MATERIALS FOR ADAPTIVE STRUCTURAL ACOUSTIC CONTROLS

Period February 1, 1993 to January 31, 1994

AD-A279 255 Annual Report
VOLUME I

OFFICE OF NAVAL RESEARCH
Contract No. N00014-92-J-1510

APPROVED FOR PUBLIC RELEASE – DISTRIBUTION UNLIMITED

Reproduction in whole or in part is permitted for any purpose of the United States Government

L. E. Cross

THE MATERIALS RESEARCH LABORATORY
UNIVERSITY PARK, PA
**REPORT DOCUMENTATION PAGE**

<table>
<thead>
<tr>
<th>4. TITLE AND SUBTITLE</th>
<th>5. FUNDING NUMBERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>MATERIALS FOR ADAPTIVE STRUCTURAL ACOUSTIC CONTROL</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>6. AUTHOR(S)</th>
<th>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L. ERIC CROSS</td>
<td>MATERIALS RESEARCH LABORATORY&lt;br&gt;THE PENNSYLVANIA STATE UNIVERSITY&lt;br&gt;UNIVERSITY PARK, PA 16802</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>8. PERFORMING ORGANIZATION REPORT NUMBER</th>
<th>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OFFICE OF NAVAL RESEARCH&lt;br&gt;GERALD T. SMITH&lt;br&gt;CODE 1513:NRI&lt;br&gt;800 NORTH QUINCY STREET&lt;br&gt;ARLINGTON, VA 22217</td>
</tr>
<tr>
<td></td>
<td>OFFICE NAVAL RESEARCH RES. REP&lt;br&gt;536 SOUTH CLARK STREET, RM 286&lt;br&gt;CHICAGO, ILLINOIS 60606-1588</td>
</tr>
</tbody>
</table>

**11. SUPPLEMENTARY NOTES**

**12a. DISTRIBUTION/AVAILABILITY STATEMENT**

**12b. DISTRIBUTION CODE**

**13. ABSTRACT (Maximum 200 words)**

SEE FOLLOWING PAGE

**14. SUBJECT TERMS**

**15. NUMBER OF PAGES**

**16. PRICE CODE**

**17. SECURITY CLASSIFICATION OF REPORT**

**18. SECURITY CLASSIFICATION OF THIS PAGE**

**19. SECURITY CLASSIFICATION OF ABSTRACT**

**20. LIMITATION OF ABSTRACT**
**GENERAL INSTRUCTIONS FOR COMPLETING SF 298**

The Report Documentation Page (RDP) is used in announcing and cataloging reports. It is important that this information be consistent with the rest of the report, particularly the cover and title page. Instructions for filling in each block of the form follow. It is important to stay within the lines to meet optical scanning requirements.

| Block 1. | Agency Use Only (Leave blank) |
| Block 2. | Report Date. Full publication date including day, month, and year, if available (e.g. 1 Jan 88). Must cite at least the year. |
| Block 3. | Type of Report and Dates Covered. State whether report is interim, final, etc. If applicable, enter inclusive report dates (e.g. 10 Jun 87 - 30 Jun 88). |
| Block 4. | Title and Subtitle. A title is taken from the part of the report that provides the most meaningful and complete information. When a report is prepared in more than one volume, repeat the primary title, add volume number, and include subtitle for the specific volume. On classified documents enter the title classification in parentheses. |
| Block 5. | Funding Numbers. To include contract and grant numbers; may include program element number(s), project number(s), task number(s), and work unit number(s). Use the following labels: |
| Block 6. | Author(s). Name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. If editor or compiler, this should follow the name(s). |
| Block 7. | Performing Organization Name(s) and Address(es). Self-explanatory. |
| Block 8. | Performing Organization Report Number. Enter the unique alphanumeric report number(s) assigned by the organization performing the report. |
| Block 9. | Sponsoring/Monitoring Agency Name(s) and Address(es). Self-explanatory. |
| Block 10. | Sponsoring/Monitoring Agency Report Number. (If known) |
| Block 11. | Supplementary Notes. Enter information not included elsewhere such as: Prepared in cooperation with…; Trans. of…; To be published in…. When a report is revised, include a statement whether the new report supersedes or supplements the older report. |
| Block 12a. | Distribution/Availability Statement. Denotes public availability or limitations. Cite any availability to the public. Enter additional limitations or special markings in all capitals (e.g. NOFORN, REL, ITAR). |
| Block 12b. | Distribution Code. |
| Block 13. | Abstract. Include a brief (Maximum 200 words) factual summary of the most significant information contained in the report. |
| Block 14. | Subject Terms. Keywords or phrases identifying major subjects in the report. |
| Block 15. | Number of Pages. Enter the total number of pages. |
| Block 16. | Price Code. Enter appropriate price code (NTIS only). |
| Block 20. | Limitation of Abstract. This block must be completed to assign a limitation to the abstract. Enter either UL (unlimited) or SAR (same as report). An entry in this block is necessary if the abstract is to be limited. If blank, the abstract is assumed to be unlimited. |

Standard Form 298 Back (Rev. 2-89)
ABSTRACT

The research goals of this ONR sponsored University Research Initiative entitled “Materials for Adaptive Structural Acoustics Control” relate directly to the sensing and actuating material which must be integrated to function in adaptive control of acoustic structures. This report documents work in the second year of the program and for convenience the activities are grouped under the headings General Summary Papers, Materials Studies, Composite Sensors, Actuator Studies, Integration Issues, Processing Studies, and Thin Film Ferroelectrics.

The general papers cover a new comprehensive description of ferroelectric ceramics and their applications, analysis of high temperature piezoelectric sensors and the possible application of nonlinearity in enhancing the “smartness” of ceramics and composites. Scale effects on ferroics are of increasing interest and the manner in which nano-scale polar regions control the properties of relaxor ferroelectrics is again emphasized.

For material studies the detailed examination of the evolution of diffuse, then relaxor behavior in lanthanum modified lead titanate has been completed. Interest in the soft PZTs, relaxor and phase switching materials continues, with a new thrust developing towards a more complete description of domain walls and morphotropic phase boundaries in perovskites. Materials issues in the wear out and fatigue effects in polarization switching systems have been subjected to detailed evaluation and the precautions necessary to fabricate long lasting materials which will stand $10^9$ switches without any fatigue are delineated.

Sensor studies have continued to focus on flexextensional composites and have demonstrated both the very high hydrostatic sensitivity and the amplified actuation response of this configuration. Integration of sensors with the “moonie” actuators has been accomplished in individual cells. Actuator studies cover the gamut from highly reproducible micro positioning using electrostrictive compositions to high strain polarization switching shape memory ceramics capable of driving a latching relay device. Studies of the destruct mechanisms in practical MLA systems complement the earlier materials work and show the importance of internal electrodes and consequent stress concentrations for crack initiation. Integration studies have focused upon more detailed evaluation of 1:3, 2:2 and tubular 1:3 composites and upon the influence of the polymer characteristic and of face plates and edge guards upon sensing and actuation capabilities. In processing, the interest in dielectrophoretic forming of composites is continuing and assembly of interesting 1:3 composites is demonstrated. Guidelines for the transducer application of electrostrictive materials have been formulated and a useful classification scheme proposed. In fiber PZTs techniques for fabricating thin (30 μ) fibers are demonstrated, the first successful technique for poling fibers is described and it is shown that properly poled fibers have electro-elastic characteristics similar to bulk material. Film papers are selected to reflect the transducer capabilities of lead titanate and of phase switching lead zirconate titanate stannate antiferroelectric compositions.
TABLE OF CONTENTS

ABSTRACT ........................................................................... 6
INTRODUCTION .................................................................... 7
1.0 GENERAL SUMMARY PAPERS ........................................ 9
2.0 MATERIALS STUDIES .................................................. 10
3.0 COMPOSITE SENSOR .................................................... 11
4.0 ACTUATOR STUDIES ...................................................... 11
5.0 INTEGRATION ISSUES ................................................... 12
6.0 PROCESSING STUDIES .................................................. 12
7.0 THIN FILM FERROELECTRICS ........................................ 13
8.0 HONORS AND AWARDS ................................................ 14
9.0 APPRENTICE PROGRAM ................................................ 14
10.0 GRADUATING STUDENTS IN THE PROGRAM ................. 15
11.0 PAPERS PUBLISHED IN REFERRED JOURNAL ............... 15
12.0 INVITED PAPERS PRESENTED AT NATIONAL AND INTERNATIONAL MEETINGS ...................... 17
13.0 INVITED PRESENTATIONS AT UNIVERSITY, INDUSTRY AND GOVERNMENT LABORATORIES ........... 20
14.0 CONTRIBUTED PAPERS AT NATIONAL AND INTERNATIONAL MEETINGS .............................. 22
15.0 BOOKS (AND SECTIONS THEREOF) ................................. 25

APPENDICES

General Summary of Papers


General Summary of Papers (continued)


Materials Studies


**Composite Sensors**


**Actuator Studies**


**Integration Issues**


**Processing Studies**

Processing Studies (continued)


Thin Film Ferroelectrics


Graduating Students in the Program


ABSTRACT

The research goals of this ONR sponsored University Research Initiative entitled "Materials for Adaptive Structural Acoustics Control" relate directly to the sensing and actuating material which must be integrated to function in adaptive control of acoustic structures. This report documents work in the second year of the program and for convenience the activities are grouped under the headings General Summary Papers, Materials Studies, Composite Sensors, Actuator Studies, Integration Issues, Processing Studies, and Thin Film Ferroelectrics.

The general papers cover a new comprehensive description of ferroelectric ceramics and their applications, analysis of high temperature piezoelectric sensors and the possible application of nonlinearity in enhancing the "smartness" of ceramics and composites. Scale effects on ferroics are of increasing interest and the manner in which nano-scale polar regions control the properties of relaxor ferroelectrics is again emphasized.

For material studies the detailed examination of the evolution of diffuse, then relaxor behavior in lanthanum modified lead titanate has been completed. Interest in the soft PZTs, relaxor and phase switching materials continues, with a new thrust developing towards a more complete description of domain walls and morphotropic phase boundaries in perovskites. Materials issues in the wear out and fatigue effects in polarization switching systems have been subjected to detailed evaluation and the precautions necessary to fabricate long lasting materials which will stand $10^9$ switches without any fatigue are delineated.

Sensor studies have continued to focus on flextensional composites and have demonstrated both the very high hydrostatic sensitivity and the amplified actuation response of this configuration. Integration of sensors with the "moonie" actuators has been accomplished in individual cells. Actuator studies cover the gamut from highly reproducible micro positioning using electrostrictive compositions to high strain polarization switching shape memory ceramics capable of driving a latching relay device. Studies of the destruct mechanisms in practical MLA systems complement the earlier materials work and show the importance of internal electrodes and consequent stress concentrations for crack initiation. Integration studies have focused upon more detailed evaluation of 1:3, 2:2 and tubular 1:3 composites and upon the influence of the polymer characteristic and of face plates and edge guards upon sensing and actuation capabilities. In processing, the interest in dielectrophoretic forming of composites is continuing and assembly of interesting 1:3 composites is demonstrated. Guidelines for the transducer application of electrostrictive materials have been formulated and a useful classification scheme proposed. In fiber PZTs techniques for fabricating thin ($30 \mu$) fibers are demonstrated, the first successful technique for poling fibers is described and it is shown that properly poled fibers have electro-elastic characteristics similar to bulk material. Film papers are selected to reflect the transducer
capabilities of lead titanate and of phase switching lead zirconate titanate stannate antiferroelectric compositions.

INTRODUCTION

This report summarizes work carried out in the Materials Research Laboratory of The Pennsylvania State University during the second year of an ONR sponsored University Research Initiative (URI) entitled “Materials for Adaptive Structural Acoustic Control.” The program has a proposed five year duration and is being carried out largely in five sections each reporting to a senior faculty member.

These sections are:

- Materials Studies: A. S. Bhalla
- Composite Sensors: R. E. Newnham
- Actuator Studies: K. Uchino
- Integration Issues: J. Dougherty
- Processing Studies: T. R. Shrout

There is of course a necessary and highly desirable overlap between many of these topic areas, the reciprocity of the piezoelectric effect which is at the base of many of our studies ensure that most actuators can also be used as excellent sensors. The composite approaches for which the laboratory is quite renowned fuzzy the edges of the integration issues and in fact most faculty practice in more than one topic area.

Following precedent established over more than seventeen earlier annual reports, this document presents a very brief narrative summary of the work which has been accomplished making reference for backup to the fifty-two published studies from the group which are included as the technical appendices which form the bulk of the report.

In this respect, for convenience in reference, the papers are grouped under the following topic headings.

1. GENERAL SUMMARY PAPERS
2. MATERIALS STUDIES
3. COMPOSITE SENSORS
4. ACTUATOR STUDIES
5. INTEGRATION ISSUES
6. PROCESSING STUDIES
7. THIN FILM FERROELECTRICS

In general discussion, a new generalization of the broad panoply of applications for ferroelectrics has been given, highlighting the mechanisms which contribute the important responses. A balanced analysis of high temperature stress/strain sensors is presented, and the
manner in which nonlinearity may enhance the “smartness” inherent in ferroelectric electroceramics and composites are emphasized. Scale effects are clearly becoming of increasing interest and the manner in which self assembling nanoscale heterogeneity on an coherent crystal lattice influences the phase behavior in relaxor ferroelectrics is again emphasized.

For materials studies interest in the soft PZTs and relaxor ferroelectrics continues, but a new developing thrust focuses upon a more complete theoretical description of domain walls and morphotrophic phase boundaries. This is in preparation for the more complete experimental information which should come available from studies of domain walls and phase boundaries with the new coherent source TEM machines now coming into use. In considering wear out and fatigue mechanism in charge switching systems it is important to separate material issues from the ancillary problems imposed in the fabrication of practical actuators. A sequence of the papers presented wraps up a very comprehensive evaluation of phenomena contributing to polarization switching fatigue in PZT and PLZT ceramics. It is intriguing to see that from grain grown PLZTs it has been possible to extract some of the first single crystal data in this system. One notes also that the continuing refinement of approaches, highlights new experimental needs, such as refinement of the d33 meter to provide phase information and the full complex d* constants.

For sensing and some actuation functions, the emphasis of the program has continued on the flexextensional moonie systems. The patent has now been issued for this technology. The first integration of the moonie into a composite sensing and actuation couple is demonstrated and the ability to control vibration explored. Several more sophisticated systems which seek to exploit nonlinear properties for very smart composite behavior have also been reported.

In actuation, the strong electrostriction in the relaxor ferroelectric families provides highly reproducible strain which can be exploited in a wide family of micropositioners. The application of more conventional piezoelectric actuators in smart systems and adaptive structures is discussed and the limiting destruct mechanisms for the practical multilayer co-fired devices explored. Clear evidence of the cracking which occurs at high strain levels is obtained from simultaneous optical studies. The basic characteristics of phase switching shape memory ceramics are discussed and their application to a bistable latching relay structure examined.

For applications where a very limited temperature range can be tolerated the extremely high induced piezoelectric effects near the Curie temperature show very interesting application possibilities.

The complexities of integration, as exemplified by the piezoceramic polymer composites, have been explored using examples in 2:2 connectivity, classic 1:3 composite and a new family of tubular type 1:3 systems. For the tubular geometry significant advantage can be obtained by control of tube diameter and wall thickness. Economical modes for fabricating these structures are being actively explored with FMI and with Material Systems Inc. A detailed study of the P(VDF-
TrFe) copolymer system initiated under funding from Sykes Associates has now been completed and a model proposed which is in good agreement with the experimental results.

Processing related problems in co-fired multilayer actuators (MLAs) are discussed, and a newer configuration using interdigitated internal electrodes is highlighted. This configuration permits the fabrication of larger actuators with longer throws. The capability of electrophoretic and dielectrophoretic forces in permitting the intelligent assembly of pseudo 1:3 composites is examined and the rheological effects in high K suspensions explored. Criteria for selecting relaxor ferroelectric composition for transducer applications have also been formalized. Lead zirconate titanate fibers are of interest for many type of 'smart' structure, techniques for fabricating fibers are discussed and the first demonstration of poling and piezoelectric response have been effected.

In related thin film work, the nature and origin of the strong orientation effects in sol-gel lead titanate thin films has been explained. Using the sol-gel method thin films of PSnZT compositions have been fabricated and the phase switching behavior from antiferroelectric to ferroelectric states under electric fields evident in the bulk ceramics has been confirmed for the film system.

1.0 GENERAL SUMMARY PAPERS

Increasing interest in the topic of high temperature vibration sensing is reflected in the balanced discussion in Appendix 1. Commercially available techniques are first reviewed concentrating on sensors with operating temperatures in excess of 650°C. New piezoelectric options are underscored in the layer structure and complex pyrochlore ferroelectrics which have $T_c > 1000°C$ and in new AlN thin film sensors which are piezoactive above 1150°C. In the series Materials Science and Technology, Vol. II, K. Uchino provides a comprehensive discussion of the fundamentals of ferroelectricity and a broad ranging discussion of the applications of ferroelectric ceramics to capacitor dielectrics, pyroelectric devices, piezoelectric sensors and actuators, electro-optic and PTC systems (Appendix 2). The topic of “smart” materials was covered in Volume 18 of the MRS Bulletin with the introduction discussing development in the field from smart, to very smart towards Intelligent Materials discussed by the guest editor R. E. Newnham (Appendix 3). The whole area of size effects in ferroic materials is of increasing interest, stimulated by the very fine scale microstructures which appear in thin film systems. Appendix 4 discusses scale effects reaching into the nanometer region and their importance for the control of nonlinear phenomena. A more detailed discussion of the unusual self-assembling self-limiting nanoscale heterogeneity which develops on the coherent crystal lattice of the relaxor ferroelectrics is given in Appendix 5. Lead magnesium niobate is the classic example exhibiting unusual glass like dielectric properties as the polar nanostructure attendant in limited ordering of the B site cations freezes in.
2.0 MATERIALS STUDIES

Examination of the properties of lanthanum modified lead titanate continues the interest in nanoscale sub-structures with evidence of a texturing in the domain structure of the ferroelectric phase as the system evolves toward diffuse then relaxor behavior with increasing lanthanum concentration (Appendix 6). A more comprehensive report will be given in the 1994 annual report as Dr. G. Rossetti writes up his excellent thesis work on the PLT system. Appendices 7-10 cover the initiation of more systematic in depth theoretical studies of two of the most important problems in piezoelectric ceramics, namely intrinsic boundary conditions on the co-existence of ferroelectric phases at the Morphotropic Phase Boundary (MPB) in PZT (Appendix 7), and that of the detailed description of domain walls by continuum theory (Appendix 9) and the light which this can throw upon the fundamentally important gradient terms in the Landau Ginsburg Devonshire Theory (Appendix 8). These approaches are particularly timely as the new coherent source Transmission Electron Microscopes promises a cornucopia of new data on internal fields in ferroics (Appendix 10).

New experimental information regarding domain wall contributions to dielectric and piezoelectric response are presented in Appendices 11-13. Since wall motion can produce no volumetric change at low field levels a separation between intrinsic and extrinsic (domain) contribution to response can be effected by considering the temperature dependence of hydrostatic versus linear piezoelectric responses. Using this method it is shown (Appendix 11) that domains make the major contribution to response in both doped and undoped PZTs at the 52:48 Zr:T i ratio. The use of acoustic emission and concurrent current pulse measurement to separate domain switching and micro-cracking which can occur in the poling process is discussed in Appendix 12. An extension of current phenomenological theory to explore nonlinearities in response associated with domain wall motion is described in Appendix 13. New measurements of nonlinearity in PZT and PLZT compositions are used to support the theoretical conclusions. Full detail of earlier studies on fatigue effects associated with polarization switching in PZT and PLZT compositions are given in Appendices 14-20. These studies focus on material problems associated with electroding, grain size effects, composition and temperature influences, the effects of porosity and the vital importance of full density, electrodes and electroding methods, and field induced stress concentration.

It is shown that with proper precautions in these areas it is possible to achieve zero fatigue after $10^9$ cycles of field application. In PLZT at the 8:65:35 composition grain grown ceramics with single grains in the range 50-100 $\mu$ meter diameter, supplied from the Shanghai Institute of Ceramics have been used to measure the anisotropy of the single crystal dielectric response (Appendix 21). Using a highly simplified model a qualitative evaluation of the extrinsic domain contribution to $d_{33}$ has also been given (Appendix 22).
For a number of polymer and composite piezoelectrics it is clear that all material constants are complex. In Appendix 23 a modification to the Berlincourt d33 meter is described which phase locks the charge detector to the AC force generator. In the phase locked mode the meter will measure d33 values down to 1 pC/N and phase angle to 0.05°.

3.0 COMPOSITE SENSORS
Sensor studies have focused upon the flextensional “moonie” type systems. A copy of United States Patent 5,276,657 detailing the several claims for the origination of this concept by Newnham, Xu, and Yoshikawa is given in Appendix 24 which covers mostly the actuation function. The design of the moonie type structure for a range of both sensing and actuation functions is discussed in Appendix 25. Resonant frequencies and finite element analysis of the stress distribution are considered and factors which affect the integration of both sensing and actuation in the same package are discussed. This theme is further developed in Appendix 26 which considers explicitly a vibration control element using a moonie actuator and separate piezoceramic sensor. The device has a dynamic range from 100 Hz to 2,500 Hz and is capable of sensing and suppressing small ~ 1μm displacements at small force levels. The topic is developed further in Appendix 27 which also considers multiple stacked flextensional structures.

The topic of composite multilayer piezoelectric:piezomagnetic structure is considered theoretically in Appendix 28 and expressions derived for the effective magneto-electric coupling in such structures are derived. Examples of electroceramic materials and composite structures which qualify for the adjective ‘smart’ are discussed in Appendix 29.

The final moonie flextensional paper (Appendix 30) discusses in more detail the design of highly reliable units using finite element methods to model shape, material and geometrical contributions to the response.

4.0 ACTUATOR STUDIES
The relaxor ferroelectric nanocomposites discussed in Appendix 5 are materials which have useful and important applications in actuator studies discussed in Appendix 31. The absence of classical stable domain structures in these materials leads to highly reproducible anhysteritic strain response for micro-positioning and optical applications. A more general discussion of conventional piezoelectric actuators and the very wide range of material systems and modes of operation is given in Appendix 32. Shape memory and semiconductor derived monomorphs are discussed along with more conventional piezoelectric stacked elements. A problem in the stacked actuators made by the co-fire process concerns the stress concentration at electrodes which terminate within the ceramic. In Appendix 33 the problem in graphically illustrated by optical observation of the cracks which initiate in the regions of tensile stress at these electrode edges. The
whole range of ceramic actuators is reviewed in Appendix 34 with examples of a wide range of practical capabilities for both simple and mechanical amplifier configurations.

The topics of actuation in smart systems is taken up briefly in Appendix 35 which is the outline of a paper presented at ADPA/AIAA/ASM/SPIE. Appendix 36 takes up in more detail the mechanical damage mechanisms which limit the performance of co-fired multilayer actuators and discusses an interesting acoustic emission test for diagnosing wear out in actuators used in highly critical applications like precision machining. It is interesting that the phase switching antiferroelectric PZT compositions show shape memory behavior and of particular importance as shown in Appendix 37 is the fact that shape recovery can be activated electrically without energetically extravagant heating and cooling required in the metallic shape memory system. Appendix 37 discusses the phenomena in PZSnT and its application to a simple latching relay. Smart control of actuators is discussed in Appendix 38, and the very high values which can be achieved in compositions close to the ferroelectric Curie point in some solid solution systems is determined in Appendix 39.

5.0 INTEGRATION ISSUES

A much more detailed analysis of the piezoceramic-polymer composite in 2:2 connectivity is given in Appendix 40. The theoretical study shows that major stress transfer takes place near the surface so that it may be desirable to have a stiffer polymer in this location. Work on the 1:3 polymer ceramic composites has been going forward with FMI (Appendix 41) who have facilities for assembling these tubular systems. The results of analysis confirm the advantage of this tubular configuration and the very high values of $d_3$ which can be achieved. The laboratory has been involved in a comprehensive experimental study of the piezoelectric PVDF copolymer (vinylidene fluoride:trifluoroethylene 75:25) and has demonstrated the complex nature of elastic, dielectric and piezoelectric constants. To explain the different observed dispersion regimes a two phase composite model is proposed (Appendix 42) and numerical calculations from the model are shown to be in good agreement with experiment.

In the final paper in this section (Appendix 43) the effects of surface face plates and edge strips on the hydrostatic response of 1:3 composite panels are considered. It is shown that the earlier shear-coupling model provides good guidelines for the design and permits the optimization of geometry and material properties.

6.0 PROCESSING STUDIES

For co-fired multilayer piezoelectric actuators it is essential to consider the processing parameters along with the design of the system (Appendix 44). For the very thin layer low voltage structures, stress concentrations at the electrode edges limit application of the simple MLC design.
and it is necessary to go to slits or gaps in these locations to relieve stress. Full plate through electrodes can only be accomplished for thicker layers and suffer also from the problems of silver migration. A new type of interdigitated longitudinal mode which can use $d_{33}$ is discussed and the performance achieved does permit longer actuators with larger throw. Manipulation of the microstructure in polymer/ceramic 0:3 composites using dielectrophoretic orientation and chaining techniques is discussed in Appendix 45. The paper highlights the use of in situ dielectric measurement to determine alignment, batch uniformity and as a general quality control technique.

Electrostriction in relaxor ferroelectric systems occurs with a number of distinct “flavors.” Appendix 46 suggests a useful classification which separates the families into four major categories. There is a growing interest in the possible advantages of PZT fibers for both passive and active smart systems in vibration control. Techniques for the fabrication by sol-gel methods, the poling and testing of very fine fibers are discussed in Appendix 47. It is gratifying to note that even at 30 $\mu$ meter diameter the properties are similar to those of an equivalent bulk PZT. The properties of electrorheological fluids using fine BaTiO$_3$ powders in silicone oil are discussed in Appendix 48. Under 60 Hz AC fields strong fibril formation was observed optically and turbulent flow was not observed for fields up to more than 20 Kv/cm. The characteristics observed in yield stress suggest a dominant dipole:dipole interaction in chain formation. More details of the application and versatility of the dielectrophoretic assembly method are given in Appendix 49 which discusses pseudo 1:3 composite assemble and the conditions required for optimum alignment.

7.0 THIN FILMS FERROELECTRICS

Following earlier established practice, thin film studies which we believe are relevant to the objectives of this program are appended. Conditions which influence the orientation of sol-gel formed lead titanate films used for high frequency transduction are discussed in Appendix 50. It is shown that both the nature of the sol and the type and condition of the substrate can have a marked influence upon the nature and the degree of film orientation.

The phase switching high zirconia PSnZT composition are of strong interest in bulk form for high strain actuation. In Appendix 51 it is demonstrated that thin films in the same composition family can be fabricated by sol-gel spin on techniques. The films also exhibit phase switching under high electric field with fast switchover times (~300 n sec) and high induced elastic strain (~0.16%).

For all perovskite type thin films, and for films like the YBCO superconductors which are in closely similar structure types, substrates with appropriate matching crystallographic structure and unit cell dimensions are of major importance. An example of the materials of interest is Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ (Appendix 52), a cubic perovskite which is shown to have exceedingly low
microwave dielectric loss. The laboratory has an extensive ONR/ARPA sponsored program on substrate materials which will be of interest to both ferroelectric and superconductor film fabricators.

8.0 HONORS AND AWARDS

Over the year 1993 the Ferroelectric Group in MRL has continued to receive excellent recognition from both Domestic and International Societies. In May 1993 Professor R. E. Newnham was awarded the Humboldt Research Award which will support his stay at the Max Plank Institute in Stuttgart during early 1994. Professor L. E. Cross and Dr. A. S. Bhalla were recipients of the Edward C. Henry Award from the Electronics Divisions of the American Ceramic Society. The award for the best paper in electroceramics published in the Journal over the period 1989-1993 and was for their paper with T. Takanaka and K. Sakata on "Dielectric Piezoelectric and Pyroelectric Properties of Lead Zirconate:Lead Zinc Niobate Ceramics."

The group has continued to be very active in the organization of both National and International Meetings. For IMF8 L. E. Cross was Vice Chairman, and orchestrated industrial support, S. J. Jang and R. E. Newnham were responsible for the Proceedings.

For ISAF9 which will be at Penn State in August 1994 A. S. Bhalla is General Chair. Dr. Bhalla was also responsible for ACerS Symposia on Materials for Smart/Intelligent Systems and for Ferroelectric Thin Films at the Fall 1993 PAC RIM Meeting in Hawaii.

9.0 APPRENTICE PROGRAM

The 1993 ONR Apprentices were:

Liza Rivera
A senior from State College High School. Her work was in the area of electrophoresis and dielectrophoretic assembly of composites.

Maria Teresa Defesdini
Maria was a graduating senior from Col. Senora Merced High School in Puerto Rico. Her studies were focused on the processing and fabrication of relaxor ferroelectric materials with a range of compositions directly relevant to work on the URI program.
10.0 GRADUATING STUDENTS ON THE PROGRAM


Jaiyu Chen, PhD, Electrical Engineering, "Electrical and Electromechanical Properties of Ferroelectric Thin Films for Microelectromechanical Applications," August 1993 (Abstract included at Appendix 54). Only the electromechanical measurement part of this work was supported on URI funding.


11.0 PAPERS PUBLISHED IN REFERRED JOURNAL


11.0 PAPERS PUBLISHED IN REFERRED JOURNAL (continued)


12.0 INVITED PRESENTATIONS AT NATIONAL AND INTERNATIONAL MEETINGS


12.0 INVITED PRESENTATIONS AT NATIONAL AND INTERNATIONAL MEETINGS (continued)


15. Newnham, R. E., Electrostrictive Materials, Seminar at the National Tsing Hua University, Hsinchu, Taiwan, Republic of China (5/3/93).

16. Newnham, R. E., Composite Electroceramics, seminar at the National Cheng-Kung University, Tainan, Taiwan, Republic of China (5/5/93).


12.0 INVITED PRESENTATIONS AT NATIONAL AND INTERNATIONAL MEETINGS (continued)


12.0 INVITED PRESENTATIONS AT NATIONAL AND INTERNATIONAL MEETINGS (continued)


13.0 INVITED PAPERS PRESENTED AT UNIVERSITY, GOVERNMENT, AND INDUSTRIAL LABORATORIES


2. Newnham, R. E., Smart Ceramics, Seminar at Engineering College, University of California, Irvine, CA (5/14/93).


4. Newnham, R. E., Smart Ceramics, Lecture at the Ceramic Science and Technology Workshop supported by the U.S. Office of Naval Research European Office, Technical Council of Turkey and the Middle East Technical University, in Ankara, Turkey (7/21-22/93).


13.0 INVITED PAPERS PRESENTED AT UNIVERSITY, GOVERNMENT, AND INDUSTRIAL LABORATORIES (continued)


9. Shrout, T., Lead Based Pb(B₁B₂)O₃ Relaxors vs BaTiO₃ Relaxors for Multilayer Capacitors, Storage Tek and AKZO-Amp.


22. Cao, Wenwu, Composite Electroceramics, Fall Meeting of the Center for Dielectric Studies, State College, Pennsylvania (September 22, 1993).

23. Cao, Wenwu, Statics and Dynamics of Ferroic Microstructures, Department of Physics, Pennsylvania State University, Solid State Seminar (September 13, 1993).
13.0 INVITED PAPERS PRESENTED AT UNIVERSITY, GOVERNMENT, AND INDUSTRIAL LABORATORIES (continued)


14.0 CONTRIBUTED PAPERS AT NATIONAL AND INTERNATIONAL MEETINGS


10. Troiler-McKinstry, S., Microstructure-Property Relations in Ferroelectric Thin Films.
14.0 CONTRIBUTED PAPERS AT NATIONAL AND INTERNATIONAL MEETINGS (continued)

95th Annual Meeting of the American Ceramic Society, Cincinnati, Ohio (April 19-21, 1993).


13. Oh, K. Y., K. Uchino, and L. E. Cross, Dynamical Observation of Domain Motion in Ferroelectric Polycrystalline Ceramics.


International Meeting on Ferroelectrics (IMF 8), NIST, Gaithersburg, Maryland (August 8, 1993).


14.0 CONTRIBUTED PAPERS AT NATIONAL AND INTERNATIONAL MEETINGS (continued)

**International Meeting on Ferroelectrics (IMF 8), NIST, Gaithersburg, Maryland (August 8, 1993).**

27. Cao, W., Domains As Nonlinear and Nonlocal Excitations.


15.0 BOOKS (AND SECTIONS THEREOF).


GENERAL SUMMARY PAPERS
APPENDIX 1
Materials for High Temperature Acoustic and Vibration Sensors: A Review


The Materials Research Laboratory, The Pennsylvania State University,
University Park, Pennsylvania 16802, USA

ABSTRACT

The industrial and scientific communities have expressed a real need for the capability of pressure, acoustic, and vibration sensing at elevated temperatures. This review compares the various commercial methods and materials for acoustic transduction, identifying their advantages and limitations. Techniques and devices include simple piezoelectric sensors, accelerometers, strain gauges, proximity sensors, fiber optics and buffer rods. Sensors with operating temperatures in excess of 650°C are readily available from commercial sources. Of the mechanisms investigated, the piezoelectric approach offers several advantages, including design cost and simplicity. Therefore, the bulk of this review concentrates on piezoelectric materials, both those that are already available commercially, and those that are presently under development. The new materials include perovskite layer structure ferroelectric ceramics, which possess the highest known Curie temperatures and thin film AlN, which has been reported to be piezoelectric at 1150°C.

1 INTRODUCTION

High-temperature electronics is an area of research offering interesting materials and design challenges and one of significant industrial importance. The major impetus for the development of high-temperature electronic materials, devices, circuits, and systems can be credited to the energy crisis of 1974, when a commitment was made to the development of national energy resources by geothermal exploration. At that time, geothermal and oil-well logging industries voiced their need for sensors and electronic
systems with higher operational temperatures for deep drilling in the earth's crust. The economic importance of world energy independence and reduced waste provided additional incentive for their development.

The aerospace and aircraft industries have especially difficult high-temperature requirements. With space and weight at a premium, engine designers and builders find it difficult to protect sensitive electronic systems in a cool, remote place. Electronic controls are to be placed directly inside jet engines because of reliability and noise requirements, so sensors need to be built that can withstand temperatures of 500–1000°C while allowing mission lifetimes up to 100 000 h.

In automotive electronics, the number of sensors and actuators continues to increase each year. Ceramic and semiconductor sensors which record temperature, oxygen pressure, and preignition knock are used in conjunction with microprocessor-based controls to improve the efficiency and reliability of internal combustion engines. Further efficiency can be realized by operating combustion engines at higher temperatures. Research on the use of ceramic components in a diesel engine has led to higher operating temperatures, resulting in a potential increase in fuel efficiency up to 65%, along with a notable reduction in exhaust pollution. Higher operating temperatures do, however, place additional requirements on the sensors. Environments of 150°C with repeated temperature cycles are at present considered the automotive norm, and higher temperatures are expected in the future.

Until the present, there has not been a review of the types of sensors commercially available for high-temperature acoustic sensing applications. The purpose of this paper is to provide such a review. Included in the discussion are the commercially available high-temperature piezoelectric materials used in many of the sensors described. In addition, new advances in materials that may permit the design of sensors which can operate at temperatures well above those currently available will be presented.

2 ACOUSTIC MEASUREMENT TECHNIQUES AND APPLICATIONS

Critical parameters for acoustic and vibration sensors involve the measurement of dynamic pressure pulses, vibrations (relative and absolute), acoustic emissions, strains, and the dynamic proximity of machine components. An example of a dynamic pulse is the rapid increase in pressure upon ignition of the air–fuel mixture in the cylinders of an internal combustion engine. The timing and the shape of the pulse have a large effect upon
engine efficiency. Transducers fitted into the cylinder head have been used for monitoring combustion pressure to optimize ignition timing. Dynamic monitoring is also employed in such machines as aircraft engines, gas turbines, and power generators, all of which have high speed rotors. Sensors strategically mounted on the machine detect destructive conditions of imbalance, or unequal loading of the rotor, enabling the possibility of corrective measures to be implemented. The sensors convert the associated mechanical energy of the vibration to electrical energy which can then be amplified and monitored. Computer coupling, allows real-time status reports of the condition of the machine while providing a comparison with an operating norm. Non-destructive testing (NDT) is another widely used application of acoustic sensors that involves either passive sensing of 'acoustic emissions', or active 'ultrasonic testing' techniques. An application of the first method involves affixing a number of acoustic sensors in strategic locations on the wall of a vessel, such as a chemical storage tank, pressurizing the vessel to create strains, and examining the acoustic emissions which result from the Kaiser effect. Cracks and poor joints can then be detected and logged so that repairs can be made. This method has also been successfully applied in the inspection of the fuselage of large aircraft to detect cracks resulting from fatigue. The ultrasonic method of NDT incorporates a transducer to generate an acoustic signal at ultrasonic frequencies that is transmitted through the test specimen. When the acoustic wave reaches an interface of the sample it is reflected back to the transmitter/sensor which, therefore, acts as a transceiver. If, however, the wave impinges upon a flaw, a portion of the wave is reflected and thus reaches the sensor ahead of the original wave. This, then, becomes a valuable tool for locating defects within a structure. Figure 1 is a simple illustration of the technique. Acoustic sensors also find use in the hostile environments of deep oil wells for seismic data logging, and in nuclear power plants to monitor the condition of heat exchange pumps and pipes. An indirect way of sensing vibration is by measuring capacitive changes in an air gap. An air gap sensor placed in close proximity to a

![Fig. 1. Detection of a flaw in a solid by ultrasonic testing (NDT).](image-url)
### TABLE 1

Acoustic and Vibration Measurement: Industrial Applications

<table>
<thead>
<tr>
<th>Industry</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerospace</td>
<td>Measure rotational speed of jet turbine rotors</td>
</tr>
<tr>
<td></td>
<td>Space vehicle acceleration</td>
</tr>
<tr>
<td></td>
<td>Trajectory monitor</td>
</tr>
<tr>
<td></td>
<td>In-flight vibration monitor</td>
</tr>
<tr>
<td></td>
<td>Nozzle pressure</td>
</tr>
<tr>
<td></td>
<td>NDT test of air frames</td>
</tr>
<tr>
<td>Automotive</td>
<td>Knock sensor</td>
</tr>
<tr>
<td></td>
<td>Fluid level sensor</td>
</tr>
<tr>
<td></td>
<td>Crash test</td>
</tr>
<tr>
<td></td>
<td>Vibration control</td>
</tr>
<tr>
<td>Industrial</td>
<td>Dynamic pressure monitors</td>
</tr>
<tr>
<td></td>
<td>Vibration detectors</td>
</tr>
<tr>
<td></td>
<td>Flow detectors</td>
</tr>
<tr>
<td></td>
<td>NDT testing</td>
</tr>
<tr>
<td></td>
<td>Proximity detectors</td>
</tr>
<tr>
<td></td>
<td>Noise &quot;fingerprinting&quot;</td>
</tr>
<tr>
<td>Medical</td>
<td>Diagnostic imaging</td>
</tr>
<tr>
<td></td>
<td>Impact sensors</td>
</tr>
<tr>
<td>Military</td>
<td>Hydrophones</td>
</tr>
<tr>
<td></td>
<td>Range finders</td>
</tr>
<tr>
<td></td>
<td>Noise detection in vehicles</td>
</tr>
<tr>
<td></td>
<td>Security systems</td>
</tr>
<tr>
<td>Power generation</td>
<td>Leak detector</td>
</tr>
<tr>
<td></td>
<td>Liquid sodium coolant pump monitor</td>
</tr>
<tr>
<td></td>
<td>Nuclear reactor monitor</td>
</tr>
<tr>
<td></td>
<td>Air gap monitoring between stator and rotor</td>
</tr>
<tr>
<td></td>
<td>Fuel rod monitor</td>
</tr>
<tr>
<td></td>
<td>Coal feeder monitor</td>
</tr>
<tr>
<td></td>
<td>NDT of pressure vessels</td>
</tr>
<tr>
<td>Commercial</td>
<td>Fish finders</td>
</tr>
<tr>
<td></td>
<td>Phonographs pick-up</td>
</tr>
<tr>
<td></td>
<td>Microphones</td>
</tr>
</tbody>
</table>

High-speed rotor will detect dynamic changes in the spacing between the two which, in effect, is an indicator of an imbalance condition or some other malfunction. This type of sensor has found wide acceptance in hydroelectric power plants.

Examples of pressure, acoustic and vibration measurement techniques described above serve to illustrate the wide variety of possible applications. Additional applications are listed by industry in Table 1. These are routinely employed in the range of $-55^\circ C$ to $125^\circ C$, however, several devices are needed to operate in much harsher thermal conditions. Sensor designs and their respective temperature limitations are described in the following section.
3 SENSOR DESIGNS

Listed in Table 2 are current commercial sensor designs. They include piezoelectric discs or plates, accelerometers, strain gauges, proximity sensors, fiber-optic sensors, and systems incorporating buffer rod extensions. Brief descriptions of these devices are as follows.

3.1 Simple disc

The most basic sensor incorporates a simple disc, or other simple shape, composed of a piezoelectric ceramic, which is attached directly to the wall or frame of an engineering structure, embedded in a recess, or mounted in a replaceable fixture. Figure 2 is a schematic construction of a piezoelectric knock sensor using a bending mode resonance to detect vibrations. The piezoelectric element ‘generates’ a voltage in response to stresses caused by the acoustic energy impinging upon it. The magnitude of the voltage generated is directly related to the product of the applied stress and the piezoelectric voltage or ‘g’ constant of the material. The electrical signal is then amplified and fed to a microprocessor in the control system. This arrangement is capable of extremely high sensitivity on the order of pico (10^-12) strains. It is also self-generating, rugged, low-cost, and simple. The temperature limitations of these sensors arise from the loss of piezoelectric properties that occur as the material approaches its transition (Curie) temperature T_m, a topic which will be discussed later. For lead zirconate-titanate, (commonly called PZT), the most widely used piezoelectric ceramic material, the maximum use temperature is ~200°C. Other temperature limitations result from the failure of the adhesives used to mount the disk, and melting of the solder used to attach the leads.

3.2 Buffer rod extensions

For many high-temperature applications, buffer rod extensions are utilized to transmit and receive acoustic signals from very hot areas, effectively

![Diagram](image)

Fig. 2. Two methods of mounting a piezoelement used in automotive knock sensors.
TABLE 2
Comparison of Commercial Strain, Vibration, and Acoustic Sensors

<table>
<thead>
<tr>
<th>Operation principle</th>
<th>Piezoelectric disc or plate</th>
<th>Accelerometer</th>
<th>Strain gauge</th>
<th>Proximity sensor</th>
<th>Buffer rod</th>
<th>Fiber-optic sensor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Piezoelectric</td>
<td>Magnetic induction</td>
<td>Resistive metal</td>
<td>Capacitive</td>
<td>Eddy current</td>
<td>Piezoelectric</td>
</tr>
<tr>
<td>Measured parameter</td>
<td>Acoustic waves vibration</td>
<td>Acceleration absolute dynamic</td>
<td>Vibration pressure</td>
<td>Load, force vibration absolute</td>
<td>Relative air gap displacement</td>
<td>Vibration</td>
</tr>
<tr>
<td>Present maximum temperature (°C)</td>
<td>400</td>
<td>650</td>
<td>480</td>
<td>850</td>
<td>150</td>
<td>450</td>
</tr>
<tr>
<td>Temperature stability</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Fair</td>
<td>Good</td>
<td>Fair</td>
</tr>
<tr>
<td>Temperature sensitivity</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Fair</td>
<td>Good</td>
<td>Fair</td>
</tr>
<tr>
<td>Resolution/sensitivity</td>
<td>High</td>
<td>High</td>
<td>Fair</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Frequency range</td>
<td>0.05–1 MHz</td>
<td>0.05–1 MHz</td>
<td>0.0015–2 kHz</td>
<td>DC-kHz</td>
<td>DC-kHz</td>
<td>DC-10 kHz</td>
</tr>
<tr>
<td>Power consumption</td>
<td>Low</td>
<td>Low</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>Cost and complexity</td>
<td>Low</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Durability</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Fair</td>
<td>Good</td>
<td>Fair</td>
</tr>
</tbody>
</table>
isolating temperature-sensitive transducers from hostile environments. The rod serves as an acoustic wave guide to couple the hot test specimen with the sensitive piezoelectric transducer. The rods are generally constructed of stainless-steel and are cooled with water or air to prevent damage to the transducers. This arrangement permits the use of a conventional piezoelectric material, which would otherwise lose its piezoelectric properties at high temperatures. This technique is widely used on NDT probes in the metals industry to detect cracks and other defects in hot steel blooms and pipes at temperatures in the neighborhood of 1100°C. A similar application employs hollow 'buffer pipes' to couple dynamic pressure sensors with jet and rocket engines.

3.3 Accelerometers

Accelerometers most often use a piezoelectric as the internal sensing element. The various designs exploit different mechanisms to translate mechanical energy to a measurable response, but all operate based on Newton’s second law:

\[ F = ma \]

The accelerometer shown in Fig. 3 differs from the simple disk piezoelectric sensor in that a seismic mass (m) is attached to the piezoelectric element and the assembly is hermetically sealed in a protective case. As a response to acceleration (a), the mass imparts a force (F) on the element, which in turn generates a voltage in proportion to the magnitude of the stress. Depending upon the sensitivity and temperature range required for the application, transducer manufacturers utilize several different piezoelectric materials. Commercial accelerometers using lithium niobate (LiNbO₃) single crystal elements are rated for continuous use up to 650°C.12,13

![Cross-section of a tubular accelerometer element](image-url)
Accelerometers based on magnetic induction, employ a permanent magnet as the seismic mass and a field coil for the active element. The mass is partially restrained by a spring, but when the mass is accelerated, it moves relative to the coil, thus inducing an electromotive force. As with the case of piezoelectric types, the resulting electric signal must be amplified and filtered before it is fed to the instrumentation. The upper temperature limit of this type of device is determined by the Curie temperature of the permanent magnet. Commercial units are rated for temperatures as high as 480°C.\textsuperscript{14}

3.4 Strain gauges

Figure 4(a) is an illustration of a bonded metallic foil strain gauge.\textsuperscript{15} Resistive strain gauges involve a change in electrical resistance ($\Delta R$) resulting from the mechanical strain ($\Delta L/L$) of the sample to which the gauge is bonded. The sensitivity is determined by the gauge factor (GF):

$$GF = \frac{\Delta R/R}{\Delta L/L}$$

With a typical gauge factor of 2, and a nominal resistance $R = 100 \, \Omega$, these gauges require an ohmmeter with very high sensitivity to measure the $\Delta R$ accompanying a strain of $1 \times 10^{-6}$. A more accurate way of measuring small changes in resistance incorporates a Wheatstone bridge as shown in Fig. 4(b).

To compensate for the nonlinear character of the thermal coefficients of expansion of the alloys used, an unstrained reference gauge is installed in an adjacent bridge arm. This second gauge is subjected to the same temperature as the first, thereby effecting electrical cancellation of the apparent strain. Commercial metal gauges are typically limited in temperature range to about 300°C; however PtW wire gauges are available for

![Figure 4(a) and 4(b) showing bonded grid resistance gauges and Wheatstone bridge circuit for measuring strain.\textsuperscript{15}](image-url)
High temperature acoustic and vibration sensors: A review

use up to 850°C, and other exotic metals such as PdCr are being studied for use up to 1000°C.

Metal strain gauges are simple in design, low-cost, and can detect static strains. Even using the Wheatstone bridge configuration, however, strain sensitivity is low compared with piezoelectric transducers.

3.5 Proximity sensors

Proximity sensors are often used to monitor the degree of rotation of the armatures of electric generators as well as the clearance between the armature and the stator. This serves as an indirect method of measuring vibration if an unbalanced condition exists. The two types of proximity sensors available commercially are (i) air gap capacitors, and (ii) eddy current detectors. Both types require electronic conditioners to supply an input signal, and processors to analyze the signals modified by the sensors.

(i) An example of an air gap capacitor is illustrated in Fig. 5. In this application on an electric power generator, the armature serves as one plate of the capacitor while the other plate is an integral part of the sensor and air is the dielectric. The plates are maintained at a close proximity with one another so that a small change in spacing results in significant changes in capacitance. The change in capacitance can then be detected by the control circuitry and acted upon accordingly. The detection of variations in air gap as small as one micron are possible in installations on hydroelectric power generators. At present, commercial units are constructed of fibreglass composites for use at temperatures up to 150°C, but it seems reasonable that units could be constructed from more refractory materials for higher temperature applications.

Fig. 5. Air gap sensors mounted on an AC generator.
(ii) The second kind of proximity sensor is the eddy current type. It determines the relative position of a rotating shaft by detecting changes in magnetic field between the sensor and the target shaft. The eddy current sensor operates in a manner similar to that of an electrical transformer. The sensing coil resembles the primary winding, and the small eddy current loops induced in the target by the variable magnetic field of the sensing coil act like the secondary windings. The small eddy currents cause a change in phase and amplitude of the sensing coil signal. The target material must therefore be metallic. The sensing coil is mounted near the rotating shaft or moving component of a machine with lead cables attached to the exterior end. Commercial models are currently rated for use up to 450°C. The temperature limitation is primarily due to the temperature coefficient of resistance of the wire used to wind the probe coil.

3.6 Fiber optic sensor Interferometers

Fiber optic sensor (FOS) interferometers or phase sensors are used to detect small strains, (in the order of $10^{-6}$) or vibrations in a sample without making physical contact. This capability allows measurements to be made inside a hostile environment, such as a furnace. A simplified schematic of a system is shown in Fig. 6. There are several different designs, but all are based on measuring a phase change in the transmitted light signal resulting from a change in length of the optical fiber. Optical fibers are typically SiO$_2$ glass; however, fibers of more heat-resistant materials such as sapphire (Al$_2$O$_3$) are commercially available. Along with the fiber, a large number of additional components, such as a laser source, phase demodulator, filters, and microprocessors, etc., are needed for these systems. High cost, complexity and sensitivity to variations in temperature are disadvantages of this approach.

![Fig. 6. Fiber-optic vibration sensor and associated electronics.](image-url)
In summary, with respect to the operational parameters listed in Table 2, piezoelectric transducers offer many advantages over the other types of acoustic sensors. Specifically, their compliment of sensitivity, stability over a wide temperature range, and simple design offers the lowest cost approach. Polycrystalline ceramics are often the material of choice because they can be readily manufactured into a variety of configurations. Therefore, the remainder of this paper concentrates on high-temperature piezoelectric materials, with a review of those currently available, and a discussion of future prospects.

4 PIEZOELECTRIC CERAMICS

4.1 Piezoelectricity

The phenomenon of piezoelectricity was first reported in 1880 by Pierre and Jacques Curie. Since that time, a number of crystalline materials have been found to exhibit piezoelectric activity, although only a few are of practical concern. The common feature of all piezoelectric crystals is that they have no center of symmetry along the piezoelectric axes. Ferroelectric ceramics possess a multitude of individual dipole domains which are distributed throughout the body in various crystallographic orientations, resulting, in a net dipole moment of zero. In a process, called poling, a relatively large electric field is applied through the body causing a common alignment of a large portion of the dipoles, thus rendering the material piezoelectric. These crystals develop an electric field when subjected to an applied stress (sensor), or conversely, exhibit a mechanical deformation with the application of an electric field (actuator). Since the details of piezoelectricity are covered in a number of excellent texts and review articles, the reader is advised to consult them for further information.\textsuperscript{11,20-22}

4.2 Electromechanical properties

In order to describe the electromechanical properties of piezoelectric materials, a large number of interrelated coefficients are used, many of which have been standardized by the IEEE.\textsuperscript{23} However, with regards to high-temperature materials, only the most important coefficients and properties will be presented in this section. (Note: where subscripts are used with coefficients, the first number refers to the axis of polarization, and the second refers to the axis of applied stress, or applied field.)
4.2.1 Ferroelectric Curie temperature
Most of the piezoelectric materials described in this paper are ferroelectric and capable of being polarized, with the polarization resulting from the asymmetry of its crystal structure. When the crystal is heated, its internal kinetic energy increases. At a certain temperature, called the Curie temperature \( T_c \), the crystal changes to a structure of a higher symmetry, the alignment of the dipoles is lost and all piezoelectric activity disappears. Upon cooling, the dipoles do not realign unless they are subjected to a strong electric field. Other consequences of increasing temperature are changes in the values of electromechanical coefficients, which become more pronounced as the \( T_c \) is neared. This can be particularly important in applications where the electrical properties of the sensor are closely matched to the instrumentation. In addition, dipoles that were polar oriented have a tendency to reverse back to their original position thus degrading the piezoelectric effect in a process known as 'thermally activated aging'. Generally, a maximum operating temperature of one-half the \( T_c \) is considered safe.

4.2.2 Resitivity and the RC time constant
High electrical resistivity is necessary so that a large field can be applied during poling without breakdown or excessive charge leakage. High insulation resistance \( 'R' \) is also required during operation of the device. The transducer must not only develop a charge for an applied stress or strain, but must also maintain the charge for a time long enough to be detected by the electronic system. The length of time the charge is maintained is proportional to the \( RC \) time constant (resistance \( \times \) capacitance). The minimum useful frequency of a sensor, known as the lower limiting frequency \( (f_{LL}) \), is inversely proportional to the time constant:

\[
f_{\text{LL}} = \frac{1}{2\pi RC}
\]

where \( C \) is the device capacitance.

Below \( f_{\text{LL}} \), the charge will drain off before it is detected because of conduction in the sensor. With low \( f_{\text{LL}} \), the dynamic bandwidth can be extended to sonic frequencies, and thus, a large \( RC \) constant is desirable for many applications.

4.2.3 Piezoelectric constants
The piezo strain \( 'd' \) constant gives the ratio of the strain developed in the specimen to the electric field applied at the electrodes, and conversely, the ratio of short circuit charge, per electrode area, to the applied stress. The stress can be applied to the body in different modes as illustrated in
Fig. 7. (a) Thickness, (b) shear, and (c) lateral mode piezoelectric sensors. P indicates the poling direction. The output voltage (V) is proportional to the applied force (F) and piezoelectric voltage coefficient (g) of the material.

Fig. 7. The piezoelectric voltage 'g' constant gives the ratio of the field developed to the stress applied, and conversely, the ratio of strain to the applied charge to the electrode area. The 'g' constant is related to the 'd' constant by the permittivity, $\varepsilon_0$.

$$g = \frac{d}{\varepsilon_0}$$

In comparing the properties of high-temperature piezoelectric materials, the 'g' constant tends to be the more meaningful coefficient.

4.2.4 Mechanical Q
The mechanical Q expresses the ratio of strain in phase with stress to strain out of phase with stress in the vibrating element, or in other words, the relative amount of input electrical energy that is converted to mechanical energy as opposed to that which is lost as heat. Piezoelectric materials with high 'Qm' factors are characterized by having narrow
resonant peaks, whereas, those with low ‘Q’ factors have broader bandwidths.

4.2.5 Sensitivity
For a given stress applied to the device, the output voltage generated by the piezoelectric ‘generator’ should be sufficiently high to be detected above background noise. The most sensitive devices produce the greatest output per unit of stress. Unfortunately, for high-temperature sensors, ferroelectric materials exhibit a considerable increase in permittivity, with increasing temperature, a condition which effectively reduces the voltage constant ‘g’. Every piezoelectric material reaches some temperature at which its voltage constant ‘g’ and resistivity are diminished to the point where the output becomes undetectable. In practice, the relatively small output signals generated by high temperature accelerometers necessitate the use of electronic charge amplifiers for enhancement, but there is a practical limit to how small a signal that can be accurately detected.

5 COMMERCIAL PIEZOELECTRIC CERAMICS

Table 3 lists typical piezoelectric ceramic materials found in commercial accelerometers and vibration sensors, along with reported room temperature properties.21,24-28 Owing to the lack of reliable published high-temperature data available for this work, samples were obtained, their electrical properties were measured at elevated temperatures, and the data reported in Table 4.25-29 In addition, the resistivity of each material was measured over a wide range of temperatures as shown in Fig. 8.25-28,30-34 Good agreement was found with values reported in the literature (as shown in Fig. 8).

A brief description of each of these piezoelectric materials, or related compositional families, is presented in this section. With the exception of quartz, all are ferroelectric.

5.1 Quartz

Quartz (SiO₂) is one of the earliest piezoelectric materials used in electronic devices. Originally, natural quartz crystals were used, but now have been widely replaced by hydrothermally-grown synthetic quartz. Because of its low mechanical loss (high Qm), narrow bandwidth, and highly temperature-stable resonant frequency, quartz is the material of choice for timing standards and monolithic filters in communication equipment. However, as seen in Table 3, the piezo ‘d’ coefficient is relatively small and thus
### TABLE 3

Reported Room Temperature Electrical Properties of Commercial High Temperature Piezoelectric Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>Curie point $T_c$ (°C)</th>
<th>Dielectric constant $K_{12}$ ($10^{-12}$ C/N)</th>
<th>Piezoelectric strain constant $d_{33}$</th>
<th>Piezoelectric voltage constant $e_{33}$</th>
<th>Electromechanical coupling constant $k_{33}$ ($10^{12}$ V/m/N)</th>
<th>Mechanical quality $Q_m$</th>
<th>Resistivity $20°C$ (Ω·cm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(Zr, Ti)O$_3$ (Soft PZT)</td>
<td>Perovskite</td>
<td>330</td>
<td>1800</td>
<td>417</td>
<td>710</td>
<td>25 $d_{33}$, 41 $d_{15}$ $e_{33}$</td>
<td>53 $e_{33}$</td>
<td>75 $k_{33}$, 30 $k_{15}$</td>
<td>N-21$^{16}$</td>
</tr>
<tr>
<td>(BaPb)NB$_2$O$_6$ (BPN)</td>
<td>Tungsten</td>
<td>400</td>
<td>300</td>
<td>85</td>
<td>100</td>
<td>32 $d_{33}$, 46 $d_{15}$ $e_{33}$</td>
<td>45 $e_{33}$</td>
<td>15 $k_{33}$, 1 $k_{15}$</td>
<td>K-81$^{23}$</td>
</tr>
<tr>
<td>PbTiO$_3$ (PT)</td>
<td>Perovskite</td>
<td>470</td>
<td>190</td>
<td>56</td>
<td>68</td>
<td>33 $d_{33}$, 32 $d_{15}$ $e_{33}$</td>
<td>45 $e_{33}$</td>
<td>1300 $k_{33}$, 10 $k_{15}$</td>
<td>LTT-3$^{38}$</td>
</tr>
<tr>
<td>Na$_2$Bi$_4$Ti$<em>4$O$</em>{13}$ (NBT)</td>
<td>Bismuth</td>
<td>-600</td>
<td>140</td>
<td>18</td>
<td>15</td>
<td>15 $d_{33}$</td>
<td>100 $k_{33}$, 1000 $k_{15}$</td>
<td>1 $k_{33}$, 1 $k_{15}$</td>
<td>1 $k_{33}$, 1 $k_{15}$</td>
</tr>
<tr>
<td>LiNbO$_3$ (LN)</td>
<td>Corundum</td>
<td>1150</td>
<td>25</td>
<td>6 $d_{33}$, 69 $d_{15}$</td>
<td>23 $d_{33}$, 91 $d_{15}$ $e_{33}$</td>
<td>23 $d_{33}$, 91 $d_{15}$ $e_{33}$</td>
<td>NR</td>
<td>10$^3$ $k_{33}$, 1000 $k_{15}$</td>
<td>7$^{27}$</td>
</tr>
<tr>
<td>SIO$_2$</td>
<td>α-Quartz</td>
<td>573</td>
<td>4·5</td>
<td>2($d_{33}$)</td>
<td>50</td>
<td>NR $e_{33}$, 50 $e_{15}$ $k_{33}$</td>
<td>NR</td>
<td>10$^3$ $k_{33}$, 1000 $k_{15}$</td>
<td>1$^{24}$</td>
</tr>
</tbody>
</table>

*High temperature acoustic and vibration sensors: A review*
<table>
<thead>
<tr>
<th>Material</th>
<th>$T_a$ (°C)</th>
<th>Vibration mode (j)</th>
<th>$g$ (RT)$^b$ (×10$^{-5}$ Vm/N)</th>
<th>TCF (ppm/°C)</th>
<th>$\rho$ (Ω-cm)</th>
<th>$\varepsilon_r$ (10 kHz)</th>
<th>tan $\delta$ (10 kHz)</th>
<th>RC (s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT (DOD II)</td>
<td>360</td>
<td>[33]</td>
<td>15 (25)</td>
<td>+200</td>
<td>$10^{12}$</td>
<td>3000</td>
<td>250</td>
<td>N-21$^{26}$</td>
<td></td>
</tr>
<tr>
<td>(Ba,Pb)Nb$_2$O$_5$</td>
<td>400</td>
<td>[33]</td>
<td>24 (30)</td>
<td>-135</td>
<td>$10^7$</td>
<td>530</td>
<td>0.036</td>
<td>0.0005</td>
<td>K-81$^{23}$</td>
</tr>
<tr>
<td>PbTiO$_3$</td>
<td>450</td>
<td>[15]</td>
<td>21 (29)</td>
<td>-97</td>
<td>$2 \times 10^5$</td>
<td>1000</td>
<td>0.35</td>
<td>0.00002</td>
<td>LTT-3$^{28}$</td>
</tr>
<tr>
<td>Na$_2$Bi$_5$Ti$<em>4$O$</em>{15}$</td>
<td>600</td>
<td>[33]</td>
<td>10 (18)</td>
<td>-118</td>
<td>$3 \times 10^3$</td>
<td>262</td>
<td>0.10</td>
<td>0.007</td>
<td>K-15$^{25}$</td>
</tr>
<tr>
<td>LiNbO$_3$</td>
<td>1150</td>
<td>[15]</td>
<td>93 (99)</td>
<td>-76</td>
<td>$3 \times 10^7$</td>
<td>100</td>
<td>0.001</td>
<td>0.0003</td>
<td>27</td>
</tr>
<tr>
<td>Sr$_2$Nb$_2$O$_7$</td>
<td>823</td>
<td>[24]</td>
<td>5 (6)</td>
<td>-74</td>
<td>$4 \times 10^9$</td>
<td>40</td>
<td>0.10</td>
<td>0.01</td>
<td>20</td>
</tr>
</tbody>
</table>

$^a$ PZT and BPN were evaluated at approximate maximum use temperatures, the others at 400°C.

$^b$ Room temperature values (RT) also shown for the voltage constant ($g$).
the amount of electric charge that can be generated is low. Although piezoelectric α-quartz has a transition temperature of 573°C, its use temperature is normally limited to 350°C. Above that temperature the crystal structure is subject to twinning, destroying its piezoelectric properties.24

5.2 Lead zirconate titanate

Lead zirconate titanate (Pb(ZrTi)O₄(PZT)) has the perovskite structure and is a solid solution of tetragonal PbTiO₃(PT) and orthorhombic PbZrO₃(PZ). Because of the large number of polarization directions available, compositions near the morphotropic phase boundary at approximately 53:47 PZ to PT are easily poled to high remanent polarization and exhibit extremely high values of electromechanical coupling coefficients and electrical permittivity. Because of its superior piezoelectric properties and higher operating temperature, PZT has largely replaced barium titanate (BT)—$T_s \sim 130°C$, the first widely used ferroelectric, in all but the lowest cost commercial products. Useful variations in properties of PZT can be obtained by compositional additives. Niobium-doped PZT (DOD Type II) is used extensively in accelerometers, hydrophones (underwater microphones), and acoustic emission instruments. Although its electrical resistivity and $RC$ time constant remain quite high
up to a $T_c$ of 360°C (Table 4 and Fig. 8), its use is kept well under 200°C because of its tendency to age very rapidly, leading to depoling.11

5.3 Lead titanate

Lead titanate (PbTiO$_3$(PT)) the solid solution end member of PZT family, has a $T_c$ of about 490°C. As in the case of PZT, a large number of modifications have been developed to optimize specific electrical and mechanical characteristics. Many commercial compositions of PT are doped with samarium or calcium for use in hydrophones, but this has the effect of lowering the $T_c$ to around 240°C. Compositions, doped with other elements, have $T_c$ values near 490°C and have found applications in knock sensors for automobile engines. The higher operating temperature of PT allows it to be mounted closer to the combustion chamber, thus giving a faster response time as compared to PZT. The data presented in Tables 3 and 4 and Fig. 8 reflects the latter composition. Evaluation at 400°C has shown it to have a resistivity of only about $10^5$ Ω-cm. Such a low value would adversely affect the $RC$ time constant.

5.4 Lead metaniobate

Lead metaniobate (PbNb$_2$O$_6$(PN)) belongs to the tungsten-bronze family. Because of its low $Q_m$ (wide bandwidth) and relatively high $d_{33}$ to $d_{31}$ ratio (high degree of anisotropy), PN finds its greatest use in transducers in NDT and medical diagnostic imaging. Commercial PN compositions are modified to enhance specific electrical characteristics but at the expense of the $T_c$. A commonly used composition contains about 10% Ba(BPN) and has a $T_c$ of about 400°C. Although BPN is reported to resist depoling up to its $T_m$, limitations are imposed by its high conductivity above 300°C. Figure 8 reveals that BPN exhibits the lowest resistivity of the materials tested. Other problems associated with this material are its high level of porosity and relatively low mechanical strength.

5.5 Bismuth titanate

Bismuth titanate (Bi$_4$Ti$_3$O$_{12}$) is the titular compound of bismuth layer structure ferroelectrics (BLSF). Modification by one or more of a large number of other elements, to enhance dielectric and piezoelectric properties, is also common. A member of the family, reported to have favorable piezoelectric properties, high resistivity and high $T_c$ (>600°C), is Na$_{0.3}$Bi$_4$Ti$_3$O$_{15}$, (NBT). Commercially available, it is used in accelerometers operated at temperatures up to 400°C. The strongest mode of vibration in NBT is the [33] mode but $d_{33}$ and $g_{33}$ are somewhat lower
than many of the perovskite ferroelectrics previously discussed (see Table 3). Nevertheless, the high $T_c$ and high resistivity make NBT an attractive, moderately high-temperature piezoelectric.

Although not commercially available, other complex variations of BLSF compounds have been reported to have Curie temperatures of over 800°C. Representative of this group is Bi$_3$TiNbO$_x$ for which room temperature values of $d_{33}$, and $g_{33}$ were reported to be near those of NBT. To date, little else has been reported about other properties, particularly at high temperature.

Unlike previously mentioned ferroelectric ceramics, BLSF materials can be made with grains having a plate-like structure. In ceramics formed and fired by conventional processes, these grains are oriented in a more or less random fashion, which leaves only a limited number of crystallographic orientation directions available for polarization due to the low symmetry of the structure. The achievement of an optimum degree of remnant polarization in polycrystalline ceramics necessitates the use of some mechanism to provide grain orientation. By employing hot forging techniques, researchers have prepared samples of several BLSF family members which display a high degree of texturing. The textured samples exhibited a twofold increase in coupling coefficient $k_{33}$ and piezoelectric constant $d_{33}$ over those from conventional sintering.

5.6 Lithium niobate

Lithium niobate (LiNbO$_3$(LN)) has the corundum structure and a reported Curie point near 1150°C. Single crystals are grown from a melt using the Czochralski technique. Single crystals are preferred because of the higher piezoelectricity, as well as difficulties encountered in conventional sintering of the polycrystalline form. As with polycrystalline ferroelectrics, single crystals of LiNbO$_3$ exhibit a multidomain structure, and must be polarized. This is accomplished by applying relatively small electric field (1 V/cm DC) at a temperature just below the $T_c$ thus converting the structure to single domain. The polarized crystal is then sliced along the desired axis indicated for the application, and the faces polished. For accelerometers, electrodes are usually applied parallel to the poling axis to take advantage of the greater value of the $d_{33}$ piezoelectric constant and to eliminate pyroelectric effects. The voltage output of LN ($g_{33} = 91 \times 10^{-3}$ Vm/N) is significantly larger than those of the other piezoelectric materials listed in Table 3 due to the inherently low dielectric constant. Sensitivity remains high up to 400°C (Table 4) but resistivity is the limiting factor for use above 650°C (Fig. 8).

The tantalum analog, LiTaO$_3$, exhibits many of the same characteristics
of LiNbO$_3$; however, the $T_c$ (720°C) and piezoelectric constants are somewhat lower, thus offers no apparent advantage for high-temperature acoustic sensors.

6 NEW HIGH-TEMPERATURE PIEZOELECTRIC MATERIALS

In general, the ferroelectric ceramics discussed thus far are limited to temperatures of approximately $T_c/2$. Therefore, applications requiring yet higher temperatures than those just presented, require other materials such as ferroelectrics with higher Curie temperatures, oriented polar non-ferroelectric materials, non-polar piezoelectric single crystals, or piezoelectric thin films. Several novel materials currently under investigation are presented below.

6.1 Perovskite layer structure (PLS) ferroelectrics

PLS ferroelectrics have the general formula $A_2B_2O_7$ and possess an anisotropic layered structure similar to the BLSF family. Single crystals of the two most recognized compounds, $\text{Sr}_2\text{Nb}_2\text{O}_7$ and $\text{La}_2\text{Ti}_2\text{O}_7$, possess the highest known ferroelectric Curie temperatures, 1342°C and 1500°C respectively. The use of solid solutions with $\text{Sr}_2\text{Ta}_2\text{O}_7$ ($T_c = -107^\circ C$), to adjust $T_c$ of the parent compound to $<900^\circ C$, aided poling and the subsequent piezoelectricity. One compound, $\text{Sr}_2(\text{Nb}_{0.5}\text{Ta}_{1.0})_2\text{O}_7$, had a $T_c$ of 820°C and demonstrated the ability to resist depoling at temperatures as high as 650°C. The electromechanical properties for $\text{Sr}_2(\text{Nb}_{0.5}\text{Ta}_{1.0})_2\text{O}_7$ are listed in Table 4. Although the room temperature $d$-coefficient is low ($d_{33} = 2.6 \times 10^{-12}$ C/N), a value similar to that of quartz, the piezoelectric voltage constant at 400°C is significant ($g_{33} = 6.3 \times 10^{-3}$ Vm/N). From Fig. 8 it is also seen that the hot-forged PLS ceramics have the highest resistivity at elevated temperatures of any of the materials tested. By using compositions of $\text{Sr}_2(\text{Nb}_{1-x}\text{Ta}_{3x})_2\text{O}_7$ with a higher Nb content, the $T_c$ can be increased to 1200°C with no loss of resistivity. Efforts to optimize the composition and processing variables are currently under way and may lead to improved properties.
6.2 Polar glass ceramics

A classification of piezoelectric materials, totally different from any previously discussed, exists in the form of polar glass ceramics. These non-ferroelectric compounds require single crystal growth or polar texturing for piezoactivity. One successful technique for obtaining oriented grains is the texturing of microscopic recrystallized polar crystals in an amorphous
glassy matrix. Using a controlled thermal gradient technique, the polar material Ba₂TiSi₂O₉ (fresonite) was recrystallized from a glass of the composition 2BaO 3SiO₂TiO₂ resulting microstructure that contained polar oriented grains. With room temperature values of $d_{13}$ and $g_{13}$ were $7 \times 10^{-12}$ C/V and $88 \times 10^{-3}$ Vm/N respectively, and relatively low density (4.01 g/cm³), these composite materials may be of interest for hydrophone applications.

It has been suggested that polar glass ceramics may also be useful for high temperature piezoelectric devices. Since they are polar, but not ferroelectric, poling is unnecessary and, consequently, there is no problem with depoling or aging effects. Foreseen problems do exist, though, including softening of the glassy phase and possible ferroelastic phase transitions that would restrict the high-temperature capabilities. Further evaluation of the electrical properties, including resistivity at high temperatures, is needed before these materials can be commercialized.

6.3 AIN thin films

In recent years, numerous studies have been made of the piezoelectric properties of thin films of several materials, including the ferroelectrics previously discussed. Thin films of non-ferroelectric materials are also of great interest, including aluminium nitride (AIN). Because of its exceptionally high thermal conductivity and dielectric breakdown strength, polycrystalline (AIN) is an important ceramic material used in substrates for hybrid microelectronics, but in the bulk form exhibits no piezoelectric activity. However, when properly oriented on a compatible substrate, AIN thin films exhibit piezoelectric properties which have been studied for their potential use as pressure transducers, speakers, and SAW devices.

Of most interest for this report are the high-temperature piezoelectric properties of AIN thin films. A recent paper reported that an AIN SAW device deposited on a fused quartz substrate, operating at 60–100 MHz, exhibited piezoelectric responses at temperatures up to 1150°C. Other reports on chemical vapor deposited (MOCVD) AIN thin films have shown room temperature $d_{33}$ values of $5.5 \times 10^{-12}$ Vm/N (about the same as LiNbO₃) and a dielectric constant $K_{33}$ of 12. Tsubouchi and Mikosheva reported room temperature resistivity values of $10^{16}$ Ω-cm, a value higher than any other piezoelectric material discussed in this paper. With this combination of very high temperature operation, high resistivity, and reasonable piezoelectric coefficients, it seems that AIN thin films warrant further investigation.
High-temperature technology is of major importance for chemical and material processing, automotive, aerospace, and power generating industries to name just a few. For many, the primary benefit of operating at higher temperatures is the direct cost savings associated with increased efficiency in fuel conversion. In a related matter, the development of advanced structural materials such as silicon nitride and carbon–carbon composites promotes a need for high-temperature electronic materials to monitor processing of these systems. This is exemplified by the recent organization of the First International High Temperature Electronics Conference by Sandia National Laboratory and Wright Laboratory.

Along with semiconductor, capacitor, magnetic, and packaging materials, electromechanical transducing materials are required to sense strains, vibrations, and noise under severe thermal conditions. Of the several different types of acoustic and strain sensors investigated, including accelerometers, strain gauge, air gap, eddy current, buffer rod, and fiber optic, piezoelectric types offer the best candidates when one considers sensitivity, cost, and design.

Figure 10 summarizes the maximum use temperature of widely commercial piezoelectric materials and the projected values of two experimental ones. If an operating temperature of 400°C or greater is required, the number of available sensor materials is clearly limited. If an operating

![Fig. 10. Approximate maximum temperature of operation for piezoelectric ceramics. Most are estimated by combined consideration of the ferroelectric Curie temperature, sensitivity, and measured electrical resistivity. Others are known with a higher degree of certainty such as barium titanate (BT) limited by its Tc of 123°C, lead zirconate titanate (PZT) known to experience accelerated depoling at 200°C and quartz (SiO2) with a maximum use temperature of 350°C.](image-url)
temperature 750°C is chosen, there is no commercial material available. It is reasonable to assume that there now exists a need for vibration sensors that can function at 750°C, or even at 1000°C, and that the need will be even more pressing in the future. The design of such sensors presents a great challenge and will require the development of new materials and novel processing techniques.

This paper has discussed two options for very high temperature piezoelectric materials. The first was the family of PLS ferroelectrics, with the highest known $T_c$ (some greater than 1500°C). The second was non-ferroelectric AlN thin film with a reported operating temperature of 1150°C. New ferroelectric compounds, also with very high $T_c$, have been predicted based on the Abrahams–Kurtz–Jameson relationship and an extensive inorganic crystal structure database. This study, and other computer assisted studies of materials, may well identify the next generation of high-temperature vibration sensor materials.

**ACKNOWLEDGMENT**

The authors wish to thank NASA-Lewis for their support under grant number NA63-125.

**REFERENCES**

24. Kistler Instruments AG Winterthur, Switzerland, 1989, General Catalog.
26. Token Corp. Tokyo, Japan, Piezoelectric Ceramic Catalog.
37. Takenaka, T. & Sakata, K., Grain oriented and Mn-doped (NaBi)_{0.97}Ca_{0.03}Bi_{2}Ti_{2}O_{7} ceramics for piezo- and pyro sensor materials. *Sensors and Materials*, 1 (1988) 35-46.
42. Turner, R. C., Work in progress.
12 Ferroelectric Ceramics

Kenji Uchino

Materials Research Laboratory, Pennsylvania State University, University Park, PA, U.S.A.

List of Symbols and Abbreviations .................................................. 637
12.1 General View of Ferroelectrics ............................................. 639
12.1.1 Crystal Structure and Ferroelectricity ................................ 639
12.1.2 Origin of Spontaneous Polarization ................................. 640
12.1.3 Origin of Field Induced Strain ....................................... 642
12.1.4 Electrooptic Effect .................................................. 643
12.1.5 Example of a Ferroelectric .......................................... 644
12.1.6 Applications of Ferroelectrics ..................................... 645
12.2 High-Permittivity Dielectrics ........................................... 646
12.2.1 Relaxor Ferroelectrics ............................................ 646
12.2.2 Multilayered Capacitors (MLC) ................................... 648
12.3 Pyroelectric Devices .................................................. 649
12.3.1 Temperature/Infrared-Light Sensors ............................... 649
12.3.2 Infrared Image Sensors ........................................... 650
12.4 Piezoelectric Devices .................................................. 651
12.4.1 Piezoelectric Materials ........................................... 651
12.4.2 Piezoelectric Resonance .......................................... 654
12.4.3 Piezoelectric Transformers ...................................... 657
12.4.4 Piezoelectric Vibrators .......................................... 658
12.4.5 Ultrasonic Transducers ........................................... 658
12.4.6 Surface Acoustic Wave Devices .................................. 658
12.4.7 Piezoelectric Actuators ........................................... 659
12.4.7.1 Deformable Mirrors ............................................. 661
12.4.7.2 Impact Dot-Matrix Printers .................................... 661
12.4.7.3 Ultrasonic Motors ............................................. 662
12.5 Electrooptic Devices .................................................. 664
12.5.1 Transparent Electrooptic Ceramics ................................ 664
12.5.2 Bulk Electrooptic Devices ........................................ 665
12.5.3 Waveguide Modulators ........................................... 666
12.6 Positive Temperature Coefficient (PTC) Materials ............... 668
12.6.1 The PTC Phenomenon ............................................. 668
12.6.2 PTC Thermistors .................................................. 669
12.6.3 Grain Boundary Layer Capacitors ................................ 669
12.7 Conclusions .......................................................... 670
12.8 Appendix 1: Tensor Representation of Physical Properties ..... 670
12.8.1 Tensor Representation .......................................................... 670
12.8.2 Crystal Symmetry and Tensor Form ........................................ 671
12.8.3 Reduction of the Tensor (Matrix Notation) ............................... 673
12.9 Appendix 2: Phenomenology of Ferroelectricity ........................... 674
12.9.1 Landau Theory of the Phase Transition ................................ 674
12.9.1.1 Second-Order Transition ............................................. 674
12.9.1.2 First-Order Transition ............................................... 674
12.9.2 Phenomenology of Electrostriction ....................................... 675
12.9.2.1 Case I: \( X = 0 \) ................................................... 675
12.9.2.2 Case II: \( X \neq 0 \) .................................................. 676
12.10 References .............................................................................. 676
**List of Symbols and Abbreviations**

- $c_p$: specific heat
- $C$: Curie–Weiss constant
- $d$: piezoelectric coefficient
- $D$: electric displacement
- $E$: electric field
- $f_A$: antiresonance frequency
- $f_R$: resonance frequency
- $F$: Landau free energy
- $g$: piezoelectric coefficient, secondary electrooptic coefficient
- $I$: light intensity
- $k$: electromechanical coupling factor
- $k, k'$: force constants
- $L$: optical pathlength
- $M$: electrostrictive coefficient
- $n$: refractive index
- $p$: pyroelectric coefficient
- $P$: dielectric polarization
- $P_s$: spontaneous polarization
- $Q$: electrostrictive coefficient
- $Q_M$: mechanical quality factor
- $r$: primary electrooptic coefficient, voltage rise ratio of a piezoelectric transformer
- $s$: elastic compliance
- $T_0$: Curie–Weiss temperature
- $T_C$: Curie temperature
- $u$: displacement of an ion from the equilibrium position
- $U$: energy
- $v$: sound velocity
- $W_{\text{dip}}$: energy of the dipole moment
- $W_{\text{elas}}$: elastic energy of displacement
- $x$: strain
- $x_s$: spontaneous strain
- $X$: stress
- $\alpha$: ionic polarizability
- $\gamma$: Lorentz factor
- $\Gamma$: phase retardation
- $\varepsilon$: relative permittivity
- $\varepsilon_0$: vacuum permittivity
- $\mu$: dipole moment of the unit cell of a crystal
- $\phi$: barrier height of the Schottky barrier
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-TGS</td>
<td>deuterated triglycine sulphate</td>
</tr>
<tr>
<td>GBL</td>
<td>grain boundary layer</td>
</tr>
<tr>
<td>MLC</td>
<td>multilayered capacitor</td>
</tr>
<tr>
<td>OA</td>
<td>office automation</td>
</tr>
<tr>
<td>PLZT</td>
<td>(Pb, La)(Zr, Ti)O₃</td>
</tr>
<tr>
<td>PMN</td>
<td>lead magnesium niobate</td>
</tr>
<tr>
<td>PTC</td>
<td>positive temperature coefficient</td>
</tr>
<tr>
<td>PTCR</td>
<td>positive temperature coefficient of resistivity</td>
</tr>
<tr>
<td>PVFD</td>
<td>polyvinylidene fluoride</td>
</tr>
<tr>
<td>PZT</td>
<td>lead zirconate titanate</td>
</tr>
<tr>
<td>rpm</td>
<td>revolutions per minute</td>
</tr>
<tr>
<td>SAW</td>
<td>surface acoustic wave</td>
</tr>
<tr>
<td>VTR</td>
<td>video tape recorder</td>
</tr>
</tbody>
</table>
12.1 General View of Ferroelectrics

12.1.1 Crystal Structure and Ferroelectricity

In so-called dielectric materials, the constituent atoms are considered to be ionized to a certain degree and are either positively or negatively charged. In such ionic crystals, when an electric field is applied, cations are attracted to the cathode and anions to the anode due to electrostatic interaction. The electron clouds also deform, causing electric dipoles. This phenomenon is called the electric polarization of the dielectrics, and the polarization is expressed quantitatively as the sum of the electric dipoles per unit volume (C/m²). Figure 12-1 shows schematically the origin of the electric polarization. There are three kinds: electron, ion and dipole reorientation-related polarizations.

Compared with vacuum capacitors, dielectric capacitors can store more electric charge due to the dielectric polarization \( P \) as shown in Fig. 12-2. The physical quantity corresponding to the stored electric charge per unit area is called the electric displacement \( D \), and is related to the electric field by the following expression:

\[
D = \varepsilon_0 E + P = \varepsilon \varepsilon_0 E
\]  

(12-1)

Here, \( \varepsilon_0 \) is the vacuum permittivity \( (= 8.854 \times 10^{-12} \text{ F/m}) \), \( \varepsilon \) is the material's relative permittivity (also simply called permittivity or dielectric constant, and in general it is a tensor).

Depending on the crystal structure, in some crystal lattices, the centers of the positive and negative charges do not coincide even without the application of external electric field. In this case, it is said that there exists spontaneous polarization in the crystal, and, especially when the polarization of the dielectric can be altered by an electric field, it is called ferroelectric.

Not every dielectric can be a ferroelectric. Crystals can be classified into 32 point groups according to their crystallographic symmetry, and these point groups can be divided largely into two classes, one with a center of symmetry and the other without. There are 21 point groups which do not have a center of symmetry. In crystals belonging to 20 of these point groups [except for the point group (432)], positive and negative charges appear on surfaces when stresses are applied. These materials are known as piezoelectrics. Pyroelectricity is the phenomenon in which, because of the temperature dependence of the spontaneous polarization, as the temperature of the crystal is changed, electric charges cor-
responding to the change of the spontaneous polarization appear on the surface of the crystal. Among the pyroelectric crystals, those whose spontaneous polarization can be reversed by an electric field (not exceeding the breakdown limit of the crystal) are called ferroelectrics. There is some ambiguity in this definition. In order to establish ferroelectricity, it is necessary to apply an electric field on a pyroelectric material and experimentally ascertain the polarization reversal. Table 12-1 shows the classification of the point groups.

### 12.1.2 Origin of Spontaneous Polarization

Why is it that crystals which, from a consideration of the elastic energy, should be stable by being non-polar, still experience the shifting of cations and anions and become spontaneously polarized? The reason is briefly explained below. For simplicity, let us assume that dipole moments result from the displacement of one kind of ion A (electric charge $q$) relative to the crystal lattice. Consider the case in which the polarization is caused by all the A ions being displaced equally in a lattice. It follows that, on any individual A ion, there exists a local field from the surrounding polarization $P$, even if there is no external field. The concept of the local field is shown schematically in Fig. 12-3. It can be shown that:

$$E_{loc} = [\gamma/(3\varepsilon_0)] P$$  \hspace{1cm} (12-2)

### Table 12-1: Crystallographic classification with respect to crystal centrosymmetry and polarity.

<table>
<thead>
<tr>
<th>Polarity</th>
<th>Centrosymmetry</th>
<th>Number of point groups</th>
<th>Crystal class</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-polar (22)</td>
<td>O ( (11) )</td>
<td>11</td>
<td>Cubic Hexagonal Tetragonal Rhombohedral Orthorhombic Monoclinic Triclinic</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$m3m$ $m3$ 6/mmm 6/m 4/mmm 4/m $D_{4h}$ $C_{4v}$ $D_{2d}$ $C_{2v}$ $D_{2h}$ $C_{2h}$ $D_{2d}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>432 622 422 $D_6$ 6 4 3 222</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$T_d$ $D_{3d}$ $D_{2d}$</td>
</tr>
<tr>
<td>Polar (pyro) (10)</td>
<td>X ( (21) )</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$6mm$ 6 4/mmm 4 3m 3 2mm $C_6$ $C_4$ $C_4$ $C_3$ $C_{2v}$ $C_{2d}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$C_{6v}$ $C_3$ $C_2$</td>
</tr>
</tbody>
</table>

* Piezoelectric crystals are those in the area enclosed by the thick line.
This is the driving force of the ion shift. Here \( \gamma \) is called the Lorentz factor. For an isotropic and a cubic system, it is known that \( \gamma = 1 \) (Kittel, 1966). \( \varepsilon_0 \) is the permittivity in vacuum and is equal to \( 8.854 \times 10^{-12} \) F/m. If the ionic polarizability of ion A is \( \alpha \), then the dipole moment of the unit cell of this crystal is:

\[
\mu = \left[ \frac{\alpha \gamma}{3 \varepsilon_0} \right] P
\]

(12-3)

The energy of this dipole moment (dipole-dipole coupling) is

\[
W_{\text{dip}} = -\mu \cdot E^{\text{loc}} = -\left[ \frac{\alpha \gamma^2}{9 \varepsilon_0^2} \right] P^2
\]

(12-4)

Per unit volume, it is:

\[
W_{\text{dip}} = N w_{\text{dip}} = -\left[ \frac{N \alpha \gamma^2}{9 \varepsilon_0^2} \right] P^2
\]

(12-5)

On the other hand, when the A ions are displaced from their nonpolar equilibrium positions, the elastic energy also increases. If the displacement is \( u \), and the force constants \( k \) and \( k' \), then the increase of the elastic energy per unit volume can be expressed as:

\[
W_{\text{elas}} = N \left( \frac{k}{2} u^2 + \frac{k'}{4} u^4 \right)
\]

(12-6)

Here, \( k' \) (> 0) is the higher-order force constant. It should be noted that in pyroelectrics, \( k' \) plays an important role in determining the magnitude of the dipole moment. By rewriting Eq. (12-6) using:

\[
P = N q u \quad (q \text{ is the electric charge})
\]

(12-7)

Combining with Eq. (12-5), the total energy can be expressed as follows (see Fig. 12-4):

\[
W_{\text{tot}} = W_{\text{dip}} + W_{\text{elas}} = \left( \frac{k}{2 N q^2} - \frac{N \alpha \gamma^2}{9 \varepsilon_0^2} \right) P^2 + \frac{k'}{4 N^3 q^4} P^4
\]

From this, one can see that if the coefficient of the harmonic term of the elastic energy is equal or greater than the coefficient of the dipole-dipole coupling, then \( P = 0 \), i.e., the A ions are stable and remain at their non-polar equilibrium positions. Otherwise, a shift from the equilibrium position \( \{ P^2 = [2 N \alpha \gamma^2/(9 \varepsilon_0^2) - k(N q^2)]/[k'(N^3 q^4)] \} \) is stable. In the perovskite-type crystal structure (as in barium titanate) as described in the next section, it is thought that because of the occurrence of a larger Lorentz factor \( \gamma \) (\( \approx 10 \)) (Kinase et al., 1969) than found for other crystal structures, spontaneous polarization can occur more easily.
two types of strain (defined by the ratio $\Delta L/L$: the amount of deformation with respect to the original length) that may be induced by an electric field depending on the nature of the interaction "springs" between the ions which is, in turn, determined by the crystal structure (Uchino et al., 1983). As shown in Fig. 12-5a, in crystals where there is no centrosymmetry, strain, $x$, is generated in proportion to the electric field $E$. This is the converse piezoelectric effect, and the tensor quantity, $d$, defined by the relationship

$$x = dE$$  \hspace{1cm} (12-9) 

is referred to as the piezoelectric coefficient. On the other hand, in centrosymmetric crystals, as shown in Fig. 12-5b, the expansion and contraction of the "spring" are such that the net response is nearly zero. However, the anharmonic nature of the "spring" motion will still bring about a small induced strain that is proportional to the square of the electric field $E$. This is referred to as the electrostriction effect which is expressed in terms of the strain, $x$, the applied electric field, $E$, and the electrostriction coefficient, $M$, as:

$$x = M E^2$$  \hspace{1cm} (12-10) 

The system pictured in Fig. 12-5a also possesses a spontaneous bias of electrical charge, or a spontaneous polarization. When a large reverse bias electric field is applied to a crystal that has a spontaneous polarization in a particular polar direction, a transition "phase" is formed which is another stable crystal state in which the relative positions of the ions are reversed (in terms of an untwinned single crystal, this is equivalent to rotating the crystal 180° about an axis perpendicular to its polar axis). This transition, referred to as polarization reversal, also causes a remarkable change in strain. This particular class of
12.1 General View of Ferroelectrics

Generally, substances are referred to as ferroelectrics, as mentioned in Sec. 12.1.1. Generally, what is actually observed as a field-induced strain, is a complicated combination of the three basic effects just described.

12.1.4 Electrooptic Effect

Since light is an alternating electromagnetic wave with electric and magnetic field directions crossing each other, it induces electric polarization in a dielectric crystal and the light itself is influenced by the crystal. The alternating frequency of the light is so high (≈ 10^{15} \text{ Hz}) that only the electronic polarization should follow the field change, and the relative permittivity of the crystal is small, not exceeding 10. The permittivity \( \varepsilon \) at this high frequency is related to the refractive index \( n \) by the following equation:

\[
\varepsilon = n^2 \quad (12-11)
\]

When an external electric field is applied to the crystal, ion shift is induced, deforming the shape of the electron cloud, and consequently the refractive index is changed. This phenomenon is called the electrooptic effect.

Generally, refractive indices are symmetrical 2-R tensor quantities and represented by using a refractive indicatrix (Eq. 12-12), where \( n_1, n_2 \) and \( n_3 \) are principal refractive indices.

\[
\frac{x^2}{n_1^2} + \frac{y^2}{n_2^2} + \frac{z^2}{n_3^2} = 1 \quad (12-12)
\]

With the application of an electric field, the change in refractive index is given by an expansion expression:

\[
1/n_i^2(E) - 1/n_i^2(0) = \sum r_{ijk} E_k + 1/2 \sum \theta_{ijk} E_k E_l \quad (12-13)
\]
Here \( r_{ijk} \) is a primary electrooptic coefficient \((\text{Pockel's effect})\) and \( g_{ijkl} \) is a secondary coefficient \((\text{Kerr effect})\).

Considering a paraelectric phase of a perovskite crystal \((m\overline{3}m)\) as an example, the Kerr coefficients are represented in the following matrix:

\[
\begin{bmatrix}
 g_{11} & g_{12} & g_{12} & 0 & 0 & 0 \\
g_{12} & g_{11} & g_{12} & 0 & 0 & 0 \\
g_{12} & g_{12} & g_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & g_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & g_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & g_{44}
\end{bmatrix}
\]

Then, the refractive indicatrix under the electric field applied along \( z \)-direction can be expressed as:

\[
x^2 + y^2 = \frac{n_0^2}{n_0^2 \left[1 - \left( \frac{n_0^2}{2} \right) g_{12} E_z^2 \right]^2} + \frac{z^2}{n_0^2 \left[1 - \left( \frac{n_0^2}{2} \right) g_{11} E_z^2 \right]^2} = 1
\]

(12-14)

When light is transmitted along the \( y \)-direction, the phase retardation \( \Gamma_r \) between an ordinary and an extraordinary light is given by:

\[
\Gamma_r = \frac{2\pi}{\lambda} \frac{n_0^2}{2} (g_{12} - g_{11}) L \left( \frac{V_z}{d} \right)^2
\]

(12-15)

\( d \) is the electrode gap and \( L \) is the optical path length (see Fig. 12-6). Putting a crystal between crossed polarizers arranged at the 45° direction with respect to \( z \)-axis, the output light intensity can be modulated as a function of applied voltage in the following way:

\[
I = I_0 \sin^2 \left( \frac{\Gamma_r}{2} \right) = \frac{1}{2} I_0 (1 - \cos \Gamma_r)
\]

(12-16)

This is the principle of a light shutter/valve, and the voltage required for the first intensity maximum (i.e., \( \Gamma_r = \pi \)) is essential and called the half-wavelength voltage.

12.1.5 Example of a Ferroelectric

A typical ceramic ferroelectric is barium titanate, which is used here as an example to illustrate some properties of the ferroelectrics.

As shown in Fig. 12-7, BaTiO\(_3\) has a perovskite crystal structure. (See also Chap. 1, Secs. 1.3.3 and 1.6.2 of this Volume for a more complete description of the crystal structures of perovskites.) In the high-temperature paraelectric phase (nonpolar phase) there is no spontaneous polarization (the symmetry is \( O_h - m\overline{3}m \)). Below the transition temperature \( T_C \) called the
Curie temperature (about 120 °C), spontaneous polarization occurs, and the crystalline structure becomes slightly elongated, that is, tetragonal (C₄ᵥ - 4mm). Figure 12-8 shows schematically the temperature dependence of the spontaneous polarization \( P_s \) and permittivity \( \varepsilon \). \( P_s \) decreases with increasing temperature and vanishes at the Curie point, while \( \varepsilon \) tends to diverge near \( T_C \). Also, the reciprocal permittivity \( 1/\varepsilon \) is known to be linear with respect to the temperature in a wide range in the paraelectric phase (so-called Curie–Weiss law),

\[
\varepsilon = C/(T - T_0) \tag{12-17}
\]

Here \( C \) is the Curie–Weiss constant and \( T_0 \) the Curie–Weiss temperature. \( T_0 \) is slightly lower than exact transition temperature \( T_C \).

It is also known that the spontaneous polarization \( P_s \) and the spontaneous strain \( x_s \) follow the relationship:

\[
x_s = Q P_s^2 \tag{12-18}
\]

\( x_s \) decreases almost linearly with increasing temperature. In the case of \( \text{BaTiO}_3 \), in the ferroelectric phase, it exhibits the piezoelectric effect, while in the paraelectric phase, it is non-piezoelectric and exhibits the electrostrictive effect.

12.1.6 Applications of Ferroelectrics

Ferroelectric materials, especially polycrystalline ceramics, are very promising for varieties of application fields such as high-permittivity capacitors, pyroelectric sensors, piezoelectric/electrostrictive transducers, electrooptic devices and PTC thermistors.

For capacitor dielectrics, the peak dielectric constant around the transition (Curie) temperature is utilized, while the strong temperature dependence of the spontaneous polarization below \( T_C \) is applied for pyroelectric sensors. Piezoelectric materials are applicable in sensors and actuators. Pressure and acceleration sensors
are now commercially available in addition to conventional piezo-vibrators. Precision positioners and pulse drive linear motors have already been installed in precision lathe machines, semiconductor manufacturing apparatus and OA equipment etc. Recent topical development is found in ultrasonic motors. Electrooptic materials will become future key components in displays and optical-communication systems. For thermistor applications, semiconductive ferroelectric ceramics with a positive temperature coefficient (PTC) of resistivity due to a junction effect have been developed from barium-titanate-based materials.

12.2 High-Permittivity Dielectrics

12.2.1 Relaxor Ferroelectrics

There are two classes of ceramic capacitors: one is used for the thermal compensation of electrical circuits, using a TiO₂-based material, and the other is a high-permittivity capacitor with BaTiO₃- or Pb(Zr,Ti)O₃-based materials. Recently relaxor ferroelectrics such as Pb(Mg₁/₃Nb₂/₃)O₃ and Pb(Zn₁/₃Nb₂/₃)O₃ have been developed for very compact chip capacitors.

The reasons why these complex perovskites have been investigated intensively for capacitor applications are: (1) their very high permittivity, and (2) their temperature-insensitive characteristics (i.e., diffuse phase transition) in comparison with the normal perovskite solid solutions.

An intuitive crystallographic model has been proposed to explain the high permittivity of the disordered perovskites (Uchino, 1980). Figures 12-9a and 12-9b show the ordered and disordered structures for an A(B₁₁/₁₂B₁₁/₁₂)O₃ perovskite crystal. Assuming a rigid-ion model, a large “rattling” space is expected for the smaller B ions in the disordered structure because the large B ions prop open the lattice framework. Much less “rattling” space is expected in the ordered arrangement where neighboring atoms collapse systematically around the small B ions.

When an electric field is applied to a disordered perovskite, the B ions with a large rattling space can shift easily without distorting the oxygen framework. A larger polarization can be expected per unit magnitude of electric field. In other words, larger dielectric constants and larger Curie-Weiss constants. On the other hand, in ordered perovskites with a very small rattling space, the B ions cannot move easily without distorting the octahedron. A smaller permittivity and Curie-Weiss constant are expected.

The reason why the phase transition becomes diffuse in the relaxor ferroelectrics has not yet been clarified, although the “microscopic composition fluctuation” model is the most widely accepted (Kanzig, 1951; Rolov, 1963, Uchino et al., 1981). Considering the Känzig region (the minimum size region in order to cause a cooperative phenomenon, ferroelectricity) to be in the range of 100–1000 Å, disordered perovskites such as Pb(Mg₁/₃Nb₂/₃)O₃ reveal a local fluctuation of the distribution

![Figure 12-9. Crystal structure models of the A(B₁₁/₁₂B₁₁/₁₂)O₃ type perovskite: (a) ordered structure with a small rattling space and (b) disordered structure with a large rattling space (○ = A and ⋄ = B₈).](image-url)
of Mg$^{2+}$ and Nb$^{5+}$ ions. Figure 12-10 shows a computer simulation of the composition fluctuation in the $A(B_{11/2}B_{11/2})O_3$-type crystal calculated for various degrees of the ionic ordering. The fluctuation of the $B_f/B_n$ fraction $x$ obeys a Gaussian error distribution. H. B. Krause reported observing the short-range ionic ordering of Pb(Mg$^{1/3}$Nb$^{2/3}$)$_3$O$_3$ by electron microscopy (Krause et al., 1979). The high-resolution image in Fig. 12-11 reveals somewhat ordered (ion-ordered) islands in the range of 20–50 Å, each of which may have a slightly different transition temperature.

Another significant characteristic of these “relaxor” ferroelectrics is dielectric relaxation (frequency dependence of permittivity) from which their name originates. Temperature dependence of the permittivity in Pb(Mg$^{1/3}$Nb$^{2/3}$)$_3$O$_3$ is plotted in Fig. 12-12 for various measuring frequencies (Smolensky et al., 1961). With in-
creasing measuring frequency, the permittivity in the low-temperature (ferroelectric) phase decreases and the peak temperature shifts towards the higher frequency; this contrasts with normal ferroelectrics such as BaTiO₃ where the peak temperature hardly changes with frequency. This is probably caused by shallow multipotential-wells in a locally distorted perovskite cell due to the disordered ionic arrangement (Skanavi-type dielectric relaxation) (Skanavi et al., 1958), in addition to a ferroelectric phase transition phenomenon.

12.2.2 Multilayered Capacitors (MLC)

Multilayer structures have been developed as part of capacitor manufacturing aimed at the integration of electrical circuit components. Figure 12-13 schematically shows a multilayer capacitor chip. Thin sheets made by the *tape casting technique*, starting from a slurry of the dielectric powder and organic solvents, are coated with Pt or Ag-Pd paste to form electrodes, then several tens of sheets are stacked together and sintered. Finally, external electrodes, used to connect the chip with the circuit, are painted on.
12.3 Pyroelectric Devices

12.3.1 Temperature/Infrared-Light Sensors

Practical applications of the pyroelectric effect in temperature sensors and infrared-light detectors have gradually been promoted, providing, together with uses in piezoelectric resonators, of the commercial market for dielectric ceramics.

The merits of pyrosensors compared to other infrared-sensor materials such as semiconductors are summarized as follows:

(a) Wide range of response frequency
(b) Use at room temperature
(c) Quick response in comparison with other temperature sensors
(d) High-grade quality (optical-grade homogeneity etc.) of ceramic pyrosensors is unnecessary.

The principle on which the pyroelectric effect is based is the measurement of the spontaneous polarization change with temperature:

\[ j = \frac{\partial P}{\partial t} = (\varepsilon \cdot \frac{c_p}{\varepsilon} \cdot \frac{\partial T}{\partial t}) = \rho \cdot \left( \varepsilon \cdot \frac{1}{c_p} \right) \]

Here, \( p \) is denoted as a pyroelectric coefficient. Two typical electrode arrangements for pyrosensors are illustrated in Fig. 12-14: (a) face electrodes with the polarization direction parallel to the infrared irradiation, and (b) edge electrodes with the polarization direction perpendicular to the irradiation. The former type has higher efficiency, but requires a sophisticated fabrication process of transparent uniform electrodes for infrared light.

The pyroelectric sensor is a device transducing optical/thermal energy to electrical energy, and its efficiency or figure of merit is evaluated in several ways; \( p \), \( \rho/c_p \), or \( \rho/(c_p \cdot \varepsilon) \). This is because the temperature change of the sample is larger for the smaller \( c_p \) material under constant heating, and the voltage generated by a certain amount of pyrocharge becomes larger for the smaller \( \varepsilon \) (permittivity) material.

Table 12-2 lists the figures of merit of several pyroelectric materials. Improvement of the characteristics has been attempted by using composites of

<table>
<thead>
<tr>
<th>Material</th>
<th>( p ) (nC cm(^{-2} ) K(^{-1} ))</th>
<th>( \varepsilon )</th>
<th>( c_p ) (J cm(^{-3} ) K(^{-1} ))</th>
<th>( \rho/c_p ) (nA cm W(^{-1} ))</th>
<th>( \rho/(c_p \cdot \varepsilon) ) (V cm(^{-2} ) J(^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGS</td>
<td>30</td>
<td>50</td>
<td>1.7</td>
<td>17.8</td>
<td>4000</td>
</tr>
<tr>
<td>LiTaO(_3)</td>
<td>19</td>
<td>46</td>
<td>3.19</td>
<td>6.0</td>
<td>1470</td>
</tr>
<tr>
<td>Sr(<em>{1/2})Ba(</em>{1/2})Nb(_2)O(_6)</td>
<td>60</td>
<td>400</td>
<td>2.34</td>
<td>25.6</td>
<td>720</td>
</tr>
<tr>
<td>PLZT (6/80/20)</td>
<td>76</td>
<td>1000</td>
<td>2.57</td>
<td>29.9</td>
<td>340</td>
</tr>
<tr>
<td>PVF(_3)</td>
<td>3</td>
<td>11</td>
<td>2.4</td>
<td>1.3</td>
<td>1290</td>
</tr>
</tbody>
</table>

\( \rho \) is denoted as a pyroelectric coefficient.
pyro-ceramics and polymers (Bhalla et al., 1981). In addition to the primary pyroelectric effect, a secondary effect is superimposed, i.e., the stress due to the thermal expansion at difference between the ceramic and polymer generates electric charge through the piezoelectric effect.

Figure 12-15 shows a typical structure of a polymer used in pyroelectric infrared sensors. In practical usage, a pyro-sensor requires an infrared-light (thermal-ray) chopper, because the electrical signal can be detected only at the transient stage of light illumination or shut off. An electromagnetic motor was conventionally used as a light-chopper mechanism, and recently a piezoelectric bimorph chopper has been developed by Y. Kuwano et al. (Shibata et al., 1985), which prompted miniaturization of the pyrosensors (Fig. 12-16).

12.3.2 Infrared Image Sensors

In Fig. 12-17 the visualization of a thermal-distribution image is exemplified by a pyro-vidicon tube (Taylor et al., 1973). The light emitted from an object is filtered with a germanium lens producing an infrared beam which is focused onto the pyroelectric target through an optical chopper. The temperature distribution of the object is represented on the target as a voltage distribution. This is monitored from the back surface of the target by electron-beam scanning using a conventional TV tube.

One of disadvantages of the pyro-vidicon is the degradation of the image over a long period of usage due to thermal diffusion on the target. Pedder et al. proposed a segmented target design in order to solve the diffusion problem (Warner et al., 1981). Figure 12-18 shows the microscopic struc-

Figure 12-15. A polymer-based pyroelectric infrared sensor.

Figure 12-16. Swing-type pyroelectric temperature sensor.
turence of a D-TGS (deuterated triglycine sulphate, \( \text{(ND}_2\text{CD}_2\text{COOD})_2\text{D}_2\text{SO}_4 \)) target, and Fig. 12-19 is an example of a picture taken in darkness.

12.4 Piezoelectric Devices

12.4.1 Piezoelectric Materials

In the early 1950s, barium titanate (\( \text{BaTiO}_3 \)) began to be utilized in Langevin-type piezoelectric vibrators. Later, at the National Bureau of Standards (NBS) in the USA (now NIST), PZT (\( \text{Pb}(\text{Zr}, \text{Ti})\text{O}_3 \)) was found to exhibit piezoelectric constants twice as large as those of \( \text{BaTiO}_3 \) around the morphotropic phase boundary between the rhombohedral–tetragonal phases (Fig. 12-20); (Jaffe et al., 1955). Subsequently, PZT modified by doping, and a ternary solid solution with a different perovskite have been intensively investigated. Examples of these ternary compositions are:

- \( \text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 \)
- \( \text{Pb}(\text{Mn}_{1/3}\text{Sb}_{2/3})\text{O}_3 \)
- \( \text{Pb}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3 \)
- \( \text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3 \)
- \( \text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3 \)
- \( \text{Pb}(\text{Sb}_{1/2}\text{Sn}_{1/2})\text{O}_3 \)
- \( \text{Pb}(\text{Co}_{1/2}\text{W}_{1/2})\text{O}_3 \)
- \( \text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3 \)

Figure 12-18. Infrared image target with divided line segments (19 µm width, 16 µm depth, 25 µm pitch).
Piezoelectric data for PZT ceramics are summarized in Table 12-3.

In polycrystalline piezoelectric ceramics, a poling process (applying a strong DC electric field) is required to rearrange the spontaneous polarization. After being poled, the ceramic can exhibit the piezoelectric effect just as single crystals do (Fig. 12-21).

Piezoelectricity is also found in polymers (Kawai, 1969). Figure 12-22 shows an example polyvinylidenefluoride (PVDF).

Figure 12-19. Images taken by a pyro-vidicon on a dark night.

Figure 12-20. Permittivity and the planar coupling factor in PbZrO$_3$-PbTiO$_3$ ceramics.

Figure 12-21. Illustration of the strain change associated with the domain reversal in a ferroelectric ceramic.
Piezoelectric polymers have the following characteristics:
(a) small piezoelectric $d$ constants (for actuators) and large $g$ constants (for sensors):
(b) Lightweight and high elasticity, leading to good acoustic impedance matching to water or the human body.
(c) Low mechanical quality factor $Q_M$, giving a wide frequency band resonance.

Table 12-3. Electromechanical parameters in PZT–PMN ceramics.

<table>
<thead>
<tr>
<th></th>
<th>PCM-5A</th>
<th>PCM-33</th>
<th>PCM-4B</th>
<th>PCM-67</th>
<th>PCM-80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electro-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mechanical</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>coupling factors</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_0$</td>
<td>0.65</td>
<td>0.65</td>
<td>0.70</td>
<td>0.32</td>
<td>0.58</td>
</tr>
<tr>
<td>$k_{31}$</td>
<td>0.38</td>
<td>0.39</td>
<td>0.43</td>
<td>0.19</td>
<td>0.35</td>
</tr>
<tr>
<td>$k_{33}$</td>
<td>0.71</td>
<td>0.74</td>
<td>0.72</td>
<td>0.48</td>
<td>0.69</td>
</tr>
<tr>
<td>$k_{33}$</td>
<td>0.70</td>
<td>0.63</td>
<td>0.37</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>$k_4$</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.40</td>
<td>0.47</td>
</tr>
<tr>
<td>Piezoelectric</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>constants</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_{31}$</td>
<td>$-186 \times 10^{-12}$</td>
<td>$-263 \times 10^{-12}$</td>
<td>$-247 \times 10^{-12}$</td>
<td>$-42 \times 10^{-12}$</td>
<td>$-122 \times 10^{-12}$</td>
</tr>
<tr>
<td>$d_{33}$</td>
<td>$375 \times 10^{-12}$</td>
<td>$575 \times 10^{-12}$</td>
<td>$490 \times 10^{-12}$</td>
<td>$109 \times 10^{-12}$</td>
<td>$273 \times 10^{-12}$</td>
</tr>
<tr>
<td>$d_{44}$</td>
<td>$579 \times 10^{-12}$</td>
<td>$599 \times 10^{-12}$</td>
<td>$131 \times 10^{-12}$</td>
<td>$412 \times 10^{-12}$</td>
<td></td>
</tr>
<tr>
<td>$\theta_{31}$</td>
<td>$-12.3 \times 10^{-3}$</td>
<td>$-8.4 \times 10^{-3}$</td>
<td>$-11.8 \times 10^{-3}$</td>
<td>$-7.7 \times 10^{-3}$</td>
<td>$-11.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\theta_{33}$</td>
<td>$-25.7 \times 10^{-3}$</td>
<td>$18.4 \times 10^{-3}$</td>
<td>$20.6 \times 10^{-3}$</td>
<td>$19.8 \times 10^{-3}$</td>
<td>$25.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\theta_{44}$</td>
<td>$33.9 \times 10^{-3}$</td>
<td></td>
<td>$29.7 \times 10^{-3}$</td>
<td>$24.7 \times 10^{-3}$</td>
<td>$31.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>Permittivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_{33}/\varepsilon_0$</td>
<td>1710</td>
<td>3530</td>
<td>2380</td>
<td>620</td>
<td>1210</td>
</tr>
<tr>
<td>$\varepsilon_{11}/\varepsilon_0$</td>
<td>1830</td>
<td>2740</td>
<td>2280</td>
<td>600</td>
<td>1460</td>
</tr>
<tr>
<td>Loss tangent $D$</td>
<td>1.50</td>
<td>2.30</td>
<td>1.40</td>
<td>0.64</td>
<td>0.64</td>
</tr>
<tr>
<td>Elastic constants</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1/\varepsilon_{11}$</td>
<td>$6.2 \times 10^{10}$</td>
<td>$6.9 \times 10^{10}$</td>
<td>$6.3 \times 10^{10}$</td>
<td>$11.0 \times 10^{10}$</td>
<td>$8.8 \times 10^{10}$</td>
</tr>
<tr>
<td>$1/\varepsilon_{22}$</td>
<td>$5.5 \times 10^{10}$</td>
<td>$5.2 \times 10^{10}$</td>
<td>$5.1 \times 10^{10}$</td>
<td>$10.8 \times 10^{10}$</td>
<td>$6.8 \times 10^{10}$</td>
</tr>
<tr>
<td>$1/\varepsilon_{44}$</td>
<td>$2.0 \times 10^{10}$</td>
<td></td>
<td>$2.2 \times 10^{10}$</td>
<td>$4.2 \times 10^{10}$</td>
<td>$3.1 \times 10^{10}$</td>
</tr>
<tr>
<td>Density $\rho$</td>
<td>7.7</td>
<td>7.7</td>
<td>7.8</td>
<td>7.7</td>
<td>7.9</td>
</tr>
<tr>
<td>Mechanical</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>quality factor $Q_M$</td>
<td>60</td>
<td>50</td>
<td>64</td>
<td>3130</td>
<td>2080</td>
</tr>
<tr>
<td>Curie temperature (°C)</td>
<td>326</td>
<td>182</td>
<td>264</td>
<td>340</td>
<td>283</td>
</tr>
</tbody>
</table>

* Elastic constant $1/\varepsilon$: N/m²; piezoelectric constants $d$: m/V, $g$: V · m/N; loss tangent $D$: %; density $\rho$: $10^3$ kg/m³.
Recent development in the field of composites of piezoceramics and polymers is remarkable (Klicker, 1981), superior piezoelectric response being achieved while still maintaining the mechanical flexibility of the polymers.

12.4.2 Piezoelectric Resonance

When an electric field is applied to a piezoelectric material, deformation (ΔL) or strain (ΔL/L) arises. When the field is alternating, mechanical vibration is caused, and if the drive frequency is adjusted to a mechanical resonance frequency of the device, large resonating strain is generated. This phenomenon can be understood as a strain magnification due to accumulating input energy, and is called piezoelectric resonance. The piezoelectric resonance is very useful for realizing energy trap devices, actuators etc. The theoretical treatment is described in the following.

If the applied electric field and the generated stress are not large, the stress \( x \) and the dielectric displacement \( D \) can be represented by the following equation:

\[
x_i = s_{ij}^p X_j + d_{mi} E_m
\]

\((i, j = 1, 2, \ldots, 6; \ m, k = 1, 2, 3) \quad (12-20)\)

\[
D_m = d_{mi} X_i + e_{mk}^s E_k
\]

\((12-21)\)

These are called piezoelectric equations. The numbers of independent parameters for a lowest symmetry trigonal crystal are 21 for \( s_{ij}^p \), 18 for \( d_{mi} \) and 6 for \( e_{mk}^s \). The number of independent parameters decreases with increasing crystallographic symmetry. Concerning the polycrystalline ceramics, the poled axis is usually denoted as the \( z \)-axis and the ceramic is isotropic with respect to this \( z \)-axis (point group \( C_{m} \)). The number of non-zero matrix elements is 10 (\( s_{111}^p, s_{112}^p, s_{123}^p, s_{223}^p, s_{333}^p, d_{31}, d_{33}, d_{15}, e_{111}^s \), and \( e_{33}^s \)).

Next, let us introduce an electromechanical coupling factor \( k \), which corresponds to the efficiency of an electro-mechanical transducer. The internal energy of a piezoelectric vibrator is given by summation of the mechanical energy \( U_m (= \int x \, dX) \) and the electrical energy \( U_E (= \int D \, dE) \). \( U \) is calculated as follows, when linear relations Eqs. (12-20) and (12-21) are applicable:

\[
U = U_m + U_E =
\]

\[
= \left( \frac{1}{2} \sum_{i,j} s_{ij}^p X_j X_i + \frac{1}{2} \sum_{m,i} d_{mi} E_m X_i \right)
\]

\[
+ \left( \frac{1}{2} \sum_{i,j} d_{mi} X_i E_m + \frac{1}{2} \sum_{k,m} e_{mk}^s E_k E_m \right)
\]

The \( s \) and \( e \) terms represent purely mechanical and electrical energies (\( U_{mm} \) and \( U_{ee} \), respectively, and the \( d \) term denotes the energy transducer from electrical to mechanical energy or vice versa through the piezoelectric effect. The coupling factor \( k \) is defined by:

\[
k = \frac{U_{me}}{\sqrt{U_{mm} \cdot U_{ee}}} \quad (12-23)\]

The \( k \) value varies with the vibrational mode (even in the same ceramic sample), and can have a positive or negative value (see Table 12-4).

Let us consider the transverse mechanical vibration of a piezo-ceramic plate as shown in Fig. 12-23. If the polarization is

![Figure 12-23. Transverse vibration in a rectangular plate.](image)
Table 12.4. Several shapes of the resonator and their electromechanical coupling factors.

<table>
<thead>
<tr>
<th>Coupling factor</th>
<th>Elastic conditions</th>
<th>Shape of the resonator</th>
<th>Definition</th>
</tr>
</thead>
</table>
| a $k_{31}$      | $X_1 \neq 0, X_2 = X_3 = 0$  
                 | $x_1 \neq 0, x_2 = 0, x_3 \neq 0$ | 3           | $\frac{d_{31}}{\sqrt{\varepsilon_{31}^2 + \varepsilon_{33}^2}}$ |
| b $k_{33}$      | $X_1 = X_2 = 0, X_3 \neq 0$  
                 | $x_1 = x_2 \neq 0, x_3 \neq 0$ | 3           | $\frac{d_{33}}{\sqrt{\varepsilon_{33}^2 + \varepsilon_{33}^2}}$ |
| c $k_p$         | $X_1 = X_2 \neq 0, X_3 = 0$  
                 | $x_1 = x_3 \neq 0, x_3 \neq 0$ | 3           | $k_{31} \sqrt{\frac{2}{1 - \sigma}}$ |
| d $k_1$         | $X_1 = X_2 \neq 0, X_3 = 0$  
                 | $x_1, x_2 = 0, x_3 \neq 0$ | 3           | $k_{33} \sqrt{\frac{\varepsilon_{33}^2}{\varepsilon_{33}^2}}$ |
| e $k_p'$        | $X_1 = X_2 \neq 0, X_3 = 0$  
                 | $x_1 = x_3 \neq 0, x_3 \neq 0$ | 3           | $k_p - \frac{A k_{33}^2}{\sqrt{1 - A^2 \sqrt{1 - k_{33}^2}}}$ |
| f $k_{31}'$     | $X_1 = 0, X_2 = 0, X_3 = 0$  
                 | $x_1 = 0, x_2 = 0, x_3 \neq 0$ | 3           | $\frac{k_{31} - B k_{33}}{\sqrt{1 - k_{31}^2}}$ |
| g $k_{33}'$     | $X_1 = 0, X_2 = 0, X_3 = 0$  
                 | $x_1 = 0, x_2 = 0, x_3 \neq 0$ | 3           | $\frac{(k_p - A k_{33})^2}{\sqrt{1 - A^2 (1 - k_{33}^2)}}$ |
| h $k_{33}$      | $X_1 = 0, X_2 = 0, X_3 = 0$  
                 | $x_1 = 0, x_2 = 0, x_3 \neq 0$ | 3           | $\frac{k_{33} - B k_{33}}{\sqrt{(1 - B^2)(1 - k_{33}^2)}}$ |
| i $k_{33}$      | $X_1 = 0, X_2 = 0, X_3 = 0$  
                 | $x_1 = 0, x_2 = 0, x_3 \neq 0$ | 3           | $\frac{d_{33}}{\sqrt{\varepsilon_{33}^2 + \varepsilon_{33}^2}}$ |
| j $k_{26} = k_{13}$ | $X_1 = X_2 = X_3 = 0, X_4 = 0$  
                 | $x_1 = x_2 = x_3 = 0, x_4 \neq 0$ | 3           | $\frac{u}{\sqrt{\varepsilon_{33}^2 + \varepsilon_{33}^2}}$ |

$A = \frac{\sqrt{\varepsilon_{33}^2}}{\sqrt{\varepsilon_{33}^2 (\varepsilon_{31}^2 + \varepsilon_{33}^2)}}, \quad B = \frac{\varepsilon_{33}^2}{\sqrt{\varepsilon_{31}^2 + \varepsilon_{33}^2}}.$

In the z-direction and the x-y planes are the planes of the electrodes, the extentional vibration in the x-direction is represented by the following dynamic equation:

$$(\partial^2 u/\partial t^2) = F = (\partial X_{11}/\partial x) + (\partial X_{12}/\partial y) + (\partial X_{13}/\partial z), \quad u \text{ is the displacement of the small volume element in the ceramic plate in the x-direction.}$$

The relations between stress, electric field (only $E_x$ exists) and the induced strain are given by:

$$x_1 = s_{11}^e X_1 + s_{12}^e X_2 + s_{13}^e X_3 + d_{31} E_x, \quad (12-24)$$
Using Eq. (12-28), the admittance for the mechanically free sample is calculated as:

\[
\frac{1}{z} = \frac{i}{V} = \frac{i}{E_s t} = \frac{j \omega w L}{t} \frac{\varepsilon_{LC}}{\varepsilon_{33}} \left[ 1 + \frac{d_{31}^2}{\varepsilon_{33} s_{11}} \left( \frac{\tan [\omega L/(2 v)]}{\omega L/(2 v)} \right) \right]
\]

\(w\) is the width, \(L\) the length, \(t\) the thickness of the sample, and \(V\) is the applied voltage. \(\varepsilon_{LC}\) is the permittivity in a longitudinally clamped sample, and is given by:

\[
\varepsilon_{LC} = \varepsilon_{33} - (d_{31}/s_{11})
\]

The piezoelectric resonance is achieved where the admittance becomes infinite or the impedance is zero. The resonance frequency \(f_R\) is calculated from Eq. (12-31), and the fundamental frequency is given by:

\[
f_R = \frac{v}{(2 L)} = \frac{1}{(2 L \sqrt{v s_{11}^E})}
\]

On the other hand, the antiresonance state is generated for zero admittance or infinite impedance:

\[
\omega_A L \cot \frac{\omega_A L}{2 v} = - \frac{d_{31}^2}{\varepsilon_{33} s_{11}} = - \frac{k_{31}^2}{1 - k_{31}^2}
\]

The final transformation is provided by the definition:

\[
\kappa_{31} = \frac{1}{2} d_{31} E_s X_1 / (L_1 \sqrt{\varepsilon_{33}^E X_1^2 \varepsilon_{33}^E E_s^2}) = \frac{1}{2} E_s \sqrt{\varepsilon_{33}^E / \varepsilon_{33}^E}
\]

The resonance and antiresonance states are described by the following intuitive model. In a high electromechanical coupling material with \(k \approx 1\), the resonance or antiresonance states appear for \(\tan [\omega L/(2 v)] = \infty\) or 0, i.e., \(\omega L/(2 v) = (m - 1/2) \pi\) or \(m \pi\) (\(m\) integer), respectively. The strain amplitude \(x_1\) distribution for each state [calculated using Eq. (12-28)] is
Resonance

- $m=1$

- $m=2$

Antiresonance

- Low coupling
- $m=1$
- $m=2$

High coupling

Figure 12-24. Strain generation in the resonant or antiresonant state.

illustrated in Fig. 12-24. In the resonance state, large strain amplitudes and large capacitance changes are induced, and the current can easily flow into the device. On the contrary, at the antiresonance, the strain induced in the device compensates in total, not causing the capacitance change, and the current can not flow easily into the sample.

In the usual case, where $k_{31} \approx 0.3$, the antiresonance state varies from the above-mentioned mode and becomes closer to the resonance mode. The low-coupling material exhibits an antiresonance mode where capacitance change due to the size change is compensated completely by the current required to charge up the static capacitance.

In general, the sound velocity $v$ of the specimen is first obtained from the resonance frequency $f_R$, then the electromechanical coupling factor $k_{31}$ is calculated from the $v$ value and the antiresonance frequency $f_A$ using Eq. (12-34). Especially in low-coupling piezoelectric materials, the following approximate equation is available:

$$k_{31}/(1 - k_{31}) = \frac{\pi^2}{4} (\Delta f/f_R) \quad (\Delta f = f_A - f_R) \quad (12-36)$$

12.4.3 Piezoelectric Transformers

One of the very basic applications of piezoelectric ceramics is a gas igniter. The very high voltage generated in a piezoelectric ceramic under applied mechanical stress can cause sparking and ignite the gas (Fig. 12-25). There are two means to apply the mechanical force; sudden application and continuous increase.

When input and output terminals are fabricated on a piezo-device and input/output voltage is changed through the vibration energy transfer, the device is called a piezoelectric transformer. Proposed by C. A. Rosen et al. (Rosen, 1957), there have been a variety of such transformers investigated: Fig. 12-26 shows a fundamental structure where two differently-polled parts coexist in one piezoelectric plate. A standing wave with a wavelength equal to the sample length is generated, a half wavelength portion of the wave existing on both

Figure 12-25. (a) Gas igniter and (b) output voltage.
A bimorph consisting of two piezoceramic plates bonded together, and a piezoelectric fork consisting of a piezo-device and a metal fork. A piezoelectric buzzer is shown in Fig. 12-27, which has merits such as high electric power efficiency, compact size and long life.

12.4.5 Ultrasonic Transducers

Ultrasonic waves are now used in various fields. The sound source is made of piezoelectric ceramics as well as of magnetostrictive materials. Piezoceramics are generally superior in efficiency and in size to magnetostrictive materials. Especially hard-type piezoelectric materials with a high $Q_M$ are preferable. A liquid medium is usually used for sound energy transfer. Ultrasonic washers and ultrasonic microphones for short-distance remote control are widely used in factories, and ultrasonic scanning detectors are useful in medical electronics.

12.4.6 Surface Acoustic Wave Devices

Surface acoustic wave (SAW) filters have been widely used for the intermediate frequency image transfer signal in color TVs, because of their excellent time delay characteristics. The fundamental structure of the SAW filter is illustrated in Fig. 12-28, where a pair of interdigital electrodes are fabricated on the piezoelectric crystal.
motors, has been rapidly increasing. The requirements for the processing accuracy of optical devices such as lasers and cameras, along with the positioning accuracy required in the processing of semiconductor chips are now typically of the order of micron and submicron levels. The need for a reliable micro-scale positioner has motivated a new surge of activity in the development of ceramic actuators which operate on the principle of electric-field-induced strain.

For actuator applications, large electric fields (≈ 1 kV/mm) are applied to the material, thereby generating large stresses (≈ 10 MPa) and strains (Δl/l ≈ 10⁻³). Therefore, in addition to an adequate electrostrictive response, electrical insulation strength and mechanical toughness are necessary material characteristics.

Lead zirconate titanate (PZT)-based ceramics are currently the primary materials for piezoelectric applications (Furuta et al., 1986). The (Pb, La)(Zr, Ti)O₃ (PLZT) (7/62/38) compound is one such material. The strain curves for this composition are shown in Fig. 12-29a. When the applied electric field is small, the induced strain is nearly proportional to the electric field. As the field becomes larger (i.e., greater than about 100 V/mm), however, the strain curve deviates from this linear trend and a significant hysteresis is exhibited due to polarization reversal. This limits the use of

![Figure 12-28. Fundamental structure of a SAW filter.](image-url)

**12.4.7 Piezoelectric Actuators**

In recent years, the need for new displacement elements, in particular, in such fields as optics, precision machinery and small

<table>
<thead>
<tr>
<th></th>
<th>LiTaO₃ (X-112°Y)</th>
<th>LiNbO₃ (128°Y)</th>
<th>PZT*</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAW velocity (m/s)</td>
<td>3295</td>
<td>3960</td>
<td>2430</td>
<td>3150</td>
</tr>
<tr>
<td>Coupling factor (k², %)</td>
<td>0.7</td>
<td>6.0</td>
<td>2.9</td>
<td>0.6</td>
</tr>
<tr>
<td>Temperature coefficient of frequency (ppm/°C)</td>
<td>-31</td>
<td>-78</td>
<td>-17</td>
<td>-15</td>
</tr>
<tr>
<td>Permittivity (εₚ)</td>
<td>47.9</td>
<td>67.2</td>
<td>350</td>
<td>8.84</td>
</tr>
<tr>
<td>Curie point (Tc, °C)</td>
<td>618</td>
<td>1210</td>
<td>300</td>
<td>1200</td>
</tr>
</tbody>
</table>

* Pb(Mn₁/₁₅Nb₂/₁₅)O₃-PbZrO₃-PbTiO₃.
the material in actuator applications that require a linear, non-hysteresis response.

Previously, electrostriction, a second-order phenomenon of electromechanical coupling, was considered to be a negligible effect and, therefore, was not studied from a practical point of view. Recent research and development on PMN [lead magnesium niobate, Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$]-based ceramics (Cross et al., 1980), however, have kindled new interest in the use of such electrostrictive materials in this area. PMN-based ceramics exhibit significant strains up to 0.1% (i.e., a 1 cm sample can elongate by as much as 10 μm). Another attractive feature of these materials is the near absence of hysteresis (Fig. 12-29b).

Piezoelectric/electrostrictive actuators may be classified into two categories based on the type of driving field applied to the device and the nature of the strain induced by that field (Fig. 12-30): (1) Rigid displacement devices for which the strain is induced unidirectionally by an applied DC field, and (2) resonating strain devices for which the mechanical resonance is excited by an AC field. The first can be further divided into two categories: (1) Servo deix-

**Figure 12-29.** Field-induced strain in ceramics. (a) Piezoelectric material PLZT(7/62/38). (b) Electrostrictive material 0.9Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-0.1PbTiO$_3$.

**Figure 12-30.** Classification of piezoelectric/electrostrictive actuators; $E$: electric field, $x$: strain.
placement transducers controlled by a feedback system through a position-detection signal, and (2) pulse-drive motors that operate in a simple ON/OFF switching mode (Uchino, 1986). Very recently, an actuator referred to as a flight actuator has been proposed which hits a steel ball strongly by means of an ON/OFF piezoelectric unit similar to that found in a pinball machine (Ota et al., 1985).

The material requirements for the three classes of devices are somewhat different and hence, certain compounds will be better suited to particular applications. The ultrasonic motor, for instance, requires almost the conventional hard-type piezoelectric with a high mechanical Q. The servodisplacement transducer suffers most from strain hysteresis and, therefore, a PMN electrostrictor is used for this device. The pulse-drive motor requires a low-permittivity material aiming at a quick response rather than a small hysteresis so that soft-PZT piezoelectrics are most suitable for this application.

In the sections to follow, three typical application examples will be taken up for examination and discussion.

12.4.7.1 Deformable Mirrors

In the field of optical information processing, deformable mirrors have been proposed to control the phase of the incident light wave. The deformable mirror can be made more convex or concave as necessary. This type of mirror, which finds application as an accessory device on observatory telescopes, effectively corrects for image distortions resulting from fluctuating airflow.

An example of a deformable mirror is a multilayered two-dimensional bimorph type like that shown in Fig. 12-31 (Sato et al., 1982). The operation of this mirror is similar in principle to a "bi-metal" device which consists of two metal plates, with different thermal expansion coefficients, bonded together. The plates will bend with a change in temperature. When three layers of thin electrostrictive ceramic (PMN) plates are bonded to the elastic plate of a glass mirror, the mirror surface is deformed in various ways corresponding to the strain induced in the PMN-layer. The nature of the deformation is determined by the electrode configuration and the distribution of the applied electric field. Trial units have been designed such that the first layer, with a uniform electrode pattern, produces a spherical deformation (i.e., refocusing), while the second layer with an electrode pattern of six minute divisions corrects for coma aberration.

12.4.7.2 Impact Dot-Matrix Printers

Among the various types of printing devices currently in use, dot-matrix printers are routinely employed. Each character formed by such a printer is initially composed of a 9 x 9 dot matrix. A printing ribbon is subsequently impacted by a multwire array. A sketch of the printer appears in Fig. 12-32a (Yano et al., 1984).

The basic actuator assumes a multilayer configuration in which roughly 100 thin piezoelectric ceramic sheets are stacked. The advantages of using a multilayer-type actuator for this particular application include a low driving voltage, large displacement, and a high electromechanical conversion efficiency. This actuator is installed in a specially designed displacement magnification unit (Fig. 12-32b) to drive the top printer pins. This unique magnification unit is based on a monolithic hinge lever with a magnification of 30 and realizes an amplified displacement of 300 μm and an energy transfer efficiency greater than 50%.
The merits of the piezoelectric impact printer compared with the conventional electromagnetic type are: (1) higher printing speed by an order of magnitude, (2) lower energy consumption by an order of magnitude, and (3) reduced printing noise since a complete sound shield may be employed with the heatless drive.

12.4.7.3 Ultrasonic Motors

Efforts have been made to develop high-power ultrasonic vibrators as replacements for conventional electromagnetic motors. Two actuators, in particular, are currently being investigated for this application: A vibratory-coupler type and a surface-wave type (Akiyama, 1986).

The basic design of the vibratory coupler is pictured in Fig. 12-33. The Langevin-type piezoelectric vibrator generates a flat-elliptical movement at the tip of the vibratory piece. When contacting a rotor at a slight angle, the vibratory piece generates a rotational torque.

This simple design, however, has several drawbacks. Defacement of the rotor caused by mechanical friction at the contact point and lack of control in both the clockwise and counter-clockwise directions are two of the most serious problems associated with this unit. The problem of
friction is alleviated by securely pressure-fitting the vibratory reed and rotor together in order to restrict, as much as possible, sliding during operation. The model picture in Fig. 12-34 is one such modified unit (Kumada, 1985). At a rotational speed of 600 rpm, this motor has performance characteristics that surpass normal electromagnetic motors with a rotational torque of 13 kgf·cm (~1.3 Nm) and an energy conversion efficiency of 80%.

The other type of motor utilizes surface wave vibrations. The operating principle of
this device is illustrated in Fig. 12-35. By means of the traveling elastic wave induced by the piezoelectric, a slider in contact with the "rippled" surface of the elastic body is driven in the direction indicated. Both linear and rotational-type motors of this type are possible. The structure of a surface-wave rotational-type motor is pictured in Fig. 12-36. Although the energy transformation efficiency (30%) and rotational torque (0.5 kgf cm) of the surface wave device are rather low as compared to the vibratory-coupler type, its merit lies in its ability to rotate in both directions and its thin design which makes it suitable for installation in video (VTR) or movie cameras as an automatic focusing device.

12.5 Electrooptic Devices

In the 1960s the nonlinear polarizability of ferroelectrics was discovered and various electrooptic and optical parametric devices have been investigated. However, problems still remaining are the difficulty of preparing high-grade optically-homogeneous single crystals, and the correspondingly high cost for a given level of performance.

12.5.1 Transparent Electrooptic Ceramics

Even with a polycrystalline microstructure, a ferroelectric ceramic can exhibit the electrooptic effect if it is sintered to a pore-free state to make it transparent. The best-known material is the (Pb, La)(Zr, Ti)O₃ system (PLZT), which has good transparancy in a wavelength range from visual to infrared, and exhibits an optical anisotropy
under applied electric voltage. Displays and light valves are promising applications. Figure 12-37 shows the phase diagram of the \((\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3\) system and the corresponding possible applications.

The PLZT solid solution exhibits both the Pockels' and Kerr electrooptic effects, depending on the composition. Some examples are shown in Fig. 12-38. The electrooptic coefficients of the PLZT system are much larger than the values in conventional crystals such as \(\text{LiNbO}_3\) and \((\text{Sr},\text{Ba})\text{Nb}_2\text{O}_6\) (SBN) (see Table 12-6), which means that the voltage required for the electrooptic shutter is much less in the PLZT.

### Table 12-6. Pockels' (1st) and Kerr (2nd) electrooptic coefficients for various materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>1st electrooptic coefficient</th>
<th>2nd electrooptic coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(r \times 10^{-10}) m/V</td>
<td>(R \times 10^{-14}) m²/V²</td>
</tr>
<tr>
<td>(\text{LiNbO}_3)</td>
<td>0.17</td>
<td>5.30</td>
</tr>
<tr>
<td>(\text{Ba}<em>4(\text{K}</em>{0.9}\text{Na}_{0.1})\text{Nb}<em>5\text{O}</em>{15})</td>
<td>0.52</td>
<td>(\text{KTa}<em>{0.63}\text{Nb}</em>{0.35}\text{O}_3)</td>
</tr>
<tr>
<td>(\text{KH}_2\text{PO}_4)</td>
<td>0.52</td>
<td>(\text{PLZT} 9/65/35) (GS = 3 μm)</td>
</tr>
<tr>
<td>((\text{Sr},\text{Ba})\text{Nb}_2\text{O}_6)</td>
<td>2.10</td>
<td>9.12</td>
</tr>
<tr>
<td>(\text{PLZT} 8/65/35) (GS = 10 μm)</td>
<td>5.23</td>
<td>(\text{PLZT} 10/65/35) (GS = 2 μm)</td>
</tr>
<tr>
<td></td>
<td>6.12</td>
<td></td>
</tr>
</tbody>
</table>

**12.5.2 Bulk Electrooptic Devices**

PLZT eye glasses for stereo TV have been fabricated using the light shutter function (Kumada et al., 1977). Lenses consist of a pair of optically isotropic PLZT (9/65/35) discs sandwiched by two crossed polarizers. When zero voltage is applied on the electrode, the light will not be transmitted. The transmitted light intensity in-
creases with increasing applied voltage, and reaches a maximum when the phase difference (retardation) of 180° is induced in the PLZT disc. The voltage required for the maximum intensity is denoted as a half-wavelength voltage.

The stereo TV image of an object is taken by two video cameras corresponding to the two eyes and the signal from each camera is mixed alternately to make a frame for the right- and left eyes. When viewing, the right and left PLZT shutters are triggered synchronously for each image frame, resulting in a stereo image.

Recent progress with high-definition TVs is remarkable, and several systems have been proposed. One of the promising devices is a projection-type TV utilizing two-dimensional PLZT displays (Ohmura, 1989). Electrooptic characteristics in PLZT ceramics are generally much superior in response speed and contrast ratio to those in liquid crystals. Moreover, the durability of ceramics under strong light illumination is excellent. However, the most significant problems in PLZT devices, which have prohibited their actual commercialization, are the high driving voltage and the cost. Therefore the development of a simple, mass-production process and the design of electrode configurations with a narrow gap are the key factors for PLZT displays.

A recently developed design for a 2-dimensional display as shown in Fig. 12-39 presents a very bright image with no cross-talk-related problems and is easy to produce. The fabrication process of the 2-dimensional PLZT light valve array is outlined in Fig. 12-40. Wet-chemically prepared (coprecipitated) PLZT 9/65/35 powders were mixed with organic solvent and binder and formed into a green sheet. The sheets were printed with electrodes and then laminated and sintered in an atmosphere with a controlled oxygen content. A transmittance of 62% could be obtained by atmosphere-controlled sintering, comparing well with a value of 63% for the ideal sample prepared by hot-pressing. Finally, the external connecting electrodes were applied to make vertical and horizontal addressing possible.

The construction of the PLZT color image projector is shown in Fig. 12-41. Three light fluxes, red, green and blue, are obtained by separating light from a xenon lamp with dichroic mirrors, and passing each through identical PLZT shutter. Then, the fluxes are superimposed to make a color image.

### 12.5.3 Waveguide Modulators

Light waveguides can be fabricated by depositing a high-refractive-index layer on a substrate. The principle of the waveguide is shown schematically in Fig. 12-42. Nb-diffused LiNbO₃ single crystals are commonly used; Fig. 12-43a and 12-43b show typical planar- and ridge-type electrooptic waveguides (Kaminow, 1975). The transmitted light intensity is easily modulated by applying a relatively low voltage. Phase modulation by 1 radian can be achieved by applying a voltage of 0.3 V with power consumption of several μW/MHz.
Figure 12-40. Fabrication process of the newly developed 2-D display.

Figure 12-41. Construction of the PLZT color image projector.
12.6 Positive Temperature Coefficient (PTC) Materials

12.6.1 The PTC Phenomenon

When barium titanate (BaTiO$_3$) is doped with a low concentration of lanthanide ions (0.3 at.%) the ceramic becomes semiconductive with a resistivity in the range of 10$^{-10^3}$ $\Omega \cdot$ cm. Moreover, the resistivity is drastically increased by 3–5 orders of magnitude with increasing temperature around the Curie point. This phenomenon was discovered in 1954, and denoted as the PTC (positive temperature coefficient of resistivity) effect, since then it has been investigated intensively by many researchers (Andrich, 1965; Heywang, 1964).

The PTC dopant is an ionic species with a larger ionic valence such as La, Sm, Ce or Gd, and replaces the Ba ions and Nb, Ta, Bi in the Ti sites. Since the temperature at which the resistivity anomaly occurs is closely related with the Curie point, the temperature coefficient can easily be designed by choosing the solid solution on the basis of BaTiO$_3$. Fig. 12-44 shows some varieties of the PTCR curves.

The theory for the PTC effect has not been established completely. The most acceptable model is illustrated in Fig. 12-45, which was initially proposed by H. Heywang et al. (Heywang, 1964). When the two semiconductive (n-type) ceramic particles are in contact through a grain boundary, an electron energy barrier (Schottky barrier) is generated and the barrier height is given by the following equation:

$$\phi = \frac{e N_d^2}{2 \varepsilon_0 \varepsilon N_s}$$

(12-38)

$N_d$ is the concentration of donor atoms and $N_s$ is the surface density of negatively
12.6 Positive Temperature Coefficient (PTC) Materials

The permittivity increases with the decrease in temperature down to the Curie point $T_C$. The permittivity $\varepsilon$ can be calculated using the Curie-Weiss law:

$$\varepsilon = C/(T - T_0)$$ (12-39)

Below $T_C$ the permittivity falls, but the spontaneous polarization appears and controls the electron concentration to reduce the barrier height. This keeps the resistivity in a rather low range.

### 12.6.2 PTC Thermistors

PTC thermistors are applicable not only for temperature-change detection but also for active current controllers. The thermistor, when self-heated, causes a decrease in the current owing to the drastic increase of resistivity. Practical applications are found in over-current/voltage protectors, starting switches for motors and automatic demagnetization circuits for color TVs.

"Ceramic heaters" have also been widely commercialized in panel heaters, electronic thermos bottles and hair dryers.

### 12.6.3 Grain Boundary Layer Capacitors

When a semiconductive BaTiO$_3$ ceramic is oxidized to make a resistive surface layer, it can be used as a high-capacitance condenser. The capacitance is adjustable in the range of 0.4–0.5 $\mu$F/cm$^2$.

---

**Figure 12-44.** Resistivity vs. temperature behavior of PTCR BaTiO$_3$ ceramics. Modifiers and additive concentrations are indicated.

**Figure 12-45.** Energy-level diagram near a grain boundary of the PTCR BaTiO$_3$. 
the sales at present, and piezoelectric vibrators such as buzzers and speakers hold the second position. The sales concerned with the other applications are negligibly small.

What does the future hold for ferroelectric devices? Ferroelectrics can be utilized in various devices but until now have failed to reach commercialization in most cases. In the light sensor, for example, semiconductive materials are superior to ferroelectrics in response speed and sensitivity. Magnetic devices are much more popular in the memory field, and liquid crystals are typically used for optical displays. Ferroelectric devices often fail to be developed in the cases where competitive materials exist. Therefore, it can be said that ferroelectrics are strong candidates for application only in those fields where no viable alternative materials exist. It is the author's opinion that the following will be promising areas:

- electromechanical devices (piezoelectric actuators, ultrasonic motors)
- thin-film hybrid sensors (pyro-, pressure, acceleration sensors)
- electrooptic devices (light waveguides, thin-film hybrid displays)

12.7 Conclusions

We have described the fundamentals and applications of ferroelectrics, including:

- high-permittivity dielectrics
- pyroelectric devices
- piezoelectric devices
- electrooptic devices
- PTC materials

From a viewpoint of commercialization, capacitor dielectrics account for most of
12.8 Appendix 1: Tensor Representation of Physical Properties

Since both the electric field and the current density are first rank tensors (i.e., vector) quantities, the conductivity should have a second rank tensor representation (i.e., with two suffixes); this is described as

\[
\begin{pmatrix}
  j_1 \\
  j_2 \\
  j_3
\end{pmatrix}
= \begin{pmatrix}
  \sigma_{11} & \sigma_{12} & \sigma_{13} \\
  \sigma_{21} & \sigma_{22} & \sigma_{23} \\
  \sigma_{31} & \sigma_{32} & \sigma_{33}
\end{pmatrix}
\begin{pmatrix}
  E_1 \\
  E_2 \\
  E_3
\end{pmatrix}
\]

or

\[
 j_i = \sum_j \sigma_{ij} E_j 
\]

or

\[
 j_i = \sum_j \sigma_{ij} E_j 
\]

A third-rank tensor is exemplified by piezoelectric coefficients, providing a relation between the applied field and the induced strain \(x\):

\[
x = d E 
\]

Since the \(E\) and \(x\) are first-rank and second-rank tensors, respectively, the \(d\) should have a third-rank tensor form represented as

\[
x_{jk} = \sum_i d_{ijk} E_i
\]

The \(d\) tensor is composed of three layers of the symmetrical matrices.

1st layer (\(i = 1\))

\[
\begin{pmatrix}
  d_{111} & d_{112} & d_{113} \\
  d_{121} & d_{122} & d_{123} \\
  d_{131} & d_{132} & d_{133}
\end{pmatrix}
\]

2nd layer (\(i = 2\))

\[
\begin{pmatrix}
  d_{211} & d_{212} & d_{213} \\
  d_{221} & d_{222} & d_{223} \\
  d_{231} & d_{232} & d_{233}
\end{pmatrix}
\]

3rd layer (\(i = 3\))

\[
\begin{pmatrix}
  d_{311} & d_{312} & d_{313} \\
  d_{321} & d_{322} & d_{323} \\
  d_{331} & d_{332} & d_{333}
\end{pmatrix}
\]

Generally speaking, if two physical properties are represented using tensors of \(p\)-rank and \(q\)-rank, the quantity which combines the two properties in a linear relation is also represented by a tensor of \((p + q)\)-rank.

12.8.2 Crystal Symmetry and Tensor Form

When we measure a physical property along two different directions, the two values measured must be equal if these two directions are crystallographically equivalent to each other. This consideration sometimes reduces the number of the independent tensor components representing the above property.

Let us again take conductivity as an example of a second-rank tensor. If the current density \(j\) in an \((x, y, z)\) coordinate system is described in an \((x', y', z')\) system as \(j'\), \(j\) and \(j'\) are related using a unitary matrix \(^1\) as follows:

\[
\begin{pmatrix}
  j'_1 \\
  j'_2 \\
  j'_3
\end{pmatrix}
= \begin{pmatrix}
  a_{11} & a_{12} & a_{13} \\
  a_{21} & a_{22} & a_{23} \\
  a_{31} & a_{32} & a_{33}
\end{pmatrix}
\begin{pmatrix}
  j_1 \\
  j_2 \\
  j_3
\end{pmatrix}
\]

The electric field is transformed in the same way:

\[
\begin{pmatrix}
  E'_1 \\
  E'_2 \\
  E'_3
\end{pmatrix}
= \begin{pmatrix}
  a_{11} & a_{12} & a_{13} \\
  a_{21} & a_{22} & a_{23} \\
  a_{31} & a_{32} & a_{33}
\end{pmatrix}
\begin{pmatrix}
  E_1 \\
  E_2 \\
  E_3
\end{pmatrix}
\]

or

\[
 E_i = \sum_j a_{ij} E_j
\]

\(^1\) A unitary matrix without an imaginary part has the following relation:

\[
\begin{pmatrix}
  a_{11} & a_{12} & a_{13} \\
  a_{21} & a_{22} & a_{23} \\
  a_{31} & a_{32} & a_{33}
\end{pmatrix}
^{-1} = \begin{pmatrix}
  a_{11} & a_{21} & a_{31} \\
  a_{12} & a_{22} & a_{32} \\
  a_{13} & a_{23} & a_{33}
\end{pmatrix}
\]

For centro-symmetry, the transformation matrix is written as

\[
\begin{pmatrix}
  -1 & 0 & 0 \\
  0 & -1 & 0 \\
  0 & 0 & -1
\end{pmatrix}
\]

and for rotation about a principal axis,

\[
\begin{pmatrix}
  \cos \theta & \sin \theta & 0 \\
  -\sin \theta & \cos \theta & 0 \\
  0 & 0 & 1
\end{pmatrix}
\]
Then, we can calculate the corresponding \( \sigma' \) tensor defined by

\[
\begin{pmatrix}
  j_1' \\
  j_2' \\
  j_3'
\end{pmatrix} = \sigma' \begin{pmatrix}
  E_1' \\
  E_2' \\
  E_3'
\end{pmatrix}
\]  

(A10)

\[
\begin{pmatrix}
  \sigma'_{11} & \sigma'_{12} & \sigma'_{13} \\
  \sigma'_{21} & \sigma'_{22} & \sigma'_{23} \\
  \sigma'_{31} & \sigma'_{32} & \sigma'_{33}
\end{pmatrix} = \begin{pmatrix}
  a_{11} & a_{12} & a_{13} \\
  a_{21} & a_{22} & a_{23} \\
  a_{31} & a_{32} & a_{33}
\end{pmatrix} .
\]  

(A11)

\[
\sigma'_{ij} = \sum_{k,l} a_{ik} a_{jl} \sigma_{kl}
\]

(A12)

When the crystal has a 2-fold axis along the z-axis, the conductivity tensor should have the same components for the transformation of

\[
\begin{pmatrix}
  -1 & 0 & 0 \\
  0 & -1 & 0 \\
  0 & 0 & 1
\end{pmatrix}
\]  

we can induce the relations:

\[
\begin{pmatrix}
  \sigma_{11} & \sigma_{12} & \sigma_{13} \\
  \sigma_{21} & \sigma_{22} & \sigma_{23} \\
  \sigma_{31} & \sigma_{32} & \sigma_{33}
\end{pmatrix} = \begin{pmatrix}
  -1 & 0 & 0 \\
  0 & -1 & 0 \\
  0 & 0 & 1
\end{pmatrix} .
\]

(A13)

we can induce the relations:

\[
\sigma_{31} = \sigma_{13} = \sigma_{32} = \sigma_{23} = 0
\]

\[
\sigma_{11}, \sigma_{22}, \sigma_{33} \neq 0 
\]

(A14)

\[
\sigma_{12} = \sigma_{21}
\]

It is very important to note that most of the physical constants have a symmetric tensor form (the proof involves thermodynamical considerations and is beyond the scope of this article).

As far as a third-rank tensor such as piezoelectric tensor is concerned, the transformation on change of the coordinate system is represented as

\[
d_{ijk} = \sum_{m,n} a_{im} a_{jn} d_{kmn}
\]

(A15)

When the crystal has a 4-fold axis along the z-axis, the transformation matrix is given by

\[
\begin{pmatrix}
  0 & 1 & 0 \\
  -1 & 0 & 0 \\
  0 & 0 & 1
\end{pmatrix}
\]  

(A16)

In consideration of the tensor symmetry with \( \sigma_{d1} = \sigma_{d2} \) and \( \sigma_{d} = \sigma_{d3} \) (each matrix of the ith layer of the \( \sigma \) tensor is symmetrical), we can obtain the relations:

\[
d_{111} = d_{222} = d_{112} = d_{121} = d_{211} = d_{122} = d_{212} = d_{123} = d_{231} = d_{133} = d_{332} = d_{232} = d_{233} = a_{132} = d_{321} = 0
\]  

(A17)

1st layer

\[
\begin{pmatrix}
  0 & 0 & d_{131} \\
  0 & 0 & d_{123} \\
  d_{131} & d_{123} & 0
\end{pmatrix}
\]

2nd layer

\[
\begin{pmatrix}
  0 & 0 & -d_{123} \\
  0 & 0 & d_{131} \\
 -d_{123} & d_{131} & 0
\end{pmatrix}
\]

3rd layer

\[
\begin{pmatrix}
  d_{111} & 0 & 0 \\
  0 & d_{111} & 0 \\
  0 & 0 & d_{333}
\end{pmatrix}
\]
12.8.3 Reduction of the Tensor
(Matrix Notation)

A general third-rank tensor has $3^3 = 27$ independent components. Since $d_{ijk}$ is symmetrical in $j$ and $k$ some of the coefficients can be eliminated, leaving 18 independent $d_{ijk}$; it also facilitates the use of the matrix notation.

So far all the equations have been developed in full tensor notation. But when calculating actual properties, it is advantageous to reduce the number of suffixes as much as possible. This is done by defining new symbols, for instance, $d_{21} = d_{211}$ and $d_{14} = 2d_{123}$: The second and third suffixes in the full tensor notation are replaced by a single suffix 1 to 6 in matrix notation, as follows:

<table>
<thead>
<tr>
<th>Tensor notation</th>
<th>11</th>
<th>22</th>
<th>33</th>
<th>23,32</th>
<th>31,13</th>
<th>12,21</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix notation</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>

In terms of these new symbols the array (A6) is rewritten as:

\[
\begin{pmatrix}
  d_{11} & \frac{1}{2} d_{16} & \frac{1}{2} d_{15} \\
  \frac{1}{2} d_{16} & d_{12} & \frac{1}{2} d_{14} \\
  \frac{1}{2} d_{15} & \frac{1}{2} d_{14} & d_{13}
\end{pmatrix}
\]

\[
\begin{pmatrix}
  0 & \frac{1}{2} d_{26} & \frac{1}{2} d_{25} \\
  \frac{1}{2} d_{26} & d_{22} & \frac{1}{2} d_{24} \\
  \frac{1}{2} d_{25} & \frac{1}{2} d_{24} & d_{23}
\end{pmatrix}
\]

\[
\begin{pmatrix}
  0 & \frac{1}{2} d_{36} & \frac{1}{2} d_{35} \\
  \frac{1}{2} d_{36} & d_{32} & \frac{1}{2} d_{34} \\
  \frac{1}{2} d_{35} & \frac{1}{2} d_{34} & d_{33}
\end{pmatrix}
\]  

(A18)

The last two suffixes in the tensor notation correspond to those of the strain components; therefore, for consistency, we make the following change in the notation for the strain components

\[
\begin{pmatrix}
  x_{11} & x_{12} & x_{31} \\
  x_{12} & x_{22} & x_{23} \\
  x_{31} & x_{23} & x_{33}
\end{pmatrix}
\]

\[
\begin{pmatrix}
  \frac{1}{2} x_6 & \frac{1}{2} x_7 & \frac{1}{2} x_5 \\
  \frac{1}{2} x_7 & x_2 & \frac{1}{2} x_4 \\
  \frac{1}{2} x_5 & \frac{1}{2} x_4 & x_3
\end{pmatrix}
\]

(A19)

The reason for the $\frac{1}{2}$s in the substitution (A19) is due to the cancellation with $\frac{1}{2}$s in (A18). Then, we have

\[
x_j = \sum_i d_{ij} E_i \quad (i = 1, 2, 3; j = 1, 2, \ldots, 6)
\]

or

\[
\begin{bmatrix}
  x_1 \\
  x_2 \\
  x_3 \\
  x_4 \\
  x_5 \\
  x_6
\end{bmatrix}
= \begin{bmatrix}
  d_{11} & d_{21} & d_{31} \\
  d_{12} & d_{22} & d_{32} \\
  d_{13} & d_{23} & d_{33} \\
  d_{14} & d_{24} & d_{34} \\
  d_{15} & d_{25} & d_{35} \\
  d_{16} & d_{26} & d_{36}
\end{bmatrix}
\begin{bmatrix}
  E_1 \\
  E_2 \\
  E_3
\end{bmatrix}
\]

(A21)

Concerning the stress components, the $\frac{1}{2}$s are unnecessary.

\[
\begin{pmatrix}
  X_{11} & X_{12} & X_{31} \\
  X_{12} & X_{22} & X_{23} \\
  X_{31} & X_{23} & X_{33}
\end{pmatrix}
\]

\[
\begin{pmatrix}
  X_1 & X_6 & X_5 \\
  X_6 & X_2 & X_4 \\
  X_5 & X_4 & X_3
\end{pmatrix}
\]

(A22)

The matrix notation has the advantage of compactness over the tensor notation, and it makes it easy to display the coefficients on a plane diagram. However, it must be remembered that in spite of their form, the $d_{ij}$s do not transform like the components of a second-rank tensor.

An example of a piezoelectric matrix for the point group 4 is written as

\[
\begin{pmatrix}
  0 & 0 & 0 & d_{14} & d_{15} & 0 \\
  0 & 0 & 0 & d_{15} & -d_{14} & 0 \\
  d_{31} & d_{31} & d_{33} & 0 & 0 & 0
\end{pmatrix}
\]

(A23)
12.9 Appendix 2: Phenomenology of Ferroelectricity

12.9.1 Landau Theory of the Phase Transition

A thermodynamical theory explaining the behavior of a ferroelectric crystal can be obtained by considering the form of the expansion of the energy as a function of the polarization $P$. We assume that the Landau free energy $F$ in one dimension should be represented formally as:

$$ F(P, T) = \frac{1}{2} \alpha P^2 + \frac{1}{4} \beta P^4 + \frac{1}{6} \gamma P^6 + \ldots $$

(A24)

The coefficients $\alpha$, $\beta$, $\gamma$ depend on the temperature in general. Note that the series does not contain terms in odd powers of $P$ because the free energy of the crystal will not change by the polarization reversal ($P \rightarrow -P$). The phenomenological formulation should be applied for all the temperature range through paraelectric and ferroelectric states.

The equilibrium polarization in an electric field $E$ satisfies:

$$ \frac{\partial F}{\partial P} = E = \alpha P + \beta P^3 + \gamma P^5 $$

(A25)

To obtain the ferroelectric state, the coefficient of the term in $P^2$ must be negative, in which the polarized state is stable, while in a paraelectric state it must be positive passing through zero at some temperature $T_0$ (Curie–Weiss temperature):

$$ \alpha = (T - T_0)/(\varepsilon_0 \cdot C) $$

(A26)

$C$ is taken as a positive constant and $T_0$ is equal to or lower than the actual transition temperature $T_C$ (Curie temperature). The variation of $\alpha$ with temperature is explained microscopically by thermal expansion and other effects of anharmonic lattice interactions.

12.9.1.1 Second-Order Transition

When $\beta$ is positive, the $\gamma$ is often neglected because nothing special is added by this term. The polarization for zero applied field (A27) is obtained from (A25) so that either $P = 0$ or $P^2 = (T_0 - T)/(\varepsilon_0 \cdot C)$.

$$ \frac{T - T_0}{\varepsilon_0 C} P + \beta P^3 = 0 $$

(A27)

For $T \geq T_0$, the unique solution $P = 0$ is obtained. For $T < T_0$ the minimum of the Landau free energy is obtained at:

$$ P = \sqrt{(T_0 - T)/(\varepsilon_0 C)} $$

(A28)

The phase transition occurs at $T_C = T_0$ and the polarization goes continuously to zero at this temperature; this is called a second-order transition.

Relative permittivity $\varepsilon$ is calculated as:

$$ 1/\varepsilon = \varepsilon_0/\partial P/\partial E = \varepsilon_0(\alpha + 3 \beta P^2) $$

(A29)

Then,

$$ \varepsilon = \begin{cases} C/(T - T_0) & (T > T_0) \\ C/[2(T_0 - T)] & (T_0 < T) \end{cases} $$

(A30)

Figure 12-A1 shows the variations of $P$ and $\varepsilon$ with temperature. It is notable that the permittivity becomes infinite at the transition temperature. Triglycine sulphate is an example exhibiting the second-order transition.

12.9.1.2 First-Order Transition

When $\beta$ is negative in Eq. (A24) and $\gamma$ is taken positive, the transition becomes first order. The equilibrium condition for $E = 0$ (A31) leads to either $P = 0$ or (A32).

$$ \frac{T - T_0}{\varepsilon_0 C} P + \beta P^3 + \gamma P^5 = 0 $$

(A31)

$$ P^2 = -\beta + \sqrt{\beta^2 - \frac{4\gamma(T - T_0)}{\varepsilon_0 C}} / (2\gamma) $$

(A32)
12.9 Appendix 2: Phenomenology of Ferroelectricity

The transition temperature $T_C$ is obtained from the condition that the free energies of the paraelectric and ferroelectric phases are equal: i.e., $F = 0$, or:

$$\frac{T - T_0}{\varepsilon_0 \varepsilon} + \frac{1}{2} \beta P^2 + \frac{1}{3} \gamma P^4 = 0 \quad (A 33)$$

Therefore:

$$T_C = T_0 + \frac{3}{16} (\beta^2 \varepsilon_0 C / \gamma) \quad (A 34)$$

Note that the Curie Temperature $T_C$ is slightly higher than the Curie-Weiss temperature $T_0$, and that the discrete jump of the $P$ appears at $T_C$. Also, the permittivity exhibits a finite maximum at $T_C$ for a first-order transition (Fig. 12-A2). Barium titanate is a good example.

12.9.2 Phenomenology of Electrostriction

Let us assume that the elastic Gibbs energy should be expanded in a one-dimensional form:

$$G_1 (P, X, T) = \frac{1}{2} \alpha P^2 + \frac{1}{2} \beta P^4 + \frac{1}{6} \gamma P^6 - \frac{1}{2} s X^2 - Q P^2 X, \ [\alpha = (T - T_0)/(\varepsilon_0 C)]$$

$P, X, T$ are polarization, stress and temperature, respectively, and $s$ and $Q$ are called the elastic compliance and the electrostrictive coefficient. Note that the piezoelectric coupling term $PX$ is omitted and the electrostrictive coupling term $P^2 X$ is introduced when the paraelectric phase has centrosymmetry (non-piezoelectric). This leads to Eq. (A 36) and (A 37).

$$E = (\partial G_1 / \partial P) = \alpha P + \beta P^3 + \gamma P^5 - 2 Q P X \quad (A 36)$$

$$x = - (\partial G_1 / \partial X) = s X + Q P^2 \quad (A 37)$$

12.9.2.1 Case I: $X = 0$

When an external stress is zero, the following equations are derived:

$$E = \alpha P + \beta P^3 + \gamma P^5 \quad (A 38)$$

$$x = Q P^2 \quad (A 39)$$

$$1/\varepsilon_0 \varepsilon = \alpha + 3 \beta P^2 + 5 \gamma P^4 \quad (A 40)$$

If the external electric field is equal to zero ($E = 0$), two different states are derived: $P = 0$ and $P^2 = (\sqrt{\beta^2 - 4 \alpha \gamma} - \beta)/(2 \gamma)$.

(I) Paraelectric phase: $P_0 = 0$ or $P = \varepsilon_0 \varepsilon E$

(under small $E$)

Permittivity:

$$\varepsilon = C(T - T_0) \quad \text{(Curie-Weiss law)} \quad (A 41)$$
Electrostriction:
\[ x = Q \varepsilon_0^2 \varepsilon E^2 \]  
\[ (A 42) \]

(II) Ferroelectric phase:
\[ P^2 = (\sqrt{\beta^2 - 4 \sigma \gamma} - \beta)/(2 \gamma) \] or \[ P = P_s + \varepsilon_0 \varepsilon E \] (under small \( E \))
\[ x = Q (P + \varepsilon_0 \varepsilon E)^2 = Q P_s^2 + + 2 \varepsilon_0 \varepsilon Q P_s E + Q \varepsilon_0^2 \varepsilon E^2 \]  
\[ (A 43) \]

Spontaneous strain:
\[ x_s = Q P_s^2 \]  
\[ (A 44) \]

Piezoelectric constant:
\[ d = 2 \varepsilon_0 \varepsilon Q P_s \]  
\[ (A 45) \]

Piezoelectricity is equivalent to the electrostrictive phenomenon biased by the spontaneous polarization. Temperature dependence of the spontaneous strain and the piezoelectric constant is plotted in Fig. 12-A 3.

\[ \begin{align*}
\text{Physical properies} \\
\text{Spontaneous strain } x_s \\
\text{Piezoelectric constant } d \\
\text{Tc Temperature} \\
\text{(Curie Temp.)}
\end{align*} \]

Figure 12-A 3. Temperature dependence of spontaneous strain and piezoelectric constant.

12.9.2.2 Case I: \( X \neq 0 \)

When a hydrostatic pressure \( p \) (\( X = -p \)) is applied, the inverse permittivity is changed in proportion to \( p \):
\[ 1/\varepsilon_p = \begin{cases} 
\alpha + 3 \beta P^2 + 5 \gamma P^4 + 2 Q_p \\
\alpha + 2 Q_p = (1 - T_0 + 2 Q \varepsilon_0 C p)/(\varepsilon_0 C)
\end{cases} \]  
\[ (Ferroelectric) \]  
\[ (Paralectric) \]  
\[ (A 46) \]  
\[ (A 47) \]

Therefore, the pressure dependence of the Curie–Weiss temperature \( T_0 \) or the transition temperature \( T_C \) is derived as follows:
\[ \frac{\partial T_0}{\partial p} = \frac{\partial T_C}{\partial p} = -2 Q \varepsilon_0 C \]  
\[ (A 48) \]

In general, the ferroelectric Curie temperature is decreased with increasing hydrostatic pressure.

12.10 References


Nikkai Mechanical (1983), Feb. 28 Ed., p. 44.


General Reading


APPENDIX 3
Smart Materials
Smart, Very Smart, and Intelligent Materials

Robert E. Newnham, Guest Editor

One of the qualities that distinguishes living systems from inanimate matter is the ability to adapt to changes in the environment. Smart materials have the ability to perform both sensing and actuating functions and are, therefore, capable of imitating this rudimentary aspect of life. Polled piezoelectric ceramics, for instance, are capable of acting as both sensor and actuator. External forces are detected through the direct piezoelectric effect, and a response is elicited through the converse piezoelectric effect, in which a voltage of suitable phase, frequency, and amplitude is applied to the same ceramic.

In this special issue, emphasis is placed on actuators, with articles on piezoelectric, electrostrictive, magnetostrictive, and shape memory materials. This is not to say that sensor materials are any less important; it is simply a matter of space. Optical fiber sensors, chemical sensors, thermistors, micromachined semiconductors, and other smart materials deserve special issues of their own.

Smart materials can be conveniently subdivided into passive smart materials that respond to external change without assistance, and actively smart materials that utilize a feedback loop enabling them to both recognize the change and initiate an appropriate response through an actuator circuit.

Zinc oxide varistors are passively smart materials capable of self-protection against high voltage breakdown. When struck by lightning, the ceramic varistor loses most of its electrical resistance, and the current is bypassed to ground. The resistance change is reversible, and acts as a standby protection mechanism. Varistors also have a self-repair mechanism through which the highly nonlinear I-V relationship can be restored by repeated voltage pulses.

Actively smart materials include vibration-damping systems for outer-space platforms and electronically-controlled auto-mobile suspension systems. Piezoelectric video tape head positioners operate on a similar principle. The positioners contain a bilaminate bender made from tape-cast PZT ceramic with a segmented electrode pattern dividing the sensing and actuating functions of the positioner. Signals appearing across the sensing electrode are analyzed and processed in the feedback circuit, resulting in a voltage across the positioning electrodes. This causes the cantilevered bender to bend, following the video tape track path.

These two examples illustrate how smart materials operate. Both sensing and actuating functions are involved in their performance—but are they really smart? Webster's Dictionary gives several definitions for the word "smart," including "alert, clever, capable," "stylish," and "to feel mental distress or irritation." All three definitions are appropriate for the currently fashionable subject "smart materials." They are "stylish," but are, in some cases, "clever," and it does cause some of us "mental distress" to think that a ceramic might somehow possess intelligence, even in rudimentary form.

How smart is "smart?" There are many words in the English language denoting various levels of intelligence. Beginning at the bottom, an intelligence scale might look like this: stupid - ignorant - trivial - sensible - smart - clever - intelligent - wise. Many modern-day materials have been cleverly designed to perform useful functions and we are, it seems to us, justified in calling them "smart." They are decidedly better than "sensible" materials, but calling them "intelligent" seems rather presumptuous and self-serving.

A number of research groups are looking for ways to raise the level of "intelligence" in materials by integrating the sensing and actuating functions with information processing systems, memories and learning mechanisms, power supplies, and various forms of self-protection. In a crude way, these materials mimic the brain, metabolism, and protective reflex reactions of the human body that augment muscle motion and the five senses.

Materials with a built-in learning function are smarter than those without. A very smart material senses a change in the environment and responds by altering one or more of its property coefficients. In this way, it can tune its sensing and actuating capabilities in time or space to optimize behavior. With the help of a feedback system, a very smart material becomes smarter with age. The distinction between smart and very smart materials is essentially one between linear and nonlinear properties. The physical properties of nonlinear materials can be adjusted by bias fields or forces to control response.

The tunable transducer developed in our laboratory illustrates the concept of a very smart material. Two of the important properties of the ultrasonic transducers used in biomedical scanners and in nondestructive testing are the resonant frequency and the electromechanical coupling coefficient. The resonant frequency is controlled by the elastic constants of the transducer, and the electromechanical coupling coefficient by its piezoelectric constants. Tunable transducers are made by sandwiching together two highly nonlinear materials: rubber and relaxor ferroelectric ceramics. Rubber, like most elastomers, is elastically nonlinear. In its unstressed compliant state, the molecules are coiled and tangled, but under stress, the molecules align and the material stiffens noticeably. Relaxor ferroelectrics, such as lead magnesium niobate, are electrically nonlinear, and exhibit huge electrostriction effects. Under electrical bias, the piezoelectric coefficient increases dramatically from zero to a value far higher than lead zirconate titanate. Both the resonant frequency and electromechanical coupling coefficient can be tuned when electric fields are applied simultaneously.

Integration and miniaturization of ceramic sensors and actuators is an ongoing process in the automotive and consumer electronics areas. Today's mid-range vehicles have about 50 sensors and actuators, and even more sophisticated functional materials are under development for exhaust gas monitoring, active suspensions, and integrated traffic guidance systems. Multilayer packages containing signal processing layers made up of low-permittivity dielectrics and printed metal interconnections are in widespread production. Further integration with embedded resistors and capacitors is under development and it seems likely that intelligent
systems will make use of this processing technology. Tape casting and screen printing are the processes used most often, and varistors, chemical sensors, thermistors, and piezoelectric transducers can all be fabricated in this way, opening up the possibility of multicomponent multifunction ceramics with both sensor and actuator capabilities. Silicon chips can be mounted on these multifunctional packages to provide all or part of the control network. The next logical step is to combine the sensor and actuator functions with the control system. This can be done by depositing electroceramic coatings on integrated circuit silicon chips—currently an active area for materials research. In the near future, when the information processing system, feedback circuitry, and power supply are integrated with the sensors and actuators, we will then perhaps be justified in calling our materials intelligent. The next goal will be to develop wise materials, that make the correct moral decision.

Robert E. Newnham, Guest Editor for this issue of the MRS Bulletin, is Alcoa Professor of Solid State Science at Pennsylvania State University's Materials Research Laboratory. He also teaches courses in the Ceramic Science Section of the Materials Science and Engineering Department. Newnham, whose research interests are in structure-property relations, electronic ceramics, and composite materials for electronic applications, holds a PhD degree from Penn State in physics and mineralogy and a PhD degree from Cambridge University in crystallography. Prior to joining the Penn State faculty, he taught at MIT, where he was a staff member of the Laboratory for Insulation Research. Newnham has authored four books and more than 300 papers, is co-editor of the Journal of the American Ceramic Society, and is a member of the National Academy of Engineering. Newnham was elected Ceramic Educator of the Year by the Ceramic Education Council and is a recipient of the John Jeppson Laboratory Medal for "Distinguished, creative, and inspiring contributions to ceramic science, technology, and education in the area of electronic ceramic materials." He is also the recipient of the First International Ceramics Prize from the Academy of Ceramics.

Arthur E. Clark, Navy Distinguished Scientist, has been head of the magnetics group at the Naval Surface Warfare Center, White Oak Laboratory, for 18 years. Since receiving his PhD in physics from Catholic University of America in 1960, he has been engaged in research on the elastic and magnetic properties of solids, particularly on the magnetoresistive properties of rare-earth ions in metals and insulators. Clark holds patents in the areas of magnetic refrigeration, magnetostrictive materials, and magnetomechanical transduction.

Kristi B. Hathaway, research physicist at the Naval Surface Warfare Center, White Oak Laboratory, and a scientific officer in the Materials Division of the Office of Naval Research, manages basic research programs in magnetic materials. Her research interests include the magnetoelastic behavior of rare-earth transition metal alloys and amorphous metallic glasses, the electronic structure of transition metals, and the magnetic properties of thin films and multilayers. Hathaway received her PhD degree in physics from Cornell University in 1976.

Susan Troller-McKinstry is an assistant professor of ceramic science at Pennsylvania State University, where she researches ferroelectric and piezoelectric films and the optical characterization of bulk and thin-film ceramic materials. Troller-McKinstry received her PhD degree in ceramic science from Penn State.
State, where she also earned her BS and MS degrees. A recipient of an MRS Graduate Student Award in spring 1992, she spent six months at the Hitachi Central Research Laboratory in Tokyo during her doctoral program, studying the development of graphoepitaxial alignment in platinum on sawtooth-profiled Si wafers for use as substrates for piezoelectric films.

Kenji Uchino is a professor of electrical and computer engineering, a professor of materials, and director of the International Center for Actuators and Transducers at Pennsylvania State University. He is also an associate professor of physics at Sophia University, Japan. Uchino received his MS and DSc degrees in physical electronics from the Tokyo Institute of Technology. His research interests cover dielectrics, ferroelectrics, and piezoelectrics, and include basic research on materials, as well as device designing and fabrication processes. An inventor holding 30 patents and the author of 24 books on piezoelectric actuators, Uchino is vice president of NF Electronic Instruments, Inc., a company formed to develop products relating to piezoelectric actuators. He is also the founder and chairman of the Society of Solid State Actuators, Japan Technology Transfer Association. Uchino has authored more than 150 publications and received the Best Paper Award of the Japanese Society of Oil/Air Pressure Control.

C.M. Wayman, professor of materials science and engineering at the University of Illinois, is a researcher in the field of martensitic transformations. He has published over 400 papers and edited numerous books. His textbook, *Crystallomorphology of Martensitic Transformations*, has been translated into Japanese and Chinese. Wayman has received the AIME Mathewson Gold Medal, The Buehler Award from the International Metallographic Society, and the Eminent Faculty Award of the College of Engineering at the University of Illinois. He is also the recipient of honorary professorships at Harbin and Balian Universities in China, and fellowships in ASM International, the Metallurgical Society of AIME, the Institution of Metallurgists, the Japan Society for the Promotion of Science, the Guggenheim Foundation, and Churchill College at the University of Cambridge.
APPENDIX 4
SIZE EFFECTS AND NONLINEAR PHENOMENA
IN FERROIC CERAMICS

R. E. Newnham, Materials Research Laboratory, Pennsylvania State University,
University Park, PA 16802, USA

ABSTRACT
Recent developments in the field of electroceramic nanocomposites are
described, placing particular emphasis on the role of the ferroic materials now
utilized as soft ferrite transformers, barium titanate multilayer capacitors, toughened
zirconia engine parts, lead zirconate-titanate transducers, and doped barium titanate
PTC thermistors. The effect of nano-scale on both the material property coefficients
of these systems and on their phase transitions is also discussed.

The concept of a fully tunable transducer is developed as an example of a
nonlinear material whose sensing and actuating functions can be tuned to optimize
behavior. By constructing the composite transducer from an elastically nonlinear
material (rubber) and an electrically nonlinear material (relaxor ferroelectric), most
of its key properties can be adjusted over wide ranges by applying DC bias fields or
mechanical prestress. These properties include resonant frequency, acoustic and
electric impedance, damping factors, and electromechanical coupling coefficients.

The origins of nonlinear properties are considered briefly using electrostriction
as an example. The nonlinearities often involve phase transformations and size-
dependent phenomena on the nanometer scale.

INTRODUCTION
Ferroic crystals have movable domain walls which impart useful properties to a
number of electroceramic materials. The properties of these materials are usually
largest near the phase transformation temperature where the ferroic domain structure
is destabilized as the crystalline structure alters to a high-temperature, high-
symmetry form. It is for this reason that the dielectric permittivity of ferroelectric
capacitors is the largest near the Curie temperature, and the magnetic susceptibility of
ferrite transformers peaks near $T_c$. PTC thermistors and toughened zirconia engine
parts also exhibit ferroic behavior (Table 1).
Table 1: Primary and Secondary Ferroic Crystals (1)

<table>
<thead>
<tr>
<th>Primary Ferroics</th>
<th>Secondary Ferroics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferromagnetism</td>
<td>Ferroelastoelectricity</td>
</tr>
<tr>
<td>Ferroelectricity</td>
<td>Ammonium Chloride (NH₄Cl)</td>
</tr>
<tr>
<td>Ferroelasticity</td>
<td>Chromium Oxide (Cr₂O₃)</td>
</tr>
<tr>
<td></td>
<td>Ferromagnetoelectricity</td>
</tr>
<tr>
<td></td>
<td>Iron Carbonate (FeCO₃)</td>
</tr>
<tr>
<td></td>
<td>Ferrobielasticity</td>
</tr>
<tr>
<td></td>
<td>Quartz (SiO₂)</td>
</tr>
<tr>
<td></td>
<td>Ferrobiomagnetism</td>
</tr>
<tr>
<td></td>
<td>Nickel Oxide (NiO)</td>
</tr>
<tr>
<td></td>
<td>Ferrobirelectricity</td>
</tr>
<tr>
<td></td>
<td>Strontium Titanate (SrTiO₃)</td>
</tr>
</tbody>
</table>

Ferroelastic solids have domains which differ in spontaneous strain. The domain walls separating these domains can be shifted with mechanical stress, leading to hysteresis between stress and strain. Analogous behavior between the polarization and the electric field is observed in ferroelectric crystals, and between magnetization and magnetic field in ferromagnetic materials.

In addition to the three types of primary ferroics, there are six types of secondaries which also have movable domain walls. Some, like ferromagnetoelectric chromium oxide, require that two fields (E and H) be applied simultaneously, while others such as ferrobielastic quartz, are higher order primary effects in which the energy difference between domain states is proportional to the square of the applied stress.

PARTICLE SIZE EFFECTS

It is anticipated that many ferroic materials undergo changes in the phase transformations as the particle size is reduced. While ferromagnetic materials are still by far the best studied, new experimental evidence is accumulating that small ferroelastic, ferroelectric and secondary ferroic particles will show similar behavior.

When prepared as large grain size ceramics (typically microns or larger), ferroelectric and ferromagnetic oxides exhibit complex domain structures, often with several different types of domain walls. As the grain size is reduced, however, the surface area grows in comparison with volume and it becomes increasingly difficult to recover the wall energy from the volume term. Consequently, the number of domains decreases as first one and then the other types of walls are eliminated. The transition from polydomain to single domain behavior is well-documented in a number of ferromagnets, occurring near 50 nm for many spherical metallic particles. For example, pure iron suspended in mercury shows a critical size for conversion to single domain behavior at -23 nm and Fe₀.₄Co₀.₆ a critical size of -28 nm (2). This is in good agreement with calculations by Kittel, who suggested a 20 nm minimum size for the appearance of ferromagnetism in particles (3). Results for acicular agglomerates of γ-Fe₂O₃ particles separated by non-magnetic grain boundaries are also consistent with these estimates; Berkowitz et al. (4) report that the stable single domain range at room temperature is centered at ~40 nm.

Studies on BaTiO₃ ceramics (which contain ferroelectric 180° walls and 90° walls which are both ferroelectric and ferroelastic) also show fewer 90° domains in small-grained samples than are observed for large grain sizes (5-7). An intermediate regime, centered at a grain size of 0.7 mm, with an increased density of small 90° domains has also been reported by Arlt et al. (8,9). Explanation for the changes in the equilibrium number of domains as a function of grain size (and in particular the effect of this on
the dielectric properties) is complicated by the fact that in a ceramic where individual grains do not possess cubic symmetry, each grain is subjected to a complex set of stresses which arise when the body is cooled through the transition temperature after firing (7). Because 90° walls are ferroelastic as well as ferroelectric, large stresses should be expected to greatly affect the number and type of domains.

For free BaTiO₃ powders, however, the boundary conditions on each particle are much simpler than those existing in a ceramic. Consequently, the changes in properties as the particle size is decreased are expected to follow the magnetic analog more closely. As far as we are aware, however, critical sizes for the disappearance of 90° domains and the transition to single domain in unconstrained ferroelectric powders have not been reported in the literature.

At still smaller sizes, ferroic particles undergo a phase change to the high temperature symmetry group and sometimes show the enhanced responsiveness characteristic of a superparamagnetic, superparaelectric, or superparaelastic solid. For example, iron exhibits superparamagnetic behavior at particle sizes near 7 nm, (2), γ-Fe₂O₃ at about 30 nm (4) and BaFe₁₂₋₂Zr₂Co₉O₃₉ at 15 - 35 nm depending on the stoichiometry and the degree of particle shape anisotropy (10). This state is characterized by a zero net magnetization, the disappearance of a magnetic hysteresis loop, and extremely high magnetic susceptibilities. These properties can be explained by assuming that the sample behaves as an unmagnetized but highly orientable single domain. Fine particle magnets are used in high frequency transformers where eddy current losses are a problem.

Although the transitions from polydomain to 180° domains in thence to single domain are not well documented for ferroelectrics, an electric analog to superparamagnetism may be found in the family of relaxor ferroelectrics (11). Compositions including many of the AlB₂₁/₄,B₁/₄O₃ and AlB₂₁/₄,B₁/₄O₃ perovskites exhibit microdomains (typically 20 - 300Å in size) of 1:1 ordering on the F₂ sublattice dispersed in a disordered matrix (12,13). It has been suggested that as a result of this local nonstoichiometry the spontaneous polarization in these materials is also disordered on a very fine scale (14). Thus a lead magnesium niobate ceramic can be regarded as a collection of disordered, but highly orientable, dipoles. The result, much like the case of superparamagnetism, is a high dielectric permittivity over a broad temperature range even though the net spontaneous polarization is zero.

Once the ordered microdomains in a relaxor grow beyond a certain size, however, the material reverts to ordinary ferroelectric (or antiferroelectric) behavior with a well defined transition temperature and a non-dispersive dielectric response. For lead indium niobate the critical domain size at which antiferroelectric ordering appears is 80 nm (12). This size may also serve as a guideline for the dimension at which a ferroelectric particle might be expected to show superparaelectric behavior.

As yet, direct observations of superparaelectric behavior in particulate ordinary ferroelectrics has not been documented. Recently, however, many investigators have attempted to determine the critical size for reversion to the high temperature prototype symmetry. Their results indicate that unconstrained BaTiO₃ particles show the transition to cubic at room temperature near 1200Å (15,16) whereas PbTiO₃ is stable in the tetragonal form to ~20 nm (17-18). However, it should be noted that it is possible to shift the observed critical size with changes in the preparation. Residual strain in particular has been shown to drastically affect the properties of BaTiO₃ (19, 20). Thus it is not surprising that milled BaTiO₃ powders with an average radius of ~10 nm have been shown to possess permanent dipole moments (21).

Saegusa et al. examined the solid solution between BaTiO₃ and PbTiO₃ to determine the critical size for stabilization of the cubic phase at room temperature as a function of composition. Assuming that crystallinity and stoichiometry were maintained for the smallest sizes, their data suggests that the critical size is not a linear function of composition. Thus, at a 1:1 Ba:Ti ratio, the ferroelectric phase was stable at least to 40 nm (16). It would be tremendously interesting to follow the magnitude of the polarization as a function of temperature in such powders to see how
its magnitude is affected by the particle size. As research of this type is pursued, it may be possible that a transition to superparaelectric behavior will be observed at still smaller sizes.

We are not aware of any reports in the literature on superparaelectricity in ceramic compositions. However, this field is potentially interesting as it holds the promise of imparting large elastic compliance to ceramics and other brittle materials.

Because ferromagnetism is a cooperative phenomenon, it is intuitively appealing to suppose that the system will be forced to revert to paramagnetic at some size at which there are simply too few atoms to sustain the cooperative interactions. Thus, at still smaller sizes, approaching atomic dimensions, superparamagnetism reverts to ordinary paramagnetism in which the magnetic susceptibility follows a Curie law with temperature. Analogous behavior is not documented for ferroelectric or ferroelastic solids.

In summary, then, we expect four regions in the size dependence of ferroic properties (Fig. 1). In large crystallites, multidomain effects accompanied by hysteresis take place. Reductions in size lead to single domain particles, and at yet smaller sizes to destabilized ferroics with large property coefficients, and finally to normal behavior as the particle size approaches the atomic scale. Similar transitions with size are expected in secondary ferroics.

<table>
<thead>
<tr>
<th>SIZE</th>
<th>FERROMAGNETIC</th>
<th>FERROELECTRIC</th>
<th>FERROELASTIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>~1 µm</td>
<td>MULTIDOMAIN</td>
<td>MULTIDOMAIN</td>
<td>MULTIDOMAIN</td>
</tr>
<tr>
<td>~0.1 µm</td>
<td>SINGLE DOMAIN</td>
<td>SINGLE DOMAIN</td>
<td>SINGLE DOMAIN</td>
</tr>
<tr>
<td>~10 nm</td>
<td>SUPER-PARAMAGNETIC</td>
<td>SUPER-PARAELECTRIC</td>
<td>SUPER-PARAELECTRIC</td>
</tr>
<tr>
<td>~1 nm</td>
<td>PARAELECTRIC</td>
<td>PARAELECTRIC</td>
<td>PARAELECTRIC</td>
</tr>
</tbody>
</table>

**Figure 1. Transitions in ferroic behavior as a function of size**

**SMART AND VERY SMART MATERIALS**

Much of the recent interest in nanoscale size effects stems from the desire to build "smart materials" for intelligent systems, utilizing nonlinear physical phenomena. The words "smart materials" have different meanings for different people, and can be smart in either a passive sense or an active sense. Passively smart materials incorporate self-repair mechanisms or stand-by phenomena which enable the material to withstand sudden changes in the surroundings.

Ceramic varistors and PTC thermistors [23] are passively smart materials. When struck by lightning or otherwise subjected to high voltage, a zinc oxide varistor loses its electrical resistance and the current is bypassed to ground. The resistance change is reversible and acts as a stand-by protection phenomenon. Barium titanate
PTC thermistors show a large increase in electrical resistance at the ferroelectric phase transformation near 130°C. The jump in resistance enables the thermistor to arrest current surges, again acting as a protection element. The R(T) behavior of the varistor and the RT(T) behavior of the PTC thermistor are both highly nonlinear effects which act as standby protection phenomena, and make the ceramics smart in a passive mode.

A smart ceramic can also be defined with reference to sensing and actuating functions, in analogy to the human body. A smart ceramic senses a change in the environment, and using a feedback system, makes a useful response (23). It is both a sensor and an actuator. Examples include vibration damping systems for space structures and energy-saving windows for homes and factories. The new electronically-controlled automobile suspension systems using piezoelectric ceramic sensors and actuators constitutes an actively smart material.

By building in a learning function, the definition can be extended to a higher level of intelligence: A very smart ceramic senses a change in the environment and responds by changing one or more of its property coefficients. Such a material can tune its sensor and actuator functions in time and space to optimize behavior. The distinction between smart and very smart materials is essentially one between linear and nonlinear properties. The physical properties of nonlinear materials can be adjusted by bias fields or forces to control response.

TUNABLE TRANSDUCER

To illustrate the concept of a very smart material, we describe the tunable transducer recently developed in our laboratory (24). Electromechanical transducers are used as fish finders, gas igniters, ink jets, micropositioners, biomedical scanners, piezoelectric transformers and filters, accelerometers, and motors.

Four important properties of a transducer are the resonant frequency f, the acoustic impedance Z_A, the mechanical damping coefficient Q, the electromechanical coupling factor k, and the electrical impedance Z_E. The resonant frequency and acoustic impedance are controlled by the elastic constants and density, as discussed in the next section. The mechanical Q is governed by the damping coefficient and is important because it controls "ringing" in the transducer. Electromechanical coupling coefficients are controlled by the piezoelectric coefficient which, in turn, can be controlled and fine-tuned using relaxor ferroelectrics with large electrostrictive effects. The dielectric "constant" of relaxor ferroelectrics depends markedly on DC bias fields, allowing the electrical impedance to be tuned over a wide range as well. In the following sections we describe the nature of nonlinearity and how it controls the properties of a tunable transducer.

ELASTIC NONLINEARITY: TUNING THE RESONANT FREQUENCY

Information is transmitted on electromagnetic waves in two ways: amplitude modulation (AM) and frequency modulation (FM). There are a number of advantages to FM signal processing, especially where lower noise levels are important.

Signal-to-noise ratios are also important in the ultrasonic systems used in biomedical and nondestructive testing systems, but FM-modulation is difficult because resonant frequencies are controlled by stiffness (c) and sample dimensions (l):

\[ f = \frac{1}{2\pi} \sqrt{c/l} \]

Neither c, l, or the density \( \rho \) can be tuned significantly in most materials, but rubber is an exception. To tune the resonant frequency of a piezoelectric transducer, we have designed and built a composite transducer incorporating thin rubber layers exhibiting nonlinear elasticity.
Rubber is a highly nonlinear elastic medium. In the unstressed compliant state, the molecules are coiled and tangled, but under stress the molecules align and the material stiffens noticeably. Experiments carried out on rubber-metal laminates demonstrate the size of the nonlinearity. Young's modulus \( E = 1 / \sigma_{1111} \) was measured for a multilayer laminate consisting of alternating steel shim and soft rubber layers each 0.1 mm thick. Under compressive stresses of 200 MN/m\(^2\), the stiffness is quadrupled from about 600 to 2400 MN/m\(^2\). The resonant frequency \( f \) is therefore double, and can be modulated by applied stress (25).

Rubber, like most elastomers, is not piezoelectric. To take advantage of the elastic nonlinearity, it is therefore necessary to construct a composite transducer consisting of a piezoelectric ceramic (PZT) transducer, thin rubber layers, and metal head and tail masses, all held together by a stress bolt.

The resonant frequency and mechanical \( Q \) of such a triple sandwich structure was measured as a function of stress bias. Stresses ranged from 20 to 100 MPa in the experiments. Under these conditions the radial resonant frequency changed from 19 to 37 kHz, approximately doubling in frequency as predicted from the elastic nonlinearity. At the same time the mechanical \( Q \) increases from about 11 to 34 as the rubber stiffens under stress (25).

The changes in resonance and \( Q \) can be modeled with an equivalent circuit in which the compliance of the thin, rubber layers are represented as capacitors coupling together the larger masses (represented as inductors) of the PZT transducer and the metal head and tail masses. Under low stress bias, the rubber is very compliant and effectively isolates the PZT transducer from the head and tail masses. At very high stress, the rubber stiffens and tightly couples the metal end pieces to the resonating PZT ceramic. For intermediate stresses the rubber acts as an impedance transformer giving parallel resonance of the PZT - rubber - metal -radiation load.

It is interesting to compare the change in frequency of the tunable transducer with the transceiver systems used in the biological world. The biosonar system of the flying bat is similar in frequency and tunability to our tunable transducer. The bat emits chirps at 30 kHz and listens for the return signal to locate flying insects. To help differentiate the return signal from the outgoing chirp, and to help in timing the echo, the bat puts an FM signature on the pulse. This causes the resonant frequency to decrease from 30 to 20 kHz near the end of each chirp. Return signals from the insect target are detected in the ears of the bat where neural cavities tuned to this frequency range measure the time delay and flutter needed to locate and identify its prey. Extension of the bat biosonar principle to automotive, industrial, medical and entertainment systems is readily apparent.

PIEZOELECTRIC NONLINEARITY: TUNING THE ELECTROMECHANICAL COUPLING COEFFICIENT

The difference between a smart and a very smart material can be illustrated with piezoelectric and electrostrictive ceramics. PZT (lead zirconate titanate) is a piezoelectric ceramic in which the ferroelectric domains are aligned in a poling field. Strain is linearly proportional to electric field in a piezoelectric material which means that the piezoelectric coefficient is a constant and cannot be electrically tuned with a bias field. Nevertheless it is a smart material because it can be used both as a sensor and an actuator.

PMN (lead magnesium niobate) is not piezoelectric at room temperature because its Curie temperature lies near 0°C. Because of the proximity of the ferroelectric phase transformation, and because of its diffuse nature, PMN ceramics exhibit very large electrostrictive effects. The nature of this large nonlinear relationship between strain and electric field, and of its underlying atomistic origin, has already been discussed in terms of a nanoscale ordering phenomenon (26).

Electromechanical strains comparable to PZT can be obtained with electrostrictive ceramics like PMN, and without the troubling hysteretic behavior
shown by PZT under high fields. The nonlinear relation between strain and electric field in electrostrictive transducers can be used to tune the piezoelectric coefficient and the dielectric constant.

The piezoelectric $d_{33}$ coefficient is the slope of the strain-electric field curve when strain is measured in the same direction as the applied field. Its value for Pb(Mg$_{0.34}$Nb$_{0.66}$O$_{3}$) ceramics is zero at zero field and increases to a maximum value of 1300 pC/N (about twice as large as PZT) under a bias field of 3.7 kV/cm (27).

This means that the electromechanical coupling coefficient can be tuned over a very wide range, changing the transducer from inactive to extremely active. The dielectric constant also depends on DC bias. The polarization saturates under high fields causing decreases of 100% or more in the capacitance. In this way the electrical impedance can be controlled as well.

**ORIGINS OF NONLINEARITY**

What do nonlinear materials have in common? The passively-smart PTC thermistor and ZnO varistor described earlier have grain boundaries a few nm thick. These insulating barriers that can be obliterated by the polarization charge accompanying a ferroelectric phase transformation, or, in the case of the varistor, the insulating boundaries so thin they can be penetrated by quantum mechanical tunneling.

Small size is also key factor in the nonlinear behavior of semiconductors. The thin gate region in a transistor allows charge carriers to diffuse through unimpeded. The p-region in an n-p-n transistor is thin compared to the diffusion length in single crystal silicon. Similar size-related phenomena are observed in quantum well structures made from GaAs and Ga$_{1-x}$Al$_x$As. Planar structures with nm-thick layers show channeling behavior of hot electrons in clear violation of Ohm's law. Current-voltage relationships are highly nonlinear in many submicron semiconductor structures. Ohm's law is a statistical law which relies upon the assumption that the charge carriers make a sufficiently large number of collisions to enable them to reach a terminal velocity characteristic of the material. When the size of the conduction path is sufficiently small, compared to the mean free path between collisions, the statistical assumption breaks down, and Ohm's law is violated.

Nonlinear behavior is also observed in thin film insulators where even a modest voltage of 1-10 volts can result in huge electric fields of 100 MV/m or more. This means that thin film dielectrics experience a far larger field than do normal insulators, and causing the polarization to saturate and electric permittivity to decline. Because of the high fields, electric breakdown becomes a greater hazard, but this is partly counteracted by an increase in breakdown strength with decreasing thickness. This comes about because the electrode equipotential surfaces on a thin film dielectric are extremely close together, thereby eliminating the asperities that lead to field concentration and breakdown.

The influence of nanometer-scale domains on the properties of relaxor ferroelectrics has already been made plain. Here the critical size parameter is the size of the polarization fluctuations arising from thermal motions near the broad ferroelectric phase transformation in PMN and similar oxides. The ordering of Mg and Nb ions in the octahedral site of the PMN structure results in a chemically inhomogeneous structure on a nm-scale, and this, in turn, influences the size of the polarization fluctuations. Tightly coupled dipoles within each Nb-rich portion of this self-assembling nanocomposite behave like a superparaelectric solid. The dipoles are strongly coupled to one another but not to the crystal lattice, and thus they reorient together under the influence of temperature or electric field. This in turn causes the large electric permittivities and large electrostrictive effects found in relaxor ferroelectrics.

The importance of nanometer-scale fluctuations and the instabilities associated with phase transformations is also apparent in the nonlinear elasticity of rubber and
other polymeric materials. The thermally-assisted movement of the randomly oriented polymer chains under tensile stress results in large compliance coefficients, but rubber gradually stiffens as the chains align with the stress into pseudo-crystalline regions. The increase in stiffness with stress gives rise to sizeable third order elastic constants in many amorphous polymers. The effect depends markedly on temperature. On cooling, to lower temperatures rubber and other amorphous polymers transform from a compliant rubber-like material to a brittle glass-like phase which is of little use in nonlinear devices.

Nonlinear behavior is also observed in magnetic and optical systems. Superparamagnetic behavior, analogous to the superparaelectric behavior of relaxor ferroelectrics, is found in spin glasses, fine powder magnets, and magnetic cluster materials. As in PMN, the magnetic dipoles are strongly coupled to one another in nanometer-size complexes, but are not strongly coupled to the lattice. Superparamagnetic solids display nonlinear magnetic susceptibilities and unusual "\(\Delta E\)" effects in which Young's modulus \(E\) can be controlled by magnetic field. The effect is especially large in metallic glasses made from Fe-St-B-C alloys. The cluster size in spin glasses is in the nanometer range like those in PMN.

Lead lanthanum zirconate titanate (PLZT) perovskites can be prepared as transparent ceramics for electrooptic modulators. Quadratic nonlinear optical behavior are observed in pseudocubic regions of the phase diagram which show relaxor-like properties.

In summary, the nonlinear properties of materials are often associated with nanometer-scale structure and diffuse phase transformations. Under these circumstances the structure is poised on the verge of an instability and responds readily to external influences such as electric or magnetic fields, or mechanical stress. The ready response of nonlinear ceramics allows the properties to be tuned in space or time to optimize the behavior of the sensor-actuator systems referred to by some as "very smart ceramics."

REFERENCES

RELAXOR FERROELECTRICS: USEFUL ELECTRONIC NANOCOMPOSITE STRUCTURES

L. ERIC CROSS
Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802-4800 USA.

Abstract: The paper will discuss the current status of understanding of the ferroelectric relaxors which are a sub group of the larger family of ferroelectrics with diffuse phase transitions. In the lead magnesium niobate (PMN) and lead scandium tantalate (PST) systems limited B site cation ordering appears to break the long range translational symmetry giving rise to the glass like behavior associated with the freeze out of polar fluctuations. In PMN and PST of major interest is the extent to which the spin glass models can describe the full range of elasto dielectric properties.

In the lead lanthanum zirconate titanate (PLZT) family the symmetry breaking phenomenon is not so clear and new work on the break up of conventional ferroelectricity in the lead lanthanum titanate (PLT) system will be discussed. A wide range of tungsten bronze family materials also exhibit relaxor ferroelectric behavior with unusual freezing behavior and switching capability.

In practical application the use of relaxor compositions in capacitor and electrostrictive actuator systems will be highlighted. New used in surface deformable mirrors and in a tilt mirror corrector for the Hubble Space Telescope will be presented.

INTRODUCTION

It is perhaps useful to begin the discussion of the interesting sub group of relaxor ferroelectrics by considering in a more general way the nature of the Curie point transition which heralds the onset of proper ferroelectric behavior. In figure 1a is illustrated first the behavior in a rather perfect single crystal which goes through an abrupt second order phase transition into the ferroelectric phase. Above $T_c$, the permittivity follows a Curie Weiss law $\varepsilon^1 = C(T - T_c)^{-1}$, at $T_c$ there is an abrupt but continuous onset of spontaneous polarization which evolves into the domain structure of the ferroelectric form. In some crystals the transition at $T_c$ is first order, there is a finite maximum of $\varepsilon$ at $T_c$ and the Curie Weiss temperature $\theta$ in the relation $\varepsilon = C(T - \theta)^{-1}$ occurs some degrees below $T_c$ e.g. 11°C in BaTiO$_3$. Again there is an abrupt loss of polarization at $T_c$ now in a discontinuous step but $\varepsilon_{\text{max}}$ and $P_s \to 0$ occur at the same temperature $T_c$.

For many practical applications it is desired to use the very large property maxima in the vicinity of the ferroelectric phase transition, to move the transition into the temperature range of interest and to broaden and diffuse the very large sharp peak values. In solid solution systems this is accomplished by trimming the mean composition to move the Curie point and at the same time
making the sample (often a ceramic) deliberately inhomogeneous. In these diffuse transition systems the dielectric maximum is now much 'rounder' and polarization persists for a short range of temperature above Tm (figure 1b). Almost all practical Z5U and Y5V capacitor dielectrics use such diffuse transitions.

In the relaxor ferroelectrics, three features of the dielectric response are qualitatively different. The transition is clearly diffuse and rounded, but the response is now markedly dispersive below T_m and T_m is a function of frequency (figure 1c). The response at weak fields above T_m is no longer Curie Weiss. In the polarization the RMS value persists to temperature (T_D) 200 to 300°C above T_m but the mean polarization $\bar{P}$ decays to zero at a temperature T_F which is well below T_m.

The weak field dielectric behavior for a typical relaxor ferroelectric in the perovskite structure family, lead magnesium niobate, is shown in more detail in figure 2a, taken from the pioneer work of Smolensky, the dispersion over the frequency range 10 Hz to $10^7$ Hz is clearly evident. That the material is ferroelectric is evident from figure 2b which traces the evolution of dielectric hysteresis under high field as a function of temperature. Unlike the sharp transition materials there are not abrupt changes and non linearity persists to temperature well above T_m. Perhaps the most puzzling feature is the absence of evidence for any macroscopic phase change below T_m either in the X-rays spectra, or the optical birefringence (figure 2c), yet clearly spontaneous polarization is impossible in cubic symmetry.

The original explanation offered by Bokov and Mylnikova for this behavior was that the diffuseness was again due to heterogeneity, giving a range of Curie points, but that now the scale was very small and therefore below the resolution of X-ray and optical probes (figure 3a). Considering this model of nano-scale polar regions, it appeared probable to us that since the energy barriers to reorientation in any ferroelectric are linearly related to the volume, at these very fine scales the electrocrystalline anisotropy energy $\Delta H_r$ might become comparable to kT leading to super-paraelectric behavior at higher temperature.
FIGURE 1  Types of Ferroelectric Phase Transitions
(a) Simple proper ferroelectric: shape second order phase change in highly perfect single crystal.
(b) Diffuse phase transition associated with macroscopic heterogeneity as in practical capacitor dielectrics.
(c) Relaxor ferroelectric defining $T_m(\omega)$, $T_D$, $T_F$.

FIGURE 2 (a) Dispersion around $T_m$ is Lead Magnesium niobate PMN, a typical relaxor ferroelectric.
(b) Slow decay of polarization with temperature.
(c) Absence of a macroscopic symmetry change.
A range of perovskite structure compounds with complex composition and a number of Tungsten bronze structure materials (Table I) show relaxor ferroelectric behavior. In perovskites the behavior occurs dominantly in lead based compositions and in both perovskites and bronzes there is always more than one type of ion occupying crystallographically equivalent sites.

For this brief review we will discuss first the origin of the symmetry breaking which occurs in the pre-cursors chemistry of these systems. It is reasonably well understood in $A(B_1B_2)O_3$ compositions but is less clear in the PLZTs and bronze family materials. Then the detail of the dielectric response which points towards a spin glass model for the freeze out of polar fluctuations as the origin of the dispersion will be considered. We then touch on some new evidence for unusual relaxor behavior in the low temperature polar phase of the tungsten bronze systems.
TABLE I  Systems Which Exhibit Relaxor Ferroelectric Behavior

PEROVSKITES OF COMPLEX COMPOSITIONS

<table>
<thead>
<tr>
<th>B-site complex</th>
<th>A-site</th>
<th>Both sites complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead magnesium niobate (PMN) PbMg(<em>{1/3})Nb(</em>{2/3})O(_3)</td>
<td>Lead lanthanum zirconate titanate (PLZT) Pb(<em>1/2)La(</em>{2x})TiO(_3)</td>
<td>Potassium lead zinc niobate K(<em>{1/3})Pb(</em>{2/3})Zn(<em>{2/9})Nb(</em>{7/9})O(_3)</td>
</tr>
<tr>
<td>Lead scandium tantalate (PST) PbSc(<em>{1/2})Ta(</em>{1/2})O(_3)</td>
<td>Lead lanthanum titanate (PLT) Pb(<em>{1-x})La(</em>{2x})TiO(_3)</td>
<td></td>
</tr>
<tr>
<td>Lead zinc niobate (PZN) PbZn(<em>{1/2})Nb(</em>{1/2})O(_3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead indium niobate (PIN) PbIn(<em>{1/2})Nb(</em>{1/2})O(_3)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TUNGSTEN BRONZE STRUCTURE COMPOSITIONS

| Strontium barium niobate (SBN) Sr\(_{1-x}\)Ba\(_x\)Nb\(_2\)O\(_6\) | Lead barium niobate (PBN) Pb\(_{1-x}\)Ba\(_x\)Nb\(_2\)O\(_6\) |

PERCUSSION CHEMISTRY

In the lead based perovskite A(B\(_1\)B\(_2\))O\(_3\) relaxors it is clear from very extensive TEM studies\(^3,4,5\) that in Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) the origin of the nanoscale heterogeneity is in a strictly limited 1:1 non stoichiometric ordering of the Mg and Nb. A crude two dimensional picture is given in figure 4a showing the scale of the region's which are of the order 5 nmeters. The dark field TEM image confirming the ordering and the scale is shown in figure 4b.

This 1:1 ordering must give rise to a significant charge imbalance and it has been suggested\(^6\) that the developing electric field limits the scale. In PbSc\(_{1/2}\)Ta\(_{1/2}\)O\(_3\) the ordering which is again 1:1 may be carried through to a highly ordered form by controlled thermal annealing, recovering full translational symmetry.\(^7\) It is important to note that the nano scale ordered PST exhibits relaxor behavior whilst the highly ordered crystal shows a first order ferroelectric phase change.

Our picture of relaxor behavior in the A(B\(_1\)B\(_2\))O\(_3\) systems is suggested schematically in figure 5. Either complete disorder, or full long range order appears to give rise to normal ferroelectric behavior. It is the limited nano-scale ordering which appears to favor the development of small scale polar regions. The fascinating feature in the PMN type compounds is that the non stoichiometry inherent in the ordering process appears to make it a self limiting nano-composite which cannot be changed by
FIGURE 4 (a) Two dimensional sketch of observed 1:1 ordering of Mg:Nb cations in PMN. (b) Dark field TEM and PMN showing the scale of the ordered regions.

FIGURE 5 Suggested dependence of relaxor behavior in perovskite Pb(B1B2)O3 compositions on limited B1:B2 ordering.
annealing. It should be emphasized that this is a most unusual nano-composite as the oxygen lattice is continuous and coherent through both ordered and disordered regions.

In the mixed A site relaxors such as the PLZTs with compositions along the 65:35 Zr:Ti mole ratio and Lanthanum concentration of more than 2 mole% (figure 6) the dielectric response is similar in many respects to the PMN system, however the symmetry breaking nanostructure is not so clear. Very careful TEM studies have revealed direct evidence of nano scale polar regions at low temperature but the precursor chemistry which forces their formation is not yet clear. Very recently Rossetti has explored the Lead lanthanum titanate system with high resolution X-ray techniques. It is clear that quite low levels of Lanthanum concentration rapidly reduce the strongly first order nature of the pure PbTiO$_3$ Curie point transition and begin to lead to a sub domain modulation of the magnitude of $P_s$ in the domain, although there is no strong evidence for ordering of the lanthanum or the associated lead site vacancies at the higher concentrations. The necessary high defct concentration in the PLZT does however lead to an aging phenomenon which modifies the relaxation response markedly making longer time measurements of response impossible to interpret unequivocally.

![PLZT Phase Diagram](image1)

![Tm and Td Separation](image2)

**FIGURE 6**

(a) PLZT phase diagram showing the trace of the x:65:35 compositions studied.
(b) Evidence of the separation of $T_m$ and $T_d$ in these relaxor compositions.
In the tungsten bronze family, Barium strontium niobate $\text{Ba}_x\text{Sr}_{1-x}\text{Nb}_2\text{O}_6$ is a prototypic relaxor where the structure is much more complex than the perovskite and more open. Again it is built on corner linked oxygen octahedra, but the sheet normal to the $c$ axis of the tetragonal paraelectric form figure 7 is markedly crumpled. Here Nb ions occupy the centers of the oxygen octahedra, Ba ions the larger 5 fold channels and strontium are distributed between 4 fold and 5 fold channels. X-ray studies using the Rietveld method\textsuperscript{11} suggest that Ba is always in the 5 fold channel but that annealing can change the Sr occupancy between 4 fold and 5 fold sites. Changing Sr occupancy has a marked effect upon the dielectric peak position $T_m$ and it is suggested that variations in distribution throughout the crystal may be responsible for a wide distribution of local Curie points. It is interesting to note that the relaxation phenomenon becomes steadily stronger with increasing Sr concentration.

Much more work is however needed to pin down the symmetry breaking nonstructures in both the PLZTs and the bronze compositions.

**FIGURE 7** Projection of the Tungsten Bronze ferroelectric structure normal to the 4 fold $c$ axis showing the sites for cation occupancy.
ELASTO-DIELECTRIC RESPONSE

Earlier studies have shown that the relaxor ferroelectric retain large values of RMS polarization to temperature some 100s of degrees above the dielectric maximum. In PMN, PLZT and SBN types measurement of lattice strain (thermal expansion) and optical refractive index\textsuperscript{12,13,14} show very good agreement in the prediction of the decay of RMS polarization. The question as to whether the residual polarization is static or dynamic has been more difficult to decide. Measurement of electrostriction in SBN above \( T_m \) strongly suggested the dynamical model\textsuperscript{15}, but it is only very recently that careful neutron spectroscopy has completely confirmed the super-paraelectric behavior at higher temperature in PMN.

**PMN-10PT AGE FREE**

\[ w = \frac{1}{\tau} = \frac{1}{\tau_0} \exp \left( -\frac{U_a}{k(T - T_f)} \right) \]

activation energy of 0.0407 eV.

pre-exponential factor of \( 10^{12} \) Hz.

freezing temperature of 291 K.

\( T_f \) and \( T_p \) are "thawing" temperature.

**FIGURE 8 (a, b)** Evidence for a glass like freezing of the dielectric response in PMN:PT solid solution lead in to Vogel-Fulcher type behavior with freezing temperature \( T_f \).

(c) Field cooled poled sample show "thawing" temperature \( T_p \).
A key feature of the dielectric response is the strong dispersion in the weak field permittivity. Studies by Viehland et al.\textsuperscript{16} have shown that the frequency/temperature characteristics are nicely described by the Vogel-Fulcher relation (figure 8a) and that the freezing temperature $T_f$ deduced from this relation agrees closely with the thawing temperature where remanent polarization is lost on heating a field cooled sample (figure 8b). Vogel-Fulcher suggests a slowing down and freezing into a glass like ensemble of nano-domains, such a behavior would also suggest that the weakly cooperating nano-polar regions should begin to depart markedly from Debye-like response towards a very long flat tail upon an $\varepsilon^{11}$ corresponding to the freezing process and this is indeed observed (figure 9).\textsuperscript{17}

For any precise dielectric studies it is essential to recognize and eliminate the aging process. As discussed earlier it is impossible to eliminate defects which couple to the polarization system in PLZT, since the La$^{3+}$ doping necessitates that the sample have equivalent lead vacancies. In Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ however the crystal is a compound, and if it is made with care from very high purity starting materials, macroscopic stoichiometry can be preserved in a fully stuffed structure. For this type of material aging can be eliminated (figure 10a), and the phenomenon can be reintroduced by a low level MnO doping. Figure 10b shows a MnO doped sample which has been aged at room temperature (20°C) then cooled to low temperature and reheated. Note the manner in which the relaxor response has been eliminated for all temperatures above the aging temperature, but is reintroduced at lower temperature. A full explanation is given in references 18 and 19 but is beyond the scope of this review. The data are emphasized however as it is clearly essential to "uncouple" aging if time dependent properties of the relaxor are to be studied without gross perturbation.

**FIGURE 9**  Glass like behavior of dielectric susceptibility $\varepsilon^{11}$. 

10
FIGURE 10 (a) "Clean" PMN:PT sample showing the absence of aging in $\varepsilon_1$ after 1,000 hours at room temperature.
(b) Aging behavior in PMN:PT reintroduced by low level doping with MnO.

FIGURE 11 (a) Structure of nano-scale polar domains revealed in PLZT at the 8.2:65:35 composition by dark field TEM.
(b) Modification
To explore the high field response it is necessary to turn to the PLZTs and to take care to always study freshly de-aged samples. For an 8:2:70:30 PLZT composition Randall\textsuperscript{20} has imaged using TEM the nano domain structure at low temperature (figure 11a) and by using charging from the beam current the evolution of nano-domains towards more normal continuous ferroelectric domains (figure 11b). Consequences of the application of static fields to PLZT samples which have been cooled in the zero field state have been explored by Yao Xi et al.\textsuperscript{21} Typical curves of switch over to a macro polar state on heating under bias are shown in figure 12a,b. If the system behaves as a spin glass the switch over should be modeled by the deAlmeida-Thouless relation\textsuperscript{22} and data taken from the measurements of Yao Xi et al are modeled in this manner in figures 13.\textsuperscript{23}

In deducing the RMS polarization it was tacitly assumed that the polarization related electrostriction constants $Q_{11}, Q_{12}$ are independent of temperature in fact this has been proven by direct measurement (figure 14).\textsuperscript{24} Clearly then in this circumstance one must expect that all the dielectric (Polarization) behavior will be reflected into the elastic response. The close relation between elastic and dielectric responses is evident in figure 15. For the high field response, it is to be expected that the high polarization values which can be induced anhysterically near $T_m$ will give rise to large elastic strains. Values of $x_{33}$ the strain in the field direction for a PMN:PT solid solution are shown in figure 16. The slope of this curve at any point is the effective d constant ($d_{33}$) which goes to very large values at relatively modest $E$ fields.\textsuperscript{25}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure12.png}
\caption{(a) Polarization and depolarization of PLZT 8:65:35 under field cooled and zero field cooled conditions as determined by integration of the pyroelectric response.}
\end{figure}
\[ Li = \lambda \left( \frac{T_f(0) - T_{DC}(0)}{T_f(0)} \right)^{3/2} \]

deAlmeida-Thouless relationship

FIGURE 13 Data of 12(a) and similar studies at different field levels fitted to the deAlmeida-Thouless relation.

![Graph showing data fitting to deAlmeida-Thouless relation.](image)

FIGURE 14 Ultramatometer measurements of the electrostrictive constants $Q_{11}, Q_{12}$ as a function of temperature in PMN:10 PT.

![Graph showing temperature dependence of $Q_{11}, Q_{12}$.](image)

FIGURE 15 (a) Elastic stiffness and damping in ceramic PMN:10 PT. 
(b) Comparison to dielectric softening associated with micro-polar behavior.
TUNGSTEN BRONZE STRUCTURE. RELAXOR FERROELECTRICS

In the solid solution system Sr Nb$_2$O$_6$:BaNb$_2$O$_6$ the end member compositions are not in the bronze structure, however in the range between Sr$_{0.8}$Ba$_{0.2}$Nb$_2$O$_6$ and Sr$_{0.3}$Ba$_{0.7}$Nb$_2$O$_6$ stable SBN bronzes form. Across this range the prototypic structure is tetragonal and for fields in the 001 (c) axis direction the characteristics are those of a relaxor ferroelectric with polarization along (001). Both optical and elastic studies confirm that large values of RMS polarization persist to temperatures well above $T_m$ and there is clear evidence of ferroelectric behavior at low temperature. Dispersion near $T_m$ becomes steadily more pronounced in compositions with increasing Strontium content. For the congruently melting Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ excellent quality single crystals have been grown and the crystal is widely used in photorefractive applications.

The bronze system Lead barium niobate Pb$_{1-x}$Ba$_x$Nb$_2$O$_6$ (PBN) is of special interest as in the vicinity of the Pb$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ composition there is a pseudo morphotropic phase boundary between orthorhombic and tetragonal ferroelectric forms (figure 17). For the tetragonal form at the 57:43 composition the permittivity for fields along (001) shows a transition with only very weak dispersion and large thermal hysteresis (figure 18a), however for fields along (100) there is now a pronounced dispersion at lower temperature (figure 18b).

In compositions on the orthorhombic side of the MPB again the upper transition exhibited for fields along 100 is reasonably sharp, however, now there is a lower temperature relaxation for field in the 001 c axis direction. There are no evidences of phase transitions in either crystal in the

FIGURE 16 Strain vs. Field curve for PMN:10 PT illustrating the large values of induced piezoelectric $d_{33}$ under DC field control.
region of the dispersion, but cooling the crystal under a poling field orthogonal to the main polarization direction produces a clear remanence of order less than \(1/20\)th of the major polarization.\(^{34}\) It is interesting to note that for compositions close to the MPB large orthogonal electric fields will switch the major component of \(P\) changing the symmetry from tetragonal to orthorhombic or vice versa. With symmetry change the lower frequency dispersion also changes axial direction always appearing normal to the major component of \(P\).

Clearly at low temperature, the field forced symmetry must be truly monoclinic in each case, as the \(P_s\) is tilted away from the primary axis (4 fold or 2 fold). Our suggestion is that in each case the micro polar regions which make up the mean polarization have \(P_s\) vectors which are slightly tilted away from the major axis. At the higher temperature transitions the energy barriers against polarization inversion are large and the dispersion weak, however the tilts perpendicular to \(P\) are random and dynamical, freezing out at the lower temperature dispersion. Crudely the energies envisaged are shown schematically for the "orthorhombic" and "tetragonal" macro symmetries in figure 19. The situation could be envisaged as that of a spin glass with two freezing temperatures for the orthogonal components of \(P\). Magnetic systems which exhibit such phenomena have been studies.\(^{35}\)
FIGURE 18 (a) Dielectric response for fields along 001 and 100 directions for a composition in the tetragonal ferroelectric phase field (57:43) of PBN.
(b) Low temperature dispersive dielectric response for fields orthogonal to the major polar direction.
(c) Dielectric response at low temperature in the orthorhombic phase for fields along 001.

Free Energy Model for Relaxor Ferroelectrics close to the MPI

FIGURE 19 Proposed simple model for the anisotropic energetics of polar regions in the 'orthorhombic' and tetragonal relaxor phase fields of PBN.
THEORETICAL UNDERSTANDING

The relaxor ferroelectrics in the oxygen octahedron families are very complex solids so that it is certainly not surprising that in spite of some thirty years of continuous effort there is no comprehensive quantitative theory. It does appear that there is reasonably general agreement of the superparaelectric character at temperatures will above \( T_m \) but the detail of the kinetics of these regions and their mutual interaction as the temperature decreases is not clear.

An appealing simple model from A. Bell at EPFL\(^{36} \) treats the micro region as a simple Devonshire ferroelectric, to calculate the activation energy \( \Delta H \) as a function of size (assuming a simple spherical region). The distribution of activation energies then comes from a specific distribution of sizes, however to get good agreement with experiment (figure 20) it is still necessary to put in weak interaction between regions.

In a more general vein, Viehland et al have pointed up the many behavior features of the relaxors which suggest spin glass like features. Table II list many of these features, the small Y suggests a yes to the nature of the common feature in each case.

An alternative model which can again explain qualitatively most features of the relaxor appeals to random electric fields associated with the composition fluctuations as the origin of the break up of normal domain structure and the tremendous slowing down of the dynamics in PMN. For large non zero electric fields, it becomes difficult to explain the aging phenomena which occur in PLZT and in suitably doped PMN. For such crystals aging under a field as little as 3KV/cm is sufficient to wipe out the relaxation at room temperature and to lead to a poled ferroelectric structure on cooling under short circuit conditions. Evidently the kinetics is very sensitive to small fields generated by defect dipole systems. Perhaps a way out of this dilemma would be the suggestion that the random field is of elastic rather than electric origin.

Recent measurements of the poling of zero field cooled PMN does suggest\(^{37} \) the presence of barkhausen pulses which could occur from the switching of ferroelectric micro-domains in concert with the random field model however it is not clear whether these measurements were carried out on aging free material.

In summary, many features of the chemo-elasto-dielectric behavior of relaxors are becoming more clear, even though there is not yet a comprehensive qualitative theory to explain the responses.
TABLE II  Comparative list of physical properties of relaxors to spin and orientational glasses.

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>RELAXOR</th>
<th>SPIN GLASS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersion of Susceptibility</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Dispersion of Tmax</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Freezing Temperature (Tf)</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Imaginary Component Frequency Independent</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>below Tf</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strong Nonlinear Response</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Maximum Nonlinearities near Tf</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Frustration</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Susceptibility &quot;diffuse&quot;</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Deviations from Curie-Weiss Behavior</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Analysis of Deviation for Local Order Parameter</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Broadening of Relaxation Time Distribution</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>on Cooling</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hysteresis, Irreversibility, and Remanence</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>below Tf</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Local polarization or magnetization</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Local correlations between moments</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Long range ordering in the Field Cooled State</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Lack of anisotropy in the Zero Field Cooled State</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>De-Almeida Thouless Analysis</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Polarization or Magnetization Viscosity</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Chemical or Structural Inhomogeneity</td>
<td>Y</td>
<td>Y</td>
</tr>
</tbody>
</table>
PRACTICAL APPLICATION

One may judge the most likely areas of application for the relaxor ferroelectrics by considering the very unusual property combinations afforded in these systems. Table III outlines these properties. The very high dielectric permittivity is properly exploited in new multilayer ceramic capacitors. The very strong electrostrictive response does not depend on a domain contribution to the strain and is thus very largely reversible, a vital feature for precise actuators which cannot be servo controlled. The slope of the electrostrictive response as a function of field is the piezoelectric constant and $d_{33}$ values much larger than those in conventional PZTs can be achieved under modest fields, giving a whole new family of potential agile transducers for sensing and actuation. Similarly under DC bias exceedingly large pyroelectric coefficients can be induced so for the bolometric long wavelength IR sensing and imaging the relaxors are of major interest.

In the following brief description we confine attention to just the capacitor and actuator potential. For capacitor dielectrics, three features of the lead based relaxors are exceedingly attractive.

TABLE III Relaxor Properties which are of Interest for Practical Application.

<table>
<thead>
<tr>
<th>PROPERTIES OF INTEREST</th>
</tr>
</thead>
<tbody>
<tr>
<td>• HIGH DIELECTRIC PERMITTIVITY.</td>
</tr>
<tr>
<td>Multilayer Ceramic Capacitors.</td>
</tr>
<tr>
<td>Co-Fires with Copper Electrodes.</td>
</tr>
<tr>
<td>• VERY STRONG ELECTROSTRICITION.</td>
</tr>
<tr>
<td>Multilayer Electrostrictive Actuators.</td>
</tr>
<tr>
<td>Optical Telescope Adaptive Optics: Hubble Corrector.</td>
</tr>
<tr>
<td>• SWITCHABLE PIEZOELECTRIC RESPONSE.</td>
</tr>
<tr>
<td>Agile Transducers for Electromedical Applications.</td>
</tr>
<tr>
<td>• SWITCHABLE STRONG PYROELECTRICITY.</td>
</tr>
<tr>
<td>Long Wavelength Infra-red Pyroelectric Imaging Systems.</td>
</tr>
</tbody>
</table>

The dielectric permittivity for a typical PMN:10 PT relaxor (figure 20a) is significantly higher than equivalent Y5V type modified BaTiO$_3$ compositions. The loss level is also higher (figure 20b), but decays rapidly under bias field where MLC type capacitors are largely used. The bias behavior is also most attractive as the material retains high permittivity to higher fields than the
FIGURE 20 (a) Dielectric permittivity as function of temperature and frequency in relaxor 
(PbMg$_{1/3}$Nb$_{2/3}$O$_3$)$_{0.9}$(PbTiO$_3$)$_{0.1}$ compared with a modified BaTiO$_3$ Y5V 
commercial composition and with pure BaTiO$_3$. 
(b) Dielectric loss in PMN:PT compared to the loss in pure BaTiO$_3$.

FIGURE 21 Dielectric saturation in the relaxor composition as compared to a BaTiO$_3$ based 
dielectric of similar permittivity.

conventional BaTiO$_3$ based materials (figure 21) and also the RC time constant is longer for the full 
range of working temperatures (figures 22). A further signal advantage for the tape case 
monomlitic MLC structures is that the PMN type compositions can be co-fired with copper 
electrodes which is impossible with the BaTiO$_3$ based systems.
FIGURE 22 RC time constant as a function of temperature for the relaxor as compared to the BaTiO$_3$ based dielectric.

It is thus not surprising that the World’s major capacitor companies are exploring a very wide range of these lead based relaxor compositions (Table IV).

In actuator application, the cardinal advantage of the PMN based relaxors is the very low hysteresis which can be obtained in the strain:voltage characteristic (figures 23a) in comparison to comparable soft PZT systems (figures 23b). A summary table for commercial actuator performance between PMN and PZT compositions is given in Table V. It is natural then to expect that electrostrictive relaxor actuators will be of most value where precise positioning is required and servo feedback control is not realizable. Such situations occur in a number of optical systems. One such system of very high visibility is a corrector for the troubled Hubble Space Telescope. This device is a tilt mirror (figure 24) which can be fully controlled from the ground by three PMN actuators. The function of a mirror is to permit precise alignment of a new optical train in the wide field camera which will contain elements configured to fully correct for the original improper figure of the primary mirror. The actuators are small multilayer PMN:PT stacks, figure 25 shows the dimension in comparison with the smallest American coin, the dime. The tilt mirror is just one of a range of optical components which begin to incorporate PMN active control and field in clearly ripe form any new products using these precise electro mechanical control elements.
TABLE IV
Composition families and associated companies involved in the application of relaxor type dielectrics to multilayer capacitors (Survey by the Penn State Dielectric Center).

<table>
<thead>
<tr>
<th>Complex Perovskite End Members for Relaxor-Based Complexes</th>
<th><strong>T_c(°C)</strong></th>
<th>++Behavior</th>
<th>Simple Perovskites</th>
<th>T_c(°C)</th>
<th>Behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PMN] -10</td>
<td>Relaxor-FE</td>
<td>PbTiO_3</td>
<td>490</td>
<td>FE</td>
<td></td>
</tr>
<tr>
<td>[PZN] 140</td>
<td>Relaxor-FE</td>
<td>PbZrO_3</td>
<td>230</td>
<td>AF</td>
<td></td>
</tr>
<tr>
<td>[PFN] -120</td>
<td>Relaxor-Fe</td>
<td>BaTiO_3</td>
<td>—</td>
<td>Para</td>
<td></td>
</tr>
<tr>
<td>[PFW] 110</td>
<td>Normal-FE</td>
<td>SrTiO_3</td>
<td>—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[PMW] 95</td>
<td>Relaxor-FE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[PFN] 38</td>
<td>AF</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

+ Transition temperatures for relaxors are averages or at 1 kHz.
++ FE-Ferroelectric, AF-Antiferroelectric, Para-Paraelectric.

**Composition Families for Relaxor-Based MLCs**

<table>
<thead>
<tr>
<th>Composition</th>
<th>EIA Temp</th>
<th>Manufacturer</th>
<th>EIG</th>
<th>Patent and Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLZT-Ag</td>
<td>X7R</td>
<td>Sprague</td>
<td>U.S. Pat. 4,027,209 (1973)</td>
<td>Ref. 9</td>
</tr>
<tr>
<td>MPW-PT-ST</td>
<td>X7R</td>
<td>DuPont</td>
<td>U.S. Pat. 4,048,546 (1973)</td>
<td></td>
</tr>
<tr>
<td>PFN-PFW</td>
<td>Y5V</td>
<td>NEC</td>
<td>U.S. Pat. 4,078,938 (1978)</td>
<td></td>
</tr>
<tr>
<td>PFN-PFW-PZN</td>
<td>Y5V</td>
<td>NEC</td>
<td>U.S. Pat. 4,236,928 (1980)</td>
<td></td>
</tr>
<tr>
<td>PFN-PMT</td>
<td>—</td>
<td>TDK</td>
<td>U.S. Pat. 4,216,103 (1980)</td>
<td></td>
</tr>
<tr>
<td>PMN-PT</td>
<td>Y5V</td>
<td>TDK</td>
<td>U.S. Pat. 4,265,668 (1981)</td>
<td></td>
</tr>
<tr>
<td>PMN-PFN</td>
<td>Y5V</td>
<td>TDK</td>
<td>U.S. Pat. 4,216,102 (1980)</td>
<td></td>
</tr>
<tr>
<td>PMN-PFN-PMW</td>
<td>Y5V</td>
<td>TDK</td>
<td>U.S. Pat. 4,287,075 (1981)</td>
<td></td>
</tr>
<tr>
<td>PFW-PZ</td>
<td>ZSU</td>
<td>TDK</td>
<td>U.S. Pat. 4,235,635 (1980)</td>
<td></td>
</tr>
<tr>
<td>PFW-PT-MIN</td>
<td>ZSU</td>
<td>Hitachi</td>
<td>U.S. Pat. 4,308,571 (1981)</td>
<td></td>
</tr>
<tr>
<td>PFN-PFW-PbGe (MSC)</td>
<td>X7R</td>
<td>Ferro</td>
<td>U.S. Pat. 4,379,319 (1983)</td>
<td></td>
</tr>
<tr>
<td>PFN-PFN-PNN</td>
<td>ZSU, Y5V</td>
<td>NEC</td>
<td>U.S. Pat. 4,450,240 (1984)</td>
<td>Ref. 11</td>
</tr>
<tr>
<td>PMN-PT-PN</td>
<td>ZSU</td>
<td>Matsushita</td>
<td>Japan Pat. 59-203759 (1984)</td>
<td></td>
</tr>
<tr>
<td>PZN-PT-ST</td>
<td>—</td>
<td>Toshiba</td>
<td>Ref. 13</td>
<td></td>
</tr>
<tr>
<td>PMN-PFN-PbGe</td>
<td>ZSU</td>
<td>Union Carbide</td>
<td>U.S. Pat. 4,550,086 (1985)</td>
<td></td>
</tr>
<tr>
<td>PFN-PNN</td>
<td>Y5V</td>
<td>NTT</td>
<td>Refs. 15-17</td>
<td></td>
</tr>
<tr>
<td>PFW-PFN (MSC)</td>
<td>ZSU</td>
<td>Matsushita</td>
<td>Ref. 18</td>
<td></td>
</tr>
<tr>
<td>PMN-PT-PNW</td>
<td>ZSU</td>
<td>NEC</td>
<td>Ref. 19</td>
<td></td>
</tr>
<tr>
<td>PMN-PT-PZ</td>
<td>X7R</td>
<td>Toshiba</td>
<td>Japan Pat. 61-155245 (1986)</td>
<td></td>
</tr>
<tr>
<td>PZN-PMN-PT-BT_ST</td>
<td>ZSU</td>
<td>Toshiba</td>
<td>Japan Pat. 61-250904 (1986)</td>
<td></td>
</tr>
<tr>
<td>PZN-PT-BT-ST</td>
<td>X7R</td>
<td>Toshiba</td>
<td>Ref. 20</td>
<td></td>
</tr>
<tr>
<td>PMN-PLZT</td>
<td>ZSU</td>
<td>Matsushita</td>
<td>Japan Pat. 62-113817 (1986)</td>
<td>Ref. 21</td>
</tr>
<tr>
<td>PMN-CT, ST, BT</td>
<td>ZSU</td>
<td>Matsushita</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFW-PFN-PT</td>
<td>Y5V</td>
<td>Toshiba</td>
<td>U.S. Pat. 4,760,732 (1988)</td>
<td></td>
</tr>
<tr>
<td>PT-PMN-PZM (MSC)</td>
<td>X7R, X7S</td>
<td>Matsushita</td>
<td>Refs. 22-23</td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 23 (a) Anhysteretic nonlinear strain ($x_3$) versus field cure for PMN:PT relaxor multilayer actuator.

(b) Strongly hysteretic response of a comparable multilayer soft PZT piezoelectric actuator.
TABLE V
Comparison of the salient features of the relaxor based actuator as compared to the more conventional soft PLZT system.

Comparative Parameters of Piezoelectric vs Electrostrictive Stacks (Both 20mm long, 6mm diam, 150 V Rated)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition</th>
<th>Electro</th>
<th>Piezo</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacitance</td>
<td>25°C</td>
<td>4</td>
<td>1</td>
<td>μ-F</td>
</tr>
<tr>
<td>Diss. Factor</td>
<td>25°C</td>
<td>8</td>
<td>3</td>
<td>%</td>
</tr>
<tr>
<td>Frequency</td>
<td>Lose &lt;10% strain</td>
<td>100</td>
<td>1000</td>
<td>Hz</td>
</tr>
<tr>
<td>Force</td>
<td>Lose &lt;10% strain</td>
<td>700</td>
<td>450</td>
<td>Newtons</td>
</tr>
<tr>
<td>Extension</td>
<td>at 150 VDC</td>
<td>16.5</td>
<td>15</td>
<td>Microns</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>%</td>
</tr>
<tr>
<td>Hysteresis</td>
<td>25°C</td>
<td>&lt;2</td>
<td>&gt;15</td>
<td>%</td>
</tr>
<tr>
<td>Creep</td>
<td>After 24 hours</td>
<td>&lt;2</td>
<td>=5</td>
<td>%</td>
</tr>
<tr>
<td>Temp Range</td>
<td>Keep 75% strain</td>
<td>±20</td>
<td>0-100</td>
<td>°C</td>
</tr>
<tr>
<td>TCE</td>
<td>25 - 125°C</td>
<td>&lt;1</td>
<td>1.6</td>
<td>ppm/°C</td>
</tr>
<tr>
<td>Youngs Modulus</td>
<td>25°C</td>
<td>16</td>
<td>4</td>
<td>10^6 PSI</td>
</tr>
<tr>
<td>Response Time</td>
<td>25°C</td>
<td>&lt;100</td>
<td>&lt;5</td>
<td>μ-sec</td>
</tr>
</tbody>
</table>

JPL WF/PC-2 ARTICULATING FOLD MIRROR (AFM)

FIGURE 24 Plan and elevation views of the JPL Articulated fold mirror driven by PMN:PT actuators (Corrector to be flown December 1993).
FIGURE 25  Scale of the multilayer PMN:PT actuator as compared to an American dime coil.
REFERENCES


MATERIALS STUDIES
APPENDIX 6
MICROSTRUCTURAL CHARACTERISTICS AND DIFFUSE PHASE
TRANSITION BEHAVIOR OF LANTHANUM-MODIFIED LEAD TITANATE

G. A. ROSSETTI, JR., W. CAO, AND C. A. RANDALL
Materials Research Laboratory, The Pennsylvania State University
University Park, Pennsylvania 16802
† Now with the Department of Geological and Geophysical Sciences and
Princeton Materials Institute, Princeton University, Princeton, New Jersey 08544

Abstract: The introduction of structural disorder into perovskite ferroelectrics leads
to the observation of diffuse phase transition behavior. In this paper, the
microstructural characteristics and phase transition behavior of lanthanum-
modified lead titanate are discussed. It is shown that the diffuse nature of the
transition is connected with the appearance of ferroelectric domain structures
exhibiting texture on the mesoscopic (≈10 nm) length scale. The theoretical
implications of these results are briefly discussed.

INTRODUCTION

Diffuse phase transitions in perovskite ferroelectrics occur as a consequence of
some level of structural disorder that breaks the translational invariance of the
lattice. The type of diffuse transition observed depends both on the nature and scale
of the structural disorder. Impurities, point defects, extended defects, incomplete or
inhomogeneous cation ordering, macroscopic fluctuations in chemical
composition, core/shell structures etc. can all lead to smearing of the ferroelectric
phase transition. The physical origin of the smearing and the behavior of the
ferroelectric properties in each particular case, however, may be very different. In
chemically complex compounds and solid solutions, several types of structural
disorder are often present simultaneously. To establish structure-property
relationships in these materials therefore requires characterization at all the relevant
length scales, including the macroscopic (crystal symmetry, chemical homogeneity,
core/shell structures), the microscopic (ferroelectric domain structures, extended
defects), the mesoscopic (cation order domains, texture within ferroelectric
domains), and the atomic (point defect chemistry, local environment).

For ferroelectrics such as lanthanum-modified lead strontium titanate (PLZT),
the structural disorder arises as a consequence of the complex defect chemistry
associated with the divalent A-site substitution of lanthanum. Keiser, Lanskik
and Burggraaf have shown that the nature of the ferroelectric transition in
ceramic specimens of the end member Pb1−xLa7TiO3 (PLT) changes smoothly from
that expected in a sharp first-order phase change to that of a diffuse transition as
the lanthanum concentration is increased. Figure 1 shows that, when characterized by the exponent $\gamma$ in the generalized Curie-Weiss law, the anomalous dielectric behavior onsets at $y = 0.05$ and becomes typical of diffuse transitions (i.e., $\gamma = 2$) when $y > 0.23$. Although the numerical values of $\gamma$ depend somewhat on the lead elimination factor ($a$) as well as on the grain size, the general trend towards increasingly diffuse behavior with lanthanum substitution is intrinsic.

In order to better understand how structural disorder evolves and relates to the dielectric properties in PLT, we have recently undertaken transmission electron microscopy (TEM) and powder x-ray/neutron studies, the details of which are reported elsewhere$^{3-5}$. In this paper, we draw on these results and speculate on some possible interconnections between the microstructure, dielectric properties, and the phase transition behavior.

RESULTS AND DISCUSSION

High resolution X-ray diffraction studies$^4$ of sol-gel derived powders have shown that the addition of lanthanum to lead titanate results in broadened diffraction profiles showing a marked profile asymmetry. The degree of asymmetry can be quantified by fitting the profiles to split Pearson distributions$^6$. The split Pearson function gives two values for the full width at half maximum, $\beta^L$ and $\beta^H$, which are characteristic of the peak shape on the low and high angle sides of the peak maximum, respectively. Figure 2 shows that both the peak asymmetry and the peak breadth renormalize as a function of lanthanum concentration. The asymmetry ($\beta^H/\beta^L$) changes markedly between $y = 0$ and $y = 0.01$, but then decreases and becomes constant for samples with $y > 0.05$. At the same time, the profile breadth decreases. Corresponding to the changes in the diffraction profiles, the crystal tetragonality ($c/a$) begins to deviate from the linear composition dependence as expected based on Vegard's law. These observations cannot be easily explained by macroscopic variations in chemical composition, nor by particle size effects.

Alternatively, recent TEM studies$^3$ (Figure 3) reveal that the development of sub-domain texture in PLT materials closely parallels the changes observed both in the X-ray studies and in the dielectric behavior. For samples with $y < 0.05$, no sub-domain texture is observed, and the transition behavior is sharp. For samples with $y \geq 0.05$, sub-domain texture becomes apparent, and increases in degree with lanthanum concentration. As the sub-domain texture becomes more pronounced, the dielectric behavior near the transition becomes correspondingly more
MICROSTRUCTURE AND DIFFUSE TRANSITION BEHAVIOR OF PLT

![Graph 1](image)

**Figure 1.** Composition dependence of the exponent $\gamma$ in the generalized Curie-Weiss law for $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$ (After Reference 2).

![Graph 2](image)

**Figure 2.** Breadth and asymmetry of the 002 powder XRD profile (a) and crystal tetragonality (b) of $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$. 
Figure 3. Transmission electron micrographs of Pb$_{1-y}$La$_y$TiO$_3$:
(a) $y = 0.01$ (b) $y = 0.05$ (c) $y = 0.10$ and (d) $y = 0.25$. 

G. A. ROSSETTI, JR., W. CAO, AND C. A. RANDALL
anomalous. For compositions with $y > 0.25$, the microstructure degenerates into a cross-hatched or tweed texture. For these compositions, the dielectric behavior is typical of that for diffuse phase transitions. Note that these textures disappear on heating above the transition temperature, and so cannot be identified with exsolution lamellae.

The tweed structures observed for the higher lanthanum concentrations would appear to be precursors for the mottled and poorly defined vestiges of sub-domain texture as observed for PLZT\textsuperscript{7}. The Zr-rich PLZT compositions exhibit strongly frequency-dispersive diffuse transitions similar to those of the complex B-site perovskites such as PbMg\textsubscript{1/3}Nb\textsubscript{2/3}O\textsubscript{3} (PMN) and related compounds. In the latter case, however, it is the cation order domains persisting on a $\sim 10$ nm length scale that lead to the breakdown of the ferroelectric domain structure\textsuperscript{8-10}. The similarity in mesoscopic domain texture of the PLZT and PMN type materials\textsuperscript{11-13} is intriguing, since at the atomic level, the origin of the structural disorder in these two materials is very different.

With regard to the nature of the phase transition in PLT, the first-order character also follows the changes in structural properties as revealed in the X-ray data. The development of a Landau-Devonshire\textsuperscript{14} formulation for the phase transition in PLT requires the expansion coefficients to depend on spatial variables, which results in a distribution of transition temperature. As a macroscopic average, one expects that the first-order discontinuity of the transition will be drastically reduced as the transition becomes diffused. The Landau theory is valid, however, only when the sub-domain modulations are weak, otherwise the gradient related (Gilinskii) terms must be included. Using the methodology described previously\textsuperscript{15}, the coefficients in the Landau-Devonshire expansion were estimated for compositions with $y < 0.05$, where judging from Figure 3, this condition is approximately satisfied. As shown in Figure 4, the coefficient of the quartic term in the elastic Gibbs function ($a_{11}^{2}$) increases rapidly toward zero between $y = 0$ and $y = 0.01$ but then changes at a much lower rate. This increase reflects the apparent loss in the first-order character of the transition as the structure relaxes to the defects and the long range order is disrupted. The coefficient of the sixth-rank term also renormalizes, but to a much lesser extent. Large changes in the coefficient of the quartic term were also observed for PLZT compositions\textsuperscript{16}.

For the compositions with $y > 0.05$, the Ginsburg terms must be included in the formalism. The inclusion of the gradient energy can describe both the domains and their modulations. Periodic domain structures can be excited for a finite
Figure 4. Coefficients of the elastic Gibbs free energy density function of Pb$_{1-x}$La$_x$TiO$_3$.

Figure 5. Observed relationships between the first-order character of the transition, the crystal tetragonality, the sub-domain texture, and the dielectric properties of Pb$_{1-x}$La$_x$TiO$_3$. 
system due to the competition between nonlinearity and nonlocality. Modulated structures and tweed textures can be described in terms of crest riding periodons. However, the modulated structures such as those in Figure 3c do not seem to follow the expected temperature variation pattern of the crest riding periodon excitations, which are unstable and can survive only in a finite temperature range near the transition. One possible explanation could involve an interaction of the defects with the periodons. These excitations might be stabilized by the lanthanum/vacancies if the defects are appropriately aligned. The alignment can be driven, on the other hand, by the field gradient created at the walls of the periodons. Consistent with this notion, the modulations have preferred orientations (although not perfect), and are nearly periodic, as shown in Figure 3. Further studies will be required to confirm this picture.

At the higher lanthanum concentrations (y > 0.25) the microstructure breaks down on still finer scales and more degenerate states are created. This will effectively increase the dielectric response of the system, as observed. For these materials, however, arguments based on the continuum theory as summarized above may not be used because the density representation (both in terms of energy and polarisation) is no longer valid. Instead, discrete models must be developed.

The results described above can be represented schematically as shown in Figure 5, where the observed relationships between the first-order character of the transition, the crystal tetragonality, the sub-domain texture, and the dielectric properties are shown. Here it is worth mentioning that, in the Landau-Devonshire formalism, close inter-relationships exist between the curvature of the energy surface, the order of the transition, and the symmetry of the ferroelectric phase. In this connection, it is of interest to consider how the scenario depicted in Figure 5 may change as strontium, which lowers the tetragonality of the system and further flattens the energy surface, is added to the system. Based on the above discussion, we might expect that lanthanum will become more effective at breaking down the domain structure as the rhombohedral side of the PLET diagram is approached, leading to a large number of degenerate states and additional contributions to the dielectric response even at modest lanthanum concentrations.

**SUMMARY**

The breakdown of conventional ferroelectric phase transition behavior in lanthanum-modified lead titanate has been correlated with the appearance of
domain structures exhibiting texture on a nanometer scale. It was suggested that this type of mesoscopic sub-domain texture is a common feature of ferroelectrics showing diffuse/frequency dispersive transitions. The theoretical implications of the relationships existing between the curvature of the energy surface, the order of the transition, the symmetry of the ferroelectric phase, the development of the sub-domain texture, and the resulting dielectric properties were discussed.

ACKNOWLEDGEMENT

This work was supported by contracts administered through the Office of Naval Research. The authors are grateful to Professor L. E. Cross for his support of, and interest in, this study. Thanks also to Mr. N. Kim for fabricating the ceramic specimens used in the TEM studies.

REFERENCES

18. W. Cao (to be published).
Distribution functions of coexisting phases in a complete solid solution system

Wenwu Cao and L. Eric Cross
Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

(Received 18 June 1992; accepted for publication 8 December 1992)

In the phase diagram of a binary system one often encounters a compositional region in which two phases coexist. A common practice is to use the Lever Rule to describe the distributions of the two coexisting phases. However, if the binary system is a complete solid solution system, the Lever Rule cannot be used. A new type of distribution has been derived for a solid solution system without solubility gap. Application of the theory to pure and modified lead-zirconate-titanate (PZT) systems shows excellent agreement with the experimental data. Several disputed facts about PZT are also explained satisfactorily.

I. INTRODUCTION

A general phase diagram of a binary system A-B is given in Fig. 1(a). There is one liquid phase L and two solid solutions a and y. A and B are completely miscible in the liquid phase, but in the solid phase there is a solubility gap in which the two solid solutions a and y coexist. At temperature T, for any composition x inside the solubility gap, g < x < h, the molar percentages f_a and f_y of the two coexisting phases are governed by the Lever Rule,

\[ f_a : f_y = x_h : x_g, \]

\[ f_a + f_y = 1. \]  

The two special points g and h on the isothermal tieline at T = T_1 represent the boundaries of the solubility gap. The corresponding free-energy versus composition plot is shown in Fig. 1(b). One can see that the two boundary compositions g and h are located at the common tangent points of the two free energies for the a and y phases. For compositions falling inside this solubility gap, two-phase mixtures will be formed consisting of g and h compositions, with the ratio of the two phases obeying the Lever Rule [Eq. (1)].

Figure 1(c) is another type of phase diagram for an A-B binary compound. Looking at the subsolidus region we have three solid solutions, β, α, and y. This is a complete solid solution system, viz., no miscibility gaps and no solubility gaps; however, there is a structural phase transition from β to either α or y depending on the composition of the solid solution. The well-known lead zirconate titanate (PZT) and its derivatives are examples of this situation. For this system, the free energies of α and β phases are monotonic functions of composition. Because there are no chemical decompositions in the complete solid solution system, for simplicity we only consider the relative stability of the α and β phases. We know that in this system, the difference of the two low-temperature phases is characterized by the polarization which is the primary order parameter in the paraelectric-ferroelectric phase transition; hence, to analyze the relative stability we only need to know the free energy associated with the polarization. Using Landau–Devonshire type phenomenological theory, the compositional dependence of the free energies associated with the polarization for the α and β phases may be drawn as in Fig. 1(d) at T_1.\(^1\) One can see from Fig. 1(d) that the coexistence of the α and y phases should be allowed only for one composition k, but not for a finite compositional region according to thermodynamics.

To some extent, Fig. 1(d) may be deceiving at first glance, because if the composition is taken as an independent variable, the transition from α to y is obviously first order and the transition hysteresis with respect to the change of composition will result in a coexistence region. In fact, this is one of the explanations given for the coexistence region found in the PZT system.\(^2\) Unfortunately, the composition cannot be changed in the subsolidus temperature region. Once a compound is formed at much higher temperature ( > 800 °C), the composition variable is frozen in the subsolidus region. The polarization related free energy for each phase at T_1 [Fig. 1(d)] is obtained independently for each composition from the corresponding prototype phase following the change of temperature. Therefore, in order to study this problem we must look at the temperature-induced phase transition from β to α and β to y.

From Fig. 1(d) we can see that both free energies for the α and y phases are monotonic functions of composition, and there is one crossover point k which is termed the morphotropic phase boundary (MPB). From energy minimization principles only one phase is stable in the low-temperature region for any given composition, which is to say that at T_1, the β phase will be transformed into either the α or y phase depending on the composition of the solid solution. However, when the transition temperature is reasonably high and the phase transition from β to α or y is of second order, thermal energy could induce some amount of the second metastable phase at the transition, especially when the difference of the free energies of the two low-temperature phases is small, such as for those compositions near the MPB [see Fig. 1(d)]. It is our opinion that the phase coexistence observed in the PZT system near the MPB is the result of a frozen-in second metastable phase as elaborated below.

One must note that the phase mixing is completely different in the cases of Figs. 1(a) and 1(c). In the former
we mix two phases of different structures and of different chemical compositions but in the latter we mix two different structures of the same chemical composition. Because of the different chemical compositions in the former case, the conservation of matter leads to the Lever Rule. But for the case in Fig. 1(c), the distribution functions cannot be obtained straightforwardly because the condition of identical chemical composition invalidates the arguments used to derive the Lever Rule.

A new approach has been proposed to calculate the partitioning of the rhombohedral and tetragonal phases at the MPB when the structural phase transition from $\beta$ to $\alpha$ or $\gamma$ is of second order. Here we will try to extend that model to address the phase coexistence near the MPB in a complete solid solution system by incorporating classical statistics. This proposed theory is applicable to the PZT system because the piezoelectric-ferroelectric phase transitions for PZT solid solutions of composition near the MPB are indeed second order.

II. THEORY

For simplicity, we will study a statistical ensemble of independent particles, for example, a ceramic powder system or even (to first-order approximation) a ceramic system (an ensemble of grains) may be considered to be such ensembles. For each particle, we assume it is a single-phase system both before and after the phase transition. In what follows we will calculate the probabilities of one of the particles transforming from the high-temperature phase $\beta$ into one of the low-temperature phases $\alpha$ or $\gamma$, and use these probability functions as the new distribution functions for the statistical ensemble with compositions near the MPB.

In order to visualize the concept let us look at a hypothesized 2D problem of a complete solid solution system AC-BC. The high-temperature phase is a nonferroelectric square phase as shown in Fig. 2(a) and the two low-temperature phases are rectangular and oblique ferroelectric phases as shown in Figs. 2(b) and 2(c), respectively. The phase diagram in the subsolidus region is given in Fig. 2(d). For convenience we call the starting point of the morphotropic phase boundary the "eutectoid point."

Assuming that the phase transition from the square phase to either the oblique or rectangular phase is of second order near the eutectoid point, strong thermal fluctuations will occur near the transition temperature $T_c$. Sufficiently below $T_c$ the system will be frozen into one of the low-temperature phases. In a way we are dealing with a "quenching" problem from the fluctuating state to a ferroelectric state. Hence, the probabilities of transforming from the square to the rectangular or oblique phases are predetermined in the fluctuating state. This situation is depicted in Fig. 3. The profile of the fluctuating state near $T_c$ and the final low-temperature states are shown in Figs. 3(a) and 3(b), respectively, in the order parameter space.

![Diagram](image-url)
thicker line in Fig. 3(a) illustrates the profile for the case of square-rectangular transition [near the BC end of the composition region in Fig. 2(d)] and the thinner line is for the case of square-oblique transition [near the AC end of the composition region in Fig. 2(d)]. In the compositional region near the eutectoid point, the profile of the fluctuation will look like the outer rim of the pattern in Fig. 3(a).

There is a link between the situations described in Figs. 3(a) and 3(b), which becomes apparent if we assume that the thermal fluctuations have no orientational preference. In other words, although the magnitude of the fluctuation is regulated by the potential well, the orientation probability of thermally induced instant polarization $P_{int}$ should have no directional preference. Thus the probability of attaining a particular low-temperature state in Fig. 3(b) on cooling from the fluctuating state [Fig. 3(a)] is proportional to the effective angle that state corresponds to in the fluctuating state. A polygon may be constructed to calculate the effective angle of each low-temperature state in the 2D problem where each edge of the polygon subtends an effective angle for each of the low temperature states. An important task is to define the boundaries between these effective angles. A method for defining the boundary has been given when the low-temperature states are degenerate. Considering the picture in Fig. 3(a), if $P_{int}$ is oriented inside a particular angular region while being frozen into the low-temperature phase, the final state should be one of the states in Fig. 3(b) whose polarization has the smallest angle with $P_{int}$. Therefore, the probability of becoming one of the states in Fig. 3(b) on cooling from the fluctuating state is equal to a corresponding effective angle in Fig. 3(a) divided by $2\pi$—the normalization constant.

This concept can be easily generalized to a three-dimensional case, for which the probability of attaining a low-temperature state when frozen from the fluctuating state is proportional to a corresponding effective solid angle divided by $4\pi$. For the three-dimensional case, a polyhedron may be constructed in the order parameter space to calculate these effective solid angles; it has been named the "probability polyhedron." The solid angle calculations may be carried out on the surface of the polyhedron. Utilizing the relatively high symmetry of the problem, we only need to derive a general formula for the solid angle subtended by a right triangle surface as shown in Fig. 4; the solid angle is given by

$$\Omega_{\triangle ABC} = \iint_{\Delta ABC} \frac{a\, ds}{(\rho^2 + a^2)^{3/2}}.$$  

(2)

where $ds$ is the area element on the surface of $\triangle ABC$ and $\rho$ is the distance of this area element from point A. The integration may be conveniently carried out using cylindrical coordinates

$$\Omega_{\triangle ABC} = a \phi_0 \int_0^\infty \frac{\rho \, d\rho}{(\rho^2 + a^2)^{3/2}} + a \int_0^{h/\cos \phi_0} \frac{\phi_0 - \arccos \frac{h}{\rho} \, \rho \, d\rho}{(a^2 + \rho^2)^{1/2}}$$

$$= \phi_0 - \frac{\pi}{4} \frac{1}{2} \arcsin \left( \frac{1 - 2 \cos^2 \phi_0 - (h/a)^2}{1 + (h/a)^2} \right).$$  

(3)

For the study of the coexistence of nondegenerate

![FIG. 4. Solid angle subtended by a right-angle surface \(\triangle ABC\) with respect to the point O.](image)

![FIG. 5. Probability polyhedron for complete solid solution systems with coexisting rhombohedral and tetragonal phases, such as PZT, with the parameter \(\delta\) in the ranges (a) \(1 - \sqrt{3} < \delta < 1 - (2/3)\) and (b) \(1 - (2/3) < \delta < 1 - (1/3)\).](image)
states, we use the following arguments to define the boundaries between different effective solid angles in the fluctuating states.

(i) At $T_r$ the thermal energy is of the order of $kT_p$, so that there are probabilities for the non-lowest-energy states to be occupied; this probability is proportional to $\exp(-\{(G_i-G_L)/kT_r\})$, where $G_i$ and $G_L$ are the free energies of the $i$th low-temperature state and the ground (lowest free energy) state, respectively. Here we have assumed that configurational tunneling near $T_r$ is allowed to achieve global equilibrium, because the system is very "soft" near $T_r$.

(ii) The solid angle $\Omega_i$, subtended by a given surface area with respect to a fixed point in space is inversely proportional to the square of the distance $r_i$ between this surface and that point.

Since the solid angle $\Omega_i$ is equivalent to the probability of attaining the $i$th low-temperature state, using the arguments (i) and (ii) above we may assume the following relationship between the distance variable $r_i$ and the free energies:

$$r_i \propto \frac{1}{\sqrt{\Omega_i}} \exp\left(\frac{G_i-G_L}{2kT_c}\right).$$  \hspace{1cm}  \text{(4)}$$

It can be proved that only one parameter $\delta$ is needed to calculate a binary system, such as the $P\leq L$ system, where $\delta$ is the relative distance,

$$\delta = \frac{r_T-r_G}{r_T} = 1 - \exp\left(\frac{G_R-G_T}{2kT_c}\right).$$  \hspace{1cm}  \text{(5)}$$

$G_R$ and $G_T$ are the free energies of the rhombohedral and tetragonal phases, respectively.

The probability polyhedron for the PZT system is given in Figs. 5(a) and 5(b). One must note that the representative surfaces for the rhombohedral and tetragonal phases change their shape for $\delta > 1 - (2/\sqrt{3})$ and $\delta < 1 - (2/\sqrt{3})$. When $r_T \geq (1/\sqrt{3})$, the six representative surfaces for the tetragonal phase will meet each other to form a cube, which implies that only a tetragonal phase can be formed. Vice versa, when $r_T < (1/\sqrt{3})$, the representative surfaces of the rhombohedral phase will form a closed octahedron so that only a rhombohedral phase can be formed. This restricts the $\delta$ values in the following range:

$$1 - \sqrt{3} < \delta < 1 - (1/\sqrt{3}).$$  \hspace{1cm}  \text{(6)}$$

For $\delta$ values out of this range, the low-temperature phase will be single phase.

Using the formula Eq. (3) the distribution functions $f_T$ and $f_R$ in terms of this single parameter $\delta$ can be obtained for the polyhedron in Figs. 5(a) and 5(b):

$$f_T = \frac{\pi}{6} \arcsin\left(\frac{\sqrt{3}(1-6\delta)}{2(1-6\delta)^2 + (\sqrt{3})^2-1}\right), \quad 1 - \sqrt{3} < \delta < 1 - \frac{2}{\sqrt{3}},$$

$$f_R = 1 - f_T.$$  \hspace{1cm}  \text{(7)}$$

At the MPB we have $G_T=G_R$ or $\delta=0$, so that the probability ratio for a particle of the cubic phase to transform into the rhombohedral and tetragonal phases becomes

$$f_R = \pi - 6 \arcsin\left[\frac{(3-\sqrt{3})/6}{\pi}\right] \approx 1.45.$$  \hspace{1cm}  \text{(9)}$$

When we have an ensemble of the particles, such as a powder ceramic system, Eq. (9) represents the molar ratio of the two low-temperature phases at the MPB composition.

III. COMPARISON WITH EXPERIMENTS

Because the difference of the two free-energy densities is small near the MPB we may write it as a series expansion of the composition about the MPB composition $x_0$.

$$\delta = \frac{1}{v} (G_R-G_T) = \sum_{n=1}^{\infty} \alpha_n (x-x_0)^n,$$  \hspace{1cm}  \text{(10)}$$

where $v$ is the volume of the individual element in a statistical ensemble and $x_0$ is the composition at which the free energies of the two low-temperature phases become equal. Looking at Fig. 1(d) one finds that Eq. (10) may be well represented by a linear function near $x_0$.

$$\delta = \alpha_1 (x-x_0).$$  \hspace{1cm}  \text{(11)}$$

Using this relation and Eqs. (5) and (6) we can derive the width of the coexistence region $\Delta x$.

$$\Delta x = (2kT_p/|\alpha_1|v)\ln 3.$$  \hspace{1cm}  \text{(12)}$$

An important conclusion can be drawn from Eq. (12): The width and the boundary compositions of the coexistence region are not well defined in a complete solid solution system, they depend on the volume $v$ of the statistical elements. This fact marks the physical difference between the phase coexistence inside a solubility gap and near the MPB of a complete solid solution system [see Figs. 1(a) and 1(c)]. A corollary from this conclusion is that the coexistence region will be infinitely sharp for a single-crystal system, but for a small-grain system the coexistence
region will become considerably wider. For a fixed volume, if the free-energy difference of the two low-temperature phases changes drastically away from the MPB, i.e., \(|\alpha_1|\) is large, there should be a very narrow coexistence region, otherwise the coexistence region could be wide. Substituting Eq. (13) into Eq. (11) we can rewrite Eq. (5) in the following form:

\[ \delta = 1 - \exp\left(\frac{(x - x_0)\ln 3}{\Delta x}\right). \]  

The parameters \(x_0\) and \(\Delta x\) may be fitted from experimental data using Eqs. (13) and (7) [or Eq. (8)]. Two examples are given below to demonstrate the procedures.

It is known from experience that the coexistence region in the pure PZT system is very narrow because the grain growth is difficult to control. Therefore, due to the limitations of x-ray resolution it is difficult to obtain a reliable molar ratio of the rhombohedral and tetragonal phases from x-ray-diffraction measurements. However, when small amounts of dopants are added to the PZT system (within the limit of not destroying the solid solution characteristic), the coexistence region usually becomes wider and the x-ray-diffraction peaks become relatively easier to separate from each other.

We have found two sets of experimental data in the literature. The data points in Fig. 6 were measured by Hanh, Uchino, and Nomura on the complete solid solution system 0.1Pb_{0.8}K_{0.2}(Zn_{0.6}Nb_{0.4})O_{2.85}-(0.9-x)PbZrO_3-xPbTiO_3. (Note that the compositional variable \(x\) refers to the mole percent of PbZrO_3 in Ref. 5 but refers to the mole percent of PbTiO_3 in this article; all data points have been converted accordingly.) The squares and circles are the molar fractions of the rhombohedral and tetragonal phases, respectively. The authors of Ref. 5 have fitted their experimental data to the Lever Rule, which is shown in Fig. 6 as the solid curves. The two edge compositions are \(x_1=0.45\) and \(x_2=0.57\). Although it appears that the fitting is reasonably good for these limited data points, the kinks at \(x_1\) and \(x_2\) are in contradiction with the nature of a complete solid solution system. As mentioned above, the two edge compositions in the Lever Rule actually define a solubility gap, and one cannot explain the physical meaning of these two edge compositions for a complete solid solution system. The dotted curves are fitted using the theory presented in this article, and the two fitted parameters are \(x_0=0.5027\) and \(\Delta x=0.2066\). We can see that the fittings are surprisingly good. More important, the kinks have been smoothed out, which is more consistent with the nature of the complete solid solution systems.

In comparison the width of the coexisting region obtained from the current theory, \(\Delta x=0.2066\), is wider than that given by the Lever Rule, \(x_1-x_2=0.12\). Both theories agree reasonably well if the second phase has more than 20%, but they deviate severely from each other near the edges of the coexistence region. In practice, the long tails in our theory may be difficult to observe because of the limited resolution of conventional x-ray techniques. For this reason we give a useful relation to estimate the width parameter \(\Delta x\),

\[ \Delta x \approx 18.87 (x_m-x_0), \]

where \(x_0\) is the MPB composition at which \(f_R:f_T=60:40\), and \(x_m\) is the equal fraction composition at which \(f_R:f_T=50:50\). These two compositions can be easily obtained from experiments and are indicated in Fig. 6.

Unlike the Lever Rule, the distribution functions, Eqs. (7) and (8), are asymmetric with respect to the equal fraction composition \(x_m\) and one may notice this point by looking at the dotted curves in Fig. 6. This asymmetric feature has been verified by experiments in other systems, for example, the experimental results of Ari-Gur and Benguigui for the PZT solid solution system (Fig. 7). One can clearly see this asymmetry from their data. Although it seems that some errors might have occurred in their experiments because the MPB composition has been shifted further to the rhombohedral side (which might be caused by the presence of impurities in their chemicals), the data can still be well fitted using Eqs. (7) and (8). The two fitted parameters are \(x_0=0.4212\) and \(\Delta x=0.2354\).
IV. SUMMARY AND CONCLUSIONS

The distribution functions have been derived for the coexisting phases near the morphotropic phase boundary in a complete binary solid solution system. It is shown that the phase coexistence near the MPB in a complete solid solution is different from the phase coexistence inside a solubility gap. The latter has two special compositions \( x_1 \) and \( x_2 \) specifying the edges of a solubility gap, and the distribution inside the gap can be described by the Lever Rule. While for the former, only the MPB composition \( x_0 \) is well defined, the width of the coexisting region is inversely proportional to the volume of individual element in a statistical ensemble.

Explicitly, we can see the difference between the two theories through the following example. Assume we have a binary system AC-BC and assume they form solid solutions \( \alpha \) and \( \beta \) for A- and B-rich compounds, respectively. Then, for any given composition \( x \) inside the coexistence region of \( \alpha \) and \( \beta \) we have the two theories describe the following situations:

(a) Lever Rule:

\[
x_{AC} + (1-x)_{BC} = f_{\alpha} A_{x_1} B_{1-x_1} C (\alpha \text{ structure})
+ f_{\beta} A_{x_2} B_{1-x_2} C (\beta \text{ structure}),
\]

(b) Present theory:

\[
x_{AC} + (1-x)_{BC} = f_{\alpha} A_{x_{\alpha}} B_{1-x_{\alpha}} C (\alpha \text{ structure})
+ f_{\beta} A_{x_{\beta}} B_{1-x_{\beta}} C (\beta \text{ structure}).
\]

The Lever Rule specifies a solubility gap from \( x_1 \) to \( x_2 \), and the two coexisting phases have different chemical compositions as shown on the right-hand side (rhs) of the first equation, while the current theory deals with the structural phase mixing with the same chemical composition as indicated on the rhs of the second equation. It is our belief that the observed coexisting phases in a complete solid solution system actually consist of a second metastable structure that was frozen in at the paraelectric-ferroelectric phase transition.

Compared to the Lever Rule, the current theory does not give those kinks in the distribution functions, therefore it is more consistent with the nature of a complete solid solution system (no solubility gap). The distribution functions [Eqs. (7) and (8)] are asymmetric with respect to the middle point \( x_m \), which is another major difference from the Lever Rule. Experimental results show that this asymmetry indeed exists (see Figs. 6 and 7). In addition to the surprisingly good agreement between the theory and the available experimental data, the current theory also provides a reasonable explanation to the controversy regarding the width of the coexistence region in the PZT system, which has been an issue of debate since the appearance of PZT. We conclude that a well-defined width cannot exist in a complete solid solution system because \( \Delta x \) is inversely proportional to the volume of the element in a given statistical ensemble, such as the grain size in a ceramic. Since the grain size depends strongly on the ceramic processing procedures, it is no surprise to see those reported experimental discrepancies regarding the width of the coexistence region.

ACKNOWLEDGMENTS

The authors would like to thank Professor Manfred Wuttig for his constructive comments on this manuscript. This research was supported in part by the Office of Naval Research under Grant No. 00014-92-J-1510.

APPENDIX 8
Polarization Gradient Coefficients and the Dispersion Surface of the Soft Mode in Perovskite Ferroelectrics

Wenwu Cao
Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

Abstract

The gradient coefficients in the Landau-Ginzburg theory are crucial for quantitative description of domain walls in ferroelectrics. The magnitude of these gradient coefficients are a measure of nonlocal coupling strength of the polarization. In this paper, we intend to explain the physical meaning of these gradient coefficients in terms of lattice dynamics and give some relationships between these gradient coefficients and the dispersion surface of the soft mode. The implications for the study of over damped soft modes are also discussed.

PACS Numbers: 64.60.-i, 63.20.Dj, 64.90.+b
Many ferroelectric materials have perovskite structure with a cubic symmetry in the paraelectric phase. The symmetry of the low temperature ferroelectric phase can be tetragonal, rhombohedral or orthorhombic. Ferroelectric phases usually have more than one variants and these variants may coherently coexist within the symmetry frame of the parent phase, forming the so called twin structures. It is shown that these twin structures can be well described by Landau-Ginzburg (LG) type models. \(^1,2\) All the expansion coefficients in the Landau theory correspond to certain macroscopic physical quantities and can be obtained experimentally. However, the physical meaning of the gradient coefficients, which regulate the domain wall formation and control the domain wall width in the twin structures, still needs to be specified.

A paraelectric-ferroelectric phase transition is characterized by a softening of a transverse optic mode at the Brillouin zone center due to the cancelation of the long range Coulomb forces and the short range repulsive forces.\(^3\) The soft mode is stabilized above the phase transition temperature by the anharmonic interactions whose strength weakens as the temperature decreases. Using mean field theory, one can still formally retain the terminology of normal modes if the "soft mode" frequency is assigned to be temperature dependent.

Close to the phase transition temperature, the dominant contribution in the lattice Hamiltonian is from the soft mode. Therefore, one may simply study the soft mode behavior to characterize the phase transition near \(T_c\). For an inhomogeneous system, the spatial variation of the order parameter must be considered. This is done by adding an energy term induced by the order parameter gradients. Because the inclusion of both nonlinear and nonlocal terms in the energy expansion, one may expect to obtain large amplitude soliton-like solutions which can describe the domain walls (the transition region between coherent twin structures).\(^4,5,6\) The physical meaning of these gradient coefficients can be seen from the study of small amplitude oscillations for which the nonlocal coupling can be treated as perturbations.\(^6,7\) We will show in
this paper how these polarization gradients can be derived from a simplified lattice dynamical model.

Since polarization is the density of dipoles per unit volume, it is proportional to the magnitude of the associated optical mode. As will be shown in the third section of this paper that the lattice potential for a given optical mode can be written in terms of the polarization vector. Therefore, the Landau-Ginzburg potential can be directly used in the lattice dynamical calculations in the small representation of the soft mode.

II. Gradient Coefficients and Dispersion Surface of the Soft Mode

From soft mode theory, the potential energy for a cubic system may be expanded in terms of the eigenvector of the soft mode

\[ G = \frac{\kappa}{2} (u_1^2 + u_2^2 + u_3^2) \]  

where \( \kappa \) is related to the temperature dependent soft mode frequency, \( \kappa \propto (T-T_c) \), and \( u_i \) (i = 1,2,3) are the components of the eigenvector of the soft mode. For the ferroelectric phase transition \( u \) is a relative displacement field.

If \( u \) is inhomogeneous, we must include the gradient energy in the energy expansion. For cubic symmetry the gradient energy may be written as follows,

\[ G_g = \frac{\delta_{11}}{2} (u_1^2 + u_2^2 + u_3^2) + \delta_{12} (u_{1,1} u_{2,2} + u_{1,1} u_{3,3} + u_{2,2} u_{3,3}) \]

\[ + \frac{\delta_{44}}{2} (u_{1,1}^2 + u_{2,2}^2 + u_{3,3}^2) \]  

(2)

Assuming the effective mass for the mode is \( M \) then the equations of motion become

\[ M \ddot{u}_1 + \kappa u_1 - \delta_{11} u_{1,11} - \delta_{12} (u_{2,21} + u_{3,31}) - \delta_{44} (u_{1,22} + u_{2,12} + u_{1,33} + u_{3,13}) = 0, \]  

(3a)

\[ M \ddot{u}_2 + \kappa u_2 - \delta_{11} u_{2,22} - \delta_{12} (u_{1,12} + u_{3,32}) - \delta_{44} (u_{1,21} + u_{2,11} + u_{2,33} + u_{3,23}) = 0, \]  

(3b)

\[ M \ddot{u}_3 + \kappa u_3 - \delta_{11} u_{3,33} - \delta_{12} (u_{1,13} + u_{2,23}) - \delta_{44} (u_{1,31} + u_{3,11} + u_{2,32} + u_{3,22}) = 0, \]  

(3c)

Eq.(3a-c) have plane wave solution of the form

\[ u = U \exp \left[ j (\alpha x - \kappa \cdot \mathbf{x}) \right] \]  

(4)
Substituting eq. (4) into eqs. (3a-c) gives the eigenvalue problem

\[ \text{M} \omega^2 \text{U} = \vec{D}(k) \text{U} \]  

(5)

where \( \vec{D}(k) \) is the dynamical matrix

\[
\begin{pmatrix}
\kappa + \delta_{11} k_1^2 + \delta_{44} (k_2^2 + k_3^2) & \delta_{12} k_1 k_2 & \delta_{12} k_1 k_3 \\
\delta_{12} k_1 k_2 & \kappa + \delta_{11} k_2^2 + \delta_{44} (k_1^2 + k_3^2) & \delta_{12} k_2 k_3 \\
\delta_{12} k_1 k_3 & \delta_{12} k_2 k_3 & \kappa + \delta_{11} k_3^2 + \delta_{44} (k_1^2 + k_2^2)
\end{pmatrix}
\]  

(6)

If the depolarization field is included, the equations of motion (3a-c) will contain one more term representing this contribution, which will split the longitudinal and transverse optical modes. The depolarization field is given by

\[ E(k) = - \frac{(P \cdot k)}{\varepsilon_0} \frac{k}{k^2} \]  

(7)

The additional contribution is a linear function of the polarization vector \( P \) which is proportional to the relative displacement field \( u \). Adding eq. (7) to the r.h.s. of eq. (3a-c) leads to the dynamical matrix for a given \( k \). In what follows, we will treat three \( k \)-values in the three principle directions of the \( k \)-space.

A. \( k = [k, 0, 0] \).

Define \( P = Z e u \), where \( Z \) is a constant which has a unit of inverse volume and \( e \) is the electron charge unit. The meaning of \( Z \) will be clear from later derivations. For this \( k \) value, the dynamical matrix can be simplified to the following form

\[
\begin{pmatrix}
\kappa + A + \delta_{11} k^2 & 0 & 0 \\
0 & \kappa + \delta_{44} k^2 & 0 \\
0 & 0 & \kappa + \delta_{44} k^2
\end{pmatrix}
\]  

(8)

where \( A \) is a constant defined by

\[ A = (1/\varepsilon_0) (Ze)^2 \]  

(9)
From Eq. (8) one can easily derive the dispersion relations for the longitudinal ($\omega_L$) and transverse ($\omega_T$) modes respectively:

\[
\omega_L^2 = \frac{1}{M} (\kappa + \Delta + 6_{11} \ k^2) \quad \text{(10a)}
\]
\[
\omega_T^2 = \frac{1}{M} (\kappa + 6_{44} \ k^2) \quad \text{(10b)}
\]

B. $k = \frac{k}{\sqrt{2}} \ [1, 1, 0]$

The electrostatic force from the depolarization field is now given by

\[
\frac{Z e (P_1 + P_2)}{2 \ e_0} [1, 1, 0] = \frac{A (u_1 + u_2)}{2} [1, 1, 0] \quad \text{(11)}
\]

Therefore the dynamical matrix is

\[
\tilde{D}(k) = \begin{pmatrix}
\kappa + A/2 + (\delta_{11} + \delta_{44}) k^2 / 2 & A/2 + \delta_{12} k^2 / 2 & 0 \\
A/2 + (\delta_{12} / 2) k^2 & \kappa + A/2 + (\delta_{11} + \delta_{44}) k^2 / 2 & 0 \\
0 & 0 & \kappa + \delta_{44} k^2
\end{pmatrix} \quad \text{(12)}
\]

and the dispersion relations are

\[
\omega_L^2 = \frac{1}{M} \left[ \kappa + \Delta + \frac{1}{2} (\delta_{11} - \delta_{12} + \delta_{44}) k^2 \right] \quad \text{(13a)}
\]
\[
\omega_T^1 = \frac{1}{M} \left[ \kappa + \frac{1}{2} (\delta_{11} + \delta_{12} + \delta_{44}) k^2 \right] \quad \text{(13b)}
\]
\[
\omega_T^2 = \frac{1}{M} \left[ \kappa + \delta_{44} k^2 \right] \quad \text{(13c)}
\]

Here the two transverse modes are not degenerate.

C. $k = \frac{k}{\sqrt{3}} \ [1, 1, 1]$.

For this case the Coulomb force from the depolarization field is

\[
\frac{Z e (P_1 + P_2 + P_3)}{3 \ e_0} [1, 1, 1] = \frac{A (u_1 + u_2 + u_3)}{3} [1, 1, 1] \quad \text{(14)}
\]
and the dynamical matrix becomes

$$\tilde{D}(k) = \begin{pmatrix}
\kappa + A/3 + (\delta_{11}/3 + 2 \delta_{44}/3) k^2 & A/3 + (\delta_{12}/3) k^2 & A/3 + (\delta_{12}/3) k^2 \\
A/3 + (\delta_{12}/3) k^2 & \kappa + A/3 + (\delta_{11}/3 + 2 \delta_{44}/3) k^2 & A/3 + (\delta_{12}/3) k^2 \\
A/3 + (\delta_{12}/3) k^2 & A/3 + (\delta_{12}/3) k^2 & \kappa + A/3 + (\delta_{11}/3 + 2 \delta_{44}/3) k^2
\end{pmatrix}$$

(15)

The dispersion relations are therefore given by

$$\omega_L^2 = \frac{1}{M} [\kappa + A + \frac{1}{3} (\delta_{11} + 2 \delta_{12} + 2 \delta_{44}) k^2 ]$$  \hspace{1cm} (16a)

$$\omega_T^2 = \frac{1}{M} [\kappa + \frac{1}{3} (\delta_{11} - \delta_{12} + 2 \delta_{44}) k^2 ]$$  \hspace{1cm} (16b)

Note that the dispersion relations derived above are for the cubic phase near $k=0$ but not for the low temperature ferroelectric phase.

III. The Expansion Coefficients and Lattice Dynamics

Taking the limit $k \to 0$ in the dispersion relations derived above, one finds that the coefficient $\kappa / M$ becomes the soft transverse mode frequency square,

$$\lim_{k \to 0} \omega_T^2 = \kappa / M$$  \hspace{1cm} (17)

The longitudinal mode will not become soft at $T = T_c$ because of the depolarization field contribution $A$,

$$\lim_{k \to 0} \omega_L^2 = \frac{1}{M} (\kappa + A)$$  \hspace{1cm} (18)

The simplest model to calculate these coefficients in terms of microscopic quantities is to study the $k=0$ mode for a biatomic system using rigid ion model, in which the soft mode represents the relative displacement field, the mass is the relative mass, and the polarization is equal to the ionic charge times the relative displacement then divided by the unit cell volume.
However, in the perovskite structure there are three different types of ions, hence, a more realistic model would be a three body system model. In what follows we will use a one dimensional rigid ion model for BaTiO$_3$ as an example to illustrate the relationship between the coefficients in Eq. (1) and the microscopic quantities.

According to the structural work of Shirane et al,$^{10}$ the soft optical mode in BaTiO$_3$ consists of the relative motion of Titanium, Barium and Oxygen (Fig. 1a). Because the center of mass and the center of charge for each type of ions coincide, we can effectively treat this system as a three-body system in the lattice dynamical calculations. For convenience the ion groups are labeled as follows (see Fig. 1b): Ba --- 1; Ti --- 2; and 3 O --- 3.

The potential energy represents the $k = 0$ mode for this three-body system is

$$\Phi = \frac{k_1}{2} (x_1 - x_2)^2 + \frac{k_2}{2} (x_2 - x_3)^2$$  \hspace{1cm} (19)

In order to derive the equations of motion one should also consider the Lorentz field, which leads to the following differential equations:

$$m_1 \ddot{x}_1 = - \kappa_1 (x_1 - x_2) + \frac{1}{3e_0} q_1 P$$  \hspace{1cm} (20 a)

$$m_2 \ddot{x}_2 = - \kappa_1 (x_2 - x_1) - \kappa_2 (x_2 - x_3) + \frac{1}{3e_0} q_2 P$$  \hspace{1cm} (20 b)

$$m_3 \ddot{x}_3 = - \kappa_2 (x_3 - x_2) + \frac{1}{3e_0} q_3 P$$  \hspace{1cm} (20 c)

$$q_1 + q_2 + q_3 = 0$$  \hspace{1cm} (21)

$$P = (q_1 x_1 + q_2 x_2 + q_3 x_3) / a_0^3$$  \hspace{1cm} (22)

where $a_0$ is the lattice constant, $q_1$, $q_2$, $q_3$ are the charges of the three ion groups, $P$ is the polarization.

For convenience let us introduce two new variables

$$u = x_1 - x_3; \hspace{1cm} v = x_2 - x_3.$$

Using eqs. (21) and (22), and the new variables $u$ and $v$ the equations of motion (20a-c) can be simplified to become
\[ \ddot{u} = au + bv \quad (23a) \]
\[ \ddot{v} = cu + dv \quad (23b) \]

where
\[
\begin{align*}
    a &= - \frac{k_1}{m_1} + \frac{q_1}{3 e_o a_3} \left( \frac{q_1}{m_1} + \frac{q_1 + q_2}{m_3} \right) \\
    b &= - \left( \frac{k_2}{m_3} - \frac{k_1}{m_1} \right) + \frac{q_2}{3 e_o a_3} \left( \frac{q_2}{m_2} + \frac{q_1 + q_2}{m_3} \right) \\
    c &= \frac{k_1}{m_2} + \frac{q_1}{3 e_o a_3} \left( \frac{q_2}{m_2} + \frac{q_1 + q_2}{m_3} \right) \\
    d &= - \left( \frac{k_1 + k_2}{m_2} + \frac{k_2}{m_3} \right) + \frac{q_2}{3 e_o a_3} \left( \frac{q_2}{m_2} + \frac{q_1 + q_2}{m_3} \right)
\end{align*}
\]

Eqs (23a,b) have the harmonic oscillator solution
\[ u = u_0 \exp(j\omega t) \quad (24) \]
\[ v = v_0 \exp(j\omega t) \quad (25) \]

and the eigenfrequency \( \omega \) is given by:
\[
\omega_0^2 = \frac{1}{2} \left[ -a - d \pm \sqrt{(a + d)^2 - 4(ad - bc)} \right] \quad (26)
\]

In any given mode the relative displacement \( u \) and \( v \) are proportional to each other. For the coordinate system in Fig. 1, \( u \) and \( v \) always have the same sign. Assuming one of the modes, for example \( \omega_n \), becomes soft at lower temperatures due to the decrease of the coupling strength between different ions, then, their magnitudes have the following relationship:
\[
v_0 = \frac{1}{2b} \left( d - a + \sqrt{(a + d)^2 - 4(ad - bc)} \right) u_0 \quad (27)
\]

From Eqs. (21) and (22) the polarization \( P \) is given by
\[
P = \frac{(q_1 u + q_2 v)}{a_3^2} = \left[ q_1 + \frac{q_2}{2b} \left( d - a + \sqrt{(a + d)^2 - 4(ad - bc)} \right) \right] u/a_3^2 \quad (28)
\]

Therefore, in this mode
\[
Z_e = \left[ q_1 + \frac{q_2}{2b} \left( d - a + \sqrt{(a + d)^2 - 4(ad - bc)} \right) \right] / a_3^2 \quad (29)
\]

The value of \( P \) can be obtained from pyroelectric measurements and \( u \) may be calculated from
X-ray diffractions of the low and high temperature phases, hence, Ze can also be obtained experimentally.

Since \( v \) and \( P \) are linearly proportional to \( u \), we could simplify the problem by constructing a new single variable potential \( G= (\kappa/2) u^2 \) which gives rise to the following equation of motion.

\[
\ddot{u} = a \, u + b \, v = \frac{1}{2} \left\{ -(a+d) - \sqrt{(a+d)^2 - 4(ad-bc)} \right\} u = \frac{\kappa}{M} u
\]  

(30)

where \( \kappa \) has the dimension of force constant and \( M \) has the dimension of mass according to the definition of \( a, b, c \) and \( d \). For a three dimensional system, the constructed potential which leads to Eq.(30) will have the same form as Eq. (1) according to symmetry. Because \( u \) is also proportional to the polarization \( P \) [eq. (28)], we may also write down the constructed potential in terms of the polarization vector \( P \), which becomes the Landau potential for a ferroelectric system \( G= (\alpha/2) P^2, \alpha = \kappa / (Ze)^2 \).

For longitudinal vibrations, we have to add the depolarization field \( -P/\varepsilon_0 \) to the equation of motion Eq.(20 a -c), which will add a positive contribution to the eigenfrequency preventing it to become soft like the transverse mode. Formally, the relationship between \( \omega_L \) and \( \omega_T \) may be written as

\[
\omega_L^2 = \omega_T^2 + \frac{A}{M}
\]  

(30)

where \( A \) is a positive constant reflecting the contribution of the depolarization field.

IV. Summary and conclusions

It is shown that the polarization gradient coefficients in the Landau-Ginzburg theory can be directly related to the dispersion surface of the soft mode. Therefore, their physical meaning becomes apparent. The correspondence between the Landau theory and the lattice dynamic potential was illustrated through a simple one dimensional rigid ion model for BaTiO\(_3\) at \( k=0 \). Since the polarization and the relative displacement field have a linear relationship, the polarization
coefficients in the Landau-Ginzburg theory may be calculated from the measured dispersion curves near the soft mode. For cubic symmetry there are only three independent gradient coefficients, the dispersion anisotropy of the soft mode can be determined through measurements along the three principal directions. These gradient coefficients in principle can be obtained through inelastic neutron scattering experiments. However, in many cases these dispersion curves are very difficult to measure because of the high transition temperature. To my knowledge, a complete set of the dispersion relations do not exist in the literatures for the known ferroelectric materials. One of the intentions of this paper is to re-emphasize the importance to measure these dispersion curves which can be used for the study of domain walls in ferroelectrics.

An interesting point should be also mentioned is the possibility of obtaining the dispersion surface of the soft mode through direct measurements on the domain wall profiles(11). Because the gradient coefficients can be extracted from fitting the measured polarization profiles to the soliton-like solutions of nonlinear nonlocal continuous medium theory,(2,6) This could be very useful to study the dispersion surface of the over damped soft mode, such as in BaTiO3, which can not be obtained through inelastic neutron scattering.

Acknowledgements

This research is sponsored by the Office of Naval Research under Grant No 00014-92-J-1510.

Reference

Figure Captions

Figure 1. (a) Illustration of the ionic displacements in BaTiO$_3$ from ref. 10.
(b) One dimensional model for the soft mode.
Figure 1.
NONLINEAR AND NONLOCAL CONTINUUM THEORY ON
DOMAIN WALLS IN FERROELECTRICS

WENWU CAO AND L. E. CROSS
Materials Research Laboratory, The Pennsylvania State University,
University Park, PA 16802

Abstract The domain structures in ferroelectrics can be described by a
Landau-Ginzburg type theory with the twin and twin band (domain) structures
being nonlinear and nonlocal excitations of the ferroelectric phase. The
polarization gradients in the theory reflect the degree of nonlocal coupling
along different crystallographic orientations. These gradient parameters can be
obtained either from the dispersion surface of the soft mode or through fitting
the polarization profile measured by the holographic electron microscopy.

INTRODUCTION

The understanding of domain structures is essential for the design and applications of
ferroelectrics. It has been long recognized that the piezoelectric and dielectric properties
of ferroelectric ceramics are mainly determined by the behavior of domain structures.
The formation of domains in ferroelectrics is due to the existence of multi-variants in the
ferroelectric phase. Atomic coherency is usually maintained across the domain
boundaries, which make it possible to switch domain orientations from one to the other
using external (either mechanical or electrical) fields. This switching gives rise to the so
called extrinsic contributions to the materials properties. The formation of domain walls
in ferroelectrics may be treated in terms of solitory wave excitations in a nonlinear and
nonlocal system. Single kink-like and periodic solitory wave solutions for the twin and
periodic domain structures can be derived using the continuum theory.1-4 Since all the
expansion coefficients in the Landau-Devonshire model can be expressed in terms of
measurable macroscopic quantities, the continuum theory can give quantitative
description of the domain wall properties, including the profile of polarization across the
domain wall, domain wall width, energy stored in the multi-domain structure, and the
stress build up at the domain wall region, once the polarization gradient coefficients are
obtained.
THE MODEL

The Landau-Devonshire type phenomenological theory for ferroelectrics has been developed for the ferroelectric phase transition.\(^5\),\(^6\),\(^7\) For a cubic system, such as perovskite ferroelectrics, the elastic Gibbs free energy can be expressed in the following form:

\[
G = G_p + G_{el} + G_c
\]

where

\[
G_p = A (P_1^2 + P_2^2 + P_3^2) + B (P_1^4 + P_2^4 + P_3^4) + C (P_1^6 + P_2^6 + P_3^6)
\]

\[
+ D (P_1^2 P_2^2 + P_2^2 P_3^2 + P_1^2 P_3^2) + E (P_1^4 P_2^2 + P_1^2 P_2^4 + P_2^4 P_3^2 + P_2^2 P_3^4 + P_3^2 P_1^4 + P_1^2 P_3^4)
\]

\[
+ H P_1^2 P_2^2 P_3^2
\]

\[
G_{el} = -\frac{s_{11}}{2} (X_{11}^2 + X_{22}^2 + X_{33}^2) - s_{12} (X_{11} X_{22} + X_{22} X_{33} + X_{11} X_{33})
\]

\[
-\frac{s_{44}}{2} (X_{12}^2 + X_{13}^2 + X_{23}^2)
\]

\[
G_c = Q_{11} (X_{11} P_1^2 + X_{22} P_2^2 + X_{33} P_3^2) + Q_{12} (X_{11} (P_2^2 + P_3^2) + X_{22} (P_1^2 + P_3^2) + X_{33} (P_1^2 + P_2^2))
\]

\[
+ Q_{44} (X_{12} P_1 P_2 + X_{13} P_1 P_3 + X_{23} P_2 P_3)
\]

(4)

where \(A, B, C, D, E, H\) are the linear and nonlinear dielectric constants, \(s_{ij}\) are the elastic compliance coefficients, \(Q_{ij}\) are the electrostriction constants, \(P_i\) and \(X_{ij}\) are the components of polarization and stress, respectively. All the coefficients are assumed to be independent of temperature except \(A\) which is a linearly function of \(T\),

\[
A = \alpha (T - T_0)
\]

(5)

In a homogeneous system, a paraelectric-ferroelectric phase transition occurs at \(T_c\). Under stress free condition, the phase transition temperature \(T_c\) and the spontaneous polarization \(P_c\) at the transition can be derived by minimizing Eq. (1),

\[
T_c = T_0 + \frac{B^2}{4 C \alpha}
\]

(6)

\[
P_c^2 = \frac{-B}{2C}
\]

(7)

One of the low temperature ferroelectric phases is the tetragonal phase. There are six energetically degenerate variants in the tetragonal phase: \((\pm P_s, 0, 0)\), \((0, \pm P_s, 0)\) and \((0, 0, \pm P_s)\), where \(P_s\) is the spontaneous polarization given by

\[
P_s = \sqrt{-B + \sqrt{\frac{B^2 - 3AC}{3C}}}
\]

(8)

These energetically degenerate variants can coexist in the ferroelectric phase to form the twin structures. Electron microscopy reveals that the ionic coherency is maintained across domain walls, but domain walls are not atomically sharp. Domain wall width is determined by the nonlocal coupling strength of the ferroelectric system.
Since the nonlinearity has been included in the model [see Eqs. (1)-(4)], if we add the contributions of nonlocal coupling, then from soliton theory, we may expect solitary wave excitations in the ferroelectric phase. These excitations are indeed found and they represent the ferroelectric domain walls.

For a perovskite system, the symmetry of the high temperature phase is cubic, therefore, the Gibbs energy representing the nonlocal coupling can be written as follows:

$$G_g = \frac{1}{2} g_{11} (P_{1,1}^2 + P_{2,2}^2 + P_{3,3}^2 ) + g_{12} (P_{1,1} P_{2,2} + P_{1,1} P_{3,3} + P_{2,2} P_{3,3} )$$

$$+ \frac{1}{2} g_{44} [ (P_{1,2} + P_{2,1})^2 + (P_{1,3} + P_{3,1})^2 + (P_{2,3} + P_{3,2})^2 ]$$  \hspace{1cm} (9)

here the indices after the comma represent derivatives with respect to space variable along that axis. Upon the minimization of the total free energy of the system Eqs. (1) and (9), one can obtain the solutions for the domain walls.

**90° DOMAIN WALLS**

There are two types of domain walls in the tetragonal ferroelectrics. One is the 180° domain wall which divides a twin domain with identical strain but opposite polarization, and the other is the 90° domain wall which divides two domains whose polarization and spontaneous strain are nearly 90° from each other. Solutions for the 180° domain walls can be easily obtained since the problem is one-dimensional. Here we only solve the problem of 90° domain walls for which the problem can be rendered to quasi-one-dimensional.

From transmission electron microscopy studies, domain walls tend to broaden or bent near the surface, however, inside the sample they have well defined wall-like

**FIGURE 1. A tetragonal-twin structure and the coordinate system used in this paper.**
structure with translational symmetry parallel to the wall plane. Therefore, while dealing with a <110>-type domain walls in tetragonal ferroelectrics we can rotate the \( x_1, x_2 \) coordinates about the \( x_3 \) coordinate by 45° so that the properties of the domain walls only depend on one space variable (s-coordinate as indicated in Fig. 1) only.

In the new coordinate system the equilibrium conditions are governed by the following equations:

\[
\frac{\partial}{\partial x_j} \left[ \frac{\partial G}{\partial P_{i,j}} \right] = 0, \quad (i, j = s, r, 3) \tag{10}
\]

\[
X_{ij,j} = 0, \quad (i, j = s, r, 3) \tag{11}
\]

and we also need the elastic compatibility relations

\[
\varepsilon_{ijkl} \varepsilon_{jmn} x_{ln,km} = 0 \quad (i, j, k, l, m, n = s, r, 3) \tag{12}
\]

to insure the elastic continuity since in our model the domain walls are intrinsic excitations, no defects are created in the domain wall region. \( x_{ln} \) is the component of elastic strain tensor and \( \varepsilon_{ijkl} \) is the Levi-Civita density.

Eqs (11) and (12) have three nontrivial solutions:

\[
X_{33} = 0 \tag{13}
\]

\[
X_{rr} = \frac{1}{2} \left( \frac{2 s_{12} Q_{12} - s_{21} (Q_{11} + Q_{12})}{s_{11} s_{ss} - s_{f1}^2} \right) \left\{ [2 s_{12} Q_{12} - s_{21} (Q_{11} + Q_{12})] P_0^2 - [2 s_{12} Q_{12} - s_{21} (Q_{11} + Q_{12} + Q_{44})] P_{f1}^2 \right\} \tag{14}
\]

\[
X_{33} = \frac{1}{2} \left( \frac{2 s_{12} Q_{12} - 2 s_{ss} Q_{21}}{s_{11} s_{ss} - s_{f1}^2} \right) \left\{ [s_{12} (Q_{11} + Q_{12}) - 2 s_{ss} Q_{12}] P_0^2 - [s_{12} (Q_{11} + Q_{12} + Q_{44}) - 2 s_{ss} Q_{12}] P_{f1}^2 \right\} \tag{15}
\]

where

\[
s_{ss} = \frac{1}{2} (s_{11} + s_{12} + s_{44}) .
\]

It can be easily verified that the two stress components \( X_{rr} \) and \( X_{33} \) are nonzero only in the vicinity of the domain wall. These nonzero stress components near the domain wall region is the cause of the faster etching rate which makes the domain walls visible through chemical etching technique.

In order to see the general trend of the variation of polarization profile without specifying the coefficients to a particular system, we normalize the polarization and the space variable \( s \) into dimensionless forms by the following substitutions:

\[
P_r = \sqrt{-\frac{B}{2C}} f_r = P_c f_r \quad P_s = \sqrt{-\frac{B}{2C}} f_s = P_c f_s \tag{16a,b}
\]

\[
s = \gamma \xi, \quad \gamma = \left( \frac{G_{ss} G_{ff}}{4 A_c^2} \right)^{1/4} \tag{17a,b}
\]

where
and define the dimensionless temperature as

\[ \tau = \frac{T - T_0}{T_c - T_0} \]  \hspace{1cm} (18)

then the equilibrium condition Eq. (10) can be written in the following form for a 90° twin structure,

\[
a f_{12}, b_{12} = \tau_1 f_{12} + c f_{12}^2 + df_{12}^3 + \frac{(8 - \frac{2}{3} d) f_{12} f_{12}^2 + (4 - \frac{1}{3} d) f_{12}^2}{(2) (19)}
\]

\[
a f_{12}, b_{12} = \tau_1 f_{12} + c f_{12}^2 + df_{12}^3 + \frac{(8 - \frac{2}{3} d) f_{12} f_{12}^2 + (4 - \frac{1}{3} d) f_{12}^2}{(2) (20)}
\]

where the coefficients are given by

\[ a = \sqrt{\frac{G_{ss}}{G_{rs}}} \]  \hspace{1cm} (21)

\[ \tau_1 = \frac{(1+\sqrt{1-\frac{3}{4} \tau_1})}{2} \left[ (Q_{11} + Q_{12} - Q_{44})[2s_{12}Q_{12} - s_{11}(Q_{11} + Q_{12})] + 2Q_{12}[s_{12}(Q_{11} + Q_{12}) - 2s_{ss}Q_{12}] \right] \]  \hspace{1cm} (22)

\[ \tau_1 = \frac{(1+\sqrt{1-\frac{3}{4} \tau_1})}{2} \left[ (Q_{11} + Q_{12} + Q_{44})[2s_{12}Q_{12} - s_{11}(Q_{11} + Q_{12})] + 2Q_{12}[s_{12}(Q_{11} + Q_{12}) - 2s_{ss}Q_{12}] \right] \]  \hspace{1cm} (23)

\[ b_s = -2 - \frac{D_1 + \sqrt{1-\frac{3}{4} \tau_1}}{B_2} \left[ (Q_{11} + Q_{12} - Q_{44})[2s_{12}Q_{12} - s_{11}(Q_{11} + Q_{12} - Q_{44})] + 2Q_{12}[s_{12}(Q_{11} + Q_{12} - Q_{44}) - 2s_{ss}Q_{12}] \right] \]  \hspace{1cm} (24)

\[ b_r = -2 - \frac{D_1 + \sqrt{1-\frac{3}{4} \tau_1}}{B_2} \left[ (Q_{11} + Q_{12} + Q_{44})[2s_{12}Q_{12} - s_{11}(Q_{11} + Q_{12} + Q_{44})] + 2Q_{12}[s_{12}(Q_{11} + Q_{12} + Q_{44}) - 2s_{ss}Q_{12}] \right] \]  \hspace{1cm} (25)

\[ c = -6 + \frac{D_1 + \sqrt{1-\frac{3}{4} \tau_1}}{B_2} \left[ (Q_{11} + Q_{12} - Q_{44})[2s_{12}Q_{12} - s_{11}(Q_{11} + Q_{12} - Q_{44})] + 2Q_{12}[s_{12}(Q_{11} + Q_{12} - Q_{44}) - 2s_{ss}Q_{12}] \right] \]  \hspace{1cm} (26)

\[ d = \frac{3}{4} \left( 1 + \frac{E}{C} \right) \]  \hspace{1cm} (27)

RESULTS AND DISCUSSIONS
Using the normalized equations, we can study the influence of different parameters to the polarization profile and obtain a conceptual understanding on the nature of the polarization variation in the domain wall region. Fig. 2 shows the variation of the polarization components with the parameter $a$ across a $90^\circ$ domain wall. One can see that the domain wall becomes wider as $a$ increases. In real dimensions, because the scaling factor of the space variables, $\gamma$, is directly related to the product $G_{ss}*G_{rs}$ [see eq.(17)], domain wall becomes wider as the gradient coefficients become larger.

**FIGURE 2.** Variation of polarization components $f_s$ and $f_r$ induced by the change of parameter $a$ across a $90^\circ$ domain wall. The gradient parameter $a$ determines the width of the domain wall.

**FIGURE 3.** Variation of polarization components $f_s$ and $f_r$ with temperature $\tau$ across a $90^\circ$ domain wall. The asymptotic values of the polarization components increase and the domain wall width decrease while lowering temperature.
FIGURE 4. Variation of polarization components $f_s$ and $f_r$ induced by the change of parameter $d$ across a 90° domain wall. The nonlinear parameter $d$ influences the magnitude of the polarization variation in the domain wall region.

FIGURE 5. (a) Polarization components $f_1$ and $f_2$ across a 90° domain wall, and (b) Illustration of the variations of the polarization vector and the unite cell distortion across a 90° domain wall.
Fig. 3 shows the variation of the polarization with temperature $T$. The asymptotic values of the magnitude of the polarization components increase and the domain wall thickness decreases as the temperature is lowered. The temperature dependence is strong near the transition and gradually becomes insensitive when the temperature is far below $T_c$. Fig. 4 shows the variation of the polarization components $f_s$ and $f_r$ induced by the change of parameter $d$. We can see that the magnitude of $f_s$ is very sensitive to $d$ while the domain wall thickness is relatively insensitive to $d$. We can also calculate the polarization components $f_1$ and $f_2$ in the original coordinates. One example is given in Fig. 5(a) for a set of chosen parameters. The corresponding unit cell distortion and the polarization variation across the domain wall are illustrated in Fig. 5(b). The polarization vector rotates gradually from one orientation into the other accompanied also by a change of the magnitude.

All properties of the domain walls can be quantitatively calculated using this model once the expansion coefficients are known. As we have mentioned above that the polarization gradient coefficients are most crucial for the study of domain walls, which may be derived from the measurements on the dispersion surface of the soft mode. In general, inelastic neutron scattering to probe the soft mode may be difficult due to the relatively high transition temperature in many systems of interest and in some cases, the soft mode is over-damped. An alternative way to obtain these coefficients would be to probe the polarization profile across the domain wall and then fitting the unknown coefficients using the differential equations (19) and (20). The recently emerged new technique, electron holography, may offer an option to this end.

ACKNOWLEDGEMENTS

This research is sponsored by the Office of Naval Research.

REFERENCES

5. A. F. Devonshire, Phil. Mag., 40, 1040 (1949); 42, 1065 (1951).
THEORY ON THE FRINGE PATTERNS IN THE STUDY OF FERROELECTRIC DOMAIN WALLS USING ELECTRON HOLOGRAPHY

Wenwu Cao and Clive Randall
Materials Research Laboratory, The Pennsylvania State University
University Park, Pennsylvania 16802

Received March 10, 1993 by A. Pinczuk

The realization of electron holography provides a new powerful tool to probe the subtle and local changes of electric and magnetic fields inside a crystal structure through the phase variation of electron wave function. For a ferroelectric system the interference fringe patterns across a domain wall are very strongly affected by the presence of surface charge compensations. If the compensation is incomplete, a residue depolarization field will be present in the direction parallel to the electron beam, which can induce kink-like fringe bending. Earlier reported holographic images of ferroelectric domain walls revealed an asymmetry fringe bending. This behavior is explained through phase shifts induced by both the depolarization field and the strain field.

1 - Introduction

Electron holography provides us with a new methodology for the study of electric and magnetic field variations at the atomic scale.1 In the past few years, the electron holography technique has demonstrated its power in the study of magnetic domain walls, p-n junctions, and fluxons in superconducting materials.2-7 Recently, this method has been introduced into the study of ferroelectric materials, with particular interest to ferroelectric domain walls and defect dopants.8 The kink-like phase change profile observed in the interference fringes qualitatively agrees with the continuum theoretical descriptions of ferroelectric domain wall profiles.9,10 However, quantitative agreement has not been obtained and the experimental results are not consistently reproducible. In this paper, a theoretical analysis is carried out, which intends to provide some basics for future studies on ferroelectric domain walls using electron holography.

Due to the existence of free charges, the study of polarization related electric field variations is much more complicated than the study of magnetic field variation using electron holography. The density of these free charges varies with the electric potential distribution and depends strongly on boundary conditions. The observed electron interference fringe patterns reflect the total electric potential distribution, therefore, in order to correlate them to the variation of polarization across a domain boundary one must separate different charge sources.

2 - Electron holography

The fundamental principle in electron holography is the interference of coherent high energy electrons. To a good approximation the transmission of high energy electrons through a thin foil sample can be treated as a one-dimensional problem. Define z to be the electron traveling direction, then the phase change in the electron wave function due to the existence of an electric potential \( V(x, y, z) \) is given by

\[
\Phi(x, y, z) = \frac{2\pi}{\lambda} \int \left( \sqrt{1 - \left( \frac{V(x, y, z)}{\Sigma} \right)^2} - 1 \right) dz
\]

(1)

where \( \lambda \) is the electron wave length, \( x_0 \) and \( y_0 \) define the point on the sample foil, \( \Sigma \) is the electron energy and \( V(x_0, y_0, z) \) represents the electric potential produced by the object. When the electron energy, \( \Sigma \), is much greater than the magnitude \( |V(x_0, y_0, z)| \max \) of the potential barrier, the phase shift of the electron wave can be simplified as

\[
\Phi(x_0, y_0) = \frac{-\pi}{2\lambda\Sigma} \int V(x_0, y_0, z) \, dz
\]

(2)

Since the energy of the electron beam is very large, ~200 keV, Eq. (2) is usually sufficient to calculate the phase change.

The most important characteristic of a ferroelectric is a reversible spontaneous polarization. Generally, the spontaneous polarization results from a displacive or order-disorder phase transition. Without external electric fields, the macroscopic spontaneous polarization is developed in domains within the crystal, forming the so-called twin structures. There are two main types of twins. One has an inversion symmetry about the twin boundary but with equal strain in both variants. The second type is a twin of two variants with both different orientation of polarization and of spontaneous strain. The internal potential \( V(x_0, y_0, z) \) in a domain depends on the polarization and the boundary conditions at the crystal surfaces.
3. Theory

From electrodynamics we know that the macroscopic electric field \( E \), polarization \( P \), and the electric displacement \( D \), are all interrelated by the following equation,

\[
D = \varepsilon_0 E + P
\]

Generally speaking, polarization \( P \) depends on local electric field which is different from the macroscopic electric field \( E \). A ferroelectric system has a number of additional considerations owing to the spontaneous polarization and boundary conditions. Two extreme cases are shown below to illustrate this situation. For simplicity we assume the spontaneous polarization, \( P_s \), is perpendicular to the sample plane.

Case I. Complete charge compensation.

The simplest case is when the sample surfaces are electroded and the two electrodes were short circuited during the development of the spontaneous polarization. For this system we have the condition \( E = 0 \), so that

\[
D = P_s
\]

Since \( P_s \cdot \pi \) is the surface "bound charge" density and \(- D \cdot \pi \) equals the surface "free charge" density, the polarization is completely compensated by the generated free charges. The system is in equilibrium and has a fully developed spontaneous polarization throughout the whole crystal. When the temperature is kept constant, there is no macroscopic electric field present either inside or outside of the ferroelectric crystal. Therefore, no fringe variations are expected.

Case II. Completely uncompensated polarization.

The other simple but unrealistic case is the polarization being completely uncompensated, i.e., \( D = 0 \). Then there will be a very strong depolarisation field being produced inside the sample,

\[
E = - \frac{P_s}{\varepsilon_0}
\]

which is equal to the microscopic field. This field is too large to be sustained. For example, the depolarisation of \( \text{BaTiO}_3 \) is 18 \( \mu \text{C/cm}^2 \), from Eq.(5) the depolarization field can be as large as 2 \( \times 10^8 \) \( \text{V/cm} \). Under such a large field, either the polarization will be destroyed (which suppresses the structural phase transition) or the system will obtain free charges (from the environment or within the crystal) to reduce the field level.

As free charges are readily available, a real system is more like Case I above, even when the sample is not being electroded. This is to say that the phase shift induced by the depolarization field difference across a domain boundary is being counterbalanced by the phase shift produced by the field of compensation charge. However, charge compensation in a non-electroded sample is a relaxation process, the rate can be very slow as the equilibrium is approached. In addition, since most of the ferroelectrics are also improper ferroelastic, a small level of the depolarization field could be sustained through elastic distortion of the structure. In other words, the system is sometimes not fully compensated, at least in a finite time period. This situation can also happen in an already compensated system through the change of temperature (pyroelectric effect) or mechanical stress (piezoelectric effect).

The depolarization field in the partially compensated system can be expressed as

\[
E = -(P_0 - D)\varepsilon_0 = (1-\eta)P_0/\varepsilon_0
\]

Here we have defined a compensation factor \( \eta = D/P_0 \) (in our problem the vectors \( D \) and \( P_0 \) are in the same direction) which is less or equal to unity, \( 0 < \eta \leq 1 \). The compensation factor \( \eta \) depends strongly on temperature, stress, and also on time. Since the net field in Eq. (6) is non-zero if \( \eta < 1 \), and proportional to the polarization, one may use holographic electron microscopy to study the variation of polarization inside a twin domain structure, through the residue field and the associated phase shift. The basic requirement is that \( \eta \) changes slowly with time.

The associated spontaneous polarization profiles can be determined using Landau-Ginsburg theory. As an example, in a 180° twin structure with the polarization in the z-direction (the electron beam direction), the profile can be described by

\[
P(x) = \frac{P_s \sinh (x/\xi)}{\sqrt{A + \sinh^2 (x/\xi)}}
\]

where \( x \) is the space variable in the domain wall normal direction and \( \xi \) is the characteristic width of the domain wall; the parameter \( A \) is a constant which reflects the sharpness of the first order transition. For a second order phase transition \( A = 1 \) and Eq. (9) reduces to a hyperbolic tangent function

\[
P = P_s \tanh (x/\xi)
\]

From Eqs. (3), (6), and (7) or (8), one can calculate the phase profile across a domain wall:

\[
\Delta \phi(x_s) = \frac{(1-\eta)x_s^2}{\lambda \Sigma} P(x_s)
\]

Here \( x_s \) defines the coordinate on the sample surface and the phase reference is chosen at the domain wall center. Since phase variations are proportional to the polarization, the fringe patterns should be kink-like as observed in \( \text{BaTiO}_3 \). For later convenience, we define these kink-like patterns as type I fringes for domain walls, which is asymmetric.

Most ferroelectrics are also improper
Fig. 1. The polarization profiles for the polarization components perpendicular and parallel to the domain wall in a 90° twin structure.

ferroelastics, i.e., the strain is the secondary order parameter and coupled to the polarizations; hence, it also changes in the domain wall region. The relationship between the spontaneous polarization \( P \) and the spontaneous strain \( \epsilon \) can be written as:

\[
S_{ij} = Q_{ijkl} P_i P_j (i,j,k,l = 1,2,3) \tag{10}
\]

where \( Q_{ijkl} \) is the electrostriction constant. The non-zero strain components are defined by the crystal symmetry and boundary conditions. For the 180° ferroelectric twin discussed above the strain variation in the domain wall region is

\[
\Delta S_i = Q_{i30} (P^2_i - P^2(x)) \tag{11}
\]

Due to the symmetric nature of Eq. (11), the phase profile reflecting the strain variation will be symmetric about the center of the domain wall. We define the hump-like symmetric fringes as type II fringes for domain walls. Additional contribution to the type II fringes may come from the polarization component perpendicular to the domain wall, which is non-zero for all non-180° domain walls. The profile of this component is hump-like as illustrated in Fig. 1. Also, because the strong polarization gradient at the domain wall region, charge defects and vacancies tend to be trapped by the domain walls, these point charge defects can also contribute to the type II fringes as summarised in Table I.

In general, the fringe patterns observed across a ferroelectric domain wall will be a mixture of type I and type II, so that the resultant fringe patterns will be non-symmetric. For example, assuming the polarization is given by Eq. (8), then the resultant normalized fringe profile is illustrated in Fig. 2. The circles in Fig. 2 represent type I profile and the dashed lines represent type II profile, \( \alpha = 1 \Delta \phi_0/1 \Delta \phi_{-1} \) is the ratio of the maximum phase shifts of type II versus type I. One can see that the resultant phase shift becomes more and more asymmetric as \( \alpha \) increases from 0 to 1, and the total profile moves to the left. This asymmetric feature is obviously seen in the results reported in ref. 5 for BaTiO₃ (see the data points in Fig. 3). According to the above analysis, we propose the fringes to be fitted in the following equation:

<p>| Table I |</p>
<table>
<thead>
<tr>
<th>Shape</th>
<th>Symmetry</th>
<th>Source of Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>Antisymmetric</td>
<td>Polarization parallel to domain wall</td>
</tr>
<tr>
<td>Type II</td>
<td>Symmetric</td>
<td>Polarization perpendicular to domain wall; point charge defects; strain variation across the domain wall</td>
</tr>
</tbody>
</table>
Fig. 3. Comparison of the theory with the experimental data of ref. 8. The circles are the experimental data, the thin line is the fitting to a simple hyperbolic tangent and the thick line was obtained using Eq. (12).

\[
\Delta \phi(x)/\Delta \phi_0 = \tanh\left(\frac{x-x_d}{\xi}\right) + \alpha \left(1 - \tanh^2\left(\frac{x-x_d}{\xi}\right)\right) + \beta
\]

where \(x_d\) and \(\beta\) are respectively the horizontal and vertical deviations of the domain wall center from the reference center used in the experiment. A different characteristic length \(\xi_a\) for the type II fringe is introduced, which may not be the same as \(\xi\). Fig. 3 shows the comparison between the fitting of ref. 8 (thin line) and the fitting using Eq. (12) (thick line). One can see that the current fitting is quite satisfactory with the following fitting parameters: \(x_d = 0.0285 \xi; \alpha = 0.323; \xi_a = 0.31 \xi\) and \(\beta = 0.1285\). Here we like to emphasize that the functional form for the first order phase transition in BaTiO\(_3\) would be more appropriate to use eq. (7) instead of eq. (8) if the constant \(A\) can be determined.

Fig. 4. Calculated fringes across a domain wall for different \(a\) assuming \(|\Delta \phi_0| = \pi/2\).

Fig. 5. Calculated fringes across a domain wall for different \(a\) assuming \(|\Delta \phi_0| = \pi/2\).

Figures 4 and 5 show some of the expected fringe patterns across a ferroelectric domain wall using the current analysis. The fringes in Fig. 4 were calculated by assuming \(|\Delta \phi_0| = \pi/2\) while the fringes in Fig. 5 were calculated by assuming \(|\Delta \phi_0| = \pi/2\). One can see the nature of the fringes changes from type I to type II as the parameter \(a\) increases from 0 to \(\infty\).

4 - Conclusions

As the electron holography technique is very sensitive to the local electric potential variations, the incompletely compensated depolarization field in domain wall regions can be measured. The fringe patterns can be directly correlated to the space profile of polarization variation in a twin structure. The sample should not be electroded and the electron energy must be very high. For a compensated sample, one may vary the temperature to destroy the charge balance and make the domain wall visible through the electron phase shift. In general, the fringe bending observed is a mixture of type I and type II, one must separate the two types of contributions in order to extract useful information from electron holography. Eqs. (9) and (12) can be used to fit the fringe patterns across a 180° and a non-180° domain wall, respectively.

Acknowledgments

The author is indebted to Drs. X. Zhang, D. Joy and L. F. Allard for many helpful discussions on the electron holography technique and Dr. L. E. Cross for discussions on ferroelectrics. This research was supported by Air Force Office of Scientific Research under Grant No. AFOSR-91-0433.
References

APPENDIX 11
Direct evaluation of domain-wall and intrinsic contributions to the dielectric and piezoelectric response and their temperature dependence on lead zirconate-titanate ceramics

Q. M. Zhang, H. Wang, N. Kim, and L. E. Cross
Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

(Received 12 July 1993; accepted for publication 17 September 1993)

By making use of the fact that domain-wall motions do not produce volumetric changes, an experimental method is introduced to directly and quantitatively determine the domain-wall and intrinsic contributions to the piezoelectric and dielectric responses of a ferroelectric material. Utilizing this method, the contributions from the domain walls and intrinsic part as well as their temperature dependence for lead zirconate-titanate (PZT) 52/48 and PZT-500 ceramics are evaluated. The data show that at temperatures below 300 K, the large change in the dielectric and piezoelectric constants with temperature is due to the change in the domain-wall activities in the materials. The results confirm that most of the dielectric and piezoelectric responses at room temperature for the materials studied is from the domain-wall contributions. The data also indicate that in PZT-500, both 180° wall and non-180° walls are possibly active under a weak external driving field.

I. INTRODUCTION

For most ferroelectric materials, the existence of domain structures or domain walls makes a significant influence on the material properties. For example, in lead zirconate-titanate (PZT) solid solution system, the material properties can be modified over a wide range by using different dopants or by different processing conditions. Such changes in the material properties are believed to be the result of changes in the domain-wall response in the materials. From the Landau-Devonshire phenomenological theory, it has been proposed that for PZT at compositions near the morphotropic phase boundary, the domain-wall contribution accounts for more than half of the room-temperature dielectric and piezoelectric responses.

In the literature, the material properties from a single-domain material are denoted as the intrinsic properties (or volume contribution) of the material, while the contributions from the other parts of the material, mainly from domain walls, are lumped as extrinsic properties of the material. Under this convention, the dielectric constant $\varepsilon$, piezoelectric constant $d$, and elastic compliance $s$, can be written as a summation of two terms:

$$\varepsilon = \varepsilon_\text{ex} + \varepsilon_\text{in},$$
$$d = d_\text{ex} + d_\text{in},$$
$$s = s_\text{ex} + s_\text{in},$$

where the subscripts ex and in denote the extrinsic and intrinsic contributions, respectively.

To understand how domain structures and domain-wall motions are influenced by different processing conditions and dopants so that the material properties can be better tailored, one needs to quantitatively describe the changes of $\varepsilon_\text{ex}, \varepsilon_\text{in}, d_\text{ex}, d_\text{in}, s_\text{ex}, s_\text{in}$ with the processing conditions and dopants. That is, to distinguish the intrinsic and extrinsic contributions from the experimental data which usually contain both parts. Currently, two methods are commonly used in separating the extrinsic properties and intrinsic properties in ceramics: One is based on the frequency dispersion characteristics of the dielectric constant and the other is based on the properties measured near 0 K temperature. Since dielectric dispersion only describes the dielectric property of a material, it cannot provide information on the piezoelectric responses from different parts and the difference between 180° domain-wall response and non-180° domain-wall response. While the results derived from the second method are only related to the material properties at near 0 K and may not be directly related to the material properties at higher temperatures.

In this article, we introduce a new experimental methodology which can directly and quantitatively determine the domain-wall and intrinsic contributions to the material properties and their temperature dependence. Using this method, the piezoelectric and dielectric responses from both the intrinsic and domain-wall contributions were investigated for both doped and pure PZT ceramics near the morphotropic phase boundary in the temperature range from 10 to 300 K. The basic principle of this method is that in contrast to the intrinsic response where any polarization change will be accompanied by a change in the unit-cell volume, the polarization change induced by domain-wall motion will not cause volume changes. As a consequence, the domain-wall motion will not contribute to the hydrostatic response of a material and the change in the piezoelectric hydrostatic coefficient $d_0$ will not be related to the response from domain walls; therefore, $d_0$ provides a very sensitive means to separate the intrinsic and extrinsic material responses. By combining these results with the data measured near 0 K, we can get the temperature dependence of the extrinsic response and intrinsic response of
these PZT samples. In addition, making use of both dielectric and piezoelectric responses, one is able to gain information on the change of domain-wall responses of 180° type and non-180° type as the processing conditions or dopants are varied.

II. EXPERIMENTS

The piezoelectric constants \( d_{33} \) and \( d_{31} \), dielectric constant \( \varepsilon_{33} \), and remanent polarization \( P_r \) were characterized for pure PZT at the composition near the morphotropic phase boundary (PZT 52/48), and a soft PZT in the temperature range from 10 to 300 K. The PZT 52/48 ceramic samples were made through the standard solid-state processing. The samples were poled at an electric field of 50 kV/cm and a temperature of 375 K for 5 min. All the samples were aged for more than 1 week at room temperature before any measurement. The soft PZT ceramic samples were purchased from Piezo Kinetics, Inc. (Bellefonte, PA 16823) and were poled by the manufacturer.

The piezoelectric constants \( d_{33} \) and \( d_{31} \) were acquired through the resonance technique using a HP impedance analyzer (HP 4194A) for bar-shaped samples and the resonance frequencies were around 150 kHz. These constants were also measured at room temperature by a laser dilatometer. The results from the two measurements were in good agreement. The temperature regulation for the resonance experiment was provided by a helium closed-cycle refrigerator (APD Cryogenics, Model HZC-2).

The dielectric constant measurement was carried out using a HP multifrequency RLC meter (HP 4274A) and the temperature dependence of the remanent polarization \( P_r \) was obtained by combining the data acquired using the Byer-Roundy technique and from polarization hysteresis loop measurements. Since the ferroelectric-paraelectric transition temperature (Curie temperature) for these samples is far above the upper operation temperature for the setup which is at 500 K, the Byer-Roundy technique cannot provide the absolute value of the remanent polarization of the samples. To establish the absolute scale of the remanent polarization, the polarization hysteresis loop was measured at room temperature using a modified Sawyer-Tower circuit. A homemade temperature chamber was used to regulate the temperature for the polarization measurement. The temperature range of the measurement was from 100 to 470 K for PZT-500 and 100 to 340 K for PZT 52/48. In all experiments, the sample thickness was about 1 mm and the sample area was about 5 \( \times \) 5 mm\(^2\). The electrodes were made by sputtering gold on both surfaces of the samples.

III. RESULTS AND DISCUSSION

A. Temperature dependence of the piezoelectric constants

Shown in Figs. 1(a) and 1(b) is the temperature dependence of the piezoelectric constants \( d_{33} \) and \( d_{31} \) for PZT 52/48 and PZT-500 samples, respectively. For PZT 52/48, as the temperature increases from 10 K to room temperature (300 K), \( d_{33} \) increases about two and a half times (from about 105 to 245 pC/N). In the same temperature range, \( d_{31} \) has about a threefold increase (from about 40 to 114 pC/N). From the relation \( d_{33}=d_{33}+2d_{31} \), \( d_3 \) can be determined in the same temperature range and clearly, unlike \( d_{33} \) and \( d_{31} \), \( d_3 \) does not increase with temperature. Instead, from low temperature to room temperature, \( d_3 \) exhibits a slight decrease from about 24 to 20 pC/N, which is shown in Fig. 1(a). The data for \( d_3 \) in Fig. 1(a) also shows larger scattering than those of \( d_{33} \) and \( d_{31} \). This is understandable since both \( d_{33} \) and \( d_{31} \) are much larger than \( d_3 \), any small data scattering in \( d_{33} \) and \( d_{31} \) will induce a relative large scattering in \( d_3 \) when it is obtained by the difference between \( d_{33} \) and \( d_{31} \). In spite of that, the data clearly shows that \( d_3 \) has a much smaller temperature variation compared with both \( d_{33} \) and \( d_{31} \).

Similarly, for PZT-500, in the temperature range from 15 K to room temperature, \( d_{33} \) increases from about 132 to 360 pC/N and \( -d_{31} \) from 54 to 170 pC/N, while \( d_3 \) stays almost a constant around 23 pC/N in the same temperature range, as shown in Fig. 2. By relating this behavior to the discussions above, one can immediately draw the conclusion that in both pure and doped PZT ceramics, the large change in the piezoelectric activity (\( d_{33} \) and \( d_{31} \)) in this temperature range is caused by the extrinsic contribution, most likely by the non-180° domain-wall motions.

B. Temperature dependence of the dielectric constant and remanent polarization

In Fig. 2, the temperature dependence of \( \varepsilon_{33} \) for both PZT 52/48 and PZT-500 is plotted from 15 to 300 K. For
PZT 52/48, except for a broad anomaly at a temperature near 260 K, $e_{33}$ shows a large increase, from about 370 at 15 K to near 1200 at room temperature, which is a more than threefold increase. For PZT-500, $e_{33}$ is 375 at 15 K and increases to 1800 at room temperature. Therefore, the dielectric constants of the two PZT materials are almost the same at temperatures near 0 K. This is consistent with an earlier experimental result in which all the dielectric constants measured from PZTs with different dopants converged to a common value as the temperature approached 0 K. In contrast, at a temperature near 0 K, the piezoelectric constants for the two materials are not the same, which is probably caused by different degree of poling and different distribution of polarization about the poling direction in the materials. As is shown later, the remanent polarization of PZT-500 is higher than that of PZT 52/48. Apparently, dopants in PZT-500 facilitate the domain-wall movement and increase the degree of poling.

The piezoelectric response in a single-domain material can be viewed as polarization-biased electrostriction. Hence, the intrinsic piezoelectric and dielectric response are related through the electrostrictive coefficient $Q_f$ and the remanent polarization $P_r$,

$$d_{33} = 2\epsilon_{33}e_{33}Q_fP_r, \quad (2a)$$

$$d_{31} = 2\epsilon_{33}e_{31}Q_fP_r, \quad (2b)$$

and

$$d_{33} = 2\epsilon_{33}e_{33}Q_fP_r, \quad (2c)$$

where $\epsilon_s$ is the vacuum permittivity. These relations are derived from single-domain materials and should be valid for ceramics where the quantities in Eq. (2) are the averaged ones. Although the piezoelectric constants $d_{ij}$ vary widely as the composition or temperature changes, the polarization-related electrostrictive coefficients $Q_f$ hardly change with composition and temperature in PZT ceramics. Therefore, once the temperature dependence of $P_r$ is determined, the temperature dependence of the intrinsic dielectric response can be evaluated through Eq. (2c). Similarly, $d_{33}$ and $d_{31}$ from the intrinsic contribution can also be determined from Eqs. (2a) and (2b).

For the two PZTs, the remanent polarization $P_r$ as a function of temperature is shown in Fig. 3. Since the lowest temperature measured for the $P_r$ was at 100 K, the data were fitted using a polynomial and the low-temperature (0 K) $P_r$ was extrapolated from the fitting. As can be seen from Fig. 3, the $P_r$ is a smooth function of temperature and from the theoretical consideration, one does not expect any irregular changes in $P_r$ as the temperature is lowered, which justifies the extrapolation. At temperatures near and above room temperature, there is a small irregular change in the $P_r$ for PZT 52/48. This is likely caused by the internal stress field in the material, which increasingly realigns the domain as the temperature is raised. Hence, for PZT 52/48 the higher-temperature data are not plotted here.

C. Discussion

From the results presented in Secs. III A, and III B, the temperature dependence of the piezoelectric and dielectric constants from both the intrinsic and domain-wall contributions can be determined. Assuming at 0 K, $d_{11}$ and $e_{33}$ are from the intrinsic contribution, $Q_{11}$, $Q_{12}$, and $Q_{33}$ for the PZT ceramics are calculated using Eq. (2), and the results (listed in Table 1) are close to those of an earlier experimental result. In the calculation, the data of $d_{11}$ and $e_{33}$ at 0 K are extrapolated from the higher-temperature data and are very close to those measured at 15 K. Making use of Eq. (2), the temperature dependence of the dielectric constant $e_{33}$ and piezoelectric constants $d_{11}$ and $d_{33}$ from the intrinsic contribution are calculated and they are shown in Figs. 4 and 5 for the dielectric constant and the piezoelectric constants, respectively. In all these calculations we as-

<table>
<thead>
<tr>
<th>TABLE I. The electrostrictive coefficients for PZT-500 and PZT 52/48 ceramics used in this experiment.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{11}$ (mC/cm²)</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>PZT-500</td>
</tr>
<tr>
<td>PZT 52/48</td>
</tr>
</tbody>
</table>
hat the electrostrictive coefficients $Q_{ij}$ were inde-

of temperature. Clearly, in the temperature range
there is very little increase in the intrinsic dielectric
ity. For PZT 52/48, it stays at about 300 in this
ature range and for PZT-500, it increases slightly
perature from 350 at 0 K to 430 at 300 K. This is

it with the experimental results from Bottger and
3d from Kersten and Schmidt on PZT ceramics, in
the low-frequency dielectric constant $\varepsilon_{33}$ showed a
change with temperature, while at frequencies above
lectric relaxation peak (near 1 GHz) $\varepsilon_{33}$ was nearly
ant of about 400 at temperatures below 300 K for
2/48. Since the dielectric relaxation at frequency
GHz is believed to be due to the relaxation from
walls, at frequencies above that one expects that
main-wall contribution will die out and the major
bution to the dielectric response will only be the in-
p:art. In addition, $\varepsilon_{33}$ value of about 400 is almost
me as what we observed here at temperatures near 0
herefore, in spite of different techniques used, the two
measurements yield almost the identical results. Be-
that, the dielectric constants measured from single-
samples of PZT also stayed almost constant at low
atures.12

The results presented here provide direct evidence that
om temperature, domain walls make major contribu-
to the dielectric and piezoelectric responses of PZT
ials. This is consistent with the theoretical prediction
Landau–Devonshire theory.4 At room temperature
trinsic dielectric and piezoelectric contributions are
than 25% and about 37% of the total responses for
500, and 30% and $\frac{1}{2}$ for PZT 52/48.

In PZT, there exist two groups of domain walls: 180°
wall and non-180° wall. A major difference between these
two groups of walls is that 180° walls are not ferroelastic
active, while non-180° walls are ferroelastic active. As a
result, 180° wall motion will affect only the dielectric prop-
and non-180° wall will affect both dielectric and piezo-
electric properties. Hence, when one discusses domain-wall
contributions to the material responses, it is important to
know which kind of wall is active under weak driving field
because by enhancing only the non-180° wall activity one
can greatly improve the electromechanical coupling factor
of the material, and on the other hand, by enhancing only
the 180° wall activity, the dielectric response of the mate-
rial can be improved significantly without introducing
large dielectric losses, which are mostly caused by non-180°
wall motions.13 Currently, it seems to be widely believed
that for PZT and other ferroelectrics with perovskite struc-
ture, under weak external driving fields, the major part of
the domain-wall response is from non-180° walls and 180°
walls are almost idle. The reason is that 180° wall width is
much narrower (probably on the order of one unit cell) in
comparison with non-180° walls,14,15 which implies that
there is a much steeper potential well for 180° walls; there-
fore, a weak external field may not be able to induce sub-
stantial changes in the 180° wall structure. Experimentally,
there was no direct evidence to prove or disprove this;
however, the results presented here may not be consistent
with the idea that 180° walls in PZT ceramics are idle.

From the results presented above, at room temperature,
the extrinsic contribution to the dielectric constant is larger
than that to the piezoelectric constant for PZT-500, while

![Graph](image-url)

**FIG. 4.** The calculated intrinsic (O) and extrinsic (■) dielectric con-
tant for (a) PZT-500 and (b) PZT 52/48. For the comparison, the total
dielectric constant (□) measured is also presented.

![Graph](image-url)

**FIG. 5.** The calculated intrinsic and extrinsic piezoelectric constants
for (a) PZT-500, and (b) PZT 52/48: open circles are intrinsic $d_{33}$,
solid circles intrinsic $d_{33}$, open squares extrinsic $d_{33}$, and solid squares
extrinsic $d_{33}$.
for PZT 52/48 they are almost the same (the ratio $d_{31}^P/d_{31}^K$ and $e_{31}^P/e_{31}^K$). That is, increased domain-wall activities in PZT-500 raise the dielectric constant more than the piezoelectric constant. The large increase in $d_{31}$ is apparently due to the increased activity in non-180° walls in PZT-500; however, the disproportionate increase in $e_{31}$ may reflect the fact that there are substantial increases in the 180° wall activity, too. In addition, as illustrated in Fig. 6, the extrinsic piezoelectric and dielectric contributions show a similar temperature dependence for both PZT-500 and PZT 52/48; however, the ratio of $d_{31}$ to $e_{31}$ ($d_{31}/e_{31}$) for the two materials is quite different. At room temperature, this ratio is 0.2 pC/N for PZT 52/48 and less than 0.15 pC/N for PZT-500. In other words, on average, corresponding to the same polarization change, the domain-wall motions will produce much less piezoelectric response in PZT-500 than in PZT 52/48 even though the poling level in PZT-500 is higher. From the analysis by Haun, Arlt, Dederichs, and Herbiet, Zhang et al. and the earlier experimental results, which showed that as the poling level increases this ratio should increase if there are only non-180° domain walls active, the phenomenon observed here strongly suggests that there is a substantial increase in 180° wall activity in PZT-500, which raises the dielectric constant of the material while keeping the piezoelectric constant unchanged; therefore, both the non-180° wall and 180° wall should be active in PZT-500.

We would like to emphasize that the notion introduced here that the domain-wall motions do not contribute to the volume change may not be applicable when the wall motions are related to the polarization switch, which may introduce significant local stress and result in some volume change. This kind of volume change may provide information on the local stress distribution and themselves detailed studies. In addition, for ceramic materials like pores which can change the local stress path cause volume changes as the wall moves. How well-fabricated materials, this probability is very small and should not significantly alter the conclusions presented in this article. The consistency between the results of earlier experimental results confirms this point.

IV. SUMMARY

In this article, we presented a new method, based on the notion that domain-wall induced by weak external fields will not contribute to the hydrostatic piezoelectric response, to directly evaluate the intrinsic and domain-wall contributions in a piezoceramic sample. Using this method, the domain-wall contributions to the piezoelectric and dielectric responses and their temperature dependence for PZT-500 ceramics are evaluated quantitatively. The data show that at temperatures above 300 K the large change in the dielectric and piezoelectric properties with temperature is from the domain-wall contribution. The results confirm that most of the piezoelectric responses at room temperature for materials studied are from the domain-wall contributions; data also show that in PZT-500, both 180° walls are most likely active under weak external fields.

The experimental methods presented in this article can be extended to a wide range of materials and temperature range to study how various external fields change the extrinsic and intrinsic contributions to their temperature-dependence behavior. In conclusion, the analysis similar to that employed by co-workers and the information of the polar contribution in a material, one can quantitatively how the 180° wall and non-180° wall activities vary under various conditions.

ACKNOWLEDGMENTS

The authors wish to thank Dr. R. E. Newnham, A. Randall, and Dr. Wenwu Cao for critical reading of the manuscript and suggestions concerning this work. This work was supported by the Office of Naval Research.

---

J. Zhang, S. J. Jang, and L. E. Cross, J. Appl. Phys. 63, 2807
F. Jonas and G. Shirane, Ferroelectric Crystals (Dover, New York,
1993).
Q. M. Zhang, W. Y. Pan, S. J. Jang, and L. E. Cross, J. Appl. Phys. 64,
6445 (1988).
DOMIAN SWITCHING AND MICROCRACKING  
DURING POLING OF LEAD ZIRCONATE  
TITANATE CERAMICS  

E. C. SUBBARAO,† V. SRIKANTH, W. CAO and L. E. CROSS  
Materials Research Laboratory, The Pennsylvania State University,  
University Park, PA 16802-4800 USA  
(Received December 17, 1992)  

The application of a DC electric field (poling) to a ferroelectric lead zirconate titanate (PZT) ceramic aligns domains in the field direction. The non 180°-domain switches involve mechanical deformations, which are detected as acoustic emission signals. Concurrent with AE signals, electrical current pulses arise from domain reorientations. When the poling field is large and domain switches are extensive, the resulting deformations, under the constraint of neighboring domains or grains, may exceed the elastic limit and cause microcracking. The onset and propagation of microcracking during poling of PZT is signalled by the appearance of continuous AE signals, unaccompanied by current pulses, in contrast to intermittent AE signals accompanied by corresponding current pulses during domain switching. The onset and extent of microcracking established by this method is confirmed by scanning electron micrographs and decrease in the value of piezoelectric coefficient (d33) and mechanical quality factor (Q_m). The amplitude of AE signals due to domain switches are spread widely, while that of AE signals caused by microcracking occur in a narrow range around 50 db.  

Keywords: Acoustic emission, PZT, domain switching, microcracking  

INTRODUCTION  

The polar direction of ferroelectric crystals can be changed by an applied electric field. Due to the existence of many variants in the low temperature ferroelectric phase, a ceramic (polycrystalline) sample contains many randomly oriented regions of uniform polarization, called domains, upon transforming from the high temperature non-ferroelectric (paraelectric) phase, thus eliminating net polarization. For many practical applications such as a piezoelectric device, the ceramic must be poled (i.e., subjected to a DC electric field) to align the polar axes as fully as possible in the field direction so that the ceramic acquires a net (non-zero) polarization. The fact that only partial alignment of domains is possible in a ceramic is reflected in the rounded D-E hysteresis loop compared to a square loop of a ferroelectric single crystal, and in a spontaneous polarization (P_s) value of about 8 μC/cm² for a ceramic versus 26 μC/cm² for a single crystal of BaTiO₃.  

Associated with the spontaneous polarization (P_s), there is a spontaneous strain (e_s), which is proportional to P_s². This strain is a consequence of the fact that the polar axis is elongated compared to other crystallographic axes. When the ferroelectric domain switches by 180°, there is no strain change and hence does not affect its neighbors. On the other hand, domain reorientations by 90° cause max-
imum strain change, leading to intergranular stresses (Figure 1). Thus, domain switching during the poling process proceeds to minimize the total energy and accommodate the elastic deformation. For example, only 12% of the domains switch by 90° upon application of an electric field to ceramic BaTiO$_3$ and half of them revert back on removal of the field. This constraint by surrounding grains does not affect domain switches by 180°, since no strain is involved in this case.

Extensive studies on BaTiO$_3$ single crystals have shown that the domain switching is a nucleation and growth process. It starts with a wedge shaped domain of the new polarization state, proceed with a fast forward growth rate and slow sidewise growth rate, finally the wedge taking the shape of a stripe across the grain or crystal. Ultimately the two 180° domain walls move sidewise to widen the new polar region to complete the switching process.

Lead zirconate titanate (PZT) is a solid solution of ferroelectric lead titanate (PbTiO$_3$) and antiferroelectric lead zirconate (PbZrO$_3$). A composition at 48% PbTiO$_3$—52% PbZrO$_3$ exhibits a morphotropic phase boundary (MPB), separating a tetragonal PbTiO$_3$-rich and a rhombohedral PbZrO$_3$-rich ferroelectric phases. Many properties (dielectric constant, piezoelectric coefficients, etc.) peak at this

---

**FIGURE 1** Schematic of domain structure of a ferroelectric ceramic before and after poling.
SWITCHING AND MICROCRACKING OF PZT DURING POLING 273

FIGURE 2  Schematic of experimental arrangement used for simultaneous detection of acoustic emission and current pulses during poling of a ferroelectric ceramic.

FIGURE 3  Acoustic emission count rate (a) and total AE counts (b) as a PZT ceramic (sample C) is poled to successively higher fields. The current pulses were observed at times indicated by triangles in this and succeeding figures (4 and 5).

TABLE I
Microcracking and electrical properties of poled PZT

<table>
<thead>
<tr>
<th>Sample</th>
<th>Remarks of Poling and Microcracking</th>
<th>$d_{33}$ (10$^{-12}$ C/N)</th>
<th>Qm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Poled but no onset of microcracking</td>
<td>333</td>
<td>89</td>
</tr>
<tr>
<td>SS</td>
<td>Poled till microcracking barely starts</td>
<td>350</td>
<td>65</td>
</tr>
<tr>
<td>B</td>
<td>Poled till microcracking starts</td>
<td>200</td>
<td>49</td>
</tr>
<tr>
<td>E</td>
<td>Poled till extensive microcracking occurred</td>
<td>119</td>
<td></td>
</tr>
</tbody>
</table>
composition, presumably due to the increase in the number of energetically degenerate states which makes the switching of domains easier under the influence of an electric field. The higher Curie temperature (360°C vs 120°C), remanent polarization (47 vs 8 μC/cm²) and piezoelectric coefficients make PZT far superior to BaTiO₃ for piezoelectric applications. In fact, PZT is the leading electromechanical transducer material for over a quarter century and therefore is chosen for the present study.

The effect of electric field on the extent of domain reorientations in PZT is somewhat different in the tetragonal and rhombohedral phase regions. In tetragonal PZT, it is estimated that 66% of all dipoles instead of the initial 16% become aligned within the sextant around the poling direction. On the other hand, dipoles switch by 71°, 109° and 180° in the rhombohedral phase. For PZT modified by Nb⁺ ion addition, it is suggested that 74% of the dipoles are present in the octant around the policy direction. The larger P₀ value and the higher degree of domain orientation in PZT make the remanent polarization of PZT substantially higher than that of BaTiO₃. The improvement in planar coupling coefficient (kₚ) of PZT as a function of poling conditions (field, time and temperature) has been studied by Chiang et al.¹⁰

As already pointed out, the non-180° domain switches involve strain changes and hence demand the coordination of neighbor domains. The microdeformations arising from the domain wall movements, though small in magnitude, are detectable by sensitive acoustic emission methods.¹¹,¹² The poling effects on acoustic velocity and attenuation in poled and unpoled PZT ceramics were studied as a function of temperature and frequency.¹³ Application of a large electric field (or mechanical stress) can lead to microcracking, due to internal stresses.¹⁴ Electrically induced microcracking in PZT has been shown to be dependent on grain size and tetragonality¹⁵,¹⁶,¹⁷,¹⁸,¹⁹ and is detected by microscopy and dielectric measurements. The external parameters influencing the extent of microcracking are the poling conditions (field, time and temperature).¹⁹,²¹ Microcracking results in a deterio-
FIGURE 5  Same as in Figure 3 for sample SS but the electric field is maintained even after the onset of continuous AE counts, signifying beginning of microcracking. The regime just before [Figures (c) and (d)] and just after [Figures (e) and (f)] the onset of microcracking is shown in detail.
ration of electrical and mechanical properties of the ceramic and hence should be minimized if not eliminated. Uchino et al. have studied AE signals in piezoelectric and electrostrictive actuators subjected to bipolar and unipolar electric fields and also after repeated cycles of thermal shocking. They found that the unipolar field does not lead to acoustic emission, unless the samples have suffered mechanical damage as by thermal shocking.

The acoustic emission technique has recently been applied to the study of domain switching, as well as the occurrence and recombination of microcracks in ferroelectric PbTiO$_3$ ceramics as it is heated and cooled.

From the above discussion it is clear that poling is a critical process for achieving optimum piezoelectric properties of a ferroelectric ceramic. The domain reorientations which give rise to enhanced piezoelectric behavior also give rise to mechanical stresses, which can lead to microcracking, if the induced stresses exceed the elastic limit of the material. Therefore poling should be carried out to obtain maximum domain reorientation, but without the onset of the microcracking process, provided there is a simple, reliable means to distinguish the two deformation processes.

The purpose of the present study is to delineate the microdeformations accompanying domain switching from those due to microcracking during poling of PZT ceramics, as a contribution toward a better understanding and optimization of the poling process. Simultaneous detection of acoustic emission and electrical current pulses were employed in the study and the results are substantiated by scanning electron micrographs and electrical property measurements.

EXPERIMENTAL

Ceramic lead zirconate titanate (PZT) composition (52% PbZrO$_3$, 48% PbTiO$_3$) at the morphotropic phase boundary (MPB) was prepared by conventional method.
Stoichiometric proportions of reagent grade oxides (PbO from Hammond Lead Products, Potterstown, Pennsylvania, ZrO$_2$ from Harshaw Chemical Co., Cleveland, Ohio, and TiO$_2$ from J. T. Baker Chemical Co., Phillipsburg, New Jersey) were mixed in a polyethylene bottle for 12 hours using ethyl alcohol as wetting agent and $\frac{1}{4}$" diameter zirconia balls as grinding media. Excess lead oxide (0.5 wt%)
was added to compensate for lead loss during calcination. The milled powder was
dried at 80°C for 24 hours and calcined at 900°C for 24 hours. X-ray diffraction
examination confirmed the formation of the perovskite phase. After mixing with
2% polyvinyl alcohol binder, the powder was pressed into pellets at 105 MPa. The
binder was removed by heating at 350°C for three hours and 550°C for three hours.
The pellets were sintered at 1250°C for five hours in closed crucibles in PbO
atmosphere, at a rate of 5°C/min during heating and 3°C/min during cooling.

Sintered PZT ceramic discs were polished to obtain two parallel faces, which
were then electrode with sputtered gold. The electrode disc is located in a suitable
holder and immersed in a silicone oil bath at 50°C. High DC field is applied in a
stepwise fashion from a power supply (Tred COR-A-TROL), while an alumina
rod serving as a wave guide rests on the ceramic disc. A transducer is mounted at
the other end of the wave guide. Acoustic emission signals are collected, filtered
and analyzed by appropriate electronic circuitry and displayed as counts or count
rate as a function of time (Locan 320 System from Physical Acoustics Corp.). The
schematic of the experimental arrangement is shown in Figure 2. A microammeter
is placed in the voltage input lead of the poling circuit, to detect current pulses
arising from domain switching, superimposed on leakage current.

After various stages of poling, the samples were examined for piezoelectric
coefficient, $d_{33}$, using a Berlincourt $d_{33}$ meter, for mechanical quality factor, $Q_m$,
using IRE standard method, and for microstructure and microcracks from scanning
electron micrographs.

RESULTS AND DISCUSSION

A PZT ceramic sample (C) was poled in successive steps of increasing DC field at
intervals of 100 sec, while acoustic emission signals and current pulses were recorded.
SWITCHING AND MICROCRACKING OF PZT DURING POLING

(Figure 3). No AE signals were detected until a poling field of 41 kV/cm was applied (though a few current pulses were observed as soon as poling field ≥ 16 kV/cm was applied). The current pulses (2–12 mA) were superimposed on a steady leakage current of 0.5 to 3 mA. It can be seen that a substantial number of AE signals occur as soon as the poling field is increased, though a smaller number of AE counts were recorded at irregular time intervals during the application of a fixed poling field, in agreement with earlier reports.12 Everytime AE counts occurred, there were accompanying current pulses. Evidently both the AE and current pulses arise from domain reorientations. After 800 sec, the field was reduced in steps to zero at 1200 sec. While no AE counts were detected till the applied field was dropped to zero, AE counts were indeed recorded nearly 60 sec after removal of the field and these AE events may reflect domain reversals. The piezoelectric coefficient, $d_{33}$, of this sample was $333 \pm 7 \times 10^{-12}$ C/N. The scanning electron micrograph of this sample [Figure 7(b)] is similar to that of a virgin sample [Figure 7(a)] and does not show clear microcracking, though grain boundaries become more obvious. The sample has a mechanical quality factor ($Q_m$) of 89 (Table 1).

An example of a sample (B) which was subjected to a stepwise increase of the poling field till microcracking just starts, as evidenced by continuous AE counts instead of intermittent AE signals, is shown in Figure 4. The field was quickly reduced to zero soon after the appearance of continuous AE counts. While current pulses were observed corresponding to the intermittent AE signals, no current pulses were observed during the continuous occurrence of AE counts. The $d_{33}$ value of this sample is lower at $-200 \times 10^{-12}$ C/N and the scanning electron micrograph does not show any significant microcracking [Figure 7(c)].

These results were confirmed with another PZT ceramic sample (SS) which shows a large number of AE counts as soon as a poling field of 8 kV/cm is applied (poling temperature 50°C), but no further AE counts till the field applied was 25 kV/cm at 300 sec (Figure 5). There were intermittent AE signals as the poling field was increased stepwise from 25 kV/cm to about 37 kV/cm at 600 sec [Figures 5(c) and (d)]. In this regime AE counts were invariably accompanied by current pulses up to 60 mA. As soon as continuous AE counts started appearing at about 620 sec, the poling field was turned off. The AE counts continued which may indicate domain reversals [Figures 5(e) and (f)]. Since the microcracking process was quickly interrupted, the $d_{33}$ was nearly unaffected (350).

The stepwise poling of another sample (E) was continued beyond the occurrence of intermittent AE signals accompanied by associated current pulses (of up to ~40 mA) to the regime where AE counts occur continuously but no current pulses are detected (Figure 6). We believe that the onset of continuous AE counts must signify the beginning of microcracking due to excessive mechanical stresses generated by extensive domain switching. The poling field was reduced to zero at 480 sec but AE counts persisted for sometime (at least up to 640 sec) suggesting further microcracking or propagation of cracks till adequate stress relief is attained. Due to the extensive microcracking, the $d_{33}$ value ($119 \times 10^{-12}$ C/N) and $Q_m$ were severely affected (Table 1). The scanning electron micrograph of this sample [Figure 7(d)] shows extensive intergranular cracking.

The threshold amplitude for the AE experiments was set at 45 db. The distribution of the magnitude of the detected AE signals for three samples is given in
Figure 8. It can be seen that the number of hits increases and the amplitude spread decreases as the extent of microcracking changes from none to minor to extensive. When acoustic emission signals arise from domain reorientations, their amplitude reflects a wide range of accompanying microdeformations, depending upon the original domain orientations and the magnitude of the poling field [Figure 8(a)]. On the other hand, the initiation and propagation of microcracking is driven by stress concentrations in the ceramic and the corresponding AE signals occur in a narrow amplitude range [Figure 8(c)]. The case where domain reorientations and initial microcracking occur simultaneously represents an intermediate situation [Figure 8(b)]. This is in agreement with the observation of Pan and Cao,13 who state that the AE signal amplitude is maximal at the polarization switching and minimal when the poling is established. Iwasaki and Izumi11 also find that the peak of AE counts occurs at lower amplitude range and the spread of amplitude narrow as the poling field is increased.

CONCLUSIONS

Application of a DC field to ferroelectric ceramics (poling) causes domain reorientations in the field direction. All but the 180° domain switches involve dimensional changes leading to mechanical stresses due to the constraint of the neighboring grains in a ceramic. When the stresses exceed the bonding strength between grains, the ceramic suffers microcracking, resulting in deterioration of electrical (d_{33}, k_p, e, etc.) and mechanical (Q_M, strength, etc.) properties. The present study established that concurrent AE counts and current pulses are observed when domain switches take place during poling. The onset and progress of microcracking is signalled by continuous AE counts but no accompanying current pulses. The delineation of domain switching from microcracking by this approach is corroborated by changes in electrical and mechanical properties and scanning electron micrographs and constitutes a simple, reliable, non-destructive in-situ means to control the poling process to achieve optimum piezoelectric properties in a ferroelectric ceramic.

ACKNOWLEDGEMENT

The authors are grateful to the Office of Naval Research for financial support.

REFERENCES

SWITCHING AND MICROCRACKING OF PZT DURING POLING