AD-A256 290

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 9/29/92	3. REPORT TYPE AND DATES COVERED April 1, 1991 to March 31, 1992

4. TITLE AND SUBTITLE

LONG TERM STABILITY IN THIN FILM FERROELECTRIC MEMORIES

5. FUNDING NUMBERS

Grant N00014-91-J-1755

6. AUTHOR(S)

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533644 Annual

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

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10. SPONSORING/MONITORING AGENCY REPORT NUMBER

N/A

11. SUPPLEMENTARY NOTES

92-26313

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unlimited
Copies available upon request

TRIBUTION CODE

N/A

13. ABSTRACT (Maximum 200 words)

The mechanism and control of the fatigue of remanent polarization in thin film ferroelectric memories is being investigated. The predicted detrimental effect of acceptor-dopants and beneficial effect of donor-dopants has been confirmed in thinned samples of $BaTiO_3$. A similar but reduced effect has been observed in thin films of PZT, and the possible effect of PbO-loss on reducing the beneficial effect of donor dopants is being investigated. It has become apparent that under high temperature equilibration conditions for perovskite titanates, the concentration of trapped holes exceeds that of free holes, contrary to earlier expectations. This means that the amount of nonstoichiometry and of trapped charge is considerably higher than previously thought. This is being explored with bulk samples of PZT. Reported problems with retention of polarization in PZT films integrated into circuits, i.e. the nonvolatile feature of the memories, has led to a new program to determine the conditions to which PZT films can be exposed without loss of essential properties. Direct observation of the motion of ferroelectric domains by transmission electron microscopy has been achieved, and a new field stage is being designed. Thin films of $Pb(Mn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (90% PMN) have been prepared with greater than 99% perovskite phase.

14. SUBJECT TERMS

Thin-films   Ferroelectrics   Defects
Fatigue   PZT

15. NUMBER OF PAGES
36

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UNLIMITED

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I. SUMMARY

A. Goals

The main goal of this project is to apply the concepts of defect chemistry to improvement of the switching stability of thin-film ferroelectric memories incorporated into Si and GaAs devices. These memories are based on the switching of the direction of polarization in a ferroelectric film, and are intended to be nonvolatile. The main material of choice is $Pb(Zr_{1-x}Ti_x)O_3$, PZT, and attention has been focused on this material with $x = 0.50$. In excess of 10^{12} switching cycles are desired; however, PZT devices typically begin to degrade after 10^8-10^{10} cycles. The degradation is in the form of a decrease in the amount of switched charge, until the sense circuit can no longer determine the polarization direction. The premise of this project is that the degradation results from an accumulative migration of charged lattice defects due to the extremely high switching fields, e.g. 5×10^5 v/cm. The most obvious candidate for the mobile species is the oxygen vacancy, which has been identified as being responsible for the degradation of the leakage resistance in capacitors based on similar materials. Thus our primary goal is to reduce the concentration of oxygen vacancies by control of the composition ("doping") and processing conditions. Another major goal is to observe ferroelectric domain motion directly in the TEM using a specially designed field stage, and to determine the effects of composition, microstructure, and processing on that motion. A secondary goal has been to prepare thin films of $Pb(Mn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$, PMN-PT, with minimal amounts of the undesirable pyrochlore phase, and to optimize their electrical properties. Such films are of interest as gate dielectrics because of their high dielectric constants.

B. New Developments

Since the beginning of this project, a little over a year ago, there have been several changes in the status of the field, and this has suggested some additional goals:

> As attempts have been made to integrate the PZT thin films into actual devices, the remanent polarization has been found to be unstable, i.e. the nonvolatile feature is lost.

> The development of nonfatiguing ferroelectric films has been claimed, but the identity of the material has not been disclosed.

> New aspects of the defect chemistry of PZT have been discovered.

There are several hypotheses about the cause of the loss of nonvolatility. Our own best guess is that processing of the devices subsequent to the deposition of the PZT films involves chemical environments that are detrimental to the properties of the

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films. PZT capacitors not subjected to the subsequent processing steps do not suffer from this problem. The insertion of a sensitive new material into an existing processing scheme, without concern for the effects on that material, has not been successful. As a result, we are initiating a program to determine the boundaries of the conditions to which the PZT films can be exposed without loss of their desirable properties.

A nonfatiguing ferroelectric thin film is obviously of great interest. We intend to study the properties of this material as soon as the composition is disclosed.

Two new aspects of the defect chemistry of PZT are under study. The predominance of trapped holes even under high temperature equilibrium conditions, as pointed out by Waser [1], means that the degree of nonstoichiometry is considerably larger than previously thought. This is of importance for all perovskite titanates, and implies that insulating material can be obtained for much more reducing conditions than previously predicted. The second aspect is the possibility that the predicted effect of donor doping on reducing the oxygen vacancy concentration may be negated by excessive loss of PbO. This is currently under study.

C. Achievements to Date

1. A system has been developed for the deposition of PZT thin films with variable composition and doping by the spin-on sol-gel process. Electrodes are deposited by cathodic sputtering. Electrical apparatus has been acquired and set up for the measurement of switching fatigue.

2. The fundamental premise of the effects of acceptor and donor dopants on the rate of switching fatigue has been demonstrated.

3. The basic defect chemistry of PZT has been studied and new aspects are being examined. It has been possible to separate the effects of the formation of both trapped and free holes under equilibrium conditions, by means of sealed-cell, constant-composition measurements. These results have confirmed the dominance of hole-trapping even under equilibrium conditions (up to 700°C). These concepts will be applied to other perovskite titanates with other support.

4. It has been realized that excessive loss of PbO during processing of PZT films can negate the ability of donor dopants to reduce the oxygen vacancy concentration. So far it has been determined that the donor dopant (La^{+3} substituted for Pb^{+2}) is effective if care is taken to avoid PbO-loss. Studies are underway to determine the effect of controlled amounts of PbO-loss.

5. The direct observation of domain motion in a TEM equipped with an electric field stage has been achieved, and video tapes are being acquired.

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6.   As a parallel project, carried out by a graduate student not supported by the DARPA/ONR program, we have been studying the preparation of PMN-PT films. Films with the composition 90PMN-10PT have been prepared at 750°C with perovskite phase contents as high as 98%.

D.   Plans for the Future

1. Fatigue Studies: The study of switching fatigue is being transferred from thinned, bulk $BaTiO_3$ to thin films of PZT prepared by the spin-on sol-gel technique. This involves an extensive experimental matrix with doping, equilibration conditions, and PbO activity as the primary variables. Particular attention will be paid to the possible interactions between donor-doping and PbO-loss.

2. Defect Chemistry: The study of the defect chemistry of PZT will continue in order to obtain a detailed understanding of the defect equilibria and interactions, and the conduction mechanisms. This will include an examination of the possible deleterious effects of PbO-loss on donor-doped PZT.

3.   A major new program will be initiated to determine the range of conditions to which PZT films can be exposed without harm to the properties that are essential for reliable, nonvolatile memories.   The retention of remanent polarization will be the primary focus, in response to reported serious difficulties in this area.

4.   New Materials: Any important new candidates as materials for ferroelectric thin films will receive parallel attention in terms of switching behavior and defect chemistry. This specifically includes the reported "nonfatiguing ferroelectric" whenever its identity is disclosed.

5. Observation of Domain Motion: We are now prepared to use the experience gained with the facility at AT&T Bell Laboratories to obtain our own field stage for installation in our TEM. Access to this existing facility has been extremely helpful in optimizing the design of our equipment. We will continue to collect videotapes of domain motion in materials prepared with different compositions. Of particular interest is the pronounced hysteresis observed in the switching behavior.
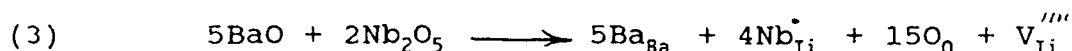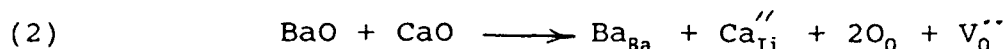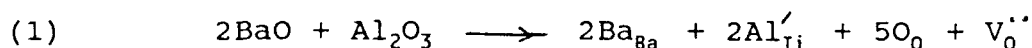
6.   In a separate but related project, we will continue to study the preparation of films in the PMN-PT system, and to characterize their electrical properties.

II. EXPERIMENTAL RESULTS

A. The Effects of Aliovalent Dopants on Switching Stability

It is proposed that the loss of remanent polarization after many switching cycles is due the migration of oxygen vacancies in the high applied switching fields. This is a direct transfer of the accepted model for the degradation of leakage resistance in multilayer ceramic capacitors. Therefore, it is expected that the rate of degradation of remanent polarization should be a function of the oxygen vacancy concentration in the dielectric film. As a first test of this assumption, thinned samples of doped and undoped ceramic $BaTiO_3$ have been subjected to repeated switching cycles. $BaTiO_3$ was tested initially because its defect chemistry is well understood, there is almost no variability in the Ba/Ti ratio and hence no defects from that source, and there are no volatile components. The samples were subjected to both unipolar pulses, and pulses of alternating polarities, with applied fields in the range of 20-30 kV/cm. These two techniques were found to give comparable results, as shown in Fig. 1.

The sample compositions were undoped, acceptor-doped (0.1% Al and 2% Ca), and donor-doped (3% Nb). The undoped material is known to contain a small excess of naturally-occurring acceptor impurities, such as Al, Fe, Mg, and Na (2,3). The incorporation reactions for the dopants, all of which are substituted for Ti, are as follows (4):

(1) $\qquad 2BaO + Al_2O_3 \longrightarrow 2Ba_{Ba} + 2Al'_{Ti} + 5O_O + V_O^{\cdot\cdot}$

(2) $\qquad BaO + CaO \longrightarrow Ba_{Ba} + Ca''_{Ti} + 2O_O + V_O^{\cdot\cdot}$

(3) $\qquad 5BaO + 2Nb_2O_5 \longrightarrow 5Ba_{Ba} + 4Nb^{\cdot}_{Ti} + 15O_O + V''''_{Ti}$

It should be noted that in the case of the Ca-doped sample, the composition was adjusted so that the Ca was forced to substitute for Ti, rather than for Ba where it would be charge-neutral. Ca substituted for Ti gives one of the most strongly acceptor-doped behaviors that has been observed (5).

For the acceptor-doped samples, the oxygen vacancy content is directly related to the acceptor concentration, and should correspond to $[V_O^{\cdot\cdot}] = 1/2[Al'_{Ti}]$ and $[V_O^{\cdot\cdot}] = [Ca''_{Ti}]$, respectively. For the donor-doped sample, the oxygen vacancy concentration will be suppressed through a mass-action relationship for intrinsic Schottky disorder.

The results of unipolar pulse tests on these samples are shown in Fig. 2. The heavily acceptor(Ca)-doped sample has degraded the most, and the donor-doped sample was by far the most stable. The undoped and lightly acceptor-doped samples fall between the extremes.

This confirmation of the expected effects of doping on a well-

characterized material indicates that the study is on the right path. The investigation is now proceeding with thin films of doped and undoped PZT.

The precise amount by which the oxygen vacancy content is reduced by donor-doping cannot be determined without accurate information on the mass-action constant for Schottky disorder. The power of this effect can be demonstrated by the following estimate, however. The reaction for the formation of Schottky disorder in $PbTiO_3$ is

$$(4) \qquad nil \rightleftharpoons V_{Pb}'' + V_{Ti}'''' + 3V_O^{\bullet\bullet}$$
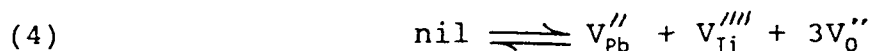
where nil refers to the perfect crystal. The mass-action expression is

$$(5) \qquad [V_{Pb}''][V_{Ti}''''][V_O^{\bullet\bullet}]^3 = K_s(T)$$

where $K_s(T)$ is the mass-action constant. For the ideal crystal, the concentrations of the vacancies are linked

$$(6) \qquad [V_{Pb}''] = [V_{Ti}''''] = 1/3[V_O^{\bullet\bullet}]$$

so that

$$(7) \qquad [V_O^{\bullet\bullet}] = (9K_s)^{1/5}$$

This would be the oxygen vacancy concentration in an ideally pure crystal, and dopant concentrations significantly less than this would have no effect on the defect concentrations. A reasonable estimate for this value at the sintering temperature would be 10^{-6} (1 ppm) based on formula units (6). The effect of the donor dopant can be estimated from the mass-action expression, the donor incorporation reaction, Eq.(3), and the approximate relationship

$$(8) \qquad [Nb_{Ti}^{\bullet}] = 4[V_{Ti}''''] = 4[V_{Pb}'']$$

to give

$$(9) \qquad [V_O^{\bullet\bullet}] = (16K_s)^{1/3}/[Nb_{Ti}]^{2/3}$$

The oxygen vacancy content should decrease with the 2/3 power of the donor concentration. The net effect is best seen graphically, and is shown in Fig. 3. Thus, relative to an ideally pure sample, a donor content of 1% would be expected to suppress the oxygen vacancy concentration by a factor of 10^4, while relative to a real sample with a net excess of 10^{-4} (100 ppm) naturally-occurring acceptors, the suppression would be by a factor of 10^6. Relative to a sample doped with 1% acceptor, the difference is a factor of 10^{10}. While only approximate, the effect of donor-doping is clearly very substantial.

B. The Interaction of Donor-Doping and the Loss of PbO

The treatment of donor-doping as outlined above is appropriate for

a model compound such as $BaTiO_3$, which has virtually no phase width in terms of Ba/Ti ratio, and which contains no volatile components. The same should be true of PZT if the PbO content is kept at the ideal level. However, because of the volatility of PbO, and the tolerance of PZT for a deficiency of Pb in the lattice (7), the situation may be quite different if appropriate care is not taken.

The effect of the incorporation of a donor oxide can be viewed as being due to its excess oxygen content relative to the component oxide it replaces, e.g. Nb_2O_5 substituted for $2TiO_2$. Eq. (3) is an example of what happens if the excess oxygen is retained in the crystal. This yields an insulating material with a suppressed oxygen vacancy content. If the excess oxygen is expelled from the crystal, as is the case for $BaTiO_3$ with donor contents less than 0.5%, it leaves behind an equivalent charge of electrons that give semiconducting properties

$$(10) \qquad 2BaO + Nb_2O_5 \longrightarrow 2Ba_{Ba} + 2Nb'_{Ti} + 6O_0 + 1/2O_2 + 2e'$$
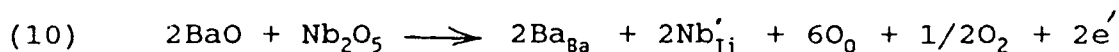
If the crystal already contains a large concentration of oxygen vacancies, due to acceptor-doping or to a loss of PbO

$$(11) \qquad Pb_{Pb} + O_0 \rightleftharpoons PbO + V''_{Pb} + V^{\cdot\cdot}_O$$
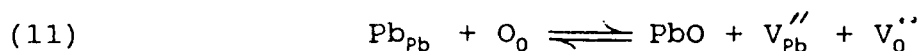
then the excess oxygen of the donor oxide can be retained in the crystal by occupying some of these vacancies, and no other defects need to be formed

$$(12) \qquad 2PbO + Nb_2O_5 + V^{\cdot\cdot}_O \longrightarrow 2Pb_{Pb} + 2Nb^{\cdot}_{Ti} + 7O_0$$
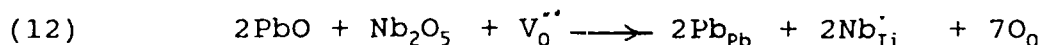
If the chemical equivalents of PbO lost exceed the amount of donor added, all of the excess oxygen of the donor oxide can be accommodated in the crystal lattice, and there will be oxygen vacancies left over. Thus if the crystal has lost 2% PbO, and is doped with 1% donor, the reduction in oxygen vacancy concentration will be only 25%, not the factor of 10^4-10^6 expected for the case of no loss of PbO. The lead vacancy, V''_{Pb}, can be viewed as an acceptor center, just like Ca''_{Ti}, and it can compensate an equivalent amount of donor impurities.

From the above analysis, it is clear that unless the loss of PbO is almost entirely avoided, donor-doping may have a negligible effect on the oxygen vacancy content. This is the price that must be paid for the use of a ferroelectric with a volatile component oxide. Thin films with a very large surface/volume ratio will be particularly susceptable to this problem. The crucial question is how much PbO is typically lost during exposure to the relatively moderate device processing temperatures of 600-700°C? Formulations with modest amounts of excess PbO may be adequate to avoid the problem. In any case, it is unlikely that device engineers will look kindly on the prospect of exposing their devices, covered with SiO_2 films, to PbO-rich atmospheres during processing.

The limits of the above problem clearly need investigation. A

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preliminary study was initiated this summer by Ms. Susan Schaffer-Smith, an undergraduate from Indiana University of Pennsylvania, supported by an NSF-funded summer undergraduate program through the Lehigh Chemistry Department. The experiments are being run on bulk powders and sintered samples of PLZT prepared with either great care to avoid loss of PbO, or with deliberate loss of PbO. The equilibrium conductivity is measured to look for the characteristic behavior of samples with excess donor or acceptor content. This behavior is based on the oxidation reaction that involves the filling of extrinsic oxygen vacancies

(13) $$V_0^{\cdot\cdot} + 1/2O_2 \rightleftharpoons O_0 + 2h^{\cdot}$$
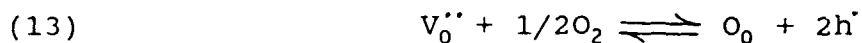
with the mass-action expression

(14) $$p^2/[V_0^{\cdot\cdot}] = K_p P(O_2)^{1/2}.$$

The hole concentration, p, is then given by

(15) $$p = (K_p[V_0^{\cdot\cdot}])^{1/2}P(O_2)^{1/4}$$

Thus the hole concentration, and hence the p-type conductivity is proportional to the square root of the oxygen vacancy concentration. The first samples were made with 1% and 5% La^{+3} substituted for Pb^{+2}. One set was prepared with 5 mol% excess PbO and was sintered in a closed container containing a large amount of powder of the same composition, while the other set was prepared with no excess PbO, and the powder was heated in an open container (in a well-ventilated hood) until substantial PbO-loss had occurred as indicated by a measured weight-loss. The equilibrium conductivities of the 1% doped sample as a function of oxygen activity at 700°C are compared with previous values obtained for undoped PZT in Fig. 4. The conductivities of the donor-doped sample is about an order of magnitude less than that of the undoped material, and, according to Eq. (15), this indicates that the oxygen vacancy content has been reduced by about a factor of 100. This is not as much as expected, but is still substantial. The biggest surprise is that the sample that had lost several mol% PbO is virtually indistinguishable from the sample for which PbO loss was avoided. The predicted negation of the effect of the donor by the loss of PbO did not occur, at least not in this case. While not understood at this point, this is an encouraging sign for the switching stability of donor-doped PZT films. The conductivity data for the 5% doped samples showed a further decrease in conductivity, but the data were too scattered for quantitative interpretation. Obviously, work will continue on this aspect of the defect chemistry of PZT.

C. The Defect Chemistry of PZT

In order to apply the principles of defect chemistry to the stability of thin PZT films, it is necessary to understand that defect chemistry in detail. While $PbTiO_3$, $PbZrO_3$, and their solid-solutions, PZT, have not been thoroughly studied, it was expected

that their defect chemistry would be very similar to that of $BaTiO_3$ and $SrTiO_3$, which have been extensively studied, and were thought to be well-understood (5,8,9). In the meantime, new aspects of the defect chemistry of the latter compounds have come to light, and it appears that PZT may have some difference in behavior, although that is not yet entirely clear.

Since PZT seems to be stable only in the oxygen-excess, p-type region, we need only consider that part of the defect model. In the model that has been generally accepted for nearly 20 years, it is assumed that the undoped titanates actually contain a small, but significant, excess of acceptor impurities, due to their naturally-occurring impurity content (2,3,9). The lower-valent cations that function as acceptors in these compounds are much more abundant in nature than the higher-valent cations that serve as donors. These acceptors are incorporated into the lattice according to Eq. (1), and in the stoichiometric, doped material are compensated by oxygen vacancies. Over the conditions of interest, charge-neutrality is dominated by these defects

(16) $$[A'] = 2[V_O^{\cdot\cdot}]$$

Where A' is a generalized acceptor. Oxidation then occurs by the partial filling of these oxygen vacancies with the formation of holes

(17) $$V_O^{\cdot\cdot} + 1/2O_2 \rightleftharpoons O_O + 2h^{\cdot}$$
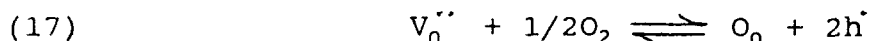
(This identical to Eq. (13), but is repeated here in the interest of having a self-contained Section.) For practical conditions, only a very small fraction of the vacancies are filled, and the condition shown in Eq. (16) is not significantly disturbed. The mass-action expression for the oxidation reaction is

(18) $$p^2/[V_O^{\cdot\cdot}] = K_p \exp(-\Delta H_p/kT) P(O_2)^{1/2}$$

where $p = [h^{\cdot}]$, and ΔH_p is the standard enthalpy of the oxidation reaction. The combination of Eqs. (16) and (18) gives the hole concentration as a function of temperature and oxygen activity

(19) $$p = (K_p[A']/2)^{1/2} \exp(-\Delta H_p/2kT) P(O_2)^{1/4}$$

In this original model, it was thought that each excess oxygen created two holes that were free to conduct in the valence band under equilibrium conditions.

Since the perovskite titanates are insulators near room temperature, the holes created by oxidation must no longer be mobile, and it is assumed that they are trapped by the acceptor centers, which lie substantially above the valence band. The ionization of these centers can be written as

(20) $$A^x \rightleftharpoons A' + h^{\cdot}$$

where A^x is the neutral combination of an acceptor with a trapped hole. The mass-action expression for this reaction is

$$(21) \qquad [A']p/[A^x] = K_a \exp(-E_a/kT)$$

where E_a is the ionization energy. At this point, the model had an inconsistency. Any ionization energy that was large enough to cause trapping of almost all of the holes near room temperature, was too large to allow almost all of the holes to be free at the equilibration temperatures. Because the model fit the experimental observations so consistently in all other respects, this problem was ignored. The impass has been resolved by Waser (1), who has pointed out that the introduction of substantial trapping of holes under equilibrium conditions does not change the form of the model, nor its apparent agreement with experiment. Thus we can accept the fact that the change in conductivity from equilibrium to ambient temperatures requires an ionization energy of about 0.5 eV, and that this will result in only about 1% of the trapped holes being ionized at 1000°C.

The defect model needs to be modified to account for a substantial, and probably dominant, concentration of trapped holes under equilibrium conditions. The oxidation reaction to form trapped holes is

$$(22) \qquad V_0^{\cdot\cdot} + 2A' + 1/2O_2 \rightleftharpoons O_0 + 2A^x$$
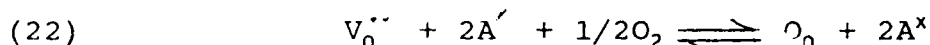
with the mass-action expression

$$(23) \qquad [A^x]^2/[A']^2[V_0^{\cdot\cdot}] = K_{ox} \exp(-\Delta H_{ox}/kT) P(O_2)^{1/2}$$

when this is combined with the expression of charge-neutrality, Eq. (16), the concentration of trapped holes is given by

$$(24) \qquad [A^x] = (K_{ox}/2)^{1/2}[A']^{3/2} \exp(-\Delta H_{ox}/2kT) P(O_2)^{1/4}$$

The oxidation reactions to form trapped holes, Eq. (22), and free holes, Eq. (17), are linked by the ionization reaction, Eq. (20), such that their enthalpies are related as

$$(25) \qquad \Delta H_p = \Delta H_{ox} + 2E_a$$

An idealized defect diagram for this model is shown in Fig. 5. It differs from the previous model only by the inclusion of the line representing trapped holes.

Eq. (17) is still a valid reaction for the formation of free holes, and their concentration is still given by Eq. (19), but it must be realized that these are not all of the hole species created by oxidation. In fact, the amount of excess oxygen is now seen to be twice the trapped hole concentration, and is larger than previously estimated. Also, the stoichiometric composition occurs when $n = [A^x]$, not when $n = p$, as previously thought. Since insulating material can be obtained for oxygen activities above that at the

stoichiometric composition, Fig. 5 shows that insulating properies can be obtained at lower oxygen activities than previously thought possible, i.e. below the conductivity minima. This resolves the puzzle of how the manufacturers of multilayer ceramic capacitors with nickel electrodes can fire their components at oxygen activities that appear to be substantially below the conductivity minimum and still have insulating dielectrics.

We have expanded our study of the defect chemistry of PZT (50% Ti and 50% Zr) in order to obtain a complete picture of the modified model. This work will also impact our study of the conditions to which PZT can be exposed without loss of essential properties for memory elements. A basic study of the related defect chemistry of $BaTiO_3$ and $SrTiO_3$ is being carried out with support from NSF. In the latter compounds, it is clear that the electron and hole mobilities are not thermally activated and the conduction can be viewed as taking place in the conduction and valence bands. It has been suggested that the holes in $PbTiO_3$, and thus presumably in PZT, are small polarons, and that their mobility is thermally activated. The evidence has been not clear, and we hope to be able to resolve the question, but, in the meantime, the model will allow for the possibility of a thermally-activated hole mobility, which will be expressed as

$$(26) \qquad \mu = \mu_o \exp(-\Delta H_m/kT)$$

where ΔH_m is the enthalpy of motion.

The experimental results include the following:

Equilibrium electrical conductivity: This has been done, and the results are shown in Fig. 6. This essentially tracks the free hole concentration, and the logarithmic slopes are close the the value of 1/4 predicted by Eq. (19). The apparent enthalpy of conduction obtained from an Arrhenius plot of the conductivity at constant oxygen activity, ΔH_c, may contain the enthalpy of motion of the holes as well as the enthalpy of formation, ΔH_p. Thus ΔH_c, which has the experimental value 0.71 eV, as shown in Fig. 7, may be expressed as

$$(27) \qquad \Delta H_c = \Delta H_p/2 + \Delta H_m = 0.71 \text{ eV}$$

Equilibrium oxygen activity at constant composition: This has also been accomplished. The experiment is based on a rearrangement of Eq. (24) to give

$$(28) \qquad P(O_2) = 4[A^x]^4/([A']^3 K_{ox})^2 \exp(2 \Delta H_{ox}/kT)$$

If the defect concentrations can be kept sufficiently constant with changing temperature, an Arrhenius plot of the equilibrium oxgen activity will give $2\Delta H_{ox}$. This requires that the sample be hermetically sealed in a cell whose gas volume is as small as possible relative to the sample mass. The oxygen that enters or leaves the sample to establish the equilibrium oxygen activities as

a function of temperature must not result in significant changes in the defect concentrations. In our cell, shown schematically in Fig. 8, the concentrations change by less than 1% over the experimental temperature range. The hermetic seal is accomplished by compression of the glass gaskets that soften at the experimental temperatures. The electroded stabilized zirconia lid serves as an electrolyte for measurement of the oxygen activity inside the cell. The experimental results are shown in Fig. 9, and the Arrhenius slope is given by

$$(29) \qquad\qquad 2\Delta H_{ox} = -0.85 \text{ eV}$$

Coulometric titration: This has also been attempted, but with only partial success. The experiment uses the same sealed cell just described, but the zirconia lid is used to electrochemically pump known amounts of oxygen into and out of the cell. This changes the amount of excess oxygen, δ, as expressed in $PbTiO_{3+\delta}$, and establishes a new equilibrium oxygen activity that is measured by the zirconia cell. The requirement is that essentially all of the added oxygen be absorbed by the PZT, and that the added amount that stays in the gas phase be negligible; that is fulfilled by our cell. According to the defect model, δ is half the concentration of trapped holes, as given by Eq. (24). For a known change in δ, there is a measured change in P(O2), and they are related by

$$(30) \qquad\qquad \Delta \delta = \delta (1 \text{ atm}) \Delta P(O_2)^{1/4}$$

δ(1 atm) is half of the coefficient of $P(O_2)^{1/4}$ in Eq. (24), which is a constant at a given temperature, and corresponds to the amount of excess oxygen at that temperature in 1 atm of oxygen. It is the slope of $\Delta \delta$ vs. $\Delta P(O_2)^{1/4}$, as shown in Fig. 10. The results indicate that δ is of the order of 10^{-4} (100 ppm) near 700°C for P(O2) = 1 atm. The temperature dependence of this value would be another measure of ΔH_{ox}, but, unfortunately, the behavior at different temperatures has so far been erratic and unreproducible, so that dependable values have not been obtained. Work continues on this aspect.

The temperature dependence of conductivity at constant composition: This can be accomplished in the same sealed cell arrangement. Constant composition would give a constant concentration of trapped holes. The temperature dependence would then depend on the ionization energy and the enthalpy of motion, $E_a + \Delta H_m$. This measurement is underway, but definitive results have not yet been obtained.

The Seebeck coefficient at constant P(O2): The Seebeck coefficient (thermoelectric power) is the voltage generated across a sample in a temperature gradient. It is directly related to the carrier concentration, although some assumption must be made for the value of a thermal transport term that depends on the conduction mechanism. In this case, a small polaron mechanism has been assumed. Preliminary experiments have been carried out in air, with the results shown in Fig. 11. At equilibrium in a

constant oxygen activity, the apparent enthalpy, ΔH_Q = 0.3 eV, should be given by

(31) $\Delta H_Q = \Delta H_{ox}/2 + E_a = 0.3$ eV

From the results obtained to date, a very tentative set of thermodynamic parameters can be given as follows:

ΔH_p, the enthalpy of formation of free holes, Eq. (17)   0.6 eV

ΔH_{ox}, the enthalpy of formation of trapped holes, Eq, (22) -0.42 eV

E_a, the ionization energy of trapped holes, Eq. (20)   0.5 eV

ΔH_m, the enthalpy of motion of holes, Eq. (26)   0.4 eV

The latter two values must be considered as uncertain until more extensive data ire obtained.

The negative sign of the value of ΔH_{ox} indicates that the amount of excess oxygen is actually increasing with decreasing temperature at constant $P(O_2)$. This has not been experimentally verified, by thermogravimetric measurements, for example. The equilibrium conductivity increases with increasing temperature, because of an increasing amount of ionization of a decreasing concentration of trapped holes, and apparently because of an increasing hole mobility.

Work will continue on this project in order to obtain as complete a picture of the defect chemistry and conduction mechanisms in PZT as possible.

    D. Direct Observation of Domain Motion by Electron Microscopy

In order to understand switching behavior in ferroelectric films, it is of interest to observe directly the motion of domains under the influence of applied fields, and the effects on that motion of composition, microstructure, thermal history, successive switching operations, and ultimately of fatigue. For that purpose, our research program includes the design, assembly, and operation of a field stage for the transmission electron microscope. This plan contains some challenges, particularly in how to apply an electric field to a thin sample in such a way that the domains can still be observed in an electron transparent region. We have had the good fortune to have the cooperation of Dr. Robert Hull of AT&T Bell Laboratories, Murray Hill, who had recently constructed a field stage for an entirely different purpose. We have had generous access to his system to try out various sample configurations and to learn the problems that must be surmounted. This has been a valuable learning experience, and the acquisition of our own field stage has been postponed until the second year of the project to take advantage of it. We are now moving forward on our own.

The sample holder configuration and the electrode system that has

evolved is shown in Fig. 12. The electrodes are applied to opposite sides of the thin sample by evaporation, such that there is a lateral gap between them of 50-100 microns that serves as the viewing area. The stage can also be heated to study the effects of temperature, and, in the case of thinned $BaTiO_3$ samples, to cross back and forth over the ferroelectric-paraelectric transition. The domain motion is recorded in real time by a video recording system.

Examples of domain motion are shown in Fig. 13 as a series of still photographs. Of course, the effect is much more dramatic in the dynamic video version. The sample in this case was $BaTiO_3$, which was used in the preliminary studies because of its relatively simple domain structure, and modest Curie temperature. The sample was initially cooled from the paraelectric state without an applied field to generate a fresh domain pattern, and an area was selected that included the free end of a domain, as shown in 13a. As the voltage was gradually increased to -1 v, the domain tip moved forward until it merged with another domain that was oriented in the same direction, 13b. When the voltage was removed, the domain remained in its new position, 13c. Even when an opposite voltage of +40 v was applied, the domain remained pinned. The application of 100 v resulted in distortion of the sample and loss of the domain contrast, but when the voltage was dropped to +9 v, the domains were observed to separate and return to approximately their original positions, 13e. When the polarity was changed to about -1 v, the original motion was repeated, and the two domains combined again, 13h-i. There was no further motion when the voltage was removed, 13j. Of particular interest, it was noted that after a domain was moved back and forth a few times, a higher field was always required to initiate further motion. This would seem to be of particular interest with regard to fatigue. In addition, the general hysteretic behavior of the domain motion, and its lack of ready reversibility, indicates that switching is a very complex process. We are looking forward to a systematic study of the effects of doping, processing, microstructure, thermal history, electric field, successive switching operations, and fatigue on the movement of domains.

E. Preparation of PMN-PT Thin Films

Mr. C.-H. Jiang, who is supported by the Republic of China, has been studying the preparation of thin films of the $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) system by the spin-on sol-gel process in order to characterize their electrical properties. The initial focus has been on the composition 90%PMN-10%PT, which we will designate as 90PMNT. The main problem, of course, is to suppress formation of the pyrochlore phase and to obtain phase-pure perovskite (10,11).

The following procedure has been found to give films with perovskite contents of 98-99%: Mg and Nb ethoxides are reacted in absolute ethanol, and then an excess of 2-methoxyethanol (2-MOE) is added. The ethanol and excess 2-MOE are removed by distillation. Pb precursor solution (Pb acetate in 2-MOE) is added and the

13

concentration is adjusted to 1M. 1M PT stock solution is prepared from Pb acetate and Ti isopropoxide dissolved in 2-MOE, and is added to the PMN stock solution. This mixture is then reacted with a mixture of water, ammonium hydroxide, and excess Pb precursor. After aging for 12 to 24 hours, the sol is ready for use.

The dried spun-on films are annealed in a slow stream of wet oxygen in a preheated quartz tube furnace. The water was found to enhance the low temperature crystallization of the films. A three-layer film, with a two minute anneal at $800^{\circ}C$ for each layer, had >99% perovskite phase, according to the x-ray pattern. Even a four-layer film annealed for two minutes at $750^{\circ}C$ had >98% perovskite. The electron diffraction patterns of these films showed faint superlattice lines indicating partial ordering of the Mg and Nb atoms. An SEM photo of the surface of a film is shown in Fig. 14. The grain sizes fall in the range 0.1-1 micron. Some "bad" areas are still seen, as shown in Fig. 15. These regions contain a dispersion of fine particles that have been identified as pyrochlore. They are not removed by further annealing. Although bulk 90PMNT shows very slim hysteresis loops, the thin films do not exhibit any hysteresis.

III. REFERENCES

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9. D. M. Smyth, Prog. Solid State Chem. 15, 145 (1984).

10. K. D. Budd. S. K. Dey, and D. A. Payne, Brit. Ceramic Proc. No. 36, "Electrical Ceramics", 107 (1985).

11. L. F. Francis and D. A. Payne, in Ferroelectric Thin Films, E. R. Myers and A. I. Kingon, Eds., Mat. Res. Soc. Symp. Proc. 200, Pittsburgh (1990), p. 173.

IV. FIGURE CAPTIONS

1. Comparison of the switching fatigue behavior of thinned, polycrystalline, Ca-doped $BaTiO_3$ samples with unipolar and bipolar applied pulses.

2. Switching fatigue behavior for various thinned samples of doped and undoped $BaTiO_3$ subjected to 30 kV/cm unipolar pulses.

3. Schematic representation of the effect of acceptor and donor dopants on the oxygen vacancy concentration of a hypothetical oxide with 1 ppm intrinsic lattice disorder.

4. The effect of PbO-loss on the equilibrium conductivity at 700°C of donor-doped PZT (50-50). The dashed line represents undoped PZT (see Fig. 6), while the data points are for PZT doped with 1% La. The sample prepared with care to minimize PbO-loss is represented by the solid points, while the open points represent the sample with deliberate loss of PbO.

5. A schematic Kroger-Vink diagram for an acceptor-doped oxide in which the majority of the holes are trapped by acceptor centers even under equilibrium conditions. Both high temperature (HT) and low temperature (LT) concentrations are shown. This figure is taken from Waser (1).

6. The equilibrium conductivity of PZT (50-50) as a function of oxygen activity. The slopes represent the exponent of the oxygen activity in Eq. (15).

7. Arrhenius plots of the equilibrium conductivity of PZT taken at two different oxygen activities. The activation enthalpy is indicated to be 0.71 eV.

8. Diagramatic representation of the sealed cell used for coulometric titration and constant composition experiments.

9. The equilibrium oxygen activity of PZT as a function of temperature at constant composition. The activation enthalpy is 0.85 eV.

10. Coulometric titration results for PZT plotted according to Eq. (30). The slopes $K(O_2)$ represent the fractional oxygen excess in equilibrium with 1 atm oxygen.

11. The normalized Seebeck coefficient of PZT in air as function of temperature. The activation enthalpy is given as 0.3 eV.

12. The sample holder used for the observation of domain motion in the transmission electron microscope.

13. Examples of domain motion with various applied voltages, as described in the text.

14.   The surface of a PMN-PT (90-10) thin film as observed in the scanning electron microscope. The area depicted is a "good" region of essentially pure perovskite phase.

15.   The surface of a "bad" region of a PMN-PT film showing finely dispersed particles of the pyrochlore phase.
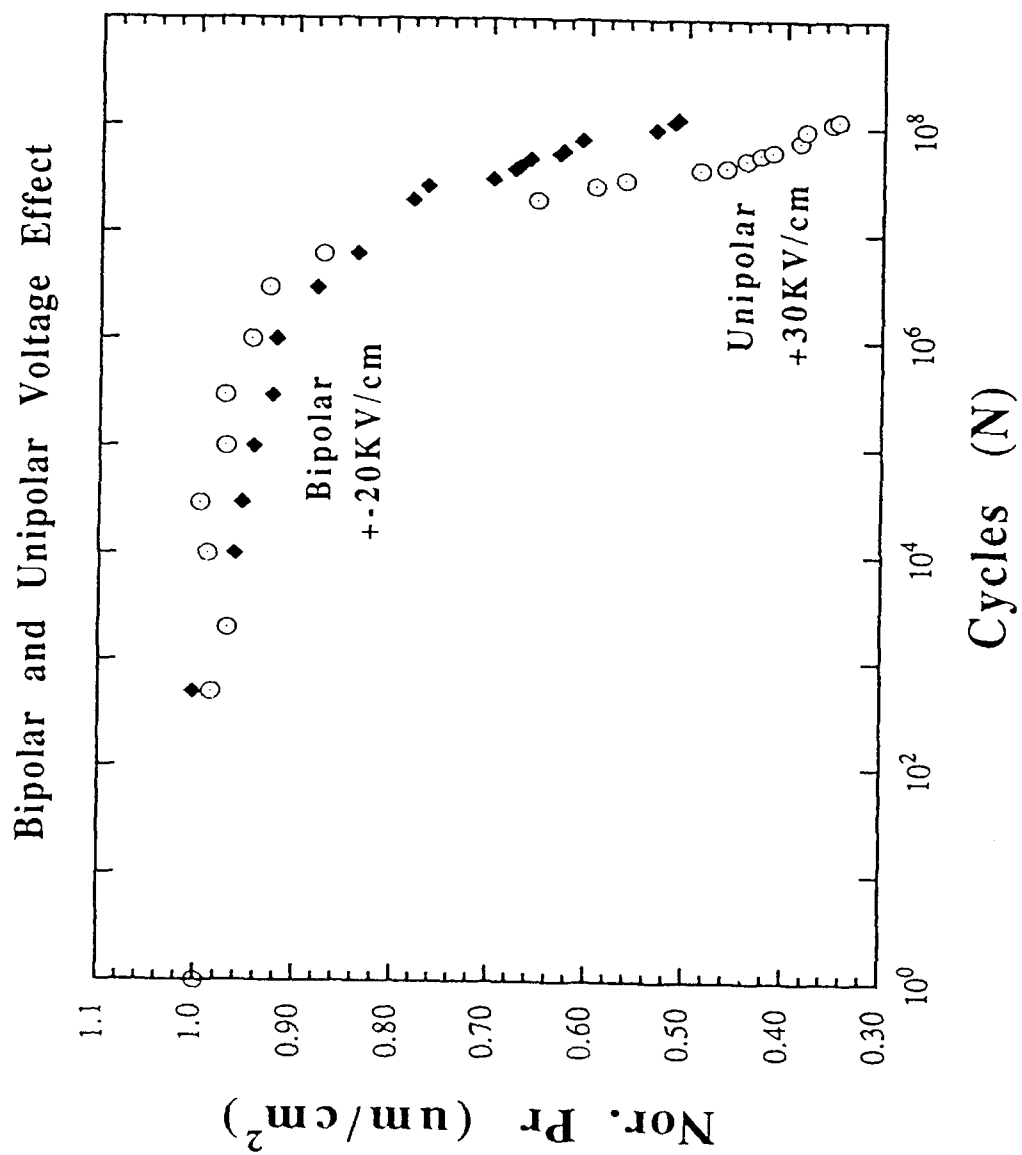
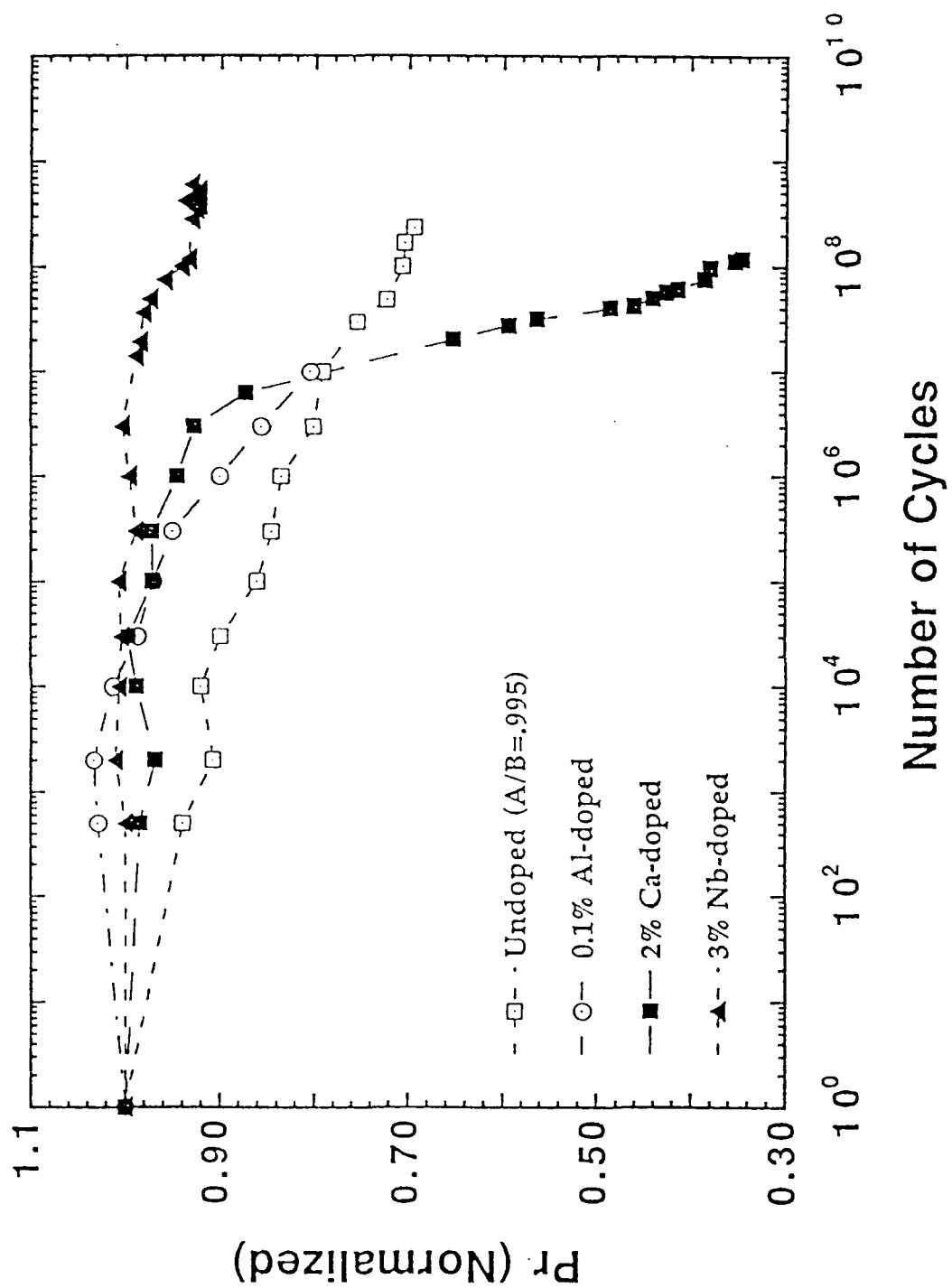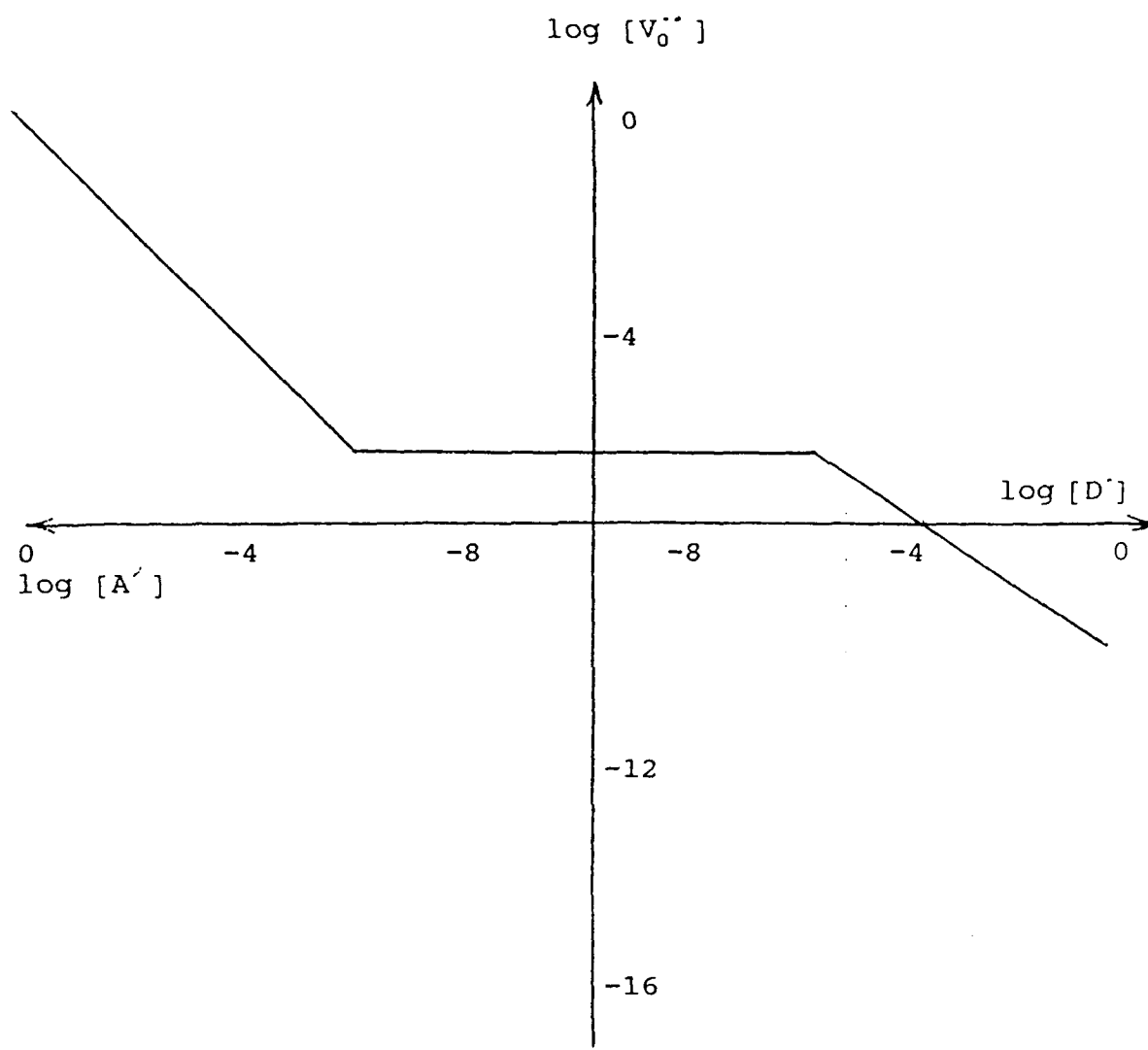Bipolar and Unipolar Voltage Effect

Figure 1

Figure 2

19

Figure 3

Figure 4

21

Figure 5

log relative P$_{O_2}$

log relative defect conc.

[A']

[V$_O^{\cdot\cdot}$]

[A$^\times$]

P$_{HT}$

n$_{HT}$

P$_{LT}$

n

[A$^\times$]$_{HT}$

n$_{LT}$

×10^2

×10^5

Equilibrium electrical conductivity for PZT + 1.5 mol% PbO
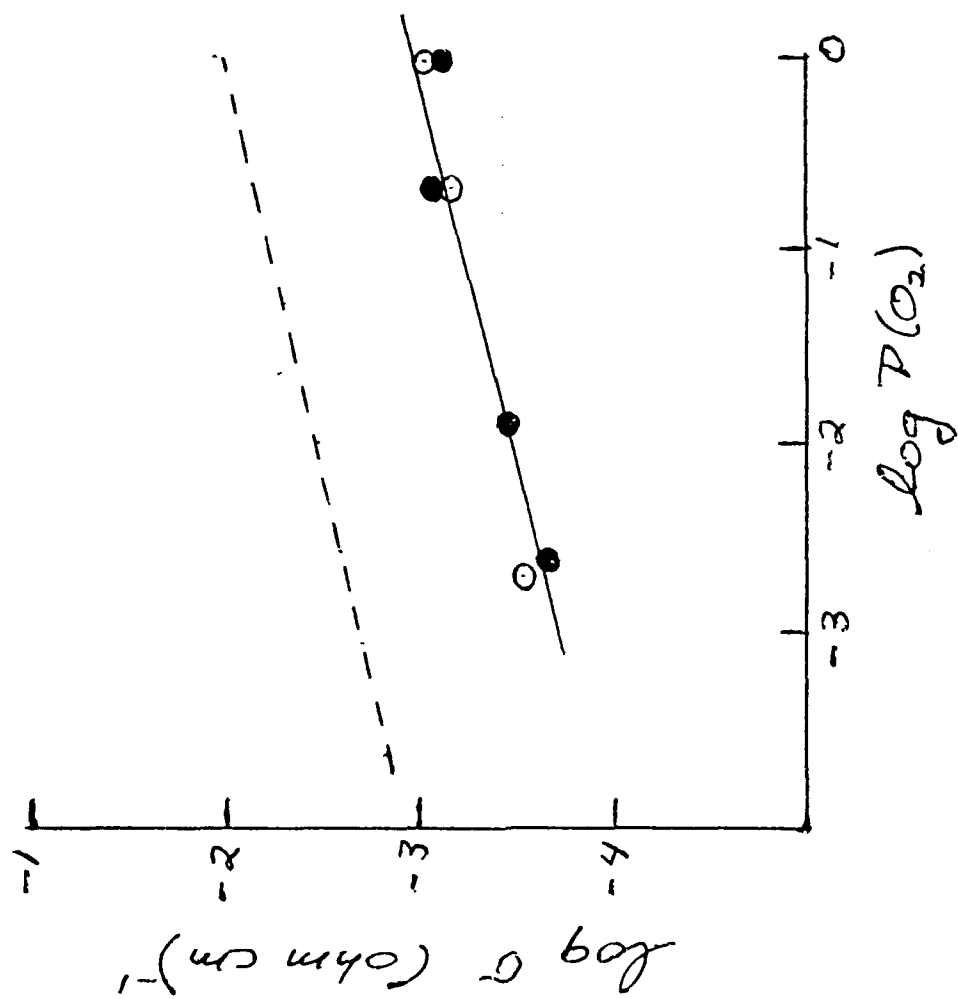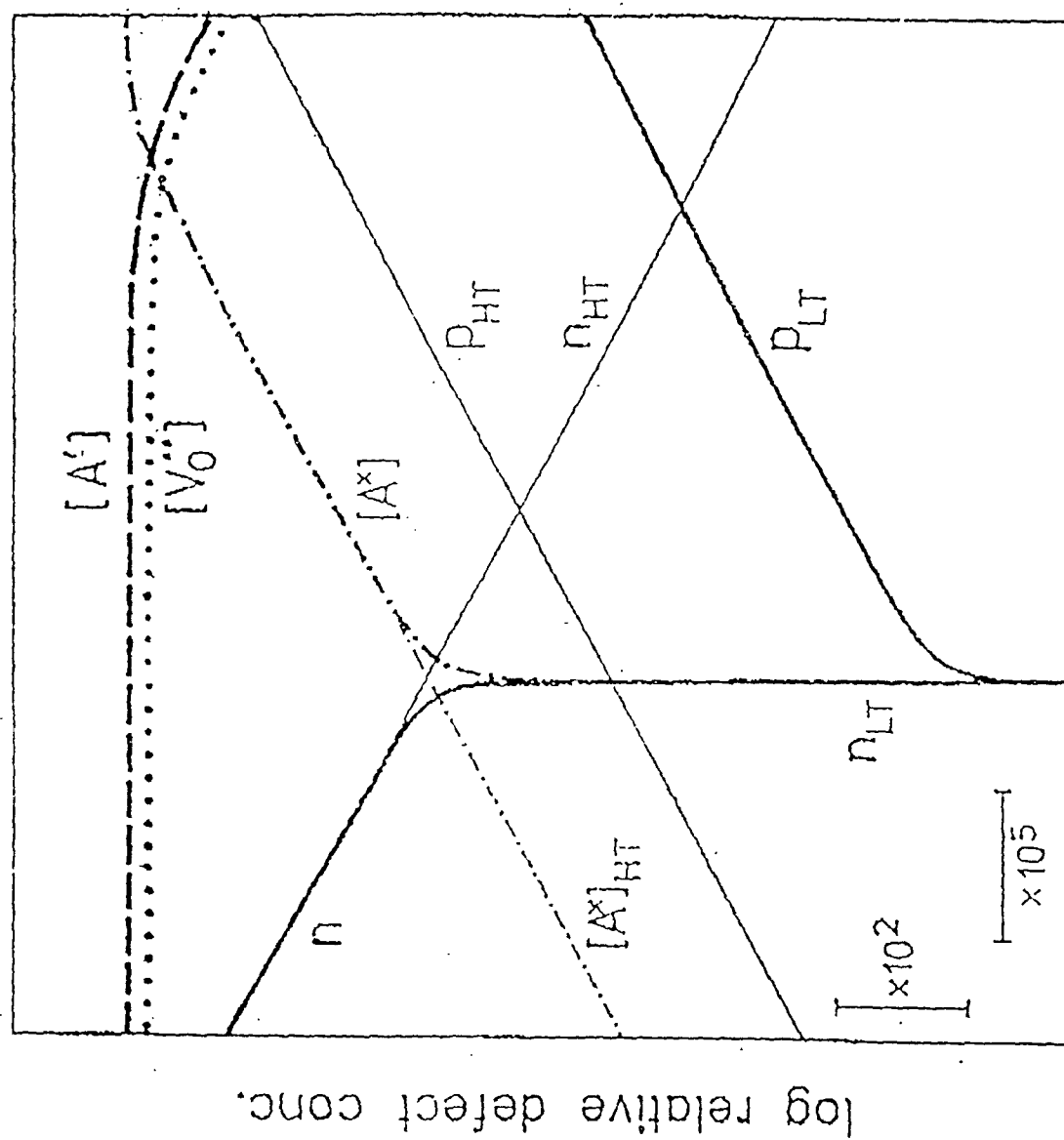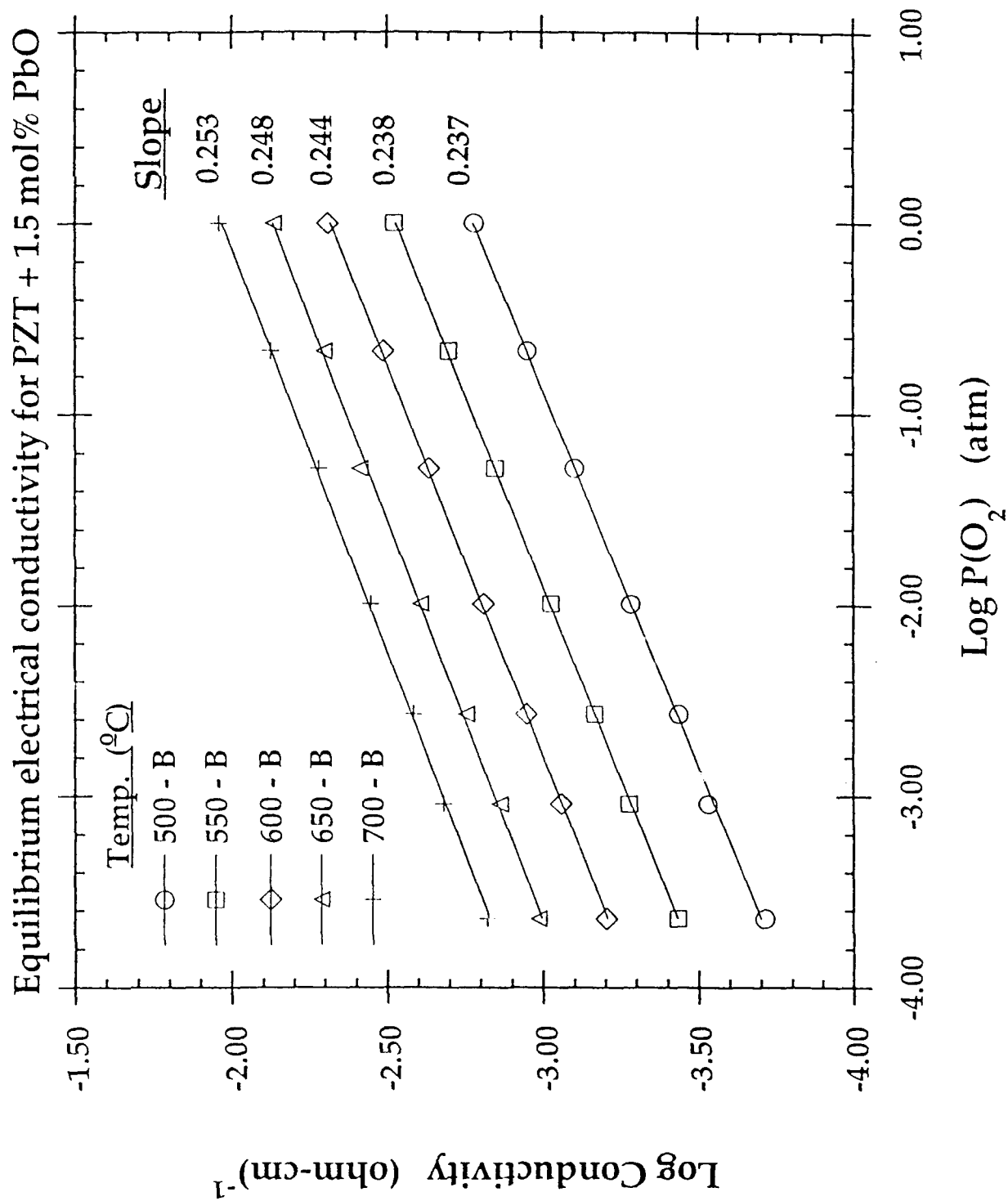
Figure 6

Arrhenius plot of conductivity for PZT + 1.5 mol% PbO

$(\Delta H_p/2)_{ave} = 0.71$ eV

$P(O_2) = 1$ atm

$P(O_2) = 10^{-3.64}$ atm

Log (Sigma * T) (ohm^{-1} cm^{-1} T)

1000/T (K^{-1})

Figure 7

Glass rings

Yittria stabilized Zirconia
electrolyte with Pt electrodes
and leads

PZT specimen

Alumina ring, tube and disk
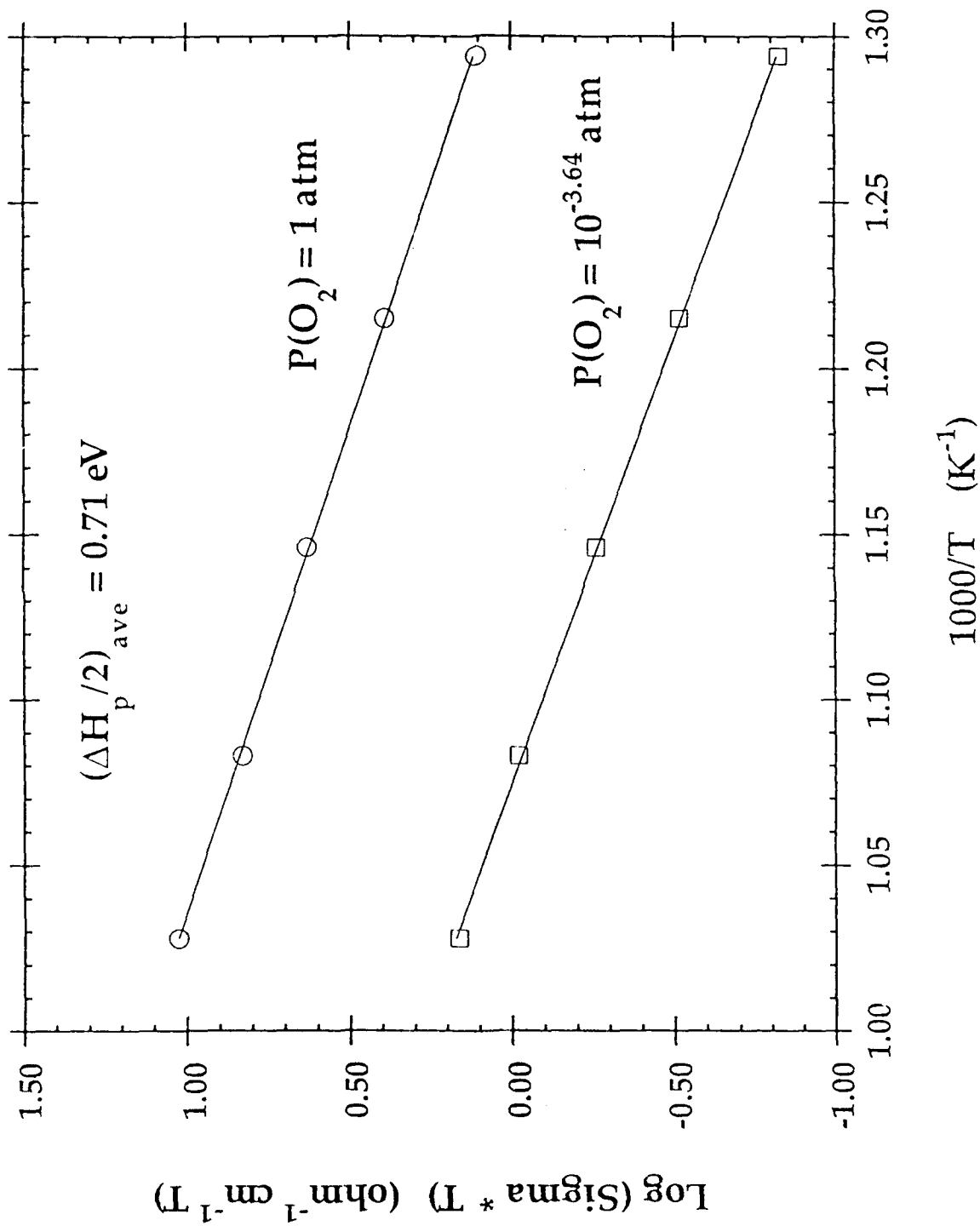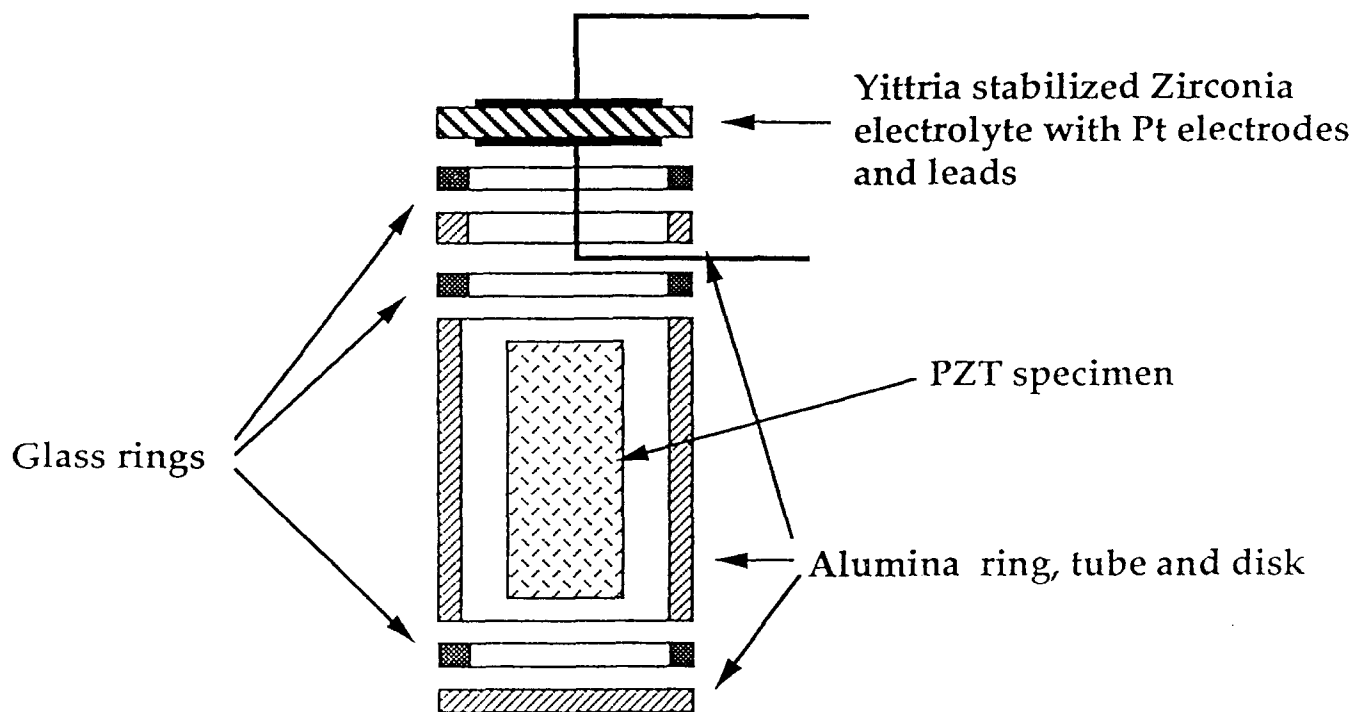
Schematic diagram of the sealed cell apparatus

Figure 8

Constant Composition Measurement of
PZT + 1.5 mol% PbO

$2 \Delta H_{ox} = -0.85$ eV

Log P(O$_2$) (atm)

1000/T (K^{-1})

Figure 9

26
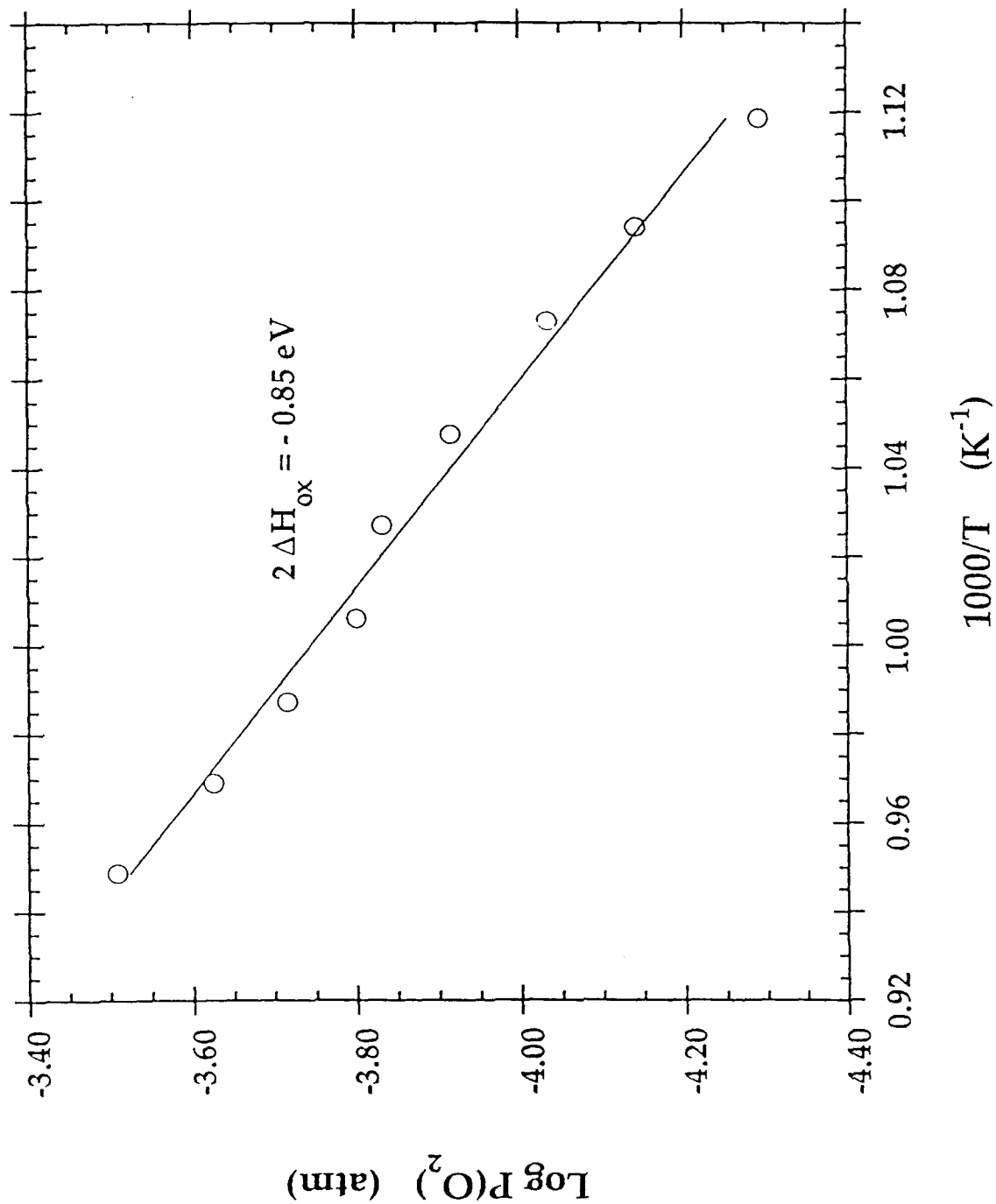
Coulometric Titration isotherms for PZT + 1.5 mol% PbO. Slopes indicate nonstoichiometry at $P(O_2) = 1$ atm

	$\underline{K(O_2)}$
680 C	72.5×10^{-6}
700 C	92.5×10^{-6}
720 C	107.2×10^{-6}

ΔDelta (10^{-6})

$P(O_2)^{1/4} - P(O_2)_{ref}^{1/4}$ $(atm^{1/4})$
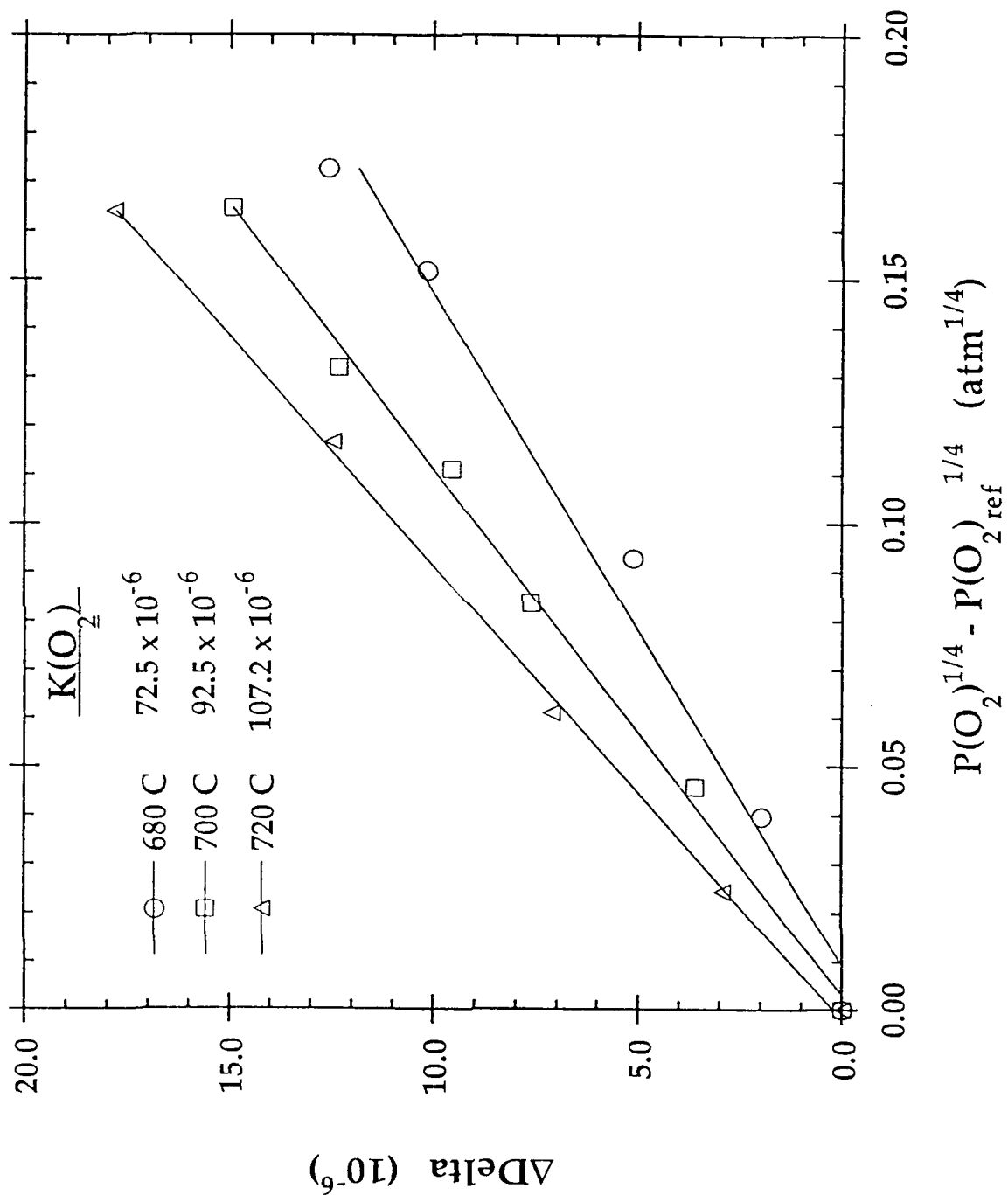
Figure 10

Arrhenius plot of $-eQ/2.3k_B$ in Air for
PZT + 1.5 mol% PbO sinter lot B-034

$y = -2.6351 + -1.4933x$ R= 0.9669
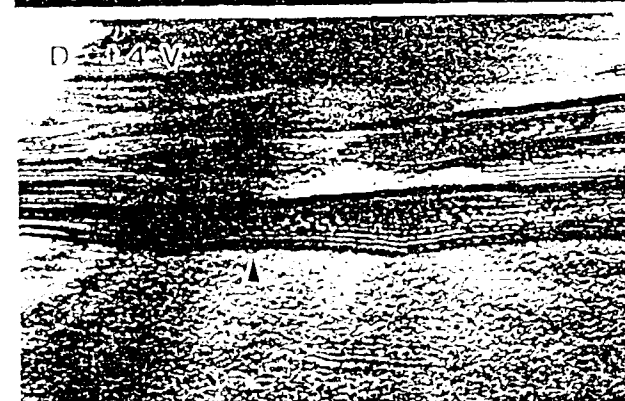
$\Delta H_Q = 0.30eV$

$-eQ/2.303k$

1000/T (K^{-1})

Figure 11

front surface electrical contact (wire ring)

mica ring with hole

Au top and bottom electrodes

BaTiO3 thin foil

heater coils

Ta washer

back surface electrical contact (locking nut)

electron transparent region

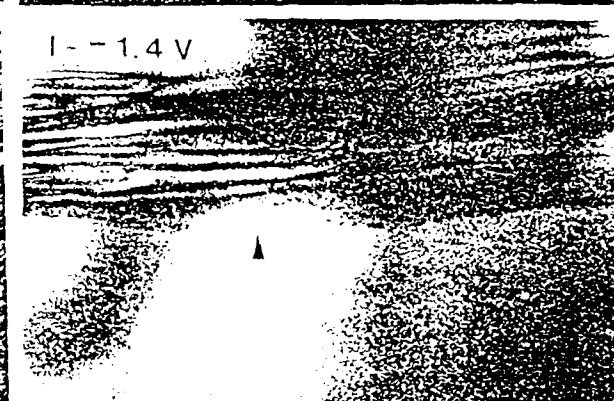3.0 mm disc

Figure 12

B -1V G 0V
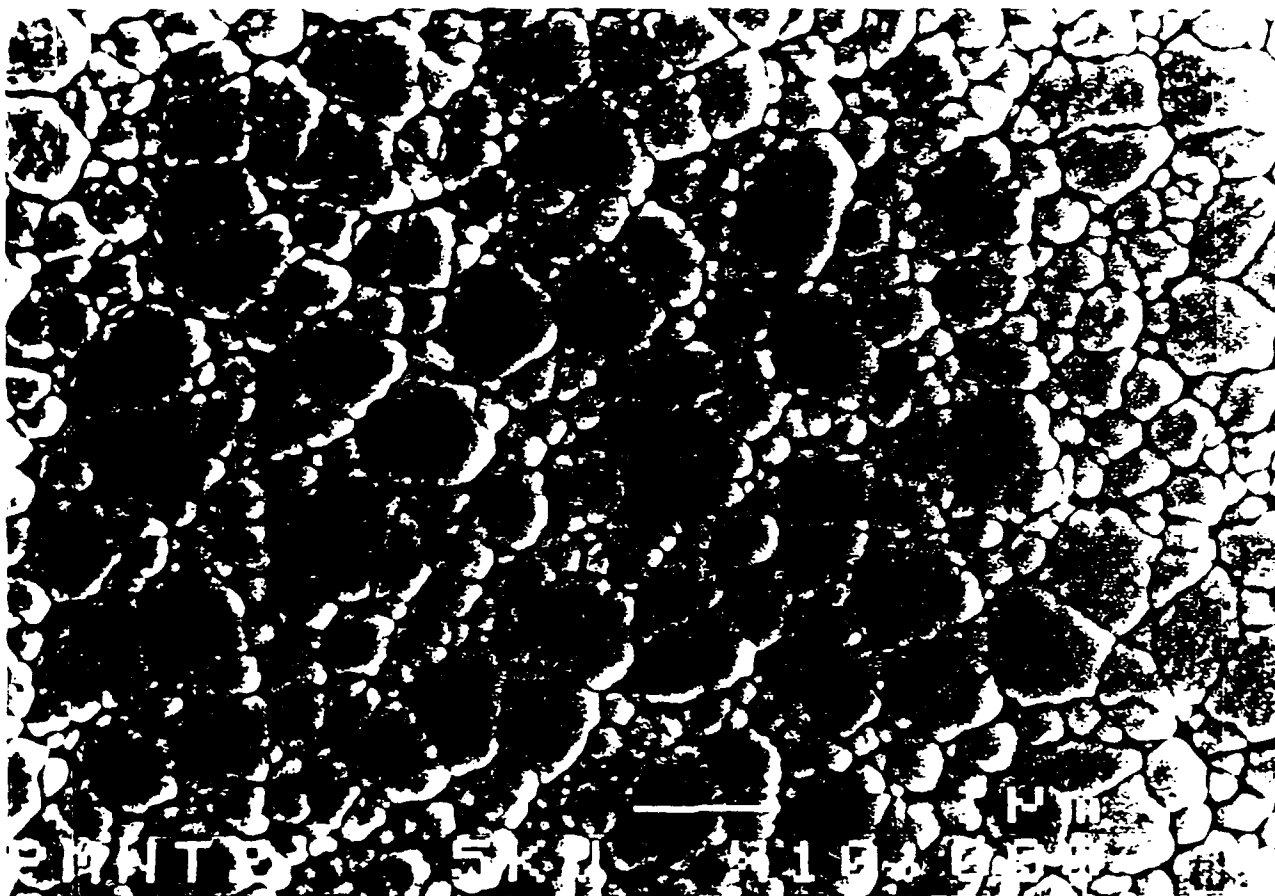C 0V H 0.9V
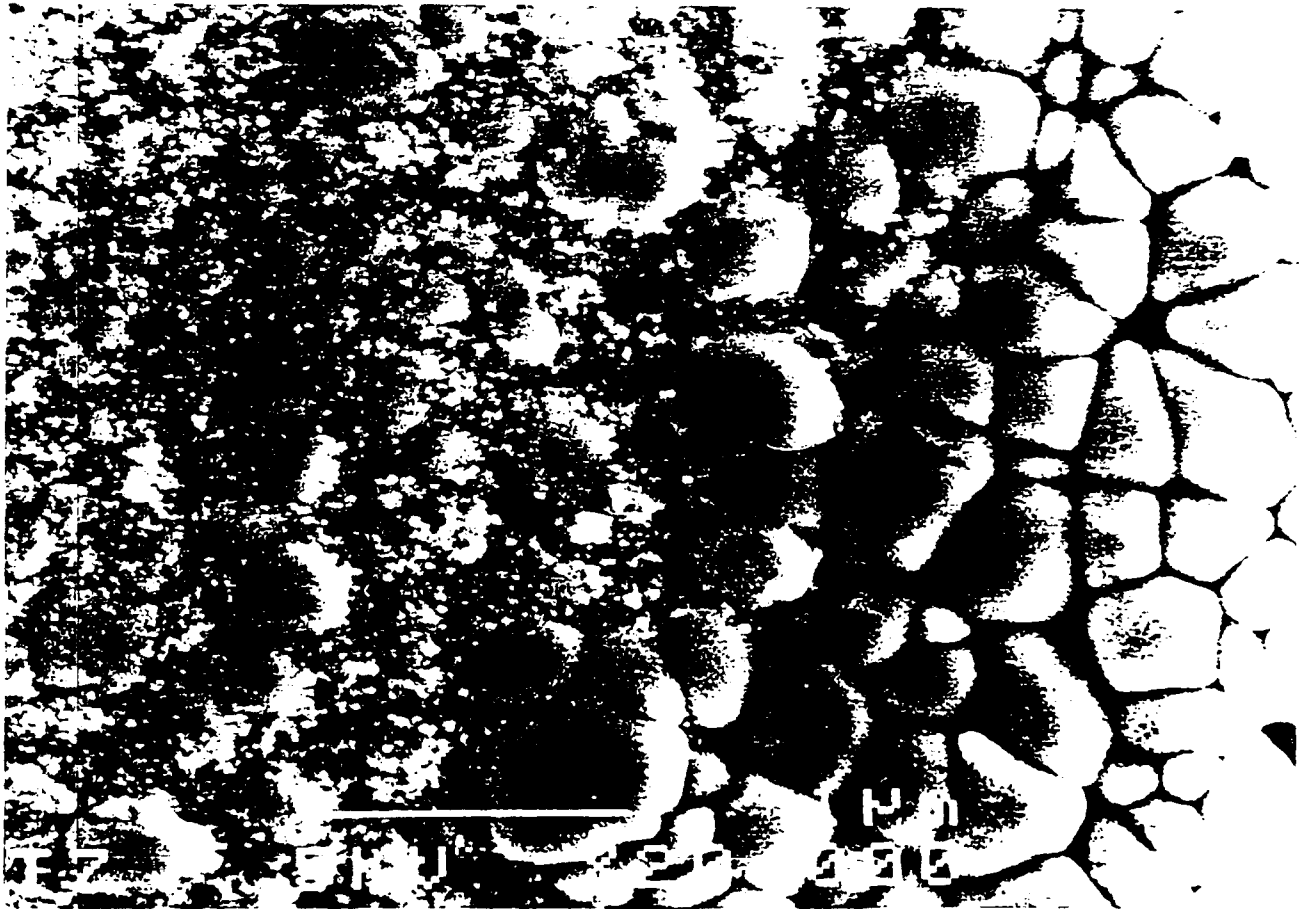D 0.4V I -1.4V
E -9V J 0V

1.0 μm
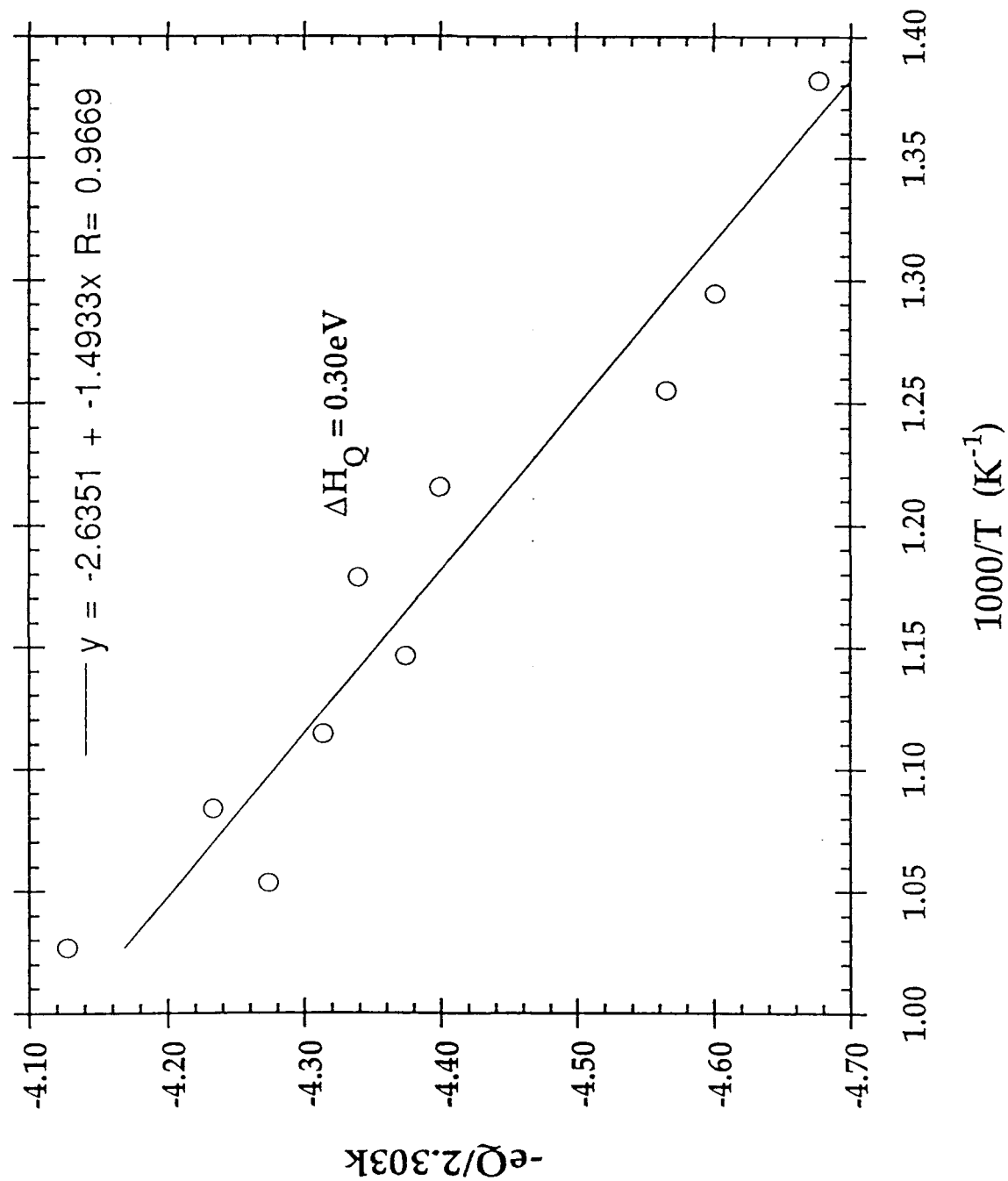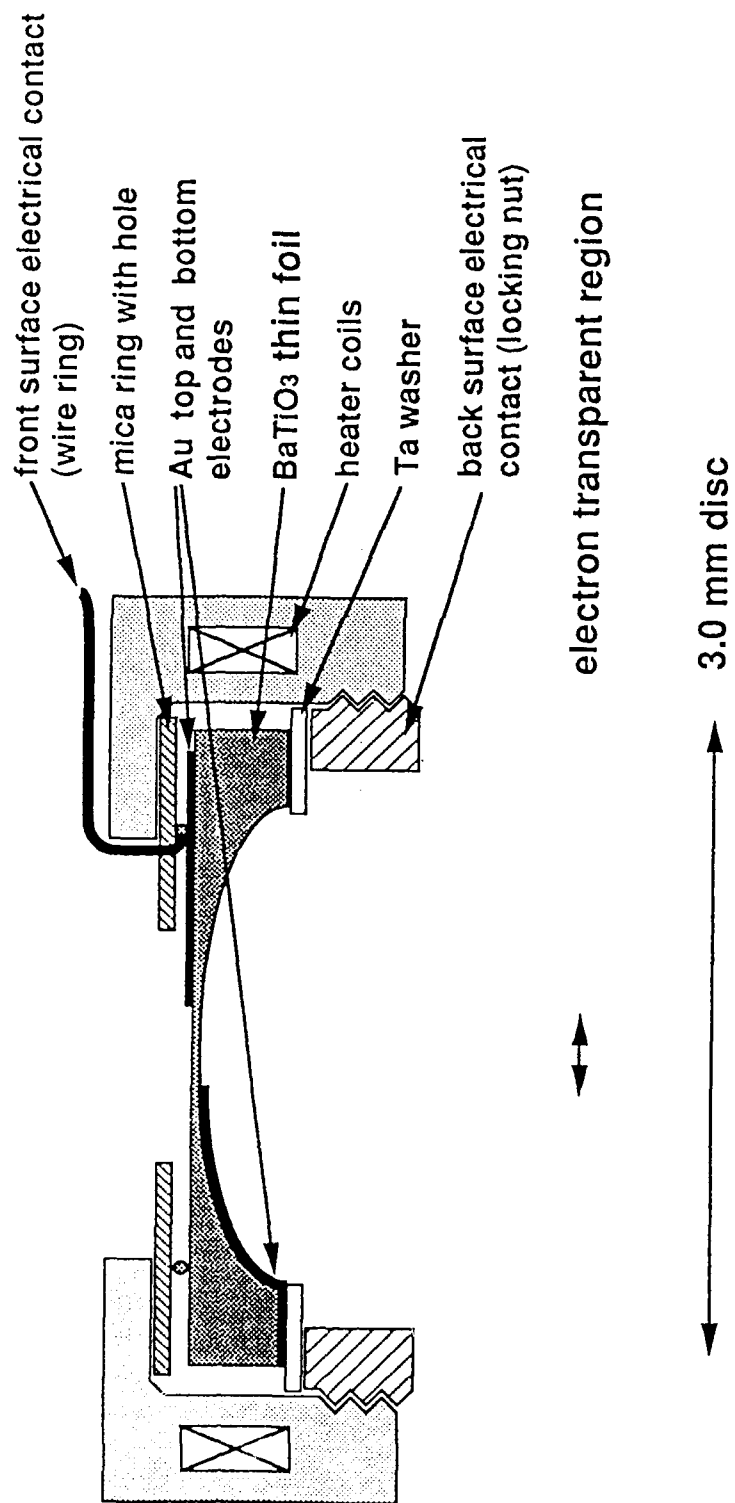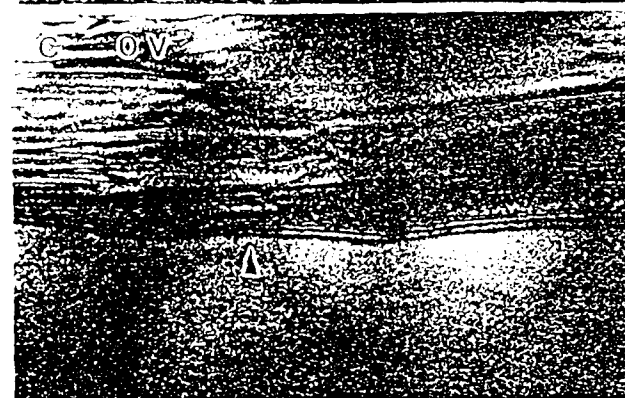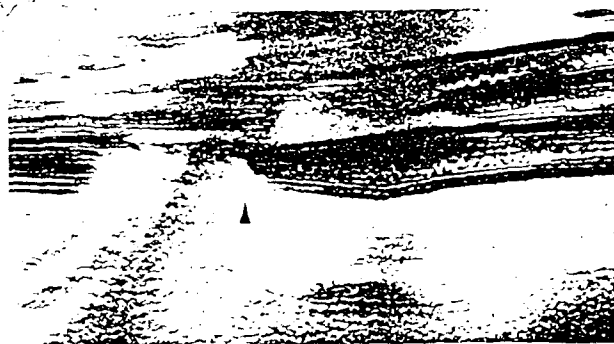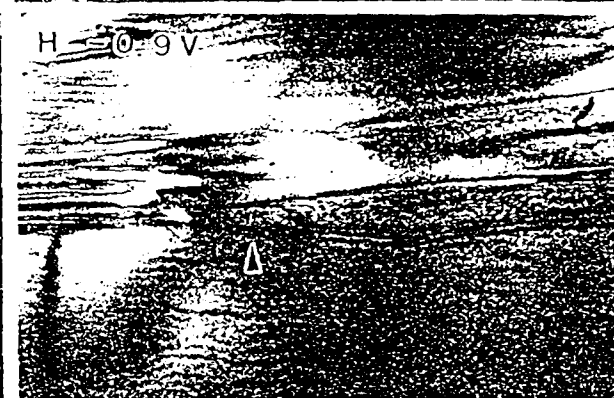
Figure 13
30

Figure 14

Figure 15

V. PRESENTATIONS AND PUBLICATIONS

A. Presentations

1. "Recent Results on the Defect Chemistry of Ferroelectric Oxides", D. M. Smyth, Third Internat. Symp. on Integrated Ferroelectrics, Colorado Springs, CO, April 1991, Invited.

2. "Defect Chemistry Analysis of $Pb(Zr_{1-x}Ti_x)O_3$ and Its Application to Thin Films", M. V. Raymond* and D. M. Smyth, Third Internat. Symp. on Integrated Ferroelectrics, Colorado Springs, CO, April 1991.

3. "Defect Chemistry Analysis of Lead-Based Ferroelectrics", 93rd Annual Meeting of the American Ceramics Society, Cincinnati, Ohio, April 1991.

4. "Defect Chemistry Analysis of $Pb(Zr_{1/2}Ti_{1/2})O_3$", M. V. Raymond and D. M. Smyth, Fourth Internat. Symp. on Integrated Ferroelectrics, Monterey, CA, March 1992.

5. "Defects and Charge Transport in $Pb(Zr_{1/2}Ti_{1/2})O_3$", M. V. Raymond and D. M. Smyth*, Joint U.S.-C.I.S. Seminar on Ferroelecticity, St. Petersburg, Russia, June, 1992.

6. "Polarization Degradation in Perovskite Ferroelectric Ceramics and Thin Films", J. Chen*, M. P. Harmer, and D. M. Smyth, Eighth Internat. Symp. on the Application of Ferroelectrics, Greenville, SC, September 1992.

B. Publications

1. D. M. Smyth, "Charge Motion in Ferroelectric Thin Films", Ferroelectrics 116, 117 (1991).

2. J. Chen, M. P. Harmer, and D. M. Smyth, "Polarization Degradation in Perovskite Ferroelectrics and Thin Films", submitted to Proceedings Eighth Internat. Symp. on the Application of Ferroelectrics.

3. D. M. Smyth and R. Waser, "Defect Chemistry, Conduction, and Breakdown Mechanism of Perovskite-Structure Titanates", invited chapter submitted to a volume on Integrated Ferroelectrics, edited by J. Scott.

4. M. V. Raymond and D. M. Smyth, "Defects and Charge Transport in $Pb(Zr_{1/2}Ti_{1/2})O_3$", in preparation, to be submitted to the Proceedings of the Joint U.S. - C.I.S Seminar on Ferroelectricity.

VI. PERSONNEL

Dr. Donald M. Smyth, Paul B. Reinhold Professor of Materials Science and Engineering and of Chemistry, and Director of the Materials Research Center (to June 30, 1992)

Dr. Martin P. Harmer, Alcoa Professor of Materials Science and Enegineering, and Director of the Materials Research Center (from July 1, 1992)

Dr. Don Young, Professor of Electrical Engineering and Computer Science

Dr. Jie Chen, Postdoctoral Research Associate

Dr. Christine Dong, Visiting Research Scientist

Mr. Mark Raymond, Doctoral Candidate, Materials Science and Engineering

Mr. C.-H. Jiang, Doctoral Candidate, Materials Science and Engineering

Mr. Cengiz Palanduz, Doctoral Candidate, Materials Science and Engineering (joined the project on June 1, 1992)

Ms. Susan Shaffer-Smith, undergraduate summer student