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14. ABSTRACT
Piezoelectric single crystals in the lead ytterbium niobate-lead titanate and BiScO3-PbTiO3 systems were grown and characterized as high temperature piezoelectrics. The properties were quite good, with d33 coefficients as high as 2500 pm/V in PY N-PT. Epitaxial and fiber textured thin films were prepared by pulsed-laser deposition and chemical solution deposition, respectively. These films show the highest reported c31,f coefficients for high Tc films. In addition, it was determined that the amplitude dependence of the dielectric and piezoelectric response of the films can be described using a frequency-dependent Rayleigh approach.

15. SUBJECT TERMS
piezoelectric, single crystals, thin films

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<td>Principal Investigator</td>
<td>T. R. Shrout and S. Trolier-McKinstry</td>
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<td>Organization</td>
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Technical Objectives

The objective of the program was the growth and characterization of high transition temperature ($T_c$) single crystal perovskites in both bulk and thin film form. Specifically, the Pb(Yb$_{1/2}$Nb$_{1/2}$)O$_3$–PbTiO$_3$ (PYN-PT) and BiScO$_3$–PbTiO$_3$ (BS-PT) were targeted. These materials offer significantly higher transition temperature ($T_c$) and thus working temperature ranges, as compared to PMN-PT and PZN-PT Relaxor-based compositions.

Specific objectives for the program were the following:

- Growth of PYN-PT and BS-PT using high temperature flux method.
- Dielectric and piezoelectric characterization of single crystals, including capacitance vs. temperature and $d_{33}$ from direct strain measurement.
- Electromechanical characterization using IEEE resonance.
- Growth of (001) PYN-PT and BS-PT thin films by sol-gel and pulsed laser deposition methods.
- Dielectric and electromechanical characterization of films

Technical Approach

Crystal growth parameters were arrived at based on differential thermal analysis (DTA) carried out on polycrystalline sample on the PYN-PT and BS-PT systems. Using a DSC 2920 Differential Scanning Calorimeter from 30 to 1350°C, the thermal hysteresis between melting crystallization points was determined. From these results, stoichiometric mixtures of the desired composition(s) were mixed
with various amounts of flux (Pb₃O₄ and/or Bi₂O₃) and loaded into platinum (PT) crucibles. Growth was carried out in a high temperature furnace with automated temperature control. A typical run was a soak temperature at 1200°C, followed by cooling to ~900°C and subsequent furnace cooling to room temperature. Figure (1) shows optical photograph of PYN-PT rhombohedral crystal.

From crystals 3–5 mm in size, samples for dielectric and piezoelectric properties were first oriented using real-time Laue and polished into flat and parallel surface onto which electrodes were sputtered. High temperature dielectric behavior was determined using a multi-frequency LCR meter (HP 4289G) with a computer-controlled temperature chamber. High field measurements included polarization and strain hysteresis using a modified Sawyer-Tower circuit and linear variable differential transducer (LVDT). The piezoelectric coefficient d₃₃ was calculated from the slope of strain versus field curves. Electromechanical coupling coefficients were determined on longitudinal and lateral mode bars and plates, as specified by IEEE standards.

![Figure 1. Optical photograph of PYN-xPT rhombohedral single crystals.](image)

Thin films have been grown both by pulsed laser deposition (PLD) and by sol-gel methods. (001) orientation was achieved in PLD films was achieved by growing epitaxial films on SrRuO₃/LaAlO₃ or SrRuO₃/SrTiO₃ substrates. Orientation control is being approached in sol-gel films on Pt/coated Si (where no epitaxial match is available) by control of nucleation. Dielectric and piezoelectric properties have been measured using low frequency LCR meters (HP 4192) with a hot-plate for temperature control. High field measurements were made using a Radiant Technologies RT66A Ferroelectrics tester. e₃₁₅-coefficients were measured by the wafer flexure method.
Summary

Among the accomplishments on the program are:

- Crystal growth PYN-xPT in the compositional range of x=0.2 – 0.75PT as shown in Figure 2. Note the composition of the morphotropic phase boundary (~ x= 0.5).
- Confirmed the transition temperature behavior in the PYN-PT system, as shown in Figure 3.
- Confirmed high $T_c$ of MPB coupled by $T_c > 330^\circ$C, as originally observed for polycrystalline materials.
- Determined the dielectric and piezoelectric properties as a function of composition, noting the performance enhancement near MPB (see Fig. 4).
- Contrasted the temperature stability of PYN-PT with PZN-PT, as seen in Figure 5.
- Crystal growth of BS-PT tetragonal crystals with $T_c > 460^\circ$C, the highest (see Fig. 6).
- Demonstrated epitaxial film growth and crystal anisotropy in PYN-PT films (See Fig. 7).
- Demonstrated epitaxial film growth in BS-PT films (See Fig. 8).
- Demonstrated good piezoelectric properties ($e_{31,t} = -12$C/m$^2$) in BS-PT films (See Fig. 9).
- Developed a sol-gel process for preparing PYN-PT films on platinum – coated Si (See Fig. 10).
- Demonstrated that sol-gel PYN-PT films on platinum – coated Si show the best (100) orientation when the heating rate during the crystallization is <20$^\circ$C/sec.
- Demonstrated good piezoelectric properties in (100) sol-gel derived PYN-PT films on MgO ($e_{31,t} = -10.2$ C/m$^2$) and Pt-coated Si (~8 C/m$^2$)
- Demonstrated that PYbN-PT films show dielectric and piezoelectric nonlinearity can be described by Rayleigh approaches (See Fig. 11). (100) films show larger amounts of nonlinearity than do (111) oriented films.
- Determined conditions under which 180$^\circ$ domain walls can contribute to the piezoelectric response.
Figure 2. XRD of PYN-xPT single crystals in the range $0.4 \leq x \leq 0.75$ with 1 mol% Ba$^{2+}$ additive.

Figure 3. Curie temperature of PYN-xPT ($0.2 \leq x \leq 0.8$) single crystals measured at 10 kHz (Δ polycrystalline data).
Figure 4. Piezoelectric coefficient of PYN-xPT (0.2 ≤ x ≤ 0.8) single crystal series.

Figure 5. Electromechanical coupling factor k₁₅ as a function of temperature for PYNT4 and PZNT4.5 crystals.
Figure 6(a). The photo of BSPT single crystals with rectangular shape.

Figure 6(b). Dielectric constant and dielectric loss of BSPT66 single crystal as the function of temperature.
Fig. 7: Crystal anisotropy in PYbN-PT films.
Fig. 8: X-ray diffraction pattern of epitaxial film growth in BS-PT50/50 film grown by pulsed laser deposition.

Fig. 9: Piezoelectric properties of BS-PT 40/60 films.
Yb-source + 2 MOE

Refux at 120 °C for 1 h

Add Nb ethoxide

Refux at 120 °C for 3 h

Add Ti-isopropoxide

Refux at 120 °C for 5 h

Add dehydrated Pb- acetate

Refux at 120 °C, for 5 h add AcAc

Complex PYbN-PT Solution

PYbN-PT Solution

Spin on a substrate (3000 r.p.m. for 30s)

Pyrolyze at $T_p$

Anneal by RTA at 750°C

PYbN-PT film

Fig. 10: Flow chart for sol-gel deposition of PYN-PT films

![Figure 11: Dielectric Nonlinearity in sol-gel PYbN-PT films](image)

Fig. 11: Dielectric Nonlinearity in sol-gel PYbN-PT films
ONR Database Statistics

Papers published in refereed journals citing ONR support: 12
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Technical Reports & Non-refereed papers: 5
Patents granted citing ONR support: 0
Presentations: 26
Papers in press in refereed journals citing ONR support: 1
Books or chapters in press citing ONR support: 0
Invention disclosures citing ONR support: 0
Patents pending citing ONR support: 0

Degrees granted: 0 (Nazanin Bassiri Gharb is expected to defend her Ph.D. in May 2005).

PI-CoPI: 2 total, 1 woman
Post-docs: 2 total, 1 minority
Grad students: 1 woman

Publications


Books and Chapters


Technical Reports


3. T. Yoshimura and S. Trolier-McKinstry, “Piezoelectric Properties of Pb(Yb1/2Nb1/2)O3 - PbTiO3 Epitaxial Films with (100) and (111) Orientation,” poster presentation at the US-Japan Meeting on Dielectric and Piezoelectric Ceramics, Sept. 26 – 29, 2001, Providence, RI


Articles in Press

1. N. Bassiri Gharb and S. Trolier-McKinstry, “Dielectric Nonlinearity of Pb\(_{1/2}\)Yb\(_{1/2}\)Nb\(_{1/2}\)O\(_3\)-PbTiO\(_3\) Thin Films with \{100\} and \{111\} Crystallographic Orientation,” accepted by the Journal of Applied Physics

Honors/Awards/Prizes


- Susan Trolier-McKinstry, promoted to full professor, July 2002

- Susan Trolier-McKinstry, fellow of the American Ceramic Society, 2004.