Micro-Raman and dielectric phase transition studies in antiferroelectric $PbZrO_3$ thin films

P. S. Dobal and R. S. Katiyar[a)]
Department of Physics, University of Puerto Rico, San Juan, Puerto Rico 00931

S. S. N. Bharadwaja and S. B. Krupanidhi
Materials Research Centre, Indian Institute of Science, Bangalore-560 012, India

Antiferroelectric materials are found to be good alternative material compositions for high-charge-storage devices and transducer applications. Lead zirconate (PZ) is a room-temperature antiferroelectric material. The antiferroelectric nature of PZ thin films was studied over a temperature range of 24–300 °C, in terms of Raman scattering, dielectric constant, and polarization. Temperature-dependent dielectric and polarization studies indicated a nonabrupt phase transition. To alleviate the extrinsic effects influencing the phase transition behavior, Raman scattering studies were done on laser-ablated PZ thin films as a function of temperature and clear phase transformations were observed.

Most recently, active studies towards the antiferroelectric thin films, such as lead zirconate ($PbZrO_3$) (Refs. 1 and 2) and La-modified lead zirconate[3] are being enhanced for the next-generation ''smart'' systems, such as high-charge-coupled devices and microelectromechanical systems consisting of sensors and actuators.[4] Antiferroelectric materials are characterized by the antiparallelly aligned adjacent dipoles with zero polarization in the equilibrium. The antiferroelectric phase can spontaneously be polarized into a ferroelectric phase by a sufficient application of electric field, since the associated free-energy difference between the two phases is small enough to be excited by an external field.[5] Such a field-induced phase transition property in antiferroelectric compositions could be utilized for high-charge-coupled devices and transducer applications.[6]

The transformation from the antiferroelectric to paraelectric phase may be realized through temperature dependence. In a pragmatic sense, dielectric and polarization studies indicated a diffused phase transition, which may either be attributed to extrinsic effects such as defect pinning, interface effects, etc., or any sort of structure-residue effect above the transition temperature. A systematic temperature-dependent study of phase variation should lead to a clear understanding, and Raman scattering studies were carried out to offer such knowledge with more accuracy. The present letter reports the studies of Raman scattering on laser-ablated $PbZrO_3$ (PZ) thin films as a function of temperature, and the findings were correlated to dielectric and polarization phase transitions.

Antiferroelectric $PbZrO_3$ thin films were deposited by the excimer laser-ablation technique (KrF; 248 nm). A phase-pure dense target of PZ was used for the deposition. Thin films of PZ were deposited at a substrate temperature of 300 °C and were annealed in a conventional annealing furnace at 650 °C for 5 min to induce perovskite crystallization. 100% pure oxygen gas was employed at a partial pressure of 50 mTorr, and a laser fluence of 3 J/cm^2 was maintained during deposition. Details of the entire deposition procedure have been described elsewhere.[7] Several thicknesses of the films were considered, keeping the grain size unchanged.

Circular gold electrodes of 500–600 μm diam were deposited using an evaporation system. The dielectric impedance and electrical measurements were carried out on the PZ films in metal–insulator–metal configuration. The polarization hysteresis behavior of the antiferroelectric PZ thin films was analyzed using a ferroelectric test system RT66A, over a wide range of temperature, 24–300 °C, in order to exemplify the variation of the dielectric and hysteresis properties. The variation of the dielectric constant over a frequency range of 0.1–100 kHz was studied using a Keithley LCZ meter (model:3330) at various temperatures.

The Raman measurements were performed using an ISA T64000 triple monochromator. An optical microscope with 80× objective was used to focus the 514.5 nm line of a Coherent Innova 99 Ar^+ laser on the sample. The same microscope objective collected the backscattered radiation. The scattered light, dispersed by the spectrophotometer, was detected by a charge-coupled-device detection system. The spectral resolution of the Raman system was less than 1 cm^{-1}. A microscope-compatible heater from Leitz Welzlar was used for temperature-dependent Raman measurements in the range 24–400 °C.

Polarization hysteresis measurements were done on antiferroelectric laser-ablated PZ thin films at different temperatures, and the results are shown in Fig. 1. The presence of a typical double hysteresis loop in the polarization versus electric field at room temperature establishes the antiferroelectric nature in the present PZ thin films [Fig. 1(a)]. The maximum value of the saturation polarization (P_S) is 36 μC/cm^2 at an applied electric field of 200 kV/cm with zero remnant polarization, at room temperature. The critical fields for the antiferroelectric-to-ferroelectric state and for the re-

a)Electronic mail: rkatiyar@upracd.upr.clu.edu

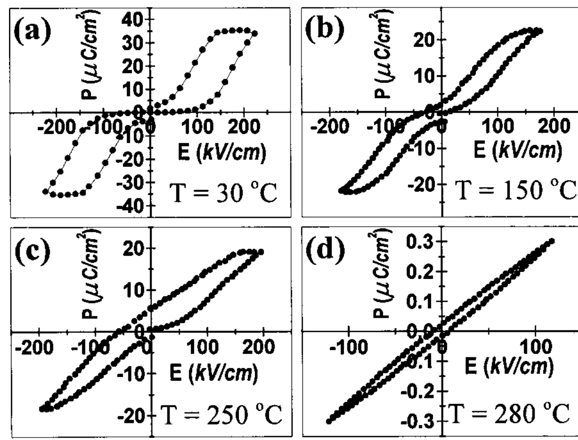

FIG. 1. Temperature-dependent polarization of $PbZrO_3$ thin films.

verse process were 84 and 156 kV/cm, respectively. As the temperature of the sample increased, the PZ films gradually started losing the double hysteresis behavior [Fig. 1(b)]. A single hysteresis loop, similar to that normally observed in a ferroelectric thin film, was observed near the Curie-transition temperature of the PZ single crystal [Fig. 1(c)]. This single-loop behavior could be attributed to the presence of an intermediate ferroelectric phase in PZ. The films exhibited a slim linear loop indicating a paraelectric phase at 280 °C [Fig. 1(d)].

The variation of dielectric constant and the associated dissipation factor with temperature was also studied. The room-temperature dielectric constant was 220 with a dissipation factor of 0.02 at a frequency of 100 kHz. The value of the dielectric constant obtained in the present study was in good agreement with the earlier reports on PZ thin films processed by other deposition techniques.[8] Also, this value of the dielectric constant was found to be larger than the bulk ceramic.[9,10] This difference in the reported values could be due to the grain–grain-boundary interaction in the polycrystalline materials, which in turn is related to the disparity in the conductivity ranges between the grain and the grain boundaries.

The temperature variation of the dielectric constant is plotted in Fig. 2. The observed dielectric phase transition temperature was found to be slightly higher than the bulk PZ ceramic, which could be attributed to the finer grain size of the PZ thin film that affects the surface-to-volume energy.[11] The accumulation of space charge near the film–electrode and/or grain-boundary interfaces, similar to a blocking electrode with heat dissipation during the phase transition process, may be assumed responsible for such behavior. However, Raman spectroscopy results of these films favor the bulk nature of the phenomena involved in the dielectric phase transition.

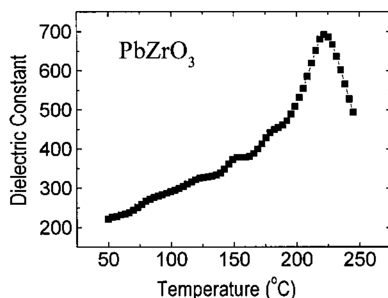

FIG. 2. Dielectric constant variation with temperature.

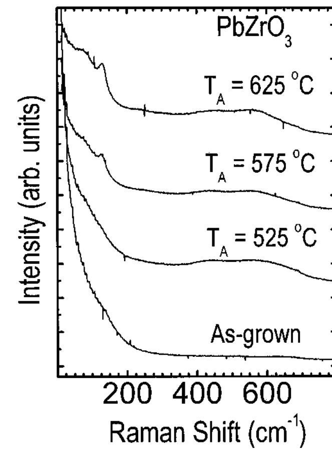

FIG. 3. Room-temperature unpolarized Raman spectra of as-grown and annealed $PbZrO_3$ thin films.

At room temperature, $PbZrO_3$ has an orthorhombic structure belonging to the space group D_{2h}^9.[12] Raman spectra from single-crystal PZ have shown certain external modes in the low-frequency region ($\nu < 100\ \mathrm{cm}^{-1}$) related to Pb lattice modes.[13] In the high-frequency region, internal modes related to certain polyatomic groups of the material appeared in the spectra. Based on the single-crystal work, the bands at 204 and 232 cm^{-1} have been associated with Zr–O bonding; the bands at 285, 330, and 344 cm^{-1} have been assigned to ZrO_3 torsions; and those at 501 and 532 cm^{-1} are due to the Zr–O stretching.[14] The room-temperature Raman spectra from the as-grown PZ film and those annealed at different temperatures are shown in Fig. 3. The as-grown film shows its amorphous nature. Annealing this film at higher temperatures results in orthorhombic PZ, indicating the best crystallization in the 625 °C annealed film. The low-frequency modes that have been observed in the Raman spectra of bulk material were not observed from these films. Additionally, weak and broad bands appear in the high-frequency region. This is due to less scattering volume and film–substrate interactions in the present films.

The existence of two phase transitions and the intermediate ferroelectric phase between the antiferroelectric and paraelectric phase in PZ has been evidenced from x-ray diffraction and neutron scattering investigations.[15,16] Light scattering in single-crystal PZ was studied in the vicinity of the intermediate phase.[14] However, no such information of phase transitions exists for thin films of PZ. The temperature-dependent Raman spectra of the PZ films are shown in Fig. 4. A sharp mode at about 136 cm^{-1} softens noticeably with increasing temperature. The frequency shift with temperature for this mode is shown in the inset of Fig. 4 after fitting the peak with a damped harmonic-oscillator-type phonon function corrected for the Bose–Einstein factor. The decreasing mode intensity with increasing temperature reflects a phase transition near 250 °C. This mode has been associated with the antiferroelectric (orthorhombic) to ferroelectric (rhombohedral) phase transition at 234 °C in PZ single crystal[17] and $PbZr_{0.95}Ti_{0.05}O_3$ ceramics.[18] The low-frequency ($\nu < 100\ \mathrm{cm}^{-1}$) PZ modes are very sensitive to temperature and

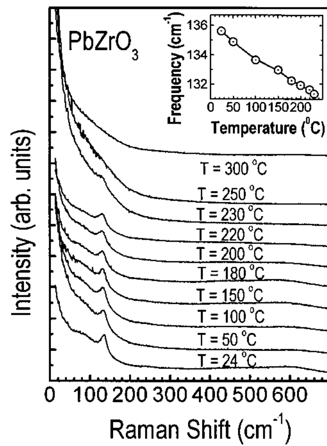

FIG. 4. Raman spectra at different temperatures for a $PbZrO_3$ film annealed at 625 °C. Inset shows the frequency variation of the 136 cm^{-1} mode.

reflect a ferroelectric rhombohedral to paraelectric cubic phase at about 245 °C in bulk material.[17,18] These modes were not resolved in the Raman spectra of the PZ films due to quasielastic scattering. The changes near the rhombohedral to cubic phase transition temperature, therefore, are not distinct in the film spectra. However, these films show a ferroelectric hysteresis near 250 °C that indicates the presence of an intermediate phase in the material. Kojima and Dong[18] explained the presence of high-frequency Raman modes (above the transition temperature) of $PbZr_{0.95}Ti_{0.05}O_3$ ceramics in terms of defects and local distortions near the grain boundaries. No high-frequency Raman band was detected above 250 °C in our films, which indicates a microlevel homogeneity of the material. The temperature-dependent micro-Raman results, therefore, confirm the intermediate ferroelectric phase as observed from polarization measurements.

In summary, temperature-dependent dielectric and polarization studies were performed on pulsed-laser-deposited PZ thin films. The films exhibited a clear temperature-dependent phase transition from the antiferroelectric-to-paraelectric state through a ferroelectric phase. The phase evolution and phase transition in these films were also studied by Raman spectroscopy. The temperature dependence of Raman spectra at a higher wave number confirms the existence of an intermediate ferroelectric phase in these films prior to the paraelectric phase.

This work was supported in part by Grant Nos. DAAG55-98-1-0012, NASA-NCC5-518, and NSF-DMR-9801759.

[1] T. Tani, J.-F. Li, D. Viehland, and D. A. Payne, J. Appl. Phys. **75**, 3017 (1994).
[2] S. S. N. Bharadwaja and S. B. Krupanidhi, Mater. Sci. Eng., B **64**, 54 (1999).
[3] N. G. Pai, B. Xu, and L. E. Cross, Integr. Ferroelectr. **22**, 501 (1998).
[4] B. Xu, N. G. Pai, Q. M. Wang, and L. E. Cross, Integr. Ferroelectr. **22**, 545 (1998).
[5] D. Berlincourt, H. H. A. Krueger, and B. Jaffe, J. Phys. Chem. Solids **25**, 659 (1964).
[6] Bernard Jaffe, Proc. IRE **49**, 1264 (1961).
[7] S. S. N. Bharadwaja and S. B. Krupanidhi, J. Appl. Phys. **86**, 5862 (1999).
[8] K. Yamakawa, S. T. McKinstry, J. P. Dougherty, and S. B. Krupanidhi, Appl. Phys. Lett. **67**, 2014 (1995).
[9] M. T. Lanagan, J. H. Kim, S.-J. Jang, and R. E. Newnham, J. Am. Ceram. Soc. **71**, 311 (1988).
[10] M. J. Haun, T. J. Harvin, M. T. Lanagan, Z. Q. Zhuang, S. J. Jang, and L. E. Cross, J. Appl. Phys. **65**, 3173 (1989).
[11] P. Buffat and J. P. Borel, Phys. Rev. A **13**, 2287 (1976).
[12] H. Fujishita, Y. Shiozaki, N. Achiwa, and E. Sawaguchi, J. Phys. Soc. Jpn. **51**, 3583 (1982).
[13] C. C. Nedelec, I. E. Harrad, J. Handerek, F. Brehat, and B. Wyncke, Ferroelectrics **125**, 483 (1992).
[14] A. E. Pasto and R. E. Condrate, J. Am. Ceram. Soc. **56**, 436 (1993).
[15] C. Cochran and A. Zia, Phys. Status Solidi **25**, 273 (1968).
[16] R. W. Whatmore and A. M. Glazer, J. Phys. C **12**, 1505 (1979).
[17] K. Roleder, G. E. Kugel, J. Handerek, M. D. Fontana, C. Carabatos, M. Hafid, and A. Kania, Ferroelectrics **80**, 161 (1988).
[18] S. Kojima and X. Dong, Jpn. J. Appl. Phys., Part 1 **37**, 5400 (1998).