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Phase transitional studies of polycrystalline $Pb_{0.4}Sr_{0.6}TiO_3$ films using Raman scattering

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$Pb_{0.4}Sr_{0.6}TiO_3$ films with submicron size grains have been prepared on Pt substrates by the metalorganic decomposition method. X-ray diffraction analysis reveals that the films are polycrystalline with a perovskite crystal structure and negligible tetragonal splitting at room temperature. The room temperature Raman spectrum, however, shows all the characteristic phonon modes of a tetragonal ferroelectric phase. These modes lose their intensity with an increase in temperature but persist even up to 150 °C. This is in agreement with the dielectric permittivity versus temperature data which show a broad peak–room temperature, and ferroelectric hysteresis persisting up to ~140 °C. Both Raman and dielectric data are interpreted as due to the presence of a distribution of phases in the film perhaps caused by a variation in Pb content along the film thickness and/or near grain boundary regions.
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INTRODUCTION

Ferroelectric thin films have potential in microelectronics applications, including memory devices, sensor technologies, and optoelectronic devices.[1,2] Thin films of lead titanate $PbTiO_3$ (PT) and its related solid solutions offer key advantages for a wide variety of applications.[3,4] The mixed system of lead strontium titanate, i.e., $Pb_{1-x}Sr_xTiO_3$ (PST) is very similar to the barium strontium titanate (BST) system in that the Curie temperature for the cubic to tetragonal transition can be adjusted over an exceedingly large temperature range by adjusting the Pb to Sr ratio. Solid solutions of PST in the bulk form have been studied for $0 \leqslant x \leqslant 1$ and the ferroelectric to paraelectric transition temperature has been shown to decrease linearly with an increase in Sr concentration.[5,6] With a Pb:Sr ratio of 4:6 the Curie temperature (T_c) of the PST bulk material is found to be around room temperature.

Raman spectroscopy has been a valuable technique in studying ferroelectric materials because of the close relationship between ferroelectricity and lattice dynamics. PT has been a textbook example of a displacive-type ferroelectric and has been well studied by Raman spectroscopy.[7–11] The lowest E(1TO) and A_1(1TO) lines shift continuously to smaller wave number as the temperature increases from 20 °C to 495 °C and then abruptly disappear with a transition to the cubic phase similar to any first-order line. The temperature dependence of the Raman spectra of ceramic bulk and thin-film samples of polycrystalline $Ba_{1-x}Sr_xTiO_3$ has been used to estimate the ferroelectric to paraelectric transition temperatures.[12] It has been shown that for BST bulk ceramic samples the T_c values from Raman measurements coincide with the corresponding T_c values as determined by the anomaly in the dielectric constant versus temperature data. On the other hand, temperature dependent Raman studies on BST thin film samples have shown consistently higher T_c values than corresponding BST bulk samples of the same composition. The discrepancy in the T_c values has been attributed to intergrain stresses arising from grain boundaries in the thin film samples, which prevent a complete phase transformation from the tetragonal to cubic phase as in the bulk ceramics.[13]

In this paper we report the temperature dependent (−80 °C to 350 °C) Raman spectra and the temperature dependence of dielectric permittivity and the spontaneous polarization of $Pb_{0.4}Sr_{0.6}TiO_3$ films. There have been no temperature dependent Raman studies reported on the $Pb_{1-x}Sr_xTiO_3$ mixed system in either bulk or thin film form. We demonstrate that Raman scattering can be used as an alternate easy tool to probe the ferroelectric properties without a need for additional sample preparation such as the deposition of electrodes and the contacts necessary for electrical measurements.

EXPERIMENT

The $Pb_xSr_{1-x}TiO_3$ films were prepared on Pt substrates using the metalorganic decomposition (MOD) method. Separate metalorganic precursor solutions of PT and ST were

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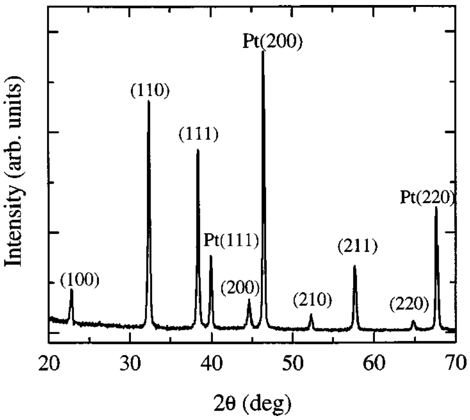

FIG. 1. XRD pattern of $Pb_{0.4}Sr_{0.6}TiO_3$ on a Pt substrate.

prepared using titanium (IV) 2-ethylhexoxide (liquid), lead (II) neodecanoate (60% in naphthalene), and strontium neodecanoate (solid) dissolved in xylene. These solutions were combined in proper proportions to obtain the desired stoichiometric balance of lead to strontium. The $Pb_{0.4}Sr_{0.6}TiO_3$ films were prepared by dispensing the metalorganic solution onto substrates, which were then spun at a rate of 4000 rpm for 15 seconds. After each coat, the film was pyrolized at 550 °C for 1 minute in air. Multiple coatings were made to obtain the desired thickness. Final annealing of the sample was done at 950 °C for 60 minutes in air. The details of electrical measurements have been described previously.[12,13] The Raman spectra were recorded using a single monochromator (Instruments SA-Triax 550), equipped with conventional optics, holographic supernotch filters, and a charge coupled device detector. A 514.5 nm excitation line was used to record spectra in a nearly back-scattering geometry.

X-ray diffraction analysis of $Pb_{0.4}Sr_{0.6}TiO_3$ film showed that the films are polycrystalline in nature with a perovskite crystal structure at room temperature and no observable tetragonal diffraction peak splitting ($c/a \sim 1$) as shown in Fig. 1. Scanning electron microscopy revealed that the film thickness ~ 4 μm (cross-sectional, figure not shown) with the average grain size ~ 150 nm, showing a significant amount of grain boundary regions (see Fig. 2). The dielectric permittivity versus temperature graph (Fig. 3) shows a broad peak around room temperature, indicating a rather diffuse phase transition, whereas ferroelectric hysteresis persists up to ~ 140 °C.

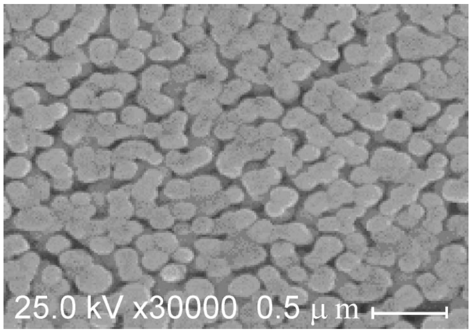

FIG. 2. Scanning electron micrograph of $Pb_{0.4}Sr_{0.6}TiO_3$ film.

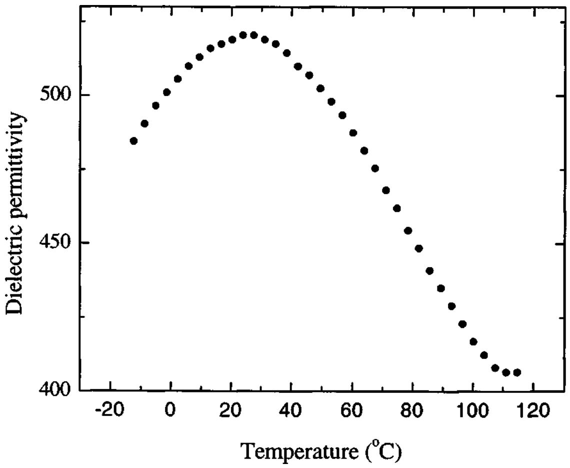

FIG. 3. Temperature dependence of dielectric permittivity (normalized to vacuum) of $Pb_{0.4}Sr_{0.6}TiO_3$.

RESULTS AND DISCUSSION

Figure 4 shows the Raman spectra of $Pb_{0.4}Sr_{0.6}TiO_3$ as a function of temperature. The symmetry assignments for the observed optical phonons have been made based on the earlier work on PT by Foster and co-workers, and Burns and Scott[7,8] and also by the observed changes in the Raman spectra of PST films at room temperature, as a function of Sr concentration (x).[14] As x increases, the separation between the higher E(TO) and A_1(TO) modes decreases and they seem to merge into a single broad band for $x=0.6$, reflecting a cubic structure. According to the Raman selection rules all the modes should disappear for the cubic phase. However,

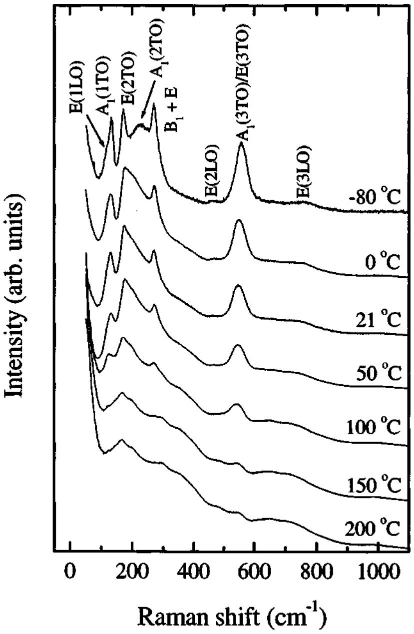

FIG. 4. Raman spectra of $Pb_{0.4}Sr_{0.6}TiO_3$ film recorded between −80 °C and 200 °C.

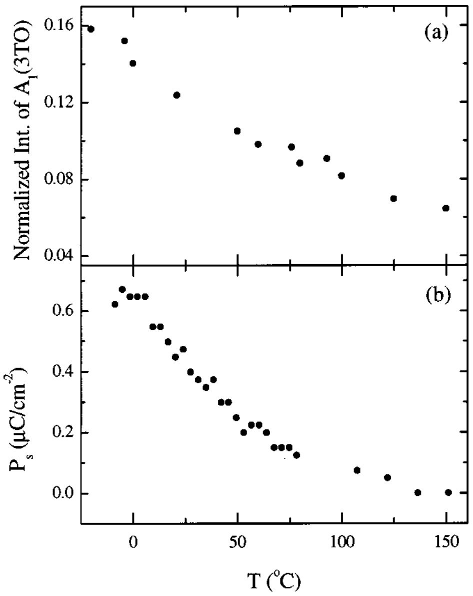

FIG. 5. Temperature dependence of (a) normalized integrated intensity of the A_1(3TO)/E(3TO) phonon peak, and (b) spontaneous polarization measured from ferroelectric hysteresis loops.

we observe all the phonon modes in $Pb_{0.4}Sr_{0.6}TiO_3$ corresponding to a tetragonal perovskite ferroelectric phase. This indicates that the film is tetragonal at the microscopic scale at which the Raman scattering probes the structure, but with an average ''cubic'' structure at the coherence length of the x-rays, perhaps due to large Debye–Waller factors.

The intensity of the Raman modes decreases with the increase in temperature (Fig. 4), but the intensity of the modes does not vanish even at temperatures well beyond 150 °C. This is consistent with the observation of a diffuse phase transition in the mixed perovskites, where there is more than one type of atom per crystallographic site.[15,16] The statistical composition fluctuations, which must occur because different cations can occupy crystallographically equivalent sites, are believed to be the reason for diffuse transitions.[17] In addition, several of the modes in the Raman spectrum show some softening with an increase in temperature. Unlike the soft phonon mode behavior of A_1(1TO) and E(1TO) in PT system,[7,8,10] the lowest A_1(1TO) mode observed at $\sim$130 cm^{-1}, does not show significant softening.

Various Raman modes in the spectrum between 50–1000 cm^{-1} were fitted using a damped harmonic oscillator model for line shapes at various temperatures.[10] As the temperature is increased from -80 °C, the splitting between the E(2TO) and A_1(2TO) modes decreases from 55 cm^{-1} to 35 cm^{-1} at room temperature. At higher temperatures the splitting remains constant. We have chosen, however, the A_1(3TO)/E(3TO) mode observed at $\sim$550 cm^{-1} to investigate as a function of temperature, as this mode is well isolated in the spectrum compared to lower frequency region. This mode softens by $\sim$15 cm^{-1} over a temperature range of -80 °C to 100 °C, and merges into a broad continuum (second order Raman scattering) for temperatures above 100 °C. Figure 5(a) shows the temperature dependence of the normalized integrated intensity (i.e., the fractional area of the peak to the total area of the spectrum between 50–1000 cm^{-1}) of A_1(3TO)/E(3TO) phonon mode, along with the spontaneous polarization measured from ferroelectric hysteresis loops [Figs. 5(b)]. Clearly both sets of data exhibit a gradual decrease with increasing temperature, without any discontinuity in slope indicating a gradual elimination of tetragonal phase in favor of cubic form. This observation suggests that the sample has a distribution of phases with different phase transformation temperatures. The presence of a distribution of tetragonal phases in film could be due to compositional changes near the grain boundary regions in comparison to grain interior and/or variation of Pb concentration along the growth direction in the film due to its volatility during the high temperature annealing process. In an earlier study with potassium tantalum niobate films, prepared by MOD process, a gradient in potassium composition was observed along the film normal which led to an up or down shift in the hysteresis loops.[18] In our recent studies on PST films,[19] a similar shift in the hysteresis loops has been observed, suggesting a Pb composition gradient along the film normal.

In summary, MOD grown $Pb_{0.4}Sr_{0.6}TiO_3$ films exhibit a diffuse type of phase transition. The dielectric constant versus temperature plot shows a broad peak centered around room temperature. The x-ray diffraction shows peaks that are characteristic of the cubic phase whereas the Raman scattering shows the characteristic phonon modes of the tetragonal phase. The persistence of the hysteresis loops at and well above room temperature also confirms the presence of tetragonal phase. The x-ray data is interpreted as due to the film being tetragonal at the microscopic level with in an average ''cubic'' structure at the coherence length of the x rays. Both Raman and dielectric data are interpreted as due to the presence of a distribution of phases in the film caused by the variation of Pb content near grain boundary regions and/or the presence of a composition gradient along the film normal resulting from the high temperature annealing process.

ACKNOWLEDGMENTS

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