Investigation in SrTi'O IND.3'-CaTi'O IND.3'-PbTi'O IND.3' ternary thin films by dielectric properties and Raman spectroscopy
Investigation in SrTiO$_3$-CaTiO$_3$-PbTiO$_3$ ternary thin films by dielectric proprieties and Raman spectroscopy

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Abstract Dielectric and Raman scattering experiments were performed on polycrystalline Pb$_{1-x-y}$Ca$_x$Sr$_y$TiO$_3$ thin films as a function of temperature. Temperature-dependent dielectric measurements revealed a decreasing ferroelectric-to-paraelectric phase transition temperature and peak dielectric permittivity showed a broad phase transition near room temperature with increasing levels of CaO$_{12}$ and SrO$_{12}$ clusters. Therefore, for higher levels of substitution, the possible random position of the CaO$_{12}$ and SrO$_{12}$ clusters leads to a diffuse state. At 100 kHz, the ferroelectric-to-paraelectric phase transition temperatures were 633, 495 and 206 K for PCST$_{90}$ (Pb$_{0.90}$Ca$_{0.05}$Sr$_{0.05}$TiO$_3$), PCST$_{70}$ (Pb$_{0.70}$Ca$_{0.15}$Sr$_{0.15}$TiO$_3$) and PCST$_{30}$ (Pb$_{0.30}$Ca$_{0.35}$Sr$_{0.35}$TiO$_3$) thin films, respectively. The evolution of the Raman spectra was also studied as a function of temperature. The temperature dependence of the E(1TO) soft mode frequencies was used to characterize the phase transition. Raman peaks were observed above the ferroelectric-to-paraelectric phase transition temperature, although all optical modes should be inactive in Raman scattering. The origin of these modes was interpreted as a breakdown of the local cubic symmetry by the random distribution of CaO$_{12}$ and SrO$_{12}$ clusters.

Keywords Thin films · Phase transition · Ferroelectric · Raman spectroscopy

1 Introduction

Ferroelectric thin films continue to attract much attention in theoretical and experimental investigations due to their interesting practical applications in memory devices, infrared sensors, and piezoelectric sensors and actuators [1–3].

Despite the existence of various compound ferroelectric thin films, the main advantage of the PbTiO$_3$ perovskite structure is that it can readily display a variety of structural phase transitions. Such transitions can be achieved by replacing the A (Pb$^{2+}$) and/or (Ti$^{4+}$) B elements by other A’ and/or B’ elements in AO$_{12}$ and/or BO$_6$ sites with different radii and charges, thereby forming other types of compounds, i.e., PbZr$_{1-x}$Ti$_x$O$_3$ (PZT), Pb$_{1-x}$Ca$_x$TiO$_3$ (PCT), Pb$_{1-x}$Sr$_x$TiO$_3$ (PST), Pb$_{1-x}$Ba$_x$TiO$_3$ (PBT), PbNb$_{0.04}$Zr$_{0.28}$Ti$_{0.68}$O$_3$ (PNZT), Pb$_{1-x}$La$_x$Zr$_{1-y}$Ti$_y$O$_3$ (PLZT), and Pb$_{0.25}$Ba$_x$Sr$_{0.75-y}$TiO$_3$ (PBST) [4–11]. It is also interesting to note that many ferroelectric materials, including PbTiO$_3$, exhibit relaxor behavior as a function of the type and concentration of dopant. This phenomenon is manifested by a strong
frequency dispersion of the dielectric constant at temperatures around the phase transition temperature [12, 13]. These materials show a relaxation-type phase transition. Lead magnesium niobate (PMN), lead zinc niobate (PZN), Pb(Sc1/2Nb1/2)O3 (PSN) and their solid solutions with lead titanate (PT) are the most widely studied relaxor materials [14–18]. In addition, with the increasing emphasis on ferroelectric thin films for various applications, especially memory storage devices, it is becoming increasingly important to understand the phenomenon of phase transitions in ferroelectric thin films. Vanderbilt and Zhong [19] applied the first-principles theory in a theoretical study of Pb(Sc1/2Nb1/2)O3 (PSN) and their solid solutions with lead magnesium niobate (PMN), lead zinc niobate (PZN), titanium (PT) are the most widely studied relaxor materials [14–18]. In addition, with the increasing emphasis on ferroelectric thin films for various applications, especially memory storage devices, it is becoming increasingly important to understand the phenomenon of phase transitions in ferroelectric thin films. Vanderbilt and Zhong [19] applied the first-principles theory in a theoretical study of Pb(Sc1/2Nb1/2)O3 (PSN) and their solid solutions with lead magnesium niobate (PMN), lead zinc niobate (PZN), titanium (PT) are the most widely studied relaxor materials [14–18]. In addition, with the increasing emphasis on ferroelectric thin films for various applications, especially memory storage devices, it is becoming increasingly important to understand the phenomenon of phase transitions in ferroelectric thin films. Vanderbilt and Zhong [19] applied the first-principles theory in a theoretical study of Pb(Sc1/2Nb1/2)O3 (PSN) and their solid solutions with lead magnesium niobate (PMN), lead zinc niobate (PZN), titanium (PT) are the most widely studied relaxor materials [14–18].

Recently, Sun et al. [20] reported on the preparation and characterization of Pb0.25Ba0.75TiO3 thin films with x = 0.05, 0.1, 0.15 and 0.2 on Pt/Ti/SiO2/Si substrates, pointing out that the structural, microstructural and electrical properties were strongly dependent on the Ba content. Currently, special attention focuses on the preparation of ternary compounds using materials with a perovskite structure. For example, Zhang et al. [20] reported on the preparation and characterization of BaTiO3–CaTiO3–SrTiO3 (BSCT) ceramics, while Li et al. [21] analyzed the effect of (Ca1–2xNa2x)TiO3 A-site substituted perovskite compounds on the structure of the phase transition at room temperature. Abdelmoula et al. [22] showed that the simultaneous substitution of Ba2+ ions in the A-site by Sm3+ and Na+ ions had a significant effect on the dielectric behavior. These authors reported that the material showed a classic ferroelectric phase transition at 0 ≤ x ≤ 0.10 and x ≥ 0.50, while a relaxor ferroelectric phase transition occurred at 0.20 ≤ x < 0.40.

So far no detailed study aimed at investigating the temperature dependence of the dielectric permittivity and Raman spectra of Pb1–x–yCa2Sr2TiO3 thin films has been reported.

2 Experimental procedure

Our procedure for synthesizing Pb1–x–yCa2Sr2TiO3 (abbreviated as PCST) thin films consisted of producing a polymeric resin using the soft chemistry method known as the polymeric precursor route. Details of the preparation method can be found in the literature [23].

The viscosity of the deposition solutions was adjusted to 12 mPa/s. After preparing the polymeric precursor, the solution was spin-coated onto 10 × 10 mm substrates [Pt/Ti/SiO2/Si] using a commercial spinner operating at 7000 rev./min for 20 s (spin-coater KW-4B, Chemat Technology) and equipped with a syringe filter to avoid particulate contamination. A two-stage heat treatment was carried out as follows: initial heating at 400 °C for 4 h at a heating rate of 5 °C/min in an air atmosphere to pyrolyze the organic materials, followed by heating at 600 °C for 4 h at a heating rate of 5 °C/min for crystallization. These steps were repeated four times to obtain the desired thickness of about 180–240 nm.

Electrical measurements were taken of PCST90 (Pb0.90Ca0.05Sr0.05TiO3), PCST70 (Pb0.70Ca0.15Sr0.15TiO3) and PCST30 (Pb0.50Ca0.35Sr0.35TiO3) thin films with thicknesses of 180, 230 and 240 nm, respectively. The temperature-dependent dielectric constant of the thin films was measured in a metal–ferroelectric–metal configuration and the films were characterized using a G"{u}nth Instek LCR 819 m at temperatures ranging from 50 to 665 K. For these measurements, circular Au electrodes with an area of approximately 4.9 × 10–2 mm2 were deposited (using a shadow mask) by evaporation on the surfaces of the heat-treated films, serving as top electrodes. The measurements of the temperature-dependent dielectric constant of the PCST30 thin films were taken at temperatures varying from 50 to 300 K, using a closed-cycle helium cryostat.

The Raman measurements were taken with a T-64000 Jobin–Yvon triple-monochromator coupled to a charge-coupled detector (CCD). An optical microscope with a 50X objective was used to focus the 514.5 nm line of a Coherent Innova 70 argon laser onto the sample. The laser output power was kept at about 20 mW. The thin films were mounted in a TMS 93 furnace (Linkam Scientific Instruments Ltd) with controlled temperature in the range of 298–773 K. In addition, low temperature Raman spectra were obtained using a closed-cycle helium refrigerator for the measurements in the 10–300 K temperature range.

3 Results and discussion

The phase transition temperature of the various PCST thin films is shown in Fig. 1. Several interesting features are apparent from the dielectric constant (ε) versus temperature curves of the PCST90, PCST70 and PCST30 thin films with different Ca2+ and Sr2+ concentrations. As can be seen (see Fig. 1), the phase transition of the PCST90 thin film from ferroelectric to paraelectric was rather sharp and occurred at around 633 K. However, there is a tendency for the maximum peak of the dielectric constant to broaden as the concentration of in Ca2+ and Sr2+ increase in the A-site, indicating that the phase transition may be of a diffuse type close to the transition temperature. Recently, Ke et al. [23] used a Lorentz-type relation to describe the dielectric permittivity of the normal ferroelectric with or without diffuse phase transition in perovskite ceramics samples of the type Ba(ZrxTi1–x)O3, PMN and BaTiO3.
It is known that a sharp or diffuse phase transition in material with an ABO$_3$ perovskite structure is more dependent on the electronic charge density in the octahedral and dodecahedral sites, BO$_6$ and AO$_{12}$, respectively. In all the PCST thin films, the A-site showed a 12-fold oxygen coordination containing three types of PbO$_{12}$, CaO$_{12}$ and SrO$_{12}$ clusters. The random distribution of these clusters in the A-site leads to heterogeneity of the nanoscale composition in thin films, thus inducing a broadening of the phase transition peak. As Fig. 1 shows, the PCST90 and PCST70 thin films displayed a Curie temperature above room temperature, i.e., 633 and 495 K, respectively, indicating their ferroelectric nature at room temperature. On the other hand, the PCST30 thin films exhibited a stronger signature of typical diffuse phase transition behavior, with its maximum at a temperature of about 206 K. This temperature is related to the ferroelectric-to-paraelectric phase transition temperature.

Figure 2 shows the characteristic dielectric permittivity-bias curves of the PCST30 thin films measured at around 50 K. The curve shows typical hysteresis behavior, indicating that the dielectric thin film has a ferroelectric property at lower temperatures. Furthermore, the hysteresis behavior increased as the temperature decreased, indicating that the dipolar clusters continued to grow during cooling to room temperature, and suggesting that the disorder of the CaO$_{12}$, SrO$_{12}$ and PbO$_{12}$ localized in the AO$_{12}$-site favors the randomization of the orientation of the Ti–O dipolar cluster. These randomly distributed domains then cause a large range of phase transition temperatures.

On the other hand, PCST30 thin films have a Curie temperature below room temperature, which is indicative of the paraelectric nature of PCST30 thin films at room temperature. Shao et al. [24] also reported a diffuse phase transition for complex Pb$_{0.40}$Sr$_{0.60}$Zr$_{0.52}$Ti$_{0.48}$O$_3$ (PSZT) thin films on Pt/Si substrates, with a maximum at a temperature of 204 K. By comparison with previously published results of the temperature-dependence of the dielectric constant of Pb$_{1-x}$Ca$_x$TiO$_3$ and Pb$_{1-x}$Sr$_x$TiO$_3$ films, we also identified a diffuse-type phase transition as a function of Ca and Sr content [12, 25–30]. Table 1 summarizes the values of the phase transition temperature obtained for the PCST, PCT and PST thin films.

It is a well known fact that perovskite-type relaxor ferroelectric thin films are characterized by the diffuse nature of their ferroelectric-to-paraelectric phase transition and by their frequency-dependent transition temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase transition temperature (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$<em>{0.90}$Ca$</em>{0.05}$Sr$_{0.05}$TiO$_3$</td>
<td>650</td>
<td>This work</td>
</tr>
<tr>
<td>Pb$<em>{0.70}$Ca$</em>{0.15}$Sr$_{0.15}$TiO$_3$</td>
<td>570</td>
<td>This Work</td>
</tr>
<tr>
<td>Pb$<em>{0.50}$Ca$</em>{0.30}$Sr$_{0.20}$TiO$_3$</td>
<td>206</td>
<td>This Work</td>
</tr>
<tr>
<td>Pb$<em>{0.90}$Ca$</em>{0.10}$TiO$_3$</td>
<td>688</td>
<td>27</td>
</tr>
<tr>
<td>Pb$<em>{0.80}$Ca$</em>{0.20}$TiO$_3$</td>
<td>623</td>
<td>27</td>
</tr>
<tr>
<td>Pb$<em>{0.70}$Ca$</em>{0.30}$TiO$_3$</td>
<td>533</td>
<td>27</td>
</tr>
<tr>
<td>Pb$<em>{0.60}$Ca$</em>{0.40}$TiO$_3$</td>
<td>463</td>
<td>27</td>
</tr>
<tr>
<td>Pb$<em>{0.70}$Sr$</em>{0.30}$TiO$_3$</td>
<td>573</td>
<td>28</td>
</tr>
<tr>
<td>Pb$<em>{0.50}$Sr$</em>{0.50}$TiO$_3$</td>
<td>413</td>
<td>29</td>
</tr>
<tr>
<td>Pb$<em>{0.30}$Sr$</em>{0.70}$TiO$_3$</td>
<td>288</td>
<td>30</td>
</tr>
<tr>
<td>Pb$<em>{0.70}$Sr$</em>{0.30}$TiO$_3$</td>
<td>573</td>
<td>31</td>
</tr>
<tr>
<td>Pb$<em>{0.60}$Sr$</em>{0.40}$TiO$_3$</td>
<td>463</td>
<td>32</td>
</tr>
<tr>
<td>Pb$<em>{0.40}$Sr$</em>{0.60}$TiO$_3$</td>
<td>343</td>
<td>32</td>
</tr>
</tbody>
</table>
Therefore, Fig. 3 shows the temperature dependence of the dielectric constant of PCST30 thin films at different frequencies. Figure 3 shows the value of the dielectric constant increasing gradually to a maximum value as the temperature rises to the phase transition temperature and thereafter decreasing, indicating a phase transition. For the PCST30 thin films, the dielectric constant maximum and the corresponding temperature maximum were independent of the measured frequency. This particular property is typical of classical ferroelectric thin films. All the compositions showed similar characteristics, indicating that these compounds are of the classical ferroelectric type. However, for typical relaxor, there is a strong frequency dependence of the temperature corresponding to maximum permittivity in agreement with the studies accomplished by Ke et al. [23].

Another important point about the PCST thin films is that their phase transition temperature shifted downward in response to simultaneous increases in randomly connected CaO12 and SrO12 clusters in the AO12 sites, which may be attributed to factors such as cluster size, coordination and configuration. As many researchers well know, the dipoles that allow for the ferroelectric effect in PbTiO3 perovskite occur through these slightly distorted TiO6 octahedral clusters, which give rise to polar macro, micro and nano-regions. In addition to the PbTiO3 perovskite structure, the stronger distortion of the octahedron lead to the high polarizability of PbO12 clusters and the possibility that they become strongly deformed in an electric field; hence, PbO12 clusters are strongly polar. The origin of this polarity is based on the partial alignment of local PbO12 clusters. These effects give rise to a highly distorted unit cell. Therefore, the presence of SrO12 and CaO12 clusters of different sizes and electronic configurations than the PbO12 cluster in the A-site perovskite structure caused an abrupt drop in the phase transition temperature. This effect on the phase transition temperature may be correlated with the contribution of new SrO12 and CaO12 clusters in the crystalline lattice, which induced: (1) a relative reduction of the unit cell volume; (2) consequently, a weaker distortion of the octahedron; and (3) formation of nonpolar clusters in which the long-range Ti–O dipoles disappear at room temperature.

To study the ferroelectric-to-paraelectric phase transition by Raman spectroscopy, Raman spectra of Pb1−x−y-CaxSr0.15TiO3 thin films were obtained at different temperatures, and the results are shown in Figs. 4, 5 and 6. An examination of Raman scattering profiles of PCST90...
and PCST70 thin films at 10 and 300 K reveals a qualitative similarity to the profiles observed in the PbTiO₃ thin films, showing all Raman active transversal and longitudinal optical modes, as expected for a tetragonal structure (P4 mm space group). Unlike the PCST90 and PCST70, the PCST30 exhibits only broad Raman peaks, indicating a high degree of local disorder from low to high temperatures. Furthermore, a important signature of the tetragonal ferroelectric-to-cubic paraelectric phase transition is the softening of the lowest-frequency mode (the E₁TO soft mode), whose frequency tends to zero as it approaches the Curie temperature. For PCST90 and PCST70, these modes, located at 89 and 83 cm⁻¹ at 10 K, respectively, clearly show a red shift indicating increasing temperature, as illustrated in Figs. 4 and 5. The temperature dependence of the square of the soft mode frequency is shown in Fig. 7. By extrapolating these curves, the transition temperature was estimated to be about 650 and 520 K for PCST90 and PCST70, respectively. In addition, Torgashev et al. [31] reported that single-crystal samples of the Pb₀.₅₀Ca₀.₅₀TiO₃ solid solution undergoes two phase transitions at 392 K (T₁) and 452 K (T₂).

The effect of temperature on the all Raman modes of PCST90 and PCST70 is shown in Fig. 8. Two distinct behaviors can be identified in this figure: modes slightly sensitive to temperature changes—E(2TO), B₁ + E, E(2LO) + A(2LO), E(3TO)—and modes highly sensitive to temperature changes—A₁(3TO) and A₁(2TO)—showing a significant red shift to increasing temperature, a behavior normally attributed to the coupling of these modes with the E(1TO) soft mode. In the particular case of A₁(3TO) mode, both Ti and O ions move against Pb ions along the z direction in BO₆-type clusters [32]. Hence, the frequency of the mode may be affected by the contents of new CaO₁₂ and SrO₁₂-type clusters.

For temperatures above Tc, in which the optical modes should be inactive in Raman scattering, broad Raman bands are still visible for the three compositions. The presence of such Raman peaks in the globally averaged cubic or pseudocubic phase can be attributed to local structural disorder. This effect has been observed frequently in materials with a high degree of chemical disorder, particularly in short-range localized polar entities arising from randomly distributed CaO₁₂ and SrO₁₂ clusters. This reflects the fact that more than one kind of dodecahedral cluster competes for the A-site in PbTiO₃ (for example, PbO₁₂, CaO₁₂ and SrO₁₂). These randomly connected CaO₁₂ and SrO₁₂ clusters destroy the perfect local cubic symmetry, causing the breakdown of Raman selection rules. Forbidden polar modes were also observed in the PCST30 thin film paraelectric phase far above the phase transition temperature, although they were very weak at room temperature and the second-order contribution dominated. Therefore, in the case of the PCST30 thin films, the presence of Raman lines should be attributed to the non-cubic local structure at and below room temperature. This distorted or noncubic local structure was not detected by XRD and FT-IR analysis, but it was visible in the Raman spectra through the presence of symmetry-forbidden Raman lines. Furthermore, in the case of PCST30, X-ray diffraction and FT-IR analyses at room temperature suggested that the structural phase was most likely the SrTiO₃ perovskite cubic structure. Also, in the case of PCST30 thin films, an analysis of the evolution of the Raman spectra depicted in Figs. 6 and 9 indicates that all the Raman lines were present and remained almost temperature-independent in
the 10–300 K range. Further investigations are needed to understand the effects in cosubstituted PCST30 multi-clusters in order to determine the phase transition temperature through Raman studies.

Figure 10 shows a phase diagram for the PCST90, PCST70 and PCST30 thin films based on the results of the dielectric and Raman measurements as a function of temperature.

4 Conclusions

In summary, we demonstrated the strong influence of CaO_{12} and SrO_{12} clusters on the temperature-dependent structural and dielectric properties of Pb_{1-x-y}Ca_{x}Sr_{y}TiO_{3} (PCST) thin films. The dielectric study revealed that the dielectric permittivity peak in PCST90 and PCST70 thin films is fairly sharp, unlike that of PCST30 thin films, where the phase transition becomes diffuse without
frequency dependence: this is a typical ferroelectric-to-paraelectric phase transition. The diffuseness increased with increasing contents of CaO$_{12}$ and SrO$_{12}$ clusters in the dodecahedral-site. This phenomenon is likely related with the existence of short-range localized polar domains, since the possible random positions of CaO$_{12}$ and SrO$_{12}$ clusters in the A-site favor randomization of the octahedral dipoles, leading to nanoscale dipolar heterogeneity. The phase transition temperature decreases with increasing CaO$_{12}$ and SrO$_{12}$ cluster contents due to the decreasing polarity of these clusters.

Raman spectroscopy was employed to study the effect of the substitution of CaO$_{12}$ and SrO$_{12}$ clusters on the structural properties as a function of temperature. Structural analyses of the PCST thin films by Raman spectroscopy revealed a decrease in the tetragonal distortion of the unit cell with an increase in CaO$_{12}$ and SrO$_{12}$ cluster content. Accordingly, a decrease in the ferroelectric phase transition temperature was detected by temperature-dependent Raman spectroscopy. The phase transition temperature of the PCST90 and PCST70 thin films was estimated using the softening of the $E$(TO) mode of the tetragonal phase. Unlike the dielectric permittivity measurements, the PCST30 thin films showed a diffuse Raman scattering response, making it difficult to estimate the phase transition temperature. In the PCST30 thin films, the substitution of CaO$_{12}$ and SrO$_{12}$ clusters resulted in a Raman spectrum with broad bands, which are characteristic of a highly structured locally disordered material.

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References