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A comparative Raman study of $0.65(\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3) - 0.35(\text{PbTiO}_3)$ single crystal and thin film

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Abstract. We report a comparative Raman study of $0.65(\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3) - 0.35(\text{PbTiO}_3)$ (PMN-0.35PT) single crystal and thin film. Raman spectra investigation indicates a change in bulk from the high temperature cubic to the tetragonal phase and then to the low temperature Mc monoclinic phase. The transition temperatures are in good agreement with the ones previously observed by dielectric measurements on the same sample. In contrast, we observe no phase transition to the monoclinic phase in the PMN-0.35PT 4000 Å thick film and only a cubic to tetragonal diffuse transition has been determined at high temperature. The enhanced stability of the tetragonal phase and the absence of low temperature monoclinic phase have been attributed to the in plane strain.

1 Introduction

The solid solution $(1 - x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3 - x\text{PbTiO}_3$ (PMN- x PT) constituted by the relaxor PMN and the ferroelectric PT presents fascinating electromechanical properties [1,2]. Such high properties are linked to a complex phase diagram [2]. As the parent compound PMN, PMN- x PT remains pseudo-cubic and relaxor for $x < 0.1$. Rhomboedral and tetragonal phase are observed on increasing titanium content (respectively for $x < 0.3$ and $x > 0.38$) while PMN- x PT is cubic at high temperatures whatever the PT content. A monoclinic phase has been discovered at the morphotropic phase boundary which acts as a structural “bridge” between the rhomboedral phase and the tetragonal phase [3–5]. For unpoled PMN-0.35PT a Mc monoclinic phase has been demonstrated by Kiat et al. [5] (polarization confined in the (101) plane). Such low symmetry is responsible of the ultra high electromechanical response through a mechanism of polarization rotation under an applied electric field [6]. The piezoelectric constant for PMN-0.35PT is one order of magnitude higher ($d_{33} > 2500\text{pC/N}$) than what is usually observed for $\text{Pb}(\text{Zr,Ti})\text{O}_3$ ($d_{33} > 250\text{pC/N}$) and can thus open the route to ultra high performance actuators or ultrasonic imagery systems [1]. Unfortunately the piezoelectric properties observed in PMN- x PT thin films show a drop of one or two orders of magnitude compared to the bulk [7–11]. Nagarajan et al. explain this reduction of the electromechanical performances by the presence of an in plane stress [7]. Stress induced structural modifica-

tions have also been observed in PMN thin films or PMN layers in PMN/PT superlattices. In these studies tetragonal distortion, orthorhombic and PT-like 90° domains have been discovered in the PMN layers [12–14]. Two-dimensional clamping or tensile stress may profoundly change the phase-transition sequence in thin films with respect to the bulk and a better understanding of the correlations between various strain factors is required to achieve reliability of physical properties for practical applications. Raman spectroscopy is a powerful technique to study phase transition and local structure in solid solutions. The temperature dependence of bulk PMN- x PT Raman spectra has been the subject of numerous Raman studies [15–20], while the lattice dynamics of thin films has not yet been studied.

We report here a comparative Raman investigation of the PMN-0.35PT system in bulk and thin film form grown on an MgO substrate buffered with a conductive $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (LSCO) layer. To better understand strain effects induced by the substrate on the thin film we have coupled X-ray diffraction and Raman spectroscopy. While we observe the cubic-tetragonal and tetragonal-monoclinic transitions in the PMN-0.35PT bulk, only a diffuse cubic to tetragonal phase transition is observed for the thin film and no monoclinic phase is detected down to 80 K.

2 Experimental procedure

The PMN-0.35PT single crystal was grown by the flux method and cut with the faces perpendicular to cubic

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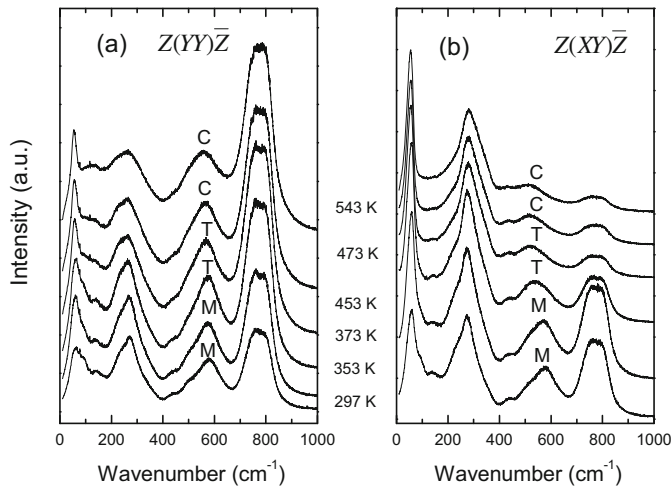


Fig. 1. Raman spectra versus temperature in (a) parallel $Z(YY)\bar{Z}$ polarization and (b) crossed $Z(XY)\bar{Z}$ polarization for the (100) oriented PMN-0.35PT single crystal. C, T and M correspond, respectively, to the cubic, tetragonal, and monoclinic phases.

axes. Thin films were grown by pulsed laser deposition using a Spectra Physik 248-nm laser in a MECA 2000 UHV chamber. A 1500 Å thick LSCO/electrode layer was deposited on the MgO substrate at a temperature (T_s) of 700 °C and 0.2 mbar oxygen partial pressure (P_{O_2}). The temperature and oxygen pressure for the PMN-0.35PT layer were, respectively, $T_s = 595$ °C and $P_{O_2} = 0.3$ mbar. The thickness of the film is about 4000 Å. X-ray measurements were performed using an in-house designed goniometer permitting high resolution measurements of out of plane lattice parameters up to 600 °C. Raman spectra were recorded in a backscattering microconfiguration, using the 514.5 nm-radiation from an argon ion laser focused to a spot of 2 μm in diameter. The scattered light was analyzed using a Jobin Yvon T64000 spectrometer and collected with a charge-coupled device. The temperature dependence from liquid nitrogen up to 600 °C was measured using a Linkam stage.

3 Experimental results

Figure 1 shows the Raman spectra of PMN-0.35PT single crystal measured at different temperatures in parallel ($Z(YY)\bar{Z}$) and crossed ($Z(XY)\bar{Z}$) polarization. X , Y and Z are parallel to the cubic axes of the PMN-0.35PT crystal. We refer to the work by Kamba et al. for the mode assignments and will only discuss the temperature behaviour of the Raman spectra [17]. Apart the high and mid frequency modes, the spectra do not change drastically and are polarized from high temperature down to 373 K.

Below 373 K strong depolarization of the Raman spectra occurs along with changes in band shape in the mid frequency range (450–650 cm^{-1}). Depolarization is particularly clear below 373 K on the high frequency side of the Raman spectra. We indeed evidenced a significant

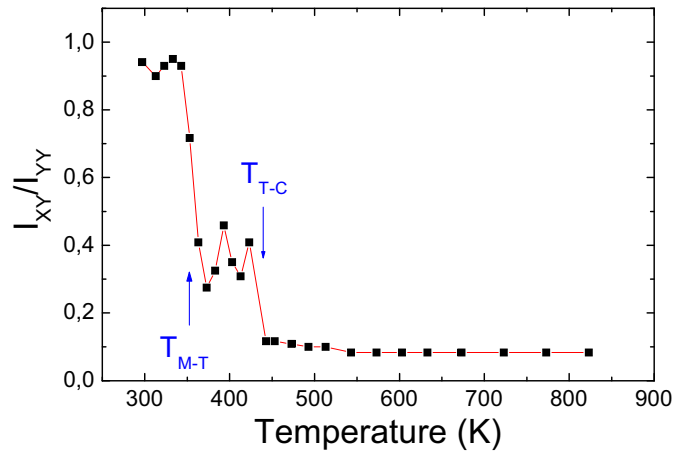


Fig. 2. (Color online) Temperature dependence of the depolarization ratio I_{XY}/I_{YY} for the Raman band at 780 cm^{-1} .

variation in the intensity of the 780 cm^{-1} phonon band in crossed (I_{XY}) polarization. The depolarization ratio between crossed and parallel polarized spectra (I_{XY}/I_{YY}) of the 780 cm^{-1} mode has already been used to investigate phase transitions in PMN-PT single crystals [16]. Figure 2 shows the temperature dependence of I_{XY}/I_{YY} for the 780 cm^{-1} band observed in PMN-0.35PT single crystal. The $T_{T-C} = 442$ K temperature corresponds to the cubic-tetragonal phase transition determined by dielectric measurements on the same sample [21].

The small increase in the depolarization ratio below 442 K is attributed to light scattering by 90° ferroelectric domain walls appearing below the Curie temperature. On further cooling a strong increase of I_{XY}/I_{YY} is observed at the tetragonal-monoclinic phase transition ($T_{M-T} = 365$ K). In the monoclinic phase the depolarization ratio remains constant and close to one (the Raman spectra in crossed and parallel polarizations are similar). Therefore, polarized Raman spectroscopy has enabled us to determine the cubic to tetragonal transition at $T_{T-C} = 442$ K followed by the tetragonal to monoclinic transition at $T_{M-T} = 365$ K that take place in the oriented (001) PMN-0.35PT single crystal.

In the following we discuss the temperature dependent behavior of a PMN-0.35PT thin film. Prior to presenting the Raman results we present X-ray diffraction characterization of a PMN-0.35PT/LSCO/MgO heterostructure. Figure 3 shows the room temperature $\theta-2\theta$ X-ray pattern. LSCO epitaxial cube on cube growth on MgO(001) substrate has been previously demonstrated [12–14]. We detect, in Figure 3, primarily 00 l diffraction peaks; only a low intensity (110) reflection is present and no secondary phases can be detected. This diffraction pattern indicates epitaxial growth. A rocking curve performed on the 001 reflection of the PMN-0.35PT layer indicates good crystallographic orientation with a FWHM = 0.81° as compared to 0.15° for the MgO substrate (not shown here). Moreover φ scans taken on the (101) family of planes (not shown here) of the substrate, the buffer layer, and the PMN-0.35PT layer indicate a

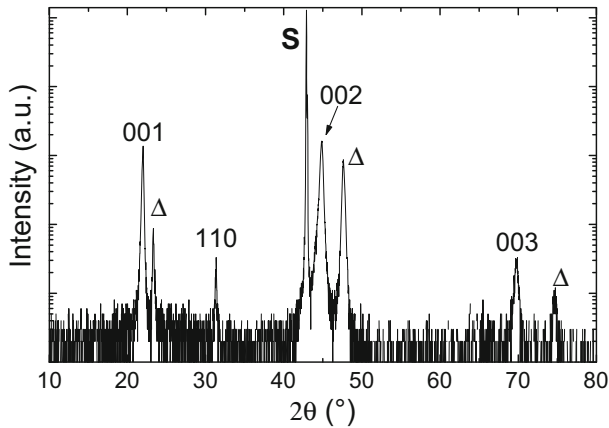


Fig. 3. θ - 2θ X-ray diffraction pattern on a 4000 Å PMN-0.35PT thick film deposited on MgO buffered with 1500 Å LSCO. **S** and Δ correspond to the substrate and LSCO 00l reflection, respectively.

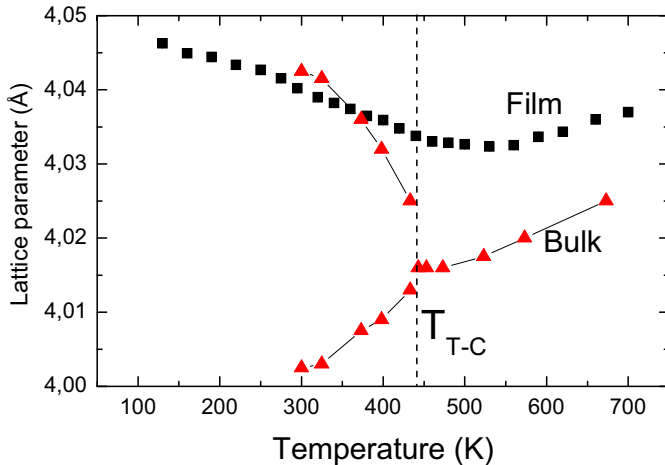


Fig. 4. (Color online) Temperature variation of the out of plane lattice parameter (\blacksquare) of the PMN-0.35PT thin film. Lattice parameters as a function of temperature in the bulk (\blacktriangle) are shown for comparison [22,23]. (Vertical dashed line indicates the Bulk Curie temperature T_{T-C}).

cube on cube growth. The out-of-plane lattice parameter calculated from the 2θ diffraction angle is 4.040 Å.

Figure 4 shows the temperature dependence of the out of plane lattice parameter of the PMN-0.35PT thin film in the temperature interval 100–700 K together with the temperature dependence of the bulk PMN0.35PT lattice parameters [22,23]. The cubic to tetragonal phase transition in bulk occurs at 442 K, while a diffuse cubic-to-tetragonal transition is observed in the range of 450–550 K for the thin film. In the ferroelectric phase we observe, on cooling, a progressive increase of the out of plane lattice parameter without any signs of a phase transition into the monoclinic phase: no anomalies could be detected on lattice parameters or widths of the diffraction peaks. Furthermore an asymmetric rocking curve analysis indicates an increase of the tetragonal distortion on cooling down

to 100 K ($c/a = 1.006$ at 295 K and 1.008 at 130 K; for an introduction on the method see Ref. [24]). The in-plane lattice parameters are deduced from this asymmetric rocking curve analysis ($a = 4.016$ Å at 295 K and $a = 4.013$ Å at 130 K) and could be used for comparison with theoretical calculations of phase diagram changes under in plane strain.

We now present the Raman investigation of the PMN-0.35PT thin film to confirm the diffuse nature of the cubic to tetragonal transition but also to check whether the tetragonal to monoclinic transition takes place. Figure 5 shows the Raman spectra in crossed and parallel polarizations between 673 K and 295 K. The spectra are polarized for the whole range of temperatures investigated and no significant changes are observed across the diffuse transition ($450 \text{ K} < T < 550 \text{ K}$) detected by X-ray Diffraction. The depolarization ratio variation is small as demonstrated by the comparison with the bulk in Figure 6. Figure 6 clearly demonstrates the absence of depolarization down to 100 K and depolarization ratio values are close to those observed in the bulk tetragonal phase. Figure 7 presents Raman spectra obtained on the thin film at 100 K. Stabilization of the tetragonal phase against the monoclinic one is clearly observed with polarized Raman spectra in the film at 100 K similar to those observed in the bulk tetragonal phase.

4 Discussions

Using Raman spectroscopy, we have been able to observe different phase transitions in the PMN-0.35PT $\langle 001 \rangle$ oriented single crystal. We used the depolarization ratio of the high frequency band to emphasize changes in the temperature behavior of a $\langle 001 \rangle$ oriented PMN-0.35PT single crystal. It was previously evidenced that the temperature evolution of this depolarization ratio can indicate phase transitions in relaxor-based ferroelectric materials [16,25–29]. The depolarization of Raman spectra is due to light scattering by domain walls and/or birefringence of light induced by the presence of a ferroelectric polarization neither parallel nor perpendicular to the polarization of the incident light. In our configuration the incident laser light is polarized along the pseudo-cubic $\langle 100 \rangle$ direction. Therefore we have attributed partial depolarization of Raman spectra between 435 K and 365 K to the formation of 90° and 180° ferroelectric domain walls in the tetragonal phase. Moreover the complete loss of polarization of Raman spectra below T_{M-T} confirms the formation of a multi domain state and the appearance of a symmetry lower than tetragonal, namely, the monoclinic Mc phase [5].

The phase transitions sequence in the PMN-0.35PT thin film is obviously different. X-ray diffraction indicates a diffuse transition from the paraelectric-cubic to the ferroelectric-tetragonal phase in the range 450–550 K. The shift of the transition to higher temperatures ($T_c = 442 \text{ K}$ in bulk) can be explained by a stabilization of the tetragonal phase by the strain induced by the substrate and the buffer layer. Indeed both thermal and epitaxial stress impose an in plane compressive stress in the

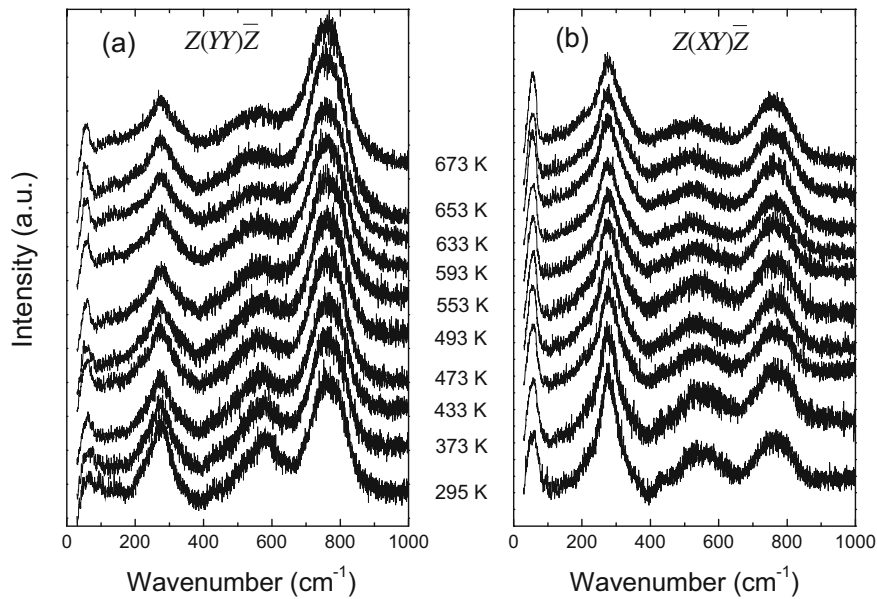


Fig. 5. Temperature dependence of the Raman spectra of the PMN-0.35PT thin film in (a) parallel polarization and (b) crossed polarization.

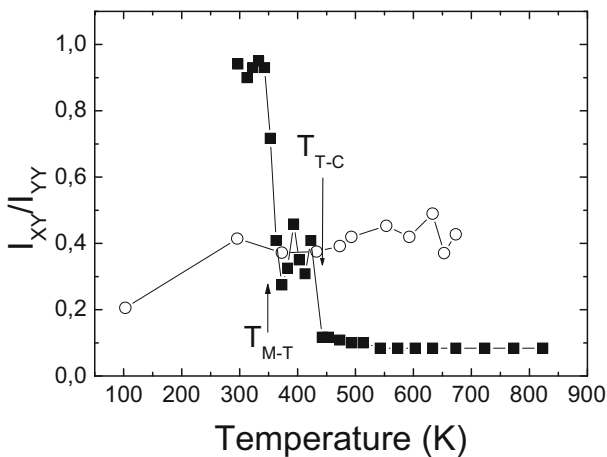


Fig. 6. Temperature dependence comparison of the depolarization ratio I_{XY}/I_{YY} for the Raman band at 780 cm^{-1} for the thin film and the bulk crystal.

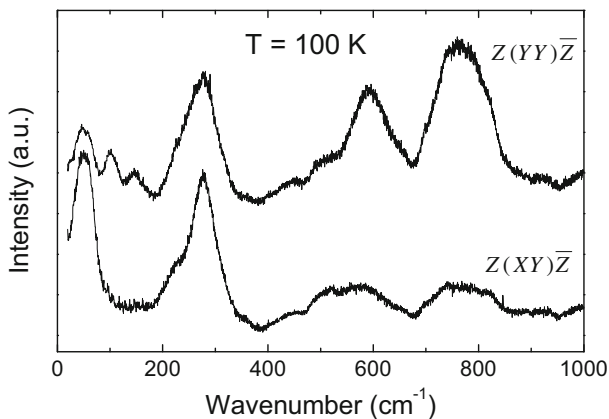


Fig. 7. Raman spectra of PMN-0.35PT thin film at 100 K in parallel $Z(Y\bar{Y})\bar{Z}$ and crossed $Z(X\bar{Y})\bar{Z}$ polarizations.

film. For comparison, the thermal expansion of the substrate (14 ppm K^{-1}) is higher than PMN-0.35PT ($\alpha < 1\text{ ppm K}^{-1}$ below 473 K [22,23]) while the lattice parameter of LSCO (3.805 \AA at 300 K) is smaller than PMN-0.35PT ($c = 4.043\text{ \AA}$ and $a = 4.000\text{ \AA}$ at 300 K). The PMN-0.35PT and LSCO values are those found for the bulk but they provide an idea of the elastic interaction between the layers in the heterostructure. The diffuse nature of the phase transition is usually explained in ferroelectric thin films by the presence of defects, dislocations and smaller grain sizes compared to the bulk [29].

In contrast to X-rays which demonstrate a stabilization of the polar tetragonal phase up to 550 K , no anomalies are observed by Raman spectroscopy across the diffuse transition and up to 673 K . Indeed up to this temperature the depolarization ratio of the 780 cm^{-1} band remains in the range of $0.3\text{--}0.4$ which is characteristic of the tetragonal phase observed in the bulk. This apparent contradiction between the X-ray results (polar tetragonal to non polar tetragonal phase transition) and Raman spectroscopy data (no signs of phase transition for $450\text{ K} < T < 550\text{ K}$) can be explained if we consider the fact that X-ray diffraction is sensitive to long range structure while Raman spectroscopy probes structure at the nanoscale level. It is thus possible that locally there remain some regions with a polar tetragonal distortion. Moreover the larger out of plane lattice parameter in the film compared to the bulk indicate a non polar tetragonal distortion due to the 2D clamping by the substrate (see Fig. 4). Such non polar tetragonal distortion and ferroelastic domain walls might also contribute to depolarization of the Raman spectra.

In the low temperature range, we did not observe any indications of a tetragonal to monoclinic phase transition neither in the out of plane lattice parameter behavior nor in the Raman spectra. In bulk the tetragonal to monoclinic phase transition takes place at $\sim 365\text{ K}$ while no anomaly

is observed at that temperature for the thin film (Fig. 4). As known from phenomenological and first-principles calculations [30,31], the two-dimensional clamping or tensile stress may profoundly change the phase-transition sequence in thin film with respect to the bulk [30–34].

The monoclinic phase has been explained by Vanderbilt et al. in relaxor-ferroelectric bulk solid solution phase via an eighth-order expansion of the free energy in the polar order parameter [30]. To our knowledge a theoretical treatment which include the strain induced by the substrate is still lacking and thus our results can not be rigorously compared with the theoretical phase diagrams [30,31,33,34]. Therefore we hope our results will stimulate such theoretical models applicable to relaxor-ferroelectric thin films.

In summary we performed a comparative study of a PMN-0.35PT single crystal and thin film. We evidenced by Raman spectroscopy different phase transitions in PMN-0.35PT single crystal using the depolarization ratio of the phonon modes. Our Raman and X-ray diffraction investigations show a phase transition from the high temperature paraelectric phase to the low temperature ferroelectric phase in the thin film. We have demonstrated the diffuse nature of this phase transition and a tetragonal distortion existing above the Curie temperature. No monoclinic phase transition down to 100 K has been evidenced. It is to our knowledge the first observation of a strain induced phase diagram modification in a relaxor-ferroelectric thin film and could thus explain the lower electromechanical response commonly observed in films compared to the bulk.

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