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Raman Study in $Pr_{0.5}Ca_{0.5}MnO_3$ Thin Films

A. Tatsi[a], E.L. Papadopoulou[a], D. Lampakis[a],
E. Liarokapis[a], W. Prellier[b] and B. Mercey[b]

[a]Department of Physics, National Technical University of Athens
15780 Athens, Greece
[b]Laboratoire CRISMAT, CNRS UMR 6508
Bd Marechal Juin, 14050 Caen Cedex, France

We report novel Raman measurements made on $Pr_{0.5}Ca_{0.5}MnO_3$ thin films grown on $SrTiO_3$ and $LaAlO_3$ (PCMO/STO and PCMO/LAO, respectively). The measurements were performed for a temperature range 78 K< T <295 K. Different scattering polarizations (xx, xz, $x'x'$, and $x'z'$) have been selected for certain temperatures in order to make the assignment of the modes, appearing in the Raman spectra. X-ray diffraction measurements have shown that the PCMO/STO film is [010]-oriented and the PCMO/LAO film is [101]-oriented due to the lattice mismatch. Close to the transition temperature to the charge ordered state, $T_{\rm CO}$, an increase in relative intensities of the high energy modes has been observed with decreasing temperature.

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1. Introduction

In the past decade the interest in doped manganites has increased due to the discovery of the colossal magnetoresistance effect (CMR) [1]. One of the most exciting phenomena of these materials is the charge-ordering (CO). This phenomenon is observed when the electrons become localized in real space and the heterovalent cations in the two sublattices (Mn^{3+} and Mn^{4+}) become ordered.

The $Pr_xCa_{1-x}MnO_3$ system has a more distorted structure than other CMR materials, in addition to a rich phase diagram. The charge ordering in $Pr_xCa_{1-x}MnO_3$ occurs in the regime $0.3 \leq x \leq 0.75$. The transition temperature takes place at approximately 220–240 K, depending on the amount of Ca doping.

The charge-ordering phenomenon is optimized for $x = 0.5$, where the carriers are exactly commensurate with the 1:1 ordering of the Mn^{3+}:Mn^{4+} species [2].

Most of the technological applications require thin films, which have different physical properties compared to the bulk [3]. This has been attributed to the strain effects induced by the substrate on the film. Moreover, the orientation of the film may induce changes in the structural and physical properties of the material.

An extensive amount of Raman data exists for various compounds of the $R_{1-x}A_xMnO_3$ series (R being a trivalent rare earth and A a divalent alkaline earth) and an assignment for the phonons has been proposed [4–7]. To the best of our knowledge, for the $Pr_{1-x}Ca_xMnO_3$ compound, the Raman data exist only for $x \approx 0.35$ [8] and $x \approx 0.37$ [9]. In a previous work [10] we have pointed out a correlation between the Raman spectra modifications due to the charge-ordering, studying thin films of $Pr_{1-x}Ca_xMnO_3$, of 180 nm thickness, as a function of temperature and hydrostatic pressure.

In this work, we have oriented the research in pointing out the assignment of the Raman active phonons, since there has been no anambiguous assignment for most of the modes. For this purpose, systematic measurements have been carried out using different scattering selection rules, resulting in the disclosure of the assignment for certain modes. Furthermore, the temperature dependence of the Raman spectra has been studied in the films of 100 nm thickness. Finally, the effects from the substrates are briefly discussed.

2. Experimental

Films of $Pr_{0.5}Ca_{0.5}MnO_3$ (PCMO) were measured on two different substrates, one $SrTiO_3$ (STO) and one $LaAlO_3$ (LAO). The films were grown *in-situ* using pulsed laser deposition (PLD) and had a thickness of 100 nm and 180 nm. The substrates were kept constant during deposition. A more detailed optimization of the growth procedure is described elsewhere [11, 12].

X-ray diffraction studies have shown that the films were of a single phase and highly crystalized. Furthermore, it was shown that the films on the STO substrate were oriented with the [010] axis perpendicular to the substrate, while the one on the LAO substrate the [101] axis was perpendicular to the substrate, which was [100]-oriented. The specific orientation of the films was a result of the lattice mismatch between the films and the substrates [13]. Using the XRD results, the out-of-plane lattice parameter of the substrates was calculated to be 3.778 Å for STO and 3.834 Å for LAO, confirming that the film is under tensile stress on STO and under compression on LAO. The structure of bulk $Pr_{0.5}Ca_{0.5}MnO_3$ is orthorombic (*Pnma*), with the lattice constants $a = 5.395$ Å, $b = 7.612$ Å and $c = 5.403$ Å [14].

The Raman spectra were obtained using a T64000 Jobin Yvon triple spectrometer, equipped with a liquid nitrogen cooled charge coupled device (CCD) and a microscope. The 514.5 nm laser line of an Ar^+ laser was used for excitation, at low power of ~ 0.1 mW on the surface of the film. Raman spectra were obtained at a temperature range of 20–295 K. A backscattering geometry was used with the sample placed under the microscope with $a \times 100$ magnification lens. For the low temperature measurements, an Oxford cryostat was used, appropriately modified for the application of the scattering selection rules. The temperature instability was less than 1 K and the local heating due to the laser beam was estimated to be less than 10 K [15, 16]. All presented spectra have been corrected for the Bose thermal factor at the nominal temperatures, but any uncertainties from a laser local heating could not induce appreciable changes in the shapes of the peaks.

3. Results and discussion

In Figs. 1 and 2 typical low temperature Raman spectra of the PCMO/STO and PCMO/LAO films, respectively, are shown, excited by the 514.5 nm laser line. The films had a thickness of 100 nm. The spectra shown here are typical of all

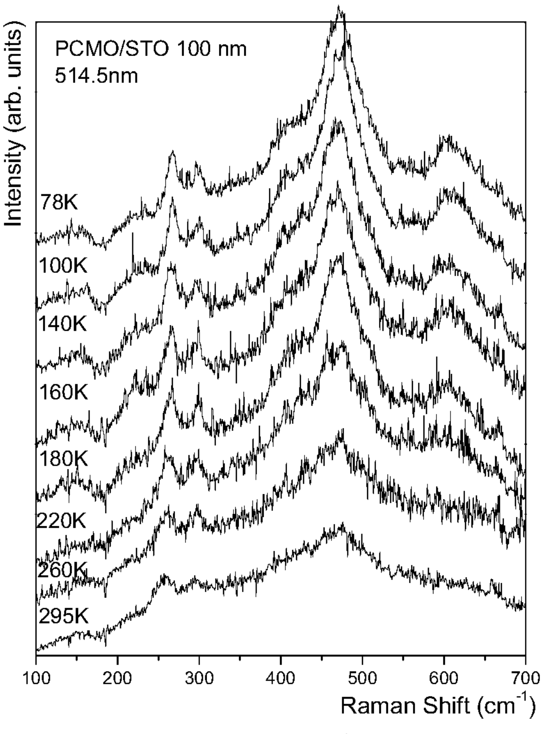

Fig. 1. Typical Raman spectra from the PCMO/STO film with the 514.5 nm excitation wavelength in a temperature range of 78–295 K. The spectra have been corrected with the Bose thermal factor.

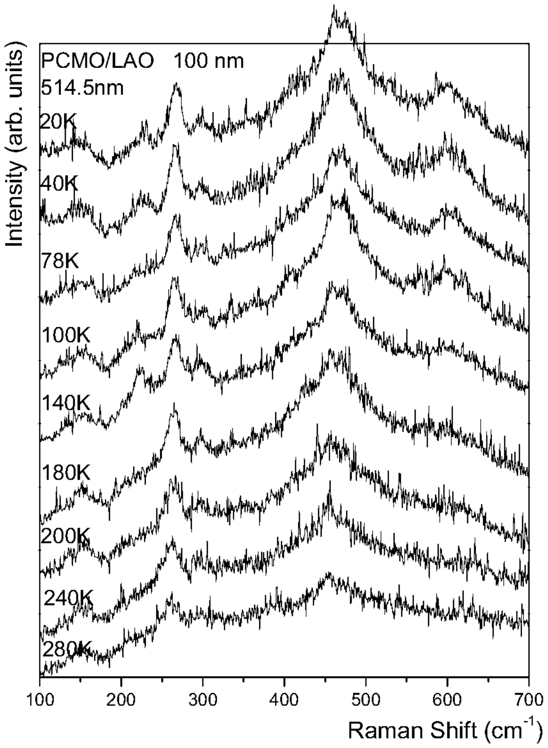

Fig. 2. Typical Raman spectra from the PCMO/LAO film with the 514.5 nm excitation wavelength in a temperature range of 20–280 K. The spectra have been corrected with the Bose thermal factor.

disordered manganites. The crystal structure of $Pr_{0.5}Ca_{0.5}MnO_3$ is the same as that of $LaMnO_3$, the symmetry assignment thus used here, is the one used by Iliev et al. for $LaMnO_3$ [4].

The most pronounced peaks exhibited for the entire temperature range, at 78 K, are centered approximately around 143 cm^{-1}, 268 cm^{-1}, 300 cm^{-1}, 403 cm^{-1}, 430 cm^{-1}, 460 cm^{-1}, 476 cm^{-1}, and 610 cm^{-1}. In addition, below approximately 200 K an additional peak appears at 220 cm^{-1}. Similar measurements have been performed at thicker PCMO/STO and PCMO/LAO films (180 nm) [10] using the 530.9 nm, 488 nm, and 647.1 nm laser lines for excitation. It was seen that the excitation photon energy does not modify considerably the spectra. However, in the thicker films the modes at 403 cm^{-1} and 430 cm^{-1} was not observed, while the 143 cm^{-1} was only observed with the 647.1 nm laser line.

In Fig. 3 the Raman spectra of the PCMO/STO film are shown for different scattering configurations (xx, xz, $x'x'$, and $x'z'$) for 300 K and for 78 K. The first symbol indicates the direction of the polarization of the incident light and the second, the polarization of the scattered light. The spectra taken at xx and zz

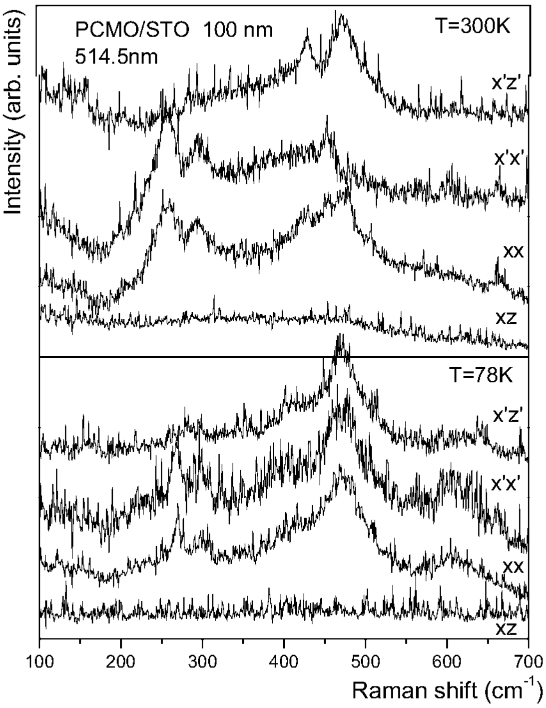

Fig. 3. Polarized Raman spectra measured on the PCMO/STO film at 300 K and 78 K, using the 514.5 nm laser line. The scattering configuration for each spectrum is indicated.

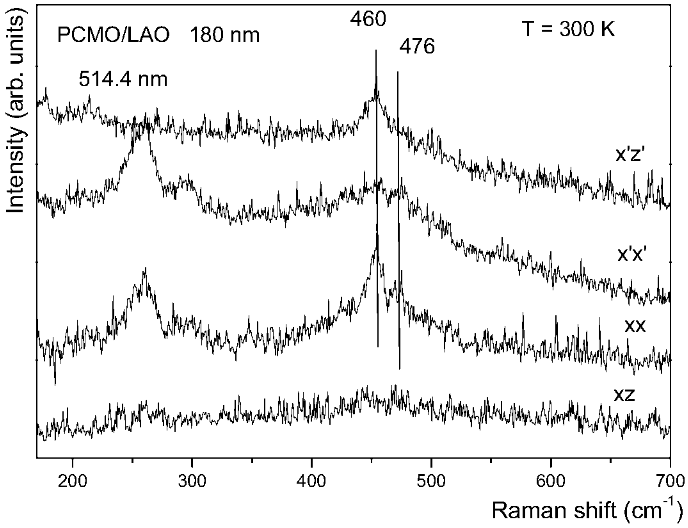

Fig. 4. Polarized Raman spectra measured on the PCMO/LAO film at 300 K, using the 514.5 nm laser line. The scattering configuration for each spectrum is indicated.

(or $x'x'$ and $z'z'$) scattering configurations (not shown in the figure) are identical and therefore the x and z directions are equivalent. In Fig. 4 similar spectra for different selection rules are shown for the PCMO/LAO film, for 300 K. However, the PCMO/LAO film is [101]-oriented, resulting in a mixture of polarizations in the Raman scattering. Using the spectra of the different scattering configurations, it is possible to determine the symmetry of the Raman lines, depending on their relative intensities on the different spectra.

There are two high energy bands, centered around 610 cm^{-1} and 470 cm^{-1} which consist of several overlapping modes. These modes appear at 640 cm^{-1}, 600 cm^{-1}, 476 cm^{-1}, 460 cm^{-1}, 430 cm^{-1} and $\sim$ 403 cm^{-1}.

From the different scattering configurations in PCMO/STO (Fig. 3) comes out that the mode at 640 cm^{-1} is of B_{2g}, whereas the 600 cm^{-1} is of A_g symmetry. The line at 600 cm^{-1} correspond to the 611 cm^{-1} seen by Iliev et al. [4] in $LaCaMnO_3$ and is of breathing type. The peak at 640 cm^{-1} has also been observed by the same authors in $YMnO_3$, and is believed to be of defect origin.

The modes at 430 cm^{-1} and 476 cm^{-1} are pronounced in both xx and $x'z'$ and thus have a B_{2g} symmetry. Similarly, the peak at 403 cm^{-1} is a weak mode, displayed at $x'x'$ and $x'z'$ and thus must be of B_{2g} symmetry. A corresponding line has been observed by Abrashev et al. [6] on the bulk $La_{0.5}Ca_{0.5}MnO_3$ and has been assigned to the same symmetry.

Comparing Figs. 1 and 2, it becomes obvious that there are differences in the relative intensities of the high energy modes of the two samples. In the PCMO/STO film, the 476 cm^{-1} mode is stronger than the 460 cm^{-1} one, while in the PCOM/LAO film the reversed situation is realized and the mode at 460 cm^{-1} is slightly stronger than the 476 cm^{-1} one. This result is shown clearer in Fig. 3, where the spectra from different scattering configurations are shown for the two films. In the $x'z'$ spectrum of PCMO/STO, the 476 cm^{-1} phonon is quite strong, whereas the 460 cm^{-1} one is absent. In the PCMO/LAO case, the 460 cm^{-1} mode is present, while the 476 cm^{-1} one is absent. This points out the B_{2g}-like symmetry of the 476 cm^{-1} phonon and the B_{1g} or the B_{3g} symmetry of the 460 cm^{-1} one. However, Abrashev et al. in measurements on thin films of $CaMnO_3$/LAO and $CaMnO_3$/STO [7] and on the bulk $La_{0.5}Ca_{0.5}MnO_3$ [6] have assigned the lower energy mode, of the two corresponding modes, to B_{2g} and the higher energy one to A_g. In our case however, the different growth orientation of the two films has made possible to differentiate the B_{1g} (or B_{3g}) symmetry of the 460 cm^{-1} mode from the B_{2g} of the 476 cm^{-1} one.

The assignment of the low energy modes is more straightforward. As shown in Fig. 3, the phonon at 300 cm^{-1} only appears at parallel polarizations, so it is of A_g symmetry as well. Relating this mode with the assignment of Iliev et al. [4], it can be attributed to the tilting vibrations of the octahedra, represented by the A_g mode at 284 cm^{-1} in $LaMnO_3$.

The mode at 268 cm^{-1} is very well defined at parallel polarizations (xx and $x'x'$), while it is not observed at crossed polarizations (xz and $x'z'$). It is hence of A_g symmetry. A corresponding mode is also observed in the case of $LaMnO_3$ [4] and has been assigned to the rotations of the b axis of the octahedra.

The low energy mode at 143 cm^{-1} is more like a wide band, which is temperature independent. It appears to be quite weak at all temperatures and no definite assignment could be carried out.

As seen from the Raman spectra in Figs. 1 and 2, there is an additional mode appearing below $T \sim 160$ K at ~ 220 cm^{-1}. This phonon is more well defined at PCMO/LAO film. It has been sometimes observed by other authors as well [6, 8] and has been identified as a soft mode. However we have not observed any softening of this mode.

From the temperature dependence of the spectra there is some evidence for the transition of the materials to the CO state. It has been shown previously [10] that below $T \sim 225$ K a rapid softening takes place for the mode at 268 cm^{-1}, decreasing in energy by 12 cm^{-1} in the temperature range of 78–300 K. The temperature, at which the rapid softening occurs, is close to the transition temperature to the CO state, T_{CO}. As seen in Figs. 1 and 2, the high frequency bands around 470 cm^{-1} and 610 cm^{-1} consist of different overlapping modes. With decreasing temperature, their relative intensities to the lower energy modes increase considerably and the different peaks become clearer. This behavior has been attributed to the formation of the CO state [8, 10]. Hence, the transition to the charge ordered state, where the carriers are more localized, results in an increase in relative intensities of the modes in this phase.

Moreover, we have performed measurements under high hydrostatic pressure, at room temperature, disclosing the anharmonicity of certain phonons [10]. It was seen that both phonons at 268 cm^{-1} and 300 cm^{-1} show a strong dependence on the hydrostatic pressure due to the anharmonic behavior of the corresponding rotations of the octahedra. In contrast, however, to the 268 cm^{-1} mode, the 300 cm^{-1} one is temperature independent.

As mentioned before, in the Raman spectra of the PCMO/STO film, there appears a strong band centered at ~ 610 cm^{-1}. It consists of a main mode at approximately 600 cm^{-1} and an accompanying one at ~ 640 cm^{-1}. These modes are clearer seen with decreasing temperature. This situation is changed in the PCMO/LAO film, where the accompanying mode can hardly be seen. We believe that these spectral modifications are mainly due to the different orientations of the two films, as well as the lattice mismatch [7].

4. Conclusions

The Raman spectra of two thin films of $Pr_{0.5}Ca_{0.5}MnO_3$ developed on $SrTiO_3$ and $LaAlO_3$ substrates, respectively, have been studied, and there has been an attempt for the assignment of all the modes appearing, carrying out measurements with different scattering configurations. Furthermore, the transition to the CO state has been briefly discussed in relation with the Raman spectra taken as a function of temperature.

We have not observed major spectra modifications, as shifts or splitting of the modes, due to the different substrates, but only minor ones due to the different orientations of the two films. Two modes at 403 cm^{-1} and 430 cm^{-1} gain considerably in intensity for the thinner films. However, further measurements are necessary for a fuller insight into this matter.

Acknowledgments

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References

[1] A.P. Ramirez, *J. Phys., Condens. Matter* **9,** 8171 (1997).

[2] Y. Tomioka, A. Asamitsu, H. Kuwahara, Y. Moritomo, Y. Tokura, *Phys. Rev. B* **53,** R1689 (1996).

[3] W. Prellier, Ph. Lecoeur, B. Mercey, *J. Phys., Condens. Matter* **13,** R915 (2001).

[4] M.N. Iliev, M.N. Abrashev, H.-G. Lee, V.N Popov, Y.Y. Sun, C. Thomsen, R.L. Meng, C.W. Chu, *Phys. Rev. B* **57,** 2872 (1998).

[5] L. Martin-Carron, A. de Andres, M.J. Martinez-Lope, M.T. Casais, J.A. Alonso, *J. Alloys Compd.* **323-324,** 494 (2001).

[6] M.N. Abrashev, J. Backstrom, L. Borjesson, M. Pissas, N. Kolev, M.N. Iliev, *Phys. Rev. B* **64,** 144429 (2001).

[7] M.V. Abrashev, J. Backstrom, L. Borjesson, V.N. Popov, R.A. Chakalov, N. Kolev, R.-L. Meng, M.N. Iliev, *Phys. Rev. B* **65,** 184301 (2002).

[8] V. Dediu, C. Ferdeghini. F.C. Matacotta, P. Nozar, G. Ruani, *Phys. Rev. Lett.* **84,** 4489 (2000).

[9] Rajeev Gupta, G. Venketeswara Pai, A.K. Sood, T.V. Ramakrishnan, C.N.R. Rao, cond-mat/0108476.

[10] A. Tatsi, E.L. Papadopoulou, D. Lampakis, E. Liarokapis, W. Prellier, B. Mercey, *Phys. Rev. B* **68,** 024432 (2003).

[11] W. Prellier, A.M. Haghiri-Gosnet, B. Mercey, Ph. Lecoeur, M. Hervieu, Ch. Simon, B. Raveau, *Appl. Phys. Lett.* **77,** 1023 (2000).

[12] A.M. Haghiri-Gosnet, M. Hervieu, Ch. Simon, B. Mercey, B. Raveau, *J. Appl. Phys.* **88,** 3545 (2000).

[13] W. Prellier, Ch. Simon, A.M. Haghiri-Gosnet, B. Mercey, B. Raveau, *Phys. Rev. B* **62,** R16337 (2000).

[14] Z. Jirak, S. Krupicka, Z. Simsa, M. Doulka, S. Vratislma, *J. Magn. Magn. Matter.* **53,** 153 (1985).

[15] M. Lax, *Appl. Phys. Lett.* **33,** 786 (1978).

[16] E. Liarokapis, Y.S. Raptis, *J. Appl. Phys.* **57,** 5123 (1985).