Available online at www.sciencedirect.com
ScienceDirect
Journal of Luminescence 128 (2008) 992–994
JOURNAL OF LUMINESCENCE
www.elsevier.com/locate/jlumin

# Electron-phonon coupling through the orthorhombic to rhombohedral phase transition in $La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO_3$ manganites

A. Espinosa[a,*], M. Otero-Leal[c], F. Rivadulla[b], J. Rivas[c], A. de Andrés[a]

[a]*Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Campus de Cantoblanco, 28049 Madrid, Spain*
[b]*Department of Physical-Chemistry, Universidad de Santiago de Compostela, 15782-Santiago de Compostela, Spain*
[c]*Department of Applied-Physics, Universidad de Santiago de Compostela, 15782-Santiago de Compostela, Spain*

Available online 19 November 2007

**Abstract**

We present a systematic study of the Raman modes of a ferromagnetic series of manganites, $La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO_3$ with $0 \leqslant x \leqslant 1$, that presents two different regimes for the variation of the ferromagnetic order temperature, $T_C$, with Sr doping. This change occurs for $x \sim 0.5$ when the temperature of the orthorhombic, *Pbnm,* to rhombohedral, *R*-3*c,* structural phase transition, $T_t$, coincides with $T_C$. We have analyzed the evolution of the frequencies and widths of the observed Raman modes as a function of Sr doping and temperature. At room temperature, features of the *Pbnm* structure are detected for compounds up to $x = 0.6$, over the orthorhombic phase limit $x = 0.45$ at 300 K. Octahedra bending modes behave as expected with doping while the tilt mode, which is related to Mn–O–Mn angles and therefore to electronic conduction mechanisms, presents different behaviors in both structures. The tilt frequency is much less sensitive to Mn–O–Mn angle in *R*-3*c* than in *Pbnm* structure indicating a reduction of electron-phonon coupling. Its width presents an anomalous behavior both as a function of doping and temperature with unexpectedly large width in the rhombohedral phase.


*Keywords:* Electron-phonon coupling; Jahn-Teller distortion; Manganites; Phase transition; Raman

## 1. Introduction

The $La_{1-y}Sr_yMnO_3$ perovskite system with $y > 0.17$ has been shown [1] to be a double-exchange ferromagnet with itinerant electrons in a narrow $e_g$ band coupled to localized $t_{2g}$ Mn electrons in a high spin configuration. On the other hand, early experiments [2] on the system $(La_{1-x}Pr_x)_{0.7}Ca_{0.3}MnO_3$ showed a remarkable decrease of $T_C$ and a colossal magnetoresistance (CMR) effect above $T_C$ that increased with decreasing $x$ until a transition to an orbitally ordered, antiferromagnetic-insulator phase. This striking evolution with $x$ of magnetic and transport properties was interpreted [3] to result from the stabilization of phase fluctuations of itinerant and localized electronic regions due to lattice instabilities associated with a first-order transition at the crossover from polaronic to itinerant electron behavior. We carried out a systematic study of the ferromagnetic system $La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO_3$, which shows a similar CMR phenomenon and variation of $T_C$ with $x$, in order to provide a quantitative description of the evolution of $T_C$ with x (Fig. 1). In a previous study [4] from Raman spectroscopy, magnetization, and thermal-expansion, we have been able to provide a quantitative basis for the dynamic phase segregation into hole-rich itinerant-electron regions and hole-poor localized-electron regions that accounts for the evolution of $T_C$ in the whole $x$ range.

The system $La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO_3$ presents either the *Pbnm* orthorhombic structure or *R*-3*c* rhombohedral structure depending on $x$ doping and temperature. Both are structurally distorted with respect to the cubic perovskite and present tilt and bending modes of the $MnO_6$ octahedra, but the stretching modes are only observed in the paramagnetic insulating phase of the *Pbnm* structure that presents cooperative Jahn-Teller distortion, due to the localization of $e_g$ electrons in $Mn^{3+}$ ions [5]. As the Sr doping is increased, the Jahn-Teller distortion decreases and at $x = 0.45$ at 300 K, a phase transition occurs to *R*-3*c* (Fig. 1a). The structure becomes more

*Corresponding author.
*E-mail address:* anaespinosa@icmm.csic.es (A. Espinosa).

0022-2313/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2007.10.031

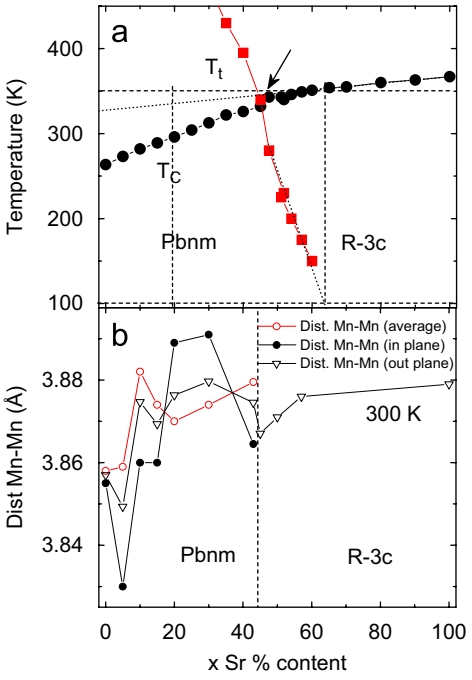


Fig. 1. (a) Variation of the ferromagnetic ($T_C$) and structural ($T_t$) transition temperatures with Sr content ($x$). Dotted line is the extrapolation of $T_C$ behaviour vs $x$ to low $x$ content. Dashed lines are examples of series of Raman experiment conditions, at fixed $x$ and varying $T$ or fixed $T$ and varying $x$. (b) Distance between Mn ions, as a function of Sr doping at room temperature. In *Pbnm* phase: out of plane (solid circles) and in plane (triangles).

regular with octahedra tilting and almost identical Mn-O bonds, characteristic of the *R*-3*c* rhombohedral structure.

In this report, we present an exhaustive study the evolution of phonon modes as a function of Sr doping and temperature through the structural phase transition.

## 2. Experimental

Raman spectra were acquired with a Jobin-Yvon HR 460 monochromator and a nitrogen cooled CCD. The excitation light was the 514.5 nm line of an Ar–Kr laser from Spectra Physics. The incident and scattered beams were focused using an Olympus microscope and a Kaiser Super-Notch-Plus filter was used to suppress the elastic scattered light. The incident power was reduced to few mW in order to avoid local heating of the samples. A continuous He flow Oxford cryostat was used for temperature control down to 10 K.

## 3. Results

The $La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO_3$ series ($0 \leqslant x \leqslant 1$) presents two different regimes for the variation of the ferromagnetic order temperature, $T_C$, with Sr doping. (see Fig. 1a). This change occurs for $x \sim 0.45$ when the temperature of the orthorhombic, *Pbnm*, to rhombohedral, *R*-3*c*, structural phase transition, $T_t$, coincides with $T_C$. The structural transition temperatures were obtained for Sr concentrations up to $x = 0.60$. From the fits of X-ray powder diffraction reference patterns [4] we have obtained Mn–Mn distances at 300 K, Fig. 1b, which give also an indication on how Mn–O octahedra volume is varying. In the *Pbnm* phase Mn–Mn distances rapidly increase while in the rhombohedral phase this distance is almost constant. We can conclude that Mn-Mn mean distance is not linearly related to Sr content.

Because of strong electron-phonon coupling in these systems, the behavior of phonons through the structural phase transition is of special relevance in the mechanisms of magnetic coupling and electronic conductivity. Two kinds of Raman experiments have been performed: (i) for constant temperatures along the series of compounds and (ii) for selected compositions varying the temperature, as dashed lines indicate in Fig. 1a. Fig. 2a shows the Raman spectra of several compositions at 350 and 100 K. The drastic changes in spectra between 100 and 350 K are due to the phase transition from ferromagnetic metallic (100 K) to paramagnetic insulator (350 K) [5]. At 350 K, the stretching modes observed as wide high frequencies bands in *Pbnm* compounds ($x = 0.05$ and 0.2) are related to MnO octahedra distortions due small polaron hoping in the paramagnetic regime of the orthorhombic structure. A fit to a combination of Lorentz functions, as described in Ref. [6], reproduces these weak modes,

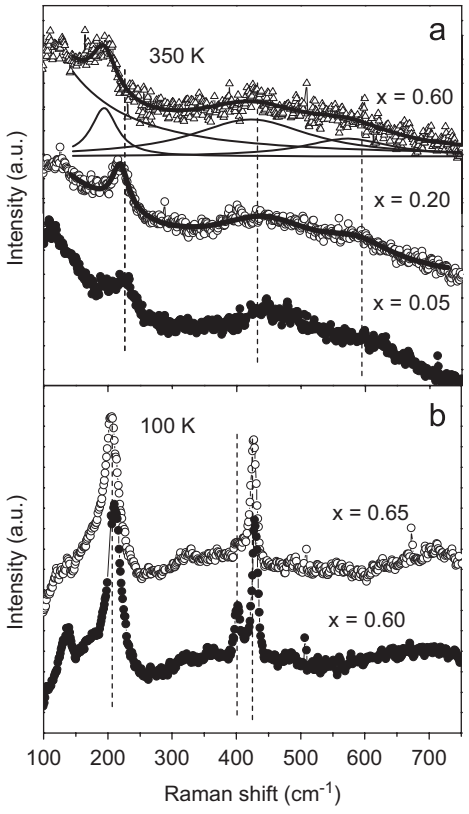


Fig. 2. (a) Phonon modes spectra for 5, 20 and 60% of Sr doping measured at 350 K. A fit to a combination of Lorentz functions has been performed in order to evidence the different modes. (b) Octahedra bending modes and tilt mode for 60 and 65% of doping at 100 K.

observed surprisingly, even for compounds up to $x = 0.6$ (Fig. 2a). A detail analysis is presented in this last case. These wide bands indicates that Mn–O octahedra are suffering fluctuations in spite of being in the *R*-3*c* phase. At low temperatures (Fig. 2b) these modes are not observable as it corresponds to metallic phases.

At 100 K, a tilt mode, around 220 $cm^{-1}$, and two bending modes, around 420 $cm^{-1}$, are detected in the *Pbnm* phase (Fig. 2b, $x = 0.60$) whereas only one bending mode is seen, in $x = 0.65$ sample. The evolution of these three phonons, $\omega_1$ (tilt) and $\omega_2$ and $\omega_3$ (bending), as a function of Sr content at 100 K is represented in Fig. 3a and b. The introduction of Sr in the system produces a shift to lower frequencies of all modes as expected from the increase of Mn–Mn distances (Fig. 1b). The extinction of $\omega_2$, as well as the change in $\omega_1$ dependence with $x$ are revealing that the structural transition from *Pbnm* to *R*-3*c* takes place between $0.6 < x < 0.65$ at 100 K (Fig. 3b). This value coincides with the extrapolation of $T_t$ at low temperatures of diffraction data (Fig. 1a). The tilt mode presents a remarkable decrease only in the orthorhombic phase *Pbnm*.

Another anomaly of the tilt mode is its temperature evolution in the *R*-3*c* phase. The frequency and width of the tilt mode for $x = 0.05$ and 0.2 samples, in the *Pbnm* phase, and $x = 0.6$, with a structural phase transition around 110 K, are displayed in Fig. 4. While for $x = 0.05$ and 0.20 the phonon frequency and width follow the temperature dependence of a simple quasiharmonic model [6], for $x = 0.60$, a clear deviation from this model occurs, especially in the *R*-3*c* regime where the phonon width increases to unexpectedly high values. This behaviour is especially surprising in the rhombohedral phase where no fluctuations of Mn–O octahedra are expected and these are more regular than in the *Pbnm* phase. We cannot give an explanation for this behaviour that would rather correspond to the compounds in the *Pbnm* structure where phase coexistence of itinerant and localized Mn $e_g$ electrons is established.

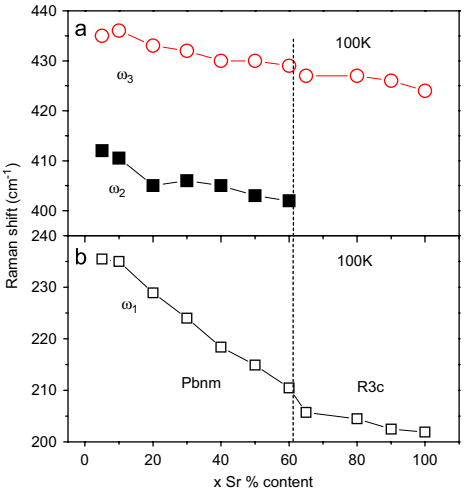


Fig. 3. (a) and (b) Evolution of the phonon modes with the Sr content measured at 100 K. The mode $\omega_1$ corresponds to tilt mode and $\omega_2$ and $\omega_3$ are the bending modes.

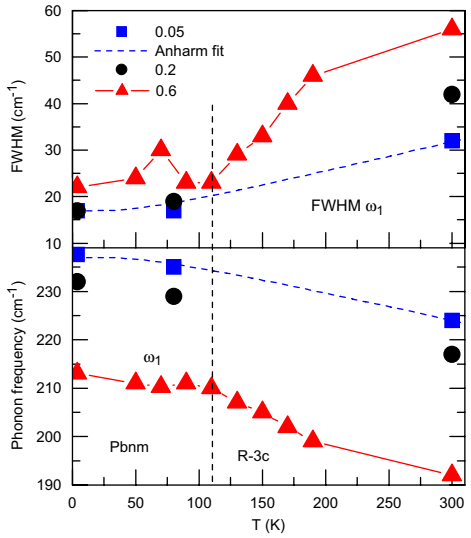


Fig. 4. Temperature evolution of the tilt frequency and width for $x = 0.05$, 0.2 and 0.6 of Sr content. Vertical line indicates the structural transition for $x = 0.6$ compound. The dashed blue lines present the temperature dependence of a simple anharmonic model for frequency and width.

## 4. Conclusions

We have shown the evolution of the Raman modes of the metallic and insulating phases of the $La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO_3$ series through the structural phase transition. The decrease of all phonon frequencies is partially supported by the increase of Mn–Mn distance as Sr content augments. The number of bending modes is a useful tool to follow the *Pbnm* to *R*-3*c* structural phase transition in manganites. We have shown the extreme sensitivity of the tilt mode with Sr doping and its anomalous and unexpected behaviour with temperature in the rhombohedral phase.

## References

[1] J.S. Zhou, J.B. Goodenough, A. Asamitsu, Y. Tokura, Phys. Rev. Lett. 79 (1997) 3234.
[2] H.Y. Hwang, S.-W. Cheong, P.G. Radaelli, M. Marezio, B. Batlogg, Phys. Rev. Lett. 75 (1995) 914.
[3] J.B. Goodenough, Localized to itinerant electronic transition in perovskite oxides, in: J.B. Goodenough (Ed.), Structure and Bonding, Vol. 98, Springer, Berlin, 2001 (Chapter 2).
[4] F. Rivadulla, M. Otero-Leal, A. Espinosa, A. de Andrés, C. Ramos, J. Rivas, J.B. Goodenough, Phys. Rev. Lett. 96 (2006) 016402.
[5] L. Martín-Carrón, A. de Andrés, M.J. Martínez-López, M.T. Casais, J.A. Alonso, Phys. Rev. B 66 (2002) 174308.
[6] L. Martín-Carrón, A. de Andrés, Eur. Phys. J. B 22 (2001) 11.