Available online at www.sciencedirect.com
SCIENCE DIRECT®
Physica B 354 (2004) 47–50
PHYSICA B
www.elsevier.com/locate/physb

Characterization of the charge order to ferromagnetic crossover behavior in $(La_yPr_{1-y})_{0.5}Ca_{0.5}MnO_3$

J. Curiale[a,*], C.A. Ramos[a], P. Levy[b,1], R.D. Sánchez[a,1], F. Rivadulla[c], J. Rivas[c]

[a]*Centro Atómico Bariloche, CNEA, Av. Bustillo 9500 (8400) S. C. de Bariloche, RN, Argentina*
[b]*Centro Atómico Constituyentes, CNEA, Av. Gral Paz 1499 (1650) San Martín Bs. As., Argentina*
[c]*Departamento de Física Aplicada. Universidad de Santiago de Compostela, (15706) Santiago de Compostela, Spain*

Abstract

We present structural and magnetization measurements in large-grain ceramic samples of the family $(La_yPr_{1-y})_{0.5}Ca_{0.5}MnO_3$ with $y=0$, 0.15, 0.3, 0.5, 0.7, 0.85 and 1.0. In this series, a change of the ionic radius in site A (r_A) modifies the structural parameters, which strongly affect the physical properties of these compounds. While the Néel temperature remains essentially constant through the series, the ferromagnetic (FM) critical temperature (T_C) decreases rapidly and the charge-order (CO) temperature (T_{CO}) increases on decreasing y. The crossover of T_C and T_{CO} determines a critical tolerance factor ($t_c \approx 0.975$) consistent with previous reports on other systems with the same Mn^{3+}/Mn^{4+} ratio. For tolerance factors t near t_c we observe coexistence of a FM and CO phases of varying degrees depending on y. For $y \leqslant 0.15$ we find no evidence of ferromagnetism.

PACS: 75.30.Kz; 75.47.Lx; 75.50.−y

Keywords: Manganites; Phase separation; $(La_yPr_{1-y})_{0.5}Ca_{0.5}MnO_3$; Critical tolerance factor

The study of manganese perovskites, particularly those in which there is a competition and coexistence of charge order (CO) and ferromagnetic (FM) states, has received renewed attention recently. Among these systems are the half-doped manganites, having a ratio $Mn^{3+}/Mn^{4+}=1$: $La_{0.5}Ca_{0.5}MnO_3$ (LCMO) and $Pr_{0.5}Ca_{0.5}$ MnO_3 (PCMO) [1–5]. At low temperatures LCMO shows the coexistence of different phases, as antiferromagnetic with charge order (AFM-CO) and ferromagnetic (FM), while only AFM-CO phase is observed in PCMO. This change of behavior is related with the departure of these perovskites from the ideal cubic structure due to the mismatch induced by the difference in ionic radii between the

*Corresponding author. Tel.: +54 2944 44 5158; fax: +54 2944 44 5299.
E-mail address: curiale@cab.cnea.gov.ar (J. Curiale).
[1]CIC-Conicet.

0921-4526/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2004.09.018

A-site (occupied by the rare earth and Ca) and the Mn site. This can be quantified in terms of the tolerance factor, t, which approached $t=1$ in the ideal cubic structure (aristotype). As a function of t this change of regime (from FM to CO) defines a critical tolerance factor, $t_c=0.975$ [5,6] at which T_C and T_{CO} coincide.

In this work we present the structural and magnetic characterization of $(La_yPr_{1-y})_{0.5}Ca_{0.5}MnO_3$ with $y=0.0$, 0.15, 0.3, 0.5, 0.7, 0.85, and 1.0. In this series t varies from 0.967 ($y=0$) to 0.979 ($y=1$) [7], across t_c.

The samples were prepared by solid-state reaction technique with a final annealing at 1400 °C and slowly cooling to room temperature. From analysis of SEM images the average grain size for all the samples was found to be between $5.0\pm0.3\,\mu m$ and $7.0\pm0.7\,\mu m$ for $y=0.5$ and 0.85, respectively, observing a good intergranular connection. The X-ray diffractions were obtained in a Phillips PW3020 apparatus with CuKα radiation, $20^\circ<2\theta<80^\circ$, at room temperature. The X-ray patterns were refined using the Fullprof [8] program. The reflections observed are consistent with a single phase, characterized as Pbnm space group. The lattice parameters are shown in Fig. 1. The cell volume evolution is consistent with the larger ionic radius of La. We note that the structure changes from $a<b$ ($y=0$) to $a>b$ ($y=1$), passing through a tetragonal phase near $y=0.7$. The smooth changes in the lattice parameters indicate that the octahedral distortions also change gradually, from a less distorted ($y=1$) to a more distorted phase ($y=0$), in fair agreement with previous published results [3,4]. Indeed, we found the Mn–O(1)–Mn distortion (ϕ) to be larger in PCMO than in LCMO, $10.9^\circ\pm0.1^\circ$ and $9.9^\circ\pm0.1^\circ$, respectively; and also the in-plane distortion Mn–O(2)–Mn which was $9.5^\circ\pm0.4^\circ$ and $8.7^\circ\pm0.5^\circ$ for PCMO and LCMO, respectively [9].

In Fig. 2 we show the magnetization data of all samples measured while cooling under $H=1\,T$ applied field in order to maximize the FM phase. The arrows indicate the critical temperatures of $y=1$ sample. All samples at room temperature are paramagnetic, with a positive Curie–Weiss temperature indicating predominant ferromagnetic interactions.

In particular, the $y=1$ sample undergoes first a ferromagnetic order at T_C ($\approx255\,K$). T_C was defined as the maximum temperature at which we observed a non-zero extrapolation of the low-field M vs. H virgin curve (see Fig. 3). Decreasing T the CO manifests as a reduction of $M(T)$. This

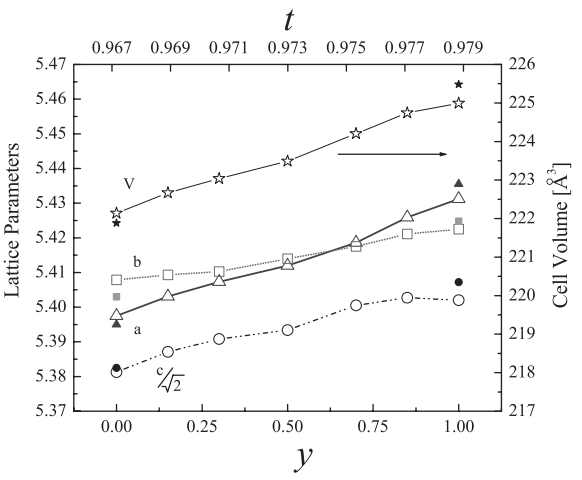

Fig. 1. Lattice parameter and unit cell volume of all samples of the series at room temperature. The error bars are smaller than the symbols. The solid symbols correspond to Refs. [3,4] for $y=1$ and $y=0$, respectively.

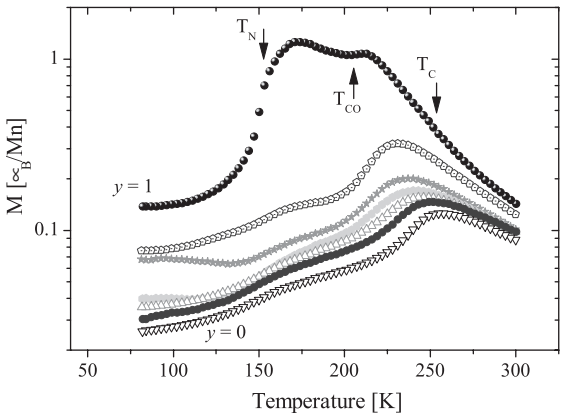

Fig. 2. Magnetization versus temperature (on cooling.) under an applied field of $H=1\,T$. The Pr^{3+} contribution, assumed to be paramagnetic, was discounted from the measurements. T_{CO} and T_N were defined as the temperature at which dM/dT show local maxima (which also coincide with maxima in resistivity derivatives) T_C was defined as the maximum temperature at which a non-zero remanence was observed.

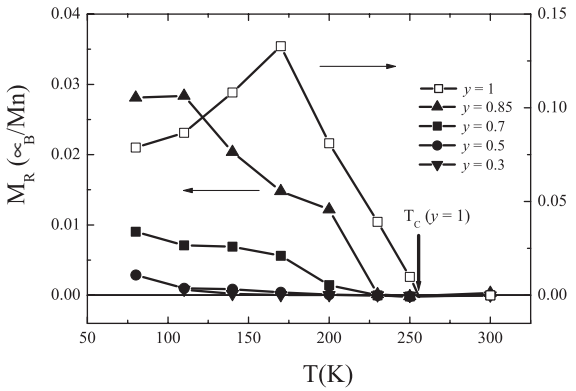

Fig. 3. Extrapolation from low-field magnetization versus temperature extracted of virgin curve of M vs. H cycles (see text). The right scale is only for $y=1$ sample.

T_{CO} (≈ 205 K for $y=1$) coincides with a maximum slope in the resistivity as a function of T which was measured, but not shown in this work. At T_N (≈ 155 K) we observe a second decrease of the magnetization as the sample undergoes AFM order. In this sample, however, we observed that a small fraction of a FM phase is retained, to judge from the low-field extrapolation of $M(H)$, even below T_N. This is characteristic of a phase-separated (PS) behavior. On the other extreme of the series, the $y=0$ sample, we did not observe any FM signal down to 80 K under a maximum applied field of $H=1$ T. Also for the $y=0$ sample the CO transition takes place at $T_{CO}\approx 240$ K and the AFM phase is established at $T_N\approx 155$ K.

While T_N remains essentially constant through the series, T_{CO} increases and T_C decreases on decreasing y. For the $y=0.15$ as well as the $y=0$ sample we did not observe signs of FM phase.

In Fig. 3, we show the magnetization, M_0, extracted from a linear extrapolation of the low-field virgin magnetization data. This data was obtained excluding the regions where a significant curvature is observed (typically between 0.0–0.2 T and 0.5–1.0 T) requiring a linear correlation better than 0.9999. In this way, we obtain information about the spontaneous magnetization at low-field in a ZFC condition. We observed $M_0\neq 0$ only for $y\geqslant 0.3$. However, the percentage of the expected FM magnetization decreases rapidly from the $y=1$ sample, compared with $3.5\,\mu_B$/Mn expected at $T=0$ K. At this composition it reaches 3.8% near 170 K, while for the $y=0.85$ and 0.7 samples is 0.8% and 0.26% at 80 K respectively. We observe for all the samples, except $y=1$, that M_0 does not diminish below T_N.

Also, we found that the sample with T_C closest to T_{CO} corresponds to $y=0.7$ which has a tolerance factor $t=0.9755$.

We observe that, as the tolerance factor diminishes from the LCMO value, the ferromagnetic interactions weakens which yields a decrease of the ferromagnetic fraction and the Curie temperature.

We used the initial low-field magnetization measurements to estimate the existence of a FM phase (and its magnetization). This method is useful to determine small fractions of a spontaneous FM phase and its T_C. In this way we established that PS is observed for samples with $y\geqslant 0.3$.

We have shown that for this $(La_yPr_{1-y})_{0.5}Ca_{0.5}MnO_3$ series the crossover from FM to CO behaviour through t_c is governed by the phase separation and its proportion. This, in turn is determined by the subtle equilibrium between the coexisting phases, which are a function of the applied magnetic field and the structural distortion that is directly related to the tolerance factor.

Acknowledgements

This work was partially supported by the ANPCyT PICT 05266. We would like to thank L. Morales for help in performing the RX characterization and refinement, and E. Winkler for helpful discussions.

References

[1] S.-W. Cheong, H.Y. Hwang, in:Y. Tokura, (Ed.), Colossal Magnetoresistance Oxides, Monographs in Condensed Matter Science, Gordon & Breach, London, 1999.
[2] Q. Huang, J.W. Lynn, R.W. Erwin, A. Santoro, D.C. Dender, V.N. Smolyaninova, K. Glosh, R.L. Greene, Phys. Rev. B 61 (13) (2000) 8895.
[3] P.G. Radaelli, D.E. Cox, M. Marezio, S.-W. Cheong, Phys. Rev. B 55 (5) (1997) 3015.

[4] Z. Jirák, S. Krupicka, Z. Simsa, M. Dlouhá, S. Vratislav, J. Magn. Magn. Mater. 53 (1985) 153.
[5] H. Kuwahara, Y. Tokura, in: C.N.R. Rao, B. Raveau (Eds.), Charge Ordering and Related Properties of Manganese Oxides, World Scientific, Singapore, 1998.
[6] F. Rivadulla, E. Winkler, J.S. Zhou, J.B. Godenough, Phys. Rev. B 66 (2002) 174432.
[7] J. Coey, M. Viret, S. von Molnar, Adv. Phys. 48 (1999) 167.
[8] J.R. Carvajal, T. Roisnel, FullProf program, Laboratoire Léon Brillouin (CEA-CNRS) v/nov 2002 LLB-LCSIM.
[9] This distortion (ϕ), is defined as $\phi = (180^\circ - \alpha)/2$, where α is the Mn–O–Mn angle.