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Magnetic and transport properties of $La_{0.7}Cd_{0.3}(Mn_{0.9}TM_{0.1})O_3$ transition metal doped manganites

A. Peña[a,*], J. Gutiérrez[b], J.M. Barandiarán[b], J.L. Pizarro[c], L.M. Rodríguez-Martínez[a], M. Insausti[a], T. Rojo[a]

[a]*Departamento Química Inorgánica, Facultad de Ciencias, Universidad del País Vasco/EHU, Apartado 644, E-48080 Bilbao, Spain*
[b]*Departamento de Electricidad y Electrónica, Facultad de Ciencias, Universidad del País Vasco/EHU, Apartado 644, E-48080 Bilbao, Spain*
[c]*Departamento Mineralogía-Petrología, Facultad de Ciencias, Universidad del País Vasco/EHU, Apartado 644, E-48080 Bilbao, Spain*

Abstract

In this work we present structural and magnetic properties of $La_{0.7}Cd_{0.3}Mn_{0.9}TM_{0.1}O_3$ (TM=Fe, Co, Ni) manganites. Samples were prepared by the sol–gel low temperature method. Preliminary room temperature structural characterization of these compounds shows a mixture of rhombohedral ($R\bar{3}c$) and orthorhombic (Pnma) phases. The low value of the tolerance factor already indicates a distorted structure of the perovskite cell. Different kinds of magnetic interactions have been observed as the doping TM element is changed. Thus, respect to the undoped $La_{0.7}Cd_{0.3}MnO_3$ composition, the Curie temperature decreases for the Fe doped sample, but progressively increases as Mn ions are substituted by Co or Ni, respectively. The measured low temperature magnetic moment values are interpreted in terms of ferro- (for the Co and Ni doped samples) or antiferromagnetic (for the Fe doped sample) TM^{3+}-Mn^{3+}/Mn^{4+} interactions. Despite their ferromagnetic character, all compositions show insulating behaviour in the whole temperature range studied.

Keywords: Magnetically ordered materials; X-ray diffraction; Electronic transport; Exchange and superexchange; Magnetic measurements

The appearance of colossal magnetoresistance in mixed manganese oxides of composition $Ln^{3+}_{1-x}A^{2+}_xMnO_3$ (Ln= La, Sm, Nd . . . ; A=Ca, Pb, Ba, Sr . . .) gave rise to new efforts in the understanding of the fundamental physics involved in their transport properties [1]. The ferromagnetic behaviour of these compounds was explained by the double exchange mechanism (DE) [2], while the magnetoresistance is related to the simultaneous presence of ferromagnetism and metallic state [3]. In general, the octahedral distortions from the ideal cubic symmetry on these perovskite-like materials have been proved to affect markedly their magnetic properties [4,5]. On the other hand, the substitution of the Mn ions by other transition metal ions gives rise to changes in the Mn^{3+}/Mn^{4+} ratio and, as a consequence, to changes in their magnetic and transport properties. In this work we present results concerning the partial substitution of Mn by different trivalent ions of the 3d group (Fe^{3+}, Co^{3+} and Ni^{3+}), in perovskites of the $A^{2+}=Cd^{2+}$ family.

The $La_{0.7}Cd_{0.3}Mn_{0.9}TM_{0.1}O_3$ (TM=Fe, Co, Ni) phases have been synthesised by the sol–gel method using stoichiometric amounts of analytical grade of La_2O_3, $Cd(NO_3)_2 4H_2O$, $Mn(C_2H_3O_2)_2 4H_2O$, $Fe(NO_3)_3 9H_2O$, $Co(NO_3)_2 6H_2O$ and $Ni(NO_3)_2 2H_2O$. Citric acid and ethylene glycol were used as gelling agents for the La and Mn ions in a nitrate solution. After drying in a sand bath for 24 h, the gel obtained was heated consecutively at different temperatures, each of them for 10 h. In order to measure the electrical properties of the samples, the powder thus obtained was pelletized with a pressure of 3 tonn/cm^2 and sintered at 1173 K for 10 h in flowing oxygen.

Preliminary crystallographic characterization of the phases was performed by X-ray powder diffraction with a Philips XPert diffractometer using Cu $K\alpha_1$ and Cu $K\alpha_2$ radiation. Soller slits of 0.25 rad and receiver and divergence slits of 0.02° were chosen to improve resolution. Powder diffraction patterns were Rietveld fitted using the GSAS program. The shape of the Bragg peaks was

*Corresponding author. Tel.: +34-94-601-5349; fax: +34-94-464-8500.

E-mail address: qibpezoa@lg.ehu.es (A. Peña).

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described by a pseudovoigh function. The background was modelled using a linear interpolation function. Small amounts of impurity phases were found to be present in the phases doped with Co and Ni, corresponding to approximately 2% of $Cd_2Mn_3O_8$ (ICSD 16-957). All the studied compounds show the coexistence of rhombohedral (around a 85%) and orthorhombic Pnma (around a 15%) phases. Refined cell parameters, relative rhombohedral to orthorhombic phase fractions, selected distances and angles and goodness of fits are reported in Table 1. The *R* values for these refinements, despite the good agreement between observed and calculated patterns, are large. This is due to background values very close to zero, which affect the denominator in the expressions used to calculate R_{wp} and R_p.

The low value of the tolerance factor *t* observed for these compositions (above 0.97 in all cases) indicates a significant degree of distortion in the perovskite cell [6]. However, the similar values of the determined Mn/TM-O-Mn/TM bond angles and Mn/TM-O distances (see Table 1) for the three doped samples, indicates that the origin of that structural distortion comes from the presence of the Cd^{2+} as divalent ion in the composition of these samples, in comparison with other related compositions [7]. As a first consequence, the double exchange ferromagnetic mechanism turns out to be less efficient in this family of Cd-containing compounds.

Magnetic and resistance measurements were conducted in a Quantum Design MPMS-7 SQUID magnetometer. The zero field cooling (ZFC) and field cooling (FC) curves were performed under an applied field of 10 mT. The ordering temperature, T_C, was determined from the ZFC curves as the temperature where the minimum of the dM/dT derivative occurs. Hysteresis loops measured at 10 K and up to 7 Tesla were also obtained. The value of the low temperature magnetic moment was determined by Arrott plots. The resistance and magnetoresistance measurements versus temperature were taken by using a dc four-wire system with the current flowing parallel to the applied field.

All measured magnetic data are summarized in Table 2.

Table 2
Values of the Curie temperature, magnetic moment (at low temperature) and temperature of blocking, for all the compositions

TM	T_C(K)	$\mu(\mu_B)$	T_b(K)
Fe	80	1.39	60
Co	135	3.05	130
Ni	140	3.13	105

For the undoped $La_{0.7}Cd_{0.3}MnO_3$ sample, previously studied by the authors [8], values of 1.59 μ_B and 100 K for the low temperature magnetic moment and order temperature, respectively, were reported.

There is a remarkable similarity in the ZFC-FC behaviour (see Fig. 1) for the samples containing Fe and Co. The measured behaviour is very close to the observed one for the $La_{0.7}Sr_{0.3}CoO_3$ composition [9]: there is a cusp in the ZFC curve that corresponds to a blocking temperature of clusters, T_b, followed by a quick decrease of the magnetization as temperature decreases. This fact indicates a collective freezing of cluster moments. This behaviour is not so marked for the 10% Ni doped sample. In the same

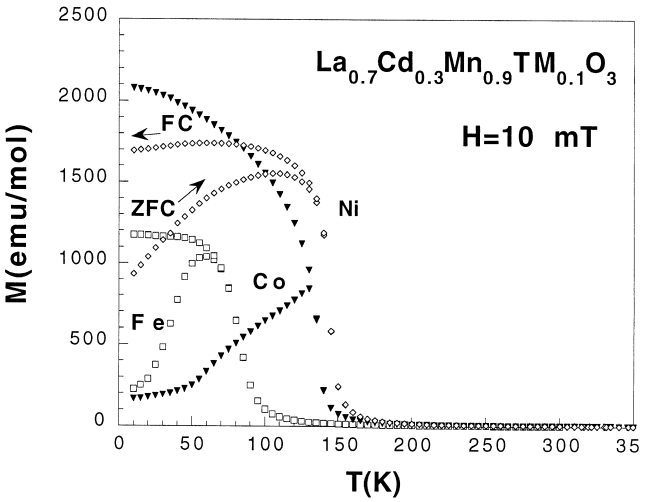

Fig. 1. Zero Field Cooling and Field Cooling curves measured for all the compositions.

Table 1
Refined cell parameters obtained from the first crystallographic characterization

TM	Fe	Co	Ni
Space group/%	$R\bar{3}c$/86(1)%	$R\bar{3}c$/85(1)%	$R\bar{3}c$/85(1)%
a (Å)	5.4835(2)	5.4876(3)	5.4858(3)
c (Å)	13.3291(5)	13.3209(8)	13.3135(9)
Mn/TM-O (Å)	1.965(1)	1.967(2)	1.964(2)
Mn/TM-O-Mn/TM (°)	159.5(5)	159.2(7)	159.7(5)
Space group	*Pnma*/14(1)%	*Pnma*/15(1)%	*Pnma*/15(1)%
a (Å)	5.465(1)	5.473(2)	5.483(3)
b (Å)	7.722(2)	7.708(2)	7.706(2)
c (Å)	5.495(1)	4.487(2)	5.483(2)
χ^2	1.44	1.37	1.60
Rwp (%)	26.78	26.00	27.78
Rp (%)	15.23	15.39	13.21

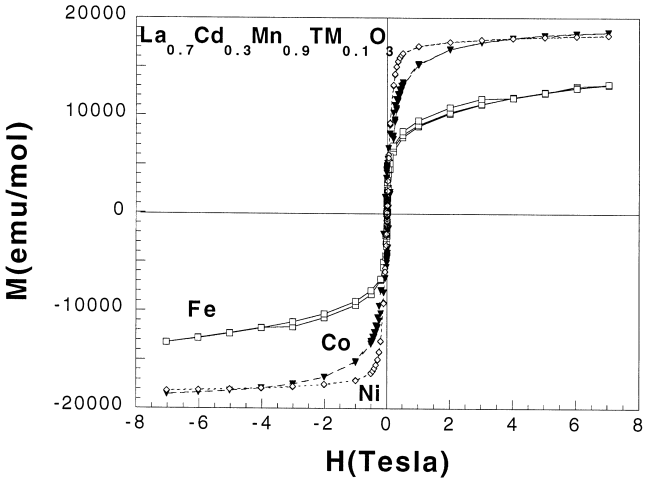

Fig. 2. Hysteresis loops measured at 10 K and up to 7 Tesla, for all the compositions.

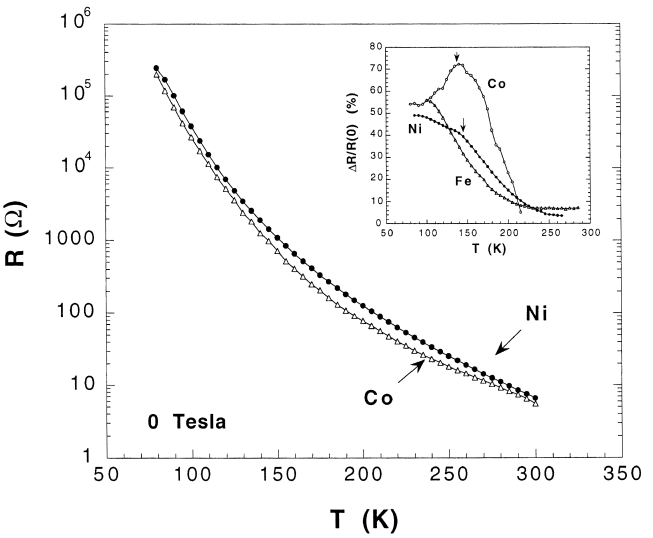

Fig. 3. Resistance measured under 0 Tesla applied field, for the Co and Ni doped compositions. The curve corresponding to the Fe doped composition superimposes the Co one. The inset shows the measured magnetoresistance for all compositions studied in this work.

way, measured hysteresis loops have shown the same ferromagnetic character for the three compositions (see Fig. 2), but reaching quickly the magnetic saturation only for that Ni-containing composition. From the low temperature values of the magnetic moment, it is clear that different kinds of magnetic interactions appear as the doping element changes; always regarding to the undoped composition, Fe still helps to suppress the long range magnetic order. On the contrary, Co and Ni ions favour strongly the ferromagnetic character of the samples. For these two samples, it has to be noticed that the magnetic contribution to the measured low temperature magnetic moment arising from the detected impurity has been measured to be around a 0.1% of the total measured value, for each composition.

The temperature dependence of the resistance measured under zero and 6 Tesla applied field has been also measured. However the samples remain as an insulator down to 50 K where resistance is too high to be measured within our possibilities (see Fig. 3). Similar results have been observed in other (LaCa) [10] and (LaPb) [11] phases with a spin-glass like state at low temperature. The obtained magnetoresistance shows a peak (for the Co doped sample, reaching a 72% magnitude change) and a small shoulder (for the Ni doped composition) close to the corresponding Curie temperature, for each composition. This indicates an intrinsic contribution to the magnetoresistance due to the fact that these granular perovskite compounds behave in the ferromagnetic state similar to a granular transition metal [12]. The Fe and Ni doped samples show a continuous increase of the magnetoresistance when lowering the temperature, with values about the 50% at 90 K (see Fig. 3).

In conclusion, the magnetic behaviour of the $La_{0.7}Cd_{0.3}Mn_{0.9}TM_{0.1}O_3$ (TM=Fe, Co, Ni) phases must be understood as arising from both structural effects, due to the distortion of the perovskite cell because of the presence of divalent Cd^{2+} in the composition of the samples, and the different types of magnetic coupling appearing as the doping TM element is changed. This different coupling effect reflects in the measured low temperature magnetic moment values: thus, Fe enters in these compositions hindering the double-exchange mechanism, while Co and Ni strongly favour the ferromagnetic character of these compounds. Despite this ferromagnetic character, all samples show insulating behaviour in the range of temperatures studied in this work.

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