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(La,Ca)(Mn,M)O_3 (M = Ni, Cr) compounds investigated by means of XRPD and DC magnetic measurements

Alberto Martinelli[a,*], M. Ferretti[a,b], C. Castellano[c], C. Mondelli[d], M.R. Cimberle[e], M. Tropeano[e]

[a] *INFM-LAMIA, C.so Perrone 24, I-16152 Genova, Italy*
[b] *Dip. Chimica e Chimica Industriale, Via Dodecaneso 31, I-16146 Genova, Italy*
[c] *Università di Roma "La Sapienza", Dipartimento di Fisica and INFM, P.le A. Moro 2, 00185 Rome, Italy*
[d] *INFM-OGG, Institute Laue Langevin, 6 rue Jules Horowitz, 38042 Grenoble Cedex 9, France*
[e] *CNR—IMEM sezione di Genova c/o Dipartimento di Fisica, Via Dodecaneso 33, I-16146 Genova, Italy*

Abstract

$(La_{1-x}Ca_x)(Mn_{1-y}M_y)O_3$ ($x = 0.37, 0.50, 0.75$; M = Cr, Ni; $y = 0.03, 0.08$) compounds have been prepared reacting stoichiometric amounts of binary oxides at high temperature. The samples were characterised by means of XRPD analysis at room temperature, followed by Rietveld refinements, revealing that all these compounds crystallize with an orthorhombic structure.

Magnetic characterization as a function of the temperature (ZFC and FC measurements from $T = 5$ K up to $T = 350$ K) and of the magnetic field (up to $\mu_0 H = 5.5$ T) was performed; various behaviours were observed depending on composition: in particular the different effects of Ni and Cr as dopant are shown and discussed.

Keyword: X-ray powder diffraction

1. Introduction

Many interesting phenomena are not yet well understood when studying manganites of general formula $(La_{1-x}Ca_x)MnO_3$. Complicate magnetic structures arise as the concentration of different cations changes. In a similar way, the substitution of Mn ions by other metal ions alters their magnetic coupling, with important modifications in the structural, magnetic and transport properties. In this work we investigate the effect of Mn site doping with Cr and Ni on the crystallographic and magnetic properties.

2. Experimental

The samples were prepared by means of a solid state reaction at high temperature: stoichiometric powder mixtures of high purity binary oxides underwent four thermal treatments in ambient air, the first at 1523 K for 15 h and the remaining at 1603 K for 18 h. These treatments were selected in order to obtain homogenous compositions of the final products; after each annealing treatment the powders were crushed in an agate mortar, since they aggregated during reaction. As a final result the following compounds were obtained: $(La_{0.63}Ca_{0.37})(Mn_{0.97}Ni_{0.03})O_3$, $(La_{0.63}Ca_{0.37})(Mn_{0.92}Ni_{0.08})O_3$, $(La_{0.63}Ca_{0.37})(Mn_{0.92}Cr_{0.08})O_3$, $(La_{0.50}Ca_{0.50})(Mn_{0.92}Ni_{0.08})O_3$, $(La_{0.50}Ca_{0.50})(Mn_{0.92}Cr_{0.08})O_3$, $(La_{0.25}Ca_{0.75})(Mn_{0.92}Cr_{0.08})O_3$.

Phase identification was performed by X-ray powder diffraction analysis (XRPD: PHILIPS PW1830; Bragg–Brentano geometry; Cu Kα; Ni filtered; range 20–80° 2θ; step 0.025° 2θ; sampling time 10 s); the crystalline structures were refined according to the Rietveld method[1] in the *Pnma* space group using the FULLPROF program.

The magnetization measurements were carried out using a commercial (Quantum Design) Superconducting Quantum Interference Device (SQUID) magnetometer. The tempera-

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* Corresponding author. Tel.: +39 010 3538737/6598780; fax: +39 010 3628252.
E-mail address: amartin@chimica.unige.it (A. Martinelli).

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ture dependence of the magnetization was measured from $T = 5$ K up to $T = 300$ K both in field cooled (FC) and zero field cooled (ZFC) conditions at a field $\mu_0 H = 0.05$ T. Magnetization versus magnetic field measurements were performed from zero to 5.5 T at $T = 5$ K.

3. Results and discussion

3.1. $(La_{0.63}Ca_{0.37})(Mn_{1-y}M_y)O_3$

Structural data obtained after Rietveld refinements for the samples with nominal composition $(La_{0.63}Ca_{0.37})(Mn_{1-y}M_y)O_3$ (M = Cr, Ni; $y = 0.03$, 0.08) are reported in Table 1. The Ni-doped samples are characterised by extremely similar structural features, cell parameters and atomic positions being practically the same for both samples. This similarity reflects on the geometry of the MnO_6 octahedra, whose structural features are reported in Table 2: both Mn–O distances, Mn–O–Mn and O–Mn–O angles are the same for both compositions. The comparison of the Ni- and Cr-doped samples ($y = 0.08$) evidences a sensible expansion of the cell parameters for the Cr-doping, especially of *b* and *c* (Table 1). In addition the Mn–O(1) bond distances are the same for the three samples (Table 2), whereas the Mn–O(2) bond lengths are strongly dependent on the chemical nature of the dopant. This phenomenon is related to the increased Jahn–Teller cooperative distortion of the MnO_6 octahedra. Assuming stoichiometric compositions and Ni and Cr in the bi-valent and tri-valent state, respectively, the nominal percentage of the Jahn–Teller Mn^{3+} cation is ∼59% in $(La_{0.63}Ca_{0.37})(Mn_{0.97}Ni_{0.03})O_3$, ∼51% in $(La_{0.63}Ca_{0.37})(Mn_{0.92}Ni_{0.08})O_3$ and ∼60% in $(La_{0.63}Ca_{0.37})(Mn_{0.92}Cr_{0.08})O_3$. Using the Mn–O bond lengths reported in Table 2 it is possible to calculate the Jahn–Teller parameter[2] (σ_{JT}) for each sample at room temperature; as a result σ_{JT} is almost the same for the Ni-doped samples (0.05 Å) and much lower compared to that with Cr-doping (0.14 Å). Hence the cooperative Jahn–Teller distortion seems not to be mainly dependent on the $[Mn^{3+}]/[Mn^{4+}]$ ratio, but on the chemical nature of the dopant. This cooperative distortion leads to lengthening of two Mn–O(2) bond (occupied $3d_{z^2}$ orbitals); the mutual orientation of the occupied $3d_{z^2}$ and empty $3d_{x^2-y^2}$ orbitals leads to the formation of a zig-zag pattern in the *ac* plane.

Table 1
Structural data obtained after Rietveld refinement for $(La_{0.63}Ca_{0.37})(Mn_{1-y}M_y)O_3$

			Ni = 0.03	Ni = 0.08	Cr = 0.08
a (Å)			5.44421(20)	5.44424(20)	5.44484(23)
b (Å)			7.68896(26)	7.68896(26)	7.69251(32)
c (Å)			5.46291(16)	5.46289(16)	5.46604(19)
R_{wp}			0.0509	0.0510	0.0510
La/Ca	Site 4*c*	*x*	0.01930(33)	0.01930(33)	0.01846(37)
		y	1/4	1/4	1/4
		z	0.99647(99)	0.99650(100)	0.99467(95)
Mn/M	Site 4*b*	*x*	0	0	0
		y	0	0	0
		z	1/2	1/2	1/2
O(1)	Site 4*c*	*x*	0.98005(244)	0.97999(245)	0.98422(273)
		y	1/4	1/4	1/4
		z	0.44035(300)	0.44005(301)	0.43815(339)
O(2)	Site 8*d*	*x*	0.72649(349)	0.72625(351)	0.74755(313)
		y	0.96648(160)	0.96655(160)	0.96821(174)
		z	0.29128(242)	0.29089(246)	0.29773(201)

Table 2
Selected bond distances and angles as obtained after Rietveld refinements for $(La_{0.63}Ca_{0.37})(Mn_{1-y}M_y)O_3$; bond multiplicities are indicated by the number after the multiplication signs

	Bond length (Å) and angles (°)		
	Ni = 0.03	Ni = 0.08	Cr = 0.08
Mn—O(1) × 2	1.953	1.953	1.954
Mn—O(2) × 2	1.893	1.895	1.781
	2.029	2.027	2.127
O(1)—Mn—O(2)	89.41	89.35	89.64
	88.40	88.43	89.50
	90.59	90.65	90.35
	91.60	91.56	90.49
O(2)—Mn—O(2)	90.67	90.68	90.10
	89.33	89.32	89.90
Mn—O(1)—Mn	159.74	159.64	159.44
Mn—O(2)—Mn	158.88	158.93	161.48

The temperature dependence of the magnetization *M* for the undoped sample ($y = 0.00$) shows the typical and expected transition from paramagnetic (PM) to ferromagnetic (FM) ordering at $T_M = 272$ K (this value determined by the maximum of the derivative dM/dT). The magnetization versus magnetic field measurements at $T = 5$ K indicates a saturation values of $m = 3.9\mu_B$.

The *M* versus *T* measurements of the Cr doped samples show the typical effect of disorder: a broadening of the PM to FM transition and a shift of the ordering temperature down to $T_M = 231$ K. The effect of a different type of interaction between the Cr^{3+} and Mn^{4+} ions, typically antiferromagnetic, may explain the decrease in the value of the saturation magnetization that goes down to $m = 3.5\mu_B$.

In the Ni doped samples magnetic measurements show the same PM to FM transition, wider respect to that of the parent sample and at lower temperatures: $T_M = 239$ K and $T_M = 182$ K, respectively. Even in this case, the wideness of the transition and the lower values of the ordering temperature may be explained in the light of the disorder introduced in the system. The saturation magnetization for the sample with $y = 0.03$ remains substantially unchanged, $m = 3.9\mu_B$, while, for the sample with $y = 0.08$, it decreases up to $m = 3.6\mu_B$.

Table 3
Structural data obtained after Rietveld refinement for $(La_{0.50}Ca_{0.50})(Mn_{0.92}M_{0.08})O_3$

			Ni	Cr
a (Å)			5.42277(72)	5.42816(14)
b (Å)			7.63454(103)	7.63773(16)
c (Å)			5.41015(77)	5.41340(16)
R_{wp}			0.0439	0.0409
La/Ca	Site 4*c*	*x*	0.01689(41)	0.01712(38)
		y	1/4	1/4
		z	0.00685(103)	0.00012(139)
Mn/M	Site 4*b*	*x*	0	0
		y	0	0
		z	1/2	1/2
O(1)	Site 4*c*	*x*	0.99320(265)	0.99308(252)
		y	1/4	1/4
		z	0.43055(447)	0.39903(274)
O(2)	Site 8*d*	*x*	0.71530(339)	0.71218(195)
		y	0.97774(133)	0.98921(238)
		z	0.27511(454)	0.24902(328)

3.2. $(La_{0.50}Ca_{0.50})(Mn_{0.92}M_{0.08})O_3$

Table 3 reports the structural data obtained after Rietveld refinements for the samples with nominal composition $(La_{0.50}Ca_{0.50})(Mn_{0.92}M_{0.08})O_3$ (M = Cr, Ni). The Cr-doped sample exhibits expanded cell parameters compared to those of the Ni-doped sample. Also in this case the MnO_6 octahedra in the Cr-doped sample are strongly affected by cooperative Jahn–Teller distortion, as evidenced by the Mn–O distances reported in Table 4 and by the values of the σ_{JT} parameters (0.03 Å and 0.12 Å for Ni- and Cr-doping, respectively); as a consequence empty and occupied orbitals lead to the formation of a zig-zag pattern in the *ac* plane, resulting in the expansion of the unit cell parameters. For both samples a distortion of the O(1)–Mn–O(2) bond angles is observed, but this behaviour is more evident after Cr-doping.

Table 4
Selected bond distances and angles as obtained after Rietveld refinements for $(La_{0.50}Ca_{0.50})(Mn_{0.92}M_{0.08})O_3$; bond multiplicities are indicated by the number after the multiplication signs

	Bond length (Å) and angles (°)	
	Ni	Cr
Mn—O(1) × 2	1.946	1.986
Mn—O(2) × 2	1.973	2.072
	1.899	1.775
O(1)—Mn—O(2)	87.17	81.00
	92.98	98.75
	92.83	99.00
	87.02	81.25
O(2)—Mn—O(2)	90.57	90.61
	89.43	89.39
Mn—O(1)—Mn	157.62	147.98
Mn—O(2)—Mn	163.05	170.19

Magnetic measurements for the undoped compound $(La_{0.50}Ca_{0.50})(Mn_{0.92})O_3$ show a transition from PM to FM ordering at $T_M = 265$ K and a saturation value at $T = 5$ K of $m = 3.5\mu_B$.

The Cr-doping effect is to broaden the transition and to lower the T_M ($T_M = 194$ K). The *M* versus *H* measurement shows a saturation value of $3.5\mu_B$.

The Ni-doped sample behaves differently. The temperature dependence of the magnetization shows a behaviour that may be attributed to a spin-glass state or to the coexistence of CO with FM cluster at $T = 50$ K. Magnetization versus magnetic field measurement at $T = 5$ K shows an hysteretic behaviour with a non saturated $m = 2.7\mu_B$ at $\mu_0 H = 5.5$ T. Moreover at lower temperature ($T = 2.5$K) the $M(H)$ curve shows a sharp step-like transition reported also by several authors (see for example Hebert et al.[3])

We point out that, at 50% Ca-percentage, we are at the border line between CO- and FM-states and, as remarked by several authors (see for example Roy et al.[4]), samples with the same nominal Ca content can present completely different behaviours. So the different behaviours observed in the samples doped with Cr or Ni must take into account this problem. Referring to the Ni-doped sample its behaviour could be explained by the disorder effect which hinders the long-range charge and orbital ordering.

3.3. $(La_{0.25}Ca_{0.75})(Mn_{0.92}Cr_{0.08})O_3$

Tables 5 and 6 report structural data and selected bond distances and angles obtained after Rietveld refinement of the XRPD data of the $(La_{0.25}Ca_{0.75})(Mn_{0.92}Cr_{0.08})O_3$ sample. Cooperative Jahn–Teller distortion is revealed by the Mn–O bond distances. As expected the value of the σ_{JT} parameter for this sample (0.08 Å) is lower compared to those of the other Cr-doped samples on account of the decreased concentration of the Jahn–Teller Mn^{3+} cation; in

Table 5
Structural data obtained after Rietveld refinement for $(La_{0.25}Ca_{0.75})(Mn_{0.92}Cr_{0.08})O_3$

a (Å)			5.33410(26)
b (Å)			7.56618(29)
c (Å)			5.34351(30)
R_{wp}			0.0441
La/Ca	Site 4*c*	*x*	0.01870(75)
		y	1/4
		z	0.99449(210)
Mn/Cr	Site 4*b*	*x*	0
		y	0
		z	1/2
O(1)	Site 4*c*	*x*	0.98910(300)
		y	1/4
		z	0.45283(346)
O(2)	Site 8*d*	*x*	0.70662(310)
		y	0.96360(258)
		z	0.26547(617)

Table 6
Selected bond distances and angles as obtained after Rietveld refinements for $(La_{0.25}Ca_{0.75})(Mn_{0.92}Cr_{0.08})O_3$ bond multiplicities are indicated by the number after the multiplication signs

	Bond length (Å) and angles (°)
Mn—O(1) × 2	1.909
Mn—O(2) × 2	2.024 1.817
O(1)—Mn—O(2)	91.69 86.24 88.31 93.76
O(2)—Mn—O(2)	92.01 87.99
Mn—O(1)—Mn	164.43
Mn—O(2)—Mn	158.70

general for the Cr-doped samples the value of the σ_{JT} parameter decreases with the increase of the [La]/[Ca] ratio, that is the decrease of the amount of Mn^{3+}; this observation holds also for the $(La_{0.63}Ca_{0.37})(Mn_{0.92}Ni_{0.08})O_3$ and $(La_{0.50}Ca_{0.50})(Mn_{0.92}Ni_{0.08})O_3$.

Magnetic measurements for the undoped compound ($y = 0.00$) shows very low values of magnetization, the expected typical bump of the OO–CO phase around $T_{CO} \sim 240$ K and the appearance, at lower temperatures, of a magnetic irreversibility with the separation of the ZFC and FC curves, probably due to the presence of small ferromagnetic clusters. The M versus H measurements at $T = 5$ K and $T = 2$ K are quite linear with a value $m = 0.06\mu_B$ at $\mu_0 H = 5.5$ T.

The Cr-doping effect is very strong. The OO–CO state is suppressed, the temperature dependence of the magnetization shows a signal increase of one order of magnitude and, at low temperatures, a typical behaviour related to the presence of FM clusters. The M versus H measurements do not show any saturation signal, $m = 0.8\mu_B$ at $\mu_0 H = 5.5$ T, but, at low fields, a concavity typical of ferromagnetic interactions.

4. Conclusions

The crystal structures at room temperature of $(La_{0.63}Ca_{0.37})(Mn_{0.97}Ni_{0.03})O_3$, $(La_{0.63}Ca_{0.37})(Mn_{0.92}Ni_{0.08})O_3$, $(La_{0.63}Ca_{0.37})(Mn_{0.92}Cr_{0.08})O_3$, $(La_{0.50}Ca_{0.50})(Mn_{0.92}Ni_{0.08})O_3$, $(La_{0.50}Ca_{0.50})(Mn_{0.92}Cr_{0.08})O_3$ and $(La_{0.25}Ca_{0.75})(Mn_{0.92}Cr_{0.08})O_3$ were refined using XRPD data applying the Rietveld method. Cooperative Jahn–Teller distortion of the MnO_6 octahedra was found to be strongly dependent both on the chemical nature of the dopant (Cr, Ni) and on the Mn^{3+} amount. In the La-rich part of the $LaMnO_3$–$CaMnO_3$ phase diagram, where the parent compound is ferromagnetic, the effect of doping, both with Cr or Ni is a broadening of the transition and a lowering of its temperature. In the Ca-rich side of the phase diagram, where the parent compound exhibits a OO–CO state, the doping destroys this state and induces ferromagnetic interactions.

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