

**(La,Ca)(Mn,M)O₃ (M = Ni, Cr) compounds investigated by means of XRPD and DC
magnetic measurements**

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Abstract

(La_{1-x}Ca_x)(Mn_{1-y}M_y)O₃ ($x = 0.37, 0.50, 0.75$; $M = \text{Cr, Ni}$; $y = 0.03, 0.08$) 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.

KEYWORDS: B X-ray powder diffraction; C Magnetic measurement; D Manganite.

1. Introduction

Many interesting phenomena are not yet well understood when studying manganites of general formula $(\text{La}_{1-x}\text{Ca}_x)\text{MnO}_3$. In particular the actual main object of research is the identification at all Ca dopings of the real nature of the inhomogeneous phase present at low T ; it could be based on a mixed charge ordered and metallic phase with a variable coherence length as a function of the concentration of the different A-site cations^{1,2}.

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 fact we can reasonably assume that the partial substitution of the magnetic ion Mn could amplify a phase component respect to the other. This result can be obtained both due to the strong coupling between charge ordering and Jahn-Teller lattice distortion (induced by the presence of the Mn^{3+} ion or of its substitute ion of the same valence) and due to the effect of the different ionic radius of the B site element on the conduction bandwidth along the Mn-O-Mn bond length³. In this work we investigate the effect of Mn site doping with Cr and Ni on the crystallographic and magnetic properties of these compounds.

The substituting ions are able to determine the strengthening of the metallic-ferromagnetic phase component, as happens after the introduction of Cr not linked with a Jahn-Teller distortion. Otherwise Ni can determine a different internal pressure due to its different ionic radius respect to that of Mn or Cr. The substituting ion acts as a random or effective magnetic field in the (Cr/Mn) case or differently, due to the different ionic radius, in the (Ni/Mn) one⁴.

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.

As a result the following compounds were obtained: $(\text{La}_{0.63}\text{Ca}_{0.37})(\text{Mn}_{0.97}\text{Ni}_{0.03})\text{O}_3$, $(\text{La}_{0.63}\text{Ca}_{0.37})(\text{Mn}_{0.92}\text{Ni}_{0.08})\text{O}_3$, $(\text{La}_{0.63}\text{Ca}_{0.37})(\text{Mn}_{0.92}\text{Cr}_{0.08})\text{O}_3$, $(\text{La}_{0.50}\text{Ca}_{0.50})(\text{Mn}_{0.92}\text{Ni}_{0.08})\text{O}_3$, $(\text{La}_{0.50}\text{Ca}_{0.50})(\text{Mn}_{0.92}\text{Cr}_{0.08})\text{O}_3$, $(\text{La}_{0.25}\text{Ca}_{0.75})(\text{Mn}_{0.92}\text{Cr}_{0.08})\text{O}_3$.

Phase identification was performed by X-ray powder diffraction analysis (XRPD: PHILIPS PW1830; Bragg-Brentano geometry; $\text{CuK}\alpha$; Ni filtered; range $20 - 80^\circ 2\theta$; step $0.025^\circ 2\theta$, sampling time 10 s); the crystalline structures were refined according to the Rietveld method⁵ 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 temperature 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 $(\text{La}_{0.63}\text{Ca}_{0.37})(\text{Mn}_{1-y}\text{M}_y)\text{O}_3$

Structural data obtained after Rietveld refinements for the samples with nominal composition $(\text{La}_{0.63}\text{Ca}_{0.37})(\text{Mn}_{1-y}\text{M}_y)\text{O}_3$ ($M = \text{Cr}, \text{Ni}$; $y = 0.03, 0.08$) 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 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 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 di-valent and tri-valent state, respectively, the nominal percentage of the Jahn-Teller Mn^{3+} cation is $\sim 59\%$ in $(\text{La}_{0.63}\text{Ca}_{0.37})(\text{Mn}_{0.97}\text{Ni}_{0.03})\text{O}_3$, $\sim 51\%$ in $(\text{La}_{0.63}\text{Ca}_{0.37})(\text{Mn}_{0.92}\text{Ni}_{0.08})\text{O}_3$ and $\sim 60\%$ in $(\text{La}_{0.63}\text{Ca}_{0.37})(\text{Mn}_{0.92}\text{Cr}_{0.08})\text{O}_3$. Using the Mn-O bond lengths reported in Table 2 it is possible to calculate the Jahn-Teller parameter⁶ (σ_{JT}) for each sample at room temperature; as a result σ_{JT} is almost the same for the Ni-doped samples (0.05 \AA) and much lower compared to that with Cr-doping (0.14 \AA). Hence the cooperative Jahn-Teller distortion seems not to be mainly dependent on the $[\text{Mn}^{3+}]/[\text{Mn}^{4+}]$ 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.

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 $T_M = 272 \text{ K}$ (this value determined by the maximum of the derivative dM/dT). The magnetization versus magnetic field measurements at $T = 5 \text{ K}$ indicates a saturation values of $m = 3.9 \mu_B$.

The M versus T measurements of the Cr doped samples shows the typical effect of disorder: a broadening of the PM to FM transition and a shift of the ordering temperature down to $T_M = 231 \text{ K}$. 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: $T_M = 239 \text{ K}$ and $T_M = 182 \text{ K}$ 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 $m = 3.6 \mu_B$.

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 exhibit 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 more 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 for the Cr-doping. 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 coexistence between CO states and 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 show a sharp steplike transition reported also by several authors (see for example Hebert *et al.*⁷).

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.*⁸), 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 orbitals ordering.

3.3(La_{0.25}Ca_{0.75})(Mn_{0.92}Cr_{0.08})O₃

Table 5 and VI 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})O₃ 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 Mn³⁺ cation; in 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 Mn³⁺; this observation holds also for the (La_{0.63}Ca_{0.37})(Mn_{0.92}Ni_{0.08})O₃ and (La_{0.50}Ca_{0.50})(Mn_{0.92}Ni_{0.08})O₃ samples.

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 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 don't 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 $(\text{La}_{0.63}\text{Ca}_{0.37})(\text{Mn}_{0.97}\text{Ni}_{0.03})\text{O}_3$, $(\text{La}_{0.63}\text{Ca}_{0.37})(\text{Mn}_{0.92}\text{Ni}_{0.08})\text{O}_3$, $(\text{La}_{0.63}\text{Ca}_{0.37})(\text{Mn}_{0.92}\text{Cr}_{0.08})\text{O}_3$, $(\text{La}_{0.50}\text{Ca}_{0.50})(\text{Mn}_{0.92}\text{Ni}_{0.08})\text{O}_3$, $(\text{La}_{0.50}\text{Ca}_{0.50})(\text{Mn}_{0.92}\text{Cr}_{0.08})\text{O}_3$ and $(\text{La}_{0.25}\text{Ca}_{0.75})(\text{Mn}_{0.92}\text{Cr}_{0.08})\text{O}_3$ 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.

Table 1. Structural data obtained after Rietveld refinement for $(\text{La}_{0.63}\text{Ca}_{0.37})(\text{Mn}_{1-y}\text{M}_y)\text{O}_3$.

		Ni = 0.03	Ni = 0.08	Cr = 0.08
<i>a</i>	[Å]	5.44421(20)	5.44424(20)	5.44484(23)
<i>b</i>	[Å]	7.68896(26)	7.68896(26)	7.69251(32)
<i>c</i>	[Å]	5.46291(16)	5.46289(16)	5.46604(19)
<i>R_{wp}</i>		0.0509	0.0510	0.0510
La/Ca site 4c				
	<i>x</i>	0.01930(33)	0.01930(33)	0.01846(37)
	<i>y</i>	¼	¼	¼
	<i>z</i>	0.99647(99)	0.99650(100)	0.99467(95)
Mn/M site 4b				
	<i>x</i>	0	0	0
	<i>y</i>	0	0	0
	<i>z</i>	½	½	½
O(1) site 4c				
	<i>x</i>	0.98005(244)	0.97999(245)	0.98422(273)
	<i>y</i>	¼	¼	¼
	<i>z</i>	0.44035(300)	0.44005(301)	0.43815(339)
O(2) site 8d				
	<i>x</i>	0.72649(349)	0.72625(351)	0.74755(313)
	<i>y</i>	0.96648(160)	0.96655(160)	0.96821(174)
	<i>z</i>	0.29128(242)	0.29089(246)	0.29773(201)

Table 2. Selected bond distances and angles as obtained after Rietveld refinements for $(\text{La}_{0.63}\text{Ca}_{0.37})(\text{Mn}_{1-y}\text{M}_y)\text{O}_3$; bond multiplicities are indicated by the number after after the multiplication signs.

Bond length [\AA] and angles [deg]	Ni = 0.03	Ni = 0.08	Cr = 0.08
Mn-O(1) \times 2	1.953	1.953	1.954
	1.893	1.895	1.781
Mn-O(2) \times 2	2.029	2.027	2.127
	89.41	89.35	89.64
	88.40	88.43	89.50
O(1)-Mn-O(2)	90.59	90.65	90.35
	91.60	91.56	90.49
	90.67	90.68	90.10
O(2)-Mn-O(2)	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

Table 3. Structural data obtained after Rietveld refinement for $(\text{La}_{0.50}\text{Ca}_{0.50})(\text{Mn}_{0.92}\text{M}_{0.08})\text{O}_3$.

		Ni	Cr
<i>a</i> [Å]		5.42277(72)	5.42816(14)
<i>b</i> [Å]		7.63454(103)	7.63773(16)
<i>c</i> [Å]		5.41015(77)	5.41340(16)
<i>R_{wp}</i>		0.0439	0.0409
		<i>x</i>	<i>x</i>
		0.01689(41)	0.01712(38)
La/Ca	site 4c	<i>y</i>	<i>y</i>
		¼	¼
		<i>z</i>	<i>z</i>
		0.00685(103)	0.00012(139)
		<i>x</i>	<i>x</i>
		0	0
Mn/M	site 4b	<i>y</i>	<i>y</i>
		0	0
		<i>z</i>	<i>z</i>
		½	½
		<i>x</i>	<i>x</i>
		0.99320(265)	0.99308(252)
O(1)	site 4c	<i>y</i>	<i>y</i>
		¼	¼
		<i>z</i>	<i>z</i>
		0.43055(447)	0.39903(274)
		<i>x</i>	<i>x</i>
		0.71530(339)	0.71218(195)
O(2)	site 8d	<i>y</i>	<i>y</i>
		0.97774(133)	0.98921(238)
		<i>z</i>	<i>z</i>
		0.27511(454)	0.24902(328)

Table 4. Selected bond distances and angles as obtained after Rietveld refinements for $(\text{La}_{0.50}\text{Ca}_{0.50})(\text{Mn}_{0.92}\text{M}_{0.08})\text{O}_3$; bond multiplicities are indicated by the number after after the multiplication signs.

Bond length [\AA] and angles [deg]	Ni	Cr
Mn-O(1) \times 2	1.946	1.986
	1.973	2.072
Mn-O(2) \times 2	1.899	1.775
	87.17	81.00
	92.98	98.75
O(1)-Mn-O(2)	92.83	99.00
	87.02	81.25
	90.57	90.61
O(2)-Mn-O(2)	89.43	89.39
Mn-O(1)-Mn	157.62	147.98
Mn-O(2)-Mn	163.05	170.19

Table 5. Structural data obtained after Rietveld refinement for $(\text{La}_{0.25}\text{Ca}_{0.75})(\text{Mn}_{0.92}\text{Cr}_{0.08})\text{O}_3$.

<i>a</i> [Å]			5.33410(26)
<i>b</i> [Å]			7.56618(29)
<i>c</i> [Å]			5.34351(30)
<i>R_{wp}</i>			0.0441
		<i>x</i>	0.01870(75)
La/Ca	site 4c	<i>y</i>	¼
		<i>z</i>	0.99449(210)
		<i>x</i>	0
Mn/Cr	site 4b	<i>y</i>	0
		<i>z</i>	½
		<i>x</i>	0.98910(300)
O(1)	site 4c	<i>y</i>	¼
		<i>z</i>	0.45283(346)
		<i>x</i>	0.70662(310)
O(2)	site 8d	<i>y</i>	0.96360(258)
		<i>z</i>	0.26547(617)

Table 6. Selected bond distances and angles as obtained after Rietveld refinements for $(\text{La}_{0.25}\text{Ca}_{0.75})(\text{Mn}_{0.92}\text{Cr}_{0.08})\text{O}_3$ bond multiplicities are indicated by the number after after the multiplication signs.

Bond length [Å] and angles [deg]	
Mn-O(1) × 2	1.909
	2.024
Mn-O(2) × 2	1.817
	91.69
	86.24
O(1)-Mn-O(2)	88.31
	93.76
	92.01
O(2)-Mn-O(2)	87.99
Mn-O(1)-Mn	164.43
Mn-O(2)-Mn	158.70

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