Influence of Mn substitution with Co or Fe on transport mechanisms in some manganites

M. L. CRAUS[a,b], N. CORNEI[c], M. LOZOVAN[a*], A. ISLAMOV[b]

[a]National Institute of Research and Development for Technical Physics, Iasi, 700050, Romania
[b]Joint Institute for Nuclear Research, Dubna, 141980, Russia
[c]"Al.I.Cuza" University, Chemistry Faculty, 700506, Iasi, Romania

Manganites with perovskite structure are today the subject of intensive research, their properties being of fundamental scientific importance and of interest for technological applications. Some manganites, as $La_{1-x}Sr_xMnO_3$, are known as ferromagnetic materials, with a "bad metal" behavior, and a transition temperature close to Curie temperature. The manganites with $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{1-x}(Co/Fe)_xO_3$ were prepared by means of sol-gel methods. The treated samples were monitorized by XRD, using a diffractometer preview with a data acquisition system, at room temperature. The XRD data were handled with CeckCell program, to proof the space group and the presence of superstructure, while lattice constants, atom positions in the unit cell, average size of the coherent blocks and microstrains were determinate with Rietveld (PowderCell and GSAS) programs. Magnetic properties of the samples were investigate with a Foner type magnetometer, between 77 and 400 K, using a magnetic field H=4 kOe. Magnetoresistance data were obtained with a four probe method, in a magnetic field H_{max} = 20 kOe, between 7 and 300 K. Treated samples contain only perovskite type phases, depending on the Mn substitution. Curie temperature has a maximum value for the smallest amount of Co/Fe. The transition temperature are smaller as Curie temperature with 70 -100 K. Transport mechanisms are discussed, in agreement with the Fe/Co doping. The effect of Co/Fe substitution on the magnetic/crystalline structure of $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{1-x}(Co/Fe)_xO_3$ manganites was investigated.

1. Introduction

Simple perovskites with ABO_3 structure are known as potential magnetoresistive materials (B = Mn or transition elements). Electronic phase diagrams of these oxides are complex; various electric/magnetic states are stabilized by changing the carrier concentration. Ferromagnetism and metallic behavior appear due Zener mechanism, which implies a transfer of e_g electron from Mn^{3+} to Mn^{4+} cation via 2p O^{2-} orbitals [1]. Near Curie temperature was observed a large decrease of resistivity with increase of the magnetic field intensity. However, for technological applications it is need an increase of critical temperatures (Curie temperature (T_C) and transition from metal to insulator state temperature (T_{MI})) by a factor two. The Curie temperature increases with bandwidth, determined by d_{MnO} distances and $\angle(Mn-O-Mn)$ angles.

Tolerance factor ($t = d_{AO}/\sqrt{2}.d_{MnO}$) is an indicator of the departure of ideal structure of the simple perovskites. For an ideal cubic structure $t=1$, while for distorted structure (due to the Mn^{3+} cation presence on B places) $t \neq 1$. If the A or/and B places are occupied by more cations, local structure can be quite different by the observed crystallographic structure. A strong dependence exists between the Curie/transition temperature, on a side, and tolerance factor and chemical disorder degree ($\sigma^2 = \sum y_i r_{i,A}^2 - \langle r_A \rangle^2$; y_i - concentration of i cation on A place, $r_{i,A}$ - radius of i cation on A place), on other side [2]. The substitution of Mn with Co or Fe should lead to disorder on B places, a local modification of the B-O distances and B-O-B angles, due to different crystalline radii of Mn and Co cations. Co cation has a magnetic moment and can interact with Mn by means O^{2-} 2p orbitals [2]. We will to investigate the influence of substitution of Mn with Co or Fe on the crystalline/magnetic structure and transport mechanisms in $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{1-x}(Co, Fe)_xO_3$ (LHSMCO and LHSMFO) manganites.

2. Experimental

The samples were prepared by sol gel method to improve the purity and homogeneity of the samples: stoichiometric amounts of La_2O_3, Ho_2O_3, $SrCO_3$, MnO_2, CoO and Fe_2O_3 (99.9%) were dissolved in nitric acid. The mixture was heated giving a black-brown powder. Resulted powder was pressed, calcined at 800°C 17 hours, grinded, cold pressed and finally sintered in air at 1200°C for 8 hours.
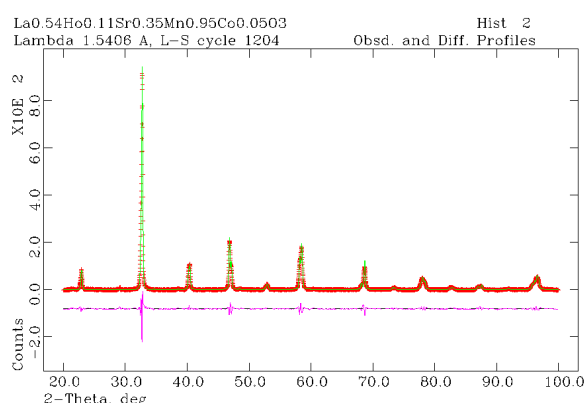
Fig. 1. Difractogram of LHSMCO (x=0.05) manganite (observed data – red; calculated data-green; difference between observed and calculated data - magenta; Rp=0.0235; Dwd=0.056; Aver.Int.=0.933).

The sintered samples were investigated by XRD, to determine phase composition, atoms positions, lattice parameters, microstrains and average size of coherent lattice blocks. XRD data were handled by means of CellRef, Powder Cell and GSAS programs (s. Fig.1 and Fig.2).
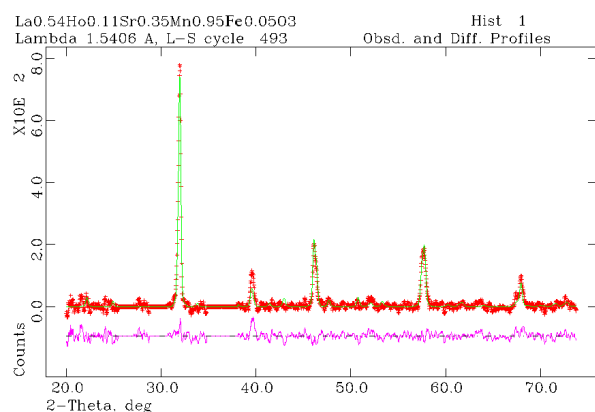

Fig. 2. Difractogram of LHSMFO (x=0.05) manganite (observed data – red; calculated data-green; difference between observed and calculated data - magenta; Rp=0.0465; Dwd=0.176; Aver.Int.=0.913).

Some different structures (unit cells) were tested by means of GSAS program. Typical atom positions in unit cell are presented in Table 1.

The resistance of the samples, depending on temperature and intensity of the magnetic field, was also determined by four probes method between 7 and 300 K, in a magnetic field H_{max} = 2 T.

Table 1. Atom positions parameters in Pnma unit cell of managites.

Atom	Wyckoff position	Atom coordinates		
		x	y	z
La/Ho/Sr	(4c)	0.505	0.250	0.494
Mn/Co(Fe)	(4b)	0.000	0.000	0.500
O_{ap}	(4c)	0.004	0.250	0.493
O_{eq}	(8d)	0.306	0.029	0.759

Molar magnetization was de terminated with a Foner type magnetometer between 77 and 350 K.

3. Results and discussions

Investigations performed by XRD shown that the treated LHSMCO and LHSMFO manganites are formed mainly by an orthorhombic (Pnma) phase (s. Fig.1 and 2). A second phase was observed in Fe doped manganites. Substitution of manganese with other transition elements, as Co or Fe, should lead to a modification of bandwidth due to the different ionic radii and electronic configuration. In the case of Co, a change of spin state could take place; from low spin state (LS) to intermediate (IS). At temperature higher as 230 K a mixture between intermediate state and high spin state (HS) appears. At the variation of the unit cell volume with Co or Fe concentration contributes the increase of Co^{3+}/Mn^{4+} concentrations ($r_{Co3+/HS}$=0.75 Å; $r_{Mn3+/HS}$=0.785 Å; r_{Mn4+}=0.67 Å), which leads to a decreases of lattice constants and 2) the increase of Co^{3+} concentration in intermediate state of spin (IS), which leads also to a decrease of lattice constants (s. Tab.2).

Table 2. Lattice constants (a, b, c) and unit cell volume (V) for LHSMCO and LHSMFO manganites.

x	a(Å)	b(Å)	c(Å)	V(Å³)
LHSMCO				
0.05	5.4946	7.7064	5.4595	231.175
0.10	5.4929	7.6993	5.4580	230.827
0.15	5.4894	7.7011	5.4554	230.625
0.20	5.4867	7.6938	5.4558	230.309
LHSMFO				
0.05	5.4850	7.6905	5.4503	229.907
0.10	5.4922	7.7251	5.4732	232.216

The Fe doped manganites contain a small amount of magnetite, which is in agreement with increase of lattice constants and unit cell volume with Fe concentration (s. Tab.2). We considered that, even in the presence of an important amount of foreign phases, magnetoresistive effect can be observed. Average size of coherent blocks, microstrains and the presence of a foreign phase influence the observed transition temperature and the ratio between extrinsic and intrinsic magnetoresistance components. Average size of mosaic blocks and microstrains are larger at Co doped manganites, possible and due to the Jahn-Teller effect (s. Tab.3). Minimum of d_{AO}, respectively, maximum of d_{BO} distances are in agreement with an observed minimum of Curie and transition temperatures of Co doped manganites (s. Tabs.3 and 4). A decrease of the transition and Curie temperatures takes places with the increase of Fe concentration in the samples (s. Tab.4).
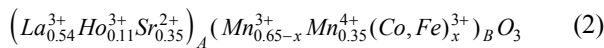
Table 3. *Average size of mosaic blocks (D), microstrains (ε), B-O and A-O distances (d$_{BO}$, d$_{AO}$) and B-O-B angles (∠BOB) for LHSMCO and LHSMFO manganites.*

x	D (Å)	ε	d$_{BO}$(Å)	d$_{AO}$(Å)	∠BOB (°)
LHSMCO					
0.05	802	0.00193	1.9611	2.5929	160.72
0.10	846	0.00177	1.9760	2.5731	155.92
0.15	824	0.00138	1.9593	2.6064	160.73
0.20	754	0.00078	1.9456	2.6726	167.57
LHSMFO					
0.05	409	0.00058	1.9818	2.6195	153.80
0.10	601	0.00052	1.9812	2.5496	152.66

Bandwidth, implicitly the Curie and transition temperatures, is determined by the average Mn-O distance and Mn-O-Mn bonds angle with relation [7]:

$$w \propto \frac{\cos\left(\frac{\pi - \angle Mn-O-Mn}{2}\right)}{d_{Mn-O}^{3.5}} \qquad (1)$$

A good correlation there is between the calculated bandwidth (w) and Curie and transition temperatures (s. Tab.4 and Figs.3 and 4). In agreement with the literature, the substitution of Mn with Co or Fe should destroy the double exchange interaction (DE), leading to the decrease of the specific magnetization and the Curie temperature [4, 5, 6]. If we suppose that Co and Fe are present only as Co^{3+} and Fe^{3+}, the cation distribution is given by:

$$\left(La_{0.54}^{3+}Ho_{0.11}^{3+}Sr_{0.35}^{2+}\right)_A \left(Mn_{0.65-x}^{3+}Mn_{0.35}^{4+}(Co,Fe)_x^{3+}\right)_B O_3 \qquad (2)$$

In this case, the magnetic moment, calculated without Co^{3+} or Fe^{3+} contributions, should decrease relatively slowly. A minimum and a continuous decrease of the magnetic moment with the increase of the Co, respectively, Fe concentrations were observed (s. Tab.4).

Table 4. *Curie and transition temperature (T$_C$, T$_{IM}$), observed and calculated magnetization per formula unit (p$_{max, obs}$, p$_{max, calc}$) or LHSMCO and LHSMFO Manganites.*

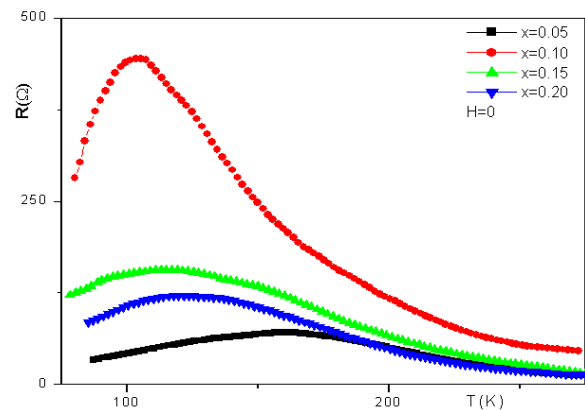| x	T$_C$ (K)	T$_{IM}$ (K)	p$_{max, obs}$ (μ$_B$/f.u.)	p$_{max, calc}$ (μ$_B$/f.u.)	w
LHSMCO					
0.05	254	161	2.623	3.45	0.0894
0.10	205	103	1.859	3.25	0.0842
0.15	216	115	1.730	3.05	0.0897
0.20	194	124	1.894	2.85	0.0951
LHSMFO					
0.05	282	165	1.926	3.45	0.0819
0.10	184	151	1.113	3.25	0.0812
0.15	134	44	0.977	3.05	-
0.20	136	<20	0.232	2.85	-

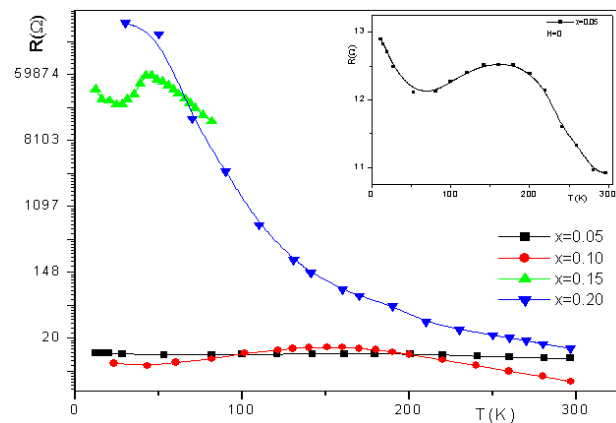Fig. 3. *Variation of resistance with temperature (T) and chemical composition for LHSMCO manganites.*

Fig. 4 *Variation of resistance with temperature (T) and chemical composition for LHSMFO manganites (Inlet; R(T) for x=0.05).*

The behavior of molar magnetization with the Co/Fe concentration can be explained by the presence of two electronic phase: a ferromagnetic metallic (based on Mn^{3+}-O-Mn^{4+} bonds) phase and other antiferromagnetic (ferrimagnetic) insulator phase (based on $Mn^{4+}/Co^{3+}(Fe^{3+})$-O-$Mn^{3+}/Co^{4+}(Fe^{3+})$ bonds.

Table 5. *Variation of activation energy (E$_p$) and constant R$_α$ for LHSMCO (I) and LHSMFO (II) manganites*

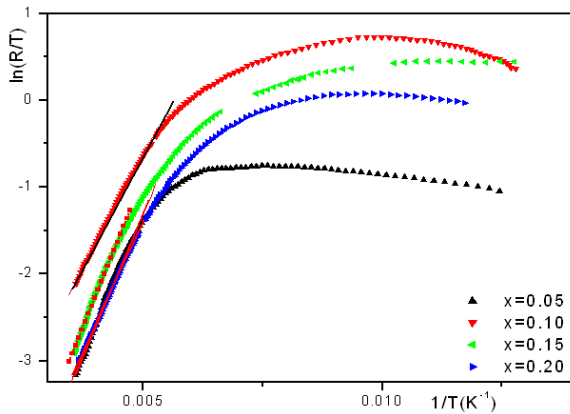| x	E$_p$ (eV)		R$_α$ (Ω)	
	I	II	I	II
0.05	0.111	0.028	4.42*10^{-4}	0.012
0.10	0.090	0.058	3.04*10^{-3}	2.12*10^{-3}
0.15	0.118	0.025	4.43*10^{-4}	5.6
0.20	0.103	0.071	6.47*10^{-4}	3.31*10^{-3}

Fig. 5. Test of SPH model for LHSMCO manganites.

We explained the observed behavior of charge transport at low temperature ($T<T_{IM}$) by means of small polaron hopping model (SPH). In agreement with this model, variation of resistance with temperature is given by:

$$R = R_\alpha T \exp\left(\frac{E_p}{kT}\right) \tag{3}$$

where R_α is a constant depending on charge density and E_p – the activation energy of charge transport [7]. The SPH process can describe the behavior of the samples near Curie temperature (s. Fig. 5 and 6).
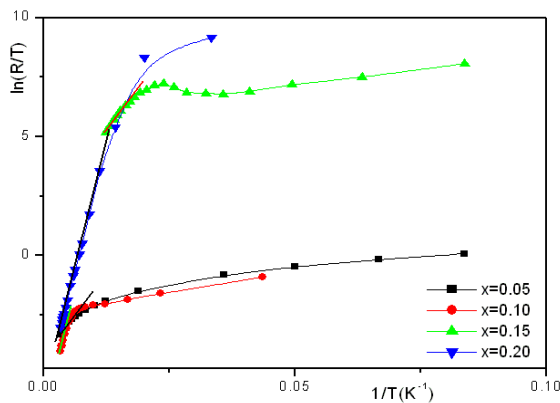

Fig. 6. Test of SPH model for LHSMFO manganites.

Activation energy is higher for Co doped samples, but the R_α constant is one order smaller as for Fe doped samples, that means a more small density of charge (s. Tab.5).

4. Conclusions

Two series of simple perovskites with $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{1-x}(Co/Fe)_xO_3$ was obtained by sol-gel method. On other hand, the bandwidth and, implicitly, Curie temperature, are influenced by the presence of Co and Fe on the B sites, which destroys the DE interaction. The magnetization behavior is due to a mixture of ferromagnetic metallic and an antiferromagnetic (ferromagnetic) insulator phases. Fe cation enhances the superexchange interaction and the appearance of a larger amount of insulator phase. Charge transport takes place by a small polaron hopping mechanism. Fe substitution leads to a decrease of charge density as compared with Co substituted samples.

References

[1] C. Zener, Phys.Rev. **82,** 403 (1951).
[2] N. X. Phuc, L. V. Bau, N. V. Khiem, L. H. Son, D. N. H. Nam, Physica **B 327**, 177 (2003).
[3] L. M. Rodriguez-Martinez, J. P. Attfeld, Phys. Rev. B **54,** R15622 (1996).
[4] E. Syskakis, G. Choudalakis, C. Papastaikoudis, J. Phys.: Condens. Matter **15**, 7735 (2003).
[5] N. X. Phuc, L. V. Bau, N. V. Khiem, L. H. Son, D. N. H. Nam, Physica B **327**, 177 (2003).
[6] X. J. Fan, J. H. Zhang, X. G. Li, W. B. Wu, J. Y. Wan, T. J. Lee, H. C. Ku, J. Phys.: Condens. Matter **11**, 3141 (1999).
[7] C. M. Srivastava, S. Banerjee, T. K. GunduRao, A. K. Nigam, D. Bahadur, J. Phys.: Condens. Matter **15**, 2375 (2003).

*Corresponding author: loz@phys-iasi.ro