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Microstructure of $La_{0.54}Ho_{0.11}Ca_{0.35-x}Na_xMn_{1-y}Cu_yO_3$ manganites

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Manganese perovskites, $Re_{1-x}Alk_xMnO_3$ (Re= rare earth; Alk= alkali earth/alkali elements) were intensively investigated in the last ten years, due to the observed colossal magnetoresistance (CMR) near the ferromagnetic-paramagnetic transition temperature. The CMR effect is most prominent for $x\approx0.3$. It is observed a correlation between the radius and distribution of the cations in the unit cell, on one side, and physical properties on other side for $La_{0.54}Ho_{0.11}Ca_{0.35-x}Na_xMn_{1-y}Cu_yO_3$ manganites, obtained by sol-gel method. Powders resulted from gel calcinations were presintered and finally sintered at 1200°C in air and investigated by X-ray analysis to determine begin of solid-state reaction, the phase composition, and other microstructure parameters. XRD data were handled with DICVOL, CellRef and Rietveld type programs. Magnetic were performed with a Foner type magnetometer between 77 and 600 K. The sintered samples contain only perovskite phases. The substitution of Ca with Na leads to a decrease of the unit cell volume, while the Cu substitution produced a non-monotonous variation of the unit cell. We discussed the dependence between the tolerance factor (experimental and calculated) and the chemical disorder degree, on one side, and the Curie temperature on other side.

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1. Introduction

Substitution of La with bi-/monovalent cations (Ca, Sr, Ba, Na, and K) in $LaMnO_3$ leads to a change of the carrier's concentration, while a substitution with isovalent rare earth elements produces a variation of carrier bandwidth. Curie temperature, implicitly, the transition from the metallic to insulator state, should increase with the bandwidth [1]. On other hand the band width is determined by the Mn-O distances (d_{MnO}), Mn-O-Mn bond angles ($\angle(Mn-O-Mn)$), tolerance factor ($t=d_{AO}/\sqrt{2}.d_{MnO}$), A sites size variance (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) and the hole concentration. $La_{1-x}Ca_xMnO_3$ system has a complex electronic phase diagram, characterized by the presence of five different regions, in agreement with x values. For x_1 =3/8 there is a ferromagnetic metallic state (FM) at T<260 K and a paramagnetic insulator (PI) for T>260 K. For x_2=4/8, a transition takes place from the FM to antiferromagnetic state (AF). Between x_2=4/8 and x_3=7/8 there are, depending on temperature, AF, charge ordering (CO) or PI states. For larger Ca concentration a canted spin (CAF) or a PI state is produced[1]. In the double exchange model the maximum for the Curie temperature corresponds to x=4/8, while the experimental data for $La_{1-x}Ca_xMnO_3$ system give a maximum of the Curie temperature at x=3/8. $La_{1-x}Ca_xMnO_3$ manganites are considered as intermediate-low bandwidth compounds, with the largest negative magnetoresistive (CMR) effect, but with smaller Curie temperature, as comparing with $La_{1-x}Sr_xMnO_3$ manganites. The structure and magnetoresistance of the La-Ca-Mn-O perovskiteswith Cu substitution were studied in our previous paper [2]. The paper aims to investigate the correlation between the modifications, induced in the bandwidth of the $La_{1-x}Sr_xMnO_3$ by the substitution of Ca with Na and Mn with Cu, having the magnetic properties of $La_{0.54}Ho_{0.11}Ca_{0.35-x}Na_xMn_{1-y}Cu_yO_3$ 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, $CaCO_3$, MnO_2 , CuO and NaOH (99.9%) were used. Citric acid and ethylene glycol were added in the oxides mixture to the previous solution. The mixture was heated giving a black-brown powder. Resulted powder was pressed, heated at 800 °C 17 hours, grinded, cold pressed and finally sintered in air at 1200 °C for 8 hours. 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 DICVOL, CellRef and a Rietveld type programs. Several different structures (unit cells), as Pnma, R3c etc were tested by means of GSAS program. It was established that the samples contain only simple perovskite phase, characterized by a Pbnm orthorhombic unit cell. The magnetic measurements were performed with a Foner type magnetometer, between 77 and 300 K, at H_{max} = 1 T.

3. Results and discussion

Sintered samples, with $La_{0.54}Ho_{0.11}Ca_{0.35}Mn_{1-y}Cu_yO_3$ composition, contain only a perovskite phase and are characterized by a Pbnm unit cell (GS 62) (Table 1 and Fig. 1, for unit cell presentation). The values of lattice constants, unite cell volume and atomic positions in unit cell are close to those of the $La_{0.6}Ca_{0.4}MnO_3$ manganite [3].

Table 1. Atomic position and occupation factor of cations and anions in $La_{0.54}Ho_{0.11}Ca_{0.35}Mn_{0.97}Cu_{0.03}O_3$ manganites.

Atom	Wyckoff positions	Atomic coordinates			Site occupation
		x	y	z	
La	4c	0.50773	0.49147	0.25000	0.54
Ho					0.11
Ca					0.35
Mn	4b	0.50000	0.00000	0.00000	0.97
Cu					0.07
O1*	4c	0.05420	0.48128	0.25000	1.0
O2**	8d	0.72305	0.27645	0.05089	1.0

*apical position; **equatorial position

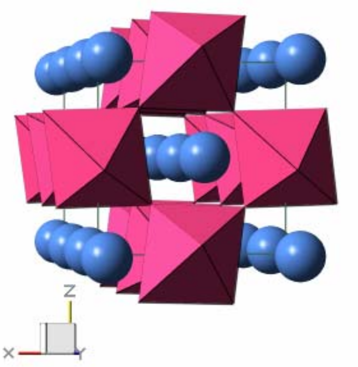

Fig. 1. Pbnm unit cell (BO_6 – polyhedra (red); A sites – alkaline earth cations (blue)).

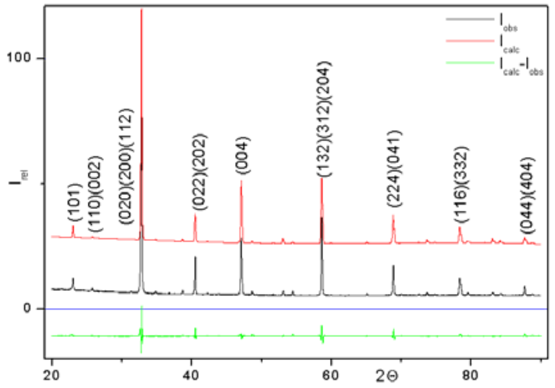

Fig. 2. Observed, calculated and difference between calculated and observed diffracted intensities of $La_{0.54}Ho_{0.11}Ca_{0.35}Mn_{0.94}Cu_{0.06}O_3$ manganite (GSAS).

Lattice constants, B-O distances (d_{B-O}) and B-O-B bonds angles (∠B-O-B) were determinate by using GSAS procedure to handle XRD data (Table 2). $La_{0.54}Ho_{0.11}Ca_{0.35-x}Na_x$ $Mn_{0.97}Cu_{0.03}O_3$ sintered samples contain small quantities of foreign phases (Fig. 3).

The substitution of Mn^{3+}/Mn^{4+} cations (r_{Mn3+}=0.785 Å; r_{Mn3+}=0.53 Å) with Cu^{2+} cations (r_{Cu2+}=0.87 Å) led to a monotonous increase of unit cell volume, but the B-O (Mn/Cu-O) distances exhibit a maximum with Cu concentration (Table 2).

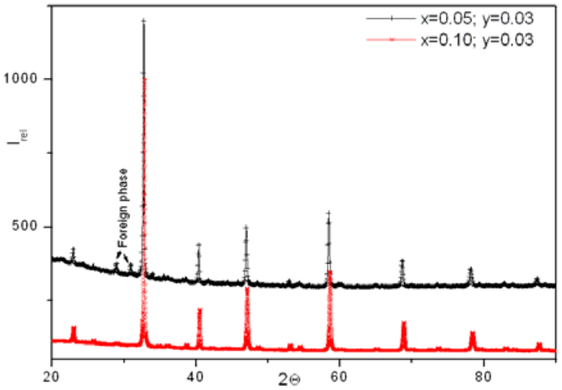

Fig. 3. Difractograms of $La_{0.54}Ho_{0.11}Ca_{0.35-x}Na_x$ $Mn_{0.97}Cu_{0.03}O_3$ sintered manganites.

Table 2. Variation of lattice constants (a, b, c), unit cell volume (V), B-O distances (d_{B-O}) and B-O-B bonds angles (∠B-O-B) with Na/Cu (x, y) concentration in the LHCNMCO manganites.

x	y	Lattice constants			V (Å^3)	d_{B-O} (Å)	d_{A-O} (Å)	<B-O-B (°)
		a(Å)	b(Å)	c(Å)				
0.0	0.03	5.441	5.445	7.687	227.808	1.9421	2.6512	164.208
0.0	0.06	5.445	5.452	7.697	228.212	1.9433	2.6528	164.215
0.0	0.10	5.443	5.448	7.686	228.304	1.9412	2.6529	164.194
0.05	0.03	5.460	5.468	7.734	230.876	1.9509	2.6633	164.232
0.10	0.03	5.442	5.451	7.713	228.724	1.9449	2.6553	164.203

The average distance A-O, implicitly the average size of A places (r_A), increases monotonously with x, despite the fact that the same cations occupy A places in all $La_{0.54}Ho_{0.11}Ca_{0.35}Mn_{1-y}Cu_yO_3$ manganites (Table 2). We have explained r_A variation by a possible change of the vacancy concentration on A places. B-O-B bond angle remains practically unchanged, for both Cu and Na substitution (Table 2).

A r_A increase should be enhanced by the substitution of Ca^{2+} cations (r_{Ca2+}=1.32 Å: we used the Shannon crystalline radii, considering CN=9 for A places and CN=6 for B places) with Na^+ cations (r_{Na+}= 1.38 Å). We have observed a decrease of the unit cell volume, of the d_{B-O} and d_{A-O} distances (Table 2, for x=0.05 and 0.10), despite the fact that the second sample of $La_{0.54}Ho_{0.11}Ca_{0.35-x}Na_x Mn_{0.97}Cu_{0.03}O_3$ sintered manganites (x=0.1) contains only a very small amount of a foreign phase (Fig. 3).

Table 3. Variation of observed and calculated tolerance factors (t_{obs}, t_{calc}), A places size variance (chemical disorder degree, σ^2) and bandwidth (w) with Na/Cu (x, y) concentration in the LHCNMCO manganites.

x	y	t_{obs}	t_{calc}	σ^2	w
0.0	0.03	0.965	0.936	0.0019	0.09700
0.0	0.06	0.968	0.938	0.0019	0.09683
0.0	0.10	0.966	0.941	0.0019	0.09653
0.05	0.03	0.965	0.943	0.0021	0.09551
0.10	0.03	0.965	0.950	0.0022	0.09654

A disagreement exists between the observed and calculated values of tolerance factor: while t_{calc} monotonously increases with the Na/Cu concentrations (x, y), observed values of tolerance factor have a maximum, respectively, remain constant (Table 3). However, the calculated values remain smaller as those observed: we considered that it could be attributed to a decrease of the Mn^{3+}/Mn^{4+} concentration ratio.

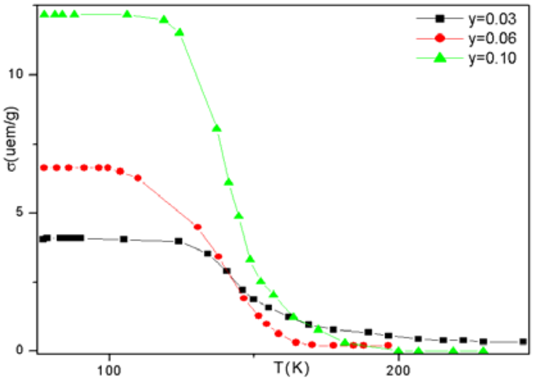

Fig. 4. Variation of the specific magnetization vs. temperature of $La_{0.54}Ho_{0.11}Ca_{0.35}Mn_{1-y}Cu_yO_3$ sintered manganites.

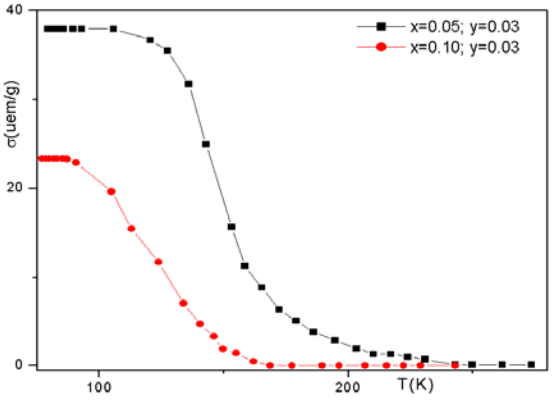

Fig. 5. Variation of the specific magnetization vs. temperature for $La_{0.54}Ho_{0.11}Ca_{0.35-x}Na_x Mn_{0.97}Cu_{0.03}O_3$ sintered manganites.

Variation of the specific magnetization with the temperature indicate an increase of σ_{max} and, respectively, a decrease of the Curie temperature with Cu concentration, for x=0 (Fig. 4 and Table 4).

To calculate molar magnetization (p_{calc}) we supposed that: 1) Cu exists only as Cu^{2+}; 2) Cu^{2+} does not participate to the double exchange interaction and 3) manganite is stoichiometric as oxygen concentration. In this case the cation distribution can be considered as given by:

$$La_{0.54}^{3+}Ho_{0.11}^{3+}Ca_{0.35}^{2+}Mn_{0.35+y}^{4+}Mn_{0.65-2y}^{3+}Cu_y^{2+}O_3^{2-} \qquad (1)$$

$$La_{0.54}^{3+}Ho_{0.11}^{3+}Ca_{0.35-x}^{2+}Na_x^{+}Mn_{0.38+x}^{4+}Mn_{0.59-x}^{3+}Cu_{0.03}^{2+}O_3^{2-} \qquad (2)$$

By comparing our data concerning magnetic properties with those due to $La_{0.65}Ca_{0.35}MnO_3$, the specific magnetization and the Curie temperature of $La_{0.54}Ho_{0.11}Ca_{0.35}Mn_{1-y}Cu_yO_3$ manganites are much smaller. A dependence of the specific magnetization of the magnetic field intensities could exist, but, in agreement with the magnetic data concerning similar manganites, an 1 T field intensity is enough to attain the saturation [4]. Damay et al. [5] investigated $La_{0.7-x}Y_xCa_{0.3}MnO_3$ system and obtained for x<0.1 a molar magnetization of 3.6 μ_B/f.u., in a magnetic field H≈4 kOe. We attribute the behavior of magnetic properties to the substitution of La^{3+} with Ho^{3+}, a cation with a smaller crystalline radius than that of La^{3+}.

The substitution of Mn with Cu destroys the double exchange bonds or leads to a decrease of the double exchange interaction as compared with super exchange interaction (SE). For low Cu concentration the increase of the specific/molar magnetization can be explained taking into account the decrease of SE interaction due to the increase of B-O average distances with Cu concentration in $La_{0.54}Ho_{0.11}Ca_{0.35}Mn_{1-y}Cu_yO_3$ manganites (see Tab.2) and the contribution of Cu^{2+} cations to the appearance of Mn^{3+}-Mn^{4+} pars (Table 2 and 4). Causa et al. have compared the magnetic properties and the structure of $La_{0.67}Ca_{0.33}MnO_3$, $La_{0.67}Sr_{0.33}MnO_3$ and $Pr_{0.67}Sr_{0.33}MnO_3$ manganites [6]. They found that Curie temperature decrease from T_C = 376 K for $La_{0.67}Sr_{0.33}MnO_3$ to T_C = 260 K, for $La_{0.67}Ca_{0.33}MnO_3$. However, the compounds are structurally different, probably due to the difference between the Sr^{2+} and Ca^{2+} radii (r_{Sr2+}= 1.45 Å; r_{Ca2+}=1.32 Å; CN=9; Shannon crystalline radii were considered).

Table 4. Variation of the specific magnetization maximum (σ_{max}), observed maximum molar magnetization ($p_{obs,\ max}$), calculated molar magnetization (p_{calc}), Mn^{3+}/Mn^{4+} pair concentration ($C_{Mn3+/Mn4+}$) and Curie temperature with Na/Cu concentrations (x/y).

x	Y	σ_{max} (uem/g)	$p_{obs,\ max}$ (μ_B)	$C_{Mn3+/Mn4+}$	p_{calc}* (μ_B)	T_C (K)
0.0	0.03	4.06	0.153	0.0235	3.50	145.4
0.0	0.06	6.65	0.251	0.0358	3.35	139.4
0.0	0.10	12.19	0.460	0.0657	3.15	137.8
0.05	0.03	38.03	1.426	0.2037	3.45	148.0
0.10	0.03	23.39	0.874	0.1248	3.40	119.1

Substitution of La with Ho with (r_{Ho3+}=1.212 Å) in $La_{0.65}Ca_{0.35}MnO_3$ leads to a decrease of the average radii of A sites and a decrease of Curie temperature (Tab.4), in agreement with Causa et al. data [6]. On other hand, the increase of Cu concentration, produces a decrease of the DE interactions, as compared with SE interactions, implicitly, a decrease of the Curie temperature (Tab.4). In $La_{0.54}Ho_{0.11}Ca_{0.35}Mn_{1-y}Cu_yO_3$ manganites only a small amount of Mn^{3+}/Mn^{4+} cations contributes to the magnetic moment of the samples (see Table 4). We consider these manganites as formed by a small amount of ferromagnetic metallic clusters, based on Mn^{3+}-O-Mn^{4+} pairs, into an antiferromagnetic/paramagnetic matrix. Concerning the manganese cations, which exist into the matrix, we are performing supplementary investigations.

The Ca substitution with Na (r_{Na+}=1.38 Å) should increase Mn^{4+} concentration (r_{Mn4+}=0.67 Å). Despite the increase of the average radius of A places, the unit cell volume and the observed tolerance factor decrease, respectively, remain constant (Table 3), in agreement with Abdelmoula et al. data [7]. The change of T_C is due to the increase of Mn^{4+} concentration over 30%, which leads to a decrease of DE interaction, enhancing the Mn^{4+}-O-Mn^{4+} superexchange interactions [7]. We should remark that, despite of an increase of the A site size variance of $La_{0.54}Ho_{0.11}Ca_{0.35-x}Na_xMn_{0.97}Cu_{0.03}O_3$ as compared with $La_{0.54}Ho_{0.11}Ca_{0.35}Mn_{1-y}Cu_yO_3$ manganites (Table 3), the values of specific magnetization are higher for the samples, where Ca was substituted by Na.

4. Conclusions

We obtained by sol-gel method two series of manganites ($La_{0.54}Ho_{0.11}Ca_{0.35-x}Na_xMn_{0.97}Cu_{0.03}O_3$, $La_{0.54}Ho_{0.11}Ca_{0.35}Mn_{1-y}Cu_yO_3$ manganites), with contain practically only the Pbnm orthorhombic phase.

Substitution of La with Ho leads to a decrease of Curie temperature and specific/molar magnetization of $La_{0.54}Ho_{0.11}Ca_{0.35-x}Na_xMn_{0.97}Cu_{0.03}O_3$ and $La_{0.54}Ho_{0.11}Ca_{0.35}Mn_{1-y}Cu_yO_3$ manganites, as compared with $La_{0.65}Ca_{0.35}MnO_3$ manganites. Substitution of Mn with Cu prevents the forming of Mn^{3+}-O-Mn^{4+} bonds and enhances the antiferromagnetic bonds.

Small substitution of Ca with Na has an opposite effect, leading to an increase of the DE interaction. However, for larger Na concentration, the increase of Mn^{4+} concentration enhances the superexchange interactions Mn^{4+}-O-Mn^{4+}, and a rapid decrease of the specific magnetization and of Curie temperature occur.

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