

# Structure and magnetoresistance of $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_3$ manganites

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It is investigated the effect of Mn substitution with Cu on the structure, magnetic and transport properties of  $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_3$  manganites obtained by standard ceramic technology. The phase composition of the samples was monitored by X-ray diffraction. The cell parameters, Mn-O distances, Mn-O-Mn angles, position of the atoms in the unit cell and the microstructure were determined and refined by means of CELLREF and FULLPROF programs. The increase of the La concentration leads to a decrease of the  $\text{Mn}^{4+}$  concentration, an increase of the unit cell volume and of the average radii of A and B places. Specific magnetization strongly depends on the thermal treatment and chemical composition. The Cu substitution produces very important change of the magnetic and transport properties, indicating very high values of magnetoresistance at temperatures higher than room temperature.

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## 1. Introduction

The  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  manganites, where A=RE or Alk (RE=rare earth as Nd, Sm, Tb, Ho, Dy etc and Alk=Sr, Ba, Ca) are known as magnetoresistive materials: a change of the resistivity is possible when is applied a magnetic field [1,2]. The transport and magnetic properties of manganites can be explained by means of double exchange mechanism, proposed by Zener and later developed by Anderson and Hasegawa.

The aim of this work is the study of the structure and magnetic properties of some  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  manganites, where Mn is partially substituted with Cu.

## 2. Experimental

The  $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_3$  (LCMCO) manganites were sinterized by standard ceramic technology, using as precursors CaO,  $\text{La}_2\text{O}_3$ ,  $\text{MnO}_2$ , CuO (99.9%) oxides. The phase composition of the presintered and sintered samples was monitored by X-ray diffraction. The unit cell parameters, Mn-O distances, Mn-O-Mn angles, position of the atoms in the unit cell and the microstructure (microstrains and coherent distances) were determined and refined by means of the DICVOL, CELLREF and FULLPROF programs. A diffractometer with data system acquisition and Cu anode X-ray tube was used. X-ray measurements were performed at room temperature. The magnetic measurements (specific magnetization, Curie temperature) were performed with a Foner type

magnetometer, with a data acquisition system, between 77 and 300 K. A nickel sphere (Erba – Italy) was used as standard. The resistance was measured at temperatures higher as room temperature, by using the four probe method, in magnetic field. Corresponding data were recorded with an acquisition data system. The performances of the bridge were tested with standard etalons.

## 3. Results and discussion

$\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  manganites are particularly interesting, since its can be prepared over the whole range of doping ( $0 < x < 1$ ). For relatively small Ca concentration ( $0.2 < x < 0.4$ ) these manganites exhibit a large magnetoresistance associated with a ferromagnetic transition. At higher Ca concentration, the charges become localized due to Coulomb and electron-phonon interactions:  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  cations are ordered in the periodic crystalline lattice, the antiferromagnetic interactions prevailing on the double exchange interaction. The sintered in air manganites contain a single phase, characterized by an ortorhombic unit cell, GS 62, Pbnm (see Figs. 1 and 2). We consider that the Cu cations are bivalent, with a 87 pm radius, Mn cations are trivalent (78.5 pm) and tetravalent (67 pm), respectively (on Shannon).

The increase of the La concentration leads to a decrease of the  $\text{Mn}^{4+}$  concentration, an increase of the unit cell volume and of the average radii of A and B places (see Table 1).

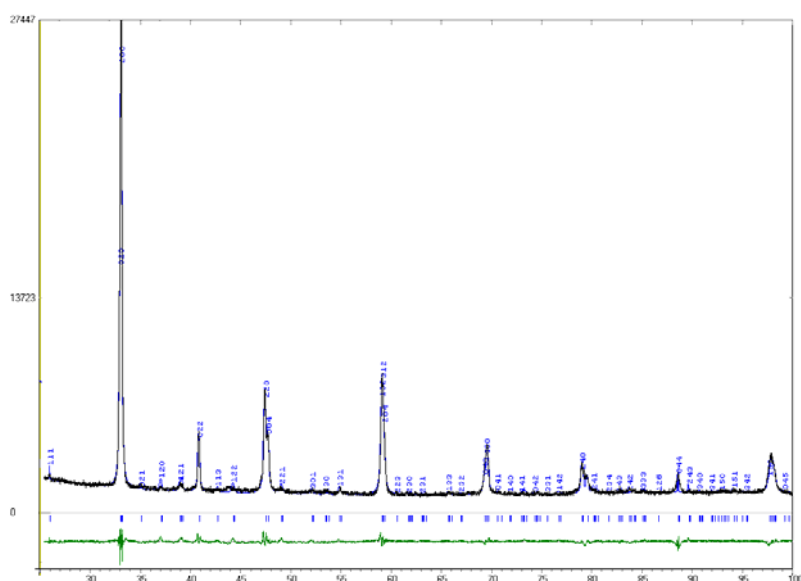


Fig. 1. Diffractogram observed (black), calculated (blue) and the difference between the observed and calculated diffractogram for  $\text{La}_{0.4}\text{Ca}_{0.6}\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_3$ .

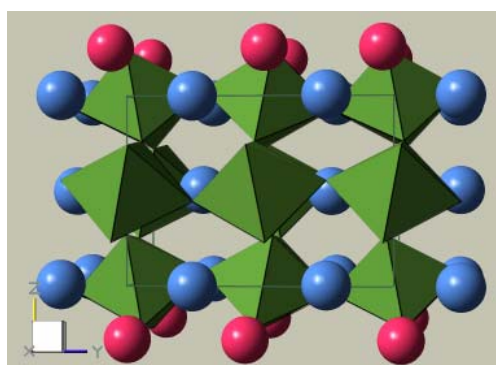


Fig. 2. The  $Pbnm$  unit cell of manganites Oxygen anions – red; Ca (La) cations – blue;  $\text{MnO}_6$  octahedra – green.

Table 1. The variation of the lattice constants ( $a, b, c$ ) and of the of LCMCO manganites.

x	a(Å)	b(Å)	c(Å)	V(Å <sup>3</sup> )	D(nm)	$\epsilon$ ( $\cdot 10^{-3}$ )
1.0	5.272 <sub>4</sub>	5.288 <sub>1</sub>	7.466 <sub>9</sub>	208.87	65.50	0.494
0.8	5.307 <sub>1</sub>	5.312 <sub>0</sub>	7.515 <sub>1</sub>	211.86	55.34	0.108
0.6	5.407 <sub>0</sub>	5.412 <sub>5</sub>	7.603 <sub>4</sub>	223.94	48.07	0.409
0.5	5.421 <sub>5</sub>	5.436 <sub>5</sub>	7.643 <sub>7</sub>	225.53	54.70	0.502

Table 2. The Mn(Cu)-O distances and Mn-O-Mn angles of some  $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_3$  manganites.

	x=1.0	x=0.8	x=0.6	x=0.5
Mn-O <sub>ap</sub> (Å)	1.9030	1.9016	1.9476	1.947
Mn-O <sub>eq</sub> (Å)	1.9642, 1.7978	1.9783, 1.8105	2.040, 1.954	2.017, 1.938
Mn-O <sub>ap</sub> -Mn (°)	165.929	164.778	154.852	154.641
Mn-O <sub>eq</sub> -Mn (°)	157.600	161.778	146.609	146.950

Table 3. The average radii of A ( $\langle r_A \rangle$ ) and B ( $\langle r_B \rangle$ ) places and tolerance (t) factors for  $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_3$  manganites (calculated by using crystalline radii on Shannon).

x	$\langle r_A \rangle$ (Å)	$\langle r_B \rangle$ (Å)	t
1.0	1.260	0.690	0.932
0.8	1.270	0.690	0.930
0.6	1.280	0.713	0.914
0.5	1.285	0.725	0.907

Our structure data are on unit-cell parameters are in agreement with those founded by Alons et al on  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  [4]. The differences are due: 1) the substitution of Mn cations with Cu cations and 2) the thermal treatment. The lattice constants and the unit cell volume increase with the increase of the La concentration in the sample (s. Table 1), in agreement with the ratio between the ionic radii of La and Ca, respectively  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ . The FullProf procedure allowed us to determine the positions of the cations and anions in the unit cell [3], the distances Mn-O and the Mn-O-Mn bond angles (s. Table 2). The cation distribution and the average radii of A ( $\langle r_A \rangle$ ) and B ( $\langle r_B \rangle$ ) places calculated in agreement with [3] are given in Table 3.

The increase of the distortion on B places should be due to the increase of the  $\text{Mn}^{3+}$  or  $\text{Cu}^{2+}$  concentration (associated with John-Teller effect) in the sample. Because the radius of  $\text{Mn}^{3+}$  are higher as those of  $\text{Mn}^{4+}$ , the increase of the  $\text{Mn}^{3+}$  concentration should lead to an increase of the B radius. It is in agreement with the observed values of the Mn(Cu) $\text{O}_6$  octahedra distortions (see ref. [3], for atomic coordinates and Table 2 for Mn-O<sub>ap</sub> and Mn-O<sub>eq</sub> distances). The local structure of some  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  manganites was investigated by Subias et al [5], means of XANES and circular magnetic X-ray dichroism techniques at MnK edge. They shown that only one kind of Mn cations there is on the B places,

independently of  $Mn^{3+}/Mn^{4+}$  ratio. They evidenced the  $MnO_6$  regular octahedra in the metallic ferromagnet phase for the  $La_{1-x}Ca_xMnO_3$  manganites. The actual X-ray data, performed in the paramagnetic region, indicate a distorted orthorhombic phase ( $Pbnm$ ), with a  $Mn(Cu)O_6$  distorted octahedra (s. Tab.2 for  $Mn(Cu)-O$  distances and  $Mn(Cu)-O-Mn(Cu)$  angles). The variation of the deformation of the octahedra associated with B places is quite complex. At small La concentration, where  $Mn^{3+}$  concentration is very small, the deformation is practic constant and can be associated only with Cu cations, because the  $Mn^{4+}$  cations present no Jahn-Teller effect. The increase of La concentration in the manganites leads to the appearance of the  $Mn^{3+}$  cations, supporter of a large Jahn-Teller effect, which should augments the octahedra deformation (s. Table 2). An intriguing behaviour presents the compound corresponding to  $x=0.6$ , which has the smallest deformation from the investigated manganites. This is connected probably with the increase of the unit cell volume, when the La concentration increases. At temperatures higher as Curie temperature ( $T_C$ ),  $La_{1-x}Ca_xMn_{0.9}Cu_{0.1}O_3$  manganites are dinamically distorted, but can stabilize this distortion, in agreement with Alonso et al [4] and Subias et al [6].

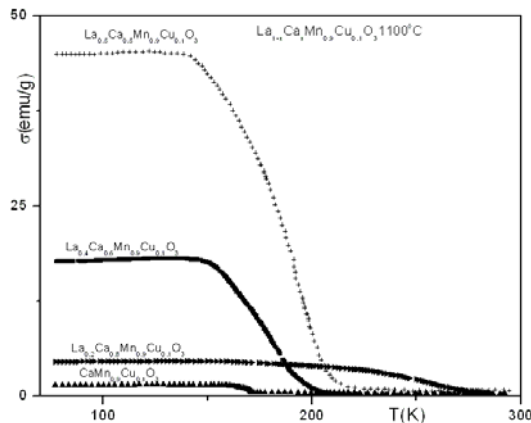


Fig. 3. The dependence of the specific magnetization on the chemical composition and the temperature for LCMCO system (sample with  $x=0.8$  was sintered at  $1200^\circ C$ ).

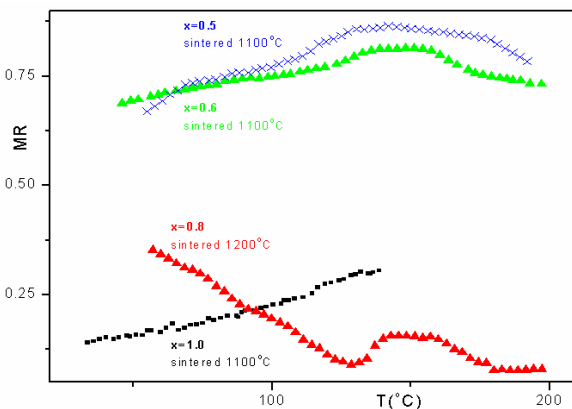


Fig. 4. Magnetoresistance vs temperature and chemical composition for the LCMCO system.

There is a good correspondence between the crystalline average radii (s. Tab.3) and the Mn-O distances (s. Table 2). The differences, which appear for the samples corresponding to  $x=0.6$  and  $x=0.5$ , are due to the oxygen concentration in the samples, implicitly to the  $Mn^{3+}/Mn^{4+}$  concentrations ratio. By comparing the calculated average radii of B places with the average Mn-O distances for the samples corresponding to  $x=0.6$  and  $x=0.5$ , respectively, we can conclude that the  $Mn^{3+}$  concentrations should be higher, respectively, lower as those calculated. However, the observed molecular magnetizations are lower as those calculated (s. Fig. 3 and Table 4).

Table 4. The variation of the magnetic properties of the  $La_{1-x}Ca_xMn_{0.9}Cu_{0.1}O_3$  system.

Chemical composition	$\sigma$ (uem/g)	$T_C$ (K)	$P_{obs}$ ( $\mu_B/f.u.$ )	$P_{cal}$ ( $\mu_B/f.u.$ )	$\delta^{**}$
$CaMn_{0.9}Cu_{0.1}O_{2.9}$	1.5	170.6	0.038	0.230	0.006
$La_{0.2}Ca_{0.8}Mn_{0.9}Cu_{0.1}O_{2.95}^*)$	4.6	255.1	0.126	0.230	0.018
$La_{0.4}Ca_{0.6}Mn_{0.9}Cu_{0.1}O_3$	18.0	176.2	0.589	1.630	0.084
$La_{0.5}Ca_{0.5}Mn_{0.9}Cu_{0.1}O_3$	45.3	193.9	1.561	2.330	0.235

<sup>\*</sup>) sintered at  $1200^\circ C$ ; <sup>\*\*</sup>) oxygen deficit, calculated with  $La_{1-x}Ca_xMn_{0.9}Cu_{0.1}O_{3-\delta}$ , by using  $p_{obs}$  data

Because the samples were sintered in the same conditions, except the sample corresponding to  $x=0.8$ , the amount of oxygen in the samples should be practically the same for all the samples. The increase of the La concentration in the samples leads to an increase of the Mn-O distances and a decrease of the Mn-O-Mn angles (s. Table 2). On other hand, the calculated average radii of B places increase also (s. Table 3). It means a decrease of the antiferromagnetic interactions as comparing with the ferromagnetic interactions, which leads to an increase of the Curie temperature and of the magnetic moment (s. Table 4 and Fig. 3).

A relative small increase of the  $Mn^{3+}$  concentration, as compared with the rest of samples, takes place in  $La_{0.2}Ca_{0.8}Mn_{0.9}Cu_{0.1}O_{3-\delta}$  manganite, due to a higher sintering temperature. It corresponds to the highest Curie temperature, implicitly to a stronger Mn-O-Mn bond interactions (s. Fig. 3 and Table 4). The specific magnetization decreases monotonously with the increase of La concentration in the samples (s. Fig. 3, in agreement with data of ref. [4] and the  $Mn^{3+}/Mn^{4+}$  concentrations). Concerning the variation of the resistance of the samples vs temperature, at temperature near room temperature prevails the semiconductor behavior, specially for the samples with higher Ca concentration ( $x=1.0$  and  $x=0.8$ ); the metallic behavior appears clearly at  $La_{0.5}Ca_{0.5}Mn_{0.9}Cu_{0.1}O_3$  [3]. Despite the dominating semiconductor behavior, all the samples present an important negative magnetoresistive effect, which increase with the decrease of the Ca concentration (s. Fig. 4). The resistance of the samples increases with the increase of the Ca concentration, implicitly with the increase of the  $Mn^{3+}$  concentration. In agreement with the model of Alonso et al

the magnetic behavior of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_y$  manganites depend on the  $\text{Mn}^{4+}/\text{Mn}^{3+}$  concentrations. The localization of  $\text{Mn}^{4+}$  cations around  $\text{Ca}^{2+}$  cations, respectively of  $\text{Mn}^{3+}$  cations around  $\text{La}^{3+}$  cations should leads to the formation of the ferromagnetic clusters that are locally conducting. On Aslam et al [7] for the composition near  $x \approx 0.5$  the microstructure formed during the thermal treatment behaves in the paramagnetic state, too. In agreement with the literature [5,6,7] we suppose that at low temperatures exist an antiferromagnetic insulating phase and a ferromagnetic phase, very close in energy. The metallic cluster volume increases with the increase of the applied magnetic field, even at the temperature higher als Curie temperature.

#### 4. Conclusions

A new type of manganites,  $\text{La}_{1-x}\text{Ca}_x\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_3$ , with Pbnm structure were obtained by standard ceramic technology. The substitution of Mn with Cu and the treatment conditions influence the manganite structure and the magnetic properties, via the change of  $\text{Mn}^{3+}/\text{Mn}^{4+}$  concentrations. The sintered perovskites present an important magnetoresistive effect at temperature equal or higher as room temperature. Effect of magnetic field was observed even for the samples with smaller La concentration and was attributed to the formation of ferromagnetic clusters, which are present in the samples above Curie temperature. The efect of Cu substitution is the improvement of the transport properties.

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