JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 5, May 2007, p. 1582 - 1585

Extrinsic magnetoresistance near room temperature in the La-Ca manganites doped with Cu

M.-L. CRAUS[a,b], M. LOZOVAN[b*], C. BACIU[c]
[a]*Joint Institute for Nuclear Research-Laboratory of Neutron Physics, Dubna, Joliot-Curie 6, 141980 Dubna, Region Moskva, Russia*
[b]*National Institute of R&D for Technical Physic s- IFT, Iasi, 47, Mangeron Blvd. Iasi, Romania*
[c]*"Gh. Asachi" University, 11 Carol I Boulevard, 700050, Iasi, Romania*

The $La_{1-x}Ca_xMn_{0.9}Cu_{0.1}O_3$ perovskites were sintered by means of standard ceramic technology. The final sintering took place between 1100 and 1200°C in air. The sintered samples were analysed with a STOE (Guinier type) diffractometer, by using $CuK\alpha_1$ radiation. The position of the cations and anions in the unit cell, the average size of the coherent blocks and the microstrains were obtained by means a Rietveld program. The variation specific magnetization with temperature was determined with a Foner type magnetometer, between 77 and 400 K, while the transport properties were performed between 300 and 450 K. The investigated compounds have an orthorhombic structure (Pbnm, SG 62), with an increase of the lattice constants with the La concentration in the samples. The average radii of A and B places (r_A and, respectively, r_B) increase with the La^{3+} concentration, while the increase of the oxygen concentration leads to a decrease of r_B. The microdistorstions exhibt a dependence on the sintering conditions. We proposed a model which explains the observed variation of the transport behavior of the investigated manganites.

(Received November 14, 2006; accepted April 12, 2007)

Keywords: Extrinsic magnetoresistance, Crystalline and magnetic structure, La-Ca manganites

1. Introduction

The $La_{1-x}Ca_xMnO_3$ manganites crystallize at high temperatures in Pm3m cubic structure. At low temperature these compounds could crystallize in orthorhombic (Pnma, Pbnm), hexagonal (R-3c) or monoclinic ($P2_1/m$) structure [1]. In agreement with the data of Pissas and Kallias, the structure of samples corresponding to $0.5 \le x \le 0.9$ can be characterized by Pnma (GS 62) unit cell: La/Ca occupy the 4c sites ($x \approx 0.025$;1/4 ; $z \approx -0.005$), Mn – (4a) sites (0 ;0 ;0), O – (4c) sites ($x \approx 0.55$;1/4 ; $z \approx 0.065$) and (8d) sites ($x \approx 0.28$;$y \approx 0.03$; $z \approx 0.72$). The lattice constants and Mn-O distances (d_{Mn-O}) monotonously decrease with the increase of dopping level [1]. On Ling et al the decrease of Ca concentration lead to an increase of a secondary phase, with $P2_1/m$ structure, with the same chemical composition as the major phase [2]. The Jahn-Teller (J-T) distortions of the MnO_6 octahedra or charge ordering determine the crystallographic transitions at low temperature. More attention was paid to the compounds corresponding $x \approx 0.3$, where the magnetoresistance attains its maximum value. In the $x > 0.5$ region, where the magnetic moment is zero and the resistivity very high, have been performed relatively less investigations, including on the substituted manganites. Above the Curie temperature, the interactions local J-T distortions with the charge carrierrs determine the transport behavior [3]. Between the super exchange (SE) and double exchange (DE) interactions takes place a competition, which also enhance the charge transport.

The partial substitution of Mn with Fe in $La_{0.5}Ca_{0.5}MnO_3$, with Fe contributes to the suppression of CO phase and the percolation/ stabilization of the metallic magnetic phase [4]. The increase of the Fe concentration in the samples leads to a weakening of the double exchange (DE) interaction. The appearance of metallic magnetic clusters in the paramagnetic region (PM) was also put in evidence by X-band EMR measurements on $La_{0.8}Ca_{0.2}MnO_3$ and $La_{0.2}Ca_{0.8}MnO_3$ manganites [5].

The aim of present paper is to investigate the correlation between the crystalline and magnetic structure, on one hand, and the transport mechanism characteristics, on other hand.

2. Experimental

The manganites were sinterized by standard ceramic technology, using as precursors CaO, La_2O_3, MnO_2, CuO (99.9%) oxides. The phase composition of the presintered and sintered samples was monitorized 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.

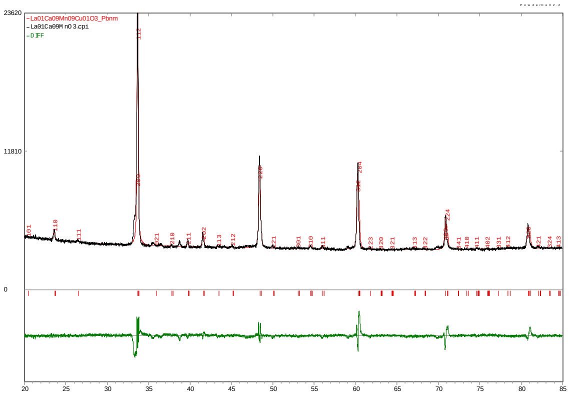

Fig. 1. The observed and calculated difractograms of the $La_{0.1}Ca_{0.9}Mn_{0.9}Cu_{0.1}O_3$ manganite (PowderCell program).

The resistance was measured at temperatures higher than 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

The $La_{1-x}Ca_xMn_{0.9}Cu_{0.1}O_3$ manganites structure can be described by using orthorhombic Pbnm (GS 62) unit cell (Table 1 and Fig. 2).

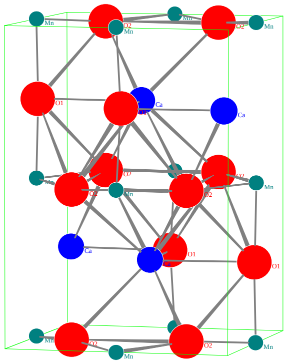

Fig. 2. The unit cell (Pbnm GS 62) of $La_{1-x}Ca_xMn_{0.9}Cu_{0.1}O_3$.

The actual data are in agreement with crystallographic data concerning $La_{1-x}Ca_xMn_{0.9}O_3$ manganites [7,8]. The decrease of the oxygen concentration in the manganites leads to an increase of the Mn^{3+} concentration, implicitly to an increase of the lattice constants and unit cell volume. The substitution of Mn cations with Cu cations, which have a larger ionic radius, explains the increase of the lattice constants in $La_{1-x}Ca_xMn_{0.9}Cu_{0.1}O_3$ as comparing with those of $La_{1-x}Ca_xMnO_3$ manganites (Table 1). The average blocks size, D, and the microstrains (ε) vary chaotically with the doping level (Table 1).

Table 1. Lattice constants (a, b, c), volume of the unit cell (V), average size of the crystalline blocks (D) and microstrains (ε) vs. Ca concen-tration (x) in $La_{1-x}Ca_xMn_{0.9}Cu_{0.1}O_3$ manganites.

x	a(Å)	b(Å)	c(Å)	V(Å^3)	D(Å)	ε (.10^{-3})
0.5	5.422	5.437	7.644	225.53	547	0.502
0.6	5.407	5.413	7.603	223.94	481	0.409
0.7	5.347	5.347	7.542	215.64	562	0.706
0.8	5.307	5.312	7.515	211.86	553	0.108
0.9	5.322	5.307	7.503	212.66	468	0.641
1.0	5.272	5.288	7.467	208.87	655	0.494
a*)	5.264	5.279	7.448			
b*)	5.265	5.282	7.452			

a*) $CaMnO_3$ [7]; b*) $CaMnO_{2.98}$ [8]

Table 2. Average radii of A and B places (⟨r$_A$⟩, ⟨r$_B$⟩) and average distances ⟨d$_{A-O}$⟩ and ⟨d$_{Mn-O}$⟩ vs Ca concentration (x) in $La_{1-x}Ca_xMn_{0.9}Cu_{0.1}O_3$ manganites.

x	⟨r$_A$⟩(Å)	⟨r$_B$⟩(Å)	⟨d$_{A-O}$⟩(Å)	⟨d$_{Mn-O}$⟩(Å)
0.5	1.280	0.725	2.5459	1.9605
0.6	1.276	0.713	2.5380	2.0215
0.7	1.272	0.702	2.5399	1.8780
0.8	1.268	0.690	2.5660	1.8968
0.9	1.264	0.690	2.5480	1.9320
1.0	1.260	0.690	2.5746	1.8926

On the other hand, the D values are rather high; it's supposing a large size of the crystallites. Because the microstrains are relatively small, the sintered manganites will contain small concentrations of defaults, with corresponding effects on the extrinsic magnetoresistance. The sample corresponding to x=0.8 was treated at higher temperatures (1200°C) as the other samples [9].

Table 3 Chemical disorder factor (σ^2), observed tolerance factor (t_{obs}), observed Mn-O-Mn bonds angles (⟨∠Mn-O-Mn⟩) and the band width (w) vs. doping level (x).

x	σ^2 (Å^2)	t_{obs}	⟨∠Mn-O-Mn⟩	w (a.u.)
0.5	0.000400	0.902	149.514	0.082
0.6	0.000384	0.891	149.357	0.073
0.7	0.000336	0.956	152.297	0.098
0.8	0.000256	0.957	162.778	0.102
0.9	0.000144	0.995	168.231	0.106
1.0	0.000000	0.962	161.710	0.102

The sample sintered at higher temperatures has a higher amount of Mn^{3+} as comparing with the same sample sintered at lower temperature. The cell volume is smaller, probably due to a smaller oxygen concentration (s. [9]). For x≥0.8 there are only small amounts of Mn^{3+} in the samples, in agreement with the magnetic data (Table 1 and ref. [9]). The increase of the Mn^{4+} concentration is associated with flattening of the MnO_6 octahedra, observed from the variation of relative elongation;

$$\left[\left\langle d^{eq}_{Mn-O}\right\rangle - d^{ap}_{Mn-O}\right] \Big/ d^{ap}_{Mn-O} \qquad (1)$$

with Ca concentration (d^{ap}_{Mn-O} is the distance between Mn and apical oxygen) (s. ref. [9]), in agreement with Pissas and Kallias structure data on $La_{1-x}Ca_xMnO_3$ ($x\in[0.5\div0.9]$) [1].

The increase of La concentration in the samples leads also to an sudden increase of the band width ($w \propto \cos\theta/(d_{Mn-O})^{3.5}$) for $x\geq0.8$, due to d_{Mn-O} (s.Tab.3), implicitly to a diminish of the Curie temperature and exchange interaction (s. ref.[9]).

At the temperatures higher as the Curie/MI transition temperatures some manganites exhibit activated transport. Around Mn^{3+} Jahn-Teller (JT) cations appear a strong electron-lattice interaction, which diminishes with the increase of bivalent cations substitution on A places.

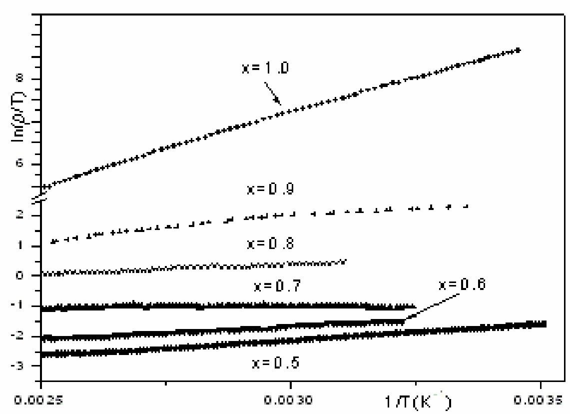

Fig. 3 The variation of the resistivity with T and chemical composition, at 2T.

Jain et al have tasted more transport mechanisms on $La_{1-x}Ca_xMnO_3$ ($x\in[0.1\div0.3]$) manganites monocrystalls at $T>T_C$[6] . They observed that in this region the transport is characterized by the variable rage hopping (VRH) mechanism.

The substitution of Ca with La in $La_{1-}Ca_xMn_{0.9}Cu_{0.1}O_3$ manganites increases the resistivity of the samples (s. Fig. 3). The resistivity values at room temperature are between 10^2 and 10^6 Ω.cm (s.Tab.4). Near room temperature the best fit for the dependence resistivity-temperature was obtained for the small polaron-hopping mechanism (SPH) (s.Fig. 4):

$$\rho = \rho_0 T \exp\left(\frac{E_p}{k_B T}\right) \qquad (2)$$

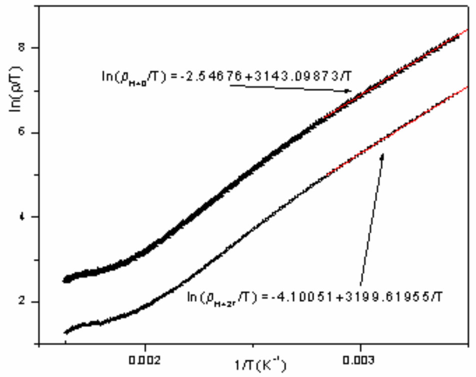

Fig. 4. The variation of the resistivity with the temperature and intensity of magnetic field of $CaMn_{0.9}Cu_{0.1}O_3$ manganite

All the investigated samples exhibit a negative magnetoresistance (s. ex. Fig.4), the variation of the resistivity depending on the chemical composition. An exponential decrease of the resistivity values at room temperature with the La/Ca concentration was observed. The activation energy of the transport process depends chaotically on the chemical composition (s.Tab.4).

Table 4. Resistivity (ρ_{300K}) and activation energy (E_p) of the charge transport near room temperature for the $La_{1-}Ca_xMn_{0.9}Cu_{0.1}O_3$ manganites

x	ρ_{300K} (Ω.cm)		E_p (eV)	
	H=0	H=2T	H=0	H=2T
0.5	100	51	0.09_8	0.09_5
0.6	313	184	0.07_2	0.05_8
0.7	117	110	0.06_1	0.03_9
0.8	1048	520	0.10_8	0.05_8
0.9	3034	2971	0.07_3	0.08_0
1.0	-	-	0.27_1	0.27_3

In the polycrystalline samples the resistivity component due to the boundaries layers or the defaults concentration of the crystalline "core" can mask intrinsic transport behavior. This affirmation is sustained by the observed resistivity values of the polycrystalline samples, which are a factor of two higher than that of the single crystals with the same chemical composition. The thickness of the boundary layer is less dependent on thermal treatment or chemical composition, as crystalline "core" of the crystallites. A large, without defaults crystalline "core" should exhibits only the intrinsic transport behavior. A suitable sintering/treatment temperature is generally enough to diminish the influence of the boundaries layers on the resistivity behavior. The $La_{1-}Ca_xMn_{0.9}Cu_{0.1}O_3$ manganites have an uncommon transport behavior: despite the observed semiconductor-like variation of the resistivity with the temperature, a large negative magnetoresistance near room temperature is present. We have explained the effect of the magnetic field, by the presence of the magnetic clusters, formed by Mn^{3+} -Mn^{4+} pairs, confirmed by the magnetic measurements [9]. The relative volume of the magnetic clusters varies with the La/Ca concentration and the thermal treatment. The presence of the magnetic clusters in the paramagnetic range in $La_{1-x}Ca_xMnO_3$ manganites was put in evidence by Shames et al. [10]. We have demonstrated that the substitution of Mn with Cu allows us to obtain ferromagnetic $La_{1-}Ca_xMn_{0.9}Cu_{0.1}O_3$ manganites (x>0.5) with Curie temperatures lower as room temperature [9]. $La_{1-x}Ca_xMnO_3$ manganites with x>0.5 are in antiferromagnetic ground state, but in the paramagnetic region EMR data put in evidence the presence of magneto-impurity-like clusters [10]. Since, in agreement with Shames et al, in the paramagnetic state of $La_{0.8}Ca_{0.2}MnO_3$ the magnetic clusters are formed by double-exchange coupled Mn^{3+}-Mn^{4+} ions, we suppose that our $La_{1-}Ca_xMn_{0.9}Cu_{0.1}O_3$ ferromagnetic-like manganites, above Curie temperature, are formed by a nonmagnetic matrix, where exist short-ranged DE coupled Mn^{3+}-Mn^{4+} clusters. A study performed by Aselage et al on $La_{0.75}Ca_{0.25}MnO_{3-\delta}$ indicated a decrease of the conductivity with the increase of the oxygen vacancy concentration [11]. The calculated oxygen deficit, on the basis of specific magnetization at low temperatures, decreases with the increase of Ca concentration in the samples [9]. On other hand, the increase of Ca concentration leads to a monotonous increase of Mn^{4+} concentration, while the Mn^{3+}-Mn^{4+} pars decrease monotonously with x. On Jonker the picture is even more complicated, the ferromagnetism, implicitly the DE interactions, being induced by the microstrains due the presence of different cations in crystalline lattice. In the absence of Cu, the $La_{1-x}Ca_xMnO_3$ manganites (x>0.5) are antiferromagnets. The substitution of Mn with Cu (also a Jahn-Teller cation) seems to decrease the superexchenge interactions between B cations as comparing with double-exchange interactions. Taking into account that the Cu radii are much larger as Mn radii, it is possible that a non-uniform distribution of the Cu/Mn cations takes place across the boundary layer of the crystallites. It will contribute to the conduction, implicitly to the extrinsic magnetoresistivity effect. A non-uniform distribution of Cu/Mn cations near the crystallites surface can explain the observed values of the microstrains and their relatively small impact on the magnetoresistivity.

4. Conclusions

We have sintered by ceramic technology $La_{1-}Ca_xMn_{0.9}Cu_{0.1}O_3$ manganites, with Pbnm orthorhombic structure. The substitution of Mn with Cu leads to destroying of the superstructure observed at low temperatures. Near room temperature the samples exhibit large negative magnetoresistance. The samples can be considered as formed by a mixture of ferromagnetic clusters in an insulating matrix. In the paramagnetic region the behavior of transport is characterized by small polaron hopping mechanism.

References

[1] M. Pissas, G. Kallias, Phys. Rev. **B 68**, 134414 (2003).

[2] C. D. Ling, E. Granado, J. J. Neumeier, J. W. Lynn, D. N. Argyriou, Phys.Rev. **B68**, 134439 (2003).

[3] N. D. Mathur, P. B. Littlewood, Solid State Communications **119**, 271 (2001).

[4] P. Levy, L. Granja, E. Indelicato, D. Vega, G. Polla, F. Parisi, J. M. M. M. **226-230**, 794 (2001).

[5] A. I. Shames, E. Rozenberg, M. Auslender, G. Gorodetsky, C. Martin, A. Maignan, Ya. M. Mukovskii, J. M. M. M. **290–291**, 910 (2005).

[6] H. Jain, A. K. Raychaudhuri, Ya. M. Mukovskii, D. Shulyatev, Sol. State Comm. **138**, 318 (2006)

[7] K. R. Pöppelmeier, M. E. Leonowicz, J. C. Scalon, J. M. Longo, W. B. Yelon, J. Solid State Chem. **45**, 71 (1982).

[8] H. Taguchi, M. Nagao, T. Sato, M. Shimada, J. Solid State Chem.**78**, 312 (1989).

[9] M. -L. Craus, M. Lozovan, communication at ANMM2005, 2005 Iasi, Romania (in print)

[10] A. I. Shames, E. Rozenberg, M. Auslender, G. Gorodetsky, C. Martin, A. Maignan, Ya. M. Mukovskii, J. M. M. M. **290–291**, 910 (2005).

[11] T. L. Aselage, D. Emin, S. S. McCready, E. L. Venturini, M. A. Rodriguez, J. A. Voigt, T. J. Headley, Phys. Rev. B**68**, 134448 (2003)

[12] A. Aslam, S. K.Hasanain, M. Zubair, M. J. Akhtar, M. Nadeem, J. Phys.: Cond. Matter, **14,** 10305 (2002).

---

[*] Corresponding author: loz@phys-iasi.ro