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Electronic diagram modification in $La_{0.54}Ho_{0.11}Ca_{0.35}Mn_{1-x}(Co/Cr)_xO_3$ manganites

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The substitution of Mn with Co cations produces the segregation of electronic phases (two defective AFM phases) in PrCa manganite doped with Co. Magnetic phase is stabilized by the microstrains induced by the Co cations. We have prepared $La_{0.54}Ho_{0.11}Ca_{0.35}Mn_{1-x}(Co/Cr)_xO_3$ manganites by sol-gel method. The samples were monitorized by means of X-ray diffractometry (Cu Kα) at room temperature and XRD data were handled by means of Rietveld type programs. The phase composition and structure (unit cell type and parameters, position of the atoms in unit cell, Mn-O distances and Mn-O-Mn bonds angles, microstrains and average size of mosaic blocks) were determined. Magnetic data (variation of specific magnetization with temperature) were obtained with a Foner type magnetometer between 77 and 500 K, at 1T magnetic field intensity. Transport phenomena (variation of resistivity with temperature and magnetic field intensity) were performed by four probes method between 77 and 300 K. Transport properties, including the resistivity values and the transition temperature from metallic to insulator state strongly depend on the concentration of Co/Cr in the samples. The transition temperature decrease slower for doped with Cr samples as for those doped with Co. We discussed the influence of Co/Cr cations on the electronic phase diagram of the $La_{0.54}Ho_{0.11}Ca_{0.35}Mn_{1-x}(Co/Cr)_xO_3$ manganites.

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1. Introduction

Colossal magnetoresistance (CMR) observed in doped manganites ($La_{1-x}A_xMnO_3$, A = Ca, Sr, Ba) are generally attributed to a double exchange interaction (DE) between Mn^{3+} and Mn^{4+} cations via 2p oxygen orbitals [1]. The magnetoresistance phenomena cannot be explained only on the basis of DE theory. In the regions with large default concentrations, a large magnetoresistance can be also observed. Substitution of La by Ca in antiferromagnetic (AFM) $LaMnO_3$ results in stable $La_{1-x}Ca_xMnO_3$ systems, in which ferromagnetic (FM) double exchange (DE) Mn^{3+}–O–Mn^{4+} competes with AFM superexchange (SE): Mn^{3+}–O–Mn^{3+} [2]. Among the 3d-elements, Cr substitution is particularly interesting as Cr^{3+} (a non-Jahn–Teller ion) is isoelectronic with Mn^{3+}. In addition, the nature of the magnetic interaction between Cr^{3+}–O–Mn^{3+} is known to favour ferromagnetism through superexchange interaction (a large difference exists between the magnetic moments of trivalent Cr and Mn). Hence, one might expect to induce a ferromagnetic phase in an otherwise antiferromagnetic, charge-ordered ground state for the electron-doped manganites, depending upon the Mn^{3+}/Mn^{4+} ratio [3, 4]. The purpose of present work is to study the influence of the substitution of Mn with Co/Cr on the magnetic and crystalline structure of $La_{0.54}Ho_{0.11}Ca_{0.35}Mn_{1-x}$ (Co, Cr)$_x$ O_3 (LHCMCoMO/ LHCMCrMO) manganites.

2. Experimental

The samples with the chemical composition $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{1-x}$ $(Co/Cr)_xO_{3-\delta}$ (x=0.05, 0.10, 0.15) were prepared by sol-gel method, using as precursors rare earth oxides (La_2O_3 and Ho_2O_3) (purity: 99.99%), the Sr, Mn acetates (purity: 99.00%) and Cr nitrate (purity: 99.00%). The details of the preparation were already communicated [4]. After grinding, the samples were sintered finally at 1200 °C for 5 hours in air. The phase composition, structure, and lattice parameters were determined by powder X-ray diffraction using a diffractometer, equipped with a Co X-ray tube and a data acquisition system. The precision of the interplanar distances was better as 0.001 Å. The magnetic measurements were performed with a vibrating sample magnetometer between 77 and 600 K. The measuring systems were previewed with a data acquisition system.

The Mn-O distances, Mn-O-Mn angles, position of the atoms in the unit cell and were determined and refined by means of the DICVOL, POWDER Cell and FULLPROF programs.

3. Results and discussions

The sintered samples contain only a phase, which have an orthorhombic structure (SG 62 – Pnma) (s. Figs. 1a and 1b), in agreement with the literature [5]. The cell parameters were refined by Rietveld method (Figs. 1 and Table 1).

The lattice constants and the microstrains vary non monotonously vs. cobalt concentration in the samples, while average size of the crystalline blocks show a maximum, corresponding to x=0.15 (s. Table 1 and 2). A similar behavior present the doped with Cr samples. A small difference exists between the lattice constants of two series.

The Mn-O_{ap} and Mn-O_{eq} distances have a minimum, respectively, remain constant for the studied range of composition, while the Mn- O_{ap} -Mn and Mn- O_{eq}-Mn angles show a minimum, respectively, a monotonous decrease with the cobalt concentration (s. Table 2).

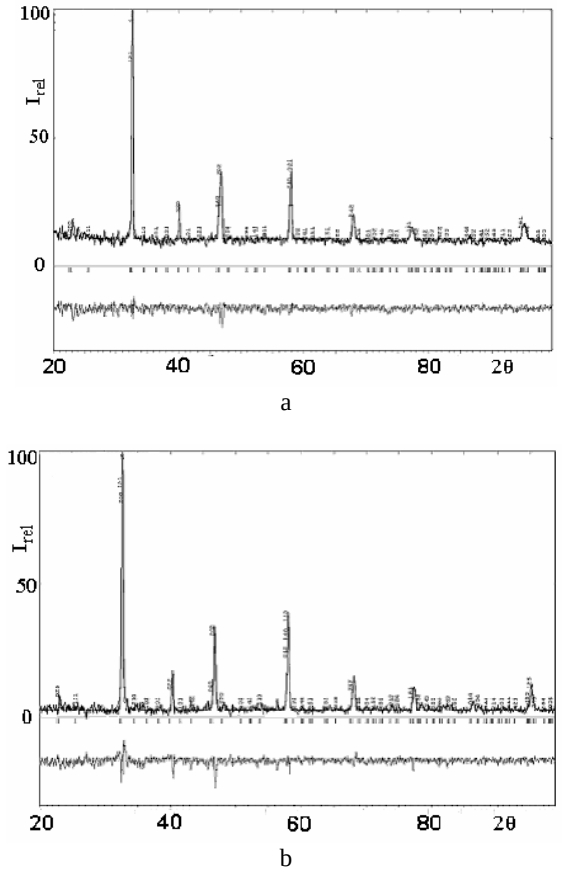

Fig. 1. Calculated and observed difractograms of LHCMCoMO (difference at bottom) (a) x=0.0; (b) x=0.2.

Table 1. Dependence of the lattice constants (a, b, c) and unit cell volume (V) on the Co concentration (x) in LHCMCoMO.

x	a(Å)	b(Å)	c(Å)	V(Å^3)
0.00	5.5296	7.8559	5.5190	239.745
0.05	5.5500	7.8608	5.5184	240.780
0.10	5.5083	7.8318	5.5175	238.024
0.15	5.5208	7.8469	5.5402	240.008
0.20	5.5218	7.8522	5.5363	240.044

Table 2. Dependence of the average size of mosaic blocks (D) and of themicrostrains (ε) with the Co concentration (x) in LHCMCoMO.

x	D(Å)	ε
0.00	521	0.001193
0.05	573	0.000475
0.10	647	0.000973
0.15	855	0.001037
0.20	522	0.000087

Table 3. Mn-O_{ap} (d_{MnOap}) , Mn-O_{eq} (d_{MnOeq}) distances and Mn-O_{ap} -Mn ($\angle$Mn- O_{ap} –Mn= α_{ap}), Mn- O_{eq} -Mn ($\angle$Mn- O_{eq} - Mn= α_{eq}) angles to LHCMCoMO manganites.

x	d_{MnOap} (Å)	d_{MnOeq} (Å)	α_{ap} (^{o})	α_{ap} (^{o})
0.00	1.9915	1.9787	160.950	161.333
0.05	1.9926	1.9822	160.957	161.350
0.10	1.9855	1.9745	160.903	161.393
0.15	1.9894	1.9808	160.865	161.372
0.20	1.9902	1.9806	160.873	161.614

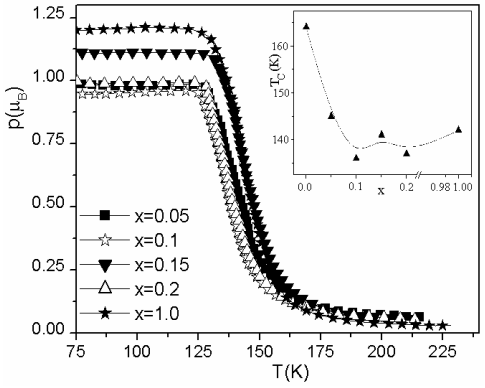

Fig. 2. Variation of molar magnetization vs T and Co concentration in LHCMCoMO manganites. In inlet – variation of Curie temperature on Co concentration.

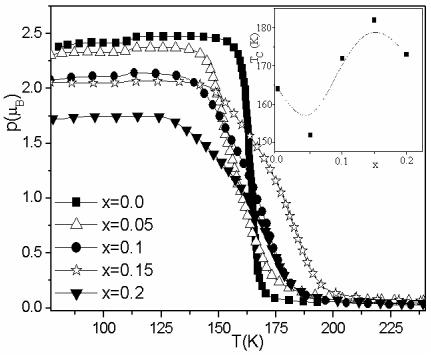

Fig. 3. Variation of molar magnetization vs T and Cr concentration in LHCMCrMO manganites. In inlet – variation of Curie temperature on Cr concentration.

The substitution of Co with Cr did not enhance large crystalline transformation because the radii of Co and Cr are close one to other: r_{Co3+}=0.75 Å, r_{Cr3+}=0.755 Å; r_{Co4+}=0.67 Å; r_{Cr4+}=0.69 Å. Data concerning the difference between crystallographic properties of LHCMCoMO and LHCMCrMO are sent to be published [7]. However, it seems that the crystallographic differences have a small influence on the magnetic/electric properties of $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{1-x}(Co/Cr)_xO_{3-\delta}$ manganites.

The lattice constants and the microstrains vary non monotonously vs. cobalt concentration in LHCMCoMO samples, while average size of the crystalline blocks show a maximum, corresponding to x=0.15 (Table 2). A similar behavior present the doped with Cr samples. A small difference exists between the lattice constants of two series.

Magnetic properties of LHCMCrMO manganites, are showing a monotonous decrease of the maximum molar magnetization, with the increase of the Cr concentration. The molar magnetization of LHCMCoMO manganites have a minimum vs Co concentration in the samples (s. Fig.4). The observed minimum of Curie temperature for LHCMCoMO manganites seems to be in agreement with the minimum of Mn-O distances and Mn-O-Mn bond angles (s. Table 3).

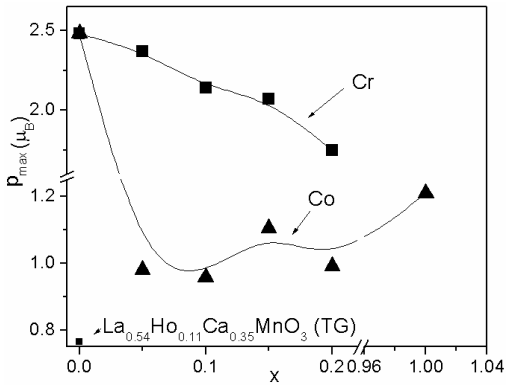

Fig. 4. Variation of maxumum molar magnetization of the $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{1-x}$ $(Co/Cr)_xO_{3-\delta}$ manganites. Undoped manganite was measured after 400 °C treatment (TG) and normal treatment.

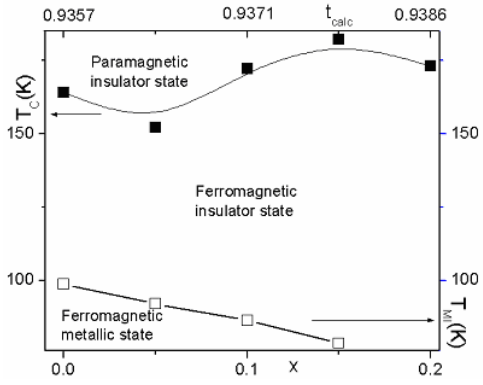

Fig. 5. Electronic phase diagram of LHCMCrMO manganites.

A large difference exists between magnetic properties of samples treated at high temperature and those treated at low temperature (Fig. 4: LHCMCrMO (x=0.0) treated at 400 °C, noted TG). This behaviour was attributed to the large defaults concentration present in the samples treated at low temperatures: diminishing of the Mn-O-Mn bond angles and increase of Mn distances lead to decrease of DE interactions, as comparing with SE interactions. If we consider that the cation distribution as given by the formula:

$$La^{3+}_{0.54}Ho^{3+}_{0.11}Ca^{2+}_{0.35}Mn^{4+}_{y}Mn^{3+}_{1-y-x}(Co/Cr)^{3+}_{x}O^{2-}_{3+\delta} \quad (1)$$

molecular magnetization will be given by $p_{max} = 3.65\text{-}2\delta\text{-}4x$ or $p_{max} = 2.45+14\delta$ if all Mn cations, respectively, only Mn^{3+}-Mn^{4+} pars participe to the magnetic moment of the molecule. The last relations can justify the molar magnetization of undoped, treated samples (s. Fig. 4). On other hand, on the last relation the substitution of Mn with Cr/Co should have no direct effect on the molecular magnetization, which are not in agreement with literature. If cobalt or chrom appear as Co^{4+}/ Cr^{4+} , molar magnetization will be given by:

$$p_{max} = 2.45+21\delta\text{-}7z \quad (4)$$

where z is the Co^{4+}/Cr^{4+} amount in the LHCMCoMO/ LHCMCrMO manganites. At least for small doping level with Cr, the Cr cations do not contribute to the magnetic moment of the samples. The presence of Co on the B places seem to distroy the interactions Mn-O-Mn not only by direct usbstitution of Mn with Co, but also by the effect of the Co on the lattice symmetry, that have a larger effect as Cr substitution (for x <0.2) (s.Fig.4). Curie temperatures are smaller for Co doped as for Cr doped manganites, that justifies our suppositions (s.Fig. 2 and 3).

The difference between the observed and calculated values of the molar magnetization of Cr doped manganites can be attributed also to the presence of a large amount of insulator/antiferromagnetic state and/or the change of the oxidation degree of Mn cations, favorites by the substitution of Mn with Cr. The behavior of the Co doped manganites, for large values of doping level, can be associated with an increase of the Co contribution to the magnetic moment. In both cases, if we attribute the magnetic moment only to Mn^{3+}-Mn^{4+} par, the magnetization should be influenced by the oxidation degree: a decrease of the oxygen concentration can lead very quickly to a diminish of the magnetic moment of the samples. Tolerance factor varies very little with the substitution of Mn with Co or Cr, because the crystalline radii of Mn^{3+}, Co^{3+} and Cr^{3+} are very close one together (s. Fig. 5). Chemical disorder degree has no influence, because the average radii of A cations remains unchanged for both series of manganites. The factors which could influence the magnetic state of the sample are the disorder of cations on the B places (that implies appearance of Co^{3+}-O-Co^{4+} or Co^{3+}-O-Mn^{4+} etc bonds in a crystallite region) and the oxygen deficit. A large difference was

observed between the Curie temperature and the transition from the metal to insulator state: we consider that the contribution of the large defaults concentration zone (as boundary layers), with more distorted Mn-O-Mn bonds and a lower associated Curie temperature, and predominates (Fig. 5). The transition temperatures for Co doped manganites are lower than the inferior limits of actual measurements range. Measurement will be performed for both series between 10 –77 K, to clarify the behavior of magnetoresistance and the transport mechanism at low temperatures

4. Conclusions

The subtitution of Mn with Co and Cr have different influence on the electronic state of $La_{0.54}Ho_{0.11}Ca_{0.35}Mn_{1-x}(Co/Cr)_xO_3$ manganites. Co substitution have a larger influence on the bandwidth and, implicitly, on the double exchange interaction, as compared with Cr substitution. It seems probably that, at large Co substitution, a DE interaction takes places between the Co cations (via oxygen orbitals). The substitution of Mn with Cr leads only to the diminishing of the Mn-O-Mn bonds and to the decrease of the magnetic moment of the samples.

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