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THE INFLUENCE OF THE SINTERING CONDITIONS ON THE TRANSPORT PROPERTIES OF $La_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$ AND $Nd_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$ COMPOUNDS

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The $La_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$ and $Nd_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$ compounds were obtained by sol-gel method. The structure, magnetic and transport characteristics were investigated between 77 and 600 K. The lattice parameters of the sintered in air samples are smaller then those of the sintered in O_2 samples. An important increase of the chemical disorder, in the same time with the decrease of the tolerance factor, was observed at the substitution of the La with Nd. The substitution of La with Nd leads to a decrease of the specific magnetization and of the Curie temperatures of the samples. The transition temperature from the metallic to the semiconductor state decreases for the samples sintered in air as compared with those sintered in O_2. A decrease of the activation energy of the charge transport at temperatures higher than the transition temperature takes place also when the La is substituted with Nd.

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1. Introduction

The perovskite manganite compounds, have received much attention because of their colossal magnetoresistance (CMR) and charge ordering properties [1-4], and due to their technological oportunities and interesting electronic and magnetic properties.

Within the double – exchange interaction model [5] the itinerant charge carriers (holes) in the substituted $La_{1-x}A_xMnO_3$ (A is divalent cation) oxide provide the mechanism for ferromagnetic interaction between Mn^{3+}/Mn^{4+} ions. Zener [5] – de Gennes [6] mechanism for double exchange offers a clear indication of convenient way to control the coupling between the mobile holes and the localized t_{2g}^3 electrons. This coupling should be controlled by the transfer integral t_{ij} between Mn^{3+} - O – Mn^{4+} cations; it can be expected that this coupling be strongly dependent on the angle subtended by the Mn – O – Mn bond.

The ferromagnetic Curie temperature is related to the strength of the transfer integral t_{ij} between Mn^{3+}/Mn^{4+} ions which itself controls the electronic (hole) conductivity. It follows that in this system one should expect a strong interplay between magnetic, transport and structural properties.

Stationary ferromagnetic clusters, under the form of small regions formed from Mn^{3+}-Mn^{4+} pairs, are present in many perovskites with B = Mn. They are growing with the decrease of the temperature, as the mobile species are progressively condensed into more conductive ferromagnetic clusters. The CMR occurs because the volume of these clusters grows also with the intensity of the applied magnetic field [7].

It is known that at a low carrier density the ferromagnetic metallic regions can be imagined as isolated droplets in an insulator antiferromagnetic matrix [8]. The increase of the electron density

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leads to the increase of the ferromagnetic metallic regions and finally to the percolation of the ferromagnetic order in the crystal [8].

Decrease of the oxygen partial pressure leads to the decrease of oxygen content and to the increase of Mn(III) cations concentration, respectively [9]. On the other hand, the increasing of the treatment temperature is followed by the decreasing of the oxygen concentration of the samples [10]. For the samples with excess of the oxygen, it can adopt the metallic vacancies model, while for the samples with deficit in oxygen is taken in account the oxygen vacancies model [10]. It is known that the increase of the oxygen vacancies content leads to the stabilization of the antiferromagnetic state, due to the strong superexchange interaction between the manganese surrounded by the oxygen vacancies and the manganese occupying the oxygen octahedra [11].

The purpose of present paper is to study the influence of the substitution of La with Nd and the synthesis conditions on the structure, magnetic and electric properties, including magnetoresistance, of $(Ln,Nd)_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$ compounds.

2. Experimental

The samples with the chemical composition $La_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$ and $Nd_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$ were prepared by means of sol-gel method, using as precursors rare earth oxides (La_2O_3, Nd_2O_3 and Ho_2O_3) (purity: 99.99%) and the Sr and Mn acetates (purity: 99.00%). The details of the preparation were already communicated [12, 13].

The resulted powders were ground and pressed into pellets and presintered at 700°C for 15 hours in air. A part of the presintered samples were again grounded and finally sintered at 1200°C for 5 hours in O_2 atmosphere; another part of the grounded and pelletized samples were sintered at 1200°C for 5 hours in air. The Mn^{4+} concentration was determined by the iodometric titration, using sodium thiosulphate [14]. The presintered and sintered samples were monitorized by X-ray analysis, to determine the begin of the solid-state reaction, the phase composition, the structure, lattice constants and the volume of the lattice cell. We used a diffractometer, equipped with a Co X-ray tube and a data acquisition system. The interplanar distances were corrected for the goniometer zero and the off set of the sample against the goniometer axis. The precision of the interplanar distances was better as 0.001 Å. The average size of the A places radius was calculated with:

$$\langle r_A \rangle = c_{La(Nd)} \cdot r_{La(Nd)} + c_{Ho} \cdot r_{Ho} + c_{Sr} \cdot r_{Sr} \tag{1}$$

where $c_{La(Nd)}$ etc represents the concentration of La(Nd) cations on A sites etc. The tolerance factor, t, and the chemical disorder, σ^2, were calculated with the formula (2) [15], respectively, after Terai et al. [16].

The electrical measurements were carried out between 77 and 450 K using the four probes method. The magnetic measurements were performed with a vibrating sample magnetometer between 77 and 600 K. The measuring system of the magnetoresistance and the magnetometer were also provided with a data acquisition system.

3. Results and discussion

The sintered samples contain only a phase, which have a tetragonal structure (SG – I4/mcm) for the $La_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$ and an orthorhombic phase (SG – Pmna) for the $Nd_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$ (s. Fig. 1), in agreement with the literature data [17,18]. The lattice constants are influenced by the sintering atmosphere (Table 1).

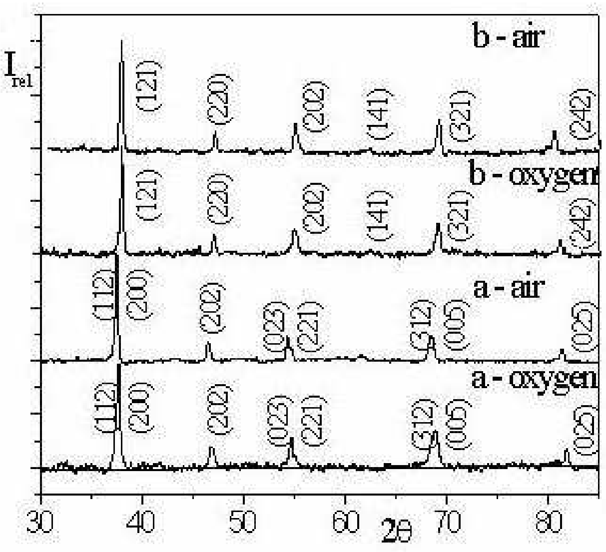

Fig. 1. The difractogramms of (a) $La_{0.44}Ho_{0.11}Sr_{0.45}MnO_{2.99}$ and (b)$Nd_{0.44}Ho_{0.11}Sr_{0.45}MnO_{2.992}$ manganites sintered in air and O_2.

The increase of the distortion degree of the perovskite lattice due to the substitution of La with Nd leads to a transition from a tetragonal to an orthorhombic cell. The average radius of the A type places, $<r_A>$, diminishes when the Nd cation substitutes the La cation, producing a decrease of the tolerance factor and an increase of the chemical disorder degree (s.Tab.1). In the same time takes places an important decrease of the volume of the unit cell, implicitly of the length of cation-anion bonds and of the Mn-O-Mn angle (Table 1 and Table 2). The unit cell parameters are smaller for the samples sintered in air, than for those sintered in O_2 (Table 1). The tolerance experimental factors, calculated taking into account the observed distances between the Mn and O, and, respectively, La (Ho, Sr, Nd) and O, are independent practically on the sintering atmosphere. On other hand, there is a difference between the observed and calculated tolerance factors, probably due to the difference in true radii of the cations and the assumed radii.

Table 1. The lattice parameter (a, b, c), the unit cell volume (V), the experimental (t^1) and calculated tolerance factors (t^2) for the sintered manganites

Chemical composition	Treatment atmosphere	a (Å)	b (Å)	c (Å)	V (Å^3)	t^1	t^2
$La_{.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$	O_2	5.477	7.847	5.477	235.390	0.961	0.947
	air	5.473	7.844	5.743	234.960	0.961	
$Nd_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$	O_2	5.424	7.613	5.413	223.527	0.931	0.934
	air	5.418	7.612	5.449	224.670	0.932	

The variation of the specific magnetization vs. temperature shows a diminishing of both Curie temperature and of the magnetization associated with the decrease of the unit cell parameters, when the La is substituted with Nd (Fig. 2).

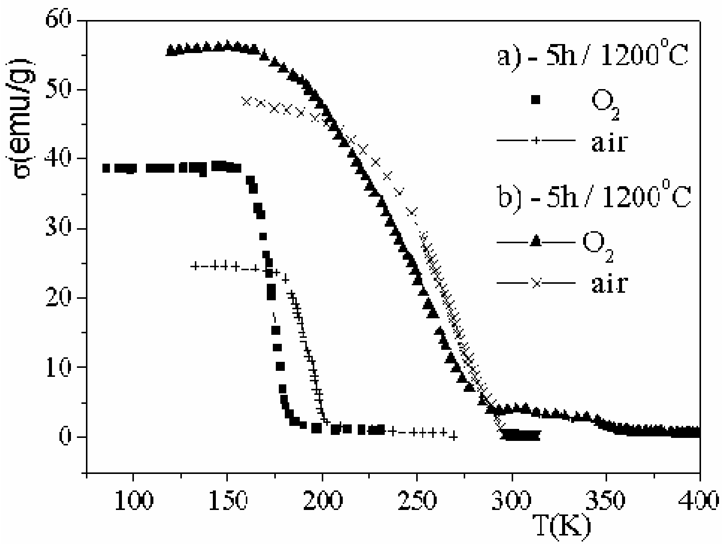

Fig. 2. The dependence of specific magnetization vs. temperature for the samples treated in O_2 and in air: a) $La_{0.44}Ho_{0.11}$ $Sr_{0.45}MnO_{3-\delta}$;b) $Nd_{0.44}Ho_{0.11}$ $Sr_{0.45}MnO_{3-\delta}$.

The samples sintered in air show a specific magnetization smaller than for the samples sintered in O_2. The samples sintered in air contain a larger concentration of Mn^{4+} than the samples sintered in O_2 (Table 4). This behavior is in agreement with the results of Cherif et al. [19], which indicated that the Curie temperature decreases with the increase of the Nd concentration in $(La_{1-x}Nd_x)_{0.7}Sr_{0.3}MnO_{3-\delta}$, implicitly with the increase of the chemical disorder and of the average radius of A places.

A small decrease of the Mn-O accompanied by a larger decrease of the Mn-O-Mn angle takes places when La is substituted with Nd (Table 2). The chemical disorder increases in the same time with the decrease of the average radius of A places.

Table 2. The Mn-O length, Mn-O-Mn angle and average radius of A places for sintered manganites.

Chemical composition	Treatment atmosphere	d_{Mn-O} (Å) <110>	d_{Mn-O} (Å) <001>	$\alpha_{Mn-O-Mn}$ (°) <110>	$\alpha_{Mn-O-Mn}$ (°) <001>	<r_A> (Å)
$La_{.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$	O_2	1.9534	1.9618	164.91	179.98	1.51
	air	1.9520	1.9610	164.866	180.00	
$Nd_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$	O_2	1.9365	1.924	162.78	165.58	1.47
	air	1.9367	1.925	162.664	165.63	

Table 3. The magnetization of the unit cell (p), Curie temperature (T_C), the transition temperature(T_t) and the chemical disorder (σ^2) vs. chemical composition.

Chemical composition	Treatment atmosphere	p(μ_B)	T_C (K)	T_t(K)	σ^2 (Å^2)
$La_{.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$	O_2	2.260	266	190	0.41×10^{-2}
	air	1.980	296	125	
$Nd_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$	O_2	1.560	178	135	1.19×10^{-2}
	air	0.985	204	112	

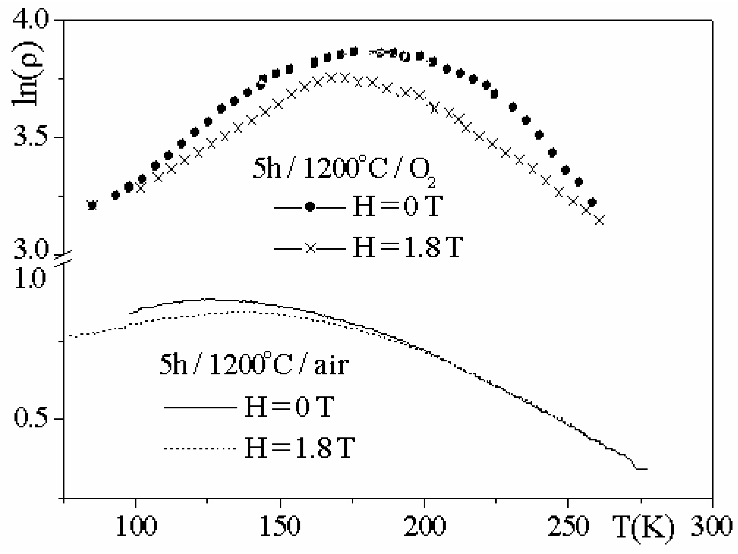

Fig. 3. The variation of the resistivity vs. temperature and magnetic field for $La_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$ sintered in O_2 and air.

After Cherif et al [19] an enhancement of the effective band gap takes places and, consequently, a reducing of the transfer interaction of the e_g electrons. Its implies also a reducing of the specific moment of the samples. The value of the molecular magnetization (p) is less than that due to the associated magnetic moments of Mn^{3+} and Mn^{4+}, decreasing monotonously with the average angle of the Mn-O-Mn bonds along <110> (Table 2 and 3).

By substituting the smaller Nd cation for La, it can suppose that the MnO_6 octahedra elongate along the c axis, favoring the $d_{3z^2-r^2}$ orbital of Mn^{3+} [20]. It results a decrease of the FM interaction, that can lead to the destroying of the FM state [20].

For the same composition, the Curie temperatures increase for the samples sintered in air, while the specific magnetization decreases (Fig. 2, Table 3). The Curie temperatures increase at sintered in air samples comparing with those sintered in O_2, which means an increase of the double – exchange interaction. That could be explained by the small increase of the Mn-O-Mn angle, for the sintered in air samples, as comparing with the sintered in O_2 samples (Table 2 and 3).

The theoretical magnetic moment for a parallel spin alignment gives a 3.57 μ_B/ molecule, far from the experimental values of the specific magnetization per molecule (Table 3). The substitution of the La with Nd leads to an increase of the chemical disorder and a decrease of the Mn-O-Mn angle bonds. In agreement with the Liu et al. [21], the angle of Mn-O-Mn bonds and the distortion degree of the crystals play an important role in the double – exchange mechanism, leading to a diminish of the Curie temperature with the increase of the chemical disorder. Its could lead to a modification of the angle between the magnetic moments corresponding to Mn cations, in agreement with the Solovyov et al. [22], implicitly to a diminishing of the specific magnetization of the sample.

Table 4. The activation energy (E_a) of the electrical transport of the $La(Nd)_{.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$ samples and the concentration ratio Mn^{3+}/Mn^{4+}.

Chemical composition	Treatment atmosphere	δ	C_{Mn3+}/ C_{Mn4+}	E(eV)
$La_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$	O_2	0.0100	1.325	0.143
	air	0.0080	1.304	0.046
$Nd_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$	O_2	0.0098	1.324	0.117
	air	0.0090	1.315	0.165

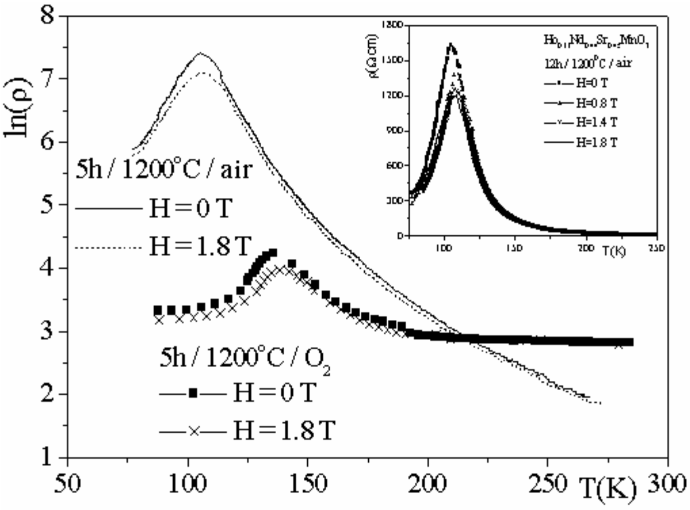

Fig. 4. The variation of the resistivity vs. temperature and magnetic field for $Nd_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$ sintered in O_2 and air.

The transition temperature decreases and the maximum of the resistivity increases with the decrease of the average size of the A places, in agreement with the decrease of the Mn-O-Mn bond angle [19]. The concentration of the Mn^{3+} and Mn^{4+} and the oxygen concentration also, remain practically unchanged to La with Nd substitution (Table 4). The measurement of resistivity vs. temperature at temperature higher as Curie temperature, where the samples behave as semiconductor, allowed us to find the activation energy of the charge transport. A decrease takes place when the average distance between Mn^{3+} and Mn^{4+} decrease, i.e. when the average radius of A places decrease. A flatter maximum of the resistivity vs. temperature was observed for the $La_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$ sample (Fig. 4), corresponding to a better approach of the average size of A places radius comparing with the A radius of the ideal perovskite.

4. Conclusion

The transition and Curie temperatures of the investigated manganites rapidly decrease when La is substituted with Nd. The decrease of the specific magnetization was attributed to an increase of the chemical disorder and of the decrease of the tolerance factor. For the sintered in O_2 samples an increase of the specific magnetization takes place simultaneously with the decrease of the Curie and transition temperatures, for the same chemical composition. The magnetoresistive effect near the room temperature is higher for $La_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$ as for $Nd_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$. On the other hand, the transition temperatures (T_t) are far from the corresponding Curie (T_C) temperatures. The difference could be due to the preparation methods.

We are preparing now the $La_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$ and $Nd_{0.44}Ho_{0.11}Sr_{0.45}MnO_{3-\delta}$ samples by standard ceramic technology, to determine the influence of the synthesis conditions on the structure and physical properties.

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