

# SYNTHESIS AND STRUCTURAL ANALYSIS OF La-Sr MANGANITES DOPED WITH Ho<sup>★</sup>

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We have synthesized by sol-gel method  $(La_{1-x}Ho_x)_{1-y}Sr_yMnO_3$  magnetoresistive bulk manganites. The samples contain only a perovskite phase, with Pnma orthorhombic structure. The unit cell volume and the Mn-O distances increase with Sr concentration and decrease with the Ho concentration. The substitution of La with Ho and the increase of the Sr concentration lead to the bathochromic shift of the Mn-O frequencies, due to the decreasing of  $MnO_6$  octahedra.

*Key words:* manganites; magnetoresistance, crystalline structure; magnetization.

## INTRODUCTION

Electronic and magnetic properties of rare earth manganites of the type  $Ln_{1-x}A_xMnO_3$  ( $Ln$  = rare earth,  $A$  = alkaline earth) have received wide attention in the last few years because of the variety of interesting phenomena exhibited by these materials [1, 2]. The origin of CMR effect is often thought to be based on the double exchange mechanism [3]. Potential applications of modern colossal magnetoresistive materials as magnetic sensors or read heads, for information storage and actuator maintain intense research of manganite components with different forms [4]. The magnetoresistive effect is indirectly influenced by the distortion degree of the lattice, because it determines both the bond length of Mn-O and Mn-O-Mn angle. The presence of the different concentrations of the Sr cations changes the chemical degree of disorder and, implicitly, the specific magnetization, the resistivity and the magnetoresistance [5].

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The energies of the states resulted by the splitting of the energetic levels are conditioned by the symmetry of  $\text{MnO}_6$  octahedra. The non-equivalence of the atoms in the crystalline lattice of the manganites have as consequence the modification of the dipole moment of Mn-O bonds, which lead to the change of the values and the intensities of the active vibrations in the IR range.

The purpose of present paper is to compare the influence of Sr concentration on the structure, magnetic and electric properties of  $(\text{La}_{1-x}\text{Ho}_x)_{1-y}\text{Sr}_y\text{MnO}_3$ .

### EXPERIMENTAL

Samples with the chemical composition  $(\text{La}_{1-x}\text{Ho}_x)_{1-y}\text{Sr}_y\text{MnO}_3$  ( $x = 0.11$ ;  $0.22$  and  $y = 0.45, 0.55$ ) were prepared by means of a sol-gel method [6]. The details of the preparation were already communicated elsewhere [7, 8]. The resulted powders were ground and pressed into pellets and were firstly heated at  $700^\circ\text{C}$  for 15 h. After grinding, they were heated again at  $1200^\circ\text{C}$  for 5 hours in oxygen atmosphere. Chemical composition and the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  concentrations ratio were obtained by van Santen methods.

The samples were investigated by IR methods using a JASCO 660 Plus FT-IR spectrophotometer in KBr pellets, X-ray diffraction using a DRON 2.0 diffractometer with a  $\text{CoK}\alpha$  radiation. Lattice constants, space group, positions of cations/anions in the unit cell were determined by using DICVOL and CELREF programs. The precision of the interplanar distances was better as  $0.001 \text{ \AA}$ . The tolerance factor and the chemical disorder degree were determined by using the corresponding formula due to Goodenough *et al.* [9] and, respectively, Terai *et al.* [10].

### RESULTS AND DISCUSSIONS

The sintered samples contain only a phase, which have an orthorombic structure Pnma (Fig. 1÷3). The volume of the unit cell, the tolerance factor and the average radius of A places increase with the increase of Sr concentration in the samples, (Table 1 and 2). On other hand, an increase of the average radius of the A places can be associated with an increase of the Mn-O-Mn bond angle (Table 2).

The substitution of La with Ho leads also to a decrease of unit cell volume, tolerance factor and Mn-O distances (Table 1 and 2). The chemical disorder degree increases also with the increase of the Sr concentration (Table 3). The increase of the Mn-O distances can be associated with the decrease of the superexchange interaction and an increase of double exchange interaction (Table 2 and ref. [11]). The decrease of the unit cell parameters for the same Sr concentration is due to the increase of Ho concentration in the samples.

Table 1

Dependence of lattice parameter ( $a$ ,  $b$ ,  $c$ ), the unit cell volume ( $V$ ), the average size of coherent blocks ( $D$ ) and the microstrains ( $\epsilon$ ) on the La, Ho and Sr concentrations in the  $(\text{La}_{1-x}\text{Ho}_x)_{1-y}\text{Sr}_y\text{MnO}_3$  system

Chemical composition	$a$ [Å]	$b$ [Å]	$c$ [Å]	$V$ [Å <sup>3</sup> ]	$D$ [nm]	$\epsilon$
$\text{Ho}_{0.11}\text{La}_{0.44}\text{Sr}_{0.45}\text{MnO}_{3-\delta}$	5.512 <sub>4</sub>	7.719 <sub>1</sub>	5.493 <sub>0</sub>	233.73 <sub>1</sub>	48.24	0.000138
$\text{Ho}_{0.22}\text{La}_{0.33}\text{Sr}_{0.45}\text{MnO}_{3-\delta}$	5.407 <sub>4</sub>	7.744 <sub>1</sub>	5.412 <sub>0</sub>	226.63 <sub>0</sub>	31.56	0.004086
$\text{Ho}_{0.09}\text{La}_{0.36}\text{Sr}_{0.55}\text{MnO}_{3-\delta}$	5.452 <sub>3</sub>	7.816 <sub>3</sub>	5.516 <sub>5</sub>	235.09 <sub>6</sub>	98.30	0.000126
$\text{Ho}_{0.18}\text{La}_{0.27}\text{Sr}_{0.55}\text{MnO}_{3-\delta}$	5.458 <sub>8</sub>	7.775 <sub>1</sub>	5.507 <sub>3</sub>	233.74 <sub>5</sub>	33.90	0.000812

Table 2

Tolerance factors ( $t$ ), Mn-O distances ( $\langle d_{\text{Mn-O}} \rangle$ ) and Mn-O-Mn bond angles ( $\langle \angle \text{Mn-O-Mn} \rangle$ ) for  $(\text{La}_{1-x}\text{Ho}_x)_{1-y}\text{Sr}_y\text{MnO}_3$  sintered manganites

Chemical composition	$t$	$\langle d_{\text{Mn-O}} \rangle$ [Å]	$\langle \angle \text{Mn-O-Mn} \rangle$ [°]
$\text{Ho}_{0.11}\text{La}_{0.44}\text{Sr}_{0.45}\text{MnO}_{3-\delta}$	0.957	1.965 <sub>7</sub>	162.72
$\text{Ho}_{0.22}\text{La}_{0.33}\text{Sr}_{0.45}\text{MnO}_{3-\delta}$	0.953	1.955 <sub>1</sub>	162.72
$\text{Ho}_{0.09}\text{La}_{0.36}\text{Sr}_{0.55}\text{MnO}_{3-\delta}$	0.962	1.966 <sub>6</sub>	162.68
$\text{Ho}_{0.18}\text{La}_{0.27}\text{Sr}_{0.55}\text{MnO}_{3-\delta}$	0.955	1.960 <sub>4</sub>	163.41

Fig. 1 – The diffractograms of  $(\text{La}_{1-x}\text{Ho}_x)_{1-y}\text{Sr}_y\text{MnO}_3$  manganites.

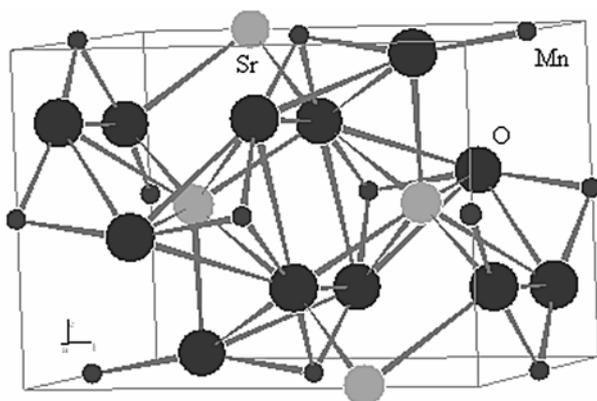
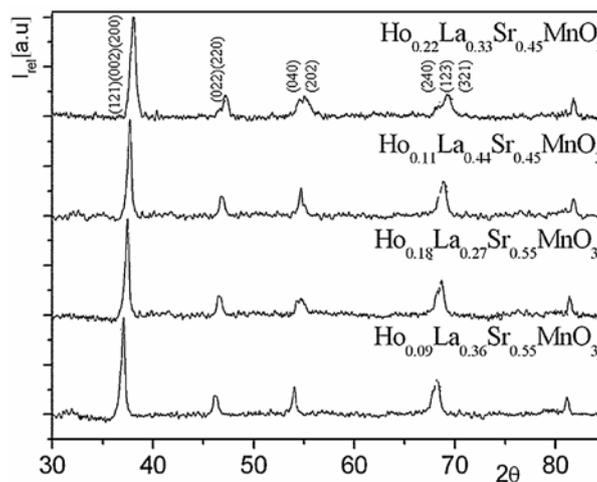


Fig. 2 – The unit cell (Pnma) of the  $(\text{La}_{1-x}\text{Ho}_x)_{1-y}\text{Sr}_y\text{MnO}_3$  manganites.

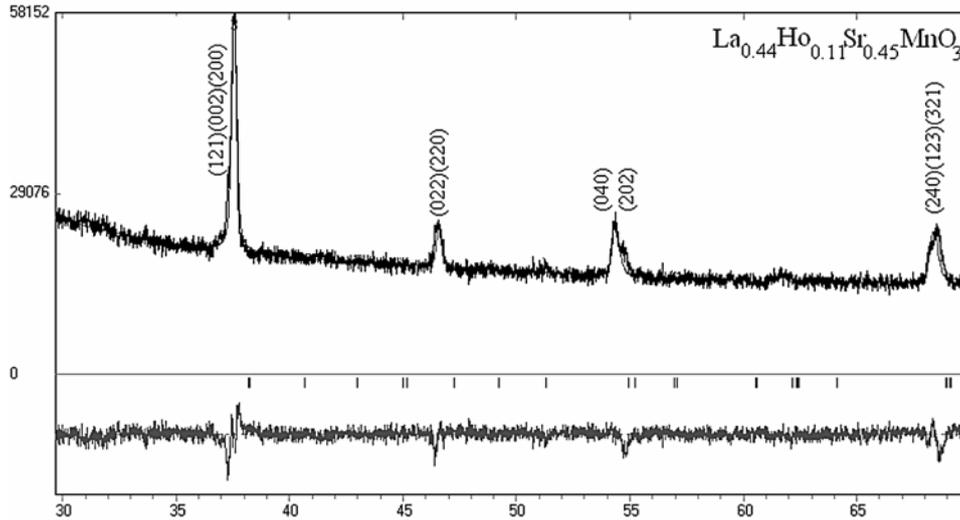


Fig. 3 – The obtained and calculated diffractogram of the  $\text{La}_{0.44}\text{Ho}_{0.11}\text{Sr}_{0.45}\text{MnO}_3$  manganite.

Table 3

The Curie temperature ( $T_C$ ), magnetization of the unit cell ( $p$ ), the chemical disorder ( $\sigma^2$ ),  $\text{Mn}^{3+}/\text{Mn}^{4+}$  concentrations ratio and average radius of A sites vs. chemical composition

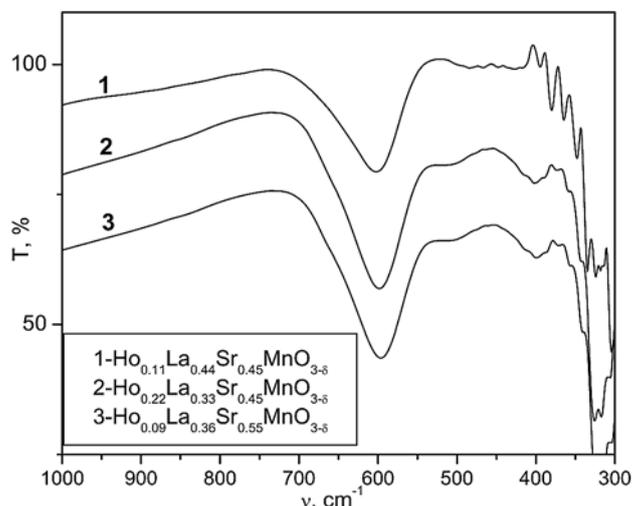
Chemical composition	$T_C$ [K]	$p$ [ $\mu_B/\text{mol}$ ]	$\sigma^2$ [ $\text{\AA}^2$ ]	$\text{Mn}^{3+}/\text{Mn}^{4+}$	$\langle r_A \rangle$ , $\text{\AA}$
$\text{Ho}_{0.11}\text{La}_{0.44}\text{Sr}_{0.45}\text{MnO}_3$	266	2.26	$0.912 \cdot 10^{-2}$	1.325	1.51
$\text{Ho}_{0.22}\text{La}_{0.33}\text{Sr}_{0.45}\text{MnO}_3$	345	1.13	$1.530 \cdot 10^{-2}$	1.304	1.48
$\text{Ho}_{0.09}\text{La}_{0.36}\text{Sr}_{0.55}\text{MnO}_3$	335	1.93	$0.820 \cdot 10^{-2}$	0.923	1.52
$\text{Ho}_{0.18}\text{La}_{0.27}\text{Sr}_{0.55}\text{MnO}_3$	–	0.11	$1.390 \cdot 10^{-2}$	0.901	1.50

We have observed also an increase of the average size of the coherent blocks and a decrease of the microstrains with increase of Sr concentration, respectively, with the decrease of Ho concentration in the manganites (Table 1).

The experimental infrared patterns show in the  $1000\text{--}300\text{ cm}^{-1}$  range two main peaks, attributed to stretching vibrational mode  $\Delta\nu_{\text{Mn-O}}$  and, respectively, the bending mode of Mn-O-Mn bond angle. For the samples with  $x = 0.22$  we observed an apparent splitting of the  $\nu_{\text{Mn-O}}$  band (Fig. 4). It was interpreted as a structural doublet, allowed by the non-centrosymmetric  $\text{MnO}_6$  octahedric groups [12, 13]. At high values of Sr ( $y = 0.55$ ) could be observed only one symmetric band around  $596\text{ cm}^{-1}$  (Fig. 4).

The symmetry of  $\text{MnO}_6$  groups is correlated with the existence of manganese ions into a mixture of two valence states,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ , the Jahn-Teller effects, partly related to the average ionic radius of the A sites (Table 3). The intensity of peaks increase with the increase of  $x$  and  $y$  values (Fig. 4).

Fig. 4 – The FT-IR spectra of  $(\text{La}_{1-x}\text{Ho}_x)_{1-y}\text{Sr}_y\text{MnO}_3$  samples.



The explanation is based on the association with a supplementary polarization (dipole moment) of Mn-O bonds. The substitution of La with Ho cations produces the shifting of  $\nu_{\text{Mn-O}}$  to higher frequencies determined by an decrease of symmetry of the lattice. This is the effect of the increase of the crystallites concentration per volume unit and the decrease of the  $\text{MnO}_6$  groups symmetry, in agreement with the XRD data.

The samples with the smallest Ho concentration and characterized by the smallest chemical disorder degree and largest average radius of the A places have the largest magnetic moment (Table 3). The increase of Sr concentration is associated with the decrease of the magnetic moment. On other hand, the Curie temperature of magnetic samples are high (295 K – 345 K) comparable with the best similar data from the literature (Table 3).

The increase of chemical disorder leads to a local modification of the Mn-O-Mn angles and Mn-O distances, which are responsible by the double exchange interaction, and, implicitly, to a decrease of the specific magnetization of the samples.

The observed Curie temperature should increases with the Sr concentration, for the same Ho concentration, in agreement with Abramovich *et al.* [11] and with data from Table 3, which correspond to  $\text{Ho}_{0.11}\text{La}_{0.44}\text{Sr}_{0.45}\text{MnO}_3$  and  $\text{Ho}_{0.09}\text{La}_{0.36}\text{Sr}_{0.55}\text{MnO}_3$ . However, for  $\text{Ho}_{0.18}\text{La}_{0.27}\text{Sr}_{0.55}\text{MnO}_3$  manganite no paramagnet-ferromagnet transition was observed (the data will be published elsewhere).

For the samples with  $x > 0.20$  and  $y > 0.45$  the transition temperatures are lower as 77 K, the samples having still a negative magnetoresistance behavior (the data will be published elsewhere). The sudden decrease of the specific magnetization and the increase of the observed resistivity could be associated

with the decrease of the ferromagnetic clusters concentration below the percolation limit or/and an increase of the extrinsic magnetoresistance contribution. This supposition is justified by the observed values of chemical disorder degree (Table 3), which is twice as large for the the samples with  $C_{\text{Ho}} \approx 0.2$  as comparing with those corresponding to the samples with  $C_{\text{Ho}} \approx 0.1$ . However, a large negative magnetoresistive effect has been observed for  $\text{Ho}_{0.22}\text{La}_{0.33}\text{Sr}_{0.45}\text{MnO}_3$  (10%) and  $\text{Ho}_{0.09}\text{La}_{0.36}\text{Sr}_{0.55}\text{MnO}_3$  (75%) manganites, in agreement with magnetoresistive data of  $\text{Ho}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  [14]. We attribute this behavior to a much smaller ferromagnetic cluster concentrations or a smaller paramagnet-ferromagnet transition at the samples with higher Ho concentration as comparing with those, which contain a smaller Ho concentration.

### CONCLUSIONS

The volume of the unit cell and the symmetry of  $\text{MnO}_6$  groups decrease with the increase of Ho concentration and increase with the Sr concentration in the samples. The substitution of La with Ho have three effects: 1) the increase of the chemical disorder degree, 2) the decrease of the magnetic moment of the samples and the decrease of the symmetry of  $\text{MnO}_6$  octahedra. It is in agreement with the observed variation of average radius of A places with the chemical composition of the manganites. Although for the compounds with higher Ho amount a characteristic maximum of resistivity could not be observed, the samples have a negative magnetoresistance. The substitution of the rare earth with Sr cations leads to an increase of the resistivity with the increase of the Sr concentration in the samples. The polarity of the Mn-O bonds are determined by the chemical composition and the crystalline structure of the investigated manganites.

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