Features of structure transformations in $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_{3+\delta}$ ($x = 0.05 – 0.30$)

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Abstract. The change in the structure properties of lanthanum manganite $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_{3+\delta}$ ($x = 0.05–0.30$) depending on the Sr concentration and heat treatment conditions has been systematically investigated by Mössbauer spectroscopy and X-ray diffraction analysis. The features of structure transformations in the given compound have been compared to those of the undoped compound $\text{LaMnO}_{3+\delta}$.

1. Introduction
The lanthanum manganite compounds doped with bivalent impurities are the materials with colossal magnetoresistance and widely used in different fields of modern engineering.

To understand the behavior of doped systems, it is necessary to systemize data of the parent $\text{LaMnO}_{3+\delta}$ compound. According to the literature data a series of structural modifications can be obtained in the undoped $\text{LaMnO}_{3+\delta}$ compound depending on the synthesis and heat treatment conditions, the main of which are two orthorhombic $\text{PnmaI}$ and $\text{PnmaII}$ (total space group $\text{Pnma}$) and rhombohedral (space group $\text{R-3c}$) modifications. Manganese ions in lanthanum manganites have a mixed valence, $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$. Each phase has the definite $\text{Mn}^{3+}$ concentration (less than 10% for $\text{PnmaII}$, less than 20% for $\text{PnmaI}$, and 20-30% for $\text{R-3c}$) [1,2]. A portion of $\text{Mn}^{3+}$ transfers into $\text{Mn}^{4+}$ under oxidation and structural phase transitions occur which are reversible under heat treatment [3]. All positions in the lattice are occupied and additional oxygen coming with $\text{Mn}^{4+}$ will be placed in interstitial positions and distort the local environment of $\text{Fe}$ [3]. In $\text{R-3c}$ a quantity of $\text{Mn}^{4+}$ and, consequently oxygen is maximal that results in greater distortion of the local environment as compared to $\text{PnmaI}$ [3].

The presence of Jahn-Teller $\text{Mn}^{3+}$ ions coexisting with not Jahn-Teller $\text{Mn}^{4+}$ ions is one of the features of the compounds based on lanthanum manganite [4]. The doping of cation positions actively affects the structure and, correspondingly, the fundamental physical properties of these compounds. The change in the structure leads to significant changes in physical properties (conductivity, magnetization) since there is a strong correlation between lattice and electron subsystems in lanthanum manganites.

2. Experimental
Polycrystalline powder samples $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_{3+\delta}$ were prepared by sol-gel method. Preparation of the samples was described in detail in [5].
X-ray diffraction (XRD) patterns of powder samples were measured using a diffractometer Siemens D-500 (Cu Kα and Fe Kα radiation). The lattice parameters were calculated using the program PowderCell (Werner Kraus & Gert Nolze, BAM Berlin).

The 57Fe Mössbauer measurements were carried out at room temperature using a conventional Mössbauer spectrometer operating in the constant acceleration mode.

3. Results and discussion

La and Sr ion radii are close, therefore they should not induce notable distortions in the lattice. The synthesized La1-xSrxCnx0.98Fe0.02O3+δ samples with x = 0.05, 0.10 and 0.20 were single phase and had the rhombohedral structure. It follows from the XRD data (Fig.1) that all the mentioned phases Pnmal, PnmaII and R-3c are formed for the small Sr concentration up to 10% with polymorphous reversible transformations under heat treatment. The lattice parameters change insignificantly for Pnmal and R-3c with an increase in Sr concentration. For PnmaII the lattice parameters b and c change insignificantly with an increase in Sr concentration, whereas the a parameter and cell volume notably decrease (Fig.2). For 10%Sr the a and c parameters approach.

Figure 1. Standard X-ray diffraction patterns for R-3c, Pnmal, and PnmaII phases (CuKα1 radiation).

When Sr concentration is higher than 10%, PnmaII is not formed. When Sr concentration is 20%, only the rhombohedral phase is formed which is stable at any heat treatment.

There are some substantial differences as compared to the undoped compound. It follows from XRD data that the monoclinic phase (distorted cube) appears in addition to R-3c for 30%Sr.

Figure 2. Dependence of the lattice parameters for PnmaII in La1-xSrxCnx0.98Fe0.02O3+δ on the Sr concentration.

The obtained Mössbauer data are in a good agreement with the XRD results.

The linewidth of Mössbauer spectra for Pnmal and R-3c of the polycrystalline Sr-doped samples is rather narrow (Γ = 0.33 mm/s) and the spectra were fitted by single doublet. The lines of Mössbauer spectra for the PnmaII phase represent strongly broadened quadrupole-split doublets (Fig.3). It can be due to the presence of several subspectra. In [5] we tried to fit qualitatively similar spectra by three doublets. Since the spectra are smooth, some uncertainty in a choice of linewidths appears. In addition, the lattice distortions can be due to several reasons. (1) We can assume that not Jahn-Teller Mn4+ ions have a concentration dispersion within the PnmaII phase which results in the formation of the regions with a different degree of distortion and, consequently in the Δ distribution. (2) We have previously shown [6] that particles of PnmaII are nanosized, therefore a surface of nanoparticles will also
contribute. (3) Interstitial oxygen will distort the local environment. It is quite difficult to separate all these contributions. Therefore it is more correctly to determine the quadrupole splitting ($\Delta = 2\varepsilon$) distribution probability (Fig.3). For this purpose the DISTRI code from the software MSTools [7] was used. Note that with an increase in Sr concentration, i.e. with an increase in the Mn$^{4+}$ ion portion, within the $Pnmn$II phase the maximum probability of distribution is displaced towards a decrease in the $\Delta$ value. It means a decrease in distortion of the local symmetry.

In the Sr-doped compound an increase in the Sr$^{2+}$ concentration leads to an increase in the Mn$^{4+}$ concentration and to a decrease in lattice distortions. For R-3c the $\Delta$ value decreases with an increase in Sr concentration and has the minimal value for 20%Sr ($\Delta = 0.23$ mm/s) (Fig.4, Table 1). It means that for this Sr concentration the quantity of interstitial oxygen is small and the lattice distortions are insignificant.

For the sample with 30%Sr the additional subspectrum appears in the Mössbauer spectrum in addition to the doublet corresponding to the R-3c phase which can be attributed to the magnetic component with $H = 3.41$ T (Fig.4). It is known from literature that $T_c$ increases with an increase in impurity concentration, $T_c = 375$ K for 33%Sr [8] and $T_c$ is lower than room temperature for 18%Sr [9]. As for the monoclinic phase observed in the XRD patterns, it is most probable that the $\Delta$ values for rhombohedral and monoclinic phases are close and it is not possible to determine the contribution of each of them in the Mössbauer spectrum. A small asymmetry of the spectra can be related to the sample texture [2].

**Figure 3.** Mössbauer spectra (at the top) and distribution probability of quadrupole displacement $P(\varepsilon)$ (at the bottom) for the $Pnmn$II phase in La$_{1-x}$Sr$_x$Mn$_{0.98}$Fe$_{0.02}$O$_{3+\delta}$ for $x = 0$ (a), 0.05 (b), and 0.1 (c).

**Figure 4.** Mössbauer spectra for the rhombohedral phase in La$_{1-x}$Sr$_x$Mn$_{0.98}$Fe$_{0.02}$O$_{3+\delta}$ for $x = 0.05$ (a), 0.1 (b), 0.2 (c), and 0.3 (d).
Comparing the experimental data for the Sr-doped and undoped compounds we can conclude the following. Lattice distortions in the undoped LaMnO$_{3+\delta}$ compound with a stoichiometric composition and a small Mn$^{4+}$ portion ($PnmaII$) are due to the cooperative Jahn-Teller effect. With an increase in Mn$^{4+}$ ion concentration the breaking of orbital order occurs and lattice distortions related to them decrease. However lattice distortions related to oxygen coming with Mn$^{4+}$ ions and occupying only interstitial positions in the undoped compound appear which are maximal for the rhombohedral phase.

Table 1. Parameters of the $^{57}$Fe room-temperature Mössbauer spectra for the $R$-3$c$ phase of La$_{1-x}$Sr$_x$Mn$_{0.98}$Fe$_{0.02}$O$_{3+\delta}$. $\Delta$ and IS are quadrupole splitting and isomer shift which is relative to bcc Fe at room temperature; $A$ is relative intensity.

| %Sr | $\Delta$, mm/s | IS, mm/s | $\Gamma$, mm/s | A, % | Sextet |
|-----|----------------|----------|---------------|-----|--------|
| 5   | 0.31±0.01      | 0.37±0.01| 0.33±0.01     |     |        |
| 10  | 0.29±0.01      | 0.37±0.01| 0.33±0.01     |     |        |
| 20  | 0.23±0.01      | 0.37±0.01| 0.33±0.01     | 47  | H=3.41 T |
| 30  | 0.24±0.01      | 0.37±0.01| 0.33±0.01     |     |        |

The introduction of bivalent impurity occupying trivalent La positions leads to the appearance of vacant oxygen sites in the lattice. Therefore a part of Mn$^{3+}$ ions transfers to Mn$^{4+}$ already during synthesis. When the Mn$^{4+}$ and Sr$^{2+}$ quantity is the same, the oxygen stoichiometric phase is formed and all extra oxygen first of all occupies vacant oxygen lattice sites. In this case lattice distortions are minimal. However, for the fixed Sr concentration in the doped sample the Mn$^{4+}$ ion concentration can increase up to the maximum value under oxidation, the rest extra oxygen will now occupy interstitial sites and the lattice is notably distorted. Thus in the Sr-doped sample one can obtain both the minimum Mn$^{4+}$ concentration equal to the bivalent impurity concentration and the maximum one under oxidation. While oxidized, the Mn$^{4+}$ portion increases and the phase transitions from $PnmaII$ to $PnmaI$ and to $R$-3$c$ occurs for small Sr concentration. An increase in the Sr$^{2+}$ concentration, on the one hand, increases the Mn$^{4+}$ ion concentration, and on the other hand, decreases the quantity of extra oxygen occupying interstitial positions, which results in a decrease in lattice distortions and, respectively, in the $\Delta$ value.

The work was supported by the Russian Foundation for Basic Research, project no. 09--02--00767 and the Russian Academy of Sciences (program Properties of Condensed Matter).

4. References
[1] Huang Q, Santoro A, Lynn J W, et al.1997 Phys. Rev. B 55 14987
[2] Sedykh V D, Smirnova I S, Bagautdinov B Sh, et al.2002 J. Surf. Inv. 12 9
[3] Sedykh V, Shekhtman V Sh, Zverkova I I, et al.2006 Physica C 433 189
[4] Kugel K I, Khomskii D I 1982 UFN 136 621 (in Russian)
[5] Sedykh V D, Shekhtman V Sh, Dubovitskii A V, et al.2009 Phys. Sol. State 51 373
[6] Aristova I M, Sedykh V D, Shekhtman V Sh, et al.2008 Mat. Lett. 62, 1036
[7] Rusakov V S 1999 Bulletin Russian Academy of Science Physics 7 1093; Rusakov V S and Kadyrzhanov K K 2005 Hyperfine Interactions 164 87. Rusakov V S 2000 Mössbauer spectroscopy of locally inhomogeneous compounds INPNNCRK, Almaty, 431
[8] Kim Ch S, Shim I-B, Kim S B 2003 JMMM 254-255 568
[9] Tkachuk A, Rogacki K, Brown D E, et al. 1998 Phys. Rev. B 57 8509