
ELECTRICAL AND MAGNETIC
PROPERTIES

The Interrelation between Iron Valence and Oxygen Vacancies in Substituted Orthoferrite $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_{3-\gamma}$ during Heat Treatment

V. D. Sedykh^{a,*}, V. S. Rusakov^b, T. V. Gubaidulina^b, O. G. Rybchenko^a, and V. I. Kulakov^a

^a Osipyan Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, 142432 Russia

^b Moscow State University, Moscow, 119991 Russia

*e-mail: sedykh@issp.ac.ru

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Abstract—In this paper, we studied substituted lanthanum orthoferrite $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_{3-\gamma}$ by Mössbauer spectroscopy using X-ray diffraction data. A series of vacuum annealings was performed in the temperature range of $t_{\text{ann}} = 200\text{--}650^\circ\text{C}$, after which no significant changes in the structure of the samples were detected. The Mössbauer measurements at room temperature show that the Fe ions are in an average valence state between Fe^{3+} and Fe^{4+} . Upon vacuum annealing, as the temperature t_{ann} increased, the average hyperfine magnetic field on the ^{57}Fe nuclei and the isomer shift of the spectrum increased, which is associated with an increase in the number of vacancies and, accordingly, a decrease in the amount of Fe^{4+} . Mössbauer measurements at 85 K showed that the average valence state of iron does not manifest itself. The hyperfine parameters of the low-temperature Mössbauer subspectra obtained from the model interpretation indicate that one of them belongs to Fe^{4+} ions, and the rest belong to Fe^{3+} . The presence in the spectra of several sextets related to Fe^{3+} ions is due to the appearance of oxygen vacancies (breaking of the $\text{Fe}^{3+}\text{--O}^{2-}\text{--Fe}$ exchange bond) and Fe^{4+} ions (weakening of the $\text{Fe}^{3+}\text{--O}^{2-}\text{--Fe}$ exchange bond) in the nearest ionic neighborhood of Fe atoms. Both factors cause a decrease in the hyperfine magnetic field and a change in the isomer shift of the spectrum. As a result of model interpretation of the Mössbauer spectra, the numbers of oxygen vacancies and Fe^{4+} ions per formula unit depending on vacuum annealing temperature t_{ann} were determined for all samples. It was shown that at t_{ann} above 450°C , the process of oxygen leaving the lattice ends and only Fe^{3+} ions are detected.

Keywords: substituted lanthanum ferrites, valence states, oxygen vacancies

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INTRODUCTION

Perovskite compounds of type $\text{R}_{1-x}\text{A}_x\text{BO}_{3-\gamma}$ where R is a rare earth element, A is Ba, Ca, or Sr and B is Fe, Mn, Co or Ni are promising materials in various fields due to their unusual electrical, magnetic and catalytic properties [1, 2,] for example, as electrode materials for fuel cells, catalysts, chemical sensors, optoelectronic devices, magnetic memory devices, etc. [3–7]. In these systems, transition-metal ions have mixed-valence states. Such states can lead to significant oxygen nonstoichiometry, which is a result of the low partial pressure of oxygen over the oxide under specified synthesis conditions. Mixed valency can be caused either by the introduction of divalent ions (A) in place of a trivalent element (R) or by the formation of oxygen vacancies [8]. The magnetic properties of these compounds are assumed to be the result of a superexchange interaction involving $3d$ electrons of

transition metal ions and oxygen p orbitals [9]. Thus, oxygen plays a very important role in the formation of the magnetic order of these compounds.

Orthoferrite LaFeO_3 belongs to this family of compounds. Here, Fe ions are in a trivalent state. Iron atoms have an octahedral oxygen neighborhood. Oxygen anions located at the vertices of the octahedron participate in the superexchange interaction between $\text{Fe}^{3+}\text{--O}^{2-}\text{--Fe}^{3+}$ iron ions, which, according to Goodenough's theory [10], is antiferromagnetic and stronger than that between Fe^{4+} and Fe^{3+} ions, as well as between Fe^{4+} and Fe^{4+} ions.

When trivalent La^{3+} is partially replaced by divalent Sr^{2+} , the structural and charge order in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\gamma}$ compounds is disturbed at the local level. The consequence of the ionic substitution $\text{La}^{3+} \rightarrow \text{Sr}^{2+}$ in $\text{LaFeO}_{3-\gamma}$ is an increase in the degree of oxidation of

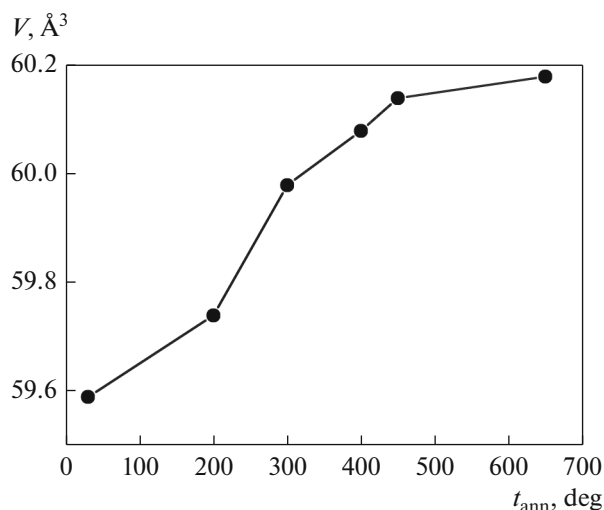


Fig. 1. The dependence of pseudocubic cell volume V_{cell} of $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_{3-\gamma}$ on vacuum annealing temperature t_{ann} .

Fe ions from Fe^{3+} to Fe^{4+} , which weakens the antiferromagnetic order due to the superexchange interaction of Fe^{3+} ions [11–15]. With an increase in the Sr content, the Neel temperature decreases [12, 16].

Mössbauer spectroscopy is an effective method for studying the states of iron ions, as well as changes in their nearest oxygen neighborhood in substituted lanthanum ferrites. In these compounds, the Mössbauer spectra of Fe ions that have different valence states represent a set of magnetic subspectra with different Mössbauer parameters (the effective magnetic fields, isomer shifts, and quadrupole shifts).

It is of interest to study the behavior of the valence states of iron and oxygen vacancies depending on the heat treatment conditions for substituted lanthanum ferrites at a fixed La/Sr ratio.

In this paper, the nature of structural changes, valence states of iron atoms, and transitions to a magnetically ordered state in substituted orthoferrite $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_{3-\gamma}$ in the course of vacuum heat treatment were studied by Mössbauer spectroscopy using data from X-ray diffraction analysis.

EXPERIMENTAL

A polycrystalline sample of $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_{3-\gamma}$ was obtained in air by the sol-gel method at 1100°C using strontium, iron, and lanthanum nitrates in a stoichiometric ratio and glycine as initial reagents. The synthesis details were described in [17]. After synthesis, the sample was slowly cooled together with the furnace to room temperature. Then, the samples were annealed in vacuum (10^{-3} Torr) at $200\text{--}650^\circ\text{C}$ and slowly cooled.

Structural certification of the synthesized polycrystalline samples was carried out at room temperature on a Siemens-D500 diffractometer using $\text{CoK}\alpha$ radiation. Powder Cell 2.4 and Match3 programs were used to perform phase analysis, calculate X-ray diffraction patterns, and refine unit cell parameters.

Mössbauer measurements of polycrystalline $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_{3-\gamma}$ samples were performed at room temperature and 85 K on a SM 1101 spectrometer operating in the constant acceleration mode. The $^{57}\text{Co}(\text{Rh})$ radioactive source was used in the experiment. The processing and analysis of the spectra was carried out by the methods of model interpretation and restoration of the distribution of hyperfine parameters of the spectrum using the SpectrRelax program [18].

RESULTS AND DISCUSSION

An LaFeO_3 sample has an orthorhombic structure with space group $Pbnm$ (JCPDS 82-1958) and cell parameters $a = 5.553\text{ \AA}$, $b = 5.566\text{ \AA}$, $c = 7.851\text{ \AA}$. The diffraction patterns of all studied $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_{3-\gamma}$ samples are similar to each other. This indicates that the structure does not undergo any significant changes in the course of vacuum annealing. The spectra have common features, in particular, markedly broadened diffraction lines, especially at large diffraction angles. The broadening can be partly due to both the inhomogeneous distribution of the substituting strontium atoms in the lanthanum positions over the sample and variations in the oxygen content and, as a consequence, the inhomogeneity of the structure. The X-ray diffraction pattern of the initial sample can be described by a rhombic cell with space group $Pbnm$ (JCPDS 89-1269) and parameters $a = 5.502\text{ \AA}$, $b = 5.544\text{ \AA}$, $c = 7.811\text{ \AA}$. However, its interpretation under the assumption of a two-phase mixture, which additionally includes a certain fraction of the rhombohedral phase $R-3c$ (JCPDS 49-0285), produces the best result. This is in accordance with the literature data [14, 19]. The same structure is registered for the samples subjected to vacuum annealing at temperatures from 200 to 400°C , only the phase lattice parameters and cell volumes change. The diffraction patterns of the samples annealed at 450 and 650°C are practically the same; this suggests that the main structural changes end at 450°C . In this case, the last sample from the series has a rhombic lattice with $a = 5.535\text{ \AA}$, $b = 5.548\text{ \AA}$, $c = 7.838\text{ \AA}$, with almost no admixture of the rhombohedral phase. Figure 1 shows the dependence of pseudocubic cell volume V_{cell} on the vacuum annealing temperature. It can be seen that V_{cell} continuously increases, which is associated with a decrease in the oxygen content in the lattice (i.e., with an increase in the number of oxygen vacancies) and an increase in the content of Fe^{3+} cations. Annealing at

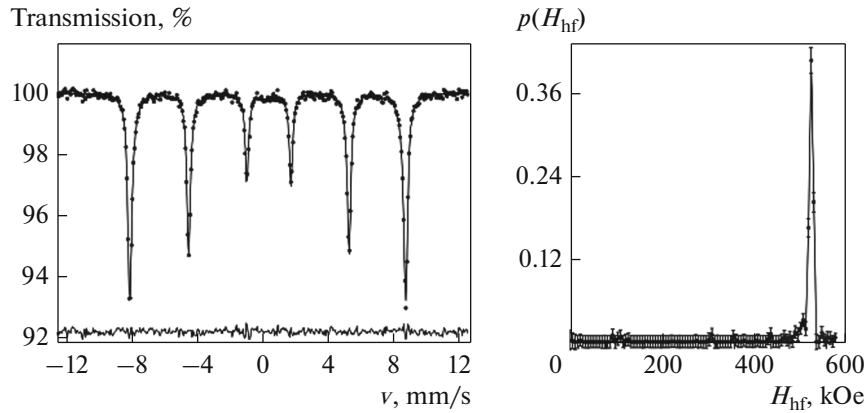


Fig. 2. The Mössbauer spectrum of LaFeO_3 measured at room temperature and the reconstructed $p(H_{\text{hf}})$ hyperfine magnetic field distribution.

200–450°C leads to the greatest changes in the cell volume; at a higher temperature, the changes are already insignificant. The oxygen content probably reaches the equilibrium value.

Model interpretation of the Mössbauer spectra of $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_{3-\gamma}$ measured at room temperature presents significant difficulties due to the uncertainty in both the number of subspectra and in the values of their hyperfine parameters. Therefore, to process the spectra, we utilized the method of restoring the distribution of spectrum parameters using the SpectrRelax program [18]. For each Mössbauer spectrum of the studied samples, the $p(H_{\text{hf}})$ distribution of hyperfine magnetic field H_{hf} was reconstructed with allowance for its linear correlation with the δ isomer shift of the spectrum at the required average value of the ϵ quadrupole shift of its components. The coefficient of linear correlation between the δ isomer shift and the H_{hf} hyperfine magnetic field was found to be positive, $\sim 10^{-3}$ mm/s/kOe.

The Mössbauer spectrum of unsubstituted LaFeO_3 is a typical Zeeman sextet associated with the magnetic ordering of lanthanum ferrite at room temperature (Fig. 2). The hyperfine parameters of the spectrum are in good agreement with the known literature data [20] and correspond to Fe^{3+} ions in the high-spin state in an octahedral oxygen neighborhood.

The 33% $\text{La}^{3+} \rightarrow \text{Sr}^{2+}$ substitution leads to a significant change in the Mössbauer spectrum compared to that of unsubstituted lanthanum ferrite (Fig. 3a). The splitting of the spectrum noticeably decreased while the resonance lines broadened significantly, which corresponds to the appearance of a wide distribution of the hyperfine magnetic field. Figure 3b also shows the Mössbauer spectrum of the $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_{3-\gamma}$ sample annealed at 650°C. Subsequent annealings after synthesis lead to an increase in the splitting, as

well as to narrowing and better resolution of the resonance lines in the spectrum.

Changes in the hyperfine parameters of the spectra of $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_{3-\gamma}$ samples synthesized and annealed at 650°C: average values (H_{av} , δ_{av}) and values at the distribution maximum (H_{max} , δ_{max}) with vacuum annealing temperature in comparison with data for lanthanum ferrite LaFeO_3 are shown in Fig. 4.

The difference between the hyperfine parameters of the spectra of both synthesized and annealed $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_{3-\gamma}$ samples from the parameters of lanthanum ferrite LaFeO_3 is directly related to the possible appearance of high-valence iron ions and oxygen vacancies in the structure upon substitution of $\text{La}^{3+} \rightarrow \text{Sr}^{2+}$ and a change in their number in the course of further vacuum annealing.

Several factors of a cardinal change in the spectra in comparison with lanthanum ferrite should be noted. For the synthesized sample, first, a strong decrease of both H_{max} and H_{av} is observed upon the 33% $\text{La} \rightarrow \text{Sr}$ substitution (Fig. 4a), second, a very wide $p(H_{\text{hf}})$ distribution occurs, and third, a decrease in the isomer shift occurs (Fig. 4b). The value of the isomer shift indicates that the iron ions are in the average valence state, i.e., with a fractional degree of oxidation. This may be due to fast (with a characteristic time of $< 10^{-8}$ s) electron transfer between iron ions at room temperature [21, 22]. The very wide distribution $p(H_{\text{hf}})$ can be due to two main factors. First, is the distribution of Sr^{2+} ions over the positions of La^{3+} ions, which, in turn, is accompanied by the distribution of Fe^{4+} ions over the positions of Fe atoms and the appearance of oxygen vacancies in the structure of substituted ferrite $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_{3-\gamma}$. This distribution of ions and vacancies in the structure leads to a strong local inhomogeneity in the neighborhood of iron atoms. The second factor affecting the $p(H_{\text{hf}})$ distribution width is the fast electron transfer between the

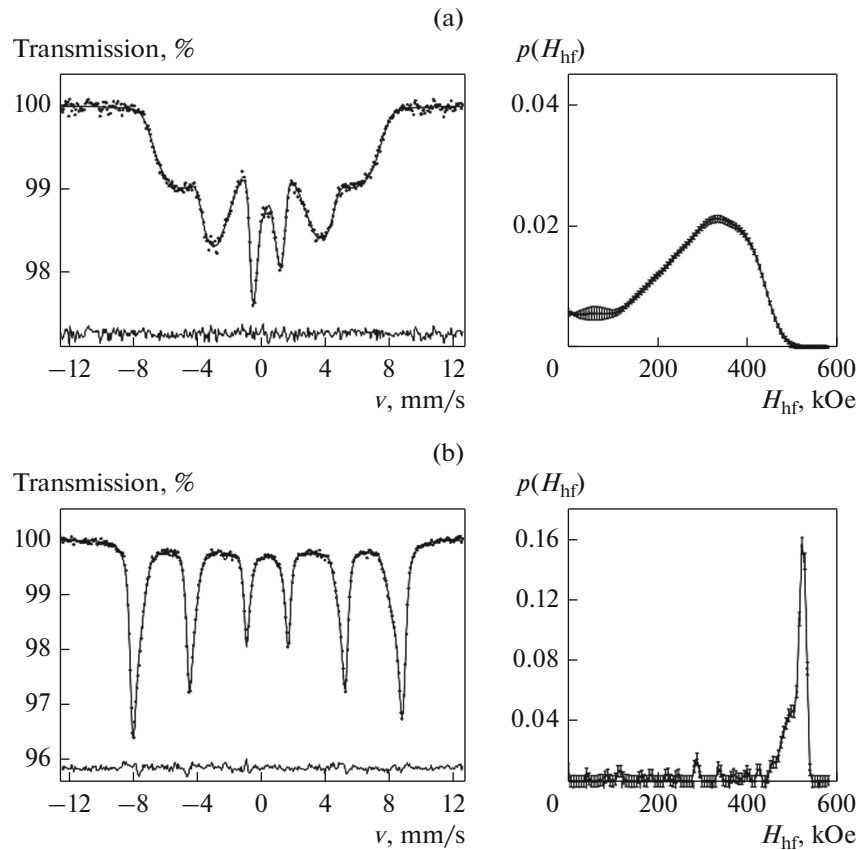


Fig. 3. The results of reconstructing the $p(H_{\text{hf}})$ distributions of the H_{hf} hyperfine magnetic field for the Mössbauer spectra of the $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_{3-\gamma}$ samples: (a) synthesized and (b) annealed in vacuum at 650°C.

Fe^{3+} and Fe^{4+} ions, which leads to the average valence state of the iron atoms. The difference in the values of the H_{max} and H_{av} fields can be due to the strong local inhomogeneity in the neighborhood of iron atoms. As the vacuum annealing temperature t_{ann} increases, i.e., with an increase in the number of oxygen vacancies, the average values of H_{av} and δ_{av} , as well as the values at the maximum of the H_{max} and δ_{max} distribution increase. This indicates that the amount of Fe^{4+} ions decreases.

The Mössbauer spectra measured at 85 K of samples synthesized and annealed at 300 and 650°C, as well as the results of model interpretation, are shown in Figs. 5. In the general case, the spectra of $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_{3-\gamma}$ samples consist of a set of several subspectra. Taking into account the possible values of the number of oxygen vacancies (γ) and the number of Fe^{4+} ions (y), the experimental spectra were interpreted assuming the presence of four subspectra of Fe^{3+} and one subspectrum of Fe^{4+} (Fig. 5). As a result of vacuum heat treatment of the synthesized sample, the content of oxygen vacancies and Fe^{4+} ions

changes, leading to a corresponding change in the Mössbauer spectra. The appearance of the Fe^{4+} ion in the nearest cationic neighborhood of the Fe^{3+} ion weakens the $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}$ exchange bond, and the appearance of an oxygen vacancy in the nearest anionic neighborhood of the Fe^{3+} ion breaks the $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}$ exchange bond. Both lead to a decrease in hyperfine magnetic field H_{hf} and a change in the isomer shift of the spectrum [23, 24].

Figure 6 shows the dependences of the relative intensities of all subspectra of Fe^{3+} and Fe^{4+} ions on the annealing temperature obtained as a result of model interpretation of the experimental Mössbauer spectra. As the annealing temperature increases, the intensity of the subspectrum corresponding to Fe^{4+} decreases and tends to zero at $t_{\text{ann}} = 650^\circ\text{C}$ (Fig. 6a).

At an increase in the vacuum annealing temperature, the contributions to the spectrum from different states of Fe^{3+} are also redistributed. The relative intensity of the $I(\text{Fe}^{3+}; 0)$ subspectrum corresponding to Fe^{3+} ions with all six exchange bonds $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$ ($m = 0$) noticeably increases while the intensities of the

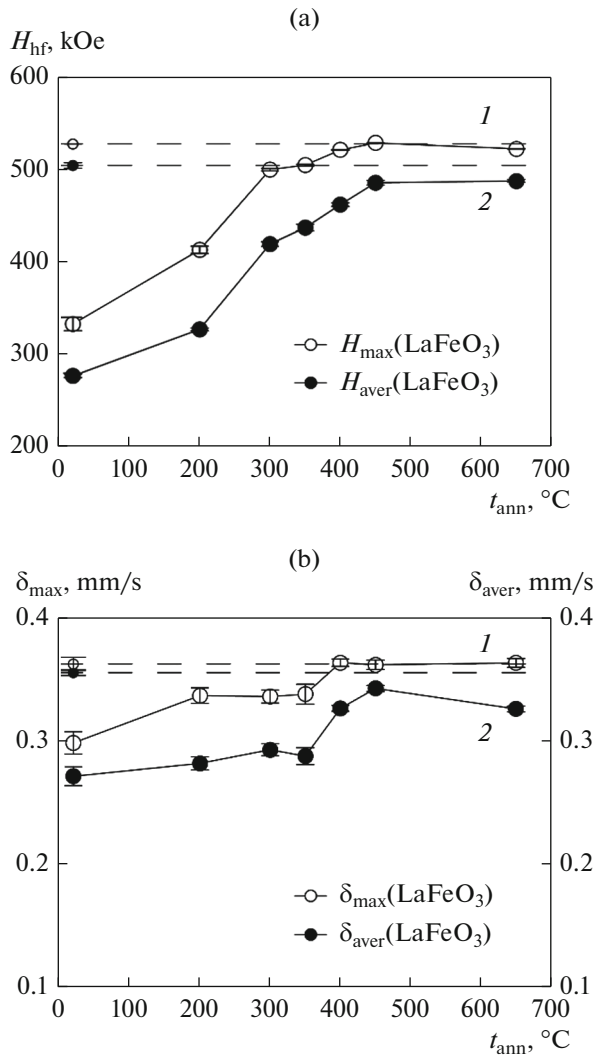


Fig. 4. Changes in the hyperfine parameters of the Mössbauer spectrum of $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_{3-\gamma}$ with vacuum annealing temperature: (1) values at the distribution maximum (max), (2) average values (av), for (a) a hyperfine magnetic field H_{hf} and (b) isomer shift δ in comparison with the data for lanthanum ferrite LaFeO_3 .

subspectra of Fe^{3+} ions with broken or weakened bonds ($m = 1, 2, 3$) decrease (Fig. 6b). The experimentally observed behavior of the relative intensities of the subspectra (Fig. 6) indicates a decrease in the number of Fe^{4+} ions in the sample and a decrease in the probability of breaking or weakening of the $\text{Fe}^{3+}-\text{O}_2-\text{Fe}$ exchange bonds upon vacuum annealing. In this case, the main changes occur in the annealing temperature range of 200–400°C. Upon a further increase of t_{ann} , the changes decelerate.

If we assume that the probabilities of the Mössbauer effect for the ^{57}Fe nuclei belonging to Fe^{3+} and Fe^{4+} ions are practically the same, then the relative

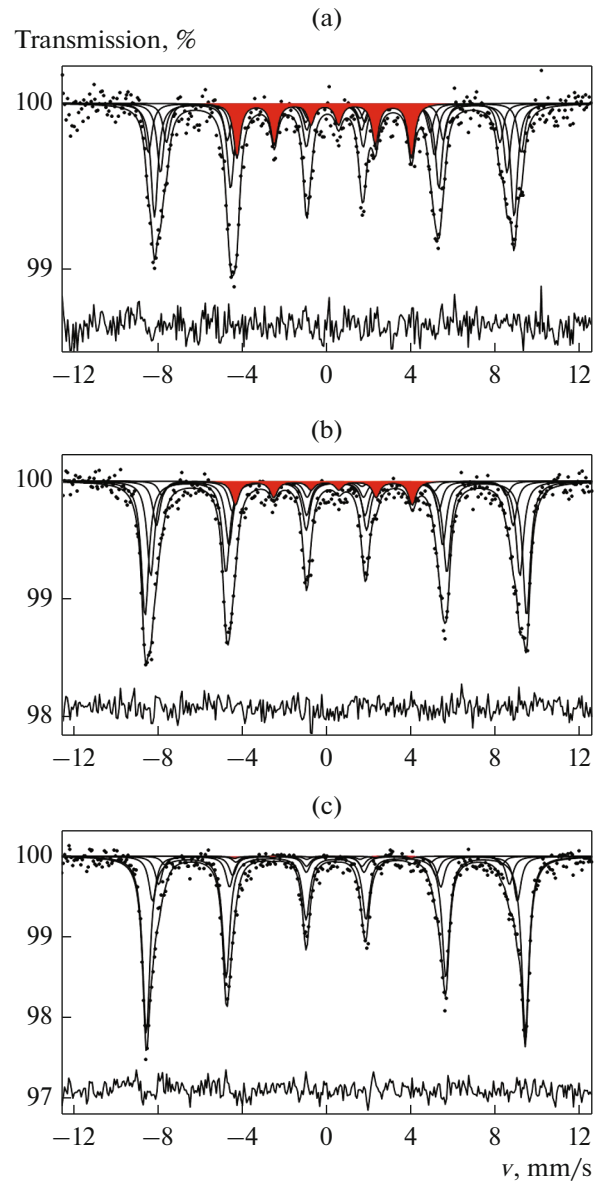


Fig. 5. The results of model interpretation of the Mössbauer spectra measured at 85 K of $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_{3-\gamma}$ samples: (a) synthesized and annealed in vacuum at 85 K, (b) 300 and (c) 650°C. The subspectrum of Fe^{4+} ions is highlighted in red.

intensities of their subspectra make it possible to determine for each sample both the number of Fe^{4+} ions and, for a specified substitution of Sr^{2+} ions for La^{3+} ions, the number of oxygen vacancies and the number of anions O^{2-} per formula unit. Their dependence on vacuum annealing temperature t_{ann} is shown in Fig. 7.

Assuming a linear dependence of the hyperfine parameters of the subspectra of Fe^{3+} ions on the number m of breaking or weakening of exchange bonds, the

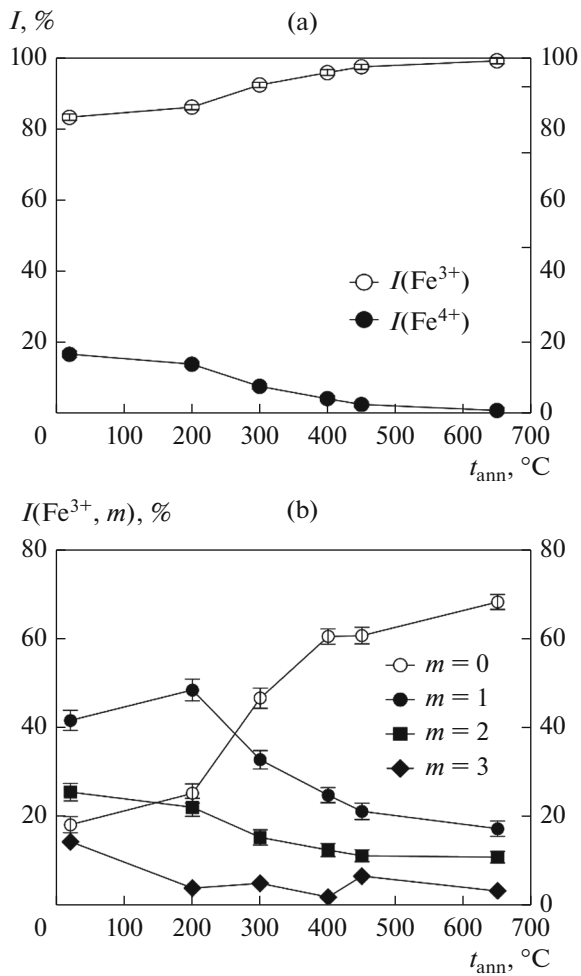


Fig. 6. The dependences on annealing temperature t_{ann} of the relative intensities of subspectra: (a) all Fe^{3+} ions and Fe^{4+} ions, as well as (b) Fe^{3+} ions, in the nearest neighborhood of which $m = 0, 1, 2, 3$ breaking or weakening of exchange bonds occurred.

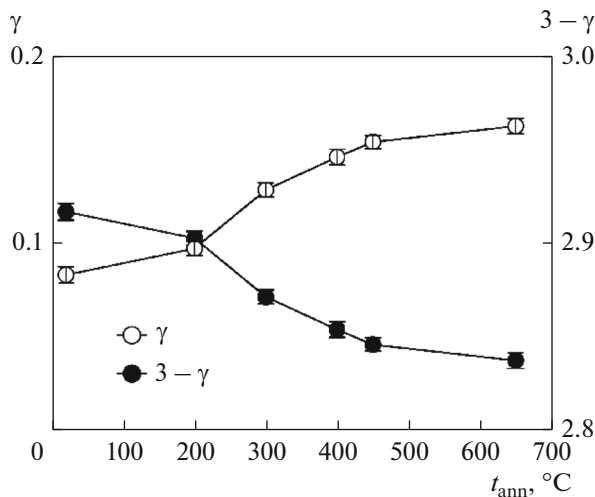


Fig. 7. The dependences on annealing temperature t_{ann} of the number of oxygen vacancies (γ) and the number of oxygen ions ($3 - \gamma$) per formula unit of substituted lanthanum ferrite.

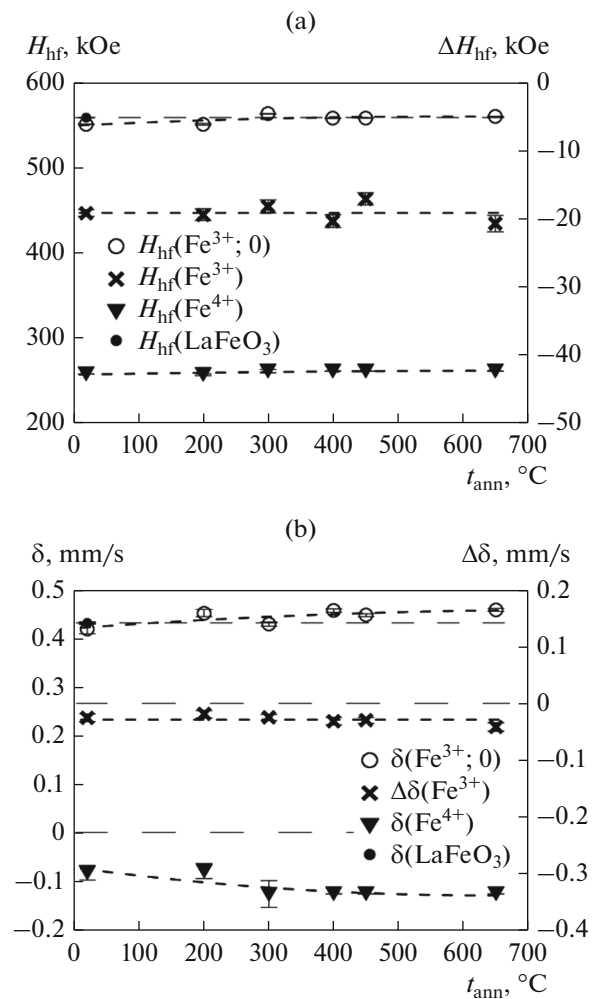


Fig. 8. The dependences on vacuum annealing temperature t_{ann} of the hyperfine parameters of the subspectra of Fe^{3+} and Fe^{4+} ions: (a) $H_{\text{hf}}(\text{Fe}^{3+}; 0)$, $\Delta H_{\text{hf}}(\text{Fe}^{3+})$, $H_{\text{hf}}(\text{Fe}^{4+})$ and (b) $\delta(\text{Fe}^{3+}; 0)$, $\Delta\delta(\text{Fe}^{3+})$, $\delta(\text{Fe}^{4+})$.

values of $H_{\text{hf}}(\text{Fe}^{3+}; 0)$ (550 kOe) and $\delta(\text{Fe}^{3+}; 0)$ for the subspectrum of Fe^{3+} ions with six $\text{Fe}^{3+}\text{-O}_2\text{-Fe}^{3+}$ exchange bonds, as well as changes in the hyperfine field $\Delta H_{\text{hf}}(\text{Fe}^{3+}) = -19.2(4)$ kOe and the isomer shift $\Delta\delta(\text{Fe}^{3+}) = -0.029(3)$ mm/s, upon either a breaking, or weakening of one exchange bond for all studied samples of substituted lanthanum ferrite (Fig. 8) are determined from the model interpretation of the spectra.

CONCLUSIONS

The valence states of Fe atoms and the formation of oxygen vacancies in $\text{La}_{0.67}\text{Sr}_{0.33}\text{FeO}_{3-\gamma}$ in the course of vacuum heat treatment in the temperature range of 200–650°C were studied by Mössbauer spectroscopy.

At room temperature, the presence of Fe^{4+} ions manifests itself as an average valence state of Fe atoms, which is due to the rapid transfer of electrons between Fe^{3+} and Fe^{4+} ions in a locally inhomogeneous ionic neighborhood.

In the course of vacuum annealing, the number of vacancies increases with increasing temperature, and the oxidation state of Fe shifts towards Fe^{3+} ; the amount of Fe^{4+} decreases. At temperatures above 450°C , only Fe^{3+} occurs, and the process of oxygen leaving the lattice terminates.

As the measurement temperature decreases (85 K), a subspectrum corresponding to Fe^{4+} atoms occurs. The presence in the spectra of several sextets related to Fe^{3+} ions is due to the appearance of oxygen vacancies and Fe^{4+} ions in the nearest ionic neighborhood of Fe atoms.

Based on the analysis of the Mössbauer data, the number of oxygen vacancies and oxygen ions depending on the vacuum annealing temperature was estimated for all samples.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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