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Structural Features of a Substituted Strontium Ferrite $Sr_{1-x}La_xFeO_{3-\delta}$: I. $Sr_2LaFe_3O_{9-\delta}$

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Abstract—The structure and the valence states of iron in substituted strontium ferrite $Sr_{2/3}La_{1/3}FeO_{3-\delta}$ or $Sr_3LaFe_3O_{9-\delta}$ at various condition synthesis and heat treatment have been studied using X-ray diffraction and the Mössbauer spectroscopy. A series of vacuum annealing (10^{-3} Torr, $400-650^{\circ}C$) allows the observation of the evolution of the structure from the rhombohedral (for the $Sr_2LaFe_3O_9$) to the orthorhombic ($Sr_2LaFe_3O_8$) via intermediate multiphase states and also the redistribution of valence iron states.

Keywords: substituted strontium ferrite, X-ray spectra, Mössbauer spectra, perovskites, oxygen vacancies **DOI:** 10.1134/S1063783421100322

1. INTRODUCTION

Recently the interest to perovskites based on strontium ferrite have markedly increased due to a possibility of their applying as cathode materials for fuel elements, in spintronics, opto- and microelectronics [1-3]. There is information that these compounds have power antibacterial properties related to the existence of oxygen vacancies in the lattice [4]. In the applied area, it is very important to understand the influence of the oxygen content on the structure and properties of these anion-deficient compounds.

In the perovskite-like oxides, the conditions of synthesizing and heat treatment can substantially influence their structure and properties, controlling the valence state of iron by introducing oxygen vacancies.

Undoped strontium ferrite $SrFeO_3$ is a metallic perovskite, which is ordered antiferromagnetically at $T_N = 134$ K. In this compound, iron is in the fourvalent state. This compound has the cubic symmetry with space group Pm-3m [5, 6], and it is unchanged to 4.2 K [7, 8]. A partial substitution of Sr^{2+} for La^{3+} $(Sr_{1-x}La_xFeO_{3-\delta})$ leads to a mixed iron valence and an increase in the Néel temperature [9]. The incorporation of oxygen vacancies into the lattice during vacuum annealings can cause the phase transformations and the formation of various magnetic structures. The magnetic properties of these compounds are a result of the superexchange mechanism including 3*d* electrons of transition metal ions and the oxygen *p* orbitals [10], i.e., here oxygen plays a very important role.

According to [11], there are three phase regions in $La_{1-x}Sr_xFeO_{3-\delta}$ in the dependence on *x*: the ortho-

rhombic phase for $0 \le x \le 0.2$, rhombohedral phase for $0.3 \le x \le 0.5$, and the cubic phase for $0.6 \le x \le 1.0$. It was indicated in some more recent works [9, 12–15] that this compound has the rhombohedral structure at x = 2/3. According to [12], the rhombohedral modification of LaSr₂Fe₃O_{8.94} (space group *R*–3*c* with parameters a = 5.4784 Å, c = 13.3928 Å in the hexagonal or $a_{\text{rhomb}} = 5.4712$ Å and $\alpha_{\text{rhomb}} = 60.09^{\circ}$ in the rhombohedral axes) is the perovskite distorted by very insignificant compression along one of the space diagonals of the cubic cell. The proximity to the cubic lattice (small distortion) is likely to be precisely the reason of the ambiguousness in the determination of the structure in this case.

Annealings at various temperatures and in various media lead to structural transformations. According to [9], as the treatment temperature increases (and, correspondingly, the oxygen content decreases), first, the phase forms that those authors called conventionally "tetragonal" (a = 3.910 Å, c = 3.867 Å); as a result of a vacuum annealing, the anion-deficient oxide Sr₂LaFe₃O₈ forms with the orthorhombic lattice (space group *Pmma*, a = 5.508 Å, b = 11.884 Å, c = 5.603 Å) [9].

Oxide $Sr_2LaFe_3O_{9-\delta}$ has a mixed valance of iron. According to [13], as temperature decreases, the first order transition with a jump in the electrical resistance is observed from the paramagnetic almost metallic state with the oxidation level $Fe^{3.7+}(d^{4.3})$ to the antiferromagnetic dielectric state due to the disproportionation of Fe^{4+} to $Fe^{3+}/Fe^{5+} = 2/1$. However, according to the Mössbauer data [14], there are not any evident of the existence of Fe^{5+} as was noted in some works

Sample	T, °C and t , h	Notation
Synthesis, slow cooling to room temperature	1300, 10	(1300SC)
Synthesis, fast cooling to room temperature	1300, 10	(1300FC)
Vacuum annealing	400, 4	(400AV)
Vacuum annealing	450, 4	(450AV)
Vacuum annealing	500, 4	(500AV)
Vacuum annealing	650, 4	(650AV)

Table 1. Sr₂LaFe₃O_{9- δ} samples studied in this work: the synthesis and vacuum annealing conditions

[15–18]. The Sr₂LaFe₃O_{9- δ} was studied in most detail in [9, 12], where samples were synthesized by the solid-phase method in air and then they were quenched into liquid nitrogen from various temperatures to minimize the oxidation. However, the quenching can lead to a nonequilibrium state and to the appearance of stresses and defects.

Since oxygen in strontium ferrites is the nearest neighbor of iron, a smallest change in its content must substantially influence the valence state of iron and also the symmetry of its surrounding. In this case, a slow cooling of a sample during its synthesis or its quenching can lead to different degrees of distortion of the local iron surroundings. Such even insignificant change in the local surrounding of iron and its valence state are well observed by the Mössbauer spectroscopy. Because the methods of preparing the samples are, as a rule, different in different works [9, 12, 14, 15, 18, 19], it is difficult to compare the literature, in particular, the Mössbauer data to each other.

There are no detailed studies of the influence of the method and the synthesis conditions (synthesis temperature and the cooling rate of the samples) on the formation of oxygen vacancies, the structure and the valence states of iron in lanthanum-substituted strontium ferrite.

In this work, the structural features and the valence states of iron in the substituted strontium ferrite $Sr_2LaFe_3O_{9-\delta}$ are studied by the X-ray diffraction and the Mössbauer spectroscopy for various conditions of the synthesis and the heat treatment.

2. EXPERIMENTAL

Polycrystalline $Sr_2LaFe_3O_{9-\delta}$ was prepared in air by sol gel method using strontium nitrate, iron, and lanthanum taken in the stoichiometric ratio, and glycine as initial reagents. The synthesis was described in detail in [20]. After the synthesis at 1300°C in air, different cooling conditions were used: slow cooling (SC) with furnace up to room temperature and fast cooling (FC) in air. The samples synthesized with slow cooling were annealed then in vacuum (AV) (10⁻³ Torr) at 400°C, 450°C, 500°C, and 650°C and slowly cooled. The conditions of the synthesis and heat treatments of the samples under study are given in Table 1. The Mössbauer measurements were carried out on the polycrystalline samples on a CM 1101 spectrometer operating in the constant acceleration mode. The Mössbauer absorption spectra were analyzed using the MössFit (version 3.1) program of processing Mössbauer spectra for decomposition of the Mössbauer spectra into the partial spectra using the approximations by the sum of analytic functions. The program algorithms correspond to the thin absorber approximation. In some cases, the processing and analysis of the spectra were performed using the method of model interpretation of the partial spectra and the recovery of the distribution of hyperfine spectrum parameters using the SpectrRelax [21].

The structural attestation of the synthesized polycrystalline samples was performed at room temperature on a Siemens-D500 diffractometer using the Fe K_{α} and Co K_{α} radiations. The phase analysis, the calculation of the X-ray diffraction patterns, and the refinement of the unit cell parameters were performed using the Powder Cell 2.4 and Match3 programs.

3. RESULTS AND DISCUSSION

According to the X-ray data, the initial $Sr_2LaFe_3O_{9-\delta}$ sample synthesized with slow cooling (1300SC) has the rhombohedral structure (space group R-3c) with lattice parameters a = 5.483 Å, c = 13.408 Å in the hexagonal setting (Table 2) or a = 5.475 Å, $\alpha = 60.07^{\circ}$ in the rhombohedral setting; the diffraction pattern is shown in Fig. 1. The attempt to describe the sample structure by the cubic cell (Pm-3m, lattice parameter a = 3.874 Å) also gives a good result, and the difference in the fitting perfection is insignificant. Angle α is close to 60° ; thus, this cell is a result of very weak distortion of the cubic structure, or "pseudocube" as it is often called in the literature.

The Mössbauer spectrum of the $Sr_2LaFe_3O_{9-\delta}$ 1300SC sample measured at room temperature (Fig. 2a) is, as a first glance, one singlet with isomer shift IS = 0.12 mm/s, which corresponds to the average iron valence Fe^{3.7+}.

However, a more careful analysis shows insignificant asymmetry and broadening of the spectrum. The decomposition of the spectrum into two singlets gives the lowest error. The isomer shift of one singlet is

	Phases, space group						
Sample	R-3c		Cmmm, close	to $Sr_4Fe_4O_{11}$	Sr ₂ LaFe ₃ O ₈ , <i>Pmma</i>		
-	cell parameters,	phase fractions,	cell parameters,	phase fractions,	cell parameters,	phase fractions,	
	(Å)	%	(Å)	%	(Å)	%	
1300SC	<i>a</i> = 5.483	100	—	—	—	—	
	c = 13.408						
1300FC	<i>a</i> = 5.487	100	_	_	—	_	
	c = 13.425						
400AV	<i>a</i> = 5.489	64	<i>a</i> = 11.048	36	-	—	
	c = 13.463		b = 7.728				
			c = 5.510				
450AV	<i>a</i> = 5.497	16	a = 11.050	52	<i>a</i> = 5.519	32	
	c = 13.567		b = 7.729		b = 11.899		
	—		c = 5.534		c = 5.605		
500AV	a = 5.529	10	<i>a</i> = 11.056	36	<i>a</i> = 5.516	54	
	c = 13.509		b = 7.728		<i>b</i> = 11.895		
	—		c = 5.520		c = 5.605		
650AV	—	-	—	—	<i>a</i> = 5.516	100	
					b = 11.894		
					<i>c</i> = 5.603		

Table 2. $Sr_2LaFe_3O_{9-\delta}$ structures after various heat treatment

typical for Fe^{4+} in the symmetrical octahedral coordination. Another subspectrum shows the average iron valence state $Fe^{3.5+}$. It is more regular to consider the valence state $Fe^{3.5+}$ as an oxidation level which can be fractal. This state cannot be proved by chemical tests, since its valence is actually mixed for which



Fig. 1. (*a*) Calculated X-ray diffection pattern of R-3c, (*b*) X-ray diffraction pattern of the Sr₂LaFe₃O_{9- δ} 1300SC sample.

PHYSICS OF THE SOLID STATE 2021

 Fe^{3+} : $Fe^{4+} = 1$: 1. The behavior of the oxide containing Fe⁴⁺ or Fe^{3.5} in the chemical reactions will be identical: such oxides are typical oxidants. A main proof of valence state Fe^{3.5+} follows from the Mössbauer spectra: the value of the isomer shift is between the values of the corresponding shifts of Fe³⁺ and Fe⁴⁺. According to [9, 18], such an average valence state of Fe is due to fast electron transfer (time constant $<10^{-8}$ s), although it is assumed that there is the electron trapping near the oxygen vacancies in the average-valence state. Table 3 gives the parameters of the obtained subspectra. This spectrum is similar to the spectrum of strontium ferrite $SrFeO_{2.875}$ which has the tetragonal structure and ratio $Fe^{4+}/Fe^{3.5+} = 1/1$ [20]. In the substituted $Sr_2LaFe_3O_{9-\delta}$ compound, the ratio of the iron valence states is slightly different: $Fe^{4+}/Fe^{3.5+} =$ 46%/54%; moreover, there is no Fe⁴⁺ with the pyramidal oxygen environment. That is, at the substitution of 33% Sr for La, the distortion of the iron local surrounding decreases as compared to that in SrFeO_{2 875}. The substitution is also leads, according to the X-ray diffraction data, to the transition from the tetragonal structure for $SrFeO_{2.875}$ to the rhombohedral structure for $Sr_2LaFe_3O_{9-\delta}$. The estimation of the oxygen content in the synthesized compound on the base of the Mössbauer data gives the composition $Sr_2LaFe_3O_{9.04}$; i.e., we have almost the stoichiometric proportion by oxygen within the error (Table 3). The same oxygen



Fig. 2. Mössbauer spectra of $Sr_2LaFe_3O_{9-\delta}$ (a, b) 1300SC and (c) 1300FC samples measured at (a, c) 300 K and (b) 90 K.

content is obtained as we take the average oxidation level of iron $Fe^{3.7+}$.

From the Mössbauer spectrum of the synthesized sample measured at 90 K (Fig. 2b), it follows that a decrease in temperature leads to the transition to the magnetically ordered state: the spectrum processing demonstrates the existence of two magnetic subspectra (Table 3). Comparing the isomer shifts of the subspectra measured at 300 K and 90 K (Table 3), we can ascribe the subspectrum with a higher effective magnetic field to Fe³⁺ ions, and the subspectrum with lower effective magnetic field, to ions Fe⁴⁺. In addition, from the isomer shifts, it follows that, as temperature decreases, Fe^{3.5+} transits to Fe³⁺ during the magnetic transition. Assuming that the averaged valence state $Fe^{3.5+}$ is due to the fast electron transfer [9, 18], then the transition to Fe³⁺ at a decrease in the temperature demonstrates the "freezing" of this process. The low-temperature Mössbauer spectrum confirms the data for the sample measured at 300 K that there are two valence states of iron in the structure.

The oxygen content in the sample at the synthesis temperature must differ from the value at room tem-

perature. Therefore, the cooling rate after the synthesis can substantially influence the oxygen content and, as result, the structure and valence states of iron. For comparison, we carried out the synthesis with fast cooling in air (sample 1300FC). The 1300FC sample has the rhombohedral structure (Table 2). The diffraction pattern is slightly different from the X-ray diffraction pattern of the previous sample (some lines at the side of small angles demonstrate slightly marked broadening). This is likely to be due to the formation of some fraction of the additional phase, the structure of which will be discussed below.

The calculation of the unit cell volumes of the 1300SC and 1300FC samples shows that the volume of the first sample (349.05 Å³) is smaller than that of the second sample (350.17 Å³), which correlates to the oxygen contents: it is lower in the fast-cooled sample.

The Mössbauer spectrum of the 1330FC sample is noticeably broadened and a noticeable asymmetry of the spectrum forms (Fig. 2c). The decomposition of the spectrum into two singlets and two doublets, parameters of which are given in Table 3, gives the minimal error. According to the isomer shift, singlet

Commis	Valence of Fe	300 K				Oxygen content,
Sample	(subspectrum)	IS	Δ	H_n	А	9-δ
1300SC	4+ (S1)	0.04(1)	_	—	46	9.04(2)
	3.5+ (S2)	0.18(1)	—	—	54	
1300FC	3.8+ (S1)	0.10(1)	—	—	26	8.91(2)
	3.8+ (D1)	0.10(1)	0.22(1)	_	48	
	3.5+ (D2)	0.15(3)	0.66(3)	_	5	
	3+ (D3)	0.36(1)	—	—	21	
400AV	4+ (S1)	0.07(1)	_	_	15	8.73(2)
	4+ (D1)	0.05(1)	0.23(1)	—	23	
	3.5+ (D2)	0.16(1)	0.77(1)	—	16	
	3.5+ (D2')	0.17(3)	1.18(3)		6	
	3+ (D3)	0.32(1)	0.17(1)	_	18	
	3+ (Sx1)	0.3(1)4	0.77(1)	423(2)	22	
450AV	4+ (D1)	-0.02(1)	0.53(1)		30	8.46(2)
	3+ (Sx1)	0.30(1)	0.82(1)	424(2)	35	
	3+ (O) (Sx2)	0.34(1)	0.37(1)	508(2)	24	
	3+ (T) (Sx3)	0.26(1)	_	388(2)	11	
			0.84(1)			
500AV	4+ (D1)	-0.01(1)	0.65(1)	_	15	8.33(2)
	3+ (Sx1)	0.27(1)	0.81(1)	424(2)	31	
	3+ (O) (Sx2)	0.31(1)	0.38(1)	510(2)	36	
	3+ (T) (Sx3)	0.14(1)	-	376(2)	18	
			0.71(1)			
650AV	4+ (D1)	0.09(4)	0.35(4)	—	4	8.00(2)
	3+ (O) (Sx2)	0.33(1)	0.39(1)	510(1)	65	
	3+ (T) (Sx3)	0.15(1)	—	375(1)	31	
			0.71(1)			
90 K						
1300SC	4+	0.00(1)	0.03(1)	255(1)	36	
	3+	0.37(1)	0.05(1)	442(1)	64	

*IS is the isomer shift (with respect to bcc Fe at 300 K), mm/s; Δ is the quadrupole splitting, mm/s; H_n is the effective magnetic field at a ⁵⁷Fe nucleus, kOe; A is the contribution of a given subspectrum, %. S, D, and Sx are singlet, doublet and sextet, respectively.

S1 and doublet D1 can be ascribed to iron ions with the average oxidation level Fe^{4+} with the symmetric and distorted oxygen surroundings, as in $SrFeO_{2.875}$ [20], doublet D2, to $Fe^{3.5+}$ and singlet S2 to Fe^{3+} . That is, the increase in the cooling rate of the sample leads to a distortion of the local surrounding of Fe, several valence states of Fe form and their redistribution takes place (Table 3).

Taking into account the obtained X-ray diffraction data, it can be assumed that doublet for Fe^{3+} belongs to an additional phase. The estimation of the oxygen content in this compound on the base of the Mössbauer data gives the composition $Sr_2LaFe_3O_{8.95}$; taking

into account the isomer shift, we use for the estimation the averaged valence $Fe^{3.8+}$, not Fe^{4+} .

The vacuum annealing 400AV of the samples leads to some changes in the X-ray diffraction pattern: we observe a clear broadening of some lines at small angles and the appearance of additional weak lines (Fig. 3*d*). This is due to the fact that, in parallel with the rhombohedral phase, the abovementioned additional phase manifests itself more clearly. The exact identification of its structure is hampered, since it is a part of the two-phase mixture and the phase lines significantly overlap in the diffraction pattern. However, the attempts to describe this additional phase structure

Table 3. Mössbauer parameters of subspectra at 300 and 90 K of $Sr_2LaFe_3O_{9-\delta}$ samples



Fig. 3. Calculated X-ray diffraction patterns: (*a*) R-3c, (*b*) *Cmmm* close to Sr₄Fe₄O₁₁, (*c*) Sr₂LaFe₃O₈; X-ray diffraction patterns of the sample annealed in vacuum: (*d*) 400AV, (*e*) 450AV, and (*f*) 500AV.

by any of two close lattices known for pure $SrFeO_3$, namely, orthorhombic $Sr_4Fe_4O_{11}$ and tetragonal $Sr_8Fe_8O_{23}$ [20], give almost similar good result. It is possible that both these close lattices simultaneously coexist in the system, and the transition to the orthorhombic phase occurs via the stage of the tetragonal phase as the oxygen content decreases. However, in this work, it is impossible to trace this complex process in the multiphase mixture.

The same additional phase was observed before in [9]. Those authors conventionally called it "tetragonal" (with parameters a = 3.910 Å and c = 3.867 Å), indicating, however, that the existence of the broadened lines and weak superstructure reflections can show a lower symmetry of the phase or a larger elementary cell volume. We obtained a good agreement with the experiment, describing in our case the additional phase using a model close to Sr₄Fe₄O₁₁. The lattice parameters of this phase are a = 11.048 Å, b =7.728 Å, c = 5.510 Å, and its fraction in the two-phase mixture is about 36% (Table 2).

The Mössbauer spectrum of the 400AV sample becomes complex: in addition to the paramagnetic part, a magnetic sextet (22%) appears with the effective magnetic field $H_n = 42.3$ T that correspond to Fe^{3+} , according to the isomer shift Fig. 4a. It can be concluded that the incorporation of La increases the Néel temperature as compared to a nonsubstituted oxide. To elucidate the fine structure of the paramagnetic part, the spectrum was also measured at low velocity (Fig. 4b). It is similar in part to the spectrum of the synthesized sample with fast cooling but more broadened. The spectrum was decomposed into five subspectra: singlet S1 and doublet D1 corresponding to Fe⁴⁺ with the octahedral symmetric and distorted oxygen surroundings, doublets D2 and D2' corresponding to Fe^{3.5+} with various degrees of distorting the surroundings, and doublet D3 corresponding to Fe^{3+} with the octahedral surroundings. There is also insignificant contribution (3%) of D4 from two internal lines of the sextet. Based on the Mössbauer data, the estimation of the oxygen content in the sample after vacuum annealing at 400°C gives Sr₂LaFe₃O_{8.75}; i.e., the vacuum annealing at 400°C leads to the appearance of oxygen vacancies. Taking into account the obtained X-ray phase analysis data (36% orthorhombic phase close to $Sr_4Fe_4O_{11}$), we can ascribe doublet D3 (16%) and sextet (22%) corresponding to Fe^{3+} , to this phase. Other subspectra (S1, D1, D2, and D2') belong to the rhombohedral phase. Taking this assumption, we see good agreement of the X-ray and the Mössbauer data. The appearance of the sextet shows that the sample undergoes a partial transition to the magnetic state; i.e., the Néel temperature increases.

The increase in the vacuum annealing temperature to 450°C (450AV) and then to 500°C (500AV) leads to a significant change in the X-ray diffraction pattern (Figs. 3e, 3f). The beast agreement with the experiment in both the cases is obtained for a three-phase mixture consisting of the rhombohedral phase, orthorhombic phase close to $Sr_4Fe_4O_{11}$ (whose content reaches a maximum at 450AV), and the orthorhombic $Sr_2LaFe_3O_3$ phase known in the literature [22], Fig. 3, Table 2. In this phase, all the iron is in state 3+. The fraction of the orthorhombic phase $Sr_2LaFe_3O_8$ increases with the annealing temperature. The proportions of the contents of these phases are ~16/52/32 for the 450AV sample and ~10/36/54 for 500AV.

Figure 5 shows the Mössbauer spectra of the 450AV and 500AV samples. From Fig. 5, it follows that the content of the paramagnetic phase in the samples decreased significantly. The magnetic part of the spectrum consists of three subspectra: magnetic sextet with $H_n = 42.4$ T corresponding to Fe³⁺ with the octahedral surroundings, the content of which gradually decreases as the vacuum annealing temperature increases, and two sextets similar to the corresponding



Fig. 4. Mössbauer spectrum of the 400AV sample measured at various velocities: (a) from -12 to +12 mm/s, (b) from -2 to +2 mm/s.



Fig. 5. Mössbauer spectra of samples (a) 450AV, (b) 500AV, and (c) 650AV.

spectra of the brownmillerite phase of nonsubstituted $Sr_2Fe_2O_5$, in which Fe^{3+} has two local oxygen surroundings: octahedral ($H_n(O) = 49.6$ T) and tetrahe-

dral ($H_n(T) = 42.0 \text{ T}$) [20]. They have different effective magnetic fields (in Sr₂LaFe₃O_{9- δ}, $H_n(O) = 51.2 \text{ T}$ and $H_n(T) = 38.8 \text{ T}$) and different contributions of the



Fig. 6. (*a*) Calculated X-ray diffraction patterns of $Sr_2LaFe_3O_8$, *Pmma*; (*b*) X-ray diffraction pattern of the 650AV sample.

corresponding subspectra, Table 3. The increase in the annealing temperature only by 50°C (from 450°C to 500°C) substantially increases the contributions of these two latter subspectra. Taking into account the X-ray data, one can be concluded that the paramagnetic contribution corresponds to the rhombohedral $Sr_2LaFe_3O_{9-\delta}$ phase, the content of which decreases as the vacuum annealing temperature increases, and the sextet with $H_n = 42.4$ T, to the orthorhombic phase with the structure close to the $Sr_4Fe_4O_{11}$, and two sextets with $H_n(O)$ and $H_n(T)$, to the orthorhombic Sr₂LaFe₃O₈ phase, whose content strongly increases with temperature; i.e., there is a good agreement of the Mössbauer and X-ray data. Based on the Mössbauer data, the estimation of the oxygen content in the 450AV and 500AV samples gives Sr₂LaFe₃O_{8.46} and Sr₂LaFe₃O_{8.33}, respectively (Table 3). The Mössbauer spectra of these samples substantially differ from the spectra in [9] of the samples prepared by another method (quenching from 1400°C in air).

The vacuum annealing of the sample 650AV leads to the formation of the pure orthorhombic $Sr_2LaFe_3O_8$ with lattice parameters a = 5.516 Å, b = 11.894 Å, and c = 5.603 Å. The sample X-ray diffraction pattern is shown in Fig. 6.

The Mössbauer spectrum of the 650AV sample is shown in Fig. 5c. This spectrum consists of two magnetic subspectra ($H_n(O) = 51.0$ T and $H_n(T) = 37.5$ T) and a small (4%) paramagnetic addition; i.e., vacuum annealing 650AV leads to the transition to the magnetically ordered phase, in which trivalent Fe³⁺ has two oxygen surroundings: the octahedral and tetrahedral, as in Sr₂Fe₂O₅. The subspectra lines are broader than those for the brownmillerite Sr₂Fe₂O₅ phase, which



Fig. 7. Dependence of the phase composition of $Sr_2LaFe_3O_{9-\delta}$ on the oxygen content, according to X-ray phase analysis data. The vertical lines indicate the oxygen content in the samples estimated from the Mössbauer data: (*1*) rhombohedral phase, (*2*) orthorhombic $Sr_2LaF_3O_8$ phase, (*3*) orthorhombic phase close to $Sr_4Fe_4O_{11}$.

can be related to disordered distributions of La and Sr. Based on the Mössbauer data, an estimate of the amount of oxygen in the sample after annealing in vacuum at 650°C gives Sr₂LaFe₃O₈. The obtained spectrum is similar to the spectrum of the sample with the same composition in oxygen in [22]. An analysis of the data obtained for the samples shows that both the samples with the edge compositions in the oxygen contents Sr₂LaFe₃O₉ and Sr₂LaFe₃O₈ are singlephase, and the intermediate states are not singlephase. Figure 7 clearly shows how the phase composition of the samples is dependent on the oxygen content after a series of vacuum annealing at various temperatures. In addition, it follows from Fig. 7 that the pure "tetragonal" phase, which is proposed in [9] for the $Sr_2LaFe_3O_{8.5}$ composition (the quenched sample), is not obtained at any oxygen contents in the samples with slow cooling after the synthesis. For all intermediate compositions, phase mixtures form. As oxygen vacancies appear, the additional phase (or the mixture of two phases) forms along with the rhombohedral phase. The additional phase content becomes maximal near the Sr₂LaFe₃O_{8.5} composition and, then, begins to decrease (Fig. 7).

Summing the obtained Mössbauer data shown in Fig. 8, it can be seen that the valence states of iron and is surroundings are dependent on the oxygen content.

From Fig. 8, it follows that Fe^{4+} presents at all intermediate oxygen concentrations, exception for the edge orthorhombic $Sr_2LaFe_3O_8$ phase. The appearance of vacancies strongly decreases the content of $Fe^{3.5+}$, and it disappears in the $Sr_2LaFe_3O_{8.46}$ compo-



Fig. 8. Valence state of iron as a function of the oxygen content in $\text{Sr}_2\text{LaFe}_3\text{O}_{9-\delta}$. The vertical lines indicate the oxygen content in the samples estimated from the Mössbauer data: (1) Fe⁴⁺, (2) Fe^{3.5+}, (3) Fe³⁺ in the orthorhombic phase close to $\text{Sr}_4\text{Fe}_4\text{O}_{11}$, (4) Fe³⁺ in the orthorhombic phase close to the brownmillerite $\text{Sr}_2\text{Fe}_2\text{O}_5$ phase.

sition. In the Sr₂LaFe₃O_{8.73} composition, a Fe³⁺ ion appears from the additional phase; i.e., in this composition, there are three valence states of iron: Fe⁴⁺, Fe^{3.5+}, and Fe³⁺. As the vacancy content increases (Sr₂LaFe₃O_{8.46}), Fe³⁺ appears from the orthorhombic Sr₂LaFe₃O₈ phase; the content of Fe³⁺ increases with the vacancy concentration (Sr₂LaFe₃O_{8.34}). In this case, the contents of Fe⁴⁺ and Fe³⁺ from the additional phase decrease.

Using the Mössbauer data, only the Sr₂LaFe₃O₈ phase, in which the iron valence, its surroundings, and the hyperfine fields on the iron nuclei differ from all other phases, can be identified quite correctly. The problems in the identification of other phases appear, because the same valence states can be in various phases, and the error in the identification of the phase composition increases. According to the X-ray phase analysis data, the additional phase is close in structure to $Sr_4Fe_4O_{11}$ of pure strontium ferrite or to $Sr_8Fe_8O_{23}$; it is also possible that a mixture of these phases forms. It is known that the Sr₈Fe₈O₂₃ phase of the strontium ferrite contains Fe⁴⁺ in the octahedral and pyramidal oxygen environment and $Fe^{3.5+}$, and the $Sr_4Fe_4O_{11}$ phase contains Fe⁴⁺ in the pyramidal environment and Fe^{3+} [20]. The set of the valence states of iron in similar phases for $Sr_2LaFe_3O_{9-\delta}$ is close to that for pure $SrFeO_{3-\delta}$, although the quantitative ratio of various valence states must differ due to a partial replacement of Sr²⁺ for La³⁺. Thus, based on the obtained X-ray and Mössbauer data, the additional phase can be identified as the orthorhombic phase close in structure to $Sr_4Fe_4O_{11}$, or as the tetragonal phase close to $Sr_8Fe_8O_{23}$, or their mixture forms.

Analyzing the obtained data, we can assume the following scheme of the transition from the rhombohedral $Sr_2LaFe_3O_9$ structure to the orthorhombic $Sr_2LaFe_3O_8$. The appearance and further increase in the oxygen vacancy content lead to the distortion of the "pseudocubic" (rhombohedral lattice with very insignificant distortion) lattice toward the orthorhombic structure close to $Sr_4Fe_4O_{11}$, it is likely, through the stage of the tetragonal lattice similar in structure to the $Sr_8Fe_8O_{23}$ phase of pure strontium ferrite. Whether only one of the abovementioned lattices or both lattices are realized sequentially, cannot be concluded on the base of the results of this work. To elucidate the nature of the additional phase (or phases), further studies are necessary.

The additional phase fraction increases up to the $Sr_2LaFe_3O_{8.5}$ composition, as the orthorhombic $Sr_2LaFe_3O_8$ phase appears with one vacancy per three perovskite cells. After its formation, the additional phase fraction starts to decrease. In this case, the content of the initial rhombohedral phase also decreases monotonically.

4. CONCLUSIONS

Thus, the X-ray data show that both samples with edge compositions in oxygen contents (Sr₂LaFe₃O₉ and $Sr_2LaFe_3O_8$) are single-phase and have the rhombohedral and orthorhombic structures, respectively. The addition of oxygen vacancies during vacuum annealings of the rhombohedral Sr₂LaFe₃O₉ leads to a change in the structural state: the samples intermediate in composition are multiphase, and the ratio of the phase contents in a mixture is changed as oxygen content decreases. As the oxygen vacancy concentration becomes equal to one vacancy per three perovskite cells, the edge orthorhombic $Sr_2LaFe_3O_8$ phase forms. The process of the transformation goes through the formation of the intermediate phase, which has, supposedly, the structure close to the $Sr_4Fe_4O_{11}$ phase structure of pure strontium ferrite. It is also possible that the system contains the phase close in structure to the tetragonal $Sr_8Fe_8O_{23}$ phase or that both these close lattices coexist simultaneously, and the transition to the orthorhombic phase goes through the stage of the tetragonal phase.

According to the Mössbauer data, iron ions in the sample with the rhombohedral $Sr_2LaFe_3O_9$ structure have two valence states: Fe^{4+} with the octahedral symmetric oxygen surroundings and the averaged valence state $Fe^{3.5+}$. The sample with the orthorhombic $Sr_2LaFe_3O_8$ structure is magnetic, according to the Mössbauer data and iron has the valence state Fe^{3+} with two oxygen surroundings, namely, octahedral

and tetrahedral, as well as, in the brownmillerite phase of the unsubstituted $Sr_2Fe_2O_5$. The analysis of the complete set of the valence states of iron, their redistribution with a decrease in the oxygen content, and also the transitions from the paramagnetic state to the magnetically ordered state made it possible to correlate the information on the local surroundings of iron cations with the structural data.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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