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Oxygen Vacancies and Valence States of Iron in $\text{SrFeO}_{3-\delta}$ Compounds

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Abstract—The brownmillerite phase has been studied by X-ray diffraction and Mössbauer methods. The available data on single-phase compounds with the perovskite structure in strontium ferrite $\text{SrFeO}_{3-\delta}$ are analyzed. All the valence states of iron for any phase state of strontium ferrite are found to be determined by its local oxygen environment. This fact enables us to understand the regularity of transitions of iron from one valence state to another state when adding oxygen vacancies and to explain the structural states of iron in strontium ferrite, such as the single-phase and two-phase compositions. This approach is a more general case for description of all known compounds and phase combinations synthesized in $\text{SrFeO}_{3-\delta}$ than the formula for single-phase structures that is considered in the literature and fit well into the scheme proposed in this work.

Keywords: strontium ferrite, X-ray spectra, Mössbauer spectra, perovskites, oxygen vacancies

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1. INTRODUCTION

Perovskite solid solutions with general formula $\text{A}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ ($\text{A} = \text{La}^{3+}, \text{Bi}^{3+}, \text{Ba}^{2+}$) are promising objects as cathode materials in solid oxide fuel cells (SOFCs) and oxygen permeation membranes [1–3]. Strontium ferrite $\text{SrFeO}_{3-\delta}$ is one of initial materials for these solid solutions, and first it should be closely studied to investigate the properties of complex cathode materials. The compositions of this material are strongly dependent on the oxygen content. According to [4–10], the oxygen-deficient strontium ferrite $\text{SrFeO}_{3-\delta}$ has four single-phase structures: SrFeO_3 (cubic system), $\text{SrFeO}_{2.86}$ (tetragonal system), $\text{SrFeO}_{2.73}$ (orthorhombic system), and $\text{SrFeO}_{2.50}$ (brownmillerite-type orthorhombic system). These single-phase structures are described by the general scheme proposed in [4]: $\text{SrFeO}_{3-1/n}$ ($n = \infty, 8, 4,$ and 2), where there are n initial perovskite cells per one vacancy. The phases obtained experimentally are close in the oxygen content to ideal single-phase compositions SrFeO_3 ($n \rightarrow \infty$), $\text{Sr}_8\text{Fe}_8\text{O}_{23}$ (or $\text{SrFeO}_{2.875}$, $n = 8$), $\text{Sr}_4\text{Fe}_4\text{O}_{11}$ (or $\text{SrFeO}_{2.75}$, $n = 4$), and $\text{Sr}_2\text{Fe}_2\text{O}_5$ (or $\text{SrFeO}_{2.50}$, $n = 2$). At $n \rightarrow \infty$, the compound has the stoichiometric composition in oxygen (without vacancies) and contains only cations Fe^{4+} [4, 5]. At $n = 2$, the compound contains only Fe^{3+} cations. The intermediate states have a mixed valence of iron.

It should be noted that the scheme shown above is applicable only to the single-phase structures, in

which there is only one vacancy per n perovskite cells. The structures of phases $\text{Sr}_8\text{Fe}_8\text{O}_{23}$, $\text{Sr}_4\text{Fe}_4\text{O}_{11}$, and $\text{Sr}_2\text{Fe}_2\text{O}_5$ are superlattices that consist of several perovskite cells. These structures are oxygen-deficient ordered, which was shown by the combination of X-ray and electron diffraction methods [4, 8, 11, 12]. Thus, there are four single-phase structures with certain sets of iron atoms with various valences with different local oxygen environment. It also follows from the literature data that a part of Fe atoms have the octahedral oxygen environment FeO_6 and another part, the quadratic-pyramidal environment FeO_5 [13–15], depending on the structure. However, up to now, there is no unambiguous opinion regarding the valence of Fe atoms having one or another oxygen environment. For example, it is assumed in [7, 16] that, in $\text{SrFeO}_{2.75}$, Fe^{3+} ions have the pyramidal oxygen environment and all Fe^{4+} ions, the octahedral environment. As the oxygen content decreases (oxygen vacancies appear), the iron valence state and its oxygen environment are changed; the significant change in the composition in oxygen leads to phase transitions.

Besides the single-phase structures, strontium ferrite contains also a whole set of poorly studied compounds with intermediate compositions in oxygen which are considered in the literature as mixture consisting of two phases [4, 9, 11, 14, 17–19], and these compounds are not described by the abovementioned formula. At the same time, it is a complete study of

single-phase and also two-phase structural states that enable us to trace the character of the transition of iron from one valence state to another state as the oxygen content is changed, in other words, as vacancies are added.

Thus, it is impossible to trace the character of the transition of iron from one valence state to another and the change its local oxygen environment when adding vacancies over entire oxygen range including both single-phase and two-phase compositions based on the formula for single-phase structures with different oxygen contents proposed in the literature.

The information about all possible valence states of iron, its local environments can be obtained by the Mössbauer spectroscopy. The structure, the crystal lattice parameters, and the phase composition are usually obtained from X-ray diffraction and neutron diffraction data.

Taking into account the foregoing, we propose a new approach different from the scheme proposed in [4]. This approach is based on the consideration of the character of the change in the iron valence state in oxide $\text{SrFeO}_{3-\delta}$ that is determined by the number of vacancies in the oxygen range of existence of the structural states ($0 \leq \delta \leq 0.5$) independent of the phase state of the sample. The Mössbauer spectroscopy is the most informative and exact method of obtaining the iron valence states. The proposed approach enables us not only observe the character of the change in the valence state of Fe as the number of vacancies is changed, but also to quantitative estimate the fractions of these states. Knowing the types and the number of the valence states in the single-phase structures, we can, using this approach, to estimate the contributions of each phase in the two-phase samples. It is precisely the possibility that differ the proposed approach from the scheme of [4]. In addition, the knowledge of the character of the change in the iron valence with addition of vacancies can be useful for studying the physical properties, in particular, anomalous properties of strontium ferrite. To construct our scheme we should obtain the Mössbauer data for the brownmillerite phase and the mixture of the brownmillerite and orthorhombic phases. For this purpose, we additionally prepared the brownmillerite phase and the mixture of the brownmillerite and orthorhombic phases and performed the X-ray diffraction and Mössbauer studies for them. We also have analyzed the available data on the single-phase and two-phase samples.

2. EXPERIMENTAL

To obtain the brownmillerite phase, the strontium ferrite synthesized by the sol-gel method was annealed in vacuum at two temperatures 450 and 650°C. The sample synthesis is described in detail in [20].

The structural certification of the polycrystalline samples was carried out at room temperature on a Sie-

mens D-500 diffractometer (CoK_α radiation) The phase composition of the samples was determined using the PowderCell 2.4 and Match 3 programs.

The Mössbauer measurements were performed at room temperature on the polycrystalline samples using an SM 1101 spectrometer operating in the constant acceleration mode using a $^{57}\text{Co}(\text{Rh})$ radioactive source. The Mössbauer absorption spectra were analyzed using the MossFit program (Version 3.1) for the decomposition of the spectra into the partial spectra by their approximation by the sum of analytical functions. The program algorithms correspond to the thin absorber approximation.

3. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction Analysis

Figure 1a shows the X-ray diffraction pattern of strontium ferrite $\text{SrFeO}_{3-\delta}$ annealed at 450°C. The sample contains two phases: $\text{Sr}_4\text{Fe}_4\text{O}_{11}$ that has the orthorhombic lattice with space group $Cmmm$ [13] and unit cell parameters $a = 10.982 \text{ \AA}$, $b = 7.708 \text{ \AA}$, $c = 5.478 \text{ \AA}$ and $\text{Sr}_2\text{Fe}_2\text{O}_5$ (or $\text{SrFeO}_{2.5}$ with the brownmillerite structure [21] (space group $Ibm2$, lattice parameters $a = 5.674 \text{ \AA}$, $b = 15.584 \text{ \AA}$, $c = 5.530 \text{ \AA}$). The quantitative estimation performed using the PowderCell 2.4 program gives the proportion of these phases 55% : 45%.

The sample annealed in vacuum at 650°C (Fig. 1b) is an almost pure $\text{Sr}_2\text{Fe}_2\text{O}_5$ (the brownmillerite structure, space group $Ibm2$, unit cell parameters $a = 5.673 \text{ \AA}$, $b = 15.592 \text{ \AA}$, $c = 5.529 \text{ \AA}$).

3.2. Mössbauer Spectroscopy

The Mössbauer spectrum of any object under study is the sum of partial spectra, where each subspectrum corresponds to a certain local environment of a Mössbauer atom. The Mössbauer spectrum does not give a direct information on the structural state of a sample. However, knowing the valence states of iron and their fractions in a single-phase sample, we can estimate the phase composition of two-phase samples from the Mössbauer data. In strontium ferrites, oxygen is in the nearest environment of iron atoms.

Figure 2a shows the Mössbauer spectrum of the synthesized $\text{SrFeO}_{3-\delta}$ sample annealed in vacuum at 450°C. It consists of two magnetic subspectra whose isomer shifts correspond to the trivalent iron in the brownmillerite phase with two oxygen environments (octahedral and tetrahedral) in the proportion 23% and 26%, respectively. In addition, there is a paramagnetic part (51%) in the spectrum consisting of two subspectra the parameters of which correspond to the local environment intrinsic to orthorhombic phase $\text{Sr}_4\text{Fe}_4\text{O}_{11}$ [20], i.e., the sample is two-phase and the ration of the local environments for the brownmillerite

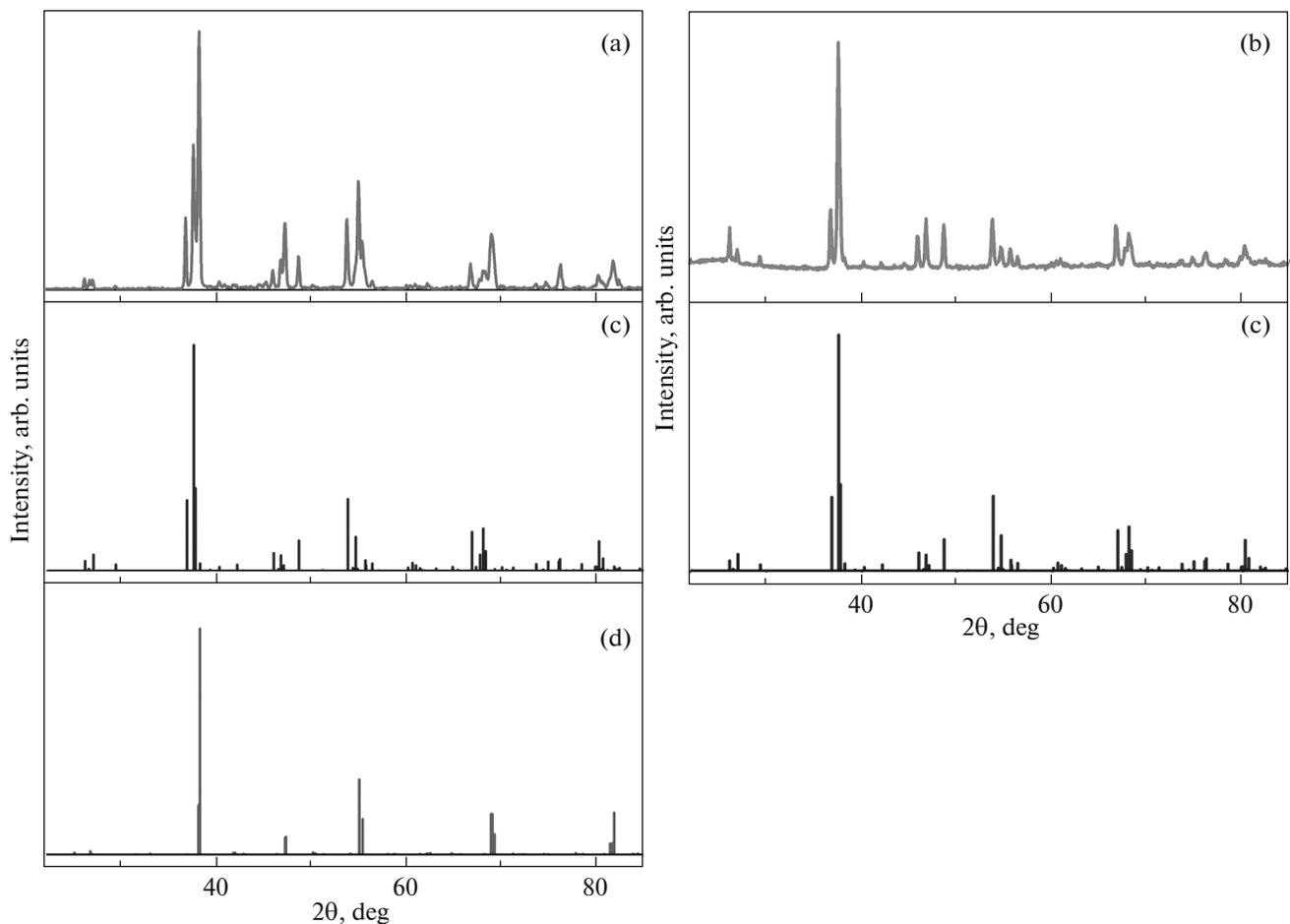


Fig. 1. X-ray diffraction pattern of the $\text{SrFeO}_{3-\delta}$ sample annealed in vacuum at temperatures (a) 450 and (b) 650°C; for comparison, the bar-diagrams are shown: (c) $\text{Sr}_2\text{Fe}_2\text{O}_5$ (Match! no. 96-200-2241) and (d) $\text{Sr}_4\text{Fe}_4\text{O}_{11}$ (Match! no. 96-152-1172).

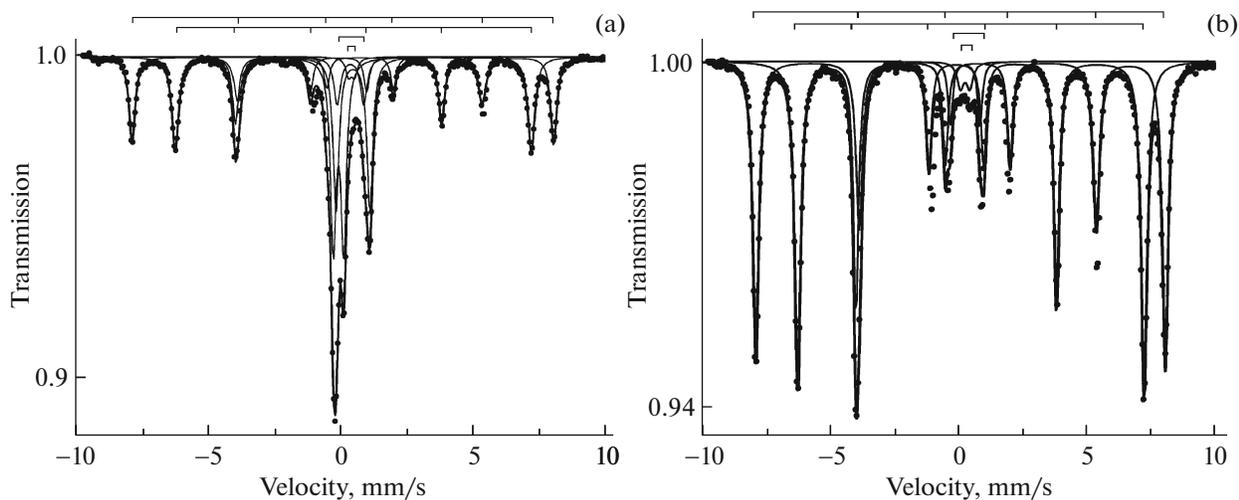


Fig. 2. Mössbauer spectra measured at 300 K for the sample annealed in vacuum at temperatures (a) 450 and (b) 650°C.

and orthorhombic phases is almost the same. After the vacuum annealing at 650°C, two magnetic subspectra corresponding to the brownmillerite phase comprise

94% (Fig. 2b). The paramagnetic part of the spectrum corresponds to the remainder of the $\text{Sr}_4\text{Fe}_4\text{O}_{11}$ phase. Table 1 gives the parameters of the Mössbauer spectra

Table 1. Parameters of the Mössbauer partial spectra at 300 K of the $\text{SrFeO}_{3-\delta}$ annealed in vacuum at 450°C (450AV) and 650°C (650AV)

Annealing	Phase	Partial spectrum	IS, mm/s	Δ , mm/s	H_n , kOe	A, %
450AV	B	Sx-1	0.38(1)	0.66(1)	496(1)	23
		Sx-2	0.17(1)	-0.56(1)	419(1)	26
	Ortho	D-1	-0.09(1)	0.39(1)		24
		D-2	0.42(1)	1.28(1)		27
650AV	B	Sx-1	0.38(1)	0.67(1)	496(1)	44
		Sx-2	0.17(1)	-0.57(1)	420(1)	50
	Ortho	D-1	0.23(5)	0.36(5)		2
		D-2	0.24(5)	1.17(5)		4

*Ortho is the orthorhombic phase, B is the brownmillerite phase; Sx-1 and Sx-2 are sextets, D-1 and D-2 are doublets; IS is the isomer shift (with respect to bcc Fe at 300 K), Δ is the quadrupole splitting, H_n is the effective magnetic field on a ^{57}Fe nucleus for various iron ion positions in the lattice; A is the contribution of a given subspectrum.

for both samples. These results agree well with the available data [4, 5, 8, 22, 23].

As follows from the Mössbauer data [20], in all phases of oxide $\text{SrFeO}_{3-\delta}$, there are in sum three valence states of iron: Fe^{4+} , $\text{Fe}^{3.5+}$, and Fe^{3+} and four oxygen environments: Fe^{4+} ions have two oxygen environments namely, the octahedral ($\text{Fe}^{4+}(\text{O})$) and the pyramidal ($\text{Fe}^{4+}(\text{P})$) and $\text{Fe}^{3.5+}(\text{O})$ and $\text{Fe}^{3+}(\text{O})$ have the octahedral environment. Besides, in the brownmillerite phase, ions Fe^{3+} have two environments: octahedral and tetrahedral. Each structural composition has its own set of valence states of iron with a certain oxygen environment. As the oxygen content is changed or, more correctly, oxygen vacancies appear, iron transfers from one valence state to another oxygen environment, their proportion is changed, the composition is changed, and a part of the valence states disappear, and other states appear. In this case, the noticeable changes in the oxygen content are accompanied by structural transformations. Based on a quite large quadrupole splitting for Fe^{3+} ($\Delta = 1.2\text{--}1.3$ mm/s) in the $\text{Sr}_4\text{Fe}_4\text{O}_{11}$ configuration, we can say that Fe^{3+} is in a distorted octahedral environment. If Fe^{3+} ion were in the pyramidal environment, as assumed in [7, 16], the quadrupole splitting would be much larger (~ 1.8 mm/s) as, for example, for the iron-alloyed superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ [24].

3.3. Model Approach

Before proceeding to the approach proposed above, we consider all valence states of iron and its oxygen environment in the single-phase compositions obtained from the Mössbauer spectroscopy. In the single-phase SrFeO_3 composition (there are no vacancies), there is only one oxygen environment of iron atoms of the only valence: $\text{Fe}^{4+}(\text{O})$; in $\text{Sr}_8\text{Fe}_8\text{O}_{23}$ (one vacancy per 8 cells), there are three oxygen environments (three partial Mössbauer spectra): two for Fe^{4+}

($\text{Fe}^{4+}(\text{O})$ and $\text{Fe}^{4+}(\text{P})$) and $\text{Fe}^{3.5+}(\text{O})$ (Fig. 3a); in $\text{Sr}_4\text{Fe}_4\text{O}_{11}$ (one vacancy per four cells), there are two oxygen environments (two partial spectra): $\text{Fe}^{4+}(\text{P})$ and $\text{Fe}^{3+}(\text{O})$ (Fig. 3b) [20]; in the brownmillerite phase $\text{Sr}_2\text{Fe}_2\text{O}_5$ (one vacancy per two cells), $\text{Fe}^{3+}(\text{O})$ has, as shown above, two local environments (two magnetic partial spectra): octahedral $\text{Fe}^{3+}(\text{O})$ and tetrahedral $\text{Fe}^{3+}(\text{T})$ environments (Fig. 3d). The Mössbauer parameters for structures $\text{SrFeO}_{2.875}$ and $\text{SrFeO}_{2.75}$ are given in [20]. Figures 3b and 3c show that, in addition to the main partial spectra, there are subspectra with very low intensities. The existence of these subspectra is related to the fact that the obtained sample can insignificantly differ from the ideal compositions.

In [20] the studies were performed for the synthesized $\text{SrFeO}_{2.8}$ sample in which there are four main local oxygen environment of iron intrinsic to phases $\text{Sr}_8\text{Fe}_8\text{O}_{23}$ and $\text{Sr}_4\text{Fe}_4\text{O}_{11}$, i.e., $\text{Fe}^{4+}(\text{O})$, $\text{Fe}^{4+}(\text{P})$, $\text{Fe}^{3.5+}(\text{O})$ and one $\text{Fe}^{3+}(\text{O})$ environments (Fig. 3c), which correspond to four partial spectra. The Mössbauer parameters of this sample are given in [20]. According to the available data, the sample with this composition in oxygen is considered to be two-phase. However, the X-ray diffraction studies [20] showed the sample is single-phase. The fact that it is single-phase is confirmed by the data of [9], in which the sample with the same composition in oxygen was synthesized. Based on the proportion of local environments of iron atom in this structure, one more single phase composition $\text{Sr}_{16}\text{Fe}_{16}\text{O}_{45}$ was proposed; in this composition, there are three vacancies for 16 initial perovskite cells. There are no data on the oxygen-vacancy ordering in this composition, and this composition intermediate in oxygen between $\text{Sr}_8\text{Fe}_8\text{O}_{23}$ and $\text{Sr}_4\text{Fe}_4\text{O}_{11}$ can be realized in this structure as a random distribution of additional vacancies. The obtained composition does not fit in the framework of the abovementioned general formula for ideal single-

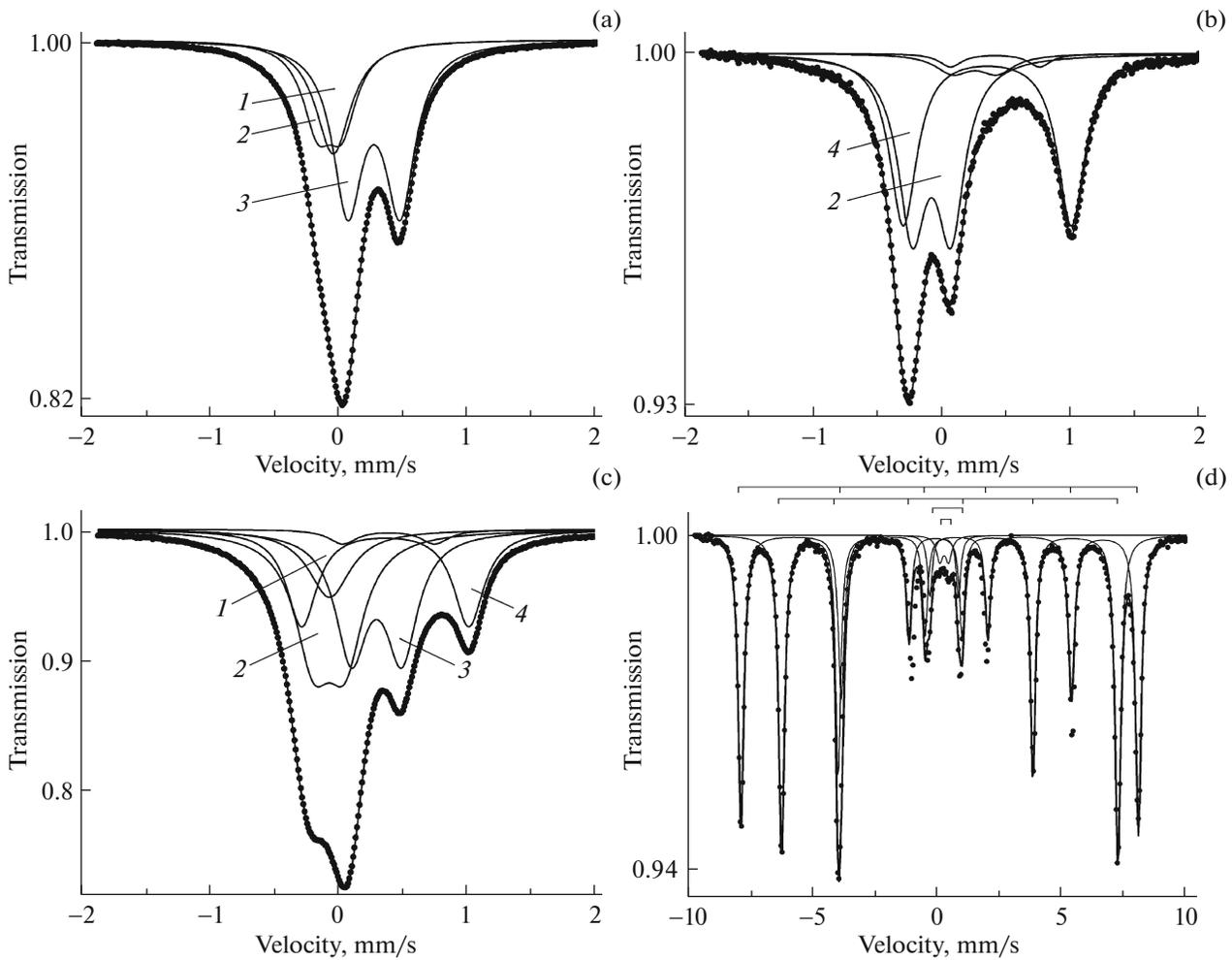


Fig. 3. Mössbauer spectra measured at 300 K for the samples: (a) $\text{SrFeO}_{2.875}$, (b) $\text{SrFeO}_{2.75}$, (c) $\text{SrFeO}_{2.8}$ [15], and (d) brownmillerite $\text{SrFeO}_{2.5}$; 1–4 are numerals of the subspectra.

phase compositions. In addition, according to the available data, there is also a number of two-phase structures with various oxygen contents which also are not described by this formula.

To combine all the available data on the structural states of oxide $\text{SrFeO}_{3-\delta}$, we propose an approach based on the consideration of all possible local oxygen environments of iron atoms with various valences in different structures. This approach makes it possible to trace the manner in which the iron transition occurs from one valence state to another valence state and in which its local environment is changed in this case as the vacancies are added, and also to estimate the compositions in oxygen as the number of the vacancies is changed.

In terms of this approach and based on the Mössbauer data, we choose the configuration with the maximum number of the perovskite cells, in which there is a whole set of the valence states of iron with various oxygen environments and in which all known single-

phase configurations fit. The $\text{Sr}_{16}\text{Fe}_{16}\text{O}_{45}$ configuration consisting of 16 cells obey the above conditions. These 16 cells are chosen as a fixed parameter for all the configurations. We begin to add by one vacancy in this configuration. We consider first all known single-phase structures. According to this scheme, configuration $\text{Sr}_8\text{Fe}_8\text{O}_{23}$ should be doubled, $\text{Sr}_4\text{Fe}_4\text{O}_{11}$ should be increased by four times, and $\text{Sr}_2\text{Fe}_2\text{O}_5$, by eight times. For these configurations, the numbers of the vacancies are 2, 4, and 8 for 16 perovskite cells, respectively. The general formula for the complete set of the oxygen environments in the ideal compositions of strontium ferrite in the dependence on the number of oxygen vacancies can be written as $\text{SrFeO}_{3-k/16}$ (or $\text{Sr}_{16}\text{Fe}_{16}\text{O}_{48-k}$, where k is the number of the vacancies per 16 perovskite cells. Thus, all the single-phase compositions fit in this scheme: $k = 0$ for $\text{Sr}_{16}\text{Fe}_{16}\text{O}_{48}$ (or SrFeO_3), $k = 2$ for $\text{Sr}_{16}\text{Fe}_{16}\text{O}_{46}$ (or $\text{Sr}_8\text{Fe}_8\text{O}_{23}$), $k = 3$ for $\text{Sr}_{16}\text{Fe}_{16}\text{O}_{45}$, $k = 4$ for $\text{Sr}_{16}\text{Fe}_{16}\text{O}_{44}$ (or $\text{Sr}_4\text{Fe}_4\text{O}_{11}$), and $k = 8$ for $\text{Sr}_{16}\text{Fe}_{16}\text{O}_{40}$ (or $\text{Sr}_2\text{Fe}_2\text{O}_5$) (Table 2). Table 2

Table 2. Change in the number of the valence states of Fe in the dependence on the number of vacancies in 16 perovskite cells

1	2	3	4	5	6	7	8
<i>k</i>	SrFeO _{3-k/16}	SrFeO _{3-1/n}	Quantity of Fe valence state				Phase ratio
			Fe ⁴⁺ (O)	Fe ⁴⁺ (P)	Fe ^{3.5+} (O)	Fe ³⁺ (O)	
0	Sr ₁₆ Fe ₁₆ O ₄₈ (SrFeO ₃)	16(SrFeO ₃)	16	0	0	0	Single phase
1	Sr ₁₆ Fe ₁₆ O ₄₇ (SrFeO _{2.94})	mix	10 (2 + 8)	2	4	0	4(C)/1(Tetra)
2	Sr ₁₆ Fe ₁₆ O ₄₆ (SrFeO _{2.875})	2(Sr ₈ Fe ₈ O ₂₃)	4	4	8	0	Single phase
3	Sr ₁₆ Fe ₁₆ O ₄₅ (SrFeO _{2.81})	Sr ₁₆ Fe ₁₆ O ₄₅	2	6	4	4	Single phase
4	Sr ₁₆ Fe ₁₆ O ₄₄ (SrFeO _{2.75})	4(Sr ₄ Fe ₄ O ₁₁)	0	8	0	8	Single phase
5	Sr ₁₆ Fe ₁₆ O ₄₃ (SrFeO _{2.69})	mix	0	6	0	10 (6 + 4)	3(Ortho)/1(B)
6	Sr ₁₆ Fe ₁₆ O ₄₂ (SrFeO _{2.625})	mix	0	4	0	12 (4 + 8)	1(Ortho)/1(B)
7	Sr ₁₆ Fe ₁₆ O ₄₁ (SrFeO _{2.56})	mix	0	2	0	14 (2 + 12)	1(Ortho)/3(B)
8	Sr ₁₆ Fe ₁₆ O ₄₀ (SrFeO _{2.5})	8(Sr ₂ Fe ₂ O ₅)	0	0	0	16 (8Fe ³⁺ (O) + 8Fe ³⁺ (T))	Single phase

Column 1: the number of vacancies *k* per 16 perovskite cells; column 2: the new formula for configurations (*k* vacancies per 16 cells); column 3: the old formula for the single-phase configurations (one vacancy per *n* cells); column 4: the number of Fe⁴⁺(O) in a configuration; column 5: the number of Fe⁴⁺(P) in a configuration; column 6: the number of Fe^{3.5+}(O) in a configuration; column 7: the number of Fe³⁺(O) in a configuration; column 8: the proportion of phases in the mixture of two phases; O is octahedral oxygen environment, P is pyramidal oxygen environment, T is tetrahedral environment, C is cubic phase, Tetra is tetragonal phase, Rh is orthorhombic phase, and B is brownmillerite phase.

lists all possible valence states of iron with different oxygen environments and shows the change in their number in the dependence on the number of the vacancies in 16 perovskite cells. The general formula from the literature fits well into the scheme proposed in this work.

The main advantage of this approach is the fact that we obtain the set of valence states of iron with the corresponding local oxygen environment and their fraction proportion for each ideal single-phase configuration, based on the Mössbauer data.

Based on the proposed scheme and the Mössbauer data on the iron valence states with different local environments, we can describe, for the single-phase compositions, the number of all possible iron valence states with the corresponding local oxygen environments for different numbers of the vacancies and to trace the manner in which the transition from one structure to another takes place (Table 2). So, based on the relation of the contributions of the partial

Mössbauer spectra of various local environments of Fe atoms, the relation of the three local environments of Fe atoms (Fig. 3a) for configuration Sr₈Fe₈O₂₃ (in the new scheme, Sr₁₆Fe₁₆O₄₆ (*k* = 2)) is 4Fe⁴⁺(O), 4Fe⁴⁺(P), and 8Fe^{3.5+}(O). For configuration Sr₄Fe₄O₁₁ (in the new formula, Sr₁₆Fe₁₆O₄₄ (*k* = 4)), the relation of two local environments of iron atoms (Fig. 3b) is 8Fe⁴⁺(P) and 8Fe³⁺(O). For configuration Sr₁₆Fe₁₆O₄₅ (*k* = 3)), the relation of four local environments of iron atoms (Fig. 3c) is 6Fe⁴⁺(O), 2Fe⁴⁺(P), 4Fe^{3.5+}(O), and 4Fe³⁺(O). For configuration Sr₂Fe₂O₅ (in the new formula, Sr₁₆Fe₁₆O₄₀ (*k* = 8)), the relation of the local environments of iron atoms in a magnetic state (Fig. 3d) is 8Fe³⁺(O) and 8Fe³⁺(T).

In parallel with the single-phase samples, the series of known two-phase samples [4, 9, 11, 14, 17–19] agrees well in the oxygen composition in the proposed scheme for *k* = 1, 5, 6, and 7.

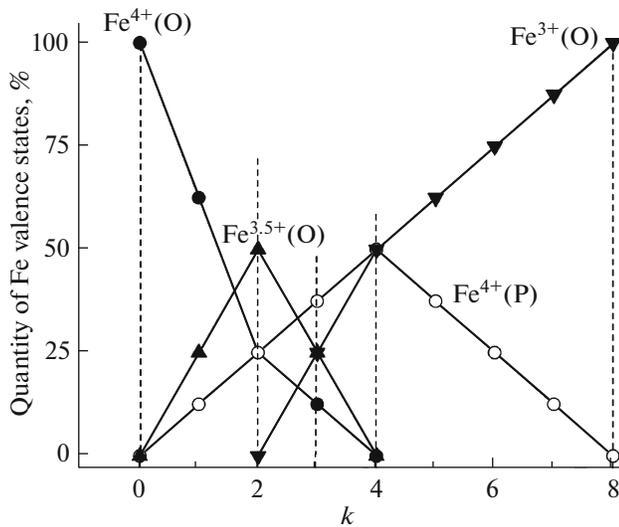


Fig. 4. Quantity of the Fe valence states as a function of the quantity of vacancies per 16 perovskite cells. The vertical dashed lines indicate the Fe valence states in the ideal single-phase configurations with $k = 0, 2, 3, 4,$ and 8 .

Using the data on the local environments of iron atoms in the single-phase samples ($k = 0, 2, 3, 4,$ and 8), we can build the pattern of the local environments for the remainders $k = 1, 5, 6,$ and 7 . The sequence of the transitions of iron ions from one valence state to another state can be built completely and the relation of the local environments for the two-phase samples can be estimated depending on the number of the vacancies in the configurations consisting of 16 perovskite cells (Table 2). Then, according to the proposed scheme, at $k = 1$ (the mixture of the cubic and tetragonal phases [4, 11, 17], Fe^{4+} must decay into three valence states of iron with the relation of the local environments indicated in Table 2. The oxygen composition of this configuration ($\text{SrFeO}_{2.94}$) estimated from the Mössbauer data agrees well with the experimental data [4, 11, 17]. Similar situation takes place for $k = 5, 6,$ and 7 , where there is a mixture of the orthorhombic and brownmillerite phases (Table 2). The estimated oxygen composition will be $\text{SrFeO}_{2.69}$ for $k = 5$, $\text{SrFeO}_{2.625}$ for $k = 6$, and $\text{SrFeO}_{2.56}$ for $k = 7$, which agree well with the experimental data for $\text{SrFeO}_{2.69}$ [4, 17], $\text{SrFeO}_{2.60}$ [18], and $\text{SrFeO}_{2.57}$ [4].

Using the scheme proposed above and the Mössbauer data on the local environments, we determine the relation of the phases in the two-phase structures (Table 2). According to the available data [4, 11, 17], we have a mixture of the cubic and tetragonal phases at $k = 1$. The tetragonal phase with configuration $\text{Sr}_8\text{Fe}_8\text{O}_{23}$ has eight Fe ions ($2\text{Fe}^{4+}(\text{O})$, $2\text{Fe}^{4+}(\text{P})$, and $4\text{Fe}^{3.5+}(\text{O})$). According to the proposed scheme (Table 2), the total number of $\text{Fe}^{4+}(\text{O})$ for $k = 1$ is 10. Then the remainder eight $\text{Fe}^{4+}(\text{O})$ ions belong to the

cubic phase SrFeO_3 , and the proportion of the phases at $k = 1$ is 4/1.

For $k = 5, 6,$ and 7 , we have a mixture of the orthorhombic and brownmillerite (brm) phases. The rhombic phase with configuration $\text{Sr}_4\text{Fe}_4\text{O}_{11}$ contain 4Fe ions ($2\text{Fe}^{4+}(\text{P})$ and $2\text{Fe}^{3+}(\text{O})$); then, according to the scheme, at $k = 5$, the configuration and, correspondingly, the number of Fe ions increases by a factor of three. The total number of $\text{Fe}^{3+}(\text{O})$ for $k = 5$ in this scheme is 10. Four $\text{Fe}^{3+}(\text{O})$ ions remain for the brownmillerite phase. The brownmillerite phase with configuration $\text{Sr}_2\text{Fe}_2\text{O}_5$ has two Fe^{3+} ion (with the octahedral ($\text{Fe}^{3+}(\text{O})$) and tetragonal ($\text{Fe}^{3+}(\text{T})$) oxygen environments). As a result, the ratio of the phases at $k = 5$ is 3/1. For $k = 6$, configuration $\text{Sr}_4\text{Fe}_4\text{O}_{11}$ and, correspondingly, the number of Fe ions is doubled. From 12 common Fe^{3+} ions, eight ions remain for the brownmillerite phase, and the ratio of the phases is 1/1. Above we presented the results of the studies of a mixture of the brownmillerite and orthorhombic phases performed in this work. The proportion of the phases estimated from the experimental data fit well in the proposed scheme for $k = 6$. For $k = 7$, from 14 Fe^{3+} ions, 12 ions remain for the brownmillerite phase, and the ratio of the phases is 1/3 (Table 2). For clarity, the data of Table 2 are shown in the graphical form in Fig. 4. Here, the discrete structural compositions shown in Table 2 calculated with a step in one vacancy ($k = 1$) are the reference points in the quantitative dependences for the oxygen environments. Using the plots, we can estimate the composition proportions also for intermediate cases.

Thus, we obtain the unique pattern of the sequential transitions of iron from one valence state to another state when adding vacancies and all possible oxygen environments of iron independent of the number the phases obtained from the Mössbauer spectroscopy data. Certain sets of the valence states of iron with a certain local oxygen environment correspond to each structural state (single-phase or two-phase). Knowing the proportion of the valence states of Fe for single-phase ideal configurations, we can estimate the proportion of the phases for the two-phase compositions (Table 2).

4. CONCLUSIONS

The structural studies of the brownmillerite phase have been performed for the samples annealed in vacuum at various temperatures. It is found that all possible valence states of iron in the oxygen-deficient oxide $\text{SrFeO}_{3-\delta}$ (the single- and two-phase systems) are unambiguously determined by their oxygen-vacancy environments.

We built the sequence of the transitions of Fe from one valence state to another one when adding the vacancies.

The scheme that we propose is a more total case for the description of all known $\text{SrFeO}_{3-\delta}$ compounds, and the formula for the single-phase structures considered in the literature fit well in this scheme. The available data on the single- and two-phase compositions fit well in this scheme.

Using this scheme for the ideal compositions, we can estimate the proportion of the valence states of iron and the proportion of the phases in the experimentally prepared the two- and single-phase systems with different oxygen contents and different phase compositions.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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