ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 6, pp. 973–978. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © I.A. Zvereva, I.V. Otrepina, V.G. Semenov, E.A. Tugova, V.F. Popova, V.V. Gusarov, 2007, published in Zhurnal Obshchei Khimii, 2007, Vol. 77, No. 6, pp. 881–886.

Mechanism of Formation of the Complex Oxide $Gd_2SrFe_2O_7$

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Received October 26, 2006

Abstract — The mechanism of formation of the perovskite-like layered structure of the oxide $Gd_2SrFe_2O_7$ was studied. The limiting stages are those of formation of phases with perovskite ($GdFeO_3$, $SrFeO_{3-x}$) and K_2NiF_4 ($GdSrFeO_4$) structures. The Mössbauer study has shown that iron atoms exist in a heterovalent state (Fe^{3+} and Fe^{4+}) only in the structure of $SrFeO_{3-x}$.

DOI: 10.1134/S1070363207060011

One of priority fields of the modern chemistry is synthesis and study of inorganic compounds that can form a basis for ceramic materials prepared by solid-phase reactions. Prospects for applications of ceramic materials are extremely wide owing to multifunctionality of their physical and chemical properties and to mechanical and thermal stability.

The choice of the most suitable method and conditions for the synthesis of solid-phase compounds is largely determined by the chemical composition and required properties of the formed substance. Polycrystalline powder materials are most often synthesized by the direct reaction of a mixture of the starting solid reactants, occurring at an appreciable rate only on heating to 1000–1500°C [1, 2]. This fact suggests that the course of solid-phase reactions is equally determined by both thermodynamic and kinetic factors. A calculation of the Gibbs energy of a solid-phase reaction allows us to evaluate whether the reaction is principally possible, whereas the kinetic factor determines its rate. The first step in the development of processes for synthesizing new and poorly studied compounds, whose thermodynamic characteristics are unknown, is the experimental determination of the mechanism of solid-phase reactions and the rate of intermediate stages. That is why studying the mechanism of formation of a complex compound is of not only fundamental but also applied importance.

Materials based on layered compounds, in particular, layered perovskite-like oxides constructed by a block principle from simpler fragments, form a promising type of ceramic materials. These oxides have a number of unique electrophysical properties. Processes of their formation are still poorly studied, although the data on the mechanism and kinetics of formation of layered compounds are necessary for the development of optimal methods of their synthesis and make it possible to answer certain questions concerning the determination of their chemical and thermal stability.

The mechanism of formation of aluminates $Ln_2SrAl_2O_7$ in which all the elements are in stable oxidation states [3–5] is the best studied. The mechanisms of formation of iron-containing layered oxides remain poorly understood, although "ferrite ceramics" based on structurally simpler compounds is used in memory chips of computer equipment, as catalysts in chemical industry, and also in power engineering and electronics. To develop effective technology of ferrite products with the required magnetic and other characteristics, it is necessary to provide not only the preset crystal-chemical characteristics (structure and distribution of cations over various structural positions), but also stability of the valence state of iron atoms.

In this study we examined the mechanism of formation of the complex oxide $Gd_2SrFe_2O_7$ by a ceramic technology at atmospheric pressure. The sequence of phase transformations was studied by performing isothermal annealing–quenching runs followed by X-ray phase analysis. The oxidation states of iron atoms in intermediate products and in the synthesized complex oxide $Gd_2SrFe_2O_7$ were determined by Mössbauer spectroscopy. The method also allowed us to obtain information on the nearest surrounding of iron atoms

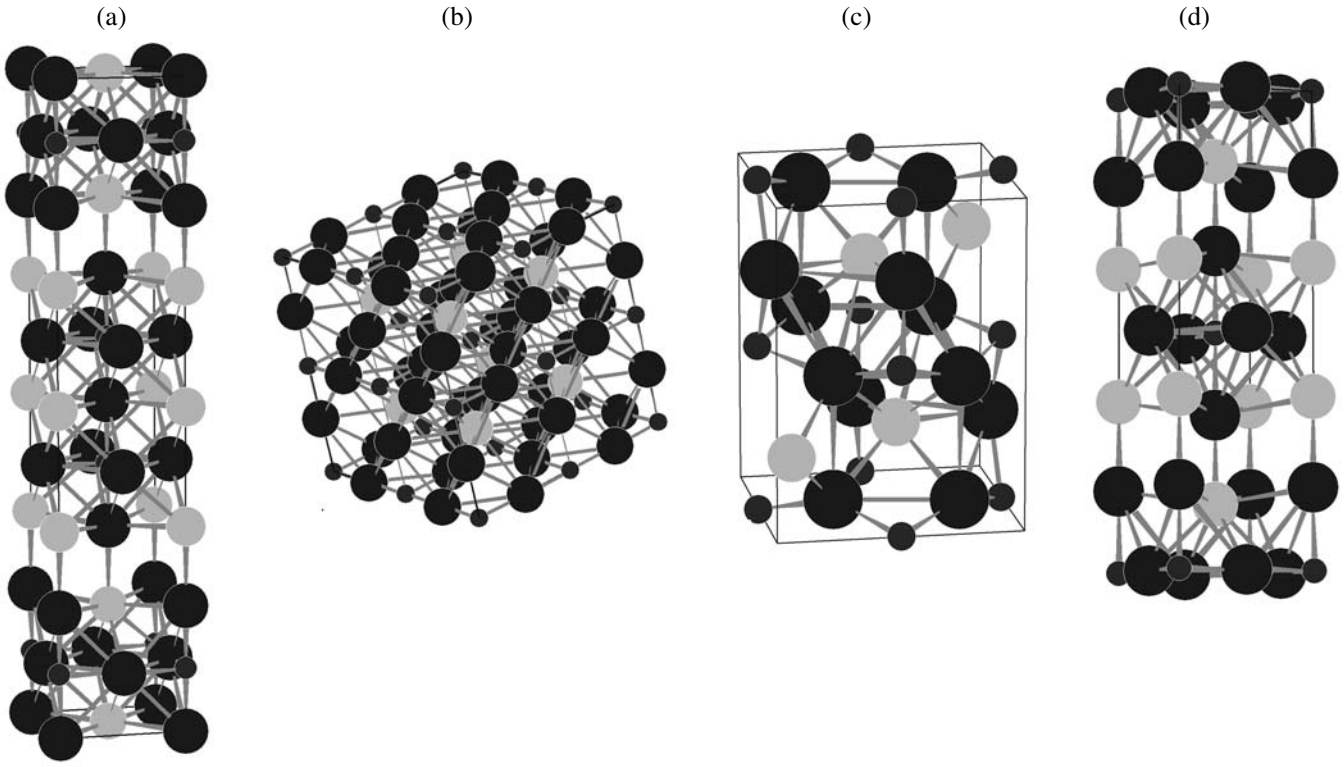

Fig. 1. Unit cell of complex oxides obtained in the course of ceramic synthesis: (a) $GdFeO_3$, (b) $SrFeO_{3-x}$, (c) $GdSrFeO_4$, and (d) $Gd_2SrFe_2O_7$.

in the crystal structure of the compounds involved in studying the mechanism of the solid-phase reaction.

According to the published data [6], the oxide $Gd_2SrFe_2O_7$ crystallizes in the $Sr_3Ti_2O_7$ structural type and belongs to Ruddlesden–Popper phases [7, 8]. These phases have the general formula $A_{n+1}B_nO_{3n+1}$ (n = 1, 2, 3) and are constructed by a block principle from interpenetrating structural fragments of perovskite (P) ABO_3 and rock salt (RS) AO [for the $Sr_3Ti_2O_7$ structural type, with the sequence ...(P)(P)(RS)(P)(P)(RS)...]. In the $Sr_3Ti_2O_7$ structure, strontium atoms occupy two nonequivalent crystallographic positions, being in 9- or 12-coordinate surrounding. Titanium atoms are arranged in the oxygen TiO_6 octahedra forming layers perpendicular to the axis of the structure (Fig. 1a). In the complex oxide $Gd_2SrFe_2O_7$, the AO_9 and AO_{12} polyhedra are populated by gadolinium and strontium atoms, whereas iron atoms are in the centers of FeO_6 octahedra.

The oxide $Gd_2SrFe_2O_7$ is isostructural to well-studied aluminates $Ln_2SrAl_2O_7$ (Ln = La–Ho) [9]; however, the possible existence of iron atoms in different valence states can give rise to certain specific features of the formation mechanism of the oxides $Ln_2SrFe_2O_7$.

The phase composition of samples after heat treatment of the starting mixture corresponding in its chemical composition to the stoichiometry of $Gd_2Sr \cdot Fe_2O_7$ is presented in Table 1, which shows that, after heat treatment for 3 h at 1200, 1300, and 1400°C, the mixture exhibits reflections of the compounds Gd_2O_3, $GdFeO_3$, $SrFeO_{3-x}$, and $Gd_2SrFe_2O_7$.

The mechanism of formation of the complex oxide $Gd_2SrFe_2O_7$ is not similar to that of the aluminate $Gd_2SrAl_2O_7$. The complex aluminate $Gd_2SrAl_2O_7$ is formed by the reaction of an intermediate compound of the spinel structure with gadolinium oxide:

$$SrAl_2O_4 + Gd_2O_3 \longrightarrow Gd_2SrAl_2O_7, \quad (1)$$

A specific feature of the formation reaction of the structurally related ferrite is the fact that, unlike the formation of aluminate (1), compounds of the perovskite structure [$GdFeO_3$ and $SrFeO_3$ (Figs. 1b, 1c)] are detected in the reaction mixture, whereas compounds of the layered structure of the K_2NiF_4 type are absent.

$$Gd_2O_3 + SrCO_3 + Fe_2O_3 \longrightarrow Gd_2SrFe_2O_7 + CO_2. \quad (2)$$

Table 1. Phase composition of samples after heat treatment of the starting mixture with the chemical composition corresponding to the stoichiometry of $Gd_2SrFe_2O_7$

Heat treatment mode		Phase composition of reaction mixture
T, °C	Time, h	
1200	3–10	Gd_2O_3, $GdFeO_3$, $SrFeO_3$, $Gd_2SrFe_2O_7$ (traces)
1300	3–5	$Gd_2SrFe_2O_7$, Gd_2O_3, $GdFeO_3$, $SrFeO_3$
1400	3	$Gd_2SrFe_2O_7$, Gd_2O_3, $GdFeO_3$, $SrFeO_3$
	5	$Gd_2SrFe_2O_7$
1500	3	$Gd_2SrFe_2O_7$

Table 2. Unit cell parameters of oxides $Gd_2SrFe_2O_7$, $SrFeO_{3-x}$, $GdFeO_3$, and $GdSrFeO_4$

Compound	Unit cell parameters, Å		Space group
	experiment	published data	
$Gd_2SrFe_2O_7$	a 3.8953 c 19.736	a 3.8953 c 19.736 [6]	$I4mmm$
$GdFeO_3$	a 5.614 b 7.667 c 5.345	a 5.616 b 7.669 c 5.349 [10]	$Pbnm$
$GdSrFeO_4$	a 3.8439 c 12.439	–	$I4mmm$
$SrFeO_{3-x}$	a 7.966	a 7.951–7.963 (1148–1223 K) [14]	$Fm3c$
		a 5.6727 b 15.582 c 5.5303 [15]	$Icmm$

The composition of the reaction mixture and the structural characteristics of intermediate compounds indicate that reaction (2) is a complex multistep process, as well as the majority of solid-phase reactions [1], and allow us to suggest the following mechanism [steps (3)–(6)] for the solid-phase synthesis of the complex oxide $Gd_2SrFe_2O_7$:

$$Gd_2O_3 + Fe_2O_3 \longrightarrow 2GdFeO_3, \quad (3)$$

$$2SrCO_3 + (1 - 2x)O_2 + Fe_2O_3 \longrightarrow 2SrFeO_{3-x} + 2CO_2, \quad (4)$$

$$Gd_2O_3 + 2SrFeO_{3-x} \quad 2GdSrFeO_4 + (1 - 2x)O_2, \quad (5)$$

$$GdFeO_3 + GdSrFeO_4 \longrightarrow Gd_2SrFe_2O_7. \quad (6)$$

The fact that the compound $GdSrFeO_4$ virtually is not detected in the reaction mixture by X-ray diffraction can be accounted for by a high rate of its reaction (6) with $GdFeO_3$.

The principal possibility of the realization of the suggested mechanism was proved by performing reactions (3)–(6) in succession. For this purpose we prepared four individual compounds, including $Gd_2SrFe_2O_7$, by reactions (3)–(6), which were carried out under conditions identical to the conditions of reaction (2). Thus, the complex oxide $Gd_2SrFe_2O_7$ was synthesized from $GdSrFeO_4$ and $GdFeO_3$ at 1400°C within 10 h. The reaction occurs also at 1300°C, but somewhat more slowly.

The unit cell parameters of the synthesized oxides are given in Table 2. The parameters of the oxides $GdFeO_3$ and $Gd_2SrFe_2O_7$ agree well with the published data [6, 10]. Data for $GdSrFeO_4$ are lacking, and its reflections were indicated in the $I4mmm$ space group by analogy with the oxide $NdSrFeO_4$ (Fig. 1d) [11]. The lack of data on $GdSrFeO_4$ is caused by its instability and by complexity of its direct synthesis from iron and gadolinium oxides and strontium carbonate, whereas oxides of the lightest lanthanides (La and Nd) can be prepared by reaction (7) [11, 12].

$$Ln_2O_3 + Fe_2O_3 + 2SrCO_3 \longrightarrow 2LnSrFeO_4 + 2CO_2. \quad (7)$$

It is important that the gadolinium-containing oxide is the last representative of the series of isostructural aluminates $LnSrAlO_4$ (Ln = La–Gd) [13].

The structure of the compound $SrFeO_{3-x}$, as well as the valence state of iron atoms in the system Fe_2O_3–SrO, were comprehensively studied [14–18]. If more complicated Ruddlesden–Popper phases $Sr_{n+1}Fe_n \cdot O_{3n+1}$ (n = 1, 2, 3) and compounds with ordered oxygen vacancies $Sr_nFe_nO_{3n+1}$ (n = 2, 4, 8) are excluded from consideration and only the perovskite structure (n = 1) is taken into account, then, as follows from the extensive review [19], oxygen-deficient phases $SrFeO_{3-x}$ consist of alternating layers of FeO_6 octahedra and FeO_5 pyramids. The structure of the compounds $SrFeO_{3-x}$ changes from cubic perovskite (x 0) through tetragonal (x 0.125) and orthorhombic perovskite (x 0.25) to orthorhombic brownmillerite (x 0.5), which is already presented by the formula $Sr_2Fe_2O_5$. The structure and composition of compounds $SrFeO_{3-x}$ depend on both the temperature and partial oxygen pressure [20].

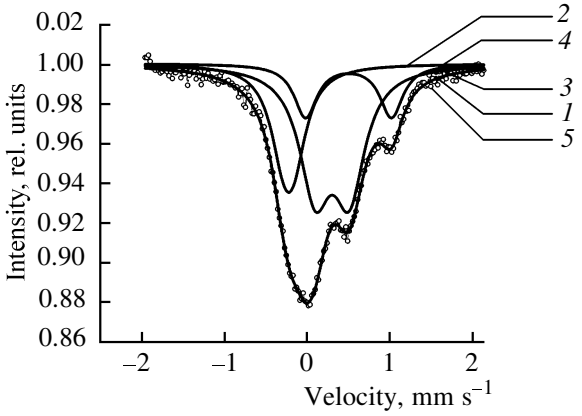

Fig. 2. Mössbauer spectrum of the compound $SrFeO_{3-x}$: (*1*) calculation, (*2*) Fe^{4+}, (*3, 4*) Fe^{3+}, and (*5*) experiment.

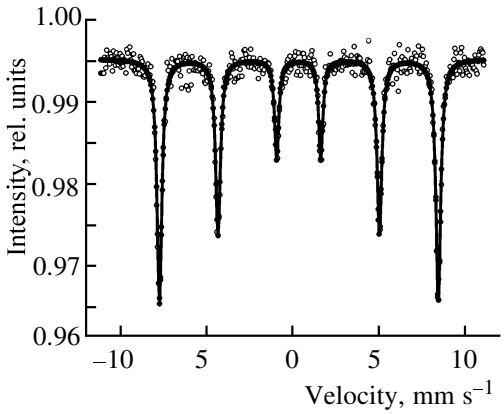

Fig. 3. Mössbauer spectrum of $Gd_2SrFe_2O_7$.

Just for this reason we set a problem of determining the oxidation state of iron in the compound $SrFeO_{3-x}$ obtained under the conditions as similar as possible to the conditions of reaction (2). The only difference was that the reaction mixture contained no gadolinium oxide. Our confidence that the iron oxidation state does not change in samples that were quenched and then studied at room temperature is based on the results of a comparative study of the Mössbauer spectra of quenched and unquenched $SrFeO_{3-x}$ samples and solid solutions based on them [21].

A systematic study of the compound $SrFeO_{3-x}$ by Mössbauer spectroscopy showed that Fe^{3+} coexists in this compound with Fe^{4+}. The total spectrum and its resolution into components are shown in Fig. 2. It is seen that, along with the single line corresponding to Fe^{4+} atoms, there are two doublets characteristic for Fe^{3+} atoms in two fields of different symmetry. The Fe^{4+} ions whose octahedral surrounding should be additionally distorted by the Jahn–Teller effect are nevertheless in a more symmetric environment than the Fe^{3+} atoms. A decrease in the symmetry of the surrounding of Fe^{3+} atoms is attributable to the presence of oxygen vacancies. The parameters of the components of the $SrFeO_{3-x}$ Mössbauer spectrum are given in Table 3. Table 3 also shows that in other complex oxides, as well as in the reaction product $Gd_2SrFe_2O_7$, iron atoms are only in the Fe^{3+} state, which is magnetically ordered, as shown by the characteristic fine structure in the spectra of these compounds (Fig. 3).

Table 3. Parameters of Mössbauer spectra of $SrFeO_{3-x}$, $GdFeO_3$, $GdSrFeO_4$, and $Gd_2SrFe_2O_7$

Oxide	Ion Fe	Chemical shift, mm s^{-1}	Quadrupole splitting mm s^{-1}	Content, %
$SrFeO_{3-x}$	Fe^{+4}	–0.235	0.123	27.3
	Fe^{+3}	0.291	0.414	54.8
	Fe^{+3}	0.488	1.038	17.9
$GdFeO_3$	Fe^{+3}	0.358	–0.007	100
$GdSrFeO_4$	Fe^{+3}			100
$Gd_2SrFe_2O_7$	Fe^{+3}	0.343	0.430	100

The ratio of iron atoms in different oxidation states can be used for estimating x, although accurate chemical determination of the strontium and iron content is necessary to find its more precise value, in view of the fact that nonstoichiometric compounds $Sr_{1+x}FeO_{3-\delta}$ are known [16]. Even at 5% error of strontium determination, the index at the oxygen atom can be estimated to within 0.05. Therefore, the 27 : 73 ratio of Fe^{4+} and Fe^{3+} atoms suggests the composition of the compound under study $SrFeO_{2.64\pm0.05}$. This composition is close to that of the compound $SrFeO_{2.5}$ or $Sr_2Fe_2O_5$, whose structure attracts much researchers' attention. The most detailed neutron diffraction study of its structure at high temperatures [14] showed that, at temperatures exceeding 1223 K, the cubic form crystallizes, in which layers with Fe^{3+} atoms in the centers of octahedra and tetrahedra alternate. Therefore, Fe^{3+} atoms in fields of different symmetry are detected in the spectrum of strontium ferrite prepared in air at 1300°C and quenched.

Thus, our structural and Mössbauer study of the formation of perovskite-like layered oxide $Gd_2SrFe_2O_7$ revealed an essential difference in the mechanisms of

formation of aluminates and ferrites. The limiting stages of the formation of the oxide $Gd_2SrFe_2O_7$ are the formation of phases with the perovskite structure ($GdFeO_3$ and $SrFeO_{3-x}$). The possibility of the existence of iron atoms in different oxidation states gives rise to certain specific features of the intermediate compounds, resulting in the fact that Fe^{3+} and Fe^{4+} atoms are present in the structure of $SrFeO_{3-x}$ synthesized in air. The successful synthesis in air shows that it is not necessary to increase appreciably the oxygen pressure as it was described in [6], because it will lead only to an increase in the Fe^{4+} content. However, it is a subject of a special study. It should be noted that understanding of the mechanism of the $Gd_2SrFe_2O_7$ synthesis allowed us to synthesize the previously unkwown oxide $GdSrFeO_4$ whose instability (or high reactivity) complicates its detection as an intermediate product.

The study has shown that the layered perovskite-like structure of the oxide $Gd_2SrFe_2O_7$ is formed via perovskite-like phases of simpler structural types; their instability at the temperatures of the synthesis determines the features of the mechanism and its limiting steps, thus opening opportunities to control the course of the multiphase solid-phase process.

EXPERIMENTAL

The mechanism of formation of the oxide $Gd_2Sr \cdot Fe_2O_7$ was studied by performing isothermal annealing–quenching runs in the temperature range 1200–1500°C, followed by determination of the qualitative composition of the reaction mixture.

$Gd_2SrFe_2O_7$ was prepared by a solid-phase reaction between the components [1] in air at atmospheric pressure. As the starting reagents we used ultrapure 7–2 grade strontium carbonate [TU (Technical Specification) 6-09-01-659-91], Gd_2O_3 (SST grade, main substance content 99.99%, calcined at 900°C for 4 h before use), and Fe_2O_3 (analytically pure grade, dried at 300°C for 2 h). The charge prepared from the starting components in the stoichiometric ratio was pressed in 0.5-g pellets 0.7 cm in diameter. The samples were sintered in a Silit furnace whose temperature was controlled with a platinum–rhodium thermocouple. The isothermal mode of the heat treatment was ensured with the accuracy of ±1°C using a TP 403 programmed temperature regulator.

To prepare intermediate compounds revealed in the course of the study and to perform the intermediate reactions involving them, we also used the method of solid-phase reactions. The oxide $GdFeO_3$ was prepared by sintering at 1300°C for 15 h with the subsequent quenching in air. The complex oxide $GdSrFeO_4$ was synthesized from the preliminarily prepared $SrFeO_{3-x}$ by sintering at 1300°C for 48 h.

The phase composition and the sequence of phase changes were monitored by the X-ray method using a DRON-3 diffractometer (FeK_α and CuK_α radiation).

The Mössbauer spectra were taken at room temperature using the ^{57}Co isotope in a Rh matrix as a source. The isomer shifts were measured relative to α-Fe. When estimating fractions of various paramagnetic centers, the intensity of signals was determined to within the factor of resonant absorption.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 04-03-32 176).

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