

The Physical Model of Formation of Hexagonal Ferrites BaFe₁₂O₁₉

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To identify the features of structural transformations occurring during the formation of the crystal lattice of hexagonal barium ferrite were studied the following issues: a) component defined that are structural element in the reaction of solid-phase synthesis of ferrites BaFe₁₂O₁₉; b) the phase composition set of the reaction products formed in mixtures of BaCO₃ – α-Fe₂O₃; c) a crystal-chemical model developed allows visually describe the transformation of α-Fe₂O₃ – BaFe₁₂O₁₉.

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1. INTRODUCTION

The obtaining submicron particulate materials with a specific particle shape is a rather difficult task, because of practical application of the powders are generally multi-component with a specific composition. Therefore the synthesis often lead to multiphase the final product because of the incompleteness of diffusion processes occurring at low temperatures range. Increasing the temperature of synthesis inevitably leads to an increase in particle size. The second important point the synthesis of multicomponent powders is the need to preserve the various stages of the process a high degree of homogeneity of the distribution of the starting components.

Analyzing the reasons that, despite there being quite unique synthesis methods hexaferrites, the lower limit of the size of the particles is still high, we come to the assumption that their education requires a fairly high temperature. It is connected to the fact that the crystal structure hexaferrites relating to the space group P6₃/mmc, is quite complex. Their unit cell consists of blocks R, S, R*, S* (* - denotes the rotation by 180° around the axis c). The blocks S have a spinel structure with the general formula for barium hexaferrite [Fe₆O₈]²⁺, blocks R correspond to the general formula [BaFe₆O₁₁]²⁻. Fe³⁺ cations occupy in this structure, five non-equivalent magnetic states. For the formation of such a structure in the synthesis must be substantial redistribution by diffusion of ions, which can be realized only at high temperatures.

The aim of this study was to determine the characteristics of structural transformations taking place in the formation of the crystal lattice of the hexagonal barium ferrite.

2. EXPERIMENTAL RESEARCH METHODOLOGY

Hexaferrite powders prepared by mixing barium carbonate BaCO₃ GOST 2149-75 «analytical grade» with iron oxide Fe₂O₃ TU6-09-4783-83 «MM-1» in conical mixer. The resulting mixture was milled in a vibrating mill M-200 for 2 hours and then calcined in an oven with a rotating tube «Hyperbola» at 930-950 °C. Syn-

thesized batch milled at attritor «Bekas» with the addition of water and surfactants.

The mass spectrometric studies of the gas phase above the mixture of α-Fe₂O₃-BaCO₃ during their solid-state interaction for elucidate the mechanism of formation of gratings BaFe₁₂O₁₉ were performed.

Ferritization performed in ampoules made of stainless steel, which through dosing valves connected to a mass spectrometer MI-12-1.

Investigations of the kinetics formation BaFe₁₂O₁₉ was performed by Mossbauer spectroscopy it allows up to 2 % judged on the content of hexaferrite mixture. The phase composition of the mixtures was determined after isothermal hold at different temperatures (1100-1550 K) and subsequent quenching in an aqueous solution of NaCl. Holding temperature it has been selected by a differential thermal analysis.

3. RESULTS AND DISCUSSION

Fig. 1 shows the mass spectra of the gas phase above the mix BaCO₃ – αFe₂O₃ after isothermal exposure for 10 and 20 minutes at a temperature of 1100 K.

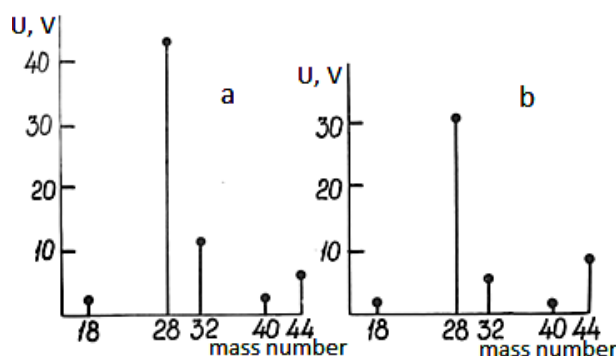


Fig. 1 – The mass spectra of the gas phase of the mixture of α-Fe₂O₃-BaCO₃ after isothermal aging at 1100 K for: a – 10, b – 20

Comparison of the spectra indicate that by heating the mixture in the gas phase change O₂ content (wt. H. 32) and CO₂ (wt. H. 44). It is connected to the fact that

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in the process the ferritization barium carbonate decomposes according to the scheme $BaCO_3 \rightarrow BaO + CO_2$. Moreover mixture reacts with oxygen in the gas phase content in the gas medium by exposing a mixture of reduced (Fig. 1b).

The amount of generated ferrite $BaFe_{12}O_{19}$ correlated with the mass of decarbonated $BaCO_3$. This suggests that the formation of the lattice $BaFe_{12}O_{19}$ is the result of the interaction of $\alpha-Fe_2O_3$ and BaO with the participation of gas-phase oxygen.

Fig. 2 shows the curves of differential thermal analysis.

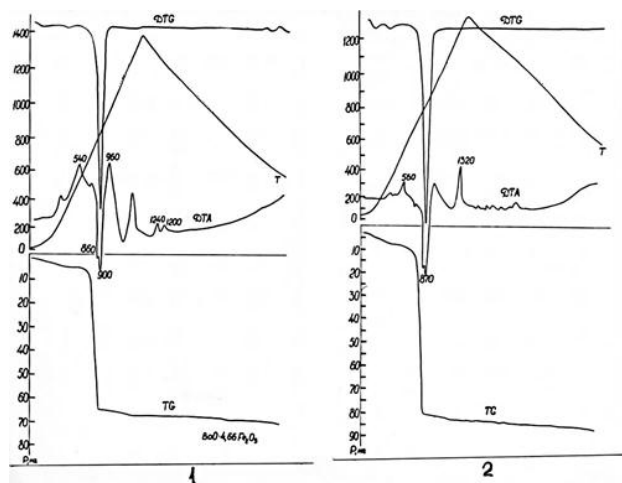


Fig. 2 – The curves of differential thermal analysis of mixtures of $BaCO_3$ and $\alpha-Fe_2O_3$: 1 – (analytical grade); 2 – chemically pure 7.5 heating rate of $^{\circ}C/min$

Behavior of the curves coincides with the literature data. However, the transformation temperatures for mixtures with different histories differ by 10 – 150 $^{\circ}C$. The lowest temperature ferritization were obtained in mixtures containing $\alpha-Fe_2O_3$ analytical grade mark (Fig. 2, 1). Number of hexaferrite mixture after ferritization determined from the relative intensities of the components of the sublattice 12 K. As an example, the Mossbauer spectrum shows after the ferritization mixtures at 1100 K for 2-90 minutes and then quenched in aqueous NaCl (Fig. 3).

Analysis of the series of Mössbauer spectra allowed to establish the following:

- in the spectra of compounds synthesized at 1100 and 1200 K contains components from the nucleus of iron ions located in the 12 k positions ferrite $BaFe_{12}O_{19}$;
- in the initial stages of the synthesis samples at

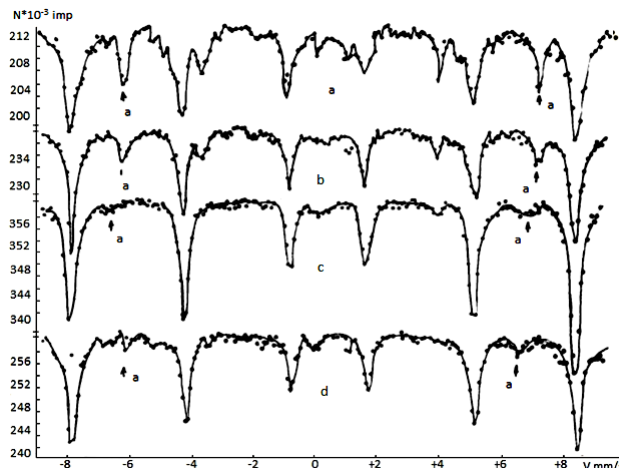


Fig. 3 – The Mossbauer spectra of samples $BaCO_3 + 5,6 Fe_2O_3$ after exposure at 1100 K for (min): 90 (a), 60 (b), 10 (c), 2 (d)

1000, 1100 and 1200 K has been detected component from the external phases rich in barium ions;

- $BaFeO_4$, $BaFeO_3$, $BaFe_2O_5$ absent in mixtures synthesized at $T = 1300 K$ on the basis of $\alpha-Fe_2O_3$ recognized analytical grade mark.

The results obtained in phase composition mixtures synthesized at various temperatures are shown in Table 1.

These findings indicate that the lattice $BaFe_{12}O_{19}$ in the range of 1000-1200 K can not be formed on the basis of BaO. Moreover, it can take place without the formation of the provisions of the intermediates. In support of this assertion evidenced by the following facts:

1. In the spectra of compounds synthesized at 1100 and 1200 K for 2-5 min observed anomalously large values of the quadrupole splitting for the sublattice 12 K $BaFe_{12}O_{19}$ $\Delta = 0,65 mm/s$ instead 0,44 mm/s. This can be attributed to significant distortion of the oxygen octahedral in a lattice $\alpha-Fe_2O_3$ as a result of ion implantation Ba^{2+} and O^{2-} . Mössbauer researches $\alpha-Fe_2O_3$ at a temperature range 800 $^{\circ}C$ indicate high «mobility» structure of $\alpha-Fe_2O_3$.

2. In experiments to study the diffusion of radionuclides Ba^{133} and Fe^{59} [1] in $BaFe_{12}O_{19}$ at 1400 K convincingly shown that self-diffusion coefficient $D_{Ba^{133}} = 7,7.10^{-10} cm^2 \cdot s$ more than this value for Fe^{59} ($D_{Fe^{59}} = 4,1.10^{-11} cm^2 \cdot s$) [2]. Excess more on the order for the ion diffusion coefficient Ba indicates that the structure-forming component is Fe_2O_3 , which diffuse ions Ba^{2+} and O^{2-} [3].

Table 1 – Phase composition $BaCO_3$ mixture and $\alpha-Fe_2O_3$ (analytical grade) of iron after the ferritization at different temperatures (according Mössbauer spectroscopy)

T_s, K	The annealing time, min						Footnote
	2	10	20	30	60	90	
1000	F	F	F	F	F	F	F- $\alpha-Fe_2O_3$
1100	F+BF ₆	F+BF ₆	F+BF ₆	F+BF ₆	F+BF ₆	F+BF ₆ +C	BF ₆ - $BaFe_2O_4$
1300	F+BF ₆	F+BF ₆	F+BF ₆	F+BF ₆	F+BF ₆	F+BF ₆	BF ₆ - $BaFe_{12}O_{19}$
1400	F+BF ₆	F+BF ₆	F+BF ₆	F+BF ₆	F+BF ₆	F+BF ₆	X – unidentified phase
1450	F+BF+BF ₆	F+BF ₆	F+BF ₆	F+BF ₆	F+BF ₆	BF ₆	
1500	BF ₆ +BF+ F	X+ BF ₆	BF ₆	BF ₆	BF ₆	BF ₆ +BF+F	C – Fe_3O_4
1530	BF ₆ +BF+X	BF ₆ +X	BF ₆ +C	BF ₆ +C	BF ₆ +C	BF ₆ +BF+C	

Note that in mixtures containing $\alpha\text{-Fe}_2\text{O}_3$ other marks in the initial stage of isothermal exposure, revealed the emergence BaFe_2O_4 , (Table 1). With increasing temperature, the synthesis mixtures, and other compounds appear richer barium.

For a quantitative description of solid-phase transformations in the system $\alpha\text{-BaO-Fe}_2\text{O}_3$ were obtained a series of kinetic dependences degree ferritization mixtures ($\alpha(\tau)$) (Fig. 4).

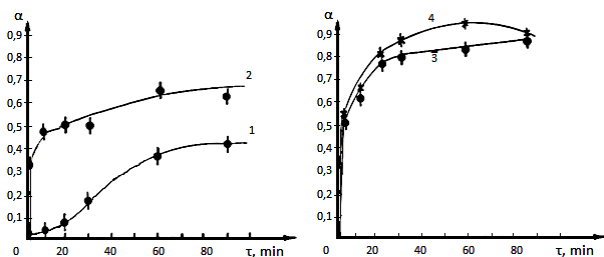


Fig. 4 – Kinetic dependence of the degree ferritization

The analysis shown in Fig. 4 is set dependencies:

1. At 1000-1100 K ferritization speed depends on the size of the crystallites $\alpha\text{-Fe}_2\text{O}_3$ and of its history.

2. In the range of 1000-1100 K ferrite is formed mainly in the surface layers of particles of $\alpha\text{-Fe}_2\text{O}_3$, thickness is 0,9-1,0 mm, which is consistent with literature data.

These curves were obtained by many authors on the basis of differential thermal and X-ray analysis [1, 4].

Consider the possibility of describing the transformations in the series: $\alpha\text{-Fe}_2\text{O}_3 \rightarrow \text{BaFe}_{12}\text{O}_{19} \rightarrow \text{BaFe}_2\text{O}_4 \rightarrow \text{BaFe}_{12}\text{O}_{19}$.

We will pay attention only to the geometry of the crystal lattice $\alpha\text{-Fe}_2\text{O}_3$, $\text{BaFe}_{12}\text{O}_{19}$, BaFe_2O_4 . Also, we use the results of γ -resonance studies of phase composition and structural states oxide mixtures. Based on the parameters of the Mössbauer spectra, we can as-

sume:

1. The advent of the extended component of the sublattice 12 K with high values of the quadrupole splitting in the background sextuplets $\alpha\text{-Fe}_2\text{O}_3$ associated with the formation of oxygen layers with hexagonal packing of anions. This assumption is based on the fact that Fe^{3+} ions in the sublattice 12 k located on the boundary of the hexagonal and spinel blocks in the structure $\text{BaFe}_{12}\text{O}_{19}$.

Therefore, a significant distortion of coordination polyhedra and their non-equivalence of evidence of marked deformation of the oxygen environment of Fe^{3+} ions in the lattice – Fe_2O_3 , which may occur during the deformation of R-block. Note that such distortions are detected when heated Fe_2O_3 , containing a high concentration of defects.

2. The introduction of ions Ba^{2+} , and O^{2-} ions – distortions are stimulated, thereby increasing the covalent component of the chemical bond for Fe^{3+} ions in the sublattice to 12 k, and the emergence of a fivefold coordination ions Fe^{3+} .

The formation of the spindle unit in the lattice of $\alpha\text{-Fe}_2\text{O}_3$ is formed by analogy with the lattice $\gamma\text{-Fe}_2\text{O}_3$ as a result of the collective displacement of Fe^{3+} ions and O^{2-} from its original position and displacement of the oxygen ions in the Ba layer. The proposed mechanism can be easily illustrated by considering sandwiched $\text{BaFe}_{12}\text{O}_{19}$ and structure of the layers (Fig. 5a and b). In this case, a distribution layers of iron ions in the lattice $\text{BaFe}_{12}\text{O}_{19}$ resembles the distribution of ions of iron and oxygen in the lattice of $\alpha\text{-Fe}_2\text{O}_3$ (Fig. 6).

It is evident that without the displacement of ions, lattice $\text{BaFe}_{12}\text{O}_{19}$ and $\alpha\text{-Fe}_2\text{O}_3$ different structure of wüstite block, which in the hexagonal ferrite, transformed into a hexagonal block R. This transformation may result organization wüstite block Fe-O additional oxygen layer, wherein a portion of the positions occupied

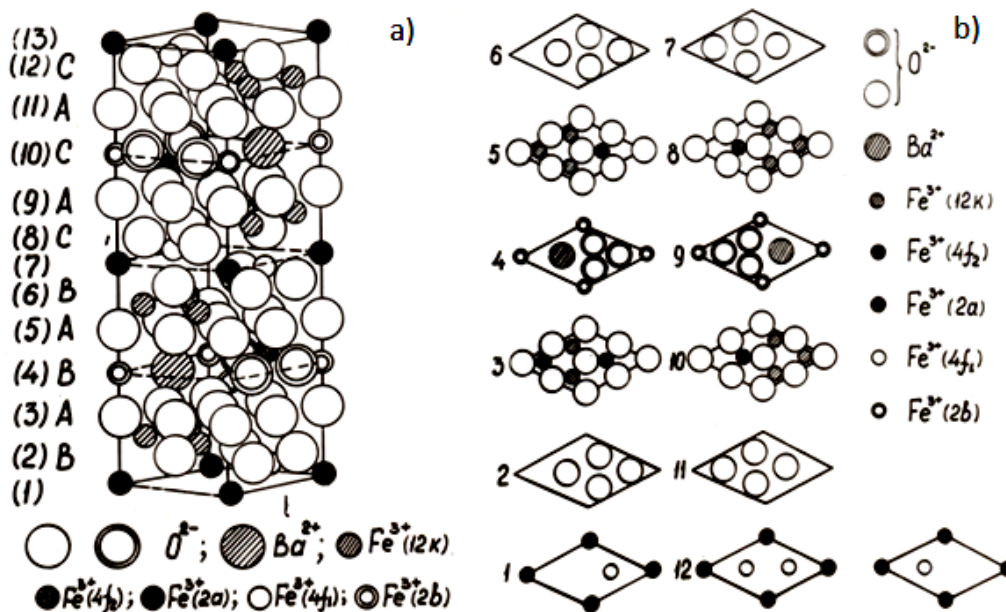


Fig. 5 – a) The crystal structure of the hexagonal ferrite $\text{BaFe}_{12}\text{O}_{19}$; b) the sequence of layers in the lattice $\text{BaFe}_{12}\text{O}_{19}$ (layer numbers correspond to the numbers in Fig. 5b)

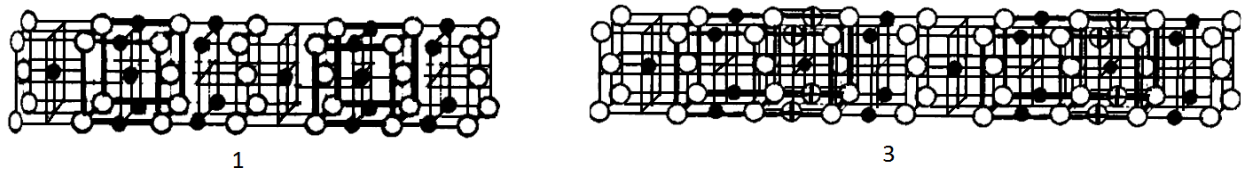


Fig. 6 – The alternation layers of oxygen and metal in the lattice $\alpha\text{-Fe}_2\text{O}_3$ (1) and in the lattice $\text{BaFe}_{12}\text{O}_{19}$ (3): ● – $\text{Fe}^{2+(3+)}$; ○ – O^{2-} ; ⊕ – Ba^{2+}

by oxygen ions Ba^{2+} and subsequent displacement of Fe^{3+} ions in the R-block. This shift translates iron ion of the octahedral position in a five-fold. The degree of saturation of an additional layer depends on the relationship between the diffusion mobility of Ba^{2+} ions and oxygen, that is, from prehistory $\alpha\text{-Fe}_2\text{O}_3$, temperature, oxygen partial pressure, the size of crystallites $\alpha\text{-Fe}_2\text{O}_3$ and the ratio of $\text{BaO} : \text{Fe}_2\text{O}_3$. Ions of barium slowly saturate wüstite layer at a relatively low temperature synthesis 700-800 °C and high partial pressure of oxygen. The result is a hexagonal block R. In this case, the formation $\text{BaFe}_{12}\text{O}_{19}$ based on $\alpha\text{-Fe}_2\text{O}_3$ at result of diffusion Ba^{2+} and O^{2-} in the layer lattice hematite with the maximum distortion. The introduction of barium into the lattice of $\alpha\text{-Fe}_2\text{O}_3$ causes displacement of Fe^{3+} ions in octahedral coordination fivefold and promotes the formation of a layer with hexagonal packing of anions. As a result, the lattice $\alpha\text{-Fe}_2\text{O}_3$, representing a plurality of layers $3\text{Fe}_4\text{O}_4 + 2\text{Fe}_2\text{O}_6 = 8 \text{Fe}_2\text{O}_3$, is reconstructed in the lattice $2\text{BaFe}_{12}\text{O}_{19} = 5\text{Fe}_4\text{O}_4 + 3\text{Me}_2\text{O}_6$. The rate of adjustment is limited by diffusion processes Ba^{2+} and O^{2-} , depends on the thermodynamic parameters of the gas phase and the prehistory of Fe_2O_3 . This assumption is confirmed by the following experimental facts:

1. Formation rate of $\text{BaFe}_{12}\text{O}_{19}$ depends on the partial pressure of oxygen in the gas phase according to the authors [5].

2. Mössbauer investigations of mixtures of $\text{BaCO}_3\text{-Fe}_2\text{O}_3$ synthesized at temperatures up to 900 °C only indicate the presence of $\alpha\text{-Fe}_2\text{O}_3$ and $\text{BaFe}_{12}\text{O}_{19}$.

3. The monoferrite BaFe_2O_4 registered at synthesis temperatures above 1000 °C during the initial stage of

solid state reactions. Moreover, at higher temperatures of synthesis may be other phase enriched barium.

4. CONCLUSION

It was established experimentally that depending on synthesis mode $\text{BaFe}_{12}\text{O}_{19}$ parameters at initial stages may occur phase enriched barium. In this case, $\text{BaFe}_{12}\text{O}_{19}$ formation may occur through an intermediate stage. An important role in the mechanism of formation of the surface layer of the particles played $\alpha\text{-Fe}_2\text{O}_3$, which is characteristic of the high degree of disorder in the lattice, its significant distortion. A huge influence on the state of the layer has grinding technology. This fact can explain the cause of the inconsistency of the results investigations by various authors, as well as a significant influence of temperature on the rate of synthesis of solid phase transformation. Indeed BaFe_2O_4 in different temperature ranges has a different structure. The most stable low-temperature modification phase is $\gamma\text{-BaFe}_2\text{O}_4$. However, the structure of this modification is still not fully established. When heated $\gamma\text{-BaFe}_2\text{O}_4$ enters $\beta\text{-BaFe}_2\text{O}_4$ and then $\alpha\text{-BaFe}_2\text{O}_4$. It is the presence of $\alpha\text{-BaFe}_2\text{O}_4$ in mixed $\text{BaO-Fe}_2\text{O}_3$ provides a high rate of formation barium hexaferrite. However, a mechanism for converting $\alpha\text{-BaFe}_2\text{O}_4$ in $\text{BaFe}_{12}\text{O}_{19}$ remains unclear.

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