

Magnetic Properties and Local Parameters of Crystal Structure for BaFe₁₂O₁₉ and SrFe₁₂O₁₉ Hexagonal Ferrites

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It is shown that difference between magnetic properties of hexagonal ferrites BaFe₁₂O₁₉ and SrFe₁₂O₁₉ is connected with difference of electronic configurations of Ba²⁺ and Sr²⁺ ions, and their ionic radii. Replacement of Ba²⁺ ions by Sr²⁺ ions that are smaller in size effects the degree of distortions of octahedrons located either in a hexagonal R-block or at its boundary with S-block. It contributes to a preferred localization of electrically active vacancies at the boundary of R- and S-blocks or in a surface layer of crystallites, and provides residual polarization of ferrites with hexagonal structure.

Key words: Hexagonal ferrites, Crystal structure, Mössbauer spectroscopy, X-Ray diffraction, Solid phase reactions, Vacancies, Diffusion.

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1. INTRODUCTION

Multi-sublattice hexagonal ferrites with their sandwich structure present a suitable object for investigation of different effects. They are used widely in machinery because they are characterized by special magnetic properties. Structure of replaced BaFe₁₂O₁₉ and SrFe₁₂O₁₉ hexagonal ferrites is isomorphic to magnetoplumbite MeFe₁₂O₁₉ (Me²⁺: Ba²⁺, Sr²⁺, Pb²⁺, Ca²⁺) mineral and presents a complex of oxygen layers of two kinds: spinel (S) and hexagonal (R), containing Me²⁺ [1, 2].

Though BaFe₁₂O₁₉ and SrFe₁₂O₁₉ ferrites have been examined many times, there is no common approach until present time to explanation of differences of their magnetic properties [3, 4]. So ambivalent explanations of differences in structurally-sensitive parameters (such as coercitive force, magnetic energy) of these ferrites are connected with complexity of the effect of electronic configuration of Ba²⁺ and Sr²⁺ ions on material magnetic structure. The observed variations of such parameters during replacement of Ba²⁺ by Sr²⁺ are mostly often connected with difference of their ionic radii and, respectively, with internal stresses arising at the boundary of R- and S-blocks or inside R-block [4]. At the same time, the mechanism of influence of internal stresses on magnetic properties is still not clear, because they not only have effect on crystallographic anisotropy, but also provide special location of point and volumetric defects and configuration variations in the nearest Fe³⁺ ions' surrounding them and, consequently, measure their magnetic state.

2. METHODS AND EXPERIMENTS

Magnetic properties and local parameters of the crystal structure of BaFe₁₂O₁₉ (BaM) and SrFe₁₂O₁₉

(SrM) ferrites are examined in this work. Monocrystals, isotropic and anisotropic polycrystals are presented as the objects of investigation in this paper. The samples were fabricated according to the known ceramic technology and didn't contain extraneous phases in correspondence with the data of X-ray diffraction analysis. Mössbauer spectroscopy, X-ray diffraction and synchronous thermal analysis in magnetic field were used for examination of the features of crystal structure and determination of Curie temperature. Magnetic parameters (specific magnetization σ_s , coercitive force H_c , residual magnetization σ_r , form of hysteresis loop) were measured via the standard technique: vibration magnetometer VS M250 in the magnetic field with intensity 20 kE at temperature 300 K. Mössbauer investigations were conducted with the help of Ms-104 Em spectrometer with spectra processing via the program Univem Ms.

3. OBTAINED RESULTS AND DISCUSSION

Based on the results of conducted researches, it was established that specific magnetization σ_s and residual magnetization σ_r of BaFe₁₂O₁₉ ferrite are lower than the same parameters for SrFe₁₂O₁₉ ferrite (see Table 1).

Table 1 – Magnetic parameters of anisotropic hexagonal ferrites BaFe₁₂O₁₉ and SrFe₁₂O₁₉ at a temperature of 300 °C

Ferrite	σ_s , $\frac{\text{Am}^2}{\text{kg}}$	σ_r , $\frac{\text{Am}^2}{\text{kg}}$	H_c , $\frac{\text{kA}}{\text{m}}$	P , $\frac{\text{kE.e}}{\mu}$	$\frac{M_r}{M_s}$	H_K
BaM	68.8	52.27	231.8	92.5	0.76	107
SrM	62.34	39.95	273.0	116	0.64	132

σ_s – specific saturation magnetization, σ_r – specific residual magnetization, H_c – coercitive force, P – magnetic power, M_r/M_s – ratio of rectangularity of magnetic

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hysteresis loop. Parameters characterizing magnetic hysteresis loop (see Figures 1*a* and 1*b*) also distinguish substantially.

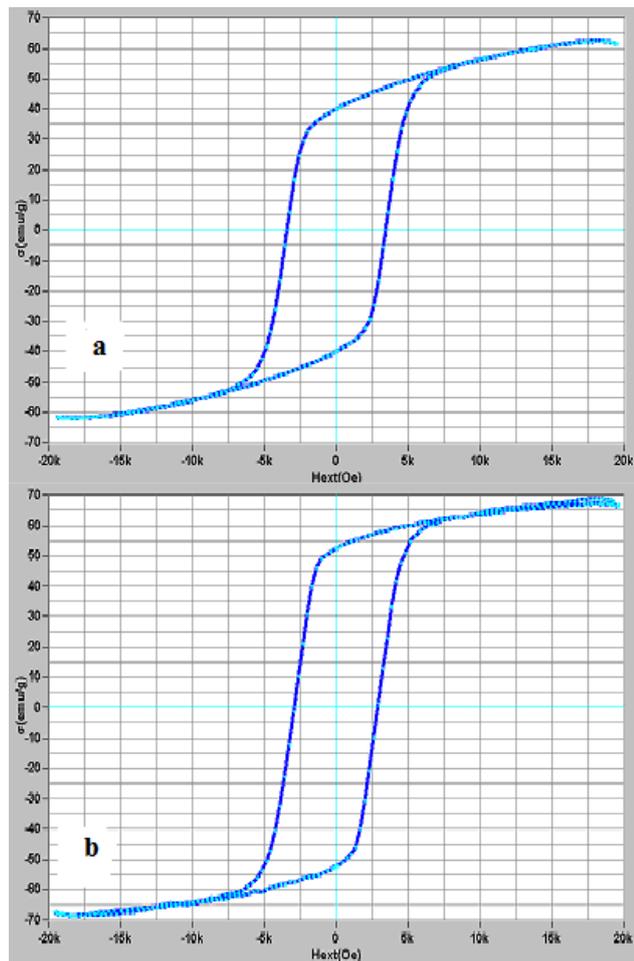


Fig. 1 – Magnetic hysteresis loops of anisotropic hexagonal ferrites: *a* – BaFe₁₂O₁₉, *b* – SrFe₁₂O₁₉

To reveal the causes of observed difference of magnetic properties, Mössbauer investigations of BaM and SrM ferrites were conducted. Mössbauer spectra of examines samples present superposition of sextets from Fe⁵⁷ ions located in the five non-equivalent positions (Figure 2).

Sextets appear most distinctly from nuclei of Fe³⁺ ions located in 12k (*a*) and 2b (*e*) sublattices that limit the magnetization. This circumstance stipulates the necessity of evaluation of relative population of these positions by Fe ions. Table 2 testifies that different values anisotropy constant of hexaferrites and their residual of integral intensity of sextets' components from 12k- and 2b-sublattices, are observed for sublattice 12k in polycrystalline samples BaM and SrM. It is known in this case that Fe³⁺ ions localized on the boundaries of R- and S-blocks (in octahedrons of 12k sublattice) are also characterized by lower values of effect probability, that testifies a more weak relation of Fe³⁺ ions with ligand environment comparing with other sublattices [1].

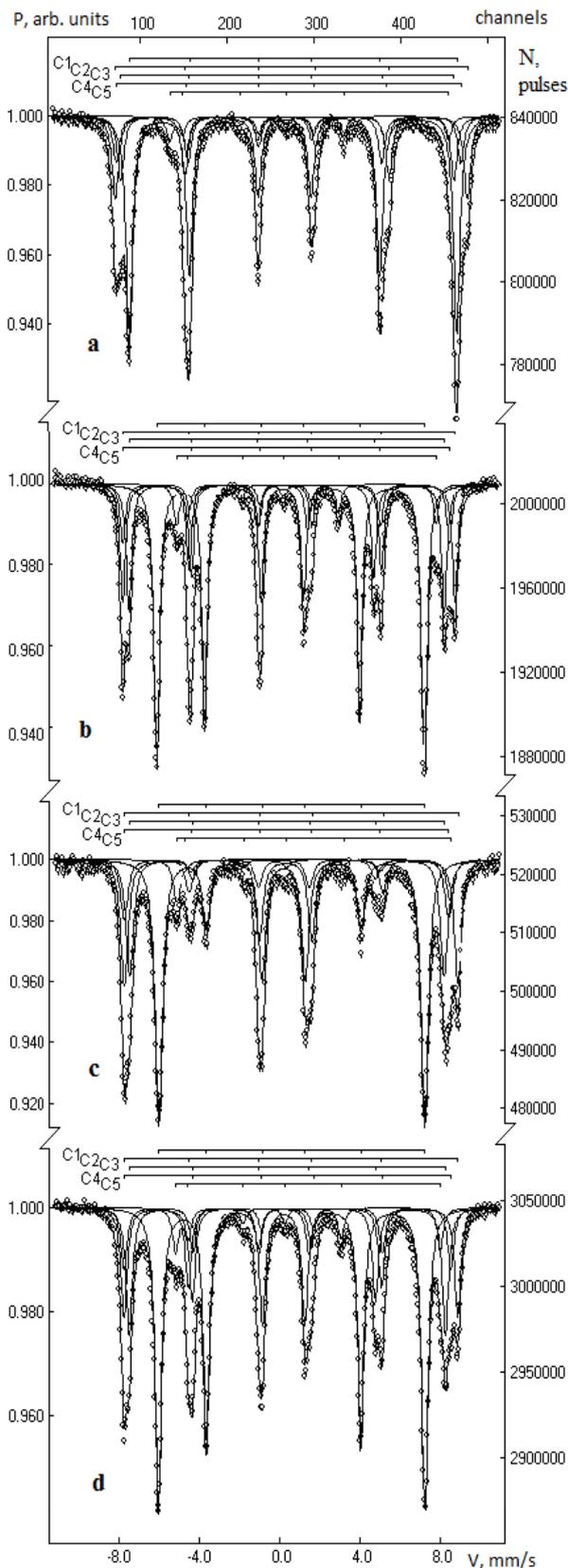


Fig. 2 – Mössbauer spectra of anisotropic hexagonal ferrites: *a* – BaFe₁₂O₁₉ at 87 K, *b* – BaFe₁₂O₁₉ at 300 K, *c* – monocrystal SrFe₁₂O₁₉ at 300 K, *d* – polycrystal SrFe₁₂O₁₉ at 300 K

Table 2 – Results of Mössbauer investigations for hexagonal ferrites BaFe₁₂O₁₉ and SrFe₁₂O₁₉

Sample, temperature K, kind of material	Sublattice, spectrum component	Isomeric shift d , mm/s	Quadru-pole splitting D , mm/s	Magnetic fields in nuclei Fe ⁵⁷ H, kE	Squares of coponents S , %	$\sum S_{bcd}/S_a$ $f_{f/bcd}$	$S_e/\sum S_{bcd}$ $f_{e/fbcd}$
SrFe ₁₂ O ₁₉ Monocrystal , 300	a-C1(Fe3+)VI	0.35	0.39	413	45.1	0.77	0.65
	b-C4(Fe3+)VI	0.28	0.04	500	11.1		
	c-C3(Fe3+)IV	0.24	0.14	485	16.7		
	d-C2(Fe3+)VI	0.39	0.27	515	20.7		
	e-C5(Fe3+)V	0.38	2.39	422	6.4		
SrFe ₁₂ O ₁₉ anisotropic, 300, powder	a-C1(Fe3+)VI	0.35	0.39	412	46.5	0.82	0.69
	b-C4(Fe3+)VI	0.24	0.03	506	9.3		
	c-C3(Fe3+)IV	0.26	0.17	489	20.8		
	d-C2(Fe3+)VI	0.37	0.28	516	16.9		
	e-C5(Fe3+)V	0.28	2.16	409	6.5		
BaFe ₁₂ O ₁₉ Anisotropic, 300, powder,	a-C1(Fe3+)VI	0.35	0.41	414	47.7	0.85	0.61
	b-C4(Fe3+)VI	0.32	0.02	506	7.8		
	c-C3(Fe3+)IV	0.26	0.21	488	19.4		
	d-C2(Fe3+)VI	0.39	0.18	514	19.4		
	e-C5(Fe3+)V	0.28	2.17	403	5.7		
BaFe ₁₂ O ₁₉ anisotropic powder, 87 K	a-C1(Fe3+)VI	0.47	0.42	507	50.2	0.94	0.61
	b-C4(Fe3+)VI	0.40	0.11	533	8.2		
	c-C3(Fe3+)IV	0.34	0.12	516	17.2		
	d-C2(Fe3+)VI	0.48	0.21	544	19.0		
	e-C5(Fe3+)V	0.35	2.28	431	5.4		

12k sublattice in BaM and SrM is characterized by more high values of quadrupole splitting equals to 0.39-0.42 (in comparison with other sublattices); it testifies substantial deviation of symmetry of Fe³⁺ ions local environment from cubic one, as well as essential part of a covalent relation between Fe³⁺ ions and ligands. Anomalous high value of quadrupole splitting for 12k- and 2B-sublattices are connected with the effects of overlapping of electronic planes of Fe³⁺ ions with the nearest oxygen ions. It is suggested in this case that the main input in the electronic part of the electric field gradient (EFG) on Fe⁵⁷ nucleus is stipulated by 3p-electrons of Fe³⁺ ions [1, 3]. However, electronic configuration of the nearest Ba²⁺ and Sr²⁺ ions is not taken into account. In the meantime these ions can effect not only an overlapping anisotropy of electronic orbits of Fe³⁺ ions (and, consequently, a magnetic state of ions and anisotropy constants), but also indirect interactions Fe³⁺_{12k}-O-Fe³⁺_{2b}.

Moreover, it is considered that Me²⁺ cation type in a hexagonal block has a weak effect on electronic configuration of Fe³⁺ ions. Indeed, H_r values for octahedral and tetrahedral sublattices in SrM and BaM are correlated with the similar values for spinel ferrites. At the same time such differences are observed for 2B-sublattice (10 kE) and 12k-sublattice (6 kE), located in an R-block and at its boundary with an S-block. Therefore, replacement of Ba²⁺ by Sr²⁺ effects the main exchange couplings Fe_{2b}-O-Fe_{4f2} and Fe_{2b}-O-Fe_{12k}. One of the causes of such differences is connected with distortions of the crystal lattice, arising due to different ion radii R (R_{Ba²⁺} = 1.43 Å and R_{Sr²⁺} = 1.15 Å) [1].

Indeed, in case of replacement of Ba²⁺ by Sr²⁺, displacement of oxygen ions in the direction of the plane where Sr²⁺ ions are located increases due to a great difference between O²⁻ (1.36 Å) and Sr²⁺ radii. It has to lead to additional distortion of oxygen octahedrons for 12k- and 2b-sublattice in SrFe₁₂O₁₉. At the same time, quadrupole splitting for these sublattices in SrM and

BaM has close values. Differences in dipole-dipole or spin-orbital interaction can be additionally attracted for explanation of the observed differences H_{eff} for 12k and 2b sublattices. However, such suggestion is hardly true owing to close values of isomeric shifts and quadrupole splitting for 12k- and 2b-sublattices in SrM and BaM ferrites. This fact displays the necessity of taking into account the difference in electronic configurations of Ba²⁺, Sr²⁺ ions during interpretation of differences of SrM and BaM magnetic properties. These Ba²⁺, Sr²⁺ ions distinguish in energy of atomic levels and in the effect of elastic stresses arising in the hexagonal R block on concentration and state of structural defects in this block.

It is evident that the complexes Ba-O₄ and Sr-O₄ existing in the hexagonal block differ essentially in their balance of overlapping of cation shells; it provides differences in the crystal lattice power that can vary due to presence of defects [5, 6]. Additionally, there are six octahedral 12k-nodes, not occupied by Fe³⁺ ions and "prohibited" in the magnetoplumbite lattice containing in the elementary cell of barium hexaferrite. Such positions are characterized by substantial distortions of ligand environment due to close location to barium ions. If Ba²⁺ ions are replaced by Sr²⁺ ions, quadrupole splitting for 2B- and 12k-positions varies from 2.32 mm/s to 2.16 mm/s and from 0.41 mm/s to 0.39 mm/s respectively. Decrease of deformation power of a crystal lattice in SrFe₁₂O₁₉ can occur as a result of transition of oxygen ions in oxygen layers to new locations. It is resulted in transformation of valent shells for Fe³⁺ ions neighbor to Ba²⁺ and Sr²⁺ ions and varying of their magnetic torques.

Concentration of local ferrite sections by cations takes place during preferred localization of defects in separate sublattices providing decrease of internal stresses. Such sections can't be identified via X-ray diffraction due to their small extension. However, this process is demonstratively confirmed by difference in ferrite coercitive force as well as by comparison of parameters of

ultra-thin interactions in monocrystals and polycrystal samples. Table 2 displays that relative intensity of spectrum lines from Fe^{3+} ions (located in 12k-sublattice) for $\text{SrFe}_{12}\text{O}_{19}$ monocrystal is lower than that for polycrystal. It is stipulated by the features of structure of a surface layer of crystallites in polycrystal, forming mainly by Fe^{3+} and O^{2-} ions of 12k-sublattice. This fact correlates with the observing widening of Mössbauer spectrum lines from nuclei of Fe^{3+} ions located in 12k-sublattice. This widening of lines can be connected with variation of the angle between direction of magnetic torque of ions and the axis of electric field gradient (EFG) and, consequently, the angle of super-exchange interaction between Fe^{3+} ions located in 12k- and 4f₂-sublattice. Therefore, visible difference of magnetic properties of Ba^{2+} and Sr^{2+} ions is observed, in spite of the fact that replacement of Ba^{2+} ions by Sr^{2+} ions in hexagonal ferrite doesn't lead to apparent variation of parameters of their Mössbauer spectra. It is shown that even small H_{\perp} increase for 12k- and 2b-sublattices of $\text{SrFe}_{12}\text{O}_{19}$ displays strengthening of exchange links between $\text{Fe}_{12\text{k}}\text{-O-Fe}_{4\text{f}_2}$ and $\text{Fe}_{12\text{k}}\text{-O-Fe}_{2\text{b}}$ in this ferrite comparing with BaM. It can be connected with varying of bond angles and distances between the nearest magnetic active neighbours, owing to ordering of defects caused by convergence to lowering of internal stresses at the boundary of R- and S-blocks. That's why $\text{SrFe}_{12}\text{O}_{19}$ in the most part presents a metastable system with its state depending on external parameters and concentration of Fe-replacing ions.

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4. CONCLUSION

The results of conducted investigations display that the difference between magnetic properties of hexagonal ferrites $\text{BaFe}_{12}\text{O}_{19}$ and $\text{SrFe}_{12}\text{O}_{19}$ is connected with the difference of electronic configurations of Ba^{2+} and Sr^{2+} ions, and their ionic radii. The replacement of Ba^{2+} ions by Sr^{2+} ions that are smaller in size effects the degree of distortions of octahedrons located in a hexagonal R-block or at its boundary with S-block. Elastic stresses arises as a result of non-correspondence of ionic radii, they cause an appearance of additional single-axial anisotropy and stimulate preference of Fe^{3+} ions to occupation of non-centrosymmetric octahedral positions. It contributes to a preferred localization of electrically active vacancies at the boundary of R- and S-blocks or in a surface layer of crystallites, and provides residual polarization of ferrites with hexagonal structure [10]. It is mostly typical for $\text{SrFe}_{12}\text{O}_{19}$ ferrite that displays a stronger multi-ferroic effect in comparison with $\text{BaFe}_{12}\text{O}_{19}$ [11]. That's why we can suggest a substantial variation of magnetic properties of strontium ferrites in consequent increase of defect concentration in an R-block and their ordering due to forced diffusion of Sr^{2+} and O^{2-} ions under the influence of the external effects or heterovalent replacement of Fe^{3+} ions.

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