

Obtaining and Properties of Hexaferrite BaFe₁₂O₁₉ for High-coercivity Permanent Magnets and Substrates Microstrip Microwave Devices of mm-Range

V.G. Kostishyn^{1,*}, V.V. Korovushkin¹, D.N. Chitanov¹, Yu.M. Korolev

¹ National University of Science and Technology "MISiS", 4, Leninsky Prosp., 119049 Moscow, Russia

² Institute of Petrochemical Synthesis of A.V. Topchieva Russian Academy of Sciences,
29, Leninsky Prosp., 119991 Moscow, Russia

(Received 24 September 2015; published online 24 December 2015)

In the work by ceramic technology produced samples isotropic and anisotropic polycrystalline hexaferrite BaFe₁₂O₁₉ and investigated their properties. It is shown that as the permanent magnets can be used both types of samples, whereas for substrates microstrip microwave devices mm-range expedient to use only anisotropic polycrystalline hexaferrite BaFe₁₂O₁₉.

Keywords: Barium hexaferrite, Microwave, Crystal anisotropy, Coercive force, Microstructure.

PACS numbers: 75.50.Gg, 75.75. + a

1. INTRODUCTION

Hexagonal ferrites BaFe₁₂O₁₉ have a crystal structure of magnetoplumbite type [1] and the high values of the magnetic anisotropy H_K and coercive force H_C [2]. Availability of high values of H_K and H_C allows to use these materials as effective permanent magnets [3].

The advantage of permanent magnets based on BaFe₁₂O₁₉ are able to exercise at them multipolar magnetisation on one-piece compact unit and high values of operational characteristics in high frequency magnetic fields.

In recent years, due to the high value of H_K, the polycrystal BaFe₁₂O₁₉ regarded as a perspective material for substrate microstrip microwave devices mm-range [2].

The purpose of this work was to obtain and research samples of polycrystalline hexaferrite BaFe₁₂O₁₉ for use as permanent magnets and substrate microstrip ferrite decouplers devices mm-range wavelength.

2. OBTAINING RESEARCH OBJECTS

Method of production objects of the research was to obtain a compound of BaO·6Fe₂O₃ by the solid phase reaction between the iron oxide and barium oxide in the heat treatment process briquetted raw material mixture, in the subsequent grinding briquettes, pressing and sintering of parts. The first stage of the process - providing a mixture of oxides in the proper proportions of the most performed in a simple way - mechanical mixing iron oxide and barium carbonate salt. The powder mixture of iron oxide and barium carbonate briquetted and subjected to thermal treatment at $T = 1300$ °C with delay for several hours and subsequent quenching in water; during the heat treatment resulted in the formation compounds BaO·6Fe₂O₃. Briquettes subjected to ball milling in a vibrating mill to a finely dispersed state (the particle size of a few microns). The pressed parts of the powder were sintered at temperatures of 1150-1250 °C. Pressing the powder in conventional compression molds results in isotropic

magnets, pressing in the molds provided with the magnetizing device, – to obtain anisotropic, with advantageous properties in the direction of the applied field. In this paper we were obtained as isotropic and anisotropic samples.

On the properties of barium oxide magnets significantly affected the percentage of oxides and the presence of impurities, grain size, the condition of pressing and sintering regime; in the manufacture of anisotropic magnets is very large role and shape of the particles.

The composition of the barium ferrite, determined by the formula BaO·6Fe₂O₃, as follows (in wt. %): BaO – 13,77, Fe₂O₃ – 86,23 [4].

3. METHODS OF EXPERIMENTAL RESEARCH

In order to study characteristics of the crystal and magnetic structure using X-ray diffraction, Mossbauer spectroscopy, magnetometry and simultaneous thermal analysis.

Magnetic parameters were measured by standard methods on vibration magnetometer VSM 250.

X-ray diffraction studies were performed on the object X-ray diffractometer DRON-3M (Russia) and D8 Advance Bruker AXS (Germany).

During the X-ray diffraction was used CuK α radiation, as well as a tube with an iron anode (working current – 25 mA, power – 25 kW). Wavelength 0.193728 nm. When shooting samples used the filter Mn. Focusing was performed by the method of Bragg-Brentano with two slits Soller. Measurements were made at room temperature.

Identification intense peaks in the diffraction pattern was performed using software package PDWin 4.0. X-ray diffraction analysis of samples was limited to the determination of the series-spacings, and compared them with the reference data base of powder diffraction data, which is based on the card index PDF2.

Mossbauer spectrometer studies performed Ms-1104 Em with automatic processing the spectra of the program Univem Ms in the temperature range 87-300 K.

* drvgkostishyn@mail.ru

4. THE RESULTS OF EXPERIMENTAL RESEARCH

X-ray studies have confirmed that as a result of the used technology obtained polycrystalline isotropic and anisotropic hexagonal ferrites BaFe₁₂O₁₉. Characteristic X-ray diffraction patterns are presented in Fig. 1 and 2.

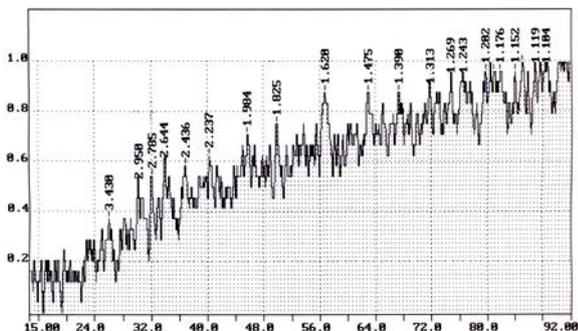


Fig. 1 – The characteristic X-ray diffraction of the sample of polycrystalline isotropic hexaferrite BaFe₁₂O₁₉

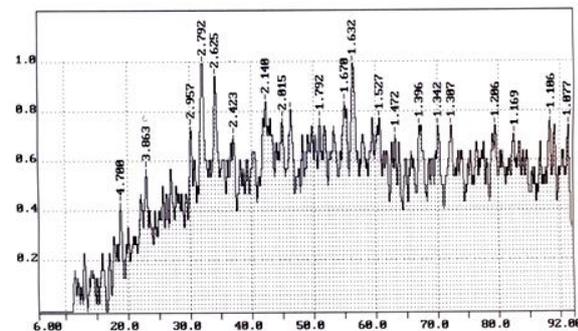


Fig. 2 – The characteristic X-ray diffraction of polycrystalline sample anisotropic hexaferrite BaFe₁₂O₁₉

Table 1 shows the values of the basic parameters for the isotropic magnetic ferrites of barium IZ-1 and IZ-2 with an energy of up to 1,25·10⁶ G·Oe and anisotropic ANIZ-1 and ANIZ-2 with energies up to 3,6·10⁶ G·Oe.

Fig. 3 shows the magnetization curve and hysteresis loop to one of the samples ANIZ-2.

Fig. 4 shows the typical fraktogrammy obtained in the isotropic and anisotropic barium hexaferrite.

Mossbauer spectroscopy was investigated samples isotropic and anisotropic hexaferrites BaFe₁₂O₁₉ as starting powders, milled from massive plates and rings, and in the form of foil at 300 and 87 K. As an example, Fig. 5 shows the Mossbauer spectra of isotropic and anisotropic barium hexaferrite measured at 300 and 87 K.

With the program spectra processing «Univem Ms» spectra were arranged on 5 sextets. The criterion for optimal decomposition served minχ², characterizing the convergence of the experimental spectrum and the results of approximation. Processing of the spectra

Table 1 - Basic magnetic parameters isotropic barium oxide magnets

| The sample type | <i>B_r</i> , G | <i>bH_c</i> , Oe | (<i>BH</i>) _{max} ·10 ⁻⁶ , Oe | <i>K₁</i> ·10 ⁻⁶ , e/cm ³ | <i>ρ</i> , Ω·cm | Density, g/cm ³ |
|-----------------|--------------------------|----------------------------|-----------------------------------------------------|------------------------------------------------------------|---------------------|----------------------------|
| IZ-1 | 1800-2100 | 1600-1400 | 0,8-0,9 | 1,2 | 1,2·10 ⁷ | 4,4-4,6 |
| IZ-2 | 1900-2100 | 1800-1600 | 0,9-1,25 | 1,5 | 1·10 ⁷ | 4,6-4,7 |
| ANIZ-1 | 3200-3500 | 2700-2300 | 2,0-2,8 | 3,5 | 7·10 ⁶ | 4,5-4,8 |
| ANIZ-2 | 3600-4000 | 2200-1600 | 3,0-3,6 | 3,7 | 8·10 ⁶ | 4,8-4,9 |

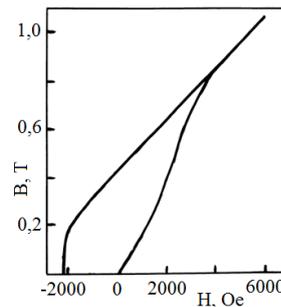


Fig. 3 – The magnetization curve and hysteresis loop for an anisotropic sample ANIZ-2

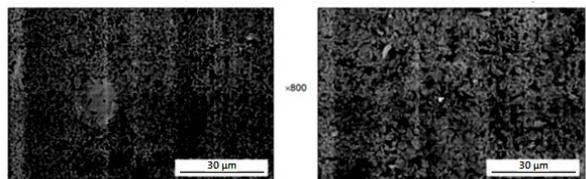


Fig. 4 – Typical fraktogrammy obtained in the isotropic (a) and anisotropic (b) barium hexaferrite

allowed us to estimate the parameters characterizing the chemical bond ions Fe³⁺-O, local distortions of the crystal lattice, the magnetic state of nonequivalent ions Fe³⁺, the population of the items iron ions over the sublattices a, b, c, d and e. Table 2 shows the parameters studied hexagonal ferrites BaFe₁₂O₁₉.

Theoretical occupancy sublattice Fe³⁺ ions are shown in Table 3. The table above shows that iron ions Fe³⁺ in BaFe₁₂O₁₉ localized in five non-equivalent positions (sublattice a, b, c, d, e), the population of which differs from the theoretical. The difference the relative intensity of the component sextet for different sublattices of the expected population may be associated with different probability of the Mossbauer effect for sublattices (a) by the presence of vacancies Fe³⁺ ions in these sublattices [5].

The comparison relative intensities of the components of the Mossbauer spectra of single crystals suggests that within the error of cation vacancies are statistically distributed in all positions except 2b (e sublattice). Lower values for the probability of the Mossbauer effect sublattice (e) due to the specifics of the vibrations of iron ions sublattice. According to X-ray diffraction fivefold-coordinated ions are located not only at the center of symmetry of the tetrahedral pyramid and its base plane – quadrangle. These provisions are separated by distance and 0,156 Å, respectively, a potential barrier. At room temperature, ion Fe³⁺ oscillates between these positions, which provides a reduced probability of the Mossbauer effect, and an abnormally large value of the quadrupole splitting (2,17-2,32) mm/s [6].

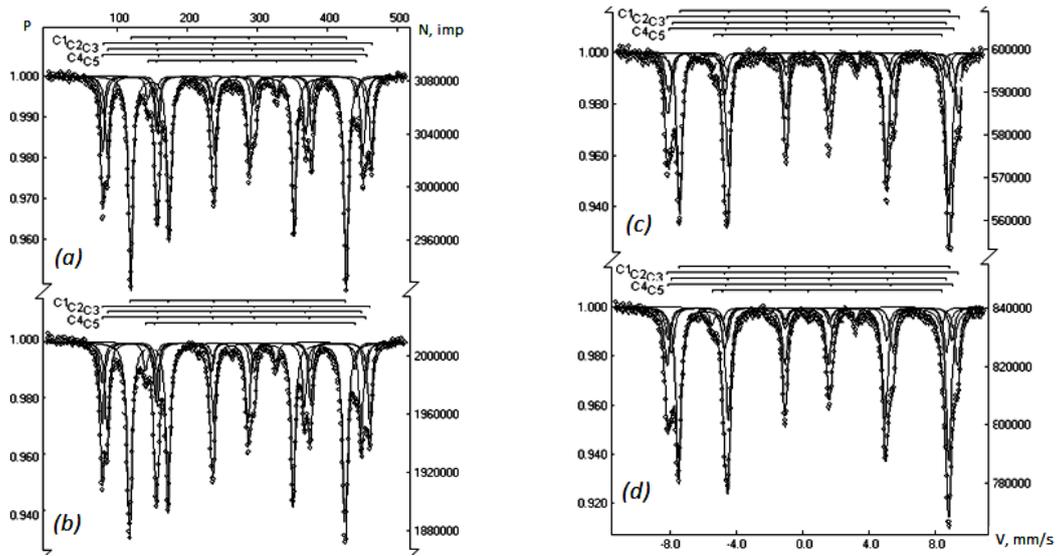


Fig. 5 – Mossbauer spectra of hexagonal ferrites $\text{BaFe}_{12}\text{O}_{19}$: a – isotropic (300 K); b – anisotropic (300 K); c – isotropic (87 K); d – anisotropic (87 K)

Table 2 – Mossbauer research parameters of isotropic and anisotropic hexagonal ferrites $\text{BaFe}_{12}\text{O}_{19}$ at 300 and 87 K

| Sample, temperature K, kind of material, T_c | Sublattice component spectrum | The isomer shift, δ , mm/s | Quadrupole splitting Δ , mm/s | The magnetic fields at the nuclei, Fe^{57} H, kOe | Squares component t , S, %. | $\sum S_{bcd}/S_a$, f_{al}/f_{bcd} | $S_e/\sum S_{bcd}$, f_{el}/f_{bcd} |
|------------------------------------------------|-------------------------------|-----------------------------------|--------------------------------------|------------------------------------------------------------|-------------------------------|---------------------------------------|---------------------------------------|
| Isotropic, 300 K, No 1 powder $T_c = 601$ K | a-C1(Fe^{3+})VI | 0,35 | 0,42 | 414 | 49,9 | 0,92 | 0,57 |
| | b-C4(Fe^{3+})VI | 0,33 | 0,00 | 507 | 8,8 | | |
| | c-C3(Fe^{3+})IV | 0,26 | 0,22 | 491 | 18,6 | | |
| | d-C2(Fe^{3+})VI | 0,39 | 0,20 | 516 | 17,6 | | |
| | e-C5(Fe^{3+})V | 0,29 | 2,21 | 400 | 5,1 | | |
| Anisotropic, 300 K, powder $T_c = 720$ K | a-C1(Fe^{3+})VI | 0,35 | 0,41 | 414 | 47,7 | 0,85 | 0,61 |
| | b-C4(Fe^{3+})VI | 0,32 | 0,02 | 506 | 7,8 | | |
| | c-C3(Fe^{3+})IV | 0,26 | 0,21 | 488 | 19,4 | | |
| | d-C2(Fe^{3+})VI | 0,39 | 0,18 | 514 | 19,4 | | |
| | e-C5(Fe^{3+})V | 0,28 | 2,17 | 403 | 5,7 | | |
| Isotropic, 90 K, powder | a-C1(Fe^{3+})VI | 0,47 | 0,43 | 508 | 50,0 | 0,94 | 0,65 |
| | b-C4(Fe^{3+})VI | 0,44 | 0,08 | 539 | 9,6 | | |
| | c-C3(Fe^{3+})IV | 0,33 | 0,15 | 519 | 17,8 | | |
| | d-C2(Fe^{3+})VI | 0,49 | 0,21 | 546 | 16,8 | | |
| | e-C5(Fe^{3+})V | 0,37 | 2,32 | 427 | 5,8 | | |
| Anisotropic, 90 K, powder | a-C1(Fe^{3+})VI | 0,47 | 0,42 | 507 | 50,2 | 0,94 | 0,61 |
| | b-C4(Fe^{3+})VI | 0,40 | 0,11 | 533 | 8,2 | | |
| | c-C3(Fe^{3+})IV | 0,34 | 0,12 | 516 | 17,2 | | |
| | d-C2(Fe^{3+})VI | 0,48 | 0,21 | 544 | 19,0 | | |
| | e-C5(Fe^{3+})V | 0,35 | 2,28 | 431 | 5,4 | | |
| Isotropic, 300 K, No 2 powder | a-C1(Fe^{3+})VI | 0,35 | 0,42 | 414 | 49,5 | | |
| | b-C4(Fe^{3+})VI | 0,33 | 0,0 | 507 | 9,1 | | |
| | c-C3(Fe^{3+})IV | 0,26 | 0,22 | 491 | 18,7 | | |
| | d-C2(Fe^{3+})VI | 0,39 | 0,20 | 516 | 17,6 | | |
| | e-C5(Fe^{3+})V | 0,29 | 2,21 | 400 | 5,1 | | |
| Isotropic, powder, $T_c = 722$ K | a-C1(Fe^{3+})VI | 0,35 | 0,41 | 409 | 49,4 | | |
| | b-C4(Fe^{3+})VI | 0,31 | 0,01 | 502 | 9,8 | | |
| | c-C3(Fe^{3+})IV | 0,26 | 0,21 | 487 | 17,7 | | |
| | d-C2(Fe^{3+})VI | 0,39 | 0,17 | 412 | 17,8 | | |
| | e-C5(Fe^{3+})V | 0,28 | 2,19 | 399 | 5,3 | | |

Table 3 – The occupancy position iron ions in the structure of $\text{Me}^{2+}\text{Fe}_{12}\text{O}_{19}$

| Sublattice | The number of ions in the el. cell | Theoretical squares sextets by Fe^{3+} ions | Encirclement | The coordination number | The direction of spin |
|---------------------|------------------------------------|------------------------------------------------------|---------------|-------------------------|-----------------------|
| 2a(b) | 2 | 8,3 | octa (S) | 6 | up |
| 4f ₁ (c) | 4 | 16,7 | tetra (S) | 4 | down |
| 12k(a) | 12 | 50 | octa (RS) | 6 | up |
| 4f ₂ (d) | 4 | 16,7 | octa (R) | 6 | down |
| 2b(e) | 2 | 8,3 | bipyramid (R) | 5 | up |

5. CONCLUSION

The work by ceramic technology obtained samples isotropic and anisotropic hexagonal ferrite $\text{BaFe}_{12}\text{O}_{19}$ and studied their properties.

It is established that the samples in powder characteristics Mossbauer isotropic and anisotropic ferrite differ slightly.

Analysis of magnetic sampling parameters allows to conclude that as the permanent magnets can be used as

isotropic and anisotropic ferrite $\text{BaFe}_{12}\text{O}_{19}$. For substrates microstrip microwave devices mm-range use of an isotropic ferrite $\text{BaFe}_{12}\text{O}_{19}$ - is impractical due to the small value of the magnetic anisotropy.

Work is executed in NUST "MISIS" with the financial support of the Ministry of Education of the Russian Federation within the grant agreement № 14.575.21.0030 on 27 June 2014 (RFMEFI57514X0030).

REFERENCES

1. V.N. Antsiferov, L.M. Letyuk, V.G. Andreev, A.N. Dubrov, A.V. Gonchar, V.G. Kostishyn, A.I. Satin, *The problems-we Powder Materials. H IV / Materials polycrystalline ferrites* (Ekaterinburg: UB RAS: 2004).
2. L.M. Letyuk, V.G. Kostishin, A.V. Gonchar, *Technology magnetoelectronic ferrite materials* (M.: MISA: 2005).
3. *Permanent magnets: A Handbook* (Ed. Y.M. Pyatina) (M.: Energia, 1980).
4. B.E. Levin, Y.D. Tretyakov, L.M. Letyuk, *Physical and chemical bases of reception, properties and applications of ferrites* (M.: Metallurgy: 1979).
5. V.I. Archarov, V.P. Pashchenko, *Math. USSR Academy Sci., Ser. Inorg. Mater.* **11** No 9, 2022 (1977).
6. Yu.A. Mamaluy, L.P. Ol'khovik, L.F. Checherskaya, *Ukr. J. Phys.* **27** No 9, 1396 (1982).