Influence of Plasma Treatment Conditions on Structural-Phase Composition and Magnetic Properties of Barium Hexaferrite (M-type) Films on C-Sapphire

© *M.KH. Gadzhiev* [1], *A.E. Muslimov* [2]

[1] Joint Institute for High Temperatures, Russian Academy of Sciences, Moscow, Russia
[2] Federal Research Center „Crystallography and Photonics", Russian Academy of Sciences, Moscow, Russia
E-mail: makhach@mail.ru

In the work investigated the influence of plasma treatment conditions on the structural-phase composition and magnetic properties of barium hexaferrite films (0001) $BaFe_{12}O_{19}$ on C-sapphire. Two treatment modes were used: with a weight average plasma temperature of $4-5\,kK$ and $8-10\,kK$. It has been shown that the films obtained at the low treatment temperature have a pronounced magnetic anisotropy and saturation magnetization of $42\,emu/g$. The films obtained at high temperature have weak magnetic anisotropy, but have a higher saturation magnetization value of $62\,emu/g$. All films have low coercive fields of less than $500\,Oe$, which indicates the low magnetic hardness of barium hexaferrite samples and the possibility of their use as magnetic conductors of transformers, electromagnets, in measuring devices. The presented results demonstrate the promise of the plasma treatment technique in the formation of coatings with high anisotropy.

Keywords: barium hexaferrite, sapphire, plasmatron, magnetization.

The progress in current electromagnetic technology (transformers, field magnets, high-density magnetic recording, sensors, probes) is associated with the search for novel magnetic materials with unique properties. Substituted M-type barium hexaferrite $BaFe_{12}O_{19}$ (BaM) with high values of crystalline anisotropy ($17\,kOe$) and the coercive field (its theoretical value exceeds $7\,kOe$) [1] belongs to the group of materials of this kind that are being studied extensively. Being a classical magnetically hard material with a high magnetization, barium hexaferrite has long been applied in the fabrication of permanent magnets for electric, radio, automatic, and electronic equipment and instrumentation. In view of this, early studies were focused on enhancing the magnetic properties of BaM further. For example, Eu- and Sc-substituted BaM exhibits elevated values of magnetization of coercive fields [2,3]. If BaM was a magnetically soft material, its range of application would be no less wide. Magnetically soft materials are used to fabricate inductor and transformer cores through which alternating currents flow. Core losses may be minimized by suppressing coercive fields and enhancing the resistance of the core material. The resistivity of pure BaM is on the order of $10^7\,\Omega \cdot cm$ [4]. In addition, materials with reduced coercive fields and a high saturation magnetization may find application in high-density magnetic recording. The production of a BaM-type material with a well-pronounced magnetic anisotropy, a high saturation magnetization, and a weak coercive field is a challenging task. The suppression of coercive fields in BaM by way of a complex substitution has been achieved only in a few studies [5], and the

problem remains relevant to this day. A rising tide of interest in BaM stemmed from its potential application as a high-temperature multiferroic. Magnetically induced ferroelectricity and giant magnetoelectric effects, which are especially well-pronounced in substituted BaM, were discovered [6].

In modern materials science, the search for materials with novel properties is associated primarily with partial substitution of matrix elements. This approach was applied in a series of studies [7–9] to synthesize efficient absorbers of electromagnetic radiation of the millimeter range (with a frequency of $30-100\,GHz$) based on M-type barium hexaferrites. In our view, an extreme external influence (e.g., plasma treatment, which is basically high-power high-temperature processing accompanied by thermochemical reactions) could be no less efficient. One may adjust the properties of synthesized materials within a wide range by altering the process parameters and changing the plasma-supporting gas. In addition, the impact intensity is so high that the needed result may be achieved in a short span of time. In the present case, the processing procedure may be outlined in the following way: an insufficiently oxidized polycrystalline BaM film is deposited onto a thermally resistant sapphire substrate and is then subjected to short-term treatment in plasma generated by a plasmatron. For additional safety, nitrogen may be used as the plasma-supporting gas, and the process itself may be conducted in the open air. Owing to its high activity, oxygen of the surrounding atmosphere, which is heated by plasma, exerts the primary chemical influence on the sample. In

the present study, we examine the influence of conditions of processing with low-temperature nitrogen plasma on the structural-phase composition and magnetic properties of Ba*M* films on sapphire.

Sapphire wafers of basal orientation (0001) were subjected to chemical-mechanical polishing. A Ba*M* film was then deposited onto these sapphire samples at a temperature of 350°C by magnetron sputtering of a ceramic $BaFe_{12}O_{19}$ target in argon atmosphere ($p_{Ar} \sim 5.6 \cdot 10^{-3}$ Torr). An anion-deficient polycrystalline film was formed this way.

A DC plasmatron with vortex stabilization and an expanding channel of the output electrode was used as a source of nitrogen plasma. It produced a weakly diverging nitrogen plasma jet with diameter $D = 8-10$ mm [10]. The samples were treated in the open air in two plasma regions: *L* (with a mass-average plasma temperature of $4-5$ kK) and *H* (with a mass-average plasma temperature of $8-10$ kK). The treatment time was shorter than 0.5 min. A longer treatment resulted in the destruction of samples.

A JCM-6000 desktop scanning electron microscope (SEM) was used for microscopic studies. X-ray tests were performed using an X'PERTPRO (PANalytical, Netherlands) diffractometer in the „reflection" Bragg−Brentano geometry with Cu*K*$_\alpha$ radiation ($\lambda = 1.54$ Å) and a Ni β-filter. Magnetic hysteresis curves were measured with a NUVO Mk2 (Fairgrieve Moulding, Ltd, Great Britain) vibration magnetometer in the magnetizing field range from -5000 to 5000 Oe in out-of-plane and in-plane geometries.

According to the X-ray diffraction (XRD) data, a Ba*M* film with the structure of magnetoplumbite formed first in the process of magnetron deposition in argon atmosphere. The anion deficiency of this film is verified by the XRD data: interplanar distance *d* along texture axis [0001] of the initial film is 0.2846 nm, which is lower than *d* for a stoichiometric sample (0.29 nm) [11]. The film structure is close to a polycrystalline one; weak texturing along axis *c* [0001] was observed. Oriented films with a well-marked texture along axis *c* (Fig. 1) formed after plasma treatment in modes *L* and *H* (in what follows, they are referred to as type *L* and *H* films). According to the electron microscopy data, the surface topology of samples differed in the parameters of relief features (Fig. 2). Crystallites grew larger after high-temperature plasma treatment in mode *H*. The thickness of samples differed greatly in their thickness: 2.8 and 1.3 μm for type *L* and *H* films, respectively. Since oxygen is contained both in films and in the substrate, it is rather hard to compare the elemental compositions of Ba*M* samples on sapphire substrates. This is the reason why films were compared in the atomic barium and iron content. According to the microanalysis data, type *L* and *H* films had the same Ba/Fe ratio of 0.1; the nitrogen content was below 1%. Although the analysis was semi-quantitative in nature, it is fair to say that nitrogen plasma treatment of anion-deficient Ba*M* samples does not result in any significant doping with nitrogen. Figure 3 shows the magnetic hysteresis curves of Ba*M* films. The results
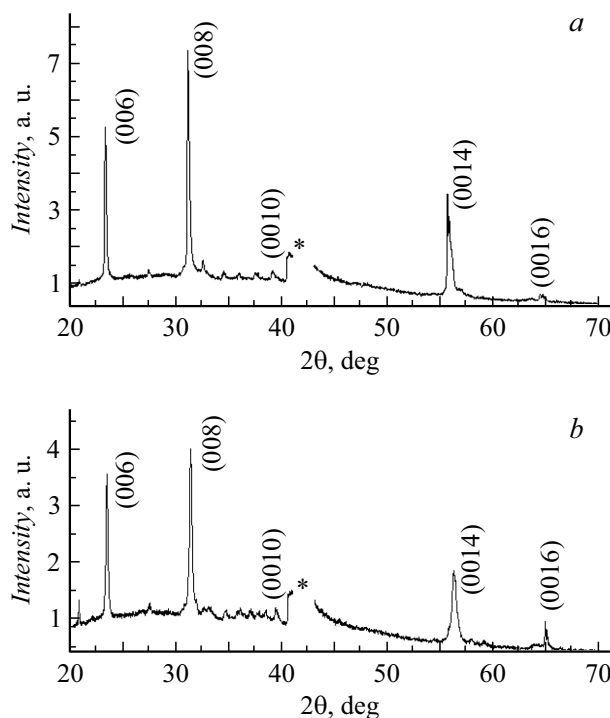

Figure 1. Diffraction patterns of type *L* (*a*) and *H* (*b* samples). The reflection of the *c*-sapphire substrate is denoted by an asterisk. JCPDS: 84-0757.

of examination of magnetic properties are listed in the table (M_s is the magnetization in 5 kOe fields, M_r is the remanent magnetization, M_r/M_s is the rectangularity, and H_c is the coercive field). The magnetization was determined in accordance with the law of approach to saturation [12].

It can be seen that type *L* films produced at a relatively low temperature feature a well-marked magnetic anisotropy (Fig. 3, *a*). This anisotropy in type *H* films produced at a high temperature is very weak (Fig. 3, *b*), although the magnetization in 5 kOe fields is higher and reaches 62 emu/g. It should be noted that the theoretical saturation magnetization value for Ba*M* is 72 emu/g [13]. The coercive fields are lower than 500 Oe for all samples (Figs. 3, *a*, *b*). This value is more than 10 times lower than the theoretical one (6700 Oe) [13]. Although magnetic anisotropy was observed for type *L* films, the rectangularity of the magnetic curve is relatively low (~ 0.28). Samples were treated in thermodynamically heterogeneous conditions. Thermo-chemical reactions proceed at a high rate of propagation of the oxidation front from the surface deeper into a sample. At the same time, since the exposure time is too short for intense diffusion processes, the anion deficiency is expected to be retained. The results of calculation of interplanar distance *d* along texture axis [0001] for type *H* and *L* films based on the XRD data were as follows: $d_H = 0.288$ nm, $d_L = 0.2855$ nm. The cell parameter along axis [0001] in both films is lower than the one corresponding to a stoichiometric crystal. This is attributable to the stoichiometry violation due to the oxygen deficiency. Since
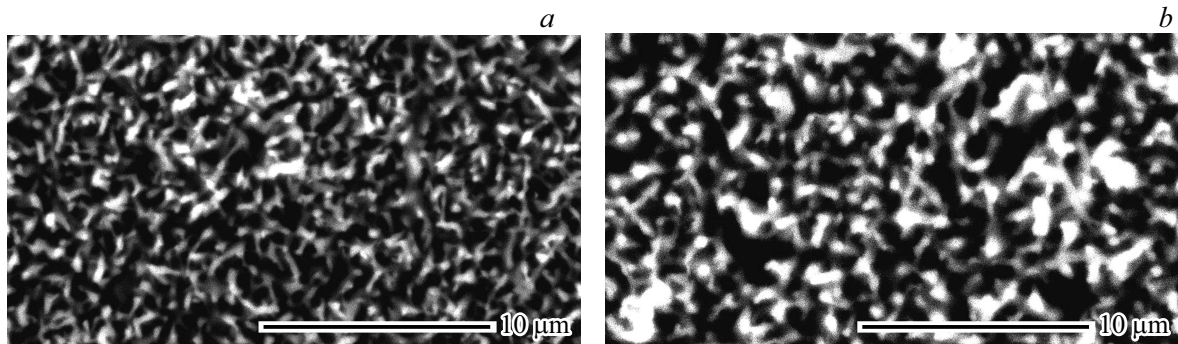
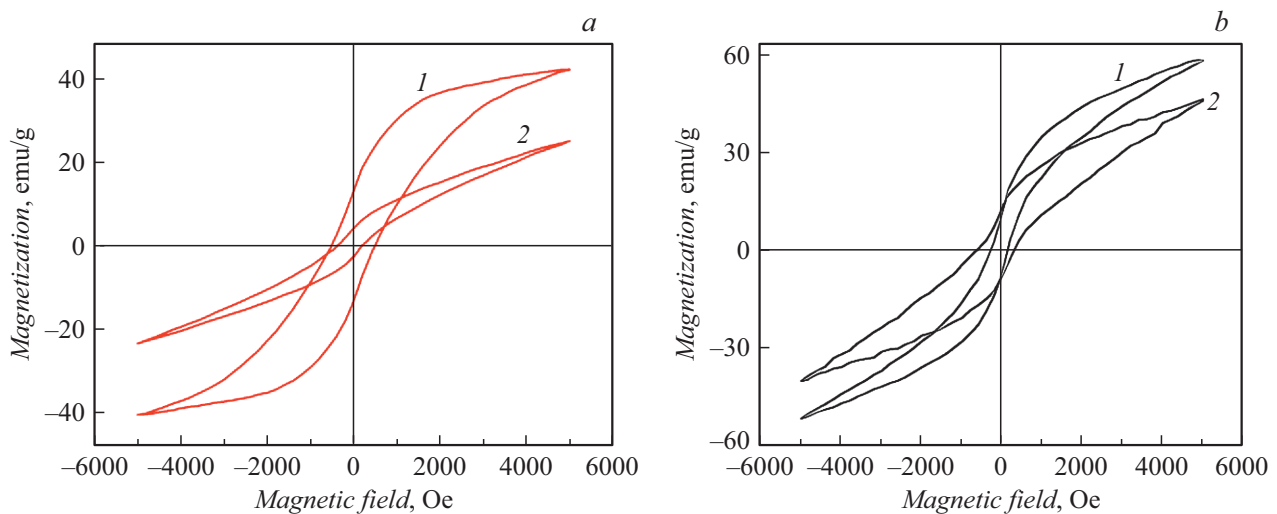**Figure 2.** SEM images of the surface of type *L* (*a*) and *H* (*b* samples).

Figure 3. Magnetic hysteresis curves of Ba*M* films processed in modes *L* (*a*) and *H* (*b*). Curve *1* — out-of-plane geometry; curve *2* — in-plane geometry.

a processed type *H* film becomes much thinner while retaining the initial Ba/Fe ratio, congruent evaporation from the film surface occurs in the process of high-temperature treatment. High-temperature sintering, which induces the growth of crystallites, proceeds in deeper layers (Fig. 2, *b*). The lower FWHM of $\{000n\}$ reflections of type *L* films is indicative of the fact that they feature larger crystallites. Direct calculations of the coherent scattering region in accordance with the Scherrer formula yield the following estimates of the crystallite size: 87 nm for a type *L* film and 29 nm for a type *H* film. The magnetic anisotropy of type *L* films (Fig. 3, *a*) is related to this increase in crystallite size. The general weakening of coercive fields (see the table) in all samples is attributable to the magnetic structure frustration and the attenuation of exchange interactions (reduction in the number of Fe−O−Fe bonds). Although the same factors should influence the magnetization in 5 kOe fields, it can be seen that it is maximized in a type *H* film (Fig. 3, *b*), which features a significant nonstoichiometry and a reduced parameter *d* along axis [0001]. This feature is difficult to explain at present; additional studies are needed. The specifics of plasma high-temperature sintering

are likely to have a significant effect here. The standard high-temperature sintering procedure envisages long-term sample treatment. In the process of slow sintering, grain-boundary diffusion in solid samples gives way to bulk diffusion. This transition helps establish a thermodynamically stable state with the minimum grain surface area. In short-term plasma treatment, the sample processing most closely resembles quenching, a feature of which is the fixation of mechanical stresses. These stresses contribute to the retention of the coercive field in films with even a significantly weakened magnetocrystalline anisotropy. The melting temperature is 1580°C for stoichiometric Ba*M* [14] and could be lower for anion-deficient samples. A molten phase, which forms in the process of high-temperature treatment, first reduces the porosity of a sample and then, in the course of subsequent crystallization, forms regions of a localized tensile stress. As is known, tensile stresses facilitate an increase in the saturation magnetization [15]. Mechanical stresses are maximized in the film plane, thus enhancing the coercive field in the in-plane scanning geometry (Fig. 3, *b*, curve *2*).

A plasma treatment technique, which induces a many-fold reduction in the magnetic hardness of samples, was pro-

Magnetic properties of Ba*M* films on sapphire in fields up to 5 kOe

Sample type	Out-of-plane				In-plane			
	M_s, emu/g	M_r, emu/g	M_r/M_s	H_c, Oe	M_s, emu/g	M_r, emu/g	M_r/M_s	H_c, Oe
L	42	12	0.28	490	25	5	0.2	210
H	62	11	0.18	180	50	11	0.22	430

posed above. The influence of conditions of processing with low-temperature nitrogen plasma on the structural-phase composition and magnetic properties of (0001) barium hexaferrite $BaFe_{12}O_{19}$ films on *c*-sapphire was examined. Two treatment modes with a mass-average plasma temperature of $4-5$ and $8-10$ kK were used. It was demonstrated that films processed at a low temperature feature a well-marked magnetic anisotropy and a magnetization on the order of 42 emu/g in 5 kOe fields. Although magnetic anisotropy was observed, the rectangularity of the magnetic curve was relatively low (~ 0.28). Films processed at a high temperature featured a weak magnetic anisotropy, but their magnetization in 5 kOe fields was higher (on the order of 62 emu/g). All films had weak coercive fields lower than 500 Oe. The potential for application of plasma treatment for altering radically the properties of materials was demonstrated through the example of magnetically hard barium hexaferrite.

Funding

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] D. Vinnik, A. Tarasova, D. Zherebtsov, S. Gudkova, D. Galimov, V. Zhivulin, R. Niewa, Materials, **10** (6), 578 (2017). DOI: 10.3390/ma10060578

[2] F. Khademi, A. Poorbafrani, P. Kameli, P., H. Salamati, J. Supercond. Novel Magn., **25** (2), 525 (2011). DOI: 10.1007/s10948-011-1323-1

[3] X. Dong, X. Zuo, Y. Wang, X. Cao, Y. Wang, M. Feng, J. Magn. Magn. Mater., **513**, 167073 (2020). DOI: 10.1016/j.jmmm.2020.167073

[4] S. Kumar, S. Supriya, M. Kar, Mater. Res. Express, **4** (12), 126302 (2017). DOI: 10.1088/2053-1591/aa9a51

[5] A. Gurbuz, N. Onar, I. Ozdemir, A.C. Karonglanli, E. Celik, Mater. Technol., **46** (3), 305 (2012).

[6] T. Kimura, G. Lawes, A.P. Ramirez, Phys. Rev. Lett., **94** (13), 137201 (2005). DOI: 10.1103/PhysRevLett.94.137201

[7] A.V. Trukhanov, V.G. Kostishyn, L.V. Panina, V.V. Korovushkin, V.A. Turchenko, P. Thakur, A. Thakur, Y. Yang, D.A. Vinnik, E.S. Yakovenko, L.Yu. Matzui, E.L. Trukhanova, S.V. Trukhanov, J. Alloys Compd., **754**, 247 (2018). DOI: 10.1016/j.jallcom.2018.04.150

[8] A.V. Trukhanov, V.O. Turchenko, I.A. Bobrikov, S.V. Trukhanov, I.S. Kazakevich, A.M. Balagurov, J. Magn. Magn. Mater., **393**, 253 (2015). DOI: 10.1016/j.jmmm.2015.05.076

[9] S.V. Trukhanov, A.V. Trukhanov, V.A. Turchenko, A.V. Trukhanov, E.L. Trukhanova, D.I. Tishkevich, S.A. Gudkova, Ceram. Int., **44** (1), 290 (2018). DOI: 10.1016/j.ceramint.2017.09.172

[10] E.Kh. Isakaev, O.A. Sinkevich, A.S. Tyuftyaev, V.F. Chinnov, High Temp., **48** (1), 97 (2010). DOI: 10.1134/S0018151X10010141.

[11] P. Sharma, R.A. Rocha, S.N. Medeiros, B. Hallouche, A. Paesano, J. Magn. Magn. Mater., **316** (1), 29 (2007). DOI: 10.1016/j.jmmm.2007.03.207

[12] T. Kahmann, E.L. Rösch, K. Enpuku, T. Yoshida, F. Ludwig, J. Magn. Magn. Mater., **519**, 167402 (2021). DOI: 10.1016/j.jmmm.2020.167402

[13] B.T. Shirk, W.R. Buessem, J. Appl. Phys., **40** (3), 1294 (1969). DOI: 10.1063/1.1657636

[14] Y. Goto, T. Takada, J. Jpn. Soc. Powder Powder Met., **7** (2), 35 (1960). DOI: 10.2497/jjspm.7.35

[15] G. Huang, Q. Zhang, M. Yu, Results Phys., **28**, 104572 (2021). DOI: 10.1016/j.rinp.2021.104572