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Magnetic and magneto-optical properties of thin films BaM hexaferrite grown on $Al_2O_3(0001)$ substrates by laser molecular beam epitaxy

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The results of a study of the structural, magnetic and magneto-optical properties of thin (thickness $h = 50-500$ nm) BaM ($BaFe_{12}O_{19}$) hexaferrite films grown on α-Al_2O_3 (0001) sapphire substrates by laser molecular beam epitaxy are presented. The crystal structure of the grown layers was studied by X-ray diffraction methods, and the static magnetic properties by a vibration sample magnetometer. The spectral dependences of the magneto-optical polar Kerr effect (PMOKE), transverse Kerr effect (TKE) and magnetorefractive effect (MRE^S) are presented.

Keywords: hexaferrites, thin films, magnetization processes, laser molecular beam epitaxy.

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Hexaferrites form a large class of ferrimagnetic materials that have various, often unique, magnetic properties, thanks to which they found wide application in creating various devices for transmitting and processing information using magnetostatic waves, creating permanent magnets, magnetic field sensors, etc. [1]. The presence of a 6th order symmetry axis in the crystal structure causes the appearance, depending on the chemical composition and type of crystal structure, of magnetic anisotropy of the type „easy axis" (easy magnetization axis), or „easy plane" (easy magnetic plane). Hexaferrite BaM ($BaFe_{12}O_{19}$) has high values of saturation magnetization ($4\pi M_s \approx 4.7$ kG) and uniaxial anisotropy field ($H_a \approx 17$ kOe), tending to orient the magnetization along the sixth-order axis. This makes it a promising material for creating thin-film structures in which the magnetization can be oriented normally to the plane without the magnetic field application. The frequency of ferromagnetic resonance (FMR) of thin-film structures based on hexaferrite $F \sim 50$ GHz [2].

Hexaferrite films were grown by laser molecular beam epitaxy on $Al_2O_3(0001)$ substrates. As our studies have shown by the methods of reflected electron diffraction (RHEED) and the polar magneto-optical Kerr effect (PMKE), the crystal structure of hexaferrite and the ferromagnetic properties of such films appear after their annealing in air at a temperature of 1000°C. To obtain information about the annealing effect on the crystal structure of films and their magnetic characteristics, in this paper, BaM films were studied using X-ray diffraction (XRD), magnetometric and magneto-optical methods.

XRD measurements were carried out on D2 Phaser powder X-ray diffractometer (Bruker AXS, Karlsruhe, Germany), in a vertical $\theta-\theta$ Bragg–Brentano geometry, equipped with a linear semiconductor position-sensitive detector LYNXEYE (Bruker AXS). Cu-K_α-radiation (wavelength $\lambda = 1.5418$ Å) of X-ray tube with a copper anode, filtered by a nickel foil filter was used.

XRD studies were also carried out using reciprocal space mapping. For this purpose Super Nova diffractometer (Agilent Technologies, Inc., Santa Clara, USA) with two-dimensional (2D) detector (CCD Atlas S2) and X-ray emitter with a copper anode ($\lambda = 1.5418$Å) was used. Mapping consisted of measuring a series of X-ray patterns depending on the angle of rotation around the normal to the sample.

Magnetization curves were measured using a vibrating-sample magnetometer (VSM) (Lake Shore Cryotronics, Westerville, USA) with the magnetic field oriented both along the normal („out-of-plane") and in plane of the structure („n-plane"). The magnetic field H varied from $+20$ to -20 kOe.

The spectral and field dependences of PMOKE were measured in the photon energy range 1.5–4 eV at room temperature in magnetic fields below $H = 15$ kOe. During measurements the magnetic field was perpendicular to the sample plane. The linearly polarized light incident from the monochromator was S-polarized. The spectral dependences of the transversal Kerr effect (TKE) were measured in „in-plane" magnetic field H oriented perpendicular to the plane of light incidence. The value $\mathrm{TKE} = \Delta I/I_0$, where $\Delta I = I(+H) - I(-H)$ and I_0 is the intensity of the reflected light in the demagnetized state. The magnetorefractive effect (MRE^S) was measured in the TKE geometry for S-polarization of the incident light. value $MRE^S(H) = \Delta I_{MRE}/I_0$, where $\Delta I_{MRE} = I(0) - I(H)$.

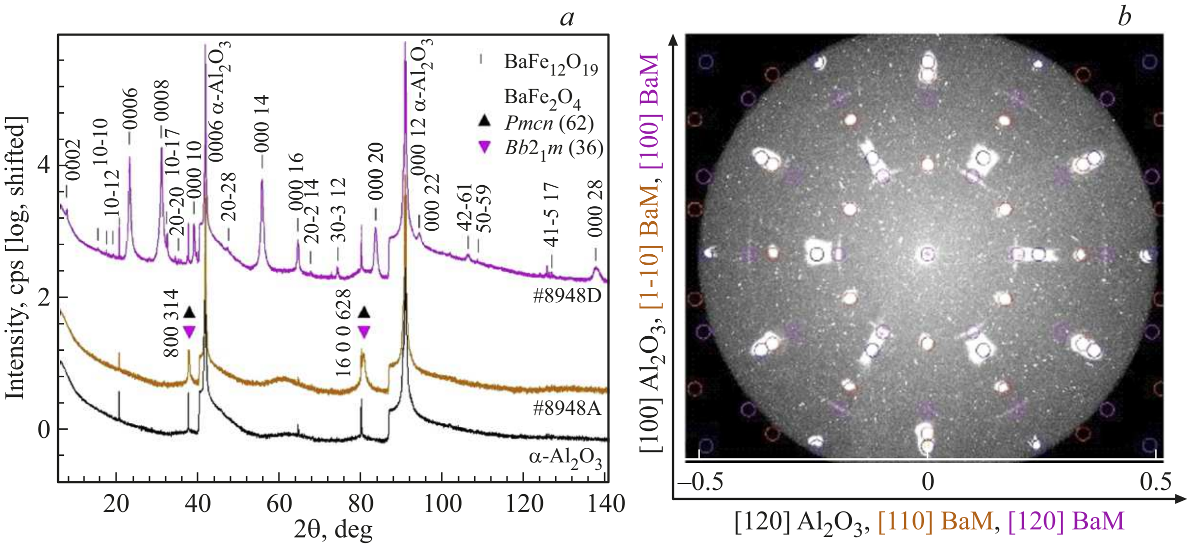

Figure 1. (*a*) XRD $\theta-2\theta$-scans from substrate α-$Al_2O_3(0001)$ and sample #8948 before (#8948A) and after (#8948D) annealing at 1000°C for 10 min. The Miller–Bravais indices *hkil* of the observed reflexes of BaM and the substrate α-Al_2O_3 and the Miller indices *hkl* of the observed reflexes of modifications $BaFe_2O_4$ are indicated. (*b*) Reciprocal space maps of an annealed sample 300 nm thick in various planes. Blue, red and purple circles correspond to Al_2O_3, the dominant BaM phase and the textured BaM phase, respectively.

Figure 1, *a* shows XRD $\theta - 2\theta$ scans from substrate $Al_2O_3(0001)$, („as-grown") structure #8948 after preparation, and of the same structure after annealing in air at temperature $T_{\text{ann}} = 1000^\circ$C. The X-ray diffraction pattern of „as-grown" film contains only two reflections, which are identified as reflections of different orders from similar parallel atomic planes of two possible orthorhombic modifications $BaFe_2O_4$ (space groups (sp. gr.) $Bb2_1m$ (36) and $Pmcn$ (62)). Reflections from a set of planes of another type are not observed, which indicates a strong main orientation of „as-grown" film. As per the Miller indices of reflexes, for two possible modifications of $BaFe_2O_4$ there is a predominant orientation along the directions [100] and [314], respectively. Annealing leads to the crystallization of hexaferrite $BaFe_{12}O_{19}$ (sp. gr. $P6_3/mmc$ (194)) with a predominant orientation along the direction $[hkil] = [0001]$ (Figure 1, *a*).

The results of XRD studies using the reciprocal space mapping method for the annealed sample 300 nm thick (Figure 1, *b*) show a good agreement between the model reciprocal lattice of BaM and the observed reflection reflexes. We can conclude that the dominant lattice of the BaM film is rotated by 30° relative to the sapphire lattice in the sample plane. However, it is clear that in the section made in the plane of the sample (Figure 1, *b*), in addition to the dominant BaM lattice (red circles), there are slightly textured domains with the same crystal lattice as the dominant one, but without turning by 30 degrees.

Studies of magnetization curves using VSM showed (Figure 2) that in annealed films $h = 50$ nm thick at orientation of the magnetic field H perpendicular to the plane of the structure („out-of-plane") almost rectangular hysteresis loops are observed. In annealed films $h = 350-500$ nm thick, the hysteresis loops are much wider, and their shape is far from rectangular. A significant difference in the magnetization curves of thin and thick films is observed when the magnetic field is directed in the plane of the film („in-plane") (Figure 2, *b*). Structurally perfect BaM hexaferrite films on $Al_2O_3(0001)$ substrates should have uniaxial anisotropy with the easy magnetic axis normal to the surface, therefore switching magnetization in „in-plane" geometry should occur in a reversible manner due to the magnetization rotation. A pronounced hysteresis loop in structure $h = 500$ nm thick (Figure 2, *b*) indicates a significant scattering in the orientation of the easy magnetic axis. The presence of a significantly weaker loop in the thin film #8948C in this geometry (Figure 2, *b*) indicates that orientation scattering of easy magnetic axis in it is significantly lower, i. e. the structure of this film is much closer to ideal.

Figure 3, *a* shows the spectral dependences of the polar (PMOKE) and transverse (TKE) Kerr effects in the structure #8948C. The spectrum of MRE^S is shown in Figure 3, *b*. A characteristic feature of PMOKE spectrum in BaM hexaferrite is the appearance of strong bands of different signs in the region $E_{ph} \sim 3.18$ eV (PMOKE $\approx -0.15^\circ$) and $E_{\text{ph}} \sim 4.6$ eV (PMOKE $\approx 0.28^\circ$) [3]. These bands were also observed in BaM films grown by organometallic decomposition [4] (at $E_{\text{ph}} \sim 3.15$ and 4.25 eV), as well as in $PbFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ prepared by sputtering [5]. The nature of these bands is associated with optical transitions with charge transfer (from Fe^{3+} ion to O^{2-}) for Fe^{3+} ions in octahedral and tetrahedral positions [3]. In Figure 3, *a* one can clearly see the manifestation of the PMOKE band at $E_{\text{ph}} \sim 3.2$ eV, a change in PMOKE sign at $E_{\text{ph}} \sim 3.6$ eV, and an increase in positive PMOKE values

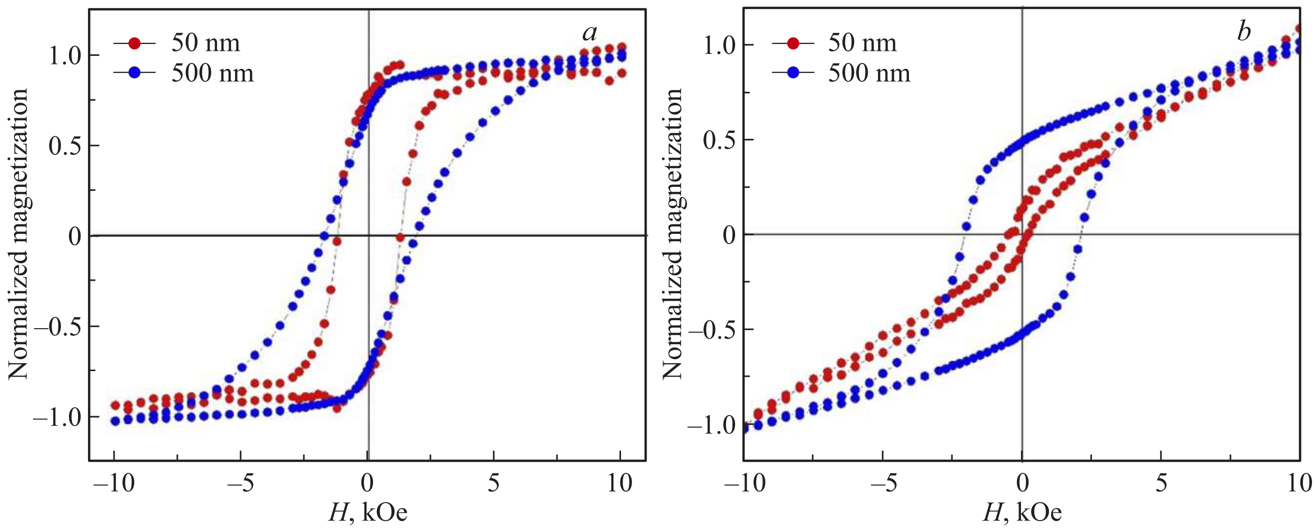

Figure 2. VSM-measured magnetization curves in annealed structures $h = 50$ nm thick (red dots) and $h = 500$ nm thick (blue dots) in (a) „out-of-plane“ and (b) „in-plane“ geometry.

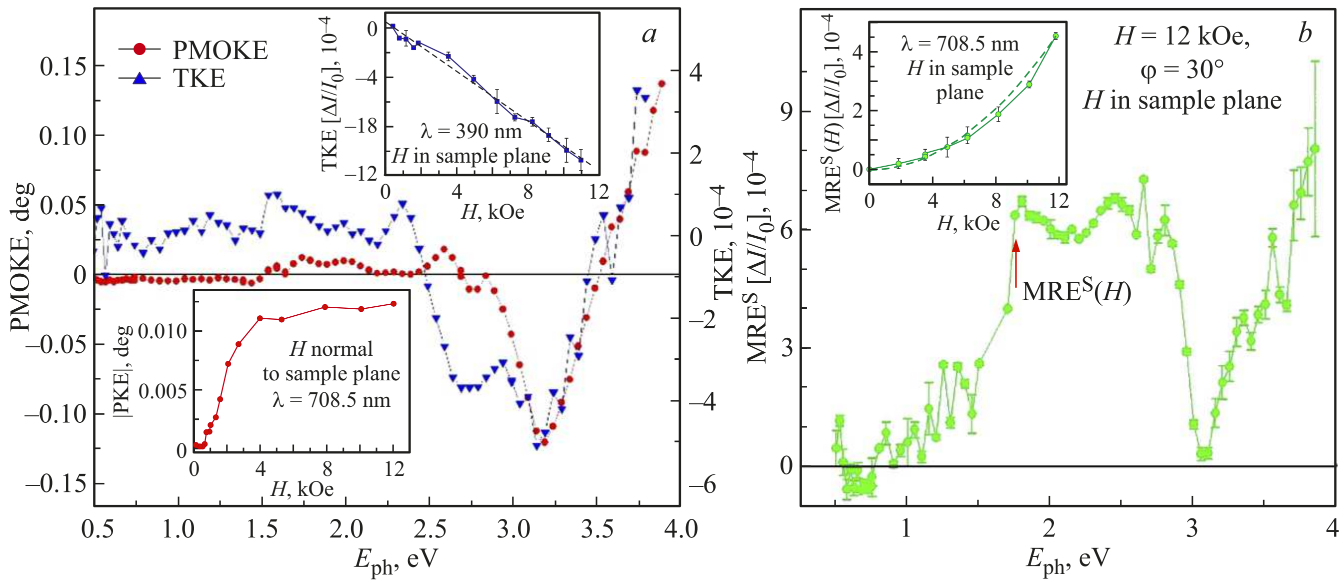

Figure 3. (a) Spectral dependences of the polar (PMOKE) and transverse (TKE) magneto-optical Kerr effect and (b) magnetorefractive effect spectrum (MRES) in the annealed structure #8948C (1 h, 1000°C). The lower left insert in (a) shows PMOKE vs. magnetic field H. The upper right insert in (a) shows TKE vs. H measured at $\lambda = 390$ nm. The dashed line corresponds to a linear line as per H fitting of the experimental points. The insert in (b) shows MRE^{S} vs. H at $\lambda = 708.5$ nm. Dashed line corresponds to square one as per H fitting of the experimental points.

above $E_{ph} \sim 3.6$ eV. Also, the band at $E_{ph} \sim 3.2$ eV appears in spectrum of TKE (Figure 3, a) and MRE^{S} (Figure 3, b).

The FMR band of the annealed structure #8948C at the frequency $F = 50$ GHz consists of a set of narrow lines with resonant fields in the range $H_{res} = 5.6-5.8$ kOe. The resonant field and main line width of FMR are $H_{res} = 5.76$ kOe, $\Delta H_{res} = 20$ Oe. The presence of lines at lower fields is apparently associated with the magnetic inhomogeneity of the layer due to the scattering of the anisotropy field, the direction of the easy magnetic axis, etc. Using the resonant field values for the main line $H_{res} = 5.76$ kOe, saturation magnetization $4\pi M_s = 4.3$ kG obtained using VSM, the measurement frequency $F = 50$ GHz, we obtained the estimate of the anisotropy field $H_a \cong 16.4$ kOe, which is close to the values $H_a = 17.0$ kOe in the structure $BaFe_{10.5}Mn_{1.5}O_{19}/Al_2O_3(0001)$ [6].

Thus, the study showed that in unannealed samples there is an orthorhombic phase of $BaFe_2O_4$ in one of two possible modifications. After annealing, the $BaFe_2O_4$phase disappears, and the hexagonal $BaFe_{12}O_{19}$ phase appears.

Only annealed structures exhibit magnetic properties. They contain loops with high remanent magnetization, which is necessary for microwave devices based on direct bulk spin waves. The narrowest and most rectangular loops appear in structures with thin ($h = 50$ nm) layers of hexaferrite. They exhibit narrow FMR lines with a half-width $\Delta H_{\text{res}} = 20$ Oe. In structures with layer thickness $h = 350-500$ nm the rectangularity of the loop decreases with h increasing. Magneto-optical spectra of annealed films show the presence of bands associated with electronic transitions with charge transfer in hexaferrite BaM.

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Conflict of interest

The authors declare that they have no conflict of interest.

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