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The phase composition and structure of the $BiFeO_3$ film grown on MgO(001) substrate by high frequency cathode deposition in oxygen atmosphere

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The crystal structure and Mossbauer spectroscopy studies results for $BiFeO_3$ film growth on the MgO(001) single crystal substrate are present in the paper. It been shown that film have high crystal perfection and low defectiveness which results in appearing of narrow lines during the $\theta - 2\theta$ and φ scanning and the small (lower than 0.7°) disorientation of film and substrate crystal axes. It is been revealed that unit cell of $BiFeO_3$/MgO(001) heterostructure possess monoclinic symmetry and deformation of unit cell is negligible. The Mossbauer study shows that magnetic subsystem of film has spatial spin-modulated structure with zero value of anharmonicity parameter (m). This indicate that at room temperature the magnetic anisotropy changes from the „easy axis" type to „easy plane" type.

Keywords: thin films, bismuth ferrite, Mossbauer effect.

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1. Introduction

As for now, the most well-known single-phase multiferroic is bismuth ferrite, $BiFeO_3$ (BFO), where ferroelectric and antiferromagnetic orderings are implemented at room temperature [2]. Temperatures of both phase transitions of BFO are considerably higher than room temperature ($T_C \sim 1100$ K; $T_N \sim 640$ K) [1–5], and residual polarization along the polar direction [111] achieves values, which are significant for ferroelectric materials $P_r \sim 100\,\mu C/cm^2$ [3,4]. This fact makes bismuth ferrite a prospective candidate for the use in high-density ferroelectric memories. In addition, many other properties were discovered in BFO, such as magnetoelectric, magnetodielectric, and photovoltaic effects, birefringence, which, in future, can promote application of this material in new functional electronics and various sensors. The history of BFO research dates back more than 50 years, it has been successfully produced in the form of ceramic, single crystals, thin films, and various nanostructures. However, it must be admitted that exactly with producing BFO in the form of thin film from the year 2003 [5], when unexpectedly large P_r and presence of ferromagnetism ($\sim 1.0\,\mu_B$ in the unit cell was shown), it became one of the most prospective multiferroics in the modern material physics. As of today, BFO thin films are already produced using various evaporation technologies: pulsed laser evaporation [6,7], sol-gel method [8], magnetron sputtering [9]. Due to the presence of numerous impurity phases emerging in the process of BFO synthesis, the technological cycle of heterostructures manufacturing based on it uses, for example, additional annealing after the synthesis [7,8] or preliminary evaporation of sublayers [6,9], which makes considerably more complicated the implementation of BFO in a real production cycle.

In this work, we have reported the results of research activities using mutually complementary methods of X-ray diffraction analysis and Messbauer spectroscopy of crystal and magnetic structures of BFO thin films grown on the surface of MgO(001) substrate by single-stage method in the atmosphere of oxygen.

2. Research targets. Methods of obtaining and research

$BiFeO_3$ films were evaporated by high-frequency sputtering in „Plasma 50 SE" plant (Shared Use Center SSC RAS № 501994) in the atmosphere of oxygen. MgO square single-crystal plates cut along its (001) plane with a thickness of 0.5 and an edge size of 12 mm were used as a substrate. Structural perfection of films, parameters of the unit cell and orientation relationships between the film and substrate were determined by X-ray difractometer RIKOR (Cu-radiation). Diffractometer was equipped with Ni filter, thus all X-ray patterns presented in this work have double reflections due to scattering of $CuK_\alpha 1$ and $CuK_\alpha 2$ components of the radiation. Messbauer spectra are measured using MS1104E Messbauer spectrometer. ^{57}Co in a Rh matrix was used as a source of γ-quanta. The

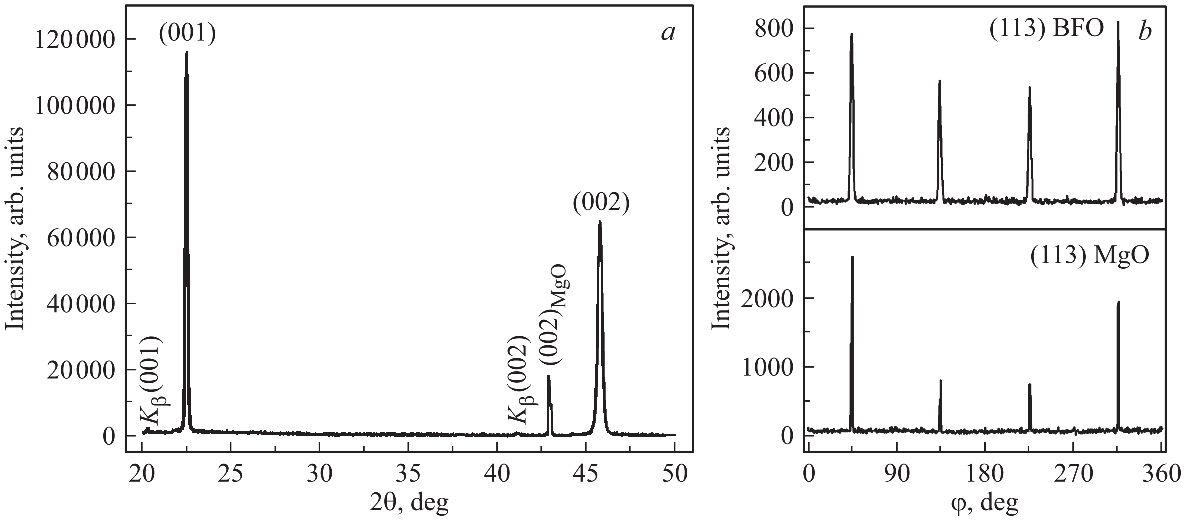

Figure 1. Diffraction pattern of BFO/MgO(001) heterostructure.

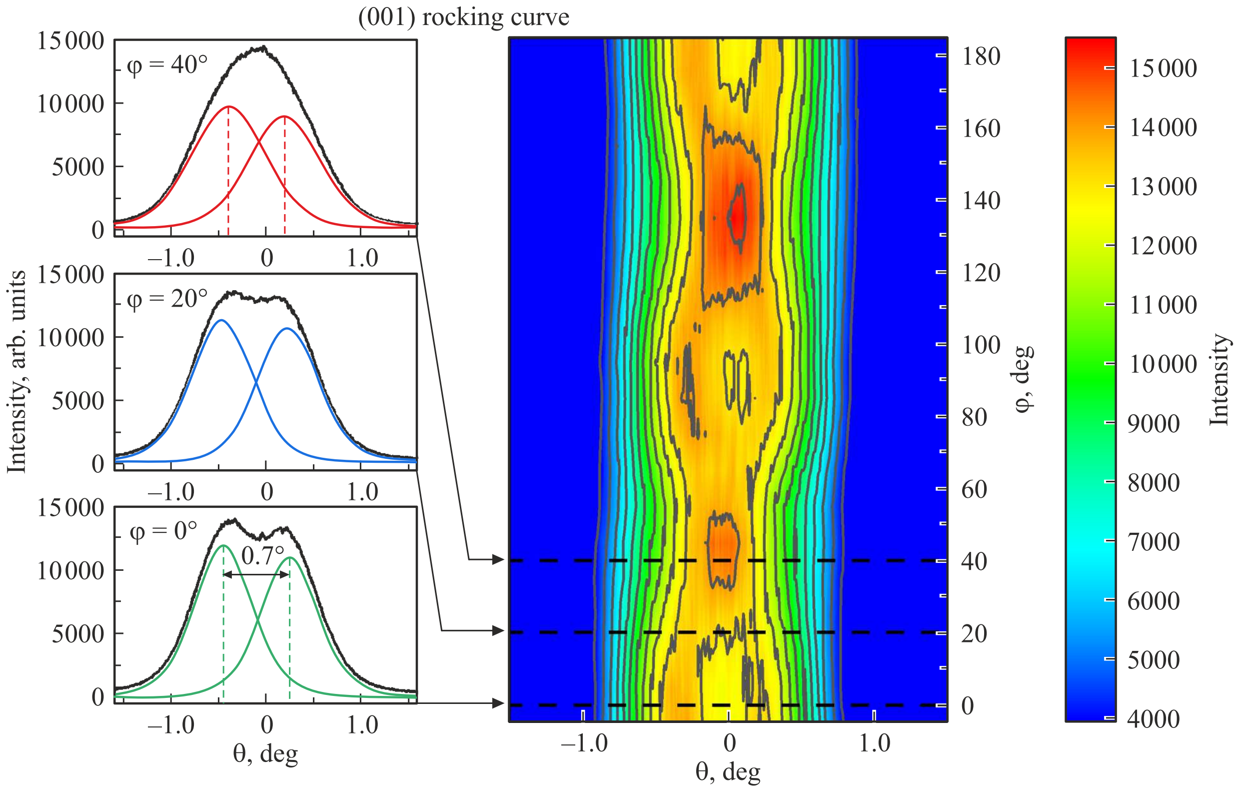

Figure 2. Rocking curves around the (001) reflection of BFO/MgO film recorded at different angles of φ.

model identification of spectra was carried out by means of SpectrRelax software [10]. Isomer shifts are referenced to α-Fe metal.

3. Experimental results and discussion

Results of X-ray diffraction measurements of a BFO/MgO film have shown that oriented growth is observed along with complete absence of impurity phase traces according to the data of $\theta - 2\theta$ scanning (Fig. 1, *a*). The results of φ scanning (Fig. 1, *b*) confirmed heteroepitaxial growth of the film (crystallographic axes of the film are directed parallel to axes of the substrate). However, a peculiarity was detected while recording the rocking curves — double peaks were observed instead of expected single peaks (Fig. 2). Moreover, with rotation in φ angle these peaks

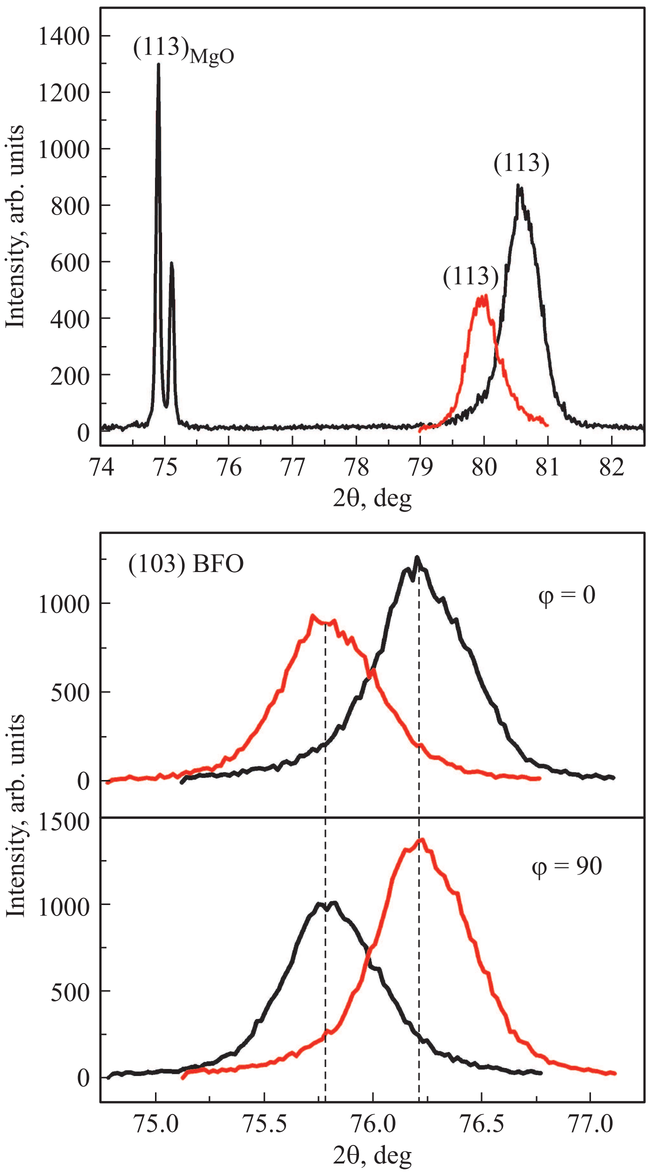

Figure 3. $\theta - 2\theta$ X-ray patterns of (113) and (103) reflections of BFO/MgO film; black and red lines are recorded at different angles of shift of the asymmetric geometry.

become closer to each other and then break up again. The specimen was installed in the diffractometer in such a way that angle $\varphi = 0$ corresponded to the specimen position when the X-ray beam was directed along axis [100] of MgO substrate, thus the recorded rocking curves with a rotation by φ represent 4 peaks oriented along axes [100] and [010] of the substrate. Similar pattern is observed for all (001) reflections. The distance between peaks at $\varphi = 0°$ is 0.7°, and each peak full width at half maximum that characterizes vertical misorientation of film axes, is not more than 1°. The presence of these peaks on the rocking curves along [100] and [010] axes of the substrate is related to the tilt of [001] axis by 0.35°. To investigate parameters of the unit cell in the interface plane, we recorded X-ray patterns of (113) and (103) reflections in the asymmetric geometry (Fig. 3). The analysis has identified two peaks in each of reflections, located at different shift angles of the asymmetric geometry. Locations of these peaks are independent on rotation by 90° in φ, however shift angles are swapped around. Locations of these peaks and shift angles of the asymmetric geometry confirm the guess of [001] film axis tilt by 0.35° along [100] and [010] axes. Based on the angular positions of X-ray lines, parameters of the unit cell were determined along normal to the surface and in the interface plane, which were found equal to each other: $a = b = 3.96 \pm 0.01$ Å, $c = 3.964 \pm 0.001$ Å. Thus, in a BFO film there are 4 types of grow units with monoclinic cells where [001] axis is tilted by 0.35°, and these units are rotated by 0, 90, 180 and 270° relative to each other. In the selected laboratory coordinate system it corresponds to four monoclinic cells with identical parameters $a = b = c = 3.964$ Å, but with different angles: 1) $\alpha = \gamma = 90°$, $\beta = 89.65°$; 2) $\alpha = \gamma = 90°$, $\beta = 90.35°$; 3) $\alpha = 89.65°$, $\beta = \gamma = 90°$; 4) $\alpha = 90.35°$, $\beta = \gamma = 90°$. The obtained parameters of the unit cell are almost coincident with those of the bulk BFO in pseudocubic approximation ($a = b = c = 3.965$ Å $\alpha = 89.3°$), which corresponds to almost full relaxation of stresses. These results were used in specimen positioning and in the analysis of results of Messbauer effect of BFO film presented below.

Fig. 4 shows Messbauer spectra of BFO/MgO film measured at room temperature. The antiferromagnetic ordering in bismuth ferrite and in solid solutions based on it has spatial spin-modulated structure (SSMS). The existence of SSMS results in an asymmetric structure and inhomogeneous broadening of Messbauer spectral lines. For the model identification of spectra like these a cycloid type SSMS model is applied. This model allows taking into account distortion of the Messbauer spectrum structure and determining parameters of the SSMS cycloid. The model uses spatial dependence of the $\vartheta(x)$ angle between the antiferromagnetism vector and the symmetry axis [11,12]:

$$\cos(\vartheta(x)) = sn\left(\frac{4K(m)}{\lambda}x, m\right) \quad \text{at} \quad K_u > 0, \qquad (1)$$

$$\sin(\vartheta(x)) = sn\left(\frac{4K(m)}{\lambda}x, m\right) \quad \text{at} \quad K_u < 0. \qquad (2)$$

where x — coordinate along the direction of wave propagation, λ — length of anharmonic wave of spin modulation, $0 \le m \le 1$ — parameter (anharmonicity) of Jacobian elliptic function $sn(x, m)$, $K(m)$ — full elliptic integral of the first kind.

In the SpectrRelax software [13] each value of $\vartheta(x)$ from the interval of $0 \le x \le \lambda$ corresponds to a Zeeman sextet with its isomer shift, quadrupole shift (ε) and hyperfine magnetic field $H_n(\vartheta)$. Quadrupole shift takes into account the quadrupole shift caused by local lattice distortions ε_{lat}, as well as the shift due to distortions caused by strong magnetoelectric interaction ε_{magn} [13]. Magnetic hyperfine

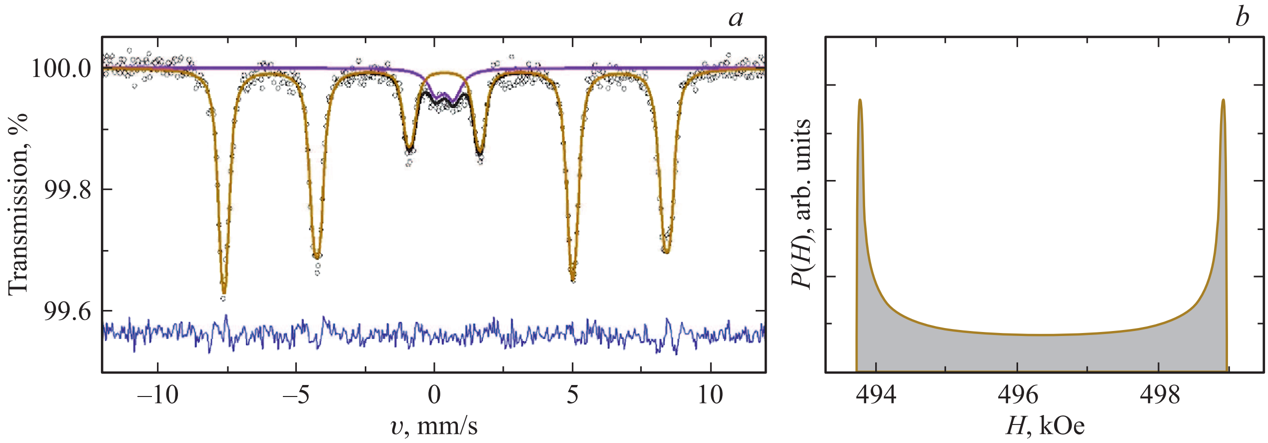

Figure 4. Messbauer spectrum of BFO/MgO film (*a*) and distribution of hyperfine fields (*b*) restored for this spectrum.

field is expressed as

$$H_n(\vartheta) = H_{is} + H_{an}\,\frac{(3\cos^2(\vartheta) - 1)}{2}, \qquad (3)$$

where H_{is} — isotropic contribution defined by contact Fermi interaction with s-electrons polarized by magnetic moment of ion, H_{an} — anisotropic contribution arising due to magnetic dipole-dipole interaction with magnetic moments of ions and anisotropy of the hyperfine magnetic interaction of nucleus with electrons of the ion core.

During the measurement of Messbauer spectrum the BFO film was installed with its (001) plane normal to the direction of γ-quanta propagation. Messbauer spectrum of the film specimen consists of a paramagnetic doublet and a SSMS-sextet. The doublet component with parameters of isomer shift $\delta = 0.39 \pm 0.01$ mm/s and quadrupole splitting $\Delta = 0.64 \pm 0.01$ mm/s corresponds to the paramagnetic impurity containing Fe^{3+} ions. Doublet area is $7 \pm 1\%$. Taking into account that X-ray diffraction measurement of the film, which was focused mainly on its central part in contrast to Messbauer measurement, has not detected signs of impurity presence, most probably it is localized at the substrate edges, where, as known, maximum temperature inhomogenuity exists due to technological reasons. SSMS-sextet has an isomer shift $\delta = 0.39 \pm 0.01$ mm/s, which corresponds to Fe^{3+} ions in the oxygen octahedron. The lattice contribution into the quadrupole shift is $\varepsilon = 0.21 \pm 0.01$ mm/s. At the same time, in this specimen the contribution from magnetoelectric interaction ($\varepsilon_{\text{magn}}$) is non-zero and equal to $\varepsilon_{\text{magn}} = -0.04 \pm 0.01$ mm/s. The emergence of this contribution is probably related to amplification of the magnetoelectric interaction in the specimen under research. The parameter of anharmonicity of the spatial spin-modulated structure is equal to zero, i.e. the cycloid is harmonic. Zero parameter m corresponds to the intermediate type of magnetic anisotropy ($K_u = 0$) between the „easy axis" ($K_u < 0$) type and the „easy plane" ($K_u > 0$) type [14]. The change of the magnetic anisotropy type is related to two competing contributions into the effective magnetic anisotropy. The first contribution is the constant anisotropy of antiferromagnetism, and the second contribution is defined by the weak ferromagnetic Dzyaloshinskii–Moriya interaction [14]. An increase in temperature will result in emergence of magnetic anisotropy of the „easy plane type, and a decrease in temperature will result in the „easy axis"type of anisotropy [14].

4. Conclusion

1. Using the HF-cathode evaporation method epitaxial films of BFO on MgO(001) substrate were produced. It is found that the unit cell has monoclinic symmetry; at the same time the evaporation of film with a thickness greater than 1 mkm made it possible to achieve almost full strain relaxation of the unit cell.

2. In the BFO film antiferromagnetic ordering with spatial spin-modulated structure of cycloid type is implemented. The anharmonicity parameter of the cycloid is equal to zero, which corresponds to the case of zero constant anisotropy $K_u = 0$.

3. A guess is made that in the specimen under research in the vicinity of room temperature the type of magnetic anisotropy changes from the „easy axis" to the „easy plane".

4. It makes sense to use the obtained results in producing heterostructures based on bismuth ferrite thin films and investigating their properties.

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Conflict of interest

The authors declare that they have no conflict of interest.

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