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Influence of the ZnO buffer layer on the magnetic properties of the BiFeO₃ thin film on sapphire

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Thin layers of bismuth ferrite on an Al₂O₃ (C-plane) sapphire substrate with a ZnO zinc oxide buffer layer were synthesized by gas-discharge high-frequency cathode sputtering of a ceramic target of stoichiometric composition BiFeO₃ in an oxygen atmosphere. The structure, magnetic and optical properties of the BiFeO₃/ZnO/Al₂O₃ film are investigated. X-ray diffraction measurements and Raman spectra of the deposited films confirm the formation of a crystalline phase of thin layers of BiFeO₃ and ZnO. Based on the results of optical studies, the band gap for the direct transition is 2.51 eV. Magnetic hysteresis loops ($M - H$) of a thin BiFeO₃ film with a ZnO buffer layer exhibit the behavior characteristic of ferromagnets. It is shown that the magnetization of BiFeO₃ is significantly higher (almost five times) in a BiFeO₃/ZnO/Al₂O₃ film compared to a film without a buffer layer, which indicates the important role of the ZnO buffer layer in improving the magnetic properties of bismuth ferrite for practical applications.

Keywords: multiferroics, BiFeO₃, ZnO, thin films, magnetic properties.

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1. Introduction

Ferroelectromagnetic compounds-multiferroic materials are treated as promising materials for creation of data storage devices for next generation nanoelectronic and spintronic applications [1]. One of the most promising compounds are multiferroic materials based on BiFeO₃ (BFO), which is to a great extent associated with high temperatures of antiferromagnetic ($T_N \sim 643$ K) and ferroelectric ordering ($T_C \sim 1103$ K) [2]. In the range of temperatures below the Neel point T_N , bismuth ferrite has a complex cycloid type spatially modulated magnetic structure which avoids the presence of ferromagnetic properties [3,4]. Destruction of the spatially modulated spin structure is a prerequisite for the magnetoelectric effect to occur, which can be achieved by doping bismuth ferrite with rare earth elements, creating nanocrystalline materials (thin films), etc. Certain success in the improvement of multiferroic properties of BFO has been achieved over the past decade, however, BiFeO₃ has a set of problems, in particular, those associated with the presence of accompanying phases with nonstoichiometric oxygen deficiency [5–7], etc.

Keen interest is currently shown to low-dimensional BFO-based multiferroic materials demonstrating high magnetoelectric effect [8–10]. Some studies show that, for

enhancement of magnetization and polarization (i.e. magnetoelectric effect) of BFO films, buffer layers (in particular, zinc oxide) may be used, which expands the range of applications of these materials [11]. Creation of heterostructures on the basis of ZnO and BiFeO₃ films as a functional component offers great opportunities for various applications, in particular, creation of high-performance broadband-response photovoltaic devices and light-controlled nonvolatile memory [12–14]. ZnO is a semiconductor oxide that demonstrates a piezoelectric wurtzite structure and, therefore, irreversible spontaneous polarization. Thus, it is important to study potential use of ZnO as a buffer layer for the BiFeO₃ thin film growth and potential future applications. Moreover, there are few studies reporting formation of ZnO ferroelectric materials, in particular, BiFeO₃ multiferroic materials. ZnO is a semiconductor oxide that demonstrates a piezoelectric wurtzite structure and, therefore, irreversible spontaneous polarization. The objective of this study is to synthesize BFO thin layers with a ZnO buffer layer to increase magnetization (and, thus, to enhance the magnetoelectric effect).

The work describes the examinations of the structure and magnetic properties of BiFeO₃ thin films on sapphire with a ZnO buffer layer fabricated by the magnetron sputtering method.

2. Samples and research methods

Gas-discharge RF sputtering of BiFeO₃ films was performed using the „Plazma 50SE“ unit (ELITEKH, Russia) designed to fabricate thin single-crystal complex oxide films by the reactive RF sputtering method. Single-crystal Al₂O₃ (0.5 mm thick) with a buffer layer made of ZnO thin film was used as a substrate. Initial substrate temperature was ~ 670 K, oxygen pressure in the chambers was 80 Pa, input RF-power was 140 W. A ceramic disc of the stoichiometric BiFeO₃ compound with a diameter of 50 mm and thickness of 3 mm was used as a target. It is introduced into the service volume from the vertical support and is perpendicular to the axis. The target is attached to an aluminum alloy holder using an adhesive composition consisting of the K-400 high-temperature vacuum-tight adhesive and boron nitride powder filling used to increase dielectric permittivity of the adhesive bonding joint and to reduce the voltage drop. The ZnO thin film buffer layer was deposited onto the Al₂O₃ sapphire substrate (a-section 0001) by the magnetron sputtering method with the following synthesis parameters: substrate temperature ~ 650 K and sputtering time 30 min. Chamber pressure — 1.2×10^{-2} mm Hg, service gas-O₂. Thickness of the film fabricated in this way was equal to 150 nm.

X-ray diffraction pattern of the thin film sample on the substrate was recorded using the XRD-7000 diffractometer (Shimadzu, Japan). The sample was placed on a thin film examination module for radiography. The following radiography parameters were used: X-ray tube voltage 30 kV, current 30 mA; Z-ray wavelength CuK = 1.5406 Å; beam focusing configuration — Grazing Incidence X-Ray Diffraction — GIXD; incident beam slit DS = 0.15; graphite reflected beam monochromator. Measurements were conducted at room temperature $T = 25^\circ\text{C}$ (298 K).

The Ntegra Spectra atomic-force microscope was used for measuring the surface topology of the grown samples and recording the Raman scattering spectra ($\lambda = 532$ nm laser). Magnetic measurements were performed at room temperature using the Lakeshore VSM 7404 vibration magnetometer. Chemical analysis of the film was performed by the energy-dispersive X-ray spectroscopy method (EDX spectra, ASPEX Express). Optical properties were measured using the Avasphere-50 integrating sphere (Avantes, Apeldoorn, Nederland) in the wavelength range $\lambda \sim 350\text{--}1000$ nm. The AvaLight-DH-S-BAL combined deuterium/halogen bulb (Avantes, Apeldoorn, Nederland) was used as a source of light to deliver the light to the samples via a 600 μm fiber-optic lightguide. Photon signals were collected using a 600 μm bifurcated waveguide and recorded by the MS3504i spectrometer (SOL-Instruments, Minsk, Belarus) combined with the HS-101(HR)-2048 $\times$ 122 CCD camera (Hamamatsu, Japan) and a PC.

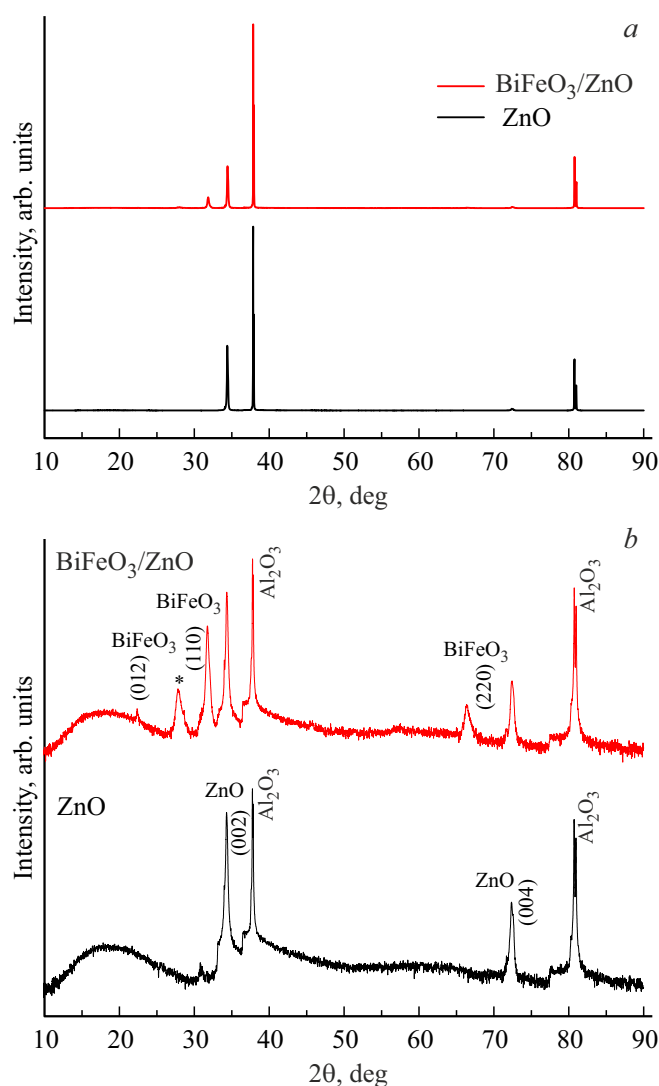


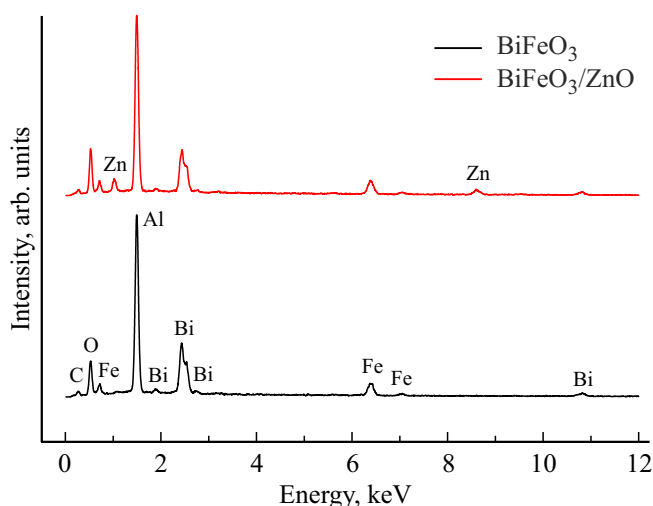
Figure 1. X-ray diffraction pattern of the BiFeO₃/ZnO and ZnO film on the Al₂O₃ substrate.

3. Findings and discussion

X-ray diffraction patterns of the ZnO and BiFeO₃/ZnO films are shown in Figure 1 (for better resolution of low intensity peaks, the curves are shown in the semi-logarithmic scale, Figure 1, b). The ZnO film, besides the diffraction peaks assigned to the sapphire substrate (37.88° and 80.76°), has typical diffraction peaks (002) and (004) or the ZnO films located at approx. 34.4° and 72.4°. ZnO film demonstrates typical peaks of the hexagonal wurtzite structure that are indicative of formation of a well crystallized pure ZnO phase. The BiFeO₃/ZnO film in turn demonstrates a similar diffraction picture as the ZnO film with an additional set of peaks assigned to the BiFeO₃ phase: (012) ~ 22.54°, (110) ~ 31.86°, (220) ~ 66.42°. In addition, a peak at ~ 27.92° assigned to the Bi₂₅FeO₄₀ phase is also observed.

Table 1.

Modes	BiFeO ₃ /ZnO	Film BiFeO ₃ /c-sapphire [9]	Film [10]	Powder [11]	Calculated values [12]	Single crystal [13]
E-1	—	75		72	102	77
A1-1	145.82	142	139	139	152	147
A1-2	172.36	172	170	170	167	176
A1-3	220	219	217	216	237	227
E-2	253.12	260	261	—	266	136
E-3	276.5	275	274	270	274	265
E-4	306.2	—		—	318	279
E-5	348	343	346	344	335	351
E-6	381.86	370	370	—	378	375
A1-4	413.65	522	430	466	409	490
E-7	480.1	468	470	—	—	437
E-8	527.45	548	522	547	509	473
E-9	617.9	609	605	621	517	525

Figure 2. EDX spectra of the BiFeO₃ and BiFeO₃/ZnO films.

Moreover, chemical analysis of films was performed using the energy-dispersive X-ray (EDX) spectroscopy. EDX spectra (Figure 2) were recorded in some selected areas on the sample and all they showed the expected presence of Bi, Fe, Zn and O content of which additionally demonstrates the purity and co-existence of BFO and ZnO in the BiFeO₃/ZnO film.

Raman scattering (RS) is one of the essential tools used to examine structural features. Despite the fact that BFO was widely studied by the Raman-scattering spectroscopy method, there is discrepancy in results reported in the literature. Figure 3 shows the Raman scattering spectra of the BiFeO₃/ZnO thin film at room temperature. According to the group theory [15], rhombohedral BFO with space group *R3c* is characterized by thirteen ($4A_1 + 9E$) active modes. For better peak resolution and position refinement, the spectrum was fitted using the Gaussian function and decomposed into separate peaks.

Observed and recorded Raman scattering modes for BiFeO₃ are listed in Table 1. A total of 12 modes were identified: The modes with the most intense peaks at 146.64, 170.59, 218, and one weak peak at 413.65 cm⁻¹ may be assigned to transverse optical (TO) modes *A*₁, while the other peaks may be assigned to E(TO) modes as shown in Table 1.

The observed results agree with the previous results in [15–20], however, there are some differences in positions and intensities of peaks which may result from the presence of high angular dispersion between the incident laser light and the [111] direction of the pseudo cubic crystal [16,21]. The differences might be probably associated with the use of different film deposition methods and types of substrates.

RS spectra of the studied material correspond to the expected ones and confirm that BiFeO₃ has been formed.

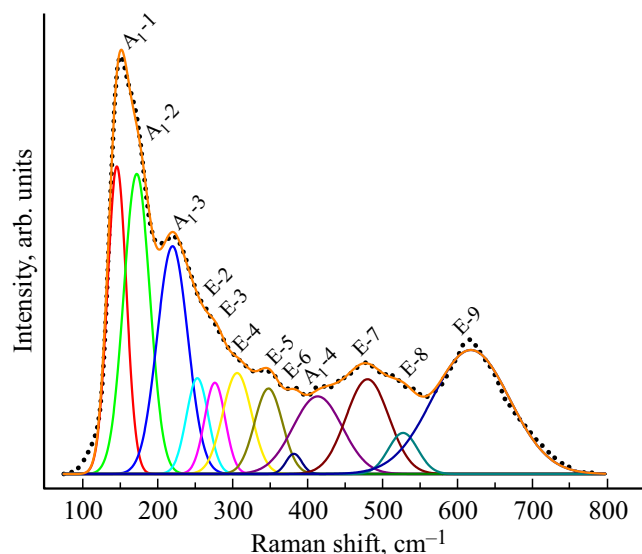
Figure 3. Raman scattering spectrum of the BiFeO₃/ZnO thin film.

Table 2.

Sample	M_s , (emu/cm ³)	M_r , (emu/cm ³)	H_c , (Oe)	M_r/M_s
BiFeO ₃	4.92	1.13	99.46	0.23
BiFeO ₃ /ZnO	21.88	4.26	74.5	0.19

Note that there are no peaks typical of ZnO probably due to the thickness of the BiFeO₃ layer.

Optical properties of the BiFeO₃/ZnO thin film were studied in the wavelength range of $\lambda \sim 350\text{--}1000$ nm. The absorption spectrum is shown in Figure 4, *a*. The sample demonstrates ultraviolet and visible absorption. Optical band gap (E_g) may be estimated using the Tauc relation [22]:

$$(\alpha h\nu) = K(h\nu - E_g)^n,$$

where α is the absorption coefficient, $h\nu$ is the photon energy, K is the constant, n is the coefficient characterizing the direct or indirect optical transition. Band gap is defined

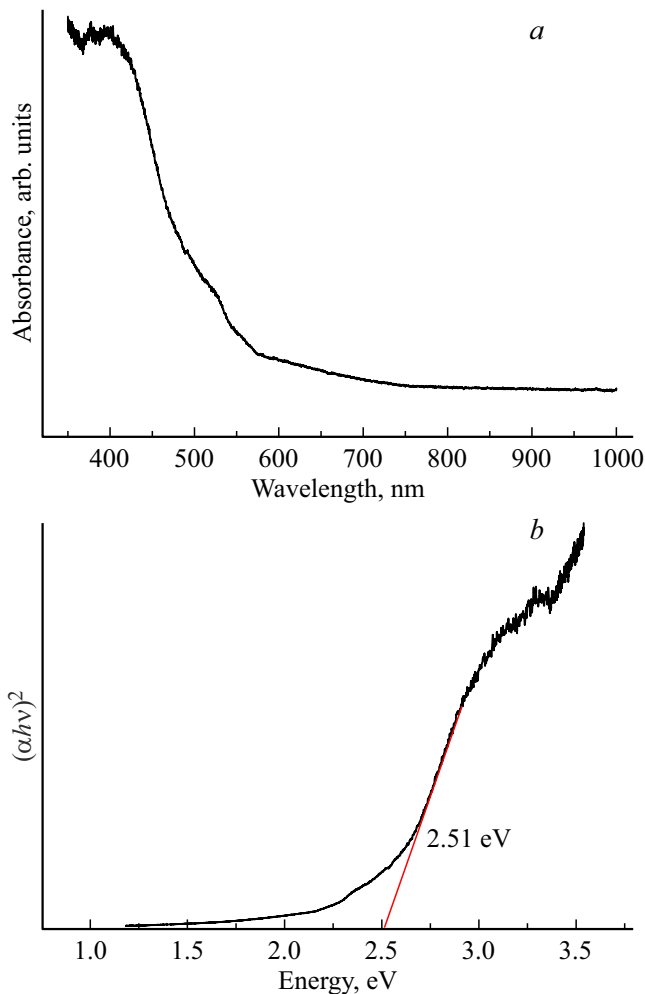


Figure 4. UV visible spectrum of the BiFeO₃/ZnO thin film (*a*) and the Tauc plot $(\alpha h\nu)^2$ depending on $h\nu$ (*b*).

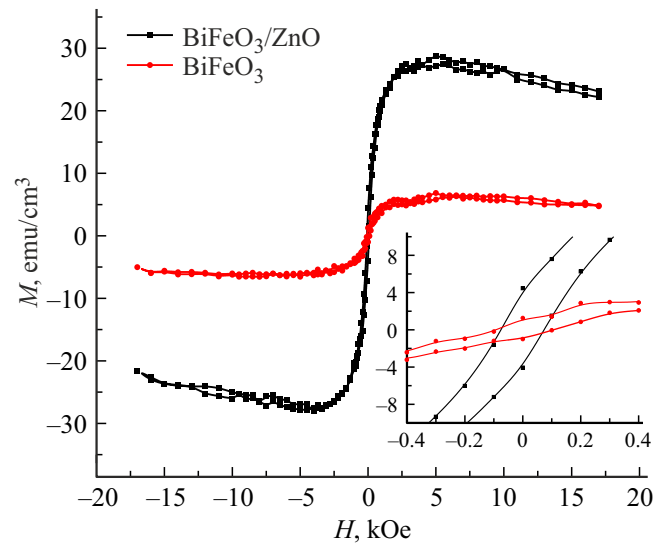


Figure 5. Magnetic hysteresis loops $M-H$ of the BiFeO₃/ZnO and BiFeO₃ films.

by interpolation of the linear section of the plot on the X axis (Figure 4, *b*).

In this case, direct optical transition with the band gap of 2.51 eV is observed. The existing literature indicates a wide band gap range (2.1–2.8 eV) for BiFeO₃ and reports that both direct and indirect electronic photoexcitation exist in BiFeO₃ at room temperature. However, the indirect charge transfer mechanism is believed to prevail at low room temperatures [23].

Figure 5 shows the magnetization curves ($M-H$) of the BiFeO₃/Al₂O₃ and BiFeO₃/ZnO/Al₂O₃ films demonstrating the ferromagnetic behavior of magnetization.

Coercive force (H_c), saturation magnetization (M_s) and residual magnetization (M_r) of films determined from ratios ($M-H$) are listed in Table 2. It can be seen that the saturation magnetization ($M_s \sim 21.88$) and residual magnetization ($M_r \sim 4.26$) of a film with the BiFeO₃/ZnO buffer layer are almost five times higher than those of the BiFeO₃ film ($M_s \sim 4.92$, $M_r \sim 1.13$).

As shown in Figure 5, the saturation magnetization decreases slightly as the magnetic field increases to 2 T, which might be associated with strong anisotropic effects in the BiFeO₃/ZnO film. In [11], study of the BiFeO₃/ZnO/Si films also showed increased saturation magnetization compared with the BiFeO₃/Si film. This indicates that the spin structure of our BiFeO₃ film is to a great extent changed by the bottom ZnO layer in the BiFeO₃/ZnO/Al₂O₃ film. Magnetization strengthening in BiFeO₃ is generally limited to the size effects (when the grain size becomes smaller than the spin cycloid ~ 62 nm) or to the existence of Fe²⁺ valence (together with Fe³⁺) at thicknesses lower than 100 nm due to the presence of oxygen vacancies [24,25]. Work [25] studies in detail the effect of content of Fe²⁺ on the magnetization of the BiFeO₃ films in the thickness range from 30 to 120 nm. The X-ray photoelectron spectroscopy

method shows that at film thicknesses more than 100 nm the content of Fe^{2+} resulting from oxygen vacancies, i.e. magnetization in the films with thickness BiFeO_3 100 nm is much lower [25]. In our case, the thickness of the deposited BiFeO_3 films was ≈ 150 nm, therefore possible influence of Fe^{2+} due to the oxygen vacancies may be ignored.

Thus, the nanostructured ZnO buffer layer used in the BiFeO_3 film presumably leads to disturbance of the antiferromagnetic order with suppression of the cyclod spin structure, which induces additional magnetic moment that strengthens the magnetization.

4. Conclusion

The study used gas-discharge radio-frequency cathode sputtering of a ceramic target with the stoichiometric BiFeO_3 composition in oxygen atmosphere to synthesize BiFeO_3 thin films on the Al_2O_3 sapphire substrate with the ZnO buffer layer. Structure and magnetic properties of the $\text{BiFeO}_3/\text{ZnO}$ thin layers on the Al_2O_3 substrate were investigated. magnetization of the $\text{BiFeO}_3/\text{ZnO}$ film is approximately five times higher than that of a film without a buffer layer. Such ferromagnetism strengthening might result from suppression of the antiferromagnetic spin screw structure by the ZnO buffer layer. Strengthening of the BFO magnetization due to the ZnO buffer layer is an effective method to control the magnetoelectric effect of BiFeO_3 -based multiferroic materials.

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Conflict of interest

The authors declare no conflict of interest.

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