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# Lattice Dynamics of Heterostructures Based on Bismuth Ferrite and Barium Strontium Titanate

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**Abstract**

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Compounds that exhibit simultaneously at least two of the three types of ordering: ferromagnetic, antiferromagnetic, or ferroelectric Ferroelastic called multiferroics. Magnetoelectric interaction ordered subsystems in them leads to the appearance of new physical effects which are of interest for spin electronics. Bismuth ferrite $BiFeO_3$ (BFO) belongs to the class of multiferroics with coupled magnetic and ferroelectric properties. Bismuth ferrite belongs to the first order type of multiferroics, in which the ferroelectric phase transition temperature ($T$c = 1083 K) exceeds the temperature of antiferromagnetic ordering ($T_N$ = 643 K), but the existence of the cycloid leads to the fact that the volume-averaged linear magnetoelectric effect and spontaneous magnetization are zero, which makes it impossible for practical use. Abnormally high values of the spontaneous polarization and the magnetoelectric effect were achieved in epitaxial thin films of $BiFeO_3$ due to distortions of the crystal structure, resulting in the destruction of the cycloidal ordering and existence of antiferromagnetic ordering of G-type with weak ferromagnetism.

The number of substrates for the deposition of thin films of complex oxides with a perovskite structure is very limited, so the distortion of the crystal structure during the deposition of epitaxial films of bismuth ferrite are possible due to the use intermediate (buffer) layer between the film and the substrate. Thus, the features of structure and lattice dynamics of multilayer heterostructures based on multiferroics can be detected using an effective method of Raman spectroscopy (RS).

In the **introduction** the relevance of the topic, purpose and objectives formulated, shows scientific novelty and practical significance of the main results and conclusions are presented the basic scientific principles for the defense, probation work and personal contribution of the author. In the **first** section of the thesis an analytical review is presented, the known features of structure and lattice dynamics of bismuth ferrite in the form of ceramics, crystals and thin films were analyzed. From the analysis of the available literature, it is clear that the sequences of phase transitions in epitaxial BFO, as well as the temperature coexistence region of magnetic and polar orders may differ significantly from that observed in bulk materials. Below the Curie temperature ($T_C$ =1083 K), the crystal structure of single crystal bismuth ferrite is described by the space group *R3c*. The rhombohedral unit cell (a = 0.562 nm, α = 59.35°) contains two formula units. In recent years, epitaxial BFO films have been synthesized on various substrates and buffer layers. It has been found that, apart from the rhombohedral phase, in epitaxial BFO films, there are different structural distortions not observed in the bulk material, such as tetragonal, orthorhombic, and monoclinic.

In the **second** section the author presents the results of studies of surface morphology, lattice parameters and Raman spectra on stagesof sequential formation of a three-layer heterostructure BST / BNFO / BST on (001) MgO substrates. The multilayer heterostructures BST, BNFO/BST and BST/BNFO/BST with thicknesses of each layer of 80 nm on (001) MgO single crystals were fabricated using two high-frequency sputtering systems. The structural perfection of the films, unit cell parameters in the direction normal to the plane of the substrate, and orientation relationships between the film and the substrate at room temperature were established using X-ray diffraction on a Rigaku Ultima IV diffractometer (high-resolution configuration for the investigation of thin films; Ge primary beam monochromator; $CuK\alpha_1$ radiation). The X- ray diffraction investigations were performed in the $2\theta$–$\omega$ scan mode and the $\phi$ scan mode. The surface morphology of the epitaxial thin films BST, BNFO/BST и BST/BNFO was examined with an Integra atomic force microscope (AFM). The measurements were carried out in the contact mode using a CSG10 cantilever. The Raman scattering spectra were excited by polarized radiation from an argon laser ($\lambda$ = 514.5 nm) and recorded on a single-pass Raman spectrometer (Renishaw) equipped with a NExT filter (Near-Excitation Tuneable filter) for the analysis in the low-frequency region of the spectra. The exciting radiation was focused on the sample using a Leica optical microscope. The diameter of the focused beam on the sample was 2 μm. The polarized micro-Raman spectra were measured on the samples precisely oriented in accordance with the crystallographic axes of the substrate: $X \parallel [100]$, $Y \parallel [010]$, and $Z \parallel [001]$.

At thicknesses of layers BST and BNFO about 80 nm it was observed their interaction, in which the crystal structure is distorted during sequential deposition of layers. Thus, when deposition BNFO layer on the surface of the film BST the degree of tetragonal distortion of BST layer increases, indicating the occurrence of compressive stresses in the BST due to difference in the lattice parameters of the upper and lower epitaxial layers. From X-ray diffraction and Raman studies it was found that deposition of the third layer BST on the surface of the heterostructure BNFO / BST / (001) MgO results in a partial relaxation of the compressive stress and a decrease in the tetragonal distortion of the first layer. Furthermore, from the polarized Raman spectra of epitaxial heterostructures BFNO / BST / MgO and BST / BFNO / BST / MgO identified particular structural distortion of their layers and found that the symmetry of the BNFO layer in the heterostructure BFNO / BST / MgO is lowered from rhombohedral to orthorhombic or monoclinic.

In the **third** section the author presents the study of the temperature dependences of the Raman spectra of epitaxial films BFO grown by pulsed laser deposition on the substrate (001) MgO and (111) MgO using buffer layers SRO and STO. For the epitaxial growth a buffer layers of STO 10 nm, and then SRO 20 nm were deposited on the substrate. A 45-nm-thick BFO film was deposited under an oxygen pressure of 0.3 mbar at a temperature of 750°C. Phonons of the first order in the Raman spectra of the film BFO / SRO / STO / (001) MgO are observed at frequencies below 600 $cm^{-1}$, while the region of 600 ... 1200 $cm^{-1}$ corresponds to the two-phonon transitions. In the Raman spectra of the film BFO / SRO / STO / (001) MgO the observed line 610 $cm^{-1}$ corresponds to the maximum density of states of magnon branch at the Brillouin zone boundary. This line is activated in the Raman spectra due to violations of the wave vector selection rules due to defects in the film studied. Intense band in the second-order spectra of the BFO / SRO / STO / (001) MgO film with a maximum of ~ 1270 $cm^{-1}$ corresponds to the density of states of two-magnon excitations. From the temperature dependence of the Raman spectra of the film BFO / SRO / STO / (001) MgO it was found that two-magnon scattering band is observed up to ~ 650 K. The temperature dependence of the intensity and half-width of the two-magnon peak in the film BNFO are similar to those previously observed in a number of antiferromagnets. In the film BNFO / (111) MgO the two-magnon scattering was observed significantly higher $T_N$ of bulk BFO, which indicates the presence of spin correlations up 900 K.

In the **fourth** section the author showed the temperature dependence of the Raman spectra of the bismuth ferrite films, doped with neodymium ($Bi_{0.98}Nd_{0.02}$) $FeO_3$ (BNFO), grown on MgO substrates of different orientations, as well as BNFO films, grown on buffer layers BST. All samples studied were fabricated by rf cathode sputtering in SSC RAS. Despite the differences in the structural distortions BNFO films in heterostructures BNFO / BST / (111) MgO and BNFO / BST / (001) MgO the temperature behavior of the two-magnon scattering in them reveals general features. The intensity of the two-magnon band decreases rapidly with increasing temperature, but above $T_N$ = 643 K this band does not disappear until 900 K.

Temperature dependence of the two-magnon scattering in Raman scattering indicates the existence of spin correlations above the antiferromagnetic transition in several samples studied.

In conclusion, we can say that due to compressive stresses arising in the heterostructure BST / BNFO / BST / (001) MgO at deposition layer BNFO thickness of 80 nm on the film BST / (001) MgO, the lattice parameter c of BST layer is increased by 0.2%, but with a further deposition on two-layer structure BNFO / BST / (001) MgO another layer of BST its lattice parameter c decreases by 0.12%. In the films of bismuth ferrite the two-magnon excitation dominate with respect to two-phonon, as evidenced by the spectral response in the Raman spectrum with a peak in the region 1260 $cm^{-1}$, corresponding to the density of states of two-magnon excitations. As well, the intense magnon scattering in the films of bismuth ferrite is observed up to the Neel temperature and does not depend on the nature of the cut of the substrate or by doping neodymium, which proves the stability of the antiferromagnetic order in this class heterostructures. In addition, it was demonstrated that the Raman spectroscopy can be used to control the presence of the magnetically ordered state by examining the temperature dependence of the two-magnon scattering.