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Correlation of magnetoelectric coupling in multiferroic BaTiO₃-BiFeO₃ superlattices with oxygen vacancies and antiphase octahedral rotations

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Multiferroic (BaTiO₃-BiFeO₃) × 15 multilayer heterostructures show high magnetoelectric (ME) coefficients α_{ME} up to 24 V/cm-Oe at 300 K. This value is much higher than that of a single-phase BiFeO₃ reference film ($\alpha_{ME} = 4.2$ V/cm-Oe). We found clear correlation of ME coefficients with increasing oxygen partial pressure during growth. ME coupling is highest for lower density of oxygen vacancy-related defects. Detailed scanning transmission electron microscopy and selected area electron diffraction microstructural investigations at 300 K revealed antiphase rotations of the oxygen octahedra in the BaTiO₃ single layers, which are an additional correlated defect structure of the multilayers. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4905343>]

In the design of advanced multiferroic materials, multi-phase multilayers are an attractive and successful approach to overcome the limitations of intrinsic single phase multiferroics such as the small magnetoelectric coupling coefficient of BiFeO₃.¹ Composite structures including multilayers may “take advantage of the specific coupling between the individual components”¹ to obtain properties that are absent in the individual constituent phases. Among the possibilities to obtain an enhanced magnetoelectric effect, interfacial strain coupling between the ferroelectric and magnetic phases via the piezoelectric effect and magnetostriction in multilayers and nanocomposites is the most widely investigated route. Beside the complicated and not well understood interplay of ferroic properties, conductivity, and sample history, there is an extreme variability of geometrical phase arrangement in such composites. For example, ten different connectivity schemes exist for two coupled piezoelectric and magnetostrictive phases according to their dimensionalities, i.e., 0–0, 1–0, 2–0, 3–0, 1–1, 2–1, 3–1, 2–2, 3–2, and 3–3, as pointed out by Vaz *et al.*¹

Recently, we demonstrated magnetoelectric coefficients α_{ME} up to 20.75 V/cm-Oe at 300 K in a μm -thin nanocomposite film, i.e., a mixture consisting of BaTiO₃ and BiFeO₃.² Similarly, high magnetoelectric (ME) coupling was obtained for approximately 50 nm thin manganite films clamped to substrates with high piezoelectric response such as Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT) or BaTiO₃ at structural phase transitions.^{3–5} However, many multiferroic materials including composites show lower α_{ME} values, see Ref. 2 and references therein.

Up to now, very little is known about the correlation between magnetoelectric coupling and microstructural features of the samples. In this letter, we correlate still higher

ME coefficients up to 24 V/cm-Oe at 300 K in 2–2 composites, in particular (BaTiO₃-BiFeO₃) × 15 multilayers grown at various oxygen partial pressures ranging from 0.01 to 0.25 mbar, with the oxygen-related defect structure of the multilayers at 300 K. The defects involve antiphase tilting of the TiO₆ octahedra in the BaTiO₃ single layers in the superlattices. The understanding of such microstructural correlations with magnetoelectric coupling is essential for the design of artificial multiferroic composites with higher, i.e., practically exploitable ME coefficients.

The (BaTiO₃-BiFeO₃) × 15 multilayers were grown by pulsed laser deposition (PLD)⁶ from single phase BaTiO₃ and BiFeO₃ targets. The optimal growth temperature for highly crystalline films is 680 °C.² In our PLD approach, four very similar films (marked a, b, c, and d) were grown simultaneously in a multi-substrate holder on various conducting substrates, namely, epi-polished SrTiO₃(001) (STO) without and with a thin SrRuO₃ layer, SrTiO₃:Nb(001) with 0.5% or 0.1% Nb content, and MgO(001). From x-ray diffraction (XRD) 2 Θ – ω scans, minor changes of the out-of-plane lattice constant depending on the used substrate were found, see Table II in Ref. 2. More details of the growth process, as well as of the structural, ferroelectric, and magnetic response of the samples can be found in Ref. 2, and in supplementary material of this paper.²⁰

XRD reciprocal space maps (RSM) and rocking curves were measured at 300 K employing a PANalytical X’pert PRO MRD with Cu K α radiation from a parabolic mirror with divergence slits of 1/8° or 1/32°, respectively. The PIXcel^{3D} array detector with a selectable number of active channels allowed fast scanning of large area RSMs.

Scanning transmission electron microscopy (STEM) investigations were performed for multilayers grown at either 0.25 mbar or 0.01 mbar oxygen partial pressure. About 100 nm thick lamellae were prepared using the focused ion

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beam (FIB) of a field emission scanning electron microscope (FEM) FEI NOVA Nanolab 200. Further thinning up to 200 kV electron transparency was done by Ar^+ ion milling in a Gatan PIPS. The STEM experiments were carried out at 300 K in a Philips CM 200 STEM with a super-twin objective lens and point resolution of 0.23 nm. The distribution of elements was determined by EDX mapping (EDAX system). Selected area electron diffraction (SAED) patterns were taken from various regions of the cross sections. The simulation of SAED patterns was done by means of the JEMS software package.⁷ The structure data for oxygen deficient BaTiO_3 needed for simulations were taken from Ref. 8, data code ICSD 54785.

Figure 1 shows typical XRD RSMs of symmetric (002) and asymmetric (-103) reflections of the multilayer sample G4729c grown at 0.25 mbar oxygen partial pressure. The lack of vertical alignment of (-103) film and substrate peaks indicates at least a partial relaxation of the film lattice, i.e., no pseudomorphic (no in-plane lattice matched) growth. In comparison to the substrate peaks, the film peaks in Fig. 1 show vertical and horizontal broadening due to microstrain

FIG. 1. XRD RSMs around the centered (a) (002) and (b) (-103) SrTiO_3 substrate peaks (red with $K\alpha_{1/2}$ splitting) of the $(\text{BaTiO}_3\text{-BiFeO}_3) \times 15$ multilayer (G 4729c) grown at 0.25 mbar. The superlattice peaks indicate a regularly arranged multilayer with smooth interfaces. From the lack of vertical alignment of (-103) film and substrate peaks in (b) we conclude partly relaxed films. BTO-BFO in the RSMs stands for $\text{BaTiO}_3\text{-BiFeO}_3$, and STO for SrTiO_3 .

TABLE I. Total multilayer thickness taken from Rutherford backscattering spectrometry of samples marked with d, and FWHM of XRD ω -scans of (002) film peaks of two simultaneously grown samples marked b and c, together with oxygen growth pressure and PLD growth no.

PLD growth no.	$p(\text{O}_2)$ (mbar)	Total thickness (nm)	FWHM ω (002)
G5090	0.01	1020	$1.12^\circ/0.90^\circ$
G5089	0.05	750	$1.28^\circ/1.31^\circ$
G5088	0.1	600	$0.23^\circ/0.35^\circ$
G4729	0.25	450	0.14°

distributions and tilt mosaicity, respectively. A more quantitative discussion of mosaicity is provided below with Fig. 4 and Table I. As additional complication, the lattice relaxation may be different at the interfaces and in the bulk of the multilayer. The XRD RSMs of the multilayer show superlattice peaks according to the double layer thickness of (13.8 ± 0.7) nm, for details, see Fig. S4 in supplementary material.²⁰ This value is in excellent agreement with the averaged single layer thicknesses of 6.1 nm (BaTiO_3) and 7.7 nm (BiFeO_3) measured by STEM on cross sections with thickness labeling of another sample (G 4174, cf. Fig. S3) grown with identical PLD parameters. This agreement illustrates the excellent reproducibility of our PLD process over a time span of 14 months.

The STEM, SAED, and EDX mapping results of the $(\text{BaTiO}_3\text{-BiFeO}_3) \times 15$ multilayer (G 4178) are depicted in Fig. 2. The STEM cross section and the corresponding EDX maps of Ba, Ti, Bi, and Fe confirm the presence of 15 double layers $\text{BaTiO}_3\text{-BiFeO}_3$ with reasonably smooth interfaces. The [110] zone axis SAED patterns taken from the region of

FIG. 2. STEM dark-field image of sample G4178 $(\text{BaTiO}_3\text{-BiFeO}_3) \times 15$ grown at 0.01 mbar on MgO with (110) azimuth. The green, orange, and blue circles define the region in the cross section where the corresponding SAED patterns (right) were taken from. The weak reflections, some of them highlighted by red circles, that appear in addition to the fundamental perovskite-type reflections arise from antiphase tilting of oxygen octahedra.⁹⁻¹² The EDX maps (bottom) show the regular distribution of elements in the multilayer sequence. The enlarged SAED reflections in the box (top left) split in vertical direction.

the multilayers and the interface show weak reflections corresponding to a pseudocubic superstructure ($h + 1/2$, $k + 1/2$, $l + 1/2$) in addition to the perovskite-type reflections. The superstructure corresponds to a *klassengleiche* displacive phase transition from $R3m$ to $R3c$ which involves the tilting of oxygen octahedra around [001] of the structure in the hexagonal setting of $R3m$ (which corresponds to $\langle 111 \rangle$ in a pseudocubic setting) as discussed in detail for $\text{Pb}(\text{Zr,Ti})\text{O}_3$ and $\text{BiScO}_3\text{-PbTiO}_3$ ceramics in Refs. 13, 11, and 12, and confirmed by superstructure reflections in calculated SAED patterns.^{9,14} The octahedral tilt involves both clockwise and counterclockwise rotations around [111], which is parallel to the ferroelectric dipole displacements of the $R3m$ phase as predicted from neutron diffraction, see Ref. 4. The STEM dark-field contrast of the antiphase boundaries that are a consequence of superstructure formation is too weak to be visible here. The difference between the lattice parameters of the tetragonal BaTiO_3 ¹⁵ and rhombohedral BiFeO_3 ¹⁶ layers can be detected by reflection splitting along the growth direction (see inset in Fig. 2, top). Because the splitting is pronounced only in vertical direction, i.e., along the reciprocal space direction perpendicular to the sample surface, we conclude an in-plane lattice matched growth of the single BaTiO_3 films on the BiFeO_3 layers with single layer thicknesses around 15 and 20 nm, respectively (see Fig. S2 in supplementary material²⁰). Strain in the $\text{BaTiO}_3\text{-BiFeO}_3$ multilayer thus occurs only in perpendicular direction, i.e., along the growth or c -axis direction. The superstructure reflections of sample G4178 (0.01 mbar) shown in Fig. 2 are more intense than those of sample G4174 (0.25 mbar, shown in supplementary material Fig. S1²⁰). This hints at increased lattice distortions including more pronounced antiphase tilt of the oxygen octahedra in the BaTiO_3 single layers at lower oxygen partial pressure during growth.

To further quantify the less pronounced tilting of oxygen octahedra at increasing oxygen growth pressure $p(\text{O}_2)$ as indicated by the different reflection intensities in SAED patterns (cf. Fig. 2 vs. Fig. S1, *vide supra*), the full widths at half maximum (FWHM) of (002) rocking curves of the most intense multilayer peaks of two simultaneously deposited films on $\text{STO:0.1\%Nb}$ (marked b) and $\text{STO:0.5\%Nb}$ (marked c) are given in Table I.

As mentioned in the introduction, little is known about correlations of crystal defects and magnetoelectric coupling in multiferroics. Zhai *et al.* have recently correlated interfacial octahedral rotations with magnetism in $\text{LaMnO}_3/\text{SrTiO}_3$ superlattices and found maximum ferromagnetic saturation magnetization with minimum octahedral rotation.¹⁷ Probably, the octahedral rotations can be considered as lattice distortions which may influence not only magnetism, as shown in Ref. 17, but also strain-mediated magnetoelectric coupling. Indeed, in our $\text{BaTiO}_3\text{-BiFeO}_3$ multilayer samples, we observe a clear dependence of the ME coefficient on oxygen partial pressure during PLD growth, see Fig. 3.

The ME coefficients were measured by the inductive AC method described in Refs. 18 and 2. Fig. 3(a) and the inset in 3(b) clearly demonstrate the key message of this work, namely, the increasing ME coefficient with increasing oxygen growth pressure from 0.01 to 0.25 mbar, i.e., decreasing oxygen-related defects, for temperatures from

FIG. 3. ME coefficient vs. temperature @ zero DC bias magnetic field (a); and vs. DC bias magnetic field @ 300 K (b) and (c); of $(\text{BaTiO}_3\text{-BiFeO}_3) \times 15$ multilayers grown at the indicated oxygen partial pressures on $\text{SrTiO}_3\text{:Nb}$ (see Table I). In addition to (a), the inset in (b) shows the increasing ME coefficient in V/cm-Oe with increasing oxygen partial pressure at 300 K, i.e., decreasing defect density including antiphase tilting of oxygen octahedra.

about 200 K to 300 K. For the three higher growth pressures, this applies even for the whole temperature range from 3 to 300 K. However, the temperature dependence of the lowest pressure curve, i.e., 0.01 mbar (black) in Fig. 3(a), results in a cross over with higher pressure curves below 200 K. This phenomenon requires further scrutiny in order to be fully understood. Most likely, differences in structural phase changes in the BaTiO_3 layers such as the orthorhombic to rhomboedric transition around 190 K play a role here. The maximum ME coefficient at 300 K of the multilayer (G4729)

FIG. 4. XRD reciprocal space maps around the symmetric STO(001) peaks (i.e., $K\alpha_{1/2}$ splitted points with highest intensity in each subfigure) of $(\text{BaTiO}_3\text{-BiFeO}_3) \times 15$ multilayers grown at (a) 0.01, (b) 0.05, (c) 0.1, and (d) 0.25 mbar oxygen partial pressure. The decreasing horizontal layer peak broadening indicates decreasing multi-layer mosaicity with increasing growth pressure. This correlates clearly with increasing ME coefficient, see Fig. 3. The corresponding FWHM of the (002) rocking curves and the total multilayer thickness values are given in Table I.

grown at 0.25 mbar is 22.8 V/cm·Oe for zero DC bias magnetic field (Fig. 3(a)), and increases up to 23.9 V/cm·Oe for fields of several T (Fig. 3(b)). For reference, a similarly grown, 455 nm thick BiFeO₃ film grown at 0.25 mbar (G 5087d) showed an ME coefficient of 4.2 V/cm·Oe at 300 K and for DC magnetic fields below 0.5 T. This comparison demonstrates that our designed BaTiO₃-BiFeO₃ superlattices show a considerably enhanced magnetoelectric effect compared to single phase multiferroics. Figures 3(b) and 3(c) provide a closer look on the DC bias magnetic field dependence of α_{ME} at 300 K. The increase of α_{ME} in DC field from 0 T to 6 T amounts to 1.2%; 1.8%; 7.9%; and 5.3% for the 0.01; 0.05; 0.1; and 0.25 mbar graphs, respectively. Obviously, the DC bias field effect is remarkably higher for the higher pressure samples.

In Ref. 19, we have measured the trigonal distortion of oxygen tetrahedra of oxygen deficient, weakly Mn-doped ZnO thin films. Lower oxygen partial pressure in PLD growth is clearly correlated to increasing density of oxygen vacancies, which is accompanied by more pronounced structural distortions, expressed locally by increasing variation of bond lengths and by variation of out-of-plane and in-plane lattice constants and rocking curve widths.¹⁹

In order to transfer these findings to our BaTiO₃-BiFeO₃ multilayers and to further illustrate the impact of oxygen partial pressure on microstructure of multilayer films, Fig. 4 shows XRD RSMs around the symmetric STO(001) peaks of samples grown with four different oxygen partial pressures, with clear indication of superlattice peaks as discussed in Fig. 1 for the (002) and (−103) reflections. Interestingly, the horizontal broadening of the superlattice film peaks in Fig. 4, i.e., the tilt mosaicity of the multilayers, shows a clear dependence on the oxygen partial pressure, i.e., the oxygen vacancies and related structural distortions. The FWHM

values of the (002) rocking curves given in Table I quantitatively support the increasing mosaicity with decreasing growth pressure which is clearly visible in Fig. 4.

In summary, we clearly correlate increasing magneto-electric coupling expressed by the ME coefficient α_{ME} of $(\text{BaTiO}_3\text{-BiFeO}_3) \times 15$ multilayer composites with crystal defects in the compounds that form the superlattices as controlled by the oxygen partial pressure during sequential PLD growth. Compared to previous work,² a still higher ME coefficient of up to 24 V/cm·Oe at 300 K was achieved here. The ME coefficient shows different temperature dependence within the covered range of PLD growth pressure and questions remain open, in particular, for the lowest growth pressure sample at low temperatures below 200 K. Systematic room-temperature studies by XRD and STEM/SAED could identify increasing tilt mosaicity of the multilayers and increasing antiphase tilt of the oxygen octahedra in the BaTiO₃ single layers with decreasing oxygen partial pressure. Mosaicity and octahedral tilt are up to now the most prominent crystal defects which obviously influence the strain-mediated magnetoelectric coupling in our superlattices. With that, this work increases the understanding and allows control of application-relevant magnetoelectric coupling in multiferroic composites. The results are important for the design of artificial composites with further increased ME coefficient, which are suitable for application as magnetoelectric storage and sensor devices.

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- ²⁰See supplementary material at <http://dx.doi.org/10.1063/1.4905343> for additional TEM, SAED, HR-XRD, AFM, FE-hysteresis data of the discussed multiferroic multilayer samples.