Epitaxy, texturing, and second-harmonic generation in $BiFeO_3$ thin films

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We have made epitaxial and polycrystalline thin films of multiferroic $BiFeO_3$ on different substrates [(001) and (111) $SrTiO_3$, (001) and (111) $LaAlO_3$, (001) MgO, and (0001) sapphire] by pulsed-laser deposition. We investigated the second harmonic generation (SHG) in these films and find that the SHG was smallest in epitaxially grown films on (001) $SrTiO_3$ and largest in epitaxial films grown on (111) $SrTiO_3$ and (111) $LaAlO_3$. We discuss these results in terms of the crystal structure as well as the film microstructure.

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There has been much recent work on multiferroic oxides due to the promise of utilizing the bifunctionalities that these compounds possess.[1] While thin films are the key to many new devices such as for information storage, it is challenging to investigate the magnetoelectric properties in thin films because the values of the measurable quantities (electric-field-induced change in the magnetic moment and magnetic-field-induced change in voltage) are small. Second harmonic generation (SHG) is a sensitive probe of magnetoelectric properties[2] as the allowed tensor elements for optical frequency doubling are strongly dependent on symmetry, as is the case for magnetoelectric coupling. SHG has successfully been used to image multiferroic domains in $HoMnO_3$.[3] One of the more well-known and studied multiferroic materials is $BiFeO_3$,[4–6] which displays ferroelectricity and antiferromagnetism at room temperature. Here we present an investigation of the structure and microstructure of thin films of $BiFeO_3$ on different substrates by SHG.

Films of $BiFeO_3$ were grown by pulsed-laser deposition on an (001) and (111) $SrTiO_3$, (001) and (111) $LaAlO_3$, (0001) sapphire, as well as (001) MgO. We ablated a stoichiometric $BiFeO_3$ target with a KrF excimer laser (wavelength $\lambda=248$ nm) with a typical fluence of 2 J/cm^2. The substrate temperature was 650 °C and the O_2 pressure was 20 mTorr during deposition. The film thicknesses were ~200 nm. Both two-theta and four-circle x-ray diffraction were performed. Topography was investigated by atomic force microscopy.

Measurements of the second harmonic intensity were completed with a coherent Ti:sapphire pulsed laser.[7] A schematic of the setup is shown in Fig. 1. The wavelength of the incident light was 780 nm and the average power was about 300 mW. A half waveplate was used to change the polarization of the incident beam. The light was chopped at a frequency of 2 kHz and focused to a spot of about 50 μ. The incident and reflected beams were in the xz plane (inset Fig. 1) at nearly normal incidence (3°–5°). The light from the sample was sent through a polarizer and the SHG was measured with a photomultiplier tube and lock-in detection after filtering by both broadband and narrow band filters. Measurements were made at room temperature with p and s polarized light (p_{in} and s_{in}, respectively) with an applied magnetic field of up to 3 kOe along the x direction (inset Fig. 1). The angle θ of the analyzer was measured with respect to the x axis; i.e., 0° and 180° correspond to p polarization (p_{out}) and 90° and 270° to s polarization (s_{out}). Films grown on (001) substrates were aligned with the (100) direction of the substrate along the x axis while films grown on (111) substrates were aligned with the $(1\bar{1}0)$ direction along the x axis. We checked that the contribution to the SHG from the substrates could be ignored in all cases.

Figure 2 shows the x-ray diffraction pattern of the various films. The epitaxial films grown on (111) substrates [Fig. 2(a)] were rhombohedral while x-ray diffraction shows that $BiFeO_3$ film on (001) $LaAlO_3$ [Fig. 2(b)] was a mixture of epitaxial and polycrystalline components. The epitaxial component of that film was indexed with tetragonal lattice constants $a=3.935$ Å and $c=3.985$ Å. The films on sapphire and MgO [Fig. 2(b)] were polycrystalline. The film on (001) $SrTiO_3$ was epitaxial [Fig. 2(c)] and the diffraction pattern could be indexed to a tetragonal structure with (001) orientation with in-plane and out-of-plane lattice constants $a=3.935$ Å and $c=3.968$ Å, respectively. Transmission electron microscopy,[8] however, indicated a small monoclinic (0.5°) distortion. Table I gives a list of the lattice constants of the $BiFeO_3$ and the cubic (pseudocubic) substrates. Obviously, the lattice mismatch between MgO is too large for epitaxial growth of $BiFeO_3$.

Figures 3 and 4 show the SHG for films grown on (111)

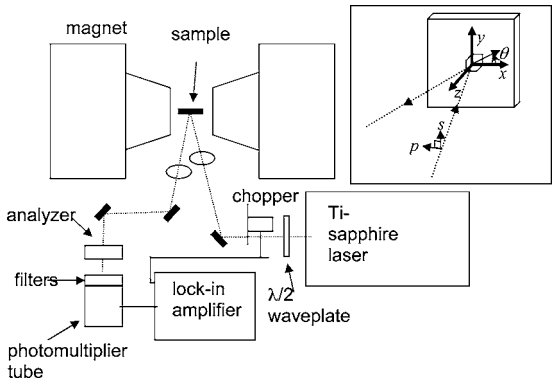

FIG. 1. Schematic of the experimental setup. The inset shows the geometry. Note that the s polarization is along the y axis.

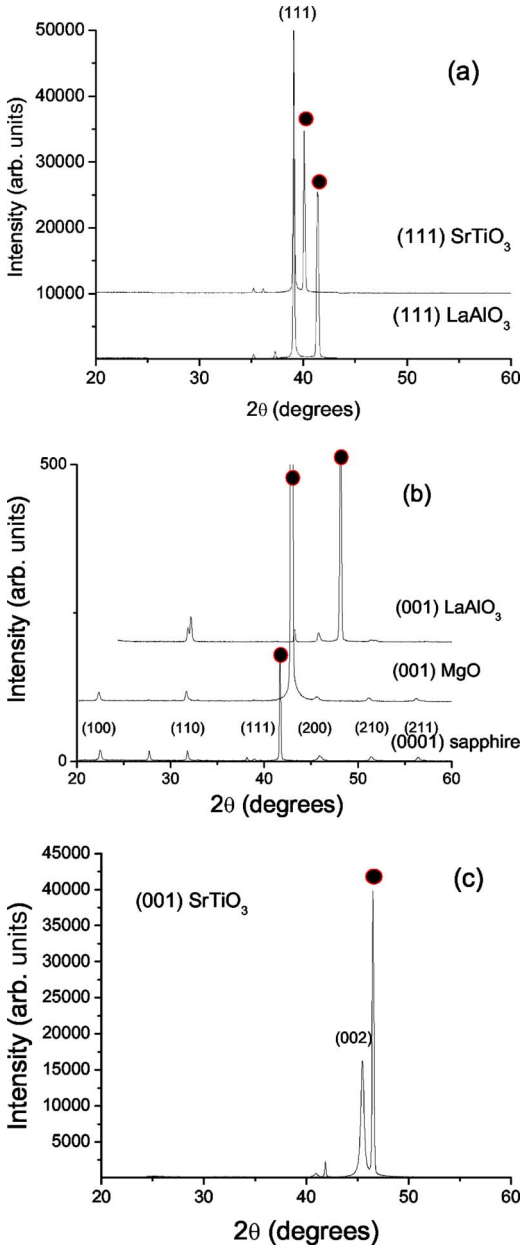

FIG. 2. (Color online) X-ray diffraction patterns of $BiFeO_3$ films on (a) (111) $SrTiO_3$ and (111) $LaAlO_3$; (b) (001) $LaAlO_3$, (001) MgO, and (0001) sapphire, and (c) (001) $SrTiO_3$. The pseudocubic Miller indices of $BiFeO_3$ are noted and the dots represent peaks from the substrates. The small peaks in (a) and (c) are from CuK_β.

$SrTiO_3$ and $LaAlO_3$ substrates, respectively. Figure 5 shows the results for the polycrystalline films grown on (001) MgO, (001) $LaAlO_3$, and (0001) sapphire, while Fig. 6 shows the results of the film grown on (001) $SrTiO_3$. In no case was any field dependence observed.

The electric dipole contribution to the SHG signal is usually by far the largest.[9] Since there was no magnetic field dependence, it seems likely that all SHG arises from electric dipole transitions. For electric dipole SHG,

$$P_i = \chi_{ijk} E_j E_k, \tag{1}$$

where P is the polarization, E the electric field, and χ_{ijk} the second harmonic electric susceptibility tensor. The allowed

TABLE I. Lattice mismatch of $BiFeO_3$ with selected substrates.

Compound	Bulk pseudocubic lattice constant (Å)	Lattice mismatch with $BiFeO_3$ (%)
$BiFeO_3$	3.95	–
$SrTiO_3$	3.905	1.1
$LaAlO_3$	3.79	4.1
MgO	4.22	−6.4

tensor elements are constrained by the symmetry,[10] and SHG becomes a direct probe of the local lattice and magnetic structure. This is particularly true when investigating single crystals by polarized light, where the incoming electric field and outgoing polarization are well defined with respect to the crystal lattice; however, valuable information on symmetry can be obtained from SHG investigations, even without single crystals.

The first study of SHG in $BiFeO_3$ was done by Kurtz and Perry[11] using the powder method, where they indicated that there was a reasonably large SHG. This observation was in direct contradiction to its then assigned point group $\bar{3}\mathbf{m}$, for which χ_{ijk} vanishes. The currently assigned space group of $BiFeO_3$ is $R3c$, point group **3m**, which has nonzero tensor elements, in agreement with the early SHG results.

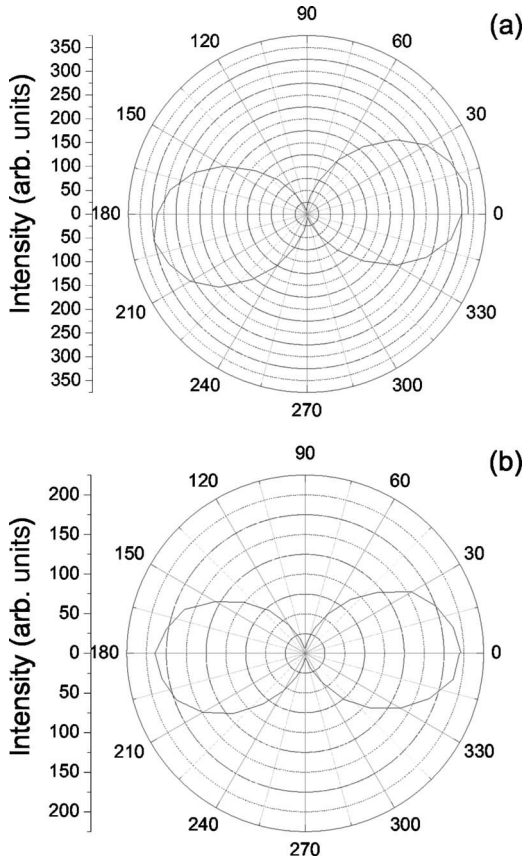

FIG. 3. Polarization dependence of the SHG intensity from a $BiFeO_3$ film on (111) $LaAlO_3$ for incident (a) p polarization and (b) s polarization.

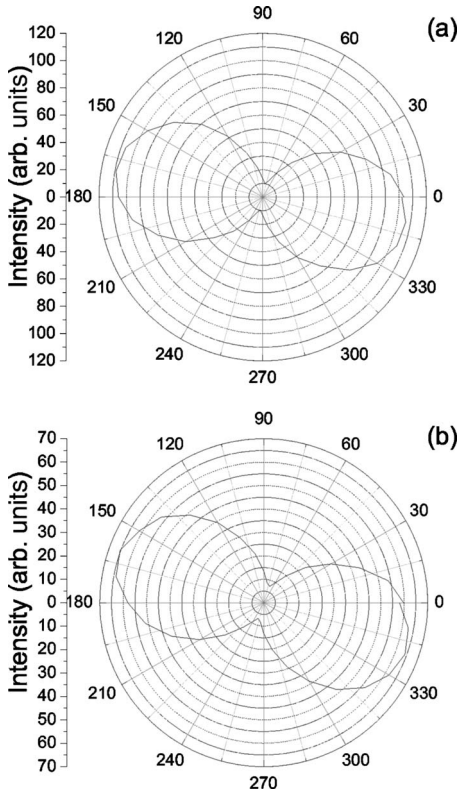

FIG. 4. Polarization dependence of the SHG intensity from a $BiFeO_3$ film on (111) $SrTiO_3$ for incident (a) p polarization and (b) s polarization.

The SHG from the epitaxial films grown on a (111) substrate was nearly linearly polarized and sizable. Since these films were rhombohedral, the threefold symmetry was in the film plane and the z axis was normal to it and the film was aligned with s along the y direction. The results require the diagonal element χ_{xxx} ($p_{\text{in}}p_{\text{out}}$). The linear polarization of the signal from the film on $LaAlO_3$ also requires that χ_{yyy} ($s_{\text{in}}s_{\text{out}}$) as well as χ_{yxx} ($p_{\text{in}}s_{\text{out}}$) be zero. This suggests point group **3m** as confirmed by measurements done away from normal incidence, which indicated that χ_{zzz} was nonzero. This result is consistent with the space group of the bulk material $R3c$. Note that in this symmetry also $\chi_{xxx}=-\chi_{yyx}$ ($s_{\text{in}}p_{\text{out}}$) as seen by the similar size signals for the two polarizations at the same orientation.

For the film on (111) $SrTiO_3$, both χ_{xxx} and χ_{yyy} are nonzero. Since $|\chi_{xxx}|=|\chi_{yyx}|$ and $|\chi_{yyy}|=|\chi_{xyy}|$, the point group must be **3**, which would suggest that the space group is $R3$. This would indicate that the lattice strain on the film from the substrate on the film has created a distortion in the structure along the c axis. It might be due to strain relaxation, but recent theoretical predictions[12] indicate that there should be minimal lattice distortions and negligible effect on the ferroelectric polarization. Perhaps the easiest explanation is to suggest that there are many ferroelectric domain walls in the film that give rise to the broken symmetry along the c axis.

The SHG is rather large for the films on (001) $LaAlO_3$ and sapphire but comparatively smaller for the film on (001) MgO. Like the films grown on (111) substrates, these polycrystalline films also had rhombohedral crystal symmetry.

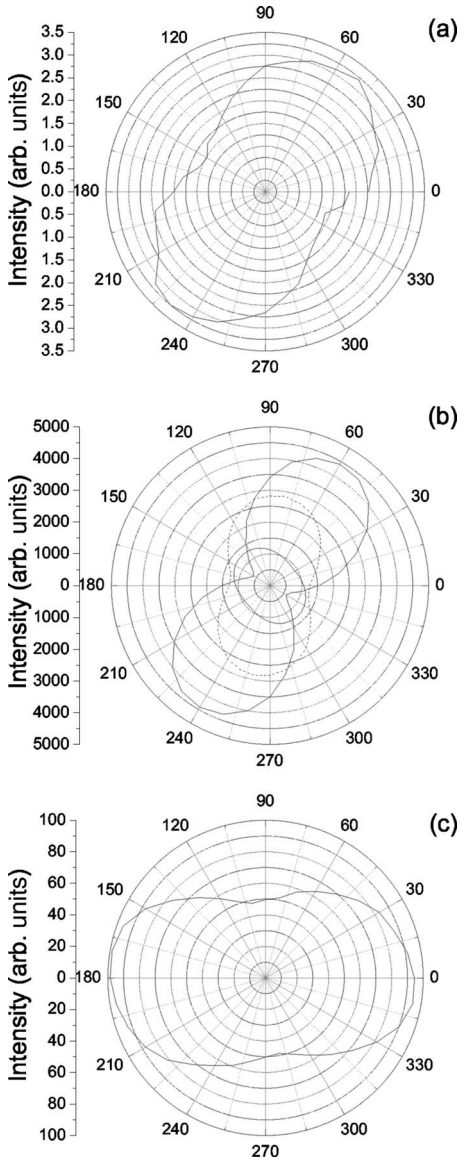

FIG. 5. Polarization dependence of the SHG intensity for incident p polarization from a $BiFeO_3$ film on (a) (001) MgO, (b) (001) $LaAlO_3$, and (c) (0001) sapphire. The data for the film on (001) $LaAlO_3$ shows significant variation from spot to spot.

AFM images indicated that the grain size was very small for the films on (001) MgO and (001) $LaAlO_3$ ($\sim$500 nm) but somewhat larger for the film on sapphire (Fig. 7), approximately 1 μ wide and several microns long. The fact the SHG was small for the film on MgO is consistent with the fact that the SHG should scale with the crystallite size for crystallites smaller than the coherence length $\sim\lambda/4(n_{2\omega}-n_{\omega})$, where $n_{2\omega}$ and n_{ω} represent the refractive index at angular frequency 2ω and ω, respectively, and λ is the wavelength.[11] While the refractive index of $BiFeO_3$ was not measured, it is highly unlikely, in the visible, that $n_{2\omega}-n_{\omega}$ would be more than 0.1 and more likely much less, yielding a coherence length of over two microns, significantly smaller than the measured grain size. This result would suggest that the film on (001) $LaAlO_3$ should also display small SHG; however, that film on (001) $LaAlO_3$ also had an epitaxial component. The align-

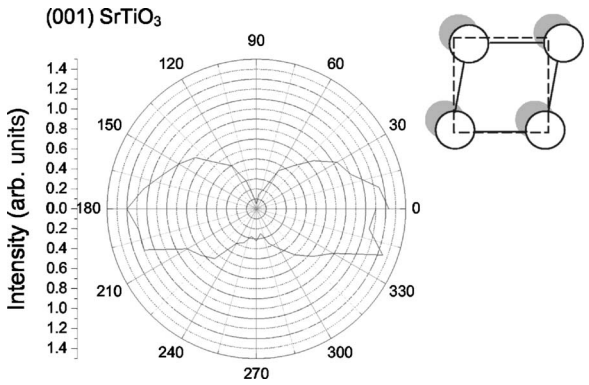

FIG. 6. Polarization dependence of the SHG intensity from a $BiFeO_3$ film on (001) $SrTiO_3$. The inset displays a schematic of the distortion of the unit cell viewed from the z axis, as required for obtaining the observed SHG intensity.

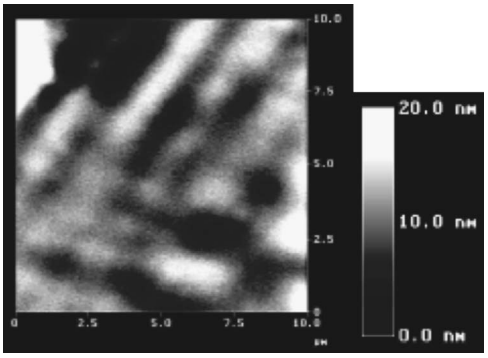

FIG. 7. Atomic force microscopy images of the surface of a $BiFeO_3$ film on a (0001) sapphire. The crystallites are about one micron wide and relatively long (several microns), and they appear to have a preferential orientation.

ment from the epitaxial parts produced coherence in the second harmonic polarization that must account for the large SHG observed from the film. This also explains the significant variation in both the polarization dependence and the intensity from spot to spot [Fig. 5(b)].

For the film on sapphire, which showed large SHG, the grain size is significantly larger. This would produce larger SHG than the film on MgO. However, the polarization dependence of the SHG in the film on sapphire, unlike that for the polycrystalline films on other substrates, cannot be written as a sum of $\cos^2\theta$ and $\sin^2\theta$ terms, as expected for a random distribution of orientations. The AFM image did show some indications of in-plane alignment, as there were long microstructures at angles of 60° (Fig. 7), as might be expected for growth on the surface of the (0001) sapphire. This would not only enhance the SHG but also give rise to a nontrivial polarization dependence.

For the film grown on (001) $SrTiO_3$, the SHG signal was the smallest of any. The observed polarization dependence of the SHG requires diagonal elements of the nonlinear susceptibility tensor χ_{xxx} or χ_{yyy}, where z is the axis of symmetry (normal to the film). No tetragonal point groups[10] have elements of this form. Therefore, the symmetry must be lower; i.e., monoclinic or triclinic. This is in agreement with transmission electron microscopy of these films[8] as well as detailed x-ray diffraction[13] on similar films, which indicated a small (0.5°) monoclinic distortion. The fact the signal is small is consistent with the fact that the distortion is minimal. If the distortion is monoclinic and the film normal is the axis of symmetry, the point group must be 2.

For the epitaxial film on (100) $SrTiO_3$, the measured magnetization in the plane was small ($\sim$20 emu/cm^3) but nonzero, so the magnetic point groups must allow for weak ferromagnetism. If one assumes that the film plane is a symmetry plane, only magnetic point groups **1**, $\underline{\mathbf{1}}$, **2**, $\underline{\mathbf{m}}$, and $\underline{\mathbf{2/m}}$ allow for magnetization in the plane. This result agrees with the prediction by Ederer and Spaldin[14] that the magnetic space group for the bulk material is one of the monoclinic groups *Bb* or *Bb′*, both of which belong to magnetic point group $\underline{\mathbf{m}}$. The fact that no magnetic field dependence was observed for the SHG may be due to the small magnetization, which corresponds to a canting angle of 1° or so. On the other hand, it may be that the magnetic contribution to the SHG is very small compared to that of the structural contribution since different spots on the epitaxial films gave the same response—interference between the two contributions would cause the polarization of the SHG to vary with the different antiferromagnetic domains.[9]

In conclusion, we have investigated the properties of thin films of $BiFeO_3$ via second-harmonic generation. Both the structure and microstructure play important roles in the SHG. Epitaxial films grown on (111) $SrTiO_3$ and $LaAlO_3$ confirm rhombohedral symmetry; however, the two films belong to different point groups, suggesting distortions related to strain. Polycrystalline films show very different SHG that results from their microstructure, i.e., grain size and texturing. The epitaxial film on (001) $SrTiO_3$ is nearly tetragonal; however, a small monoclinic distortion is evident from the SHG measurements. These results demonstrate the importance of strain when developing thin film multiferroic devices since the local symmetry dictates the magnetoelectric coupling.

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