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Probing mixed tetragonal/rhombohedral-like monoclinic phases in strained bismuth ferrite films by optical second harmonic generation

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Epitaxial strain can induce the formation of morphotropic phase boundary in lead free ferroelectrics like bismuth ferrite, thereby enabling the coexistence of tetragonal and rhombohedral phases in the same film. The relative ratio of these phases is governed by the film thickness and theoretical studies suggest that there exists a monoclinic distortion of both the tetragonal as well as the rhombohedral unit cells due to imposed epitaxial strain. In this work we show that optical second harmonic generation can distinguish the tetragonal-like phase from the rhombohedral-like phase and enable detection of monoclinic distortion in only a pure tetragonal-like phase. © *2010 American Institute of Physics*. [doi:10.1063/1.3483923]

An alternative route to achieve large piezoelectric responses that is fundamentally different from chemical alloying is of particular interest to the ferroelectrics community. Epitaxial strain has recently been demonstrated to drive the formation of a morphotropic phase boundary and create large piezoelectric responses in lead-free ferroelectrics.[1] Theoretical calculations of the effect of biaxial strain on $BiFeO_3$ (BFO) films reveal two distinct structures in the high and low strain regime with a discontinuous first-order transition between them at 4.5% compressive strain. The phases that evolve above and below this critical strain are pseudotetragonal (T-phase) and pseudorhombohedral (R-phase) respectively with a small monoclinic distortion of the unit cells.[2–4] The T phase can be reversibly converted to a mixed T and R phase via the application of an external electric field.[1] Both phases have the same space group symmetry and hence such phase transitions are known as *isosymmetric* and are necessarily first order. So, in reality, strained $BiFeO_3$ is monoclinic, with tetragonal-like (T-phase) and rhombohedral-like (R-phase) distortions.

This paper describes how optical second harmonic generation (SHG)[5] can distinguish the T-like phase from the R-like phase, as well as detect possible monoclinic distortion in the pure T-like phase. First we show that SHG can distinguish a T-like phase from a pure rhombohedral phase. Using molecular beam epitaxy (MBE), the T-like phase was a 25 nm film of $(001)_T$ $BiFeO_3//(110)_O YAlO_3$, with in-plane orientations of $[100]_T BiFeO_3//[001]_O YAlO_3$, and $[010]_T BiFeO_3//[1\bar{1}0]_O YAlO_3$. (Subscripts T and O refer to tetragonal and orthothombic indices.) The $BiFeO_3$ film was under -6.5% strain (compressive) as determined from x-ray diffraction. Piezoelectric force microscopy (PFM) indicates that the film is self-poled in the single domain "down" state.[1] The pure rhombohedral phase film was a 25 nm $(001)_p BiFeO_3//(001)SrTiO_3$ grown by MBE, with in-plane orientations of $\langle 100\rangle_p BiFeO_3//\langle 100\rangle SrTiO_3$.[6] This film was unstrained and possessed eight different domain variants along the eight $\langle 111\rangle_p$ directions.

Optical SHG (Ref. 5) involves the conversion of light (electric field E^{ω}) at a frequency ω into an optical signal at a frequency 2ω by a nonlinear medium, through the creation of a nonlinear polarization $P_i^{2\omega} \propto d_{ijk} E_j^{\omega} E_k^{\omega}$, where d_{ijk} represents the nonlinear optical coefficients. The SHG experiment was performed with a fundamental wave generated from a tunable Ti-sapphire laser with 100 fs pulses of wavelength 800 nm and 1 kHz repetition rate incident from the film side at an angle θ to the sample surface normal with $[100]_p$ film axis lying in the plane of incidence. The polarization direction of the incident light was at an angle $90° - \varphi$ from the incidence plane and was rotated continuously using a $\lambda/2$ waveplate (inset of Fig. 1).

First we ignore the monoclinic distortion, and treat the T-like phase as pure T-phase and R-like as pure R-phase, which as we shall see later is justified. The d_{ijk} tensors are distinctly different for the tetragonal versus rhombohedral phases. For the *p*-in-*p*-out SHG polarization geometry, shown in the inset of Fig. 1, the expected SHG intensity for the two phases, including various domain variants, is given as follows:

$$I_{pp}(\theta) = I_0^2 t_p^2 (A f_x^2 \cos^2 \theta + B f_z^2 \sin^2 \theta + C f_x f_z \sin 2\theta)^2, \quad (1)$$

where for the tetragonal phase $A = d_{31}\tilde{f}_z$, $B = d_{33}\tilde{f}_z$, and $C = d_{15}\tilde{f}_x$. Here, $f_{x,z}$ are the linear and $\tilde{f}_{x,z}$ are the nonlinear Fresnel coefficients, which are functions of the refractive indices of the film and substrate and the angle of incidence,[7] t_p is the Fresnel coefficient for transmission of *p*-polarized SHG at the substrate-air interface, and I_0 is the intensity of the fundamental light. For the rhombohedral phase $A = \tilde{f}_x[(\delta A_{13} + \delta A_{24})\tilde{d}_1 - 2\sqrt{2}(\delta A_{13} - \delta A_{24})d_{22}] + \tilde{f}_z[(\delta A_{12} + \delta A_{34})\tilde{d}_3 + \sqrt{2}d_{22}]$, $B = \tilde{f}_z[(\delta A_{13} + \delta A_{24})\tilde{d}_3 + \sqrt{2}(\delta A_{13} - \delta A_{24})d_{22}] + \tilde{f}_z[(\delta A_{12} + \delta A_{34})\tilde{d}_1 - 2\sqrt{2}d_{22}]$, and $C = \tilde{f}_x[(\delta A_{12}$

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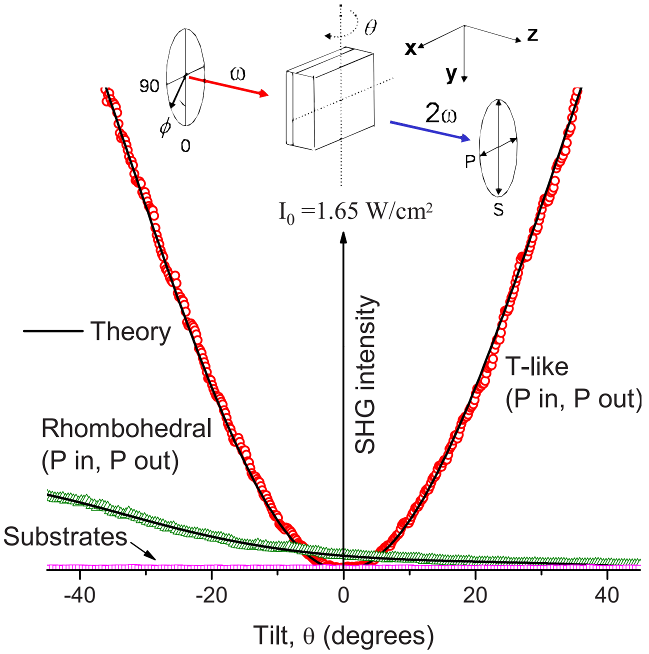

FIG. 1. (Color online) Angular tilt dependence of SHG signal obtained in p-in-p-out configuration for a 25 nm T-phase $(001)_T\mathrm{BiFeO_3}//\mathrm{YAlO_3}$ (open circles) compared to a purely rhombohedral 25 nm $(001)_{pc}\mathrm{BiFeO_3}//\mathrm{SrTiO_3}$ film (open triangles). The experimental setup is shown in the inset.

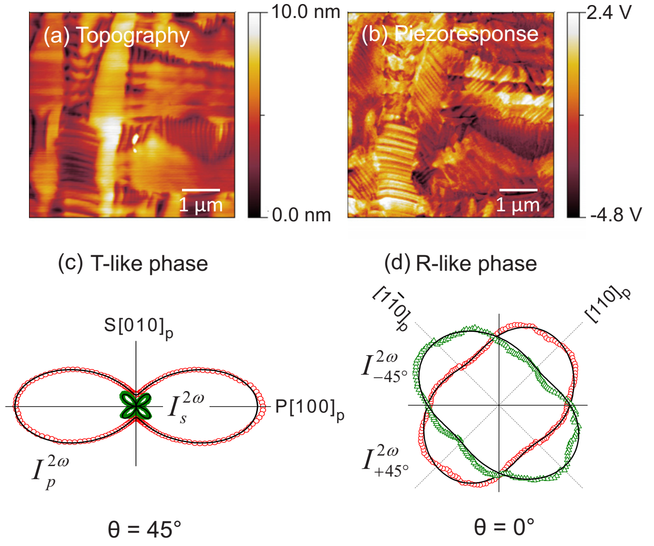

FIG. 2. (Color online) (a) Topography and (b) piezoresponse from a 160 nm mixed phase $\mathrm{BiFeO_3}//(001)_{pc}\mathrm{LaAlO_3}$. (c) Polarization dependence of SHG signal for the film tilted at an angle of $\theta=45°$ with respect to the surface normal of the film in s and p configurations. The signal is mostly dominated by the T-phase at this tilt. (d) Polarization dependence of SHG signal for the film with no tilt with respect to the surface normal and analyzer positions at $\varphi=45°$ and $-45°$. The signal arises entirely due to the R-phase in this configuration. The dark lines show excellent theoretical fits to the data.

$+\delta A_{34})\tilde{d}_2+\sqrt{2}d_{22}]+\tilde{f}_2[(\delta A_{13}+\delta A_{24})\tilde{d}_2+\sqrt{2}(\delta A_{13}-\delta A_{24})d_{22}]$. Here, δA_{ij} are the differences $i-j$ of the area fractions of the 4 domain variants with polarization along $[111]_p$, $[11\bar{1}]_p$, $[\bar{1}\bar{1}1]_p$, and $[\bar{1}\bar{1}\bar{1}]_p$ labeled 1–4, respectively, and $\tilde{d}_1=4d_{15}+2d_{31}+d_{33}$, $\tilde{d}_2=d_{15}-d_{31}+d_{33}$, and $\tilde{d}_3=-2d_{15}+2d_{31}+d_{33}$. Figure 1 shows the p-polarized SHG intensity as a function of the sample tilt, θ, for an incident average power density of 1.65 W/cm² for both film systems. For this power density, the substrates $\mathrm{YAlO_3}$ and $\mathrm{SrTiO_3}$ do not generate any SHG signal as shown in the same figure. The theoretical fits of the experimental data to Eq. (1) are also shown. As can be seen from the above equation, in normal incidence ($\theta=0°$) $I_{pp}(0)\propto A^2$ which is zero for the pure tetragonal phase ($\tilde{f}_z=0$ for $\theta=0$) and nonzero for the pure rhombohedral phase ($\tilde{f}_x\neq 0$ for $\theta=0$).[7] This is also confirmed by the experiments. Thus, in normal incidence geometry, the pure rhombohedral phase component in a mixed phase film can be uniquely probed. Although our film is not purely tetragonal, but rather tetragonal-like monoclinic phase (T-phase), it behaves predominantly like a pure tetragonal phase, with negligible SHG intensity at normal incidence for the above power density. Possible evidence for the monoclinic distortion in the T-phase is seen at ten times the above power density as discussed toward the end of this Letter.

Figures 2(a) and 2(b) depict a mixed phase system of 160 nm $\mathrm{BiFeO_3}//(001)_p\mathrm{LaAlO_3}$. This thickness is greater than the critical thickness (~30 nm) for which pure T-phase can exist. Hence a mixture of T-like and R-like phases coexist. These phases can be imaged using topography and PFM as shown in Figs. 2(a) and 2(b).[1] Figures 2(c) and 2(d) show the SHG intensity as a function of the incident polarization angle φ for two different values of sample tilt, θ, namely $\theta=45°$ (to probe the T-phase), and $\theta=0°$ (to probe the R-phase). The fits to these polar plots are based on the following equations:

$$I_{\langle 110\rangle}(\varphi)=K_1(\cos^2\varphi+K_2\sin^2\varphi)^2+K_3\sin^2(2\varphi)+K_4\sin 2\varphi(\cos^2\varphi+K_2\sin^2\varphi)\quad\text{(rhom.)},\tag{2}$$

$$\begin{aligned}I_p(\varphi)&=(P\cos^2\varphi+Q\sin^2\varphi)^2\\ I_s(\varphi)&=R\sin^2 2\varphi\end{aligned}\quad\text{(tet.)},\tag{3}$$

where for the tetragonal phase $P\propto d_{31}\sin\theta$, $Q\propto(2d_{15}+d_{31})\cos^2\theta\sin\theta+d_{33}\sin^3\theta$, $R\propto d_{15}\sin\theta$, and for the rhombohedral phase $K_1^x\propto d_{31}^2$, $K_1^y\propto(2d_{15}+d_{31}+2d_{33})^2$, $K_2^x=1/K_2^y=(2d_{15}+d_{31}+2d_{33})/d_{31}$, $K_3^x\propto K_3^y\propto d_{15}^2$, $K_4^x\propto d_{31}d_{15}$, and $K_4^y\propto(2d_{15}+d_{31}+2d_{33})d_{15}$ (with $x\equiv[1\bar{1}0]_p$ and $y\equiv[110]_p$). For $\theta=0°$, the signal is purely from the R-like phase, and for the $\theta=45°$, the signal appears to be dominated by the T-phase. This is confirmed by the excellent theoretical fits to Eqs. (2) and (3), and thus allows a clean distinction between the T-like and the R-like phases.

We now discuss the possible detection of the monoclinic distortion in a pure T-like phase film. (The monoclinicity in the R-like phase is not considered in this work due to its multiple domain variants which complicates analysis.) Although the pure T-like phase has a SHG signature that predominantly behaves as a pure tetragonal phase, nonetheless, symmetry considerations and higher incident power densities can allow us to test whether monoclinic distortion is present. The monoclinic phase[2] with point group m will have four possible twin variants with their mirror plane perpendicular to the substrate and parallel to the $(100)_p$ and $(010)_p$ planes. The expected governing SHG response for this system has identical functional dependence on φ as Eq. (2) except that now the coefficients K_{1-4} in the expression contain the nonlinear optical susceptibility tensor components of the point

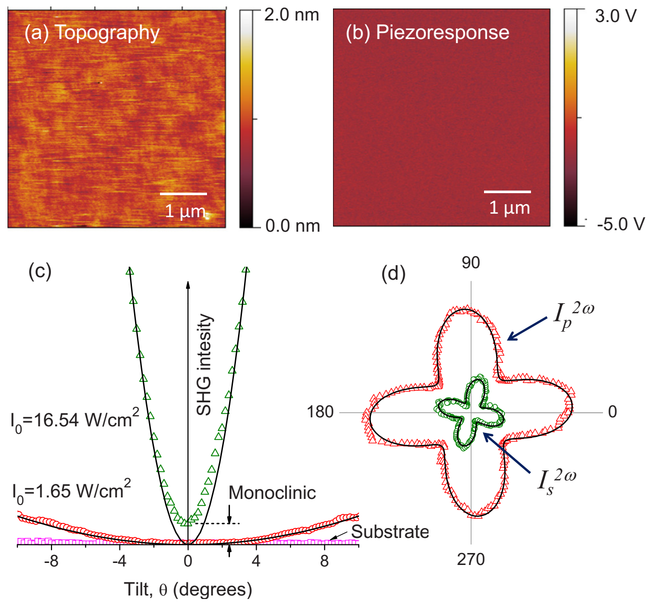

FIG. 3. (Color online) (a) Topography and (b) piezoresponse from a 25 nm T-phase $(001)_T BiFeO_3//YAlO_3$. (c) Angular tilt dependence of SHG signal for the film obtained at different input power densities in *p*-in-*p*-out configuration $[I_p^{2\omega}(\varphi=90°)]$. The nonzero signal observed at higher power density shows evidence of monoclinic distortion in the film. (d) Polarization dependence of the SHG signal obtained from the film at higher power density (I_0=16.54 W/cm^2) in normal incidence fit to monoclinic model. The dark lines show good theoretical fits to the data.

group *m* and the area fractions of the eight possible ferroelectric domain variants in the monoclinic phase arising from the four possible twin variants: $K_1^x \propto d_{12}^2$, $K_1^y \propto d_{11}^2$, $K_2^x = 1/K_2^y = d_{11}/d_{12}$, $K_3^x \propto K_3^y \propto d_{26}^2$, $K_4^x \propto d_{26}d_{12}$, and $K_4^y \propto d_{26}d_{11}$ (with $x \equiv [100]_p$ and $y \equiv [010]_p$).

Thus, in normal incidence ($\theta=0°$), the monoclinic phase is expected to result in some signal. However, the presence of any rhombohedral phase in the film can corrupt this monoclinic signature. Hence we performed atomic force microscopy (AFM) topography and PFM imaging of our nominally pure T-like phase film, as shown in Figs. 3(a) and 3(b). Within the detection resolution limit of our AFM/PFM system (~1 nm for AFM and ~10 nm for PFM), no secondary rhombohedral phases are observed. Thus we proceed to interpret the normal incidence signal as the monoclinic distortion in this pure T-like phase film. Figure 3(c) shows *p*-polarized SHG signal similar to that in Fig. 1, but at two different power densities of the incident fundamental light. Although at a power density of 1.65 W/cm^2 no signal is observed in normal incidence, at higher power densities of 16.5 W/cm^2 a very small signal is observed in normal incidence. Theoretical fit to this curve using Eq. (1) clearly shows that near normal incidence, the signal does not correspond to a pure tetragonal phase. We can interpret this difference as the signature of monoclinic distortion in the T-like phase. Figure 3(d) shows polar plots of SHG intensity versus the incident polarization angle φ, and the corresponding theoretical fits based on the monoclinic model. The theoretical fit is excellent. Thus, barring the presence of undetectable rhombohedral phases not observed in our AFM/PFM experiments, one can interpret this as evidence of monoclinic distortion in the pure T-like phase, as has been predicted by theory. We note that this small SHG signal at normal incidence disappears at ~380 °C, which is the antiferromagnetic transition temperature of rhombohedral $BiFeO_3$. Thus either monoclinicity disappears at the same temperature, or it indicates trace amounts of rhombohedral phase. The detection of monoclinicity is, therefore, not unequivocal.

In summary, we show that optical second harmonic generation can elegantly distinguish T-like and R-like distortions in mixed phase strained $BiFeO_3$ films. The monoclinic distortion of these strained films, as predicted by theory, can only be detected by SHG in films with pure T-like phase in single domain films with no rhombohedral phase component; since SHG can detect trace amounts of secondary phases, monoclinicity is difficult to prove unequivocally. The same symmetry arguments also hold for other morphotropic systems with tetragonal, rhombohedral and potentially monoclinic phases, such as in Pb_xZrTiO_3 (PZT), PMN-PT, etc. Given the large tunability in piezoelectric and ferroelectric properties expected in mixed phase systems, SHG can prove to be a valuable probe of dynamical properties of these phases under external stimuli such as electric fields and temperature.

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