

Anomalous low-energy phonons in nearly tetragonal BiFeO₃ thin films

K.-Y. Choi,^{1,*} S. H. Do,¹ P. Lemmens,² D. Wulferding,² C. S. Woo,³ J. H. Lee,³ K. Chu,³ and C.-H. Yang³

¹*Department of Physics, Chung-Ang University, Seoul 156-756, Republic of Korea*

²*Institute for Condensed Matter Physics, TU Braunschweig, D-38106 Braunschweig, Germany*

³*Department of Physics, KAIST, Daejeon 305-701, Republic of Korea*

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We present evidence for a concomitant structural and ferroelectric transformation around $T_S \sim 360$ K in multiferroic BiFeO₃/LaAlO₃ thin films close to the tetragonal phase. Phonon excitations are investigated by using Raman scattering as a function of temperature. The low-energy phonon modes at 180–260 cm⁻¹ related to the FeO₆ octahedron tilting show anomalous behaviors upon cooling through T_S : (i) a large hardening amounting to 15 cm⁻¹, (ii) an increase of intensity by one order of magnitude, and (iii) an appearance of a dozen new modes. In contrast, the high-frequency modes exhibit only weak anomalies. This suggests an intimate coupling of octahedron tilting to ferroelectricity leading to a simultaneous change of structural and ferroelectric properties.

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The multiferroic compound BiFeO₃ (BFO) is in the focus of experimental and theoretical research directed toward room-temperature multifunctional devices.^{1–4} The distinct multiferroic properties of BFO rely on the high ferroelectric ($T_c \sim 1100$ K) and antiferromagnetic ($T_N \sim 640$ K) transition temperature as well as their mutual couplings.^{5,6} Bulk BFO has a rhombohedral structure with $R3c$ symmetry.

With increasing strain above 4%, a structural phase transition takes place from a rhombohedral (R)- to a supertetragonal (T)-like structure. Although the symmetry of strained films is more likely to be monoclinic, we adopt the convention to label the respective phases as R like and T like to stress the symmetry of their parent structures.^{7,8} The relative fraction of the T and the R phases is controllable as function of both film thickness and an electric field.^{2,9} It has been shown that the magnetic transition temperature hardly varies but the ferroelectric Curie temperature is strongly reduced with strain.⁴ Octahedron tilting is suggested to be responsible for the anomalous strain dependence of ferroelectricity. First-principles calculations uncovered a wealth of low-symmetry structures (Cc , Cm , Pc , or $Pna2_1$), which are nearly degenerate in energy.⁸ X-ray diffraction, Mössbauer spectroscopy, and piezoresponse force microscopy studies indicate that the majority T-like phase concomitantly undergoes structural, magnetic, and ferroelectric transitions around $T_S \sim 360$ K.¹⁰

Raman spectroscopy can serve as a sensitive, local probe of structural and multiferroic properties. Single crystalline and low-strain BFO film exhibited an exceptional coupling of multimagnon, phonon, and electronic excitations.^{11,12} Raman scattering on highly strained BFO films showed monoclinic distortions from the T phase and a first-order structural transition to a new T phase at about 370 K.^{7,13} Although a previous Raman scattering study evidenced the temperature-induced phase transition, the underlying mechanism is not fully clarified.

In this study, we report on enormous anomalies of low-frequency FeO₆ octahedra rotation modes. The concomitant, drastic change of the phonon parameters through T_S suggests the mutual coupling of structural and multiferroic properties.

Two BiFeO₃ thin films of different thickness (30 and 80 nm) were grown on (001) LaAlO₃ (LAO) substrates by using pulsed laser deposition at the growth temperature of

650 °C and at the oxygen partial pressure of 100 mTorr. The surface morphologies were investigated by scanning probe microscopy (Veeco Multimode V) with Ti/Pt coated Si tips (MikroMasch). Clear step terrace structures, as shown in Fig. 1, reveal that both films were grown in a step flow mode, indicating good crystallinity. The thinner film mainly consists of the T-like BFO, while the thicker one contains mixed phase areas (darker areas in the AFM) where the T-like phase and the R phase alternate on nanolength scales. We conclude a strain relaxation in the thicker film. The surface morphologies and the thickness dependence of the phase evolution match well to previous results.²

Raman scattering experiments have been performed in backscattering geometry with the excitation line $\lambda = 532$ nm of Nd:YAG solid-state laser by using a micro-Raman spectrometer (Jobin Yvon LabRam HR). The light beam was focused to a few- μ m-diameter spot on the surface of the BFO thin films using a 50-times-magnification microscope objective. The temperature is varied between 10 and 390 K by using a helium cryostat.

Figure 2 compares unpolarized Raman spectra of BFO (30 nm) and BFO (80 nm) thin films measured at $T = 10$ K and $T = 390$ K. Due to the small thickness of the studied films, we observe Raman signals from both the substrate and the BFO film. The substrate peaks are identified by measuring separately the LAO crystal. At 390 K we observe six phonon modes at 221, 231, 275, 365, 594, and 690 cm⁻¹.

For the $P4mm$ tetragonal structure, the factor group analysis yields eight Raman-active modes of $3A_1 + B_1 + 4E$. In the backscattering geometry normal to the (001) surface, $3A_1 + B_1$ modes of them are symmetry allowed. In comparison to Ref. 7, the 221, 275, 365, and 690 cm⁻¹ modes are assigned to the tetragonal phase. The two extra modes might be due to either monoclinic distortions or the R phase. This indicates that for temperatures above $T_S \sim 360$ K the BFO film ($t \leq 100$ nm) has a nearly tetragonal structure. At 10 K we identify a total of 22 phonon modes for frequencies above 170 cm⁻¹, which match well with 27 expected modes ($\Gamma = 14A' + 13A''$) for the monoclinic (Cc) symmetry. This suggests that a more monoclinic-like phase is stabilized at low temperatures.^{7,8,14,15} Both the BFO (30 nm) and the BFO (80 nm) films show the same number of phonons and no noticeable shift in the

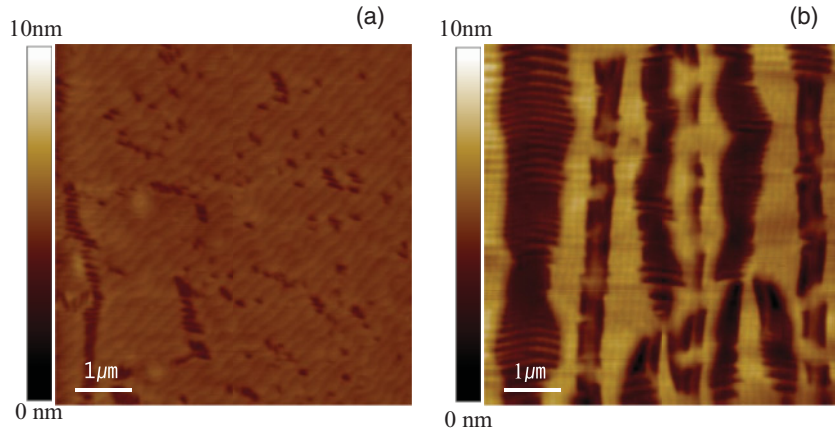


FIG. 1. (Color online) Surface morphologies taken by scanning probe microscopy for the BFO films with thickness of (a) 30 and (b) 80 nm.

phonon frequency. The distinct difference is seen in the relative intensities of the 177, 227, 244, 274, 365, 409, 516, and 598 cm^{-1} modes, which are enhanced in the BFO (80 nm) film. It is noteworthy that the numbers and frequencies of them are very close to those obtained from a rhombohedral crystal structure (compare to Table I of Ref. 16). Since the substrate strain is released with increasing thickness, these

modes are attributed to the minority R-phase. This evidences the coexistence of the T-like and the R-like phase.

Figures 3(a) and 3(b) zoom into the low- and the high-energy part of the Raman spectra. The low-energy modes below 300 cm^{-1} show a drastic temperature dependence in their number, frequency, and intensity while the high-energy modes exhibit a moderate change. To investigate the evolution of the phonon modes in detail we fit them to Lorentzian profiles [see Fig. 5(a)]. The resulting frequency, linewidth, and intensity are plotted as functions of temperature for the two lines at 180 and 690 cm^{-1} in Fig. 4.

With lowering temperature, the 180-cm^{-1} mode undergoes a large hardening by 15 cm^{-1} , starting at around T_S . Its linewidth decreases monotonically and its scattering intensity grows by one order of magnitude. As the Raman scattering intensity is proportional to the square of the derivative of the dielectric function with respect to the amplitude of the normal mode, the strong intensity increase means that the low-energy

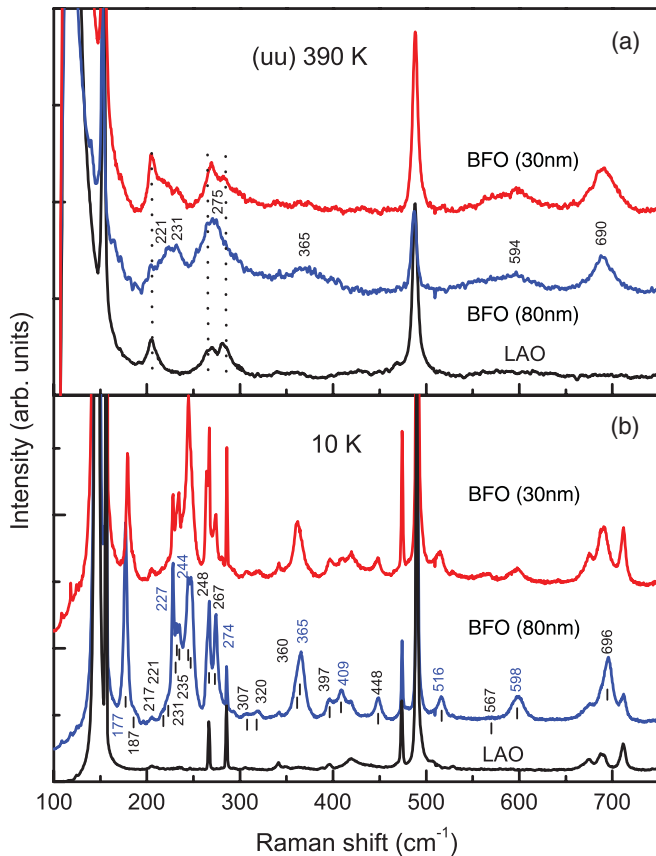


FIG. 2. (Color online) (a) Comparison of unpolarized Raman spectra between BFO (30 nm) and BFO (80 nm) thin films at 390 K. The given numbers are the phonon frequencies of the BFO (80 nm) film. For reference, a Raman spectrum of an LAO substrate is also shown. (b) Unpolarized Raman spectra of BFO (30 nm), BFO (80 nm), and LAO at 10 K. The bars denote the peaks from the BFO (80 nm) film.

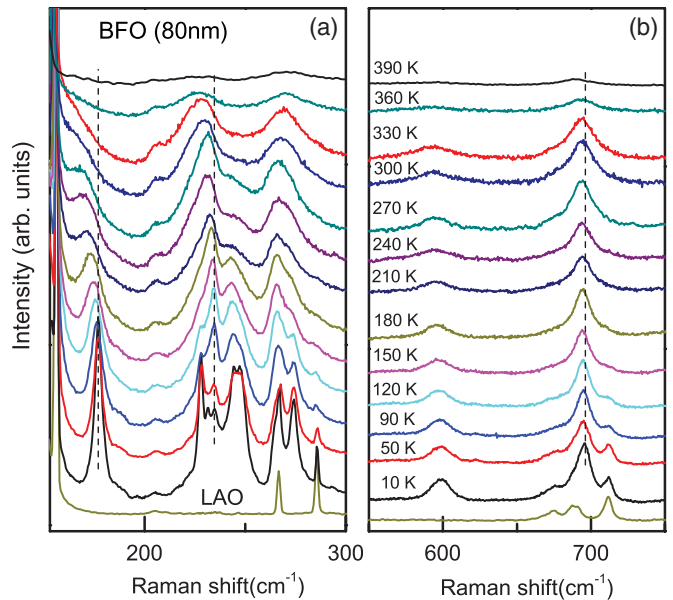


FIG. 3. (Color online) (a) Temperature dependence of the low-frequency Raman spectra of the BFO (80 nm) thin film. The dashed vertical lines are guide to the evolution of phonon frequencies. (b) Temperature dependence of the high-frequency part of Raman spectra.

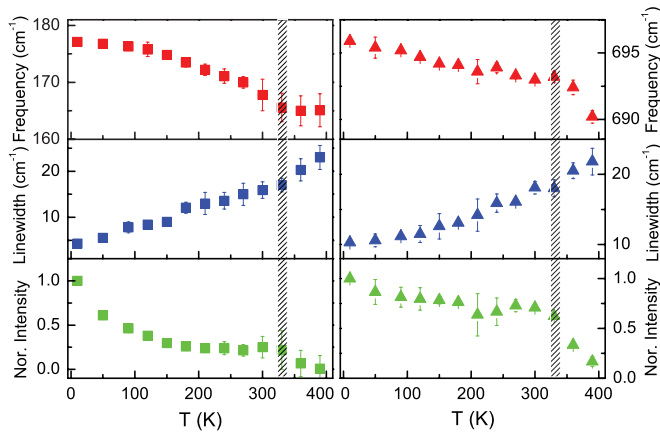


FIG. 4. (Color online) (Left panel) Temperature dependence of the frequency, the linewidth, and the normalized intensity of the low-energy 180 cm^{-1} mode for the BFO (80 nm) film. (Right panel) Temperature dependence of the phonon parameters of the high-energy 690 cm^{-1} mode. The shaded bars indicate the structural transition temperature.

modes are susceptible to a change of ferroelectricity. Since the low-energy modes are associated with the external vibrations of the FeO_6 octahedra¹⁷ and polar cation displacements,¹⁸ they provide a measure of the tilting degree of the FeO_6 octahedra.¹⁹ In this light, the concomitant change of intensity and frequency suggests that the increase of octahedral tilting accompanies the polar cation displacements. Exactly this cross-coupling effect has been discussed as an origin of the reduction of the ferroelectric transition temperature under strain.⁴

The high-frequency modes are related to the internal vibrations of the FeO_6 octahedra and are susceptible to a change in the Fe-O bond distance and angle. The phonon parameters of the 690 cm^{-1} mode show only small anomalies at about T_S .

Since the Fe-O bond angle and length determines a strength of superexchange interactions, we conclude that the magnetic interactions are rather weakly coupled to ferroelectricity.

In Fig. 5 we focus on the evolution of the low-frequency phonons with $\Delta\omega = 220\text{--}260\text{ cm}^{-1}$. With decreasing temperature, several anomalies develop. For temperatures below T_S , several extra modes appear at 231, 244, and 248 cm^{-1} . Between T_S and 150 K the phonon frequencies undergo a substantial hardening and the linewidths strongly narrow. Noteworthy is the large enhancement of the 222-- and 234 cm^{-1} modes upon cooling through T_S and the small drop of their intensity for temperatures below $170\text{--}240\text{ K}$. The concomitant, drastic change of the phonon number and intensity indicates a complex nature of the phase transition. The increased number of the phonon modes is due to a transition from the more T-like phase to the monoclinic-like one.^{10,13} The structural change can also lead to the enhancement of phonon scattering intensity. However, the observed huge anomalies invoke the strong change of electronic polarizabilities beyond the structural transformation.

Notably, the recent first-principles calculations by Diéguez *et al.*⁸ suggest that antiferroelectric patterns and twisting modes of the FeO_6 octahedra are important in determining the relative stability of the low-symmetry T-like phases. Such so-called secondary modes can also fine-tune polarization. Therefore the intensity-polarizability enhancements and the hardening of the low-energy tilting modes are evidence for the coupled structural-ferroelectric transition. Actually, Infante *et al.*¹⁰ showed that a hard-to-soft ferroelectric transition accompanies the structural transition. The low-frequency internal modes exhibit the soft-mode-like behavior as the temperature is increased to T_S [see Figs. 4 and 5(b)]. The corresponding Raman shifts are fitted to the relation, $\Delta\omega \propto |T - T_S|^\beta$ with the critical exponent β . We find no reasonable agreement between the experimental data and the

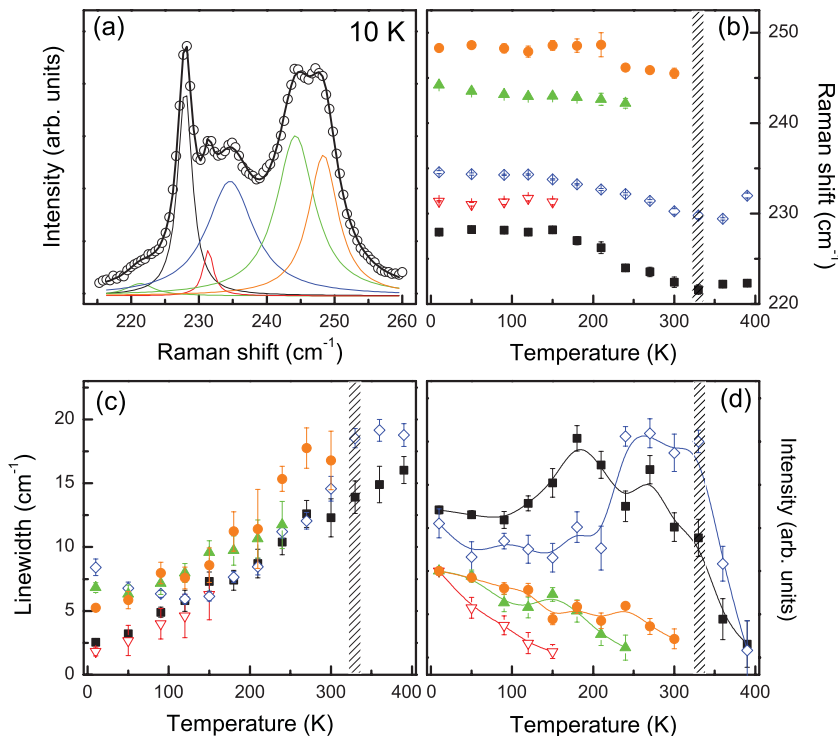


FIG. 5. (Color online) (a) Fit of the low-energy Raman spectrum to Lorentzian profiles at 10 K. (b), (c), and (d) Temperature dependence of the optical phonon frequencies, linewidths, and intensities.

fitted curve (not shown here). This might be due to the fact that the structural transition involves a number of competing, metastable phases.⁸

In summary, we have presented a Raman scattering study of nearly tetragonal BFO thin films in the temperature range of 10–390 K. We observe large anomalies of the internal phonon modes of 180–300 cm⁻¹, which are susceptible to the tiltings of the FeO₆ octahedron. The most salient feature is the strong enhancement of phonon intensity and the increase of

the phonon number through a structural phase transition. Our study suggests that the structural and ferroelectric transitions are intimately tied because the low symmetry of the strained films can afford a large number of metastable structural phases with different polar distortions and rotation patterns.

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*kchoi@cau.ac.kr

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¹⁷Although Fe³⁺ ions of the T-like phase are thought to be coordinated in FeO₅ pyramids, isomer shift values of Mössbauer spectroscopy indicate that Fe³⁺ ions of both the T- and R-like phases are in octahedral environments.¹⁰

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