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## Polarized Raman scattering of multiferroic BiFeO<sub>3</sub> epitaxial films with rhombohedral *R3c* symmetry

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Highly (111)-oriented rhombohedral BiFeO<sub>3</sub> (BFO) thin films were grown on (111) SrTiO<sub>3</sub> substrates by pulsed laser deposition. Polarized Raman-scattering study of the (111)-oriented epitaxial BFO thin film with rhombohedral *R3c* symmetry was carried out by employing two distinct backscattering geometries. The *A*<sub>1</sub>-symmetry transverse-optical [*A*<sub>1</sub>(TO)] phonons were selectively isolated from the *E*-symmetry transverse-optical [*E*(TO)] phonons by employing *Y'*(*ZZ*)*Y'* polarization configuration in a novel side-view backscattering. By comparing the *Y'*(*ZZ*)*Y'* spectrum with the *Z*(*X'X'*)*Z* polarization spectrum in a normal backscattering, we were able to assign most of *A*<sub>1</sub> and *E*-symmetry normal modes of *R3c* BFO. In addition, we found that there was a negligible LO-TO splitting in the *A*<sub>1</sub>-symmetry normal modes. © 2006 American Institute of Physics. [DOI: 10.1063/1.2168038]

Multiferroic materials combine two or more of the properties of ferromagnetism, ferroelectricity, and ferroelasticity.<sup>1,2</sup> Under the action of an external magnetic field, such materials would show electric polarization while an external electric field would induce magnetization.<sup>1</sup> Multiferroism is currently the subject of intensive investigation because multiferroic materials potentially offer a whole range of new applications, including the emerging field of spintronics, new data-storage media,<sup>3</sup> and multiple-state memories.<sup>1</sup> However, there are very few systems existing in nature because transition-metal *d* electrons reduce the tendency for an off-centering ferroelectric distortion.<sup>1</sup>

BiFeO<sub>3</sub> (BFO) is known to be the only material that exhibits multiferroism at room temperature.<sup>2</sup> It is a rhombohedrally distorted ferroelectric perovskite (*T*<sub>c</sub> ≈ 1100 K) with the space group *R3c* (Ref. 4) and shows *G*-type antiferromagnetism up to 643 K (*T*<sub>N</sub>).<sup>5</sup> The rhombohedral unit cell parameters are *a* = 5.63 Å and *a* = 59.35°. In this distorted structure, the *R3c* symmetry permits the development of a spontaneous polarization (*P*<sub>s</sub>) along the pseudo-cubic [111] direction. Bi<sup>3+</sup> and Fe<sup>3+</sup> cations are displaced from their centro-symmetric positions along this threefold rotation axis.<sup>6</sup> However, BFO shows unexpectedly small values of the ferroelectric polarization with ~3.5 μC/cm<sup>2</sup> along [100] and ~6.1 μC/cm<sup>2</sup> along [111] even in a single crystal.<sup>7</sup>

A few recent studies reported<sup>8,9</sup> that the (111)-oriented rhombohedral BFO thin film fabricated on a (111) SrTiO<sub>3</sub> (STO) exhibited a giant polarization of ~100 μC/cm<sup>2</sup> along the principal [111] polarization direction. According to these studies,<sup>8,9</sup> the easy axis of *P*<sub>s</sub> lies close to [111], and the polarization value measured along [100] or [101] is simply a geometrical projection onto this orientation.

Raman-scattering technique can provide us with a very useful insight to the “softening” of dynamic ferroelectric modes<sup>10</sup> and the spin-phonon coupling<sup>11,12</sup> in ABO<sub>3</sub>-type perovskites. In spite of its importance, however, the normal mode assignment of rhombohedral BFO by employing polar-

ized Raman-scattering method has not been reported yet. This is mainly due to the well-known difficulty in the preparation of a (111)-oriented single crystal of rhombohedral BFO. In view of this difficulty, it is highly desirable to prepare a (111)-oriented epitaxial BFO thin film. In this letter we report polarized Raman-scattering study of the (111)-oriented rhombohedral BFO thin films that have been known to possess giant *P*<sub>s</sub> values.<sup>8,9</sup> We have assigned the *A*<sub>1</sub>-symmetry transverse-optical [*A*<sub>1</sub>(TO)] phonons by employing a side-view backscattering geometry. On the contrary, we have assigned the *A*<sub>1</sub>-symmetry longitudinal-optical *A*<sub>1</sub>(LO) phonons and the *E*-symmetry transverse-optical [*E*(TO)] phonons by employing a normal backscattering geometry.

Epitaxial BFO thin films were grown on (111) STO substrates by employing pulsed laser deposition (PLD) method. The deposition conditions used in the present study are essentially the same as those employed in the preparation of (001)-oriented epitaxial BFO thin films.<sup>13</sup> The lattice-constant mismatch between the BFO film and the STO layer is very small (~1.4%), resulting in a slightly tensile in-plane stress in the (111)-oriented BFO films. The average thickness of these films, as estimated using field-emission scanning electron microscopy, was 600 ± 30 nm.

To examine the structure of the PLD-grown BFO thin film on a STO (111) substrate, theta-2theta (*θ*-2*θ*) x-ray diffraction (XRD) and *Φ*-scan experiments were carried out, and their results are shown in Fig. 1. As presented in Fig. 1(a), the film is exclusively characterized by the [111] growth. The degree of in-plane orientation was assessed by examining XRD *Φ*-scan spectra. As presented in Fig. 1(b), the peaks for (022) reflection of the (111)-oriented domain occur at the same azimuthal *Φ* angle as those for STO (022) reflection and are 120° apart from each other. This clearly indicates the presence of threefold symmetry along the [111] direction and a “cube-on-cube” epitaxial growth of BFO on a STO (111) substrate.

Room-temperature magnetic hysteresis loop of the (111)-oriented epitaxial film was measured by employing a superconducting quantum interference magnetometer (Quan-

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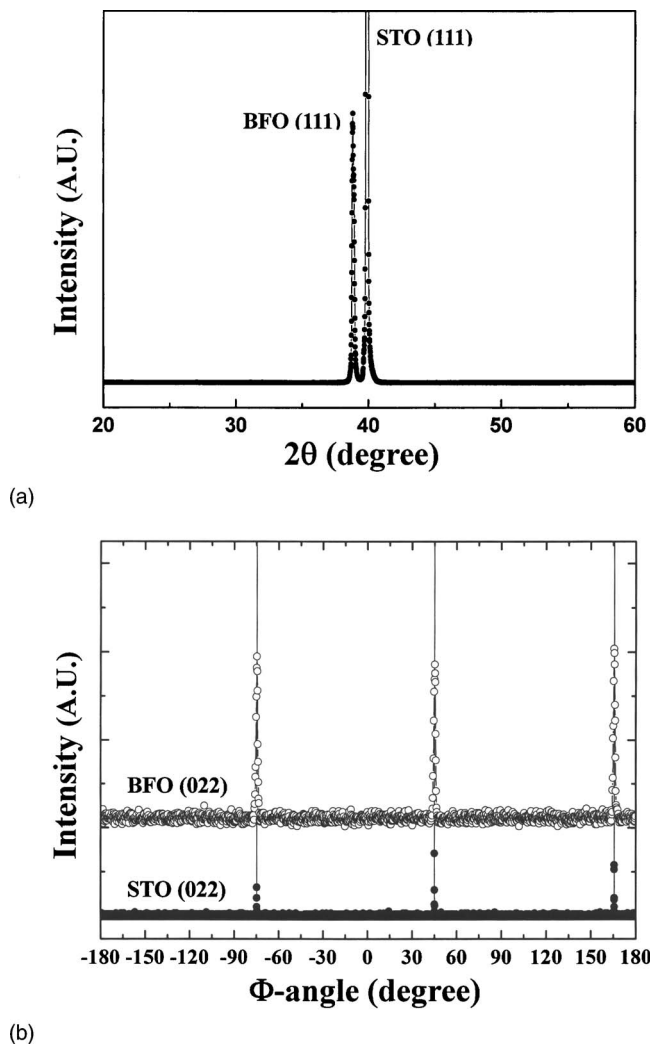


FIG. 1. (a) Theta-2theta ( $\theta$ - $2\theta$ ) XRD pattern of a PLD-grown BiFeO<sub>3</sub> thin film on a SrTiO<sub>3</sub> (111) substrate. (b)  $\Phi$ -scan diffraction pattern of a 600-nm-thick BiFeO<sub>3</sub> film and of a SrTiO<sub>3</sub> substrate on (022) planes.

tum design MPMS-5S) with the magnetic field applied parallel to the film plane. The film showed a saturated weak ferromagnetic response similar to the magnetic hysteresis loop of the (001)-oriented epitaxial BFO film.<sup>13</sup>

Polarized Raman-scattering data were obtained using a NRS-2100 spectrometer (JASCO, Japan) equipped with a triple-grating monochromator and a Coherent Innova 90C Ar<sup>+</sup> laser at 514.5 nm. The measurement was performed with a micro-Raman option using a LN<sub>2</sub> cooled charge coupled device. Linear polarization of the Raman signal was analyzed by employing two distinct backscattering geometries: (i) normal backscattering in which the direction of the incident and scattered light is parallel to the principal [111] polar axis, and (ii) side-view backscattering in which the direction of the incident and scattered light is perpendicular to the [111] direction of the epitaxial BFO thin film, as schematically represented in Figs. 2(a) and 2(b), respectively. Since the BFO thin film exhibits a cube-on-cube epitaxial growth on a STO (111) plane (Fig. 1), the Z direction is parallel to the principal [111] direction, whereas X' and Y' represent two orthogonal directions that are parallel to experimental stage but are perpendicular to the polar axis (Z direction) of rhombohedral BFO films. On the other hand, X, Y and Z are three mutually perpendicular directions. Thus,

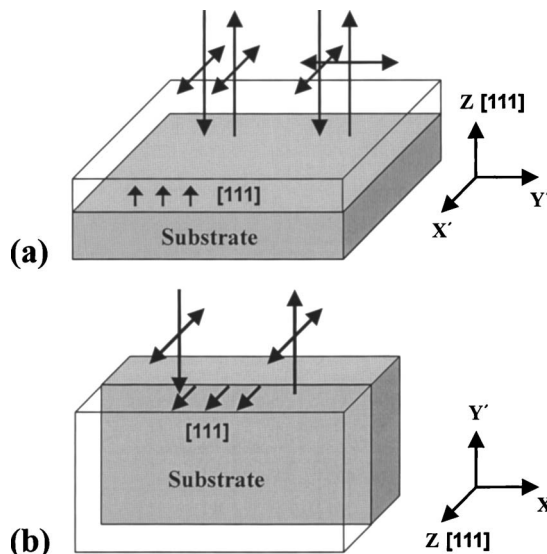


FIG. 2. Two backscattering geometries used in polarized Raman-scattering study of the (111)-oriented epitaxial BiFeO<sub>3</sub> thin film with rhombohedral  $R3c$  symmetry. (a) normal backscattering in which the propagation direction of relevant phonons is parallel to the principal [111] polar axis. (b) Side-view backscattering in which the propagation direction of relevant phonons is perpendicular to the principal [111] polar axis.

if Z is parallel to [111], X and Y are parallel to  $[1\bar{1}0]$  and  $[\bar{1}\bar{1}2]$ , respectively.

As discussed previously, the (111)-oriented epitaxial BFO film is characterized by rhombohedral symmetry (Fig. 1) with the point group  $3m(C_{3v})$  and the space group  $R3c(C_{3v}^6)$ . The Raman active modes of the rhombohedral BFO ( $R3c$ ) can be summarized using the following irreducible representation:  $\Gamma = 4A_1 + 9E$ . According to the Raman selection rule, the  $A_1$  normal modes are expected to appear in the parallel  $XX$ ,  $YY$ , and  $ZZ$  polarization configurations while they should not be seen in the cross  $XY$  configuration. On the other hand, the nine doubly degenerate  $E$  modes are allowed in  $XX$ ,  $YY$  and  $XY$  polarization configurations. Since X' and Y' are not parallel to X and Y, respectively, all four possible polarization configurations, i.e.,  $(XX)$ ,  $(YY)$ ,  $(XY)$ , and  $(YX)$ , can be obtained by  $Z(X'X')Z$  or  $Z(X'Y')Z$  normal backscattering geometry.<sup>14</sup>

Figure 3 presents room-temperature (298 K) polarized

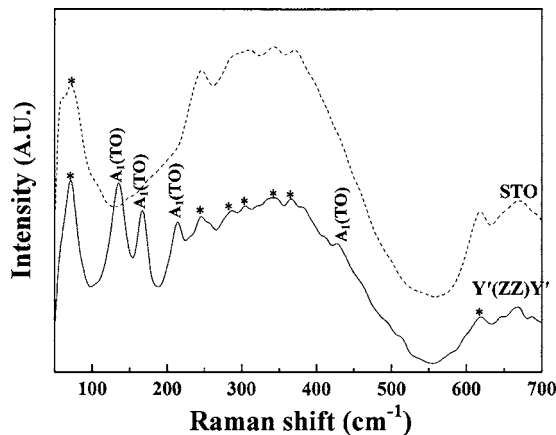


FIG. 3. Room-temperature polarized Raman spectrum of the 600-nm-thick (111)-oriented rhombohedral BiFeO<sub>3</sub> thin film and of a (111) SrTiO<sub>3</sub> substrate, as obtained by employing Y'(ZZ)Y' backscattering geometry.

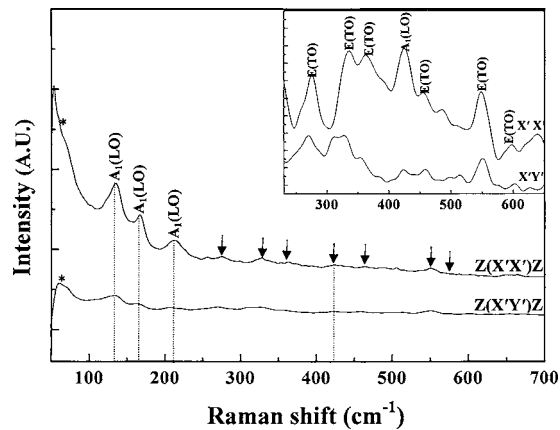


FIG. 4. Room-temperature polarized Raman spectra of the 600-nm-thick (111)-oriented rhombohedral BiFeO<sub>3</sub> thin film obtained by employing two distinct normal backscattering Z(X'X')Z and Z(X'Y')Z geometries. The inset presents a magnified view, showing one A<sub>1</sub>(LO) and six E(TO) modes.

Raman-scattering data of the 600-nm-thick (111)-oriented epitaxial BFO thin film, as obtained by employing the side-view Y'(ZZ)Y' backscattering geometry. An intense peak observed at 72 cm<sup>-1</sup> originates from a STO substrate. Considering the scattering tensors for A<sub>1</sub> and E normal modes, one can readily conclude that for the [111]-oriented rhombohedral film with 3m symmetry, only A<sub>1</sub>(TO) normal modes are allowed in the Y'(ZZ)Y' parallel polarization configuration.<sup>14</sup> Thus, the three relatively intense peaks appeared at 136, 168, and 212 cm<sup>-1</sup> and one weak peak at 425 cm<sup>-1</sup> in the Y'(ZZ)Y' spectrum can be assigned to A<sub>1</sub>(TO) modes. These mode frequencies (136, 168, and 212 cm<sup>-1</sup>) are essentially the same as the three mode frequencies of A<sub>1</sub>(TO) modes observed in the (001)-oriented pseudo-tetragonal BFO film.<sup>15</sup> In addition to these A<sub>1</sub>(TO) peaks, the Y'(ZZ)Y' spectrum also shows several other peaks originating from the (111) STO substrate, as marked with the asterisk (\*).

Polarized Raman-scattering data of the (111)-oriented epitaxial BFO thin film were also obtained by employing two distinct normal backscattering Z(X'X')Z and Z(X'Y')Z geometries, and their results at room temperature are presented in Fig. 4. In these polarization configurations, the propagation direction of the relevant phonon wave vector *k* is parallel to the principal [111] axis of rhombohedral BFO. Because the phonon-propagation direction for Z(X'X')Z backscattering is parallel to the [111] direction (i.e., Z direction), the A<sub>1</sub> normal mode whose eigenvector is parallel to the Z direction should be purely longitudinal.<sup>14</sup> As presented in Fig. 4, we observed three intense peaks at 136, 168 and 212 cm<sup>-1</sup> and a weak-intensity peak at 425 cm<sup>-1</sup> in the Z(X'X')Z spectrum. Comparing these values with the mode frequencies of A<sub>1</sub>(TO) phonons (Fig. 3) and considering a normal degree of the LO-TO splitting in weakly ionic ABO<sub>3</sub>-type perovskites,<sup>16</sup> one can clearly conclude that these four peaks at 136, 168, 212, and 425 cm<sup>-1</sup> in the Z(X'X')Z spectrum are the manifestation of longitudinal-optical A<sub>1</sub>(LO) modes rather than transverse-optical E(TO) modes.

In addition to A<sub>1</sub>(LO) peaks, both Z(X'X')Z and Z(X'Y')Z spectra show several weak signals. The inset presents the Raman spectra in the higher frequency region (above 230 cm<sup>-1</sup>), clearly showing the six peaks at 275, 335, 363, 456, 549 and 597 cm<sup>-1</sup>. These are common in both spectra and thus are assigned to E(TO) phonons. We also

notice that the E(TO) peaks appearing in the Z(X'X')Z and Z(X'Y')Z spectra (Fig. 4) are absent in the Y'(ZZ)Y' spectrum (Fig. 3), which is consistent with our prediction that the E-symmetry phonon cannot be observed under the side-view Y'(ZZ)Y' scattering.<sup>14</sup>

The Raman-scattering data clearly show that there is a negligible LO-TO splitting of A<sub>1</sub>-symmetry phonons in the rhombohedral BFO with R3c symmetry. The splitting between A<sub>1</sub>(LO) and A<sub>1</sub>(TO) modes can be understood in terms of the Born effective charges (BEC). According to Zhong, King-Smith and Vanderbilt,<sup>16</sup> anomalously large BEC values are generic to weakly ionic oxides that tend to have some covalent character. The BEC values of Bi, Fe, and O ions are 4.37, 3.49, and -2.61, respectively, in the rhombohedral BFO, as estimated by Neaton *et al.*<sup>17</sup> These anomalous BEC values of Bi, Fe, and O ions in BiFeO<sub>3</sub> indicate the relative importance of covalent character,<sup>16</sup> as compared with ionic nature, in Bi-O and Fe-O bonds. Thus, the observed negligible LO-TO splitting of A<sub>1</sub> normal modes indicates that the short-range interatomic force dominates over the long-range ionic force in the rhombohedral 3m phase of BFO.

In conclusion, we have assigned most of A<sub>1</sub> and E-symmetry normal modes of R3c BFO by comparing the Y'(ZZ)Y' spectrum with the Z(X'X')Z spectrum. The A<sub>1</sub>(TO) phonons were isolated from the E(TO) phonons by employing a side-view backscattering geometry.

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<sup>1</sup>N. A. Hill, J. Phys. Chem. B **104**, 6694 (2000).

<sup>2</sup>J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, Science **299**, 1719 (2003).

<sup>3</sup>M. Fiebig, Th. Lottermoser, D. Fröhlich, A. V. Goltsev, and R. V. Pisarev, Nature (London) **419**, 818 (2002).

<sup>4</sup>F. Kubel and H. Schmid, Acta Crystallogr., Sect. B: Struct. Sci. **46**, 698 (1990).

<sup>5</sup>P. Fischer, M. Połomska, I. Sosnowska, and M. Szymański, J. Phys. C **13**, 1931 (1980).

<sup>6</sup>C. Michel, J.-M. Moreau, G. D. Achenbach, R. Gerson, and W. J. James, Solid State Commun. **7**, 701 (1969).

<sup>7</sup>J. R. Teague, R. Gerson, and W. J. James, Solid State Commun. **8**, 1073 (1970).

<sup>8</sup>J. Li, J. Wang, M. Wutting, R. Ramesh, N. Wang, B. Ruetter, A. P. Pyatakov, A. K. Zvezdin, and D. Viehland, Appl. Phys. Lett. **84**, 5261 (2004).

<sup>9</sup>F. Bai, J. Wang, M. Wutting, J. Li, N. Wang, A. P. Pyatakov, A. K. Zvezdin, L. E. Cross, and D. Viehland, Appl. Phys. Lett. **86**, 032511 (2005).

<sup>10</sup>S. M. Cho and H. M. Jang, Appl. Phys. Lett. **76**, 3014 (2000).

<sup>11</sup>M. N. Iliiev, A. P. Litvinchuk, H.-G. Lee, C. L. Chen, M. L. Dezaneti, C. W. Chu, V. G. Ivanov, M. V. Abrashev, and V. N. Papov, Phys. Rev. B **59**, 364 (1999).

<sup>12</sup>E. Granado, A. García, J. A. Sanjurjo, C. C. Rettori, I. Torriani, F. Prado, R. D. Sánchez, A. Caneiro, and S. B. Oseroff, Phys. Rev. B **60**, 11879 (1999).

<sup>13</sup>D. Lee, M. G. Kim, S. Ryu, H. M. Jang, and S. G. Lee, Appl. Phys. Lett. **86**, 222903 (2005).

<sup>14</sup>H. Yi, M. G. Kim, J. H. Park, and H. M. Jang, J. Appl. Phys. **96**, 5110 (2004).

<sup>15</sup>M. K. Singh, S. Ryu, and H. M. Jang, Phys. Rev. B **72**, 132101 (2005).

<sup>16</sup>W. Zhong, R. D. King-Smith, and D. Vanderbilt, Phys. Rev. Lett. **72**, 3618 (1994).

<sup>17</sup>J. B. Neaton, C. Ederer, U. V. Waghmare, N. A. Spaldin, and K. M. Rabe, Phys. Rev. B **71**, 014113 (2005).