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# Optical anisotropy and charge-transfer transition energies in BiFeO<sub>3</sub> from 1.0 to 5.5 eV

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## ABSTRACT

We discuss uniaxial optical anisotropy in single-crystal BiFeO<sub>3</sub> determined by spectroscopic ellipsometry from 1.0 to 5.5 eV. The dielectric function  $\epsilon = \epsilon_1 + i\epsilon_2$  and refractive index  $N = n + ik$  spectra of BiFeO<sub>3</sub> are extracted for the tensor components along its ordinary and extraordinary principal axes. Using the standard lineshape analysis, we also obtain the energies of the major optical structures associated with the charge-transfer transitions in BiFeO<sub>3</sub>.

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Bismuth ferrite ( $\text{BiFeO}_3$ ) is so far the only known compound that exhibits both antiferromagnetism and a strong ferroelectricity at room temperature.<sup>1-3</sup> Such a unique multiferroic characteristic has made  $\text{BiFeO}_3$  a very attractive material for fundamental physics studies.<sup>1-4</sup> For practical applications,<sup>3</sup> possible electrical manipulation of the magnetic states (*magneto-electric coupling*) has stimulated an intense effort to realize various novel devices in magnetoelectric memory storage and electric-field control of magnetic sensors for example. Also, the large saturation polarization and the smaller bandgap (than many other ferroelectric perovskite compounds) of  $\text{BiFeO}_3$  open a new path toward the oxide-based photovoltaic devices.<sup>5,6</sup>

Crystal  $\text{BiFeO}_3$  forms in the *pseudocubic* rhombohedral structure belonging to the  $R3c$  space group, but the unit cell can also be described as the hexagonal structure with the  $c$ -axis lying in the  $[111]$  axis of the *pseudocubic* reference frame.<sup>3</sup> The electric polarization vector  $\vec{P}$  of this compound is also along  $[111]$ . Thus, the  $[111]$  axis is distinguished from the remaining three  $\langle 111 \rangle$  axes. In the *pseudocubic* reference frame, there are six equivalent  $\langle 1\bar{1}0 \rangle$  axes normal to the  $[111]$  direction that form a plane. Since a second-rank polarizability tensor cannot support a 3-fold rotational anisotropy, the optical properties are essentially the same for any polarization in this plane. Consequently,  $\text{BiFeO}_3$  has uniaxial optical anisotropy with the optic axis along the  $[111]$  axis.

Spectroscopic ellipsometry (SE) is a highly suitable method of determining complex optical functions over a wide range of photon energy and therefore, many interesting SE studies<sup>7-9</sup> have recently been performed on epitaxial  $\text{BiFeO}_3$  thin films. However, no systematic SE study has yet been reported on the optical anisotropy in  $\text{BiFeO}_3$ . The mixed ferroelectric domain structures presented in thin films probably obscured the anisotropic nature of this crystal in previous SE work.<sup>7</sup>

Here, we apply SE to determine the ordinary and extraordinary components of the dielectric function  $\varepsilon = \varepsilon_1 + i\varepsilon_2$  and refractive index  $N = n + ik$  tensor for  $\text{BiFeO}_3$ . Our spectra exhibit distinct optical structures associated with the charge-transfer transitions. The energies of these transitions are accurately obtained by using the standard lineshape analysis.<sup>10</sup>

A single-domain BiFeO<sub>3</sub> bulk crystal was grown by the flux growth method where Bi<sub>2</sub>O<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub>/B<sub>2</sub>O<sub>3</sub> were mixed and sintered at around 870°C. The as-grown crystal was first cut and polished, followed by a dilute nitric acid etch and a 10-hour anneal at 300°C in argon to relieve any strain from the polishing. This procedure left a platelet with facets normal to [001] larger than 1 mm<sup>2</sup>. The formation of a single domain structure was explicitly verified using polarized optical microscopy. Additional details of the growth and structural characterization can be found in Ref. 5.

Generalized variable-angle SE (g-VASE) measurements<sup>11</sup> were performed with the sample at room temperature from 1.0 to 5.5 eV using a rotating compensator-type SE (M2000-DI model, J.A. Woollam Inc.) equipped with a manual *in-plane* rotation sample stage. Data were recorded at multiple crystallographic orientations by rotating the sample about the surface normal in steps of 15°. The incident angle of the probing light was also varied from 45 to 75° with an increment of 15° per orientation.

We reduced the surface overlayer artifacts<sup>12</sup> in the SE data to the maximum extent possible by polishing the surface using a colloidal silica suspension with 0.02-μm particles, followed by de-ionized water, acetone, and methanol rinses. Immediately prior to the SE measurements, we further cleaned the surface for 20 min in an ultraviolet (UV) ozone cleaner. This UV ozone cleaning procedure has been proven to effectively remove carbon-related contaminants from the surface of oxide compounds.<sup>13</sup> Nitrogen gas was continuously flowed onto the sample during the measurements to minimize the possible recontamination of the surface.

Figures 1(a) and 1(b) show the real and imaginary parts of the *pseudodielectric function*  $\langle \epsilon \rangle = \langle \epsilon_1 \rangle + i\langle \epsilon_2 \rangle$  spectra, respectively, recorded at an incident angle of 75° along four different crystallographic orientations: [100], [110], [010], and  $[\bar{1}10]$ . The crystal orientations were determined by measuring the unique Bragg angles of the four asymmetric {113} planes using high-resolution x-ray diffraction. Two pronounced optical structures at around 3 and 4 eV with a small shoulder at ~2.5 eV are commonly seen from all the spectra. Our  $\langle \epsilon_2 \rangle$  spectra reveal that the optical structure at ~4 eV has two

contributions that vary in relative strengths for different crystallographic directions. This effect has not been probed in previous thin film studies.<sup>7-9</sup>

Even though all the spectra share common optical features, our results show a clear dependence of  $\langle \epsilon \rangle$  on the crystallographic orientation. The SE measurement is very sensitive to the projection of the  $\epsilon$  tensor along the segment defined by the intersection of the plane of incidence and the sample surface.<sup>14</sup> Therefore, the strong orientation-dependence of the  $\langle \epsilon \rangle$  spectrum suggests the presence of optical anisotropy. Two orthogonal axes [100] and [010] are optically equivalent with respect to the optic axis [111], and the  $\langle \epsilon \rangle$  spectra recorded along these two axes are identical within experimental error. A schematic depicting the measurement along the [110] axis is given in Fig. 1(c). For this specific measurement geometry, the optic axis, [111], of BiFeO<sub>3</sub> (also the electric polarization vector  $\mathbf{P}$ ) lies in the plane of incidence. We note that Pisarev *et al.*<sup>15</sup> have also observed multiple contributions in the optical structure at  $\sim 4$  eV and an orientation-dependence of the  $\langle \epsilon \rangle$  spectra from their standard SE studies of bulk BiFeO<sub>3</sub>, but no discussion has been made on the optical anisotropy.

For a SE measurement, the optical response of materials can be expressed mathematically using the Jones matrix:<sup>11</sup>

$$\begin{bmatrix} E_p \\ E_s \end{bmatrix}_{out} = \begin{bmatrix} r_{pp} & r_{sp} \\ r_{ps} & r_{ss} \end{bmatrix} \cdot \begin{bmatrix} E_p \\ E_s \end{bmatrix}_{in}. \quad (1)$$

Here,  $E$  represents an electric field,  $r$  is a reflection coefficient, and the subscripts  $p$  and  $s$  are the  $p$ - and  $s$ -polarization, respectively. For isotropic crystals, the off-diagonal components in the matrix vanish and the standard SE measures the ratio of the two diagonal terms  $r_{pp}/r_{ss}$ . When the principal axes of an anisotropic crystal are not aligned with the laboratory's coordinate system, however, the off-diagonal components in the Jones matrix are no longer zero and the matrix is normalized to a diagonal element to express the 3 measured values as<sup>11</sup>

$$\rho_{pp} = r_{pp}/r_{ss} = \tan \Psi_{pp} \exp(i\Delta_{pp}), \quad (2.1)$$

$$\rho_{ps} = r_{ps}/r_{pp} = \tan \Psi_{ps} \exp(i\Delta_{ps}), \quad (2.2)$$

$$\rho_{sp} = r_{sp}/r_{ss} = \tan \Psi_{sp} \exp(i\Delta_{sp}). \quad (2.3)$$

Hence, the six independent parameters  $\Psi_{pp}$ ,  $\Delta_{pp}$ ,  $\Psi_{ps}$ ,  $\Delta_{ps}$ ,  $\Psi_{sp}$ , and  $\Delta_{sp}$  should be determined to describe the optical response of anisotropic crystals whereas only two parameters  $\Psi$  and  $\Delta$  are sufficient for isotropic crystals. It is the g-SE method that measures the full components of the Jones matrix.<sup>11</sup>

Figures 2(a) and (b) show experimental spectra (symbols) and the modeled curves (solid lines) for the six g-SE parameters of BiFeO<sub>3</sub> crystal measured along the  $[0\bar{1}0]$  direction at the incident angle of 75° as an example. Our model, consisting of a surface roughness layer and two optical functions  $\epsilon_a$  and  $\epsilon_c$ , shows good agreement with the experimental results, in particular for the diagonal components  $\Psi_{pp}$  and  $\Delta_{pp}$ . The surface roughness, estimated to be  $\sim 10\text{\AA}$ , was modeled as a virtual layer whose optical functions are a 50-50 mixture of the underlying material and void using the Bruggeman effective medium approximations.<sup>16</sup> This procedure is based on the assumption that the absorption vanishes below the bandgap. The  $\epsilon_a$  and  $\epsilon_c$  spectra were first obtained from the *wavelength-by-wavelength* inversion method, then parameterized by the generalized oscillator method.<sup>17</sup>

In order to fully analyze the uniaxial anisotropic data, it is necessary to determine two Euler angles  $\Phi_E$  and  $\Theta_E$ .<sup>11</sup> The angle  $\Phi_E$  corresponds to the in-plane orientation of the crystal with respect to the plane of incidence, and  $\Theta_E$  is the angle between the optic axis and the measurement surface.  $\Phi_E$  is usually defined as the angle between the plane of incidence and the projection of the optic axis onto the measurement surface. Assuming the perfect (001) surface, the predicted Euler angles  $\Phi_E$  and  $\Theta_E$  are 135° and 55°, respectively, for experimental data shown in Figs. 2(a) and 2(b). Our best-fit  $\Phi_E$  and  $\Theta_E$  values were 134.4° and 61.6°, respectively. The small difference in  $\Theta_E$  is in part due to the imperfect (001) surface, which was probably caused by the surface polishing.

The  $\epsilon_{a,c} = \epsilon_{a,c1} + i\epsilon_{a,c2}$  and  $N_{a,c} = n_{a,c} + ik_{a,c}$  spectra, extracted mathematically for the tensor components along the ordinary (*a*) and extraordinary (*c*) principal axes of the BiFeO<sub>3</sub> crystal, are

presented in Figs. 3(a) and 3(b). Our data shown in Fig. 3(b) indicate that the BiFeO<sub>3</sub> crystal has negative uniaxial anisotropy ( $n_a > n_c$ ) below the fundamental absorption edge ( $\leq 2.25$  eV), which is consistent with the results from a previous optical study.<sup>18</sup> We note that Rivera *et al.*<sup>18</sup> have measured the below-bandgap birefringence dispersion  $dn' = n_a - n_c'$ , which requires a scaling factor to obtain the birefringence  $dn = n_a - n_c$ . We suggest a scaling factor of about 2.2 by comparing our  $dn$  values with the  $dn'$  values reported in Ref. 18.

One of the primary objectives in solid-state spectroscopy is to determine the parameters of the optical structures shown in the  $\epsilon$  spectrum. For BiFeO<sub>3</sub>, it is known<sup>15,19</sup> that those optical structures are better described by the  $p$ - $d$  and  $d$ - $d$  charge-transfer (CT) transitions rather than the interband-transitions in semiconductors. The optical information obtained can then be used to verify the predictions made from the electronic structure calculations.

Lineshape analysis of the  $d^2\epsilon/dE^2$  spectrum is a common approach in SE study, where the  $\epsilon$  spectrum is differentiated and smoothed numerically using the Savitzky-Golay type<sup>20</sup> algorithms followed by least-squares fitting of standard lineshape expressions:<sup>10</sup>

$$\frac{d^2\epsilon}{dE^2} = \begin{cases} n(n-1)Ae^{i\phi}(E - E_g + i\Gamma)^{n-2}, & n \neq 0 \\ Ae^{i\phi}(E - E_g + i\Gamma)^{-2}, & n = 0 \end{cases} \quad (3)$$

where  $A$  is the amplitude,  $E_g$  the threshold energy,  $\Gamma$  the broadening parameter, and  $\phi$  the phase angle. The exponent  $n$  has the values of -1, -1/2, 0, and +1/2 for excitonic, one-, two-, and three-dimensional lineshapes, respectively. Here, we calculated the derivative of the  $\epsilon$  data that were obtained from the *wavelength-by-wavelength* inversion method. An appropriate level of smoothing was achieved with 11 data points to suppress noise in the derivative spectra.

Both real and imaginary parts were fitted simultaneously. Our data did not show any noticeable difference in the CT transition energies between the  $\epsilon_a$  and  $\epsilon_c$  spectra, so we only present the results from the  $\epsilon_a$  spectrum here. The  $d^2\epsilon_a/dE^2$  spectra calculated from our experimental data and the corresponding best-fit curves are shown in Fig. 4. The open circles and squares represent the  $d^2\epsilon_{a1}/dE^2$  and  $d^2\epsilon_{a2}/dE^2$ ,

respectively, whereas the solid and dash-dotted lines are the best-fit curves of the real and imaginary parts. Four lineshapes were used to fit the data from 2 to 5 eV, which are indicated by the arrows and labeled using a notation established in a recent first principles calculations by Wang *et al.*<sup>19</sup>

The physical origin of the unidentified structure (“?”) at  $\sim 2.5$  eV is not clearly understood. It has been attributed to the defect states due to oxygen vacancies or collective excitations in previous SE<sup>8,9</sup> and theoretical<sup>21</sup> studies. However, a recent study<sup>15</sup> of BiFeO<sub>3</sub> and related iron oxides suggests that this structure has an intrinsic nature and originates from a dipole-forbidden  $p$ - $d$  CT transition. A positive identification of this structure would require further theoretical investigations, which is beyond the scope of this work.

The  $A$ ,  $B$ , and  $C$  CT structures were fit with the two-dimensional lineshape ( $n = 0$ ) whereas the unknown structure “?” was best represented by the excitonic lineshape ( $n = -1$ ). The origin of the structure  $A$  has been suggested as the CT transitions from either the occupied O  $2p$  states to the unoccupied Fe  $3d$  states or the  $d$ - $d$  transition between  $3d$  valence and conduction bands.<sup>19</sup> The structures  $B$  and  $C$  have been identified as the transitions from O  $2p$  valence band to Fe  $3d$  or Bi  $6p$  conduction band.<sup>19</sup> The CT energies that we obtained are listed in Table I together with the values reported previously.<sup>8,9,15,19</sup> We note that many theoretical studies<sup>19,21</sup> calculated  $\varepsilon$  along the  $[100]$ ,  $[010]$ , and  $[001]$  axes of the *pseudocubic* frame and reported the averaged linear  $\varepsilon = (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})/3$ , which possibly resulted in the observed discrepancies in the CT energy values. It is one of our goals to provide theoreticians with the information needed to calculate  $\varepsilon$  along the ordinary and extraordinary principal axes of BiFeO<sub>3</sub>.

In conclusion, we reported the ordinary and extraordinary components of the optical tensor for single-domain BiFeO<sub>3</sub> crystal determined by SE. The  $\varepsilon$  spectra exhibited three CT transition structures from 1.0 to 5.5 eV along with an unknown weak feature at 2.5 eV. The CT transition energies were obtained from the standard lineshape analysis. Our results also suggest that crystal BiFeO<sub>3</sub> has negative uniaxial optical anisotropy.

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## FIGURE CAPTIONS

**FIGURE 1. (Color online)** (a) Real and (b) imaginary parts of the pseudodielectric function  $\langle \epsilon \rangle$  spectra measured along 4 different orientations of a single-domain BiFeO<sub>3</sub> (001) crystal. The dependence of  $\langle \epsilon \rangle$  on crystallographic orientation is clearly seen. (c) A schematic depicting the SE measurement along the [110] direction.

**FIGURE 2. (Color online)** Experimental spectra (symbols) and best-fit curves (solid lines) for g-SE parameters (a)  $\Psi$  and (b)  $\Delta$ . The measurements were done along  $[0\bar{1}0]$  direction at the incident angle of 75°.

**FIGURE 3. (Color online)** (a) Dielectric function  $\epsilon = \epsilon_1 + i\epsilon_2$  and (b) refractive index  $N = n + ik$  spectra extracted mathematically for the tensor components along the ordinary ( $\epsilon_a$  and  $N_a$ ) and extraordinary ( $\epsilon_e$  and  $N_e$ ) principal axes of BiFeO<sub>3</sub>.

**FIGURE 4. (Color online)** Best-fit curves for the second-energy-derivative of  $\epsilon_{a1}$  (solid line) and  $\epsilon_{a2}$  (dash-dotted line) of BiFeO<sub>3</sub>. The open circles and open squares represent data for  $d^2\epsilon_{a1}/dE^2$  and  $d^2\epsilon_{a2}/dE^2$ , respectively. Energies of each CT transition are indicated by the arrows and labeled using a notation established in a recent theoretical study.<sup>19</sup> The physical origin of the structure at  $\sim 2.5$  eV labeled by “?” is not clear, but has been suggested as a defect-related one.

**TABLE I.** Charge-transfer transition energies for BiFeO<sub>3</sub> at room temperature.

| CT transitions     | A               | B               | C               |
|--------------------|-----------------|-----------------|-----------------|
| Ref. 8 (thin film) | 2.97            |                 | 4.19            |
| Ref. 9 (thin film) | 3.2             |                 | 4.3             |
| Ref. 15 (bulk)     | 2.90            | 3.95            | 4.54            |
| Ref. 19 (theory)   | 3.09            | 4.12            | 4.45            |
| This work          | $2.83 \pm 0.01$ | $3.77 \pm 0.01$ | $4.27 \pm 0.03$ |

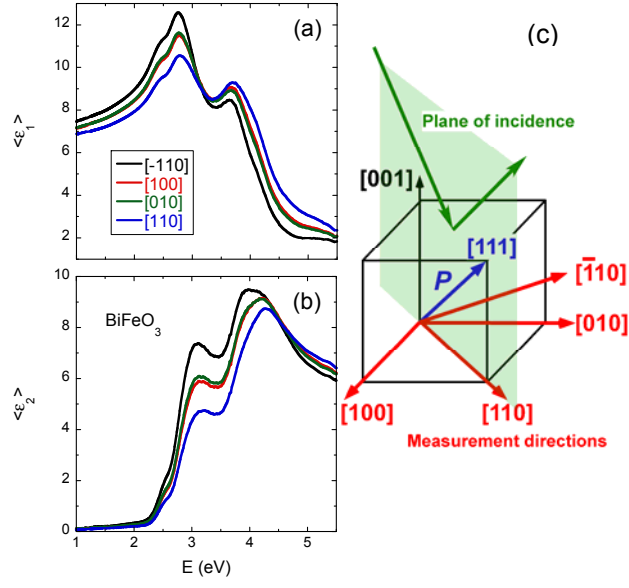


FIG. 1. Choi *et al.*

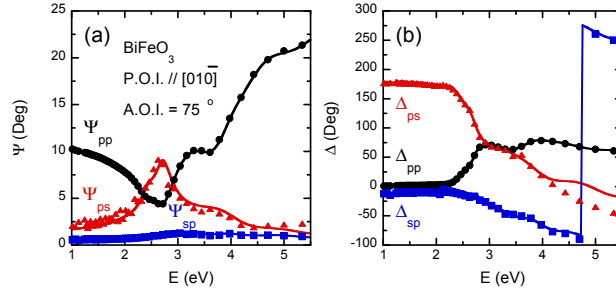


FIG. 2. Choi *et al.*

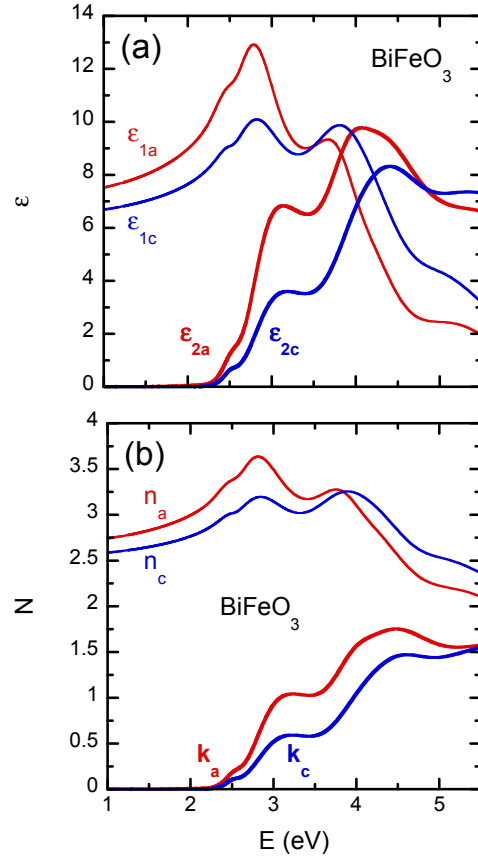


FIG. 3. Choi *et al.*

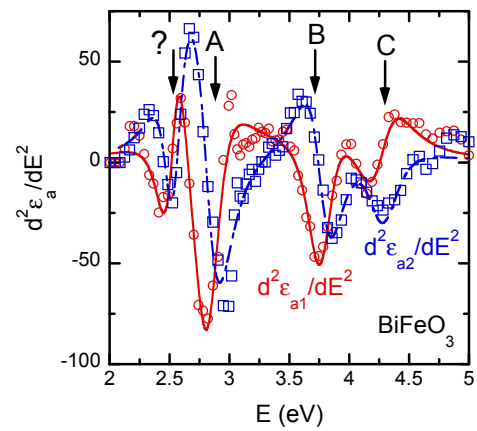


FIG. 4. Choi *et al.*