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Optical properties of quasi-tetragonal $BiFeO_3$ thin films

P. Chen,[1,a)] N. J. Podraza,[2] X. S. Xu,[1,b)] A. Melville,[3] E. Vlahos,[4] V. Gopalan,[4] R. Ramesh,[5,6] D. G. Schlom,[3] and J. L. Musfeldt[1]
[1]*Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, USA*
[2]*Department of Electrical Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, USA*
[3]*Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853-1501, USA*
[4]*Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, USA*
[5]*Department of Materials Science and Engineering, University of California-Berkeley, Berkeley, California 94720, USA*
[6]*Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

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Optical transmission spectroscopy and spectroscopic ellipsometry were used to extract the optical properties of an epitaxially grown quasi-tetragonal $BiFeO_3$ thin film in the near infrared to near ultraviolet range. The absorption spectrum is overall blue shifted compared with that of rhombohedral $BiFeO_3$, with an absorption onset near 2.25 eV, a direct 3.1 eV band gap, and charge transfer excitations that are ~0.4 eV higher than those of the rhombohedral counterpart. We interpret these results in terms of structural strain and local symmetry breaking. © *2010 American Institute of Physics*. [doi:10.1063/1.3364133]

The physical properties of polar oxides are of foundational importance for investigations of coupling in functional materials. This is because the rich tunability in these systems arises from the interplay between charge, structure, and magnetism. In thin film oxides, strain is well known to modify hybridization and bonding and, as a consequence, the bulk properties.[1–3] It can also stabilize nonequilibrium (metastable) phases. In this work, we focus on bismuth ferrite, the only known single phase room temperature multiferroic. $BiFeO_3$ displays many exotic properties including magnetoelectric coupling,[4,5] a large remanent polarization,[6,7] and photovoltaic current,[8] and it is already incorporated in polar oxide-based solar cells and actuators.[9,10] In both applications, the different phases of the parent material play a vital role, either to achieve better match with the solar spectrum or to define a morphotropic phase boundary. In this work, we investigate the optical properties of quasi-tetragonal[11] $BiFeO_3$, a phase stabilized by compressive strain.[10]

Bulk $BiFeO_3$ is ferroelectric ($T_C \sim 1100$ K) and antiferromagnetic ($T_N \sim 640$ K) at 300 K. The structure is that of a rhombohedrally distorted perovskite[12] belonging to the $R3c$ space group. Each Fe^{3+} center is coordinated by six O^{2-} ions [Fig. 1(a)], although the distortion along [111] yields a quasi-octahedral arrangement. A slight tetragonal distortion reduces the space group to $P4mm$ (Ref. 14) and modifies the overall perovskite structure so that the local Fe^{3+} environment is quasi-square pyramidal [Fig. 1(b)]. Theoretical calculations predict an unusually large tetragonality ratio for this system.[10,14,15] In practice, the nonequilibrium tetragonal phase can be stabilized by compressive strain, and epitaxial films with different c/a ratios have been reported.[10,15,16]

In order to investigate the impact of strain on the charge excitations of a model polar oxide, we measured the optical properties of tetragonal $BiFeO_3$ and compared the results with rhombohedral films[17–20] and recent first principles electronic structure calculations.[14,15] We find that the optical response of tetragonal $BiFeO_3$ is overall blue shifted, with an absorption onset near 2.25 eV and a direct band gap and charge transfer excitations that are ~0.4 eV higher than those of the rhombohedral material. These results can be understood in terms of symmetry breaking and local structure strain.

A series of tetragonal $BiFeO_3$ films with thicknesses between 23 and 38 nm were deposited on (110) $YAlO_3$ substrates using conventional and laser molecular-beam epitaxy.[10] The pure tetragonal phase with small monoclinic distortion is stabilized by the large epitaxial stain due to lattice mismatch with the substrate.[10] X-ray results show only substrate and film peaks, and these films have a c/a ratio of 1.27. Rocking curves show partial relaxation but with a full width at half max that is virtually the same as the substrate. We employed both optical transmission spectroscopy and spectroscopic ellipsometry to elucidate the optical properties of this nonequilibrium phase. A combination of techniques was employed due to the challenges inherent in a thin film measurement. These include (i) important reflectance contributions in a normal-incidence transmittance measurement when the absorption coefficient is low and (ii) surface rough-

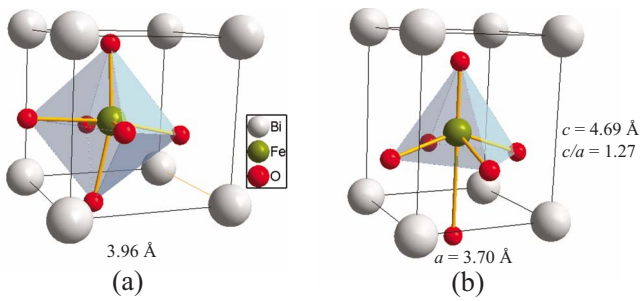

FIG. 1. (Color online) Schematic view of the local structure around the Fe^{3+} center of (a) rhombohedral (Ref. 13) and (b) tetragonal (Ref. 14) $BiFeO_3$.

a)Electronic mail: pchen@ion.chem.utk.edu.
b)Present address: Oak Ridge National Laboratories, Oak Ridge, TN.

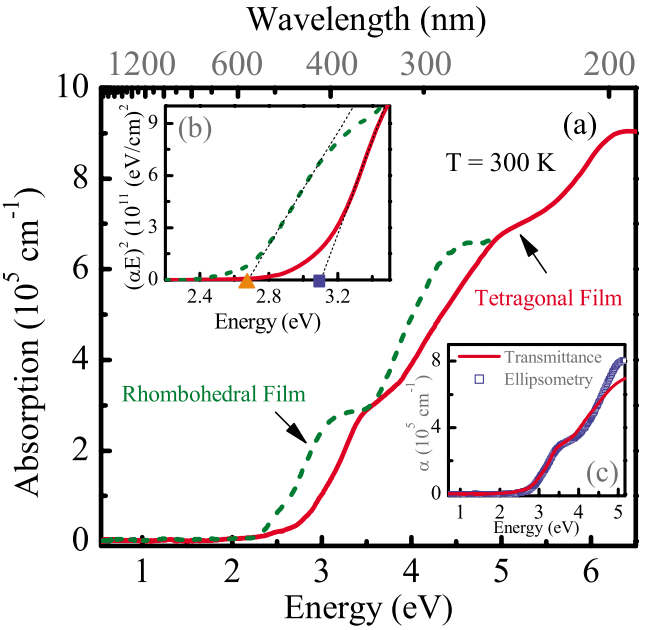

FIG. 2. (Color online) (a) Absorption coefficient of tetragonal $BiFeO_3$ compared with that of the rhombohedral system (Ref. 17). (b) Direct band gap analysis of both materials. The triangle marks the 2.67 ± 0.02 eV charge gap of the rhombohedral film whereas the square marks the 3.10 ± 0.02 eV gap of tetragonal $BiFeO_3$. (c) $\alpha(E)$ obtained by optical transmittance compares well with that obtained by ellipsometry.

ness sensitivity and the difficulty in characterizing low absorption coefficients via ellipsometry.[21,22] Room temperature transmittance and reflectance spectra were collected using a Perkin-Elmer Lambda-900 spectrometer (3000–190 nm; 0.41–6.53 eV). We calculated the absorption coefficient $\alpha(E)$ from combined transmittance and reflectance measurements.[23] Ellipsometric spectra (in Δ, ψ) were extracted at four angles of incidence, $\Theta = 50°$, 60°, 70°, and 80°, using a variable-angle dual rotating-compensator multichannel spectroscopic ellipsometer[24] over a spectral range from 0.75 to 5.15 eV. $\alpha(E)$ was also determined from spectroscopic ellipsometry analysis and compared with the complementary data obtained from optical transmittance.

Figure 2(a) displays the 300 K absorption spectrum of the tetragonal $BiFeO_3$ film compared with that of the rhombohedral analog.[17] We assigned the observed excitations based on recent first-principles calculations.[14,15,25] Although the overall absorption profiles are similar, the familiar 3.2 and 4.5 eV electronic excitations of the rhombohedral material, assigned as minority channel dipole-allowed charge transfer features,[17,18,25] are blue shifted by ~0.4 eV in tetragonal $BiFeO_3$. The blue shift of these strongly hybridized O p to Fe d excitations is a consequence of the strained nature of the nonequilibrium tetragonal phase. The quasi-tetragonal film displays an additional electronic feature centered at ~6.2 eV that we assign as a strongly hybridized majority channel O p+Fe $d \rightarrow$ Bi p state excitation. The direct band gap is extracted by a linear extrapolation of an $(\alpha \cdot E)^2$ versus E plot to zero [Fig. 2(b)].[21] We find the band gap in tetragonal $BiFeO_3$ to be 3.10 ± 0.02 eV, ~0.4 eV larger than that in rhombohedral $BiFeO_3$ (2.67 ± 0.02 eV). This result is different from the recent theoretical calculations[14,15] that predict a smaller band gap in tetragonal $BiFeO_3$. The 2.5 eV sub band gap absorption feature in the rhombohedral system[17] is also present in the tetragonal material. This feature contributes to the onset of optical absorption at ~2.25 eV and is probably a collective excitation.[26]

TABLE I. Dielectric function parameters for rhombohedral and tetragonal $BiFeO_3$. All Tauc–Lorentz (TL) oscillators (Ref. 29) share a common Tauc gap $E_g = 2.14$, $\varepsilon_\infty = 2.24$ for the rhombohedral film and $E_g = 2.30$, $\varepsilon_\infty = 2.49$ for the tetragonal film, where ε_∞ is the high frequency permittivity a constant additive term to ε_1. SO, E_0, A, and Γ are, respectively, the Sellmeier oscillator (Ref. 30), resonance energy, amplitude, and broadening. All parameters are in units of energy (electron volts).

	Rhombohedral $R3c$ [a]			Tetragonal $P4mm$		
Oscillator	E_0	A	Γ	E_0	A	Γ
TL_1	2.39	9.54	0.31	3.01	1.05	0.24
TL_2	2.97	36.10	0.70	3.37	33.50	0.98
TL_3	4.19	44.03	1.63	4.91	47.03	1.77
TL_4/SO	6.15	38.66	3.47	6.50	6.04	0

[a]Reference 20.

The experimental ellipsometric spectra were fit to a parameterized optical and structural model using a least-squares regression analysis with an unweighted error function[27] in order to extract the complex dielectric function spectra and microstructural parameters. The latter include bulk film and surface roughness thicknesses. The optical properties of the surface roughness layer were represented by the Bruggeman effective medium approximation consisting of fractions of bulk material and void.[28] The fitting parameters of both materials are given in Table I. The average unweighted error function obtained from the least-squares regression fitting is sufficiently low with a value of 6.4×10^{-3}, indicating that the fit using this model is reasonable. Dielectric functions were extracted by numerical inversion from each (Δ, ψ) spectra using the bulk film and surface roughness thicknesses determined from the parameterized fit. Figure 3 displays $\varepsilon_1(E)$ and $\varepsilon_2(E)$ for the quasi-tetragonal $BiFeO_3$ film compared to similar results on the rhombohedral material.[19] Tetragonal $BiFeO_3$ exhibits higher energy charge transfer excitations that are also broadened compared with the rhombohedral phase, a result that is overall consistent with the absorption spectra in Fig. 2(c).

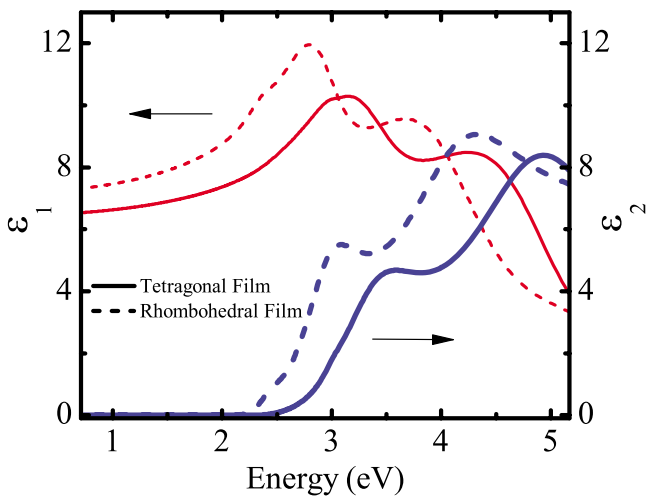

FIG. 3. (Color online) Complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) vs photon energy (E) obtained for tetragonal $BiFeO_3$ (solid line). ε_1(E) and ε_2(E) of rhombohedral $BiFeO_3$ (dashed line) are shown for comparison (Ref. 19).

We can also compare the optical properties of tetragonal $BiFeO_3$ with a local structure analysis [Fig. 1], simple crystal field theory, and first principles electronic structure calculations.[14,15] We begin by considering the FeO_6 structure in rhombohedral $BiFeO_3$ as an ideal octahedron. It is well-known that, in an octahedral crystal field, the $3d$ orbital states split into t_{2g} and e_g levels. Strain has important consequences for the local structure. In tetragonal $BiFeO_3$, one of the Fe–O axial distances increases to ~2.80 Å, and the Fe–O equatorial bond lengths are reduced to ~1.93 Å.[14] These modifications split the t_{2g} states into a doubly-degenerate pair (d_{xz},d_{yz}) and a singly-degenerate d_{xy} level, and the e_g states break symmetry to yield a lower energy d_{z^2} state and a higher energy $d_{x^2-y^2}$ level. The net effect is to move the empty Fe^{3+} $3d$ states closer to the occupied ones. Band structure calculations[14,15] confirm this trend, predicting that the unoccupied Fe^{3+} $3d$ states broaden and move closer to the Fermi level in the quasi-tetragonal system. At the same time, the calculations predict that the O^{2-} $2p$ states move further away from the Fermi level.[14] Together, these competing density of states shifts define the predicted charge gap. In other words, this is a joint density of states effect. Based upon our measurement of a larger band gap in quasi-tetragonal $BiFeO_3$ compared to that in the rhombohedral analog, the calculations either overestimate the strain-induced shift in the Fe^{3+} $3d$ states or underestimate the shift of the O^{2-} $2p$ states.

To summarize, both optical transmission spectroscopy and spectroscopic ellipsometry were used to reveal the optical properties of quasi-tetragonal $BiFeO_3$. Due to the structure strain and symmetry breaking induced distortions of the local Fe^{3+} crystal field and shifts in the O $2p$ states, the band gap and charge transfer excitations are blue shifted compared with those in the rhombohedral material. Although compressive strain stabilizes a non-equilibrium phase, its optical properties are unfortunately a less attractive match with the solar spectrum. On the other hand, an applied electric field can drive a morphotropic phase transition,[10] a result that may allow the development of an electro-optic switch.

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