Optical properties of ferroelectric $Bi_4Ti_3O_{12}$

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We report optical properties of ferroelectric $Bi_4Ti_3O_{12}$ based on spectroscopic ellipsometry and calculations with the recently developed density functional of Tran and Blaha. We find a close accord between the experiment and the calculated results with this functional, including the energy onset of optical transitions and the scale of the optical conductivity. The band gap is indirect, with a value of 2.9 eV, and an onset of direct optical transitions at 3.1 eV.

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There has been recent interest in the optical properties of ferroelectric oxides, particularly those with relatively low band gaps. This has been motivated by observations of interesting photovoltaic effects that may be of practical importance especially if light absorption can be increased and band gaps decreased.[1–5] $Bi_4Ti_3O_{12}$ is an interesting material from this point of view. It has a polarization of $P \sim 50$ $\mu C/cm^2$ at room temperature,[6–8] and is thought to have a moderately low band gap of ~ 3 eV,[9] although higher values have also been reported.[10,11] Unfortunately, although there are a number of thin-film studies based on primarily reflection measurements, there is a general lack of bulk optical spectroscopic data for this compound in the visible and ultraviolet range, perhaps in part due to difficulties in preparing suitable bulk samples. On the other hand, $Bi_4Ti_3O_{12}$ has a layered structure based on a stacking of perovskite $BiTiO_3$ and fluoritelike bismuth oxide blocks (see below) and can be grown in very high-quality thin-film form.[12] The presence of separated oxide blocks in a material amenable to thin-film growth allows more possibilities for chemical modification while retaining the ferroelectric function.[13,14] This has been of considerable importance in modifying the material for electronic applications.[12,15,16]

In fact, the optical properties have been observed to change with the addition of dopants, including reductions in the apparent optical band gap.[10] However, it is unknown whether these reductions are primarily due to changes in the fundamental gap or the effects of disorder in an indirect gap material. Furthermore, unlike $BiFeO_3$ and $PbVO_3$, there are no correlated magnetic ions in the structure. As such, there will not be magnetic scattering that would reduce the mobility at ambient temperature.

Here we report application of a recently developed density functional to obtain the optical properties of ferroelectric $Bi_4Ti_3O_{12}$ and compare with spectroscopic ellipsometry. The purpose of the present study is to more firmly establish the intrinsic absorption edge of $Bi_4Ti_3O_{12}$ and to investigate to what extent a recently developed density functional that improves band gaps provides a sufficiently accurate description of the electronic structure to use in computational studies of optical properties of this material and modifications of it.

Computational studies can potentially be important in interpreting optical measurements, understanding the effects of substitutions and possibly in finding dopants that produce the desired changes in optical absorption. However, as is well known, standard density-functional techniques underestimate the band gaps of most semiconductors and simple oxides while more sophisticated methods can be very computationally demanding especially for large cells that may be needed in defect studies. Recently, Tran and Blaha[17] have developed a semi-local functional and applied it to a variety of materials showing that this functional, which we denote TB-mBJ, greatly improves the calculated fundamental band gaps over standard density functionals. This functional has been recently applied to calculate the optical properties and band structures in quantitative agreement with experiment of a variety of halides and other materials, although some problems were noted, especially with some *d*- and *f*-band materials.[18,19] These problems could be of importance for $Bi_4Ti_3O_{12}$ since the conduction-band edges of titanates typically have *d* character. However, as we show below, the description of this compound appears to be accurate, based on comparison of calculated and experimental spectra.

The experiments were done using a *c* axis (with the orthorhombic setting, i.e., stacking of the fluorite and perovskite layers along *c*) oriented $Bi_4Ti_3O_{12}$ film, which was epitaxially grown by pulsed laser deposition on a (001) $SrTiO_3$ substrate. The dielectric function of the film was investigated using spectroscopic ellipsometry (Woollam's M-2000). This simultaneously measures refractive indices and extinction coefficients of a sample without the need for Kramers-Kronig analysis. We recorded ellipsometric angles spectra $[\Psi(\omega)$ and $\Delta(\omega)]$ at two incident angles, $\theta = 60°$ and $\theta = 70°$. The spectral parameters, $\tan \Psi(\omega)$ and $\cos \Delta(\omega)$, give the ratio between the amplitude attenuation and the change in angles between the phase shift due to reflections by *p* and *s* polarizations, respectively. The optical spectrum of a $SrTiO_3$ substrate was also measured independently using the same procedure in order to extract the dielectric functions, $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, of the film. For this we used a numerical iteration process from the $\Psi(\omega)$ and $\Delta(\omega)$ spectra using an isotropic film on an isotropic substrate model (Ref. 21). The validity of the dielectric functions is supported by the fact that the resulting real and imaginary parts satisfy the causality relationship.

The calculations were done using the general potential linearized augmented plane-wave (LAPW) method,[22] as implemented in the WIEN2K code.[23] We used well converged Brillouin-zone samplings and basis sets with LAPW sphere radii of 2.3 bohr for Bi, 1.75 bohr for Ti, and 1.5 bohr for O. The electronic structure and optical calculations were performed relativistically including spin orbit.
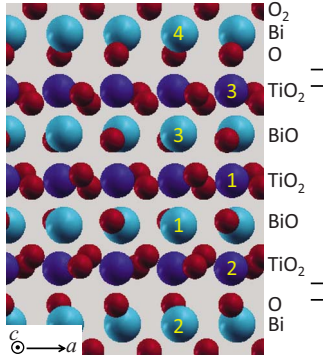
FIG. 1. (Color online) Relaxed structure of $Bi_4Ti_3O_{12}$. Bi is denoted by large light gray spheres, O by small dark red spheres, and Ti by dark blue spheres. The cations are numbered as in Table I.

We used the experimental lattice parameters and relaxed all internal coordinates using the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE). The relaxed structure is shown in Fig. 1 and values for the internal coordinates of all atoms are given in Table I. We then used this PBE relaxed structure in our electronic-structure calculations with the TB-mBJ functional. The relaxed structure is monoclinic. This is in agreement with the conclusion of Shrinagar *et al.*,[24] who performed a detailed density-functional study considering both monoclinic and ortho-

TABLE I. Internal structural coordinates of monoclinic $Bi_4Ti_3O_{12}$, space group Pc. The lattice parameters were fixed at a =5.4500 Å, b=16.6406 Å, c=5.4059 Å, and monoclinic angle, γ=80.575°. This is equivalent to the $B1c1$ with lattice parameters given in Ref. 20. The coordinates are in terms of the monoclinic lattice vectors.

|	x	y	z
Bi1	0.7340	0.6110	0.7462
Bi2	0.8874	0.3240	0.7334
Bi3	0.6009	0.8764	0.7481
Bi4	0.4636	0.1667	0.7659
Ti1	0.6355	0.7407	0.2472
Ti2	0.7547	0.4855	0.2458
Ti3	0.4983	0.0009	0.2504
O1	0.8055	0.3795	0.3062
O2	0.5000	0.5208	0.5325
O3	0.4342	0.4913	0.0542
O4	0.3978	0.7212	0.5327
O5	0.1614	0.2426	0.4963
O6	0.6471	0.6233	0.1745
O7	0.3098	0.7571	0.0401
O8	0.6600	0.2462	0.0036
O9	0.5305	0.8577	0.3173
O10	0.4443	0.1064	0.1967
O11	0.2724	0.9648	0.9783
O12	0.1991	0.9908	0.4585
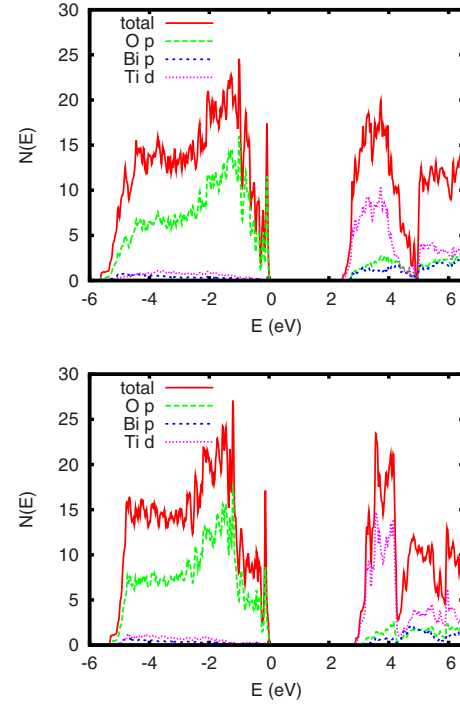
FIG. 2. (Color online) Electronic DOS in eV^{-1} per f.u. as obtained using the PBE (top) and TB-mBJ (bottom) functionals. The projections are onto the LAPW spheres.

rhombic structures, as well as a variety of experimental studies,[6,20,25,26] although there are conflicting reports.[27,28] The monoclinicity is not large and this is reflected in the optical properties. In an orthorhombic system the dielectric tensor is diagonal with three independent components. In a monoclinic system with a fixed Cartesian coordinate system, there is a fourth independent component. This off-diagonal component reflects the monoclinicity. Here we find an off-axis component of the refractive index that is less than 10^{-3}. We show only the diagonal parts of the optical tensors. These were calculated from the electronic structure using the optical package of the WIEN2K code.

The electronic densities of states (DOS) are shown in Fig. 2 for both the PBE and TB-mBJ functionals. There have been several prior first-principles studies of $Bi_4Ti_3O_{12}$.[24,26,29–32] Our calculated PBE results are consistent with those studies. The absolute band gap, defined as the energy difference between the conduction-band minimum and the valence-band maximum with the PBE functional is 2.44 eV. This is increased to 2.88 eV with the TB-mBJ functional. In both cases this is an indirect gap. The onset of direct optical transitions is at 3.05 eV with the TB-mBJ functional. This value is in accord with prior measurements[9] that indicate a gap near 3 eV. As mentioned, there is a lack of measurements on high-quality crystals and so the experimental value is based on studies of powders and films. Considering the sample dependence in the studies and the size of the below gap (Urbach) absorption, there is an uncertainty in the experimental value of at least ~0.2 eV, based on comparison of results of different studies and taking the samples with the lowest below gap absorption and highest gap values as most representative of the intrinsic behavior. However, the
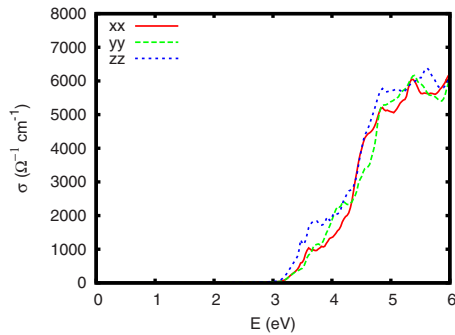
FIG. 3. (Color online) Optical conductivity with the TB-mBJ functional and a 0.025 eV broadening. The xx direction is the Pc a-axis direction, the yy direction is perpendicular to the a and c axes, i.e., the c-axis direction of the doubled cell with the $B1a1$ setting and the zz direction is along c.

uncertainty could be larger. In particular, Jia et $al.$[10] reported films with a band gap of 3.64 eV based on optical transmittance while Wang et $al.$[11] reported 3.56 eV for Nd-doped films.

The main difference between the PBE and TB-mBJ results, besides the change in band gap, is a narrowing of the mainly Ti d derived bands comprising the conduction-band edge, as may be seen from the projected DOS. There is noticeable cross-gap hybridization of Bi $6p$ and Ti $3d$ states with the O p orbitals as may be seen both from the metal character in the valence bands and the O p character in the conduction bands.

As mentioned, the structure of Bi$_4$Ti$_3$O$_{12}$ consists of an intergrowth of fluorite and perovskite blocks, as shown in Fig. 1. This is important for the electronic structure because the trilayer blocks Bi$_2$Ti$_3$O$_8$ have a net charge of +2, while the fluorite bilayer blocks Bi$_2$O$_4$ have a net charge of −2, with Bi^{3+} and Ti^{4+}. While this is no doubt important for stabilizing a well-ordered intergrowth structure, it also effectively shifts the band edges closer together because the negatively charged region is unfavorable for anions, bringing up the valence-band edge and the positively charged region is unfavorable for cations, bringing down the conduction-band edge. This provides a qualitative explanation for the low band gap compared to most other oxide ferroelectrics. In our calculations the DOS at the conduction-band edge comes primarily from Ti d states in addition to Bi p states from the Bi1 and Bi3 sites, which are in the positively charged perovskite blocks with a lower contribution from the fluorite Bi2 and Bi4 sites. A difference between the Bi sites was noted previously by Postnikov et $al.$[29] in regard to the Bi $6s$ positions and hybridization with O.

The optical conductivity spectrum as obtained with the TB-mBJ functional is given in Fig. 3. The calculated refractive index is shown in Fig. 4. The experimental optical conductivity and dielectric function are given in Fig. 5. Both the experimental and theoretical data are on an absolute scale, allowing direct comparison. The calculated TB-mBJ direction averaged low-frequency refractive index is $n=2.37$. This corresponds to a low-frequency optical dielectric constant $\epsilon_1=5.6$, which is smaller than but in reasonable accord with the extrapolated experimental value of $\epsilon_1=6.0$. There is a
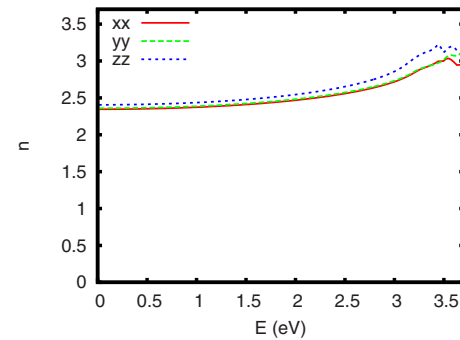

FIG. 4. (Color online) Refractive index with the TB-mBJ functional and a 0.025 eV broadening.

close correspondence in the scale of the optical conductivity above the band edge. Both the theoretical and experimental data show an onset above 3 eV and a leveling-off to a value $\sigma \sim 6000-7000$ Ω^{-1} cm^{-1} above ~ 4.5 eV. While the experimental spectrum is broad and has a noticeable Urbach tail, an enhanced conductivity may be noted as a shoulder between 3.5 and 4 eV. This corresponds to the structure in the calculated optical conductivity in this range, in particular, the direction-dependent peak at ~ 3.5 eV. The close correspondence of the theoretical and experimental spectra both in shape and absolute magnitude of the optical conductivity and refractive index support the view that our film is representative of intrinsic Bi$_4$Ti$_3$O$_{12}$ and that measurements indicating a lower refractive index and much higher band gap of ~ 3.6 eV are not.

A very remarkable result of this study is the close correspondence in the onset of optical transitions between the experiment and the results with the TB-mBJ density functional. Extrapolation of the experimental spectrum above the Urbach tail to zero gives an estimated onset of 3.3 eV, as compared to the calculated 3.05 eV. This means that the well-known density-functional band-gap error has been almost entirely corrected by the TB-mBJ functional in this compound. Considering the shape of the calculated optical conductivity near the band edge in relation to the experimental data, we estimate that the intrinsic absorption onset is 3.1 eV.

To summarize, we compared optical properties calculated with the TB-mBJ functional and spectroscopic ellipsometry
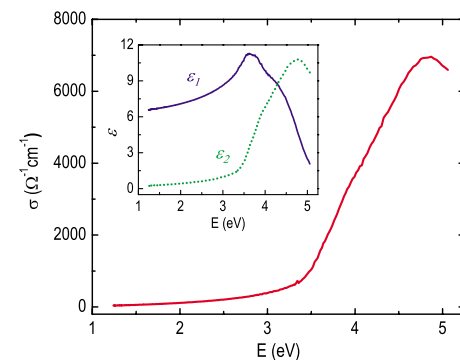

FIG. 5. (Color online) Experimental optical conductivity and dielectric function for Bi$_4$Ti$_3$O$_{12}$.

data. The direct absorption onset is at 3.1 eV. We find that the TB-mBJ functional provides an accurate description of the optical properties including the band gap. Therefore it is likely to be useful in more detailed studies of this compound and modifications of it.

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