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Linear and nonlinear optical properties of BiFeO$_3$

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Using spectroscopic ellipsometry, the room temperature refractive index and absorption versus
wavelength of the ferroelectric antiferromagnet bismuth ferrite, BiFeO$_3$, are reported. The material
has a direct band gap at 442 nm wavelength (2.81 eV). Using optical second harmonic generation,
the nonlinear optical coefficients were determined to be $d_{15}/d_{22}=0.20 \pm 0.01$, $d_{31}/d_{22}$
$=0.35 \pm 0.02$, $d_{33}/d_{22}=-11.4 \pm 0.20$, and $|d_{22}|=298.4 \pm 6.1$ pm/V at a fundamental wavelength

BiFeO$_3$ (BFO) is an antiferromagnetic, ferroelectric with Neel temperature $T_N=643$ K, and ferroelectric Curie temperature $T_C=1103$ K. It is presently one of the most studied multiferroic materials due to its large ferroelectric polarization of $\sim 100 \mu$C/cm$^2$ in thin films and the possibility of coupling between magnetic and ferroelectric order parameters, thus enabling manipulation of one through the other. Linear and nonlinear optical spectroscopy tools are ideally suited to study such coupling. While the mean refractive index for bulk single crystal BiFeO$_3$ has been previously investigated, the optical constants of thin films have not been presented, thus far. Also, an indirect gap at 673 nm (1.84 eV) was reported before, which is shown here to be an absorption onset potential due to a joint density of states effect and not associated with phonon participation. In our analysis, the material appears to have a direct gap with a band edge at 442 nm instead. No studies of nonlinear optical coefficients of BFO, in any form, exist. In this letter, we measure large second order optical nonlinearities in BFO.

Epitaxial and phase-pure BFO thin films were synthesized by pulsed-laser deposition as well as molecular-beam epitaxy (MBE) on (111) SrTiO$_3$ (STO) substrates. The films studied here are epitaxial with orientation relationship BFO(0001)//STO(111) and [2110]BFO|[110] STO. We specifically note that unlike many epitaxial thin films, these films do not have any additional structural variants, including any rotational variants within the film growth plane. Thus, these (0001) oriented films have nearly single crystalline perfection, with three well-defined crystallographic $x$-[2110], and $y$-[1100] axes within the film plane, and the $z$-[0001] axis normal to the plane. The three $y$-$z$ mirror planes in the 3$m$ point group symmetry for BFO are thus well-defined and allow us to precisely extract nonlinear coefficients without ambiguity. Typical film stoichiometry, as determined by Rutherford backscattering spectrometry, was stoichiometric within $\sim 3\%$ error of the measurement (Bi:Fe $=0.98-0.99:1$). There were no amorphous or secondary phases as confirmed by transmission electron microscopy.

Ellipsometric spectra in $(\Delta, \Psi)$ were collected ex situ for a BiFeO$_3$ film prepared by MBE on (111) SrTiO$_3$ at $\theta_i=55^\circ$ and $70^\circ$ angles of incidence using a variable-angle rotating-compensator multichannel spectroscopic ellipsometer with a spectral range from 190 to 1670 nm. The optical properties $(n, k)$ shown in Fig. 1(a) and the corresponding dielectric function spectra $(\varepsilon_1, \varepsilon_2)$ are extracted by using a least squares regression analysis and a weighted root mean square error to fit the ellipsometric spectra to a four-medium optical model consisting of a semi-infinite STO.

![Diagram](Image)

FIG. 1. (Color online) (a) Index of refraction $(n)$ and extinction coefficient $(k)$ for BiFeO$_3$ deposited on (111) SrTiO$_3$ over a spectral range from 190 to 1670 nm. Also shown are the dielectric function parameters for the three Tauc–Lorentz oscillators (TL 1, TL 2, and TL 3) within the spectral range. The parametrization also includes an additional oscillator outside the spectral range with $E_0=7.29 \pm 0.06$ eV, $\Gamma=4.28 \pm 0.34$ eV, and $A=51.19 \pm 2.78$ eV. (b) Plot of $(\alpha E)^2$ and $(\alpha E)^3$ vs photon energy $E$ where a linear extrapolation of $(\alpha E)^3$ to 0 suggests a direct band gap at 2.81 eV.
substrate/bulk film/surface roughness/air ambient structure. The free parameters correspond to the bulk and surface roughness thicknesses of the film and a parametrization of the BiFeO₃ dielectric function. The dielectric function parameterization of BiFeO₃ consists of four Tauc–Lorentz oscillators, sharing a common band gap and a constant additive term to \( e_1 \) denoted by \( e_0 \) (equal to 0 for this model). The parameters corresponding to each oscillator include an oscillator amplitude \( A \), broadening parameter \( \Gamma \), resonance energy \( E_0 \), and a Tauc gap \( E_g \) common to all oscillators. The optical properties of the surface roughness layer are represented by a Bruggeman effective medium approximation.

It should be noted that although BiFeO₃ is uniaxially anisotropic, this model to be a direct gap at 2.81 eV (442 nm), as shown in Fig. 1(b). This value is in good agreement with that obtained from more recent optical measurements. Band gap measurements on different MBE-grown BiFeO₃ films grown on (001) and (111) SrTiO₃ substrates revealed a direct band gap in all cases with \( E_g = 2.77 \pm 0.04 \) eV. The presence of two distinct slopes in \((\alpha E)^{1/2} \) vs \( E \) characteristic of an indirect band gap is not observed. We obtain the linear complex indices from recent optical measurements. Band gap measurements on different MBE-grown BiFeO₃ films grown on (001) and (111) SrTiO₃ substrates revealed a direct band gap in all cases with \( E_g = 2.77 \pm 0.04 \) eV.

As shown in Fig. 2, the intensity \( I_{2\omega}^{\text{NL}} \) of the output SHG signal at 400 nm wavelength from the film was detected along either \( j = p, s \) polarization directions as a function of polarization angle \( \phi \) of incident light. The resulting polar plots of SHG intensity for \( p \) and \( s \) polarized outputs, \( I_{p}^{\text{NL}}(\phi) \) and \( I_{s}^{\text{NL}}(\phi) \), at tilt angles \( \theta = 0^\circ \) and \( 45^\circ \) are shown in Figs. 2(b) and 2(c), respectively. If the incident beam has an intensity \( I_0 \), then the nonlinear polarizations for BFO(111) film with \( x \) axis perpendicular to the plane of incidence is given by

\[
P_{x}^{\text{NL}} = I_0 f_x \sin 2\phi (d_{15} f_z \sin \theta - d_{22} f_y \cos \theta),
\]

\[
P_{y}^{\text{NL}} = I_0 (-d_{22} \cos^2 \phi f_y^2 + d_{22} f_x^2 \cos^2 \theta \sin^2 \phi + d_{15} f_z \sin 2\theta \sin^2 \phi),
\]

\[
P_{z}^{\text{NL}} = I_0 (d_{31} \cos^2 \phi f_y^2 + d_{31} f_x^2 \cos^2 \theta \sin^2 \phi + d_{15} f_z \sin^2 \theta \sin^2 \phi),
\]

where \( d_{ij} \) are nonlinear coefficients and \( f_j \) are effective linear Fresnel coefficients. The measured intensity of the \( p \) and \( s \) polarized SHGs in transmission geometry (neglecting birefringence) is proportional to nonlinear polarization. The expected SHG intensity expressions for \( p \) and \( s \) output polarizations in the predicted 3m symmetry system of BFO are

\[
I_{p}^{\text{NL}} = A(\cos^2 \phi + B \sin^2 \phi)^2,
\]

\[
I_{s}^{\text{NL}} = C \sin^2 2\phi,
\]

where \( B \) and \( C \) are given by

\[
B = \frac{K_{15} f_z f_x \sin 2\theta \cos \theta_R + K_{31} f_x^2 \cos^2 \theta \sin \theta_R + K_{33} f_z^2 \sin^2 \theta \sin \theta_R + f_z^2 \cos^2 \theta \cos \theta_R}{K_{33} f_z^2 \sin \theta_R - f_z^2 \cos \theta_R},
\]

\[
C = D(K_{15} f_z f_x \sin \theta - f_z f_x \cos \theta).
\]
extract the ratios $K_{15}=0.20 \pm 0.01$, $K_{31}=0.35 \pm 0.02$, and $K_{33}=-11.4 \pm 0.20$. By taking absorption into account, the estimated effective coefficients are

$$|d_{22}| = 298.4 \pm 6.1 \text{ pm/V}, \quad |d_{31}| = 104.4 \pm 8.1 \text{ pm/V},$$

$$|d_{15}| = 59.7 \pm 4.2 \text{ pm/V}, \quad |d_{33}| = 3401 \pm 129 \text{ pm/V}.$$  

Note that only the signs of the ratios $K_{15}$, $K_{31}$, and $K_{33}$ were unambiguously determined. The absolute signs of the $d_{ij}$ coefficients were not determined, except to state that the $d_{33}$ coefficient has the opposite sign to the other coefficients. The large values of $d_{ij}$ coefficients most likely arise due to electronic resonances at the 400 nm SHG wavelength.

To conclude, we report the complex index of refraction versus wavelength and optical SHG coefficients in BiFeO$_3$ thin films. These studies will be important in performing further linear and nonlinear optical spectroscopies of the magnetism and ferroelectricity in this material.

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Here, $K_{15}=d_{15}/d_{22}$, $K_{31}=d_{31}/d_{22}$, and $K_{33}=d_{33}/d_{22}$ are the ratios of the nonlinear optical coefficients, $A$ and $D$ are scaling parameters, and $\theta$ is the angle that the generated second harmonic wave makes with the surface normal inside the film. Theoretical fits to the experimental polar plots based on Eq. (2) are excellent both in normal incidence and tilted configuration, as shown in Figs. 2(b) and 2(c), respectively, for both $p$ and $s$ polarized SHG outputs. In normal incidence ($\theta=0^\circ$), only the $d_{22}$ coefficient is involved in the generated $I_p(\varphi=0^\circ)$. By using the $d_{22}=1.672 \text{ pm/V}$ coefficient of a single crystal $z$-cut LiTaO$_3$ used as a reference, the $d_{22}$ coefficient of the BFO film is calculated by employing the following equation:

$$\frac{d_{22}^2}{d_{11}^2} = \frac{P_{22}^2}{P_{11}^2} \frac{A_{22}^2}{A_{11}^2} \frac{\int f_1^{\alpha}(x)^2 e^{-\alpha_2(x,\varphi_2,\theta)} dx}{\int f_1^{\alpha}(x)^2 e^{-\alpha_2(x,\varphi_2,\theta)} dx}, \quad (4)$$

where the subscripts $r$ and $f$ refer to the reference and the film, respectively, $P_{22}(P_{11})$ are the second harmonic (fundamental) signal powers measured, $T$ is the transmission coefficient of the fundamental, $A$ is the area of the probed beam, $n$ are the indices of refraction, $l_1$ the coherence lengths, and $\alpha=4\pi k/\lambda$ is the absorption coefficient at $2\omega$. For this experiment, $A_1=A_2=(60 \mu m)^2$ and the coherence length of the film $l_1$ is equal to the film thickness.

The $B$ and $C$ parameters, which contain the ratios of nonlinear coefficients, are experimentally obtained by collecting the $p$-in-$p$-out $I_p^{\alpha}(\varphi=90^\circ)$, $s$-in-$p$-out $I_p^{\alpha}(\varphi=0^\circ)$, and $45$-in-$s$-out $I_p^{\alpha}(\varphi=45^\circ)$ SHG signals for different angles of tilt $\theta$ about the $x$ axis. The experimental data for $B$ and $C$ parameters (Fig. 3) is then fitted to Eq. (3) to

$$B = \frac{K_{22}}{K_{12}}, \quad C = \frac{K_{32}}{K_{12}}.$$