BiFeO₃ (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 BiFeO₃ 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 potentially 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 bandedge at 442 nm instead. No studies of nonlinear optical coefficients of BiFeO₃, 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 (PLD) 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 note specifically 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 \( z \)-[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 \( 3m \) point group symmetry for BFO are thus well defined and allow us to extract nonlinear coefficients precisely without ambiguity. Typical film stoichiometry, as determined by Rutherford backscattering spectrometry (RBS), was stoichiometric within \( \pm 3 \) \% 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 $\theta_0 = 55^\circ$ 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 substrate / bulk film / surface roughness / air ambient structure. The free parameters correspond to the bulk and surface roughness thicknesses of the film and a parameterization of the BiFeO$_3$ dielectric function. The dielectric function parameterization of BiFeO$_3$ consists of four Tauc-Lorentz oscillators sharing a common band gap and a constant additive term to $\varepsilon_1$ denoted by $\varepsilon_\infty$ (equal to 1 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 consisting of a 0.50 bulk film / 0.50 void mixture. This model yields the common Tauc gap $E_g = 2.15 \pm 0.06$ eV, bulk thickness $d_b = 468.93 \pm 0.78$ Å, and surface roughness thickness $d_s = 75.39 \pm 0.4$ Å.

We note that though the Tauc gap at 2.15 eV (577 nm) represents the onset of absorption, it is not the direct gap, as claimed in literature. A plot of $\alpha^2 E^2$ vs. photon energy $E$ ($\alpha = 4\pi k/\lambda$) and the linear extrapolation to $\alpha^2 E^2 = 0$ indicates 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 BiFeO$_3$ films grown on (001) and (111) SrTiO$_3$ 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 this model to be $N = 2.836 + 0i$ and $N^2 = 3.444 + 0.981i$ for corresponding wavelengths of 800 and 400 nm, respectively. It should be noted that although BiFeO$_3$ is uniaxially anisotropic, only the optical properties of the ordinary index of refraction have been obtained for this film.

The crystal symmetry of epitaxial BFO(111) films has been shown to be point group 3m using optical SHG and diffraction techniques. Optical SHG involves the conversion of light (electric field $E$) at a frequency $\omega$ into an optical signal at a frequency $2\omega$ by a nonlinear medium, through the creation of a nonlinear optical signal. BFO film thickness of about 50 nm grown on STO(111) substrates was used for this study. STO is centrosymmetric (cubic) and does not contribute SHG signals of its own for the incident powers used. The SHG experiment was performed with a fundamental wave generated from a tunable Ti-sapphire laser with 65 fs pulses of wavelength 800 nm incident from the substrate side at variable tilt angles to the sample surface normal.

As shown in Fig. 2, the crystallographic $y-z$ plane in the BFO film was aligned with the incidence plane. The polarization direction of incident light is at an angle $\phi$ from the $x$ axis, which was rotated continuously using a half-wave plate. The intensity $I_p$ of the output SHG signal at 400 nm wavelength from the film was detected in the p-polarization. The expected SHG intensity expressions for BFO(111) film with $x$-$y$ polarization are:

$\tilde{I}_p = A(\cos^2 \phi + B \sin^2 \phi)^2$

where $B$ and $C$ are given by...
the BFO film is calculated by employing the following
\[
B = \frac{K_{15} f_x f_z \sin 2\theta \cos \theta_B + K_{31} f_y^2 \cos^2 \theta \sin \theta_B + K_{33} f_z^2 \sin^2 \theta + f_y^2 \cos^2 \theta \cos \theta_B}{K_{33} f_x^2 \sin \theta_B - f_x^2 \cos \theta_B}
\]
\[
C = D(K_{15} f_x f_z \sin \theta - f_x f_y \cos \theta)
\]

The B and C parameters, which contain the ratios of nonlinear coefficients, are experimentally obtained by collecting the p-in-p-out \(I_{22}^p(\phi = 90^\circ)\), s-in-p-out \(I_{22}^p(\phi = 0^\circ)\) and 45-in-s-out \(I_{22}^p(\phi = 45^\circ)\) 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 extract the ratios \(K_{15} = 0.20 \pm 0.01\), \(K_{31} = 0.35 \pm 0.02\) and \(K_{33} = -11.4 \pm 0.20\). Taking absorption into account, the estimated effective coefficients are

\[
|d_{22}| = 298.4 \pm 6.1 \text{ pm/V}, \quad |d_{31}| = 59.7 \pm 4.2 \text{ pm/V},
\]
\[
|d_{15}| = 104.4 \pm 8.1 \text{ pm/V}, \quad |d_{33}| = 3401 \pm 129 \text{ pm/V}.
\]

Note that only the signs of the ratios \(K_{15}, K_{31}\) and \(K_{33}\) were determined unambiguously. 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 second harmonic generation coefficients in BiFeO\(_3\) thin films. These studies will be important in performing further linear and nonlinear optical spectroscopy of the magnetism and ferroelectricity in this material.

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