Bismuth tri-iodide (BiI₃) is an intermediate band gap semiconductor with potential for room temperature gamma-ray detection applications. Remarkably, very different band gap characteristics and values of BiI₃ have been reported in literature, which may be attributed to its complicated layered structure with strongly bound BiI₆ octahedra held together by weak van der Waals interactions. Here, to resolve this discrepancy, the band gap of BiI₃ was characterized through optical and computational methods and differences among previously reported values are discussed. Unpolarized transmittance and reflectance spectra in the visible to near ultraviolet (UV-Vis) range at room temperature yielded an indirect band gap of 1.67 ± 0.09 eV, while spectroscopic ellipsometry detected a direct band gap at 1.96 ± 0.05 eV and higher energy critical point features. The discrepancy between the UV-Vis and ellipsometry results originates from the low optical absorption coefficients (σ ≈ 10^2 cm⁻¹) of BiI₃ that renders reflection-based ellipsometry insensitive to the indirect gap for this material. Further, electronic-structure calculations of the band structure by density functional theory methods are also consistent with the presence of an indirect band gap of 1.55 eV in BiI₃. Based on this, an indirect band gap with a value of 1.67 ± 0.09 eV is considered to best represent the band gap structure and value for single crystal BiI₃.

I. INTRODUCTION

Bismuth tri-iodide (BiI₃) is a semiconductor material for room temperature gamma-ray detection, primarily due to its intermediate band gap, high density, and high effective atomic number.¹⁻³ At room temperature, BiI₃ has a rhombohedral crystal structure (space group R₃̅, No. 148) with six formula units per unit cell (Z = 6).⁴ Within each unit cell, BiI₃ adopts a layered structure with highly ionic Bi-I bonds in the layers and weak van der Waals bonding between layers. The band gap energy of the semiconductor material determines the number of electron-hole pairs generated under the radiation, and affects the energy resolution of the radiation detector.⁵ The experimentally and computationally determined band gap energy of BiI₃ has been reported with very different values ranging from 1.43 eV to 2.2 eV, as summarized in Table I. For instance, Vashchenko and Timofeev investigated the absorption and reflection spectra of BiI₃ single crystals and reported an indirect band gap energy of 1.730 ± 0.005 eV at room temperature. They also observed the temperature dependence of the band gap energy to be $-9.2 \times 10^{-4}$ eV/K in the 85–293 K range.⁵,⁷ Jellison et al. measured the optical functions of BiI₃ single crystal using two-modulator generalized spectroscopic ellipsometry. By modeling the complex dielectric functions, a band gap energy of 1.991 ± 0.005 eV at room temperature was determined.⁸ Schluter et al. theoretically studied the electronic band structure of BiI₃ by the empirical pseudopotential method.⁹ Their calculation indicated that BiI₃ has a direct band structure with an energy of 2.2 eV. However, recent first-principles pseudopotential calculations by Yorikawa and Muramatsu suggest that BiI₃ has an indirect band gap with a much smaller energy of 1.6652 eV.¹⁰ The first-principles linearized augmented plane-wave calculations by Singh used three different potentials and found band gaps of 1.43, 1.67, and 1.82 eV.¹¹ Thus, there is a clear discrepancy in the electronic structure and band gap values reported for BiI₃ in the literature. The present work investigates the band gap energy of BiI₃ single crystal by studying its optical transmission and reflection spectra in the visible to near ultraviolet (UV-Vis) spectral range and ellipsometric spectra from the near infrared to near ultraviolet range. As a supplement to the experimental work, the electronic band structure of BiI₃ was also studied using density functional theory (DFT). On the basis of the present work, the nature of the discrepancy on the previously reported band gap energy values is identified and the most likely characteristics of BiI₃ are determined.
II. EXPERIMENTAL PROCEDURE

BiI$_3$ single crystals for the optical characterization were grown by a modified vertical Bridgman method. For the crystal growth, BiI$_3$ powder (99.999%, MV Laboratories) was vacuum-sealed in a 3/4 in. diameter borosilicate glass ampoule at a pressure of approximately 10$^{-5}$ Torr. The ampoule was placed vertically in a programmable 24 heating zone vertical furnace (EDG-13, Mellen Company). A temperature profile was pre-established in the furnace with the temperature gradient of 10°C/cm at the solidification frontier. The melting point of BiI$_3$ is 408°C. The growth ampoule was first kept at 460°C for 24 h then cooled to 420°C at a rate of 10°C/h. During crystal growth, the temperature profile was controlled to move along the vertical axis with a speed of 0.5 mm/h. This simulated the ampoule movement in the conventional vertical Bridgman method. A polycrystalline ingot was obtained after the growth, and single crystals were cleaved perpendicular to the [001] direction from the ingot.

In this study, the band gap at room temperature was characterized by two different experimental methods: UV-Vis spectroscopy and spectroscopic ellipsometry. The UV-Vis spectroscopy method involved measuring optical transmission and reflection spectra over a range of 1.55 to 4.13 eV using a Xe lamp as the light source. The sample is a freshly cleaved single crystal with thickness of 0.900 ± 0.003 mm. A parallel monochromatic light beam from a Newport Cornerstone™ 260 monochromator was incident on the crystal surface at an angle of 3° to the crystal optic axis. The intensities of the incident, reflected, and transmitted beams were measured separately by a Newport UV-silicon detector.

Room temperature ellipsometric spectra (both in $\Delta$, $\Psi$ and the complete Mueller matrix) were collected ex situ at four angles of incidence, $\Theta_i = 50°, 60°, 70°,$ and $80°$, using a variable-angle dual rotating-compensator multichannel spectroscopic ellipsometer over a spectral range from 0.75 to 5.15 eV (Ref. 13) for three BiI$_3$ single crystals (A, B, C). Sample A is the smallest in area and significant incoherent reflections are observed from the back surface, making spectra below 1.78 eV unusable. Samples B and C are larger and the back surfaces have been roughened in order to prevent the incoherent reflections observed for sample A. The complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) and microstructural parameters were extracted using a least squares regression analysis and a weighted error function, to fit the experimental ellipsometric spectra to an optical model consisting of a semi-infinite BiI$_3$/BiI$_3$ + void layer/surface roughness/air ambient structure. When analyzing spectra collected for a uniaxial material with the optic axis perpendicular to the sample surface, the measurement is primarily sensitive to the ordinary values of $\varepsilon$. Simultaneous analysis of measurements at multiple angles of incidence can be used to extract both the ordinary and extraordinary $\varepsilon$, however, the presence of relatively large surface roughness and BiI$_3$ + void layers prevent accurate determination of the principal values of $\varepsilon$ in samples B and C. The large amplitude of $\varepsilon$ prevents accurate determination of the principal indices for sample A, even though the BiI$_3$ + void layer is not present and the surface roughness is small in magnitude. Thus, only an effective $\varepsilon$ is measured. In this work, only effective $\varepsilon$ will be discussed, and the loss of sensitivity at low values of $\varepsilon$ is apparent for all $\varepsilon$ extracted by reflection based spectroscopic ellipsometry measurements of BiI$_3$.

III. RESULTS AND DISCUSSION

A. Band gap determined by transmission and reflection spectra

The UV-Vis transmission and reflection spectra measured from 1.55 to 4.13 eV at room temperature are shown in Fig. 1. The absorption coefficient $\alpha$ was determined from the experimental spectra by

$$ T = \frac{(1 - R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}}, $$

where $T$ is the transmittance, $R$ is the reflectance, and $d$ is the total sample thickness. The relation between the absorption coefficient $\alpha$ and incident photon energy ($h\nu$) near the fundamental absorption edge can be written as

<table>
<thead>
<tr>
<th>Characterization method</th>
<th>Band gap nature</th>
<th>Band gap (eV)</th>
<th>T (K)</th>
<th>Crystal growth method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPM</td>
<td>Direct</td>
<td>2.2</td>
<td>0</td>
<td></td>
<td>...</td>
</tr>
<tr>
<td>First-principles pseudopotential</td>
<td>Indirect</td>
<td>1.6652</td>
<td>0</td>
<td></td>
<td>...</td>
</tr>
<tr>
<td>First-principles linearized augmented plane-wave</td>
<td>Direct</td>
<td>1.43-1.82</td>
<td>0</td>
<td></td>
<td>...</td>
</tr>
<tr>
<td>Density functional theory</td>
<td>Indirect</td>
<td>1.55</td>
<td>0</td>
<td></td>
<td>This work.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.730</td>
<td>293</td>
<td></td>
<td>...</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.922</td>
<td>85</td>
<td></td>
<td>...</td>
</tr>
<tr>
<td>Optical absorption</td>
<td>Indirect</td>
<td>2.029</td>
<td>20.4</td>
<td>Vertical Bridgman</td>
<td>Vashchenko and Timofeev</td>
</tr>
<tr>
<td>Optical absorption</td>
<td>Direct</td>
<td>1.72</td>
<td>298</td>
<td>Vertical Bridgman</td>
<td>Dmitriev et al.</td>
</tr>
<tr>
<td>Optical absorption</td>
<td>Indirect</td>
<td>1.67</td>
<td>298</td>
<td>Modified vertical Bridgman</td>
<td>This work.</td>
</tr>
<tr>
<td>Optical transmission</td>
<td>Direct</td>
<td>1.73</td>
<td>298</td>
<td>Vapor transportation</td>
<td>Schieber et al.</td>
</tr>
<tr>
<td>Spectroscopic Ellipsometry</td>
<td>Direct</td>
<td>1.991</td>
<td>298</td>
<td>Vapor transportation</td>
<td>Jellison et al.</td>
</tr>
<tr>
<td>Spectroscopic Ellipsometry</td>
<td>Direct</td>
<td>1.94-1.96</td>
<td>298</td>
<td>Modified vertical Bridgman</td>
<td>This work.</td>
</tr>
</tbody>
</table>

The dependence of \((zh\nu)^{1/2}\) or \((zh\nu)^2\) on the photon energy is shown in Fig. 2(a). Straight lines with different slopes were observed in the \((zh\nu)^{1/2}\) versus \(h\nu\) plot, representing the absorption or emission of phonons during interband transitions. This behavior clearly indicates the indirect characteristics of the BiI\(_3\) band structure. The two interceptions of the straight lines on the energy axis give the values of \(E_g - E_p\) and \(E_g + E_p\), where \(E_p\) is the phonon energy. The band gap value was then determined to be \(1.67 \pm 0.09\) eV at room temperature by taking the average of the two intercepts. This value is in general agreement with experimental values determined by optical absorption or transmission spectra, but smaller than the previously reported value determined by spectroscopic ellipsometry, as listed in Table I. In addition, to further investigate the pre-absorption edge, an Urbach tail analysis was also performed and it is presented in Fig. 2(b); it can be seen that the tail cannot be fit accurately with a single slope in the log(\(\alpha\)) vs photon energy plot, thus further supporting the indirect characteristics of the of the band structure.

### B. Band gap determined by spectroscopic ellipsometry

Example ellipsometric spectra in \(\Delta, \psi\) and corresponding fits using the parameterized structural and optical models are shown in Figs. 3–5 for sample A. Due to back side reflection effects in the experimental data below 1.78 eV, only higher photon energies have been included in the fitting procedure. A variety of parameterizations for \(\varepsilon\) and structural models have been applied, and that which provides the lowest error function, \(\chi^2\), while maintaining physically realistic parameters and a Kramers-Kronig consistent shape of \(\varepsilon\) is used. The complex dielectric function parameterization of BiI\(_3\) is represented by several Tauc-Lorentz oscillators.
where $A$ is the amplitude, $\Gamma$ is the broadening, $E_0$ is the resonance energy, and $E_g$ represents a band gap determined from a parabolic band, constant momentum matrix element. The low energy Sellmeier oscillator is represented by

$$
e = \frac{A^2}{E^2 - E_0^2},$$

(4)

where $A$ and $E_0$ are similar to Tauc-Lorentz oscillator parameters, but $E_0$ must be outside the spectral range. A constant additive term to $\epsilon_1$ represented by $\epsilon_{\infty}$ is also included. The optical properties of the surface roughness and BiI$_3$ + void layers are represented by Bruggeman effective medium approximation\cite{24} consisting of variable fractions of BiI$_3$ and void. These parameterizations are used to extract an effective $\epsilon$, which is likely strongly related to the ordinary value of $\epsilon$.\cite{8} Measurements of these samples are not sensitive to optical anisotropy due to the position of the optic axis perpendicular to the sample surface and the experimental $\Delta$, $\psi$ spectra being dominated by the presence of the surface roughness and BiI$_3$ + void layers.

The fit in Fig. 3 for sample A is only valid in the region where no backside reflections are observed, namely at photon energies greater than 1.78 eV. The experimental spectra collected at all angles of incidence are fit simultaneously to the same optical and structural model, with results given in Table II. Fig. 4 shows there is good qualitative agreement between $\epsilon$ obtained from the parameterization and from direct numerical inversion of $\Delta$, $\psi$ spectra collected at $\Theta_i = 80^\circ$. Effective $\epsilon$ has been extracted for each angle of incidence, shown in Fig. 5, and little angular dependence is observed. The large values of $\epsilon$ for BiI$_3$ leads to a smaller angle of refraction, thus predominately sampling only the ordinary values of $\epsilon$. This comparison indicates that ellipsometric measurements of BiI$_3$ with the optic axis perpendicular to the sample surface do not have sufficient sensitivity to anisotropy, even utilizing angles of incidence from 50$^\circ$ to 80$^\circ$.

Effective $\epsilon$ at 50$^\circ$ and 80$^\circ$ angles of incidence were calculated using reference spectra for the ordinary and extraordinary properties using the analytic expressions described in Ref. 25 and the optical response predicted using the Berreman formalism for a uniaxial material.\cite{26} The results of these two approaches indicate a maximum difference in the real and imaginary parts of the effective $\epsilon$ at 50$^\circ$ and 80$^\circ$ of less than 0.013. This small difference is at the sensitivity

![FIG. 4. Complex dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$) spectra for single crystal BiI$_3$ sample A obtained via the parametric fit (solid lines) and by direct numerical inversion of ($\Delta$, $\psi$) spectra collected at $\Theta_i = 80^\circ$.](image)

![FIG. 5. Complex dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$) spectra for single crystal BiI$_3$ sample A obtained by direct numerical inversion of ($\Delta$, $\psi$) spectra at each angle of incidence.](image)

TABLE II. (Sample A) Complex dielectric function and microstructural parameters (surface roughness thickness $d_s = 13 \pm 1$ Å, void fraction in surface roughness = 0.50) for the BiI$_3$ sample obtained by fitting experimental spectra (in $\Delta$, $\psi$) collected at $\Theta_i = 50^\circ$, $60^\circ$, $70^\circ$, and $80^\circ$ from 1.78 to 5.15 eV to the structural model using a least squares regression analysis with a weighted error function, $\chi^2 = 3.637$, $\epsilon_{\infty} = 1.90 \pm 0.01$, $E_g = 1.80 \pm 0.09$ eV.

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>$E_0$ (eV)</th>
<th>$\Gamma$ (eV)</th>
<th>$A$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tauc-Lorentz</td>
<td>1.99 ± 0.01</td>
<td>0.16 ± 0.01</td>
<td>140.77 ± 0.70</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>2.40 ± 0.01</td>
<td>0.77 ± 0.01</td>
<td>97.49 ± 0.99</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>3.10 ± 0.01</td>
<td>0.38 ± 0.03</td>
<td>1.45 ± 0.20</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>3.78 ± 0.01</td>
<td>0.53 ± 0.03</td>
<td>2.64 ± 0.33</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>4.41 ± 0.01</td>
<td>2.09 ± 0.03</td>
<td>32.76 ± 1.79</td>
</tr>
</tbody>
</table>
The fits for samples B and C, shown in Fig. 6, are similar in quality to that shown in Fig. 3 for sample A, except that the full spectral range can be accurately fit. Tables III and IV show the fit parameters to the experimental data using the complex dielectric function and structural models for samples B and C.

The microstructural parameters indicate these samples had significant surface roughness due to scattering via features on the surface such as lattice dislocations or defects due to cleaving. Several hundred angstroms of BiI$_3$ + void material between the surface roughness and bulk of the samples indicate a slightly less dense material perhaps related to defects near the surface arising from environmental contamination, deeper damage due to cleaving, or other effects arising from processing. Numerical inversion has been used to extract $\varepsilon$ from the $(\Delta, \Psi)$ spectra using the microstructural parameters deduced from the parameterized fit in the same manner as for sample A.

The effective $\varepsilon$ obtained by numerical inversion from $\Theta_i = 80^\circ$ measurements are shown in Fig. 6. There are qualitative similarities between the effective $\varepsilon$ for all three samples, with significant differences in relative amplitudes of features above 2.0 eV. These variations may be attributed to surface defects arising during sample processing and indicate that BiI$_3$ surfaces may have long-term stability issues and is highly sensitive to processing conditions. There is relatively good agreement in $\varepsilon$ for samples A, B, and C at photon energies less than ~2.0 eV. The penetration depth of light into BiI$_3$ is large in this range near the band edge. This larger penetration depth makes the low energy region less sensitive to surface effects and allows for probing the properties of the bulk material.

Overall, the effective $\varepsilon$ reported in this work has similar critical point features compared to the ordinary $\varepsilon$ reported in Jellison et al.$^8$ over most of the spectral range. $\varepsilon$ obtained for sample A is quite similar to the ordinary $\varepsilon$ from Ref. 8. The relative amplitudes of features vary, with deviations at higher energies for samples B and C. These differences can potentially be attributed to a loss of sensitivity to the true “bulk” material in the sample studied here due to screening by the surface roughness and BiI$_3$ + void layers or by damage to the samples during cleaving, back-side roughening, or other handling for reflection measurements. This loss of sensitivity also prevents accurate determination of the ordinary and extraordinary values of $\varepsilon$ and results in the deviation of the effective $\varepsilon$ from the principal values in Ref. 8.

The absorption coefficient, $\alpha$, can be obtained after $\varepsilon$ is obtained from numerical inversion. Fig. 7 presents $(\varepsilon\omega)^2$ and $(\varepsilon\omega)^2$ plotted as functions of photon energy, and extrapolated using a linear relationship to $(\varepsilon\omega)^2$ for samples A, B, and C. For these evaluations, linearity in the spectral region near where $\alpha \sim 10^2$–$10^4$ cm$^{-1}$ was examined. In this situation, the results of Fig. 7 would indicate that BiI$_3$ possesses a direct gap at 1.94 ± 0.05 eV for sample A and

![Graph showing complex dielectric function (\(\varepsilon = \varepsilon_1 + i\varepsilon_2\)) spectra for single crystal BiI$_3$ samples obtained by direct numerical inversion of \((\Delta, \Psi)\) spectra collected at \(\Theta_i = 80^\circ\).](image)

**TABLE III.** (Sample B) Complex dielectric function and microstructural parameters (BiI$_3$ + void thickness = 750 ± 7 Å, void fraction in BiI$_3$ + void layer = 0.03 ± 0.01, surface roughness thickness $d_s = 133 ± 6$ Å, void fraction in surface roughness = 0.68 ± 0.04) for the BiI$_3$ sample obtained by fitting experimental spectra (in $\Delta, \Psi$) collected at $\Theta_i = 80^\circ$ from 0.75 to 5.15 eV to the structural model using a least squares regression analysis with a weighted error function, $\chi^2 = 6.399$, $\varepsilon_{\infty} = 2.03 ± 0.03$, $E_g = 1.86 ± 0.12$ eV.

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>$E_0$ (eV)</th>
<th>$\Gamma$ (eV)</th>
<th>$A$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tauc-Lorentz</td>
<td>2.01 ± 0.01</td>
<td>0.14 ± 0.01</td>
<td>168.53 ± 3.02</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>2.47 ± 0.01</td>
<td>0.77 ± 0.01</td>
<td>91.28 ± 1.90</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>3.13 ± 0.01</td>
<td>0.30 ± 0.03</td>
<td>1.27 ± 0.20</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>3.79 ± 0.01</td>
<td>0.26 ± 0.03</td>
<td>0.89 ± 0.13</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>4.87 ± 0.05</td>
<td>1.75 ± 0.08</td>
<td>45.96 ± 4.12</td>
</tr>
<tr>
<td>Sellmeier</td>
<td>0.001</td>
<td>...</td>
<td>0.26 ± 0.1</td>
</tr>
</tbody>
</table>

**TABLE IV.** (Sample C) Complex dielectric function and microstructural parameters (BiI$_3$ + void thickness = 723 ± 9 Å, void fraction in BiI$_3$ + void layer = 0.04 ± 0.01, surface roughness thickness $d_s = 93 ± 17$ Å, void fraction in surface roughness = 0.74 ± 0.08) for the BiI$_3$ sample obtained by fitting experimental spectra (in $\Delta, \Psi$) collected at $\Theta_i = 80^\circ$ from 0.75 to 5.15 eV to the structural model using a least squares regression analysis with a weighted error function, $\chi^2 = 6.036$, $\varepsilon_{\infty} = 1.48 ± 0.04$, $E_g = 1.87 ± 0.25$ eV.
1.96 ± 0.05 eV for samples B and C, which are in agreement with the work by Jellison et al.8

The discrepancy on the band gap characterization by UV-Vis spectra and ellipsometry method is obvious for sample B, given that the experiments were conducted on the same crystal. The comparison suggests that the origin of the discrepancy in the values here obtained and those reported in literature lies in the sensitivity of the characterization techniques employed as discussed in Sec. III C.

C. Comparison between UV-Vis and ellipsometry

Spectroscopic ellipsometry has proven to be useful in extracting the material microstructure in the form of surface features, the index of refraction below the band gap, and the critical point features above the band gap.27–29 Transmission and reflection measurements have been widely used to determine the band gap values of materials18,19,30 but generally lack sensitivity to the material microstructure. A comparison between spectroscopic ellipsometry and UV-Vis spectroscopy measurements highlights the relative strengths and weaknesses of the two techniques. Fig. 8 shows the absorption coefficient extracted from the spectroscopic ellipsometry and UV-Vis measurements in the present work. As is typical of reflection-based techniques, spectroscopic ellipsometry loses sensitivity when the absorption coefficient is low, in this case near \( \chi \approx 10^3 \text{ cm}^{-1} \) as has been observed by Jellison et al.8 When the absorption coefficient is extracted using UV-Vis spectroscopy, sensitivity is retained between \( \chi \approx 1 \) and 200 cm\(^{-1}\). The different \( \chi \) sensitivity originates from the nature of the techniques. Oblique angle reflection-based techniques, such as spectroscopic ellipsometry, are inherently more microstructure-sensitive than are transmission-based approaches. It is likely that small differences in the surface microstructure used in the ellipsometry modeling would produce differences in the numerically inverted optical data. Thus, from numerical inversion of the ellipsometric spectra the sensitivity to \( \chi \) is lost at small values. In this particular material, the value of \( \nu_2 \) and thus \( \chi \) extracted below \( \approx 1.88 \text{ eV} \) from spectroscopic ellipsometry is zero, which is not the case when the sample is measured by unpolarized transmittance spectroscopy. When the crystal is measured by UV-Vis spectroscopy at near-normal incident angle, the effect of BiI\(_3\) + void layer is much smaller compared to spectroscopic ellipsometry. Thus, UV-Vis spectra can maintain the sensitivity to smaller \( \chi \) values. Therefore, the different band gap values obtained by UV-Vis and spectroscopic ellipsometry in this study and Jellison et al.8 can be attributed to the different range of absorption coefficient used for the data fitting, which results from the sensitivity of the respective technique. As indicated in Fig. 2, the band gap characteristics of BiI\(_3\) appear near \( \chi \approx 10^2 \text{ cm}^{-1} \) and below photon energy of 2 eV. Thus, the value determined by UV-Vis spectroscopy more accurately represents BiI\(_3\), which has an indirect band gap with energy of 1.67 ± 0.09 eV.

It should be noted that while the exact data and fitting parameters by Jellison et al. are not available, it is most likely that they faced the same sensitivity limitations discussed here.

D. Computational band structure

The previous sections focused on experimental determination of the band gap. Here, DFT calculations were employed to further investigate the band structure of BiI\(_3\) crystal. However, as was discussed in the introduction, there are quite different predictions reported for the band gap of BiI\(_3\) using first-principles calculations. Schluter et al. determined a direct band gap of 2.2 eV in BiI\(_3\) (Ref. 9) but work by Yorikawa and Muramatsu suggested that BiI\(_3\) has a much smaller indirect band gap 1.6652 eV.10 Recent work by Singh11 reported the band gap energy for various halide scintillators, including BiI\(_3\), using first-principles calculations.
The work used the linearized augmented plane-wave (LAPW) method with three different functionals, the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE), the Engel-Vosko (EV), and the semilocal functional of Tran and Blaha (TB-mBJ), and found a band gap 1.43 eV, 1.67, and 1.82, respectively.

To understand the discrepancy between these studies, DFT calculations were performed using projector augmented wave (PAW)\textsuperscript{31,32} pseudopotentials within the general gradient approximation with the PBE parameterization.\textsuperscript{33} The bismuth 5d\textsuperscript{10}6s\textsuperscript{2}6p\textsuperscript{3} and iodine 5s\textsuperscript{2}5p\textsuperscript{5} were treated as valence electrons and spin orbit coupling was included for the electronic structure. A plane-wave cutoff energy of 400 eV was used along with a 6 × 6 × 3 k-mesh. Test calculations done with 500 eV cutoff and a 8 × 8 × 4 k-mesh resulted in differences less than 0.02 eV in the total energy and 0.01 eV in the band gap. The equilibrium structure lattice parameters were found to be a = 7.823 Å and c = 22.812 Å, which overestimate the values of a = 7.519 Å and c = 20.721 Å determined by X-ray diffraction.\textsuperscript{4}

To calculate the band structure, reciprocal space was divided by discrete points between high symmetry sites and is shown in Fig. 9. Γ, K, H, A, M, and Λ correspond to critical points of (0, 0, 0), (0.5, 0, 0), (0.5, 0, 0.5), (0, 0.5, 0), (0.5, 0.5, 0), and (0.5, 0.5, 0.5) in the first Brillouin zone, respectively. The conduction band is very flat between A and Γ near the minimum at 0.5 Å, with low lying states surrounding the minimum. The A and the Γ point connect along the z direction, as seen in Fig. 9(b), crossing through the I-Bi-I layers and van der Waals interactions layer. The conduction band minimum occurs just above the iodine, outside of the I-Bi-I layer. By contrast, the top of the valence band is more pronounced than the conduction band and the maximum is found at 0.7 Å, which occurs within the I-Bi-I layer along the x-y plane. These calculations indicate BiI\textsubscript{3} has an indirect band gap, which is consistent with the experimental results obtained by UV-Vis spectroscopy in this work but in disagreement with Schluter et al.\textsuperscript{9} The top and bottom dashed lines in Fig. 9(a), is 1.55 ± 0.01 eV, which is smaller than experimental results of 1.67 eV presented here. In comparison to the computational reports, the band gap predicted here is in agreement with Singh\textsuperscript{11} and Yoikawa,\textsuperscript{10} and significantly lower than Schluter et al.\textsuperscript{9} The work by Schluter et al.\textsuperscript{9} excluded spin orbit effects, without which the calculations performed here predicted a direct band gap of 2.2 eV. Therefore, the discrepancy between predictions is attributed to the missing spin orbit feature. In addition to the indirect band gap, a direct band gap of 1.61 eV was found at 0.1 Tm, corresponding to the van der Waals interactions between the I-Bi-I layers. The indirect band gap of 1.55 eV predicted by DFT gives strong supporting evidence to the experimentally determined band gap of 1.67 eV because DFT usually underestimates the band gap,\textsuperscript{34} since excited states are not accurately captured.

**IV. CONCLUSIONS**

Discrepancies among the nature and values of the band gap in BiI\textsubscript{3} have been discussed. Through optical methods, the band gap nature of BiI\textsubscript{3} single crystals was confirmed to be indirect. The different band gap energy values and characteristics obtained by UV-Vis and spectroscopic ellipsometry were found to originate from the nature of the techniques that retain sensitivity to different ranges of absorption coefficient. The calculated band structure from DFT found an indirect band gap of 1.55 ± 0.01 eV. Along the van der Waals interactions direction, a very flat conduction band profile was observed between the A and Γ points. In conclusion, the band structure of BiI\textsubscript{3} is best represented by an indirect band gap of 1.67 ± 0.09 eV.

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