



# Article Structural Analysis, Characterization, and First-Principles Calculations of Bismuth Tellurium Oxides, Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>

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Abstract: A single crystal of  $Bi_6Te_2O_{15}$  was obtained from the melt of the solid-state reaction of  $Bi_2O_3$ and TeO<sub>3</sub>. Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub> crystallizes in the *Pnma* space group (No. 62) and exhibits a three-dimensional network structure with a = 10.5831(12) Å, b = 22.694(3) Å, c = 5.3843(6) Å,  $\alpha = \beta = \gamma = 90^{\circ}$ , V = 1293.2(3) Å<sup>3</sup>, and Z = 4. The structure was determined using single-crystal X-ray diffraction. An asymmetric unit in the unit cell, Bi<sub>3</sub>Te<sub>1</sub>O<sub>7.5</sub>, uniquely composed of four Bi<sup>3+</sup> sites, one Te<sup>6+</sup> site, and nine O<sup>2-</sup> sites, was solved and refined. As a bulk phase,  $Bi_6Te_2O_{15}$  was also synthesized and characterized using powder X-ray diffraction (XRD), infrared (FT-IR) spectrometry, and the thermogravimetric analysis (TGA) method. Through bond valence sum (BVS) calculations from the single crystal structure, Bi and Te cations have +3 and +6 oxidation numbers, respectively. Each Bi<sup>3+</sup> cation forms a square pyramidal structure with five  $O^{2-}$  anions, and a single Te<sup>6+</sup> cation forms a six-coordinated octahedral structure with O<sup>2-</sup> anions. Since the lone-pair electron (Lp) of the square pyramidal structure,  $[BiO_5]^{7-}$ , where the Bi<sup>+</sup> cation occupies the center of the square base plane, exists in the opposite direction of the square plane, the asymmetric environments of all four Bi<sup>3+</sup> cations were analyzed and explored by determining the local dipole moments. In addition, to determine the extent of bond strain and distortion in the unit cell, which is attributed to the asymmetric environments of the Bi<sup>3+</sup> and Te<sup>6+</sup> cations in Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>, bond strain index (BSI) and global instability index (GII) were also calculated. We also investigated the structural, electronic, and optical properties of the structure of Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub> using the full potential linear augmented plane wave (FP-LAPW) method and the density functional theory (DFT) with WIEN2k code. In order to study the ground state properties of Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>, the theoretical total energies were calculated as a function of reduced volumes and then fitted with the Birch-Murnaghan equation of state (EOS). The band gap energy within the modified Becke-Johnson potential with Tran-Blaha parameterization (TB-mBJ) revealed a value of 3.36 eV, which was higher than the experimental value of 3.29 eV. To explore the optical properties of  $\text{Bi}_6\text{Te}_2O_{15}$ , the real and imaginary parts of the dielectric function, refraction index, optical absorption coefficient, reflectivity, the real part of the optical conductivity extinction function, and the energy loss function were also calculated.

Keywords: Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>; bismuth tellurium oxides; crystal growth; first-principles calculation

# 1. Introduction

Bismuth tellurium oxides, including solid solution phases, have been synthesized and reported in the literature: Bi<sub>2</sub>TeO<sub>5</sub> [1–7], Bi<sub>2</sub>TeO<sub>6</sub> [1,8–10], Bi<sub>2</sub>Te<sub>2</sub>O<sub>7</sub> [2,11,12], Bi<sub>2</sub>Te<sub>2</sub>O<sub>8</sub> [8,10, 13], Bi<sub>2</sub>Te<sub>4</sub>O<sub>11</sub> [4,11,12], Bi<sub>10</sub>Te<sub>2</sub>O<sub>19</sub> [4], Bi<sub>16</sub>Te<sub>5</sub>O<sub>34</sub> [4], Bi<sub>6</sub>Te<sub>2</sub>O<sub>13+ $\delta$ </sub> ( $\delta$  = 0 or 2) [14,15], Bi<sub>1-x</sub>Te<sub>x</sub>O<sub>(3+x)/2</sub> (0.333 < x < 0.500) [16], etc. Among these, Bi<sub>2</sub>TeO<sub>5</sub> has garnered attention for its applications in nonlinear microphotonic and holographic devices [5,6], particularly with recent findings highlighting the ferroelectric domains observed at room temperature in two-dimensional (2D) Bi<sub>2</sub>TeO<sub>5</sub> grown via chemical vapor deposition (CVD) [7].

In terms of the structural composition of bismuth tellurium oxides, the oxidation number of Te cations is either 4+ or 6+, while Bi cations exhibit a consistent oxidation state of



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3+. Bismuth tellurium oxides are formed through the combination of  $Bi^{3+}$  and  $Te^{4+}$  cations or the combination of  $Bi^{3+}$  and  $Te^{6+}$  cations. In the case of the structure of  $Bi_2Te_2O_8$  [13], both  $Te^{4+}$  and  $Te^{6+}$  cations coexist within the compound. The distinction between these cations is evident through bond valence sum (BVS) calculations based on the crystal structure. A  $Te^{6+}$  cation produces a six-coordinated octahedral structure as  $[Te^{6+}O_6]^{6-}$ . Generally, transition metal cations in the reported transition metal oxides have shown distorted octahedral structures. However, the octahedral structure of  $[Te^{6+}O_6]^{6-}$  shows no distortion because the six coordinated bonds have roughly the same bond distances. As an example, the  $Te^{6+}$  cation of  $Bi_2TeO_6$  has an undistorted octahedral structure [9]. In contrast, the  $Te^{4+}$  cation exhibits three- or four-coordinated structures as  $[Te^{4+}O_3]^{2-}$  or  $[Te^{4+}O_4]^{6-}$ , which corresponds to a trigonal pyramid or a seesaw shape, respectively. For the  $Bi^{3+}$  cation, a square pyramid  $[Bi^{3+}O_5]^{7-}$  structure with five coordinates is also available. In addition, a lone-pair electron also exists in  $Te^{4+}$  and  $Bi^{3+}$  cations, which induces distorted structures related to the second-order *Jahn–Teller* (SOJT) effect in  $Bi_2TeO_5$  [3].

For  $Bi_6Te_2O_{13+\delta}$  ( $\delta = 0$  or 2), it was reported that two different phases according to the synthetic temperature conditions and the transition from  $Bi_6Te_2O_{15}$  (orthorhombic) to  $Bi_6Te_2O_{13}$  (cubic) occurs around 860 °C, which is driven by a shift in the oxidation state of the Te cation [15]. The literature also shows that  $Bi_6Te_2O_{15}$  is composed of  $Bi^{3+}$  and  $Te^{6+}$  cations and  $O^{2-}$  anions using powder XRD or a single crystal structure using natural *pingguite* crystals [14]. However, for  $Bi_6Te_2O_{13}$ , it was difficult to analyze the exact atomic coordinates of Bi, Te, and O due to the disorder of the Bi and Te atoms. Thus, we have demonstrated the growth of single crystals in two phases,  $Bi_6Te_2O_{13}$  and  $Bi_6Te_2O_{15}$ , to determine the exact atomic coordinates in the unit cell.

In this paper, we report the structure of  $Bi_6Te_2O_{15}$  from a single crystal grown using conventional solid-state methods. Pure  $Bi_6Te_2O_{15}$  as a bulk phase was also synthesized and characterized via powder X-ray diffraction (XRD), infrared (IR) spectrometry, and the thermogravimetric analysis (TGA) method. The structure of  $Bi_6Te_2O_{15}$  was explored using the bond valence sum (BVS) calculation, the dipole moment calculation, and a calculation for the extent of the distortion and bond strain in a unit cell using the global instability index (GII) and the bond strain index (BSI). In addition, based on the determined crystal structure of  $Bi_6Te_2O_{15}$ , the volume-optimized structures, density of state (DOS), band structure, and optical properties were calculated and investigated via the first-principles method.

### 2. Materials and Methods

Reagents  $Bi_2O_3$  (Alfa Aesar, Haverhill, MA, USA, 99%) and  $H_2TeO_4 \cdot 2H_2O$  (Alfa Aesar, Haverhill, MA, USA, 99+%) were used without any further purification.

Crystal Growth Crystals of  $Bi_6Te_2O_{15}$  were obtained from a melt of the solid-state reaction of  $Bi_2O_3$  and  $TeO_3$ . Amorphous  $TeO_3$  was prepared by heating  $H_2TeO_4 \cdot 2H_2O$  at 400 °C for 12 h in air. Stoichiometric amounts of  $Bi_2O_3$  and  $TeO_3$  were thoroughly ground and pressed into a pellet. The pellet was placed into a Pt crucible with extra amounts of  $Bi_2O_3$ , which acted as flux. The crucible was heated to 800 °C for 24 h, then cooled slowly to 450 °C at a rate of 3.5 °C/h, and then the furnace was turned off. Colorless plate-shaped crystals of  $Bi_6Te_2O_{15}$  and unidentified glassy products were obtained.

Single-Crystal X-ray Diffraction. A colorless plate-shaped crystal ( $0.030 \times 0.040 \times 0.150 \text{ mm}^3$ ) was selected for single crystal data collection. The data were collected with a Bruker SMART APEX CCD diffractometer with graphite-monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 100 K. A hemisphere of data was collected using a narrow-frame method with scan widths of  $0.30^\circ$  in  $\omega$  and an exposure time of 30 s per frame. The data were integrated using the SAINT program [17], with the intensities corrected for Lorentz, polarization, and air absorption. Numerical methods were used for the absorption correction on the hemisphere of data. The structure was solved using direct methods (SHELXS-2014) [18,19]. As an asymmetric unit in the unit cell, the Bi<sub>3</sub>Te<sub>1</sub>O<sub>7.5</sub> model was used, and all atoms were refined with anisotropic thermal parameters using the program SHELXL (2018) [18,19]. Data were converged for I > 2 $\sigma$  (I), and all calculations were performed

using the WINGX-98 crystallographic software package [20]. Relevant crystallographic data and selected bond distances for  $Bi_6Te_2O_{15}$  are given in Tables 1 and 2, with additional details found in the Supporting Information (see Supporting Information, Tables S1 and S2). The structural figure for  $Bi_6Te_2O_{15}$  was drawn using the VESTA crystal structure drawing package [21].

Table 1. Crystallographic data and structure refinement for Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>.

| Empirical formula                        | Bi Ta O  |  |  |
|--|--|--|--|
| Empirical formula                        | 1740.08  |  |  |
| Tomporature                              | 1/49.00<br>100(2) V                                  |  |  |
| lemperature                              | 100(2) K   |  |  |
| Wavelength                               | 0.71073 A  |  |  |
| Crystal system                           | Orthorhombic   |  |  |
| Space group                              | <i>Pnma</i> (No. 62)                                 |  |  |
| Unit cell dimensions                     | $a = 10.5831(12) A$ $\alpha = 90^{\circ}$            |  |  |
|  | $b = 22.694(3) \text{ Å}  \beta = 90^{\circ}$        |  |  |
|  | $c = 5.3843(6) \text{ Å} \qquad \gamma = 90^{\circ}$ |  |  |
| Volume                                   | 1293.2(3) Å <sup>3</sup>                             |  |  |
| Z  | 4  |  |  |
| Density (calculated)                     | $8.984 \text{ Mg/m}^3$                               |  |  |
| Absorption coefficient                   | $85.869 \text{ mm}^{-1}$                             |  |  |
| F(000)                                   | 2888   |  |  |
| Crystal size                             | $0.150	imes 0.040	imes 0.030~\mathrm{mm^3}$          |  |  |
| Theta range for data collection          | $1.795 \text{ to } 26.372^{\circ}$                   |  |  |
| Index ranges                             | $-12 \le h \le 13, -28 \le k \le 28, -6 \le l \le 6$ |  |  |
| Reflections collected                    | 7178   |  |  |
| Independent reflections                  | 1316 [R(int) = 0.0384]                               |  |  |
| Completeness to theta = $25.242^{\circ}$ | 96.90%   |  |  |
| Absorption correction                    | Numerical  |  |  |
| Max. and min. transmission               | 0.13931 and 0.02840                                  |  |  |
| Refinement method                        | Full-matrix least squares on F <sup>2</sup>          |  |  |
| Data / restraints / parameters           | 1316/0/110   |  |  |
| Goodness-of-fit on $F^2$                 | 1.079  |  |  |
| Final R indices [I>2sigma(I)]            | $R_1 = 0.0364$ , $wR_2 = 0.0744$                     |  |  |
| R indices (all data)                     | $R_1 = 0.0475, wR_2 = 0.0791$                        |  |  |
| Extinction coefficient                   | 0.00196(8)   |  |  |
| Largest diff. peak and hole              | 2.415 and $-1.457$ e Å <sup>-3</sup>                 |  |  |

Powder X-ray Diffraction The powder XRD data of  $Bi_6Te_2O_{15}$  were collected on a PANalytical X'pert pro diffractometer using CuK $\alpha$  radiation in the 2 $\theta$  range 5–65°. A step size of 0.008 degrees (deg) with a scan time of 0.3 s/deg was used.

FT-IR Spectroscopy FT-IR spectra of  $Bi_6Te_2O_{15}$  were obtained using a Thermo Scientific Nicolet 6700 FT-IR spectrometer in the range of 400–4000 cm<sup>-1</sup>.

Thermal Analysis Thermogravimetric analysis (TGA) of  $Bi_6Te_2O_{15}$  was carried out on a TA Instruments TGA 2050. About ~10 mg of the sample was placed into a Pt crucible and heated under nitrogen atmosphere at a rate of 10 °C min<sup>-1</sup> to 900 °C.

Computational Methods All calculations were performed using the all-electron fullpotential linearized augmented plane-wave (FP-LAPW) method implemented with the WIEN2k package [22,23]. Generalized gradient approximation, including the Perdew–Burke– Ernzerhof (GGA-PBE) [24,25], Perdew–Burke–Ernzerhof for solids (GGA-PBESol) [26], and Wu–Cohen (GGA-WC) [27] functionals, was used for the treatment of exchange-correlation electron interactions. To achieve an accurate electronic structure for optical properties, the modified version of the original Becke–Johnson exchange potential with Tran–Blaha parameterization (TB-mBJ) was also used [28,29]. In addition, the electron configuration for each atom was as follows: Bi:  $[Xe]4f^{14}5d^{10}6s^26p^3$ , Te:  $[Kr]4d^{10}5s^25p^4$ , and O:  $[He]2s^22p^4$ . The muffin tin radii (R<sub>MT</sub>) for Bi, Te, and O were 2.04, 1.81, and 1.56 Bohr, respectively, to avoid the overlapping of atomic spheres [23]. The number of plane waves in the potential of the interstitial region between the atomic spheres was restricted to R<sub>MT</sub> × k<sub>max</sub> = 7, where R<sub>MT</sub> is the muffin tin radii and k<sub>max</sub> indicates the highest *k*-vector for plane wave expansion. Valence wave functions inside MT-spheres were expanded up to  $l_{\text{max}} = 10$ , and the charge density was Fourier expanded up to  $G_{\text{max}} = 16 \text{ Bohr}^{-1}$ . In order to optimize the cell structure, more precise calculations were performed using the first Brillouin zone sampling with 200 *k*-points mesh according to the Monkhorst–Pack scheme [30]. The total energy convergence criterion was also set to  $10^{-4}$  Ry.

| Cation | Cation Anion Bond Length |           | BVS                      |
|--------|--------------------------|-----------|--------------------------|
| Bi(1)  | O(7)#1                   | 2.168(9)  | 3.01 (Bi <sup>3+</sup> ) |
| Bi(1)  | O(7)                     | 2.200(8)  |                          |
| Bi(1)  | O(5)                     | 2.265(9)  |                          |
| Bi(1)  | O(2)#1                   | 2.335(9)  |                          |
| Bi(1)  | O(4)#2                   | 2.530(9)  |                          |
| Bi(2)  | O(8)                     | 2.098(12) | 2.94 (Bi <sup>3+</sup> ) |
| Bi(2)  | O(1)#3                   | 2.221(9)  |                          |
| Bi(2)  | O(1)#4                   | 2.221(9)  |                          |
| Bi(2)  | O(6)#5                   | 2.583(9)  |                          |
| Bi(2)  | O(6)                     | 2.583(9)  |                          |
| Bi(3)  | O(8)#6                   | 2.148(12) | 2.89 (Bi <sup>3+</sup> ) |
| Bi(3)  | O(6)#2                   | 2.226(9)  |                          |
| Bi(3)  | O(6)#7                   | 2.226(9)  |                          |
| Bi(3)  | O(3)                     | 2.531(10) |                          |
| Bi(3)  | O(3)#5                   | 2.531(10) |                          |
| Bi(3)  | O(7)                     | 2.142(9)  |                          |
| Bi(4)  | O(4)#8                   | 2.226(9)  | 2.77 (Bi <sup>3+</sup> ) |
| Bi(4)  | O(3)#1                   | 2.269(9)  |                          |
| Bi(4)  | O(5)#9                   | 2.536(9)  |                          |
| Bi(4)  | O(2)#10                  | 2.585(9)  |                          |
| Bi(4)  | O(2)                     | 1.906(8)  |                          |
| Te(1)  | O(4)                     | 1.912(8)  | 5.80 (Te <sup>6+</sup> ) |
| Te(1)  | O(1)                     | 1.929(9)  |                          |
| Te(1)  | O(5)                     | 1.938(9)  |                          |
| Te(1)  | O(3)                     | 1.938(9)  |                          |
| Te(1)  | O(6)                     | 1.958(9)  |                          |
| Te(1)  | O(7)#1                   | 2.168(9)  |                          |

Table 2. Selected bond distances (Å) and bond valence sums (BVS) for Bi6Te2O15.

# 3. Results and Discussion

#### 3.1. Single-Crystal Structure

Compared to the structure of  $Bi_6Te_2O_{15}$  obtained from the crystal fragment of natural *pingguite* [14], the structure of  $Bi_6Te_2O_{15}$  synthesized using the conventional solid-state method described above was similar, except that the bond distance information of the synthesized structure was better. Thus, only a brief description of the structure of  $Bi_6Te_2O_{15}$  is given here. In the binary system,  $Bi_6Te_2O_{15}$  exhibited a three-dimensional network consisting of one unique  $Te^{6+}$  and four unique  $Bi^{3+}$  cations (see Figure 1). The  $Te^{6+}$  cation showed an octahedral structure with six  $O^{2-}$  anions, and the bond distances of Te–O ranged from 1.912 to 1.958 Å. Although the  $Te^{4+}$  cation from  $TeO_2$  was used as a starting reagent, it was expected that the relatively higher temperature condition would induce the oxidation of  $Te^{4+}$  cations to  $Te^{6+}$ , accompanied by a structural change from trigonal pyramidal to octahedral. It was also proved that Te has an approx. 6+ oxidation (5.80) from the bond valance sum (BVS) calculation [31–33] (see Table 3). Each  $Bi^{3+}$  cation had a five-coordinated square pyramidal structure with asymmetric environments, and the bond distances of Bi-O ranged from 2.098 to 2.585 Å.

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z+1; #2 x-1/2, y, -z+3/2; #3 x, y, z-1; #4 x, -y+3/2, z-1; #5 x, -y+3/2, z; #6 x-1/2, y, -z+1/2; #7 x-1/2, -y+3/2, -z+3/2; #8 -x+3/2, -y+1, z-1/2; #9 -x+1, -y+1, -z+2; #10 -x+3/2, -y+1, z+1/2.



Figure 1. Ball-and-stick representation of Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub> in the *ab*-plane.

**Table 3.** Calculated local dipole moments of polyhedral structure of  $Bi_6Te_2O_{15}$  (D = Debye).

| Species             | Dipole Moment (D) | Species        | Dipole Moment (D) |
|---------------------|-------------------|----------------|-------------------|
| Bi(1)O <sub>5</sub> | 18.3              | $Bi(1)O_5(Lp)$ | 9.3               |
| Bi(2)O <sub>5</sub> | 13.2              | $Bi(2)O_5(Lp)$ | 7.9               |
| Bi(3)O <sub>5</sub> | 16.2              | $Bi(3)O_5(Lp)$ | 8.8               |
| $Bi(4)O_5$          | 16.2              | $Bi(4)O_5(Lp)$ | 6.8               |
| $Te(1)O_6$          | 0.5               |                |                   |

Lp indicates lone-pair electron. The local dipole moment for the square pyramidal of  $[BiO_5]^{7-}$  is calculated without Lp or with Lp.

Each square pyramidal was also connected to the six oxygen atoms of the TeO<sub>6</sub> octahedral via corner sharing. In addition, there was an edge-shared connection between the two square pyramidals of Bi(3) and Bi(4), and it formed the three-dimensional network structure along the *ab*-plane of the unit cell. Bond valence sum calculations, weighted to reflect occupancies, resulted in values of 3.01, 2.94, 2.89, and 2.77 for the Bi(1), Bi(2), Bi(3), and Bi(4) cations, respectively. In addition, all four Bi<sup>3+</sup> cations were in asymmetric coordination environments, owing to their unbonded electron pair (lone-pair electron) in the square pyramidal (see Figure 2).



**Figure 2.** ORTEP representations (50% probability ellipsoids) of  $Bi(1)^{3+}$ ,  $Bi(2)^{3+}$ ,  $Bi(3)^{3+}$ ,  $Bi(4)^{3+}$ , and  $Te(1)^{6+}$  cations.

## 3.2. Characterization

The bulk phase of  $Bi_6Te_2O_{15}$  was also synthesized using the conventional solidstate method described above. The impurities were not observed, and the calculated and experimental powder XRD patterns were in agreement (see Supporting Information, Figure S1). The FT-IR spectra of  $Bi_6Te_2O_{15}$  revealed Te–O and Bi–O vibrations between 700 and 400 cm<sup>-1</sup>. The bands occurring between 670 and 570 cm<sup>-1</sup> and 540 and 400 cm<sup>-1</sup> can be assigned to Te–O and Bi–O vibrations, respectively. These assignments of vibrations were consistent with the corresponding bonds for previously reported compounds [34]. The IR spectra and assignments were deposited in the Supporting Information (see Figure S2). The thermal behavior of  $Bi_6Te_2O_{15}$  was also investigated using thermogravimetric analysis (TGA) under a nitrogen atmosphere.  $Bi_6Te_2O_{15}$  was thermally stable up to around 775 °C, and beyond that, the sample decomposed. A TGA diagram for  $Bi_6Te_2O_{15}$  was also deposited in the Supporting Information (see Figure S3). After cooling the heated sample, the final residue products,  $Bi_2TeO_5$  and  $Bi_2O_3$ , were also confirmed via powder XRD (see Supporting Information, Figure S4).

#### 3.3. Local Dipole Moment and Structural Distortion

To determine the contribution of the lone-pair electron to the asymmetric coordination environments of the square pyramidal, the direction and magnitude of the lone-pair polyhedral were quantified and investigated by determining the local dipole moments [35,36] (see Table 3). The method uses a bond-valence approach to calculate the direction and magnitude of a local dipole moment. This approach was also extended to include the polarization of lonepair electrons. With the square pyramidal including the lone-pair electron, the lone-pair electron was given a charge of 2– and was localized 0.98 Å from the Bi<sup>3+</sup> cation [37–39]. Using this methodology, the dipole moments for the Bi(1)O<sub>5</sub>, Bi(2)O<sub>5</sub>, Bi(3)O<sub>5</sub>, and Bi(4)O<sub>5</sub> square pyramidals in which the lone-pair electron (Lp) was included had dipole moments of 9.3, 7.9, 8.8, and 6.8 Debye (D), respectively (see Table 3). In addition, similar to the octahedral for the transition metal oxide, the local dipole moment of the Te(1)O<sub>6</sub> octahedral containing six Te–O bonds also had a dipole moment of 0.5 Debye (D). This shows that the TeO<sub>6</sub> octahedral was slightly distorted, and the deviation of the Te<sup>5+</sup> cation from the center of the octahedral was smaller [40]. The calculation of dipole moments is also described in the Supporting Information (see Table S3).

Two indices, global instability index (GII) and bond strain index (BSI), were also calculated to measure the extent to which a real structure violates its ideal structure using the difference between the real bond valence sum ( $\Sigma S_{ij}$ ) and the theoretical bond valence sum ( $\Sigma S_{ij}$ ) [32,41,42]. This difference indicates the extent of distortion and bond strains in its unit cell. After solving the topological loop equations using the BONDVAL program [43]

(see Supporting Information, Table S4), we calculated theoretical bond valences  $(s_{ij})$  for the six Bi<sup>3+</sup> cations, two Te<sup>6+</sup>cations, and fifteen O<sup>2-</sup> anions from the formula of Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>. The equation  $[\langle (S_{ij} - s_{ij})^2 \rangle]^{1/2}$ , where the symbol  $\langle \rangle$  indicates the average of  $(S_{ij} - s_{ij})^2$  and 42 chemical bonds exist in the topological loop equations, determines the value of the BSI. The calculated value of 0.172 was significantly larger than 0.05, which means that Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub> was structurally strained [41]. Because two Bi(4) cations and two Te cations had relatively larger values for  $(S_{ij} - s_{ij})^2$  in the table containing the BSI and GII calculations, which is depicted in the Supporting Information (see Table S4), it is proposed that the structural strain in Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub> is attributed to the Bi(4)–O(2), Bi(4)–O(5), and Te(1)–O(1) bonds. For GII, the equation  $[(\Sigma S_{ij} - \Sigma s_{ij})^2/N]^{1/2}$ , where N is the number of atoms in the formula, was used. Since 23 atoms exist in the formula of Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>, N corresponded to 23. The calculated GII also was 0.279, which is larger than 0.20, meaning that the structure of Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub> was unstable and distorted in the unit cell [32,44].

#### 3.4. Structural Optimization

The atomic coordinates in the unit cell of a single crystal structure of  $Bi_6Te_2O_{15}$  were used to determine the theoretical equilibrium geometry and the minimized total energy by varying the *c/a* ratio and the volume in the WIEN2k package [23]. After running the volume optimization under three different exchange-correlation potentials, the estimated equilibrium lattice parameters ( $a_0$ ,  $b_0$ , and  $c_0$ ), volume, bulk modulus ( $B_0$ ), derivative of the bulk modulus ( $B_0'$ ), and ground state total energy ( $E_0$ ) were obtained and tabulated in Table 4. The calculated total energies were also fitted with the Birch–Murnaghan equation of state (EOS) to obtain the theoretical lattice parameters [45–47]. The total energy as a function of the volume for  $Bi_6Te_2O_{15}$  is shown in the Supporting Information (see Figure S5). From the volume optimization calculations, the theoretical structure with the lowest optimal energy was thought to be the ground state structure, and this structure was selected for further calculations.

**Table 4.** Estimated equilibrium lattice parameters  $(a_o, b_o, c_o)$ , volume, bulk modulus  $(B_o)$ , derivative of bulk modulus  $(B_o')$ , and ground state energy  $(E_o)$ .

|                          | <sup>1</sup> GGA-PBE | <sup>2</sup> GGA-PBESol | <sup>3</sup> GGA-WC | Single Crystal |
|--------------------------|----------------------|-------------------------|---------------------|----------------|
| a <sub>o</sub> (Å)       | 10.791               | 10.618                  | 10.688              | 10.583         |
| b <sub>o</sub> (Å)       | 23.139               | 22.769                  | 22.919              | 22.694         |
| c <sub>o</sub> (Å)       | 5.490                | 5.402                   | 5.438               | 5.384          |
| Volume (Å <sup>3</sup> ) | 4895.046             | 4664.148                | 4756.507            | 4617.674       |
| B <sub>o</sub> (GPa)     | 145.337              | 159.234                 | 154.845             |                |
| B <sub>o</sub> ′(Gpa)    | 4.101                | 5.762                   | 4.170               |                |
| E <sub>o</sub> (Ry)      | -1,153,695.25        | -1,153,345.57           | -1,153,604.27       |                |

<sup>1</sup> GGA-PBE: generalized gradient approximation using Perdew–Burke–Ernzerhof functional. <sup>2</sup> GGA-PBESol: generalized gradient approximation using Perdew–Burke–Ernzerhof functional for solids. <sup>3</sup> GGA-WC: generalized gradient approximation using Wu–Cohen functional.

#### 3.5. Electronic Band Structure and Density of State

The band structure of  $Bi_6Te_2O_{15}$  was calculated with the volume-optimized structures along highly symmetrical points of the first Brillouin zone,  $\Gamma$ -X-S-Y- $\Gamma$ -Z-U-R-T-Z, using different exchange-correlation potentials [48,49] (see Figure 3 and Table 5). To get the band-gap energy to match with the experimental one, the modified potential (TB-mBJ) was also used [29,50,51]. However, the calculated band gap was slightly higher than the experimental result by 0.07 eV (see Table 5). To further explain the nature of the electronic structure, the total density of state (TDOS) and partial density of state (PDOS) were also calculated with the GGA-PBE and the TB-mBJ potential. Figure 4 shows the plots of the TDOS and PDOS of  $Bi_6Te_2O_{15}$  with the Fermi level (EF), as illustrated by the vertical dot line at 0 eV. The lowest part of the valence band region (from -10.3 to -5.5 eV) was formed mainly by Bi-, Te-, and O-PDOS and attributed to the electrons occupying the Bi-6s, Te-5s, and O-2s orbitals, while the middle part (from -5.5 to -4.2 eV) was created by the electrons occupying the Bi-6p, Te-6p, and O-2p orbitals. In addition, the O-PDOS caused by the electrons occupying the O-2p orbitals was perceived as the main contributor to the highest part of the valence band region (from -4.2 to 0 eV). The conduction band (from 3.3 to 6.8 eV) was attributed to the empty electron orbitals of Bi-6p, Te-5p, and O-2p.

Table 5. Calculated and experimental band-gap energy of Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>.

| XC           | Band-Gap Energy (eV) |  |  |
|--------------|----------------------|--|--|
| GGA-PBE      | 2.53                 |  |  |
| GGA-WC       | 2.78                 |  |  |
| GGA-PBESOL   | 2.54                 |  |  |
| TB-mBJ       | 3.36                 |  |  |
| Experimental | 3.29                 |  |  |

XC represents the exchange-correlation functional (potential). The band-gap energies were calculated for the four functionals. It is also well known that the band-gap energies calculated using local density approximation (LDA) and generalized gradient approximation (GGA) strongly underestimate the experimental band-gap [52]. To get a good estimate of the band-gap energies, the modified version of the original Becke–Johnson exchange potential with the Tran–Blaha parameterization (TB-mBJ) was also used [29].



**Figure 3.** Band structure of  $Bi_6Te_2O_{15}$ . The calculated band gap of  $Bi_6Te_2O_{15}$  was obtained by analyzing the energy difference from the maximum of valence band at point S to the minimum of conduction band at point X. The band gap shows 3.36 eV within TB-mBJ potential.



**Figure 4.** Total density of state (TDOS) and partial density of state (PDOS) of Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>. Depicted as a vertical dot line, E<sub>F</sub> represents the Fermi level. TDOS and PDOS were also calculated using the TB-mBJ potential. TDOS, Bi-PDOS, Te-PDOS, and O-PDOS curves were drawn with black, red, green, and blue lines, respectively.

# 3.6. Optical Properties

The interaction of incident light with Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub> was investigated using the complex dielectric function  $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ , where the real part  $\varepsilon_1(\omega)$  defines the energy dissipation and wave damping and the imaginary part  $\varepsilon_2(\omega)$  is related to the polarization and the capacity of a material to store energy [53]. Regarding the orthorhombic symmetry of Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>, the three polarization directions showed the following relation:  $\varepsilon^{xx} \neq \varepsilon^{yy} \neq \varepsilon^{zz}$ . The imaginary part  $\varepsilon_2(\omega)$  was calculated from the electronic band structure according to the photon energy along three polarization directions:  $\varepsilon^{xx}$ ,  $\varepsilon^{yy}$ , and  $\varepsilon^{zz}$  [54–56]. The real part  $\varepsilon_1(\omega)$  was also computed from  $\varepsilon_2(\omega)$  using the Kramers–Kronig relation. As shown in Figure 5, the calculated static dielectric function,  $\varepsilon_1(0)$ , is 4.06, 4.24, and 4.13 along the three polarization directions. The real part,  $\varepsilon_1(\omega)$ , also increases with increasing photon energy until it reaches its maximum value near 3.3 eV. The imaginary part,  $\varepsilon_2(\omega)$ , remains at zero below the calculated band gap. It starts to increase sharply over the band gap at -3.3 eV, and the maximum values of  $\varepsilon_2^{xx}$  (near 6.3 eV),  $\varepsilon_2^{yy}$  (near 6.7 eV), and  $\varepsilon_2^{zz}$  (near 6.8 eV) are 6.3, 6.8, and 6.1, respectively, as shown in Figure 5.

Both the real and imaginary parts of the dielectric function allow the calculation of other optical functions such as refractive index n ( $\omega$ ), optical absorption coefficient I( $\omega$ ), reflectivity R( $\omega$ ), the real part of optical conductivity  $\sigma(\omega)$ , and the energy-loss function L( $\omega$ ) [55,57]. As depicted in Figure 5, the static refraction index n(0) of Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub> is ~2.1 for three components. The maximum peaks of n<sub>xx</sub>( $\omega$ ), n<sub>yy</sub>( $\omega$ ), and n<sub>zz</sub>( $\omega$ ) are 2.5, 2.7, and 2.6, respectively, near 4 eV of photon energy. Given that n( $\omega$ )  $\rangle$  1 for a given type of matter, the speed of the photons is reduced when they enter the matter because the photons interact with electrons. Thus, the higher electronic density of a material also increases its n( $\omega$ ). The calculated absorption coefficient I( $\omega$ ) is also shown in Figure 5. The threshold point at which matter begins to absorb electromagnetic radiation is 3.16, 3.30, and 3.22 eV, according to the three polarization directions for the structure of Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>. The maximum absorptions for I<sub>xx</sub>, I<sub>yy</sub>, and I<sub>zz</sub> are also diverse at different photon energies. Other optical properties, such as reflectivity R( $\omega$ ), the real part of optical conductivity  $\sigma(\omega)$ , and the energy-loss function L( $\omega$ ) described above, are summarized in Table 6, and their spectra are also depicted in the Supporting Information (see Figure S6).



**Figure 5.** Calculated real part ( $\varepsilon 1(\omega)$ ) and imaginary part ( $\varepsilon 2(\omega)$ ) of the dielectric function, refractive index n ( $\omega$ ), and optical absorption coefficient I ( $\omega$ ) of Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>.

**Table 6.** Summary of the calculated real part ( $\varepsilon_1(\omega)$ ) and imaginary part ( $\varepsilon_2(\omega)$ ) of the dielectric function, refractive index n (0), optical absorption coefficient I( $\omega$ ), reflectivity R( $\omega$ ), the real part of optical conductivity  $\sigma(\omega)$ , and the energy-loss function L( $\omega$ ) within the TB-mBJ potential for Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>.

| Components | ε <sub>1</sub> (0)<br>(eV) | n(0) | Ι(ω)<br>(eV) | R(0) | σ(ω)<br>(Ω cm) <sup>-1</sup> | L(ω)<br>(eV) |
|------------|----------------------------|------|--------------|------|------------------------------|--------------|
| xx         | 4.06                       | 2.05 | 3.16         | 0.10 | 5763                         | 3.22         |
| уу         | 4.24                       | 2.08 | 3.30         | 0.12 | 6247                         | 3.24         |
| ZZ         | 4.13                       | 2.06 | 3.22         | 0.11 | 6202                         | 3.23         |

# 4. Conclusions

We reported that the structure of Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub> was precisely determined using the singlecrystal diffraction method, and it had a three-dimensional network structure as an orthorhombic space group (No. 62, *Pnma*) with a =10.583 Å, b = 22.694(3) Å, c = 5.3843(6) Å,  $\alpha = \beta = \gamma = 90^{\circ}$ , V = 1293.2(3) Å<sup>3</sup>, and Z = 4. It was also composed of six  $[BiO_5]^{7-}$  and two [TeO<sub>6</sub>]<sup>6-</sup> moieties. Each Bi<sup>3+</sup> cation exhibited a five-coordinated square pyramidal structure under asymmetric environments, and each Te<sup>6+</sup> cation had an octahedral structure. Due to the asymmetric and distorted environments of the Bi<sup>3+</sup> and Te<sup>6+</sup> cations, the dipole moments of the square pyramidal of Bi<sup>3+</sup>, including the lone-pair electron (Lp), ranged from 6.8 to 9.3 Debye (D), and the  $Te^{6+}$  cation had a dipole moment of approximately 0.5 D. Additionally, the calculated values of the global instability index (GII) (0.172 a.u.) and bond strain index (BSI) (0.279 a.u.) indicated that the structure of Bi6Te2O15 was strained and distorted in the unit cell, which was attributable to the distortion of the square pyramidal of the  $[BiO_5]^{7-}$  moiety and the octahedral of the  $[TeO_6]^{6-}$  moiety. Finally, using the WIEN2k code (FP-LAPW), the electronic and optical properties of Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub> were investigated. The optimized structural parameters agreed with the experimental ones. The modified version of the original Becke–Johnson exchange potential (TB-mBJ) yielded a match between the calculated and experimental band-gap energies from the bulk phase of  $Bi_6Te_2O_{15}$ . Regarding optical properties, the refraction index (n(w)), the optical absorption coefficient  $(I(\omega))$ , reflectivity (R( $\omega$ )), the real part of the optical conductivity extinction function ( $\sigma(\omega)$ ), and

the energy loss function  $(L(\omega))$  were calculated from the real and imaginary parts of the dielectric function.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/cryst14010023/s1. Table S1: Atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>. Table S2: Anisotropic displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) for Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>. Table S3: Local dipole moment calculation. Table S4: Table of the calculation for BSI (Bond Stability Index) and GII (Global Instability Index). Figure S1: Experimental and calculated X-ray powder diffraction patterns for Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>. Figure S2: FT-IR spectra of Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>. Figure S3: Thermogravimetric analysis (TGA) diagram for Bi<sub>6</sub>Te<sub>2</sub>O<sub>15</sub>. Figure S4: PXRD pattern for final residuals after TGA experiments. Figure S5: Dependence of total energy versus the unit cell volume by selected potential. Figure S6: Other optical properties.

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**Data Availability Statement:** The corresponding crystallographic information file (CIF) has been deposited with the Cambridge Crystallographic Centre (CCDC) and can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk) with the following depository number: 2313042. The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy.

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