Ab initio calculations and crystal structure simulations for mixed layer compounds from the tetradymite series

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ABSTRACT

Density functional theory (DFT) is used to obtain structural information of seven members of the tetradymite homologous series: Bi₂Te₃ (tellurobismuthite), BiTe (tsumoite), Bi₄Te₃ (pilsenite), Bi₅Te₃, Bi₆Te, Bi₇Te₃ (hedleyite) and Bi₈Te₃. We use the formula S(Bi₂kTe₃)•L[Bi₂(k+1)Te₃] as a working model (k=1-4) where S and L are short and long modules in the structures. The relaxed structures show an increase in the a parameter and decrease in the interlayer distance (d_{sub}) from Bi₂Te₃ (2.029 Å) to Bi₈Te₃ (1.975 Å). DFT-derived formation energy for each phase indicates they are all thermodynamically stable. Scanning transmission electron microscopy (STEM) simulations for each of the relaxed structures show an excellent match with atom models. Simulated electron diffractions and reflection modulation along c* are concordant with published data, where they exist, and with the theory underpinning mixed-layer compounds. Two modulation vectors, q=γ • c_{sub}^{*} (γ =1.800-1.640) and q_{F}=γ_{F} • d_{sub}^{*} (γ_{F} =0.200-0.091),
describe the distribution of reflections and their intensity variation along \(d_{\text{sub}}^* = 1/d_{\text{sub}}\). The \(\gamma\) parameter reinforces the concept of \(\text{Bi}_{2k}\text{Te}_3\) and \(\text{Bi}_{2(k+1)}\text{Te}_3\) blocks in the double module structures and \(\gamma\) relates to \(d_{\text{sub}}\) variation. Our model describing the relationship between \(\gamma\) and \(d_{\text{sub}}\) allows prediction of \(d_{\text{sub}}\) beyond the compositional range considered in this study, showing that phases with \(k>5\) have \(d_{\text{sub}}\) values within the analytical range of interlayer distance in bismuth. This in turn allows us to constrain the tetradyminite homologous series between \(\gamma\) values of 1.800 (\(\text{Bi}_2\text{Te}_3\)) and 1.588 (\(\text{Bi}_{14}\text{Te}_3\)). Phase compositions with higher \(\text{Bi}/\text{Te}\) should be considered as disordered alloys of bismuth. These results have implications for mineral systematics and classification as they underpin predictive models for all intermediate structures in the group and can be equally applied to other mixed-layer series. Our structural models will also assist in understanding variation in the thermoelectric and topological insulating properties of new compounds in the broader tetradyminite group and can support experimental work targeting a refined phase diagram for the system Bi-Te.

**Keywords:** tetradyminite series, mixed layer compounds, crystal structure, Density Functional Theory, STEM simulations

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**INTRODUCTION**

The tetradyminite series [generally \(\text{Bi}_x(\text{Te},\text{Se},\text{S})_y\); where \(\text{Te}, \text{Se}, \text{S}\) are chalcogens] comprises phases with crystal structures derived from the tetradyminite archetype [\(\text{Bi}_2\text{Te}_2\text{S}\), a 5-atom-thick layer, ‘mod5’] (Cook et al. 2007, and references therein). Ciobanu et al. (2009) considers the tetradyminite series a “metal- or Bi-rich” series within a larger group of phases derived from the same tetradyminite archetype. For the sake of simplicity and the purpose of this contribution, we chose Te as the only chalcogen. There are two models describing crystal structure modularity within the Bi-rich series (or tetradyminite series *sensu stricto*). The first, proposed by Imamov and Semiletov (1971), considers the combination of \(\text{Bi}_2\) and \(\text{Bi}_2\text{Te}_3\) blocks (hereafter referred to as the “Mod2 and 5 model”), later formalised as \(n\text{Bi}_2\bullet m\text{Bi}_2\text{Te}_3\) by
Shelimova et al. (2000). The second model was introduced by Amelinckx et al. (1989) and Frangis et al. (1990) as 5- and 7-layer lamellae based upon the electron diffraction properties indicating one dimensional, interface modulated mixed layer compounds. This was subsequently formalised by Ciobanu et al. (2009) for modules of incremental thickness, as an accretional homologous series with formula: 

\[ S(Bi_{2k}Te_3) \cdot L[Bi_{2(k+1)}Te_3] \]

where S and L are the number of short and long modules, respectively. This model allows for definition of building modules with incremental thickness extending from module 5 to 7, 9, 11, and so on. These modules have a fixed number of chalcogen atoms and are incrementally enriched in Bi, i.e., \( Bi_4Te_3 \) (7), \( Bi_6Te_3 \) (9), \( Bi_8Te_3 \) (11), relative to the 5-atom archetype, \( Bi_2Te_3 \), explaining why this is referred to as the Bi-rich series.

Transmission electron microscopy (TEM) study of phases in the compositional range \( Bi_2Te_3 - Bi_8Te_3 \) are complemented by high angle annular dark field (HAADF) scanning TEM (STEM) studies of \( Bi_8Te_3 \) and \( Bi_4(Te,Se,S)_3 \) that show the correlation between composition and structural modulation (Ciobanu et al. 2009, 2021; Cook et al. 2021). Diffraction patterns show that all phases are N-fold superstructures (N = layers in the stacking sequence) of a rhombohedral subcell with \( c/3 = d_0 \approx 2.000 \) Å. The structures are characterised by two modulation vectors showing monotonic decrease in d-subcell (\( d_{sub} \)) with increasing Bi composition.

Several named minerals and other unnamed phases in the tetradymite group are reported from natural assemblages, particularly from gold deposits (Cook et al. 2007; 2009; Ciobanu et al. 2010) yet remarkably few have been subject to crystal structure determination or crystallographic information data file (cif). Compounds from this series are intensely studied for their thermoelectric and/or topological insulating properties (Bos et al., 2007; 2012; Goldsmid, 2014). To better understand the series, we perform \textit{ab initio} calculations and structure simulations for phases with single and double modules across the compositional range \( Bi_2Te_3 \) to \( Bi_8Te_3 \) (k=1-4). We use simulations of images and electron diffraction patterns to assess the validity of the accretional model versus the “Mod 2 and 5” model and apply the
formation energies to evaluate phase stability of the seven phases. The determined crystal structure parameters are used to develop a model for the series that involves variation in $d_{sub}$ relative to modulation.

**Crystal structure data and selection of input files**

Table 1 indicates the phases under consideration and published information on their crystal structures. The symmetry and the number of layers in each structure can be derived from the explicit chemical formula given by Ciobanu et al. (2009). In the present work, four structures with $S=1$, $L=0$, and $k=1, 2, 3, 4$ (Bi$_2$Te$_3$, Bi$_4$Te$_3$; Bi$_6$Te$_3$ and Bi$_8$Te$_3$), and three structures with $S=1$, $L=1$, and $k=1, 2, 3$ (Bi$_6$Te$_6$; Bi$_{10}$Te$_6$ and Bi$_{14}$Te$_6$) are included. These correspond to single and double module structures: (i) 5, 7, 9 and 11; and (ii) combinations of these with notation 5.7, 7.9 and 9.11, respectively. The number of layers in the asymmetric unit cell is $N_1 = S(2k+3)+L(2k+5)$. If the number of atoms in the explicit formula is divisible by 3, as in the case of Bi$_6$Te$_6$ (BiTe, tsumoite) and Bi$_6$Te$_3$ (unnamed Bi$_2$Te), the symmetry changes from $R\bar{3}m$ (hereafter called R) to $P\bar{3}m1$ (hereafter called H). The total number of layers in the structure is $N = N_1 \times 3$ for R phases and $N = N_1$ for H phases. Knowing that the distance between two consecutive layers (Imamov and Semiletov 1971), the ideal $d_0$, approximates to 2.000 Å, we can calculate the $c$ parameter using the formula: $c = N_1 \times 2.000$ Å.

We selected 12 published crystal structures for the phases targeted here that have been documented from x-ray powder or single crystal diffraction studies, and two from (S)TEM data (Table 2). Published data are unevenly distributed among the seven phases. For example, there are five studies of Bi$_2$Te$_3$ (tellurobismuthite) but no x-ray diffraction studies for either Bi$_5$Te$_3$ or Bi$_8$Te$_3$. Most of the published studies were carried out on synthetic material and only a single study was performed on natural tellurobismuthite (Nakajima 1962), highlighting the difficulty in finding natural material suitable for crystal structure determination of these phases. We observe that $a$ increases slightly from Bi$_2$Te$_3$ to Bi$_8$Te$_3$ whereas the $c$ parameter varies widely as it is dependent upon $N$ and symmetry. However, using
the $c$ parameter we can calculate the variation in the interlayer distance defining the subcell from which
the layers are derived ($d_{\text{sub}}$). This interval, calculated from analytical measurements, shows a decrease
from $\sim 2.000 \text{ Å}$ to $1.910 \text{ Å}$ across the Bi$_2$Te$_3$-Bi$_8$Te$_3$ range, with some fluctuations (Table 1).

**METHODS**

**Ab initio calculations**

To explore the correlation between crystal structural modularity and chemical variation in a series
of mixed-layer compounds, we have employed *ab initio* total energy calculations and structure relaxation
using density functional theory (DFT) (Hohenberg and Kohn 1964; Kohn and Sham 1965). Input data
for structure optimisation comprised crystallographic information files (cif) from the literature (Table 1).
An exception was the Bi$_3$Te$_3$ phase, for which a predicted structure was obtained using CrystalMaker
(CM) (Palmer 2015) and Findsym software (Stokes and Hatch 2005).

The DFT calculations were performed with the Vienna *ab initio* simulation package (VASP) (Kresse
and Furthmüller 1996; Kresse and Joubert 1999), using the projector augmented wave (PAW) method
(Blöchl 1994). A plane wave basis set with energy cut-off of 500 eV was employed for all calculations.

The electronic exchange and correlation energy were estimated by the generalized gradient
approximation (GGA) with Perdew, Burke and Ernzerhof (PBE) parameters (Perdew et al. 1996). We
included van der Waals interactions between atoms of the same type (Te-Te and Bi-Bi) using the method
of Grimme et al. (2010), which adds a small dispersion energy correction to the total energy in the system.

This is also shown in a recent publication in which the electronic structure of Bi$_4$Te$_3$ phase is predicted
to be a semimetal (Nabok et al., 2022).

The Brillouin zone (BZ) was sampled at $\Gamma$-centred dense k-point grids based on the Monkhorst-Pack
scheme (Pack and Monkhorst 1977). The set of k-points was considered dependent upon the cell
parameters and symmetry of each structure (Table 1) to maximize the total energy accuracy while aiming
to minimize computational cost.

Volumes from each input file were considered as \( V_i \) for each structure. The lattice parameters \((a, c)\)
in each case were subsequently scaled in the range 95 to 101\% to obtain a series of volume values. For
consistency, the volume relaxation was performed at constant energy cut-off. Total energy calculations
and structural optimization for the atomic positions and cell parameters \((c, a)\) were carried out for
individual volumes with energy tolerance <10\(^{-5}\) eV between two ionic steps and force less than 0.02 eV/Å
per atom. After volume relaxation, a static calculation is performed to obtain the total energy at each
volume.

To obtain the equilibrium volume and ground state energy we used the Murnaghan (1944) equation
of state (EOS) as being most appropriate for compounds with trigonal symmetry (e.g. the same EOS used
by other studies of Bi-tellurides; Nakayama et al. 2009). The Birch-Murnaghan (1947) EOS was
introduced for phases with cubic symmetry. Equilibrium volume and ground state energy were found by
fitting the Murnaghan (Murnaghan 1944) equation of state (EOS):

\[
E(V) = E_0 + \frac{K_0}{K_0'} \left( \frac{V_0}{V} \right)^{K_0'} - \frac{K_0 V_0}{K_0' K_0'} - \frac{1}{K_0'} \left( \frac{V_0}{V} \right) \left( \frac{V_0}{V} \right)^{K_0'},
\]

where \(K_0\) and \(K_0'\) are the bulk modulus and its pressure derivative, \(V_0\) represents the equilibrium volume
and \(E_0\) is the reference energy. The calculated parameters after EOS fitting are given in Table 3. The
optimized lattice parameters for each structure were obtained by performing relaxation at the
corresponding equilibrium volume.

**Crystal structure models**

All the relaxed crystal structures were modelled and assessed using CM and Findsym was used to
generate the cif data files. Electron diffractions and STEM image simulation were performed using
HREM STEM software for structure visualization. A computer subroutine was written in Python for intensity calculations and simulations of reflections.

RESULTS

Crystal structure relaxation

We have selected six of the structures given in Table 1 as a basis for crystallographic file input (cif) in the DFT calculations. For Bi$_5$Te$_3$ we use experimental parameters given by Ciobanu et al. (2009) and obtain atom coordination by applying $1/N_1 = 1/16$ derived from the 7.9 modular structure with equal intervals along the $c$ direction for the $z$ coordinates.

To constrain the seven crystal structures, we determined the equilibrium volume for each phase (Figure 1) by fitting the total energy volume curves using equation (1), with the minimum well constrained. The equilibrium volumes and EOS parameters are listed and compared with published data in Table 3.

The fitted volumes are within 2% of the reference structures, except for Bi$_5$Te$_3$ for which the difference is 9%. The main reason is that the parameters for this were obtained from S/TEM data which carries a higher uncertainty. Our calculated bulk moduli ($K_0$) range from 33-40 GPa, concordant with studies of elastic properties using ab initio calculations of bismuth-based alloys (Woodcox et al. 2019). This is seen from a comparison for phases with the same composition, e.g., 40 GPa vs. 41 GPa (Woodcox et al. 2019) for BiTe, as well as from the small variation of $K_0$ across the compositional range.

After the fitting step we calculated the structure parameters at $V_0$ (Table 4), with differences of ±1% for $a$ and $c$ relative to most reference structures, although differences were higher (a few %) for Bi$_5$Te$_3$ and Bi$_8$Te$_3$. Comparable discrepancies between DFT calculations and input files for a crystal structure are reported in other studies, e.g., for Bi$_2$Te$_3$ (Cheng and Ren 2011).
We also note that after relaxation, the $a$ parameter is expanded whereas $c$ contracts relative to the input data (Tables 1 and 4). The comparison of the $a$ parameter with published data (Figure 2a) shows that relaxed structures follow a smooth trend, increasing with Te content across the range $\text{Bi}_2\text{Te}_3$ to $\text{Bi}_8\text{Te}_3$, with values systematically larger – by a small amount – than published measurements (Table 1). An appreciation of published DFT data (Cheng and Ren, 2011) relative to analytical data is shown for tellurobismuthite ($\text{Bi}_2\text{Te}_3$), the most intensively studied of the seven structures. Our data plots close to the mean of published DFT data; the TEM-based lattice parameter $a$ is smaller than both analytical and DFT curves (Figure 2a).

The calculated $d_{\text{sub}}$ parameter from DFT data (range 1.975 to 2.029 Å) also follow a smooth trend, although with an inverse trend compared to $a$, i.e., decreasing with Bi content (Figure 2b). This curve shows a steep downwards slope from tellurobismuthite ($\text{Bi}_2\text{Te}_3$) to tsumoite ($\text{BiTe}$), followed by a gentle decreasing trend intersecting the $d_{\text{sub}}$ axis at $\sim 1.960$ Å for a 0 atom.% Te composition (native bismuth). The analytical data is noisier, but generally consistent (Figure 2c). The largest difference occurs for $\text{Bi}_2\text{Te}$ between our DFT results and the XRD data by Bos et al. (2012) with 0.012 Å difference (1.2 %), if we ignore the TEM data for $\text{Bi}_8\text{Te}_3$, which differs from the present calculated range of $d_{\text{sub}}$ by 0.050 Å (Ciobanu et al. 2021). A good fit is obtained between DFT and the $d_{\text{sub}}$ of $\text{Bi}_2\text{Te}$ given by Zavylov et al. (1976). Excellent agreement is obtained for tsumoite ($\text{BiTe}$) and tellurobismuthite ($\text{Bi}_2\text{Te}_3$) with data from Yamana et al. (1979) and Atuchin et al. (2012), respectively.

To assess the differences between the DFT and experimental data we also undertook the PBEsol functional method (Perdew et al., 2008). The results show that the for the endmember $\text{Bi}_2\text{Te}_3$, its interlayer distance $d_{\text{sub}}$ is underestimated relative to experimental data (i.e., 3.1%) although it reduces the difference to $a$ parameter (i.e., 0.5%). In contrast, the chosen PBE functional method gives a better fit with the analytical data for $d_{\text{sub}}$ (i.e., 0.2%, and by inference for the $c$ parameter), which is most important for the topic addressed here.
Models and simulations for the relaxed structures

The relaxed structures were plotted as models on the [11\(\bar{2}0\)] zone axis to show the incremental width of the 2k+3 modules and the bond topology across the range Bi\(_2\)Te\(_3\)-Bi\(_8\)Te\(_3\) (Figures 3 and 4). Crystal structure models for any phase in the group can be obtained from generic atomic coordinate calculations following the same approach applied here for phases without initial cif files (i.e., Bi\(_5\)Te\(_3\) and hedleyite). The bond topology in such models would be orthogonal whereas the optimized structures, either obtained from measurements or DFT relaxation will show slight distortions (Figures 3 and 4; left column). The structural modules are schematically shown using the accretional formalism \([S(Bi_{2k}Te_3)\cdot L(Bi_{2(k+1)}Te_3)]\), but these are not necessarily constrained relative to models using the nBi\(_2\)•mBi\(_2\)Te\(_3\) formula. This is particularly apparent for phases such as BiTe tsumoite where two Bi\(_2\)Te modules (m=2) are linked by one Bi\(_2\) block (n=1) (Figure 4, upper panel). The atom fill models are shown for purposes of comparison with the STEM simulations in Section 4.4 (Figures 3 and 4; right column).

Bond analysis

Bond distances for atoms in the asymmetric unit cells are shown in Figures 5 and 6. A comparison of the minimum and maximum bond lengths for each structure is given in Figure 7. All seven structures contain Bi-Te bonds but only two have Te-Te bonds and only six have Bi-Bi bonds. The Te-Te bonds are longer than all other bonds and virtually the same for tellurobismuthite (3.694 Å) and tsumoite (3.692 Å) (Figure 7b). The relative proportion of Bi-Bi versus Bi-Te bonds increases from 1/6 in pilsenite to 5/6 in Bi\(_8\)Te\(_3\) when considering the neighbouring bonds (Figure 5). The double module structures all fall within this range, except for tsumoite which has a Bi-Bi / Bi-Te ratio of 1/10 (Figure 6).

The minimum for Bi-Te bond lengths increases by ~0.027 Å, from tellurobismuthite (3.080 Å) to Bi\(_8\)Te\(_3\) (3.107 Å), but this is stepwise, with the largest difference between tsumoite and pilsenite and no discernible difference between Bi\(_2\)Te and hedleyite (Figure 7a). The maximum Bi-Te bond lengths increase sharply between tellurobismuthite and pilsenite (~0.303 Å) but decrease gently towards Bi\(_8\)Te\(_3\).
(Figure 7b). The minimum Bi-Bi bond lengths increase with Bi content, giving a relatively smooth curve between tsumoite and Bi$_8$Te$_3$ with a difference of $\sim$0.013 Å (Figure 7c). The maximum Te-Te bond lengths are significantly longer than the Bi-Bi bonds (~0.159 Å; Figure 7d). In the four phases with more than one Bi-Bi bond, the maximum Bi-Bi length tend to decrease with Bi content from Bi$_5$Te$_3$ to Bi$_8$Te$_3$, but not continuously. Overall, minimum bond lengths show a consistent variation across the range Bi$_2$Te$_3$-Bi$_8$Te$_3$, whereas the maximum is complicated by the presence of phases with Te-Te bonds (Figure 7). Bond lengths are important for understanding the variation of interlayer distances ($d_{sub}$), and the analysis above indicates a strong split between phases that contain Te-Te bonds (larger $d_{sub}$ values) and those that do not.

**Simulation of STEM images and electron diffractions**

The relaxed structures are shown as simulations of STEM images and electron diffraction (ED) patterns on the [1100] zone axis in Figures 8 and 9. The images show a very good agreement with the atom fill models on the same zone axis shown in Figures 3 and 4. The $d_{sub}$ interval is also shown as two simulations, one cropped from the ED patterns (upper strips) and a second one computed using the displacement introduced by the fractional shift method of Amelinckx et al. (1989) and Frangis et al. (1990) (lower strips) (see Ciobanu et al. 2009 for more details). The $d_{sub}$ interval is important for defining the modulation underpinning the increase in width of the modules. In this interval the number of reflections ($n_r$) corresponds to $N_1$-1, equally distributed along $d_{sub}^*$ interval. The length of the asymmetric unit cell ($d_{N_1}$) along c corresponds to the layer stacks defining each unit cell. This is also marked as the smallest interval, $d_{N_1}^*$ between two adjacent reflections along $d_{sub}^*$. The $d_{N_1}$ interval for the structures with double modules (S, L=1) approximates to the sum of S and L lengths.

All ED patterns show the two brightest reflections about the middle of $d_{sub}^*$ with monotonic decrease of the interval between them as the Bi concentration increases. Two modulation vectors are shown for
each phase. The $\mathbf{q} = \gamma \cdot \mathbf{c}_{sub}^*$ vector defined by Lind and Lidin (2003) is based on displacive modulation between chalcogen (Te, Se, S) and Bi atoms, where $q$ is the homoatomic interval. The $\mathbf{q}$ modulation is depicted up to third-order reflections along $c^*$ (ED patterns in Figures 8 and 9). The $\gamma$ values (1.800-1.640 for the range Bi$_2$Te$_3$-Bi$_8$Te$_3$) are calculated as $3\cdot\left[(N_1+1)/2\right]/N_1$ for single modules (Figure 8) and $3\cdot\left[(N_1+2)/2\right]/N_1$ for double modules (Figure 9). The $\gamma$ values correlate with the chemical formula by the relation $\gamma=3[S(k+2)+L(k+3)]/N_1$. The same $\gamma$ range was shown by Ciobanu et al (2009) as selected area electron diffraction (SAED), and accompanying TEM images, for natural phases where an ideal $d_{sub} \sim 2.000$ Å was assumed. The relaxed structures presented here show excellent agreement with those SAEDs. Here, however, the STEM image simulations complement the ED patterns. Such simulations, reproducing the atom models, efficiently describe the nature of phases from the tetradymite group documented in prior STEM studies, e.g., Medlin et al. 2014 for tellurobismuthite, Ciobanu et al. (2021) for Bi$_8$Te$_3$, and Cook et al., 2001 for Bi$_4$(Te,S,Se)$_3$ phases.

The second modulation vector $q_F = \gamma_F \cdot d_{sub}^*$ and $q_F = i/N_1 \cdot d_{sub}^* = i \cdot d_{N_1}^*$ ($\gamma_F = i/N_1; i = S + L$), introduced by Frangis et al (1990), relates changes in module size and their respective number to displacements in the basic substructure. This is particularly instructive for depicting the correlation between the building modules (S, L) and electron diffractions patterns. We show that the interval defined by the two brightest reflections about the middle of $d_{sub}^*$ can be divided into two for all the double module structures (Figure 9). The intensity variation along $d_{sub}^*$ is simulated using the fractional shift method following the adapted $\mathbf{q}_F$ model to include the homology for S, L modules related by $k$ given in Ciobanu et al. (2009). The displacements are quantifiable by fractional shifts between reflections in the derived and basic structures (e.g., module ‘7’ derived from module ‘5’, module ‘9’ derived from module ‘7’, etc.). The adapted model stipulates that the distance between the two brightest reflections, about the middle of $d_{sub}^*$, equals $i \cdot d_{N}^*$ only when the shift at this position is minimal (equal to $1/N_b$; $N_b=$layers in the basic structure).
A correlation between electron diffractions and chemical modules for a series group of phases is typical of mixed layer compounds (Amelinckx et al. 1989). If we use the model with blocks of constant width, as in the “Mod2 and 5” model of Imamov and Semiletov (1971) and Shelimova et al. (2000), the number of component modules cannot be correlated with the modulation along $d_{sub}^*$. For example, tsumoite would have $n=1$ and $m=2$, requiring three distinct modules instead of two (the ‘5’ and ‘7’ modules considered here).

**DISCUSSION**

**Phase stability**

An evaluation of phase stability for each of the seven phases uses formation energy relative to chemical composition. The stability of related compounds can be assessed by the convex hull method of Gibbs (1973), with recent DFT applications to complex metallic compounds (Ma et al. 2017). The phase stability is assessed by the distance between calculated formation energy $\Delta E_f$ and the energy of the convex hull $E_{hull}$:

\[
\Delta E_{distance} = E_{hull} - \Delta E_f, \quad (2)
\]

and those compounds plotting above the hull are considered unstable. We employ the model of Woodcox et al. (2019) that stipulates a simple relationship between $\Delta E_f$, the energy of phase $E_{\text{phase}}$ and the energy of composing atoms, in this case the energies of $E_{Bi}$ and $E_{Te}$ using the equation (3):

\[
\Delta E_f = \frac{E_{\text{phase}} - pE_{Bi} - qE_{Te}}{p+q}, \quad (3)
\]

where $p$ or $q$ represent the number of Bi and Te atoms in the unit cell (phase), respectively (Table 2). Calculated $\Delta E_f$ for the seven relaxed structures (Table 5) are plotted relative to atom.% Te in Figure 10a. The convex hull is defined by the lines between endmembers and the compound with minimum $\Delta E_f$, in our case, bismuth, tellurium, and $\text{Bi}_2\text{Te}_3$ (tellurobismuthite), respectively. The calculated $\Delta E_f$ values are negative for all phases and show a quasi-linear relationship along the $\text{Bi}_2\text{Te}_3$-Bi branch of the hull.
The alternative alloy approach to Bi-Te phases (Woodcox et al. 2019) gives another hull that plots above the one obtained here (Figure 10a). In this approach, the Bi$_2$Te$_3$-Te branch hosts two phases (BiTe$_2$ and BiTe$_{4.88}$) and the branch towards Bi hosts three phases corresponding to BiTe (tsumoite), Bi$_2$Te and Bi$_{4.88}$Te. Our data show lower ground state energy for phases of the same composition and is thus more plausible in terms of thermodynamic stability. This is also because our input structures are more appropriate than the simple, Bi-Te alloy-type substitution used by Woodcox et al. (2019).

A second model for evaluation of phase stability was introduced by Park et al. (2021), using the mixing energies of the 2- and 5-atom modules according to the formula,

$$E_{\text{mixing}} = \frac{\sum n_{\text{atom}}}{N_{\text{atom}}} \left( E = \sum n_{\text{total}} - m_{\text{total}} - E_{\text{total}} \right),$$

where $N_{\text{atom}}$ = total number of atoms in a given phase. In this case, the hull is determined between endmembers Bi$_2$Te$_3$ (tellurobismuthite) and bismuth, rather than bismuth and tellurium. The diagram obtained for the six phases using the relaxed structures when calculating $E_{\text{mixing}}$ values for each compound (Table 5, Figure 10b) shows Bi$_4$Te$_3$ (pilsenite) as the minimum of the hull (Figure 10b). The energy for each compound represents the ground state energy ($E_0$ in Table 3). The other compounds plot below the branch between pilsenite and bismuth, indicating they are stable. BiTe (tsumoite) plots slightly above the branch towards Bi$_2$Te$_3$. However, the distance between the point and the hull is $\sim$1.400 meV/atom, a small offset indicating that tsumoite may be stable.

Park et al. (2021) calculate $E_{\text{mixing}}$ for the nine phases defined as superstructures in Bos et al. (2007) but using lattice parameters ($a$ and $c$) from previous experimental studies. Park et al. (2021) obtained a hull centered on Bi$_2$Te, rather than pilsenite as the minimum $E_{\text{mixing}}$ point (Figure 10b). Except for hedleyite, all the other five intermediate phases plot above the hull. Nonetheless, Park et al. (2021) considered these phases as stable since the distance to the hull is within a cutoff of $\sim$4.500 meV/atom.

We point at the significant differences between the results of Park et al. (2021) and our own, particularly
when comparing the same compounds, Bi$_7$Te$_3$ (hedleyite), Bi$_2$Te, and BiTe (tsumoite). We consider that
the energy differences are due to the lattice parameters used, which were fixed lattice parameter values
in Park et al. (2021) rather than obtained as the result of structure relaxation as in our study. Our data
show a better fit to the convex hull and are therefore more credible in terms of energetic stability.

Following the ideas of Park et al. (2021) that intermediate compounds in a modular series can be
obtained by mixing energies of the constituent units, we formulate the energy of mixing using the
accretional model as follows:

\[
E_{mixing} = \frac{E_{Total}^{S BI_{2(k)} Te_3 L BI_{2(k+1)} Te_3} - E_{Total}^{S BI_{2(k)} Te_3 L BI_{2(k+1)} Te_3}}{N_{atom}}.
\] (5)

Applying this to the three double module phases (S=1, L=1), we obtained $E_{mixing}=1.420$ meV/atom for
tsumoite (5.7), -0.040 meV/atom for Bi$_3$Te$_3$ (7.9), and -0.020 meV/atom for hedleyite (9.11), values very
close to zero. This implies that mixing between the incremental modules is close to ideal. Further
calculation for other intermediate phases (S>1, L>1) would test this statement.

The $\gamma$ - $d_{sub}$ relationship: where does the series end?

The “Mod2 and 5” model of Imamov and Semiletov (1971) and Shelimova et al. (2000) is popular
because it allows the separation of two blocks with different thermoelectric properties and electronic
band structures (e.g., Bos et al. 2007; 2012; Park et al. 2021). In this model, if m=0, bismuth becomes
the end member of the series. This is, however, impossible in the mixed layer compound model, or the
homologous series described by the accretional modules (Frangis et al. 1989; Ciobanu et al. 2009), in
which Te will always be part of the component modules. This implies the end of the series is close to but
never meets native bismuth.

The incremental decrease in $d_{sub}$ across the series (Figure 2b, c) shows the size of this interval
moves towards a constant value for phases within the compositional range ~45 to 27 atom.% Te. A better
description of $d_{sub}$ across the series is obtained using $\gamma$ modulation (Figure 11). The fitted curve shows
that $d_{sub}$ becomes a de facto constant of ~1.973 Å from Bi$_{20}$Te$_3$ (k=10) onwards, up to Bi$_{100}$Te$_3$ (k=50), for example. Taking the values for interatomic distances in native bismuth reported for $R\overline{3}m$ space for temperatures between 4.2 K and 298 K we note that these are in a comparable range (1.966-1.977 Å; Wyckoff, 1963; Schiferl and Barrett, 1969). The $d_{sub}$ of Bi$_7$Te$_3$ (hedleyite) is at the upper limit whereas $d_{sub}$ for single module phases with $k\geq$4 falls within the range reported for native bismuth.

The incremental decrease in $d_{sub}$ corresponds to phases lacking Te-Te bonds, i.e., towards Bi-rich compositions from Bi$_8$Te$_9$, a phase with 5.7.7 module stack (Figure 12). Such behavior can be rationalized in terms of the relative contributions of Bi-Bi and Bi-Te bond lengths to the interlayer intervals across the asymmetric unit cell along $c$ (Figure 12). If we consider the ideal $d_0$ =2.000 Å as a baseline, the weighted, average values of Bi-Te bonds for each phase lead to an increase of $d_{sub}$ whereas the Bi-Bi bonds have the opposite effect. The total contribution (sum of the two calculated values for each phase) shows a gentle slope from Bi$_4$Te$_3$ (pilsenite) to Bi$_8$Te$_3$ (Figure 12). The offset of $d_{sub}$ decreases relative to ideal $d_0$ and we predict it will stay constant for phases with $k \geq$ 10.

Based on this consideration, we define three subgroups in terms of slope variation in $d_{sub}$, the crystal-structural parameter that defines derivation of the series from the archetypal tetradymite structure:

(i) Bi$_2$Te$_3$ (tellurobismuthite) -Bi$_8$Te$_9$ – steep slope; (ii) Bi$_8$Te$_9$-Bi$_{14}$Te$_3$-gentle slope, and (iii) Bi$_{14}$Te$_3$ to Bi$_{100}$Te$_3$, expanding to Bi$_{100}$Te$_3$ – almost flat (values <<0.001 Å). This implies that phases in range (iii), i.e., $k>7$, should be considered as disordered native bismuth rather than discrete members of the tetradymite group. The structures of Bi-tellurides with $k>7$ would be indistinguishable from native Bi since they would have the same $d_{sub}$ values. On the other hand, regular insertion of Te layers at such large intervals into a bismuth matrix must be considered as very unlikely.

**SUMMARY AND IMPLICATIONS**
We have used density functional theory to obtain seven structures spanning the range Bi$_2$Te$_3$-Bi$_8$Te$_3$ in the tetradymite homologous series with formula: S[Bi$_{2k}$Te$_3$]L[(Bi$_{2(k+1)}$Te$_3$)]; k=1-4. The structures represent single modules [S=1, L=0; Bi$_2$Te$_3$ (tellurobismuthite), Bi$_4$Te$_3$ (pilsenite), Bi$_2$Te and Bi$_8$Te$_3$] and double modules [S=1, L=1; BiTe (tsumoite), Bi$_5$Te$_3$ and Bi$_7$Te$_3$ (hedleyite)] within this range. The relaxed structures show systematic increase in $a$ and decrease in interlayer distance ($d_{sub}$). We observe a sharp decrease in $d_{sub}$ between tellurobismuthite (2.029 Å) and tsumoite (1.996 Å), followed by an incremental decrease to Bi$_8$Te$_3$ (1.975 Å) with Bi content.

Models for the relaxed structures are used to show representative atomic arrangements, bonding, and bond distances for the asymmetric unit cells. Variation in minimum and maximum bond lengths show the series can be split into two parts, corresponding to structures with and without Te-Te bonds. The latter are larger than the Bi-Bi and Bi-Te bonds, reflecting the variation in $d_{sub}$.

Scanning transmission electron microscopy simulations for the relaxed structures show a perfect match with the atom models. Simulated electron diffractions and the reflection modulation along the $c^*$ show a good fit with published analytical data and the mixed-layer compound theory. The distribution of reflections and their intensity variation along $d_{sub}^* = 1 / d_{sub}$ is described by two modulation vectors, $\mathbf{q} = \gamma \cdot c_{sub}^*$ ($\gamma = 1.800-1.640$) and $\mathbf{q}_F = \gamma_F \cdot d_{sub}^*$ ($\gamma_F = 0.200-0.091$). The $\gamma_F$ parameter underpins the S, L building blocks as Bi$_{2k}$Te$_3$ and Bi$_{2(k+1)}$Te$_3$ for the double module structures instead of Bi$_2$ and Bi$_2$Te$_3$, whereas $\gamma$ relates to variation of the $d_{sub}$.

Density functional theory is also used to calculate the formation energies of the seven phases. This shows that the phases in the range BiTe-Bi$_8$Te$_3$ lie on the Bi-Bi$_2$Te$_3$-Te convex hull, implying they are thermodynamically stable. However, further studies employing phonon calculations are required to assess whether these phases can be experimentally synthesised.

We have built a model that describes the relationship between $\gamma$ and $d_{sub}$. This allows us to predict values for $d_{sub}$ beyond the compositional range considered here, e.g., for $k$ values of 5, 7, 10, or even
These values are within the analytical range of interlayer distance in native bismuth. The tetradymite group is therefore constrained within the $\gamma$ range between 1.800 (tellurobismuthite) to 1.588 (Bi$_{14}$Te$_3$), beyond which $\gamma$ no longer represents the tetradymite group but rather disordered native bismuth.

The present study carries implications for mineral nomenclature and classification as well as for the technological applications of Bi-chalcogenides. The framework presented here allows for the prediction of structures for any intermediate phases within the Bi-rich series of the tetradymite group. The same approach can be extended to other series comprised of mixed-layer compounds, e.g., the aleksite series (Cook et al. 2019) and other chalcogen-rich series within the tetradymite group, or REE-fluorocarbonates of the bastnäsite-synchysite group (Ciobanu et al. 2017; 2022).

Applying the correct structural model should also help to understand the variation in the thermoelectric or topological insulating properties of new compounds in the tetradymite group (Bos et al., 2007; 2012; Goldsmid, 2014).

Crystal structures are also fundamental for calculation of thermodynamic properties, which in turn places constraints on phase relations in the system Bi-Te (Mao et al., 2018; Hasanova et al., 2021). A refined phase diagram for the system Bi-Te is important for synthesis of new compounds and for understanding the strong association between Bi-tellurides and gold observed in nature.

**Deposit items:** The following are available online at https://xxxx/xxxxxx: cif files for seven structures.

**ACKNOWLEDGMENTS AND FUNDING**

This work was supported by the Australian Research Council through Linkage grant LP200100156 “Critical Minerals from Complex Ores”, co-supported by BHP Olympic Dam. We acknowledge access to the Phoenix high-performance computer (HPC) at the University of Adelaide and thank Fabien Voisin and Mark Innes for the assistance with VASP installation and HPC configuration. We appreciate the constructive comments of two anonymous reviewers and editorial handling by Jianwei Wang.
REFERENCES CITED


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**Figure captions**

**Figure 1.** Energy versus volume curves for the nine crystal structures corresponding to phases as labelled, including elemental Bi and Te. Open black circles are total energies calculated from DFT. Solid black curves are constructed by fitting the equation of state (1). The parameters listed in Table 3 are obtained from the fitted curve. Native bismuth and tellurium are included for the calculation of formation energy in equation (3).

**Figure 2.** Lattice parameters $a$ (a) and $d_{sub}$ (b,c) as a function of atom.% Te for the seven studied phases. Data from literature (Table 1 and additional DFT studies) are indicated for comparison. The value of $d_{sub}$ for Bi$_8$Te$_3$ from Ciobanu et al. (2021) is included although is out of the range calculated here. (a) The present data plots along a curve above the one refined from literature (dashed line). The DFT data for tellurobismuthite is given with error bars. Note that the mean value for previously published DFT data (Cheng and Ren 2011; Vilaplana et al., 2011; Zurhelle et al., 2016) is midway between other published data and present study. The plot in (c) is a close up of (b). Abbreviations: Hed—hedleyite; Pls—pilsenite; Tbs—tellurobismuthite; Tsm—tsumoite.

**Figure 3.** Atom models (ball and stick to the left, atom filling to the right) for the relaxed structures of the single module phases ($k=1-4$; $S=1$; $L=0$) as labelled viewed on [1120] zone axis. Atom-layer modules and their respective widths are marked by numbers at the top. The
sequence of atoms (red—Bi; green—Te) typifying the structure is shown along \((hki\ell)\) planes, \(i=-(h+k)\). Corresponding crystallographic information data files (cif.) included as Deposit items.

**Figure 4.** Atom models (ball and stick to the left, atom filling to the right) for the relaxed structures of the double module phases \((k=1-3; S=1; L=1)\) as labelled viewed on \([11\bar{2}0]\) zone axis. Atom-layer modules and their respective widths are marked by numbers at the top. The sequence of atoms (red—Bi; green—Te) typifying the structure is shown along \((hki\ell)\) planes, \(i=-(h+k)\). Corresponding crystallographic information data files (cif.) included as Deposit items.

**Figure 5.** Bonds and their respective lengths for atoms (red—Bi; green—Te) within the asymmetric unit cell (viewed on \([11\bar{2}0]\) zone axis) for single module phases as labelled. Maximum and minimum bond lengths are marked in red and tabulated for each phase to enable an easier comparison. Projection of bond lengths along the \(c\) axis is marked for pilsenite, \(\text{Bi}_2\text{Te}_3\) and \(\text{Bi}_8\text{Te}\) to illustrate the contribution of Bi-Bi and Bi-Te bonds to the \(d\)-subcell plotted on Figure 12). Note that Te-Te bonds (with greatest length) are present only in tellurobismuthite.

**Figure 6.** Bonds and their respective lengths for atoms (red—Bi; green—Te) within the asymmetric unit cell (viewed on \([11\bar{2}0]\) zone axis) for double module phases as labelled. Maximum and minimum bond lengths are marked in red and tabulated for each phase to enable an easier comparison.

**Figure 7.** Minimum and maximum bond lengths for all seven structures (data from Figures 5 and 6) plotted against atom.\% Te. Differences between largest and smallest values are marked adjacent to each diagram. (a, b) Minimum and maximum Bi-Te bonds. Note that all seven phases contain such bonds. (c,d) Minimum Bi-Bi and maximum Bi-Bi and Te-Te bonds. Note that tellurobismuthite lacks Bi-Bi bonds (in (c) and that pilsenite has only one Bi-Bi bond with value
within the range of minimum Bi-Bi bonds (not plotted on d). See text for additional details.

Abbreviations: Hed—hedleyite; Pls—pilsenite; Tbs—tellurobismuthite; Tsm—tsumoite.

**Figure 8.** STEM simulations (left) and electron diffraction (ED) patterns (right) obtained on [11\(\bar{2}0\)] zone axis for the relaxed structures corresponding to the single module phases as labelled. Values for \(a\), \(c\) and \(d_{\text{sub}}\) parameters correspond to those given in Table 4. The two strips under each image show the \(d'_{\text{sub}}\) interval cropped from ED patterns (area rectangle) and computed intensity variation for reflections across this interval, displaying the number of reflections and the two modulation vectors (as marked). The atom sequence corresponding to each structure is marked by overlays on the images. Compare the simulations with the models shown in Figure 3. Third order satellite reflections underpin the \(q\) modulation along \(c^*\) (marked by arrows and circles). Note that the simulations for unnamed Bi\(_2\)Te were performed using space group \(P1\) instead of \(P\bar{3}m1\). See text for additional details.

**Figure 9.** STEM simulations (left) and electron diffraction (ED) patterns (right) obtained on [11\(\bar{2}0\)] zone axis for the relaxed structures corresponding to the double module phases as labelled. Values for \(a\), \(c\) and \(d_{\text{sub}}\) parameters correspond to those given in Table 4. The two strips under each image show the \(d'_{\text{sub}}\) interval cropped from ED patterns (area rectangle) and computed intensity variation for reflections across this interval, displaying the number of reflections and the two modulation vectors (as marked). The atom sequence corresponding to each structure is marked by overlays on the images. Compare the simulations with models shown in Figure 4. Third order satellite reflections underpin the \(q\) modulation along \(c^*\) (marked by arrows and circles). Note that the simulations for tsumoite were performed using space group \(P1\) instead of \(P\bar{3}m1\).

**Figure 10.** Phase stability diagrams using the convex Hull approach. (a) Plot showing formation energy from DFT calculations (Table 5) versus atom.% Te for the seven studied phases shown
in red (single modules) and green (double modules). A convex hull is defined by bismuth (Bi),
tellurobismuthite (Tbs) and tellurium (Te). The other six phases lie on the Bi-Tbs side (full line),
whereas the Tbs-Te side (marked by dashed line) is empty. The convex hull Bi-BiTe-Te
obtained from DFT calculations of Bi-Te alloys (marked as blue circles) (Woodcox et al. 2019)
is shown for comparison. (b) Plot showing energy mixing (equation 4 from Park et al. 2021)
versus n/(n+m) using the Mod 2 and 5 model. The convex hull (red line) from our data (phases
as red circles) is between Tbs, pilsenite (Pls) and Bi. All phases, except tsumoite (Tsm) plot
underneath the Pls-Bi side, indicating stability. Tsumoite, plotting above the Pls-Tbs side, is
also likely stable given the distance to the hull (~1.400 meV/atom). In contrast, DFT data from
Park et al. (2021), using fixed lattice constants for the structures is defined by a Tbs-Bi$_2$Te-Bi
convex hull (data in blue). The distances to the hull for Tsm is larger than the fit obtained here
for relaxed structure of this compound. Abbreviation: Hed—hedleyite.

**Figure 11.** Model for the relation between d subcell and parameter γ showing that the
tetradymite series extends from tellurobismuthite to Bi$_{14}$Te$_3$ (k=7). The fitted curve ($d_{sub} =$
6.457e-10 $\gamma^{31.15} + 1.973$) using calculated d subcell and γ values for the seven phases (in red)
allows prediction of d subcell for phases with higher k (k=5, 7, 10, 50 shown in green). The
slope of this curve has three domains with sharp, gentle, and flat trends, respectively (marked
as slopes 1-3). The boundary between slope 1 and 2 is marked by the first phase in which the
stacking sequence indicates a lack of Te-Te bonds (Bi$_8$Te$_9$, stack modules 5.7.7, shown in blue).
The boundary between slope 2 and 3 is marked by the composition Bi$_{14}$Te$_3$, the point on the
curve from where d-subcell becomes constant. Therefore, the phases in the slope 3 region should
be considered disordered native bismuth rather than compounds from the tetradymite series.
Interval of analytical data for interlayer distance in native bismuth in yellow.
Figure 12. Contribution of bond lengths to d-subcell for the three single module phases without Te-Te bonds, pilsenite (Pls), Bi$_2$Te, and Bi$_8$Te$_3$. This can be seen as the difference between weighted average bond lengths and reference $d_0$ which is taken as a baseline. The Bi-Te and Bi-Bi bonds show opposing trends, and the total contribution of the two bond types decreasing from Pls to Bi$_8$Te$_3$, in agreement with calculated $d_{sub}$ values (Table 4).
Table 1. Background and crystal structures with published information on unit cell parameters.

<table>
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<tr>
<th>Formula, Mineral name</th>
<th>Explicit formula</th>
<th>k</th>
<th>Module stacks</th>
<th>N₁</th>
<th>Space Group</th>
<th>N total</th>
<th>c calc (Å)</th>
<th>Reference(s)</th>
<th>c (Å)</th>
<th>a (Å)</th>
<th>d subcell (Å)</th>
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* structure given with rhombohedral axes as \(a=b=c=10.45 \text{ Å}, \alpha=\beta=\gamma=24.13^\circ\)

b S/TEM data

c Zav’ylov et al. (1976) given as for hedleyite

The first listed for each phase (in italics) was used as input data for DFT structure calculations.
Table 2. Number of atoms and chemical formula units applied in each simulation box and KPOINTS grids chosen in the DFT computations for all seven Bi-tellurides structures, native bismuth and tellurium.

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<th>Bi₈Te₃</th>
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Table 3. Equation of state parameters fitted from the energy volume relation for the seven Bi-tellurides, native bismuth and tellurium. \( V_0 \) represents the equilibrium volume for each simulation cell, \( K_0 \) and \( K'_0 \) are the bulk modulus and its derivative. The \( V_0 \) and bulk modulus are compared with experimental and previously published calculations.

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All bulk modulus data are from Woodcox et al. (2019)
Table 4. Calculated lattice constants $a$, $c$, volume, $Z$, and density for the seven relaxed Bi-telluride structures based on density functional theory. Values for $d_{sub}$ are obtained from the $c$ parameter and number of layers (N1) for each phase.

<table>
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<tr>
<th>Name</th>
<th>Explicit formula, $\text{(N1)}$</th>
<th>Space group</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>Volume (Å$^3$)</th>
<th>$Z$</th>
<th>density (g/cm$^3$)</th>
<th>$d_{sub}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tellurobismuthite</td>
<td>$\text{Bi}_2\text{Te}_3 (5)$</td>
<td>$R\bar{3}m$</td>
<td>4.431</td>
<td>30.433</td>
<td>517.561</td>
<td>3</td>
<td>7.7079</td>
<td>2.029</td>
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<tr>
<td>Tsumoite</td>
<td>$\text{Bi}_6\text{Te}_6 (12)$</td>
<td>$P\bar{3}m1$</td>
<td>4.468</td>
<td>23.950</td>
<td>414.059</td>
<td>6</td>
<td>8.0995</td>
<td>1.996</td>
</tr>
<tr>
<td>Pilsenite</td>
<td>$\text{Bi}_4\text{Te}_3 (7)$</td>
<td>$R\bar{3}m$</td>
<td>4.487</td>
<td>41.678</td>
<td>726.691</td>
<td>3</td>
<td>8.3552</td>
<td>1.985</td>
</tr>
<tr>
<td>Bi$_3$Te$_3$</td>
<td>$\text{Bi}_{10}\text{Te}_6 (16)$</td>
<td>$R\bar{3}m$</td>
<td>4.499</td>
<td>95.133</td>
<td>1667.607</td>
<td>6</td>
<td>8.5309</td>
<td>1.982</td>
</tr>
<tr>
<td>Bi$_2$Te</td>
<td>$\text{Bi}_8\text{Te}_3 (9)$</td>
<td>$P\bar{3}m1$</td>
<td>4.508</td>
<td>17.811</td>
<td>313.463</td>
<td>3</td>
<td>8.6709</td>
<td>1.979</td>
</tr>
<tr>
<td>Hedleyite</td>
<td>$\text{Bi}_{14}\text{Te}_6 (20)$</td>
<td>$R\bar{3}m$</td>
<td>4.514</td>
<td>118.613</td>
<td>2093.081</td>
<td>6</td>
<td>8.7863</td>
<td>1.977</td>
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<tr>
<td>Bi$_3$Te$_3$</td>
<td>$\text{Bi}_{16}\text{Te}_3 (11)$</td>
<td>$R\bar{3}m$</td>
<td>4.519</td>
<td>65.182</td>
<td>1152.771</td>
<td>3</td>
<td>8.8798</td>
<td>1.975</td>
</tr>
</tbody>
</table>

Table 5. DFT calculated formation energy ($E_f$) and energy of layer mixing ($E_{mixing}$) for seven phases from the tetradyomite series. Equations (3) and (4) are given in the text.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$E_f$ (eV)</th>
<th>Bi$_2$Te$_3$</th>
<th>BiTe</th>
<th>Bi$_4$Te$_3$</th>
<th>Bi$_5$Te$_3$</th>
<th>Bi$_3$Te$_5$</th>
<th>Bi$_7$Te$_3$</th>
<th>Bi$_8$Te$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$Te$_3$</td>
<td>-242.533</td>
<td>-205.250</td>
<td>-181.048</td>
<td>-158.563</td>
<td>-141.000</td>
<td>-126.667</td>
<td>-114.909</td>
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</tr>
<tr>
<td>Bi$_3$Te$_3$</td>
<td></td>
<td>-3.139</td>
<td>-7.810</td>
<td>-6.979</td>
<td>-6.259</td>
<td>-5.400</td>
<td>-4.667</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1
Figure 3
Tsumoite BiTe

Unnamed Bi$_5$Te$_3$

Hedleyite Bi$_7$Te$_3$

Figure 4
Tellurobismuthite Bi$_2$Te$_3$
- max Te$_2$-Te$_2$ = 3.694 Å
- min Bi$_1$-Te$_2$ = 3.080 Å
- max Bi$_1$-Te$_1$ = 3.263 Å

Pilsenite Bi$_2$Te$_3$
- min Bi$_2$-Bi$_2$ = 3.073 Å
- min Bi$_1$-Te$_2$ = 3.098 Å
- max Bi$_2$-Te$_2$ = 3.566 Å

Unamed Bi$_2$Te
- min Bi$_1$-Bi$_2$ = 3.080 Å
- max Bi$_2$-Bi$_2$ = 3.553 Å
- min Bi$_3$-Te$_1$ = 3.105 Å
- max Bi$_1$-Te$_1$ = 3.531 Å

Figure 5
Figure 6
Figure 7
Figure 8
Figure 9
Figure 10
Figure 11