1   *Revision 1*

2   ***Ab initio* calculations and crystal structure simulations for mixed layer**

3   **compounds from the tetradymite series**

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12   **ABSTRACT**

13   Density functional theory (DFT) is used to obtain structural information of seven members of the

14   tetradymite homologous series: Bi_2Te_3 (tellurobismuthite), $BiTe$ (tsumoite), Bi_4Te_3 (pilsenite), Bi_5Te_3,

15   Bi_2Te, Bi_7Te_3 (hedleyite) and Bi_8Te_3. We use the formula $S(Bi_{2k}Te_3) \cdot L[Bi_{2(k+1)}Te_3]$ as a working model

16   (k=1-4) where S and L are short and long modules in the structures. The relaxed structures show an

17   increase in the *a* parameter and decrease in the interlayer distance (d_{sub}) from Bi_2Te_3 (2.029 Å) to Bi_8Te_3

18   (1.975 Å). DFT-derived formation energy for each phase indicates they are all thermodynamically stable.

19   Scanning transmission electron microscopy (STEM) simulations for each of the relaxed structures show

20   an excellent match with atom models. Simulated electron diffractions and reflection modulation along

21   c^* are concordant with published data, where they exist, and with the theory underpinning mixed-layer

22   compounds. Two modulation vectors, $\mathbf{q}=\gamma \cdot c^*_{sub}$ (γ =1.800-1.640) and $\mathbf{q_F}=\gamma_F \cdot d^*_{sub}$ (γ_F =0.200-0.091),

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23 describe the distribution of reflections and their intensity variation along $d^*_{sub} = 1/d_{sub}$. The γ_F

24 parameter reinforces the concept of $Bi_{2k}Te_3$ and $Bi_{2(k+1)}Te_3$ blocks in the double module structures and γ

25 relates to d_{sub} variation. Our model describing the relationship between γ and d_{sub} allows prediction of

26 d_{sub} beyond the compositional range considered in this study, showing that phases with k>5 have

27 d_{sub} values within the analytical range of interlayer distance in bismuth. This in turn allows us to

28 constrain the tetradymite homologous series between γ values of 1.800 (Bi_2Te_3) and 1.588 ($Bi_{14}Te_3$).

29 Phase compositions with higher Bi/Te should be considered as disordered alloys of bismuth. These

30 results have implications for mineral systematics and classification as they underpin predictive models

31 for all intermediate structures in the group and can be equally applied to other mixed-layer series. Our

32 structural models will also assist in understanding variation in the thermoelectric and topological

33 insulating properties of new compounds in the broader tetradymite group and can support experimental

34 work targeting a refined phase diagram for the system Bi-Te.

35 Keywords: *tetradymite series, mixed layer compounds, crystal structure, Density Functional Theory,*

36 *STEM simulations*

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37   **INTRODUCTION**

38   The tetradymite series [generally $Bi_x(Te,Se,S)_y$; where Te, Se, S are chalcogens] comprises phases

39 with crystal structures derived from the tetradymite archetype [Bi_2Te_2S, a 5-atom-thick layer, 'mod5']

40 (Cook et al. 2007, and references therein). Ciobanu et al. (2009) considers the tetradymite series a "metal-

41 or Bi-rich" series within a larger group of phases derived from the same tetradymite archetype. For the

42 sake of simplicity and the purpose of this contribution, we chose Te as the only chalcogen. There are two

43 models describing crystal structure modularity within the Bi-rich series (or tetradymite series *sensu*

44 *stricto*). The first, proposed by Imamov and Semiletov (1971), considers the combination of Bi_2 and

45 Bi_2Te_3 blocks (hereafter referred to as the "Mod2 and 5 model"), later formalised as $nBi_2 \cdot mBi_2Te_3$ by

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46   Shelimova et al. (2000). The second model was introduced by Amelinckx et al. (1989) and Frangis et al.

47   (1990) as 5- and 7-layer lamellae based upon the electron diffraction properties indicating one

48   dimensional, interface modulated mixed layer compounds. This was subsequently formalised by Ciobanu

49   et al. (2009) for modules of incremental thickness, as an accretional homologous series with formula:

50     $S(Bi_{2k}Te_3) \bullet L[Bi_{2(k+1)}Te_3]$, where S and L are the number of short and long modules, respectively. This

51   model allows for definition of building modules with incremental thickness extending from module 5 to

52   7, 9, 11, and so on. These modules have a fixed number of chalcogen atoms and are incrementally

53   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,

54   explaining why this is referred to as the Bi-rich series.

55   Transmission electron microscopy (TEM) study of phases in the compositional range Bi_2Te_3-Bi_8Te_3

56   are complemented by high angle annular dark field (HAADF) scanning TEM (STEM) studies of Bi_8Te_3

57   and $Bi_4(Te,Se,S)_3$ that show the correlation between composition and structural modulation (Ciobanu et

58   al. 2009, 2021; Cook et al. 2021). Diffraction patterns show that all phases are N-fold superstructures (N

59   = layers in the stacking sequence) of a rhombohedral subcell with $c/3 = d_0 \sim 2.000$ Å. The structures are

60   characterised by two modulation vectors showing monotonic decrease in d-subcell (d_{sub}) with

61   increasing Bi composition.

62   Several named minerals and other unnamed phases in the tetradymite group are reported from natural

63   assemblages, particularly from gold deposits (Cook et al. 2007; 2009; Ciobanu et al. 2010) yet

64   remarkably few have been subject to crystal structure determination or crystallographic information data

65   file (cif). Compounds from this series are intensely studied for their thermoelectric and/or topological

66   insulating properties (Bos et al., 2007; 2012; Goldsmid, 2014). To better understand the series, we

67   perform *ab initio* calculations and structure simulations for phases with single and double modules across

68   the compositional range Bi_2Te_3 to Bi_8Te_3 (k=1-4). We use simulations of images and electron diffraction

69   patterns to assess the validity of the accretional model versus the "Mod 2 and 5" model and apply the

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70   formation energies to evaluate phase stability of the seven phases. The determined crystal structure

71   parameters are used to develop a model for the series that involves variation in d_{sub} relative to

72   modulation.

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

74   Table 1 indicates the phases under consideration and published information on their crystal

75   structures. The symmetry and the number of layers in each structure can be derived from the explicit

76   chemical formula given by Ciobanu et al. (2009). In the present work, four structures with S=1, L=0, and

77   k=1, 2, 3, 4 (Bi_2Te_3, Bi_4Te_3; Bi_6Te_3 and Bi_8Te_3), and three structures with S=1, L=1, and k=1, 2, 3

78   (Bi_6Te_6; $Bi_{10}Te_6$ and $Bi_{14}Te_6$) are included. These correspond to single and double module structures: (i)

79   5, 7, 9 and 11; and (ii) combinations of these with notation 5**.**7, 7**.**9 and 9**.**11, respectively. The number

80   of layers in the asymmetric unit cell is N_1=S(2k+3)+L(2k+5). If the number of atoms in the explicit

81   formula is divisible by 3, as in the case of Bi_6Te_6 (BiTe, tsumoite) and Bi_6Te_3 (unnamed Bi_2Te), the

82   symmetry changes from $R\bar{3}m$ (hereafter called R) to $P\bar{3}m1$ (hereafter called H). The total number of

83   layers in the structure is $N=N_1$ x 3 for R phases and $N = N_1$ for H phases. Knowing that the distance

84   between two consecutive layers (Imamov and Semiletov 1971), the ideal d_0, approximates to 2.000 Å,

85   we can calculate the *c* parameter using the formula: $c = N_1$ x 2.000 Å.

86   We selected 12 published crystal structures for the phases targeted here that have been documented

87   from x-ray powder or single crystal diffraction studies, and two from (S)TEM data (Table 2). Published

88   data are unevenly distributed among the seven phases. For example, there are five studies of Bi_2Te_3

89   (tellurobismuthite) but no x-ray diffraction studies for either Bi_5Te_3 or Bi_8Te_3. Most of the published

90   studies were carried out on synthetic material and only a single study was performed on natural

91   tellurobismuthite (Nakajima 1962), highlighting the difficulty in finding natural material suitable for

92   crystal structure determination of these phases. We observe that *a* increases slightly from Bi_2Te_3 to

93   Bi_8Te_3 whereas the *c* parameter varies widely as it is dependent upon N and symmetry. However, using

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94 the c parameter we can calculate the variation in the interlayer distance defining the subcell from which

95 the layers are derived (d_{sub}). This interval, calculated from analytical measurements, shows a decrease

96 from ~2.000 Å to 1.910 Å across the Bi_2Te_3-Bi_8Te_3 range, with some fluctuations (Table 1).

97   **METHODS**

98 **Ab initio calculations**

99   To explore the correlation between crystal structural modularity and chemical variation in a series

100 of mixed-layer compounds, we have employed *ab initio* total energy calculations and structure relaxation

101 using density functional theory (DFT) (Hohenberg and Kohn 1964; Kohn and Sham 1965). Input data

102 for structure optimisation comprised crystallographic information files (cif) from the literature (Table 1).

103 An exception was the Bi_5Te_3 phase, for which a predicted structure was obtained using CrystalMaker

104 (CM) (Palmer 2015) and Findsym software (Stokes and Hatch 2005).

105   The DFT calculations were performed with the Vienna *ab initio* simulation package (VASP) (Kresse

106 and Furthmüller 1996; Kresse and Joubert 1999), using the projector augmented wave (PAW) method

107 (Blöchl 1994). A plane wave basis set with energy cut-off of 500 eV was employed for all calculations.

108 The electronic exchange and correlation energy were estimated by the generalized gradient

109 approximation (GGA) with Perdew, Burke and Ernzerhof (PBE) parameters (Perdew et al. 1996). We

110 included van der Waals interactions between atoms of the same type (Te-Te and Bi-Bi) using the method

111 of Grimme et al. (2010), which adds a small dispersion energy correction to the total energy in the system.

112 This is also shown in a recent publication in which the electronic structure of Bi_4Te_3 phase is predicted

113 to be a semimetal (Nabok et al., 2022).

114   The Brillouin zone (BZ) was sampled at Γ-centred dense k-point grids based on the Monkhorst-Pack

115 scheme (Pack and Monkhorst 1977). The set of k-points was considered dependent upon the cell

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116   parameters and symmetry of each structure (Table 1) to maximize the total energy accuracy while aiming

117   to minimize computational cost.

118   Volumes from each input file were considered as V_i for each structure. The lattice parameters *(a, c)*

119   in each case were subsequently scaled in the range 95 to 101% to obtain a series of volume values. For

120   consistency, the volume relaxation was performed at constant energy cut-off. Total energy calculations

121   and structural optimization for the atomic positions and cell parameters (*c* and *a*) were carried out for

122   individual volumes with energy tolerance $<10^{-5}$ eV between two ionic steps and force less than 0.02 eV/Å

123   per atom. After volume relaxation, a static calculation is performed to obtain the total energy at each

124   volume.

125   To obtain the equilibrium volume and ground state energy we used the Murnaghan (1944) equation

126   of state (EOS) as being most appropriate for compounds with trigonal symmetry (e.g. the same EOS used

127   by other studies of Bi-tellurides; Nakayama et al. 2009). The Birch-Murnaghan (1947) EOS was

128   introduced for phases with cubic symmetry. Equilibrium volume and ground state energy were found by

129   fitting the Murnaghan (Murnaghan 1944) equation of state (EOS):

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

131   where K_0 and K_0' are the bulk modulus and its pressure derivative, V_0 represents the equilibrium volume

132   and E_0 is the reference energy. The calculated parameters after EOS fitting are given in Table 3. The

133   optimized lattice parameters for each structure were obtained by performing relaxation at the

134   corresponding equilibrium volume.

135   **Crystal structure models**

136   All the relaxed crystal structures were modelled and assessed using CM and Findsym was used to

137   generate the cif data files. Electron diffractions and STEM image simulation were performed using

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138   HREM STEM software for structure visualization. A computer subroutine was written in Python for

139   intensity calculations and simulations of reflections.

140   **RESULTS**

141   **Crystal structure relaxation**

142   We have selected six of the structures given in Table 1 as a basis for crystallographic file input (cif)

143   in the DFT calculations. For Bi_5Te_3 we use experimental parameters given by Ciobanu et al. (2009) and

144   obtain atom coordination by applying $1/N_1 = 1/16$ derived from the 7.9 modular structure with equal

145   intervals along the c direction for the z coordinates.

146   To constrain the seven crystal structures, we determined the equilibrium volume for each phase

147   (Figure 1) by fitting the total energy volume curves using equation (1), with the minimum well

148   constrained. The equilibrium volumes and EOS parameters are listed and compared with published data

149   in Table 3.

150   The fitted volumes are within 2% of the reference structures, except for Bi_8Te_3 for which the

151   difference is 9%. The main reason is that the parameters for this were obtained from S/TEM data which

152   carries a higher uncertainty. Our calculated bulk moduli (K_0) range from 33-40 GPa, concordant with

153   studies of elastic properties using *ab initio* calculations of bismuth-based alloys (Woodcox et al. 2019).

154   This is seen from a comparison for phases with the same composition, e.g., 40 GPa vs. 41 GPa (Woodcox

155   et al. 2019) for BiTe, as well as from the small variation of K_0 across the compositional range.

156   After the fitting step we calculated the structure parameters at V_0 (Table 4), with differences of $\pm 1\%$

157   for a and c relative to most reference structures, although differences were higher (a few %) for Bi_5Te_3

158   and Bi_8Te_3. Comparable discrepancies between DFT calculations and input files for a crystal structure

159   are reported in other studies, e.g., for Bi_2Te_3 (Cheng and Ren 2011).

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160   We also note that after relaxation, the a parameter is expanded whereas c contracts relative to the

161   input data (Tables 1 and 4). The comparison of the a parameter with published data (Figure 2a) shows

162   that relaxed structures follow a smooth trend, increasing with Te content across the range Bi_2Te_3 to

163   Bi_8Te_3, with values systematically larger – by a small amount – than published measurements (Table 1).

164   An appreciation of published DFT data (Cheng and Ren, 2011) relative to analytical data is shown for

165   tellurobismuthite (Bi_2Te_3), the most intensively studied of the seven structures. Our data plots close to

166   the mean of published DFT data; the TEM-based lattice parameter a is smaller than both analytical and

167   DFT curves (Figure 2a).

168   The calculated d_{sub} parameter from DFT data (range 1.975 to 2.029 Å) also follow a smooth trend,

169   although with an inverse trend compared to a, i.e., decreasing with Bi content (Figure 2b). This curve

170   shows a steep downwards slope from tellurobismuthite (Bi_2Te_3) to tsumoite (BiTe), followed by a gentle

171   decreasing trend intersecting the d_{sub} axis at ~1.960 Å for a 0 atom.% Te composition (native bismuth).

172   The analytical data is noisier, but generally consistent (Figure 2c). The largest difference occurs for Bi_2Te

173   between our DFT results and the XRD data by Bos et al. (2012) with 0.012 Å difference (1.2 %), if we

174   ignore the TEM data for Bi_8Te_3, which differs from the present calculated range of d_{sub} by 0.050 Å

175   (Ciobanu et al. 2021). A good fit is obtained between DFT and the d_{sub} of Bi_2Te given by Zavylov et al.

176   (1976). Excellent agreement is obtained for tsumoite (BiTe) and tellurobismuthite (Bi_2Te_3) with data

177   from Yamana et al. (1979) and Atuchin et al. (2012), respectively.

178   To assess the differences between the DFT and experimental data we also undertook the PBEsol

179   functional method (Perdew et al., 2008). The results show that the for the endmember Bi_2Te_3, its

180   interlayer distance d_{sub} is underestimated relative to experimental data (i.e., 3.1%) although it reduces

181   the difference to a parameter (i.e., 0.5%). In contrast, the chosen PBE functional method gives a better

182   fit with the analytical data for d_{sub} (i.e., 0.2%, and by inference for the c parameter), which is most

183   important for the topic addressed here.

Models and simulations for the relaxed structures

184

185   The relaxed structures were plotted as models on the $[11\bar{2}0]$ zone axis to show the incremental width

186   of the 2k+3 modules and the bond topology across the range Bi_2Te_3-Bi_8Te_3 (Figures 3 and 4). Crystal

187   structure models for any phase in the group can be obtained from generic atomic coordinate calculations

188   following the same approach applied here for phases without initial cif files (i.e., Bi_5Te_3 and hedleyite).

189   The bond topology in such models would be orthogonal whereas the optimized structures, either obtained

190   from measurements or DFT relaxation will show slight distortions (Figures 3 and 4; left column). The

191   structural modules are schematically shown using the accretional formalism $[S(Bi_{2k}Te_3)\bullet L(Bi_{2(k+1)}Te_3)]$,

192   but these are not necessarily constrained relative to models using the $nBi_2\bullet mBi_2Te_3$ formula. This is

193   particularly apparent for phases such as BiTe tsumoite where two Bi_2Te modules (m=2) are linked by

194   one Bi_2 block (n=1) (Figure 4, upper panel). The atom fill models are shown for purposes of comparison

195   with the STEM simulations in Section 4.4 (Figures 3 and 4; right column).

Bond analysis

196

197   Bond distances for atoms in the asymmetric unit cells are shown in Figures 5 and 6. A comparison

198   of the minimum and maximum bond lengths for each structure is given in Figure 7. All seven structures

199   contain Bi-Te bonds but only two have Te-Te bonds and only six have Bi-Bi bonds. The Te-Te bonds

200   are longer than all other bonds and virtually the same for tellurobismuthite (3.694 Å) and tsumoite (3.692

201   Å) (Figure 7b). The relative proportion of Bi-Bi versus Bi-Te bonds increases from 1/6 in pilsenite to 5/6

202   in Bi_8Te_3 when considering the neighbouring bonds (Figure 5). The double module structures all fall

203   within this range, except for tsumoite which has a Bi-Bi / Bi-Te ratio of 1/10 (Figure 6).

204   The minimum for Bi-Te bond lengths increases by ~0.027 Å, from tellurobismuthite (3.080 Å) to

205   Bi_8Te_3 (3.107 Å), but this is stepwise, with the largest difference between tsumoite and pilsenite and no

206   discernible difference between Bi_2Te and hedleyite (Figure 7a). The maximum Bi-Te bond lengths

207   increase sharply between tellurobismuthite and pilsenite (~0.303 Å) but decrease gently towards Bi_8Te_3

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208   (Figure 7b). The minimum Bi-Bi bond lengths increase with Bi content, giving a relatively smooth curve

209   between tsumoite and Bi_8Te_3 with a difference of ~0.013 Å (Figure 7c). The maximum Te-Te bond

210   lengths are significantly longer than the Bi-Bi bonds (~0.159 Å; Figure 7d). In the four phases with more

211   than one Bi-Bi bond, the maximum Bi-Bi length tend to decrease with Bi content from Bi_5Te_3 to Bi_8Te_3,

212   but not continuously. Overall, minimum bond lengths show a consistent variation across the range

213   Bi_2Te_3-Bi_8Te_3, whereas the maximum is complicated by the presence of phases with Te-Te bonds (Figure

214   7). Bond lengths are important for understanding the variation of interlayer distances (d_{sub}), and the

215   analysis above indicates a strong split between phases that contain Te-Te bonds (larger d_{sub} values) and

216   those that do not.

217   **Simulation of STEM images and electron diffractions**

218   The relaxed structures are shown as simulations of STEM images and electron diffraction (ED)

219   patterns on the $[11\bar{2}0]$ zone axis in Figures 8 and 9. The images show a very good agreement with the

220   atom fill models on the same zone axis shown in Figures 3 and 4. The d_{sub} interval is also shown as two

221   simulations, one cropped from the ED patterns (upper strips) and a second one computed using the

222   displacement introduced by the fractional shift method of Amelinckx et al. (1989) and Frangis et al.

223   (1990) (lower strips) (see Ciobanu et al. 2009 for more details). The d_{sub}^* interval is important for

224   defining the modulation underpinning the increase in width of the modules. In this interval the number

225   of reflections (n_r) corresponds to N_1-1, equally distributed along d_{sub}^*. The length of the asymmetric unit

226   cell (d_{N_1}) along c corresponds to the layer stacks defining each unit cell. This is also marked as the

227   smallest interval, $d_{N_1}^*$ between two adjacent reflections along d_{sub}^*. The d_{N_1} interval for the structures

228   with double modules (S, L=1) approximates to the sum of S and L lengths.

229   All ED patterns show the two brightest reflections about the middle of d_{sub}^* with monotonic decrease

230   of the interval between them as the Bi concentration increases. Two modulation vectors are shown for

10

231   each phase. The $\mathbf{q}=\gamma \bullet c_{sub}^*$ vector defined by Lind and Lidin (2003) is based on displacive modulation

232   between chalcogen (Te, Se, S) and Bi atoms, where q is the homoatomic interval. The $\mathbf{q}$ modulation is

233   depicted up to third-order reflections along c^* (ED patterns in Figures 8 and 9). The γ values (1.800-

234   1.640 for the range Bi_2Te_3-Bi_8Te_3) are calculated as $3\bullet[(N_1+1)/2]/N_1$ for single modules (Figure 8) and

235    $3\bullet[(N_1+2)/2]/N_1$ for double modules (Figure 9). The γ values correlate with the chemical formula by the

236   relation $\gamma=3[S(k+2)+L(k+3)]/N_1$. The same γ range was shown by Ciobanu et al (2009) as selected area

237   electron diffraction (SAED), and accompanying TEM images, for natural phases where an ideal

238   d_{sub}~2.000 Å was assumed. The relaxed structures presented here show excellent agreement with those

239   SAEDs. Here, however, the STEM image simulations complement the ED patterns. Such simulations,

240   reproducing the atom models, efficiently describe the nature of phases from the tetradymite group

241   documented in prior STEM studies, e.g., Medlin et al. 2014 for tellurobismuthite, Ciobanu et al. (2021)

242   for Bi_8Te_3, and Cook et al., 2001 for $Bi_4(Te,S,Se)_3$ phases.

243   The second modulation vector $q_F = \gamma_F \bullet d_{sub}^*$ and $q_F = {}^i/_{N_1} \bullet d_{sub}^* = i \bullet d_{N_1}^*$ $(\gamma_F = {}^i/_{N_1} ; i =$

244    $S + L$), introduced by Frangis et al (1990), relates changes in module size and their respective number to

245   displacements in the basic substructure. This is particularly instructive for depicting the correlation

246   between the building modules (S, L) and electron diffractions patterns. We show that the interval defined

247   by the two brightest reflections about the middle of d_{sub} can be divided into two for all the double module

248   structures (Figure 9). The intensity variation along d_{sub}^* is simulated using the fractional shift method

249   following the adapted $\mathbf{q_F}$ model to include the homology for S, L modules related by k given in Ciobanu

250   et al. (2009). The displacements are quantifiable by fractional shifts between reflections in the derived

251   and basic structures (e.g., module '7' derived from module '5', module '9' derived from module '7',

252   etc.). The adapted model stipulates that the distance between the two brightest reflections, about the

253   middle of d_{sub}^* , equals $i \bullet d_N^*$ only when the shift at this position is minimal (equal to $1/N_b$; N_b=layers

254   in the basic structure).

255   A correlation between electron diffractions and chemical modules for a series group of phases is

256   typical of mixed layer compounds (Amelinckx et al. 1989). If we use the model with blocks of constant

257   width, as in the "Mod2 and 5" model of Imamov and Semiletov (1971) and Shelimova et al. (2000), the

258   number of component modules cannot be correlated with the modulation along d^*_{sub}. For example,

259   tsumoite would have n=1 and m=2, requiring three distinct modules instead of two (the '5' and '7'

260   modules considered here).

261   **DISCUSSION**

262   **Phase stability**

263   An evaluation of phase stability for each of the seven phases uses formation energy relative to

264   chemical composition. The stability of related compounds can be assessed by the convex hull method of

265   Gibbs (1973), with recent DFT applications to complex metallic compounds (Ma et al. 2017). The phase

266   stability is assessed by the distance between calculated formation energy ΔE_f and the energy of the

267   convex hull E_{hull}:

268
$$\Delta E_{distance} = E_{hull} - \Delta E_f, \qquad (2)$$

269   and those compounds plotting above the hull are considered unstable. We employ the model of Woodcox

270   et al. (2019) that stipulates a simple relationship between ΔE_f, the energy of phase E_{phase} and the energy

271   of composing atoms, in this case the energies of E_{Bi} and E_{Te} using the equation (3):

272
$$\Delta E_f = \frac{E_{phase} - pE_{Bi} - qE_{Te}}{p+q}, \qquad (3)$$

273   where p or q represent the number of Bi and Te atoms in the unit cell (phase), respectively (Table 2).

274   Calculated ΔE_f for the seven relaxed structures (Table 5) are plotted relative to atom.% Te in Figure 10a.

275   The convex hull is defined by the lines between endmembers and the compound with minimum ΔE_f, in

276   our case, bismuth, tellurium, and Bi_2Te_3 (tellurobismuthite), respectively. The calculated ΔE_f values are

277   negative for all phases and show a quasi-linear relationship along the Bi_2Te_3-Bi branch of the hull.

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278   The alternative alloy approach to Bi-Te phases (Woodcox et al. 2019) gives another hull that plots

279   above the one obtained here (Figure 10a). In this approach, the Bi_2Te_3-Te branch hosts two phases ($BiTe_2$

280   and $BiTe_{4.88}$) and the branch towards Bi hosts three phases corresponding to BiTe (tsumoite), Bi_2Te and

281     $Bi_{4.88}Te$. Our data show lower ground state energy for phases of the same composition and is thus more

282   plausible in terms of thermodynamic stability. This is also because our input structures are more

283   appropriate than the simple, Bi-Te alloy-type substitution used by Woodcox et al. (2019).

284   A second model for evaluation of phase stability was introduced by Park et al. (2021), using the

285   mixing energies of the 2- and 5-atom modules according to the formula,

286
$$E_{mixing} = \frac{E_{Total}^{nBi_2 \cdot mBi_2Te_3} - nE_{Total}^{Bi_2} - mE_{Total}^{Bi_2Te_3}}{N_{atom}}, \qquad (4)$$

287   where N_{atom} = total number of atoms in a given phase. In this case, the hull is determined between

288   endmembers Bi_2Te_3 (tellurobismuthite) and bismuth, rather than bismuth and tellurium. The diagram

289   obtained for the six phases using the relaxed structures when calculating E_{mixing} values for each compound

290   (Table 5, Figure 10b) shows Bi_4Te_3 (pilsenite) as the minimum of the hull (Figure10b). The energy for

291   each compound represents the ground state energy (E_0 in Table 3). The other compounds plot below the

292   branch between pilsenite and bismuth, indicating they are stable. BiTe (tsumoite) plots slightly above the

293   branch towards Bi_2Te_3. However, the distance between the point and the hull is ~1.400 meV/atom, a

294   small offset indicating that tsumoite may be stable.

295   Park et al. (2021) calculate E_{mixing} for the nine phases defined as superstructures in Bos et al. (2007)

296   but using lattice parameters (*a* and *c*) from previous experimental studies. Park et al. (2021) obtained a

297   hull centered on Bi_2Te, rather than pilsenite as the minimum E_{mixing} point (Figure 10b). Except for

298   hedleyite, all the other five intermediate phases plot above the hull. Nonetheless, Park et al. (2021)

299   considered these phases as stable since the distance to the hull is within a cutoff of ~4.500 meV/atom.

300   We point at the significant differences between the results of Park et al. (2021) and our own, particularly

13

301   when comparing the same compounds, Bi_7Te_3 (hedleyite), Bi_2Te, and $BiTe$ (tsumoite). We consider that

302   the energy differences are due to the lattice parameters used, which were fixed lattice parameter values

303   in Park et al. (2021) rather than obtained as the result of structure relaxation as in our study. Our data

304   show a better fit to the convex hull and are therefore more credible in terms of energetic stability.

305   Following the ideas of Park et al. (2021) that intermediate compounds in a modular series can be

306   obtained by mixing energies of the constituent units, we formulate the energy of mixing using the

307   accretional model as follows:

308
$$E_{mixing} = \frac{E_{Total}^{S \cdot Bi_{2k}Te_3.L \cdot Bi_{2(k+1)}Te_3} - S \cdot E_{Total}^{Bi_{2k}Te_3} - L \cdot E_{Total}^{Bi_{2(k+1)}Te_3}}{N_{atom}}. \qquad (5)$$

309   Applying this to the three double module phases (S=1, L=1), we obtained E_{mixing}=1.420 meV/atom for

310   tsumoite (5.7), -0.040 meV/atom for Bi_5Te_3 (7.9), and -0.020 meV/atom for hedleyite (9.11), values very

311   close to zero. This implies that mixing between the incremental modules is close to ideal. Further

312   calculation for other intermediate phases (S>1, L>1) would test this statement.

313   **The γ - d_{sub} relationship: where does the series end?**

314   The "Mod2 and 5" model of Imamov and Semiletov (1971) and Shelimova et al. (2000) is popular

315   because it allows the separation of two blocks with different thermoelectric properties and electronic

316   band structures (e.g., Bos et al. 2007; 2012; Park et al. 2021). In this model, if m=0, bismuth becomes

317   the end member of the series. This is, however, impossible in the mixed layer compound model, or the

318   homologous series described by the accretional modules (Frangis et al. 1989; Ciobanu et al. 2009), in

319   which Te will always be part of the component modules. This implies the end of the series is close to but

320   never meets native bismuth.

321   The incremental decrease in d_{sub} across the series (Figure 2b, c) shows the size of this interval

322   moves towards a constant value for phases within the compositional range ~45 to 27 atom.% Te. A better

323   description of d_{sub} across the series is obtained using γ modulation (Figure 11). The fitted curve shows

14

324   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),

325   for example. Taking the values for interatomic distances in native bismuth reported for $R\overline{3}m$ space for

326   temperatures between 4.2 K and 298 K we note that these are in a comparable range (1.966-1.977 Å;

327   Wyckoff, 1963; Schiferl and Barrett, 1969). The d_{sub} of Bi_7Te_3 (hedleyite) is at the upper limit whereas

328   d_{sub} for single module phases with k≥4 falls within the range reported for native bismuth.

329   The incremental decrease in d_{sub} corresponds to phases lacking Te-Te bonds, i.e., towards Bi-rich

330   compositions from Bi_8Te_9, a phase with 5.7.7 module stack (Figure 12). Such behavior can be rationalized

331   in terms of the relative contributions of Bi-Bi and Bi-Te bond lengths to the interlayer intervals across

332   the asymmetric unit cell along *c* (Figure 12). If we consider the ideal d_0 =2.000 Å as a baseline, the

333   weighted, average values of Bi-Te bonds for each phase lead to an increase of d_{sub} whereas the Bi-Bi

334   bonds have the opposite effect. The total contribution (sum of the two calculated values for each phase)

335   shows a gentle slope from Bi_4Te_3 (pilsenite) to Bi_8Te_3 (Figure 12). The offset of d_{sub} decreases relative

336   to ideal d_0 and we predict it will stay constant for phases with $k \gtrsim 10$.

337   Based on this consideration, we define three subgroups in terms of slope variation in d_{sub}, the

338   crystal-structural parameter that defines derivation of the series from the archetypal tetradymite structure:

339   (i) Bi_2Te_3 (tellurobismuthite) -Bi_8Te_9 – steep slope; (ii) Bi_8Te_9-$Bi_{14}Te_3$-gentle slope, and (iii) $Bi_{14}Te_3$ to

340     $Bi_{100}Te_3$, expanding to $Bi_{\infty}Te_3$ – almost flat (values <<0.001 Å). This implies that phases in range (iii),

341   i.e., k>7, should be considered as disordered native bismuth rather than discrete members of the

342   tetradymite group. The structures of Bi-tellurides with k>7 would be undistinguishable from native Bi

343   since they would have the same d_{sub} values. On the other hand, regular insertion of Te layers at such

344   large intervals into a bismuth matrix must be considered as very unlikely.

345   **SUMMARY AND IMPLICATIONS**

346

347   We have used density functional theory to obtain seven structures spanning the range Bi_2Te_3-Bi_8Te_3

348   in the tetradymite homologous series with formula: $S[Bi_{2k}Te_3)L[(Bi_{2(k+1)}Te_3)]$; k=1-4. The structures

349   represent single modules [S=1, L=0; $Bi_2Te_{3(}$ tellurobismuthite), Bi_4Te_3 (pilsenite), Bi_2Te and Bi_8Te_3] and

350   double modules [S=1, L=1; BiTe (tsumoite), Bi_5Te_3 and Bi_7Te_3 (hedleyite)] within this range. The

351   relaxed structures show systematic increase in a and decrease in interlayer distance (d_{sub}). We observe

352   a sharp decrease in d_{sub} between tellurobismuthite (2.029 Å) and tsumoite (1.996 Å), followed by an

353   incremental decrease to Bi_8Te_3 (1.975 Å) with Bi content.

354   Models for the relaxed structures are used to show representative atomic arrangements, bonding, and

355   bond distances for the asymmetric unit cells. Variation in minimum and maximum bond lengths show

356   the series can be split into two parts, corresponding to structures with and without Te-Te bonds. The

357   latter are larger than the Bi-Bi and Bi-Te bonds, reflecting the variation in d_{sub}.

358   Scanning transmission electron microscopy simulations for the relaxed structures show a perfect

359   match with the atom models. Simulated electron diffractions and the reflection modulation along the $c*$

360   show a good fit with published analytical data and the mixed-layer compound theory. The distribution

361   of reflections and their intensity variation along $d^*_{sub} = 1 / d_{sub}$ is described by two modulation vectors,

362    $\mathbf{q}=\gamma \bullet c^*_{sub}$ (γ =1.800-1.640) and $\mathbf{q_F}=\gamma_F \bullet d^*_{sub}$ (γ_F =0.200-0.091). The γ_F parameter underpins the S, L

363   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_2Te_3,

364   whereas γ relates to variation of the d_{sub}.

365   Density functional theory is also used to calculate the formation energies of the seven phases. This

366   shows that the phases in the range $BiTe$-Bi_8Te_3 lie on the Bi-Bi_2Te_3-Te convex hull, implying they are

367   thermodynamically stable. However, further studies employing phonon calculations are required to

368   assess whether these phases can be experimentally synthesised.

369   We have built a model that describes the relationship between γ and d_{sub}. This allows us to predict

370   values for d_{sub} beyond the compositional range considered here, e.g., for k values of 5, 7, 10, or even

16

371   50. These values are within the analytical range of interlayer distance in native bismuth. The tetradymite

372   group is therefore constrained within the γ range between 1.800 (tellurobismuthite) to 1.588 ($Bi_{14}Te_3$),

373   beyond which γ no longer represents the tetradymite group but rather disordered native bismuth.

374   The present study carries implications for mineral nomenclature and classification as well as for the

375   technological applications of Bi-chalcogenides. The framework presented here allows for the prediction

376   of structures for any intermediate phases within the Bi-rich series of the tetradymite group. The same

377   approach can be extended to other series comprised of mixed-layer compounds, e.g., the aleksite series

378   (Cook et al. 2019) and other chalcogen-rich series within the tetradymite group, or REE-fluorocarbonates

379   of the bastnäsite-synchysite group (Ciobanu et al. 2017; 2022).

380   Applying the correct structural model should also help to understand the variation in the

381   thermoelectric or topological insulating properties of new compounds in the tetradymite group (Bos et

382   al., 2007; 2012; Goldsmid, 2014).

383   Crystal structures are also fundamental for calculation of thermodynamic properties, which in turn

384   places constraints on phase relations in the system Bi-Te (Mao et al., 2018; Hasanova et al., 2021). A

385   refined phase diagram for the system Bi-Te is important for synthesis of new compounds and for

386   understanding the strong association between Bi-tellurides and gold observed in nature.

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

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515   **Figure captions**

516   **Figure 1.** Energy versus volume curves for the nine crystal structures corresponding to phases

517   as labelled, including elemental Bi and Te. Open black circles are total energies calculated from

518   DFT. Solid black curves are constructed by fitting the equation of state (1). The parameters

519   listed in Table 3 are obtained from the fitted curve. Native bismuth and tellurium are included

520   for the calculation of formation energy in equation (3).

521   **Figure 2.** Lattice parameters a (a) and d_{sub} (b,c) as a function of atom.% Te for the seven

522   studied phases. Data from literature (Table 1 and additional DFT studies) are indicated for

523   comparison. The value of d_{sub} for Bi_8Te_3 from Ciobanu et al. (2021) is included although is out

524   of the range calculated here. (a) The present data plots along a curve above the one refined from

525   literature (dashed line). The DFT data for tellurobismuthite is given with error bars. Note that

526   the mean value for previously published DFT data (Cheng and Ren 2011; Vilaplana et al., 2011;

527   Zurhelle et al., 2016) is midway between other published data and present study. The plot in (c)

528   is a close up of (b). Abbreviations: Hed—hedleyite; Pls—pilsenite; Tbs—tellurobismuthite;

529   Tsm—tsumoite.

530   **Figure 3.** Atom models (ball and stick to the left, atom filling to the right) for the relaxed

531   structures of the single module phases (k=1-4; S=1; L=0) as labelled viewed on $[11\bar{2}0]$ zone

532   axis. Atom-layer modules and their respective widths are marked by numbers at the top. The

23

533   sequence of atoms (red─Bi; green─Te) typifying the structure is shown along ($hkil$) planes, i=-

534   (h+k). Corresponding crystallographic information data files (cif.) included as Deposit items.

535   **Figure 4.** Atom models (ball and stick to the left, atom filling to the right) for the relaxed

536   structures of the double module phases (k=1-3; S=1; L=1) as labelled viewed on [$11\bar{2}0$] zone

537   axis. Atom-layer modules and their respective widths are marked by numbers at the top. The

538   sequence of atoms (red─Bi; green─Te) typifying the structure is shown along ($hkil$) planes, i=-

539   (h+k). Corresponding crystallographic information data files (cif.) included as Deposit items.

540   **Figure 5.** Bonds and their respective lengths for atoms (red─Bi; green─Te) within the

541   asymmetric unit cell (viewed on [$11\bar{2}0$] zone axis) for single module phases as labelled.

542   Maximum and minimum bond lengths are marked in red and tabulated for each phase to enable

543   an easier comparison. Projection of bond lengths along the c axis is marked for pilsenite, Bi_2Te

544   and Bi_8Te to illustrate the contribution of Bi-Bi and Bi-Te bonds to the d-subcell plotted on

545   Figure 12). Note that Te-Te bonds (with greatest length) are present only in tellurobismuthite.

546   **Figure 6.** Bonds and their respective lengths for atoms (red─Bi; green─Te) within the

547   asymmetric unit cell (viewed on [$11\bar{2}0$] zone axis) for double module phases as labelled.

548   Maximum and minimum bond lengths are marked in red and tabulated for each phase to enable

549   an easier comparison.

550   **Figure 7.** Minimum and maximum bond lengths for all seven structures (data from Figures 5

551   and 6) plotted against atom.% Te. Differences between largest and smallest values are marked

552   adjacent to each diagram. (a, b) Minimum and maximum Bi-Te bonds. Note that all seven phases

553   contain such bonds. (c,d) Minimum Bi-Bi and maximum Bi-Bi and Te-Te bonds. Note that

554   tellurobismuthite lacks Bi-Bi bonds (in (c) and that pilsenite has only one Bi-Bi bond with value

24

555   within the range of minimum Bi-Bi bonds (not plotted on d). See text for additional details.

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

557   **Figure 8.** STEM simulations (left) and electron diffraction (ED) patterns (right) obtained on

558    $[11\bar{2}0]$ zone axis for the relaxed structures corresponding to the single module phases as

559   labelled. Values for a, c and d_{sub} parameters correspond to those given in Table 4. The two

560   strips under each image show the d^*_{sub} interval cropped from ED patterns (area rectangle) and

561   computed intensity variation for reflections across this interval, displaying the number of

562   reflections and the two modulation vectors (as marked). The atom sequence corresponding to

563   each structure is marked by overlays on the images. Compare the simulations with the models

564   shown in Figure 3. Third order satellite reflections underpin the **q** modulation along c^* (marked

565   by arrows and circles). Note that the simulations for unnamed Bi_2Te were performed using space

566   group $P1$ instead of $P\bar{3}m1$. See text for additional details.

567   **Figure 9.** STEM simulations (left) and electron diffraction (ED) patterns (right) obtained on

568    $[11\bar{2}0]$ zone axis for the relaxed structures corresponding to the double module phases as

569   labelled. Values for a, c and d_{sub} parameters correspond to those given in Table 4. The two

570   strips under each image show the d^*_{sub} interval cropped from ED patterns (area rectangle) and

571   computed intensity variation for reflections across this interval, displaying the number of

572   reflections and the two modulation vectors (as marked). The atom sequence corresponding to

573   each structure is marked by overlays on the images. Compare the simulations with models

574   shown in Figure 4. Third order satellite reflections underpin the **q** modulation along c^* (marked

575   by arrows and circles). Note that the simulations for tsumoite were performed using space group

576    $P1$ instead of $P\bar{3}m1$.

577   **Figure 10.** Phase stability diagrams using the convex Hull approach. (a) Plot showing formation

578   energy from DFT calculations (Table 5) versus atom.% Te for the seven studied phases shown

579   in red (single modules) and green (double modules). A convex hull is defined by bismuth (Bi),

580   tellurobismuthite (Tbs) and tellurium (Te). The other six phases lie on the Bi-Tbs side (full line),

581   whereas the Tbs-Te side (marked by dashed line) is empty. The convex hull Bi-BiTe-Te

582   obtained from DFT calculations of Bi-Te alloys (marked as blue circles) (Woodcox et al. 2019)

583   is shown for comparison. (b) Plot showing energy mixing (equation 4 from Park et al. 2021)

584   versus n/(n+m) using the Mod 2 and 5 model. The convex hull (red line) from our data (phases

585   as red circles) is between Tbs, pilsenite (Pls) and Bi. All phases, except tsumoite (Tsm) plot

586   underneath the Pls-Bi side, indicating stability. Tsumoite, plotting above the Pls-Tbs side, is

587   also likely stable given the distance to the hull (~1.400 meV/atom). In contrast, DFT data from

588   Park et al. (2021), using fixed lattice constants for the structures is defined by a Tbs-Bi_2Te-Bi

589   convex hull (data in blue). The distances to the hull for Tsm is larger than the fit obtained here

590   for relaxed structure of this compound. Abbreviation: Hed—hedleyite.

591   **Figure 11.** Model for the relation between d subcell and parameter γ showing that the

592   tetradymite series extends from tellurobismuthite to $Bi_{14}Te_3$ (k=7). The fitted curve (d_{sub} =

593   6.457e-10* $γ^{31.15}$ + 1.973) using calculated d subcell and γ values for the seven phases (in red)

594   allows prediction of d subcell for phases with higher k (k=5, 7, 10, 50 shown in green). The

595   slope of this curve has three domains with sharp, gentle, and flat trends, respectively (marked

596   as slopes 1-3). The boundary between slope 1 and 2 is marked by the first phase in which the

597   stacking sequence indicates a lack of Te-Te bonds (Bi_8Te_9, stack modules 5.7.7, shown in blue).

598   The boundary between slope 2 and 3 is marked by the composition $Bi_{14}Te_3$, the point on the

599   curve from where d-subcell becomes constant. Therefore, the phases in the slope 3 region should

600   be considered disordered native bismuth rather than compounds from the tetradymite series.

601   Interval of analytical data for interlayer distance in native bismuth in yellow.

602 **Figure 12.** Contribution of bond lengths to d-subcell for the three single module phases without

603 Te-Te bonds, pilsenite (Pls), Bi_2Te, and Bi_8Te_3. This can be seen as the difference between

604 weighted average bond lengths and reference d_0 which is taken as a baseline. The Bi-Te and Bi-

605 Bi bonds show opposing trends, and the total contribution of the two bond types decreasing from

606 Pls to Bi_8Te_3, in agreement with calculated d_{sub} values (Table 4).

Table 1. Background and crystal structures with published information on unit cell parameters.

Formula, Mineral name	Explicit formula	k	Module stacks	N_1	Space Group	N total	c calc (Å)	Reference(s)	c (Å)	a (Å)	d subcell (Å)
Bi_2Te_3 tellurobismuthite	Bi_2Te_3	1	5	5	$R\bar{3}m$	15	30	*Atuchin et al. (2012)*	30.502	4.390	2.033
								Nakajima (1963)	30.497	4.386	2.033
								Feutelais et al (1993)	30.440	4.395	2.029
								Imamov and Semiletov (1971)	30.57	4.380	2.038
								[a]Lange (1939)	30.423	4.369	2.028
$BiTe$ tsumoite	Bi_6Te_6	1	5.7	12	$P\bar{3}m1$	12	24	*Yamana et al. (1979)*	24.002	4.423	2.000
								Imamov and Semiletov (1971)	23.97	4.400	1.998
Bi_4Te_3 pilsenite	Bi_4Te_3	2	7	7	$R\bar{3}m$	21	42	*Yamana et al. (1979)*	41.888	4.451	1.995
								Imamov and Semiletov (1971)	41.870	4.43	1.994
Bi_5Te_3 (unnamed)	$Bi_{10}Te_6$	2	7.9	16	$R\bar{3}m$	48	96	[b]*Ciobanu et al. (2009)*	95.05	4.500	1.980
Bi_2Te (unnamed)	Bi_6Te_3	3	9	9	$P\bar{3}m1$	9	18	*Bos et al. (2012)*	17.922	4.469	1.991
								[c]Zav'ylov et al. (1976)	17.805	4.4733	1.978
Bi_7Te_3 hedleyite	$Bi_{14}Te_6$	3	9.11	20	$R\bar{3}m$	60	120	*Imamov and Semiletov (1971)*	119.04	4.47	1.984
								Warren and Peacock (1945)	119	4.47	1.983
Bi_8Te_3 (unnamed)	Bi_8Te_3	4	11	11	$R\bar{3}m$	33	66	[b]*Ciobanu et al. (2021)*	63.000	4.400	1.909

[a] structure given with rhombohedral axes as $a=b=c=10.45$ Å, $\alpha=\beta=\gamma=24.13°$

[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.

	Bi_2Te_3	BiTe	Bi_4Te_3	Bi_5Te_3	Bi_2Te	Bi_7Te_3	Bi_8Te_3	Bi	Te
Number of atoms	15	12	21	48	9	60	33	6	3
Formula units	3	6	3	6	3	6	3	1	1
KPOINTS mesh	14x14x2	20x20x4	18x18x2	21x21x1	16x16x4	26x26x1	30x30x2	18x18x6	12x12x12

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.

	E_0/atom (eV)	V_0/atom ($Å^3$)	K_0 (GPa)	K_0'	Ref.
Bi_2Te_3	-3.96	34.50	33	6.3	This work
		33.93	41		[1]
BiTe	-4.00	34.51	40	5.0	This work
		33.89	41		[2]
Bi_4Te_3	-4.03	34.60	40	5.2	This work
		34.22	41		[2]
Bi_5Te_3	-4.05	34.74	39	5.2	This work
		33.18	41		[3]
Bi_2Te	-4.07	34.83	38	5.6	This work
		34.44	39		[4]
Bi_7Te_3	-4.08	34.88	39	5.1	This work
		34.32	36		[5]
Bi_8Te_3	-4.09	34.93	39	5.1	This work
		32.00	33		[3]
Bi	-4.19	35.49	36	5.7	This work
		35.07	38		[6]
Te	-3.41	33.30	29	5.8	This work
		33.94	48		[7]

[1] Atuchin et al. (2012)
[2] Yamana et al. (1979)
[3] Ciobanu et al. (2009)
[4] Bos et al. (2012)
[5] Imamov and Semiletov (1970)
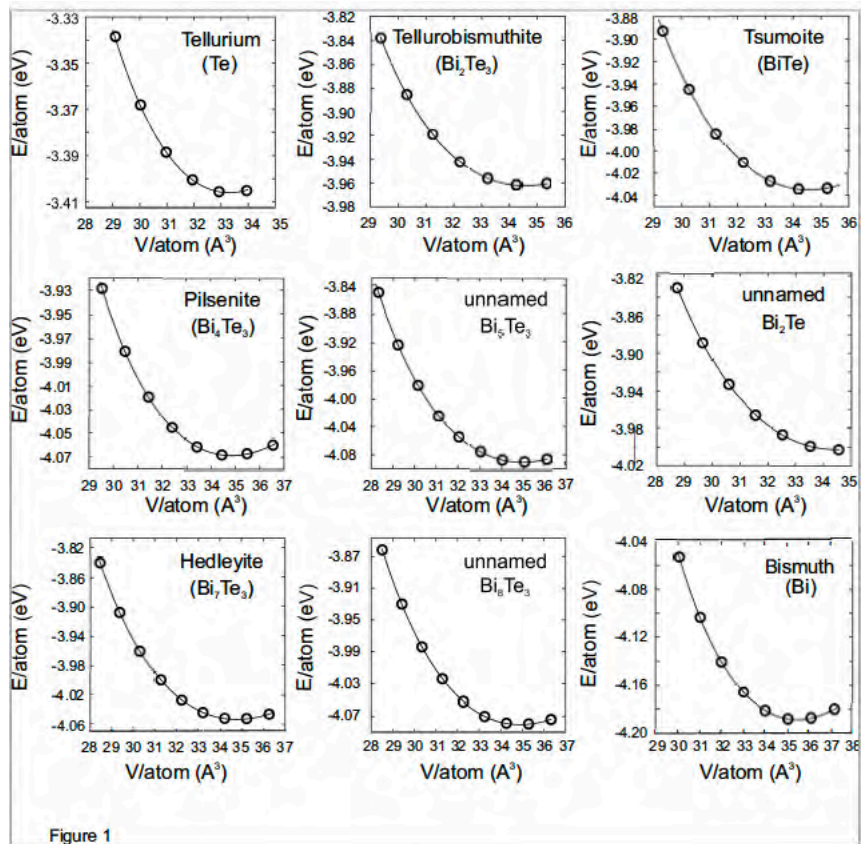[6] Schiferl and Barrett (1969)
[7] Adenis et al. (1989)
All bulk modulus data are from Woodcox et al. (2019)

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.

Name	Explicit formula, (N1)	Space group	a (Å)	c (Å)	Volume (Å³)	Z	density (g/cm³)	d_{sub} (Å)
Tellurobismuthite	Bi_2Te_3 (5)	$R\bar{3}m$	4.431	30.433	517.561	3	7.7079	2.029
Tsumoite	Bi_6Te_6 (12)	$P\bar{3}m1$	4.468	23.950	414.059	6	8.0995	1.996
Pilsenite	Bi_4Te_3 (7)	$R\bar{3}m$	4.487	41.678	726.691	3	8.3552	1.985
Bi_5Te_3	$Bi_{10}Te_6$ (16)	$R\bar{3}m$	4.499	95.133	1667.607	6	8.5309	1.982
Bi_2Te	Bi_6Te_3 (9)	$P\bar{3}m1$	4.508	17.811	313.463	3	8.6709	1.979
Hedleyite	$Bi_{14}Te_6$ (20)	$R\bar{3}m$	4.514	118.613	2093.081	6	8.7863	1.977
Bi_8Te_3	Bi_8Te_3 (11)	$R\bar{3}m$	4.519	65.182	1152.771	3	8.8798	1.975

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

	Bi_2Te_3	BiTe	Bi_4Te_3	Bi_5Te_3	Bi_2Te	Bi_7Te_3	Bi_8Te_3
E_f (eV)	-242.533	-205.250	-181.048	-158.563	-141.000	-126.667	-114.909
E_{mixing} (meV/atom)	0.000	-3.139	-7.810	-6.979	-6.259	-5.400	-4.667

Figure 1

(a)

Bi₈Te₃ Hed Bi₂Te Bi₅Te₃ Pls Tsm Tbs

a (Å)

atom.% Te

(b)

△ Warren and Peacock (1945)	▲ Ciobanu et al. (2021)
○ Nakajima (1962)	◇ Bos et al. (2012)
□ Imamov and Semiletov (1970)	○ This study
◇ Zav'ylov et al. (1976)	◆ other DFT data
△ Yamana et al. (1979)	
○ Feutelais et al. (1993)	
△ Ciobanu et al. (2009)	

d subcell (Å)

Bi₈Te₃ Hed Bi₂Te Bi₅Te₃ Pls Tsm Tbs

shifted 0.02

atom.% Te

(c)

d subcell (Å)

Tsm
Pls
Bi₅Te₃
Bi₂Te
Hed
Bi₈Te₃
upper limit d Bi

atom.% Te

Figure 2

Tellurobismuthite Bi_2Te_3

5

5

$(1\bar{1}05)$

5 atoms

c

Unnamed Bi_2Te

9

9

$(1\bar{1}06)$

9 atoms

c

Pilsenite Bi_4Te_3

7

7

$(1\bar{1}07)$

7 atoms

c

Unnamed Bi_8Te_3
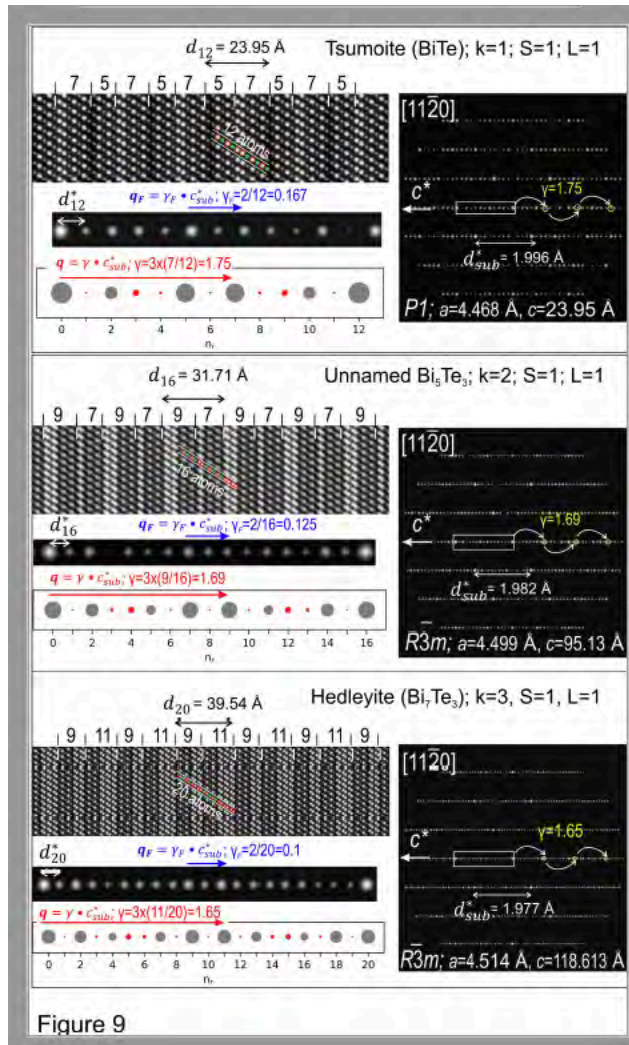
11

11

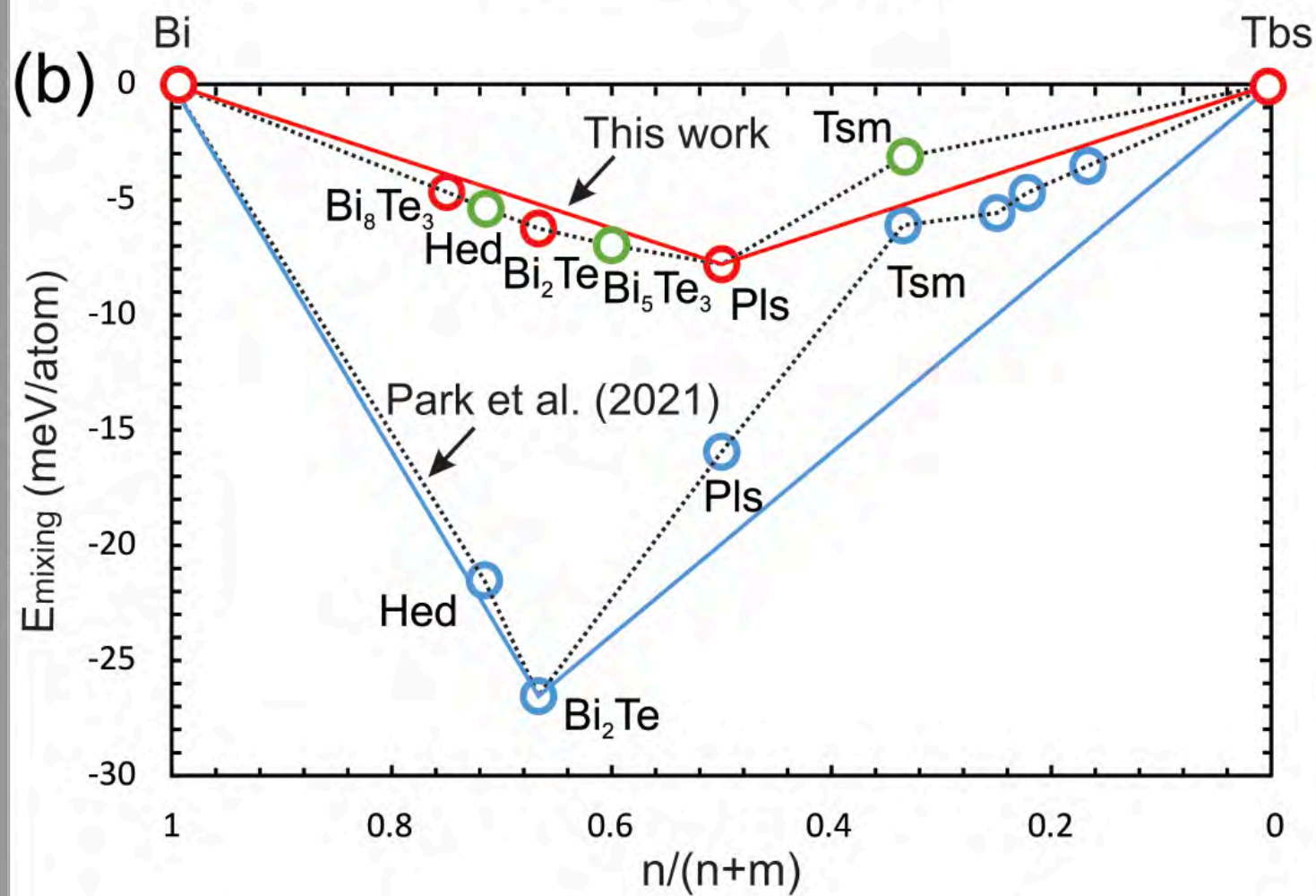$(1\bar{1}0.11)$

11 atoms

c

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7
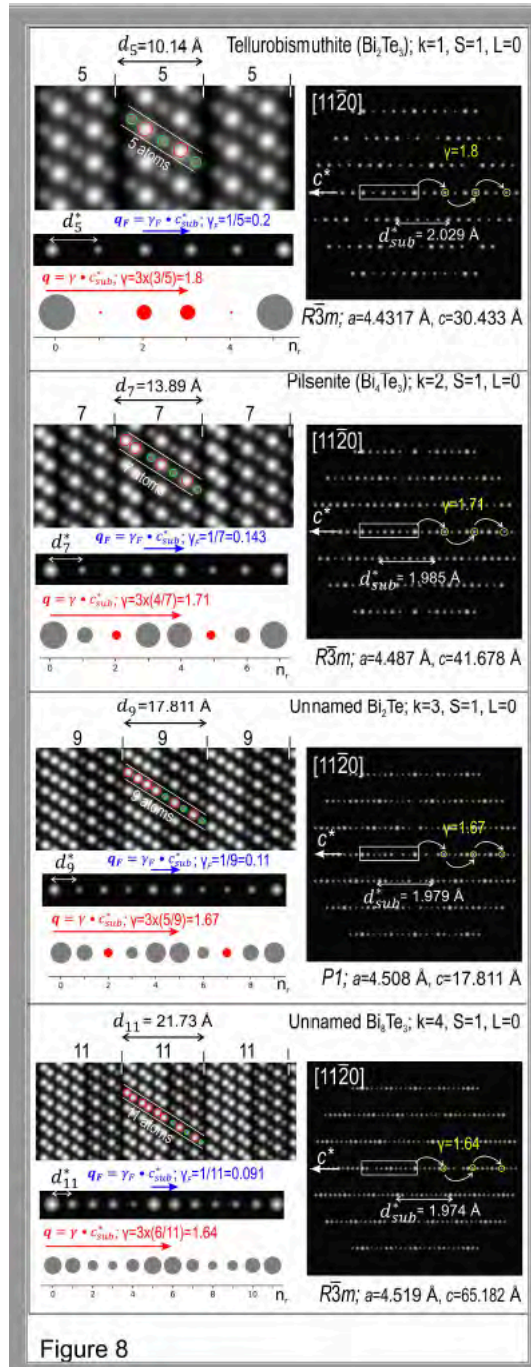
Figure 8

Figure 9

Figure 10

Figure 11

Figure 12