**Abstract:** $\text{Bi}_8\text{Te}_3$ is a member of the tetradymanite homologous series, previously shown to be compositionally and structurally distinct from hedleyite, $\text{Bi}_7\text{Te}_3$, yet inadequately characterized structurally. The phase is identified in a sample from the Hedley district, British Columbia, Canada. Compositions are documented by electron probe microanalysis and structures are directly imaged using high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM). Results confirm that $\text{Bi}_8\text{Te}_3$ has an 11-atom layer structure, in which three Bi-Bi pairs are placed adjacent to the five-atom sequence (Te-Bi-Te-Bi-Te). $\text{Bi}_8\text{Te}_3$ has trigonal symmetry (space group $R\overline{3}m$) with unit cell dimensions of $a = ~4.4$ Å and $c = ~63$ Å calculated from measurements on representative electron diffraction patterns. The model is assessed by STEM simulations and ED5 mapping, all displaying good agreement with the HAADF STEM imaging. Lattice-scale intergrowths are documented in phases replacing $\text{Bi}_8\text{Te}_3$, accounting for the rarity of this phase in nature. These results support prior predictions of crystal structures in the tetradymanite homologous series from theoretical modeling and indicate that other phases are likely to exist for future discovery. Tetradymanite homologues are mixed-layer compounds derived as one-dimensional superstructures of a basic rhombohedral sub-cell. Each member of the series has a discrete stoichiometric composition and unique crystal structure.

**Keywords:** $\text{Bi}_8\text{Te}_3$; lattice-scale intergrowths; tetradymanite homologous series; HAADF STEM

1. Introduction

The tetradymanite homologous series ($\text{Bi}_x\text{X}_y$, where $X = \text{Te, Se, S}$) comprises phases derived from a simple 5-atom layer represented by tellurobismuthite, $\text{Bi}_2\text{Te}_3$, and isostructural phases, including tetradymanite, $\text{Bi}_2\text{Te}_5$ [1,2]. To provide a systematic homology for the series enabling prediction of the structural arrangements for any stoichiometry, Ciobanu et al. [2] presented a model drawing on seminal work by many authors since the 1960s [3–9], in which constituent layer stacks of different size (5-, 7-, 9-, 11-atom, etc.) are combined in various proportions: $S'(\text{Bi}_{2k}X_3)L'(\text{Bi}_{2(k+1)}X_3)$ ($k \geq 1$; $X = \text{chalcogen}; S', L'$ = number of short and long modules, respectively).

This approach was introduced as a working model based on a high-resolution transmission electron microscopy (HR-TEM) study of phases in the extended compositional range $\text{Bi}_2\text{Te}_3$–$\text{Bi}_8\text{Te}_3$ [2]. This study showed that each phase is a $N$-fold superstructure of a rhombohedral sub-cell with $c/3 = d~0.2$ nm, where $N$ is the number of layers in the stacking sequence. Electron diffraction (ED) patterns, displaying the two brightest reflections about the middle of $d^*$, are described by a monotonic decrease of two displacive modulations with an increase in Bi. Such displacements are quantifiable by fractional shifts between reflections in the derived and basic structures [2].
All structures of named minerals in the tetradymite homologous series, their synthetic analogues, and other experimental products in the system Bi-X (e.g., [10–12]) can be interpreted in the same way, allowing derivation of a systematic group homology (e.g., [1,2]). Such an approach also infers that each individual member of the series should be stoichiometric in composition.

In this scheme [2], tetradymite and isostructural Bi$_2$X$_3$ phases, such as tellurobis-muthite, paraganajautilite (Bi$_2$Se$_3$), kawazulite (Bi$_2$Te$_2$Se), and skippenite (Bi$_2$Se$_2$Te), are represented by simple repeats of a single 5-atom X-Bi-X-Bi-X layer. Members of the Bi$_4$X$_3$ subgroup (ikunolite, laitakarite, pilsenite, joséite-A, and joséite-B) share 7-atom layers only [13]. Named phases in the Bi$_3$X$_3$ (BiX) subgroup, tsumoite, ingodite, nevskite, and telluronevskite, are composed of a combination of 5- and 7-atom layers. Towards Bi-rich compositions in the system Bi-X, hedleyite (Bi$_7$Te$_3$) was previously the only named phase and is proposed to consist of a combination of 9- and 11-atom layers [2]. This has prompted efforts to obtain empirical support for the compositions Bi$_2$Te (i.e., Bi$_6$Te$_3$) and Bi$_8$Te$_3$ reported in the literature [14,15] as the ‘missing’ 9- and 11-atom only structures.

This contribution describes and provides a direct visualization of Bi$_8$Te$_3$ in a specimen from the Good Hope Mine, Hedley, British Columbia, Canada, using high-angle annular dark field scanning transmission electron microscopy (HAADF STEM) imaging and STEM simulations. The crystal structure model built for Bi$_8$Te$_3$ using measurements from electron diffractions is in agreement with the modularity in the series, and this model is used for STEM simulations. Bi$_8$Te$_3$ co-exists with joséite-B and features an 11-atom layer stack (Bi-Bi-Bi-Te-Bi-Te-Bi-Te-Bi-Bi-Bi), thus making it compositionally and structurally distinct from hedleyite. This contribution evaluates the role of lattice-scale intergrowths that can be correlated with non-stoichiometric compositions in the Bi$_4$Te$_3$–Bi$_2$Te range and identifies the likely existence of other, additional members of the tetradymite homologous series.

2. Microanalytical Methodology

Two polished blocks were analyzed: (1) H163b, containing patches of bismuth minerals within skarn, and (2) H1-H2, a mounted chip with lamellae of Bi$_8$Te$_3$ within joséite-B. The same lamellae in H1-H2 were also analyzed by [2] using conventional HR TEM. The nanoscale study was carried out on three foils prepared from the two polished blocks.

2.1. Electron Probe Microanalysis

Quantitative compositions were determined using a Cameca SX-Five electron probe microanalyzer (EPMA), equipped with five tunable wavelength-dispersive spectrometers. The instrument runs PeakSite v6.5 software for microscope operation, and Probe for EPMA software (distributed by Probe Software Inc., Eugene, OR, USA) for all data acquisition and processing. Operating conditions utilized were 20 kV/20 nA with a focused beam.

The full list of elements analyzed along with count times, nominal detection limits, and primary and interference standards are presented in the Supplementary Materials, Tables S1 and S2. Matrix corrections of Armstrong-Love/Scott $\varphi(pz)$ [16] and Henke MACs were used for data reduction.

Traditional two-point backgrounds were acquired. Due to complex off-peak interferences in these sample matrices, the shared background function of Probe for EPMA was utilized. This function allows the collected background positions of elements on the same spectrometer be used for all elements on that spectrometer, allowing multipoint backgrounds to be applied to each element. However, in simple background regions, a traditional 2-point linear fit was still used.

In addition, the first elements acquired on each spectrometer were analyzed using the Time-Dependent Intensity (TDI) correction feature of Probe for EPMA (e.g., [17]). Using this method, the decay of X-ray counts over time is measured and modeled to return a $t = 0$ intercept, and from this a concentration is calculated, minimizing the impact of element migration.
2.2. Nanoscale Analysis

Thinned (<100 nm) foils for TEM investigation were prepared from polished blocks using a FEI-Helios nanoLab dual-focused ion beam and scanning electron microscope (FIB-SEM), as outlined by Ciobanu et al. [18]. Each TEM foil was attached to a copper grid.

Foils were analyzed using high-angle annular dark field (HAADF) scanning TEM (STEM) imaging and energy dispersive X-ray spectrometry (EDS) STEM mapping using an ultra-high-resolution, probe-corrected, FEI Titan Themis S/TEM, operated at 200 kV. This instrument is equipped with a X-FEG Schottky source and Super-X EDS geometry. The Super-X EDS detector provides geometrically symmetric EDS detection with an effective solid angle of 0.8 sr. Probe correction delivered sub-Ångstrom spatial resolution, and an inner collection angle greater than 50 mrad was used for HAADF imaging with a Fischione detector. Image acquisition was undertaken using FEI software, TIA (v4.15), and complementary imaging by the drift-corrected frame integration package (DCFI) included in the Velox (v. 2.13.0.1138) software. Various filters (Radial Wiener, high-pass, average, and Gaussian blur) were used to eliminate noise and/or enhance the images. EDS data acquisition and processing was carried out using Velox software. Indexing of diffraction patterns was conducted with WinWulff © (v1.6) (JCrystalSoft) and publicly available data from the American Mineralogist Crystal Structure Database (http://rruff.geo.arizona.edu/AMS/amcsd.php, accessed between April and August, 2021). Crystal structure models were generated in CrystalMaker® (v10.5.7) and image simulations using STEM for xHREM™ (v4.1) software.

All instruments are housed at Adelaide Microscopy, The University of Adelaide.

3. Results

3.1. Specimen Petrography

Bi$_8$Te$_3$ occurs within disseminations of bismuth minerals (dominantly joséite-B and native bismuth, with subordinate hedleyite and traces of joséite-A) in a hedenbergite skarn (Figures 1 and 2). Micron- to nano-scale compositional and structural characterization of joséite-A and -B is described by Cook et al. [13].

| Table 1. Microprobe data for hedleyite and unnamed Bi$_8$Te$_3$. |
|---------------|-----------------|---------------|---------------|-----------------|-----------------|
|               | Hedleyite (Bi$_7$Te$_3$) ($n = 11$) |               | * Unnamed Bi$_8$Te$_3$ ($n = 7$) |
|               | Mean       | Minimum   | Maximum   | Mean       | Minimum   | Maximum   |
| Pb            | 0.19       | 0.08      | 0.25      | 0.02       | 0.00      | 0.09      |
| Bi            | 80.65      | 80.26     | 81.45     | 83.16      | 81.85     | 83.82     |
| Sb            | 0.10       | 0.04      | 0.16      | 0.13       | 0.04      | 0.29      |
| Te            | 20.47      | 18.37     | 20.80     | 18.75      | 18.58     | 18.87     |
| Se            | <mdl       | -         | -         | <mdl       | -         | -         |
| S             | 0.09       | 0.00      | 0.92      | 0.04       | 0.00      | 0.19      |
| Total         | 101.50     | 100.86    | 101.86    | 102.11     | 100.91    | 102.59    |

|               | Formula on basis of 10 atoms |               | Formula on basis of 11 atoms |
| Pb            | 0.02       | 0.01      | 0.02       | 0.00       | 0.00      | 0.01      |
| Bi            | 7.01       | 6.92      | 7.03       | 8.00       | 7.90      | 8.06      |
| Sb            | 0.01       | 0.01      | 0.02       | 0.02       | 0.01      | 0.05      |
| Pb + Bi + Sb  | 7.04       | 6.93      | 7.06       | 8.02       | 7.94      | 8.07      |
| Te            | 2.91       | 2.56      | 2.96       | 2.95       | 2.93      | 2.98      |
| Se            | -          | -         | -          | -          | -         | -         |
| S             | 0.05       | 0.00      | 0.51       | 0.03       | 0.00      | 0.12      |
| Te + Se + S   | 2.96       | 2.94      | 3.07       | 2.98       | 2.93      | 3.06      |

* Of the seven points representing the Bi$_8$Te$_3$ phase, five are from the patch in Figure 1B (sample H163b) and two (one each) are from the two lamellae (sample H1-H2) shown in the Supplementary Material, Figure S1.
In reflected light, Bi$_8$Te$_3$ displays high reflectance, anisotropy, and is indistinguishable from hedleyite in air. It is, however, brighter than joséite-B and has a distinct grey color relative to native bismuth (Figure 1B). Unnamed Bi$_8$Te$_3$ is also identified as distinct within much smaller patches of bismuth minerals within the same polished block using high-magnification backscatter electron (BSE) imaging (Figure 2) and subsequent nanoscale analysis (see below). The smaller bismuth mineral patches occur along micron-scale trails following brecciation of gangue minerals (Figure 2A) and are often associated with lamellae of molybdenite (Figure 2B). In detail, each of the multi-component patches display complex relationships among coexisting phases, with narrow slivers of native bismuth along mutual contacts between joséite-B and Bi$_8$Te$_3$ (Figure 2C). FIB-SEM cross-sectioning during extraction of a S/TEM sample from one of these patches shows one of the sub-µm-sized bismuth inclusions embedded within Bi$_8$Te$_3$, close to the boundary with joséite-B (Figure 2D–F).

The Bi$_8$Te$_3$ phase was also analyzed in a mounted chip of material from the same locality and previously documented by Ciobanu et al. [2] (Supplementary Materials, Figure S1). In this case, the Bi$_8$Te$_3$ occurs as lamellae of a few µm in width within joséite-B.
Figure 2. Back-scattered electron (BSE) images (A–D) showing aspects of the patch (sample H163b) from which Bi$_8$Te$_3$ was analyzed at the nanoscale. (A) Patches and trails of bismuth minerals within quartz and hedenbergite. (B,C) Details of the analyzed Bi-patch (marked by rectangle in (A)), showing that this is dominantly joséite-B attached to a thin lamella of molybdenite (in (B)). The Bi$_8$Te$_3$ is limited to the tip of this patch (in (C)). (D) Detail of (C) showing the FIB cut location from which foil #1 was obtained (in red). (E,F) Secondary electron images showing the FIB slice attached to the copper grid at the beginning of thinning. This shows the shape of the Bi$_8$Te$_3$ phase embedded within joséite-B and a thin sliver of native bismuth on one side. Note, this lies within the Bi$_8$Te$_3$ and not at the direct contact to joséite-B. Abbreviations: Bi—native bismuth; Bi-min.—bismuth minerals; Hdl—hedleyite; Hd—hedenbergite; Js-B—joséite-B; Mol—molybdenite; Qz—quartz.

3.2. Chemical Composition

Electron probe microanalytical data for Bi$_8$Te$_3$ and associated hedleyite are provided in Table 1. The data show that the two phases have distinct compositions. Both phases contain minor S and Sb but no detectable Se.

3.3. Nanoscale Characterization

Nanoscale characterization of the Bi$_8$Te$_3$ phase was carried out on three S/TEM foils: foil #1 (Figure 3) and foils #2 and #3 (Supplementary Materials, Figure S2). These were obtained from the specimens shown in Figure 2 and Supplementary Materials, Figure S1. Attempts to analyze the stacking sequences within Bi$_8$Te$_3$ and hedleyite from the larger Bi-mineral patch in Figure 1B were unsuccessful due to the [0001] orientation of the two phases, prohibiting access to zone axes of interest for the stacking sequences within either phase (tilting > 30°, beyond the capability of the double-tilt holder of the instrument).

However, bright field (BF) TEM imaging for the stacking sequence and ED pattern typical of hedleyite from Hedley was shown in [2].
Figure 3. (A) HAADF STEM image of foil #1 (sample H163b) showing the Bi$_8$Te$_3$ phase within joséite-B. The stars with labels a1–a6 show areas that have been documented in detail. (B,C) BF STEM images showing the sliver of native bismuth within the Bi$_8$Te$_3$ (in (B)), and the contact between Bi$_8$Te$_3$ and a disordered sequence (FFT as inset), with composition changing from joséite-B to ~Bi$_{4.6}$X$_3$. Arrows in (B) mark lattice distortion in Bi$_8$Te$_3$ at the contact with native bismuth. (D) HAADF STEM image showing the contact between joséite-B (Js-B) and Bi$_8$Te$_3$. Selected area electron diffraction (SAED) as inset shows the ordered 7-atom layer (7 equal intervals along the d* shown at the bottom) at this location after tilting the specimen on the [2T10] zone axis. (E) High-resolution image of native bismuth in (B) tilted on the [2T10] zone axis (FFT as inset). Note the typical dumbbell Bi-atom pairs. Structural data for native bismuth from [19]: space group R$ar{3}$m, a = 4.533 Å, b = 11.797 Å.
3.3.1. Stacking Sequences and Crystal Structure of the Bi$_8$Te$_3$ Phase

The Bi$_8$Te$_3$ phase is well-exposed in the middle part of foil #1 (Figure 3), which was obtained from the location shown in Figure 2D. This foil also exposes grain contacts with joséite-B and native bismuth. Bi$_8$Te$_3$ exhibits a funnel-shaped morphology in the cross-section (Figure 3A) and displays ordered stacking sequences across a distance of >10 µm, as confirmed by imaging of the upper part of the foil. Sets of defects are noted in Bi$_8$Te$_3$ on both sides of the native bismuth (Figure 3B). Changes in the layer orientation across the boundary contacts to joséite-B (Figure 3C,D) indicate non-epitaxial growth. Joséite-B displays strong stacking disorder on one side of the foil (Figure 3C) and regular 7-atom layer sequences on the other (Figure 3D). The simple dumbbell motif of native bismuth is shown on the [210] zone axis (Figure 3E) for the purpose of comparison with Bi$_8$Te$_3$ (see below).

Thin bands of Bi$_8$Te$_3$ are also exposed at the top of each of the other two foils studied here (Supplementary Materials, Figure S2). These show regular stacking sequences with a repeat of ~2.1 nm (Figure 4). In detail, each repeat shows brighter and darker slabs corresponding to 5- and 6-atom arrays, respectively, for each interval (Figure 4A). These correspond to (i) the chalcogen-bearing, Te-Bi-Te-Bi-Te five-atom array (hereafter called mod5, following [2]), and (ii) three Bi-Bi dumbbell pairs (hereafter called 3 × mod2), together forming the 11-atom layer. A profile across the length of this sequence (Figure 4B) shows a ‘harmonic’ variation in the HAADF signal which can be broadly associated with the intensity variation from low (mod5) to high (3 × mod2).

![Figure 4](image-url)

**Figure 4.** (A) HAADF STEM image (obtained by DCFI procedures and filtered to eliminate noise) showing 14 repeats of ~2.1 nm width representing the 11-atom layer on the [210] zone axis. Each unit consists of darker and brighter slabs representing the mod5 and 3 × mod2 marked by purple and green overlays. (B) Intensity profile across the sequence (yellow line in (A)) showing a harmonic-like variation (7 rhythms) which is correlated with the image by the green and purple lines separating the 11-layer repeats. At this resolution, the signal reflects the signal swing between the mod5 and 3 × mod2 across two 11-atom units. Abbreviation: a.u.—arbitrary units.
The ~2.1 nm distance represents a good approximation of the 11-atom layer width ($d_{11}$). Considering the 3R symmetry, space group $R3m$ of this phase [2], and using measured $d_{11}$ to calculate $c (=3 \times d_{11} = 63 \ \text{Å})$, we have built a crystal structure for the $\text{Bi}_8\text{Te}_3$ phase using Crystal Maker software (Figure 5). The $a$ parameter (~4.4 Å) is relatively constant across all members of the series. The asymmetric unit cell comprises six unique atom positions, two for Te, and four for Bi, with distribution as shown in Figure 5A. The crystal structure of $\text{Bi}_8\text{Te}_3$ is shown on two projections (Figure 5B,C), both of which are relevant for the definition of stacking sequences for phases in the tetradymite group. This model is in good agreement with incremental layer expansion within the group via addition of $n \times \text{mod}2$ (Bi-Bi pairs) to the mod5 slab common to all structures [1,2,13].

![Crystal structure model for $\text{Bi}_8\text{Te}_3$ with cell parameters and symmetry from [2] and built using Crystal Maker software](image)

**Figure 5.** Crystal structure model for $\text{Bi}_8\text{Te}_3$ with cell parameters and symmetry from [2] and built using Crystal Maker software (see Supplementary Material .cif file for more information). (A) Distribution of the six unique atoms in the asymmetric unit cell (area marked by rectangle in (B)) representing the $\text{Bi}_8\text{Te}_3$ structure. (B,C) Ball and stick models (shown for the length of a single cell along the c axis) showing the structure projected on two zone axes displaying the layer stacks in the structure. Note the tight atom packing on the [1100] relative to the [2110] projection, indicating that the latter is best-suited for resolving atomic positions by HAADF STEM imaging. For simplicity and sake of comparison with other defined structures in the series, the unit cell is centered relative to the 5-atom repeat.

Assessment of the $\text{Bi}_8\text{Te}_3$ crystal structure was carried out using high-resolution HAADF STEM imaging and simulation tilting the specimen on the [2110] zone axis (Figure 6A). Simulations were performed using the crystallographic information file (.cif) obtained for the model presented here (Supplementary Materials, .cif file). There is an excellent match between the STEM simulation and the image (compare upper and lower parts of Figure 6A) obtained from the upper part of foil #1.
Figure 6. (A) HAADF STEM image (top) and simulation (bottom) showing a regular sequence of 7 repeats of the 11-atom layer on the [21\(\bar{1}0\)] zone axis. Yellow lines mark the seven repeats on the image and simulation. Note the very good correlation between image and simulation. (B) SAED pattern for Bi\(_8\)Te\(_3\) on the [2\(\bar{1}0\)0] zone axis. Indexing of 11-atom supercell and the rhombohedral sub-cell marked in yellow and white, respectively. Reflections along the \(d^*\) interval (\(d = 1/d^* \approx 1.9 \text{ Å}\)) shown underneath the SAED are drawn schematically to reflect intensity variation. The 11-atom layer has 11 equal intervals with \(d_{11}^* = q_F^*\) (\(q_F^*\) = modulation vector). These reflections display modulation in agreement with a displacement vector (\(q_F^*\)) typical for the mixed-layer compounds in the tetradymite series and related series (see [2,6]). This is shown by the intensity variation matching the calculated values for sum intensities for this phase given in [2], i.e., intensity reflections from 0000 to 000.15 along 1/2d* are: 1.0506, 0.9063, 0.5956, 0.5059, 0.7450, and 1.0208 (see Table 3 in Ciobanu et al. [2]). Additional explanation is provided in the text.

The layer sequence in mixed-layer compounds with interface modulated structures can be calculated from electron diffractions using the correlation between the displacement vector (\(q_F^*\)) and the rhombohedral sub-cell defined by the \(d^*\) interval (\(d = 1/d^* = \approx 2 \text{ Å}\)) along the \(c^*\) axis in the tetradymite homologous series ([2,6]; Figure 6B). The \(q_F^*\) parameter corresponds to the distance between two brighter satellites in the center of \(d^*\), and the layer stack is defined by the number of divisions (\(i\)) within this interval. The smallest distance between any two reflections (\(d_{N}^*\)) across \(d^*\) corresponds to the width of a given \(N\) layer type (\(N = \) number of atoms in the layer) and can be calculated from:

1. \(q_F^* = i \times d_{N}^* = (i \times d^*)/N\), leading to:
2. \(d_{N} = q_F^*/i\) and \(N = (i \times q_F^*)/d\)

The selected area electron diffraction (SAED) shows a single-layer stack (\(i = 1\)) with 11 divisions across \(d^*\) (Figure 6B). In this case, \(d_{N}^* = q_F^*\) and \(d_{N} = d \times N = \approx 2.1 \text{ nm}\) for the 11-atom layer (\(d = \approx 1.9 \text{ Å}\) and \(N = 11\)). Therefore, the results calculated from measured values for \(d_{11}\) have a good fit with one another. The measured value of \(d_a\) (3.8 Å; see Figure 6B) was used to calculate \(a\) by the function \(a = d_a/cos30^\circ\), where \(a\) is 4.4 Å.
Indexing of the 11-atom layer supercell is marked along the d* interval (drawing at the bottom of Figure 6B). The modulation with respect to intensity of reflections along d* is concordant with the variation of sum of intensities for (N−i)/2 reflections calculated by Ciobanu et al. (Table 3 and Figure 9h in [2]) using the fractional shift method of van Landuyt et al. [4].

3.3.2. Atom Identity within the 11-Atom Layer

A clearer separation between the mod5 and mod2 slabs within the 11-atom layer is evident from high-resolution HAADF STEM images (Figure 7A). In this structure, the chalcogen-bearing mod5 slab is smaller than the 3 × mod2 (6-atom), Bi-only slab, and the two are well-separated as darker and brighter strips on the image.

Figure 7. (A) Atomic-scale resolution image (obtained by DCFI procedures and filtered to eliminate noise) on the [2101] zone axis showing the 5- and 6-atom slabs (mod5 and 3 × mod2) in the Bi₈Te₃ phase. (B,C) Crystal model and STEM simulation for a single unit of Bi₈Te₃ showing the distribution of the 11 atoms along the <0.1.11> direction. (D,E) HAADF STEM image and intensity profile showing the decrease in HAADF signal for Te relative to Bi.

The sequence of atoms representing the structure: (Te-Bi-Te-Bi-Te)(Bi-Bi-Bi-Bi-Bi), is shown along the <0.1.11> lattice direction on the crystallographic model and STEM simulation representing the [2101] zone axis for Bi₈Te₃ (Figure 7B,C). This sequence is
replicated by variation in size and intensity along a profile encompassing the mod5 slab at the center of two $3 \times \text{mod2}$ (6-atom) slabs (Figure 7D,E).

The relative variations in the HAADF signal interpreted as Te and Bi atoms along the profile in Figure 7E (lower and higher intensity, respectively) show a very good match with the structure and STEM simulation (Figure 7B,C). This interpretation is also confirmed by high-resolution EDS mapping across three 11-layer repeats (Figure 8). These show that the distribution of Te and Bi reproduces the 5- and 6-atom slabs in Bi$_8$Te$_3$.

3.3.3. Stacking Disorder among Bi-Rich Layers

Disordered stacking sequences observed in the sulphotelluride enclosing the Bi$_8$Te$_3$ phase were studied in closer detail from area 7 in foil #1 (sample H163b; Figure 3A,C).

The stacking sequences along a ~130 nm-long profile (Figure 9) show blocks of up to 20 regular repeats of a 7-atom (Bi$_4$X$_3$; X = chalcogen) layer (third frame in Figure 9) within a sequence that comprises various stacks of 9-atom layers (composition Bi$_6$X$_3$ or Bi$_2$X [1,2]) that alternate with the 7-atom layer ($d_9$~1.7 nm; $d_7$~1.3 nm). These comprise slabs that are compositionally equivalent in terms of Bi:X ratio, such as 9.9.9.9.7.7.7 and 9.7.9.9.7.9.7 (first frame in Figure 9), but are mostly alternating single or double units of 7- and 9-atom layers (e.g., 7.9.7.7.9.7.7.9.7.9.7 in the middle part of frame 2, Figure 9). The 11-atom layer is also observed as single units with random distribution among the 7- and 9-atom layers (frame 4 in Figure 9).

The 9-atom layer (Bi$_6$X$_3$) comprises two pairs of Bi atoms enclosing the mod5 slab: Bi-Bi-Bi-Bi-(X-Bi-X-Bi-X)/Bi-Bi-Bi-Bi . . . [1,2]. The stacking sequences identified were used to calculate the composition for each frame: Bi$_5$X$_3$, Bi$_{4.88}$X$_3$, Bi$_{4.29}$X$_3$, and Bi$_{4.53}$X$_3$, obtaining an average of Bi$_{4.67}$X$_3$. Among these, Bi$_5$X$_3$ has the simplest configuration (7.9-layer sequence [2]), but other polytypes can also be present (see [20]).

High-resolution images of the disordered sequences (Figure 10) show dark lines clearly separating individual layer units with central arrays of single or double Bi-Bi dumbbells (Figure 10A). Such dark lines are attributable to sulfur occurring in the middle part of josite-B (7-atom layer [13]). The sequence can be identified using $d_7$ and $d_9$ layer widths of ~13.5 and ~17 Å. The 9-atom layer is irregularly distributed, and this stacking disorder can be recognized on Fast Fourier Transform (FFT) patterns obtained from the images.
(Figure 10B). As shown above, single 11-atom units also occur alongside the 9- and 7-atom units (Figure 10C). The single-, double-, and triple-arrays of Bi-atom pairs are separated by the chalcogen-bearing mod5 slabs marked as overlays in Figure 10C. The different layers are distinguished in the figure by their asymmetric rather than centered arrangements of the double-Bi \((n \times \text{mod2})\) arrays relative to the mod5 slab. In stacking sequences involving different chalcogens (e.g., S and Te in joséite-B), layer units can be readily recognized using the centered approach even if the double-Bi rows are slightly distorted and more difficult to count. Unit widths are, however, effectively identical irrespective of which method is considered, as shown in Figure 10D.

![Figure 9. HAADF STEM images showing the stacking sequence along a profile (area 7 in Figure 3A) comprising dominantly 7- and 9-atom layers. This sequence has an average composition of Bi\(_{4.67}X_3\), with the composition of individual frames (1–4) calculated from the layer sequence observed in each. One 11-layer unit is shown in frame 4. Abbreviation: L—layer.](image-url)
Figure 10. (A,C,D) Atomic-scale resolution HAADF STEM images (obtained by DCFI procedures and filtered for noise) and FFT pattern (B) showing disordered intergrowths among the 7-, 9-, and 11-atom layers from the sequence in Figure 9. (A) Sequence of 7- and 9-atom layers characterized by different widths, i.e., ~13.5 and ~17 Å, respectively. The layers are well-separated by dark bands (marked by yellow lines) representing S, a chalcogen with lesser atomic weight than Te. (B) FFT pattern for the sequence in (A), showing streaks along c* indicative of high stacking disorder. (C) Detail of a short sequence comprising all layer units (11-, 9-, and 7-atoms), showing epitaxial relationships with one another. The mod5 and n × mod2 slabs are highlighted by overlays: (i) triple, double, and single pairs of Bi arrays as red lines for the Bi-only mod2 slabs, and (ii) Te and S chalcogens as green and yellow lines for the mod5 slab. The width of the units is marked considering asymmetric units rather than using the position of the central chalcogen in the mod5 slab, as considered in (A). (D) Separation of 9- and 7-atom units using both asymmetrical and symmetrical approaches, represented by white and yellow lines, respectively.
4. Discussion

4.1. The Bi-Rich End of the Tetradymite Series

This study is focused on one of the closest natural species known towards the Bi-rich side of the tetradymite homologous series. It thus complements existing compositional and structural data obtained from electron diffractions provided previously for the Bi₆Te₃ phase from the same locality [2], but adds HR HAADF STEM imaging and a crystal structure model. Other studies have addressed a generalized structural model for synthetic compounds analogous to the tetradymite series but without extending the model to the Bi-rich side of the system. Among these, the studies of Frangis et al. [6] and Lind and Lindin [9] are relevant for the discussion here. Based on HR TEM studies of compounds of M₂ₓ₈X₃ type, where M = Bi, Sb, Ge, X = Te, Se, and 0 ≤ δ ≤ 0.4, Frangis et al. [6] describe a continuous series of one-dimensional structures using the fractional shift method of van Landuyt et al. [4]. Lind and Lindin [9] later introduced a general structural model for Bi-Se phases using a super-space formalism based on X-ray diffraction study of phases in the compositional range Bi₂Se₃–Bi₄Se₃, extrapolated to Bi₃Se₂ (=Bi₄.₅Se₃), but thus not including the Bi-rich side of the system.

The structural model built for the Bi₆Te₃ phase (space group R3m; a = 4.4 Å, c = 63 Å; Figure 3; Supplemental Materials, .cif file) was assessed by measurements of cell parameters from electron diffractions and confirmed by direct atomic-scale imaging and STEM simulations (Figures 6 and 7). STEM EDS mapping is in agreement with the atom specification considered for this structure (Figure 8). The Bi₆X₃ phase represents the k = 4 structure within the series described by the general formula Bi₂ₓX₃, where k is an integer value ≥ 1 [2].

The data presented here support the homology model based on fractional shift theory proposed for phases in the tetradymite series (whereby the number of layers within each unit constrains modulation along the d interval, representing the c/subcell common to all phases) [2]. An alternative model for homology in the tetradymite series is provided as nBi₂·mBi₂X₃ by Shelimova et al. [8]. This correlates with the Bi₂ₓX₃ modules of [2] by the relationship: n/m = k−1. Ciobanu et al. [2] draw attention to the fact that although intuitive in terms of imaging, the generalized formula nBi₂·mBi₂X₃ does not account for the qₜ modulation underpinning homology within the series. For example, native bismuth (Figure 3E), which displays identical imagery in terms of the Bi-only mod2 slabs of tetradymite species, would be part of the tetradymite series with k→∞ if we consider the model of Shelimova et al. [8] rather than the homology proposed by [2].

Whichever model is best-suited to describe the tetradymite series, recognition of layered compounds within a homologous series allows new structures to be accurately predicted from compositional data and the specific characteristics of electron diffractions, an intrinsic feature of mixed-layer compounds [21]. The data presented here further emphasize that Z-contrast imaging techniques such as HAADF STEM are optimally suited for characterization of mixed-layer compounds [13,20,22–25].

4.2. Relationships between BiₓTe₃, Hedleyite, and Other Species with Higher Bi/X > 1 Ratios

Remarkably, the Bi₆Te₃ phase is very well-ordered over a distance of >10 μm, confirming the compositional data presented here and in [2] for the Hedley material. Like all other phases in the series representing single-layer stacks, this should be more stable than those species formed by combinations of two types of modules, i.e., S'(Bi₂ₓX₃)·L'(Bi₂(x+1)X₃), where k ≥ 1, X = chalcogen, and S' and L' are the number of short and long modules, respectively. Paradoxically, one such phase, hedleyite, with a 9.11 stacking sequence (k = 3, S' = 9, and L' = 11), has been the most commonly reported phase at the Bi-rich end of the series. As initially defined [26] from the type locality (Good Hope claim, Hedley, B.C., Canada), hedleyite has the chemical formula BiₓTe₃. Subsequent work questioned the validity of this formula, suggesting that Bi₂ₓ+δTe₁−ₓ (x = 0.13–0.19) represents a more appropriate formula [27]. Structural data for hedleyite [26] indicate unit cell dimensions of a = 4.4733(20) Å and c = 17.805(11) Å, Z = 3.

≥
The literature contains several prior references to unnamed Bi₉Te₃ (e.g., [14,15,28]), or to microprobe data which were ascribed to hedleyite, yet where Bi is clearly in excess of stoichiometry (e.g., [29,30]). Some authors have chosen to assume that compositions closer to Bi₉Te₃ than Bi₇Te₃ were hedleyite (e.g., [28]), or referred specifically to ‘bismuthian hedleyite’ (see review in [1]). The Bi₉Te₃ phase was, however, clearly shown to be a distinct phase, different from and coexisting with hedleyite, in the example presented by Cabral and Corrêa-Neto [15]. Likewise, we show here the co-existence of the two species in the same area (Figure 1B), defined by their distinct compositions (Table 1).

The scarcity of both phases could be related to a decreasing probability of maintaining a regular stacking sequence during growth with a larger number of layers involved. However, the relative scarcity of Bi₉Te₃ relative to hedleyite or other associated phases typical of high-grade gold ores (e.g., [31]) is the chance of preservation during deposit evolution or over a protracted geological history. Interaction with late, S-bearing fluids can lead to replacement of Bi₉Te₃ by hedleyite + joséite-B, the most common association in Au skarns such as Hedley [32]. The lack of epitaxial relationships and the change in layer orientation across the boundary between Bi₉Te₃ and disordered joséite-B/Bi₄₋₆X₃ (Figure 3A,C) is evidence that these phases did not form at the same time. One example of relict Bi₉Te₃ would be the lamellae preserved within joséite-B (Supplementary Materials, Figure S2).

In contrast, 11-atom layer units, epitaxial with 7- and 9-atom layers within the disordered sequences of slabs with an average composition of ~Bi₄₋₆X₃ (Figures 9 and 10), are more likely part of a newly formed assemblage. Such sequences may show some degree of stack ordering if analyzed over larger intervals, as for example the phases Bi₄₋₆X₃ and Bi₅X₃ representing both distinct polysome slabs and a combination thereof (~Bi₄₋₆X₃) [2]. Note that some of the disordered stacks presented here (Figure 9) have the same compositions as (quasi)ordered sequences shown in [2], e.g., the [777.9] layer stack for Bi₄₋₆X₃, or 7.9 for Bi₅X₃.

It is likely that stacking sequences involving layer units of different size will be more disordered than those composed of a single module type (e.g., 7-, 9-, or 11-atoms), thus explaining the deviation from ideal stoichiometry in some Bi-rich compounds such as hedleyite (see above). Nonetheless, stacking disorder induced to accommodate compositional variation during cycles of growth is likely to be far more common in nature. The data here draw attention to the fact that tetradyomite series specimens with compositions in the range between those of single-layer structures require assessment by S/TEM or X-ray diffraction methods before they can be considered as distinct phases. On the other hand, the mutual relationships between layers across and within a stacking sequence can be suggestive of primary versus secondary origin, if analyzed at the nanoscale.

4.3. Prospects for Other Phases in the Tetradyomite Homologous Series

Based on observed crystal structures and theoretical arguments, Ciobanu et al. [2] predicted an extended family of single-module phases with incremental k increase with compositions from Bi₂Te₃ (k = 1, 5-atom layer) to Bi₁₄Te₃ (k = 7, 17-atom layer), each with distinct structures defined by different c parameters.

These include named phases with relatively simple structures, such as tsumoite, Bi₃Te₃ (BiTe, a combination of 5- and 7-atom layers), and pilsenite, Bi₄Te₃ (7-atom layers only). Compositions corresponding to Bi₅Te₃ (e.g., [33]) and Bi₆Te₃ (Bi₇Te) (e.g., [15,33]) are reported from natural samples and similarly ascribed to a combination of 7- and 9-atom layers, and 9-atom layers, respectively [2]. More complex structures are also predicted, particularly in the narrow compositional range close to ~BiTe. The latter includes phases such as Bi₄X₅, Bi₅X₆, Bi₆X₇, Bi₇X₈, Bi₈X₉, Bi₉X₁₀, Bi₁₀X₁₁, Bi₁₁X₁₂, and several others.

Although they are not named minerals, several phases in the tetradyomite homologous series with higher Bi/Te ratios have been reported in nature, including Bi₉Te₃ (Bi₃Te) and Bi₁₂Te₃ (Bi₄Te) [34], and Bi₇Te₂ (Bi₁₀.₅Te₃) [35]. Other phases have been synthesized experimentally, including Bi₁₁Te₃ nanowire arrays [36].
Whether phases that share a structure with Bi₈Te₃, but with compositions including S and/or Se (i.e., Bi₈S₃, Bi₈Se₃, Bi₈TeS₂, Bi₈TeSe₂, Bi₈Se₂Te, and Bi₈Te₂Se), also exist in nature is unknown at present. We note that no reports of unnamed phases of S- or Se-bearing analogues of Bi₈Te₃ (or indeed, Bi₇Te₃) have been published, with the single exception of unnamed Bi₂₋₂₄₃S₀₋₋₀.₇₄₂₋₋₀.₁₁₃ (≡Bi₇₋₇₋₀(S₂₋₀₋₀.₄₋₋₀.₃) mentioned by Fuksová et al. [37]. The present study shows that the 11-atom layer structure may accommodate chalcogens other than Te, e.g., S, as suggested by the HR-STEM images (Figure 10C).

5. Conclusions and Implications

Bi₈Te₃ is a new member of the tetradymite homologous series and is compositionally and structurally distinct from hedleyite (Bi₇Te₃). HAADF STEM imaging showed that Bi₈Te₃ has an 11-atom layer structure, in which three Bi-Bi pairs (3 × mod 2) are placed adjacent to a 5-atom sequence (mod 5, Te-Bi-Te-Bi-Te). This is an 11-fold superstructure of a rhombohedral sub-cell with d ~ 1.9 Å, and the trigonal symmetry (space group R3m) for the unit cell, a is ~ 4.4 Å and c is ~ 63 Å (=3 × 11 × d, or 3 × d₁₁), as calculated from d₂₄₃, d₣, and d⁺₁₁, measured from electron diffraction patterns. STEM simulations based on the crystal structure model matched the images and showed the distribution of the 11 atoms along <0.1.1.1> directions. Intensity profiles and STEM EDS mapping showed a very good match with assumed atom speciation within the structure.

Lattice-scale intergrowths are documented as epitaxial growth of single 11-atom layer units within a strongly disordered sequence of 7- and 9-atom layer units of average composition, Bi₄₋₆₇X₃. Disordered sequences such as this, replacing Bi₈Te₃, likely account for the rarity of this phase in nature and show how compositional non-stoichiometry, although not represented by a discrete phase, is nevertheless interpretable in terms of layer stacks.

Results support predictions of crystal structures from theoretical modeling of the series and indicate that multiple phases likely exist but are yet to be discovered and named. Each has a discrete stoichiometric composition and unique crystal structure. These types of modular structures can be predicted from their basic principles as mixed-layer compounds derived as one-dimensional superstructures of a basic rhombohedral sub-cell. Although their stabilities are unknown, there is likely a continuous range of compositions and compounds extending towards native bismuth.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/min11090980/s1, Table S1: Details of EPMA set-up; Table S2: EPMA standards; Figure S1: Back-scatter electron images showing aspects of the Bi₈Te₃ lamellae and location of samples extracted for nanoscale study; Figure S2: Secondary electron images showing the FIB slices; Crystallographic Information File (.cif file) for Bi₈Te₃.

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