



Article Bi₈Te₃, the 11-Atom Layer Member of the Tetradymite Homologous Series

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Abstract: Bi₈Te₃ is a member of the tetradymite homologous series, previously shown to be compositionally and structurally distinct from hedleyite, Bi₇Te₃, 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 Bi₈Te₃ 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). Bi₈Te₃ 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 EDS mapping, all displaying good agreement with the HAADF STEM imaging. Lattice-scale intergrowths are documented in phases replacing Bi₈Te₃, accounting for the rarity of this phase in nature. These results support prior predictions of crystal structures in the tetradymite homologous series from theoretical modeling and indicate that other phases are likely to exist for future discovery. Tetradymite 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: Bi₈Te₃; lattice-scale intergrowths; tetradymite homologous series; HAADF STEM

1. Introduction

The tetradymite homologous series (Bi_xX_y , where X = Te, Se, S) comprises phases derived from a simple 5-atom layer represented by tellurobismuthite, Bi_2Te_3 , and isostructural phases, including tetradymite, Bi_2Te_2S [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'($Bi_{2k}X_3$)·L'($Bi_{2(k+1)}X_3$) ($k \ge 1$; X = 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 $Bi_2Te_3-Bi_8Te_3$ [2]. This study showed that each phase is a N-fold superstructure of a rhombohedral sub-cell with $c/3 = d\sim0.2$ 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].



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). 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_2X_3 phases, such as tellurobismuthite, paraguanajuatite (Bi_2Se_3), kawazulite (Bi_2Te_2Se), and skippenite (Bi_2Se_2Te), are represented by simple repeats of a single 5-atom X-Bi-X-Bi-X layer. Members of the Bi_4X_3 subgroup (ikunolite, laitakarite, pilsenite, joséite-A, and joséite-B) share 7-atom layers only [13]. Named phases in the Bi_3X_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_7Te_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_2Te (i.e., Bi_6Te_3) and Bi_8Te_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_8Te_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_8Te_3 using measurements from electron diffractions is in agreement with the modularity in the series, and this model is used for STEM simulations. Bi_8Te_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 $Bi_4Te_3-Bi_2Te$ 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_8Te_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 $\varphi(\rho z)$ [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-Angstrom 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 xHREMTM (v4.1) software.

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

3. Results

3.1. Specimen Petrography

Bi₈Te₃ 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].

	Hedleyite (Bi_7Te_3) ($n = 11$)			* Unnamed Bi_8Te_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< td=""><td>-</td><td>-</td><td><mdl< td=""><td>-</td><td>-</td></mdl<></td></mdl<>	-	-	<mdl< td=""><td>-</td><td>-</td></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

Table 1. Microprobe data for hedleyite and unnamed Bi₈Te₃.

* Of the seven points representing the Bi₈Te₃ 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.



Figure 1. Reflected light photomicrographs showing aspects of specimen H163b petrography. (**A**,**B**) Larger patch of bismuth minerals containing both the Bi_8Te_3 phase and hedleyite (compositions from EPMA data; Table 1) in hedenbergite skarn. Note the difference in color and reflectivity between the two phases and native bismuth in the middle and joséite-B on the outside. Dark squares are FIB cuts. (**C**,**D**) Joséite-B associated with native gold and bismuth. Note the perceptual change in color for joséite-B depending upon the association. Abbreviations: Au—native gold; Bi—native bismuth; Bi-min.—bismuth minerals; Hdl—hedleyite; Hd—hedenbergite; Js-B—joséite-B; Sch—scheelite.

In reflected light, Bi_8Te_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_8Te_3 is also identified as distinct within much smaller patches of bismuth minerals within the same polished block using highmagnification 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_8Te_3 (Figure 2C). FIB-SEM cross-sectioning during extraction of a S/TEM sample from one of these patches shows one of the sub-µmsized bismuth inclusions embedded within Bi_8Te_3 , close to the boundary with joséite-B (Figure 2D–F).

The Bi_8Te_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_8Te_3 occurs as lamellae of a few μ m in width within joséite-B.



Figure 2. Back-scattered electron (BSE) images (**A**–**D**) showing aspects of the patch (sample H163b) from which Bi_8Te_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_8Te_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_8Te_3 phase embedded within joséite-B and a thin sliver of native bismuth on one side. Note, this lies within the Bi_8Te_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_8Te_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_8Te_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_8Te_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 Bi₈Te₃ 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 Bi₈Te₃ (in (**B**)), and the contact between Bi₈Te₃ and a disordered sequence (FFT as inset), with composition changing from joséite-B to ~Bi₄.₆X₃. Arrows in (**B**) mark lattice distortion in Bi₈Te₃ at the contact with native bismuth. (**D**) HAADF STEM image showing the contact between joséite-B (Js-B) and Bi₈Te₃. 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 [2110] zone axis. (**E**) High-resolution image of native bismuth in (**B**) tilted on the [2110] zone axis (FFT as inset). Note the typical dumbbell Bi-atom pairs. Structural data for native bismuth from [19]: space group $R\overline{3}m$, a = 4.533 Å, b = 11.797 Å.

The Bi₈Te₃ 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. Bi₈Te₃ exhibits a funnel-shaped morphology in the cross-section (Figure 3A) and displays ordered stacking sequences across a distance of >10 μ m, as confirmed by imaging of the upper part of the foil. Sets of defects are noted in Bi₈Te₃ 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 [2110] zone axis (Figure 3E) for the purpose of comparison with Bi₈Te₃ (see below).

3.3.1. Stacking Sequences and Crystal Structure of the Bi₈Te₃ Phase

Thin bands of Bi_8Te_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. (**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 $[2\overline{110}]$ 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 3*R* symmetry, space group $R\overline{3}m$ of this phase [2], and using measured d_{11} to calculate c (=3 × d_{11} = 63 Å), we have built a crystal structure for the Bi₈Te₃ 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 Bi₈Te₃ 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 × mod2 (Bi-Bi pairs) to the mod5 slab common to all structures [1,2,13].



Figure 5. Crystal structure model for Bi_8Te_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 Bi_8Te_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 Bi₈Te₃ crystal structure was carried out using high-resolution HAADF STEM imaging and simulation tilting the specimen on the $[2\overline{110}]$ 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 $[2\overline{11}0]$ 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 Bi₈Te₃ on the $[2\overline{11}0]$ zone axis. Indexing of 11-atom supercell and the rhombohedral sub-cell marked in yellow and white, respectively. Reflections along the d* interval $(d = 1/d^* - 1.9 \text{ Å})$ 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 ($d = 1/d^* = ~2 \text{ Å}$) 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 $d_N = d \times N = -2.1$ nm for the 11-atom layer (d = ~1.9 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 $a = d_a / \cos 30^\circ$, 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 $3 \times \text{mod2}$ (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 [2110] zone axis showing the 5- and 6-atom slabs (mod5 and $3 \times \text{mod2}$) 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 <0.1.1.11> 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 $<0.1.\overline{1}.11>$ lattice direction on the crystallographic model and STEM simulation representing the [2110] 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 Bi₈Te₃.



Figure 8. HAADF STEM image and STEM EDS element maps for Te/Bi (overlain), Bi, and Te. Note the good match between Te- and Bi-rich bands with the darker and brighter ribbons on the image.

3.3.3. Stacking Disorder among Bi-Rich Layers

Disordered stacking sequences observed in the sulphotelluride enclosing the Bi_8Te_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 (Bi₄X₃; X = chalcogen) layer (third frame in Figure 9) within a sequence that comprises various stacks of 9-atom layers (composition Bi₆X₃ or Bi₂X [1,2]) that alternate with the 7-atom layer (d₉~1.7 nm; d₇~1.3 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., 7.9.7.7.9.7.7.9.7.7.9.7.9.7 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_6X_3) comprises two pairs of Bi atoms enclosing the mod5 slab: Bi-Bi-Bi-(X-Bi-X)/Bi-Bi-Bi-Bi-Bi ... [1,2]. The stacking sequences identified were used to calculate the composition for each frame: Bi_5X_3 , $Bi_{4.89}X_3$, $Bi_{4.29}X_3$, and $Bi_{4.5}X_3$, obtaining an average of $Bi_{4.67}X_3$. Among these, Bi_5X_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 joséite-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 ($n \times mod2$) 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 $Bi_{4.67}X_{3,7}$ 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.



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 Bi₈Te₃ 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 Lidin [9] are relevant for the discussion here. Based on HR TEM studies of compounds of $M_{2+\delta}X_3$ type, where M = Bi, Sb, Ge, X = Te, Se, and $0 \le \delta \le 0.4$, 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 Lidin [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 Bi₈Te₃ 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 speciation considered for this structure (Figure 8). The Bi₈X₃ phase represents the k = 4 structure within the series described by the general formula Bi_{2k}X₃, 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 $nBi_2 \cdot mBi_2 X_3$ by Shelimova et al. [8]. This correlates with the $Bi_{2k}X_3$ 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 $nBi_2 \cdot mBi_2 X_3$ does not account for the q_F 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 $k \rightarrow \infty$ 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 Bi_8Te_3 , Hedleyite, and Other Species with Higher Bi/X > 1 Ratios

Remarkably, the Bi₈Te₃ 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., $S'(Bi_{2k}X_3)\cdot L'(Bi_{2(k+1)}X_3)$, where $k \ge 1$, 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 Bi₇Te₃. Subsequent work questioned the validity of this formula, suggesting that Bi_{2+x}Te_{1-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 Bi_8Te_3 (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 Bi_8Te_3 than Bi_7Te_3 were hedleyite (e.g., [28]), or referred specifically to *'bismuthian hedleyite'* (see review in [1]). The Bi_8Te_3 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 Bi_8Te_3 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 Bi_8Te_3 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 Bi_8Te_3 and disordered joséite-B/ $Bi_4._6X_3$ (Figure 3A,C) is evidence that these phases did not form at the same time. One example of relict Bi_8Te_3 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 \sim Bi_{4.67}X₃ (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 Bi_{4.5}X₃ and Bi₅X₃ representing both distinct polysome slabs and a combination thereof (\sim Bi_{4.63}X₃) [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 Bi_{4.5}X₃, 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 tetradymite 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 Tetradymite 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 Bi_2Te_3 (k = 1, 5-atom layer) to $Bi_{14}Te_3$ (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, Bi_3Te_3 (BiTe, a combination of 5- and 7-atom layers), and pilsenite, Bi_4Te_3 (7-atom layers only). Compositions corresponding to Bi_5Te_3 (e.g., [33]) and Bi_6Te_3 (Bi_2Te) (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 Bi_4X_5 , Bi_5X_6 , Bi_6X_7 , Bi_7X_8 , Bi_8X_7 , Bi_7X_6 , Bi_6X_5 , and several others.

Although they are not named minerals, several phases in the tetradymite homologous series with higher Bi/Te ratios have been reported in nature, including Bi_9Te_3 (Bi_3Te) and $Bi_{12}Te_3$ (Bi_4Te) [34], and Bi_7Te_2 ($Bi_{10.5}Te_3$) [35]. Other phases have been synthesized experimentally, including $Bi_{11}Te_3$ nanowire arrays [36].

Whether phases that share a structure with Bi_8Te_3 , but with compositions including S and/or Se (i.e., Bi_8S_3 , Bi_8Se_3 , Bi_8Te_2S , Bi_8Te_2S , Bi_8Se_2S , Bi_8Se_2S , Bi_8Se_2Te , and Bi_8Te_2Se), also exist in nature is unknown at present. We note that no reports of unnamed phases of S- or Se-bearing analogues of Bi_8Te_3 (or indeed, Bi_7Te_3) have been published, with the single exception of unnamed $Bi_{2.243}S_{0.742}Se_{0.113}$ (= $Bi_{7.87}(S_{2.6}Se_{0.4})_3$) 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 ($3 \times mod2$) are placed adjacent to a 5-atom sequence (mod5, 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 $R\overline{3}m$) for the unit cell, *a* is ~4.4 Å and *c* is ~63 Å (= $3 \times 11 \times d$, or $3 \times d_{11}$), as calculated from d^*_{a} , 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, $Bi_{4.67}X_3$. Disordered sequences such as this, replacing Bi_8Te_3 , 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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References

- 1. Cook, N.J.; Ciobanu, C.L.; Wagner, T.; Stanley, C.J. Minerals of the system Bi-Te-Se-S related to the tetradymite archetype: Review of classification and compositional variation. *Can. Mineral.* **2007**, *45*, 665–708. [CrossRef]
- Ciobanu, C.L.; Pring, A.; Cook, N.J.; Self, P.; Jefferson, D.; Dima, G.I.; Melnikov, V. Chemical-structural modularity in the tetradymite group: A HRTEM study. *Am. Mineral.* 2009, 94, 517–534. [CrossRef]
- 3. Brown, A.; Lewis, B. The systems bismuth-tellurium and antimony-tellurium and the synthesis of the minerals hedleyite and wehrlite. *J. Phys. Chem. Solids* **1962**, *23*, 1597–1604. [CrossRef]
- 4. van Landuyt, J.; De Ridder, R.; Gevers, R.; Amelinckx, S. Diffraction effects due to shear structures: A new method for determining the shear vector. *Mater. Res. Bull.* **1970**, *5*, 353–362. [CrossRef]
- 5. Imamov, P.M.; Semiletov, S.A. The crystal structure of the phases in the system Bi-Se, Bi-Te, and Sb-Te. *Sov. Phys. Crystallogr.* **1971**, *15*, 845–850.
- 6. Frangis, N.; Kuypers, S.; Manolikas, C.; Van Tendeloo, G.; Amelinckx, S. Continuous series of one-dimensional structures in compounds based on M₂X₃ (M = Sb, Bi, X = Se, Te). *J. Solid State Chem.* **1990**, *84*, 314–334. [CrossRef]
- Gaudin, E.; Jobic, S.; Evain, M.; Brec, R.; Rouxel, J. Charge balance in some Bi_xSe_y phases through atomic structure determination and band structure calculations. *Mat. Res. Bull.* 1995, 30, 549–561. [CrossRef]
- 8. Shelimova, L.E.; Karpinsky, O.G.; Kosyakov, V.I.; Shestakov, V.A.; Zemskov, V.S.; Kuznetsov, F.A. Homologous series of layered tetradymite-like compounds in Bi-Te and GeTe-Bi₂Te₃ systems. *J. Struct. Chem.* **2000**, *41*, 81–87. [CrossRef]
- 9. Lind, H.; Lidin, S. A general structure model for Bi-Se phases using a superspace formalism. *Solid State Sci.* 2003, *5*, 47–57. [CrossRef]
- 10. Bos, J.-W.G.; Faucheux, F.; Downie, R.A.; Marcinkova, A. Phase stability, structures and properties of the (Bi₂)_{*m*} (Bi₂Te₃)_{*n*} natural superlattices. *J. Solid State Chem.* **2012**, *193*, 13–18. [CrossRef]
- 11. Kuznetsov, P.I.; Yapaskurt, V.O.; Shchamkhalova, B.S.; Shcherbakov, V.D.; Yakushcheva, G.G.; Luzanaov, V.A.; Jitov, V.A. Growth of Bi₂Te₃ films and other phases of the Bi-Te system by MOVPE. *J. Cryst. Growth* **2016**, 455, 122–128. [CrossRef]
- 12. Mao, C.; Tan, M.; Zhang, L.; Wu, D.; Bai, W.; Liu, L. Experimental reinvestigation and thermodynamic description of Bi-Te binary system. *Calphad* **2018**, *60*, 81–89. [CrossRef]
- 13. Cook, N.J.; Ciobanu, C.L.; Slattery, A.; Wade, B.P.; Ehrig, K. The mixed-layer structures of ikunolite, laitakarite, joséite-B and joséite-A. *Minerals* **2021**, *11*, 920. [CrossRef]
- 14. Oberthur, T.; Weiser, T.W. Gold-bismuth-telluride-sulphide assemblages at the Viceroy Mine, Harare-Bindura-Shamva greenstone belt, Zimbabwe. *Mineral. Mag.* 2008, 72, 953–970. [CrossRef]
- Cabral, A.R.; Corrêa Neto, A.V. Empirical Bi₈Te₃ and Bi₂Te from the São Sebastião Gold Deposit, Brazil: Implications for lode-gold mineralization in Minas Gerais. *Can. Mineral.* 2015, *53*, 1061–1072. [CrossRef]
- Armstrong, J.T. Quantitative analysis of silicate and oxide minerals: Comparison of Monte Carlo, ZAF, and φ(ρz) procedures. In *Microbeam Analysis*; Newbury, D.E., Ed.; San Francisco Press: San Francisco, CA, USA, 1988; pp. 239–246.
- 17. Donovan, J.J.; Rowe, M. Techniques for Improving Quantitative Analysis of Mineral Glasses. *Geochim. Cosmochim. Acta* 2005, 69 (Suppl. 1), A589.
- 18. Ciobanu, C.L.; Cook, N.J.; Utsunomiya, S.; Pring, A.; Green, L. Focussed ion beam—Transmission electron microscopy applications in ore mineralogy: Bridging micron- and nanoscale observations. *Ore Geol. Rev.* **2011**, *42*, 6–31. [CrossRef]
- 19. Schiferl, D.; Barrett, C.S. The crystal structure of arsenic at 4.2, 78 and 299 K. J. Appl. Cryst. 1969, 2, 30–36. [CrossRef]
- Cook, N.J.; Ciobanu, C.L.; Liu, W.Y.; Slattery, A.; Wade, B.P.; Mills, S.; Stanley, C.J. Polytypism and polysomatism in mixed-layer chalcogenides: Characterization of PbBi₄Te₄S₃ and inferences for ordered phases in the aleksite series. *Minerals* 2019, *9*, 628. [CrossRef]
- 21. van Tendeloo, G.; van Dyck, D.; Kuypers, S.; Amelinckx, S. Electron diffraction effects in mixed layer compounds. I. Theorteical considerations. *Phys. Stat. Sol.* (*A*) **1989**, *101*, 339–354. [CrossRef]
- 22. Medlin, D.L.; Snyder, G.J. Atomic-scale interfacial structure in rock salt and tetradymite chalcogenide thermoelectric materials. JOM 2013, 65, 390–400. [CrossRef]
- Medlin, D.; Erickson, K.; Limmer, S.; Yelton, W.; Siegal, M.P. Dissociated dislocations in Bi₂Te₃ and their relationship to seven-layer Bi₃Te₄ defects. *J. Mater. Sci.* 2014, 49, 3970–3979. [CrossRef]
- 24. Medlin, D.L.; Yang, N.; Spataru, C.D.; Hale, L.M.; Mishin, Y. Unraveling the dislocation core structure at a van der Waals gap in bismuth telluride. *Nat. Comms.* **2019**, *10*, 1820. [CrossRef] [PubMed]
- Ciobanu, C.L.; Kontonikas-Charos, A.; Slattery, A.; Cook, N.J.; Ehrig, K.; Wade, B.P. Short-range stacking disorder in mixed-layer compounds: A HAADF STEM study of bastnäsite-parisite intergrowths. *Minerals* 2017, 7, 227. [CrossRef]
- 26. Warren, H.V.; Peacock, M.A. Hedleyite, a new bismuth telluride from British Columbia, with notes on wehrlite and some bismuth-tellurium alloys. *Univ. Tor. Stud. Geol. Ser.* **1945**, *49*, 55–69.
- 27. Zav'ylov, E.N.; Begizov, V.D.; Nechelyustov, G.N. New data on hedleyite. Dokl. Acad. Nauk SSSR 1976, 230, 1439–1441. (In Russian)
- 28. Gu, X.-P.; Watanabe, M.; Hoshino, K.; Shibata, Y. Mineral chemistry and associations of Bi-Te(S,Se) minerals from China. *N. Jb. Mineral. Monatsh.* **2001**, *7*, 289–309.
- 29. Casari, L. Cobalt pyrite ores in the upper Martello Valley (Alto Adige, Northern Italy). *Rend. Soc. Ital. Mineral. Petrol.* **1986**, *41*, 15–23.

- Mayorova, T.; Kuznetsov, S. Native gold paragenesis with bismuth and tellurium minerals in subpolar Ural placers (Russia). In Proceedings of the 17th International Multidisciplinary Scientific GeoConference SGEM 2017, Albena, Bulgaria, 29 June–5 July 2017; Issue 11 (Geol., Mineral Proc.). pp. 359–366.
- Ciobanu, C.L.; Birch, W.D.; Cook, N.J.; Pring, A.; Grundler, P.V. Petrogenetic significance of Au–Bi–Te–S associations: The example of Maldon, Central Victorian gold province, Australia. *Lithos* 2010, 116, 1–17. [CrossRef]
- 32. Meinert, L.D. Gold in skarns related to epizonal intrusions. Rev. Econ. Geol. 2000, 13, 347–375.
- 33. Houzar, S.; Litochleb, J.; Sejkora, J.; Cempírek, J.; Cícha, J. Unusual mineralization with noibian titanite and Bi-tellurides in scheelite skarn from Kamenné doly quarry near Pisek, Moldanubian Zone, Bohemian Massif. J. Geosci. 2008, 53, 1–16.
- Ivashchenko, V.I.; Sundblad, K.; Toritsin, A.N.; Golubev, A.I.; Lavrov, O.B. Rajonkoski gold-telluride ore occurrence: A new high prospective type of complex noble metal mineralization in the Karelian Proterozoic. *Dokl. Earth Sci.* 2008, 423, 1187–1193. [CrossRef]
- 35. Strakhovenko, V.D. Bismuth mineralization of rare-metal deposits Kokten–KoL', Severnyi Katpar, and Verkhnee Kairakty (central Kazachstan). *Geol. Ore Depos.* **1996**, *38*, 401–408.
- Reeves, R.D.; Crosser, L.A.; Chester, G.E.; Hill, J.J. Thermoelectric property enhancement via pore confinement in template grown bismuth telluride nanowire arrays. *Nanotechnology* 2017, 28, 505401. [CrossRef]
- Fuksová, A.; Dolníček, Z.; Gadas, P. Mineralogy of sulphide, arsenide and telluride mineralization in cordierite-bearing pegmatite from the Bory quarry near Velké Meziříčí (Strážek Moldanubicum). *Geol. Vyzk. Mor. Slez. Brno* 2011, 2, 125–127. (In Czech with English abstract).