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Bismuth Tellurides: BiTe and Bi_4Te_3

By Kazuo Yamana,* Kuniaki Kihara and Takeo Matsumoto

Department of Earth Sciences, Faculty of Science, Kanazawa University, 1–1 *Marunouchi, Kanazawa* 920, *Japan*

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Abstract. BiTe, trigonal, $P\bar{3}m1$, a = 4·423 (2), c = 24·002 (6) Å, Z = 6, D_x = 4·966 Mg m^{-3}, μr(Mo $K\alpha$) = 4·2; Bi_4Te_3, rhombohedral, $R\bar{3}m$, $a_{\rm hex}$ = 4·451 (1), $c_{\rm hex}$ = 41·888 (5) Å, $Z_{\rm hex}$ = 3, D_x = 5·087 Mg m^{-3}, μr(Mo $K\alpha$) = 5·9. Both structures are characterized by the combination of 5-layers (TeBiTeBiTe) and 2-layers (BiBi). The unit cell of BiTe contains 12 atomic layers stacked along the c axis in the order Te(1)Bi(1)Te(2)-Bi(2)Te(3)Bi(3)Bi(3)Te(3)Bi(2)Te(2)Bi(1)Te(1). Interatomic distances between the nearest pairs are 3·044 Å for Te(1)–Bi(1), 3·355 Å for Bi(1)–Te(2), 3·137 Å for Te(2)–Bi(2), 3·166 Å for Bi(2)–Te(3), 3·326 Å for Te(3)–Bi(3), 3·267 Å for Bi(3)–Bi(3) and 3·679 Å for Te(1)–Te(1). One third of the unit cell of Bi_4Te_3 has seven layers in the order Te(1)Bi(1)Te(2)Bi(1)Te(1)-Bi(2)Bi(2): the rhombohedral cell contains three such stacks. The interatomic distances are 3·327 Å for Te(2)–Bi(1), 3·115 Å for Bi(1)–Te(1), 3·401 Å for Te(1)–Bi(2) and 3·098 Å for Bi(2)–Bi(2).

Introduction. Mixtures of Bi and Te ingots were sealed in evacuated silica tubes, with ratios corresponding to BiTe and Bi_4Te_3, respectively. They were melted at a temperature higher than 1073 K, and then cooled in liquid nitrogen. The solidified materials were ground to powders and again sealed into silica tubes under vacuum. After heating at a temperature higher than the melting point for a few days, the temperature was gradually lowered to 823 K in 3 d for BiTe, and to 733 K in 1 d for Bi_4Te_3. The tubes, which were held at those temperatures for 14 d for BiTe and 53 d for Bi_4Te_3, were then quenched in ice water.

Crystals used for recording diffraction patterns and intensity measurements were cut from aggregates of crystals. Both kinds of crystals were ground into spheres, and dipped into a mixture of H_2SO_4, HNO_3 and HCl to eliminate powder lines on X-ray photographs due to grinding. Spheres with diameters of 0·13 and 0·15 mm were obtained for BiTe and Bi_4Te_3, respectively. Lattice constants and diffraction symbols for them correspond to those reported by Ozawa & Shimazaki (1974). Each of the synthesized products was confirmed to consist of a single phase.

The intensity data were collected on an automatic four-circle diffractometer (Philips PW 1100), up to 2θ = 70° (graphite-monochromated Mo $K\alpha$ radiation), adopting the ω–2θ scan mode. Scan speed was 5° min^{-1} in ω for BiTe and 3° min^{-1} for Bi_4Te_3. The scan widths were determined according to the formula $(a + b \tan \theta)^\circ$, where a = 1·0, b = 0·5 for BiTe and a = 1·5, b = 0·8 for Bi_4Te_3.

For BiTe, the intensity data were collected for 272 reflections satisfying the condition $I_{\rm top} - 2I_{\rm top}^{1/2} \geq I_{\rm bck}$, where $I_{\rm top}$ is intensity in counts s^{-1} measured at the top of the reflection and $I_{\rm bck}$ is mean intensity in counts s^{-1} of both background measurements. For Bi_4Te_3, all the 463 reflections were measured. Lorentz, polarization and absorption corrections were applied to both sets of intensity data.

According to Imamov & Semiletov (1971), crystal structures in the system Bi–Te consist of 5-layers (TeBiTeBiTe) and 2-layers (BiBi), which are stacked along the c axis of a hexagonal lattice. For BiTe and Bi_4Te_3, they gave only the stacking sequences of the atomic layers: TeBiTeBiTeBiBiTeBiTeBiTe in the former and TeBiTeBiTeBiBi in the latter. These models were also confirmed by the Patterson-like method (Kihara & Matsumoto, 1978). The structures of BiTe and Bi_4Te_3, were refined by the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970), starting from the models where each atomic layer is separated by an equal distance. Scattering factors for non-ionized atoms and dispersion corrections were taken from *International Tables for X-ray Crystallography*

Table 1. *The atomic coordinates with estimated standard deviations in parentheses*

(*a*) BiTe

	x	y	z
Te(1)	$\frac{1}{3}$	$\frac{2}{3}$	0·0552 (3)
Bi(1)	0	0	0·1242 (3)
Te(2)	$\frac{2}{3}$	$\frac{1}{3}$	0·2149 (5)
Bi(2)	$\frac{1}{3}$	$\frac{2}{3}$	0·2908 (3)
Te(3)	0	0	0·3687 (6)
Bi(3)	$\frac{2}{3}$	$\frac{1}{3}$	0·4575 (3)

(*b*) Bi_4Te_3

	x	y	z
Te(2)	0	0	0
Bi(1)	$\frac{2}{3}$	$\frac{1}{3}$	0·0505 (1)
Te(1)	$\frac{1}{3}$	$\frac{2}{3}$	0·0927 (2)
Bi(2)	0	0	0·1460 (1)

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* Present address: The Institute of Scientific and Industrial Research, Osaka University, Yamadakami, Suita, Osaka 565, Japan.

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(1962). All the 272 measured reflections for BiTe were used in the course of the least-squares refinement. The 290 reflections with $|F|$'s larger than $3\sigma|F|$ were used in the refinement for Bi_4Te_3. Isotropic extinction parameters were introduced into these calculations. The final R values of BiTe and Bi_4Te_3 were 0·064 and 0·068, respectively. The final atomic coordinates are given in Table 1.* The interatomic distances and the bond angles of BiTe and Bi_4Te_3 are listed in Tables 2 and 3, respectively, with those of Bi_2Te_3 (Lange, 1939) for comparison.

Discussion. In the system Bi–Te, only the crystal structure of Bi_2Te_3 has been determined accurately (Lange, 1939; Nakajima, 1963). Recently, minerals with compositions BiTe and Bi_4Te_3 were found by Ozawa & Shimazaki (1974). Both compositions are included in a range of the mineral wehrlite, $Bi_{2+x}Te_{3-x}$.

The structures of Bi_2Te_3, BiTe and Bi_4Te_3 are shown schematically in Fig. 1. They consist of layers of Bi and Te atoms perpendicular to the c axis of a hexagonal lattice, where atoms are located on nearly cubic-close-packing positions.

The crystal structure of BiTe consists of twelve layers with six Bi and six Te atomic layers stacked in the order: Te(1)Bi(1)Te(2)Bi(2)Te(3)Bi(3)Bi(3)Te(3)-Bi(2)Te(2)Bi(1)Te(1). The order of atomic layers, TeBiTeBiTe as seen in Bi_2Te_3, is also retained in this structure. The 2-layers composed of Bi(3) are sandwiched by the 5-layers. Such a 2-layer arrangement of Bi atoms is seen in the structure of bismuth. Te(1) is surrounded by six neighbors in adjacent layers, of which three are Bi(1) atoms at a distance of 3·044 Å and the others are Te(1) atoms at a distance of 3·679 Å. Whereas Te(1)–Te(1) is the longest bond distance for neighboring atomic pairs, it is much shorter than the theoretically estimated van der Waals separation, 4·40 Å (Von Hippel, 1948). Te(3) located on the other side of the 5-layer is surrounded by six Bi atoms. The bond distance Te(3)–Bi(3), 3·326 Å, is longer than 3·166 Å for Te(3)–Bi(2) and 3·267 Å for Bi(3)–Bi(3), but slightly shorter than the bond Bi(1)–Te(2), 3·355 Å in the 5-layer. Thus, it is suggested that the bonding between the 5- and 2-layer stacks is stronger than that between the 5-layer stacks.

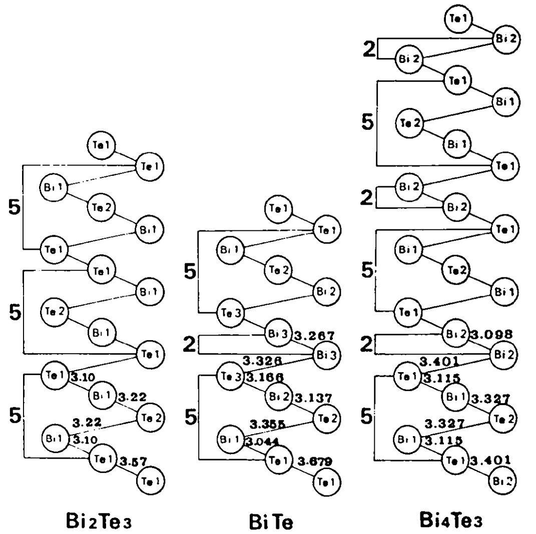

Fig. 1. Projections of structures of Bi_2Te_3, BiTe and Bi_4Te_3 on (110). 5- and 2-layer stacks are expressed by the numbers 5 and 2, respectively.

The crystal structure of Bi_4Te_3 is composed of atomic layers in the following order: Te(1)Bi(1)Te(2)-Bi(1)Te(1)Bi(2)Bi(2). In this structure, the 5-layer stacks and the 2-layer stacks are also retained and alternately stack along the c axis. There are three 5-layer stacks and three 2-layer stacks in the unit cell. The 5-layer stacks are centrosymmetrical with respect to the Te(2). The bond distance between the 5- and 2-layer stack, 3·401 Å, is the longest for all neighboring atomic pairs and longer than the corresponding one in BiTe. Thus, this structure has the weakest bonding at the boundary between the 5- and 2-layer stacks.

As seen above, whereas the structures of Bi_4Te_3 and BiTe are both composed of the 5- and the 2-layer stacks, the nature of the bonding within them is apparently affected by the stacking order of these stacks.

Table 2. *Bond lengths of* Bi_2Te_3, BiTe *and* Bi_4Te_3 (Å)

Parallel values in the table correspond to the same kind of bond in both structures.

Bi_2Te_3*		BiTe		Bi_4Te_3	
Te(1)–Te(1)	3·57	Te(1)–Te(1)	3·679 (6)		
Te(1)–Bi(1)	3·10	Te(1)–Bi(1)	3·044 (5)		
Bi(1)–Te(2)	3·22	Bi(1)–Te(2)	3·355 (6)		
		Te(2)–Bi(2)	3·137 (5)	Te(2)–Bi(1)	3·327 (2)
		Bi(2)–Te(3)	3·166 (9)	Bi(1)–Te(1)	3·115 (5)
		Te(3)–Bi(3)	3·326 (6)	Te(1)–Bi(2)	3·401 (6)
		Bi(3)–Bi(3)	3·267 (6)	Bi(2)–Bi(2)	3·098 (4)

* Lange (1939).

Table 3. *Bond angles*

BiTe		Bi_4Te_3	
Te(1)–Te(1)–Te(1)	73° 54′ (11′)	Te(2)–Bi(1)–Te(2)	83° 50′ (5′)
Te(1)–Bi(1)–Te(1)	93° 10′ (9′)	Bi(1)–Te(1)–Bi(1)	91° 03′ (11′)
Bi(1)–Te(2)–Bi(1)	82° 47′ (15′)	Te(1)–Bi(2)–Te(1)	81° 36′ (8′)
Te(2)–Bi(2)–Te(2)	89° 40′ (14′)	Bi(2)–Bi(2)–Bi(2)	91° 42′ (7′)
Bi(2)–Te(3)–Bi(2)	88° 36′ (20′)		
Te(3)–Bi(3)–Te(3)	83° 24′ (15′)		
Bi(3)–Bi(3)–Bi(3)	85° 11′ (11′)		

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* Lists of structure factors, anisotropic temperature factors and the mean-square displacements have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33902 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Divalent-Europium Metaborate

By K. Machida, G. Adachi* and J. Shiokawa

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565, Japan

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Abstract. EuB_2O_4, orthorhombic, *Pnca*; $a = 6{\cdot}593\,(1)$, $b = 12{\cdot}063\,(2)$, $c = 4{\cdot}343\,(1)$ Å, $Z = 4$, $D_x = 4{\cdot}57$, $D_m = 4{\cdot}61$ Mg m^{-3}, $\mu(\mathrm{Mo}\,K\alpha) = 18{\cdot}15$ mm^{-1}. EuB_2O_4 is isostructural with CaB_2O_4. The structural framework consists of endless chains of BO_3 groups, $(BO_2)_\infty$, along the *c* axis. Each Eu atom is surrounded by eight O atoms to form an EuO_8 dodecahedron. The mean Eu–Eu distances between Eu nearest neighbors and between Eu next-nearest neighbors are 4·080 and 6·632 Å, respectively. The final *R* value was 0·029 for 334 observed reflections.

Introduction. Compounds containing divalent europium (Eu^{2+}) have been of interest because of their magnetic and spectroscopic properties. The magnetic exchange interactions in highly symmetrical compounds such as rock salt-type EuO or perovskite-type $EuTiO_3$ have been evaluated on the basis of the Eu^{2+}–Eu^{2+} interactions, and Eu^{2+}–O^{2-}–Eu^{2+} angles, 90 and 180°, between Eu nearest neighbors and next-nearest neighbors respectively. These exchange interactions are sensitive to the distances between Eu^{2+} ions (Wolf, McGuire & Shafer, 1964; McGuire, Shafer, Joenk, Alperin & Pickart, 1966). Divalent-europium borates in the EuO–B_2O_3 system, *i.e.* EuB_4O_7, EuB_2O_4, $Eu_2B_2O_5$ and $Eu_3B_2O_6$, have been synthesized and EuB_2O_4 is an antiferromagnet with the Néel temperature, $T_N = 3$ K (Hata, Adachi & Shiokawa, 1977; Machida, Hata, Okuno, Adachi & Shiokawa, 1978).

The preparation of single crystals has been described in detail elsewhere (Machida *et al.*, 1978). They were grown in the form of light-yellow needles. Weissenberg photographs exhibited the following systematic absences: $k + l = 2n + 1$ for $0kl$, $l = 2n + 1$ for $h0l$ and $h = 2n + 1$ for $hk0$.

The intensity data were measured on a Rigaku automated four-circle diffractometer with a crystal of dimensions 0·15 × 0·15 × 0·30 mm. Reflections within $(\sin\theta)/\lambda = 0{\cdot}71$ Å^{-1} were collected using the ω–2θ scan technique with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) monochromated by a graphite plate. 495 independent reflections were measured, among which 334 observed reflections were above background. The intensity data were corrected for Lorentz and polarization factors. No correction was made for absorption.

The location of the Eu atom was determined by a three-dimensional Patterson synthesis. Successive Fourier syntheses revealed the positions of the O and B atoms. All the atomic parameters were refined by the block-diagonal least-squares method with *HBLS*-V

Table 1. *Final positional parameters*

Standard deviations are given in parentheses.

	x	*y*	*z*
Eu	$\frac{1}{4}$	0	0·2610 (1)
B	0·1247 (13)	0·1944 (6)	0·8281 (18)
O(1)	0·0935 (9)	0·0914 (4)	0·7350 (9)
O(2)	0·1440 (9)	0·2111 (4)	0·1470 (12)

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* To whom correspondence should be addressed.

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