

Tsumoite, BiTe, a new mineral from the Tsumo mine, Japan

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Abstract

Tsumoite, BiTe, is trigonal, $P\bar{3}m1$, $a = 4.422(2)\text{Å}$, $c = 24.05(2)\text{Å}$, $Z = 3[\text{Bi}_2\text{Te}_2]$, and is a new mineral with a sheet structure composed of 12 monoatomic layers in a cubic close-packed stacking sequence analogous to synthetic BiSe. It is silver-white in color, luster metallic and streak steel-grey, and has perfect basal cleavage. Specific gravity is 8.16 ± 0.05 (meas), 8.23 (calc). Vickers hardness is in the range 51–90 kg/mm² (15 g load). Under the ore microscope it is white with creamy tint, very weakly pleochroic, and moderately anisotropic. The reflectivity is higher than that of associate tetradyomite. It occurs as tabular crystals associated with tetradyomite, bismuthinite, cosalite, and galena in a clinopyroxene–garnet–quartz skarn from the Tsumo mine, Shimane Prefecture, Japan. The principal X-ray powder diffraction lines are: 4.78(w), 3.23(vs), 2.36(s), 2.21(s), 1.825(s), and 1.408(s); these being essentially identical with those of synthetic BiTe and distinct from, but very similar to, those of 15-layered hexagonal bismuth chalcogenide.

Introduction

Although natural occurrences of minerals compositionally close to BiTe have been reported under the name wehrlite, the authors' study on topotypic wehrlite (Ozawa and Shimazaki, in preparation) has proved it to be a mixture of Bi₄Te₃ and hessite. The natural occurrence of structurally-verified BiTe is here described under the new name tsumoite, with the approval of the Commission on New Minerals and Mineral Names, IMA; the type locality is the Tsumo mine, Shimane Prefecture, Japan. Type material is deposited in the University Museum, University of Tokyo, Hongo, Tokyo, Japan.

Prior to the natural occurrence, the compound BiTe was studied by Stasova (1964, 1967) from its analogy with synthetic Bi₂Se₂ and Sb₂Te₂. The present structural study on natural BiTe substantiates the structural analogy between them.

Besides wehrlite from the type locality, Deutsch-Pilsen, Hungary, several wehrlites have been reported in previous papers (e.g. Thompson, 1949; Sarkar and Deb, 1969; Sakharova, 1971). Due to lack of adequate X-ray diffraction data in the original papers, it

is not clear whether these wehrlites are tsumoite or not. As will be shown below, tsumoite is characterized by c of about 24Å. Wehrlite reported from Treadwell Property, Ontario (Berry and Thompson, 1962) has c of about 30Å, and is clearly not tsumoite. The mineral seems to be rather close to tellurobismuthite on the basis of the X-ray powder diffraction data.

Occurrence

The Tsumo mine is located about 50 km northwest of Hiroshima City. The area comprises Paleozoic sedimentary rocks, their metamorphic equivalents, and acidic igneous rocks of late Cretaceous age. The ore deposits are pyrometasomatic, and comprise skarns composed principally of grandite garnet and clinopyroxene with disseminated copper, zinc, and lead minerals (Shimazaki, 1968). The studied material was collected from the –60 m level of Tsumo adit. Tsumoite is found as irregular aggregates up to one cm across in a clinopyroxene–garnet–quartz skarn. The aggregates include tablets of tsumoite up to a few millimeters across in the center, surrounded

Table 1. Electron probe microanalyses of minerals found in the tsumoite-bearing aggregate

| | 1 | 2 | 3 | 4 | 5 | 6 |
|-------|------|------|------|-------|------|-------|
| Bi | 61.1 | 61.0 | 60.9 | 60.6 | 45.4 | 81.4 |
| Pb | 1.0 | 1.1 | 1.1 | 0.0 | 36.4 | 1.1 |
| Ag | 0.0 | 0.0 | 0.0 | 0.0 | 1.0 | 0.0 |
| Cu | 0.0 | 0.0 | 0.0 | 0.0 | 0.4 | 0.2 |
| Fe | 0.0 | tr. | 0.0 | 0.0 | 0.0 | 0.0 |
| Te | 37.6 | 37.3 | 37.8 | 35.5 | 0.1 | 0.0 |
| S | 0.0 | 0.1 | 0.1 | 4.4 | 16.3 | 18.6 |
| Total | 99.7 | 99.5 | 99.9 | 100.5 | 99.6 | 101.3 |

| | | |
|----------------|---|-------------------------------|
| 1 Tsumoite | $(\text{Bi}_{0.99}\text{Pb}_{0.02})_{1.01}\text{Te}_{1.00}$ | } Based on Bi+Pb+Te+S=2.00 |
| 2 Tsumoite | $(\text{Bi}_{0.99}\text{Pb}_{0.02})_{1.01}(\text{Te}_{0.99}\text{S}_{0.01})_{1.00}$ | |
| 3 Tsumoite | $(\text{Bi}_{0.98}\text{Pb}_{0.02})_{1.00}(\text{Te}_{1.00}\text{S}_{0.01})_{1.01}$ | |
| 4 Tetradymite | $\text{Bi}_{14.4}\text{Te}_{13.8}\text{S}_{6.9}$ | Bi+Te+S=35.0 |
| 5 Cosalite | $\text{Bi}_{2.13}(\text{Pb}_{1.76}\text{Ag}_{0.09}\text{Cu}_{0.07})_{1.92}(\text{S}_{4.95}\text{Te}_{0.01})_{4.96}$ | Bi+Pb+Ag+Cu+S+Te=9.00 |
| 6 Bismuthinite | $(\text{Bi}_{1.99}\text{Pb}_{0.03}\text{Cu}_{0.01})_{2.03}\text{S}_{2.97}$ | Bi+Pb+Cu+S=5.00 |

by monomineralic tetradymite bands up to 0.2 mm thick and rimmed by a mixture of cosalite and bismuthinite, in direct contact with skarn minerals. In some cases tsumoite is in contact with skarn minerals. Galena is found along the basal cleavage of tsumoite crystals as lamellae a few microns thick and up to 200 microns long.

Chemical and physical properties

By means of JEOL XMA-5 electron probe micro-analyzer with take-off angle 40°, chemical compositions were determined for the minerals found in the aggregates described in the previous section. The accelerating voltage was 25 kV, and the standards used were pure elemental Bi, Te, and Ag; synthetic PbS for Pb; natural chalcopyrite of known composition for Cu, Fe, and S. No other elements were detected through qualitative tests. The X-ray intensities for each point were measured five times for a fixed interval of 10 sec. The averaged values were corrected for dead time and background, and intensities of samples relative to standards were obtained. Quantitative corrections for atomic number, absorption, and fluorescence effects were performed by the method proposed by Sweatman and Long (1969). Preliminary scanning on tsumoite showed that the mineral is quite homogeneous in composition.

Examples of analyses of the minerals are shown in Table 1. Tsumoite has a composition close to Bi:Te = 1:1. Although precise quantitative analysis could not be accomplished because of its thin bleb-like

form, the galena was checked by the probe and found to consist essentially of lead and sulfur.

Tsumoite is silver-white in color, luster metallic, $G = 8.23$ (calc), 8.16 ± 0.05 (meas). Vickers hardness range is 51–90 kg/mm² (15 g load). Cleavage is basal perfect. Under the ore microscope, the mineral is white with a faintly creamy tint, and with very weak reflection pleochroism. The reflectivity is higher than that of associated tetradymite. Tsumoite is moderately anisotropic between crossed nicols, and is etched with HNO₃ and FeCl₃ solutions.

As shown clearly by Strunz (1963), Stasova and Karpinskii (1967), and Imamov and Semiletov (1970, Table 2), the numbers of layers in the phases in the systems Bi–Se, Bi–Te and Sb–Te can be calculated from their compositions: that is, the number of layers in the unit cell is three times of number of atoms in the unit formula. According to this rule, the unit formula of tsumoite should be written as Bi₂Te₂ instead of BiTe, because it has a 12-layer structure, as shown later, given by 3 × (2Bi + 2Te). In fact, many previous investigators adopted the formulas as Bi₂Te₂ and Bi₂Se₂. However, for simplicity, the chemical composition of tsumoite is expressed as BiTe in the present paper.

X-ray diffraction results

Stasova (1967) analyzed the crystal structure of synthetic BiSe, which belongs to the space group $P\bar{3}m1$. The structure is composed of a Bi–Bi double layer alternating with two five-layer packs of the form

Table 2. Crystal data for tsumoite

| | | | | |
|--|-----|--|-----------|--------|
| BiTe, trigonal $P\bar{3}m1$ | | | | |
| $a=4.422(2)$ Å, $c=24.05(2)$ Å, $V=407.3$ Å ³ , $Z=6$ | | | | |
| Atomic coordinates and isotropic temperature factors | | | | |
| atom | x | y | z | B |
| Te ₁ | 1/3 | 2/3 | 0.0530(6) | 1.0(3) |
| Te ₂ | 2/3 | 1/3 | 0.2111(9) | 1.7(3) |
| Te ₃ | 0 | 0 | 0.3631(9) | 1.3(4) |
| Bi ₁ | 0 | 0 | 0.1252(4) | 0.7(2) |
| Bi ₂ | 1/3 | 2/3 | 0.2922(4) | 0.7(2) |
| Bi ₃ | 2/3 | 1/3 | 0.4593(6) | 2.3(3) |
| Interatomic distances | | | | |
| Te ₁ –Te ₁ ' = 3.61(2) Å | | Bi ₂ –Te ₃ = 3.07(2) | | |
| Te ₁ –Bi ₁ = 3.09(1) | | Te ₃ –Bi ₃ = 3.45(2) | | |
| Bi ₁ –Te ₂ = 3.28(2) | | Bi ₃ –Bi ₃ ' = 3.22(2) | | |
| Te ₂ –Bi ₂ = 3.21(2) | | | | |

Se-Bi-Se-Bi-Se. The unit cell contains 12 close-packed layers along the *c* axis. In relation to these results she mentioned that synthetic BiTe is clearly isostructural with BiSe. Yamana *et al.* (1975) confirmed the suggestions by Stasova in their study of synthetic BiTe. In order to clarify the structural character of the present material, powder and single crystals were studied with X-ray techniques.

A Laue photograph taken perpendicular to the cleavage plane showed the Laue symmetry to be $\bar{3}m$. Precession photographs of *h0l* and *hhl* yielded results similar to those reported for synthetic BiSe (Stasova, 1967). The lack of systematic absence permits $P\bar{3}m1$, $P321$, and $P\bar{3}m1$ as possible space groups. There are strong reflections which define a rhombohedral substructure, plus some relatively weak ones due to the stacking of substructure units. The diffraction intensities of *h0l* reflections were measured on the precession photographs (CuK α radiation) using a microdensitometer with reference to a calibrated intensity strip. In addition, several very weak reflections were visually estimated in the range of densities where the densitometer was insensitive. However, only 100 of a total of 281 independent reflections had an intensity above the detectable limit, since the existence of accumulated substructure led to the absence of many reflections. Corrections for Lp and absorption effects were applied (ACACA, Wuensch and Prewitt, 1965, $\mu_{Cu} = 2195$). Since the lattice parameters and intensity distribution in reciprocal space were closely similar to BiSe, the atomic coordinates of Bi and Se in BiSe were employed for the initial model, and then refined in the space group $P\bar{3}m1$ (ORFLS, Busing *et al.*, 1962). Several cycles of refinement for positional parameters and isotropic temperature factors reduced the R index to 0.106 for the observed 100 *h0l* reflections. Neutral-atom form factors given in *International Tables*, Vol. 3, p. 211 and 212 (1968) were used. Anomalous dispersion terms were considered. Our results are summarized in Table 2, together with interatomic distances (ORFFE, Busing *et al.*, 1964) and other crystallographic data. Attempts to refine the model proposed by Gobrecht *et al.* (1964) for BiSe were unsuccessful. Although minor differences in unit-cell dimensions and interatomic distances are observed between tsumoite and synthetic BiTe (Stasova, 1967; Yamana *et al.*, 1975), it may safely be said that the present material is the natural equivalent of synthetic BiTe. The unit cell of tsumoite contains 6 BiTe and it is composed of 12 monoatomic layers. All atoms occupy the special position (c) or (d) of the space group. The layer stacking and the arrangement

Table 3. X-ray powder patterns of tsumoite from the Tsumo mine and synthetic BiTe

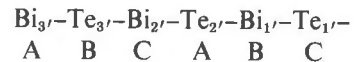
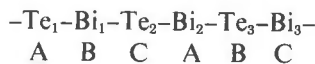
| 1 | | | 2 | | | hkl |
|------|------------------|-------------------|------|------------------|-------------------|--------|
| I | d _{obs} | d _{calc} | I | d _{obs} | d _{calc} | |
| w | 4.78 | 4.81 | m | 4.78 | 4.81 | 005 |
| vw | 3.78 | 3.78 | w | 3.79 | 3.79 | 101 |
| vs | 3.23 | 3.23 | vs | 3.24 | 3.24 | 104 |
| s | 2.36 | 2.36 | s | 2.37 | 2.37 | 108 |
| s | 2.21 | 2.21 | s | 2.22 | 2.22 | 110 |
| | | | w | 2.18 | 2.19 | 109 |
| m | 2.01 | 2.00 | s | 2.00 | 2.00 | 0.0.12 |
| s | 1.825 | 1.825 | s | 1.830 | 1.828 | 204 |
| vw | 1.663 | 1.666 | w | 1.663 | 1.666 | 1.0.13 |
| m | 1.617 | 1.615 | s | 1.620 | 1.618 | 208 |
| | | | vw | 1.556 | 1.559 | 209 |
| s | 1.487 | 1.485 | s | 1.487 | 1.486 | 1.1.12 |
| s(b) | 1.408 | 1.407 | m | 1.413 | 1.410 | 214 |
| | | | m | 1.401 | 1.399 | 1.0.16 |
| | | | vw | 1.362 | 1.357 | 1.1.14 |
| | | | vw | 1.333 | 1.332 | 2.0.13 |
| w | 1.306 | 1.304 | m | 1.309 | 1.307 | 218 |
| vw | 1.277 | 1.277 | w | 1.280 | 1.280 | 300 |
| | | 1.192 | | | 1.192 | 1.1.17 |
| vw | 1.185 | 1.182 | w | 1.190 | 1.183 | 2.0.16 |
| | | 1.147 | | | 1.147 | 1.0.20 |
| vw | 1.140 | 1.140 | w | 1.149 | 1.142 | 2.1.13 |
| vw | 1.106 | 1.106 | vw | 1.111 | 1.108 | 220 |
| vw | 1.076 | 1.077 | w | 1.080 | 1.078 | 3.0.12 |
| | | 1.046 | | | 1.048 | 314 |
| w(b) | 1.045 | 1.043 | w(b) | 1.042 | 1.044 | 2.1.16 |
| | | | vw | 1.018 | 1.019 | 2.0.20 |
| w | 1.001 | 1.002 | w | 1.001 | 1.004 | 318 |
| | | | w | 0.9678 | 0.9697 | 2.2.12 |
| | a=4.422(2) A | | | a=4.433(3) A | | |
| | c=24.05(2) | | | c=24.04(3) | | |

1 Tsumoite from the Tsumo mine, Shimane Prefecture, Japan.

Cu/Ni radiation. Camera method ($\phi = 114.59$ mm).

2 Synthetic BiTe. Cu/Ni radiation. Camera method ($\phi = 114.59$ mm).

of atoms are expressed simply as follows:



Weak van der Waals bonding between $\text{Te}_1-\text{Te}_1'$ (Imamov and Semiletov, 1970) would account for the perfect basal cleavage. The distance (3.61A) is comparable with those in tetradymite, $\text{Bi}_2\text{Te}_2\text{S}$ (3.77, 3.77, 4.10, 4.21A, Pauling, 1975), tellurobismuthite, Bi_2Te_3 (3.57A, Lange, 1939) and Sb_2Te_2 (3.60A, Stasova, 1967).

Powder diffraction data for tsumoite are listed in Table 3, with comparable data for synthetic BiTe prepared as follows. Bismuth and tellurium metals of 99.999 percent purity were weighed and sealed into

an evacuated silica glass tube. After being heated for 7 days at 640°C, the tube was quenched, the contents ground under acetone, again sealed and reheated to the same temperature. After 2 days the tube was cooled to 413°C and kept at that temperature for 6 days. Homogeneity of the product was examined with the electron probe microanalyzer. The unit-cell dimensions were determined using a least-squares program.

The X-ray powder data for tellurobismuthite (Berry and Thompson, 1962), hedleyite (Warren and Peacock, 1945), and redefined pilsenite, Bi_4Te_3 (Ozawa and Shimazaki, in preparation) are very similar to those for tsumoite because of the existence of a substructure unit common to all. One of the most distinctive characteristics of the tsumoite pattern is the position of (005), which varies near 4.8Å as a function of the Bi/Te ratio. This relation is also found in the materials of Bi-Se binary system (Stasova and Karpinskii, 1967).

A hexagonal bismuth chalcogenide from Treadwell Property, Canada, described under the name "wehrlite" (Berry and Thompson, 1962), has a unit cell with $c \approx 30\text{Å}$, in which the existence of 15 layers is expected. The X-ray powder data are very close to those for tsumoite except the reflection near 4.8Å, which appears near 5.0Å with the index (006). In view of this fact, the chemical composition of this wehrlite may be close to that of tellurobismuthite.

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