The Formula, Structure, and Chemical Bonding of Tetradymite, Bi$_{14}$Te$_{13}$S$_8$, and the Phase Bi$_{14}$Te$_{13}$S$_8$

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Abstract

Consideration of bond-angle strain in the structure proposed for tetradymite by Harker leads to the suggestion that the strain can be relieved by substituting a sulfur atom for every seventh tellurium atom in the two outermost layers of the 5-layer sheet and a tellurium atom for every seventh sulfur atom in the middle layer. This substitution leads to Bi$_{14}$Te$_{13}$S$_8$, rather than Bi$_2$Te$_2$S, for tetradymite. Similar structures are also suggested for other phases in the Bi$_2$Te$_2$-Bi$_2$S$_3$ system.

Introduction

The rhombohedral mineral tetradymite, assigned the formula Bi$_2$Te$_2$S, was studied by the X-ray diffraction method by Harker (1934). He reported the unit of structure to be rhombohedral, with $a = 1031$ picometers (pm) and $\alpha = 24^\circ 10'$, and to contain 1 Bi$_2$Te$_2$S, with S at 0,0,0, 2Bi at $\pm(u,u,u)$, $u = 0.392$, and 2 Te at $\pm(v,v,v)$, $v = 0.788$. The structure is based on successive close-packed layers ABCABCABC . . . . It was described as containing sheets of five layers, with the sequence TeBiSBiTe in each sheet (in layers BCABC, for example). The bond lengths corresponding to Harker’s values of $u$ and $v$ and the accurate cell dimensions given by Glatz (1967) are Bi–S = 301 pm and Bi–Te = 308 pm, with the tellurium–tellurium contact distance between sheets equal to 364 pm.

This X-ray investigation seemed to assure the correctness of the formula Bi$_2$Te$_2$S. In 1974, however, Professor Hennes H. Soonpaa of the University of North Dakota told me that he had been unable to grow crystals with the composition Bi$_2$Te$_2$S, but had grown crystals containing somewhat less tellurium and more sulfur, to which he assigned the formula Bi$_2$Te$_2$S$_3$ (Soonpaa, 1962). I then attacked the problem by the methods of theoretical structural chemistry, as described in the next sections, and reached the conclusion that the ideal formula for tetradymite is Bi$_{14}$Te$_{13}$S$_8$, and that another phase in the Bi$_2$Te$_2$–Bi$_2$S$_3$ system, reported by Glatz (1967), has the ideal formula Bi$_{14}$Te$_{13}$S$_8$.

Harker (1934) pointed out that the bond lengths Bi–S and Bi–Te in tetradymite are somewhat greater than the sums of the single-bond covalent radii (Pauling and Huggins, 1934; Pauling, 1960), and suggested that the substance is an example of the metallic state. The theory of chemical bonding in metals and alloys has been developed during recent decades (Pauling, 1938, 1947, 1950, 1970), and can be applied to tetradymite with considerable confidence. It has been found that in metals and some other substances the interactions between adjacent atoms can be described as involving bonds of fractional bond number, $n$, which can be described as resulting from the resonance of bonds (shared electron pairs) among alternative positions. The bond length, $R_{AB}$, for a bond with bond number $n$ between atoms $A$ and $B$ has approximately the value

$$R_{AB}(n) = R_A(1) + R_B(1) + 60 \text{ pm} \log (1/n)$$

In this equation $R_A(1)$ and $R_B(1)$ are the single-bond covalent radii of atoms $A$ and $B$ and the last term is the correction for fractional bond number, equal to 29 pm for $n = 1/3$ and 11 pm for $n = 2/3$ (Pauling, 1947).

The single-bond covalent radii for S, Te, and Bi are 104, 137, and 151 pm, respectively (Pauling, 1960, p. 228, 403), and the values from the shortest contacts in the elementary substances are 103, 142, and 154 pm, the increase for Te and Bi being attributed to bond numbers somewhat smaller than 1, with some bonding to the nearest neighbors. With ligancy 6 for the atoms in the three inner layers of the 5-layer sheet, some increase in bond lengths is expected, and I have selected as the likely values of the effective
single-bond radii in tetradyomite the values 104 pm for S, 140 pm for Te, and 153 pm for Bi. These three elements are all hyperelectronic (Pauling, 1950), so that electron transfer between them would not occur. Their normal covalences are 2 for S and Te and 3 for Bi. The sulfur atom, with valence 2, is bonded to six Bi; the two single covalent bonds resonate among the six positions, leading to bond number \( n = 1/3 \). The corresponding value of the bond length Bi-S is 286 pm, from Equation 1. The bismuth atom uses one of its three covalences in the bonds to sulfur, leaving two for the bonds to the three adjacent tellurium atoms, which thus have \( n = 2/3 \). The calculated Bi-Te bond length is 304 pm. This value agrees with Harker’s value, 308 pm, but the Bi-S bond length, 286 pm, is less than Harker’s value, 301 pm, by more than the experimental error.

For the atoms in the three middle layers, with octahedral ligation, bond angles close to 90° would be expected. In the outer layers, with ligancy 3 and bond number 2/3, a larger bond angle would be expected. The observed value for elementary tellurium is 103°, and with two bonds resonating among three positions the value 94° for Bi-Te-Bi and Te-Bi-Te would not be unreasonable, with consideration of the increase in bond length associated with bond number 2/3. The value of this angle for bond length 304 pm and \( a = 425 \) pm (the edge of the hexagonal cell reported by Glatz, 1967) is, however, only 88.7°, with the calculated angle Bi-S-Bi = S-Bi-S equal to 96.0°. These deviations from the expected values of the angles might make the substance with composition Bi\(_2\)Te\(_2\)S and the Harker structure unstable, relative to other phases, as reported by Soonpaa (1962) and by Glatz (1967).

The \( \alpha \) Phase

The substance Bi\(_2\)Te\(_3\) has the tetradyomite structure, with sheets of atoms in the sequence TeBiTeBiTe. The calculated bond lengths for Bi-Te, namely, 304 pm for \( n = 2/3 \) and 322 pm for \( n = 1/3 \), correspond to bond angles 92.6° and 86.0°, respectively. The strain from the small value of the second angle would be relieved by the introduction of some sulfur atoms.

The \( \beta \) Phase

Glatz made a thorough study of the system Bi\(_2\)Te\(_3\)-Bi\(_2\)S\(_3\) by differential thermal analysis and X-ray diffraction of samples that had been annealed at 400°C for several weeks. He found a phase (\( \alpha \)) with 0 to 4 mole percent of Bi\(_2\)Te\(_3\), one with 25 to 30 percent (\( \beta \)), and one with 34 to 50 percent (\( \gamma \)). There was no phase with 33.3 percent, corresponding to the formula Bi\(_2\)Te\(_2\)S. The hexagonal cells have \( a = 438.4 \) to 437.9 pm and \( c = 3050 \) to 3045 pm for the \( \alpha \) phase, \( a = 425.5 \) pm and \( c = 2959 \) pm for the \( \beta \) phase, and \( a = 425.5 \) to 424 pm and \( c = 2960 \) to 2957 for the \( \gamma \) phase.

Formulation of Structures

The nature of the structure, a sequence of close-packed hexagonal layers, is such that there is only one parameter, the hexagonal cell edge \( a \), determining the interatomic distances in the various layers. The value of \( a \) corresponding to the greatest stability for the two outermost layers of a sheet (occupied by tellurium atoms in the tetradyomite structure) might differ from that corresponding to the greatest stability for the middle layer (occupied by sulfur atoms), leading to a compromise involving some strain. This strain might be relieved by the substitution of part of the atoms in a layer by atoms of another kind. Sulfur atoms and tellurium atoms have the same valence but differ in size. Accordingly strain of this sort might be relieved by introducing some sulfur atoms in a tellurium layer or some tellurium atoms in a sulfur layer.

One reasonable way to introduce a few atoms of one kind in a layer containing mainly atoms of a second kind is shown in Figure 1. The hexagonal unit of structure contains seven atoms, ST\(_{e6}\) or TeS\(_6\), with the atoms of each kind equivalent. In ST\(_{e6}\), for example, each sulfur atom has six tellurium neighbors, and each tellurium atom has one sulfur and five tellurium neighbors. The axes of the 7-atom unit are rotated by 19.11° and have a length \( \sqrt{7} \) times those of the one-atom unit.

The \( \beta \) Phase

The substance Bi\(_2\)Te\(_3\) has the tetradyomite structure, with sheets of atoms in the sequence TeBiTeBiTe. The calculated bond lengths for Bi-Te, namely, 304 pm for \( n = 2/3 \) and 322 pm for \( n = 1/3 \), correspond to bond angles 92.6° and 86.0°, respectively. The strain from the small value of the second angle would be relieved by the introduction of some sulfur atoms.

FIG. 1. The 7-atom unit of a close-packed layer in relation to the 1-atom unit.
in the middle layer of the 5-layer sheet. This substitution might be either random or ordered. A reasonable ordered structure is that for STe shown in Figure 1. I suggest that this is the structure for the high-sulfur limit of the α phase, which would have the formula Bi₁₄Te₂oS, with 4.76 mole percent Bi₂S₃, a little larger than the 4 percent reported by Glatz. The average bond length to bismuth for the atoms STe in the middle layer is 317 pm, which corresponds to 87.4° for the average bond angle, an improvement over the value 86.0° for Bi₄Te₃.

The β Phase

Additional improvement in the bond angle is achieved by going to the composition TeS₄ for the middle layer; the average bond length 291 pm leads to the acceptable value 93.8° for the average bond angle. This structure corresponds to the formula Bi₁₄Te₂oS, with 28.6 mole percent Bi₂S₃, near the middle of the range 25 to 30 percent for the β phase. The sequence of layers in a sheet is Te₄-Bi₄-TeS₄-Bi₄-TeS₄.

The γ Phase

In the β compound Bi₁₄Te₂oS, the angle for the middle layer, 93.8°, is satisfactory, but that for the outer layer, 88.9° (calculated for Bi-Te = 304 pm, n = 2/3), is too small. Its value can be increased by replacing the two outer Te₄ layers by TeS₄ layers, leading to the average Bi-(TeS) bond length 299 pm and the acceptable value 90.6° for the average bond angle. The layers of the sheet have the composition TeS₄-Bi₄-TeS₄-Bi₄-TeS₄, giving the formula Bi₁₄Te₂oS. This formula corresponds to 38.1 mole percent Bi₂S₃, within the range 34 to 50 percent for the β phase. It lies close to Soonpaa's formula Bi₆Te₃S₆, with 38.5 percent.

I suggest that this formula, Bi₁₄Te₂oS, is the ideal formula also for natural tetradymite.

Natural Tetradymite

The results of several chemical analyses of natural tetradymite cited by Palache, Berman, and Frondel (1944, p. 162) have been normalized to Bi + Pb = 14.00 atoms (Table 1). It is seen that the number of tellurium atoms is found to be 12.99 or 13.20, much closer to the value for the proposed formula Bi₁₄Te₂oS than to the old formula Bi₂Te₅S = Bi₁₄Te₃S₆. The average reported value for S + Se, 7.18, agrees more closely with the old formula than with the proposed one. It is possible that there are systematic errors in the analyses, since the sum Te + S + Se, with average value 20.17 or 20.38, almost certainly should equal 21. If the error is in the determination of S + Se the analyses would correspond closely with the formula Bi₁₄Te₃S₆.

None of the analyses of natural tetradymite lie close to the ideal composition of the β phase, Bi₁₄Te₂oS.

Description of the Structure of Bi₁₄Te₂oS

The structure of a 5-layer sheet of Bi₁₄Te₂oS is similar to that found by Harker, except for the distortions caused by the substitutions of a sulfur atom for tellurium in each of the two outer layers and of a tellurium atom for sulfur in the middle layer. The distortions are such as to give the expected bond lengths.

The space group is R3. The rhombohedral unit, containing 1 Bi₁₄Te₂oS, has a₃ₙ = 1124 pm, α = 56.83°. For convenience I use the corresponding hexagonal unit, with a = 425 pm and c = 2960 pm, containing 3 Bi₁₄Te₂oS. The predicted atomic positions are given in Table 2.

The short interatomic distances have the values assumed in deriving the structure, 268 and 286 pm for Bi-S and 304 and 322 pm for Bi-Te, the longer bonds being those to the middle layer.

The Te-Te contacts between sheets are at 377, 377, 410, 410, and 421 pm, as compared with 349 pm in elementary tellurium. The Te-S contacts between

### Table 1. Chemical Analyses of Tetradymite*

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Bi</th>
<th>Pb</th>
<th>Te</th>
<th>S</th>
<th>Se</th>
<th>S+Se</th>
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<tbody>
<tr>
<td>Bradshaw City, Arizona, 1890</td>
<td>14.00</td>
<td>--</td>
<td>12.25</td>
<td>6.60</td>
<td>6.60</td>
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<td>Caslava, Hungary, 1935</td>
<td>13.84</td>
<td>0.16</td>
<td>12.49</td>
<td>6.30</td>
<td>0.88</td>
<td>7.18</td>
</tr>
<tr>
<td>Schubka, Hungary, 1897</td>
<td>14.00</td>
<td>--</td>
<td>13.39</td>
<td>6.35</td>
<td>trace</td>
<td>6.35</td>
</tr>
<tr>
<td>Nornengo, New South Wales, 1908</td>
<td>13.81</td>
<td>0.19</td>
<td>12.57</td>
<td>6.85</td>
<td>--</td>
<td>6.85</td>
</tr>
<tr>
<td>West Gwanda, Rhodesia, 1928</td>
<td>14.00</td>
<td>--</td>
<td>13.65</td>
<td>7.63</td>
<td>trace</td>
<td>7.63</td>
</tr>
<tr>
<td>Caslava, Hungary, 1931</td>
<td>14.00</td>
<td>--</td>
<td>13.94</td>
<td>7.33</td>
<td>--</td>
<td>7.33</td>
</tr>
<tr>
<td>Trail Creek, Idaho, 1925</td>
<td>13.64</td>
<td>0.36</td>
<td>14.13</td>
<td>6.91</td>
<td>1.39</td>
<td>8.30</td>
</tr>
</tbody>
</table>

**Numbers of atoms, referred to Bi + Pb = 14.00
***From Palache, Berman, and Frondel (1944).

The weighted average gives this line the weight 4.

### Table 2. Predicted Atomic Positions for Tetradymite*

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Bi₁₄Te₂oS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₆ in α, z = 0.000</td>
<td>0.215</td>
<td>0.268</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>Bi₄ in α, z = 0.0520</td>
<td>0.215</td>
<td>0.268</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>Bi₂ in α, z = 0.0057</td>
<td>0.215</td>
<td>0.268</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>Bi in α, z = 0.0057</td>
<td>0.215</td>
<td>0.268</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>Te₁ in ω, x = 0.441</td>
<td>y = 0.301, z = 0.0020</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te in ω, x = 0.441</td>
<td>y = 0.301, z = 0.0020</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi₁ in ω, x = 0.0520</td>
<td>0.215</td>
<td>0.268</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
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</tr>
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<td>Bi in ω, x = 0.0520</td>
<td>0.215</td>
<td>0.268</td>
<td>0.007</td>
<td></td>
</tr>
</tbody>
</table>

*All + 000, 0.5, 0.5, 0.5, 0.5, 0.5, 0.5.
sheets have a length of 425 pm. There is presumably some bonding in the Te-Te contacts, since the distance is less than that expected for pure van der Waals interaction, 440 pm, but not so much as in the elementary substance. The Te-S distance, 425 pm, is a little larger than the sum of the van der Waals radii, 405 pm.

It is likely that weak X-ray reflections indicating the large unit could be obtained from natural tetradymite and from thoroughly annealed synthetic crystals. They should appear clearly on Laue photographs. One weak reflection requiring a unit larger than the Harker unit was reported by Soonpaa (1962).

In Bi₂Te₃, with \(a = 438.4\) pm and \(c = 3050\) pm, the assumed bond lengths lead to the values \(z = 0.0653\) for Bi and \(0.1203\) for Te, and to the Te-Te contact distance 379 pm. The values of \(z\) agree reasonably well with those of Airapetyants and Efimova (1958), 0.0662 and 0.1209; of Wiese and Muldawer (1960), 0.0680 and 0.1238; and of Lange (1939), 0.066 and 0.125.

For Bi₂Se₃, with \(a = 415\) pm and \(c = 2865\) pm (Schubert and Fricke, 1953), we use the value 117 pm for \(R(1)\) of selenium to obtain the bond lengths Bi-Se = 281 pm \((n = 2/3)\) and 299 pm \((n = 1/3)\) and the corresponding values 0.0624 and 0.1136 for \(z\) of bismuth and selenium, respectively, in rough agreement with the values 0.066 and 0.127 reported by Semiletov (1954). The Se-Se contacts between sheets are at 387 pm, somewhat less than the van der Waals contact distance, 400 pm.

The general agreement with experiment of the structures predicted by use of interatomic distances calculated for bond numbers 1/3 and 2/3 supports the assumption that tetradymite and related substances are normal-valence compounds, bismuth having covalence 3 and tellurium and its congeners covalence 2, with the bonds resonating among three or six positions. There is no evidence for assigning a significant amount of transaragononic character to the atoms, as was suggested by Drabble and Goodman (1958).

References


Harker, D. (1934) The crystal structure of the mineral tetradymite, Bi₂TeS₃. Z. Kristallog. 89, 175-181.


———, and M. L. Huggins (1934) Covalent radii of atoms and interatomic distances in crystals containing electron-pair bonds. Z. Kristallog. 87, 205-238.


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