

## The Formula, Structure, and Chemical Bonding of Tetradymite, $\text{Bi}_{14}\text{Te}_{13}\text{S}_8$ , and the Phase $\text{Bi}_{14}\text{Te}_{15}\text{S}_6$

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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  $\text{Bi}_{14}\text{Te}_{13}\text{S}_8$ , rather than  $\text{Bi}_2\text{Te}_2\text{S}$ , for tetradymite. Similar structures are also suggested for other phases in the  $\text{Bi}_2\text{Te}_3\text{-Bi}_2\text{S}_3$  system.

### Introduction

The rhombohedral mineral tetradymite, assigned the formula  $\text{Bi}_2\text{Te}_2\text{S}$ , 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  $\text{Bi}_2\text{Te}_2\text{S}$ , 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 TeBiS<sub>2</sub>BiTe 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  $\text{Bi}_2\text{Te}_2\text{S}$ . In 1974, however, Professor Henn H. Soonpaa of the University of North Dakota told me that he had been unable to grow crystals with the composition  $\text{Bi}_2\text{Te}_2\text{S}$ , but had grown crystals containing somewhat less tellurium and more sulfur, to which he assigned the formula  $\text{Bi}_8\text{Te}_7\text{S}_5$  (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  $\text{Bi}_{14}\text{Te}_{13}\text{S}_8$ , and that another phase in the  $\text{Bi}_2\text{Te}_3\text{-Bi}_2\text{S}_3$  system, reported by Glatz (1967), has the ideal formula  $\text{Bi}_{14}\text{Te}_{15}\text{S}_6$ .

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 tetradymite 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  $90^\circ$  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  $103^\circ$ , and with two bonds resonating among three positions the value  $94^\circ$  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  $88.7^\circ$ , with the calculated angle Bi-S-Bi = S-Bi-S equal to  $96.0^\circ$ . These deviations from the expected values of the angles might make the substance with composition  $Bi_2Te_2S$  and the Harker structure unstable, relative to other phases, as reported by Soonpaa (1962) and by Glatz (1967).

### The $Bi_2(Te,S)$ Phase Diagram

Glatz made a thorough study of the system  $Bi_2Te_3$ - $Bi_2S_3$  by differential thermal analysis and X-ray diffraction of samples that had been annealed at  $400^\circ C$  for several weeks. He found a phase ( $\alpha$ ) with 0 to 4 mole percent of  $Bi_2Te_3$ , 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  $Bi_2Te_2S$ . 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 tetradymite 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,  $STe_6$  or  $TeS_6$ , with the atoms of each kind equivalent. In  $STe_6$ , 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  $19.11^\circ$  and have a length  $7^{1/2}$  times those of the one-atom unit.

### The $\alpha$ Phase

The substance  $Bi_2Te_3$  has the tetradymite 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  $92.6^\circ$  and  $86.0^\circ$ , respectively. The strain from the small value of the second angle would be relieved by the introduction of some sulfur atoms

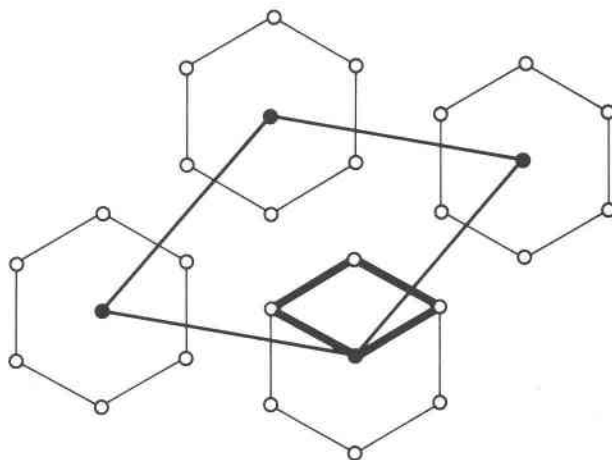


FIG. 1. The 7-atom unit of a close-packed layer in relation to the 1-atom unit.

in the middle layer of the 5-layer sheet. This substitution might be either random or ordered. A reasonable ordered structure is that for  $\text{STe}_6$  shown in Figure 1. I suggest that this is the structure for the high-sulfur limit of the  $\alpha$  phase, which would have the formula  $\text{Bi}_{14}\text{Te}_{20}\text{S}$ , with 4.76 mole percent  $\text{Bi}_2\text{S}_3$ , a little larger than the 4 percent reported by Glatz. The average bond length to bismuth for the atoms  $\text{STe}_6$  in the middle layer is 317 pm, which corresponds to  $87.4^\circ$  for the average bond angle, an improvement over the value  $86.0^\circ$  for  $\text{Bi}_2\text{Te}_3$ .

### The $\beta$ Phase

Additional improvement in the bond angle is achieved by going to the composition  $\text{TeS}_6$  for the middle layer; the average bond length 291 pm leads to the acceptable value  $93.8^\circ$  for the average bond angle. This structure corresponds to the formula  $\text{Bi}_{14}\text{Te}_{15}\text{S}_6$ , with 28.6 mole percent  $\text{Bi}_2\text{S}_3$ , near the middle of the range 25 to 30 percent for the  $\beta$  phase. The sequence of layers in a sheet is  $\text{Te}_7\text{-Bi}_7\text{-TeS}_6\text{-Bi}_7\text{-Te}_7$ .

### The $\gamma$ Phase

In the  $\beta$  compound  $\text{Bi}_{14}\text{Te}_{15}\text{S}_6$ , the angle for the middle layer,  $93.8^\circ$ , is satisfactory, but that for the outer layer,  $88.9^\circ$  (calculated for  $\text{Bi-Te} = 304$  pm,  $n = 2/3$ ), is too small. Its value can be increased by replacing the two outer  $\text{Te}_7$  layers by  $\text{Te}_6\text{S}$  layers, leading to the average  $\text{Bi-(Te}_6\text{S)}$  bond length 299 pm and the acceptable value  $90.6^\circ$  for the average bond angle. The layers of the sheet have the composition  $\text{Te}_6\text{S-Bi}_7\text{-TeS}_6\text{-Bi}_7\text{-Te}_6\text{S}$ , giving the formula  $\text{Bi}_{14}\text{Te}_{13}\text{S}_8$ . This formula corresponds to 38.1 mole percent  $\text{Bi}_2\text{S}_3$ , within the range 34 to 50 percent reported by Glatz. It lies close to Soonpaa's formula  $\text{Bi}_8\text{Te}_7\text{S}_5$ , with 38.5 percent.

I suggest that this formula,  $\text{Bi}_{14}\text{Te}_{13}\text{S}_8$ , 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  $\text{Bi} + \text{Pb} = 14.00$  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  $\text{Bi}_{14}\text{Te}_{13}\text{S}_8$  than to the old formula  $\text{Bi}_2\text{Te}_2\text{S} = \text{Bi}_{14}\text{Te}_{14}\text{S}_7$ . The average reported value for  $\text{S} + \text{Se}$ , 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  $\text{Te} +$

TABLE 1. Chemical Analyses of Tetradymite\*

Analysis**	Bi	Pb	Te	S	Se	S+Se
Bradshaw City, Arizona, 1890	14.00	--	12.25	6.60	--	6.60
Csiklova, Hungary, 1935	13.84	0.16	12.49	6.30	0.88	7.18
Schubkau, Hungary, 1897	14.00	--	13.39	6.35	trace	6.35
Norongo, New South Wales, 1908	13.81	0.19	12.57	6.85	--	6.85
West Gwanda, Rhodesia, 1928	14.00	--	13.65	7.63	trace	7.63
Csiklova, Hungary, 1931	14.00	--	13.94	7.33	--	7.33
Trail Creek, Idaho, 1925	13.64	0.36	14.13	6.91	1.39	8.30
Average			13.20			7.18
Weighted average***			12.99			7.18
Ideal formula	14		13			8

\*Numbers of atoms, referred to  $\text{Bi+Pb} = 14.00$

\*\*From Palache, Berman and Frondel (1944).

\*\*\*The second line gives the average of four closely agreeing analyses. The weighted average gives this line the weight 4.

$\text{S} + \text{Se}$ , with average value 20.17 or 20.38, almost certainly should equal 21. If the error is in the determination of  $\text{S} + \text{Se}$  the analyses would correspond closely with the formula  $\text{Bi}_{14}\text{Te}_{13}\text{S}_8$ .

None of the analyses of natural tetradymite lie close to the ideal composition of the  $\beta$  phase,  $\text{Bi}_{14}\text{Te}_{15}\text{S}_6$ .

### Description of the Structure of $\text{Bi}_{14}\text{Te}_{13}\text{S}_8$

The structure of a 5-layer sheet of  $\text{Bi}_{14}\text{Te}_{13}\text{S}_8$  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  $R\bar{3}$ . The rhombohedral unit, containing 1  $\text{Bi}_{14}\text{Te}_{13}\text{S}_8$ , has  $a_{\text{rh}} = 1124$  pm,  $\alpha = 56.83^\circ$ . For convenience I use the corresponding hexagonal unit, with  $a = 425$  pm and  $c = 2960$  pm, containing 3  $\text{Bi}_{14}\text{Te}_{13}\text{S}_8$ . 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  $\text{Bi-S}$  and 304 and 322 pm for  $\text{Bi-Te}$ , the longer bonds being those to the middle layer.

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

TABLE 2. Predicted Atomic Positions for Tetradymite\*

3 Te 1 in $a$ , 000
18 Te 2 in $f$ , $x, y, z; \bar{y}, x-y, z; y-x, \bar{x}, z; \bar{x}, \bar{y}, \bar{z}; y, y-x, \bar{z}; x-y, x, \bar{z}$ $x = 0.220, y = 0.044, z = 0.1115$
18 Te 3 in $f$ , $x = 0.407, y = 0.504, z = 0.1169$
6 S 1 in $c$ , $\frac{1}{3}, \frac{2}{3}, z; \frac{2}{3}, \frac{1}{3}, z; z = -0.1007$
18 S 2 in $f$ , $x = 0.441, y = 0.301, z = 0.0020$
6 Bi 1 in $c$ , $z = 0.0520$
18 Bi 2 in $f$ , $x = 0.215, y = 0.268, z = 0.0557$
18 Bi 3 in $f$ , $x = 0.464, y = 0.097, z = 0.0527$

\*  $a11 + 000, \frac{2}{3}, \frac{1}{3}, \frac{2}{3}; \frac{1}{3}, \frac{2}{3}, \frac{2}{3}$

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  $\text{Bi}_2\text{Te}_3$ , 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 Muldower (1960), 0.0680 and 0.1238; and of Lange (1939), 0.066 and 0.125.

For  $\text{Bi}_2\text{Se}_3$ , 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 transargononic character to the atoms, as was suggested by Drabble and Goodman (1958).

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