

## Pressure-Induced Te<sub>7</sub>S<sub>10</sub>: A Cocrystallization of Sulfur and Tellurium Helices

**Abstract.** *The first and only known phase in the tellurium-sulfur system has been obtained at high pressures. Evidence is presented to support the hypothesis that this phase consists of a cocrystallization of sulfur and tellurium helices in 1 : 1 ratio.*

In a continuing investigation of the metastably retainable pressure-induced phases involving Group VI-A elements, a new phase in the tellurium-sulfur system has been found. It is the only known phase of tellurium and sulfur of fixed stoichiometry, but does not involve Te-S chemical bonding; rather, it is evidently formed by a cocrystallization of sulfur and tellurium helices in 1 : 1 ratio.

Thus far, three pressure-induced phases of sulfur have been found (1). A structural analysis (2) has been made of one of these phases that is fibrous and appears to be the same as the so-called S<sub>v</sub> phase (1-4). No new phases of Se or of Te that can be retained metastably at room temperature were expected, nor were any such expected of Te-Se. However, no difference from the solid solution formed at ordinary pressure was observed when Te<sub>0.5</sub>Se<sub>0.5</sub> at 40 kb was melted at 700°C, held at 300°C for 2 hours, followed by quenching and removal of pressure.

A new sulfur-selenium phase was obtained (5) with formula S<sub>0.55</sub>Se<sub>0.45</sub>. Although crystals of this phase have neither the structure of hexagonal selenium nor that of any of the sulfur phases, the phase is a solid solution; the helical molecules contain both Se and S atoms (chemically bonded). The experiments carried out on the S-Se system indicated also that there was a range of solid solution involving the same structure. They also showed, in fact, that some Se could be dissolved in the fibrous sulfur phase and that some S could be dissolved in hexagonal Se. The quantitative extents of these solid-solution ranges were not determined. Preliminary discussion of the new S-Se crystal structure was given earlier (5).

While a compound TeO<sub>2</sub> and its crystal structures are known (6), there is no known compound of Te and S, and I thought that one could be made at high pressures. If so, the probability was high that it might be retained metastably at ordinary conditions.

It was found early in the experiments

that, although a new phase appeared, the phase could not be obtained homogeneously by melting a mixture of Te and S before annealing it, as we had done in the S-Se cases (5). Melting before annealing caused a separation of the two elements. It was thus necessary to depend on solid-state reaction involving rather long holding periods at high pressure and at temperatures below the melting points of either Te or S.

The experiments showed that the formula of the new phase was not TeS<sub>3</sub>, TeS<sub>2</sub>, or Te<sub>2</sub>S<sub>3</sub>. After pressure was removed, the specimens made with these proportions of Te and S contained the new phase and excess sulfur. This indicated that the new phase was not a valence compound like TeO<sub>2</sub>. If the phase contained some mixed Te-S molecular species, solid-solution range should be expected but was not observed. The new phase was not TeS; the specimen with this attempted stoichiometry contained excess Te. Similarly, a specimen made up to be Te<sub>3</sub>S<sub>4</sub> contained excess Te, but this one seemed to be close to single phase, and, in view of the difficulty in obtaining homogeneous starting mixtures, this could possibly be the correct formula. But I could not account for such a formula on any logical structural basis.

I reviewed the facts. As to the size of the sulfur, selenium, and tellurium atoms, the sulfur atom is smallest and the tellurium atom is the largest. Sulfur forms solid solutions with selenium (7) and selenium forms solid solutions with tellurium (8), even at atmospheric pressure. That the pressure-induced tellurium-sulfur phase is not a valence compound and does not have a solid-solution range implies that there is no chemical bonding between the sulfur and tellurium atoms. It seemed that only one logical possibility remained, namely that the sulfur and tellurium helical molecules are cocrystallizing in exactly a 1 : 1 ratio.

I now present evidence in support of this hypothesis. The lattice constants of hexagonal tellurium (9, 10) are  $a = 4.457$ ,  $c = 5.929$  Å. The pseudoorthorhombic axes of fibrous sulfur (1) are

$a = 13.8$ ,  $b = 32.4$ ,  $c = 9.25$  Å; in fibrous sulfur (1-3, 11) there are ten S atoms in three turns of a helix of period 13.8 Å and pitch,  $P_s$ , 4.6 Å. It is immediately seen that  $7/3 P_{Te} = 3 P_s$  within the experimental error of 3  $P_s$ . That is, the length of a seven-atom increment of Te helix is equal to that of a ten-atom increment of sulfur helix (Fig. 1). However, for a lattice period

Table 1. X-ray diffraction powder data for Te<sub>7</sub>S<sub>10</sub> indexed on pseudoorthorhombic cell (CuK $\alpha$  radiation). Abbreviations: w, weak; m, medium; s, strong; v, very.

hkl	d(Å)		I <sub>rel</sub>
	Calculated	Observed	
002	4.62	4.62	m
10,0,0	4.149	4.146	w
462.	3.295	3.291	m
912	3.246	3.245	w-m
372	3.146		
880	3.145	3.144	m-s
881	2.977	2.979	m
6,10,0	2.877		
4,10,1	2.876		
10,4,2	2.876	2.876	m-s
513	2.876		
791	2.874		
16,0,0	2.593		
8,10,1	2.593	2.592	w
2,10,2	2.590		
16,0,1	2.497		
14,0,2	2.494	2.497	s
11,7,2	2.454		
12,6,2	2.451	2.451	m*
15,5,2	2.222		
11,11,1	2.220	2.221	w
514	2.220		
5,13,2	2.084		
19,3,1	2.083		
12,10,2	2.083		
13,11,1	2.082	2.081	m*
3,11,3	2.078		
16,6,2	2.078		
18,2,2	2.045		
11,13,0	2.045		
12,2,1	2.045	2.045	w
5,15,0	2.044		
7,11,3	1.981		
14,6,3	1.979	1.980	vw*
0,16,0	1.978		
15,5,3	1.957		
10,4,4	1.956	1.956	vw*
14,8,3	1.879		
974	1.878	1.877	m*
13,9,3	1.875		
625	1.774		
16,8,3	1.773		
445	1.773	1.773	ms*
155	1.772		
9,15,2	1.771		
7,15,3	1.670		
285	1.669		
11,17,0	1.669	1.668	m*
10,14,3	1.668		

\* Broad

parallel to the helix axis, the tellurium helix must have  $3n$  atoms. Therefore, the lattice constant in this direction must be close to  $7c_{Te} = 41.49 \text{ \AA}$  or  $9P_S = 41.4 \text{ \AA}$ , and the formula of the phase is  $Te_7S_{10}$ .

Now we look at the van der Waals or packing diameter of the Te and S helices. In the Te case, this diameter is simply equal to the lattice constant  $a = 4.457 \text{ \AA}$ . In the fibrous sulfur case, the sulfur helices are essentially hexagonally close-packed, although perhaps somewhat more efficiently (11) than those of Te, because of the simultaneous presence of both right- and left-handed helices. Examination of a scale model indicates that a very probable arrangement of helices is similar to that (2, 11) in fibrous sulfur, namely rows of right(left)-handed sulfur and left(right)-handed tellurium helices alternating along the pseudoorthorhombic  $b$ -axis (Fig. 2). If this is the case, then the pseudoorthorhombic  $c$ -axis would be equal to that of sulfur, namely  $9.25 \text{ \AA}$ . Along the  $b$ -axis, one sulfur helix accounts for  $4.05 \text{ \AA}$ ; in tellurium  $a_{Te} \sqrt{3}/2 = 3.860$ . The average of these two values is  $3.955 \text{ \AA}$  which, when multiplied by 8, predicts  $31.64 \text{ \AA}$  for the pseudoorthorhombic  $b$ -axis of  $Te_7S_{10}$ .

In our earlier experiments we had established that the new phase melts incongruently at high pressure, which, in retrospect, is a logical consequence of the absence of chemical bonding between the tellurium and sulfur atoms. Thus it appeared that it would not be possible to obtain single crystals of a size suitable for obtaining diffraction data. But the weight of the evidence nevertheless favors the plausibility of the conclusion that the structure consists of a cocrystallization of tellurium and sulfur helices in 1 : 1 ratio.

Tellurium and sulfur of 99.999+ percent purity (obtained from American Smelting and Refining Company) were finely ground. Amounts of each appropriate to  $Te_7S_{10}$  and for two high-pressure runs (to obtain sufficient material for a density measurement) were weighed out (the total weight being about 0.41 g) and thoroughly mixed. The specimens were pressurized at 40 kb and  $400^\circ$  to  $412^\circ\text{C}$  for 4 to 5 days. The powder x-ray diffraction photographs indicated that the resulting material was single phase. The material from the two runs was ground in an agate mortar and then highly compressed in a cylindrical die with a nominal

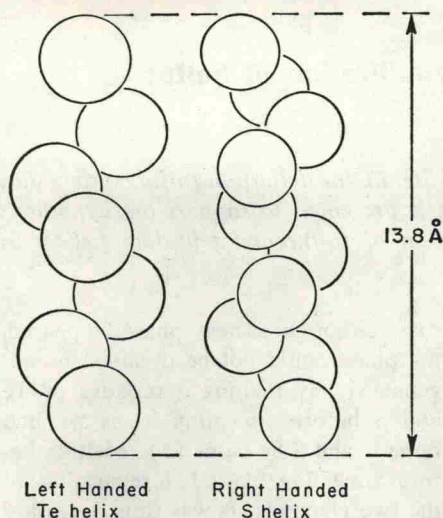


Fig. 1. The relation of the sizes of a seven-atom increment of Te helix to a ten-atom increment of S helix.

inal diameter of 0.25 inches (0.64 cm). The resulting pill had high metallic luster (as does tellurium itself) and, I believe, was close to theoretical density. The dimensions of the pellet were measured, and the pellet was weighed. The measured density was  $4.017 \text{ g/cm}^3$ .

Now, if the reasoning presented earlier is correct, the pseudoorthorhombic cell of  $Te_7S_{10}$  should have lattice constants  $a = 41.49$ ,  $b = 31.64$ ,  $c = 9.25 \text{ \AA}$ ; in indexing of the powder photograph (Table 1), I reduced  $c$  to  $9.24 \text{ \AA}$ . With  $8 \times 30 = 240$  S atoms, and  $8 \times 21 = 168$  Te atoms in this cell, the calculated x-ray density is  $3.99 \text{ g/cm}^3$ , which is within less than 1 percent of the measured value.

It should be emphasized that it is really impossible for the structure of the  $Te_7S_{10}$  phase to have orthorhombic symmetry (2). The monoclinic cell de-

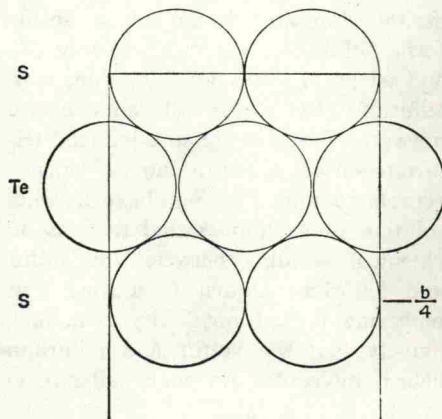


Fig. 2. Idealized packing of the S and Te helices. The circles, drawn to scale, represent projections of the van der Waals "cylinders" circumscribing the helices.

rived from the end-centered pseudoorthorhombic cell has lattice constants:  $a = 41.49$ ,  $b = 9.24$ ,  $c = 26.09 \text{ \AA}$ ,  $\beta = 142.7^\circ$ . To have monoclinic symmetry, the twofold symmetry of some of the sulfur helices must be used. For efficient packing of the tellurium and sulfur helices, however, this could turn out not to be possible, and in view of our results on the fibrous sulfur (2), improbable. In this case, the most probable space group for the phase would be  $P1$ .

One further point should be made regarding the fibrous sulfur itself. In my earlier report (1), I had indicated that the pressure-induced modifications were obtained only when the sulfur was first melted and then held at temperature and pressure for some time. For the temperatures given in that report, this is correct. However, I could not escape the logical conclusion that the formation of the new  $Te_7S_{10}$  phase below the melting point of either sulfur or tellurium implied that melting is not required for the formation of helical sulfur molecules. I therefore ran an experiment in which sulfur was pressurized to 40 kb and held at  $400^\circ\text{C}$  for 4 days. The resultant product was indeed the fibrous modification. Sclar *et al.* (4) have also reported obtaining this phase without having first melted the sulfur (see also 12).

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