Pressure-Induced Te₇S₁₀: 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_Ψ 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 $Te_{0.5}Se_{0.5}$ 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 $S_{0.55}Se_{0.45}$. 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_2 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_3, TeS_2, or Te_2S_3. 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_2. 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_3S_4 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 pseudoortho-rhombic axes of fibrous sulfur (*1*) are

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

Table 1. X-ray diffraction powder data Te₇S₁₀ indexed on pseudoorthorhombic (CuKα radiation). Abbreviations: w, w m, medium; s, strong; v, very.

| hkl | d(Å) | | I_{rel} |
	Calculated	Observed	
002	4.62	4.62	
10,0,0	4.149	4.146	v
462	3.295	3.291	
912	3.246	3.245	w
372	3.146		
880	3.145	3.144	m
881	2.977	2.979	
6,10,0	2.877		
4,10,1	2.876		
10,4,2	2.876	2.876	m
513	2.876		
791	2.874		
16,0,0	2.593		
8,10,1	2.593	5.92	
2,10,2	2.590		
16,0,1	2.497		
14,0,2	2.494	2.497	
11,7,2	2.454		
12,6,2	2.451	2.451	n
15,5,2	2.222		
11,11,1	2.220	2.221	
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	v
5,15,0	2.044		
7,11,3	1.981		
14,6,3	1.979	1.980	v
0,16,0	1.978		
15,5,3	1.957	1.956	v
10,4,4	1.956		
14,8,3	1.879		
974	1.878	1.877	
13,9,3	1.875		
625	1.774		
16,8,3	1.773		
445	1.773	1.773	n
155	1.772		
9,15,2	1.771		
7,15,3	1.670		
285	1.669	1.668	
11,17,0	1.669		
10,14,3	1.668		

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