

Pressure-Induced Phase of Sulfur-Selenium

Abstract. Crystals of a fibrous phase of sulfur-selenium obtained at 20 kilobars and 280°C are trigonal, the most probable space groups being $P3_1$ and $P3_2$, with $a = 7.85$, $c = 4.62 \pm 0.01$ Å. The unit cell contains nine atoms, and the measured density of 3.20 g/cm³ implies five sulfur and four Se atoms. The structure contains mixed atom helices of 1.54 Å pitch and 0.91 Å average radius.

In a continuing investigation of group VIA elements a new pressure-induced sulfur-selenium phase has been found. The phase is fibrous but is not isostructural with the fibrous sulfur phase (II) (1). In fact, we have also found that some selenium does dissolve in the fibrous sulfur phase.

Starting materials were pure (99.999+ percent) Se and S (American Smelting and Refining Company). A one-to-one mixture (atom percent) was put into a fused silica tube, evacuated, and sealed. The mixture was melted and kept at 250°C for 2 hours and annealed at 80°C for 110 hours. It was then removed from the tube and ground and mixed thoroughly in an attempt to insure homogenization. Some of this material was then packed into tantalum containers and subjected to pressure and heating in furnaces and piston cylinder devices similar to those described by others (1, ref. 1). The fibrous S-Se phase reported here was prepared in a furnace (2.54 cm diameter) at 20 kb. The temperature was raised to 550°C and held there for 10 minutes; the temperature was then reduced to 280°C and maintained

there for 56 hours. The resulting material was not homogeneous but that part of the sample in the bottom portion of the sample capsule was red-brown, crystalline, and fibrous. A measurement of the density of isolated crystals of the fibrous form by the flotation technique gave 3.20 g/cm³.

An apparently single crystal of the fibrous sulfur-selenium was aligned along the fiber axis with oscillation photography; $\text{CuK}\alpha$ radiation was used, and Weissenberg photographs were taken. Lattice constants were determined from Buerger precession camera photographs ($\text{MoK}\alpha$ radiation). The diffraction symmetry of all the photographs is $6/m$, the only systematic absences being those reflections ($00l$) for which l is not equal to $6n$. The lattice constants of the particular crystal photographed are: $a = 7.85$, and $c = 4.62 \pm 0.01$ Å. Hexagonal selenium has $a = 4.355$, $c = 4.949$ Å. The sublattice obtained by a 30° rotation from the unit cell of the sulfur-selenium phase has lattice constants $a = 4.53$ Å and $c = 4.62$ Å. It appears then that the sulfur-selenium unit cell must contain nine atoms. A cell content of five S and

four Se atoms gives an x-ray density of 3.20 g/cm³ equal to the measured density.

Any space group giving diffraction symmetry $6/m$ satisfying the conditions for these helices must contain screw axes. Further, because of the length of the c -axis, the helices in the sulfur-selenium phase must have three atoms per turn as in hexagonal selenium itself. No hexagonal space group giving diffraction symmetry $6/m$ can satisfy the requirements for this structure. Thus it appears that the $6/m$ is only an apparent diffraction symmetry; the more probable diffraction symmetry is $\bar{3}$. When crystals with this symmetry are 120° rotation-twinned, they give the apparent symmetry observed. This is analogous to the case of selenium itself (2) in which the twinning of crystals with diffraction symmetry $\bar{3}m$ leads to apparent symmetry $6/mmm$.

Thus the most probable space groups to which the fibrous $\text{S}_{0.555}\text{Se}_{0.444}$ belongs are $P3_1$ or $P3_2$. It is possible also that the two enantiomorphs are cocrystallizing in the twinned crystals.

Thus far the preliminary refinement of the x and y parameters with the use of the Busing-Martin-Levy (3) program (modified for use on the IBM 360 computer) and only the $hk0$ intensity data (for which there is no overlapping of nonequivalent reflections) indicates that the helix radius is close to 0.91 Å; the pitch, given by $c/3$ is 1.54 Å. This implies an average S-Se distance (4) of 2.20 Å as compared with a calculated one of 2.18 Å based on a value of 2.34 Å for an Se-Se distance and 2.05 Å for an S-S distance.

For Se, the pitch and radius of the helix are 1.65 and 0.95 Å, respectively (4). Thus the larger a -axis of the subcell (see above) implies poorer packing efficiency of the sulfur-selenium phase than of the hexagonal Se phase.

Spacings were calculated with the lattice constants determined from the Buerger precession camera photographs. It is seen in Table 1 that the calculated spacings compare well with those measured on an x-ray powder photograph of the material. All nonequivalent sets of indices are given.

There appears to be a range of solid solutions having the same fibrous structure, but the limits have not yet been determined. The new phase is not nearly as stable as the fibrous sulfur phase, in which case a specimen 15 months

Table 1. Powder data for pressure-induced fibrous sulfur-selenium ($S_{0.56}Se_{0.44}$); $CuK\alpha$ radiation. Abbreviations: w, weak; m, medium; s, strong; v, very.

hkl	d(Å)		I_{rel}
	Calc.	Obs.	
100	6.80	6.80	vw
110	3.93	3.93	vs
111, 121	2.99	2.99	vs
201, 021	2.74	2.73	s
210, 120	2.57	2.56	m
300	2.27		
211, 121	} 2.25	} 2.25	ms
231, 131			
102, 012	2.19	2.19	m
301, 031	2.03	2.03	s
220	1.96	1.95	w
202, 022	1.91	1.91	w
310, 130	1.885	1.879	w-m
221, 241	1.806	1.803	m
131, 311	} 1.746	} 1.742	s
141, 341			
212, 122	} 1.718	} 1.718	s
132, 232			
302, 032	1.618	1.615	w
401, 041	1.595	1.591	w
320, 230	1.560	1.555	m
103, 013	1.502	1.505	w-m
410, 140	1.483		
321, 231	} 1.478	} 1.477	w-m
251, 351			
203, 023	1.403	1.404	vvw
402, 042	1.369	1.370	vvw
330	1.308		
501, 051	} 1.304	} 1.305	w
420, 240			
412, 142	} 1.248	} 1.248	w
152, 452			
511, 151	} 1.180	} 1.177	vw
161, 561			
403, 043	1.141		
104, 014	1.139	1.141	vw
422, 242	} 1.123	} 1.122	vw
262, 462			
114, 124	1.108	1.106	w-m
521, 251	} 1.060	} 1.056	w
271, 571			
214, 124	} 1.053	} 1.056	w
134, 234			

old and having been irradiated with 35-kv x-rays for about 1500 hours still remains unaltered in any observable manner. When examined about 3 months after it was made, the "single" crystal of the sulfur-selenium phase on which x-ray data had been collected had altered. It had gone partially to the fibrous sulfur (II) type phase.

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References and Notes

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2. R. E. Marsh, L. Pauling, J. D. McCullough, *Acta Cryst.* **6**, 71 (1953).
3. W. R. Busing, K. O. Martin, H. A. Levy, *Oak Ridge National Laboratory Report ORNL-TM-305* (1962).
4. The values given for the helix radius and average S-Se distance should be taken as tentative Limits of error for these are now approximately ± 0.05 Å.
5. We thank P. B. Crandall for technical assistance.