

Novel Chain Structures of Sulfur at High Pressure

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Introduction

Polymorphism of sulfur has been studied over the years by a wide range of techniques. Different experiments, however, have produced conflicting results, mostly because all structural studies on lower pressure phases have been performed only on quenched samples [1]. In fact, some 12 solid and 5 liquid phases have been reported, making the phase diagram of sulfur one of the most complicated among the elements [2].

In situ high-pressure diffraction studies on metallic phase of sulfur report a base-centered orthorhombic (bco) structure above 86 GPa [3,4], which transforms at 162 GPa to a β -Po structure [4]. These metallic phases of sulfur are isostructural with the high-pressure metallic phases of the heavier group-VI elements Se and Te [5-7]. The crystal structure of sulfur in the intermediate pressure range below metallization is unclear. Some *in-situ* diffraction experiments [8] indicated a pressure induced amorphization at 25 GPa, however, the energy-dispersive x-ray diffraction technique used in that study can be misleading if large crystallites with preferred orientation form. Indeed, a phase with large crystallites has been reported above 25 GPa in angle-dispersive x-ray diffraction study on S but without structural determination [3].

The most recent *in situ* study on the low-pressure phase diagram of sulfur [9,10] provided the first high-quality diffraction data on high-pressure sulfur. This study showed a transformation of the ambient-pressure S_8 ring molecule of the orthorhombic $Fddd$ phase S-I to a new phase S-II, consisting of chains with trigonal geometry. Phase S-II is reported to form only on heating of S-I (because of a kinetic barrier) at pressures above 1.5 GPa. This study [9,10], however, was restricted to pressures of 5 GPa, leaving the high-pressure behavior of S-II unknown. Thus, the crystal structure of sulfur in the pressure range between 5 and 86 GPa still remains unknown. In order to understand the high-pressure behavior of sulfur, we have conducted several angle-dispersive x-ray diffraction experiments using diamond anvil cells and monochromatic high-energy high-brilliance synchrotron radiation over a broad P-T range.

Methods and Materials

Samples of 99.999% purity of S from Puratronic were loaded in high-temperature Mao-Bell cells with different opening allowing probing up to 22 degrees of 2θ . Different pressure transmitting media (*i.e.*, He, Ne, N_2 and no medium) were used for different loadings. To determine the pressure, we used *in situ* fluorescence measurements of ruby chips loaded in the sample chamber. In the case of heating experiments pressure was measured before and after heating and did not change appreciably. The temperatures were measured to within ± 5 K by thermocouple. Powder diffraction data were collected at beamline 16-ID-B (HPCAT) at the Advanced Photon Source. Focused, monochromatic beams of different wavelengths ($\lambda = 0.36$ - 0.42 Å) were used and the data were recorded on a MAR

CCD or image plate calibrated with a CeO_2 or Si standard. Diffraction data were integrated azimuthally using FIT2D [11], and structural information was obtained by Rietveld refinement of the integrated profiles using GSAS [12].

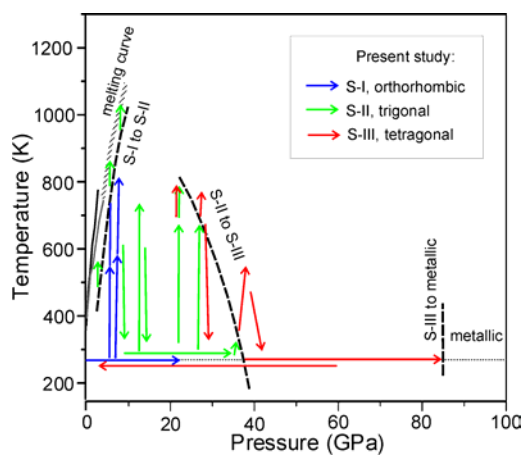


Fig. 1. Reaction and transformation diagram of sulfur. Selected P-T paths of this study are shown with arrows, where the direction of the arrows indicates the increase/decrease of pressure/temperature. Blue arrows indicate the S-I phase, green arrows - S-II, and red arrows indicate the S-III phase. Melting curve up to 3 GPa, shown by black solid line, is taken from Ref. [1], melting curve up to 5 GPa, shown by grey solid line, is taken from [10] and melting curve from 5 GPa to higher pressures, shown by dashed area, is taken from Ref. [13]. The boundaries for the transition S-I to S-II and S-II to S-III observed in the present study are shown by dashed lines.

Results and Discussion.

Figure 1 shows the thermodynamic paths followed during this study. In all the runs, our diffraction data show that the starting material was always the known ambient S-I phase. Upon heating at pressures above 3 GPa, S-I transforms to S-II, at temperatures very close to the melting line of sulfur (Fig. 1). The phase transition from S-I to S-II is of first order, and is associated with very significant changes in the diffraction pattern. The diffraction patterns of phase S-II (Fig. 2) were indexed with trigonal unit cell [$a=6.9082(3)$ Å, $c=4.2593(6)$ Å, atomic volume $V=19.54$ Å³ at 5.8 GPa and 800 K]. Rietveld refinement confirmed that the S-II phase forms trigonal structure with space group $P3_221$, reported in [9], that consists of triangular chains, running parallel to the trigonal c -axis, with 3 atoms per turn (Fig. 3). Our Rietveld refinement (Fig. 2) showed that the atoms occupy the following positions: $3(b)$ (0.876(4) 0 1/6) and $6(c)$ (0.230(3) 0.534(2) 0.051(3)), close to those reported in [9] and yielded R-factors $R_{wp}=7.6\%$, $R_p=5.4\%$.

S-II closely resembles ambient polymorphs of the heavier group VI elements Se and Te [2], consisting of atomic chains with very similar geometry (Fig. 3). The bond angle and the torsion angle in S-II are very similar to those in Se-I and Te-I. However, the structure of S-II with two symmetry-independent spirals per unit cell is more complex than the structure of Se-I and Te-I with one spiral per unit cell, where the spirals of S-II are rotated around the c -axis, if compared to those in Se-I (Fig. 3).

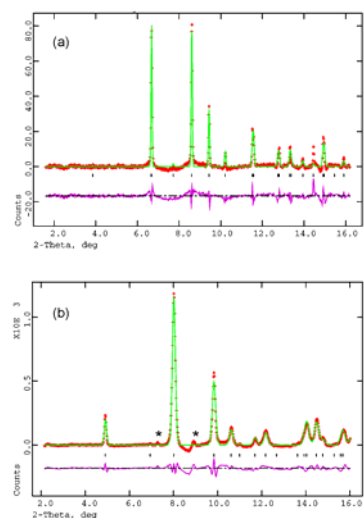


Fig. 2. X-ray spectra of (a) S-II at 5.8 GPa and 800 K collected on pressure increase and (b) S-III taken on pressure decrease at 12 GPa and 300 K. The spectrum of S-II is taken with $\lambda=0.4028 \text{ \AA}$, the spectrum of S-III is taken with $\lambda=0.3683 \text{ \AA}$. Full structure Rietveld refinement is shown, where red crosses, green solid lines, and purple line represent experimental, modeled and difference spectra. The ticks below profiles indicate the predicted peak positions. Asterisks in the S-III profile indicate the reflections from the pressure transmitting medium N_2 .

If sulfur is pressurized above 36 GPa at 300 K or heated at pressures between 22 to 35 GPa to temperatures shown in Fig. 1, it transforms into a body-centered tetragonal phase S-III, quenchable in temperature down to 300 K (Fig. 2). The transformation also appears to be of first order. S-III is stable up to 86 GPa at 300 K, where it transforms to the known metallic S-IV phase [3,4]. On pressure decrease at 300 K, S-III can be retained in a metastable form down to 3 GPa, where it transforms to another (metastable) phase with very broad diffraction peaks, the structure of which could not be determined. This phase transforms to S-I on decompression. The patterns of S-III were indexed with the cell parameters $a=8.5939(9) \text{ \AA}$, $c=3.6179(5) \text{ \AA}$ and $V=16.70 \text{ \AA}^3$ at 12 GPa and 300 K on pressure decrease. One should note that the diffraction pattern of sulfur at 76.3 GPa reported in Ref. [3] is likely to correspond to the S-III phase. The Rietveld refinement for S-III (Fig. 2) shows that the S atoms occupy $16(f)$ position ($x \ x+1/4 \ 1/8$) of the space group $I4_1/acd$ (origin choice 2), with $x=0.1405(3)$ at 12 GPa and 300 K (R-factors $R_{wp}=5.1\%$, $R_p=3.4\%$). The S-III structure consists of squared chains, running parallel to tetragonal c -axis, with 4 atoms per turn (Fig. 3). This is a novel structure type.

We have reproduced the S-I to S-II transition several times at different pressures and temperatures (Fig. 1). The S-II phase always forms just below melting line and after re-crystallisation

from the liquid state, and is quenchable in temperature down to 300 K. S-II is stable at 300 K up to 36 GPa, and has a negative slope of transformation to S-III, similar to that observed in molecular phases of N_2 [14]. The experiments carried out at high pressures with loading sulfur in different pressure transmitting media and following different P-T paths by heating S-I or S-II at different pressures all resulted in formation of S-III above 36 GPa at room temperature.

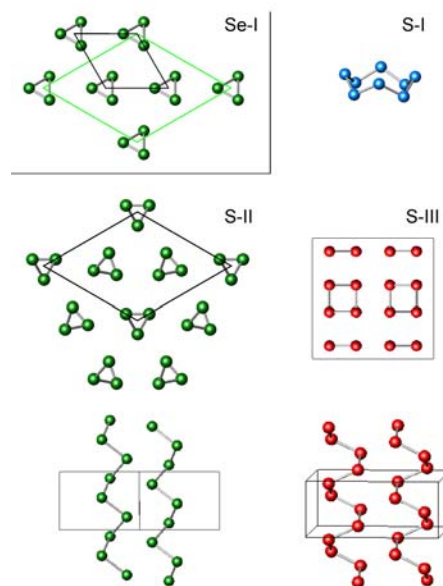


Fig. 3. Crystal structures of Se and S. Structure of Se-I with black line indicating Se-I cell and green line indicating S-II cell; S_8 ring molecule of S-I; trigonal chain structure of S-II and tetragonal chain structure of S-III. The bonds up to 2.10 \AA for S and 2.32 \AA for Se are shown. The structures of Se-I and S-I are drawn based on the data from Ref. [15].

Acknowledgments

We acknowledge V.F. Degtyareva for helpful discussions. This work and HPCAT is supported by DOE-BES, DOE-NNSA, DOD-TACOM, NSF, NASA, and the W.M. Keck Foundation. The authors acknowledge financial support from NSF, through grant EAR-0217389. The Advanced Photon Source is supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

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