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## Brief Reports

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# X-ray-diffraction study of sulfur to 32 GPa: Amorphization at 25 GPa

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The orthorhombic form of sulfur ($S_8$) has been studied in a diamond anvil cell to 32 GPa at room temperature by energy-dispersive x-ray-diffraction techniques using a synchrotron source. An orthorhombic-to-monoclinic phase transition was observed at about 5 GPa. The monoclinic phase could be followed until 24 GPa. Our previous optical results indicted a phase transition around this pressure. The diffraction patterns above 25 GPa showed the characteristics of an amorphous phase. This crystalline-amorphous phase change was found to be reversible with hysteresis upon decreasing pressure. The mechanism of this pressure-induced amorphization of sulfur is proposed. The equation of state was determined to 24 GPa.

With a very rapid development in high-pressure experimental technology during the past decade, especially with the applications of diamond anvil cell (DAC) and x-ray diffraction using synchrotron sources, a number of elements and their compounds have been studied under high pressures with information such as pressure-induced structural transitions, equation of state, and pressure-induced amorphization and metallization obtained. Sulfur, as one of the most abundant elements in the Earth and an important chemical element, was among the first group of samples to be studied under high pressure and has still received extensive attention in recent years. The earlier studies regarding the phase transition were mostly done in a low-pressure range below 5 GPa with very confusing and inconsistent results, as summarized in Refs. 1 and 2. Recent independent Raman measurements[3–7] under high pressures have indicated several phase transitions in the pressure range 4–28 GPa. Optical transmission and reflection studies[8] to 120 GPa at room temperature have shown a phase transition at about 23 GPa and an insulator-metal transition at 95 GPa. In addition to several phase transitions above 5 GPa, a solid-to-solid photoreaction,[4] amorphization[5] at $P > 5$ GPa and $T \leq 200$ K, and $S_6$-featured Raman spectra[6] have been reported based on the Raman studies. However, the crystalline structure information on sulfur at high pressures is still absent, especially in the higher pressure range above 5 GPa, and the phase transitions reported by Raman studies are inconsistent and even controversial. The equation of state above 5 GPa has not been determined, which is of importance for both theoretical and experimental analyses. Part of the reasons for the confusing high-pressure behavior and incomplete results of sulfur are (1) a puckered ring-type sulfur molecule containing eight S atoms; (2) a very large unit cell with 128 S atoms at the ambient conditions. These together make structural determination very difficult if not impossible for the sample in a diamond anvil cell.

As a continuation of our efforts to study the behavior of sulfur under high pressure, we present the results of an x-ray diffraction study of sulfur to 32 GPa at room temperature. It should be mentioned that it was not our primary goal to determine the complete crystal structure (i.e., actually to locate the atomic positions in the unit cell) for the reasons stated above plus the existence of inevitable preferred orientations in the sample under pressure.

Sulfur powders of orthorhombic structure with a purity of 99.9995% were placed in a diamond anvil cell without using other pressure-transmitting media. Three independent experiments have been made, each to about 30 GPa. Attention has been made for each experiment to ensure a sufficient sample amount in a sample chamber of 150–250 $\mu$m diameter and 80–100 $\mu$m depth in order to obtain a good diffraction pattern. In all three experiments the sample pressure was determined by the ruby fluorescence method.[9] The ruby fluorescence was excited by using a 488 nm line of an $Ar^+$ laser under a low output power. The x-ray data were taken from the Cornell High Energy Synchrotron Source (CHESS) using the energy-dispersive x-ray-diffraction (EDXD) method. Details of the experimental apparatus and techniques can be found in Refs. 10 and 11.

The original orthorhombic structure of S has 16 $S_8$ molecules or 128 S atoms per unit cell. The large number of atoms in the unit cell and a low symmetry of the lattice plus preferred orientations in the sample in the DAC prevented us from making a determination of the atomic

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positions in the unit cell. However, based on the room pressure crystalline structure from the literature[12] we could index the lattice and therefore obtain the unit cell volume up to 24 GPa.

The original orthorhombic lattice could be followed up to 4.9 GPa with 20–34 diffraction lines indexed. The lattice parameters obtained at $P \approx 0$ GPa are close to those of the literature values.[12] A selected diffraction pattern of the orthorhombic phase is shown in Fig. 1(a) with the peak indexes marked. At $P = 5.3$ GPa the diffraction data indicated a phase transition. The new phase could be assigned as a monoclinic lattice with 20 diffraction lines fitted. (Note that the phase assignment and peak indexing may not be unique, but they allow us to fit all the diffraction peaks and still obtain reasonable lattice parameters and the unit cell volume.) A selected diffraction spectrum of the monoclinic phase is shown in Fig. 1(b). The monoclinic phase at 5.3 GPa has lattice parameters $a = 9.83$ Å, $b = 10.33$ Å, $c = 20.65$ Å, $\beta = 79.34°$, and $V_{\text{unit cell}} = 2060.6$ Å$^3$. For comparison, the orthorhombic phase at 4.9 GPa has $a = 10.17$ Å, $b = 11.51$ Å, $c = 23.53$ Å, $\beta = 90°$, and $V_{\text{unit cell}} = 2756$ Å$^3$. The monoclinic phase could be followed with increasing pressure until about 24 GPa. However, at above ~18 GPa the diffraction peaks from the sample have a significant decrease in intensity and increase in width resulting in less diffraction peaks being observed. The relation of the reduced cell volume $V/V_0$ vs pressure is plotted in Fig. 2 along with the first-order Birch[13] fit to the data points. The parameters fitted to the Birch equation are given in Table I. Using these fitted curves, we obtain $-\Delta V/V \sim 24\%$ at 5.3 GPa. Since the number of atoms per cell is not necessarily the same in the two structures, the actual volume fraction per atom can be different. (If the number of atoms in the monoclinic cell is 96, the volume per atom discontinuity at the phase transition would be negligible.

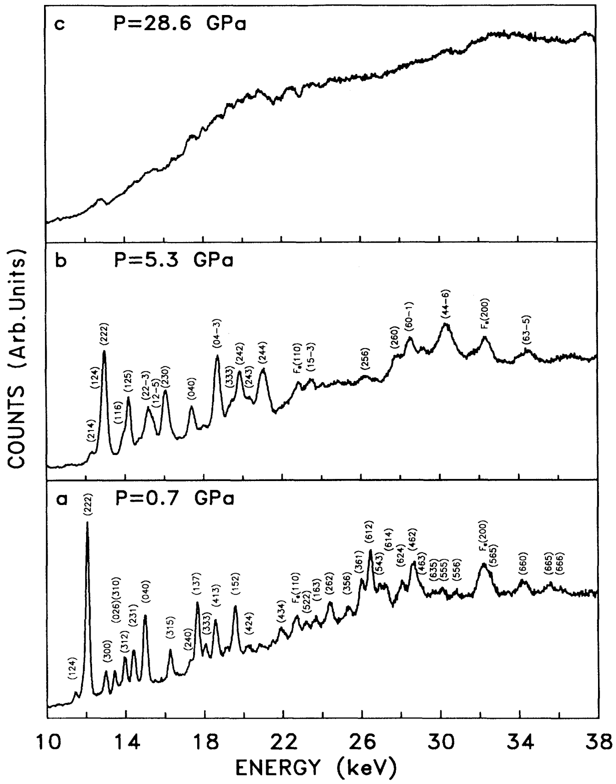

FIG. 1. Energy-dispersive x-ray-diffraction spectra of sulfur at three selected pressures. (a) Orthorhombic phase at 0.7 GPa, (b) monoclinic phase at 5.3 GPa, (c) amorphous phase at 28.6 GPa. The spectrum contains dips or negative peaks as a result of diamond Laue reflections which cause losses of x-ray intensity at corresponding energies. The diffraction angle ($2\theta$) for all spectra was 15.81°.

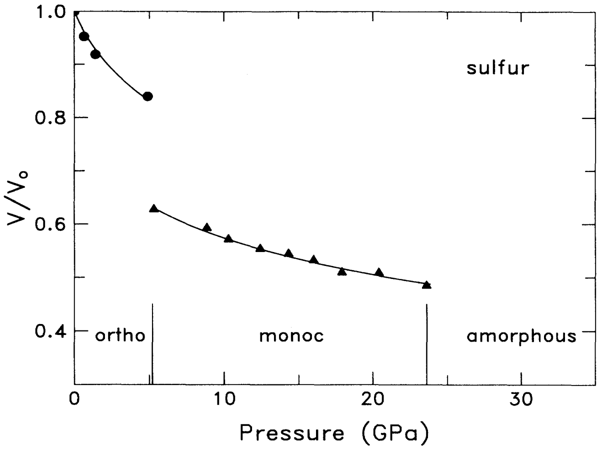

FIG. 2. Plot of the reduced cell volume $V/V_0$ vs pressure for sulfur. Fits of the data points to the first-order Birch (Ref. 13) equation are shown by the solid curves. Circles are for the orthorhombic phase and triangles are for the monoclinic phase. The $V_0$ used for both phases is 3282 Å$^3$. The fitting parameters are listed in Table I. An extrapolation of the $P$-$V$ relation of the monoclinic phase to zero pressure leads to a unit cell volume of 2500 Å$^3$. At $P \geq 25$ GPa, the sample transforms to an amorphous phase.

At $P \geq 25$ GPa, the diffraction spectra showed a characteristic of amorphous phase with extremely weak and broad diffraction peaks. A typical spectrum in this pressure range is shown in Fig. 1(c). Because of increasing intensities of the Compton scattering from diamonds relative to the sample diffraction as a result of reduction of the sample thickness, we are not able to make any quantitative analysis of the spectra above 25 GPa. Based on the diffraction data, the amorphous phase could start at pressures below 25 GPa and increase its content with increasing pressure until the transition is complete at about 25 GPa. This amorphous phase persisted to, at least, 32 GPa, the highest pressure attempted in the ex-

TABLE I. Parameters obtained by a fit of the first-order Birch equation to the reduced cell volume vs pressure data points of sulfur.

| Phase | Pressure range (GPa) | $B_0$ (GPa) | $B_0'$ | $(V/V_0)_{P=0}$ |
|---|---|---|---|---|
| Orthorhombic | 0–4.9 | 14.5 | 7 | 1 |
| Monoclinic | 5.3–24 | 17.3 | 5 | 0.76±0.05 |

periments. Upon decompression of the samples from the amorphous phase, the reverse transition to the crystalline phase was observed with pressure hysteresis. However, we could not make any indexing to the decompression spectra from 32 GPa except at $P \approx 0$ GPa, because the diffraction was weak and the background was high. A totally recovered diffraction pattern from the sample in DAC at $P=0$ is shown in Fig. 3 with 17 peaks indexed to an orthorhombic lattice, which gives the lattice constants $a=10.45$ Å, $b=12.80$ Å, and $c=24.64$ Å, in agreement with $a=10.45$ Å, $b=12.84$ Å, and $c=24.46$ Å, the lattice constants of orthorhombic sulfur at ambient conditions from the literature.[12] The totally recovered sample at $P=0$ GPa (still in DAC) showed sharp diffraction peaks although the background (primarily from the Compton scattering of diamond anvils) was as high as that at 25–32 GPa (see Fig. 3), which indicated that the recrystallization process in sulfur during decompression was mostly, if not completely, finished at $P=0$ GPa. Based on these observations and other previous experimental results (discussed below), we conclude that a pressure-induced amorphization in sulfur starts at about 18 GPa and completes at about 25 GPa.

Eckert *et al.*[5] have reported an amorphous phases of sulfur by Raman study at pressures above 5 GPa and temperatures below 200 K. If one considers the effect of lowering temperature to be similar to increasing pressure toward the phase transition between crystalline and amorphous phases (which is indeed the case in sulfur according to Eckert *et al.*[5]), then it is reasonable that at room temperature, amorphization of sulfur would need higher pressure than 5 GPa. Our previous optical studies[8] showed a discontinuity in the absorption edge $E_g$ vs pressure curve at about 23 GPa, which changes the slope $dE_g/dP$, and hence delays the closure of the band gap to a very high pressure. On the mechanism of the pressure-induced amorphization in sulfur there are two possibilities. The first is that instead of transforming to another crystalline phase with higher symmetry, sulfur changes to a disordered amorphous phase because of insufficient kinetic energy and large ring-type $S_8$ molecules. This type of mechanism for amorphization during compression has been attributed to quartz[14] and $CaSiO_3$,[15] etc., as they transform to amorphous phases. The second is that the S-S bond within a $S_8$ molecule is broken by compression resulting in the formation of new types of bonds and structures. A C-C bond breaking, and hence a formation of an amorphous phase, have been observed in solid benzene ($C_6H_6$) under pressure between 25–30 GPa.[16] The benzene molecule is also of a ring type. Considering the bonding energy, it is known that a C-C single bond has a bonding energy of 3.6 eV in comparison to 2.7 eV of a single S-S bond. Therefore it is logical that opening of the sulfur rings occurs at a lower pressure than that of the benzene rings. According to Wolf *et al.*[4] and Rossmanith *et al.*,[6] the Raman spectra above 10 GPa have indicated some characteristics of dissociation of $S_8$ molecules and the high-pressure phase of sulfur may have a chain structure. To confirm which mechanism discussed above is more likely, further spectroscopic measurements are required.

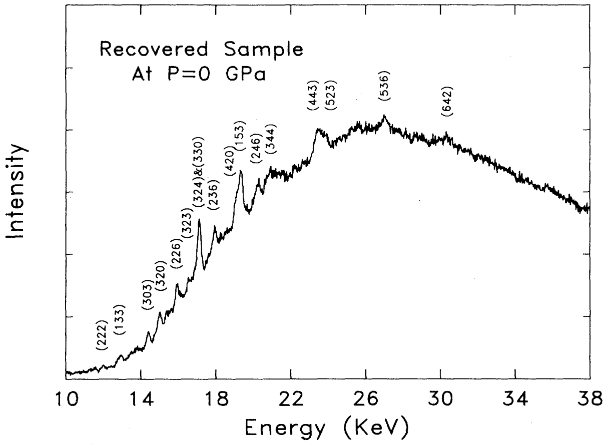

FIG. 3. Energy-dispersive x-ray-diffraction spectrum of sulfur at $P=0$ GPa decompressed from 32 GPa. The high background comes primarily from the Compton scattering of diamond anvils. The peak indexing confirms an orthorhombic lattice with $a=10.45$ Å, $b=12.80$ Å, and $c=24.64$ Å.

In our earlier paper of optical studies on sulfur,[8] we discussed several possibilities based on dislocation and defect states for the weak conducting behavior observed by Dunn and Bundy[17,18] in their electrical resistance measurements at 50 GPa. The creation of numerous dangling bands and defects during the amorphization leads to a near continuum of energy levels in the band gap and a positive slope of $d\rho/dT$, where $\rho$ is resistivity and $T$ is temperature, and a high resistance compared to a metal. This is consistent with the experimental findings that $\rho=0.03\ \Omega\,\mathrm{cm}$ and $dR/dT>0$ at $P=50$ GPa.[17] The Goldhammer-Herzfeld (GH) criterion[19,20] has been successful in predicting pressure-induced metallization of insulators, such as Xe[21] and BaTe[22]. For sulfur, the GH criterion gives $V_M/V_0=0.48$. Based on extrapolation of our fitted equation of state of the monoclinic phase from 24 GPa (assuming the monoclinic structure has 128 atoms per unit cell), we obtain, at the metallization pressure of 95 GPa, $V_M/V_0=0.35$.

In summary, we have obtained the following results based on our x-ray-diffraction experiments and the previous optical and Raman results on sulfur.

(1) The original orthorhombic sulfur undergoes a phase transition to a monoclinic phase at about 5 GPa. This monoclinic phase persists to 24 GPa.

(2) An onset of amorphization of sulfur starts at about 18 GPa and completes at about 25 GPa during compression at room temperature.

(3) The crystalline-amorphous phase transition in sulfur was found to reverse during decompression but with hysteresis. The recovered sample at $P=0$ GPa was found to be recrystallized in its original form.

(4) Two possible mechanisms for the pressure-induced amorphization have been proposed and discussed.

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