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X-ray powder diffraction study of CS₂ at high pressures

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Abstract

X-ray powder diffraction experiments were performed at pressures up to 14 GPa and at room temperature. The orthorhombic lattice was retained at pressures up to 10 GPa. Above 10 GPa, however, a broad glassy background developed. The lattice constants, a , b , c , and the orientation angle at 2.72 GPa are 5.845, 5.220, 8.296 Å and 41.3°, respectively. The orientation angle at high pressure is smaller than that of the low-temperature phase.

1. Introduction

Carbon disulphide (CS₂) crystallizes into an orthorhombic $Cmca$ structure with two molecules per primitive cell at atmospheric pressure below 173 K [1]. The orthorhombic phase is stable at temperature down to 5.3 K [2]. The liquid–solid boundary at room temperature is crossed at 1.26 GPa and CS₂ crystallizes also into the orthorhombic $Cmca$ structure [3]. Therefore it was confirmed that the low-temperature phase and the high-pressure one are the same. With further increasing pressure, it transforms irreversibly into a black solid compound at pressure around 9 GPa. This black solid is generally known as the Bridgman's Black, which is a kind of polymer of CS₂ [4, 5]. There have been many spectroscopic studies of crystalline CS₂ at high pressures and high temperatures. However, few previous x-ray studies of CS₂ at high pressures have been reported. The orthorhombic phase is a layered structure because the linear molecules lie in the bc -planes perpendicular to the a -axis, and it also has a freedom of the orientation angle (φ): between the molecular axis and the b -direction.

In this paper, powder x-ray diffraction results on CS₂ at pressures up to 14 GPa and room temperature are presented; the study was undertaken to investigate the irreversible transformation into the black solid.

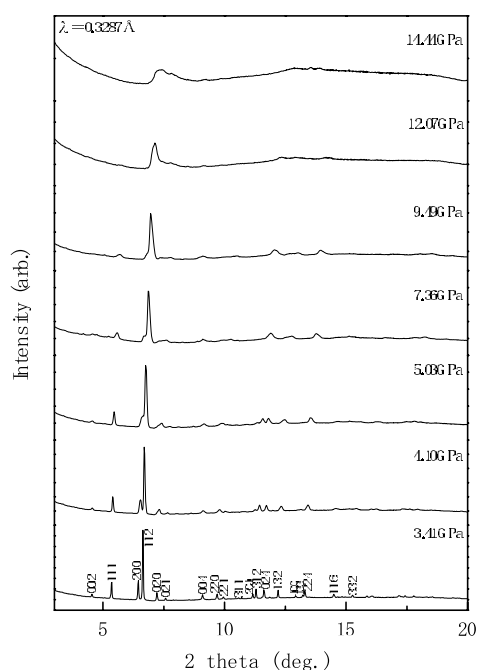


Figure 1. Typical diffraction patterns of solid CS₂ at selected pressures. The wavelength of the x-ray source was 0.3287 Å.

2. Experimental details

A diamond anvil cell (DAC) with a cone-shaped aperture was used for generation of high pressure. The top surface of the anvils was 0.6 mm in diameter. Solid CS₂ was ground into fine powder on a cooled agate mortar and loaded with a ruby chip into a hole in the metal gasket (U-700) fixed on a lower anvil in the DAC, which was cooled by liquid nitrogen in a dry box. X-ray diffraction experiments at room temperature were carried out with synchrotron radiation sources on the beamline BL10XU and BL04B2 stations at SPring-8. The wavelength was tuned with a Si(111) double-crystal monochromator. Powder patterns were obtained by an angle-dispersive method with an image plate detector. The diffraction images obtained were analysed using integration software described as ‘the powder pattern analyser for an imaging plate’ (PIP) [6]. The pressure was determined by the ruby fluorescence method [7]. The results presented below were obtained in three experimental runs up to 4.05, 10.0 and 14.44 GPa.

3. Results and discussion

Figure 1 shows the diffraction of solid CS₂ at pressures up to 14.4 GPa and room temperature. The pattern at 3.41 GPa depicted in the lowest panel was assigned to an orthorhombic *Cmca* structure. With increasing pressure, the patterns did not change appreciably, and there was no smearing out of the diffraction peaks due to the increasing of the peak width. The *d*-values of all lines exhibited smooth changes and the relative intensities of the reflections remained almost constant at pressures up to 10 GPa. These results indicate that the orthorhombic lattice is still retained at pressures up to 10 GPa.

The result of there being no solid-state phase transitions at pressures up to 10 GPa and room temperature is consistent with the previous spectroscopic studies [8]. Above 10 GPa, however, a broad glassy background developed, which corresponds to the formation of the Bridgman’s Black polymer.

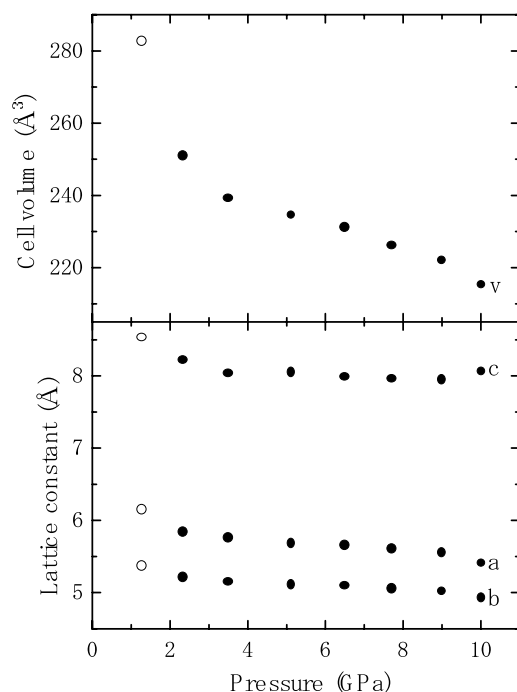


Figure 2. Pressure dependences of the lattice constants and cell volume. Open circles are from [3].

Table 1. Lattice parameters, C–S bond lengths (l) and orientation angles (φ) between the molecular axis and the b -direction for solid CS₂ at 2.72 GPa and 300 K. The data at 150 K and 1 bar obtained by Powell *et al* [2] are listed in the bottom line.

	a (Å)	b (Å)	c (Å)	l (Å)	φ (deg)
This work	5.8451(10)	5.2201(11)	8.2959(14)	1.535	41.3
150 K [2]	6.4141(7)	5.5787(7)	8.8928(14)	1.518	43.2

Figure 2 shows the pressure dependences of the cell volume and lattice constants. The cell volume decreases only slightly at higher pressures after dropping rapidly below 4 GPa. The pressure dependence of the lattice constants exhibits slight anisotropy, which is depicted in figure 3. The a -axis is more compressible and the b/c ratio remains almost constant under application of pressure. This represents a striking contrast to the low-temperature phase, with the elongation of the c -axis and the constant a/b ratio with decreasing temperature [2]. The compressible behaviour of the a -axis under high pressure is predictable because the molecules lie in the bc -planes perpendicular to the a -axis.

Lattice constants at 2.72 GPa obtained from a Rietveld refinement fit are tabulated in table 1 together with the data at 1 bar and 150 K in reference [2]. At high pressure, the orientation angle (φ) becomes smaller, which indicates that the molecules orient so as to reduce the steric hindrance between the two molecules in the bc -plane. The Bridgman's Black contains zigzag chains of C(=S)–S units. These chains would be realised if the polymerization takes place toward the b -axis direction. The large reduction of the interlayer spacing under pressure is favourable for the formation of polymers.

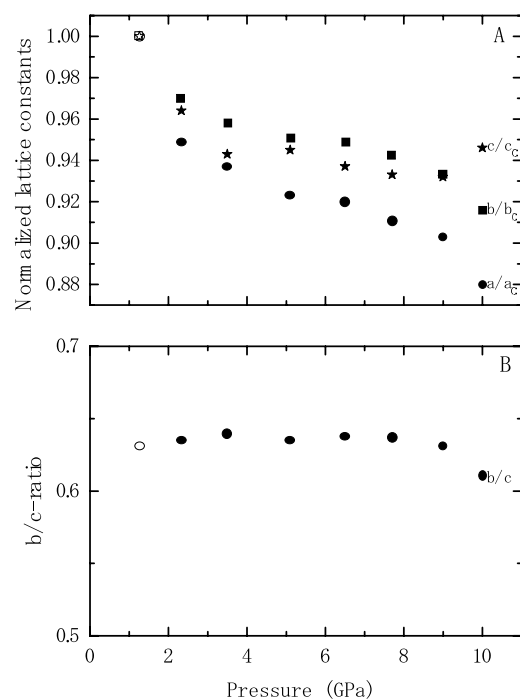


Figure 3. Normalized lattice constants (A) and the lattice constant ratio b/c (B) as a function of pressure. The reference values of a_0 , b_0 and c_0 are from [3].

Acknowledgments

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