



Study of the reaction products of SF₆ and C in the laser heated diamond anvil cell by pair distribution function analysis and micro-Raman spectroscopy

N. Rademacher^{a,*}, L. Bayarjargal^a, W. Morgenroth^a, J.D. Bauer^a, V. Milman^b, B. Winkler^a

^a Institut für Geowissenschaften, Goethe-Universität Frankfurt, 60438 Frankfurt am Main, Germany

^b BIOVIA, Dassault Systèmes, 334 Science Park, Cambridge CB4 0WN, United Kingdom

ARTICLE INFO

Article history:

Received 21 August 2014

Received in revised form

8 November 2014

Accepted 15 December 2014

Available online 24 December 2014

Keywords:

Sulfur hexafluoride

Pair distribution function

Diamond anvil cell

High pressure

ABSTRACT

The decomposition of SF₆ in the presence of glassy carbon was induced in laser heated diamond anvil cells at 10–11 GPa and 2000–2500 K. The reaction products were characterised by synchrotron X-ray diffraction, including high pressure pair distribution function analysis, and micro-Raman spectroscopy combined with atomistic model calculations. The decomposition leads to elemental amorphous helical sulfur and crystalline CF₄-III. Two different sulfur phases, namely helical S_μ and crystalline α-S₈, were observed after recovering the laser heated samples of different experiments at ambient conditions.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Chemical reactions of small molecules at extreme pressure and temperature conditions have been studied extensively because the reaction products have interesting chemical, physical and mechanical properties [1–3]. Well-known examples include the polymerisation of CO₂ [4], N₂ [5] and CO [6,7]. Polymerised CO and N₂ for instance are potential high-energy materials [6,5] and the quartz-like CO₂ polymer is proposed to be a super-hard material [8].

Sulfur hexafluoride, SF₆, is a very stable and inert compound and hence widely used, for example as insulator material in electric equipment [9]. The high-pressure behaviour of SF₆ has been studied by Sasaki et al. [10] up to 10 GPa by Raman spectroscopy who found two different crystalline phases, denoted as phase I and phase II. We recently explored the phase diagram of SF₆ by means of X-ray diffraction and micro-Raman spectroscopy up to 32 GPa and observed two additional phase transformations at 10 GPa and 19 GPa, respectively [11]. The SF₆ molecule was stable up to the highest applied pressure at ambient temperature.

CO is an example which showed that the reaction products at high pressures are not always crystalline but may be poorly crystalline or amorphous. Total-scattering techniques have been demonstrated to be a powerful tool for the determination of accurate structural parameters of crystalline as well as disordered, amorphous and nanocrystalline materials [12,13] also at high

pressures [14,15]. The pair distribution function (PDF, $G(r)$) gives the probability of finding atoms separated by a distance r . $G(r)$ is experimentally obtained by a Fourier transformation of corrected and normalised powder diffraction data, $S(Q)$:

$$G(r) = 4\pi r [\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ \quad (1)$$

$\rho(r)$ is the microscopic pair density, ρ_0 is the average number density, $S(Q)$ is the total scattering structure function and Q is the magnitude of the scattering vector, which is given by $Q = 4\pi \sin \theta / \lambda$ with θ being the scattering angle and λ the wavelength of the radiation. Detailed information on the procedures can be found in Egami and Billinge [16].

In the current study, we explored the stability field of SF₆ at high pressures and high temperatures. The reaction products are analysed by X-ray diffraction, including pair distribution function analysis, and micro-Raman spectroscopy combined with atomistic model calculations.

2. Experimental details

A binary gas mixture of SF₆ and He with 10.4(2) vol% SF₆ was obtained from Praxair and loaded without further purification with the gas loading system in Frankfurt. Boehler-Almax [17] type DACs with opening angles of 48–70° and culet sizes of 350 μm were employed. Tungsten gaskets with an initial thickness of 200 μm were preindented to 50–52 μm and holes of 133–140 μm were drilled with a laser lathe. The pressure was determined with the ruby fluorescence method [18,19].

* Corresponding author.

E-mail address: rademacher@kristall.uni-frankfurt.de (N. Rademacher).

The laser heating experiments were performed in Frankfurt using a pulsed CO₂ laser ($\lambda = 10.6 \mu\text{m}$, 250 W) and at the Extreme Conditions Beamline P02.2 [20] (PETRA III, DESY, Hamburg) using a Yb fibre laser ($\lambda = 1070 \text{ nm}$, 100 W). Two different samples containing the SF₆–He mixture and glassy carbon, which was used as laser absorber (coupler), were heated at 11.3(3) GPa and 10.0(2) GPa, respectively. KCl was used

for thermal insulation. The temperature during laser heating was determined to be between 2000(100) K and 2500(100) K by fitting a Wien function to thermal emission spectra.

Raman spectra of the starting materials inside the DAC as well as the laser heating products inside the DAC at high pressures and recovered at ambient conditions after unloading the DAC were

Table 1

Lattice parameters of the sulfur phases and CF₄-III at different pressures and temperatures from DFT, experiment and literature.

Model	<i>p</i> (GPa)	<i>T</i> (K)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)
α -S ₈ , exp. ^a	0	300	10.457(6)	12.785(4)	24.655(7)	–	3296(2)
α -S ₈ , exp. [33]	0	298	10.4646(1)	12.8660(1)	24.4860(3)	–	3296.73
α -S ₈ , exp. [45]	0	300	10.45	12.80	24.64	–	3295.85
α -S ₈ ^b	0	–	10.714	13.169	25.173	–	3551.7
α -S ₈ ^c	0	–	10.751	13.113	24.264	–	3420.7
α -S ₈ ^b	11	–	9.0666	11.4200	22.3889	–	2318.2
α -S ₈ ^c	11	–	8.9154	11.2600	22.1676	–	2225.3
ϵ -S ₆ ^b	11	–	9.8568	–	3.6261	–	305.1
S-II ^b	3	–	7.2019	–	4.3356	–	194.7
S-II, exp. [35]	3	673	7.0897	–	4.3024	–	187.3
S-II ^b	11	–	6.5549	–	4.2126	–	156.8
CF ₄ -III, exp. [36]	6.2	300	6.776	4.423	6.818	102.97	199.1
CF ₄ -III ^c	6.2	–	6.8163	4.4553	6.8603	102.78	203.2
CF ₄ -III, exp. ^d	11.6(2)	300	6.51(1)	4.332(6)	6.63(1)	102.1(1)	182.9(4)
CF ₄ -III ^c	11	–	6.5589	4.3164	6.5972	102.44	182.4

^a This study, Le Bail refinement.

^b This study, GGA-PBE+TS.

^c This study, GGA-WC.

^d This study, Rietveld refinement.

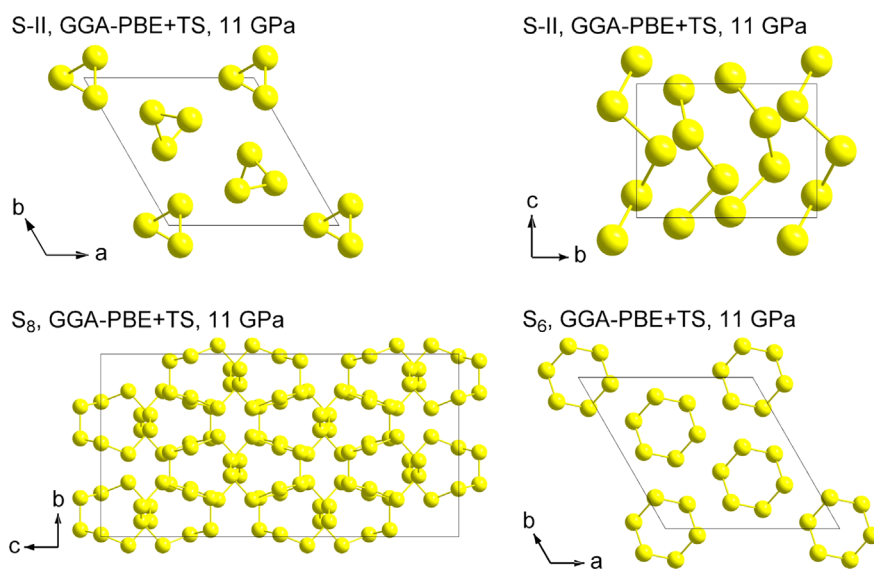


Fig. 1. Crystal structures of the DFT-optimised sulfur allotropes S-II shown along *c* and along *a*, α -S₈ along *a* and ϵ -S₆ along *c*.

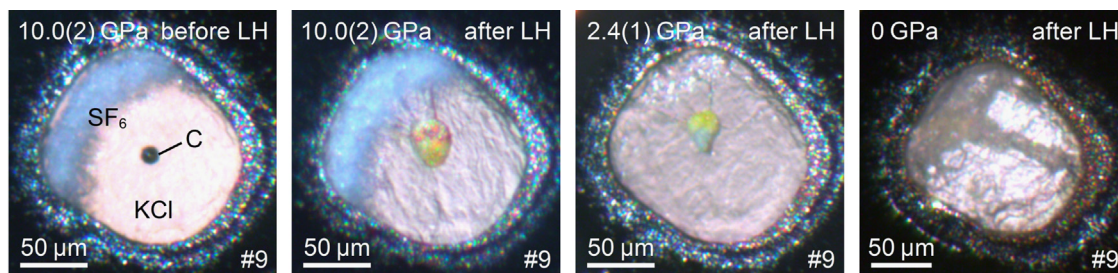


Fig. 2. SF₆ and a glassy carbon sphere before and after laser heating and during decompression.

Download English Version:

<https://daneshyari.com/en/article/1331612>

Download Persian Version:

<https://daneshyari.com/article/1331612>

[Daneshyari.com](https://daneshyari.com)