

Liquid-Liquid transition in P_4S_n ($n=3, 7, 10$) melts at high pressure. Part 2

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Pressure-induced structural change of P_4S_3 liquid was studied by in-situ x-ray diffraction up to 10 GPa. The FSDP decreases dramatically with increasing pressure and exhibits a shift to higher Q , although it remains at 10 GPa.

キーワード : 液体、相転移、X線回折、高温、高圧

1. 目的

The first-order liquid-liquid transition remains an exciting challenge to be addressed to *in situ* diffraction and spectroscopic experiments as a function of high pressure and/or temperature. In an October 2008 Science publication [1], yttria-alumina melts were believed to show a first-order liquid-liquid transition at 1788 K. The observed findings have not been confirmed later for high-T melts with similar composition [2]. The above controversy shows a difficulty in getting the reliable and reproducible data to answer definitely a much debated issue. The main purpose of our Part 2 experiment was to reach a maximum available pressure (about 10 GPa) and to observe a possible first-order liquid-liquid transition in P_4S_n ($n = 3, 7, 10$) molecular liquids at high pressure and temperature. Our previous measurements below 8 GPa [3] have shown dramatic changes in the First Sharp Diffraction Peak (FSDP) position and amplitude but the maximum available pressure was not sufficient to transform the molecular liquid into a network one.

2. 方法

For our experiment, we have used P_4S_3 . This cage compound exhibits the lowest melting point (165 °C) between the three known cage molecules (P_4S_3 , P_4S_7 and P_4S_{10}) in the P-S system. Two series of measurements using cubic anvil cells with 4 and 6 mm anvils have been carried out. The applied load varied between 20 and 100 tons. The resulting pressure was measured using Bragg reflections of NaCl and depending on the cell and load was changing between 1.1 and 10.0 GPa. At applied pressure of about 4 GPa, samples become liquid above 450 °C, but then suddenly crystallize and become liquid again at 800 °C. Most experiments have been carried out therefore at 800-850 °C. Diffraction measurements have been performed in energy dispersive mode at 9 scattering angles in the range from 3 to 18 degrees.

3. 研究成果

Typical diffraction pattern of a P_4S_3 liquid at 820 °C taken at the scattering angle of 3° are shown in Fig. 1. Two main features are clearly visible: (i) an intense First Sharp Diffraction Peak (FSDP) of the molecular liquid, reflecting P-P correlations between the neighbouring cages, and (ii) a Bragg peak of pyrolytic BN, used as a sample container in the cell. Two series of measurements in the cells with 4 and 6 mm anvils represent a compression experiment between 1.9 and 10.0 GPa. A dramatic monotonic decrease of the FSDP and its shift to higher Q with increasing pressure is observed. The FSDP amplitude decreases at least by a factor of 10 but still remains visible at 10 GPa. The FSDP position Q_1 as a function of applied pressure is shown in Fig. 2. One observes a monotonic increase of Q_1 with pressure from 1.02(3) Å⁻¹ (ambient P) to 1.39(5) Å⁻¹ (10 GPa). We should also note that at high P (> 8 GPa) the Q_1 position tends to saturate, i.e., $\partial Q_1/\partial P \rightarrow 0$. Further data analysis is in progress.

4. 結論・考察

Without further detailed and systematic data analysis, we cannot respond definitively whether a liquid-liquid transition in liquid P_4S_3 is taking place in the P-range between ambient pressure and 10 GPa. On the one hand, we have still observed a weak FSDP at the highest available pressure of 10 GPa and $Q_1(P)$ changes are monotonic. On the other, the observed trend of $Q_1(P)$ to saturation above 8 GPa suggests some structural changes or, at least, a critical region just before a possible transition. Experiments with higher pressure or with softer cage molecules are necessary to verify these two alternatives.

5. 引用(参照)文献等

1. G.N. Greaves, M.C. Wilding, S. Fearn et al., Science **322** (2008) 566.
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3. E. Bychkov, M. Milochova, A. Bychkov, S. Kohara, Y. Katayama, Spring-8 Experimental report 2007B-E22.

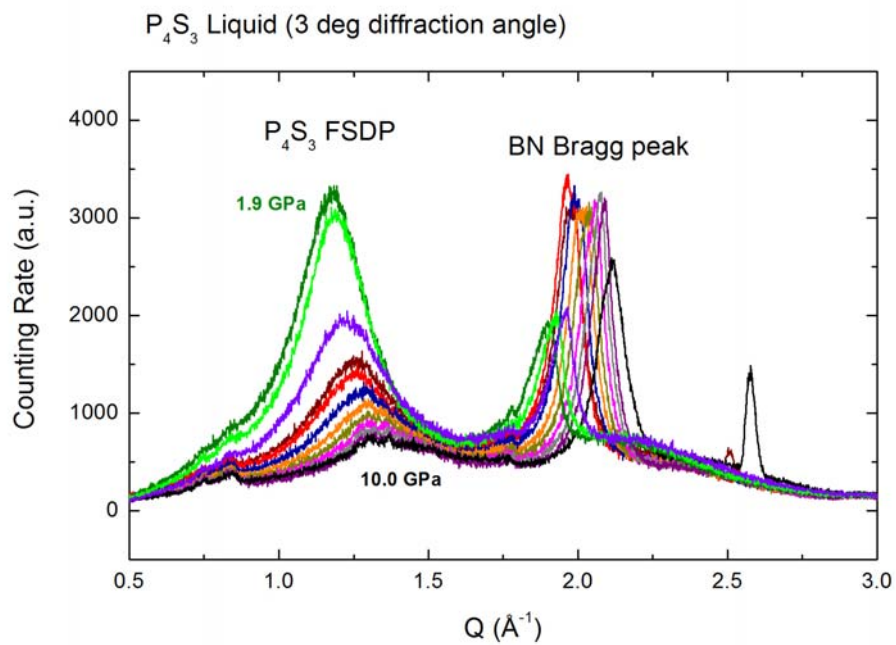


Fig.1

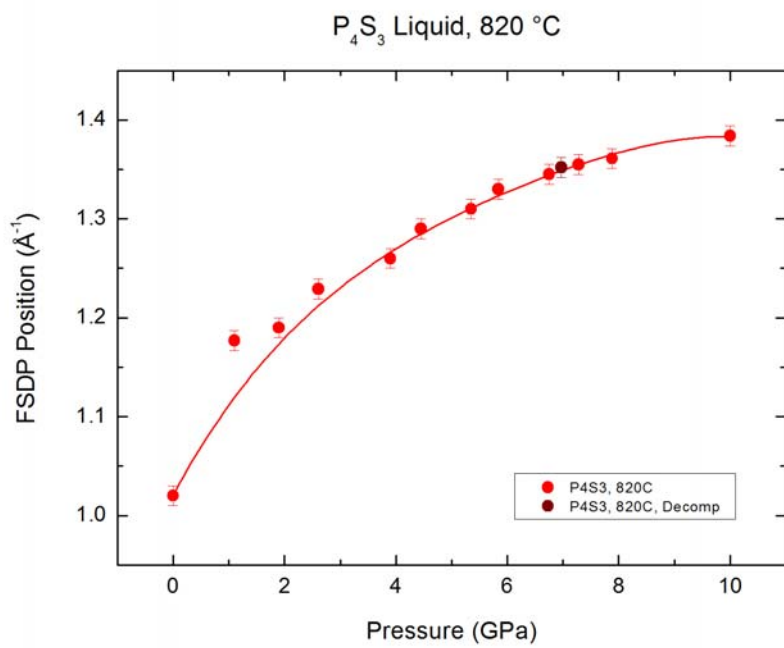


Fig.2