Liquid-liquid transition in P_4Se_3 melts at high pressure

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Pressure-induced structural change of P_4Se_3 liquid was studied by in-situ x-ray diffraction up to 5 GPa. The FSDP decreases dramatically with increasing pressure and exhibits a shift to higher Q.

キーワード: Liquid, Phase transition, X-ray diffraction, High temperature, High pressure

１．目的

The main purpose of our *in situ* x-ray diffraction measurements of a molecular liquid P_4Se_3 in the pressure range up to 10 GPa was to study a possible liquid-liquid transition. The previous measurements with P_4S_n (n = 3, 7) liquids 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. The P-Se system appears to be softer and we expected to observe liquid-liquid transition using a P_4Se_3 molecular cage in the available pressure range.

２．方法

The experiments were conducted at BL14B1 of SPring-8. 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 cell and load was changing between 1 and 10 GPa. The sample diffraction measurements have been performed in energy dispersive mode at 10 scattering angles in the range from 2.5 to 18 degrees.

３．研究成果

At applied pressure of about 1 GPa, samples become liquid at 300 °C. It is interesting to note that the melting point of P_4Se_3 cages at ambient pressure is 246 °C. It was the first substantial difference compared to P_4S_3 liquids for which the melting point at ambient pressure was 165 °C but at 4 GPa samples first melted at 450 °C, then crystallized and become liquid again only at 800 °C.Typical diffraction pattern of a P_4Se_3 liquid at 406-430 °C taken at the scattering angle of 2.5° are shown in Fig. 1. Two main features are clearly visible: (i) an intense First Sharp Diffraction Peak (FSDP) of the low-P liquid, reflecting P-P correlations between the neighbouring cages, and (ii) a Bragg peak of pyrolitic BN, used as a sample container in the cell. A dramatic monotonic decrease of the FSDP and its shift to higher Q with increasing pressure from 1.1 to 5.0 GPa is observed. The FSDP amplitude decreases at that temperature by a factor of 3.5 but at 5.0 GPa the liquid starts to crystallize. Increasing the temperature from 400 to 800 °C, the FSDP amplitude decreases further and the second peak in the diffraction pattern becomes smaller and broader, and also shifts to lower Q (Fig. 2). Decreasing the pressure and temperature restores the original low-P pattern.

４．結論・考察

Similar changes were observed for liquid As_4S_4 under high pressure and were attributed to first to polymerization of the molecular liquid and then to its metallization [1]. Recent viscosity measurements at high pressure [2] confirm the observed phenomena. Further data analysis of the obtained P_4Se_3 data is in progress. However, the performed experiments with softer P_4Se_3 cages molecules seem to show liquid-liquid transitions at high pressure.

５．引用(参照)文献等

1. V.V. Brazhkin, Y. Katayama, et al., Phys. Rev. Lett. **100** (2008) 145701.
2. V.V. Brazhkin, M. Kanzaki, K. Funakoshi, Y. Katayama, Phys. Rev. Lett. **102** (2009) 115901.

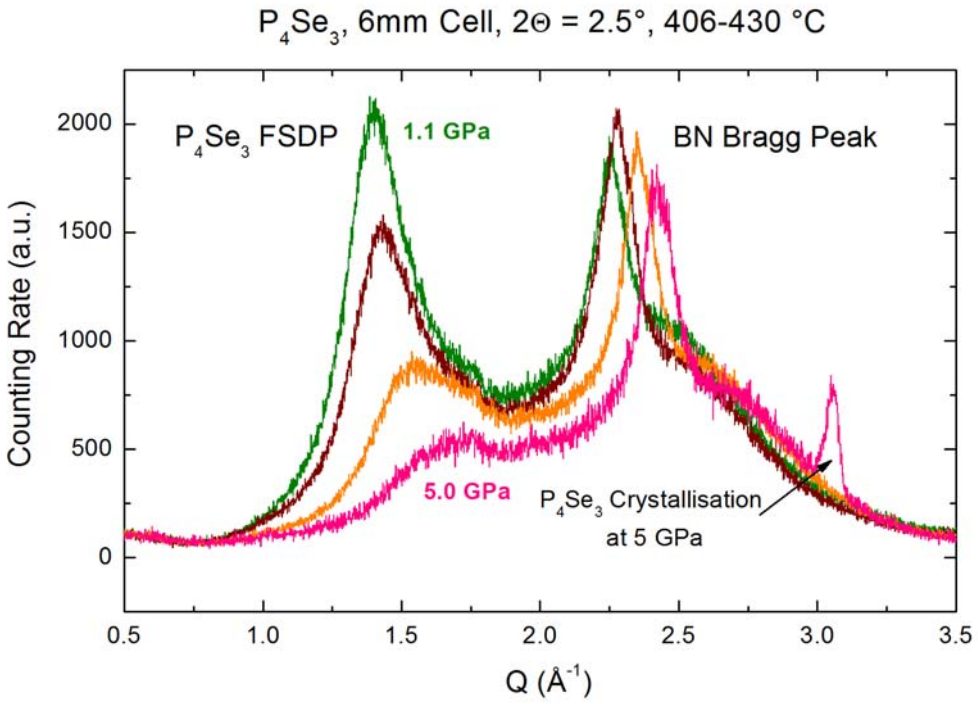
P4Se3, 6mm Cell, 2Θ = 2.5°, 406-430 °C
P4Se3 FSDP
1.1 GPa
BN Bragg Peak
5.0 GPa
P4Se3 Crystallisation
at 5 GPa
Counting Rate (a.u.)
Q (Å-1)

Fig. 1

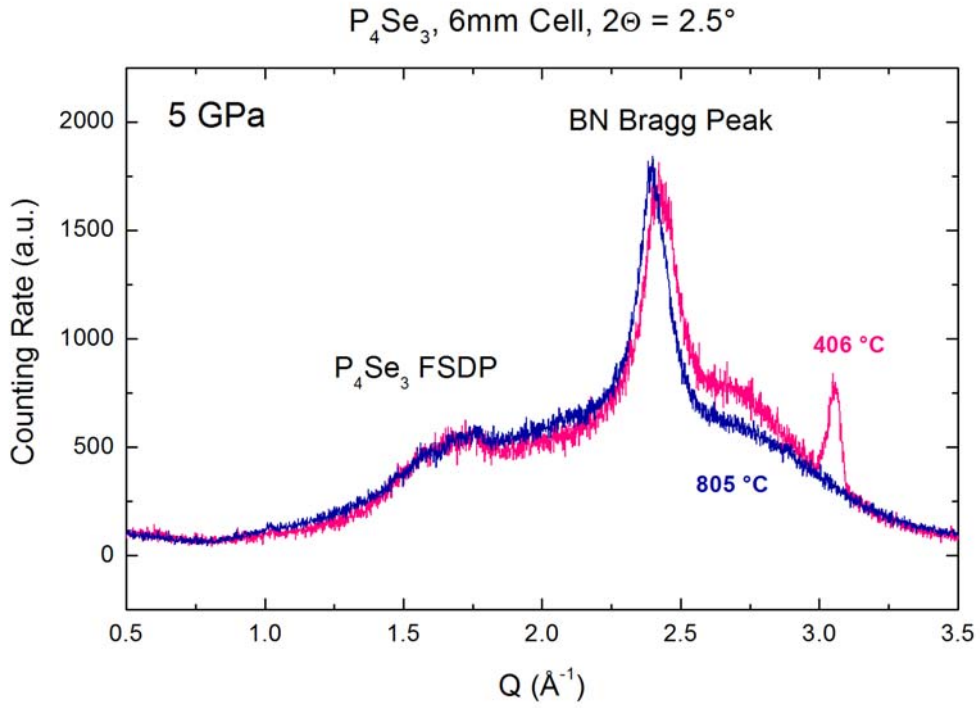
P4Se3, 6mm Cell, 2Θ = 2.5°
5 GPa
BN Bragg Peak
P4Se3 FSDP
406 °C
805 °C
Counting Rate (a.u.)
Q (Å-1)

Fig.2