Liquid-Liquid transition in P_4S_n (n=3,10) melts at high pressure

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Pressure-induced structural change of P_4S_7 liquid was studied by in-situ x-ray diffraction up to 8.3 GPa. The FSDP decreases dramatically with increasing pressure and exhibits a shift to higher Q. The cage structure of P_4S_7 remains intact at the highest pressure.

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. Recent structural studies of the pressure-induced transformation in liquid phosphorus have shown a first-order phase transition at ≈1 GPa and ≈1000 °C from a low-density molecular liquid consisting of uncorrelated P_4 molecules to a network liquid with a structure similar to that in amorphous red P or liquid As [1]. In later experiments, the observed phenomenon was attributed to a first-order transition between a dense molecular fluid and a polymeric liquid [2]. The aim of our experiment was to verify whether a similar (presumably liquid-liquid) transition can be observed in the binary P-S system at much lower temperatures. Three congruently melting compounds in this system (P_4S_3, P_4S_7 and P_4S_{10}) have the melting point below 310 °C and preserve their cage-like molecular structure, derived from a P_4 tetrahedron, in the melt.

２．方法

For our experiment, we have used P_4S_7. Three series of measurements using cubic anvil cells with 10, 6 and 4 mm anvils have been carried out. The applied load varied between 8 and 100 tons. The resulting pressure was measured using Bragg reflections of NaCl and depending on the cell and load was changing between 0.5 and 8.3 GPa. At applied pressure of 1.5-2.0 GPa, samples become liquid above 500 °C. Most measurements have been carried out at 550-600 °C. In some cases, temperature was increased to 730 °C without apparent changes in diffraction pattern. 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 P_4S_7 liquid at 600 °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 pyrolitic BN, used as a sample container in the cell. This series of measurements represents a decompression experiment in the 10 mm anvil cell. A dramatic monotonic increase of the FSDP and its shift to lower Q with pressure release from 2 GPa (100 tons load) to a nearly ambient pressure indicates that the cage structure of P_4S_7 remains intact.

A typical compression experiment in the 4 mm anvil cell is shown in Fig. 2. In this experiment, a maximal pressure of 8.3 GPa was obtained for a 100 tons load. The FSDP decreases dramatically with increasing pressure and exhibits a shift to higher Q, but this process seems to be coherent with the decompression experiment shown in Fig. 1. The FSDP amplitude in the compression and decompression series differs by a factor of 10 at least. Further data analysis is in progress.

４．結論・考察

The above experimental results lead us to the following conclusion. The P_4S_7 liquid at 550-730 °C and applied pressure up to 8.3 GPa preserves its molecular structure consisting of P_4S_7 cages. The compression and decompression processes seem to be completely reversible in this pressure range. These results are consistent with our high-pressure Raman measurements carried out in cooperation with Professor Yarger group. The Raman measurements show only some distortions in geometry of P_4X_n (n = 3-10, X = S, Se) cages in the pressure range below 8-10 GPa and a complete recovery after pressure release [3]. Irreversible changes occur above 10 GPa.

５．引用(参照)文献等

1. Y. Katayama, T. Mizutani, W. Utsumi et al., Nature **403** (2000) 170.
2. G. Monaco, S. Falconi, W.A. Crichton et al., Phys. Rev. Lett. **90** (2003) 255701.
3. E. Soignard, E. Bychkov, J. Yarger, Arizona State University (Tempe, USA), unpublished Raman results.

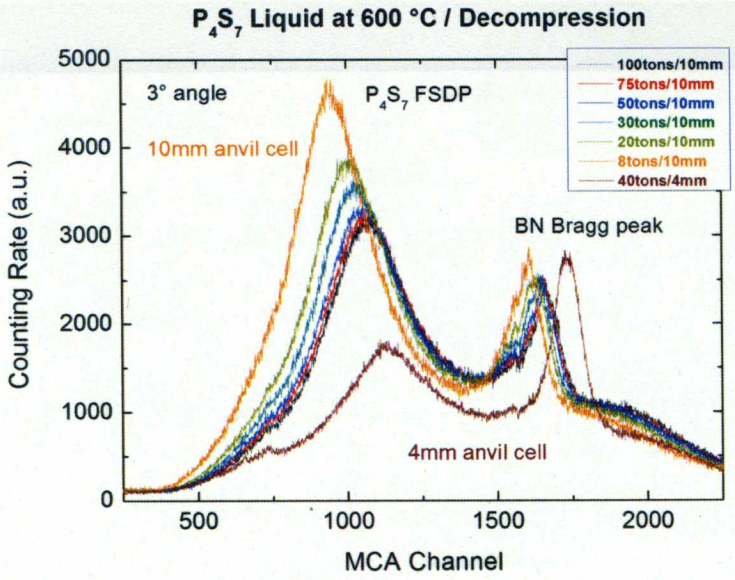

Fig.1

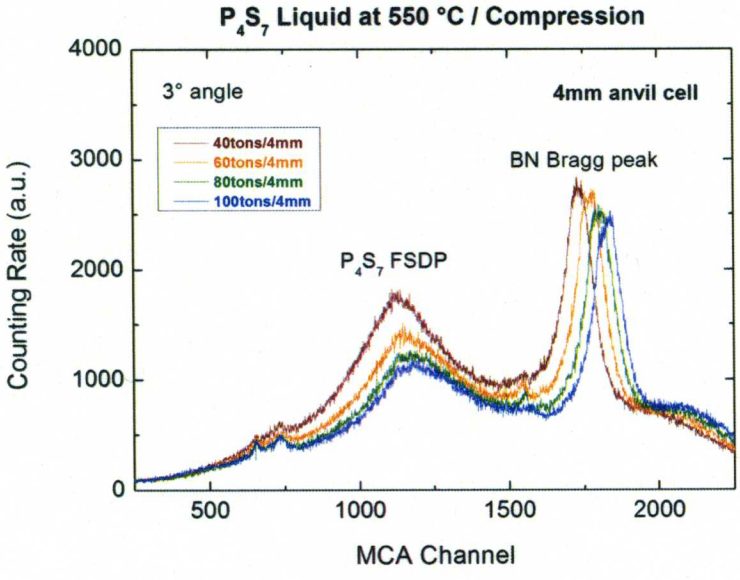

Fig.2