Liquid-liquid transition in P_4Se_3 melts at high pressure. Part 2.

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Summary
We have carried out *in situ* x-ray diffraction measurements of molecular liquid P_4Se_3 above the melting point as a function of high pressure up to 8 GPa and temperature, and established the P,T-phase diagram. The most significant feature appears to be a solid-state amorphisation of P_4Se_3 taking place at 300-330C and weakly depending on pressure. The solid-state amorphisation is followed by crystallization of a high-pressure form of P_4Se_3 with subsequent incongruent melting. In a limited P,T-range, the polymeric liquid coexists with solid black phosphorus. At higher temperatures, the polymeric and probably metallic liquids are stable.

key words: P_4Se_3 P,T-phase diagram, solid-state amorphisation, *in situ* x-ray diffraction measurements, molecular-to-polymeric transition

1. Objectives

Liquid-liquid phase transition is remaining exciting challenge in condensed matter physics and chemistry, and the question of whether it could be the first order or rather a gradual transition is a highly debated issue [1-3]. In our previous *in situ* x-ray diffraction measurements of a molecular liquid P_4Se_3 in the pressure range up to 10 GPa, a possible liquid-liquid transition was observed [4]. The main goal of the current experiments was to investigate the P_4Se_3 P,T-phase diagram and to study in details the structure of the melts in region of possible phase transformations from a molecular to a network liquid.

2. Methods

Energy-dispersive x-ray diffraction experiments have been carried out on the JAEA BL14B1 beamline using the cubic anvil type high-pressure high-temperature apparatus (SMAP2). P_4Se_3 samples were placed in a sample container made of boron nitride. Boron-epoxy cubes of different size have been used as containers. We have measured data sets for P_4Se_3 samples in 4 and 6mm anvil cells using compression/decompression cycles for each configuration. The samples have been heated by a graphite heater and the temperature was monitored by a thermocouple. The pressure has been determined using the lattice constant of sodium chloride.

3. Results

A preliminary P,T-phase diagram for P_4Se_3 obtained in this study is shown in Figure 1. The most significant feature appears to be a solid-state amorphisation of P_4Se_3 taking place at 300-330C and weakly depending on pressure. The solid-state amorphisation is followed by crystallization of a high-pressure form of P_4Se_3 with subsequent incongruent melting. In a limited P,T-range, the polymeric liquid coexists with solid black phosphorus. At higher temperatures, the polymeric and probably metallic liquids are stable. Typical diffraction pattern at $2\Theta = 6°$, shown in Figure 2, illustrate the solid-state amorphisation of P_4Se_3 molecular crystal and subsequent crystallization of amorphous solid on further heating.

The diffraction patterns of stable liquids above the melting point, i.e., 715C for 4.5GPa, appear to be

quite similar to their amorphous counterparts and glasses obtained by rapid quenching of the high-pressure melt. It means that the solid-state amorphisation transforms the P_4Se_3 molecular crystal into a polymeric amorphous form.

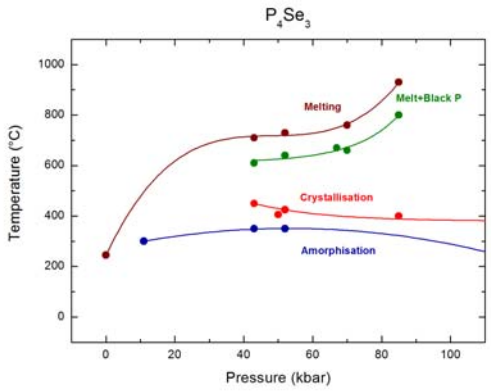

Figure 1. Preliminary P,T-phase diagram for P_4Se_3.

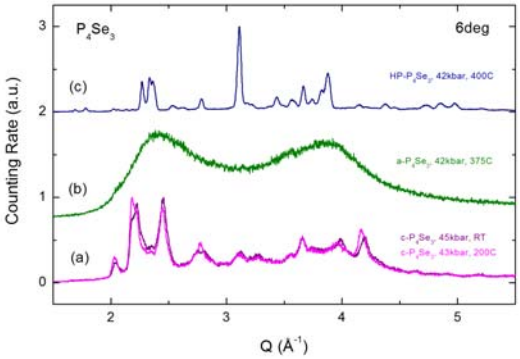

Figure 2. P_4Se_3 transformations at 4.2-4.5GPa on heating: (a) P_4Se_3 molecular crystal, (b) amorphous P_4Se_3, (c) HP-P_4Se_3 crystal; $2\Theta = 6°$.

4. Discussion and Conclusion

The obtained results indicate that a liquid-liquid phase transition for P_4Se_3 cages is hardly probable within the investigated P,T-range. The molecular organization is changing to a polymeric and then presumably to a metallic network via an intermediate step, the solid-state amorphisation. In fact, in a separate experiment we have succeeded to obtain a HP-P_4Se_3 glass at room temperature but at much higher pressure, 16GPa [5]. The interpolated results for this P,T-point are shown in Fig. 1 for solid-state amorphisation and crystallization lines, consistent with our results carried out in the investigated P,T-range: RT-950C, 0.1-8GPa.

5. References

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