

Structural changes in liquid and glassy P-Se alloys at very high pressures and temperatures.

In a previous EXAFS experiment (see report for HS2105) we attempt to look at the structural changes in solid, liquid and glassy P_4Se_3 as a function of pressure and temperature. In this experiment we observed a considerable amount of hysteresis and meta-stability in the EXAFS spectra as a function of temperature and pressure. For example, the EXAFS spectra at 4.5 GPa were different after the sample had been melted and refrozen. The subsequent relaxation of the pressure to 1 GPa also gave a markedly different spectrum compared to the sample at 1 GPa before it was pressurised. However, melting and re-solidification of the sample at 1 GPa recovered the original 1 GPa ambient temperature spectrum. Unfortunately, it was not possible from the EXAFS spectra alone, to identify what was happening to the material during these cycles. The primary aim of this experiment was to observe, by diffraction, what was happening to the structure of the material through these heat-pressure cycles.

The starting material used in these experiments was crystalline P_4Se_3 produced in our laboratory in an identical way to that produced for the previous EXAFS experiments. Analysis of the diffraction pattern of the as prepared sample confirmed that it was predominately the α phase with a small proportion of the β phase. As this sample was heated the β phase became more predominant. The diffraction pattern also showed an increasing amount of diffuse scattering which we attribute either to large strains developing in the crystal or induced rotational disorder of the P_4Se_3 molecular units. On cooling to room temperature the β phase along with a large amount of diffuse scattering again dominated as has been previously reported in the literature. Following the ambient pressure measurements at the beginning we then explored the P-T phase diagram. Figure 1 shows the, uncorrected diffraction patterns observed for liquid P_4Se_3 obtained at low pressure (< 0.2 GPa) and high pressure (> 5 GPa). It can immediately be seen that the two diffraction patterns are dramatically different. The low pressure sample shows a strong first sharp diffraction peak (FSDP) that has almost completely disappeared at high pressure. On quenching the liquid at high pressure the amorphous diffraction pattern remained without the observation of any Bragg peaks (the Bragg peaks seen in the figure come from the BN sample container in the Paris-Edinburgh Cell). This suggested the formation of a new, previously unreported, glass phase of P_4Se_3 produced via this route. After the sample was depressurised we measured the recovered material and confirmed the existence of this glass which had only a small FDSP. The existence of this glass phase explains the unusual observations we made in the EXAFS experiments. Following the measurements on P_4Se_3 , we also carried out measurements on as prepared glassy PSe. A similar pattern of behaviour was observed – namely a noticeable decrease in the size and intensity of the FSDP as a function of applied pressure (see figure 2).

At the current time we are carrying out a detailed analysis of all of the data we collected and comparing this with the previously obtained EXAFS data.

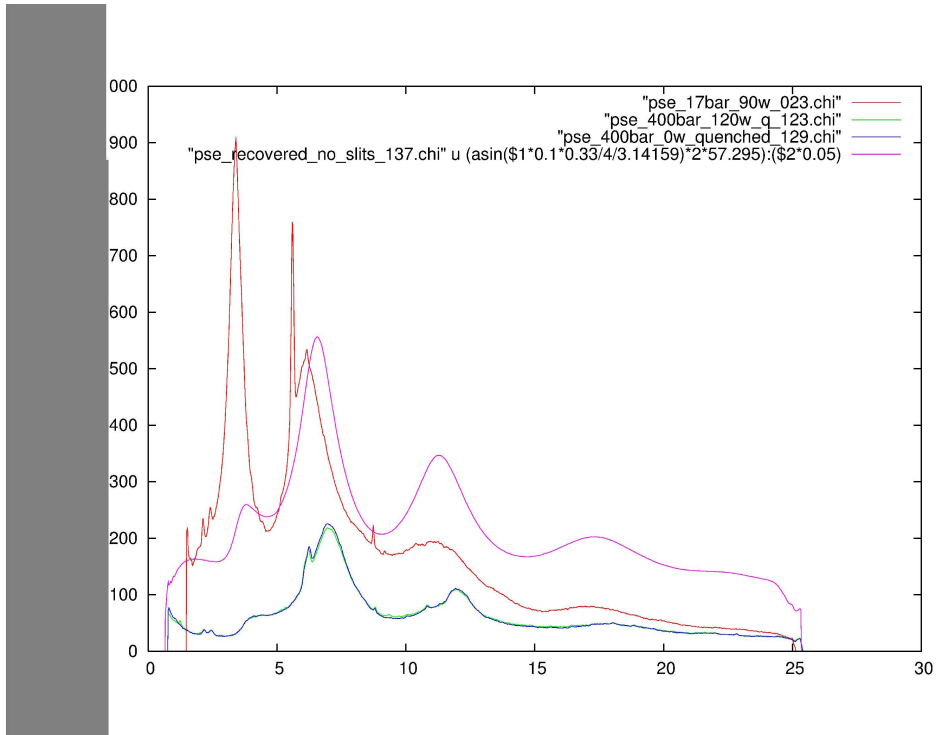


Figure 1. The figure shows the low pressure liquid phase of P_4Se_3 (red), the high pressure liquid and glass phases (blue and green) and the room temperature recovered glass phase of P_4Se_3 . Note the very strong FSDP in the low pressure liquid phase that has almost completely disappeared in the high pressure liquid and glass phases. Note, the FSDP is slightly recovered in the recovered glass phase and the shift of the peaks to smaller Q (in agreement with the expansion of the sample).

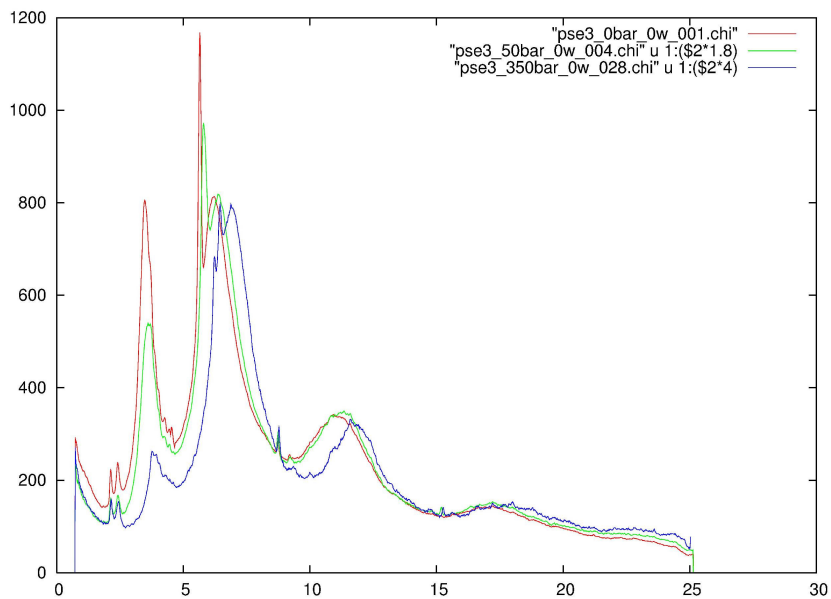


Figure 2. The diffraction patterns obtained from glassy PSe after the application of pressure (no heating). Note how the first sharp diffraction peak decreases in intensity and the shift of the peaks in $S(Q)$ to high Q as the sample volume decreases.