ESRF	**Experiment title:** X-ray diffraction study of amorphous and crystalline $GeSe_2$ at high pressures and high temperatures	**Experiment number:** HS 919
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Report:

The structures of most germanium and silicon dioxides, disulfides, and diselenides are based on tetrahedral AB_4-structural units. Their long range order depends on the connectivity of the tetrahedra and a number of different structures is observed as a function of temperature and pressure. Tetrahedra typically share faces, edges or corners. Edge sharing reduces the cross-linking between the AB_4 units and at ambient pressures SiS_2 and $SiSe_2$ have one-dimentional structures with edge-sharing SiX_4-tetrahedras only. The connectivity of the $GeSe_4$-units in $GeSe_2$ is rather unique, 50 % of the tetrahedra is edge sharing, while the other half is corner sharing. Hence, $GeSe_2$ has a two-dimentional structure. At atmospheric pressure, GeS_2 with 100 % corner sharing is observed at room temperature whereas its high-temperature modification is reported to be isostructural with $GeSe_2$. In general, the glassy analogues of the silicon and germanium dioxides are examples of random continuous networks of the AB_4 tetrahedra. On the other hand, the structure of amorphous germanium and silicon diselenides and disulfides is still debated (1).

The purpose of our experiments on a high pressure and high temperature behavior of two-dimensional $GeSe_2$ was manifold. First, we wanted to obtain information both on the existence of distinct crystalline modifications with different connectivity schemes in the pressure range up to 6 GPa and on the tentative phase diagram of this material. Second, determined equations of state, bulk moduli, and densities for all the polymorphs, together with the P-T slopes of the phase transitions between them, could be used to calculate the entropies and enthalpies of the phase transitions. Third, the structures of the crystalline modifications and the relations between them could be helpful to understand the structural properties of amorphous $GeSe_2$.

When two-dimensional $GeSe_2$ is compressed at the pressure range up to 6 GPa at temperatures 295-1200 K, three new crystalline modifications are observed. From the obtained high quality data, we have already determined the structure of two of them using classical direct methods for X-ray powder diffraction. The solved structures were refined using a full profile Rietveld method as implemented in GSAS (Figure 1). The two solved structures are three-dimensional -- the crystobalite type and distorted variants (Figure 1) of the structure already reported for the quenched GeS_2 and $GeSe_2$ products from high pressure and high temperature syntheses to ambient conditions (2). Their structural variations can be explained by anisotropic lattice distortions due to cooperative tiltings of the rigid corner-sharing $GeSe_2$ tetrahedra. We were also able to establish the existence of a triple point for the crystalline and liquid phases. We also drew a tentative phase diagram of crystalline $GeSe_2$ The investigation have also revealed the anomalous compressibilty of molten $GeSe_2$.

Since the structural information inferred so far from our experiments is promising to fulfill our goals, we hope to study the structural properties of glasses as well as liquids at high pressures and high temperatures (modeling of structure factors, etc.).

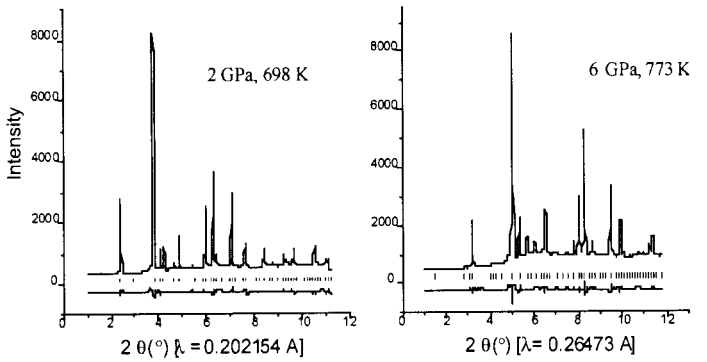

Figure 1 Observed and difference XRD profiles for $GeSe_2$ at different conditions – $I\boxed{X}$ space group (left) and $P\boxed{X}$ space group (right). Vertical markers indicate Bragg reflections.

References

(1) A. Grzechnik, S. Stølen, and T. Grande, J. Solid State Chem. 141, 248 (1998)
(2) T. Grande et al., J. Solid State Chem. 145, 167 (1999)