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Pressure-induced structures of PbS and Pb₆Bi₂S₉.
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Many sulphosalts are composed of modules of the PbS archetype combined into bulk crystal structures by structure-building operators at the sub-unit cell level [1]. Thus, their structural (in)stability at non-ambient conditions is determined by the behaviour of the PbS-like building blocks. In this communication, we will present the results of our work on the pressure-induced phase transitions in PbS (galena) and Pb₆Bi₂S₉ (heyrovskyite).

At ambient conditions, PbS has the NaCl (B1) structure (Fm $\bar{3}$ m, $Z = 4$). It undergoes a reversible first-order phase transition to a new polymorph at about 2.2 GPa [2]. A further transformation to the CsCl (B2) structure (Pm $\bar{3}$ m, $Z = 1$) occurs at 22.0 GPa.

The structure of the intermediate phase of PbS was solved using single-crystal x-ray diffraction in a diamond anvil cell mounted on a STOE diffractometer IPDS-2T (Mo-K α). It is described in space group Cmcm ($Z = 4$) with a twin law corresponding to a 180° rotation around the orthorhombic [21 $\bar{2}$] direction, which in turn corresponds to the cubic [110] direction in space group Fm $\bar{3}$ m. The Pb atom is surrounded by seven S atoms in the form of a capped trigonal prism (the coordination 1+4+2). The S atom that caps the prism gives the shortest Pb-S distance along the b axis. When only the Pb-S distances below 3 Å are taken into account, the structure could be considered as a stack of layers in the b direction.

Heyrovskyite Pb₆Bi₂S₉ (Bbmm, $Z = 4$) is built of distorted moduli of the PbS (galena) type structure at ambient conditions. The moduli are cut parallel to (311)_{PbS} and combined by mirror planes parallel to (010). Pb₆Bi₂S₉ undergoes a reversible first-order phase transition at about 4 GPa. Its new structure was solved using single-crystal x-ray diffraction in diamond anvil cells combining the data measured at laboratory (IPDS-2T, Mo-K α) and synchrotron (D3 beamline, HASYLAB/DESY, Hamburg, $\lambda = 0.4$ Å) facilities. The phase transition was expressed by the appearance of new reflections at $h/2 k l$ accompanied by the change from a B-centred to a primitive lattice, space group Pna2₁ ($Z = 8$). This new structure consists of two types of moduli with their structures related to the orthorhombic polymorph of PbS (Cmcm, $Z = 4$). In general, the mechanism of pressure-induced phase transitions involving the transformation of the modules from the galena type to the Cmcm type could be common to other sulphosalts.

[1] Ferraris G., Makovicky E., Merlino S., *Crystallography of modular materials*, Oxford University Press, Oxford (2004). [2] Chattopadhyay T., von Schnering H.G., Grosshans W.A., Holzapfel W.B., *Physica B*, 1986, 139/140, 386.

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Investigation of the Demixing Process in the System Fe₃O₄ (Magnetite)-FeAl₂O₄ (Hercynite). G. Eckold, H. Ritter, J. Davaasambuu, F. Güthoff. *Institute of Physical Chemistry, University of Göttingen, Germany.*
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The system Fe₃O₄(Mag)-FeAl₂O₄(Hec) exhibits a well defined miscibility gap at temperatures below 867°C. According to Putnis et al.[1], the early stages of chemical demixing are characterized by the mechanism of spinodal decomposition. Results from transmission electron microscopy and susceptibility measurements suggest a characteristic timescale of several hours.

The present work aims at a further investigation of the demixing kinetics of this system by X-ray powder diffraction. Mag₅₀Hec₅₀ samples were synthesized from hematite, corundum, iron and magnetite following a modified route of hercynite synthesis[2]. The purity of magnetite was tested by refinement from X-ray powder diffraction data as well as Raman spectroscopy. There was no indication for any impurity phase like maghemite. The sample was characterized by X-ray powder diffraction. After quenching from the homogeneous phase at about 1000°C to room temperature, the diffractogram remains almost unchanged. No significant broadening or line splitting is observed compared with a diffractogram obtained well above the critical temperature. This indicates that the mixture is still homogeneous. The lattice constant was determined by Rietveld refinement as 8.31Å which is between the values of magnetite(8.39Å) and hercynite(8.17Å). The deviation from Vegard's Law is probably due to the change of spinel site occupation. While Fe₃O₄ exhibits basically an inverse spinel structure, the cation distribution in FeAl₂O₄ corresponds to the normal spinel type. In order to obtain information about the kinetics of phase separation, in situ X-ray diffraction experiments were performed in a temperature interval from 300°C to 800°C. During this time-interval up to 9 days after quenching, no significant changes in the diffractograms could be observed at any temperature. For the investigation of the long time behaviour, another sample was annealed ex-situ at 600°C for 25 days before it was cooled to room temperature. The Bragg peaks of this sample are shifted to smaller angles and the lines are considerably broadened due to the phase separation. However, a complete demixed state is not achieved. These results indicate that demixing needs at least more than one week to be observed by Bragg reflections and is definitely not finished after more than three weeks. In view of the findings of Putnis et al. who observed compositional fluctuations already within several hours by transmission electron microscopy, the present data show that the growth of those fluctuations and the formation of well defined demixing structure needs much longer times.

Small angle scattering as well as inelastic neutron scattering experiments are planned in order to check if this behaviour is a two-stage mechanism like in silver-alkali halide systems[3-4].

[1] Putnis A. et al., *Am. Mineral.*, 2005, 90, 1278. [2] Hill R., *Am. Mineral.*, 1984, 69, 937. [3] Eckold G., *J.Phys.:Cond.Matter*, 2001, 13, 217. [4] Eckold G. et al., *J.Phys.:Cond.Matter*, 2004, 16, 5945.

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