FA2-MS15-P01

Pressure-induced structures of PbS and Pb,Bi,S
Andrzej Grzegorzek\textsuperscript{a}, Lars A. Olsen\textsuperscript{b}, Emil Makovicky\textsuperscript{b},
Tonci Balic-Zunic\textsuperscript{c}, Wolfgang Morgenroth\textsuperscript{b}, Karen
Friese\textsuperscript{a}, \textsuperscript{\textcopyright}Condensed Matter Physics, University of
the Basque Country, Bilbao, Spain; \textsuperscript{b}Dept. of Geography
and Geology, University of Copenhagen, Denmark;
\textsuperscript{c}Institute of Geosciences, Crystallography Group,
Goethe University, Frankfurt am Main, Germany.
E-mail: andrzej.grzegorzek@ehu.es

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 Pb,Bi,S (heyrovskite).

At ambient conditions, PbS has the NaCl (B1) structure
(Fm\textit{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 (Pt\textit{3}m, \(Z = 1\))
occurs at 22.0 GPa.

The structure of the intermediate phase of PbS was solved
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
distribution in FeAl\textsubscript{2}O\textsubscript{4} corresponds to the normal spinel type.

Keywords: phase transitions, high pressure, single-crystal
X-ray diffraction

FA2-MS15-P02

Investigation of the Demixing Process in the System
Fe\textsubscript{2}O\textsubscript{3}(Magnetite)-FeAl\textsubscript{2}O\textsubscript{4}(Hercynite).
G. Eckold, H. Ritter, J. Davassaambuu, F. Guthoff. Institute of Physical
Chemistry, University of Göttingen, Germany.
E-mail: geckold@gwdg.de

The system Fe\textsubscript{2}O\textsubscript{3}(Mag)-FeAl\textsubscript{2}O\textsubscript{4}(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.
Mag\textsubscript{50}Hec\textsubscript{50} 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
Fe\textsubscript{2}O\textsubscript{3} exhibits basically an inverse spinel structure, the cation
distribution in FeAl\textsubscript{2}O\textsubscript{4} 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].


Keywords: spinel, demixing, kinetics