High pressure in situ XRD study of the disproportionation of SnO

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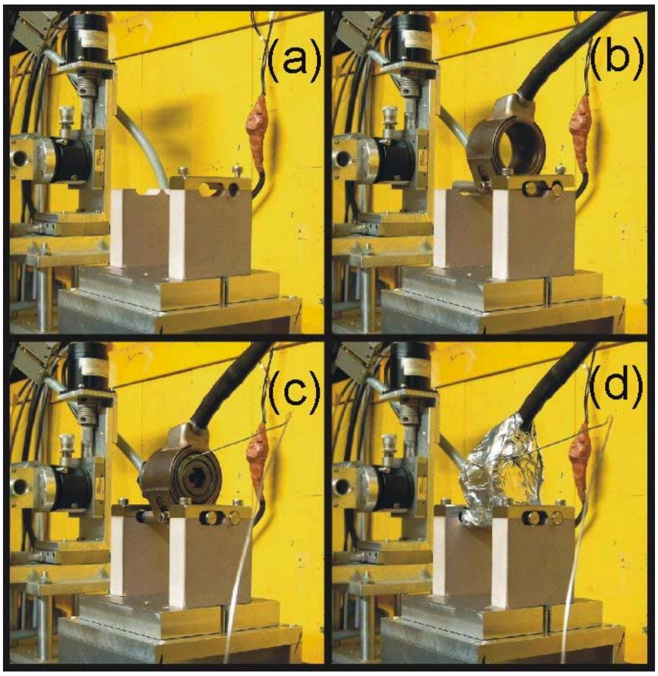

Figure 1: *Setup for high pressure/high temperature in situ XRD studies of disproportionation reactions of SnO at beamline F3.*
(a) Ceramic spacers for thermal insulation.
(b) Heating band connected with a PID temperature controller.
(c) DAC with thermocouple.
(d) Aluminum foil for thermal insulation.

The present study is a continuation of previous *in situ* and *ex situ* XRD studies of the disproportionation reaction of SnO [1]. Here we report on the disproportionation of SnO to SnO_2 and Sn at temperatures up to 370 °C and for the first time pressures up to 15 GPa. We used the *in situ* setup described in [1] with liquid N_2 as chemically inert and pressure transmitting medium for hydrostatic compression. Up to 8 GPa NaCl was used as pressure marker and above 8 GPa MgO. Gold as pressure marker could not be used due to the fact that the occurring metallic tin alloys with gold. The diamond anvil cell (DAC) had diamonds with 1.0 and 0.5 mm flat and gasket hole diameters of 0.4 and 0.2 mm, respectively. We used a 0.05 mm thick inconel gasket with only a little amount of ground sample of SnO from ChemPur inside the gasket hole for hydrostatic pressure and to avoid pressure drop due to the volume collapse during the disproportionation reaction of SnO to SnO_2 and Sn. The huge number of spectra was evaluated with the computer program EDXPowd [2].

Compared to the experiments at ambient pressure [1], no synchrotron radiation induced disproportionation of SnO was observed. This means that pressure stabilizes SnO against the radiation induced segregation into Sn and SnO_2. Another difference we observed was that no intermediate oxide (Sn_2O_3) occures during the disproportionation. Moreover under pressure metallic tin appears in the β-Sn structure and in the tetragonal high-pressure phase and SnO_2 in the high-pressure phase SnO_2-IV [3] which is a modified fluorite structure.

We measured at beamline F3 the time dependence of the disproportionation reaction of SnO at 20 different pressure/temperature conditions, altogether about 1100 EDXRD spectra. Some typical spectra from two series are shown in Fig. 2. At pressures above 5 GPa diffraction lines (*hkl*) with $h \neq k$ of SnO become broader due to tensile stress conditions in the high pressure cell [4]. The appearing Sn is not always visible in the diffraction spectra as in the case of the 14.8 GPa spectra (Fig. 2). Several strong diffraction peaks are used for SnO and SnO_2 in order to determine the composition of the sample (see Fig. 3) while the X-ray fluorescence of Sn serves as internal intensity standard. This is the advantage of EDXRD kinetic studies especially under pressure. The yield fraction of SnO_2 was used to derive the value of reaction progress α. A Sharp-Hancock plot of α [5] reveals the reaction rate *k* and the reaction exponent *m*. The reaction exponent *m* reflects the rate determining process. In the case of SnO *m* starts at a value of 1.8 at ambient pressure, decreasing to 0.3 at 3 GPa and increasing to 1.6 at 15 GPa. This shows that with applying pressure the rate determining process changes dramatically from a nucleation and growth mechanism to a diffusion controlled one and back to a nucleation and growth mechanism at higher pressures. The aggregate state of the occurring Sn can not be the reason for ths behavior, as shown for ca. 2.3 GPa at 232 °C (β-Sn) and 370 °C (liquid-Sn) where *m* is 0.3 and 0.5, respectively. In contrast to the behavior of *m* both the values of the reaction rate *k* and the pressure dependence of *k* depend strongly on the physical state of Sn. The reaction rate *k* has a larger value when Sn is liquid compared to the case when Sn is solid. The pressure dependence of *k* is large and positive for the liquid case and nearly zero when Sn is solid. This behavior is caused by the higher diffusion rate of liquid Sn.

To conclude the above finding, the reaction mechanism from SnO to SnO_2 and Sn is strongly influenced by the applied pressure, while the reaction rate strongly depends on the physical state of the appearing Sn.

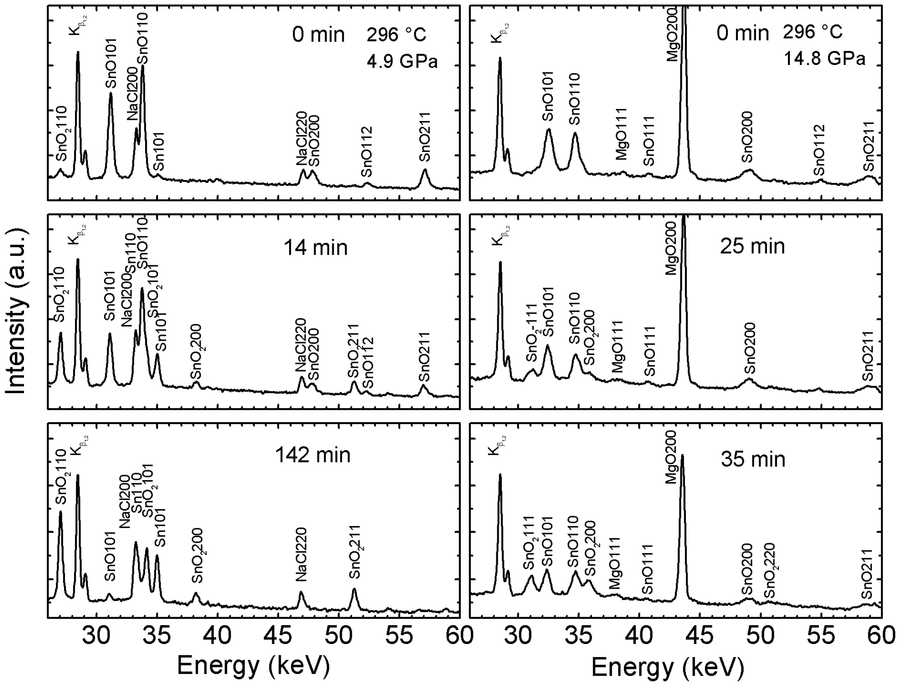

Figure 2: Disproportionation of SnO to Sn and SnO_2. (left): At 4.9 GPa and 296 °C Sn has the bct high-pressure phase. NaCl was used as pressure-marker (right): At 14.8 GPa and 296 °C the occurring Sn is not visible. SnO_2 has the high pressure SnO_2-IV phase. MgO was the pressure marker. This series could not be finished because a diamond anvil broke after 35 min.

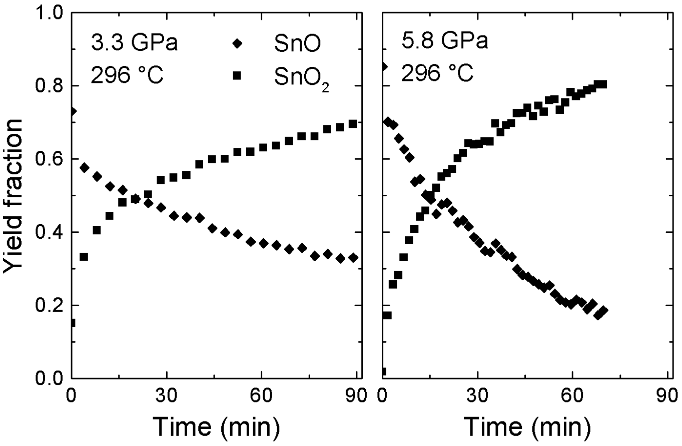

Figure 3: In situ measurements of the time evolution of the reactants at 296 °C under pressure. The initial substance was ground SnO. The accumulation time per point was 240 s for the 3.3 GPa series and 100 s for the 5.8 GPa series. In this presentation the yield fraction of SnO_2 corresponds to the reaction progress α.

References

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