Supplementary Information

Phase segregation in Mn-doped In_2O_3: in-situ high-pressure high-temperature synchrotron studies in multi-anvil assemblies

Maged F. Bekheet, Marcus R. Schwarz, Mathis M. Müller, Stefan Lauterbach, Hans-Joachim Kleebe, Ralf Riedel, and Aleksander Gurlo

Experimental details

The solid solution c-$In_{1.85}Mn_{0.15}O_3$ was synthesized hydrothermally by applying the following procedure. 0.37 mmol of $InCl_3 \times 4H_2O$ (97%, Aldrich) 0.03 mmol of $Mn(CH_3COO)_3 \times 2H_2O$ (97%, Aldrich) and 3.2 mmol of hexamethylenetetramine (HMTA, 99.5%, Fluka) are added to a solution of 2 ml ethylenediamine (EN, 99%, Aldrich) in 4 ml distilled water (DW) and stirred for 30 min. The resulting solution is transferred into a Teflon-lined stainless-steel autoclave (10 mL) and maintained at 180°C for 16 h. After cooling to 25°C the solid product was separated by centrifugation, washed three times with distilled water and isopropanol, dried at 80°C for 5 h and calcined at 500°C for 3 h in air.

High pressure high temperature experiments were performed with a 6-8 DIA-type multianvil press MAX200X at beamline W2, HASYLAB/DESY, Hamburg, Germany. In-situ energy-dispersive diffraction pattern were collected with a white beam with the spot size of 0.7 mm in the energy range 20-150 keV using a high purity Ge detector covered in a 6 mm lead capsule to shield scattered radiation. Synchrotron radiation was directed perpendicularly to the uniaxial press axis through the holes in the first-stage steel anvils. Figure 2 shows a cross-sectional schematic of the pressure cell, based on semisintered MgO-5%Cr_2O_3 octahedron (Ceramic Substrates & Components LTD., Isle of Wight) with 18 mm edge length. The material alongside the X-ray beam path was replaced by amorphous Si-B-C-N X-ray windows, cemented into the cell. The cylindrical zirconia sleeve for thermal insulation and the graphite heater were perforated also for this purpose. Temperature was measured with a Type C (W5Re:W26Re) thermocouple (Newport Electronics GmbH), which is inserted coaxially to the axis of the furnace [1] and protected against the pressure standard and sample chamber with thin molybdenum foil and two BN sheets. Thermocouples readings are reported without correction of the influence of high pressure to the e. m. f. or additional thermopower exerted by copper protection coils. [2] Samples and pressure standard (NaCl) [3] were placed in amorphous SiBCN capsules located in the center of the beam pathway. Samples were separated from the pressure standard inside the capsules with thin Pt foil serving as an additional standard.

After the experiment, the amorphous capsules containing HP/HT-treated samples were recovered by cutting the octahedral cell by using a diamond disc. In the next step the amorphous capsules were broken by using hard metal tool. The quenched samples were extracted and ground in a mortar to obtain a fine powder for subsequent characterizations.

X-ray powder data were collected in capillary-sample transmission geometry on a STOE STADI P with Mo$K\alpha_1$ radiation and a position sensitive detector with 6° aperture. Rietveld refinement was performed using the FULLPROF program. [4]

Transmission electron microscopy (TEM) characterization was performed with a FEI CM20 microscope, equipped with a Gatan double tilt holder at a nominal acceleration voltage of 200 kV. TEM samples were prepared from a small amount of powder that was dispersed in ethanol by ultrasonic treatment for 5 minutes. A drop of the suspension was applied to a copper grid covered with a holey carbon film. SEM images were recorded with Scanning Electron Microscopy (SEM, XL 30 FEG).

Raman spectra

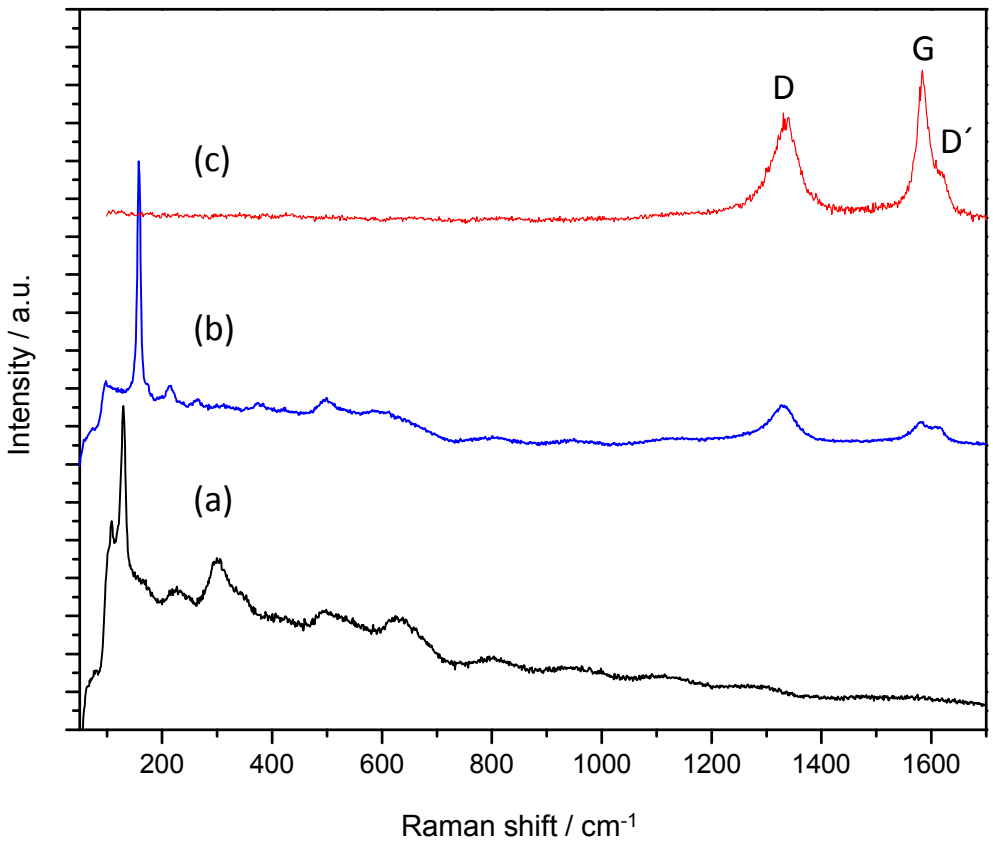

Figure 1: Micro-Raman spectra of initial bixbyite-type c-$In_{1.85}Mn_{0.15}O_3$ (a), recovered specimen (b) and SiBCN crucible (c) after compression to 8 GPa and heating to 950 °C, showing the main Raman features of carbon, the D, G, D´ bands. Raman spectra are taken with a red laser (632.8 nm).

References

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