ESRF	**Experiment title:** **High pressure synthesis of corundum-type In_2O_3 and new SiC_2N_4 phases**	**Experiment number**: HS-3413
Beamline: ID27	**Date of experiment**: from: 30-OCT-2007 to: 03-NOV-2007	**Date of report**: 29-FEB-2008
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Names and affiliations of applicants (* indicates experimentalists):

Alexander GURLO*, Elisabeta HORVATH-BORDON, Dmytro DZIVENKO*

FB Material- und Geowissenschaften, TU Darmstadt, Petersenstr. 23, D-64287 Darmstadt, Germany

Andreas ZERR*

LPMTM - CNRS, Université Paris Nord, av. J. B. Clement, F-93230 Villetaneuse, France

Report:

Indium oxide

In-situ angle-dispersive X-ray diffraction (AD-XRD) experiments were performed in a diamond anvil cell (DAC) up to ~33 GPa. The sol-gel synthesized cubic (bixbyite-type) In_2O_3 was loaded into a cavity of 100 µm in diameter and 20-30 µm thickness, drilled in stainless steel gaskets. Pressure was calculated from the equation of state of crystalline argon served as a quasi-hydrostatic pressure medium. Pressure was additionally controlled using the ruby fluorescence method. An *ex-situ* laser heating system (Nd-YAG laser) was used to heat the sample. After heating the samples were quenched to ambient temperature by closing laser shutter. *Unfortunately, it was not possible to perform in-situ heating experiments as it was planned in the proposal.* Focused monochromatic beam (λ=0.3738 Å) with beam size of approximately 10 µm diameter was used at the X-ray source for AD-XRD experiments. The diffraction patterns were collected using MAR-CCD detector and processed with Fit2D (ESRF) and FullProf[1] software.

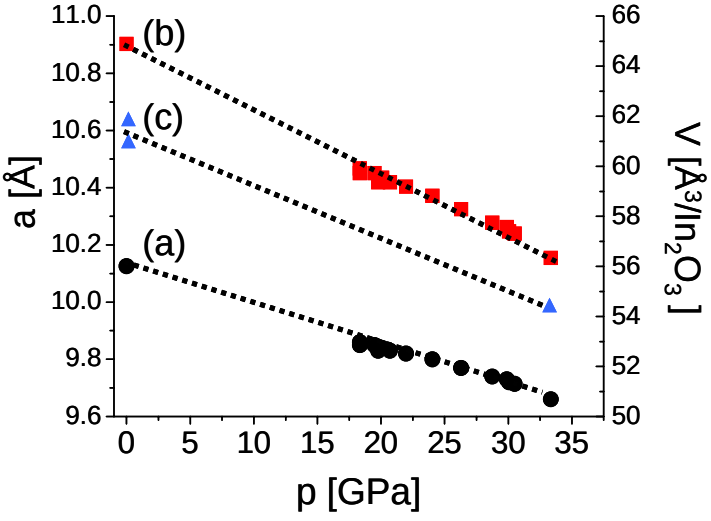

Figure 1. Variation of lattice constant (a) and unit-cell volume (b) with pressure of the c-In_2O_3 in a DAC. The solid lines are shown to guide the eye. (c) Triangles indicate the volume of a new orthorhombic polymorph.

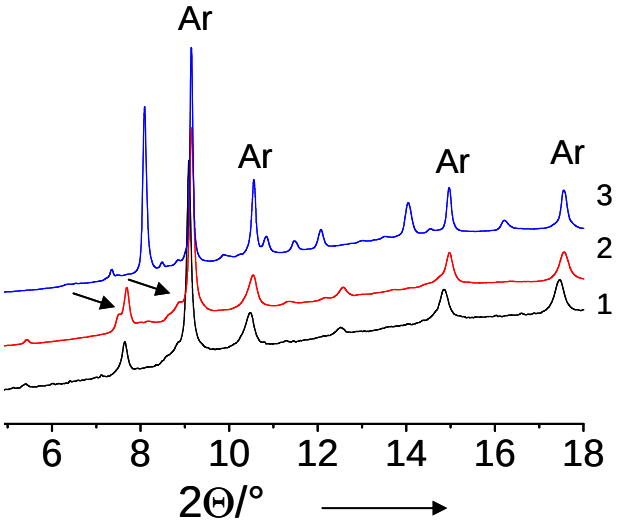

Figure 2. *In-situ* XRD diffraction patterns of c-In_2O_3 in DAC compressed to 33 GPa (1), and after laser-heating (2), (3). "Ar" indicates the reflexes of crystalline argon.

The first remarkable observation is the stability of the c-In_2O_3 up to ~33 GPa at RT. The lattice constant decreases by approximately 5% and, accordingly, the volume- by ~15% (Figure 1). Thus, c-In_2O_3 is found to be more compressible as compared to other bixbyite-type oxides (see for example, Mn_2O_3[2]).

A short *ex-situ* laser heating of the compressed (33 GPa) sample induced splitting of the diffraction reflexes, while longer heating (1 min) induced the appearance of a new diffraction pattern (Figure 2). The latter differ significantly from XRD patterns of the rh-In_2O_3 compressed to the same pressure (not shown here) as well as of c-In_2O_3. Two-dimentional XRD pattern of the compressed laser-heated sample consists of two types of diffraction rings (besides the pattern of compressed argon) (): (i) almost continuous rings similar to ones observed in the initial powdered sample (i.e. initial c-In_2O_3) and (ii) individual spots which appears only in a laser heated sample. The spots, which are characteristic feature of highly textured samples, indicate the crystallisation of several microcrystals of a new phase under high pressure conditions. The sample was recovered to ambient conditions without any changes in the texture (b). The appearance of two types of diffraction patterns in a laser-heated sample suggested a two phase composition. c-In_2O_3 was verified to remain in the sample even after laser-heating. The strong texture causes the variation in diffraction intensities and complicates the full profile Rietveld refinement. Unfortunately the quality of the x-ray diffraction patterns was not sufficient for an unequivocal solving of crystal structure of the new In_2O_3 phase.

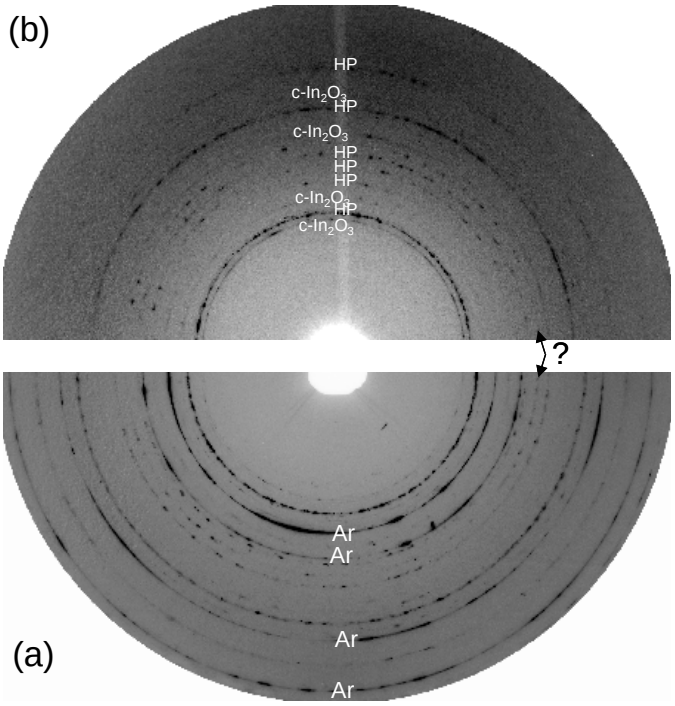

Figure 3. Two dimensional images of laser-heated sample In_2O_3 sample (a) in a DAC at 33 GPa and (b) recovered to ambient conditions.

The results obtained during our beamtime at the ID27 showed the existence of a new high pressure In_2O_3 polymorph. They call for the reinterpretation of In_2O_3 phase diagram, especially the stability regions of different structures and conditions for their synthesis.

Silicon carbonitride

We also performed high-pressure high-temperature experiments with nanocrystalline silicon-(carbodiimide)-nitride, Si_2CN_4. This Si-C-N phase crystallizes in orthorombic structure which contain carbodiimide unit (–N=C=N–), i.e. it can be expressed as $Si_2N_2(NCN)$.[3] Recent theoretical studies have indicated that –N=C=N– units are unstable on commpression and can condensate with Si atoms at high pressures, thus resulting in formation of new denser crystalline Si-C-N phase.[4] [REF]

The pellets of nanocrystalline Si_2CN_4 powder were loaded in a DAC in argon pressure medium and compressed up to about 20 GPa. The samples were investigated *in-situ* using AD-XRD. The diffraction lines of Si_2CN_4 broaden and weaken considerably with pressure increase, in accordance with earlier high-pressure multi-anvil experiments.[5] At pressures above 9 GPa the diffraction lines have almost disappeared. We presume that this observation is due to complete amorphization of Si_2CN_4. At maximal pressures of about 20 GPa the samples were annealed *ex-situ* using CO_2-laser. The heating time was very short (10-20 seconds) due to instabilities of stainless steel gaskets. The heating, however, had no effect on the diffraction patterns. The SI-C-N samples recoverd to ambient conditions were found to maintain amorphous state.

References

[1] C. Frontera, J. Rodriguez-Carvajal, *Physica B* **2003**, *335*, 219.

[2] T. Yamanaka, T. Nagai, T. Okada, T. Fukuda, *Z. Kristallogr.* **2005**, *220*, 938.

[3] R. Riedel, A. Greiner, G. Miehe, W. Dressier, H. Fuess, J. Bill, F. Aldinger, *Angew. Chem. Int. Edit.* **1997**, *36*, 603.

[4] P. Kroll, J. Gracia, A. Gurlo, R. Riedel, "Phase Transitions in Silicon-Carbon-Nitride Compounds", presented at *2007 MRS Fall Meeting*, Boston, MA, USA, November 26-30, **2007**.

[5] V. L. Solozhenko, M. Schwarz, R. Riedel, *Solid State Commun.* **2004**, *132*, 573.