



	<b>Experiment title:</b> High pressure nitrides of Si and Al	<b>Experiment number:</b> HC-1328
<b>Beamline:</b> ID06-LVP (C05)	<b>Date of experiment:</b> from: 25.04.2014 to: 29.04.2014	<b>Date of report:</b> 06.03.2015
<b>Shifts:</b> 21	<b>Local contact(s):</b> Wilson A. Crichton, Jeremy Guignard	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> Marcus Schwarz* <i>Freiberg High Pressure Research Centre / Institute for Inorganic Chemistry TU-Bergakademie Freiberg, Leipziger Straße 29, 09599 Freiberg, Germany marcus.schwarz@chemie.tu-freiberg.de</i>  Christian Schimpf* <i>Institute for Materials Science, TU-Bergakademie Freiberg, Gustav-Zeuner-Str. 5, 09599 Freiberg, Germany</i>		

## In-situ X-ray investigation of the high pressure-induced phase transformation of a AlN single crystals

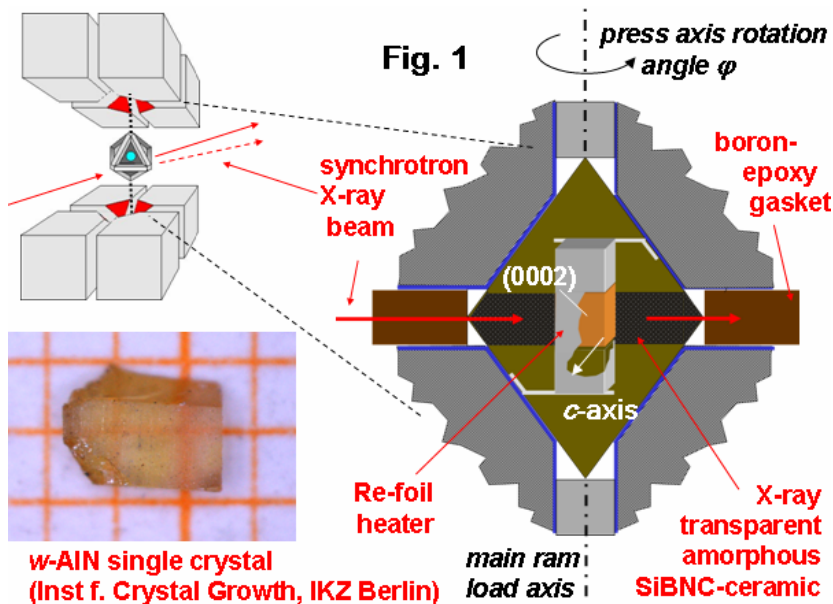
### Introduction

Although AlN and Si<sub>3</sub>N<sub>4</sub> are well-known non-oxide ceramic materials with high technological relevance, their high pressure forms, *rs*-AlN and  $\gamma$ -Si<sub>3</sub>N<sub>4</sub>, have been discovered only two decades ago [1,2]. Like diamond and cBN, their mechanical properties are superior to those of their low pressure counterparts [3,4]. In the recent time we concentrated on the rocksalt-type AlN phase [4], because still many properties of this metastable phase have not been experimentally determined. In Ref. [4] we propose a revised experimental *p*-*T* phase diagram of AlN, using an amorphous Al-N-H precursor which would easily decompose into that modification of AlN which is stable at the given *p*,*T* conditions. By using this technique, we could show that the phase boundary between the ambient-pressure wurtzite-type (*w*-AlN) and *rs*-AlN has a negative clapeyron slope and commences between 11 and 12 GPa (at *T* = 1000–2000 K). This is at least 1 GPa lower than reported in other recent works [5], which, like all previous studies, had been conducted with *w*-AlN as starting material. Thus the direct *w*-AlN → *rs*-AlN phase transition, which is displacive in nature (see [6] and references therein), appears to have a considerable kinetic barrier, requiring high overpressures and temperatures to proceed. In this study we attempted to follow the conversion of a high purity single crystal of *w*-AlN at pressures above 15 GPa and very high temperatures, using the large volume multianvil press at beamline ID06 and angle-dispersive X-ray diffractometry. Preliminary evaluation of the collected data presented in this report shows that at 17 GPa and *T* ≈ 1800–2000°C, the *w*-AlN crystal indeed slowly transforms into a cluster of highly oriented *rs*-AlN nanocrystallites. Repetition of the experiment using one X-ray transparent anvil in the second high pressure stage revealed that multiple (00 $\ell$ ) reflections and all reciprocal axes of the hexagonal *w*-AlN crystal lattice are accessible. To the best of our knowledge, this is the first time that an *in-situ* X-ray diffraction experiment on a macroscopic single crystal at high pressure and high temperature, using a multianvil apparatus has been successfully conducted.

Additionally, at the end of the report, first results on the equation of state (EoS) of the Cu-Mn-Ni alloy manganin, which have been obtained in one preliminary experiment during the same measurement stay are provided. Although manganin is a well-known piezoresistive material and used to determine pressure and deformation in static and dynamic high pressure experiments for a long time, a literature research shows that EoS data is not available up to the present day.

## Experimental

**Fig.1** shows a scheme of the experimental setup used for the multianvil high pressure experiments on the macroscopic *w*-AlN single crystals. The second high pressure stage of the multianvil press is indicated in the

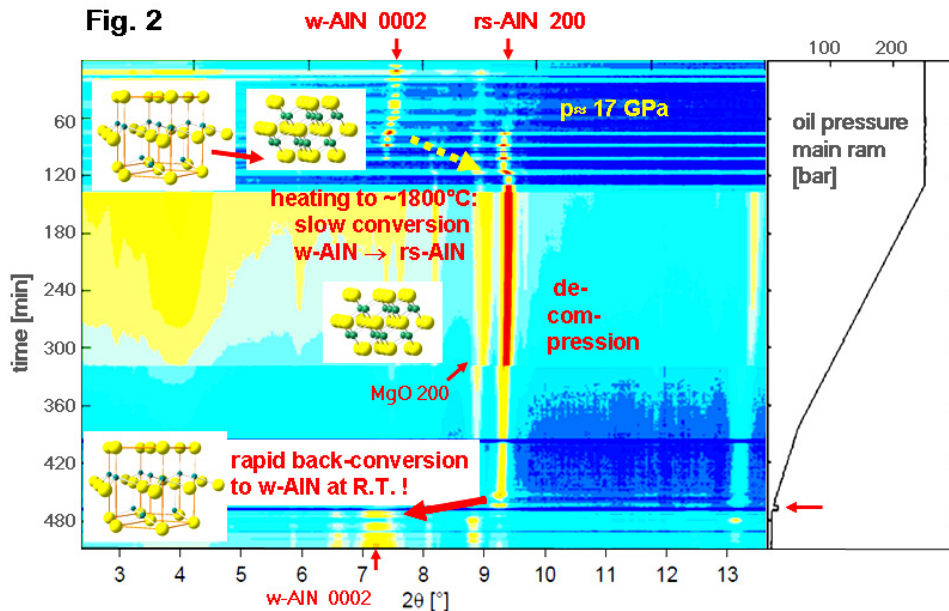


upper left, consisting of a cluster of 8 tungsten carbide cubes with truncated corners towards an octahedral pressure cell located within their common center. Assemblies with truncation edge length (TEL) to octahedron edge length (OEL) combinations of 10/5, 10/4.5 or 7/4 were used. The synchrotron x-ray beam passes through the equatorial plane between the anvils. Low absorption boron epoxy gaskets and highly transparent amorphous Si/B/C/N ceramic [7] inserts in the pressure cell in beam direction were used to achieve high transmission, leading to small collecting times and an excellent signal-to-noise ratio of the collected X-ray pattern, without interfering reflections

from the sample environment. High quality *w*-AlN crystals produced by a physical vapor transport method [8] were kindly provided by the Leibnitz Institute for Crystal Growth (IKZ, Berlin, Germany). The crystals were cut into rectangular blocks, so that their natural smooth growth surface of the *w*-AlN (0002) basal plane formed one face of the block. The crystals were then wrapped into a rhenium-foil box furnace and inserted into the octahedral pressure cell, oriented so that (0002) was coplanar to the plane formed by the beam and the main ram axis (*c* axis normal to paper plane in Fig. 1) Thus, reflection conditions for 0002 and higher order reflections could be matched upon a small rotation of the press around the angle  $\varphi$ . In addition to the very incompressible Re, a thin strip of h-BN and MgO from the cell served as pressure and/or temperature calibrants. While a first experiment was terminated by a violent blowout due to gasket failure, a second run could be safely compressed to 17.5 GPa within 280 min at room temperature and was then gradually heated up to  $\sim 1800^\circ\text{C}$ . The electric heating power was kept constant until all X-ray reflections of the wurtzite phase had vanished and then reduced to zero within 6 min. Decompression was accomplished at room temperature within 340 min. Throughout the entire run, diffractograms were routinely recorded every 20 seconds. At specific stages of the experiment, pattern with longer exposure times were recorded.

## Results and Discussion

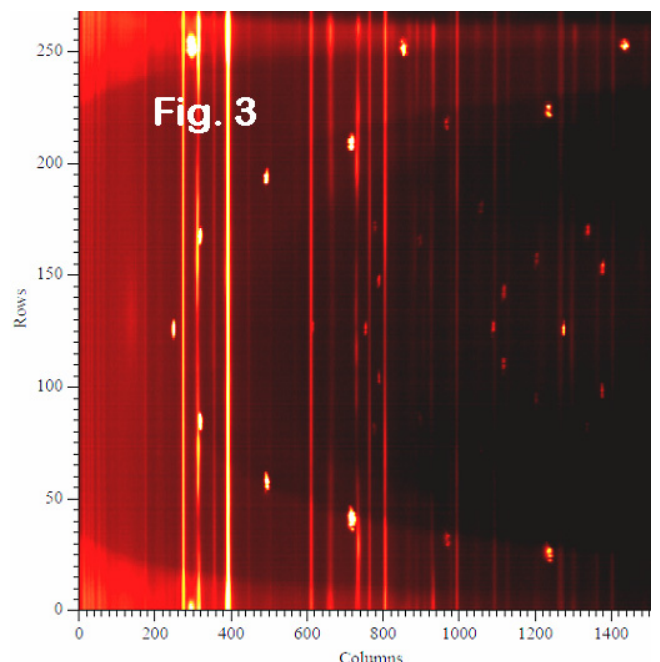
In the left part of **Fig. 2**, the development of X-ray pattern of the AlN sample during heating at constant ram load and decompression is shown, along with schematic representations of the corresponding changes in crystal structure. On the right hand side, the (un)loading history is represented by the oil pressure of the main ram of the press. As already mentioned, loading the 10/4.5 (OEL/TEL) assembly to 250 bars oil pressure resulted in a sample pressure of  $\sim 17$  GPa. Initially, only the 0002 reflection of the *w*-AlN phase is present. Upon temperature increase the reflection shifts to lower diffraction angle, corresponding to thermal expansion. Then a *rs*-AlN 200 peak emerges and while heating is continued both phases coexist. Further



displacement of the *w*-AlN reflection towards lower diffraction angle possibly indicates pressure relaxation due to the ~20% volume shrinkage during the phase transformation. Eventually the *w*-AlN 0002 reflection faints and only the *rs*-AlN reflection can be observed. At this stage, the temperature was decreased to ambient within 6 minutes as already mentioned. Due to re-location of the beam relative to the contents of the pressure cell upon decompression, also the 200 reflection of the MgO pressure medium becomes visible as a broad (yellow) band at the left of the *rs*-AlN peak. Both reflections persist down to a hydraulic pressure of about 7 bars, at which a blowout—usually associated with a rapid pressure drop inside the cell—occurred, as indicated by the small hump in the oil pressure curve and marked by the red arrow. Remarkably, after this instant, the *rs*-AlN 200 reflection was almost completely vanished, while that of MgO was still in place and a strong *w*-AlN 0002 reflection discernible again. Other *w*-AlN reflections such as the 1000 (between channel No. 400 and the red arrow) were much weaker or not visible, indicating that the resulting *w*-AlN material still had the same orientation as the original single crystal, while the broadness of the reflections resembled that of a very fine grained material.

The observed rapid back-conversion from *rs*-AlN to *w*-AlN is very remarkable in several regards. First, being not thermally activated and orientation-conserving, it is clear that it must be of martensitic nature. Second, given the fact that it took about 40 minutes for the forward conversion until all *w*-AlN had vanished, the speed with which the reverse transformation must have proceeded is quite remarkable, particularly when keeping in mind that it is associated with a ~20% increase in volume. Third: Our results shed light on the small fractions or even absence of (residual) *rs*-AlN observed in *post-mortem* investigations of material retained from static [9] and dynamic [10] HP/HT experiments which used (polycrystalline) *w*-AlN as starting material. On the other hand *rs*-AlN as such was shown to have sufficient kinetic stability under ambient conditions: In a prior study we have successfully recovered the phase both as a nanocrystalline powder in high yields from shock wave treatment of nanocrystalline *w*-AlN as well as crystallites with sizes up to several microns via static HPHT-treatment of a Al-N-H precursor [4]. The nano *rs*-AlN powder had a high thermal stability up to ~1100°C [4]. The ease of the back conversion of material obtained by transforming a larger crystallographically coherent volume of *w*-AlN must therefore be associated with a "memory" on the parent phase, given by the mutual orientation relationship of the created domains of the high pressure phase and residual (frozen-in) stresses, similar to the shape memory effect in metallic alloys.

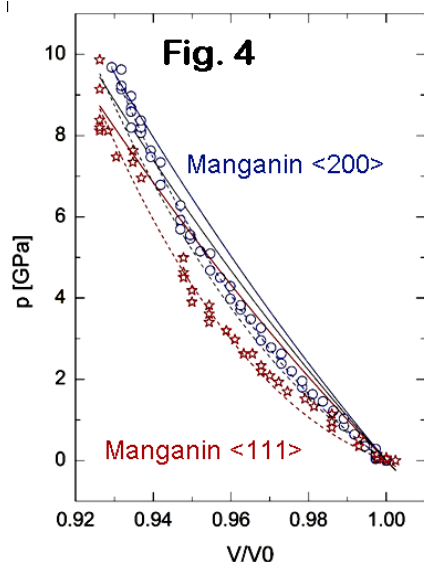
Two further high pressure runs with *w*-AlN single crystals associated with this measurement stay were unfortunately terminated by blowouts before the target pressure for *w*-AlN → *rs*-AlN conversion was reached. However, utilization of one X-ray transparent anvil in these experiments revealed that with omega slicing all reflections of the *w*-AlN single crystal which would be expected within the respective solid angle are in fact visible (Fig.3) [11], thus enabling single crystal diffraction in a multianvil press.



In a continuation of this project at ESRF observation of the changes in lattice site positions, buildup and release of anisotropic strain in the forward and backward transitions may become possible. Also, in order to study this phenomenon on the microscopic level, the material recovered from the successful conversion experiment is marked for examination via (high resolution) transmission electron microscopy by our partners at the Leibnitz Institute for Crystal Growth, Berlin.

## Preliminary investigation of the equation of state of manganin

The alloy Cu-Mn12-Ni4 (Manganin™ [12]) is being used in static [13] and shock wave [14] high pressure experiments for many decades, however to the best of our knowledge an isothermal high pressure equation of state has never been published. During our last stay at ID-06 we conducted preliminary X-ray measurements



<b>Manganin &lt;111&gt;</b>		
BM3:	$B_0 = 64.4 \text{ GPa}$	$B' = 24.7$
BM2:	$B_0 = 113.7 \text{ GPa}$	$B' = 4$
<b>Manganin &lt;200&gt;</b>		
BM3:	$B_0 = 34.4 \text{ GPa}$	$B' = 50.3$
BM2:	$B_0 = 97.8 \text{ GPa}$	$B' = 4$
<b>Manganin isotropic</b>		
BM3:	$B_0 = 60.7 \text{ GPa}$	$B' = 23.3$
BM2:	$B_0 = 105.7 \text{ GPa}$	$B' = 4$

on a coiled-up 0.2 mm manganin wire embedded in epoxy resin with CsBr pressure standard up to ~10 GPa. Simultaneous resistance measurements yield a piezoresistive coefficient of  $\Delta R/R = 0.023 \text{ GPa}^{-1}$ , nearly identical to that reported previously [12]. However, fitting the obtained diffraction data to second and third-order Birch Muraghan (BM) equations of state (Fig. 4) results in unphysically

high values for the first pressure derivatives  $B_0'$  and bulk moduli which would represent a significant deviation from the rule of mixtures:  $B_0(\text{Cu, Mn, Ni}) = 140, 120$  and  $180 \text{ GPa}$ , respectively.

- [1] Vollstädt, H.; Ito, E.; Akaishi, M.; Akimoto, S. & Fukunaga, O., High Pressure Synthesis of Rocksalt Type of AlN, *Proc. Japan Acad.*, **1990**, *66 B*, 7-9.
- [2] Zerr, A.; Miehe, G.; Serghiou, G.; Schwarz, M.; et al. Synthesis of cubic silicon nitride *Nature*, **1999**, *400*, 340-342.
- [3] Zerr, A.; Kempf, M.; Schwarz, M.; Kroke, E.; Göken, M., Riedel, R., Elastic Moduli and Hardness of Cubic Silicon Nitride, *J. Am. Ceram. Soc.*, **2002**, *85*, 86-90.
- [4] Schwarz, M.; Antlauf, M.; Schmerler, S.; Keller, K.; Schlothauer, T.; Kortus, J.; Heide, G. & Kroke, E. Formation and properties of rocksalt-type AlN and implications for high pressure phase relations in the system Si-Al-O-N, *High Pressure Research*, **2014**, *34*, 22-38.
- [5] Bayarjargal L, Winkler B. High (pressure, temperature) phase diagrams of ZnO and AlN from second harmonic generation measurements. *Appl Phys Lett*. **2012**, *100*, 021909.
- [6] Schmerler, S.; Kortus, J. Ab initio study of AlN: Anisotropic thermal expansion, phase diagram, and high-temperature rocksalt to wurtzite phase transition, *Phys. Rev. B*, **2014**, *89*, 064109.
- [7] Baldus, H.; Jansen, M., Novel high-performance ceramics - Amorphous inorganic networks from molecular precursors, *Angew. Chem. Int. Ed.*, **1997**, *36*, 329-343.
- [8] Hartmann, C.; Dittmar, A.; Wollweber, J., Bickermann, M., Bulk AlN growth by physical vapour transport, *Semiconductor Science and Technology*, **2014**, *29*, 084002.
- [9] Vollstädt, H.; Ito, E.; Akaishi, M.; Akimoto, S.; Fukunaga, O., High Pressure Synthesis of Rocksalt Type of AlN, *Proc. Japan Acad.*, **1990**, *66 B*, 7-9.
- [10] Sekine, T., Kobayashi, T., Phase Transitions in Ceramics under Shock Wave Compression *New Diamond and Frontier Carbon Technology*, **2003**, *13*, 153-160
- [11] W. Crichton, private e-mail correspondence. Fig. 3 shows the sum of all omega slices at all azimuth positions.
- [12] Fujioka, N.; Mishima, O.; Endo, S.; Kawai, N., Electrical Resistance of Manganin under High Static Pressures *Journal of Applied Physics*, **1978**, *49*, 4830-4832.
- [13] Keough, D. D.; Wong, J. Y., Variation of the Shock Piezoresistance Coefficient of Manganin as a Function of Deformation, *Journal of Applied Physics*, **1970**, *41*, 3508-3515.