

In situ SYNCHROTRON X-RAY DIFFRACTION STUDIES OF HP-HT SYNTHESIS OF SUPERHARD PHASES IN THE B-C-N SYSTEM

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The present paper briefly reviews results of our very recent studies of high-pressure high-temperature synthesis of superhard phases in the B-C-N system using powder X-ray diffraction with synchrotron radiation.

Materials Science under extreme conditions is one of the most important lines of research using the third-generation synchrotron radiation sources. The high resolution and improved sensitivity resulting from the use of high-intensity synchrotron-derived X-ray radiation from these sources are indispensable for *in situ* studies of phase formation and reaction kinetics of compounds of low-Z elements at high pressures and temperatures.

Here we report the results of *in situ* studies of synthesis of superhard phases in the B-C-N system that have recently been performed at the high-pressure beamline ID30.

SYNTHESIS OF NEW SUPERHARD PHASE, CUBIC BC₂N

Phase transitions of graphite-like BN-C solid solutions (g-BC_xN) were studied up to 32 GPa and 3000 K using a laser heated diamond anvil cell and angle-dispersive X-ray diffraction [1]. At room temperature an increase in pressure is accompanied by a pronounced decrease in the line intensities of the turbostratic g-BC₂N (Figure 1). Upon compression to 19.9 GPa, the intensity of the strongest 002 line decreases by a

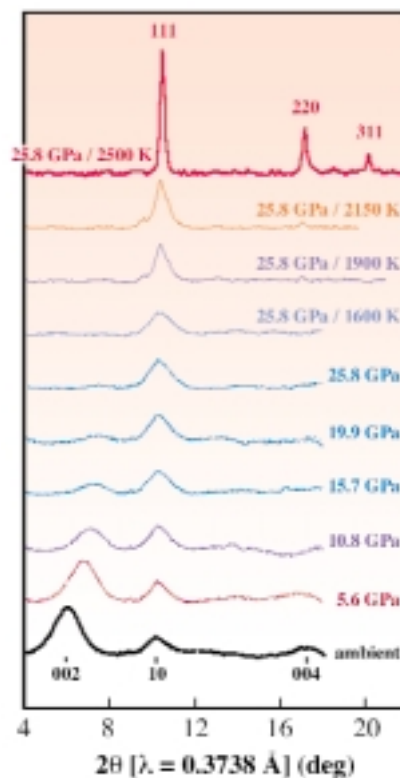
factor of 6, and at 25.8 GPa this line almost disappears. Also, with increasing pressure, a variation in the 10 asymmetric line of the turbostratic structure is observed. The intensity of scattering in this region increases, the profile of the line becomes increasingly symmetric and its peak shifts towards a value of 2.07 Å which is close to those observed for the 111 reflections of diamond-like phases. These effects point to the reconstruction of the graphite-like sp²-structure into the diamond-like sp³-structure, which starts at about 5 GPa and ends at about 25 GPa.

At 25.8 GPa, the heating of g-BC₂N up to 1600 K is not accompanied by any change in the diffraction patterns which exhibit only a broad line in the region of 111 reflections of diamond-like phases. At higher temperatures, the profile of this broad line changes to a rather complicated fine structure, and two new weak lines with d_{hkl} = 1.26 and 1.09 Å (at ambient temperature) also appear. Finally, above 2200 K a drastic change in the spectrum is observed (Figure 1, top pattern) which clearly points to the

formation of a new phase. The diffraction pattern of the quenched sample exhibits only 111, 220, and 311 lines of the cubic lattice, which indicates that the sample is single-phase.

Laser heating experiments at different pressures have shown that the formation of c-BC₂N is observed only at pressures

Fig. 1: Laser-heating sequence of diffraction patterns taken at several pressures and temperatures. Bottom and top patterns correspond to g-BC₂N and c-BC₂N, respectively.



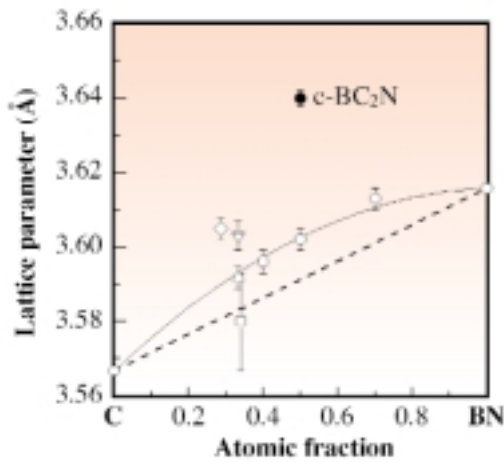


Fig. 2: Lattice parameters of *c*-BC₂N (solid circle) and “cubic BN-C solid solutions” reported by Kakudate *et al.* [3] (open down triangle), Knittle *et al.* [4] (open circles), Nakano [5] (open up triangle), Kagi *et al.* [6] (open square) and Komatsu *et al.* [7] (open diamond). The dashed line represents ideal mixing between *c*BN and diamond, while solid curve shows the deviation from ideality for the data reported by Knittle *et al.* [4].

above 18 GPa. At 14.5 GPa and temperatures above 2000 K *g*-BC₂N decomposes to form a mixture of cubic boron nitride (*c*BN) and diamond. On further decrease in pressure down to 11.0 GPa, thermal decomposition of *g*-BC₂N proceeds to form *c*BN and disordered graphite, as reported previously [2].

The lattice parameter of *c*-BC₂N at ambient conditions is $a = 3.642(2)$ Å, which is larger than those of both diamond and *c*BN. The large deviation of the lattice parameter of cubic BC₂N from the value expected from ideal mixing between diamond and *c*BN testifies that the synthesised phase differs from the so-called “diamond-*c*BN solid solutions” reported earlier [3-7] (Figure 2).

The bulk modulus of *c*-BC₂N is 282(15) GPa which is exceeded only by the bulk moduli of diamond and *c*BN [8,9]. The Vickers hardness of *c*-BC₂N is 76 GPa, which makes it the hardest known solid after diamond.

CBN CRYSTALLISATION FROM BN SOLUTIONS IN SUPERCRITICAL FLUIDS

In situ studies of the BN-N₂H₄ system at pressures to 5 GPa and temperatures to 1500 K using a Paris-Edinburgh press and X-ray diffraction (energy- and angle-dispersive) provided us the ability to investigate the local structure of boron nitride solutions in supercritical fluid, and BN crystallisation from these solutions on cooling.

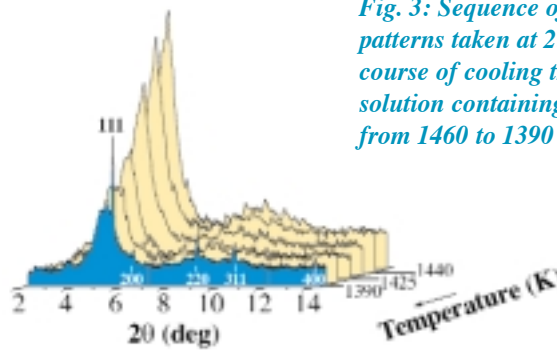


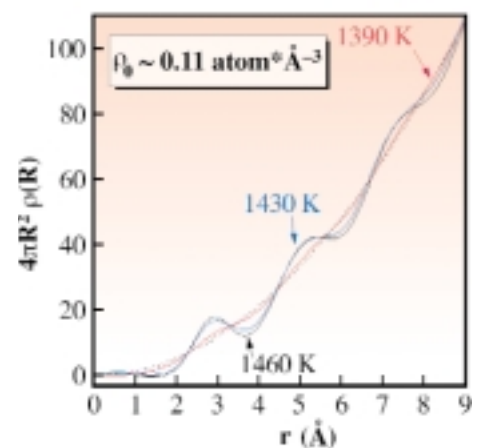
Fig. 3: Sequence of ADX diffraction patterns taken at 2.1 GPa in the course of cooling the supercritical solution containing 74.5 mol.% BN from 1460 to 1390 K.

At 4.1 GPa, cooling the solution containing 81 mol.% BN is accompanied by spontaneous crystallisation of cubic boron nitride. The emergence of *c*BN lines is accompanied by a change in the shape of the solution spectrum, in particular by the appearance of a broad halo with a maximum at $d_{hkl} = 1.1$ Å. A similar change in the shape of the solution spectrum was also observed at 4 GPa and 1350 K by cooling the solution containing 33 mol.% BN. In this case, however, no formation of any crystalline phase was recorded even on cooling the solution down to room temperature. This fact should be attributable to the formation of an unknown amorphous phase of the BN-N-H system (phase X). A subsequent heating up to 1600 K in both cases gave rise to a recovery of the characteristic shape of the solution spectrum due to dissolution of solid phase(s) which

is unambiguous evidence for the reversibility of the observed precipitation/dissolution processes.

Our findings show that spontaneous crystallisation of *c*BN is observed down to 2.1 GPa (Figure 3). This is the lowest pressure of *c*BN crystallisation ever reported before, though the process occurs without any catalyst. At 1.7 GPa, cooling of the solution containing 73 mol.% BN is accompanied by crystallisation of graphite-like hexagonal boron nitride (*h*BN) with a simultaneous formation of the phase X. This fact points to the predominant nucleation of metastable *h*BN in the region of *c*BN thermodynamical stability. The broad halo of phase X disappears upon quenching down to ambient conditions. This fact allows the suggestion that phase X is metastable at low pressures.

Fig. 4: The radial distribution functions for the supercritical solution containing 74.5 mol.% BN at 2.1 GPa. Dash line is the $4\pi r^2 \rho_0$ curve. The average atomic density ρ_0 was estimated from the linear fit to the reduced RDF $G(r)$ in the range of $r = 0-1$ Å.





The radial distribution function $4\pi r^2\rho(r)$ (RDF) was used to characterise BN solutions in supercritical fluid at different pressures and temperatures. Our findings have shown that above 1450 K between 2.1 and 4.8 GPa in the concentration range from 74.5 to 82.5 mol.% BN, interference function $i(s)$ for BN solutions exhibits a sharp first maximum ($s = 2.84 \text{ \AA}^{-1}$) with a small shoulder on its high- s side, a second maximum at 5.1 \AA^{-1} and a third maximum at about 7 \AA^{-1} .

RDFs for the solution containing 74.5 mol.% BN at 2.1 GPa and different temperatures are presented in Figure 4. In cooling the solution, the intensities of the maxima in the RDFs decrease, and at 1390 K the maxima nearly disappear while the most prominent 111 line of cBN becomes visible in the corresponding X-ray pattern (Figure 3), *i.e.* this temperature can be considered as the temperature of cBN liquidus at the above pressure and concentration of the solution. Thus, the cBN crystallisation is accompanied (or even preceded) by disappearance of short-range order in the solution.

Similar changes of RDFs of solutions close to BN liquidus are observed over the whole ranges of concentrations and pressures being studied. Therefore, it can be suggested that crystallisation of boron nitride is preceded by decomposition of the BN associated solutions in the supercritical fluid of the N-H system.

KINETICS OF DIAMOND CRYSTALLISATION FROM METAL-CARBON MELTS

In situ studies of diamond crystallisation from the Fe-Ni-C melt at pressures up to 6 GPa and temperatures up to 1700 K were performed using a Paris-Edinburgh press and energy-dispersive X-ray diffraction. At 5.2 GPa and the heating rate of 25 K/min, spontaneous crystallisation of diamond starts at 1510 K immediately after the halo of the liquid phase appears, and is fully completed at 1605 K (Figure 5). We note that despite the presence of a liquid in the system over the whole temperature range of diamond crystallisation, all diffraction patterns exhibit lines of the solid phase that can be ascribed to the fcc Fe-Ni-C solid solution (γ -phase).

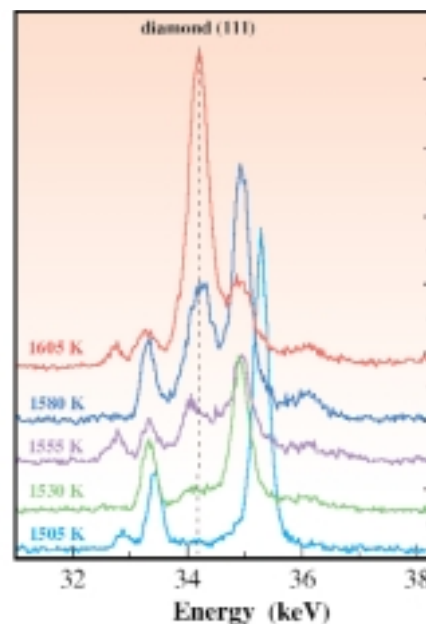
Fig. 5: Diffraction patterns of the Fe-Ni-C system taken at 5.2 GPa in the course of a linear heating at a rate of 25 K/min.

This fact indicates that in accordance with the p,T-phase diagram of the Fe-Ni-C system [10], under experimental conditions the $L = C + \gamma$ monovariant eutectic reaction takes place. In this case, the melt is in equilibrium with both diamond and γ -phase.

Diamond crystallisation in the system under study is very fast and proceeds in a narrow temperature range that plagues essentially isothermal kinetics studies. Because of this, the present work describes a non-isothermal approach. As all the diffraction patterns exhibited diffraction lines of graphite, we state that diamond crystallisation from the Fe-Ni-C melt occurs at the constant carbon supersaturation with respect to diamond, which is ensured by dissolution of the initial graphite. Based on this, the degrees of the graphite-to-diamond conversion proceeding via melt has been calculated by normalising integral intensities of the (111) reflection of diamond at various temperatures to the appropriate value at 1605 K ($\alpha = 1$).

From the non-isothermal kinetic data it follows that at 5.2 GPa diamond crystallisation is controlled by carbon diffusion in the melt to the surface of a growing crystal. Kinetic data might be best fit by the model that assumes a constant nucleation rate and three-dimensional growth of the resulting nuclei. From the temperature dependence of the rate constant in the 1505-1605 K range, the activation energy of diamond crystallisation from the Fe-Ni-C melt at 5.2 GPa was calculated to be 148(64) kJ/mole.

These studies firmly establish synchrotron radiation experiments at the third-generation sources as a powerful tool for studies of materials synthesis in



the B-C-N system at high pressures and temperatures on a real timescale. ■

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