ESRF	**Experiment title:** High-Pressure High-Temperature Synthesis of Novel Utrahard Phases in the B-C-N System	**Experiment number**: HS 918
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Shifts: 15	**Local contact(s)**: Daniel HAUSERMANN	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Vladimir SOLOZHENKO *   Institute for Superhard Materials, Kiev, Ukraine

Denis ANDRAULT *   Laboratoire des Géomatériaux, Institut de Physique du Globe, Paris, France

Guillaume FIQUET *   Laboratoire de Mineralogie et Cristallographie, Université Paris-VI, Paris, France

Mohamed MEZOUR *   ESRF, Grenoble, France

Report:

The data on attempted synthesis of B-C-N dense phases reported by different authors are rather contradictory and up to date there is no unambiguous answer to the question of whether the synthesis products are diamond-like solid solutions between carbon and boron nitride, or just mechanical mixtures of highly dispersed diamond and cBN. It should be especially noted that all previous results on the subject have been obtained from quench experiments, without any *in situ* control of the process of phase formation.

In the present work for synthesis of cubic BC_2N, novel ternary phase of the B-C-N system, a laser-heated diamond anvil cell has been applied. Angle-dispersive X-ray diffraction patterns were recorded using on-line image-plate FastScan detector at the ID30 beamline. As the starting material, we have used turbostratic graphite-like BC_2N (g-BC_2N) synthesized by simultaneous nitridation of boric acid and carbonization of saccharose in molten urea.

An increase in pressure at room temperature is accompanied by a pronounced decrease in the line intensities of g-BC_2N (Figure). 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 more and more symmetric and its peak shifts towards a value of 2.07 Å close to those observed for the *111* reflections of diamond-like phases. These effects point to the reconstruction of the graphite-like sp^2-structure into the diamond-like sp^3-structure, which starts at about 5 GPa and ends at about 25 GPa.

At 25.8 GPa the heating of g-BC_2N up to 1600 K is not accompanied by any variation in diffraction patterns which exhibit only a broad line in the region of *111* reflections of diamond-like phases (Figure). At higher temperatures, the profile of this broad line somewhat changes to show 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, 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. From this one can assume that the composition of the high-pressure cubic phase is the same as that of the starting graphite-like material, namely, BC_2N.

The lattice parameter of the as-synthesized cubic phase at ambient conditions is a = 3.642±0.002 Å, which is larger than those of both diamond (3.5667 Å) and cBN (3.6158 Å). So large a deviation of the lattice parameter of cubic BC_2N (c-BC_2N) from the value that could be expected from ideal mixing (Vegard's law) between diamond and cBN

(3.583 Å) testifies that the new phase has nothing to do with all the diamond-cBN solid solutions reported earlier.[1-3] Analysis of these papers has shown that due to insufficient resolution of used X-ray detection systems the reported products can be interpreted equally likely as mechanical mixtures of dispersed (Bragg scattering area less then 50 Å) diamond and cBN. The positive deviations of the lattice parameter from Vegard's law (0.25-0.68%) observed in [1-3] are evidently caused by a high concentration of structural defects just as it has been reported for ultradispersed powders of cubic BN [4] and diamond.[5] In our case, it is clear that a ternary phase was synthesized, as ID30 provides a sufficient resolution to track the occurrence of a mixture of cBN and diamond.

For the c-BC_2N phase, we observe presence of *111*, *220* and *311* Bragg lines, that corresponds to the Fd-3m space group. Apparent lack of the *200* line is an important feature, as it determines a space group between Fd-3m and F-43m, found for diamond and cBN, respectively. Indeed, for a B-C-N diamond-like phase, the most sensitive to the atom distribution are the lines, for which $h + k + l = 2n$, where n is the odd number (the *200* line is the strongest of them). The intensities of these lines are defined by the $F = 4 (f_1 - f_2)$ structure amplitude, where f_1 and f_2 are the atomic scattering factors of two *fcc* sublattices of the zinc-blende lattice. The absence of the *200* line for c-BC_2N is indicative of the fact that $\langle f_1 \rangle = \langle f_2 \rangle$, which is possible in the case that B, C and N atoms are statistically uniformly distributed over both the sublattices. Another possibility is that BN pairs are randomly distributed over one *fcc* sublattice, with C-C pairs on the other sites. Our experimental results, however, do not help to distinguish between these two cases.

Figure Laser-heating sequence of diffraction patterns taken at several pressures and temperatures. Bottom and top patterns correspond to g-BC_2N and c-BC_2N, respectively.

Laser heating experiments at different pressures have shown that the formation of c-BC_2N is observed only at pressures above 18 GPa. At 14.5 GPa and temperatures above 2000 K g-BC_2N decomposes to form a mixture of cBN and diamond. On further decrease in pressure down to 11.0 GPa, thermal decomposition of g-BC_2N proceeds to form cBN and disordered graphite in much the same way as reported earlier by Solozhenko.[6]

For compressibility measurements, a sample of cubic BC_2N synthesized at 25.8 GPa and 3000 K was compressed at room temperature in the DAC using 4:1 methanol-ethanol pressure medium to maintain quasi-hydrostatic conditions. High-pressure X-ray patterns were collected to 30 GPa. The experimental pressure-volume data were fitted to the two-parameter Birch equation of state. The parameters of the fit are $B_0 = 282\pm15$ GPa and $B_0' = 4.3\pm1.1$, with cell volume $V_0 = 48.49\pm0.08$ Å^3. The bulk modulus of cubic BC_2N is smaller than that expected for ideal mixing between diamond and cBN (420 GPa). However, c-BC_2N still has one of the largest bulk moduli known for any solid.

References

1. Knittle, E. *et al. Phys. Rev. B* **51**, 12149-12156 (1995).

2. Nakano, S. in *Proc. 3rd NIRIM Int. Symp. on Advanced Materials*. 287-292 (NIRIM, Tsukuba, Japan, 1996).

3. Kagi, H. *et al.* in *Proc. XV AIRAPT Int. Conf.* 258-260 (World Scientific, Singapore, 1996).

4. Borimchuk, N.I. *et al. Doklady AN SSSR*, **306**, 1381-1383 (1989).

5. Gamarnik, M.J. *Phys. Stat. Sol.* **b161**, 457-462 (1990).

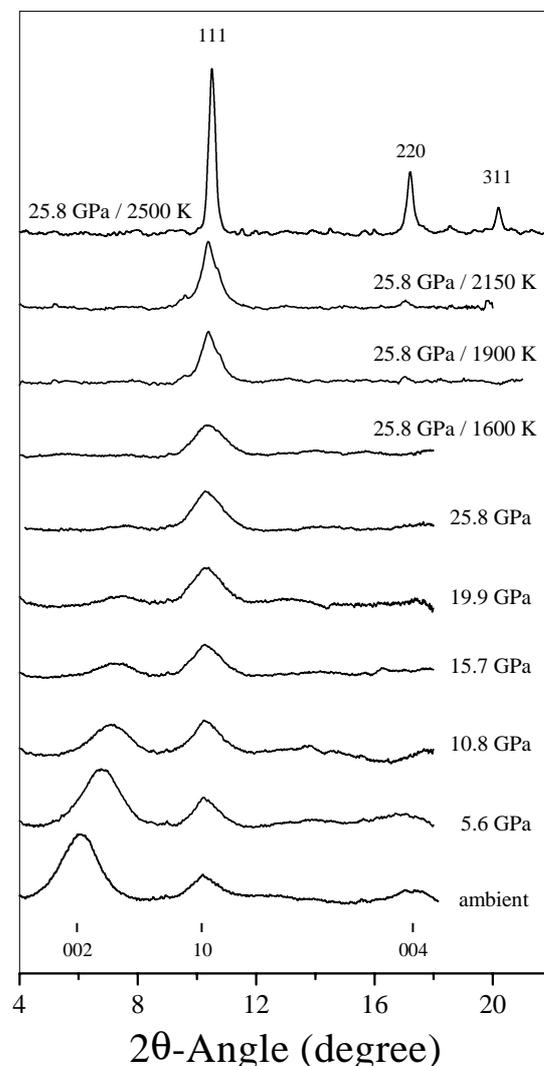6. Solozhenko, V.L. *Eur. J. Solid State Inorg. Chem.* **34**, 797-807 (1997).