ESRF	**Experiment title:** **Crystallization of boron nitride from its solutions in supercritical hydrazine at high temperature and pressure. In situ studies**	**Experiment number**: HS 1084
Beamline: ID30	**Date of experiment**: from: 04.10.1999 to: 09.10.1999	**Date of report**: 25.08.2000
Shifts: 12	**Local contact(s)**: Mohamed MEZOUAR	*Received at ESRF:*

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Report:

Pressure evolution of phase diagram of the BN - N_2H_4 system and local structure of BN solutions in supercritical hydrazine have been studied *in situ* to 5 GPa and 1600 K using angle-dispersive X-ray diffraction with synchrotron radiation. The experiments have been done using large-volume Paris-Edinburgh press and FastScan detector at beamline ID30. The results obtained are briefly described below.

Phase diagram of the BN-N_2H_4 system – evolution with pressure

Our data on cBN crystallization in the 2.1-4.8 GPa pressure range from solutions containing from 74.5 to 82.5 mole% BN have shown that a pressure decrease results in the shift of the cBN liquidus to the low-concentration region (~2.7 mole% per 1 GPa at 1400 K). At the pressure of about 2.5 GPa, this shift inevitably leads to the change in the type of the phase ***X***[1] melting from the congruent to the incongruent one, and results in expansion of the concentration field of cBN crystallization. In all the cases, the emergence of cBN lines is accompanied by appearance of broad halo of amorphous phase ***X*** ($d_{hkl} \approx 1.1$ Å) in much the same way as we observed earlier at 4.1 GPa [1,2]. Thus, pressure decrease causes the type of the L ⇆ ***X*** + cBN reaction to change from the eutectic to the peritectic one, and the temperature of the corresponding solidus to decrease as is shown in Fig. 1.

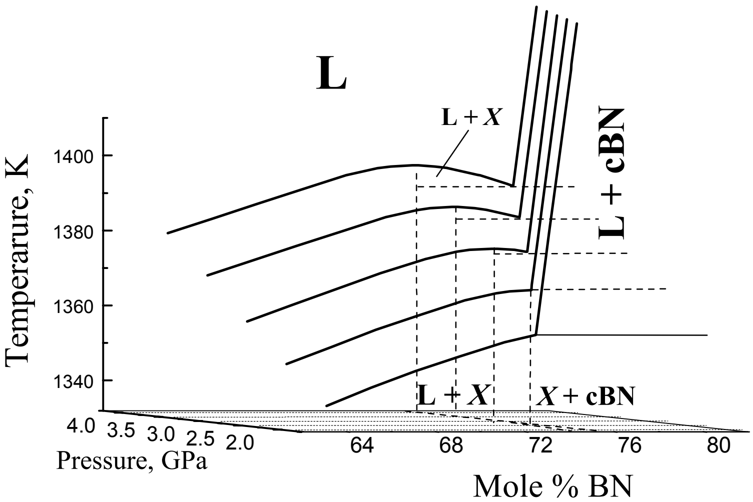

Figure 1

[1] amorphous high-pressure phase with stoichiometry of $3BN{\cdot}N_2H_4$ revealed by us in the course of our previous experiment (HS-494)

At 1.5 GPa in cooling of the solution containing 71 mole% BN, no precipitation of crystalline phase(s) is observed but only broad halo of phase ***X*** appears. This halo disappears, however, upon quenching down to ambient conditions. This fact allows the suggestion that phase ***X*** is metastable at low pressures. To evaluate the temperature of the phase ***X*** liquidus under the above p,***c*** –conditions, we have calculated RDFs of the solution at different temperatures (for more details, see below). The results obtained clearly show that the short-range order in the solution disappears at about 1340 K which evidently can be considered as the liquidus temperature.

Threshold pressure of cBN crystallization in the BN-N_2H_4 system

Previously we have shown that at 1.7 GPa the L ⇆ ***X*** + hBN metastable eutectic reaction is realized that results in crystallization of graphite-like hexagonal boron nitride and a simultaneous formation of the phase ***X*** [3,4]. Our present findings show that cBN spontaneous crystallization is observed down to 2.1 GPa. Thus, the threshold pressure of crystallization of cubic boron nitride from BN solutions in supercritical hydrazine can be estimated as 1.9±0.2 GPa. This is the lowest pressure of cBN crystallization ever reported before, though the process occurs without any catalyst.

Radial distribution functions for BN solutions in hydrazine

The radial distribution function $4\pi r^2\rho(r)$ (RDF) was used to characterize BN solutions in hydrazine at different pressures and temperatures. The experimental diffraction data after corrections for background scattering, polarization and absorption were scaled into electronic units by the so-called "high-angle" method [3], and the interference function *i(s)* was calculated according to Pings & Waser [4]. The reduced RDF *G(r)* was calculated as a Fourier transform of the *i(s)* while the average atomic density ρ_0 was estimated from the linear fit to the *G(r)* in the range of r = 0-1 Å. 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 mole% BN, *i(s)* curves for BN solutions exhibit a sharp first maximum (s = 2.84 Å^{-1}) with a small shoulder on its high-s side, second maximum at 5.1 Å^{-1} and low third maximum at about 7 Å^{-1}.

RDFs for the solution containing 74.5 mol. % BN at 2.1 GPa and different temperatures are presented in Fig. 2.[2] In cooling the solution, the intensities of the maxima in the RDFs decreases, and at 1390 K all the maxima almost disappear while the strongest 111 line of cBN becomes visible in the corresponding X-ray pattern, 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 crystallization is accompanied (or even preceded) by disappearance of short-range order in the solution. Similar changes of RDFs of solutions close to cBN liquidus (or liquidus of phase ***X***) are observed over the whole ranges of concentrations and pressures being studied. Therefore, it can be suggested that precipitation of a solid phase (cBN, hBN or phase ***X*** depending on pressure and solution concentration) is preceded by decomposition of the BN-N_2H_4 associated solution.

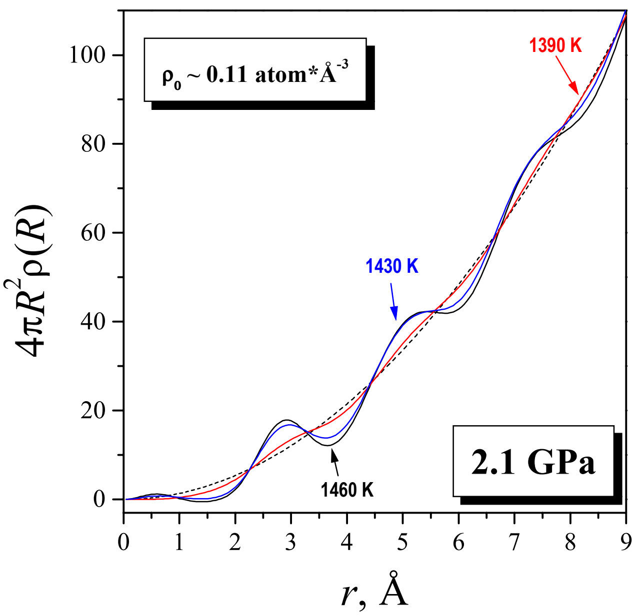

Figure 2

References

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2. Y. Le Godec, V.L. Solozhenko, M. Mezouar, J.-M. Besson, and G. Syfosse, in: *"Science and Technology of High Pressure"*. Universities Press, Hyderabad, India, 2000, vol. 2, pp. 1031-1034
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[2] dash line in Fig. 2 is the $4\pi r^2\rho_0$ curve