



	<b>Experiment title:</b> New Type of a High-Pressure Transformation of One-Dimensional Disordered Layered Structures: <i>In Situ</i> Studies	<b>Experiment number:</b> HS-1693
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<b>Shifts:</b> 9	<b>Local contact(s):</b> Tristan LE BIHAN	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b>  Vladimir L. SOLOZHENKO *      ISM, Kiev (Ukraine) & LPMTM-CNRS, Villetaneuse (France) Denis ANDRAULT *                Laboratoire des Géomatériaux, IPGP, Paris (France) Mohamed MEZOUAR *            ESRF, Grenoble (France) Oleksandr O. KURAKEVYCH      LPMTM-CNRS, Villetaneuse (France)		

## Report:

Room-temperature structure changes in the turbostratic (one-dimensionally disordered) BN–C solid solutions have been *in situ* studied up to 30 GPa using angle-dispersive X-ray diffraction with synchrotron radiation. The experiments have been done using diamond anvil cell and on-line image-plate FastScan detector at beamline ID30.

Pressure increase at room temperature is accompanied by a pronounced decrease in the intensity of the *00l* lines of the initial graphite-like BN–C solid solutions. Upon compression to 20 GPa, the intensity of the strongest *002* line of graphite-like BC<sub>2</sub>N (g-BC<sub>2</sub>N) decreases by a factor of 6, and at 25 GPa this line almost disappears. At the same time, a change of the diffraction pattern in the region of the *10* asymmetrical line of the turbostratic structure is observed. The intensity of scattering in this region increases, the profile of the line becomes increasingly symmetrical and its maximum shifts towards a value of 2.07 Å, which is close to those observed for the *111* reflections of diamond and cubic boron nitride. The structure reconstruction proceeds at room temperature and completely terminates at pressures of the order of 25 GPa. The similar evolution of diffraction patterns under pressure has been observed for other turbostratic BN–C phases.

Another set of *in-situ* experiments have shown that the changes in diffraction patterns of turbostratic BN–C solid solutions are fully reversible up to pressures of the order of 30 GPa. The fact unambiguously indicates that the total disappearance of the *002* lines under pressure is caused not by the destruction of the layered structure. Thus, one should speak about the reversible phase transformation of turbostratic g-BC<sub>2</sub>N into a high-pressure phase, which proceeds over a wide pressure range and terminates at 25–30 GPa. However, up to date room-temperature pressure-induced phase transformations have been observed only for highly ordered layered structures of carbon and boron nitride while in the case of turbostratic BN–C solid solutions, the transformation cannot be implemented by any of known crystallographic mechanisms.

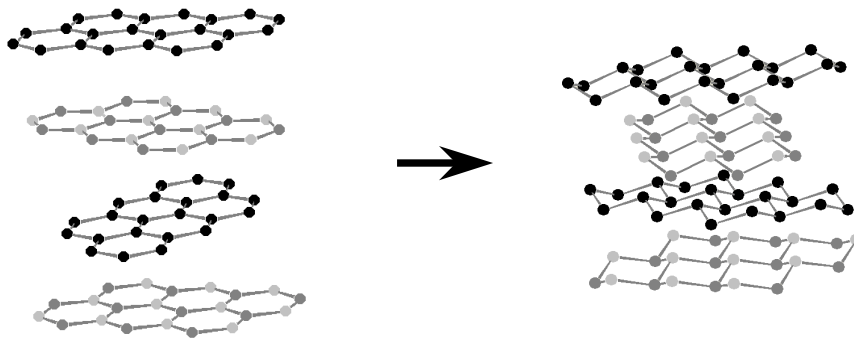
With the aim of explaining the experimentally observed evolution of diffraction patterns, we have performed the Rietveld analysis of the experimental patterns and have simulated diffraction patterns of layered finite-size B–C–N clusters with lattice defects of various types.

The Rietveld refinement of the graphite-like structure reveals that the experimentally observed relation between intensities  $J_{002} \geq J_{10}$  in diffraction patterns of turbostratic g-BC<sub>2</sub>N up to 10 GPa can be satisfactorily

explained under the assumption that the initial structure is disordered with respect to interlayer spacings. A similar type of disordering has been previously observed for partially graphitized carbon. In our case, it is likely that in the course of the g-BC<sub>2</sub>N compression, a non-uniform change in the relative orientation of the layers takes place, which is accompanied by approaching of layers to each other. This gives rise to a layered structure with various interlayer spacings. The relation  $J_{002} < J_{10}$ , which is experimentally observed at pressures above 10 GPa, can be explained only on the assumption that the layers are buckled. It should be noted that in the framework of the Rietveld formalism an increase in  $J_{10}$  stems from the appearance of additional intense lines with  $l = 0$  near the  $10$  line of the initial turbostratic phase, which points to a decrease in the symmetry of the pseudo unit cell under pressure. However, the  $002$  line still remains intense. Thus, the assumption of the “random” buckling is not sufficient for the explanation of the total disappearance of the  $002$  line in the patterns of turbostratic g-BC<sub>2</sub>N at high pressures.

The results of the simulation of diffraction patterns have shown that for a compressed turbostratic structure, the change-over from flat to buckled layers is accompanied by a decrease in the  $002$  line intensity and a rise in the  $10$  line intensity. However, with the ordered buckling, a total disappearance of the  $002$  line has not been observed as well as in case of “random” buckling.

To describe the experimental diffraction patterns at pressures above 25 GPa, which are characterized by intensive band in the region of  $111$  line of diamond-like phases and by the absence of bands in the region of other lines ( $220$ ,  $311$ ), we have simulated patterns of layered structures with interlayer spacings of 2.1 Å. It has been found that the disturbance of the ordering along  $c$ -axis of the properly buckled layers of a diamond-like structure tends to increase the intensity of the  $10$  line of the resulting disordered layered structure in comparison with other lines at higher angles.



For ordered graphite-like phases, the buckling of layers under pressure is a necessary stage of the martensitic transformation at room temperature. In a similar manner the buckling of layers should proceed in the course of the compression of turbostratic structures. Under pressure, the layers approach each other and the interlayer interaction intensifies (the role of the repulsion forces increases), with the result that the atoms tend to occupy the most preferable positions in terms of energy by displacement relative to each other, and finally at some sufficiently high pressure, the buckling occurs. Then the abrupt approaching of buckled layers gives rise to the structure shown in Figure, to which there correspond patterns taken at pressures above 20 GPa. This may be caused by the achievement of some critical value of buckling, which allows the layers to approach each other, or by change in mutual orientation of layers because of the rotation and displacement. The change of mutual orientation occurs because of increasing the role of repulsive forces between the layers and leads to other type of one-dimensional disorder than in the original turbostratic phase. As the diffraction patterns corresponding to the initial turbostratic phase completely recover their original shape as soon as the pressure is released, one may conclude that the layers remain in the region of the elastic forces over the whole range of pressures under study, and the formation of covalent bonds between layers does not occur.

Thus, in the case of turbostratic BN–C solid solutions, we deal with a reversible diffusionless transformation of the initial turbostratic phase into the disordered high-pressure phase consisting of close-packed buckled layers with a diamond-like structure (Figure).