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In situ observation of the crystallization of amorphous boron nitride at high pressures and temperatures

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Abstract

The formation processes of cubic boron nitride (cBN) from disordered turbostratic BN are observed in situ under high pressures and temperatures. It is found that cBN grows directly from an amorphous matrix and not from different BN polymorphs as previously proposed. Only during quench and pressure release do new structural phases occur.

Keywords: Boron nitride; Polymorphic phase transition; High pressure; Amorphous state

1. Introduction

Cubic boron nitride, cBN, a valuable material with interesting properties and several technological applications, is usually produced in a high pressure–high temperature process. Mostly, the hexagonal modification, hBN, is used as the starting material. The introduction of various catalyst/solvent materials allows for a new way of reducing the pressure and temperature required for cBN formation but, on the other hand, includes the disadvantage of introducing contamination of the final product with traces of the catalysts used. For very high quality BN materials a direct transition is preferable, which up until now has required rather high pressures and temperatures. But a better knowledge of the particular processes during the phase transition could contribute to an optimization of the necessary conditions, such as structure of the starting material, pressure, and temperature. One possibility is the use of an initial BN material with high defect concentration and poor crystallinity as e.g. turbostratic (tBN) or amorphous (aBN) material [1–5].

However, the mechanism of the transition reaction is still under discussion. One key question is how sp^2-bonded hBN transforms into sp^3-bonded cBN—whether this is a direct process that proceeds via an amorphous phase or if there exists at least one intermediate structure between hBN and cBN. The crucial role of diffusion processes during nucleation and growth is another point of interest. Recent HRTEM observations of the synthesis products suggest the importance of a disordered stage so that cBN would nucleate from an amorphous matrix [3,4,6]. Nevertheless, other authors find hints of the existence of intermediate stages with a distinct crystalline structure like monoclinic 'compressed hBN' [7]. Several authors also found the wurtzitic form, wBN, in their recovered samples and thus argued that hBN first transforms into wBN under pressure and temperature by the so-called 'puckering' mechanism [8], followed by the transformation into cBN by a dislocation mechanism [1,2]. Most of these various proposed mechanisms are based on structural similarities or relations between

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the different crystalline structures. However, other structures that are possibly metastable and thus only occur in a specific pressure–temperature range cannot be excluded [4]. As of today this may only be discussed theoretically. Most experimental results described so far [1–4,6,7] suffer from one clear disadvantage. The transition reaction was not observed in situ since all experiments were carried out in a closed high pressure chamber. Only the final products after quench and pressure release were analyzed and only these results can be taken into account to model the transition mechanism. But the final process of pressure and temperature release may have an important influence. If the products can only be analyzed after the experiment, transient stages and metastable phases may occur or vanish or other phases could undergo phase transitions thus leading to incorrect conclusions about the appropriate mechanism. These disadvantages are avoided if the observations are carried out under in situ conditions as described in the following.

2. Experiments

To obtain some more information about basic physical mechanisms, experiments on the cBN formation in disordered turbostratic boron nitride were carried out. The high pressure–high temperature experiments were performed using the cubic multi-anvil high pressure apparatus MAX-80 at HASYLAB, Hamburg. Thus the observations could be done in situ using synchrotron radiation for energy dispersive X-ray diffraction. The description of the applied setup may be found elsewhere [9]. After the isothermal pressure application the temperature was increased stepwise up to the region between 1000 °C and 1700 °C. The conditions were kept constant for several minutes to observe the kinetics of the processes by subsequently taking X-ray diffractograms at constant time intervals. Details of the evaluation procedure are also described in Ref. [9].

3. Results and discussion

Fig. 1 shows energy dispersive XRD patterns at 8 GPa, at 1000 °C and 1300 °C. Turbostratic BN shows rather poor crystallinity as expressed by the low intensity and rather large width of the diffraction lines. Here, only the (0 0 2) reflex is clearly visible (superimposed with the same reflex from the graphite heater). At that pressure the temperature leads only to a small fraction of recrystallized hBN. At about 1300 °C a clear cBN formation begins. All other reflections vanished, especially the (10×) lines of hBN and a broad and intense amorphous background occurs around the cBN (1 1 1) reflex. No formation of any other intermediate BN structure is observed. The disordered tBN is nearly completely amorphous. That leads to the conclusion that cBN forms directly from an amorphous matrix. Increasing temperature leads to growing cBN content. The amorphous background decreases slightly.

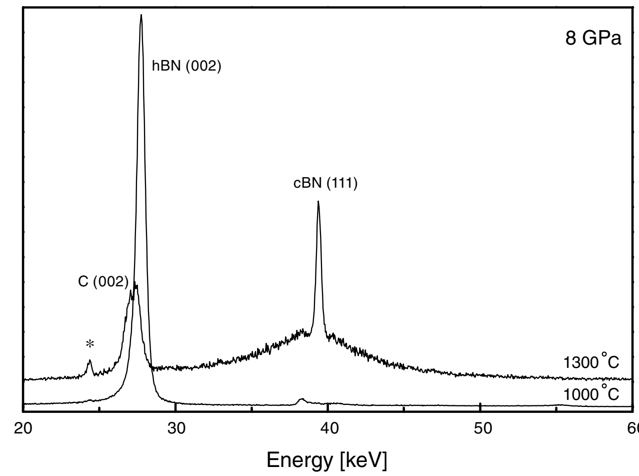

Fig. 1. XRD patterns for the BN phase transition. The cBN formation at 8 GPa proceeds directly from the amorphous matrix. The asterisk denotes a fluorescence from the detector.

After a quench at high pressure a new and yet unknown structure forms. The background decreases. New lines are observed in the diffractogram besides those of cBN, hBN and the graphite heater as Fig. 2 demonstrates in comparison to Fig. 1. This indicates that a new phase formed from the remaining amorphous BN material during temperature release after the transformation to cBN was nearly completed, and not prior to it. Further restructuring with slight modifications of the diffractogram occurs during full pressure release. Investigations of the recovered sample by powder X-ray methods result in the explicit identification of cBN and hBN and another crystalline phase. The formation

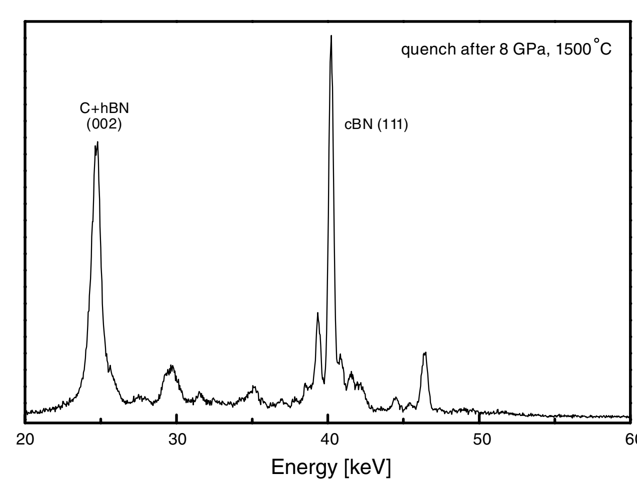

Fig. 2. Formation of a new BN phase during the quench and pressure release.