

Is there a new form of boron nitride with extreme hardness?

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Abstract

In the course of an investigation of boron nitride, its phase diagram and its synthesis at high pressure and high temperature some particles of BN of extreme hardness were extracted. Tests for hardness showed that the samples were actually harder than diamond. In ensuing checks the X-ray and electron diffraction patterns revealed that the material possesses amorphous structure, i.e. no diffraction lines were observed. An attempt is made here to understand the structural nature of such a material which can explain the findings and to predict the likely hardness for such structures. We have defined hardness as the decrease in total energy as deformations of representative clusters of atoms are simulated. Calculations have been tested previously for diamond and cubic boron nitride and now have been applied to calculate the expected hardness of the present models. We find that a promising generative model is a cage system consisting of truncated boron–nitrogen octahedrons connected to each other in a random arrangement over the four- and six-membered rings, thus leading to amorphous diffraction patterns. The model manifested hardness which surpassed both that of cBN and of diamond. It appears moreover, that the cages can be stiffened even further by the incorporation of foreign atoms in the model. The inclusion of calcium as such a foreign atom was tested and this is predicted to increase the hardness. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the binary boron-nitride system four crystalline polymorphs are known as well as some amorphous modifications. Cubic boron nitride, cBN, is the most important form and is the second hardest material after diamond. It does not occur in nature. The compound crystallizes with a zinc blende structure which closely resembles that of diamond, each atom being tetragonally linked to four neighboring boron or nitrogen atoms by strong covalent bonds. Charge accumulates strongly between the atoms due to the strong interatomic overlap of s and p orbitals (Fig. 1) [1]. Very accurate and detailed study of charge deformation den-

sities from X-ray diffraction data [1] show that, in cBN, a formal charge transfer of 0.46 electrons occurs from boron towards nitrogen as expected from their respective electronegativities. In concurrence with this result, Perkins et al. [2] derived from solid state calculations with molecular wave functions, the value of 0.36 electrons transferred from boron to nitrogen. The large charge accumulation between the atoms is responsible for the extreme hardness in both diamond and cBN, and it also gives a reasonable explanation for the somewhat lower hardness of cBN in comparison with diamond. Cubic BN is synthesized similarly to diamond from the hexagonal polymorph, hBN, by applying high pressure in the range of approximately 60 kbar at a temperature near 1500°C. As in the diamond synthesis ‘catalysts’ are used here: in boron nitride these are generally Mg compounds although sometimes Li compounds have been used. In this study Mg and/or Li

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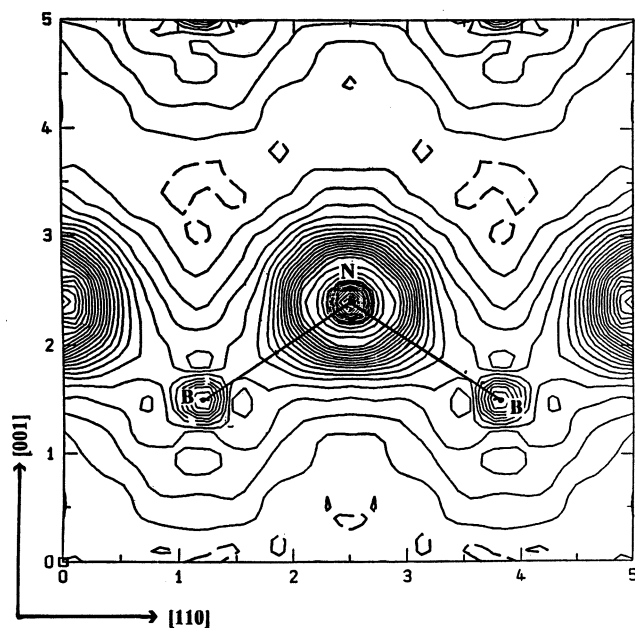


Fig. 1. Deformation electron density between boron and nitrogen in cubic BN extracted from X-ray diffraction data by multipole refinement.

compounds were used. The graphite heater was separated from the reaction chamber by a thin pyrophyllite tube, thus no carbon atoms from the heater could penetrate to the boron nitride.

The hexagonal polymorph, hBN, is routinely used as starting material for the high pressure–high temperature synthesis of cBN. Hexagonal BN is generally referred to as being ‘graphite-like’, but there is a significant difference in the structure between hBN and graphite, i.e. the arrangement is AA’AA’ in hBN but ABAB in graphite. The two forms above are commonly found in published phase diagrams of boron nitride.

Two further crystalline polymorphs, a *rhombohedral* form, rBN, and a *wurtzitic* one, wBN, are known. Both closely resemble the hexagonal form and are only of academic interest. There is at least one amorphous form of boron nitride, referred to as aBN, which was used, for example, in our experiments to ameliorate the conditions for forming cBN [3]. There is another so-called *turbostratic* form, which is just a highly disordered hexagonal arrangement, or, of course, a highly ordered amorphous BN.

The phase diagram of boron nitride was first published by Wentorf and co-workers in several publications [4–7], with contradicting results. We established the phase diagram in recent years in a number of experiments using in situ high pressure/high temperature X-ray diffraction with synchrotron radiation [8–10]. We also conducted extensive studies on the synthesis of cBN, and, in the course of these investigations we discovered a form of boron nitride of extreme hardness

not previously known. We do not yet know the chemical composition of this material but we assume BN with a 1:1 ratio.

X-Ray and electron diffraction afforded no diffraction lines, but a broad ring in the forward region as is common with amorphous compounds. This new form turned out to be of extreme hardness, possibly even harder than diamond. The material was named aBN2 [11]. Very little material was available when the investigation was eventually terminated. An important issue is to secure the hardness and several tests were performed.

The first indication came when we tried to polish the insert from the high pressure runs by grinding with diamond wheels. We then manually extracted splinters, approximately 100 μm in size, for further examinations by X-ray and electron diffraction indicating amorphous, or at least nano-crystalline character. The first indication of a new superhard material came when we could scratch the faces on diamond crystals. Next we conducted mechanical hardness tests by diamond indentation, which were performed outside our laboratory. They gave the expected indentation in cBN crystals, used as reference material, but showed aBN2 to be harder than diamond. Further mechanical experiments were conducted by fabricating drilling tools, which were used to drill holes into sintered corundum, with aBN2 and parallel also with a diamond drill. These experiments showed convincingly aBN2 being harder than diamond: After 30 s we reached a depth of 6 mm with aBN2 compared to 2.2 mm with the diamond drill [11].

The finding of extreme hardness was surprising for an amorphous material taking the example of carbo-nado. It predicates, first of all, a need to understand the geometrical ‘structure’ of such a compound and, furthermore, to find a reason how an ‘amorphous’ compound such as this can be harder than diamond. The problem has been approached here by theoretical methods and we have developed models for the compound which take into account, and could possibly represent, its amorphous nature. Using this model we have attempted to calculate its hardness in comparison to diamond and cBN and to illuminate some of the structural possibilities which emerge.

2. Hardness on a microscopic scale

Hardness is difficult to define theoretically on a microscopic scale in a way which correlates with experimental data. Hardness in mechanical terms is measured by the indentation made into a material by a diamond spike under a well-defined force. If we take for example the Vickers hardness used in engineering this works well for metals because of the simple nature

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