

Superhard B–C–N materials synthesized in nanostructured bulks

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We report here the high-pressure synthesis of well-sintered millimeter-sized bulks of superhard BC₂N and BC₄N materials in the form of a nanocrystalline composite with diamond-like amorphous carbon grain boundaries. The nanostructured superhard B–C–N material bulks were synthesized under high *P–T* conditions from amorphous phases of the ball-milled molar mixtures. The synthetic B–C–N samples were characterized by synchrotron x-ray diffraction, high-resolution transmission electron microscope, electron energy-loss spectra, and indentation hardness measurements. These new high-pressure phases of B–C–N compound have extreme hardnesses, second only to diamond. Comparative studies of the high *P–T* synthetic products of BC₂N, BC₄N, and segregated phases of diamond + *c*BN composite confirm the existence of the single B–C–N ternary phases.

I. INTRODUCTION

The synthesis of novel superhard materials (Vickers hardness, $H_v \geq 40$ GPa) with superb properties has been one of the most important high-pressure science and technology frontiers. Superhard materials are usually made of light elements such as boron, carbon, nitrogen, and oxygen.^{1–8} The intrinsically strong and directional covalent bonds between these light elements lead to tight, three-dimensional crystalline networks with extreme resistance to shear. The search for novel superhard materials has been ongoing following the successful synthesis of man-made diamonds⁹ and cubic boron nitride (*c*BN).¹⁰ Theoretical studies suggest the existence of B–C–N phases having hardness approaching that of diamond.¹¹ These phases are expected to resist oxidation and graphitization to higher temperatures and, thus, to remain strong for hardened-steel cutting. The technological

importance of these products has led to the synthesis of superhard B–C–N compounds by sintering various starting materials at high pressure and temperature.^{12–16} But it is still unclear whether the synthesized products are real B–C–N ternary single phase or simply mechanical mixtures of highly dispersed diamond and *c*BN.^{16,17} In addition, well-sintered B–C–N bulk samples are in high demand for hardness and thermal stability tests. Determination of morphology, crystallography, bonding structure, and chemical composition are exceedingly important in the search for novel B–C–N superhard materials.

Superhard nanocrystallites embedded in a strong amorphous matrix is currently the most promising concept for the synthesis of novel superhard material, as shown in a recent preparation of nanocomposite TiN/Si₃N₄ coating¹⁸ of about 100 GPa nanoindentation hardness. It is known that the achievable strength and hardness of engineering materials are usually orders-of-magnitude lower than the theoretical values.^{19,20} The reason for this is that deformation and fracture occur

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through the multiplication and propagation of vacancies and dislocations in crystalline materials. The initiation and growth of microcracks in grain boundaries of ceramics and metal alloys lead to significantly lower practical hardness, toughness, and strength than the theoretical values. Nanocrystalline and amorphous phases greatly minimize these drawbacks and enhance their mechanical performance substantially.^{11,18,21} The amorphous boundary has significant advantages over the crystalline boundary, including (i) relaxing mismatches from adjacent unit cells corresponding to different phases, (ii) absorbing vacancies, dislocations, and impurities at boundaries, and (iii) diminishing surface energy and reducing residual stresses among the nanocrystalline grains. The amorphous boundaries, therefore, substantially improve the stability and mechanical performance of nanostructured bulk materials. Appropriate design of nanocomposites with strong nanocrystalline/amorphous grain boundaries can increase the strength and hardness by a factor of 3 to 8.^{18–20} In this work, we focus not only on the synthesis of the B–C–N superhard ternary phase but also on the formation of well-sintered nanostructured bulk samples with strong nanocrystalline/amorphous grain boundaries.

II. EXPERIMENTAL

Our starting materials for the preparation of the BC₂N and/or BC₄N samples were in stoichiometric 2:1 and/or 4:1 molar ratio mixture of graphite and hexagonal boron nitride (hBN). The mixture was ball-milled in a tungsten carbide (WC) vial for 34 h. The long ball-milling process leads to extreme homogeneity in the starting materials and enhances the chances of the B–C–N atoms to randomly bond with one another. We expected to break the *sp*² bonding among the hexagonal rings of the graphite and hBN crystal structures and to introduce some initial amount of hybrid *sp*³ bonding seeds during the high power point impacts of the ball-milling process. The ball-milled mixture was dark in color, and no obvious crystalline morphology was observed upon examination with scanning electron microscopy and Raman spectroscopy, and the amorphized particles had a median size of about 2–3 nm. X-ray diffraction (XRD) studies of the ball-milled mixture showed that the BC₂N and BC₄N starting material was completely amorphized, and no contamination from WC was observed within the resolution limit of the instrument.

The amorphous form of the B–C–N fine powder was compressed to a pressure of 20 GPa and heated to a temperature of 2200 K for 5 min using a multianvil press. The recovered synthetic product was a well-sintered bulk cylinder chunk 1.5 mm in height and 1.2 mm in diameter. The products are all well sintered and extremely hard to cut and polish, even with diamond saws and diamond

pastes. The high-pressure synthesized BC₂N samples were examined by synchrotron XRD in angle-dispersive mode with a short monochromatic wavelength of $\lambda = 0.4246 \text{ \AA}$. One obvious feature of the x-ray pattern is that the diffraction peaks are significantly broadened (Fig. 1). Using the Scherrer equation, we obtained a crystallite size for the synthetic BC₂N sample in the range of 4–8 nm. This indicates that our unique sample preparation procedure does indeed result in superhard material bulks that are nanostructured.

For comparison purposes, we also synthesized a segregated diamond + cBN composite from a raw mixture of hBN + 2 graphite that had not been subjected to ball-milling process. This sample was synthesized under the same *P–T* conditions (20 GPa, 2200–2250 K) as the B–C–N samples. The synchrotron XRD data in Fig. 2 show clear splitting of the diffraction peaks for the separated phases of diamond and cBN and contrast significantly with the single peaks of the BC₂N and BC₄N samples. The breadth of the peaks of the nanostructured BC₂N and BC₄N samples covers the range of the diffraction peaks of the diamond and cBN. However, it is very clear from the detailed comparison of each individual diffraction peak that the BC₂N peak falls just between the diamond and cBN peaks and the BC₄N peak moves slightly toward the diamond peak with smaller *d*-spacing, just as expected for the solid solution product. The peaks of both BC₂N and BC₄N exhibit similar symmetric shapes, strongly suggesting that the synthesized

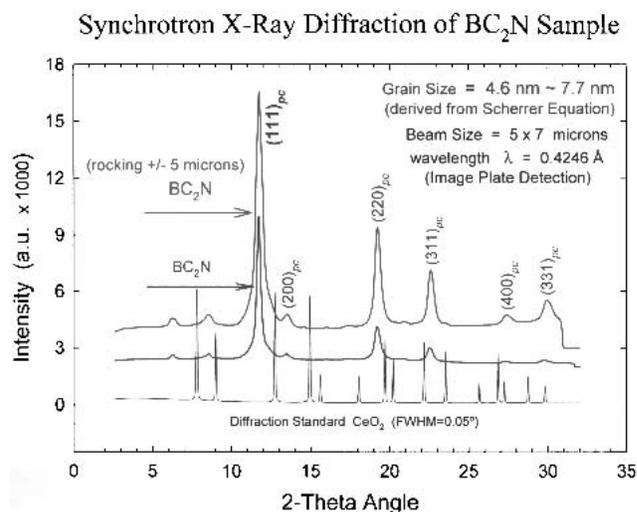


FIG. 1. Monochromatic synchrotron XRD patterns taken in angle-dispersive mode at the Advanced Photon Source at Argonne National Laboratory. The top diffraction pattern was taken with the nanostructured superhard BC₂N sample rocking with amplitude of 5 μm . The middle pattern was taken with a stationary sample. The bottom pattern is a standard diffraction pattern (CeO₂) and shows instrumental resolution. The grain size of the BC₂N sample deduced from the Scherrer equation ranges from 4 to 8 nm. Two minor peaks between $2\theta = 5^\circ$ and 10° and appearance of the (220)_{pc} peak may reflect the existence of superstructure of BN– layers.

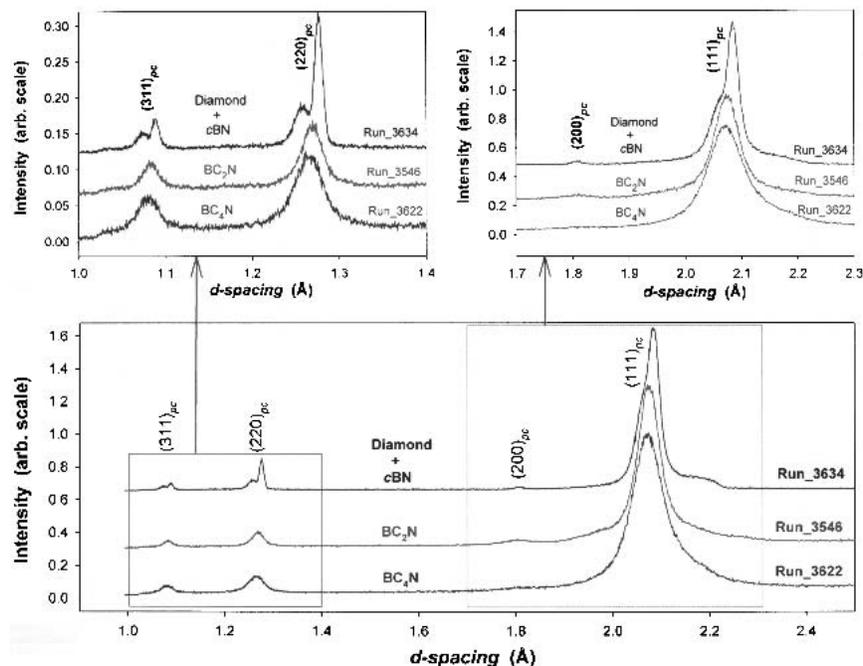


FIG. 2. Synchrotron XRD patterns of BC_2N , BC_4N , and diamond + cBN composite samples taken in energy-dispersive mode at National Synchrotron Light Source (NSLS). The bottom panel shows the overall patterns, and the top two panels show details of the comparison, in terms of position and symmetric of the diffraction peaks, among these three samples. The synthesis conditions for all these samples were 20 GPa and 2200–2250 K. The peak splitting for the segregated phases in diamond + cBN composite is not observed for the BC_2N and BC_4N samples. Comparison of the patterns clearly indicates the existence of single B–C–N ternary phases with cubic and zinc-blende structure.

sample is not a mixture of diamond and cBN. If the sample were a mixture, the contribution from diamond and cBN would affect the symmetry of the diffraction peaks as carbon concentration changes. This provides strong evidence for the successful synthesis of a single B–C–N ternary phase in the form of well-sintered nanostructured BC_2N and BC_4N superhard bulks.

III. RESULTS AND DISCUSSION

Interestingly, the $(200)_{pc}$ peak reported in our study was not shown in the data of Komatsu *et al.*,¹⁵ Solozhenko *et al.*,¹⁶ and Utsumi *et al.*,²² significantly, their starting materials were all graphitic BC_2N .²³ We also note that Knittle *et al.*¹⁴ reported the appearance and disappearance of the $(200)_{pc}$ peak in their synthesis products depending on their use of various proportions of “graphitic” and “mixed” starting materials. We have observed a significant reduction of the diffraction intensity of $(200)_{pc}$ diffraction peak and two other peaks at large d -spacing with increasing carbon concentration, from BC_2N to BC_4N . On the basis of these observations, we believe that the appearance of the $(200)_{pc}$ peak and two minor peaks at large d -spacing ($2\theta = 5^\circ$ – 10°) are the indication of the existence of superstructure BN– layers within the crystal structure, as suggested by many theoretical modeling studies.^{1,24}

The major diffraction peaks of the crystalline BC_2N and BC_4N are consistent with a face-centered-cubic zinc-blende (ZnS) structure with unit cell parameters of $a = 3.595(7) \text{ \AA}$ and $a = 3.586(9) \text{ \AA}$, respectively. These unit cell dimensions lie between diamond ($a = 3.567 \text{ \AA}$) and cBN ($a = 3.616 \text{ \AA}$), as predicted for the high-pressure phases of B–C–N in solid solution. Our observation contradicts the results of Solozhenko *et al.*,¹⁶ who measured a unit cell ($a = 3.642 \text{ \AA}$) for BC_2N even larger than that of cBN. Our result agrees with Knittle *et al.*'s¹⁴ report of $a = 3.602 \text{ \AA}$ and Komatsu *et al.*'s¹⁵ report of $a = 3.605 \text{ \AA}$. A recent synthesis experiment conducted by Utsumi *et al.*²² at 21 GPa and 2300 K yielded the same unit-cell parameter for BC_2N as the present study. A plot of unit-cell parameters as a function of chemical composition for all data^{14,15,23} measured in the B–C–N system, including the present study, shows good agreement with Vegard's law (Fig. 3),²⁵ with the exception of Solozhenko *et al.*'s (2001) data,¹⁶ which deviate significantly from the line on Fig. 3. This deviation suggests that the composition of Solozhenko *et al.*'s sample was not the solid solution of BC_2N and clearly had a different chemistry.

The well-sintered BC_2N and BC_4N chunks synthesized at high-pressure were translucent with light-yellowish color. We measured Vickers indentation hardness of the synthesized BC_2N and BC_4N chunks at a loading force up to 9.8 N. The measured hardness (nominal

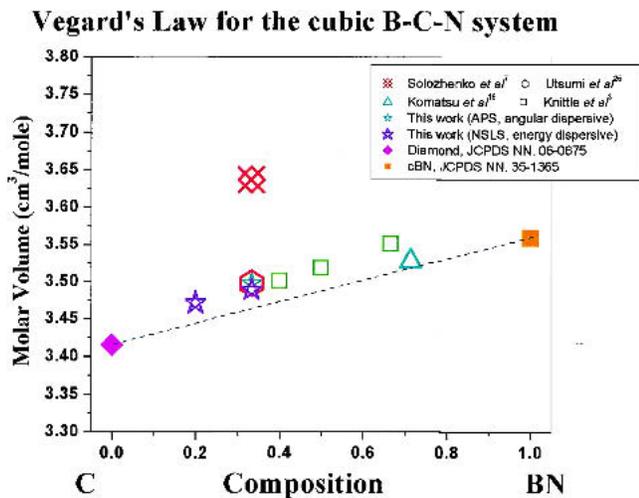


FIG. 3. Plot of all observed unit-cell volumes in the B–C–N system of cubic zinc-blende structure. The relationship of unit-cell volume versus chemical composition shows a clear trend closely obeying Vegard's law for ideal solid solutions, except for Solozhenko *et al.*'s (2001) data.

value) was about 62 GPa for the BC₂N samples and about 68 GPa for the BC₄N samples (Fig. 4). The superb performance of our nanostructured superhard B–C–N material makes it the second hardest material known, second only to diamond. Optical observations on segregated diamond + cBN sample clearly showed visible differences between diamond and cBN phase regions. The indentation hardness measurements were taken on diamond and on the cBN phases and the measured hardness (at 9.8 N loading) was 85 GPa for diamond and 47 GPa for cBN, respectively.

Solozhenko *et al.* (2001) measured the hardness for their large-volume synthesis of BC₂N¹⁶ and obtained a hardness of $H_v = 76$ GPa. However, their large-volume synthesized sample had massively reacted with the MgO capsule. Therefore, their hardness measurement probably does not reflect a pure BC₂N phase but rather the hardness of a phase mixture. In contrast to their hardness measurement, Solozhenko *et al.*'s (2001) measured bulk modulus of 282 GPa for their BC₂N sample is much smaller than Knittle *et al.*'s (1995) and Utsumi *et al.*'s (2001) measurements of 350 GPa. It is doubtful that Solozhenko *et al.*'s (2001) low-density and low-bulk

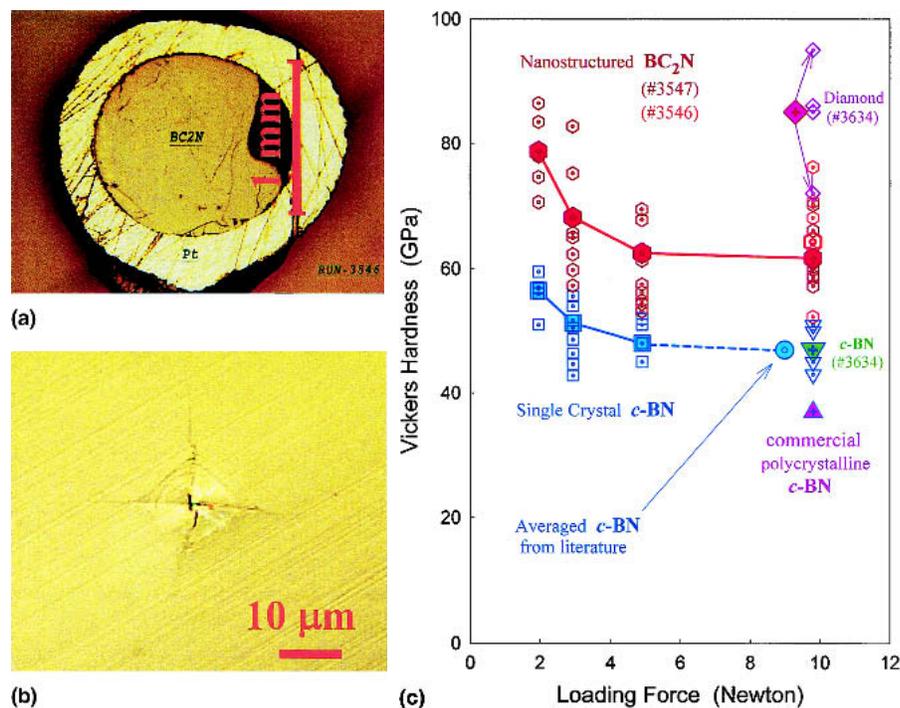


FIG. 4. (a) Optical micrograph of the BC₂N sample synthesized under high *P–T* conditions. The yellow ring is the cross section of the platinum holder. (b) Vickers indentation produced by a diamond indenter using a loading force of 9.8 N. (c) Vickers hardness data. Empty symbols show individual measurements, whereas filled symbols are averaged data. For comparison, the figure also shows hardness measurements for cBN single crystals and for polycrystalline diamond and cBN from the synthesized composite sample (run no. 3634). The circle denotes the average hardness of cBN at a loading force of 9.8 N taken from the literature.¹¹ The empty inverted triangles show the measurement on cBN from the diamond + cBN composite, and the filled inverted triangle shows the average of the measurements. These measured data agree exactly with the highest hardness on well-sintered, polycrystalline cBN sample measured to date.³³ The upright triangle denotes the hardness of currently available commercial polycrystalline cBN (Valenite Polycrystalline Products). The empty diamond symbols show the measurement on diamond from the synthesized diamond + cBN composite, and the filled diamond symbol shows the average of the measurements.

modulus $c\text{BC}_2\text{N}$ structure could be harder than $c\text{BN}$, as pointed out by theoretical modelers.¹ Additionally, it is important to note that, unlike our results, the experiments conducted by Knittle *et al.* (1995),¹⁴ Komatsu *et al.* (1999),¹⁵ and Utsumi *et al.* (2001)²² did not produce large bulks of well-sintered samples. These authors were therefore unable to measure hardness on their BC_2N superhard flakes.

We also performed a high-resolution transmission electron microscopy (HRTEM) examination of the BC_2N sample synthesized at high pressures. HRTEM shows clear evidence of the presence of nanoscale crystallites with an average size of 5 nm (Fig. 5), consistent with the results of the synchrotron XRD study. The electron diffraction pattern of the nanocrystalline BC_2N sample shows the same zinc-blende structure revealed by synchrotron XRD. The volume ratio between the nanocrystalline phase and amorphous phase is estimated to be less than 5%.

In conjunction with the HRTEM study, we carried out an electron energy-loss spectroscopy (EELS) analysis—a technique especially suitable for obtaining local chemical composition and chemical bonding information in light-element materials.^{17,26,27} EELS is conducted with an electron beam focused to 3–4 nm in diameter in such a way that individual nanocrystalline grains can be analyzed. The EELS results indicate that the nanocrystallites

shown in Fig. 5 contain the complete B–C–N ternary system in that the K-edges of boron, carbon, and nitrogen appear concurrently in the EELS spectra of individual nanograins (Fig. 6). Up to 50 individual observations on single-phase nanograins demonstrate conclusively that the BC_2N nanocrystallites synthesized at high pressure are a single B–C–N ternary phase compound rather than a mixture of diamond and $c\text{BN}$. Furthermore, the EELS pattern of single grains very clearly shows the concurrent existence of the boron, carbon, and nitrogen K-edge peaks of the BC_2N sample, just as observed in the polycrystalline sample. We have also focused an electron beam on amorphous boundaries and observed the corresponding EELS pattern. It is very obviously shown that there only exists a single carbon K-edge peak for the amorphous boundary of the sample; we thus conclude that the grain boundaries of the polycrystalline BC_2N sample are formed by diamond-like amorphous carbon.

We quantitatively analyzed the EELS spectra to determine the chemical composition of the $c\text{BC}_2\text{N}$ phase. The relative composition ratio, C_A/C_B , of element A and B can be calculated from the integrated intensity under the edge and above the background measured over an energy-loss window ΔE and for a spectrometer acceptance angle β .²⁸ The energy window, acceptance angle, and convergence angle used in the experiments were 50 eV, 5.6 mrad, and 6.8 mrad, respectively. Analyses of

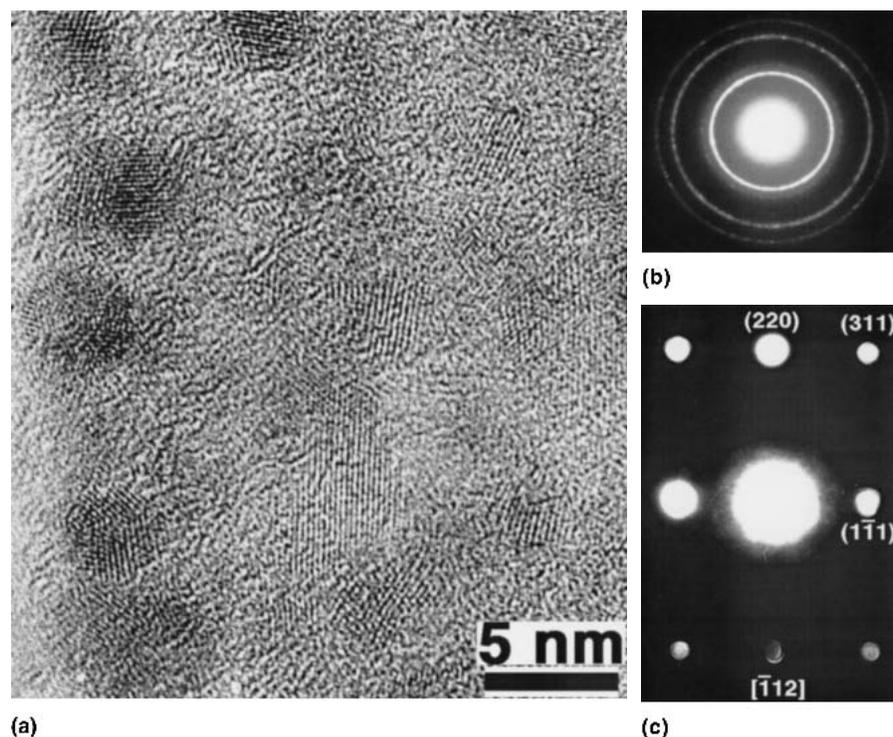


FIG. 5. (a) HRTEM image of the nanostructured BC_2N superhard material. The zinc-blende structure is confirmed by (b) electron polycrystalline diffraction pattern of a selected area and by (c) electron diffraction of a single-grain crystal. The grain boundaries between nanocrystallites appear to be amorphous (see text for details). The average crystallite size ranges from 3 to 8 nm, consistent with the XRD observations.

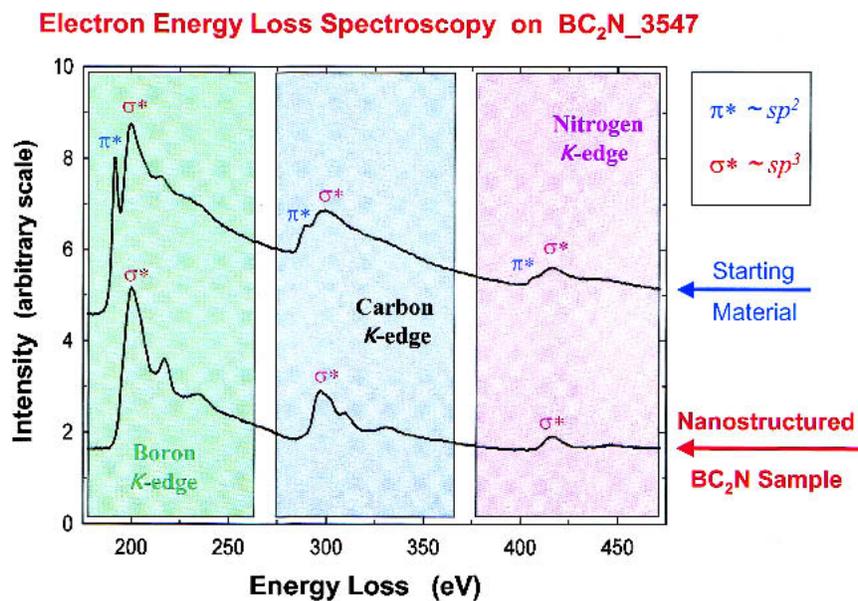


FIG. 6. EELS comparing the starting material with the nanostructured BC₂N superhard material. The spectrum for the starting material (after ball-milling) clearly shows the presence of sp^2 bonding (π^* peaks), whereas the spectrum for the final product (after reaction at high P – T) shows only the presence of sp^3 bonding (σ^* peaks only). The EELS data were collected with a beam approximately 3 nm in size and focused on individual nanoparticles. All three K edges (B, C, and N) appear simultaneously in the spectra. This indicates that the material is a true B–C–N ternary compound rather than segregated phases of diamond and cBN. The EELS patterns observed on amorphous grain boundaries only show a single carbon K-edge peak indicating that the grain boundaries of the nanostructured polycrystalline BC₂N sample are formed by diamond-like amorphous carbon.

ten spectra gave an average atomic composition close to B₂₇C₅₀N₂₃, which is within experimental error of $\pm 10\%$ for theoretical composition of BC₂N. The EELS spectra thus confirm that our superhard BC₂N phase has a chemical composition very close to ideal atomic ratio.

The grain boundaries of the nanostructured BC₂N bulk materials were identified as diamond-like amorphous carbon (DLC) by HRTEM and EELS. This is an unexpected result and is the first time DLC has been observed in a high P – T synthesized bulk nanostructured material. DLC is typically produced by vacuum arc or pulsed laser deposition methods in film form, and this material has stimulated great interest because of its high hardness, chemical inertness, thermal stability, wide optical gap, and negative electron affinity.^{29,30} The DLC grain boundary between nanoparticles significantly enhances the mechanical strength of our bulk superhard nanocomposite. The content of DLC resulting from high P – T synthesis process in the BC₂N sample is quite small (less than 5%) according to the HRTEM, EELS, and XRD data. Nevertheless, extremely strong subnanoscale bonds must have formed between the BC₂N nanocrystallites because no extensive cracks were induced at the corners of the indentation pyramid in the hardness measurement. Such enhanced fracture toughness is likely due to the disappearance of vacancies and dislocations in the nanocrystallites and to the difficulty of propagating microcracks in amorphous grain boundaries.³¹ This is a

very desirable mechanical property, and it is one of the major reasons for pursuing the synthesis of new nanostructured superhard materials.

Our results show that the amorphous–nanocrystalline transformation under high- P – T conditions is a novel approach to fabricate bulk nanostructured, single-phase, well-sintered, superhard materials of the B–C–N ternary system with greatly enhanced mechanical properties. Crystallization of the amorphous starting materials is thermodynamically favored under high pressure—especially the formation of crystalline nuclei—because amorphous phases have a lower density and a higher compressibility than their corresponding crystalline states.³² Conversely, the growth of a crystalline nucleus is usually accompanied by long-range atomic rearrangements and is kinetically hindered by external pressure. As pressure and temperature reach a critical point, the crystallization process is initiated simultaneously throughout the sample due to the extreme homogeneity of our amorphous starting materials after the long ball-milling process. We speculate that the massive and sudden appearance of superhard B–C–N nuclei, the so-called “copious nucleation” in the amorphous matrix, and the high-pressure “braking” of the diffusion process of crystallization are essential to the formation of nanostructured superhard materials. Pressure promotes the nucleation of crystallites and effectively restricts grain growth. The subtle interplay between temperature and

pressure allows for much finer control of the crystallization process of amorphous materials and should open up new avenues in the design and synthesis of novel nanostructured materials with outstanding properties.

IV. CONCLUSION

In summary, we have successfully synthesized nanostructured superhard material bulks in the boron–carbon–nitrogen system at high pressures and high temperatures. The starting material for the synthesis experiments was a mixture of graphite and hexagonal boron nitride in 2:1 and/or 4:1 molar ratio for BC₂N and/or BC₄N, rendered completely amorphous following 34 h of ball-milling in a WC vial. The final products are well-sintered chunks of millimeter size and are translucent and yellowish in color. Synchrotron XRD and high-resolution transmission electron microscopy with EELS all show that the BC₂N samples synthesized under high-*P–T* conditions are nanocrystalline with a grain size approximately 5 nm. Comparative studies of synchrotron XRD, HRTEM, EELS, and Vegard's law of unit-cell volume versus chemical compositions all indicate that the BC₂N and BC₄N samples synthesized at high-*P–T* conditions are single B–C–N ternary phases, significantly in contrast to the phase segregation of diamond + *c*BN composite. The synthesized BC₂N and BC₄N material have the zincblende structure and face-centered cubic unit cell with a unit-cell dimension of $a = 3.595(7)$ Å and $a = 3.586(9)$ Å, respectively. The hardness measurements show that the BC₂N and BC₄N samples synthesized under high-*P–T* conditions have a nominal hardness of 62 and 68 GPa, respectively, which is very close to diamond and far higher than cubic boron nitride. This result establishes the nanostructured B–C–N superhard material as the second hardest material known, second only to diamond.

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REFERENCES

- H. Sun, S. Jhi, D. Roundy, M.L. Cohen, and S.G. Louie, *Phys. Rev. B* **64**, 094108 (2001).
- Y. Tateyama, T. Ogitsu, K. Kusakabe, and S. Tsuneyuki, *Phys. Rev. B* **55**, 10161 (1997).
- H.T. Hall and L.A. Compton, *Inorg. Chem.* **4**, 1213 (1965).
- R.H. Wentorf, R.C. DeVries, and F.P. Bundy, *Science* **208**, 873 (1980).
- A.Y. Liu and M.L. Cohen, *Science* **245**, 841 (1989).
- D.M. Teter and R.J. Hemley, *Science* **271**, 53 (1996).
- H. Hubert, B. Devouard, L.A.J. Garvie, M. O'Keeffe, P.R. Buseck, W.T. Petuskey, and P.F. McMillan, *Nature* **391**, 376 (1998).
- D. He, M. Akaishi, B.L. Scott, and Y. Zhao, *J. Mater. Res.* **17**, 284 (2002).
- F.P. Bundy, H.T. Hall, H.M. Strong, and R.H. Wentorf, Jr., *Nature* **176**, 51 (1955).
- R.H. Wentorf, Jr., *J. Chem. Phys.* **26**, 956 (1957).
- S. Veprek, in *Handbook of Ceramic Hard Materials*, edited by R. Riedel (Wiley-VCH Verlag GmbH, Weinheim, Germany, 2000), pp. 104–139.
- A.R. Badzian, *Mater. Res. Bull.* **16**, 1385 (1981).
- S. Nakano, M. Akaishi, T. Sasaki, and S. Yamaoka, *Chem. Mater.* **6**, 2246 (1994).
- E. Knittle, R.B. Kaner, R. Jeanloz, and M.L. Cohen, *Phys. Rev. B* **51**, 12149 (1995).
- T. Komatsu, M. Samedima, T. Awano, Y. Kakadate, and S.J. Fujiwara, *Mater. Process. Technol.* **85**, 69 (1999).
- V.L. Solozhenko, D. Andrault, G. Fiquet, M. Mezouar, and D.C. Rubie, *Appl. Phys. Lett.* **78**, 1385 (2001).
- J. Huang, Y.T. Zhu, and H. Mori, *J. Mater. Res.* **16**, 1178 (2001).
- S. Veprek, *J. Vac. Sci. Technol., A* **17**, 2401 (1999).
- R.W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials* (Wiley, New York, 1989).
- A. Kelly and N.H. MacMillan, *Strong Solids* (Clarendon, Oxford, U.K., 1986).
- E.A. Ekimov, A.G. Gavriluk, Z. Palosz, S. Gierlotka, P. Dluzewski, E. Tatianin, Y. Kluged, A.M. Naletov, and A. Presz, *Appl. Phys. Lett.* **77**, 954 (2000).
- W. Utsumi, S. Nakano, K. Kimoto, T. Okada, M. Isshiki, T. Taniguchi, K. Funakoshi, M. Akaishi, and O. Shimomura, *Proceedings of AIRAPT-18*, Beijing, China, 2001 (2001), p. 186.
- S. Nakano, M. Akaishi, T. Sasaki, and S. Yamaoka, *Chem. Mater.* **6**, 2246 (1994).
- M. Mattesini and S.F. Matar, *Comput. Mater. Sci.* **20**, 107 (2001).
- L. Vegard, *Z. Phys.* **5**, 17 (1921).
- Ph. Redlich, J. Loeffler, P.M. Ajayan, J. Bill, F. Aldinger, and M. Rühle, *Chem. Phys. Lett.* **260**, 465 (1996).
- M. Wibbelt, H. Kohl, and Ph. Kohler-Redlich, *Phys. Rev. B* **59**, 11739 (1999).
- L.A.J. Garvie, H. Hubert, W.T. Petuskey, P.F. McMillan, and P.R. Buseck, *J. Solid State Chem.* **133**, 365 (1997).
- J.S. Lannin, V.I. Merkulov, C.H. Munro, S.A. Asher, V.S. Veerasamy, and W.I. Milne, *Phys. Rev. Lett.* **78**, 4869 (1997).
- M.P. Siegal, D.R. Tallant, L.J. Martinez-Miranda, J.C. Barbour, R.L. Simpson, and D.L. Overmyer, *Phys. Rev. B* **61**, 10451 (2000).
- J. Schiøtz, F.D. Di Tolla, and K.W. Jacobsen, *Nature* **391**, 561 (1998).
- D. He, Q. Zhao, W.H. Wang, R.Z. Che, J. Liu, X.J. Lou, and W.K. Wang, *J. Non-Cryst. Solids* **297**, 84 (2002).
- T. Taniguchi, M. Ahaishi, and S. Yamaoka, *J. Mater. Res.* **14**, 162 (1999).