Elastic moduli of the superhard cubic BC_2N phase by Brillouin scattering

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(Received 18 April 2003; published 29 August 2003)

Brillouin scattering measurements on the nanocrystalline cubic phase of BC_2N, the hardest known solid after diamond, have been successfully performed using the ''emulated'' platelet scattering geometry. We were able to measure both longitudinal (V_p) and shear (V_s) velocities independent of refractive index, and thus obtained values of 13.09 ± 0.22 and 8.41 ± 0.14 km/s, respectively. Using these values, we calculated the bulk and the shear moduli as 259 ± 22 and 238 ± 8 GPa, respectively.

DOI: 10.1103/PhysRevB.68.052104 PACS number(s): 78.35.+c, 78.20.Ci, 62.20.−x

Following the successful synthesis of the superhard phase of cubic nanocrystalline BC_2N (c-BC_2N) both in a diamond-anvil cell and in a large-volume press,[1] it became possible to characterize its mechanical properties by microindentation and nanoindentation.[2–4] The Vickers hardness of 76 GPa measured for nanocrystalline c-BC_2N has been found to lie between 115 GPa (Refs. 5, 6) for the (111) face of a single-crystal diamond and 62 GPa for the (111) face of a single-crystal cubic boron nitride (c-BN).[2–4] Based on the nanohardness measurements, the value of the shear modulus of the c-BC_2N was predicted to be 447 ± 18,[2] which is even higher than that of diamond. The bulk modulus derived earlier from the x-ray diffraction data was as low as 280 GPa.[1] These results appear to differ from recent theoretical simulations,[7,8] which show that the phases of the cubic BC_2N with high shear moduli, without exception, have very high bulk moduli. Despite several reports on the synthesis of diamondlike phases in the B-C-N system, no experimental data on the elastic properties of these new phases are available.[9–13] In this paper, we report on experimental data on the elastic moduli of nanocrystalline bulk c-BC_2N obtained by Brillouin spectroscopy.

The sample used in this study is the same one used for hardness and refractive index measurements, a nanocrystalline sample of c-BC_2N.[1,2,14] It was synthesized[1] by direct conversion of graphitelike $(BN)_{0.48}C_{0.52}$ solid solution at 25 GPa and 2100 K using a large-volume multianvil system and Sumitomo 1200-ton press at the Bayerisches GeoInstitut. One side of the recovered c-BC_2N sample (1.1 mm in diameter and 0.9 mm thick disk) was polished by a cast iron scaife and 15- to 2-μm diamond grit, and finished with 0.5-μm diamond paste. The polishing of the specimen reduced sample size to approximately 0.3 mm depth from the exposed surface to the bottom of encapsulated surface. The transmission electron microscopy (TEM) of the sample[4,15] shows that the grain size ranges from 10 to 30 nm with a narrow size distribution.

The presence of microcracks (inclined at $10°-15°$ to the polished plane), visible both at the surface and within the encapsulated sample, yielded some artifacts in the Brillouin spectra. To overcome such a problem, the formerly open side of the sample was attached to a reflective mirror by epoxy and the sample was thinned from ~300 down to ~90 μm by polishing the encapsulated side. At the end of this process, several areas, ranging from 50 to 100 μm in size, appeared to be especially well cleared of microcracks and, thus, were chosen to emulate the platelet scattering configuration. In this specific assemblage the laser beam reflected from the mirror serves as incident light for giving rise to a signal scattered in platelet geometry.[16–18] The frequency shift Δf thus obtained is related to the bulk sound velocity V as

$$V = \frac{\lambda \Delta f}{2 \sin \theta}, \tag{1}$$

where θ is the angle between the incident wave vector and normal to the sample surface, and λ is the wavelength of the incident light. The advantage of the ''emulated'' geometry enables measurements of the longitudinal (V_L) and transverse (V_T) velocities independent of refractive index n. Moreover, mounting the sample with only one side exposed has significantly reduced the risk of disintegrating the brittle specimen. Measurements done with ''emulated'' platelet geometry also confirmed that the elastic anisotropy, revealed in preliminary surface Brillouin scattering measurements prior to polishing, was an artifact attributed to the light scattering from inclined microcracks.

The Brillouin scattering (BS) experimental setup is an improved version of the system utilized in a recent study[19] on bulk amorphous carbon samples. It is a fully automated, self-aligning spectrometer with increased stability and flexibility,[20] and it operates on the basis of a Sandercock-type tandem six-pass Fabry-Perot interferometer.[21] The beam from an argon ion laser ($\lambda = 514.5$ nm and beam power of 70 mW) was focused on the sample with 1:1.4 ($f = 50$ mm) lens. The high-resolution spectra were typically accumulated for 1–2 h.

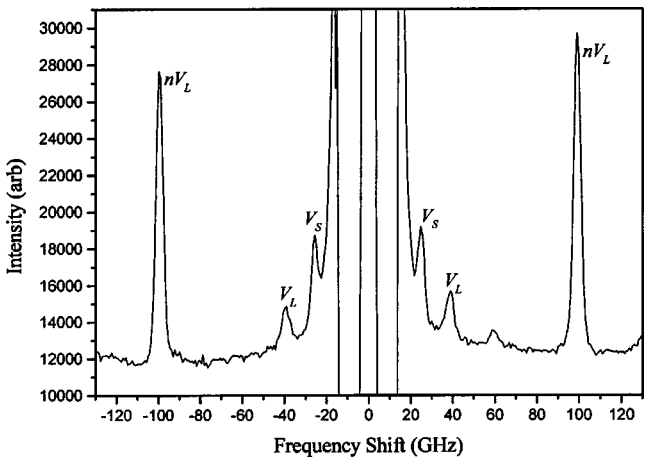

FIG. 1. Experimental BS spectrum ($\theta = 50°$) of nanocrystalline c-BC_2N. An asymmetric peak at ≈ 60 GHz resulted from the saturation of the system by the strong elastic scattering (Ref. 19).

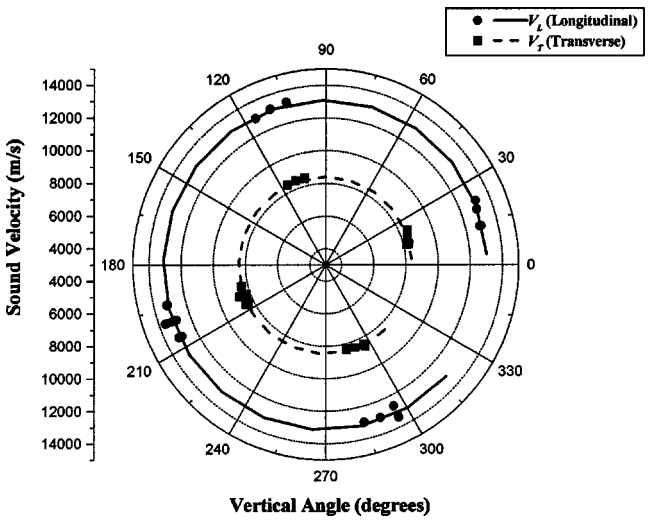

FIG. 2. Experimental azimuth dependence of longitudinal (solid circles) and shear velocities (solid squares) in c-BC_2N. Thick lines are linear fits to present data.

A typical Brillouin spectrum of the nanocrystalline c-BC_2N sample (Fig. 1) shows well-defined peaks associated with both longitudinal and transverse acoustic modes. The azimuth dependencies of V_L and V_S (Fig. 2) do not indicate velocity anisotropy and therefore provide evidence that the nanocrystalline cubic BC_2N phase is elastically isotropic. Using average V_L and V_S values of 13.09 ± 0.22 and 8.41 ± 0.14 km/s, respectively, we calculated bulk and shear moduli, Poisson's ratio, and the Young's modulus. The results and relevant data from the literature are compiled in Table I with the standard deviations indicated as uncertainties. We find good agreement among the presently obtained bulk modulus and the corresponding value obtained from independent x-ray compressibility measurements.[1]

Experimental spectra show also a strong peak around 100 GHz (Fig. 1). This peak is attributed to interaction between laser light and longitudinal phonons in backscattering geometry.[22] In such a geometry, the longitudinal velocity is related to the frequency shift Δf, by the expression

$$V_L = \frac{\lambda \Delta f}{2n}. \tag{2}$$

From the measured value of the frequency shift, we obtained $nV_L = 25.65 \pm 0.4$ km/s. The refractive index of c-BC_2N has been determined to be 2.06, using the multi-angle-of-incidence ellipsometry measurements.[14] Thus, from these measurements, the longitudinal velocity can be determined independently. The value is 12.45 ± 0.31 km/s, and it agrees reasonably well with $V_L = 13.09 \pm 0.33$ km/s obtained by ''emulated'' platelet geometry. We can also calculate n from measured values of nV_L. Results presented in Fig. 3 clearly show that the nanocrystalline c-BC_2N is optically isotropic as well, with an average value of $n = 1.96 \pm 0.03$. This is in agreement with multi-angle-of-incidence ellipsometry measurements.[14]

The cubic BC_2N phase has an unusual combination of mechanical properties: its elastic moduli measured by Brillouin scattering and x-ray diffraction are lower than those of c-BN, whereas its hardness measured independently by microindentation technique[2] is higher than that of the single-crystal c-BN and only slightly lower than that of diamond. The fact that the values of bulk and shear moduli of c-BC_2N are lower than those for c-BN and diamond may be attrib-

TABLE I. Summary of experimental data on V_L, V_S, density (ρ), K, G, and ν of c-BC_2N, c-BN, and diamond. Elastic moduli and Poisson's ratio of c-BC_2N were calculated using Brillouin scattering data and value of density measured in Ref. 1. Acoustic velocities and elastic moduli of c-BN and diamond were calculated using experimentally measured parameters for single crystals.

Phase	ρ (g/cm^3)	V_L (km/s)	V_S (km/s)	ν	K (GPa)	G (GPa)
c-BC_2N	3.358[a]	13.09 ± 0.22[b]	8.41 ± 0.14[b]	0.149[c]	259 ± 22[c]	238 ± 8[c]
c-BN[d]	3.500	15.82	10.39	0.121	372.3	377.8
Diamond[e]	3.512	18.17	12.238	0.071	442	538

[a]Reference 1.
[b]Present study.
[c]Calculated using V_L and V_S from current measurements and density from Ref. 1.
[d]Reference 24.
[e]Isotropic (Voigt-Reuss-Hill) average using elastic moduli reported in Ref. 25.

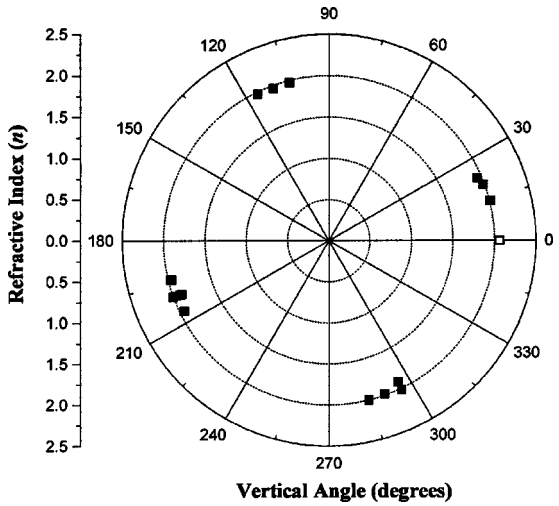

FIG. 3. Experimental azimuth dependence of refractive index (n) in c-BC_2N. Solid squares are present data; open square is the value of n determined from multi-angle-of-incidence ellipsometry measurements (Ref. 14).

uted to the lattice parameter of c-BC_2N being larger than those in diamond and c-BN.[1] The shear modulus value of (447 GPa) for the c-BC_2N evaluated from the nanohardness measurement[4] is most likely an overestimate due to distinct deformation of the diamond indenter. Clearly the Oliver-Pharr relation between the experimentally measured stiffness and projected area of the elastic contact[23] cannot be used to estimate Young's modulus for superhard phases ($H_V > 40$ GPa). Nonetheless, it is to be noted that for the diamondlike B-N-C phases synthesized by shock compression at pressure higher than 30 GPa and temperature above 3000 K, very high bulk modulus values were reported for c-$BC_{2.5}N$ ($K_0 = 401$ GPa) (Ref. 13) and for $BC_{0.9\pm0.2}N$ ($K_0 = 412$ GPa).[4] These results indicate that the elastic properties of diamondlike B-C-N phases are dependent upon the structure of the phases and, hence, upon the synthesis p-T routes. Further studies are needed to establish any relationship between properties and structure and, hence, the synthesis conditions.

We thank John Balogh for technical assistance and Dr. D. Frost and Dr. D.C. Rubie for their assistance with synthesizing the bulk c-BC_2N sample. Multianvil synthesis was performed at the Bayerisches GeoInstitut under the EU ''IHP-Access to Research Infrastructures'' Program under Contract No. HPRI-1999-CT-00004 (D.C. Rubie). This work was supported by the National Science Foundation Grants Nos. DMR-0102215 and EAR-0074285, and U.S. Army Contract No. DAAD19-00-1-0569.

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[1] V. L. Solozhenko, D. Andrault, G. Fiquet, M. Mezouar, and D. C. Ruby, Appl. Phys. Lett. **78**, 1385 (2001).
[2] V. L. Solozhenko, S. N. Dub, and N. V. Novikov, Diamond Relat. Mater. **10**, 2228 (2001).
[3] V. L. Solozhenko, S. N. Dub, and N. V. Novikov, J. Superhard. Mater. **23**, 72 (2001).
[4] V. L. Solozhenko, Int. J. High Pressure Res. **22**, 519 (2002).
[5] N. V. Novikov and S. N. Dub, J. Hard Mater. **2**, 3 (1991).
[6] C. A. Brooks, in *Properties and Growth of Diamond*, edited by G. Davies (INSPEC, London, 1994), p. 36.
[7] M. Mattesini and S. F. Matar, Int. J. Inorg. Mater. **3**, 943 (2001).
[8] H. Sun, S.-H. Jhi, D. Roundy, M. L. Cohen, and S. G. Louie, Phys. Rev. B **64**, 094108 (2001).
[9] S. Nakano, T. Sasaki, M. Akaishi, and S. Yamaoka, Mater. Sci. Eng., A **209**, 26 (1996).
[10] E. Knittle, R. B. Kaner, R. Jeanloz, and M. L. Cohen, Phys. Rev. B **51**, 12 149 (1995).
[11] T. Komatsu, J. Chem. Soc., Faraday Trans. **94**, 101 (1998).
[12] T. Komatsu, M. Nomura, Y. Kakadate, and S. Fujiwara, J. Chem. Soc., Faraday Trans. **94**, 1649 (1998).
[13] T. Komatsu, M. Samedima, T. Awano, Y. Kakadate, and S. Fujiwara, J. Mater. Process. Technol. **85**, 69 (1999).
[14] V. L. Solozhenko, O. S. Kondratenko, V. G. Litovchenko, and N. L. Dmitruk, Superhard Mater. **2**, 77 (2002).
[15] F. Langenhorst and V. L. Solozhenko, Phys. Chem. Chem. Phys. **4**, 5183 (2002).
[16] C. H. Whitfield, E. M. Brody, and W. A. Bassett, Rev. Sci. Instrum. **47**, 942 (1976).
[17] J. Bak and R. Sooryakumar, High Press. Res. **11**, 329 (1994).
[18] C. S. Zha, T. S. Duffy, H. K. Mao, and R. J. Hemley, Phys. Rev. B **48**, 9246 (1993).
[19] M. H. Manghnani, S. Tkachev, P. V. Zinin, X. Zhang, V. V. Brazhkin, A. G. Lyapin, and I. A. Trojan, Phys. Rev. B **64**, 121403(R) (2001).
[20] B. Hillebrands, Rev. Sci. Instrum. **70**, 1589 (1999).
[21] J. R. Sandercock, in *Light Scattering in Solids III. Recent Results*, edited by M. C. a. G. Guntherodt (Springer-Verlag, Berlin, 1982), Vol. 51, p. 173.
[22] M. Grimsditch, in *Handbook of Elastic Properties of Solids, Liquids, and Gases. Volume I: Dynamic Methods for Measuring the Elastic Properties of Solids*, edited by M. Levy, H. Bass, R. Stern, and V. Keppens (Academic Press, New York, 2001), Vol. I, p. 331.
[23] W. C. Oliver and G. M. Pharr, J. Mater. Res. **7**, 1564 (1992).
[24] M. H. Manghnani, in *The 5th NIRIM International Symposium on Advances Materials (ISAM' 98)* (National Institute For Research in Inorganic Materials, Chicherster, 1998), p. 73.
[25] H. J. McSkimin, P. Andreatch, and P. Glynn, J. Appl. Phys. **43**, 985 (1972).