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Effect of nanostructuration on compressibility of cubic BN

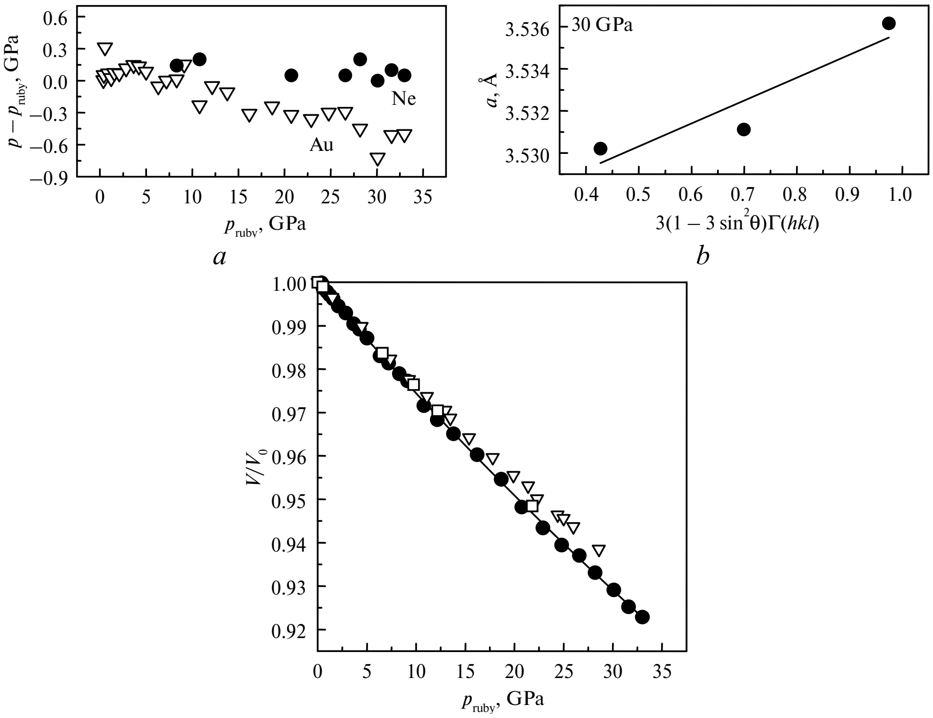
Compressibility of high-purity nanostructured cBN has been studied under quasi-hydrostatic conditions at 300 K up to 35 GPa using diamond anvil cell and angle-dispersive synchrotron powder X-ray diffraction. It has been found that the data fit to the Vinet equation of state yields the values of the bulk modulus B_0 *of 375(4) GPa with its first pressure derivative* B_0' *of 2.3(3), thus, the nanometer grain size (~ 20 nm) results in a decrease of the bulk modulus by ~ 9%.*

***Keywords**: nanostructuration, cubic boron nitride, equation of state, superhard materials.*

Flexible grain-size control of cubic boron nitride (cBN) sintered bulks has been recently achieved by Solozhenko et al. [1] by simultaneous applying very high pressure and high temperature to pyrolytic graphite-like BN precursors of various structural faults. At 20 GPa and 1770 K the high-purity nano-cBN (grain size ~ 20 nm) has been successfully synthesized [1]. New material shows superior wear resistance, fracture toughness, and extremely high hardness as compared to microcrystalline cBN (micro-cBN). In the present work, we report the 300-K equation of state (EOS) of nano-cBN.

In situ X-ray diffraction experiments in a large-aperture membrane-type diamond anvil cell were conducted at ID27 beamline, European Synchrotron Radiation Facility (ESRF). A small particle (~ 10 μm) of nano-cBN (grain size ~ 20 nm) preliminary selected using its specific Raman signal [1], was loaded together with a small ruby ball (less than 5 μm in diameter) and a gold crystal grain (10 μm size). Nano-cBN sample and the pressure markers were placed within a few micrometers to each other close to the center of diamond culet. Neon pressure medium has been used to maintain quasi-hydrostatic conditions. Pressure was determined in situ from the calibrated shift of the ruby R_1 fluorescent line [2] and equations of state of gold [3] and neon [4]. High-brilliance focused synchrotron radiation (8×8 μm^2) was set to a wavelength of 0.3738(1) Å. X-ray patterns were collected using on-line large-area Bruker CCD detector (exposure time from 5 to 10 min).

All three pressure gauges indicated very close pressures (figure, *a*), which points to the negligible strains and stresses, as well as inessential pressure gradients all over the cell. The small differences between apparent lattice parameters for different Bragg peaks (figure, *b*) indicate the quasi-hydrostatic conditions during the measurements. Uniaxial stress (difference between diagonal elements of the pressure tensor) has been evaluated using equation $\sigma_3 - \sigma_1 \approx -3\dfrac{M_1}{\alpha M_0 S}$ [3], where M_1 and M_0 are determined by the equation $a_m(hkl) = M_0 + M_1[3\ (1 - 3\sin^2\theta)\ \Gamma(hkl)]$ with $\Gamma(hkl) = \dfrac{h^2k^2 + k^2l^2 + l^2h^2}{(h^2 + k^2 + l^2)^2}$. $S = (-1/C + 1/C')/2$ where $C = C_{44}$, $C' = (C_{11} - C_{12})/2$. For cBN $C_{44} = 469$ GPa, $C_{11} = 798$ and $C_{12} = 172$ GPa [5], therefore, $S = 5.3 \cdot 10^{-4}$ GPa^{-1}. The fit (figure, *b*) gives the estimate for $\sigma_3 - \sigma_1 \sim -6$ GPa, i.e. $p \sim \sigma_1 - 2$ (GPa). The absolute value seems to be quite reasonable for such superhard and low-compressible phase as cubic BN.



a *b*

c

Deviation of pressure by EOS of Ne and Au from the ruby gauge (*a*); lattice parameter of nano-cBN as a function of *hkl* at 30 GPa (*b*); the 300-K equation of state data for nano-cBN (present work (●), fit to the Vinet EOS – solid line) and micro-cBN (from [9] (∇) and [10] (□)) (*c*).

Three EOS were used to establish isothermal bulk modulus B_0 and its first pressure derivative B_0', i.e. those of Vinet [6], Birch-Murnaghan [7], and Holzapfel [8]. The fitting results are listed in table, while the Vinet fit is presented in figure, *c*. In the compression range probed here, all three models fit the data equally well and give almost the same values for B_0 and B_0'. Figure, *c* also shows equation-of-state data of microcrystalline cBN [9, 10] measured in similar experimental conditions. The bulk modulus of nano-cBN ($B_0 = 375(4)$ GPa) is smaller than the 395(2) GPa value for micron-sized cBN crystals [9].

Since the B_0' value of nano-cBN might not be very well constrained due to the relatively narrow pressure range explored in our study, the reliable comparison of the B_0 values could be obtained by constraining B_0' to the same value as for micro-cBN i.e. 3.62 [9, 11–13]. However, fits with both fixed and variable B_0' are indistinguishable in the pressure range under study, and B_0 of nano-cBN remains lower than B_0 of micro-cBN by 8.9%.

Our result confirms recent experimental [14, 15] and theoretical [16–18] studies, which have demonstrated that in numerous cases elastic moduli of nanomaterials are lower than those of their bulk counterparts (for example, in the same grain size range, B_0 of nanocrystalline Mg_2SiO_4, MgO, Ni and γ-Al_2O_3 are smaller than B_0 of their bulk counterparts by 4.9 % [15], 8.3% [14], 9% [19] and 34.5% [20], respectively). This may be attributed to the presence of a significant volume fraction of grain boundaries and triple junctions, which are more compressible than the crystalline grains, in nanocrystalline materials.

Comparison of equation-of-state data of nano-cBN and micro-cBN fitted to various EOS [6–8]. The zero-pressure volume V_0 was fixed to 5.910 Å^3/atom

Model	Vinet	Birch-Murnaghan	Holzapfel's AP2	Vinet (B_0' = 3.62)
Nano-cBN (this study)	B_0 = 375(4) GPa B_0' = 2.3(3)	B_0 = 375(4) GPa B_0' = 2.4(3)	B_0 = 376(4) GPa B_0' = 2.2(3)	B_0 = 360(2) GPa
Micro-cBN [9]	B_0 = 395(2) GPa B_0' = 3.62(5)	B_0 = 396(2) GPa B_0' = 3.54(4)	B_0 = 397(2) GPa B_0' = 3.50(5)	

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Сжимаемость высокочистого наноструктурированного cBN была изучена в квазигидростатических условиях при 300 K до 35 GPa в алмазных наковальнях с помощью угловой дисперсионной рентгеновской дифракции синхротронного излучения. Описание полученных данных уравнением состояния Винэ дает значение модуля сжимаемости B_0 = 375(4) ГПа и его первой производной по давлению B_0' = 2.3(3). Наноразмер зерна (~ 20 нм) приводит к уменьшению модуля сжимаемости на ~ 9 %.

Ключевые слова: *наноструктурирование, кубический нитрид бора, уравнение состояния, сверхтвердые материалы.*

Стисливість високочистого наноструктурованого cBN була вивчена в квазігідростатичних умовах при 300 K до 35 ГПа в алмазних ковадлах за допомогою кутової дисперсійної рентгенівської дифракції синхротронного випромінювання. Опис одержаних даних рівнянням стану Віне дає значення модуля стисливості B_0 = 375(4) ГПа і його першої похідної по тиску B_0' = 2.3(3). Нанорозмір зерна (~ 20 нм) приводить до зменшення модуля стисливості на ~ 9 %.

Ключові слова: *наноструктурування, кубічний нітрид бору, рівняння стану, надтверді матеріали.*

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