Critical pressure for weakening of size-induced stiffness in spinel-structure Si_3N_4 nanocrystals

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We demonstrate that the compressibility of spinel Si_3N_4 nanocrystals increases when the pressure is raised above ~40 GPa. Si_3N_4 nanocrystals initially exhibit an extremely high bulk modulus of 685(45) GPa. But, above 40 GPa, the bulk modulus is reduced to 415(10) GPa. Thus, a critical pressure of ~40 GPa was determined that signifies the onset of size-induced weakening of elastic stiffness in nanocrystalline Si_3N_4. Enhanced surface energy contributions to the shell layers of nanoparticles and the resulting effect on the corresponding large *d*-spacing planes are used to explain the observed phenomenon. Upon decompression, the bulk modulus of the Si_3N_4 spinel remained at its lower value of 415 GPa. This study provides a reasonable explanation for the different compressibility properties of numerous nanocrystals. [DOI: 10.1063/1.1618365]

Nanocrystalline materials with particle sizes of 1–100 nm are of current interest because they display physical and chemical properties that may differ from those of their corresponding bulk materials. The structural stability of nanocrystalline material is of particular interest, especially when related to first-order transformations, because of its relevance to many research areas, including the engineering of materials with enhanced mechanical properties.[1] Previous high-pressure studies indicated a correlation between increasing transition pressure and decreasing particle size,[2,3] or vice versa.[4,5] These nanocrystals exhibit a higher bulk modulus than their bulk counterparts.[1–5] However, recent investigations demonstrate that the compressibilities of materials with a large stability range of pressures (i.e., they do not undergo first-order transformations), such as MgO, CuO, and Ni,[6–8] does not change with particle size. In order to explore the potential mechanism and connection between these two types of compression behaviors, we selected recently synthesized cubic-spinel structure Si_3N_4 nanocrystals,[9] a superhard material with applications in industry and applied physics as well as material science.[10–12] The sample was studied by high-resolution synchrotron radiation to pressures over 1 Mbar. Our results indicate that the particle size effect on compressibility becomes insignificant above a critical pressure. An analysis of this observation provides a feasible explanation and builds a close connection for these two different compression behaviors of nanocrystalline solids.

A sample of Si_3N_4 was synthesized from its hexagonal polymorph (β-phase) by using the shockwave impacting technique.[9] Raman spectroscopy and x-ray diffraction indicate that the obtained Si_3N_4 crystallizes in the cubic-spinel structure. Transmission electron microscopy reveals that Si_3N_4 has a nearly spherical particle size of 30 nm, on average.[9] The sample is almost free of porosity, and has no preferred orientation texture. High-pressure x-ray diffraction measurements were carried out at room temperature by using a gasketed high-pressure diamond anvil cell (DAC). The sample without pressure medium was placed in a T301 steel gasket hole, 60 μm in initial thickness, and 100 μm in diameter. A small piece of platinum was also loaded as a pressure marker. Energy dispersive synchrotron radiation at Cornell High-Energy Synchrotron Source (CHESS) was used for the x-ray diffraction experiments.[3,5] Energy calibrations were made using well-known radiation sources (^{55}Fe and ^{133}Ba), and angle calibrations were made from the six peaks of standard Au powder. Powder x-ray diffraction patterns were collected at pressures to ~120 GPa and cell parameters were refined.

Cell parameters calculated from individual *d* spacings of the observed diffraction peaks from nanocrystalline Si_3N_4 at one atmosphere are shown in Fig. 1(a). As observed previously, bulk materials usually exhibit consistent cell parameters, within small errors, from each of the observed peaks.[13] In nanocrystalline Si_3N_4, however, the cell parameter decreases as the *d* spacing increases. Since nanocrystals include only a small number of unit cells relative to their bulk counterparts, the diffraction planes with large *d* spacings are important determinants of the nanoparticle shell layers. It has been well documented that, upon a decrease in particle size, surface energy is significantly enhanced.[1,2] Such an enhanced surface energy results in a remarkable variation of the sur-

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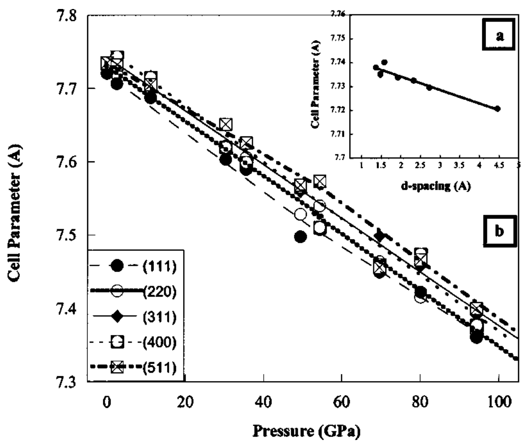

FIG. 1. (a) Relationship between *d* spacing and cell parameter (*a*) of nanocrystalline spinel Si_3N_4 at ambient conditions. (b) Pressure dependences of the cell parameter (*a*) calculated from the observed diffraction planes of nanocrystalline spinel Si_3N_4. Note: Since the other peaks become broad and weak upon compression, a large error may exist, so we did not use those peaks in this plot.

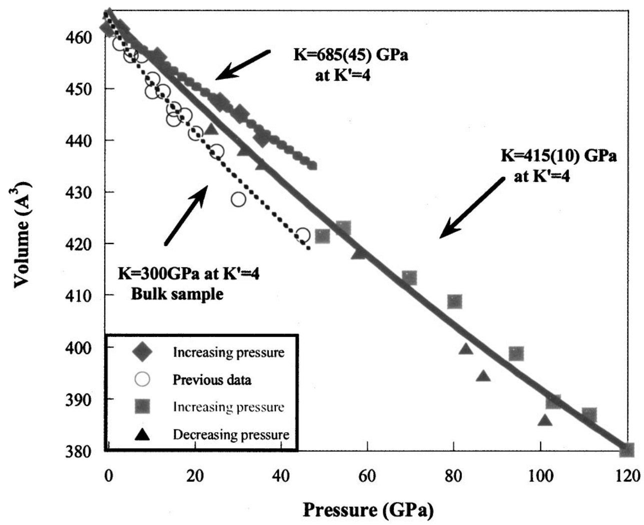

FIG. 2. The EOS curves fitted from the volumetric data obtained at pressures below and above 40 GPa, respectively. Note: Data obtained previously and at decompression in this study are also presented for comparison.

face structural characteristics of nanocrystalline particles, which are reflected in an apparent contraction of the particle surface. This in turn leads to a decrease in the large *d* spacings of the corresponding diffraction planes from the shell layers. Such a size-induced effect is significantly illustrated in nanocrystalline Si_3N_4 [Fig. 1(a)]. The volume of the unit cell was calculated to be 461.7(6) Å^3, which is smaller than a previously reported value of 463.3 Å^3, in which the samples consisted of submicron sized particles.[10,11]

We also calculated cell parameters based on each observed diffraction peak of spinel Si_3N_4 under pressure. As is plotted in Fig. 1(b), the diffracting plane (111), which has the largest *d* spacing, initially exhibits significant compression, whereas the plane (511), which has the smallest *d* spacing, displays lesser compression. At pressures above 40 GPa, the compression of each of the diffraction planes became equivalent. These results imply that significant size-induced effects in Si_3N_4 occur only at pressures below 40 GPa; upon additional compression (>40 GPa), the size-induced effect appears to be suppressed, indicating a considerable weakening of the elastic stiffness.

A third-order Birch–Murnaghan equation of state (EOS) was fit to the observed pressure–volume ($P-V$) data. As is shown in Fig. 2, a noticeable discontinuity appears at ~40 GPa. Therefore, we fit the $P-V$ data with two distinct EOS curves that appear to be reasonably constrained (Fig. 2). It is noticeable that the curve fit to the data above 40 GPa is also consistent with the data obtained upon release of pressure. This curve also matches previous data.[11,12] Upon compression, the bulk modulus below 40 GPa is 685(45) GPa with $K' \equiv 4$, which is greater than that of sintered polycrystalline diamond (490 GPa). Such an extremely high bulk modulus is likely due to the nanocrystalline effect, as is also observed for nanosized (partially amorphous) C_{60} molecular crystals with an extremely high bulk modulus of 800–900 GPa.[14–16] Thus, we find that the application of pressure on Si_3N_4 systematically alters large *d* spacings (i.e., surface effects), while producing a lesser effect on smaller *d* spacings. However, cell parameters are most influenced by the values of the small *d* spacings. Therefore, the initial effect of pressure is to alter the surface to a greater extent than the cell volume. Combining the data from above 40 GPa with that obtained at decompression, the bulk modulus is calculated to be 415(10) GPa with $K' \equiv 4$; somewhat higher than the previous reported value of ~300 GPa for bulk material.[11,12] This suggests that pressure lowers the size-induced effect, rather than eliminating it.

Upon release of pressure, the trend of the collected data is comparable to that collected above 40 GPa in the compression run (Fig. 2). It is shown in Fig. 3(a) that the cell parameters, calculated from the observed peaks during decompression, exhibit a similar pressure dependence, suggesting that the effect in Si_3N_4 is pressure quenchable. Moreover, as for the pressure-quenched sample, the cell parameters corresponding to each diffraction plane are presented in Fig. 3(b). The values of the cell parameter are now consistent, indicating that the size-induced compaction effect on nanoparticle

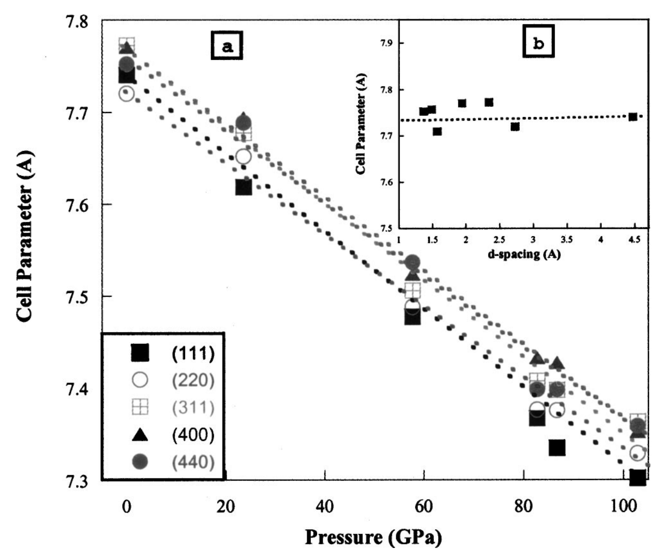

FIG. 3. (a) Pressure dependence of the cell parameter (*a*) calculated from the observed diffraction planes of nanocrystalline spinel Si_3N_4 upon release of pressure. Note: We did not use some broad low intensity peaks, as described in Fig. 1(b). (b) Correlation between *d* spacing and cell parameter (*a*) of the pressure-quenched nanocrystalline spinel Si_3N_4.

shell layers no longer exists. This contrasts the phenomenon observed in the starting sample, as shown in Fig. 1(a).

Previous high-pressure studies identified two types of nanocrystalline materials: One exhibits a larger bulk modulus with a reduction in particle size;[1–5] while the other displays the same compressibility as that in the bulk counterpart.[6–8] As for the first type, all previously studied materials were investigated only at lower pressures.[1–5] A key factor is the low transition pressures in their bulk counterparts. In contrast, the second type of nanocrystal was studied under extreme compression,[6–8] since their bulk counterparts are stable over a wide range of pressure. Nevertheless, the mechanism and connection between those two types of nanocrystals still remain ambiguous. The cubic Si_3N_4 spinel is considered a potential superhard material, so it has recently been studied using several high-pressure techniques, including multianvil, DAC, and shockwave impact.[9–12] Results show that this phase is stable in the cubic-spinel structure at least to 1 Mbar.[9] Therefore, the cubic Si_3N_4 nanocrystals were expected to exhibit the same compressibility as their bulk counterpart. However, our study has demonstrated an unexpected result; at a critical pressure of $\sim$40 GPa, there is a significant weakening of the pressure-induced incompressibility of the spinel Si_3N_4 nanocrystals. The bulk modulus of the nanocrystals is still greater than that previously found for bulk material, but the fitted curve is quite close to the previous data, considering that large errors exist in the high-pressure range (Fig. 2).[11,12] This observation is strongly supported by a recent radial x-ray diffraction measurement,[17] in which the yield strength of nanocrystalline Si_3N_4 increases rapidly with increasing pressure to 45 GPa, and then increases at a much lower rate at higher pressures. Therefore, our interpretation can be used to explain the observed phenomena of other nanocrystals. It is suggested that the size-induced effect plays a vital role in the particular properties of nanocrystals only below the critical pressure, and correspondingly results in an enhancement of the bulk modulus. Upon additional pressure, the size-induced effect weakens and apparently vanishes, consequently leading to the occurrence of the weak and same incompressibility as the bulk counterpart. The disappearance of nanoeffects has also been observed in spinel-structure Ge_3N_4 nanocrystals.[13] The Si_3N_4 spinel is much more incompressible than Ge_3N_4, and the corresponding mechanical and physical properties may persist to very high pressure. This may be one factor that results in the weakness of nanocrystals Si_3N_4, rather than a complete disappearance at a critical pressure. Moreover, the bulk modulus (K) involves both the Young's modulus (E) and Poisson's ratio (μ), and either increase of Young's modulus or Poisson's ratio can lead to an increase of the bulk modulus. Previous studies indicate that a reduction of particle size results in a significant enhancement of both Young's modulus and Poisson's ratio,[18–20] but below a critical size, both of them exhibit a remarkable softening effect.[19,20] Thus, this may suggest that an enhanced bulk modulus in this study results from the size-induced increase of both Young's modulus and Poisson' ratio. However, above the critical pressure, pressure-induced compression in volume makes the grain size approach the critical size, which further results in a significant softening of the bulk modulus. However, our result can further explain why the two types of nanocrystals were observed in previous studies.[1–8] An important consideration is whether the peak pressures in previous runs reached the critical pressure or not. Moreover, our interpretation also suggests why the transition pressure does not change as particle size decreases in those nanocrystals, in which their bulk phases have a large structural stability.[6–8]

In summary, we have carried out *in situ* synchrotron x-ray diffraction to explore a size-induced compressional effect of nanocrystalline cubic spinel Si_3N_4 to pressures over 1 Mbar. Results indicate that at a critical pressure of $\sim$40 GPa, there is a significant weakness of the size-induced effect in nanocrystalline spinel Si_3N_4. Below and above this pressure, the bulk moduli were calculated to be 685(45) and 415(10) GPa, respectively. Upon release of pressure, the weakened properties induced by pressure are retained in Si_3N_4. The size-induced compact effect does not exist in the quenched sample. This result provided a reasonable explanation for the existing irreconcilable compression behaviors of different nanocrystals.

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