Threshold Pressure for Disappearance of Size-Induced Effect in Spinel-Structure Ge_3N_4 Nanocrystals

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We demonstrate that the incompressibility of spinel Ge_3N_4 nanocrystals decreases when the pressure is elevated above ~20 GPa. Ge_3N_4 nanocrystals initially exhibit a higher bulk modulus of 381(2) GPa. But, above 20 GPa, the bulk modulus is apparently reduced to 268(4) GPa, which is similar to the reported bulk modulus of 208−296 GPa for the bulk Ge_3N_4. Thus, a threshold pressure of ~20 GPa was determined that signifies the onset of size-induced disappearance of elastic stiffness in nanocrystalline Ge_3N_4. Enhanced surface energy contributions to the shell layers of nanoparticles and resulting effect on the corresponding large *d* spacing planes are used to elucidate the observed phenomenon. This study provides a reasonable explanation for the different compressibility properties of numerous nanocrystals.

Introduction

Nanocrystalline materials with particle size of 1−100 nm are of current interest in discovering novel physical and chemical properties of materials that may differ from those of the corresponding bulk materials.[1] The structure stability of the nanocrystalline material is of interest for an understanding of the first-order structure transition, which is relevant to many research areas, including the engineering of materials with enhanced mechanical properties.[1,2] Previous high-pressure studies indicate a correlation between increasing transition pressure and decreasing particle size, [3,4] or vice versa.[5,6] These nanocrystals exhibit a higher bulk modulus than their bulk counterparts.[2−6] However, recent investigations demonstrate that the compressibilities of materials with a large stability range of pressures (i.e., they do not undergo first-order phase transformation), such as MgO, CuO, and Ni,[7−9] do not change with particle size. To explore the potential mechanism and connection between these two types of compression behaviors, we selected the newly synthesized cubic-spinel structure Ge_3N_4 nanocrystals,[10] a potential superhard material, similar to the spinel Si_3N_4, with applications in industry and applied physics, as well as material science.[11] The sample was studied by the high-resolution synchrotron radiation to 69.2 GPa. Our results indicate that the size-induced effect on compressibility significantly vanishes above a certain pressure. Analysis of this observation provides a feasible explanation and builds a close connection for these two different compression behaviors of nanocrystalline solids.

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Experimental Section

The sample used here was synthesized from their hexagonal polymorphs (99.99%) by using a 30 mm bore propellant gun with impact velocities up to ~2.0 km/s.[10] Raman spectroscopy and X-ray diffraction indicate that the obtained Ge_3N_4 crystallizes in the cubic-spinel structure without any oxidation. TEM indicates that the spinel has the average nearly spherical particle size of 15 nm (10−20 nm).[10] 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, 70 μm in initial thickness and 120 μm in diameter. A small piece of platinum was also loaded as a pressure marker. An angle dispersive synchrotron radiation at High Pressure Collaborative Access Team (HP-CAT) beam line, Argonne National Laboratory (APS), was used for the X-ray diffraction measurements. A monochromatic beam with a wavelength of 0.3688 Å, which is 10 times the intensity of other comparable third-generation synchrotron facilities, was focused to be 10 μm in size on the sample. A CCD detector located at 249 mm distance from the sample served for collecting the X-ray diffraction pattern. Calibration was made by the standard CeO_2 powder. The collected X-ray diffraction images were integrated by Fit2d program. The reduced X-ray diffraction patterns were thus fitted by the Peakfit package for further refinement of the structure and cell parameters.

Results and Discussions

Cell parameters calculated from individual *d* spacings of the observed diffraction peaks from nanocrystalline and bulk Ge_3N_4

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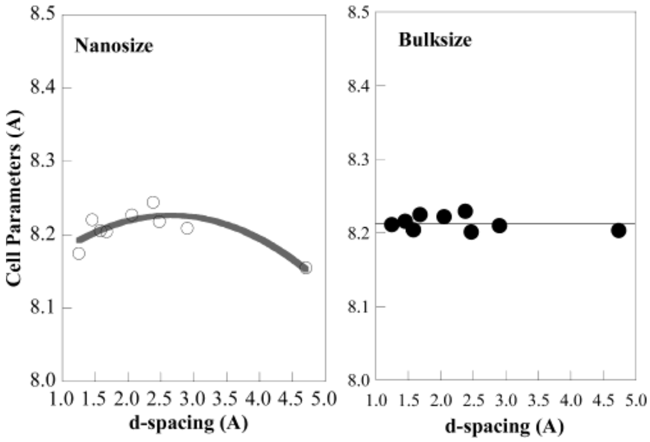

Figure 1. Relationship between *d* spacing and cell parameter (*a*) of spinel Ge_3N_4 at ambient conditions: (a) nanocrystalline; (b) bulk Ge_3N_4.

at 1 atm are shown in Figure 1. As observed previously, bulk materials usually exhibit consistent cell parameters, within small errors, from each of the observed peaks. Results from bulk Ge_3N_4 demonstrate such a conclusion (Figure 1b). In nanocrystalline Ge_3N_4, however, the cell parameter decreases as the *d* spacing increases or decreases (Figure 1a). 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 decrease of particle size, the surface energy is significant elevated.[1,2] Such an enhanced surface energy results in a remarkable variation of the surface 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 Ge_3N_4 (Figure 1a). This mostly results in the variation of the surface structural characteristics of nanocrystalline particles, such as the occurrence of the apparent contraction of the particle surface. As for the observed decrease of the small *d* spacings (Figure 1a), it may be caused by an accumulated effect. The small *d* spacing planes usually are not significantly affected by the size-induced surface contraction. But, if we consider that the shell layers include the small *d* spacing planes more than others, an accumulated effect may result in an observed decrease of the small *d* spacings. Such an analysis can reasonably explain the observation as shown in Figure 1a.

We also calculated cell parameters based on each observed peak of spinel Ge_3N_4 under pressure. As is plotted in Figure 2, the diffracting planes (111) and (220), which have the largest *d* spacings, and the diffracting planes (440) and (533), which have the smallest *d* spacings, initially exhibit significant weak compression, whereas the other planes display higher compression. At pressure above 20 GPa, the compression of each of the diffraction planes became equivalent. These results imply that significant size-induced effects in Ge_3N_4 occur only at pressures below 20 GPa; upon additional compression (>20 GPa), the size-induced effect appears to be suppressed, indicating a remarkable disappearance of the elastic stiffness.

A third-order Birch−Murnaghan equation of state (EOS) was fit to the observed pressure−volume data. As is shown in Figure 3, a noticeable discontinuity appears at ∼20 GPa. Therefore, we fit the *P*−*V* data with two distinct EOS curves that appear to be reasonably constrained (Figure 3). It is noticeable that the curve fit to the data above 20 GPa is also consistent with

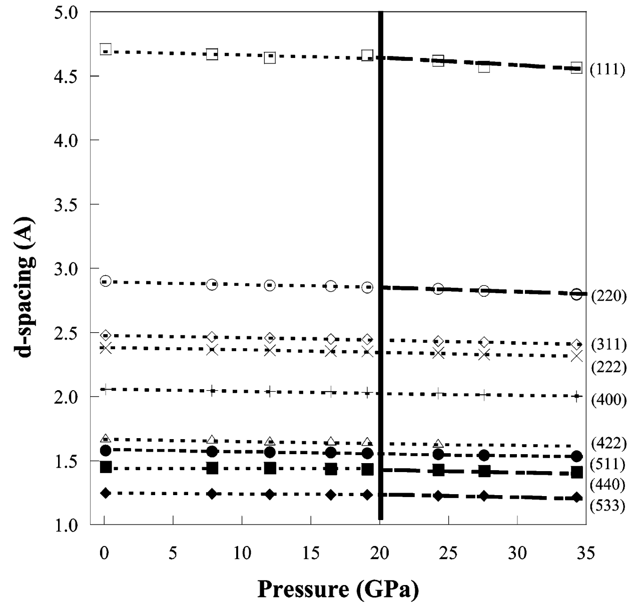

Figure 2. Pressure dependences of *d* spacings calculated from the observed diffraction peaks of nanocrystalline spinel Ge_3N_4.

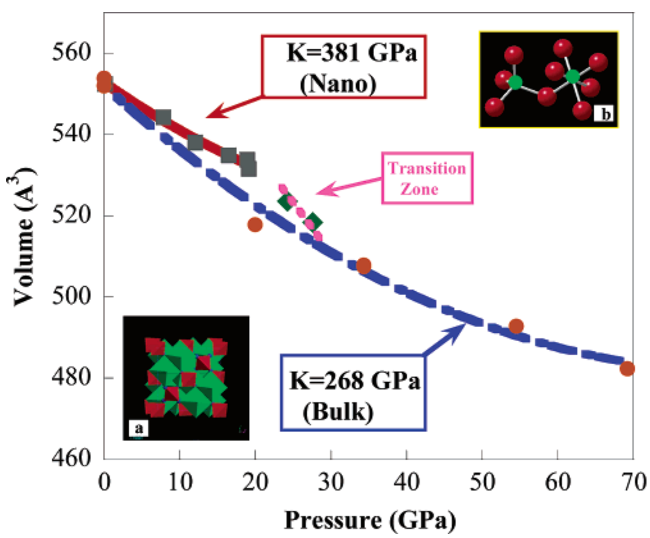

Figure 3. The EOS curves fitted from the volumetric data obtained at pressures below and above 20 GPa. Note: two data points for bulk Ge_3N_4 at 0 and 20 GPa are from refs 12 and 13. Inset a shows the structure of spinel Ge_3N_4 with octahedron (green) and tetrahedron (red); inset b shows details of octahedron and tetrahedron of spinel: green balls represent Ge atoms and red balls represent N atoms.

previous data, obtained from microsize spinel Ge_3N_4.[12,13] Upon compression, the bulk modulus below 20 GPa is 381(2) GPa with $K' = 7.9(1.2)$, which is greater than that of microsize polycrystalline Ge_3N_4 (208−296 GPa). [12,13] Such a high bulk modulus is likely due to the nanocrystalline effect, as also observed for nanosized Si_3N_4 crystals with an extremely high bulk modulus of 684 GPa.[16] Thus we found that application of pressure on Ge_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 20 GPa with previous data, we calculate the bulk modulus to be 268(4) GPa with K' $= 8.1(1.6)$, consistent with the previously reported value of

208−296 GPa for bulk Ge_3N_4 spinel.[12,13] It is noticeable that the K' values fit to $P-V$ data are quite large and greater than the normal value of $K' = 4$ for most solids. Such an unusual result obtained from this study still remains unclear. However, since those two K' values are close and the curve fit to the data above 20 GPa matches bulk data (Figure 3), the comparison is reliable. This suggests that pressure eliminates the size-induced effect at pressures above 20 GPa.

Previous high-pressure studies identified two types of nanocrystalline materials: one exhibits a larger bulk modulus with reduction in particle size,[2−6] while the other displays the same compressibility as that in the bulk counterpart.[7−9] As for the first type, all previously studied materials were investigated only at lower pressures.[2−6] A key factor is the low transition pressures in their bulk counterparts. In contrast, the second type of nanocrystals was studied under extreme compression,[7−9] 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 Ge_3N_4 spinel is considered a potential superhard material, so it has recently been studied using several high-pressure techniques, including multianvil, diamond anvil cell, and shock wave impact.[10,12,13,15] Results show that this phase is stable in the cubic-spinel structure at least to 65 GPa.[10] Therefore, the cubic Ge_3N_4 nanocrystals were expected to exhibit the same compressibility as their bulk counterpart. However, our study has demonstrated an unexpected result; at a threshold pressure of ∼20 GPa, there is a significant disappearance of the pressure-induced incompressibility of the spinel Ge_3N_4 nanocrystals. Such a finding can be applied to explain the observed phenomenon of other nanocrystals. It is suggested that the size-induced effect plays a vital role in the particular properties of nanocrystals only below the threshold pressure and correspondingly results in an enhancement of the bulk modulus; upon additional pressure, the size-induced effect apparently vanishes, consequently leading to the occurrence of the same incompressibility as the bulk counterpart. Moreover, the bulk modulus (K) involves both the Young's modulus (E) and Poisson's ratio (μ), and enhancement of either 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 Young's modulus and of Poisson's ratio,[17−19] but below a critical size, both of them exhibit a remarkable softening effect.[17,18] 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's ratio, but at the above critical pressure, pressure-induced compression in volume makes the grain size approach the critical size, which further results in a significant softening of bulk modulus. However, our result can further explain why the two types of nanocrystals were observed in previous studies.[2−9] An important consideration is whether the peak pressures in previous runs reached the threshold pressure. 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.[7−9]

Conclusion

In summary, we have carried out in situ synchrotron X-ray diffraction to explore the size-induced compressional effect of nanocrystalline cubic-spinel Ge_3N_4 to pressures as high as 69.2 GPa. Results indicate that at a threshold pressure of ∼20 GPa, there is a significant disappearance of the size-induced effect in nanocrystalline spinel Ge_3N_4. Below and above this pressure, the bulk moduli were calculated to be 381(2) and 268(4) GPa, respectively. This result has provided a significant explanation on the existing irreconcilable compression behaviors of different nanocrystals.

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References and Notes

(1) Alivisatos, A. P.; Barbara, P. F.; Castleman, A. W.; Chang, J.; Dixon, D. A.; Klein, M. L.; McLendon, G. L.; Miller, J. S.; Ratner, M. A.; Rossky, P. J.; Stupp, S. I.; Thompson, M. E. *Adv. Mater*. **1998**, *10*, 1297.

(2) Chen, C. C.; Herhold, A. B.; Johnson C. S.; Alivisatos, A. P. *Science* **1997**, *276*, 398.

(3) Tolbert S. H.; Alivisatos, A. P. *Annu. Rev. Phys. Chem.* **1995**, *46*, 595.

(4) Wang, Z. W.; Saxena, S. K.; Pischedda, V.; Liermann, H. P.; Zha, C. S. *J. Phys: Condens. Matter* **2001**, *13*, 8317.

(5) Jiang, J. Z.; Olsen, J. S.; Gerward, L.; Morup, S. *Europhys. Lett*. **1998**, *44*, 620.

(6) Wang, Z. W.; Saxena, S. K.; Pischedda, V.; Liermann, H. P.; Zha, C. S. *Phys. Rev. B* **2001**, *64*, 012102.

(7) Rekhi, S.; Saxena, S. K.; Atlas, Z. D.; Hu, J. *Solid State Commun*. **2000**, *117*, 33.

(8) Wang, Z. W.; Pischedda, V.; Saxena, S. K.; Lazor, P. *Solid State Commun*. **2002**, *121*, 275.

(9) Chen, B.; Penwell, D.; Kruger, M. B. *Solid State Commun*. **2000**, *115*, 191.

(10) He, H. L.; Sekine, T.; Kobayashi, T.; Kimoto, K. *J. Appl. Phys*. **2001**, *90*, 4403.

(11) Zerr, A.; Miehe, G.; Serghiou, G.; Schwarz, M.; Kroke, E.; Riedel, R.; Fuess, H.; Kroll, P.; Boehler, R. *Nature (London)* **1999**, *400*, 340.

(12) Leinenweber, K.; O'Keeffe, M.; Somayazulu, M.; Hubert, H.; McMillan, P. F.; Wolf, G. H. *Chem.*−*Eur. J.* **1999**, *5*, 3076.

(13) Deb, S. K.; Dong, J.; Hubert, H.; McMillan, P. F.; Sankey, O. F. *Solid State Commun*. **2000**, *114*, 137.

(14) Dong, J.; Sankey, O. F.; Deb, S. K.; Wolf, G. H.; McMillan, P. F. *Phys. Rev. B* **2000**, *61*, 11979.

(15) Serghiou, G.; Miehe, G.; Tschauner, O.; Zerr A.; Boehler, R. *J. Chem. Phys.* **1999**, *111*, 4659.

(16) Wang Z. W.; Zhao, Y.; Schiferl, D.; Zha, C. S.; Downs, R. T.; Sekine, T. *Appl. Phys. Lett.* **2003**, *83*, 3174.

(17) Villain, P.; Goudeau, P.; Renault, P. O.; Badawi, K. F. *Appl. Phys. Lett*. **2002**, *81*, 4365.

(18) Shen, T. D.; Koch, C. C.; Tsui T. Y.; Pharr, G. M. *J. Mater. Res.* **1995**, *10*, 2892.

(19) Zhou, Y.; Erb, U.; Aust, K. T.; Palumbo, G. *Scr. Mater*. **2003**, *48*, 825.