Size-Induced Reduction of Transition Pressure and Enhancement of Bulk Modulus of AlN Nanocrystals

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An in situ X-ray-diffraction study of AlN nanocrystals under hydrostatic (or quasihydrostatic) conditions was performed to pressures of 36.9 GPa, using an energy dispersive synchrotron-radiation technique in a diamond-anvil cell (DAC). Hexagonal AlN nanocrystals have a particle size of 10 nm on average, and display an apparent volumetric expansion as compared to the bulk AlN polycrystals. Upon compression to 14.5 GPa, AlN nanocrystals start to transform to a rocksalt structure phase. This pressure is significantly lower than the transition pressure of 22.9 GPa observed from the bulk AlN by using the same technique. The nanosized wurtzite phase has a bulk modulus (B_0) of 321 ± 19 GPa, larger than that of the bulk AlN crystals with a B_0 of 208 GPa. There is a large volumetric decrease of 20.5% upon the wurtzite-to-rocksalt phase transformation. Combination of the size-induced volumetric expansion and resulting softening of the Poisson ratio and shear modulus may explain the reduction of transition pressure in this type of nanomaterials.

Because of the relevance to the engineering of materials with enhanced mechanical properties, nanocrystals have been of considerable interest for current studies in terms of pressure tuning. Previous studies indicate that, as for a large number of materials, decrease of particle size results in an enhancement of elastic modulus,[1–4] but their pressure-induced phase transformations exhibit the two reversal trends: the reduction verses the elevation of the phase transition pressure.[2–4] Enhancement of the bulk modulus and of transition pressure was previously explained by an increased surface energy contribution,[2] but the mechanism resulting in the reduction of transition pressure still remains unclear.[3,4] However, it is observed that the studied nanocrystalline materials that display a weakened transition pressure have the particle size below 15 nm,[3,4] and this is coincidently smaller than the critical size of 15 nm that was observed from numerous nanocrystals.[5–8] Below the critical size, nanocrystals exhibit several reverse properties, such as the volumetric expansion and softening of the Poisson ratio and shear modulus.[5–7] These are different from the nanosize induced volumetric contraction and the enhanced shear modulus. Therefore, we expect that the nanocrystals with a particle size smaller than the critical size may display a reduction of transition pressure for the pressure-induced first-order solid–solid phase transformation. To explore the reliability of such an assumption and any potentially novel mechanism for the ultrafine nanocrystals (<15 nm), AlN nanocrystals with an average particle size of 10 nm were studied by using a Diamond Anvil Cell (DAC) coupled with the high-energy synchrotron X-ray diffraction to 36.9 GPa. The results demonstrate that AlN nanoc-
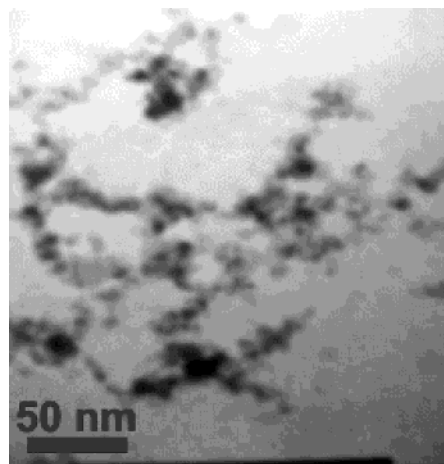
Figure 1. The transmission electronic microscopy (TEM) image of AlN nanocrystals.

rystals exhibit a significant reduction of transition pressure for the wurtzite-to-rocksalt phase transformation, and still display an enhanced bulk modulus.

A sample of AlN used in this study has a nearly spherical particle size of 10(±2) nm, on average (Figure 1). X-ray diffraction characterized that AlN nanocrystals have a hexagonal wurtzite structure. High-pressure X-ray diffraction measurements were performed at room temperature by using a gasketed high-pressure Diamond Anvil Cell (DAC).[1,4] A mixture of ~97% AlN nanopolycrystals and ~3% platinum with the liquid pressure transmission medium (methanol/ethanol 4:1) was loaded in a T301 steeliness gasket hole that is 80 μm in initial thickness and 150 μm in diameter. The liquid pressure medium

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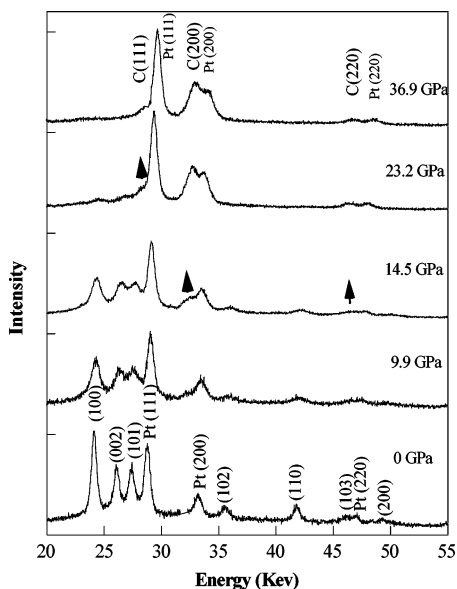**Figure 2.** High-pressure X-ray-diffraction spectra of AlN nanocrystals. Note: The upward arrows (↑) denote the occurrence of the new peaks of the cubic rocksalt AlN phase.
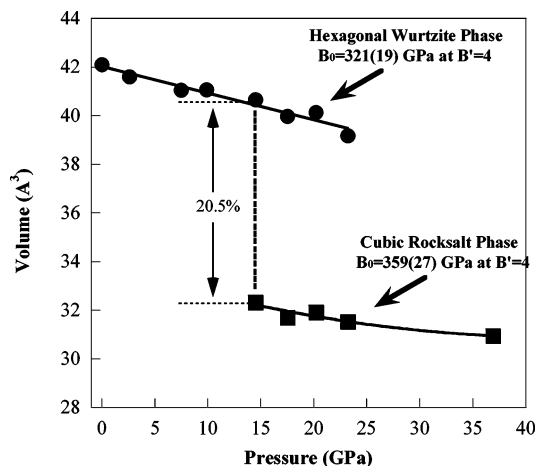

Figure 3. Equation of state (EOS) curve and the relative volumetric variation of AlN upon the phase transformation at 14.5 GPa. Note: For better comparison of the volumetric variation between the two phases, the volumes of the wurtzite and rocksalt phases are shown by the same units of 2AlN, which corresponds to one wurtzite unit cell ($M = 2$) and a half rocksalt unit cell ($M = 4$). M denotes the unit number of AlN in one unit cell.

is used to maintain the sample having a hydrostatic or quasihydrostatic state under pressure, to circumvent the interaction between the particles and possibly resulting enlargement of the particle size, as well as the generation of the large pressure gradient in the sample. Platinum serves to read the pressure at each X-ray diffraction collection. Energy dispersive synchrotron radiation at CHESS was used for X-ray diffraction measurements.[1,4] Energy calibrations were made by using well-known radiation sources (^{55}Fe and ^{133}Ba), and angle calibrations at a fixed angle of 11° (2θ) were made from the six peaks of standard Au powder. Powder X-ray diffraction patterns were collected to pressures of ∼36.9 GPa for the determination of structure and refinement of cell parameters.

Figure 2 shows X-ray diffraction patterns of AlN nanocrystals to pressures of 36.9 GPa. The unit cell parameters are calculated from the X-ray diffraction peaks of the starting sample at 1 atm of pressure, which show a pure hexagonal wurtzite phase with $a_0 = 3.1203(9)$ Å, $c_0 = 4.9921(12)$ Å, and $V_0 = 42.09(8)$Å^3. As compared to the reported unit cell parameters of the AlN macrocrystals with $a_0 = 3.114$ Å, $c_0 = 4.9792$ Å, and $V_0 = 41.74$Å^3,[9] it is clear that both the a- and c-axis exhibit an apparent enlargement, and that the enlargement of the c-axis is slightly greater than that of the a-axis. The unit cell volume is 0.8% larger than that of the bulk AlN crystal. This confirms that the size-induced volumetric expansion apparently occurs in such ultrafine nanocrystals, and differs from the volumetric contraction observed from the large numbers of nanocrystalline materials that have the particle size larger than the critical size of 15 nm.

Upon elevation of pressure to 14.5 GPa, several new peaks of the high-pressure phase started to emerge. This pressure is drastically lower than the phase transition pressures of 22.9 and 21 GPa, which were observed from the bulk AlN polycrystals by using the same technique and the shock wave impact technique, respectively.[10-12] Previous studies have demonstrated that the cold compression DAC data are quite compatible with the shock wave-impacted data, so the comparison between this study and the above two types of high-pressure results is reliable. But, one pressure study performed at in situ pressure heating conditions produces a quite low transition pressure of 16.5 GPa.[12] As is well-known, in situ heating can significantly

overcome the existing energy gap upon the phase transformation, and correspondingly lead to the occurrence of the lower transition pressure and further speed up the accomplishment of the phase transformation, so it is reasonable to observe a lower transition pressure at in situ heating conditions relative to that under cold compression.[10,12] Moreover, we have to consider the effect of the pressure-induced nonhydrostaticity in the sample, because the large pressure gradient can result in a significant decrease of transition pressure. In this study, we use the liquid pressure transmission medium to maintain a hydrostatic condition, and this type of pressure medium (M:E 4:1) is able to maintain a hydrostatic state up to 15 GPa, and above 15 GPa, the solidification of the liquid medium leads to the occurrence of the quasihydrostaticity in the sample chamber. Because the observed transition pressure of 14.5 GPa is located within the hydrostatic pressure range, it is thus believed that such a reduced transition pressure is not caused by the large pressure gradient across the sample. As a result, it is guaranteed that the observed transition pressure is truly lower than that of the bulk AlN crystals.

The high-pressure phase of AlN was indexed to the cubic rocksalt structure with the unit cell parameters of $a = 4.0133$ Å and $V = 64.64$ Å^3 and four units of AlN per unit cell at a pressure of 14.5 GPa. The bulk modulus of the rocksalt phase was calculated to be 359(27) GPa at a fixed $B_0' = 4$, which is slightly higher than the B_0 of 285−329 GPa obtained from the bulk AlN polycrystals.[13] At the phase transition pressure of 14.5 GPa, the high-pressure rocksalt phase is 20.5% denser than the hexagonal wurtzite phase (Figure 3). Upon release of pressure, the rocksalt phase was preserved at 1-atm pressure conditions. Previous study indicates that the high-pressure rocksalt phase is not quenchable upon decompression to zero pressure in the case of no in situ heating under pressure.[10] However, it should be pointed out that the peak pressure in that study was reached only to 30 GPa. Thus, combining previous results with this study that reached the peak pressure of 36.9 GPa, it is reasonably suggested that a critical pressure representing the completion of the phase transition is around 35 GPa. At ambient conditions, the cell parameters of the rocksalt phase were calculated to be $a_0 = 4.0445(3)$ Å and $V_0 = 66.16$ Å^3, which has no significant difference from that obtained from in situ high-temperature high-

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TABLE 1: Parameters for the Transition and Equation of State (EOS) Data of the Wurtzite-to-Rocksalt Phase Transformation

method	particle size	transition pressure (GPa)	ΔV (%)	B_0 (GPa)	B'	ref
X-ray diffraction	bulk	22.9	18.0	208	6.3	10
quench (1400−1600 °C)	bulk	16.5	20.6			12
shock wave	bulk	21.0	22.0			11
X-ray diffraction	nanosize	14.5	20.5	321	4.0	*a*

a This study.

pressure conditions.[12] This is likely caused by a pressure-induced increase of particle size.[14]

Figure 3 shows the equation of state (EOS) data of AlN nanocrystals to pressures of 36.9 GPa. A fit to the Birch−Murnaghan EOS of the hexagonal wurtzite phase gives the bulk modulus $B_0 = 321(19)$ GPa at a fixed $B_0' = 4$. This is significantly greater than the B_0 of 208 GPa observed from the bulk AlN crystals (Table 1).[10−12] Therefore, this indicates that the reduction of particle size can significantly lead to an enhancement of the bulk modulus. This is consistent with the previous studies on a significant ratio of nanocrystals.[1−4]

Numerous studies on nanosized materials indicate that the decrease of particle size leads to an apparent elevation of phase transition pressure and of bulk modulus as compared to their bulk counterparts.[1,2] But, recent studies on γ-Fe$_2$O$_3$ and CeO$_2$ nanocrystals reveal that the decrease of particle size results in a significant reduction of the phase transformation pressure for the pressure-induced first-order solid−solid-phase transformation.[3,4] The enhancement of bulk modulus can easily be explained by a higher surface energy contribution, but the mechanism resulting in a reverse variation of phase transition pressure remains unclear. Moreover, at 1-atm pressure conditions, studies uncovered the existence of a critical size for a large number of nanocrystalline materials, and such a critical size was observed mostly to be around 15 nm.[5−7] Above the critical size, nanocrystals typically exhibit an apparent volumetric contraction, but below the critical size, they display a reverse volumetric expansion together with a noticeable softening of the Poisson ratio and of shear modulus.[5−8] It is also noticed that, as for these nanocrystals (e.g. γ-Fe$_2$O$_3$ and CeO$_2$) that exhibit a reduced transition pressure in the pressure-induced first-order solid−solid-phase transformation, the particle sizes of the nanocrystals studied previously are coincidently smaller than the critical size of 15 nm.[3,4] Thus, it is logically suggested that the combination of the size-induced volume expansion and softening of the Poisson ratio and shear modulus may play a crucial role in the reduction of the transition pressure for the first-order solid−solid-phase transformation in these nanomaterials, such as γ-Fe$_2$O$_3$, AlN, and CeO$_2$. Since these nanomaterials continue to exhibit an enhanced bulk modulus, while the particle size is smaller than the critical size, it is implied that the higher surface energy contribution still puts a considerable impact on the enhanced bulk modulus. It must be pointed out that CdSe nanocrystals with a particle size of 4.4 nm do not

exhibit a reduced transition pressure, and instead an increased transition pressure was observed.[2] However, recent study indicates that CdSe nanocrystals with a particle size ranging from 2.5 to 6 nm unexpectedly display an apparent volumetric contraction,[15] rather than an expansion. Thus, this allows us to conclude that the reduction of phase transition pressure observed in these ultrafine nanocrystals (e.g. γ-Fe$_2$O$_3$, AlN, and CeO$_2$) results from the size-induced volumetric expansion and the softening of both the Poisson ratio and shear modulus.

In summary, we have investigated the AlN nanocrystals to 36.9 GPa at room temperature and at a hydrostatic or quasihydrostatic condition by using high-energy synchrotron X-ray diffraction. AlN nanocrystals have an average particle size of 10 nm and exhibit a noticeable volumetric expansion, which is 0.8% larger than the bulk AlN. The wurtzite AlN nanocrystals initially transform to the rocksalt structure at 14.5 GPa, which is significantly lower than that observed from the bulk AlN polycrystals. The bulk modulus of the wurtzite phase is 321(19) GPa at a fixed $B_0 = 4$, which is notably greater than that of the bulk AlN of 208 GPa. It is suggested that the combination of the volume expansion and the softening of the Poisson ratio and shear modulus results in the reduction of the phase transition pressure, and that a higher surface energy contribution still casts a crucial effect on the enhanced bulk modulus of these types of nanomaterials.

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