Lack of the critical pressure for weakening of size-induced stiffness in 3C–SiC nanocrystals under hydrostatic compression

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Using *in situ* high-pressure x-ray diffraction methods, the compressibility of 30 nm 3C–SiC nanocrystals was studied under hydrostatic conditions while helium was used as pressure transmitting medium, as well as under nonhydrostatic conditions without pressure medium. No threshold pressure phenomenon was observed for the compressibility of the nanocrystals during compression in hydrostatic conditions, while the critical pressure around 10.5 GPa was observed during nonhydrostatic compression. These indicate that the threshold pressure phenomena, recently reported that the nanocrystals initially exhibited much higher bulk modulus below the threshold pressure during compression [Appl. Phys. Lett. **83**, 3174 (2003); J. Phys. Chem. **107**, 14151 (2003)], were mainly caused by the nonhydrostatic effect instead of a specific feature of nanocrystals upon compression. The bulk modulus of 3C–SiC nanocrystals is estimated as 220.6±0.6 GPa based on the hydrostatic compression data. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1789240]

Studies of compressibility and pressure induced phase transitions for nanocrystalline materials can improve our understanding of the stable state of materials down to nanometer scale. This field has drawn extensive attention in the last decade, and numerous types of samples with various nanoscale grain sizes were reported for high pressure study.[1–15] Very recently, a threshold pressure phenomenon was proposed as a general compressing behavior of nanocrystals based on the high pressure *in situ* x-ray diffraction (XRD) studies on Si_3N_4 (with average grain size about 30 nm) and Ge_3N_4 (with average grain size about 15 nm).[16,17] The nanocrystals initially exhibited extremely high bulk moduli below the threshold pressure, then the bulk moduli were significantly reduced above the corresponding threshold pressure during compression. However, this conclusion is doubtable because both of these high pressure studies were carried out under nonhydrostatic conditions without using any pressure medium.[16,17] It is well known that "harder to compress" behavior of materials under nonhydrostatic conditions than the corresponding (quasi-)hydrostatic conditions, and this behavior was well documented in numerous high pressure experimental reports. For example, Duffy *et al.* summarized compression behavior of four materials (Mg_2SiO_4, MgO, $Mg(OH)_2$, and Re) representative of different class of solids under nonhydrostatic and quasihydrostatic conditions. In all cases, the nonhydrostatic compression curve yields a volume above the quasihydrostatic curve at a given pressure. As a result, the bulk modulus determined under nonhydrostatic conditions may be incorrect.[18] Therefore, it is necessary to critically exam the nonhydrostatic effect on the compressibility study on nanoscale materials before conclude to the proposed "threshold pressure" as a specific feature for nanocrystals.

In this report, 3C–SiC nanocrystals were chosen as a samples to clear the hydrostatic and nonhydrostatic effect on the compressibility of nanocrystals. Nanocrystalline 3C–SiC sample in the present study was synthesized by laser induced vapor phase reactions, and was characterized as nearly spherical particles with mean grain size about 30 nm.[19] Three *in situ* high pressure XRD experiments were designed to simulate hydrostatic, quasihydrostatic and nonhydrostatic conditions by using helium as pressure medium, silicone oil as pressure medium, and without pressure medium, respectively. The high pressure experiments were carried out in a diamond anvil cell (DAC) apparatus at room temperature. The sample was loaded in a hole of T301 steel gasket. The pressure was calibrated by the ruby luminescence method.[20] For helium medium experiments, the angle-dispersive x-ray powder diffraction (ADXRD) experiments ($\lambda = 0.4228$ Å) in a DAC were performed at beam line ID-B, HPCAT, Advanced Photon Source (APS), Argonne National Laboratory. Diffraction patterns were recorded on an image plate and then integrated by using the program FIT2D.[21] The energy dispersive x-ray diffraction (EDXRD) experiments for silicone oil medium and no medium cases were carried out at beamline X17C of National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Ge solid state detector was used to collect diffraction patterns.

The lattice parameters of nanocrystalline 3C–SiC under various pressure conditions were refined based on the whole patterns LeBail refinement. Figure 1 demonstrates the corre-

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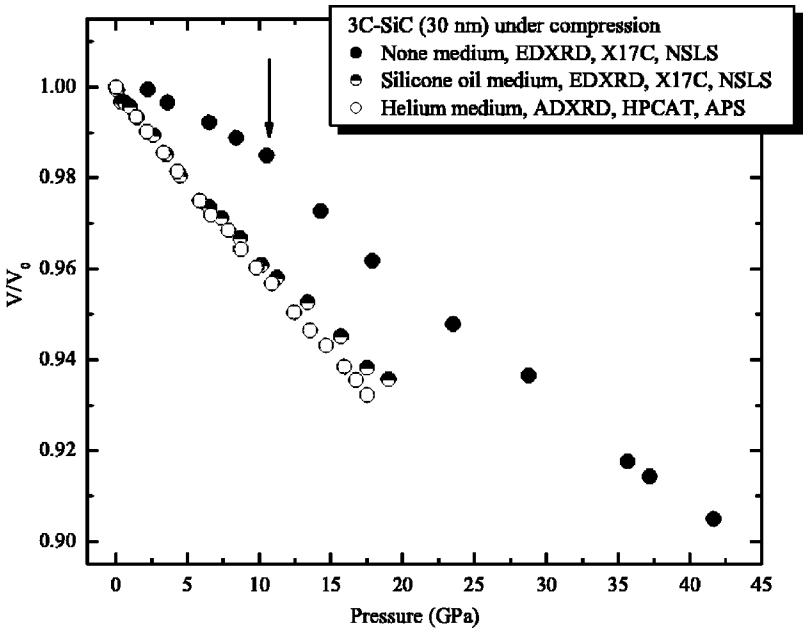

FIG. 1. Change of the relative volume of 30 nm 3C–SiC as a function of pressure, in which open circles, half filled circle, and solid circles represent experimental data obtained in hydrostatic (helium medium), quasihydrostatic (silicone oil medium) and nonhydrostatic (no pressure medium) compression processes in this study, respectively. The error bars are omitted since smaller than the symbol size.

sponding relative volumes of sample under three conditions change as a function of pressure. In the no pressure medium compression, the "critical pressure" phenomenon was observed for the nanocrystalline 3C–SiC and the critical pressure is about 10.5 GPa (marked by an arrow in Fig. 1). However, this phenomenon did not appear when pressure medium of silicone oil or helium were used. This clearly indicates that the critical pressure phenomenon caused mainly by the nonhydrostatic effect, and not caused by the size effect from the nanocrystalline sample.

In fact, for the bulk materials samples, the nonhydrostatic unaxial stress could generate so called "critical pressure" phenomenon during compression. For example, four cubic Laves phases of $PrCo_2$, $NdCo_2$, $SmCo_2$, and $TbCo_2$ were studied by comparison their compressibility under nonhydrostatic and quasihydrostatic by using different pressure media,[22] in which the threshold pressures could also be assigned for the nonhydrostatic compression processes. On the other hand, generating nonhydrostatic conditions combined with high pressure radial diffraction technique, more elasticity and shear strength information of the sample under nonhydrostatically compression in an opposed anvil cell device could be obtained,[23] and lots of interesting materials, such as Au and Re,[18] MgO,[24] Pt,[25] etc. were studied in last decade. The effect of the plasticity on the elasticity measurement from high pressure radial diffraction data was pointed out recently,[26] and this will limit the radial diffraction technique to the relative lower pressure range before the stress fields higher than the yield strength of the materials only if researcher targets to obtain the actual values of the elastic moduli.

The equation of state (EoS) parameters of nanocrystalline 3C–SiC were fitted according to Birch EoS,[27] and results were summarized in Table I, together with the measured results for bulk 3C–SiC for comparison.[28–30] The bulk modulus of the nanocrystalline 3C–SiC is estimated as 220.6 ± 0.6 GPa when kept B_0' as 4 based on the hydrostatic data. If fitting via third order Birch EoS, the $B_0 = 226.8\pm2.3$ GPa while $B_0' = 3.0\pm0.3$. These results are in good agreement with the result for bulk 3C–SiC from high pressure XRD under helium medium in Ref. 28. These indicate that there is no obvious difference on compressibility between nanocrystalline (~30 nm) and bulk 3C–SiC. Helium is the best pressure transmitting medium which could generate hydrostatic pressure conditions to at least 50 GPa.[31] However, a carefully loading sample to avoid "bridging" diamond anvils is still critical for the hydrostatic high pressure experiment, otherwise a detectable nonhydrostatic stress component could be observed at a relatively low pressure range.[32] The reliable equation of state parameters could be

TABLE I. Summary of equation of state parameters (bulk modulus and its pressure derivative) of 30 nm nanocrystalline and bulk 3C–SiC at room temperature measured by XRD methods.

3C–SiC sample type	B_o(GPa)	B_0'	Pressure medium	Pressure range (GPa)	Reference and year
Nanocrystal (30 nm)	721±50	4 (fixed)	no medium	10.5	This work, 2004
	362±13	4 (fixed)		41.7	
	243.3±1.8	4 (fixed)	silicone oil	19.0	
	220.6±0.6	4 (fixed)	helium	17.5	
	226.8±2.3	3.0±0.3			
Bulk	227±3	4.1±0.1	helium	42.5	28, 1991
	260±9	2.9±0.3	methanol/ethanol/water	95	29, 1993
	248±9	4.0±0.3	methanol/ethanol	25	30, 1987

obtained when care is taken during sample loading even helium is used as pressure medium.

In principle, physical meaningful EoS parameters could not be deduced based on the relative volume versus pressure data obtained under nonhydrostatic conditions. However, it is interesting to compare the bulk modulus difference between the nonhydrostatic, quasihydrostatic, and hydrostatic conditions. Table I lists the B_0 values of nanocrystalline 3C–SiC estimated by fitting Birch EoS at various pressure medium conditions. It is clear that the overestimation trend of B_0 under quasi- and nonhydrostatic conditions. In particular, B_0 can be estimated as 721 ± 50 GPa based on the V–P data within the "critical pressure" range (<10.5 GPa) under nonhydrostatic conditions, which is about 320% higher than its bulk modulus value deduced from hydrostatic data. This extremely high bulk modulus value has no directly link with the 'size-induced stiffness' in nanocrystals.

From nonhydrostatic conditions high pressure XRD, the macro- and microstrain and their dependence on grain size of nanometer SiC, were studied, by taking advantage of the nonhydrostatic conditions could highlight the effects of generation of strains originating at the contacts between the nanoscale grains.[33–36] The core-shell model was proposed to explain, beside the nonhydrostatic effect, the stages relation between the compressibility and the microstructure of the nanometer SiC.[33] The "apparent lattice parameter" method was developed for the diffraction research on nanometer 3C–SiC.[34–36] It is noticed that the lattice parameter in grain size of 30 nm has no severe dependence on the diffraction vector compared to a smaller grain size such as 3 nm.[33] Hence in the present work, the lattice parameters of 30 nm nanocrystalline 3C–SiC obtained by whole pattern LeBail refinements could deduced reliable EoS parameters of nanometer SiC. If nano-SiC with much smaller average grain size, for example, around 3 nm, is studied, atomic pair distribution function technique could be used to analyze its broad Bragg peaks and diffuses scattering patterns after the background is carefully removed.[37] Then the EoS parameters will be a challenge to be estimated, but it will be interesting to highlight the size effect down to several nanometer scale.

In summary, the "threshold pressure" phenomenon was not observed for the compressibility study of the 30 nm 3C–SiC nanocrystals during compression in hydrostatic conditions, while the critical pressure around 10.5 GPa was observed during nonhydrostatic compression. These indicate that the recently reported threshold pressure phenomena in nanocrystals were mainly caused by the nonhydrostatic effect instead of a specific feature of nanocrystals upon compression. The bulk modulus of 3C–SiC nanocrystals is estimated as 220.6 ± 0.6 GPa based on the hydrostatic compression data, which has no obvious difference with its bulk counterpart.

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