

The effect of particle size on the structural transitions in zinc sulfide

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(Received 10 July 2000; accepted for publication 29 September 2000)

Studies of pressure induced phase transformations of ZnS nanoparticles using diamond anvil cells and synchrotron radiation were carried out to 20.0 GPa. Nanoparticles initially in the zinc-blende and wurtzite phases both transformed to the NaCl phase under the application of pressure. The zinc-blende particles, which were of 2.8 nm size, and the wurtzite particles, which were of 25.3 nm size, transformed to the NaCl phase at 19.0 and 15.0 GPa, respectively. Nanoparticles of the wurtzite phase never regained their initial wurtzite structure but returned to the zinc-blende phase upon downloading the pressure. The resultant zinc-blende nanoparticles transformed to the NaCl phase upon the reapplication of a pressure of 15.0 GPa. Nanoparticles initially in the zinc-blende phase returned to their original phase. © 2001 American Institute of Physics.
[DOI: 10.1063/1.1328066]

I. INTRODUCTION

Semiconductors with dimensions in the nanometer realm are important because their optical, electrical, and chemical properties can be tuned with particle size. This feature makes them attractive candidates for device applications. Interest in these materials is further heightened by the fact that their electro-optical properties arise from quantum confinement effects and because their thermodynamic properties are dominated by surface effects.¹ Nanometer-sized particles of PbS, CdS, and CdSe show lattice distortions from their bulk counterparts as well as the presence of residual strain.²⁻⁵ Recently, Goldstein *et al.* reported that nanoparticles of CdS melt at a temperature which is substantially below that of the bulk material.⁶

The II–VI semiconductor ZnS is used in many applications primarily for its luminescent properties. Although it has been reported to exist in a variety of polytypes, at standard temperature and pressure (STP) it is known to adopt a crystal structure of either cubic, zinc-blende phase (B3 phase in the *Strukturbericht* notation), or the hexagonal, wurtzite phase (B4). The luminescent properties of the B4 phase are considerably greater than the B3 phase, however the B3 phase is the more stable structure at STP. Upon application of 1020 °C and 0.1 MPa to bulk ZnS, the B3 phase transforms into the B4 phase. Recent high temperature experiments performed at the Naval Research Laboratory revealed a significant reduction in the B3 to B4 transition temperature with reduced particle size.⁷ Nanoparticles of ZnS were found to undergo zinc-blende to wurtzite transformation at a temperature at least 600 °C below that of the bulk phase transition

temperature. Commercial phosphors are often fired at temperatures near 1000 °C to optimize luminescence. A potential advantage, therefore, exists in using nanoparticles of ZnS since the high temperature wurtzite phase can be attained by heating to relatively low temperatures, around 400–500 °C, thus reducing the cost of processing. Another advantage is that the particles can be annealed directly on glass screens, which typically soften at temperatures above 600 °C. It is subsequently important to find the pressure tolerance for nanoparticles in the B4 phase, in order to determine their operational limits in the presence of high pressure conditions.

In previous studies the semiconductor-to-metal transition pressure (P_t) of bulk ZnS was reported to be in the range from 14.0 to 24.0 GPa.^{8,9} From shock studies, P_t was estimated to be 17.4 ± 1.2 GPa.¹⁰ Recent angle dispersive and energy dispersive x-ray diffraction experiments have indicated a transition from the B4-to-B3 phase in the 8–12 GPa range followed by a transition from B3 to the cubic NaCl (B1) phase at 12.4–13.5 GPa. Particles initially in the B3 phase showed the onset of the B1 phase at 8 GPa. The B3 and B1 phases coexisted up to 13 GPa. at which point the transition from B3 to B1 was completed. In their study, the authors do not mention the particle size.¹¹ Recent high pressure experiments based on resistivity measurements of ZnS revealed the strong dependency of P_t on the particle size, where P_t varied between 15.6 ± 0.3 , 19.0 ± 0.4 , and 20.5 ± 0.6 GPa for particles of 10 μm , 36 nm, and 11 nm, respectively. The experiments stressed the need to specify the particle size when reporting the transition pressure of a II–VI

semiconductor.¹² In this article we report the effect of particle size on the B3-to-B1 transition pressure of ZnS. We also study the stability of nanoparticles in the wurtzite phase upon the application of pressure and present the compressibilities of the B4 and B3 phases.

II. EXPERIMENT

The ZnS:Mn (Mn ~0.5 at. %) nanometer-sized particles were synthesized using a technique in which the bicontinuous cubic phase exhibited by some lipids and surfactants is used as a matrix to provide a uniform nanometer-sized reaction chamber for the formation of the particles.¹³ Powders of two different particle sizes were used in this work: 2.8 ± 0.1 nm and 25.3 ± 0.9 nm. Particle sizes were obtained by using x-ray diffraction scans on a powder diffractometer and by high resolution transmission electron microscopy. The ZnS powders were mixed with a pressure calibrant of either NaCl or Au (both 1–2 μm) and loaded in a 100 μm diameter hole in a stainless steel gasket of a diamond-anvil pressure cell. Methanol–ethanol 4:1 fluid was used as hydrostatic-pressure medium for all the runs. Pressure was determined from the appropriate equation of state.

Data were collected using energy dispersive diffraction facility on the superconducting-wiggler beam line (X17C) at the National Synchrotron Light Source, Brookhaven National Laboratory. The detector was set at an angle of $2\theta = 13.0^\circ$ for all the measurements. Additional details are reported elsewhere.¹⁴

III. RESULTS

In the absence of strain, the particle sizes can be determined from the full width at half maximum (FWHM) of the standard x-ray diffraction peaks using Scherrer's formula.¹⁵ We have modified the standard Scherrer's equation for energy dispersive x-ray diffraction spectra as follows:

$$\tau = \frac{0.94 * Ed}{\Delta E}, \quad (1)$$

where τ is the particle size in angstrom, ΔE is the FWHM of the Bragg peak in keV, and d is the interplanar spacing in angstrom.⁴ The instrumental broadening was deconvoluted from the measured peaks using the Bragg peaks of the pressure calibrant NaCl whose particle size was 1–2 μm . The corrected FWHM for the ZnS peak can be computed from the following equation:

$$[(\Delta E_{\text{ZnS}})_m]^2 = [(\Delta E_{\text{NaCl}})]^2 + [(\Delta E_{\text{ZnS}})_c]^2, \quad (2)$$

where the subscripts m and c refer to the measured and calculated FWHMs of the ZnS peaks respectively, and ΔE_{NaCl} is the FWHM of the NaCl peak closest to the ZnS peak in the spectrum under consideration.

In the presence of strain, the contribution of strain and particle size to the FWHM of the diffraction peaks, can be calculated by using the following equation for the energy-dispersive x-ray diffraction case:¹⁶

$$\Delta E^2 = K_\epsilon E^2 + \left(\frac{c}{\tau}\right)^2, \quad (3)$$

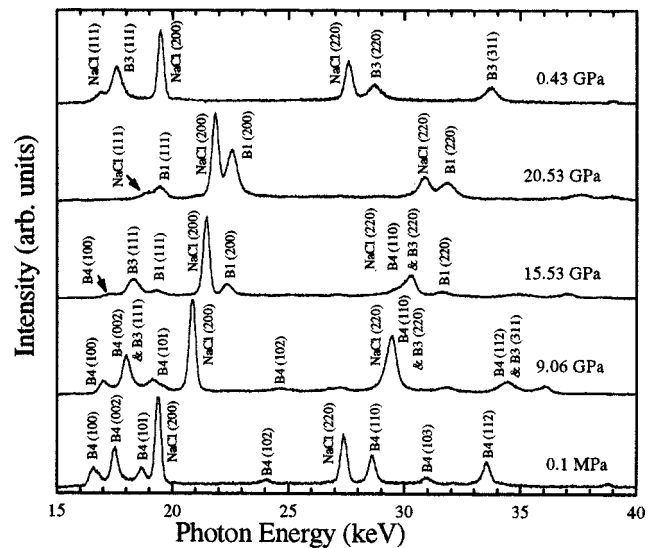


FIG. 1. Diffraction spectra for the 25.3 nm ZnS particles recorded at selected pressures showing the onset of the B4-to-B3-to-B1 transitions using NaCl as the internal pressure calibrant.

where ΔE is the FWHM of the diffraction peak in keV after removing the experimental broadening, K_ϵ the strain, and $c = Ed = 6.1992/\sin \theta$ (a constant). In order to determine K_ϵ and τ from the experimental data, ΔE^2 should be plotted as a function of E^2 . The particle size can be calculated from the intercept of a linear least square fit to the data and the slope gives information about the strain. If the slope is zero then there is no strain and Eq. (3) is essentially the same as Eq. (2) and the particle size can be calculated from either of them.

A. ZnS particles of 25.3 nm size

The 25.3 nm particles in the B4 phase were observed to undergo gradual B4-to-B3-to-B1 transitions as they were placed under increasing pressure. A series of energy dispersive x-ray spectra at selected pressures is shown in Fig. 1 where NaCl is used as an internal pressure calibrant. The NaCl (111) peak is merged with the B4 (002) peak so that only one peak is visible. As the B3 phase appears, the B3 (111), (220), and (311) peaks overlap with the B4 (002), (110), and (112) peaks, respectively. The onset of the B3 phase is, therefore, manifested by the relative increase in the overlapping B3 and B4 peaks, such as B4(002)/B3(111), to the nonoverlapping B4 peaks such as B4 (100) and B4 (101). Our experiments with nanoparticles using angular dispersive x-ray diffraction and an image plate detector showed continuous diffraction rings indicating the absence of preferred orientation in the nanoparticles while under pressure using a diamond-anvil cell. At a pressure above 0.5 GPa, peaks corresponding to the B3 phase begin to appear in the spectrum as indicated by the relative increase of the merged B4(002) and B3(111) peak with respect to the B4 (100), (101), (102), and (103) peaks. The B4 and B3 phases coexist, with a continuous shift towards the B3 phase as the pressure increases, until approximately 16 GPa where all nonoverlapping B4 peaks finally disappear from the spectrum. At 15 GPa, peaks corresponding to the B1 phase appear. The B3 and B1 phases

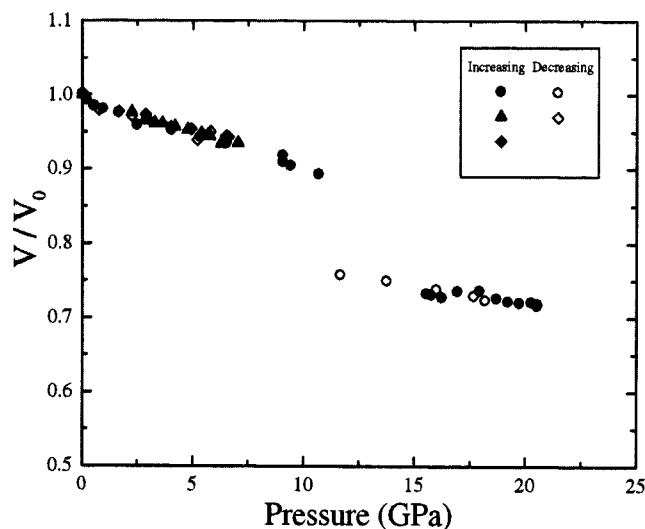


FIG. 2. V/V_0 as a function of pressure for 25.3 nm ZnS particles.

coexist as a mixed phase with a continuous shift towards B1 as the pressure increases until 18.7 GPa where the transition to the B1 phase is completed and all peaks in the spectrum correspond to the ZnS B1 phase or to the internal pressure calibrant, NaCl. Upon the release of pressure the B4 phase was not recovered but instead the B3 phase was retained. This is evident since all B4 specific peaks are absent from the spectrum and because the previously merged B3(111), B4(002), and NaCl(111) can be distinguished as separate B3(111) and NaCl(111) peaks. Figure 2 shows the reduced V/V_0 as a function of pressure for the nanoparticles of ZnS initially in the B4 structure. Different symbols in this figure correspond to different pressure runs and the open symbols correspond to data taken on the decreasing pressure cycle. Since only the B3 phase was retained on the decreasing cycle the reduced V/V_0 corresponds to only the B3 phase. It is clear from this figure that the compressibilities of the B3 and B4 phases are equivalent. Reapplication of pressure to the recovered B3 nanoparticles again caused an onset of a transformation to the B1 phase at a pressure of 15.0 GPa, and there was a likewise return to the B3 phase as the pressure was decreased. In order to observe the B4-to-B3 transition without the interference of the NaCl peaks, we loaded the 25.3 nm B4 ZnS particles into the diamond-anvil cell and ran a separate trial. The pressure was estimated by comparing the ZnS d spacings with those of our previous trial where NaCl was used as an internal pressure calibrant. Figure 3 shows the series of spectra as a function of pressure along with a spectrum at ambient conditions after downloading the pressure. In this figure, the peaks corresponding to the B4 phase have been identified along with those of ZnO. The small quantity of ZnO is generated during the synthesis of ZnS in the B4 phase. The small ZnO peaks were present in all data runs using the B4 nanoparticles, but usually less distinguishable where internal pressure calibrants were used. Upon application of pressure, the peaks rapidly disappear. The onset of the B3 phase can be observed at 0.5 GPa where the merged B3(111) and B4(002) peak becomes significantly larger than the diminishing B4(100) and (101) peaks. After

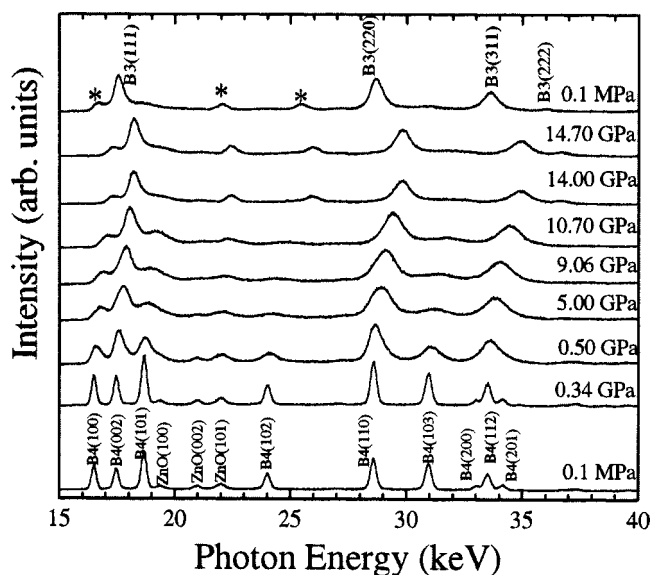


FIG. 3. Diffraction spectra for the 25.3 nm ZnS particles recorded at selected pressures showing the onset of B3 phase and its coexistence with B4 phase. B3 phase is retained at 0.001 GPa.

downloading the pressure the B4 phase was not recovered, however, the maximum pressure of the experiment was not sufficient to complete an absolute B4-to-B3 transition, which was observed at about 16 GPa in the previous trial, therefore some remnant B4 nanoparticles remain as indicated by the continuous presence of the B4(100) peak. The experiment showed that the wurtzite phase is unstable when subjected to pressures even as low as 0.5 GPa. Similar results were reported in the experiments conducted by Desgreniers *et al.*¹¹ where they found that merely grinding the synthetic B4 ZnS was sufficient to cause some of the sample to revert to B3. In addition, Desgreniers *et al.* reported the same B4-to-B3-to-B1 transition sequence observed in our experiments. The peaks marked with an asterisk can be identified with the high pressure phase of ZnO as reported by Jiang *et al.*¹⁷ The lattice parameter of the B3 phase was calculated to be 5.395 ± 0.005 Å based on (111), (220), (311), and (222) peaks; it is less than 0.2% from the bulk lattice parameter of 5.405 Å. The slightly reduced parameter may be due to the fact that there is still some remnant pressure on the sample. By plotting the ΔE^2 versus E^2 we observed a straight line with zero slope indicating the absence of strain. X-ray diffraction measurements of the recovered sample in a regular powder diffractometer showed a lattice parameter of 5.406 ± 0.002 Å in very good agreement with the bulk value.

In our recent studies⁷ on the size-induced phase transformations in ZnS, we observed a significant reduction in the B3-to-B4 transition temperature, as compared to the bulk value. Postanneal x-ray diffraction studies revealed an increase of crystallite size, accompanied by a partial transformation from the B3 structure to the hexagonal, the B4 structure at temperatures as low as 400 °C. This was significantly less than accepted bulk transition of 1020 °C. In the present studies, we started with ZnS particles synthesized in the hexagonal wurtzite structure and found that as soon as the pressure is applied the particle size decreases and a phase change

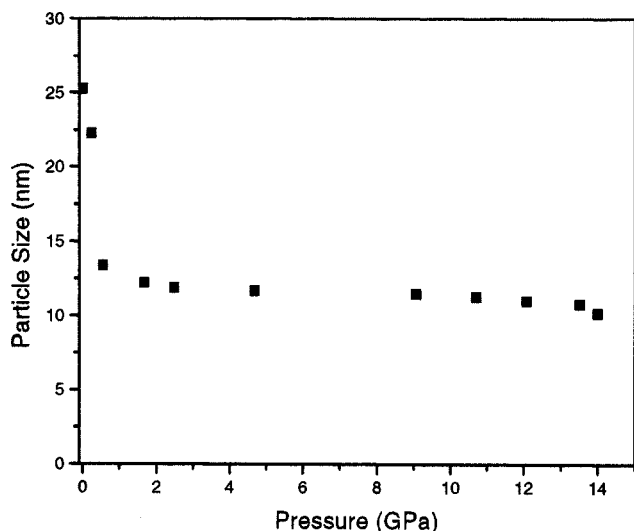


FIG. 4. Crystallite size as a function of increasing pressure.

to the B3 phase is induced. As the pressure is increased, the FWHM of the ZnS (101) peak increased, suggesting a decrease in the crystallite size, while the NaCl (200) peak remains invariant with pressure suggesting hydrostatic pressure conditions. Thus, the ZnS particles appear to be fragmented into smaller particles with the application of pressure inducing the B3 phase transition. The crystallite sizes, calculated based on Eqs. (1) and (2), are shown as a function of pressure in Fig. 4. In our previous studies, we observed mixed phases of B3 and B4 for a crystallite size of 7.4 nm. An analysis of the x-ray diffraction peaks showed absence of strain. In the present study we find that the crystallite size is reduced to 13.4 nm from 25.3 nm with a pressure of 0.5 GPa with a concomitant appearance of peaks corresponding to the B3 phase. Further increase of pressure resulted in the reduction of the crystallite size with a subsequent increase in the intensities of B3-phase peaks. At a pressure of 10.7 GPa, the crystallite size was reduced to 11.3 nm. There was no significant change in the crystallite size up to 15.0 GPa, at which point we observed the onset of the B3-to-B1 transition which was complete at 18.7 GPa. Upon release of the pressure, the B4 phase was not recovered and the B3 phase was retained. The crystallites of this B3 phase were of the order of 10.3 nm in size. No further reduction in the particle size was observed as the pressure was increased to 20.0 GPa and followed by releasing to the ambient conditions as the transitions from B3 to B1 and B1 to B3 were cycled.

The bulk modulus B_0 and its pressure derivative B'_0 were obtained by fitting the measured V_0/V data to the Muraghan equation of state

$$P = \frac{B_0}{B'_0} \left[\left(\frac{V_0}{V} \right)^{B'_0} - 1 \right], \quad (4)$$

where V is the volume at pressure P , and V_0 is the zero-pressure volume. A least square fit of the above equation to the experimental pressure-volume data gives $B_0 = 68.5 \pm 6.8$ GPa, and $B'_0 = 7.09 \pm 0.7$. The value of B_0 is slightly less than that for the bulk B3 phase which is calculated to be

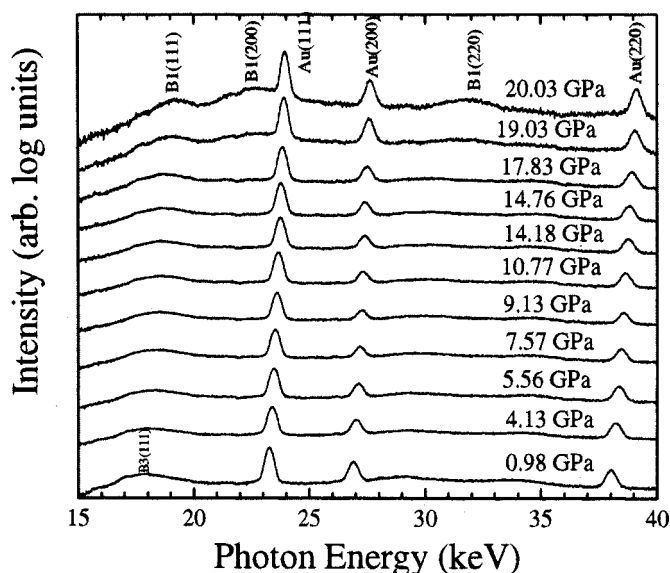


FIG. 5. Diffraction spectra for the 2.8 nm ZnS nanoparticles recorded at various pressures showing the B3-to-B1 phase transition.

78.4 GPa from the elastic constants c_{11} and c_{12} reported by Berlincourt *et al.*¹⁸ and using the expression $B_0 = 1/3[c_{11} + 2c_{12}]$. The B_0 and B'_0 values were reported by Desgreniers *et al.*¹¹ to be 80.1 and 4, respectively, for the bulk modulus of the wurtzite phase. The smaller B_0 value for our experiment may be attributed to a reduced particle size.

B. ZnS particles with 2.8 nm size

ZnS particles with a nominal diameter of 2.8 nm that were initially in the B3 phase transformed to the B1 phase at elevated pressure. The transition was sluggish; onset was observed at 18.0 GPa and was not complete until 21.0 GPa. Both NaCl and Au were used as internal pressure calibrants in separate runs. Figure 5 shows a series of spectra taken as a function of increasing pressures using Au as internal pres-

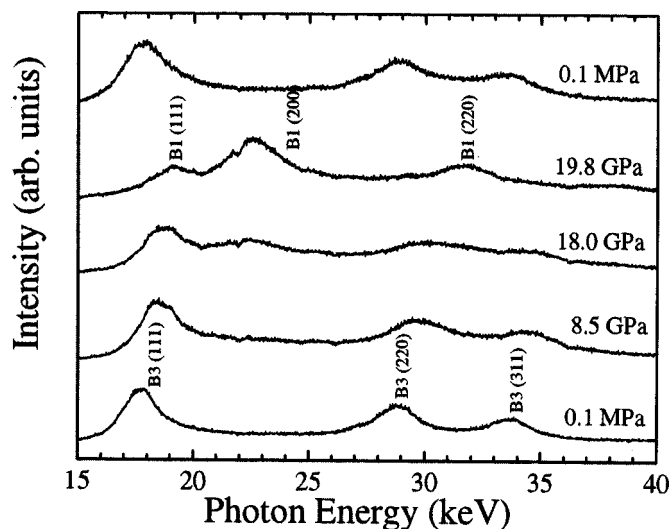


FIG. 6. Energy dispersive diffraction spectra of 2.8 nm ZnS particles recorded at selected pressures without any pressure calibrants. Sample peaks were used to determine the pressures.

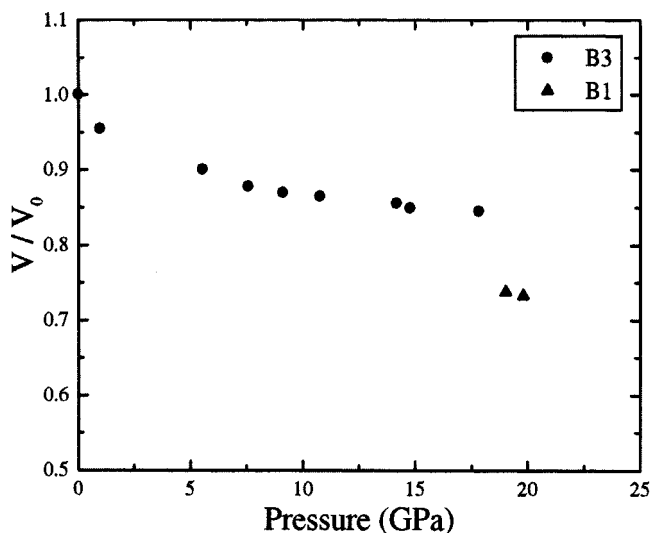


FIG. 7. V/V_0 vs pressure for 2.8 nm ZnS particles.

sure calibrant. The onset of the B1 phase at 18.0 GPa can be easily seen in this figure. In order to see the B3-to-B1 transition with no interference from the calibrants peaks, we made a separate run with only ZnS. Figure 6 shows the spectra at various pressures. The pressure was estimated from the B3(111) peak which was calibrated using the data taken with NaCl and Au as the internal pressure calibrants. The FWHMs of the peaks remained invariant with a change of pressure which suggests that the smaller particles did not fragment upon application of pressure in contrast to the case of 25.3 nm crystallite size ZnS. Upon release of pressure, the sample reverted back to the B3 phase with no apparent change in the particle size, as determined from the diffraction peak widths. Figure 7 shows the V/V_0 versus pressure of the B3 phase along with a few data points corresponding to B1 phase. A least square fit of the V/V_0 data of the B3 phase to the Eq. (3) gave $B_0 = 60.0$ GPa and $B'_0 = 4.0$. The value of B_0 is even smaller than the one for 25.3 nm crystallite size ZnS suggesting that these particles are more compressible. The B_0 and B'_0 values were reported by Desgreniers *et al.*¹¹ to be 79.5 and 4, respectively, for the bulk modulus of the zincblende phase and its pressure derivative. The smaller B_0 value in our experiment indicates an increased compressibility of the B3 ZnS particles and is likely due to a reduced particle size.

The enhancement in the transition pressure of B1 phase with decreasing particle size seems to be consistent with the observation that the band gap increases for the smaller particles.^{19,20} Following Jamieson's rule,²¹ the transition to the conducting state (high pressure phase) would be predicted to occur at higher pressures if there were an increase in the energy gap in the relation $P\Delta V = \Delta E/2$, where ΔE is the energy gap and ΔV is the change in the unit cell volume at P_t . These results are also consistent with the more recent studies on the finite size effects on the transition pressure of CdSe, Si, and PbS nanocrystals.^{3,4,22} The transition pressures are largely controlled by the surface energy of the particles associated with any given phase of the nanocrystalline particles.

Most of the theoretical studies based on *ab initio* calculation have been on the bulk II–VI compounds. Our results suggest the need for theoretical calculations of structural phase transitions within the limits of reduced particle size. It is also very important to investigate the transition pressures of II–VI compounds as a function of crystallite size as more and more of the nanoparticles are synthesized.

IV. CONCLUSIONS

Pressure induced transformations in nanoparticles of ZnS with two particle sizes of 2.8 and 25.3 nm were carried out using energy dispersive x-ray diffraction and a diamond-anvil cell. The particles with 25.3 nm size which were initially in the B4 phase showed transformation to the B3 phase as soon as a small pressure of 0.5 GPa was applied and then to the B1 phase at a pressure of 15.0 GPa. Upon release of the pressure the sample did not return to the wurtzite phase; instead the B3 phase was retained at the atmospheric pressure. The nanoparticles with a particle size of 2.8 nm which were initially in the B3 phase showed an onset of transition to B1 phase at a pressure of 18.0 GPa indicating that the transition pressure increases for ZnS as the particle size is reduced. The initial B3 phase and the particle size were retained after release of the pressure.

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