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ZnS nanotetrapods synthesized via a solvothermal route have a octahedral core with a zincblende (ZB) structure and four hexprism-shaped arms consisting of alternately stacking ZB and wurtzite (WZ) phases, where the WZ phase has a higher volume percentage. *In situ* angular-dispersive X-ray diffraction (ADXRD) measurements were carried out to study the structural behavior of ZnS nanotetrapods under high pressure up to 41.3 GPa. The initial WZ structure exhibits a very high mechanical stability to ∼11.3 GPa. Both the WZ and ZB structures transform to the rocksalt (RS) structure at ∼15.4 GPa. The bulk moduli of the WZ (148.2 ± 8.9 GPa) and RS (165.6 ± 9.9 GPa) phases are both larger than the previously reported values. These phenomena are discussed based on the alternating epitaxial growth of the WZ and ZB phases in the arms of nanotetrapods. Our study suggests that the internal structure of nanomaterials could also greatly affect their stability and transition behavior.

Keywords: ZnS nanotetrapods; phase-transition behavior; high pressure *in situ* ADXRD

1. Introduction

Nanomaterials with special morphologies have attracted great attention in the past few decades due to their extraordinary properties.[1,2] In recent years, many efforts have been devoted to nanotetrapods due to their ability of integrating different functionalities into one material under the "bottom-up" architecture.[3] And they have exhibited novel behaviors in charge migration, field electron emission and so on.[4–6]

As a wide-band-gap (∼3.7 eV) semiconductor, ZnS has been used as an important material in the electronics industry with a wide range of applications including light-emitting diodes, efficient phosphors in flat panel displays, injection lasers and electroluminescent devices.[7,8]

At ambient conditions, ZnS has two common polymorphs: cubic zincblende (ZB) and hexagonal wurtzite (WZ). The latter is metastable and easily transforms to the cubic form under normal conditions,[9] but it is much more desirable for its better optical properties. However,

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previous investigations have revealed that nanostructured WZ ZnS may be stable at room temperature.[10,11] Since the properties of materials are closely related to their structure, it is valuable to explore the structural behavior of materials. Upon the application of pressure, both ZB and WZ ZnS transform to a rocksalt (RS) structure, and WZ ZnS starts the transformation to the ZB phase even when grinding or under a slight pressure. Similar behavior was also observed in ordinary nanocrystalline ZnS.[12] But there is something different in ZnS nanomaterials with special morphologies. In the case of ZnS nanobelts,[13] high mechanical stability of WZ ZnS is observed. And ZnS nanorods undergo a direct phase transition from the WZ phase to the RS phase without the ZB phase in the transition process.[14] ZnS nanotetrapods synthesized via a solvothermal method have a octahedral core with the ZB structure and four hexprism-shaped arms consisting of alternately stacking ZB and WZ phases along WZ (001)/ZB (111) direction, where the WZ phase has a higher volume percentage.[15] Considering their special morphology and internal structure, ZnS nanotetrapods are expected to show special pressure behavior rather different from that of the bulk sample.

2. Experiments

The preparation details and the structural characterization results of ZnS nanotetrapods were reported elsewhere.[15] Powder XRD data were recorded on a Philips X'Pert Pro diffractometer with Cu Kα radiation.

In situ high pressure angular-dispersive X-ray diffraction (ADXRD) measurements on ZnS nanotetrapods were carried out at 4W2 High Pressure Station of Beijing Synchrotron Radiation Facility with the incident monochromatic X-ray beam wavelength of 0.6199 Å. High pressure was produced within a diamond anvil cell with culets of 300 µm in diameter, and determined by the shift of the ruby R_1 line. The diffracted X-rays were recorded with a MAR345 image plate detector placed at a distance of about 377.62 mm, which was calibrated by CeO_2. The FIT2D program was used to display and integrate the diffraction rings on the image plate. The pressure–volume data were fitted to the Birch–Murnaghan equation of state using the EosFit software.[16] No pressure-transmitting medium was used in our experiments.

3. Results and discussion

Figure 1 shows the XRD pattern of ZnS nanotetrapods. The preferred growth direction of the WZ and ZB structures in nanotetrapods is clearly evidenced by the significantly strong WZ (002)/ZB (111) peak on the spectra. Since the ZB (111), (022) and (113) peaks merged with the WZ (002), (110) and (112) peaks, respectively, only one peak is visible at the corresponding position.

A series of ADXRD spectra under different pressures are illustrated in Figure 2. Below 11.3 GPa, all the peaks gradually shift to the higher angle region as the pressure increases, which is related to the compression of the lattice. Since no relative increase in the merged WZ (002)/ZB (111) or WZ (110)/ZB (022) peak with respect to the WZ (010), (011) and (013) peaks is observed, it is reasonable to assume that the WZ structure remains stable up to 11.3 GPa, different from the general instability exhibited by the bulk and spherical nanoparticles with the WZ structure. Similar high structural stability has also been observed in nanobelts [13] and nanorods,[14] and well explained based on their special morphologies. In these two kinds of nanomaterials, only one or two dimensions are at the nanoscale, so there is a significant difference between the confinement effects in different directions, which is believed to be the reason for the high mechanical stability of the WZ phase. However, the WZ phase in nanotetrapods is

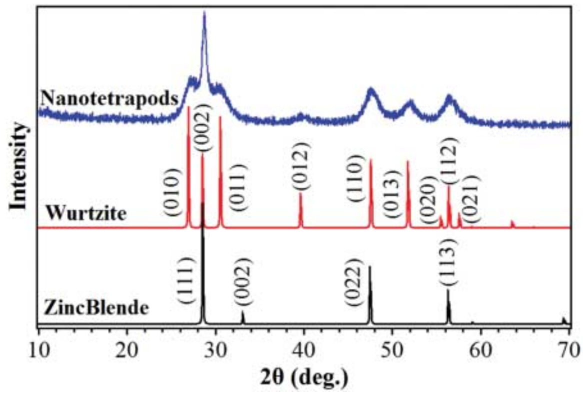

Figure 1. XRD pattern of ZnS nanotetrapods at ambient conditions. The patterns of wurtzite and zincblende are from JCPDS card 79-2204 and 77-2100, respectively.

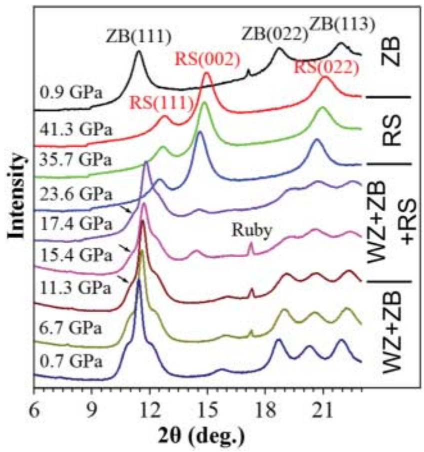

Figure 2. ADXRD spectra of ZnS nanotetrapods recorded at selected pressures showing the WZ + ZB – RS phase transition. The arrows indicate the position of the WZ (010) peak.

a three-dimensional nanostructure. Therefore, we assume that the enhanced stability of the WZ phase in nanotetrapods mainly results from the alternating epitaxial growth of the WZ and ZB phases in the arms of nanotetrapods, which usually helps to stabilize the metastable phase in the film field.[17]

When the pressure increases up to 15.4 GPa, a new peak ascribed to the RS (002) peak appears, which indicates that the transformation to the RS structure occurs at this pressure. The initial WZ and ZB structures coexist with the RS structure until 23.6 GPa, and the RS structure exists until the highest pressure of 41.3 GPa in our experiment without any other phase transition. After releasing the pressure, the initial WZ phase is not recovered, only the peaks related to the ZB phase are observed on the diffraction pattern.

On the spectra over the transition region, a small relative decrease in the WZ (010) peak with respect to the WZ (002)/ZB (111) peak is observed with the increase in the RS-related peaks. This phenomenon may indicate the direct transition from WZ to RS, which is very rare in ZnS materials, but was observed in ZnS nanaorods by Li et al.[14] Due to the similar morphology between the arms of nanotetrapods and nanorods, it is reasonable to assume that the transition from WZ to RS may also occur in ZnS nanotetrapods. However, according to the analysis stated below, this transition path is less probable in nanotetrapods.

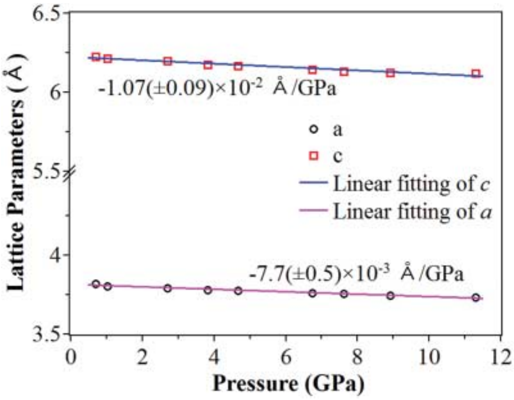

Figure 3. Pressure dependence of lattice parameters *a* and *c* of the WZ phase of ZnS nanotetrapods. The parameters of *c* and *a* are calculated using the *d* spacings of the WZ (002) and (110) planes, respectively.

The WZ phase is located in the four arms of the nanotetrapods, which are of 40–50 nm in length and ∼5 nm in diameter. This morphology is similar to that of the nanorods. According to Li's model, the compressibility in the *c*-axis direction is relatively large due to the different confinement effects in the longitudinal and radial directions of ZnS nanorods, so the atom layers get close obviously than that in *a*-axis direction and finally all atoms evolve into the arrangements of the RS structure. In both nanotetrapods and nanorods, the lattice parameters *c* and *a* of the WZ phase decrease linearly with the increase in pressure as shown in Figure 3. All the corresponding data are summarized in Table 1. Compared with nanorods, the decreasing rates (k_c and k_a) of *c* and *a* are smaller in nanotetrapods. With decreasing particle size, surface energy increases and provides a significant contribution to total internal energy, resulting in a noticeable enhancement of the structural stability. As a result, the pressure-induced lattice change is relatively small in smaller size materials. Previous studies have revealed that the transition pressure increases as the particle size decreases in ZnS nanomaterials.[12,18].

On the other hand, the difference between the confinement effects in the *c*- and *a*-axis directions in nanotetrapods should be smaller than that in nanorods considering the smaller ratio of length to diameter of the WZ part in nanotetrapods as seen in Table 1. As a result, the ratio of k_c/k_a for nanotetrapods should be smaller than that for nanorods. However, the obtained value for nanotetrapods is not significantly small due to data uncertainties. Nevertheless, it is reasonable to assume that the direct transformation from WZ to RS in nanotetrapods should occur at a higher or equal pressure compared with that of in nanorods. However, the transition pressure is 15.4 GPa for our sample, significantly lower than that of the nanorods which is 19.6 GPa. Hence, the indirect transition path with the ZB phase in the process seems more probable in nanotetrapods. It should be mentioned that non-hydrostatic stress resulting from the lack of transmitting medium in our experiments may also contribute to the lower transition pressure.

Table 1. Comparison of the size, compressibility in different directions, and the transition pressure of ZnS nanotetrapods and ZnS nanorods.

	Size (nm) diameter	Size (nm) Length	k_c (Å/GPa)	k_a (Å/GPa)	k_c/k_a	Transition pressure (GPa)	Reference
Nanotetrapods	∼5	40–50	$-1.07 \pm 0.09 \times 10^{-2}$	$-7.7 \pm 0.5 \times 10^{-3}$	1.39	15.4	This study
Nanorods	∼20	∼300	$-1.4 \pm 0.17 \times 10^{-2}$	$-9.3 \pm 0.88 \times 10^{-3}$	1.51	19.6	Ref. [14]

Note: The size of nanotetrapods given is the size of the arms. k_c and k_a are the slope of the lines that best fit the *c* and *a*, respectively, versus pressure data.

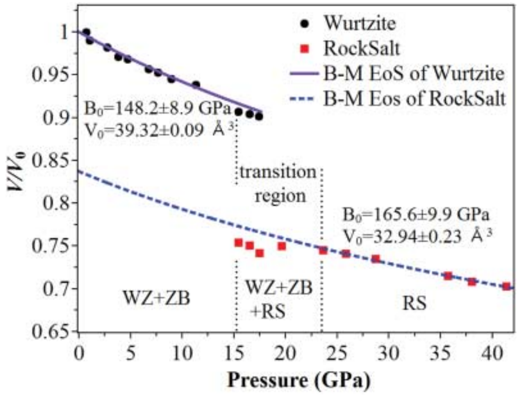

Figure 4. Experimental equation of state of ZnS nanotetrapods. The lattice parameter *a* of the RS structure was obtained by averaging the values calculated from the *d* spacings of the (111), (002) and (022) planes. And the pressure–volume data points after the transition were used to fit the Birch–Murnaghan equation of state. Thus, a large deviation is observed in the phase-transition region.

One possible evidence for the indirect transition to the RS structure is the wide transition-pressure range of $\sim$8.2 GPa. This value is much larger than that of the nanorods ($\sim$2.5 GPa), but in agreement with the sluggish transition from WZ to ZB observed in bulk and nanoparticle ZnS forms.[9,12,18]

The Zn coordination is almost identical in both WZ and ZB structures, room condition unit-cell volumes and bulk moduli for both the phases are close. Besides, the WZ phase has a higher volume percentage in nanotetrapods, and the appeared peaks of the ZB phase are all merged with the peaks of the WZ phase. Therefore, for the low-density phase, we just obtained the equation of state of the WZ phase. The experimental pressure–volume data were fitted using the Birch–Murnaghan equation of state which is expressed by

$$P = \frac{3B_0}{2}\left[\left(\frac{V}{V_0}\right)^{-7/3} - \left(\frac{V}{V_0}\right)^{-5/3}\right]\left\{1 + \frac{3}{4}(B_0' - 4)\left[\left(\frac{V}{V_0}\right)^{-2/3} - 1\right]\right\},$$

where V_0 is the zero-pressure volume of the primitive cell, B_0 and B_0' are the bulk modulus and its pressure derivative, respectively.

The measured V/V0 data points and the fitted curves are all plotted in Figure 4 for both the initial WZ phase and the denser RS phase. The B_0 value of the WZ phase with the fixed B_0' of 4 is 148.2 $\pm$ 8.9 GPa, which is significantly larger than that of the ZnS bulk sample ($\sim$80 GPa) [9] and nanomaterials ($\sim$60 GPa).[12,18] The enhancement of the bulk modulus of the nanotetrapods should result from the alternating epitaxial growth of the WZ and ZB phases in the arms, which usually induces an increase in the hardness of the sample.[19] For the RS structure, the bulk modulus is 165.6 $\pm$ 9.9 GPa with the fixed B_0' of 4 and the zero-pressure volume is 32.94 $\pm$ 0.23 Å^3. Both the values are larger than the previously reported values.[9,14] We suggest that the large modulus of the high pressure phase may be caused by the possible high-concentration dislocations formed during the phase-transition process due to the special morphology and alternately stacking structure of nanotetrapods.

4. Conclusions

The pressure-induced structural behavior of ZnS nanotetrapods was studied using XRD by synchrotron radiation up to 41.3 GPa. Both the initial WZ and ZB structures of nanotetrapods remain stable up to $\sim$11.3 GPa and transform to the RS phase at $\sim$15.4 GPa. The transformation from WZ to RS should be an indirect transition with the ZB phase in the process. By fitting the Birch–Murnaghan equation of state, the bulk modulus of the low-pressure WZ phase (148.2 $\pm$ 8.9 GPa) and the high pressure RS phase (165.6 $\pm$ 9.9 GPa) are obtained, in which both are larger than the previously reported values. These phenomena should be ascribed to the alternating epitaxial growth of the WZ and ZB phases in the arms of the nanotetrapods. Our study suggests that the internal structure of nanomaterials could also greatly affect their stability and transition behavior.

Disclosure statement

No potential conflict of interest was reported by the authors.

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