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Solvothermal synthesis of ZnS nanorods and their pressure modulated photoluminescence spectra

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Abstract

ZnS nanorods in a wurtzite structure with an average diameter of 10 nm were synthesized via a solvothermal method. *In situ* photoluminescence and Raman spectra measurements on the ZnS nanorods under high pressure were carried out using a diamond anvil cell. The disappearance of the photoluminescence (PL) band and longitudinal-optical (LO) phonon mode indicates that the ZnS nanorods transform to the rock salt phase near 16.7 GPa. A visible change in the pressure dependence of the full width at half magnitude for the PL band and LO phonon was found near 9 GPa, indicating that a phase transition of the ZnS nanorods from the wurtzite phase to the zinc blende phase probably occurs. High pressure can obviously modulate the PL band of the ZnS nanorods—it shifts to a long wavelength band with increasing high pressure.

1. Introduction

Nanostructured materials have attracted a great deal of attention in the last few years due to their excellent properties that are different from the bulk materials [1–4]. Zinc sulfide (ZnS) is an important wide-band-gap (3.6 eV) semiconductor that has been used as an important material in ultraviolet light-emitting diodes and injection lasers [5], flat-panel displays [6], electroluminescent devices and infrared (IR) windows [7, 8]. Thus, study of the properties and synthesis of ZnS nanomaterials is of considerable importance and great efforts have been focused on this topic [9–12]. Among the ZnS nanomaterials, quasi-one-dimensional nanomaterials such as nanobelts, nanotubes, nanoribbons and nanorods are given special attention due to their unique nanostructure and luminescence properties, and study of their synthesis and properties have also been reported [13–24]. As typical one-dimensional ZnS nanomaterials, ZnS nanorods attract much attention and have been synthesized by various

methods [17–24]. The solvothermal method is an important method for wet chemistry, featuring low temperature, simplicity and good yield, and has also been employed for the preparation of ZnS nanomaterials—products with a narrow size distribution and good crystallization can be obtained. The synthesis of the ZnS nanorods with a small diameter and good crystallization is still a challenging topic using this method [20, 21]. Very recently, we have succeeded in synthesizing ZnS nanorods with small diameter and high crystallinity by simply changing the ratio of the reactants in the solvothermal method [24]; the diameters of the ZnS nanorods with a relatively narrow distribution in the range of 10–20 nm are much smaller than those in the literature [20, 21]. In this report, we find that ZnS nanorods with much smaller diameter can be fabricated by mainly adjusting the ratio of the solvents.

High pressure can change the structure and morphology of ZnS nanomaterials and further change their properties. The pressure induced phase and semiconductor-to-metal transition of ZnS nanoparticles has been widely studied. For example, Pan *et al* [25] studied ZnS nanoparticles initially in the wurtzite structure with a size of 6 nm and found the phase transition from the wurtzite to the zinc blende structure at 11.5 GPa followed by a transition from the zinc blende to the rock salt structure at 16 GPa; Qadri *et al* [26] found that ZnS nanoparticles with a size of 25.3 nm initially in the wurtzite structure transformed to the rock salt structure at a pressure of 15.0 GPa. Qadri *et al* also studied the phase transition of ZnS nanoparticles with a size of 2.8 nm initially in the zinc blende structure and found that the nanoparticles showed a transition to the rock salt structure at 18 GPa. Studies of one dimensional ZnS nanomaterials under high pressure would be very interesting due to their unique nanostructure. However, there are few reports on one dimensional ZnS nanomaterials. Wang *et al* [9] reported that nanobelts initially in the wurtzite structure transformed to the zinc blende structure at 6.8 GPa and they also gave the mechanism of the phase transition. Jiang *et al* [27, 28] reported that the grain-size effect can elevate the transition pressure in a large pressure range. The phase transition and photoluminescence under high pressure for ZnS nanorods have not been studied.

In this paper we report the synthesis by the solvothermal method of single crystalline ZnS nanorods with an average diameter of 10 nm. *In situ* photoluminescence measurements and Raman spectra determinations were carried out under high pressure on the ZnS nanorods using a diamond anvil cell up to 19.4 GPa. High pressure can obviously modulate the PL band of the ZnS nanorods. The ZnS nanorods transform to the rock salt phase near 16.7 GPa and the transition from the wurtzite to the zinc blende structure probably occurs near 9 GPa.

2. Experimental details

The detailed process for the synthesis of the ZnS nanorods is similar to that in our very recent report [24]. In this experiment ZnCl₂ is chosen as the zinc source instead of Zn(NO₃)₂, and the volume ratio of the ethylenediamine (C₂H₄(NH₂)₂)–deionized water is changed to 1.5:1. In addition, the reaction temperature and time are changed to 170 °C and 8 h, instead of 200 °C and 12 h. X-ray powder diffraction (XRD) is used to characterize the product with Cu K α radiation ($\lambda = 0.15406$ nm). A scanning rate of 0.05° s⁻¹ is applied and the scanning range is 20°–80°. A Hitachi H-8100 transmission electron microscope (TEM) with accelerated voltage 200 kV is employed to observe the morphology of the products.

In the high-pressure experiments, hydrostatic pressures up to 19.4 GPa were generated by a diamond anvil cell (DAC) with a methanol–ethanol mixture with a volume ratio of 4:1 as the pressure-transmitting medium. The pressure was calibrated by the shift of the ruby R_1 line. The Raman and PL spectra of the ZnS nanorods were recorded using a Renishaw spectrometer with a 325 nm He–Cd laser providing the excitation wavelength.

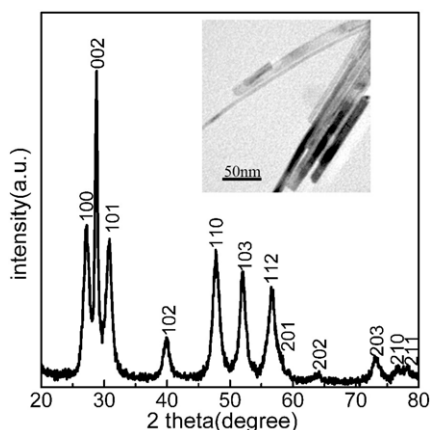


Figure 1. XRD pattern and the TEM image (inset) of the ZnS nanorods synthesized by the solvothermal method.

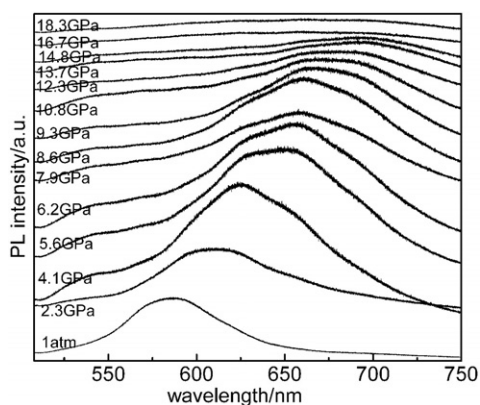


Figure 2. The pressure dependence of the PL spectra of the ZnS nanorods.

3. Results and discussion

The final products fabricated in the solvothermal process are characterized by x-ray powder diffraction (XRD) and transmission electron microscopy (TEM) (figure 1). As shown in the TEM image (inset) in figure 1, the ZnS products are nanorods and each nanorod has a uniform diameter along its entire length with an average diameter of 10 nm. This diameter is smaller than those in our recent report [24] and other literature, which indicates that our ZnS nanorod sample is of much smaller diameter. In the XRD pattern, all the diffraction peaks can be indexed easily to wurtzite phase ZnS (space group $P63mc$) and the calculated unit cell parameters are $a = 0.3803$ nm and $c = 0.620$ nm, in agreement with reports in the literature (Joint Committee on Powder Diffraction Standards (JCPDS) card no. 75-1534). The XRD and TEM data indicate that the synthesized ZnS nanorods are single crystals.

Figure 2 gives the PL spectra of the ZnS nanorods at ambient conditions and under high pressure. At ambient conditions, the PL spectrum reveals that the nanorods have a strong emission band centered at 587 nm which is not the band gap emission. It is well known that the PL spectrum of ZnS is sensitive to the synthesis condition, shape and size of the

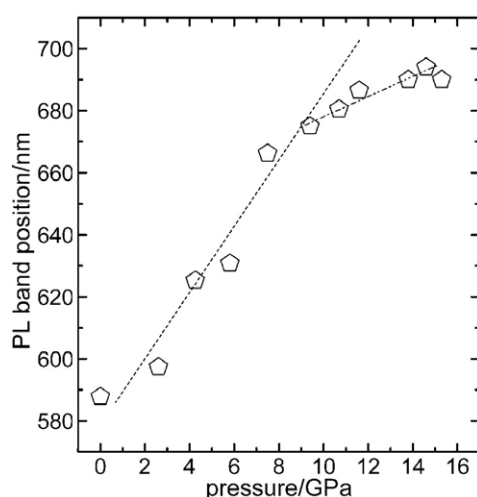


Figure 3. Pressure dependence of PL band position of ZnS nanorods.

products, and the PL spectra have differences from each other [29–31]. Uchida [32] studied the photoluminescence of bulk ZnS with varying stoichiometries and found that both excess Zn^{2+} and S^{2-} emit at about 350 nm. Becher and Bard [33] attributed the blue emission band of 428 nm to S^{2-} vacancies. Murase *et al* [34] ascribed the blue emission band at 470 nm to a Zn^{2+} vacancy related acceptor. Kar and Chaudhuri [35] reported the emission bands at 394 and 458 nm as being due to the interstitial lattice defects and the trapped luminescence arising from the surface states. Yao *et al* [36] reported the yellow–green emission at 578 nm in the PL spectra of the ZnS nanosphere. The PL band of the ZnS nanorods synthesized here is different from those in the literature and its origin is still an open question. The emission might be caused by vacancy states, interstitial states or surface-related reasons due to the peculiar nanostructure, and should be further investigated in detail.

The pressure-dependent PL spectra of the ZnS nanorods with the increase of pressure up to 18.3 GPa is shown in figure 2. A redshift of the emission band with increasing pressure is clearly observed. At ambient conditions, the center of the emission band is 587 nm, and the emission band shifts to 591 nm when the pressure is up to 15.3 GPa. From figure 2, we see that the PL emission band disappears at 16.7 GPa. In previous studies, bulk ZnS transformed to the rock salt phase in the range from 15 to 16 GPa [37–39] and ZnS nanoparticles initially in the wurtzite structure transformed at a pressure of 15.0 GPa [26]. It is well known that the rock salt phase in ZnS is an indirect band gap phase and has no PL emission. Comparing the disappearance of the PL emission with the transition pressure reported, we deduce that the ZnS nanorods transform to the rock salt phase near 16.7 GPa which is higher than those of the ZnS bulk and the nanoparticles initially in the wurtzite phase [25, 26, 37–39].

The pressure dependence of the PL band position of the ZnS nanorods is shown in figure 3. We can observe the redshift of the emission band directly. Additionally, in the low-pressure region, the position of the emission band versus pressure changes obviously near 9.3 GPa. The fitted pressure coefficient of the PL band position in the region of low pressure is $10.1 \pm 1.2 \text{ nm GPa}^{-1}$, which is larger than that in the region of high pressure ($2.8 \pm 0.6 \text{ nm GPa}^{-1}$). The pressure dependence of the full width at half magnitude (FWHM) of the PL band has also been analyzed in figure 4. It is noted that the FWHM of the PL emission band under pressure has an abrupt change near 9.3 GPa which is consistent with the pressure

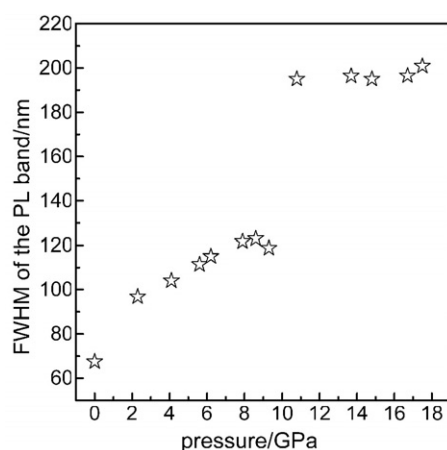


Figure 4. The pressure dependence of the FWHM of the PL band.

dependence of the emission band position. The pressure coefficient of FWHM for the PL band in the region of low pressure is $5.35 \pm 0.8 \text{ nm GPa}^{-1}$, much larger than that in the region of high pressure ($0.65 \pm 0.4 \text{ nm GPa}^{-1}$). ZnS initially in the wurtzite structure usually undergoes a phase transition from the wurtzite structure to the zinc blende structure before the transition to the rock salt structure under high pressure [9, 25, 26], and the phase transition pressure from the wurtzite phase to the zinc blende phase is reported to be in the range of 6.8–11.5 GPa. Compared with the wurtzite–zincblende transition pressure in the literature, the obvious change of the position and the FWHM of the PL emission band indicates that the wurtzite–zincblende transition probably occurs near 9 GPa.

Zinc sulfide with a wurtzite structure belongs to the space group C_{6v}^4 and all atoms occupy C_{3v} sites. The possible optical modes of the four-atom primitive cell have the following symmetries: $1A_1 + 2B_1 + 1E_1 + 2E_2$. A_1 , E_1 and E_2 are Raman active and B_1 is Raman inactive. Under ambient conditions, the transverse optic (TO) mode of the wurtzite phase ZnS is not visible because the Raman spectrum is excited by the 325 nm laser line. The pressure-dependent Raman spectra of the ZnS nanorods are shown in figure 5 with the Raman spectrum under ambient conditions. The Raman peak at 348 cm^{-1} is assigned to the vibration of the longitudinal-optical (LO) phonon mode, which is agreement with the reports in the literature. Xiong *et al* [40] observed the LO mode of A_1/E_1 at 346.4 cm^{-1} and Lu *et al* [15] reported the LO(A_1/E_1) mode at 350 cm^{-1} . The other peak of the ZnS nanorods at 694.3 cm^{-1} is attributed to the second order of the longitudinal-optical mode (2LO).

In the pressure dependence of the Raman spectra of the ZnS nanorods shown in figure 5, the frequency of the LO phonon mode of the ZnS nanorods becomes larger with increase in pressure. As the pressure increases, the LO phonon mode starts to disappear near 16.7 GPa, which is the same pressure at which the PL emission band disappeared. From previous discussion on the PL emission band under high pressure we have concluded that the ZnS nanorods transformed to the rock salt phase near 16.7 GPa. The disappearance of the LO mode confirms the phase transition to the rock salt structure near 16.7 GPa because the LO phonon mode of ZnS with a rock salt structure is Raman inactive.

In the region of low pressure, we have deduced that the phase transition from the wurtzite to the zinc blende structure probably occurs from the obvious changes of emission position and FWHM of the PL band near 9 GPa. We then studied the pressure dependence of the position

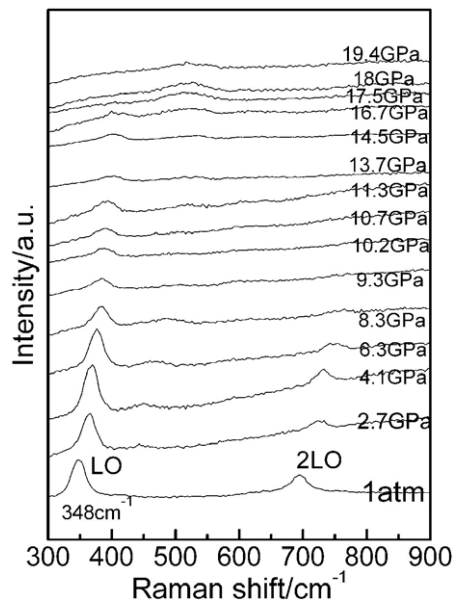


Figure 5. Pressure dependence of Raman spectra of ZnS nanorods.

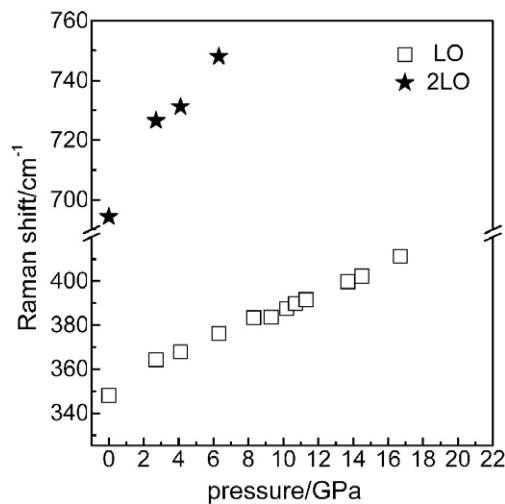


Figure 6. Pressure dependence of LO and 2LO mode position of the ZnS nanorods.

of the LO mode shown in figure 6. The LO phonon mode of the ZnS nanorods exists with increasing pressure until the pressure reaches 16.7 GPa, and the pressure coefficient of the LO mode under high pressure shows no obvious change. As reported in the literature [41], the LO phonon modes of both the wurtzite and zinc blende ZnS structures are Raman active, and have a similar frequency. It is thus difficult to figure out the phase transition from the wurtzite to the zinc blende structure according to the change of frequency under high pressure. We then further studied the pressure-dependent FWHM of the LO and 2LO modes shown in figure 7. The FWHM of the LO mode changed abruptly near 9.3 GPa, which is the same

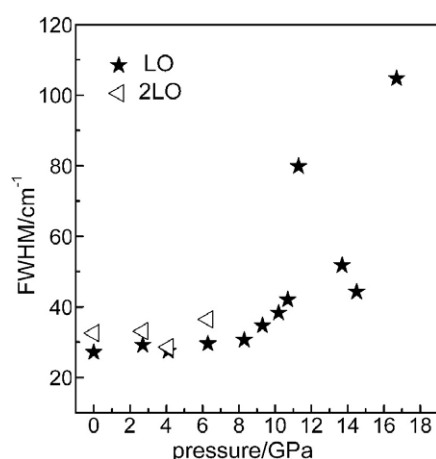


Figure 7. Pressure dependence of the FWHM of the LO and 2LO mode of the ZnS nanorods.

pressure at which the pressure-dependent emission position and the FWHM of the PL band show an abrupt change. The pressure coefficients of the FWHM of the LO phonon mode in the region of low and high pressure are 0.38 ± 0.2 and $6.54 \pm 3.2 \text{ cm}^{-1} \text{ GPa}^{-1}$, respectively, which change greatly near 9 GPa. Compared with the obvious changes of the position and FWHM of the PL emission band near 9 GPa, we further deduce that the wurtzite–zincblende phase transition probably occurs.

4. Summary

In summary, we have synthesized ZnS nanorods with a wurtzite structure and an average diameter of 10 nm via a facile solvothermal method. *In situ* photoluminescence measurements and determination of the Raman spectra under high pressure on the ZnS nanorods were carried out using a diamond anvil cell. The disappearance of the PL band and LO phonon mode indicates that the ZnS nanorods transformed to the rock salt phase near 16.7 GPa, and the phase transition pressure is higher than that of the bulk ZnS and ZnS nanoparticles initially in the wurtzite structure. A visible change in the pressure dependence of the full width at half magnitude (FWHM) for the PL band and LO phonon was found near 9 GPa, indicating that the phase transition of the ZnS nanorods from the wurtzite phase to the zinc blende phase probably occurs. High pressure can obviously modulate the PL band of the ZnS nanorods; it shifts to a long wavelength band with increasing high pressure.

Acknowledgments

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