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Structural stability and Raman scattering of ZnSe nanoribbons under high pressure

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ABSTRACT

The high-pressure *in situ* angular dispersive x-ray diffraction (ADXD) study on the zinc blende (ZB) type ZnSe nanoribbons were implemented using image-plate technique and diamond-anvil cell up to about 32 GPa. The pressure-induced structural transition from the ZB to a rocksalt (RS) type phase occurs at about 12.6 GPa, and the relative volume reduction at the transition point is close to 13%. Moreover, the variation in the relative volume with pressure seems discontinuous at about 5.5 GPa, which indicates an unidentified transition. The bulk modulus B_0 for the ZB and RS phases were determined through fitting the relative volume–pressure experimental data by Birch–Murnaghan equation of states. High-pressure Raman scattering experiments revealed that the transverse optical (TO) phonon mode splits into two peaks at about 5.5 GPa, which is compatible with the result of ADXD. The disappearance of the longitudinal optical peak above 13 GPa is due to the semiconductor–metal transition. Surprisingly, all Raman scattering peaks begin to become broad from the lower pressure (5–6 GPa) relative to the bulk ZnSe (normally ∼11 GPa), and the corresponding TO phonons become invisible beyond 14.7 GPa. Using the values of the bulk modulus from ADXD experiments, the corresponding mode Grüneisen parameters can be obtained for the ZB phase.

1. Introduction

The II–VI semiconductors such as zinc or cadmium chalcogenides, as a class of important functional semiconductor materials, have always attracted great interest of researchers in several decades, not only due to the potential application [1] but also their close relevance to key problems in physics [2–5]. For the application of these semiconductor materials in photoelectronic devices a deep understanding of their structural, electronic and lattice-dynamic properties is essential. Hence, a number of theoretical and experimental researches [6–9] focused on respectively structural properties in recent years. At the same time, the crystal structures of these compounds were extensively studied under different conditions as well [10–12]. For instance, Leoni et al. [12] recently reported that nanodomain fragmentation and local rearrangements in CdSe occur under pressure. Generally, almost all of zinc or cadmium chalcogenides crystallize either as zinc blende (ZB) or as wurtzite structures at ambient conditions, but they can change into the rocksalt (RS) structure phase under high external pressure. Therefore, the structural transition of these semiconductors under pressure is a highlighted subject in the high-pressure research field. Thus, they have also attracted great interest and have been studied extensively.

As a typical example in II–VI semiconductors, the direct wide band gap semiconductor ZnSe generally occurs in the ZB-type structure at ambient conditions. However, Smith and Martin [10] and Piermarini et al. [11] reported that the bulk ZnSe undergoes a pressure-induced phase transition from fourfold coordination ZB to sixfold coordination RS type structure at about 13 GPa. Moreover, Itkin et al. [13] found the pressure-induced metallization of ZnSe at the transition pressure, indicating that the electronic structural transition is companied by crystal structural transition. In addition to the experimental studies, some theoretical methods, such as the self-consistent pseudopotential approach [14], the local model pseudopotential method under the virtual crystal approximation [9], the full potential linearly augmented plane wave approach, and numerical atomic orbital band structure calculations within the local-density approximation [15], were also employed in the study of ZnSe at high pressure. Later, the dependence of lattice vibration on high pressure has been studied by Raman scattering experiments for the ZnSe powders. For instance, Greene et al. [16]

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observed the discontinuity of transverse optical (TO) and longitudinal optical (LO) phonon frequencies in the ZB phase of ZnSe at about 5 GPa. Furthermore, Lin et al. [17] found the splitting of TO phonon modes at 4.65 and 7.61 GPa and the disappearance of LO at about 14.35 GPa, and pointed out that the latter is attributed to the semiconductor–metal phase transition. Recently, several research groups [18–20] tried to tune the physical properties (such as LO plasmon coupling, etc.) of ZnSe and ZnSe-based ternary compounds using the powerful high-pressure approach.

However, the above-mentioned studies mainly focused on ZnSe bulk materials or powders rather than low dimensional material. It is suggested that nanomaterials exhibit many promising physical properties such as strength, thermal, electronic and magnetic properties in contrast with the conventional bulk materials. Especially, surface features and energy band structures show significant differences. So the property of structural transition of nanomaterials under pressure has become a subject of intense investigations. In this work, we report the observation of structural stability of the ZnSe nanoribbons using the high-pressure *in situ* angular dispersive x-ray diffraction (ADXD) technique. In addition, the linear pressure coefficients and mode Grüneisen parameters of ZnSe nanoribbons phonons were determined by Raman spectroscopy.

2. Experiments

ZnSe was synthesized in an electrical furnace with a horizontal quartz tube by physical evaporation of ZnSe powder with Au as catalyst. The details are described elsewhere [21]. The ZnSe nanoribbons have a thickness of 20–80 nm, widths of 0.2–2 μm, and lengths up to several tens of micrometers.

The ADXD experiment on ZnSe nanoribbons at external pressure was carried out at room temperature on the bending magnet beam line 3W1A of the Photon Factory in the High Energy Accelerator Research Organization. The x-ray was monochromatized to a wavelength of 0.061651 nm with two Si (1 1 1) crystals, and focused in horizontal and vertical directions with two curved mirrors. A pinhole collimator placed in front of the diamond-anvil cell (DAC) was used to limit the final beam size to 25 μm in diameter. The diffracted x-ray was detected with an imaging plate placed at a distance of about 238.89 mm, which was calibrated by CeO_2. High pressure was generated using an improved Mao-Bell-type DAC with 400 μm culets. Silicon oil was used as pressure transmitting medium to obtain hydrostatic pressure conditions. Pressures were calibrated by ruby luminescence technique. In this experiment, a series of x-ray diffraction patterns were obtained under different pressures up to about 32.0 GPa.

In Raman scattering experiments, the ZnSe nanoribbons were carefully loaded into a 250 μm stainless-steel gasket hole and then installed into the improved Mao-Bell-type DAC with 400 μm culets. Pressures were calibrated by ruby luminescence technique. Raman spectra were collected in backscattering geometry in the frequency region from 100 to 600 cm^{-1}, using a LABRAM-HR confocal laser Micro-Raman spectrometer (HR800). The 532 nm line of the Verdi-2 solid-state laser was used as a Raman excitation source. A 25×-microscope objective lens was applied in order to focus the laser beam and collect the scattered light. The instrument resolution was 1 cm^{-1}. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. High-pressure in situ ADXD

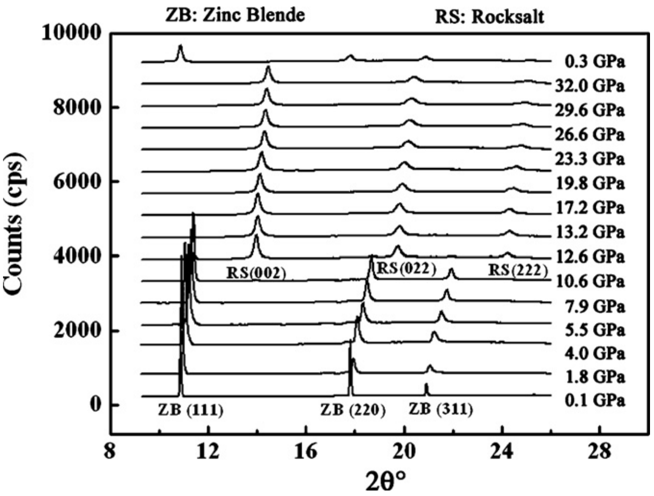

Fig. 1. High-pressure *in situ* ADXD patterns for the ZnSe nanoribbons.

At ambient conditions, ZnSe crystallizes in the ZB-type structure with lattice parameter $a \approx 0.5618$ nm and space group *F*-43*m*. Certainly, ZnSe nanoribbons have the same structure as the ZnSe bulk material. The results of the high-pressure *in situ* ADXD studies on the ZnSe nanoribbons at up to 32.0 GPa are shown in Fig. 1. For the diffraction pattern at lower pressure (∼0.1 GPa), all the diffraction peaks can be indexed to a cubic ZB structure. With the increase of pressure, a right shift of the diffraction peaks was observed due to the reduction of unit cell volume. Upon the application of pressure, the ZB phase persists up to about 10.6 GPa. Above 12.6 GPa, three peaks related to the ZB phase become significantly weak and three new peaks appear, indicating that a phase transition occurs. Beyond 13.2 GPa, the original peaks belonging to the ZB phase disappear completely, while the three new peaks are detectable up to the maximum experimental pressure (∼32.0 GPa). According to previous reports [16,22], these new peaks can be assigned to (0 0 2), (0 2 2) and (2 2 2) reflections of the RS structure. Moreover, the lattice parameter *a* is close to 0.5090 nm at about 12.6 GPa. Thus it is identified that the ZnSe nanoribbons undergo a structural transition from the ZB to RS phase at about 12.6 GPa, which is close to the corresponding results for the ZnSe bulk material (∼13.5 GPa) [16,23]. In fact, it was suspected that ZnSe might also undergo a similar structural transition like ZnTe from the ZB through a cinnebar, an orthorhomic (*Cmcm*) to a final RS structure according to theoretical calculations [24]. However up to now, there is no detailed experimental data confirming these transitions. As shown in Fig. 1, the ADXD results of our experiments only demonstrate the transition from the ZB to a RS phase.

We also studied the relative volume change of the ZnSe nanoribbons as a function of pressure, as shown in Fig. 2. For the ZB phase, the relative volume exhibits a monotonous reduction with increasing pressure up to 12.6 GPa. Thereby, a noticeable discontinuity was observed at about 5.5 GPa, as reported by Ves et al. [23] and Greene et al. [16] successively. However, the detailed interpretation remains unknown for this phenomenon. Obviously, in Fig. 2, there is a drastic decrease of about 13% in the relative volume at 12.6 GPa accompanied by the phase transition from the ZB to the RS type. In general, it is considered that ZnSe undergoes a direct phase transition from the ZB to the RS phase, thus the unidentified transition at lower pressure is commonly ignored during the fitting

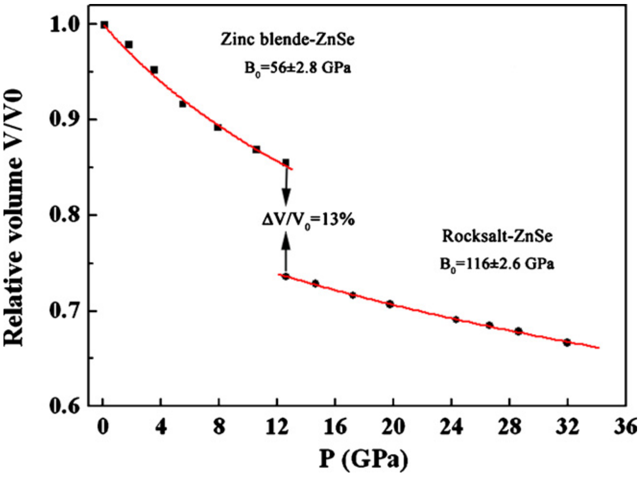

Fig. 2. The relative volume of ZnSe nanoribbons as a function of pressure.

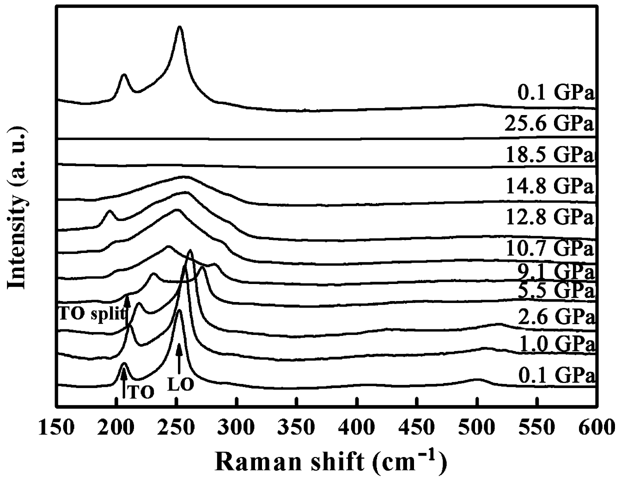

Fig. 3. High-pressure Raman scattering spectra for the ZnSe nanoribbons.

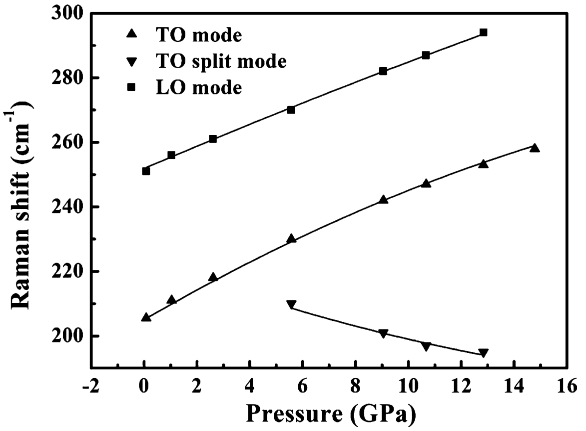

Fig. 4. The variation of the Raman modes as a function of pressure for the ZnSe nanoribbons.

by equation of states. The bulk modulus B_0 was obtained through fitting the relative volume–pressure experimental data related to the ZB and RS phases to Birch–Murnaghan equation of states. The values of B_0 are 56 GPa ($B'_0 = 4$) and 116 GPa ($B'_0 = 4$) for the ZB and RS phases, respectively. For the ZB phase, our results are slightly lower than that of ZnSe bulk materials (~62 GPa).

3.2. High-pressure Raman scattering

The Raman spectra at room temperature and at different pressures are presented in Fig. 3. At the lower pressure like 0.1 GPa, the LO and TO phonon modes are observed at about 251 and 205 cm^{-1}, respectively, which are in agreement with related reports [19,25]. With increasing pressure up to about 5.5 GPa, the TO phonon mode splits into two peaks. The lower one resulted from the mode softening and decreases with increasing of pressure, while the upper one continues to shift to higher frequency with pressure. Although the splitting of the TO phonon mode corresponds to the apparent discontinuity in the relative volume–pressure curve at about 5.5 GPa, no calculations have been reported for a phase transition at the corresponding pressure, so generally it is considered that ZnSe undergoes directly a phase transition from the ZB to the RS phase. Certainly, the LO phonon in ZB structure is non-degenerate. Thus, there is no splitting for the LO phonon mode, and its Raman shift only rises monotonously with increasing pressure. As the pressure is close to 12.8 GPa, the LO peak becomes invisible, which is attributed to the semiconductor–metal transition [13]. In the previous study for the bulk ZnSe, the related TO modes and the splitting of the TO phonon modes might persist up to higher pressures (>30 GPa). Therefore, those were considered not to be influenced by the metallization transition. However, for the ZnSe nanoribbons strongly broadened peaks centered at about the TO phonon modes can be observed in the Raman spectra at pressures beyond ~5.5 GPa. These Raman peaks related to the TO modes become very weak and invisible above 14.8 GPa. The related report [26] pointed out that the broadening of the peaks under pressure is higher than expected for the mixing of resonant three phonons. The possible reasons for this are attributed to disorders and localization in ZnSe associated with primary stages of nucleation of sixfold coordinated domains. Certainly, the related grain boundary effect should be considered as an influencing factor on the broadening of the peaks for the ZnSe nanoribbons. The broadening effect occurs at notable lower pressure (5–6 GPa) for the ZnSe nanoribbons than for the bulk ZnSe (normally ~11 GPa). In the Raman spectra at lower pressure the broadening of the peaks can be associated with non-homogeneous surface strains or the effect of interparticle dipole–dipole coupling on phonon modes in the ZnSe nanoribbons [26]. In our experiments, as the pressure is gradually released to the lowest pressure, the original peaks corresponding to the ZB phase reappear, thus confirming the reversible transition between the ZB and RS phases for the ZnSe nanoribbons.

The variation of the Raman modes as a function of pressure is shown in Fig. 4. The Raman modes corresponding to the TO, TO split and LO phonons are marked by triangles, inverted triangles and squares, respectively. Generally, the frequencies versus pressure can be expressed by a quadratic relationship for most semiconductors. Here, the frequencies of the phonon modes can be fitted by using the following formulae:

$$\text{TO}: \omega_1 = 205.1 + 4.76p - 0.075p^2$$

$$\text{TO split}: \omega_2 = 224.1 - 3.10p + 0.06p^2$$

$$\text{LO}: \omega_3 = 251.8 + 3.38p - 0.008p^2$$

where ω_i is the frequency of the i_{th} phonon mode in cm^{-1}, and p is the external pressure in GPa. According to the reports by Blackman and Daniels [27,28], the Grüneisen parameter (γ_i) can be defined as $\gamma_i = -(\partial \ln \omega_i / \partial \ln V) = (B_0/\omega_{i0})K_i$, where the values of $K_i = (\partial\omega_i/\partial p)_{p=0}$ can be gained by the slopes of phonon frequency versus pressure. The frequencies at zero pressure ω_{i0} are regressed by the fittings. In the above ADXD experiments, the obtained bulk modulus B_0 is 56 GPa ($B'_0 = 4$) for the ZB phase, thus the corresponding mode Grüneisen parameters are listed in Table 1. The values for the different modes are close to the results by Lin et al. [19]. With the exception of TO split mode, the values of K_i for other two modes are positive, thus the corresponding Grüneisen parameters are positive as well. Similar cases were usually reported for ZB-type semiconductors [29]. Moreover, it is also found that the Grüneisen parameter for the TO phonon modes is larger than the one for the LO phonon mode. Recently, Saib et al. [30] gave theoretical data about the mode Grüneisen parameters of AlN, and pointed out that the pressure dependence of the phonon frequencies and the mode

Table 1
Effect of pressure on the different Raman vibrational modes of ZnSe nanoribbons at room temperature. The values of mode frequencies ω_{i0}, pressure dependence K_i, and mode Grüneisen parameters γ_i were extrapolated at ambient conditions using the value of the bulk modulus from the high-pressure ADXD experiments.

Modes	ω_{i0} (cm^{-1})	K_i (cm^{-1} GPa^{-1})	γ_i
TO	205.1	4.76	1.30
TO split	224.1	−3.10	−0.77
LO	251.8	3.38	0.75

Grüneisen parameters are related to behavior of ionicity. Considering that both ZnSe and AlN belong to the wide band gap materials with high ionicity character, the results of Saib et al. [30] can be assigned to our experiments. Thus, the larger Grüneisen parameter for the TO phonon modes in comparison to the LO phonon mode points to a decrease in ionicity with rising pressure for the ZB-type ZnSe. This is in close correlation to the behavior of ZB-type ZnO as reported by Serrano et al. [29].

4. Conclusions

The high-pressure *in situ* ADXD experiments were carried out for the ZB-type ZnSe nanoribbons at pressures up to about 32.0 GPa and at ambient temperature. From the analysis of the ADXD patterns, it is verified that the ZnSe nanoribbons undergo a structural transition from the ZB to a RS phase at about 12.6 GPa, accompanying by a drastic decrease of 13% in the relative volume. The variation in the relative volume with pressure seems discontinuous at about 5.5 GPa, which indicates an unidentified transition similar to the related reports [16,19]. According to the results fitted by Birch–Murnaghan equation of states, the bulk modulus B_0 is ~56 GPa ($B_0' = 4$) for the ZB phase and the bulk modulus B_0 is ~116 GPa ($B_0' = 4$) for the RS phase. In high-pressure Raman scattering experiments, the TO phonon mode splits into two peaks at about 5.5 GPa, which is consistent with the results of the ADXD. The lower TO split phonon mode begins to soften and reduce with increasing pressure, while the upper component continues to shift to higher frequency with pressure. Upon the pressure of about 12.8 GPa, the LO peak disappears due to the semiconductor–metal transitions (accompanied by the transition of the ZB phase to the RS phase). Moreover, above 14.8 GPa, all the TO phonons become invisible, which is due to the related grain boundary effect, non-homogeneous surface strain or the effects of interparticle dipole–dipole coupling on phonon modes in the ZnSe nanoribbons. The mode Grüneisen parameters are obtained for the ZB phase on the basis of the bulk modulus from the ADXD experiments. The phenomenon on the larger Grüneisen parameter for the TO phonon modes points to a decrease in ionicity with rising pressure.

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