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High pressure photoluminescence and Raman studies of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ quantum dots

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Abstract

Raman and photoluminescence (PL) studies of wurtzite alloy $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ ($x = 0.2$) quantum dots (QDs) with size ~ 4.7 nm were carried out under hydrostatic pressure up to 130 kbar using the diamond anvil cell technique. The structural phase transition from wurtzite to rock-salt was observed at 71 kbar, indicated by the disappearance of both PL and Raman peaks. In addition, the abrupt change of PL pressure coefficient and Raman peak splitting were observed at about 25.8 kbar, which may indicate a new unidentified structural phase transition of the alloy QDs. This new unidentified phase transition was discussed and possible explanations were proposed. The results of alloyed ZnCdSe QDs differ greatly from that of bare CdSe or ZnSe QDs as well as the corresponding bulk materials, implying that the quantum size effect plays an important role in the structural stability of the alloy QDs.

1. Introduction

II–VI wide bandgap semiconductors (such as CdSe , ZnSe) have attracted much attention in the past decade. Their optical properties make them suitable for visible light-emitting diodes (LEDs), lasers and other optoelectronic devices [1, 2]. The alloy $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ is also a very important semiconductor: its compositional dependent bandgap can be tuned to cover the entire visible range. Recently, different nanostructured $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ have also been synthesized, such as $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ quantum wells, nanowires, nanorods and QDs [3–7]. The nanoscale structures bring out new properties. High-quality $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ QDs have been successfully prepared by the high temperature solution method [7]. These alloy QDs show high PL efficiency (70–85%) and narrow bandwidth (22–30 nm), which are comparable to the best reported CdSe -based QDs [8]. The $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ QDs can be very promising nanomaterials for applications as biological labels and short

wavelength optoelectronic devices such as quantum dot lasers and photovoltaic cells [7].

As is well known, the stability of QDs is not only essential in understanding their fundamental physical processes related to emission and Raman scattering, but is also vital to their applications. The alloy $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ QDs have demonstrated higher thermal and chemical stability due to its larger particle size, high crystallinity and ‘hardened’ lattice structure, compared with bare CdSe QDs. However, the structural stability of such alloy QDs is little known.

High pressure PL and Raman spectroscopy are the popular way to study the electronic structure and phase transition of semiconductor materials related to their structural stability. Tolbert and Alivisatos have reported the pressure-induced wurtzite to rock-salt structural transformation in CdSe QDs [9, 10]. They showed that both the thermodynamics and kinetics of this transformation were strongly altered in QDs due to their small size and high surface energy. For the alloy materials, three phase transitions were observed by Arora *et al* on $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ under pressure [11, 12]. It seems that the alloy

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sample may behave in a more complicated manner than binary structures (like CdSe) under high pressure. Li *et al* performed micro-Raman and PL investigations on $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ films ($x = 0.68$) and quantum wells ($x = 0.74$) under high pressure [13, 14]. They reported the pressure coefficients of the materials, but did not observe any phase transition up to 66 kbar. Camacho *et al* also studied the pressure dependence of optical phonons in zinc-blende ZnCdSe films ($x = 0.5$ and 0.6) at low temperature [15]. They did not observe any phase transition up to 75 kbar either.

In this paper, we performed high pressure Raman and PL experiments on the wurtzite $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ ($x = 0.2$) QDs (size ~ 4.7 nm, size distribution $< 10\%$) up to 130 kbar. Two structural phase transitions were observed and discussed: a new unidentified structural phase transition at 25.8 kbar and a wurtzite to rock-salt structural phase transition at 71 kbar. The experimental results of ZnCdSe QDs show significant differences from those of bare CdSe or ZnSe QDs as well as the corresponding bulk materials.

2. Experimental details

High-quality $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ QDs were successfully prepared at high temperature by incorporating stoichiometric amounts of Zn and Se into pre-prepared CdSe QDs [7], and the size of the $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ ($x \sim 0.2$) QDs was ~ 4.7 nm as shown by the transmission electron microscopy (TEM) image inserted in figure 1(a). Energy-dispersive x-ray analysis (EDX) shows that the mole ratio of zinc:cadmium:selenium is 9.8:40:50.2, so the zinc composition is around $x = 0.2$. X-ray diffraction (XRD) results reveal that the $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ QDs ($x \sim 0.2$) have a hexagonal wurtzite structure [7]. High pressure was generated by a diamond anvil cell (DAC), with a 4:1 methanol–ethanol mixture as the pressure medium. Pressure was calibrated by the energy shift of the R_1 luminescence line of a ruby crystal. The micro-Raman and PL measurements were carried out with a Renishaw inVia Raman system using a 532 nm DPSSL laser. The laser was focused on the sample with a $20\times$ objective lens. The Raman and PL signals are collected by the same lens in the backscattering geometry. The signals are then directed to the spectrograph and detected with a charge coupled device (CCD) detector. The laser power at the sample is below 1 mW to avoid laser-induced sample heating [16].

3. Results and discussion

Figure 1(a) shows the absorption and PL spectrum of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ ($x = 0.2$) QDs at ambient pressure. The absorption band of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ ($x = 0.2$) QDs is around 2.12 eV, which is blueshifted compared to that of the corresponding bulk $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ with the same zinc composition (1.83 eV) [17] due to the quantum confinement effect. The PL spectrum was excited by a 532 nm laser line. The band-edge emission is at about 2.04 eV (609 nm). The PL peak at 609 nm is quite symmetrical and has a full width at half-maximum (FWHM) of about 30 nm, indicating that the sample is of high quality, with a narrow distribution in the size of QDs. Compared to other wurtzite structure QDs, such as ZnO, the

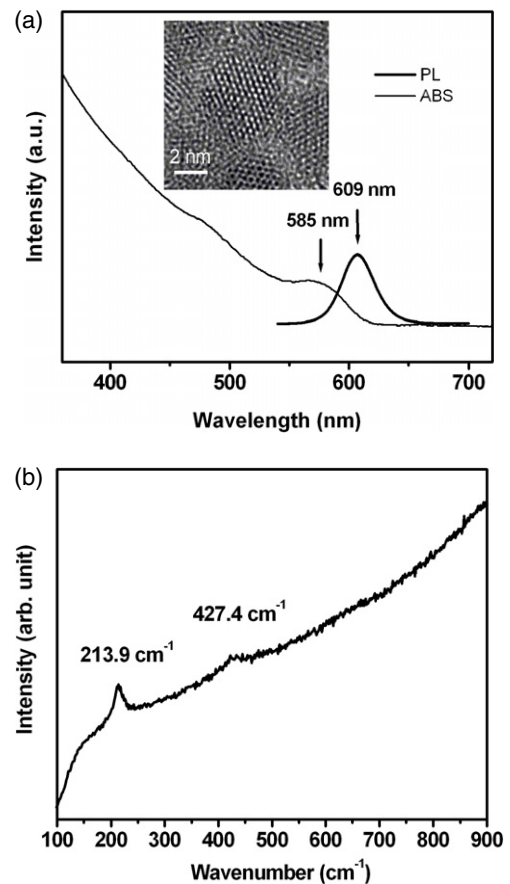


Figure 1. PL (a) and Raman (b) spectra of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ ($x = 0.2$) QDs at ambient pressure excited by using a 532 nm laser line.

ZnCdSe QDs have emission bands between 450 and 650 nm which can be tuned by their size and Zn composition. The ZnO QDs have a near-band-edge UV emission at ~ 400 nm and a very broad emission band at 500–600 nm caused by defects such as oxygen vacancies [18].

Figure 1(b) shows the Raman spectrum of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ ($x = 0.2$) QDs at ambient pressure. There are two peaks in the spectrum; the stronger one at 213.9 cm^{-1} is the A_1 longitudinal–optical (LO) mode of the alloy QDs, while the weaker peak at 427.4 cm^{-1} is the overtone of the LO mode, which is exactly twice the frequency of the LO mode. The sharp drop at about 150 cm^{-1} is caused by the notch filter and the upward slope background is caused by the strong broad photoluminescence, whose maximum is located at about 600 nm, as shown in figure 1(a). The FWHM of the LO peak is about 26 cm^{-1} . Compared to the ZnCdSe bulk materials with similar Zn composition (FWHM $\sim 8\text{ cm}^{-1}$, peak position $\sim 219\text{ cm}^{-1}$) [19], the LO mode of ZnCdSe QDs shifts to lower frequency and becomes broader. These are due to small physical dimensions of the QDs which lead to the breakdown of the $q = 0$ selection rule of phonon dispersion, causing the first-order Raman line to shift and broaden [20, 21]. According to the calculation results, the quantum confinement induced redshift of CdSe with size about 5 nm is $\sim 4\text{ cm}^{-1}$ [20], which is close to our observed value of 5 cm^{-1} redshift for ~ 4.7 nm ZnCdSe QDs.

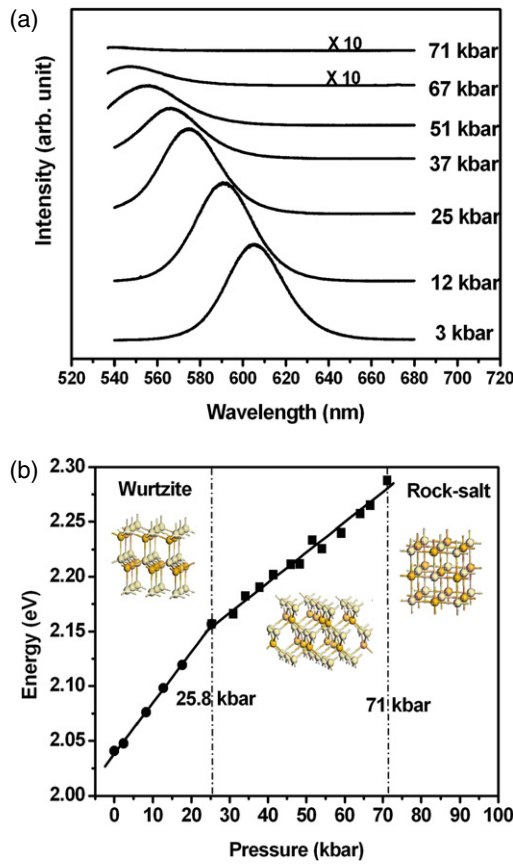


Figure 2. (a) PL spectra taken from $Zn_xCd_{1-x}Se$ ($x = 0.2$) quantum dots under high pressure at room temperature. Above 71 kbar, the PL peak cannot be observed because of the phase transition. (b) PL peak energy of $Zn_xCd_{1-x}Se$ ($x = 0.2$) QDs as a function of pressure. At 25.8 kbar, the pressure coefficient changed from 4.64 to 2.76 meV kbar⁻¹.

(This figure is in colour only in the electronic version)

Next, we studied PL spectra of $Zn_xCd_{1-x}Se$ ($x = 0.2$) QDs under pressure. Figure 2(a) shows the PL spectra with increasing pressure. A large blueshift of the PL peak was observed due to the pressure-induced blueshift of bandgap energy. Above the pressure of 71 kbar, the PL peak disappeared, indicating that the QDs undergo a phase transition from a direct-bandgap wurtzite structure to an indirect-bandgap rock-salt structure, which will cause the annihilation of PL emission [22–25]. We also repeated the high pressure PL experiment using a 488 nm excitation laser. The results were quite similar to those of using a 532 nm excitation laser. Most of the wurtzite/zinc-blende semiconductors (including CdSe and ZnSe) have the wurtzite/zinc-blende to rock-salt phase transition under high pressure and this phase transition was observed in corresponding nanoscale semiconductors too [9, 26, 27]. Here the phase transition pressure of $Zn_xCd_{1-x}Se$ QDs (71 kbar) is higher than that of CdSe QDs (20–49 kbar) [9, 26, 27] and lower than that of ZnSe QDs (95–130 kbar) with various sizes [27]. Moreover, this phase transition has not been observed for $Zn_{0.5}Cd_{0.5}Se$ up to 75 kbar, which has a higher zinc composition than our sample [15]. Apparently for $Zn_xCd_{1-x}Se$ alloy, the pressure

of wurtzite/zinc-blende to rock-salt phase transition increases as the zinc composition increases.

The PL energy as a function of pressure is shown in figure 2(b). We fitted the data with the following formula:

$$E_P = E_0 + \alpha P$$

where E_0 is the ambient pressure PL energy, α is the PL pressure coefficient and P is the applied hydrostatic pressure in kbar. It was found that, at lower pressure, the PL energy of $Zn_xCd_{1-x}Se$ ($x = 0.2$) QDs shifted linearly with a pressure coefficient of 4.64 meV kbar⁻¹. However, above 25.8 kbar, the pressure coefficient changed to 2.76 meV kbar⁻¹ and the PL peak also shifted quite linearly with pressure. Obviously there is an electronic structure change at this critical pressure, which may be due to an unidentified structural transition induced by pressure.

High pressure Raman spectroscopy studies of ZnCdSe alloy QDs were also carried out. The Raman LO mode shifted to higher frequencies with pressure, and disappeared at 71 kbar, the same pressure at which the PL disappears. The disappearance of the LO mode is also attributed to the wurtzite to rock-salt phase transition as Raman scattering of the rock-salt phase is inactive. In order to study the possible structural phase transition at 25.8 kbar, the Raman spectra of ZnCdSe QDs before and after 25.8 kbar were compared. Figure 3(a) shows the Raman spectra at 0 and 32 kbar, in which a Raman peak splitting is clearly observed. By fitting all the Raman spectra at different pressures, we find that the peak splitting also began at 25.8 kbar. Figure 3(b) shows the Raman peak position of the LO peak as a function of pressure. The pressure coefficient of the LO mode before 25.8 kbar was about 0.525 cm⁻¹ kbar⁻¹, with a linear fit of $\omega = 214.3 \text{ cm}^{-1} + 0.525 P \text{ cm}^{-1} \text{ kbar}^{-1}$. After splitting, the higher frequency peak has a pressure coefficient of 0.517 cm⁻¹ kbar⁻¹, with a linear fit of $\omega = 221.5 \text{ cm}^{-1} + 0.517 P \text{ cm}^{-1} \text{ kbar}^{-1}$; and the lower frequency peak has a coefficient of 0.473 cm⁻¹ kbar⁻¹, with a linear fit of $\omega = 201.7 \text{ cm}^{-1} + 0.473 P \text{ cm}^{-1} \text{ kbar}^{-1}$. The Raman LO mode splitting as well as the PL pressure coefficient sudden change at the same pressure (25.8 kbar) indicates that there is a new structural phase transition. This phase transition has not been observed in bulk $Zn_xCd_{1-x}Se$ as well as in bulk or nanoscaled CdSe and ZnSe. Zhao *et al* [28] have also investigated the high pressure PL spectra of ZnCdSe QDs and they did not observe this new phase transition, partially because the PL change is not very obvious for this phase transition. On the other hand, Raman spectroscopy is easy and efficient to use to identify a structural phase transition.

As is well known, the II–VI semiconductors (such as CdSe) have two stable structures at ambient conditions, which are wurtzite and zinc-blende. Sometimes there is a mixture of these two structures. Under high pressure, the wurtzite/zinc-blende structured II–VI semiconductors have their first-order phase transition to rock-salt structure, followed by the cinnabar or orthorhombic Cmc₂m phase [29–32]. The structure of our ZnCdSe QDs at ambient condition is wurtzite, while at 25.8 kbar, it went through an unidentified phase transition. The observed new phase transition is below that of the wurtzite

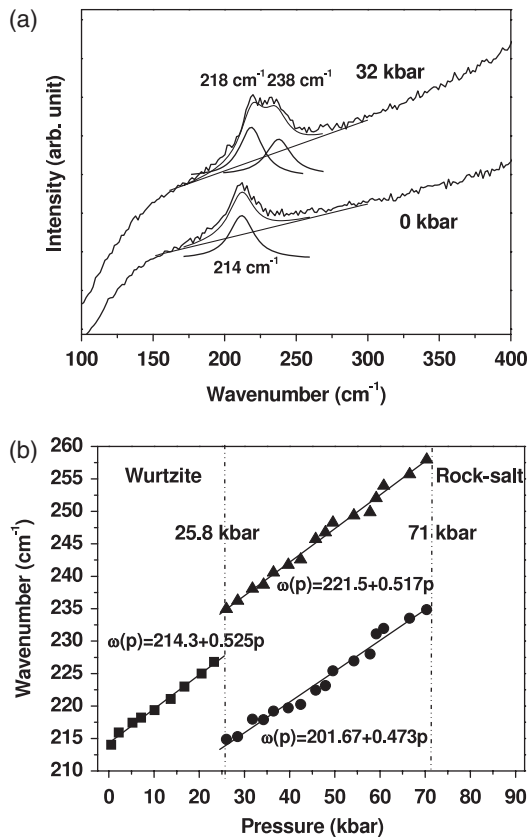


Figure 3. (a) Raman spectra of $Zn_xCd_{1-x}Se$ ($x = 0.2$) QDs at pressures of 0 and 32 kbar. The smooth solid curves are the Lorentzian fitting of the peaks. (b) Raman shift of the LO mode of $Zn_xCd_{1-x}Se$ ($x = 0.2$) QDs as a function of pressure. After 25.8 kbar, a peak splitting was observed. Above 71 kbar, the Raman peaks cannot be observed because of the semiconductor–metal phase transition.

to rock-salt phase transition at 71 kbar, which is confirmed by the disappearance of both Raman and PL intensity. The structure between 25.8 and 71 kbar cannot be cinnabar or Cmc_m either, as the energies of these two structures are usually similar or higher than rock-salt [30], and they are also indirect-bandgap structures without PL. Recently, an intermediate phase between wurtzite and rock-salt, which is known as the h-MgO phase, has been widely studied theoretically [33–36]. The h-MgO phase was considered as a possible intermediate phase in several semiconductors, such as MgO, GaN and CdS [33–35]. Although the h-MgO phase is found to be unstable in bulk CdSe because of its high energy [35], there was a theoretical prediction that this intermediate phase is accessible during the phase transition of nanocrystalline CdSe, mainly because of its high surface area [37]. However, according to our calculation, the h-MgO structured II–VI semiconductors (CdSe and ZnCdSe) are indirect-bandgap structures, which do not emit PL. In that case, the phase between 25.8 and 71 kbar of ZnCdSe QDs cannot be the intermediate h-MgO phase either.

A possible structure would be zinc-blende. Zinc-blende is a direct-bandgap structure, which has a strong PL just like wurtzite. This is consistent with our results that the

PL signals between 25.8 and 71 kbar were still strong. The wurtzite to zinc-blende phase transition has been observed under pressure by Pan *et al* [38] on nanocrystalline ZnS and Wang *et al* [39] on ZnS nanobelts with synchrotron x-ray diffraction experiments. Moreover, the ZnCdSe alloy has a phase transition from wurtzite to zinc-blende by increasing the zinc composition [40]. Different zinc compositions result in different structures, implying that the wurtzite to zinc-blende phase transition is a smooth transition that can easily happen for $Zn_xCd_{1-x}Se$ alloy. Note that, if the QDs were in the zinc-blende phase between 25.8 and 71 kbar, the deduced bandgap of the zinc-blende structure at ambient pressure (2.08 eV) is slightly higher than that of the wurtzite structure (2.04 eV), which deviates from the normal case [41]. The lower bandgap energy of the wurtzite structure (~ 0.04 eV) could be caused by the different positions of the elements in the two structures, or the size changing of the QDs during the phase transition. Besides zinc-blende, there may also be other possible explanations for the new phase transition, such as a new high pressure structure, and a tilted wurtzite structure [42]. Further experiments, such as high pressure x-ray diffraction, are necessary to clarify this new phase transition. The quantum size effects on the structure stability of QDs have been demonstrated on the wurtzite to rock-salt phase transition studies of CdSe QDs. Both the thermodynamics and kinetics of transformation were strongly altered in QDs. The smaller size QDs have a higher phase transition pressure, which was attributed to its higher surface energy [9]. Another size-dependent high pressure experiment also showed that the structural metastability in CdSe QDs is dependent on their size [43]. Since, for the bulk ZnCdSe, no new phase was observed between the wurtzite and rock-salt phases, we propose that the quantum size effects also play an important role in the new phase transition at ~ 25.8 kbar for ZnCdSe QDs.

Upon decreasing the pressure, the Raman and PL peaks can be observed at 22 kbar and below. The splitting Raman LO modes recovered one peak, which means that the QDs transform directly from rock-salt back to wurtzite structure. The wurtzite to rock-salt phase transition of ZnCdSe alloy QDs has a hysteresis of about $71 - 22 = 49$ kbar, which is broader than that of CdSe QDs (20–40 kbar) [9]. After releasing the pressure, the recovered LO Raman peak is at about 210 cm^{-1} , which is 4 cm^{-1} lower than the peak position before the pressure was applied, as shown in figure 4(a). The main PL peak energy is at ~ 1.99 eV after releasing pressure, which is 0.05 eV lower than peak energy before pressure, as shown in figure 4(b). Besides, the PL peak becomes asymmetric with a tail to the low energy side. The redshift of the Raman peak cannot be caused by the smaller size of dots through the phase transition [10], because smaller size QDs will accompany a higher electronic transition energy, hence the blueshift of PL [44, 45], which is not in accord with our result. Both redshifts in Raman frequency and PL energy were caused by lattice defects that formed under the pressure and phase transition. The bandgap shrinkage (redshift of absorption edge) and redshift of the Raman bands were also observed in the high pressure experiments on CdS, which were attributed to the lattice defects after phase transition and upon release of

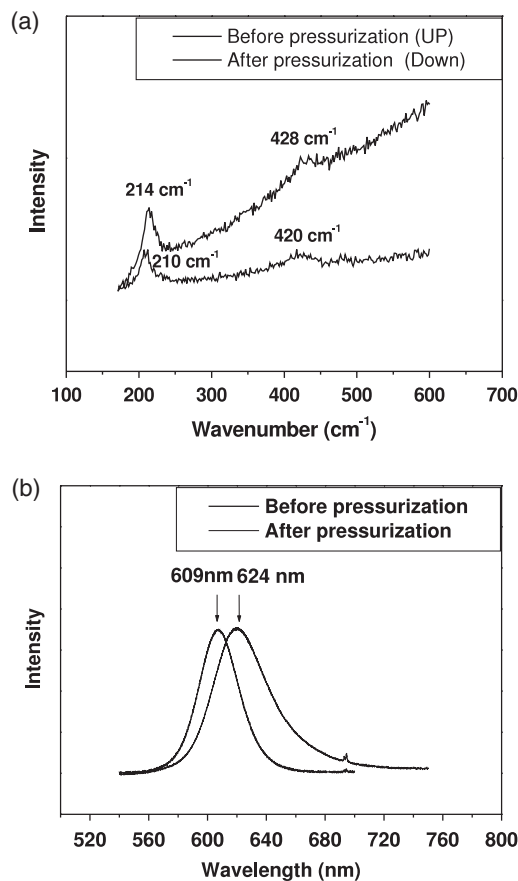


Figure 4. Raman (a) and PL (b) spectra of $Zn_xCd_{1-x}Se$ ($x = 0.2$) QDs before and after applying the pressure.

pressure [24]. Such lattice defects would cause the shrinkage of the bandgap, hence the redshift of the PL peak in our experiments. The asymmetry of the recovered PL peak may be due to the increased emission of surface states, which are formed by the rearrangement of the surface during the phase transition [10].

4. Conclusion

In summary, Raman and PL experiments have been carried out on $Zn_xCd_{1-x}Se$ ($x = 0.2$) QDs under hydrostatic pressure up to 130 kbar at room temperature. Two structural transitions were observed in the pressure range. The wurtzite to rock-salt was observed at about 71 kbar, indicated by the disappearance of PL and Raman peaks. A new unidentified phase transition was also observed at about 25.8 kbar. At this pressure, the PL coefficient has a sudden change from 4.64 to 2.76 meV kbar⁻¹, and also a split in the Raman peak was observed. These results for $ZnCdSe$ QDs show a significant difference from those of bulk $ZnCdSe$ as well as $CdSe$ and $ZnSe$ QDs, implying that the quantum size effect plays an important role in the structural stability of the alloy QDs.

References

[1] Klimov V I, Mikhailovsky A A, Xu S, Malko A, Hollingsworth J A, Leatherdale C A, Eisler H J and Bawendi M G 2000 *Science* **290** 314

[2] Coe S, Woo W K, Bawendi M and Bulovic V 2002 *Nature* **420** 800

[3] Matsumura N, Yasui K and Saraie J 2002 *J. Cryst. Growth* **237** 1536

[4] Zhang X T, Liu Z, Li Q and Hark S K 2005 *J. Phys. Chem. B* **109** 17913

[5] Lee H, Holloway P H and Yang H 2006 *J. Chem. Phys.* **125** 164711

[6] Venugopal R, Lin P I and Chen Y T 2006 *J. Phys. Chem. B* **110** 11691

[7] Zhong X H, Han M Y, Dong Z L, White Timothy J and Knoll W 2003 *J. Am. Chem. Soc.* **125** 8589

[8] Reiss P, Bleuse J and Pron A 2002 *Nano Lett.* **2** 781

[9] Tolbert S H and Alivisatos A P 1994 *Science* **265** 373

[10] Tolbert S H and Alivisatos A P 1995 *J. Chem. Phys.* **102** 4642

[11] Arora Akhilesh K and Sakuntala T 1995 *Phys. Rev. B* **52** 11052

[12] Arora Akhilesh K, Suh E K, Debska U and Ramdas A K 1988 *Phys. Rev. B* **37** 2927

[13] Li W S, Shen Z X, Shen D Z and Fan X W 1998 *J. Appl. Phys.* **84** 5198

[14] Li W S, Chi Y B, Li Y M, Fan X W, Yang B J, Shen D Z and Lu Y M 1995 *Thin Solid Films* **266** 307

[15] Camacho J, Loa I, Cantarero A, Syassen K, Hernandez-Calderon I and Gonzalez L 2003 *Phys. Status Solidi b* **235** 432

[16] Alim K A, Fonoberov V A and Balandin A A 2005 *Appl. Phys. Lett.* **86** 053103

[17] Kim Y D, Klein M V, Ren S F and Chang Y C 1994 *Phys. Rev. B* **49** 7262

[18] Fonoberov V A, Alim K A, Balandin A A, Xiu F X and Liu J L 2006 *Phys. Rev. B* **73** 165317

[19] Brafman O 1972 *Solid State Commun.* **11** 447

[20] Tanaka A, Onari S and Arai T 1992 *Phys. Rev. B* **45** 6587

[21] Hwang Y N, Shin S, Park H L, Park S H and Kim U 1996 *Phys. Rev. B* **54** 15120

[22] Jacobs K, Zaziski D, Scher E C, Herhold A B and Alivisatos A P 2001 *Science* **293** 1803

[23] Tolbert S H, Herhold A B, Johnson C S and Alivisatos A P 1994 *Phys. Rev. Lett.* **73** 3266

[24] Venkateswaran U, Chandrasekhar M and Chandrasekhar H R 1984 *Phys. Rev. B* **30** 3316

[25] Zhao X S, Schroeder J, Bilodeau T G and Hwa L G 1989 *Phys. Rev. B* **40** 1257

[26] Shan W, Walukiewicz W, Ager J W III, Yu K M, Wu J and Haller E E 2004 *Appl. Phys. Lett.* **84** 67

[27] Mujica A, Rubio A, Munoz A and Needs R J 2003 *Rev. Mod. Phys.* **75** 863

[28] Zhao Z, Zeng J, Ding Z J, Wang X P, Hou J G and Zhang Z M 2007 *J. Appl. Phys.* **102** 053509

[29] Zakharov O, Rubio A and Cohen M L 1995 *Phys. Rev. B* **51** 4926

[30] Côté M, Zakharov O, Rubio A and Cohen M L 1997 *Phys. Rev. B* **55** 13025

[31] Nemes R J and McMahon M I 1998 *Semicond. Semimet.* **54** 145

[32] Fan H M, Ni Z H, Feng Y P, Fan X F, Kuo J L, Shen Z X and Zou B S 2007 *Appl. Phys. Lett.* **90** 021921

[33] Limpjumnong S and Lambrecht Walter R L 2001 *Phys. Rev. B* **63** 104103

[34] Limpjumnong S and Lambrecht Walter R L 2001 *Phys. Rev. Lett.* **86** 91

[35] Knudson M D, Gupta Y M and Kunz A B 1999 *Phys. Rev. B* **59** 11704

[36] Shimojo F, Kodiyalam S, Ebbsjo I, Kalia Rajiv K, Nakano A and Vashishta P 2004 *Phys. Rev. B* **70** 184111

[37] Grunwald M, Rabani E and Dellago C 2006 *Phys. Rev. Lett.* **96** 255701

[38] Pan Y W, Qu S C, Dong S S, Cui Q L, Zhang W W, Liu X Z, Liu J, Liu B B, Gao C X and Zou G T 2002 *J. Phys.: Condens. Matter* **14** 10487

- [39] Wang Z W, Daemen L L, Zhao Y S, Zha C S, Downs R T, Wang X D, Wang Z L and Hemley R J 2005 *Nat. Mater.* **4** 922
- [40] Nasibov A S, Korostelin Y V, Shapkin P V, Suslina L G, Fedorov D L and Markov L S 1989 *Solid State Commun.* **71** 867
- [41] Yeh C Y, Wei S H and Zunger A 1994 *Phys. Rev. B* **50** 2715
- [42] Bae I T, Seong T Y, Park Y J and Kim E K 1999 *J. Electron. Mater.* **28** 873
- [43] Chen C C, Herhold A B, Johnson C S and Alivisatos A P 1997 *Science* **276** 398
- [44] Vossmeier T, Katsikas L, Giersig M, Popovic I G, Diesner K, Chemseddine A, Eychmüller A and Weller H 1994 *J. Phys. Chem.* **98** 7665
- [45] Alivisatos A P 1996 *Science* **271** 933