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Pressure-induced phase transition in Thiol-capped CdTe Nanoparticles

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Abstract

Phase transitions for CdTe nanoparticles (NPs) under high pressure up to 37.0 GPa have been studied using fluorescence measurements. The phase transition from cinnarbar to rocksalt phase has been observed in CdTe NPs solution at 5.8 GPa, which is much higher than the phase transition pressure of bulk CdTe (3.8 GPa) and that of CdTe NPs in solid form (0.8 GPa). CdTe NPs solution therefore shows elevated phase transition pressure and enhanced stability against pressure compared with bulk CdTe and CdTe NPs in solid forms. The enhanced stability of CdTe NPs solution has been attributed to possible shape change in the phase transition and/or inhomogeneous strains in nanoparticle solutions.

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1. Introduction

II-VI semiconductors such as CdS, CdSe, and CdTe have been found to undergo phase transitions by applying pressure[1-5]. Since the band structure changes with phase, the studies on pressure-induced phase transition will provide information not only on how the phase stability of the materials can be affected by factors such as surface, size, and shape, but also on the nature of the states involved in electronic relaxations. One of the critical issues in these studies is how the phase stability will change with surface or size.

CdS and CdSe nanoparticles (NPs) in colloidal suspension exhibit enhanced phase stability against pressure, compared with corresponding bulk materials[1-3,6,7]. For example, the pressure-induced wurtzite to rock salt phase in bulk CdS and CdSe normally occurs at ~ 2-3 GPa and shifts up to 4-8 GPa in CdS and CdSe NPs. Different groups agree that preparation method is very important for the phase stability. However, it is not clear yet whether the method simply affects the defect density or surface intension. Haase and Alivisatos proposed that surface tension alone is responsible for the stabilization in 4-5 nm CdS NPs using methanol as pressurizing fluid[1]. Rock salt phase has been shown to have a higher surface tension than wurtzite phase due to the shape change in phase transition. While Arai et al. studied very large CdS NPs (75-315 nm) in colloidal solution using resonant Raman scattering, with 4.3 to 4.0 GPa transition pressures for small and large NPs, respectively[2]. They suggested that higher defect density in NPs might be responsible for the enhanced stability relative to bulk and that the size dependence of the phase transition can not be explained by any single mechanism. Controversies still exist regarding the mechanisms of the stabilization.

Bulk CdTe has two successive phase transition over a narrow pressure range at 3.5-4 GPa: first zinc-blende to cinnabar and then cinnabar to rocksalt phase[4,8-11]. At about 11.4 GPa, the rocksalt

phase changes to a metallic high-pressure β-tin phase[12,13]. The cinnabar phase is not present in the phase transitions in other II-VI compounds, where the zinc-blende or wurtzite phase at low pressures and the β-tin phase at high pressures are separated by an intermediate rocksalt phase only. The energy gap of the CdTe cinnabar phase is found to be similar to that of zinc-blende phase since there is no discontinuity in the direct energy gap in the pressure range of 3.5-4.2 GPa[9]. Although the pressure-induced phase transitions in bulk CdTe have been well addressed and relatively well understood, so far there is no such study reported in CdTe NPs, to our knowledge. How would factors such as size and surface influence the phase transitions in CdTe NPs still remain open.

In this paper, we report the first measurement of the pressure dependence of the energy gap in CdTe NPs. The transition pressure from cinnarbar to rocksalt has been elevated from the bulk transition pressure of 3.8 GPa to 5.8 GPa in CdTe NPs solutions. However, CdTe NPs in solid form exhibit a reduced transition pressure to 0.8 GPa. Two possible mechanisms can account for the enhanced phase stability in CdTe NPs solutions. One is the possible shape changes involved in the phase transitions, leading to a higher surface tension in rocksalt than in cinnabar phase. The other possibility is that the crystallinity for CdTe NPs solution is not as good as bulk CdTe and solid CdTe NPs, resulting in a remarkable increase of inhomogeneous strain in CdTe NPs solutions.

2. Experimental

Synthesis of the water soluble thiol-capped CdTe NPs has been described in details previously [14,15]. Thiol-capped CdTe NPs have been transferred from aqueous solution to chloroform by modifying a published recipe [16]. Briefly, 5 ml of the thiol-capped CdTe NPs solution was diluted to 50 ml with milli-Q water and the pH was adjusted to 6 by adding HCl. CdTe NPs were then transferred from water to chloroform using a phase transfer agent (DODABr,

dimethydioctadecylammonium bromide) in a separatory funnel. We modified the recipe by change the ratio of CdTe NPs/DODABr. The transfer was completed when the organic phase turned from colorless to yellow and the aqueous phase changed from yellow to almost colorless.

Static electronic absorption and fluorescence spectra were obtained using a Hewlett-Packard 8452A Diode Array UV-visible spectrometer and a Perkin-Elmer fluorometer (LS50B), respectively. High pressure fluorescence measurements have been performed using a diamond anvil cell with liquid Ar as the pressure medium.

Optical measurements were made on a solution of CdTe nanocrystals in chloroform loaded in a Merrill Bassett diamond anvil cell (DAC) [17] along with a $SrB_4O_7:Sm^{2+}$ pressure marker. The *in situ* pressure was determined using a $SrB_4O_7:Sm^{2+}$ scale [18]. In addition solid CdTe nanocrystals were studied using argon as a pressure medium. The 488 nm line from a Coherent Inova 90 argon ion laser was used to populate excited state electronic levels in CdTe nanoparticles. Photoemission measurements were conducted on a Jobin Yvon Horiba LabRam spectrograph using a 1200 g/mm diffraction grating and a high-performance CCD multichannel matrix detector. CdTe fluorescence spectra were collected from 490 – 850 nm and corrected for instrument response using a 3000K halogen bulb. In addition a spectral intensity correction accounting for Blackbody radiation was subtracted from the instrument response data. All high pressure measurements were made at room temperature.

3. Results and Discussion

Figure 1 represents the static electronic absorption and fluorescence spectra of CdTe NPs in chloroform solution recorded at room temperature. The absorption spectrum shows an excitonic peak at around 530.0 nm, indicating a particle size of around 3 nm in diameter[19]. The

fluorescence spectrum shows strong bandedge emission at around 538.5 nm and hardly any deep trap emission. Here we assume the direct energy bandgap is approximately equal to the energy of bandedge emission since the difference between them is found to be small (in a few tens of meV) and normally is difficult to distinguish bandedge states from the bottom of conduction band or the top of valence band[20].

The energy bandgaps obtained from the high pressure fluorescence measurements have been plotted in Figure 2 as a function of pressure. The bandgap increases linearly with pressure from 0.01 to 3.5 GPa. With further increasing of the pressure, it then becomes saturated and at the pressure of 5.8 GPa, it starts to decrease with increasing pressure.

The data in the lower pressure range from 0 to 6 GPa can be fit to a quadratic form as shown in Figure 3:

$$\Delta E = E_0 + bP + cP^2 \qquad (1)$$

with a linear pressure coefficient b = 6.79×10^{-2} eV GPa^{-1}, which is consistent with the literature values obtained for bulk CdTe from other groups (b = 6.45×10^{-2}-8.57×10^{-2} eV GPa^{-1}) [4,9,10,21-28]. Since the shallow trap state wave function can be well-represented by the superposition of free particle wave functions with a narrow distribution of wave vectors, it makes sense that the pressure coefficients for these shallow trap states is close to that of the corresponding bandgap. The fact that the pressure coefficient for CdTe NPs is close to that of bulk CdTe indicates similarity between the bandgap of CdTe NPs and that of bulk CdTe.

In addition to the similarity, pressure-induced phase transitions in CdTe NPs also show differences from that of bulk CdTe. It has been shown that bulk CdTe has two phase transitions over a narrow pressure range ~ 3.5 GPa, first from zinc-blende to cinnabar and then from cinnarbar to rocksalt phase[8,9]. However, the energy gap exhibits a sublinear increase with pressure during the

first transition (zinc-blende to cinnarbar). The lack of discontinuity in the energy bandgap during the transition suggests that the band structure of the reported CdTe cinnarbar phase is similar to that of zinc-blende phase. At around 4 GPa, the energy gap drops by about 1.84 eV due to a direct to indirect bandgap transition (zinc-blende/cinnarbar to rocksalt). Similar large and abrupt red shift in the bandgap has been observed in other II-VI bulk and NPs materials such as CdS and CdSe when they transform to rocksalt phase at high pressure[9,29-31]. We therefore ascribe the observed turning point at around 5.8 GPa in Figure 2 to the transition from cinnarbar/zincblende to rocksalt phase. CdTe NPs solution seems to have an elevated transition pressure from that of bulk CdTe (~ 3.8 GPa).

A phase transition can only occur between phases 1 and 2 when they have equal Gibbs free energy $G_1=G_2$, that is:

$$U_1 + PV_1 - TS_1 = U_2 + PV_2 - TS_2 \qquad (2)$$

where U is the internal energy, and P, V, T and S are the pressure, volume, temperature, and entropy as usual. At low temperature, the third term can be abbreviated and the transition pressure P_T is given by:

$$P_T = \frac{U_2 - U_1}{V_2 - V_1} \qquad (3)$$

When the size goes into the regime of nanometer, surface tension becomes increasing important because the number of atoms on the surface increases relative to the ones inside. Surface tension provides additional pressure and therefore can reduce the external pressure needed for a phase transition. Eq. (3) can be modified if taking surface tension into consideration:

$$P_T = \frac{(U_2 + \tilde{a}_2 A_2) - (U_1 + \tilde{a}_1 A_1)}{V_2 - V_1} \qquad (4)$$

where γ is the surface tension and A is the surface area. The phase transition pressure will be elevated if the product phase has a high surface tension than the starting phase.

Alivisatos and collaborators are the first to report the elevated phase transition pressure and enhanced stability in CdS and CdSe NPs from that of the bulk[1,6,32]. They proposed a mechanism for the transition from wurtzite or zincblende to rocksalt phase, which involves a dramatic shape change. The rocksalt phase therefore has a larger surface tension than wurtzite or zincblende phase and surface tension alone is responsible for the stabilization.

Another group studied the phase transition in CdS NPs with much larger sizes.(in tens or hundreds of nm) Samples with poorer crystallinity have been found to have an elevated phase transition pressure due to significant inhomogeneous strain. They proposed that inhomogeneous strains as well as defects and surface condition might be responsible for the enhanced stability and size dependence of the phase transition could not be explained by any single mechanism.

To answer if the crystallinity of NPs affects the phase transition, we evaporate the solvent (chloroform) of CdTe NPs solution and measurement the changes of fluorescence under high pressures. As shown in Figure 4, CdTe NPs in solid form show a reduced transition pressure at around 0.8 GPa. Since the samples were prepared by evaporating the solvent and using CdTe powders re-crystallized from the CdTe NPs solution, we expect the crystallinity in the powders is better than that in the mother solution. The atomic arrangement in the powders is then more ordered, resulting in less inhomogeneous strain and reduced phase transition pressure. Our results seem to indicate that crystallinity also plays an important role in the pressure-induced phase transitions in CdTe NPs. A comparison of XRD patterns between the liquid and solid samples would be helpful in determining the crystallinity. Further experiments are underway.

Above 5.8 GPa, the energy bandgap decreases with increasing pressure, as shown Figure 2. Since most studies of II-VI CdS and CdSe NPs have been focused on the transition from zinc-blende/wurtzite to rocksalt phase, no one has ever reported the decrease of energy gap with pressure in any II-VI NPs. The only report of such behavior has been found for InP NPs, which has been ascribed to the direct-to-indirect bandgap transition[33]. This could be the reason for the decrease of energy bandgap with pressure observed here for CdTe NPs. At pressures above 5.8 GPa, the fluorescence peak could shift to red and trap state emission could dominate the fluorescence spectra. Beyond 10 GPa, CdTe NPs could transform from indirect rocksalt to metallic β-tin phase. The fluorescence peak then could shift to near IR/IR region or even redder position, which can be out of our detection limit. In a few high pressure measurements of bulk CdTe, the bandgap has been found to increase with pressure for the phase of rocksalt. If we can detect the high pressure fluorescence signal in the redder wavelength, we might be able to address the phase transition behavior above 5.8 GPa in more detail. Our current detections in visible range only indicate the transition from a direct bandgap to an indirect bandgap structure at around 5.8 GPa.

Conclusions:

As a summary, we performed the first measurements of the pressure-induced phase transitions in CdTe NPs. At low pressures, CdTe NPs show similar linear pressure coefficients to that of bulk CdTe. In addition to the similarities, the behaviors of CdTe NPs are different from bulk in the elevated transition pressure from cinnarbar to rocksalt phase and the decrease of energy bandgap with increasing pressures above 5.8 GPa. The elevation of phase transition pressure has been attributed to factors such as surface tension, inhomogeneous strain and defect density. While the

decrease of bandgap with pressure at above 5.8 GPa has been ascribed to changes in band structure from direct bandgap to indirect bandgap structure or metallic phase.

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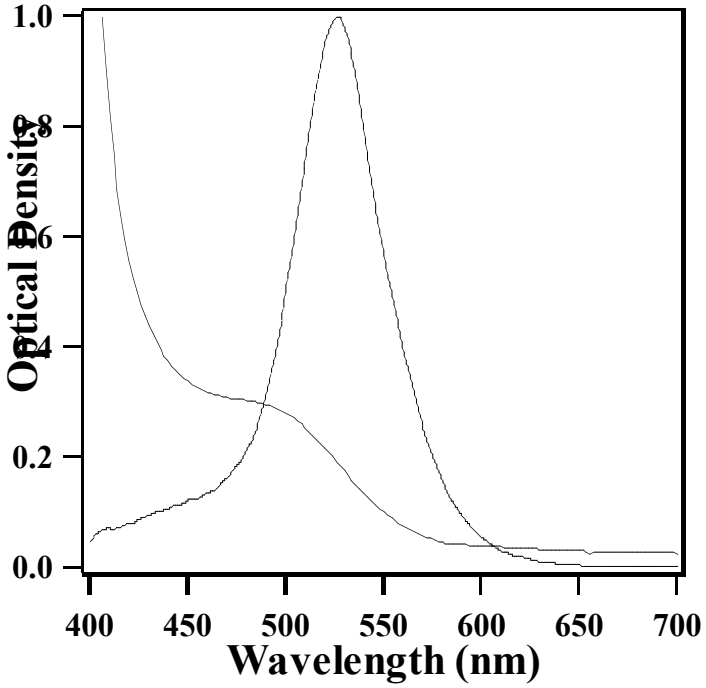
Figure captions:

Figure 1. Static electronic absorption (left) and fluorescence (right) spectra of CdTe NPs in chloroform obtained at room temperature and atmosphere pressure. Signals are normalized for comparison.

Figure 2. The pressure dependence of fluorescence peak energy for CdTe NPs in chloroform solutions.

Figure 3. The pressure dependence of fluorescence peak energy for CdTe NPs in chloroform solutions at the pressure range 0-5.8 GPa. The dots are the experimental data and the solid line is the fit to $\Delta E = E_0 + bP + cP^2$.

Figure 4. The pressure dependence of fluorescence peak energy for CdTe NPs in solid form.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0.2
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Optical Density
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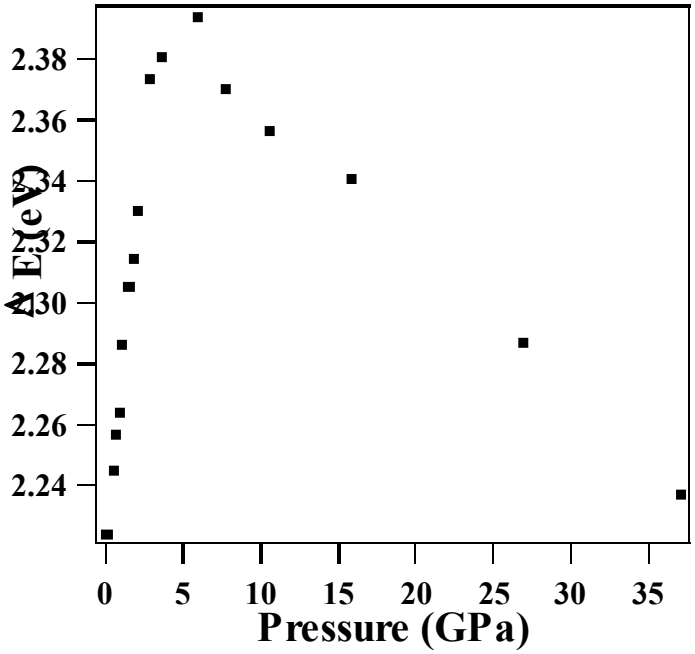
450
500
550
600
650
700
Wavelength (nm)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2.32
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Δ E(eV)
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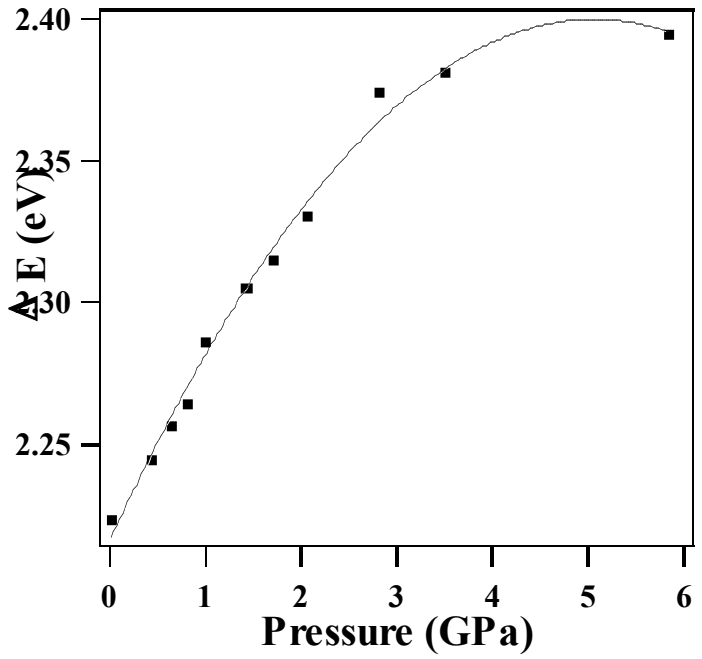
35
Pressure (GPa)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ΔE (eV)
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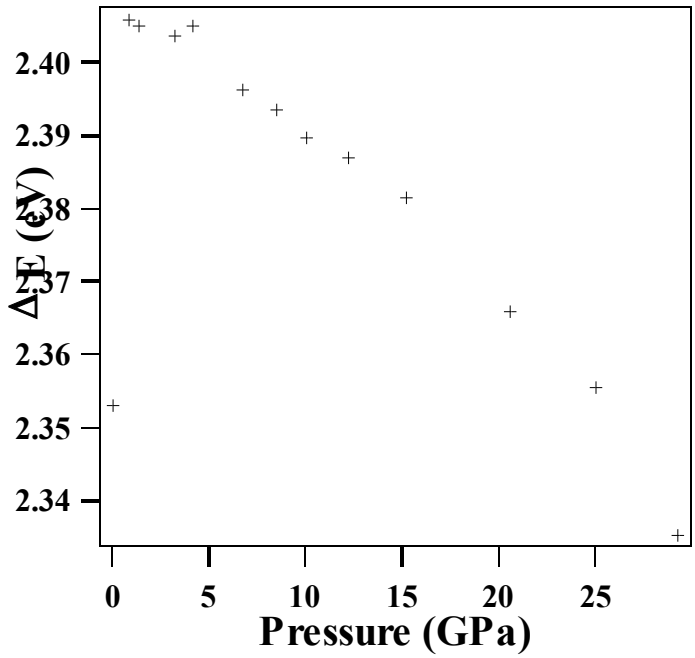
Pressure (GPa)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ΔE (eV)
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25
Pressure (GPa)

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