Effect of the surfactant CTAB on the high pressure behavior of CdS nano particles

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Abstract. Angle dispersive x-ray diffraction studies on CTAB capped cadmium sulphide (CdS) nano particles of sizes 70 nm, 44 nm and 10 nm have been carried out up to ~39, ~30 and ~28 GPa respectively. All the three types of nano particles transform to the rocksalt phase at pressures higher than that of bulk CdS. Our analysis of the x-ray diffraction data indicates that the phase transition pressure as well as the bulk modulus of the rocksalt phase of CdS exhibits a non monotonous behaviour as a function of the size of the nano particles. Our high pressure Raman scattering studies on the 10 nm CdS nano particles are in agreement with the x-ray diffraction studies. The presence of the Raman mode in the high pressure rocksalt phase may be attributed to a disorder activated scattering in this phase or to the formation of a core shell structure beyond the transformation pressure.

1. Introduction

Studies of II-VI or III-VI binary semiconductors like ZnS, ZnO CdS GaN, InP etc are of fundamental interest because of their technological importance and also from a basic physics point of view. It has been observed that reducing particle size to the nano meters either modifies their physical properties or introduces some novel properties making them much sought after materials for applications like disease detection, quantum computing etc [1]. Reduction of size results in an increase in the surface to volume ratio and therefore the surface energy plays an important role in deciding the stability, structure and properties of the nano materials. It is often found that depending on the size of the nano particle a particular compound can exhibit a myriad of structures even at ambient temperature and pressure [2]. For eg. CdS nano particles < 2 nm are amorphous whereas 2 nm and ≥ 4 nm particles of CdS crystallize in the rocksalt and zinc blende/wurtzite structures respectively.

Knowledge of the phase stability of these nano semiconductors is important and has been a central issue in nano science and technology. In nano particles the phase stability, not only depends on stimuli of pressure, temperature and composition of the specimen but also on the size of these particles [3]. There are several studies where it has been demonstrated that solid-solid phase transition pressures or the high pressure behavior itself is affected by the size of the nano particles. It has been shown that the phase stability of nano particles also depends upon the capping surfactant as the surface energy of these particles is altered by different surfactants.

Cadmium sulphide (CdS), a direct band gap semiconductor, is extensively used in the electronic industry especially in the nano crystalline form [4]. As in the nano form it is commercially used as a phosphor, heterojunction laser, field effect transistor, photovoltaic cell, fabrication of optoelectronic devices, it is important to understand its structural behaviour under different thermodynamic conditions. There are several studies on CdS which have shown that the wurtzite or zinc blende form
of bulk CdS transforms to the rocksalt form at \( \sim 3.1 \) GPa. It has been shown by Alivisatos et al. that size reduction enhances the stability range of the initial structure, thus delaying the transformation to the rocksalt phase [5].

These authors have also shown that surfactants play a vital role in the high pressure structural behavior of CdS. They observed that CdS nano particles (4.5 nm) stabilized by sodium polyphosphate transformed to rocksalt structure at 8.0 GPa, where as tetrabutylammonium-EDTA (4 nm) stabilized particles transformed at 6.5 GPa. However, since the effect of CTAB (cetyl trimethyl ammonium bromide) surfactant on the high pressure behavior of CdS nano particles has not been studied so far, we have carried out angle dispersive x-ray diffraction and Raman scattering studies on these nano particles.

2. Method

Nano-sized particles of CdS (in CTAB matrix) were prepared using wet chemical routes [6]. The samples yielded different particle sizes when annealed from different temperatures. We have studied three samples annealed at 500\(^\circ\)C (A), 300\(^\circ\)C (B) and 20\(^\circ\)C (C). The x-ray diffraction pattern of ‘A’ type and ‘B’ type sample could be indexed to pure wurtzite phase while that of ‘C’ to a mixture of wurtzite and zinc blend phase. The lattice parameters of the different phases were determined by carrying out a Rietveld refinement using GSAS [7] and have been tabulated in table 1.

Table 1.

| Type of CdS nano particles | Phase (at ambient) | Space group | Lattice parameter |
|----------------------------|-------------------|-------------|------------------|
| ‘A’ type                   | Wurtzite          | P6\(_{3}\)mc | \(a = 4.147(2)\ \text{Å}, c = 6.733(3)\ \text{Å}\) |
| ‘B’ type                   | Wurtzite          | P6\(_{3}\)mc | \(a = 4.141(4)\ \text{Å}, c = 6.713(3)\ \text{Å}\) |
| ‘C’ type                   | Wurtzite + Zinc blend | P6\(_{3}\)mc + F 43m | \(a = 4.181(3)\ \text{Å}, c = 6.843(2)\ \text{Å}\) |
|                            |                   |             | \(a = 5.838(2)\ \text{Å}\) |

The particle size of these three types samples was determined by using the Deby-Scherrer formula given below

\[
\text{Particle size (t)} = \frac{K \times \lambda}{(W \times \cos(\theta_B))}
\]

where \(K\) is a dimensionless constant with typical value of 0.94, \(W\) is FWHM of the x-ray diffraction peak used to determine the particle size and \(\theta_B\) is the corresponding Bragg angle. The Scherrer equation relying on FWHM of diffraction peaks is generally used as a quick and reliable method for the particle size determination in case of bulk as well as nano crystalline samples using x-ray diffraction pattern. Since other factors such as instrumental broadening, strain broadening etc. also contribute to the peak width, the FWHM needs to be deconvoluted in order to get reliable particle size. In this study we have obtained particle size by factoring out instrumental broadening only as other contributions are negligible under ambient conditions.

However the contribution to FWHM of x-ray diffraction peak due to instrument broadening was factored out during determination of the particle size. The particle size of the A, B and C type samples were determined to be 70nm, 44 nm and 10nm respectively.

For the high pressure experiments, nano crystalline samples of CTAB capped CdS along with a few specs of gold were loaded in a hole of ~100 \(\mu\)m diameter drilled in a pre-indented (~ 80 micron thick) tungsten gasket of a diamond-anvil cell (DAC). Methanol: ethanol (4:1) mixture was used as the pressure transmitting medium. The pressure was determined from the known equation of state of gold [8]. High-pressure angle dispersive x-ray-diffraction experiments, were carried out at 5.2 R (XRD1) beamline of Elettra Synchrotron source using monochromatized x-rays of \(\lambda = 0.6888\ \text{Å}\). The
Diffraction patterns were recorded using the MAR345 imaging plate detector kept at a distance of ~20 cm from the sample. Two-dimensional x-ray diffraction patterns were transformed to one-dimensional diffraction profiles by the radial integration of diffraction rings using the FIT2D software [9].

High pressure Raman scattering studies were carried out using our indigenously developed micro Raman set up with confocal optics. The Raman scattered light, excited by 532nm DPSS laser, is collected using CCD based single stage spectrograph and a supernotch filter. 4:1 methanol:ethanol mixture was used as pressure transmitting medium and ruby fluorescence lines were used for monitoring the pressure [10].

### 3. Results and Discussion

Figure 1(a, b & c) show the x-ray diffraction patterns of 70 nm (A), 44 nm (B) and 10 nm (C) CdS nano particle respectively stacked at a few representative pressures. The x-ray diffraction (xrd) peaks marked with G and Au represents the xrd peaks from gasket and gold pressure marker respectively.

In case of 70 nm CdS particles the transformation to the rocksalt (face centered cubic) phase takes place at 6.7 GPa which is higher than that of bulk CdS. The rocksalt phase was found to be stable up to the highest pressure of measurement (39 GPa) of this study. On release of pressure, the diffraction peaks of the rocksalt phase became very broad and were hardly discernible below 15 GPa. This could be an indicative of amorphization of the 70 nm CTAB capped CdS nano particles on release of pressure.

However, in the case of the 44 nm sized particles the transformation to the rocksalt phase takes place at ~4.4 GPa whereas for the 10 nm particles the transformation takes place at pressures beyond ~6.7 GPa as shown in Fig. 1b & 1c. As in the case of the 44 nm particle, the rocksalt phase was found to be stable upto ~30 GPa and on release it reverts back to wurtzite phase but in contrast to the 70 nm particles the high pressure phase was retained on release of pressure for 10 nm particles. This shows that the high pressure behavior of the 70 nm particles of CdS is distinct from that of the 44 and 10 nm particles. This implies that the CTAB surfactant tends to increase the stability range of the CdS nano particles when compared to that of tetrabutylammonium-EDTA surfactant but decreases with respect to the sodium polyphosphate surfactant [5].
Figure 2: Variation of phase transition pressure with particle size. Here dotted line corresponds to the phase transition pressure of bulk CdS sample. It is interesting to note that transition pressure decreases as the particle size increases from 10 to 44 nm. However it increases again for 70 nm crystals, for which it becomes comparable to that of 10 nm. It is noteworthy that, annealing of the samples at different temperatures does affect the particle size. However, effect of the annealing temperature on the state of the surfactant cannot be ruled out. Therefore the variation in transition pressures of the nano crystalline CdS particles may be attributed to both particle size and state of the surfactant.

The observed pressure induced variations of volume has been fitted with third order Birch Murnaghan equation of state to determine the bulk modulus of rocksalt phase for all the three types of CdS nano particles. Figure 3 shows the plot for the bulk modulus of rock salt phase as a function of pressure. The dotted line corresponds to the bulk modulus of rock salt phase of bulk CdS sample.

Figure 3: Variation of bulk modulus of rocksalt phase with particle size.

Figure 4: Raman spectrum of 10 nm CdS nano particles at a few representative pressures.

Figure 5: Variation of Raman shift for A1 (LO) mode with pressure.

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The bulk modulus for rock salt phase is lowest for the 44 nm particles size thus the variation of bulk modulus with particle size is also non monotonous.

Raman scattering studies were carried out on the 10 nm particles upto 18.4 GPa. Representative Raman spectra at a few pressures are shown in Fig. 4. The black square symbols represent the observed data while the red line corresponds to the Lorentzian fit for the observed Raman mode. The letter (r) adjacent to some pressure values represents the release run. As expected, we have observed a Raman mode at ~302 cm\(^{-1}\) assigned as A\(_1\) (LO) corresponding to the cation-anion (Cd-S) longitudinal vibration. On application of pressure the observed Raman mode at 302 cm\(^{-1}\) stiffens and broadens and at 6.9 GPa it appears to soften by ~23 cm\(^{-1}\) which is indicative of a phase transition. As our x-ray diffraction measurements show that the high pressure phase has rocksalt structure and it does not have any Raman active mode, this softened Raman mode could be due to the coexisting surface wurtzite motifs and the rocksalt phase as core beyond this pressure. Softening of the A\(_1\)(LO) Raman mode at the phase transformation could be due to surface relaxation caused by the large volume collapse (~18%) of the core. Though our x-ray diffraction studies do not show coexistence of the wurtzite and rocksalt phases, this possibility cannot be ruled out as Raman scattering is a local probe and more sensitive to local coordination whereas x-ray diffraction probes the long range ordering. However, to ascertain this further surface sensitive studies on the released samples should be carried out.

Other possibility is that this Raman mode beyond transformation pressure could be a disorder activated, symmetry forbidden Raman mode of rock salt phase as was observed in case of GaN [11]. For Bulk samples wurtzite to rocksalt phase transition has been proposed to proceed via an orthorhombic cell. One of the notable aspects of this phase transition is the large reduction in volume that occurs. During this transition the (001) plane of rocksalt structure could have a high degree of disorder as there is an arbitrariness in the relationship between the initial crystallographic a/b plane of wurtzite and (001) plane of rocksalt. This poor long range order in the lattice would allow relaxation of k-selection rules in the Raman scattering; resulting in disorder activated Raman scattering. This mode was found to stiffen on further application of pressure as shown in figure 5. Here the closed symbol corresponds to the compression while the open ones are from the released run. Slope of this Raman mode is 7.4±0.8 cm\(^{-1}\)/GPa for the ambient phase while for high pressure phase it is 3.9±0.2 cm\(^{-1}\)/GPa. It is interesting to note that the \(\rho d\omega/dP\) for bulk CdS is 5.0 ± 0.2 cm\(^{-1}\)/GPa.

4. Conclusions

Our high pressure studies on CTAB capped CdS nano particles of different sizes show that the range of stability of the ambient phase can be controlled by using different surfactants like CTAB, EDTA [5] etc. The detailed x-ray diffraction analysis suggests that the size variation of CdS nano-particles has a non monotonous effect on the pressure of transformation to the rocksalt phase. However, further work needs to be carried out with several particle sizes to ascertain this non monotonous behavior. Our Raman results are in agreement with the x-ray diffraction results. The presence of the Raman mode in the high pressure phase may be attributed to the coexisting wurtzite shell and rocksalt core as interpreted in the earlier reports or it could be due to the disorder activated scattering from the rocksalt phase itself. Our measurements also suggest that the 70 nm particles of CTAB capped CdS amorphize on release of pressure.

5. References

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