CHAPTER 5

HIGH PRESSURE STUDIES ON NANO CRYSTALLINE SEMICONDUCTORS

5.1 INTRODUCTION

In the past two decades nanocrystalline semiconductor particles have been the focus of scientific research because of their special properties such as surface-volume ratio, increased activity, special electronic properties and unique optical properties as compared to those of the bulk materials (Henglein 1989, Agfeldt and Gratzel 1995). Nanocrystals consisting of small crystallites with diameter 1-100 nm often have novel physical and chemical properties differing from those of the corresponding bulk materials. In recent years, sulphides, selenides and oxides semiconductors with nano meter size dimensions are of great interest due to the quantum size effect exhibited by these nanosized semiconductors (Gorer and Hoders 1994, Empedocles 1999, Ludolph et al 1998). The chemical preparation method used plays a significant role in controlling the size distribution, structure and crystallinity of these particles (Vossmeyer et al 1994, Murrary et al 1993). In the nanocrystals, approximately half the atoms are on the surface. Since half of the atoms are on the surface in the nanocrystals, it is important to understand the surface structure, so that it can be modified if one has to develop any device using these materials. The surface structure of a nanoparticle, and its shape, are determined by minimization of the surface energy. This is accomplished by maximizing the amount of low-energy low–index facets of the crystal. One way of inducing changes in the shape and structure of
nanoparticles is to apply high pressure. The systematic study on the nanomaterials under high pressure is important to understand nanosized structures and their structural metastabilities, as well as their properties. At the same time, different phases and properties of nanomaterials can be understood. In contrast to the bulk materials, the pathway of the first-order solid-solid phase transition for the nanomaterials depends on both thermodynamic and the kinetic parameters of the substances. Because the space groups of two phases in the phase transition frequently exhibit a relationship of group-subgroup, the transformation from one phase to another must involve the specific atomic motions that change the solid from one symmetry to another accompanied by a change of properties. Actually, one can accurately predicts the ground state structure of a solid if a given composition is known but cannot evaluate the lifespan of a metastable state. To know the metastability of different bonding geometries in solid, it is necessary to study on the microscopic mechanism of such solids which transform between crystal structures under high pressure.

In the present work, the nanocrystalline semiconductor like lead chalcogenides (PbS and PbSe) and mercury chalcogenides (HgS, HgSe and HgO) are investigated under high pressure and the results obtained are analysed.

5.2 METHODS FOR PREPARING SULPHIDES, SELENIDES AND OXIDE NANOCRYSTAL

5.2.1 Microwave Assisted Method

Mercury Sulphide (HgS) is a very useful material, which is widely used in ultrasonic transducers, electrostatic image materials (Tokyo 1975) and photoelectric conversion devices. Lead Sulphide (PbS) is also an attractive semi conducting material because of its applications in potential photonic
material (Wang 1991) and Pb$^{2+}$ ion-selective sensor (Gademne et al 1989). Due to wide applications of these semiconductors, developments of techniques such as chemical route, electro deposition in acidic medium (Sharon et al 1997), the ion-exchange colloidal method (Zhou et al 1999), ion beam method and mechanochemical method (Jiang et al 2000) have led to the preparation of lead and mercury sulphides. Though lot of methods are available to prepare metal sulphides, it’s still a challenge to synthetic chemists and material scientists to find out a fast and energy efficient methods. The microwave assisted route is a novel method which is faster and energy efficient. This method is used to prepare the metal sulphides (Wang et al 2001 and Liao et al 2001). The microwave is an electromagnetic wave and it has both electric and magnetic components. The electric field applied creates a force on charged particles as a result of which the charged particles start to migrate or rotate. Due to the movement of charged particles, further polarization of polar particles takes place. The concerted forces applied by the electric and magnetic components of microwave are rapidly changing in direction, which creates friction and collisions of the molecules. The microwave radiation includes thermal and non thermal effects which is an added advantage to this method (Saskia 1997). Compared with conventional methods, microwave synthesis has the advantages such as short reaction time, small particle size, narrow particle size distribution and high purity. Hence, it has been found to be a fast, convenient, mild, energy efficient and environmental friendly route to produce HgS and PbS nanoparticles.

5.2.2 Sonochemical Method

Semiconductor selenides have attracted considerable attention due to their interesting properties and potential applications. They have been widely used as thermoelectric cooling materials, optical filters, optical recording materials, solar cells, super ionic materials, sensors and laser
materials (Wang et al 1999). PbSe is one of the most attractive selenide for a wide variety of applications in IR detectors, photographic plates, selective and photovoltaic absorbers. HgSe has a unique combination of properties which makes it a candidate material for detailed investigations of solid state phenomena (Broerman 1969) and its electrical properties lead to the wide applications in optoelectronic technology including photoconductive photovoltaic, Infra red (IR) detector, IR emitter, tunable lasers and thermoelectric coolers (Willardson and Beer 1981). HgO also has a wide application in the field of batteries.

Some of the conventional methods for the preparation of selenides and oxides are gas-phase reactions between the element and its compounds and gaseous H$_2$-Se (Metcalf et al 1982), solid state reaction (Ohmiya and Suge 1970), chemical bath deposition and pyrolysis of single source precursors (Ptatschek et al 1997, Steigerwald et al 1998). Solid state reaction usually requires elevated reaction temperature and the reaction is not easily controllable and aqueous solution reaction is highly toxic. Since the above said reactions and methods have limitations it’s still a challenge for the chemists and materials scientists in the preparation of selenides of nanoparticle size. Hence, a mild and fast reaction rate method is necessary for the production of nanocrystalline materials.

Ultrasound method has become an important tool in chemistry in recent years which provide a solution to the problem of producing nanoparticles. The sonochemical (ultrasound) method has been used extensively to generate the novel materials with unusual properties since they form particles of a much smaller size and higher surface area than reported by other methods (Suslick 1988). The sonochemical method offers a very attractive method for the preparation of nanosized materials and has shown very rapid growth in its application to materials science due to its unique
reaction effects. This method is a promising one for the preparation of PbSe, HgSe and HgO. It is a convenient and efficient route to produce (i) monodispersed nanoparticles with controllable morphologies in a single step and (ii) to obtain the pure and narrow size distribution of the samples at low cost.

The chemical effects of ultrasound arise from acoustic cavitation i.e. the formation, growth and implosive collapse of bubbles in a liquid. The implosive collapse of the bubbles generates a localized hotspot through adiabatic compression or shock wave formation within the gas phase of the collapsing bubbles. When solutions are exposed to strong ultrasound irradiation, bubbles in the solution are implosively collapsed by acoustic fields producing high temperature and high pressure fields at the centre of the bubbles. The temperature is estimated to be 5000 K and the pressure reaches over 1800 atm. These extreme conditions attained during bubble implode enables many chemical reactions to occur and this mechanism help to obtain the nanocrystals of narrow size.

5.3 MATERIALS

5.3.1 Lead Chalcogenides

Lead chalcogenides (PbX, X = S, Se and Te), which are also known as lead salts are very promising materials for technological applications in the field of infrared (IR) devices, diode lasers and thermophotovoltaic energy converters. The lead chalcogenides crystallize in the rocksalt structure and are polar semiconductors. They posses some unusual electronic and structural properties such as very narrow energy gaps, high carrier mobility, high dielectric constants and positive temperature coefficients and negative pressure coefficients of the gap (Dalven 1973, Suzuki et al 1995). It has narrow energy gaps and this is one of the most important properties leading to great experimental interest in these materials (Nabi et al 2000). Knowledge of
electronic and structural properties of these materials under pressure is important in the semiconductor device industry.

PbS and PbSe nanocrystals have attracted much attention due to their tunability over a wide spectrum (Wang et al. 1987). Relative to bulk crystals, the band gap of the PbS nanoparticles is significantly blue shifted from the near IR into the visible and near UV region with decreasing particle size.

5.3.2 Mercury Chalcogenides

Mercury Chalcogenides belongs to IIB – VI group. Most of the IIB – VI compounds, which have either the zinc blende or wurtzite crystal structure (four fold coordinated) at atmospheric pressure will transform to the NaCl crystal structure (six fold coordinated) under high pressure (Jayaraman et al. 1963). The valence electronic configuration of Hg is (n-1) d$^{10}$ ns$^2$ and has covalent bonding with sp$^3$ hybridization similar to that of Cd and Zn elements. Among these IIB – VI compounds, mercury chalcogenides have discrimination. First HgSe is semimetal instead of semiconductors at atmospheric pressure though it has sp$^3$ bonding and transform to cinnabar structure at very low pressures (Kafalas et al. 1962). Secondly HgS has a metastable zincblende phase at atmospheric pressure, while the cinnabar structure is the stable phase for other elements in this group. The effects of high pressure on the crystal structure of bulk IIB – VI compounds have been widely studied (Ray 1969, Huang and Ruoff 1983).

5.3.2.1 Mercury Sulphide

Normally the HgS can be found in three different phases. Cinnabar (or) α-HgS or HgS-III is red in colour. It has a hexagonal structure with space
group P3121 (154). The structure of cinnabar can be considered as a distorted NaCl-type structure. The lattice constants of the bulk material are $a_0 = 4.1495\,\AA$, and $c_0 = 9.497(3)\,\AA$. Werner et al (1983) have shown that the $c/a$ ratio increases with increasing pressure. They have determined the bulk modulus ($B_o$) and its pressure derivative ($B_o'$) as 19.4 at 5 GPa and 11.1 at 7 GPa respectively. Thus, cinnabar is very compressible (i.e. low $B_o$ value) but it hardens rapidly because of the high $B_o'$ value. Huang and Ruoff (1985) have shown that bulk cinnabar transforms to the NaCl-type structure (HgS-IV) at 13 GPa and the lattice constant ($a$) is found to be 5.070(5) Å at 30 GPa.

Metacinnabar ($\beta$-HgS or HgS-II) is black in colour. It has a cubic structure, (ZnS type) and its space group is F43m (216). Lattice constant of bulk material is $a_0 = 5.8517\,\AA$. So far the $B_o$ and $B_o'$ are not calculated for this phase of HgS. The metacinnabar is stable at high temperature whereas the cinnabar type is stable at low temperature. In many natural and contaminated surface anoxic environments cubic HgS has been recognized as the stable phase (Barnett et al 1997, Charnock et al 2003).

Hypercinnabar ($\gamma$-HgS or HgS-I) is violet-red in colour. It has a Hexagonal structure. Lattice constant of bulk material is $a_0 = 6.86\,\AA$ and $c_0 = 14.07\,\AA$.

### 5.3.2.2 Mercury Selenide

HgSe have tetrahedrally co-ordinated zinc blende (Zb) structure at ambient pressure and transform to the cinnabar structure under applied pressure. This transformation involves a substantial structural rearrangement and a 9% increase in density, and is quite sluggish in both systems at room temperature (Jayaraman et al 1963). The ambient pressure semi-metallic zinc-blende phase transform first into a semiconducting cinnabar-type
structure at ~ 1 GPa. (Kafalas et al 1962) which on further compression transforms to NaCl phase (Ohtani et al 1982, Werner et al 1983, Huang and Ruoff 1985). The second transition which takes place from Zinc blende to an orthorhombic phase with space group C222_1 has been reported at pressures slightly higher than the Zb → cinnabar transition pressure (Mc Mahon et al 1996). This hidden C222_1 transition is therefore formed when the zinc blende phase is thermodynamically unstable with respect to the cinnabar phase. The hidden “high-to-low cristobalite phase further transforms into the cinnabar phase upon slight increase of pressure. There is a further transition at 25 – 30 GPa in HgSe (Nelmes et al 1997, McMohan et al 1996).

5.3.2.3 Mercuric Oxide

Among II-VI semiconductors, mercury oxide probably is the most unusual one in terms of its ambient-pressure structural properties. These are largely determined by the strong tendency for linear coordination of Hg when forming Hg–O bonds. The common transition sequence in these compounds for increasing pressure is given as zincblende (phase I), cinnabar (phase II), NaCl type (phase III) and body centered tetragonal (phase IV). In phase II these materials are found to be metallic. But HgO violates this sequence of transition.

HgO crystallizes in the orthorhombic structure and the space group is Pnma (D_{16h}^2) (Decamps 1972). This structure is built up of planar O-Hg-O zigzag chains running parallel to the a-axis and lying in the ac plane. Figure 5.1 show the structure of HgO. Within a chain the Hg atoms are linearly coordinated by two oxygen atoms at a distance d ~ 203 pm. One unit cell contains two chains lying on two adjacent ac planes resulting in four formula units per cell (Zhou et al 1998). The closest inter chain Hg-O distances are 287 pm within ac planes and 282 pm for neighboring ac planes.
The band gap energy is approximately 2.2 eV at room temperature for bulk HgO and it has n-type electrical conductivity (Zhou et al 1998).

![Crystal structure of orthorhombic HgO](image)

**Figure 5.1** View of crystal structure of orthorhombic HgO

5.4  EXPERIMENT

5.4.1  Sample Preparation

5.4.1.1  Preparation of nano PbS and HgS

About 1.6 g of lead acetate (Pb (Ac₂).3H₂O) and 1.5 g of mercury acetate (Hg (Ac₂₀)) are added to 60 ml of polyethylene glycol (PEG-200). All the reagents used in the experiment are of analytical grade and used without any purification. About 0.2 g of sulphur powder is introduced into the two PEG solvents. The amount of entire reagent is optimized. The two mixtures are then placed in the microwave refluxed system and the reaction is performed under ambient air for 20 minutes. The microwave oven followed a working cycle of 9 seconds ‘on’ and 21 seconds ‘off’ i.e. 30% power. At the end of the reaction, the black precipitates are collected and centrifuged, washed with distilled water and absolute acetone and finally dried in air. The
final products are collected for characterization using XRD, TEM and XPS. Figures 5.2 and 5.3 show the XRD pattern and TEM photographs of PbS and HgS. According to TEM observation thus prepared, PbS and HgS nanoparticles are mostly spherical in shape. The average sizes of HgS and PbS particles are in the range 10-20 nm and 15-20 nm respectively. They are in good agreement with those estimated by the Debye-Scherrer equation. The XPS is employed to investigate the composition and purity of the prepared nanoparticles. The Pb:S ratio is 42:58 which shows that the surface of the products is rich in sulphur and for Hg : S the ratio is 58:42. The probable reaction mechanism of HgS and PbS is consolidated as follows:

\[
\begin{align*}
&\text{PEG as reducing agent} \\
&\text{Hg}^{2+}, \text{Pb}^{2+} \quad \text{Microwave irradiation} \\
&\text{In PEG solvent} \\
&\text{Hg or Pb} + \text{S} \quad \text{Microwave irradiation} \\
&\text{HgS or PbS}
\end{align*}
\]

Figure 5.2  XRD pattern of (a) PbS and (b) HgS nanoparticles prepared in PEG solvent
5.4.1.2 Preparation of nano Lead Selenide (PbSe)

All the reagents used are of analytical purity and used without further purification. Pb \((\text{CH}_3\text{COO})_2 3\text{H}_2\text{O}\), trisodium citrate (TSC) and Na\(_2\)SO\(_3\) are taken in the stoichiometric ratios. The aqueous solution of lead acetate is mixed with 0.2 M Na\(_2\)SeSO\(_3\) solution in a 150 ml round bottom flask. Along with the solution 20 mM lead acetate solution, 40 mM complexating agents and 20 mM of Na\(_2\)SeSO\(_3\) are added to increase the concentration. The pH is adjusted to 10 by using KOH and the total volume of the solution is reduced to 100 ml. The Na\(_2\)SeSO\(_3\) solution is prepared by stirring 0.2 M Se and 0.5 M Na\(_2\)SO\(_3\) at 70°C for 24 h. The complexing agents used in the experiments are TSC and NTA. Then the mixture solution is exposed to high intensity ultrasound irradiation under ambient air for 30 minutes (Zhu et al 2002). Ultrasound irradiation is accomplished with a high intensity ultrasonic probe (Xinzhi Co., China, JY92-2D, 0.6 cm diameter, Ti horn 20 kHz, 60 W/cm\(^2\)) immersed directly into the reaction solution. A great amount of black precipitates is obtained. After the mixture is cooled to room temperature, the precipitates are centrifuged, washed by distilled water, absolute ethanol and acetone in sequence and dried in air. The final products are collected and characterizations are carried out with the help of X-ray powder diffraction and TEM. The average particle size of PbSe is found to 8-25 nm and is in agreement with Debye-Scherrer equation.
According to TEM images the diameter of the particles are in the range of 10 -15 nm. Figure 5.4 shows the XRD and TEM of PbSe.

The probable reaction process for the sonochemical formation of PbSe nanoparticles in aqueous solution can be summarized as follows:

\[
\begin{align*}
\text{Pb} (\text{TSC})_2^{4-} & \rightarrow \text{Pb}^{2+} + 2\text{TSC}^{3-} \\
\text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{OH}^- \\
2\text{H} + \text{SeSO}_3^{2-} & \rightarrow \text{Se}^{2-} + 2\text{H}^+ + \text{SO}_3^{2-} \\
\text{Pb}^{2+} + \text{Se}^{2-} & \rightarrow \text{PbSe} \\
\text{n PbSe} & \rightarrow (\text{PbSe})_n
\end{align*}
\]

Figure 5.4  (a) Powder XRD pattern of nano PbSe
(b) TEM image of PbSe nanoparticles prepared by ultrasound irradiation
5.4.1.3 Preparation of nano Mercury Selenide (HgSe)

An aqueous solution of Hg (CH₃COO)₂ in the presence of complexing agents is mixed with 0.2 M Na₂SeSO₃ solution in a 150 ml round-bottom flask to give a final concentration 20 mM Hg(CH₃COO)₂. 20 mM Na₂SeSO₃ solution is prepared by stirring 0.2 M of Se and 0.5 M Na₂SO₃ at 70°C for 24 h. This solution is irradiated with a high intensity ultrasonic probe under ambient air for 30 minutes and black precipitates are obtained. After cooling to room temperature, the precipitates are centrifuged, washed by distilled water and acetone in sequence and dried in air. The products are characterized by X-ray powder diffraction (XRD) and TEM. The average size of thus prepared nanocrystal is found to be 100-200 nm. Figure 5.5 shows the XRD pattern and TEM image of HgSe. The probable reaction mechanism can be explained as follows

\[
\begin{align*}
H_2O & \rightarrow H^+ + OH^- \\
2H^- + SeSO_3^{2-} & \rightarrow Se^{2-} + H_2SO_3 \\
Hg(TEA \text{ or } NH_3) + Se^{2-} & \rightarrow HgSe + n \ (TEA \text{ or } NH_3) \\
nHgSe & \rightarrow (HgSe)^n
\end{align*}
\]
Figure 5.5  (a) XRD pattern of HgSe nanoparticle  
(b) TEM image of HgSe nanoparticle
5.4.1.4 Preparation of nano Mercuric Oxide (HgO)

0.6 grams of Mercuric acetate is dissolved in 50 ml water, and then ammonia and NaOH are added. Finally, distilled water is added to the total volume of 100 ml of the solution and sonocate for 1 hour. The product is yellow turbid. The product is centrifuged with distilled water and ethanol and then dried in air. The product is characterized by XRD and the pattern is shown in the Figure 5.6. The average size of the crystal is about 150 nm to 200 nm.

Figure 5.6 XRD spectra of HgO nanoparticle
5.4.2 Experimental Set-up for Electrical Resistivity Studies

The high-pressure electrical resistivity is studied using the standard two-probe for PbS, PbSe and HgO by using Bridgman Opposed anvil device. The set up is arranged as explained in Section 4.4.2. HgS and HgSe are semimetallic in nature and they have resistance in the range of ohms. Hence the high pressure electrical resistivity measurement is carried out using four probe method as explained in Section 3.6. The resistivity measurements are carried out up to a pressure of 10 GPa and up to a temperature of 300ºC.

5.4.3 Experimental Set-up for High Pressure EDXRD Studies

The high-pressure EDXRD studies for PbX (X=S, Se) and HgX (X = S, Se, O) samples are carried out with the help of Mao–Bell type Diamond anvil cell upto 15 GPa as explained in Section 4.4.3. The spectra are taken at room temperature by fixing the detector at an angle $2\theta = 16^\circ$. The Scherrer equation used for calculating the particle size from the energy dispersive x-ray diffraction spectra is modified as follows

$$P = \frac{(0.94 \times 6.1992)}{\Delta E (\sin \theta)}$$

(5.1)

where, $p$ is the particle size in Å, $\Delta E$ is the FWHM of the Bragg peak in keV, and $\theta$ is the Bragg angle.

5.4.4 Experimental Set-up for High Pressure Raman Studies

The high pressure Raman studies are carried out using the diamond anvil cell (Dia cell) as explained in Section 4.4.4. The Renishaw Raman spectrometer is used for recording the Raman spectrums. The 514 nm line of
the Argon ion laser with a power of 100 mW is used. Raman spectrum is obtained for both loading and unloading pressures.

5.5 EXPERIMENTAL RESULTS

5.5.1 High Pressure Investigation of Nanocrystalline Lead Chalcogenides

5.5.1.1 Electrical resistivity results of nano lead chalcogenides

The resistivity measurements are carried out using Bridgmann anvil cell upto a pressure of 10 GPa using two probe method. In general, the resistivity of PbX (X= S, Se or Te) increases abruptly first and drop as the pressure is increased (Samara and Drickamer 1962). Similar result is observed in the nanocrystalline lead salts. Figure 5.6 show the change in resistivity values with high pressure and high temperature. Initially, the resistivity value does not show any significant change with pressure. It shows a gradual increase and at 5.8 GPa it increases sharply with three orders of magnitude for every pressure upto 8 GPa. On further increase of pressure, the resistivity of the nanocrystalline PbS decreases. The same result is obtained for PbSe nanoparticles of size 8 nm. According to Figure 5.7, the resistivity increases abruptly and on further increase tends to decrease. The sharp increase in both the graphs indicates the structural phase transition of the lead chalcogenides. The bulk PbS and PbSe is transformed from B1 to B16 structure at pressures 2.8 and 4.2 GPa respectively. In nanoparticles the same transition is obtained at 5.8 GPa and 6.2 GPa for PbS and PbSe respectively. The decreasing trend of the graph indicates the phase transition from semiconductor–metal. On increasing the temperature transition pressure is slightly shifted towards the left or in other words to the lower pressure side.
Figure 5.7  Variation of resistivity under pressure for nano (a) PbS and (b) PbSe at different temperatures

Figure 5.8 shows the pressure and temperature curve of the PbS and PbSe. This gives a clear idea of the transition pressure for different temperature upto 300°C. Figure 5.9 shows the energy gap of the lead chalcogenides with pressure at different temperatures. It is found that the gap
decreases for different temperatures for pressures upto 10 GPa. The lead chalcogenides have narrow band gap and the band gap energy decreases with increase in pressure. The bulk lead chalcogenides PbS and PbSe have forbidden gaps of 0.286 eV and 0.16 eV respectively (Ovsyannikov et al 2003). The forbidden energy gap of nano crystalline lead salts PbS and PbSe is calculated at ambient condition and is found to be 0.5 eV for 10-20 nm particle size and 0.07 eV for 8-25 nm particle size respectively.

**Figure 5.8**  Temperature – Pressure phase diagram of nano (a) PbS and (b) PbSe

**Figure 5.9**  Variation in energy gap with pressure for nano (a) PbS and (b)PbSe at different temperatures
5.5.1.2 High Pressure EDXRD Results of nano Lead Chalcogenides

Figures 5.10 and 5.11 show EDXRD pattern of PbSe and PbS at high pressure. At ambient pressure in both the samples, the NaCl structure is obtained and the peaks are indexed to cubic phase (B1). The lattice constant (\(a_0\)) at ambient condition is found to be 5.91 Å for PbS and 6.051 Å for PbSe. PbS and PbSe are transformed to orthorhombic phase (B16) at 5.8 GPa and 6.2 GPa respectively. Both B1 and B16 structural peaks are obtained at this pressure. Exactly at 7 GPa orthorhombic peaks alone are monitored in both the cases. The calculated volume and the lattice constants are in good agreement with that of the bulk samples.

![EDXRD pattern of nano PbS for different pressures](image)

**Figure 5.10** EDXRD pattern of nano PbS for different pressures
Figure 5.11 High pressure EDXRD pattern of nano PbSe

Figure 5.12 shows the pressure–volume graph of PbS and PbSe. It is clear from the discontinuity of the graph that there is a structural transition from B1 to B16. The bulk modulus of PbS and PbSe is found to be 49.89 GPa and 50.001 GPa respectively. The compressibility of the sample is 2% for PbS and 1.9% for PbSe. Table 5.1 shows the comparison of parameters for bulk and nanocrystalline states of PbS and PbSe.
Figure 5.12 Pressure vs reduced volume graph of (a) PbS and (b) PbSe

Table 5.1 Comparison of parameters for bulk and nanocrystalline PbS and PbSe

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice constant (a) Å</th>
<th>Bulk modulus(B₀) GPa</th>
<th>Transition pressure(P_T) GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk</td>
<td>Nano</td>
<td>Bulk</td>
</tr>
<tr>
<td>PbS</td>
<td>5.929</td>
<td>5.912</td>
<td>52.9</td>
</tr>
<tr>
<td>PbSe</td>
<td>6.117</td>
<td>6.051</td>
<td>54.1</td>
</tr>
</tbody>
</table>

5.5.2 High Pressure Investigation of Nanocrystalline Mercury Chalcogenides (HgS, HgSe and HgO)

The present study is made on nano mercury chalcogenides namely HgS, HgSe and HgO. Table 5.2 shows the comparison between the bulk and the nanosized mercury chalcogenides.
Table 5.2  Comparison of bulk and nanoparticle Mercury Chalcogenides

<table>
<thead>
<tr>
<th>Sample</th>
<th>Parameters</th>
<th>Lattice parameter(a) Å</th>
<th>Bulk modulus(B_o) GPa</th>
<th>Transition Pressure(P_T) GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>Nano</td>
<td>Bulk</td>
<td>Nano</td>
<td>Bulk</td>
</tr>
<tr>
<td>β-HgS</td>
<td>5.851</td>
<td>5.853</td>
<td>-</td>
<td>23.93</td>
</tr>
<tr>
<td>HgSe</td>
<td>6.102</td>
<td>6.067</td>
<td>50</td>
<td>45.47</td>
</tr>
<tr>
<td>HgO</td>
<td>a=6.61</td>
<td>b=5.52</td>
<td>c=3.52</td>
<td>43.12</td>
</tr>
</tbody>
</table>

5.5.2.1 High pressure EDXRD results of nano β-HgS

The nano metacinnabar HgS is characterized by EDXRD and the peaks obtained are indexed to cubic structure. Figure 5.13 shows the EDXRD pattern of β - HgS at high pressure. The lattice constant (a₀) is found to be 5.853Å and the volume (V₀) is found to be 200.57 Å³. The high pressure measurements are carried out upto 15 GPa. No transition is observed during this pressure range. The emerging peaks are indexed to the cubic structure of β- HgS. At 13 GPa some of the peaks such as (331) and (311) vanishes. The intensity of those peaks decreases as the pressure is increased. This shows that the β - HgS may undergo structural transition from NaCl to distorted NaCl at higher pressure range.
Figure 5.13 EDXRD pattern of nano $\beta$-HgS for different pressures

Figure 5.14 shows the pressure-volume graph of $\beta$-HgS. As the pressure is increased, the volume decreases monotonically. The bulk modulus ($B_0$) of the nano crystalline $\beta$-HgS is found to be 23.43 GPa using “Birch-Murnaghan equation”. The compressibility is found to be 4.2% at 7 GPa.
5.5.2.2 High pressure electrical resistivity results of nano $\beta$-HgS

HgS and HgSe are semimetal in nature. They are called as zero band gap semiconductors. At ambient conditions, the resistivity of mercury sulphide is in the range of ohms. Initially, the resistivity of HgS is found to 2.006 $\Omega$m. On increasing the pressure, the resistivity decreases upto 5.7 GPa and becomes almost constant upto 10 GPa. This shows that the mercury sulphide becomes conductor with very low resistance. When the temperature is increased along with pressure the transition pressure shift towards the left. The phase transition from semiconductor to metallic is enhanced on application of pressure. The temperature is increased upto 300°C in steps of 100°C. Figure 5.15 shows the high pressure and high temperature resistivity measurements of nano sized $\beta$-HgS. Figure 5.16 shows pressure vs temperature diagram. The transition pressure for different temperature is clearly known from the graph. Figure 5.17 shows the pressure vs energy gap of the HgS. The energy gap decreases on increase of pressure.
Figure 5.15 Variation of resistivity with pressure for nano $\beta$-HgS at different temperatures

Figure 5.16 Pressure vs temperature diagram of nano $\beta$-HgS
5.5.2.3 High pressure EDXRD results of nano HgSe

At normal condition the nanocrystalline mercury selenide have a zinc-blende (zb) structure. The low pressure transition from zb $\rightarrow$ cinnabar is obtained at 2.8 GPa whereas this transition takes place at $\sim$1 GPa for bulk HgSe. The hidden transition of zb $\rightarrow$ orthorhombic phase is not monitored. The cinnabar phase obtained at 2.8 GPa remains unaltered upto 15 GPa. The spectrum obtained at normal condition is indexed to zincblende structure and the lattice constant ($a_o$) and volume ($V_o$) is found to be 6.067 Å and 223.35 Å$^3$ respectively. The structure is transformed to cinnabar structure at 2.8 GPa. The lattice constants are found to be $a = 4.555$ Å, $c = 9.731$ Å and $c/a$ ratio is found to be 2.136. The volume ($V$) of the transformed structure is found to be $174.92$ Å$^3$. Figure 5.18 shows the EDXRD pattern of nano HgSe for different pressures upto 15 GPa. The pressure volume data of the sample is shown in the Figure 5.19. The volume decreases as the pressure is increased. The $c/a$ ratio also decreases as the pressure is increased. This shows that the compression is along x and z axis and y axis remains unaltered. For
nanocrystalline HgSe, the onset of the transition starts at 2.8 GPa and remains constant. The intermolecular (d) spacing decreases as the pressure is increased. The bulk modulus ($B_o$) of the sample is found to be 45.47 GPa. The compressibility of the sample is found to 2.3% at 3.2 GPa.

Figure 5.18  EDXRD pattern of nano- HgSe at different pressures
5.5.2.4 High pressure and high temperature electrical resistivity results of nano HgSe

HgSe is initially semimetal and it becomes semiconductor on application of pressure. At normal condition it has resistance in the range of ohms. On application of pressure the resistivity increases sharply by several orders of magnitude. It shows a structural transition from NaCl to cinnabar structure at modest pressures. On further increase in pressure, there is a gradual drop in the resistivity. This shows that there is a phase transition from semiconductor to metallic nature. The resistivity value is found to be 0.102 $\Omega$m at ambient condition. Though the temperature is increased upto 300ºC, the resistivity follows the same path as that of the resistivity curve for room temperature. Due to high temperature the transition pressure is shifted towards the lower pressure range. Figure 5.20 shows the resistivity measurements at high pressure and high temperature. Figure 5.21 shows the
temperature and pressure phase diagram which clearly indicates the transition pressure at particular temperature. Figure 5.22 show the energy gap vs pressure of nano HgSe and it is found that the energy gap decreases with increase in pressure.

Figure 5.20 Variation of resistivity with pressure in nano HgSe at elevated temperature

Figure 5.21 Phase diagram of nano HgSe at different temperature
5.5.2.5 High pressure EDXRD results of nano HgO

The HgO undergoes a structural transition from orthorhombic to a phase that has been tentatively characterized as a slight tetragonal distortion of the NaCl structure with space group I4/mmm or a very close variant of NaCl structure at 14 GPa. (Zhou et al 1998). According to Nelmes and McMohan (1998), a second transition towards an undistorted NaCl phase begins at 26 GPa and it undergoes a new structural transition above 34 GPa (Zhou et al 1998).

The same results are expected for the nanosized mercuric oxide. The high pressure experiment is carried out upto 15 GPa. Figure 5.23 shows the EDXRD pattern of the nano-HgO upto 15 GPa. It is found that nano HgO has no structural transition upto the working pressure range. The peaks shift towards the left due to the application of pressure and this confirms that the inter atomic distance decreases and the lattice constant decreases with increase in pressure. The emerging peaks are indexed to orthorhombic
structure with $a_0 = 6.621 \, \text{Å}$, $b_0 = 5.577 \, \text{Å}$ and $c_0 = 3.55 \, \text{Å}$ and the volume ($V_o$) is calculated to be $131.13 \, \text{Å}^3$. Figure 5.24 shows the pressure-volume change of nano HgO and the volume decreases monotonically as the pressure increases. The bulk modulus ($B_o$) is calculated to be 41.89 (4) GPa. The compressibility of the nano HgO is found to be 2.3% at 4 GPa.

![Figure 5.23 EDXRD of nano HgO at elevated pressure](image)

Figure 5.23 EDXRD of nano HgO at elevated pressure
5.5.2.6 High pressure and high temperature electrical resistivity results of nano HgO

Figure 5.25 shows the high pressure high temperature resistivity measurement of nano HgO. At ambient condition the resistivity of HgO is found to $1.33 \times 10^6$ Ωm. Its value lies on the megaohm range and hence ‘two probe’ method is used to obtain the results. On application of pressure the resistivity decreases and at 8 GPa resistivity value becomes almost constant at room temperature. At 10 GPa the resistivity decreases to $7.38 \times 10^2$ Ωm. At high temperature, the graph shifts towards the lower pressure range. The temperature is increased in steps of 100°C upto 300°C. Figure 5.26 shows the variation of energy gap with pressure at different temperatures for nano-HgO. As the pressure increases, the energy gap decreases. Pressure exerted on nano HgO result in the reduction of forbidden gap and the resistivity value reduces to kilo ohms.
Figure 5.25 Variation of electrical resistivity of nanocrystalline HgO at different temperatures and pressures

Figure 5.26 Pressure vs energy gap graph of nano HgO at different temperatures
5.5.3 High Pressure Raman Results on Sulphide Nanocrystals

Figure 5.27 and 5.28 shows the Raman spectrum of nano PbS and HgS. Raman Study is carried out upto a pressure of 15 GPa. Upto 15 GPa no transition is observed in both samples. The peaks are shifted towards the right due to the application of pressure.

![High pressure Raman spectra of nano PbS](image)

Figure 5.27  High pressure Raman spectra of nano PbS
For nano PbS using XRD as a method of probing, new structural peaks indicating the transition from B1 structure to B16 structure is monitored. Raman spectrum for PbS reveals the amorphous nature of the sample up to 1.05 GPa. The appearance of peaks on increase of pressure indicates the crystalline nature of the sample. The same result is obtained for nano HgS and no transition is monitored upto 15 GPa.

Figure 5.28  Raman spectra of nano HgS at different pressures
It is very difficult to obtain the Raman spectra for nanocrystals, since the mixing between the interior lattice modes and a surface mode that causes a significant broadening of the vibration band. This results in the major failing of Raman technique for exploring high pressure phase transitions in nanocrystals.

5.6 DISCUSSION

According to the results obtained, the transition pressure for the nanocrystalline semiconductor is greater than that of the bulk semiconductor. This is in accordance with the researchers who reported in their work carried out earlier. The effects along the transition path play a major role in both the dynamic and the stable phases of nanometer-scale materials. By means of \textit{insitu} observation, such research on nanocrystals provides an opportunity to observe the effects of transition path masked in a bulk system. In bulk semiconductors first-order solid-solid phase transformation under pressure involves the multiple nucleation and fracture. Similar behaviour is observed for nanocrystals under pressure, and the atoms in nanocrystals tend to vibrate at lower frequency. The elevation in pressure transition is due to single nucleation effect and can be explained with the help of surface energy and shape changes.

On application of pressure the peak width before and after the transition remains the same. This indicates that the nanocrystals transform coherently without domain fracture. In solid-solid phase transition, there is a specific path through which the atoms follow when transforms from one phase to the next. This path acts as the reaction coordinate for the phase transition. In bulk, where most of the atoms are in the interior the change in surface energy is negligible. However, in a nanocrystal, large fraction of the atoms is on the surface and this result in shape change. If all the atoms are
moving in a well-defined path, this causes the crystal to change shape. This is not observed in macroscopic crystals because multiple nucleations will cause the crystal to break into many domains, thus obscuring any overall change in shape. The shape change will change the position of the atoms on the surface as well as in the interior, which in turn change the surface energy of the crystal. Therefore the surface energy is increased at the solid-solid phase transition which impedes the formation of the high pressure phase and thus elevates the phase transition pressure as the particle size is decreased. These two effects contribute to the elevation of transition pressure in semiconductor nanocrystal.

The electronic structures of substances vary with their phase structures, so a phase transition may be accompanied by a sharp variation of electric conductivity of the substances. For nanocrystals, the size effect leads to band edge blueshift and interfacial charge increment which would influence the transition pressure. The different transition pressures indicate different transition energies and different conditions by which nanocrystals undergo the first order transition.

The resistance changes in nanomaterial is a complicated phenomena, which depends on many factors such as crystal boundary, band gap, density of state of intrinsic and others like surface state, dangling bonds, doping and electrodes contacts of nanocrystals etc. When the pressure is exerted on the nanocrystals, the particles start to move closer and distribute between the two electrodes or probes. If the particles go away from the region between the probes no conducting signal could be obtained. In the pressure dependent resistance measurement, the critical point of electric resistance under pressure is generally between the equilibrium point of two phases in bulk materials. The two phases coexist at the equilibrium point. In terms of the shape change theory of nanocrystal, the shape of the material will change
when the phase transition takes place. This shape change will occur before the critical point of transition pressure change when the imposed pressure is elevated, and the change of shape will also be reflected in other characterizations. When nanocrystals are compressed to higher pressures, the resistance of the nanocrystal should decrease sharply, but no such reduction of resistance value is obtained when compared with bulk. The reason for the resistance increase before the phase transition may be due to the surface charging effect and surface amorphization, which blocks the conducting electrons near the surface of nanocrystals.

5.7 CONCLUSION

Above experimental work on semiconductor nanocrystals show that the transition pressure increases as the particle size decreases. This increase in transition pressure is found to be a major effect obtained due to surface energy and shape effect. The major role of nucleation effect results in the enhanced transition pressure. The stability of the high pressure phases obtained under high pressure is high for nanocrystals when compared with the bulk materials. The nanocrystals remain stable at the high pressure phase on release of pressure. This helps to obtain desired phases at high pressure and instrumentation of devices.