Chapter 2

Synthesis and Structural Characterization of Nanoparticles and Nanorods of CdS and ZnS

2.1 Introduction

The novel properties of nanomaterials strongly depend on their dimensions [1-2]. Along with quantum confinement effects, surface and interface effects also play a major role in deciding the properties of materials in the nano-regime [3-4]. While the size induced quantum confinement of charge carriers makes the electronic energy levels discrete, large density of defects at the surface of nanomaterials introduce a stress field which can strain the lattice. These effects influence the electronic structure of materials, thereby alters their physical properties. The strength of quantum confinement and the density of surface states are directly related to size and shape of nanomaterial. Therefore, the structure of a nanomaterial has to be studied thoroughly and correlated to the modified physical properties before predicting their technological applications.

Although there are different methods for fabricating nanomaterials, wet chemical methods are the most widely used due to their relatively mild preparative conditions. Among these, hydrothermal methods have attracted considerable attention as they are simple, controllable and low temperature processes for producing uniform sized particles [5]. Therefore, in this work a hydrothermal technique has been used for preparing the nanostructures of CdS and ZnS. Structural characterization is mainly done via X-ray
diffraction, high resolution transmission electron microscopy (HR-TEM), energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM). XRD studies are done to understand the crystal structure and to extract the value of the average crystallite size. Williamson-Hall technique is used to get an estimate of the strength of lattice strain in the samples. HR-TEM and SEM are employed to study the morphology of the samples. Chemical composition of the material is confirmed using EDS. This chapter also describes a series of structural changes observed in CdS nanoparticles during annealing. A model for an unusual phase transformation in CdS nanoparticles observed at a relatively low annealing temperature is proposed. This has greatly aided in tracing the nature and origin of lattice strain in nanomaterials and their concomitant effects on physical properties.

2.2 Hydrothermal synthesis of nanoparticles and nanorods of ZnS and CdS

2.2.1 Hydrothermal method: An introduction

For preparing nanomaterials, a variety of techniques are used by researchers [6-7]. Out of them hydrothermal method decorates an important position owing to its simplicity, large yield and simple growth conditions. The term ‘hydrothermal’ normally refers to any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high temperature and pressure conditions to dissolve and recrystallize materials which are relatively insoluble under ordinary conditions. In this method the
crystallization occurs inside an autoclave (sealed vessel) and is carried out from superheated aqueous solutions at high pressure.

Hydrothermally prepared 0D and 1D materials have extremely smooth edges unlike those produced by techniques like ball milling and sol-gel [8]. Also nanomaterials with different shapes and sizes can be produced through this method [9-10]. The samples so produced are also reported to have uniform shape and size distribution [11]. It is a cost effective method which can produce high purity products. These reasons encouraged me to adopt this very useful technique to create nanorods and nanoparticles of CdS and ZnS.

2.2.2 Synthesis of CdS nanoparticles and nanorods

Analytical grade cadmium nitrate-dihydrate (Cd(NO$_3$)$_2$.2H$_2$O) and thiourea ((NH$_2$)$_2$.CS) were used to prepare CdS nanoparticles and nanorods. The reagents were mixed in 1:3 molar ratios (0.1M: 0.3M) along with ethylenediamine using a magnetic stirrer and simultaneously heated at 363 K in a sealed bottle for six hours. The products were then washed with ethanol and water and dried at 373 K for four hours. For preparing the nanorods, the aforementioned solution of Cd (NO$_3$)$_2$.2H$_2$O and (NH$_2$)$_2$.CS mixed in 1:3 ratio was transferred into a stainless steel autoclave and placed in a preheated oven at 433 K for 8 hours. The products were then washed and dried exactly in the same way as adopted for CdS nanoparticles.
Annealing the samples: For studying the effect of annealing on the properties of nanomaterials, the as-prepared nanoparticles were subsequently annealed at three different temperatures 623 (sample B), 773 (sample C) and 973 K (sample D) for one hour, separately in a muffle furnace. The samples were then collected and washed with distilled water for several times before drying them at 373 K for four hours. In this chapter, wherever a comparison of the properties of these samples has to be made with CdS nanoparticles, the latter will be addressed sample A.

2.2.3 Synthesis of ZnS nanoparticles and nanorods

ZnS nanoparticles were synthesized using zinc acetate \([\text{Zn(CH}_3\text{COO)}_2 \ 2\text{H}_2\text{O}]\) and thiourea \([\text{SC(NH}_2)_2]\). Both the chemicals were of analytical grades. In this experiment the concentration of zinc acetate and thiourea were 0.1M and 0.3M, respectively. Both solutions were mixed vigorously in the presence of 10 ml ethylenediamine using a magnetic stirrer for thirty minutes. The mixture was then transferred to a stainless steel autoclave which is filled up to 80% of its volume and kept in a high accuracy furnace at 453 K for ten hours. For preparing nanorods the same solution was heated at 473 K for 24 hours. The resulting products were then washed using water and ethanol and dried at 373 K for four hours.
2.3 X-Ray diffraction technique: Instrument and theory

2.3.1 Introduction to XRD

X-ray diffraction is a powerful tool for investigating the fine structure of matter. In the early years of the 20th century, the pioneering work of Max Von Lau and the Braggs made XRD a popular technique for studying crystals. Today this method is employed, not only for structure determination, but also for such diverse problems as stress measurement, chemical analysis, crystallite size calculations, and phase composition studies of both single crystals and polycrystalline aggregate [12-13]. Wavelength of X-rays is on the atomic scale which makes X-ray diffraction the primary tool for probing structure of nanomaterials. X-ray diffraction method offers unparalleled accuracy in the measurement of atomic spacing and is the technique of choice for determining lattice strain in nanomaterials. The intensity of XRD peaks can give quantitative and precise details of the arrangements of atoms at interfaces.

A typical powder XRD instrumentation consist of four main parts: 1) an X-ray source, 2) specimen stage, 3) receiving optics and 4) X-ray detector as shown in figure 2.1.
The source, detector and their associated optics lie on the circumference of focusing circle, while the sample stage is at the center of the circle. Bragg’s law is the basis of XRD analysis [14]. According to this law, although the crystal diffracts the X-rays striking the crystal planes, constructive interference occurs only when the path difference (2d sinθ) between the interfering rays equals an integral multiple of the X-rays wavelength (λ). That is 2d sinθ = nλ. This relation is a mathematical statement of the Braggs law, clearly stating that the diffraction effects cannot be observed from a family of planes for arbitrary angle of incidence. X-ray diffraction from parallel atomic planes of crystal is shown in figure 2.2.
2.3.2 Determination of average crystallite size and lattice strain:

Williamson-Hall equation

In the year 1918, Paul Scherrer investigated the effect of limited particle size on X-ray diffraction patterns and published his results in a paper that included what became known as the Scherrer equation. Scherrer equation relates the peak width to crystallite size as...
\[ \beta = \frac{K \lambda}{L \cos(\theta)} \]  

(1)

where \( \beta \) is the FWHM in radians, \( \lambda \) the wavelength of X-ray, \( K \) is the shape factor with a value close to unity and \( L \) the average crystallite size [15]. \( K \) value depends on the shape of the crystallites, and hence in the absence of detailed shape information, it is plausible to fix it as 0.9.

It is clear from equation 1 that as the crystallite size decreases, a broadening of diffraction peaks takes place. However, Scherrer equation was derived for ideal crystal, ignoring the crystal imperfections and instrumental error. Although the latter’s role can be ignored, the former has significant contribution to peak broadening, especially in nanomaterials due to their enhanced surface to volume ratio which generates a lattice strain. This results in the broadening or narrowing of X-ray diffraction peak depending on the nature of lattice strain. Scherrer equation only takes into account, the broadening of diffraction peaks due to particle size. A modified equation was proposed by Williamson and Hall which takes into account the broadening due to both particle size and strain. This equation is given by

\[ \beta_{total} = 4 \varepsilon \tan(\theta) + \frac{0.9 \lambda}{L \cos(\theta)} \]  

(2)

where \( \varepsilon \) is the lattice strain [15-16].
In the present work, equation (2) is employed to extract details of lattice strain and average crystallite sizes of the samples.

2.4 X-Ray diffraction studies of nanoparticles and nanorods of CdS and ZnS

2.4.1 XRD studies of CdS nanoparticles and nanorods

![Diagram](image)

**Fig 2.3:** (a) Normalised XRD pattern of CdS nanoparticles and nanorods (b) W-H plot and (c) the schematic diagram of Cd-terminated CdS quantum dot.
Figure 2.3 (a) shows the XRD patterns of as-prepared CdS nanoparticles and nanorods. From XRD it is evident that the obtained CdS has hexagonal wurtzite phase (International centre for diffraction data (ICDD) CAS NO: 41-1049). The average crystallite sizes of both nanoparticles and rods calculated using Scherrer equation are 9 and 20 nm, respectively. However, in nanomaterials the presence of defects at the grain boundaries can produce a short range stress field which acts as a source of lattice strain [17]. This results in the broadening of X-ray diffraction peaks. Since Scherrer equation only takes into account the broadening of diffraction peaks due to particle size, Williamson-Hall plots are used to deconvolute the strain and particle size broadening. The W-H plots of CdS nanoparticles and nanorods are shown in figure 2.3 (b).

The values for strain and average crystallite size are -0.00521 and 7.05 nm, respectively for nanoparticles while they are -0.00155 and 15.76 nm, respectively for nanorods. It is to be noted that the slop of Williamson-Hall plot is negative which might be an indicative of the presence of compressive strain in as-prepared nanostructures [18-19]. In spite of the fact that the formation of inherent compressive lattice strain in nanomaterials due to surface defects is reported by many authors [18, 20-21], there is no clear idea as to how and what extent these defects can compress the crystal lattice. Origin of compressive strain in the surface layers of CdS nanostructures can be attributed to their cadmium terminated surface and sulfur vacancies. The heavy cadmium atoms together with sulfur vacancies at surface can compress the immediate layers close to it according to continuum theory of elasticity [22]. This can give rise to interstitials which will distort the surface of nanostructures. The concept of hydrostatic stress, which always holds in
the case of bulk solids, is not valid in nanomaterials because of the fact that their defect
density and lattice distortion are not uniform over the surface. Figure 2.3 (c) shows a
schematic diagram of CdS quantum dot which has Cd-terminated surface with broken
(dangling) bonds.

In unpassivated nanostructures density of surface defects depends on the surface to
volume ratio. Nanoparticles have higher surface to volume ratio than nanorods as the
former’s particle size is lower than that of the latter’s. Hence, nanoparticles experience
more compressive strain than nanorods which is evident from the W-H analysis.
However, it is worth keeping in mind that the values of ε obtained from W-H plot may
not represent an extremely accurate estimate of lattice strain since this is not the perfect
method to study the nature of lattice strain. Hence, further support to the assumptions
made above regarding the formation of lattice strain in the samples has to be obtained
from EDS and TEM studies. This will be discussed in the later part of this chapter.

The lattice parameters a and c of CdS nanoparticles are obtained as 4.11 and
6.684 Å, respectively, whereas those for nanorods are 4.16 and 6.679 Å, respectively. A
comparison of the values of lattice parameters to the values reported in ICDD is made by
many authors. However, such a comparison is meaningless as the values of a, b and d
reported by different authors in ICDD vary from each other. A discrepancy in the values
of lattice parameters of CdS nanoparticles and nanorods arises mainly due to the
difference in their surface morphology and size which directly depends on the preparation
technique and reaction conditions. In this study a comparison of lattice parameters has
been done with those of bulk CdS which is hydrothermally prepared. This is shown in Table 2.1.

**Table 2.1:** The values of lattice constants and d spacing obtained from XRD

<table>
<thead>
<tr>
<th>h k l</th>
<th>a=b (Å)</th>
<th>C (Å)</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk</td>
<td>Nano rods</td>
<td>Nano particles</td>
</tr>
<tr>
<td>1 0 0</td>
<td>4.14</td>
<td>4.11</td>
<td>4.07</td>
</tr>
<tr>
<td>1 1 0</td>
<td>2.075</td>
<td>2.057</td>
<td>1.999</td>
</tr>
<tr>
<td>0 0 2</td>
<td>3.354</td>
<td>3.342</td>
<td>3.306</td>
</tr>
<tr>
<td>1 0 1</td>
<td>3.131</td>
<td>3.1379</td>
<td>3.137</td>
</tr>
</tbody>
</table>

From these results it is obvious that the values of lattice constants and d spacing for CdS nanoparticles are lower compared to those obtained for nanorods and bulk CdS. Also, these values obtained for CdS nanorods are lower than those of its bulk analogue. This substantiates our earlier assumption that the effect of the stress field on the surface of as-prepared nanostructures is to compress the lattice which is in agreement with the W-H analysis. However, it is to be noted that only the surface layers of nanomaterials are influenced by stress field. The interior remains well ordered. Since XRD only gives an average estimate of the values of lattice constants and d spacing, HR-TEM studies have been employed to confirm the existence of surface strain which will be discussed in the forthcoming sections.
2.4.2 Effect of annealing on the structure of CdS nanoparticles: A hexagonal to cubic phase transformation.

Stability of the structure of nanomaterials is of great significance in deciding their technological applications. For high temperature applications, it is imperative that the structure remains stable at all operating temperatures. Phase transformation at high temperatures modifies the physical properties of a material, thereby making it inappropriate for high temperature applications. While studying the properties of annealed CdS nanoparticles it is observed that a phase transformation from cubic to hexagonal structure takes place at an annealing temperature of about 500 K. Such a transformation from hexagonal to cubic phase is unusual at low annealing temperatures due to the high stability of the former phase [23]. Although there are many reports on the pressure-induced phase transformations in II–VI semiconductor nanostructures, reports on thermal instability at comparatively low temperatures are rare [24-25]. Available reports on the thermal instability of nanomaterials show that the studies conducted so far are not well focused [26-27]. The exact reason for such phase transformation is yet to be perceived. A phase transformation might induce or eliminate defects in a material. However, the nature of defects thus formed will be different from that of inherent lattice imperfections such as surface defects. Since bandstructure of semiconductors is strongly influenced by defect-induced lattice strain [28], any change in lattice strain will strongly affect the physical properties of a semiconductor. Unfortunately, no sufficient efforts have been taken so far to correlate surface stress field in nanomaterials with the modification in properties. Hence, a detailed study on such a phase transformation and its
influence on the physical properties have been pursued in this work. This section mainly discusses the structural changes that have taken place in CdS nanoparticles during annealing. Efforts have been made to comprehensively study and understand the nature of defects generated in the material. A model for phase transformation observed in CdS nanoparticles has been proposed. Even so, investigation of lattice defect induced changes in physical properties is narrated only in the next few chapters.

**Fig 2.4:** (a) XRD of samples, (b) TGA of unannealed CdS nanoparticles and (c) EDS spectra of the samples
From the XRD patterns shown in figure 2.4(a), it can be inferred that sample A (unannealed CdS nanoparticles) has hexagonal-wurtzite structure, which during annealing, transforms to cubic-zinc blende structure. Contrary to an earlier report on the thermal instability of very small CdS nanoparticles, it is observed that the hexagonal phase remains stable up to a temperature of 500 K [29]. However, after 500K phase transformation occurs during which the cubic phase evolves. A comparison of the XRD patterns of samples B (CdS nanoparticles annealed at 623 K) and C (CdS nanoparticles annealed at 773 K) clearly indicate that the latter has much improved cubic nature. This suggests that the phase transformation is complete only for sample C and due to low annealing temperature sample B does not retain crystallinity. Figure 2.4 (a) also shows that sample D (CdS nanoparticles annealed at 973 K) exhibits multiphase (mixed hexagonal and cubic) which indicates the formation of CdO at the surface layers due to chemical decomposition of CdS. This is verified using the thermogravimetric analysis (TGA) as shown in figure 2.4(b). The weight loss at around 963 K (690°C) indicates the chemical decomposition of CdS. A complete transformation to cubic phase is hindered due to the formation of CdO at surface layers as it obstructs the displacement of atomic chains which is the cause of phase transformation. This helps the sample to retain most of its hexagonal phase. However, additional phase is observed due to the formation of cubic-CdO at the surface.

The Williamson-Hall plots of samples A, B and C are used for deconvoluting the size and strain broadening. The values of lattice strain and actual crystallite size are obtained using least square fitting with equation (2) and are given in table 2.2. Although the values
of strain obtained from W-H plot are not so reliable for a comparison, their sign can give us an idea about the nature of lattice strain.

Table 2.2: The parameters obtained from Williamson-Hall analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Crystallite size from Scherrer equation (nm)</th>
<th>Lattice Strain</th>
<th>Actual Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>9.1</td>
<td>-0.00521</td>
<td>7.05</td>
</tr>
<tr>
<td>B</td>
<td>11.2</td>
<td>0.00463</td>
<td>13.23</td>
</tr>
<tr>
<td>C</td>
<td>13.8</td>
<td>0.00071</td>
<td>14.71</td>
</tr>
</tbody>
</table>

From table 2.2 it is evident that the stress field in unannealed sample (sample A) is strong enough to compress and deform its atomic layers. However, annealing reduces compressive strain and introduces tensile strain (values with a positive sign) in the crystal lattice. At this point, it is useful to present the results of EDS – the theory of which is discussed only in section 2.5.2 - in order to comprehend the root cause of the observed phase transformation. From the EDS spectrum of sample A shown in figure 2.4 it has been found that its surface is probably cadmium terminated with 56% cadmium atoms. This results in the formation of compressive surface strain in surface layers. Other samples (samples B and C) also have a higher atomic percentage of Cd. Still, the lattice strain is positive (tensile) in sample B which certainly has a connection with the incomplete ordering of lattice chains which occurred during the phase transformation. Phase transformation in this sample is incomplete because the annealing temperature is not sufficient enough to make the process happen quickly. Consequently, defects are
introduced inside the nanoparticle due to which the nature of strain will mainly be tensile. In sample B, the phase is not entirely zinc blende and contains slight wurtzite phase also. Hence, the interfaces separating both faces will experience strong tensile strain. In sample C, high temperature annealing expands the lattice and completes phase transformation due to which the material becomes crystalline. As a result, lattice strain is very weak in sample C which is apparent from table 2.2. For sample D, the EDS spectrum shows a strong peak corresponding to oxygen which suggests the formation of CdO. The oxidation of Cd atoms in the surface layers happens at a relatively low annealing temperature because of their unsatisfied bonds. This is analogous to the inference made from TGA results.

2.4.3 XRD studies of ZnS nanoparticles and nanorods

![XRD patterns and W-H Plots of ZnS nanoparticles and nanorods](image)

**Fig 2.5:** (a) XRD patterns and (b) W-H Plots of ZnS nanoparticles and nanorods
Figure 2.5(a) shows the XRD patterns of as-prepared ZnS nanoparticles and nanorods. The patterns apparently suggest that the obtained material is wurtzite ZnS (ICDD CAS NO: 36-1450). From the W-H plots shown in figure 2.5(b), the values for strain and average crystallite size are obtained as -0.0031 and 9.5 nm, respectively for nanoparticles, and -0.0017 and 13.2 nm, respectively for nanorods. Just like the case of unannealed CdS nanoparticles and nanorods, negative value of strain has been obtained for ZnS nanostructures implying the presence of compressive strain. However, a comparison of the magnitude of values cannot be done as the values obtained from W-H plots are not so reliable. Calculated values of lattice constants and d spacing are given in table 2.3 and are compared to the values of bulk ZnS which are produced hydrothermally.

Table 2.3: The values of lattice constants and d spacing obtained from XRD

<table>
<thead>
<tr>
<th>h k l</th>
<th>a=b (Å)</th>
<th>c (Å)</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk</td>
<td>Nano rods</td>
<td>Nano particles</td>
</tr>
<tr>
<td>1 1 0</td>
<td>3.867</td>
<td>3.841</td>
<td>3.822</td>
</tr>
<tr>
<td>1 0 1</td>
<td>2.9617</td>
<td>2.9436</td>
<td>2.9368</td>
</tr>
</tbody>
</table>

The reduction in the values of d spacing and lattice constants may be an indication that the crystal has slightly compressed under the effect of strain produced by surface
defects. Even so, as discussed earlier, XRD is not the best tool to provide information about the nature of strain in the samples. Some supporting evidences for the XRD predictions in the form of EDS results are already presented in the case of CdS nanoparticles. The EDS studies of ZnS nanostructures will be discussed along with SEM and TEM studies in the forthcoming sections.

2.5 Electron microscopy and energy dispersive spectroscopy: An introduction

2.5.1 Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

Scanning electron microscopy is a widely used technique for inspecting topographies of specimens at very high magnifications using equipment called the scanning electron microscope. SEMs can magnify at maximum of 300,000 times the size of the object studied. This technique is widely employed to study the morphology of nanomaterials. The schematic diagram of SEM is shown in figure 2.6 (a). Scanning electron microscope consists of an electron gun, which produce a stream of monochromatic electrons. The current in the beam is controlled by the condenser lens which also eliminates the high angle electrons. A set of scanning coils enables the movement of beam back and forth across the specimen. When the beam of electrons hit the specimen, secondary electrons are emitted from its surface which is detected by a
detector and the resulting signal is fed to an amplifier. The image of the sample is constructed from the number of electrons emitted from each spot of it [30].

![Fig 2.6: Schematic diagrams of (a) SEM and (b) TEM](image)

A transmission electron microscope works the same way as SEM except that instead of scanning the specimen, the electrons are transmitted through the specimen. Depending on how they are affected by the specimen, electrons continue down their journey through further electromagnetic lenses and produce the image. This image is either magnified and focused onto an imaging device, such as a fluorescent screen, or
detected by a sensor such as a CCD camera. The schematic diagram of a TEM is shown in figure 2.6(b).

Modern TEMs equipped with a STEM facility are capable of resolving 0.2 nm at magnifications of up to one million times. This is much higher than the maximum magnification that the best SEM can provide. The high resolution TEM can provide a maximum resolution of 0.08 nm [30]. The focus of analysis is also different. SEM focuses only on the surface and composition of the samples. On the other hand, TEM is powerful enough to explore what is inside or beyond the surface. SEM is mainly used to study the average morphology of the particles, while TEM provides detailed information about the structure of even a single particle. SEM with sufficient attachment can provide a three-dimensional image while TEM can provide only a two-dimensional picture.

2.5.2 Energy dispersive spectroscopy (EDS)

Energy dispersive X-ray spectroscopy is a powerful technique used to determine the elemental composition of a sample. This technique is based on the fact that each element has unique atomic structure, and hence produces unique set of peaks in the X-ray spectrum. These characteristic X-rays result from the electron transitions between inner electronic orbits. However, under normal circumstances these orbitals are completely filled. When the electron beam strikes the sample, it may excite an inner shell electron and eject it from the shell thus creating a vacancy. This vacancy will be filled by an electron from an outer shell. The difference in energy between the two shells is released as X-rays [31]. This is shown in figure 2.7.
The EDS equipment is normally attached to the SEM or TEM. This enables the equipment to detect the X-rays that are produced by the sample when bombarded with a focused beam of electrons. The instrument then determines the number and energy of the X-rays given off by the atoms. Since these parameters are characteristics of the atomic structure of the element from which they are emitted, they enable us to measure the elemental composition.
2.6 Electron microscopic and energy dispersive spectroscopic studies of CdS and ZnS nanoparticles and nanorods

2.6.1 SEM, EDS and TEM analysis of CdS nanoparticles and nanorods

![SEM images of CdS nanoparticles and nanorods](image)

**Fig 2.8:** The SEM images of CdS (a) nanoparticles and (b) nanorods. The EDS patterns of nanoparticles and nanorods are shown in (c) and (d), respectively

The SEM images are taken using JEOL Model JSM-6390LV scanning electron microscope. Figure 2.8(a) reveals the almost spherical morphology of CdS nanoparticles. The rod-like morphology of CdS nanorods is shown in figure 2.8 (b). However, determination of the exact particle size is hardly possible due to the low resolution of
SEM. It can also be seen that the nanoparticles have agglomerated as a consequence of their high surface energy. EDS spectra of the samples are shown in figure 2.8 (c) and (d). These spectra are taken by focusing the electron beam to different locations of the samples, and a consistency in calculated atomic percentages is observed. The atomic percentages of cadmium and sulfur in CdS nanoparticles are 56 and 44, respectively while those in CdS nanorods are 54 and 48, respectively. Although a 50:50 ratio is expected in the ideal case, slight deviations from this ratio occurs in practical cases owing to the high surface to volume ratio of nanomaterials. However, the huge difference in atomic percentages observed in these samples undoubtedly points towards the fact that very high density of sulfur vacancies decorates their outermost atomic layers. Thus it can be concluded from the EDS studies that as-prepared samples are devoid of impurities, but rich in sulfur vacancies. This is analogous to the XRD results and supports the earlier assumption that sulfur vacancies (or the cadmium terminated surface) could be the possible generators of compressive surface strain. To authenticate the claim that the surface strain is ‘compressive’, HR-TEM studies of CdS nanoparticles are conducted. This will be discussed in section 2.6.3.

HR-TEM images are recorded using the JEOL model-JEM-2100 transmission electron microscope. Figure 2.9(a) shows nanorods with an average diameter of 25 nm and lengths in the range of 90-180 nm. The diameters of nanorods are very close which is of great importance. From figure 2.9 (b) the average particle size of CdS nanoparticles is 11.5 nm. The figure also reveals that the particles have a spherical shape and almost uniform size distribution. The selected area electron diffraction (SAED) patterns of both
the samples are shown in figure 2.9(c) and (d). The values of d spacing are calculated from the pattern. The hexagonal structure of samples are confirmed and the rings are indexed.

**Fig 2.9:** The HR-TEM and SAED images of CdS (a) (c) nanorods and (b) (d) nanoparticles. The inset of (b) shows a single spherical CdS nanoparticle

### 2.6.2 SEM, EDS and TEM analysis of ZnS nanoparticles and nanorods

The SEM images of ZnS nanoparticles recorded using JEOL Model JSM-6390LV scanning electron microscope are shown in figure 2.10. Figure 2.10(a) and (c) reveals the spherical and rod-like morphology of ZnS nanoparticles and nanorods,
respectively. The figure also shows that both nanoparticles and rods are agglomerated owing to their enhanced surface energy. The resolving power of SEM is not enough to clearly show the distribution of these agglomerated nanostructures. EDS patterns of the samples are presented in figure 2.10(b) and (d). Both figures show strong peaks corresponding to zinc and sulfur. No impurity peaks are observed indicating the high purity of the samples. The atomic percentages of zinc and sulfur in ZnS nanoparticles are 54 and 46 percentages, respectively, whereas those in ZnS nanorods are 52 and 48 percentages, respectively. From this calculation it is evident that both samples, similar to CdS nanostructures, possess high density of sulfur vacancies. These vacancies exist mainly on the surface of nanostructures as proposed earlier.

**Fig 2.10:** The SEM images of ZnS (a) nanoparticles and (c) nanorods. (b) and (d) are the EDS spectra nanoparticles and nanorods, respectively
The TEM images of ZnS nanoparticles and nanorods shown in figure 2.11 confirm their spherical and rod-like shapes, respectively. It is found from these images that the diameters of ZnS nanoparticles is in the range 10-20 nm while those of ZnS nanorods lies in the range 20-35 nm. The ZnS nanorods have a length between 80-120 nm. The SAED rings are indexed as shown in figure 2.11(c) and (d) confirming the hexagonal structure of as-prepared samples. Both TEM and EDS studies point towards the fact that the average diameter of CdS nanorods is smaller than that of its ZnS counterpart. Similarly, CdS nanoparticles are smaller than ZnS nanoparticles. Due to this the surface to volume ratio, and hence the defect density (from EDS) will be higher for CdS nanostructures. This will definitely affect the search for a consistent and similar pattern in the enhanced properties of semiconductors. Attempts to further reduce the size of ZnS nanostructures turned out to be futile as traces of ZnO has been found in the sample on reduction of molarity of precursors. A different preparation technique has not been employed as the surface defect density will be greatly affected on doing so and the comparison of properties of the samples will become irrelevant. Although this comparative study of CdS and ZnS nanostructures may not help us to fully understand the general trend observed in nanosized II-VI semiconductors, it would certainly help to track some common trends and phenomena observed in these semiconductors. From this point it will be easy to pursue the underlying reasons.
2.6.3 TEM studies of annealing induced hexagonal to cubic phase transformation in CdS nanoparticles: Understanding the mechanism of phase transformation

As discussed in section 2.4.2, it is observed from the XRD studies that CdS nanoparticles, during annealing, undergo a transition from hexagonal to cubic phase. At very high annealing temperatures; however, a mixed phase of the sample has been found to exist.
To get a detailed picture of the morphological changes that has taken place in CdS nanoparticles during annealing, high resolution transmission electron microscopy is used. Figure 2.12 shows the HR-TEM images and SAED patterns of the samples. From these TEM images, the average particle sizes of samples A, B, and C are obtained as 11.5, 30, and 50 nm, respectively. The figure proves beyond any doubt that annealing has not only increased the size of nanoparticles but also changed its shape. In figure 2.12 (a) the particles are almost spherical in shape with smooth edges. Yet, during annealing the particle size increases significantly. One reason for this size change is the thermal expansion of the lattice. Nevertheless, thermal expansion cannot be the sole reason for such a large change in particle size. At high temperatures grain boundaries of two or more grains can fuse together to form a single grain causing the particle size to increase \[32\]. If the sample is heated for a sufficient period, fused grain boundaries can retain their crystalline nature. The shape of particles, however, gets deformed as shown in figure 2.12(c). The SAED patterns are indexed which confirms the hexagonal to cubic transformation.
A transformation from hexagonal phase to cubic phase is unusual at low annealing temperatures due to the stability of the former. However, such a transformation is not forbidden. Atoms in wurtzite and rock salt CdS are four fold coordinated and the 2H to 3C transformation only requires a slight displacement of atomic layers. The stacking sequence of wurtzite (2H) structure can be represented as ABABAB along the [001]
direction, whereas that of the zinc blende (3C) structure is ABCABC along the [111] direction [33-34]. The 2H to 3C transformation involves a displacement of four successive layers after every two layers as shown below

Initial structure (2H) – ABABABABABAB

Final structure (3C) – ABCABCABCABC

The atomic arrangements of wurtzite and zinc blende CdS are shown in figure 2.13(a) and (b), respectively. As discussed earlier, a slight displacement of the four atomic chains marked in figure 2.13(a) transforms it to the structure shown in figure 2.13(b). There is yet another model in which twinning can induce a phase transformation [25]. However, this process requires very high energy due to which twinning-model cannot be used to explain the phase transformation observed in the present study. The generation of stacking faults needs less energy compared to other types of dislocations. Hence, this model is apt to explain the observed phase transformation. The HR-TEM images of atomic chains in sample A and sample C are shown in figure 2.13 (c) and 2.13(d), respectively, which once again confirms the phase transformation.
Fig 2.13: Schematic representation of (a) wurtzite and (b) zinc blende CdS. The HR TEM images of the atomic chains of (c) wurtzite and (d) zinc blende CdS are also shown.

Evidence for the existence of compressive strain in unannealed nanoparticles and the evolution of tensile strain in the sample during annealing is obtained by carefully analyzing the HR-TEM data. Figure 2.14 (a) depicts the compressed surface layers of sample A. The insets of this figure also show its distorted surface layers. Now a clear
picture of the phase transformation is evolving. Due to the large density of defects and dangling bonds at the surface, nanomaterials have high surface energy [35]. The crystal will always try to reduce its free energy [36]. In sample B, temperature treatment expands the lattice which gives rise to dislocations for minimizing its energy. This results in the formation of stacking faults and triggers the phase transformation. This transformation only requires low energy and happens according to the model presented in the previous paragraph. The TEM image of the lattice of sample B, similar to the XRD results, suggests that the crystal experiences tensile strain. Figure 2.14(b) clearly shows deformed atomic layers in the interior of the sample. Tensile strain arises due to incomplete ordering of lattice during the occurrence of dislocations as the annealing temperature is insufficient to make the process happen quickly. Figure 2.14(c) reveals that only weak compressive/ tensile strain exists in sample C which is a clear sign that the material has acquired good crystallinity. Thus it becomes clear that the nanoparticles have finally gone to an ordered low energy state through a phase transformation. It is also to be noted that the lattice spacing (d) has increased during annealing due to thermal expansion of lattice.
Fig 2.14: The HR-TEM images of (a) sample A (b) Sample B and (c) Sample C. The values of d spacing and corresponding plains are marked. The arrows indicate the strained lattice

2.7 Summary

Nanoparticles and nanorods of CdS and ZnS have been prepared via hydrothermal method. The average crystallite size and lattice strain are calculated using the
Williamson-Hall analysis. The morphology is studied using SEM. From TEM studies the average particle size of CdS nanoparticles and nanorods are obtained as 25 and 11.5 nm, respectively, whereas those of ZnS nanoparticles and nanorods are found to fall in the range 10-20 and 20-40 nm, respectively. Lengths of CdS nanorods are in the range of 90-180 nm while that of ZnS nanorods are between 80-120 nm. EDS analysis has shown that the as-prepared samples are rich in sulfur vacancies. Evidence of the existence of ‘compressive’ type lattice strain is obtained from XRD and HR-TEM analyses. The lattice strain takes its origin in the surface layers of nanomaterials as a result of their Cd/Zn terminated surface. Another important observation is that of a low temperature phase transformation from hexagonal to cubic phase during the annealing of CdS nanoparticles. A model of phase transformation mechanism is presented in this chapter which attributes the phase change to thermally arisen dislocations. Such dislocations induce tensile strain which acts against the surface defect induced compressive strain in the surface layers. HR-TEM and XRD studies clearly show that compressive strain exists in the surface layers of unannealed CdS nanoparticles, whereas dislocation introduced tensile strain persist in the interior of its annealed version. This observation has played a crucial role in understanding the defect induced changes in the properties of nanomaterials which will be discussed in the forthcoming chapters.

2.8 References


