CHAPTER – 2

GROWTH AND STRUCTURAL CHARACTERIZATION OF CADMIUM SULFIDE (CdS) CRYSTALS
2.1 Introduction

Over the years, uses for crystals have not really changed and they are still being used in the same way as the ancients. However, we do now have the modern-day benefit of discoveries such as the silicon chip for computer technology and quartz to power clocks and watches. Crystals are used by scientists in emergent technological fields such as holographic computers. Crystals are particularly valuable for their amplifying and absorbing properties, as well as their pronounced ability to conduct energy from one source to another. The actual word crystal comes from a Greek word Crystallos, from “Krysos” meaning “ice cold” as it was originally thought that crystals were a type of ice that was so cold it would never melt [1].

As in the present day, the regular polyhedral forms were the ones that roused the most interest. Pythagoras, for example, used the word crystal to imply perfection, harmony, and beauty; and Plato listed his famous five polyhedra, related to fire, earth, air, water, and the universe. Around the late 1700’s this theory was superseded by the idea that crystals “grew” by the addition of layers. Now science has been able to calculate physical laws which clarify this theory. When a crystal is shattered, each piece may vary in size, but the fragments all have the same shape. How our understanding of morphology and growth mechanism of crystals has developed since the time of Kepler and Steno has recently been summarized by Sunagawa [2].

Snow crystals and rock crystals are naturally formed crystals under uncontrolled, fluctuating, and often sharply changing growth conditions. Any mineral crystals constituting the solid earth and planetary bodies were formed under such conditions and in impure, complicated, and complex systems. Also, inorganic and organic crystals are formed in various organs and cells of animate bodies, through biological processes necessary to sustain life or to eliminate unnecessary waste compounds. How crystals nucleate and grow, and how their forms are controlled in such complicated and complex systems are problems still waiting for proper answers at the atomistic level.

Crystals may be partially dissolved during the process of formation, or experience transformation in their post growth histories. We are unable to observe in situ the growth or post growth process of mineral formation, but we can investigate samples that experienced these processes, provided that these processes are recorded in the samples in some form and can be visualized by appropriate methods. In nearly
perfect single crystals, these are recorded in the form of various physical imperfections and chemical heterogeneities, preserving the records of morphological evolution during the growth or post growth processes. Information obtainable from such samples is equally important and informative in understanding the formation of solid earth and planetary materials, provided that such information can be evaluated properly.

The evolution of our knowledge of crystal growth requires not only scientific understanding, but the driving force of applied technology which so often provides a significant influence in highlighting our lack of scientific knowledge and the need for a more refined science and indeed the development of new concepts. Crystal growth now embraces an immense field of materials and technologies, which could not be covered in-depth by any one book. Nevertheless the present study does provide more comprehensive coverage. Natural crystals of many materials are available in nature but they cannot be used directly for devise applications.

Instead they should give some sort of treatment because of the main problem of purity and perfection. The crystal growth study in last 10 years [3 - 7] led to the conclusion that the artificial crystals of most of the materials can be grown in laboratories. To satisfy the modern days need of science and technology the crystals are produced artificially crystal. The crystal growth processes have been described in many books [8-17].Crystals grown by different methods can be used in several applications and hence the growth procedure and the characteristics of crystalline solids are very significant for scientific and industrial development. Therefore, it is always essential to characterize and evaluate the properties and behaviour of the grown crystals.

The important properties of the materials are physical, chemical, structural, mechanical, electrical and optical properties. They are characterized with the help of different experimental techniques. In Present chapter, the different experimental techniques have been used for the stoichiometry confirmation and the structural characterization of grown crystals. This includes energy dispersive analysis of X-rays (EDAX), X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM). Experimental details and apparatus used in the respective analysis and results sequentially will be mentioned here.
2.2 Different Growth Techniques

Before proceeding with the discussion, it must be emphasized that speaking of the superiority of one crystal growth technique over another would not be appropriate without clearly specifying the types of and expected physical and chemical properties from the grown crystal since each class of a material brings its own special difficulties. A technique that results in a successful growth for a particular semiconductor crystal may fail in the growth of another material. Briefly, there exists no such a universal technique, which guaranties the growth of all kinds of single crystal semiconductor materials. Therefore, here, each technique is introduced, in general sense, to provide the reader with some background knowledge.

The quality of the crystals is the most important aspect of electronic device design. So far, many growth techniques have been developed to grow high-quality crystals. Significant improvements have been made in bulk crystal growth with regard to uniformity, reproducibility, thermal stability, diameter control, and impurity and dopant control[18,19].Crystal growth, in principle, involves controlled phase transformation from disordered fluid phase to with high atomic mobility and hence we may define four categories of crystal growth processes. Different techniques for crystal growth are classified as below:

1. Vapour Growth: Growth form the vapour phase
2. Solution Growth: Growth from an aqueous solution
3. Melt Growth: Growth from a supercritical or fluid phase
4. Solid Growth: Growth from one or more solid phases

These techniques are adequately described in various textbooks and reviews [20-43]. Figure 2.1 shows these main categories with their subfamilies. From the literature survey, it has been found that many materials have been grown using different techniques. Most of the basic techniques of crystal growth and their modification are described at length by Brice [44] and Peiser [45]. Recently, melt growth techniques are the main methods of industrial manufacture for the most compound of semiconductor materials. This is because they are appropriate to grow large single crystals quickly. In the case of solution growth techniques and vapor phase growth techniques, growth rates are rather lower compared to melting growth techniques and they are in general limited to growing compound semiconductor materials which are difficult to grow by the melt growth technique from the viewpoint
of physical properties such as high melting temperature and/or high decomposition vapor pressure.

Common to almost all growth techniques, the natural convection driven by density and temperature variations occurs in the melt. Convection in the melt enhances the transport of species giving rise to a faster growth rate, which is desirable, but at the same time it results in uneven concentration distributions, unstable interface formation and inclusion trapping in the solid. Crystal growth from the vapor phase is the most basic technique. It has advantages that growth can be performed at lower temperatures. This can prevent from phase transition and undesirable contamination. Therefore, this technique has commonly been used to grow II–VI compound semiconductor especially for CdS, ZnSe, CdSe, CdTe etc. [46-48].
2.3 Growth from Vapour Transport Techniques

The vapor phase is considered to be an important technique to obtain stoichiometric crystalline materials from inexpensive and readily available raw materials. The vapour growth method is mostly preferred for the growth of layered single crystals as well as for the fabrication of thin layers of metals, insulators and semiconductor type materials. Elements or compounds which are relatively volatile can be grown from the vapour phase.

In this technique, the materials from which the crystals are to be grown are transported to the growth zone, kept at comparatively lower temperatures from the source.
zone which is kept at comparatively high temperature in the form of volatile compounds, which reacts or decomposes to give the material in crystal form and a by-product. Most II–VI compounds are high melting point materials which may be grown as single crystals by careful use of vapor phase and it offers a considerable number of advantages over melt growth listed below:

- The relatively high vapour pressures below the melting point allow growth to take place at low temperatures. In principle, this leads to a reduction in the density of precipitates and inclusions (due to temperature fluctuations) as well as limiting the amount of thermal stress applied to the crystal.
- Contaminations from the crucible are smaller than in melt techniques due to the low temperatures used.
- Non-volatile impurities present in the source charge are not transported to the crystal, i.e. the growth process is to some extent also a purifying one.

2.3.1 Classification of Vapour Transport Technique

The growth of crystal from vapor phase can be divided [49] into various categories:

1. Sublimation or evaporation, in which the vapor is obtained from the pure condensed phase at an appropriate temperature;
2. If a transporting reaction is used for one or more of the constituents of the crystal, the process is termed either chemical vapor transport (CVT) or
3. The direct vapour transport (DVT) technique.

Crystals with good perfection can be obtained from the vapor phase. This technique is used for production of thin crystals and those materials with van der waals bonds. In this technique, the materials from which the crystals are to be grown are transported to the growth zone, kept at comparatively lower temperatures from the source zone which is kept at comparatively high temperature in the form of volatile compounds, which reacts or decomposes to give the material in crystal form and a by-product. The grown of cadmium sulfide from the vapour phase has been described in many articles [50-53]. The brief description of this technique adopted in the present work is given below.
2.3.1.1 Sublimation Technique

This method is carried out in either a static or in a floating gas system. In a static system, the material is sealed in a tube and placed in a furnace with thermal gradient. The sublimation takes place in hotter portion of the furnace and the crystal growth in the colder portion. In a float system, an inert gas is passed through the tube over the material in the hot zone, carrying the gaseous species into the colder zone where it deposits. Crystals grown in this manner are of extremely high purity. The method may be applicable to a material that has reasonably high vapour pressure at temperature up to 1000 °C.

2.3.1.2 Chemical Vapour Transport (CVT) Technique

This is a widely applicable method. Several compounds which are not accessible by usual crystal growing methods such as modified Czochralski or Bridgman - Stockbarger techniques can be prepared by this method. It is particularly suited for compounds having a high melting point or for those which decompose without melting. Application of this technique stems on the growth of metal single crystals in halogen atmospheres. This technique has been used for the growth layer compound by various research groups [54-56].

CVT technique mainly relies on a chemical reaction between the source material to be crystallized and a transporting agent. The reaction product is volatile and can be transported in the vapour phase at temperature well below the melting point of the compound. Transportation occurs between two zones having different temperatures. Usually the starting reaction occurs at a higher temperature and is reversed at lower temperature to deposit molecules of the compound at the most favorable crystalline sites. Initially random deposition occurs until seed crystals are formed. Thereafter, growth preferentially occurs in these seeds, and large single crystals are formed. The transportation of the reaction products in the vapour phase can be obtained by a continuous gas flow from external supplies or by its recirculation within a closed tubular ampoule. Improvement in the quality of crystals can be made by lowering the growth temperature and by appropriate choice of the transporting agent.
2.3.1.3 Direct Vapour Transport (DVT) Technique

This technique is classified as a better method to obtain pure crystals, where in the transport of material takes place directly from the source zone to the growth zone due to the temperature gradient set across the encasing tube without using any transporting agent. The CVT technique is very useful for the growth of large sized single crystals, but the grown crystals are usually incorporated with an active impurity in the form of a small amount of the transporting agent. This affects the thermal and electrical properties of the grown crystals at a considerable extent. In order to avoid the contamination by the transporting agent and hence to obtain pure crystals, a better technique is the direct vapour transport technique.

Many researchers [50-52] have used the direct vapour transport technique in order to avoid the contamination due to the transport agent. Their work showed that it is possible to grow fairly large crystals of transition metal chalcogenides and their solid solutions. A useful procedure for the calculations of the rate of the transport of solid, based on knowledge of initial condition as well as thermodynamic and diffusion coefficient data has been derived by Mabdel [57]. Crystal growth can be carried out either by an open system technique or a closed system technique. Initially, the Piper–Polich technique was developed, in 1961 [58]. Prior [59] improved the PVT technique using a reservoir to control the deviation from stoichiometry. Detailed study of transport reactions occurring during the growth process has been carried out by Shafer [60]. The reaction taking place to form AB compound can be given as:

$$A(s) + B(s) \xrightarrow{T} A(g) + B(g) \xrightarrow{T} AB(g) + A(s) + B(g) \xrightarrow{T} AB(g)$$

One of the elements has a lower melting point. So it goes into vapor form at lower temperatures. This vapor reacts with the other elements at high temperature forming the compound where the proper growth conditions in the growth zone would lead to the growth of the crystal.

2.4 Earlier Research Work on CdS Crystals by Various Growth Techniques

In this section we present some of the main results obtained on the growth and characterization of CdS crystals using various types of crystal growth techniques.
Table 2.1: Earlier work on CdS crystals with important results obtained by using different growth techniques [47,48,50,52,61-79].

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Author</th>
<th>Technique</th>
<th>Results</th>
<th>Reported year</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>E.Tiede et al.</td>
<td>HP-VGF</td>
<td>First melt growth of CdS</td>
<td>1920</td>
</tr>
<tr>
<td>2</td>
<td>D.R.Boyd et al.</td>
<td>PVT</td>
<td>CdS thin platelets, rod and whiskers, polygonal crystals, polycrystalline crystals and single crystals.</td>
<td>1959</td>
</tr>
<tr>
<td>4</td>
<td>F. Kaldis</td>
<td>Sublimation &amp; CVT</td>
<td>A comparative study of the sublimation and CVT</td>
<td>1969</td>
</tr>
<tr>
<td>5</td>
<td>Z. Blank et al.,</td>
<td>gel-growth PVT</td>
<td>Orange dendrites, Small dendritic clusters, Small red of polycrystalline hexagonal CdS, size 0.1—0.2 mm.</td>
<td>1971</td>
</tr>
<tr>
<td>6</td>
<td>L. Rouse et al.</td>
<td>PVT</td>
<td>Hexagonal crystals of CdS have been grown in sealed ampoules containing argon.</td>
<td>1972</td>
</tr>
<tr>
<td>7</td>
<td>G. H. et al.</td>
<td>PVT</td>
<td>Growth mechanism of CdS platelets in a stream of argon.</td>
<td>1972</td>
</tr>
<tr>
<td>8</td>
<td>Kenneth A. Jones</td>
<td>PVT</td>
<td>CdS powder was evaporated at 1100 °C and re-deposited at 900 °C. Needles were the initial stage of growth platelets</td>
<td>1973</td>
</tr>
<tr>
<td>9</td>
<td>C. Kim et al.</td>
<td>CVT</td>
<td>CdS platelets with and without halogen dopants</td>
<td>1974</td>
</tr>
<tr>
<td>10</td>
<td>G.J. Russell et al.</td>
<td>sublimation CVT</td>
<td>Platelet CdS crystals grown in a continuous stream of argon.</td>
<td>1979</td>
</tr>
<tr>
<td>11</td>
<td>Koichi M. et al.</td>
<td>CVT</td>
<td>CdS prisms, pyramids, platelets, dendrites, or irregular-shaped crystals were obtained by using iodine as a transporting agent</td>
<td>1983</td>
</tr>
<tr>
<td>No.</td>
<td>Authors</td>
<td>Method</td>
<td>Details</td>
<td>Year</td>
</tr>
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<td>-------------------------------------------------------------------------</td>
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</tr>
<tr>
<td>13</td>
<td>N.V. Klimova et al.</td>
<td>sublimation</td>
<td>Growth of Large CdS single crystals with a high optical strength</td>
<td>1995</td>
</tr>
<tr>
<td>14</td>
<td>M.J. Tafreshi et al.</td>
<td>sublimation</td>
<td>Mechanical and Optical Properties studies on CdS single crystals</td>
<td>1995</td>
</tr>
<tr>
<td>15</td>
<td>T.S. et al.</td>
<td>sublimation</td>
<td>Growth of hexagonal CdS without a seed crystal</td>
<td>1995</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>The carrier concentration and mobility obtained from Hall measurements at RT were $2.90 \times 10^{16} \text{cm}^{-3}$ and 316 (cm$^2$/V s), respectively</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>K.-T. Chen et al.</td>
<td>PVT</td>
<td>Two types of as-grown crystals, one &quot;dark&quot; and the other &quot;clear&quot; were obtained both having a medium resistivity of $10^6$-$10^8 \Omega \cdot \text{cm}$</td>
<td>1996</td>
</tr>
<tr>
<td>17</td>
<td>K.J. Hong et al.</td>
<td>sublimation</td>
<td>Growth of hexagonal CdS without a seed crystal</td>
<td>2000</td>
</tr>
<tr>
<td>18</td>
<td>L.v.B. et al.</td>
<td>flux</td>
<td>Growth and investigation of CdS single crystals</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>XRD characterization</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>N. Sankar et al.</td>
<td>PVT</td>
<td>Single and polycrystalline CdS grown by versatile technique</td>
<td>2002</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>The carrier concentration and mobility obtained from Hall measurements at RT were $1.86 \times 10^{16} \text{cm}^{-3}$ and 335 (cm$^2$/V s), respectively</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>A. P. Odrinskii</td>
<td>Czochralski (CZ)</td>
<td>Investigation of high-resistivity CdS single crystals</td>
<td>2004</td>
</tr>
<tr>
<td>22</td>
<td>B. Bou. et al.</td>
<td>Czochralski (CZ)</td>
<td>Growth of CdS nanocrystals</td>
<td>2004</td>
</tr>
<tr>
<td>23</td>
<td>Cheng H. et al.</td>
<td>PVT</td>
<td>Growth of large-size CdS crystals</td>
<td>2009</td>
</tr>
</tbody>
</table>
2.5 Selection of Growth Technique

The choice of technique basically depends upon the properties of the material to be synthesized. Materials in crystalline form required in modern devices need to be of high purity, high degree of perfection with minimum defects. II-VI compound have higher melting points. Due to their high ionicity, the overheating phenomenon occurs when they are heated to their melting point. Owing to the higher vapor pressures at their melting points, it is difficult to grow bulk crystals from melt.

On the other hand, it is easy to grow bulk crystals as well as their films from the vapor phase. In addition to this, the majority of compounds belonging to II-VI group is insoluble in water and decomposes before their melting points are reached. Therefore, the growth of such crystals from the melt and aqueous solution is not possible and hence the growth of single crystals of these compounds, using vapour phase technique was found to be most suitable [80]. Since, the present investigation is oriented towards the applications part of CdS, i.e. the fabrication of Schottky diodes and the study of its interface properties, the purity of the grown material is the prime factor to be taken into account. In light of the above discussion, the direct vapour transport technique seems to be a better, easier and comparatively an economical method for the growth of pure crystals, this technique has been used for the growth of CdS crystals in the present case.

2.5.1 Limitations and Requisites for DVT Technique

As discussed earlier, the growth of crystals by the vapour transport technique takes place as a result of the transport of material in vapour form from one region to another region of an enclosed system. This can be accomplished only if certain requirements of the growth mechanism through this technique concerning the encasing tube as well as the furnace constructions are satisfied. The requirements of the growth process of the direct vapor transport technique are given below.

1. Since the technique involves the transport of materials in the vapor form from one region to the other within the enclosed tube placed inside the furnace, it is necessary that the furnace should essentially have two different zones of temperature with a proper temperature gradient between them.

2. Since the material is transported in this technique is in vapor form, the encasing assembly should be vacuum-sealed. This would provide an impurity
free environment for the growth of crystals to ensure the purity of the grown crystal.

3. The material used to make the encasing assembly should sustain high temperature above 1000 °C (which must be essentially higher compared to the melting / boiling point of the material to be grown) and at the same time it should not react with the vapor or get corroded by the vapor.

4. Since the temperatures of the two different zones of the furnace are kept at different temperatures, it is necessary that they should be independently controlled using two different temperature controllers.

5. Considering the above requirements a two-zone furnace has to be constructed using windings of a material which can withstand temperatures up to 1200 °C. Also, the encasing tube should be of the material which does not melt at high temperatures. The material should be non-reactive at these temperatures in order to avoid contamination of the grown crystals. Under these circumstances, quartz was considered as the best choice for making the encasing tube. The following sections cover the furnace design as well as the fabrication of the encasing assembly as per the above requirements.

2.6 Experimental Setup

2.6.1 Dual Zone Horizontal Furnace

Taking into account the above limitations, a two-zone furnace was found to be convenient to produce an appropriate temperature gradient over the entire ampoule. Normally the temperatures employed are fairly high. The temperature gradient within the furnace is required over a length of about 25 cm. Stability of temperature plays an important role, therefore, for this purpose electronic temperature controllers were used. The furnace was constructed in our university science and instrumentation center (USIC) by using special sillimanite threaded tube of grade KR 80 GA HG. This muffle tube is closed at one end and has 500 mm in length, 70 mm outer diameter, 56 mm inner diameter with threaded pitch of 3 mm (Koppers Fabriken Feuerfester, Germany). Super Kanthal A-1 wire of 17 SWG was wound directly on the furnace tube into two different zones or regions. These wires can withstand temperatures up to 1400 °C. The tube (Muffle) was enclosed in the glass wool jacket, hot face insulating brick slabs constructed locally and the brick shell was fully enclosed in thick asbestos sheets, and this entire assembly was supported in a steel framework. This arrangement
is shown in figure 2.2. The power supplied to the furnace windings was regulated by the control circuit shown in figure 2.3.

![Figure 2.2: The dual zone horizontal furnace with axially loaded ampoule.](image)

![Figure 2.3: Schematic diagram of complete furnace structure with temperature controlling system.](image)
The two regions of windings were provided with independent power supplies and temperature controllers. Transformers with 70V, 80V and 100V taps with 20A current capacity in secondary windings were used to supply sufficient power in order to achieve the required higher temperature.

2.6.2 Ampoule Preparation

Quartz is considered as the best choice for making the encasing tube. High quality fused quartz tubes of various diameters, having a melting point of about 1500 °C were used for the growth of crystals. Tubes having internal diameter 22 mm, outer diameter 25 mm and length 250 mm were found to be more suitable. One end of the ampoule was sealed and the other end was drawn into a neck and joined to another 8 mm inner, 2 mm thickness and 10 mm outer diameter glass tube to connect it to the vacuum system for evacuation after introducing the source materials. Such a quartz tube and an ampoule generally used for the crystal growth are shown in figure 2.4.

![Figure 2.4: A quartz tube and an ampoule used for crystal growth.](image)

2.6.3 Cleaning Process of Ampoules

Cleaning of ampoule is an important step in the crystal growth process. The employees were cleaned prior to filling them with the stoichiometric mixture of required materials. The cleaning steps have been monitored below:

1. They were first washed with boiling water along with a suitable detergent.
2. They were rinsed with concentrated H₂SO₄ and washed with double-distilled water once again.
3. A further rinsing was done with the mixture of concentrated HNO₃ and concentrated HCl taken in equal proportion.

4. They were washed with double distilled water two to three times.

5. Then, the ampoules were filled with concentrated HF and heated at 70 °C in order to make the inner surface of the ampoules slightly rough due to etching. These rough surfaces are absolutely essential to enhance growth sites for preferential nucleation during the crystal growth.

6. A thorough and final washing was done again with double-distilled water to remove any residue of these chemicals for 3 to 7 times.

7. The so-cleaned ampoule was then kept in a SICO constant temperature oven at 100 °C for 24 hours to make it moisture free.

2.6.4 Sealing of Ampoules

For the crystal growth of cadmium sulfide (CdS), the required materials shown in the table 2.2, were taken in a stoichiometric proportion using the “AFCOSET” electronic weighing machine and filled up in a transparent ampoule duly cleaned and dried by the process explained above. A total amount of constituent materials used was 15 gm in experiment. The ampoule containing the source material was evacuated to a pressure of 10⁻⁵ Torr to minimize the reaction of the elements with the atmosphere at elevated temperatures and also to create an inside pressure very low so that the vapor pressure developed at high temperature within the ampoule does not lead to its blasting. Proper care was taken while evacuating the ampoule so that material from ampoule does not enter into the vacuum system. Once the required vacuum was reached, the loaded ampoule was sealed off at the neck. Proper mixing of the contents was ensured by shaking thoroughly the sealed ampoule.

2.7 Growth of Cadmium Sulfide (CdS) Crystals

2.7.1 Seeds Preparation

In the present work, the author had first prepared the charge of the compounds of Cd and S. The materials used for preparing the charge of crystals are shown in table 2.2. In the sealed ampoule, the mixture in the powder form was then distributed uniformly all over the length and kept in the horizontal furnace co-axially in the center. The temperatures and the period for which the ampoule was kept in the furnace depended upon the material, which was being grown. A slow heating was
necessary to avoid any possibility of explosion due to the strong exothermic reaction between the elements.

After some stipulated time of keeping the ampoule at elevated temperatures, a slow cooling process was carried. The rate of cooling should be as slow as possible for enhancing the nucleation and growth process. The typical temperature profile of the growth run of grown crystals is shown in figure 2.5. Crystal growth occurs in three steps any one of which may be rate limiting [81]:

1. Vaporization of the charge,
2. Diffusion of the vapors,
3. Condensation on the crystal surface.

In the present case, the required temperature was 1000 °C. The ampoule was kept at this constant temperature for 13 days. After this period, the furnace was slowly cooled down to room temperature at the rate 50 °C /hr and then switched off. As a result fine free flowing; shiny homogenous polycrystalline material was achieved for the compound.

Table 2.2 Material used and their supply source

<table>
<thead>
<tr>
<th>Material</th>
<th>Purity</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium (Cd)</td>
<td>99.999% Pure</td>
<td>Alfa Aesar, U.K.</td>
</tr>
<tr>
<td>Sulfide (S)</td>
<td>99.999% Pure</td>
<td>Alfa Aesar, U.K.</td>
</tr>
</tbody>
</table>

Figure 2.5: The temperature profile used for the growth CdS seeds by (DVT).
2.7.2 Crystal Growth

The sealed ampoule containing stoichiometric mixture of a fine charge form was placed in the two zone horizontal furnace and the temperatures of both the zones were raised slowly for reaction between elements. The typical temperature profile used in the present investigation is shown in figure 2.6. Where, the temperatures of both the zones were raised to 700 °C at the rate of 10 °C per hour. The furnace was left at this temperature for 24 hours to ensure the reaction. Afterwards, the temperatures of both the zones were raised to 980 °C at the rate of 10 °C per hour. The ampoule was left at this temperature for 24 hours. Thereafter, the temperature of the growth zone was lowered down to 930 °C at the rate of 5 °C per hour. Thereby setting a temperature difference of 50 °C between the growth and the source zones. Later on, the growth zone temperature was again brought back to 980 °C at the rate of 5 °C per hour.

Figure 2.6: (a) Placement of the ampoule in the furnace; (b) the temperature profile used for the growth of CdS by (DVT).
Such oscillations of temperature were carried out thrice with a gap of 12 hours between each cycle. The temperature oscillation method preferentially evaporates small nuclei and allows large crystals to grow at the expense of smaller ones. Such oscillation cycles were adopted for the growth of some semiconducting materials [82]. After these oscillations, the temperature of the growth zone and the source zone were set to 930 °C and 980 °C respectively. The furnace was left with this temperature distribution for about 168 hours. Then, both the zones were slowly cooled down to room temperature with rate of 10 °C/hour.

**Table 2.3:** Growth parameters for grown crystals.

<table>
<thead>
<tr>
<th>The quantity</th>
<th>Temperature distribution (°C)</th>
<th>Transport growth time (hrs)</th>
<th>Crystals obtained (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS (15gm)</td>
<td>Source Zone: 1000</td>
<td>Growth Zone: 930</td>
<td>312</td>
</tr>
<tr>
<td>CdS (10gm)</td>
<td>Source Zone: 980</td>
<td>Growth Zone: 930</td>
<td>168</td>
</tr>
</tbody>
</table>

The growth parameters such as temperature distribution, growths period etc used for the growth of CdS have been given in table 2.3. Once the temperatures of both the zones are come down to the room temperature, the furnace was switched off. The ampoule was carefully taken out of the furnace. It was seen that in the growth zone, the material was sublimed and deposited at the coldest part of the employee. The quality of the grown crystals was found to be good. This could be due to the stability of the flow of the materials transported from the source to the growth zone by using such a growth program as mentioned here.

The grown CdS crystals were orange and brown in color, transparent and their habits were mostly regular and irregular shaped of crystals platelet with dendrite on its surface. The grown crystals were carefully taken out by breaking the ampoule. The crystal dimensions of CdS grown in this manner were of (3 × 12) mm² and a few micrometers thick. Figure 2.7 shows some of as grown CdS crystals.
Figure 2.7: Photograph of as grown CdS crystals by DVT technique.
2.8 Chemical Composition Analysis of Grown CdS Using EDAX

Energy Dispersive X-Ray Analysis (EDX), referred to as EDS or EDAX, is an X-ray technique used for identification of chemical composition of materials. Applications include materials and product research, troubleshooting. The data generated by EDX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the sample being analyzed. This technique detects the X-rays produced as the result of the electron beam interactions with the sample. Mapping of the distribution of the different chemical elements constituting the specimen can be obtained. X-ray data are processed to obtain the percentage of each measured element present in the individual particles. Most scanning / transmission electron microscopes and electron microprobes are equipped with energy dispersive spectrometer (EDS) facilities. The EDS system is capable of identifying elements with atomic number (Z) ≥ 11 in a few minutes.

The EDAX technique detects X-rays emitted from the sample during bombardment by an electron beam to characterize the elemental composition of the analyzed volume. This technique generates a spectrum in which the peaks correspond to specific X-ray lines and the elements can be easily identified. Quantitative data can also be obtained by comparing peak heights or areas in the unknown with a standard material. Data collection and analysis with EDAX is a relatively quick and simple process because the complete spectrum of energies is acquired simultaneously.

When a beam of electrons strikes the sample specimen, a fraction of the incident electrons excites the atoms in the sample. This, in turn, emits the characteristic X-rays in the process of returning to the ground state. The EDS detector collects the entire X-ray spectrum and a multichannel analyzer where the pulses are sorted by voltage. The energy of these X-rays is strictly related to the atomic number of the elements that have got excited, while the intensity of X-rays is related to the concentration of elements in the sample. The energy, as determined from the voltage measurement, for each incident X-ray is sent to a computer for display and further data evaluation. The spectrum of X-ray energy versus counts is evaluated to determine the elemental composition of the sampled volume. Figure 2.8 shows an experimental arrangement of EDAX attached to SEM (Model: Phillips, Model: XL 30 ESEM) at Sophisticated Instrumentation Center for Applied Research and Testing (SICART), Vallabh Vidyanagar used in experiment study. An EDAX system
comprises four basic components that must be designed to work together to achieve optimum results: the beam source, the X-ray detector, the pulse processor and the analyzer. X-ray detector measures the relative abundance of emitted X-rays versus their energy. The detector is typically lithium-doped silicon, a solid state surface barrier device.

![Figure 2.8: Experimental setup of energy dispersive analysis of X-rays (EDAX).](image)

❖ **Specifications:**

- Emission current: 0 to 200 μA
- Accelerating Voltage: 0.2 to 30 KV
- Resolution: With LaB6 filament 2nm at 30 KV, With W filament 3.5nm at 30 KV
- Magnification: 10x to 400000x or higher
- Automatic scaled micron marker
- Eucentric goniometer stage
- Specimen movement: X=50mm, Y=50mm
- Rotation: n x 360 degrees
- Z movement: 25mm internal & external
- Secondary and back scattered electron detectors
2.8.1 Results and Discussions

The energy dispersive spectra for determining the chemical composition of the grown crystals are shown in figures 2.9 (a, b). The results obtained for CdS charge form as well as crystal form is shown in table 2.4.

![EDAX spectra of CdS crystals grown by DVT technique.](image)

From the results of energy dispersive analysis of X-ray confirms that the chemical composition in both charge and crystal forms are stoichiometrically good agreement with the calculated data. A spectrum of EDAX reveals that there is no presence of any extra impurity. So it is free from the other impurities. This analysis shows the proportion of the constituent elements and its comparison with starting elements used in stoichiometric proportion which is given in table 2.4. This
comparison shows that there is a slight excess of cadmium occurred due to nucleation process.

**Table 2.4:** Chemical composition (wt. %) of CdS crystals grown by DVT technique.

<table>
<thead>
<tr>
<th>Stoichiometric proportion Wt (%)</th>
<th>Cd</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt % of elements Calculated</td>
<td>77.80</td>
<td>22.19</td>
</tr>
<tr>
<td>Obtained from EDAX for</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CdS charge form</td>
<td>78.63</td>
<td>21.37</td>
</tr>
<tr>
<td>Obtained from EDAX for</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CdS crystal form</td>
<td>78.06</td>
<td>21.94</td>
</tr>
</tbody>
</table>

### 2.9 Structural Characterization of DVT Grown CdS

It is always important to characterize and evaluate the properties and behavior of the grown crystals. In this section, structural characterization of CdS crystals includes X-ray diffraction (XRD) and transmission electron microscopy (TEM) were carried out using these characterization tools, very useful information related to the crystal structure, morphology, chemical composition and size of crystals is obtained.

#### 2.9.1 X-Ray Diffraction (XRD)

X-ray diffraction is a versatile, non-destructive analytical technique for identification and quantitative determination of the various crystalline forms of compounds present in powdered and solid samples, including lattice constant and geometry, preferred orientation of polycrystals, defects, etc. X-rays can interact with a solid in several ways; they can be absorbed, emitted, reflected or transmitted.

In the case of diffraction of rays from a periodic structure, the diffraction peaks can give us much valuable information about the crystal structure. X-rays primarily interact with electrons in atoms. When X-ray radiations collide with electrons, the X-rays are scattered “diffracted” by electrons present in the material. Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic structure, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern therefore allows us to deduce the distribution of atoms in a material.
The peaks in an X-ray diffraction pattern are directly related to the atomic distances. In order to make use of this technique, the material must be composed of regularly spaced atoms acting as scattering centers for X-rays. Another condition required to be satisfied is that the wavelength of the X-rays and the space between atoms must be in the same order. The conditions of diffraction are as follow [83].

i. The angle made by the diffracting planes (h k l) with the incident and diffracted beams are equal.

ii. The directions of the incident and diffracted beams and the normal to the diffracting planes are coplanar.

iii. The waves emitted by individual atoms in the direction of diffracted beams are in phase.

The diffraction condition is given by Bragg's law,

\[ n\lambda = 2d \sin \theta \]  

Derived by the English physicist W. H. Bragg and his son W. L. Bragg in 1933 so as to explain why the X-ray beam reflects at certain angle of incidence (\( \theta \)). \( n \) is the order of the diffracted beam and is numerically equal to the path difference in wavelengths for successive planes, \( d \) is the interplanar spacing of the diffracting planes and \( \lambda \) is the wavelength of incident X-rays. \( \theta \), the Bragg's angle, is the angle between the incident X-rays and diffracting planes. The Bragg's law is one of the most important laws used for interpreting X-ray diffraction data.

Let us consider an incident X-ray beam interacting with the atoms arranged in a periodic manner as shown in two dimensions in figure 2.10 [84]. The atoms, represented as spheres in the graph, can be viewed as forming different sets of planes in the crystal (lines).
2.9.1.1 Powder Method (Debye and Scherrer Method)

X-ray Powder Diffraction is a non-destructive technique widely applied for the characterization of crystalline materials [83, 85-87]. The Powder method was developed by Debye and Scherrer in Germany and by Hill in America simultaneously. This method is used to study the structure of the crystals which cannot be obtained in the form of perfect crystals of appreciable size. Therefore, the sample used is in the form of a fine powder containing a large number of tiny crystallites with random orientations. To obtain X-ray diffraction data, the diffraction angles of the various cones, 2θ, must be determined. The main techniques are: Debye-Scherrer camera (photographic film) or powder diffractometer.

In practice, this would be a time consuming operation to reorient the crystal, measure the angle θ, and determine the d-spacing of all atomic planes. A faster way is to use a method called the powder method. In this method, a mineral is ground up to a fine powder. In the powder, are thousands of grains that have

---

**Figure 2.10:** Bragg's law and schematic representation of constructive interference between X-Rays.
random orientations. With random orientations, we might expect most of the different atomic planes to lie parallel to the surface in some of the grains. Thus, by scanning through an angle 0 of incident X-ray beams form 0 to 90°, we would expect to find all angles where diffraction has occurred, and each of these angles would be associated with a different atomic spacing. X-ray diffractometer (figure 2.11) consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. The instrument used to do this is an X-ray powder diffractometer. It consists of an X-ray tube capable of producing a beam of monochromatic X-rays that can be rotated to produce angles from 0 to 90°. A powdered mineral sample is placed on a sample stage so that it can be irradiated by the X-ray tube. To detect the diffracted X-rays, an electronic detector is placed on the other side of the sample from the X-ray tube, and it too is allowed to rotate to produce angles from 0 to 90°. As the sample is rotated, the count rates will reflect the flux of diffracted X-ray photons for that orientation.

When the geometry of the incident X-rays impinging the sample satisfies the Bragg equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate, which is then output to a device such as a printer or computer monitor [83, 88-90]. Strong peaks are expected when the Bragg condition is satisfied. After a scan of the sample the X-ray intensity can be plotted against the angle θ (usually reported as 2θ because of the way older diffractometers were made) to produce a chart, like the one shown here. The angle 2θ for each diffraction peak can then be converted to d-spacing, using the Bragg equation. The instrument used to rotate both the X-ray tube and the detector is called a goniometer. The goniometer keeps track of the angle θ, and sends this information to a computer, while the detector records the rate of X-rays coming out the other side of the sample (in units of counts/sec) and sends this information to the computer.
Figure 2.11: (a) Schematic of X-ray diffractometer; (b) ‘X’PERT MPD’ Powder Diffractometer.

- **Essential Parts of the Diffractometer**:
  - X-ray Tube: the source of X Rays
  - The goniometer: the platform that holds and moves the sample, optics, detector.
  - The sample & sample holder.
  - Software: JCPDF database for powder diffractometry
  - Detector: Xe-filled Counterate or Proportional detector
  - Diffractometer radius: 130 to 230 mm
  - 2θ° Measurement range: 3o to 136o
  - Accuracy:±0.002
Since every compound with the same crystal structure will produce an identical powder diffraction pattern, the pattern serves as a kind of a "fingerprint" for the substance, and thus comparing an unknown mineral to those in the Powder Diffraction file known as the Joint Committee on Powder Diffraction Standards (JCPDS) enables easy identification of the unknown.

In the present study, we have used this technique. The crystals are reduced to a very fine powder and it is exposed to a beam of monochromatic X-rays. For every set of crystal planes, by chance, one or more crystal will be in the correct orientation to give the correct Bragg angle in order to satisfy Bragg's relation. Hence, every crystal plane is capable of diffraction. Using the powder method, we can determine the unknown structure by finding the structural parameters such as interatomic spacing $d$ for each peak and considering relative intensities matched with known components.

### 2.9.1.2 Specimen Preparation for XRD

In order to record the X-ray pattern of the charge and crystal samples, synthesized product was crushed homogeneously with the help of mortar and pestle. The pulverized samples were filled in a specially designed quartz sample holder for XRD measurements. Generally, All peaks found in the Powder Diffraction File (PDF) pattern must also be seen in in the diffractogram, otherwise it is not a valid match. In the present analysis, 20 and 21 sharp peaks are detected at varying intensities for CdS charge and crystal form respectively. Therefore, a lot of aspects need detailed explanations in particular with the sample preparation where must be taken into account, whether the specimen is pulverized or they used the as-grown crystals for XRD measurements. Here, will be listed some of the specific advantages and Possible exceptions below:

1. An ideal powder sample should have many crystallites in random orientations.
2. If there are enough crystals, it will get enough diffraction to determine the material.
3. If the crystallites in a sample are very large, there will not be a smooth distribution of crystal orientations. You will not get a powder average diffraction pattern, it means crystallites should be <10mm in size to get good powder statistics.
4. If the crystallites in a powder sample have a plate or needle like shapes it can be very difficult to get them to adopt random orientations.

5. Large crystallite sizes and non-random crystalline orientations, both lead to peak intensity variation, so the measured diffraction pattern will not agree with that expected from an ideal powder and the measured diffraction pattern will not agree with reference patterns in the Powder Diffraction File (PDF) database.

6. Top-loading, where you press the powder into a holder can cause problems with preferred orientation.

7. In samples such as metal sheets or wires, there is almost always preferred orientation due to the manufacturing process.

8. Small peaks may be no detectable if the noise level is too high.

9. Missing peaks may be the result of a very strong preferred orientation effect, if this is the case; the relative intensities in general are changed and show a systematic dependence from $hkl$.

10. Missing peaks may be the result of anisotropic disorder, if this is the case, the FWHM of the peaks should show a systematic dependence from $hkl$ (some reflections become so broad and low that they are not recognized anymore).

### 2.9.1.3 Phase Identification and Lattice Parameters Determination

To identify a particular phase, both peak positions and relative intensities must fit. The X-ray diffractogram (XRD) of the grown materials were obtained using the Philips X’ Pert MPD diffractometer of Cu-Kα wavelength (1.5405Å) to verify the crystallinity of the compounds within the range of 3-100°. The typical X-ray diffractogram with indexing using Powder X” obtained are shown in figure 2.12 for CdS charge and crystal form contains 20 and 21 sharp peaks respectively for varying intensities (given in table 2.5).

All peaks associated to each specimen possess hexagonal (wurtzite); furthermore, the analytical indexing of the pattern thus obtained was done to calculate the lattice parameters for hexagonal (wurtzite) structure. It is evident from the diffractograms that for each grown CdS form, (110) reflections are of maximum intensity indicates the most preferred orientation of the crystal grains. The interplaner distance ‘d’, relative intensities, peak width and angle 2θ corresponding to different hkl planes were calculated from the respective diffractograms and are recorded in...
which agrees with JCPDS cards for CdS [91,92]. On the other hand, as we observed needles shape in the initial stage of grown, probably the (0 0 2) preferred orientation could be seen in the diffraction pattern in case of used as-grown crystal. Therefore supports their suggestion of some grown of needles which will be seen by SEM in chapter 3. But by using the pulverized of crystals for XRD measurement, indeed the (0 0 2) preferential growth could not be observed. In general, the X-ray diffraction data indicate that growth in intensity of the peaks is related to improvement in the crystallinity.

From figure 2.12, it’s clearly observed that a more intense and sharp of peaks appears in CdS crystal grown from the charge form possess 21 peaks generated by XRD signals, which indicates an improvement in the crystallinity of CdS crystal. Generally, in X-ray diffraction, the main reasons of deviations in peak positions are presented of substitutional impurities and thermal expansion but as verify sample's composition which does not have any extra impurities (ref. section 2.8.1). Therefore, in the present analysis, a reason of some deviations in peak positions is the thermal expansion.

The analytical indexing of the pattern, thus obtained, was done to calculate the lattice parameters for the hexagonal structures. The results obtained for ‘a’ and ‘b’ and the unit cell volume has been calculated with the help of the equation 2.2, are given in table 2.6. The calculated values are in good agreement with that reported in the JCPDS - X-ray powder diffraction database and other workers [77, 91-93]. From this analysis, it is found that the effect of the growth process in lattice parameters and the unit cell volume is more remarkable in comparison to the parameters calculated in CdS crystals and reported by JCPDF file.

The lattice parameters and the unit cell volume values for CdS crystals are revealed that the improvement of the values in comparison with the charge form to be near the reported by JCPDS file.

\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad 2.2
\]

\[
V = \frac{\sqrt{3}}{2} a^2 c \quad 2.3
\]
Figure 2.12: X-ray diffractogram of CdS charge and crystals grown.
Table 2.5: Comparison of observed data for CdS charge and crystals with JCPDS data sheet.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Standard Values</th>
<th>CdS charge</th>
<th>CdS crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2θ (h k l)</td>
<td>d-spacing (Å)</td>
<td>2θ (h k l)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>(1 0 0)</td>
<td>3.583</td>
<td>24.79 (1 0 0)</td>
</tr>
<tr>
<td>2</td>
<td>(0 0 2)</td>
<td>3.367</td>
<td>26.70 (0 0 2)</td>
</tr>
<tr>
<td>3</td>
<td>(1 0 1)</td>
<td>3.160</td>
<td>28.20 (1 0 1)</td>
</tr>
<tr>
<td>4</td>
<td>(1 0 2)</td>
<td>2.450</td>
<td>36.80 (1 0 2)</td>
</tr>
<tr>
<td>5</td>
<td>(1 1 0)</td>
<td>2.068</td>
<td>43.84 (1 1 0)</td>
</tr>
<tr>
<td>6</td>
<td>(1 0 3)</td>
<td>1.898</td>
<td>47.98 (1 0 3)</td>
</tr>
<tr>
<td>7</td>
<td>(2 0 0)</td>
<td>1.791</td>
<td>51.04 (2 0 0)</td>
</tr>
<tr>
<td>8</td>
<td>(1 1 2)</td>
<td>1.761</td>
<td>52.01 (1 1 2)</td>
</tr>
<tr>
<td>9</td>
<td>(2 0 1)</td>
<td>1.731</td>
<td>53.0 (2 0 1)</td>
</tr>
<tr>
<td>10</td>
<td>(0 0 4)</td>
<td>1.679</td>
<td>----</td>
</tr>
<tr>
<td>11</td>
<td>(2 0 2)</td>
<td>1.581</td>
<td>58.39 (2 0 2)</td>
</tr>
<tr>
<td>12</td>
<td>(1 0 4)</td>
<td>1.520</td>
<td>----</td>
</tr>
<tr>
<td>13</td>
<td>(2 0 3)</td>
<td>1.398</td>
<td>66.89 (2 0 3)</td>
</tr>
<tr>
<td>14</td>
<td>(2 1 0)</td>
<td>1.354</td>
<td>69.52 (2 1 0)</td>
</tr>
<tr>
<td>15</td>
<td>(2 1 1)</td>
<td>1.327</td>
<td>71.10 (2 1 1)</td>
</tr>
<tr>
<td>16</td>
<td>(1 1 4)</td>
<td>1.303</td>
<td>72.54 (1 1 4)</td>
</tr>
<tr>
<td>17</td>
<td>(1 0 5)</td>
<td>1.257</td>
<td>75.64 (1 0 5)</td>
</tr>
<tr>
<td>18</td>
<td>(3 0 0)</td>
<td>1.194</td>
<td>80.48 (3 0 0)</td>
</tr>
<tr>
<td>19</td>
<td>(2 1 3)</td>
<td>1.159</td>
<td>83.34 (2 1 3)</td>
</tr>
<tr>
<td>20</td>
<td>(3 0 2)</td>
<td>1.12</td>
<td>86.54 (3 0 2)</td>
</tr>
<tr>
<td>21</td>
<td>(2 0 5)</td>
<td>1.074</td>
<td>91.79 (2 0 5)</td>
</tr>
<tr>
<td>22</td>
<td>(2 2 0)</td>
<td>1.034</td>
<td>96.46 (2 2 0)</td>
</tr>
</tbody>
</table>
Table 2.6: The calculated and reported lattice parameters, unit cell volume for CdS charge and crystals.

<table>
<thead>
<tr>
<th></th>
<th>a = b (Å)</th>
<th>c (Å)</th>
<th>Cell Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reported (JCPDS)</td>
<td>4.136</td>
<td>6.713</td>
<td>99.450</td>
</tr>
<tr>
<td>CdS charge</td>
<td>4.102</td>
<td>6.674</td>
<td>97.266</td>
</tr>
<tr>
<td>CdS crystal</td>
<td>4.125</td>
<td>6.720</td>
<td>98.955</td>
</tr>
</tbody>
</table>

2.9.1.4 Grain Size Determination

Crystallite (grain) Size and micro-strain can be indicated by peak broadening, while the other defects (stacking faults, etc.) can be measured by analysis of peak shapes and peak width. Currently, to obtain an idea about the grain size distribution in our grown crystals, the grain size \( t \) for each sample has been determined, using the Scherrer formula [83].

\[
\theta = \frac{k \lambda}{\beta_{2\theta} \cos \theta}
\]

Where, \( k \) is the geometrical factor arising from the shape of the grain. Here, we assume that each grain possesses spherical symmetry; \( \lambda \) is the wavelength of incident radiation (\( \lambda = 1.54056 \) Å), \( \beta \) is full width at half maximum intensity measured in radians (FWHM) and \( \theta \) is the Bragg angle that is the angle between the incident and the scattered X-ray.

2.9.1.5 Strain and Dislocation Density Determination

Lattice strain (micro-strain) is caused by lattice defects like dislocations, vacancies, interstitials, substitutionals, etc. These defects lead to displacements of atoms from their sites in the idealized crystal structure, thus causing a variation in the lattice plane d-spacings. Since there is a possibility for the generation of strain among the grains. Therefore, Scherer’s formula is again used to calculate the amount of micro-strain (\( \varepsilon \)) among the grains by [83, 94]:

\[
\varepsilon = \frac{\beta_{2\theta} \cos \theta}{4} \tan \theta
\]

Where all the notations are same as mentioned above.

The peak broadening due to strain is assumed to have the following dependence:

\[
\beta = 4 \times \varepsilon_0 \times \tan \theta
\]

2.9
The value of the dislocation density ($\delta$) which is related to the number of
defects in the grown crystals was calculated from the average values of the grain size
$r$ by the relationship [95-97],

$$\delta = \frac{1}{t^2}$$

Where, $r$ is the average grain size.

The average grain size ($t$), micro strain ($\varepsilon$) and dislocation density ($\rho$) for CdS
charge and grown crystals are given in comparison table 2.7.

However, above mentioned method for determining the grain size and micro-
strain is valid only when the interfacial stress contributes. However, in those cases
where both interfacial stress and particle size lead to broadening of the diffraction
peaks, a more comprehensive method must be used to look into their contributions.
The most common method used to determine grain size and accompanying micro-
strain in such cases is Hall- Williamson method [98].

A shift in the peak of XRD profile arises due to the presence of micro-strains
in the growth crystals resulting of thermal expansion [99]. However, at the same time
line broadening might also be observed. It is commonly accepted that XRD line
broadening may be the result of pure size, or micro-strain, or both size and micro-
strain broadening [100]Hall [101] Hall and Williamson [102]and Williamson and Hall
[98] have suggested a method combining both the domain size and lattice micro-strain
effects on line broadening. It permits the separation of these contributions to this
broadening. This method or its modification [103] has been widely used in bulk
WH approach considers the case when the grain effect and lattice deformation are
both simultaneously operative, and their combined effects give the final line
broadening ($\beta_{2\theta}$), given as the sum,

$$\beta_{2\theta} (\text{grain size}) + \beta_{2\theta} (\text{Lattice distortion})$$

This relation assumes a negligibly small instrumental contribution compared
to the sample-dependent broadening. Equation 2.7 may be expressed in the form,

$$\frac{\beta_{2\theta} \cos\theta}{\lambda} = \frac{1}{<t^2>} + \frac{4\varepsilon \sin\theta}{\lambda}$$

Where $<t>$ is the average grain size, $\varepsilon$ is the micro-strain. From a plot of $\beta_{2\theta}\cos\theta/\lambda$
vs. $4\sin\theta/\lambda$, one can evaluate the contribution of micro-strain and grain size to the
XRD line broadening. The intercept of the plot 2.13 (a, b) with the ordinate (the values are expressed in radians) represents the reciprocal of the average grain size, and, from the slope of the line, \( \varepsilon \) can be obtained, which is related to the micro-strains present in the CdS grown crystals.

In present case average grain size and average micro-strain has been calculated using both methods (Scherer's method and WH method) and the results are given in table 2.7. From table 2.7, it can be seen that the improvement of grain size of crystals in comparison with the charge form whereas the strain and dislocation density decreased.

**Figure 2.13:** Hall Williamson plots for CdS (a) in charge form; (b) crystal form.
Table 2.7: XRD results of grain size, micro-strain and dislocation density calculated for CdS grown crystals.

<table>
<thead>
<tr>
<th>Crystalline phase</th>
<th>Grain Size (nm)</th>
<th>Micro strain (m$^{-2}$) $\times 10^{-4}$</th>
<th>Dislocation Density (m$^{-2}$) $\times 10^{+15}$</th>
<th>Grain Size (nm)</th>
<th>Micro strain (m$^{-2}$) $\times 10^{-3}$</th>
<th>Dislocation Density (m$^{-2}$) $\times 10^{+15}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS charge</td>
<td>283</td>
<td>0.14</td>
<td>1.37</td>
<td>286</td>
<td>0.13</td>
<td>1.22</td>
</tr>
<tr>
<td>CdS crystal</td>
<td>296</td>
<td>0.13</td>
<td>1.23</td>
<td>303</td>
<td>0.11</td>
<td>1.10</td>
</tr>
</tbody>
</table>

2.9.1.6 Estimation of Growth and Deformation Fault Probabilities

Perfect crystalline structure is an ideal concept since perfect crystals are neither available in nature nor can be grown in the laboratory. Several types of defects are always present in crystal, e.g. point defects, stacking fault, etc. The study of stacking fault is very important because it plays a fundamental role in the description of defects. Warren [110] and Agarwal et.al. [111, 112] have shown that in case of hexagonal close packed metals, it is possible to make a realistic estimation of the deformation fault probability ‘$\alpha$’ and the growth fault probability ‘$\beta$’ by measuring the half width of X-ray diffraction lines. Reflections having h-k=3n, where ‘n’ is an integer, are independent of stacking faults, whereas reflections having h-k=3n ± 1 and $l \neq 0$ depend upon the stacking faults in the crystal structure. An estimation of the deformation and growth fault probability can be obtained from the (hkl) values using following formula [113,114].

$$(3\alpha + 3\beta) = \frac{\beta_{2\theta} \times x^2 \times c^2}{360 \times d^2 \times \tan \theta}$$

for ‘$l$’ even

$$(3\alpha + \beta) = \frac{\beta_{2\theta} \times x^2 \times c^2}{360 \times d^2 \times \tan \theta}$$

for ‘$l$’ odd

Where ‘$\beta_{2\theta}$’ is the full width at half maximum intensity expressed in degrees, $c=2d_{002}$, ‘$l$’ is the Miller index in the (h k l) plane, $\alpha$ and $\beta$ are the deformation fault probability and the growth fault probabilities respectively. $d$ is the interplaner spacing between two (h k l) planes, $\theta$ is the Bragg’s angle corresponding to this (h k l) plane. Thus, from equation 2.10 and 2.11, the stacking fault probabilities, i.e. deformation fault probability ($\alpha$) and growth fault probability ($\beta$) for the two samples of CdS have been estimated and the resultant values are given in table 2.8. The values of the both probabilities, i.e. $\alpha$ and $\beta$ are nearly of the same order of values. The value of $\alpha$
presented in table 2.8 clearly indicated that a low density of deformation faults was introduced into the specimen and the actual number depends upon the amount of deformation introduced into the sample during an experiment.

The opposite sign of probability ($\beta$) indicated that the created stacking fault is an intrinsic type in CdS [115], because existence of stacking fault leads to a localization of electron states.

The calculations of the stacking faults may be considered as one of the guidelines for further detailed study of defects and various properties of crystals. Whatever, the increment in deformation fault probability ($\alpha$) with respect to the sample form and the decrement in growth fault probability ($\beta$) that is an insignificant variation, where it does not represent any contraindications for the improvement in crystal surface and structure.

**Table 2.8:** Deformation and growth fault probabilities for 1000 atomic layers in CdS crystals.

<table>
<thead>
<tr>
<th>Sample form</th>
<th>Deformation Fault ($\alpha$)</th>
<th>Growth Fault ($\beta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS charge</td>
<td>9.87</td>
<td>1.41</td>
</tr>
<tr>
<td>CdS crystal</td>
<td>11</td>
<td>-0.71</td>
</tr>
</tbody>
</table>

### 2.9.2 Transmission Electron Microscopy (TEM)

In this form of microscopy, a beam of electrons transmits through an extremely thin specimen, and then interacts with the specimen when passing through it [116]. The sample must be thin enough to transmit sufficient electrons such that enough intensity falls on the screen to give an image. Before knowing the detailed working principles of a TEM it is a pre-requisite to have basic knowledge of the electron-matter interactions. Electron microscopy is not just a single technique, but a diversity of electron-matter interactions with unique properties are used to gain insight in structure, morphology and chemical composition, where the latter is obtained via spectroscopic techniques.

Unlike electromagnetic radiation-object interaction, interaction of electrons with matter is much stronger because of the electrostatic (Coulomb) interaction between the incident electrons and the atoms in the matter. As a result, numerous elastic and inelastic scattering events occur. Figure 2.14 shows the products of
electron beam specimen interaction for fast electrons traveling through matter. Elastic scattering arises from interactions of incident electrons with the electrostatic potential of the atom (the result of Coulomb interaction between electron-electron and electron-nuclei) and provides the most important contribution to the contrast in (S)TEM images. Elastically scattered electrons suffer virtually no energy loss.

Interaction of incoming electrons with the electrons of the atom results in inelastic scattering of the incident electrons. Inelastically scattered electrons, on the other hand, lose energy and become concentrated within smaller scattering angles. Any event between the electron beam and matter results in a loss of energy, and/or a change in momentum of the incident beam electrons must produce an equivalent amount of energy in some other form. There are numerous forms of energy phenomena produced during electron beam–matter interaction, and all of these have the potential to provide important information about the nature of the specimen. The inelastic events may result from many electron–matter interactions, e.g. phonon excitations, plasmon excitations, intraband and interband excitations, ionization of inner shell electrons, and Bremsstrahlung. Among all these inelastic events listed above, ionization of inner-shell electrons is the most important one because the produced signals directly reflect the chemical state of the analyzed specimen. This occurs when a primary electron beam has enough energy to "knock out" an electron from one of the tightly bonded inner atomic shells.

Figure 2.14: Schematic representation of the signals generated when a high energy electron beam is incident on a thin specimen.
An atom that loses its inner-shell electron, usually called an ionized atom, is highly unstable. The empty state will then be filled by an electron from one of the outer shells. The atom is relaxed by emitting X-rays with corresponding energy. As the energies of the emitted X-rays will be different for each element, they are called characteristic X-rays and thus can be used to determine atomic species in the analyzed volume [117]. The electron column (figure 2.15(b)) consists of an electron gun and set of five or more electromagnetic lenses operating in vacuum. It is convenient to divide up the TEM into three components: the illumination system, the objective lens/stage, and the imaging system.

The illumination system comprises the gun and the condenser lenses and its role is to take the electrons from the source and transfer them to the specimen. The electron beam is accelerated to energy in the range 20 - 1000 keV in the electron gun then the electron beam passes though set of condenser lenses in order to produce a beam of electrons with a desired diameter. The illumination system can be operated in two principal modes: parallel beam and convergent beam. The first mode is used primarily for TEM imaging and selected-area diffraction (SAD), while the second is used mainly for scanning (STEM) imaging, analysis via X-ray and electron spectrometry, and convergent beam electron diffraction.

The objective lens and the specimen holder/stage system is the heart of the TEM. Here is where all of the beam-specimen interactions take place and the two fundamental TEM operations occur, namely, the creation of the various images and diffraction patterns (DP) that are subsequently magnified for viewing and recording.

The imaging system uses several lenses to magnify the image or the DP produced by the objective lens and to focus these on the viewing screen or computer display via a detector, CCD, or TV camera. Images are recorded on a conventional film positioned either below or above the fluorescent screen or digital capture can be utilized using CCD or TV cameras.

The lenses are the crucial components in the electron microscope, which allow us to utilize the electron beam in either forming images in the TEM or focusing the beam in a spot. Electron lenses are situated beyond the electron gun(figure 2.15(b)). In TEM the function of the lenses is to transform a point in an object to a point in an image and to focus parallel rays to a point in the focal plane of the lens. Electrons can be focused either by electrostatic or magnetic field. Most electron microscopes employ electromagnetic lenses. Regardless of their nature electrostatic, magnetic or
electromagnetic electron lenses are notoriously poor lenses compared to visible light lenses, where most aberrations can be corrected whereas in electron lenses they cannot be corrected.

The practical resolution of a TEM normally depends on the accelerating voltage and the design of the objective lens. The performance of electron lenses is relatively much poorer than optical lenses because of the aberrations in the electron lens system. Williams and Carter in their book compared the electron lenses to the quality obtained from the bottom of the Coca Cola bottle [118]. In reality perfect lenses for TEM are not produced. The most common defect in the lenses is chromatic and spherical aberration. These aberrations are not allowing the electrons to focus in a single focal point. In the case of spherical aberration, the electrons originating from a point source and scattered/diffracted further away from the optic axis (i.e. coming closer to the electromagnetic pole pieces) are focused more strongly back to the optic axis, compared to the electrons closer to the optic axis. This creates a series of focal points rather than a single finite focal point and results in broadening of an original point into a point-spread disk in the image plane.

Compared to an exact in-focus image the size of the point-spread disk can be reduced (by a factor of two) to its minimum size by taking an image at an optimum under focus. In that case the point-spread disk is called the disk of minimum confusion. The positive value of the spherical aberration constant (Cs) is the key factor limiting the resolution in high resolution TEM imaging. Although somewhat less important than Cs for TEM imaging, the other important aberration is chromatic aberration (Cc). The electron beam generated from an electron source has a certain energy spread. Electrons having different energies at the same location in the column will experience different forces. An electromagnetic lens will bend and focus the electrons of lower energy more strongly than those of higher energy. Recently both Cs and Cc corrected microscopes have become available commercially, which will open up a new era for TEM research.
The TEM sample is placed in front of the objective lens in a form of thin foil, thin section, or fine particles transparent for the electron beam. The objective lens forms an image of the electron density distribution at the exit surface of the specimen based on the electron optical principles. A diffraction pattern is formed in the back focal plane of the objective lens and the recombination of the diffracted beams forms an image in the image plane of the objective lens. The diffraction, projection, and intermediate lenses below the objective lens are used to focus and magnify either the diffraction pattern or the image onto a fluorescent screen, which converts the electrons into visible light signal figure 2.16.

The transmission electron microscope may be operated to produce either a diffraction pattern from a specific region of the specimen or one of several types of images, where quantitative information about the microstructure of the material is required, and a detailed correlation is made between the diffraction pattern and the image. The essential features of the diffraction and image modes of operation can be
explained in terms of a geometric optics treatment of the situation at the objective lens. Figure 2.16 shows the comparison of the lens conditions between TEM diffraction and TEM imaging modes. Those two modes are the basic modes in TEM operations. The difference between the two modes may only be the strength of the intermediate lens. The action of forming the image brings both the transmitted and the diffracted beam to a focus in the back focal plane of the objective lens. Thus a diffraction pattern is produced here. Because both a diffraction pattern and an image of the specimen are always produced by the objective lens, a magnified image of either may be produced on the viewing screen by focusing the next lens in the magnification system on one or the other. When we focus the diffraction lens at the image plane of the objective lens and introduce an aperture in the back focal plane of the objective lens an image of the sample is produced on the screen. The differential scattering and absorption of electrons creates intensity variations at the exit surface of the sample and these variations are magnified and imaged on the fluorescent screen by the lens system. In addition to formation of electron diffraction patterns there are three important mechanisms, which produce image contrast in the electron microscope: mass-thickness contrast, phase contrast, and diffraction or amplitude contrast.

To study the electron diffraction pattern of CdS sample, Philips – Technai 20 electron microscope shown in figure (2.15(a)) is used which is housed in Sophisticated Instrumentation Centre for Applied Research and Testing (SICART) – Vallabh Vidyanagar. In this microscope, Tungsten (LaB6) filament is used as an emitter of electrons. The accelerating voltage is 200 KV. The point resolution and line resolution of this microscope is better than 0.27 nm and 2 nm respectively with magnifications of 25 X to 750000 X. The produced image or diffraction patterns are recorded with inbuilt CCD camera [117].
2.9.2.1 Specimen Preparation for TEM

Specimen preparation for TEM investigations is a crucial and complex task. It involves many steps before bringing the specimen down to the thickness of electron transparency, typically 100 nm or smaller. This is achieved by conventional technique involving cutting, grinding, polishing, dimpling and ion milling as described below. Most often the quality of the image is determined by the quality of the prepared specimen and not directly limited by the resolution of TEM itself. Necessary care is required at each step during preparation in order to avoid artifacts due to polishing and ion milling. There is a fair chance of creating defects at the atomic scales in the samples during the various stages of specimen preparation. Threading and/or misfit dislocations can be produced during the grinding and ion milling stages of specimen preparation. It is not always necessary that the defects are imbedded in the sample itself. The ion milling can produce heat up to 100 °C. Specimen preparation for TEM is an art, at the same time technical skills alone are not enough for good specimen preparation.
preparation; one should have basic knowledge about the material and the preparation process may vary depending on the properties and nature of the specimen. Different methods are applied for different materials such as metals, ceramics, polymers, powder samples, thin films, bulk specimens etc. [118, 120].

2.9.2.2 Results and Discussions

In the present study, we have been using both modes of TEM i.e. diffraction mode, and image mode to find structure and the crystalline size of grown CdS crystals respectively. Figures 2.17 represent the typical electron diffraction patterns of CdS crystals. The nature of these diffraction patterns (observed rings) confirms that the grown crystals are polycrystalline in nature. According to the rings diffraction, one can say the samples do not contain tens of thousands of grains, which clearly seen from the incompletely diffraction cone because there are not a statistically relevant number of grains being irradiated i.e. due to the amount limitation of samples used or due to non-randomly oriented of grains which have needle like shapes. Figure 2.18 shows that the initial stage of growth CdS platelets was very thin needles with diameters from around 14 to 35nm and lengths from around 64 to 214nm. The diffraction patterns have also been studied to estimate the ‘d’ spacing values and the indexing of reflections. For this purpose, the patterns were placed on the platform of a comparator for the measurement of the diameter of the rings and by using equation 2.12,

\[ d = \frac{2\lambda L}{D} \]

The value of ‘d’ spacing were calculated. Here ‘D’ is the diameter of the rings, ‘L’ is the distance between photographic film and the specimen, and ‘\(\lambda\)’ is the wavelength of the electron beam which is calculated from the equation,

\[ \lambda = \frac{1.50}{U(V)} \]

Where \(U(V)\) is the accelerating volt 200kV giving the wavelength of the electron \(\lambda\) as 0.0274Å.
Figure 2.17: Diffraction patterns of CdS for (a) charge and (b) crystals.

The ‘d’ spacing and that corresponding (h k l) planes for all rings in the diffraction patterns have been calculated by putting distance between photographic film and the specimen L as 320cm, wavelength of electron $\lambda = 0.0274\text{Å}$, in equation 2.12.
The result obtained are listed in table 2.9 which is in good agreement with standard JCPDS data and supported to the XRD results [91, 92].
Figure 2.18 (a-d): A typical TEM image of CdS crystals shows the initial stage of CdS crystal growth were very thin needles with diameters of about 14-35\(nm\) and lengths of about 64-214\(nm\).
Table 2.9: Results of electron diffraction for CdS compound.

<table>
<thead>
<tr>
<th>CdS form</th>
<th>Diameter of rings(cm)</th>
<th>d - spacing d=2λL/D (Å)</th>
<th>Standard d - spacing (Å)</th>
<th>( h k l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.08</td>
<td>3.24</td>
<td>3.34</td>
<td>(002)</td>
<td></td>
</tr>
<tr>
<td>8.18</td>
<td>2.01</td>
<td>2.06</td>
<td>(110)</td>
<td></td>
</tr>
<tr>
<td>8.89</td>
<td>1.85</td>
<td>1.89</td>
<td>(103)</td>
<td></td>
</tr>
<tr>
<td>Crystal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.08</td>
<td>3.24</td>
<td>3.34</td>
<td>(002)</td>
<td></td>
</tr>
<tr>
<td>7.42</td>
<td>2.22</td>
<td>2.43</td>
<td>(102)</td>
<td></td>
</tr>
<tr>
<td>8.05</td>
<td>2.04</td>
<td>2.06</td>
<td>(110)</td>
<td></td>
</tr>
<tr>
<td>8.25</td>
<td>1.99</td>
<td>1.89</td>
<td>(103)</td>
<td></td>
</tr>
<tr>
<td>8.89</td>
<td>1.85</td>
<td>1.75</td>
<td>(112)</td>
<td></td>
</tr>
<tr>
<td>13.54</td>
<td>1.21</td>
<td>1.19</td>
<td>(300)</td>
<td></td>
</tr>
</tbody>
</table>

Summary

At the beginning of this chapter, Literature survey on CdS crystals with important results obtained by using different techniques were made. Also, a review of some of the different techniques of crystal growth was done. Accordingly, the appropriate growth technique which was selected for CdS material is direct vapour transport (DVT) technique. This followed by the explanation of the experiment which used for growth of CdS crystals. A good stoichiometric confirm by the energy dispersive analysis of X-ray (EDAX). The investigation of the hexagonal crystalline for the grown CdS crystal was done by (XRD) and that was confirmed by TEM. The lattice parameters and the unit cell volume values for CdS crystals were calculated and that was compared with JCPDS file. The grain size, micro-strain and dislocation density parameters for CdS grown crystals were calculated using two method i.e. Scherer’s method and Hall Williamson method. Finally, the initial stage of growth CdS platelets was observed by TEM images of CdS crystals.

References


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