Structural parameters of \((\text{CdSe})_{1-x}(\text{ZnS})_x\) mixed semiconductors

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ABSTRACT

The electrical, photoelectric and other properties of compound semiconductor are highly structure sensitive as they influence the device performance. The structural parameters are strongly dependent on composition and other related properties. In this paper, we report the study of structural parameters of \((\text{CdSe})_{1-x}(\text{ZnS})_x\), like crystallinity, crystal phase, lattice constant, average internal stress, strain, grain size etc. XRD, SEM, EDAX techniques were used for the characterization of the compound.

Key words: Mixed semiconductors; Co-precipitation; X-ray and optical characterization; Lattice parameters.

INTRODUCTION

Binary, ternary and quaternary semiconductors like \(\text{CdSe},\text{CdS},\text{Cd}_{1-x}\text{Zn}_x\text{Se},\text{Cd}_{1-x}\text{Zn}_x\text{S},\text{CdSe}_{1-x}\text{Te}_{x},\text{In}_{1-x}\text{Ga}_{x}\text{Sd}_{1-y}\text{As}_{y}\) were prepared in thin film form by several authors using different techniques to help in miniaturization of electronic devices made out of these compounds. The techniques used were Successive ionic layer absorption and reaction process, Spray pyrolysis, Molecular beam epitaxy, Radiofrequency sputtering and Thermal vacuum evaporation. Recently the authors have prepared bulk \(\text{CdSe}_{1-x}\text{Zn}_x\text{S}:\text{Cu}\) polycrystalline materials by co-precipitation method and characterized them using XRD, SEM, EDAX, electrical conductivity, optical absorption. The results are comparable very much with those of bulk material prepared by sophisticated techniques like melting and vapor transport methods. This technique gave reproducible results. An attempt is also therefore made to prepare alloys or solid solutions of \(\text{CdSe}\) and \(\text{ZnS}\) by co-precipitation method. The X-ray results indicated that the quality of \((\text{CdSe})_{1-x}(\text{ZnS})_x\) polycrystalline samples was good and consisted several phases. Among them \(\text{CdSe}(H),\text{CdSeS}(H),\text{ZnSe}(H)\) and \(\text{ZnS}(H)\) phases were dominating over the other phases like \(\text{ZnS}(C),\text{ZnSe}(C),\text{SeS}\). The results on structural parameters were discussed under the light of these phases.

The photoelectric and other properties of compound semiconductors are highly structure sensitive and thus effect the device performance. In turn the structural parameters such as crystallinity, crystal phase, lattice constant, average stress, strain, grain size orientation etc. depend strongly on composition and its related parameters. Although many investigations in thin film as well as in bulk form have been carried out by many researchers, it is felt that no attention is paid on the correlation of structural parameters with the composition of the mixed crystals. Keeping in view of these aspects, an experimental study on co-precipitated \((\text{CdSe})_{1-x}(\text{ZnS})_x\) polycrystalline compounds has been undertaken. Finally a
correlation between composition (x = 0 to 1) and different structural parameters has been highlighted with suitable explanation.

**EXPERIMENTAL**

(CdSe)$_{1-x}$(ZnS)$_x$ powder was prepared by controlled co-precipitation method. In this method equimolar (1 mole) solutions of Cadmium acetate, Zinc acetate, Thiourea and Selenium dioxide (all are of AR grade) were prepared using double distilled water and were mixed proportionately. The mixed solution was made alkaline by adding 25% of liquid ammonia under constant stirring process. The solution was then heated at about 90°C (±2°C) while stirring the solution constantly for 1 hour. The colour of the mixed solution of all composition (with x = 0 – 1) changed from yellow to grey, indicating the beginning of the formation of precipitate. The bath was heated further for 3 hour to complete the reaction. The precipitate was filtered through Wattman filter paper No. 41 and was rinsed with doubly distilled water repeatedly. The precipitate was then collected and dried at room temperature for 24 hours. The dried precipitate was transferred into a clean and dry quartz boat and was kept in a quartz tube of 3 cm. diameter and 1 m length arranged in a high temperature tubular furnace (1000°C). Both the ends of quartz tube were provided with two metal caps to pass inert gas through the tube. The precipitate was heated in Nitrogen atmosphere for 3 hours at 300°C. Furnace was then allowed to cool naturally to room temperature (slow cooling). The precipitate was grind in a pestle and mortar to form a fine powder and the process is repeated in order to obtain uniform particle size. The powder was made into pellets at 10 tons per square centimeter pressure by using a punch die of diameter 1.5 cm. The pressure was applied for 10 minutes. Necessary amount of powder was taken every time to obtain pellets of about 1 mm thickness. The pellets were then heated at 800°C for 2 hours under the Nitrogen atmosphere. The pressure of the gas was maintained uniform throughout the heating process and the furnace was cooled very slowly (1°C/minute) to room temperature.

The optical absorption was studied using UV-VIS-NIR recording spectrophotometer. Schimadzu diffractometer was used to record the X - ray diffractograms. Elemental analysis was carried out using EDAX (OXFORD LINK ISIS). Scanning electron micrographs were taken by the SEM Model NO.J.Col. JSM-54011.

A four probe technique was used to perform the electrical conductivity at 300K under inert atmosphere. Kiethley nanovoltmeter model 182 was used to measure potential drop across the sample and a Kiethley multimeter model 2000 was used to measure the output of the temperature sensor (Copper – Constantan thermocouple). A Kiethley constant source model No.224 was used to pass the current through the sample.

**RESULTS AND DISCUSSION**

Synthesis and Characterization

**Synthesis**

Bulk polycrystalline samples of (CdSe)$_{1-x}$(ZnS)$_x$ are prepared by the decomposition of thiourea in an alkaline solution containing Cadmium, Zinc and Selenium salts of low concentration. The preparation process is based on the slow release of Cd$^{+2}$, Se$^{-2}$, Zn$^{+2}$, and S$^{-2}$ ions in solution. The ions condensed on an ion-ion basis in the solution. The slow release of Cd$^{+2}$ and Zn$^{+2}$ ions is achieved by the dissociation of a complex species of Cd / Zn such as the Tetra amine cadmium / Tetra amine Zinc complex$^{14-17}$ ion $\left[[\text{Cd(NH}_3\text{)}_4]^{2+}/\text{[Zn(NH}_3\text{)}_4]^{2+}\right]$. The S$^{-2}$ ions are supplied by the decomposition of an organic sulphur containing liquid such as thiourea and Se$^{-2}$ ions are obtained by the decomposition of SeO$_2$ in the aqueous solution.

(CdSe)$_{1-x}$(ZnS)$_x$ precipitate was formed by controlled precipitation method. The S$^{2-}$, Se$^{2-}$ ions react with Cd$^{+2}$ and Zn$^{+2}$ ions in alkaline medium and (CdSe)$_{1-x}$(ZnS)$_x$ precipitate is formed as per the following chemical reaction.

\[
(1-x)[\text{Cd(NH}_3\text{)}_4]^{2+}+x[\text{Zn(NH}_3\text{)}_4]^{2+}+2\text{SeO}_2+6\text{NH}_3\rightarrow \text{(CdSe)}_{1-x}(\text{ZnS})_x+6\text{NH}_3\cdot\text{CO}_2+\text{H}_2\text{O}
\]

The complex formed with 1M concentration of $[\text{Cd(NH}_3\text{)}_4]^{2+}$, $[\text{Zn(NH}_3\text{)}_4]^{2+}$, SeO$_2$, thiourea and triethanolamine solution with ammonia gives controlled number of ions of Cd$^{+2}$ and Zn$^{+2}$ in which they combine with S$^{2-}$ and Se$^{2-}$ ions to form (CdSe)$_{1-x}$(ZnS)$_x$ powder.
**Chemical Analysis**

The chemical analysis of polycrystalline (CdSe)$_{1-x}$(ZnS)$_x$ samples with $x = 0 - 1$ was checked using energy dispersive analysis of X-rays (EDAX) at various locations on the bulk samples. A typical EDAX spectra of (CdSe)$_{0.6}$(ZnS)$_{0.4}$ is shown in Fig.1. The numerical data of the percentage of atoms obtained from the analysis on six samples is given in Table 1. It indicates that the chemical composition of the initial solution of the mixture is maintained in the bulk samples. It is also observed from the EDAX of all the (CdSe)$_{1-x}$(ZnS)$_x$ samples that the increase in the atomic contents of Zn and S and the decrease in Cd and Se occurred systematically while varying the value of $x$ from 0 - 1. In addition to these atoms negligibly small amounts of oxygen impurity (4.20%) is also observed uniformly in all the samples (not indicated in the Table -1).

**X-ray Analysis**

X-ray diffraction patterns of (CdSe)$_{1-x}$(ZnS)$_x$ samples with $x = 0 - 1$ are shown in Fig. 2 (a) and (b). Comparison of prominent peak positions of the observed XRD spectra with the positions given in JCPDS -ICDD data file of both cubic and hexagonal phases of CdSe, CdS, ZnSe, ZnS, CdZnS, CdSeS and SeS is given in Table - 2. It is clear from the Table that the observed diffraction peaks of mixed crystals with $x = 0 - 0.2$ coincide mostly with the peaks corresponding to CdSe(H) and few others with the positions of CdS(H) and SeS. Crystals with $x = 0.3$ contain few number of peaks corresponding to CdSe(H) and no single peak of CdSe(H) appears in samples with $x > 0.3$. Samples with $x = 0.3 - 0.4$ consists dominant peaks of CdSeS(H) and some peaks of ZnS(H). The peaks have continued to correspond with those of CdSeS(H) in samples of $x$ up to 0.7. In addition, some peaks have corresponded with the peaks of ZnSe(H) and ZnSe(C) in samples with $x = 0.5 - 0.7$. In samples with $x = 0.8$, few peaks have corresponded with those of ZnSe(H) whereas they corresponded with those of ZnS(C) in samples with $x = 0.9 - 1.0$. Randomly some peaks with lower intensities have matched with the peaks of SeS. The $d$ values and the intensities corresponding to the observed diffraction peaks were computed and assigned the Miller indices by comparing them with JCPDS - ICDD values of CdSe, CdS, ZnSe, ZnS binary compounds and also CdSeS ternary compound with hexagonal and cubic phases.

The prominent X-ray diffraction peak observed in (CdSe)$_{1-x}$(ZnS)$_x$ with $x = 0$ crystal corresponding to $d = 3.72$ Å is indexed as (100) of CdSe hexagonal phase. Apart from the prominent peak other peaks assigned are (002), (101), (102), (110), (103), (200), (112), (201), (210), (211) and (212) of CdSe with hexagonal phase. Similarly the prominent X-ray diffraction peak corresponding to $d = 3.123$ Å in the crystal of end composition with $x = 1$ is indexed as (111) of ZnS cubic phase. Apart from this peak other peaks assigned to ZnS are (200C), (311C), (110H). Some other peaks corresponding to the reflections of SeS with $d = 3.22$Å, 3.06Å and 3.13Å were also observed in mixed samples with $x = 0.1$ to 0.7. Table 2 also shows the comparison of observed $d$ value and
intensities of (CdSe)$_{1-x}$(ZnS)$_x$ with $x = 0$ - 1.0 compounds with the reported data of some peaks of CdSe, CdSSe, ZnSe and ZnS and find a good matching in terms of both intensities and $d$ values. The lattice parameters for different compositions of (CdSe)$_{1-x}$(ZnS)$_x$ with $x = 0$ - 1 calculated using X-ray data are given in Table - 3. The graphical variation of lattice parameters $a$ and $c$ for $0 \leq x < 1.0$ is shown in Fig. 3. It may be noted from the figure that the parameter $a$ decreases linearly with $x$ and the parameter $c$ increases with the increase in $x$ till 0.2 and then decreases nonlinearly till the end composition.

**Optical absorption studies**

The optical energy gap, $(E_g)$ of (CdSe)$_1$. 
\( (\text{ZnS}) \), samples was estimated from the graph showing the variation of optical absorption coefficients as a function of wavelength. The optical absorption measurements were conducted using the fine particles (powder) of the compound spread on the scotch tape. A typical optical absorption spectrum of \((\text{CdSe})_{1-x}(\text{ZnS})_x\) is shown in Fig. 4. The Absorption coefficients at different frequencies were obtained from optical absorption and plots of \((ahn)^2\) verses \(hn\) were drawn for different alloys and observed that the energy gap in all of them is about 5.2 eV.

A typical graph of \((ahn)^2\) verses \(hn\) is shown in Fig. 4. This figure indicates that there are number of trapping centers present in the samples which trap the charge carriers leading to smaller mobilities and the conduction to occur due to small polarons rather than electrons or holes. Therefore, measuring the Hall effect was not possible due to the formation of feeble amount of Hall voltage. Hence an alternate method i.e. thermoelectric power study was made use to compute the mobilities in different samples.

**Scanning electron microscope studies**

Figure 5 (a – f) represent SEM micrographs of sintered \((\text{CdSe})_{1-x}(\text{ZnS})_x\) pellets with \(x = 0, 0.2, 0.4, 0.7, 0.9\) and 1. It is evident from the micrographs that the grains are like platelets and their size decreases with the increase of \(x\) from 0 - 0.6 and later it remains almost same till \(x\) reaches 0.9. Samples with \(x = 1\) show crystallites of small grain size. The shape of the crystallites can be identified as hexagonal mixed with cubic structure under higher magnification. A similar conclusion was also drawn from the calculations of grain size using the X-ray diffraction data. The values of grain size obtained are also given in Table - 3. It may be concluded from these studies that the grain size decreases with the increase of \(x\). Lower resistivity and higher mobility may be achieved by doping these samples with metal ions as observed by the authors in Cu doped \(\text{Cd}_{1-x}\text{Zn}_x\text{S}\) ternary compounds.

**Lattice Constant**

The \(d\) values corresponding to the set of planes responsible for the observed diffraction peaks were compared from the peak position \(2q\) of the XRD pattern of the Samples \((\text{CdSe})_{1-x}(\text{ZnS})_x\) prepared by co-precipitation and assigned the Miller indices by comparing them with the JCPDS – ICDD values of CdSe and ZnS with hexagonal and Cubic phases. The lattice constant \(a\) and \(c\) for the hexagonal phase structure of CdSe and \(a\) for the cubic structure of ZnS are determined using the assigned Miller indices \((h k l)\) to the diffraction peaks of experimentally known \(d\) values by
\[ \frac{1}{d^2} = \frac{1}{3a^2} (h^2 + k^2 + l^2) + \frac{1}{c^2} \]  \hspace{1cm} \text{(1)}

\[ a = d(h^2 + k^2 + l^2) \frac{1}{\sqrt{2}} \]  \hspace{1cm} \text{(2)}

respectively. The corrected values of lattice constants for a particular composition are estimated from the Nelson-Riley plots drawn between the calculated values of ‘a’ and their corresponding error function \( f(q) \) related to the angular position (\( q \)) of

Fig. 5(a-f): SEM micrographs of sintered (CdSe\(_{1-x}\) (ZnS)\(_x\)) compounds with \( x = 0.02, 0.04, 0.7, 0.9 \& 1 \)
Various structural parameters such as lattice constant, average internal stress, micro strain, dislocation density, grain size, and preferred orientations of \((\text{CdSe})_{1-x} (\text{ZnS})_x\) bulk samples are calculated using the relevant formulae and are systematically represented in Table - 4. These parameters of each sample are correlated with the composition. The variation of lattice parameter with the composition is shown in Fig. 6 (a-b) (The correct

\[
f(\theta) = \frac{1}{2} \left[ \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right] ...(3)
\]

A least square fit is made to this curve and the straight line is extrapolated to the y-axis. The Y-intercept of the line gives the corrected value of lattice constant. The lattice constants of all \((\text{CdSe})_{1-x} (\text{ZnS})_x\) samples are determined.
values of lattice constant of different samples are estimated from the Nelson-Riley plots drawn independently for every sample. A typical graph is shown in Fig 7.) The values of $a$ and $c$ corresponding to ZnS(H) are found to vary within the range of 4.078Å to 4.296Å and 6.656Å to 7.018Å respectively. Similarly the range in 5.390Å to 3.978Å for a ZnS(C) with in the composition range

Fig. 8a: Variation of average internal stress of ZnS(II) phase in (CdSe)$_{1-x}$ (ZnS)$_x$ compounds with $x = 0.1-0.5$

Fig. 8b: Variation of average internal stress of ZnS(C) phase in (CdSe)$_{1-x}$ (ZnS)$_x$ compounds with $x = 0.7-0.1$

Fig. 9: Variation of micro strain of (CdSe)$_{1-x}$ (ZnS)$_x$ compounds with $x = 0-1.0$

Fig. 10: Variation of grain size in (CdSe)$_{1-x}$ (ZnS)$_x$ compounds with $x = 0-1.0$

Fig. 11: Variation of dislocation density in (CdSe)$_{1-x}$ (ZnS)$_x$ compounds with $x = 0-1.0$
Table 1: Atomic Percentages in different (CdSe)$_{1-x}$(ZnS)$_x$ compounds

| Compound           | Atomic Percentage |
|--------------------|-------------------|
|                    | Cd   | Se   | Zn   | S    |
| (CdSe)$_{1.0}$ (ZnS)$_{0.0}$ | 50.77 | 49.02 | -    | -    |
| (CdSe)$_{0.8}$ (ZnS)$_{0.2}$ | 38.55 | 37.84 | 12.73 | 10.69 |
| (CdSe)$_{0.6}$ (ZnS)$_{0.4}$ | 29.05 | 37.41 | 20.03 | 13.31 |
| (CdSe)$_{0.4}$ (ZnS)$_{0.6}$ | 25.06 | 32.14 | 24.74 | 17.86 |
| (CdSe)$_{0.2}$ (ZnS)$_{0.8}$ | 20.92 | 25.21 | 29.49 | 24.18 |
| (CdSe)$_{0.0}$ (ZnS)$_{1.0}$ | -    | -    | 48.49 | 49.92 |

x = 0.7 to 1.0 shown in Fig. 6(c). It may be noted from Fig. 6 (a) & (b) that a and c parameters decrease linearly with the increase of x till x = 0.5. For x > 0.5 the sample undergoes a crystalline transition from Hexagonal structure of ZnS to Cubic structure. The decreasing nature of lattice parameter with increase in concentration indicates an improvement in the compact arrangement of atoms in the crystals.

Average internal stress and micro-strain

Thronton and Hoffmann\textsuperscript{18} revealed that all vacuum evaporated films are in a state of stress. The total stress is composed of a thermal stress and an intrinsic stress due to the difference in thermal expansion coefficients of the film and substrate material. The intrinsic stress is due to the accumulating effect of the crystallographic flaws that are built in the film during deposition. The thermal stress developed in the films prepared at higher temperatures is normally observed to be 5% of the total stress. Therefore, it is believed that for a compound semiconductor of high melting temperature like ZnSe, (CdSe)$_{1-x}$(ZnS)$_x$ the internal stress accumulates and tends to dominate over thermal stress. Hence thermal stress in films is negligible when compared to internal stress. A similar argument also holds good for bulk materials. The average stress is given by the relation\textsuperscript{19},

$$\sigma = \frac{E}{2\sigma} \left[ \frac{a_0 - a}{a_0} \right] \quad \ldots(4)$$

where $E$, $s$ and $a_0$ are the Young’s modulus, poisson’s ratio and bulk lattice constant of ZnS/ CdSe samples respectively and standard bulk values of $E$, $s$ and $a_0$ are used in the calculation of stress. While calculating stress in ZnS(C) and ZnS(H) phases $a_0$ and $a$ are substituted with the standard and observed lattice parameters along X, Y and Z - axis.

The micro-strain $\varepsilon$ developed in (CdSe)$_{1-x}$(ZnS)$_x$ compounds is calculated from the relation

$$\varepsilon = \frac{1}{4} \left( \beta_{2\theta} \cos \theta \right) \quad \ldots(5)$$

where $\beta_{2\theta}$ is the full width at half maximum (FWHM) of a prominent peak. In our calculations peaks corresponding [100] and [111] are considered in case of CdSe (H) and ZnS(C) respectively.

The internal stress of (CdSe)$_{1-x}$(ZnS)$_x$ consisting a mixture of Zns (H) and ZnS(C) phases with $0 \leq x \leq 1$ is calculated by considering the stress with reference to two lattice parameters ($a$, $c$) of Hexagonal phase and one single lattice parameter ($a$) of Cubic phase. These values are given in Table - 4. The variation of stress with composition for these two structures are shown in 8 (a) and 8(b). From these graphs and Table - 4, it is observed that the stress is elongational in nature in Hexagonal phase, whereas it is compressional in Cubic phase. Also it may be observed that the variation of stress along two different directions in Hexagonal phase is more or less coinciding at lower concentrations except at concentrations nearing 0.5 and in general,
Table 2: Comparison of the observed d values and intensities with the JCPDS-ICDD values and their (hkl) values

| Compound            | Observed       | JCPDS-ICDD Values                                                                 |
|---------------------|----------------|----------------------------------------------------------------------------------|
|                     | d(A0)          |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | l       |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | I/I0  |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | hkl   |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | I/I0  |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | d(A0) |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | hkl   |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | I/I0  |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | d(A0) |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | hkl   |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | I/I0  |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | d(A0) |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | hkl   |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | I/I0  |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | d(A0) |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | hkl   |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | I/I0  |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
| (CdSe)1.0(ZnS)0.0  | 3.690 | 100                |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 3.477 | 86                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 3.264 | 65                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 3.923 | 4                  |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 3.531 | 22                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 2.311 | 3                  |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 2.137 | 81                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 2.050 | 6                  |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 1.959 | 43                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 1.865 | 4                  |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 1.842 | 19                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 1.814 | 52                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 1.780 | 11                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 1.439 | 12                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 1.389 | 9                  |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 1.294 | 7                  |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
| (CdSe)0.9(ZnS)0.1  | 3.725 | 100                |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 3.591 | 12                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 3.509 | 67                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 3.397 | 16                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 3.289 | 73                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 3.094 | 23                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 2.675 | 7                  |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 2.552 | 33                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 2.150 | 77                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 1.979 | 64                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 1.861 | 10                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
|                     | 1.832 | 42                 |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |                     |
| 1.797 | 10 | 1.800 (201) | 12 |
| 1.456 | 13 | 1.456 (203) | 20 |
| 1.380 | 7  | 1.380 (210) | 8  |
| 3.724 | 100| 3.720 (100) | 100|
| 3.819 | 24 | - - - - - - |
| 3.586 | 51 | - - - - - - |
| 3.505 | 82 | 3.51 (002) | 70 |
| 3.401 | 60 | - - - - - - |
| 3.289 | 70 | 3.29 (101) | 75 |
| 3.095 | 65 | - - - - - - |
| 3.005 | 39 | - - - - - - |
| 2.753 | 20 | - - - - - - |
| 2.674 | 16 | - - - - - - |
| 2.552 | 29 | - - - - - - |
| 2.391 | 12 | - - - - - - |
| 2.148 | 59 | 2.151 (110) | 85 |
| 2.008 | 16 | - - - - - - |
| 1.970 | 56 | 1.980 (103) | 70 |
| 1.830 | 30 | 1.834 (112) | 50 |
| 1.511 | 15 | - - - - - - |
| 1.457 | 14 | 1.456 (203) | 20 |
| 3.632 | 100| - - - - - - |
| 3.439 | 97 | - - - - - - |
| 3.223 | 58 | 3.29 (101) | 75 |
| 2.500 | 11 | - - - - - - |
| 2.369 | 5  | - - - - - - |
| 2.105 | 92 | - - - - - - |
| 1.938 | 34 | - - - - - - |
| 1.792 | 52 | - - - - - - |
| 1.654 | 5  | 1.645 (202) | 8  |
| 1.595 | 6  | - - - - - - |
| 1.449 | 8  | 1.407 (210) | 8  |

Table 1. Cont.
| Wavelength (Å) | Intensity | Crystallographic Plane |
|---------------|-----------|------------------------|
| (CdSe)0.6(ZnS)0.4 | 3.557 100 | 3.583 (100) 75 3.6 (100) 98 |
|               | 3.367 (002) 60 3.38 (002) 93 | 3.309 (100) 100 |
|               | 3.160 (101) 100 3.18 (101) 97 | 3.128 (002) 86 |
| (CdSe)0.5(ZnS)0.5 | 3.524 100 | 3.524 (100) 98 |
|               | 3.34 (100) 100 | 3.34 (100) 100 |
|               | 3.25 (002) 90 | 3.25 (002) 90 |
| (CdSe)0.3(ZnS)0.7 | 6.473 11 | 6.67 10 |
|               | 3.34 (100) 100 | 3.34 (100) 100 |
|               | 3.25 (002) 90 | 3.25 (002) 90 |
|               | 3.05 (101) 70 | 3.05 (101) 70 |

Table 1. Cont.
Table 1. Cont.

| 1.987 75 | - | - | - | - | - | - | - | - | 1.97 | 1.0 | - | - | - | - | - | - | - | - | 2.004 (220) 65 |
| 1.834 37 | - | - | - | - | - | - | - | - | 1.909 (103) 42 | - | - | - | - | - | - | - | - | - | - |
| 1.696 31 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 1.670 17 | - | - | - | - | - | - | - | - | 1.66 | 20 | - | - | - | - | - | - | - | - | - |
| (CdSe)\textsubscript{0.2}(ZnS)\textsubscript{0.8} | 3.422 100 | - | - | - | - | - | - | - | - | 3.43 (100) 100 | - | - | - | - | - | - | - | - | - |
| 3.229 94 | - | - | - | - | - | - | - | - | - | 3.25 (002) 90 | - | - | - | - | - | - | - | - | - |
| 3.023 69 | - | - | - | - | - | - | - | - | - | 3.05 (110) 70 | - | - | - | - | - | - | - | - | - |
| 2.345 23 | - | - | - | - | - | - | - | - | 2.24 | 20 | - | - | - | - | - | - | - | - | - |
| (CdSe)\textsubscript{0.1}(ZnS)\textsubscript{0.9} | 3.339 65 | - | - | 3.367 (002) 60 | - | - | - | - | - | - | 1.911 (110) 75 | - | - | - | - | - | - | - | - |
| 3.156 100 | - | - | - | - | - | - | - | - | - | - | - | - | 3.123 (111) 100 | - | - | - | - | - |
| 2.953 43 | - | - | - | - | - | - | - | - | - | 2.925 (101) 54 | - | - | - | - | - | - | - | - | - |
| 2.297 14 | - | - | - | - | - | - | - | - | - | 2.723 (102) 29 | - | - | - | - | - | - | - | - | - |
| 1.929 78 | - | - | - | - | - | - | - | - | - | 1.911 (110) 74 | 1.912 (220) 51 | - | - | - | - | - | - | - | - | - |
| 1.780 26 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| (CdSe)\textsubscript{0.0}(ZnS)\textsubscript{1.0} | 3.130 100 | - | - | - | - | - | - | - | - | - | - | 3.123 (111) 100 | - | - | - | - | - | - | - | - |
| 2.732 18 | - | - | - | - | - | - | - | - | - | - | - | - | 2.705 (200) 10 | - | - | - | - | - | - | - | - |
| 1.913 73 | - | - | - | - | - | - | - | - | - | - | - | - | 1.911 (110) 74 | - | - | - | - | - | - | - | - |
| 1.766 12 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 1.631 45 | - | - | - | - | - | - | - | - | - | - | - | - | 1.630 (112) 45 | 1.633 (311) 30 | - | - | - | - | - | - | - | - |
Table 3: Lattice Parameters and grain size of (CdSe)$_{1-x}$(ZnS)$_x$ crystals with $x = 0-1$

| Compound             | $a$ (Å) | $c$ (Å) | Grain Size (D) (Å) |
|----------------------|---------|---------|--------------------|
| (CdSe)$_{1.0}$(ZnS)$_{0.0}$ | 4.348   | 6.954   | 257                |
| (CdSe)$_{0.9}$(ZnS)$_{0.1}$ | 4.296   | 7.018   | 240                |
| (CdSe)$_{0.8}$(ZnS)$_{0.2}$ | 4.285   | 7.010   | 168                |
| (CdSe)$_{0.7}$(ZnS)$_{0.3}$ | 4.193   | 6.868   | 124                |
| (CdSe)$_{0.6}$(ZnS)$_{0.4}$ | 4.122   | 6.954   | 125                |
| (CdSe)$_{0.5}$(ZnS)$_{0.5}$ | 4.078   | 6.656   | 130                |
| (CdSe)$_{0.3}$(ZnS)$_{0.7}$ | 3.978   | 6.490   | 193                |
| (CdSe)$_{0.2}$(ZnS)$_{0.8}$ | 3.942   | 6.458   | 193                |
| (CdSe)$_{0.1}$(ZnS)$_{0.9}$ | 5.409(c) | -       | 196                |
| (CdSe)$_{0.0}$(ZnS)$_{1.0}$ | 5.390(c) | -       | 155                |

the stress increases with the increase in concentration. Whereas the compressional stress belonging to cubic structure decreases with increase in concentration observed (reducing nature of lattice parameters) in ZnS (C) structure.

The variation of Microstrain of (CdSe)$_{1-x}$(ZnS)$_x$ compounds with the increase of $x$ is shown in Fig. 9. The strain, as shown in figure, initially increases and attains maximum when $x = 0.3$ then decreases gradually, reaches minimum at $x = 0.9$ and afterwards increases slowly.

Grain Size

It is observed that the XRD patterns of all (CdSe)$_{1-x}$(ZnS)$_x$ samples show the most preferred orientation along (100) in CdSe(H) and (111) in ZnS(C). The [100] and [111] directions are the close-packed directions of the hexagonal (w) and Zinc blend (C) structures. The grain size of the samples is estimated using Scherrer formula

$$D = \frac{k \lambda}{\beta \cos \theta} \quad \ldots(6)$$

Here $k$ is taken as 1, $\lambda$ is the wavelength of X-rays used ($\lambda = 1.78892$ Å) and $\beta$ the full width at half maximum of [100] or [111] peak of XRD pattern.

The variation of Grain size of (CdSe)$_{1-x}$(ZnS)$_x$ samples with the increase of $x$ is shown in the Fig. 10. This variation appears to be conjugate when compared to the variation of strain. i.e it first decreases, attains minimum at $x = 0.4$, increases thereafter, reaches maximum when at $x = 0.8$ and decreases for higher values of $x$. The peak value of strain at $x = 0.3$ (or a minimum of grain size) appears to be an anomaly arising due to different combinations of crystal structures that are developed in the compound. Afterwards, the decrease in strain and attaining minimum (or the increase in grain size to a maximum value) at $x = 0.9$ may indicate the formation of stable structure. A similar result was also observed by others.

Dislocation Density

A dislocation is an imperfection in a crystal associated with the misregistry of the lattice in one part of the crystal with that in another part. Unlike vacancies and interstitial atoms, dislocations are not equilibrium imperfections i.e., thermodynamic considerations are insufficient to account for their existence in the observed densities. In fact the growth mechanism involving dislocation is a matter of importance. In the present study the dislocation density for both hexagonal and cubic (CdSe)$_{1-x}$(ZnS)$_x$ crystals is estimated from Williamson and Small man method using the relation (De and Mishra).

$$\rho = \frac{15 \varepsilon}{aD} \quad \ldots(7)$$
The variation of dislocation density with the composition is given in Fig. 11. The dislocation density, as shown in figure, initially increases and attains maximum when \( x = 0.3 \), then decreases gradually and reaches minimum at \( x = 0.8 \) and afterwards increases slowly beyond this concentration. This type of change may be due to the fact that the increase of average internal stress which corresponds to a decrease in dislocation density. It is also observed that the microstrain (\( \varepsilon \)) and dislocation density (\( \rho \)) exhibit a slow decrease at higher composition i.e for \( x > 0.9 \). This decrease of (\( \varepsilon \)) and (\( \rho \)) for \( 0.3 \leq x < 0.9 \) may be due to the movement of interstitial ZnS atoms from the crystallites to grain boundaries leading to the reduction in the concentration of lattice imperfections.

**CONCLUSIONS**

- Homogeneous and polycrystalline (CdSe), \(_x(ZnS)_x\) mixed compounds are grown by controlled co-precipitation method. All the compounds have shown semiconductor nature.
- The compounds have hexagonal and cubic structure whose lattice parameters \( a \) and \( c \) are found to decrease with increase in \( x \). This agrees well with the fact that crystallite size of ZnS is relatively smaller compared to that of CdSe.
- Both Hexagonal and Cubic phases are present in (CdSe), \(_x(ZnS)_x\) mixed crystals with \( 0 \leq x \leq 0.5 \) and a dominant Cubic structure of ZnS with \( 0.5 < x < 1 \).
- The average internal stress of (CdSe), \(_x(ZnS)_x\) is a mixture of stress in ZnS(H),ZnS(C)phases. In mixed crystals, the stress is elongational in nature in Hexagonal phase, whereas it is compressional in cubic phase.
- Arrangement of atoms in (CdSe), \(_x(ZnS)_x\) crystals becomes compact with the increase in ZnS concentration.
- The peak value of strain at \( x = 0.3 \) (or a minimum of grain size) is an anomaly arising due to different combinations of crystal structures developed in the compound.
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