Structural and dc conductivity Studies of Cd$_{0.8-x}$ Pb$_x$Zn$_{0.2}$S Mixed Semiconductor Compounds

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Abstract: Cd$_{0.8-x}$Pb$_x$Zn$_{0.2}$S ($x = 0-0.8$) semiconductor powders have been prepared by controlled Co-precipitation Method in an alkaline medium using Thiourea as a sulphide source. Pellets of these powders are sintered at 800°C for 2hours in nitrogen atmosphere. X-Ray Diffractograms of these samples showed that they possess polycrystalline nature and its phase varied from Hexagonal to Cubic. Lattice parameters of all the compounds are determined. The dc electrical Conductivity of these bulk pellets has been studied using the Keithley electrometer over the temperature range 77-300K. It is observed that electrical conductivity increases with the increase in Pb concentration. The electrical conductivity measurements show that Cd$_{0.8-x}$Pb$_x$Zn$_{0.2}$S compounds possess mixed conduction at low temperatures and is observed that the conductivity of Cd$_{0.8-x}$Pb$_x$Zn$_{0.2}$S, mixed Semiconductors is enhanced with the inclusion of Pb. The results are explained based on the defects included by Pb atoms.

Keywords: Cd$_{0.8-x}$Pb$_x$Zn$_{0.2}$S, Co-Precipitation, dc conductivity, quaternary semiconductors, XRD, VRH.

I. Introduction

The Binary semiconductors have attracted much attention due to their novel properties and promising applications. For some optoelectronic applications, it is important to be able to tune the emission wavelength. Wavelength tunable emission can be achieved from ternary compounds by simple adjustment of composition. The tunability can be achieved through composition modulation [1]. In Compounds which exist in a single phase wurtzite Structure such as Cd$_{1-x}$Zn$_x$S, the value of x plays an important role in determining their structural, electrical and optical properties. Due to rapid increase in the resistivity/energy gap of Cd$_{1-x}$Zn$_x$S with increase in x which limits its usage in conductivity related applications like near infrared solar cells [2-6]. It is interesting to prepare samples of higher energy gap with reasonably good electrical conductivity. One way of achieving such compounds is by selecting suitable dopant. Hence we have taken up the preparation and characterization of Cd$_{0.8-x}$Pb$_x$Zn$_{0.2}$S system and the XRD and electrical studies have been investigated due to very little information available on the ternary CdPbZnS system [7-11]. The results are explained based on the defects incorporated with Pb.

II. Experimental Details

2.1 Growth of samples

Samples of Cd$_{0.8-x}$Pb$_x$ Zn$_{0.2}$S ($x = 0-0.8$) have been prepared by controlled Co-Precipitation method [12-15]. In this method equimolar solutions of Lead acetate, Cadmium acetate, Thiourea and Triethanolamine were taken in different compositions. The solution mixture was made alkaline by adding 30 percent of liquid Ammonia under constant stirring process. The solution was heated at about 80$^0$ C for one hour. The colour of the solution changed from yellow to grey indicating the starting of precipitation. The bath was heated further for 1hour to complete the reaction. The filtered precipitate was collected and dried at room temperature for 24hours. Then the dried precipitate was heated for 2hours at 300°C under Nitrogen atmosphere and then slowly cooled to room temperature. The dried precipitate was ground to fine powder and the powder was made into pellets under 10 ton pressure per sq.cm by using punch dye of 1.0cm diameter. The pellets were heated at 800°C for 2hours in Nitrogen atmosphere. The furnace is cooled slowly to room temperature at the rate of 2°C per minute. These pellets are used for XRD and conductivity studies. The reaction mechanism and other experimental details of the preparation are given in our earlier paper [5].
2.2 X-ray Diffraction studies

Panalytical X-pert powder X-ray diffractometer with CuKα Radiation (λ = 1.514 Å) was used to study the crystal structure and composition of Cd_{0.8-x}Pb_{x}Zn_{0.2}S samples in the angular range of 20°–80° at a scan speed of 0.02°/Sec.

2.3 Conductivity Measurements

The dc conductivity of Cd_{0.8-x}Pb_{x}Zn_{0.2}S (x = 0-0.8) was measured by two probe method using a conductivity cell fabricated in the laboratory. Keithley nano volt meter (Model 2000), constant current source (model 6220) were used for conductivity studies. A constant current of 0.2mA is passed through the samples. Conductivity measurements were made at different temperatures ranging (77-300K).

III. Results and Discussion

3.1 X-Ray Diffraction

Fig. (1) shows XRD patterns of Cd_{0.8-x}Pb_{x}Zn_{0.2}S, these XRD patterns confirm the formation and composition of Cd_{0.8-x}Pb_{x}Zn_{0.2}S ternary compounds with x = 0 - 0.8. The presence of sharp peaks confirms good polycrystalline nature of the compounds. The experimental d values for the different composition of Cd_{0.8-x}Pb_{x}Zn_{0.2}S (x=0-0.8) are compared with JCPDA data (PDF No. 400835 and PDF No. 050592) values of Cd_{0.8}Zn_{0.2}S and PbS with hexagonal and cubic phases respectively and assigned miller indices. It is found that both the phases (Hexagonal and Cubic) are present in Cd_{0.8-x}Pb_{x}Zn_{0.2}S mixed crystals. Hexagonal Structure of Cd_{0.8}Zn_{0.2}S is assigned with major peaks occurring due to the reflections from (100) (002) and (101) planes. Face centered cubic structure of PbS is assigned with the major peaks (111) and (200) planes. The peaks were in good agreement with the values reported by other researchers [11,16]. Lattice parameters of Cd_{0.8-x}Pb_{x}Zn_{0.2}S for different compositions are calculated by using the relation [17].

\[ \frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2+k^2+l^2}{a^2} \right) + \frac{\beta^2}{\lambda^2} \]  

(for hexagonal) \hspace{1cm} (1)

\[ \frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \]  

(for cubic) \hspace{1cm} (2)

For Cd_{0.8-x}Pb_{x}Zn_{0.2}S the lattice parameters with x=0 are a = 4.141 Å, c = 6.729 Å whereas only parameter obtained for the compound with x=0.8 is a = 5.933 Å. For an intermediate compound with x=0.4 the hexagonal phase has values of a and c are 4.119 Å and 6.695 Å respectively and an additional phase of cubic has a = 5.954 Å.

The average crystallite size of compounds is calculated using Scherer relation [17].

\[ D = \frac{0.94\lambda}{\beta \cos \theta} \]  

(3)

Where D is the average crystallite size, λ is X-Ray wavelength, θ is the Bragg’s angle and β is FWHM. For particles smaller than 100nm, FWHM should be corrected by using FWHM for larger grain silicon sample using the relation

\[ \beta_{\text{corrected}} = \left( \text{FWHM}^2_{\text{Sample}} - \text{FWHM}^2_{\text{Si}} \right) \]  

(4)

FWHM of silicon is 0.15 Å. Crystallite size of the compounds found to lie between 35.5 nm and 54.5 nm as x varies from 0–0.8.
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3.2. dc conductivity studies

The electrical conductivity of Cd$_{0.8-x}$ Pb$_x$ Zn$_{0.2}$ S samples is measured in the region (77-300K). A Plot drawn between log $\sigma$ and 1000/T is shown in Fig.2. These plots show three linear regions of conductivity in each sample. A similar type of variation was also observed by H.A Zayed et al [19] and D.PathinettamPadiyan et al [20]. The plot exhibits Arrhenius behavior in two different temperature ranges (i) 300K – 170K and (ii) 170 -100 K and obeys the equation.

$$\sigma = \sigma_0 \exp \left[ \frac{-E_a}{kT} \right]$$  (5)

Where $E_a$ is activation energy, $k$ is the Boltzmann constant and $T$ is temperature in Kelvin.

![Fig.1. XRD Diffractograms of Cd$_{0.8-x}$ Pb$_x$ Zn$_{0.2}$ S compound](image1)

![Fig.2.(A) A Plot of Log $\sigma$ versus 1000 / T for different compositions of Cd$_{0.8-x}$ Pb$_x$ Zn$_{0.2}$ S compound. (B) A Plot of Log $\sigma$ versus 1000 / T for 0.2 composition, showing three conduction mechanisms.](image2)
The activation energies calculated for two regions are shown in Table.1. Below 100K the conductivity is almost constant indicating the freezing of charge carriers. It can be observed from the Fig.2 that the dc conductivity increases with increase in Pb content. This increase can be attributed to the fact that the addition of Pb to CdZnS creates defect levels close to the conduction band with in the forbidden energy gap. As concentration of Pb increases the defects created are such that their corresponding energy levels move closer to the conduction band and hence there is a decrease in the activation energy. The electrical conductivity in compounds below room temperature follows different types of mechanisms [21] namely

(i) The ordinary conductivity due to the drifting of charge carriers in the applied field which normally occurs at higher temperature (above room temperature)
(ii) Conductivity due to thermally assisted hopping
(iii) Conductivity due to hopping of charge carriers due to existence of localized states around EF and
(iv) Variable range hopping (VRH) conduction.

In Cd$_{0.8-x}$Pb$_x$Zn$_{0.2}$S compounds three types of conduction are observed. In the log $\sigma$ vs 1000/$T$ Plot the deviation in the straight line below 100K indicates the existence of VRH conduction. The Greaves [22] conductivity expression for the VRH model applicable to low temperature is

$$\sigma T^{1/2} = C \exp \left(\frac{-T^0}{T}\right)^{1/4}$$  \hspace{1cm} (6)

where $C$ and $T_0$ are constants related to the density of localized states $N(E_F)$ given by

$$T_0 = \frac{16\alpha^3}{KN(E_F)}$$  \hspace{1cm} (7)

In which $\alpha^{-1}$ is the measure of the spatial extension of the wave function $\exp(-\alpha x)$ associated with the localized states. Plots of log($\sigma T^{1/2}$) vs $T^{-1/4}$ in the temperature range 100K-77K are drawn for different Pb content [Fig.3]. The graphs are found to be straight lines indicating the validity of hopping conduction mechanism. This is in good agreement with MOTT’s VRH Process. The slopes of the curves give the values of $T_0$ and are shown in Table.1.

![Fig.3](image_url)

**Fig.3.** Log $(\sigma T^{1/2})$ versus $T^{-1/4}$ for different compositions of Cd$_{0.8-x}$Pb$_x$Zn$_{0.2}$S compound.

It is also found that the activation energy of the compounds varies from 100meV to 34meV in the temperature range 300K-170K, which suggests the conduction due to the thermally assisted hopping and in the temperature range 170-100K the conduction is due to hopping of charge carriers due to existence of localized states around $E_F$ and is supported by the values of activation energies ranging from 68meV to 6meV.
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Fig.4. Composition dependence of activation energy in Cd$_{0.8-x}$Pb$_x$Zn$_{0.2}$S compound.

Table.1. The activation energy and T$_0$ values of different compositions of Cd$_{0.8-x}$Pb$_x$Zn$_{0.2}$S compound.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Sample</th>
<th>Activation Energy (meV)</th>
<th>T$_0$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>300-170K</td>
<td>170-100K</td>
</tr>
<tr>
<td>1</td>
<td>Cd$<em>{0.8}$Zn$</em>{0.2}$S</td>
<td>100</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
<td>Cd$<em>{0.7}$Pb$</em>{0.1}$Zn$_{0.2}$S</td>
<td>50</td>
<td>22</td>
</tr>
<tr>
<td>3</td>
<td>Cd$<em>{0.6}$Pb$</em>{0.2}$Zn$_{0.2}$S</td>
<td>47</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>Cd$<em>{0.5}$Pb$</em>{0.3}$Zn$_{0.2}$S</td>
<td>44</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>Cd$<em>{0.4}$Pb$</em>{0.4}$Zn$_{0.2}$S</td>
<td>43</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>Cd$<em>{0.3}$Pb$</em>{0.5}$Zn$_{0.2}$S</td>
<td>39</td>
<td>18</td>
</tr>
<tr>
<td>7</td>
<td>Cd$<em>{0.2}$Pb$</em>{0.6}$Zn$_{0.2}$S</td>
<td>37</td>
<td>13</td>
</tr>
<tr>
<td>8</td>
<td>Cd$<em>{0.1}$Pb$</em>{0.7}$Zn$_{0.2}$S</td>
<td>36</td>
<td>11</td>
</tr>
<tr>
<td>9</td>
<td>Pb$<em>{0.8}$Zn$</em>{0.2}$S</td>
<td>34</td>
<td>06</td>
</tr>
</tbody>
</table>

IV. Conclusions

1. Bulk polycrystalline Cd$_{0.8-x}$Pb$_x$Zn$_{0.2}$S mixed semiconductor compounds are prepared by controlled Co-Precipitation method.
2. Both Cubic and Hexagonal phases are present in Cd$_{0.8-x}$Pb$_x$Zn$_{0.2}$S mixed crystals with 0<x<0.8 where as hexagonal and cubic phases are seen in compounds with x=0 and x=0.8 respectively.
3. The electrical conductivity increases with the increase in temperature, which confirms the semiconductor nature of the samples.
4. Activation energies below room temperature in temperature regions (300K – 170K) and (170 – 100K) are observed to decrease with the increase in the concentration of Pb. This supported two conduction mechanisms Viz. conductivity due to thermally assisted hopping of charge carriers, conductivity due to hopping of charge carriers due to existence of localized states around E$_F$ and below100K the conductivity is due to VRH.
5. The increase in the conductivity with the increase of Pb content finds Cd$_{0.8-x}$Pb$_x$Zn$_{0.2}$S compounds more useful in Opto-electronic devices.

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