IOSR Journal of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 6, Issue 2 Ver. III (Mar-Apr. 2014), PP 34-39
www.iosrjournals.org

Structural and dc conductivity Studies of $Cd_{0.8-x}Pb_xZn_{0.2}S$ Mixed Semiconductor Compounds

T. Shekharam[1], V. Laxminarasimha Rao, G. Yellaiah, T. Mohan Kumar And M. Nagabhushanam[2]
[1,2]*Department of Physics, University College of Science, Osmania University, Hyderabad – 500 007*

Abstract: *$Cd_{0.8-x}Pb_xZn_{0.2}S$ (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 800^0C 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 $Cd_{0.8-x}Pb_xZn_{0.2}S$ compounds possess mixed conduction at low temperatures and is observed that the conductivity of $Cd_{0.8-x}Pb_xZn_{0.2}S$, mixed Semiconductors is enhanced with the inclusion of Pb. The results are explained based on the defects included by Pb atoms.*

Keywords: *$Cd_{0.8-x}Pb_xZn_{0.2}S$, 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 $Cd_{1-x}Zn_xS$, 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 $Cd_{1-x}Zn_xS$ 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 $Cd_{0.8-x}Pb_xZn_{0.2}S$ 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 $Cd_{0.8-x}Pb_xZn_{0.2}S$ (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 300^0C 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 800^0C for 2hours in Nitrogen atmosphere. The furnace is cooled slowly to room temperature at the rate of 2^0C 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 Xpertpowder X-Ray diffractometer with CuK α Radiation (λ = 1.514 A^0) 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 20^0– 80^0 at a scan speed of 0.02^0 / Sec.

2.3 Conductivity Measurements

The dc conductivity of $Cd_{0.8-x}$ $Pb_xZn_{0.2}$ S (x= 0-0.8) was measured by two probe method using a conductivity cell fabricated in the laboratory. Keithley nano voltmeter (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 $Cd_{0.8-x}Pb_xZn_{0.2}S$, these XRD patterns confirm the formation and composition of all $Cd_{0.8-x}Pb_xZn_{0.2}S$ 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 $Cd_{0.8-x}Pb_xZn_{0.2}S$ (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 $Cd_{0.8-x}Pb_xZn_{0.2}S$ mixed crystals. Hexagonal Structure of $Cd_{0.8-x}Pb_xZn_{0.2}S$ 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 $Cd_{0.8-x}Pb_xZn_{0.2}S$ for different compositions are calculated by using the relation [17].

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+l^2}{a^2}\right) + \frac{l^2}{c^2} \quad \text{(for hexagonal)} \qquad (1)$$

and

$$\frac{1}{d^2} = \left(\frac{h^2+k^2+l^2}{a^2}\right) \quad \text{(for cubic)} \qquad (2)$$

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

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

$$D = \frac{0.94\lambda}{\beta\cos\theta} \qquad (3)$$

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

$$\beta_{corrected} = (FWHM^2_{Sample} - FWHM^2_{Si}) \text{ [18]} \qquad (4)$$

FWHM of silicon is 0.15^0 Crystallite size of the compounds found to lie between 35.5 nm and 54.5nm as x varies from 0–0.8

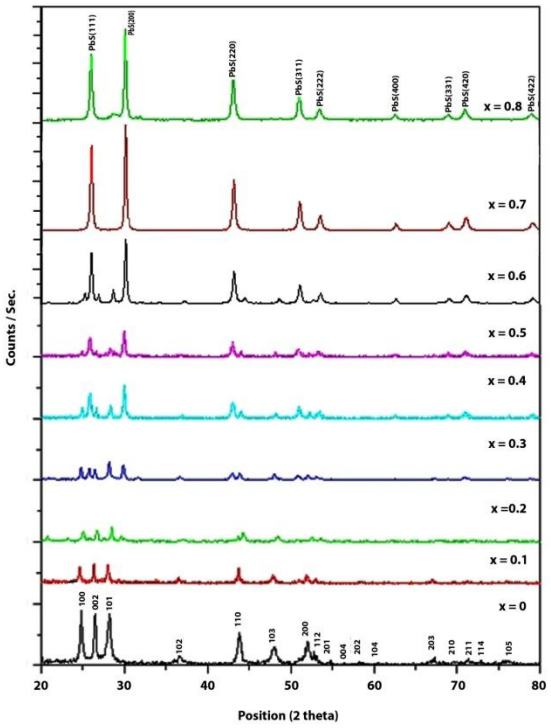

Fig.1. XRD Difractograms of $Cd_{0.8-x}Pb_xZn_{0.2}S$ compound

3.2.dc conductivity studies

The electrical conductivity of $Cd_{0.8-x}Pb_xZn_{0.2}S$ 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.

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

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

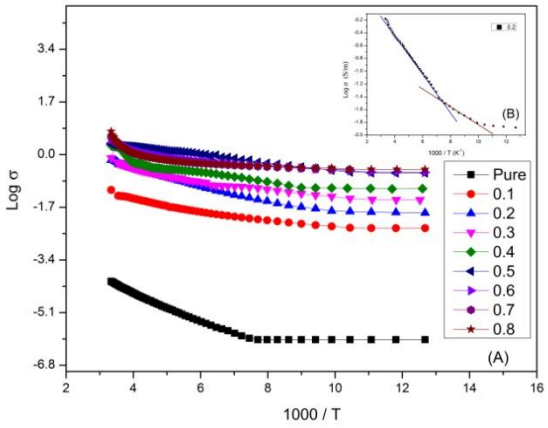

Fig.2.(A) A Plot of Log σ versus 1000 / T for different compositions of $Cd_{0.8-x}Pb_xZn_{0.2}S$ compound. (B) A Plot of Log σ versus 1000 / T for 0.2 composition, showing three conduction mechanisms.

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 E_F and
(iv) Variable range hopping (VRH) conduction.

In $Cd_{0.8-x}Pb_xZn_{0.2}S$ 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

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

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

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

In which α^{-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_o and are shown in Table.1.

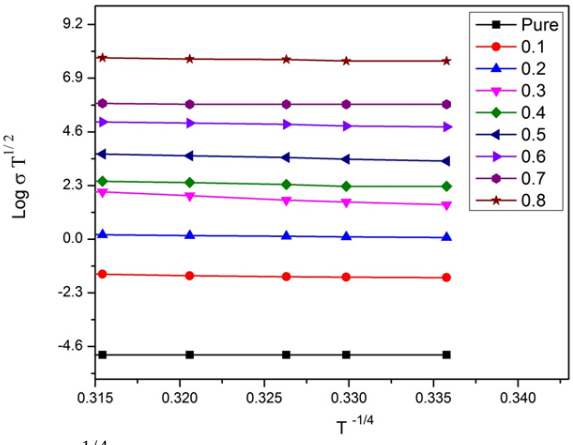

Fig.3. Log (σ $T^{1/2}$) versus $T^{-1/4}$ for different compositions of $Cd_{0.8-x}Pb_xZn_{0.2}S$ compound.

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.

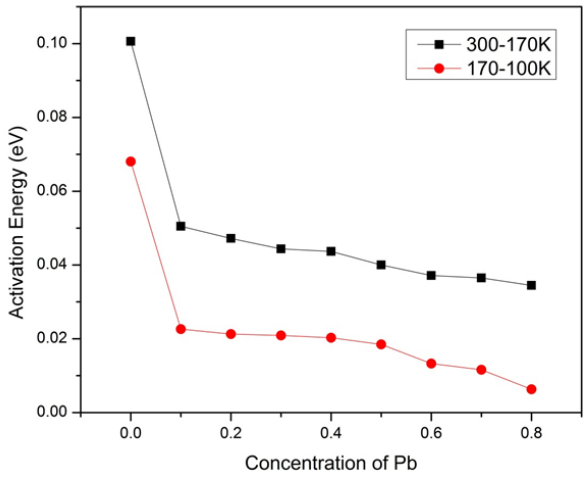

Fig.4. Composition dependence of activation energy in $Cd_{0.8-x}Pb_xZn_{0.2}S$ compound.

Table.1.The activation energy and T_o values of different compositions of $Cd_{0.8-x}Pb_xZn_{0.2}S$ compound.

S. No	Sample	Activation Energy (meV)		T_0 (K)
		300-170K	170-100K	100-77K
1	$Cd_{0.8}Zn_{0.2}S$	100	68	75
2	$Cd_{0.7}Pb_{0.1}$ $Zn_{0.2}S$	50	22	83
3	$Cd_{0.6}Pb_{0.2}$ $Zn_{0.2}S$	47	21	876
4	$Cd_{0.5}Pb_{0.3}$ $Zn_{0.2}S$	44	20	1083
5	$Cd_{0.4}Pb_{0.4}$ $Zn_{0.2}S$	43	20	1271
6	$Cd_{0.3}Pb_{0.5}$ $Zn_{0.2}S$	39	18	1519
7	$Cd_{0.2}Pb_{0.6}$ $Zn_{0.2}S$	37	13	1753
8	$Cd_{0.1}Pb_{0.7}$ $Zn_{0.2}S$	36	11	8649
9	$Pb_{0.8}$ $Zn_{0.2}S$	34	06	28323

IV. Conclusions

1. Bulk polycrystalline $Cd_{0.8-x}Pb_xZn_{0.2}S$ mixed semiconductor compounds are prepared by controlled Co-Precipitation method.
2. Both Cubic and Hexagonal phases are present in $Cd_{0.8-x}Pb_xZn_{0.2}S$ 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 $Cd_{0.8-x}Pb_xZn_{0.2}S$ compounds more useful in Opto-electronic devices.

Acknowledgements

The authors are grateful to Head, Department of Physics, University college of Science, Osmania University for providing facilities and Director CFRD, Osmania University for extending the facilities at the center.

References

[1] M.A.Barote, A.A.Yadav, E.U.Masumdar, Effect of thickness on structural, optical and electrical properties of chemically grown $Cd_{0.825}Pb_{0.175}S$ thin films, Journal of Chemical, Biological & Physical Sciences,

[2] M.A.Redwan, L.I.Soliman, E.H.Aly, A.A.EL-Shazely and H.A.Zayed, Study of Electrical and optical properties of $Cd_{1-x}Zn_xS$ thin films, Journal of Materials Science, 38, 2003, 3449-3454.

[3] D.Patidar, N.S.Saxena andT.P.Sharma, Structural, Optical and electrical properties of CdZnS thin films, Journal of Modern Optics, Vol.55, No.1,10, Jan 2008 79-88

[4] Sanjeev Kumar and B.Bhattacharya, Variation of band gap in CdPbS with composition prepared by a precipitation technique, IndianJournal of Pure & Applied Physics, Vol.43, 2005, PP. 609-611

[5] T.Shekharam, G.Yellaiah, V.LaxmiNarasimha Rao, T.Mohan Kumar and M.Nagabhushanam, Effect of Pb on Structural and optical properties of $Cd_{0.8-x}$ $Pb_xZn_{0.2}S$ mixed semiconductor compounds for optoelectronic applications, International Journal of Materials Science and Technology, Vol.3, No.2 , 2013, PP. 57-76.

[6] M.V.Gracia-Cuena and J.L.Morenza, On the electrical conductivity of Polycrystalline CdS films, Journal of Physics, D,18,10, 1985, 2081

[7] P.Marquardt, L.Borngen, G.Nimtz, R. Sonnberger, H. Gleiter and J.Zhu, Microwave absorption by small metal particles, Phys. Lett,114A 1986, 39

[8] K.Frahm, B.Muhlschlegel and R.Nemeth,Size dependent ac conductivity of small metal particles Z.Physik.B:condensed matter,78,1990,91

[9] P.J.Yetman and J.C.Gill, Size dependent threshold fields for frohlich conduction in niobium triselenide : possible evidence for pinning by the crystal surface, Solid state communications, 62,3, 1987, 201

[10] P.Marquardt, G.Nimtz, and B.Muhlschlegel, On the quasi – static conductivity of sub micrometer crystals, Solid state communications, 65, 6, 1988, 539

[11] M.Nagabhushanam, E.Nagabhushan, D.Jayaprakash, B.Rajam and K.Yadaiah, Growth characterization and transport properties of $Pb_xZn_{1-x}S$ mixed crystals, Bull.Meter.Sci., Vol.32, No.1.2009, PP.109-115

[12] K.Hadasa, G.Yellaiah and M.Nagabhushanam, Effect of Copper dopant on Structural, optical and electrical properties of $Cd_{1-x}Zn_xS$ films grown by chemical bath deposition method, Bulletin of Material Science, 2012

[13] G.Yellaiah, K.Hadasa and M.Nagabhushanam, Structural, optical and irrational studies of Na^+ doped $Cd_{0.8}Zn_{0.2}S$ Semiconductor compounds, journal of alloys and compounds, 581, 2013, 805-811

[14] G.Yellaiah, K.Hadasa and M.Nagabhushanam, Growth, Characterization, optical and vibrational properties of Sm^{3+} doped $Cd_{0.8}Zn_{0.2}S$ semiconductor compounds, journal of crystal growth,386, 2014, 62-68

[15] K.Yadaiah, K.Hadasa, G.Yellaiah, E.Nagabhushan and M.Nagabhushanam, Structural parameters of $(CdSe)_{1-x}$ $(ZnS)_x$, mixed semiconductors, journal of Material Science Research India, Vol.6 (2), 2009, 263-278

[16] S.Rajathi, N.Sankarasubramanian, K.Ramanathan and M.Senthamizhselvi, Structural and optoelectronic properties of pyralytically sprayed CdZnS thin films, Chalcogenide Letters, Vol.9, No.12, 2012, PP.495-500

[17] V.Kumar, V.Singh, S.K.Sharma, etal., Structural and optical properties of sintered $Cd_{1-x}Zn_xS$ films, Opt.Mater.,11,29,1998

[18] T.P.Sharma, Dinesh Patidar, N.S.Saxena and Kananbala Sharma, Measurement of Structural and optical band gaps of $Cd_{1-x}Zn_xS$ (x=4 and x=6) Nano materials, Indian Journal of Pure & Applied Physics, Vol.44, 2006, PP.125-128

[19] H.A.Zayed, A.M.Abo-Elsoud, B.A.Mansour and A.M.Ibrahim, Dependence of transport and optical properties of amorphous SbSe films on temperature of heat treatment, Indian Journal of Pure & Applied Physics, Vol.32, April 1994, PP.334-340.

[20] D.PathinettamPadiyan, A.Marikani and K.R.Murali, Influence of thickness and Substrate temperature on electrical and photoelectrical properties of vacuum deposited CdSe thin films, Materials Chemistry and Physics, 78, 2002, 51-58

[21] H.M.Rosenberg, The solid state, third edition (Oxford University Press, Oxford, 1989)P.285

[22] G.N.Greaves, Journal of Non-Crystalline solids, 11, 1973, 427.