Electrical and Thermoelectric properties of Cu doped $Cd_{0.8}Zn_{0.2}S$ Compound prepared by modified Co-precipitation method

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Abstract: *$Cd_{0.8}Zn_{0.2}S$ compounds doped with different mol % of Cu (1.3, 2.5, 3.8, 5.0 and 6.1) have been prepared by modified chemical co-precipitation method (CCP method). Bulk $Cd_{0.8}Zn_{0.2}S$ compounds have been prepared by adopting two different ways of mixing the solutions of constituent elements named as CCP-I & CCP-II. XRD studies have shown that the compounds grown by both methods are of polycrystalline nature. SEM micrographs have shown that the crystallites in CCP-I grown samples have needle like shape whereas the samples grown by CCP-II failed to show clear shape of the crystallites . The dc-electrical conductivity of all the samples grown by CCP-I & II are more than the undoped sample and the conductivity change in CCP-I samples is more than that of CCP-II samples. The variation in activation energy at low temperature region is more or less uniform than at high temperature region in CCP-II grown samples. TEP measurements have shown that all the samples have p-type semiconductor nature. Mobility of charge carrier was found to increase with the increase in temperature. This is governed by the scattering mechanism associated with inter-grain barrier height. It is observed In all the samples that the sum of the activation energy due to charge carriers and grain boundary potential is equal to the activation energy due to conductivity.*
Keywords: *Ternary semiconductor compounds, CCP method, Structural properties, Electrical and Thermoelectric properties.*

I.   Introduction

Solid solutions of binary or ternary alloy semiconductors are of scientific interest as their properties can be tailored to meet specific requirements in device fabrication. Particularly, II-VI compounds can form ternary and quaternary alloys with a direct fundamental band gap over the entire composition range and with high absorption coefficient. Mixed compound semiconductors like $Cd_{(1-x)}Zn_xS$, $Cd_{(1-x)}Zn_xSe$, $CdSe_{(1-X)}Te_X$, $In_{1-x}Ga_xSd_{1-y}As_y$ have potential applications in the fabrication of Photoconductive, Photovoltaic and Solar cells in the field of electronic and optoelectronic devices[1,2]. These compounds have been prepared in thin film form by using sophisticated techniques[3-5] to help the process of miniaturization of electronic devices. In general, it is also not simple to prepare bulk material over a wide range of composition due to limited solubility.

Recently, attention is directed towards low temperature chemical synthesis of high quality water soluble alloy nanocrystals. This simple chemical route gives a chance to control the crystalline size, crystalline distribution and most importantly to improve the crystallinity by altering the concentration of the reagents and their mixing rate at different temperatures [6]. Doping these materials with different activator ions gives not only the required emission properties but also creates intrinsic defects giving rise to photoconductive properties [7]. Doped semiconductor nanocrystals, as an important family of semiconductor nanocrystals, have attracted much attention due to their apparent merits, such as larger ensemble Stokes shift to reduce self-quenching and insensitivity to thermal and photochemical disturbances[8].There are numerous reports on optical properties of various metal and rare-earth ion doped CdS, ZnS, ZnSe and CdSe nanostructures, but studies on their doped alloy compounds/ nanostructures are still very limited[9-12]. To the best of our knowledge there are reports by Karar et.al. on the optical properties of Ag ion doped $Cd_{1-x}Zn_xS$ alloy systems[13], Ruchisethi et.al.on visible emission studies of Ag-doped CdZnS alloy quantum dots[14] and Alaa A.Al. Jubory on the effect of structural and optical properties of copper doped $Cd_{0.7}Zn_{0.3}S$ nano thin films prepared by chemical bath deposition[15],and studies on $Zn_x Cd_{1-x}S$ thin films doped with Cu , Sn ,In, and F [16-19].Though several techniques were used to prepare undoped/ doped CdZnS thin films/ bulk material, chemical bath deposition(CBD)/ Chemical Co-precipitation(CCP) methods have been into usage as these methods involve low temperature and avoids oxidation and corrosion. The properties of CBD/CCP grown compounds are strongly dependent on the preparation conditions such as temperature, stirring rate and time, relative concentrations, type of reactants and the mixing process of reactants [20-22].

In view of the process dependent characteristics and applications of $Cd_{0.8}Zn_{0.2}S$ compound semiconductor, an attempt has been made to prepare it in bulk form with different concentrations of Cu as

dopant by Chemical Co-precipitation method by adopting two different procedures of mixing the solutions of the constituent elements named as CCP-I & CCP-II. The compounds are characterized and their structural, electrical and thermal properties have been investigated by using XRD, SEM, EDAX, DC electrical conductivity and TEP studies. The results are explained based on altered interaction between impurity and grain boundary in CCP-I & CCP-II grown compounds.

II.   Experimental

$Cd_{0.8}Zn_{0.2}S:Cu_x$ compounds have been prepared by two methods of Chemical Co-precipitation. In the first method, aqueous solutions of Cadmium acetate(0.5M), Zinc acetate(0.5M), Thiourea(1M), Triethanolamine(0.5M) and $CuSO_4$ (0.25M) in proportionate were taken in a beaker to prepare $Cd_{0.8}Zn_{0.2}S:Cu$. The solution mixture was made alkaline by adding 25% of liquid ammonia under constant stirring process. The solution was gradually heated to 80°C(±2°) in order to complete the reaction and to obtain the compound in the form of precipitate. This method is referred as CCP-I method.

In the second method, chemicals, taken in stoichiometric weight percentage were added to preheated water (fixed volume) at 80°C(±2).Here, the fixed volume of water is the accounted volume of water that was used to make a solution mixture for the preparation of the compound by CCP-I. And then, 25% of liquid ammonia was added to make the solution alkaline. The chemical bath was continued to be at 80°C for about 90 min. After the chemical reaction, the precipitate was separated, rinsed in double distilled water, dried at room temperature for 24 hrs. This method of preparation is referred as CCP-II method.

The dried precipitates obtained by CCP-I & CCP-II methods were heated in nitrogen atmosphere for 1 hr at 300°C and made into pellets of 1.4 cm diameter and 1mm thickness. These pellets were sintered at 800°C for 2 hr in nitrogen atmosphere. Fine details of the entire process was described in our earlier publication[23,24].

$Cd_{0.8}Zn_{0.2}S$ compounds doped with different amounts of Cu (1.3, 2.5, 3.8, 5.0 and 6.1 mol %) were prepared by CCP-I & CCP-II. Structural, electrical and thermoelectric properties of these samples were made by using XRD (PHILIPS- PAN ANALYTICAL X'PERT PLUS), SEM (ZEISS EVO-18),a two-probe technique interfaced with Keithley 6220 Precision current source and Keithley 182 Sensitive digital Voltmeter and Keithley multimeter Model to measure the output of the temperature sensor(copper-constantan thermocouple) . The X-ray diffractograms are recorded with a step size 0.02 degrees/sec(2 theta) indicating an accuracy of ±0.02° in the measurement of 2θ.The dc electrical conductivity(σ) of $Cd_{0.8}Zn_{0.2}S:Cu$ compounds prepared by CCP-I & II have been determined by two-probe technique in the temperature range(77-300K).

III.   Results And Discussion

3.1 XRD Studies

X-ray diffractograms of $Cd_{0.8}Zn_{0.2}S:Cu$ compounds prepared by CCP-I and II methods are shown in Fig1(a) and (b) respectively. Both the figures show sharp diffraction peaks indicating that they have polycrystalline nature. The peaks were indexed by comparing their positions with the standard ICDD-JCPDS data(card no. 400435) of $Cd_{0.8}Zn_{0.2}S$ (Hexagonal) structure. It was found that the compounds prepared by both the methods have same Hexagonal structure and did not show any change in the crystal phase.

3.2 SEM Studies

SEM micrographs of samples prepared by CCP-I shows crystallite structures(Fig 2a), whereas such crystallites are not clearly seen in the samples prepared by CCP-II(Fig 2b). This may be due to the change in the method of compound preparation in CCP-II. The crystallites observed in CCP-I samples have needle like structure in undoped compound and the structure is hexagonal in Cu doped samples. The compositional analysis (EDAX data) has confirmed (nearly) the nominal composition of all the CCP-I & II grown samples.

3.3 Electrical Studies

The variation of electrical conductivity with temperature of all $Cd_{0.8}Zn_{0.2}S:Cu$ compounds grown by CCP-I & II are shown in Fig 3 &4 respectively.

From these figures, one can observe that the conductivity of the samples prepared by CCP-I increases with the increase in Cu concentration whereas in samples prepared by CCP-II, it increases with the Cu concentration till 3.8% of Cu and decreases slightly with further increase in Cu concentration. The conductivity of doped samples are more than the undoped in both CCP-I & II grown sample and the deviation in conductivity in CCP-I samples is more than that of CCP-II grown samples. Recently the photoconductivity results of Cu doped CdZnS are reported to have 4 orders of increase in conductivity due to incorporation of Copper[25]. The rise in conductivity in CCP-I samples at low concentrations of Cu may be due to the carrier movement along the grain boundary (grain boundary conduction). At higher concentrations of Cu, the scattering of carriers due to boundaries may increase and the Cu impurities enter into defect sites of the crystals. Hence the variation in

conductivity may be due to the above two contributions resulting in increase in conductivity with rise in Cu concentration. HankeXie et al [26] have also observed grain boundary trapping of Cu impurities in CdS films grown by thermal evaporation from the anamolous behaviour of electrical conductivity. However such anomaly is not observed in Cu doped CdZnS bulk samples by CCP-I & II methods.

In CCP-II grown samples the rise in conductivity till 3.8% of Cu may again be due to the carrier movement along the boundaries and for higher concentrations the Cu impurities may be due to trapping of Cu impurities at large number of grain boundaries. Further the possibility of the creation of more grain boundaries in CCP-II process i.e., sudden crystallization , helps the impurity trapping.

The activation energies of all the samples from the conductivity variation with temperature have been calculated using the relation

$$\sigma = \sigma_o \exp[-E_a/kT]$$ ---(1)

where E_a is the activation energy, σ_o is a constant, k is the Boltzmann constant and T is the absolute temperature. Using this equation, the activation energies are calculated at high and low temperature regions, in which the conductivity varied linearly with temperature, are given in Table.1.

From the Table.1, we observe that the activation energy in samples of different concentrations of Cu prepared by CCP-I & II is almost the same in the low temperature region. From this result one may infer that the impurity(Cu) is going to the same defect sites(grain boundary) in both CCP-I & II grown samples. At low temperatures, the carriers are bound to the lattice in CCP-I & II grown samples. The activation energy of CCP-II samples is slightly higher than those of CCP-I samples which may be due to sudden and random distribution of impurity ions and making strong bonds with the lattice atoms.

3.4 TEP Studies

The thermo emf (TEP) measurements have been carried out on these samples by establishing temperature gradient across the thickness of the sample and by measuring the open circuit voltage. The temperature dependence of TEP of $Cd_{0.8}Zn_{0.2}S$:Cu compounds prepared by CCP-I and CCP-II methods are shown in Fig 5 and 6 respectively. In all the samples, thermo emf is found to be positive which indicates that they have p-type semiconductor nature. The related equation for thermo emf is given as (Ravich et al 1968)

$$p = \frac{k}{e}\left[\left(r+\frac{5}{2}\right) + \ln 2\left(\frac{2\pi m_d kT}{nh^3}\right)\right]$$ --------------------------------------(2)

where $r + 5/2 = A$, is the thermoelectric factor, which depends on various scattering mechanisms, m_d the density of state effective mass and n the carrier density. Solving the above equation we can write the equation for the carrier concentration as

$$\log n = 3/2 \log T - 0{\cdot}005(TEP) + 15{\cdot}718.$$ -----------------------------------(3)

The carrier concentration is then calculated from the above relation. The observed carrier concentration is of the order of 10^{18}- 10^{19} cm^{-3}. Fig 7 and 8 shows the typical variation of log n vs10^3/T of$Cd_{0.8}Zn_{0.2}S$(doped with 3.8 mol% of Cu) compound prepared by CCP-I and CCP-II methods. The plots are governed by an equation $n = n_o \exp(-E_n/KT)$ and exhibit two regions showing two conduction mechanisms. The activation energies of electron density (E_{an}) in both low and high temperature regions have been determined and tabulated in Table.2. Further the data is analysed by obtaining the charge carrier mobility using the relation

$$\mu = \sigma/(ne).$$ --------------------(4)

It is observed that the mobility increases in all the samples with rise in temperature and the increase of mobility shows two different temperature regions (i.e., lower and higher) suggesting that the electrical transport properties of$Cd_{0.8}Zn_{0.2}S$:Cu samples are governed by the scattering mechanism associated with intergrain barrier height (Peritz 1956).Further the mobility in such cases is activated by temperature and obeys exponential behaviour as

$$\mu = \mu_0 T^{-1/2}\exp(-\phi_B/kT),$$ -------------------------(5)

where ϕ_B is the height of the grain barrier potential and can be determined from the slope of the variation of log ($\mu T^{1/2}$) vs 1/T (Fig 9 & 10). The heights of the grain barrier potential corresponding to both the temperature regions (lower and higher) are determined from these graphs and have been tabulated in Table.3. And μ_0 is the exponential factor, which on the assumption that the current over the barrier flows by thermo-ionic emission depends on the grain size (d) and the effective mass of electron(m*) as

$$\mu_0 = ed/(2\pi m^*kT)^{1/2}.$$ ------------------------------(6)

From the observed values of the activation energies calculated from electrical conductivity ($E_{a\sigma 1}$, $E_{a\sigma 2}$) and electron density (E_{an1}, E_{an2}) and potential barrier heights of the grain boundaries (ϕ_{B1}, ϕ_{B2})of all

theCd$_{0.8}$Zn$_{0.2}$S:Cu samples, it may be observed that they are related with each other in two regions. The observed relation for higher temperature region is

$E_{a\sigma 1} = E_{an1} + \phi_{B1}$.

It also satisfies a similar relation for lower temperature region,

$E_{a\sigma 2} = E_{an2} + \phi_{an2} + \phi_{B2}$.

These two above equations are expected from the interrelationship between electrical conductivity, carrier density and mobility (Heikes and Ure 1961; Micocci et al 1995). A similar result was also observed (Mullik et al 1996).

The variations of these activation energies calculated from electrical conductivity ($E_{a\sigma 1}$, $E_{a\sigma 2}$) and electron density (E_{an1}, E_{an2}) and potential barrier heights of the grain boundaries (ϕ_{B1}, ϕ_{B2})of all theCd$_{0.8}$Zn$_{0.2}$S:Cu samples with respect to different mol% of Cu are shown in Fig 11, 12 &13.

From the graphs, we observe that the variation of activation energies from electrical conductivity, electron density and potential barrier heights of the grain boundaries of CCP-I grown samples both at low temperature and high temperature are the same, but for CCP-II grown samples the variation of activation energies at low temperature are more or less uniform than at high temperature region. Due to stress variations, various no of defects are formed and get activated differently at high temperature region and have low activation energies.

IV.   Conclusions

1.   X-ray diffraction studies on Cd$_{0.8}$Zn$_{0.2}$S:Cu compounds revealed that they possessed   polycrystalline nature with hexagonal crystal structure.
2.   SEM micrographs showed that the crystallites in undoped Cd$_{0.8}$Zn$_{0.2}$S sample grown by CCP-I have needle like shape whereas no such crystallite shapes are seen in samples grown by CCP-II.
3.   The conductivity values of all the samples grown by CCP-I & II are more than that of undoped sample and the variation in conductivity with dopant concentration in CCP-I samples is more than the variation observed in samples grown by CCP-II. This difference may be due to the possibility of more grain boundary conduction in CCP-1 samples.
4.   The increase in mobility ,in all samples, with rise in temperature is governed by the charge carrier scattering mechanism associated with inter-grain barrier height.
1.   In all the samples, the sum of the activation energy due to charge carriers and grain boundary potential is equal to the activation energy due to conductivity.
2.   The variation of activation energies at low temperature are more or less uniform than at high temperature region in CCP-II grown samples.

Acknowledgement

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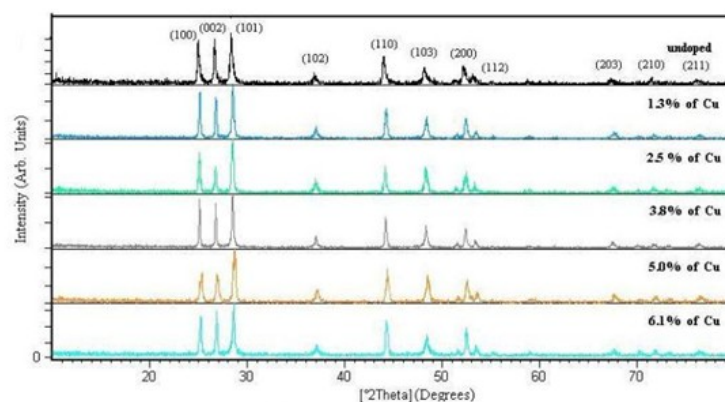
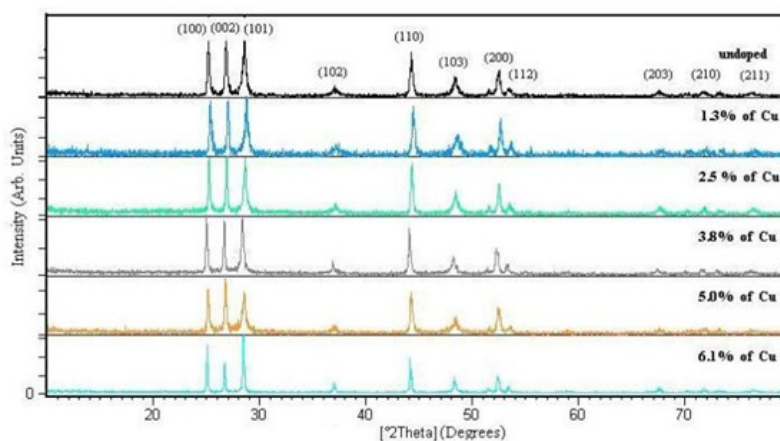Figure 1(a) XRD patterns of $Cd_{0.8}Zn_{0.2}S$:Cu compounds prepared by CCP-I method.

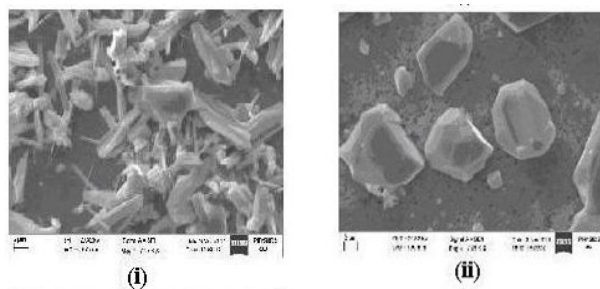Figure 1(b) XRD patterns of $Cd_{0.8}Zn_{0.2}S$:Cu compounds prepared by CCP-II method.

Figure 2(a) SEM of CCP-I grown samples (i) $Cd_{0.8}Zn_{0.2}S$ (undoped)
(ii) $Cd_{0.8}Zn_{0.2}S$ doped with 2.5 mole % of Cu
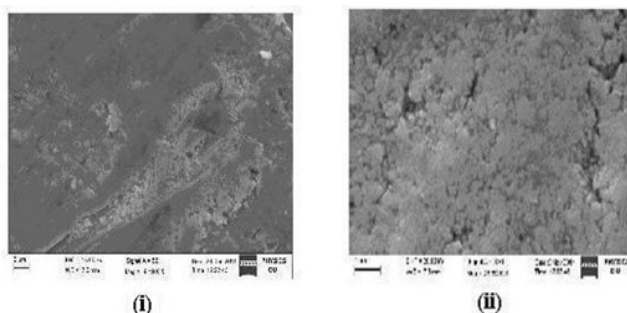

Figure 2(b) SEM of CCP-II grown samples (i) $Cd_{0.8}Zn_{0.2}S$ (undoped)
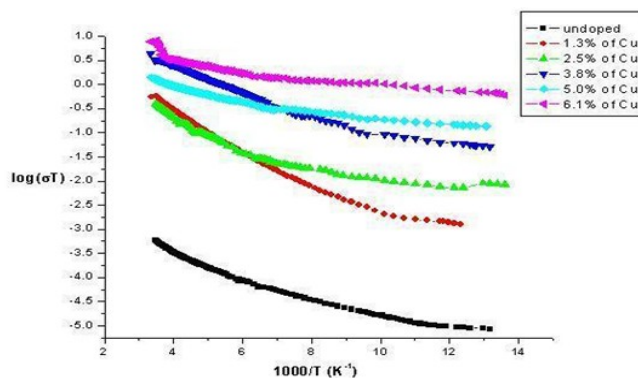(ii) $Cd_{0.8}Zn_{0.2}S$ doped with 2.5 mole % of Cu

Figure 3. Variation of Electrical conductivity with Temperature of
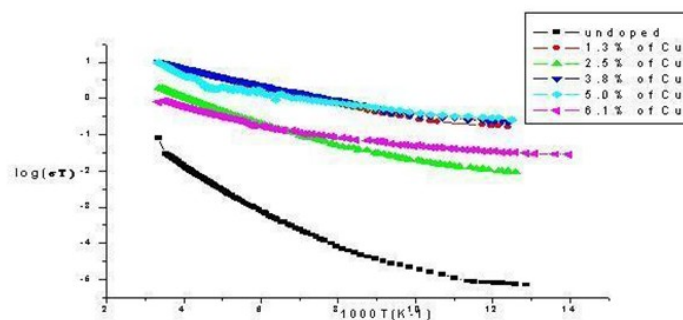$Cd_{0.8}Zn_{0.2}S$:Cu compounds prepared by CCP-I method.

Figure 4. Variation of Electrical conductivity with Temperature of
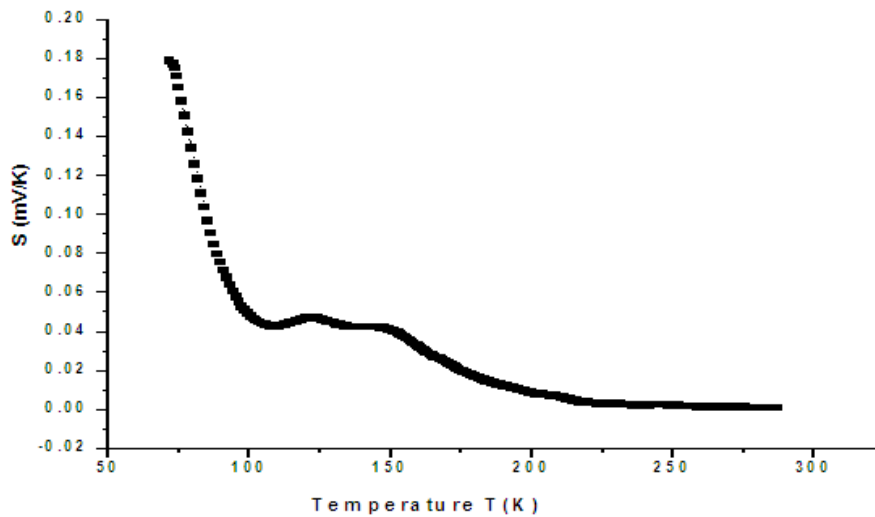$Cd_{0.8}Zn_{0.2}S$:Cu compounds prepared by CCP-II method.

Fig.5(a) TEP graph of $Cd_{0.8}Zn_{0.2}S$(undoped) compound prepared by CCP-I method.
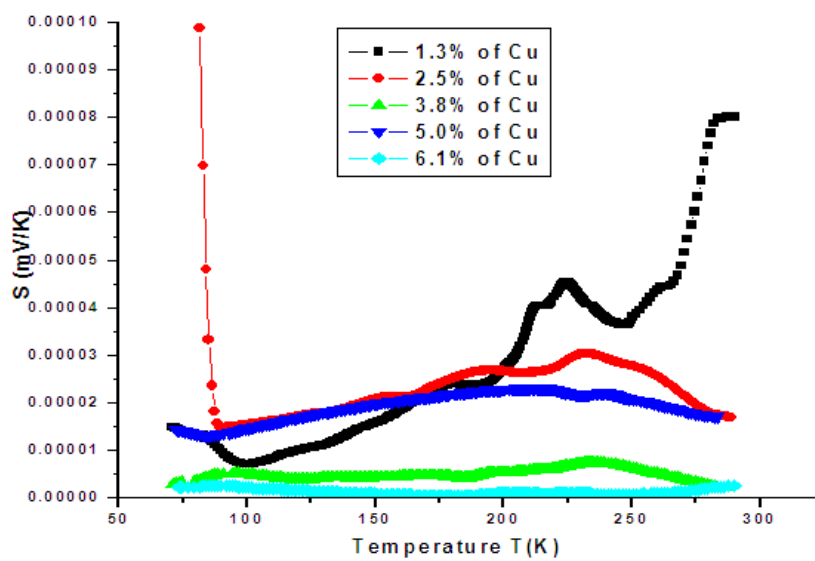
Fig.5(b) TEP graphs of $Cd_{0.8}Zn_{0.2}S$ doped with different mole% of Cu
prepared by CCP-I method.
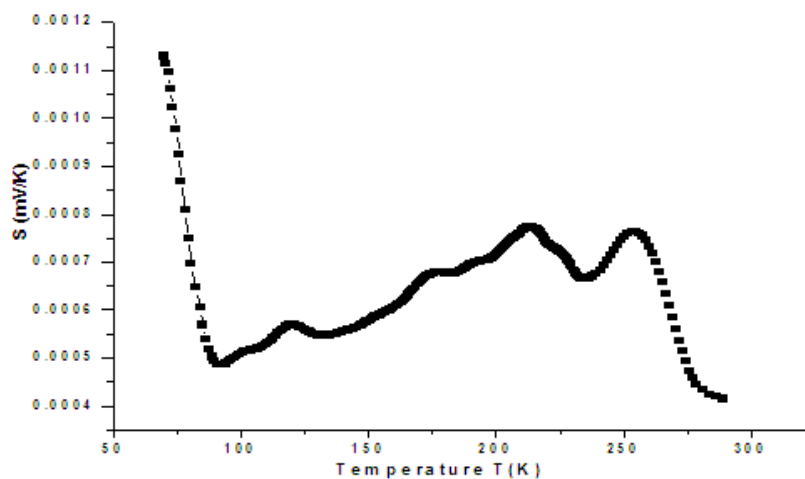
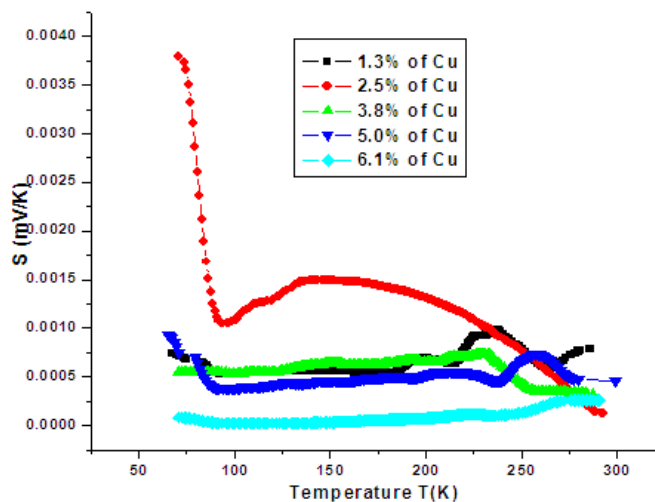**Fig .6(a)** TEP graph of $Cd_{0.8}Zn_{0.2}S$(undoped) compound prepared by CCP-II method.

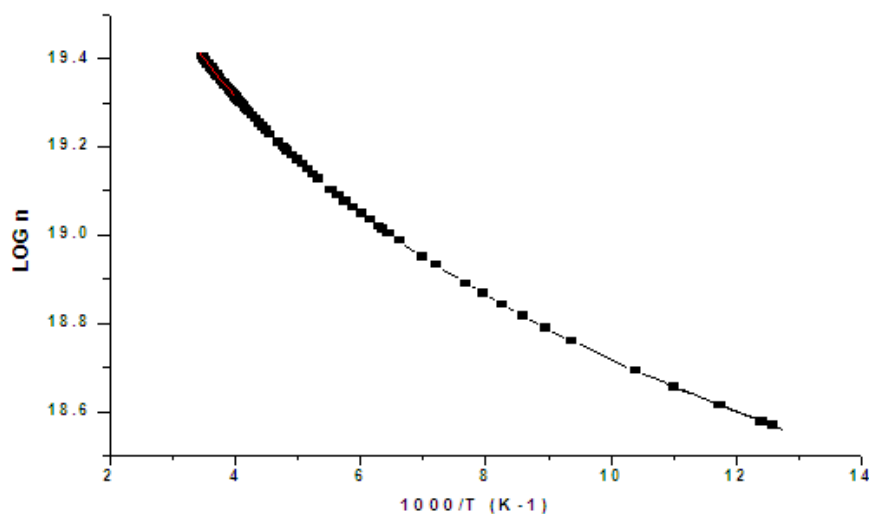**Fig.6(b)** TEP graphs of $Cd_{0.8}Zn_{0.2}S$ doped with different mole% of Cu prepared by CCP-II method.

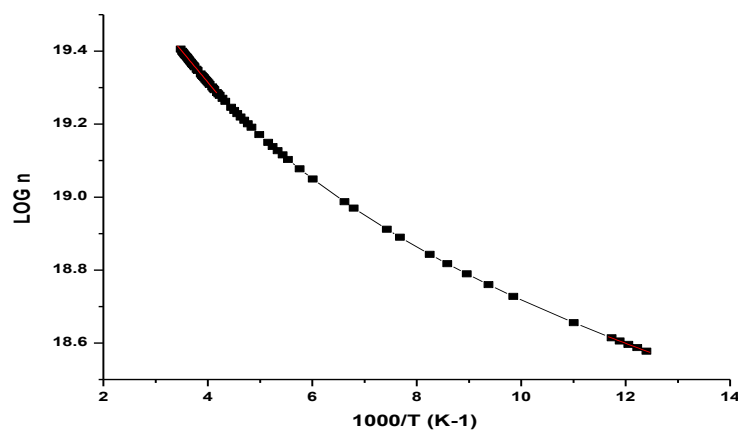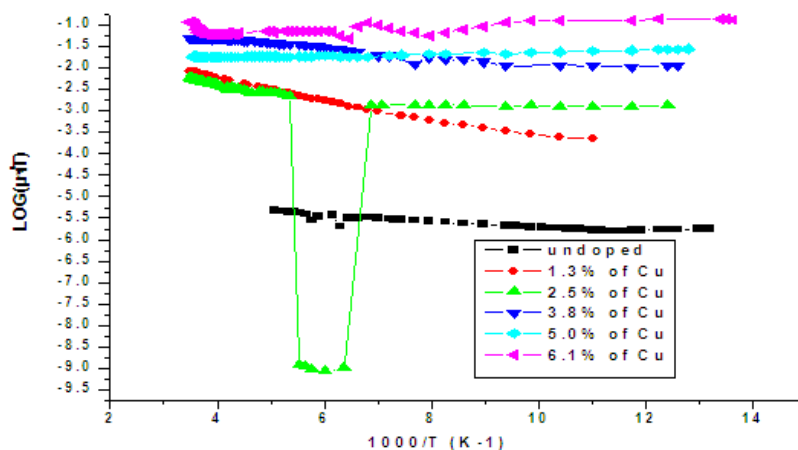Fig.7 Variation of log n vs $10^3/T$ of $Cd_{0.8}Zn_{0.2}S$ doped with 3.8 mole% of Cu prepared by CCP-I method.

Fig.8 Variation of log n vs $10^3/T$ of $Cd_{0.8}Zn_{0.2}S$ doped with 3.8 mole% of Cu prepared by CCP-II method.

Fig.9 Variation of log ($\mu T^{1/2}$) vs 1000/T of $Cd_{0.8}Zn_{0.2}S$ compounds doped with different mole% of Cu prepared by CCP-I method.
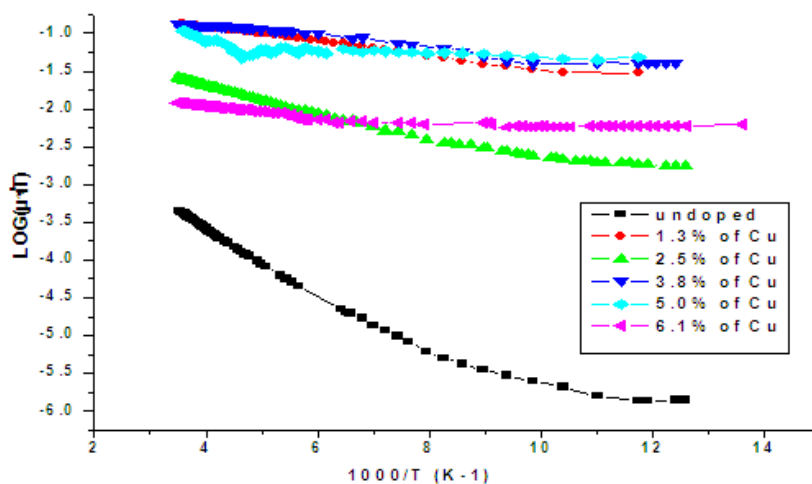

Fig.10 Variation of log ($\mu T^{1/2}$) vs 1000/T of $Cd_{0.8}Zn_{0.2}S$ compounds doped with different mole% of Cu prepared by CCP-II method.
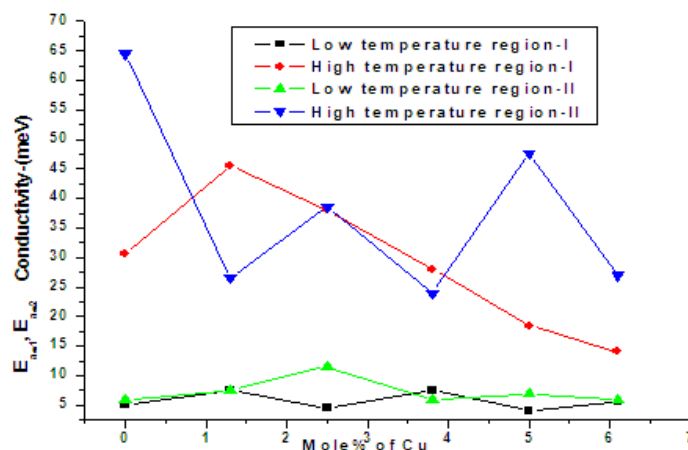

Fig.11 Variation of activation energies ($E_{a\sigma1}$, $E_{a\sigma2}$) from electrical conductivity of $Cd_{0.8}Zn_{0.2}S$:Cu compounds prepared by CCP-I & II method for different mole % of Cu.
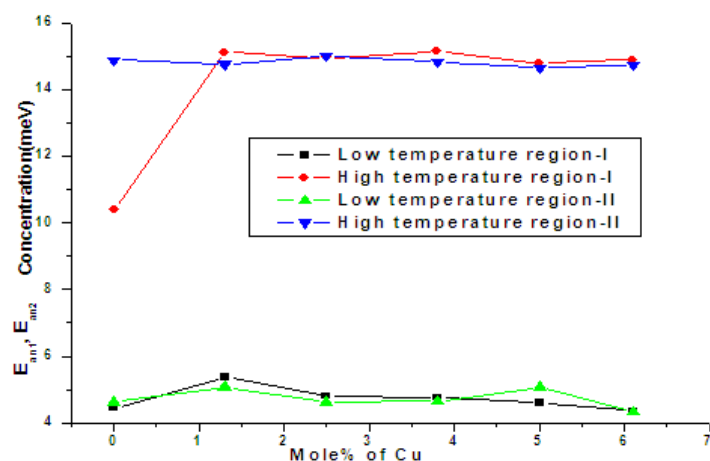
Fig.12 Variation of activation energies (E_{an1}, E_{an2}) from electron density of $Cd_{0.8}Zn_{0.2}S$:Cu compounds prepared by CCP-I & II method for different mole % of Cu.
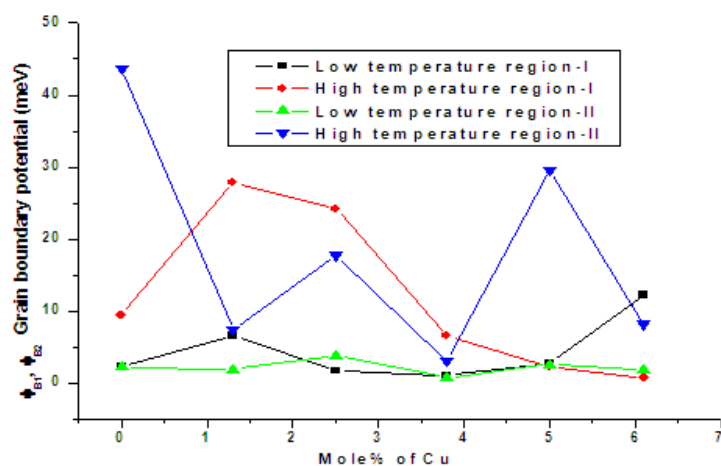

Fig.13 Variation of activation energies from potential barrier heights of the grain boundaries (ϕ_{B1}, ϕ_{B2}) of $Cd_{0.8}Zn_{0.2}S$:Cu compounds prepared by CCP-I & II method for different mole % of Cu.

Table 1: Activation energies of conductivity, concentration and grain boundary potentials of $Cd_{0.8}Zn_{0.2}S$ compounds doped with different mole% of Cu prepared by CCP-I & II methods at low and high temperature region.

Mole% of Cu	CCP-I						CCP-II					
	E_{an} I(meV)		E_{an} I(meV)		φ_B I (meV)		E_{an} II(meV)		E_{an} II(meV)		φ_B II(meV)	
	L	H	L	H	L	H	L	H	L	H	L	H
Undoped	05	30.5	4.44	10.39	2.30	9.48	06	64.5	4.62	14.89	2.30	43.78
1.3	7.5	45.5	5.38	15.12	6.59	27.80	7.5	26.5	5.08	14.76	1.96	7.57
2.5	4.5	38	4.80	14.96	1.77	24.29	11.5	38.5	4.62	15.01	3.83	17.77
3.8	7.5	28	4.76	15.14	1.10	6.60	06	24	4.65	14.84	0.82	3.08
5.0	04	18.5	4.59	14.79	2.82	2.28	07	47.5	5.08	14.66	2.64	29.64
6.1	5.5	14	4.36	14.90	12.26	0.804	06	27	4.33	14.74	1.87	8.24