

Original Research

Effect of Zinc additive on dielectric properties of Cd–Se glassy system

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Abstract

Cd₅Se_{95-x}Zn_x ($x=0, 2, 4, 6$) glassy alloy has been prepared by a melt-quenching technique. Thin films were deposited by thermal coating unit on ultraclean glass substrate under a vacuum of 10^{-6} Torr. The absence of any sharp peaks in the X-ray diffraction confirms the amorphous nature of thin films. The frequency and temperature dependence of dielectric constant and dielectric loss in the frequency range of 1 kHz to 1 MHz and in the temperature range of 290–370 K were studied. Dielectric dispersion was observed when Zinc (Zn) was incorporated into the Cd–Se system. The increase in dielectric parameter with Zn concentration may be due to increase in defect states. The DC conductivity has been reported to investigate the effect of Zn concentration on DC conduction loss. The results are interpreted in term of dipolar theory for Cd₅Se₉₅ and Cd₅Se₉₃Zn₂ samples, while the remaining samples have been explained on the basis of DC conduction loss. It was also observed that the DC conductivity increased with the increase of Zinc concentration, which may be due to the decrease in the band gap near Fermi level.

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Keywords: Amorphous semiconductor; Localized states; DC conductivity; Dielectric constant; Dielectric loss

1. Introduction

The amorphous chalcogenide (II–VI group elements) semiconductors are known for their special photovoltaic, photoconductors and optoelectronic properties [1–3]. It has been especially investigated because of their widely potential application in solar cells, electronic devices, optical detectors, sensors, narrow band filters, wave guide, coating, optical recording, imaging media in both thin films as well as bulk form [4–5]. Amorphous chalcogenide semiconductor has large number of localized states in the mobility gap, due to the absence of long range order. Therefore the measurement of the frequency dependence of electrical and dielectric properties of amorphous semiconductor has been extensively used to study the transport mechanism. Dielectric materials have been the subject of renewed attention. The study of dielectric behavior of chalcogenide semiconductors is expected to reveal structural

information, which in effect can be useful for understanding the dielectric losses as well. Alloying of chalcogenide with certain additives [6–8] like Te, Zn, Cd, etc. has produced characteristic effect on structural and transport properties. The binary alloys ZnSe and CdSe are technologically important materials due to their direct and rather large gap [9–10]. These materials can be engineered for better application purpose by varying the composition parameter (x). The addition of third element not only enhances the properties but also change the structural and compositional disorder as compare to binary alloy. The ternary alloys exhibit more flexible and are able to change their properties under the action of many external factors as light, field, particles, heat, pressure etc. Various authors have studied the structure and optical properties of CdSeZn alloy with different compositions and methods [11–14]. However the studies on dielectrics are very limited and require more understanding. In the present work, Zn is chosen as an additive because it improves the electrical, optical and dielectric properties. The dielectric study of CdSeZn reveals that dielectric dispersion exists at low frequency and high temperature. In the present work, authors reported the

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structural, dielectric and DC conductivity properties of the bulk samples (pellets) $\text{Cd}_5\text{Se}_{95-x}\text{Zn}_x$ ($x=0, 2, 4, 6$) in the temperature range of 290–370 K and in the frequency range of 1 kHz to 1 MHz.

2. Experimental

$\text{Cd}_5\text{Se}_{95-x}\text{Zn}_x$ ($x=0, 2, 4, 6$) glassy alloys were prepared by a melt-quenching technique. High purity (99.999%) elements, in appropriate amount were sealed in quartz ampoules (length ~ 13 cm and inner diameter ~ 8 mm) under a high vacuum 10^{-6} Torr. All ampoules were heated in a rocking furnace where the temperature was raised to 900 °C at a rate of 3–4 °C for 12 h followed by sudden cooling in ice cooled water. The cooling was too fast to prevent the nucleation and growth. The duration of mixing and shaking of ampoules in the furnace protect the homogeneity of the alloy. The quenched samples were removed by breaking the quartz ampoules. Thin films of these materials were prepared by thermal coating unit under a vacuum of 10^{-6} Torr on ultraclean glass substrate. Bulk samples in the form of pellets with diameter of 10mm and thickness 1 mm were obtained by finely grinding and compressing the powder by hydraulic press at a constant load of 5 t. The surface of the pellets was smoothen and coated with silver paste to obtained good electrical contacts. The bulk samples were mounted between two steel electrodes inside a metallic sample holder for dielectric measurement under a vacuum of 10^{-3} Torr. To calculate the dielectric constant (ϵ') and dielectric loss (ϵ''), the parallel capacitance and dissipation factor were measured simultaneously using LCZ (Wayne Kerr 4300 m). For DC conductivity measurement, a DC voltage of 1.5 V was applied across the sample and the resulting current was measured by a Keithley electrometer (6514). The temperature of the pellets was controlled by mounting a heater inside the sample holder and the temperature was measured by a calibrated chromel–alumel thermocouple near the electrodes.

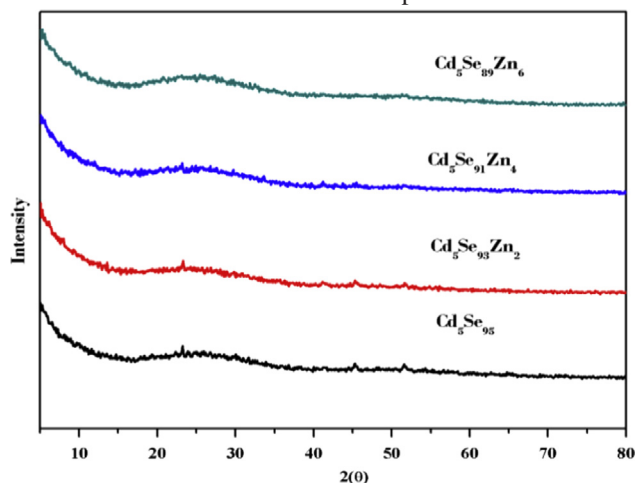


Fig. 1. XRD diffraction pattern of thin film $\text{Cd}_5\text{Se}_{95-x}\text{Zn}_x$ ($x=0, 2, 4, 6$) alloy.

3. Result and discussion

3.1. Structure investigation

X-ray diffraction patterns give valuable information about nature and structure of the samples. The copper target was used as a source of X-rays with $\lambda=1.54$ Å (Cu $K\alpha_1$). Scanning angle was in the range of 5–80°. A scan speed of 2°/min and a chart speed of 1 cm/min were maintained. X-ray diffraction pattern of $\text{Cd}_5\text{Se}_{95-x}\text{Zn}_x$ ($x=0, 2, 4, 6$) thin films are shown in Fig. 1. Absence of any sharp peak confirms the amorphous nature of thin films.

Surface morphology of the powder sample were analyzed by a scanning electron micrograph (SEM) apparatus JEOL (Model JSM 6380), which are shown in Fig. 2. SEM is a promising technique for the topographic analysis, which gives important information regarding the growth mechanism, shape and size of the samples. It can be observed that the morphology of the powdered form changes with Zinc content. The formation of contours confirms the amorphous nature of the prepared samples.

4. Temperature and frequency dependent of dielectric constant

Temperature and frequency dependence of dielectric constant ϵ' and dielectric loss ϵ'' were studied for $\text{Cd}_5\text{Se}_{95-x}\text{Zn}_x$ ($x=0, 2, 4, 6$) glassy alloys in the temperature range of 290–370 K and in the frequency range of 1 kHz to 1 MHz. The temperature dependent dielectric constant ϵ' and dielectric loss ϵ'' for $\text{Cd}_5\text{Se}_{95}$ are shown in Fig. 3(a) and (b). The values of ϵ' and ϵ'' increase with the increase of temperature and are different for different frequencies. At low temperature ϵ' and ϵ'' has been found to be almost constant and increase appreciably with increasing temperature. The increase in ϵ' with temperature may be attributed to the fact that the orientational polarization is the rotation of the dipoles in material, which involve the inelastic movement of particle, which is strongly dependent on temperature. At low temperature the dipoles do not orient themselves, as the temperature increased the orientational polarization increased, which in turn increases the ϵ' .

Fig. 4(a) and (b) shows the frequency dependence of ϵ' and ϵ'' for $\text{Cd}_5\text{Se}_{95}$ at various fixed temperatures. With the increasing frequency both ϵ' and ϵ'' decreased. The reason is that in the case of low frequency ϵ' is due to multicomponent of polarizability (electronic, atomic, orientation, space charge and hopping polarizability) [15–17]. As the frequency increase there is practically no time for building up the charges over microscopic and mesoscopic boundaries so the polarization is less. When the relaxation time is much higher than the frequency of the applied electric field, the polarization occurs instantaneously. When the relaxation time is much lower than the frequency of the applied electric field, no polarization occurs.

Fig. 5(a) and (b) shows the variation of dielectric constant (ϵ') and dielectric loss (ϵ'') with temperature at different frequencies for $\text{Cd}_5\text{Se}_{93}\text{Zn}_2$ alloy. Similar result has been observed for other concentration of Zn (result not shown here). These results show that concentration of Zinc play important role in the variation of

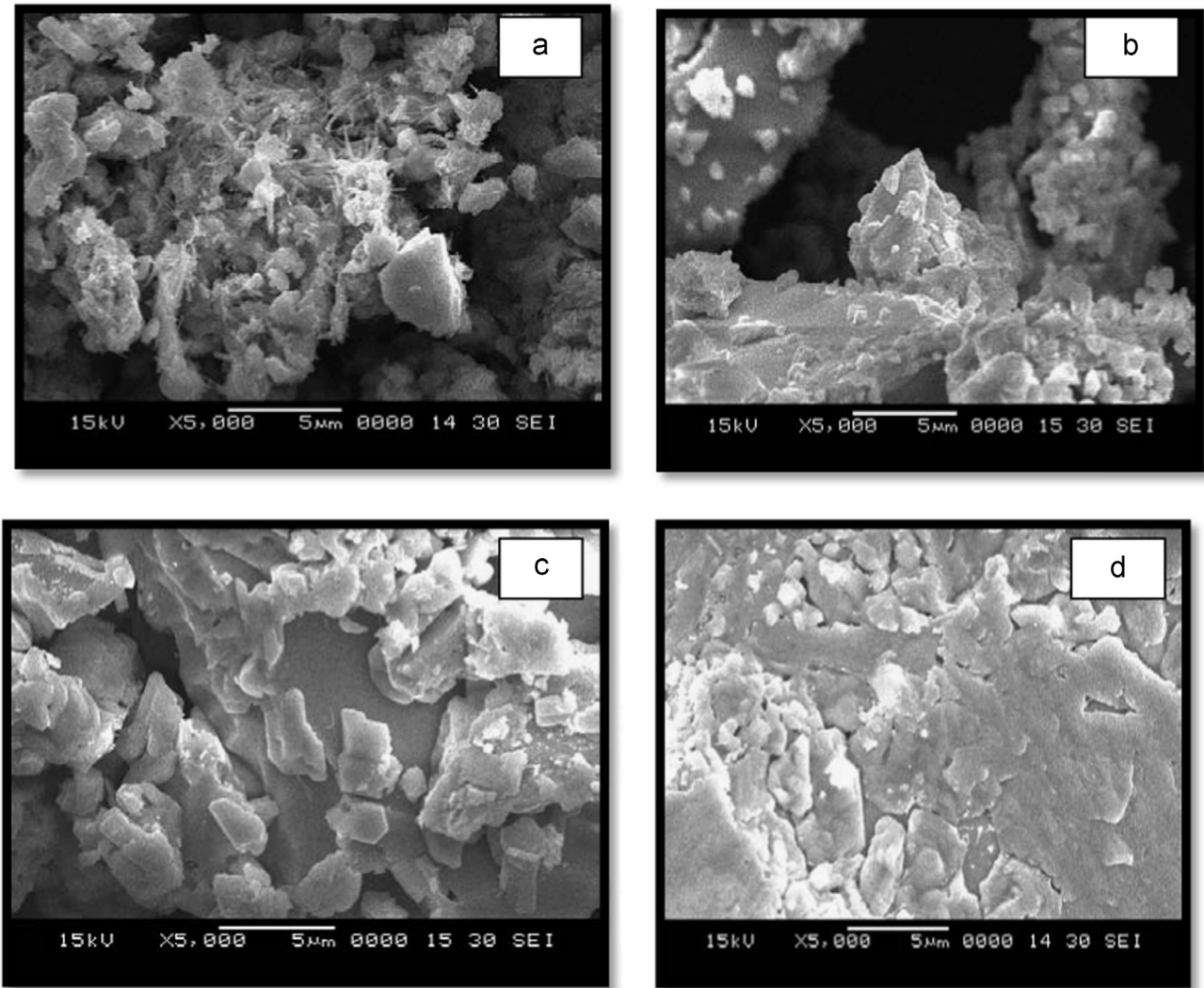


Fig. 2. SEM images of powdered form of (a) Cd_5Se_{95} (b) $Cd_5Se_{93}Zn_2$ (c) $Cd_5Se_{91}Zn_4$ and (d) $Cd_5Se_{89}Zn_6$ samples.

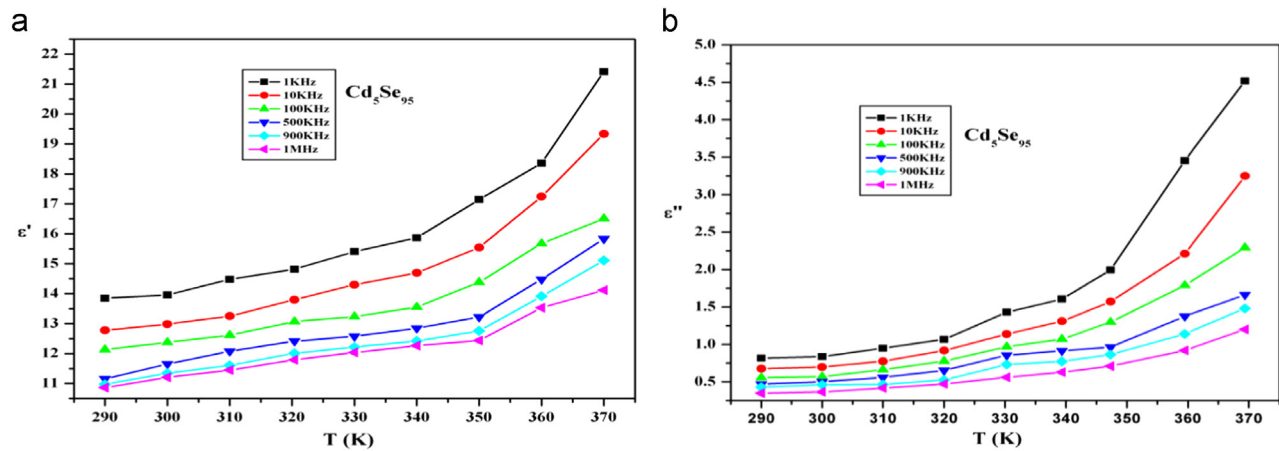


Fig. 3. (a) Dielectric constant ϵ' and (b) dielectric loss ϵ'' versus temperature at various fixed frequencies for Cd_5Se_{95} sample.

dielectric parameters with temperature. Fig. 6(a) and (b) shows the frequency dependence of dielectric constant ϵ' and dielectric loss ϵ'' at different temperature for $Cd_5Se_{93}Zn_2$.

The temperature dependence of dielectric constant ϵ' at various frequencies for CdSeZn system indicates that ϵ' varies

exponentially with temperature. The graph between $\ln \epsilon'$ versus $1/T$ is found to be a straight line (result not shown). This type of temperature dependence is generally observed in molecular solids where the Debye theory [18] for viscosity dependence of relaxation time holds quite well. According to this theory, ϵ'

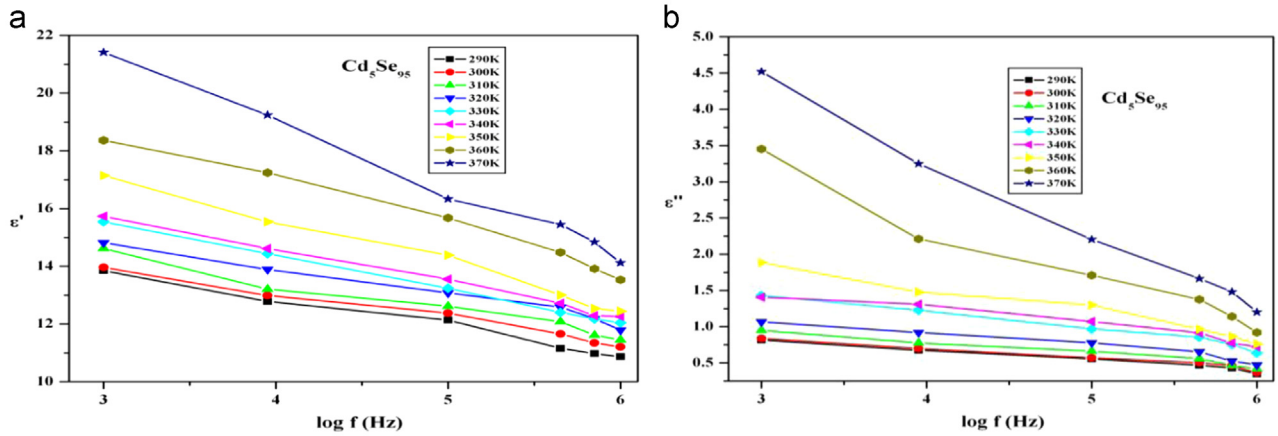


Fig. 4. (a) Dielectric constant ϵ' and (b) dielectric loss ϵ'' versus $\log f$ at various fixed temperature for $\text{Cd}_5\text{Se}_9\text{S}$ sample.

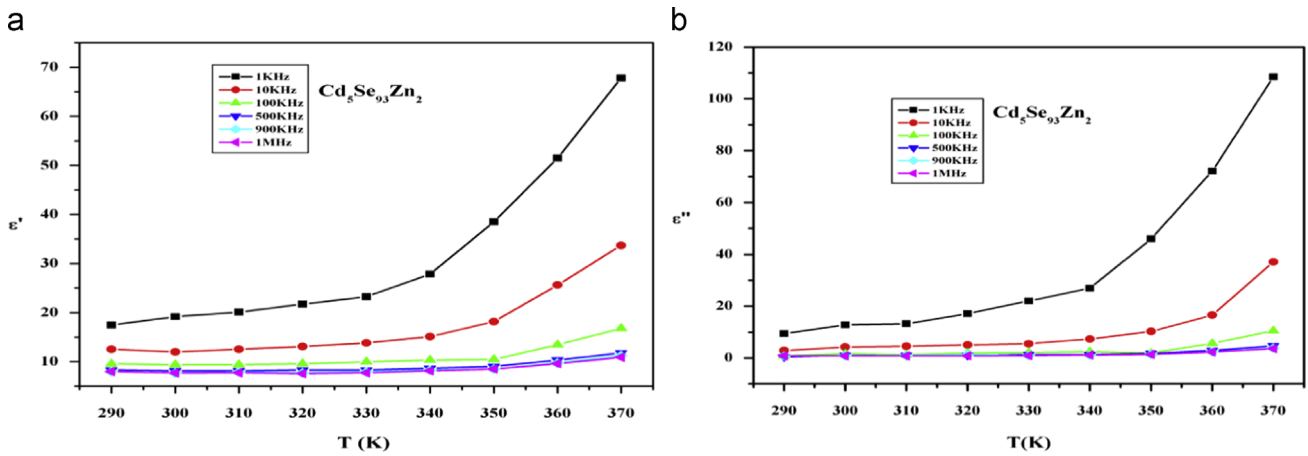


Fig. 5. (a) Dielectric constant ϵ' and (b) dielectric loss ϵ'' versus temperature at various fixed frequencies for $\text{Cd}_5\text{Se}_9\text{S}_3\text{Zn}_2$ sample.

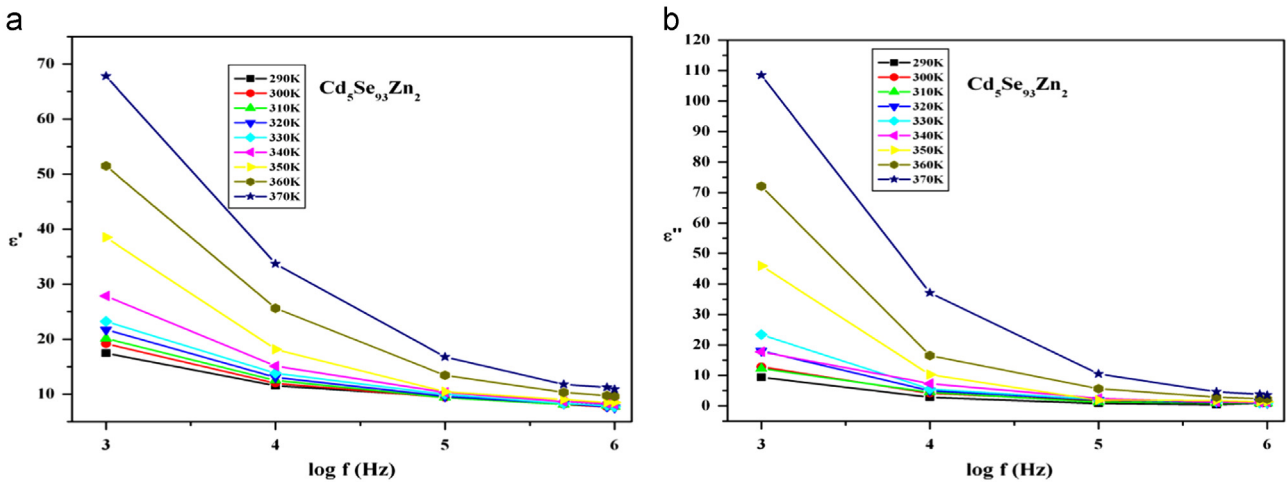


Fig. 6. (a) Dielectric constant ϵ' and (b) dielectric loss ϵ'' versus $\log f$ at various fixed temperature for $\text{Cd}_5\text{Se}_9\text{S}_3\text{Zn}_2$ sample.

should increase exponentially with temperature, and this has been found to be true in the present samples. The above discussion indicates that the dipolar-type dielectric dispersion has occurred in the present system. However, no peaks have been observed in the curve of the dielectric loss ϵ'' versus $\log f$ in the present samples as expected in the case of dipolar-type

relaxation. Such peaks may be absent because of the wide distribution of relaxation times. Guintini et al. [19] proposed a dipolar model for dielectric dispersion in chalcogenide semiconductor based on Elliott's ideas [20] of hopping of charge carriers over a potential barrier between charged defect states (D^+ and D^-) which is assume to form a dipole. Fig. 7(a) and

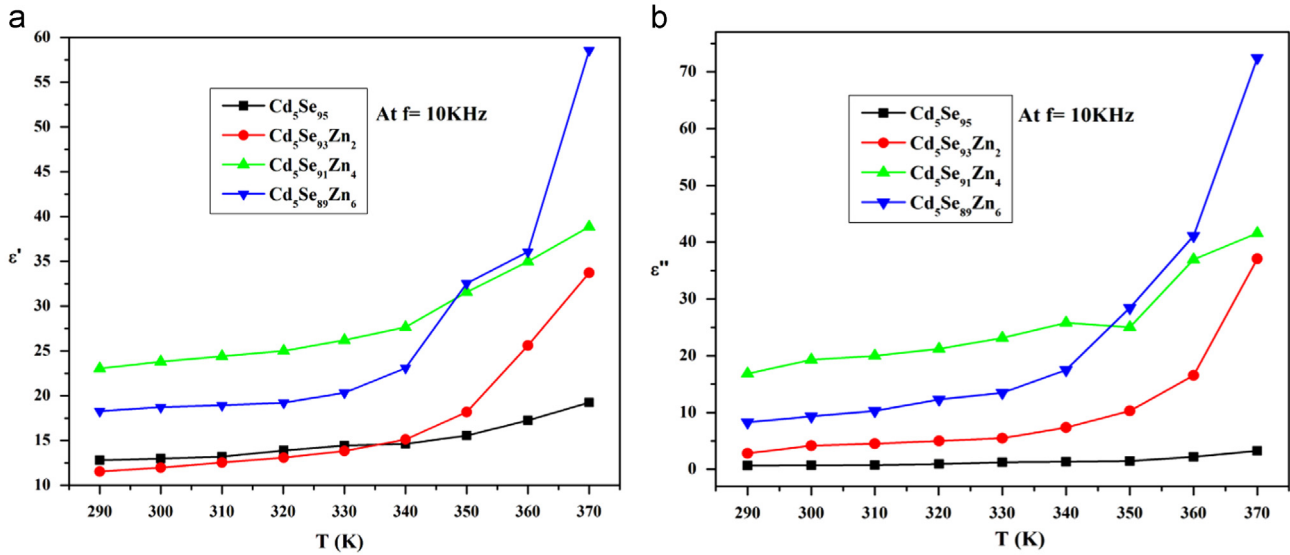


Fig. 7. (a) Dielectric constant ϵ' and (b) dielectric loss ϵ'' versus temperature at a fixed frequency of 10 kHz for $Cd_5Se_{95-x}Zn_x$ sample.

Table 1
Dielectric and electrical parameter in $Cd_5Se_{95-x}Zn_x$ at a temperature of 350 K and a frequency of 10 kHz.

Sample	ϵ'	ϵ''	$\sigma_{dc}(\Omega^{-1} \text{ cm}^{-1})$	ΔE (eV)	$\sigma_0(\Omega^{-1} \text{ cm}^{-1})$	ϵ'' (dc)
Cd_5Se_{95}	15.5	1.47	1.4×10^{-8}	0.42	8.3×10^{-3}	2.52
$Cd_5Se_{93}Zn_2$	18.1	10.28	1.9×10^{-8}	0.20	1.8×10^{-5}	3.5
$Cd_5Se_{91}Zn_4$	31.55	25.04	2.4×10^{-6}	0.28	0.0492	587
$Cd_5Se_{89}Zn_6$	33.33	28.43	2.7×10^{-4}	0.11	0.0584	6.4×10^4

(b) shows the variation of dielectric constant (ϵ') and dielectric loss (ϵ'') with different concentration of Zn at fixed frequency (10 kHz) with temperature. It is clear from the figure that both values of (ϵ') and (ϵ'') increase with the increase of Zn concentration. The numerical values are given in Table 1. These results indicate that the concentration of Zn play important role in the variation of dielectric parameters. As the concentration of Zn increases the both values of (ϵ') and (ϵ'') increase. The increase in the dielectric parameter with Zn concentration is most likely due to the increase in defect states in the band gap near the Fermi level, i.e., the hopping of charge carrier in defect state increases. Schottmiller et al. [21] have reported that in glassy Se, about 40% of atoms have ring like structure and 60% are bounded as polymeric chains. When Zn is added in Cd–Se system, it might decrease the Se ring structure and enter into the chain concentration, there by decreasing the disorderliness of Cd–Se–Zn samples. Furthermore the presence of chain concentration in the Cd–Se–Zn system results in an increasing density of defect states.

5. DC conductivity

The DC conductivity of amorphous semiconductor mostly depend on density and mobility of charge carriers. The density of carriers is small since all electrons are localized to their respective atoms, like wise mobility is also small due to the

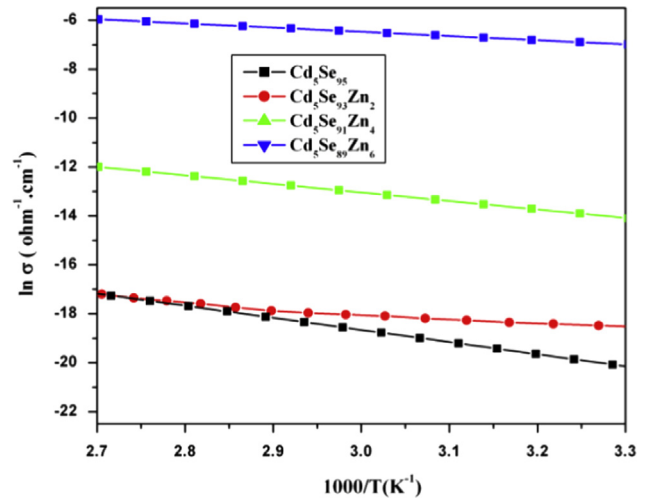


Fig. 8. $\ln \sigma_{dc}$ versus $1000/T$ for $Cd_5Se_{95-x}Zn_x$.

absence of long range order. Thus the conduction process in a-semiconductor involves a temperature dependent DC conductivity, which can be expressed by a usual relation [22]:

$$(\sigma_{dc}) = \sigma_0 \exp \left[-\frac{\Delta E}{kT} \right] \tag{1}$$

where ΔE , σ_0 , and k are the activation energy, pre-exponential factor and Boltzmann constant respectively. Fig. 8 shows the graph of $\ln \sigma_{dc}$ versus $1000/T$ in the temperature range of (300–390 K) for all samples, which were found to be straight lines, indicating that the conduction is due to thermally assisted tunneling of charge carriers in the localized states present in the band tails [23–25]. The calculated value of ΔE and σ_0 are listed in Table 1. The conducting additives in dielectric materials may have a very large effect on its electrical response. The increase in the DC conductivity with Zinc concentration is mainly due to the increase in the density of localized state in the mobility gap. The presence of additives might increase the concentration of the

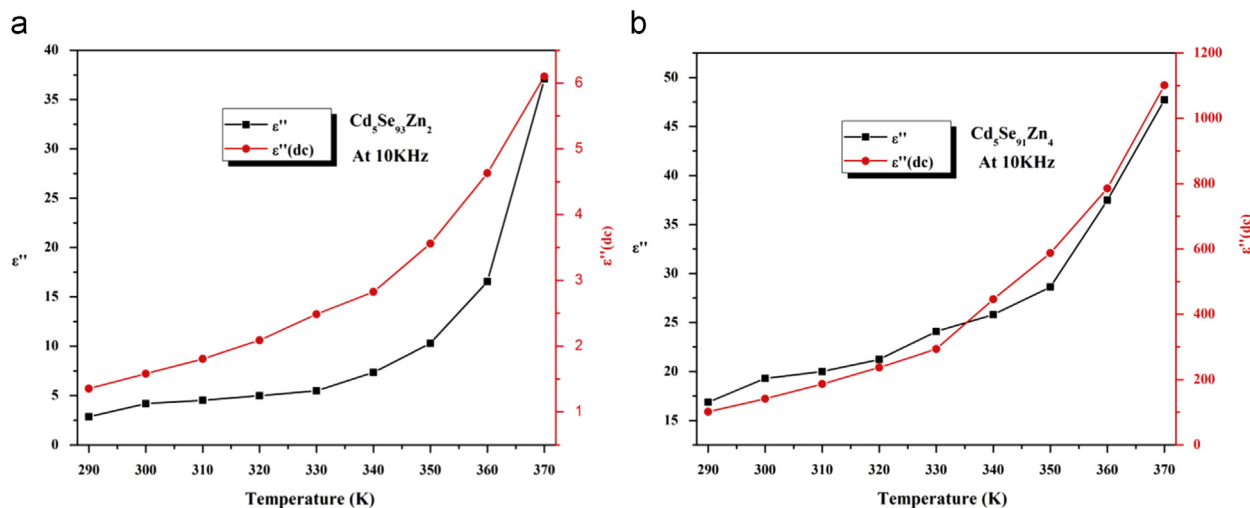


Fig. 9. Variation of observed dielectric loss and calculated DC conduction loss for $\text{Cd}_5\text{Se}_{93}\text{Zn}_2$ and $\text{Cd}_5\text{Se}_{91}\text{Zn}_4$ at a fixed frequency of 10 kHz.

charge carriers, the creation of new states takes place, which affect the Fermi level. However it has also point out that the increase in the conductivity could be caused by the increase in the portion of hopping conduction through the defect states associated with impurity atoms. This suggests that the present samples have the semiconducting nature. Mott [25] has suggested that that pre-exponential factor (σ_0) for the conduction in extended states is in the range of 10^3 – $10^4 \Omega^{-1} \text{cm}^{-1}$, low value of σ_0 indicates that the conduction is most likely in localized state.

DC conduction loss is also an important parameter to understand the dielectric dispersion in amorphous semiconductor. The dielectric loss consists of two contributions, one from the dielectric polarization processes and other from DC conduction. To study the origin of dielectric loss, the DC conduction loss was calculated using the relation [26,27].

$$\epsilon''(\text{dc}) = \sigma_{\text{dc}} / \omega \epsilon_0 \quad (2)$$

σ_{dc} is the DC conductivity.

Table 1 shows the calculated values of DC conduction loss. Fig. 9(a) and (b) shows the comparative study of DC conduction loss and the observed loss at the fixed frequency of 10 kHz for $\text{Cd}_5\text{Se}_{93}\text{Zn}_2$ and $\text{Cd}_5\text{Se}_{91}\text{Zn}_4$. This indicates that the DC conduction loss is smaller than the observed loss. However as the concentrations of Zn increases for $x > 2$, DC conduction loss dominates, which is due to the increase in DC conductivity. The conductive additives may have a very large effect on its electrical response. Thus the dielectric dispersion is interpreted in term of dipolar theory for $\text{Cd}_5\text{Se}_{95}$ and $\text{Cd}_5\text{Se}_{93}\text{Zn}_2$ samples, which is due to hopping of charge carrier over a potential barrier between charge defect states, while the remaining samples have explained on the basis of DC conduction loss.

6. Conclusions

XRD results confirmed the amorphous nature of thin films. Temperature and frequency dependence of dielectric constant and dielectric loss are studied in the $\text{Cd}_5\text{Se}_{95-x}\text{Zn}_x$ glassy system. Dielectric constant and dielectric loss both increases with Zinc

concentration which can be understood in term of increase in defect state near Fermi level. DC conduction loss is found to be much smaller than observed loss, however as Zinc concentration increases ($x > 2$) $\epsilon''(\text{dc})$ dominate over the observed loss. The increase in the DC conduction loss can be understood in terms of an increase in DC conductivity. The increase in DC conductivity with Zn concentration may due to increase in the density of localized state or decrease in the band gap. Mott parameter shows that the dominate conduction is in the localized states.

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