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Study of dielectric properties of Se-Zn -In chalcogenide glasses

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In present work we report that the dielectric property of $Se_{98-x}Zn_2In_x$ (X= 0, 2, 4, 6 and10) chalcogenide glasses. The capacitance measurements were done in frequency range 10 to 500 KHz at room temperature. Dielectric constant (ε') and dielectric loss (ε'') have been evaluated from the data of capacitance measurements. It has obtained that the dielectric constant (ε') and dielectric loss (ε'') varied with Indium concentration and applied frequencies. Frequency and concentration dependence dielectric phenomena have been also explained from cole-cole diagrams. While variations in dielectric property with Indium concentration could be explained on basis of bond formation in solids.

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1. Introduction

Chalcogenide glasses are attractive and appropriate materials due to their extensive electrical, optical and thermal properties [1-8]. Early phase of research on chalcogenide glasses were mainly devoted to binary alloys [9-18]. It is widely accepted [9-18] a few binary chalcogenides exhibit remarkably good physical properties. Despite of this, previous studies on binary chalcogenides have also demonstrated that such glasses suffered from lower thermal stability, lower crystallization temperature and aging effects [1-8]. To overcome these difficulties of binary chalcogenides investigators preferred to make ternary Se-Te-Zn, Se-Te-Sb, Cd–Se–Te, Ge–Sb–Se, Sb-As-Se, Ga-Se-Te, Ag-As-Te etc [19-30] chalcogenide glassy alloys.

Physical properties of ternary chalcogenide glasses are changes drastically with the concentration of additive elements. The change in concentration of additive elements results the modifications in structural defects such as heterogeneous particles, microcrystalline phase separation, cracks and inhomogeneities etc. Due to such structural changes electric and dielectric properties of chalcogenide glasses have attracted much attention, because it has solid state technical importance.

Dielectric properties of chalcogenide glasses related to important physical phenomena for understanding of the conduction mechanism and nature of the dielectric losses, which turn may be useful to determine the nature of defects in solids. The dielectric behaviour of chalcogenide glasses also reveals the structural information with concerning conduction mechanism. The observation of dielectric dispersion and frequency dependence dielectric constant is an interesting and important problem for understanding the origin of losses in such materials. Most of dielectric measurements have been reported at audio or radio frequencies [31-34].

Recently dielectric properties of chalcogenide glasses have been widely studied by various investigators [35]. Trnocova et al [36] have reported the composition dependence of dielectric properties for a few chalcogenide glasses. Bordovsky et al [37] have reported a comprehensive study of field dependence dielectric properties for different alloys. According to this study, the dielectric parameters of chalcogenides are varied with frequency due to their structural changes. El-Sayed et al [38] have reported that the low temperature dielectric behavior of metallic chalcogenide glasses. Kumar et al [39] have reported dielectric studies of Sn based ternary chalcogenide glasses. Their results show that the dielectric constant and dielectric losses increase with increasing Sn concentration. Sharma et al [40] have studied the dielectric relaxation of Ag containing gasses at room temperature.

In present work we have studied the dielectrics properties of $Se_{98-x}Zn_2In_x$ (X= 0, 2, 4, 6 and 10) chalcogenide glasses in wide frequency range (10-500 KHz) at room temperature.

2. Experimental

Bulk glassy materials were prepared by melt quenched technique. High purity elements (99.999%) Selenium, Zinc and Indium were used. The desired amount of elements was weighed by electronic balance. Properly weighed elements were put into clean quartz ampoules, (length 8 cm and diameter 12 mm). The material containing quartz ampoules were evacuated and sealed under a vacuum of 10^{-5} Torr. Sealed ampoules were heated in electric furnace, where furnace temperature was raised at a rate of 5-6 K $(min)^{-1}$ upto 1173 K and kept at that temperature for 10-11 h. During the heating process, ampoules were frequently rocked to ensure the homogeneity of molten materials. After desired heating time, ampoules were rapidly quenched into ice cooled water. Ingots of glassy materials were removed from the ampoules.

The amorphous nature of materials was [41] confirmed by PHILIPS XRD, which is shown in Fig. 1.For dielectrics measurements prepared glassy materials pellets was made. These pellets were mounted between two steel electrodes in specially designed sample holder. The vacuum of 10^{-2} Torr was maintained over the entire frequency range at normal room temperature. The frequency dependence of dielectrics measurements were performed in frequency range 10 KHz to 500 KHz from WAYNE-KEER, Model 4255 LCR-METER equipment. Capacitance was measured the pellets which mounted between parallel steel electrode plates. Using the experimental values of capacitance at different frequencies, the dielectric constant (ε') and dielectric loss (ε'') were calculated. Three terminal measurements were performed to avoid the stray capacitances.

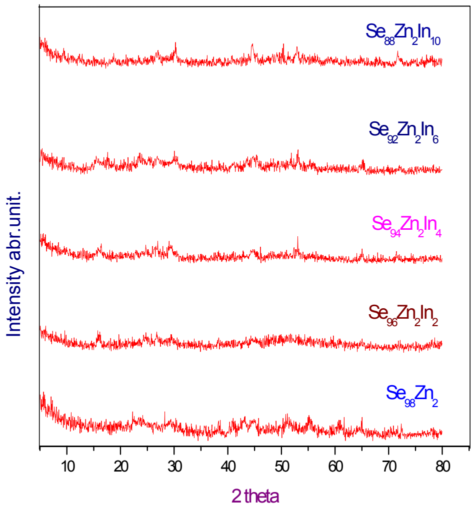

Fig. 1. XRD Patterns of $Se_{98-x}Zn_2In_x$ (X= 0, 2, 4, 6 and 10) chalcogenide glasses.

We were performed experiment on pellets rather than the bulk because macroscopic effects (gas bubbles, etc) may appear in the bulk during the preparation. The Goyal et al. [42] have shown both theoretically and experimentally, the bulk ingots and compressed pellets exhibit similar dielectric behaviour in chalcogenide glasses. They have not found any evidence of Maxwell-Wagner losses for the suspected inhomogeneities in case of compressed pellets in these materials. The number of localized sites induced by grain boundary can be neglected as compared to charge to defect states which are quit large (~ 10^{18} to 10^{19} $eV^{-1}cm^{-1}$) in such glasses.

3. Results and discussion

Guintini et al [43] have proposed a model for dielectric dispersion of chalcogenide glasses. This model based on Elliott study [44] of hopping of charge carrier over a potential barrier between charge defect states D^+ and D^-. Each pair of D^+ and D^- is assumed to form dipoles and relaxation phenomena of dipoles depend on its energy [45]. Thus the letter can be attributed to existence of a potential barrier over which the carrier hopes [46]. According to this model [43] dielectric dispersion (ε'') at particular frequency can be evaluated as

$$\varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty)\, 2\pi^2\, N(ne^2/\, \varepsilon_0)^3\, kT\tau^m{}_0\, W^{-4}{}_m\, \omega^m \qquad (1)$$

Here n is the number of electron that hope, N is the concentration of localized state, ε_0 and ε_∞ are the static and optical dielectric constants respectively, W_m is the required energy to move the electron from a site to infinity.

It is well known that the Guintini and Elliott theory of dielectric relaxation are applicable whether dielectric peak not appeared over entire frequency range [19, 47]. However present glasses exhibiting a dielectric peak in frequency range (10-100 KHz). Therefore, Debye theory of dielectric relaxation is appropriate to explain the dielectric behaviour of subjected glasses.

Debye theory of dielectric relaxation is explained the various liquid physical phenomena in such manner, the instance molecules which change position by jumps over an energy barrier. Then τ is one half of the average time (a molecule waits before jumping). Thus τ is the required quantity for dielectric interpretation on molecular scale. Dielectric constant values macroscopically can be obtained from variation of frequency (ε = ε' - iε'') [47].

Frequency dependence dielectrics (ε') of $Se_{98-x}Zn_2In_x$ (X= 0, 2, 4, 6 and 10) chalcogenides are obtained minimum at 6 at % of In, as shown Fig. 2. Generally dielectric constant of chalcogenide glasses decreases upto certain point and beyond it nearly constant. The present glasses also show such manner in rather different way, the dielectric constant profiles of present glasses are exhibiting a small peak below certain frequency range (See Fig. 2). The appearances of such peak in dielectric constant indicates that the existence of two consecutive phases within glassy alloys. The double stage glass transition peaks we were also observed in thermal characterization of present glasses [48].

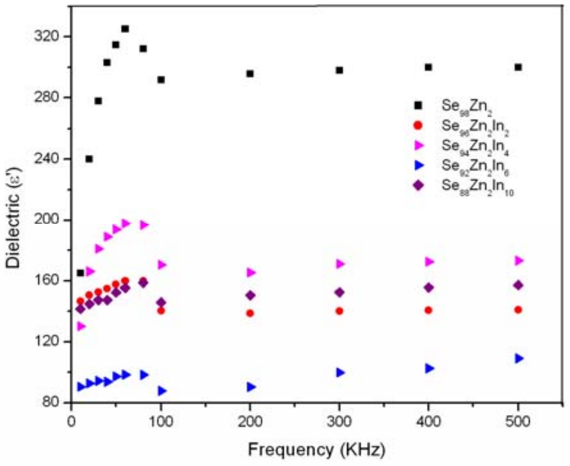

Fig. 2. Plots of dielectric constant (ε') vs frequency for $Se_{98-x}Zn_2In_x$ (X= 0, 2, 4, 6 and 10) chalcogenide glasses.

Dielectric loss (ε") vs frequency range profile also show the minimum dielectric dispersion at 6 at % of In, as shown in Fig. 3. Values of dielectric loss are widely dispersed below the 100 KHz frequency range. The clear view of dielectric dispersion loss below 100 KHz is shown in inset profile (See Fig. 3). These results show that the frequency dependence dielectric loss profile is also exhibit double phase behaviour for these glasses. The average value of dielectric constant (ε') and dielectric loss (ε") parameters is listed in Table.1.

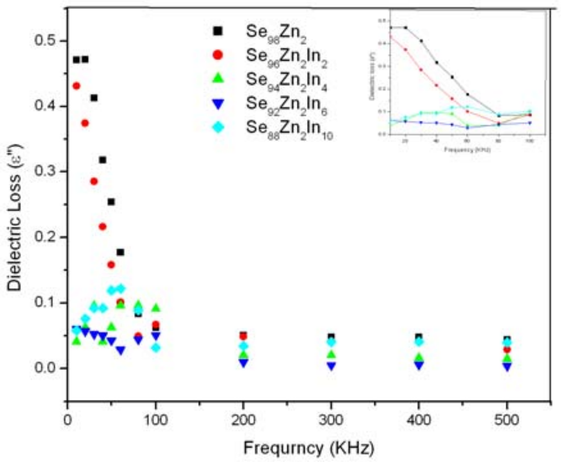

Fig. 3. Plots of dielectric loss vs frequency (the inset profile is showing clear view of dielectric loss at lower frequency) for $Se_{98-x}Zn_2In_x$ (X = 0, 2, 4, 6 and 10) chalcogenide glasses.

Table .1 Evaluated average values of dielectric constant (ε') and dielectric loss (ε") for $Se_{98-x}Zn_2In_x$ (X= 0, 2, 4, 6 and 10) chalcogenide glasses.

Indium concentration %	Mean of dielectric constant (ε')	Mean of dielectric loss (ε")
0	285.234	0.2056
2	175.652	0.1272
4	146.626	0.0548
6	95.908	0.0344
10	150.808	0.0756

In order to define the dielectric features of studied glasses, we also examined the composition dependence dielectric constant (ε') and dielectric loss (ε") at frequency 200 KHz, which is shown in Fig.. 4. The minimum values of both dielectric parameters are obtained at 6 at % of In.

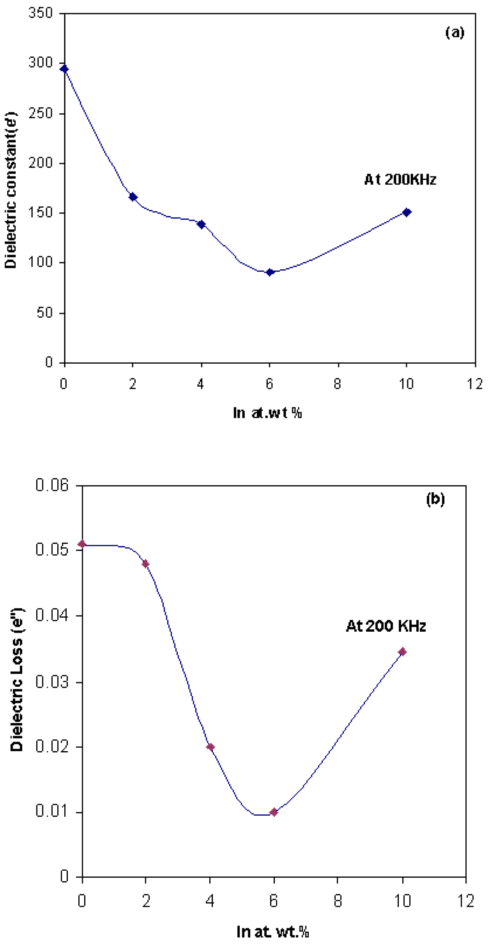

Fig. 4. (a-b) Dielectric constant and dielectric loss with Indium atomic percentage at 200 KHz.

The frequency dependence cole-cole diagrams of $Se_{98-x}Zn_2In_x$ (X= 0, 2, 4, 6 and 10) glasses are shown in Fig. 5 (a-e). The cole-cole diagrams are plotted between dielectric loss (ε") and dielectric constant (ε') over entire frequency range. The minimum cole-cole variation is obtained at 6 at % of In.

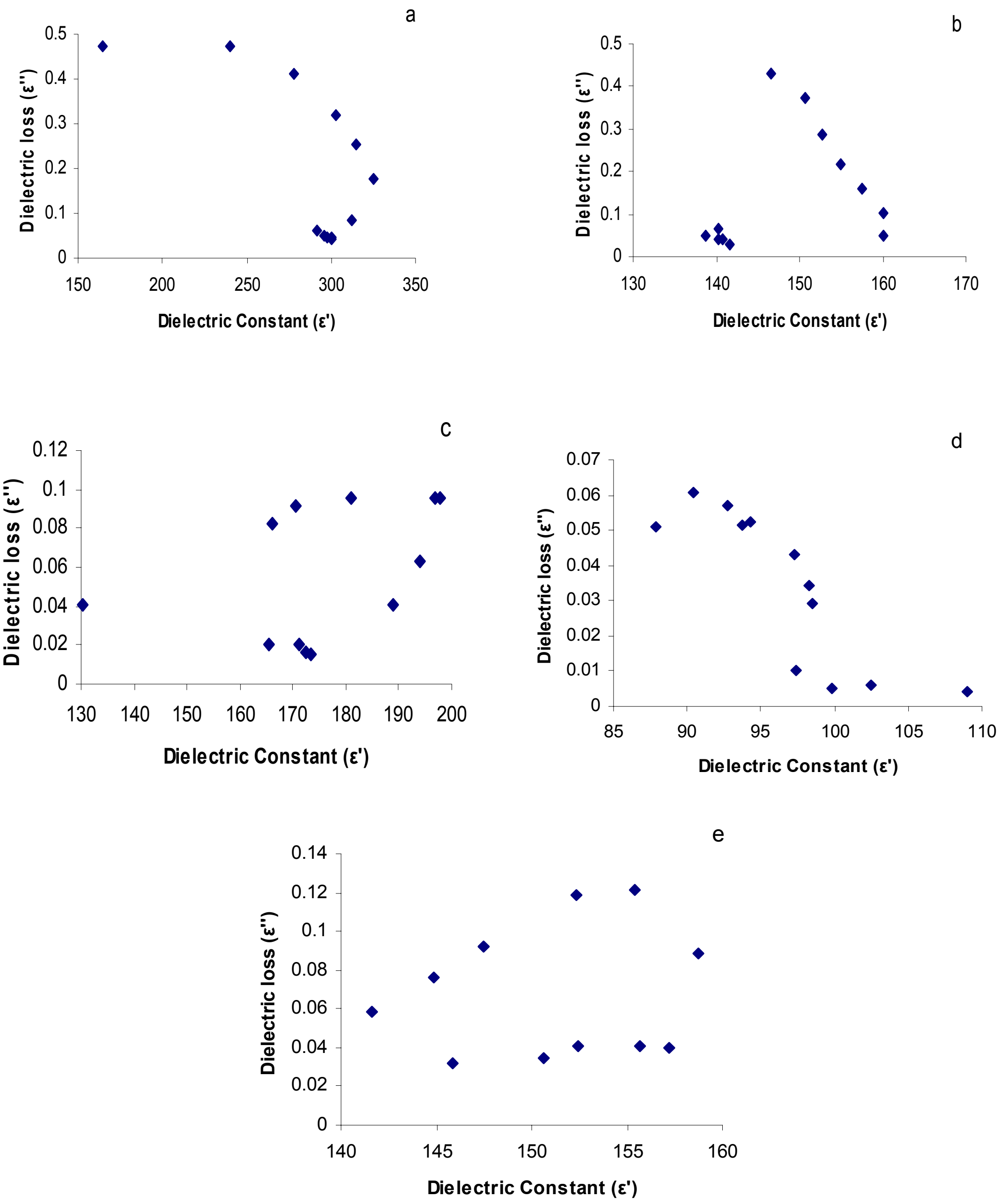

Fig. 5. (a-e) Plots of cole- cole diagrams for $Se_{98-x}Zn_2In_x$ (X= 0, 2, 4, 6 and 10) chalcogenide glasses.

Obtained coal-coal diagrams are verify with help of Onsager-Cole theory (modified Debye theory) of intrinsic relaxation time, the multiple decay time of exponential relaxation of polarization have to be taken instead of single relaxation time. Cole-cole plot curves of such dielectric spectrum always lies out side the semi circle [19, 47]. For two independent dielectric decay times exponential expression can be written as [47]

$$\alpha (t) = A_1\exp^{-t/T_1} + A_2 \exp^{-t/T_2} \qquad (2)$$

here α is the distribution parameter. T_1 and T_2 represent decay time.

The more general form of the expression is

$$\varepsilon-\varepsilon_\infty = \varepsilon_0-\varepsilon_1/\ 1+ i\ \omega T_1 + \varepsilon_1-\varepsilon_\infty/\ 1+ i\ \omega T_2 \qquad (3)$$

For bulk materials expression can be generalized [50] as

$$\varepsilon-\varepsilon_\infty= \varepsilon_I + \varepsilon_{II} \qquad (4)$$

Here ε_I and ε_{II} are respective phase dielectric parameters.

Thus, the expression (8) is convenient form to consider the plot between ε'' and ε' for two well separated dispersion regions. At the room temperature more complex semicircular curves are obtained due to two regions overlap to each others. Cole-cole diagrams [Fig. 5 (a-e)] of these glasses also show the dispersed double phase semicircular dispersion behaviour throughout the frequency range, which follows the modified Debye theory of intrinsic dielectric relaxation.

The variation of dielectric properties in $Se_{98-x}Zn_2In_x$ (X= 0, 2, 4, 6 and 10) chalcogenide glasses could be explained on basis chemical bond theory of solids [49]. It is expected that Zn dissolve in Se chains and it make Zn-Zn, Se-Se homonuclear and Se-Zn heteronuclear bonds with respective bond energies 204, 104 and 161 kJ(mole)$^{-1}$. Initially, binary Se-Zn glass forms cross-linked Se_2Zn_4 heteronuclear metastable state structure and produced more defects in density of localized state [50] due to existence of dangling bonds in combined stochiometrics.

Incorporation of In concentration in binary Se-Zn system at cost of Se results the formation of Se-In heteronuclear bonds having energy 128.4 kJ(mole)$^{-1}$ in Se chains, with strong fixed metallic Zn-In bonds (bond energy 165.17 kJ mole^{-1}), because of fixed amount of Zn. On increasing concentration of In, the structure heavily cross-linked and steric hindrance increases. Therefore, the expanse of Se chains and replacement of weak Se-Se bonds phenomena existed due to increasing strength Se-In bonds. Thus, the cohesive energy of the system is increased with increase In content, this is the probable reason to observed chemical threshold in dielectric properties at critical composition (6 at %) of In. At the chemical threshold concentration glass become chemically ordered and contains only strong Se-In bonds. Hence the maximum cross-linking in glassy structure has occurred at the concentration of Indium.

4. Conclusions

Study of dielectric properties of $Se_{98-x}Zn_2In_x$ (X= 0, 2, 4, 6 and 10) chalcogenide glasses leads to the following conclusions;

1. The present glasses have shown double phase dielectric dispersion behaviour. This double phase dielectric dispersion phenomena have been verified by Onsager-Cole model.
2. The dielectric properties such as; dielectric constant (ε'), dielectric loss (ε'') and cole-cole diagram varied with Indium concentration. Thus the dielectric properties of present glasses are widely depends on alloys concentration.
3. Dielectric characterization reveals that $Se_{98}Zn_2In_6$ can be considered a critical composition for $Se_{98-x}Zn_2In_x$ (X= 0, 2, 4, 6 and 10) chalcogenide glasses.

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