

Electrical and dielectric properties of Se-In-Sb chalcogenide glasses

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Se₉₀In_{10-x}Sb_x (x=0, 2, 4, 6, 8 &10) chalcogenide glasses were prepared by well established melt quenching technique. The glassy nature was verified by X-ray diffraction (XRD). Electrical conductivity of Se₉₀In_{10-x}Sb_x (x=0, 2, 4, 6, 8, 10) glassy systems at different temperature has been studied in bulk form through I-V characteristic curves. The dielectric properties of glassy systems at room temperature 300K to 350K and over a wide range of frequencies (50Hz to 500 kHz) have been studied. The dielectric constant (ϵ') and loss constant (ϵ'') showed frequency, temperature and Sb content dependence. The activation energies $E_{\epsilon'}$ belonging to the dielectric constant is found to be affected by both the applied frequency and the Sb content. Analysis of result on the basis of the correlated barrier hopping (CBH) model reveals that the electronic conduction in Se-In-Sb glasses takes place via bipolaron hopping.

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1. Introduction

The study of dielectric behavior of chalcogenide glasses is expected to reveal structural information which is useful for the understanding of the conduction mechanism. In addition, a study of temperature dependence of dielectric permittivity particularly in the range of frequencies where dielectric dispersion occurs can be of great importance for the understanding of the nature and origin of losses occurring in these materials [1-7]. In this work, we have measured the frequency and temperature dependence dielectric & loss component in Se₉₀In_{10-x}Sb_x with a view to understand the dielectric properties in amorphous semiconductor.

The choosing of Se was made because of its wide commercial applications like switching [8], memory [9] and xerography [10] etc. But in pure state, it has certain disadvantages because of its short lifetime, low sensitivity and low thermal instability [11]. This problem can be overcome by alloying Se with some impurity atoms (Ge, Te, Bi, Sb and In etc.). Selenium also exhibits a unique property of reversible phase transformation. This property makes these systems very useful in optical memory devices [12]. The addition of In to Se-Sb system is expected to modify the material properties to make it more suitable for reversible optical recording with an eraser time less than 1 microsecond [13-14]. It has been found that the structure of the glass is considerably modified by the addition of Sb [15].

2. Experimental details

The bulk material was prepared using well-established melt quenching technique. High purity (99.999%) Se, Sb and In in appropriate atomic percentage proportions were weighed in a quartz glass ampoule (length 10.5 cm and 8 mm internal diameter). The content of ampoule were sealed under a vacuum of 10⁻⁵ Torr and heated in a furnace where the temperature was raised at a rate of 3-4 °C per minute up to 900°C and kept at that temperature for 15 hours. The ampoule was agitated frequently in order to mix the constituents to ensure homogenization of the melt. The molten sample was then quenched in ice-cooled water. Bulk samples in the form of pellets (diameter = 1.3 cm) were obtained by finally grinding the glassy alloys and compressing the powder under a pressure of 8 tons. The amorphous nature of the alloy was ascertained through X-ray diffraction pattern of the samples using diffractometer with CuK α -radiation source ($\lambda = 1.540 \text{ \AA}$). The XRD pattern of Se₉₀In₈Sb₂ glass is shown in Fig 1. The absence of any sharp peak in the XRD pattern confirms the amorphous nature of the sample.

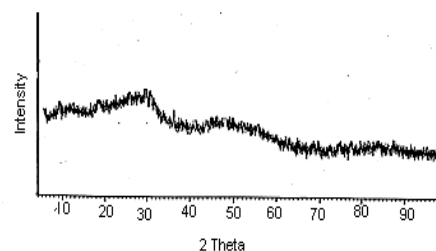


Fig. 1. XRD pattern of Se₉₀In₈Sb₂ chalcogenide glass at room temperature.

I-V characteristics of $\text{Se}_{90}\text{In}_{10-x}\text{Sb}_x$ ($x=0, 2, 4, 6, 8, 10$) glassy pellets were carried out in a temperature range from room temperature to 350 K using a Keithley electrometer 6517A. Fig. 2 shows the temperature dependence of I-V characteristic of $\text{Se}_{90}\text{In}_6\text{Sb}_4$ as a representative case.

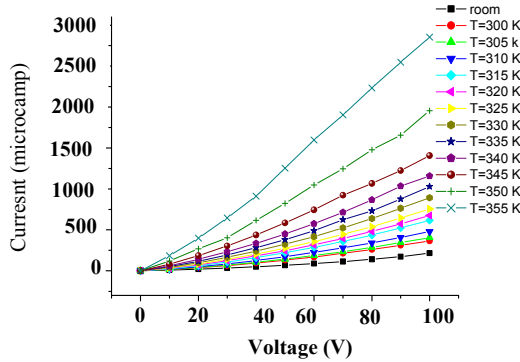


Fig. 2. I-V characteristics of $\text{Se}_{90}\text{In}_6\text{Sb}_4$ glassy pellets at different temperature.

The pellets were mounted in between two steel electrodes of a metallic sample holder for dielectric measurements. The temperature measurements were facilitated by a copper-constantan thermocouple mounted very near to the sample. A vacuum of 10^{-3} Torr was maintained over the entire temperature range (300-350 K). Dielectric measurements were made using a digital LCR meter. The parallel capacitance and dissipation factor were measured and then ϵ' and ϵ'' were calculated.

3. Results and discussion

3.1. Temperature and composition dependence of the electrical conductivity

DC electrical conductivity was calculated from the relation:

$$\sigma_{\text{DC}} = 1/\rho_{\text{DC}} = (1/R)(L/A) \quad (1)$$

where, R is the resistance of the sample, L is the thickness of the sample, A is the cross-sectional area of the sample and ρ_{DC} is the resistivity of the sample under test. It is well known that electrical conduction can take place by means of two parallel processes namely band conduction and hopping conduction. The band conduction occurs when the carriers are excited beyond the mobility edges into non-localized states at high temperatures. The excitations of carriers into localized states at band edges cause the hopping conduction. Thus the total conductivity is given as:

$$\sigma = \sigma_i + \sigma_h \quad (2)$$

where, σ_i is the intrinsic conductivity and σ_h is the hopping conductivity.

Fig. 3 shows the composition vs conductivity plots at different temperatures. It has been indicated that in Se

containing glass, there is a tendency to form polymerized network glasses and the homopolar bond is qualitatively suppressed [16]. Moreover, at lower percentage of Sb the system contains $\text{SbSe}_{4/2}$ tetrahedral units dissolved in a matrix composed of Se chains. With the increases of Sb content, the glassy matrix becomes heavily cross-linked and the steric hindrance increases. The Se-Se bonds (bond energy 205.8 kJ/mol) will be replaced by Sb-Se bonds, which have higher bond energy (214.2 kJ/mol). Hence the cohesive energy of the system increases with increasing Sb content. It is found that electrical conductivity is maximum at 4 at % of antimony (Sb). This composition can be considered as a critical composition at which the system becomes a chemically ordered alloy containing high-energy Sb-Se heteropolar bonds. Further addition of Sb favours the formation of Sb-Sb bonds (bond energy 176.4 kJ/mol) thus reducing the Sb-Se bond concentration. Thus the cohesive energy decreases resulting a decrease of conductivity.

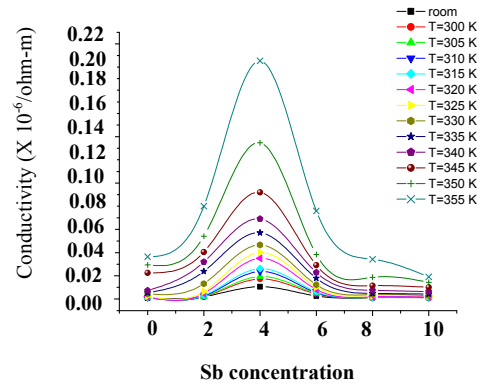


Fig. 3. Conductivity vs Sb concentration at different temperature.

The variation of electrical conductivity with temperature of different glassy alloys is shown in Fig. 4. It is found that at low temperature electrical conductivity increases linearly. The non-linearity or sharp increase in current in the temperature range 335 K to 355 K indicates that there is an effect of thermodynamic transition in the vicinity of a particular temperature.

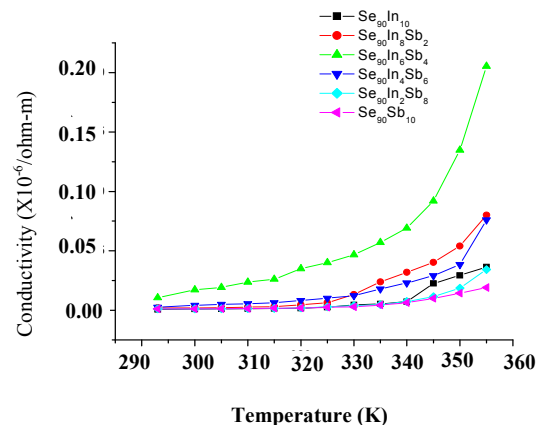


Fig. 4. The variation of electrical conductivity with temperature of different glassy alloys.

3.2. Temperature dependence of dielectric constant (ϵ') and dielectric loss (ϵ'')

Guintini et al. [17] have proposed a model for dielectric dispersion in chalcogenide glasses. This model is based on the idea of hopping of charge carriers over a potential barrier between charged defects states (D^+ and D^-). Each pair of site (D^+ and D^-) is assumed to form a dipole which has the relaxation time depending on its energy; the later can be attributed to the existence potential barrier over which the carriers hop [18].

According to the above model, at a particular frequency, in the temperature range where the dielectric dispersion occurs, is given by

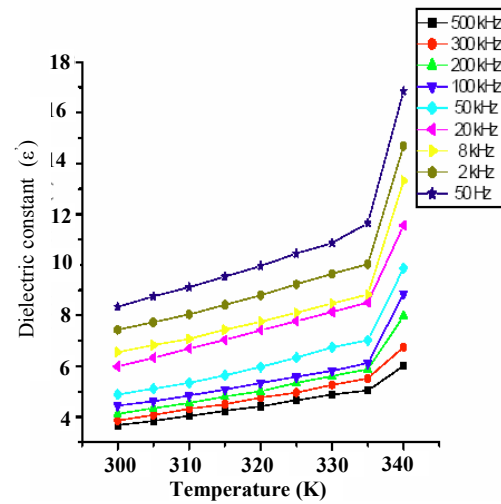
$$\epsilon'' = (\epsilon_0 - \epsilon_\infty) 2 \pi^2 N (ne^2 / \epsilon_0)^3 kT \tau_0^m W_m \omega^m \quad (3)$$

here, m is a power of angular frequency and is negative in this case and is given by

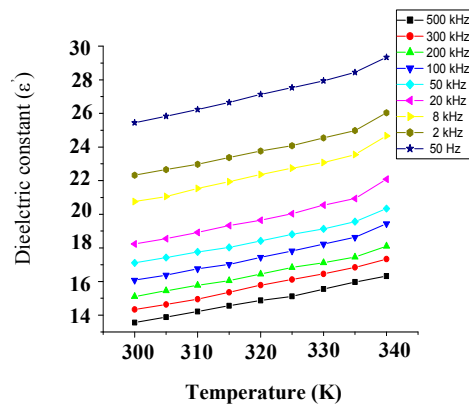
$$m = -4kT/W_m \quad (4)$$

n is the number of electrons that hop, N is the concentration of localized sites, ϵ_0 and ϵ_∞ are the static and optical dielectric constants, respectively, W_m is the energy required to move the electron from a site to infinity. It has been reported [19] that, in chalcogenide glasses, the temperature dependence of ϵ' and ϵ'' is appreciable only in a certain temperature range. At lower temperatures ϵ' is almost constant and ϵ'' is negligibly small. After a certain temperature, ϵ' and ϵ'' increase appreciably with temperature. Therefore, the present measurements have been made only in the high-temperature region where dielectric dispersion is quite appreciable. The temperature dependence of ϵ' and ϵ'' was studied at various frequencies (8–500 kHz) for all the glassy alloys reported here. The glass transition temperature of the alloys is around 350 K [20]; hence the temperature e of measurements was not more than 350 K.

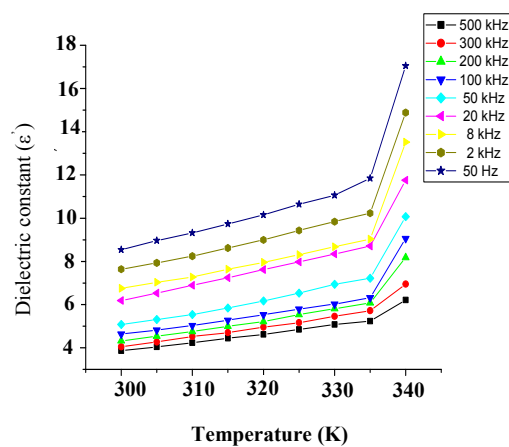
Figs. 5 and 6 show the results of the dielectric constant (ϵ') and the dielectric loss (ϵ'') measurements at different frequencies for glassy alloys below the glass transition temperature. From Figs. 5 and 6, it is clear that the temperature dependence of ϵ' and ϵ'' is appreciable in the glass transition region. In these glassy samples, dielectric constant increases with the increase in temperature, the increase being different at different frequencies. Thus, the temperature dependence of ϵ' in the present chalcogenide glass is the same as reported by various workers in other chalcogenide glasses [21-22].



(a) $Se_{90}In_{10}$

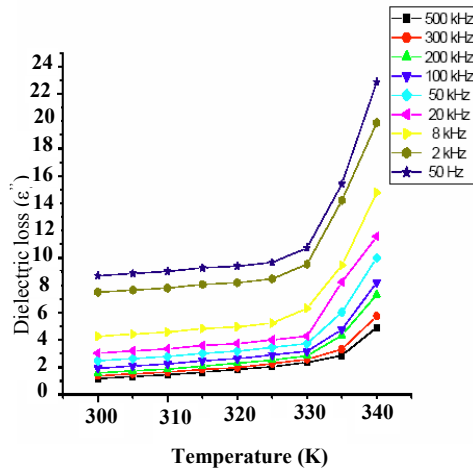


(b) $Se_{90}In_6Sb_4$

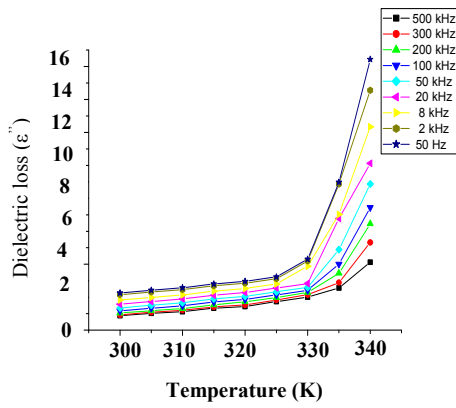


(c) $Se_{90}Sb_{10}$

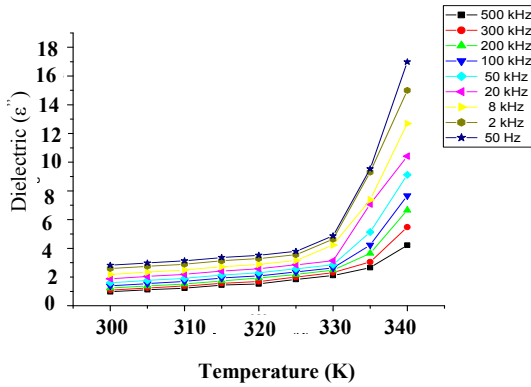
Fig. 5. Temperature dependence of dielectric constant at different frequencies in glassy alloys.



(a) $Se_{90}In_{10}$



(b) $Se_{90}In_6Sb_4$



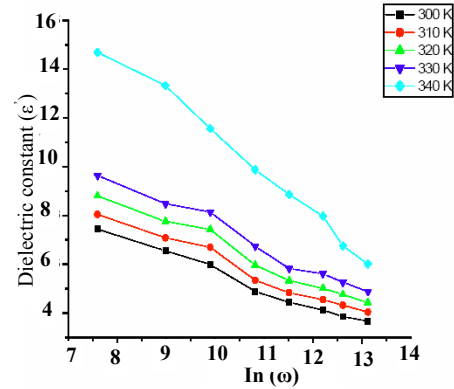
(c) $Se_{90}Sb_{10}$

Fig. 6. Temperature dependence of dielectric loss at different frequencies for glassy alloys.

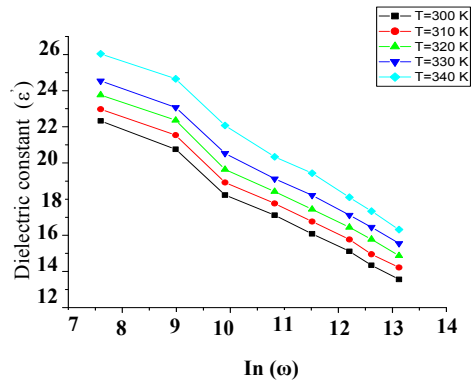
3.3. Frequency dependence of dielectric constant (ϵ') and dielectric loss (ϵ'')

Fig. 7 shows the frequency dependence of dielectric constant (ϵ') at different temperatures for glassy alloys. It is clear from the figure that ϵ' decreases with increasing frequency and increases with increasing temperature. The

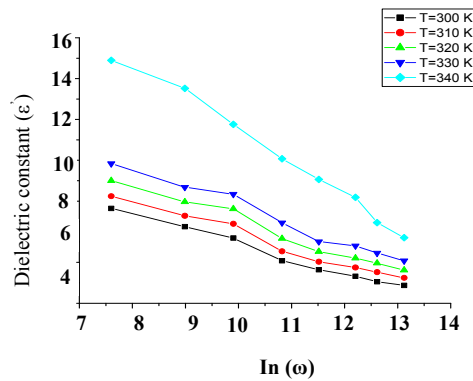
increase of ϵ' with temperature can be attributed to the fact that the orientation polarization is connected with the thermal motion of molecules, so dipoles cannot orient themselves at low temperatures. When the temperature is increased, the orientation of dipoles is facilitated and this increases the value of orientation polarization, and this increases ϵ' with increasing temperature. The frequency dependence of dielectric loss ϵ'' is shown in Fig. 8 at different temperatures for the glassy alloys. From this figure, it is clear that ϵ'' is also found to decrease with increasing frequency and increases with increasing temperature according to equation $\epsilon'' = A\omega^m$, where A is a constant and m is negative.



(a) $Se_{90}In_{10}$



(b) $Se_{90}In_6Sb_4$



(c) $Se_{90}Sb_{10}$

Fig. 7. Frequencies dependence of dielectric constant at different temperature.

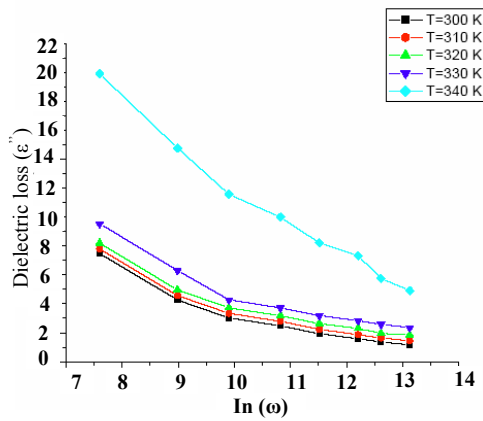
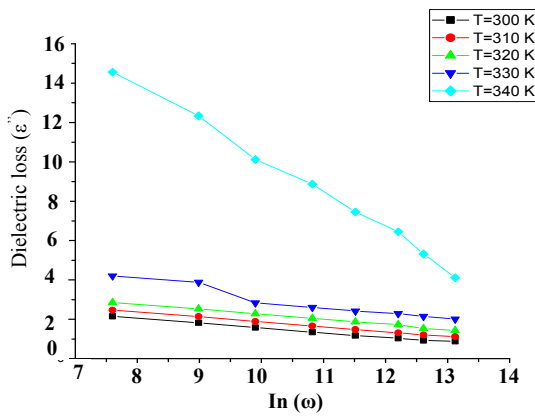
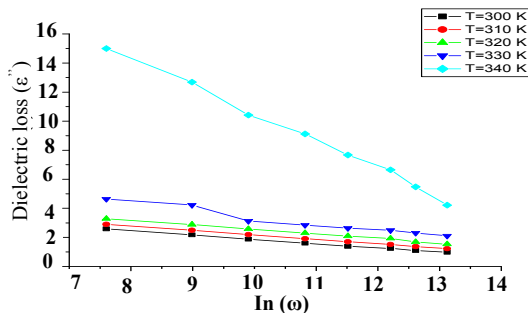
(a) $Se_{90}In_{10}$ (b) $Se_{90}In_6Sb_4$ (c) $Se_{90}Sb_{10}$

Fig. 8. Frequencies dependence of dielectric loss at different temperature.

The above behavior can be explained by the model of correlated barrier hopping (CBH) of bipolarons (i.e., two-electron hopping charged defects D^+ and D^-). According to the Guintini model [17], each pair of D^+ and D^- is assumed to form a dipole with relaxation energy E_r . This type of energy can be attributed to the existence of a potential barrier over which the carrier can hop. This observation leads to a decrease in the density of states due to the conversion of some bipolaron states (D^+ , D^-) states into a single polaron state (Do) according to the relation

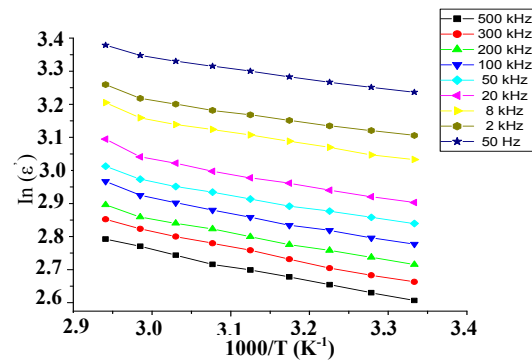
$(D^+) + (D^-) \rightarrow 2(Do)$. However, this theory does not explain the high temperature behavior so well, particularly in the low frequency range. Shimakawa [23] suggested that Do states are produced by thermal excitation of D^+ and/or D^- states and that single polaron hopping (i.e. one-electron hopping between Do and D^+ or D^-) contributes at high temperature.

The increase of ϵ' with temperature can be attributed to the fact that the orientational polarization is connected with the thermal motion of molecules, so dipoles cannot orient themselves at low temperatures. When the temperature is increased the orientation of dipoles is facilitated and this increases the value of orientational polarization and this increases ϵ' with increasing temperature.

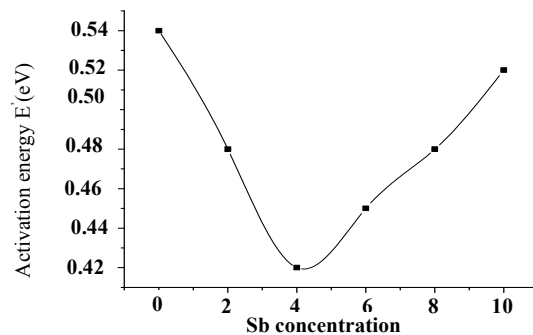
The temperature dependence of ϵ' can be suggested as:

$$\epsilon' = \epsilon_0 \exp(-E_{\epsilon'}/KT) \quad (5)$$

where $E_{\epsilon'}$ is the activation energy, K is the Boltzman's constant, ϵ_0' is the corresponding temperature independent value for the dielectric constant. Fig. 9 shows the relations between $\ln(\epsilon')$ vs $1000/T$ for the composition $Se_{90}In_6Sb_4$ as an example.

Fig. 9. Plot of $\ln(\epsilon')$ vs $1000/T$ at different frequencies for $Se_{90}In_6Sb_4$ glass.

The slope of the curve is used to calculate the activation energy $E_{\epsilon'}$. Fig.10 shows the plot of Sb concentration vs activation energy $E_{\epsilon'}$ at frequency 100 kHz. The activation energy increases with the Sb concentration

Fig. 10. Plot of sb concentration vs activation energy $E_{\epsilon'}$ at frequency 100 kHz.

The activation energy decreases as the Sb concentration increase upto 4 atomic weight percentages and more addition of Sb reduces the activation energy. As the antimony content increases beyond 4, more Sb-Sb and Se-Sb bonds may be formed, which increases the cross-link density in the structure as reported above. This in turn increases the compactness of the structure, which consequently results in an increase of the activation energy for conduction.

4. Conclusions

A systematic study of $\text{Se}_{90}\text{In}_{10-x}\text{Sb}_x$ ($x=0, 2, 4, 6, 8, \& 10$) chalcogenide glasses leads to the following conclusions: -

1. The electrical conductivity increases with the increase in temperature, which confirms the semi conducting nature of the samples. The electrical conductivity increases up to 4 at. wt % of Sb and decreases on further addition of Sb.

2. The result shows that dielectric dispersion exists in these glassy alloys suggesting the possibility of dipolar type relaxation in the glassy alloys. This is confirmed from the observed peaks in ϵ' and ϵ'' curves.

3. Dielectric constant ϵ' and loss constant ϵ'' decreases with increasing frequency and increases with increasing temperature.

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