

DIELECTRIC PROPERTIES OF $\text{Se}_{85-x}\text{Te}_{15}\text{Ge}_x$ CHALCOGENIDE GLASSESA. KUMAR^{a,b}, M. LAL^c, K. SHARMA^a, P.S.GILL^d, NAVDEEP GOYAL^{a*}^a*Department of Physics, Panjab University, Chandigarh, India-160014*^b*PG Govt. College for Girls, Sector-11, Chandigarh, India-160011*^c*GGD SD College, Chandigarh, India-160030*^d*GGS College, Chandigarh-160026, India*

Temperature and frequency dependence of dielectric constant(ϵ') and dielectric loss(ϵ'') have been studied for chalcogenide glasses $\text{Se}_{85-x}\text{Te}_{15}\text{Ge}_x$ ($x=0, 2, 6, 10, 15$) by measuring capacitance and conductance in the frequency range 5 kHz to 20 kHz and temperature range 253K to 313K. Dielectric dispersion has been found to occur in this frequency and temperature range. The variation of dielectric constant and dielectric loss with temperature shows almost similar behavior for $x=0, 2, 6$, but dielectric constant and dielectric loss show peaks for $x=10, 15$. The analysis of results indicates that dielectric losses are dipolar in nature and are explained on the basis of Guintini's theory of dielectric dispersion based on two electron hopping over a potential barrier. Results show that both dielectric constant and dielectric loss decrease with increase in Germanium concentration. This is due to the decrease in defect states with increase in Germanium concentration.

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1. Introduction

Dielectric relaxation studies are important to understand the nature and the origin of the dielectric losses which in turn, may be helpful to determine the nature of defects in the solids. Moreover, the structural information from the study of dielectric behavior of chalcogenide glasses may be used to understand the conduction mechanism in chalcogenide glasses. Chalcogenide glasses, particularly Se-Te glasses have gained much importance because of their greater hardness, high crystallization temperature and smaller aging effects [1] and their high potential for applications in electronics. Properties of chalcogenide glasses are usually affected by the addition of third element [2-9]. We have chosen Germanium dopant because Germanium doped chalcogenide glasses have more thermal stability in wide temperature range due to its high melting point. The present paper reports the temperature and frequency dependent behaviour of dielectric constant and dielectric loss in $\text{Se}_{85-x}\text{Te}_{15}\text{Ge}_x$ ($x=0, 2, 6, 10, 15$) in the temperature range 253K to 313K and frequency range from 5KHz to 20KHz. Guintini's theory [10] of dielectric relaxation in chalcogenide glasses has been used to analyse the results.

2. Experimental details

For the present work, melt quench technique has been used to prepare the $\text{Se}_{85-x}\text{Te}_{15}\text{Ge}_x$ ($x=0, 2, 6, 10, 15$) glasses. The bulk-ingots were grinded into fine powder and the powder was compressed in a die under a hydraulic press (10^3kg/m^2) to obtain the compressed pellets. A three terminal sample holder fabricated for the measurement of ac and dc conductivity of pellet-shaped samples has been used. A thermocouple inserted inside the sample holder and kept close to the sample measures correct temperature of the samples. To achieve a vacuum upto 10^{-4} to 10^{-5} Torr

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inside the sample holder, vacuum pumping system (Model VS-65D, H.H.V.India) has been used. To measure the frequency-dependent ac conductivity and dielectric constant, general radio bridge (Model 1615-A) has been used. The bridge consist of an audio oscillator (Model 1311), a tuned amplifier (Model 1232-A) and a null detector, which permits balance to a resolution of one part in million. This bridge is designed for the precise measurements of capacitance and conductance. Its direct read-out system minimizes the reading errors and permits rapid operation. Capacitance and conductance measurements were simultaneously done using GR Bridge to calculate the dielectric constant and dielectric loss of the samples.

Dielectric behavior of the samples has been studied on the pellet rather than the bulk, as macroscopic effects (gas bubbles etc.) may appear in the bulk during preparation. Goyal et al [11] have shown both theoretically and experimentally that bulk ingots and compressed pellets show similar dielectric behavior in chalcogenide glasses. No evidence of Maxwell-Wagner losses for the suspected inhomogeneity in case of compressed pellets was found by them.

3. Results and discussion

3.1 Dielectric relaxation in $\text{Se}_{85-x}\text{Te}_{15}\text{Ge}_x$ ($x=0, 2, 6$)

The temperature dependence of dielectric constant (ϵ') and the dielectric loss (ϵ'') is studied at various frequencies from 5 kHz to 20 kHz for $\text{Se}_{85-x}\text{Te}_{15}\text{Ge}_x$ ($x=0, 2, 6$) in the temperature range 253K to 313K. The dielectric constant and dielectric loss increase with increase in temperature at different frequencies for each sample (Figs.1-6). Dielectric constant (ϵ') and dielectric loss (ϵ'') decreases with increase in frequency at a particular temperature for each sample. This type of behaviour has been reported earlier in the chalcogenide glasses[12-18].

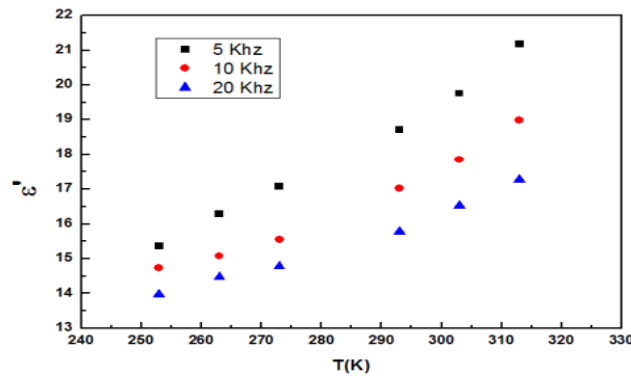


Fig. 1. Temperature dependence of dielectric constant (ϵ') in $\text{Se}_{85}\text{Te}_{15}$

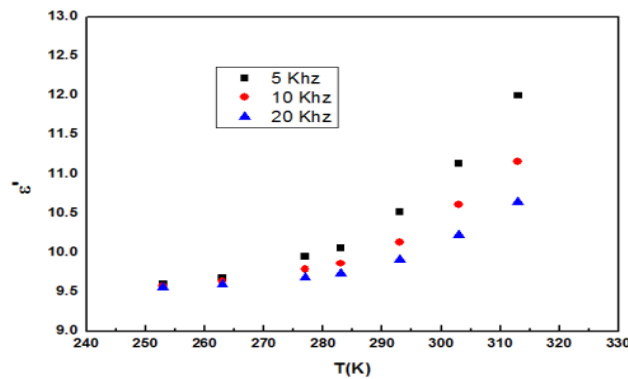


Fig. 2. Temperature dependence of dielectric constant (ϵ') in $\text{Se}_{83}\text{Te}_{15}\text{Ge}_2$

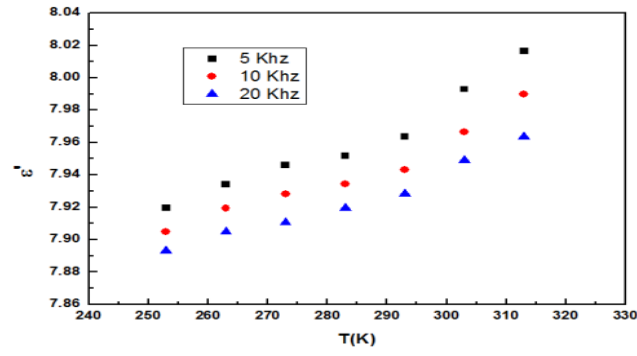


Fig. 3. Temperature dependence of dielectric constant (ϵ') in $\text{Se}_{79}\text{Te}_{15}\text{Ge}_6$

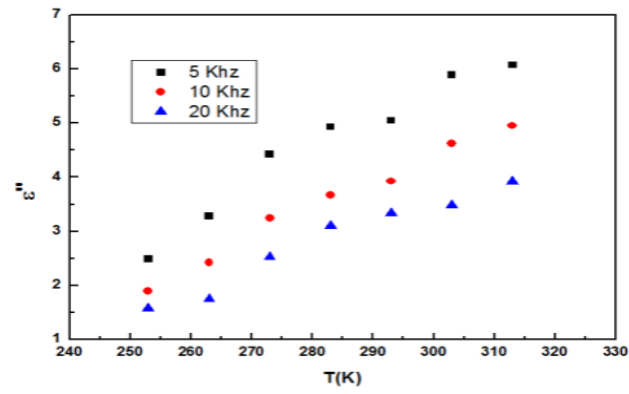


Fig. 4. Temperature dependence of dielectric loss (ϵ'') in $\text{Se}_{85}\text{Te}_{15}$

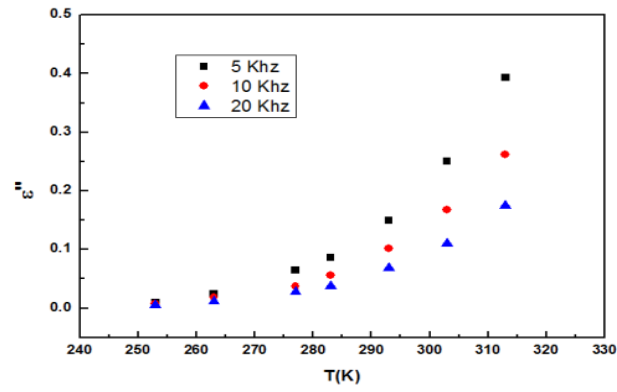


Fig. 5. Temperature dependence of dielectric loss (ϵ'') in $\text{Se}_{83}\text{Te}_{15}\text{Ge}_2$

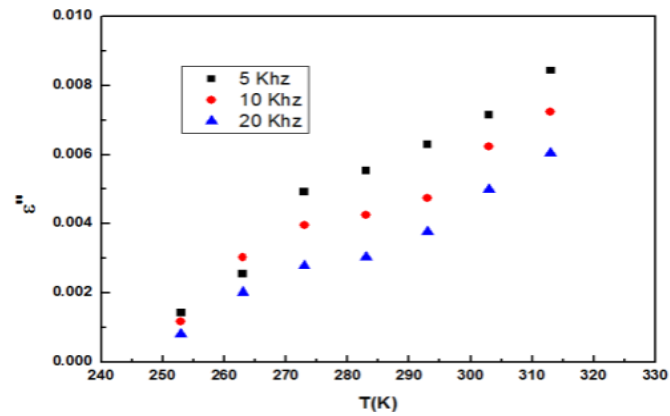


Fig. 6. Temperature dependence of dielectric loss (ϵ'') in $\text{Se}_{83}\text{Te}_{15}\text{Ge}_6$

To explain dielectric dispersion in chalcogenide glasses, Guintini et al [10] proposed a model, according to which dielectric properties of chalcogenide glasses can be interpreted by considering a set of dipoles formed by charged defect states D^+ and D^- . Each dipole has a relaxation time depending on its activation energy which can be attributed to the existence of potential barrier over which the carriers must hop. This potential barrier (proposed by Elliot) is due to columbic interaction between neighbouring sites forming a dipole. The relaxation time connected with hop is given by

$$\tau = \tau_0 \exp(W/k_B T) \quad (1)$$

Combining the imaginary part of the permittivity with the circular frequency ω of the applied field, we can write

$$\varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty) \frac{4\pi N \varepsilon_0 k T}{n e} \int_0^\infty R^4 [\omega / (1 + \omega^2 \tau^2)] d\tau \quad (2)$$

Assuming $\omega\tau \ll 1$, ε'' can be written as

$$\varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty) 2\pi^2 N \left(\frac{n e^2}{\varepsilon_0} \right)^3 k T \tau_0^m W_M^{-4} \omega^m \quad (3)$$

where m is power of angular frequency and is given as

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

and n is the number of electrons that hop, N is the concentration of localized states, ε_0 is the static dielectric constant and ε_∞ the dielectric constant at infinitely high frequencies. W_m is the energy required to move the electron from one site to infinity. Thus, an increase in frequency decreases the dielectric loss as has been observed for each sample (Figs. 4-6).

In all the glasses under study, ε'' is found to follow a power law with frequency i.e $\varepsilon'' = A\omega^m$. This is confirmed by the straight line graphs between $\log \varepsilon''$ and $\log f$ (Fig.7) for $\text{Se}_{85-x}\text{Te}_{15}\text{Ge}_x$ ($x=0, 2, 6$) at 303K. The power m is calculated from the slopes of these graphs is found to be negative (eq.4). Similar graphs have been obtained at other studied temperatures.

Therefore, it seems that the paired defect states (D^+ and D^-) behave as dipoles in the studied glasses and the results are in agreement with the theory of hopping of charge carriers over a potential barrier as suggested by Elliot[19] in case of chalcogenide glasses.

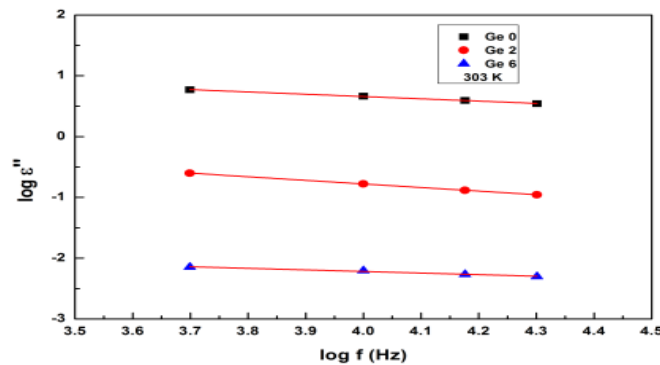


Fig. 7. Log ε'' vs log f graph for $\text{Se}_{85-x}\text{Te}_{15}\text{Ge}_x$

The value of dielectric parameters dielectric constant (ε') and the dielectric loss (ε'') at a particular frequency and temperature are given in Table 1.

Table1. Dielectric parameters for $Se_{85-x}Te_{15}Ge_x$ ($x=0, 2, 6$) at 303K and 10 kHz

Sample	ϵ'	ϵ''	m
$Se_{85}Te_{15}$	17.85	4.6271	-0.38
$Se_{83}Te_{15}Ge_2$	10.61	0.1673	-0.59
$Se_{79}Te_{15}Ge_6$	7.97	0.0062	-0.26

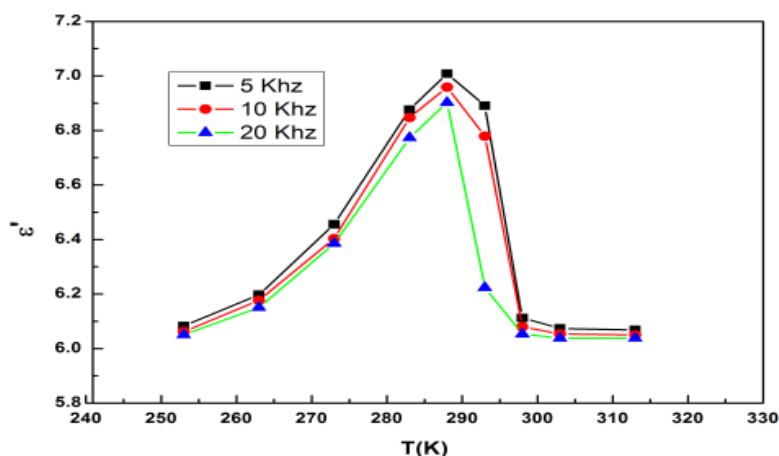
Dielectric constant (ϵ') and dielectric loss (ϵ'') decrease with increase in concentration of Germanium (Table 1). It is generally assumed that the addition of germanium to Se-Te system leads to cross linking of Se-Te chains, reducing the disorder in the system which may decrease the density of defect states i.e. decrease in number of dipoles (D^+ and D^-) and hence decrease in dielectric constant and dielectric loss.

The decrease in dielectric constant with increasing frequency can be explained on the basis of contribution of different types of polarizability; deformational (electronic, ionic) and relaxation (orientational and interfacial) polarization process [20]. Orientational polarization exists in substance whose asymmetric molecules possess permanent electric moment. The orientational polarization decreases as frequency increases as it takes more time than electronic and ionic polarization to follow alternating field. As ϵ' decreases with increase in frequency in all the samples, consequently, orientational polarization is dominant in the studied samples in the frequency range investigated as the paired defect states (D^+ and D^-) behave as dipoles in the studied glasses.

Since the orientational polarizability is associated with thermal motion of molecules, the orientation of molecular dipoles increases with increases in thermal energy which increases the dielectric constant (ϵ'). So, the dielectric constant is increasing with increase in temperature for each sample.

3.2 Dielectric relaxation in $Se_{85-x}Te_{15}Ge_x$ ($x=10, 15$)

Figures 8-9 show the temperature dependence of dielectric constant (ϵ') at different frequencies for $Se_{75}Te_{15}Ge_{10}$ and $Se_{70}Te_{15}Ge_{15}$ respectively. The graphs indicate that ϵ' increases with increase in temperature and then shows maxima for each frequency.

Fig. 8. Temperature dependence of dielectric constant (ϵ') in $Se_{75}Te_{15}Ge_{10}$

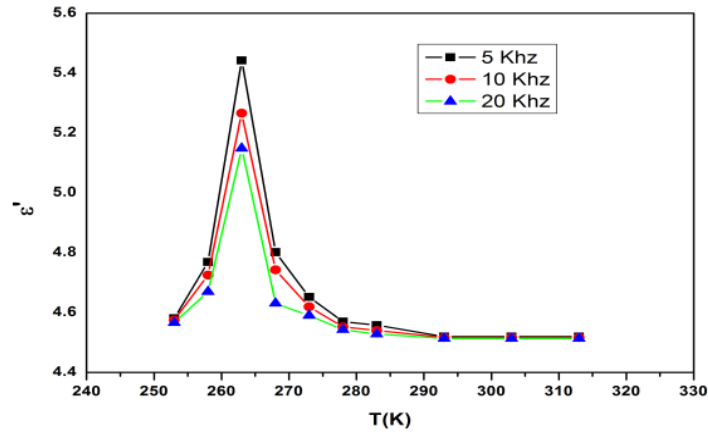


Fig. 9. Temperature dependence of dielectric constant (ϵ') in $\text{Se}_{70}\text{Te}_{15}\text{Ge}_{15}$

The average coordination number Z for glass composition $\text{Se}_{85-x}\text{Te}_{15}\text{Ge}_x$ ($x=0, 2, 6, 10, 15$) is calculated using the relation [21].

$$Z = [(85-x)N_c(\text{Se}) + 15N_c(\text{Te}) + xN_c(\text{Ge})]/100 \quad (5)$$

Where $N_c(\text{Se})$, $N_c(\text{Te})$ and $N_c(\text{Ge})$ are coordination number of Se, Te and Ge respectively. Coordination number is two for Se & Te each and four for Ge, obeying the so called 8N rule[22]. The average coordination number for the various compositions $\text{Se}_{85}\text{Te}_{15}$, $\text{Se}_{83}\text{Te}_{15}\text{Ge}_2$, $\text{Se}_{79}\text{Te}_{15}\text{Ge}_6$, $\text{Se}_{75}\text{Te}_{15}\text{Ge}_{10}$ & $\text{Se}_{70}\text{Te}_{15}\text{Ge}_{15}$ are 2.0, 2.04, 2.12, 2.20 and 2.30 respectively. The degree of covalency in the studied samples has been calculated using the relation [23].

$$C_c = 100 \exp[-0.25(\zeta_A - \zeta_B)^2] \quad (6)$$

Where ζ_A and ζ_B are the electronegativities of atoms A and B respectively. The value of covalent character of bonding in the studied materials is shown in Table 2.

Table 2. Calculated covalent character of various bonds in $\text{Se}_{85-x}\text{Te}_{15}\text{Ge}_x$.

Bond Type	Covalent Character (%)
Se-Se	100
Te-Te	100
Se-Te	95.06
Se-Ge	92.97
Te-Ge	99.80

This shows that covalent character of bonding is dominant in the samples.

Anomalous features have been observed in the physical properties [24, 25] when average coordination number reaches 2.4 for covalently bonded chalcogenide glasses [26]. From the temperature dependence of ϵ' for $\text{Se}_{75}\text{Te}_{15}\text{Ge}_{10}$ ($Z=2.20$) and $\text{Se}_{70}\text{Te}_{15}\text{Ge}_{15}$ ($Z=2.30$) at different frequencies, the existence of maxima shows some anomalous behaviour in dielectric studies of the chalcogenide glasses. This behavior can be explained on the basis that dipolar chains [27] that exist in the parent material ($\text{Se}_{85}\text{Te}_{15}$). However, the substitution of Se with Ge leads to cross linking of Se-Te chains.

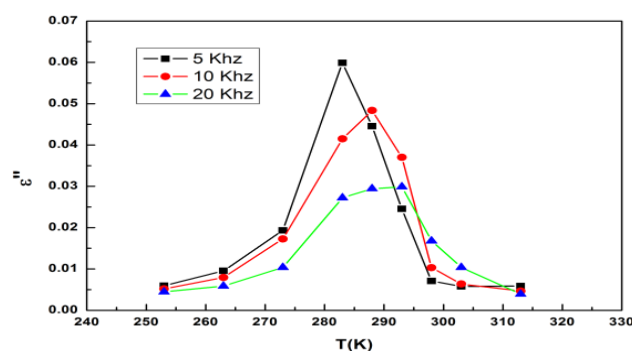


Fig. 10. Temperature dependence of dielectric loss (ϵ'') in $\text{Se}_{75}\text{Te}_{15}\text{Ge}_{10}$

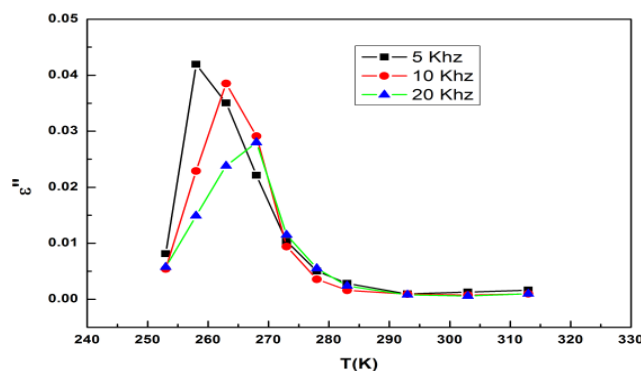


Fig. 11. Temperature dependence of dielectric loss (ϵ'') in $\text{Se}_{70}\text{Te}_{15}\text{Ge}_{15}$

Figs.10-11 show the temperature dependence of dielectric loss (ϵ'') at different frequencies for $\text{Se}_{75}\text{Te}_{15}\text{Ge}_{10}$, $\text{Se}_{70}\text{Te}_{15}\text{Ge}_{15}$ respectively. The graphs indicate that ϵ'' increases with increase in temperature and then shows maxima at a particular temperature for each frequency. The peaks of ϵ'' are obtained at higher temperatures with increases of frequency. This is consistent with the theory of dipolar relaxation [3, 25] as paired defect states (D^+ and D^-) behave as dipoles in the studied glasses.

4. Conclusions

From the dielectric studies of $\text{Se}_{85-x}\text{Te}_{15}\text{Ge}_x$ ($x=0, 2, 6$), we find that dielectric constant (ϵ') and the dielectric loss (ϵ'') are temperature and frequency dependent. Dielectric constant (ϵ') and dielectric loss (ϵ'') increases with increase in temperature, the increase being different at different frequencies. For each sample, dielectric constant (ϵ') and dielectric loss (ϵ'') decreases with increase in frequency at a given temperature. The frequency dependence of dielectric loss in the studied temperature range has been interpreted in terms of hopping of charge carriers over a potential barrier between charged defect states (D^+ and D^-). For $\text{Se}_{85-x}\text{Te}_{15}\text{Ge}_x$ ($x=10, 15$), the temperature dependence of dielectric constant (ϵ') and dielectric loss (ϵ'') show peaks which has been explained on the basis of dipolar relaxation. The dielectric constant (ϵ') is found to decrease with increase in Germanium content which may be interpreted in terms of decrease in defect states in the Se-Te glassy system with the addition of Germanium.

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