Role of Ge incorporation in the physical and dielectric properties of $Se_{75}Te_{25}$ and $Se_{85}Te_{15}$ glassy alloys

J SHARMA* and S KUMAR

Department of Physics, Christ Church College, Kanpur 208 001, India
*Corresponding author. E-mail: shjyoti_06@yahoo.com

Abstract. The effect of Ge additive on the physical and dielectric properties of $Se_{75}Te_{25}$ and $Se_{85}Te_{15}$ glassy alloys has been investigated. It is inferred that on adding Ge, the physical properties i.e., average coordination number, average number of constraints and average heat of atomization increase but lone pair electrons, fraction of floppy modes, electronegativity, degree of crosslinking and deviation of stoichiometry (R) decrease. The effect of Ge doping on the dielectric properties of the bulk $Se_{75}Te_{25}$ and $Se_{85}Te_{15}$ glassy alloys has also been studied in the temperature range 300–350 K for different frequencies (1 kHz–5 MHz). It is found that, with doping, the dielectric constant ε' and dielectric loss ε'' increase with increase in temperature and decrease with increase in frequency. The role of the third element Ge, as an impurity in the two pure binary $Se_{75}Te_{25}$ and $Se_{85}Te_{15}$ glassy alloys has been discussed in terms of the nature of covalent bonding and electronegativity difference between the elements used in making the aforesaid glassy systems.

1. Introduction

Alloying Te into a-Se results in dissociation of long polymeric chains and eight-member rings of a-Se [1]. This makes Se–Te alloys more useful than a-Se due to their distinct advantages (greater hardness, better photosensitivity, lesser ageing effects, etc.) and hence these alloys have many applications. However, limited reversibility and low crystallization temperatures are their serious disadvantages [2,3]. These can be overcome by adding a third element as a chemical modifier. The addition of a dopant can modify the lattice perfection.The Ge atom, due to its tetrahedral structure, forms spatial units with the chalcogen elements, break their characteristic configurations and contribute to the establishment of more homogeneous structure, which is quite stable compared to the chain-like structure of Se–Te.

Glasses with transparency upto 8 μm can be used for the preparation of optical fibres to transport radiation from the CO laser, and also to produce passive and active elements. For many applications, it is however advantageous to utilize radiation from the CO_2 laser. Therefore, one is looking for materials fulfilling this requirement. Se–Ge–Te glasses are useful from this point of view. Incorporation of Ge in binary Se–Te glassy system results in more thermal stability in a wide temperature range due to its high melting point. The fibres of Se–Ge–Te glasses can be used as transport medium for laser radiation.

In view of the above, the present communication reports the effect of Ge as an impurity in the dielectric properties of two well-known binary $Se_{75}Te_{25}$ and $Se_{85}Te_{15}$ glassy systems. Section 2 describes the experimental details of the measurements. The results are presented and discussed in §3. Section 4 deals with the conclusions drawn from the present work.

2. Experimental details

2.1 *Preparation of glassy alloys*

Glassy alloys of $Se_{75}Te_{25}$, $Se_{85}Te_{15}$ and $Se_{75}Te_{15}Ge_{10}$ systems were prepared by quenching technique described in our paper [4].

Pellets of ∼10 mm diameter and ∼(1–2) mm thickness were prepared by compressing the finely-grounded powder in a die in a hydraulic press under a load of ∼3–4 tons. Measurements were performed after coating the pellets with indium film deposited by vacuum evaporation technique.

2.2 *Dielectric relaxation measurements*

Measurement technique given in our paper [4] is used in the present case. Dielectric measurements were made using a 'Hioki 3532-50 LCR Hi TESTER'. The parallel capacitance and dissipation factor were measured and then ε' and ε'' were calculated. Three terminal measurements were performed to avoid stray capacitances.

3. Results and discussion

3.1 *Physical behaviour of various glassy alloys*

3.1.1 *Coordination number (r) and number of constraints in glassy network.* Glasses with varying compositions have varying coordination numbers. Hence, it is useful to calculate average coordination number $\langle r \rangle$. Average coordination number $\langle r \rangle$ is calculated by using the standard method [5,6]. For the compositions $Se_{75}Te_{25}$, $Se_{85}Te_{15}$, $Se_{75}Te_{15}Ge_{10}$, average coordination number $\langle r \rangle$ is given by

$$\langle r \rangle = \alpha N_{Se} + \beta N_{Te} + \gamma N_{Ge}/\alpha + \beta + \gamma, \tag{1}$$

where α, β, γ are concentrations (at%) of Se, Te and Ge respectively and $N_{Se} = 2$, $N_{Te} = 2$, $N_{Ge} = 4$ are their respective coordination numbers. The calculated coordination

Table 1. Values of average coordination number $\langle r \rangle$, number of constraints arising from bond stretching (N_a), number of constraints arising from bond bending (N_b) and average number of constraints (N_c) for Se₇₅Te₂₅, Se₈₅Te₁₅ and Se₇₅Te₁₅Ge₁₀ glassy systems.

Composition	$\langle r \rangle$	N_a	N_b	N_c
Se₇₅Te₂₅	2	1	1	2
Se₇₅Te₁₅Ge₁₀	2.2	1.1	1.4	2.5
Se₈₅Te₁₅	2	1	1	2

numbers (r) lie in the range $2.00 \leq r \leq 2.20$ and are given in table 1. From the calculated values of coordination numbers for the glassy system under investigation, it is inferred that $\langle r \rangle$ increases with the increase of Ge content. This reveals the compactness of the alloy.

The mechanical constraints (N_c), i.e., bond stretching (N_a) and bond bending (N_b) have great influence on covalent bonded glassy networks, which are associated with atomic bonding and effective coordination number $\langle r \rangle$. The number of constraints per atom arising from bond bending can be calculated as $N_b = 2\langle r \rangle - 3$ and from bond stretching by $N_a = \langle r \rangle / 2$ for the atomic species having coordination number (r). For different compositions of the glassy systems, the effective coordination number $\langle r \rangle$ can be determined by calculating the average number of constraints, i.e., $N_c = N_a + N_b$,

$$\langle r \rangle = \frac{2}{5}(N_c + 3). \tag{2}$$

The calculated values of N_a, N_b, N_c and $\langle r \rangle$ for the glassy systems Se₇₅Te₂₅, Se₈₅Te₁₅ and Se₇₅Te₁₅Ge₁₀ are listed in table 1. In Se₇₅Te₂₅, Se₈₅Te₁₅ and Se₇₅Te₁₅Ge₁₀ glassy systems, the average coordination number varies from 2.00 to 2.20.

3.1.2 *Role of lone pair electrons and glass-forming ability.* The numbers of lone pair electrons are calculated by using the relation

$$L = V - \langle r \rangle, \tag{3}$$

where L is the lone pair electrons, V is the valence electrons and $\langle r \rangle$ is the average coordination number. For Se₇₅Te₂₅, Se₈₅Te₁₅ and Se₇₅Te₁₅Ge₁₀ glassy systems, the number of lone pair electrons are obtained by using eq. (3) and are listed in table 2. It is observed that by adding Ge in a pure binary system, number of lone pairs electrons go on decreasing. This may be due to the interaction between Ge ion and lone pair electrons of the bridging Se atom [7]. Zhenhua [8] proposed a simple rule for a binary and a ternary system. According to him, for a binary system, the number of lone pair electrons must be greater than 2.6 and for a ternary system it must be greater than 1. In our system under investigation, the number of lone pair electrons are found to be greater than 1. So this explains the fact that the system can be obtained in glassy state.

3.1.3 *The average heat of atomization.* The heat of atomization of ternary and higher-order semiconductor compounds is a direct measure of the cohesive energy and the average bond strength for crystalline semiconductors [9] and is given by the relation

$$\langle H_s \rangle = \alpha H_s^A + \beta H_s^B + \gamma H_s^C / \alpha + \beta + \gamma, \tag{4}$$

Table 2. Values of average coordination number $\langle r \rangle$, number of lone pair electrons (L) and average heat of atomization ($H_s/\langle r \rangle$) for $Se_{75}Te_{25}$, $Se_{85}Te_{15}$ and $Se_{75}Te_{15}Ge_{10}$ glassy systems.

Composition	$\langle r \rangle$	V	$L = V - \langle r \rangle$	H_s (kJ/mole)	$H_s/\langle r \rangle$ (kJ/mole)
$Se_{75}Te_{25}$	2	6	4	219.50	109.75
$Se_{75}Te_{15}Ge_{10}$	2.2	5.8	3.6	237.50	107.95
$Se_{85}Te_{15}$	2.2	6	3.8	222.50	101.14

where α, β and γ are the atomic percentage of the elements Se, Te and Sn respectively and H_s is the heat of atomization of the element A. The average heat of atomization is calculated from eq. (4), by using the values of heat of atomization of Se, Te and Ge as 227, 197 and 377 kJ/mole, respectively from [7]. The calculated values of average heat of atomization $\langle H_s \rangle$ and average single bond energy $\langle H_s \rangle/\langle r \rangle$ are given in table 2. From table 1, it has been found that by increasing the Ge content or decreasing the Te content, the average single bond energy decreases in the case of $Se_{75}Te_{25}$ and increases in the case of $Se_{85}Te_{15}$ glassy system.

3.1.4 *Fraction of floppy modes.* Thorpe [10] has suggested that there exists a finite fraction of zero frequency normal vibrational modes, called floppy modes. These floppy modes exist in the absence of weaker long-range forces in the undercoordinated networks. The fraction of floppy modes is related to the average coordination number by the relation

$$f = 2 - \frac{5}{6} \langle r \rangle. \tag{5}$$

The values of fraction of floppy modes are calculated from eq. (5) and are given in table 3. From table 3, it is clear that the fraction of floppy modes decreases with increase in average coordination number. This shows that the system becomes more rigid with the increase in Ge content.

3.1.5 *Deviation of stoichiometry and electronegativity.* The deviation of stoichiometry (R) is the ratio of the possible covalent bonds of chalcogen atoms to that of nonchalcogen atoms in the system. The values of R decide the nature of the material, i.e., for $R > 1$,

Table 3. Values of fraction of floppy modes f, electronegativity χ, deviation of stoichiometry R and degree of cross-linking for $Se_{75}Te_{25}$, $Se_{85}Te_{15}$ and $Se_{75}Te_{15}Ge_{10}$ glassy alloys.

Composition	Fraction of floppy modes f	χ	R	Degree of cross-linking
$Se_{75}Te_{25}$	0.333	2.325	∞	2.50
$Se_{75}Te_{15}Ge_{10}$	0.166	2.29	4.5	0.70
$Se_{85}Te_{15}$	0.333	2.285	∞	2.00

the material is chalcogen-rich and for $R < 1$, the material is chalcogen-poor. The value of R is obtained by the relation [11,12]

$$R = XN_{\text{Se}} + YN_{\text{Te}}/ZN_{\text{Ge}}, \tag{6}$$

where X, Y, Z are the atomic fractions of Se, Te and Ge respectively. The calculated values of R are given in table 3. From table 3, it is observed that the minimum value of R is 21.22, which is much greater than 1, confirming that the system under consideration is a chalcogen-rich system. The electronegativity of the samples is calculated by Sanderson's principle [13]. The calculated values of electronegativity for the present system are listed in table 3. From table 3, it is clear that the electronegativity decreases on addition of Ge.

3.2 *Dielectric behaviour of various glassy alloys*

3.2.1 *Temperature and frequency dependence of various glassy alloys.* Temperature dependence of ε' and ε'' was measured at various frequencies (1 kHz–5 MHz) for different glassy alloys studied at present. Measurements have been taken in the temperature range 300–350 K. ε' and ε'' are found to be temperature-dependent in the above frequency range in all the glassy samples studied here (see figures 1–2 for all glassy alloys). ε' and ε'' increase with the increase of temperature, the increase is different at different frequencies. This can be attributed to the fact that orientational polarization is associated with the thermal motion of molecules. The orientation of the molecules of dipoles increases as the thermal energy increases, leading to the increase of ε''. The increase of ε'' with temperature may be due to the increase in conduction losses with temperature.

From figures 1 and 2, it is also found that dispersion is low at high frequencies. In dielectric spectroscopy, large frequency-dependent contributions to the dielectric response, especially at low frequencies, may be due to the build-up of charge. This, the so-called Maxwell–Wagner polarization, occurs either at the inner dielectric boundary layers on a microscopic scale, or at the external electrode–sample interface on a macroscopic scale. In both cases, this leads to a separation of charges. The charges are often separated over a considerable distance, and the contribution to dielectric response can therefore be orders of magnitude larger than the dielectric response due to molecular vibration which occurs at high frequencies because at high frequencies, the energy is too high to cause rotation, yet too low to affect electrons directly, and is absorbed in the form of molecular vibrations. This type of behaviour at low and high frequencies comes under interfacial polarization.

It has also been found that ε' and ε'' decrease with increasing frequency. This is due to the fact that in dielectric spectroscopy, all the components of polarization (electronic, ionic, dipolar or orientation and space charge) contribute for polar molecules. First, electronic polarization occurs at frequencies up to 10^{16} Hz. Secondly, ionic polarization occurs due to the displacement of negative and positive ions with respect to each other. This type of polarization occurs at 10^{13} Hz frequency. The third type is the dipolar polarization, which takes place due to the presence of molecules with permanent electric dipole moments that can change their directions of rotation to that of the applied electric field. The dipolar polarization occurs at frequencies up to about 10^{10} Hz. Finally, space-charge polarization takes place due to the diffusion of mobile charge carriers, along the
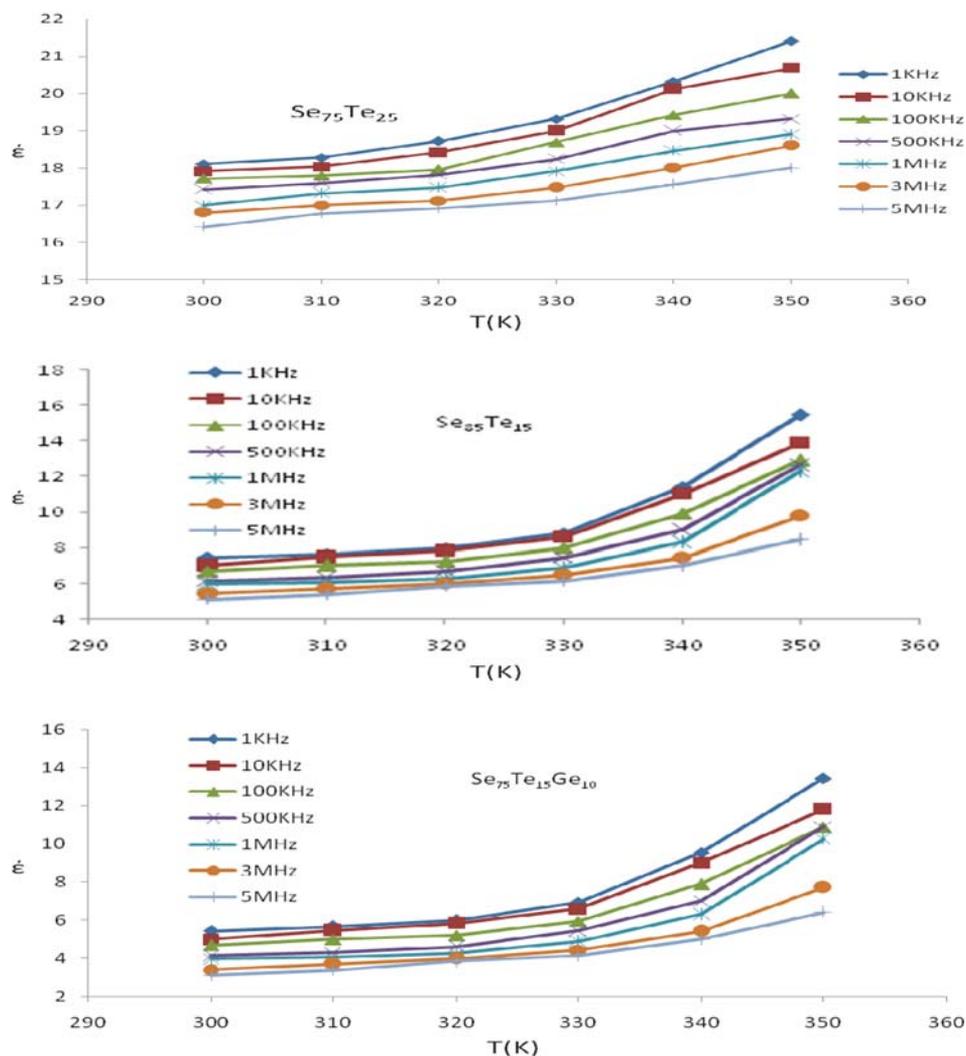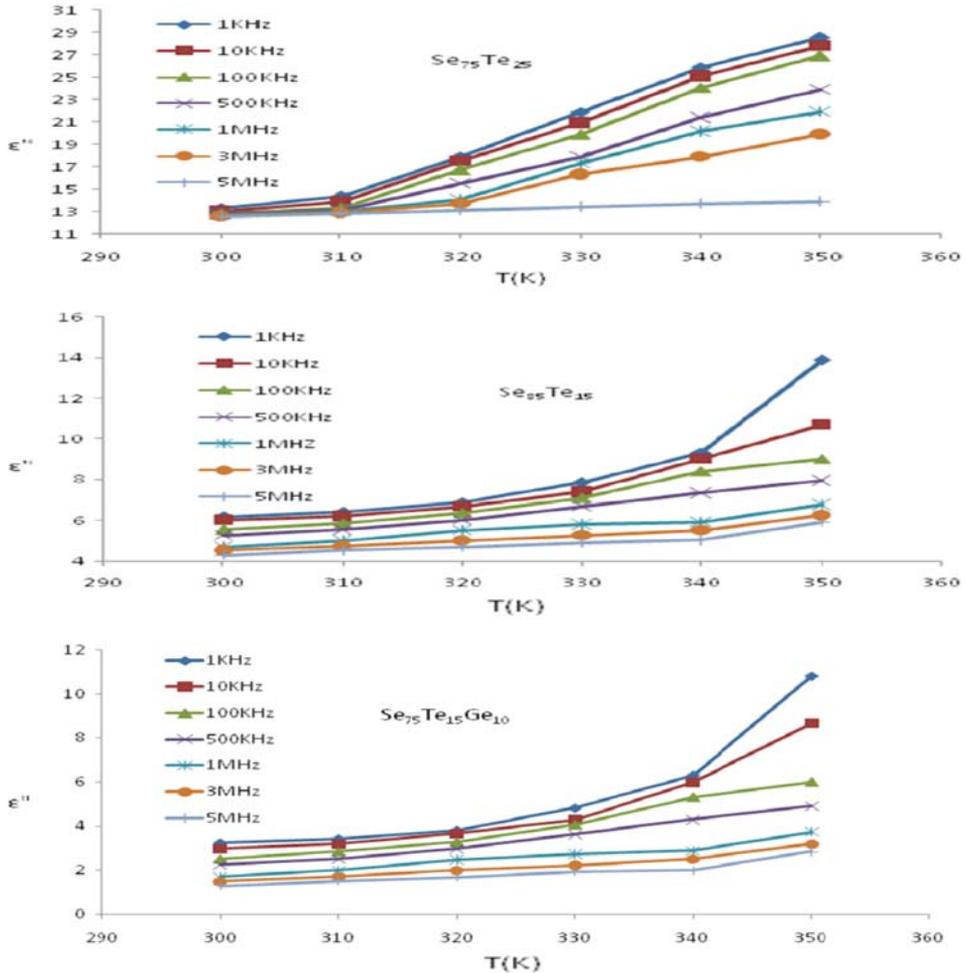
Figure 1. Plots of ε' vs. T curves for $Se_{75}Te_{25}$, $Se_{85}Te_{15}$ and $Se_{75}Te_{15}Ge_{10}$ glassy systems.

field direction at the interfaces. Space-charge polarization occurs at frequencies between 1 and 10^3 Hz. The sum of these four types of polarization represents the total polarization of a dielectric material. In the present study, it is clear that the ionic polarization does not show a pronounced effect in the total polarization because the studied composition is of covalent nature.

In these glassy alloys, ε'' is found to follow a power law with frequency, i.e., $\varepsilon'' = A\omega^m$. Figure 3 confirms this behaviour where $\ln \varepsilon''$ vs. $\ln \omega$ curves are found to be straight lines at various temperatures for all glassy alloys.

The power m is calculated from the slopes of these curves and it is found that the values of m are negative at all measuring temperatures. The magnitude of m increases with the
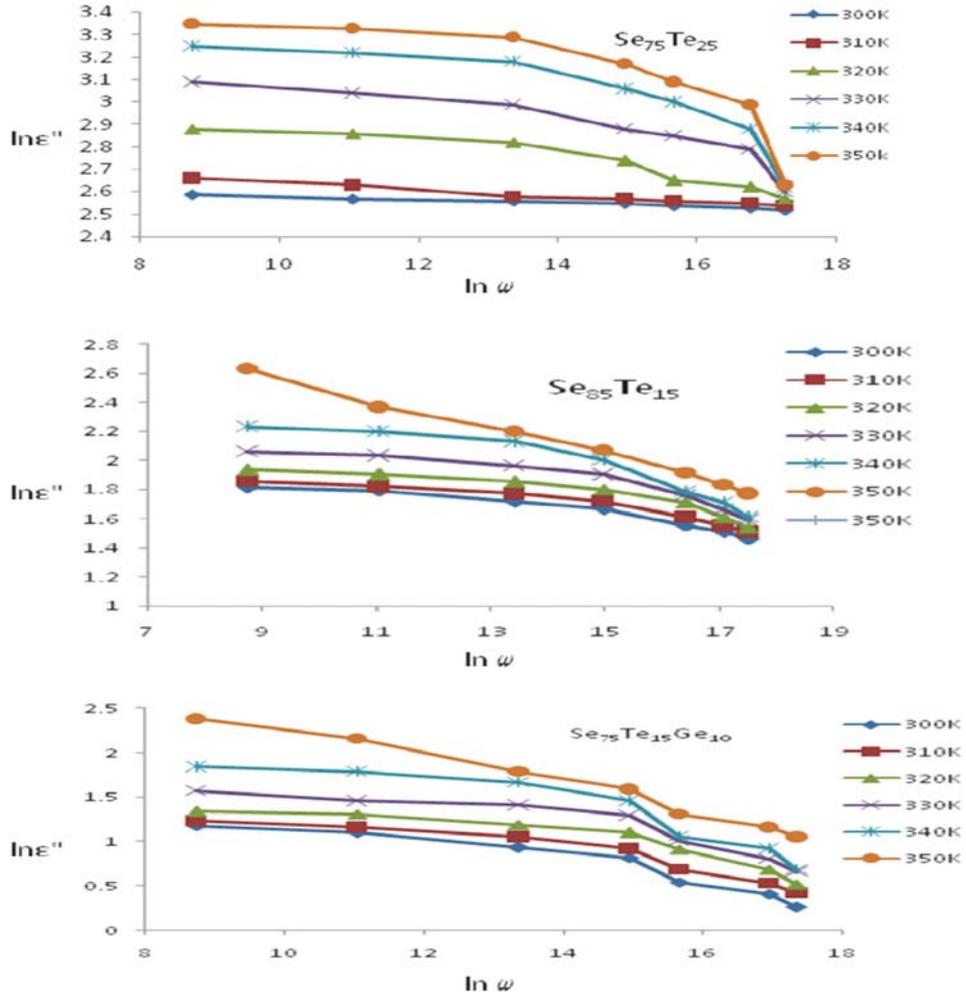
Figure 2. Plots of ε'' vs. T curves for Se$_{75}$Te$_{25}$, Se$_{85}$Te$_{15}$ and Se$_{75}$Te$_{15}$Ge$_{10}$ glassy systems.

increase in temperature in all the samples studied at present. Guintini *et al* [14] had proposed a dipolar model for dielectric dispersion in chalcogenide glasses. This model is based on Elliott's idea [15] of hopping of charge carriers over a potential barrier between charged defect states (D^+ and D^-). These defects are responsible not only for the position of the Fermi level, but also for the transport properties of the material. In addition, they act as traps and recombination centres for carriers and (D^+/D^-) is assumed to form a dipole which has a relaxation time depending on its activation energy; the latter can be attributed to the existence of a potential barrier over which the carriers hop. This potential barrier, as proposed by Elliot, is due to the Coulombic interaction between neighbouring sites forming a dipole.

The relaxation time connected with a hop is given by

$$\tau = \tau_0 \exp(W/kT). \tag{7}$$

Figure 3. Plots of ln ω vs. ln ε'' curves for $Se_{75}Te_{25}$, $Se_{85}Te_{15}$ and $Se_{75}Te_{15}Ge_{10}$ glassy systems.

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

$$\varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty)\, 4\pi N\varepsilon_0 kT/ne^2 \int_0^\infty R^4 \left[\omega/\left(1 + \omega^2\tau^2\right)\right] d\tau, \tag{8}$$

where R (a function of τ) is the distance between the localized sites. According to Guintini *et al* [16], assuming $\omega\tau \ll 1$, ε'' at a particular frequency in the temperature range where dielectric dispersion occurs, is given by

$$\varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty)\, 2\pi^2 N \left(ne^2/\varepsilon_0\right)^3 kT\tau_0^m W_m^{-4}\omega^m. \tag{9}$$

Here, m is the power of angular frequency and is negative in this case and is given by
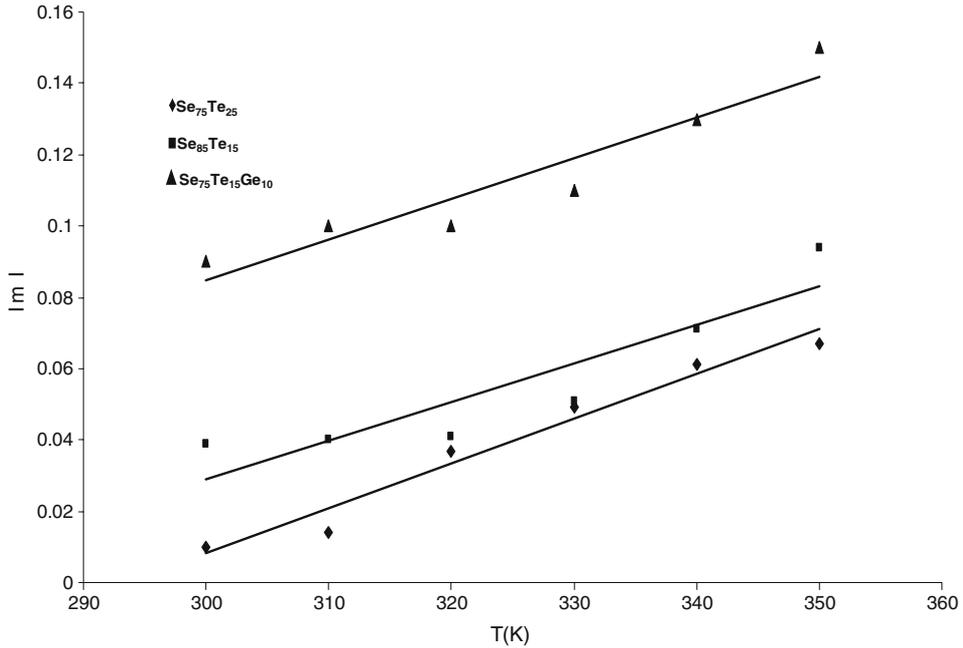
$$m = -4kT/W_m, \tag{10}$$

Figure 4. $|m|$ vs. T curves for Se$_{75}$Te$_{25}$, Se$_{85}$Te$_{15}$ and Se$_{75}$Te$_{15}$Ge$_{10}$ glassy systems.

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

The values of m at different temperatures are negative and follow a linear relation with temperature (see figure 4 for the glassy alloys studied). Using the values of m, W_m is calculated and values are given in table 4. The values of loss tangent (tan $\delta = \varepsilon''/\varepsilon'$) and capacitive reactance ($X_c = \frac{1}{2}\Pi f C$) are also calculated and the results obtained are given in table 4. It is clear from this table that W_m increases and tan δ decreases with impurity incorporation. The behaviour of W_m with increasing temperature is shown in figure 5.

3.2.2 *Impurity dependence of ε' and ε''.* When the isoelectronic atom Te is added to amorphous selenium [16], the density of defect states is increased and hence the residual

Table 4. Dielectric parameters of Se$_{75}$Te$_{25}$, Se$_{85}$Te$_{15}$ and Se$_{75}$Te$_{15}$Ge$_{10}$ glassy systems.

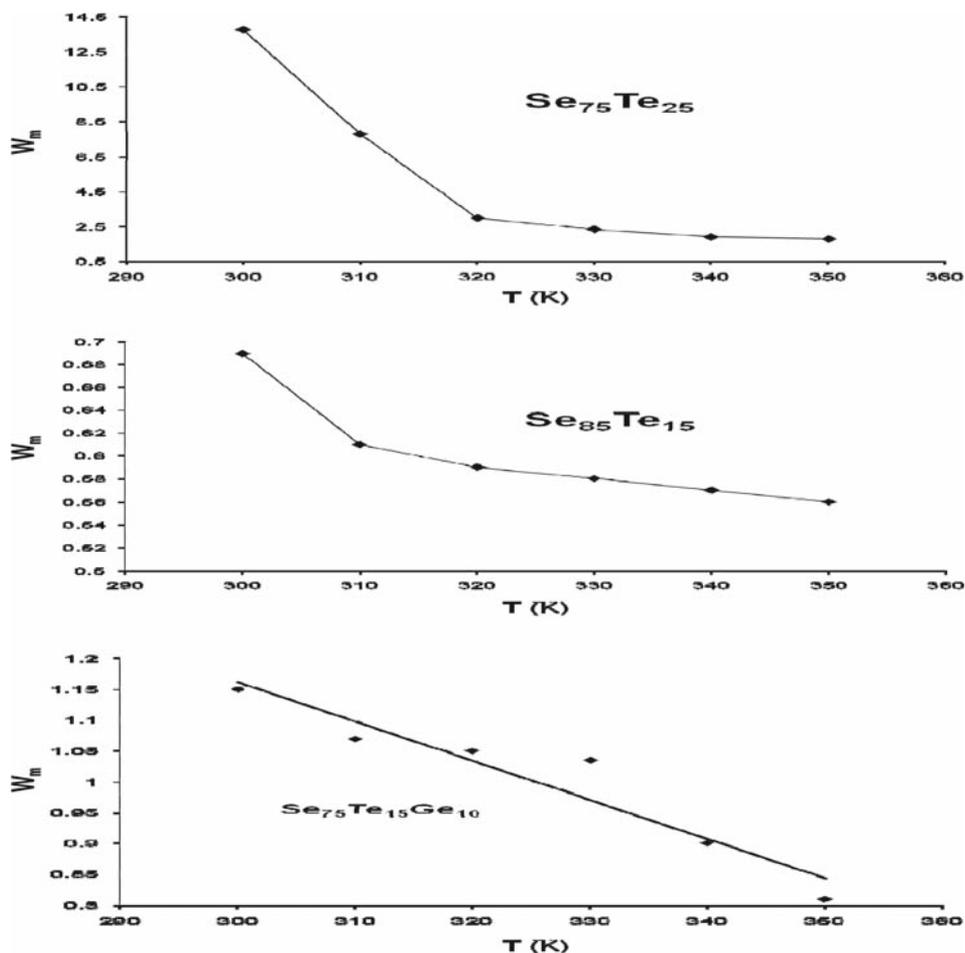| Glassy alloys	ε' (1 kHz, 300 K)	ε'' (1 kHz, 300 K)	W_m (eV)	tan δ (1 kHz, 300 K)	$X_c \times 10^6$ (1 kHz, 300 K)
Se$_{75}$Te$_{25}$	7.42	6.14	0.31	0.83	12.64
Se$_{75}$Te$_{15}$Ge$_{10}$	5.42	3.24	0.32	0.60	46.50
Se$_{85}$Te$_{15}$	18.11	13.32	0.27	0.74	28.59

Figure 5. W_m vs. T curves for $Se_{75}Te_{25}$, $Se_{85}Te_{15}$ and $Se_{75}Te_{15}Ge_{10}$ glassy systems.

potential increases in xerographic experiment. Onozuka *et al* [16] have therefore observed that on introducing Cl to the Se–Te system, the residual potential decreases again. This result was interpreted on the basis of a structural defect model where Te was assumed to form positively charged impurities due to the small electronegativity of Te as compared to Se, while Cl atoms having higher electronegavity than selenium [9] form negatively-charged impurities, thereby compensating the effect of Te.

Along the same lines, one can expect that when Ge, having lower electronegativity than Se and Te [9], is introduced in $Se_{85}Te_{15}$, positively-charged defects will be formed, but the extent of their formation will be smaller as the amount of Te is the same in both. On the other hand, when the same Ge is incorporated in $Se_{75}Te_{25}$, the density of defect states may decrease more sharply due to the decrease in percentage of Te atom in $Se_{75}Te_{15}Ge_{10}$ compared to that in $Se_{75}Te_{25}$ binary glassy system.

The values of ε' and ε'' in these glassy alloys are given in table 4. As the dielectric loss in these glasses depends upon the total number of localized sites, the decrease of dielectric

Table 5. Calculated covalent character of bonds for the considered compositions.

Different bonds	% Covalent character
Se–Se	100.00
Se–Te	97.78
Ge–Ge	100.00
Se–Ge	91.39
Te–Te	100.00
Te–Ge	79.85

loss with the Ge incorporation can be understood in terms of the decrease of density of defects on adding Ge to the Se–Te glassy system. Due to the decreased number of dipoles (D^+ and D^-) with Ge, the dielectric constant is also expected to decrease as we found in the present study.

The change in dielectric parameters with impurity can also be explained in terms of the nature of bonding in the system. The degree of covalency of the studied compositions can be estimated according to the following relation [9]:

$$\text{The proportion of covalent character} = 100\% \exp\left[-0.25(\chi_A - \chi_B)^2\right], \quad (11)$$

where χ_A and χ_B are the electronegativities of atoms A and B respectively. The values of % covalent characters of different bonds are listed in table 5.

The incorporation of Ge in the pure binary Se–Te glassy alloy leads to a decrease in the value of the dielectric parameters. It may be assumed that the incorporation of Ge in the binary alloy leads to an increase in the density of stronger bonds Ge–Ge, Se–Se, Te–Te compared to other bonds in the network structure, i.e., decreases the weaker bond density, i.e., Se–Ge and Te–Ge in the investigated compositions, which are more responsive to the electric field than the stronger bonds. Thus, ε' decreases with Ge incorporation in the studied system. The decrease in the dielectric loss may be due to the decrease in the density of defect states when the third element Ge as an impurity is incorporated in pure binary Se–Te glassy alloys.

4. Conclusions

The effect of Ge additive on the physical and dielectric properties of Se$_{75}$Te$_{25}$ and Se$_{85}$Te$_{15}$ glassy alloys has been investigated. It is inferred that by adding Ge, the physical properties, i.e., average coordination number, average number of constraints and average heat of atomization increase but lone pair electrons, fraction of floppy modes, electronegativity, degree of crosslinking and deviation of stoichiometry (R) decrease. The temperature and frequency dependences of the dielectric constants and the dielectric losses in various glassy systems in the frequency range (1 kHz–5 MHz) and temperature range (300–350 K) have also been measured. It has been found that both dielectric constant and the dielectric loss are highly dependent on frequency and temperature and

also found to be dependent with the Ge as an impurity incorporated in Se–Te glassy system. It is clear from the results obtained that the addition of Ge decreases the charged defect states in the pure Se–Te glassy network which also affects the dielectric properties. The decrease in defect states in the $Se_{75}Te_{25}$ and $Se_{85}Te_{15}$ binary glassy systems could be explained on the basis of the electronegativity difference between the constituent elements and on the nature of covalent bonding character of the elements used in making these glassy alloys.

Acknowledgement

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