DIELECTRIC PROPERTIES OF Se-Te-In GLASSES

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Frequency and temperature dependence of dielectric parameters in chalcogenide glasses $Se_{85-x}Te_{15}In_x$ (x= 0, 2, 6, 10) have been studied by measuring capacitance and conductance in the frequency range 2 kHz to 50 kHz and temperature range 223K to 293K. Results indicate that dielectric dispersion occurs in this frequency and temperature range and dielectric dispersion is more at lower frequency. Dielectric constant and dielectric loss are found to be highly frequency and temperature dependent. The analysis shows that dielectric dispersion based on two electron hopping over a potential barrier. It has been found that both dielectric constant and dielectric loss are found to increase with increase in Indium concentration and is due to the increase in defect states with increase in Indium concentration.

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1. Introduction

Chalcogenide glasses have been extensively studied due to their varied applications in solid state devices. Selenium tellurium based chalcogenides have been widely studied due to their (a) great storage capacity and fast access to information (b) the advantage to delete and introduce new information (c) electro-photographic applications such as photoreceptors in photocopying and laser printing [1]. The study of dielectric behavior of chalcogenide glasses reveals the structural information which may be used to understand the conduction mechanisms. In addition, a study of temperature and frequency dependent dielectric constant may be of importance to understand the nature and origin of losses occurring in these materials. The effect of an impurity in an amorphous semiconductor may be widely different, depending on the conduction mechanism and the structure of material [2]. The impurity may either destroy the dangling bond centres of one sign or form charged centres which are compensated by centres of opposite sign. So, the composition dependence of physical parameters like dielectric constant and dielectric loss becomes an area of interest. The present paper reports the frequency and temperature dependence of dielectric constant and dielectric loss in Se_{85-x}Te₁₅In_x (x=0, 2, 6, 10) in the temperature range 223K to 293K and frequency range from 2kHz to 50kHz. The results have been analysed in terms of the existing Guintini's theory [3] of dielectric relaxation in chalcogenide glasses.

2. Experimental Details

For the present work the glassy materials were prepared by taking the constituent elements (5N pure) in the required atomic weight percentages using electronic balance with an accuracy of 0.0001gm. The weighed components for the respective samples were put into properly cleaned (rinsed with soap solution, acetone and methanol) quartz ampoules. The ampoules were sealed in a vacuum of order of 10^{-5} mbar using diffusion pump. The sealed ampoules were heated upto $650^{\circ}C$

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in the rocking furnace initially. Later the temperature of the furnace was raised upto 700° C and maintained at this temperature for about 24hrs. Rocking was done to ensure proper mixing and homogeneity of samples. Heated ampoules were immediately cooled in ice water for the materials to go into glassy state. Samples were crushed, separated, ground and characterized for their amorphous nature using X-ray diffraction technique (Model: Philips PW 1610, Goniometer: Philips 1710, detector Cu K α). The absence of prominent peaks confirmed the amorphous nature of various samples.Compressed pellets were prepared from the fine powder of various materials and compressing the powder in a die under a hydraulic press (10^3kg/m^2) . A three terminal sample holder has been fabricated for conductivity and capacitance measurements of pellet-shaped samples. A thermocouple has been inserted inside the sample holder which has been kept close to the sample for the measurement of correct temperature .Vacuum pumping system (model VS -65D , H.H.V. India) has been used to achieve a vacuum upto 10^{-4} to 10^{-5} Torr inside the sample holder. A general radio bridge (Model 1620-A) has been used for the measurement of frequency dependent conductance and capacitance of the materials. The bridge consists 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. Its direct read-out system minimizes the reading errors and permits rapid operation. To calculate the dielectric constant and dielectric loss, the capacitance and conductance were measured simultaneously using general radio bridge.

We have preferred to measure dielectric behavior on the pellet rather than the bulk, as macroscopic effects (gas bubbles etc.) may appear in the bulk during preparation. It has been shown by Goyal et al [4], 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 has been found by them in these materials.

3. Results and Discussion

The temperature dependence of dielectric constant(ε ') and the dielectric loss(ε ") has been studied at various frequencies from 2 kHz to 50 kHz for Se_{85-x}Te₁₅In_x (x=0, 2, 6, 10) in the temperature range 223K to 293K.

The real and imaginary parts of the absolute permittivity are represented by the relation

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}' - \mathbf{j} \ \boldsymbol{\varepsilon}'' \tag{1}$$

ac conductivity is given by

$$\sigma_{ac} = \omega \varepsilon'' \tag{2}$$

Dielectric loss,

$$\varepsilon'' = \frac{\sigma_{ac}}{\omega} \tag{3}$$

The dielectric constant (ϵ ') and dielectric loss (ϵ ") have been calculated from equations (1), (2) and (3).Both dielectric constant and dielectric loss increase with increase in temperature at different frequencies for each sample (Figs.1-8).All the samples show dielectric dispersion in the studied temperature and frequency range. The dielectric dispersion is more at lower frequency.



Fig.1Temperature dependence of dielectric constant(ε') in Se₈₅Te₁₅



Fig. 2. Temperature dependence of dielectric constant (ε ') in Se₈₃Te₁₅In₂



Fig. 3. Temperature dependence of dielectric constant (ε ')in Se₇₉Te₁₅In₆



Fig. 4. Temperature dependence of dielectric constant (ε ') in Se₇₅Te₁₅In₁₀



Fig. 5. Temperature dependence of dielectric loss (ε'') in Se₈₅Te₁₅



Fig. 6. Temperature dependence of dielectric loss (ε ") in Se₈₃Te₁₅In₂



Fig. 7. Temperature dependence of dielectric loss (ε ") in Se₇₉Te₁₅In₆



Fig. 8. Temperature dependence of dielectric loss (ε'') in Se₇₅Te₁₅In₁₀

The dielectric constant and dielectric loss decreases with increase in frequency and increase with increase in temperature for each sample. Moreover dielectric constant and dielectric loss increases with increase in concentration of Indium. This type of behavior has been reported earlier in the chalcogenide glasses [5-12]. The decrease of ε' with increasing frequency can be explained on the basis of polarizability of dielectrics. The total polarizability of dielectrics is made of four different components. One or two of them are always present and at a particular frequency of electric field and temperature. The total polarizability is given by

$$\alpha_{\rm P} = \alpha_{\rm e} + \alpha_{\rm i} + \alpha_{\rm 0} + \alpha_{\rm s} \tag{4}$$

 α_e , α_i , α_0 and α_s are respectively the electronic, ionic, orientational and space charge polarizabilities.

Electronic polarizability (α_e), which exists in all dielectrics, is due to displacement of electron cloud of each atom relative to nucleus. Ionic polarizability (α_i) exists in ionic crystals because the adjacent ions of opposite sign get displaced with respect each other in external electric field. Orientation polarizability (α_0) exists in polar substance whose asymmetric molecules possess permanent electric moment. Space charge polarizability is due to accumulation of charges in the interfaces between the component layers of dielectrics. The upper limits of frequency for electronic polarization, ionic polarization, orientational polarization and space charge polarization are 10^{16} Hz, 10^{13} Hz, 10^{10} Hz, 10^{3} Hz respectively[13].

The degree of covalency in the studied samples has been calculated using the relation[14].

$$C_{c} = 100 \exp[-0.25(\zeta_{A} - \zeta_{B})^{2}]$$
(5)

Where ζ_A and ζ_B are the electronegativities of atoms A and B respectively. The values of covalent character of bonding in the studied materials is shown in Table1.

Bond	Covalent Character (%)		
Туре			
Se-Se	100		
Te-Te	100		
Se-Te	95.06		
Se-In	86.22		
Te-In	97.47		

Table 1. Calculated covalent character of various bonds in $Se_{85-x}Te_{15}In_x$.

This shows that covalent character of bonding is dominant in the samples. So, ionic polarization does not play an important role in total polarization of studied glasses. The space charge polarization does not play any important role at studied frequencies. 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.

Since the orientiational 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 increases with increases with increases in temperature for each sample.

In chalcogenide glasses, the charged defect states D^+ and D^- [15] lie close to each other and form a dipole which is responsible for dielectric behavior of these glasses. When the sample of chalcogenide glass is placed in an oscillating electric field, each pair of sites forming dipole contributes to dielectric relaxation. So, for investigated chalcogenide glasses, the frequency and temperature dependence of orientational polarizability becomes significant which results in dielectric dispersion.

When an alternating electric field is applied to a dipole, the dipole rotates to align itself with the field. As the time passes, the electric field reverses its direction and the dipole must rotate again to remain aligned with the correct polarity. As it rotates, energy is lost through the generation of the heat as well as the acceleration and deceleration of the rotational motion of the dipole which leads to dielectric loss. The dielectric loss is a function of material, frequency and temperature. The dielectric loss can be divided into three parts i.e. conduction losses, dipole losses, and vibrational losses [16]. The conduction loss is due to migration of ions over large distances. When the ions move, they give some of their energy to the lattice as heat. Conduction losses are low at low temperature because it is proportional to $\sigma_{ac}(\omega)/\omega$. As $\sigma_{ac}(\omega)$ increases with increase in temperature so conduction loss increases with increase in temperature. This leads to increase in ε " with increase in temperature. The increase of dielectric loss at low frequency is due to dipole polarization.

In all the glasses under study, ε " is found to follow a power law with frequency i.e ε "=A ω ^m. This is confirmed by the straight line graph between log ε " and log f at various temperatures (Figs.9-12) for each sample.



Fig. 9.Log ε "vs log f graph for Se₈₅Te₁₅



Fig. 10.Log ε "vs log f graph for Se₈₃Te₁₅In₂



Fig. 11. Log ε "vs log f graph for Se₇₉Te₁₅In₆



Fig. 12.Log ε " vs log f graph for Se₇₅Te₁₅In₁₀

The power m is calculated from the slopes of these graphs and it is found that m is negative at the studied temperatures for each sample. The magnitude of m has been found to increase with increase in temperature for all the samples (Fig. 13).



Fig. 13. |m| versus T graph for Se_{85-x}Te₁₅In_x

Guintini et al [3] proposed a model for dielectric dispersion in chalcogenide glasses according to which dielectric properties of chalcogenide glasses can be interpreted by considering a set of dipoles formed by charged defect stats D^+ and D^- . Each dipole has a relaxation time depending on its activation energy; the latter can be attributed to the existence of potential barrier over which the carriers must hop. This potential barrier as proposed by Elliot is due to columbic interaction between neighbouring sites forming a dipole. The relaxation time connected with hop is given by

$$\tau = \tau_0 \exp(W/kT) \tag{6}$$

Combined the imaginary part of the permittivity with the angular frequency ω of the applied field, we can write

$$\varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty) \frac{4\pi N \varepsilon_0 kT}{ne^2} \int_0^\infty R^4 [\omega/(1 + \omega^2 \tau^2)] d\tau$$
⁽⁷⁾

Where R (a function of τ) is the distance between localized states. Assuming $\omega \tau \ll 1$, ϵ " can be written as

$$\varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty) 2\pi^2 N \left(\frac{ne^2}{\varepsilon_0}\right)^3 k T \tau_0^m W_M^{-4} \omega^m$$
(8)

where m is power of angular frequency and is given as

$$m=-4kT/W_{m}$$
(9)

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.

According to equation (8), ε " should follow a power law ε " = $A\omega^m$ and m should be negative.|m| should increase with increase in temperature.

In our samples, we have found that ε " follows power law for the studied frequency and temperature range and |m| has been found to increase with increase in temperature.

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 barriers as suggested by Elliot[15] in case of chalcogenide glasses. Using equation (9), W_m has been calculated at different temperatures for all samples. For each sample W_m comes out to be almost constant i.e.(0.24 ± 0.01)eV, (0.27 ± 0.01)eV,(0.25 ± 0.01)eV, ($0.22\pm.01$)eV for Se₈₅Te₁₅,Se₈₃Te₁₅In₂,Se₇₉Te₁₅In₆, Se₇₅Te₁₅In₁₀ respectively indicative of bipolaron hopping in all the samples in the studied temperature range[17].

The values of dielectric parameters: dielectric constant (ϵ ') and dielectric loss (ϵ ") at a particular frequency and temperature are given in Table2.

Sample	3	." 3	m
Se ₈₅ Te ₁₅	17.03	3.93	0.41
Se ₈₃ Te ₁₅ In ₂	23.12	8.78	0.38
Se ₇₉ Te ₁₅ In ₆	29.73	11.58	0.39
Se ₇₅ Te ₁₅ In ₁₀	71.69	52.69	0.44

Table2. Dielectric parameters for $Se_{85-x}Te_{15}In_x$ (x=0, 2, 6, 10) at 293K and 10 kHz

Dielectric constant (ϵ ') and the dielectric loss (ϵ ") increases with increase in Indium concentration. Such a behavior can be explained on the basis of increase in number of dipoles (D^+ and D^-) at higher concentration of Indium. The dielectric constant is also expected to increase as we found in the present study.

4. Conclusion

From the dielectric studies of $Se_{85-x}Te_{15}In_x$ (x=0, 2, 6, 10), 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 dielectric relaxation is due to orientational polarization in the investigated samples. 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^-) i.e. due to dipolar polarization. The dielectric constant (ε ') and the dielectric loss (ε ") are found to increase with increase in Indium content which may be interpreted in terms of increase in the Se-Te glassy system.

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