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AC CONDUCTIVITY AND DIELECTRIC PROPERTIES OF AMORPHOUS $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ (6≤ x ≤14) GLASSY SYSTEM

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The glassy network system under investigation is prepared by using melt quench technique. The ac conductivity and dielectric behavior studied in ac frequency range (500Hz–1MHz) below glass transformation region. The correlated barrier hopping (CBH) model is used for interpreting the relation between the frequency exponent and temperature. The equation based on the Guintini model gives the value of maximum barrier height from the dielectric measurements. The compositional variation of conduction mechanism and dielectric parameters is studied to explore material's nature.

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Keywords: X-Ray diffraction, Ac conductivity, Dielectric parameters, Activation energy, Frequency exponent

1. Introduction

In the recent years the study of amorphous semiconductor glasses has become one of the interesting areas of research due to their technical applications such as memory switching devices, optical switching, electro-photography, solar cells and IR transmission devices [1-4]. Dielectric properties such as dielectric constant and dielectric loss are important in explaining the defect states and structure of glassy network [5]. The ac conductivity variation with frequency and temperature explain the conduction mechanism in glassy network through hopping. In glassy amorphous semiconductors the mechanism of ac conduction is explained by using correlated barrier hopping (CBH) model [6-8] for the charge carriers across the defect states D^+ and D^-. In correlated barrier hopping mechanism, a potential barrier is formed due to assumed dipoles of the defect states pair which carriers must have to hop. The frequency and temperature dependent dielectric constant and dielectric loss measurements explain different types of polarization in the glassy network.

Among chalcogenide elements only Se has amorphous form but has short life time and low sensitivity problem [9]. However, the addition of impurities such as Sb, Sn, In, Ge, Te etc leads to relatively stable glasses with improved physical properties [10].The fourth dopant Sb acts as chemical modifier and creates compositional as well as configurational disorder in glassy network, which will be useful in understanding the structural, thermal, electrical and optical properties of a-Se-Ge-Sn-Sb chalcogenide glassy alloys [11].

The XRD technique has been used to confirm the amorphous nature of the samples through their short range order. In present work, frequency and temperature dependence of ac conductivity and dielectric properties has been studied for $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ (6≤ x ≤14) glassy alloys with the help of Impedance Analyser.

2. Experimental details

The melt quenching technique is used for preparation of $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ (6≤ x ≤14) glassy alloys. Se, Sn, Sb in powder form with 99.999% purity (Alpha Aesar) and Ge with 99.999%

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purity (Across organics) are weighed according to their atomic percentage. These weighed materials are put in clean quartz tube and are sealed at very high vacuum pressure of 10^{-5}Torr. The sealed ampoules are heated in a furnace at a heating rate of 3°C - 4°C/minute and temperature is raised to 1000°C. The ampoules are kept at highest temperature for 15 hours and continuously rocked at an interval of 1 hour to ensure the homogenous mixture. The quenching is done in ice-cold water immediately after taking out the ampoules from the furnace. The glass sample prepared is extracted by breaking the quartz ampoules and is grinded to fine powder. The vitreous nature of samples is confirmed by using X'Pert Pro XRD. Data is collected using Ni filtered Cu-K_α (1.54 Å) radiation in the $10° < 2\theta < 70°$ range at a scanning speed of 1°/min for glasses. The XRD spectra do not contain any prominent peak which confirms that samples have amorphous nature as shown in Fig. 1.

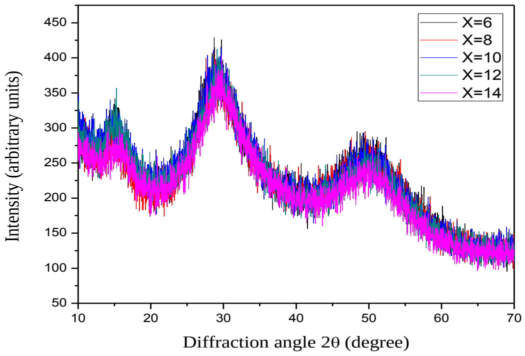

Fig.1.X-ray diffraction pattern of $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($6\leq x \leq 14$) glassy system.

The thin circular pellets (thickness=2mm and diameter=10mm) are prepared by compressing fine powder in a polished die under pressure of 3-4 tons produced by hydraulic pressure machine. The pellets are coated with silver paste on both sides to confirm good electrical contact with the electrode of the sample holder. Dielectric measurements have been done by using an instrument called Impedance Analyser (WAYNE KERR 6500B). The conducting and the dielectric properties of the samples are measured in the frequency range 500Hz to 1MHz and temperature range from 293K to 363K below glass transformation region.

3. Results and discussion

3.1. Frequency and temperature dependence of ac conductivity

The ac conductivity is calculated by using [12],

$$\sigma(\omega) = \varepsilon'\varepsilon_o\omega\tan\delta \tag{1}$$

where ε' is dielectric constant, ω is angular frequency, $\tan\delta$ is the dissipation factor and ε_o is the permittivity of free space.

The total conductivity in the glassy alloys system is given by [13],

$$\sigma_t(\omega) = \sigma_{dc} + \sigma_{ac}(\omega) \tag{2}$$

The term σ_{dc} is low frequency (dc) conductivity whose value is less as compared to ac conductivity. So σ_{dc} can be neglected in equation (2) and hence the total conductivity becomes equal to the ac conductivity. The value of ac conductivity is given by [14],

$$\sigma_{ac}(\omega) = A\omega^s \tag{3}$$

where ω = 2πf is the angular frequency, A is pre factor and s is the frequency exponent.

The frequency exponent (s≤1) is given by following equation [14],

$$S = \frac{d(\ln(\sigma_{ac}))}{d(\ln(\omega))} = 1 - \frac{6k_BT}{[W_m + k_BT\ln(\omega\tau_o)]} \qquad (4)$$

where W_m is the maximum barrier height over which the electrons hop, T is the absolute temperature and k_B is the Boltzmann constant, ω is the angular frequency and τ is the relaxation time for the electrons to hop over the barrier height (W).The conducting behavior of the glassy alloys is studied in frequency range 500Hz to 1MHz at different temperature range from 293K to 363K. The linear variation of ac conductivity with frequency is shown in Fig. 2. On analyzing compositional based results, we found increase in conducting behavior that might be due to increase in density of states or charge carriers due to dangling bonds with introduction of Sb in the network and hence the band tailing in the band structure.

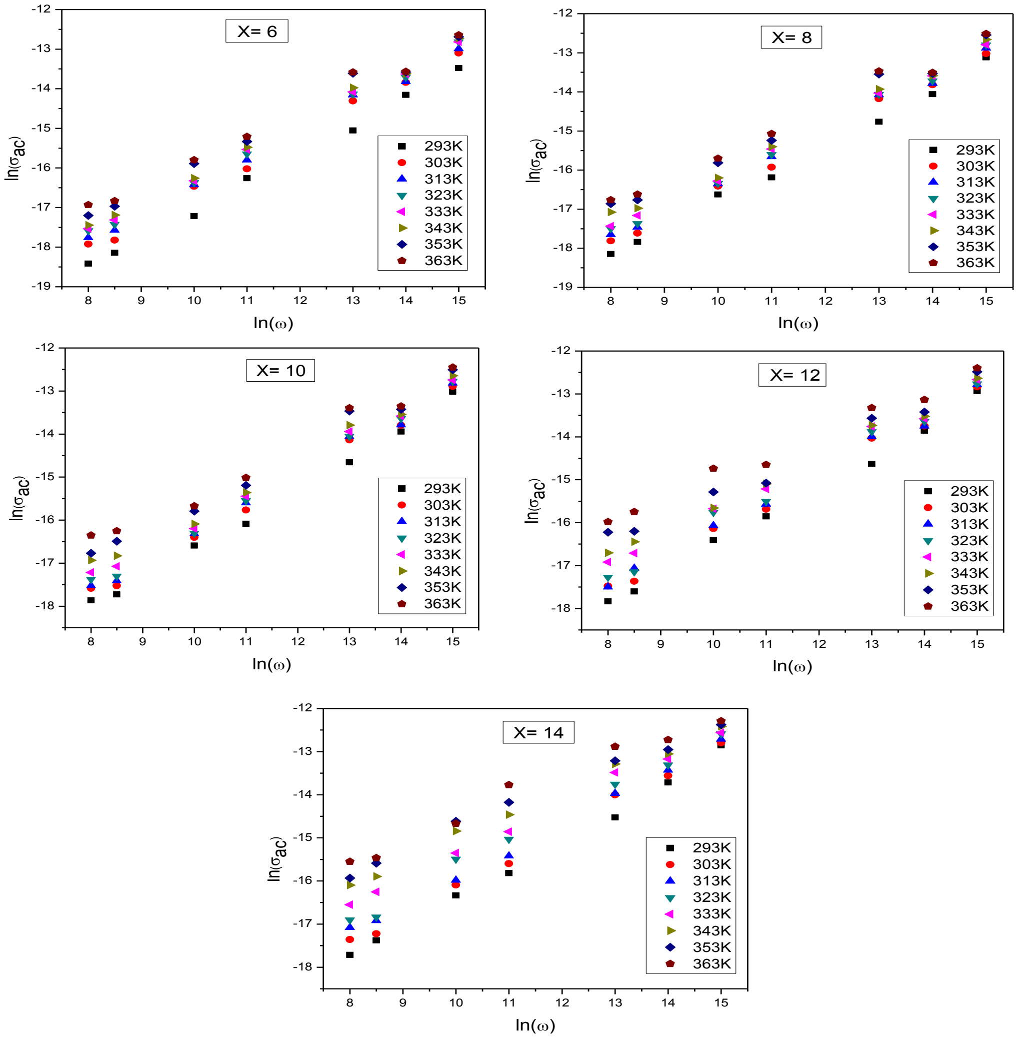

Fig.2.Variation of ln(σ_{ac}) with ln(ω) at different temperatures for $Se_{69}Sn_{10}Ge_{21-x}Sb_x$(6≤ x ≤14) glassy alloys.

The frequency exponent is calculated from the slope of the straight line plots of ln(σ_{ac}) versus ln(ω) in Fig. 2. The frequency exponent variation as function of temperature is plotted in Fig. 3. The value of s approximately equal to one at lower temperature and reduces with increase in temperature. These results can be interpreted on the basis of the correlated barrier hopping (CBH) between the intimate valence alternation pairs (IVAP) centers [15-17].

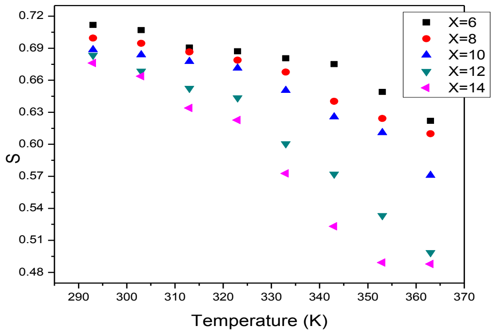

Fig.3. Variation of frequency exponent (s) with temperature for $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($6 \leq x \leq 14$) glassy alloys.

The variation of ac conductivity as function of temperature at different frequencies for glassy alloys is shown in Fig. 4. The ac conductivity increases with increase in temperature at particular frequency as listed in Table 1.

Table 1.Ac conductivity values of $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ (where x= 6, 8, 10, 12, 14) at different temperatures and frequencies.

$Se_{69}Sn_{10}Ge_{21-x}Sb_x$	Frequency	ac conductivity ($\Omega^{-1}m^{-1}$)			
		303K	313K	353K	363K
X=6	5KHz	1.57X 10^{-8}	1.68X 10^{-8}	4.11X 10^{-8}	4.88X 10^{-8}
	100KHz	1.19X10^{-7}	1.65X10^{-7}	3.10X10^{-7}	3.46X10^{-7}
	1MHz	9.75X 10^{-7}	9.95X 10^{-7}	1.22X 10^{-6}	1.28X 10^{-6}
X=8	5KHz	2.07X 10^{-8}	2.43X 10^{-8}	4.88X 10^{-8}	5.77X 10^{-8}
	100KHz	1.24X10^{-7}	1.9X10^{-7}	3.01X10^{-7}	6.19X10^{-7}
	1MHz	9.95X 10^{-7}	1.03X 10^{-6}	1.26X 10^{-6}	1.33X 10^{-6}
X=10	5KHz	2.18X 10^{-8}	2.48X 10^{-8}	6.88X 10^{-8}	7.73X 10^{-8}
	100KHz	1.69X10^{-7}	1.82X10^{-7}	3.91X10^{-7}	9.24X10^{-7}
	1MHz	9.75X 10^{-7}	1.03X 10^{-6}	1.47X 10^{-6}	1.58X 10^{-6}
X=12	5KHz	3.24X 10^{-8}	4.81X 10^{-8}	1.56X 10^{-7}	1.81X 10^{-7}
	100KHz	1.83X10^{-7}	2.26X10^{-7}	5.69X10^{-7}	1.57X10^{-6}
	1MHz	1.00X 10^{-6}	1.06X 10^{-6}	1.48X 10^{-6}	1.53X 10^{-6}
X=14	5KHz	3.49X 10^{-8}	5.42X 10^{-8}	3.57X 10^{-7}	3.89X 10^{-7}
	100KHz	2.22X10^{-7}	2.64X10^{-7}	8.61X10^{-7}	1.22X10^{-6}
	1MHz	1.29X 10^{-6}	1.06X 10^{-6}	1.48X 10^{-6}	1.53X 10^{-6}

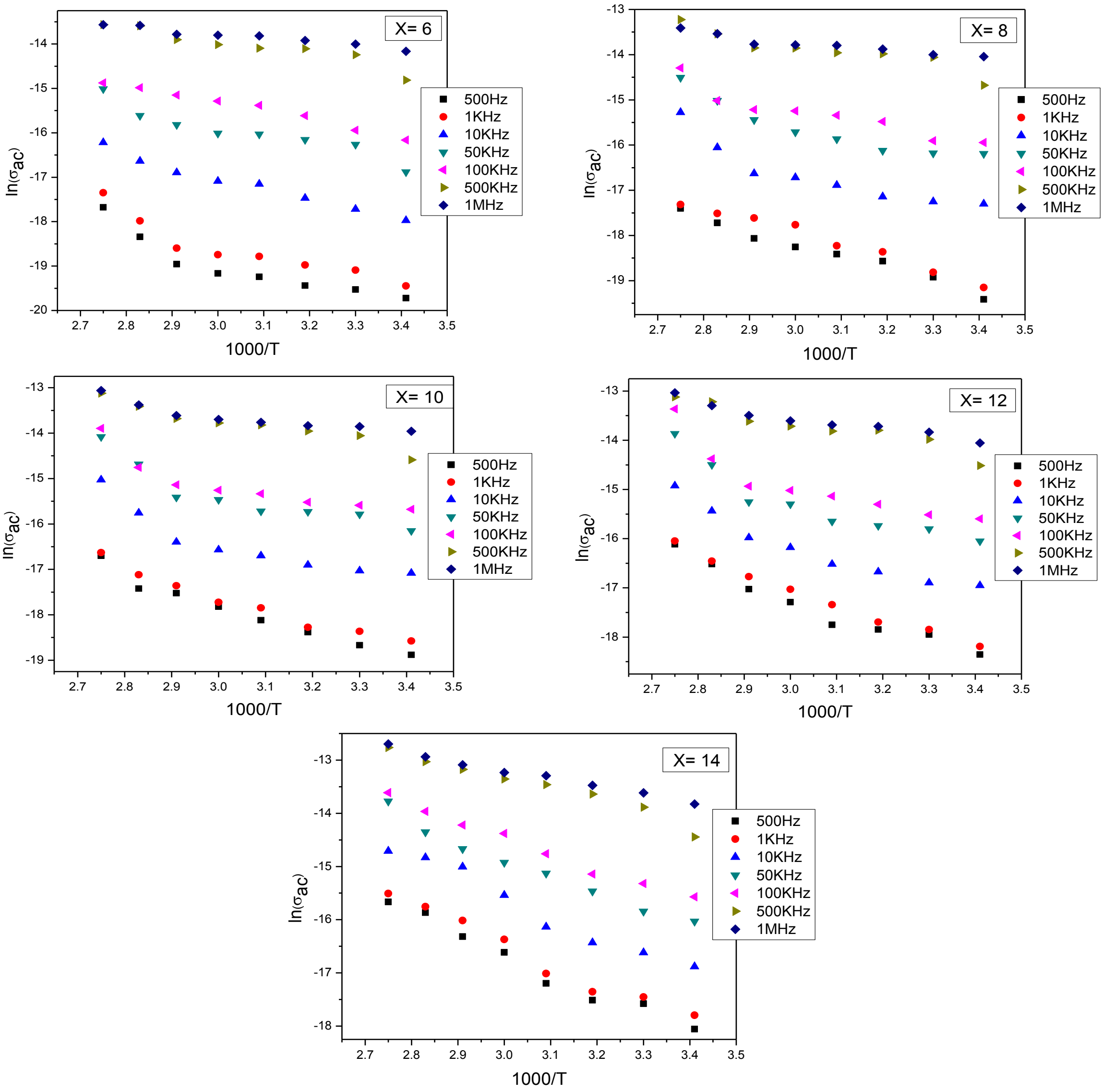

Fig.4. Variation of ln(σ_{ac}) with 1000/T at different temperatures for $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($6 \leq x \leq 14$) glassy alloys.

The density of states N(E_F) is calculated by using the equation [18],

$$\sigma_{ac} = (1/3)\, \pi e^2 k_B\, T[N(E_F)]^2\, \omega \alpha^{-5} [\ln(\upsilon_{ph}/\omega)]^4 \qquad (5)$$

where e is the electronic charge, k_B is the Boltzmann constant, T is the temperature, α is the exponential decay parameter of localized state wave function and υ_{ph} is the phonon frequency. By assuming α^{-1}=10Å and $\upsilon_{ph}=10^{12}$Hz [13]. The calculated values of density of localized states at frequency 1KHz at different temperature is listed in Table 2. It has been observed from table 2 that with addition of Sb in the glassy alloy system, Ge gets replaced by Sb thereby leading to increase in the density of localized states in the glassy network. This factor also contributes to increase the value of ac conductivity in the glassy alloy network with addition of Sb.

The value of activation energy at different frequencies can be calculated using equation [19]

$$\sigma_{ac}(\omega) = \sigma_o\, e^{\left(\frac{-\Delta E_{ac}}{k_B T}\right)} \qquad (6)$$

where σ_o is constant. The activation energy decreases with frequency as shown in Fig. 5.The calculated values of activation energy at different frequencies and temperature are listed in Table 2. The decrease in ΔE with increase in frequency is due to the increase in electronic jump between the localized states with increase in frequency [13]. The increase in ac conductivity and decrease in activation energy with frequency confirms hopping conduction mechanism.

At low temperatures, there is presence of thermally assisted tunneling of charge carriers in the band tails. The activation energy alone does not provide sufficient information as conduction takes place in extended states above mobility edge or by hopping in localized states. If the conduction happens in extended states above mobility edge, the activation energy represents the energy gap between mobility edge and the Fermi level. However, at low temperatures during hopping conduction it represents the sum of energy separation between occupied localized states and Fermi level, and the mobility activation energy [20]. The increase in value of ac conductivity with increase in the activation energy is due to shift of Fermi levels in Sb doped glassy network.

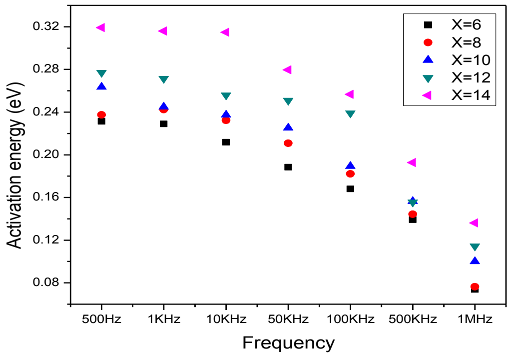

Fig.5. Variation of activation energy with frequency for $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($6 \leq x \leq 14$) glassy alloys.

Table 2. Values of the density of states $N(E_F)$, *activation energy* (ΔE_{ac}) *and maximum barrier height* (W_m) *for* $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($6 \leq x \leq 14$) *glassy alloys.*

$Se_{69}Sn_{10}Ge_{21-x}Sb_x$	$N(E_F)$ ($eV^{-1}m^{-3}$) at 1KHz		ΔE_{ac} (eV)		W_m(eV)
	293K	363K	1KHz	100KHz	
X = 6	$5.35X10^{33}$	$1.37X10^{34}$	0.2289	0.1680	0.297
X = 8	$6.22X10^{33}$	$1.39X10^{34}$	0.2424	0.1820	0.257
X= 10	$8.28X10^{33}$	$1.97X10^{34}$	0.2450	0.1892	0.213
X= 12	$1.00X10^{34}$	$2.63X10^{34}$	0.2714	0.2390	0.129
X = 14	$1.22X10^{34}$	$3.45x10^{34}$	0.3159	0.2566	0.113

3.2. Frequency and temperature dependence of dielectric loss

The dielectric loss is the imaginary part of the dielectric susceptibility which is given as [18]

$$\varepsilon'' = \varepsilon' \tan(\delta) \quad (7)$$

where $\tan(\delta)$ is the dissipation factor (D) obtained directly from the impedance analyzer which represents the dissipation of electric energy in the glassy dielectric material and ε' is dielectric constant.

The dielectric loss obeys a power law with angular frequency for all the glassy network compositions given as [7, 21]

$$\varepsilon'' = A\omega^m, \quad m < 1 \quad (8)$$

where A is constant. The variation of dielectric loss (ε'') with $\ln(\omega)$ for different glassy network is shown in Fig. 6. The dielectric loss has high values at low and moderate frequencies because of ion jump and conduction loss due to ion migration along with ion polarization loss. But at high frequencies the ion vibration is the only cause of low dielectric loss.

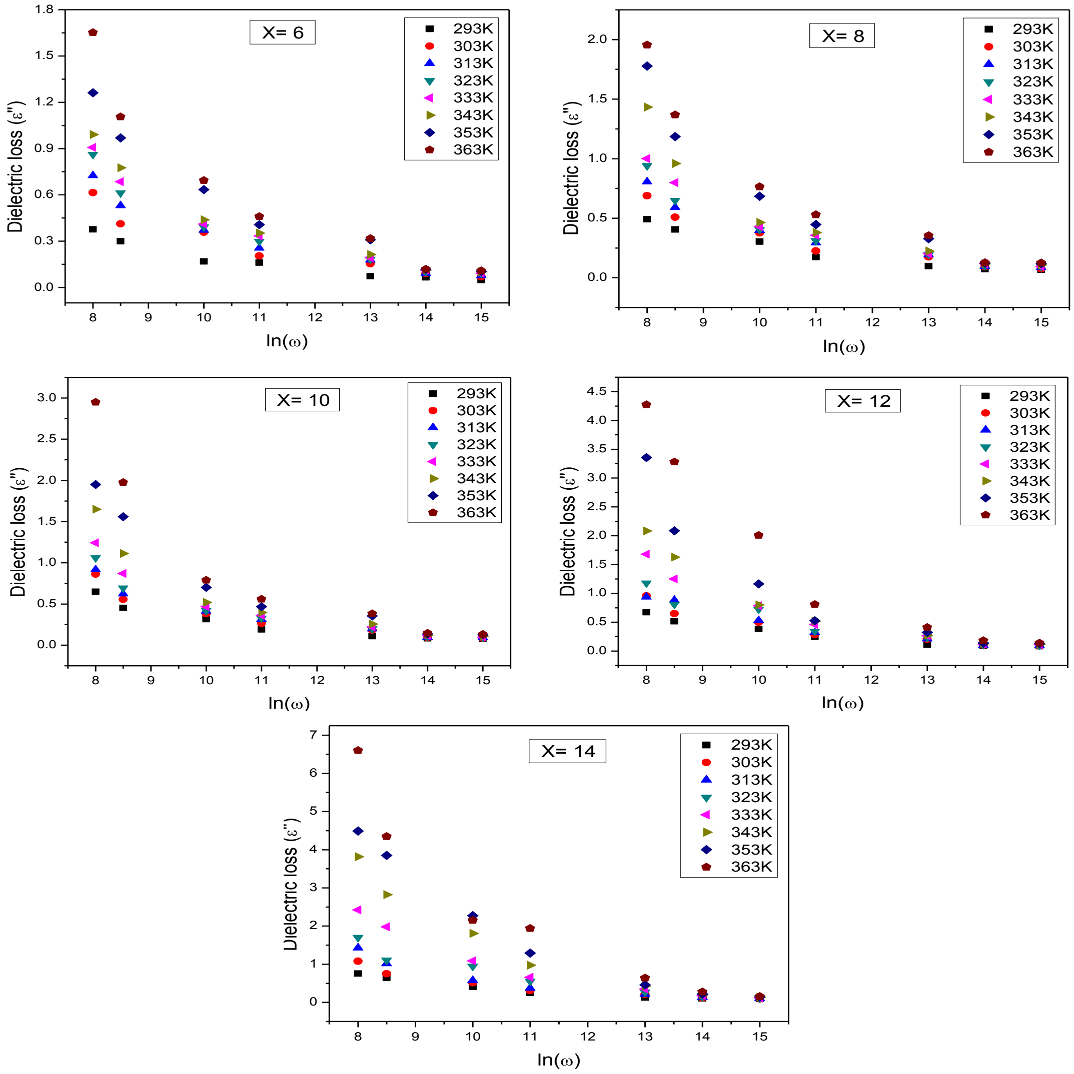

Fig.6. Variation of ε'' *with ln(ω) at different temperatures for* $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ *(6≤ x ≤14) glassy alloys.*

The dielectric loss behavior is also confirmed from the straight line plot between ln(ε″) and ln(ω) as in Fig. 7. The slope of graphs gives the value of m, which has been found negative for all compositions. Guintini [7, 21] on the basis of Elliot's [15, 22] idea proposed a model in order to explain the dielectric relaxation mechanism in chalcogenide glassy systems. The transport properties of the material are due to dipole formation by charged defect states (each pair of D^+ and D^-). The relaxation time of each dipole depends on its activation energy [23] which leads to the existence of a potential barrier for carrier hopping. The model explained the dielectric loss in dispersion region at particular frequency and the temperature is given as [7]

$$\varepsilon'' = (\varepsilon_o-\varepsilon_\infty)\, 2\pi^2 N\left(\frac{ne^2}{\varepsilon_o}\right)^3 k_B T \tau_o^m W_m^{-4} \omega^m \tag{9}$$

where n is the number of hoped electrons, N is the concentration of localized sites, ε_o is static dielectric constant, ε_∞ dielectric constant at infinitely high frequencies. W_m is the maximum barrier height whose value is obtained from the slopes of the straight lines plotted on m and temperature variation graphs as shown in Fig. 8. The relation between m and temperature is given as

$$m = \frac{-4k_B T}{W_m} \tag{10}$$

The relaxation time is given by,

$$\tau = \tau_o \exp\left(\frac{W}{k_B T}\right) \tag{11}$$

The values of W_m calculated by using equation (10) for investigated glassy alloys are listed in Table 2.

The dielectric loss increases with increase in temperature at different frequencies as shown in Fig.7. The higher dielectric loss at high temperature as compare to lower one is due to maximum contribution of conduction, dipole and vibration losses. The obtained values of dielectric loss at different frequencies and at different temperature for the glassy alloy system are listed in Table 3.

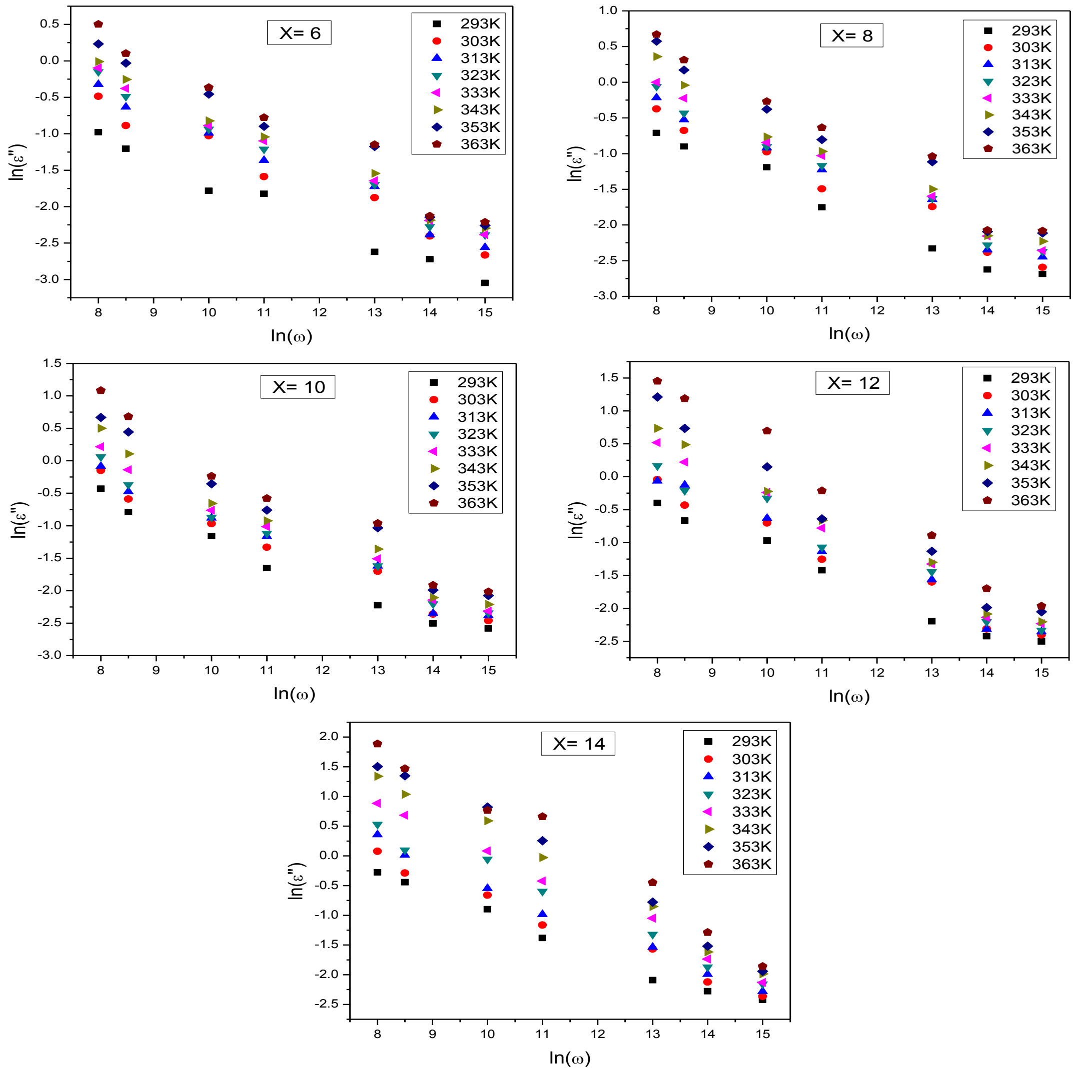

Fig.7. Variation of ln(ε'') with ln(ω) at different temperatures for $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ *(6≤ x ≤14) glassy alloys.*

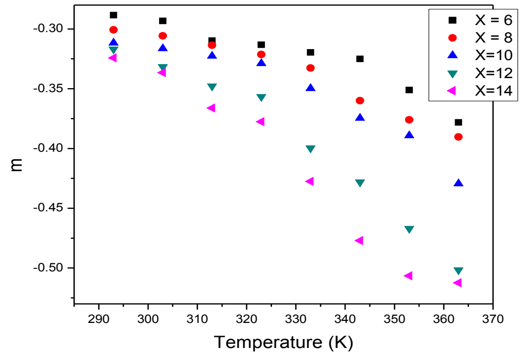

Fig.8 Variation of parameter 'm' with temperature for $Se_{69}Sn_{10}Ge_{21\text{-}x}Sb_x$ *(*$6\leq x\leq 14$*) glassy alloys.*

Table 3. Values of dielectric parameters for $Se_{69}Sn_{10}Ge_{21\text{-}x}Sb_x$ *(*$6\leq x\leq 14$*) glassy alloys.*

$Se_{69}Sn_{10}Ge_{21\text{-}x}Sb_x$	Frequency	ε′		ε″	
		293K	363K	293K	363K
X = 6	1KHz	186.42	194.62	0.403	3.302
	100KHz	185.52	193.32	0.107	0.390
	1MHz	185.41	193.23	0.079	0.144
X = 8	1KHz	195.56	200.43	0.544	3.411
	100KHz	193.60	198.73	0.134	0.700
	1MHz	193.56	198.69	0.089	0.169
X= 10	1KHz	198.34	202.75	0.966	6.765
	100KHz	196.95	201.44	0.175	1.044
	1MHz	196.85	199.98	0.097	0.239
X= 12	1KHz	206.74	208.61	1.421	12.132
	100KHz	205.04	206.22	0.190	1.772
	1MHz	204.99	206.04	0.088	0.246
X = 14	1KHz	212.15	215.75	2.113	20.783
	100KHz	210.81	212.16	0.195	1.384
	1MHz	210.74	211.93	0.111	0.345

3.3. Frequency and temperature dependence of dielectric constant

The values of dielectric constant are calculated by using the relation [24]

$$\varepsilon' = \frac{Cd}{\varepsilon_o A} \tag{12}$$

where C is the capacitance of the material, d is the thickness of the pellet, ε_o is the permittivity of the free space and A is the area of the pellet of the investigation sample. The variation of dielectric constant with frequency is shown in Fig.9.

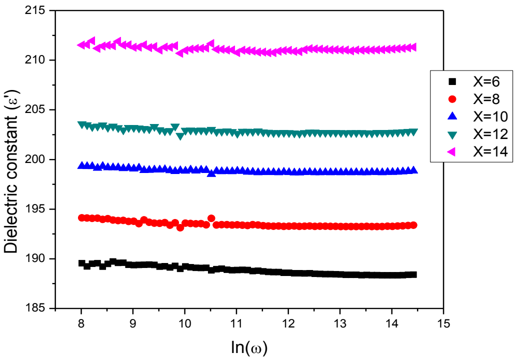

Fig.9.Frequency dependent dielectric constant variation of $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ *(*$6\leq x \leq 14$*) glassy alloys at room temperature.*

The polarization plays an important role in the explanation of decrease in dielectric constant with frequency. Various types of polarizations such as ionic, electronic, orientational and space charge polarization are responsible for such dielectric behavior [24]. Electronic polarization (10^{13}-10^{15}Hz) occurs due to displacement of valence electrons relative to positive nucleus. Ionic polarization (10^{12}-10^{13}Hz) arises from the displacement of ions (positive and negative) forming a heteropolar molecule. Orientational polarization (10^{13}-10^{10}Hz) arises due to change in the permanent dipole moments of molecules in presence of electric field. Lastly, the space charge polarization (1-10^{3}Hz) occurs due to impedance mobile charge carriers by interface. The value of total polarization is the sum of four types of polarizations [25].But in present glassy alloy system ionic polarization plays less effective role due to presence of predominant covalent nature [26].

The degree of covalency is calculated by using Pauling relation [27]

$$\text{Covalent character} = 100\%\ \exp(-0.25((\chi_A - \chi_B)^2) \qquad (13)$$

where χ_A and χ_B are the electronegativity of atoms A and B. The covalent character of different bonds (>90%) is given in Table 4 which shows the covalent nature of the samples.

Table 4.Bond energy and degree of covalency of different bonds in $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ *(*$6\leq x \leq 14$*) glassy alloys.*

Type of Chemical Bond	Bond Energy (kcal/mol)	Covalent Character (%)
Se-Ge	49.42	92.97
Se-Sb	43.95	93.94
Ge-Sb	33.75	99.96
Sb-Sn	32.38	99.98
Ge-Sn	35.93	99.94

At lower frequencies, the dielectric constant decreases with frequency due to decrease in orientational polarization as compared to electronic polarization. As frequency increases dipoles take more time to orient themselves to the applied electric field due to which orientational polarization ceases. Therefore the dielectric constant approaches to constant value at higher frequencies because of space charge polarization only [18]. On the basis of bond energy as listed in Table 4, Se-Sb bonds are weak as compared to Se-Ge bond which can easily respond to applied electric field. Therefore with addition of Sb in the glassy system values of dielectric constant increases due to increase in density of Se-Sb bonds as compare to Se-Ge bonds.

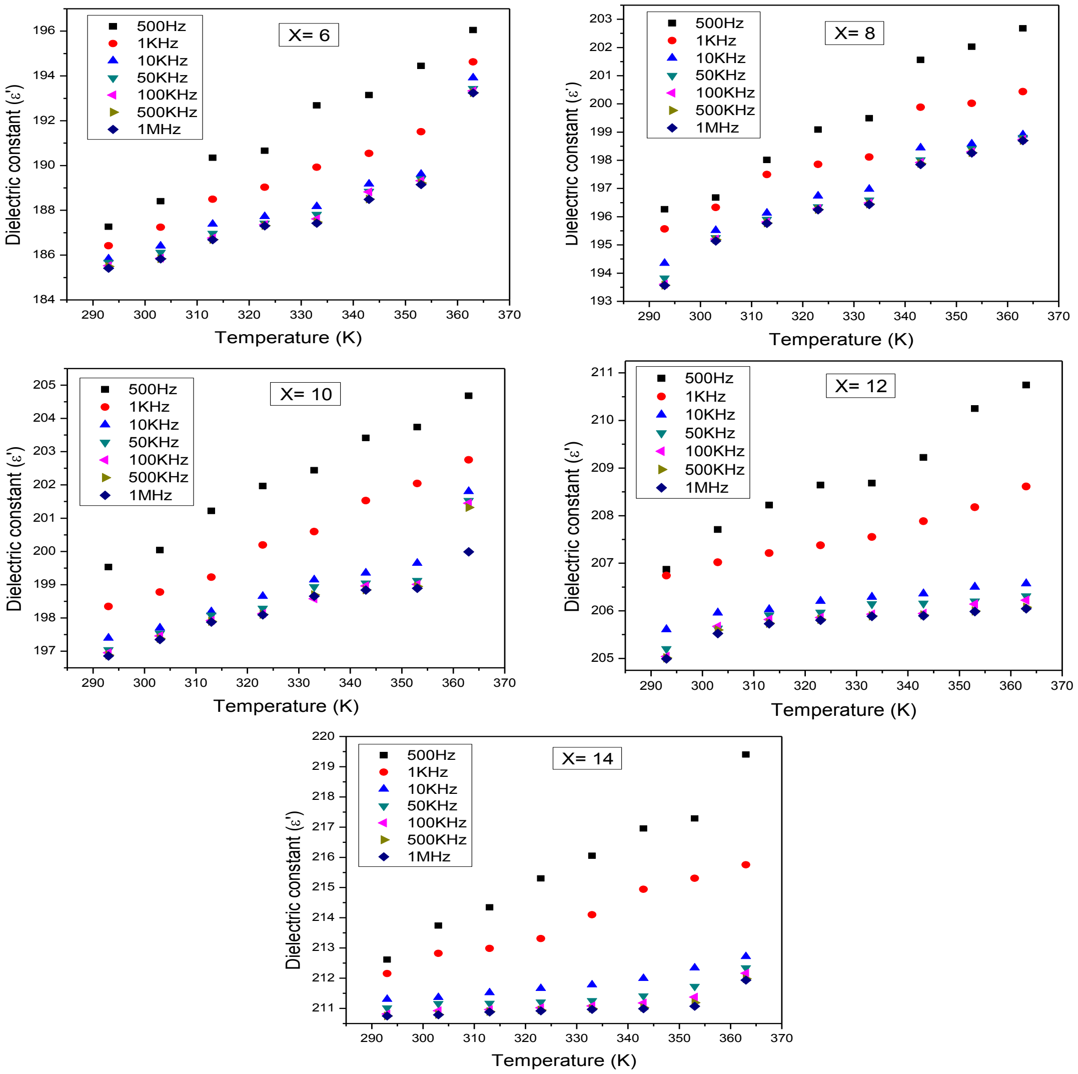

Fig.10. Temperature dependent dielectric constant variation of $Se_{69}Sn_{10}Ge_{21-x}Sb_x(6\leq x \leq 14)$ glassy alloys at different frequencies.

It is clear from Fig. 10 that with increase in temperature dielectric constant increases at particular frequency. This increase is due to increase in orientational polarization with temperature [28]. With addition of Sb in glassy network the density of defect states increases which leads to increase in dielectric constant. The calculated values of dielectric loss at different frequencies and at different temperature for the glassy alloys are listed in Table 3.

4. Conclusion

The glass material is prepared by using melt quench technique whose vitreous nature is confirmed by X-ray diffraction. The dielectric parameters of a-$Se_{69}Sn_{10}Ge_{21-x}Sb_x(6\leq x \leq 14)$ are temperature and frequency dependent. The material is semiconducting in nature that is obvious from the temperature dependence of ac conductivity. These results follow the CBH model. The dielectric parameters decreases with frequency and increases with temperature below glass transition temperature at particular concentration of Sb. On increasing the concentration of Sb, the density of defect states in the band gap increases which results in increase in ac conductivity and dielectric parameters.

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References

[1] M. Fabian, N. Dulgheru, K. Antonova, A.S zekeres, M. Gartner, Adv. in Condensed Matt. Phys. **1**, (2018).
[2] T. Kanamori, Y. Terunuma, S. Takahashi, T. Miyashita, Journal of Lightwave Technology**2**, 607 (1984).
[3] A. M. Andriesh, Semiconductors **32**, 867(1998).
[4] I. S. Yahia, N. A.Hegab, A. M.Shakra, A.M.AL-Ribaty, Physica B **407**, 2476 (2012).
[5] A.V. Nidhi, V. Modgil, V. S. Rangra, Chalcogenide Letters **13**, 359 (2016).
[6] A. E. Streen, H. Eyring, J. Chem. Phys. **5**, 113 (1937).
[7] J. C. Giuntini, J. V. Zanchetta, D. Jullien, R. Enolie, P. Houenou, J. Non-Cryst. Solids **45**, 57 (1981).
[8] M. Pollak, G. E. Pike, Phys. Rev. Lett. **25**, 1449 (1972).
[9] Saleh Ahmed Saleh, J. Mater. Sci. and Appl.**2**, 950 (2011).
[10] S. A. Fayek, M. Fadel, M. O. Abou-Helal, A. M. Shakra, Chalcogenide Letters **5**, 317 (2008).
[11] R. M. Mehra, G. Kaur, P. C. Mathur, Phy. Solid State Commun.**85**,29 (1993).
[12]J. I. Langford, A.J. C. Wilson, J. Appl. Crystallogr.**11**, 102(1978).
[13] N. A. Hegab, M. A. Afifi, H. E. Atyia, M.I. Ismael, ActaPhysicaPolonica A **119**, 416 (2011).
[14] S. R. Elliott, Adv. Phys. **36,** 135 (1987).
[15] S. R. Elliott, Solid State Commun. **27**, 749 (1978).
[16] C. Angell, Ann. Rev. Phys. Chem. **43**, 693 (1992).
[17] A. Sharma, N. Mehta, A. Kumar, J. Mater. Sci. **46**, 4509 (2011).
[18] Vivek Modgil, V. S. Rangra, Physica B, **445**, 14 (2014).
[19] N. Chandel, N. Mehta, A. Kumar, Curr. Appl. Phys. **12**,405 (2012).
[20] Satish Kumar, M. Husain, M. Zulfequar, J. Mater. Sci. **42**, 143 (2007).
[21] J. C. Giuntini, J. V. Zancheha, J. Non Cryst. Solids. **34**,419 (1979).
[22] S. R. Elliott, Philos. Mag. B **36**, 1291 (1977).
[23] M. Pollak, G. E. Pike, Phys. Rev. Lett. **28**, 1494 (1972).
[24] N. Sharma, B. S. Patial, N. Thakur, Appll. Phys. A **122**, 209 (2016).
[25] M. Barsoum, Fundamentals of Ceramics, McGraw-Hill:New York (1997).
[26] L. J. Pauling, Nature of the Chemical Bond, Cornell University Press, New York, 1960.
[27] A. Dahshan, K. A.Aly, Phil. Mag. **88**, 361(2009).
[28] D. K. Goel, C. P. Singh, R. K. Shukla, A. Kumar, J. Mater. Sci. **35**, 1017 (2000).