

AC Conductivity and Dielectric Properties of Amorphous $\text{Te}_{42}\text{As}_{36}\text{Ge}_{10}\text{Si}_{12}$ Glass

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$\text{Te}_{42}\text{As}_{36}\text{Ge}_{10}\text{Si}_{12}$ chalcogenide composition was prepared by conventional melt-quenching. The ac conductivity and the dielectric properties were carried out in the frequency range 0.5×10^3 – 4×10^6 Hz and temperature range 300–423 K. The analysis of the experimental results of the frequency dependence of ac conductivity $\sigma_{ac}(\omega)$ indicates that $\sigma_{ac}(\omega)$ is proportional to ω^s where $s > 1$. The temperature dependence of both ac conductivity and the parameter s is reasonably well interpreted by the correlated barrier hopping model. The maximum barrier height W_m calculated from ac conductivity and the density of localized states were determined. Values of dielectric constant ϵ_1 and dielectric loss ϵ_2 were found to decrease with frequency and increase with temperature. The analysis of dielectric loss leads to determine the barrier height W_m and agrees with that proposed by the theory of hopping of charge carriers over potential barrier between charged defect states as suggested by Elliott in case of chalcogenide glasses.

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1. Introduction

Chalcogenide glasses have received a great deal of attention for the last two decades due to their technological applications namely electronic, optoelectronic, optical and memory switching devices [1–4]. Chalcogens (Se, S, and Te) are basis elements in many ternary and quaternary systems in which the third or fourth components are added as a glass network former such as Ge and Si [5–7] or as an impurity to modify the investigated physical properties of amorphous materials [8–10]. This category of materials do not have long-range order, exhibit semi-conductive properties such as energy band gap, switching phenomenon and other electrical properties, which have been measured and discussed by many investigators. It is considered that many of these properties are due to the presence of localized states [11, 12]. The ac conductivity measurements represent an experimental method to obtain information about the existence and location of these states. Different models have been proposed to interpret the frequency and temperature dependence of ac conductivity in amorphous semiconductors [13–15].

The present communication reports some experimental results on ac electrical conductivity and dielectric properties over a wide range of temperature and frequency for bulk $\text{Te}_{42}\text{As}_{36}\text{Ge}_{10}\text{Si}_{12}$. These measurements provide useful information about the suitable conduction mechanism which contributed to the measured results.

2. Experimental detail

Bulk glassy $\text{Te}_{42}\text{As}_{36}\text{Ge}_{10}\text{Si}_{12}$ composition was synthesized as follows. The elementary constituents of the

composition under test of purity 99.99% were weighted in accordance with their atomic percentage and loaded in a silica tube, which was then sealed under vacuum (10^{-5} Torr). The tube was heated gradually in an oscillatory furnace to 450°C (melting point of Te) and kept constant for 2 h, then it was raised to 600°C (melting point of As) and kept constant for 2 h and finally it was raised to 1000°C (at rate 100°C/h) and kept constant for 45–50 h. Long time of synthesis and oscillation of the tube are necessary for the homogeneity of synthesized composition.

Polished bulk sample in the form of pellets was used for the measurements of ac and dc conductivity. Sample was pressed between two polished and cleaned brass electrodes coated with silver past.

The chemical composition of the investigated composition was checked by energy dispersive X-ray analysis (EDX) using a JOELE 5400 scanning electron microscope. The amorphous nature of the considered composition in powder form was confirmed by X-ray diffraction analysis and differential thermal analysis (DTA) [7].

The ac conductivity measurements was carried out using Hioki 3532 programmable automatic LCR meter bridge through the frequency range 0.5×10^3 – 4×10^6 Hz and temperature range 300–423 K which is well below the glass transition temperature [7] according to the relation: $\sigma_t(\omega) = L/za$, where z is the sample impedance, a — the cross-sectional area of the sample and L — the sample thickness. The sample temperature was measured using a chromel–alumel thermocouple with accuracy ± 1 K.

The frequency and temperature dependence of the dielectric constant ϵ_1 are determined from the observed

values of the capacitance for the sample under test. The dielectric constant ε_1 was calculated using the relation: $\varepsilon_1 = C_x L / a \varepsilon_0$, where C_x is the capacitance of the sample and ε_0 is the free space permittivity. The dielectric loss ε_2 was calculated from the relation: $\varepsilon_2 = \varepsilon_1 \tan \delta$, where $\delta = 90^\circ - \phi$, and ϕ is the phase angle.

3. Results and discussion

3.1. Ac conductivity

Ac conductivity $\sigma_{ac}(\omega)$ is related to the total conductivity $\sigma_t(\omega)$ and dc conductivity σ_{dc} according to the relation [16, 17]:

$$\sigma_{ac}(\omega) = \sigma_t(\omega) - \sigma_{dc}. \quad (1)$$

The ac component was obtained by subtracting the dc component from the measured value at different temperatures. However, the dc component σ_{dc} is negligibly small compared to the $\sigma_t(\omega)$. Thus $\sigma_t(\omega)$ considered to be $\sigma_{ac}(\omega)$. The variation of $\sigma_{ac}(\omega)$ with frequency in the range $0.5 \times 10^3 - 4 \times 10^6$ Hz for the studied composition was investigated at different temperature values 300–423 K. It was found that at constant working temperature $\sigma_{ac}(\omega)$ increases linearly with increasing frequency for temperature values as shown in Fig. 1. For most semiconductors

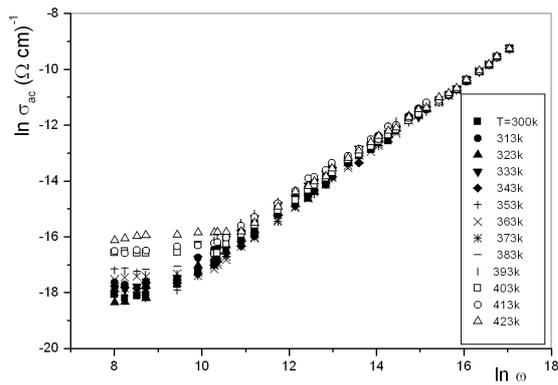


Fig. 1. Frequency dependence of σ_{ac} for $\text{Te}_{42}\text{As}_{36}\text{Ge}_{10}\text{Si}_{12}$ glass at different temperature.

[16, 17] the ac conductivity is given by the relation

$$\sigma_{ac}(\omega) = A\omega^s, \quad (2)$$

where A is constant, ω — the angular frequency ($\omega = 2\pi f$) and s — the frequency exponent. The working temperature dependence of the frequency exponent s for the investigated composition is shown in Fig. 2. It is clear that s has a value less than unity in the range 0.94 to 0.74 and decreases with increasing working temperatures. The observed behavior of $s(T)$ may be analyzed by assuming that the ac conduction mechanism is the correlated barrier hopping (CBH) model [15]. According to this model, the conduction occurs via a bipolaron hopping process where two polarons simultaneously hop over the potential barrier between two charged defect states D^+ and D^- and the barrier height is correlated with the

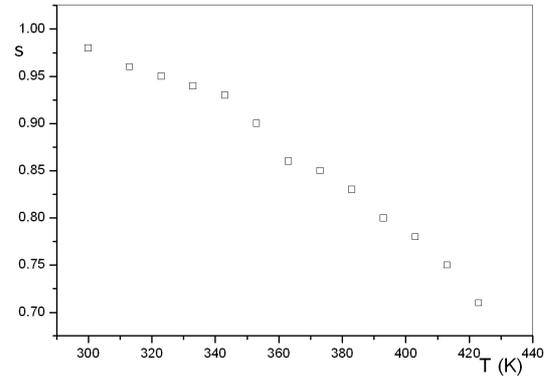


Fig. 2. Temperature dependence of the frequency exponent s for $\text{Te}_{42}\text{As}_{36}\text{Ge}_{10}\text{Si}_{12}$ glass.

inter-site separation via a Coulombic interaction. Shimakawa [18] suggested further that at higher temperature D^0 states are produced by thermal excitation of D^+ and D^- states and a single polaron hopping (i.e. one electron hopping between D^0 and D^+ and hole between D^0 and D^-) becomes the dominant process.

According to Eq. (2) the frequency exponent s is given as [15]:

$$s = d(\ln \sigma_{ac}) / d(\ln \omega) = 1 - 6k_B T / W_m \quad (3)$$

or

$$\beta = 1 - s = 6k_B T / W_m, \quad (4)$$

where k_B is the Boltzmann constant, T — the absolute temperature and W_m — the maximum barrier height which is the energy required to take two electrons from the D^- state to the conduction band in the absence of D^+ centers. To determine the value of W_m the parameter β is plotted as a function of temperature as shown in Fig. 3. The value of W_m can be calculated from the slope of the obtained straight line and is equal to 0.24 eV. It is known that the value of W_m is related to the optical band gap [11]. The obtained value of W_m is expected to be equal to $E_g/4$ ($E_g^{\text{opt}} = 0.98$ eV [19]) which is in agreement with that proposed before.

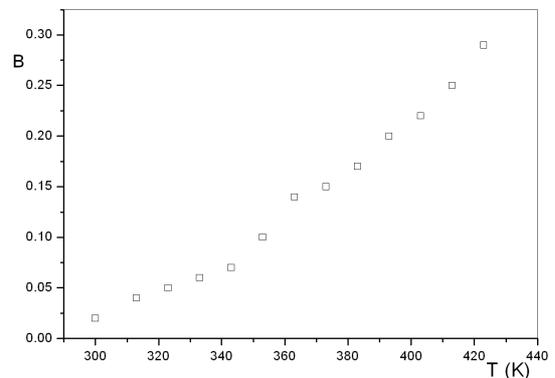


Fig. 3. Temperature dependence of the value B for $\text{Te}_{42}\text{As}_{36}\text{Ge}_{10}\text{Si}_{12}$ glass.

According to the Austin–Mott formula [20], based on CBH model, ac conductivity $\sigma_{ac}(\omega)$ can be explained in terms of the hopping of electrons between pairs of localized states at the Fermi level. $\sigma_{ac}(\omega)$ is related to the density of states $N(E_f)$ at the Fermi level by the following relation:

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

where α is the exponential decay parameter of localized state wave function, and v_{ph} is the phonon frequency, e is the electronic charge, k_B , ω , and T have the same meaning as above. By assuming $v_{ph} = 10^{13}$ Hz and $\alpha^{-1} = 10 \text{ \AA}$ [21], the density of states is calculated and it is found that $N(E_f)$ has value of order $5.74 \times 10^{21} \text{ eV}^{-1} \text{ m}^{-3}$ (at $f = 5 \text{ kHz}$ and $T = 303 \text{ K}$), which increases with frequency and temperature through the studied ranges.

The variation of $\sigma_{ac}(\omega)$ vs. $1000/T$ for studied composition was studied at different frequency values in the temperature range. The obtained relation is shown in Fig. 4 as $\ln \sigma_{ac}(\omega)$ vs. $1000/T$. It is clear from Fig. 4 that $\sigma_{ac}(\omega)$ decreased nonlinearly with the reciprocal of temperature. The shape of the curve suggests two different regimes with different activation energies. The first regime with weak temperature dependence and other with strong temperature dependence. Accordingly, the ac component of the frequency-dependent conductivity can be expressed as the sum of two different conduction mechanisms [22, 23]:

$$\sigma(\omega) = \sigma_f + \sigma_s, \quad (6)$$

where σ_f represents the relatively weak temperature dependence mechanism which has been interpreted as being due to hopping between localized states at the Fermi level, and σ_s represents the stronger temperature dependence component of ac conductivity and is obtained by subtraction σ_f from $\sigma_{ac}(\omega)$. This behavior of ac conductivity is in agreement with the results obtained before for other amorphous materials [22–24].

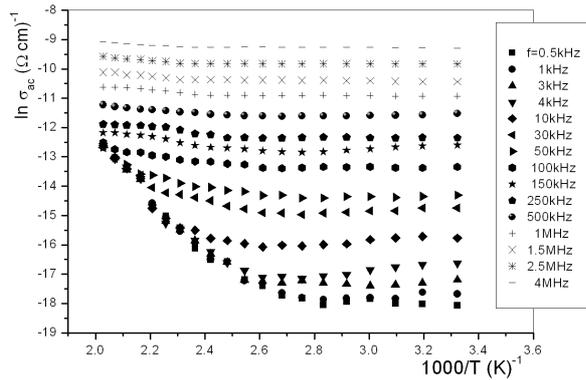


Fig. 4. Temperature dependence of $\sigma_{ac}(\omega)$ for $\text{Te}_{42}\text{As}_{36}\text{Ge}_{10}\text{Si}_{12}$ glass.

3.2. Dielectric properties

Dielectric analysis measures the electric properties of a material as a function of frequency and temperature. This analysis measures two fundamental electrical characteristics of materials: (1) the capacitive (insulating) nature, which represents its ability to store electric charge; (2) the conductive nature, which represents its ability to transfer electronic charge. Through this analysis, the dielectric constant ϵ_1 and dielectric loss ϵ_2 of a material can be determined.

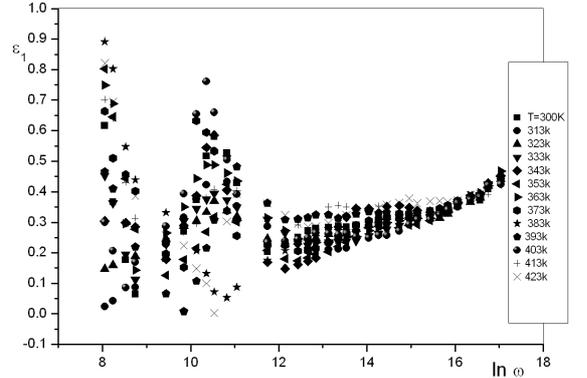


Fig. 5. Frequency dependence of the dielectric constant for $\text{Te}_{42}\text{As}_{36}\text{Ge}_{10}\text{Si}_{12}$ at different temperature.

Figure 5 shows the frequency dependence of dielectric constant ϵ_1 at different temperatures of the studied sample. It is clear from this figure that ϵ_1 decreases with frequency and increases with temperature. The decrease of ϵ_1 with frequency can be attributed to the fact that at low frequencies ϵ_1 for polar material is explained by the contribution of multi component of polarizability, deformational (electronic and ionic) and relaxation (orientational and interfacial) polarization. First, electronic polarization arises from the displacement of the valence electrons relative to the positive nucleus. This type of polarization takes place at frequencies up to 10^{16} Hz. The second type is the ionic polarization, which occurs due to the displacement of negative and positive ions with respect to each other. The maximum frequency of ionic polarization is 10^{13} Hz. Third: dipolar polarization occurs if the material contains molecules, with permanent electric dipole moment that can change orientation into the direction of the applied electric field. The dipolar polarization takes place at frequencies up to 10^{10} Hz. The final one is the space charge polarization which occurs due to impedance mobile charge carriers by interfaces. Space charge polarization typically occurs at frequency range from 1 to 10^3 Hz. The total polarization of the dielectric material can be given as the sum of these four types of polarization [25]. The obtained results in the present study referred that the ionic polarization does not play a pronounced effect in the total polarization, where the degree of covalency in the studied sample is calculated using the following relation [26]:

the proportion of covalent character

$$= 100\% \exp(-0.25(\zeta_A - \zeta_B)), \quad (7)$$

where ζ_A and ζ_B are the electronegativities of atoms A and B, respectively.

The values of covalent character of the expected bonds present in the studied sample are listed in Table, which reveals that the covalent character of bonding is predominant in the studied sample.

TABLE
Calculated covalent character of
bonds for $\text{Te}_{42}\text{As}_{36}\text{Ge}_{10}\text{Si}_{12}$.

Bond type	Covalent character
Te-Te	100
Te-As	98
Te-Ge	92.3
Te-Si	92.3
As-As	100
Ge-Ge	100
As-Si	90.9
As-Ge	90.9
Si-Si	100

When the frequency is increased, the orientational polarization decreases since it takes more time than electronic and ionic polarization. This decreases the value of dielectric constant ε_1 reaching a constant value at higher frequency correspondingly to interfacial polarization. On the other hand, the increase of ε_1 with temperature (see Fig. 5) 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 dipole is facilitated and this increases the value of orientational polarization, which leads to increases of the dielectric constant ε_1 with temperature. It can be noticed from this figure that there is a maximum in value of ε_1 ; it may be due to that the sample undergoes certain transformation.

Figure 6 shows the frequency dependence of dielectric loss ε_2 at different temperatures for the studied composition. It is clear from this figure that ε_2 decreases with frequency and increases with temperature. Dielectric loss ε_2 consists of two contributions: one from the dielectric polarization processes, and the other from the dc conduction. To study the origin of the dielectric loss ε_2 , the dc conduction loss was calculated using the relation $\varepsilon_2(\text{dc}) = \sigma_{\text{dc}}/\varepsilon_0\omega$. Taking the experimental value of dc conductivity equal to $1.37 \times 10^{-8} \Omega^{-1} \text{m}^{-1}$ at room temperature, $\varepsilon_0 = 8.85 \times 10^{-12} \text{F/m}$ and frequency equal to 5 kHz, the obtained value of $\varepsilon_2(\text{dc})$ is equal to 2.7×10^{-1} which is small compared to the observed dielectric loss ε_2 . Thus the dielectric loss ε_2 cannot be attributed to dc conduction in the entire temperature range. The frequency dependence of the dielectric loss ε_2 is found to follow the

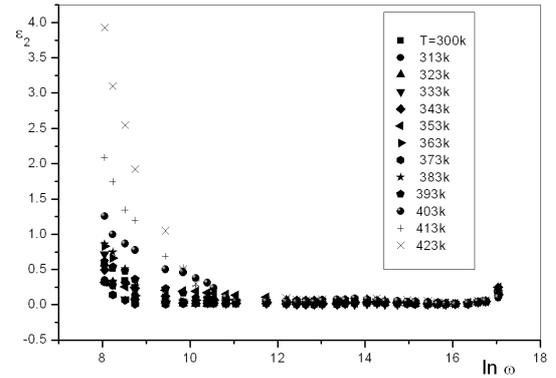


Fig. 6. Frequency dependence of the dielectric loss for $\text{Te}_{42}\text{As}_{36}\text{Ge}_{10}\text{Si}_{12}$ at different temperatures.

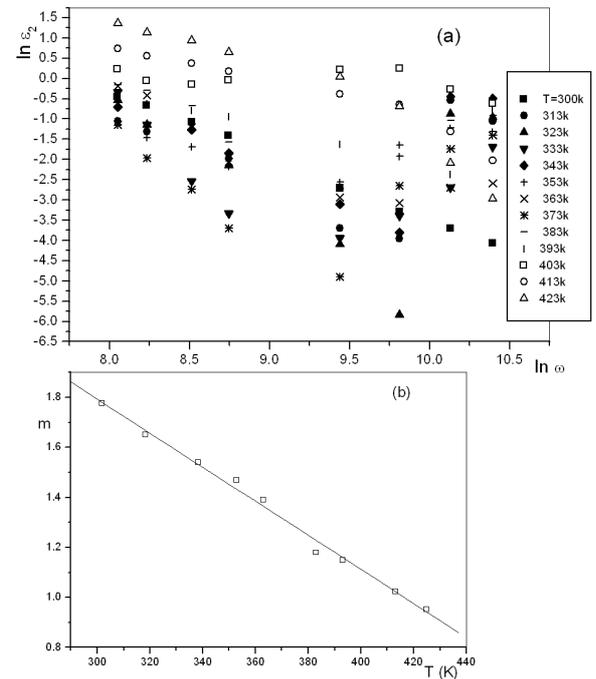


Fig. 7. (a) $\ln \varepsilon''$ versus $\ln \omega$ for $\text{Te}_{42}\text{As}_{36}\text{Ge}_{10}\text{Si}_{12}$ at different temperatures. (b) The temperature dependence of the parameter m .

relation [27]: $\varepsilon_2 = C\omega^m$, where C is a constant, therefore the obtained results can be plotted as $\ln \varepsilon_2$ vs. $\ln \omega$ as illustrated in Fig. 7a. This enables us to calculate the value of the power m from the negative slope of the obtained straight lines of Fig. 7a. The values of m should be negative and it seems to be a function of temperature, as shown in Fig. 7b. It is clear that m decreases linearly with temperature. According to Guintini equation [28] the dielectric loss ε_2 at particular frequencies in the temperature range is given by

$$\varepsilon_2 = (\varepsilon_0 - \varepsilon_\infty) 2\pi^2 N (ne/\varepsilon_0)^3 k_B T \omega^m \tau_0^m W_m^{-4}, \quad (8)$$

where $m = -4k_B T/W_m$, n — the number of electrons that hop, ε_0 — the static dielectric constant, ε_∞ — the

dielectric constant at infinitely high frequencies, N — the concentration of localized states, and W_m — the maximum barrier height. The obtained value of W_m (0.05 eV) is in agreement with that obtained according to the theory of single polaron hopping of charge carriers over a potential barrier as suggested by Elliott [15] and Shimakawa [22] in case of chalcogenide glasses. The increase of ε_2 with temperature can be explained according to Stevels [27] who divided the relaxation phenomenon into three parts: conduction losses, dipole losses and vibrational losses. At low temperatures conduction losses have minimum value since it is proportional to $\sigma_{ac}(\omega)/\omega$. As the temperature increases, $\sigma_{ac}(\omega)$ increases and so the conduction losses increase. This increases the value of ε_2 with increasing temperature.

4. Conclusion

Amorphous $\text{Te}_{42}\text{As}_{36}\text{Ge}_{10}\text{Si}_{12}$ chalcogenide glass was prepared by the conventional melt quenching technique. The ac conductivity, dielectric constant and dielectric loss of the studied composition are investigated. The experimental results were carried out through the frequency range 0.5×10^3 – 4×10^6 Hz and temperature range 300–423 K. It is found that the frequency and temperature dependences of ac conductivity support the CBH model, where the frequency exponent s is temperature dependent, decreasing with increasing temperature through the studied frequency and temperature ranges. The density of localized states was determined for the studied composition.

Both dielectric constant ε_1 and dielectric loss ε_2 increase with temperature and decrease with the frequency. Value of the maximum barrier height was estimated from the data of dielectric loss, which was in good agreement with the theory of hopping of charge carriers over a potential barrier between charged defect states. It was calculated according to the Giuntini equation based on the Elliott model for chalcogenide glasses.

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