Dielectric Relaxation in Glassy $Se_{100-x}\ Sb_x$

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Abstract

Frequency and temperature dependence of dielectric constant ε' and dielectric loss ε'' are studied in glassy $Se_{1-x}\ Sb_x$ ($x = 0$, 0.02, 0.04, 0.06, 0.08 and 0.10) in the frequency range from 1–10 kHz and in the temperature range 290 K to 360 K. The experimental results indicate that no dielectric dispersion exist in glassy Se in the operating range of frequencies. However, when Sb concentration increases in $Se_{1-x}Sb_x(x = 0.02$, 0.04, 0.06, 0.08 and 0.10) dielectric dispersion starts in the upper frequency and temperature range. The values of ε' and ε'', as functions of temperature and frequency, increase with Sb concentration to x = 0.08; at which point a discontinuity is observed. Above 8%, ε' and ε'' decrease with Sb concentration. The discontinuity is explained in terms of the mechanically stabilized structure at a particular average co-ordination number. An analysis of the observed dielectric loss shows that the Guintini's theory of dielectric dispersion based on two electron hopping over a potential barrier is applicable in the present case.

Key Words: Chalcogenide glasses, Dielectric relaxation

1.   Introduction

Chalcogenide glasses based on sulfides, selenide and telluride alloys in binary and multi-component system, have evoked much interest in terms of the understanding of basic physics of non-crystalline solids, as well as for the development of various semiconducting devices. These glasses are also promising materials for various optical and photonic applications [1]. Selenium based chalcogenide glasses have high transparency in the broad middle and far IR regions and have strong non-linear properties [2]. Apart from these applications, amorphous Se has been found to have tremendous potential in xeroxing applications and therefore a lot of attempts have been made to improve its properties by alloying [3] it with other elements.

Alloying elements produce characteristic effects depending on the electronic structure of these elements. It has been reported [4] that the effect of alloying Sb with Se drastically improves the thermal stability of the Se. Calorimetric studies in this glassy system have been made by Dimitrov et al. [5, 6]. The effect of Sb alloying on the electronic density of gap states has been studied by Mikla et al. [7], by xerographic measurements. These measurements indicate that progressive addition of Sb to a-Se increases the integrated number of deep traps. Since the electrical properties of chalcogenide glasses are strongly dependent on density and distribution of gap states, it is interesting to study electrical properties of this glassy system.

In view of the above, in the present paper, we report the study of dielectric relaxation in $Se_{1-x}\ Sb_x$ glassy system, where x is varied from 0 to 0.10. The observed dielectric loss has been analyzed in terms of

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the existing theories of dielectric relaxation. The composition dependence of the dielectric parameters has been discussed in terms of the average co-ordination number in the binary alloy.

Section 2 describes the experimental details of sample preparation and dielectric measurements. The theory of measurements is given in section 3. The results have been presented in section 4 and discussed in section 5. The last section deals with the conclusions of the present work.

2.   Experimental

2.1.   Preparation of glassy alloys

Glassy alloys of $Se_{1-x}Sb_x$ ($x = 0$, 0.02, 0.04, 0.06, 8 and 0.10) are prepared from the melt by the quenching technique. The exact proportions of high purity (99.999%) elements, in accordance with their atomic percentages, are weighed using an electronic balance with a precision of 10^{-4} g. The materials are then sealed in quartz ampoules of about 8 mm internal diameter in vacuum ($\sim 10^{-5}$ Torr). The ampoules containing materials are heated up to the melting point of the constituent elements and held at that temperature for 10–12 hours. The temperature of the furnace is raised slowly at a rate of 3–4 °C/min.

During heating, all the ampoules are rocked, by rotating a ceramic rod to which the ampoules are tucked away in the furnace. This is done to obtain homogenous glassy alloys. The obtained melts are cooled rapidly by removing the ampoules from the furnace and dropping them into ice-cooled water. The quenched samples are then taken out by breaking the quartz ampoules. The samples are characterized to be in glassy state by X-ray diffraction technique.

2.2.   Experimental details of dielectric measurements

Bulk samples, used for dielectric measurements, are obtained in disc form by compressing the powdered glassy samples in a die under a load of 3–4 tons. The diameter of the pellets are ~ 1 cm and thickness ~ 6 mm. Vacuum evaporated In films on both sides of the pellets were used as electrodes for the present study.

For dielectric measurements, the pellets are mounted in between the two electrodes of a metallic sample holder in which a vacuum $\sim 10^{-2}$ Torr could be maintained. Three terminal measurements are made to avoid stray capacitances. For this purpose, the low and high terminals of the capacitor are insulated. Co-axial connections are used and the sample holder and the bridge is grounded. The capacitance bridge knob is used in three terminal mode. A General Radio 1620 AP capacitance measuring assembly is used to measure the capacitance. The instrument is used in the parallel capacitance mode, where parallel conductance could be measured directly. The leads are coaxial wire to avoid the effect of stray capacitance. Lead capacitance is subtracted from the measured capacitance before calculating the dielectric constant.

3.   Theory of Measurements

Guintini et al. [8] have proposed a model for dielectric dispersion in chalcogenide glasses. This model is based on Elliott's idea [9] of charge carriers hopping over a potential barrier between charged defect states (D^+ and D^-). Each pair of sites (D^+ and D^-) is assumed to form a dipole which has a relaxation time depending on its energy [10, 11]; the latter can be attributed to the existence of a potential barrier over which the carriers hop [12].

According to the above model [8], at a particular frequency and temperature T where dielectric dispersion occurs, ε'' is given by

$$\varepsilon''(\omega) = (\varepsilon_\circ - \varepsilon_\infty) \, 2\pi^2 N (ne^2/\varepsilon_\circ)^3 K T \, \tau_\circ^m \, W_m^{-4} \omega^m, \tag{1}$$

were m is a power of angular frequency and is given by

$$m = -4kT/W_m. \tag{2}$$

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

According to eq. (1), ε'' should follow a power law with frequency, i.e. $\varepsilon'' = A \quad \omega^m$, where m should be negative and linear with T, as given by equation (2).

4. Results

Temperature dependence of dielectric constant and loss is measured at the different fixed frequencies 1 kHz, 2 kHz, 5 kHz and 10 kHz in the temperature range 290 K to 360 K in all the glassy alloys used in the present study. The experimental results indicate that no dielectric dispersion exist in glassy Se in the operating range of frequencies. However, when Sb concentration increases in $Se_{1-x}Sb_x(x = 0.02, 0.04, 0.06, 0.08$ and $0.10)$ dielectric dispersion starts in the upper frequency and temperature range. Figures 1 and 2 show the temperature dependence of dielectric constant ε' and loss ε'' at certain fixed frequencies in case of $Se_{.92}Sb_{.08}$. It is evident from this figure that ε' and ε'' increases with temperature; the increase being greater for lower frequencies. Similar results were obtained in other glassy alloys also.
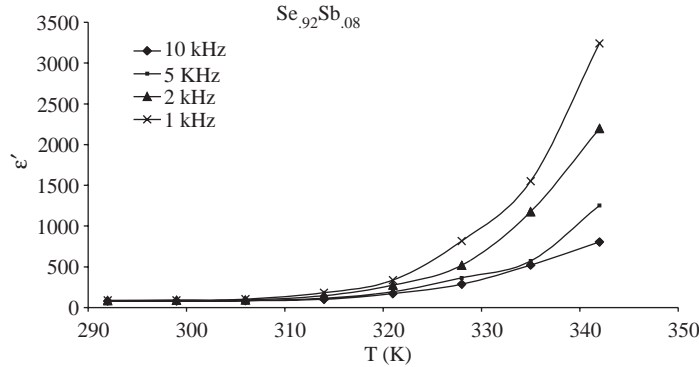

Figure 1. Temperature dependence of dielectric constant at certain fixed frequencies in glassy $Se_{.92}Sb_{.08}$. Lines are guide for the eyes (no fits).
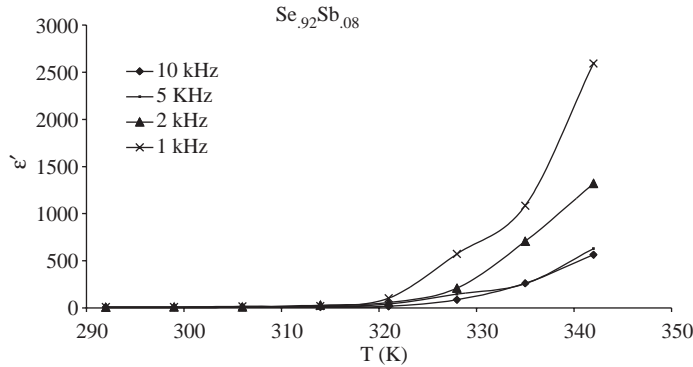

Figure 2. Temperature dependence of dielectric loss at certain fixed frequencies in glassy $Se_{.92}Sb_{.08}$. Lines are guide for the eyes (not fits).

To compare the variation of ε' and ε'' at a particular frequency, ε' and ε'' is plotted as a function of temperature in Figures 3 and 4 for different glassy alloys at 5 kHz. It is clear from these figures that, for $x < 0.08$, the values of ε' and ε'', at a particular temperature and frequency, increase with Sb concentration. However, at higher concentrations $x \geq 0.08$, the values of ε' and ε'' decrease with Sb concentration.
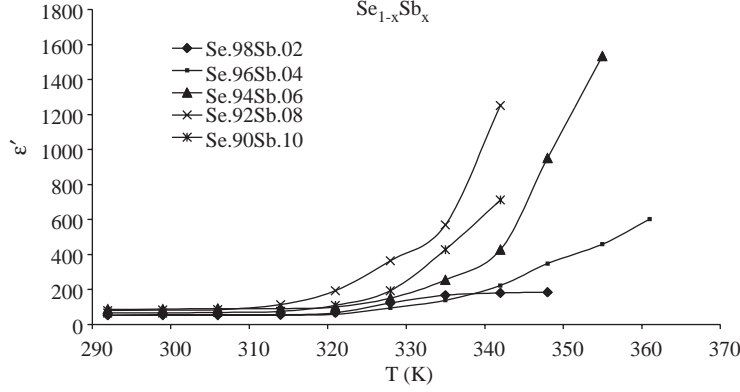

Figure 3. Temperature dependence of dielectric constant at 5 kHz for different glassy alloys. Lines are guide for the eyes (not fits).
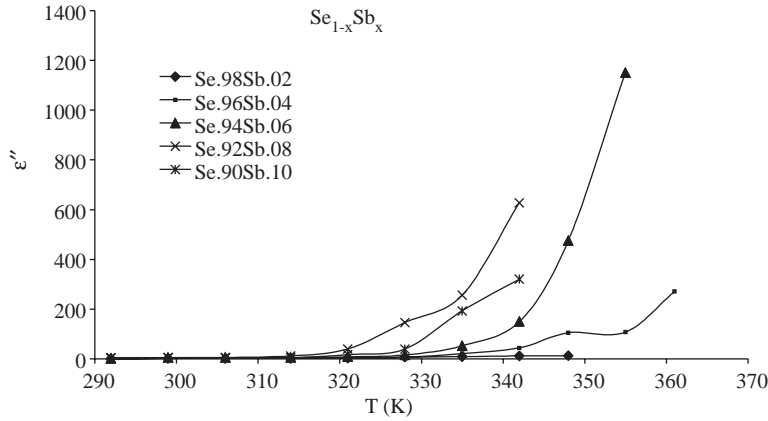

Figure 4. Temperature dependence of dielectric loss at 5 kHz for different glassy alloys. Lines are guide for the eyes (not fits).

In our samples we found that ε'' follows a power law with frequency at temperatures where dielectric dispersion occurs (see Figure 5(a) for the case of $Se_{.92}Sb_{.08}$). The values of m at different temperatures are negative and follow a linear relation with T (see Figure 5(b) in the case of $Se_{.92}Sb_{.08}$). The results for other compositions are of the same nature.

Using the values of m, W_m is calculated using eqn. (2) and the results are given in Table. It is clear from this table that the value of W_m first decreases with increase of Sb concentration upto 8 at%. Thereafter, it starts decreasing with Sb concentration. Such type of discontinuity at 8 at% has also been observed in ε' and ε''. These results have been discussed in the next section.

5.   Discussions

5.1.   Dielectric dispersion

In the present samples, ε'' follows a power law with frequency at temperatures where dielectric dispersion occurs. The values of m at different temperatures are also negative and follow a linear relation with T.
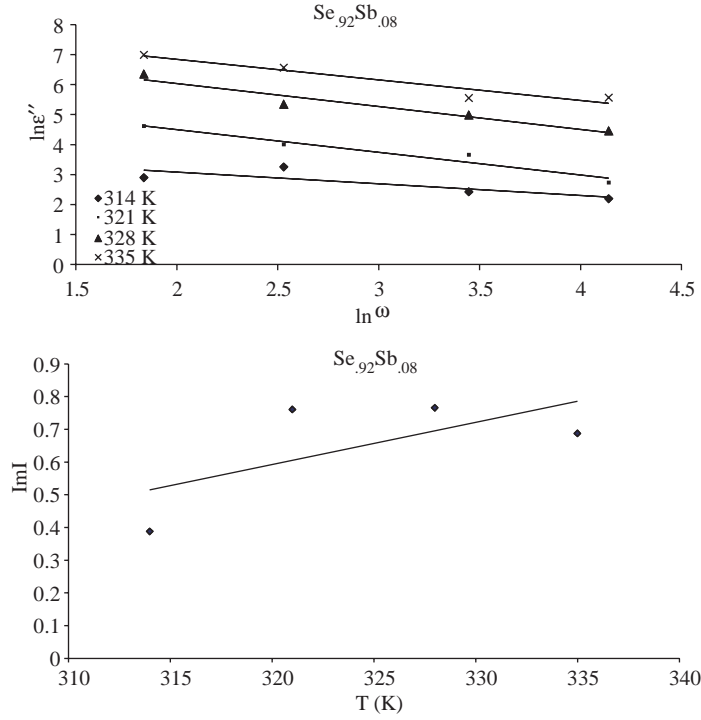
Figure 5. In glassy $Se_{.92}Sb_{.08}$ (a) $\ln \varepsilon''$ vs $\ln \omega$ curves at different temperatures; (b) m vs T curve in glassy $Se_{.92}Sb_{.08}$. Lines are best fits.

Table. Values of W_m for different glassy alloys.

Sample	W_m (eV)
$Se_{.98}Sb_{.02}$	1.08
$Se_{.96}Sb_{.04}$	0.27
$Se_{.94}Sb_{.06}$	0.19
$Se_{.92}Sb_{.08}$	0.17
$Se_{.90}Sb_{.10}$	0.19

The present results are, therefore, in agreement with the above (Elliott's) theory of dielectric dispersion as mentioned in section 3.

Arora et al. [13, 14] have reported frequency and temperature dependence of dielectric constant ε' and dielectric loss ε'' in glassy Se, $Se_{1-x}Te_x$ and $Se_{.80}Te_{.10}M_{.10}$ (M = Cd, In and Sb) glassy alloys in the audio frequency range. In these materials, ε' and ε'' are independent of temperature and frequency at low temperatures ($T < 200$ K). However, at high temperatures, they showed dielectric dispersion, except in the case of glassy Se. Goel et al. [15, 16] have also reported similar behavior in case of Se-Te-Sb and Se-Te-Ge glasses. Some more work [17–21], reported on dielectric relaxation studies; indicate that dielectric dispersion occurs in these materials in audio and/or radio frequency range. They have also explained their results based on the theory of ac conductivity and dielectric relaxation given by Guintini et al. [8]. The present results are, therefore, in agreement with the results reported in the literature on chalcogenide glasses.

5.2. Dependence of ε' and ε'' on composition

At $T = 335$ °C and $f = 5$ kHz, the values of ε' and ε'' increase with Sb concentration up to 8 at%, after which they decrease with increasing concentration (see Figure 6). A discontinuity in W_m is also observed at the same Sb fractional content (see Table).
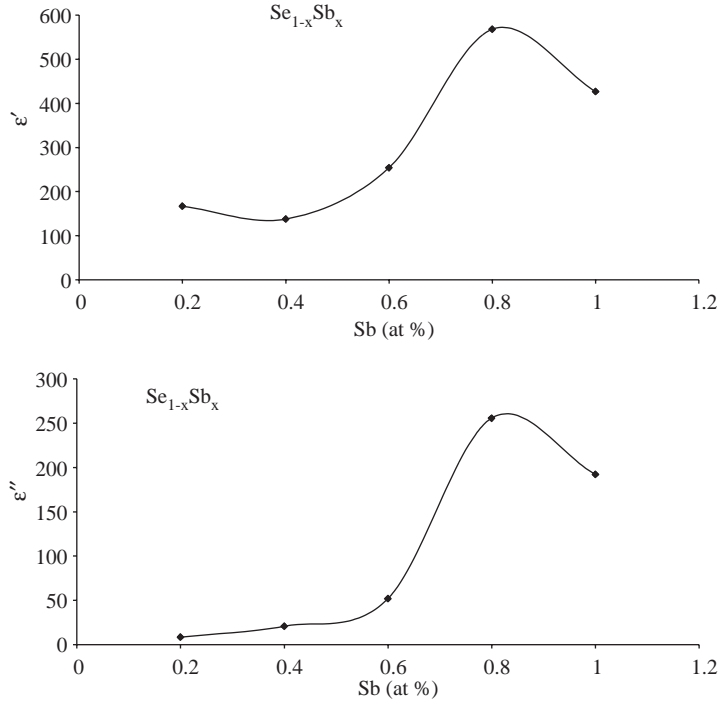
Figure 6. ε' and ε'' at 5 kHz and 335 K as a function of Sb concentration in $Se_{1-x}Sb_x$ glassy system. Lines are guide for the eyes (not fits).

In chalcogenide glasses, a discontinuity in various physical properties has been observed [22–26] at a particular composition where the average coordination number $< r >$ reaches 2.4, which is explained in terms of mechanically stabilized structure at critical glass composition. In the present glassy system, the coordination number of Se is 2, but is 3 for Sb. Hence, at a composition $Se_{.92}Sb_{.08}$, where a maxima in ε' and ε'' occurs, $< r >$ comes out to be 2.2. IV–VI glasses, however, show a threshold at $< r > = 2.4$ [27, 28]. This shows that $< r >$ at the threshold, in the present glassy system, is slightly less. However, it may be mentioned that Phillips [26, 27] considered the interaction between atoms to be purely covalent while arriving at the balance condition. Such an assumption may be valid for Ge-Se glasses, but not for systems containing heavier elements such as Sb. The presence of such a heavier element may lead to partial covalent bonding.

It should be noted that the above explanation for the above anomaly is highly qualitative and no quantitative information can be obtained from such explanations. Future experiments on the local structure of these glasses could reveal the exact origin and nature of the anomaly.

6.   Conclusions

Frequency and temperature dependence of dielectric constant ε' and dielectric loss ε'' is studied in glassy $Se_{1-x}Sb_x$ where $x = 0$, 0.02, 0.04, 0.06, 0.08 and 0.10, in the frequency range 1 kHz to 10 kHz and in the temperature range from 293 K to 360 K. The experimental results indicate that dielectric dispersion does exist in the present glassy system in the above frequency and temperature range. A detailed analysis shows that the Elliott's theory of two electron hopping over a potential barrier is applicable in the present case. The values of ε' and ε'', at a particular temperature and frequency, increase with the increase in Sb concentration with a discontinuity observed at 8 at.% of Sb. This is explained in terms of a mechanically stabilized structure at a particular average co-ordination number.

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