

## Dielectric studies on a-Se<sub>100-x</sub>Bi<sub>x</sub> (x = 0, 0.5, 2.5, 5 & 10) system

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### ABSTRACT

The dependence of dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) on temperature and frequency have been investigated for a-Se<sub>100-x</sub>Bi<sub>x</sub> (x = 0, 0.5, 2.5, 5 and 10) alloys. The measurements have been made in the temperature range 300 to 370 K and in the frequency range 0.12 to 100 kHz. A strong dielectric dispersion has been observed when Bi is incorporated into a-Se in the operating range of temperature and frequency. The increase in dielectric parameters ( $\epsilon'$  and  $\epsilon''$ ) with increase in Bi concentration in the Se-Bi system has been discussed in terms of the increase in the density of defect states in these alloys.

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*Keywords:* a-Se<sub>100-x</sub>Bi<sub>x</sub>, Dielectric constant, Dielectric loss.

### 1. INTRODUCTION

Chalcogenide glasses are well known and promising materials as they have potential applications in a variety of optoelectronic devices [1-3]. The addition of impurities to disordered systems has a pronounced effect on changing their conduction mechanisms and their structures. This effect can be widely different for different impurities. Several workers [4-6] have reported the impurity effects in various chalcogenide glasses. Due to ease of fabrication and processing, they are interesting as core materials for optical fibers used for transmission especially when short length and flexibility are required [7, 8]. Since the advent of electrophotography, amorphous selenium has become a material of commercial importance. Selenium exhibits the unique property of reversible phase transformation [9]. Its various device applications like rectifiers, photocells, vidicons, xerography, switching and

memory etc. have made it attractive, but pure selenium has disadvantages like short lifetime and low photosensitivity. This problem can be overcome by alloying Se with some impurity atoms such as Bi, Te, Ga, Sb, As, Pb which gives higher photosensitivity, higher crystallization temperature and smaller ageing effects [10-12]. Here we have chosen Bi as an additive because it readily alloys with most of the metals and modify their physical properties.

Dielectric relaxation studies are important to understand the nature and the origin of dielectric losses, which in turn, may be useful in the determination of structure and defects in solids. It is of great importance to investigate the details of dielectric response in Se-Bi alloys as the application of these materials in memory devices strongly depends on the dielectric properties. Se-Bi alloys have recently gained much importance because of their greater hardness, higher photosensitivity, higher crystallization temperature and smaller ageing effects as compared to pure glassy Se. The dielectric characterization has also been considered as an important complementary efforts contributing to a better understanding of transport mechanism in such materials. Usually in chalcogenide glasses, DC and AC conduction at high frequencies are known to have electronic characteristics. Several workers [13-16] have reported the dielectric properties of some glassy compounds and alloys. Measurements on chalcogenide glasses have indicated that the dielectric dispersion does exist in these glasses even though these materials are covalently bonded.

In the present work, the dielectric properties of a-Se<sub>100-x</sub>Bi<sub>x</sub> system (where x = 0, 0.5, 2.5, 5 and 10) have been studied. Our aim is to throw light on temperature and frequency dependence of dielectric constant and dielectric loss in this system.

## 2. EXPERIMENTAL

Glassy alloys of a-Se<sub>100-x</sub>Bi<sub>x</sub> (where x = 0, 0.5, 2.5, 5 & 10) were prepared by quenching technique. Highly pure materials (99.999%) having the desired compositional ratio of elements were sealed in quartz ampoules (length ~10 cm, internal diameter ~0.8 cm) in a vacuum of 10<sup>-3</sup> Pa. The sealed ampoules were kept inside a programmable furnace where the temperature was raised to 1100 K at a rate of 4 K/min for 10 hours with frequent rocking to ensure the homogenization of the melt. The quenching was done in ice water. Amorphous nature of the samples has been confirmed by x-ray diffractograms.

For dielectric studies, bulk samples in the form of pellets (diameter  $\sim 8$  cm and thickness  $\sim 0.8$  cm) were obtained by finely grinding the glassy alloys and compressing the powder in a die at a pressure of  $\sim 6.6$  ton. These pellets were coated on their both sides with indium by thermal evaporation to ensure good electrical contacts between samples and the electrodes of sample holder. The pellet was mounted between a pair of electrodes in the sample holder for dielectric measurements. The temperature was measured by a calibrated chromel-alumel thermocouple located very close to the sample. The pellet was annealed in vacuum of about  $10^{-1}$  Pa developed inside the sample holder. The capacitance and dissipation factor were determined by programmable LCZ meter (Keithley, model 3330) with operating frequency range from 0.12 to 100 kHz. The parallel capacitance and conductance were measured simultaneously and then  $\epsilon'$  and  $\epsilon''$  were calculated. Three terminal measurements were performed to avoid any stray capacitances. The frequency dependence of  $\epsilon'$  and  $\epsilon''$  was also measured by maintaining constant temperature inside the sample holder. A vacuum  $\sim 10^{-1}$  Pa was maintained during all these measurements. The measurements were made under the same experimental conditions for all the samples.

### 3. RESULTS AND DISCUSSION

The temperature and frequency dependence of dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) have been studied for various glassy alloys of  $\text{Se}_{100-x}\text{Bi}_x$  system (where  $x = 0, 0.5, 2.5, 5$  &  $10$ ). The temperature and frequency ranges of measurements are from 300 to 370 K and from 0.12 to 100 kHz, respectively. In glassy samples of Se, almost no variation of  $\epsilon'$  and  $\epsilon''$  has been observed in the operating range of temperature and frequency [14]. This fact is true in our case also (results not shown here). Figs. 1 and 2 exhibit the temperature dependence of dielectric parameters ( $\epsilon'$  and  $\epsilon''$ ) at different frequencies in  $\text{Se}_{100-x}\text{Bi}_x$  system. These figures indicate that the temperature dependence of  $\epsilon'$  and  $\epsilon''$  is appreciable in the high temperature region.  $\epsilon'$  and  $\epsilon''$  increase with increase in temperature; the increment being different at different frequencies. It is also observed that, at a particular temperature and frequency,  $\epsilon'$  and  $\epsilon''$  increases as the bismuth concentration increases in the  $\text{a-Se}_{100-x}\text{Bi}_x$  system. These results show that the Bi content plays a vital role in the variation of dielectric parameters with temperature. This type of behaviour has also been observed by different workers [14, 17-19] in chalcogenide glasses.

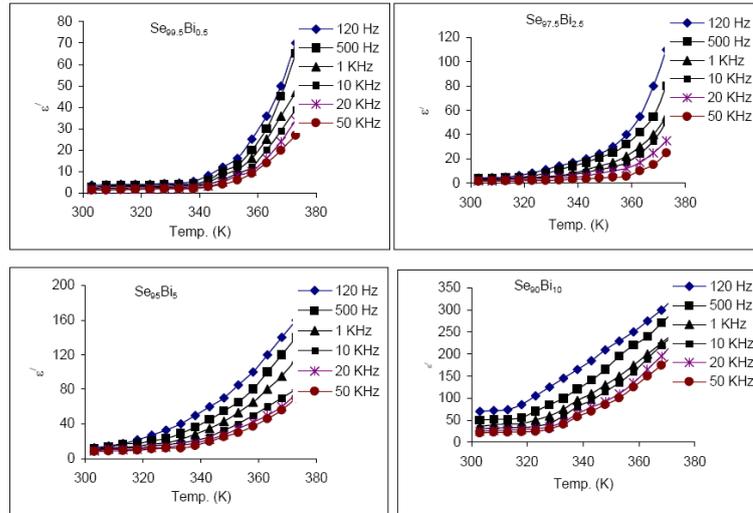


Figure 1 : Temperature dependence of ( $\epsilon'$ ) in temperature range (300-370K) at different frequencies in a- $\text{Se}_{100-x}\text{Bi}_x$  alloys.

Figs. 3 and 4 exhibit the frequency dependence of dielectric parameters at different temperatures in a- $\text{Se}_{100-x}\text{Bi}_x$  system.  $\epsilon'$  and  $\epsilon''$  remains almost independent of frequency in a-Se [14]. However, on the incorporation of Bi in a-Se, the dielectric parameters  $\epsilon'$  and  $\epsilon''$  decreases with increase in frequency. The values of dielectric parameters  $\epsilon'$  and  $\epsilon''$  in a- $\text{Se}_{100-x}\text{Bi}_x$  alloys at a particular temperature and frequency are given in Table 1.

Table 1 : Dielectric parameters in a- $\text{Se}_{100-x}\text{Bi}_x$  alloys (at  $T = 348 \text{ K}$  and  $f = 1 \text{ kHz}$ )

Composition (x)	Samples	( $\epsilon'$ )	( $\epsilon''$ )	$X_c$	m
0.0	a-Se	10.35	6.16	1.6	-0.103
0.5	a- $\text{Se}_{99.5}\text{Bi}_{0.5}$	12.47	30.68	1.8	-0.076
2.5	a- $\text{Se}_{97.5}\text{Bi}_{2.5}$	23.76	75.54	1.5	-0.132
5.0	a- $\text{Se}_{95}\text{Bi}_5$	71.07	105.21	1.7	-0.068
10.0	a- $\text{Se}_{90}\text{Bi}_{10}$	210.13	371.05	2.4	-0.185

It may be noted that  $\epsilon'$  and  $\epsilon''$  increases appreciably with increase in Bi concentration in a- $\text{Se}_{100-x}\text{Bi}_x$  system. Hence dielectric dispersion becomes strong in these alloys as the bismuth

content increases. The increase in dielectric loss with increase in Bi content may be understood in terms of the increase in the density of defect states on the incorporation of Bi in a-Se.

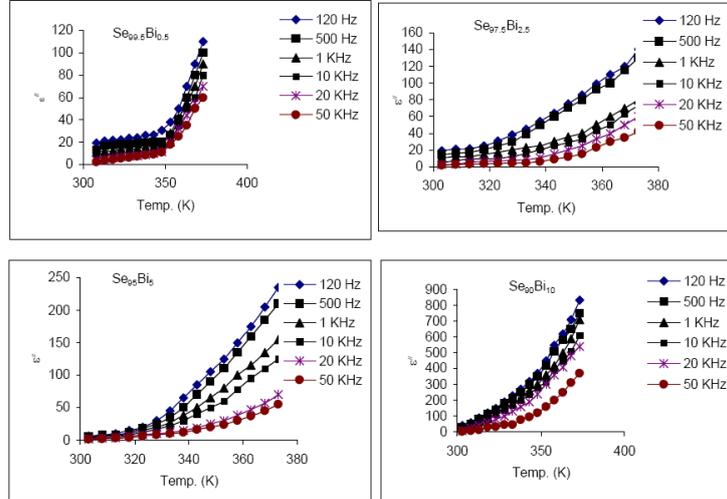


Figure 2: Temperature dependence of ( $\epsilon''$ ) in temperature range (300-370K) at different frequencies in  $a\text{-Se}_{100-x}\text{Bi}_x$  alloys.

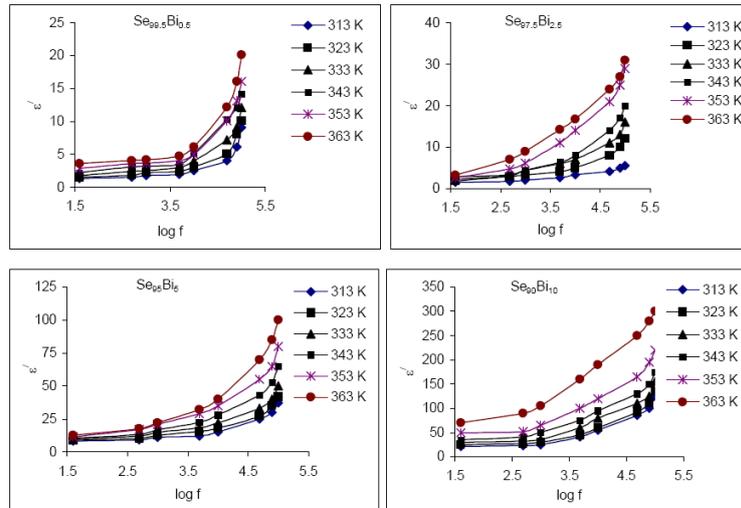


Figure 3: Frequency dependence of ( $\epsilon''$ ) in frequency range (0.12 –100 kHz) at different temperatures in  $a\text{-Se}_{100-x}\text{Bi}_x$  alloys.

The spurious dielectric dispersion may appear in semi conducting glasses if there is a poor electrical contact between the sample and the electrodes [20]. This is most likely in uncoated samples. To avoid such spurious effects, indium is coated on both the faces of the pellets. The temperature dependence of dielectric constant at various frequencies in  $a\text{-Se}_{100-x}\text{Bi}_x$  system indicated that  $\epsilon'$  varies exponentially with temperature as the  $\ln \epsilon'$  versus  $1/T$

curves as shown in Fig.5 are found to be straight lines at various frequencies in all the samples. This type of temperature dependence is generally observed in molecular solids where Debye theory [21] for the viscosity dependence of relaxation time holds good. According to this theory  $\epsilon''$  should increase exponentially with temperature and has been found to be so in the present case also. In a-Se<sub>100-x</sub>Bi<sub>x</sub> alloys, dielectric loss is found to follow a power law with frequency, that is,  $\epsilon'' = A \omega^m$ . Fig. 6 confirms this behaviour where  $\ln \epsilon''$  versus  $\ln \omega$  curves are found to be straight lines at various temperatures. The values of  $m$  are calculated from the slopes of these lines and it is found that the values of  $m$  at different temperatures are negative and less than unity.

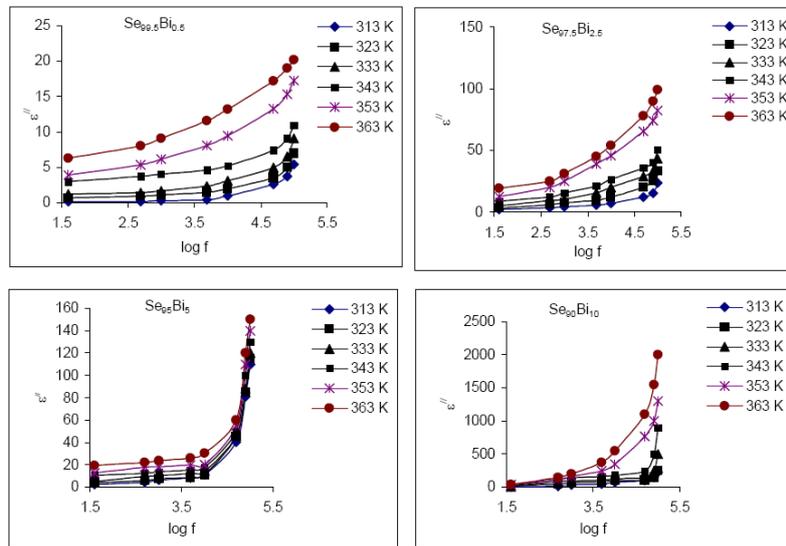


Figure 4: Frequency dependence of ( $\epsilon''$ ) in frequency range (0.12 –100 kHz) at different temperatures in a-Se<sub>100-x</sub>Bi<sub>x</sub> alloys.

In chalcogenide glasses, transfer of an electron from one chain end to another chain leads to the formation of dangling bonds, i.e., two charged defect states  $D^+$  and  $D^-$ . A dipolar model for dielectric dispersion in chalcogenide glasses has been proposed by Guintini et al [13]. This model is based on Elliott's theory [22] of hopping of charge carriers over a potential barrier between charged defect states ( $D^+$  and  $D^-$ ). Each pair of these states is assumed to form a dipole, which has a relaxation time depending on its activation energy [23]. The activation energy can be attributed to the existence of a potential barrier over which the carriers hop [24]. From the above discussion it is clear that the addition of Bi into Se increases the number of charged defect states, which may affect the dielectric properties. These paired charged defect states ( $D^+$  and  $D^-$ ) behave

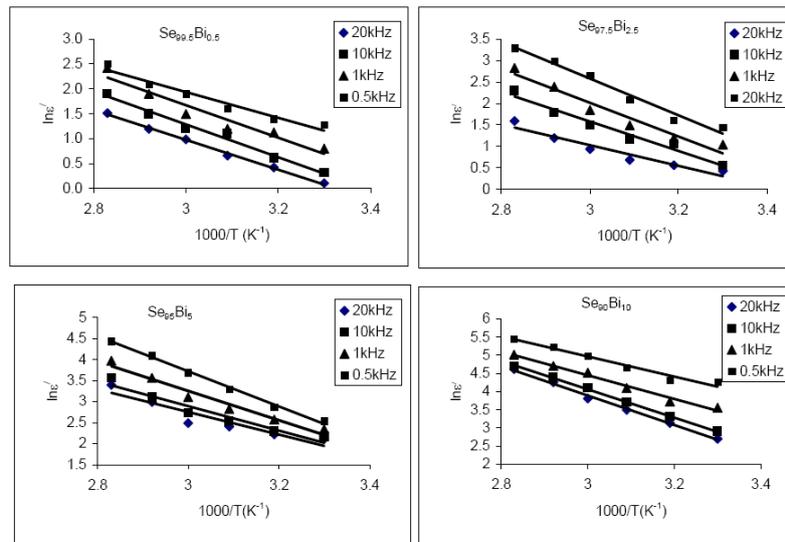


Figure 5:  $\ln \varepsilon'$  versus  $1000/T$  curves at different frequencies.

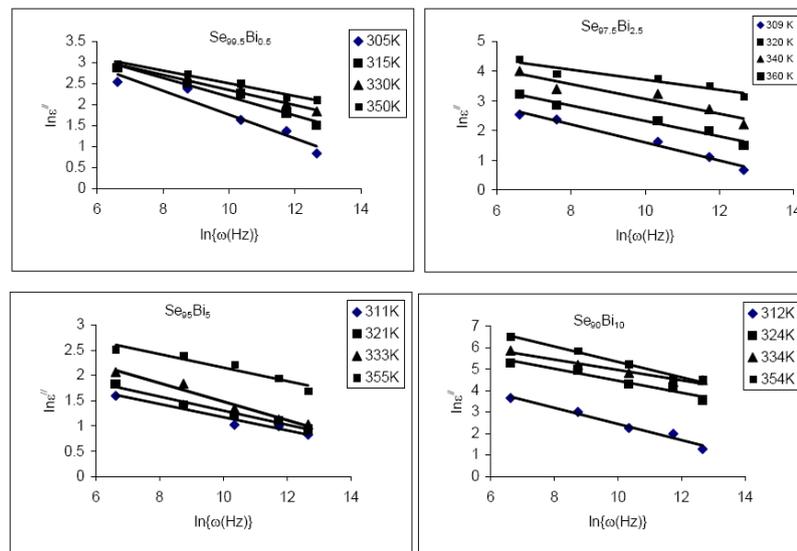


Figure 6:  $\ln \varepsilon''$  versus  $\ln \omega$  curves at different temperatures.

as dipole in a- $\text{Se}_{100-x}\text{Bi}_x$  glassy alloys. Due to an increase in the number of dipoles at higher concentration of Bi, the dielectric parameters are also supposed to increase with Bi concentration.

#### 4. CONCLUSION

It may be concluded from dielectric studies that dielectric constant and dielectric loss are temperature and frequency dependent in a- $\text{Se}_{100-x}\text{Bi}_x$  alloys.  $\varepsilon'$  and  $\varepsilon''$  increases with increase in

temperature, the increase being different at different frequencies.  $\epsilon'$  and  $\epsilon''$  decreases with increase in frequency, the decrease being different at different temperatures. The dielectric constant and dielectric loss are found to increase with increase in Bi concentration in a-Se<sub>100-x</sub>Bi<sub>x</sub> alloys. The increase in dielectric loss with Bi content in these glassy alloys may be understood in terms of the increase in the density of defect states.

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