DETERMINATION OF THERMAL DIFFUSION LENGTH IN BISMUTH DOPED CHALCOGENIDE GLASSES, BY PHOTOACOUSTIC TECHNIQUE

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The photoacoustic (PA) technique has been used to measure the thermal diffusion length in $Ge_{20}Bi_xSe_{80-x}$ ($2 \leq \times \leq 12$) and $Ge_{20}Bi_xSe_{70-x}Te_{10}$ ($2.5 \leq \times \leq 11$) glasses. The measured thermal diffusion length values show an unusual behaviour near the p to n transition. This anomaly has been explained by the effect of the percolation threshold in these systems.

1. Introduction

Photoacoustic (PA) technique is highly sensitive to optical and thermal properties of gases, liquids and solids [1]. The PA effect is based on the conversion of absorbed light energy into heat by means of non-radiative deexcitation processes. On irradiation of a sample by modulated beam of light, a heat wave of the same frequency is generated in the sample. The heat wave is transferred by diffusion to the surface of the sample, where oscillatory thermal effects are generated in the coupled gas. These can be detected as an acoustic signal by a sensitive microphone. The PA signal depends on the thermal properties of the sample like specific heat, thermal expansion and thermodynamic changes, being characterized by the magnitude of the thermal diffusion length of the solid [2].

In the past few years, there has been a great deal of interest developed in the study of chalcogenide glasses in device technology, which can be used in electrical and optical switching and optoelectronic fields [3]. The power dissipation in optoelectronic and microelectronic devices is an important mechanism limiting the device performance. The room temperature values of thermal diffusivity will help to optimize the power dissipation in such devices [4].

Chalcogenide glasses prepared by melt quenching are generally p type semiconductors [5]. These glasses are insensitive to doping because of pinning of the Fermi level by native defects [6]. Over the past few years, the sign reversal from p to n type has been observed in various amorphous thin film [7] and melt quenched chalcogenide glasses [8,9]. Still, the mechanism of this p- to n- type conduction is yet to be completely revealed.

The incorporation of Bi into Ge-Se and Ge-Se-Te glasses changes the conduction type from p to n. The characterization of electrical, optical [10] and high pressure [11,12] of these glasses have been reported. In this paper we report thermal diffusion length of Bi modified, and melt quenched germanium chalcogenide glasses with and without tellurium by photoacoustic technique. The measurements show interesting variation of diffusion length with the Bi content of the sample.

2. Experimental

Homogeneous glasses of $Ge_{20}Bi_xSe_{80-x}$ ($2 \leq x \leq 12$) and $Ge_{20}Bi_xSe_{70-x}Te_{10}$ ($2.5 \leq x \leq 11$) were prepared by melting a mixture of appropriate amounts of constituents and then rapidly quenching in liquid nitrogen. No crystalline inclusions were observed in these samples.

The apparatus for measuring thermal diffusivity consists of a 15 mW He-Ne laser $\nu = 4.74 \times 10^{14}$ Hz, mechanical light chopper (Model 194A, Eg&G, Princeton Applied Research, USA), photoacoustic cell with a condensed microphone (BT 1759, Knowles electronics, Inc., USA) and lock-in amplifier (Model SR 530, Stanford Research Systems, USA). The block diagram of the laser-photoacoustic spectrometer is shown in Fig. 1. A brief account of the experimental setup, procedure of thermal diffusivity measurements and the description of the photoacoustic cell are published elsewhere [13].
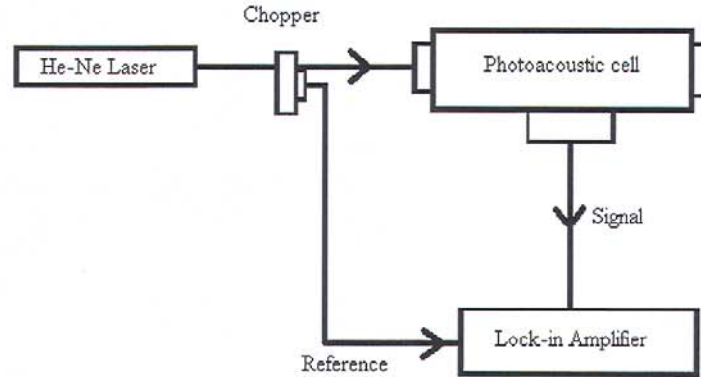

Fig. 1. Block diagram of laser-photoacoustic spectrometer.

For all compositions, measurements are made on samples having thickness in the range of 150-375 μm. The sample is fixed on the stainless steel sample holder with the help of silver paste, which is used for anchoring and providing a good thermal contact. The thermal diffusivity of the sample is determined by measuring the variation of PA amplitude as a function of chopping frequency, f_c, above which the sample is thermally thick and thereafter the signal depends on the thermal properties of the backing material. The changes at f_c leads to a bend in the log A – log f straight-line plot. According to the RG theory [2] the thermal diffusivity is calculated using the relation

$$\alpha = f_c \lambda^2$$

where λ is the geometrical thickness of the sample. The thermal diffusion length of the sample has been calculated by

$$\mu = (2 \alpha / \omega)^{1/2}$$

Where ω is the angular modulation frequency $(2\pi f)$ of the incident light.

3. Results and discussion

The reported thermal diffusion length value of $Ge_{20}Se_{80}$ melt quenched glass is approximately an order less than for Bi doped Ge-Se and Ge-Se-Te glasses [14]. The variation of thermal diffusion length as a function of Bi for $Ge_{20}Bi_xSe_{80-x}$ and $Ge_{20}Bi_xSe_{70-x}Te_{10}$ glasses is shown in Fig. 2. This also brings out the relative sensitivity of the thermal diffusion length measurement to the p to n conduction change. The anomalous behavior observed in the graph, at x = 8 at.% in GeBiSe glasses, shift to x = 9 at.% when Te (10 at.%) is added. This shift is not an unexpected one, as Toghe [15] stated that conductivity can take place anywhere between 7.5 and 9 at.% of Bi. The addition of Te decreases the thermal diffusion length value and the change is very pronounced.

An attempt was made to explain the anomalous behavior of thermal diffusion length with Bi (at.%) in these glasses. According to composition dependence of the concentration of covalent bonds [15] in these system, addition of Bi in Ge-Se system leads to a minimum concentration of Bi-Se bonds at x = 10. In GeBiSeTe systems [10] the Se-Se homopolar bonds completely vanish at x = 5,

which reflects as a higher value of thermal diffusion length. Beyond x = 5, the concentration of Bi-Se bonds increases steadily and reach the maximum at x = 10 at.%. The decrease of the thermal diffusion length value after x = 10 at.% is due to the formation of homopolar bonds and to the decrease of the Bi-Se bonds.
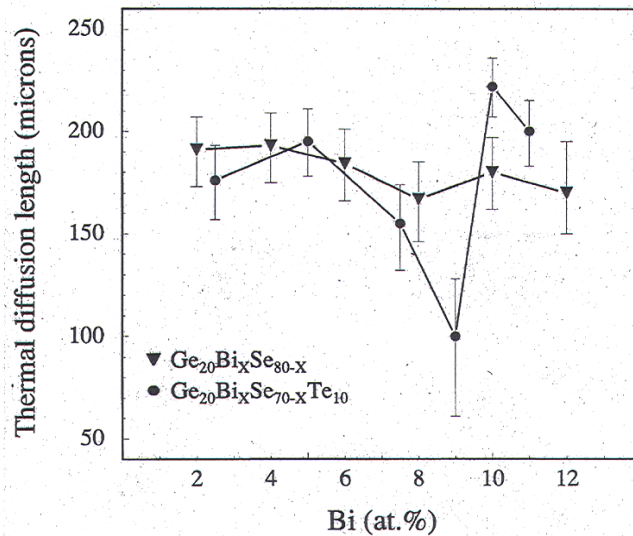

Fig. 2. Variation of thermal diffusion length with Bi composition.

According to Tichý [16] among the possible binary compounds of multicomponent chalcogenide glasses, only Bi_2Se_3 shows strong n type conduction [17]. n type conductivity of these glasses appears in the vicinity of the percolation threshold where formation of Bi_2Se_3 compound is predominant over the other binary compounds. It is an established fact that percolation threshold occurs in these glasses at x = 10 at.%. As a result, the network structure is optimally balanced and an ordered, rigid 3-d structure is formed. The phonon mean free path of this ordered network is maximum and the glassy network has minimum resistance for the propagation of the thermal wave. Because of the uniform distribution of these Bi_2Se_3 microcrystals in the glassy network, the concentration of free charge carriers is higher than in the case of lower Bi concentration. This apart, photocarrier generation also takes place during the photoacoustic process. These excess carriers diffuse through the sample and re-establish the equilibrium by disposing off the excess energy in the form of heat. The PA signal mainly depends on this heat generation. Thus, because of the presence of Bi_2Se_3 clusters, contribution from the free electrical / photo carriers may be appreciable to determine the increase of the thermal diffusion length at x = 10 at.%. The decrease of the thermal diffusion length beyond x = 10 at.% may be due to the formation of homopolar bonds, decrease of the concentration of heteropolar bonds, and decrease in the mobility of free carriers by scattering on defects.

4. Conclusions

The compositional dependence of thermal diffusion length in Bi doped chalcogenide glasses have been studied by a home made non-resonant photoacoustic cell. It was established that the thermal diffusion length is very sensitive to changes in network topology of chalcogenide glasses. At the time of p to n conversion, thermal diffusion length increases and this behavior is analogous to activation energy of thermoelectric power. The value of thermal diffusion length shows an anomalous variation with Bi concentration when the Bi content increases, and decreases up to x = 9 at.% beyond which it increases and reached a maximum at x = 10 at.%. Further addition of Bi leads to a decrease of the values of thermal diffusion length. These observations have been explained by the occurrence

of microphase separation into n type Bi_2Se_3 (microcrystalline) clusters. Addition of Te to GeBiSe system does not change the critical Bi concentration but the unusual behavior at the time of conversion is more pronounced.

Acknowledgement

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