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Optical band gap of Pb modified Ge–Se–Te glasses investigated by photoacoustic technique

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Abstract

Optical band gap (E_{opt}) for Pb modified Ge–Se–Te bulk glasses has been measured using the photoacoustic (PA) technique. The advantage of this technique over the absorption spectrophotometry technique is that this method is independent of sample thickness and provides optical band gap energy (E_{opt}) values corresponding to a high ($\sim10^4$ cm^{-1}) absorption coefficient. Hence this technique is especially suited for highly absorbing and brittle bulk semiconductors. The composition dependence of the optical energy E_{opt} of two series of glasses, namely, $Pb_xGe_{42-x}Se_{48}Te_{10}$ ($3 \leq x \leq 13$) and $Pb_{20}Ge_xSe_{70}Te_{10}$ ($17 \leq x \leq 24$) has been measured by recording the variation of the PA signal as a function of wavelength in the range 400–1200 nm. E_{opt} has a minimum value for the composition with 9 at. wt.% Pb in the $Pb_xGe_{42-x}Se_{48}Te_{10}$ series of glasses. E_{opt} exhibits a maximum for the 21 at. wt.% Ge composition in the $Pb_{20}Ge_xSe_{70}Te_{10}$ series of glasses. The above results have been interpreted in terms of the variation of the average bond energy of these glasses with change in composition. It is a matter of interest that E_{opt} shows anomalous behaviour at compositions at which the majority charge carrier reversal is observed in these glasses.

Keywords: Chalcogenide glasses; Optical band gap; Majority charge carrier reversal; Photoacoustic technique; Pb–Ge–Se–Te glasses

1. Introduction

Chalcogenide glasses form an important class of materials having extensive potential applications in science and technology due to their electrical and optical properties [1–3]. Chalcogenide glasses are generally p-type semiconductors [4]. The p-type conduction in these glasses is attributed to pinning of the Fermi energy level near the middle of the band gap by charge defects present in these glasses [5]. Tohge et al in early eighties [6,7] showed that n-type glasses could be obtained when Ge−Se glasses were prepared with appropriate amounts of Bi or Pb as additives. Murugavel et al. [8] reported the occurrence of carrier reversal in $Pb_xGe_{42-x}Se_{48}Te_{10}$ glasses at $x = 9$ at. wt.% Ge. Murugavel et al. attributed the conduction type change in Pb modified Ge–Se–Te glasses to the modification of defect states on the addition of Pb. They also addressed the role of the polarizibilty of the dopant, band structure on the majority charge carrier reversal (MCCR). The composition dependence of various physical properties of these glasses have also been studied by several investigators viz., Differential scanning calorimeter studies [9], microhardness studies [10] and Electrical studies [8] on Pb–Ge–Se–Te glasses showed that even physical properties of non-electronic nature exhibited anomalous behaviour at the MCCR composition.

The process of producing sound with light, known as ‘Photoacoustics (PA)’ was discovered by Alexander Graham Bell in the 19th century [11]. Photoacoustic techniques are essentially based upon sensing the temperature fluctuation of a given sample due to non-radiative de-excitation processes following the absorption of modulated or pulsed light. These techniques have been used extensively in the optical and thermal characterization of a wide spectrum of materials [12]. In this paper, the PA technique has been used to investigate the optical absorption of $Pb_xGe_{42-x}Se_{48}Te_{10}$ and $Pb_{20}Ge_xSe_{70-x}Te_{10}$ glasses. The composition dependence of the optical band gap of the two series of glasses has also been reported.

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Table 1
Glass transition temperature and optical band gap of E_{opt} Pb–Ge–Se–Te glasses

Sample composition	T_g (K)	E_{opt} (eV)	Sample composition	T_g (K)	E_{opt} (eV)
$Pb_{03}Ge_{39}Se_{48}Te_{10}$	536 ± 1	1.54 ± 0.01	$Pb_{20}Ge_{17}Se_{53}Te_{10}$	496 ± 1	1.53 ± 0.01
$Pb_{06}Ge_{36}Se_{48}Te_{10}$	522 ± 1	1.52 ± 0.01	$Pb_{20}Ge_{19}Se_{51}Te_{10}$	510 ± 1	1.59 ± 0.01
$Pb_{09}Ge_{33}Se_{48}Te_{10}$	517 ± 1	1.41 ± 0.01	$Pb_{20}Ge_{21}Se_{49}Te_{10}$	518 ± 1	1.62 ± 0.01
$Pb_{13}Ge_{29}Se_{48}Te_{10}$	514 ± 1	1.44 ± 0.01	$Pb_{20}Ge_{22.5}Se_{47.5}Te_{10}$	514 ± 1	1.58 ± 0.01
$Pb_{15}Ge_{27}Se_{48}Te_{10}$	515 ± 1	1.45 ± 0.01	$Pb_{20}Ge_{24}Se_{46}Te_{10}$	508 ± 1	1.44 ± 0.01

2. Experimental procedures

Bulk $Pb_xGe_{42-x}Se_{48}Te_{10}$ ($3 \leq x \leq 15$) and $Pb_{20}Ge_xSe_{70-x}Te_{10}$ ($17 \leq x \leq 24$) glasses were prepared by the melt quenching technique as described elsewhere [9]. To check the amorphous nature of these glasses, X-ray diffraction method was used. The glass transition temperature (T_g) was determined from Differential Scanning Calorimeter (Perkin-Elmer DSC 7) studies under a constant heating rate of $10\,^{\circ}C\,min^{-1}$. The T_g (on-set) values are tabulated in Table 1. The majority charge carrier type in these glasses was determined by the thermoelectric power measurement using an indigenous set-up [13]. The optical band gap of these glasses was determined from the PA signal recorded in the range 400 to 1200 nm using a photoacoustic (PA) set-up. The powdered samples under study were placed in a room temperature PA cell. A 1 kW Xe arc lamp (Oriel Instruments, Lamp Housing model 66921, Power supply model 68920, Lamp model 6269) provided the broad-band (white) light for the setup. A 0.25 m grating monochromator (Oriel Instruments Model Cornerstone^{TM} 260 1/4M) with stepper motor control was used to choose the appropriate wavelength. An optical chopper (Model SR 540, Stanford Research Systems), was used to intensity modulate the light. A dual channel lock-in amplifier (Model SR 830, Stanford Research Systems) was used for the recording the PA signal. A gas-microphone PA cell containing the sample, microphone, with its preamplifier was a minimum volume type cylindrical cell made of aluminium. The distance between the cell window and the sample was kept at 5 mm and the cell volume was $\sim 0.9\,cm^3$. The signal processing equipment consists of the lock-in amplifier and a personal computer and Labview^{TM} (Version 6.0, National Instruments) software. Carbon black PA spectrum was used to normalise the sample PA spectra. Further details of the PA set-up can be found elsewhere [14].

3. Results and discussion

The PAS spectra of bulk glassy samples of Pb modified Ge–Se–Te glasses in the wavelength range of 400 to 1200 nm

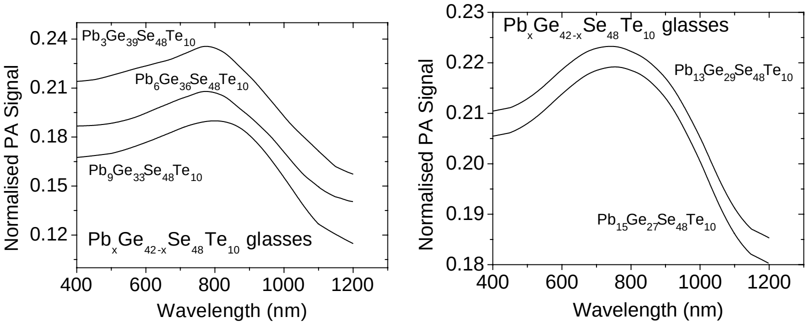

Fig. 1. Normalised PA spectra of $Pb_xGe_{42-x}Se_{48}Te_{10}$ glasses.

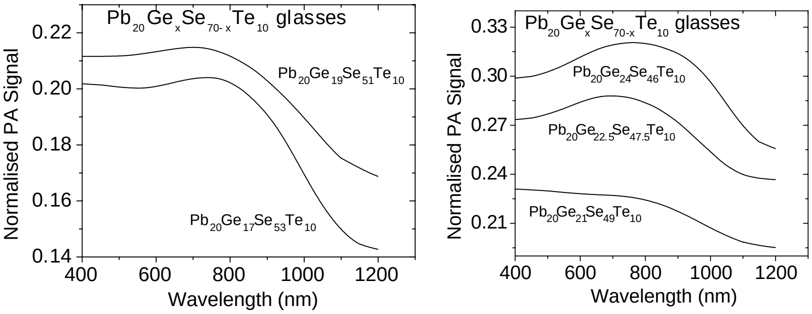

Fig. 2. Normalised PA spectra of $Pb_{20}Ge_xSe_{70-x}Te_{10}$ glasses.

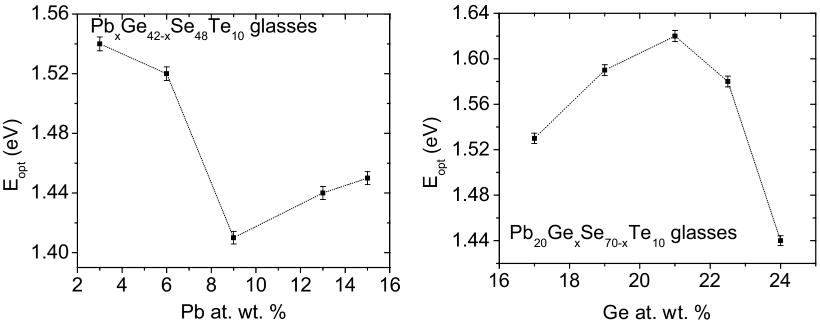

Fig. 3. Variation of optical band gap E_{opt} with composition of (a) $Pb_xGe_{42-x}Se_{48}Te_{10}$ and (b) $Pb_{20}Ge_xSe_{70-x}Te_{10}$ glasses (Dotted lines merely connect adjacent data points).

is shown in Figs. 1 and 2. The optical band gap E_{opt} is determined from the position of the knee in the PAS spectra (using the relation $E_{opt} = 1240/\lambda_g$, where λ_g is the wavelength corresponding to the knee of the PA curve). The Variation of E_{opt} with the composition for both the series of glasses is shown in Fig. 3. The variation of optical band gap energy E_{opt} of $Pb_{20}Ge_xSe_{70-x}Te_{10}$ glasses with Ge at. wt.% could be understood on the basis of the variation in the average bond energy of the glasses. As the Pb atomic weight percentage increases in $Pb_xGe_{42-x}Se_{48}Te_{10}$, the optical band gap energy decreases and attains a minimum at 9 at. wt.% of Pb (Fig. 3a). In the case of $Pb_{20}Ge_xSe_{70-x}Te_{10}$ glasses, the optical band gap energy shows a maximum at 21 at. wt.% of Ge (Fig. 3b). Optical band gap data is tabulated in Table 1.

The variation of optical band gap energy (E_{opt}) of $Pb_{20}Ge_xSe_{70-x}Te_{10}$ glasses with Ge at. wt.% could be understood on the basis of the change in the average bond energy of the amorphous solid as a function of composition. Pauling proposed [15] that single covalent bond energy of heteronuclear bonds D(A−B) can be estimated from the single covalent bond energy of homonuclear bonds D(A−A) and D(B−B) and the electronegativity, x_A of atom A and x_B of atom B using the formula,

$$D(\text{A–B}) = [D(\text{A–A}) \times D(\text{B–B})]^{1/2} + 30(x_A - x_B)^2 \quad (1)$$

The single bond energy values [16,17] of Ge−Ge (205.2 kJ mol^{-1}), Pb−Pb (85.7 kJ mol^{-1}) and Se−Se (206.1 kJ mol^{-1}) and Allred–Rockow electronegativity values were used for estimating the single covalent bond energies of Ge−Se (234.9 kJ mol^{-1}), Pb−Se (231.2 kJ mol^{-1}), etc. Since Te remains constant in both series of Pb–Ge–Se–Te glasses, the variation in average bond energy of both the series of glasses is only due to the variation in Pb, Ge and Se in these glasses. In $Pb_xGe_{42-x}Se_{48}Te_{10}$ glasses, substitution of Ge with Pb atom results in the reduction of Ge−Se bonds and an increase in Pb−Se bonds. Since Pb−Se bonds have a lower energy than Ge−Se bonds, addition of Pb results in a reduction in the average bond energy of $Pb_xGe_{42-x}Se_{48}Te_{10}$ glasses. This reduction in the average bond energy of the glasses is reflected in the reduction in the optical band gap of these glasses. Tohge et al. [7] estimated the variation in the number of Ge−Se, Ge−Ge and Se−Se bonds in bulk $Pb_{20}Ge_xSe_{80-x}$ glass system and showed that Ge−Se bonds increase in number and attain a maximum value at 20 mol % of Ge and thereafter decrease in number. Se−Se bonds decrease in number as Ge content is increased and disappear at 20 mol % Ge, whereas Ge−Ge bonds, which start appearing at 20 at. wt.% Ge, progressively increase in number with addition of Ge. Since Ge−Se bonds are maximum at 20 at. wt.% Ge, the average bond energy of the glass with this composition is the maximum in this series.

4. Conclusion

Pb–Ge–Se–Te glasses belonging to two series have been prepared by melt quenching technique. Optical band gap (E_{opt}) for two series of Pb modified Ge–Se–Te bulk glasses namely, $Pb_xGe_{42-x}Se_{48}Te_{10}$ ($3 \leq x \leq 13$) and $Pb_{20}Ge_xSe_{70}Te_{10}$ ($17 \leq x \leq 24$) has been measured using the photoacoustic (PA) technique. The E_{opt} value for $Pb_xGe_{42-x}Se_{48}Te_{10}$ ($3 \leq x \leq 13$) glasses exhibited a minimum with 9 at. wt.% of Pb, whereas for $Pb_{20}Ge_xSe_{70}Te_{10}$ ($17 \leq x \leq 24$) glasses E_{opt} exhibits a maximum for the 21 at. wt.% Ge. The variation of E_{opt} with composition has been interpreted in terms of variation in average bond energy.

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