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TRANSIENT AND STEADY STATE PHOTOCONDUCTIVITY STUDIES ON BULK GLASSES AND AMORPHOUS FILMS OF Ge-Te-Pb - COMPOSITION AND SPECTRAL DEPENDENCE

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Transient photoconductivity studies have been undertaken on bulk $Ge_{20}Te_{80-x}$ Pb_x glasses with varied lead content ($2 \leq x \leq 8$); The composition dependence of normalized photoconductivity and photo-decay have been investigated upon white light incidence. The photoconductivity rise and its decay with time indicate that the process may best be understood in terms of the recombination within the localized states. Further, it has been found that the addition of lead results in an initial decrease in the photoconductivity, showing anomalous variations at compositions x = 5, 6.5 and 7.5. Steady state photoconductivity studies on amorphous $Ge_{20}Te_{80-x}Pb_x$ thin films ($2 \leq x \leq 8$) have also been undertaken. The intensity dependence of steady state photoconductivity indicates the existence of continuous distribution of localized states in the mobility gap of this material. Further, the spectral dependence of photoconductivity has been studied using various interference filters. The composition dependence of steady state photoconductivity due to white light incidence, shows pronounced anomalies at x = 5, 6.5 and 7.5. Based on the present photoconductivity studies and other investigations, it has been proposed that the rigidity percolation occurs in $Ge_{20}Te_{80-x}$ Pb_x glasses, over an extended composition region with the composition x = 5 (x_{c1}) and x = 6.5 (x_{c2}) being the onset and completion of the rigidity percolation. The composition x = 7.5 corresponds to the chemical threshold of the system.

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1. Introduction

Chalcogenide glasses exhibit a variety of light induced effects. Photoconductivity (PC) studies are of considerable interest because they yield information about the defects and meta-stable structural states in amorphous solids [1]. The structure and bonding configuration of chalcogenide glasses can be changed by thermal treatment or light soaking which can be sometimes reversible. The reversible photo-induced change in chalcogenides is favored by the rapid localization of the photo-excited carriers. As the photoconductivity behavior is controlled by carrier localization and delocalization processes, transient photoconductivity measurements are expected to give information about the localized states in these materials. Transient photoconductivity measurements on different chalcogenide glasses have been reported earlier by various workers [2-7].

The electrical properties of chalcogenide glasses are in general not affected appreciably by the addition of impurities because the random networks of atoms can accommodate an impurity by adjusting its nearest neighbor environment, causing negligible effect on the electrical properties [8]. Also, the high density of localized states present in the forbidden gap effectively pin the Fermi level.

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However, experimental results reported by several researchers [9-12] have shown that the addition of certain selected impurities brings about notable changes in the electrical properties of chalcogenide glasses.

Studies on the composition dependence of various properties of chalcogenide glasses are expected to throw light on the two network topological thresholds exhibited by these materials, namely the rigidity percolation threshold [13] and the chemical threshold [14]. The rigidity percolation threshold corresponds to the composition at which a chalcogenide glass exhibits a sudden change in network connectivity and rigidity and the chemical threshold refers to a chemically ordered network glass [13, 14]. Though the rigidity percolation has been earlier considered to occur at a definite composition, the recent investigations reveal the possibility of it occurring over an extended composition range, with an onset and completion of the transformation [15].

In the present study, the composition dependence of normalized transient photoconductivity and photo-decay of Ge-Te bulk glasses doped with Pb, along with the steady state photoconductivity of above samples in thin film form are investigated, with the aim to study the effect of topological thresholds on these properties.

2. Experimental details

Glasses belonging to the composition tie-line $Ge_{20}Te_{80-x}Pb_x$ ($2 \leq x \leq 8$) are prepared by melt quenching technique. The amorphous nature of the glasses has been confirmed by X-ray diffraction. The transient photoconductivity measurements have been carried out on polished samples of approximately 0.5 mm thickness.

Thin films of the glassy chalcogenide $Ge_{20}Te_{80-x}Pb_x$ ($2 \leq x \leq 8$) have been deposited on glass substrates by flash evaporation technique at a base pressure of 1×10^{-5} mbar keeping the substrates at room temperature. The thickness of the film is maintained at 1500 Å using a digital thickness monitor.

Aluminum electrodes for planar gap cell are subsequently deposited on the thin film samples for the electrical contacts. The dimensions of the coplanar structures are ~ 10.59 mm long and electrode gap ~ 0.64 mm.

The samples under study were placed in a specially designed cell. The cell consisted of a metallic chamber, which can be evacuated. The setup has a provision for holding the sample, which consists of a point contact top electrode and a flat plate bottom electrode (for transient PC measurements) and a window through which sample could be illuminated. For steady state photoconductivity measurements the sample holder consisted of a copper base with two Teflon supports to hold the substrates. The transient and steady state photoconductivity measurements have been carried out at room temperature using a 200W Hg-Xe Oriel Arc Lamp (Model 8500). The electrical conductance is measured using a Keithley (model 614) electrometer.

3. Results and discussion

3.1.Transient photoconductivity studies of bulk samples

3.1.1 Composition dependence of transient photoconductivity due to white light

The normalized transient photoconductivities of $Ge_{20}Te_{80-x}Pb_x$ glasses for different Pb concentrations are shown in Fig. 1. It is clear from this figure that there is an increase in the conductivity of the sample under illumination.

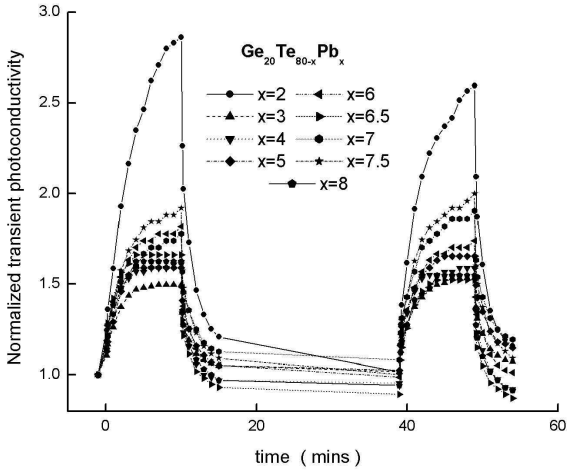

Fig. 1. Normalized transient photoconductivity as a function of time. The photo-response during illumination and the photo-decay is clearly depicted for $Ge_{20}Te_{80-x}Pb_x$ samples.

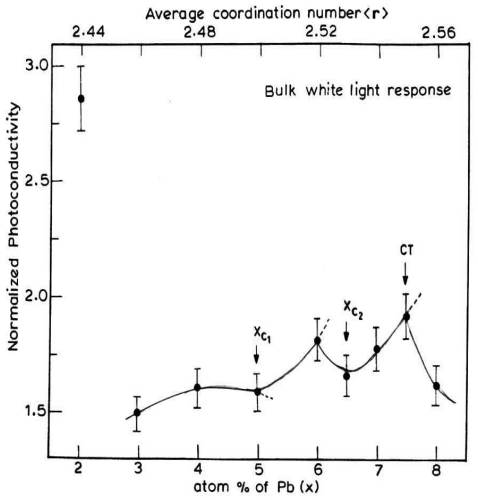

Fig. 2. Composition / average coordination number dependence of normalized transient photo-conductivity of $Ge_{20}Te_{80-x}Pb_x$ samples.

The photo-decay of the sample when the light is turned off is also shown in the figure. The photoconductivity and the photo-decay of the samples in two sequences of exposure are depicted in Fig. 1. The trend seen in the present samples has been observed earlier in $Se_{80}Te_{20}$ thin film samples [16], and also in other chalcogenide glasses [17]. The present photoconductivity rise and decay regime with time and the earlier studies by Fuhs et. al. [18,19] indicate that the photoconductivity behavior may be best understood in terms of recombination within localized states. According to Ovshinsky and Sapru [20] the lone pair electrons play an important role in the transition between bistable configurations through a change in interactions with each other and surrounding bonds caused by the photo-excitation. It is therefore plausible that the sample, which is photo-excited during the process of illumination, comes back to its normal dark condition with small changes in its conductance. Also, minor changes may occur in the valence alternation defect pairs and in the steric freedom of low coordination atoms to change their positions and bond configurations when the sample is illuminated.

Fig. 2 shows the composition/average coordination number dependence of normalized transient photoconductivity. It is noticed that the addition of Pb leads to an initial decrease in the photoconductivity. Thereafter, it increases progressively as a function of x with a subtle change at x = 5. This is followed by an inflection leading to a minimum at x = 6.5. An increase is noticed again in normalized photoconductivity, which results in a local maximum at x = 7.5. Earlier electrical switching, resistivity and differential scanning calorimetric studies on these glasses [21, 22] also reveal anomalies at x = 5, 6.5 and 7.5. Based on the present and the earlier studies, we suggest that the composition x = 5 and 6.5 correspond to the onset and completion of rigidity percolation and the composition 7.5 denotes to the chemical threshold.

3.1.2 Intensity dependence of photoconductivity

The intensity (F) dependence of photoconductivity (σ_{ph}) at room temperature is also studied for a representative $Ge_{20}Te_{78}Pb_2$ sample. It is found that σ_{ph} increases with intensity but does not follow a power law, viz., $\sigma_{ph} \alpha F^{\gamma}$.

3.2. Steady state photoconductivity studies of thin film samples

3.2.1 Composition dependence of steady state photoconductivity with time due to white light

Fig. 3 shows the time dependence of steady state photoconductivity due to white light as a function of time. The measurements have been taken maintaining a constant intensity of light. It is noticed that the photoconductivity increases with intensity as reported earlier for other chalcogenide systems [23].

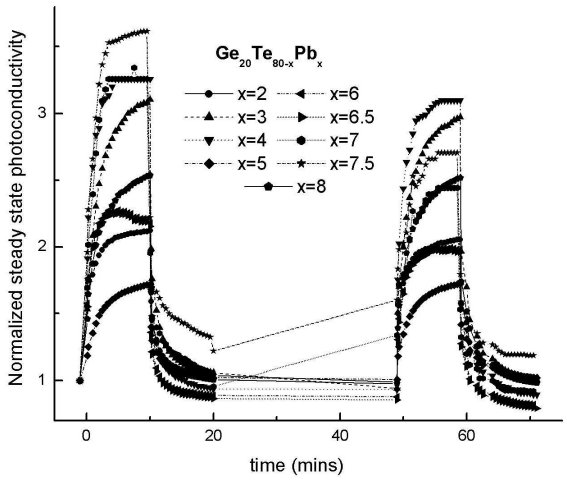

Fig. 3. Time dependence of normalized steady state photoconductivity and photo-decay for $Ge_{20}Te_{80-x}Pb_x$ ($2 \leq x \leq 8$) thin films.

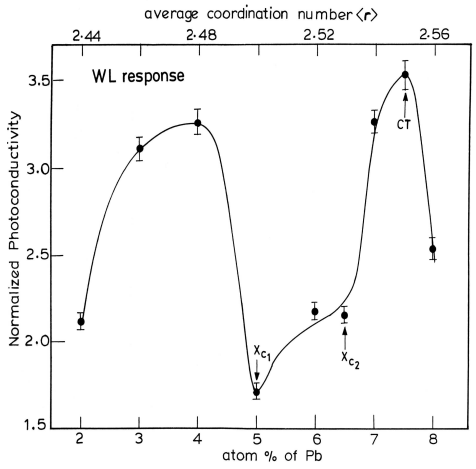

Fig. 4. Composition/average coordination number dependence of normalized steady state photo-conductivity due to white light.

The photoconductivity is found to reach saturation and the rise is found to be slow with the increase in exposure time, which is prominent in sample with 7 atom percent of Pb. Two exposures have been done on the same sample with an interval of 25 minutes, which is shown in the Fig. 3. The photo-decay is found to have two components, fast in the beginning and slow later as observed earlier for $Ge_{22}Se_{78-x}Bi_x$ chalcogenide glasses [23]. The very slow decay is non-exponential with time and may be ascribed to deep traps, which is understandable in chalcogenide glasses due to the continuous distribution of localized states in these materials. The composition dependence of normalized steady state photoconductivity due to white light is shown in Fig. 4. It can be seen that the composition dependence of normalized photoconductivity of Ge-Te-Pb thin films also exhibit anomalies at the topological thresholds of the system.

3.2.2 Spectral dependence of steady state photoconductivity with time and composition/average coordination number

The normalized steady state photoconductivity with time at different wavelengths in the visible region is shown in Fig. 5 (a-d). The spectral response for 401.97 nm and 452.67 nm is found to be hazy indicating less sensitivity of these samples at the above two wavelengths. The response is fairly smooth for other wavelengths with the increase in photoconductivity for 552 nm, attaining maximum sensitivity at 580 nm; the sensitivity is found to be only slightly less for 652.91 nm and

670 nm. It can therefore be inferred that the photosensitivity is maximum for 580 nm and it remains fairly constant at 652.91 nm and 670 nm respectively.

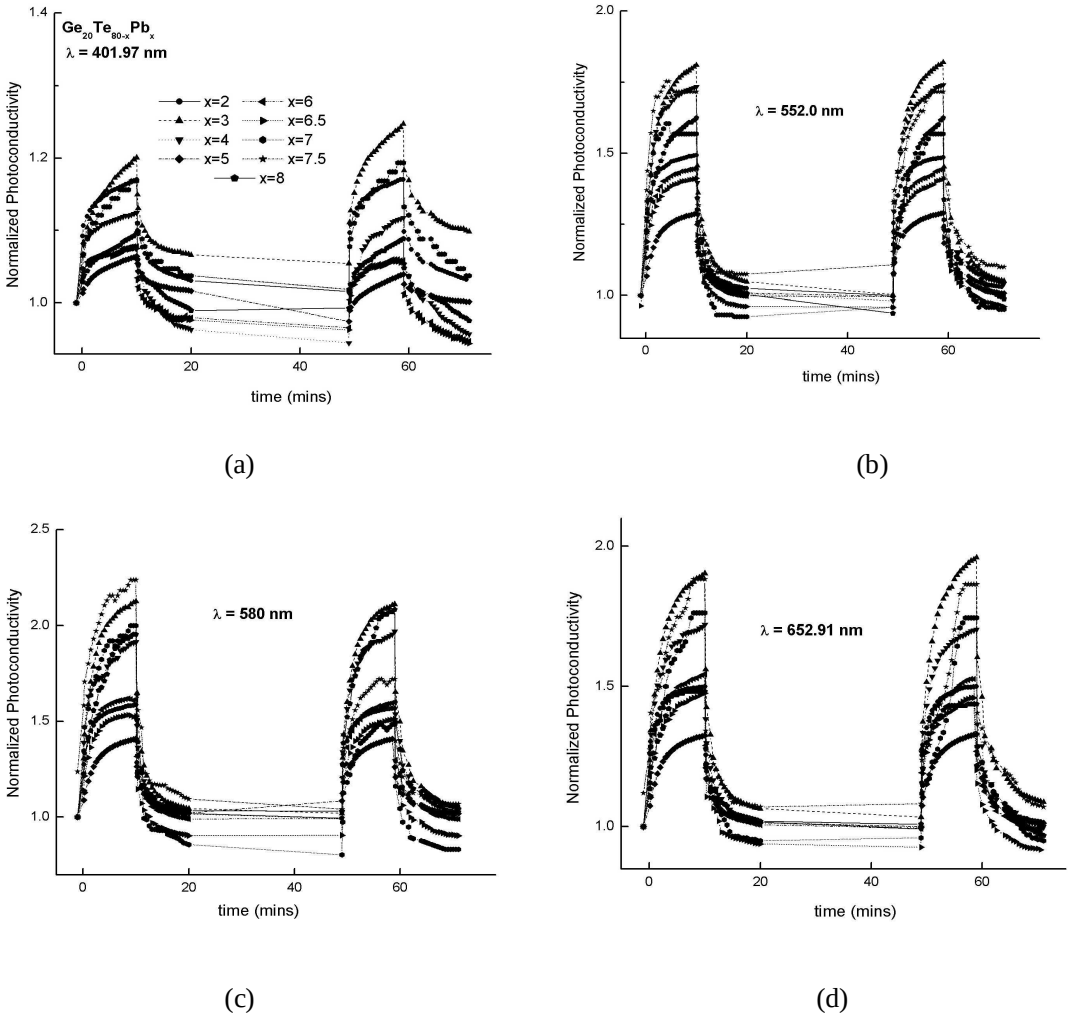

Fig. 5. Spectral dependence of normalized steady state photoconductivity at (a) 401.97 nm (b) 552.0 nm (c) 580.0 nm (d) 652.91 nm.

Fig. 6 shows the composition/average coordination number dependence of normalized photoconductivity at 401.97 nm. A broad minimum is noticed between 5 and 6.5 atom percent of Pb and a maximum at x = 7.5. A similar effect has been seen in other wavelengths also.

So far, the presence of extended rigidity percolation has been seen only in modulated differential scanning calorimetric studies. However, the present studies in the composition dependence of photoconductivity of bulk and thin film Ge-Te-Pb samples under illumination with white light and with different wavelengths reveal the presence of extended rigidity thresholds and chemical threshold in the samples.

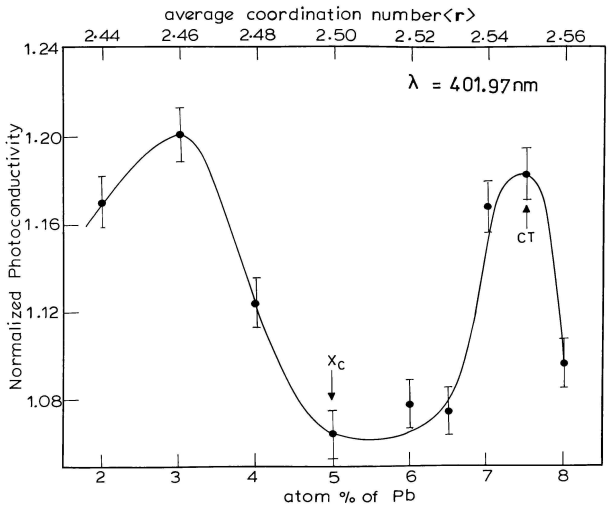

Fig. 6. Composition/average coordination number dependence of normalized steady state photoconductivity at 401.97 nm.

3.2.3 Intensity dependence of steady state photoconductivity

The intensity dependence of steady state photoconductivity for a representative $Ge_{20}Te_{78}Pb_2$ sample at ambient temperature is studied in the intensity range of 82.8mW to 156.4mW. The photoconductivity (σ_{ph}) is found to increase with increase in intensity (F) (Fig. 7) following a power law $\sigma_{ph} \alpha F^{\gamma}$, where the value of γ computed by curve fitting is found to lie in the range of 0.5 to 1.5. Fig. 7 shows the linear fit of absolute photoconductivity with intensity, which indicates the existence of continuous distribution of localized states in the mobility gap of this material as indicated by Rose [24].

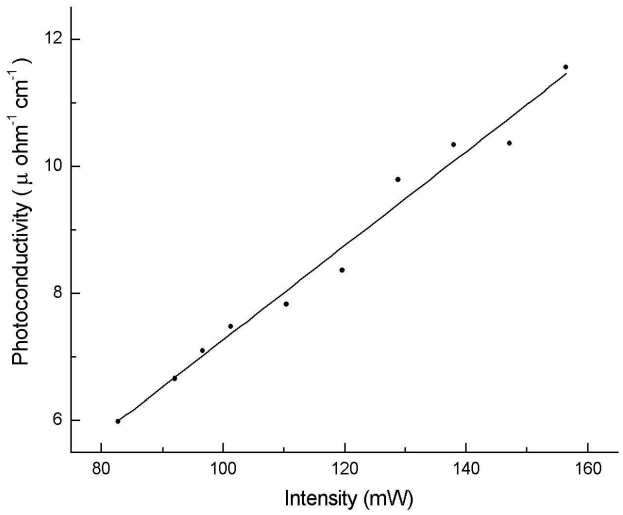

Fig. 7. Absolute steady state photoconductivity with intensity. The line shows the linear fit to the data points.

4. Conclusions

Time dependent transient photoconductivity measurements carried out on bulk $Ge_{20}Te_{80-x}Pb_x$ ($2 \leq x \leq 8$) glasses indicate that the photo response decreases rapidly with the increase in Pb, from x = 2 to x = 3 atom percent. Anomalies noticed in the composition dependence of normalized photoconductivity of bulk $Ge_{20}Te_{80-x}Pb_x$ glasses at x = 5 and x = 6.5 are possibly due to the onset and completion of rigidity percolation; the cusp seen at x = 7.5 is due to the chemical threshold. Steady state photoconductivity due to white light and for different wavelengths on $Ge_{20}Te_{80-x}Pb_x$ ($2 \leq x \leq 8$) thin films also reveals the existence of an extended rigidity percolation and the chemical threshold. The spectral dependence of normalized steady state photoconductivity with time indicates less photosensitivity of $Ge_{20}Te_{80-x}Pb_x$ thin films for 401.97nm and 452.67nm and a maximum in photosensitivity for 580.0nm. The slow non-exponential decay with time in both bulk and thin films are characteristic of the deep traps present in chalcogenide glasses. The steady state photoconductivity of thin films of $Ge_{20}Te_{80-x}Pb_x$ is found to increase with intensity following a power law with γ value lying between 0.5 and 1.5 which shows the existence of continuous distribution of localized states.

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