

THE ROLE OF DEFECTS IN CARRIER TYPE REVERSAL IN BISMUTH DOPED Ge-Se GLASSES BY PHOTOLUMINESCENCE SPECTROSCOPY

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The role played by defects in bringing out n-type conduction in $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$ and $\text{Ge}_{20}\text{Se}_{70-x}\text{Bi}_x\text{Te}_{10}$ glasses is using investigated photoluminescence (PL) spectroscopy. It was found that for both the systems, the compositions at lower Bi content exhibit luminescence with fine features associated while the compositions that show n-type conduction do not exhibit luminescence. The identification of the associated fine features, carried out by deconvoluting the experimental spectra, reveals that Bi addition brings out a relative diminishing in D^+ defects as compared to D^- ones. The study gives an overall indication for the role played by native defects in bringing out n-type conduction in Bi-doped glasses.

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1. Introduction

The physical properties of semiconducting chalcogenide glasses, that are promising materials in various applications, are profoundly influenced by the presence of inherent defects. One such property is the appearance of n-type conduction in Bi doped glasses ($\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$ and $\text{Ge}_{20}\text{Se}_{70-x}\text{Bi}_x\text{Te}_{10}$) above $x \geq 8$ [1,2]. In the past two decades, the extensive studies carried out to understand the mechanism of n-type conduction in these Bi doped glasses have lead to two different explanations. The first one among them is based on the evidences for phase separation at microscopic level, the conclusions drawn from which claim the presence of Bi_6^- atoms [1-3]. On the other hand, the second one based, on structural studies, asserts the presence of positively charged Bi_3^+ or Bi_4^+ atoms [4-6]. The n-type conduction according to the former description is due to the microcrystallites of n-type conducting c- Bi_2Se_3 embedded in the rest of the glassy matrix while on the contrary, according to the later, it is due to the relative decrease in inherent D^+ defects. Though the two contradictory ideas are addressed recently in a consistent way [7], studies on the role played by defects in bringing out n-type conduction in Bi doped glasses are very rare [8].

The inherent defects in chalcogenide glasses originate mainly from the rearrangements taking place at the prevalent chain ends and are denoted either as D^+ and D^- charged dangling bonds or equivalently as C_3^+ and C_1^- valence alternation pairs (VAP)[9,10]. Also, the VAPs that form very close to each other are called intimate valence-alternation pairs (IVAP). These defects give rise to states in the gap and are conjectured to be the luminescence centers in chalcogenide glasses[11]. In the present paper we address the role played by these defects in bringing out n-type conduction in glassy $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$ and $\text{Ge}_{20}\text{Se}_{70-x}\text{Bi}_x\text{Te}_{10}$ systems using photoluminescence spectroscopy.

2. Experimental details

Bulk glassy samples of interest were prepared by conventional melt-quenching technique from 5N pure elemental materials. The samples prepared in this way were confirmed to be x-ray amorphous. Differential scanning calorimetry scans were done on the samples to determine their glassy nature.

Samples having surface dimensions of $2 \times 2 \text{ mm}^2$ were selected for PL studies. No grinding or polishing was done because samples already had shiny surfaces in their as-prepared form.

To carry out photoluminescence studies a Fourier Transform Photoluminescence Spectrometer (MIDAC corp. USA) was used. Samples to be studied were mounted on a sample holder and then were suspended in a liquid helium cryostat and excited with an Ar⁺ laser ($\lambda = 514.5$ nm or $E \sim 2.41$ eV) with 2 mm beam diameter. The experiment was carried out at 4.2 K with 150 mW/cm^2 excitation power density. PL signals coming from the samples were analyzed using a Michelson interferometer and detected by a liquid-nitrogen cooled Ge-photodiode. The interferograms with a resolution of 2 meV were recorded by averaging out 0 coadded scans using a personal computer attached to the spectrometer. The excitation was turned on just before recording each spectrum.

3. Results and discussion

The PL spectra recorded for the two systems $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$ and $\text{Ge}_{20}\text{Se}_{70-x}\text{Bi}_x\text{Te}_{10}$ with varying Bi concentration are given in Figs. 1 and 2. For lower concentration of Bi, the range of luminescence spectra falls in a broad range 0.7 to 1.2 eV like in a-Se [12]. Again like a-Se, these compositions exhibit luminescence with fine features indicating transitions at three separate energies. However, no luminescence is observed for n-type compositions having higher Bi content.

On the whole, addition of Bi in both Ge-Se and Ge-Se-Te systems reduces the overall PL intensity with an exception of an initial increase in Ge-Se system. The initial increase in Ge-Se system resembles the trends observed when Ge and Te are added to Se, probably because the initial addition of Bi to Ge-Se can facilitate in further breaking of long Se chains. This can give rise to an increase in the concentration of under and overcoordinated inherent defects which are conjectured to be the luminescence centers in chalcogenide glasses. However, as can be seen from the figures, when the concentration of Bi is further increased beyond 4 at%, the intensity goes down to the disappearance of luminescence for compositions that show n-type conduction. Reduction in inherent defects that act as radiative recombination centers can be one of the reasons for the decrease and subsequent disappearance of luminescence intensity.

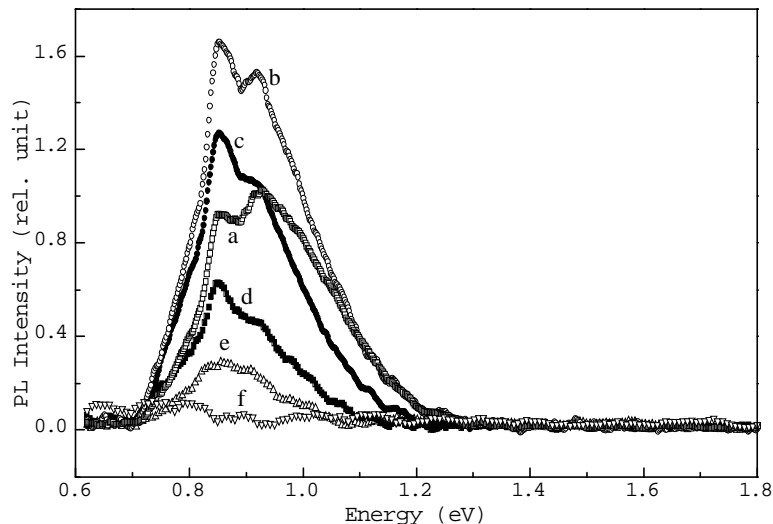


Fig. 1. Photoluminescence spectra for $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$ semiconducting glasses at 4.2 K and 150 mW cm^{-2} incident power for a. $x = 0$, b. $x = 2$, c. $x = 4$, d. $x = 6$, e. $x = 8$ and f. $x = 10$. No luminescence was observed for composition for $x = 12$ as well as in $x = 10$.

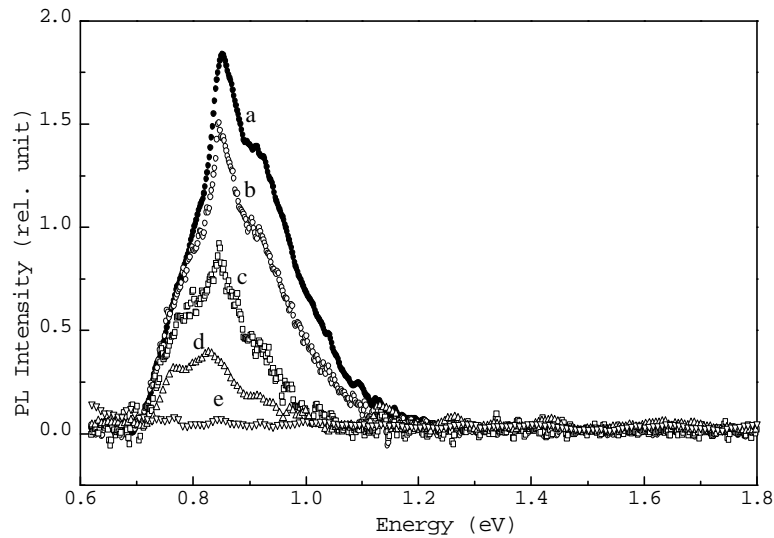


Fig. 2. Photoluminescence spectra for $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x\text{Te}_{10}$ semiconducting glasses at 4.2 K and 150 mW cm^{-2} incident power for a. $x = 0$, b. $x = 2.5$, c. $x = 5$, d. $x = 7.5$ and e. $x = 9$. No luminescence was observed for the compositions $x = 10$ and $x = 11$ as well as in $x = 9$.

Apart from a decrease in inherent defects, there can be a host of nonradiative processes which can play a significant role in reducing PL efficiency in n-type conducting samples. One such process which mostly the chalcogenide glasses is photoconduction since the quantum efficiency curves for photoluminescence and photoconductivity are complementary to each other and can be written as

$$\eta_0 + \eta_p = 1 \quad (3.1)$$

where η_0 and η_p are the quantum efficiencies for photoluminescence and photoconduction, respectively. The relation strongly holds when the excess photon energy required to quench photoluminescence is smaller than that required to ionize excitons. Hence, more the exciting photon energy greater will be the kinetic energy of the exciton created. This in turn will enhance the quantum efficiency for photoconduction with a corresponding drop in the same for photoluminescence. Earlier experimental studies have shown that addition of Bi in $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$ brings down the optical band gap from 2.0 eV at $x=0$ to nearly 1.2 eV for n-type conducting samples [1,2]. The excitation energy in the present investigations is 2.41 eV for all the samples as a result of which the excess excitation energy for n-type conducting glasses amount to nearly 1 eV and can enhance photoconduction with a simultaneous reduction in PL efficiency. The experimental reports on photoconduction in Ge-Se-Bi glasses indeed give evidences for such an increase in photoconductivity with Bi addition [13]. Besides photoconduction, there is a second possibility for absence of PL in n-type conducting glasses. Extrinsic as they are, the n-type glasses will have a significant amount of extended states occupied even at 0K. As a result, the probability of absorption near band edges will be diminished, Lesser the absorption, poorer will be the PL efficiency.

Similarities observed in the PL energy range for samples with lower Bi content and for a-Se confirms the more general nature of luminescent centers in chalcogenides vis-à-vis the inherent defects. These inherent defects include VAPs and IVAPs and are also denoted as random D^+ and D^- and nonrandom D^+ and D^- , respectively. In principle both VAPs and IVAPs can act as PL centers and luminescence energy range can be explained on the basis of these defects as luminescence centers [12]. The similarities in the three features observed in Bi-doped glasses and a-Se suggest that addition of Bi does not create any extra luminescence centers though it can give rise to some sort of defect centers which are non-radiative.

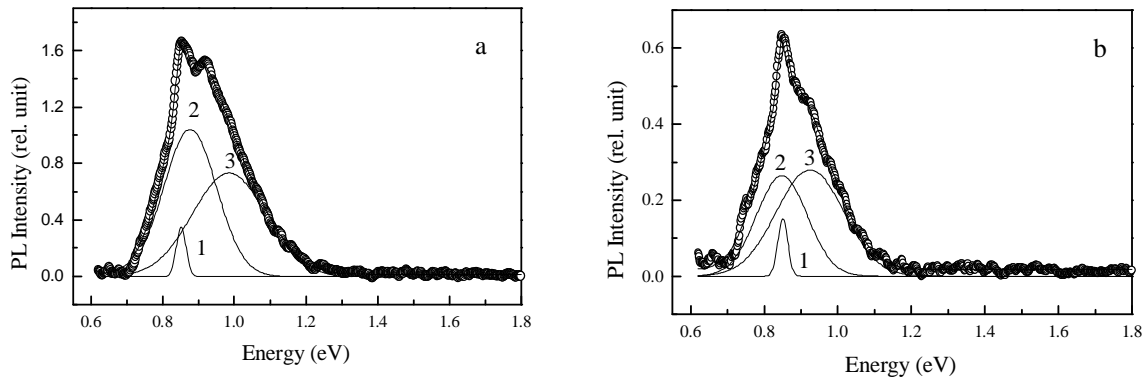


Fig. 3. Deconvoluted experimental spectra for a. $x = 2$ and b. $x = 6$ in $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$ glasses.

Conventionally, luminescent transitions at low temperatures are described by Gaussian line broadening mechanism and similar is the case proposed for chalcogenide glasses too [8]. Therefore to deconvolute the three distinct luminescence transitions embedded in the experimental PL spectra is considered a linear combination of three Gaussians (amplitude version) given by

$$y = y_0 + \sum_{i=1}^{i=3} A_i \exp\left(-0.5\left(\frac{x - xc_i}{w_i}\right)^2\right) \quad (3.2)$$

with y_0 representing offset and A_i , xc_i and $2.355w_i$ representing the amplitude, peak position and full width at half maxima (FWHM) of i th transition. The deconvoluted experimental spectra in Ge-Se-Bi and Ge-Se-Te-Bi systems for some samples that showed PL are given in figures 3 and 4. In Table 1 are listed the best fitting parameters along with the area under each deconvoluted spectra ($\sqrt{2\pi} A_i w_i$). The resultant of the three deconvoluted spectra fits very well with the experimental spectra. Identification of the three deconvoluted spectra with radiative transitions at different inherent defects is done according to the following arguments.

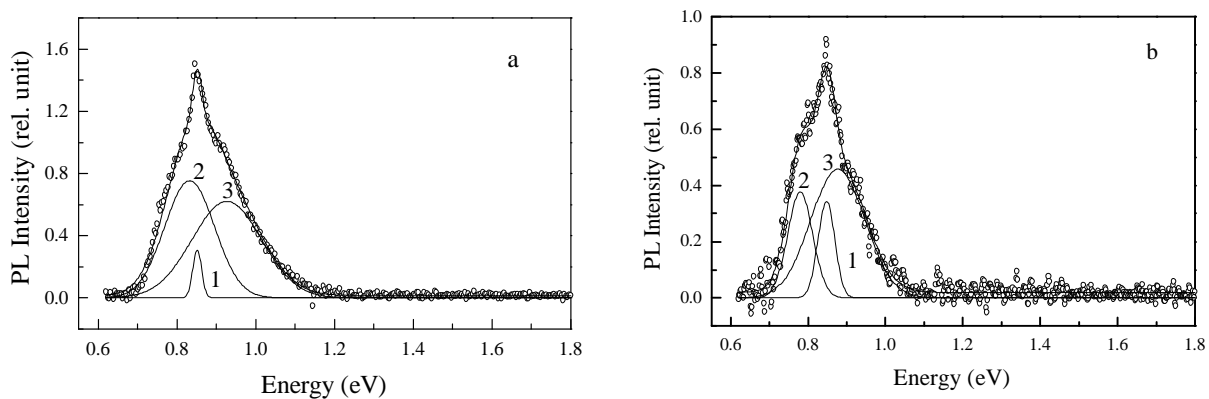


Fig. 4. Deconvoluted experimental spectra for a. $x = 2.5$ and b. $x = 5$ in $\text{Ge}_{20}\text{Se}_{70-x}\text{Bi}_x\text{Te}_{10}$ glasses.

PL in semiconductors is generally due to electron-hole recombination and its origin can be traced to six different transition [14]. They are the transition between a) a free electron and a free hole ($fe \rightarrow fh$), b) an electron trapped in a shallow or deep level and a free hole ($etsl \rightarrow fh$ or $etdl \rightarrow fh$), c) a free electron and a hole trapped in shallow or deep level ($fe \rightarrow htsl$ or $fe \rightarrow htdl$) and d) electron-hole pairs trapped at defect pairs in the gap ($etdl \rightarrow htdl$). The energy level scheme for gap states in semiconducting chalcogenide glasses is sketched in Fig. 5(a) in which the energy levels arising due to random and non-random D^- and D^+ defect centers are positioned according to the phenomenological

defect models[15]. The shallow donor and acceptor levels represent the random D^+ and D^- defects and the deep donor and acceptor levels represent non-random D^+ and D^- defects. The donor levels act as trap levels for electrons whereas the acceptor levels act as trap levels for holes.

Coming to the present results, the deconvoluted spectra in Figs. 3 and 4 are significantly Stokes-shifted from the excitation energy (2.41eV) as well as the respective optical bandgap energies. Such a large shift of half the band gap magnitude is not feasible if at all there are any band-to-band radiative transitions[16]. Interestingly, energy and width of one of the three deconvoluted spectra appears insensitive to compositional variation. According to the defect models, IVAP defect centers forming neutral defect pairs are known to be insensitive to dopant atoms[15]. The insensitive deconvoluted spectra can therefore be identified with the recombination transition at IVAPs. At the same time, according to charged defect models, there is a larger distortion associated with random D^+ than for random D^- and, therefore, the radiative transition involving D^+ will occur at lesser energy than that involving D^- . Utilizing these ideas, we identify the second deconvoluted spectra with transition occurring at D^+ (etsl \rightarrow fh) and the third one with the transition at D^- (fe \rightarrow htsl). The multiple transitions discussed above can be illustrated with the help of a configurational coordinate diagram as shown in Fig. 5(b).

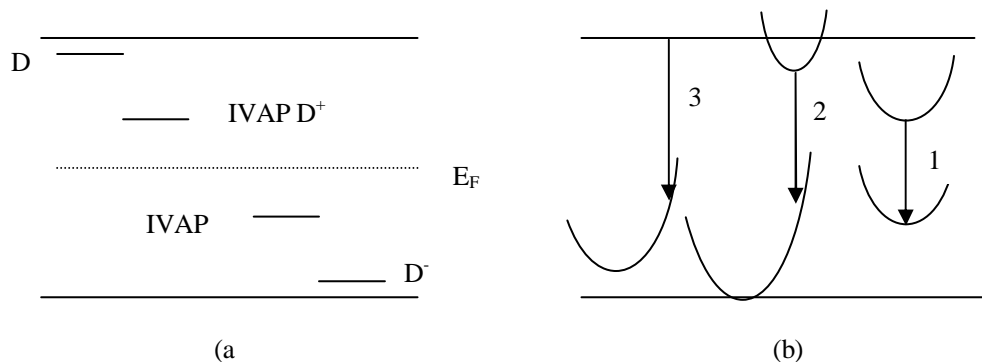


Fig. 5. (a)Energy level scheme for VAP and IVAP defects in chalcogenide glasses and (b) Configurational coordinate diagram illustration of multiple PL transitions involving gap levels denoted by 1- the IVAP pair recombination. 2 - etsl \rightarrow fh and 3- fe \rightarrow htsl.

With this identification we can now discuss the consequences of Bi addition to Ge-Se and Ge-Se-Te glasses. In both these systems addition of Bi gives rise to a reduction in the width of the two broader transitions along with a shift in their peak position to lower energy side. This is natural if we recall that the broader transitions are assigned to random VAPs which are more likely to get influenced by external dopants unlike IVAPs. The lowering of energy of transitions associated with random VAPs is probably due the higher atomic radii of Bi atoms added that can push the corresponding energy levels away from the band edges, towards the Fermi level.

From Table 1 and also from the deconvoluted spectra in Figs. 3 and 4, we can see that at 6 and 5 at% of Bi in Ge-Se and Ge-Se-Te systems, respectively, the relative area under the second deconvoluted spectra is less than that under the third. As the area under the curve depends on the density of defect centers giving rise to the corresponding PL, it can be said that the concentration of D^+ defects decreases more rapidly than the concentration of D^- as Bi replaces Se. This is possible if Bi atoms added enter the glassy matrix as positive defects. For Bi to go as positive defect it has to have a coordination number of less than its valence i.e. five. Most of the structural studies carried out in the past like EXAFS, Raman and IR have all pointed out a coordination of three for Bi with a positive charge on it. Though a recent EXAFS study has claimed the coordination of Bi to be four[6] as against all the earlier structural studies, it is interesting to note that it has in fact envisaged Bi atoms to be positively charged. The relative reduction in D^+ defects as compared to D^- defects indeed gives a clear evidence for Bi atoms entering as positively charged defects into the glassy matrix. Some earlier studies pointing out a reduction in hole drift mobility as compared to electron drift mobility with the addition of Bi[17] substantiate our findings as it is known that D^+ and D^- defects act as electron and hole traps, respectively. With this in mind a discussion on the mechanism of appearance of n-type conduction in Bi doped glasses is presented here.

Table 1 The extracted features from the experimental spectra for different compositions and the area under the respective deconvoluted spectra.

Sample	xc_1 (eV)	w_1 (eV)	Area	xc_2 (eV)	w_2 (eV)	Area	xc_3 (eV)	w_3 (eV)	Area
a-Se	0.849	0.030	0.017	0.859	0.148	0.379	0.954	0.206	0.229
Ge ₂₀ Se ₈₀	0.850	0.034	0.088	0.903	0.160	1.127	1.01	0.202	1.00
Ge ₂₀ Se ₇₈ Bi ₂	0.851	0.028	0.122	0.877	0.148	1.944	0.986	0.204	1.852
Ge ₂₀ Se ₇₆ Bi ₄	0.851	0.026	0.084	0.863	0.140	1.358	0.963	0.190	1.238
Ge ₂₀ Se ₇₄ Bi ₆	0.851	0.026	0.087	0.848	0.138	0.458	0.925	0.184	0.644
Ge ₂₀ Se ₇₀ Te ₁₀	0.851	0.024	0.129	0.859	0.144	1.989	0.956	0.192	1.414
Ge ₂₀ Se _{67.5} Bi _{2.5} Te ₁₀	0.851	0.022	0.085	0.832	0.127	1.198	0.926	0.176	1.371
Ge ₂₀ Se ₆₅ Bi ₅ Te ₁₀	0.847	0.028	0.090	0.784	0.072	0.220	0.873	0.140	0.628

From a thorough review of all the earlier studies, a coordination of three for Bi appears more convincing as it can be made consistent even with the phase separation evidences [7]. Accordingly, we envisage Bi atoms to exist as positively charged defects with three nearest Se neighbours in Ge-Se glassy matrix to bring out an imbalance in D^+ - D^- defect pairs. An additional consequence of Bi atoms entering as Bi^{+3} defects in the glassy matrix is the availability of extra electrons in the conduction band extended states, evidence for which also is available in the literature[18]. These two changes combined with the setting in of microscopic inhomogeneities in the form of a- Bi_2Se_3 [7] can lead to a condition wherein the Fermi level can no longer be pinned. A shifts in E_F towards the conduction band is the natural consequence of these effects, eventually bring out n-type conduction at higher Bi content in both Ge-Se and Ge-Se-Te glasses.

4. Conclusions

Compositional dependence of photoluminescence in $Ge_{20}Se_{80-x}Bi_x$ and $Ge_{20}Se_{70-x}Bi_xTe_{10}$ glasses is studied. It is observed that addition of Bi brings out a reduction in the relative concentration of D^+ as compared to D^- defects. The imbalance accompanied by the contribution of extra electrons brings out n-type conduction in Bi doped glasses. The observation is in good agreement with the earlier structural studies.

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