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Theoretical Investigation on Linear and Nonlinear Optical Properties of Solution-Processed GeTeBi Chalcogenide Films

Reena Gadhwal[1], Hukum Singh[1], Ambika Devi[2]

[1]Professor, Department of Applied Sciences, The NorthCap University, Sector 23-A, Gurugram 122017, Haryana, India, [2]Professor, Amity School of Applied Sciences, Amity University, Gurugram 122413, Haryana, India

Abstract

The optical study of $Ge_{20}Te_{75}Bi_5$ nano colloids is presented in this paper. Bulk chalcogenide glass was prepared by the well-known melt quenching method. Solution-based processing is proposed for nano colloid formation. Using the spin coating technique, optical-grade thin films are deposited on glass slides. The optical bandgap of films is estimated from absorbance spectra using the Tauc extrapolation method and Wemple and DiDomenico (WDD) model is used to determine the optical dispersion parameters. Tichy and Ticha approach has been employed to observe nonlinear refractive index (n_2). An increase in optical parameters and a decrease in optical bandgap with the increase in glass concentration may be attributed to cluster formation while dissolution.

Keywords: *Chalcogenide, Nano colloid, Bandgap, Dispersion parameter, Refractive Index.*

Introduction

There is currently a lot of theoretical and experimental interest in the linear and nonlinear optical characteristics of semiconductors[1]. Researchers in both the basic and technological fields are very interested in nano semiconductor materials that display distinctive characteristics that their bulk counterparts do not. Research on nanostructured semiconductors is also important because photonics is moving towards nanoscale optical functionality and integrating several components onto one chip. The photonic community is currently paying more attention to chalcogenide semiconductors. To achieve strong optical confinement, nanophotonic devices often use a high refractive index contrast, enabling wavelength-scale resonators and waveguide bends. Due to the flexibility of their atomic structure and the presence of defect states, chalcogenide glasses are known to exhibit a range of photoinduced phenomena[2,3]. Many optical and electrical characteristics of noncrystalline semiconductors are known to be governed by localized states in the band edge and bandgap [4,5]. Hence, engineering the bandgap energy and defect state density helps to control linear and nonlinear optical characteristics of chalcogenide glasses.

When dissolved in organic solvents, chalcogenide glasses enable novel and straightforward deposition methods like the spin coating process [6,7]. The production of clusters with diameters of several nanometers that retain the bulk glass stoichiometry is the outcome of the low-cost dissolution of chalcogenide glasses. The bandgap of these nanoclusters changes with size and is influenced by the solution concentration [8]. There have been several reports on the use of solution processing in devices such

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Corresponding Author:
Reena Gadhwal
Professor, Department of Applied Sciences, The NorthCap University, Sector 23-A, Gurugram 122017, Haryana, India
e-mail: reena18asd003@ncuindia.edu

as integrated single-mode mid-infrared waveguides, inverse opal photonic crystals, etc [9,10]. The identification of optical nonlinearities is crucial for practical application in optic fibers, all-optical switching elements (AOS), waveguides, optical limiting devices, and other areas In many different device engineering applications, such as optical switches, and optical limiters it is advantageous to use materials with high nonlinear refractive index (n_2) and low nonlinear absorption coefficient (β) [11,12].

Given the above, two different concentrations of $Ge_{20}Te_{75}Bi_5$ nano colloids and their spin-coated thin films are reported in this work. Optical characteristics, including refractive index, energy band gap, and WDD parameters, have been investigated utilizing the UV-visible spectrophotometer data.

Materials and Methods

Bulk $Ge_{20}Te_{75}Bi_5$ glass has been synthesized using the conventional melt-quench method [13]. To create two solution-processed $Ge_{20}Te_{75}Bi_5$ glasses with concentration S_1 = 0.525 mg/ml and S_2= 0.96 mg/ml, n-butylamine was used to dissolve finely ground glass samples. The breakdown took place in a glass container that was firmly closed to avoid evaporation. To maximize the surface area of glass samples and speed up the dissolution process, they were coarsely ground. A magnetic stirrer was used to hasten the dissolving process for at least two days. The thin films were deposited over glass microscope slides using the spin coating technique. A double-beam UV-VIS spectrophotometer (Perkin Elmer-365) was employed to detect the optical transmittance of solutions.

Results and Discussion

The transmission spectra of nanocolloidal films composed of two distinct concentration samples S_1 and S_2 are shown in Figure 1. Figure 1 clearly shows that when the concentration of the $Ge_{20}Te_{75}Bi_5$ component in the solution decreases, the transmission edge moves to the shorter wavelength side. The concentration also affects the slope of the absorption edge, which establishes the width of the localized states. This property is important because it allows amorphous composites to alter their photosensitivity from the ultraviolet to the infrared region.

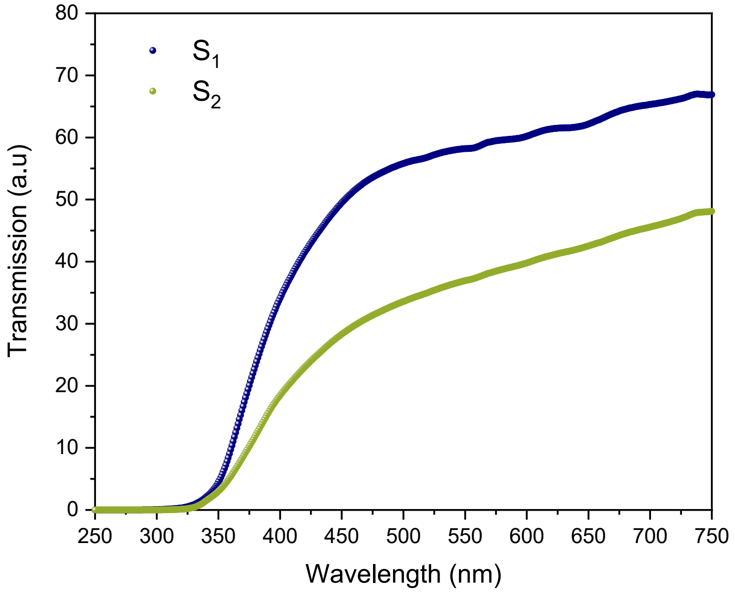

Figure 1. Transmission spectra of S_1 = 0.525 mg/ml and S_2= 0.96 mg/ml.

The optical bandgap of nanocolloidal sample (shown in Table 1) has been calculated from the optical absorption coefficient data using the equation [14]

$$\alpha h\nu = B(h\nu - E_g)^2 \quad (1)$$

where B is the band tail parameter, which is the slope of the Tauc edge. The band gap (as shown in Figure 2) significantly shifts to red when the concentration of nano colloids rises [15].

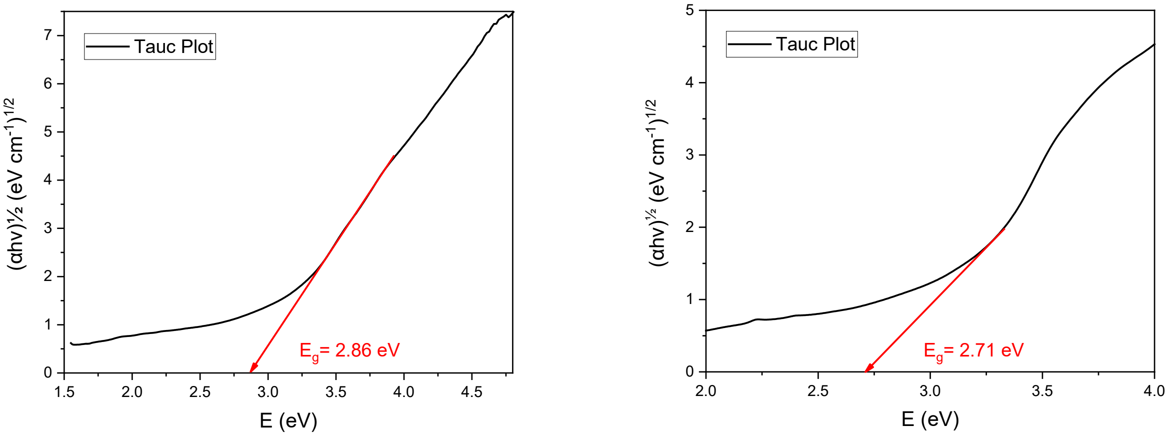

Figure 2. $(\alpha h\nu)^{1/2}$ vs E for nanocolloidal samples S_1 and S_2.

Transmission spectra can be used to determine refractive index using the well-known Swanepoel method[16]

$$n = \sqrt{H^2 + \sqrt{H^2 - S^2}} \tag{2}$$

Where $H = \frac{4s^2}{(s^2+1)T^2} - \frac{s^2+1}{2}$, where T is the transmission of nanocolloidal samples and s is the refractive index of air. Further, the extinction coefficient is calculated using the formula $k=\alpha\lambda/4\pi$.

The relationship between the extinction coefficient and oscillator amplitude decay of the incoming field depends on the absorption coefficient.

Table 1. Values of E_g, E_0 and E_d for nanocolloidal chalcogenide samples.

Sample	E_g (eV)	E_0 (eV)	E_d (eV)
S_1	2.86	2.23	31.94
S_2	2.71	3.1	38.57

Wemple Di Domenico (WDD) devised a single effective oscillator model, which is provided below equation, to study the dispersion behavior of nano colloids[17,18].

$$n^2 - 1 = \frac{E_0 E_d}{E_0^2 - h\nu^2} \tag{3}$$

Here $h\nu$ represents the photon energy, E_0 stands for the single oscillator energy, and E_d stands for the dispersion energy. The slope $(1/E_0E_d)$ and intercept (E_0/E_d) of the graph of $(n^2\text{-}1)^{-1}$ versus $(h\nu)^2$ (as shown in Figure 3) yield E_0 and E_d. E_0 and E_d values are reported in Table 1, which exhibits higher values of WDD parameters with the inclusion of a higher concentration of nano colloids. Although bonds are firmly covalent, chalcogenide nano colloids have bigger nearest neighbors than bulk chalcogenides due to the higher value of the dispersion factors [19].

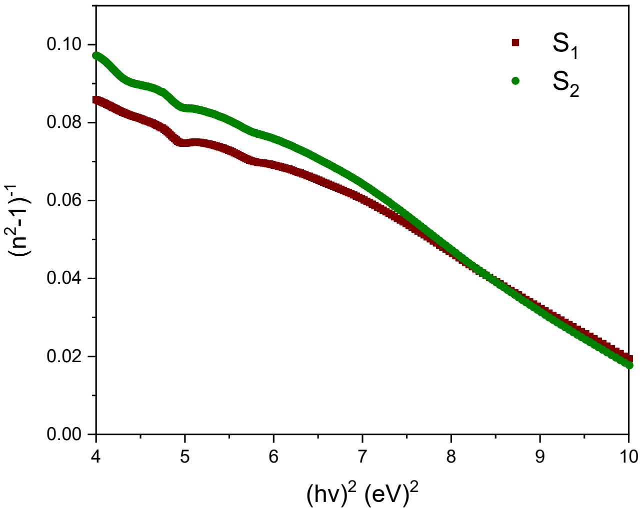

Figure 3. $(n^2 - 1)^{-1}$ vs $(h\nu)^2$ plot for two nanocolloidal samples.

Devices for shielding delicate electronics from powerful optical radiations use photonic materials with optical limiting features. Depending on their nonlinear optical properties, and bandgap particularly their two-photon absorption coefficient (β) and nonlinear refractive index (n_2), semiconductors can be employed for these purposes. The optical nonlinearity in chalcogenide glasses is mostly caused by third-order susceptibility. Amorphous chalcogenides and their nano colloids are of specific importance among them due to their value in nonlinear optical characterization.

Miller's generalized rule and the WDD parameters were used by Tichy and Ticha [20] to estimate $\chi^{(3)}$. As per this approach, for chalcogenide glasses $\chi^{(3)}$ can be measured in esu using the relation [21,22]

$$\chi^{(3)} = \frac{A(n_0-1)^4}{(4\pi)^4} \quad (4)$$

where A= 1.7 $\times 10^{-10}$. $\chi^{(3)}$ values are estimated and tabulated in Table 2.

Table 2. Value of n_0, n_2, and $\chi^{(3)}$ for $Ge_{20}Te_{75}Bi_5$ nano colloids S_1 and S_2.

Sample	n_o	n_2	$\chi^{(3)}$ (esu)
S_1	3.92	1.55×10^{-12}	1.27×10^{-13}
S_2	3.16	4.7×10^{-12}	4.89×10^{-13}

To determine the nonlinear refractive index (n_2) for photonic glasses, Tichy and Ticha proposed the empirical relation shown below [20]

$$n_2 = \frac{12\pi\chi^{(3)}}{n_0} \quad (5)$$

Here n_0 is the static refractive index whose values for samples are shown in Table 2. The n_2 values have been estimated for two nano-colloidal solution samples using the above relation and have been depicted in Table 2. Theoretically calculated nonlinear refractive index values show an increase in nonlinear refractive index values with increasing nanocolloidal concentration as is reported in experimental results[15].

Conclusion

Linear and nonlinear optical properties of $Ge_{20}Te_{75}Bi_5$ nano colloids are investigated theoretically in this paper. The Wemple and DiDomenico (WDD) model is used to calculate the optical dispersion parameters, and the Tauc extrapolation method is utilized to estimate the optical bandgap of films from absorbance spectra. To observe the nonlinear refractive index, the Tichy and Ticha technique has been used (n_2). Cluster formation during dissolving may explain why optical parameters increase and the optical bandgap decreases as glass concentration increases.

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