

Experimental and Model Studies of $\text{Ge}_{10}\text{Se}_{90}$ Sample

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Abstract

$\text{Ge}_{10}\text{Se}_{90}$ is a Group IV–VI semiconductor glassy material synthesized by the melt-quenching technique. Its optical properties were studied using UV–Visible spectroscopy. The optical band gap of the sample was found to be 1.95 eV. The increase in band gap compared to the bulk value indicates quantum confinement effects, confirming the nano-dimensional nature of the material. The wavelength dependence of the refractive index was analyzed using the Wemple–DiDomenico single-oscillator model. From this model, parameters such as the single-oscillator energy (E_0) and dispersion energy (E_d) were determined, and their values reflect the influence of nano-dimensional effects. The Sellmeier model was also applied to obtain parameters such as oscillator strength and average oscillator wavelength. The Abbe number of the glass was calculated to be 17.21, which is smaller than that of flint glass (Abbe number ≈ 25). The lower Abbe number indicates higher chromatic dispersion. The material exhibits normal dispersion behavior, as the first derivative of the refractive index with respect to wavelength ($dn/d\lambda$) is less than zero.

Keywords: Semiconductor, chalcogenide glasses, Abbe number, dispersion, nano-dimension

Introduction

Ge–Se glasses are Group IV–VI semiconducting materials that are widely used in various applications. Their transparent nature makes them particularly important for infrared applications. Long-wave infrared (LWIR) imaging plays a crucial role in medical diagnostics, monitoring, autonomous driving, and other imaging fields. A mature imaging system consists of both an optical system and a detector [1–4]. In addition to selecting suitable materials, chromatic aberration must be addressed by modifying the lens structure. The dispersion properties of chalcogenide glasses can be tuned by altering their composition. Another approach to modifying the optical properties is through nanometric size reduction, which introduces quantum

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confinement effects. Diffractive surface structures are also employed to fabricate surfaces with negative dispersion characteristics on the original lens, thereby effectively correcting chromatic aberrations [5]. The aim of this work is to report the Abbe number, which is very small for this glassy system and has not yet been reported in the literature, and to discuss the fitted optical dispersion models and their parameters for the $\text{Ge}_{10}\text{Se}_{90}$ sample.

Experiment

The $\text{Ge}_{10}\text{Se}_{90}$ glass was prepared using Ge (5N purity) and Se (5N purity) ingots as raw materials employing the traditional melt quenching technique. Initially, the raw materials weighted in compositional ratios were vacuumed (10^{-6} mbar) using a diffusion pump in quartz ampoules and then sealed the ampoule by welding torch. After that, the sealed ampoule was subjected to ramp the temperature $2^{\circ}\text{C}/\text{min}$ up to the melting process in a rotating furnace at 1000°C for 72 hours. The homogenized melt was quenched within a second by fast quenching in ice water. Disc of thickness 2 mm and 8mm diameter was cut from the glass sample and polished for optical characterization.

Results and Discussion

The energy band gap and refractive index of glassy semiconductors in the UV-Visible region allow us to study the fundamental aspects of their optical and electrical properties. Investigation of the optical band gap helps in identifying and developing materials for specific applications, particularly distinguishing between direct and indirect band gap semiconductors. The refractive index, on the other hand, describes the bending of light within the glass medium. In a dispersive medium, the behavior of light varies with wavelength, which is important for designing suitable lens systems using transparent semiconducting materials.

In optical applications, refraction and chromatic dispersion directly influence the characteristics of transmitted light and determine the practical feasibility of the prepared material. The refractive index is an important parameter that describes the speed of light within a material relative to its speed in vacuum. Knowledge of the band gap can also be used to estimate the refractive index of a material. Because of its importance in device design [6], several studies have proposed empirical relationships between the refractive index and other physical quantities [7].

In the present work, the refractive index was determined from UV-Visible experimental data. The first part of our analysis focuses on the evaluation of the Abbe number. The Abbe number is calculated using the refractive indices at three standard spectral lines in the visible region:

$\lambda_F = 486.1 \text{ nm}$ (F line),
 $\lambda_D = 589.2 \text{ nm}$ (D line), and
 $\lambda_C = 656.3 \text{ nm}$ (C line).

The Abbe number of a transparent optical material, named after the German physicist Ernst Abbe, is defined as:

$$V_D = \frac{n_D - 1}{n_F - n_C} \quad (1)$$

The Abbe number is defined as the ratio of refractivity to dispersion. The Abbe number V_D , sometimes referred to as the V-number, is calculated using the refractive indices at the standard spectral lines.

By substituting the values $n_D = 1.947$, $n_F = 1.978$, and $n_C = 1.923$, the Abbe number was calculated to be 17.21. Refractive index values for three different lines are obtained from Figure 1.

The variation of refractive index as a function of wavelength is shown in Figure 1;

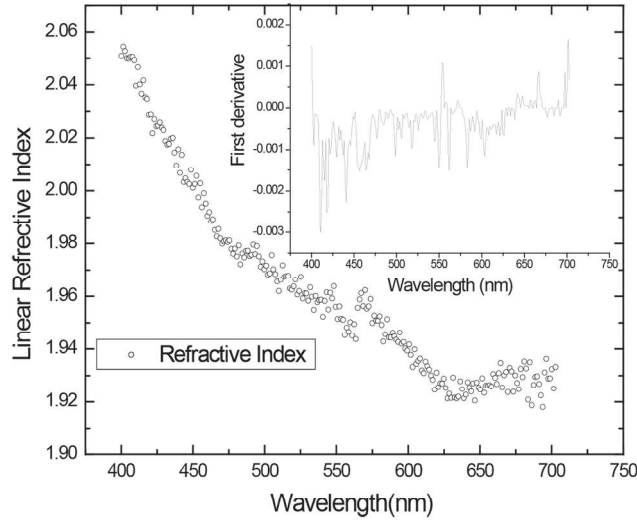


Figure 1: Variation of Refractive Index versus Wavelength; inset in Figure 1 shows first derivative of Refractive index

Dispersion refers to the broadening of the spectrum due to the variation of refractive index with wavelength, as shown in the inset of Figure 1. In the case of normal dispersion, $\frac{dn}{d\lambda} < 0$, it means that the refractive index decreases

with increasing wavelength. This behavior is clearly reflected in the inset of Figure 1. Chromatic dispersion can be investigated in greater detail through the Abbe number, which provides a quantitative measure of dispersion. Since the Abbe number is directly related to wavelength-dependent refractive index variation, it can also be correlated with the focal length of a lens made from the material. For lens design applications, understanding how chromatic dispersion varies with wavelength helps predict the extent of chromatic aberration across the spectrum. This information is essential for designing efficient optical systems. The obtained Abbe number of our sample is 17.21, indicating relatively high chromatic dispersion. Therefore, this material may be particularly suitable for applications such as prisms or other dispersion-based optical elements. For example, in a system consisting of a convex and a concave lens of the same radius of curvature (e.g., 50 mm), the focal length of the combination can be determined using the lens maker's formula.

$$\frac{1}{f} = (n_d - 1) \left(\frac{1}{R_1} - \frac{1}{R_2} \right) = (1.95 - 1) \times \frac{2}{50} = 0.038 \text{ mm}^{-1}$$

$$f = 26.3 \text{ mm}$$

We also know-

$$n^2 - 1 = \frac{P}{\epsilon_0 E} \quad (2)$$

Now, to find n , we need the ratio P/E . We also know the force exerted on charge q ; this force causes displacement of dipoles, which causes polarization. The force is given by:

$$F = q[E + v \times B] \quad (3)$$

$$|B| = \frac{|E|}{c} \quad \text{so} \quad |E| \gg |v||B| \quad \text{In this situation, the Lorentz force is neglected;}$$

$F = q E$, hence material particles absorb energy from the electromagnetic wave and hence accelerate, due to which they radiate out energy. This radiating out energy is called scattering. r is the displacement of charge particle due to the electromagnetic wave [EM]; the dipole moment can be written as $P = q.r$. More importantly, the refractive index originates from multiple microscopic resonance mechanisms such as time varying dipole moments of electrons, atoms, and other oscillators. Under the classical regime, the complex refractive index can be expressed in terms of resonance frequencies, ω_0 , of different oscillators [8].

$$n^2 = 1 + \frac{q^2 N}{m \epsilon_0} \sum \frac{1}{\omega_0^2 - \omega^2 - i \gamma \omega} \quad (4)$$

γ is the damping rate. In normal dispersion, the damping term is neglected, so the above expression can be written as:

$$n^2 = 1 + \frac{q^2 N}{m\epsilon_0} \sum \frac{1}{\omega_0^2 - \omega^2} \quad (5)$$

now put $\omega = 2\pi\nu = 2\pi c/\lambda$; $\lambda = 2\pi c/\omega$; $\lambda_0 = 2\pi c/\omega_0$

Putting the values of ω and ω_0 in the above expression, we got:

$$n^2 = 1 + \sum \frac{A_k \lambda^2}{\lambda^2 - \lambda_0^2} \quad (6)$$

Equation (6) is called Sellmeier model. We fitted the Sellmeier model to our data and found the oscillator length strength A_k and the strength of wavelength parameter λ_0 . The fitted graph of the data is shown in Figure 2.

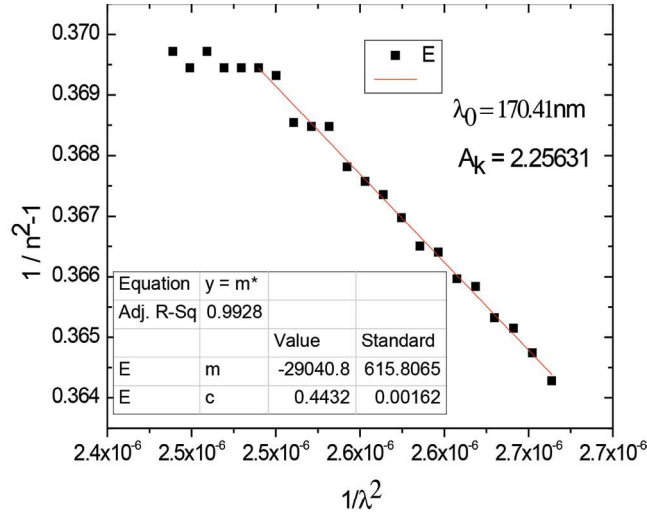


Figure 2: Sellmeier Model fitted on Data

On the y-axis, the quantity $1/(n^2-1)$ was plotted as a function of $1/\lambda^2$. The fitted model is represented by the red line superimposed on the experimental data. The adjusted R-square value of the fit is 0.99285, indicating excellent agreement between the model and the experimental data. The average oscillator strength parameter, $A_k=2.256$, is a dimensionless quantity. The parameter $\lambda_0=170.41\text{nm}$ represents the average oscillator wavelength, which is related to the energy at which direct interband electronic transitions occur. The fitted Sellmeier equation provides valuable information about the absorption peak of the glass.

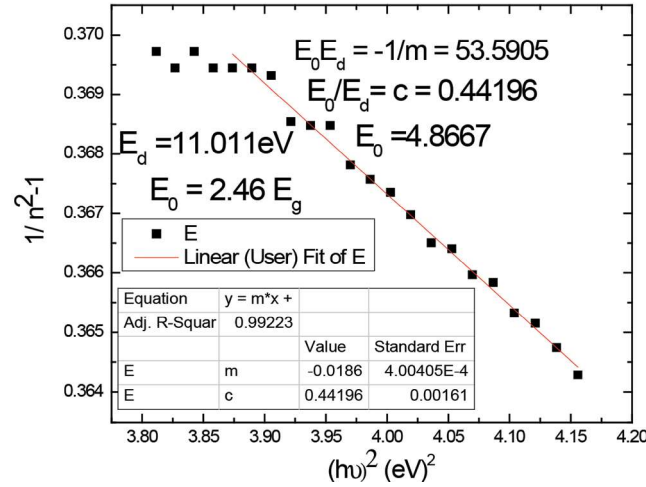


Figure 3: Wemple-DiDomenico single oscillator model fitted on experimental data

The Wemple-DiDomenico model (WDD) is widely used to study the spectral dependence of the refractive index below the interband absorption edge (i.e., below the optical band-gap energy). The dispersion parameters, namely the single-oscillator energy E_0 , and the dispersion energy E_d , were obtained by fitting a straight line to the plot of $1/(n^2-1)$ versus $(\hbar\nu)^2$, as shown in Figure 3. The adjusted R-square value of the fit was 0.9923, indicating good agreement between the model and the experimental data. The values of E_0 and E_d were calculated from the slope ($-1/E_0E_d$) and the intercept (E_0/E_d) of the fitted line. The obtained values were $E_0 = 4.8667$ eV and $E_d = 11.011$ eV. In our samples, confined acoustic phonon modes were observed in Raman scattering measurements, indicating that the particle size is in the 7-10 nanometer range. Due to this confinement effect, the absorption edge shifts toward lower wavelengths (approximately 170 nm), as confirmed by the Sellmeier analysis presented in this article. This shift may be attributed to the increased Coulomb interaction resulting from spatial localization of the electron wave functions in the synthesized nanometer-sized glass. A comprehensive literature survey of optical studies on $\text{Ge}_{10}\text{Se}_{90}$ revealed that reports on bulk glass of this composition are not available; only thin-film studies have been reported in the literature [9]. Therefore, the optical parameters obtained from thin films cannot be directly compared with those of bulk glasses, since the dispersion parameters (E_0) and (E_d) can be influenced by several experimental factors, including film thickness, substrate temperature, deposition temperature, and other deposition conditions. In the reported $\text{Ge}_{10}\text{Se}_{90}$ thin film [9], the values of (E_0) and (E_d) were 2.20 and 20.17 eV, respectively. The relatively high value of (E_d) may be associated with structural disorder, weakly bound atomic configurations, or

defect-related clusters in the thin-film sample. The comparatively low value of (E_0) ($= 2.20\text{eV}$) can be related to the average energy gap of the material. For disordered materials, the optical gap (E_g) is often approximately related to the dispersion energy through the empirical approximation ($E_0 \approx 2E_g$) [10].

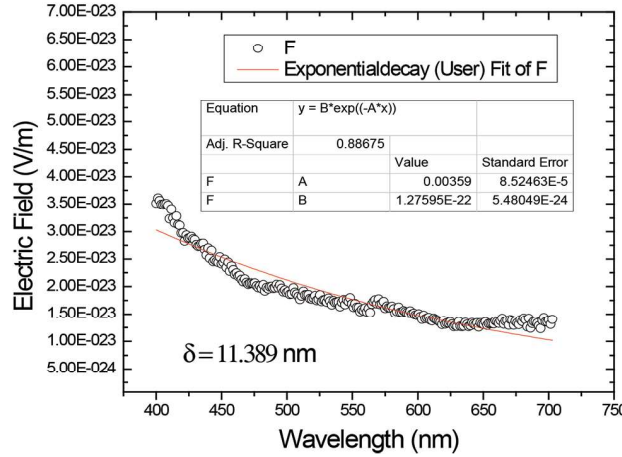


Figure 4: Skin Depth or Penetration depth plot

In the present study, a considerably higher value of $(E_0 = 4.8667\text{eV})$ was obtained. This value is approximately twice that reported for the $\text{Ge}_{10}\text{Se}_{90}$ thin film in Ref. [9]. The higher (E_0) value may be attributed to the nanoscale dimensions of the present sample, where quantum-confinement effects can modify the electronic structure and consequently influence the optical response observed in the UV-Visible region. However, since (E_0) and (E_d) are sensitive to structural and experimental conditions, the difference between the present results and those reported for thin films should be interpreted and attributed to quantum confinement. An interesting conceptual aspect of the present results is the relationship between structural disorder and optical dispersion. As the degree of structural disorder decreases and the material tends toward a more ordered or crystalline state, a reduction in optical dispersion and a corresponding decrease in the optical gap may be expected. In contrast, when the material dimensions are reduced to the nanometric scale, quantum-confinement effects can modify the electronic structure, leading to an increase in (E_0) and a decrease in (E_d) . Thus, the observed values of the dispersion parameters may reflect the combined influence of structural ordering and nanoscale confinement effects.

Nonlinearity in refractive index is related to third-order susceptibility $\chi^{(3)}$, and the nonlinear refractive index is directly proportional to E^2 . The third-order optical susceptibility and nonlinear refractive index are evaluated by using the semi-empirical relation [11, 10] based on Miller's formula and the WDD single-oscillator model:

$$\chi^{(3)} = B \left[\frac{n_0^2 - 1}{4} \right]^4 \quad (7) \quad \text{where } B \text{ is a constant } 1.7 \times 10^{-10} \text{esu}$$

$$n_2 = \frac{3\chi^3}{8n_0} \quad (8)$$

Derivation of $\chi^{(3)}$ and nonlinear refractive index: The nonlinear refractive index n_2 is directly proportional to the real part of the third-order nonlinear optical susceptibility $\chi^{(3)}$, and the overall refractive index change Δn scales directly with the square of the electric field amplitude, E^2 . The interaction of a high-intensity field with a material induces a total polarization P inside the glassy medium. This can be written as a power series expansion of the electric field E

$$P = P^{(1)} + P^{(2)} + P^{(3)} + \dots \quad (9)$$

For centrosymmetric media (such as glass, gases, or liquids), the second-order susceptibility $\chi^{(2)}$ is zero due to inversion symmetry. Keeping terms up to the third order, the total polarization becomes:

$$P = \epsilon_0 \chi^{(1)} E + \epsilon_0 \chi^{(3)} E^3 \quad (10)$$

Where: ϵ_0 is the vacuum permittivity

$\chi^{(1)}$ is the linear susceptibility

$\chi^{(3)}$ is the third-order nonlinear susceptibility

Consider a monochromatic optical electric field oscillating at an angular frequency ω :

$$E(t) = E \cos(\omega t)$$

Substituting this electric field into the third-order polarization term yields:

$$P^{(3)}(t) = \epsilon_0 \chi^{(3)} E^3 \cos^3(\omega t)$$

Using the trigonometry relation $\cos^3(\omega t) = \frac{3}{4} \cos(\omega t) + \frac{1}{4} \cos(3\omega t)$ substituting the value of $\cos^3(\omega t)$ into $P^{(3)}(t)$:

$$P^{(3)}(t) = \frac{3}{4} \epsilon_0 \chi^{(3)} E^3 \cos^3(\omega t) + \frac{1}{4} \epsilon_0 \chi^{(3)} E^3 \cos(3\omega t) \quad (11)$$

The second term describes third-harmonic generation (3ω). To study changes to the refractive index at the fundamental frequency (ω), we isolate the component oscillating strictly at ω :

$$P(\omega) = \epsilon_0 \chi^{(1)} E + \frac{3}{4} \epsilon_0 \chi^{(3)} E^3 \quad (12)$$

Factoring out the common E so that P(ω) is written as:

$$P(\omega) = \epsilon_0 (\chi^{(1)} + \frac{3}{4} \chi^{(3)} E^2) E \quad (13)$$

The total polarization is also related to the effective relative permittivity (dielectric constant) ϵ_r by the constitutive relation:

$$P = \epsilon_0 (\epsilon_r - 1)E \quad \text{or} \quad \epsilon_r = 1 + \frac{P}{\epsilon_0 E} \quad (14)$$

Substituting the value of P(ω) into the above expression yields:

$$\epsilon_r = 1 + \chi^{(1)} + \frac{3}{4} \chi^{(3)} E^2$$

We can separate this into a linear component ϵ_L and a nonlinear component $\Delta\epsilon$

$$\text{Where: } \epsilon_L = 1 + \chi^{(1)}$$

$$\Delta\epsilon = \frac{3}{4} \chi^{(3)} E^2 \quad (15)$$

Now solve for the refractive index change:

The total refractive index n is defined by $n^2 = \epsilon_r$; let the field -dependent index be expressed as a sum of its linear index n_0 and a small nonlinear perturbation Δn :

$$n = n_0 + \Delta n \quad (16)$$

Squaring both sides of this relation yields:

$$n^2 = n_0^2 + 2n_0\Delta n + (\Delta n)^2$$

As the nonlinear modification is remarkably small ($\Delta n \ll n_0$), the high-order term $(\Delta n)^2$ can be ignored. Equating this to the permittivity representation:

$$n_0^2 + 2n_0\Delta n \approx \epsilon_L + \Delta\epsilon$$

$$\text{Since, } n_0^2 = \epsilon_L; \text{ and}$$

$$\Delta\epsilon = 2n_0\Delta n \quad (17)$$

Substituting the expression for $\Delta\epsilon = 2n_0\Delta n$ into equation (15), we get;

$$\begin{aligned} 2n_0\Delta n &= \frac{3}{4} \chi^{(3)} E^2 \\ \Delta n &= \frac{3}{8n_0} \chi^{(3)} E^2 \end{aligned} \quad (18)$$

Nonlinear refractive index constant

The total refractive index can be expressed explicitly as a function of the optical field power:

$$n = n_0 + n_2 E^2 \quad (19)$$

Equating the two expressions for the change in index ($\Delta n = n_2 E^2$):

$$n_2 E^2 = \frac{3}{8 n_0} \chi^{(3)} E^2$$

Cancelling out the field component E^2 from both sides yields the relation for nonlinear refractive index:

$$n_2 = \frac{3}{8 n_0} \chi^{(3)} \quad (20)$$

Now substitute the value of $\chi^{(3)}$ from equation (7) into equation (20), so the final relation for nonlinear refractive index is written as:

$$n_2 = \frac{3}{8 n_0} B \left[\frac{3}{8 n_0} \frac{n_0^2 - 1}{4} \right]^4 \quad (21)$$

$$n - n_0 = \frac{3}{8 n_0} B \left[\frac{n_0^2 - 1}{4} \right]^4 \quad (22)$$

The value of n_0 is obtained at $h\nu \rightarrow 0$ for the composition. Figure 3 $1/n^2 - 1$ vs. $(h\nu)^2$ the straight line equation corresponding to the fit for $\text{Ge}_{10}\text{Se}_{90}$ bulk glass provides the value of n_0 by extrapolating the WDD equation to $h\nu \rightarrow 0$. To evaluate the electric field, the value of B in electrostatic units is converted to electric field units, and finally, Figure 4 shows the decay of the electric field with distance as the electromagnetic wave travels through a medium. Due to dissipative effects, the electric field decays with distance according to the equation:

$$E(x) = E_0 e^{-\alpha x}. \quad (23)$$

To determine the skin effect or penetration depth, an exponential fit is performed. However, the nonlinearity of the medium causes the field to deviate from the ideal exponential decay, as evident from the fitted plot. Penetration depth (δ) is defined as the distance at which the amplitude of the field decays to E_0/e ; it means

$$\frac{E_0}{e} = E_0 e^{-\alpha \delta} \quad (24)$$

After substituting the values, the skin depth δ is obtained, which is 11.389 nm.

The optical band gap of the $\text{Ge}_{10}\text{Se}_{90}$ sample was found to be 1.9837 eV;

detailed analysis was published [12], which is higher than the reported bulk value (1.8eV) [9]. The wavelength corresponding to maximum exciton absorption decreases with decreasing particle size due to quantum confinement of photo-generated electron-hole pairs.

Conclusions

The Ge₁₀Se₉₀ nanometric glassy sample studied in the present work was synthesized using the melt-quenching technique. The sample was characterized through X-ray diffraction (XRD) and UV-Visible spectroscopy. The XRD results confirmed the amorphous nature of the sample and indicated a nanometric grain size. The optical band gap of the material was measured to be 1.9837eV, which shows an increase compared to bulk values. Additionally, structural parameters such as the Abbe number, refractive index, dispersion, skin depth, and models like Sellmeier and WDD were fitted to the experimental data to calculate the physical parameters.

Data Availability: Data will be available on request.

Declaration: This research received no external funding.

Conflict of interest: The author declares no conflict of interest.

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