Mapana – Journal of Sciences
2025, Vol. 24, No. 1, 67-78
ISSN 0975-3303 | https://doi.org/10.12723/mjs.72.5

Nonlinearities and Dielectric constant of Ge-Se Chalcogenide Glasses

Deepak Sharma*

Abstract

We recorded a transmission spectrum of Ge-Se glasses in the UV-visible range, revealing 80-90% transmission of light at room temperature. The percentage of light absorbed by these glasses is only 15%. The applicability of these glasses for the fabrication of single-mode optical fibre is being pursued by their high transmission and nearly nonexistent normal dispersion, while a small anomalous dispersion drop in the transmission is noticed at 720 nm in the UV-visible region. Drop in transmission at higher wavelength is explained in terms of absorption/photodarkening effect. Analysis of prepared glasses reveals direct band-gap material; thus, these materials can be used directly in fibre laser preparation. The refractive index obtained from spectra is modelled by Cauchy expression, and it is valid up to 700nm; beyond 700nm, wavelength increase in refractive index is modelled by poly4. Dielectric characteristics are examined and assessed. Ge-Se glasses have a decreasing dielectric constant as the band gap widens, indicating a decreasing trend in dielectric constant with increasing frequency.

Keywords: Chalcogenide glasses, Bandgap, Refractive index, Susceptibility, Polarizability, Dielectric constant

1. Introduction

Developed and emerging nations have high demands in the field of information technology. We require optical fibre technology in order to transmit information from one location to another within a city, between cities, or across international borders. Due to a combination of low linear and nonlinear indices, silica fibre optics, which are now the standard material for optical telecommunication, need to be replaced. Chalcogenide glasses, which belong to a unique class of network glasses, are the cause of the replacement. Because of a slight variation in electronegativity between the cation and the anion, the elements that form chalcogenide glasses are covalently bound;

---

* SCRIET, C.C.S. University, Meerut, Uttar Pradesh, India; deepak22s@yahoo.com

nevertheless, the bonding strength is weaker in chalcogenide glasses than in oxide-based optical fibre materials. Chalcogenide glasses have special optical and dielectric characteristics due to the structure of the bonding; glasses with heavier chalcogen elements have a much higher refractive index and a lower bandgap [1], which is not found in traditional oxide/silicon glass. Low phonon energy [2], photosensitivity, and chemical mechanical durability exist in selenium-based chalcogenide glasses. The transparency limit was in the range of 7-8μm in oxide glasses to prolong such a limit, further chemical composition of chalcogenide glasses is required [3]. Chalcogenide glasses/fibres are exceptionally stable in liquid water/water-vapour at ambient temperature, unlike halide glasses [4], and Ge-Se-based glasses are not oxidised in air below the glass transition temperature, analogous to silicon oxidised in the air [5]. These days, a lot of research is being done to build these kinds of devices. A high linear refractive index greater than 2, nonlinear absorption losses and high transmission material are required for the current choice. Ge-Se glassy alloys are promising materials that can be used with large-scale integration technology and have good light transmission properties (85%–90%). This leads us to conduct more studies on UV-visible and far-infrared. Our initial findings on bulk Ge-Se glasses motivate us to carry out an additional study on this material and accomplish the preparation of a single-mode optical fibre for these glasses. In order to exploit or close gaps in scaling Ge-Se material in nano-fibre form, either in optical fibre or fibre laser, the primary focus of this work has been to comprehend changing compositions and variations in the characterisation of optical properties, such as transmission, refractive index, bandgap, dielectric constant, etc. of these glassy compounds. The first announcement of a room-temperature lasing glass fibre doped with rare earth ions was made at 5.2μm in 2021[6]. We identify the structural component behind these glassy alloys' high nonlinear susceptibility and polarizability.

2. Experimental

To prepare bulk glasses, elemental raw chemicals Ge (5N) and selenium (5N) purity CERAC Company U.S.A., in chunks were weighed carefully, crushed in powder form, and put together into pre-cleaned silica ampoules. Silica ampoules were dried under vacuum (10^{-6} Torr) to remove any impurities. Finally, the ampoule was sealed. The chemical reaction for the preparation of the sample is as follows:

$$x\mathrm{Ge} + (1\text{-}x)\ \mathrm{Se} \rightarrow \mathrm{Ge}_x\mathrm{Se}_{1\text{-}x} \quad \text{...} \quad (1)$$

Where x is the percentage of germanium, ampoules containing the raw materials were placed and heated in a **rocking** furnace at 1000^0C for 48 hours. The melt was homogenised for 48 hours in a rocking furnace. To avoid crystallisation, the samples were quenched very fast in ice water in a bucket. A schematic of the furnace for chalcogenide glass preparation is shown. In this work, optical measurements were carried out at room temperature for the Ge_xSe_{1-x} (bulk) glasses; spectra were collected using a UV-visible spectrometer; the sample path length was 1cm. Light-matter interaction provides the variation in properties.

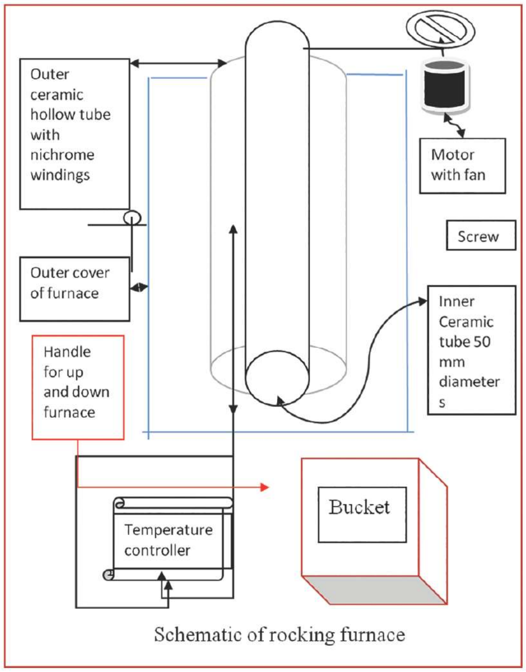

Figure Schematic of Rocking furnace for Chalcogenide glass preparation

3. Results and Discussion

For this work, UV-visible spectrums were recorded for a few selected compositions on the Ge_xSe_{100-x} glasses. The transmission spectra for Ge-Se glasses are displayed in Figure 1.

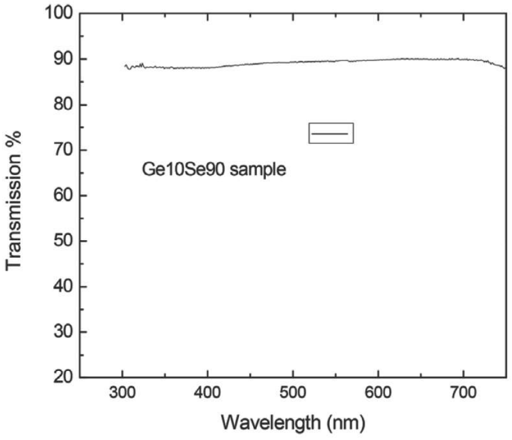

Figure 1: Transmission spectra of Ge10Se90 glass

It is observed that, at shorter wavelengths, normal dispersion was almost absent, and all the glasses showed good transparency at 89.6-93% up to 720nm wavelength. Above 720nm-800nm decrease in transparency (18%) seems to be absorption/ a photodarkening effect, and it is believed to originate from photo-induced structural transformations, fundamental understanding of this phenomenon allows local structural reorganisation of homopolar bonds to hetropolar bonds. Therefore, we can expect this effect is also due to also annihilation of localised states, enlarging the optical band gap and decreasing the material volume due to smaller lattice constants of the heteropolar bonds (Ge-Se) over homopolar bonds (Ge-Ge, Se-Se), as evident from other researchers' data up to 10μm no intensity decay was noticed [7]. 90% transparency from UV-visible data confirms that Ge-Se glasses can be used for single-mode fibre applications. Transmission edge at a longer wavelength is also known as anomalous dispersion. A transmission spectrum that fits the Boltzmann function well in the whole range is shown in Figure 2a.

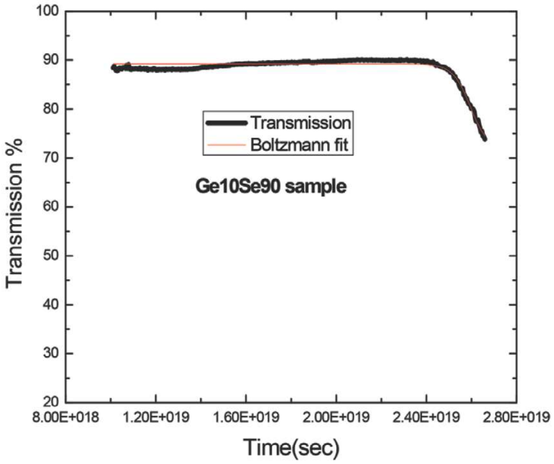

Figure 2a: Boltzmann fitted transmission spectra up to 800nm wavelength

At higher wavelengths, optical absorption edge shift has been noticed with the Ge% composition in the selenium matrix. Ge10Se90 glass composition optical absorption edge shifts towards the highest wavelength, i.e. red shift, has been noticed, while in chemical threshold composition, Ge33Se67 optical absorption edge shifts towards lower wavelength, i.e. blue shifts, has been noticed. Intermediate-range compositions show very nominal changes in optical absorption shift. It is due to this composition lies in a stress-free regime. Intermediate compositions displayed largest blue shift compared to Ge33Se67 and Ge10Se90 compositions, as shown in Figure 2b. A decrease in transmission is also explained on the basis of the photodarkening (PD) process, while the increase in transmission is explained on the basis of the photobleaching (PB) process. As we saw from transmission spectra, transmission intensity decreases, and hence, photodarkening in low germanium concentration (less than 20% Ge) is governed by lone pair (LP) excitation. At higher germanium concentrations, the mechanism of photodarkening is based on the breakage of the Ge-Ge and Ge-Se bonds. Photo darkening (PD) is of great interest due to its direct applications in optics and optoelectronics, including optical switching. Our present result on composition dependent suggests that the Ge-deficient to Ge-rich photodarkening process is observed only, as shown in Fig. (2b).

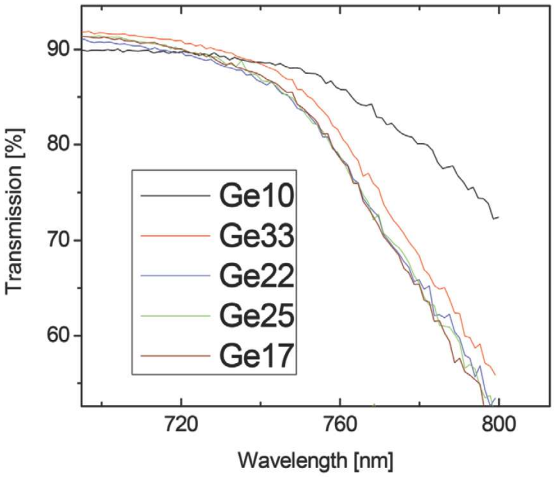

Figure 2b: Optical absorption shift at a higher wavelength with compositions

Compositional variations with at% of Ge transient effect of photodarkening are observed only. Moreover, the lower Germanium content shows la ess pronounced transient effect in magnitude, and it shits towards the higher wavelength side (red shift). The higher the germanium content, the more pronounced the magnitude of transient effects are observed, and it shifts towards a lower wavelength (blue shift).

The absorption spectrum has been determined from transmission data, and the optical band gap has been determined from the spectrum of absorption coefficient α. For band gap analysis, Tauc relation for the direct optical transition from the valence band to the conduction band has been used [8]. The following formula, known as the Tauc law, can be used to determine the optical energy gap Eg for Ge-Se glasses.

$$\alpha h\nu = A(h\nu - E_g)^m \quad \text{...} \; (2)$$

where m is a parameter that depends on the kind of electronic transition that caused the absorption, hv is the energy of incident light, and A is a constant that depends on the likelihood of the electronic transition. Direct and indirect optical transitions are permitted for values of m=0.5 and m=2, respectively. Laser-grade materials must have a direct bandgap, which is defined as one where the valence band maxima and conduction band minima fall on the same value of the k wave vector.

The direct optical band gap E_g has been obtained from the plot $(\alpha h\upsilon)^2$ vs. Energy and following a linear dependence extrapolating to the value $(\alpha h\upsilon)^2 = 0$ as shown in Figure 3.

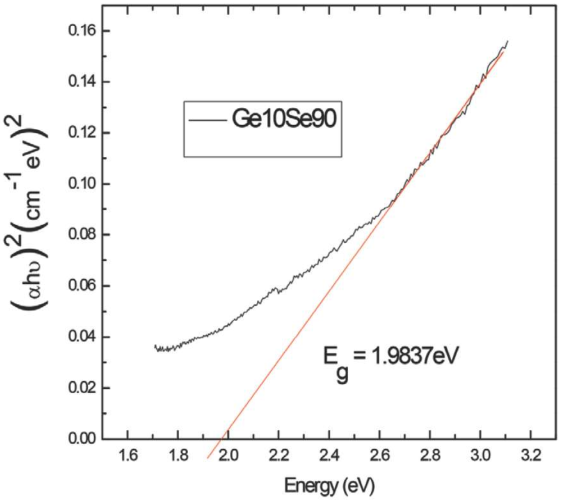

Figure 3: Direct band gap determinations from Tauc plot

It is clear that there is a significant increase in the optical band gap by increasing Ge concentration, as shown in Fig.4 in this system. This increase in band gap is attributed to the decrease of localised states in the glassy system due to germanium (Ge) addition in the Selenium matrix. It is remarkable that selenium rich compounds have a direct band gap. This increasing trend of optical band gap with composition may also be due to a shift in the Fermi level, whose position is determined by the distribution of electrons over the localised states. In covalent network glasses, the valence band (σ -bonding) arises from lone pair electron states, whereas the conduction band originates from anti-bonding (σ^*) states [9]. The variation of band gap with composition might also be responsible for bond strengths; the formation of stronger bonds could be the cause of the increase of optical band gap, network connectivity and density. Increasing bond strengths with the doping of Germanium in the host selenium matrix causes a larger splitting between the valence band and conduction band, which results in an increase in the band gap (E_g). The stoichiometric composition is usually known as chemical threshold composition Ge33Se67 the glass is made up of completely cross-linked tetrahedral-like structural units in which all the germanium is consumed by selenium, which consists of energetically favoured hetero-nuclear bonds only. Below the chemical threshol,d composition glasses are chalcogen rich, and above the chemical threshold are Ge-rich glasses [10]. An increase in network connectivity can be attributed to an increased interaction between tetrahedrons/atomic species, which results in widening the separation the n valence band and conduction band and increases E_g. Similar maxima were also reported in Ge-Se bulk glasses [11].

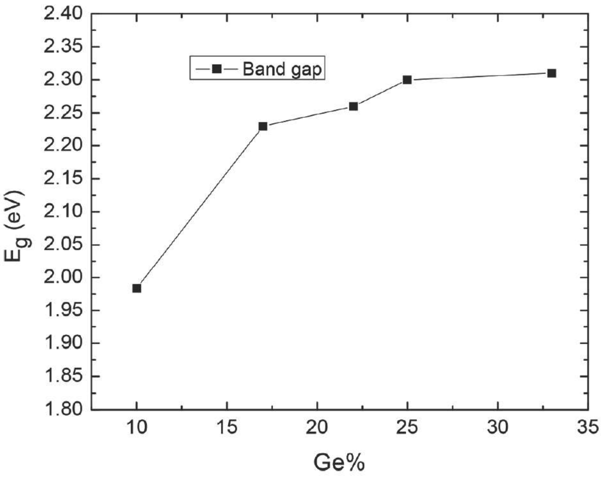

Figure 4: Variation of band gap with compositions

Polarizability calculation for different compositions has been done according to the Lorentz – Lorentz relation [12].

$$\frac{n^2-1}{n^2+1} V_M = R_m$$

Where V_M is a molar volume of compositions, n is the refractive index, and R_m is the molar refraction. Molar refraction is connected to polarizability which is a microscopic quantity α_m [13];

$$R_m = 4\pi\, \alpha_m (N_A/3) = 4.1887\, \alpha_m (N_A)$$

We get the Lorentz-Lorentz equation in terms of polarizability in this form:

$$\frac{n^2-1}{n^2+1} (V_M) = 4.1887\, \alpha_m (N_A) \quad \text{..} \quad (3)$$

N_A is Avogadro constant.

Reddy et al. [14] have proposed an empirical relation between the refractive index and band gap for a variety of compounds:

$$n = \sqrt{\frac{12.417}{E_{g-0.365}}} \quad \text{..} \quad (4)$$

Equation (4) is the modified form of the original Moss [15-17]. Refracting index determination from equation (3) calculation for different compositions has been found to decrease trends with the increasing Ge % doping in the host selenium matrix. It has been seen that a decrease in refractive index with doping of increasing Ge concentration compositions is probably due to an increase in density. Therefore, this decrease in refractive index can also be attributed to the decrease of valence in current carriers, or it might be due to the decreased polarizability. The drop in transmission, even for low intensity is results from highly metastable state structure in these bulk glasses samples. The experimental refractive index was obtained from transmission spectra, and its theoretical modelling was applicable only to the 700nm wavelength. The theoretical fit of Cauchy formula on refractive index, which gives $n = 1.862+2.8216\times10^4/\lambda^2$ as shown in Figure 5.

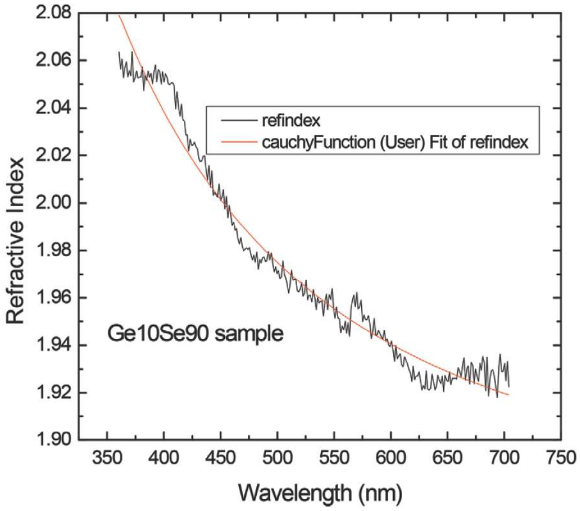

Figure 5: Refractive Index with Cauchy fit up to 700nm

An increase in refractive index for the Ge10Se90 sample beyond 700nm wavelength was modelled with poly4 fit as displayed in Figure 6. Due to an abrupt decrease in transmission intensity, these materials have been shown to exhibit a reverse/increasing trend of refractive index as contrasted to Figure 5. It indicates that absorption is increasing in this specific wavelength range, which is caused by the impact of photo-induced radiation and the sample's temperature no longer being kept at room temperature.

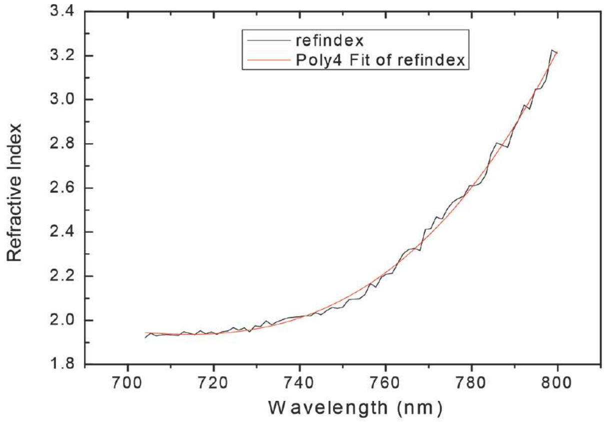

Figure 6: Refractive index with poly (4) fitting from 700-800nm

The compositional dependence of the dielectric constant ε, as shown in Figure 7 reveals that ε is decreasing with increasing Germanium concentration in Ge_xSe_{1-x} glasses. For Ge10Se90 composition, the value of dielectric constant shows a maximum while a minimum value with dielectric constant shows for Ge33Se67 glass composition. The nature of the plot of the dielectric constant, as shown in figure 7, is well-fitted with the exponential decay function. Variation of dielectric constant ε with composition is disorder-dependent.

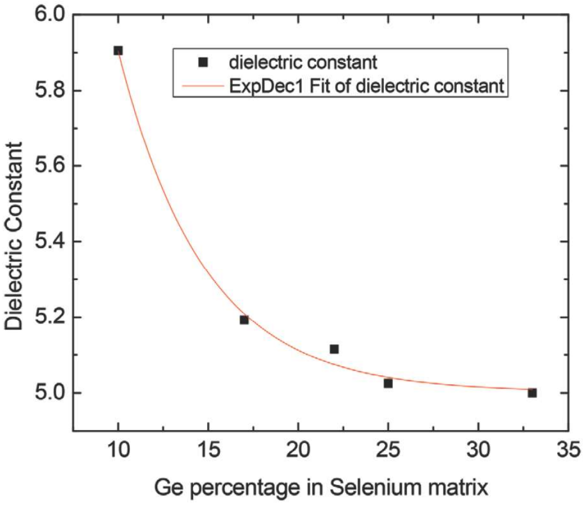

Figure 7: Variation of Dielectric constant with compositions

Materials with low germanium percentage doping or compositions rich in selenium have good charge storage capacity and can be employed in solar photovoltaic and battery applications. The decreasing trend of dielectric constant with an increase in frequency can be described with four types of polarisation such as electronic, ionic, orientation (dipolar) and space charge. At frequencies up to 10^{16} hertz, electronic polarisation occurs; it arises due to the shifting of valence electrons with respect to the positive nucleus. At a frequency of 10^{13} hertz, ionic polarisation arises due to the displacement of opposite ions relative to each other. At frequencies up to 10^{10} hertz, dipolar polarisation arises because molecules have permanent electric dipole moments that can change direction into the orientation of the applied electric field. In the frequency range, 1-10^{3}Hz space charge polarisation occurs because of impedance mobile charge carriers by interface. So the total polarisation is the sum of all the polarisation as described of the dielectric material; bonding is covalent in Ge-Se samples, decreasing trend of dielectric constant with frequency is because of the reduction of dipolar / orientation polarisation, dipoles cannot have the capacity to rotate rapidly so their oscillations lag behind those of the field. Dipoles are unable to follow the field, so the dielectric constant reduces and approaches the constant value at a higher frequency.

On analysis at low percentage doping of germanium in host selenium matrix (Ge10Se90) sample clearly discerned highly polarizability means high polarisable atoms or ions expected to have larger-nonlinear optical properties. The non-linear refractive index in glasses resulting in the highest non-linear properties, we have calculated non-linear refractive index (n_2) using the semi-empirical relation of Ticha et al. [18]

$$n_2 = \frac{B}{E_g^4} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(5)}$$

where B= 1.26×10^{-9} esu$(eV)^4$. By putting the value of band gap from data analysis, we obtain different values of non-linear refractive index for different compositions as shown in Figure 8.

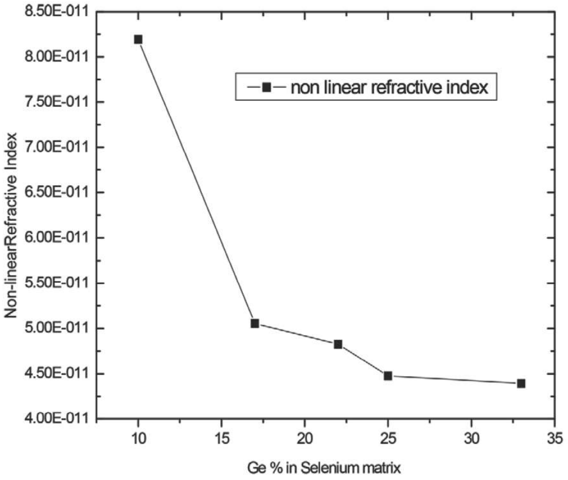

Figure 8: Variation of non-linear Refractive Index with Compositions

The decreasing trend of the nonlinear refractive index with compositions would be expected because the substitution of Germanium into selenium not only changes the network but also affects non-linear properties resulting from the widening of the band gap. Third-order non-linearity susceptibility $\chi^{(3)}$ is also obtained from the generalised Miller's formula [19] as-

$$\chi^{(3)} = 1.7\times10^{-10} (\chi^{(1)})^4$$

where ($\chi^{(1)}$) is a first-order linear Susceptibility that can be obtained by the following equation –

$$\chi^{(1)} = \frac{n^2-1}{4\pi}$$

n is a linear refractive index can be estimated from equation2. Glass is an isotropic solid with an inversion symmetry configuration so second order Susceptibility is ruled out i.e. $\chi^{(2)} = 0$. Third-order non-linear, third harmonic production and nonlinear events are caused by susceptibility, but laser light, which uses a very high electric field, can also make this feasible. Higher nonlinear susceptibilities and nonlinear phenomena, including the optical Kerr effect, which would be noticeable in compounds rich in selenium, can be easily observed in samples with lower germanium percentages. For optical switching devices, it is useful to determine nonlinear parameters. Chalcogenide glasses have a thousand times the nonlinear refractive index and third-order nonlinear susceptibility of silica-based glasses.

4. Conclusions

Our findings clearly show that adding Ge% to the selenium matrix improves the material's band gap, indicating an increase in both bond strength and networking [10]. It has been observed that the dielectric constant decreases with increased frequency or composition, and it is relevant that low doping of Ge% compositions can be used for better charge storage devices. Transmission spectra give essential details about the very transparent characteristics and nonlinearities of Ge-Se glasses, making them feasible for a variety of chalcogenide glass applications. Understanding nonlinearities will advance the physics area, how nonlinearities will affect the dielectric constant, and what will be the relationship between nonlinearities and dielectric constant is an important issue.

Declaration of Competing Interest

The author has no known conflict of interest to influence the work reported in this paper.

Author contributions

The author wrote the manuscript, did data analysis and prepared figures. Measurements were carried out at the Indian Institute of Science Bangalore.

Acknowledgement and funding

No financial support was available; we acknowledge the support of UGC DAE CSR Indore for sample preparation.

References

[1]. Jiri Jemelka, Karel Palka, Petr Janicek, Stanislev Slang, Jiri Jancalek, Michal Kurka and Miroslav Vlcek, Solution Processed Multilayered ThinFilms of Ge20Sb5S75 and Ge20Sb5Se75 chalcogenide glasses, Scientific reports13,16609(2023). https://doi.org/10.1038/s41598-023-43772-w

[2]. J.A.Savage, Optical properties of chalcogenide glasses, J of Non-Cryst. Solids Vol 47, 1, 101-115 (1982).

[3]. T.Babeva, V.Vassilev, P.Gushterova, A.Amova, G.Alexieva, V.Strashilov, P.Petkova, Optical properties of chalcogenide glasses from the system As_2Se_3-Ag_4SSe-PbTe J of optoelectronics and advanced materials vol19, no 3-4, 204-210 (2017). .

[4]. A.B.Seddon, Fluoride glasses, A.E. Comyns, ed. (Wiley 1989), chapter7

[5]. M.Morita, T.Ohmi, E. Hasegawa, M. Kawakami and M. Ohwada, J of Appl. Physics 68, 1272 (1990).

[6]. J.J. Nunes, Ł Sojka, R.W. Crane, D. Furniss, Z.Q. Tang, D. Mabwa, B. Xiao, T.M. Benson, M.C. Farries, N. Kalfagiannis, E. Barney, S. Phang, A.B. Seddon, S. Sujecki Opt. Lett. 46(15), 3504-3507(2021).

[7]. J.S.Sanghera, I.D.Agarwal, L.B.Shaw, L.E.Busse, P.Thielen, V.Nguyen, P.Pureza, S.Bayya, F.Kung, J.of Optoelectronics and Advanced Materials, vol3, no.3, p627-640,2001.

[8]. J.Tauc, R.Grigorovici, A.Vancu, Physica status solidi B, 15, 627-637, (1966).

[9]. M.Kastner, Phys.Rev.Lett. 28,355, (1972).

[10]. Ralph Chbeir, Aaron Welton, Matthew Burger, Soumendu Chakarvarti, Shreeram Dash, Siddhesh Bhosle, Kapila Gunashekra, Badriah S.Almutairi, Bernard Goodrman, Matthieu Miccoulaut, Punit Boolchand, J.Am.Ceramic Society 106, 3277-3302 (2023).

[11]. P.Tronc, M.Bensoussan, A.Brenac, C.Sebenne, Phys.Rev.B 8, 5947 (1973).

[12]. E.A Moelwyn-Hughes, Physical chemistry, Pergamon, London 1961.

[13]. H.Rawson, properties and application of glass, Elsevier, Amsterdam, 1980.

[14]. Reddy RR, Nazeer Ahammed Y,Rama Gopal K, et al.,Opt Mat, 10 (1998)95;Reddy RR & Ahammed NY,Infra Phys Technol, 36 (1995) 825.

[15]. Moss TS, Proc Phys Soc B, 63 (1950) 167.

[16]. Moss TS, Photoconductivity in Elements (Butterworth, London), 1952, 61.

[17]. Moss TS, Phys Stat Sol (B) 131(1985), 415.

[18]. H.Tichy, L.Ticha J.Opt.Adv.Mat. 4(2), 381, (2002).

[19]. J.J.Wynne, Phys.Rev.B 178, 1295, (1969).