



Optical Properties of Pure Glycine Doped Alkali Metal Nitrates

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Abstract: The present study focuses on the optical properties of glycine-doped Lithium Nitrate (LiNO_3), Sodium Nitrate (NaNO_3), Potassium Nitrate (KNO_3), Cesium Nitrate (CsNO_3) at various doping equimolar ratios (1:1, 2:1, 3:1) synthesized using the Solid-State Reaction Method and then subsequently dissolved in aqueous solutions. Optical properties of these samples were measured by using a UV-VIS-NIR Spectrophotometer (Agilent Cary Multicell Peltier) over a wavelength range of 200-900 nm. Results show that glycine-doped alkali metal nitrates exhibit significant absorption across the entire wavelength range. The direct bandgap energy of pure glycine is 5.80 eV, while glycine-doped alkali metal nitrates range from 5.12 to 5.31 eV, indicating shifts in optical bandgap energy suitable for optoelectronic applications. Transmittance spectra reveal higher transparency in the visible range for glycine-doped alkali metal nitrates as compared to pure glycine, which is essential for nonlinear optical (NLO) materials. Glycine has a lower cutoff wavelength at 244 nm, while the glycine-doped alkali metal nitrates show a lower cutoff wavelength around 258 to 262 nm approximately. Additionally, other optical parameters such as absorption coefficient, reflectance, refractive index, optical conductance, extinction coefficient, optical density, and dielectric parameters were evaluated, showing notable modifications in light behaviour within the doped matrix. The overall findings suggest that glycine Lithium Nitrate (1:1) exhibits the best optical properties, as compared to all other glycine doped alkali metal nitrates making it ideal for use in optoelectronics, NLO devices, photonic sensors, and laser technologies.

Keywords: Absorption • Transmittance • Reflectance • Energy bandgap • Optical Conductivity • Extinction Coefficient.

Introduction

In past few decades, Nonlinear optical materials are used in a wide range of applications, such as optoelectronics, optical computers, photonics, optical storage, telecommunications, and data processing. These materials exhibit unique properties for modern technological advancements. Pure organic materials, have high nonlinear optical coefficients, which make them highly efficient for NLO applications. They also exhibit excellent flexibility and easy to fabrication, making them highly adaptable for use in a variety of devices. organic material has limitations in terms of mechanical strength and physicochemical stability. Pure inorganic materials, are known for their greater strength, thermal stability, and

Chemical properties. these materials have mechanical durability and high-temperature performance, but they exhibit lower nonlinear optical efficiency compared to their organic materials. semi organic nonlinear optical materials have particularly promising class due to their ability to combine the advantages of both organic and inorganic materials. These semi organic compounds have excellent nonlinear optical properties while also have favourable mechanical strength and stability, offering a balance that is not typically found in purely organic or inorganic materials (Podder, 2002; Lin et al., 2003; Goel et al., 2013; Wang et al., 2002; Duan et al., 2002; Dinakaran & Kalainathan, 2013; Uma et al., 2013). Among the different types of semi organic nonlinear optical materials, the amino-acid family has the most potential for nonlinear optical device applications. Amino acids, considered the main components of life,



have been thoroughly researched for their capacity to create stable compounds with both organic and inorganic materials while exhibiting good second-order nonlinear optical features. Amino acids' unique chemical structures, combined with their capacity to form hydrogen bonds and interact with other molecules, make them perfect options for the synthesis of new nonlinear optical substances. Many amino acids, including glycine, alanine, and serine, exhibit strong second-order nonlinear spectral characteristics, and their derivatives have been investigated for use in a variety of photonic applications (Lydia Caroline et al., 2009; Anandan et al., 2014; Masilamani & Musthafa, 2013; Natarajan et al., 2010; Anbuezhayan et al., 2010). Researchers have been particularly interested in glycine, one of the simplest amino acids, because of its tendency to create compounds with both organic and inorganic elements. Glycine is well-known for its ability to form stable crystals and compounds, and its molecular structure, which includes both an amine and a carboxyl group, permitting it to interact with other molecules effectively. Over the years, multiple glycine-based compounds with nonlinear optical features have been discovered, including strong second-order nonlinear optical characteristics. These glycine-based nonlinear optical materials have been investigated for possible use in highspeed optical communication systems, laser technology, and optoelectronic devices (Martin Britto Dhas & Natarajan, 2007; Mary Linet et al., 2011; Esthaku Peter & Ramasamy, 2010). Glycine-based compounds comprise Bisglycine maleate, glycine picrate, calcium dibromide bis-glycine tetrahydrate, tri-glycine zinc chloride, α -glycine Sulpho-nitrate, bisglycine lithium nitrate, glycine potassium nitrate, glycine sodium nitrate, glycine silver nitrate, diglycine manganese chloride, triglycine sulphate, triglycine zinc chloride, as well as triglycine sel. These substances are synthesized by various techniques and have been reported to have

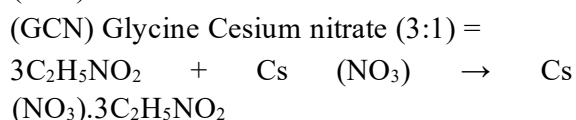
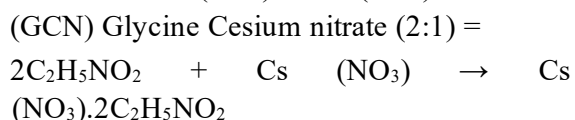
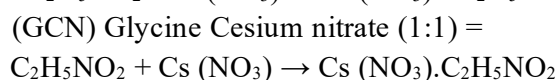
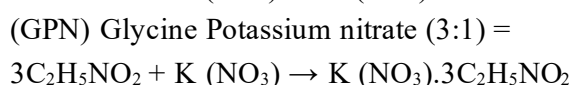
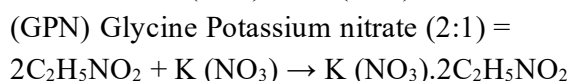
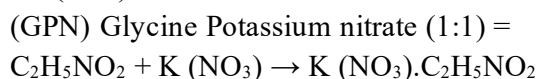
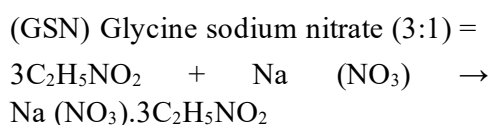
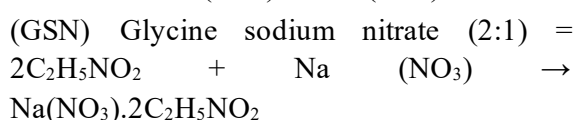
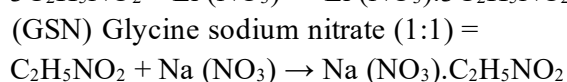
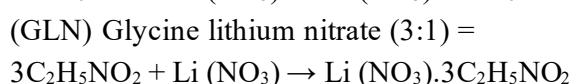
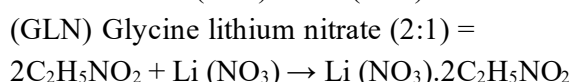
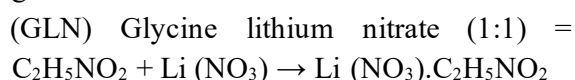
notable nonlinear optical properties (Balasubramanian et al., 2010; Shakir et al., 2009; Dhanaraj et al., 2010; Esthaku Peter & Ramasamy, 2010; Khandpekar & Pati, 2010; Shkir et al., 2014; Khandpekar & Pati, 2011; Pepinsky et al., 1957; Pepinsky et al., 1958; Sinha et al., 2012; Wojciechowski et al., 2010; Vijayakumar et al., 2008; Ozga et al., 2011). To our knowledge, no comparative research has been done on the optical parameters of pure glycine doped alkali metal nitrates by solid state reaction method. Recent studies have analysed key optical parameters, including absorption, bandgap, transmittance, reflectance, refractive index, optical conductivity, and dielectric properties.

Materials and methods

High purity analytical grade glycine ($C_2H_5NO_2$), lithium nitrate ($LiNO_3$), sodium nitrate ($NaNO_3$), potassium nitrate (KNO_3), and cesium nitrate ($CsNO_3$) starting components were weighed in stoichiometric proportions and dried at 80 degrees Celsius for a period of two hours. Then, for six hours, the glycine powders and each of these pure materials $LiNO_3$, $NaNO_3$, KNO_3 , $CsNO_3$ were mixed at various doping equimolar ratios (1:1), (2:1), (3:1) in an acetone medium using an agate mortar and pestle. The combined samples were then calcined at 100 degrees Celsius for a duration of six hours, after which calcined, powder was pressed into pellets without any binder using a hydraulic press. The prepared pellets were sintered at 130 degrees Celsius for twelve hours. After the sintering process was completed, each glycine doped alkali metal nitrate pellet was crushed to a fine powder and then mixed with 20 ml of double-distilled water, that acted as a solvent for the resulting solutions. To ensure equal mixing, the solutions were constantly swirled with the help of a magnetic stirrer for four hours at 50 degrees Celsius. After completing the procedure, the solutions were left uninterrupted at room temperature for 24



hours. During this period, the solutions were preserved from dust and contaminant-free to avoid extraneous particles from influencing the samples. Finally, the optical properties of aqueous solutions of glycine-doped alkali metal nitrate were examined utilizing the UV-VIS-NIR spectrophotometer (Agilent Cary Multicell Peltier) with a wavelength that ranges from 200- 900 *nm*. The reaction taking place in glycine doped alkali metal nitrate given as follows:



Results and discussion

Absorption and absorption coefficient

The process by which a substance absorbs incident light (or other electromagnetic radiation) and turns it into another form,

usually heat. The absorbed light energy is equivalent to the energy required to excite electrons in the material from lower to higher energy states. The amount of light absorbed is determined by the material's qualities, including its atomic structure and the wavelength of the incoming light. nonlinear optical materials are only useful if they have a broad transparency over the wavelength spectrum. The optical absorption spectra of Glycine doped alkali metal nitrates were determined within 200 - 900 *nm* utilizing an UV-VIS-NIR Spectrophotometer [Agilent Cary Multicell Peltier] that covered the entire ultraviolet, visible, and near infrared range. Figure 1 displays the absorption spectrum. The visible range has an extensive transparency window that extends from 400 - 700 *nm*, which is a favourable feature for nonlinear optical materials. A notable identified little protuberance has been found around the 299304 *nm* (Bhat & Dharma Prakash, 2002). Absorption in a nonlinear optical material near the fundamental or second harmonic signal results in a loss of SHG conversion. Because of this characteristic, glycine-doped alkali metal nitrates have potential applications in SHG, in which a ND: YAG laser 1064 *nm* creates a second harmonic signal in the green band 532 *nm* of the electromagnetic spectrum (González-Valenzuela et al., 2009; Mary Linet & Jerome Das, 2012). Absorption spectrum reveals that Glycine Lithium Nitrate (1:1) has the highest absorbance among all glycine doped alkali metal nitrates, while pure glycine has the lowest absorbance. The absorbance decreases in the following order: 1. GLN (1:1) > 2. GLN (2:1) > 3. GSN (1:1) > 4. GLN (3:1) > 5. GPN (1:1) > 6. GSN (2:1) > 7. GPN (2:1) > 8. GSN (3:1) > 9. GCN (1:1) > 10. GPN (3:1) > 11. GCN (2:1) > 12. GCN (3:1) > 13. Pure Glycine.

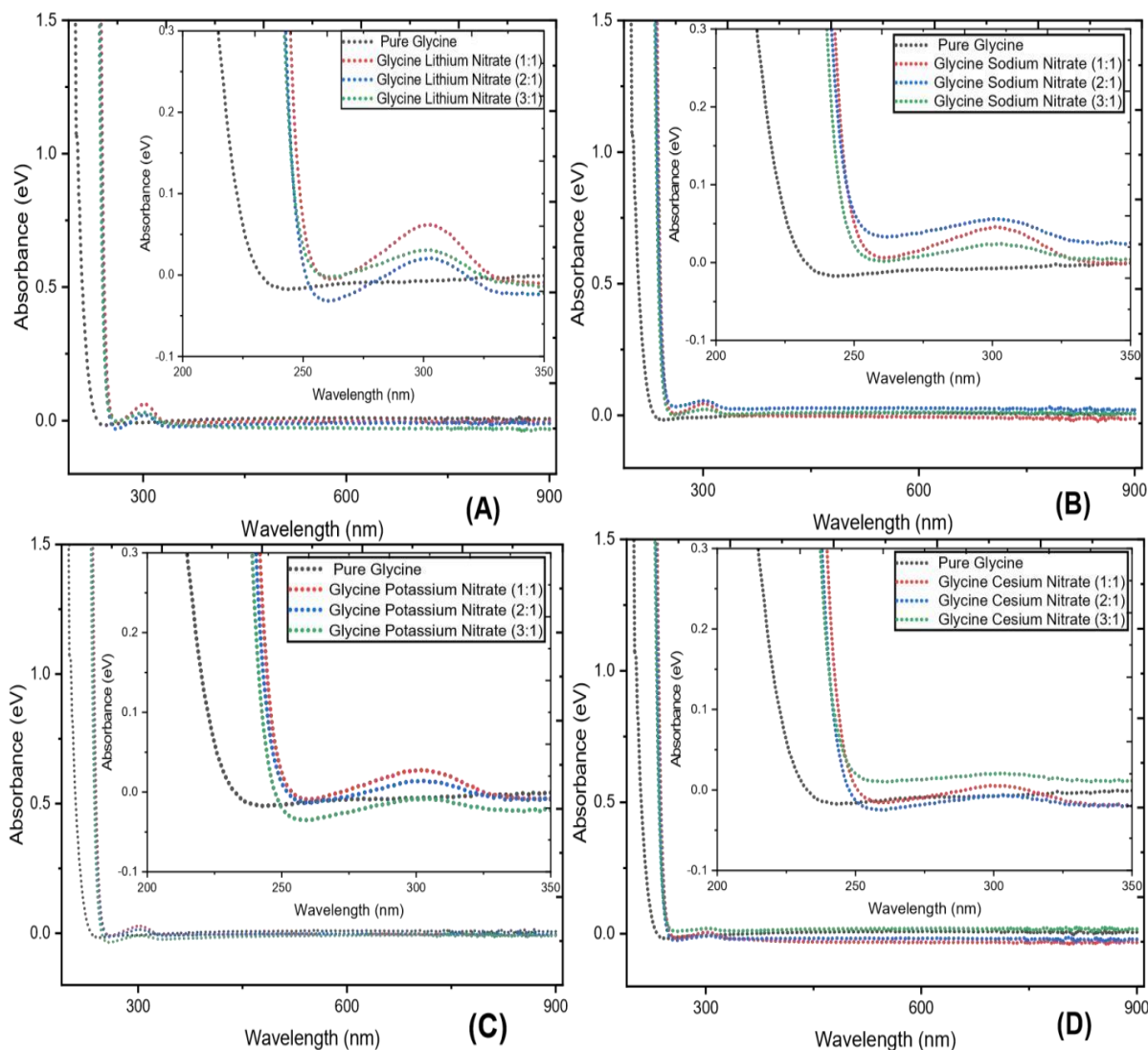


Fig.1 Optical Absorption spectrum of Pure glycine doped Alkali Metal Nitrates:

A- GLN (1:1, 2:1, 3:1), B- GSN (1:1, 2:1, 3:1), C- GPN (1:1, 2:1, 3:1), D-GCN (1:1, 2:1, 3:1)

The absorption coefficient indicates how much light is absorbed per unit length when it passes through a substance. It is determined by the wavelength of the incoming light and the features of the substance, such as its electronic

structure. The value of the absorption coefficient (α), or the power proportion of material absorption, can be used to measure optical absorption (Annapurna Devi et al., 2016).

Formula for absorption coefficient (Gnana Kiran et al., 2020).

$$\alpha = \frac{2.303}{t} \times A \quad (1)$$

Where, A - absorption value, t – width or thickness of sample.

Figure 2 illustrates the absorption coefficient vs photon energy for glycine doped alkali metal nitrates, highlighting small fluctuations up to 5 eV, after which absorption coefficient

rises with increased photon energy. Glycine lithium nitrate (1:1) has the highest absorption coefficient, whereas glycine has the lowest.

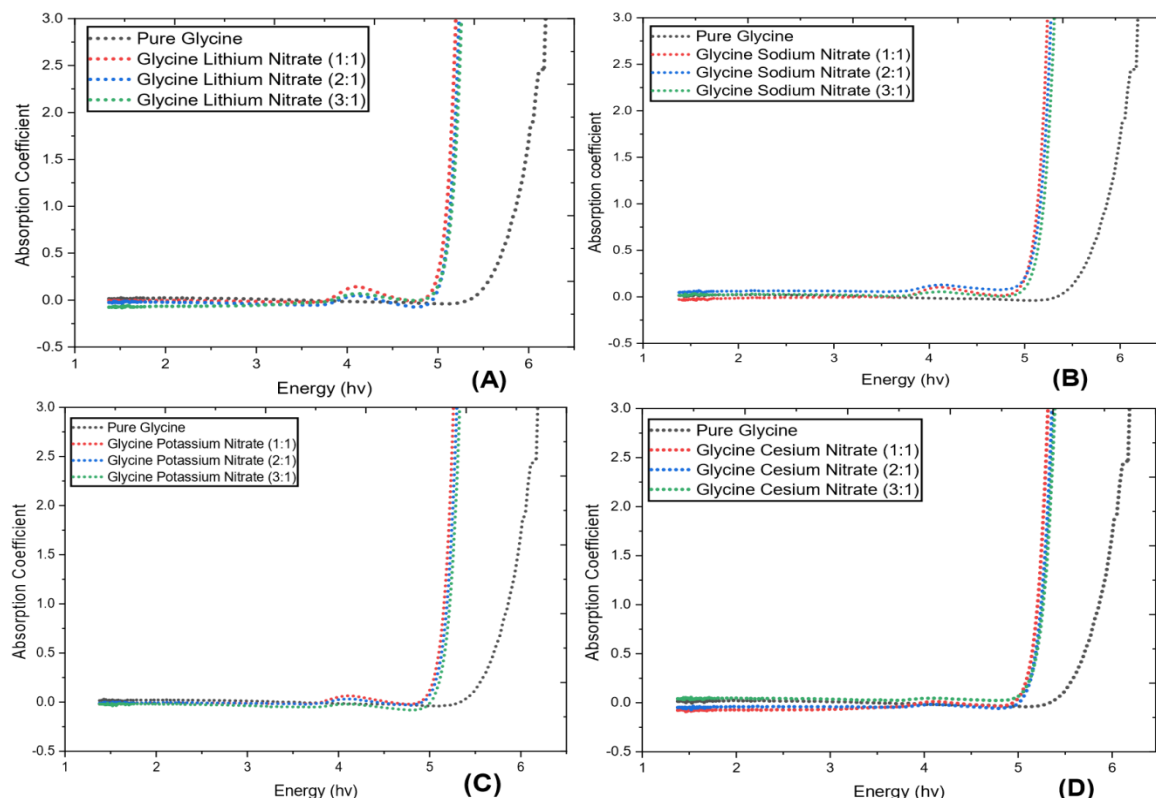


Fig.2 Optical Absorption Coefficient Spectrum of glycine doped Alkali Metal Nitrate:
A- GLN (1:1, 2:1, 3:1), B- GSN (1:1, 2:1, 3:1), C- GPN (1:1, 2:1, 3:1), D - GCN (1:1, 2:1, 3:1)

Optical Band Gap Energy

The bandgap energy of a material is defined as the quantity of energy that exists between the greatest occupied electronic state in the band of valence and the smallest vacant condition in the band of conduction. It specifies if a substance is a conductor, semiconductor, or an insulator.

Formula for Energy Band Gap (Dalal et al., 2014).

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

where, α = Absorption coefficient, h = plank constant, ν = frequency of incident radiation, A = constant, independent of photon energy, E_g - optical band gap. Optical absorption studies reveal the band structure of materials. The bandgap divides semiconductors and insulators into two major categories: direct bandgap energy and indirect bandgap energy (Abdullah & Muhammad, 2010; Bhajantri et al., 2007). the graphs showing that $(\alpha h\nu)^2$ & $(\alpha h\nu)^{1/2}$ Vs $(h\nu)$ were used by Shalliday and Davis to identify the direct and indirect bandgaps at band's fundamental boundary (Shehap, 2008). to examine the variation of $(\alpha h\nu)^2$ vs $h\nu$ was evaluated by extrapolating the linear component from the Tauc's plot (Tauc, 1974). Figure 3 demonstrates the direct bandgap energy of pure glycine is 5.80eV, while glycine-doped alkali metal nitrates ranged from 5.12 to 5.31 eV, indicating shifts in optical bandgap energy. Figures 3 also indicate that glycine lithium nitrate (1:1) has the lowest direct energy bandgap, which suggest that it is very useful for making optoelectronic application (Dalal et al., 2014).

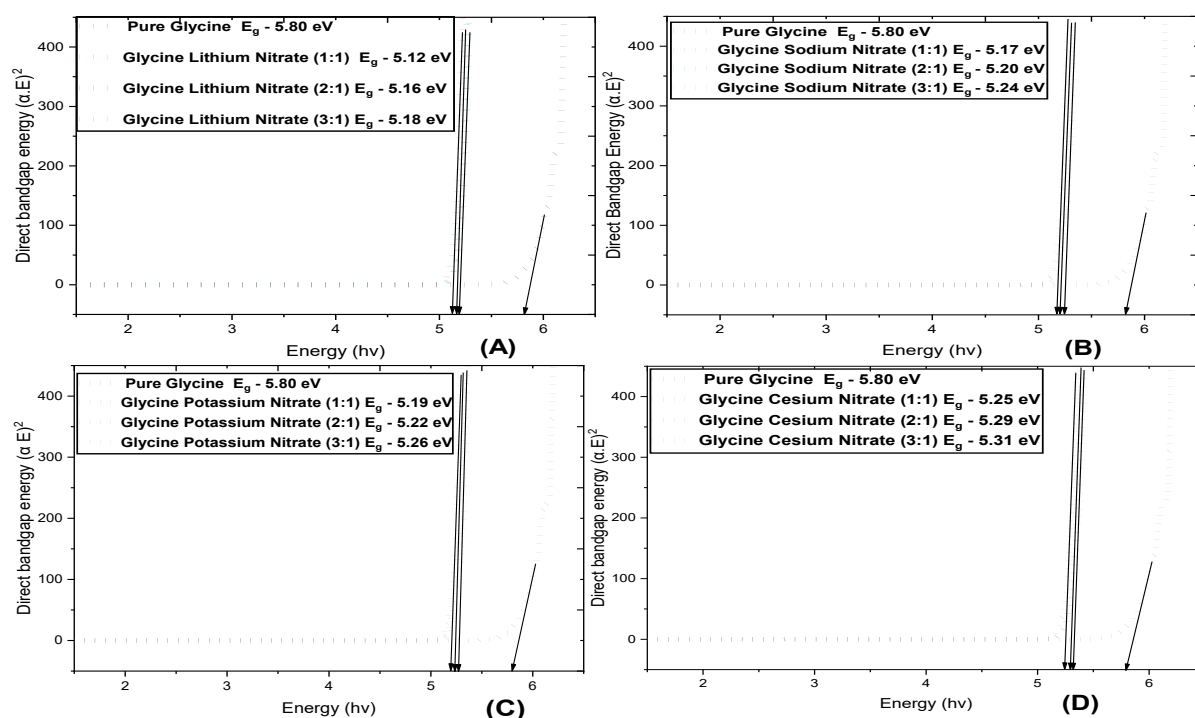


Fig.3 Optical direct bandgap energy Spectrum of glycine doped Alkali Metal Nitrates:
A- GLN (1:1, 2:1, 3:1), B- GSN (1:1, 2:1, 3:1), C- GPN (1:1, 2:1, 3:1), D- GCN (1:1, 2:1, 3:1)
Transmittance

Transmittance is the proportion of incident light that travels through a substance without being absorbed or reflected. It is often stated as a proportion of total incident light. Transmittance might be influenced by the thickness of the substance and optical characteristics. In present study, optical transmittance spectrum over a wavelength that range from 200 - 900 *nm* for glycine doped alkali metal nitrates have been determined utilizing optical absorbance values. transmittance is a combination of two phrases the power of radiant transmission (*P*) by the material being studied and power of radiant incidence (*P*₀) (Gnana Kiran et al., 2020). But, $P = P_0 T$,

$$T = e^{-\alpha t} \quad (3)$$

Where, α - optical absorption coefficient, *t*– thickness of sample

Figure 4 indicates that Glycine has a lower cutoff wavelength at 244 *nm*, while the glycine-doped alkali metal nitrates show a lower cutoff wavelength around 258 to 262 *nm* approximately. A strong absorption band at around 298 - 304 *nm* indicates the *n*- π^* transition (Dalal et al., 2014; Kriger et al., 2013; Anan'ev & Miklin, 2000). The greatest transparency appeared in the 350-900 *nm* wavelength area, while it declined greatly below 350 *nm* due to absorption. The transmittance spectra can be separated into two distinct areas: transparent exhibiting little absorbance in the visible area and intense with significant absorbance in the ultraviolet area when transmission falls extensively because of the coefficient of absorption. Transmission spectra are critical for nonlinear optical materials because a material will only be beneficial if it is transparent throughout the entire spectrum of visible range for appropriate optical applications, the lower cutoff in Ultraviolet and



visible transmittance spectrum should be within 200-400 nm (Sinha.et al., 2012). This glycine-doped alkali metal nitrate has potential for optoelectronic applications and has nonlinear optical features, demonstrated by its excellent transmission in the visible spectrum. all the finding are correlated with reported data (Shkir et al., 2014; Khandpekar & Pati, 2011; Bhat & Dharma Prakash, 2002; González-Valenzuela et al., 2009; Mary Linet & Jerome Das, 2012; Dalal et al., 2014).

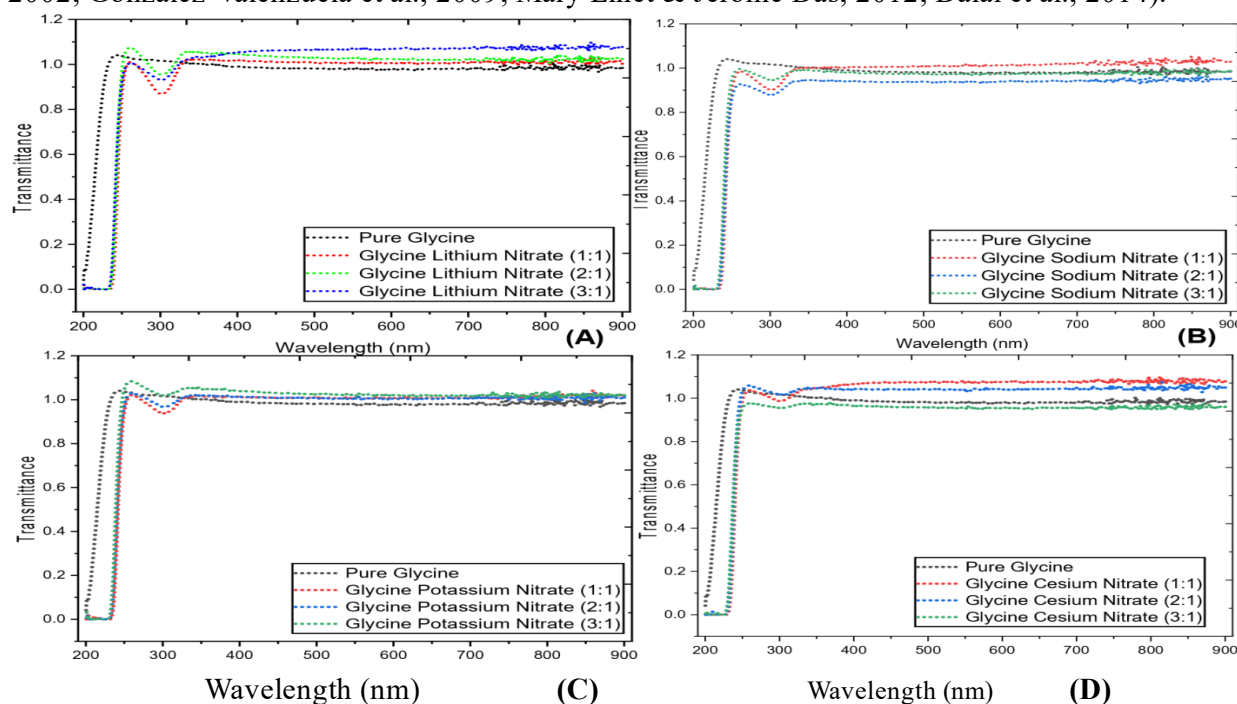


Fig.4 Optical transmittance Spectrum of glycine doped Alkali Metal Nitrates: A- GLN (1:1, 2:1, 3:1), B- GSN (1:1, 2:1, 3:1), C- GPN (1:1, 2:1, 3:1), D- GCN (1:1, 2:1, 3:1).

Reflectance and refractive index

It is the fraction of the incident light that is reflected by a surface or a material. It is a measure of how much light is returned from a boundary rather than transmitted or absorbed. Reflectance depends on factors such as the material's properties (refractive index, surface roughness, etc.) and the angle of incidence of the light. Reflectance also varies with wavelength and polarization of the incident light. Formula for reflectance (Gnana Kiran et al., 2020). $R = 1 - (T + A)$ (4)

Where, T - optical transmittance, A - optical

absorption. The refractive index, is an indicator of the amount that the speed of light decreases within a substance as compared to the speed of light in vacuum. It additionally describes the degree to which light bends or refracts when entering a new medium. optical reflectance is capable of being utilized for determining the index of refraction as well as other optical parameters. The optical constant of a material can be determined by utilizing its optical properties, such as the coefficient of extinction and refractive index the refractive index, atomic structure, electrical



properties, and electronic band structure are all related to specific optoelectronics technologies (Abdullah & Saber, 2012). optical reflectance is used to compute the optical refractive index (Gnana Kiran et al., 2020).

$$R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \quad (5)$$

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \quad (6)$$

Where, R - optical reflectance, K - coefficient of extinction, n - refractive index. Figure 5 and 6 suggest that glycine lithium nitrate (1:1) has the highest reflectance and refractive index among all glycine doped alkali metal nitrates. This conclusion implies that these materials are appropriate for the development of nonlinear optical technologies.

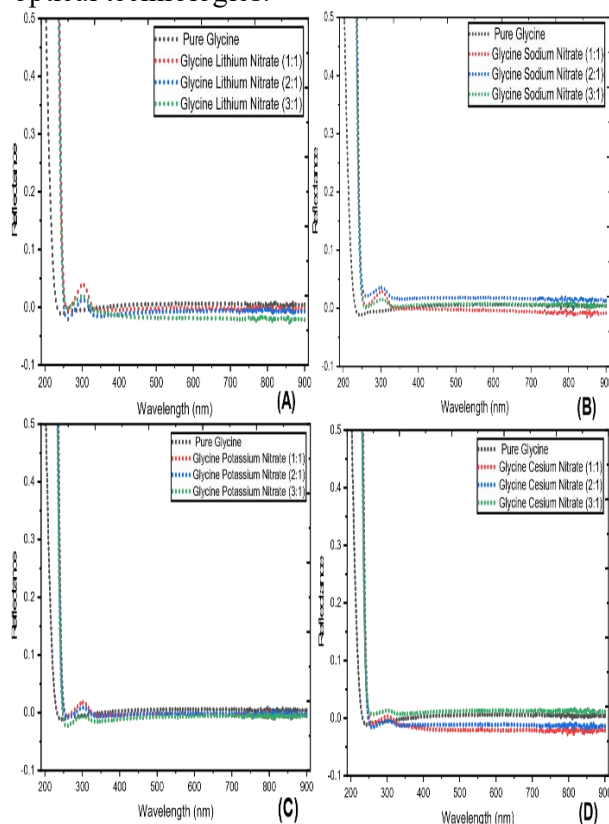


Fig.5 Optical reflectance Spectrum of glycine doped Alkali Metal Nitrates: A- GLN (1:1, 2:1, 3:1), B- GSN (1:1, 2:1, 3:1), C- GPN (1:1, 2:1, 3:1), D- GCN (1:1, 2:1, 3:1).

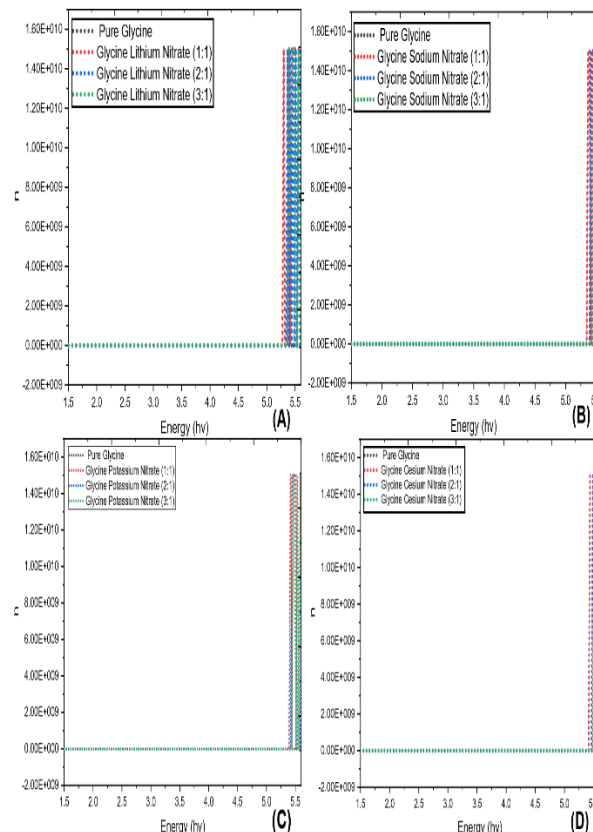


Fig.6 Optical reflective index Spectrum of glycine doped Alkali Metal Nitrates: A- GLN (1:1, 2:1, 3:1), B- GSN (1:1, 2:1, 3:1), C- GPN (1:1, 2:1, 3:1), D- GCN (1:1, 2:1, 3:1)

Optical conductivity

Optical conductivity characterizes a material's capacity for carrying electrical current when it is exposed to electromagnetic radiation. It is commonly utilized in semiconductors and light-responsive materials. As a result, the conductance increases as the photon energy value does. The orientation and polarization of the particles result in optical absorption and transmission. refractive index is modified through modifying the relative orientation of the particles. Finally, these factors influence the substance's conductivity. optical conductance quantity has been determined



utilizing the measurement of the refractive index, absorption coefficient, velocity of light as it passes through the material being studied. Formula for optical conductivity (Gnana Kiran et al., 2020).

$$\sigma = \frac{\alpha n c}{4\pi} \quad (7)$$

Where, α - absorption coefficient, n - refractive index, and c - speed of light. Figure 7 represents optical conductivity vs photon energy for glycine doped alkali metal nitrates, with small fluctuations up to 5 eV, followed by increases with higher photon energy. Glycine Lithium nitrate (1:1) has the highest optical conductivity.

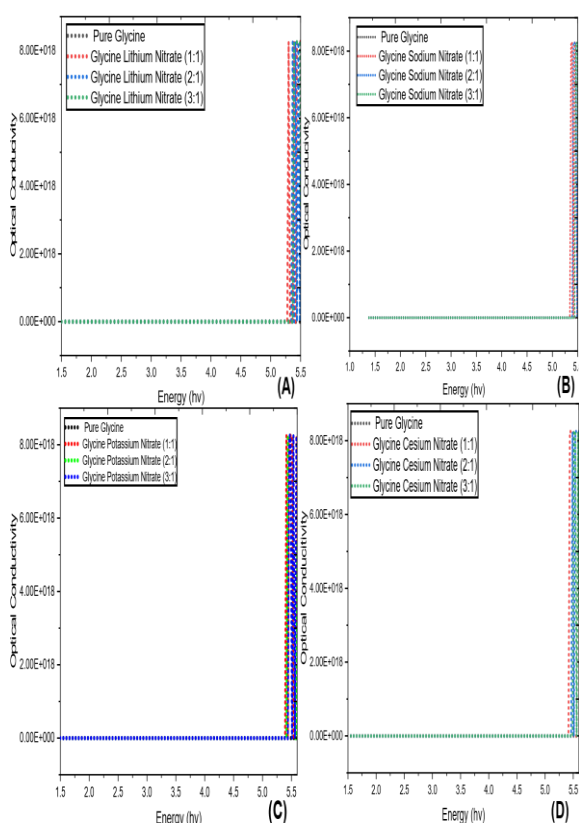


Fig.7 Optical conductivity Spectrum of glycine doped Alkali Metal Nitrates:
A- GLN (1:1, 2:1, 3:1), B- GSN (1:1, 2:1, 3:1),
C- GPN (1:1, 2:1, 3:1), D- GCN (1:1, 2:1, 3:1)

Extinction Coefficient (K)

The coefficient of extinction tells us about the amount of light is absorbed and scattered in a substance. It denotes the imaginary component of the complex refractive index and represents the material's loss of intensity of light. The extinction coefficient has been defined as the imaginary component of the optical refractive index. The fluctuation of the excitation coefficient via wavelength demonstrates the interaction between medium and photon energy. Coefficient of extinction refers to the small percentage of electromagnetic energy that is destroyed. Optical absorption influences the extinction coefficient. The extinction coefficient gets higher through raising the wavelength.

Formula for excitation coefficient (Gnana Kiran et al., 2020).

$$K = \frac{\alpha \lambda}{4\pi} \quad (8)$$

where, λ - wavelength, α - absorption coefficient.

Figure 8 plots extinction coefficient with photon energy for glycine doped alkali metal nitrates, clearly exhibiting minimal fluctuations up to 5 eV after which it increases with increased photon energy. Glycine lithium nitrate (1:1) have highest extinction coefficient which is photon or wavelength dependent. Since the wavelength significantly impacts a device's internal effectiveness, modifying the wavelength permits the development of optoelectronic devices.

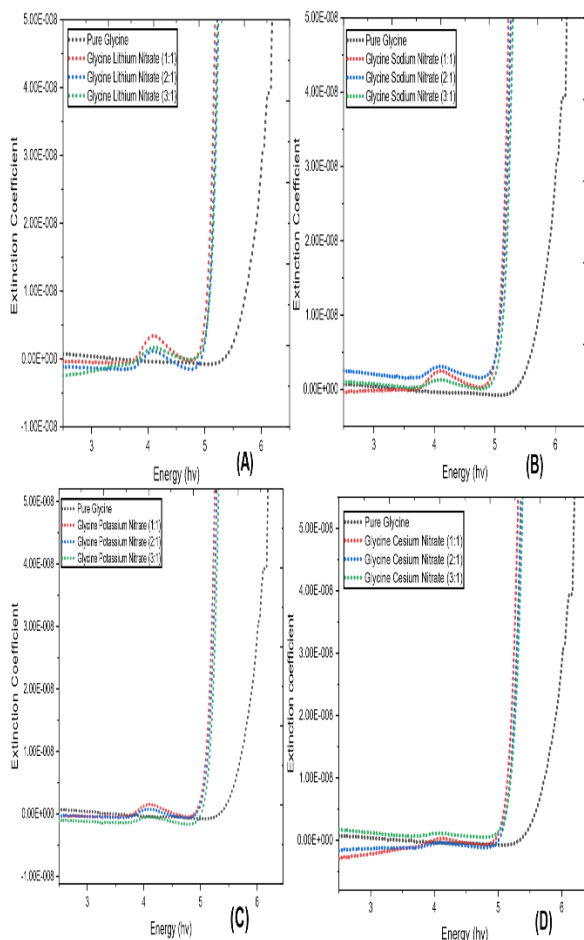


Fig.8 Optical Extinction Coefficient Spectrum of glycine doped Alkali Metal Nitrates: A- GLN (1:1, 2:1, 3:1), B- GSN (1:1, 2:1, 3:1), C- GPN (1:1, 2:1, 3:1), D- GCN (1:1, 2:1, 3:1).

Optical Density

Optical density quantifies how much light gets diminished when it passes through a material. Optical density (OD) is a measurement of light's distortion as it passes through a substance. It measures how much light the substance absorbs, hence diminishing its intensity. Formula for optical density $OD = at$ (9)

Where, a - absorption coefficient, t - thickness of sample. Optical density is often used to describe optical filters, glasses, and other materials that reduce light transmission.

Figure 9 depicts the optical density against wavelength for glycine doped alkali metal nitrates, clearly showing increases with increased wavelength. The optical density of glycine lithium nitrate (1:1) is the highest.

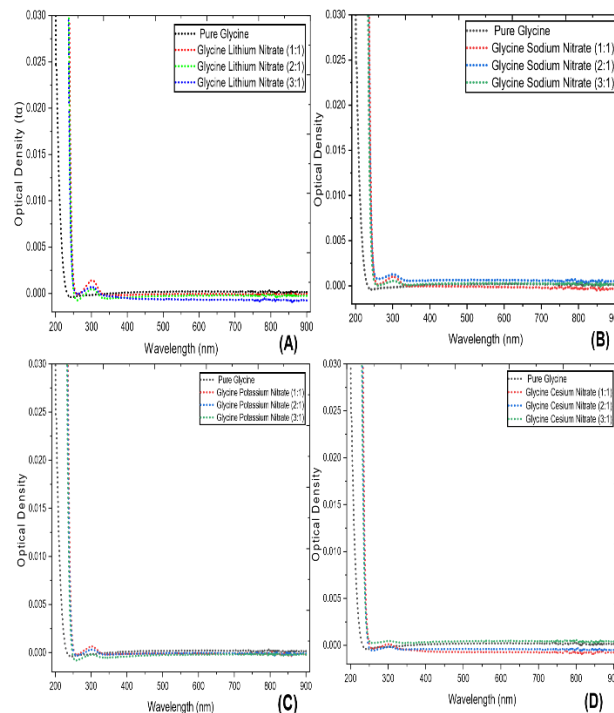


Fig. 9 Optical Density Spectrum of Glycine Doped Alkali Metal Nitrates: A- GLN (1:1, 2:1, 3:1), B- GSN (1:1, 2:1, 3:1), C- GPN (1:1, 2:1, 3:1), D- GCN (1:1, 2:1, 3:1)

Real part (ϵ_r) & Imaginary part (ϵ_i) of dielectric constant

Real part of the dielectric constant, written as ϵ_r , measures a material's polarization in the interaction to an electric field. It refers to the material's ability to store electrical energy. The real part of the dielectric constant impacts the speed of light within the substance being studied. Formula for Real Part of Dielectric Constant (Muhammad et al., 2015).

$$\epsilon_r = n^2 - k^2 \quad (10)$$

Where, n - refractive index, k - extinction coefficient.



Imaginary part of the dielectric constant (ϵ_i) indicates energy dissipation in the substance, corresponding to absorption. The imaginary component demonstrates how much of the electromagnetic wave is transformed to heat or other forms of energy as it travels through the substance being used. Formula for Imaginary Part of Dielectric Constant (Muhammad et al., 2015).

$$\epsilon_i = 2nk \quad (11)$$

where, n - refractive index, k - extinction coefficient. Figures 10 and 11 illustrate the real and imaginary parts of the dielectric constant vs photon energy for glycine doped alkali metal nitrates, exhibiting small fluctuations up to 5 eV and then increasing with increased photon energy. Glycine Lithium nitrate (1:1) has the largest real and imaginary parts of the dielectric constant.

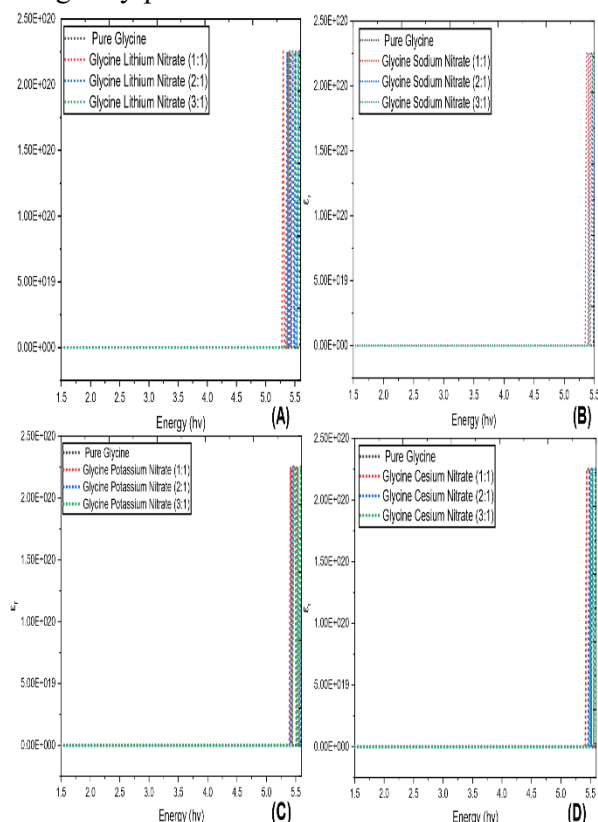


Fig.10 Real part of Dielectric Constant Spectrum of glycine doped Alkali Metal Nitrates: A- GLN (1:1,2:1,3:1),B- GSN (1:1, 2:1,3:1),C- GPN (1:1,2:1,3:1),D- GCN(1:1, 2:1, 3:1

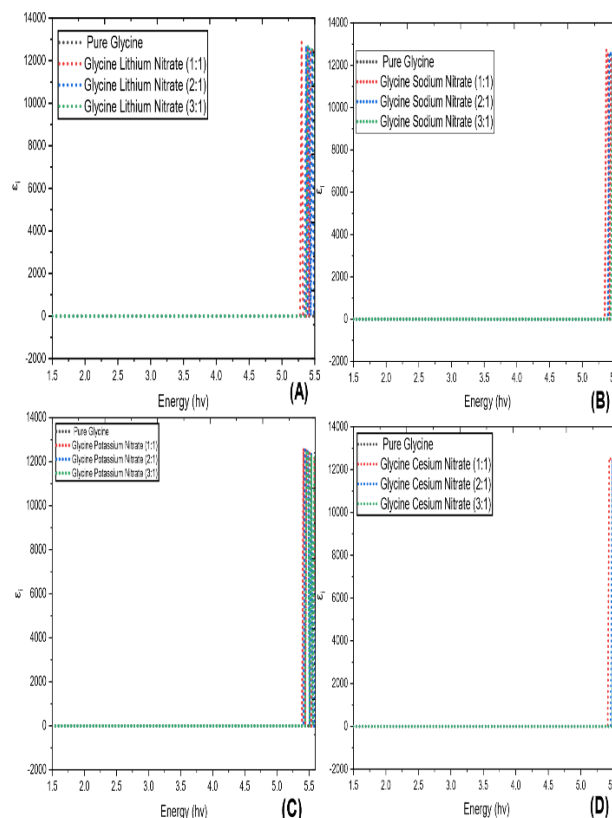


Fig.11 Imaginary Part of Dielectric Constant Spectrum of glycine doped Alkali Metal Nitrates: A- GLN (1:1, 2:1, 3:1),B- GSN (1:1, 2:1,3:1),C- GPN (1:1,2:1,3:1),D- GCN(1:1, 2:1, 3:1).

Conclusion

In conclusion, the study revealed that pure glycine-doped alkali metal nitrates exhibit promising optical properties, including significant absorption in the UV region, a wide bandgap (5.12 eV to 5.31 eV), and high transparency in the visible range. The analysis of their absorbance, transmittance, reflectance spectra, as well as their absorption coefficient,



refractive index, optical conductivity, extinction coefficient, optical density, dielectric parameters, suggests that these materials are highly suitable for optoelectronic and nonlinear optical applications. Based on the overall findings, we conclude that among all, glycine lithium nitrate (1:1) has the highest absorbance, wide bandgap, and Other optical parameters also suggest that it is highly suitable for the development of advanced device fabrication, particularly in optoelectronic and nonlinear optical applications.

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