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Optical and Dielectric Properties of Glycine Fumarate NLO Single Crystal.

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Abstract: Single crystals of the Glycine Fumarate (GFA) were from the aqueous solution by slow evaporation method at room temperature. Single crystal X ray diffraction analysis reveals that the crystal belongs to orthorhombic crystal system. Optical transmission studies show that the crystal is transparent in the entire visible region with cut off wave length 252 nm .The optical band gap is found to be 3.872 eV. Mechanical hardness studies carried out to find the Hardness number of the grown crystal and it is increase with increase in applied load. Mayer index number was calculated for the grown up crystal and found that the materials belongs to the soft material category. Dielectric constant and the dielectric loss of material were calculated by using dielectric analysis at the room temperature. Further, electrical properties, such as Plasma energy, Penn energy, Fermi energy and electronic polarizability of the growth crystals have been predicated. The optical second harmonic generation conversion efficiency of GFA was determined by Kuntz powder technique and it shows that the material is the potential candidate for the NLO applications and its efficiency found to be 0.2 times that of KDP.
Keywords: Slow evaporation, X- ray diffraction, Optical transmission, Dielectric test, NLO.

Introduction

Investigations on the growth for good quality single crystals plays an important role in the development of modern scientific world with advanced technology. Behind the development in every solid state device and the explosion in solid state device, there stands a single crystal. NLO development provides the key function of conversion, telecommunication, optical switching, signal processing, parametric light generation, optical data storage, high speed telecommunications and terahertz wave generation and detection and Photonics[1-9] Among the NLO materials, Organic materials have another advantage over inorganic materials, in that they are associated with large optical property compared with the inorganic analogues due to their larger optical susceptibilities, high optical threshold for laser power, low frequency dispersion and large optical coefficient[10-13]. Amino acids and their complexes belong to a family of organic materials have been considered for the photonic applications. Complex of amino acid with organic salts are promising materials for optical SHG as they tend to combine the advantages of organic salt. Amino acid have the Zwitterionic nature due to the presence of proton donor carboxyl acid (-COO) group and the proton acceptor amino (NH_2) group in them[14]. Glycine is the simplest amino acid which has three polymeric crystalline forms α, β, γ. There are two types of glycine group such as glycinium ions and zwitter ion. The Zwitterionic nature of the glycine useful for its optical activity[15-16].

In the present study, GFA were grown and hence the attempts were made to characterize the grown crystals by single crystals XRD, UV-Vis-NIR absorption study , dielectric, Micro hardness, SHG studies. Some of the optical properties like Band gap determination, Extinction Coefficient, Reflectance, Refractive index of the grown crystals were calculated. Electronic properties such as Valance electrons Plasma energy, Penn energy, Fermi energy and electronic polarizability are calculated for the grown crystals.

Experimental Procedure

Single crystals of GFA was crystallized form the aqueous solution of Glycine (CAS no 56406,Merck, AR) and Fumaric acid (Sigma Alrich, AR CAS no 24461323) in the ratio 1:1. The stoichiomertic amounts of the reactants were dissolved in the deionised water and stirred well for about 12 hours. The equipped solution was filtered using Whatman filter paper (Cat no. 1001-042). The solution were taken in a glass beaker and tightly closed with aluminium foil and kept in dust free compartment. The induction period for nucleation is 3-4 days the solvent was allowed to evaporate. Deionised was used as a solvent for the repeated recrystallization and optically transparent single crystal were harvested after 30 days.

Result and Discussion

Powder X ray Analaysis

The X ray diffraction study on grown crystal was used to confirm the quality and identification of cell parameter. It is found that the cell parameter are a = 14.858 Å, b = 9.480Å, c = 8.044 Å, $\alpha = \beta = \gamma = 90.00°$, and volume V = 1132.832 A^3. From the lattice parameter is it clear that the grown crystal was belongs to orthorhombic system with Centro symmetric space group $P2_12_12_1$

Density measurement

The density of GFA crystal was calculated using the equation,

$$\rho = \frac{MZ}{N\,\mathrm{abc}(\sin[\beta])} \quad (1)$$

Where, M is molecular weight of GFA and it is found to be 191.136 Kg, Total Number of atoms per unit cell Z = 4, N is Avogadro's number and a, b and c are the lattice parameters of GFA crystal. The theoretical density is found to be 1.121 g/cm^3.

UV-Vis-NIR spectroscopy analysis

Optical transmittance and the transparency cut off of the grown crystal are the important parameters of the optical application. The UV-Vis-NIR spectrum of GFA crystal has been recorded in the range between 190 to 1100 nm using Perkin-Elmer Lambda 35 UV-Vis-NIR spectrometer and is shown in Figure 1. It is seen from the transmission spectrum evident that the crystal has a transparency window from 250 nm to 1100 nm making it suitable for applications in the whole region, which is an advantage and is a desirous property of the material for NLO applications [17]. The UV absorption edge for the grown crystal was found to be 252 nm is due to the $n \rightarrow \pi^*$ transition.

The absorption coefficient α which depends on the wave length λ , can be obtained by using the following relation. When scattering effects are neglected, the absorption coefficient may be expresses by

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (2)$$

Where, A is a constant nearly independent of photon energy, h be the Planck's constant, γ be the frequency of the incident photons and E_g is the optical band gap. The band gap of the GFA crystal is found to be 3.872 eV are found from the Tauc Plot in the Figure2. Extinction coefficient can be obtained from the following formula

$$K = \frac{\lambda\alpha}{4\pi} \quad (3)$$

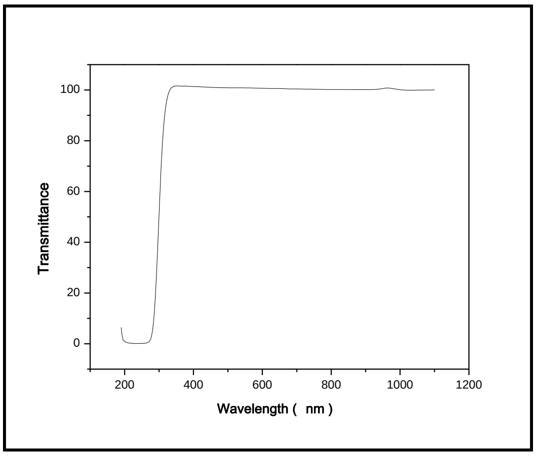

Fig.1 Optical Transmittance spectra of GFA.

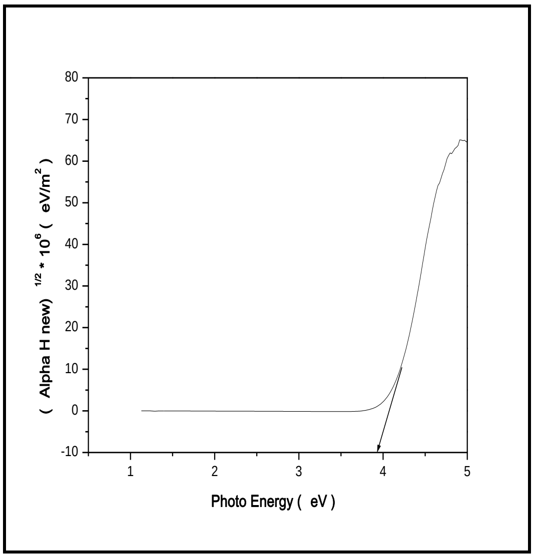

Fig.2. Tauc plot curve for GFA

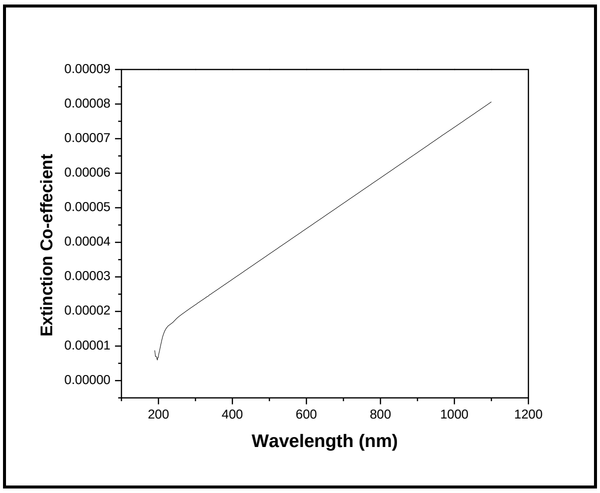

Fig.3. Extinction Coefficient Vs Wavelength curve for GFA.

Dielectric Test Analysis

The dielectric characterization studies used analysis the lattice dynamics of the GFA crystal and it were carried out at various frequencies and temperatures using HIOKI 3532-50 LCR HITESTER instrument. The cut and polished single crystal of 5 mm thickness was selected as the sample for studying dielectric constant. The sample having silver coating on the opposite faces was placed between the two copper electrodes to form a parallel plate capacitor .the crystal was heated at thermostat itself. Multi frequency LCR meter was used to measure the capacitance (C) and the dissipation factor (D) as the sample as the function of frequency. The dielectric constant and dielectric loss was calculation by the following relations,

Dielectric constant

$$\varepsilon = \frac{cd}{A\varepsilon_0} \qquad (4)$$

and

Dielectric loss

$$\tan\delta = D\varepsilon \qquad (5)$$

Where, C is the capacitance of the sample, d is the thickness of the sample, A be the area of the face in contact with the electrode and ε_∞ is the permittivity of free space

Dielectric constant and Dielectric loss measurements were carried out with the sample as the function of temperature for the function of frequencies from100 MHz to 5 Mhz. Figures 6 and 7 represent the graph of dielectric constant and dielectric loss respectively. From the graph it is observed that dielectric constant is maximum at the lower frequency since all microscopic polarizations (electronic, ionic, orientation and space charge polarization) occur at lower frequency. Dielectric loss was found to increase with the increase of temperature. Because of the inertia of the molecules and ions, the dipolar and ionic contributions are small at high frequencies. Hence the dielectric constant increases with the decrease of frequencies. These curves suggest that the dielectric loss strongly depends on the frequency of the applied field, similar to the dielectric constant in the ionic system [18-19]. The results are evident that the sample was good optical quality with lesser defect [20].

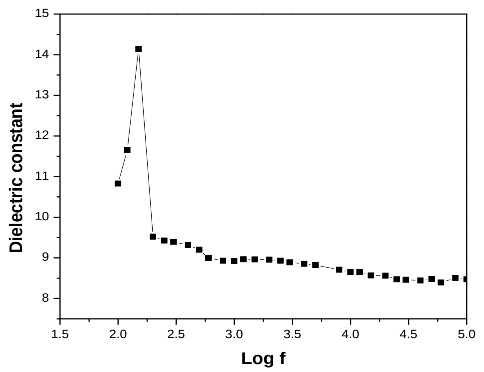

Fig.4. Dielectric constant Vs Log f curve for GFA

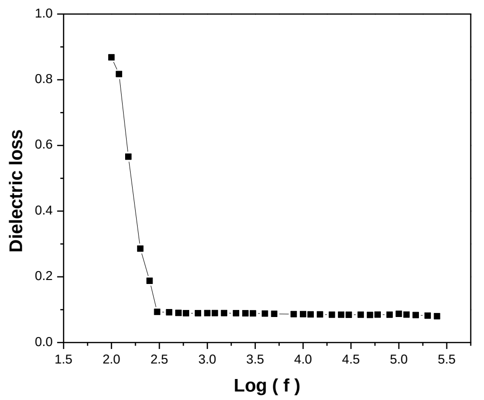

Fig.5. Dielectric loss Vs Log f Curve for GFA.

The theoretical calculations shows that the high frequency dielectric constant is clearly dependent on the free electrons Plasma energy an average energy gap referred to as the Penn energy and the Fermi energy. The Penn gap is determined by fitting the dielectric constant with the Plasmon energy [21].

The valance electron plasma energy $\hbar\omega_P$ is calculated using the relation

$$\hbar\omega_P = 28.8\left(\frac{Z\rho}{M}\right)^{1/2} \quad (6)$$

$$E_P = \frac{\hbar\omega_P}{(\varepsilon_\infty - 1)^{1/2}} \quad (7)$$

Plasma energy are the Penn energy and Fermi energy [21] given by

$$E_F = 0.2948(\hbar\omega_P)^{4/3} \quad (8)$$

Then we obtained electronic polarizability α using the relation [22-23]

$$\alpha = \left[\frac{(\hbar\omega_P)^2 S_0}{(\hbar\omega_P)^2 S_0 + 3E_P^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^3 \quad (9)$$

Where S_0 is constant given by

$$S_0 = 1 - \left[\frac{E_P}{4E_F}\right] + \frac{1}{3}\left[\frac{E_P}{4E_F}\right]^2 \quad (10)$$

The value of α obtained from the previous equation closely matches with that the Clausius – Mossotti relation.

$$\alpha = \frac{3}{4}\frac{M}{\pi N_a \rho}\left[\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right] \quad (11)$$

Table .1 Electronic Properties of GFA single crystal.

S.No	Parameters	Values
1	Plasma energy ($\hbar\omega_p$)	18.973 eV
2	Penn Energy (E_p)	6.701 eV
3	Fermi Energy (E_F)	14.772 eV
4	Electronic Polarizability (Penn analysis)	5.409 × 10^{-23} cm^3
5	Electronic Polarizability (using Clausius –Mossotti relation)	5.442 × 10^{-23} cm^3

Micro Hardness studies

Vickers microhardness test was carried out GFA crystal using microhardness tester fitted with a diamond indenter. The indentations were made using a Vickers pyramidal indenter for loads 25 *g*, 50 *g* and 100 *g*. The diagonals of the impressions were measured using Shimadzu; Model HMV-2T hardness instrument. Vickers microhardness number (Hv) was evaluated from the relation

$$H_V = 1.8544 P / d^2 kg / mm^2 \quad (12)$$

Where P is the applied load in *g* and d is the diagonal length of the impression in mm. The variation of microhardness values with applied load is shown in Figure 6. From the Vicker's microhardness studies, the hardness value is found to increase with the applied load and the cracks start at 100g. Work hardening coefficient n, a measure of the strength of the crystal, is computed from the log P-log d plot and it is found to be 2.66 are as in Figure 7. Hence the GFA crystal comes under the soft materials category.

Yield strength can also be calculated using the relation

$$\sigma y = (Hv / 3) \times (0.1)^{n-2} \quad (13)$$

Where, σy is the yield strength, Hv is the hardness of the material and n is the logarithmic exponent. According to the relation, the yield strength is found to be 6.344 MPa and hence the grown GFA crystal has relatively low mechanical strength.

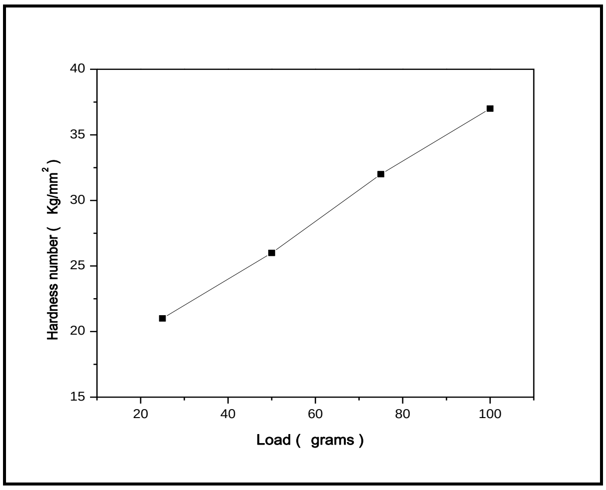

Fig.6. Mechanical Hardness curve for GFA

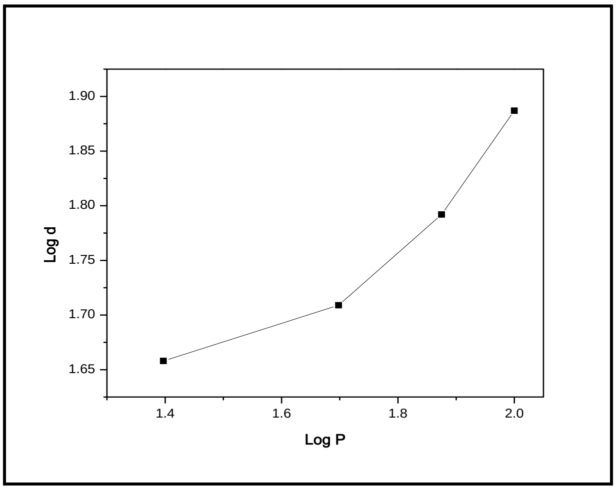

Fig.7. Log P Vs Log d curve for GFA

Second Harmonic Generation

The SHG intensity of the grown crystal was tested using the Kurtz and Perry method [24]. A high intensity Nd:YAG laser (λ = 1064 nm) with a pulse duration of 8 ns was allowed to pass through the powdered sample in a capillary tube. The SHG behaviour was confirmed from the output of the laser beam having the bright green emission (λ = 532 nm). The powder SHG efficiency of GFA crystal shows about 0.2 times that of KDP crystal. This nearly zero SHG efficiency shows that the crystal is centro symmetric as the reported value eralier[25].

Conclusion

Single crystals of GFA were synthesized and subjected to the single crystal XRD, optical and dielectric studies. From the X ray diffraction, it was confirmed that the crystal belongs to orthorhombic structure with space group $P2_12_12_1$. The optical transmittance of the crystal confirms the transparency of the crystal. The band gap energy value (3.872 eV) predicated from the UV studies confirms the dielectric behaviour of the crystal. Dielectric measurement was carried to analyse the dielectric constant and the dielectric loss at room temperature. Some electrical properties like plasma energy, Penn gap, Fermi energy and dielectric polarizability of the crystal have been calculated. The mechanical behaviour is studied by Vicker's hardness test. From the test, it is observed that the Hardness number increases with increase in load and the value of the Mayer index number (n) was calculated as 2.66 and the material belongs to soft material. The SHG efficiency tested by the Nd:YAG laser as source and GFA could be the promising NLO material.

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