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GROWTH AND CHARACTERISATION OF GLYCINUM OXALATE SINGLE CRYSTALS FOR NONLINEAR OPTICAL APPLICATIONS

4.1 INTRODUCTION

In recent years, one has witnessed increasing interest in the study of amino acids and their derivative crystals. This interest has been stimulated by the perspective of understanding a system where the hydrogen bonding plays a fundamental role and, as a result of this understanding, a better knowledge of some important biological molecules can be achieved. Amino acid crystals usually display large nonlinear optical (NLO) response and are potential candidates for applications in the emerging areas of photonics [1]. Molecules that show asymmetric polarization induced by electron donor and acceptor groups are responsible for electro optic and NLO properties [2].

Glycine (NH₂CH₂COOH amino acetic acid) is the simplest amino acid, which is hydrophilic polar in nature. It is the only protein-forming amino acid without a center of chirality. Glycine helps to trigger the release of oxygen to the energy requiring cell-making process. It is necessary for the manufacture of hormones in the human biological system that builds a strong immune system [3]. Glycine exhibits polymorphism. It grows in many forms; such as the stable α form and γ- form (optically active showing SHG) and the unstable β- form [4]. The single crystals of γ-glycine and α-glycine may be obtained by slow cooling of aqueous solution of glycine [3, 4]. The crystal of α- form is metastable in aqueous solution and it transforms into γ-form spontaneously [5]. While glycine can exist as a neutral molecule in the gas phase, it exists as zwitterions in solution and in the solid
4.2.2 CHN analysis

The chemical composition of the grown GLO crystal determined by carbon, hydrogen, nitrogen (CHN) analysis using VarioEL III CHNS serial number 11035060 is compared with the theoretical values of carbon, hydrogen and nitrogen present in the crystal and is shown in Table 4.1. From the results, the composition of the material is established as $C_4H_7NO_6$.

Table 4.1. CHN analysis data.

<table>
<thead>
<tr>
<th>Element</th>
<th>Theoretical composition (%)</th>
<th>Measured composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>29.07</td>
<td>28.72</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.24</td>
<td>4.42</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>8.48</td>
<td>8.50</td>
</tr>
</tbody>
</table>

4.2.3 X-ray powder diffraction studies

The powder X-ray diffractogram of the GLO crystal shown in Fig. 4.2 is registered with Bruker D8 advance diffractometer operated at 40 KV and 50mA, using Cu target and graphite monochromator. The intensity data is recorded by continuous scan from 5° to 60° with a step size of 0.02° and scan speed of 4°/minute. The structure, refined by Pawley method [7] using the TOPAZ R version 3 program is given in table 4.2, which agrees well with the reported values [6].
4.2.4 UV/Vis/NIR spectrum and evaluation of linear optical constants

The UV/Vis/NIR spectrum plays a vital role in identifying the potential of a NLO material because a given NLO material can be of utility only if it has a wide transparency window without any absorption at the fundamental and second harmonic wavelengths [8]. The UV-Vis-NIR spectrum of the sample in the range
200nm-2500nm is recorded with Hitachi U3140 UV-VIS-NIR spectrophotometer and is shown in Fig. 4.3. It is evident that the crystal has a transparency window from 324nm to 2500 nm making it suitable for applications in the whole region for higher harmonic generation. The absence of absorption of light in the visible region is an intrinsic property of all the amino acids [9].

![Absorbance vs Wavelength](image)

**Fig 4.3 UV/VIS/NIR Spectrum of GLO**

The absorption coefficient $\alpha$ which depends on the wavelength $\lambda$ can be obtained by using the following relation. When scattering effects are neglected, the absorption coefficient may be expressed by

$$\alpha \nu = A (\alpha \nu - E_g)^n$$

where $A$ is a constant nearly independent of photon energy and $E_g$ is the optical band gap. For the indirect allowed transitions $n = 2$, but, for the direct allowed transitions $n = 0.5$ [10]. The plot of $(\alpha \nu)^2$ versus $h\nu$ for the GLO crystal is shown in fig(4.4). The X-axis intercept of the plot will give the band gap energy. The band gap of GLO crystal is found to be 3.9 eV.
The optical constants such as refractive index \( n \) and the extinction coefficient \( k \) and the absorption coefficient \( \alpha \) are determined from the transmission \( T \) and reflection \( R \) spectrum based on the following relations [11, 12].

\[
T = \frac{(1-R)^2 \exp(-at)}{1-R \exp(-at)}
\]

(4.1)

where \( t \) is the thickness and the absorption coefficient \( \alpha \) is related to extinction coefficient \( k \) (absorption index) by

\[
K = \alpha \lambda / 4\pi
\]

(4.2)

For semiconductors and insulators (where \( k^2 \ll n^2 \)) there exists a relationship between \( R \) and \( n \) (refractive index) given by [13, 14]

\[
R = \frac{(n - 1)^2}{(n + 1)^2}
\]

(4.3)

The relationship between \( \varepsilon \) and \( k \) is given by [15] \( \varepsilon = \varepsilon_r + i\varepsilon_i = (n + ik)^2 \)

(4.4)

The real part \( \varepsilon_r \) and imaginary part \( \varepsilon_i \) of the dielectric constant is given by

\[
\varepsilon_r = n^2 - k^2
\]

(4.5)

\[
\varepsilon_i = 2nk
\]

(4.6)
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Growth and characterisation of glycineium oxalate single crystals for nonlinear optical applications

The variation of refractive index, extinction coefficient and dielectric constant with energy in the range 1-6 ev is shown in figures 4.5, 4.6 and 4.7 respectively. The linear optical constants evaluated using the present study are utilised for the determination of the nonlinear optical constants of the crystal.

Fig. 4.5 Plot of variation of n with energy

Fig. 4.6 plot of variation of k with energy
4.2.5 FTIR and FT Raman spectral analysis

The FTIR spectrum of the grown crystals, recorded in the wave number range from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) using Thermo-Nicolate Avatar 370 system is shown in figure (4.8). The FT Raman spectrum of the powdered sample (Fig. 4.9) is recorded with BRUKER RFS100/S system with a resolution of 4 cm\(^{-1}\) using a standard InGaAs detector with a laser source of 150 mW with a resolution of 4 cm\(^{-1}\) in the range 400-4000 cm\(^{-1}\).

The vibrational analysis of glycinium oxalate is performed on the basis of vibrations of the glycinium ion consisting of amino, methylene, carboxylic groups and the oxalate ion and is given in table 4.3.

For saturated amines, it is established that the asymmetric NH\(_2\) stretch will give rise to a band between 3380 and 3350 cm\(^{-1}\), while the symmetric stretch will appear between 3310 and 3280 cm\(^{-1}\) [16]. But the protonation of NH\(_2\) group can produce a shift in band position towards the range 3300-3100 cm\(^{-1}\) for
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asymmetric stretch and 3100–3000 cm\(^{-1}\) for symmetric stretch as appeared in glycine derivatives [17, 18]. Further, the \(\text{NH}_3^+\) stretching bands are broader and weaker in IR than those arising from the uncharged \(\text{NH}_2\) groups [19, 20]. The infrared spectrum shows a very broad intense band observed at 3224 cm\(^{-1}\) corresponding to \(\text{NH}_3^+\) asymmetric stretching mode. The position and broadness of this band clearly indicate the presence of \(\text{NH}_3^+\) group in the crystal. Thus, the protonation of the amino group can be inferred from the vibrational spectra. The \(\text{NH}_3^+\) symmetric stretching frequencies are overlapping with vibrations of \(\text{CH}_2\) group.

The \(\text{NH}_3^+\) asymmetric and symmetric deformation modes appear in the regions 1625–1560 cm\(^{-1}\) and 1550–1505 cm\(^{-1}\) respectively [21]. The strong bands at around 1623 cm\(^{-1}\) and band at 1593 cm\(^{-1}\) in IR and corresponding Raman bands at 1621 cm\(^{-1}\) and at 1595 cm\(^{-1}\), are assigned to the parallel and perpendicular asymmetric \(\text{NH}_3^+\) deformation modes, respectively [17]. The \(\text{NH}_3^+\) symmetric deformation mode occurs in the IR spectrum as a very strong band at 1507 cm\(^{-1}\). The corresponding Raman bands of \(\text{NH}_3^-\) are also observed in the same region. The \(\text{NH}_3^+\) rocking modes occur at frequencies around 1100 cm\(^{-1}\) for glycine and its derivatives and exact band position depends, on the position and strength of the hydrogen bond [22]. The IR bands at around 1090 and at 964 cm\(^{-1}\) and the corresponding Raman bands at around 1099 and at 962 cm\(^{-1}\) are assigned to parallel and perpendicular \(\text{NH}_3^+\) rocking modes, respectively [17]. The medium intense band in IR at 480 cm\(^{-1}\) is assigned to the \(\text{NH}_3^+\) torsion mode.

For amino acids, the asymmetric \(\text{CH}_2\) stretching vibrations are generally observed in the region 3100–3000 cm\(^{-1}\), while the symmetric stretch will appear between 3000 and 2900 cm\(^{-1}\) [24-26]. The \(\text{CH}_2\) asymmetric vibrations are observed as strong band in Raman spectrum at 3033 cm\(^{-1}\) and medium shoulder in IR at 3032 cm\(^{-1}\). The symmetric stretching also observed as an intense sharp band in Raman at 2975 cm\(^{-1}\) and medium intense shoulder in IR at 2979 cm\(^{-1}\). The bands
corresponding to scissoring, wagging and rocking vibrations of CH$_2$ appear at 1433, 1322 and 1042 cm$^{-1}$ in the IR spectrum. The frequencies at 1434, 1321 and 1039 cm$^{-1}$ in Raman spectrum are assigned to CH$_2$ scissoring, wagging and rocking modes, respectively, which are supported by the results reported on glycine derivatives [26-29].

The Carbonyl stretching vibrations are found in the region 1780–1700 cm$^{-1}$ [16, 21]. The sharp intense band in IR spectrum at 1713 cm$^{-1}$ can be assigned to C=O stretching vibration, which is also observed in Raman at 1710 cm$^{-1}$ as a strong band. The COO bending, wagging and rocking vibrations are observed as intense bands in the IR spectrum in the expected regions [24] at 712, 579 and 519 cm$^{-1}$, respectively. The less intense Raman band arising from bending is also found at 707 cm$^{-1}$. This mode has been assigned to the COO wagging mode in literature [23-26]. The absorption bands arising from C–N and C–C stretching vibrations are usually observed in the region 1150–850 cm$^{-1}$ [21]. The C–C stretching is observed as an intense band at 864 cm$^{-1}$ in IR spectrum and the corresponding Raman band at 873 cm$^{-1}$. It is assigned that the NH$_3$ rocking, CH$_2$ rocking and C–C stretching modes overlap to give the most intense band observed at 897 cm$^{-1}$ in IR and at 893 cm$^{-1}$ in Raman, respectively. Earlier reports [22, 23–26] have given this mode as C–C stretching. However, deuterated studies [30] have indicated that this band has undergone shift on deuteration of NH$_3$ group. Hence it is reasonable to assume that the vibrational interaction involving NH$_3$ rocking, CH$_2$ rocking and C–C is responsible for the most intense Raman band at 893 cm$^{-1}$ and not the pure C–C stretching as reported in literature.

The stretching vibration of the hydroxyl group of oxalate appears as a very weak shoulder in IR at 3589 cm$^{-1}$. The hydroxyl bending mode at 1370 cm$^{-1}$ in Raman and 1371 cm$^{-1}$ in IR arises due to the O–H bending of carboxylic group of oxalates while, the weak band at 1412 cm$^{-1}$ in Raman spectrum corresponds to the O–H bending of glycinium.
The present study highlights the presence of NH$_3^+$ ion in the crystal confirming protonation of the amino acid group leading to the formation of glycinium oxalate molecule. Noncentrosymmetry is one of the decisive criterion for a material to be NLO active, particularly SHG active. For a noncentrosymmetric material, there exists an exact match between the infrared and Raman wave numbers. In the vibrational spectra of GLO, there is excellent matching between vibrational bands of the infrared and Raman spectra. The result of the XRD analysis also reveals that the material is noncentrosymmetric. Thus the NLO activity of GLO crystal is confirmed from the vibrational spectrum.

Fig. 4.8 FTIR spectrum of GLO crystal
Fig. 4.9 FT Raman spectrum of GLO crystal
<table>
<thead>
<tr>
<th>IR band Positions (cm(^{-1}))</th>
<th>Raman band Positions (cm(^{-1}))</th>
<th>Assignment of vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>481</td>
<td></td>
<td>NH(_3) torsion mode.</td>
</tr>
<tr>
<td>518</td>
<td></td>
<td>COO rocking mode.</td>
</tr>
<tr>
<td>582</td>
<td>590</td>
<td>COO wagging mode/CH(_2) out of plane bend</td>
</tr>
<tr>
<td>670</td>
<td>672</td>
<td>COO out of plane bending</td>
</tr>
<tr>
<td>708</td>
<td>707</td>
<td>COO in plane bending mode.</td>
</tr>
<tr>
<td>869</td>
<td>873</td>
<td>C-C stretching mode.</td>
</tr>
<tr>
<td>901</td>
<td></td>
<td>NH(_3) rocking/CH(_2) rocking in</td>
</tr>
<tr>
<td>972</td>
<td>962</td>
<td>NH(_3) rocking</td>
</tr>
<tr>
<td>1015</td>
<td></td>
<td>O-H-O stretching mode.</td>
</tr>
<tr>
<td>1037</td>
<td>1039</td>
<td>CH(_2) rocking out vibration.</td>
</tr>
<tr>
<td>1098</td>
<td>1099</td>
<td>II NH(_3) rocking mode.</td>
</tr>
<tr>
<td>1118</td>
<td></td>
<td>C-N stretching mode</td>
</tr>
<tr>
<td>1231</td>
<td>1223</td>
<td>C-O stretch/O-H in plane bend</td>
</tr>
<tr>
<td>1322</td>
<td>1321</td>
<td>CH(_2) wagging vibration.</td>
</tr>
<tr>
<td>1429</td>
<td>1434</td>
<td>CH(_2) bending deformation.</td>
</tr>
<tr>
<td>1509</td>
<td></td>
<td>NH(_3) symmetric stretching mode.</td>
</tr>
<tr>
<td>1594</td>
<td>1595</td>
<td>NH(_3) assymmetric deformation</td>
</tr>
<tr>
<td>1716</td>
<td>1710</td>
<td>C=O stretching mode.</td>
</tr>
<tr>
<td>1922</td>
<td></td>
<td>C-C overtone</td>
</tr>
<tr>
<td>2873</td>
<td>2873</td>
<td>O-H stretching</td>
</tr>
<tr>
<td>2974</td>
<td>2975</td>
<td>CH(_2) symmetric stretching mode.</td>
</tr>
<tr>
<td>3033</td>
<td>3033</td>
<td>CH(_2) assymmetric vibration</td>
</tr>
<tr>
<td>3229</td>
<td></td>
<td>NH(_3) assymmetric stretching mode.</td>
</tr>
</tbody>
</table>

Table 4.3 Vibrational assignments
4.2.6 THERMAL ANALYSIS

The thermal properties of the GLO crystal are studied using thermo gravimetric analysis (TGA) / differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Powdered sample of 6.945 mg glycimum oxalate is analyzed in N2 atmosphere by using Perkin Elmer Diamond TGA / DTA equipment. The analysis is carried out simultaneously in air at a heating rate of 10°C / min for a temperature range of 28°C to 810°C. The TGA/DTA curve is shown in Fig. 4.10. Quite interesting and important point to be noticed is the very good thermal stability of the material up to 190°C. The absence of water of crystallization in the molecular structure is indicated by the absence of weight loss around 100°C. The endothermic peak in the DTA curve at 179°C represents the melting point of the sample. Another important observation is that there is no phase transition till the material melts and this aspect enhances the temperature range for the utility of the crystal for NLO applications. Further there is no decomposition up to the melting point. This ensures the suitability of the material for possible applications in lasers, where the crystals are required to withstand high temperatures. After 190°C, there is decomposition, illustrated by the loss of mass in the temperature range 190°C to 240°C. In this region the gaseous fragments like carbon dioxide and ammonia might be liberated.

![Fig.4.10 TGA/DTA curve of GLO crystal](image-url)
The specific heat at constant pressure $C_P$ of the crystal is estimated from the DSC curve using the ratio method [31]. In this method, base line corresponding to the temperature range of interest is first obtained. After this, two independent DSC runs are performed under identical conditions; one with weighed quantity ($m'$) of $\alpha$-$\text{Al}_2\text{O}_3$ and the other with a weighed quantity ($m$) of the sample. Then the specific heat $C_P$ of the sample can be determined by using the relation

$$\frac{C_P}{C_P'} = \frac{m'y}{my'}$$

(4.7)

where $C_P'$ is the specific heat of $\alpha$-$\text{Al}_2\text{O}_3$, $y$ and $y'$ are the ordinate deflections of the sample and reference standard respectively. Figure 4.11 depicts the DSC runs performed for the baseline, reference standard and the sample under the same heating conditions and figure 4.12 gives the variation of specific heat of the sample within the temperature range of interest.

![DSC thermogram](image-url)

Fig. 4.11 DSC thermogram
DSC run performed on the sample reveals that there is no phase transition up to its melting point and it agrees well with the TGA/DTA analysis reported earlier [32]. It is found that $C_p$ increases linearly in the temperature region of interest. The specific heat value of GLO crystal at 333 K is 898 J/kg K. Due to its relatively large $C_p$, GLO crystal needs a larger quantity of heat energy to get heated up, so that consequent damage due to localized heating can be avoided, which enhances its prospects for applications in laser assisted devices.

### 4.2.7 Vickers’ microhardness

Microhardness measurement on the (010) surface of the crystal was done for applied loads ($P$) from 5 gms to 100 gms with a dwell time of 5 seconds using Leitz Miniload Hardness tester and the average indentation diagonal length ($d$) is measured. Figure (4.13) illustrates the Vicker’s micro hardness profile [33] of the crystal calculated using the formula

$$H_v = 1.8544 \frac{P}{d^2} \text{ Kg/mm}^2$$

(4.8)
Fig. 4.13. Plot of Vickers hardness number vs. load.

Fig. 4.14. Plot of log P vs. log d.
Increase in microhardness with increase of load in the low load region can be attributed to the heaping up of material at the edges of impression made by the indentor due to the slipping of layers [34]. At higher loads, slipping of layers stops which in turn hardens the crystal. Since crack initiation and material chipping become significant beyond 50 g of the applied load, hardness test could not be carried out above this load. Elastic stiffness constant $C_{11}$ for various loads, which gives an idea about the tightness of bonding between neighboring atoms, is calculated using Wooster's empirical formula [35] and is given in table 4.4.

$$C_{11} = (H_v)^{7/4}$$ \hspace{1cm} (4.9)

<table>
<thead>
<tr>
<th>Load(gm)</th>
<th>Hv (kg/mm$^2$)</th>
<th>$C_{11}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>24</td>
<td>1.1466</td>
</tr>
<tr>
<td>10</td>
<td>28</td>
<td>3.373</td>
</tr>
<tr>
<td>15</td>
<td>33</td>
<td>10.65</td>
</tr>
<tr>
<td>25</td>
<td>42</td>
<td>57.63</td>
</tr>
<tr>
<td>50</td>
<td>59</td>
<td>62.21</td>
</tr>
</tbody>
</table>

Table 4.4 Variation of $C_{11}$ with load.

The slope of the Mayers' plot of log $P$ versus log $d$ shown in figure 4.14 yields the Mayers' index number 'n' which in the present case is found to be equal to 3.3. According to Onitsch [36] and Hanneman [37] 'n' should lie between 1 and 1.6 for hard materials and above 1.6 for softer ones. Hence GLO belongs to softer material category. According to Hays and Kendall's theory of resistance pressure [38], there is a minimum level of indentation load ($W$) also known as resistance pressure below which no plastic deformation occurs. $W$ can be found out by drawing a graph between $d^0$ and $d^2$ which yields a straight line as shown in figure 4.15 according to the equation

$$d^0 = w/k_1 + (k_2/ k_1) d^2$$ \hspace{1cm} (4.10)

Where $k_1$ and $k_2$ are material constants. The value of $W$ is calculated as 19.2 gm.
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Vickers microhardness study on solution grown GLO crystals reveals that the Vickers hardness number Hv increases with increase in load and the sample belongs to soft material category as Meyer's index number 'n' is greater than 1.6. From Hey and Kendall's theory of resistance pressure, the minimum load that induces plastic deformation in GLO crystal is 19.2 gm which shows that the mechanical property of the crystal is quite good. The stiffness constant $C_{11}$ is quite high, revealing that the binding forces between the ions are quite strong.

4.2.8 Chemical etching studies

Good optical quality crystals free from defects are used for microtopographical studies using Leica Q Win Systems metallurgical microscope to check the presence of features like spirals, hillocks, slip lines......etc as they yield considerable information about the growth mechanism [39,44]. We have observed two dimensional growth layers of small step height on the free surface of almost all the crystals (Fig.4.16.a). Patterns like spirals, striations, slip bands, etc. are absent in the present study. The transmission photomicrograph of the inclusions present in the crystal is shown in Fig.4.16.b. A variety of parameters such as non-uniform growth rates, variation in super saturation during growth due to transition from dissolution to
growth are responsible for these types of patterns. Kitamura et al. [40] pointed out that liquid inclusions getting trapped parallel to the interfaces are due to drastic changes in growth conditions. GLO crystals show sharp cleavage on (010) plane, which shows river patterns and rivulets.

Chemical etching studies are carried out on the as grown and cleaved GLO crystals to study the symmetry of the crystal face from the shape of pits and the distribution of structural defects. First, the crystal is completely immersed in the etchant and then cleaned and dried and the etch figures are observed in the reflection mode. A mixture of n-propyl alcohol and distilled water is used as chemical polishing agent. Fig.4.16.c shows the pyramidal hillock with a circle at the middle portion formed by etching with dilute propionic acid. When the surface dissolution is low, the surface is smooth and the increased dissolution at dislocations can lead to terracing [41,45]. A composition of water in acetone in the ratio 1:5 volume is found to produce triangular etch pattern on the (010) surface when etched for 5-10 seconds is shown in Fig.4.16.d. When etched with water, fast dissolution layers are formed and are shown in figure 4.16.e. When etched with a mixture of acetic acid, methanol and distilled water circular etch pits are formed Fig.4.16.f. On successive etching no spurious development of pits is observed which suggests that etch pits are produced at the emergence of dislocation. It was found that propionic acid (50%) and formic acid (60%) and sulphuric acid in the volume ratio 8: 1:1 produces etch pits with their sides parallel to [010] and [110] directions(fig.4.16.g). The shape of etch pits reflects the slow dissolution rate along the directions parallel to the sides of the pits [42, 43]. Thus the dissolution rate along a [110] direction is faster than that along a [010] direction as seen from the structure of etch pits produced by this etchant. A hackle like pattern observed on the figure upon cleavage is shown in fig. 4.16.h. When the grown crystal is taken out from the solution and dried quickly, tree like structures are formed (fig.4.16.i). These dendrites are due to fast evaporation, which cause uneven growth resulting into the formation of dendrites. An indentation fracture pattern is represented by the photomicrograph 4.16.j. Slip bands and fracture lines are clearly visible in the figure. Following interesting features are noteworthy regarding the pattern observed in dynamic indentation. It can be seen that there are four prominent cracks forming a shape of letter 'V' on two opposite sides of the indentation mark
occupied by the regions of twin bands; whereas, on two other sides there are, no such prominent cracks. The cracks observed in the regions devoid of twin bands are quite short, less prominent in appearance and frequently curved as is seen in the photograph. The cracks forming the ‘V’ shape also run mostly along the terminations of the twin bands indicating the way in which the crack nucleate and propagates.
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4.2.9 Microwave dielectric studies

Very little is known about the microwave absorption characteristics of NLO organic crystals. An understanding of the dielectric properties of the nonlinear optical GLO crystal is essential as far as device applications at various frequency ranges are concerned. Hence in the present work, the dielectric parameters of the GLO single crystals are investigated at S band microwave frequency using the resonant cavity perturbation method [46, 47].

The cavity is made from a S-band wave-guide with both ends closed. The length of the resonator cavity determines the number of resonant frequencies. The resonator is excited in the TE_{10p} mode. The resonant frequency ‘f₀’ and the corresponding quality factor ‘Q₀’ of each resonant peak of the cavity resonator, without sample placed at the maximum of the electric field, are noted. The
sample is introduced into the cavity resonator through the non-radiating slot. The resonant frequencies of the sample loaded cavity are selected and the position of the sample is adjusted for maximum perturbation (that is, maximum shift of resonant frequency with minimum amplitude for the peak). The new resonant frequency $f_s$ and quality factor $Q_s$ are determined. The procedure is repeated for other resonant frequencies. The frequency dependence of effective conductivity, dielectric constant and dielectric loss and absorption coefficient are plotted in figure 4.17.

From the figure it is clear that variation of dielectric constant with increase in microwave frequency in the S band is negligible. Dielectric loss is very negligible throughout the S band. The very low value of dielectric loss is an indication of the better crystallinity of the crystals formed [48]. Samples with low dielectric loss are needed for device applications. Conductivity is also very small indicating that sample is an insulator to microwaves in the frequency range 2-3 GHz. It is found that absorption coefficient increases slightly with frequency. The exact dielectric behaviour of the material throughout the entire microwave frequency is to be found out.

Fig. 4.17 Frequency dependence of the various dielectric parameters
4.2.10 Photoluminescence studies

Photo-luminescence spectrum (PL) is recorded with a Jobin Yvon Spectrofluorometer (Model FL3-22). A 450 W xenon lamp is used as the source and PMT (Model R928P) as the detector. Double gratings are used for the excitation and emission spectrometers. Excitation wavelength used is 260 nm. PL spectrum of GLO crystal recorded is shown in figure 4.18.

![PL spectrum of GLO](image)

Fig. 4.18 PL spectrum of GLO

The main contribution to the HOMO state comes from the mono ionised oxalate ions, while to the LUMO state comes from the NH$_3^+$ ions. In GLO molecular chains, these two molecular orbitals are at opposite extrema. So, in the interband transitions, the electron has to cross the whole chain, loosing energy to the vibrational modes of the crystal, contributing to the luminescence. Peaks in the visible region can be assigned to lattice related processes, while the peaks in the UV region can be due to the relaxation of excited molecular states. The maximum intensity peak at 470nm is assigned to a lattice related process. The intense PL emission observed at 470nm is significant from the view point of application of this material as bio compatible capping agents for nano particles in bio medical imaging and targeted drug delivery applications [49].
4.2.11 SHG in GLO crystal

The second harmonic generation behaviour of the powdered material is tested using Kurtz and Perry method [50]. A high-intensity Q switched Nd: YAG laser ($\lambda = 1064$ nm) with pulse duration of 7 ns and frequency repetition of 10 Hz is passed through the sample. The SHG behaviour is confirmed from the output of the laser beam having the bright green emission ($\lambda = 532$ nm) from the specimen. The second harmonic signal of 110 mV was obtained for an input energy of 3.0 mJ/pulse, while the standard KDP give a SHG signal of 120 mV for the same input energy. The second order nonlinear efficiency will vary with the particle size of the powder sample [51]. It has been found that vacancies influence the nonlinear optical properties of organic crystals, particularly the SHG [52].

It has been generally understood that the second-order molecular nonlinearity can be enhanced by systems with strong donor and acceptor groups [53,54]. Since a large molecular hyperpolarizability $\gamma$ is the basis of a strong second harmonic generation (SHG) response, organic molecules that usually exhibit large $\gamma$ values are certainly candidate molecules for NLO applications.

Table. 4.5 gives a comparison of the second harmonic generation in the GLO crystal with KDP crystal for different laser inputs.

<table>
<thead>
<tr>
<th>Laser input</th>
<th>KDP</th>
<th>GLO crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0 mJ</td>
<td>120mV</td>
<td>110mV</td>
</tr>
<tr>
<td>5.0 mJ</td>
<td>211mV</td>
<td>198mV</td>
</tr>
</tbody>
</table>

4.2.12 Laser damage threshold studies

One of the decisive criteria for a NLO crystal to perform as a device is its resistance to laser damage, since high optical intensities are involved in nonlinear processes [55].
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The laser damage threshold measurement is made on cleaved GLO single crystal (010) surface using a Q-switched Nd: YAG laser for 7 ns laser pulses operating in (TEM_{00}) mode at a wavelength of 1064 nm. The output intensity of the laser is controlled with a variable attenuator and delivered to the test sample located at the near focus of the converging lens. The lens with a focal length of 10 cm is used, which is useful in setting the spot size to the desired value according to the equation.

\[ d' = 2.4 \frac{f \lambda}{d} \]  \hspace{1cm} (4.11)

where \( d' \) is the diffraction limited beam diameter, \( f \) is the focal length of the lens at which the sample is placed, and \( d \) is the beam diameter at the output aperture of the laser.

The sample is mounted on a holder which is used to position the different sites in the beam. Single and multiple laser damage measurements are made on the cleaved face of the grown crystal. In the present study, the laser damage threshold energy density for the single shot is found to be 15.5 GW/cm² and that for the multiple shot is found to occur at laser power of 11.5 GW/cm². The laser damage threshold value is lower when the crystal is subjected to multiple shots. It reveals the fact that single shot damage threshold is higher than multiple shot damage. Figure 4.19 (a) and (b) depicts the laser damage pattern observed on the (010) crystal surface for single shot and multiple shot. Striation pattern of unequal width observed on the surface is depicted in figure 4.19 (c); the cause of which can be attributed to be of thermal origin. Since GLO has a room temperature specific heat of 898 J kg⁻¹ K⁻¹, one can expect a high threshold value for laser damage and that is what we have observed in our investigation. Apart from the thermal effect, multiphoton ionization is an important cause of laser-induced damage [56]. For the pulse widths of several nanoseconds, the thermal effects are unavoidable, while for the picosecond pulse widths, the thermal effects are negligible. This is because the thermal effects take several nanoseconds to buildup and could take several milliseconds to decay [57]. The observed damage threshold value is greater than that of other known NLO organic single crystals [58-60].
There is considerable interest in finding materials having large yet fast nonlinearities. This interest is driven primarily by the search for materials for all-optical switching and sensor protection applications, which concerns both nonlinear absorption (NLA) and nonlinear refraction (NLR).

The Z-scan technique is a method which can measure both NLA and NLR in solids, particularly in liquids and liquid solutions [61, 62], and has gained rapid acceptance as a standard technique for separately determining the nonlinear changes in index of refraction and changes in absorption. This acceptance is primarily due to the simplicity of the technique as well as the simplicity of the interpretation. The index change, $\Delta n$, and absorption change, $\Delta \alpha$ can be determined directly from the data without resorting to fitting.

Fig.4.19 (a) single shot damage (b) multiphoton damage (c) Thermal striation pattern

4.2.13 Z Scan measurement of the optical nonlinearity
In a typical z-scan experimental setup, a laser beam with a Gaussian profile is initially focused by a lens. The sample is then moved along the axial direction of the focused beam in such a way that it moves away from the lens, passing through the focal point. At the focal point the sample experiences the maximum pump intensity, which will progressively decrease in either direction of motion from the focus. If a light detector is placed in the far field and the transmitted intensity is measured as a function of the position of the sample, one obtains an "open aperture" z-scan curve, the shape of which will reveal the presence of any absorptive nonlinearity in the sample. On the other hand, if a properly chosen aperture is placed in front of the detector, a "closed aperture" z-scan curve is obtained which will reflect the occurrence of refractive nonlinearities.

The laser used is 532 nm, 7ns pulses from the second harmonic output of a hybrid mode-locked Nd: YAG laser operating at 10 Hz repetition rate. The crystal is fixed on a microprocessor controlled translation stage that has a range of 30 cm and a resolution of 2 microns, so that it can be accurately moved through the focal region of the laser beam. A fast photodiode monitors the input laser energy, and a large area photodiode collects the transmitted beam. For the closed aperture measurements, a suitable aperture is placed in front of the photo diode. Data acquisition is facilitated in real time by the use of a PC.

In the open aperture z scan, the open aperture transmission normalized to the linear transmission of the sample is plotted against the sample position measured relative to the beam focus is shown in figure 4.20. Nonlinear absorption in the present study is indicated by a smooth valley-shaped curve, symmetric about the focal (z=0) position. The RSA coefficient $\beta$ (m/W) can be obtained from a best fitting performed on the experimental data of the OA measurement with the equations (4.12) and (4.13)[70] where $\alpha$ and $\beta$ are the linear and effective third order NLO absorption coefficients, respectively, $\tau$ is the time, $I(z)$ is the irradiance and $L$ is the optical path length.

$$T(Z)=\frac{1}{Q(z)\sqrt{\pi}} \int_{-\infty}^{+\infty} \ln [1 + Q(z)]e^{-\tau^2} d\tau$$

(4.12)
(4.13)

where \( \frac{1-e^{-aL}}{a} \) is the effective path length \( L_{\text{eff}} \).

The value of the non linear absorption coefficient \( \beta \) is found to be equal to be 7.429 cm/GW.

Figure 4.21 shows a typical closed aperture z scan, obtained for glycinium oxalate crystal. The peak-valley structure of the curve is a clear indication of a negative refractive nonlinearity exhibited by the medium [62]. The nonlinear refraction coefficient \( n_2 \) (m\(^2\)/W) is obtained through the following equation

\[
\Delta \Phi_0 = kn_2 I_0 L_{\text{eff}}
\]

(4.14)

In the above equation the phase shift \( \Delta \Phi_0 \) is equal to \( 2\pi/\lambda n_2 I_0 L_{\text{eff}} \).

The difference between the normalized transmittance at the peak and valley is related to \( \Delta \Phi_0 \) by the relation

\[
\Delta T_{p-v} = 0.406 (1-S)^{0.25} \Delta \Phi_0
\]

(4.15)

The value of \( n_2 \) is calculated to be equal to \(-1.689 \times 10^{-13}\) m\(^2\)/W.

The molecular second hyperpolarizability, \( \gamma \), may be obtained to be \( 4.0424 \times 10^{-24} \) esu with the equation below [71]

\[
\gamma = 40\pi n_2/ c n_0
\]

(4.16)

The real and imaginary parts of the \( \chi (3) \) of the sample can also be calculated by the following equations [63-68]

\[
\text{Re } \chi^3 (\text{esu}) = (c n_0^2/120\pi^2) n_2,
\]

(4.17)

\[
\text{Im } \chi^3 (\text{esu}) = (c n_0^2 \varepsilon_0 \lambda /2\pi) \beta
\]

(4.18)
The value of the real part of nonlinear susceptibility $\text{Re } \chi^3$ (esu) and imaginary part $\text{Im } \chi^3$ (esu) is found to be equal to $1.474 \times 10^{-11}$ esu and $0.40854 \times 10^{-11}$ esu respectively.

Introducing the coupling factor $\rho$, the ratio of imaginary part to real part of third-order nonlinear susceptibility,

$$\rho = \frac{\text{Im } \chi^3}{\text{Re } \chi^3}$$

(4.19)

The value of $\rho$ in this case is found to be equal to 0.27

The observed value of coupling factor is seen to be less than 1/3, which indicates that the nonlinearity is electronic in origin [71].

The open aperture curve demonstrates a nonlinear absorption and the characteristic pattern of the curve shows that the nonlinear absorption is reverse saturation absorption (RSA) implying that the crystal can be effectively used for optical limiting applications. The peak to-valley configuration of the closed aperture curve suggests that the refractive index change is negative, exhibiting a self defocusing effect [69]. The experimental results exhibit that the GLO crystal possesses a large third-order NLO properties. The reason for the large value of RSA coefficient may be due to the delocalization resulting from the protonation of amino group leading to the formation of glycinium oxalate molecule.

![Fig. 4.20 open aperture Z scan curve of GLO](image)
4.3 CONCLUSIONS

Glycinium oxalate single crystals are grown from the saturated solution at ambient temperature. Powder XRD study on the grown crystal agrees well with the reported single crystal XRD data. CHN analysis confirms the molecular formula as $\text{C}_4\text{H}_7\text{NO}_6$. The vibrational analysis carried out using the FTIR and FT Raman spectroscopy shows the presence of $\text{NH}_3^+$ ion confirming the protonation of amino group leading to the formation of glycinium oxalate molecule. The noncentrosymmetry in the grown crystals of glycinium oxalate is established on the basis of the excellent match between the various vibrational frequencies in the vibrational spectra. Thermal studies carried out employing TGA/DTA and DSC techniques, establish that the crystal has thermal stability up to 180°C. Vickers' microhardness analysis carried out on the material suggests that the material belongs to soft material category. The value of load independent resistance to deformation is calculated as 19.2 g. Dislocation density for solution grown GLO, in the present study is about $10^4$/cm$^2$ which is quite small compared with many other solution grown inorganic semiconductors. It is established that growth mechanism of GLO single crystals in
the present work is 2D nucleation and subsequent spreading of layers. It is seen that the GLO crystal has a wide transparency window ranging from 324 nm to 2500 nm and the absorption throughout this range is very small. This aspect highlights its prospects of applications as a material for higher harmonic generation in nonlinear optics. The value of the linear optical constants, $\alpha$, $n$ and $k$ are evaluated and these values are used to compute the non linear optical parameters from the Z scan studies. The value of dielectric loss found by microwave cavity perturbation technique for this crystal is very small which is of the order of 0.006, and is an indication of the crystalline perfection of the grown crystal. The intense emission peak at 470 nm in the PL spectrum observed in GLO crystal extends ample scope for further detailed investigations in this direction. The SHG efficiency of the crystal is found to be 0.92 times that of KDP by Kurtz and Perry technique. The single shot ($P_s$) and multiple shot ($P_n$) laser damage threshold values for (010) cleaved face of GLO are found to be 15.5 and 11.5 GW cm$^{-2}$, respectively for 1064 nm, pulsed Nd: YAG laser radiation. Open aperture Z scan studies carried out using 532 nm radiation of the pulsed Nd: YAG laser of 7 ns pulse width shows that there is reverse saturable absorption (RSA) in the material and two photon absorption is the mechanism responsible for RSA. The peak-valley structure of the curve obtained in the closed aperture Z scan studies is a clear indication of a negative nonlinear refraction exhibited by the crystal.

4.4 REFERENCES

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