STRUCTURAL AND OPTICAL STUDIES OF GLYCINE BASED SINGLE CRYSTALS - A NONLINEAR OPTICAL MATERIAL

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Abstract
The glycine based single crystals such as glycine zinc sulphate (GZS) and di(glycine) barium chloride (DGBC) was synthesized and single crystals are grown by solution growth technique. The unit cell parameters of grown crystals have been analyzed by single crystal XRD. The optical properties were studied using UV-Vis and photoluminescence spectroscopies. The TG/DTA analyzes were performed and the melting point of the sample was measured. The study of microhardness was measured on a prominent plane to determine mechanical strength using Vicker's hardness test. The NLO properties measurements were carried out using Q-switched Nd: YAG laser.

Keyword: Single crystals, unit cell, microhardness, band gap, photoluminescence.

1. Introduction
The NLO material plays an important role in photonics, laser technology and optical modulation since it can produce a high value of the original frequency[1-3]. To realize many of these NLO applications, materials with large second order nonlinearities, short transparency cutoff wavelength and stable physicochemical properties are needed[4-7]. Due to their possible applications in the optoelectronic technologies, nonlinear optical materials of third order property have received much attention [8-10]. Third-order nonlinear optical materials with low nonlinear absorption but strong nonlinear refraction have attracted considerable attention because of their potential use in the optical signal processing device[11-13]. The structural, thermal, and optical properties of a GZS and DGBC semiorganic nonlinear single optical crystal were investigated.

2. Experimental Techniques

2.1 Synthesis and crystal growth
The GZS was synthesized from glycine and zinc sulfate in the ratio 1:1. The reaction as follows

\[ \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{CH}_2\text{NH}_2\text{COOH} \rightarrow \text{Zn}[\text{CH}_2\text{NH}_2\text{COOH}] \text{SO}_4 \cdot 7\text{H}_2\text{O} \]

The DGBC salt was synthesized with glycine and barium chloride in the ratio 2:1. The reaction is taken as

\[ 2(\text{NH}_2 \rightarrow \text{CH}_2 \rightarrow \text{COOH}) + \text{BaCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Ba} (\text{NH}_2 \rightarrow \text{CH}_2 \rightarrow \text{COOH})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O} \]
The molecular structure of GZS and DGBK was shown in Fig. 1(a) and (b) respectively.

![Glycine zinc sulfate](image1.png)

**Fig. 1 (a) Molecular structure of GZS**

![Di(glycine) barium chloride](image2.png)

**Fig. 1 (b) Molecular structure of DGBK**

### 2.2 Solubility Studies

The solubility test for GZS and DGBK was carried with fine different temperatures (35, 40, 45, 50, 55°C) from the solubility curve highly soluble in distilled water is observed (Fig. 2).

![Solubility curve of GZS and DGBK](image3.png)

**Fig. 2 Solubility curve of GZS and DGBK**

### 2.3 Growth of single crystals

The synthesized GZS salt was dissolved in distilled water then allowed for crystallization and a good quality single crystal with dimensions of 14×10×5 mm³ obtained within a month (Fig. 3). Similarly, the DGBK solutions were prepared then kept for crystallization. The good quality single crystals with a size of 30×15×10 mm³ are grown in 25 days (Fig. 4)
Fig. 3. As grown single crystals of GZS

Fig. 4. As grown single crystal of DGBC

3. Result and Discussion

3.1 Single Crystal XRD Analysis

The grown crystals (GZS and DGBC) were subjected to single crystal XRD analysis using ENRAF NONIUS CAD-4 X-ray diffractometer with MoKα (λ = 0.717 Å) radiation. The GZS and DGBC belong to Triclinic P and Orthorhombic P crystal system respectively (Table 1).

<table>
<thead>
<tr>
<th>Crystal</th>
<th>GZS</th>
<th>DGBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>a(Å)</td>
<td>5.98</td>
<td>8.27</td>
</tr>
<tr>
<td>b(Å)</td>
<td>6.84</td>
<td>9.32</td>
</tr>
<tr>
<td>c(Å)</td>
<td>13.35</td>
<td>14.90</td>
</tr>
<tr>
<td>α</td>
<td>85.12</td>
<td>90</td>
</tr>
<tr>
<td>β</td>
<td>83.21</td>
<td>90</td>
</tr>
<tr>
<td>γ</td>
<td>82.84</td>
<td>90</td>
</tr>
<tr>
<td>V(Å³)</td>
<td>537</td>
<td>1149</td>
</tr>
</tbody>
</table>
3.2. UV-Vis Spectral Study

The UV-Vis spectral transmission analysis of GZS and DGBC was carried out using Perkin Elmer Lambda UV-Vis spectrophotometer (Fig. 5). The lower cutoff wavelength for GZS and DGBC is 190 nm and has a good optical transmission window (190-1100 nm) throughout the UV, Visible, and Near IR region that allows for optoelectronic applications.

![Fig. 5 UV-Vis transmittance spectrum of GZS and DGBC](image)

The band gap of GZS and DGBC crystals was determined by plotting \((\alpha h\nu)^2\) vs \((h\nu)\) and then band gap energy is found to be 6.4 and 6.8 eV (Fig. 6 and Fig. 7). The extinction coefficient of glycine based single crystals was calculated from the relation:

\[
k = \frac{\alpha \lambda}{4\pi}
\]

The extinction coefficient of GZS and DGBC was decreasing with the increasing photon energy (Fig. 8).

![Fig.6 Tauc’s plot of GZS crystal](image)
3.3 Photoluminescence Spectrum

The photoluminescence study of GZS (Fig. 9) and DGBK (Fig. 10) was carried out using a Cary eclipse photoluminescence spectroscopy with excitation wavelength of 220 nm. In both crystals the maximum violet emission was observed at the peak with energy of 3eV and the peak at 465 nm shows the weak blue emission (2.7eV). The peaks at 270 nm, 325 nm and 360 nm emit the weak violet emission corresponding to the energy of 4.6 eV, 3.8 eV and 3.4 eV respectively.
3. 4. FT-IR spectral analysis

The FT-IR spectrum of GZS and DGBC was recorded in the range of 400-4000 cm\(^{-1}\) by KBr pellet technique (Fig. 11). The bands at 3788 cm\(^{-1}\) and 1474 cm\(^{-1}\) due to NH asymmetric stretching and COO\(^{-}\) stretching [7]. The band at 3003 cm\(^{-1}\) established the presence of CH group [8]. The bands at 1640 cm\(^{-1}\) and 1420 cm\(^{-1}\) established the presence of NH\(_3^+\) and C=O symmetric stretching. The band 1108 cm\(^{-1}\) confirm the presence of C-C stretching. The band at 619 cm\(^{-1}\) is assigned to the COO- out of plane bending vibration [9].

The vibration of CH\(_2\) group appears at 1474 cm\(^{-1}\). The characteristic stretching vibrations of SO\(_4^2-\) group appear at 892 and 664 cm\(^{-1}\). The carboxylate group (COO\(^-\)) asymmetric and symmetric stretching vibrations appear at 1640 and 1420 cm\(^{-1}\). The peak observed at 1312 cm\(^{-1}\) is due to the CH\(_2\) wagging vibration. The frequencies at 892 cm\(^{-1}\) are assigned to the carboxylate group. The presence of carboxylate ion and ammonium ion clearly indicated that glycine molecule exists in the zwitter ionic form in GZS [12]. In DGBC a peak at 2583 indicates the presence of NH\(_3^+\) stretching vibrations. A peak at 1572 cm\(^{-1}\) confirm NH\(_3^+\) asymmetric bending vibration in a primary amine group. The band 1334 cm\(^{-1}\) established the presence of C-N stretching vibration. The peaks at 1115 cm\(^{-1}\) and 896 cm\(^{-1}\) are due to the NH\(_3^+\) group of glycine molecule and CCN stretching groups respectively.
3.5 TG/DTA analyzes

The TG/DTA of GZS and DGBC was performed using SII Nanotechnology TG/DTA 6200. The TGA curve (Fig. 12) of GZS shows good thermal stability up to 122°C as there is 14% of weight loss is due to the removal of occluded and absorbed water molecules occurring up to 85°C. The DTA curve shows that the melting point of GZS is 123°C. The TGA curve (Fig. 13) of DGBC has good thermal stability up to 190°C as there is no weight loss below that temperature and weight loss of about 30% in the temperature range 200-320°C. The DTA curve shows the peak at 190°C to be the DGBC melting point.

3.6 Measurement of Microhardness

Microhardness studies for GZS and DGBC were conducted on the well grown plane using a SHIMADZU HMV-200 fitted with a Vicker’s pyramidal indenter (Fig. 14). The GZS and DGBC work hardening coefficient (Fig. 15) is 1.94 and 1.97 which indicates that both crystals belong to the category of soft material.
3.7 Determination of Second Harmonic Generation Efficiency

The second order nonlinear optical property (SHG) of GZS crystal was determined by Kurtz and Perry technique[13-15]. A Q-switched Nd : YAG laser beam was allowed to hit the sample, emitting a fundamental wavelength of 1064 nm (pulse width 8 ns). The SHG in the crystalline sample was confirmed by green radiation emission (532 nm) from the sample. The SHG efficiency of GZS was found to be 0.7 times of KDP. The GZS belongs to non-centro symmetric space group which exhibits SHG efficiency whereas DGBC belongs to center symmetric space group which does not exhibit second order NLO phenomena.

3.8 THG Measurement Using Z-Scan Technique

The Z-scan experiment was carried out for GZS and DGBC using 50 mW Diode pumped Nd: YAG laser with a wavelength of 532 nm [16, 17]. The closed and open aperture of the third order nonlinear optical
susceptibility $\chi^{(3)}$ for GZS and DBC are shown in Fig. 16 and 17 respectively. The ratio of an open and closed aperture of third order nonlinear optical susceptibility for GZS and DBC was shown in Fig.18. The third order nonlinear parameters of GZS and DBC are shown in Table.2.
Fig. 18 Ratio of open and closed aperture of GZS and DGBCC

Table 2. Nonlinear properties of GZS and DGBCC single crystals

<table>
<thead>
<tr>
<th>Parameters</th>
<th>GZS</th>
<th>DGBCC</th>
</tr>
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<tbody>
<tr>
<td>50 mW Diode pumped Nd:YAG Laser (λ)</td>
<td>532 nm</td>
<td>532 nm</td>
</tr>
<tr>
<td>Lens focal length (f)</td>
<td>3.5 cm</td>
<td>3.5 cm</td>
</tr>
<tr>
<td>Optical path length</td>
<td>1 mm</td>
<td>1 mm</td>
</tr>
<tr>
<td>Beam radius of the aperture (wa)</td>
<td>15 mm</td>
<td>15 mm</td>
</tr>
<tr>
<td>Aperture radius (ra) for closed aperture</td>
<td>2 mm</td>
<td>2 mm</td>
</tr>
<tr>
<td>Linear refractive index</td>
<td>1.68</td>
<td>1.629</td>
</tr>
<tr>
<td>Nonlinear refractive index (n&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>5.017×10^-8 cm²/W</td>
<td>4.346×10^-8 cm²/W</td>
</tr>
<tr>
<td>Nonlinear absorption coefficient (β)</td>
<td>0.018×10^-4 cm/W</td>
<td>0.023×10^-4 cm/W</td>
</tr>
<tr>
<td>Real part of the third order susceptibility[Re(χ&lt;sup&gt;3&lt;/sup&gt;)]</td>
<td>10.030×10^-6esu</td>
<td>9.818×10^-6esu</td>
</tr>
<tr>
<td>Imaginary part of the third order susceptibility [Im(χ&lt;sup&gt;3&lt;/sup&gt;)]</td>
<td>0.110×10^-6esu</td>
<td>0.145×10^-6esu</td>
</tr>
<tr>
<td>Third order nonlinear optical susceptibility (χ&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>10.030×10^-6esu</td>
<td>9.819×10^-6esu</td>
</tr>
</tbody>
</table>
4. Conclusion

The GZS and DGBBC single crystals were grown by evaporation method and single crystal XRD analysis confirmed that GZS and DGBBC crystals belong respectively to the triclinic P and orthorhombic P crystal systems. FTIR analysis confirmed the molecular structure of the synthesized material. The transmission spectrum reveals that GZS and DGBBC have a lower cutoff wavelength of 190 nm. The TG/DTA analysis shows that the grown crystal have good thermal stability and both crystals are belongs to soft material category. The SHG of GZS crystal was found to be 0.7 times that of KDP. The third-order nonlinear susceptibility $\chi^{(3)}$ for GZS and DGBBC crystals are found to be $10.030$ and $9.819 \times 10^{-6}$esu respectively.

Reference


