Chapter 12

Summary and Suggestions for Future Work

In the present work single crystals of glycine metal halogenides (GZC, GLC and GLB), glycine metal sulphates (GZS, GLS), γ - glycine, glycine phthalic acid (GPA), ammonium pentaborate and L - Ornithine monohydrochloride have been successfully grown. Slow evaporation and slow cooling method are employed to grow these crystals. Solubility and metastable zonewidth have been estimated at various temperatures. The primary aim of this thesis is to optimize the growth conditions of the above materials and to investigate their properties so as to find their suitability to various applications.

GZC single crystal of 16mm×10mm× 6mm size was grown from aqueous solution by slow cooling method. Its structure was elucidated from single crystal X-ray diffraction data. The powder X-ray diffraction patterns were recorded and the peaks were indexed. Vibrational frequencies of various functional groups of GZC were assigned using FTIR and FT Raman spectroscopy. Thermal properties and Vickers microhardness values were determined. The variation of dielectric constant with varying frequency was studied at room temperature. Even though the GZC belongs to centrosymmetric crystal system its relative SHG efficiency is about 0.5 times that of KDP, this may be due to the breakage of centrosymmetry when exposed to laser light. High resolution X-ray diffraction studies show that the crystal quality is quite good.

Employing slow evaporation method GZS single crystal of dimension 19mm×16mm×15mm with well defined morphology was grown by optimizing the growth parameters. Single crystal X-ray diffraction analysis reveals that GZS crystallizes in orthorhombic system. FTIR
studies were carried out to confirm the functional groups present in the grown crystals. Optical transmittance study shows that the grown crystals are highly transparent throughout the visible and near IR region. Vikers microhardness values were estimated on the (011) faces of the crystal. In TGA curve three step weight loss was found. Powder second harmonic generation efficiency of this crystal is 0.7 times that of KDP. The variations of dielectric constant with varying frequency at different temperatures were studied using LCR meter.

γ - Glycine single crystal of size 18mm×19mm×10mm was grown from a mixture of glycine, water and lithium bromide employing slow cooling method. Solubility and metastable zonewidth were estimated from aqueous solution. Lattice parameters were calculated from single crystal X - ray diffraction. Presence of various functional groups was identified from FTIR spectrum. UV -vis- NIR studies revealed that this crystal is transparent in the region 250 -1500 nm. Vickers microhardness test was carried out to study the mechanical strength of γ - glycine on the prominent (100) face. Thermogravimetric and differential scanning calorimetry analyses were carried out to study the thermal properties of γ - glycine. The powder SHG efficiency of the crystal is about three times that of KDP.

GLS single crystal of size 10mm×5mm×5mm was grown by slow cooling method. The solubility and metastable zonewidth were estimated at different temperatures. The unit cell parameters of the GLS single crystal was evaluated from single crystal XRD. The cell parameters estimated in this work agree well with the reported values. The powder X-ray diffraction was recorded and the peaks were indexed. Thermal analysis reveals that the material is stable up to 328 °C i.e. its melting point. The UV - vis - NIR spectrum shows that the crystal is transparent in the region of 400 – 1100 nm. Powder SHG efficiency of GLS single crystal was found to be 0.75 times that of KDP. Microhardness studies were carried out on (011) face of the GLS crystal.
Bulk single crystals of glycine lithium bromide with dimensions up to 19mm×9mm×8mm have been grown by optimized growth conditions. The solubility and metastable zonewidth were estimated at different temperatures. Single crystal X-ray diffraction analysis reveals that GLB crystallizes in monoclinic system with space group \(P2_1/c\). Morphology of GLB crystal was determined by single crystal XRD analysis. The powder X-ray diffraction was recorded and the peaks were indexed. FTIR spectral analysis confirmed the functional groups of the grown crystal. Microhardness studies were carried out on the (112) face of the GLB crystal. The transmittance and absorbance spectrum of GLB crystal was recorded. TG and DSC analyses were carried out to study the thermal properties. The variation in dielectric constant with varying frequency was studied at different temperatures.

Glycine lithium chloride single crystal of size 15mm×14mm×8mm was grown by slow cooling method from aqueous solution. The single crystal X-ray diffraction study reveals that the grown crystal belongs to triclinic system. Solubility studies show that the solubility of GLC in aqua solution is relatively higher than other glycine compounds taken up for study in this thesis. Metastable zonewidth of GLC was determined. FTIR spectrum was recorded to identify various functional groups present in the material. UV visible spectrum shows that the crystal has good transmittance window with a lower cut off at 230nm. Thermogravimetric analysis implies that the material is stable upto 235 °C. From the microhardness studies it is seen that the hardness of GLC on (011) face decreases with increase in load. Powder SHG efficiency of the crystal is 2.25 times that of KDP. Dielectric constant measured at room temperature shows normal dielectric behaviour.

GPA single crystal of dimensions 14mm×8mm × 6mm was grown by slow cooling method from aqueous solution. Solubility of GPA was determined at five different temperatures. Single crystal X-ray structure
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analysis was carried out for the grown crystal. In the GPA crystal structure, antiparallel linear arrays of glycinium ions are sandwiched between phthallic acid layers via N-H...O and O-H....O intermolecular hydrogen bonds. GPA crystallizes in the orthorhombic crystal system with centrosymmetric space group Pbca. Vibrational frequencies of the functional groups of GPA were assigned using FTIR spectroscopy. Powder X-ray diffraction was recorded and the peaks were indexed using the software Autox 93. Mechanical hardness of GPA single crystal was estimated on (100) face by Vickers Hardness test. Thermal properties of the sample were investigated using TG, DTA and DSC studies. Dielectric studies were carried out for the grown crystal at different temperatures for the frequencies from 40Hz to 100 kHz.

In the present investigation growth and characterization of some of the glycine compounds have been studied in detail. The single crystal structure of γ-glycine, glycine zinc chloride, glycine zinc sulphate and glycine lithium sulphate have been reported by the other investigator. Single crystal structure for glycine lithium bromide and glycine phthalic acid has been reported for the first time in this thesis. In the case of γ-glycine no reports on the physical properties are available in the literature. Hence the present thesis is devoted to investigate on the physical, linear and nonlinear optical, thermal, mechanical and dielectric properties of all the above crystals.

The results of single crystal XRD, second harmonic generation efficiency, hardness values for maximum load, UV lower cut off wavelength and melting point of the glycine complexes prepared in this work are compared in the Table 12.1. SHG efficiency of γ-glycine crystal is larger than the other glycine compounds reported in this investigation. The UV lower cut off values and the transmittance range reveal that the glycine compounds reported in this thesis are suitable for nonlinear optical applications. Among these glycine compounds glycine lithium chloride shows relatively larger SHG efficiency of about 2.3 times that of
KDP with relatively larger Vickers microhardness value. Further glycine lithium chloride is also stable up to its melting point, 235\degree C.

Single crystals of ammonium pentaborate were grown by temperature reduction method from aqueous solution. Unit cell dimensions were calculated from single crystal X-ray diffraction studies. Powder XRD spectrum was recorded and the peaks were indexed. The functional groups were identified and assigned from FTIR spectral analysis. The HRXRD studies carried on APB single crystals reveal that threading the seed crystal affects the perfection of grown crystal. The lower cut-off wavelength (230 nm) and the transmittance range (240-1500 nm) were observed from the UV-vis-NIR spectrum. TGA and DTA reveal that the compound is stable up to 165 \degree C. Hardness values estimated on (101) face by Vickers microhardness tester increases with increase of load and the crystal experience cracks for loads above 200 g. APB shows that the powder SHG efficiency is about 0.75 times that of KDP crystal.

A new nonlinear optical material L-ornithine monohydrochloride (LOMHCl) single crystal of size 18 mmx8 mmx3 mm was grown by slow evaporation technique at room temperature. The grown crystals were characterized by single crystal and powder XRD, FTIR, TGA, DTA, and DSC analyses. UV-vis-NIR spectrum shows that the crystal is transparent in the wavelength range of 300-1600 nm. Vickers microhardness test shows that the crystal withstands up to a load of 200 g and the corresponding hardness value is 75. Dielectric studies were carried out for the grown crystal for different frequencies from 40 Hz to 100 kHz at different temperatures. Its relative powder SHG efficiency tested using Nd: YAG laser is about 1.25 times that of KDP.
<table>
<thead>
<tr>
<th>Crystal</th>
<th>Cell dimensions</th>
<th>Powder SHG Efficiency (KDP times)</th>
<th>Hv (kg/mm²) [Load(g)]</th>
<th>UV lower cut off</th>
<th>Melting Point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>GZC</td>
<td>a = 14.419(2) Å, b = 6.903(2) Å, c = 12.959(2) Å, β = 17.99°, Monoclinic; Space Group – C2/c</td>
<td>0.5</td>
<td>116 (80)</td>
<td>240nm</td>
<td>228</td>
</tr>
<tr>
<td>GZS</td>
<td>a = 5.954 Å, b = 6.812 Å, c = 13.272 Å, α = 85°, β = 83°, γ = 82.92° and V = 529.1(4) Å³; Triclinic</td>
<td>0.7</td>
<td>71 (18)</td>
<td>350nm</td>
<td>Decomposes</td>
</tr>
<tr>
<td>GLS</td>
<td>a = 16.385(10) Å, b = 4.989(4) Å, c = 7.657(4) Å, ( \alpha = \beta = \gamma = 90° ) and V = 625.8(8) Å³; Orthorhombic; Space group – Pna2₁</td>
<td>0.75</td>
<td>55 (30)</td>
<td>330nm</td>
<td>320</td>
</tr>
<tr>
<td>GLC</td>
<td>a = 7.4230 Å, b = 17.5394 Å, c = 8.0303 Å, α = 89.91°, β = 115.08°, γ = 90.21° and V = 946.928 Å³; Triclinic</td>
<td>2.25</td>
<td>121 (70)</td>
<td>230nm</td>
<td>235</td>
</tr>
<tr>
<td>GLB</td>
<td>a = 7.5501(2) Å, b = 17.3863(2) Å, c = 8.2124(2) Å, ( \beta = 116° ) and V = 957.96(16) Å³; Monoclinic Space group – P2₁/c</td>
<td>NIL</td>
<td>105 (70)</td>
<td>300nm</td>
<td>238</td>
</tr>
<tr>
<td>GPA</td>
<td>a = 7.9657(5) Å, b = 11.3470(7) Å, c = 23.513(2) Å ( \alpha = \beta = \gamma = 90° ) and V = 2125.3(3) Å³; Orthorhombic Space group – Pbcå</td>
<td>NIL</td>
<td>120 (200)</td>
<td>280nm</td>
<td>180</td>
</tr>
<tr>
<td>GG</td>
<td>a = 7.0205 Å, b = 7.0240 Å, c = 5.4544 Å, ( \beta = 119.91° ) and V = 233.14 Å³; Monoclinic</td>
<td>3</td>
<td>56 (100)</td>
<td>250nm</td>
<td>220</td>
</tr>
</tbody>
</table>
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**Suggestion for Future Work**

In the present work the single crystals were grown by slow evaporation and slow cooling methods. In future attempts one can grow bulk size crystals by unidirectional growth method. By varying the pH of the solution growth habits of the crystals may be modified. The grown crystals may be characterized using SEM, AFM, Photoluminescence and ferroelectric behaviour.

Etching is a simple and powerful technique to investigate the perfection of the grown crystal. Hence etching studies can be carried out by suitable etchants to reveal perfection of the crystals. Ferroelectric properties of these crystals can be studied in detail. The electrical conductivity with varying temperature can be attempted to ascertain the electrical properties and the activation energy of the grown crystals. Laser damage threshold and third order nonlinear optical property can be studied for these crystals.