Comparative study of mechanical, dielectric and electrical properties of solution grown semi-organic NLO crystal glycine with additives-ammonium oxalate, potassium and barium nitrate

M N Ravishankar*1, M A Ahlam1, R Chandramani2 & A P Gnana Prakash1

1Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore 570 006, India
2Department of Physics, Dayananda Sagar College of Engineering, Bangalore 560 078, India

*E-mail: ravibhum2004@gmail.com

Received 13 March 2012; revised 7 August 2012; accepted 24 September 2012

The semi-organic non-linear optical (NLO) crystals of γ-glycine (G), with additives like ammonium oxalate (AO), barium nitrate (BN) and potassium nitrate (PN) were grown by aqueous solution method. The mechanical properties like Vicker’s micro hardness number ($H_v$), stiffness constant ($C_{11}$) and yield strength ($\sigma_y$) of grown crystals have been evaluated. The dielectric constant and dielectric loss of the grown crystals have been investigated in the frequency range 10 kHz-10MHz. The dependence of ac conductivity on frequency of the applied field has been established. Studies confirm that the grown NLO crystals retain the merits of organic (SHG response and flexibility) and inorganic (good hardness) properties. Glycine ammonium oxalate (GAO) is a preferred material for device application compared to glycine barium nitrate potassium nitrate (GBNPN) crystal. Based on mechanical and electrical characterization, comparison has been made between the additives ammonium oxalate (AO), barium nitrate (BN) and potassium nitrate (PN).

Keywords: Organic compound, Crystal growth, Dielectric properties, Electrical properties, Mechanical properties

1 Introduction

Non-linear optics has emerged as one of the most attractive fields of current research in view of its vital application in areas such as optical modulation, optical logic, frequency shifting, optical switching and optical data storage. Glycine is the simplest of all amino acids among the organic materials. It has been reported that some complexes of amino acids with simple inorganic salts may exhibit non-linear optical and ferroelectric properties. Semi-organic non-linear optical crystals have large mechanical strength and chemical stability when compared to organic crystals but it is difficult to grow large size and high quality crystals. The challenge faced by researchers in this emerging field is the identification of new types of functional materials by rational construction of molecular assemblies exhibiting non-linear optical effects. In addition, the new crystals should fulfill the secondary requirements such as thermal, mechanical and chemical stabilities. Various strategies have been done by the researchers to bring out the suitable materials such as formation of metal complexes and salts, or introduction of steric effects and hydrogen bonding interactions. In the present study, we have made an attempt to grow number of semi-organic non-linear optical crystals of γ-glycine (G), with additives of AR grade like ammonium oxalate (AO), barium nitrate (BN) and potassium nitrate (PN) by aqueous solution method. Additives are used in the host compound to make the crystal exhibit higher mechanical strength and chemical stability. Oxalates and nitrates are more suitable to enhance mechanical strength, chemical stability as well as non-linear optical property. We mainly focus on mechanical characterization of all grown crystals. Since micro hardness has direct correlation with the crystal structure and is sensitive to lattice perfection and interatomic spacing, mechanical properties have been studied by employing Vicker’s micro hardness tester. Various hardness parameters namely, micro hardness number ($H_v$), Mayer’s index ($n$), yield strength ($\sigma_y$) and elastic stiffness constant ($C_{11}$), have been estimated for all the grown samples. Studies such as dielectric constant and dielectric loss whose dependence on frequency confirms the grown crystal behaviour and purity, the electrical property ac conductivity has also been investigated in the present work.

2 Experimental Details

The non-linear optical crystals γ-glycine (G) with different additives like ammonium oxalate (AO),
barium nitrate (BN) and potassium nitrate (PN) were grown by slow evaporation method. Good transparent crystals of glycine ammonium oxalate (GAO) in the ratio 1:1 and glycine barium nitrate potassium nitrate (GBNPN) in the ratio 1:¼:¼ were obtained in a time span of 3 to 4 weeks. The sizes of crystals are in the range 0.5-2.5 cm and are shown in Fig. 1. The mechanical properties have been studied using Vicker’s micro hardness tester MH-5. The diagonal lengths of the indentation with various applied loads from 10 g to 200 g were measured for a constant indentation period of 10 s. Various hardness parameters such as micro hardness \((H_v)\), Mayer’s index \((n)\), yield strength \((\sigma_y)\) and elastic stiffness constant \((C_{11})\) have been estimated for the grown samples. The dielectric studies on GAO and GPNBN single crystals have been carried out using 4275A Multi-Frequency LCR meter (Hewlett-Packard) in the frequency range 10 kHz-10 MHz. The crystals were also characterized with XRD, FTIR to confirm the crystallinity and presence of the additives. The crystals also have shown very good second harmonic generation (SHG) efficiency\(^{10}.\)

3 Results and Discussion

3.1 Mechanical study

In order to understand the plasticity of the crystals, micro hardness test was carried out. The hardness of the crystals depends on the type of chemical bonding, lattice energy, Debye temperature, heat of formation and inter-atomic spacing\(^8\), which may differ along the crystallographic directions. Hardness of the material is a measure of the resistance it offers for local deformation and it plays a key role in device fabrication\(^9\). The Vicker’s micro hardness number \((H_v)\) is calculated using the relation\(^{11}:\)

\[
H_v = 1.8544P/d^2 \text{ N/mm}^2
\]

where \(P\) is the applied load in Newton and \(d\) is the diagonal length of the indentation in mm. The variation of \(H_v\) with the applied load \(P\) for both the crystals is shown in Fig. 2. The hardness number was found to increase with increase in applied load up to 100 g and then decreases slowly up to 200 g, which confirms the hardness property. The slight increase in micro hardness with increase of load could be attributed to the heaping up of material at the edges of the impression made by the diamond pyramid. This also confirms moderate stress required for homogeneous nucleation of dislocation in the small dislocation free region of indention. Whereas in case of GBNPN, \(H_v\) has decreased by a small number with increase in load up to 100 g, later increases slowly up to 200 g and again it confirms the moderate stress to dislocation. The \(H_v\) value of the crystals reveals that the grown crystals are soft materials but GBNPN is softer than GAO. Plots of \(\log P\) versus \(\log d\) for the grown crystals are shown in Fig. 3. It can be seen that

![Fig. 1 — Photograph of as grown crystals (a) glycine ammonium oxalate crystal (b) glycine barium nitrate potassium nitrate crystal](image1)

![Fig. 2 — Variation of \(H_v\) versus load \(P\) for GAO and GBNPN semi-organic NLO crystals](image2)

![Fig. 3 — Log \(P\) versus log \(d\) for GAO and GBNPN semi-organic NLO crystals](image3)
log $P$ versus log $d$ is linear for both the crystals and the slope gives the work hardening index number ‘$n$’. The values of ‘$n$’ are presented in Table 1. From the hardness value, the yield strength ($\sigma_v$) has been calculated using the relation (for $n>2$),

$$\sigma_v = \frac{H}{3}(0.1)^{n-2}$$

where $n' = n+2$

The calculated values of yield strength $\sigma_v$ for grown crystals are given in Table 2. Values of $\sigma_v$ reveal that GBNPN crystals possess higher yield strength compared to GAO.

The elastic stiffness constant ($C_{11}$) has been calculated for both the grown crystals using Wooster’s empirical relation $C_{11} = \frac{H_v}{7}$. The calculated stiffness constant for different loads from 10 g to 200 g are given in Table 3. Moderate values of $C_{11}$ compared to inorganic crystals indicate that the binding forces between the ions are quite strong.

### 3.2 Dielectric study

The dielectric properties are correlated with electro-optic properties of the grown GAO and GBNPN crystals; particularly when they are non-conducting materials. Microelectronics industry needs new low dielectric constant ($\varepsilon_r$) materials as an inter layer dielectric (ILD). In order to carry out dielectric measurements, rectangular surfaces of the grown GAO and GBNPN single crystals were well polished and coated with pure silver paste to ensure good electrical contact so that it behaved like a parallel plate capacitor. Plots of dielectric constant ($\varepsilon_r$) and dielectric loss as a function of log frequency are shown in Fig. 4(a and b).

Dielectric constant and dielectric loss of GAO and GBNPN crystals decrease with increase in frequency up to 6.5 MHz as shown in Fig. 4. The values of the dielectric constant at low frequencies are due to the contribution of all the four polarizations namely dipolar, electric, ionic and space charge polarization, which depends on frequency. The graphs exemplify the fact that both the dielectric constant and the dielectric loss are inversely proportional to frequency. The space charge contribution will depend on purity and perfection of the crystal and it has noticeable influence in the low frequency region. The low value of dielectric loss at high frequency for the grown samples suggests that the samples possess

<table>
<thead>
<tr>
<th>Load $P$ in g</th>
<th>Glycine ammonium oxalate</th>
<th>Glycine barium nitrate potassium nitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>17.364</td>
<td>20.28</td>
</tr>
<tr>
<td>25</td>
<td>18.04</td>
<td>19.622</td>
</tr>
<tr>
<td>50</td>
<td>18.726</td>
<td>19.128</td>
</tr>
<tr>
<td>100</td>
<td>19.40</td>
<td>17.811</td>
</tr>
<tr>
<td>200</td>
<td>18.38</td>
<td>18.60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Load $P$ (g)</th>
<th>Glycine ammonium oxalate</th>
<th>Glycine barium nitrate potassium nitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>51.4</td>
<td>9.86</td>
</tr>
<tr>
<td>25</td>
<td>53.6</td>
<td>10.61</td>
</tr>
<tr>
<td>50</td>
<td>55</td>
<td>11.1</td>
</tr>
<tr>
<td>100</td>
<td>57.5</td>
<td>11.82</td>
</tr>
<tr>
<td>200</td>
<td>54.5</td>
<td>10.93</td>
</tr>
</tbody>
</table>

![Fig. 4 — (a) Frequency dependence of dielectric constant ($\varepsilon_r$) of GAO and GBNPN crystal (b) Frequency dependence of dielectric loss of GAO and GBNPN crystal](image-url)
enhanced optical quality with fewer defects and this parameter is of vital importance for NLO materials\textsuperscript{18,19}. The low value of $\varepsilon_r$ and $\tan \delta$ at high frequencies indicate the purity of grown crystals. Further, the material is suitable for device applications up to frequency 2 MHz. Increase of $\varepsilon_r$ and $\tan \delta$ beyond 2 MHz may be due to the space charge which could not sustain and comply with the external varying field.

At high frequencies, the periodic reversal of the field takes place so rapidly in such a way that the space charges may not be able to sustain and comply with the external varying field.

3.3 \textit{ac} Conductivity

\textit{ac} Conductivity study is carried out to characterize the bulk resistance of the crystalline solids as a function of frequency which is analyzed in the complex impedance plane. The resulting impedance is consisting of two parts, real and imaginary part.

\[ Z = Z' + Z'' \]

\[ Z' = |Z| \cos \theta \] (Real part), \[ Z'' = |Z| \sin \theta \] (Imaginary part).

Figure 5 shows the frequency dependence of imaginary part $Z''$ of impedance of the grown GAO and GBNPN crystals. In both the crystals, $Z''$ is found to decrease with increase in frequency and the values of $Z''$ merge at higher frequencies.

From the \textit{ac} measurements, $Z'$ and $Z''$ have been evaluated and Nyquist plots (impedance plots) are shown in Figs 6 and 7. The nature of the graph confirms the suitability of the materials as good quality capacitor. Variation of $\log \sigma_{ac}$ versus $\log f$ is shown in Fig. 8 which reveals the usual behaviour.
that is, increase of $\sigma_{ac}$ with increase of frequency. The frequency dependence of $\sigma_{ac}$ is in accordance with Jonscher’s power law. Increase of $\log \sigma_{ac}$ with $\log f$ is almost linear in nature in case of GAO when compared to GBNPN crystal.

4 Conclusions
Good transparent crystals of glycine ammonium oxalate (GAO), glycine barium nitrate potassium nitrate (GBNPN) were obtained in a time span of 3 to 4 weeks. The variation of micro hardness with increase in load confirms the moderate stress to dislocation. The $H_v$ value of the crystals reveals that both the crystals are soft materials but GBNPN is softer than GAO. The GBNPN crystal posses higher yield strength compared to GAO. The moderate values of elastic stiffness constant $C_{11}$ indicate that the binding forces between the ions are quite strong in both the crystals. The low value of dielectric loss at high frequency in GAO and GBNPN crystals suggests enhanced optical quality and low density defects which are of vital importance for NLO materials. Nyquist plots of GAO and GBNPN crystals confirm the suitability of material as good quality capacitor.

Acknowledgement
The authors thank Head, Mechanical Division, NAL, Bangalore, for providing micro-hardness test facility. Authors also thank The Chairman, Department of Physics, Indian Institute of Science, Bangalore, for providing Multi-Frequency LCR meter (Hewlett-Packard) facility. Authors are grateful to the management, DSCE, Bangalore for their constant support and encouragement.

References