Crystal growth, structural, optical, mechanical and thermal properties of a third-order nonlinear material bis-glycine lithium bromide monohydrate single crystal

T. Balakrishnan\textsuperscript{a}, P. Revathi\textsuperscript{a}, S. Sakhthivel\textsuperscript{a} and K. Ramamurthi\textsuperscript{b}

\textsuperscript{a}Crystal Growth Laboratory, PG & Research Department of Physics, Periyar EVR College (Autonomous), Tiruchirappalli, India; \textsuperscript{b}Crystal growth and Thin film laboratory, Department of Physics and Nanotechnology, SRM University, Kancheepuram, India

ABSTRACT

Well-developed transparent single crystals of bis-glycine lithium bromide were grown by the slow evaporation method. The grown crystals were characterized by powder X-ray diffraction analysis, Fourier transform infrared spectroscopy, thermogravimetric analysis (TGA), differential thermal analysis and differential scanning calorimetry analyses. UV–VIS–NIR spectrum shows excellent transmission in the UV, visible and NIR regions. Mechanical properties of the grown crystals were studied using the Vickers microhardness tester. Third-order nonlinear optical properties were studied in detail by the Z-scan technique with He–Ne laser radiation of wavelength 632.8 nm and the corresponding nonlinear refractive index, absorption coefficient and optical susceptibility were calculated.

1. Introduction

Complexes of glycine have recently attracted attraction due to their potential applications in ferroelectricity [1–3], dielectric properties [4] and nonlinear optical properties [5–17]. Extensive research on metal coordination compounds of glycine exists in the literature because of its structural flexibility, good solubility in water and its amphoteric nature. To date, six complexes of glycine with inorganic lithium salts have been published. These are glycine lithium nitrate, glycine lithium sulfate [18], glycine lithium chloride monohydrate and lithium glycinate, bis (glycine) dilithium chromate monohydrate and bis (glycine) dilithium molybdate. Recently, Fleck et al. [19,20] have reported a review on glycine compounds and introduced a classification scheme. We have isolated a new compound glycine lithium bromide and its single crystal structure was described [21]. Single crystal X-ray structure solution analysis reveals that the hydrated form of glycine lithium bromide crystallizes in the monoclinic system, with space group P2\(_1\)/c. As part of continuation of our study, we report here the growth of glycine lithium bromide from aqueous solution by the solvent evaporation method. The grown crystals were characterized by powder X-ray diffraction analysis, Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), differential thermal analysis and differential scanning calorimetry (DSC) analysis. UV–VIS–NIR spectrum shows excellent transmission in the UV, visible and NIR regions. Mechanical property of the grown crystal was studied using the Vickers microhardness tester. Third-order nonlinear optical properties were studied in detail by the Z-scan technique.

2. Experimental

2.1. Synthesis

Bis-glycine lithium bromide (BGLB) salt was synthesized by dissolving Analar grade glycine and lithium bromide in a 1:1 ratio in double distilled water according to the following reaction:

\[
\text{LiBr} + \text{CH}_2\text{NH}_2\text{COOH} \rightarrow \text{Li}^+ [\text{CH}_2\text{NH}_2\text{COOH}]\text{Br}^-.
\]

The temperature of the solution was maintained at a constant temperature of 50°C, and the BGLB salt was obtained by the evaporation of the solvent. The purity of the salt was increased by successive recrystallizations.

2.2. Solubility

The solubility of BGLB was determined for six different temperatures, namely 30°C, 35°C, 40°C, 45°C, 50°C and 55°C. The solubility at 30°C was determined by dissolving the recrystallized BGLB salt in 100 ml of double distilled water, taken in an air tight container maintained at constant temperature with continuous heating and cooling.

CONTACT T. Balakrishnan balacrystalgrowth@gmail.com Crystal Growth Laboratory, PG & Research Department of Physics, Periyar EVR College (Autonomous), Tiruchirappalli, Tamil Nadu 620 023, India

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stirring. After attaining saturation, the equilibrium concentration of the solute was estimated gravimetrically. The same procedure was followed to estimate the solubility at different temperatures. The variation of the solubility with temperature is shown in Figure 1.

BGLB has a positive temperature coefficient of solubility.

2.3. Crystal growth

To obtain a single crystal of high quality, the recrystallized starting material was used for crystal growth. In the present study, BGLB crystals were grown from aqueous solutions by solvent evaporation as well as by slow evaporation. Initially, the slow evaporation method was employed to grow single crystals of BGLB at room temperature. A saturated solution of 200 ml was prepared according to solubility data and taken in a crystallizing vessel with perforated covers. It was kept in an undisturbed area for slow evaporation. The crystals were harvested after few days. The harvested crystals are transparent. The photograph of the crystal grown from the slow evaporation method is shown in Figure 2(a). BGLB crystals were also grown by the solvent evaporation method in a constant temperature bath having an accuracy of ±0.01°C. One good transparent single crystal, obtained by the slow
evaporation method at room temperature, was selected as a seed crystal. The crystal growth process was initiated in a saturated solution at 35°C by suspending a seed in the solution. During solvent evaporation, the seed crystal was rotated in a clockwise and anticlockwise directions. The crystal harvested after a growth period of 18 days is shown in Figure 2(b). The crystals of BGLB have well-developed morphology with several predominant habit faces. The morphology of the BGLB crystal depicted in Figure 2(c) is a polyhedron with eight developed faces. All the faces of the crystal were indexed after identifying them using X-ray measurements.

3. Result and discussion

3.1. Single crystal and powder X-ray diffraction analysis

BGLB single crystal structure was published by Balakrishnan and colleagues [21]. In this structure, the Li atom is coordinated to a single water molecule and three carboxylate oxygen atoms of the two glycine molecules and has distorted tetrahedral coordination geometry. One carboxylate atom, O2, from one glycine and two carboxylate oxygen atoms, O3 and O4, from the second glycine ion are involved in coordination to the Li atom. One of the oxygen atoms, O3, coordinates with a symmetry-related Li cation, hence the Li cation bridges two of the carboxylate oxygen atoms, O3 and O4. The coordinated water molecule in the bromide complex is involved in hydrogen bond with one of the carboxylate atoms, O2, and this along with the coordination sphere produces an eight-membered fused ring. The ORTEP diagram of BGLB is presented in Figure 3(a). The unit cell dimensions are \( a = 7.5396(6) \) Å, \( b = 17.4173(14) \) Å, \( c = 8.2726(12) \) Å, \( \beta = 118.138(7)^\circ \), \( V = 957.96(18) \) Å\(^3\) and \( \rho = 1.768 \) g/m\(^3\).

The powder X-ray diffraction pattern of BGLB was recorded using the SEIFERT JSODEBYEFLEX (Model2002) diffractometer with Cu K\(\alpha\) (\(\lambda = 1.5405 \) Å) radiation. A fine powder of BGLB was obtained by crushing the single crystals. The sample was scanned over the \(2\theta\) range 10–80° at a rate of 1°/min. From the X-ray diffraction data, the various planes of reflections were indexed using the software AUTOX93. The indexed X-ray diffraction pattern of BGLB is given in Figure 3(b).

![Figure 3. (a) ORTEP diagram of BGLB. (b) Powder X-ray diffraction of BGLB.](image-url)
3.2. FTIR spectral studies

The FTIR spectrum for BGLB, recorded at 300 K in the range of 450–4000 cm$^{-1}$ (JASCO FT-IR spectrometer, KBr pellet) is shown in Figure 4. The intense sharp peak at 3429 cm$^{-1}$ is due to the O–H asymmetric stretching. The absorption due to the carboxylate group of free glycine is observed at 504.2, 892.8 and 1614 cm$^{-1}$, respectively [7]. In BGLB, these peaks are shifted to 517, 896 and 1634 cm$^{-1}$, respectively. Similarly, the absorption due to the NH$_3^+$ group of free glycine is observed at 1111, 1131 and 1505 cm$^{-1}$, respectively [7]. In BGLB, the peaks for NH$_3^+$ are shifted to 1042, 1142 and 1497 cm$^{-1}$, respectively. The strong band observed at 1331 cm$^{-1}$ is due to the CH$_2$ group. The CCN asymmetric stretching frequency is observed at 1031 cm$^{-1}$. Table 1 compares the characteristic FTIR vibrational frequencies for glycine lithium bromide, with glycine and glycine lithium chloride.

3.3. UV–VIS–NIR spectral studies

The UV–VIS–NIR spectrum was recorded in the wavelength range of 200–1100 nm using the Varian Cary 5E UV–VIS–NIR spectrophotometer. In this study, BGLB crystal of thickness 3 mm was used to record the transmittance and absorbance in the range of 200–1100 nm. The crystal had attained 62% of transmittance in the UV visible region. The recorded spectrums are shown in Figure 5. The UV transparency lower cut-off occurs at 300 nm.

3.4. Thermogravimetric analysis

Thermogravimetric analysis was carried out using a STA 409 C instrument in the temperature range 55–1217°C at a heating rate of 10°C/min in a nitrogen atmosphere. The decomposition process of this crystal takes place in three steps (Figure 6). In the first step, decomposition of BGLB starts at 100°C and ends at 200°C resulting in...

Figure 4. FTIR spectrum of BGLB.
a weight loss of 7.5\% of the total weight of the material taken. This decomposition is due to the loss of one water molecule. This is also reflected in the DSC curve. The second decomposition takes place between the temperature 200°C and 400°C. In this interval, a total weight loss of 51\% is observed. The weight loss corresponds to decomposition of the glycine molecule. The calculated weight loss is 52.53\%. The remaining material (Li Br) about 38\% decomposes in the third step gradually. This decomposition starts at 600°C and ends at 900°C.

3.5. Differential scanning calorimetry

DSC was carried out on a Perkin-Elmer DSC 7 calorimeter with a heating rate of 10°C/min. For this, a small piece of the crystal weighing 13.313 mg was placed in an aluminum pan. The DSC plot (Figure 7) shows a phase transition at 135°C. This well-marked endothermic peak is due to the loss of one water molecule. The loss of water is also reflected in the TGA curve within the same temperature region. The second endothermic peak obtained near 240°C is attributed to the splitting and decomposition of part of the title compound.

3.6. Microhardness studies

Crystal hardness is the ability of a material to resist surface abrasion. One of the transparent BGLB crystals free from cracks was selected to carry out the Vickers microhardness measurements at room temperature using a Ultra microhardness tester fitted with a diamond indenter. The specimen was mounted on the stage of the Vickers pyramid indenter and indentations were made at various loads from 10 to 70 g for a descent time of 2 s. Two indentations were made for each load. The diagonal impressions were measured using a Reichert Polyvar 2 MET Microscope with a Micro duromat 4000E hardness controller. The measurements were made on the well-developed face of (001). The Vickers microhardness number was evaluated from the relation \( H_v = \frac{1.8544P}{d^2} \) kg/mm\(^2\), where \( H_v \) is the Vickers hardness number, \( P \) is the indenter load in kg, \( d \) is the diagonal length of the impression in mm and 1.8544 is a constant, which is a geometrical factor for the diamond pyramid. The hardness value was found to increase with the applied load (Figure 8) and it was observed that crack starts after a load of 70 g. The crystal hardness is load dependent and the value of the hardness increases with an increase in the applied indentation load. This phenomenon is known as the indentation size effect (ISE). In order to analyse the ISE, one needs to fit the experimental data according to Meyer’s law \[ P = Ad^n \] where \( n \) is the Meyer’s index or work hardening exponent and \( A \) is the material constant. In the present work, the plot (Figure 9) obtained between log \( P \) and log \( d \) gives a straight line. The work hardening coefficient (\( n \)) calculated by the least-square curve fitting is 1.8 [23]. The applicability of the proportional specimen resistance (PSR) model was also examined. A plot of \( P/d^n \) against \( d \) gives a straight line (Figure 10). This linear relationship confirms that the PSR model is also applicable for explaining the ISE behaviour of the BGLB crystal. The slope value of \( P/d^n \) multiplied by the Vickers conversion factor 1.8544 gives the value of the load-independent microhardness, \( H_{\text{ip}} \). In this study, the calculated load-independent microhardness is 55.6 g/mm\(^2\).

### Table 1. Vibrational band assignments of BGLB.

| IR band (cm\(^{-1}\)) | Glycine [7] | Glycine lithium chloride [10] | Glycine lithium bromide (present work) | Assignment |
|------------------------|------------|-------------------------------|--------------------------------------|------------|
| 3419                   | 3415       | 3429                          | O–H asymmetric stretching             |
| 3282                   | 3136       | –                             | O–H symmetric stretching              |
| 1614                   | 1631       | 1634                          | CO\(^{-}\) asymmetric stretching      |
| 1502                   | 1515       | –                             | NH\(^{3}\) symmetric stretching       |
| 1345                   | 1335       | 1331                          | CH\(_2\) wagging                      |
| 1112                   | 1127       | 1129                          | NH\(^{3}\) rocking                    |
| 1034                   | 1033       | 1031                          | CCN asymmetric stretching             |
| 892                    | 908        | 896                           | CCN symmetric stretching               |
| 766                    | 766        | 666                           | NH\(^{3}\) rocking                    |
| 690                    | 675        | –                             | CO\(^{-}\) scissoring                  |
| 607                    | –          | –                             | CO\(^{-}\) rocking                    |
| 504                    | –          | –                             | COO\(^{-}\) rocking                   |

Figure 5. Transmittance and absorption spectra of BGLB.
Figure 6. TGA of BGLB.

Figure 7. DSC curve of BGLB.
### 3.7. Dielectric studies

The dielectric property of the BGLB single crystal was measured on the (–11–2) face using an HIOKI LCR meter. A cut and polished crystal of dimensions 1.2 cm × 1.0 cm × 0.3 cm was used. The sample was polished with alumina (1–3 μm) powder. The opposite faces of the samples were painted using silver paste. A two-terminal copper electrode was used as the sample holder and the sample was held between the electrodes. A thermocouple was fixed in the vicinity of the lower electrode to measure the temperature of the sample. In this way, a parallel plate capacitor was formed. The capacitance of the sample was measured by varying the frequency from 40 Hz to 100 kHz. The dielectric constants for various temperatures (30°C, 35°C, 40°C and 50°C) were determined using the relation

\[ \varepsilon = \frac{C d}{\varepsilon_0 A} \]

where \( C \) is the capacitance of the crystal, \( d \) is the thickness of the crystal, \( A \) is the cross-sectional area of the flat surface of the crystal and \( \varepsilon_0 \) is the permittivity of free space. Figure 11 shows the variation of the dielectric constant with applied frequency. The dielectric constant has high values in the lower frequency region and then it decreases with applied frequency. The very high value of dielectric constant at low frequencies may be due to the presence of all the four polarizations, namely space charge, orientational, electronic and ionic polarization and its value at higher frequencies may be due to the loss of significance of these polarizations gradually [24]. It was observed from the curves that the dielectric constant of BGLB exhibits a normal dielectric behaviour. That is, the dielectric constant decreases with increasing frequency and reaches a constant value.

### 3.8. Z-scan studies

In 1989, Sheik-Bahae et al. [25,26] have reported a method, the Z-scan technique for the determination of third-order nonlinear refractive index \( n_2 \) and nonlinear absorption coefficient \( \beta \) simultaneously. In this technique, a polarized Gaussian laser beam propagating in the Z-direction is focused to a narrow waist. The sample is moved along the Z-direction and the transmitted intensity is measured through a finite
aperture in the far field as a function of the sample position $Z$, measured with respect to the focal plane. As the sample moves through the beam focus (at $Z = 0$), self-focusing or defocusing modifies the wave front phase, thereby modifying the detected beam intensity. The schematic set-up of the Z-scan technique is depicted in Figure 12(a).

The third-order nonlinear coefficient ($\beta$) of the grown BGLB crystal was calculated by using the Z-scan technique with a laser power of 20 mW and the wavelength of He–Ne laser being 632.8 nm and focused by a lens of 12 cm focal length. The transmitted beam through an aperture placed in the far field was measured using a photodetector with a digital power meter. In an open aperture method, a lens replaces the aperture to collect the entire laser beam transmitted through the sample. The sample causes an additional focusing and defocusing, depending on whether nonlinear refraction is positive or negative. The sensitivity to nonlinear refraction is entirely due to the aperture and the removal of aperture completely eliminates the effect. The enhanced transmission near the focus is suggestive of the saturation of the absorption at a high intensity. Absorption saturation in the sample enhances the peak and decreases the valley in the closed aperture Z-scan. The defocusing effect is produced due to the thermal conductivity resulting from the absorption of radiation 632.8 nm. A spatial distribution of the temperature in the crystal is produced due to the absorption of focused beam propagating through the absorbing sample medium. Hence, a spatial variation of the refractive index is produced, which acts as a thermal lens resulting in the phase distortion of the propagating beam. The closed aperture Z-scan curve of BGLB is depicted in Figure 12(b). The difference between the transmittance peak and valley transmission ($\Delta T_{p-v}$) can be written in terms of the on-axis phase shift at the focus.

$$\Delta \phi = \frac{\Delta T_{p-v}}{0.406(1 - S)^{0.25}},$$

where $\Delta \phi$ is the on-axis phase shift at the focus, $S$ is the aperture linear transmittance and it was calculated using the following relation:

$$S = 1 - \exp\left(-\frac{2r_a^2}{\omega_a^2}\right),$$

where $r_a$ is the radius of the aperture and $\omega_a$ is the beam radius at the aperture. The nonlinear refractive index ($n_2$) was calculated using the following relation [25]:

$$n_2 = \frac{\Delta \phi}{k I_0 L_{\text{eff}}},$$

where $k$ is the wave number ($k = 2\pi/\lambda$), $I_0$ is the intensity of the laser beam at the focus ($Z = 0$).

$$L_{\text{eff}} = \frac{1 - \exp\left(-\alpha L\right)}{\alpha},$$

where $L_{\text{eff}}$ is the effective thickness of the sample, $\alpha$ is the linear absorption coefficient of the sample and $L$ is the thickness of the sample. The nonlinear absorption coefficient ($\beta$) is estimated from the open aperture Z-scan data.

$$\beta = \frac{2 \sqrt{2} \Delta T}{I_0 L_{\text{eff}}},$$

**Figure 12.** (a) The schematic set-up of the Z-scan technique is depicted. (b) Z-scan (closed) spectrum of BGLB.
where $\Delta T$ is one peak value at the open aperture Z-scan curve. The value of $\beta$ will be negative for saturated absorption and positive for two photon absorption. The real and imaginary parts of the third-order nonlinear optical susceptibility ($\chi^{(3)}$) were estimated using the below equations

$$\text{Re} \chi^{(3)} = \frac{10^{-4} \epsilon_0 c^2 n_0^2 n_2}{\pi} (\text{cm}^2/\text{W}) \tag{6}$$

$$\text{Im} \chi^{(3)} = \frac{10^{-2} \epsilon_0 c^2 n_0^2 \lambda \beta}{4 \pi^2} (\text{cm}^2/\text{W}) \tag{7}$$

where $n_0$ is the vacuum permittivity, $c$ is the velocity of light in vacuum, $n_0$ is the linear refractive index of the sample and $\lambda$ is the wavelength of laser beam. The third-order nonlinear optical susceptibility was calculated using the following relation:

$$\chi^{(3)} = \sqrt{(\text{Re} \chi^{(3)})^2 + (\text{Im} \chi^{(3)})^2}. \tag{8}$$

Table 2 shows the experimental details and the values obtained from the Z-scan measurement for BGLB.

### 4. Conclusion

Single crystals of BGLB were grown by slow evaporation at room temperature and by the solvent evaporation technique. Optically transparent, BGLB crystals with dimensions up to $19 \times 9 \times 8 \text{ mm}^3$ have been grown by the solvent evaporation method. Solubility tests were carried out and show that water is a suitable solvent for growing single crystals. Powder X-ray diffraction studies were carried out and the peaks were indexed. The presence of functional groups was confirmed by FTIR analysis. Optical transmittance and the spot-size diameter in front of the aperture ($\omega_0$) were measured in Z-scan experiment.

| Parameters                              | Values                   |
|-----------------------------------------|--------------------------|
| Laser beam wavelength ($\lambda$)       | 632.8 nm                 |
| Lens focal length ($f$)                 | 12 cm                    |
| Optical path distance ($Z$)             | 115 cm                   |
| Spot-size diameter in front of the aperture ($\omega_0$) | 1 cm                        |
| Aperture radius ($r_0$)                | 4 mm                     |
| Effective thickness ($L_{\text{eff}}$)  | 0.99 mm                  |
| Nonlinear refractive index ($n_2$)      | $12.3371 \times 10^{-6} \text{ m}^2/\text{W}$ |
| Nonlinear absorption coefficient ($\beta$) | $0.3840 \times 10^{-3} \text{ m/ W}$ |
| Third-order nonlinear susceptibility ($\chi^{(3)}$) | $1.957 \times 10^{-6} \text{ esu}$ |

The authors thank the Tamil Nadu State Council for Science and Technology, Tamil Nadu, India (Ref. No. TNSCST/S&T Project/AR/PS/2013–2014) for financial support.
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