Structural and Optical Properties of (DI) Glycine Chlorides of Barium and Magnesium Crystals

Anu Elizabath Jose
Ministry of Education
United Arab Emirates

Gayathri Mohan K V
Christ Academy Institute of Advanced Studies
Bengaluru, India

Suresh Kumar M R
R V Institute of Technology and Management,
Bengaluru, India

***Abstract*—The present study attempts to investigate the structural and optical properties of (di) Glycine chlorides of Barium and Magnesium (DGCBM) crystals. Solvent evaporation technique is used to grow Single crystals of good crystalline properties. Crystalline properties and the lattice parameter values are studied using Powder X-ray diffraction (PXRD) technique. The FT-IR spectral analysis of the sample is used to confirm the presence of expected functional groups. The optical transparency and band gap of the desired sample is determined by UV-Vis analysis. The classical powder method developed by Kurtz and Perry is performed to check the nonlinear optical (NLO) properties of the grown crystal in the fine powder form.**

***Keywords*— (di) Glycine chloride of Barium and Magnesium crystals (DGCBM), PXRD, FT -IR, UV- Vis analysis, Kurtz and Perry method, NLO**

I. INTRODUCTION

All amino acids have a chiral symmetry and crystallize in non-centrosymmetric space groups, that make them good choice for a variety of applications in telecommunication, optical computing, optical data storage, chemical engineering, information processing etc. [1-2].

Nonlinear optics (NLO) is the study of the modified electro-magnetic field, altered in phase, frequency, amplitude, or any other propagation characteristics, because of the interaction of the field with the propagation medium. It became one of the key interests for many researchers after the discovery of second harmonic generation in quartz crystal [1], which in turn galvanized a series of studies for the synthesizing of various novel materials showing great nonlinear optical properties; in pursuit of replacing electrons with photons in future photonic devices [3-7].

The ubiquitous amino and acid groups in amino acids make them a good choice for many researchers to investigate different non-linear properties and to grow novel Non- Linear Optical (NLO) materials of various photonic applications. Among the various amino acid crystals, glycine, being the simplest compound, became a prime focus for several researchers [8-18]. In addition to that, many research studies proved that the addition of impurities will improve the material properties of the crystal as well [19-22].

In the present study, an attempt is made to develop novel crystals of good nonlinear properties.

II. MATERIALS AND METHODS

A. *Crystal growth*

Single crystals of the desired sample have been prepared by solvent evaporation technique. At first, pure glycine A grade crystals were dissolved in double distilled water and stirred continuously until the salts were fully dissolved. Barium chloride salts were added to this solution and stirred continuously for about an hour to get a clear solution. To this solution, magnesium chloride ($MgCl_2$) crystals were added and stirred using a magnetic stirrer, to obtain a homogenous solution. The resultant solution was filtered using Whatman Filter paper, to remove the solid impurities and then, allowed to evaporate at room temperature. Good transparent seed crystals were harvested in a period of 4 weeks. The seed crystals were taken and kept in mother solution at room temperature, to obtain crystals of required size. Figure 1 shows the image of the grown (di)Glycine chlorides of Barium and magnesium (DGCBM crystals.

$$\mathrm{MgCl_2 + 2C_2H_5NO_2 + BaCl_2 \rightarrow MgCl_2.(C_2H_5NO_2)_2.BaCl_2}$$

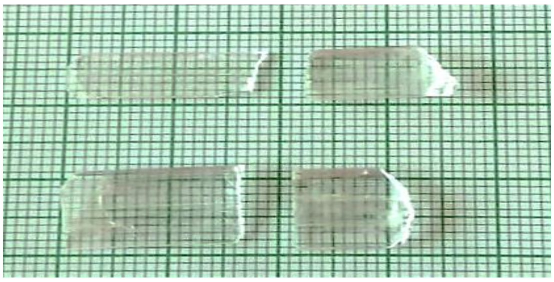

Figure 1: di Glycine chloride of barium and Magnesium crystals

III. RESULTS

A. *Powder X ray Diffraction*

Powder X ray Diffraction (PXRD) studies were carried out using Bruker D2 phaser instrument with Cu K-alpha source (wavelength- 1.5406 A°) in the range 0°-100℃. The powder X ray diffraction pattern for DGCBM crystals been shown in figure (2) shows a good crystallinity of the crystal.

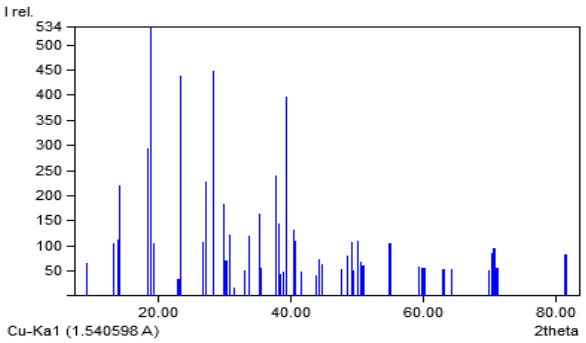

Figure 2: XRD of titled crystal.

The crystal parameters are determined using Xpert High score and are listed in the table (1) below.

TABLE 1 CRYSTAL PARAMETERS OF THE TITLED CRYSTAL

Crystal parameter	***a A°***	***b A°***	***c A°***	***α***	***β***	***γ***	***Volume***	***Crystal system***
DGCBM *crystals*	6.683	6.683	19.3	90°	90°	90°	862.1	tetragonal

B. FTIR studies

The FTIR spectrum of DGCBM crystal is analyzed using Bruker-alpha FTIR spectrophotometer revealed at room temperature in the range of 400-4000 $cm^{-1}$and is shown in Figure (3) and all the functional group assignments are summarized in Table. 2.

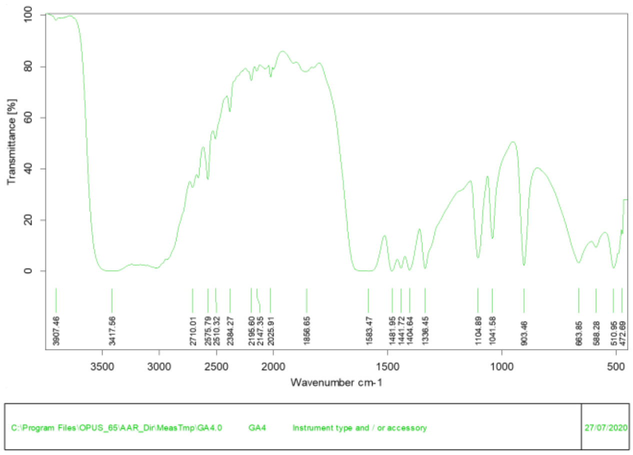

Figure 3: FTIR spectra of the crystal

TABLE 2: FTIR BAND ASSIGNMENTS OF THE TITLED CRYSTAL

Wavelength cm^{-1}	assignments
510.95	Carboxylate group
588.28	NH_3^+torsion
663.85	C-Cl stretching
903.6	Carboxylate group
1041	C-C-N C symmetric stretching
1104.89	Absorption due to NH_2^+
1336.45	COO group
1404.64	COO- symmetric stretching
1441	NH_2 deformation
1481.85	NH_3^+stretching
1583.47	NH_3^+ deformation
2710.01	CH_2 group
3417.56	N-H stretching vibrations

The absorption due to carboxylate group of free glycine is observed at 504.2 cm^{-1}, 892.8 $cm^{-1}$and 1614 cm^{-1} respectively. In $MgCl_2$ doped DGBC crystals, these peaks are shifted to 510.95, 903.6 and 1583.47 cm^{-1} respectively. Similarly, the absorption peaks due to NH_2^+ group of free glycine are observed at 1131 $cm^{-1}$and 1505 cm^{-1}respectively. In $MgCl_2$ doped DGBC crystals, these peaks are shifted to 1104.89 cm^{-1}1 and 1441.72 cm^{-1}respectively. In the same manner, the other peaks at 1481.85cm^{-1}, 2710.01 $cm^{-1}$and 3417.56 cm^{-1} are attributed to NH_3^+ group and CH_2 and N-H stretching vibrations respectively from a comparison of the spectra with that of glycine.[23].

C. Optical Studies

1) linear optical properties

The UV-Visible spectrometer from Perkin Elmer Lamda 935 was used to study the linear optical properties of the titled crystal. In UV spectral studies the optical transmittance window, the transparency and the lower cutoff wavelength is very important for the realization of SHG output in the range using diode laser. When the samples are transparent, an attempt is made to record the region in which they behave as nonlinear optical material. The ultra -violet spectra were therefore recorded from 190nm to 1100nm. If the maximum wavelength i.e., λ_{max} lies within this region, the existence of wide transparency window indicates material of NLO properties which find applications in electronic industries. For the titled compound, the λ_{max} is found to at 191nm. This remarkably low absorption property in the entire visible region, makes the compound a suitable material for optoelectronic, NLO, window materials in optical instruments, second harmonic generation and parametric oscillations applications [10-11].

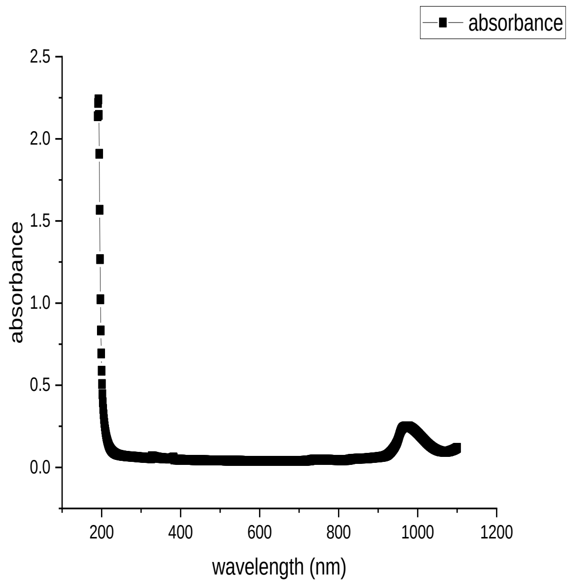

Figure 4: UV- Vis spectra of the titled crystal

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For a direct band gap crystal, the optical band gap energy (E_g) can be calculated using the Tauc relation:

$$(\alpha h\nu)^2 = A(E_g - h\nu) \text{ ....(1)}$$

Where α is the absorption coefficient. The variations of $(\alpha h\nu)^2$ versus hν in the fundamental adsorption region are plotted in Fig. 5 and E_g can be evaluated by extrapolation of the linear part [24,25].

The band gap is found to be 6.2 eV. This high band gap value indicates that the grown crystal possesses dielectric behavior to induce polarization when powerful radiation is incident on the material**.**

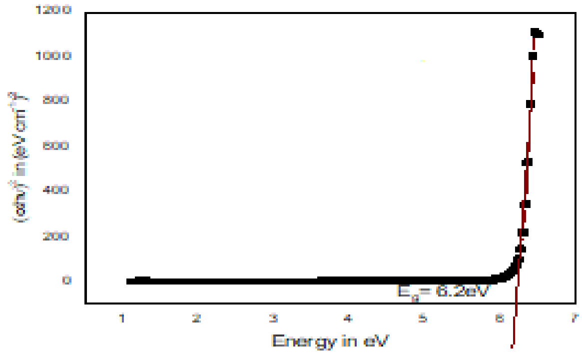

Figure 5: Tauc's plot

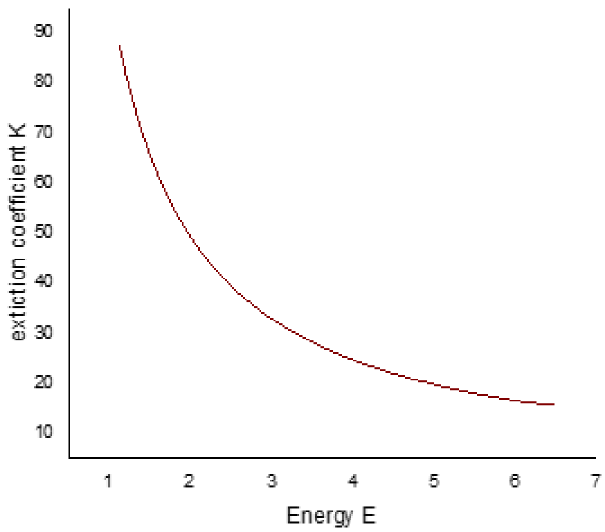

Figure 6: extinction coefficient spectra

The extinction coefficient of the crystal can be calculated by the Swanepoel's equation,

$$K = \frac{\lambda\alpha}{4\pi} \text{ ....(2)}$$

The extinction coefficient describes the loss of wave energy to the material [26,27]. The graph of extinction coefficient versus energy graph shows an exponential decay.

2) Nonlinear optical properties

SHG conversion efficiency measurements of the grown crystals have been carried out using Kurtz and Perry technique [28]. It is a popular and powerful tool for the initial screening made to evaluate the conversion efficiency of NLO material. When barium chloride crystals are added to pure Glycine, the relative SHG efficiency is reported to have 0.5 times that of KDP crystal [22]. When Magnesium Chloride is added to pure glycine, the conversion efficiency reduces to half of KDP [14]. In the present study, it has been noticed that, when Magnesium Chloride is added to DGBC crystal, the crystal showed zero conversion efficiency. To investigate the nature and magnitude of path dependent third order refraction nonlinearity in the crystal, Z scan analysis should be employed.

IV. Discussions

Present study attempts to investigate the structural and optical properties of glycine chlorides of magnesium and barium. The crystalline properties are studied by PXRD, and it is found that, the compound crystallizes in tetragonal system. The FTIR spectrum is used to analyze various functional groups in the compound. The compound shows wide transparency window, that showcases the nonlinear properties of the compound. The band gap energy and the extinction coefficient of the compound are determined from the UV- Vis spectra. The non - linear optical properties of the compound is yet to be determined using Z scan technique.

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