

Synthesis, Experimental and Theoretical Investigations on Bis Glycine Lithium Molybdate Single Crystal

A. Chitra, and J. Madhavan
Department of Physics, Loyola College, Chennai-34.

Abstract - Optically transparent nonlinear single crystal of Bis Glycine Lithium Molybdate (BGLM) has been grown by adopting slow evaporation solution growth technique at room temperature. To reveal the microscopic nonlinear optical properties, the first-order hyperpolarizability (β) was evaluated by using the density functional theory (DFT) quantum chemical calculations at B3LYP. The Fourier transform infrared (FT-IR) spectroscopic studies were performed for identifying different functional groups present in the compound.

Keywords - organic compound; FT-IR; NLO

I. INTRODUCTION

Nonlinear optical (NLO) materials utilize the nonlinear dependence of the refractive index on the applied electric field to bring forth other frequencies. The added esteem of nonlinear optical materials over lasers and electro-optics became preponderant from the early days of lasers [1]. Organic crystals with the required conjugated π electrons are attractive candidates, because of the large nonlinear optical coefficients. Their practical applications are limited by poor chemical stability due to the presence of large π -conjugated system, which causes the red cut-off wavelength [2]. In this present investigation single crystal of BGLM were grown from its aqueous solution by solvent evaporation method. The grown crystals were characterized by the Kurtz and Perry powder SHG test which was performed to confirm the second order nonlinearity of the grown crystal. A detail analysis of the molecular structure of BGLM is described along with the DFT calculations.

II. EXPERIMENTAL DETAILS

Synthesis and Solubility of BGLM

Single crystal of BGLM was synthesized by dissolving AR grade Glycine (Merck) and Lithium Molybdate (Sigma Aldrich) in the ratio of 2:1. The chemical reaction that takes place in this process is as follows



Synthesized salt was used to measure the solubility of BGLM in water. Figure 1 shows the solubility curve of BGLM. The supersaturated solution of BGLM was prepared in accordance with the solubility data (Figure 1). Single crystals of BGLM were grown from their aqueous solution using slow solvent evaporation technique. The solvent was allowed to evaporate and numerous tiny crystals were formed due to spontaneous nucleation. The transparent and defect free ones among them were chosen as the seeds for growing bulk crystals. Good optical quality crystals of dimension up to $9 \times 5 \times 7 \text{ mm}^3$ were harvested after a period of 20 - 30 days. The photograph of as grown crystal of BGLM is shown in Figure 2.

III. RESULTS AND DISCUSSION

X-ray diffraction analysis

The grown BGLM sample was crushed as fine powder for X-ray diffraction studies. The recorded X-ray diffraction pattern of BGLM sample is depicted in Figures 3. The recorded spectrum of the sample was taken at room temperature in a 2θ range of 10 to 40° using Cu $K\alpha$ radiation of wavelength 1.5418 \AA . It is confirmed that BGLM belongs to monoclinic crystal system, the unit cell parameters were found to be $a = 5.1924 \text{ \AA}$, $b = 7.7339 \text{ \AA}$ and $c = 12.492 \text{ \AA}$ with space group $P2_1$.

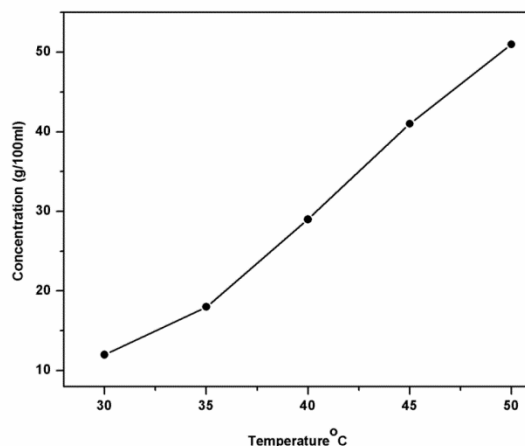


Figure 1 The solubility curve of BGLM



Figure 2 Photograph of as grown BGLM single crystal

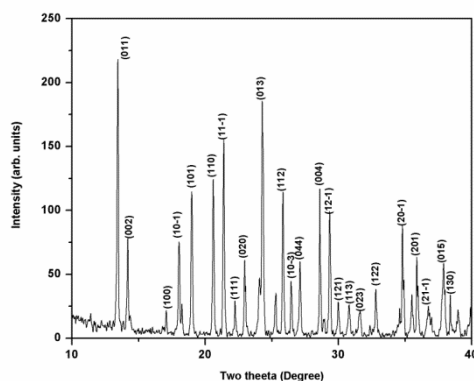


Figure 3 Powder XRD spectrum of BGLM crystal

Hyperpolarizability

The non-linear optical properties play an important role for the design of materials in modern communication technology, signal processing, optical switches and optical memory devices [3]. The non-linear optical properties of the organic molecules arise from delocalized π electrons that move along molecule. The increase of the conjugation on molecule leads to an increase in its nonlinear optical properties. One another way to increase non-linear optical properties is to add donor and acceptor groups. If the donor and acceptor groups are powerful, delocalization of π electron cloud on organic molecules increases and as a result of this the polarizability and first hyperpolarizability of organic molecules increases. The energy gap between HOMO and LUMO has an important role in getting polarizability of a molecule [4]. The increment of the strength of the donor and acceptor groups increases the non-linear optical properties of organic molecules due to the decrease in energy gap between HOMO and LUMO. First-order molecular hyperpolarizability is a third rank tensor that can be described by $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [5]. The calculated first hyperpolarizability β of BGLM is 5.9552×10^{-30} esu that is greater than that of urea (0.37289×10^{-30} esu), respectively. The calculated first order hyperpolarizability values for BGLM molecule are given in Table 1.

Table 1 The electric dipole moment μ , the average polarizability α_{tot} and First hyperpolarizability β_{tot} for BGLM

B3LYP/ 6-31G	
Dipole Moment in Debye	
μ_x	3.8956
μ_y	35.4745
μ_z	0.9639
μ_{tot}	35.7007
Polarizability in esu	
α_{xx}	147.4888264
α_{xy}	4.1253429
α_{yy}	102.3204407
α_{xz}	-0.9479697
α_{yz}	-0.7173573
α_{zz}	129.1563448
α_o	1.057×10^{-30}
Hyperpolarizability in esu	
β_{xxx}	-472.3058991
β_{xxy}	77.2129714
β_{xyy}	107.2712246
β_{yyy}	234.0803929
β_{xxz}	282.1170072
β_{xyz}	1.1352191
β_{yyz}	52.789851
β_{xzz}	38.5433817
β_{yzz}	-32.7550759
β_{zzz}	232.6587879
β_{tot}	5.9552×10^{-30}

FT-IR Analysis

FT-IR spectrum of the grown crystal was recorded in the range 500 cm^{-1} to 4000 cm^{-1} , using KBr pellet technique on BRUKKER IFS FT-IR Spectrometer. The experimental FT-IR is presented in Figure 2.6.

NH_3^+ group vibration

In zwitterionic molecules, the NH_3^+ asymmetric and symmetric stretching bands appear in the region 3330 cm^{-1} and 3080 cm^{-1} respectively [6]. The present assignment 3359 cm^{-1} agrees with the values available in literature [7]. The NH_3^+ asymmetric deformation vibrations usually appear in the region $1660\text{-}1610 \text{ cm}^{-1}$ and the symmetric deformation in the region $1550\text{-}1485 \text{ cm}^{-1}$ [8]. The peaks at 1603 cm^{-1} , 1650 cm^{-1} are assigned to NH_3^+ asymmetric deformation vibrations.

Carboxylate group vibrations

The asymmetric and symmetric stretching modes of carboxylate ion vibrations expected to occur at $1650\text{-}1550 \text{ cm}^{-1}$ and around 1440 cm^{-1} respectively [9]. The peaks at 1603 cm^{-1} and 1650 cm^{-1} are assigned to asymmetric stretching. Peak at 1408 cm^{-1} is assigned to symmetric stretching modes of carboxylate ion. The carbonyl stretching mode is simultaneously influenced by the conjugation of $\text{C}=\text{O}$ and $\text{C}=\text{O}$ with amino nitrogen and the intermolecular hydrogen bonding. The unusual lowering of the carboxylate asymmetric stretching wavenumber is also contributed by the electron releasing effect of the $\text{C}=\text{O}$ bond in the acceptor subunit due to intermolecular charge transfer effect and π conjugation which plays an important role in the NLO activity [10]. COO^- deformations are usually expected to occur in the region $650 \text{ cm}^{-1}\text{-}510 \text{ cm}^{-1}$ [11]. The deformation peaks appear at 516 cm^{-1} , 527 cm^{-1} and 586 cm^{-1} .

SHG efficiency studies

SHG efficiency of the grown BGLM crystal was determined by Kurtz-Perry powder technique with Potassium dihydrogen phosphate (KDP) crystal as reference material. The crystalline sample was taken into very fine powder and tightly packed in a micro capillary tube. Then the tube was placed in the path of Nd:YAG laser beam of wavelength 1064 nm with 8 ns pulse width and 10 Hz pulse rate. When KDP crystal in the form of powder was used as a reference material, the transmitted laser beam voltage was 24 mV . For the BGLM crystal the output voltage was 29 mV . Hence the SHG efficiency of BGLM crystal is 1.5 times of KDP crystal.

CONCLUSION

Single Crystals of Bis Glycine Lithium Molybdate (BGLM) of dimension $9 \times 5 \times 7 \text{ mm}^3$ are conveniently grown by slow evaporation technique at room temperature. A solvent of deionized water is used for the growth process. The powder XRD analysis proves that BGLM crystal belongs to monoclinic in structure with a noncentrosymmetric space group $P2_1$.

IV REFERENCES

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