Computational Study And Physicochemical Properties of A Potential NLO Crystal: Bis-Glycine Lithium Molybdate

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Abstract **- Good quality single crystals of Bis (glycine) lithium molybdate (BGLM), a semi organic NLO material have been successfully grown up to a size of 11mm x 10mm x 8mm. The crystals have been grown by slow solvent evaporation at room temperature from its aqueous solution. The DFT computations are performed with Gaussian 03 software program using the HF/6-31G (d, p) basis set to predict the molecular structure and vibrational wavenumbers. Optimized bond lengths and angles of the title molecule have been obtained. The molecular geometry, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) explains the charge transfer interactions taking place within the molecule. Melting point and the decomposition temperature of the grown crystal was premeditated from the thermal analysis. The UV–Vis studies recognized the optical transmittance window and the lower cut off wavelength of the BGLM crystal and thus it could be performed as a NLO material. The mechanical stability of the grown crystal was tested with Vicker's micro hardness tester and the work hardening coefficient of the grown material was estimated.**

KEYWORDS: BGLM, DFT, HOMO, LUMO, UV-VIS, NLO

I. INTRODUCTION

Compared to organic NLO crystals, Semi organic nonlinear optical (NLO) crystals are attracting a great deal of attention due to their high NLO coefficient, high damage threshold and high mechanical strength [1]. Complexes of amino acids with inorganic acids and salts are promising materials for optical second harmonic generation, as they tend to combine the advantages of the organic amino acid with that of the inorganic acid/salt [2]. When compared to inorganic materials, organic materials possess a high degree of nonlinearity due to π conjugation and high laser damage threshold. Simple salts of amino acids are compounds which consist of singly or doubly protonated cations of one type of amino acid and one type of anion. The majority of salts out of all the amino acids are found in the simplest amino acid glycine, except amino acids forming doubly charged cations. It is expected that hydrogen bonds have an effect on the physical properties of a crystal such as mechanical hardness, melting point, and chemical stability.Organic crystals with the required conjugated π electrons are attractive candidates, because of the large nonlinear optical coefficients. Nonlinear optical (NLO) materials are attracting a great deal of attention because of their use in optical devices. There is a great need for device quality single crystals for the materials which exhibits second order NLO effects [3, 4].

In the present investigation, single crystals of Bis Glycine Lithium Molybdate were grown by slow evaporation method and the computational study was made by using Gaussian03 program. Optical property, mechanical property and thermal stability were determined by Optical study, Hardness test and TG/DTA respectively.

II. EXPERIMENTAL DETAILS

A. SYNTHESIS METHOD

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

$2[C_2H_5NO_2] + Li_2MoO_4 \rightarrow Li_2Mo(C_2H_5NO_2)_2O_4$

Solubility and temperature plays a vital role in the rate of growth of crystals. The solubility data of a material governs the amount of material, which is available for the growth and hence, defines the total size limit. Solvent and solubility factor define super saturation, which is the driving force for the rate of crystal growth. Hence, investigating the solubility in a particular solvent is an essential criterion for a material to grow as a good quality crystal.

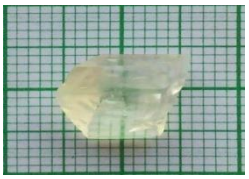

Figure 1: Photograph of as grown BGLM single crystal

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 to11 x 10 x 8 mm^3 were harvested after a period of 90 days. The photograph of as grown crystal of BGLM is shown in Figure 1.

III. RESULTS AND DISCUSSION

A. Molecular Geometry

The structural detail of BGLM with numbering of atoms is shown in the Figure 2. From the structural point of view, the molecular compound belongs to C_1 point group symmetry. The bond length and bong angles are listed in table 1 and table 2.

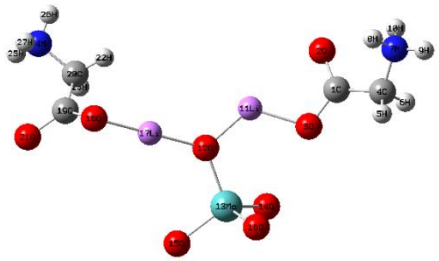

Figure 2: Atomic numbering system of BGLM molecule

Table1: Selected bond lengths

S.No	Bondlength(A°)	Gaussian
1	C1-O2	1.430
2.	O2-O3	2.476833
3.	O3-H5	2.684824
4.	C4-N7	1.470000
5.	H5-H9	2.363932
6.	H6-H8	2.911016
7.	N7-H9	1.000000
8.	H8-H10	1.632993
9.	H9-H10	1.632993
10	H22-N24	2.086720

Table 2: Selected bond angles

S.No	Bond angle(°)	Gaussian
1.	O2-C1-O3	120
2.	H5-C4-N7	109.4712
3.	O3-Li11-O12	120
4.	Li11-O12-Mo13	109.4712
5.	Mo13-O12-Li17	125.2644
6.	O18-C19-O21	120
7.	C20-N24-H26	109.4712
8.	H26-N24-H27	109.4712
9.	C20-C19-O21	120
10.	Li11-O12-O18	125.2644

B. Computational Details

The optimized molecular structure of the prepared compound calculated theoretically by computational method. GAUSSIAN 03 software was used for theoretical calculation. The quantum calculations were performed applying DFT method with Beeke-3-Lee-Yang-Parr(B3LYP) supplemented with standard 6-31 G(d ,p) basis set without any constraint on the geometry [5]. The wavenumber calculations gave positive values for all the obtained wavenumbers which confirms the stability of the optimized geometries.Experimental and Calculated B3LYP/6-31 G (d, p) level of vibrational frequencies of BGLMis shown in table 3. By combining the theoretical results vibrational frequency assignments were made with a high degree of accuracy.

Table: 3 Experimental and Calculated B3LYP/6-31 G (d, p) level of vibrational frequencies of BGLM

S. No.	Frequency cm^{-1}		Spectroscopic assignment	Force constant	Reduced mass
	B3LYP	Expt.			
1.	485.5630	481	COO^-opd+CC wag	0.1411	1.0157
2.	560.1011	516	COO^-d+COO^-opd	1.4598	7.8979
3.	568.8410	527	COO^-d+COO^-opd	0.9681	5.0778
4.	593.3596	586	COO^-d+COO^-opd	2.1421	10.3266
5.	663.0053	662	COO^- opd+NH_2 wag	0.9381	3.6221
6.	865.0129	899	CH_3opb	2.0122	4.5642
7.	948.5440	932	C=O opd	0.7892	1.4887
8.	1045.4735	1036	PhI	3.0255	4.6981
9.	1154.5393	1123	PhI	4.3137	5.4926
10.	1155.2533	1137	NH_2 v	4.5614	5.8008
11.	1468.3121	1408	COO^- symst	1.5337	1.2074
12.	1472.5870	1481	CC st(bz)+C=C st	1.5761	1.2336
13.	1627.6423	1603	NH_3^+asy d	1.6712	1.0707
14.	1646.9576	1650	NH_3^+asy d	1.7229	1.0781
15.	3359.0051	3009	NH_3^+asyst	7.0325	1.0579

asyst-asymmetric stretching, symst-symmetric stretching, asy d-asymmetric deformation, d-dformation, st-stretching, st&b-stretching&bending, wag-wagging, st(hyd)-hydroxyl stretching, opb-out of plane bending

IV. HOMO-LUMO energy gap

Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the main orbital take part in chemical stability [6]. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The HOMO and LUMO energy calculated by B3LYP/6-31G (d, p) method as shown in Figure 3.

HOMO energy (B3LYP) = -0.343 a.u.
LUMO energy (B3LYP) = -0.167 a.u.
HOMO–LUMO energy gap (B3LYP) = 0.175 a.u.

The HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule.

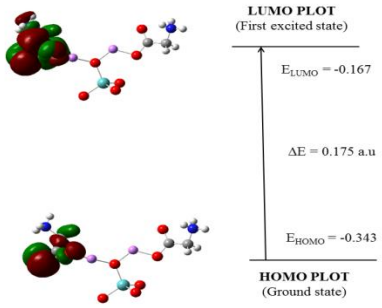

Figure 3: HOMO – LUMO plot of BGLM at B3LYP/6-31G (d, p)

A. Optical absorption spectrum

The optical absorption spectra of BGLM crystal were recorded in the range 200-1100 nm. Figure 4 shows the UV Vis spectra of the BGLM crystal. The optical cut off wavelength was found to be 320 nm. The UV spectrum shows the presence of a wide transparency window in the entire visible and the IR region which is highly suitable for NLO applications second harmonic generation, frequency doubling, etc [7]. The band gap energy was calculated from linear part of the Tauc's plot drawn between $(\alpha h\nu)^2$ and $h\nu$. The band gap energy of BGLM was found to be 3.45 eV in Figure 5.

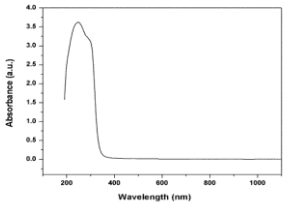

Figure 4: Optical absorption spectrum of BGLM crystal

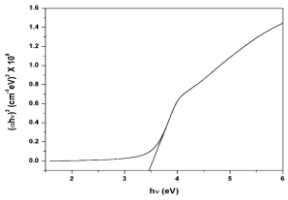

Figure 5: Optical band gap of BGLM crystal

B. Thermogravimetric analysis

Thermal analysis was performed using TG/DTA instrument in nitrogen atmosphere with heating rate of 10 °C/min. Figure 6 shows TG/DTA spectra for the BGLM crystal. It is observed from the figure that the decomposition takes place in three stages and no weight loss was observed in the temperature range between 36 °C and 200 °C. In the first stage, the material starts to dissociate at 200 °C. A weight loss of 18.14% was observed between 200 °C to 340 °C. The second decomposition stage was observed between 340 °C and 600 °C with 19.48% weight loss of the compound indicating the decomposition and burning of volatile gases produced from the thermal degradation. The third stage of weight loss of 17.89% was observed from 600°C to 870 °C is due the change of the structure of the material.

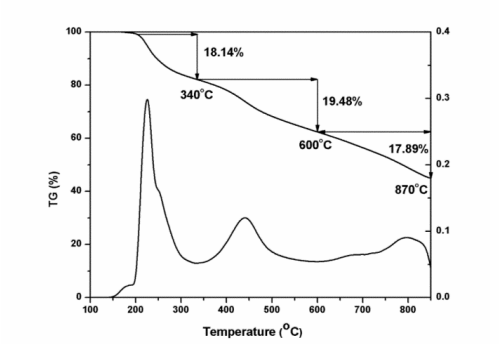

Figure 6: TGA and DTA curves of BGLM crystal

In the DTA curve, prominent endothermic peaks were observed for the title compound. The First endothermic sharp peak was observed at 200 °C which is the melting point of the compound. The second and third endothermic peaks at 450 °C and 810 °C were observed respectively. TGA/ DTA studies confirm that the crystal is stable up to 200 °C without any decomposition of the molecules and hence it is useful for optical device applications up to the temperature 200°C.

C. Microhardness studies

Vicker's microhardness indentations were made on the grown surface of the BGLM crystal at room temperature with the load ranging from 10 to 50 g with a constant indentation time of 10 s for all the trials.Using a calibrated micrometer attached to the eye piece of the microscope, diagonal lengths of the indented impressions weremeasured for various loads. Several indentation trials were made on BGLM. The average value of the diagonal lengths of the indentation mark for each load was used to calculate the hardness. The variations of H_v for various applied loads are plotted in Figure 7. The graph indicates that the microhardness number decreases with the increasing load. The decrease in microhardness number with the increasing load satisfies normal indentation size effect (ISE). The work hardening coefficient (n) was found to be 1.66 (Figure 8). According to Onitsch, if $n > 2$, the microhardness number Hv increases with increasing load and if $n < 2$, Hv decreases with increasing load [8,9]. For $1.0 \leq n \leq 1.6$ the material is regarded as hard material and $n > 1.6$ for soft materials. In the present study, n was found to be greater than 1.6, thus confirming that BGLM was a soft material.

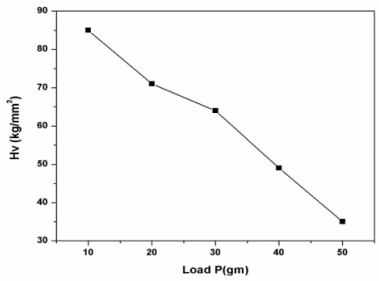

Figure 7: Variation of Vickers hardness number with load of BGLM crystal

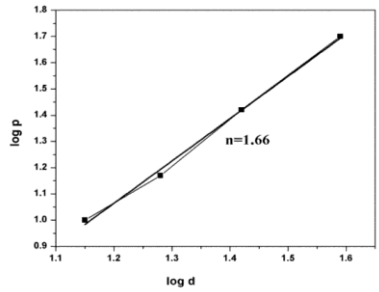

Figure 8: log d Vs log p of BGLM single crystal

V. CONCLUSION

Optically transparent single crystals of Bis Glycine Lithium Molybdate (BGLM)of dimension 11 x 10 x 8 mm^3 are conveniently grown by slow evaporation technique at room temperature. A solvent of deionized water is used for the growth process. Computational study was done using Gaussian 03 software program. Optical absorption studies confirm the UV cut-off wavelength of BGLM at 320 nm having better optical quality and the band gap energy of the sample is calculated and it is found to be 3.45 eV. The crystal is thermally stable up to 200 °C thus the material can be used in devices that works below this temperature. The microhardness reveals the mechanical properties of the grown crystal which is found to be a soft material. Thus, the observed results revealed that the grown BGLM crystals proved to be an attractive material for optoelectronic applications.

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