RJC
http://www.rasayanjournal.com

RASĀYAN *J. Chem.*
Vol.4, No.2 (2011), 387-392
ISSN: 0974-1496
CODEN: RJCABP

SPECTROSCOPIC, THERMAL AND OPTICAL PROPERTIES OF GLYCINE OXALATE (GOA) - AN ORGANIC OPTICAL CRYSTAL

J.Chandrasekaran[1], P.Ilayabarathi[2,*], P.Maadeswaran[3] and P.Mohamedkutty[1]

[1]Department of Physics, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore – 641 020, Tamil Nadu, India.

[2,*]Research and Development Center, Bharathiyar University, Coimbatore – 641 046, Tamil Nadu, India.

[3]Department of Physics, K S Rangasamy College of Technology, Tiruchengode – 637 215, Tamil Nadu, India.

*E-mail: ilayabarathipj@gmail.com

ABSTRACT

Glycine oxalate (GOA), an organic optical crystal has been synthesized and the grown crystals were subjected to various characterization studies such as Elemental analysis, FTIR analysis and UV-Vis-NIR spectrophotometer. The structure of the crystal was confirmed by powder X-ray diffraction analysis. The crystal exhibits the thermal stability up to 170 ºC using Thermal analysis.

Keywords: Crystal growth, thermal analysis, fourier transform infrared spectrum and optical properties.

INTRODUCTION

There is continuing research effort to develop the new organic crystal system for prospective novel phenomena and device adapted for laser frequency conversion, information control in optical circuit, light valves and optical switches. These potential utility of organic materials with large optical nonlinearity, excellent resistance to laser damage and high durability for very high frequency applications contrast with bandwidth limitations of conventional inorganic counterparts. Recently, the amino acids are found to have special feature such as molecular chairality, which secure acentric crystallography structures and the presence of weak Vander walls and hydrogen bond leads to wide transparency range in the visible and UV spectral regions and zwitteronic nature of the molecule which favour the physico-chemical stability.

Amino acids are interesting organic materials for NLO applications as they contain donor carboxylic acid (COOH) group and the proton acceptor amino (NH_2) group in them, known as zwitterions, which create hydrogen bonds, in the form of N–H+—O–C, which are very strong bonds. Hydrogen bonds have also been used in the possible generation of non-centrosymmetric structures, which is a prerequisite for effective NLO properties[1] .Although the salts of amino acids like L-arginine, L-histidine and L-proline are reported to have novel properties and the complexes of glycine with inorganic salts are not explored very much for Second Harmonic Generation (SHG) so far. Glycine is the simplest amino acid, it contain three kinds of polymorphs such as α, β, and γ, which exhibit different physical properties. From the γ-glycine posses non-centrosymmetric space group $P3_1$ and it exhibits NLO property[2,3] .In this article, we report the growth of glycine single crystals from aqueous solutions in the presence of oxalic acid as additive in equimolar ratio. The grown crystals were characterized by elemental analysis, FT-IR; powder XRD, optical transmittance spectrum and thermal analysis.

EXPERIMENTAL

Analytical grade glycine and oxalic acid taken in equimolar ratio was used to synthesize glycine oxalate (GOA) crystal. The chemical reaction of the synthesis is as follows:

$$C_2H_5NO_2 + C_2H_2O_4 \rightarrow C_2H_6NO_2^+ . C_2HO_4^- \quad (1)$$

The calculated amounts of the reactants were thoroughly dissolved in double distilled water and stirred well for about 4 hour using a magnetic stirrer to obtain a homogeneous solution. Then the solution was filtered well to remove the suspended impurities and allowed to crystallize by slow evaporation techniques. Thereby good optical qualities of colorless crystals were obtained in 25 to 30 days, which is shown in (Fig.1).

Table-1: Elemental analysis of GOA crystals.

Element	Experimental (%)	Theoretical (%)
C	29.07	26.02
H	6.60	7.05
N	9.57	11.06

Table-2: X-ray powder diffraction data of GOA crystal.

2θ(deg)	Experimental 'd' value
9.091	9.7192
12.004	7.3668
14.803	5.9794
16.332	5.4230
19.466	4.5565
21.316	4.1650
22.289	3.9853
24.583	3.6183
27.512	3.2394
28.968	3.0798
32.407	2.7604
35.501	2.5266
36.912	2.4332
37.942	2.3695
40.459	2.2277
42.369	2.1316
44.163	2.0490
49.459	1.8413
52.028	1.7563
54.222	1.6903
55.355	1.6583

RESULTS AND DISCUSSION

Elemental analysis

The percentage compositions of the constituent elements present in glycine oxalate [GOA] crystals were determined by Elementar Vario EL III instrument. The percentages of carbon, hydrogen and nitrogen are presented in Table 1. The experimental values are close to the theoretically values.

FTIR study

Fourier transform infrared radiation of GAO crystal was carried out in the middle IR between 4000 and 400 cm^{-1}, using a Thermo Nicolet, Avatar 370 Spectrophotometer and the spectrum is shown in Fig.2. A peak at 3231 cm^{-1} is due to NH_3^+ asymmetric stretching vibration. CH_2 stretching mode is observed at 3054 cm^{-1}. The sharpness of endothermic peak at 1720 cm^{-1} is due to C=O stretching of –COOH. The absorption bands at 1590 and 1507 cm^{-1} are due to NH_3^+ asymmetric and symmetric stretching mode respectively[4]. The C-N-H- symmetric bonding observed at 1318 cm^{-1}. The peak at 1109 cm^{-1} is assigned to rocking vibration of CH_2. C-N stretching mode and C-C stretching mode are observed at 1012 and 896 cm^{-1} respectively[5]. Free glycine exists as a zwitterion in which the carboxyl group is present as carboxylate ions and the amino group exists as ammonium ion. The absorptions due to the carboxylate group of free glycine are observed at around 511 cm^{-1}.

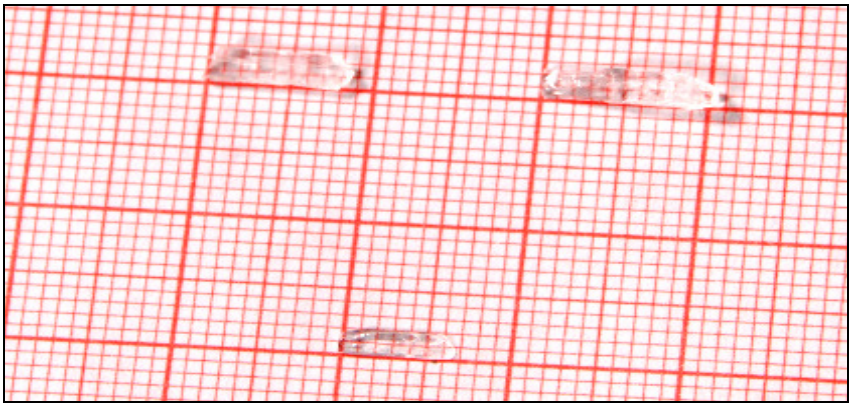

Fig.-1: GOA crystals

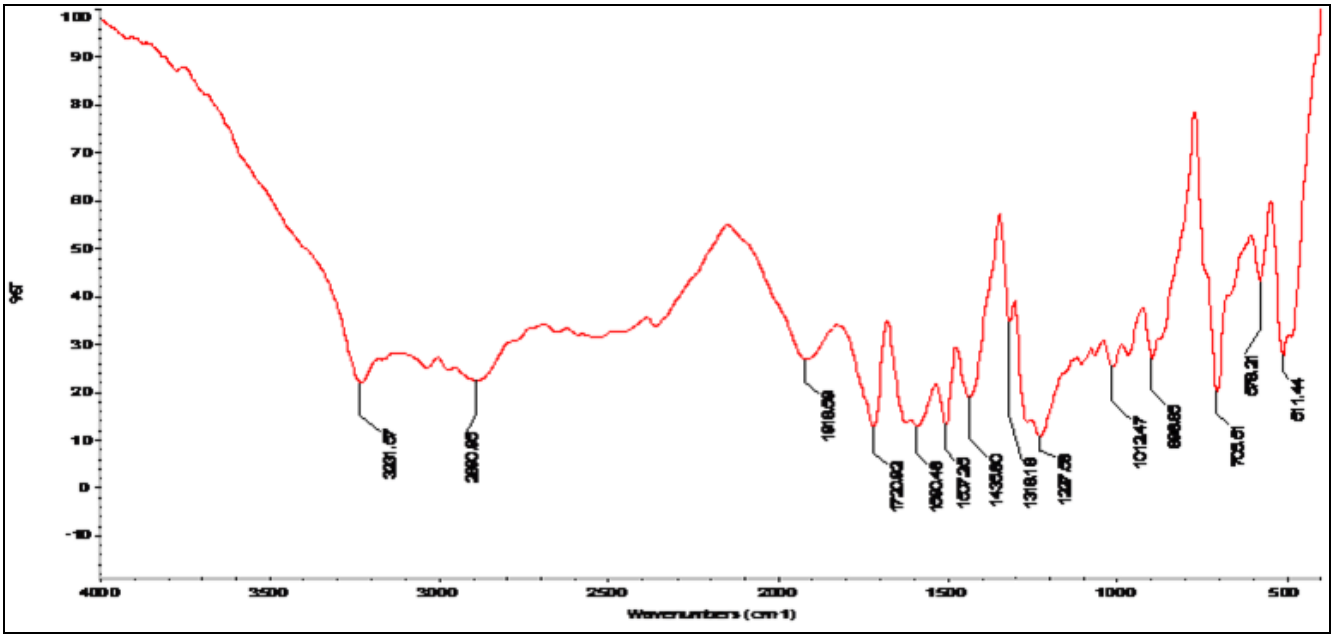

Fig.-2: FT-IR spectrum of GOA crystal

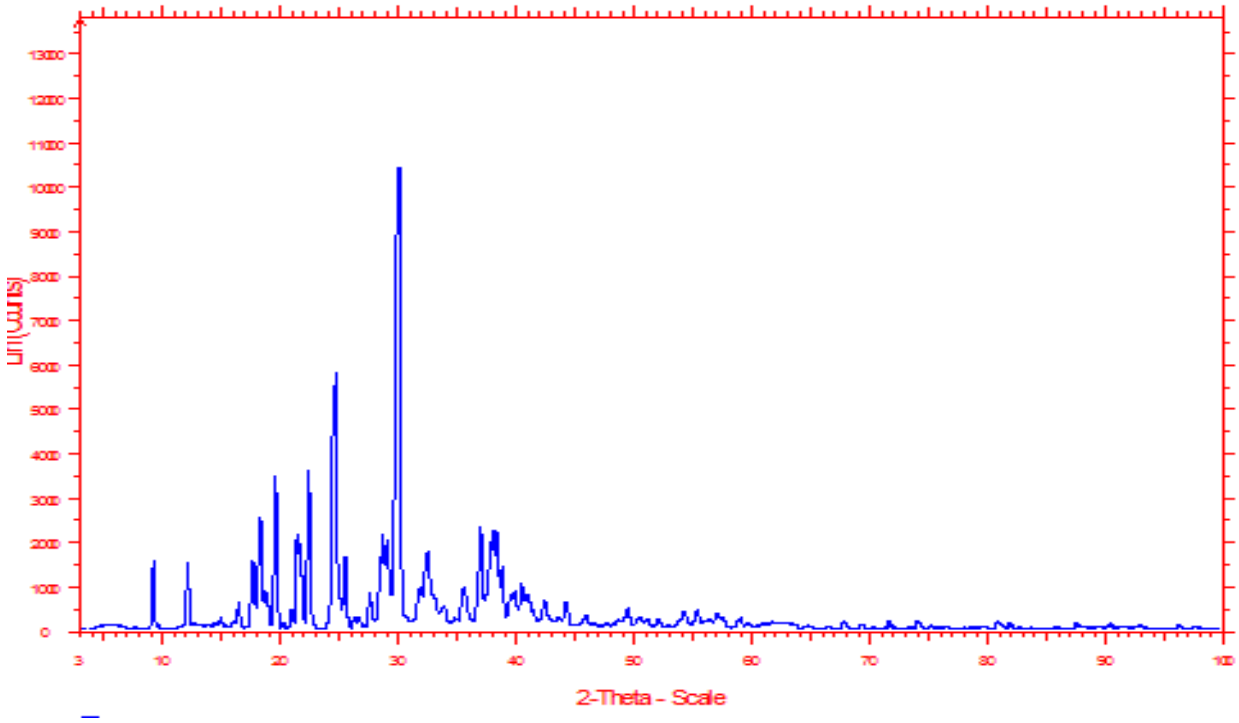

Fig.-3: X-ray powder diffraction of GOA crystal.

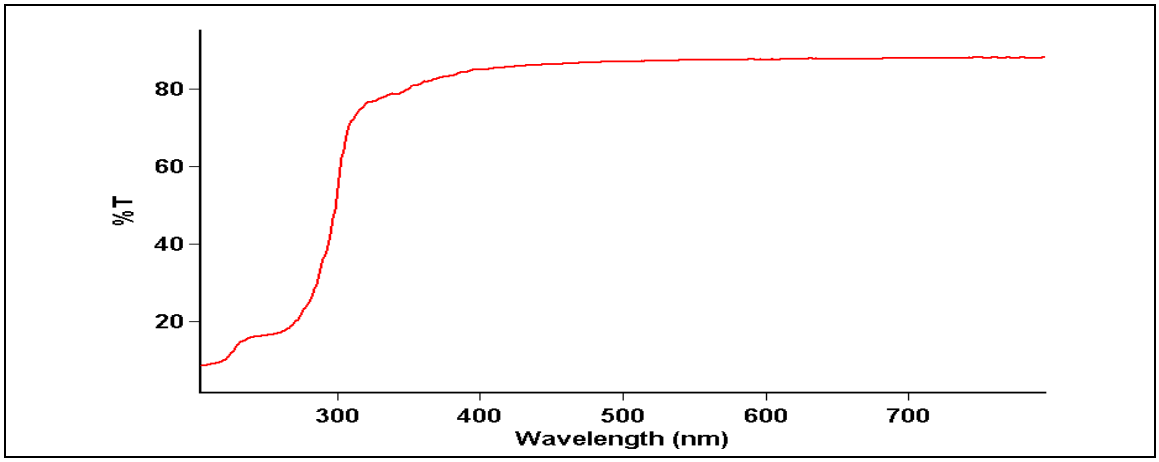

Fig.-4: Optical transmission spectrum of GOA crystal

Powder X-ray diffraction analysis

Powder XRD patterns (Fig.3) of the crystalline powder samples of GOA were recorded on a Rich-Seifert X-ray diffractometer using Bruker AXS D8 Advance Cu, Wavelength (1.5406 Å). The sample was scanned for a 2θ range of 10–80 ºC and at a scan speed of 2º C/minute. The observed 'd' values for different 2θ values of the corresponding reflective planes for the crystal are given in Table 1. The results of well defined diffraction peaks at specific 2θ angles testimonies the crystalline nature and purity of the crystal[6].

UV-Vis-NIR study

Optical transmission spectrum were recorded using (Varian, Cary 5000) in the range of 200-800nm. From the spectrum (Fig.4), it is seen that the crystal has a very low cut-off wavelength of 269 nm. The low cut-off wavelength and the wide optical transmission window are the desirous properties for NLO activity[7].

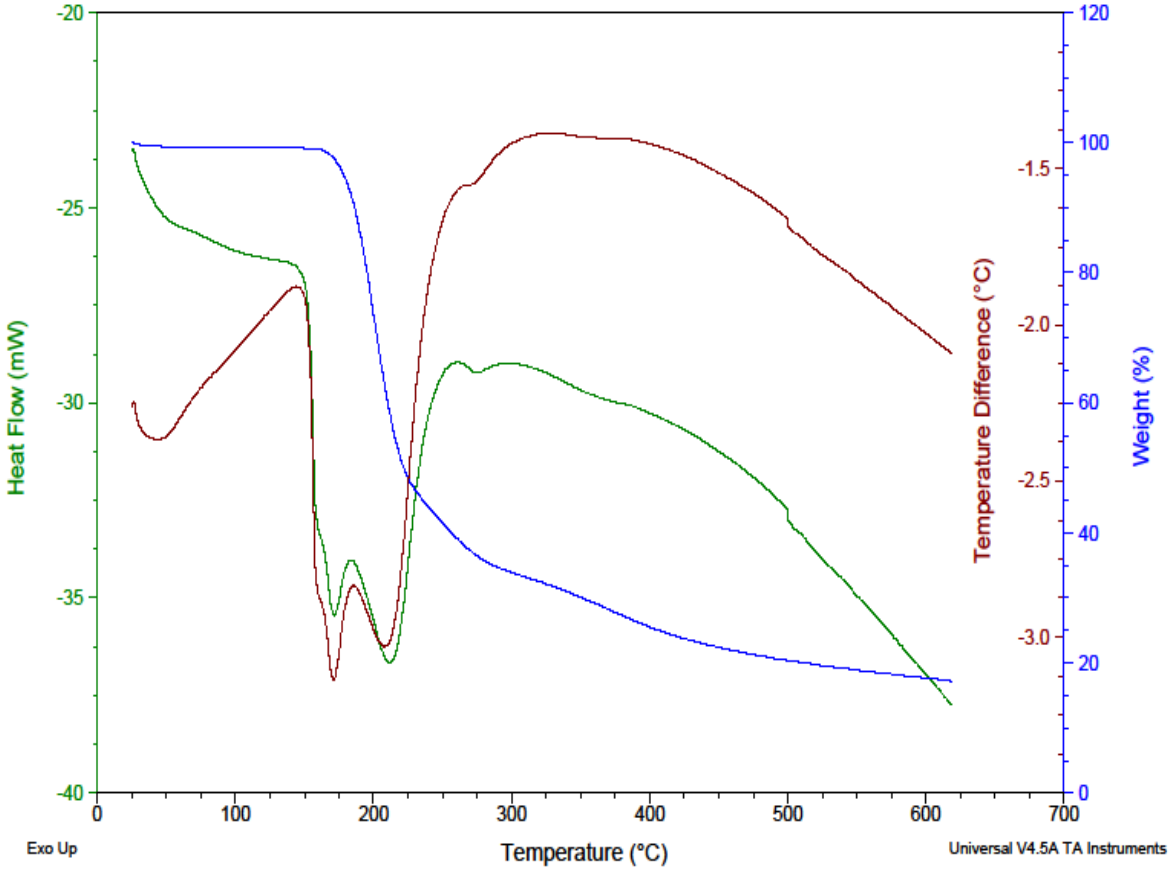

Fig.-5- TG-DTA/DSC Curve of GOA crystal.

Thermal analysis

The thermal stability of GOA crystals has been recorded using a simultaneous thermal analyzer Q600 SDT and Q20 and DSC instruments. The TG/DTA and DSC curves of GAO crystal are illustrated in Fig.5. From the DTA curve, first endothermic peak observed at 170 ºC corresponds to the melting point of GOA. The melting point is confirmed by a sharp peak at 170 ºC in the DSC trace[8,9]. The endothermic peak at 215 ºC in DTA curve is attributed to decomposition of GOA, which is also evident in the DSC curve. The TGA and DTA analysis do not show any kind of phase transition of GOA crystal. The absence of weight loss around 100 ºC in TGA response confirms that there is no crystallization of water in the molecular structure. The GOA crystal is stable up to 170 ºC and can be used for device applications up to this temperature.

CONCLUSION

Organic crystals of Glycine oxalate crystals (GOA) were grown from slow evaporation technique. The FT-IR spectrum reveals the functional groups of the grown crystals. Transmission spectra revealed that the crystal has an extended transparency cut off wavelength at 269nm. The crystalline nature was found by powder X-ray diffraction technique. The thermal studies show that the crystals good thermal stability up to 170 ºC.

ACKNOWLEDGMENTS

The authors thank sophisticated analytical Instrumentation facility (STIC), Cochin and Central Instrumentation Facility (CIF) Pondichery University, for their analytical instrument facilities.

REFERENCES

1. P.V. Dhanaraj, N.P. Rajesh, *Physica. B,* **405** ,4105(2010).
2. J. Mary Linet, S. Dinakaran, S. Jerome Das, *J. Alloys and Compounds* ,**509 ,**3832(2011).
3. P.V. Dhanaraj, N.P. Rajesh, *Physica. B,* **405,** 4105(2010).
4. T.P. Srinivasan, R.Indirajith, R.Gopalakrishnan, *J. Cryst. Growth,* **318**, 762(2011).
5. G. Anandhababu, S.K.Mohanapriya, P.Ramasamy, A.Chandramohan, *J.Cryst. Growth* **318** , 1021(2011).
6. K. Ambujam, K. Rajarajan, S. Selvakumar, I. Vetha Potheher, Ginson P. Joseph, P. Sagayaraj, *J. Cryst. Growth,* **286** ,440(2006).
7. M.M. Khandpekar, S.S. Dongare, S.B. Patil, S.P. Pati, *Optics Communications,* **284,** 1583(2011).
8. K. Ambujam, K. Rajarajan, S. Selvakumar, I. Vetha Potheher, Ginson P. Joseph, P. Sagayaraj, *J. Cryst. Growth,* **286,** 440(2006).
9. P.V. Dhanaraj, N.P. Rajesh, *Physica. B,* **406** ,12(2011).

[RJC-781/2011]