SYNTHESIS AND SPECTROSCOPIC STUDIES OF AN AMINO ACID BASED NLO CRYSTAL:GLYCINE OXALATE

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ABSTRACT

A new organic NLO crystal GOA was synthesized by slow evaporation method. Glycine and oxalic acid were combined in different molar ratios to form glycine oxalic acid (GOA) transparent crystals of sizes (2-6 cm) in 2 to 3 weeks time. The solubility studies indicates a linear increase in solubility with increase in temperature from room temp to 75 ^{0}C. The phase formation using XRD studies shows orthorhombic crystal structure. The chemical contents of the crystals were verified by CHN analysis and are seen to agree with calculated chemical unit. The presence of two hydrogen atoms belonging to NH_2 and CH_2 group have been identified in ^{1}H-NMR spectra and ^{13}C-NMR Spectra confirms the presence of CH_2 and COOH group .The IR &RAMAN assignments have been made for all the crystal and most of the peaks in IR are active in Raman indicating non-centro symmetric crystals.

Keyword: *, Glycine, oxalic acid, IR & Raman Spectra, ^{1}H-NMR & ^{13}C-NMR*

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1. INTRODUCTION

Crystal growth is a vital and fundamental part of materials science and engineering. [1-3].Organic materials are of great interest for most electronic applications and they exhibit large non-linearity enhanced NLO (non linear optical) efficiencies and structural diversity. Glycine has been the basic amino acid providing suitable matrix for many such chemical combinations of organic as well as semi-organic materials. It is interesting to grow new GOA (Glycine Oxalic acid) crystal having NLO characteristics and studying with respect to these structural and vibrational properties. An Organic crystals are made up from discrete units of organic molecules unit and these crystals are being developed with the physico-chemical stability.[4-6]. The main importance of organic NLO materials is that they are used in optical devices because of their large optical non- linearity, low cutoff wavelength, short response time and high threshold for laser power The organic NLO crystals are synthesized with non-localized Π electron system to realize nonlinear susceptibility better than inorganic crystals. The nonlinear optical (NLO) properties of organic materials are currently of great interest for application in the field of communication technologies. Owing to the tendency to replace classical electronic materials with suitable organic compound, organic crystals have non-linearity optical coefficient larger than inorganic crystals. In the field of nonlinear optical crystal growth, amino acids are playing a vital role. A number of natural amino acids exhibit the nonlinear optical properties because they have a donor NH_2 and acceptor COOH and also intermolecular charge transfer is possible [7]. α- glycine with oxalic acid forms the crystals of glycine oxalic acid .

2. GROWTH OF CRYSTALS BY SLOW EVAPORATION METHOD

Analytical reagent grade (AR) samples of glycine (NH_2CH_2COOH) and Oxalic acid $(COOH)_2$ (anhydrous) were taken in 3: 1 equimolar ratio and dissolved in double distilled water and used for growth of crystal by slow evaporation method at room temperature. The crystals were found to be stable, colorless and transparent The period of growth of crystal ranged from about 2 to 3 weeks.

3. RESULTS AND DISCUSSION

3.1 Solubility Studies

Solubility of the material in solvent decides the amount of the material, which is available for the growth and hence defines the total size limit. If the solubility is too high, it is difficult to grow bulk single crystals and too small a solubility restricts the size and growth rate of the crystals. Solubility gradient is another important parameter, which dictates the growth procedure [8]. The solubility curves for GOA crystal are almost linear within temperature limit of 303 K to 348 K

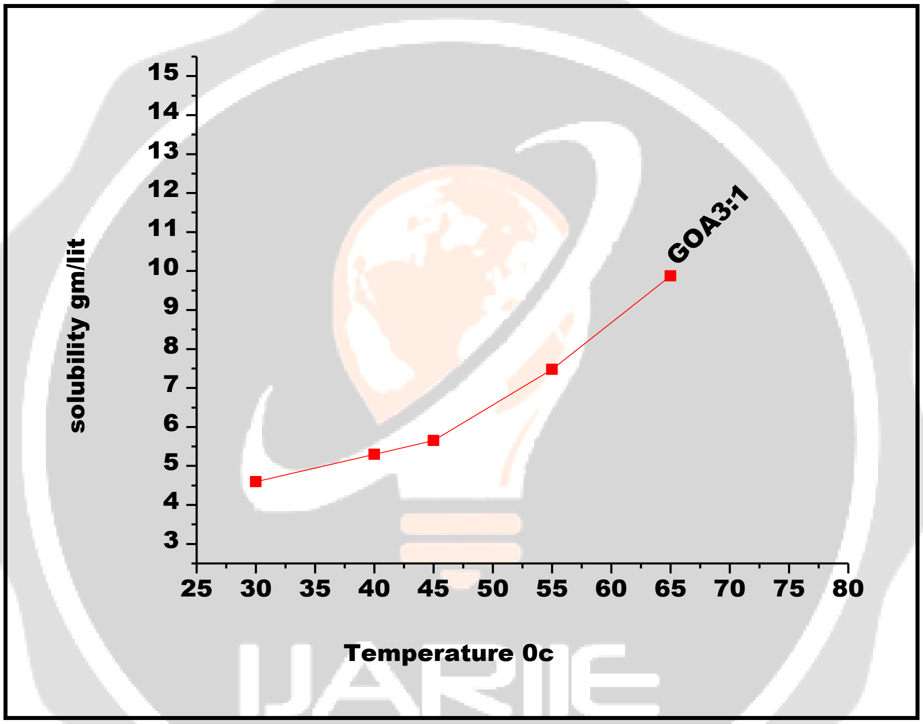

Chart- 1-Solubilty curve for GOA Crystal

3.2 Powder X-ray diffraction analysis

Powder x-ray diffraction analysis was carried out on Panalytical X-pert MPO PRO from 20 ° to 80 ^{0} with characteristics Cu-Kα radiation with λ= 1.5418 A^0. The GOA crystal belong to the orthorhombic symmetry with lattice parameters a=7.035 A^0, b=12.20 A^0, c=9.05 A^0 and volume 777.33 cc.

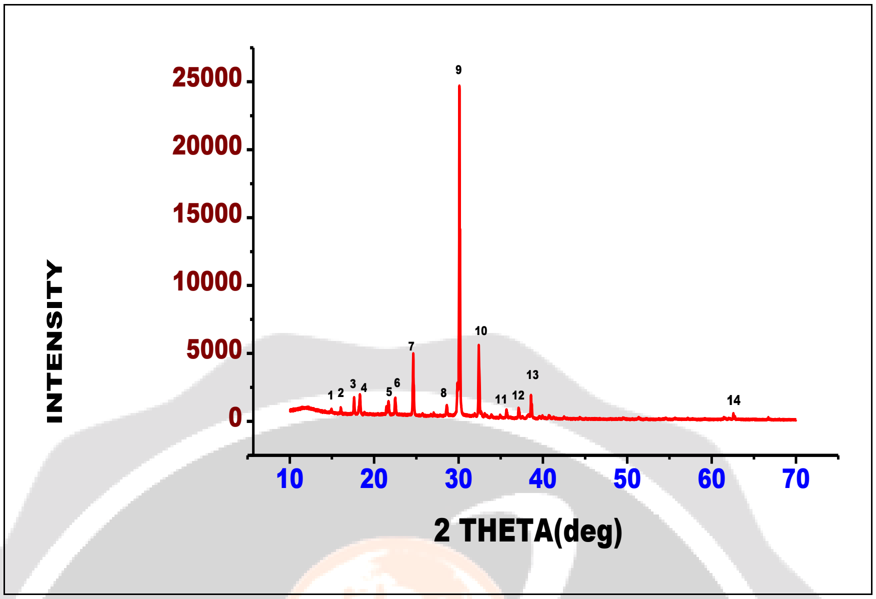

Chart- 2- X-Ray profile for GOA Crystal

3.3 CHNS Analysis

CHN analysis provides a quick and inexpensive method to check sample purity and to characterize a compound. CHN analysis is an experiment that determines the amount (typically a weight percent) of an element in a compound. The most common type of elemental analysis is for carbon, hydrogen, and nitrogen (CHN analysis).

The CHN analysis is particularly useful in determining the empirical formula of the compound and this type of analysis is especially useful for organic compounds [9].

The CHN analysis of GOA crystal was performed and the observed chemical units are seen to agree with the calculated chemical units. Table 1 below shows the percentage of respective elements in the grown materials.

Table 1 Element percentages in compound for GOA crystal

Sample	Element % in compound				Chemical formula	
GOA crystal	N%	C%	H%	O%	Calculated Formula	Observed Formula
	13.31	31.26	5.15	49.73		
					$NH_5C_3O_3$	$NH_5C_3O_3$

3.4Infrared & Raman Spectra Analysis

Infrared spectra have been an important tool to check the purity of its components, for the confirmation of salt formation, study of bonding in the crystals, the nature of glycine molecule in the complex and for the study of water of crystallisation [10].

The IR spectrum of the grown crystals was therefore taken in the range of 450 cm^{-1} to 4000 cm^{-1}, which is a characteristic range used for most of the organic samples. For spectroscopic measurements powdered crystals were mixed with KBr (spectroscopic grade) and pressed to form pellets. The Infrared spectra of glycine molecule acts as a standard, so initially glycine was subjected to infrared absorption and the assignments of fundamental groups were made in accordance with those reported. Such assignments were then used for the interpretation of fundamental vibrations of our new GOA crystal.The IR assignments were further confirmed by Raman studies; in the range 30 cm^{-1}to 3000 cm^{-1}.

Comparison of IR and RAMAN assignments are shown in tables 2 for GOA and their respective profiles are shown in figure 3 and 4 for GOA. The broad bands in the higher energy region between 3107 and 2170 cm^{-1} are due to NH_3^+ stretching vibration. The leading edge of N-H stretch at 3769 cm^{-1} in glycine shifted to about 63 cm^{-1} and 606 cm^{-1} remain unaffected by bending. Similarly no effect in frequency maxima of rocking, twisting and scissoring vibrations of CH_2 group is recorded. The COO^- antisymmentric stretch at 1610 cm^{-1} is clearly seen to split, apart from being weak and over lapped by NH_3^+ deformation vibrations showing co-ordination. The amino acid region from 2000 cm^{-1} to 3000 cm^{-1} is also seen to be affected upon by co-ordination [11-12]. For the characteristic amino acid absorption, the bands attribute to NH_3^+ groups and COO^- group exhibited absorption maxima, indicating the glycine molecules in Zwitterionic form and the absence of bands in region 870 cm^{-1} due to COOH group confirms this observations. The absence of any absorption in the 3420 cm^{-1} region shows absence of water of crystallization. The RAMAN spectra are seen distributed due to background radiation. The region from 30 cm^{-1} to 300 cm^{-1} show peaks due to lattice vibrations. The CCN symmetric & asymmetric stretch is observed form 860 cm^{-1} to 1080 cm^{-1}. The combination bands from 2950 cm^{-1} to 3050 cm^{-1} are seen prominently [13].

Raman spectra remains disturbed due to background radiation. The fundamental functional groups have been verified by FTIR spectra in agreement with the laser Raman spectral studies. Most of the vibrations are active in both IR and RAMAN spectra showing molecules lack of centre of symmetry [14].

Table 2 IR & Raman spectral assignments for GOA crystal

IR cm^{-1}	RAMAN (cm^{-1})	Band Assignment	IR cm^{-1}	RAMAN (cm^{-1})	Band Assignment	IR cm^{-1}	RAMAN (cm^{-1})	Band Assign
	37.5	Lattice vibrations	517.1	-	COO^- rocking/ torsional oscillation	1065	1050.1	CH_2 wagging
	97.4	Lattice vibrations	661.1	-	COO^- bending vibrations	1142.9	-	NH_3^+ rocking

	158.0	Lattice vibrations	720.0	702 .4	COO $^-$ wagging	-	-	-
	428.6	Lattice vibrations	-	-	814 .3	CCN symmetric stretc	-	-
1429.6	1440.2	COO $^-$ symmetric stretching /CH_2 scissoring	-	-	-	-	-	-
1745.8		C=O stretch of –COOH	-	-	-	-	-	-

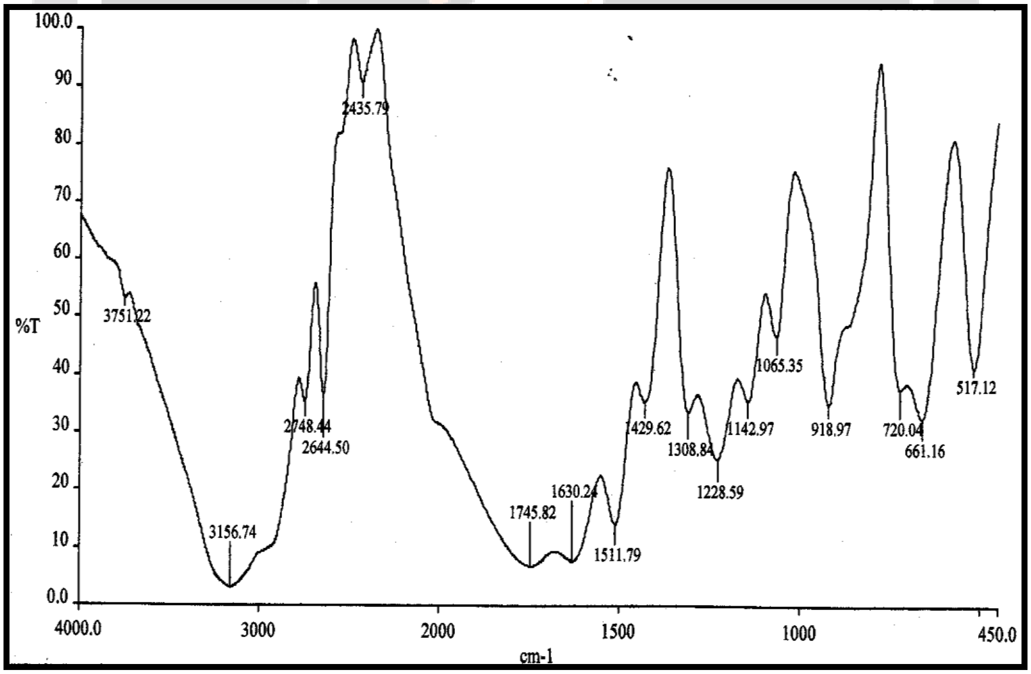

Chart- 3- Infrared spectra for GOA Crystal

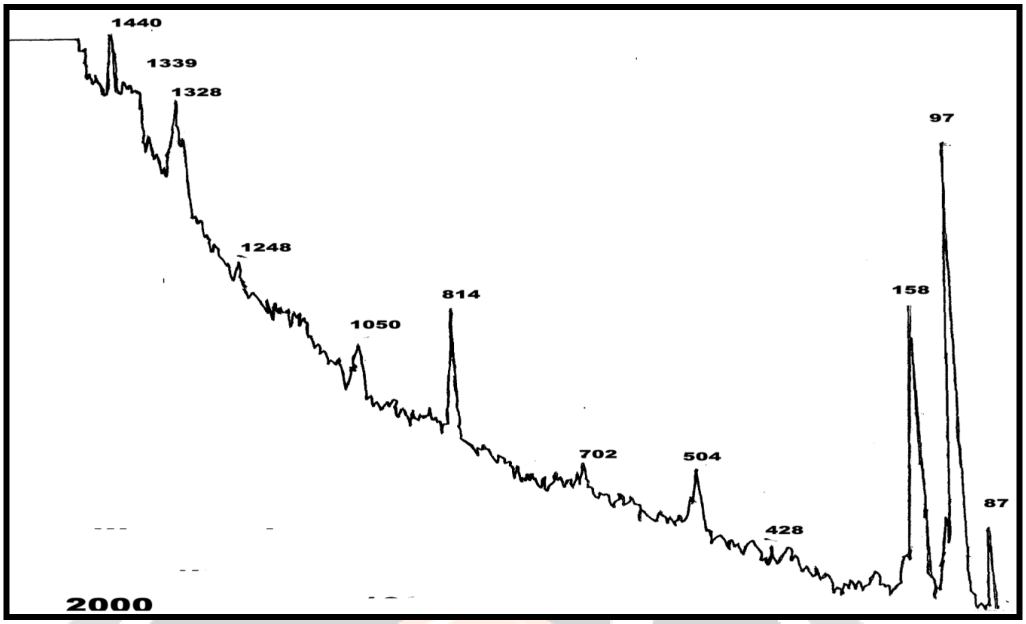

Chart- 4- Raman spectra for GOA Crystal

3.5. ^{1}H-NMR (proton-nuclear magnetic resonance)

^{1}H-NMR spectroscopy is used in identification of the proton containing group in the sample. Whenever there is no external or applied magnetic field, the nucleus spins orient randomly and when there is an applied magnetic field the nuclei orient themselves with or against the larger applied field [15].

It is observed that as the concentration of oxalic acid increases with respect to glycine, the δ values goes on increasing from lower concentration to higher concentration i.e. 3.421 to 3.630 to 3.730, appreciable change has been observed. The NH_2 peak (signal) becomes more desheilded because electronegative groups tend to move NMR signals from neighbouring proton to higher ppm values. Proton attached with nitrogen group is sensitive to concentration of compounds.

Table 3 ^{1}H-NMR Peaks For GOA crystal

PROTON CHEMICAL SHIFT (δ) ppm	
ASSIGNMENT PEAK	GOA
NH_2 peak	3.421
CH_2 peak	4.683

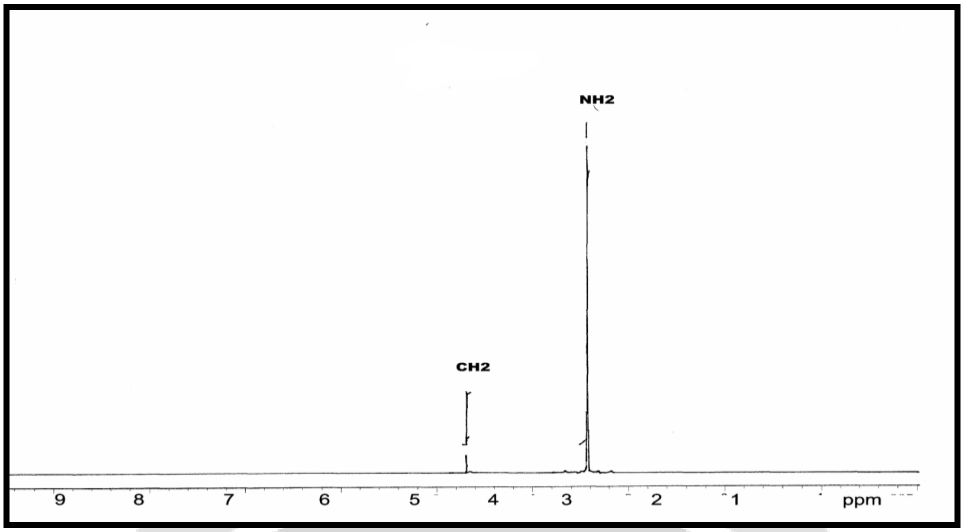

Chart 5- ^{1}H-NMR spectra for Crystal

3.6 ^{13} C- NMR (carbon-nuclear magnetic resonance)

Nuclear magnetic resonance (NMR) spectroscopy is an established technique for characterising crystalline materials. NMR investigate molecular motions in amino acid. The simplest amino acid, glycine has been subjected to of a wide range of investigations over the years. It determines crystal structure and allows to study the spectroscopic and physical properties [16].

The studies on ^{13} C-NMR are useful and can be correlated with studies of ^{1} H-NMR. In ^{13} C-NMR overlapping of peaks are less common than ^{1}H-NMR which makes it easier to determine how many types of carbon atoms are existing in the crystal [17-18]. To confirm the presence of carbon groups in the grown GOA ,^{13}C- NMR studies were undertaken. The sample GOA was subjected to ^{13}C-NMR measurement on BRUKER instrument at a frequency of 500MHz in D_2O [19].The respective peak(signal) Assignments & profiles are shown table 4 and in chart 6.

Table4 ^{13}C-NMR Peak Assignment for crystal

Sample	obs. no	Peaks δ(ppm)	^{13}c assignment	Remarks
GOA crystal	1	40.84	CH_2	Methelene group
	2	166.01	COOH	Carboxylic acid (oxalic acid)
	3	171.50	COOH	Carboxylic acid (glycine)

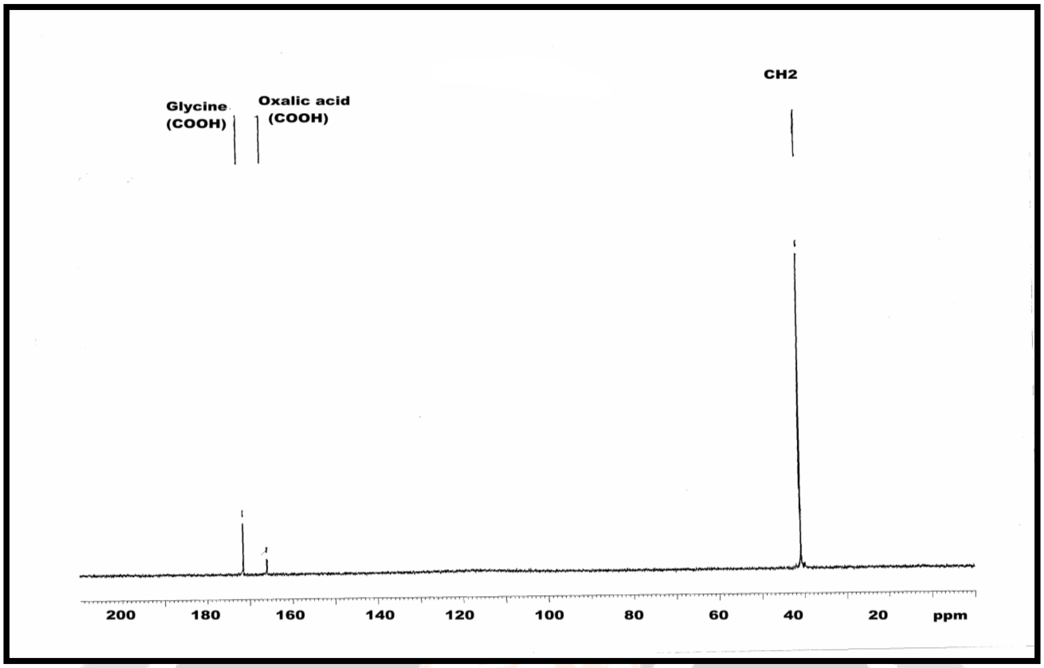

Chart 6- ^{13}C-NMR **spectra for crystal**

4. Conclusions

1. The solubility curves for GOA crystal are almost linear within temperature limit of 303 K to 348 K
2. The GOA crystal belong to the orthorhombic symmetry with lattice parameters a=7.035 A^0, b=12.20 A^0, c=9.05 A^0 and volume 777.33 cc.
3. The CHN analysis of GOA crystal was performed and the observed chemical units are seen to agree with the calculated chemical units
4. Most of the vibrations are active in both IR and RAMAN spectra showing molecules lack of centre of symmetry
5. The NH_2 peak (signal) becomes more desheilded because electronegative groups tend to move NMR signals from neighboring proton to higher ppm values. Proton attached with nitrogen group is sensitive to concentration of compounds.

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