GROWTH AND CHEMICAL BOND ANALYSIS OF DOPED GLYCINE OXALATE- AN ORGANIC NLO CRYSTAL

Dr. Jyotsna Rajiv Pandey

Assistant Professor, Department of Physics, Kishinchand Chellaram college, Churchgate Mumbai, Maharashtra, India

ABSTRACT

A new organic (NLO) Non Linear Optical crystal Glycine- Oxalate was synthesized by slow evaporation technique at room temperature . The AR grade of Glycine and oxalic acid were selected for the present work. The pure glycine and oxalic acid were mixed in 2 different molar ratios. The Homogeneous Aqueous solution of mixture kept for slow evaporation at room temperature. The glycine-oxalic acid crystals of different combinations were obtained in of sizes (2-4 cm) in 2 to 3 weeks' time. The crystallite of crystal was confirmed by powder X-ray diffraction analysis, which confirms orthorhombic structure of crystals. The functional groups present in the grown crystals were identified by FT-IR Spectral analysis and chemical Bond length of different Bonds has been studied in detail.

**Keyword : -** *Glycine, oxalic acid, FT-IR, Chemical Bond Length*

1. INTRODUCTION

Amino acid based crystals have been widely grown from slow evaporation technique(SET) from acid which shows high solubility in water and hence good quality crystals can be obtained from solution. Organic crystals of Glycine-Oxalic acid in different molar ratios like 3:1 and 3:0.11have been grown successfully. Organic crystals due to structural flexibility are good candidate of nonlinear optical crystals. Keeping this in view a new system with coupling of glycine and oxalic acid has been grown from Aqueous solution. Glycine($C_2NO_2H_5$)is a non-essential amino acid which is hydrophilic in nature. Amino acid based several hybrid crystals have recently been crystallized and their various properties have been analyzed. NLO features are caused by highly polarizable acid-base interactions of organic molecules as joining through a hydrogen bond network creates non-Centro symmetric structural system .

In the present work grown crystals of different molar ratios were subjected to Powder x-ray diffraction technique and Fourier-Transform Infrared Spectral Analysis to Confirm Different Functional groups and to determine Bond length between chemical bonds.

2. EXPERIMENTATION

Glycine is an amino acid with zwitterionic character. Its solubility at 25^0 C in water is 25.99/100gm.[3-4] The pH as well as its molar ratio in solution is an important factor in the growth process. Glycine is mixed with oxalic acid resulting in a new glycine oxalic acid crystals. Glycine powder (AR grade M.W 75.07 gm) supplied by S.D FINE chem. Pvt Ltd, Gujarat having impurity composition as insoluble matter 0.003%; sulphated ash 0.05% ;chloride 0.001% ;sulphate 0.0035% ; ammonium 0.0005% ; Iron 0.001; Lead 0.0005% ; copper 0.0005% and oxalic acid (AR Grade, M.W 126.7 gm) supplied by S.D Fine Chem. pvt Ltd were employed for growth of GOA crystals. The molar ratios were 3:1 and 3:0.1 of glycine and oxalic acid respectively and were taken in two different glass beakers . The total aqueous contents of beaker (500 ml) were filtered using good quality filter paper (Whattman 44) and were covered and kept for slow evaporation at room temperature. Crystals begin to appear after about 1 weeks and crystals of appreciable sizes are obtained within 2 to 3 weeks time.
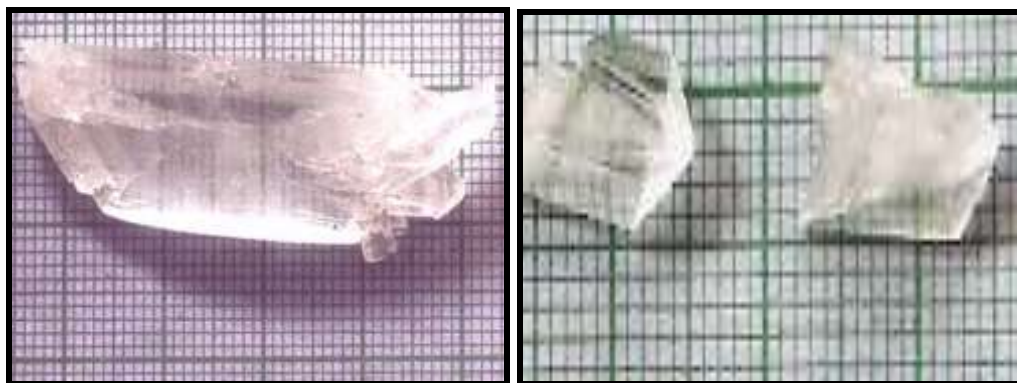
Fig -1: Grown crystals of Glycine-oxalic acid of 3:1 and 3:0.1

3. RESULT AND DISCUSSION
3.1 PH MEASUREMENT

pH is the measure of the acidity or alkalinity of a solution. It is formally a measure of the activity of dissolved hydrogen ions (H^+), but for very dilute solutions, the molarity (molar concentration) of H^+ may be used as substitute with little loss of accuracy. The attempts to grow protein crystals pH was varied in order to monitor possible effect.[5-6] The ideal growing condition for the protein is a pH between 4.0 to 6.0 . The variation of pH of the solution influences the optical, structural and NLO properties of the grown crystals as well as effects the sizes of crystals[7-9]

The growth kinetics and the quality of the crystals grown from solutions are influenced by pH of the solution. At pH 6.0 essentially the glycine is in the zwitterionic form. The amino acids contain both acidic ($-NH_3$) and basic (-COOH) groups, they are amphoteric. In an acidic solution, the COOH group and the molecule has an overall +ve charge. As pH is lowered, the –COOH loses its proton at about pH 2.0. This point is called PKa_1. The first acid – dissociation constant. As pH is raised, the –NH3+ group loses its proton at about pH 9.6. This point is called PKa2 the second acid-dissociation constant. Above this pH the molecule has an over all negative charge . For the Glycine-oxalic acid crystals, as the pH value and concentration of oxalic acid goes on increasing the sizes of crystals also increases it has been observed. The pH of the saturated solutions was determined with the help of digital pH meter. The pH of various solutions and respective sizes of crystals are tabulated in table1.

Table -1: pH Values for Crystals

Ratio of Glycine: oxalic acid	Name of the sample	pH Values	Size of crystal (cm)
3:1	GOA 3:1	4.0	3cm-4cm
3:0.1	GOA 3:0.1	5.0	1cm-1.5cm

3.2 X-ray Diffraction Analysis

X-ray diffraction (XRD) is a well-established technique for determining crystalline order in 3 dimensional solid. [10-11]The crystals in powder X-ray diffraction technique exposed to characteristics X-ray (CuKα wavelength) and output is obtained in the form of x-ray peaks where the Bragg's law is satisfied. Figure 2 and 3 shows the x-ray diffraction profile of GOA3:1 and GOA3:0.1 respectively.

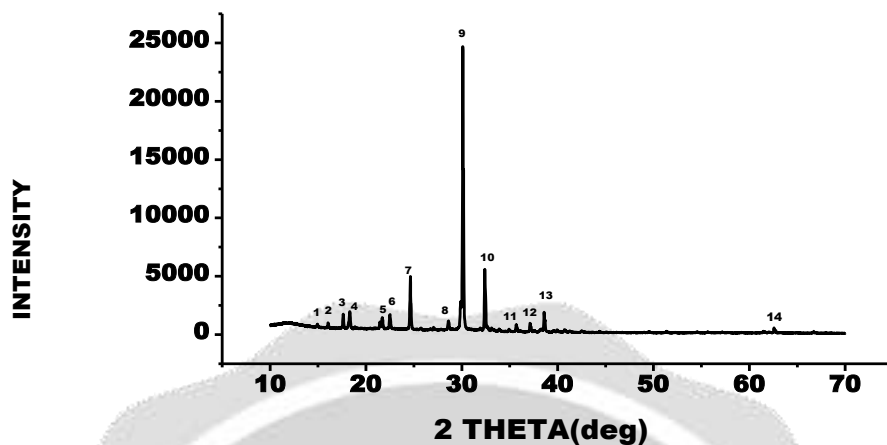**Fig -2**: X-ray diffraction profile of GOA3:1
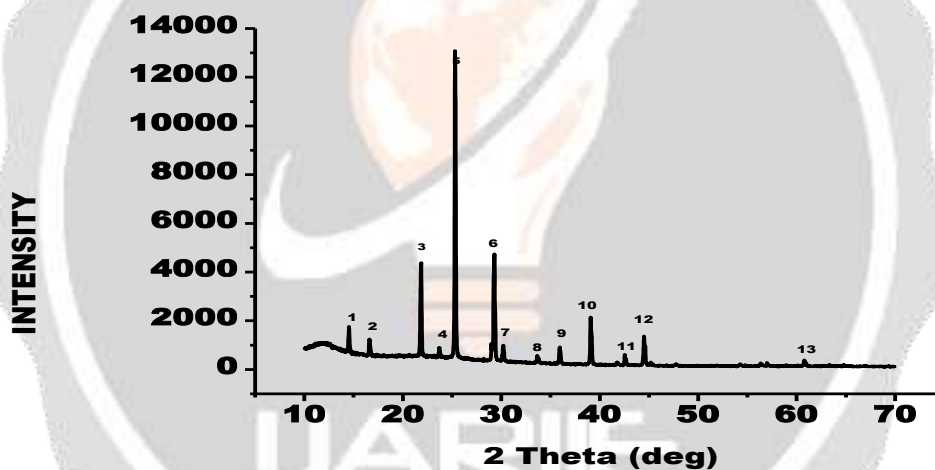

Fig -3: X-ray diffraction profile of GOA3:0.1

**Table -2: Lattice parameters for GOA3:1 and GOA3:0.1**

Name of Sample	Concentration of oxalic acid gm/ml	a (A.U)	b (A.U)	C (A.U)	Vol cc
GOA3:1	0.33	19.97	11.09	5.902	1307.5
GOA3:01	0.033	7.559	10.29	5.458	424.9

The GOA 3:1 and GOA 3:0.1 crystals belong to orthorhombic symmetry and as the concentration of oxalic acid reduces with respect to Glycine, the lattice parameters 'a', 'b' and 'c' and Volume are seen to in decreasing order. The cell parameters and Volume are dependent on the concentration of oxalic acid in the crystals.

3.3 Fourier Transform Infrared Spectral (FT-IR) and Bond Length 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 crystallization. [12-15] The IR spectrum of the grown crystals were taken in the range of 450 cm^{-1} to 4000 cm^{-1}, which is a characteristic range used for most of the organic samples. 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.[16-17] Such assignments were then used for the interpretation of fundamental vibrations of our new GOA 3:1 and GOA 3:0.1. crystals in figure 4 and figure 5 respectively.

Fig -4: Infrared spectral Profile for GOA3:1
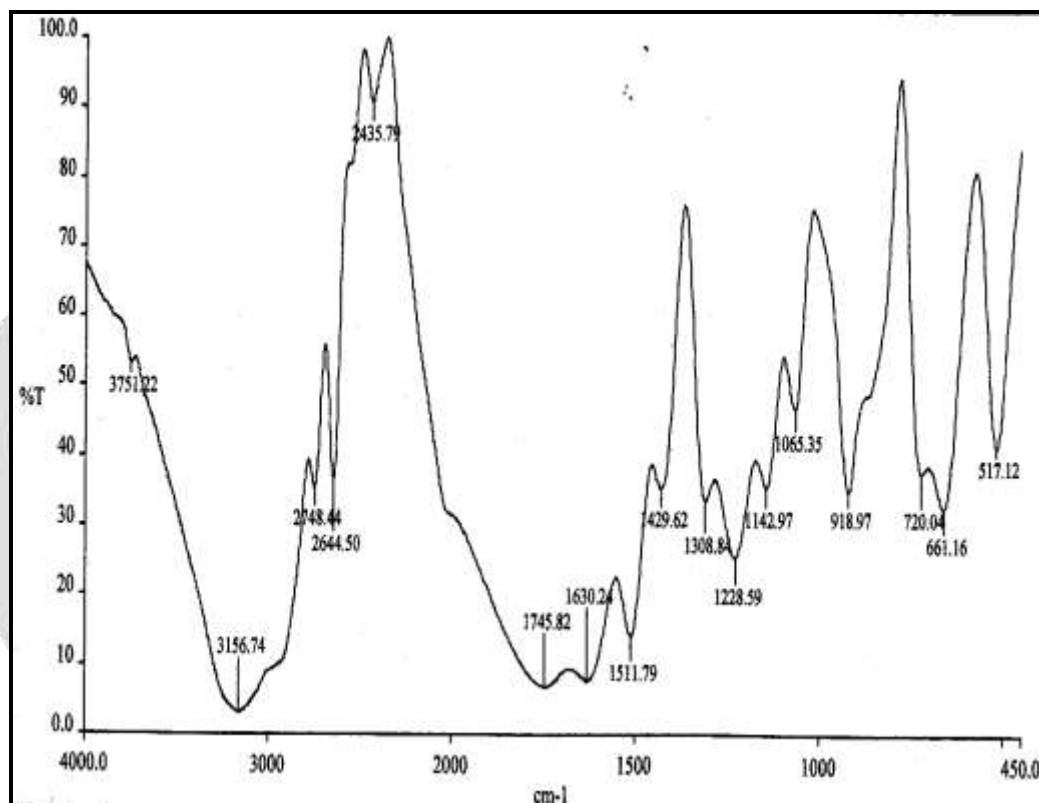
Fig -5: Infrared spectral Profile for GOA3:0.1
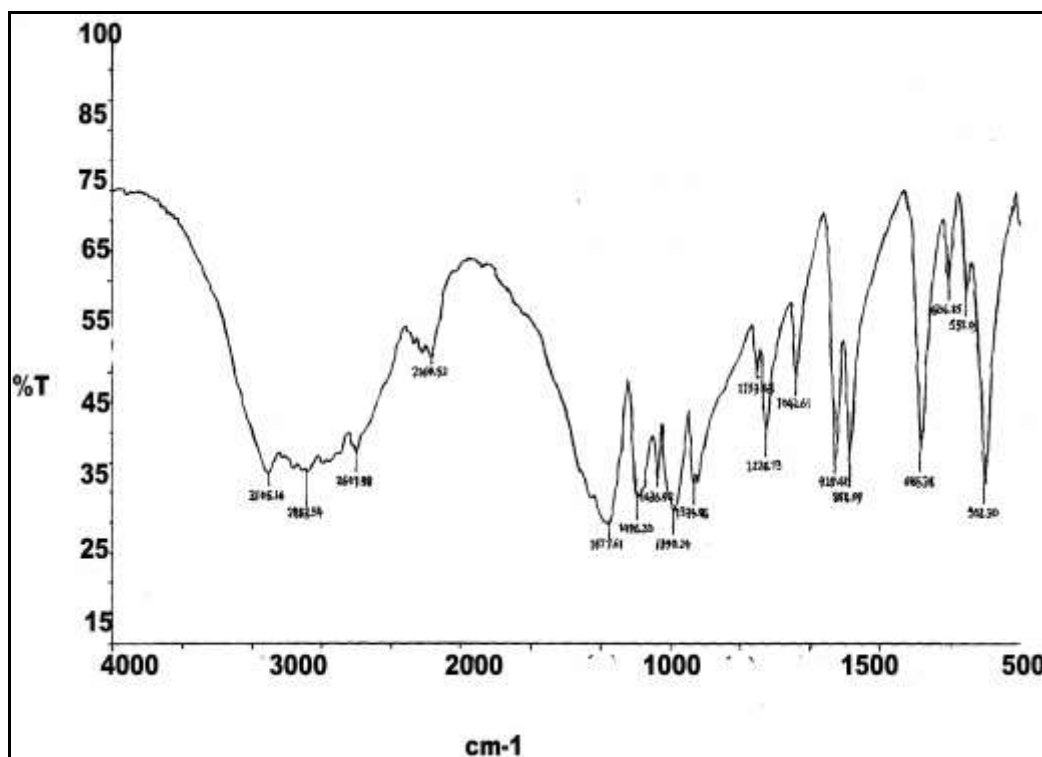
The broad bands in the higher energy region between 3107 and 2170 cm^{-1} are due to NH_3^+ stretching vibration. The leading edge of N-H stretch at 3769 cm^{-1} in glycine shifted to about 63 cm^{-1} and 606 cm^{-1} remain unaffected by bending. Similarly, no effect in frequency maxima of rocking, twisting 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 . 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 these observations.[18] The absence of any absorption in the 3420 cm^{-1} region shows absence of water of crystallization. The fundamental functional groups have been verified by FTIR spectra.

Bond Length Analysis
The vibrational frequency of different bond can be determined by the equation:

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}} \quad --------------(1)$$

where ν is wave number, c is the velocity of light, k is average force constant of the bond and μ is the effective mass of the bond

(For example, O-H) given by the relation:

$$\mu = \frac{m_O . m_H}{m_O + m_H} \quad -----------(2)$$

The force constant can be correlated with the average bond length (r) by the relation

$$K = \frac{17}{r^3} \quad --------------(3)$$

with the use of Eqations. (1) to (3), the values of effective mass, force constant and the bond lengths were calculated from the FTIR spectral data and the calculated values are shown in table3& table 4 for GOA 3:1and GOA3:0.1and comparative analysis is shown in table 5.

Table -3: Band Assignment for GOA3:1

| Wavenumber $\nu(cm^{-1})$	Band Assignment	Effective mass(μ) g	Force Constant K(N/m)	Bond Length (A^0)
3751.22	O-H Stretch	1.5626×10^{-24}	78.0197	0.6017
3156.74	N-H Stretch	1.5496×10^{-24}	54.7901	0.6769
2748.44	C-H Stretch	1.5325×10^{-24}	41.0769	0.7452
1745.82	C=O Stretch	1.1384×10^{-23}	123.1205	0.5168
1630.24	N-H bending	1.5496×10^{-24}	14.6126	1.0517
1429.62	C-H bending	1.5325×10^{-24}	11.1139	1.1521
1308.84	C-O Stretch	1.1384×10^{-23}	69.1997	0.6262
918.97	N-H opp bending	1.5496×10^{-24}	4.6433	1.5417

Table -4: Band Assignment for GOA3:0.1

Wavenumber $\nu(cm^{-1})$	Band Assignment	Effective mass(μ) g	Force Constant K(N/m)	Bond Length (A^0)
3105.14	C-H Stretch	1.5325×10^{-24}	52.4310	0.6869
2607.98	N-H Stretch	1.6099×10^{-24}	38.8537	0.7591
1577.61	C=C Stretch	8.3015×10^{-25}	7.3309	1.1326
1436.20	C-H bending	1.5325×10^{-24}	11.2164	1.1486
1334.86	C-N Stretch	1.0728×10^{-23}	67.8259	0.6304
1153.63	C-O Stretch	1.1384×10^{-23}	53.7606	0.6812
929.42	CH_2 rocking	1.5325×10^{-24}	4.6973	1.5353
881.69	N-Hoop Bending	1.5496×10^{-24}	2.5837	1.8740

Table -5: Comparative analysis of Bond-length

Band Assignment	GOA 3:1 Bond Length (A^0)	GOA 3:0.1 Bond Length (A^0)	Band Assignment	GOA3:1 Bond Length (A^0)	GOA 3:0.1 Bond Length (A^0)
N-H Stretching	0.6769	0.7591	C-H bending	1.1521	1.1486
C-H Stretching	0.7452	0.6869	N-H opp bending	1.5417	1.8740
C-O Stretching	0.6262	0.6812			
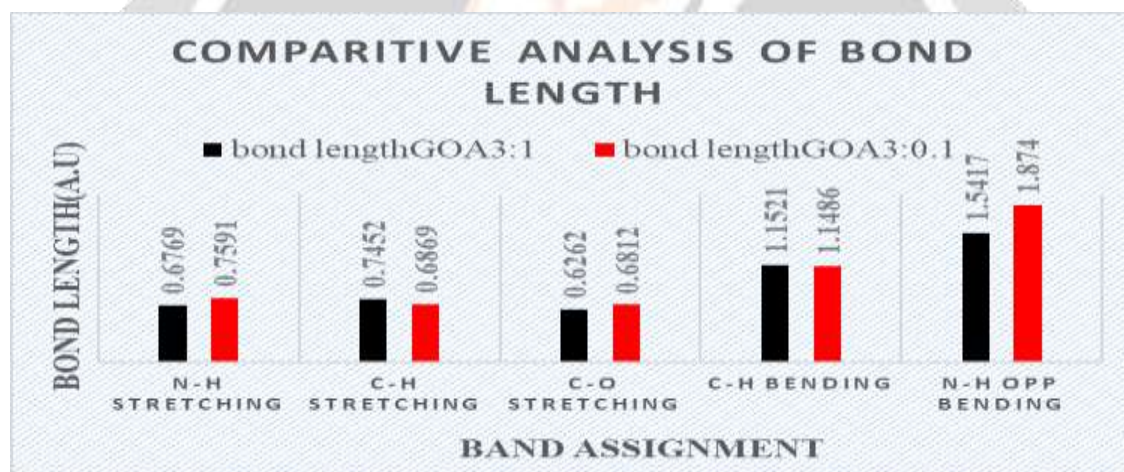
Chart -1: Comparative Analysis of Bond length

According to chart1, as the concentration of oxlip acid varies, the bond length between different chemical bonding shows no significant variation.

4. CONCLUSIONS

Organic crystals of Glycine-Oxalic acid in different molar ratios like 3:1 and 3:0.11have been grown successfully using slow evaporation technique (SET). The ideal growing condition for the protein is a pH between 4.0 to 6.0. The variation of pH of the solution influences the optical, structural and NLO properties of the grown crystals as well as effects the sizes of crystals. The GOA 3:1 and 3:0.1 crystals belong to orthorhombic symmetry and as the concentration of oxalic acid reduces with respect to Glycine, the lattice parameters 'a', 'b' and 'c'and volume are seen to in decreasing order. The cell parameters are dependent on the concentration of oxalic acid in the crystals. The variation of oxalic acid in GOA 3:1 and GOA 3:0.1 with respect to glycine shows no significant changes in the bond length of different types of chemical bonds .

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