

VICKER'S MICROHARDNESS STUDIES AND ^1H -NMR SPECTRAL ANALYSIS OF AN ORGANIC NLO MATERIAL

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ABSTRACT

A series of NLO Glycine-oxalic acid crystals have been grown by slow evaporation method at room temperature. The Solubility studies indicated a linear increase in solubility with temperature from room temperature to 75°C. The mechanical behavior of the grown crystals were studied using Vicker's microhardness tester. The PSR model was verified for all samples and it is found that all the crystal belongs to soft material category as Mayer's index (n) is greater than 1.6. The presence of two hydrogen atoms belonging to NH₂ and CH₂ group have been identified in H-NMR spectra

Keyword: - glycine, oxalic acid, Vicker's Hardness, NMR spectra, NLO

1. INTRODUCTION

Crystal growth is a vital and fundamental part of materials science and engineering. Development of crystal growth is in high demand due to its role for the development of several important components like high-efficiency photovoltaic cells in the area of alternative energy, medicine, and in the fabrication of light-emitting diodes. Organic materials are of great interest for most electronic applications. Organic crystals exhibit large non-linearity enhanced NLO (non linear optical) efficiencies and structural diversity.[1]

Glycine (C₂H₅NO₂) is a nonessential amino acid which is hydrophilic polar in nature. It is the only protein forming amino acid without centre of chirality. In the field of nonlinear optical crystal growth, amino acids are playing a vital role.[2] A number of natural amino acids exhibit the nonlinear optical properties because they have a donor NH₂ and acceptor COOH and also intermolecular charge transfer is possible. In the recent modern technologies many efforts were taken to find the higher order Nonlinear optical materials for several optoelectronic devices. [3]

In the present investigation, I am reporting the growth of Doped series of Glycine –Oxalic acid crystals by slow evaporation method. The grown series of doped Glycine-Oxalic acid crystals subjected to Vicker's Microhardness test and ^1H -NMR Spectral analysis to determine the resistance offered by the present crystal series to indentation by a relatively harder body. This techniques for determination of hardness are essentially means of giving a quantitative value to the materials ability to resist load deformation and ^1H -NMR spectroscopy is used in identification of the proton containing group in the sample and it also helps to determine the content and purity of a sample respectively.[4]

1.1 PRESENT WORK

In this present paper, Organic crystals of Glycine-oxalic acid (series 1) have been grown from slow evaporation method. Organic crystals due to structural flexibility are good candidates of non-linear optical materials. Keeping this in view a new system with coupling of α -glycine and oxalic acid has been grown for the first time from aqueous solution. This paper focuses studies on growth, Hardness and NMR spectral analysis. The pH of the solution is an important parameter during growth. The optimum value of pH is 6.0 to estimate good crystals.

α - glycine, an amino acid and oxalic acid both are soluble in water. The condition during growth has been optimised. The doped series 1 of glycine-oxalic acid crystals were labeled as GOA1,GOA2 &GOA3 with molar ratios of 3:1, 2:1, 1:1, of glycine and oxalic acid respectively and were taken in three different containers of glass. The total aqueous contents of beaker (500 ml) were filtered using good quality filter paper (Whatman 44) and clear solutions were formed in double distilled water. The filtered contents were labelled and beakers were covered and kept for slow evaporation at room temperature. Crystals begin to appear after about 2 weeks and crystals of appreciable sizes are obtained within 3 to 4 weeks time

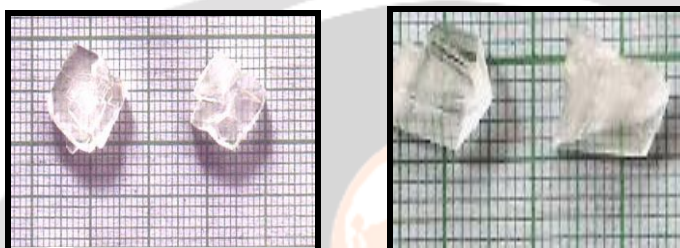


Figure 1: The Grown series of crystals

2. EXPERIMENTAL PROCEDURE

2.1 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. Neither flat nor steep solubility curve will enable the growth of bulk crystals from solutions, where the solubility is linear as temperature increases and having larger positive temperature coefficient value therefore for growth of these crystals slow evaporation is best method [5]. The solubility of the Glycine-oxalic acid (series 1) were determined for varying temperature from 30 -75 °C in double distilled water (100ml). The near linear solubility curves with temperature are shown in chart 1.

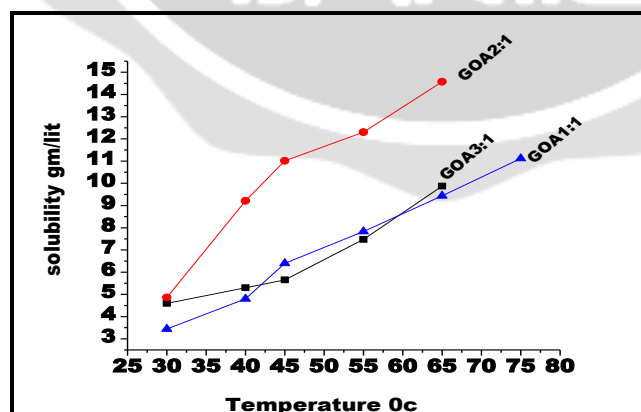


Chart 1: Solubility curve against Temperature

The solubility curves are almost linear within temperature limit of 303 K to 348 K for the given series.

3. CHARACTERISATION ANALYSIS

3.1 Vicker's Microhardness Test

Good quality, appreciable size crystals were chosen to begin with and were subjected to Vicker's indentation test after polishing on the most flat surface. The indentation test was carried out at room temperature using LECO LM – 700-hardness tester fitted with a Vickers's diamond indenter attached to a microscope. Loads varying from 10 gm to 50 gm are applied over a fixed interval of time (5 seconds). The indentation was carried out at different sites in order to avoid any mutual influence of the indentations. The diagonal length of the indented impressions was observed as d_1 and d_2 . The LECO- LM 700 consists of interchangeable color filters and automatic turret accommodates up to 4 objectives (2.5 x to 100 x) available on an advanced touch panel displays.[6]



Figure 2: LECO LM –700-hardness tester

3.2 ^1H -NMR spectroscopy

In NMR spectroscopy the interaction of electromagnetic radiation with the nuclei of certain atoms in the molecules is studied. The number of protons present in the compound can be measured using VARIAN MERCURY PLUS 300MHz, (USA) NMR spectrometer. A typical Varian Mercury 300 MHz NMR has 2 channel mercury console and unshielded magnet. The mercury 300 is capable of observing ^1H , ^{19}F , ^{13}C , & ^{31}P , but due to hardware constraints it is not capable of observing ^{19}F coupled.[7]



Figure 3: VARIAN MERCURY PLUS 300MHz, (USA) NMR spectrometer

4. RESULT AND DISCUSSION

4.1 Microhardness study

The grown Glycine oxalic acid (series1) crystals were polished on the most flat surface and are used for the micro hardness studies. The diamond indenter was used for indentation purpose at various loads and the diagonals (d₁ & d₂) can be measured directly on the digital display using the average values of measured diagonals and load applied [8-10].Vickers Hardness Number (VHN) is calculated from the relation

$$\begin{aligned}
 \text{VHN} &= \frac{W}{\text{Pyramidal area}} \text{-----(1)} \\
 &= \frac{1.8544 \times W}{d^2} \text{ , Kg/mm}^2 .
 \end{aligned}$$

It is an important use of micro hardness studies is to find the indirect estimate of other mechanical characteristics of materials having a specific correlation with the hardness. Kick proposed an analysis of results on hardness and according to him the relation between applied load ‘P’ and indentation length ‘d’ is given by

$$\boxed{P = k d^n} \text{-----(2)}$$

Where ‘k’ and ‘n’ are constant for a given material .Kick postulated a constant value n = 2 for all the indentator and for all geometrically similar impressions. Kicks law has not been accepted widely because the value of ‘n’ is usually less than 2, in low load region. If ‘n’ is less than 2 the hardness number increases with decreasing load and if ‘n’ is greater than 2 the hardness number decreases with decreasing load. The constant ‘n’ is called work hardening index /coefficient/ Meyer’s index. The value of ‘n’ is calculated by taking the slope of graph log p versus log d.From calculations It is observed GOA 1 is the softest of all crystals and GOA 2 is harder than GOA 3 and. [12]

TABLE 1 : Variations of Load and Diagonals in Vicker’s Hardness Studies

LOAD (gms)	LOAD P (newton)	GOA1	GOA2	GOA3
		Diagonals(m)	Diagonals(m)	Diagonals(m)
10 gm	0.09 N	D1=28.47 x 10 ⁻⁶	D1=14.27 x 10 ⁻⁶ (break)	D1=16.93 x 10 ⁻⁶
25 gm	0.24 N	D2=36.20 x 10 ⁻⁶	D2=23.86 x 10 ⁻⁶	D2=26.96 x 10 ⁻⁶
50 gm	0.49 N	D3=41.07 x 10 ⁻⁶	-	D3=48.55 x 10 ⁻⁶

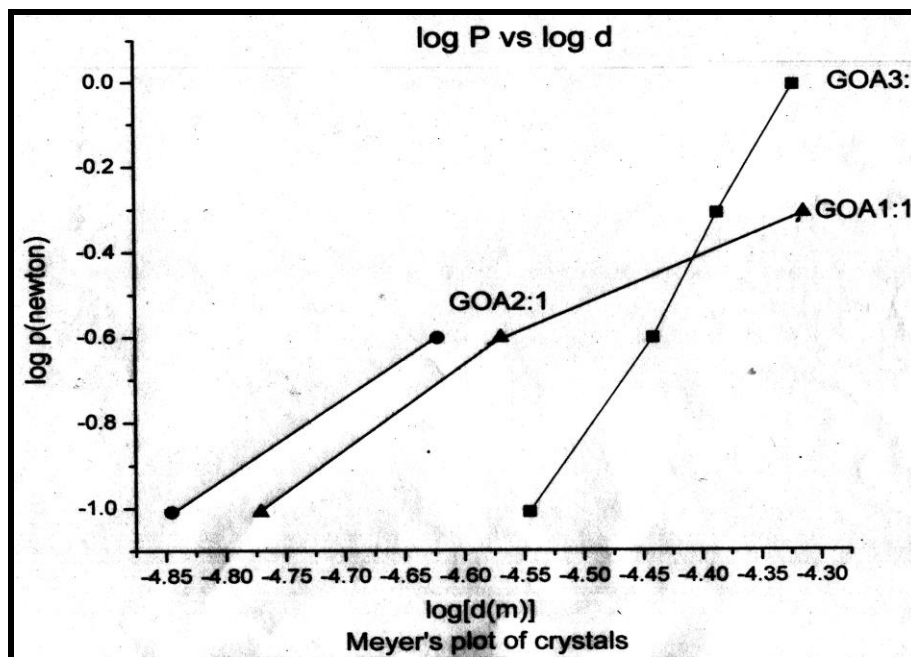


Chart 2: Mayer's Plot for doped series 1

Table 2 : The Hardness index 'n'

NAME OF SAMPLE	CONCENTRATION OF OXALIC ACID	MEYER'S INDEX 'n'
GOA 1	0.33	3.90
GOA2	0.50	1.76
GOA3	1.00	1.96

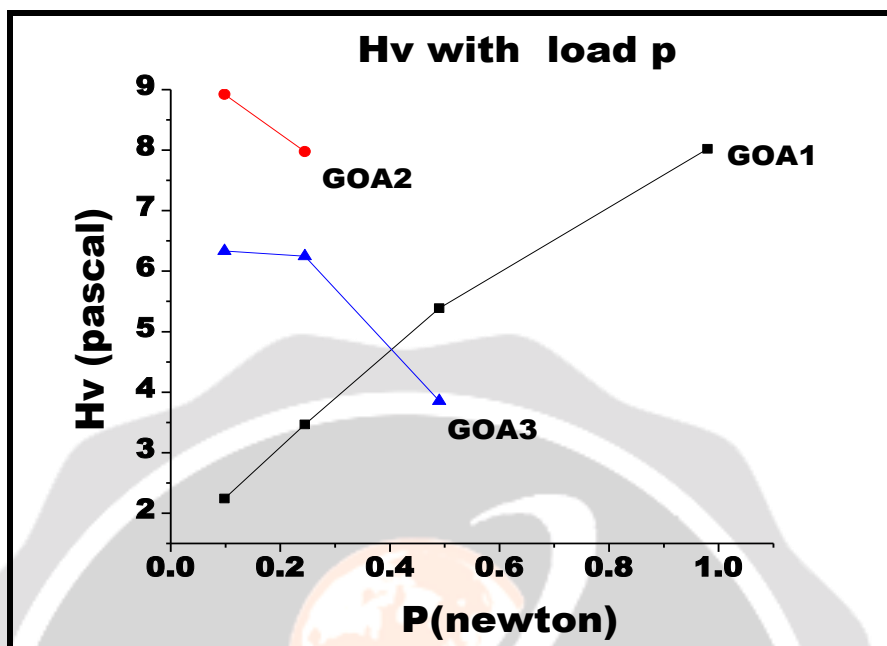


Chart 3: Variation of Vicker's Hardness Number (H_v) with load

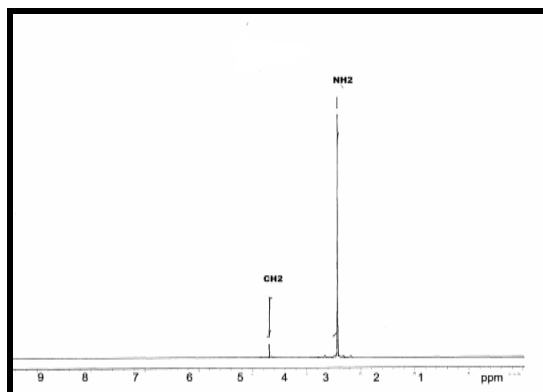
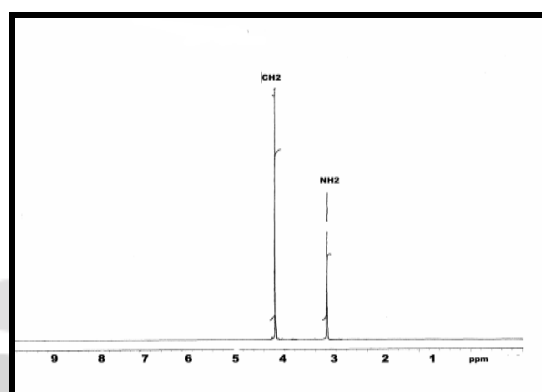
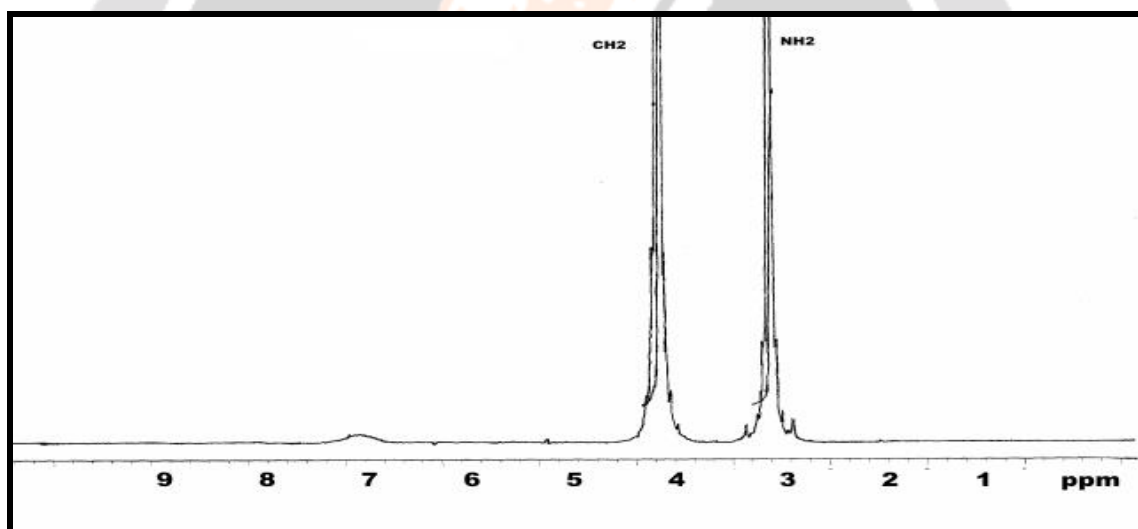
Chart 3 shows the variation of Vickers's hardness number (H_v) against the applied load. While GOA 2 & GOA 3 shows decrement in the micro hardness number (H_v) with increase in load and GOA1 crystal shows a linear increase in H_v as load is increased. According to Onitsch, for hard materials, 'n' lies between 1 to 1.6 and for soft materials it is above 1.6. So the value of 'n' enlisted in table 2 show that GOA 2 is harder than GOA 3 and GOA 1 is the softest of all crystals.

4.2 $^1\text{H-NMR}$ Spectral Analysis

$^1\text{H-NMR}$ spectroscopy is used for confirmation of the proton containing group in the sample. The $^1\text{H-NMR}$ profiles for doped series 1 are presented in chart 4 to 6. From the NMR profiles, 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. 2.971 to 3.222 to 3.330, appreciable change has been observed. The NH_2 peak (signal) becomes more deshielded because electronegative groups tend to move NMR signals from neighbouring proton to higher ppm values, Proton attached with nitrogen group is more sensitive to concentration of compounds. [13-14]

Table 3: $^1\text{H-NMR}$ Spectral assignment

PROTON CHEMICAL SHIFT (δ) ppm			
ASSIGNMENT PEAK	GOA 1	GOA2	GOA3
NH_2 peak	2.971	3.222	3.222
CH_2 peak	4.683	4.780	4.780

Chart 4: $^1\text{H-NMR}$ spectrum for GOA 1**Chart 5:** $^1\text{H-NMR}$ spectrum for GOA 2**Chart 6:** $^1\text{H-NMR}$ spectrum for GOA 3

In glycine–oxalic acid doped series1, with increase in concentration of oxalic acid, NH_2 peak shift to higher value of (δ) ppm, while no prominent effect has been observed in CH_2 bands. Shielded protons absorb at higher field and they have lower δ values. Deshielded proton absorbs at lower field and they will have higher δ values. Thus as shielding increases, δ decreases and as deshielding increases, δ tends to increase. 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.

5. CONCLUSIONS

A well defined transparent crystals of appreciable size (2-6 cm) crystals of glycine-oxalic acid doped Series 1 were grown successfully from aqueous solution at room temperature in 3-4 weeks time.) . Optimum value of pH 6 is seen to yield good crystals. Solubility studies indicates a linear increase in solubility with temperature from room temperature to 75°C . The presence of two hydrogen atoms belonging to NH_2 and CH_2 group have been identified in $^1\text{H-NMR}$ spectra. The hardness of the crystals are calculated and it is found that GOA 2 is harder than GOA 3 and GOA 1 is the softest of all crystals.

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