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XRD and FT-IR Studies on FeSO_4 and CuCl_2 Doped Glycine Picrate Crystals: A Nonlinear Optical Material

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ABSTRACT

Copper Chlorides and Ferrous sulphate doped Glycine Picrate crystals have been grown separately by slow evaporation technique at room temperature. The crystal systems and lattice dimensions have been identified and measured using X-ray diffraction analysis. The functional groups of the grown crystals were qualitatively examined using FTIR analysis.

Keywords: Crystal growth, Organic compounds, Glycine picrate, Copper Chloride, Ferrous sulphate, FTIR, X-ray diffraction.

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INTRODUCTION

It is thought that development of a new optical device is needed to satisfy the demand in the society. The large non-linear optical properties of large organic molecules and polymers have been the subject of extensive theoretical and experimental investigations during past few decades. Considerable efforts have been made to investigate organic non-linear optical materials. Organic non-linear optical materials are often formed by weak Vander walls and hydrogen bonds and hence possess high degree of delocalization. Organic materials have been demonstrated in recent years to possess superior second and third order NLO properties compared to the more traditional inorganic materials. The properties of organic compounds can be refined using molecular engineering and chemical synthesis (T. Uma Devi, N. Lawrence, R. Ramesh Babu, K. Ramamurthy, G. Bhagavannarayana Vol.8, No.10). The study of amino acid crystallizes with other organic and inorganic molecules, which presents a high non-linear optical coefficient has gained much attention in the last few years because of the possibility of using them in technological devices [1, 2]. Our work is engaged in finding new materials for NLO applications and some of these were reported recently [3-6]. Glycine picrate (GP) is an organic nonlinear optical material that belongs to monoclinic crystal system and the lattice parameters are $a = 14.968 \text{ \AA}$, $b = 6.722 \text{ \AA}$, $c = 15.165 \text{ \AA}$ and $\beta = 93.65^\circ$. GP consists of two molecules of glycine and one picric acid molecule and is formed through hydrogen bonding and the carboxyl groups of two glycine molecules share a hydrogen atom [7]. Growth of GP and the results of FTIR and XRD studies of GP were discussed in earlier report [4]. Third-order nonlinear optical (NLO) materials with weak nonlinear absorption (NLA) but strong nonlinear refraction (NLR) have attracted considerable attention because of their potential uses in the optical signal processing devices [8–13]. The dielectric behavior of a material is an important factor as it has direct influence on the NLO efficiency of the crystals. Further quality of the crystal is an important factor when the crystals are brought to the device applications. It has been demonstrated that organic crystals can have very large non-linear susceptibilities compared with inorganic crystals [14]. In this paper we have reported the growth and characterization of Copper chlorides and ferrous sulphate doped Glycine picrate crystals through XRD and FTIR studies.

EXPERIMENTAL PROCEDURE

Exactly one molar picric acid and Glycine are weighed. Equimolar solutions are prepared and heated separately for five minutes. They are mixed thoroughly with stirring while in hot Condition. It is filtered and added with the dopent copper chloride and ferrous sulphate in separate test tubes which are also maintained in the hot condition and .these are kept aside until attain the room temperature. After that these are cooled in the ice Bath till the precipitates are formed. It is filtered, dried and a portion is taken for preparing the saturated solution. The saturated solution is prepared and heated to about 60 degree centigrade for 5 Minutes. It is filtered and kept undisturbed. The induction time is noticed. The fine crystals are harvested within a span of three to five days. The Picric acid-Glycine crystals doped with Copper chloride and ferrous sulphate are characterized using FTIR and XRD studies

FTIR spectral studies

The Picric acid-Glycine crystals doped with Copper chloride

Fourier Transform Infrared spectrometry (Fig 1) (FTIR) involves examination of the twisting, bending, rotating and vibrational modes of atoms in a molecule. Upon interaction with infrared radiation, portions of the incident radiation are absorbed at specific wavelengths and the functional groups of a sample can be identified from the spectrum. The FTIR spectrum for the grown picric acid with glycine doped with CuCl_2 crystal is presented in the figure1. The CC-O bend and CC stretching vibrations are observed at 497.8 cm^{-1} and also it represents chloro alkanes. CH_3 Rocking vibrations are observed at 703.6 cm^{-1} . The NO_2 wagging vibrations are observed at 741.7 cm^{-1} . The CC stretching and C-O stretching vibrations are observed at 801.4 and 803.9 cm^{-1} . The C-H in plan bending vibrations is observed at 1077.5 cm^{-1} . The CN symmetric stretching vibrations are observed at 938.8 cm^{-1} . Strong band at 1270.7 cm^{-1} . In the FTIR spectrum could be assigned to NH_3^+ rocking vibration. Methylene vibration is observed in FTIR in 1422.2 cm^{-1} . Aliphatic C-H stretching is due to vibration at the peak in the range 2826.3 cm^{-1} . In this figure it is observed that NO_2 symmetric stretching (ν) at 1329.9 cm^{-1} . NH_3^+ symmetric deformation is due to vibration at the peak in the range 1491.7 cm^{-1} . The phenolic O vibration produces peak at 1155.3 cm^{-1} . Also it reveals that picric acid necessarily promotes the carboxyl group. There is N-H bending at 1615.9 cm^{-1} . The derivatives of carboxylic acid (acyl halide or anhydrides) vibrations are observed at 1865.9 cm^{-1} . The H-bonded OH group of $-\text{COOH}$ stretching vibrations are observed at 3297.2 cm^{-1} . The absorption peaks/bands and their assignments are provided in the table1.

Table 1

Wave numbers cm^{-1}	Functional groups
497.8	CC-O bend and CC
703.6	CH_3 Rocking
741.7	NO_2 wagging
801.4	CC stretching,
803.9	C-O stretching
938.8	CN symmetric
1077.5	C-H in plan bending
1155.3	phenolic O vibration
1270.7	NH_3^+ rocking
1329.9	NO_2 symmetric
1422.2	Methylene vibration
1491.7	NH_3^+ symmetric deformation
1615.9	N-H bending
2826.3	Aliphatic C-H stretching
1865.9	The derivatives of carboxylic acid (acyl halide or anhydrides)
3297.2	H-bonded OH group of $-\text{COOH}$ stretching

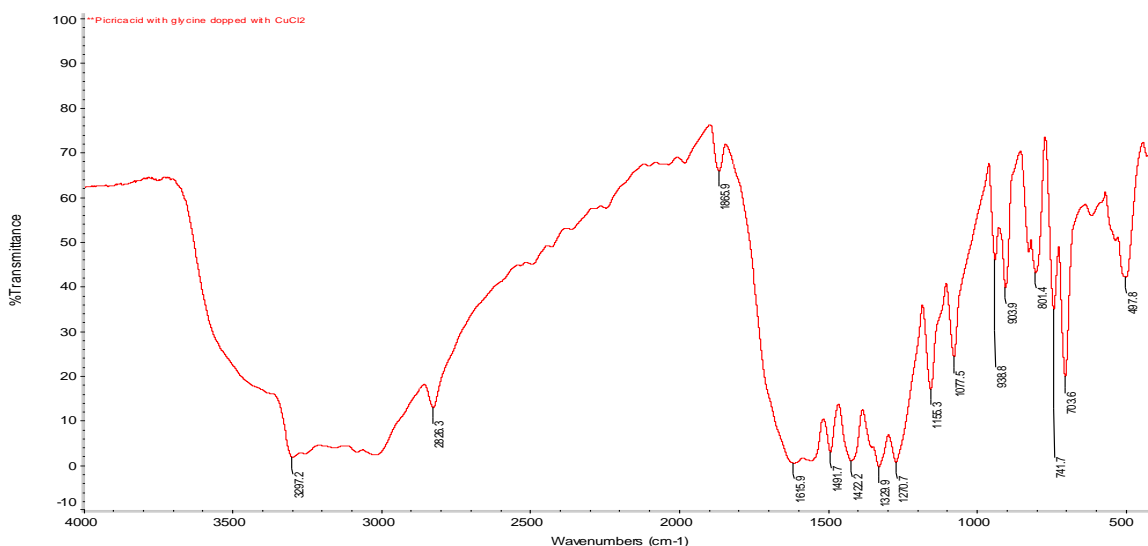


Figure 1

The Picric acid-Glycine crystals doped with ferrous sulphate

In the FTIR spectra of the complex Picric acid with Glycine doped with FeSO_4 (Fig 2), the overlap of hydrogen bonded O-H and aromatic C-H stretching vibrations are observed at 3099.8 cm^{-1} . The $-\text{NH}_2$ deformation mode is observed by the absorption at 1634.2 cm^{-1} . This band overlaps with the aromatic C=C stretching vibrations. The asymmetric and symmetric stretching vibrations of the $-\text{NO}_2$ group are observed at 1552.8 cm^{-1} and 1339.9 cm^{-1} , respectively. Normally the asymmetric stretching vibration of the $-\text{NO}_2$ group is sensitive to polar influences and the electronic states of the species. Therefore, it has been realized that the shift to lower frequency of $\nu_{\text{asym}}(\text{NO}_2)$ vibration (1552.8 cm^{-1}) in the spectrum of the complex compared with free picric acid (1606 cm^{-1}) is due to the increased electron density on the picric acid moiety owing to the charge transfer interaction in the complex. The absorption at 1634.2 cm^{-1} , 1552.8 cm^{-1} and 1428.0 cm^{-1} are due to the aromatic C=C absorption stretching vibrations. The C-O stretching vibration is observed as a band of medium intensity at 1146.8 cm^{-1} . The NH_3^+ rocking vibrations are observed at 1269.9 cm^{-1} . The C-H in-plane bending vibration is observed at 1086.3 cm^{-1} and the C-H out-of-plane bending is shown by the presence of a band at 787.5 cm^{-1} . The C- NO_2 stretching is observed at 913.3 cm^{-1} . The CH_3 rocking vibrations are observed at 710.9 cm^{-1} . The band at 787.5 cm^{-1} is due to CH_2 rocking skeletal vibration and NO_2 wagging vibration. The NH_3^+ torsion vibrations are observed at 533.1 cm^{-1} . The NO_2 wagging deformation vibrations are observed at 594.4 cm^{-1} . The CNC deformation vibrations are observed at 409 and 413.6 cm^{-1} . The derivatives of carboxylic acids or anhydrides vibrations are observed at 1864.0 cm^{-1} . The assignments of various absorption frequencies of the compound are given in the table 2.

Table 2

Wave numbers cm-1	Functional groups
3099.8 cm-1	hydrogen bonded O-H and aromatic C-H stretching
1634.2cm-1	-NH ₂ deformation, C=C stretching
1552.8 cm-1	The asymmetric stretching vibrations of the –NO ₂ group
1339.9 cm-1,	The symmetric stretching vibrations of the –NO ₂ group are observed
1634.2 cm-1,	
1552.8 cm-1 and	Aromatic C=C absorption stretching vibrations.
1428.0 cm-1	
1146.8 cm-1.	C-O stretching vibration
1269.9 cm-1.	NH ₃ ⁺ rocking
1086.3 cm-1	C-H in-plane bending
787.5 cm-1	C-H out-of-plane bending
913.3 cm-1.	C-NO ₂ stretching
710.9 cm-1.	CH ₃ rocking
787.5 cm- 1	CH ₂ rocking skeletal vibration and NO ₂ wagging vibration.
533.1 cm-1.	NH ₃ ⁺ torision vibrations
594.4 cm-1.	NO ₂ wagging deformation
409 and 413.6 cm-1.	CNC deformation
1864.0 cm-1.	The derivatives of carboxylic acids or anhydrides

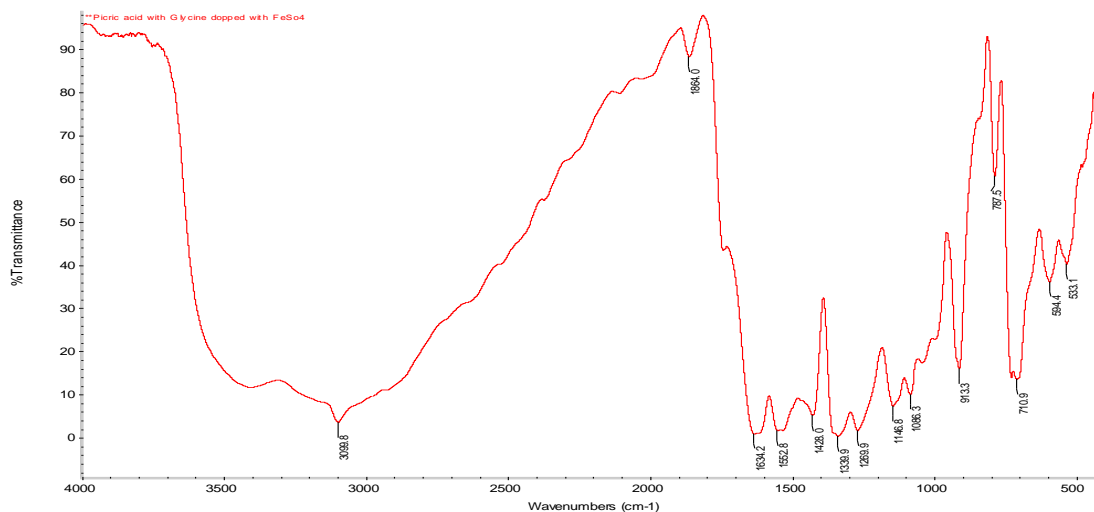


Figure 2

High-Resolution X-ray Diffractometry Study on CuCl₂ Doped GP

The grown specimen was first lapped and chemically etched in a non preferential etchant of water and acetone mixture in 1:2 volume ratio to remove the non-crystallized solute atoms remained on the surface of the crystal and also to ensure the surface planarity of the specimen. Fig. 3 shows the high-resolution rocking or diffraction curve (DC) recorded for the specimen CuCl₂ Doped GP using (001) diffracting planes in symmetrical Bragg geometry by

employing the XPERT-PRO Philips X-diffractometer with $\text{CuK}\alpha 1$ radiation. As seen in the figure, in addition to the main peak at the 40 arc s, this curve contains 17 more additional peaks. The solid line in these curves which is well fitted with the experimental points is obtained by the Lorentzian fit. The additional peaks between 11.8 and 56.8 (Table 3) arc s around the main peak are due to internal structural very low angle (≤ 1 arc min) grain boundaries [15]. The tilt angle i.e. the mis orientation angle of the boundary with respect to the main crystalline region for all the observed very low and high angle boundaries are 11.8 and 56.8 arc s. The full width at half maximum (FWHM) values for the main peak and the all other low and high angle boundaries are respectively given in the table. Though the specimen contains very low angle boundaries, the relatively low angular spread of around 5 arc min of the diffraction curve and the low FWHM values show that the crystalline perfection is (T. Uma Devi, N. Lawrence, R. Ramesh Babu, K. Ramamurthy, G. Bhagavannarayana Vol.8, No.10) reasonably good. The effect of such low angle boundaries may not be very significant in many applications, but for the phase matching applications, it is better to know these minute details regarding crystalline perfection. It may be mentioned here such very low angle boundaries could be resolved only because of the high-resolution of the X'Pert Pro Philips X-ray diffractometer used in the present investigation. Experimental d values of pure samples are in well agreement with standard JCPDS values [16]. The variations in intensity of peaks of doped crystals may be attributed to the incorporation of dopants in crystal lattice.

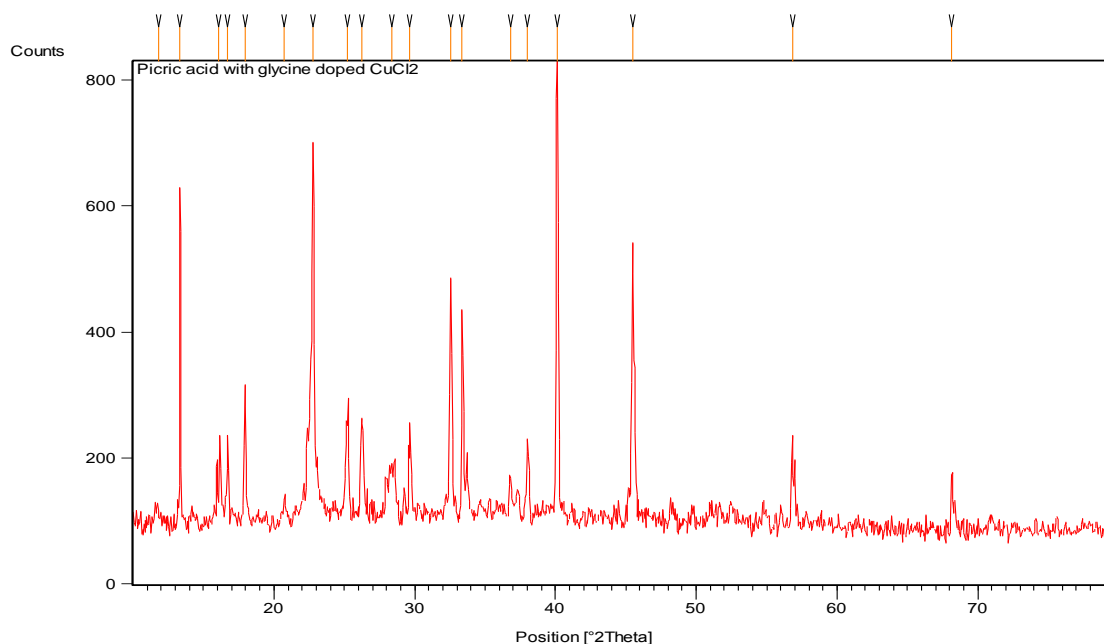


Figure 3

Table 3

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
11.8012	27.76	0.5904	7.49916	4.02
13.3374	499.51	0.0633	6.63316	72.40
16.1027	96.50	0.6105	5.49975	13.99
16.7005	116.94	0.2244	5.30423	16.95
17.9287	209.92	0.1449	4.94352	30.43
20.7412	37.75	0.2952	4.28263	5.47
22.7478	491.73	0.2960	3.90597	71.27
25.1949	181.48	0.2283	3.53186	26.30
26.2453	167.00	0.1968	3.39566	24.21
28.3437	85.01	0.7899	3.14625	12.32
29.6517	139.69	0.1968	3.01286	20.25
32.5362	370.73	0.1212	2.74977	53.73
33.3768	330.74	0.0980	2.68241	47.94
36.7894	58.58	0.2843	2.44104	8.49
38.0023	117.68	0.1601	2.36588	17.06
40.0979	689.95	0.0997	2.24693	100.00
45.4873	403.99	0.1572	1.99245	58.55
56.8267	128.39	0.2030	1.61886	18.61
68.1585	108.03	0.1270	1.37470	15.66

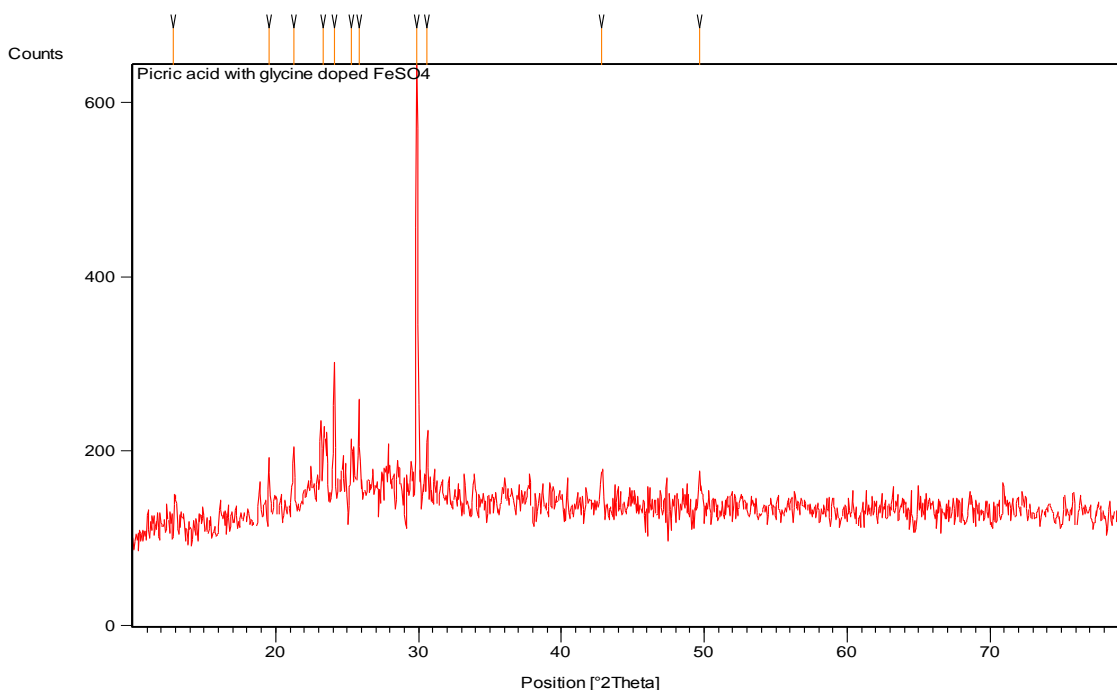
High-Resolution X-ray Diffractometry Study on FeSO₄ Doped GP

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Table 4

Pos. [$^{\circ}$ 2Th.]	Height [cts]	FWHM [$^{\circ}$ 2Th.]	d-spacing [\AA]	Rel. Int. [%]
12.8242	24.40	1.9680	6.90315	5.16
19.5264	61.51	0.1035	4.54249	13.00
21.2409	59.91	0.1353	4.17954	12.66
23.3502	75.38	0.5134	3.80654	15.93
24.0940	128.85	0.1003	3.69069	27.22
25.2761	69.75	0.1476	3.52362	14.74
25.8235	80.59	0.1528	3.44730	17.03
29.8638	473.34	0.0953	2.98947	100.00
30.5949	62.77	0.0780	2.91968	13.26
42.7931	53.85	0.2060	2.11145	11.38
49.6695	42.47	0.2984	1.83403	8.97


Figure 4

CONCLUSION

Optically good quality crystal of Copper chlorides and ferrous sulphate doped GP was grown using evaporation technique. A XPERT-PRO Philips X-diffractometer with CuK α 1 radiation

study reveals the crystalline perfection of the crystal without any internal structural grain boundaries. The functional groups were identified using FTIR technique.

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