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Research Article

SYNTHESIS AND CHARACTERIZATION STUDIES ON GLYCINE PICRATECRYSTAL DOPED WITH CDCL$_2$: A NONLINEAR OPTICAL MATERIAL

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ABSTRACT

Crystals of Glycine picrate doped with manganese chloride had grown successfully by solution growth method from its aqueous solution. The grown crystals were subjected to X-ray diffraction (XRD) studies to identify the morphology and structure. The FTIR study reveals the presence of functional groups of the sample under investigation. The NLO property of the crystals has been confirmed by UV spectrum which is established through the UV cut-off range below 490 nm that is sufficient for SHG efficiency. The XRD spectrum of the sample was indexed using the Chekcel software.

Keywords: Glycine picrate, FTIR, UV, XRD, Chekcell.

INTRODUCTION

Materials with excellent nonlinearities have been studied extensively for their possible applications in various fields like telecommunication, optical computing, optical data storage and optical information processing[1-3].Purely inorganic NLO materials have excellent mechanical and thermal properties, but possess relatively modest optical nonlinearity because of the lack of extended π-electron delocalization[3, 4]. Hence it may be useful to prepare semi organic crystals which combine the positive aspects of organic and inorganic materials, resulting in useful nonlinear optical properties.Semi organic materials structurally involve one or more kind of hydrogen bonds, which have been identified as one of the NLO functional bonds. Semi organicmaterials possess several attractive properties such as high damage threshold, wide transparency range, less deliquescence and high non-linear coefficient, which make them suitable for frequency doubling[5,6].

MATERIALS AND METHOD

Exactly one molar **Picric acid[M.F.$C_6H_3N_3O_7$]** (1M) solution is prepared by weighing accurately 22.91 g of picric acid and is dissolved in the 100 ml of doubly distilled deionised water and **Glycine [M.F. NH_2CH_2COOH].** (1M) solution is prepared by weighing exactly 7.5 g and is dissolved in 100 ml of doubly distilled deionised water. The equimolar solutions are heated separately for five minutes. They are mixed thoroughly with stirring while in hot Condition.

The **dopant Cadmium chloride[M.F. $CdCl_2$]** is added in the ratio of 0.1M by weighing about 1.83 g and is mixed with the reagents directly. After having added completely, it is kept aside until it attains the room temperature. After that it is cooled in the ice bath till the precipitate is formed.

It is filtered, dried and a portion is taken for preparing the saturated solution. The saturated solution is prepared and heated to about 60^0 C for 5 Minutes. It is filtered and kept undisturbed. The fine crystals are harvested within a span of three to five days. The Picric acid-Glycine crystals doped with Cadmium chloride are characterized using FTIR and XRD studies.

RESULTS AND DISCUSSIONS

UV VISIBLE SPECTROSCOPIC STUDIES

Figure shows the absorbance zone around

203.56 nm (Ultra-violet wavelength) where a wide band completely transparent in all the visible range is observed (Infrared wavelengths).[7,8] This means that this material presents a good non-absorbance band in the visible range for expected applications.

A little protuberance around the 356.64nm is observed.[9] This little peak is still outside the visible zone (UV zone) and it could present some absorbance if the crystal were to be excited with 600 nm (red color) trying to obtain a second harmonic of 356.64 nm (UV color).

Optical properties of the grown crystals were studied using Arithmetic UV spectrometer. Optical transmittance and absorption were recorded for the crystals of thickness approximately around 2mm.From the spectra [Figure], it is evident that crystals have UV cut off below 490 nm which is sufficient for SHG Laser validation of 1064 nm or other application in the blue region.

There is a shift in the cut off wavelength due to additive effect. The crystals have wide transparency between 200 to 1100 nm is the most desirable property of the crystals used for nonlinear optical application.The recorded transmission is almost above 95% throughout the region. This is the most desirable property of the crystals used for nonlinear optical application. The peak around 203.56 nm corresponds to π - π^* conjugation.

The depth of the peak varies with the additive present. The increased depth which is favourable for more non-linear effect is observed in this crystal at 356.64 nm. The dependence of optical absorption coefficient and the photon energy helps to study the band structure and the type of transmission of electrons.

As a consequence of wide band gap, the crystals under study have relatively longer in the visible region. The internal efficiency of the device also depends upon the absorption coefficient. Hence by tailoring the absorption coefficient and tuning the band gap of the material, one can achieve devised material, which is suitable for fabricating various layers of the optoelectronic devices as per requirements.[10]

FTIR SPECTRAL STUDIES

Fourier Transform Infrared spectrometry (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 $CdCl_2$ crystal is presented in the figure

The appearance of N-H Stretching frequency at 3442.05 cm^{-1} confirms the presence of amino group present in the amino acid, Glycine. This is further supported by the presence of two C-N Stretching frequency at 1333.53cm^{-1} and 1269cm^{-1}. The carboxylic acid functional group in the Glycine picrate is identified by the two O-H Stretching frequency and one O-H bending frequency corresponding to 2730.38cm^{-1} and 2641.02cm^{-1} and 1434.39cm^{-1} respectively.

The C-H Stretching frequency at 3082.14cm^{-1} confirms the aromatic ring in the picric acid. The hydrogen bonded O-H Stretching frequency at 3235.98cm^{-1} show the phenolic group in the picric acid. The presence of NO_2 Asymmetric stretching frequency at 1634.39cm^{-1} confirms the nitro groups present in the Glycine picrate.

From the spectral data it has been clearly established that the sample under investigation is Glycine-picrate doped with Cadmium chloride.

XRD STUDIES

The grown specimenGlycine-picratedoped with$CdCl_2$ 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. shows the high-resolution rocking or diffraction curve (DC) recorded for the specimen Glycine-picratedoped with $CdCl_2$ using (001) diffracting planes in symmetrical Bragg geometry by employing the XPERT-PRO Philips X-diffractometer with CuKα1 radiation.

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 11.913 and 76.774 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 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.

The powdered pattern XRD Spectrum of copper chloride Doped Glycine Picrate Crystal has been indexed using CHEKCELL software. The unit cell parameters are a = 14.88 Å, b = 6.69 Å, c = 15.08 Å and α=90.00°, β=93.71, γ=90.

The system belongs to monoclinic p21/A[11]. The cu K λ= 1.54060.The lowest experimental 2 θ value and the highest experimental value respectively say $2\theta1$=11.913 and $2\theta2$=76.774 have been taken to calculate the hkl values.

The 2θ positions and the d-spacings are also calculated. The table shows the comparison of the calculated and the experimental values. From the table, it is revealed that the assignment of hkl values is so accurate since there isgood agreement of calculated values with the experimental values. Experimental d values of pure samples are in well agreement with standard JCPDS values.[12] The variations in intensity of peaks of doped crystals may be attributed to the incorporation of dopant in crystal lattice.

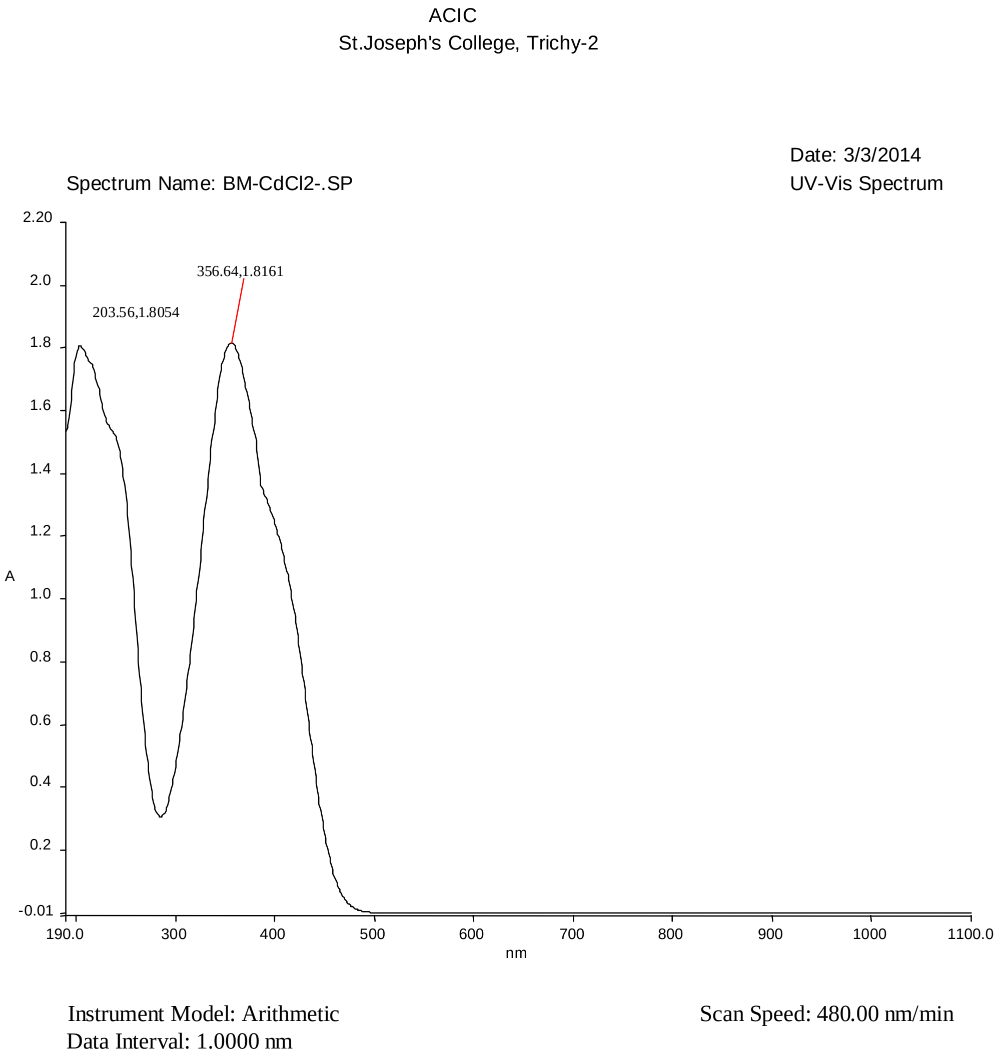

Fig. 1: UV Absorption spectrum of Glycine-picrate doped with $CdCl_2$

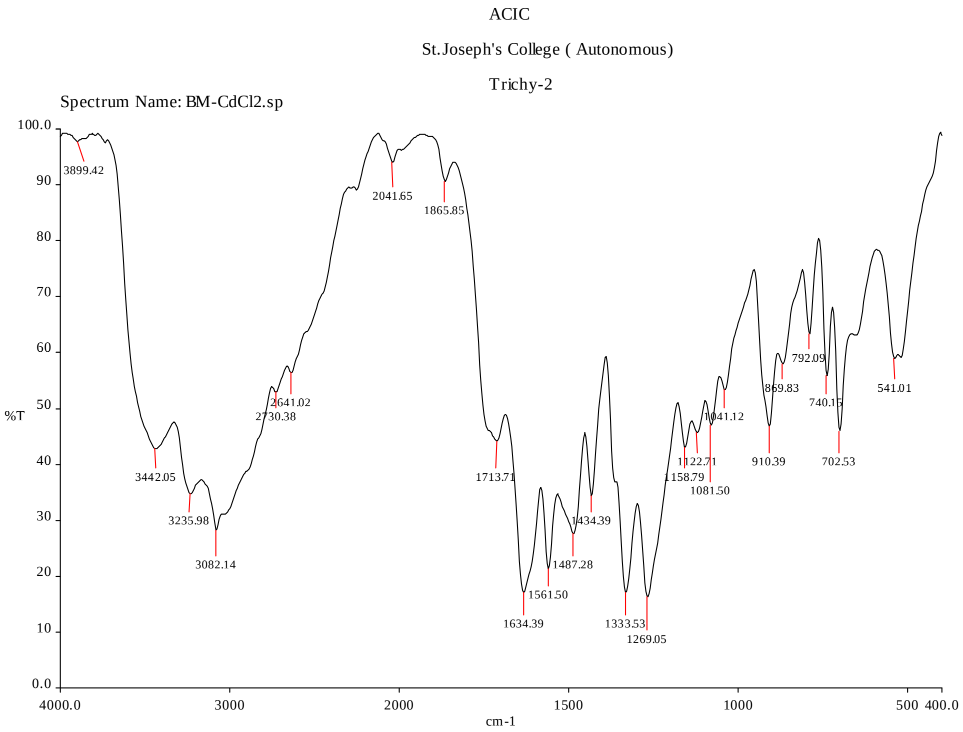

Fig. 2: FTIR spectrum of Glycine picrate doped with cadmium chloride

Table 1: Details of FTIR spectrum of Glycine picrate dopedwithcadmiumchloride

S.N	Wave No cm^{-1}	Mode	Comment
1	3442.05	N-H Stretch	Amines
2	3235.98	O-H H bonded	Phenol
3	3082.14	C-H Stretch	Aromatic ring
4	2730.38	O-H Stretch	Carboxylic acid
5	2641.02	O-H Stretch	Carboxylic acid
6	1713.71	C=OStretch	Acid
7	1634.39	No_2AsymmetricStretch	Nitro group
8	1487.28	C-H bond	Alkenes
9	1434.39	O-H bond	Carboxylic acid
10	1333.53	C-N Stretch	Amines
11	1269.05	C-NStretch	Amines
12	1158.79	C-OStretch	Carboxylic acid
13	910.39	O-H bond	Carboxylic acid
14	869.83	C-HStretch	Aromatic

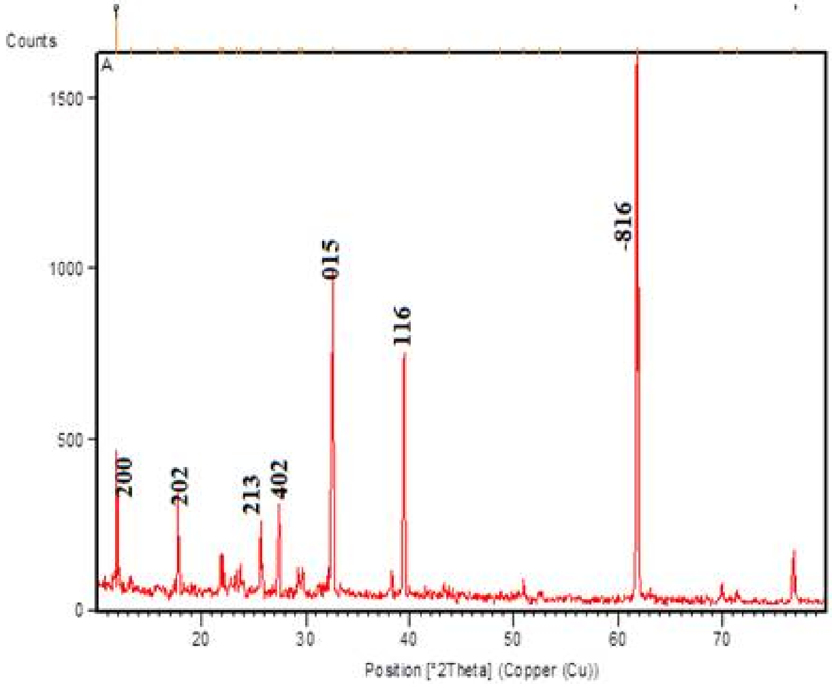

Fig 3: XR.D Spectrum of glycine picrate doped with cdcl$_2$ indexed with chekcel software

Table 2: Details ofxrd spectrum of glycine picrate doped with CdCl$_2$

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
11.913(2)	305(23)	0.075(9)	7.42284	17.21
13.23(2)	20(5)	0.24(9)	6.68637	1.15
15.80(7)	8(3)	0.4(2)	5.60318	0.48
17.39(1)	32(10)	0.07(4)	5.09530	1.81
17.783(2)	230(15)	0.100(9)	4.98375	12.98
21.829(6)	89(12)	0.12(2)	4.06834	5.03
22.122(7)	86(6)	0.100(3)	4.01500	4.87
23.32(1)	48(13)	0.11(6)	3.81103	2.73
23.72(1)	52(8)	0.16(4)	3.74833	2.96
25.675(5)	144(17)	0.12(3)	3.46694	8.16
27.417(5)	134(14)	0.13(2)	3.25043	7.57
29.30(1)	39(7)	0.21(4)	3.04548	2.19
29.68(1)	56(10)	0.17(4)	3.00757	3.16
32.532(2)	863(31)	0.117(6)	2.75012	48.75
38.20(1)	63(14)	0.14(5)	2.35386	3.56
39.388(2)	643(22)	0.132(6)	2.28576	36.34
43.81(2)	26(10)	0.06(5)	2.06470	1.48
48.74(3)	10(4)	0.08(9)	1.86663	0.57
50.90(1)	46(9)	0.13(4)	1.79270	2.61
52.50(4)	13(5)	0.2(1)	1.74160	0.71
54.47(6)	6(1)	0.1(1)	1.68332	0.33
61.7965(9)	1771(31)	0.118(3)	1.50005	100.00
69.88(1)	38(6)	0.21(5)	1.34496	2.13
71.41(1)	38(6)	0.12(3)	1.31980	2.15
76.774(4)	151(10)	0.12(1)	1.24047	8.53

Table 3: Comparision of Calculated 2 0 Values with the experimental value with hkl spectrum of glycine picrate doped with $CdCl_2$

S.No	h	k	1	20 Calculated	20 Experimental	d calculated	d Experimental
1	2	0	0	11.911	11.913	7.5242	7.42284
2	1	1	1	**15.809**	**15.80**	5.6012	5.60318
3	2	0	2	17.300	**17.39**	5.1217	5.09530
4	2	1	2	21.837	21.829	4.0667	4.06834
5	0	1	3	22.132	22.122	4.0133	4.01500
6	3	1	3	29.344	29.30	3.0412	3.04548
7	-1	2	2	29.661	29.68	3.0095	3.00757
8	0	1	5	32.598	32.532	2.7447	2.75012
9	0	1	6	38.295	38.20	2.3485	2.35386
10	1	1	6	39.166	39.388	2.2982	2.28576
11	-2	3	2	43.812	43.81	2.0647	2.06470
12	3	3	3	48.733	48.74	1.8671	1.86663
13	-7	2	1	50.966	50.90	1.7904	1.79270
14	-5	3	2	52.214	52.50	1.7505	1.74160
15	4	3	4	54.521	54.47	1.6817	1.68332
16	-8	1	6	61.748	61.7965	1.5011	1.50005
17	2	4	6	69.064	69.88	1.3589	1.34496
18	1	3	9	71.015	71.41	1.3262	1.31980
19	1	4	8	76.733	76.744	1.2410	1.24047

CONCLUSION

Transparent crystals of picric acid-glycine doped with-Cadmium chloride were grown by slow evaporation technique at low temperature. Evolution of lattice parameters and density measurements conform that the dopant, Cadmium chloride has gone into the lattice of the crystals.

The FT-IR study confirms that the presence of Glycine in the doped crystals. The spectra reveal that the Glycine additives have not destroyed the optical transference of the crystals and have sufficient transmission in the entire IR region.

It has been observed that the addition of Glycine enhances transparency, thermal stability, second harmonic generator efficiency, nonlinear optical efficiency and reduces the values of K.D.P crystals when compared. The various regions of absorption are shown in the FT-IR spectra.

The X-ray diffraction studies of glycine picrate doped with $Cdcl_2$ has revealed that the sample under investigation is conformed the crystallinity. It has been indexed using the checked application software. The hkl values are calculated and tabulated and 2θ values. The d spacing have been calculated and tabulated along with the experimental 2θ values of powdered pattern of x-ray spectrum.

The U.V. spectrum conformed that the crystal under examination is well suited for having the SHG efficiency of nonlinear optical properties.

It will be useful for fabricating suitably in optical industries.

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