INTERNATIONAL JOURNAL OF PHARMACEUTICAL, CHEMICAL AND BIOLOGICAL SCIENCES

Available online at www.ijpcbs.com

Research Article

STRUCTURAL CHARACTERIZATION STUDIES ON GLYCINE PICRATECRYSTAL DOPED WITH $MNCL_2$: A NONLINEAR OPTICAL MATERIAL

K. Rajarajan[1]*, B. Mohanadevi[1], B. Manimekalai[1] and G. Madhurambal[2]

[1]Department of Chemistry, Rajah Serfoji, GOVT College, Thanjavur, Tamil Nadu-613 005, India.
[2]Department of Chemistry, ADMCollege for women, Nagappattinam-DT, Tamil Nadu India.

ABSTRACT

Glycine Picrate crystals doped with Manganese Chlorides have been grown by slow evaporation technique at room temperature. 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 crystal system has been identified and lattice dimensions have been measured using X-ray diffraction analysis. They have been indexed using CHEKCEL software. The calculated 2theta values are compared with the experimental values. The functional groups of the grown crystals were qualitatively examined using FTIR analysis.

Keywords: Glycine picrate, Manganese Chloride, FTIR, X-ray diffraction, Nonlinear optical properties.

INTRODUCTION

Picric acid can be crystallized with amino acids toform the respective picrate crystals apart from the application of picric acid to identify the alkaloids as in the Mayer's test[1,2] and the derivatives of picric acid serve its vital role in anti-microbial activity[3].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 Å, b = 6.722 Å, c = 15.165 Å and β= 93.65º. 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 hasdirect influence on the NLO efficiency of the crystals.

MATERIALS AND METHODS

Glycine PicrateCrystalDoped with $MnCl_2$

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 deionized 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 deionized water. The equimolar solutions are heated separately for five minutes. They are mixed thoroughly with stirring while in hot Condition. The **dopant Manganese chloride[M.F. $MnCl_2$]** is added in the ratio of 0.1M by weighing about 1.25 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 Manganese 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)[14, 15]. 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.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 favorable 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.[16]

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 $MnCl_2$ crystal is presented in the figure

The appearance of O-H Stretching frequency at 2905.40 confirm the presence of carboxylic acid functional group present in the amino and glycine. This is supported by the additional one C=O Stretching frequency and one more O-H bending frequency that correspond to 1713.51 and 912.09.

The amino group in the glycine give rise to a N-H Stretching frequency that corresponds to 3398.67.This is confirmed by the one N-H bending frequency at 1630.84 and two more C-N Stretching frequency at 1332.34 and 1268.59. The appearance of two C-C Stretching frequency at 1493.54 and 1434.20 confirm the presence of aromatic ring in the picric acid.

From the available spectral date it is clearly established that the sample under investigation is Glycine-picrate doped with Manganese chloride.

XRD STUDIES

The grown specimenGlycine-picratedoped with$MnCl_2$ 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 specimenGlycine-picratedoped with$MnCl_2$ using (001) diffracting planes in symmetrical Bragg geometry by employing the XPERT-PRO Philips X-diffractometer with $CuK\alpha 1$ 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 11.8 and 56.8arc 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 ofthe 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 diffract meter used in the present investigation.

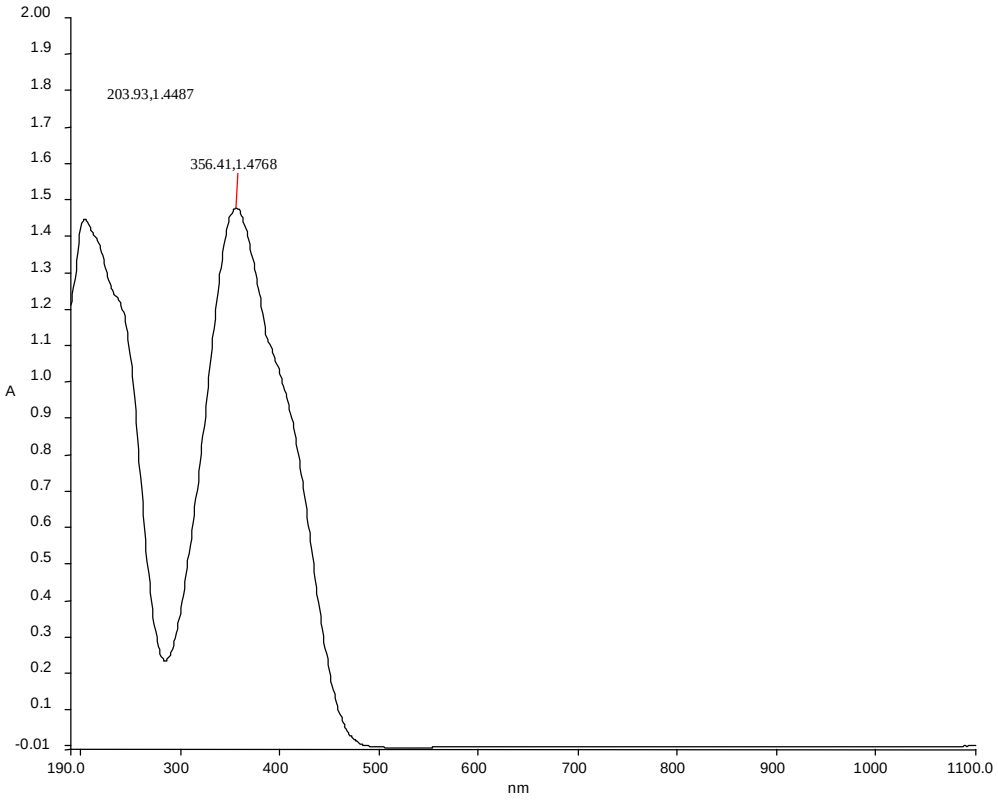
The powdered pattern XRD Spectrum of copper chloride Doped Glycine Picrate Crystal has been indexed using CHEKCELL software. The unit cell parameters are a = 14.88 Å, b = 6.69 Å, c = 15.08 Å and α=90.00º, β=93.71, γ=90.

The system belongs to monoclinic p21/A[17]. The cu K λ= 1.54060.The lowest experimental 2 θ value and the highest experimental value respectively say $2\theta 1$=11.592 and $2\theta 2$=70.597 have been taken to calculate the hkl values.

The 2θ positions and the d-spacing 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 agreementwith standard JCPDS values.[18] The variations in intensity of peaks of doped crystals may be attributed to the incorporation of dopant in crystal lattice.

ACIC
St. Joseph's College, Trichy-2

Date: 3/3/2014
Spectrum Name: KM-MnCl2-.SP
UV-Vis Spectrum



Instrument Model: Arithmetic
Data Interval: 1.0000 nm
Scan Speed: 480.00 nm/min

Fig. 1: UV Absorption spectrum of Glycine-picrate doped with $MnCl_2$

Table 1: Details of FTIR spectrum of Glycine picrate doped with $MnCl_2$

S.NO	WAVE NO CM^{-1}	MODE	COMMENT
1	3398.67	N-H Stretch	Amines
2	3084.32	C-H Stretch	Aromatic
3	2905.40	O-H Stretch	Carboxylic acid
4	1713.51	C=O Stretch	Carboxylic acid
5	1630.84	N-H Bond	1^0 Amine
6	1493.54	C-C Stretch (in ring)	Aromatic
7	1434.20	C-C Stretch (in ring)	Aromatic
8	1332.34	C-N Stretch	Aromatic Amine
9	1268.59	C-N Stretch	Aromatic Amine
10	912.09	O-H Bond	Carboxylic Acid
11	793.60	N-H Stretch	1^0, 2^0, Amine

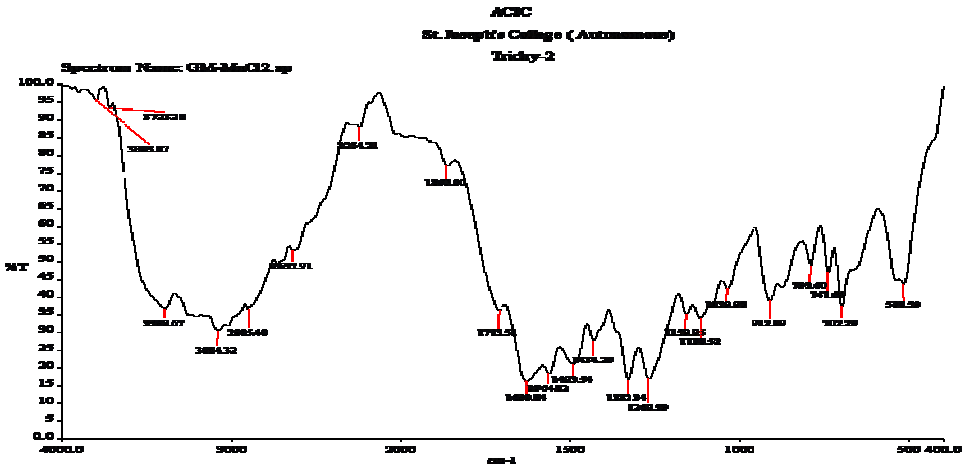


Fig. 2: FTIR spectrum of Glycine-picrate doped with Manganese chloride

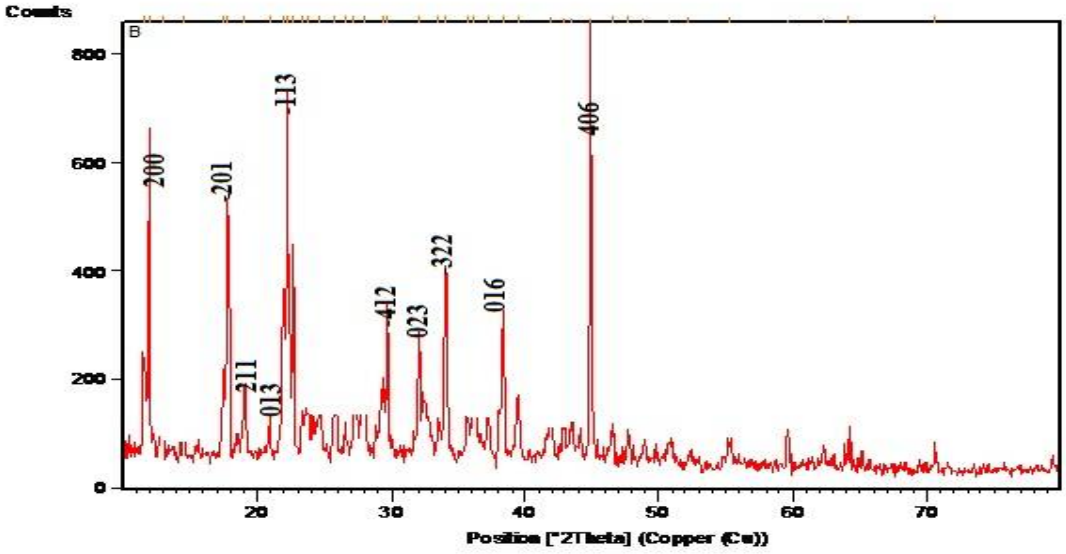


Fig. 3: XRD spectrum of glycine picrate doped with manganese chloride (indexed with checkcel)

Table 2: Details of XRD Spectrum of Glycine Picrate Doped with $MnCl_2$ Showing 2 Theta positions

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
11.592(7)	110(9)	0.20(2)	7.62803	15.63
11.944(3)	292(14)	0.16(1)	7.40386	41.52
12.951(9)	67(7)	0.22(2)	6.83027	9.50
14.570(7)	65(9)	0.13(3)	6.07480	9.28
17.474(8)	110(10)	0.23(2)	5.07106	15.60
17.807(3)	328(16)	0.135(8)	4.97694	46.61
19.060(8)	89(8)	0.22(2)	4.65257	12.72
20.93(1)	50(10)	0.13(4)	4.24089	7.09
21.921(6)	196(12)	0.23(2)	4.05138	27.86
22.268(3)	414(24)	0.15(1)	3.98900	58.93
22.689(3)	266(18)	0.13(1)	3.91596	37.79
23.38(2)	46(10)	0.16(4)	3.80221	6.52
23.728(6)	139(13)	0.18(2)	3.74672	19.71
24.56(4)	58(14)	0.43(9)	3.62134	8.20
25.77(1)	87(9)	0.24(3)	3.45439	12.34
26.54(1)	41(7)	0.08(2)	3.35587	5.82
27.231(6)	121(10)	0.22(2)	3.27219	17.23
27.976(8)	102(13)	0.17(3)	3.18678	14.57
29.32(1)	89(8)	0.29(3)	3.04318	12.65
29.715(6)	170(17)	0.13(2)	3.00410	24.19
32.046(7)	141(9)	0.30(2)	2.79073	20.10
33.53(2)	42(9)	0.20(6)	2.67071	5.99
34.031(5)	251(13)	0.23(2)	2.63234	35.76
35.635(8)	79(13)	0.10(2)	2.51741	11.28
36.11(1)	104(11)	0.34(3)	2.48564	14.85
37.185(7)	114(11)	0.17(2)	2.41595	16.16
38.286(7)	179(15)	0.23(2)	2.34902	25.52
39.398(9)	80(8)	0.23(3)	2.28521	11.44
41.94(2)	57(9)	0.28(5)	2.15244	8.05
42.88(1)	51(10)	0.20(7)	2.10749	7.29
43.46(2)	51(9)	0.32(6)	2.08041	7.30
44.903(2)	703(24)	0.150(7)	2.01701	100.00
46.50(4)	38(15)	0.2(1)	1.95133	5.35
47.71(2)	41(9)	0.15(6)	1.90458	5.81
48.84(3)	22(6)	0.2(1)	1.86317	3.07
50.81(2)	29(5)	0.36(8)	1.79535	4.19
52.2(2)	11(2)	0.01(2)	1.75152	1.51
55.24(2)	37(7)	0.27(8)	1.66146	5.22
59.616(9)	54(8)	0.11(3)	1.54959	7.70
62.24(3)	21(4)	0.4(1)	1.49045	2.96
64.13(4)	21(5)	0.5(1)	1.45094	3.04
70.549(7)	56(9)	0.11(3)	1.33386	8.03

Table 3: Comparison of calculated 2 θ values with the experimental value with hkl indexed with chekcel

S.N	h	k	l	2 θ calculated	2 θ experimental	Dcalculated	D experimental
1	2	0	0	11.911	11.944	7.4244	7.40386
2	-2	1	0	17.833	17.807	4.97694	5.07106
3	2	1	1	19.031	19.060	4.0595	4.65257
4	0	1	3	22.132	22.298	4.0133	3.98900
5	-1	1	3	22.631	22.698	3.9258	3.91596
6	-4	1	2	29.319	29.715	3.0437	3.00410
7	0	2	3	32.137	32.046	2.7830	2.79073
8	-3	2	2	34.039	34.031	2.6318	2.63234
9	0	1	6	38.295	38.286	2.3485	2.34902
10	4	0	6	44.868	44.903	2.0185	2.01701

CONCLUSION

Transparent crystals of picric acid-glycine dopant-Manganese chloride were grown by slow evaporation technique at low temperature. Evolution of lattice parameters and density measurements conform that the dopant, Manganese 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 $Mncl_2$ 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 experimental2θvalues 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.

REFERENCES

1. Sachinkumar, Hotam sing choudhari and Chandrabhanseniya . J Chem Pharm Res. 2011;3(4):854-860.
2. Chandrabhanseniya, Sumit sing trivedia and Santoshkumarverma. JChem Pharm Res. 2011;3(6): 330-336.
3. Avinashseth, NamanDhoshi, Sen DJ, Badmanathan R and Patel CN. J Chem Pharm Res. 2010;2(2): 1-12.
4. Moitra S and Kar T. J Cryst Growth. 2008;310:4539.
5. Sun ZH, Zhang GH, Wang XQ, Cheng XF, Liu XJ, Zhu LY, Fan HL, Yu G and Xu D. J Cryst Growth. 2008;310:2842 .
6. Uma Devi T, Lawrence N, Ramesh Babu R and Ramamurthi K. J Cryst Growth. 2008;310:116 .
7. Uma Devi T, Lawrence N, Ramesh Babu R and Ramamurthi K. Spectrochim ActaA. 2008;71:340.
8. Uma Devi T, Lawrence N, Ramesh Babu R, Selvanayagam S, Helen Stoeckli-Evans and Ramamurthy K. Cryst Growth Des. 2009;9:1370.
9. Uma Devi T, Lawrence N, Ramesh Babu R and Ramamurthi K. Mat Res India. 2008;5:397.
10. Kai T, Goto M, Furuhata K and Takayanagi H. Anal Sci. 1994;10:359.
11. Hales JM, Zheng SJ, Barlow S, Mrder SR and Perry JW. J Am Chem Soc. 2006;128:11362.
12. Marder SR, Kippelen B, Jen AKY and Peyhambarian N. Nature. 1997;388:845.
13. Wang Q, Han J, Gong H, Chen D, Zhao X, Feng J and Ren J. Adv Funct Mater. 2006;16:2405.
14. Lydia. J Crystal growth. 2009;311(4):1161-1165.
15. Martin Brittodhass SA and Natararajan S. Crystal Research and Technology. 43(8): 869-873.
16. Uma Devi. J Min Mat Charact Engg. 2009;8(4):393-403.
17. Thilagavathi SR and Ambujam K. Transactions of the Indian Institute of metals. 2011;64(1-2):143-14.
18. Sheik-Bahae M, Said AA, Wei T-H, Hagan DJ and Van Stryland EW. IEEE J Quantum Electron. 1990;26:760.