INTERNATIONAL JOURNAL OF PHARMACEUTICAL, CHEMICAL AND BIOLOGICAL SCIENCES

Available online at www.ijpcbs.com

Research Article

SYNTHESIS GROWTH AND CHARACTERISATION OF SUCCINIC-PICRATE CRYSTAL DOPED WITH COPPER SULPHATE (0.2M)

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ABSTRACT

Picric acid with Succinic acid resulting the Succinic picrate crystals doped with copper sulphate of (0.1M) has been reported already in this journal . The present study investigates the change in spectral and optical properties of the synthesized crystal when the concentration of the dopant copper sulphate has been increased. Succinic-Picrate crystals are synthesized in equi molar proportions of picric acid and succinic acid and incorporating a concentration of (0.2M) copper sulphate by slow evaporation technique. The grown crystals are investigated by various spectral techniques like FTIR Spectroscopy, U.V Spectroscopy. It is examined using the XRD Studies powdered pattern. The well-defined peaks at specific 2theta values show high crystallinity of the grown crystals. The values of hkl, relative intensity and 2 theta values for the reflection peaks of the powder XRD pattern are given. The crystals have wide transparency between 200 to 1100nm. 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 powdered pattern of XRD has been indexed using Chekcell software.

Keywords: Succinic picrate, Laser optics, nonlinear optics, FTIR, XRD, SEM. Checkcell.

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[1,2].The NLO phenomena occur when the optical properties of molecules change in the presence of strong external electric fields, i.e., high-energy laser beams. Most organic NLO crystals have usually poor mechanical and thermal properties and are susceptible for damage during processing even though they have large NLO efficiency.

MATERIALS AND METHODS

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 **Succinic acid [M.F. $C_4H_6O_4$]** (1M) solution is prepared by weighing exactly 11.809 g and is dissolved in 100 ml of doubly distilled deionised water. The 1:1 equimolar solutions are heated separately for five minutes. They are mixed thoroughly with stirring while in hot Condition. The dopant copper sulphate solution is added in the ratio of 0.2M by weighing about 4.9940 g and is mixed directly in to the picric acid and Succinic acid solution slowly with constant shaking. 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. Saturated solution is prepared for growing crystals. It is filtered and kept undisturbed. The fine crystals are harvested. The Succinic-Picrate crystals doped with copper sulphate are characterized using FT-IR and XRD studies, U.V-VIS, Single crystal XRD and SEM.

RESULTS AND DISCUSSIONS

UV absorption studies

Figure shows the absorbance zone around 234.91nm (Ultra-violet wavelength) where a wide band completely transparent in all the visible range is observed (Infrared wavelengths)[3, 4]. This means that this material presents a good non-absorbance band in the visible range for expected applications. A little protuberance around the 356.43 nm is observed[5] 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 356.43 nm (UV color). Other noticeable characteristic in the absorption spectrum is a wide transparency window within the range of 557 nm which is desirable for NLO crystals because the absorptions in an NLO material near the fundamental or second harmonic signals will lead to the loss of the conversion of SHG. Due to this property, LASN and DASN have potential uses for SHG using an Nd: YAG laser (1064 nm) to emit a second harmonic signal within the green region (930nm) of the electromagnetic spectra.

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 [Figure7.1.1], it is evident that crystals have UV cut off below 490 nm (260nm), which is sufficient for SHG Laser validation of 1064nm 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 1100nm.

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 234.91 nm is correspond 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 356.43 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[6].

FTIR STUDIES

The presence of O-H stretching frequency at 1697.70 confirms the presence of Succinic acid. The appearance of medium O-H bending frequency at 1380.78 shows the presence of phenolic group in the picric acid. The presence of strong Asymmetric stretching frequency at 1638.24confirm the NO2 groups present in the picric acid. The appearance of stretching frequency at 674.11 shows the aromatic nature of the sample.

From the available FTIR Spectral information, it has been established that the compound under investigation is Succinic-picrate doped with copper sulphate.

X-ray diffraction

The grown specimen Succinic-picrate doped with copper sulphate was first lapped and chemically etched in a non preferential etchent of water and acetone mixture in 1:2 volume ratio to remove the non-crystallized solute atoms remained on the surface of the crystals and also to ensure the surface planarity of the specimen. Fig.7.1.3 shows the high-resolution rocking or diffraction curve recorded for this specimen using (002) diffracting planes in symmetrical Bragg geometry by employing the multi crystal X-ray diffractometer (0000000083004288) described above with MoKα1 radiation. The powder XRD studies for the grown crystals were carried out and the collected data are provided in the table. 7.1.2.

The powder X-ray diffraction (XRD) patterns are shown in the figure. The well-defined peaks at specific 2θ values show high crystallinity of the grown crystals of Succinic-picrate doped with copper sulphate. The values of hkl, relative intensity and 2 θ values for the reflection peaks of the powder XRD pattern are given table. The resultant peaks in the diffractogram (Figure7.1.3) show an intense peak at 21.335(3) ° (intense peak). The peaks appearing in the spectrum that have not been identified can be attributed to the formation of the compound Succinic-picrate doped with copper sulphate.

As seen in the figure, in addition to the main peak at the centre, this curve contains two 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 at 34.714(6) ° and 38.066(4) ° away from the main peak are due to internal structural very low angle (≤ 1 arc min) grain boundaries.

The tilt angle i.e. the mis orientation angle of the boundary with respect to the main crystalline region for both the observed very low angle boundaries are 34.714(6)° and 38.066(4)°. The full width at half maximum (FWHM) values for

the main peak and the two low angle boundaries are respectively0.12 (1) °, 0.001(1) °and 0.10(1)°. 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 around 700 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 multi crystal X-ray diffractometer used in the present investigation.

The powdered pattern XRD Spectrum of Succinic picrate doped with copper sulphate Crystal has been indexed using **CHEKCELL** software in Table 6.3.The unit cell parameters are a = 9.21Å, b = 9.66 Å, c = 19.04 Å and α=90.00º, β=90, γ=90. The system belongs to **ORTHORHOMBIC. The cu K λ=1.54060**.The lowest experimental 2 θ value and the highest experimental value respectively say **$2\theta_1$=23.125 and $2\theta_2$=65.22** have been taken to calculate the hkl values. The 2θ positions and the d-spacings are also calculated.

The table 6.4.3. Shows the comparison of the calculated and the experimental values. From the table, it is revealed that the assignment of hkl values are so accurate since there is good agreement of calculated values with the experimental values. Experimental d values of pure samples are in well agreement with standard JCPDS values[7].

SINGLE-CRYSTAL X-RAY DIFFRACTION

A selected transparent grown crystal was subjected to single crystal X-ray diffractometer to determine Crystal structure and lattice parameters. Single crystal XRD analysis reveals that the grown crystal belongs to orthorhombic P structure. The lattice parameters were found to be a = 9.21Å, b = 9.66 Å, c = 19.04Å and α=90.00º, β=90, γ=90.with unit cell volume V = 1694Å3.

SEM ANALYSIS

The SEM micrograph of Succinic picrate doped with copper sulphate is shown in Fig. 5.3. The photograph clearly reveals the step like growth pattern on the surface of the grown crystal and also the formation of few isolated islands. Succinic picrate doped with copper sulphate, the semi organic crystal with high SHG efficiency and laser damage energy density has been grown by low temperature solution growth technique. The crystal has a moderate thermal stability and favourable optical properties. Being the semi organic material with interesting properties, Succinic picrate doped with copper sulphate will be a strong candidate for future SHG devices.

SHG MEASUREMENT

The study of nonlinear optical conversion efficiency was carried out using the experimental setup of Kurtz and Perry[8]. A Q-switched Nd: YAG laser beam of wavelength 1064 nm, with an input power of 6.1.mj. The grown crystal of Succinic-picrate doped with copper sulphate was powdered with a uniform particle size and then packed in a micro capillary of uniform bore and exposed to laser radiations. The generation of the second harmonics was confirmed by the emission of green light. A sample of potassium dihydrogen phosphate (KDP), also powdered to the same particle size as the experimental sample, was used as a reference material in the present measurement. The relative SHG conversion efficiency of Succinic-picrate doped with copper sulphate was found to be greater than that of KDP. This may be attributed to the molecular structure of Succinic-picrate doped with copper sulphate residue is engaged in a strong hydrogen bond with the picrate anion[9]. Table 7.4 shows comparison of SHG signal energy output of Succinic-picrate doped with copper sulphate.

CONCLUSION

Transparent crystals of Succinic-Picrate crystals doped with copper sulphate were grown by slow evaporation technique at low temperature. Evaluation of lattice parameters and density measurements confirm that the dopant copper sulphate has gone into the lattice of the crystals. X- ray diffraction studies are conducted on Succinic-Picrate crystals doped with copper sulphate using XPERT- PRO – Philips X-diffractometer using the powdered pattern.

The FT-IR study confirms the presence of Succinic -Picrate crystals doped with copper sulphate. The spectra reveal that the functional group additives have sufficient transmission in the entire IR region.

In the U.V absorption studies- characteristic feature in the absorption spectrum is a wide transparency window within the range of 490 nm which is desirable for NLO crystals because the absorptions in an NLO material near the fundamental or second harmonic signals will lead to the loss of the conversion of SHG. The dependence of optical absorption coefficient and the photon energy helps to study the band

structure and the type of transmission of electrons. The SHG measurement shows that Succinic-Picrate crystals doped with copper sulphate is a promising material that has the Non-linear optical properties.

ACKNOWLEDGEMENT

The authors sincerely thank to Dr. C.Sanjeeviraja, Alagappa University, and Karaikudi, Dr.Vincent sagayaraj, St. Joseph's college Trichi, Dr.P.K. Das, IPC lab, IISC, Bangalore.

Tables and Figures

Fig. 1A **Fig.1B**

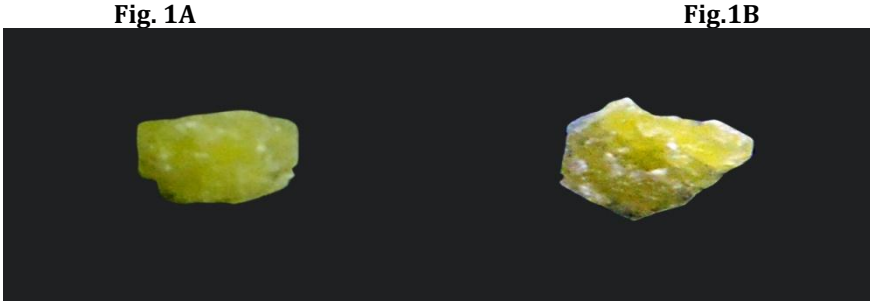

Fig. 1C **Fig. 1D**

Fig. 1A to 1D: Grown crystals of succinic-picrate-doped with copper sulphate (0.2M)

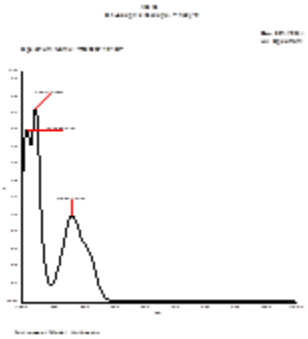

Fig. 1.1: UV Spectrum of Succinic -Picrate crystals doped with copper sulphate

Table 1.1: Details of FTIR spectrum of Succinic picrate dopped with C_USO_4

S.NO	WAVE NO.	MODE	COMMENT
1.	3429.71	O-H Stretch H- bonded	Strong band
2.	2081.84	C-D Stretch	Of variable intensity
3.	1697.70	C=O Stretch	Carboxylic acids
4.	1638.24	Strong NO2 Asy Stretch	NO2 groups
5.	1114.89	Medium C-N Stretch	Of variable intensity
6.	674.11	Ar C-H Stretch	Aromatic
7.	1380.78	Medium O-H Bending	Phenolic

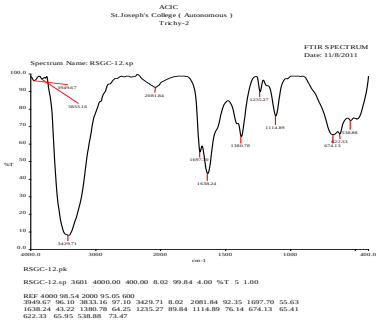

Fig. 1.2: FTIR Spectrum of Succinic - Picrate crystals doped with copper sulphate

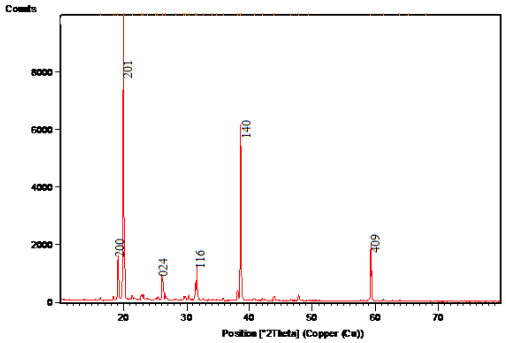

Fig. 7.1.3: XRD Spectrum of Succinic -Picrate crystals doped with Copper sulphate (0.2M)

Table 1.2: Details of 2θ positions in the XRD Spectrum of Succinic-picrate crystal doped with copper sulphate (0.2M)

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
23.74(2)	43(6)	0.32(5)	3.74533	0.54
25.03(1)	60(11)	0.16(4)	3.55508	0.77
25.41(1)	73(9)	0.20(2)	3.50275	0.93
26.165(2)	535(17)	0.214(8)	3.40306	6.82
26.636(6)	149(16)	0.12(2)	3.34400	1.90
28.26(2)	36(5)	0.19(5)	3.15560	0.46
29.587(6)	159(17)	0.12(2)	3.01680	2.02
29.812(6)	164(27)	0.07(2)	2.99457	2.09
30.323(5)	180(16)	0.064(9)	2.94528	2.30
31.376(3)	476(18)	0.180(9)	2.84872	6.07
31.629(2)	1061(41)	0.082(4)	2.82653	13.51
32.52(3)	29(5)	0.33(6)	2.75074	0.37
34.07(3)	20(11)	0.2(1)	2.62904	0.25
34.66(4)	27(15)	0.1(1)	2.58606	0.34
34.714(6)	76(2)	0.001(1)	2.58206	0.96
35.75(2)	49(14)	0.14(7)	2.50948	0.62
38.066(4)	296(21)	0.10(1)	2.36206	3.77
38.5565(6)	5655(60)	0.120(2)	2.33314	72.01
40.66(1)	69(8)	0.28(4)	2.21721	0.88
42.021(9)	75(10)	0.11(2)	2.14846	0.95
43.955(4)	199(14)	0.11(1)	2.05830	2.53
46.616(7)	68(7)	0.06(2)	1.94680	0.87
47.829(5)	168(14)	0.16(2)	1.90023	2.14
49.42(2)	39(9)	0.15(5)	1.84260	0.50
59.2574(9)	2047(32)	0.114(3)	1.55812	26.07
61.280(8)	67(8)	0.12(3)	1.51145	0.85
63.88(1)	44(11)	0.08(3)	1.45601	0.56
65.22(2)	15(7)	0.09(6)	1.42925	0.18
68.05(2)	19(25)	0.1(1)	1.37670	0.25

Table 7.1.3: Calculated hkl values, 2θ and d spacing values for Succinic picrate doped with copper sulphate (0.2M)

hkl value	2θ cal	2θ exp	d cal	d exp
023	23.122	23.125(5)	3.8436	3.84315
203	23.854	23.74(2)	3.7272	3.74533
024	26.265	26.165(2)	3.3903	3.40306
025	29.855	29.812(6)	2.9904	2.99457
205	30.436	30.323(5)	2.9346	2.94528
133	32.638	32.52(3)	2.7414	2.75074
231	34.220	34.07(3)	2.6139	2.62904
225	35.774	35.75(2)	2.5080	2.50948
409	59.270	59.2574(9)	1.5578	1.55812
611	61.292	61.280(8)	1.5112	1.51145
621	63.756	63.88(1)	1.4586	1.45601
536	65.296	65.22(2)	1.4279	1.42925

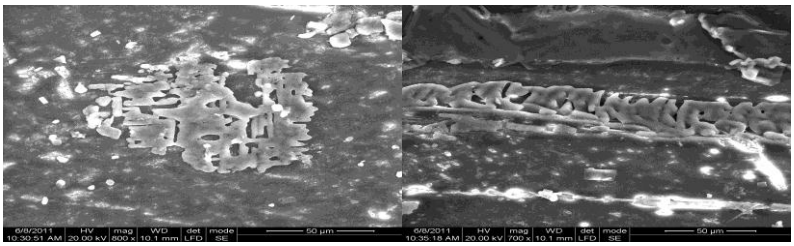

Fig. 7.1.4: SEM photographs of Succinic-picrate crystal doped with copper sulphate (0.2M)

Table 7.4: Relative SHG Conversion Efficiency of some picrate crystals. The input power (mj/pulse) is: 6.1mV

S.NO	CRYSTAL EXAMINED FOR SHG	SHG in mV
1.	**KDP REFERENCE**	**6.8 mV**
2.	Succinic picrate	7.4 mV
3.	Succinic picrate doped with C_uSO_4 0.1M	9.0 mV
4.	Succinic picrate doped with C_uSO_4 0.2M	11.0 mV

REFERENCES

1. Boyd RW. Nonlinear Optics, Academic Press, Inc. San Diego. 1992.
2. Jiang MH and Fang Q. Adv Mater. 1999;11:1147.
3. Lydia. Crystal growth J. 2009;311(4):1161-1165.
4. Martin Brittodhass SA and Natararajan S. Crystal Research and Technology. 43(8):869-873.
5. Narayanan Bhatt M and Dharmaprakash SM. J of Crystal growth. 2002;235:511-516.
6. Uma Devi. J of Minerals and Materials characterisation and Engg. 2009;8(4):393-403.
7. Franken PA, Hill AE, Peters CW and Weinrich G. Phys Rev Lett. 1961;7:118.
8. Kurtz SK and Perry TT. J Appl Phys. 1968;39:3798.
9. Bhagavannarayana G, Ananthamurthy RV, Budakoti GC, Kumar B and BartwalK S. J Appl Cryst. 2005;38:768.