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Research Article

SPECTRAL DIFFRACTION AND OPTICAL PROPERTIES OF SUCCINIC-PICRATE DOPED WITH COPPER SULPHATE- A NONLINEAR OPTICAL CRYSTAL

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ABSTRACT
Crystals that display non linear optical properties have a wide variety of potential applications in the field of laser optics and communication. Succinic-Picrate crystals doped with copper sulphate that are yielded by mixing the equi molar proportions of succinic acid and picric acid by slow evaporation method. The grown crystals are harvested and subjected to Spectral as well as X-ray diffraction studies. FTIR Spectroscopy confirm the functional groups at the appropriate absorption frequencies for the sample under examination. 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. 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. XRD studies revealed that the well-defined peaks at specific 2thetavalues 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.

Keywords: Succinic-picrate, Non-linear optical property, laser optics, XRD, FTIR.

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].
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. Also it is difficult to grow larger sizeoptical-quality crystals of these materials for device applications. 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 toprepare semi organic crystals which combine the positive aspects of organic and inorganic materials, resulting in useful nonlinear optical properties.
The basic requirements for a NLO crystal to be successfully utilized in frequency conversion are alack of centre of symmetry for the molecular charge transfer, significant change in dipole moment upon excitation from the electronic ground state to some excited states , small to moderate excitation energies of the corresponding excited states , Hammett constants of the substituents ,nonzero NLO coefficient, transparency at all wavelengths involved, efficient transfer of energy between the optical waves propagating through the crystal, and good physical (low vapour pressure, high thermo stability) and optical (high damage threshold, large birefringence, low dispersion) properties[5,6]. According to the Philips-Van Vechten-Levine-Xue bond theory[7], constituent chemical bonds of the single crystal determine its NLO responses. Semi organic materials structurally involve one or more kind of hydrogen bonds, which have been identified as one of the NLO functional bonds. Semi organic

materials 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 [8,9].

MATERIALS AND METHODS
SUCCINIC-PICRATE CRYSTAL DOPED WITH COPPER SULPHATE

Exactly one molar Picric acid and Succinic acid are weighed. Equi molar solutions are prepared and heated separately for five minutes. They are mixed thoroughly using the stirrer while in the hot condition. A 0.1M solution of copper sulphate is prepared and it is added solely to the succinic and picric acid mixture with constant shaking.

It is filtered and kept aside for five minutes. After having attained the room temperature, 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 induction time is noticed. The fine crystals are harvested.

The Succinic-Picrate crystals doped with copper sulphate are characterized using FT-IR and XRD studies, U.V-VIS.

RESULTS AND DISCUSSIONS
UV absorption studies

Figure shows the absorbance zone around 260.65 nm(Ultra-violet wavelength) where a wide band completely transparent in all the visible range is observed (Infrared wavelengths)[10,11] This means that this material presents a good non-absorbance band in the visible range for expected applications. A little protuberance around the 365.75 nm is observed[12] 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 365.75nm (UV color). Other noticeable characteristic in the absorption spectrum is a wide transparency window within the range of557nm 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 [Figure], it is evident that crystals have UV cut off below 300nm (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 260.65nm 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 365nm.

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[13]

X-ray diffraction

The grown specimen 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. shows the high-resolution rocking or diffraction curve (DC) recorded for the specimen Succinic-picrate doped with copper sulphate using (002) diffracting planes in symmetrical Bragg geometry by employing the multicrystal Xray 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.

The powder X-ray diffraction (XRD) patterns are shown in the figure. The well-defined peaks at specific 2theta values show high crystallinity of the grown crystals of Succinic-picrate doped with copper sulphate. The values of hkl, relative intensity and 2 theta values for the reflection peaks of the powder XRD pattern are given table. The resultant peaks in the diffractogram (Figure) show an intense peak at21.335(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 at34.714(6) ° and38.066(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 misorientation angle of the boundary with respect to the main crystalline region for both the observed very low angle boundaries are34.714(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 multicrystal X-ray diffractometer used in the present investigation.

INTERPRETATION OF FTIR SPECTRUM OF SUCCINIC PICRATE DOPED WITH COPPERSULPHATE.

The frequency of absorption of O-H Stretching at 3291.15 cm^{-1} confirms the presence of succinic acid. The C-H Stretching at the frequency of absorption at3079.99cm indicates the aromatic nature.

The C-O stretching frequency at 1208.30cm^{-1}establishes the presence of phenolic functional group in the picric acid. The nitro group in the picric acid is established by the N-O stretching frequency of absorption at 1536.67 cm^{-1}. The FTIR spectrum confirm the presence of picric acid, succinic acid in the grown crystal.

SHG MEASUREMENT

The study of nonlinear optical conversion efficiency was carried out using the experimental setup of Kurtz and Perry[14]. 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[15]. Table 3 shows comparison of SHG signal energy output of Succinic-picrate doped with copper sulphate

Table 1: Details of FTIR absorption frequencies of Succinic-picrate doped with copper sulphate

S. NO	WAVE NO.	MODE	COMMENT
1.	3291.15	O-H Stretching	Carboxylic acids
2.	3073.99	C-H Stretching	Aromatic
3.	2272.14	N-H Stretching	overlapping
4	1545.80	N-H Bending	amines
5.	1536.67	N-O Stretching	Nitro group in picric acid
6.	1321.54	C-N Stretching	Aromatic
7.	1208.30	C-O Stretching symm	Phenolic in picric acid

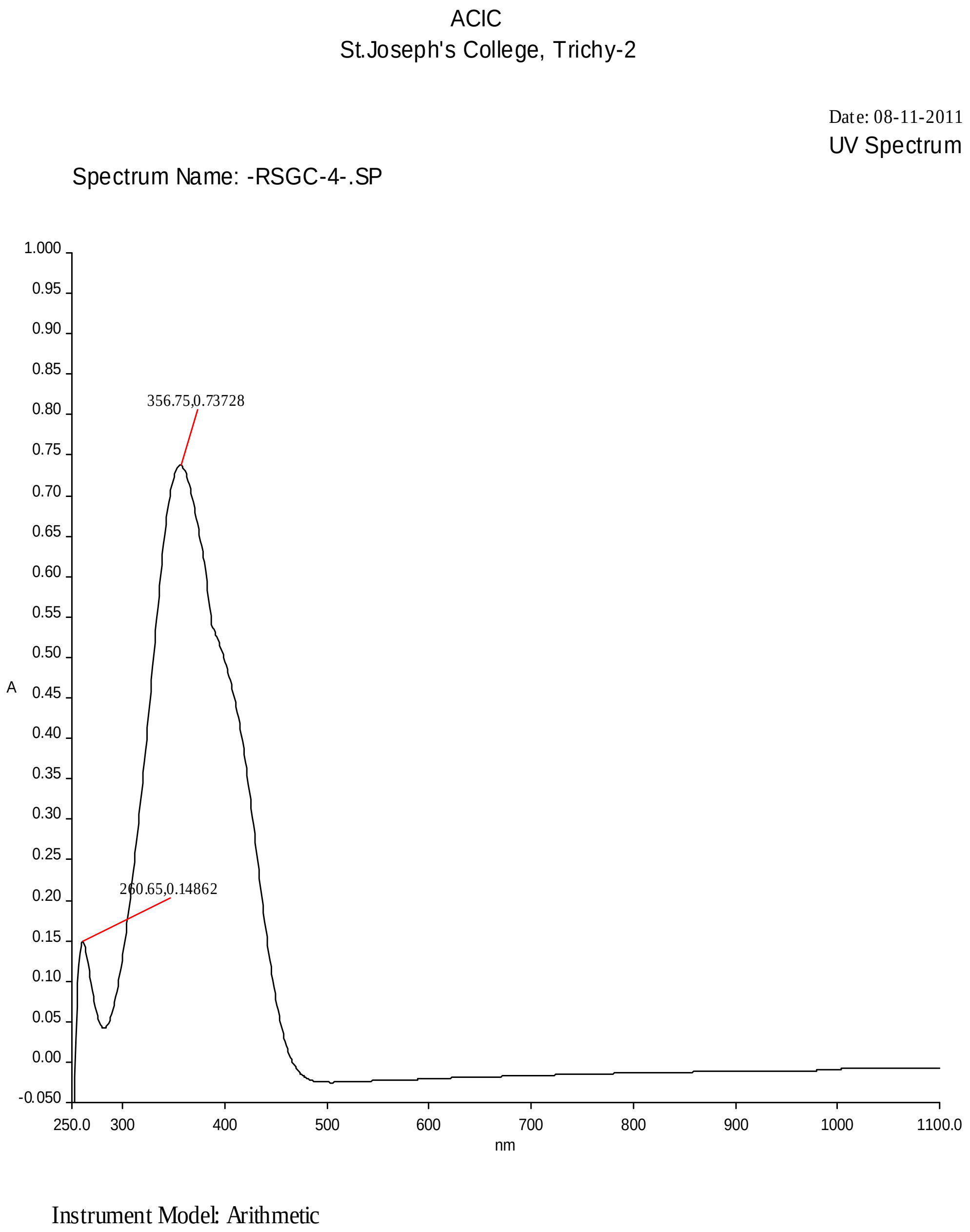


Fig. 1: UV-VIS absorption spectrum of Succinic-picrate doped with copper sulphate

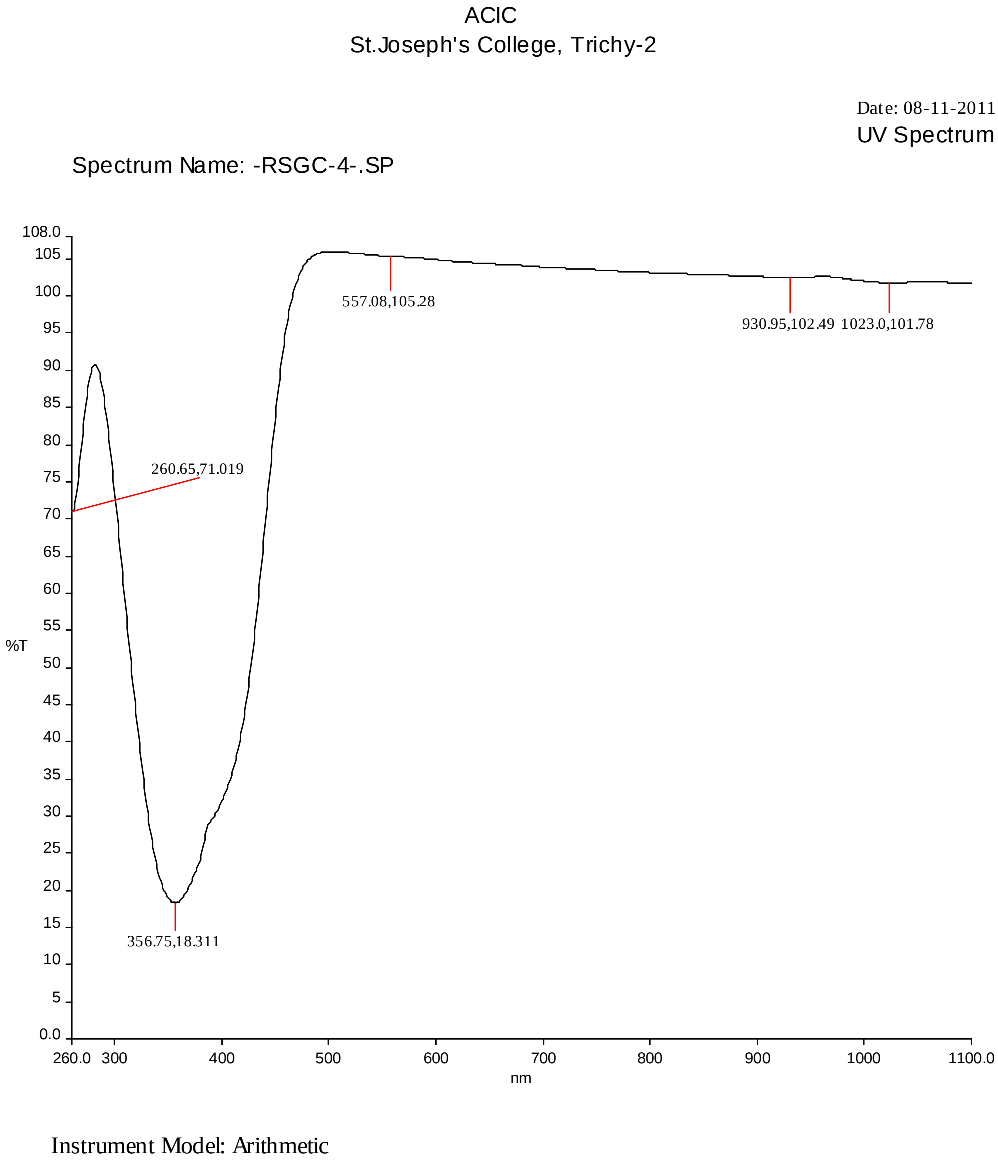
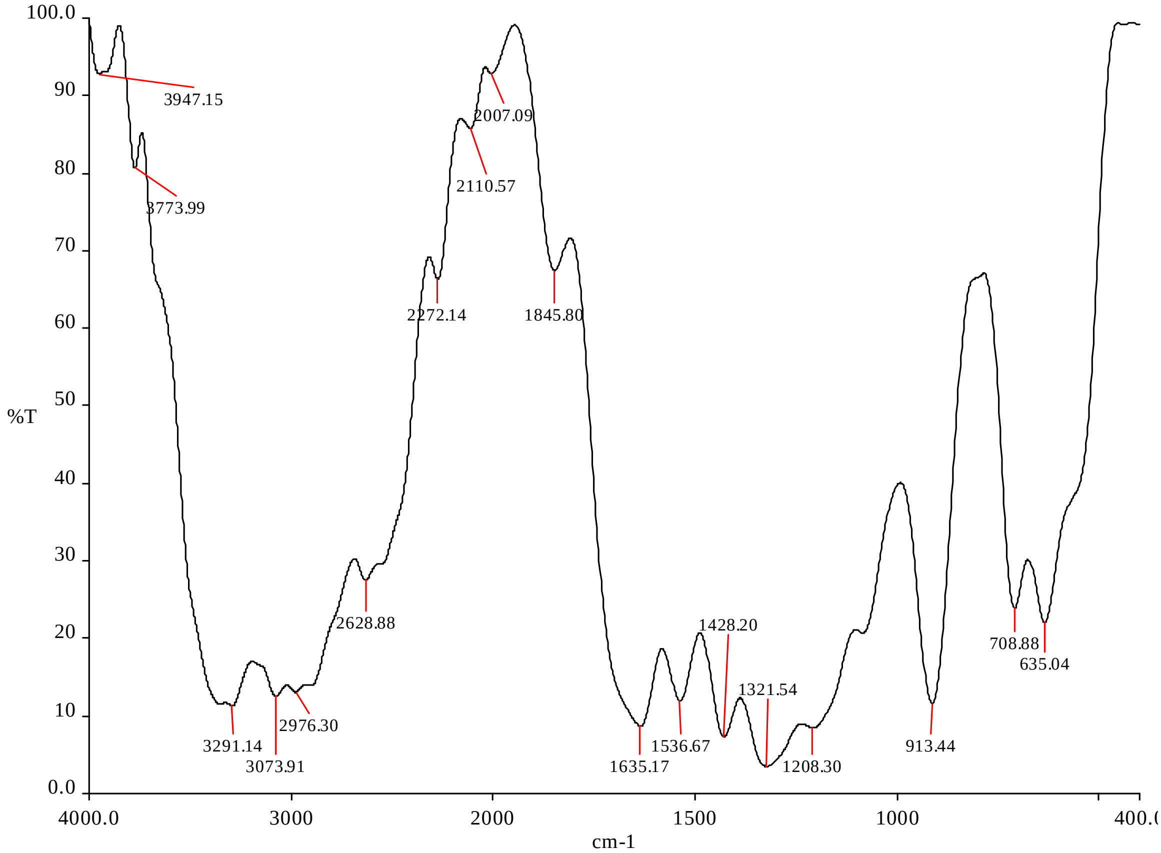


Fig. 2: UV-VIS emission spectrum of Succinic-picrate doped with copper sulphate

ACIC
St.Joseph's College (Autonomous)
Trichy-2

FTIR SPECTRUM
Date: 11/8/2011

Spectrum Name: RSGC-4.sp



RSGC-4.pk

RSGC-4.sp 1801 4000.00 400.00 3.49 99.74 4.00 %T 10 0.50

REF 4000 99.74 2000 92.95 600
3947.15 92.78 3773.99 80.64 3291.14 11.31 3073.91 12.47 2976.30 13.07
2628.88 27.48 2272.14 66.29 2110.57 85.79 2007.09 92.80 1845.80 67.41
1635.17 8.65 1536.67 11.87 1428.20 7.30 1321.54 3.49 1208.30 8.46
913.44 11.57 708.88 23.87 635.04 22.08

Fig. 3: FTIR spectrum of Succinic-picrate doped with copper sulphate

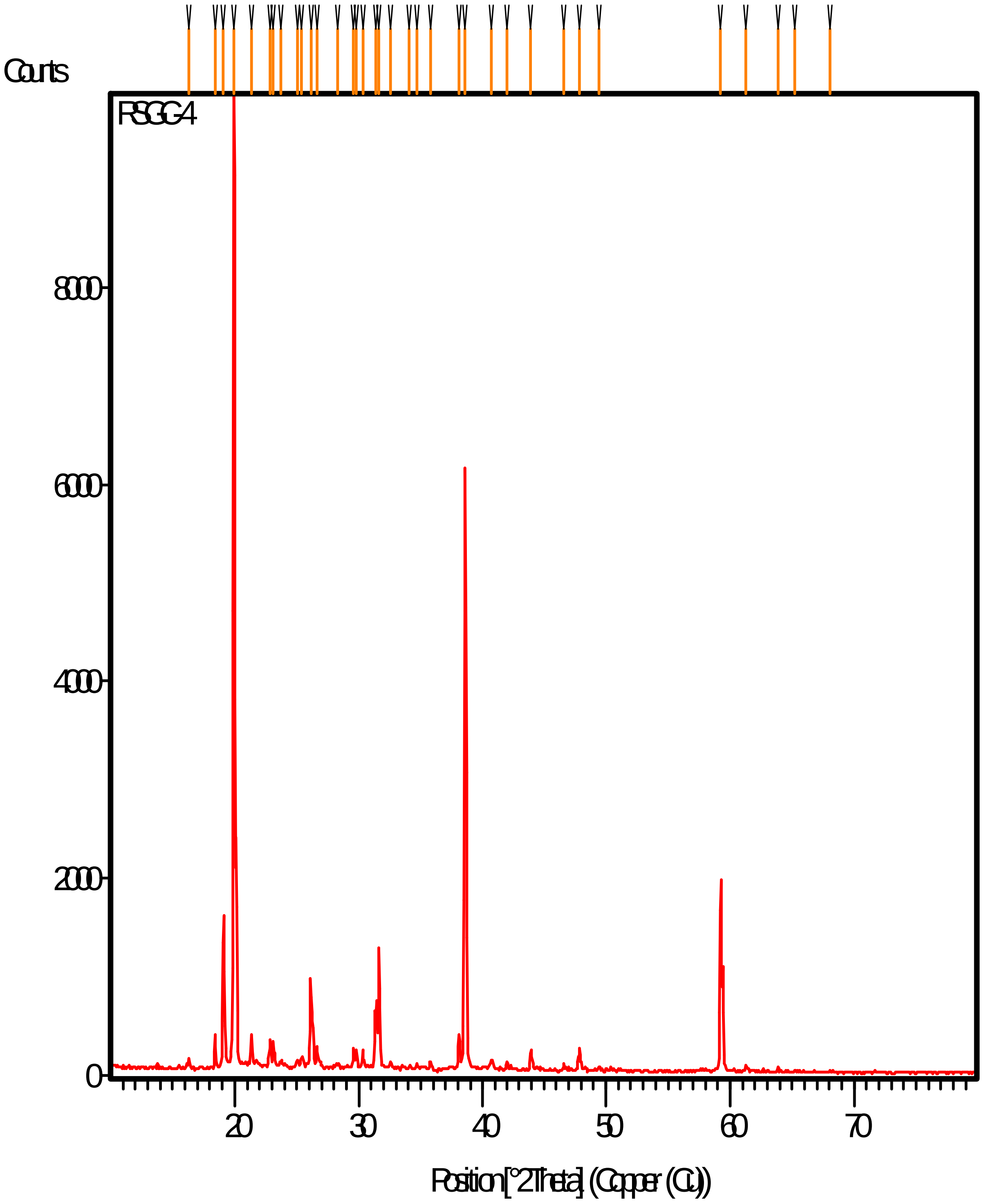


Fig. 4: XRD spectrum of Succinic-picrate doped with copper sulphate

Table 2: Details of XRD spectrum of Succinic-picrate doped with copper sulphate

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
16.288(7)	78(15)	0.09(3)	5.43758	0.99
18.417(3)	243(22)	0.08(1)	4.81343	3.09
19.104(1)	1125(29)	0.125(4)	4.64198	14.32
19.9350(4)	7853(80)	0.113(2)	4.45028	100.00
21.335(3)	262(19)	0.12(1)	4.16126	3.34
22.834(5)	178(14)	0.15(2)	3.89148	2.27
23.125(5)	180(18)	0.13(2)	3.84315	2.29
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 3: SHG Efficiency of Succinic-picrate doped with copper sulphate with respect to KDP

INPUT POWER mj /pulse	KDP mv	Succinic-picrate doped with copper sulphate mv
6.1	6.8	9.0

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 361 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.

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