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Research Article

SYNTHESIS, GROWTH AND CHARACTERIZATION STUDIES OF THIOUREA PICRATE CRYSTAL

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ABSTRACT

Picric acid with Thio urea resulting the Thio urea picrate crystals exhibit the nonlinear optical properties, which is an important parameter in laser optics. Thio urea -Picrate crystals are synthesized in equi molar proportions of picric acid and Thio urea 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

Thio urea picrate crystals are studied for its unit cell measurements by taking Single Crystal XRD measurements. SEM-EDAX studies are also carried out to study the morphology of the crystals. The powdered pattern of XRD has been indexed using Chekcell software.

Keywords: Thio urea -picrate, Laser optics, nonlinear optics, FTIR, XRD, SEM, Checkcell.

INTRODUCTION

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[1,2]. Thiourea Crystals as such do not have any nonlinear optic property of its own. But Thiourea when mixed with picric acid show excellent NLO properties. Thio urea picrate crystals are synthesised using slow evaporation technique. The grown crystals are harvested and subjected to FTIR Studies, UV-VIS-NIR Studies, XRD, SEM and Single crystal XRD analysis.

EXPERIMENTAL PROCEDURE

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 **Thio urea[M.F.CH_4N_2S]** (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. 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 induction time is noticed. The fine crystals are harvested. Picric acid-Diphenylamine crystals doped with the ferrous sulphate are characterized using FT-IR, UV, XRD &SHG studies.

RESULTS AND DISCUSSIONS

U.v-vis spectral studies

Figure shows the absorbance zone around 253.04 nm (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 357.40 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 357.40 nm (UV color). Other noticeable characteristic in the absorption spectrum is a wide transparency window within the range of 864.26 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 [Figure], it is evident that crystals have UV cut off below 490 nm (253.04 nm 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 253.04 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 357nm.

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].

8.4. FTIR STUDIES

Two absorption frequencies of N-H Stretching are observed at 3369.94 and 3155.98 confirm the presence of amide in the thio urea. The appearance of C=S Stretching frequency is observed at 1621.22 indicates the presence of thio group in the thio urea. This is further supported by the S-H Stretching frequency at 2560.69 The N=O bending frequency observed at 1324.28 confirm the presence of nitro groups in the picric acid. The absorption peaks and their assignments are shown in the table. From the spectral data it has been revealed that the sample under investigation is Thio urea picrate crystal.

X-ray DIFFRACTION STUDIES

The grown specimen Thio-urea -picrate 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. 8.4. shows the high-resolution rocking or diffraction curve (DC) recorded for the specimen Thio-urea -picrate using (002) diffracting planes in symmetrical Bragg geometry by employing the multicrystal

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 8.2. The powder X-ray diffraction (XRD) patterns are shown in the figure 8.4. The well-defined peaks at specific 2θ values show high crystallinity of the grown crystals of Thio-urea -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 show an intense peak at 28.487(5) ° (intense peak). The peaks appearing in the spectrum that have not been identified can be attributed to the formation of the compound Thio-urea -picrate 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 30.787(4) ° and 32.68(2) ° 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 respectively 0.12 (2) °, 0.22(2) °and 0.29(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.

The powdered pattern XRD Spectrum of Succinic picrate doped with copper sulphate Crystal has been indexed using **CHEKCELL** software in Table 7.3.The unit cell parameters are a = 5.46Å, b = 7.63 Å, c = 8.59 Å and α=90.00º, β=90, γ=90. The system belongs to **ORTHORHOMBIC P. The cu K λ= 1.54060**.The lowest experimental 2 θ value and the highest experimental value respectively say **$2\theta_1=19.537$and $2\theta_2=58.20$** have been taken to calculate the hkl values. The 2θ positions and the d-spacings are also calculated.

The table 7.3. 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 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 XRD STUDIES

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 = 5.46Å, b = 7.63 Å, c = 8.59 Å; with unit cell volume V = 3.58Å^3 with α=90.00 β=90.20 ϒ=90.00.

8.7. THERMAL STUDIES

The TGA-DSC thermogram of thiourea picrate crystal is shown in figure 4. When the compound heated from room temperature the compound decomposes into two stages. The compound is stable up to 150° C. Afterwards the compound decomposes almost 90%. The first weight loss occurring between 150 and 170° C. The low temperature DSC (heating and cooling) curves of the compound is depicted in figure Thermal anomalies are observed at 150^0 C, 170^0C, 240^0C in the cooling and heating cycles, respectively. The occurrence of thermal hysteresis during the cooling and heating cycles indicates a first order phase transition. The first order phase transition may be due to the occurrence of thermal changes in the compound. A first order transition is defined as the one in which a discontinuity occurs in the first derivatives of the free energy with respect to temperature and pressure. First order phase transitions are associated with thermal hysteresis[8].

SHG MEASUREMENT

The study of nonlinear optical conversion efficiency was carried out using the experimental setup of Kurtz and Perry[9]. 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 Crystal was found to be greater than that of KDP. When the dopant concentration is increased the SHG efficiency is also increased in this case.

At the same time this was compared with the un doped Succinic picrate crystal under the same experimental condition and with the same KDP as the reference material. In that case the SHG efficiency was found to be lower for the un doped crystal.This may be attributed to the molecular structure of Succinic picrate doped with copper sulphate Crystal residue is engaged in a strong hydrogen bond with the picrate anion[10]. Table 7.4 shows the comparison of SHG signal energy output of Succinic -picrate doped with copper sulphate.

CONCLUSION

Transparent crystals of Thiourea-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 Thio-urea Picrate crystals using XPERT- PRO – Philips X-diffractometer using the powdered pattern.The FT-IR study confirms the presence of Thio-urea -Picrate crystals. The spectra reveal that the functional group additives have sufficient transmission in the entire IR region.

In the U.V absorption studies the 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 a Thiourea Picrate crystal is a promising material that has the Non-linear optical properties.

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Tables and Figures

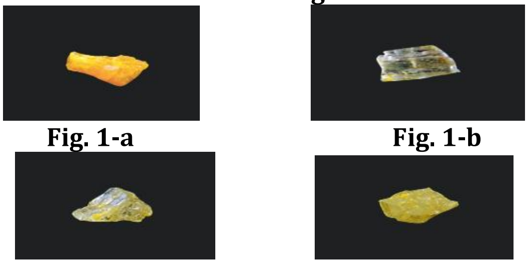

Fig. 1-a Fig. 1-b

Fig. 1-c Fig. 1-d

Fig. 1-a to 1-d: Grown crystals of Thiourea picrate

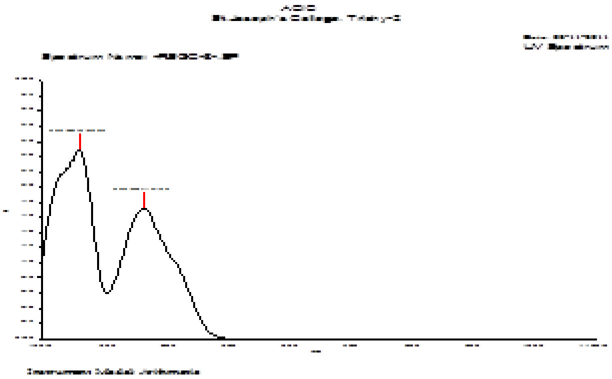

Fig. 1.2: UV Spectrum of Thio urea picrate crystal

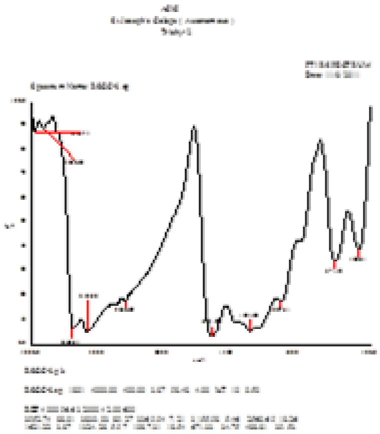

Fig. 1.3: FTIR Spectrum of
Thio urea picrate crystal

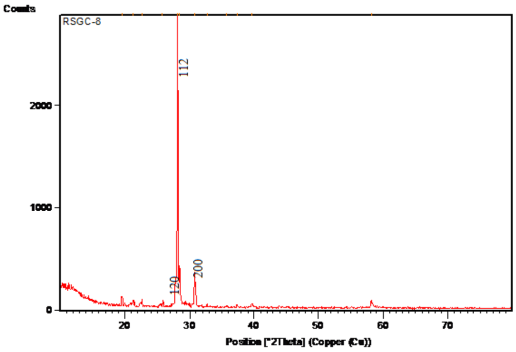

Fig. 1.4: XRD Spectrum
O-Thio urea picrate crystal

Table 1.1: Details of FTIR of Thio urea picrate crystal

S.NO	WAVE NO.	MODE	COMMENT
1.	3369 cm^{-1}	N-H Stretch amides	amides
2.	3155 cm^{-1}	N-H Stretch amides	amides
3.	2560 cm^{-1}	S-H Stretch	Thio urea
4.	1621 cm^{-1}	C=S Stretching	Thio group
5.	1324 cm^{-1}	NO$_2$ Stretch symmetric	Nitro groups
6.	1087.31	C-N Stretching	Amines

Table 1.2: Details of XRD of Thio urea picrate crystal

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
19.537(3)	168(12)	0.13(1)	4.54002	8.43
21.238(9)	58(9)	0.17(4)	4.18005	2.93
22.59(2)	35(7)	0.31(5)	3.93364	1.75
25.71(3)	31(6)	0.70(8)	3.46199	1.54
28.116(1)	1988(34)	0.172(4)	3.17121	100.00
28.487(5)	254(28)	0.12(2)	3.13078	12.80
30.787(4)	230(13)	0.22(2)	2.90188	11.56
32.68(2)	18(5)	0.29(8)	2.73828	0.92
35.69(2)	16(3)	0.27(8)	2.51367	0.78
37.36(1)	29(8)	0.11(3)	2.40507	1.48
39.62(2)	22(2)	0.54(6)	2.27294	1.08
58.20(1)	50(7)	0.32(8)	1.58392	2.53

Table 1.3: Calculated hkl values, 2θ and d spacing values with Experimental values for Thiourea picrate

hkl value	2θ cal	2θ exp	d cal	d exp
111	22.523	22.59(2)	3.9444	3.93364
021	25.527	25.71(3)	3.4866	3.46199
120	28.520	28.116(1)	3.1272	3.17121
112	28.527	28.487(5)	3.0871	3.13078
121	30.339	30.787(4)	2.9386	2.90188
200	32.778	32.68(2)	2.7300	2.73828
122	35.480	35.69(2)	2.5281	2.51367
113	37.339	37.36(1)	2.4064	2.40507
023	39.311	39.62(2)	2.2901	2.27294
043	58.055	58.20(1)	1.5875	1.58392

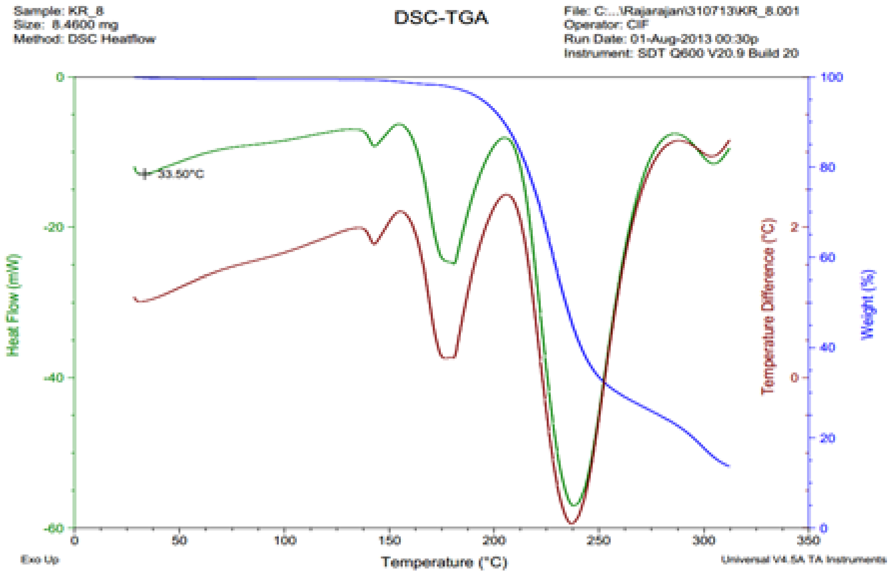

Fig. 1.5: DSC TGA Thermogram of Thio urea picrate crystals

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