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Growth and Characterization Studies on Acetamide-Picrate Doped With Copper Sulphate-A Nonlinear Optical Crystal

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ABSTRACT

Picric acid and Acetamide with dopant copper sulphate resulting the Acetamide picrate –copper sulphate crystals exhibit the nonlinear optical properties, which is an important parameter in laser optics.Acetamide-Picrate crystals are synthesized in equi molar proportions of picric acid and acetamide 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. It is revealed from the analysis that the dopant copper sulphate which gets in to the crystal is confirmed by ftir by the S-O stretching frequency. The well-defined peaks at specific 2theta values show high crystallinity of the grown crystals.. 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 applicationThe acetamide picrate crystals doped with copper sulphate were studied for its unit cell measurements by taking Single Crystal XRD measurements. SEM-EDAX studies were also carried out to study the morphology of the crystals.SHG Efficiency of this crystal has been tested in IPC Lab, IISC, and Bangalore.

Keywords: Acetamide-picrate, Laser optics, nonlinear optics, FTIR, XRD, SEM.

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INTRODUCTION

Materials answering for high optical nonlinearity are a potential area which has attracted many theoretical and experimental researchers. At present the trend is towards semi organic material compared to inorganic and organic since they possess higher mechanical strength and chemical stability [1] Pure inorganic NLO material, Potassium di hydrogen phosphate (KDP) and its isomorphs are representative of hydrogen bonded materials which possess important piezoelectric, electro-optic and nonlinear optical properties with excellent mechanical and thermal properties, but possess relatively modest optical nonlinearity [2-4]. Hence it is appropriate to grow semi organic crystals which possess the aspects of organic and inorganic materials resulting in promising NLO properties [5].

In this present study, it has been revealed that Acetamide-picrate doped with copper sulphate crystal has excellent Non linear optical properties. The SHG conversion efficiency was found to be higher than that of KDP which has been taken as the reference compound. On the contrary the SHG efficiency of undoped Acetamide-picrate, that is without the addition of copper sulphate was found to be zero with respect to KDP. The semi organic crystals always found to be the materials that possess excellent non linear optical properties [6-9].

MATERIALS AND METHODS

Exactly one molar Picric acid and Acetamide 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 slowly to theAcetamide 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 Acetamide-Picrate crystals doped with copper sulphate are characterized using FT-IR and XRD studies, U.V-VIS and SHG Efficiency.

RESULTS

FTIR studies

A sharp N-H stretching band appears in the 3275.34 cm^{-}1 clearly indicates the presence of amide. The absorption of C-H stretching frequency at 3009.76 cm^{-}1 indicates that the compound is aromatic. The band at 1196.82 cm^{-}1 confirms the presence of phenolic functional group. The C=O stretching frequency of absorption at 1691.40 cm^{-1} shows the presence of NH_2 and C=O groups confirming the presence of an amide. The C-H in plane bending frequency of absorption at 1423.26 cm^{-1} gives an intense peak which reveal the presence of CH3 and C=O Present in the amide compound.

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A sharp peak at 1542.63 cm^{-1} and 1313.12 cm^{-1} shows the presence of Nitro groups. A peak at 719.98 cm^{-1} indicates the modified deformation of aromatic ring. The S-O stretching frequency of absorption at 801.65 cm^{-1} shows the presence of sulpur which is from the dopant CUSO4. The band is of variable intensity.

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St.Joseph's College (Autonomous)
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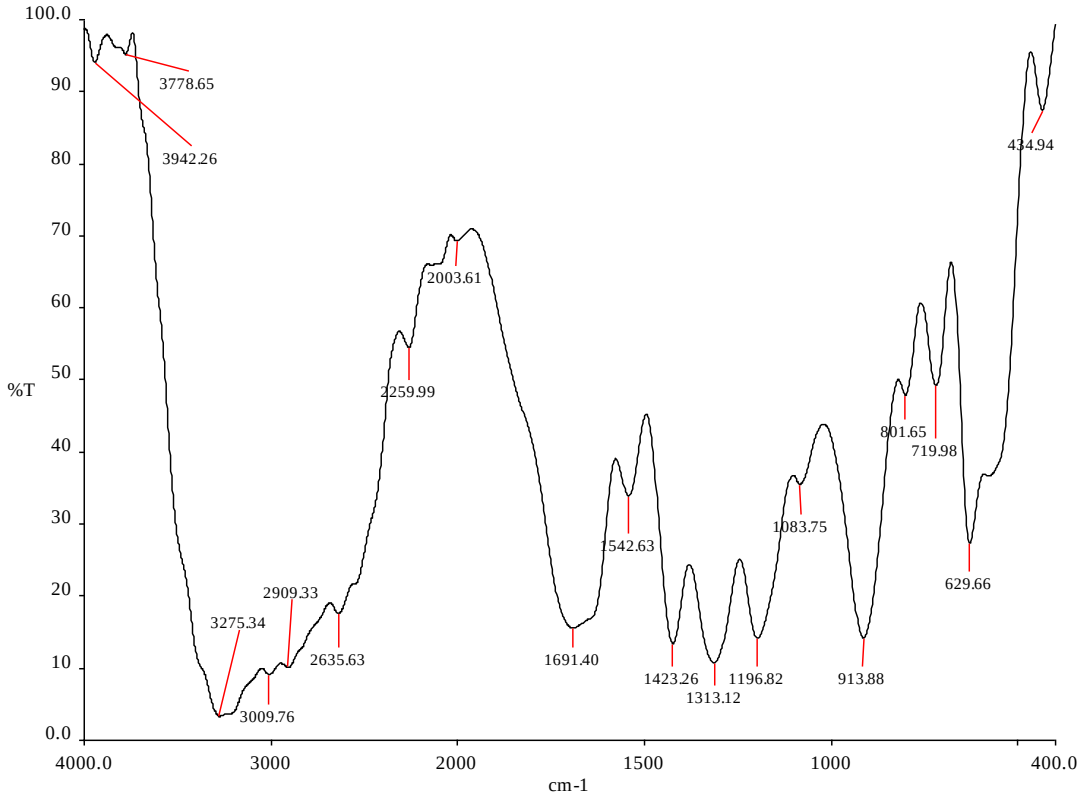
FTIR SPECTRUM
Date: 11/8/2011

Spectrum Name: RSGC-6.sp



RSGC-6.pk

RSGC-6.sp 1801 4000.00 400.00 3.33 99.39 4.00 %T 10 0.50

REF 4000 98.64 2000 69.34 600
3942.26 94.07 3778.65 95.14 3275.34 3.33 3009.76 9.18 2909.33 10.12
2635.63 17.57 2259.99 54.56 2003.61 69.31 1691.40 15.55 1542.63 33.93
1423.26 13.43 1313.12 10.78 1196.82 14.10 1083.75 35.53 913.88 14.20
801.65 47.89 719.98 49.31 629.66 27.28 434.94 87.49

FIG-I: FTIR Spectrum of Acetamide-picrate doped with copper sulphate

ISSN: 0975-8585

Table FTIR Absorption frequencies of Picric acid-Acetamide Doped with $CuSO_4$

S.NO	WAVE NUMBER cm^{-1}	MODE	COMMENT
1.	3275.34 cm^{-1}	N-H stretch	Sharp stands alone , Amide
2.	3009.76 cm^{-1}	C-H stretch	Aromatic
3.	2909.33 cm^{-1}	C-H stretch	Non specific band,
4.	2635.63 cm^{-1}	$N\text{-}H^{+}$ stretch	Major maximum
5.	2259.99 cm^{-1}	C= N stretch	Medium,broad,highly structured
6.	2003.61 cm^{-1}	C≡ C C ≡ O C ≡ N	Medium,broad,highly structured
7.	1691.40 cm^{-1}	C=O stretch	Primary amides,NH_2C= O,strong
8.	1542.63 cm^{-1}	NO_2 aromatic	Nitro group
9.	1423.26 cm^{-1}	C-H in Plane bend	CH_3C= O
10.	1313.12 cm^{-1}	C-H in plane bend	C-NO_2 Aromatic nitro
11.	1196.82 cm^{-1}	C-O stretch	Phenols
12.	1083.75 cm^{-1}	C-N stretch aryl	Amines
13.	801.65 cm^{-1}	S-O stretch	Of variable intensity
14.	719.98. cm^{-1}	Ring	Modified deformation of aromatic ring

From the FTIR Spectral evidence cited above the presence of picric acid, acetamide and the dopant CUSO4 have clearly established.

UV-VIS-NIR Absorption Studies

Figure shows the absorbance zone around 237.83 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 354.71 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 354.71 nm (UV color). Other noticeable characteristic in the absorption spectrum is a wide transparency window within the range of 415 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 300nm (260nm), which is sufficient for SHG Laser validation of 1064nm or other application in the blue

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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 237.83nm 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 354.71nm.

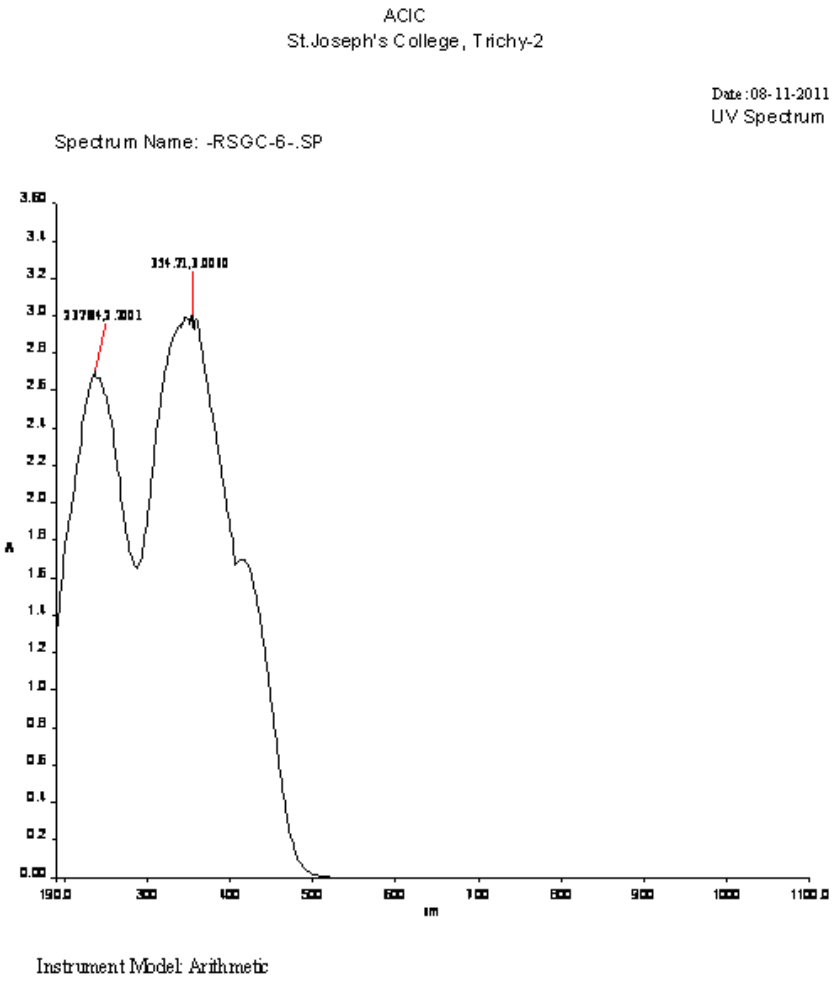

FIG-2 : U.V-VISIBLE Spectrum of Acetamide-picrate doped with copper sulphate

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]

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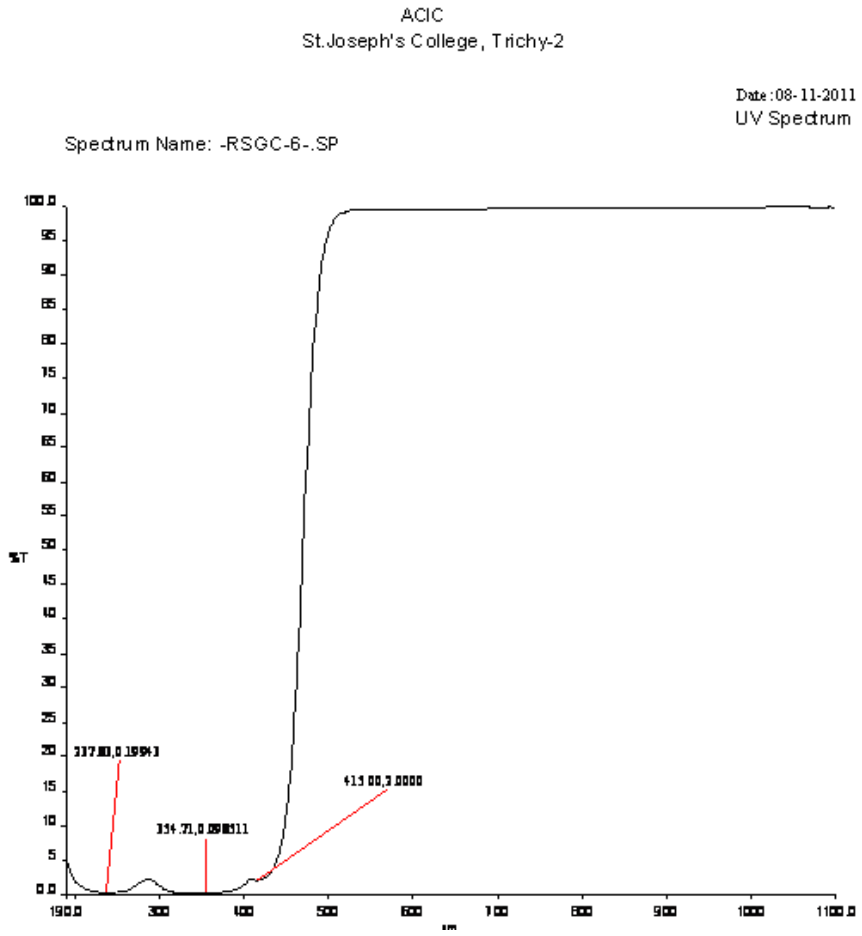

FIG-3 : U.V-VISIBLE Spectrum of Acetamide-picrate doped with copper sulphate

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 Picric acid acetamide 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) pattern Picric acid acetamide copper sulphate crystals are shown in the figure. 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 table. The resultant peaks in the diffractogram (Figure) show an intense peak at 20.0915°(intense peak). The peaks appearing in

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the spectrum that have not been identified can be attributed to the formation of the compound Picric acid acetamide copper sulphate crystal.

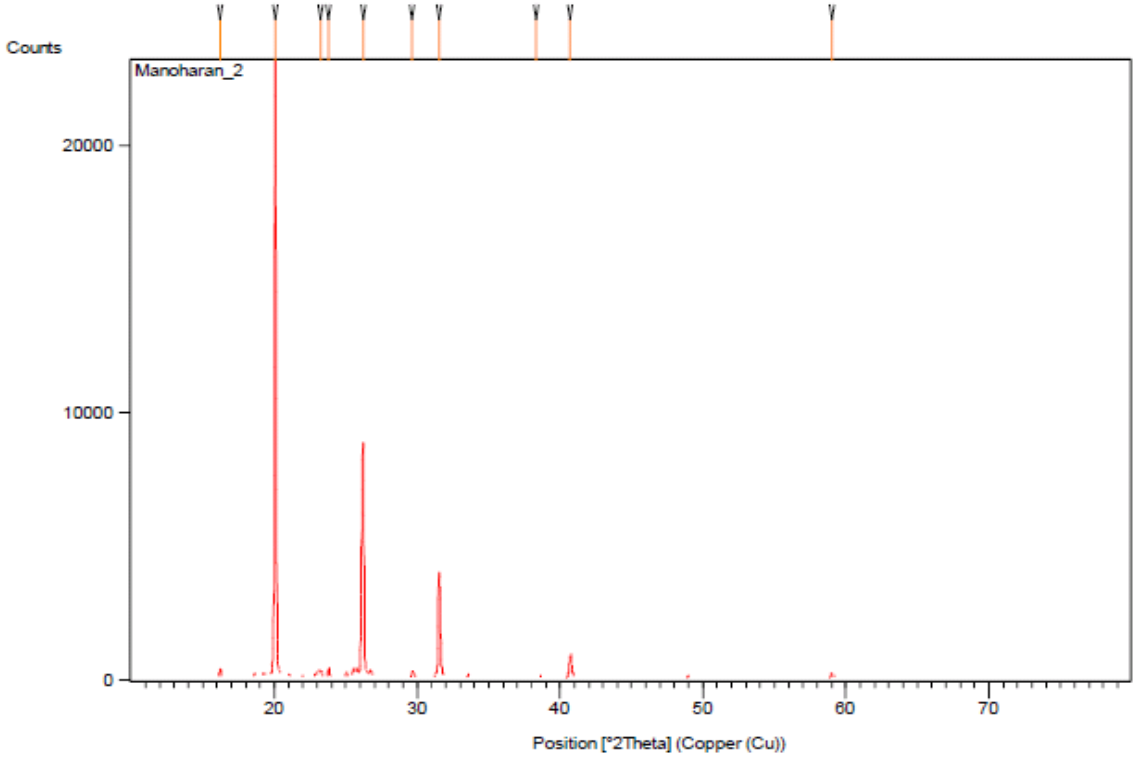

FIG-4: XRD spectrum of Picric acid acetamide doped with copper sulphate

TABLE-2: Details of XRD Studies of Picric acid acetamide doped with copper Sulphate

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
16.2259	299.27	0.1338	5.46280	1.30
20.0915	23078.45	0.1338	4.41965	100.00
23.2142	182.39	0.4015	3.83171	0.79
23.8142	349.87	0.1338	3.73651	1.52
26.2150	8792.37	0.1004	3.39951	38.10
29.6744	245.58	0.2342	3.01060	1.06
31.5150	3822.36	0.0836	2.83885	16.56
38.3547	55.24	0.8029	2.34689	0.24
40.7143	917.99	0.2007	2.21616	3.98
59.0168	158.90	0.4896	1.56390	0.69

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 26.2150° and 31.5150° 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 are 26.2150° and 31.5150 °.

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The full width at half maximum (FWHM) values for the main peak and the two low angle boundaries are respectively 0.1338°, 0.1004°and 0.0836 °. 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 .The affect 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.

SHG MEASUREMENT

Table-3 SHG CONVERSION EFFICIENCY

INPUT POWER mj /pulse	KDP mv	SHG EFFICIENCY
6.1mv	6.8 mv	PICRIC ACID-ACETAMIDE 0 mv
6.1mv	6.8 mv	PICRIC ACID-ACETAMIDE DOPED WITH CUSO4 8.8 mv

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 Acetamide-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 dihydrogenphosphate (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 Acetamide-picrate doped with copper sulphate was found to be greater than that of KDP. At the same time this was compared with the undoped Acetamide-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 zero for the un doped crystal .This may be attributed to the molecular structure of Acetamide-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 Acetamide-picrate doped with copper sulphate.

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 monoclinic structure. The lattice parameters were found to be a = 5.10Å, b = 5.59Å, c = 11.06 Å; with unit cell volume V = 307Å^3 with α=82.0 β=79.20 ϒ=85.63

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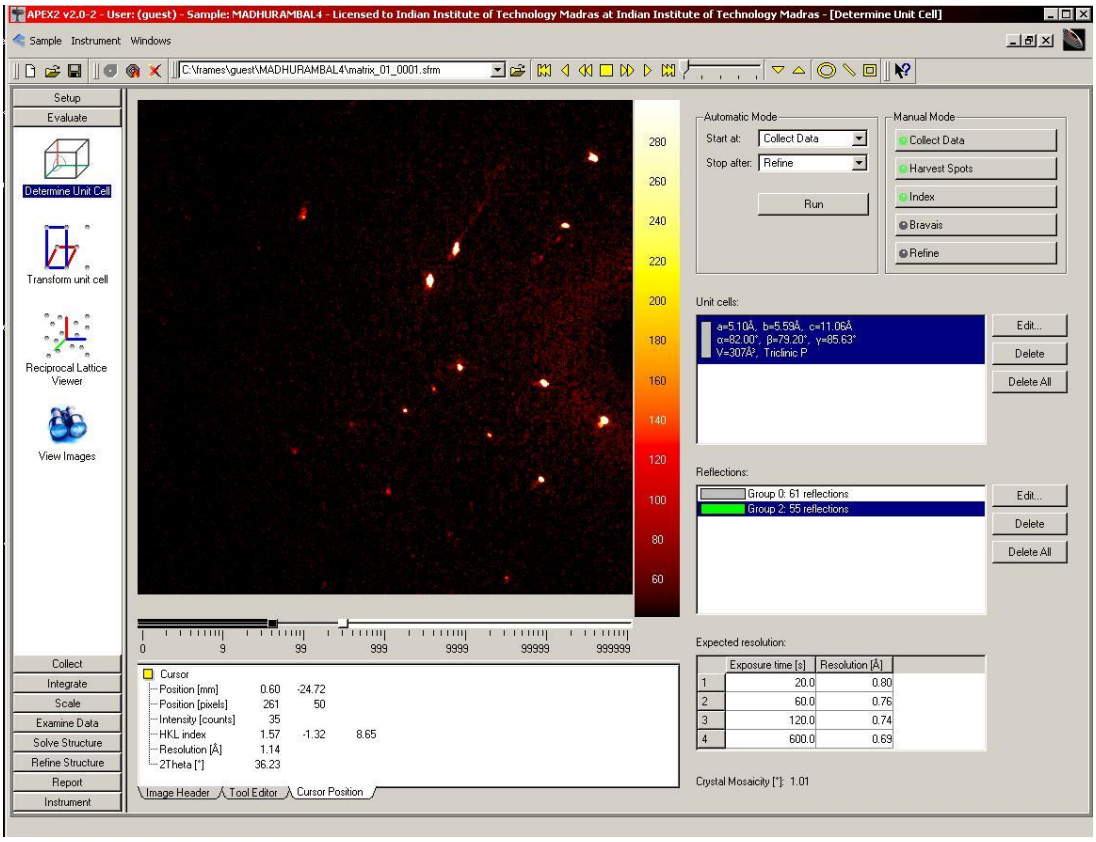
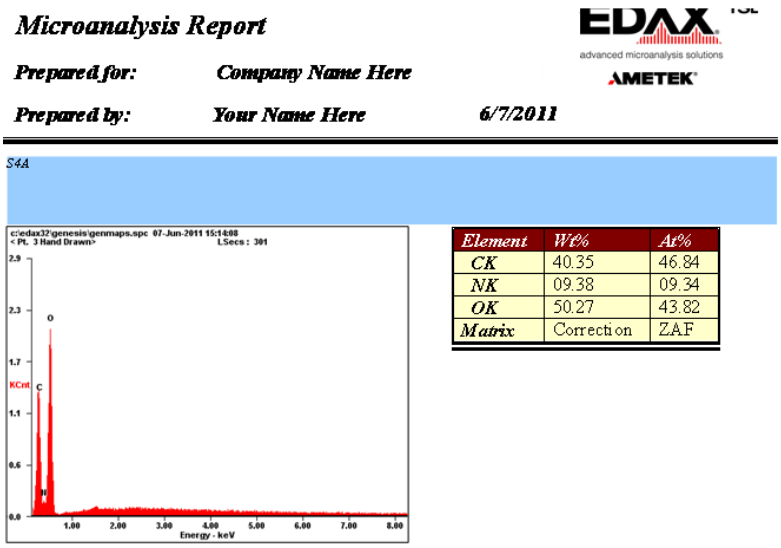


FIG-5: Single crystal XRD of Acetamide-picrate doped with copper sulphate

SEM EDAX ANALYSIS



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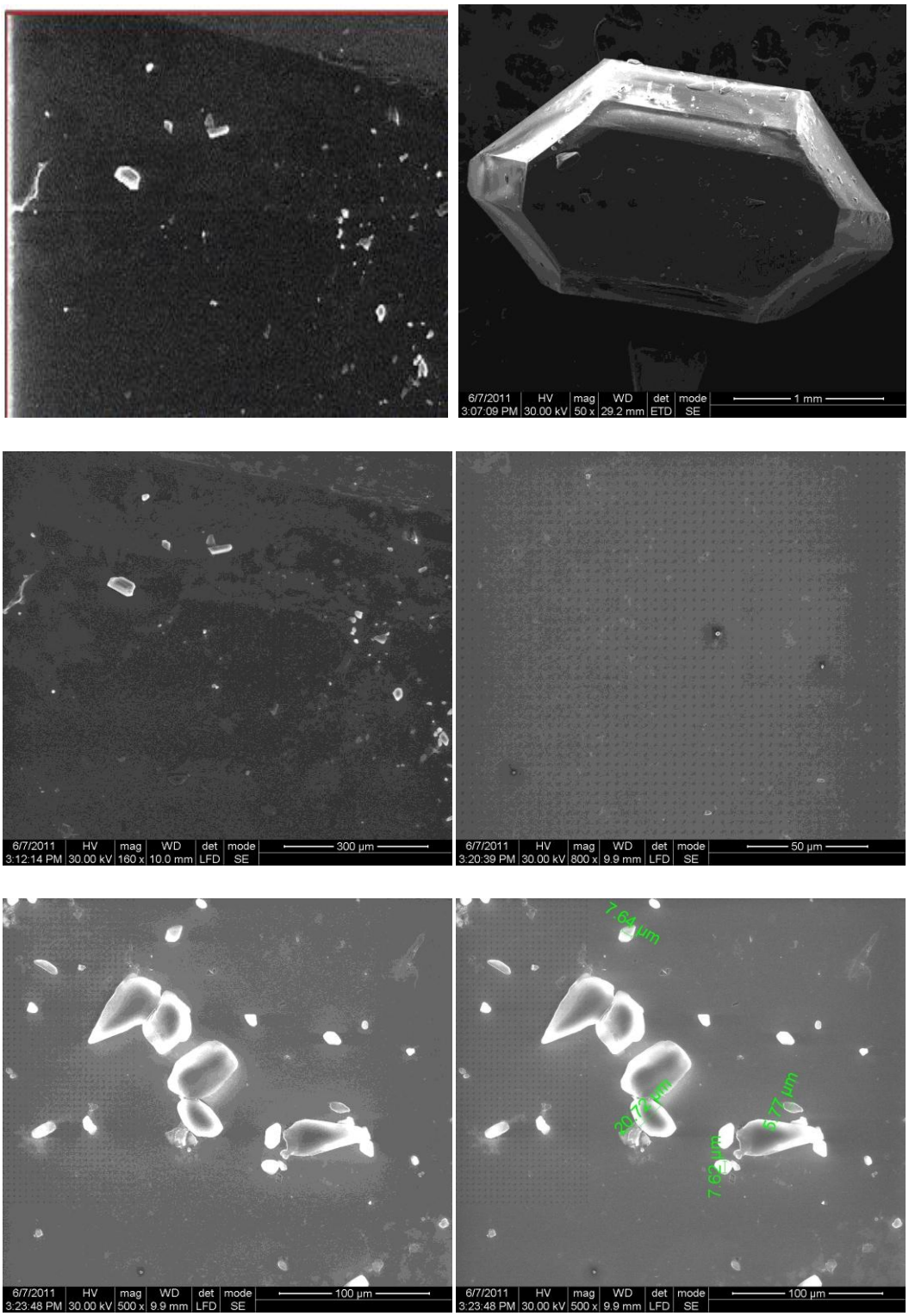

The Scanning electron microscope views of the Acetamide-picrate crystals doped with copper sulphate is shown.

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CONCLUSION

Transparent crystals of Acetamide-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 Acetamide-Picrate crystals doped with copper sulphate using XPERT- PRO – Philips X-diffractometer using the powdered pattern.

The FT-IR study confirms the presence of Acetamide-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 Acetamide-Picrate crystals doped with copper sulphate is a promising material that has the Non-linear optical properties.

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