Growth and Characterization of Potassium Thiou-reaDichromate(PTDC) and Copper Thiourea Sulphate (CTS) Single Crystals

[1]Arvind R. Bajaj, [2]Dr. K.C.Poria,
[1]Research Scholar (& Associate Professor), [2]Professor and Head
[1]Department of Physics,VeerNarmad South Gujarat University,
U.M.Road,Surat -395007

Abstract: With an aim to synthesize environmentally stable material possessing non- linear optical properties, we have grown Potassium Thiourea Dichromate (PTDC) and Copper Thiourea Sulphate (CTS) single crystals of good quality by inexpensive slow evaporation growth technique. The morphological analysis of grown crystal has been carried out to find the effect of dopant species on growth process. The XRD analysis of these crystals has been performed by powdered X-ray diffraction method which indicate the variations in lattice parameters and cell size to some extent with induction of metal salts in Thiourea ligand but without appreciably changing the crystal systems .FTIR and UV-Vis analysis of pure Thiourea,PTDC and CTS has been carried out to compare transmission and absorption abilities and to explore its suitability for NLO applications.

Key Words: Non- linear optical properties, Single Crystals, Slow evaporation technique, PTDC, CTS ,XRD characterization-Vis spectrum etc.

1. Introduction:

In recent emerging trends of photonics and optoelectronic device technologies three is an increased demand of materials suitable for non- linear optical applications. Thiourea is an important semi organic matrix modifier material having large dipole moment. It has property to form hydrogen bonds with extensive network structure. Due to such nature of Thiourea it is reported to have non- linear optical properties in the form of frequency conversion with reasonable efficiency. Though Thiourea possess adequately efficient NLO properties but its modest mechanical and thermal thresholds make it less viable material for devices based on non- linear optical properties.Materials having non- centro-symmetric molecules usually with dipolar $D-\pi-A$ structure are most likely to produce efficient second order non- linear effect, where electron donor group D is conjugated to electron acceptor group A via π con-jugated bridge. Metal ligand combinations which have non- centrosymmetric molecules are an emerging class of materials suitable for non- linear optical applications.Compared toorganic molecules, there is possi-bility of larger variety of molecular and bulk structures with high environmental suitability and a diversity of electronic properties by virtue of the coordinated metal centres Such compounds are more stable mechan-ically and thermally. The degree of variability of using different metal centers with suitable ligands is quite large.

With an aim to synthesize materials with such improved mechanical, thermal and optical properties, metal doped Thiourea crystals using metal salt solutions of $CuSo_4$ and $K_2Cr_2O_7$ has been grown successfully named as PTDC and CTS by slow evaporation growth technique along with crystals of pure Thiourea. The grown crystals were subjected to XRD analysis by powdered X-ray method to confirm and identify crystal structure. The analysis of experimental results obtained are presented and discussed in this paper.UV-Vis spectroscopic test for PTDC,CTS single crystal as well as pure Thiourea crystal is also carried out and ana-lyzed for comparing optical absorption and transmission abilities.SHG test on grown materials were also performed by Kurtz method and show encouraging results.

2. Experimental Methods:

2.1 Synthesis: The single crystals of pure Thiourea and metal doped Thiourea were grown by slow evapora-tion method. The single crystals of pure Thiourea were grown by supersaturated solution of analytical grade Thiourea in doubled distilled water. The K-Thiourea and Cu –Thiourea crystals were grown by adding $K_2Cr_2O_7$and $CuSo_4$ solutions into pure Thiourea solution taken in molar ratio 1:1 .The beaker containing

double distilled water was kept on magnetic stirrer and the finely powdered AR grade Thiourea was added in pinches for uniform and homogeneous solution at ambient temperature of around 30^0 C. The solution prepared in 6 to 8 hours were filtered using double fold filter papers to discard local impurities and were poured in peltry dishes covered with perforated polythene lid. Thesolutions of Thiourea and metal salts were also prepared by same method. The solutions so prepared were kept in isolation inside a wooden box for 3 to 4 weeks. The single crystals of different size were harvested with an average growth period of three to four weeks. The grown crystals posses well defined morphology and reasonable sizes. The photographs of grown crystals are shown in figures 1(a) to 1(c).

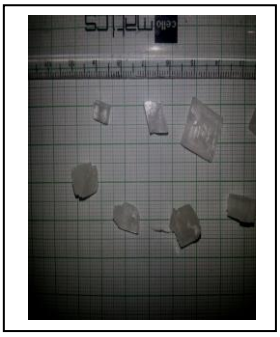

Fig1 (a)
Pure Thiourea

Fig1(b).
PTDC

Fig1(c).
CTS

2.2X-Ray Diffraction Experiment:
The X-ray diffraction analysis plays a vital role in elucidating the arrangements and spacing of atoms in crystalline material.XRD analysis was carried out forthe grown crystal samples by powdered diffraction technique. The samples were finely powdered and an x-ray beam of wavelength $1.5405A^0$ from CuKαsource was incident on in the diffractometer(Model-Miniflex -50/60Hz).The observations of The intensity of diffracted beam was measured at various 2θ angles ranging from 10^0up to 80^0 in step size of 0.10^0,where θ is the angle made by the incident beam with crystal surface. Using computer software (ASTM) the XRD pattern in graphical form wasobtained. The dominant peaks are indexed. Observations recorded for PTDC and CTS single crystalsfor some specific peaks positions are presented in table-1.The comparison with standard pattern using JCPDS card data was also carried out. The lattice parameters were calculated and compared with experimental values.

2.3 **FT-IR and UV –Vis spectroscopy:** In order to identify functional groupsand molecular structure of the grown samples, Fourier transform infrared spectrum was obtained by direct sampling method.The samples were exposed to IR radiation in spectrometer and observation obtained were Fouriertransformed using computer software .Plots of relative transmittance (%) against the wave number in the range 4000 $cm^{-}1$ to 500 cm^{-1} were obtained. Peaks are compared with standard references to identify molecular structure group to which they belong. The UV, visible and near IR absorption spectroscopic observations were also obtained

2.3 **Non Linear optical (SHG) Experiment:**
The optically transparent and defect freegrown crystals of metal doped Thiourea were tested for second harmonic generation by Kurtz and Perry method. The experimental setup consisted of ND-YAG laser source of 1064nm fundamental wavelength with pulse width of 10ns and repetition rate of 10Hz. The crystal samples were crushed to fine powdered form and were filled in fine capillaries separately. These samples in capillaries were exposed to laser beam and the intensity of output beam synchronized to monochromator at wavelength 532 nm (green radiation) was measured through digital storage oscilloscope. The instrument was calibrated for standard microcrystalline KDP crystals so that relative efficiency of the samples could be found. All the samples exhibit non vanishing output which confirmed the SHG of grown materials.

3. Results and Discussions:

The XRD pattern shown in fig 1(a) and 1(b) clearly indicate the single crystal structure of K-doped and CTS which broadly resembles the pattern of pure Thiourea except some minor changes in intensity values and

lattice parameter. Thus metal Thiourea ligand compound retains crystalline structure with slight variation in cell size due to presence of metal atom.

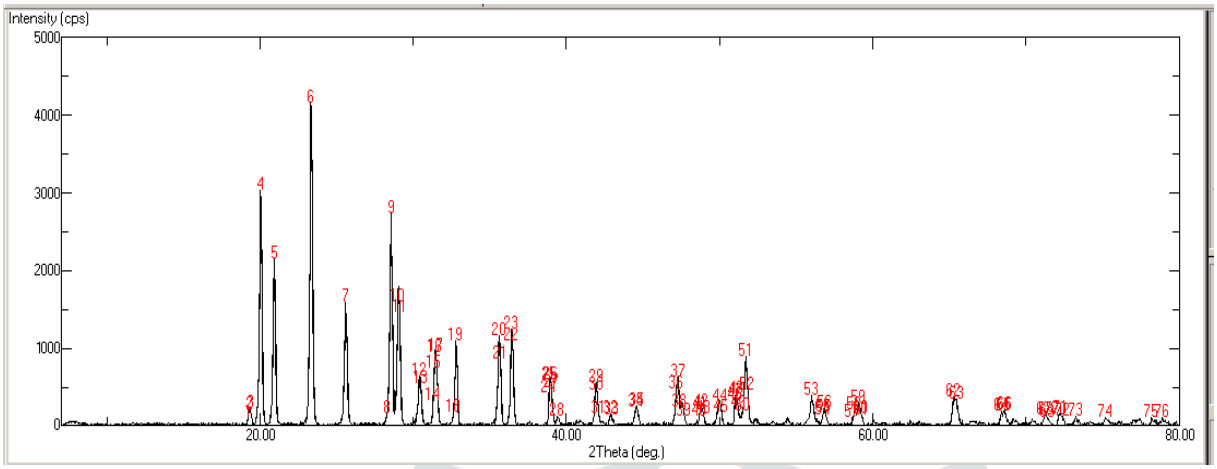

Figure 1(a): XRD K-Thiourea

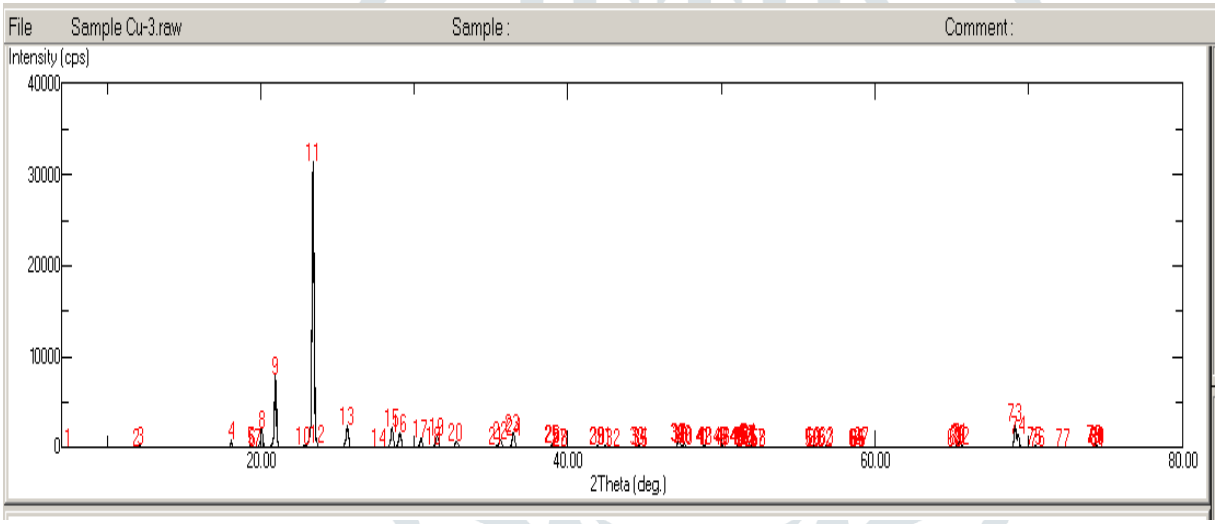

Figure 1(b): XRD Cu-Thiourea

Table-1 shows the data of XRD experiment for K-Thiourea and Cu-Thiourea.the peak has been indexed using data reference from JCPDF card. Most of the peak positions (2θ- values) broadly resemble with pure Thiourea but variation in relativesharpness (I/I_0- values) was observedfor K-doped and CTScrystals. The variation in relative sharpness may be attributed to dopant metal atom and its preferred orientation in diffractometer measurements. Also the mosaic spread of powdered pattern may result in intensity variations as compared to single crystal patterns. Overall XRD pattern signify the good crystalline and single phase nature of Thiourea crystals with added metal dopants.

Table-1: XRD data of grown crystals for some specific peaks

K-Thiourea					Cu-Thiourea				
2(Theta)	**d-space**	**Intensity**	**(hkl)**	**I/I_0(%)**	**2(Theta)**	**d-space**	**Intensity**	**(hkl)**	**I/I_0(%)**
20.04	4.43	3043	020	73.3	20.06	4.42	2055	020	6.54
20.94	4.24	2151	020	51.84	20.96	4.23	7951	020	25.28

23.32	3.81	4149	210	100	23.40	3.80	31440	210	100
25.60	3.48	1590	210	38.32	25.64	3.47	2511	210	7.99
28.56	3.12	2727	121	65.73	28.54	3.12	2185	121	6.95
28.98	3.08	1596	121	38.46	29.06	3.07	1767	121	5.62
30.44	2.93	610	121	14.70	30.44	2.93	997	121	3.17
31.38	2.85	745		17.96	31.50	2.84	1306		4.15
32.80	2.73	1100		26.51	36.44	2.46	1699		5.40
35.60	2.52	1155	131	27.84	36.50	2.46	1225	131	3.90

FT-IR spectra obtained for pure Thiourea and Cu-Thiourea are shown in fig 2(a) and 2(b) respectively. The graphs exhibit recorded transmittance against various wave numbers in the range 500 cm^{-1} to 3500 cm^{-1}.Various peak positions corresponding to particular range of wave numbers can be assigned to different functional groups referring to standard data. Table -2 shows theobservedpatterns of pure and doped Thiourea which resembles broadly and confirm the presence of various functional groups. Their interactions among various groups expected to be preserved except for a small shift in peak positions. In higher frequency range of 3000cm^{-1} to 3400 cm^{-1},the peak positions almost match which corresponds to NH_2- asymmetric stretching. There is shift in C = S symmetric stretching at 1456.74cm^{-1} for pure Thiourea to 1407.65 $cm^{-1}$for CTSwhich may be indicative of C = S asymmetric stretching. Thus the shift in frequency establishes the presence of Cu^{2+} ion in the lattice.

UV,Visible and near IR spectroscopic results are shown in Fig 2(a) and 2(b) which exhibits the absorption against the radiation in wavelength range from 200 nm to 800 nm.The response of pure and CTS matches to great extent.. The near zero absorbance in entire visible and near IR region are indicative of crystals with good optical transparency. The UV cut-off is below 200nm presenting a broad transparency window in UV,Visible and near IR region which is an important feature for NLO material to be viable for optoelectronic devices.

The results obtained for SHG for the doped samples presented in table-3. The non –zero output confirms the second harmonic generation. The output power was compared with standard KDP. The efficiency as higher as 23.4% for PTDC and 20% for CTS was recorded.

Table-2: FT-IR Analysis

Pure Thiourea		**Cu-Thiourea**	
Wave Number Cm^{-1}	**Band assignment**	**Wave Number Cm^{-1}**	**Band assignment**
3362.62	NH_2 asymmetric stretching	3364.62	NH_2 asymmetric stretching
3264.10	NH_2 asymmetric stretching	3258.01	NH_2 asymmetric stretching
3154.39	NH_2 asymmetric stretching	3143.82	NH_2 asymmetric stretching
1604.22	NH_2 bending	1603.73	NH_2 bending
1551.54	NH_2 bending	1463.47	NH_2 bending
1456.74	C = S symmetric stretching	1407.65	C = S asymmetric stretching
1078.21	C - N symmetric stretching	1078.61	C - N symmetric stretching
726.73	N – C- N asymmetric bending	727.45	N – C- N asymmetric bending
621.25	N – C- N asymmetric bending	627.09	N – C- N asymmetric bending

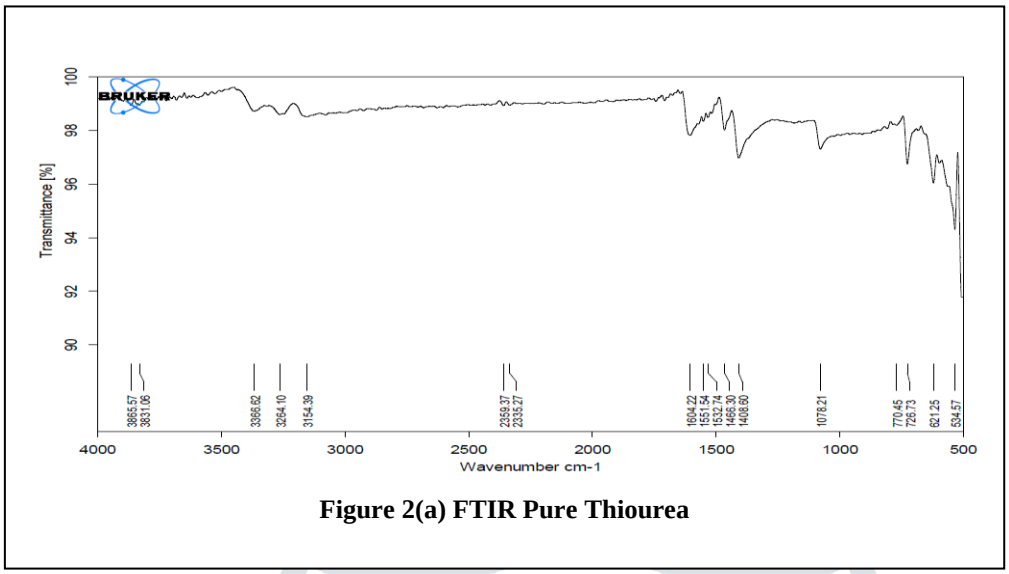

Figure 2(a) FTIR Pure Thiourea

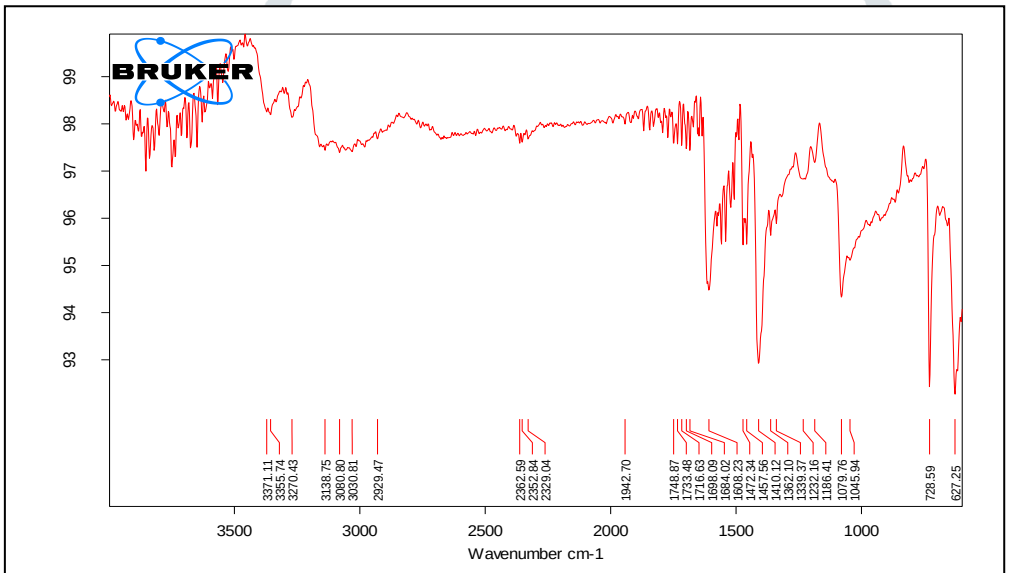

Figure 2(b) FTIR (PTDC)

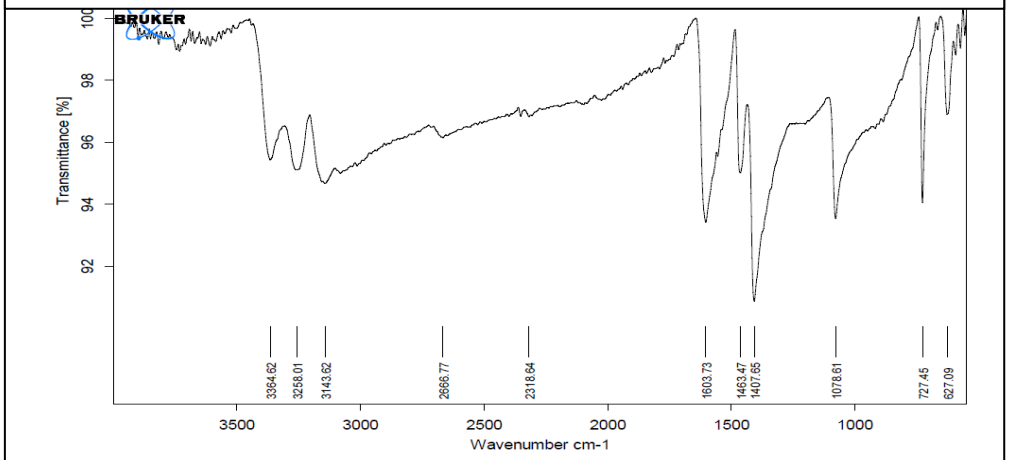

Figure 2(c) FTIR (CTS)

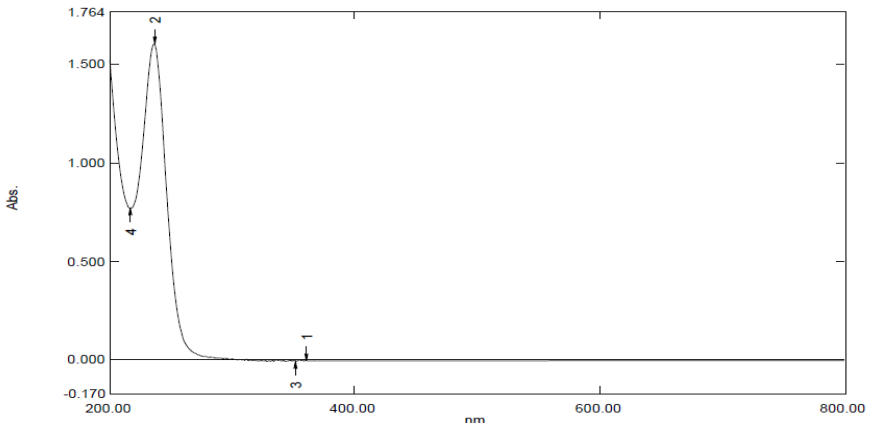

Figure 3(a) UV-Vis Pure thiourea

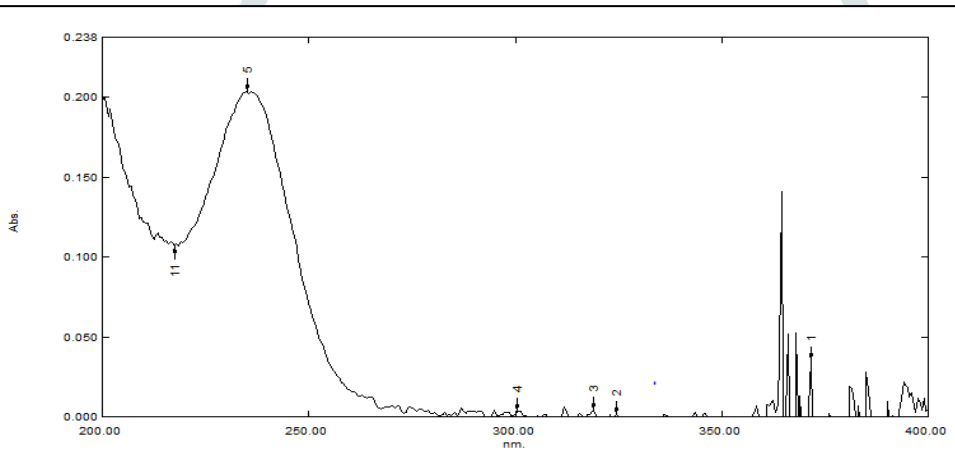

Figure 3(b) UV-Vis PTDC

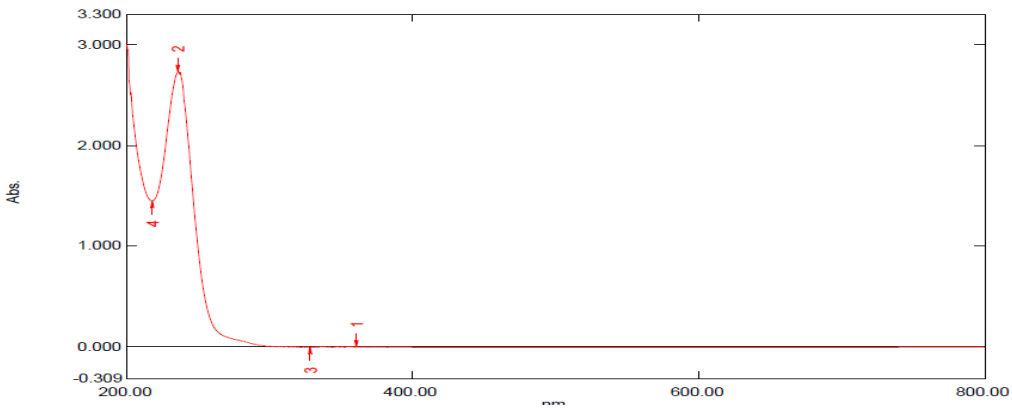

Figure 3(c) UV-Vis Cu-Thiourea

5.Conclusions:

Good quality non linear optical semi organic single crystals of K-doped and CTS have been synthesized by slow evaporation method using doubled distilled water as solvent. The unit cell structure of grain crystals were confirmed by XRD analysis and reveals that the crystals belong to orthorhombic and tetragonal systems. The good crystalline nature is confirmed by well defined sharp peaks in powder XRD plots. The dominant peaks were indexed and matched with reference data.FTIR and UV-Vis spectroscopic studies reveals that the materials grown are optically suitable for non linear applications. The non linear optical studies reveal that the grown samples have reasonably good efficiency. There is ample scopeof growing such materials under better growth conditions and improved performance.

6. Acknowledgement: The author working as an associate professor at**V.S.Patel college of Arts & Science,Bilimora**,Gujarat is thankful to college management and Department of Physics,**Veer Narmad South Gujarat University, Surat**for providing necessary infrastructure to perform experiments for growth of crystals and logistic support.

I am also thankful to Prof. **P.K.Das**,senior scientist atPhysical Chemistry Department of **Indian Institute of Science,Bangaluru**for his assistance to performsecond harmonic generation experiment in his laboratory.

REFERENCES:

[1]GENERATION OF OPTICAL HARMONICS :P.A.Franken,A.E.Hills,C.W.Peters and G Wienriech,Physical Review letters,Volume7,Number4 1961

[2] K.Kurtz,T.T.Perry,J.Appl.Phys.39,(1968),3798,3814

[3].Non Linear Optics,Sec.Edi.,RobertW.Boyd,AcademicPress,Elsevier Science(2003) ,1-56.

[4].D.Rajasekharan,R.Mohankumar,R.Jayavel, P.Ramaswamy,Jour. Of Crystal Growth,Vol-252,issue1-3,(2003), 317-327

[5]Synthesis and characterization of bis(thiourea)zinc chloride doped with l-arginine; SwetaMoitra, TanusreeKar:Materials Chemistry and Physics 117 (2009) 204–208,Elsevier

[6] SHG in Zinc tris (thiourea) sulphate: H.O.Marcy,L.F.Warren,M.S.Webb,C.A.Ebbers,S.P.Vaiska, G.C.kannady and G.C.Catella: Applied Optics,Vol-3,Issue-24,P 5051-5056

[7]YandingLu,ZhengpingWang,Xinguangxu and Xian zhoo,Optical Material ExpressVol.4 Issue-9(2014),1787-1793

[8] Growth and characterization of pure and metal doped bis thiourea zinc acetate (BTZA) single Crystals; A kangavalli,J. Thomas Joseph Prakash,T.Seethalakshmi; International journal of research in pharmaceutical and nano sciences;5(6),2016,326-336

[9] M.NarayanBhat,S.M.Dharmprakash,Journal of Crystal Growth,2002,Vol-235,511-516

[10] B.Ravi*et al* Rayasan J. Chem ; Vol-7/No.3 ,2014 P -287-294

[11] S.Surentherbabu&P.Rajasekaran;Optoelectronics and Advanced Materials-Rapid Communications;Vol-6/No.7-8;2012 P 768-770

[12] Saha J K and Podder J, *J Bangladesh Academy of Sciences*, 2011, 35(2), 203-210;

[13]B. Senthilkumaran, S.Arivoli and G. Thanapathy; Chemical Science Transactions 2017, **6(3),** 473-479

[14] Professor Dr. Alexander A. Chernov;Modren Crystallography III ; Crystal Growth;Springer-Verlag Berlin Heidelberg Voi-1;1984; P 353-414

[15] P. Sagayaraj and S. Selvakumar, Studies on the growth and characterization of novel organometallic NLO crystal *Journal of Materials Science: Materials in Electronics*, **20**, S1, (299), (2009).

[16]Growth and characterization of pure and metal doped bis(thiourea) zinc chloride single crystals S.Selvakumar *et al;Crystal Research and Technology Vol-48 issue-8;2006 P 766-770*