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Synthesis and Characterization of Cerium Doped Urea Thiourea Naphthylamine Single Crystal Developed by Slow Evaporation Method

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Abstract

A single crystal of cerium doped urea thiourea naphthylamine has been grown successfully from its aqueous solution. The grown crystals have been subjected to X-ray diffraction studies to identify the morphology and structure. The TGA-DTA studies showed the thermal properties of the crystals. The functional group of the grown crystals was found by UV - Visible double beam spectra, FT-IR analysis, NMR and XRD studies.

Key words : Urea, Thiourea, Naphthylamine, Cerium chloride, Cerium Naphthylamine Thiourea Urea single Crystal (CeNTU), X-Ray diffraction, UV-Vis, FT-IR, NMR, TGA, NLO and micro hardness.

1. Introduction

Crystals are the essential pillars of modern technology. Without crystals, there would be no electronic and photonic industry and fibre optical communications, which depend on crystals such as semiconductors, superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries. Crystal growth is an interdisciplinary subject covering physics, chemistry, material science, chemical engineering, metallurgy, crystallography, mineralogy, etc. In the past few decades, there has been a growing interest on crystal growth processes, particularly in view of the increasing demand of materials for technological applications[1-10]. Atomic arrays that are periodic in three dimensions, with repeated distances are called single crystals. It is clearly more difficult to prepare single crystal than poly-crystalline material and extra effort is justified because of the outstanding advantages of single crystals[2]. The reason for growing single crystals is, many physical properties of solids are obscured or complicated by the effect of grain boundaries. The chief advantages are the anisotropy, uniformity of composition and the absence of boundaries between individual grains, which are inevitably present in polycrystalline materials. The strong influence of single crystals in the present day technology is evident from the recent advancements in the above mentioned fields. Hence, in order to achieve high performance from the device, good quality single crystals are needed. Growth of single crystals and their characterization towards device fabrication have assumed great impetus due to their importance for both academic as well as applied research. To enable a material to be potentially useful for NLO applications, the material should be available in bulk single crystal form[9]. So, crystal growth of new nonlinear optical materials and investigation into their properties has become most indispensable and efficacious disciplines in the field of materials science and engineering. The rapid development of optical communication system has led to a demand for Nonlinear Optical (NLO) materials of high performance for use as components in optical devices. NLO materials are used in frequency conversion, which is a popular technique for extending the useful wavelength range of lasers. The search for new materials has identified novel semi organic systems of considerable potential and high performance[11-21]. There are three major stages involved in this research. The first is the production of pure materials and improved equipment associated with the preparation of these materials. The second is the production of single crystals first in the laboratory and then extending it to commercial production. The third is the characterization and utilization of these crystals in devices. In this paper, the method of crystal growth with emphasis on low temperature solution growth technique was described.

2. Experimental Method

2.1. Material Preparation :

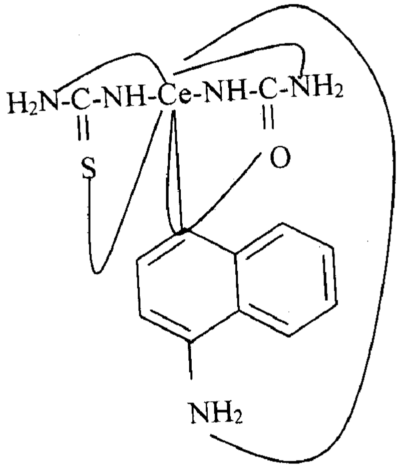
An essential prerequisite for success in crystal growth is the availability of material of the highest purity. Solute and solvents of high purity are required, since impurity may be incorporated into the crystal lattice resulting in the formation of flaws and defects. Sometimes impurities may slow down the crystallization process by being adsorbed on the growing face of the crystal, which changes the crystal habit. A careful repetitive use of standard purification methods of recrystallization followed by filtration of the solution would increase the level of purity.

2.2. Seed Preparation :

0.909 g of urea, 2.15 g of naphthylamine, 5.7 g of thiourea and 2.58 g of Cerium chloride were dissolved in 30 ml of double distilled water. The solution was thoroughly mixed using a magnetic stirrer. A crystalline substance was formed. The Urea, Thiourea, naphthylamine cerium chloride solution was prepared in water and maintained at 30°C with continuous stirring to ensure homogeneous temperature and concentration. The solution was kept at 30°C for ten days in order to get the cerium doped naphthylamine thiourea and urea doped single crystal.

Crystal growth : large single crystals can be grown from slow evaporation solution growth. Single crystals of cerium doped naphthylamine thiourea and urea are grown by slow evaporation of the saturated aqueous solution at room temperature. Good quality single crystals were grown within ten days.

$CeCl_3 + NH_2CONH_2 + NH_2CSNH_2 + C_{10}H_7NH_2 \rightarrow CeNHCSNH_2.NHCONH_2.NHC_{10}H_7 + 3HCl$



Molecular structure of CeNTU

Fig. 1-Shape of CeNTU

2.2 Uv-Vis Spectral Analysis :

The optical transmittance range and transparency cut-off wavelength are the main requirements for device applications.

2.3 Thermal Analysis :

Thermo Gravimetric Analysis (TGA) gives the information regarding the phase transition and different stages of decomposition of the crystal system.

2.4 Ft-Ir Spectral Analysis :

FT-IR Spectroscopic studies were effectively used to identify the functional groups present in the synthesized compound and to determine the molecular structure.

2.5 NMR

^{1}H NMR Chemical Shifts :

Molecular structure of the grown crystal was investigated by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrums indicate the presence of different proton environments in the title crystal.

^{13}C NMR Chemical Shifts :

^{13}C NMR spectrum arises in the same way as in the proton NMR spectrum. Each carbon nucleus has its own electronic environment, different from the environment of other, non-equivalent nuclei; it feels a different magnetic field, and absorbs at different applied fields strength.

3. Results and Discussion

3.1. X-Ray Diffraction Analysis :

Single crystal X-ray diffraction study was performed for the grown CeNTU crystal. It was found that CeNTU crystal belongs to orthorhombic system (α= β= γ= 90°). Lattice parameter values of CeNTU are compared with reported TU in Table 1. In the case of doped sample, a slight variation in the cell parameters is observed, which may be due to the incorporation of urea and thiourea ligands. This analysis revealed that the induction of urea and thiourea ligand in the CeNTU crystal does not change the crystal system though there is a small change in the lattice parameters. The powder sample of CeNTU was scanned over the range 10-80° at a rate of 1° per minute and the powder X-ray diffraction patterns were indexed using Check cell software (Fig. 2). The Lattice parameter (a) was calculated by selecting the (102) plane using the formula[2]

$$Sin^2\theta = \frac{\lambda^2}{4a^2}\,(h^2 + k^2 + l^2)$$

Sample	**System**	**2θ(degree)**	**FWHM**	**hkl**	**Lattice parameter (Å)**	
					Calculated	Reference
TU	Orthorhombic	23.25	0.16	200	7.644	7.644
		20.81	0.16	020	8.527	8.559
		32.57	0.24	002	5.493	5.492

Sample	**System**	**2θ(degree)**	**FWHM**	**hkl**	**Lattice parameter (Å)**	
					Calculated	Reference
CeNTU	Orthorhombic	29.305	0.7119	200	3.0451	3.0800
		48.209	0.6037	020	1.8861	1.9061
		57.073	0.6036	002	1.6124	1.6323

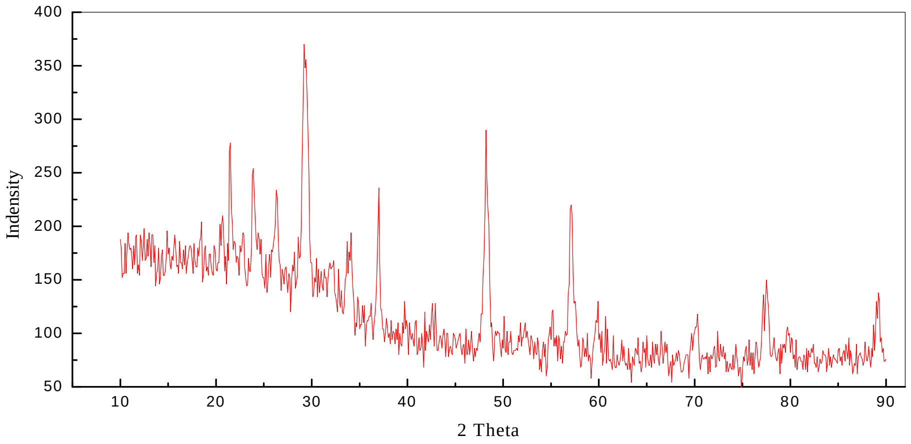


Fig. 2-XRD-pattern of CeNTU

3.2. Fourier Transforms Infrared Spectroscopy :

The FT-IR spectra of cerium urea thiourea naphthylamine grown crystals are shown in figure 3. In the higher wavelength region, the peak at 3490cm^{-1} is assigned to C-H, N-H stretching vibration. The region 3450 cm^{-1} and 3128 cm^{-1} with strong intensity represents N-H stretching mode. The broad envelope positioned in between 3450 cm^{-1} and 2700 cm^{-1} corresponds to the symmetric and asymmetric stretching modes of NH$_2$ group. The peak at 2950 - 2900 cm^{-1} with medium intensity refers C-H asymmetric stretching. Combinational overtones extend to the bands from 2450 - 2320 cm^{-1}. The peak at 1740 cm^{-1} indicating the C=O stretching mode of vibration. The NH$_2$ bending vibrations occur at 1620, 1613 and 780 cm^{-1}. The peak at 1500 cm^{-1} is due to NH$_2$ bending vibration. The peaks at 1470-1420 cm^{-1} corresponds to the C=S stretching. The C-C stretching mode of vibration occurs in 1358 cm^{-1} peak. The peak at 1205 cm^{-1} gives rise to C-N stretching mode of vibration. The spectra show absorption bands in the region of 1165 cm^{-1} and 1050 cm^{-1} which are due to in-plane C-H bending vibration. The band 1125 cm^{-1} signifies the N-H symmetric bending. The bands at 850 cm^{-1} and 800 cm^{-1} revealed that C-N deformation mode. The ring deformation occurs the peak at 828 cm^{-1}. C=O deformation is identified by the band at 690 cm^{-1}. C-H out-of plane bending peaks obtained at 660 cm^{-1} and 648 cm^{-1}. The bands 635-628 cm^{-1} represents C-C deformation. The absorption bands in the region of 486-471 cm^{-1} are due to N-C stretching vibration. The assignments confirm the presence of various functional groups present in the material. The absorption around 1610 cm^{-1} is NH$_2$ bending and this band would be shifted into lower wavelength region 1618 cm^{-1}. The absorption bands in the region of 900-820 cm^{-1} are due to the presence of aromatic ring. Our investigations were well compared with earlier reports$^{10-19}$.

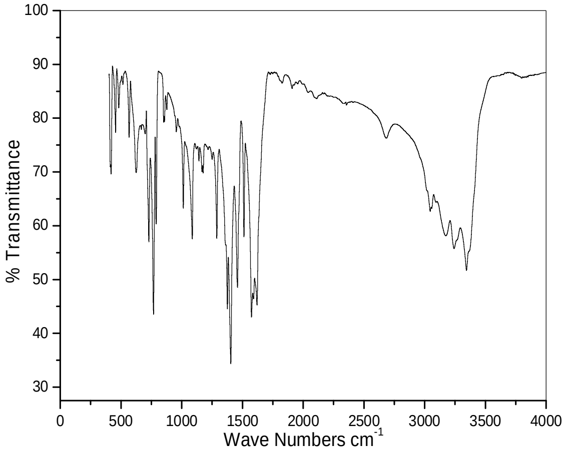


Fig. 3-FT-IR spectrum of CeNTU single crystal

Table 1-IR Spectrum data's

Crystal	Wavenumber (cm^{-1})	Band Assignment
CeNTU single Crystal	3500	C-H, N-H
	3500 and 3123	N-H
	3490 and 2711	NH_2
	2995 - 3000	C-H
	1750	-C=O
	1420 - 1470	-C=S
	1350	-C-C-
	1215	-C-N-

3.3 Uv- Visible Studies :

The UV-Visible spectrum of the single crystal CeNTU indicates Low absorption in the entire visible and near infrared region of the crystals. This is a desirable property for NLO applications since a wider optical transparency in these regions enhances the frequency conversion efficiency in the corresponding wavelengths.

The cuts off wavelengths of CeNTU single crystal were found to be 383.6 nm, 490.8 nm and 975 nm respectively. The presence of aromatic ring is confirmed by the cut of wavelength around 975 nm. The good optical transmittance in the entire visible region and the cut off wavelength (λ_{cut}) was observed as this is due to π-π^* transition in the compounds. The band gap energy ($E_g = hc/\lambda$) was found to be 9.58 eV for pure and CeNTU crystals. The large transmission in the entire visible region and short cut off wavelength enables it to be a potential material for second and third harmonic generation[20-27].

Crystal	Wavelength (nm)	% Transmittance
CeNTU	383.6	98.3
	490.8	115.6
	975.0	89.4

3.4 Nuclear Magnetic Resonance Spectroscopy (Nmr) :

NMR spectrum of CeNTU was recorded using FT-NMR spectrometer. CeNTU crystal was powdered and dissolved in deuterated dimethyl sulfoxide (DMSO). FT-NMR spectrum recorded for CeNTU is shown in figure 4. A chemical shift at 8.015, 7.995, 6.980 ppm is due to Ar-H proton. The chemical shift at 7.058 – 7.716 ppm is assigned to =C-NH-C= proton. Chemical shift at 6.552 - 6.670 ppm is due to H-N–C=O. A chemical shift at 1.032 ppm is due to =C-H proton [12]. The chemical shift at 7.742-7.763 is due to H–N-C=O. A chemical shift at 3.79 is due to –C=S. The above values confirm the structure of CeNTU.

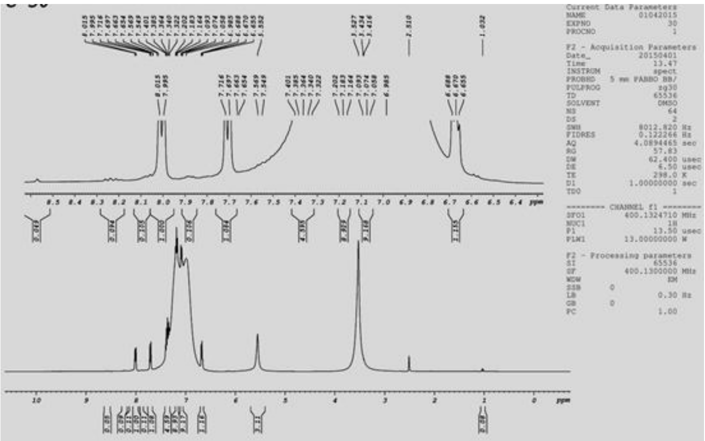


Fig. 4-NMR spectrum of CeNTU

3.5 Thermal Analysis :

TGA analysis of the CeNTU crystal was carried out in the temperature range 10- 900°C. The recorded thermogram is shown in Fig. 5. From TGA curve it is observed that the weight loss start from 200°C. There is 35.5 % weight loss is due to the liberation of naphthylamine molecule at 210°C. There is 6.56 % weight loss between 310°C to 370°C. This weight loss is due to the liberation of NH_3. There is 11.5 % weight loss between 555°C to 680°C. This weight loss is due to the liberation of CO. There is 13.4 % weight at 820°C. This weight loss is due to the liberation of H_2S. This endothermic event is in good agreement with the TGA trace[21].

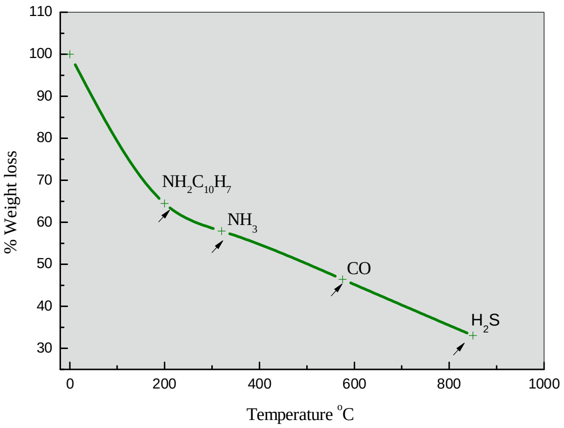


Fig. 5. Thermogravimetric analysis for the determining the weight loss

3.6 Micro Hardness Studies :

Hardness of the material is a measure of resistance that offers to deformation. The transparent polished crystal free from cracks was selected for hardness measurements. The indentations were made on the flat surface with the load ranging from 10 to 100 g using Shimadzu make-model-HMV-2 fitted with Vicker's pyramidal indenter and attached to an incident light microscope. The indentation time was kept as 5s for all the loads. The Vicker's hardness (Hv) was calculated from the relation[21],

$$Hv = \frac{1.8544P}{d^2} \qquad P/d^2 \ kg/mm^2$$

Where, P is the applied load and d the average length of the diagonal of the indentation mark. With P in g and d in µm, the units of Hv turned out to be kg/mm^2. The variation of micro hardness with applied load for the prominent (102) plane of the CeNTU crystal is shown in Fig. 6. It is found that the hardness values increases with the increase of the applied load. This behaviour of increasing micro hardness with the load known as reverse indentation size effect (RISE)[21], which is also attributed due to existence of distorted zone near crystal medium interface, effect of vibrations, specimen chipping etc., and the plastic deformation is dominant. At low loads or strains, plastic deformation of crystals mainly involves the nucleation of dislocations along a particular slip system. The RISE effect can be qualitatively explained on the basis of the depth of penetration of the indenter[21]. At small loads, the indenter penetrates only the surface layers and therefore, the effect is shown sharply at the early stages. When the applied load increases, the penetration depth also increases and the overall effect must be due to the surface and inner layers. When only one slip system is active during plastic deformation at low loads, the number of active parallel glide planes during indentation is low. Therefore the nucleating dislocations rapidly propagate into the material without experiencing substantial mutual interaction stress between them. Consequently in this stage, indentation depth increases proportionally with applied pressure.

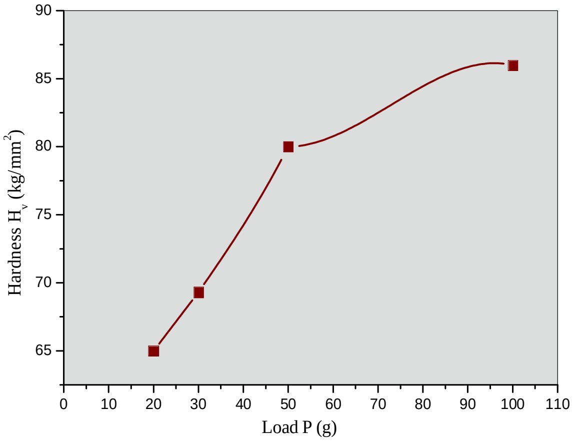


Fig. 7 : Variation of hardness number with load

3.7 Nlo Studies :

The second harmonic signal, generated in the crystals was confirmed from the emission of yellow radiation by the crystals. The NLO SHG values of the CeNTU single crystals were determined and compared to the reported SHG value of pure KDP[21].

Crystal	Second harmonic signal output (mJ)	SHG efficiency (compared to SHG efficiency of pure KDP)
CeNTU	9.3	3.4

4. Conclusions

The good quality single crystals of Cerium Naphthylamine Thiourea Urea single Crystal are successfully grown by slow evaporation method at room temperature. The UV-Vis spectra showed that the crystals had a wide optical window, no absorbance and good optical transmittance in the entire visible region. FT-IR analysis confirmed the presence of functional groups in the grown crystals. TGA thermo gram revealed the thermal stability of the materials. The powder X-Ray diffraction study confirms the lattice parameter values. The good optical quality and their suitability for NLO applications. Kurtz-Perry powder SHG test was employed to determine the SHG efficiency of the samples and the values were compared to the reported SHG efficiency of pure KDP.

References

1. J.K. Saha and J. Podder, “Crystallization of zinc sulphate single crystals and its structural, thermal and optical characterization” *Journal of Bangladesh Academy of Sciences*, Vol. *35*, No. 2, 203-210 (2011).
2. G. Viruthagiri, P. Praveen, S. Mugundan, M. Anbuvannan, “Growth and Characterization of L-Histidine Doped Thiourea Single Crystals by Slow Evaporation method” *Indian Journal of Advances in Chemical Sciences, 1 (4),* 193-200 (2013).
3. R.S. Sundararajan, M. Senthilkumar, C. Ramachandraraja, “Growth and Characterization of Bisthiourea Nickel Bromide-New Semi organic Nonlinear Optical Crystal” *Journal of Crystallization Process and Technology*, *3,* 56-59 (2013).
4. S. Gunasekaran, G. Anand, R. Arun Balaji, J. Dhanalakshmi and S. Kumaresan, “Crystal growth and comparison of vibrational and thermal properties of semi-organic nonlinear optical materials” *Journal of Physics*, Vol. *75,* No. 4, 683-690 (2010).
5. J. Thomas Joseph Prakash, L. Ruby Nirmala, “Synthesis, spectral and thermal properties of bisthiourea zinc acetate (BTZA) single crystals”, *International Journal of Computer Applications*, *6,* 0975-8887 (2011).
6. X. E. Duan, X. H. Wei, H. B. Tong, S. D. Bai, “Ferrocene-modified pyrimidine acyl-thiourea derivatives: Synthesis, structures and electrochemistry”, *Journal of Molecular Structure,* 1005: 91-99 (2011).
7. M.N. KrishnaMoha, K. Jagannathan, S. Ponnusamy, C. Muthamizhchelvan, “Effect of urea and thiourea on nonlinear optical hippuric acid crystals”, *Journal of Physics and Chemistry of Solids, 72,* 1273-1278 (2011).
8. K. Muthu, S. P. Meenakashisundaram, “Growth and characterization of Hexakis (thiourea) nickel (II) nitrate crystals”, *Journal of Crystal Growth, 352,* 158-162 (2012).
9. J. Chandrasekaran, P. Ilayabarathi, P. Maadeswaran, P. Mohamed Kutty, S. Pari, “Growth and characterization of L-histidine cadmium chloride monohydrate asemiorganic nonlinear optical crystals”, *Optics Communications,* 285: 2096-210 (2012).
10. J.Chandrasekaran, P.Ilayabarathi, and P. Maadeswaran, “Synthesis, growth, spectroscopic and optical studies of a new semi organic nonlinear optical crystal: l-valine potassium chloride” *Rasayan J. Chem. 4(2),* 320-326 (2011).
11. V. Krishnakumar and Nagalakshmi, “Crystal Growth and Characterisation of $K[CS(NH_2)_2]_4Br$-A Semi organic Non-Linear Optical Crystal,” *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, Vol. *68,* No. 3,, pp. 443-453 (2007).
12. N. Vijayan and R. Ramesh Babu, “Some Studies on the Growth and Characterization of Organic Nonlinear Optical Acetoacetanilide Single Crystals,” *Journal of Crystal Growth*, Vol. *267,* No. 3-4, 646-653 (2004).
13. R. Mohankumar and D. Rajanbabu, “Studies on the Growth Aspect of Semi organic 1-Alanine Acetate a Promising Nonlinear Optical Crystal,” *Journal of Crystal Growth*,Vol. *275,* No.1-2, p. 1935-1939 (2005).

14. H.O. Merry, L. F. Warren,, “Liquid Level Sensor with Optical Fibers,” *Applied Optics*, Vol. *31*, p. 5051 (1992).
15. 16) V. Venkataraman, G. Dhavaraj, H. L. Bhat,, “Crystal Growth and Defect Characterization of Zinc Tris(thio-urea) Sulphate: A Novel Metal-Organic Nonlinear Optical Crystal,” *Journal of Crtystal Growth*, Vol. *154*, No. 1-2, p. 92-97 (1995).
16. V. Venkataraman, S. Maheswaran, “Crystsal Growth and Physical Characterization of the Semi organic Bis (Thiourea) Cadmium Chloride Crystal,” *Journal of Crystal growth*, Vol. *174*, No. 3-4, p. 605-610 (1997).
17. D. Cu, M. Jiaog and Z. Taus, “A New Phase Match able NLO Crystal 1-Arginine Monohydrate,” *Acta Chimica Sinica*, Vol. *41*, p. 570 (1983).
18. C. Ramachandraraja and R. S. Sundararajan, “Growth, Characterization, Vibrational Spectroscopic and Thermal Studies of a New Metal-organic Non-Linear Optical Crystal-Bisthiourea Cadmium Bromide,” *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, Vol. *71*, No. 4, pp. 1286-1289 (2008).
19. S. K. Kurtz and T. T. Perry, “A Powder Technique for the Evaluation of NoOnlinear Optical Materials,” *Jounal of Applied Physics*, Vol. *39*, No. 8, p. 3798-3814 (1968).
20. S. A. Martin Britto Dhas, J. Suresh, G. Bhagavannarayana, S. Natarajan, Growth and characterization of a new organic non-linear optical (NLO) material: l-histidinium tri fluoro acetate, *The Open Crystallography Journal*, *1*, 46-50 (2008).
21. A. Ruby and S. Alfred Cecil Raj, ’Growth, spectral, optical, thermal and mechanical properties of thiourea doped tri glycine zinc chloride nonlinear optical crystal, *International journal of Scientific Research Publications*, *3(3)*,1-5 (2013).
22. G. M. Lawrence, J. Thomas Joseph Prakash, Growth and characterization of pure and glycine doped cadmium thiourea sulphate (GCTS) crystals, *Spectrochimica Acta Part A*, *91*, 30-34 (2012).
23. J. D. Patel, F. Mighri, A. Ajji, Aminocaproic acid mixed methanolic lead-thiourea complex precursor and its thermal decomposition to star-shaped lead sulfide crystals, *Materials Letters*, *74*, 183-186 (2012).
24. J. D. Patel, F. Mighri, A. Ajji, T. K. Chaudhurid, Orphology and sizecontrol of lead sulphide nanoparticles produced using methanolic lead acetate trihydrate-thiourea complex via different precipitation techniques, *Materials Chemistry and Physics*, *132*, 747-755 (2012).
25. P. Anandan, R. Jayavel, T. Saravanan, G. Parthipan, C. Vedhi, R. Mohan Kumar, Crystal growth and characterization of L-histidine hydrochloride monohydrate semiorganic nonlinear optical single crystals, *Optical Materials*, *34*, 1225 (2012).
26. S. E. Joema, S. Perumal, S. Ramalingam, Studies on structural, optical, mechanical and thermal properties of un doped and urea-doped L-Histidine bromide (lhb) in science and single crystals, *Recent Research Technology*, 3: 2076-5061 (2011).
27. J. Ramajothi, S. Dhanuskodi, M. Akkurt, Crystal growth of phase matchable new organic nonlinear optical material for UV laser generation, *Spectrochimica Acta Part A*, *69*, 1271-1276 (2008).