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CRYTALLIZATION AND CHARACTERIZHTION OF ORGANIC LIGAND THIOUREA SINGLE CRYSTALS

Dr.A.Prabumarachen

Assistant professor,Department of Physics, Vivekananda college, Agasteeswaram-629701.Affiliated to Manonmaniam Sundaranar University,Tirunelveli,abishekapatti, Tamilnadu, India.

Dr.T.S.Jayanthi

Associate professor,Department of Physics, Vivekananda college, Agasteeswaram-629701.Affiliated to Manonmaniam Sundaranar University,Tirunelveli,Abishekapatti, Tamilnadu, India.

ABSTRACT

Thiourea single crystals have been grown from aqueous solution by slow evaporation technique. The solubility of thiourea with different temperatures were measured. Thiourea with two distinct morphologies were observed. The structural, optical and elemental analysis was carried out by X-ray diffraction, FT-IR and elemental ICPA analysis.

Keywords: nonlinear optical materials,ligand,morphology.

Introduction

Recent advances in organic Non-Liner Optical (NLO) materials have involved a large revival of interest in this area on account of their widespread industrial potential such as their high nonlinearity, high flexibility in terms of molecular structure ,high optical damage threshold and low cost[(1)] .In particular thiourea and its co-ordination compounds formed is of great interest.

The origin of nonlinearity in NLO materials arises due to the presence of delocalized π electrons system, connecting donor and acceptor groups and responsible for enhancing their asymmetric polarizability[(2)]

Single crystals of thiourea are being extensively used and have vast demand in the electronic industry as polarization filter,electro-optic and electro-acoustic devices.Thiourea crystals also exhibit pyroelectric effect,which is utilized in infrared,ultraviolet,scanning electron microscopy detection and infrared imaging[(3)]

Thiourea belongs to orthorhombic crystal system with lattice primitive space group Pnma.The Unit cell parameters are a=7.657A^o,b=8.588 A^o and c=5.485 A^o [(4)]

Thiourea is soluble in water and its solubility at 13^{o}C is 9.8 parts by weight by parts by weight of water. Its molecular weight and density were 76.12 and 1.405 gm/cc[(4)] respectively.More than 700 structures of metal thiourea complexes were reported by Cambridge structural database[(5)] .Spectroscopic and microscopic studies of thiourea single crystals were performed[(6)].

In crystallization process, the feed solution contains unwanted dissolved impurities. The ability of these impurities to change the kinetics of nucleation, the growth and the crystal morphology is well known in crystallization technology.

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An attempt has been made in the present investigation to crystallize pure thiourea crystals and also to study the unwanted dissolved impurities on the crystal morphology.

Solubility of thiourea.

Analytical reagent Grade thiourea and deionised water(solvent),were used in the present crystallization experiment.The solubility of thiourea was determined for different temperatures viz.30, 35, 40, 45 and 50^0C.The measurement was performed by dissolving pure thiourea in deionised water in an airtight container with constant stirring using magnetic stirrer. After achieved saturation the equilibrium concentration of thiourea was determined gravimetrically. The solubility curve for different temperatures are presented in Fig.1.

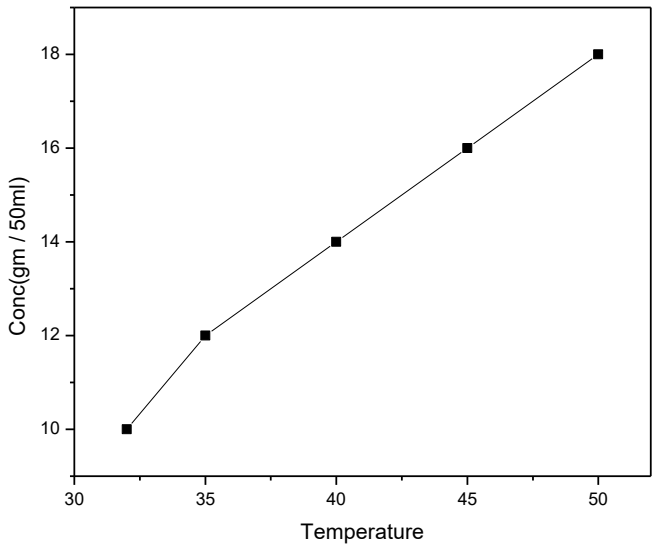

Fig1.Solubility curve of thiourea

Experimental.

200 ml of saturated solution of thiourea was prepared at constant stirring using magnetic stirrer for 6 hours at 30^0C.The saturated solution was filtered using Wattman filter paper. The filtered solution was poured in two beakers (100 ml each).The pH of the solution was found to be 7.5.

The beaker was covered with perforated polythene paper. The solution was allowed to evaporate at 30^0C.Due to the slow evaporation of the solvent, the solution get evaporated and get supersaturated. Hence the nucleation starts. The nucleus grows in size and within a period of 17-20 days Thiourea crystals with well defined morphologies could be grown.

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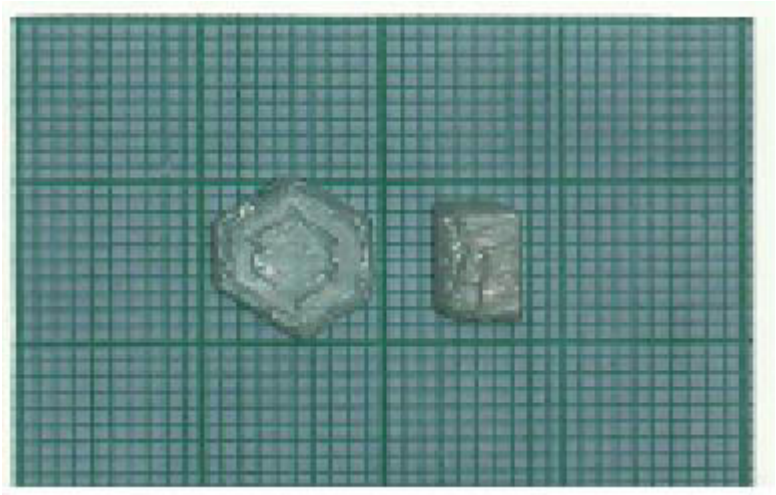

Fig (2a) thiourea with hexagonal morphology (2b) thiourea with rectangular morphology.

Results and Discussion.

Morphological studies.

Thiourea single crystals with two distinct morphologies were observed from the grown crystals. Fig. 2(a) shows hexagonal morphology with dimensions of ---------- and thickness----------.The crystal was found to be well faceted with high transparency. Where as Fig .2 (b) Shown rectangular morphology with dimensions ---------- breath with less transparency. The poor transparency may be due to the presence of dissolved impurities in the solution itself.

The influence of impurities on the Growth of thiourea crystals.

The nucleation and hence the growth of a crystal in various directions is a function of a parameters such as temperature, the degree of super saturation of the mother solution, P^H, concentration of various impurities in solution and other physico-chemical properties (7).

The crystals with two distinct morphologies were analyzed with ICP-AES analyses in which thermo Electron IRIS Intrepid II xsp DUO was used.

The given two samples were dissolve in HNO_3 and make up into 100ml using HPLC grade water and analyzed with ICP-AES system. The elements measured (ppm)were presented in table 1.

No	Sample Name	Cu3275	Fe2599	k-7664	Mg2852	Na5889
1	Hexagonal	BDL	49.14	64.22	14.89	145.2
2	Rectangular	29.09	360.95	109.09	27.10	157.4

On comparing the elements present in both Hexagonal and rectangular crystals,CU3275 was present in rectangular morphology crystals and in Hexagonal the same elements was below

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the detectable Limit. The other elements present in rectangular morphology crystal were higher in concentration in compared with hexagonal morphology. The formation of rectangular morphology is may be due to the influence of the higher level of concentration of the impurities and may due to the formation of complex with Cu3273 and Fe2599 element.

FTIR studies.

The FT-IR analysis was carried out by Peskin Elmer spectrometer by KBr pellet technique in the range 500-400cm.The FTIR spectra of Hexagonal shaped and rectangular shaped thiourea is shown in Fig 3a and b respectively. The vibration frequency of various functional groups of hexagonal and rectangular shaped thiourea single crystals is presented in Table 2.

To identify the functional groups in determining the molecular structure of the grown crystals.

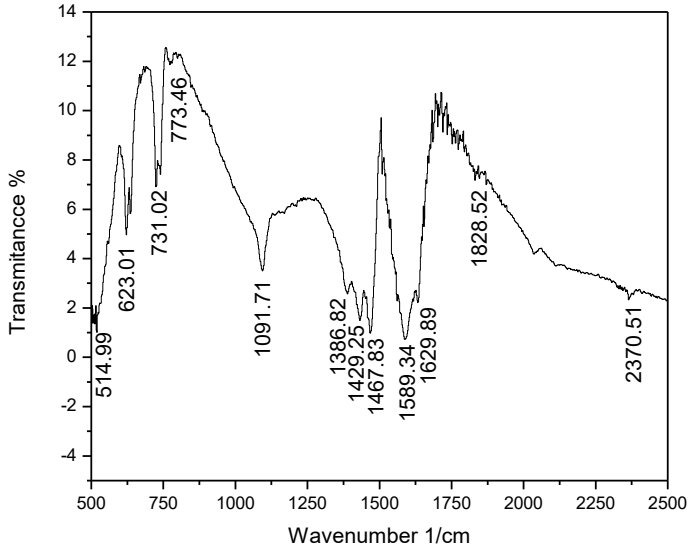

Fig 3a-Hexagonal shaped thiourea
b-rectangular shaped thiourea

Table 2.Vibrational band assignments in wave number cm^{-1}

Hexagonal(cm^{-1})	Rectangular(cm^{-1})	Assignment
1589.34	1591.271	NH_2 bending
1091.71	1091.71	COH Stretching
1467.29	1467.83	N-C-N-assymetric Stretching
729.02	731.02	C=S stretching and N-C-N stretching
495.71	-	N-C-N deformation

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The CH_2 asymmetrical deformation or CH_2 bending vibration.

X-ray Diffraction.

The powder diffraction patterns of the Hexagonal and rectangular shaped thiourea single crystals differed in their relative intensity and in the lattice spacing of the crystals(Fig-4a,b).The obtained diffraction peaks were compared with JCPDS card and hkl planes were indexed. The lattice parameters were calculated by fitting the XRD data with "least square method" using "CELN"program.

The calculated lattice parameters for the Hexagonal and rectangular shaped thiourea are presented in table 3.

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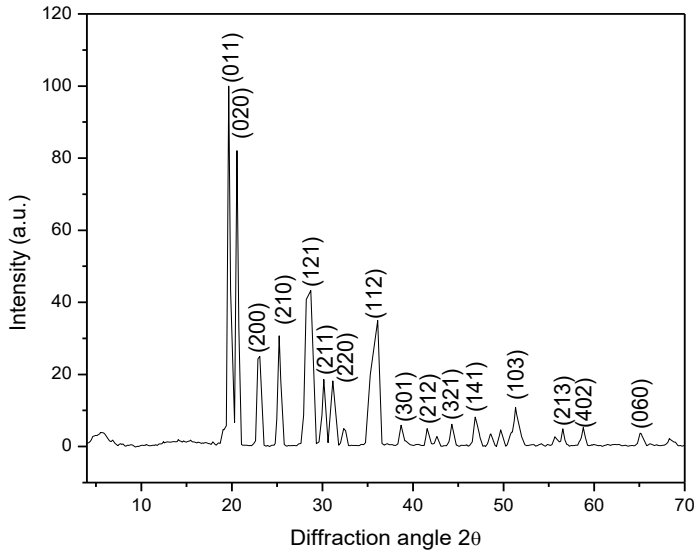

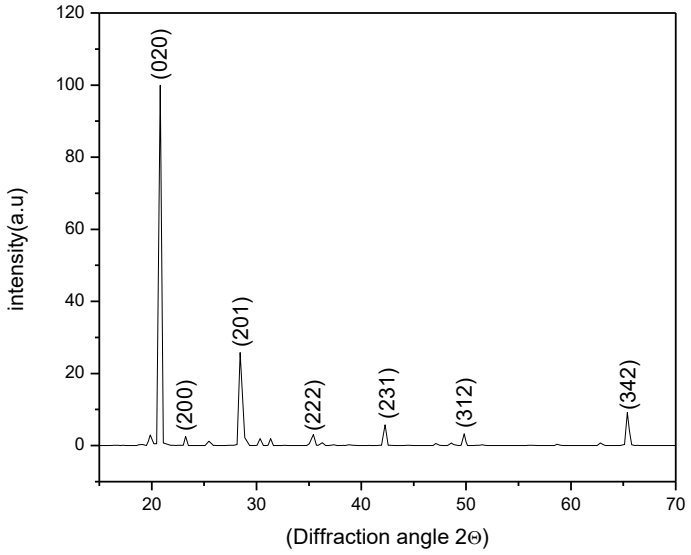

Conclusion:

The solubility of thiourea was determined for different temperatures and it has positive coefficient of solubility.

Thiourea with two distinct morphologies such as hexagonal and rectangular has been found.ICP-IES analysis confirmed that the formation of rectangular morphology is due to the influence of the higher level of concentration of impurities and may be due to the formation of complex with CU and Fe.The FTIR studies confirms the presence of functional groups present in both hexagonal and rectangular shaped thiourea.The powder X-ray diffraction analysis shows that both the samples were crystalline and the variation in relative intensities

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and the absence of many peaks in the rectangular shaped thiourea shows the incorporation of higher level of impurities in the crystal lattice.

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