AN INVESTIGATION ON THE GROWTH AND CHARACTERIZATION OF THIOUREA SINGLE CRYSTAL GROWN FROM AQUEOUS SOLUTIONS

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ABSTRACT

Thiourea single crystals have been grown from aqueous solution by slow cooling technique. The stability of the saturated solutions of different pH values has been assessed by measuring the metastable zone width (MSZW) by a nucleation method. MSZW has been enhanced by the influence of pH of thiourea solution. The growth rate of the thiourea crystal along the c-direction [001] was found faster for the higher pH value of the solution. The structural, optical and mechanical properties of the grown crystals were characterized by FT-IR spectroscopy, UV-Vis spectroscopy and powder X-ray diffraction. FT-IR and UV-Vis spectra provide information about the presence of functional groups. The Vicker's micro-hardness study has been performed on the grown crystals and the results reveal the softening nature according to Onistch concept. The growth features of the thiourea crystals were observed by etching study. A hexagonal spiral growth was observed on the [001] faces of thiourea crystals.

1. INTRODUCTION

Crystallization of organic materials for use in non-linear optical (NLO) devices is of great interest due to their high nonlinearity, high flexibility in terms of molecular structure, high optical damage threshold and low cost [(1)]. Single crystals of thiourea are being used extensively and have vast demand in the electronic industry as polarization filter, electronic light shutter, electronic modulator, optical voltmeter and as elements of electro-optic and electro-acoustic devices. 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)]. Thiourea crystals also exhibit pyroelectric effect, which is utilized in infrared (IR), ultraviolet (UV), scanning electron microscopy (SEM) detection and infrared imaging [(3)].

Pure and thiourea added potassium dihydrogen phosphate (KDP) single crystals were grown by the gel method and their lattice vibration and thermal properties were studied [(4)]. Spectroscopic and microscopic studies of thiourea single crystals were performed [(5)]. Growth of bis (thiourea) cadmium chloride (BTCC) single crystals and growth and characterization of zinc thiourea chloride (ZTC) have already been investigated [(6-7)]. In view of finding good quality thiourea crystal, in the present investigation, an attempt has been made to grow an optical quality thiourea single crystal by low temperature solutions growth technique. The effect of pH of solution on the growth rate and morphology has been discussed. In addition, FT-IR, XRD and optical transmission studies, mechanical hardness, and etching studies, etc. have been performed in details.

2. EXPERIMENTAL

2.1 Solubility of thiourea

The solubility of thiourea was determined for five different temperatures viz. 30, 35, 40, 45 and 50 °C. The measurement was performed by dissolving the Analar grade thiourea salt in double distilled water in an airtight container maintained at a constant

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temperature bath with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute was analysed gravimetrically. The solubility curves for different temperatures are shown in Fig.1.

2.2 ***Metastable zone width measurement***

A constant volume of 50 ml of thiourea salt solution was used in all the experiments. The solution was prepared at 5 K above the saturation temperature for 1 hour before cooling. It was continuously stirred using a hot magnetic plate to ensure homogeneous concentration and temperature through the entire volume of the solution. Metastable zone width (MSZW) of the thiourea was measured by polythermal method [8, 9]. Saturated solution of thourea was prepared in accordance with the presently determined solubility data for the nucleation experiments. In this method, the equilibrium saturated solution was cooled from the overheated temperature until the first visible crystal is observed. Since the time taken for the formation of the first visible crystal after the attainment of critical nucleus is very small, the first crystal observed may be taken as the critical nucleus. The MSZW width depends not only on the temperature but also on the type of the crystal and its physico-chemical properties. The temperature interval in between the solubility (equilibrium concentration) and nucleation temperature is known as the MSZW.

2.3 ***Crystallization of thiourea crystal***

The growth of thiourea single crystal was carried out from aqueous solution by slow cooling technique in a constant temperature bath with an accuracy of ± 0.1 K. 300 ml saturated solution was prepared at 45°C and then filtered to remove any insoluble impurities. The spontaneous nucleation was avoided during the filtration process. The temperature was reduced at the rate of 0.25K per day as the growth progressed. Seed crystals were prepared by an isothermal process. The saturated solutions were kept in the Petri dish and the outer face was covered by perforated transparent polythene paper or filter paper. The Petri dishes were kept at the room temperature until small transparent well-shaped crystals were obtained. It takes about 3-6 days to form good seed crystals. The growth period of single crystal takes 2–3 weeks. The grown crystals possess well defined morphology with reasonable size of about 2 x 1.5 x 0.75 cm^3 along all the three crystallographic directions. The grown crystals are shown in Fig. 2.

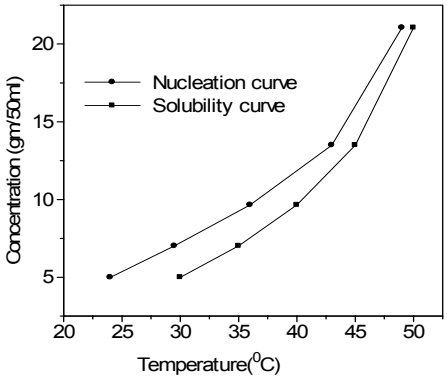

Fig. 1. Solubility and metastable zone width of thiourea.

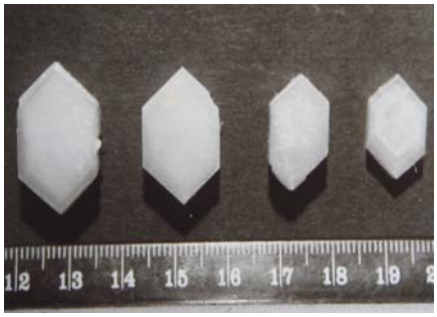

Fig.2. Photograph showing some of the grown thiourea crystals.

2.4 Influence of pH on the solubility

The growth rate of a crystal plane is a function of a set of growth parameters like temperature, the degree of super saturation of the solution, pH, concentration of impurities in solution and other physico-chemical properties [10]. In general, the following equation can be used to express the functional relation, R = F (t, s, pH, c), where R expresses the growth rate of the crystal and t, s and c express the temperature, super saturation and concentration of the impurity in the solution respectively. To study the influence of pH on the growth rate t, s and c were kept constant during the growth runs. In order to investigate the influence of pH, crystal growth experiments were carried out with pH values ranging from 3.5 to 5.0, which are shown in figure 3. The pH of the solutions was measured with a Microprocessor Bench-top pH meter (HANNA Instruments) Model No HI8417 with a resolution of ± 0.01. The electrode was calibrated using a buffer before and after each experiment. The pH, growth rate and l/w (length/width) of pure thiourea are shown in Table 1.

2.5 Mass Growth Rate

Growth rate of the grown crystals was determined by weighing method [11]. The growth rate is defined as

$$G_s = \frac{(m - m_0)}{(m_0 \Delta t)}$$

where m_o is the initial mass of the crystal (Kg), m is the final mass (Kg), and Δt is the growth time. The mass growth rate of the grown crystal at different time for slow cooling process is shown in Fig. 4.

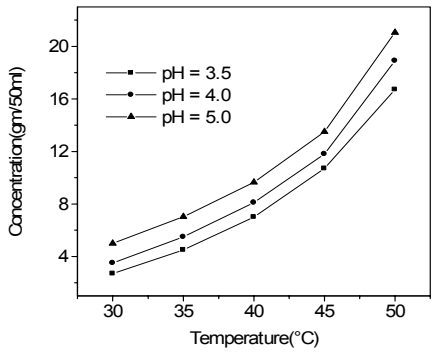

Fig. 3. Solubility of thiourea at different temperatures and pH values.

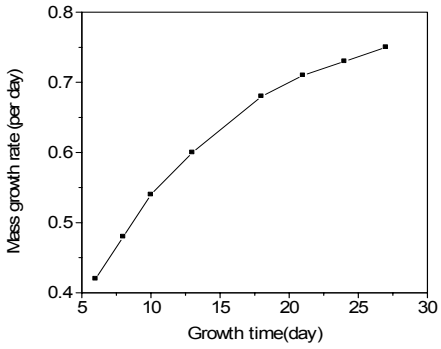

Fig.4. Variation of mass growth rate with time for thiourea grown crystal

Table. 1.
The pH, growth rate and l/w of pure thiourea

Material	pH	Growth rate (mm/day)	l/w
Thiourea	3.5	0.39	1.5
(sample 1)	4.0	0.48	2.3
"	5.0	0.66	3.2
(Sample 2)	3.5	0.36	1.5
"	4.0	0.44	1.6
"	5.0	0.59	2.2

3. RESULTS AND DISCUSSION

3.1 FT-IR spectroscopy

The Fourier transform infrared (FT-IR) spectrum of thiourea was recorded by using KBr pellet technique to identify the functional groups in determining the molecular structure of the grown crystals. The FT-IR spectrum was recorded by using Shimadzu FT-IR 8400 spectrophotometer in the region 400-4000 cm^{-1} and presented in Fig. 5. The symmetric and asymmetric C = S stretching vibrations of thiourea are observed at 729 cm^{-1}. The H_2O twisted is occurred at 488 cm^{-1}. The CH_3 asymmetrical deformation, or CH_2 bending vibration or N-C-N asymmetric stretching mode is assigned at 1466 cm^{-1}. The combination band occurred at 1389 cm^{-1}. The COH stretching mode occurred at 1092 cm^{-1} in the spectrum. The absorption band at 1589 cm^{-1} is due to NH_2 in-group deformation. The = CH valence and ≡ CH valence of thiourea are observed at 3161 cm^{-1} and 3261 cm^{-1} respectively. The ≡ CH symmetrical band is assigned at 3373 cm^{-1} in the spectrum. The symmetric NH_2 stretching is assigned to the band at 3360 cm^{-1}.

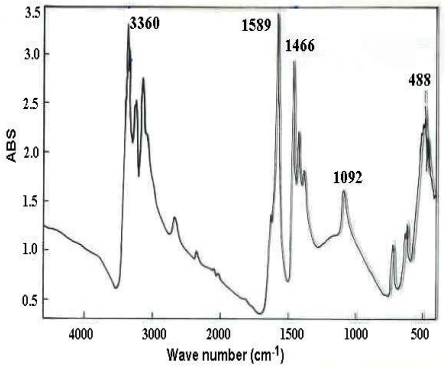

Fig. 5. FT-IR spectrum for pure thiourea single crystal.

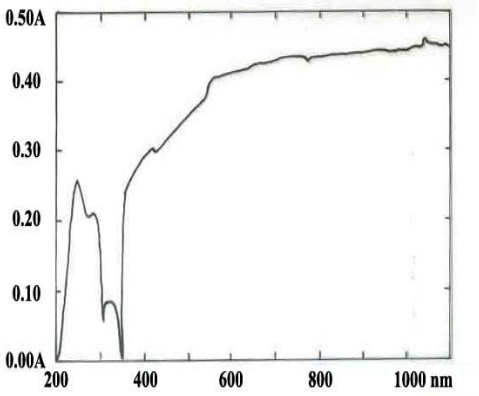

Fig.6. UV- Vis spectrum for pure thiourea single crystal

UV-VIS Spectroscopy

An optical transmission spectrum was taken at room temperature using a 2 mm thick crystal plane by Shimadzu-160 spectrometer (UV-VIS-NIR). Optical transmission spectrum gives valuable information about the structure of the molecule because the absorption of UV and visible light involves promotion of electron in σ and π orbital from the ground state to higher energy state. From device point of view, the transmission spectrum is important, as the grown crystal can be used only in the highly transparent region. The transmission is uniformly high (60%) for light in the visible region of the electromagnetic spectrum, which is useful for device application. In the present investigation UV transmittance spectrum was recorded in the wavelength range of 200-1100 nm shown in Fig.6. The peak appears in the transmission spectrum in the ultraviolet region (265 nm) may be attributed to the first over tone of N-H groups of every thiourea molecule of strongly hydrogen bonded. The transmission spectrum of thiourea crystals have been centered at 350 nm, which arrives from harmonic absorption of the N-H stretch

which cut-off at 300 nm makes the onset of electronic absorption with resonance centered on 325 nm.

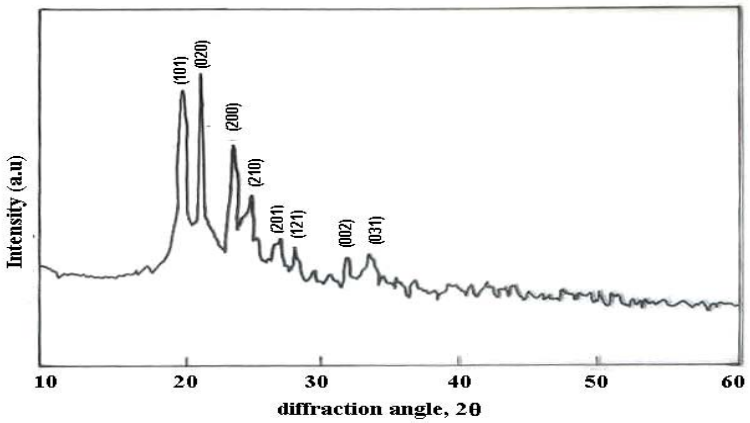

Fig.7. X-ray diffractogram for pure thiourea crystal.

X-ray Diffraction

X-ray diffraction pattern for the powder samples of grown pure thiourea crystals was carried out using Siefert XRD 3000 P, CuK_α radiation at 30 mA/ 35KV, shown in Fig. 7. The lattice parameters were determined and the values are: a = 7.466 Å, b = 8.255 Å and c = 5.342 Å and cell volume = 329.237 $Å^3$ for thiourea sample. These values are more or less same and are in good agreement with the ASTM standard values.

Micro-Hardness Test

The hardness of a material is influenced by various parameters such as lattice energy, Debye temperature, heat of formation and interatomic spacing. Micro-hardness measurement is a general microprobe technique for assessing the bond strength. Micro-hardness studies were carried out along the growth plane (001) at room temperature using a Micro hardness tester (Type M–80380, Company–Shimadzu, Japan), fitted with a diamond pyramidal indentor attached to an incident light microscope. For a static indentation test, load varying from 25 to 175 gm and the time of indentation is kept constant at 10 seconds for all trials. The diagonal lengths of indented impressions obtained at various loads were measured using a micrometer eyepiece. The Vicker's Hardness Numbers (H_v) were calculated using the formula [12]

$$H_V = \frac{1.8544P}{d^2} \quad Kg/mm^2$$

where *P* is the applied load in Kg and *d* is the average diagonal length of the indentation mark in mm. Fig. 8 shows the photographs of indentation marks on faces of thiourea crystals at different loads.

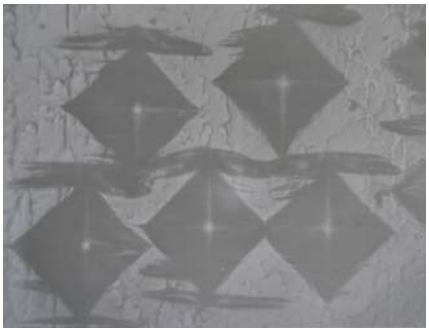

Fig.8. Photograph showing indentation mark on (001) face of thiourea crystal at different loads.

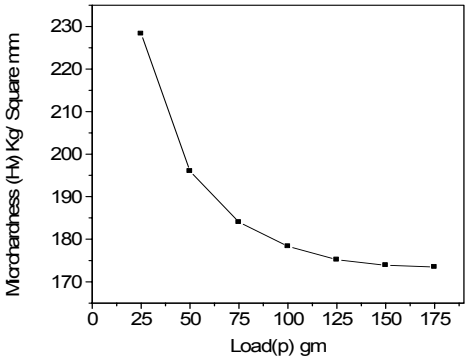

Fig. 9. Variation of H_v with load

The variations of H_v with loads are shown in Fig. 9. When indenter just touches the surface, dislocations are generated in the indenter region so micro hardness decreases initially. At lower load, there is an increase in the hardness with load, which can be attributed to the work hardening of the surface layers. Above a particular load, the micro-hardness attains nearly a constant value due to the rearrangement of dislocations and mutual interaction of dislocations. The plot of log (d) against log (P) is given in Fig. 10. The plot yields a straight line. The value of the slope (n) is found less than two, for all the samples of thiourea crystals and it is in good agreement with Onistch concept. It reveals that the Vicker's hardness decreases, indicating their softening nature.

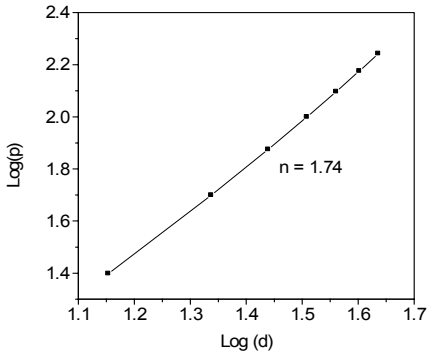

Fig.10. Variation of log (P) with log (d)

Fig.11. Photograph showing the growth features on the (001) face of thiourea single

Etching Studies

The study of identification, origin and characteristics of crystalline defects such as grain boundaries, slip planes, dislocations and plastic flow relies heavily on etching phenomena [13].

The single crystals of pure thiourea have been etched with water. The etched crystals were examined under optical microscope. Etching with water for 20 seconds resulted in the formation of pits of hexagonal shape on the (001) faces of thiourea crystals. Etched pits of layer growth are seen in Fig. 11. The size of the pits is found to increase with the time of etching.

4. CONCLUSIONS

The crystallization of thiourea and its solubility, the MSZW at various temperatures were measured. The MSZW was found to be wider at lower temperature and narrow down at higher temperature. Faster growth rates were achieved with higher pH values and yielding bigger size crystals. The grown crystals were found well faceted. FT-IR spectrum of grown thiourea crystal exhibits all the salient features reported in literature. The UV-Vis spectrum shows that it has a good optical transmittance in the entire visible region (350 to 1100 nm) and it is a potential candidate for optoelectronics application. Powder X-ray diffraction peaks obtained for single crystals were compared with the ASTM standard values. This indicates that the impurity content in the crystal is minimum. The Vicker's micro-hardness measurement satisfies the Onistch concept. The micro-hardness study revealed that the grown crystals are mechanically soft.

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