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Nucleation, Growth and structural studies of Non Linear Optical crystals - Potassium Thiourea Chloride (PTC)

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ABSTRACT

In the recent past semiorganic nonlinear optical single crystals are getting more attention due to its inherent physical and chemical properties. The title compound of potassium thiourea chloride (PTC) is one of the potential semiorganic compounds and it was synthesized by conventional chemical reactions and then grown by slow cooling technique. The lattice dimensions and crystal system was identified from the single crystal X-ray diffraction technique and found that it crystallizes in orthorhombic crystal structure. The Fourier Transform Infrared analysis confirms the presence of functional groups in the synthesized compound. Solubility measurements have been performed at different temperatures and observed that it increases with temperature. Metastable zonewidth and induction period values have been determined in order to optimize the growth parameters. The Interfacial tension values were determined from induction period measurements and found that it is comparable with the theoretical values. Bulk size single crystal of potassium thiourea chloride was successfully grown by optimizing the above said growth parameters.

Keywords: Solubility, Nucleation, X-ray diffraction, Growth from solutions, Metal-organic crystal

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INTRODUCTION

Nowadays efficient nonlinear optical materials can have a significant impact on laser technology, optical communication and optical data storage technology. The search for new frequency conversion materials primarily concentrated on organic compounds [1, 2] and many organic NLO materials with high nonlinear susceptibilities have been discovered. However, the

implementation of organic single crystal in practical device applications has been impeded by their often inadequate transparency, poor optical quality and low laser damage threshold. Hence recent search is concentrated on semi organic materials due to their large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [3, 4]. Recently metal complexes of thiourea analogs were investigated thoroughly and found that its nonlinear optical properties better than that of standard potassium dihydrogen orthophosphate (KDP). Recently, potassium thiourea chloride single crystals have been grown by slow evaporation solution growth technique and their thermal and optical properties have been reported [5]. The unit cell dimensions are a=20.4854 Å, b=20.6430 Å, c=8.5278 Å and they confirmed the tetragonal structure though there was some variation in a and b. However, to the best of our knowledge there is no growth related studies such as metastable zonewidth, induction period have been provided so far. In the present study, we have attempted the growth of potassium thiourea chloride to form a new semi organic nonlinear optical material and its crystal structure was confirmed by single crystal XRD analysis. In order to optimize the growth parameters for growing bulk size crystals, a systematic investigation has been made on the experimental determination of solubility, metastable zone width and induction period values. The interfacial energy has been estimated using the experimentally determined induction period values and compared with theoretical results. The bulk crystals of size 21mm x 19 mm x 16 mm have been grown for the first time.

MATERIALS AND METHODS

2.1 Material synthesis and solubility measurements

The commercially available raw materials of potassium chloride and thiourea have taken in the ratio of 1:4 and its purity was improved by repeated recrystallization processes. The purified salt was synthesized by dissolving it in deionized water of resistivity 18.2MΩ cm. The chemical reaction is given below:

$$KCl + 4\,[(CSNH_2)_2] \rightarrow K\,[CS\,(NH_2)_2]_4Cl$$

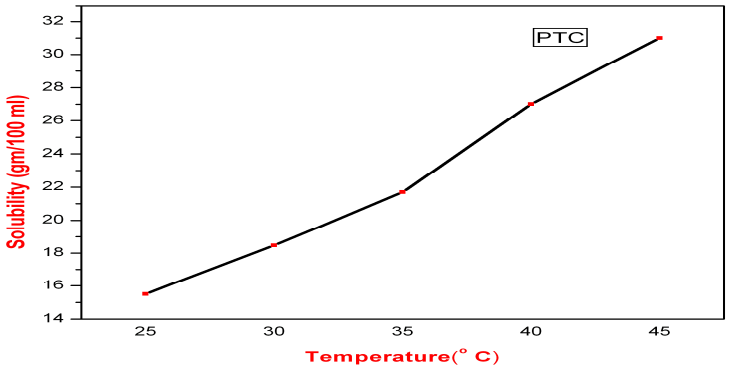

Fig.1 Temperature dependence of the solubility curve for PTC

Since thiourea has the coordinating capacity to form different phases of metal–thiourea complexes, the mixture of the reactants had to be stirred well to avoid co-precipitation of multiple phases. In solution growth technique, the size of a crystal depends on the solubility of the material. We have determined the solubility of the synthesized material in deionized water. This was performed by adding a known quantity of material into 100 ml of water maintained at a constant temperature. This process was repeated till the material is completely dissolved. Using this technique, we have evaluated solubility of PTC for various temperatures between 25°C and 45°C, in steps of 5°C and it is shown in Fig. 1.

2.2. Metastable zone width and induction period measurements

Saturated solution of PTC has been prepared in accordance with the presently determined solubility data for the nucleation experiments. The studies were carried out in a constant temperature bath controlled with an accuracy of ±0.01°C, provided with a cryostat for cooling below room temperature. A constant volume of 100 ml of salt solution was used in all the experiments. The solution was preheated to 5 °C above the saturation temperature for homogenization and left at the superheated temperature for 1 h before cooling. It was continuously stirred using a motorized stirrer to ensure homogeneous concentration and temperature through the entire volume of the solution. Metastable zone width of PTC was measured by the conventional polythermal method [6]. In this method, the equilibrium-saturated solution was cooled from overheated temperature till a first visible crystal was observed. Time taken for the formation of first visible nucleus was very short and hence it may be taken as the critical nucleus.

Induction period of saturated PTC solution at 30°C, 35°C and 40°C was determined by employing the isothermal method [7]. Normally, the time required for the growth of critical nucleus to a detectable size is very short compared to the time interval between the achievement of supersaturation and the appearance of crystal nucleus. Therefore, the total time elapsed between the achievement of supersaturation and the appearance of nucleus of detectable size can be measured as induction period (τ). In this method, the saturated solution was cooled to desired temperature and maintained at that temperature. The time taken for the first observed crystal was measured. Experiments were repeated several times to obtain the optimized values.

2.3. Interfacial tension

Interfacial tension of the crystal–solution interface is an important parameter involved in the theory of nucleation and growth kinetics. The classical homogeneous nucleation theory has been successfully tested for the nucleation of liquid solution and for crystal formation in melts [8]. In the present investigation, interfacial tension has been calculated using the experimentally determined induction period values by the following relation on the basis of classical theory for homogeneous formation of spherical nuclei [9]

$$\ln \tau = \ln B + \frac{16\pi\gamma^3 \mathrm{v}^2 N_A}{3R^3T^3(\ln S)^2} \qquad (1)$$

Where B is a constant, γ is the interfacial tension, v is the molar volume of the crystals, NA is the Avogadro's number, R is the universal gas constant and S is the supersaturation ratio. τ is the

induction period of PTC solution at temperature T and the supersaturation ratio S. B is a constant. A plot of 1/(ln S)2 against ln τ is a straight line. The intercept of straight line on the y-axis gives the value of ln B. The equation suggests a straight line fit for ln τ against 1/ (ln S)2 with a slope given by

$$m = \frac{16\pi\gamma^3 \mathrm{v}^2 N_A}{3R^3T^3} \qquad (2)$$

Since ln B weakly depends on the temperature

$$\gamma^3 = \frac{3R^3T^3m}{16\pi \mathrm{v}^2 N_A} \qquad (3)$$

where m is the slope of the straight line.

Several empirical expressions for the interfacial tension using physico-chemical data have been reported in literature. Bennema et al. [10] proposed a relation between interfacial tension and solubility as

$$\gamma = \frac{kT}{a_0^2}\{0.173 - 0.248 \ln X_m\} \qquad (4)$$

where X_m is the molefraction and a_o is the interionic distance
Sangwal [11] reported the relation between the surface tension and molefraction of the solute as

$$\gamma = kT\frac{\{3 - \ln X_m\}}{8d^2} \qquad (5)$$

where d is the mean diameter of ions.

The interfacial tension values are estimated in the present study by using the experimentally determined induction period values and have been compared with the above theoretical values.

Fig.2 As grown crystal of PTC

2.4 Bulk growth of PTC

The purified raw material of PTC was dissolved in deionized water in accordance with solubility data. The bulk crystal growth of PTC was carried out by slow cooling technique, in a constant temperature bath with an accuracy of ±0.01º C. An amount of 400 ml of the solution was saturated at 40ºC and the solution was maintained at 40ºC for two days before seeding. The seed crystal with well defined morphology was suspended in the solution. The temperature reduction was at the rate of 0.02º C per day as growth progressed. After 35 days a good quality single crystal size 21mm x 19 mm x 16 mm was harvested (Fig. 2) at 37.22º C.

RESULTS AND DISCUSSION

The grown PTC single crystal was subjected to single crystal X-ray analysis. The unit cell dimensions determined are a = 5.503 Å, b = 7.651 Å, c = 8.530 Å and V = 359.1 Å3 and α = β = γ = 90˚ which confirms that PTC crystallizes in orthorhombic structure. The morphology of the grown crystal is shown in Fig. 3. The FTIR shows (Fig. 4) the presence of all functional groups in PTC. The study of the spectra of PTC shows a shift in frequency band in the low frequency region. The broad envelope positioned between 2682 and 3380 cm^{-1} corresponds to the symmetric and asymmetric stretching modes of NH2 grouping of thiourea. The bonds of thiourea were not shifted to lower frequencies on the formation of the potassium thiourea complex. Comparison of the vibration of thiourea and PTC is shown in Table 1.

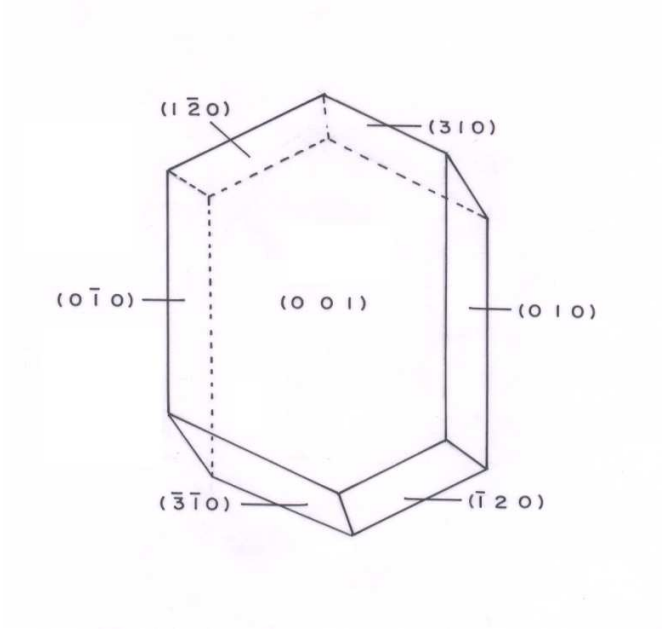

Fig.3 Typical morphology of PTC

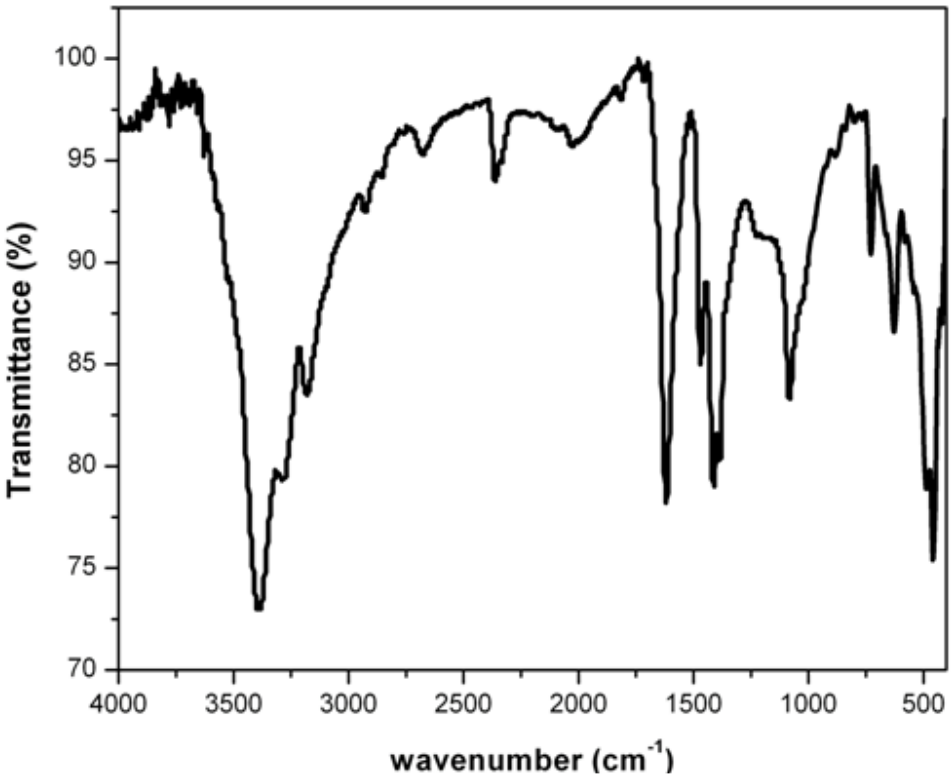

Fig.4 FTIR spectra of PTC

Table 1 Comparison of the vibration of thiourea and PTC

Wavenumbers (cm^{-1})		Assignments
Thiourea	PTC	
1625	1619	NH2 bending
1470	1468	N–C–N stretching
1417	1413	C=S stretching
1083	1083	N–C–N stretching
730	729	C=S stretching

The metastable zone width of PTC as a function of temperature is shown in Fig. 5 and it is seen that the metastable zone width becomes narrower with increasing solute concentration. Fig.6 shows the induction period as a function of supersaturation ratios for various temperatures. Interfacial tension is an important parameter in the nucleation studies. The interfacial tension has been calculated at various constant temperatures from the graph drawn between ln τ and $1/(\ln S)^2$ (Fig. 7).Using the interfacial tension value, the radius of critical nucleus, the Gibbs free energy for the formation of the critical nucleus (ΔG*), number of molecules in the critical nucleus (i*) can be calculate. The measured interfacial tension varies from 2.10 to 2.54 mJm^{-2}. The numerical values of solubility, metastable zone width and interfacial tension for different temperatures are given in Table 2.

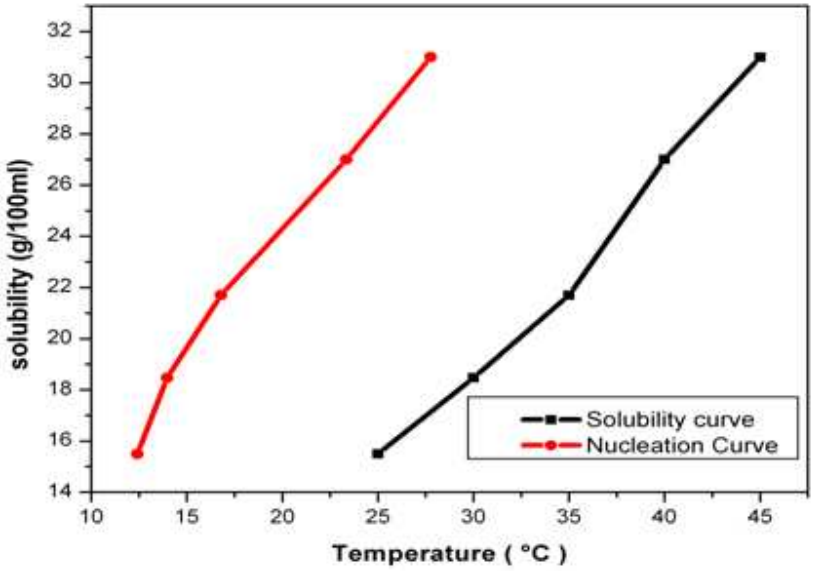

Fig.5 Metastable zonewidth of PTC solution

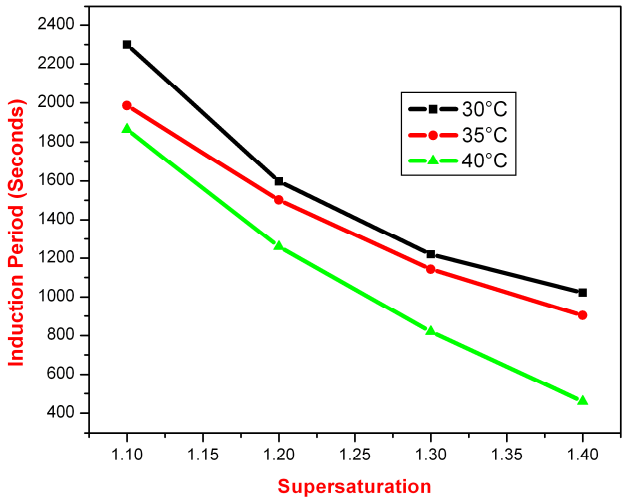

Fig.6 Induction period measured at different super saturation conditions for the PTC solution

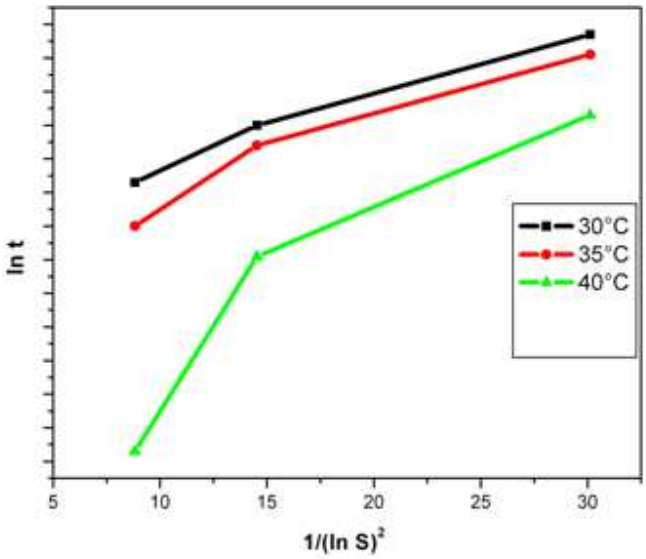

Fig.7 Relation between ln τ and 1/(ln S)^2

Table 2 Nucleation parameters of PTC

Temperature (°C)	Solubility g/100ml	Metastable zonewidth (°C) ΔTc	Interfacial tension (m J /m^2)		
			Theoretical results		Present work [experimental values]
			Bennema et al.[10]	Sangwal [11]	
30	18.47	16.03	1.233	2.927	2.1086
35	21.70	18.21	1.254	2.975	2.1562
40	27.01	16.65	1.274	3.024	2.5420

CONCLUSION

Fundamental growth parameters have been carried out for crystallization of PTC from aqueous solution. The solubility of PTC in aqueous solution has been estimated for different temperatures. The metastable zone width and induction period have been experimentally determined. Experimentally determined interfacial tensions are in good agreement with the theoretical results of Bennema et al and Sangwal. The experimental result shows that the induction period values decrease with increase in temperature. The interfacial tension varies from 2.10 to 2.54 mJm^{-2}. PTC single crystals have been grown by slow cooling technique for the first time. Bulk crystals of size 21 x 19 x 16 mm3 have been grown by optimized growth conditions. The single crystal X-ray diffraction study reveals that the potassium thiourea chloride crystal crystallizes in orthorhombic structure and it is not getting hygroscopic in ambient atmosphere.

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