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Experimental Determination of Metastable Zone Width, Induction Period, Interfacial Energy, Growth and SHG Efficiency of N-[(propan-2-ylidene) amino] Thiourea

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ABSTRACT

N-[(propan-2-ylidene) amino] thiourea an organic crystal which is grown by solution growth technique by adopting slow evaporation method from the solvent methanol.Nucleation parameters such as metastable zone width, induction period and interfacial energy have been determined for N-[(propan-2-ylidene) amino] thiourea single crystals. The induction period was measured at various super saturations and hence the interfacial energies were evaluated. Using the interfacial tension value, the nucleation parameters such as radius of the critical nuclei(r*), the Gibbs free energy for the formation of a critical nucleus (ΔG*) and the number of molecules in the critical nucleus (i*) were also calculated for methanol at two different temperatures. The effect of surface tension, viscosity and density of these solvents are correlated with interfacial tension. FT-IR studies confirm the structure and presence of functional groups in the grown crystals. The optical transparency was examined by UV-Spectral analysis. The grown crystal was examined by X-ray diffraction to determine its crystalline nature. Second harmonic generation efficiency of the powdered N-[(propan-2-ylidene) amino] thioureawas tested using Nd:YAG laser and it is found to be 1.8 times that of potassium dihydrogen phosphate.

Keywords: Nucleation, induction period, Solubility, SHG efficiency

I. INTRODUCTION

In recent days the field of opto electronics, optic communication have experienced tremendous advancements. The research on new organic nonlinear optical materials has attracted more research groups to them for their advantages over the inorganic nonlinear optical materials. The organic nonlinear optical molecules are widely used in many applications such as optical communication, information storage, and optical switching [1-5]. In recent days organic molecular crystals are direct imparting attention due to large optical property, bulk in size, hard and stable. Due to these properties, these crystals are needed in many electronic devices like colour displays and optical memories. From this background, it is needed to search organic crystals with optical property. Generally, recent researches have mentioned that organic crystals are bulk in size, hard, stable, and large Nonlinear optical susceptibilities compared to the inorganic crystals but they have poor mechanical properties. Considering all these parameters the modern scientists have concentrated on the growth of organic crystals. In addition thiosemicarbazone molecules containing π-electron conjugation system asymmetrized by the electron donor and acceptor groups are highly polarizable entities for NLO applications. Hence the N-[(propan-2-ylidene) amino] thiourea is the one of the potential organic optical materials.

Which belongs to the carbonyl group of compounds .The Ketone group is asymmetrical (Chiral carbon). Therefore in the present studieswe report on the induction period, nucleation parameters and SHG efficiency of organic optical N-[(propan-2-ylidene) amino] thioureacrystals by slow evaporation solution growth technique (SESGT) [6-16]. Metastable zone width is an essential parameter for the growth of good crystals from solution. Because it is the direct measure of the stability of the solution in its saturated region. The

growth and the metastable zone width of N-[(propan-2-ylidene) amino] thioureain methanol, as solvent were determined. The harvested crystals were subjected to FT-IR, UV studies. The nucleation parameters for solution grown N-[(propan-2-ylidene) amino] thioureawere determined using the interfacial tension and reported for the first time.

II. METHODS AND MATERIAL

An organic crystal of N-[(propan-2-ylidene) amino] thiourea was prepared by adopting the standard procedure [6-10]. To a hot solution of thiosemicarbazone in methanol, a solution of acetone in methanol was added drop wise for 30 minutes. The mixture was stirred and refluxed for four hours. Then it was filtered and the filtrate was concentrated to half the volume. Then the filtrate allowed for slow evaporation at room temperature, crystals were collected by filtration, washed with cold ethanol and dried the crystals in vacuo. The harvested crystals are shown in Fig.1.

Figure 1: Photograph of N-[(propan-2-ylidene) amino] thiourea.

III. RESULTS AND DISCUSSION

A . FT-IR Spectral Analysis

The Infrared spectral analysis has been carried out to understand the chemical bonding and it provides useful information regarding the molecular structure of the compound. The purified form of N-[(propan-2-ylidene) amino] thioureawas subjected to Fourier Transform Infra-Red Spectroscopy analysis for the analysis of functional groups present in grown crystal and the spectra were recorded using KBr pellettechnique between 400cm-1 and 4000cm-1.The recorded FT-IR spectrum of N-[(propan-2-ylidene) amino] thiourea is shown in fig.2.The sharp peak at 3377cm-1 shows C-H stretching of alkynes [11-16].The peak at 1512cm-1shows corresponding imine group (C=N) which confirm the bond between ketone and Hydrazide is imine group. The peak below 1500cm-1 indicates C=N and N-N stretching vibration. And also the peak at 1466 cm-1 and 1429cm-1 shows two CH3 deforms. The C=S stretching of thiosemicarbazide moiety is observed at 1161cm-1. The absence of band at 2720cm-1 indicates the absence of ketone function.

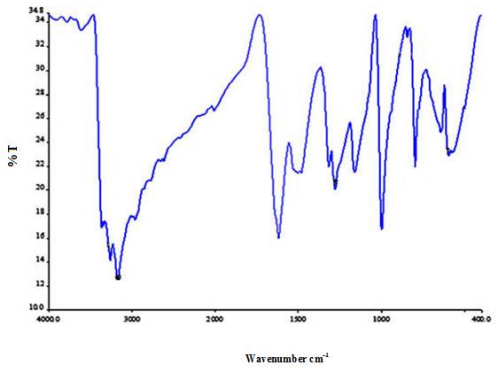

Figure 2 : FT-IR Spectrum of N-[(propan-2-ylidene) amino] thiourea

B. UV-Visible spectral studies

UV-Visible spectral analysis gives useful information about electronic transitions in the compound [17].The grown crystals were subjected to UV-Visible spectral analysis for studying the optical properties and transparency of a substance. The UV-visible spectrum of N-[(propan-2-ylidene) amino] thiourea crystal was recorded using Lambda 25 spectrometer is shown in figure 3.In the spectrum the characteristic absorption of N-[(propan-2-ylidene) amino] thiourea crystal is found at 267.61nm and there is no absorbance between 325 and 800 nm. The recorded UV spectrum proves the highly transparent nature of the material between 325-800nm [18, 19].This confirms the characteristic property of N-[(propan-2-ylidene) amino] thiourea, which is suitable for optical applications.

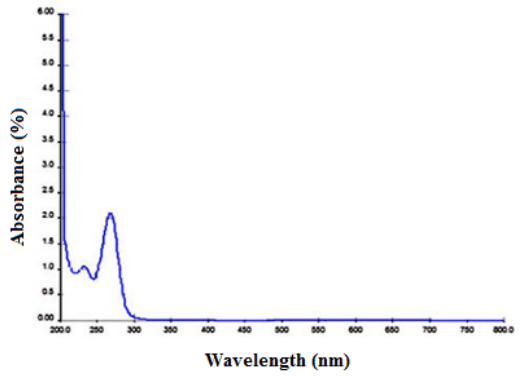

Figure 3 : UV-Visible spectrum of N-[(propan-2-ylidene) amino] thiourea.

C. **X-ray diffraction studies**

The grown organic crystal of N-[(propan-2-ylidene) amino] thiourea was recorded using Bruker D8 ADVANCE POWDER diffractometer with Cu Kα radiation (α=1.5418A) the sample was scanned at a rate of 1o/min in the range of 10-70o. The crystalline nature and purity of the grown crystals usually determined with the knowledge of X-ray diffraction studies [20-23]. The Crystalline nature of the grown crystal is confirmed by the diffraction pattern shown in figure 4. The obtained values are in good agreement with the standard values, which confirm the purity of the grown crystal and its application related properties.

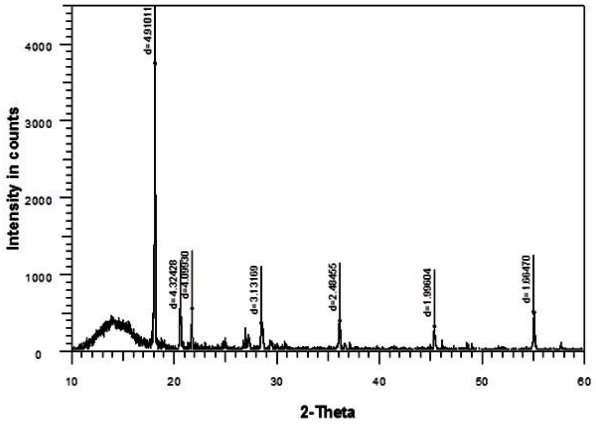

Figure 4 : X-ray diffraction pattern of N-[(propan-2-ylidene) amino] thiourea.

D. Determination of solubility and metastable zone width

Metastable zone width is an important parameter for the growth of good crystals from slow evaporation solution growth technique. It is very useful direct measure of the stability of the solution in the supersaturated region [24-28].The metastable zonewidth of N-[(propan-2-ylidene) amino] thioureamethanol was determined. Saturated solution of N-[(propan-2-ylidene) amino] thioureain these solvent ratio at different temperatures were allowed fo systematic slow cooling.The temperature at which the first nucleation was observed which corresponding to their width of the metastable zones. The metastable zonewidth of N-[(propan-2-ylidene) amino] thiourea in methanol shown in figure.5.Blue line indicates metastable zone width and red line indicates solubility.

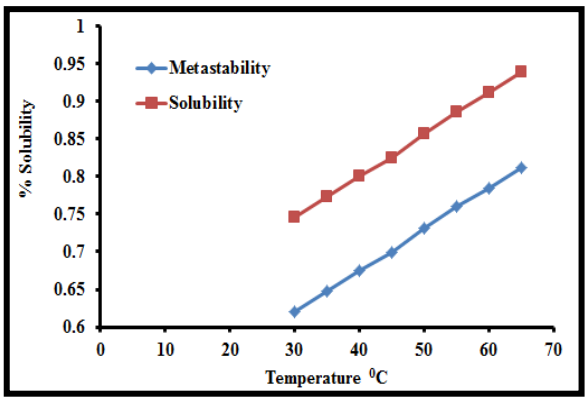

Figure 5 : Solubility and metastability of N-[(propan-2-ylidene) amino] thiourea in methanol

Table.1. Solubility and metastability of N-[(propan-2-ylidene) amino] thiourea in methanol

Temperature ^{0}C	Metastability	Solubility
30	0.6204	0.746
35	0.6473	0.7729
40	0.6754	0.801
45	0.6995	0.8251
50	0.7306	0.8562
55	0.7604	0.886
60	0.785	0.9106
65	0.8124	0.938

E. Experimental determination of Induction period and Interfacial energies and nucleation parameters

There are several methods of measuring the induction period depending upon the solubility of the materials. Here the visual observation method was followed. Solutions of N-[(propan-2-ylidene) amino] thiourea in methanol at different supersaturation values were

prepared and subjected to systematic slow evaporation. The time period that elapses between the achievement of supersaturation and appearance of visual nuclei is taken as the induction period (t). Several trial runs were performed to minimize the error. Experiments were repeated for supersaturation (s) like 1.15, 1.17, 1.20 and 1.25at two different temperatures. From the results obtained a plot of lnt against 1/(lns)2 is drawn and is shown in figure.6.The interfacial tension was calculated from the slope of the curves using the equation

$\ln t = \ln A + 16\pi r^3 V^2 N / 3RT(\ln s)^2$

Where A is a constant related to the pre-exponential factor of the nucleation rate expression. V is the molar volume, N is the Avogadro number and R is the gas constant. The factor $16\pi r^3$ in the above equation refers to the spherical nuclei [29-31]. The interfacial tension between the N-[(propan-2-ylidene) amino] thiourea and methanol is calculated by measuring the slope value of the curve obtained at the two temperatures. The effect of solvent and temperature on interfacial tension is presented in Table.2.

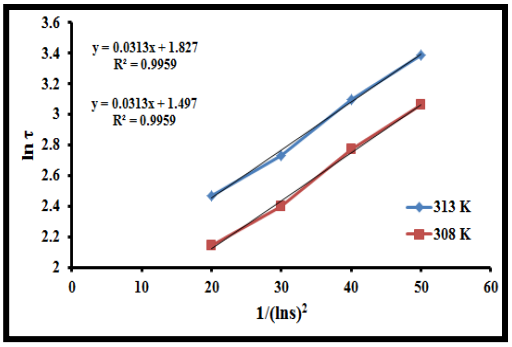

Figure 6 : A plot of ln τ Vs1/ $(\ln s)^2$ for N-[(propan-2-ylidene) amino] thiourea grown from methanol at 308 and 313K.

Table.2. Effect of temperature and solvent on interfacial tension.

Solvent	Temperature/K	Slope value	Interfacial tension/mJ/m^2 × 10^{-13}
Methanol	308	0.267	1.84
	313	0.027	1.97

Using the interfacial tension value. The radius, of the critical nuclei(r*), the Gibbs free energy change for the formation of a critical nucleus (ΔG^*) and the number of molecules (i*) were calculated at different temperature for N-[(propan-2-ylidene) amino] thioureain methanol and presented in Table.3.

It was noted that with the increase in super saturation, the Gibbs free energy change for the formation of a critical nucleus (ΔG^*) decreases with radius(r*).This favours the easy formation of nucleation in methanol at higher super saturations.

Table 3. Nucleation parameters of N-[(propan-2-ylidene) amino] thiourea crystal in methanol.

Super turation tio S=C/C*	308 K			313 K		
	r*/m X 10^{12}	△G* X 10^{12}	i* X 10^{38}	r*/m X 10^{12}	△G* X 10^{12}	i* X 10^{38}
1.15	7.027	4.567	2.906	7.383	5.384	3.370
1.17	6.285	3.654	2.079	6.604	4.307	2.412
1.20	5.443	2.740	1.350	5.719	3.230	1.566
1.25	4.444	1.827	0.735	4.669	2.153	0.853

The surface tension of the solvent methanol is in increasing order with decreasing concentration. The effect of surface tension on interfacial tension is given in Table .4.The interfacial tension between the methanol is also in decrease ng order. The effect of viscosity of solvents on interfacial tension is given in Table.5.As viscosity increases the interfacial tension decreases.The effect of density of solvents on interfacial tension is presented in Table.6. As density increases the interfacial tension decreases.

Table.4. Effect of surface tension of solvents on interfacial tension.

Solvent	Viscosity, m.pa.s	Interfacial tension at 35^{0}C /mJ/m^2 ×10^{-13}
Methanol	0.544	1.8525

Table 5. Effect of viscosity of solvents on interfacial tension

Solvent	Viscosity, m.pa.s	Interfacial tension at 35^{0}C /mJ/m^2 ×10^{-13}
Methanol	0.544	1.8525

Table 6 : Effect of density of solvents on interfacial tension

Solvent	Density,Kg/ l	Interfacial tension at 35^{0}C /mJ/m^2 ×10^{-13}
Methanol	0.7893	1.8525

The metastable zone width can also be correlated with interfacial tension. As the metastable zone width increases. The interfacial tension decreases. This work gives the general idea of systematic study of the correlation of the important parameters of the crystal growth and thereby suitable designing of growth conditions of the crystals of required specificity.

F. Nonlinear Optical Studies

The second harmonic generation efficiency of N-[(propan-2-ylidene) amino] thiourea crystal was measured by using Kurtz-Perry powder SHG technique [32] with potassium dihydrogen phosphate (KDP) crystal as reference material. The grown crystal was powdered with a uniform particle size and packed in a micro capillary of uniform bore and was illuminated using spectra physics quanta ray DHS2.Nd:YAG laser is used to test second harmonic generation (SHG) of grown crystal, The SHG efficiency obtained for N-[(propan-2-ylidene) amino] thiourea is about 1.8 times higher than that of potassium dihydrogen orthophosphate crystal.

IV. CONCLUSION

The metastable zonewidth of methanol were determined for the first time it was found that the metastable zone width dependence on solvent concentrations. The effect of temperature and solvent on interfacial tension was determined using the interfacial tension value the nucleation parameters such as radius of the critical nuclei (r*), the Gibbs free energy for the formation of a critical nucleus (ΔG*) and the number of molecules in the critical nucleus(i*) were also calculated for various concentration of solvent at two different temperatures. The effect of surface tension, viscosity and density of these solvents are correlated with interfacial tension optically good grade of an organic N-[(propan-2-ylidene) amino] thiourea crystal were successfully grown using slow evaporation solution growth technique, using acetone and thiosemicarbazide using methanol as a solvent. The methanol grown crystals are good quality. The FT-IR spectral report confirms the purity and functional group of the crystal. The UV-Visible spectrum proves the transparent nature of the crystal between 325-800nm.The grown crystal of N-[(propan-2-ylidene) amino] thiourea was confirmed by X-ray diffraction analysis. The optical transparency and crystalline nature of N-[(propan-2-ylidene) amino] thiourea confirm its various applications.

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