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Growth and Characterization of L-Glutamic Acid Thiourea Crystal for NLO Applications

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Abstract

The L-Glutamic acid doped thiourea single crystals were grown successfully by slow-evaporation technique. The structure and morphology identified through XRD analysis. The functional group and cut-off wavelength are performed thorough FTIR and UV-Visible spectroscopical analysis. The non-linear behavior analysed with second harmonic generation set up. The thermal stability of the growned crystal studied with thermo-gravimetric analysis(TGA), differential thermo-gravimetric analysis(DTA). The 1hysic-mechanical nature of crystal also studied.

Keywords: L- Glutamic acid; Crystal; NLO, XRD, FTIR

1. Introduction

In recent years, the need of non-linear optical crystals [1] in many areas, electronic components, physics, microelectronic devices, smart devices and etc., [2,3]. High efficiency, optical quality based non-linear optical materials with dopant to polarize the organic molecules. The property of semi organics helps charge transfer, larger polarization, enhancing charge density and susceptibilities [4-6]. The semi-organic coordination complexes can also enhancing the physic-chemical stability with the breaking up of the centro-symmetry of the ligand in the crystal and an increase in NLO intensity [7]. Organic crystals were used for frequency doubling and tripling of laser systems, switching optical devices, acoustic-optical devices [8-11]. Semi organic crystals, which have larger non linearity, high resistance, low angular sensitivity and good mechanical hardness [12, 13]. In the present study, an investigation was made on the solubility and metastable zone width for pure and L-Glutamic acid doped thiourea saturated solutions. The results of the investigations form a basis for the growth of bulk thiourea crystals. The effect of seed of different orientations on the habit of c and the change of morphology while doping with amino acids has also been investigated.

2. Sample Preparation

The crystals are synthesized by dissolving thiourea with L- Glutamic acid in triple distilled water. Typical growth conditions involve temperature stabilization to about ±0.05°C and rates of evaporation of a few mm^3/hr. The evaporation techniques of crystal growth have the advantage that the crystals grow at a fixed temperature. A 100 ml glass beaker was used as nucleation cell. The nucleation cell was placed in a cryostat and the temperature was thermostatically controlled to a controlled to an accuracy of ± 0.05° C- The solutions were stirred by means of a motor. Aqueous solutions of pure and doped thiourea were prepared by dissolving the required amount of thiourea salt in 100 ml of water at a temperature slightly higher than their respective saturation temperatures. The solution was continuously stirred for at least 24 hours before use.

3. Characterization

Powder X-ray diffraction studies were carried out for the as grown crystals using a Rich Seifert X-ray diffractometer with CuK_α (λ = 1.5405 Å) radiation (Kurtz 1968). The FT-IR spectra of pure and L-Glutamic acid thiourea crystals on a Bruker IFS 66V model spectrophotometer using 1064 nm output of a cw diode pumped Nd: YAG laser as a source of excitation in the region 450 – 4000 cm^{-1} operating at 200 mW powers at the samples with a spectral resolution of 2 cm^{-1}. The transmission spectra were taken at room temperature using Varian Cary 2300 Spectrometer (UV-VIS-NIR). The transmission spectra were recorded in the range 200-1200 nm. Microhardness measurements were carried out using Leitz Weitzler hardness tester fitted with a diamond indenter and the Non-Linear Optical effect can be studied by Kurtz and Perry method.

4. Results and discussion

Powder X-ray diffraction spectra of the grown crystals from pure and L-Glutamic acid doped thiourea are shown in Figure 1. Powder XRD spectra for the pure and Glutamic acid doped Thiourea revealed that the structures of the doped crystals were slightly distorted compared to the pure thiourea crystal. This may be attributed to strain on the lattice by the absorption or substitution of dye. It is observed that the reflection lines of the doped dye crystal correlate well with those observed in the individual parent compound with a slight shift in the Bragg angle. The doping of crystals affects the growth rate and morphology. In the case of L-Glutamic acid doped thiourea crystal the growth rate in the [101] direction was restrained, leading to a wide (101) plane; the crystal was thinner than pure thiourea. While doping with L-Glutamic acid the growth rate along (010), (001) and (100) were less compared to that of pure thiourea crystal [2, 14, 15].

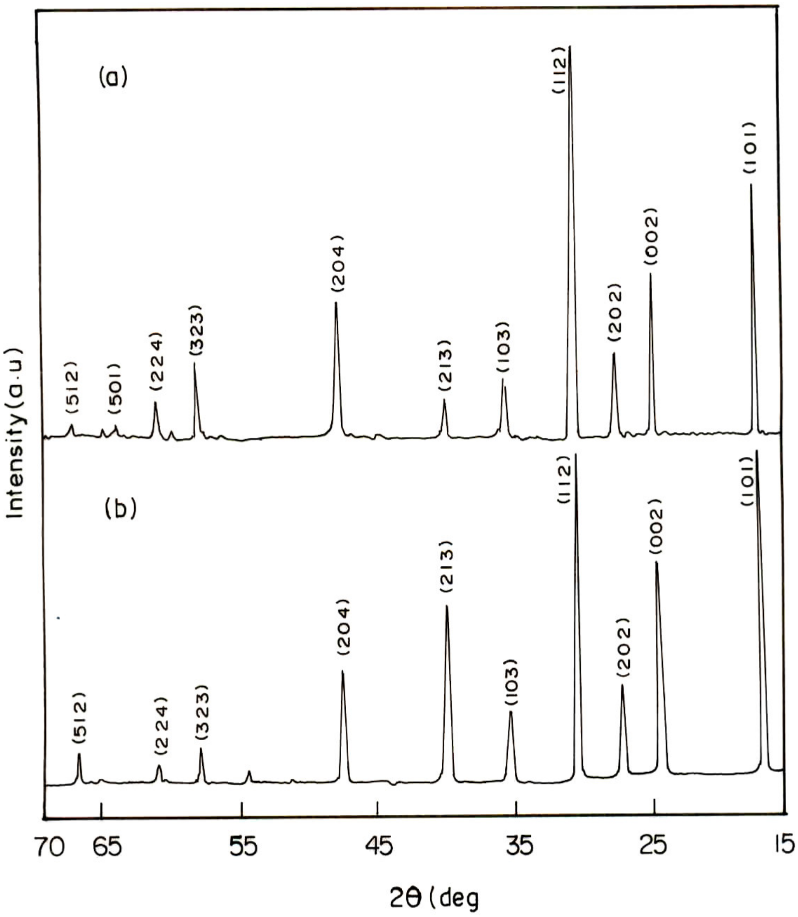

Figure.1. XRD Spectra of (a) pure and (b) Glutamic acid doped Thiourea crystal

The observed FT-IR spectra of pure and doped thiourea are shown in Figure 3.5.

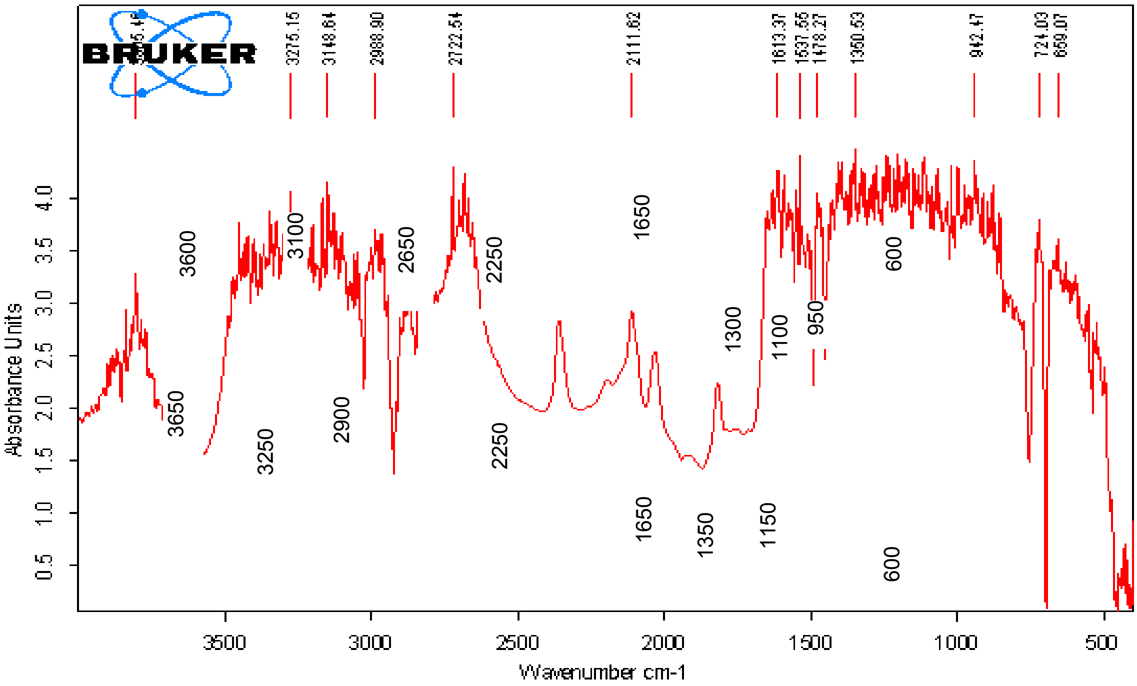

Figure.2. FT-IR spectrum of L-Glutamic acid doped Thiourea crystal

In doped thiourea spectra, broad peak around 3650 cm^{-1} was due to free –OH stretching vibration. It reveals that at least one of the –OH group of thiourea was remain unaltered after that doped with thiourea. Due to the greater mass of sulpher in TGS the C=S stretching vibration was expected to occur at 625 cm-1, it was considerably lower frequency that the usual C=O stretching vibration at 1710 cm^{-1} because of the C=N group is less polar than the C=O group and has a considerably weaker bond [16, 17].

The strong vibrational coupling was operative in the case of nitrogen containing thiocarbonyl group of thiourea and that the C=S vibration was not located in the spectra. The comparison of FT-IR studies on pure and amino acid doped thiourea crystals are shown in Figure.2.

Calculated frequency (cm^{-1})	Pure Thiourea	L-Glutamic acid doped Thiourea	Assignments
3615	3600(w)	3650(w)	Free O-H stretching
3200	-	3250(vw)	N-H asymmetric stretching
3100	3100(br)	-	Intramolecular H-bonded O-H stretching
2900	-	2900(br)	N-H symmetric stretching in NH_2 group
2650	2650(br)	-	O = P – OH asymmetric stretching of KDP
2250	2250(w)	2250(br)	P-O-H asymmetric stretching
1600	1650(br)	1650(vs)	O = P – OH symmetric stretching of KDP
1350	1300(sh)	1350(vs)	P=O symmetric stretching (aliphatic)
1150	1100(sh)	1150(vs)	P-O-H symmetric stretching
975	950(s)	-	O = P – OH bending
625	600(sh)	600(sh)	HO – P – OH bending

Table.1. FT-IR Assignments of pure and dye doped TGS crystals

The transmission spectra for 1 mm thick c-cut plates of pure and doped thiourea was shown in Figure.3.

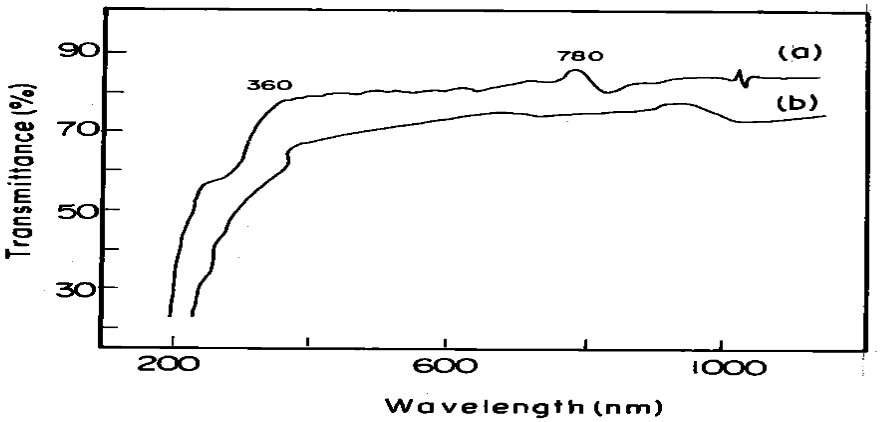

Figure. 3. UV-Visible spectra of (a) L-Glutamic acid doped Thiourea and (b) pure Thiourea Crystal

All the crystals irrespective of the dopants are transparent in the entire visible region. The UV-Visible spectrum of L-Glutamic doped thiourea crystal, maximum wavelength of absorption (λ_{max}) appeared at 780 cm^{-1}. Therefore, it reveals that after incorporation of dye, the UV absorption was shifted to Red region. The Bathochromic shift (Red shift) increases in accordance of mole fractions of dopants. The pure thiourea crystal has about 70% of transmission. The L-Glutamic acid doped Thiourea crystal is invariably has higher transmission percentage compared to pure thiourea crystal. From the UV-Visible spectrum, transmission percentage increases due to addition of doped in Thiourea crystal, which would enhances the optical property of Thiourea crystal [18, 19].

The well-polished doped thiourea crystal was placed on the platform of the Vickers micro hardness tester and the loads of different magnitudes were applied over a tester at a fixed interval of time. The indentation time was kept as 8 sec for all the loads. The microhardness value was calculated using the relation $H_v = 1.8544 \times P/d^2$ kg/mm^2, where P is the applied load in kg and d is the diagonal length of the indentation impression in mm. L-Glutamic acid doping in thiourea improves the mechanical strength of thiourea microhardness value of pure and amino acid doped thiourea are tabulated in Table 3.2.

S.No	Crystal	Microhardness (kg/mm^2)
1.	Thiourea	145.79
2.	L-Glutamic doped Thiourea Crystals	155.56

Table.2. Microhardness values of doped Thiourea crystals

Figure.4. illustrates the Differential Thermal Analysis (DTA) and Thermo-Gravimetric Analysis (TGA) curves for the grown amino acid doped thiourea crystal. The DTA curve implies that the material undergoes an irreversible endothermic transition at 200°C where the melting begins. This peak was endothermic peak, represents the temperature at which the melting terminates which corresponds to its melting point at 210°C.

Ideally, the melting point of the trace corresponds to a vertical line. The sharpness of the endothermic peak shows good degree of crystallinity of the grown ingot. The exothermic peak at 290°C indicates a phase change from liquid to vapour state as evident from the loss of weight of about 87% in TG curve [20, 21].

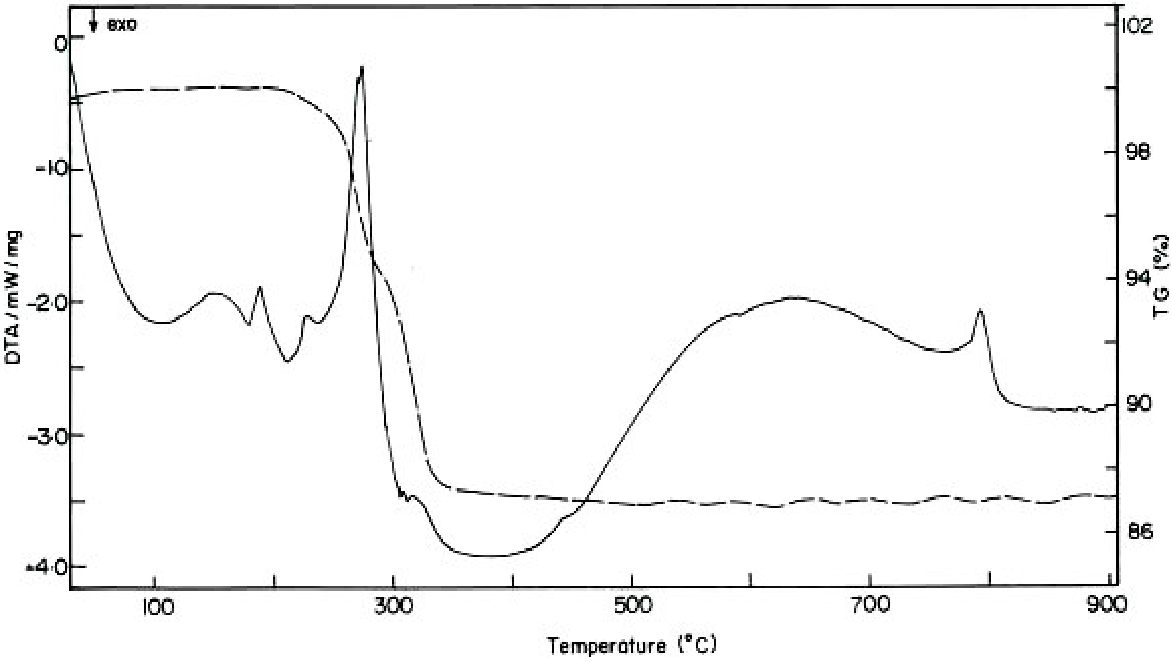

Figure.4. TGA-DTA curves of L-Glutamic acid doped Thiourea Crystal

The efficiency of doped thiourea crystals were compared with pure thiourea and also show that dye doped thiourea crystal has higher efficiency. A sample of thiourea, also powdered was used for the same experiment as a reference material in the SHG measurement. It was found that the frequency doubling efficiency of the doped thiourea was better than KDP. From the Table.3, shown the SHG efficiency of thiourea crystal with L-Glutamic doped thiourea crystal has larger compared to KDP crystal [22].

S.No.	Compound	SHG efficiency
1.	KDP	1.00
2.	L-Glutamic acid doped thiourea	1.68

Table.3. Comparison of SHG of pure and L-Glutamic acid doped thiourea crytstals.

5. Conclusions

Good optical quality single crystals of L-Glutamic acid doped thiourea have been grown from solution by slow solvent evaporation technique. The crystallinity of the grown sample was confirmed by single crystal X-ray diffraction analysis. The functional groups present in the grown crystals have been confirmed by FT-IR spectral analysis. The observed frequencies were assigned on the basis of symmetry operation on the molecule and normal coordinate analysis.

Thermal stability of the grown sample was studied by TG and DTA analysis. The results from TG and DTA studies L-Glutamic acid doped thiourea crystals were stable up to 210°C. The exothermic peak at 290°C indicates a phase change from liquid to vapour state as evident from the loss of weight of about 87% in TG curve. Optical transmission UV-Visible spectral) range of amino acid doped thiourea was measured and the doped thiourea crystal has a good optical transmission in the entire visible region. The powder SHG measurement shows that the grown doped thiourea crystal has 1.68 times higher SHG efficiency than KDP. Vickers micro hardness was calculated in order to understand the mechanical stability of the grown crystals.

The non-linear response of the physical properties with respect to the electric field and temperature is a unique characteristic of ferroelectric materials. This makes them extremely attractive materials for a variety of applications, particularly based on their anomalous electrical and optical properties. The solubility and stability of pure and amino acid doped thiourea crystals have been experimentally investigated. It has been found that while doping with amino acids both the solubility and stability were reduced. This has been attributed to the increase in the rate of formation of nuclei while doping with amino acids. The effect of seeds of different orientations on the habit of the crystal has been investigated. It has been found that while using a (001) seed the crystal ends with a wide b-plane - a suitable one for NLO applications.

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