

# Irradiation effect on dye doped Thiourea crystals for NLO applications

P. DAMODARAN<sup>a,b</sup>, P. KUMARESAN<sup>a\*</sup>, R. RAJASEKARAN<sup>b</sup>, R. JAYAVEL<sup>c</sup>

<sup>a</sup>Department of Physics, Thiru. A.Govindasamy Government Arts College, Tindivanam-604 002, Tamil Nadu, India

<sup>b</sup>Department of Physics, Government Arts College, Tiruvannamalai, Tamil Nadu, India

<sup>c</sup>Centre for Nanoscience and Technology, Anna University, Chennai-600 025, India

Most irradiation studies in the hydrogen bonded ferroelectrics have been concentrated on the transient defects induced by ionising radiation such as UV light, where the defects are closely related to the optical properties [1]. On the other hand, ion beam irradiation effects have rarely been studied.  $\text{Li}^{3+}$  irradiations lead to the development of a well-defined surface H peak in dye doped thiourea crystals. Due to beam interaction, electron moves to the conduction band leaving behind the free hole, which can get self-trapped and configurationally changes occurring in the neighbouring structural units. Irradiation effects diffuse the dyes uniformly in the crystal due to lattice disorder. The NLO efficiency is increased in dyes doped thiourea crystals after irradiation. The stability of thiourea single crystal was improved by doping organic dyes [2]. The structural, chemical, optical, mechanical and non-linear optical properties of the doped crystals were analyzed with the characterization studies such as powder XRD, FT-IR, UV-Visible, SEM and SHG measurements, respectively. The results for doped thiourea crystal are compared with the results of the pure thiourea crystals.

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## 1. Introduction

Non-linear optical (NLO) materials have a significant impact on laser technology, optical communication, optical storage technology and electro optic modulation. The search for new frequency conversion materials over the past decade has led to the discovery of many semi organic materials. These materials possess large nonlinearity, high resistance laser induced damage and low angular sensitivity [4, 5]. The semi organic NLO materials gain importance over organic and inorganic NLO materials because of their large polarizability and wide transmission window. Extensive investigation in this direction resulted in the discovery of a new phase match semi organic NLO crystals [6].

Thiourea crystal finds widespread use as frequency doublers in laser applications and was studied in great detail. Improvement in the quality of the thiourea crystals and the performance of this crystal-based device can be realized with suitable dopants. To analyze the influence of dye based dopant on the non-linear optical property of Thiourea crystals; efforts were made to dope Thiourea with Rhodamine B dye. The effects of impurity atoms on the quality and performance of the crystals were analyzed [7]. Bulk crystals of Thiourea and dye doped Thiourea crystals were grown by solution growth technique.

## 2. Experimental procedure

### 2.1 Crystal growth

Pure Thiourea crystals were grown from aqueous solution by slow evaporation and also by slow cooling method ( $0.5^{\circ}\text{C}/\text{Day}$ ). The same method is followed for doped Thiourea crystals (0.1 mole % of Rhodamine-B). The solubility of doped Thiourea in the solvent was measured for each dopant, it was found to be 31.5-gms/100 ml at  $42^{\circ}\text{C}$  for Rhodamine-B. The seed crystals are prepared at low temperature by spontaneous nucleation. The seed crystals with perfect shape and free from macro defects were used for growth experiments. Large single crystals of Thiourea and doped Thiourea were grown using constant temperature bath (CTB) controlled with an accuracy of  $0.01^{\circ}\text{C}$ . The mother solution was saturated with the initial pH value, 4.2 for Rhodamine-B. The growth was carried out for more than 22 days by keeping the bath at a temperature of  $39^{\circ}\text{C}$ .

Well-polished, transparent, single crystalline Thiourea samples, procured from the Thiru. A.Govindasamy Government Arts College, Tindivanam, Tamil Nadu India, were used for  $\text{Li}^{+}$  irradiation at room temperature. The samples were irradiated with 20 MeV Li ions by using a 15 UD Pelletron Accelerator. These studies were performed at room temperature in an experimental chamber under vacuum better than  $10^{-7}$  Torr. The beam was scanned a  $10\text{ mm} \times 10\text{ mm}$  area on the sample using a magnetic beam scanner. The dose of charge accumulated in the sample was measured separately in terms of the fluences and the following fluences were used:  $1 \times 10^{11}$ ,  $1 \times 10^{12}$ ,  $1 \times 10^{13}$  and  $1 \times 10^{14}$  ions  $\text{cm}^{-2}$ . According to the

calculation of stopping and ranges of ions in matter (SRIM) [8], the projected range ( $R_p$ ) of the 20 MeV Li ions in Thiourea is 7.5- $\mu$  m. Also the corresponding end of range lateral distribution of straggling is 4.567MeV ( $\text{mg cm}^{-2}$ )<sup>-1</sup> and the longitudinal distribution of straggling is 7.5 MeV ( $\text{mgcm}^{-2}$ )<sup>-1</sup>. The atomic force microscopy (AFM) image was acquired using the Veeco Digital Nanoscope III AFM in the show mode.

## 2.2. Characterisation studies

Powder X-ray diffraction studies were carried out for the as grown crystals using Rich Seifert X-ray diffractometer with  $\text{CuK}\alpha$  ( $\lambda = 1.5498 \text{ \AA}$ ) radiation. The FT-IR spectra of all the crystals were recorded from solid phase samples 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 400 – 4000  $\text{cm}^{-1}$  operating at 200mW power at the samples with a spectral resolution of 2  $\text{cm}^{-1}$ . The IR spectra were also recorded on Shimadzu-800, FTIR spectrometer series of Japan in the region 400 – 4000  $\text{cm}^{-1}$ . The frequencies for all sharp bands are accurate to  $\pm 1 \text{ cm}^{-1}$ . The UV-VIS spectrum of Thiourea, doped Thiourea crystals were taken in the wavelength 200nm-1200nm ranges using the Varian CARY5E UV-VIS-NIR Spectrophotometer. Nd-YAG laser test was performed to find the non-linear optical property of dye doped Thiourea crystals. The crystal was illuminated using spectra – physics Quanta-Ray DHS2Nd-YAG laser using the first harmonics out put of 1064 nm with a pulse width of 8 ns.

### 2.2.1 X-Ray diffraction investigation

Powder XRD spectra (Fig.1) for the pure and dyes doped Thiourea revealed that the structures of the doped crystals are slightly distorted compared to the pure Thiourea crystal. This may be attributed to strains on the lattice by the absorption or substitution of dyes. It is observed that the reflection lines of the doped Thiourea crystal correlate well with those observed in the individual parent compound [8, 9] with a slight shift in the Bragg angle.

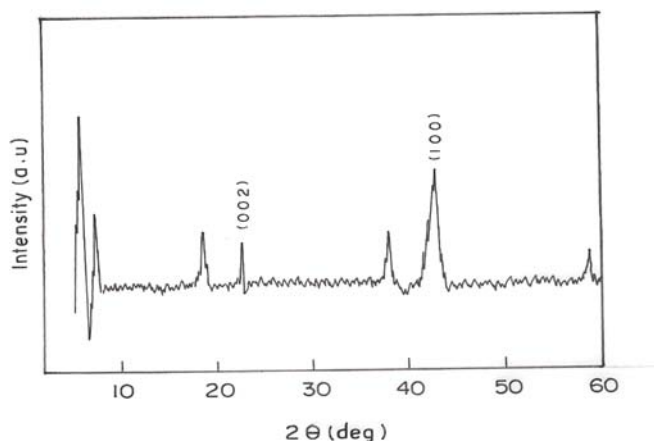


Fig. 1. XRD of dye doped Thiourea crystal.

### 2.2.2 FTIR Studies

The FTIR [Fig.2] of all of them were recorded from solid phase samples on a Bruker IFS 66V model spectrophotometer using 1064nm output of a cw diode pumped Nd:YAG laser as a source of excitation in the region 400 – 4000  $\text{cm}^{-1}$  operating at 200mW power at the samples with a spectral resolution of 2  $\text{cm}^{-1}$ . The IR spectra were also recorded on Shimadzu-800, FTIR spectrometer series of Japan in the region 400 – 4000  $\text{cm}^{-1}$ . The frequencies [10-12] for all sharp bands are accurate to  $\pm 1 \text{ cm}^{-1}$ . The observed spectra of single and doped Thiourea shown in Fig. 2.

It was confirmed that broad envelope positioned in between 2750-3500  $\text{cm}^{-1}$  corresponds to symmetric and asymmetric stretching modes of  $\text{NH}_2$  grouping of zinc and cadmium coordinated thiourea. The bond of thiourea was not shifted to lower frequency on formation of metal thiourea complex. The NH and N-C-N stretching vibrations were also seen in these crystals

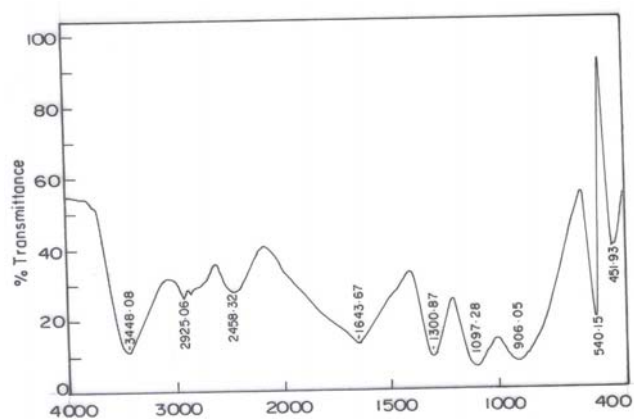


Fig. 2. FT-IR spectra of dye doped Thiourea Crystal

### 2.2.3 UV-Visible investigation

UV-visible spectral studies The UV-visible spectral studies of grown crystals were carried out using Shimadzu 1601UV-V spectrophotometer. The UV-visible absorbance spectra of doped Thiourea crystals are shown in figure 3. The absorption spectra reveal that all three crystals have lower cut off wavelengths at around 290nm. The wide transmission in the entire visible region (190nm-1100nm) enables it be a potential candidate for optoelectronics applications. It shows that, near absorption edge the absorption coefficient increases rapidly with energy.

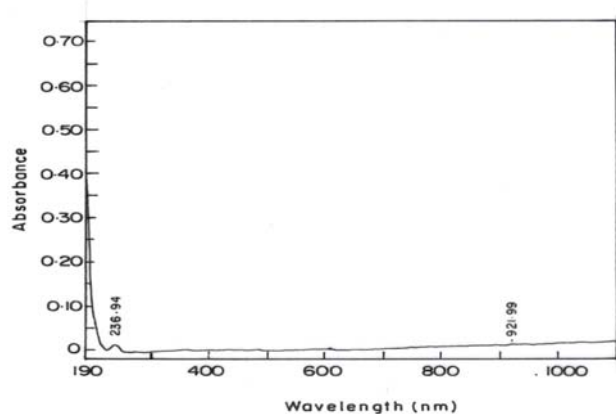


Fig. 3. Absorbance spectra of dye doped Thiourea crystal

### 2.2.4 TGA-DTA investigations

Fig. 4 illustrates the differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) curves for the grown dye doped Thiourea samples. The DTA curve implies that the material undergoes an irreversible endothermic transition at 200°C where the melting begins. The peak of the endothermic [10-12] 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 TG curve of this sample indicates that the sample is stable up to 220°C and above this temperature; the weight loss is not due to self-degradation of doped Thiourea but merely to its evaporation after its melting.

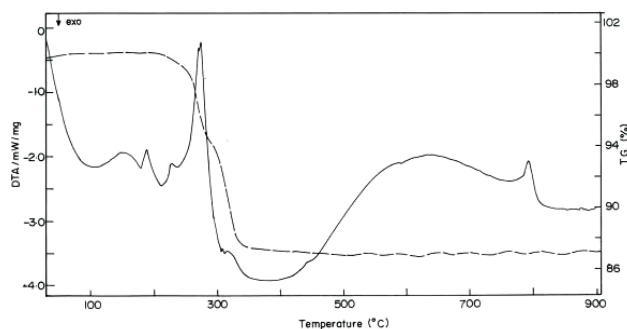


Fig. 4. TGA-DTA spectra of dye doped Thiourea crystal

### 2.2.5 SEM investigations

The SEM picture (Fig.5) confirms the formation of a layer on the surface of the crystal due to impurities. The SEM studies reveal that the Rhodamine-B present in the solution creates a surface layer, which prevents the entry of impurities and thereby it helps to grow the crystal with high crystalline quality. The crystal surface morphology of pure and Li<sup>+</sup> ion irradiated Thiourea sample was investigated by SEM and it is shown in Fig. 5.

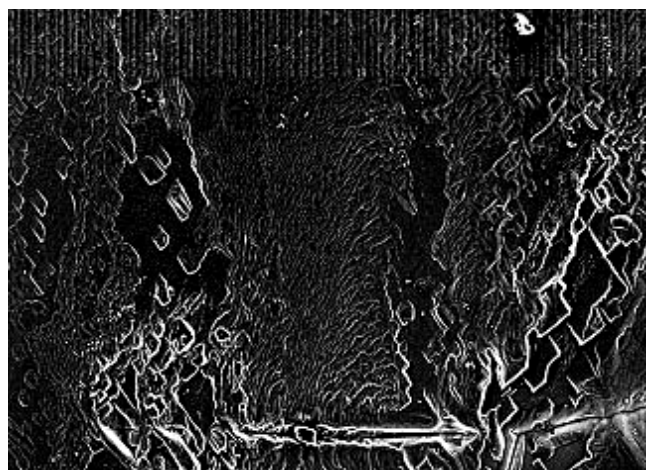


Fig. 5. SEM photograph of Rhodamine-B doped Thiourea crystal (after irradiation)

### 2.2.6 NLO properties

In order to confirm the NLO property the doped Thiourea crystal has been tested using the Nd-YAG laser. Small crystals of amino acids doped Thiourea was placed on the sample holder and the red color laser beam was made to pass through the crystal and the incoming beam passing through the crystal converted into the green light. The efficiency of doped Thiourea a crystal was compared with pure [13-14]. Thiourea and also shows that Rhodamine -B doped Thiourea crystals have higher efficiency. It was observed that the irradiation process enhance the NLO property of dye doped Thiourea crystals.

## 3. Results and discussion

We have grown single crystals of Thiourea and organic dyes doped Thiourea and characterized them by employing FT-IR and X-Ray diffraction methods. The doped crystals show good second harmonic generation efficiency. There is a different class of non-linear optical materials, which possess important optoelectronic properties. However, to fabricate optical devices using these materials, a detailed study of ion induced stoichiometric and structural changes occurring in them are necessary. Most irradiation studies in the hydrogen bonded ferroelectrics have been concentrated on the transient defects induced by ionizing radiations such as X-

ray and UV light, where the defects are closely related to the optical properties.

On the other hand, heavy ion beam irradiation effects have rarely been studied. In this paper, it has been shown that irradiation modifies the optical properties of Thiourea crystal [15-17].  $\text{Li}^+$  irradiation leads to the development of a well-defined surface H peak. The depletion of hydrogen from the Thiourea sample in terms of the possible bond-breaking mechanism occurs. Due to beam interaction, an electron moves to the conduction band leaving behind the free hole, which can get self-trapped and configurationally changes occurring in the neighboring structural units. The irradiation determines diffusion of the dyes uniformly in the crystal. The sharpness of the endothermic peak shows good degree of crystallinity of the grown ingot. The endothermic peak at  $250^\circ\text{C}$  indicates a phase change from liquid to vapor state as evident from the loss of weight in TG curve.

#### 4. Conclusions

Most irradiation studies in the hydrogen bonded ferroelectrics have been concentrated on the transient defects induced by ionizing radiations such as X-ray and UV light, where the defects are closely related to the optical properties. On the other hand, heavy ion beam irradiation effects have rarely been studied. In this paper, it has been shown that irradiation modify the optical properties of Thiourea crystal. The depletion of hydrogen from the Thiourea sample is attributed to the possible bond-breaking mechanism. Due to beam interaction, electron moves to the conduction band leaving behind the free hole, which can get self-trapped and configurationally changes occurring in the neighboring structural units. On the other hand, light beam irradiation effects have been studied. A recent study has been shown that irradiation on a Thiourea - type crystal,  $\text{Li}^+$  irradiations, and leads to the depletion of hydrogen with possible bond-breaking mechanism. Because of doping organic dyes, the stability of Thiourea is strong enough and such effect is likely to be reduced. Irradiation effects diffuse the dyes uniformly in the crystal. The nano-islands of dyes in Thiourea are likely to be dissolved and enhance the nonlinear optical properties of these materials.

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\*Corresponding author: logeshkpmaresan@yahoo.com