BULK GROWTH AND PHYSICAL PROPERTIES OF NONLINEAR OPTICAL MATERIAL: THIOUREA SULPHAMIC ACID CRYSTAL

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ABSTRACT

Nonlinear optical crystals of Thiourea Sulphamic Acid (TS) crystals have been successfully grown by employing slow evaporation technique. The grown crystals were characterized using powder X-Ray diffraction analysis for the crystal system and lattice parameter values. The vibrational behavior was analyzed by means of FTIR spectral technique. UV–Vis–NIR spectral study revealed that the grown crystals have a wide transmission window in the entire visible region with the lower cutoff wavelength 237 nm. The Vicker's microhardness test was carried out on the grown crystals to study the mechanical strength therein, the Vicker's hardness number (Hv) were calculated. The grown crystals of thiourea sulphamic were subjected to thermal studies to confirm that the decomposition of crystals takes place in three different stages making them suitable for device fabrication for frequency conversion applications. Surface Morphology of the grown crystal was confirmed through SEM analysis. The second harmonic generation of the crystals was confirmed by employing Kurtz powder technique to ascertain the nonlinear optical property.

Keywords: Thiourea, Sulphamic Acid, XRD, FTIR, UV-Visible, Thermal, SHG.

INTRODUCTION

Nonlinear optics plays a central role in the developing era of photonics. Photonics includes the application of photons for information and image processing. Non-Linear optical crystal is an important part in research arena due to their hands-on applications such as optical computing, optical information processing, optical communication, medical diagnostics, laser remote sensing, optical disk data storage, laser fusion reactions, color display, etc. Nonlinear optical processes have applications in vital functions such as frequency conversion and optical switching.[1] Organic crystals can have very large nonlinear susceptibilities relative to inorganic crystals, but exhibit low damage threshold and poor processibility.[2-6] For overcoming these difficulties, the search for new materials with high optical nonlinearities is an everlasting process.

In semiorganic materials, the organic ligand is ionically bonded with the inorganic host. Organic nonlinear materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultra-fast response times and high optical thresholds for laser power as compared with inorganic materials.[7] Sulphamic acid is a classical inorganic compound and an important industrial chemical with a yearly production of several kilotons.[8] Sulphamic Acid is used to Descaler, Detergent & Corrosion Remover, Removing additional cement on tiles, efflorescence and other mineral deposits etc. Industrial uses of thiourea include the production of flame retardant resins and vulcanization accelerators. Thiourea is used as an auxiliary agent in diazo paper, light-sensitive photocopy paper and almost all other types of copy paper. It is also used to tone silver-gelatin photographic prints. The main application of thiourea is in

textile processing. Urea (N₂H₄CO) and Thiourea (N₂H₄CS) are simple organic molecules with immense dipole moment and have the ability to form a large scale network of hydrogen bonds. Dopant is added to occupy the interstitial positions in the lattice and in turn this may lead to distinctive changes in the physical properties of thiourea sulphamic acid.[9-12] Due to its interesting property, in the present investigation, an attempt made to grow thiourea sulphamic acid crystals. The primary aim of the article is to investigate the influence of thiourea on the optical and thermal properties of thiourea sulphamic acid crystals.

EXPERIMENTAL

Synthesis and Solubility of Thiourea Sulphamic Acid Crystals

TS was synthesized from Thiourea Sulphamic Acid taken in the molar ratio of 1:1 by slow evaporation technique. The reactants were thoroughly dissolved in double distilled water and stirred well using a temperature controlled magnetic stirrer to yield a homogeneous mixture of the solution. Then the solution was allowed to evaporate at room temperature, which results in the yield of white crystalline salt of TS due to super saturation followed by nucleation:
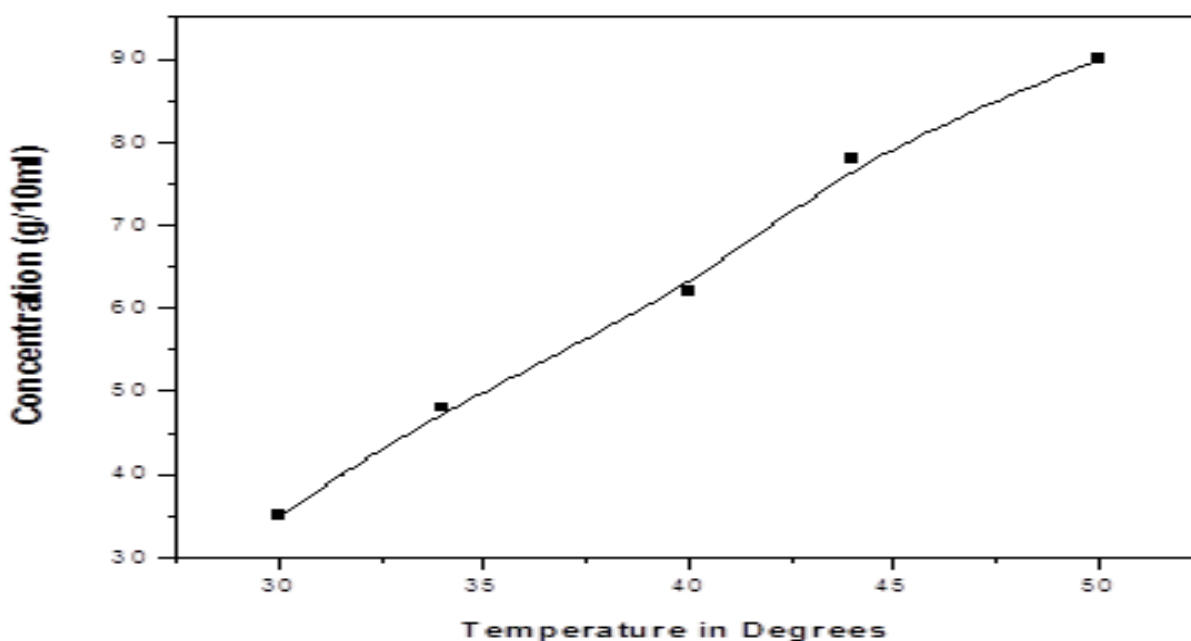
$$H_2N - CS - NH_2 + HO - SO_2 - NH_2 \rightarrow (H_2N - CS - NH_3)SO_3 - NH_2$$
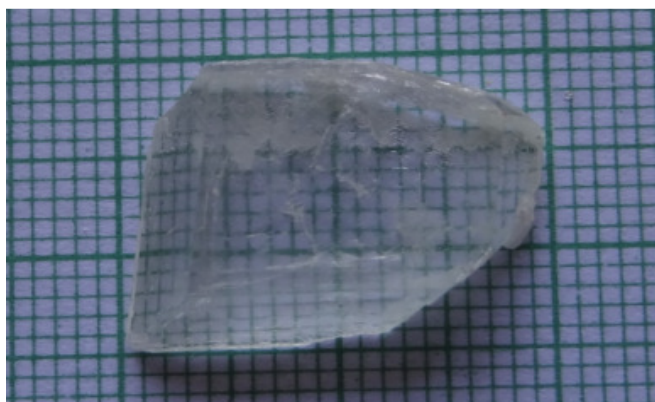

Fig.-1: Solubility Curves of TS Crystal

Fig.-2: Image of Grown TS Crystal

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The seed crystals were harvested from the solution after eight days and a suitable seed was selected. The selected seed was suspended in the freshly prepared solution. After a period of 15 days, optically transparent defect-free crystals were obtained from the mother solution. Fig.-1 shows the Solubility curves of TS. Fig.-2 shows the as-grown crystal of TS with an optimized solution pH value of 3.2.

Characterization Studies
The grown pure and doped TS single crystals have been subjected to numerous characterization studies. The Rigaku ultima III X-Ray diffractometer with $CuK\alpha_1(\lambda = 1.5406$ Å) was used to estimate the cell parameters. The Fourier transform infrared spectroscopy (FTIR) spectrum was recorded using a Perkin Elmer make model Spectrum Rx1 spectrophotometer using KBr pellet technique in the region 4000–400 cm^{-1}. The UV-vis absorption spectrum was studied in the range 190– 1100 nm by Perkin Elmer make model Lambada 35 UV-Vis-NIR spectrophotometer in the range 190-1100 nm. Microhardness study of the crystals was carried out using MUTUTOYOM112 microhardness tester fitted with a diamond pyramidal indenter. The thermal gravimetric analysis (TGA)/differential scanning calorimetry (DSC) studies showed the thermal properties of grown crystal carried using TA instruments (model: Q600 SDT and Q20 DSC thermal analyser) are carried out at the room temperature to 700°C at a heating rate of 10°C min in the nitrogen atmosphere. Nonlinear optical property of the crystal was confirmed using the Kurtz and Perry powder technique by passing the fundamental beam of Q-switched, mode-locked Nd:YAG laser operating at 1.06 μm and pulse width of 8 ns laser pulse with a spot radius of 1 mm.

RESULTS AND DISCUSSION
Powder X-Ray Diffraction
The structural properties of single crystals of TS have been studied by X-Ray Powder diffraction technique. The X-Ray diffraction studies were carried out using Rigaku ultima III X-Ray diffractometer with $CuK\alpha_1$ ($\lambda = 1.5406$ Å) radiation. The powdered samples were scanned over the range 10°-80 ° at a rate of 1° per minute. From the powdered X-ray data, the various planes of reflections were indexed using XRDA 3.1 program and the lattice parameters were evaluated.
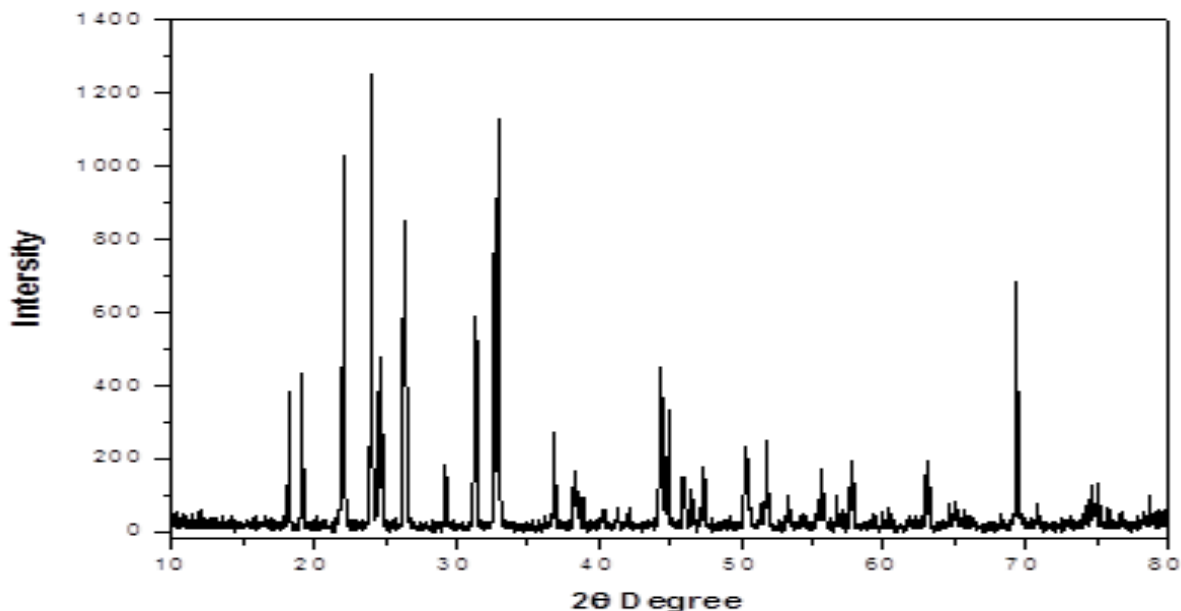

Fig.-3: The XRD Pattern of TS Crystal

The lattice parameters are a(Å) = 25.077, b(Å) = 10.092 and c(Å) = 9.288 and the unit cell volume is 2153.9 A^3. TS belongs to the primitive Triclinic system, The Powder X-ray diffraction pattern is shown in Fig.-3. The results are good agreement with the reported values.[13]

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FTIR Measurements

The FTIR spectrum of TS is shown in Fig.-4 and the vibrational modes and frequencies. The frequency observed at 3949 and 3829 cm^{-1} is due to the intermolecular hydrogen bonding as well as asymmetric NH$_2$ stretching vibration present in the compound.
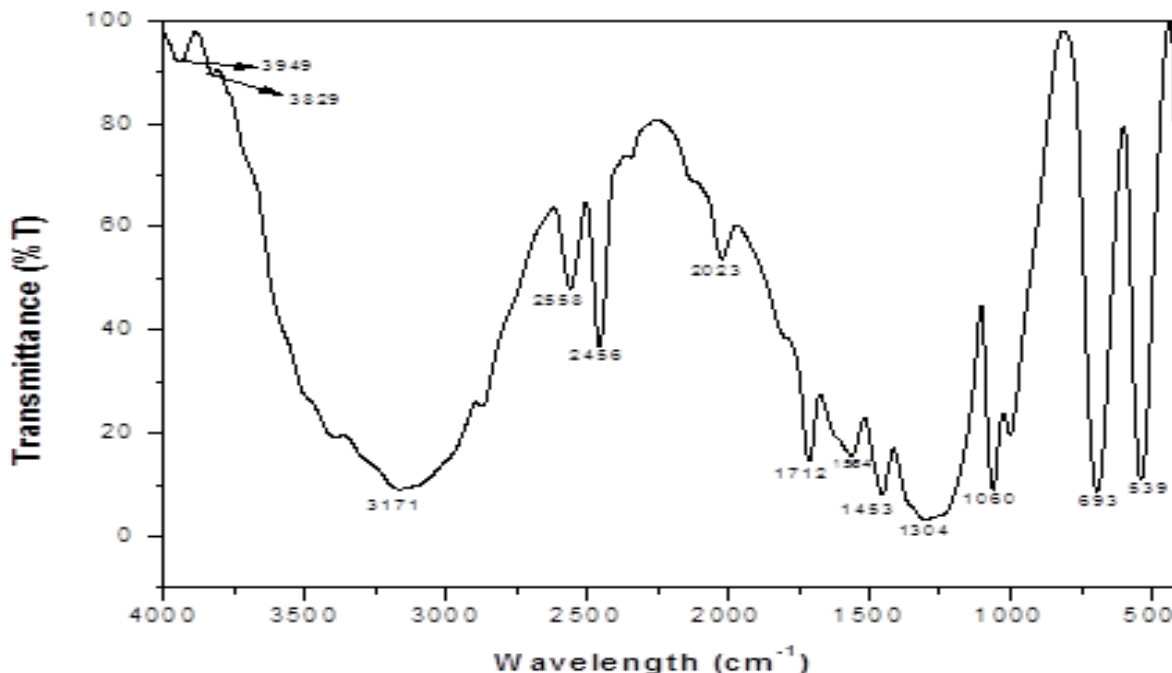

Fig.-4: FTIR Spectrum of TS Crystal

The absorption frequency at 3171, 2558 and 2456 cm^{-1} is due to the symmetric O–H stretching vibration mode. The absorption frequency at 2023 and 1712 cm^{-1} is due to the C–N stretching present in the aromatic nucleus. The frequency at 1564 cm^{-1} which appear in SO$_3^-$ deformation vibration. The absorption frequency at 1453 and 1304 cm^{-1} is due to O–H bending vibration. The absorption frequencies at 1060, 1000 and 693 cm^{-1} are due to the C–S stretching vibration mode. The peaks observed at 539 cm^{-1} is N-S stretching vibration mode.[14-17]

UV-Vis Spectrum

The UV-vis transmittance and absorption spectra Fig.-5 was recorded using Perkin Elmer make model Lambada 35 UV-Vis-NIR spectrophotometer in the range 190-1100 nm. Optically clear single crystal was used for this study and the crystal is transparent and there is no absorption in the entire region. The lower cut-off wavelength is 237 nm. As there is no absorption in the visible and near infrared region it can be used as a potential material for frequency doubling.[18]

Vicker's Hardness Test

Hardness is one of the important mechanical properties of the solid material. It can be used as a suitable measure of the plastic properties and strength of the material. Microhardness analysis was carried out using Vickers Microhardness tester fitted with a diamond indentor. The well-polished TS crystal was placed on the platform on the Vicker's Microhardness tester and loads of different magnitude (25-100 gm) were applied over a fixed interval of time.[19] The indentation time was kept at 5 sec. for all the loads. The Vicker's hardness number of the grown crystals was calculated using the relation:

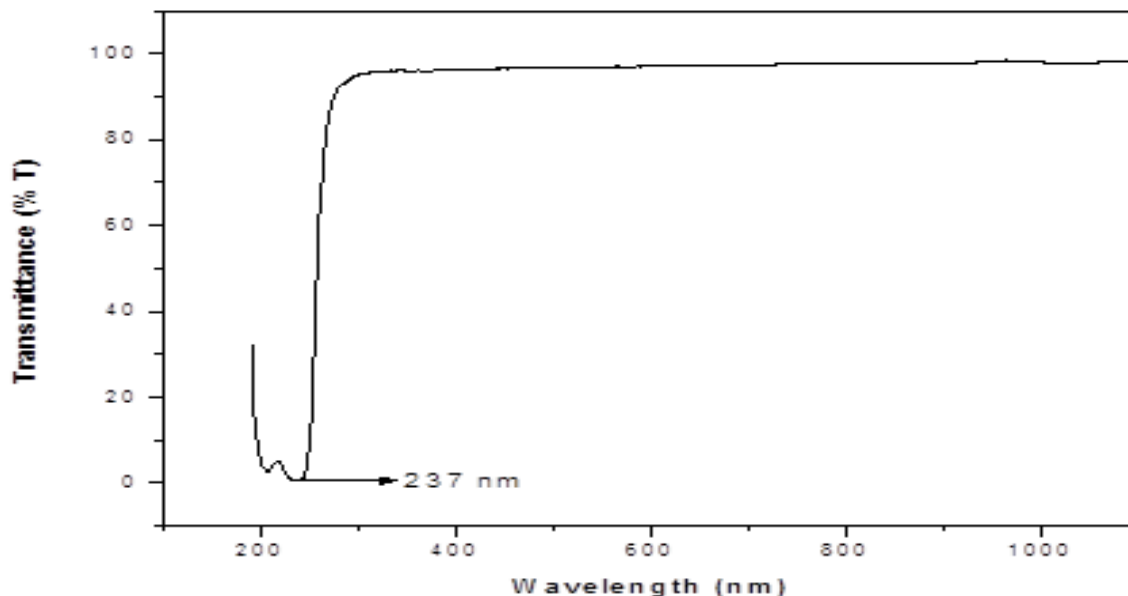$$H_v = \frac{1.8544P}{d^2} Kg/mm^2$$

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Fig.-5: UV-Vis Spectrum of TS Crystal

P is the applied load in kg, d is the average diagonal length in mm of the indentation impression. The relation between hardness number (H_v) and load (P) for TS is shown in Fig.6. The hardness increases gradually with the increase of load and above 100 g cracks develops on the smooth surface of the crystal due to release of the internal stresses generated locally by indentation.
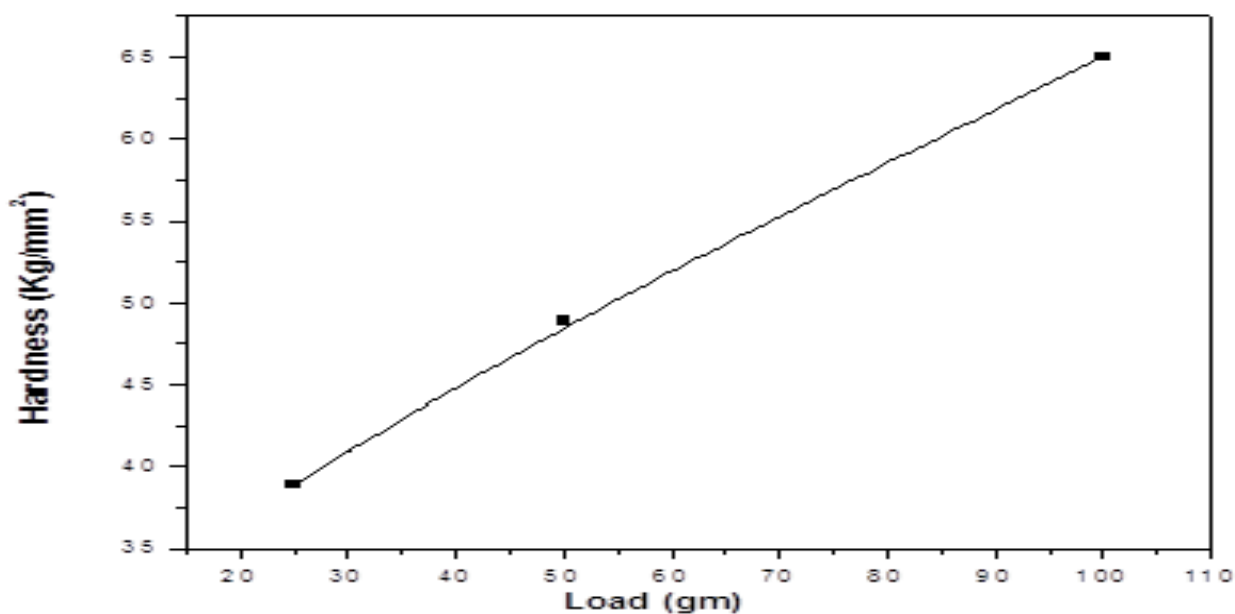
Fig.-6: Vickers Hardness Vs Load for TS Crystal

Scanning Electron Microscopy Studies (SEM)

Chemical analysis and morphological studies were carried out using scanning electron microscopy (SEM model JSM 840A). Fig.-7 illustrates the SEM image of the crystal. It shows some darker and brighter uneven areas. This might be due to solvent inclusions, which is most commonly observed in solution growth. Interesting features of surface morphologies are observed in SEM, actually, exhibits stepped

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structure.[20-21] Variations in step directions and the appearance of wider steps could be attributed to the general roughness / grain boundary.
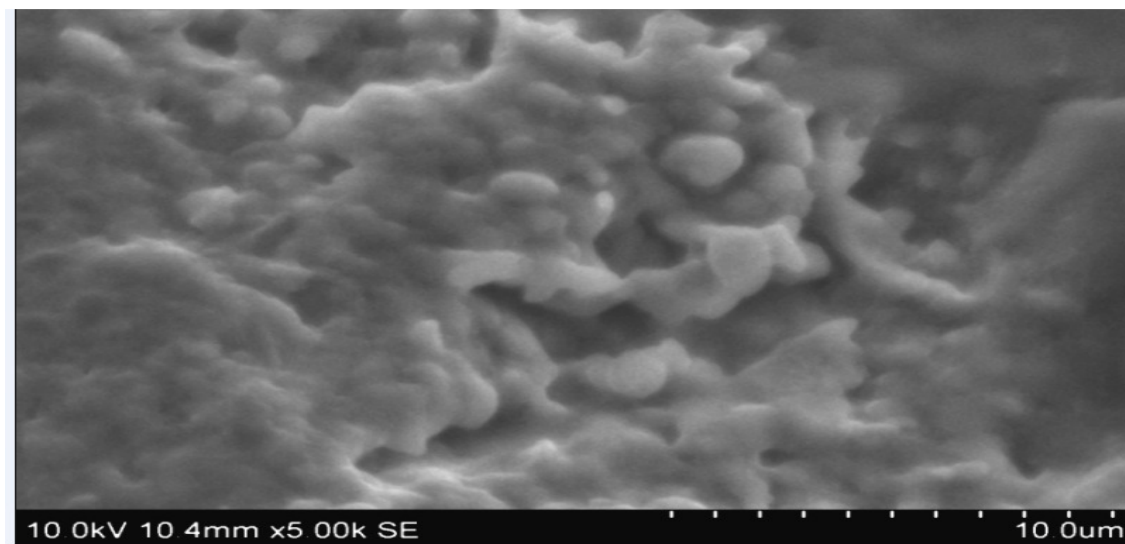

Fig.-7: SEM Image of TS Crystal

Thermal Studies
TGA Analysis
The TGA response curves for the powder sample TS is shown in Fig.-8. In the TGA trace, there is a major weight loss of 100 % starting at about 10-15°C. It is due to the decomposition and volatilization of the compound. The next weight loss occurs between 17 and 22°C shows that that the decomposition is almost complete. The other endotherms or exotherms observed coincides exactly with the decomposition observed in TGA trace.[22] It is concluded that the TS crystal is suitable for NLO applications up to 39°C.
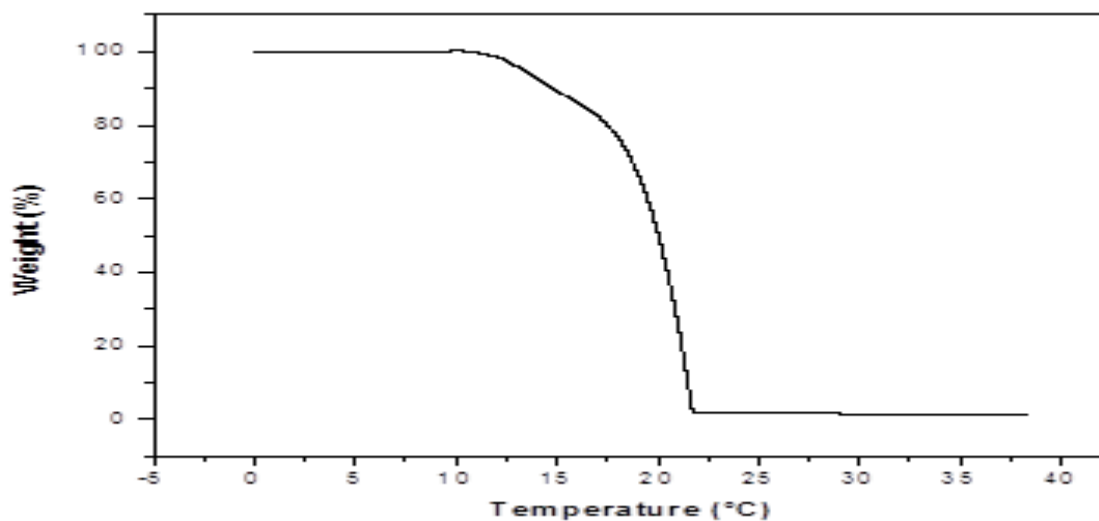

Fig.-8: TGA Curve of TS Crystal

DSC Analysis
The DSC curve shown in Fig.-9 shows that there is no phase transition up to 200°C. There is second weight loss at a temperature of 242°C and after that one distinct anomaly of heat was observed at 290°C. The first endothermic curve corresponds to a loss of water. The thermogram also shows the decomposition temperature at 290°C. The reduction in decomposition value of doped TS crystal as compared to pure TS may be attributed to decrease in bond energy caused by the addition of a dopant.[23]
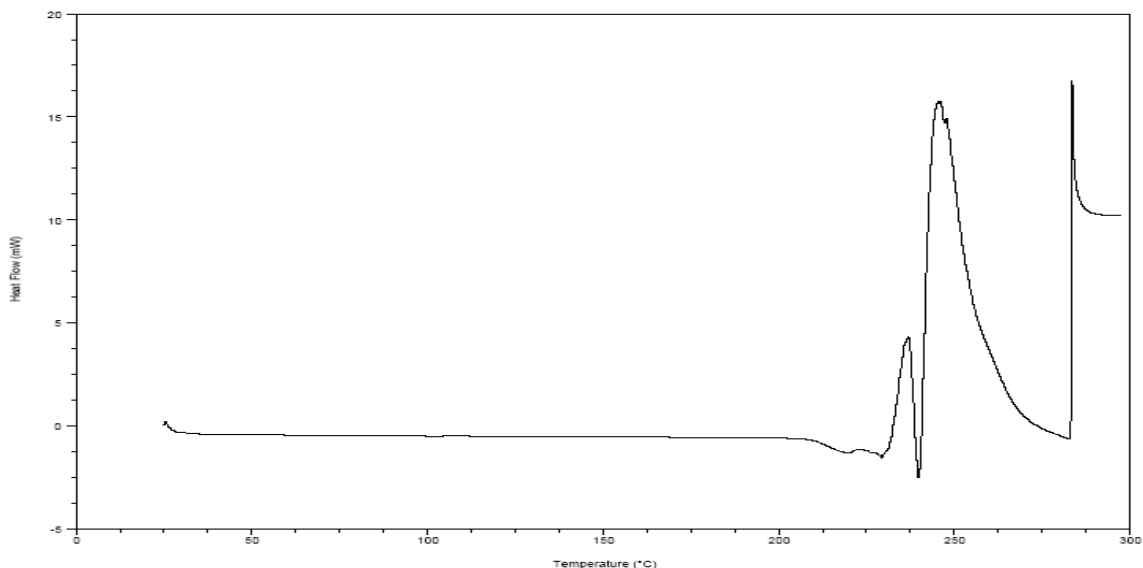
Fig.-9: DSC Curve of TS Crystal

Dielectric Studies

The dielectric constant of the TS crystals was studied at different temperatures using HIOKI 3532 LCR HITESTER. Fig.10 shows the plot of dielectric constant (ε_r) vs log frequency. The dielectric constant has high values in the lower frequency region and then decreases with the applied frequency. The very high value of ε_r at low frequencies may be due to the presence of all the four polarizations namely, space charge, orientation, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually.[24-27] From the plot, it is also observed that dielectric constant decreases with increasing frequency, attributed to space charge polarization near the grain boundary interfaces, which depends on the purity and perfection of the sample.
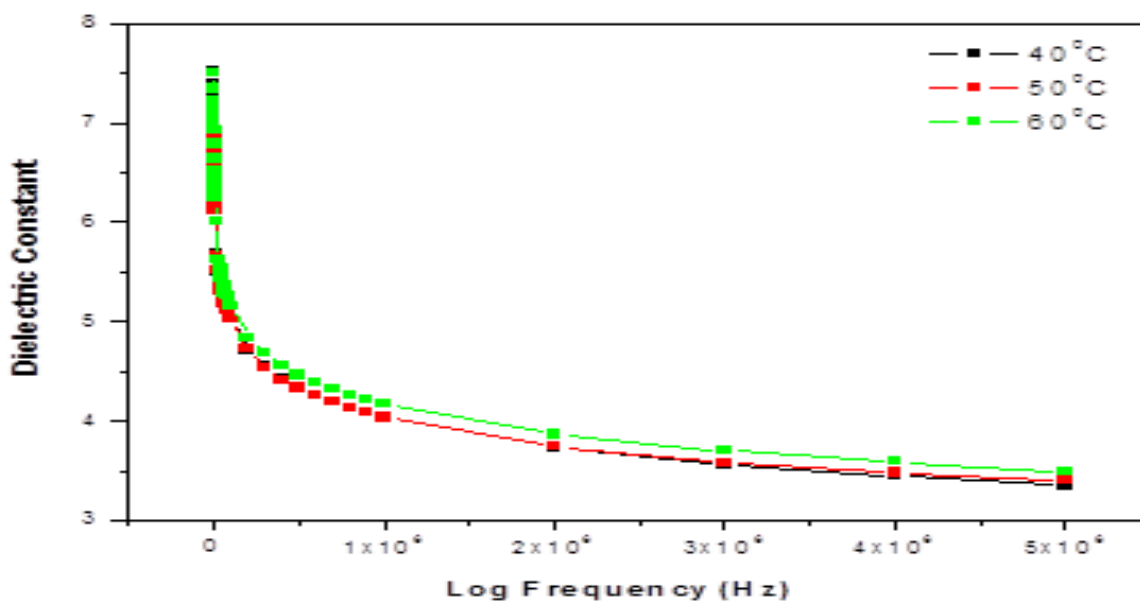

Fig.-10: Variation of Dielectric Constant with Frequency for TS Crystal

Second Harmonic Generation NLO Study

In order to confirm the NLO behavior of this material, the powder sample was subjected to Kurtz and Perry technique.[28] A fundamental beam of wavelength 1064 nm with a pulse duration of 10 ns and the

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frequency repetition of 10 Hz from Q-switched Nd:YAG laser has been used as a source and passed through the powder sample of particle size 1.2 nm for second harmonic generation efficiency (SHG) study. Pulse energy and pulse width are maintained as 321 mJ s^{-1} and 8 ns respectively.

The 532 nm radiation was collected by a monochromator, after separating the 1064 nm pump beam with an infra-red blocking filter. The second harmonic radiation generated by the randomly oriented microcrystals was focused by a lens and detected by a photomultiplier tube. The second harmonic generation is confirmed by the emission of green radiation from the crystal. The second harmonic out signal was 98 mV and was obtained from an input energy 2.149mJ/pulse with a pulse width of 8 ns. The second harmonic generation (SHG) of the TS crystal was demonstrated by Kurtz Perry method using Nd: YAG laser and the result confirms that the grown crystal is 140% as that of KDP.

CONCLUSION

After careful optimization crystal of TS is successfully grown by slow evaporation technique. X-ray diffraction analysis confirms the improvement in the crystalline quality of grown doped TS crystals. The presence of dopants has slightly retailored the lattice parameters without affecting the basic arrangement of crystals. It is noticed that the dopants thiourea has improved the hardness which shows the importance of doping in the mechanical stability of optical applications. The presence of various functional groups of the molecules was confirmed by FTIR analysis. The thermal analysis shows that there is no phase transformation or vaporization before melting point and stable 29° C doped crystals. The Dielctric behavior of the grown crystals were confirmed form the dielectric test. The SHG efficiency of thiourea doped SA was found to be equal to the reference material KDP.

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