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Growth, Spectral, Optical and Thermal Characterization of NLO Organic Crystal – Glycine Thiourea

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Abstract: Optical quality single crystals of glycine thiourea (GT), a new organic nonlinear optical (NLO) crystal, were grown from aqueous solution by slow evaporation method. Solubility of GT was determined at various temperatures. Single crystal X-ray diffraction studies indicate that GT crystallizes in the monoclinic crystal system. Various diffracting planes of the grown crystal were identified from the powder X-ray diffraction study. The various functional groups of molecules present in GT were identified from FT-IR studies. The elemental analysis confirmed the stoichiometry of the compound. Optical characterization of the crystal shows the cut off wavelength near the UV region. Thermal stability and melting point of the grown crystal were found by thermal analyses. The powder second harmonic generation test of GT revealed its relative NLO efficiency is approximately 0.5 times that of potassium dihydrogen orthophosphate. The mechanical strength of the grown crystal is estimated by Vicker's hardness test.
Key words: single crystals, slow evaporation, X- ray diffraction, FT-IR, Thermal analyses, second harmonic generation.

1. Introduction

In the recent years, nonlinear optical (NLO) crystals have attracted the researchers due to their potential applications in the fields of high-energy lasers for inertial confinement fusion research[1], electro-optic switches, frequency conversion[2], color display and photonics including optical information processing[3- 6]. Organic materials have been known for their potential applications in semiconductors, superconductors and nonlinear optical devices[7]. Organic compounds exhibit larger NLO response than inorganic materials due to the presence of active π-bonds. Organic NLO crystals with high conversion efficiency for second harmonic generation and transparency in UV-Vis region are required for numerous device applications mainly in optical telecommunications and optical storage device[8]. Amino acid crystals are potential NLO materials as they have donor carboxyl group and acceptor amino group, which form an extensive hydrogen bond networks within the crystal[9]. Glycine is the only amino acid without a centre of chirality. The gas phase of glycine molecule is a neutral molecule, but in liquid and in solid phase glycine exists as zwitterions[10].

Nonlinear optical crystals of glycine such as benzoyal glycine[11], glycine zinc sulphate[12], glycine lithium sulphate[13], glycine picrate[7] and glycine sodium nitrate [14] were reported. Among these

crystals, the second harmonic generation efficiency (SHG) of glycine sodium nitrate crystal was two times that of potassium dihydrogen orthophosphate (KDP) and the SHG efficiency of benzoyal glycine crystal was 1.5 times that of KDP. Ferroelectric properties were reported for glycine silver nitrate[15] and glycine phosphate[16]. Hoshino et al.[17] reported about the dielectric properties of trisglycine fluroberyllate. Thiourea is a centro symmetric molecule and has the ability to form an extensive network of hydrogen bonds[18]. Most of the thiourea complexes are metal organic coordination complexes[19]. Some of the nonlinear crystals of the metal complexes of thiourea reported are bisthiourea zinc chloride[20], bisthiourea cadmium chloride [21] and zinc thiourea sulphate[22]. Recently Prakash et al.[23] reported on the synthesis and characterization of glycine thiourea. The single crystal XRD results of their work reveal that the crystal belongs to orthorhombic crystal system with cell parameters of a=5.546Å, b= 7.774Å and c= 8.637Å. In this work results of the detailed studies carried out on the synthesis, growth, structural, vibrational, thermal and optical properties of glycine thiourea crystal are presented.

2.Experimental

2.1. Synthesis

Glycine thiourea (GT) was synthesized by dissolving high purity thiourea and glycine in the equimolar ratio in aqueous medium. Thiourea was first dissolved in Millipore water and then glycine was added with continuous stirring. The prepared solution was slightly heated up and the beaker containing the solution was suitably closed and the solvent was allowed to evaporate at room temperature. The product was obtained as per the following reaction.

$CS(NH_2)_2 + NH_2CH_2COOH \rightarrow CH_2CS(NH_2)_2NH_3^+COO^-$

The impurity content of GT was minimized by the process of recrystallization.

2.2.Crystal growth

Solubility studies were carried out using the synthesized salt of GT and double distilled water as solvent. Saturated solution was prepared at various temperatures (35- 45°C) with the help of a constant temperature bath (±0.01°C) and the amount of solute was measured gravimetrically [24]. The variation of solubility with temperature is given in Fig.1 which shows that the solubility increases linearly with temperature, exhibiting a high solubility coefficient. Bulk single crystals of GT were grown by slow evaporation technique from aqueous solution. The saturated solution prepared at 30°C was filtered and taken in a beaker and closed with a parafilm and was kept in a constant temperature bath maintained at 30°C. The solvent was allowed to evaporate slowly. Single crystals of GT obtained in a growth period of 20 days are shown in Fig. 2.

Figure 1- Solubility Curve of GT

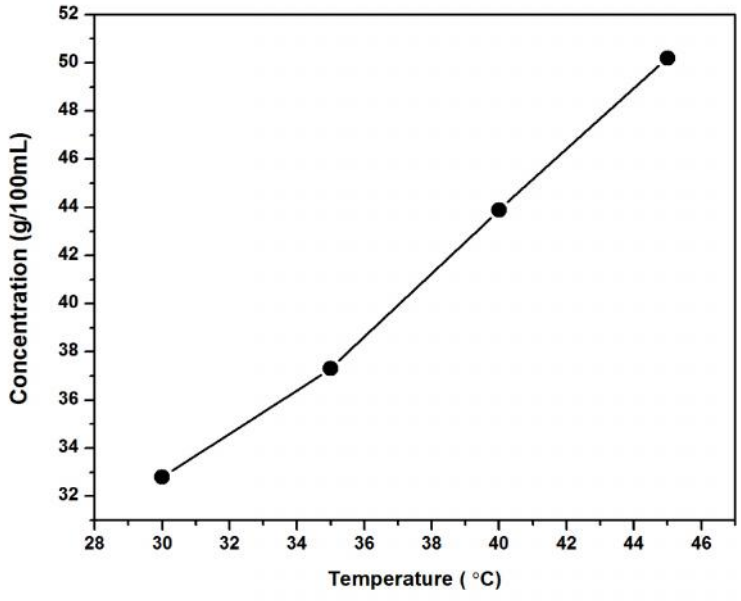
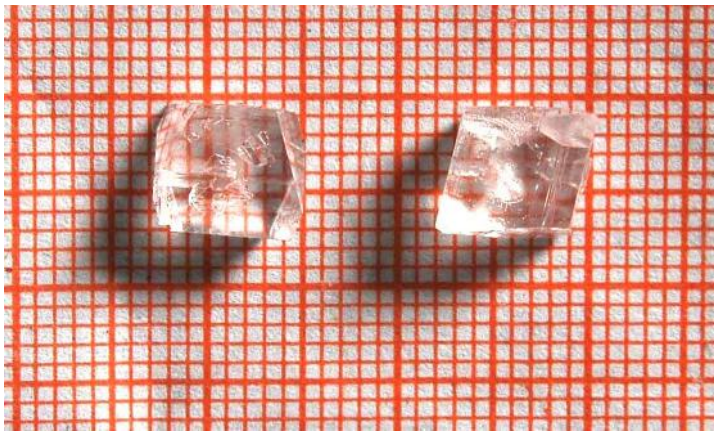


Figure 2- As grown crystals of GT



2.3. Characterization

The lattice parameters of the grown GT single crystal were determined by single crystal X-ray diffraction (XRD) studies using an ENRAF NONIUS CAD-4 diffractometer with Mo Kα (λ=0.71073Å) radiation at room temperature. Powder XRD analysis was also carried out using a Rich Seifert diffractometer with Cu Kα (λ=1.54059Å) radiation. Fourier transform infrared (FT-IR) spectrum of GT was recorded with a Perkin-Elemer RXI spectrophotometer using KBr pellet technique in the wavenumber range of 400-4000 cm^{-1} for the functional groups identification of the sample. Chemical composition of crystal was estimated by elemental analysis using elementar Vario ELIII-Germany. UV-vis transmittance spectrum of GT crystal of thickness 1 mm was recorded using Perkin Elmer-lambda 35 UV-Vis spectrophotometer in the range of 190-1100 nm. Thermal analysis was carried out using SDT Q600V 8.3 build 101 simultaneous DTA/TGA analyzer in the nitrogen atmosphere. Microhardness studies were carried out using Shimadzu HMV-2 instrument.The nonlinear optical efficiency of powdered GT crystal was measured employing Q-switched Nd: YAG laser.

3.Results and Discussion

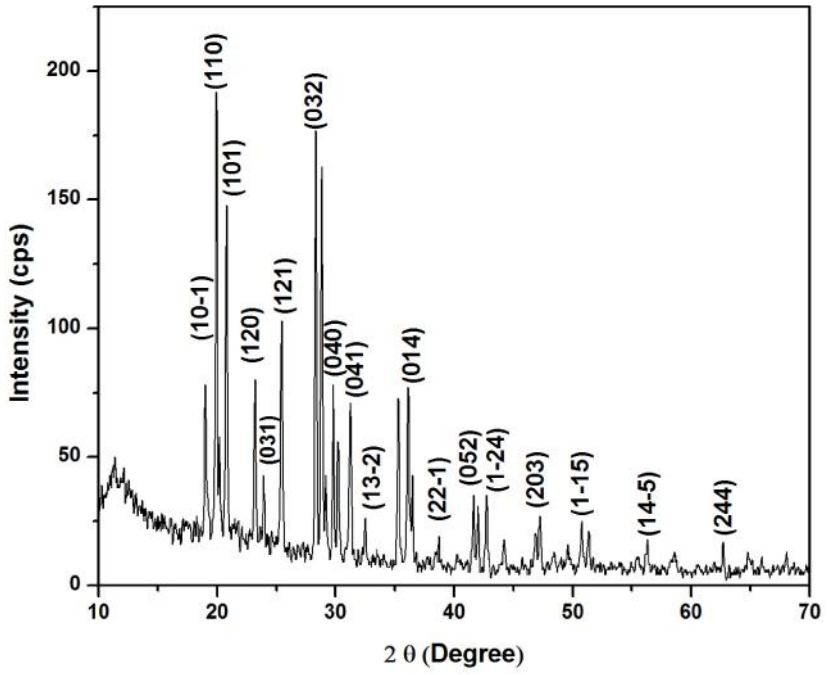
3.1. X-ray diffraction analysis

Structurally, glycine exhibits α, β and γ polymorphic forms at ambient conditions. The α- and β-forms crystallize in the monoclinic system and the γ-form crystallizes in the trigonal- hexagonal system[25]. At ambient conditions, α-form is the stable one and the β-form is the most unstable one. The γ-form occurs from aqueous solution only in the presence of a selective additive[26, 27]. In the present work the single crystal XRD study reveals that GT belongs to monoclinic crystal system. The observed lattice parameters of GT are compared with that of glycine (α,γ) and thiourea (TU)[28] in Table 1. The powder sample of GT was scanned over the range 10-80° at a rate of 1° per minute and the powder X-ray diffraction patterns were indexed using Check cell software (Fig. 3).

Table 1-Comparison of lattice parameters of glycine, TU and GT

S. No	Samples	a (Å)	b (Å)	c (Å)	Angle	Crystal system	Melting Point (°C)	Unit cell Volume ($Å^3$)	Ref
1	α-glycine	5.197	12.071	5.474	β=112.91°	Monoclinic	226.8	315.01	[25]
2	γ-glycine	7.004	7.004	5.447	α=β=γ=90°	Hexagonal	178.9	231.46	[25]
3	TU	7.66	8.54	5.52	α=β=γ=90°	orthorhombic	176.0	360.73	[28]
4	GT	5.32	11.90	5.85	β =95.78°	Monoclinic	156.3	370	Present Work

Figure 3- Powder XRD spectrum of GT



3.2. Elemental and FT-IR analyses

Elemental analysis of GT was carried out with elemental Vario EL III - Germany. GT weighing 8.0620 g was used for the analysis. Carbon (C), hydrogen (H), nitrogen (N) and sulphur(S) percentage composition was determined and presented in **Table 2**. Experimentally determined value of the elements of GT is in good agreement with the corresponding theoretical values, which confirms the formation of GT. FT-IR spectrum of GT was recorded at room temperature in the range 400-4000 cm^{-1} at a resolution of 4 cm^{-1} using KBr pellet technique and is given in **Fig. 4.** The thiourea molecule has a sulphur atom and two nitrogen atoms which are capable of having coordination with glycine. This coordination is expected to affect NH_2 and C= S stretching vibrational bands of GT. N- H stretching vibrations observed in GT at 3369 and 3258 cm^{-1} are shifted from that of 3380 and 3279 cm^{-1} of thiourea respectively. In the thiourea coordinated crystals N-H band participate in the hydrogen bonding and hence the vibrational frequencies of N- H stretching is shifted to lower number side[29]. The absorption peak due to NH_3^+ asymmetric stretching vibration is observed at 3160 cm^{-1} in GT which is shifted to that of 3175 cm^{-1} of glycine[30,31]. The NH_3^+ absorption, characteristic of amino acids, occurring at higher wave number is more often shifted to lower wave number side due to the formation of amino salts. The NH_2 group of glycine is protonated by COOH group giving rise to NH_3^+ and COO^- group during the formation of the salt[32]. The symmetric and asymmetric stretching frequencies of COO^- group appear at 1421 and 1587 cm^{-1} respectively and COO^- wagging vibration occurs at 624 cm^{-1} [33,34].

The absorption observed at 1087 cm^{-1} in the spectrum of GT corresponds to the N- C- N stretching vibration. The increase in the frequency can be attributed to the greater double bond character of the carbon to nitrogen bond on complex formation[35]. It is observed that the C= S stretching vibration is shifted to 724 cm^{-1} in GT from 730 cm^{-1} of thiourea. If the bonding is through sulfur, there will be decrease in CS stretching frequency and an increase in CN stretching frequency[36]. The vibration frequencies of GT are compared with the frequencies of glycine (GLY) and thiourea (TU) [37] in **Table 3** which confirms the formation of GT.

Table 2-Elemental analysis of GT

Element	Composition (%)	
	Experimental	Theoretical
Carbon	22.61	23.83
Hydrogen	6.552	6.00
Nitrogen	30.51	27.79
Sulphur	23.41	21.21

Figure 4- FTIR spectrum of GT

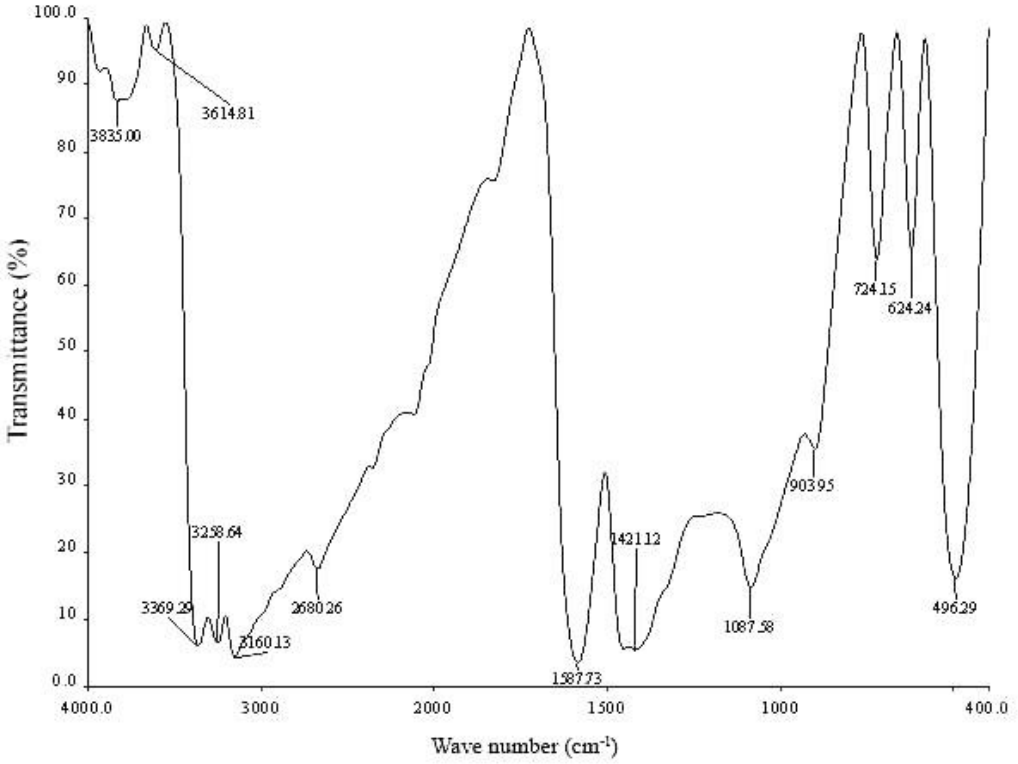


Table 3-Comparison of vibrational frequencies (cm^{-1}) of GT with the corresponding values of glycine and thiourea.

GLY[19]	TU[33]	GT[Present work]	Assignments
-	487	496	$(N\text{-}C\text{-}N)^{b}$
607	-	624	$(COO^{-})^{w}$
-	730	724	$(C{=}S)^{s}$
910	-	903	$(CH_2)^{r}$
1100	1083	1087	$(N\text{-}C\text{-}N)^{s}$, $(NH_3^{+})^{r}$
1413	1417	1421	$(C{=}S)^{s}$, $(COO^{-})^{ss}$
1605	1617	1587	$(NH_2)^{b}$, $(COO^{-})^{ass}$
2614	-	2680	$(NH_3^{+})^{s}$, $(C\text{-}H)^{s}$
3175	3177	3160	$(N\text{-}H)^{s}$, $(NH_3^{+})^{ass}$
-	3279	3258	$(N\text{-}H)^{s}$
-	3380	3369	$(N\text{-}H)^{s}$

[b] bending; [r] rocking; [w] wagging; [s] stretching; [ss] symmetric stretching; [ass] asymmetric stretching

3.3. UV-Vis studies

The optical transmittance of GT single crystal of 1 mm thickness was measured using Perkin Elmer Lamda 35 UV-Vis spectrophotometer in the range of 190-1100 nm and is shown **in Fig. 5.** The absence of absorption of light in the visible region is an intrinsic property of all the amino acids. Also low absorbance behavior shows the colorless nature of the crystal. The percentage of transmission enables the suitability of materials for optoelectronic applications. The lower UV cutoff wavelength is below 250 nm and the crystal is transparent in the range 300- 1100 nm. So GT crystal could be used for generation and mixing of frequencies over a wide range of electromagnetic spectrum including the UV and for bluegreen laser application [38].

3.4. Thermal analyses

The thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out for a sample of weight 2.2760 mg in the temperature range 20-1200°C at a heating rate of 20°C/min in nitrogen atmosphere (**Fig. 6).** From TGA it is evident that the compound GT has good thermal stability up to 180.57°C as there is no weight loss below that temperature. The TGA curve also shows that there was a weight loss of about 81.95% in the temperature range 180.57- 286.50°C due to the liberation of volatile substance in the compound. The DTA curve shows the first exothermic peak at 156.34°C, the melting point of the substance an then it undergoes two irreversible endothermi transitions. The first endothermic peak at 182.42° in the DTA curve may be due to the liberation o thiourea and the second endothermic peak a 229.84°C may be due to the liberation of glycine i GT, as glycine is known to decompose at 233°C[3 The second exothermic peak at 296.97°C in the DT curve indicates the major decomposition of th material. The heat capacity at constant pressure, Cp of GT crystal was measured by differential scannin calorimetric (DSC) analysis in the temperature rang 20-1200°C at the heating rate for the syster calibration. Powdered sample weight of 2.2760 m was placed in a sealed aluminum DSC pan. Th DSC curve of GT is shown in **Fig. 7**. The specifi heat of GT crystal at 230.03°C was found to be 100 J/g/°C.

3.5. Micro hardness Measurements

Micro hardness testing is one of the best methods for understanding the mechanical properties of materials [40]. Hardness of the material is a measure of resistance, that offers to deformation[41]. The transparent polished crystal free from cracks was selected for hardness measurements. The indentations were made on the flat surface with the load ranging from 25 to 100 g using Shimadzu make-model-HMV-2 fitted with Vicker's pyramidal indenter and attached to an incident light microscope. The indentation time was kept as 5s for all the loads. The Vickers's hardness number H_v was calculated from the following expression.

$H_v = (1.8544\ P)/d^2\ kg/mm^2$

Where P is the applied load in kg and d is the diagonal length of the indentation impression in millimeter and 1.8544 is a constant of a geometrical factor for the diamond pyramid. A plot obtained between the hardness number and the load is shown in **Fig. 8.** The relation connecting the applied load and diagonal length'd' of the indentor is given by Meyer's law $P= ad^n$, where n is the Meyer's index or work hardening coefficient. A plot obtained between log (P) and log (d) gives a straight line. Meyer's index is calculated from the slope of straight line. From many observations on various materials Onitsch [42] pointed out that 'n' lies between 1 and 1.6 for moderately hard materials, and it is more than 1.6 for soft materials, The observed value of Meyer's index for GT is 4 and hence GT belongs to the soft materials category.

Figure 5- Transmittance spectrum of GT Crystal

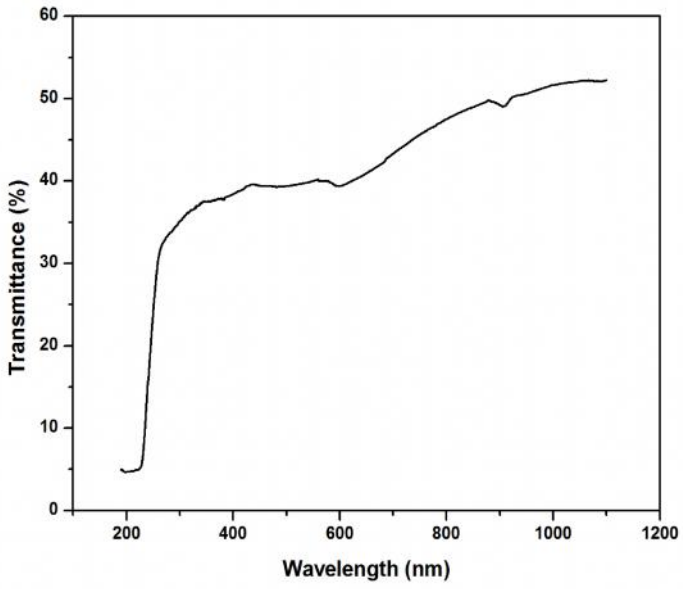


Figure 6- TGA / DTA spectrum of GT

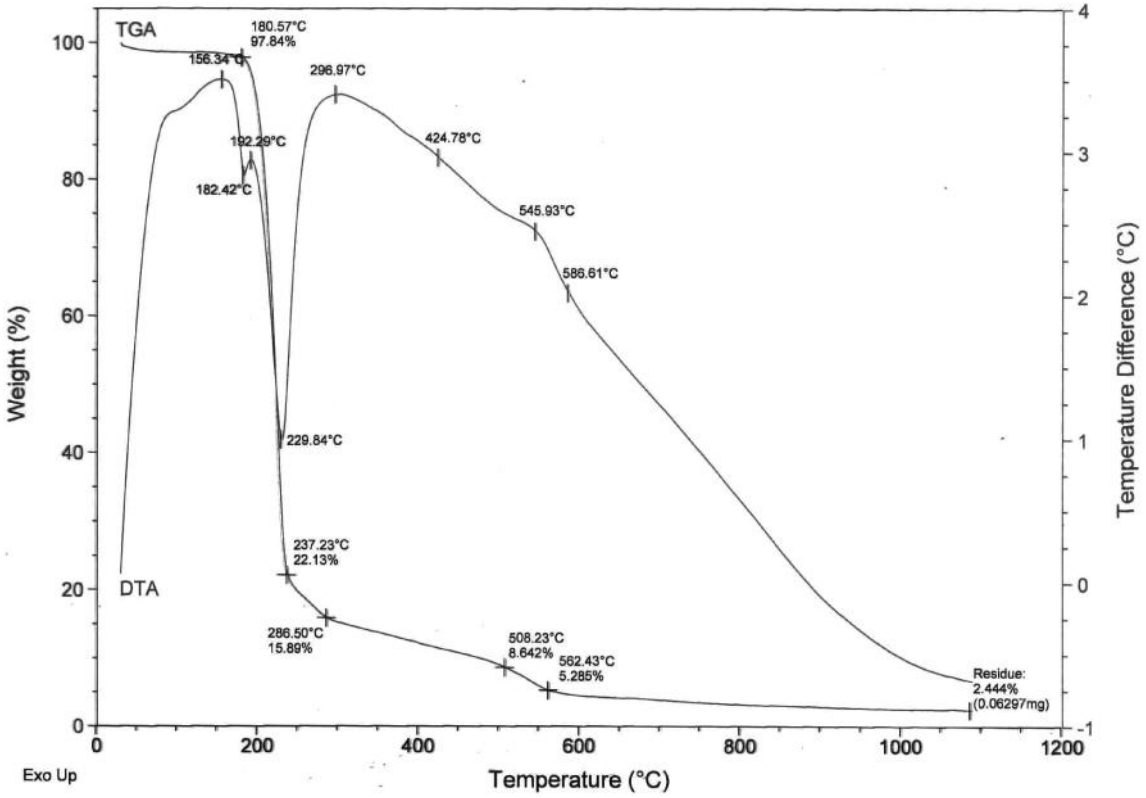


Figure 7 -DSC spectrum of GT

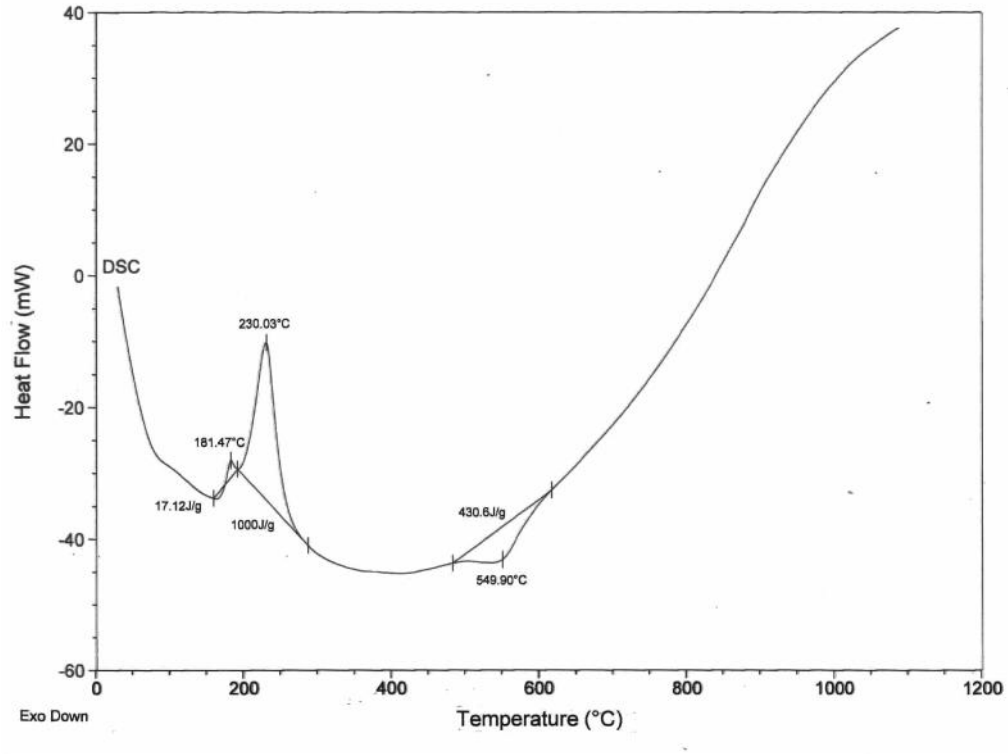
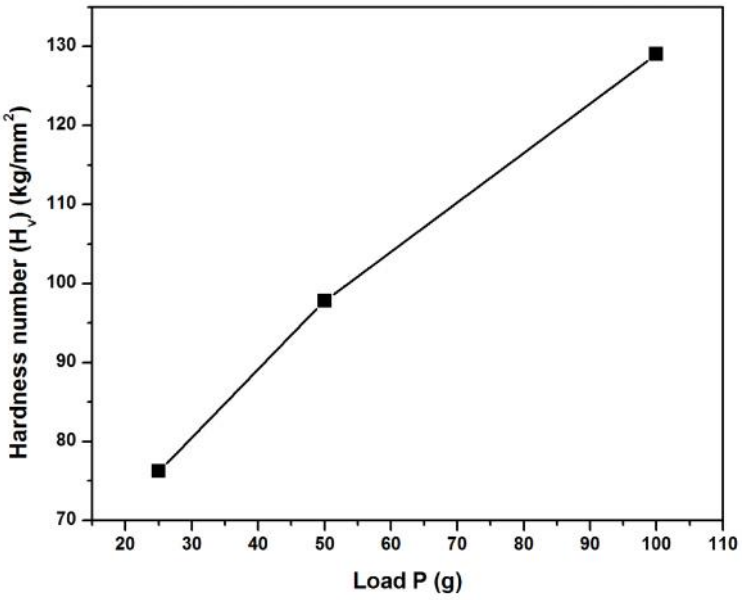


Figure 8 -Plot of Vicker's hardness H_v verses load P for GT crystal



3.6. Nonlinear optical studies

A quantitative measurement of the second harmonic generation (SHG) efficiency of GT crystal was determined by the modified version of powder technique developed by Kurtz and Perry[43]. The GT crystal was made into powder and it was packed densely between two transparent glass slides. Nd: YAG laser was used as a light source. A fundamental laser beam of 1064 nm wavelength, 8 ns pulse in depth with 10Hz pulse rate was made to fall on sample cell. The power of the incident beam was measured using a power meter and it was 5.7 m J/pulse. The transmitted fundamental wave was passed over a monochromater which separates 532 nm (SHG signal) from 1064 nm. The green light of 532 nm was detected by a photo multiplier tube and displayed on a storage oscilloscope. KDP crystal was powdered to the identical size of GT and was used as reference material in the SHG measurement. The SHG efficiency of GT (8 mV) is approximately 0.5 times that of KDP (15 mV).

4. Conclusion

Optical quality single crystals of glycine thiourea were grown from aqueous solution by slow evaporation at room temperature. Unit cell parameters of GT obtained from single crystal XRD show that the crystal belongs to monoclinic system. Sharp peaks of powder XRD of the crystal show good crystalline nature of the compound. The chemical composition of the compound estimated by CHN analysis is in good agreement with the expected composition of GT, thus showing the formation GT crystal. FT-IR spectrum of the grown GT crystal confirmed the vibrational frequencies of various functional groups of GT. The TGA/DTA analyses revealed the melting point and the thermal stability of the GT crystal. From DSC spectrum the specific heat of GT at 230.03°C was found to be 1000 J/g/$^{\circ}$ C. The optical transmittance window and lower cut off wavelength of GT crystal were identified by UV-Vis-NIR studies. The Vicker's micro hardness test of GT shows that the hardness value increases with load which confirms the reverse indentation size effect and soft nature of the material. Second harmonic generation test conducted for the powdered GT crystal using Nd: YAG laser showed its relative SHG efficiency is approximately 0.5 times that of KDP.

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