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Growth, Spectral, Optical, Thermal and Mechanical Properties of Thiourea doped Trisglycine Zinc Chloride Nonlinear Optical Crystal

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Abstract- Single crystals of thiourea doped trisglycine zinc chloride (TuTGZC) were grown from aqueous solution by slow evaporation technique. Single crystal X-ray diffraction analysis reveals that TuTGZC crystals belong to orthorhombic system. Various diffracting planes of the grown crystal were identified from the powder X-ray diffraction study. The FT- IR spectral analysis confirmed the presence of the functional groups present in the grown TuTGZC crystal. Optical studies showed that the TuTGZC crystal has good transparency in the entire UV and visible range of the spectrum. The relative second harmonic generation (SHG) efficiency of TuTGZC crystal was found by Kurtz – Perry powder technique. Thermal stability and melting point of the grown crystal were found by thermal analyses. The mechanical strength of the grown crystal is estimated by Vicker's micro hardness test.

Index Terms- Single crystal, slow evaporation technique, single crystal X- ray diffraction, FT-IR, optical studies, Thermal, micro hardness.

I. Introduction

Highly efficient nonlinear optical (NLO) materials with good mechanical strength and chemical stability are essentially required for opto electronic applications such as optical communications, high speed information processing and optical data storage [1, 2]. Nowadays, high storage capacity optical devices require laser sources at short wavelengths typically around blue region [3- 6]. Semiorganic nonlinear optical materials are reputed candidates for device fabrication, owing to their large nonlinear coefficient, high laser damage threshold and exceptional mechanical and thermal stability. Semiorganic materials are metal- organic coordination complexes in which the organic ligand plays a dominant role for the NLO effect. As for the metallic part, the focus is on group II B metals (Zn, Cd and Hg) as these compounds usually have a high transparency in the UV region, because of their closed shell [7, 8]. Also, in metal-organic compounds the mechanical and thermal stability are considerably enhanced due to the organic ligand is ionically bonded with inorganic host [9]. In the organo- metallic compounds, the metal centre is engaged in π- bonding with the organic ligand which allows metal to ligand charge transfer, and produce excellent second harmonic generation devices.

Among amino acids, glycine forms crystals with structures that frequently lead to dielectric instabilities, which in turn lead to the formation of ferroelectric phases [10]. The inherent polarity and the zwitterionic nature of the glycine molecule are useful prerequisites for the synthesis of new non-centrosymmetric crystals. Compounds of glycine with metal halogenide zinc chloride ($ZnCl_2$) namely glycine zinc chloride hydrate, bisglycine zinc chloride dihydrate and trisglycine zinc chloride that were already published [11, 12]. The crystal structures of glycine zinc chloride hydrate and bisglycine zinc chloride dihydrate compounds are centrosymmetric space groups $P2_1/a$ and C_2/c respectively [13]. Trisglycine zinc chloride (TGZC) crystallizes in the non- centrosymmetric space group $Pbn2_1$ and the crystal structure has been reported. In that paper refractive indices, piezoelectric properties and type I and type II phase matching conditions of the TGZC crystal in the red and near IR region were discussed [14]. Detailed nonlinear properties of trisglycine zinc chloride such as many- photon stimulated Raman scattering, Cherenkov- type second harmonic generation (SHG) and third harmonic generation (THG) were discussed [15]. HRXRD and NMR spectral characterizations of TGZC were discussed [16].

Organic thiourea molecule (NH_2CSNH_2) is an interesting matrix modifier and it has the ability to form an extensive network of hydrogen bonds. In order to observe the changes in structural, optical, thermal and mechanical properties, thiourea molecule is used as dopant to tailor and improve the properties of trisglycine zinc chloride crystals and to meet the practical device fabrication requirements. In the present work, the structural, vibrational, optical, thermal and mechanical properties of TuTGZC crystal are investigated. The results of the investigations are presented in this paper.

II. EXPERIMENTAL

Trisglycine zinc chloride (TGZC) was synthesized by dissolving high purity analar grade glycine (NH_2CH_2COOH) and zinc chloride ($ZnCl_2$) in the ratio 3:1 in an aqueous medium according to the reaction.

$$3(NH_2CH_2COOH) + ZnCl_2 \rightarrow (NH_3CH_2COO)_3 . ZnCl_2 .$$

The required volume of zinc chloride was dissolved in double distilled water . Then the calculated amount of glycine salt was slowly dissolved in the zinc chloride solution. Then 0.1 mol thiourea was dissolved and stirred well. The solution temperature was always maintained below 50°C. Impurity content of the TuTGZC was minimized by recrystallization method. Extreme care was taken while crystallizing the salt to avoid oxidation of glycine.The solubility of the TuTGZC in double distilled water, ethanol and methanol in the temperature range 30- 50°C in steps of 5°C was found gravimetrically. Water was found to be suitable solvent for growth. Fig. 1 shows the solubility curves and the positive slope of the solubility curve enables growth by slow evaporation method. Saturated solution of TuTGZC was prepared. The final saturated solution was filtered using a 0.2 μm porosity filter papers after suitable preheating. The solution was kept in beaker covered with perforated sheet and loaded in the constant temperature bath set at 35°C. Transparent and good optical quality grown crystals were harvested after 25 days by slow evaporation solution growth method. Grown TuTGZC crystal of size (25x10x10) mm^3 is shown in Fig. 2.

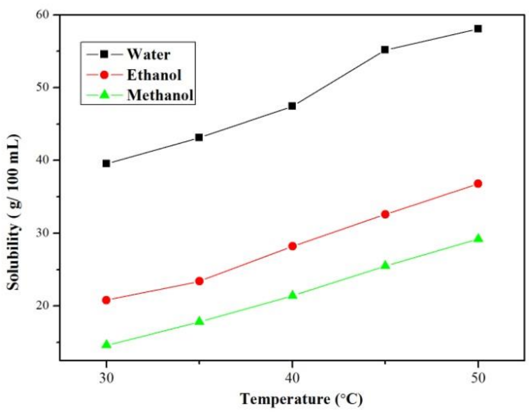

Fig. 1 : Solubility curves of TuTGZC.

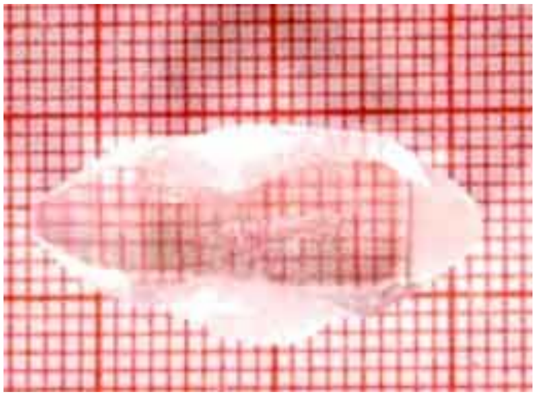

Fig. 2 : Photograph of as grown crystal of TuTGZC.

2. 1 CHARACTERIZATION TECHNIQUES

The grown crystals was subjected to single crystal X-ray diffraction using an ENRAF NONIUS CAD-4 diffractometer with MoKα (λ=0.71073 Å) 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 was recorded with a Perkin-Elemer RXI spectrometer using KBr pellet technique in the wave number range 400- 4000 cm^{-1} in order to confirm the presence of functional groups of the grown crystals. UV-vis transmittance spectrum of TuTGZC crystal was recorded using Perkin Elemer-lambda 35 UV-vis spectrophotometer in the range of 190- 1100 nm. Second harmonic generation efficiency was measured using Kurtz and Perry powder technique using Nd: YAG laser beam of energy 1.95 mJ/ pulse. Thermal analysis was carried out using SDT Q600V 8.3 build 101 simultaneous DTA/TGA analyzer in the nitrogen atmosphere. Microhardness measurements were made using Shimadzu HMV-2 microhardness tester fitted with a Vicker's diamond pyramidal indenter.

III. RESULTS AND DISCUSSION

3. 1. X-ray diffraction analysis

Single crystal X-ray diffraction study was performed for the grown TuTGZC crystal. It was found that TuTGZC crystal belong to orthorhombic system (α= β= γ= 90°). Lattice parameter values of TuTGZC are compared with reported TGZC in Table 1. In the case of doped sample, a slight variation in the cell parameters is observed, which may be due to the incorporation of thiourea ligand. This analysis revealed that the induction of thiourea ligand in the TGZC crystal does not change the crystal system though there is a small change in the lattice parameters. The powder sample of TuTGZC 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 Lattice parameters of TGZC and TuTGZC

Samples	a (Å)	b (Å)	c (Å)	Volume ($Å^3$)
TGZC[a]	11.230	15.251	15.564	2666
TuTGZC[b]	11.10	15.15	15.38	2586

[a] Ref. [14], [b] Present work.

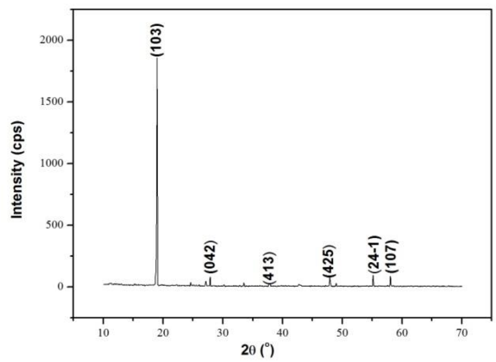

Fig. 3 : Powder XRD spectrum of TuTGZC

3. 2. FT- IR spectral analysis

The mid Fourier transform infrared (FT-IR) spectrum of TuTGZC crystal is shown in Fig. 4. The peak at 3188 cm^{-1} is considered to be due to the NH_2 group which is associated with a broad band. This broad band in high wave number region indicates the presence of intermolecular hydrogen bonds in the title crystal. The asymmetric and symmetric NH_3^+ vibrations occur at 1642 and 1501 cm^{-1} respectively [17]. The asymmetric stretching vibration of CH_2 appears at 2160 cm^{-1} [18]. The wagging and stretching vibration ofCH_2 appear at 1309 and 903cm^{-1} respectively. The asymmetric stretching vibration of CCN gave a peak at 1033 cm^{-1}. The wave number of the bands for both TGZC and TuTGZC are compared and given in Table 2. The frequencies in the high wave number region are slightly shifted for thiourea doped TGZC crystal due to N- H bands participate in the hydrogen bonding. The deprotonated carboxylic group (COO^-) symmetric stretching vibrational frequency of the TuTGZC crystal appears at 1417 cm^{-1}. But in TGZC crystal, this band appears at 1411 cm^{-1}. This variation may be due to mixing of C = S and C – N stretching vibrations in this region [19]. Deformation mode and rocking mode of COO^- are observed strongly for the title crystal at 674 and 568 cm^{-1} respectively [20]. The presence of dopants and intermolecular hydrogen bonding network between the cation and anion lead to corresponding shift of few stretching and deformation modes. The results confirmed that the glycine molecule existed as zwitter ions in the crystalline state of both TGZC and TuTGZC.

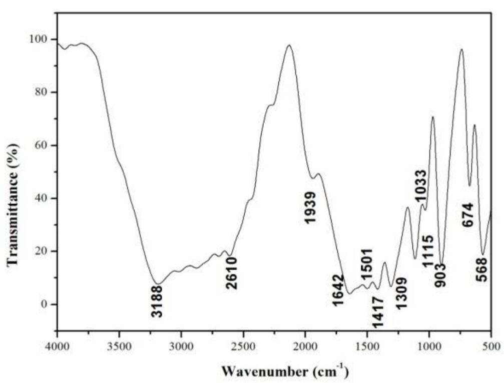

Fig. 4 : FTIR spectrum of TuTGZC

Table 2 wave number assignments for TGZC and TuTGZC.

Wave number (cm^{-1})		Assignments
TGZC [16]	TuTGZC Present work	
1560	1501	asymmetric stretching of $(NH_3)^+$
1498	-	rocking $\delta(CH_2)$
1411	1411	symmetric stretching of (COO^-)
1325	1309	wagging of (CH_2)
1134	-	rocking of $(NH_3)^+$
1126	1115	rocking of $(NH_3)^+$
1033	1033	asymmetric stretching of(CCN)
928	-	rocking of (CH_2)
918	903	rocking of (CH_2)
897	-	asymmetric stretching of (CCN)
686	674	rocking of (COO^-)
593	-	rocking of $(NH_3)^+$
561	568	rocking of (COO^-)

3. 3. Optical studies

UV- visible spectral study is a useful tool to determine the transparency which is an important requirement for a material to be optically active [21]. The optical transmittance spectrum of the grown crystal of thickness 2 mm was recorded in the wavelength range 190- 1100 nm and is shown in Fig. 5. Low absorption in the entire visible and near infrared region with the low cut- off wavelength at 248 nm suggests that the material is quite suitable for SHG generation and opto electronic applications. The good transmission of the crystal in the entire visible region suggests its suitability for NLO devices [22, 23].

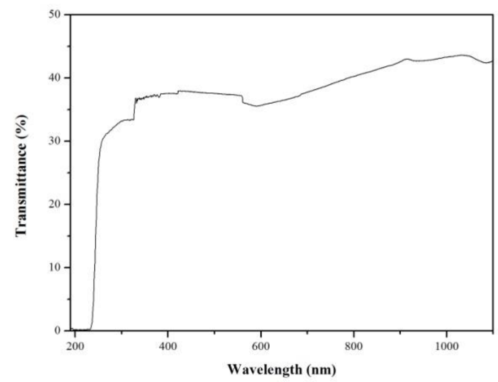

Fig.5 : UV-vis transmittance spectrum of TuTGZC.

3. 4. Nonlinear optical studies

In order to find the nonlinear optical efficiency, the second harmonic generation behaviour of the powdered TuTGZC material was tested using the Kurtz and Perry method [24]. The second harmonic generation was confirmed by emission of green light (λ = 532 nm). The output second harmonic signal of 65 mV for TuTGZC crystal sample and 60 mV for standard KDP sample were found for the same input energy. Hence the measured relative SHG efficiency for TuTGZC sample was about 1.08 times, as that of KDP. When TGZC crystals are doped with thiourea, an NLO material, it is possible that the SHG efficiency may be improved and this is observed in this work. The value of the reported SHG efficiency for TGZC crystal was 0.5 times than that of KDP [25], and hence thiourea doped TGZC crystal is a better candidate for NLO and optoelectronic applications.

3. 5. Thermal analysis

TGA/DTA analysis of the TuTGZC crystal was carried out in the temperature range 10- 800°C. The recorded themogram is shown in Fig. 6. From TGA curve it is observed that the weight loss start from 192°C. There is 53% weight loss between 269°C and 472°C. This weight loss is due to the liberation of chlorine atoms and glycine molecule. As there is no weight loss below 192°C, it indicates that the crystal is devoid of any physically adsorbed water in it. The DTA curve shows a sharp endothermic peak at 244.6°C which indicates the melting point of the crystal. This endothermic event is in good agreement with the TGA trace.

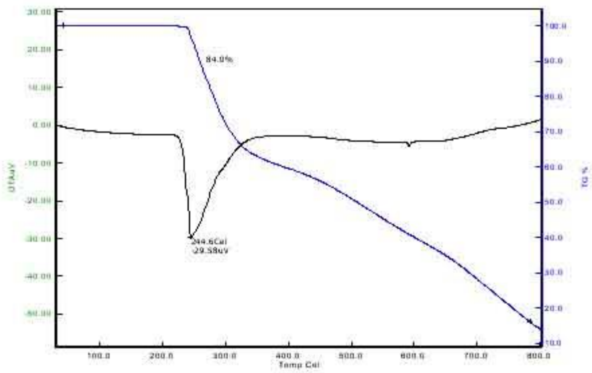

Fig. 6 : TG/DTA spectrum of TuTGZC

3. 6. Micro hardness studies

Hardness of the material is a measure of resistance, that offers to deformation. 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 Vicker's hardness (H_v) was calculated from the relation [26],

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

Where P is the applied load and d the average length of the diagonal of the indentation mark. With P in g and d in µm, the units of H_v turned out to be kg/mm^2. The variation of micro hardness with applied load for the prominent (100) plane of the TuTGZC crystal is shown in Fig. 7.

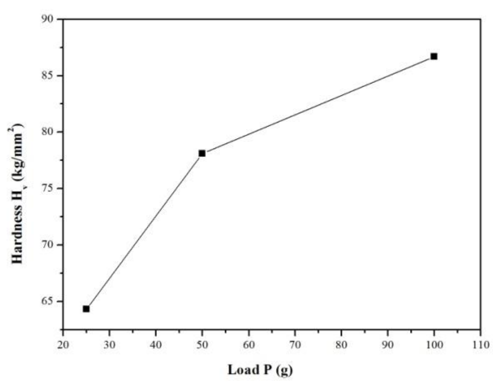

Fig. 7 : Variation of hardness number with load.

It is found that the hardness values increases with the increase of the applied load. This behaviour of increasing microhardness with the load known as reverse indentation size effect (RISE) [27], which is also attributed due to existence of distorted zone near crystal medium interface, effect of vibrations, specimen chipping etc., and the plastic deformation is dominant. At low loads or strains, plastic deformation of crystals mainly involves the nucleation of dislocations along a particular slip system. The RISE effect can be qualitatively explained on the basis of the depth of penetration of the indenter [28]. At small loads, the indenter penetrates only the surface layers and therefore, the effect is shown sharply at the early stages. When the applied load increases, the penetration depth also increases and the overall effect must be due to the surface and inner layers. When only one slip system is active during plastic deformation at low loads, the number of active parallel glide planes during indentation is low. Therefore the nucleating dislocations rapidly propagate into the material without experiencing substantial mutual interaction stress between them. Consequently in this stage, indentation depth increases proportionally with applied pressure.

IV. CONCLUSION

Single crystals of thiourea doped trisglycine zinc chloride (TuTGZC) were grown from the aqueous solution by slow and controlled solvent evaporation technique. The lattice parameters of the grown crystals were obtained by single crystal XRD. It was found that the TuTGZC crystal was crystallized in the orthorhombic system. Powder XRD spectrum shows the crystalline nature of the compound. Functional groups of the grown TuTGZC crystal were identified by FTIR spectral analysis. The good transparency in the entire visible region and low cut-off wavelength facilitate the TuTGZC crystal to be a potential material for NLO applications. Second harmonic generation test conducted for the powdered TuTGZC crystal using Nd: YAG laser showed its relative SHG efficiency is approximately 1. 08 times that of KDP. The TGA/DTA analyses revealed the melting point and the thermal stability of the TuTGZC crystal. The Vickers micro hardness study shows that hardness steadily increases with the applied load and implies the reverse indentation size effect (RISE). The above characterization and the nonlinear efficiency confirm that the TuTGZC crystal is suitable for the fabrication of various optoelectronic devices.

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