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# Comparative characterization study of pure and glycine doped potassium thiourea chloride crystal for laser frequency conversion applications

S.M. Azhar<sup>a</sup>, Mohd Anis<sup>c</sup>, S.S. Hussaini<sup>d</sup>, M.D. Shirsat<sup>e</sup>, G. Rabbani<sup>b,\*</sup><sup>a</sup> Department of Physics and Electronics, Sir Sayyed College, Aurangabad 431001, Maharashtra, India<sup>b</sup> Department of Physics and Electronics, Maulana Azad College, Aurangabad 431001, Maharashtra, India<sup>c</sup> Department of Physics, Sant Gadge Baba Amravati University, Amravati 444602, Maharashtra, India<sup>d</sup> Crystal Growth Laboratory, Department of Physics, Milliya Arts, Science and Management Science College, Beed 431122, Maharashtra, India<sup>e</sup> Intelligent Materials Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431005, Maharashtra, India

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## ABSTRACT

In current study doping of glycine (G) in potassium thiourea chloride (PTC) crystal has been firstly achieved and glycine doped PTC (G-PTC) crystal has been grown by slow solution evaporation technique. The unit cell parameters of crystals have been determined by means of single crystal X-ray diffraction technique. The functional groups of pure and G-PTC crystal have been identified using Fourier transform infrared analysis. In UV–visible studies, the increased optical transparency of G-PTC crystal has been measured within 200–900 nm and the optical constants have been determined using the transmittance data. The Kurtz and Perry test has been performed to confirm the enhancement in second harmonic generation (SHG) efficiency of G-PTC crystal as compared to KDP and PTC crystal. The temperature dependent dielectric analysis has been carried out to investigate the dielectric constant and dielectric loss of grown crystal. The thermal stability of the grown crystal has been determined using the thermogravimetric analysis.

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## 1. Introduction

In present technological era immense attention has been drawn by thiourea metal complex (TMC) crystals due to wide operating wavelength range, high mechanical and thermal stability, optically active accentric symmetry, high chemical stability, extended charge transfer and improved nonlinear optical (NLO) behavior. Owing the foresaid qualities the TMC crystals are exclusively demanded for tuning and fabricating the technologically vital optoelectronics, photonics and NLO devices [1,2]. A large number of TMC crystals namely bis-thiourea cadmium chloride (BTCC), zinc thiourea sulphate (ZTS), zinc thiourea chloride (ZTC), copper thiourea chloride (CTC), bis thiourea zinc acetate (BTZA), bis thiourea cadmium acetate (BTCA), potassium thiourea iodide (PTI) and potassium thiourea bromide (PTB) have been reported [3,4]. Recently, doping of organic and inorganic impurities to TMC

crystal has revealed significant enhancement in various properties of TMC crystals. In order to gain favorable physico-chemical properties for fabricating advanced devices, doping of amino acid glycine has been encouraged to enhance the optical, thermal, mechanical and second harmonic generation (SHG) efficiency of BTCC [6], ZTS [7], ZTC [8] and BTCA [9] TMC crystals. Amongst the TMC crystals the potassium thiourea chloride (PTC) crystal is an NLO material occurring in tetragonal symmetry with optical transparency above 60%, moderate mechanical resistance and thermal stability up to 198 °C [5]. Hitherto not a single researcher has made an attempt to uplift the characteristic properties of PTC crystal. This is the very first investigation to grow the glycine doped PTC (G-PTC) crystal and analyze its structural, UV–visible, SHG efficiency, dielectric and thermal properties to discuss its application for laser frequency doubling applications.

## 2. Experimental procedure

The host material PTC has been synthesized by dissolving thiourea and potassium chloride in 1:4 ratio in double distilled deionized water. The PTC complex was successively recrystallized to

\* Corresponding author.

E-mail addresses: [dr.grabbani@yahoo.com](mailto:dr.grabbani@yahoo.com), [hussainiss34@gmail.com](mailto:hussainiss34@gmail.com) (G. Rabbani).



Fig. 1. As grown G-PTC crystal.

Table 1  
XRD data.

Crystal	Cell parameters (Å)	Cell volume (Å <sup>3</sup> )	Crystal system
PTC	$a = 20.478, b = 20.478, c = 8.53$	3577.04	Tetragonal
G-PTC	$a = 20.491, b = 20.491, c = 8.55$	3589.98	Tetragonal

eliminate the occurring impurities. The purified PTC compound was then dissolved in double distilled de-ionized water upto supersaturation is achieved and 3 mol% of glycine was added to the solution. The glycine added PTC solution was allowed to agitate for 8 h at constant stirring speed to allow the homogeneous doping of glycine in PTC. The glycine doped PTC solution was then filtered and kept for slow solution evaporation in a constant temperature bath at 40 °C. The as grown glycine doped PTC (G-PTC) single crystals are shown in Fig. 1.

### 3. Results and discussion

#### 3.1. Single crystal X-ray diffraction (XRD) analysis

The structural parameters of the grown crystals have been determined by employing the single crystal XRD analysis using the Enraf Nonius CAD4 single crystal X-ray diffractometer. The determined XRD data is shown in Table 1 and it reveals that the pure and G-PTC crystals belong to tetragonal crystal system. The structural parameters of PTC crystal are in good agreement with literature [5]. The doping of glycine imparts the lattice strain on volumetric sites of PTC crystal leading to slight change in cell parameters of G-PTC crystal as compared to PTC.

Table 2  
Functional groups of pure and G-PTC crystal.

Wavenumber (cm <sup>-1</sup> )		Assignment
PTC	G-PTC	
681	708	C-S stretching
811	820	C-H plane deformation
1022	1042	N-C-N stretching
1462	1459	CH <sub>3</sub> antisymmetric deformation
1535	1524	N=O anti-symmetric stretching
1645	1645	C=O stretching
1692	1690	C=N stretching
	3256	NH <sub>2</sub> symmetric stretching
	3401	O-H stretching

#### 3.2. Fourier transform infrared (FT-IR) analysis

The functional groups of pure and G-PTC crystals have been identified using the FT-IR spectral analysis performed using the Bruker  $\alpha$ -ATR spectrophotometer. The recorded FT-IR spectrum of crystals is shown in Fig. 2a and b. The C-S stretching vibration associated with thiourea is observed at 708 cm<sup>-1</sup>. The absorption at 820 cm<sup>-1</sup> is attributed due to C-H plane deformation. The N-C-N bond stretching vibration is evident at 1042 cm<sup>-1</sup>. The CH<sub>3</sub> antisymmetric deformation vibration is confirmed at 1459 cm<sup>-1</sup>. The wavenumber 1524 cm<sup>-1</sup> is assigned to N=O anti-symmetric stretching. The characteristic C=O bond stretching vibration is observed at 1645 cm<sup>-1</sup>. The absorption observed at 1690 cm<sup>-1</sup> confirms the C=N stretching vibration. The NH<sub>2</sub> symmetric stretching vibration is observed at 3256 cm<sup>-1</sup>. The absorption observed at 3401 corresponds to characteristic O-H bond stretching vibration associated with carboxyl group of glycine. The N-H stretching is attributed within 3617-3850 cm<sup>-1</sup>. The identified shift in functional frequencies (see Table 2) of PTC crystal confirms the incorporation of dopant glycine in PTC crystal.

#### 3.3. UV-visible studies

The transmittance spectrum (Fig. 3a) of 2 mm pure and G-PTC crystal has been recorded using the spectrophotometer (Shimadzu UV-2450). It is observed that the transmittance window is wide and magnitude of transmittance is 67% for PTC crystal and 77% for G-PTC crystal. The rise in transmittance of G-PTC crystal by 10% indicates that the dopant glycine has significantly reduced the crystal and lattice defects which benefits the crystal quality and offers less scattering of light in crystal system [10]. The materials with high transparency over wide range of wavelength substantiate its exclusive utility for NLO applications such as laser frequency

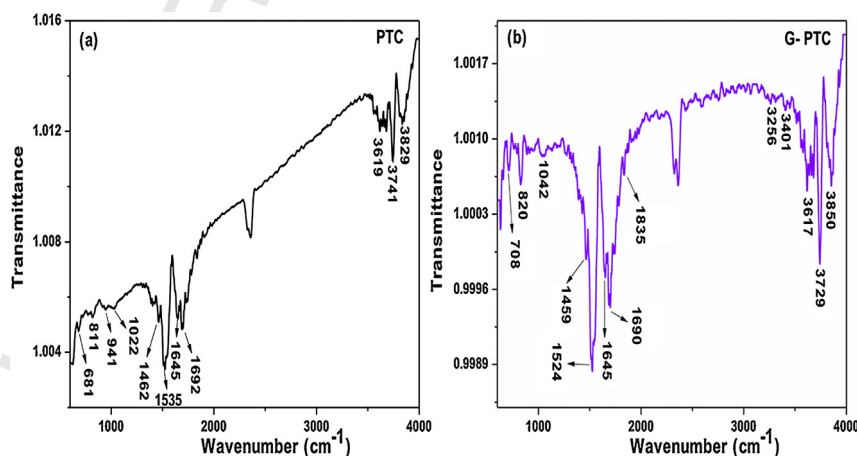


Fig. 2. FT-IR spectrum of (a) PTC (b) G-PTC.

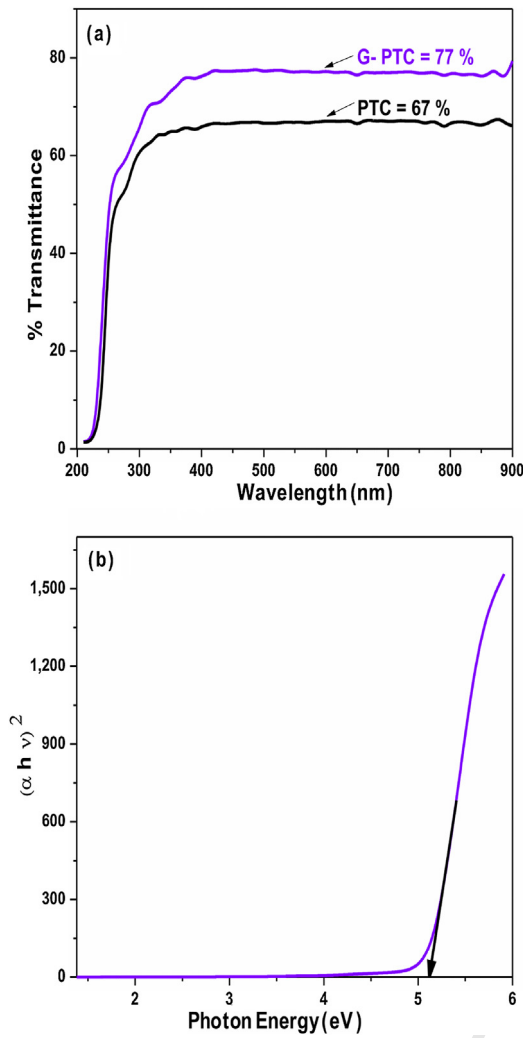


Fig. 3. (a) Transmittance spectrum (b) Tauc's plot.

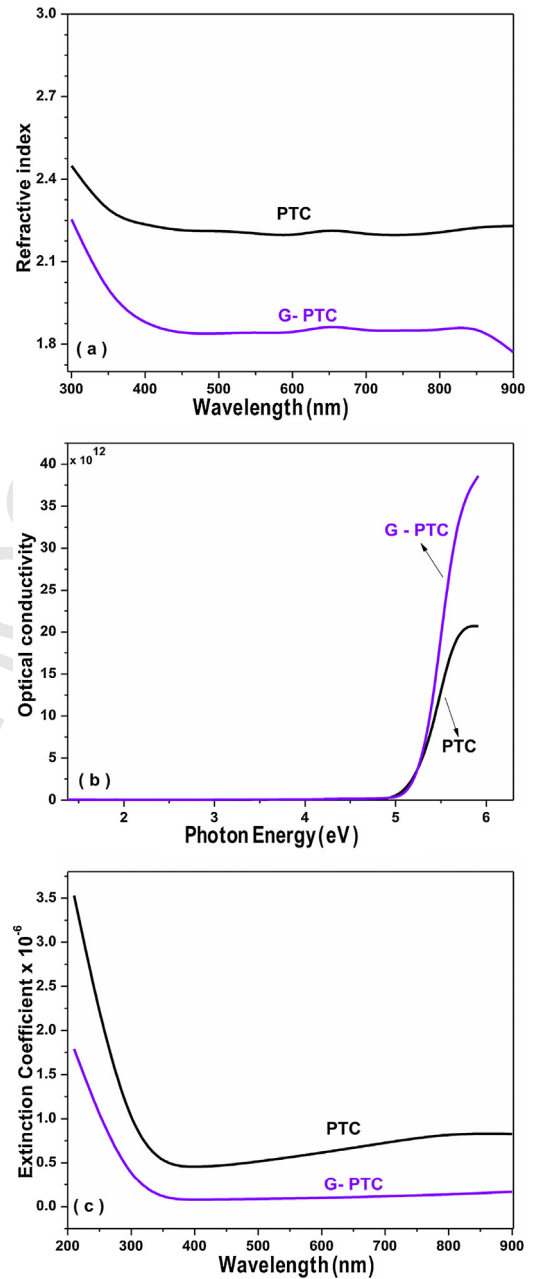


Fig. 4. (a) Refractive index vs. wavelength. (b) Optical conductivity vs. photon energy. (c) Extinction coefficient vs. wavelength.

conversion devices [11]. The inter-dependence of photon energy ( $h\nu$ ) and absorption coefficient ( $\alpha$ ) helps to identify the band gap ( $E_g$ ) of the material. The Tauc's plot shown in Fig. 3b has been drawn using the relation  $(\alpha h\nu) = A(h\nu - E_g)^{1/2}$ . The band gap of G-PTC crystal is found to be 5.1 eV. The material with high band gap is primarily advantageous for UV-tunable lasers [3]. The detail information of optical constants such as refractive index ( $n$ ), optical conductivity ( $\sigma_{op}$ ) and extinction coefficient ( $K$ ) of the material helps to identify distinct photonics device applications [12]. The variation of refractive index (Fig. 4a) of pure and G-PTC crystal in visible region determines the optical density and photo-refraction tendency of the crystal system. It is observed that the refractive index of G-PTC crystal is significantly lower than PTC crystal. The high transmittance materials with lower refractive index are largely demanded for calibrating optical filters, resonators and detectors [13]. The nature of optical conductivity and extinction coefficient is shown in Fig. 4b and c respectively. The high optical conductivity and lower extinction coefficient of G-PTC crystal vitalizes its prime usability for optical information processing and computing devices [14].

### 3.4. SHG efficiency test

The SHG efficiency of grown crystal has been determined using the standard Kurtz and Perry powder technique using the Nd:YAG laser operating at 1064 nm with repetition rate of 10 Hz and pulse

width 8 ns. The perfectly grown crystals were finely grinded to powder form and tightly filled in a micro-capillary tube of standard bore. The prepared samples were multishot normally by a laser beam and the emergence of sharp green light at the output confirms the NLO behaviour of material. The optical signal of the sample was collected through the array of photomultiplier tube and converted into voltage through digital oscilloscope. The output voltage offered by KDP, PTC and G-PTC crystal sample was 75 mV, 56 mV and 88 mV respectively. The SHG efficiency of G-PTC crystal is found to 1.57 times greater than PTC and 1.17 times greater than standard KDP material. The SHG efficiency of G-PTC crystal is significantly higher than G-BTCC crystal [6]. The high SHG efficiency of G-PTC crystal pronounces its utility for laser frequency conversion applications.

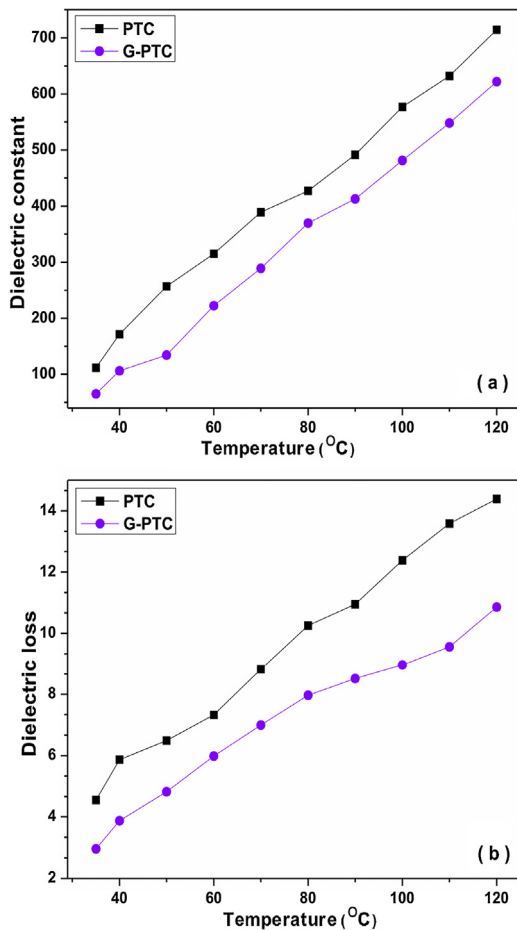


Fig. 5. Temperature dependent. (a) Dielectric constant. (b) Dielectric loss.

### 3.5. Dielectric studies

The dielectric constant and dielectric loss of pure and glycine doped PTC crystal has been evaluated at different temperatures using the HIOKI 3532 LCR tester. The surface of the crystal samples were polished and pasted by the silver paste to ensure the electrical contact and avoid the loss of data. The measurements were performed and the variation of dielectric constant with reference to temperature is shown in Fig. 5a. The dielectric constant is contributed by polarization mechanism and the electronic, ionic, dipolar and space charge polarization activity of the material is highly influenced by external frequency and applied temperature [15]. The dielectric constant of pure and G-PTC crystal increases with rise in temperature. The rise in dielectric constant of crystals is attributed by dominance of space charge polarization in high temperature range. However, the dielectric constant of G-PTC crystal is significantly lower than PTC crystal. The lower dielectric constant material facilitates low power consumption which is vital parameter for manufacturing optoelectronics, broad band electro-optic modulators and field detectors [16]. The behavior of dielectric loss of grown crystals is shown in Fig. 5b. The dielectric loss of crystals increases with increase in temperature. The lower dielectric loss indicates the decrease in lattice defects density which is essential parameter to sustain dissipation of energy through the material [17]. The lower dielectric constant and dielectric loss of G-PTC crystal suggest its potential candidature for tuning microelectronics, photonics, THz wave generators and optoelectronics devices [18].

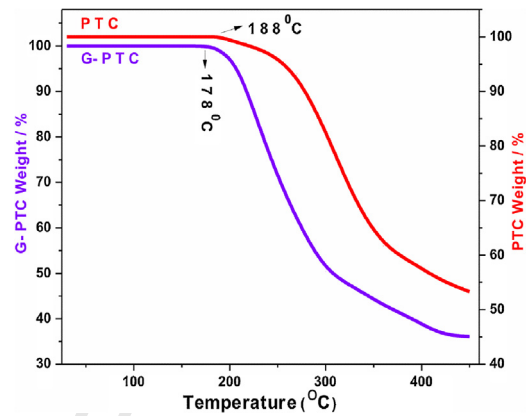


Fig. 6. Thermogravimetric curve.

### 3.6. Thermogravimetric analysis

The identification of decomposition temperature of material is of vital importance to impart it for designing high edge photonic devices. Hence, the thermal stability of grown crystal has been determined in a homogeneous nitrogen atmosphere using the Perkin-Elmer Diamond thermal analyzer constrained to operate within 30–450 °C at a heating rate of 20 °C/min. The thermogravimetric (TG) curve of pure and glycine doped PTC crystal is shown in Fig. 6. It is observed that both the crystal shown no decomposition till 100 °C which evidences the absence of water molecules in the crystal system. The decomposition temperature of PTC crystal is found to be 188 °C where as the G-PTC initiates to decompose at 178 °C. The fall in decomposition temperature of G-PTC crystal might have been occurred due to unstable nature of glycine at higher temperatures. It is notable that the weight loss of pure and G-PTC crystal is 35.4% and 54.3% respectively at 450 °C.

### 4. Conclusion

The G-PTC crystal has been grown by slow evaporation solution technique at 40 °C. The XRD analysis established the change in volume and tetragonal crystal system of G-PTC crystal. The identified functional groups in FT-IR analysis confirmed the incorporation of glycine in PTC crystal. The G-PTC crystal exhibits the optical transparency of 77% which is 10% higher than PTC crystal and band gap of G-PTC crystal is 5.1 eV. The G-PTC crystal delivers high optical conductivity, lower extinction coefficient and refractive index vitalizing its utility for photonics applications. The SHG efficiency of G-PTC crystal is 1.57 times higher than PTC and 1.17 times higher than KDP crystal. The dielectric studies revealed that the dielectric constant and dielectric loss of crystals is highly influenced by temperature. The G-PTC crystal offers notably lower dielectrics than PTC crystal. The decomposition temperature of G-PTC crystal is 178 °C. The improved optical quality, enhanced SHG efficiency and lower dielectrics make the G-PTC crystal promising for advanced photonics, optoelectronics and NLO device applications.

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