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

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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.

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

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Fig. 1. As grown G-PTC crystal.

Table 1
XRD data.

Crystal	Cell parameters (Å)	Cell volume (Å)	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^{-1})		Assignment
PTC	G-PTC	
681	708	C–S stretching
811	820	C–H plane deformation
1022	1042	N–C–N stretching
1462	1459	CH_3 antisymmetric deformation
1535	1524	N=O anti-symmetric stretching
1645	1645	C=O stretching
1692	1690	C=N stretching
	3256	NH_2 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 α-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^{-1}. The absorption at 820 cm^{-1} is attributed due to C–H plane deformation. The N–C–N bond stretching vibration is evident at 1042 cm^{-1}. The CH_3 antisymmetric deformation vibration is confirmed at 1459 cm^{-1}. The wavenumber 1524 cm^{-1} is assigned to N=O anti-symmetric stretching. The characteristic C=O bond stretching vibration is observed at 1645 cm^{-1}. The absorption observed at 1690 cm^{-1} confirms the C=N stretching vibration. The NH_2 symmetric stretching vibration is observed at 3256 cm^{-1}. 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^{-1}. 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

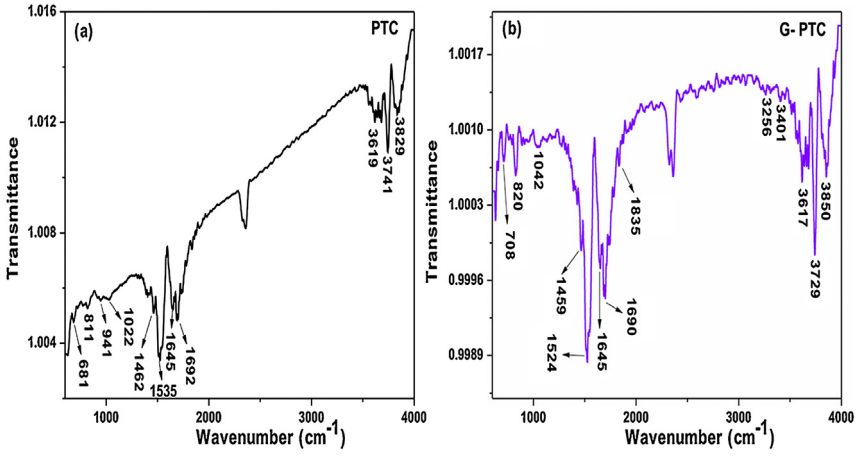

Fig. 2. FT-IR spectrum of (a) PTC (b) G-PTC.