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Dielectric, etching and Z-scan studies of glycine doped potassium thiourea chloride crystal

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Glycine doped potassium thiourea chloride (PTC) crystal has been grown by slow solution evaporation technique. The dielectric studies have been employed to examine substantial improvement in dielectric constant and dielectric loss of glycine doped PTC crystal. The etching studies have been performed to investigate the surface quality of this crystal. The Z-scan studies have been carried out at 632.8 nm to explore the third order nonlinear optical nature. The negative nonlinear refraction of glycine doped PTC crystal was found to be of 7.27×10^{-12} cm^2/W. The origin of high magnitude of third order nonlinear optical susceptibility and reverse saturable nonlinear absorption have been investigated. The obtained results were explored to discuss the nonlinear optical applications of PTC crystal.

Keywords: *PTC crystal; doping; glycine; etching; Z-scan studies; dielectric studies*

1. Introduction

In past few decades thiourea based nonlinear optical (NLO) metal complex crystals have drawn large attention due to combined benefit of organic and inorganic constituents, which rapidly enhanced the demand of thiourea metal complex (TMC) crystals for industrial applications in photonics, laser frequency conversion, signal modeling and optoelectronics devices [1, 2]. The inventory of potentially known TMC crystals includes zinc thiourea sulphate (ZTS), bis thiourea cadmium chloride (BTCC), copper thiourea chloride (CTC), zinc thiourea chloride (ZTC), bis thiourea cadmium acetate (BTCA), bis thiourea zinc acetate (BTZA) and potassium thiourea chloride (PTC) [3, 4]. The doping of precise quantity of additive plays a key role in upgrading the qualitative features in desired host material. Recent investigations also confirm that the doping of organic and inorganic impurities in TMC crystal significantly enhanced the intrinsic qualities of TMC crystals. Amino acid glycine containing the carboxyl group has a potential ability to enhance the charge mobility and photochemical stability of TMC crystal. It is evident that doping of glycine has a positive impact on characteristic features of BTCF, BTCC, ZTS, ZTC and BTCA crystals [5–9]. Potassium thiourea chloride (PTC) crystal is a promising NLO material having a tetragonal structure, good optical transparency, moderate hardness and high thermal stability [4]. It is noteworthy that till date no doping attempt has been made in case of PTC crystal as well as no investigations were accomplished

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to study the dielectric, third order nonlinear optical (TONLO) and surface characteristics of PTC crystal doped by an external impurity such as glycine. The present communication is one of the first that reports the investigation on the dielectric, TONLO and surface properties of glycine doped PTC crystal by means of dielectric measurement, Z-scan and etching studies.

2. Experimental

The potassium thiourea chloride (PTC) complex has been prepared by dissolving 1 mol.% of thiourea and 4 mol.% of potassium chloride in highly pure deionized water. The recrystallization process was adopted to obtain high purity PTC complex. A supersaturated solution of purified PTC compound was obtained and precisely measured quantity of glycine (3 mol.%) was gradually introduced to the solution. The glycine added PTC solution was constantly allowed to mix for eight hours for homogeneous doping of glycine in PTC. The glycine doped potassium thiourea chloride solution was filtered in a rinsed beaker and slow solution evaporation was achieved in an isothermal environment. A single crystal of glycine doped potassium thiourea chloride material is shown in Fig. 1.

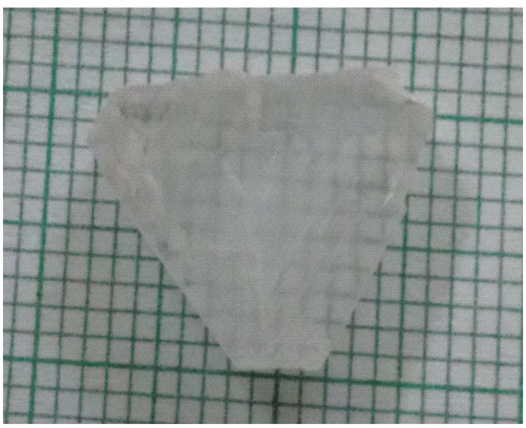

Fig. 1. Glycine doped PTC single crystal.

3. Results and discussion

3.1. Dielectric studies

The dielectric studies are vital to understand the electro-optic properties of crystalline material [10] for which the dielectric constant and dielectric loss of pure and glycine doped potassium thiourea chloride crystals have been evaluated at different frequencies using the Gwinstek-819 LCR cube meter at room temperature. To conduct good measurements, the parallel-faced single crystals were selected and covered by silver paste to avoid loss of data due to external factors. The active electronic, ionic, dipolar and space charge polarization mechanism at lower frequencies strongly influences the relaxation time of molecular dipoles in a material causing an increase of dielectric constant [11].

The frequency response of dielectric constant of the crystals is shown in Fig. 2a which evidences the decreasing behavior of dielectric constant of pure and glycine doped potassium thiourea chloride crystal with increasing frequency. The high polarization activity in lower frequency domain leads to higher dielectric constant while the low polarization activity at higher frequencies results in reduction of dielectric constant of crystals [12]. As organic groups favor lower dielectric activity, substantial reduction in magnitude of dielectric constant of glycine doped potassium thiourea chloride crystal is observed in comparison to PTC crystal. The materials with lower dielectric constant consume less power which is the decisive factor for designing NLO, photonics and electro-optic modulation devices [13]. The dissipation factor mainly depends on defect centres in crystalline material [14]. The profile of dielectric loss of the crystals is plotted in Fig. 2b. The less dielectric loss indicates that the glycine doped potassium thiourea chloride crystal possesses less defect centres than the PTC crystal [15]. The lower dielectric constant and dielectric loss of glycine doped potassium thiourea chloride crystal suggest its usefulness for optoelectronics device applications.

3.2. Etching studies

The etching studies were employed to examine surface purity, growth habit and structural defects associated with glycine doped potassium thiourea chloride crystal. A selected surface of glycine doped potassium thiourea chloride crystal was etched with water and the etch micrographs

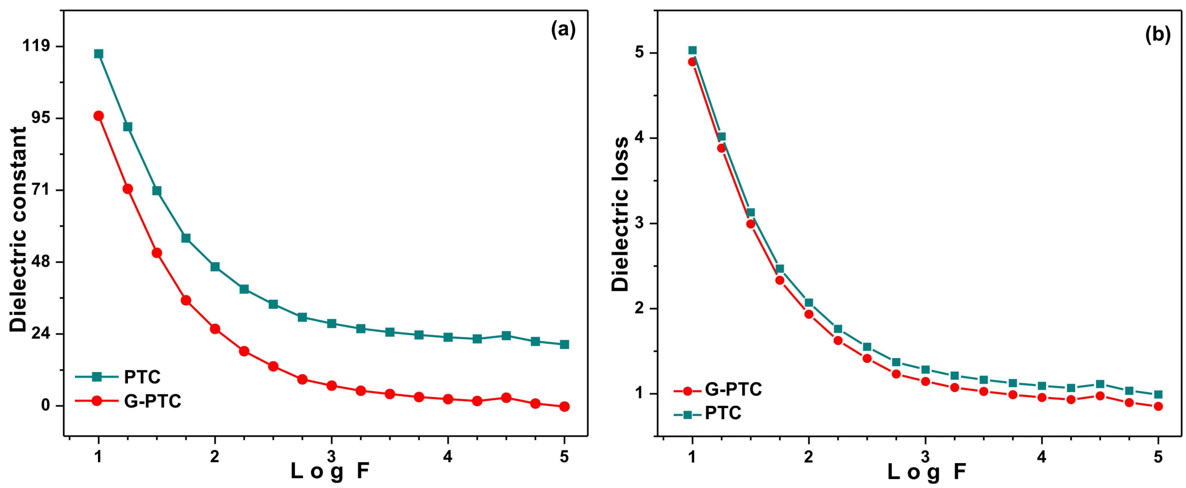

Fig. 2. (a) dielectric constant and (b) dielectric loss of PTC and glycine doped PTC crystals.

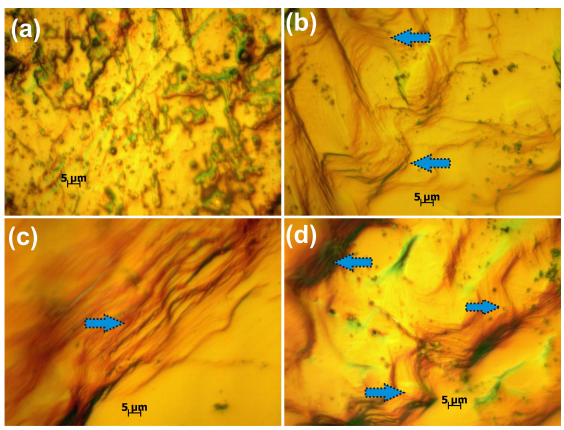

Fig. 3. Etch patterns of the crystal after (a) 0 s, (b) 10 s, (c) 20 s, (d) 40 s.

of the crystal surface were recorded after a regular interval of 10 s. The micrograph (Fig. 3a) of the grown crystal surface shows irregular micropits and intermixed patterns which might have occurred due to variation in temperature of surface during the growth. After 10 s of etching (Fig. 3b) the surface of glycine doped potassium thiourea chloride crystal reveals a symmetrically stacked step growth trend with the absence of pits and line defects. The stacked growth habit of glycine doped potassium thiourea chloride crystal is clearly observed after 20 s of etching as seen in Fig. 3c. Further etching of the surface for 40 s (Fig. 3d) confirms the step growth nucleation along the studied plane. The absence of micropits, structural defects and symmetrical step nucleation along the plane confirms the good crystalline nature of the glycine doped potassium thiourea chloride crystal.

3.3. Z-scan analysis

The TONLO properties of glycine doped potassium thiourea chloride crystal have been evaluated at 632.8 nm using the Z-scan technique developed by Bahae et al. [16]. The optical resolution of experimental Z-scan setup is given in Table 1. The closed aperture Z-scan technique provides the information about the nature and magnitude of path dependent third order refraction nonlinearity in a crystal. The tightly focused gaussian beam of He-Ne laser was irradiated through a converging lens on a crystal sample and the sample was gradually translated about the beam irradiated path focus ($Z = 0$). The shift in transmittance of the crystal about the focus along the Z path was observed. The distribution of optical energy along the crystal surface, due to localized absorption of highly repetitive optical beam, causes the phase shift in transmittance about the focus ($Z = 0$) [17]. The peak to valley phase shift about the focus confirms the negative nonlinear refraction (NLR) tendency in glycine doped potassium thiourea chloride crystal as shown in Fig. 4a. The negative NLR is characteristic of self-defocusing dominant material which is highly demanded for protective optical night vision sensor devices [18].

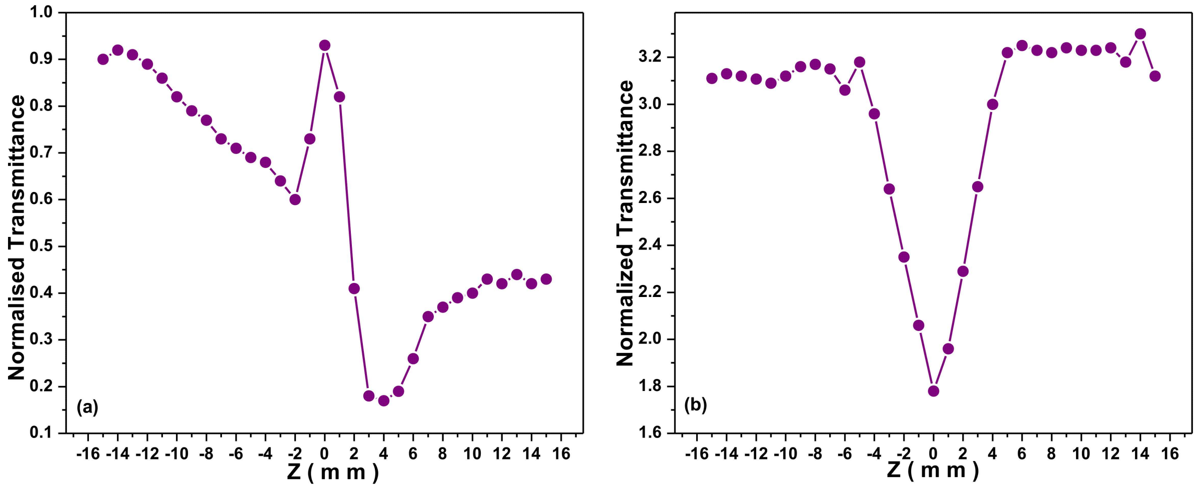

Fig. 4. Z-scan transmittance curve with (a) close and (b) open aperture.

Table 1. Z-scan setup and TONLO parameters of the grown crystal.

Parameters and notations	Magnitude
Laser wavelength (λ)	632.8 nm
Lens focal length (f)	30 mm
Optical path distance (Z)	85 cm
Beam waist radius (ω_a)	3.3 mm
Aperture radius (r_a)	2 mm
TONLO susceptibility (χ^3)	6.99×10^{-6}esu
Absorption coefficient (β)	1.61×10^{-6} cm/W
Nonlinear refraction (n_2)	7.27×10^{-12} cm^2/W

The on axis phase shift (ΔΦ) and peak to valley transmittance difference (ΔT_{p-v}) are determined using equation [16]:

$$\Delta T_{p-v} = 0.406(1 - S)^{0.25} |\Delta\phi| \tag{1}$$

where $S = [1-\exp(-2r_a^2/\omega_a^2)]$ is the aperture linear transmittance, r_a is the aperture radius and ω_a is the beam radius at the aperture. The third order NLR (n_2) of glycine doped potassium thiourea chloride crystal was calculated using the relation [16]:

$$n_2 = \frac{\Delta\phi}{KI_0L_{eff}} \tag{2}$$

where $K = 2\pi/\lambda$ (λ is the laser wavelength), $I_0 = 5$ MW/cm^2 is the intensity of the laser beam at the focus (Z = 0), $L_{eff} = ([1-\exp(-\alpha L)]/\alpha)$ is the effective thickness of the sample depending on linear absorption coefficient α and L is the thickness of the sample. The n_2 of glycine doped potassium thiourea chloride crystal is found to be 7.27×10^{-12} cm^2/W. The origin of nonlinear absorption β in glycine doped potassium thiourea chloride crystal has been investigated by means of open aperture Z-scan configuration. The open aperture Z-scan transmittance shows a significant fall at the beam irradiated path focus (Z = 0) confirming the presence of reverse saturable absorption (RSA) effect in glycine doped potassium thiourea chloride crystal as shown in Fig. 4b. The origin of RSA effect is assisted by multi photon absorption in excited states [19]. The crystals with origin of RSA phenomenon are highly desirable for biomedical and optical limiting photonic devices [20]. The nonlinear absorption coefficient β of glycine doped potassium thiourea chloride crystal is calculated using equation [16]:

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0L_{eff}} \tag{3}$$

where ΔT is the one valley value at the open aperture Z-scan curve. The glycine doped potassium thiourea chloride crystal exhibits the RSA effect with the β coefficient of a magnitude 1.61×10^{-6} cm/W. The measure of TONLO susceptibility (χ^3) determines the polarizing nature of the material determined using the equations below [16]:

$$Re\chi^{(3)}\ (\text{esu}) = 10^{-4}(\varepsilon_0 C^2 n_0^2 n_2)/\pi\ (\text{cm}^2/\text{W}) \quad (4)$$

$$Im\chi^{(3)}\ (\text{esu}) = 10^{-2}(\varepsilon_0 C^2 n_0^2 \lambda \beta)/4\pi^2\ (\text{cm/W}) \quad (5)$$

$$\chi^3 = \sqrt{(Re\chi^3)^2 + (Im\chi^3)^2} \quad (6)$$

where ε_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample and C is the velocity of light in vacuum. The χ^3 of glycine doped potassium thiourea chloride crystal is found to be of order of 6.99 × 10^{-6} esu. The photo induced mobility of charge transfer through the π-electron dominated chromophores leads to large enhancement in nonlinearity of glycine doped potassium thiourea chloride crystal [21, 22].

4. Conclusions

Single crystal of glycine doped potassium thiourea chloride material has been successfully grown by slow evaporation solution technique. The dielectric studies revealed that the frequency response of dielectric constant and dielectric loss of glycine doped potassium thiourea chloride crystal was significantly lower than that of PTC crystal. The etching studies of glycine doped potassium thiourea chloride crystal along the studied plane revealed the step growth habit with the absence of structural impurities. The Z-scan studies confirmed the promising third order nonlinear optical nature of glycine doped potassium thiourea chloride crystal. The peak to valley on axis phase shift in the grown crystal confirmed the presence of negative nonlinear refraction having a magnitude of 7.27 × 10^{-12} cm^2/W. The reverse saturable nonlinear absorption coefficient β of magnitude 1.61 × 10^{-6} cm/W has originated in grown crystal due to multi photon absorption. The high TONLO susceptibility of glycine doped potassium thiourea chloride crystal was found to be 6.99 × 10^{-6} esu. The improved dielectric quality, high TONLO response and high surface purity substantiates the utility of glycine doped potassium thiourea chloride crystal for nonlinear optical applications optoelectronics, optical night vision sensors and photonic devices.

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