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Luminescence, laser induced nonlinear optical and surface microscopic studies of potassium thiourea chloride crystal

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ABSTRACT

The present communication is aimed to explore the optical properties of organometallic nonlinear optical potassium thiourea chloride (PTC) crystal by means of UV–vis, luminescence, Z-scan, laser damage threshold and etching studies. The PTC single crystal of optimum size $(11 \times 12 \times 04)$ mm^3 has been grown from solution by slow evaporation technique. The qualitative analysis of PTC crystal has been confirmed by means of energy dispersive spectroscopic technique. The UV–vis study has been carried out to assess the optical transparency of PTC crystal in visible region of interest. The photoluminescence study has been accomplished to ascertain the color centered photoluminescence emission nature of PTC crystal in optical spectrum. The laser damage threshold (LDT) value of PTC crystal has been determined by pulse multi shot method using the Nd:YAG laser operating at 1064 nm and the LDT of PTC crystal is found to be in the range of MW/cm^2. The microscopic studies were performed by means of etching analysis to discuss the growth habit and structural defects associated with PTC crystal surface. The third order nonlinear optical nature of PTC crystal has been investigated at 632.8 nm employing the He-Ne laser assisted Z-scan studies. The third order nonlinear optical parameters such as susceptibility (χ^3), absorption coefficient (β), refractive index (n_2) and figure of merit have been evaluated using the Z-scan transmittance data. The NLO device applications of PTC crystal have been discussed in light of observed results.

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1. Introduction

The organometallic nonlinear optical (NLO) crystals predominantly retained the interest of many researchers in this 21st century. The design of organometallic crystals contribute high polarizing property and photo chemical stability of organic

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part along with excellent mechanical and thermal stability of inorganic part [1–4]. Recent research has been more focused to develop and investigate the thiourea metal complex crystals as they seek huge demand in optoelectronics, photonics, electro-optic modulation, laser frequency conversion, second harmonic generation (SHG) and image processing devices [5–7]. A large number of thiourea metal complex crystals such as bis thiourea cobalt chloride (BTCoC), bis thiourea lead acetate (BTLA), zinc thiourea chloride (ZTC), thiourea urea magnesium chloride (TUMC), bis-thiourea cadmium acetate (BTCA), copper thiourea chloride (CTC), potassium thiourea bromide (PTB), bis-thiourea cadmium chloride (BTCC), bis-thiourea zinc acetate (BTZA), potassium thiourea thiocyanide (PTT), bis-thiourea cadmium formate (BTCF) and bis thiourea bismuth chloride (BTBC) have been grown and extensively studied [8,9]. Amongst the thiourea metal complex crystals potassium thiourea chloride (PTC) outstands as a potential NLO material belonging to tetragonal crystal system with good SHG response, wide optical transparency window in visible region, high thermal stability up to 198 °C and high dislocation threshold to mechanical load [10,11]. The interaction of material with high intensity optical energies results to various nonlinear photonic effects which explores new vendors for industrial applications and hence demand a core analysis and investigation. In current scenario the ultrafast optical processes occurring at nano-, pico-, and femto-second regime of optical signals play huge role in industrial and telecommunication applications [12]. Therefore, in order to subject a crystal for laser driven device applications; the growth habitat of crystal surface, luminescence nature, optical switching response and surface tolerance to laser irradiation need to be examined, which are not reported in case of PTC crystal. The unavailability of literature on essential parameters such as optical transmittance, surface property, TONLO response and laser damage threshold of PTC crystal constrained us to grow and analyze the PTC crystal by employing UV–vis, photoluminescence, laser damage threshold, Z-scan and etching characterization techniques to explore its potential candidature for classified laser driven device applications.

2. Experimental

The material of PTC complex was synthesized by dissolving thiourea and potassium chloride in doubly distilled water in a mole ratio of 4:1. The aqueous solution was allowed to agitate for five hours to assure reaction and formation of PTC complex. The solution was later filtered by whatman filter paper in a rinsed beaker. The beaker was covered with perforated coil to avoid dust inclusion and kept for slow solution evaporation in a constant temperature bath of accuracy ±0.01 °C. The purity of PTC crystal material was achieved by recrystallization process. The solution grown $(11 \times 12 \times 04)\ mm^3$ single PTC crystal harvested within three weeks is shown in Fig. 1a.

3. Results and discussion

The elemental analysis of grown PTC crystal has been accomplished by means of EDS technique using the Hitachi S4700 instrument. For the analysis the single PTC crystal was powdered and the energy spectrum shown in Fig. 1b was recorded by applying the energy ranging from 0–10 KeV. The elements present in the crystal material were identified and indexed at respective energies in the spectrum. The presence of carbon (C), sulphur (S) and potassium (K) thus confirms the presence of constituent elements of grown PTC crystal.

The optical transparency of pure PTC crystal has been examined in the range of 190–1100 nm by means of Shimadzu UV-1601 spectrophotometer. The transparency of the material is aided by photo induced transition of electron to allowed energy states, molecular orientation along the crystal plane and the defects associated with the crystal [13–15]. The recorded absorbance spectrum of PTC crystal is shown in Fig. 2a and it reveals that the magnitude of absorbance is lowest in the range of 250–1100 nm which holds huge advantage for devices operative in visible region. The lower cut-off wavelength of PTC crystal at 250 nm advocates the potential candidature of PTC crystal for UV-tunable lasers and transmission of second and third harmonic generated signals of Nd:YAG laser (1064 nm) [16–18]. The observed lower absorbance deduces the fact that PTC crystal offer least optical scattering indicating presence of minimum concentration of structural and crystalline defects [19].

The photoluminescence (PL) analysis is a crucial tool to identify the intrinsic defects, impurity level and lifetime of electron in energy state associated with the material [20–22]. In present analysis the PTC crystal material was photo excited with energy wavelength of 235 nm (5.2 eV) and the PL emission spectrum was recorded in the visible region ranging from 325–700 nm. The PL emission spectrum (Fig. 2b) confirms that the PTC crystal has red colored emission in visible region with intensity maxima centered at 607 nm corresponding to energy of 2.04 eV. The single color emission of PTC crystal denotes the good crystalline nature of PTC crystal which is in agreement with present UV–vis study results. The material with prominent PL emission find vast applications in biochemical and medical research fields for testing the characteristic properties of different compounds [23].

In order to understand the performance of NLO crystal in high power regime the knowledge of laser induced optical damage plays a crucial role [24]. In present analysis the plane surfaced PTC crystal was multishot by the gaussian filtered beam of Nd:YAG laser operating at 1064 nm with pulse width 10 ns and frequency 10 Hz. The laser beam of 1 mm diameter was attenuated by variable attenuator and focused on PTC crystal sample through a lens of focal length 30 cm for 30 s/shot. The energy at which the crystal surface was damaged was recorded using the EPM 200 energy/power meter. In practical the PTC crystal sustained few laser shots of lower energy and eventually got damaged at energy of 193 mJ. The spot size of 1.6 mm diameter was observed on the surface of PTC crystal (Fig. 3). The induced laser damage is the complex phenomenon which originates due to combined effect (electron avalanche, multi photon absorption and thermally contributed localized

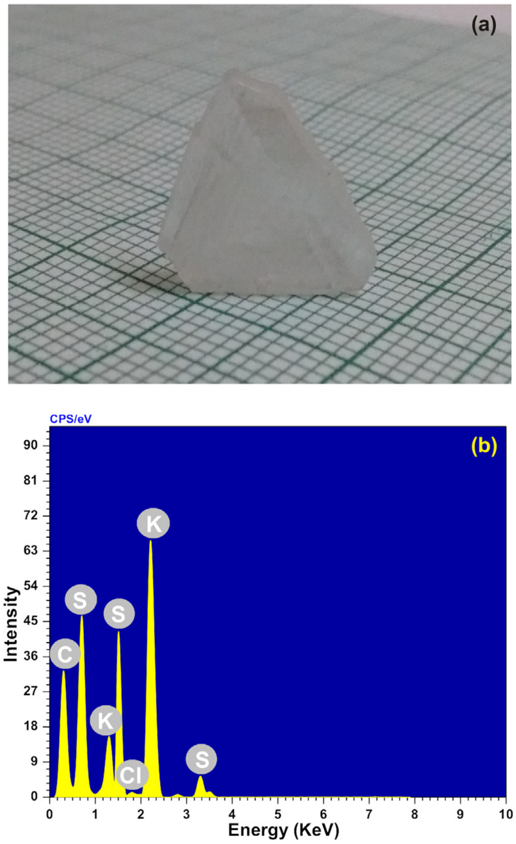

Fig. 1. (a) PTC single crystal (b) EDS spectrum of PTC.

photo-ionization of crystal material) [25,26]. The laser damage threshold (LDT) of PTC crystal is found to be 960.3 MW/cm^2. The LDT value of PTC crystal is sufficiently higher than potential crystal namely, potassium dihydrogen orthophosphate (0.2 MW/cm^2) and bis thiourea zinc acetate (12.44 MW/cm^2) [27].

The etching analysis of crystal gives an in-depth knowledge of growth feature, presence of dislocations and structural defects associated with the crystal plane [28,29]. For a crystal to be utilized for NLO applications it is very necessary to grow crystal with excellent quality. In addition the quality of the crystal highly influences the nonlinear efficiency of material as the impurities and dislocations arising during the growth results to impede the optical signal to be processed [30,31]. This urges the necessity to investigate the microstructural imperfections or crystal defects in the grown crystals. For current study the PTC crystal surface was etched by water and the etch pattern micrographs were captured after a regular interval of 10 s as shown in Fig. 4. The micrograph of as grown crystal shows a stacked growth habit of PTC crystal along the studied plane. The etch pattern reveals the absence of pits in crystal however after successive etching of crystal surface with water for 20 s, the segregation of impurities gives the clear picture of stacked growth mechanism along the studied plane. The more prominent irregular stacked pattern was observed in micrograph recorded after 30 s of etching.

The third order nonlinear optical (TONLO) properties of PTC single crystal (0.8 mm) have been investigated by means of open and close aperture Z-scan technique developed by Bahae et al. [32]. The crystals with promising TONLO properties are readily demanded for optical switching devices, hence the TONLO behavior of PTC crystal has been investigated at 632.8 nm using the He-Ne laser facilitated Z-scan set-up detailed in Table 1. Initially the nonlinear refraction behavior of PTC crystal has been investigated using the close aperture Z-scan configuration. The polished PTC crystal was positioned at

Table 1
Optical resolution of Z-scan setup.

Parameters and notations	Details
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
Incident intensity at the focus (I_o)	2.3375 KW/m^2

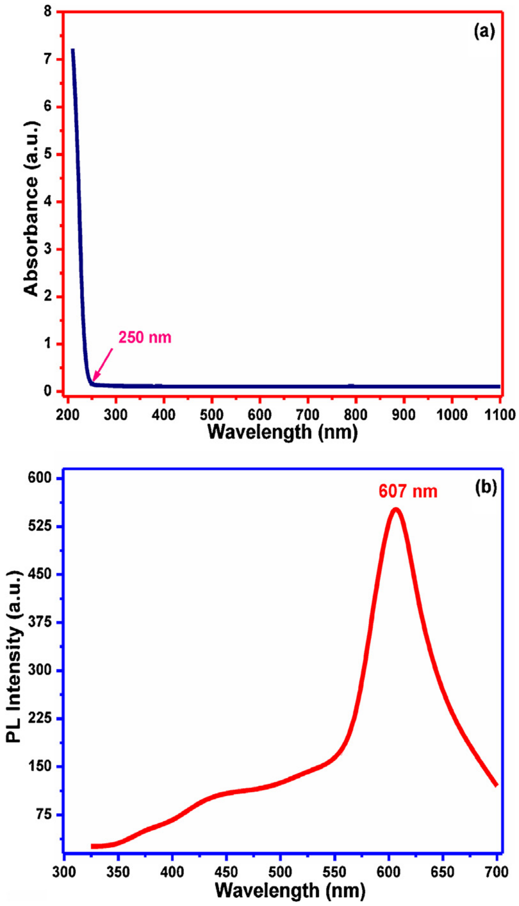

Fig. 2. (a) UV–vis absorbance spectrum (c) PL emission spectrum of PTC crystal.

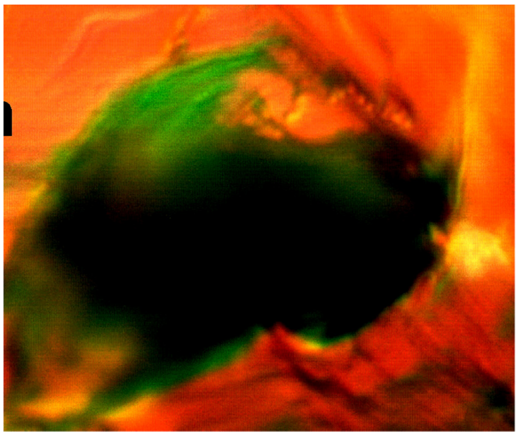

Fig. 3. Surface image of laser damaged PTC crystal.

the focus point (Z = 0) of beam irradiated path. The gaussian laser beam was made incident on the crystal sample through a convex lens and the crystal sample was translated in steps along the Z-direction. The transmitted intensity from the crystal sample was recorded using the photo-detector placed at far field. The close aperture Z-scan transmittance curve is shown in Fig. 5a. It reveals that the variation in intensity shifts from peak to valley indicating the presence of negative nonlinear refraction (NLR). The negative NLR is the characteristic parameter of material exhibiting self-defocusing effect [33]. The materials with negative nonlinear refraction are desirable candidate for optical night vision sensor devices [34]. The phase shift in nonlinear refraction is a prominent effect inculcated due to uniform energy gradient along the crystal surface causing

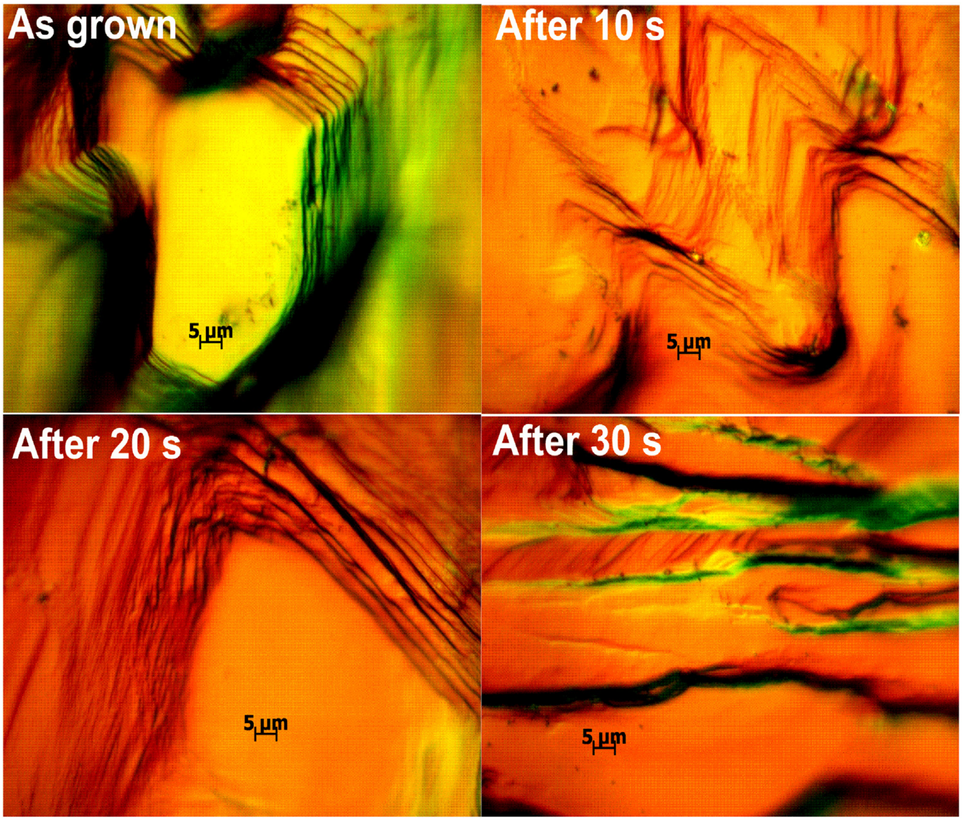

Fig. 4. Etch patterns of PTC crystal.

the thermal lensing effect originating due to irradiation of highly repetitive rate of laser beam [35,36]. The peak to valley transmission ($\Delta T_{p\text{-}v}$) can be related in terms of phase shift as [32],

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

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 waist radius in front of aperture. The NLR (n_2) of PTC crystal has been determined using the relation [32],

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

where $K = 2\pi / \lambda$, $I_0 = 2P/\pi\omega_a^2$, is the incident irradiance intensity of beam at the focus (Z = 0), the effective thickness of the sample has been determined using the equation, $L_{eff} = [1 - \exp(-\alpha L)]/\alpha$ where α is the linear absorption coefficient and L is the thickness of the sample. The n_2 of PTC crystal is found to be of magnitude 4.86×10^{-10} cm^2/W. The TONLO absorption of grown PTC crystal has been investigated using the open aperture Z-scan technique and the transmittance curve as shown in Fig. 5b. It depicts that the transmitted intensity is maximum at the focus position which confirms the occurrence of saturable absorption (SA) phenomenon in PTC crystal. The SA effect is attributed by the dominance of ground state linear absorption coefficient over the excited state absorption [37]. The magnitude of TONLO absorption coefficient (β) has been calculated using the equation given below [32],

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

where ΔT is the one valley value obtained in open aperture Z-scan curve. The β magnitude of PTC crystal is found to be 3.97×10^{-5} cm/W. The polarizing tendency of crystal can be evaluated by means TONLO susceptibility (χ^3) of the material using following equations [32],

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

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

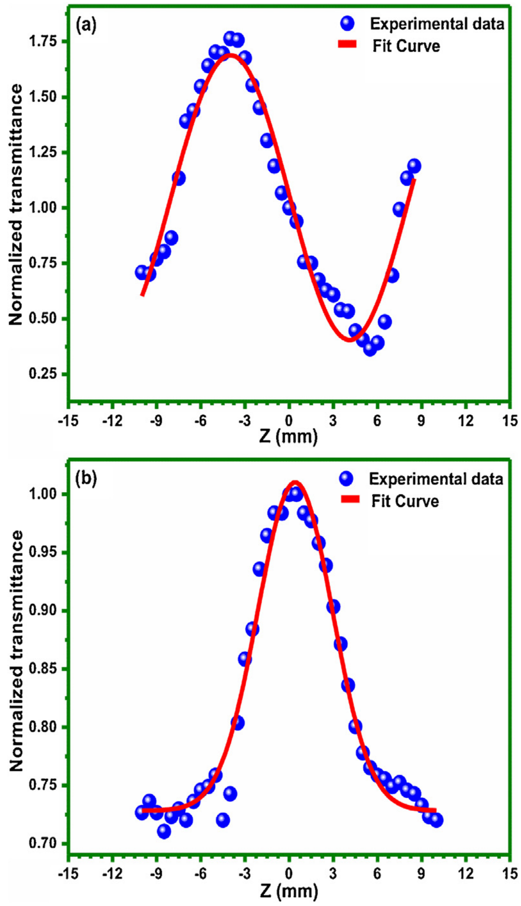

Fig. 5. Z-scan transmittance curve with aperture of detector (a) close and (b) open.

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

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 PTC crystal contributes the high magnitude of susceptibility (χ^3) of magnitude 8.71×10^{-5} esu which is significantly higher than several thiourea metal complexes reported in literature [38]. The photoinduced charge delocalization over pi bonded network is the key factor responsible for high susceptibility in material [39,40]. The figure of merit (FOM = $\beta\lambda/n_2$) provides the information regarding the dominating TONLO effect in given crystal medium which could be either nonlinear refraction or absorption [41]. The FOM of PTC crystal is found to be 5.17 which confirm the dominance of TONLO refraction over the TONLO absorption in the PTC crystal. The PTC crystal with potential TONLO parameters is most compatible material for designing night vision sensors, optical limiting and photonic devices.

4. Conclusion

In present investigation the PTC single crystal with dimension of $(11 \times 12 \times 04)$ mm^3 has been grown from solution by slow evaporation technique and optical as well as physical analysis of grown crystal is successfully accomplished. The EDS analysis confirmed the presence of constituent elements in grown PTC crystal. The observed minimum absorbance and lower cut-off wavelength at 250 nm in UV–vis studies revealed less optical scattering in PTC crystal which is vital for laser frequency conversion device applications. The photoluminescence study confirmed the prominence of red colored PL emission in PTC crystal with single peak maxima centered at 607 nm. The laser damage threshold of PTC crystal facilitated by localized thermal conductivity due to photo-ionization of crystal surface is found to be 960.3 MW/cm^2. The etching studies revealed the absence of pits and presence of stacked growth habit along the studied plane confirming the uniform 2D growth mechanism in PTC crystal. In Z-scan studies, the PTC crystal is revealed to have negative NLR with a magnitude of 4.86×10^{-10} cm^2/W. The magnitude of TONLO susceptibility and the saturable absorption coefficient of PTC crystal is found to be 8.71×10^{-5} esu and 3.97×10^{-5} cm/W respectively. The PTC crystal with least absorption tendency, excellent PL nature, unique surface habitat, sufficient LDT and excellent TONLO properties might be a better alternative crystal for laser assisted NLO and photonic devices operative in high-tech industrial applications.

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