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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.

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 $\pm 0.01\,^{\circ}C$. 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