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Nonlinear optical and microscopic analysis of Cu^{2+} doped zinc thiourea chloride (ZTC) monocrystal

S.P. Ramteke [a], Mohd Anis [a,*], M.S. Pandian [b], S. Kalainathan [c], M.I. Baig [d], P. Ramasamy [b], G.G. Muley [a,*]

[a] Department of Physics, Sant Gadge Baba Amravati University, Amravati 444602, Maharashtra, India
[b] SSN Research Centre, SSN College of Engineering, Kelavakkam 603110, Tamil Nadu, India
[c] Centre for Crystal Growth, VIT University, Vellore 632014, India
[d] Prof Ram Meghe College of Engineering and Management, Amravati 444701, Maharashtra, India

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ABSTRACT

Organometallic crystals offer considerable nonlinear response therefore, present article focuses on bulk growth and investigation of Cu^{2+} ion doped zinc thiourea chloride (ZTC) crystal to explore its technological impetus for laser assisted nonlinear optical (NLO) device applications. The Cu^{2+} ion doped ZTC bulk single crystal of dimension $03 \times 2.4 \times 0.4$ cm^3 has been grown from pH controlled aqueous solution by employing slow solvent evaporation technique. The structural analysis has been performed by means of single crystal X-ray diffraction technique. The doping of Cu^{2+} ion in ZTC crystal matrix has been confirmed by means of energy dispersive spectroscopic (EDS) technique. The origin of nonlinear optical properties in Cu^{2+} ion doped ZTC crystal has been studied by employing the Kurtz-Perry test and Z-scan analysis. The remarkable enhancement in second harmonic generation (SHG) efficiency of Cu^{2+} ion doped ZTC crystal with reference to ZTC crystal has been determined. The He-Ne laser assisted Z-scan analysis has been performed to determine the third order nonlinear optical (TONLO) nature of grown crystal. The TONLO parameters such as susceptibility, absorption coefficient, refractive index and figure of merit of Cu-ZTC crystal have been evaluated using the Z-scan transmittance data. The laser damage threshold of grown crystal to high intensity of Nd:YAG laser is found to be 706.2 MW/cm^2. The hardness number, work hardening index, yield strength and elastic stiffness coefficient of grown crystal has been investigated under microhardness study. The etching study has been carried out to determine the growth likelihood, nature of etch pits and surface quality of grown crystal.

1. Introduction

Designing and fabrication of high tech laser driven photonic and optoelectronic devices obligates the need of a potential nonlinear optical (NLO) crystal which foreshow excellent linear as well as nonlinear optical characteristics. It is astonishing observation that since past few decades the family of organometallic crystals has fascinated the research fraternity throughout the globe owing to their outstanding physical, electrical, chemical and optical traits [1–3]. Interestingly, zinc thiourea chloride (ZTC) is an exceptional organometallic crystal with promising structural, linear-nonlinear optical and physical features [4–6]. ZTC crystal has been under rigorous investigation to explore its potential liability for NLO device application. In order to enhance the overall performance of ZTC crystal the most effective technique of doping an external additive has been adopted by many researchers. An extensive literature analysis pointed out a fact that metal additives have shown influential impact on characteristic properties of ZTC crystal. The effect of univalent metal additives such as K^+ [7] and Li^+ [8] on significant properties of ZTC crystal has been explored by several research groups. The influence of bivalent impurity such as Ca^{2+} [9], Cd^{2+} [10], Mg^{2+} [11] and Ba^{2+} [12] on ZTC crystal has been extensively investigated. Very recently the doping effect of trivalent impurity Nd^{3+} on structural, optical, electrical and mechanical properties of ZTC crystal has been scrupulously studied [13]. In our earlier report the Cu^{2+} ion has been firstly doped in ZTC crystal and it has shown remarkable enhancement in UV–visible and dielectric response of ZTC crystal [14]. However the structural, SHG efficiency, third order nonlinear optical, laser damage threshold (LDT), microhardness and surface properties are yet to be investigated. Aforesaid crucial parameters play decisive role for scrutinizing the crystal for specific device application. Therefore, the

* Corresponding authors.
E-mail addresses: loganees@gmail.com (M. Anis), gajananggm@yahoo.co.in (G.G. Muley).

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current studies on Cu^{2+} ion doped ZTC crystal has been accomplished by employing X-ray diffraction, energy dispersive spectroscopy, Kurtz-Perry test, Z-scan, LDT, Vicker's microhardness and etching characterization techniques.

2. Experimental procedure

The zinc thiourea chloride (ZTC) complex has been synthesized by dissolving zinc chloride and thiourea in double distilled water having a ratio of 1:2 respectively. The ZTC crystal complex has been recrystallized to extract the impurities introduced during the growth process. The copper chloride (2 wt%) was added to the solution of ZTC crystal complex in order to achieve doping of Cu^{2+} ion. The solution was allowed to agitate for four hours in order to achieve the homogeneous doping of Cu^{2+} ion in ZTC crystal complex and the pH was maintained at 1.6 by adding the hydrochloric acid. This solution was later filtered and kept in a constant temperature (35 °C) water bath. The Cu^{2+} ion doped ZTC (Cu-ZTC) bulk single crystal of dimension $03 \times 2.4 \times 0.4$ cm^3 (shown in Fig. 1a) was grown within a period of 15 days.

3. Results and discussion

The single crystal X-ray diffraction analysis has been performed at room temperature using the crystal X-ray diffractometer (Enraf Nonius CAD4). The crystal structure and cell dimensions of pure and Cu-ZTC crystal has been determined. It reveals that the pure and Cu-ZTC crystal are orthorhombic in structure belonging to P_n2_{1a} space group. The cell dimensions of ZTC crystal are a = 13.029 Å, b = 12.764 Å, c = 5.885 Å and volume is 978.68 $Å^3$ which is in good agreement with reported work [1]. The cell dimensions of Cu-ZTC crystal are found to be a = 13.033 Å, b = 12.771 Å, c = 5.893 Å and volume is 980.85 $Å^3$. The slight change in cell dimension of Cu-ZTC with reference to ZTC indicates the influence of Cu on lattice of host material.

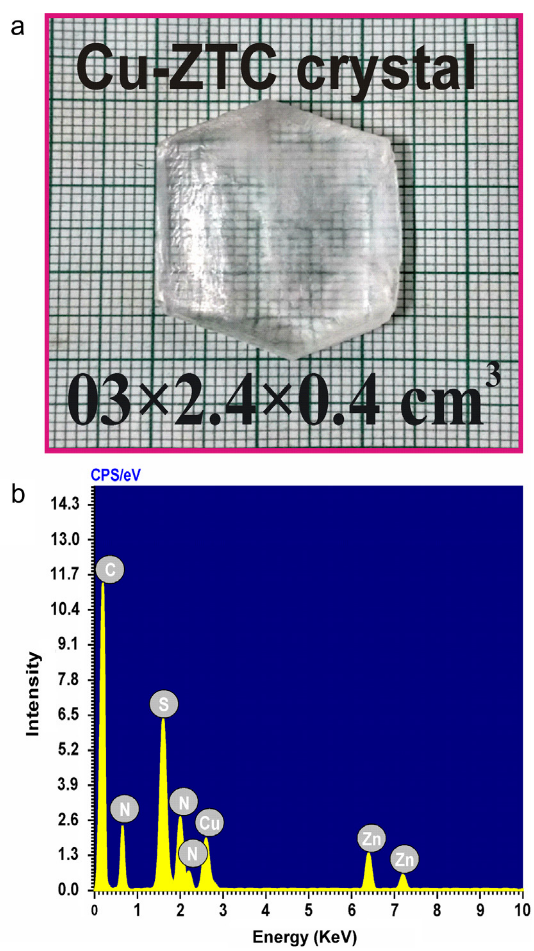

Fig. 1. (a) Bulk single crystal of Cu-ZTC. (b) EDS spectrum of Cu-ZTC.

The elemental analysis has been carried out by employing the energy dispersive spectroscopic (EDS) technique using the Hitachi S4 7000 instrument. The energy spectrum of the Cu-ZTC crystal complex has been recorded in the range of 0–10 keV. The analysis of the spectrum reveals the presence of constituent elements carbon, nitrogen and zinc of the ZTC crystal complex in addition to the presence of Cu ion confirms the incorporation of dopant in ZTC crystal. The indexed EDS spectrum of Cu-ZTC crystal is shown in Fig. 1b.

The standard Kurtz-Perry powder test [15] has been employed to determine the second harmonic generation (SHG) efficiency of grown Cu-ZTC crystal. The powder samples of the crystal were prepared by grinding the selected crystal sample in molder-pester and the same powder was packed in the quartz cavity. The quartz cavity was irradiated by the Gaussian filtered beam of Nd:YAG laser (1064 nm, 6 ns, 10 Hz, 1.1 mJ) and the green signal at the output window confirmed the successful frequency doubling phenomenon in pure and Cu-ZTC crystal material. Fig. 2a shows the intensity of generation of second harmonic signal from each characterized sample recorded using the optical fiber interfaced spectrophotometer. The SHG efficiency of Cu-ZTC crystal is found to be 5.41 times higher than KDP and 2.81 times higher than ZTC crystal. The enhanced SHG efficiency in Cu-ZTC crystal might have been attributed by the added electron density of dopant Cu^{2+} and enhanced charge delocalization over the extended bonding network of ZTC crystal matrix. Similar enhancing effect on SHG efficiency of ZTC crystal due to other dopants evident in literature is discussed in Table 1 [13,16]. The high SHG efficiency of Cu-ZTC crystal implicated its credibility for application in frequency doubling/conversion devices [17].

The nonlinearities originating in a material when irradiated with highly repetitive optical energy can be evaluated by the most crucial and sensitive Z-scan technique developed by Bahae et al. [18]. The Z-scan setup has been facilitated with He-Ne laser aligned with focusing lens and the photo detector is placed at far field. The optical resolution of Z-scan setup is tabulated in Table 2. The sample was placed at the focus (Z = 0) of the beam irradiated path and then smoothly translated in +Z and −Z direction with reference to focus. The change in intensity of nonlinear refraction attributed by Cu-ZTC crystal has been detected and recorded using the photo detector placed at far field. The closed aperture Z-scan transmittance curve is shown in Fig. 2b. It reveals that the crystal medium offers phase shift in propagating light from valley to peak (positive refraction) which is intrinsic property of material exhibiting self-focusing nature [19]. The phase shift in direction of propagating light evidences the origin of nonlinear refraction which is attributed by the spacial distribution of energy along the crystal surface due to incident laser beam giving rise to localized thermal lensing effect [20,21]. The on axis phase shift ($\Delta\phi$) in terms of peak to valley transmission ($\Delta T_{p\text{-}v}$) is given as [18],

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

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 nonlinear refraction (n_2) of Cu-ZTC crystal has been determined using the relation [18],

$$n_2 = \frac{\Delta\phi}{KI_0L_{eff}} \quad (2)$$