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Doping effect of L-cystine on structural, UV–visible, SHG efficiency, third order nonlinear optical, laser damage threshold and surface properties of cadmium thiourea acetate single crystal

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ABSTRACT

The present article is focused to investigate the influence of L-cystine (LC) on linear-non-linear optical and laser damage threshold of cadmium thiourea acetate (CTA) crystal. The structural parameters of pure and LC doped CTA crystals have been determined using the single crystal X-ray diffraction technique. The functional groups of grown crystals have been identified by means of fourier transform infrared (FT-IR) analysis. The UV–visible spectral analysis has been done in the range of 200–900 nm to ascertain the uplifting influence of LC on optical properties of CTA crystal. The second harmonic generation (SHG) efficiency of LC doped CTA crystal is found to be higher than CTA and KDP crystal. The Z-scan technique has been employed to determine the third order nonlinear optical (TONLO) nature of LC doped CTA crystal at 632.8 nm. The self focusing tendency confirmed the strong kerr lensing ability of LC doped CTA crystal. The TONLO susceptibility (χ^3), refraction (n_2) and absorption coefficient (β) has been calculated using the Z-scan data. The laser damage threshold of pure and LC doped CTA crystals has been measured using the Q-switched Nd:YAG laser and its is found to be in range of GW/cm^2. The surface analysis has been done by means of etching studies.

1. Introduction

The rapid development of nonlinear optical (NLO) thiourea metal complex (TMC) crystals has drawn huge attention due to its allied organic and inorganic features such as structural diversity, good transparency, large nonlinearity, huge laser damage threshold, high thermal stability and adequate mechanical hardness. The possession of these qualities make the TMC crystals most desirable for laser fusion systems, optical switching and data storage devices, telecommunication practices, optoelectronics and advanced NLO applications [1,2]. The growth and extensive study on TMC crystals namely zinc thiourea sulphate, bis thiourea cadmium chloride, potassium thiourea iodide, zinc thiourea chloride, bis thiourea zinc acetate, copper thiourea chloride, potassium thiourea bromide and cadmium thiourea acetate (CTA) have been reported [3,4]. As doping of external impurity plays crucial role in tuning the properties of host crystal, the most effective strategy to gain improvement in intrinsic properties of TMC crystals is to incorporate organic and inorganic impurities in a selected quantity [5]. In order to gain enhanced optical performance the TMC crystal is to be doped with organic additive offering good photo chemical stability, high charge mobility and strong polar density as such inherited by amino acids. The significant enhancement in crystal perfection, optical transparency, second harmonic generation (SHG) efficiency, mechanical strength and dielectric properties of CTA crystal has been achieved by doping amino acids (glycine and L-alanine) [6]. The L-cystine (LC) is an optically active amino acid with wide hydrogen bonding network and chiral centers which are essential qualities to enhance the optical properties of material [7]. Hitherto not a single researcher has made an attempt to investigate the influence of LC on different properties of CTA crystal. In this submission the structural, etching, UV–visible, SHG efficiency, third order nonlinear optical and laser damage threshold

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studies of LC doped CTA crystal have been concluded to explore distinguished laser assisted NLO device applications.

2. Experimental procedure

The CTA has been synthesized by dissolving cadmium acetate and thiourea 1:2 mol ratio in double distilled de-ionized water. The purity of CTA metal complex was gained by repetitive re-crystallization process. The purified CTA compound was then dissolved in water to obtain the supersaturated solution. The measured quantity of 2 mol% of LC was added to supersaturated solution of CTA and allowed to stir at homogeneous speed for six hours. The LC doped CTA solution was filtered and kept for slow solution evaporation in a constant temperature bath at 38 °C. The as grown CTA and LC doped CTA (LC-CTA) single crystals are shown in Fig. 1.

3. Results and discussion

3.1. Single crystal X-ray diffraction (XRD) analysis

The grown crystals were subjected to single crystal XRD analysis using the Enraf Nonius CAD4 single crystal X-ray diffractometer. The XRD data shown in Table 1 reveals that the pure and LC-CTA crystals belong to orthorhombic crystal system. The structural parameters of CTA crystal are in good agreement with literature [5]. The cell parameters of LC-CTA crystal are slightly changed with reference to CTA which might have been occurred due to strain imposed on lattice cites of CTA crystal by dopant LC.

3.2. Fourier transform infrared (FT-IR) analysis

The functional groups of grown crystals have been identified by means of FT-IR spectral analysis using the Bruker α-ATR spectrophotometer. The FT-IR spectrum of single crystals was recorded in the range of 600–4000 cm^{-1} and the recorded spectrum is shown in Fig. 2a. The peak observed at 687 cm^{-1} is contributed due to C–C bond deformation in thiourea. The C=S stretching vibration is attributed at 1459 cm^{-1}. The characteristic COO^- stretching vibration associated with acetate ion is expressed at 1526 cm^{-1}. The NH_2 bending vibration is evident at 1652 cm^{-1}. The functional peak observed at 1693 cm^{-1} confirms the C=O stretching vibration. The broad absorption bands associated with C=O stretching of carboxyl group of LC are expressed at wavenumber 1740 cm^{-1} and 1883 cm^{-1}. The absorption peak at 2360 cm^{-1} is contributed by the C–C bond stretching vibration. The N–H stretching is attributed within 3610–3860 cm^{-1}. In Fig. 2a, the identified shift in functional frequencies confirms the incorporation of dopant LC in CTA crystal.

Table 1
Single crystal XRD data.

Crystal	a (Å)	b (Å)	c (Å)	Volume $(Å)^3$	Crystal system
CTA	7.56	11.87	15.67	1406.18	Orthorhombic
LC-CTA	7.54	11.82	15.89	1416.16	Orthorhombic

3.3. Linear optical studies

The high optical quality is a prerequisite demand for material to possess NLO properties. The optical transmittance of unpolished 2 mm thickness pure and LC-CTA crystal has been recorded within 200–900 nm using the Shimadzu UV-2450 spectrophotometer as shown in Fig. 2b. In a bulk crystal, the transmittance is majorly influenced by chemical composition and defect density. The spectrophotometer records the maximum transmittance of 55% for CTA crystal and 72% transmittance for LC-CTA crystal in visible region. The transmittance of LC-CTA crystal is found to be enhanced by 17% as compared to CTA. This ensures that LC-CTA crystal offers less scattering and absorption of light owing to least absorption tendency of amino acid [8] and minimized defects (structural and crystalline) [9] which might have been enforced by dopant LC resulting to substantial enhancement in %transmittance of LC-CTA crystal. The high transparency and low absorption tendency as observed in LC-CTA crystal may serve advantage for UV-tunable lasers and NLO devices active in blue and green spectrum [10].

The detail analysis of optical constants gives the idea of optical quality of crystal which plays decisive role in processing, tuning, calibrating and designing the technological devices. Thus, the influence of LC on optical conductivity (σ_{op}), extinction coefficient (K), refractive index (n) and reflectance (R) of CTA crystal has been investigated using the measured transmittance data. The variation of optical conductivity and extinction coefficient with reference to photon energy is shown in Fig. 3a and b respectively. It reveals that the optical conductivity increases with increase in photon energy while the reduced extinction coefficient of LC-CTA crystal facilitates less optical loss. The quality of less optical loss with increasing optical conductivity makes LC-CTA crystal highly desirable for ultrafast optical data processing, computing and signaling devices [11]. The characteristic property of material to change the path of light when passed through a medium is termed as refractive index. The change in refractive index and reflectance of grown crystals is plotted in Fig. 3c and d. It confirms that the refractive index and reflectance of CTA has been modified by LC to lower value. The materials with low refractive index are readily used in holographic data storage utilities [12] also; they find huge application as antireflection coating material for solar thermal devices [13]. The LC-CTA crystal with improved linear optical performance is suggested as potential material to be utilized in NLO device applications.

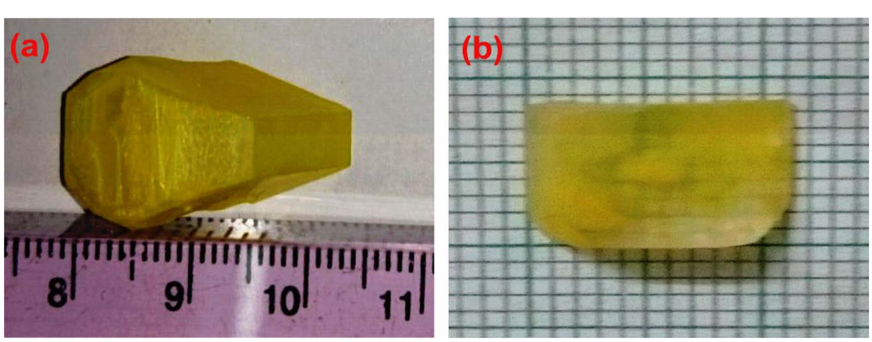

Fig. 1. Single crystal of (a) CTA (b) LC-CTA.