Optics & Laser Technology 60 (2014) 124–129

Contents lists available at ScienceDirect

Optics & Laser Technology

journal homepage: www.elsevier.com/locate/optlastec

Investigation of optical and electrical properties of L-Cystein doped zinc thiourea chloride (ZTC) crystal for nonlinear optical (NLO) applications

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ARTICLE INFO

Article history:
Received 23 October 2013
Received in revised form
4 January 2014
Accepted 14 January 2014
Available online 14 February 2014

Keywords:
Crystal growth
Growth from solution
Nonlinear optics

ABSTRACT

The single crystal of L-Cystein doped zinc thiourea chloride (ZTC) has been grown by slow evaporation technique. The optical study revealed that the doped ZTC crystal has high transmission with lowest cut off wavelength of 306 nm. The optical band gap was found to be 4.2 eV. The transition band gaps were studied using the photoluminescence spectrum. The incorporation of L-Cystein in ZTC was estimated qualitatively by FT-IR analysis. The presence of dopant was confirmed by energy diffraction X-ray analysis (EDAX) analysis. The lower dielectric characteristics of doped ZTC crystal were scrutinized by dielectric measurements. The high thermal stability of grown crystal was ascertained by TG/DTA analysis. The Second harmonic generation (SHG) efficiency measured using Nd-YAG laser is 1.96 times that of pure ZTC.

1. Introduction

In recent years, great efforts had been made to develop new organic, inorganic, and semiorganic nonlinear optical (NLO) materials due to their widespread applications in technologies like lasers, optoelectronics, frequency conversion, high-speed information processing, optical advantage of both inorganic (high thermal and mechanical stability) and organic (broad optical frequency range and second harmonic conversion efficiency) materials. Among thiourea metal complex zinc thiourea chloride (ZTC), zinc thiourea sulphate (ZTS), cadmium thiourea chloride (BTCC), copper thiourea chloride (CTC), bisthiourea zinc acetate (BTZA) and cadmium thiourea acetate (BTCA) are reported and possess moderate SHG efficiency [1–3]. The zinc thiourea chloride (ZTC) is a potential semiorganic NLO material and crystallizes in the non centrosymmetric orthorhombic space group. In the field of nonlinear optical crystal, amino acids play a vital role as they exhibit natural chiral properties and crystallize in the noncentrosymmetric space groups, which are an essential criterion for NLO applications. Optically active amino acids show high efficient optical second harmonic generation (SHG) and are promising candidates for laser and optical communication technology. Since isometrically pure and optically active substances always meet the symmetry requirements for optical second harmonic generation, there is considerable variation in efficiency for the generation of SHG, ranging from almost zero to greater than that of potassium dihydrogen phosphate crystals. The influence of L-Arginine on SHG efficiency of ZTC had been reported by Balu et al. [4].The growth and characterizations of L-Alanine and Glycine doped ZTC crystals had also been reported by our group [5,6]. L-Cystein [$C_3H_7NO_2S$], the smallest naturally occurring amino acid with a thiol group, offers a high degree of chirality due to the presence of three different functional groups. The L-Cystein occurs in both the nonionic and Zwitter ionic forms under involvement of all three functional groups. It has Zwitter ionic state in aqueous solution as well as in solid state [7]. In literature no reference has been observed in attempting L-Cystein doping in ZTC crystal. In the present communication, attention is focused on the effect of optical and dielectric properties of ZTC with addition of amino acid L-Cystein.

2. Experimental

The ZTC salt was synthesized using the AR grade zinc chloride and thiourea in molar ratio 1:2. The Calculated amount of salt was dissolved in the deionised water and allowed to evaporation at room temperature. The ZTC salt was dissolved in deionized water to achieve the supersaturated solution. The amino acid L-Cystein was doped in1, 2 and 3 weight% to the supersaturated solution of ZTC and stirred for four hours at constant speed to achieve the homogeneity throughout the volume. This doped solution is filtered and kept for evaporation at room temperature. The purity of L-Cystein doped ZTC is achieved by successive recrystallisation. The good quality transparent seed crystals were harvested within

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http://dx.doi.org/10.1016/j.optlastec.2014.01.011

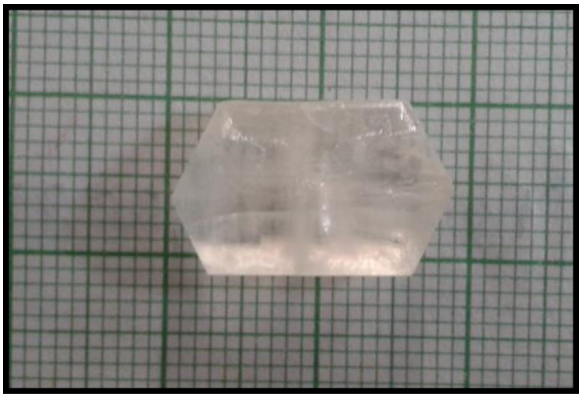

Fig. 1. Photograph of L-Cystein doped ZTC.

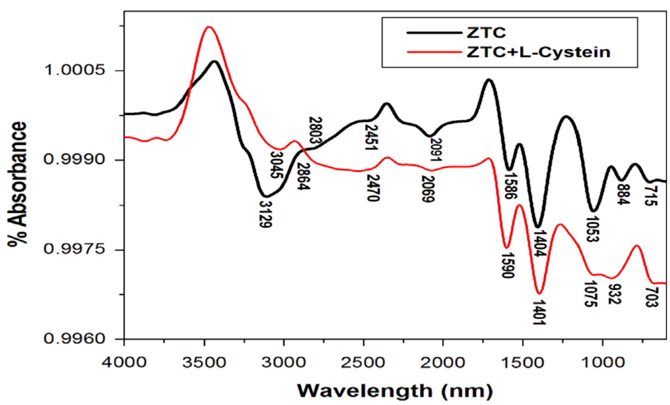

Fig. 2. FT-IR spectrum of L-Cystein doped ZTC.

15 days. The single bulk crystal of 2 wt% L-Cystein doped ZTC was grown by slow evaporation technique is shown in Fig. 1.

3. Result and discussion

3.1. SHG efficiency test

The SHG efficiency of L-Cystein doped ZTC was determined using the Kurtz and Perry powder method [8]. To elaborate, the SHG demands specific molecular alignment of the crystal to be achieved facilitating nonlinearity in the presence of a dopant. The inclusion of complexation alters the molecular alignment which is imperative for enhancing SHG [4]. The NLO behavior was confirmed from the output of the bright green emission from the powder sample. The measured output signals for pure and doped ZTC crystals were 5 mV and 9.8 mV, respectively. The SHG efficiency of Doped ZTC crystal is 1.96 times greater than that of pure ZTC.

3.2. Fourier transform infrared (FT-IR) analysis

The FT-IR spectrum was recorded using Bruker Alpha-T in the region 4000–600 cm^{-1} is shown in Fig. 2. The specific peaks of ZTC occur at 1586, 1404, 1053, 713 cm^{-1}which are in good agreement with the reported work [9]. The major band of C=S symmetric stretching is observed at 932 cm^{-1}.The C–O stretch band is observed at 1075 cm^{-1} for doped ZTC. The C–S asymmetric stretching vibration is observed at 1404 cm^{-1} and 1401 cm^{-1} for pure and doped ZTC crystal. The characteristic $-NH_2$ bending of ZTC is observed at 1586 cm^{-1}. The absorption peak at 1590 cm^{-1} is assigned to $-NH_2$ bending of doped ZTC. The N=C=S bond

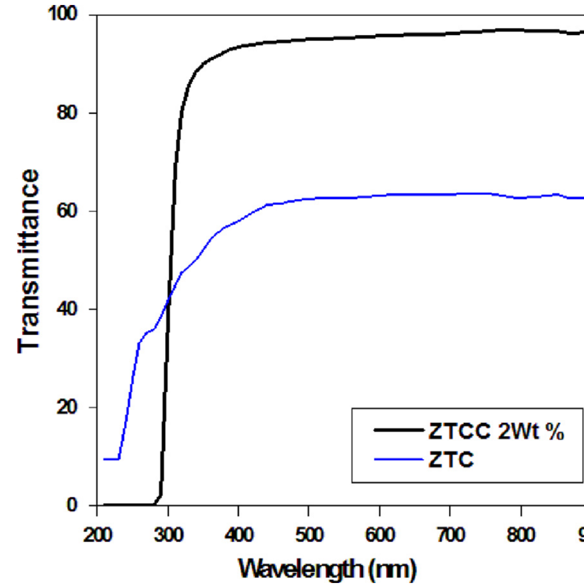

Fig. 3. UV transmittance spectrum.

stretching in the doped ZTC is assigned to absorption peak cited at 2069 cm^{-1}. The absorption observed at 2470 cm^{-1} and 2451 cm^{-1} is assigned to S–H bond stretching. The broad envelope positioned between 2864 cm^{-1} and 3500 cm^{-1} corresponds to the symmetric and asymmetric stretching modes of $-NH_2$ group of pure and doped ZTC crystals. Thus thiourea complex formation and its coordination with the amino acid have been confirmed.

3.3. Optical studies

The optical transmission spectra of the grown crystals were recorded using Shimadzu UV-2450 Spectrophotometer in the range of 200–900 nm is shown in Fig. 3. The L-Cystein doped crystal showed high transmittance of 90% in entire visible region and lower cut off wavelength of 306 nm imperative for laser frequency conversion applications. The optical band gap (E_g) can be evaluated from the transmission spectra [10] using the relation

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \tag{1}$$

where A is a constant, E_g the optical band gap, h the Planck's constant and n the frequency of the incident photon. The optical band gap of doped ZTC crystal is found to be 4.2 eV and is shown in Fig. 4. The lower absorption and high optical band gap is most desirable for UV tunable laser materials [10]. The extinction coefficient of doped ZTC crystal was observed to be decreasing with wavelength represented in Fig. 5 which confirms semiconducting nature of material [11]. The refractive index (RI) was calculated using the formula reported by Bakr et al. and plotted in Fig. 6 [12]. It was found to be 1.12 at 632 nm. The lower RI procured by doped ZTC crystal makes it more suitable than pure ZTC for antireflection coating in solar thermal devices and optical device fabrications [11]. The variation of complex dielectric constant and optical conductivity is shown in Figs. 7 and 8, respectively. The low dielectric constant and enhanced optical conductivity of doped ZTC is better for frequency conversion [11]. Hence, this crystal can be used for UV tunable laser, NLO and SHG device applications effectively.

3.4. Photoluminescence studies

The photoluminescence (PL) studies were carried to evaluate lower concentration of defects and transitional band gaps.