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Growth, SHG and Z-Scan Studies of the Pure and L-Cysteine Doped Zinc Thiourea Sulphate Crystal for Photonic Device Applications

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ABSTRACT

In the current investigation the pure and L-Cysteine (LC) doped Zinc Thiourea Sulphate (ZTS), an optically transparent single crystal has been grown by slow evaporation technique. The encouraging third-order non-linear response of grown crystals has been investigated at 632.8 nm using Z-scan technique, and vital third-order non-linear optical (NLO) constants like third order nonlinear refraction (η_2), nonlinear susceptibility (χ^3), nonlinear absorption (β) and FOM of grown crystal has been evaluated to explore the various optical applications. The χ^3 of magnitude 1.43×10^{-3}esu confirms the strong polarizing nature of doped ZTS crystal. In Kurtz–Perry powder test, the second harmonic generation (SHG) efficiency of doped ZTS crystal is found to be 1.16 times that of ZTS material.

Keywords: Slow evaporation technique, Optical studies, Z-Scan studies, SHG efficiency, NLO materials.

INTRODUCTION

The demands of the nonlinear optical (NLO) crystals have been expedited in the field of photonics technology. The progress of semi organic crystals with superior properties have been focused due to huge applications in photonics and electro-optic modulations devices. [1] Recently, large number of thiourea based organo-metallic crystals with excellent nonlinear optical, mechanical, thermal properties has been reported. The zinc thiourea chloride (ZTC), zinc thiourea sulphate (ZTS), bis-thiourea cadmium acetate (BTCA), bis-thiourea cadmium chloride (BTCC) etc are the well-known crystals reported in the literature [2,3] The ZTS crystal is technologically vital crystal with superior properties as evident in literature.[2-3] Profound research has revealed that the chiral nature of amino acids promote enrichment in properties of various organo-metallic NLO crystals. [4] The various parameters of ZTS crystal have been investigated by doping variety of amino acids namely; glycine, L-Lysine etc. [5-6] The rigorous literature survey noticed that, the effect of L-cysteine (LC) on linear and nonlinear optical properties of ZTS crystal is not investigated. The LC is predominantly chiral amino acid with a thiol group which acquires high affinity towards bonding with metal ions. [7] This bonding ability of LC might serve an advantage to enhance the optical properties of ZTS crystal. Hence, in the current research work pure and LC doped ZTS (LC-ZTS) crystals have been grown and linear and nonlinear optical (NLO) characterization studies have been performed to explore the potential utility of LC-ZTS crystal for photonic device applications.

METHODOLOGY

The analytical reagent (AR) grade zinc sulphate and thiourea in molar ratio 1:3 in deionized water has been dissolved to get the ZTS salt. The recrystallization technique has been used to enhance the purity of the ZTS salt. The LC with 0.5 wt. %, 1 wt. % and 1.5 wt. % was added into supersaturated solution of ZTS. The LC-ZTS mixture was stirred well for 4h and filtered by Whatman filter paper in large size beakers. The beakers were covered by the thin transparent film and kept in isolated vibration free space. The grown crystal obtained from slow solution evaporation technique in 25 days is shown in Fig. 1(a)

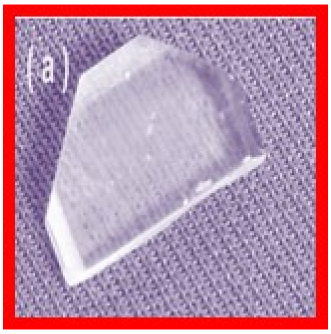

Fig.1(a) LC-ZTS Crystal

NLO Test:

The Kurtz-Perry powder technique [8] was used for evaluating the SHG efficiency of grown crystals. The Q-switched Nd: YAG laser operating at 1064 nm was allowed to incident on the fine powder sample with the repetition rate of 10 Hz. At the output window, the emergence of green output of pure ZTS and LC-ZTS was recorded with a second harmonic signal of 60 mV and 66mV respectively. Thus the SHG efficiency of LC-ZTS is found to be 1.16 times that of pure ZTS. Thus, the LC-ZTS crystal is a promising material than ZTS for laser frequency conversion devices.

Z-Scan Studies:

The determination of third-order non-linearity at single wavelength helps to explore the applications ultrafast lasers and photonic systems. A sensitive Z-scan technique has been developed by Bahae *et al.* It is a significant tool for finding the nature and magnitude of third-order non-linearity of pure and LC-ZTS crystal. [9] In order to confirm the path-dependent third-order non-linearity, the transparent crystal sample was tightly focused by the He–Ne laser beam (632.8 nm) using a convex lens, and the crystal was move along the Z-direction with reference to focus (Z = 0). The respective path-dependent transmittance was noticed by means of photo detector placed at far field. The details of Z-scan set-up are given in table 1. The close aperture Z-scan technique has been used to determined third-order non-linear refraction (NLR) (n_2) of the grown crystals. The fig.2 and 3 noticed the closed aperture Z-scan transmittance curve of pure and LC-ZTS crystal. In the crystals, the pre-focus valley and the post-focus peak evidences the signature of positive NLR which is the characteristic property of material foreshowing self-focusing nature.[10] The focused repetitive optical energy of laser beam is a crucial factor which leads to the localized absorption and spatial distribution of energy throughout the crystal surface causing a phase shift in NLR of the crystal material.[11]

The peak-to-valley transmission (ΔTp-v) can be expressedin phase shift as,

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

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 radius at the aperture. The third order non linear refractive index (n_2) of crystals has been determined using the relation, [9]

$$\eta = \frac{\Delta\varphi}{kI_0L_{eff}}$$

Where K = $2\pi/\lambda$, I_0 is the beam intensity at the focus Z = 0. The effective thickness of the sampleis determine by using the equation, $L_{eff} = [1 - \exp(-\alpha L)/\alpha$, which depends on linear.

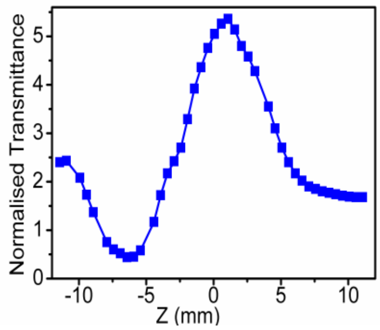

Fig.2. Closed apertures Z- scan transmittance curve of ZTS

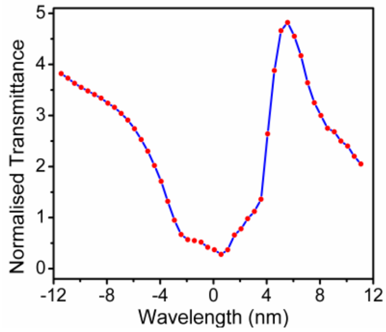

Fig.3. Closed aperture Z-scan transmittance curve of LC-ZTS

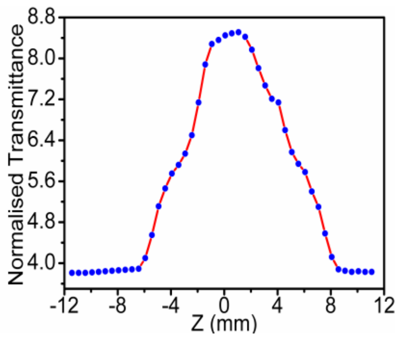

Fig.4. Open apertures Z- scan transmittance curve of ZTS

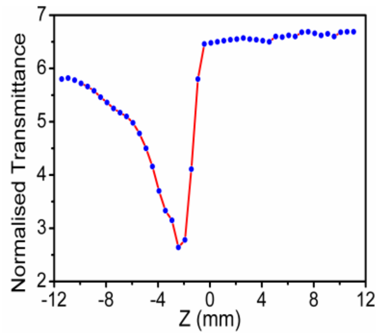

Fig.5. Closed apertures Z- scan transmittance curve of LC-ZTS

Table: 1. Optical details of Z- scan setup and measured parameters.

Laser beam wavelength (λ)	632.8nm	
Lens focal length (f)	8.5cm	
Optical path distance (Z)	115cm	
Aperture radius (r_a)	2mm	
Spot-size diameter in front of the aperture (ω_a)	1mm	
Incident intensity at the focus (Z = 0)	25MW/cm^2	
Sample thickness (L)	2mm	
Effective thickness (L_{eff})	1.81mm	
Nonlinear refractive Index (n_2)	LC-ZTS	ZTS
	3.21×10^{-7} cm^2/W	2.24×10^{-8} cm^2/W
Nonlinear absorption coefficient (β)	1.36×10^{-4} cm/W	3.91×10^{-3} cm/W
Third-order nonlinear susceptibility (χ^3)	1.42×10^{-3}esu	8.64×10^{-3}esu
Figure of Merit (FOM)	26.86	11.40

absorption coefficient (α) and thickness (L) of the sample.

The high magnitude of positive NLR relates directly to the prominent Kerr-lens mode locking (KLM) ability of the crystal. [12] The $n_2$value is found to be of the order of 10^{-7} cm^2/W, such high magnitude of NLR suggests the strong Kerr-lensing effect which advocates the prominence of pure and LC-ZTS crystals for analyzing the stability limits of continuous wave mode locked laser systems and generating the shorter laser pulses. [13]

The open aperture Z-scan trace of LC-ZTS (fig.5) crystal identifies the fall in transmittance at focus, which indicates the prominence of multi-photon absorption (MPA) assisted by excited state absorption (ESA) phenomenon. [14] The MPA is a complex effect which is triggered due to contributions from two-photon absorption (TPA) along with the absorption governed by excited singlet and triplet states. [14,15] The nonlinear absorption coefficient (β) of both pure and doped ZTS can be evaluated using the open aperture transmittance data, according to the equation shown below, [9]

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}},$$

Where, ΔT is the one valley value obtained in open aperture Z-scan curve. The non-linear absorption coefficient (β) of LC-ZTS crystal is found to be 1.36×10^{-4} cm/W which is superior to several reported materials.[16]The cubic susceptibly (χ3) of the crystals has been analyzed by solving the following equations,

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

$$Re\chi^3(esu) = \frac{10^{-2}(\varepsilon_0 C^2 n_0{}^2 \lambda\beta)}{4\pi^2(cm/w)}$$

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. Thus, we can easily obtain the absolute value of χ^3 using equation,

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

Where, ε_o, the vacuum permittivity, n_0 is the linear refractive index of the sample and c is the velocity of light in vacuum.

The LC-ZTS crystal has higher χ3 value than pure ZTS and other technologically vital crystals such as KDP, BTCF, BBO and $LiNbO_3$. [17] The observed enhancement in susceptibility of LC-ZTS crystal is an evidence of increased charge transfer through donor–acceptor channel which is the characteristic feature of strongly polarized material. The figure of merit (FOM = $\beta\lambda/n2$) is a decisive parameter to ascertain the worthiness of crystal for optical power limiting applications. [18] The pure and LC-ZTS crystals with attractive non-linear properties (see table 6.5) hold huge advantage for optical switching, calibrating optical distortions, optical logic gates and passive laser mode-locking systems. [19] The shifts observed in maximum valley transmittance of close (see figs. 6.15 and 6.16) and open (see fig.4 and5) aperture curves of LC-ZTS crystal confirm that LC is the potential dopant to tailor TONLO properties of ZTS crystal. It is interesting to note that LC has shifted the maximum valley transmittance of close and open aperture curves of ZTS crystal towards +Z direction which confirms L-cysteine as a potential dopant to tailor TONLO properties of ZTS crystal. Also, in regime of TMC crystals, the third-order non-linear susceptibility of pure and LC-ZTS crystals are remarkably greater than thiourea, BTZB, ZTS, BTZC and BTCF crystals. [8, 19].

CONCLUSION

Optically transparent pure and LC-ZTS crystals have been grown by slow evaporation solution growth technique. The enhanced SHG efficiency of LC-ZTS crystal is found to be 1.16 times that of pure ZTS crystals. The grown crystal showed potential third order nonlinear optical parameters ascertained from Z-scan technique at 632.8 nm. All above studies suggests the prominence of grown crystal for laser stabilization, microelectronics and integrated optical applications. The present studies concluded that the LC-ZTS possesses improved transparency, third order nonlinearity enhanced SHG efficiency which validates its applicability for NLO and photonic devices.

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