Exploration of third order NLO property of semi-organic optical material: Bis(L-threonine) copper (II) monohydrate [BLTCM]

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Abstract

Transparent, nonlinear Bis(L-threonine) copper (II) monohydrate [BLTCM], the semiorganic optical crystal was synthesized by a conventional slow evaporation solution growth technique. The synthesized crystals were investigated to reveals its excellent performance. The third order nonlinear optical properties of BLTCM sample in WATER was measured by the *Z*-scan technique using 532nm diode pumped solid state laser. This material exhibits negative optical nonlinearity. The sample at around 62 % transmittance exhibited non-linear refractive coefficient of the order of 10^{-9} (cm^2/W), nonlinear absorption coefficient of the order of 10^{-4} cm/W and nonlinear susceptibility of the order of 10^{-6} esu. These results show that BLTCM sample has potential applications in nonlinear optics.

Keywords

Solution growth ; Slow evaporation; Third order nonlinearity

1. Introduction

The search for new advanced materials is an important area of contemporary research in numerous disciplines of science and development of many new technologies. Nonlinear optical (NLO) crystals have been a great deal of interest in recent years due to their potential applications in the domain of optoelectronics and photonic technologies [1]. While the engineering for enhancing second order NLO efficiency is relatively well understood, the need for efficient third order molecules and materials still exists. Materials with third order NLO finds application in ultra-high-speed signal processing, information storage, optoelectronics and photonics, optical switching, microscopic imaging, and optical limiting applications as discussed in various literature. Organic nonlinearity, high value of molecular polarizability, molecular flexibility, low mobility, and wide bandgap [2] but it is difficult to grow large size crystals as it possess low mechanical stability. Inorganic NLO materials though they possess good mechanical and thermal properties, they lack delocalisation in π-electrons and hence only passable non-linearity. The advantages of inorganic and organic materials are tailored in semi-organic materials [3]. Aminoacids, are attractive organic candidates as they contain amine ($-NH_2$) and carboxylic acid (-COOH) functional groups along with a side chain (R group) specific to each amino acid [4]. There are numerous amino acid based NLO crystals have been reported and their properties were studied [5-9]. The complex of amino acids are prone to introduce a noncentrosymmetric space group in crystals. Hence, Bis(L-threonine) copper (II) monohydrate (BLTCM) [10,11] was chosen and it was synthesized within a short period of ten days. In the present investigation we report here the third-order nonlinear parameters of BLTCM, such as nonlinear absorption coefficient, nonlinear refractive index, third-order susceptibility and second-order hyperpolarizability have been analyzed using Z-scan.

2. Crystal growth

BLTCM was synthesised by mixing L-Threonine (loba chemie) and copper carbonate in equimolar ratio (2:1) in the deionized water. The homogeneous solution was obtained after stirring well for 3h using a magnetic stirrer. This solution was filtered by using Whatmann filter paper and allowed for evaporation. After a growth period of 10 days, transparent and non-hygroscopic good quality blue single crystals were obtained as shown in Fig. 1.

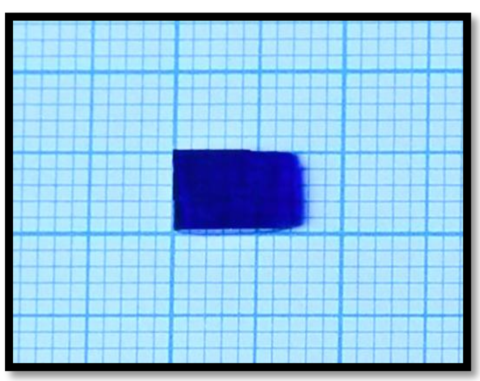


Fig. 1 As grown crystal of BLTCM

3. Nonlinear studies

The Z-scan technique [12,13] is a simple but very accurate method to determine both nonlinear index of refraction n_2 and nonlinear absorption coefficient β. Nonlinear index of refraction is proportional to the real part of the third-order susceptibility. [$Re\chi^{(3)}$] and the nonlinear absorption coefficient is proportional to [$Im\chi^{(3)}$]. The *Z*-scan experiments were performed using a 532 nm diode pumped solid state laser, which was focused by a 103 mm focal length lens. The intensity (I∘) and the beam waist (ω∘) at the focal point were calculated to be 0.0136 $MWcm^{-2}$ and 0.33 μm respectively. The Rayleigh range (Z∘ = πω∘/ λ) of the experimental setup was found to be 1.32 mm, hence satisfying the condition L < z∘ for thin sample approximation.
The schematic of the experimental set up used is shown in Fig. 2.

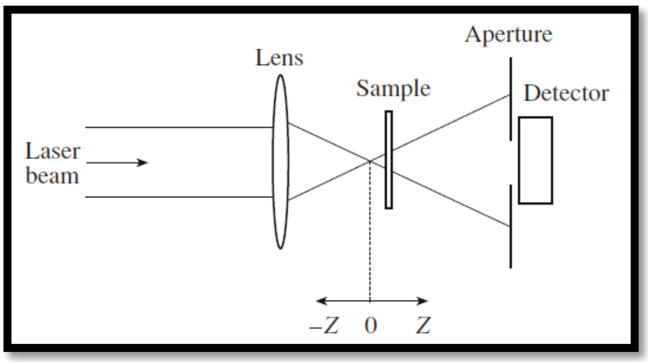
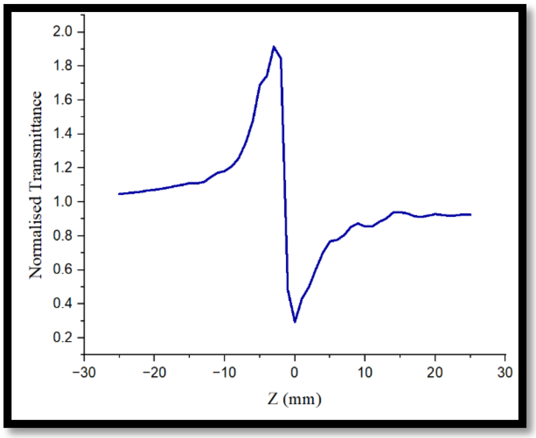


Fig.2 Schematic of experimental setup for z-scan

A 1 mm wide optical cell containing the BLTCM sample in WATER is translated across the focal region along the axial direction that is the direction of the propagation laser beam. The transmission of the beam through an aperture placed in the far field was measured using photo detector fed to the digital power meter (Field master GS-coherent). For an open aperture *Z*-scan, a lens to collect the entire laser beam transmitted through the sample replaced the aperture.
Fig.3 gives a closed, open and ratio of the closed-to-open normalized *Z*-scan of BLTCM sample in WATER at 60% transmittance. The peak followed by a valley-normalized transmittance obtained from the closed aperture *Z*-scan data indicates that the sign of the refraction nonlinearity is negative, i.e., self-defocusing. The self-defocusing effect is due to the local variation in the refractive index with the temperature. The open aperture Z-scan pattern showed transmission minimum at focus, indicating the reverse saturable absorption (RSA).



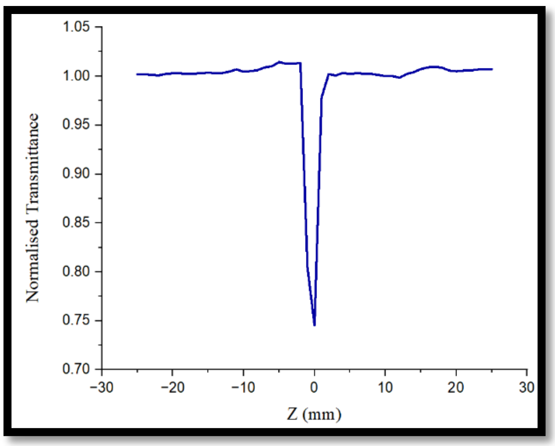


Fig. 3(a) **Fig. 3(b)**

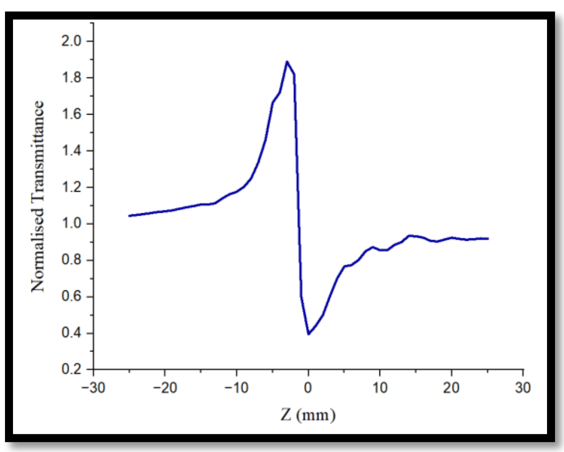


Fig. 3(c)

Fig. 3 (a) Closed aperture Z-Scan plot of BLTCM (b) Open aperture Z-Scan plot of BLTCM (c) ratio of closed to open aperture z-scan plot of BLTCM

The measurable quantity ΔT_{p-v} can be defined as the difference between the normalized peak and valley transmittances, $T_p - T_v$. The variation of this quantity as a function of $|\Delta\phi_o|$ is given by

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

where $\Delta\phi_0$ is the on-axis phase shift at the focus. S the aperture linear transmittance is given by

$$S = 1 - \exp(-2\, r^2_a/\omega^2_a) \tag{2}$$

with r_a denoting the aperture radius and ω_a denoting the radius of the laser spot before the aperture .

The on-axis phase shift is related to the third order nonlinear refractive index (n_2) [14] by,

$$|\Delta\phi_0| = kn_2\, L_{eff}\, I_0 \tag{3}$$

where $L_{eff} = (1-e^{-\alpha L})/\alpha$, with L the sample length , α is the linear absorption coefficient I_O is the intensity of the laser beam at focus $z = 0$, and k is the wave number($k=2\pi/\lambda$).

The imaginary parts of the third-order nonlinear optical susceptibility [χ^3] is estimated using the value of the nonlinear absorption coefficient β obtained from the open aperture Z-scan data and using the relations:

$$q_o(z) = \frac{\beta . I_o . L_{eff}}{(1+\frac{Z^2}{Z_o{}^2})} \tag{4}$$

$$\beta = \frac{2\sqrt{2}.\Delta T}{I_o . L_{eff}} \tag{5}$$

$Z_R = k\omega_0^2/2$ is the diffraction length of the beam, ω_0 is the beam waist radius at the focal point. Experimentally determined nonlinear refractive index n_2 and nonlinear absorption coefficient β can be used in finding the real and imaginary parts of the third-order nonlinear optical susceptibility [χ^3] [15,16] according to the following relations.

$$\text{Re}\,\chi^3(esu) = 10^{-4}\frac{\varepsilon_o c^2 n_o{}^2}{\pi} n_2 (\frac{cm^2}{W}) \tag{6}$$

$$I_m \chi^3(esu) = 10^{-2}\frac{\varepsilon_o c^2 n_o{}^2 \lambda}{4\pi^2} \beta(\frac{cm}{W}) \tag{7}$$

where ε_0 is the vacuum permittivity, and c is the light velocity in vacuum.

The absolute value of the third-order nonlinear optical susceptibility is given by the relation

$$\left|\chi^3\right| = \left[(R_e(\chi^3))^2 + (I_m(\chi^3))^2\right]^{1/2} \tag{8}$$

The nonlinear parameters calculated are as tabulated in Table 1

Table 1. Nonlinear parameters of BLTCM in water

Results						
Sample Code	n_o	n_2 (cm^2/W)	β (cm/W)	$Re\chi^{(3)}$ (cm^2/W)	$Im\chi^{(3)}$ (cm/W)	$\chi^{(3)}$ (esu)
BLTCM	1.73	1.31E-09	2.36E-04	2.34E-06	1.22E-06	2.64E-06

From the calculated values it is clear that the nonlinear absorption coefficient value is positive for the grown crystal. The crystal possess the positive third order nonlinear refractive index which is associated with self-focusing effect. The enhanced χ3 value proves that the crystal is an alternative for optical limiting and sensing, and optical storage applications.

4. Conclusion

BLTCM single crystal was grown by low temperature solution growth technique. Third order NLO susceptibility for BLTCM was investigated by Z-Scan technique. The enhanced third order optical susceptibility value supports the usage of the crystal in optical limiting applications. The values obtained suggests that the BLTCM crystal can be used for various optical data processing switching applications. As a consequence, the reported crystal opens a new pathway to investigate further the suitability in other NLO applications such as laser production and optical processing unit.

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