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Evaluate the effect of L-valine on linear–nonlinear optical and electrical properties of BTCA crystal to identify photonic device applications

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In this study, pure and L-valine (LV)-doped bis-thiourea cadmium acetate (BTCA) crystals have been grown by slow solution evaporation technique. For the first time, LV has been used as a dopant to tune the optical (linear and third-order non-linear optical) and electrical properties of BTCA crystal which are vital for various integrated optic device applications. The UV-visible spectral analysis has been performed in the range of 200–900 nm to determine the optical transparency of grown crystals. The Z-scan (open and closed apertures) studies were undertaken at 632.8 nm to ascertain the nature of third-order non-linearity in grown crystals. The third-order non-linear optical parameters such as non-linear refraction (n_2), absorption coefficient (β) and susceptibility (χ^3) of grown crystals have been calculated. The susceptibility (χ^3) of pure and LV-doped BTCA crystal is found to be 2.58×10^{-4} esu and 3.34×10^{-4} esu, respectively. The electrical studies have been carried out to analyse the dielectric constant, dielectric loss, ac resistivity and ac conductivity of pure and LV-doped BTCA crystals.

Keywords: Crystal growth, Non-linear optical materials, UV-visible studies, Z-scan studies, Dielectric studies

Introduction

The demand of materials offering excellent optical, electrical and non-linear optical (NLO) coefficient has been sustained for past few decades as they hold wide application in the field of optical signal processing, laser fusion and ultrafast laser systems, UV-tunable lasers, optoelectronics and NLO-assisted photonic devices.[1] Recently, semiorganic crystals belonging to thiourea metal complex (TMC) family have gained large attention owing to organo-metallic bond channel which offers high non-linearity, huge threshold to laser damage, fast electronic response, high mechanical strength and good thermal stability. These are the vital qualities of raw materials essential for designing high edge integrated optical devices.[2] Amongst the various reported TMC crystals, bis-thiourea cadmium acetate (BTCA) is an interesting NLO crystal. The structural, UV–visible, SHG efficiency, photoconductivity, dielectric, photoluminescence, mechanical and thermal behaviour of BTCA crystal has been extensively studied in past.[3–5] In order to achieve the enhancement in characteristic properties of BTCA crystal, many researchers have attempted to grow BTCA crystal by either using different growth techniques or using additives such as amino acids (glycine and L-alanine), urea and metal-based dopants.[6–8] The analysis revealed that the amino acid dopants have played significant role in enhancing the optical and dielectric performance of BTCA crystal; also it is interesting to note that not a single researcher has explored the third-order non-linear optical (TONLO) properties of BTCA crystal. As NLO materials with high figure of merit are largely demanded for all optical device applications, this is the first investigation to report the TONLO studies of pure and L-valine (LV)-doped BTCA crystal. The influence on LV on UV-visible, third-order non-linear optical and dielectric behaviour of BTCA crystal has been investigated, and the possible integrated optic applications of grown crystals have been discussed.

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Experimental procedure

The Merck-made AR grade salt of thiourea and cadmium acetate was dissolved in deionised water in molar (1:2) ratio to synthesise the pure BTCA crystal compound. The supersaturated solution of BTCA was prepared and gradually 0.5 mol% LV was added to it with constant stirring speed so as to achieve the homogeneous doping throughout the aqueous solution. The LV-doped BTCA solution was allowed to stir for six hours, and later the solution was filtered in a rinsed beaker using the No.1 Whatman filter paper. The slow evaporation of aqueous solutions of pure and LV-doped BTCA was maintained at 40 °C (±0.01 °C) in a constant temperature bath. The pure and LV-doped BTCA (LV-BTCA) crystals grown in a period of 3–4 weeks are shown in Fig. 1.

Results and discussion

Optical studies

UV-visible spectral analysis

In order to determine the influence of LV on optical transparency of BTCA crystal, the UV–visible absorption spectrum of grown crystals (2 mm thickness) has been recorded in the

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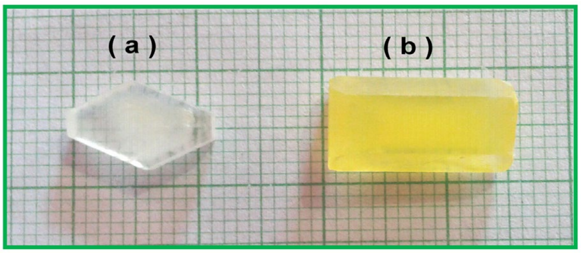
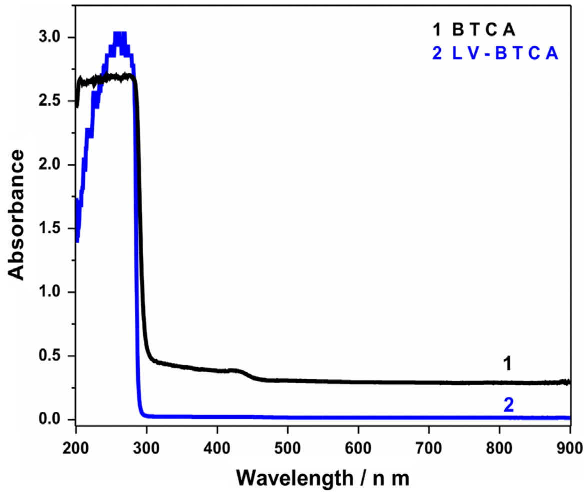


1 Crystal of (a) LV-BTCA and (b) BTCA

range of 200–900 nm using the Shimadzu spectrophotometer (UV-2450). The absorption spectrum (Fig. 2) reveals that LV has largely reduced the optical absorption of BTCA crystal to lower level which makes it highly transparent and useful for all optical devices operating in visible spectrum. The LV-BTCA crystal with lower absorption behaviour falls to the regime of materials that are desirable for UV-tunable lasers and optoelectronic applications.[9,10] The least intrinsic absorption tendency of amino acids[11] and role of dopant in eliminating the crystalline and structural defects (point and line defects, solution inclusions and void density)[7] are the principle factors responsible for minimum optical scattering leading to less optical loss and increase in optical transparency of LV-BTCA crystal. The uniform and enhanced optical homogeneity (i.e. lower optical loss) over wide range is another notable quality that advocates the stringent requirement of LV-BTCA crystal for ultrafast optical data streaming and computing devices.[12]



2 UV-visible absorption spectrum

Table 1 Optical resolution of Z-scan set-up

Parameters and notations	Details
Laser wavelength (λ)	632.8 nm
Laser power (P)	10 mW
Lens focal length (f)	20 cm
Optical path distance (Z)	113 cm
Beam waist radius (ω_a)	1 mm
Aperture radius (r_a)	15 mm
Incident intensity at the focus (I_o)	2.3375 KW/m^2

Z-scan analysis

The determination of third-order non-linearity at single wavelength helps to explore the wide spectrum of applications of the crystal material in the field of distinct NLO-assisted ultrafast lasers and photonic systems. A sensitive and influential Z-scan technique developed by Bahae *et al.*, has been used as a significant tool for finding the nature and magnitude of third-order non-linearity of pure and LV-BTCA crystal.[13] In order to confirm the path-dependent third-order non-linearity, the transparent crystal sample was tightly focused by the gaussian beam of He–Ne laser (632.8 nm) using a convex lens, and the crystal was then gradually translated along the Z-direction with reference to focus ($Z = 0$). The respective path-dependent transmittance was traced by means of photo detector placed at far field. The details of Z-scan set-up are given in Table 1. The n_2 (third-order non-linear refraction (NLR)) of the grown crystals has been determined using the close aperture Z-scan technique and the closed aperture Z-scan transmittance curve of pure and LV-BTCA crystal is shown in Figs. 3*a* and 4*a*, respectively. In both 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.[14] The focused repetitive optical energy of laser beam is a crucial factor which leads to the localised absorption and spatial distribution of energy throughout the crystal surface causing a phase shift in NLR of the crystal material.[15] The peak-to-valley transmission ($\Delta T_{p\text{-}v}$) can be expressed in phase shift as,

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

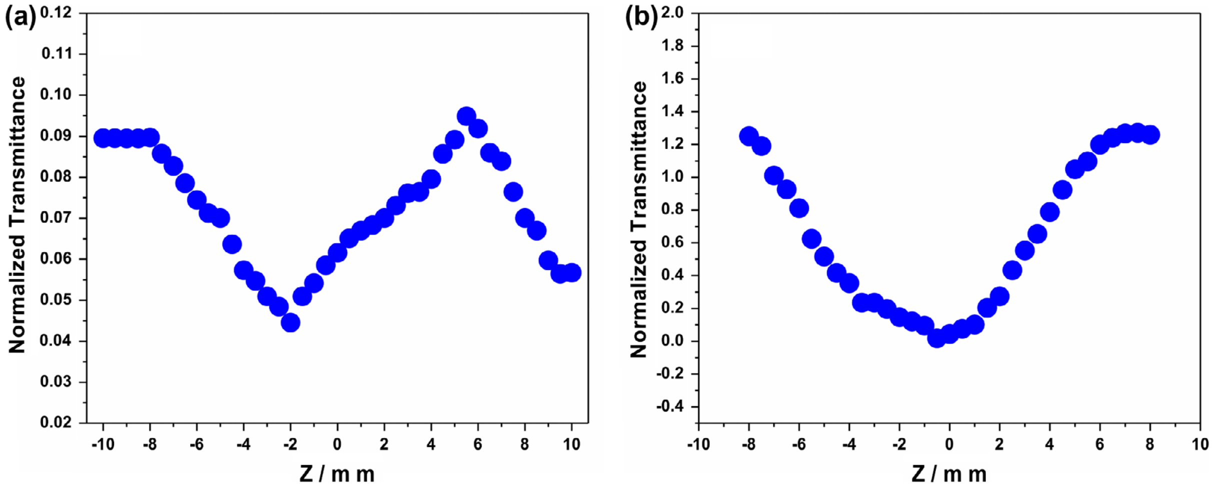
where $S = [1 - \exp(-2r_a^2/\omega_a^2)]$ is the aperture linear transmittance, r_a is the aperture radius and ω_a is the beam waist radius in front of aperture. The n_2 of crystals has been determined using the relation,

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

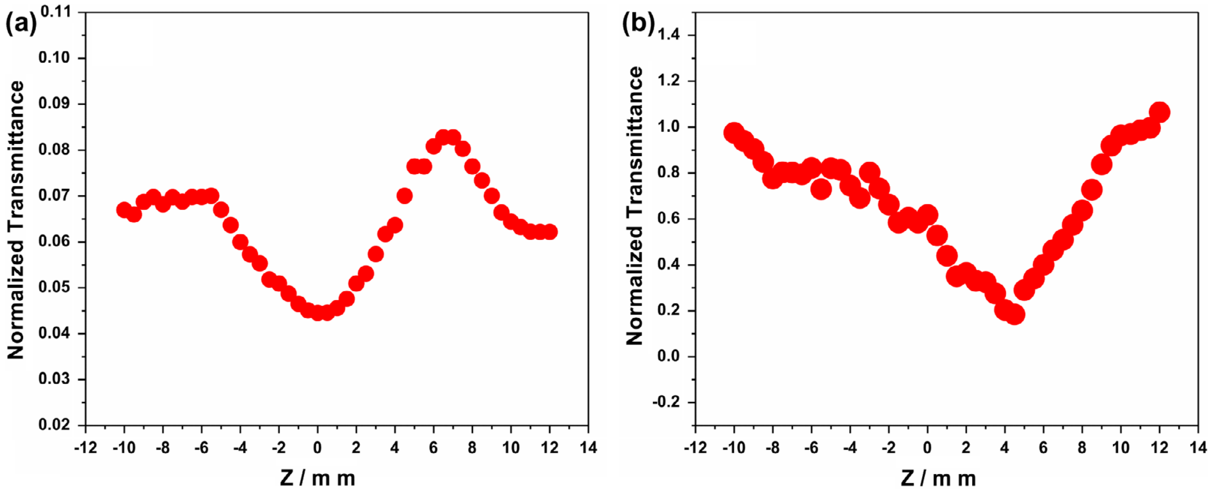
where $K = 2\pi/\lambda$, $I_0 = 2P/\pi\omega_a^2$, is the incident irradiance intensity of beam at the focus ($Z = 0$), the effective thickness of the sample, $L_{eff} = [1 - \exp(-\alpha L)]/\alpha$, depends on linear absorption coefficient (α) and L thickness of the sample. The high magnitude of positive NLR relates directly to the prominent kerr-lens modelocking (KLM) ability of the crystal. The n_2 value is found to be of the order of 10^{-11} cm^2/W, such high magnitude of NLR suggests the strong kerr-lensing effect which advocates the prominence of pure and LV-BTCA crystals for analysing the stability limits of continuous-wave mode-locked laser systems and generating the shorter laser pulses.[16] The open aperture Z-scan trace of pure (Fig. 3*b*) and LV-BTCA (Fig. 4*b*) crystal identifies the fall in transmittance at focus, which indicates the prominence of multi-photon absorption (MPA) assisted by excited state absorption (ESA) phenomenon.[17] 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.[17,18] The non-linear absorption coefficient (β) of LV-BTCA crystal is found to be 9.05×10^{-6} cm/W which is superior to several reported materials.[19] The β value can be evaluated using equation,

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0L_{eff}} \quad (3)$$

where ΔT is the one valley value obtained in open aperture Z-scan curve. The cubic susceptibly (χ^3) of the crystals has been analysed by solving the following equations,



3 ***a* Close and *b* open aperture Z-scan transmittance of BTCA crystal**



4 ***a* Close and *b* open aperture Z-scan transmittance of LV-BTCA crystal**

Table 2 TONLO parameters

Crystal	n_2 cm²/W	β cm/W	χ^3 esu	FOM
BTCA	8.37×10^{-11}	4.70×10^{-6}	2.58×10^{-4}	35.57
LV-BTCA	5.06×10^{-11}	9.05×10^{-6}	3.34×10^{-4}	113.1

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

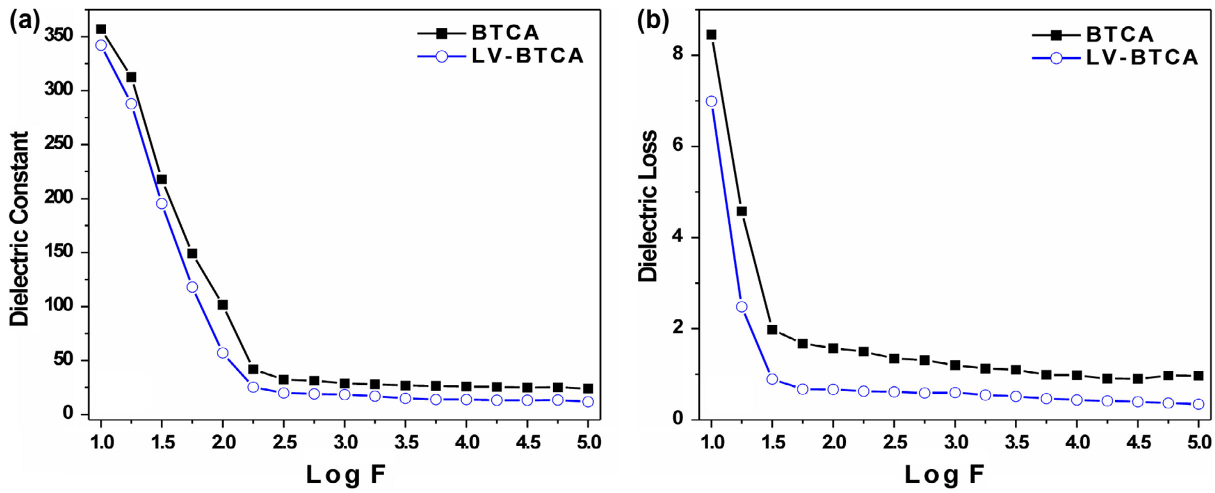
$$\mathrm{Im}\chi^{(3)}(esu) = 10^{-2}(\varepsilon_0 C^2 n_0^2 \lambda\beta)/4\pi^2(\mathrm{cm}/\mathrm{W}) \quad (5)$$

$$\chi^3 = \sqrt{(\mathrm{Re}\chi^3)^2 + (\mathrm{Im}\chi^3)^2} \quad (6)$$

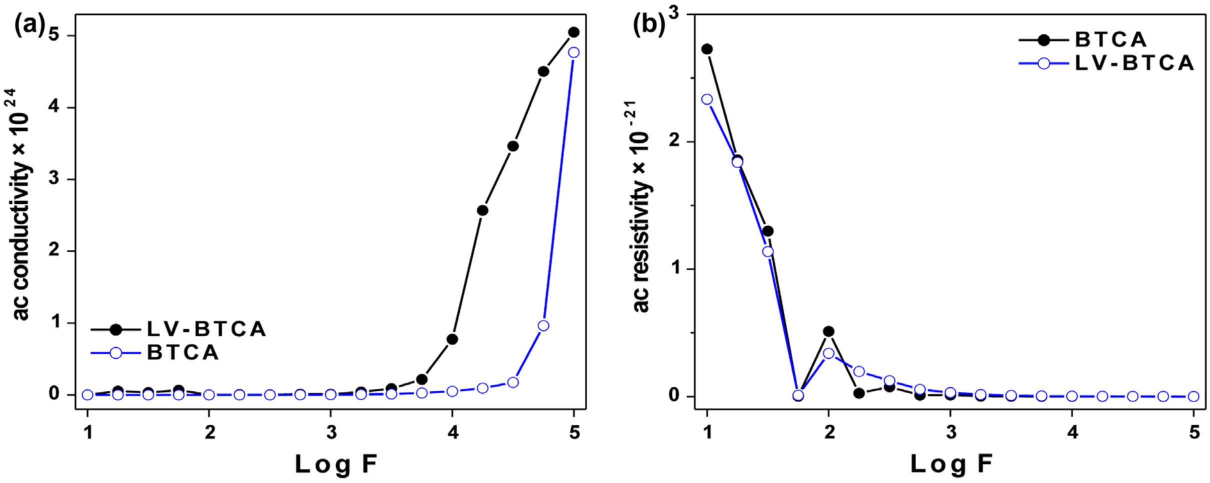
where ε_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample and c is the velocity of light in vacuum. The LV-BTCA crystal has higher χ^3 value than pure BTCA and other technologically vital crystals such as KDP, BBO and $LiNbO_3$.[20] The observed enhancement in susceptibility of LV-BTCA crystal is an evidence of increased charge transfer through donor–acceptor channel which is the characteristic feature of strongly polarised material. The figure of merit (FOM $= \beta\lambda/n_2$) is a decisive parameter to ascertain the worthiness of crystal for optical power limiting applications.[21] The pure and LV-BTCA crystals with attractive non-linear properties (see Table 2) hold huge advantage for optical switching, calibrating optical distortions, optical logic gates and passive laser mode-locking systems.[22] The shifts observed in maximum valley transmittance of close (see Figs. 3*a* and 4*a*) and open (see Figs. 3*b* and 4*b*) aperture curves of LV-BTCA crystal confirm that LV is the potential dopant to tailor TONLO properties of BTCA crystal. It is interesting to note that LV has shifted the maximum valley transmittance of close (see Figs. 3*a* and 4*a*) and open (see Figs. 3*b* and 4*b*) aperture curves of BTCA crystal towards +*Z* direction which confirms L-valine as a potential dopant to tailor TONLO properties of BTCA crystal. Also, in regime of TMC crystals, the third-order non-linear susceptibility of pure and LV-BTCA crystals is remarkably greater than thiourea, BTZB, ZTS, BTZC and BTCF crystals.[19,23]

Electrical studies

In this study, the electrical response of grown crystals has been investigated using the LCR tester (Gwinstek-819). For



5 Frequency-dependent *a* Dielectric constant and *b* Dielectric loss



6 Frequency-dependent *a* ac conductivity and *b* ac resistivity

the measurement, the flat-surfaced 2.5-mm-thickness pure and LV-BTCA crystals were coated with the highly conductive silver paste to obtain good contact with the LCR meter probes and measure accurate data. The frequency-dependent nature of dielectric constant (Fig. 5*a*) and dielectric loss (Fig. 5*b*) of grown crystals has been recorded in the range of 10 Hz–100 kHz at room temperature. The dielectric constant of material depends on various polarisation (electronic, ionic, dipolar and space charge) mechanisms. As time required for alignment of polarisation direction is larger in low-frequency domain, it contributes to higher magnitude of dielectric constant; on the other hand, the increased frequency of applied field induces the faster alignment of polarisation direction which results to profoundly lower magnitude of dielectric constant.[24]

In case of LV-BTCA crystal, the dielectric constant is significantly lower than BTCA throughout the frequency range. The lower dielectric constant is a suitable parameter for enhancing the SHG coefficient of the material[25], also the lower dielectric constant offers less consumption of electrical power which is a vital requirement for manufacturing microelectronic devices, THz wave generators, broad band electro-optic modulators and field detectors.[26,27] The LV-BTCA crystal with lower dielectric constant could be a material of interest for all foresaid industrial applications. The study of dielectric loss is a significant parameter to evaluate the extinct of electrical loss within the material medium. It is observed that the dielectric loss of both the crystals decreases with the increase in frequency, but the lower dielectric loss of LV-BTCA indicates that the crystal is of good optical quality with minimum electrically active defects.[28] The frequency response of ac conductivity and ac resistivity of grown crystals has been measured, and the behaviour is plotted in Fig. 6*a* and *b,* respectively. It reveals that the behaviour of ac resistivity and ac conductivity is opposite in nature. In accordance to small polaron hopping model theory, the conductivity of material increases at higher frequency which is in good agreement in the case of pure and LV-BTCA crystals.[29]

Conclusion

In this study, optically transparent LV-doped BTCA crystal has been successfully grown by employing slow solution evaporation technique. The UV-visible analysis revealed that LV-doped BTCA crystal has sufficiently lower optical loss than BTCA in entire visible region which vitalises its prominence for applications of ultrafast optical data transmission, processing and signalling devices. In closed aperture Z-scan study, pure and doped BTCA crystals were observed to have positive NLR behaviour which established the self-focusing tendency of materials. The obtained higher magnitude of positive NLR demonstrates the existence of strong kerr-lens modelocking effect in pure and doped BTCA crystal. The excited state absorption-assisted multi-photon absorption phenomenon was observed in both the studied crystals. The superior χ^3 and FOM of LV-doped BTCA crystal revealed the strong polarising nature and enhanced the mobility of charge transfer. The shifts observed in valley transmittance of close and open aperture Z-scan curves confirms the strong influence of LV on NLO behaviour of BTCA crystal. In electrical studies, the dielectric constant and dielectric loss of LV-doped BTCA crystal is remarkably lower than BTCA crystal. The ac conductivity and resistivity of the crystals have been investigated. Above studies infer that LV-BTCA crystal is a promising optical material which could be exceptionally advantageous for applications of passive laser modelocking systems, broad band electro-optic modulators, laser stabiliser and short pulse generation systems, optical data processing, optical limiting and all photonic devices.

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