Comparative Study on Structural, Optical, Dielectric and Thermal Properties of Pure and L-Alanine Doped Bis-Thiourea Cadmium Acetate Crystal

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Abstract- Structural, optical, dielectric and thermal properties of pure and L-alanine (LA) doped bis-thiourea cadmium acetate (BTCA) crystals have been studied in present investigation. Pure and L-alanine (LA) doped bis-thiourea cadmium acetate (BTCA) crystals have been grown by slow evaporation technique. The crystal system of pure and doped BTCA crystal has been determined by single crystal XRD technique. The shifts in the vibrational frequencies of functional groups of doped BTCA crystal have been identified by FT-IR spectral analysis. The improved optical transparency and large transmission range of doped BTCA crystal has been assessed under UV-visible study. The enhanced optical band gap of LA doped BTCA is found to be 4.83 eV. The thermal stability of doped BTCA crystal was determined by means of thermogravimetric & differential thermal analysis. The dielectric characteristics of pure and doped BTCA crystals were investigated using dielectric studies. Significant enhancement in SHG efficiency was observed after doping LA in BTCA which is determined to be 4 times that of pure BTCA crystal.

Index Terms- Crystal growth, Nonlinear material, Optical properties, Electric properties, thermal properties

I. INTRODUCTION

Nonlinear thiourea metal complexes with high mechanical hardness, structural stability, high optical and nonlinear behavior are advantageous for applications in the fields of optical information-storing devices, second harmonic generation (SHG), nonlinear optical (NLO) and telecommunication systems [1]. A large family of thiourea metal complexes include zinc thiourea sulphate (ZTS), zinc thiourea chloride (ZTC), copper thiourea chloride (CTC), bis thiourea zinc acetate (BTZA), bis-thiourea cadmium acetate (BTCA), bis thiourea cadmium formate (BTCF), potassium thiourea chloride (PTC), potassium thiourea bromide (PTB) and potassium thiourea iodide (PTI) has been reported in literature [2-7]. BTCA is a potential semiorganic metal complex crystallizing with orthorhombic crystal system exhibiting potential optical mechanical and electrical properties [5]. L-alanine is the natural amino acid with zwitterionic nature which induces potential electro-optic properties and thermo-mechanical stability. Studies on structural, optical and electrical properties of LA doped KDP crystal has been reported by Firdousi Akhter et. al. [8]. The influence of LA on SHG efficiency, optical, electrical and thermal properties of ZTC and ZTS crystal has been reported by our group in earlier investigations [9-10]. The growth and characterization studies of Zn^{2+} doped BTCA crystal have been reported by S. Selvakumar et. al. [11]. Recently, comparative studies on SHG efficiency, microhardness, HRXRD, optical and dielectric properties of 2mole% Mn(II), glycine & LA doped BTCA crystals have been explored by V. Ganesh et. al. [12]. Hitherto, no systematic comparative studies of pure and LA doped BTCA crystals are available in literature. The present manuscript is the first comparative investigation on growth, SHG efficiency, structural, optical, dielectric and thermal properties of pure and 1mole% LA doped BTCA crystal.

II. EXPERIMENTAL

Synthesis and growth

The AR grade thiourea and cadmium acetate were mixed in 2:1 molar ratio in deionised water to synthesis the pure crystalline BTCA salt. The supersaturation of pure BTCA was achieved at room temperature in deionised water. The calculated amount of 1mole% L-alanine was gradually introduced to the supersaturated solution of BTCA and allowed to stir at a constant speed for six hours to attain the homogeneity throughout the volume. The solution was filtered using number one whatman filter paper and kept for evaporation at room temperature in constant temperature bath of accuracy $\pm 0.01^{0}C$. The purity of the synthesized salt was achieved by successive recrystallisation. The pure CTA crystals were grown in 22 days while LA doped BTCA crystals were obtained within 16 days. The as grown pure and LA doped BTCA crystals are shown in Fig. 1a and 1b.

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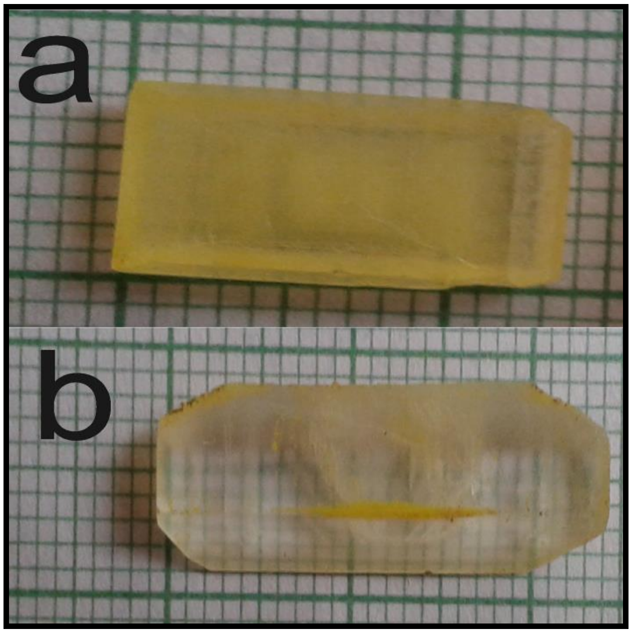

Figure 1: a) Pure BTCA, b) LA doped BTCA crystal

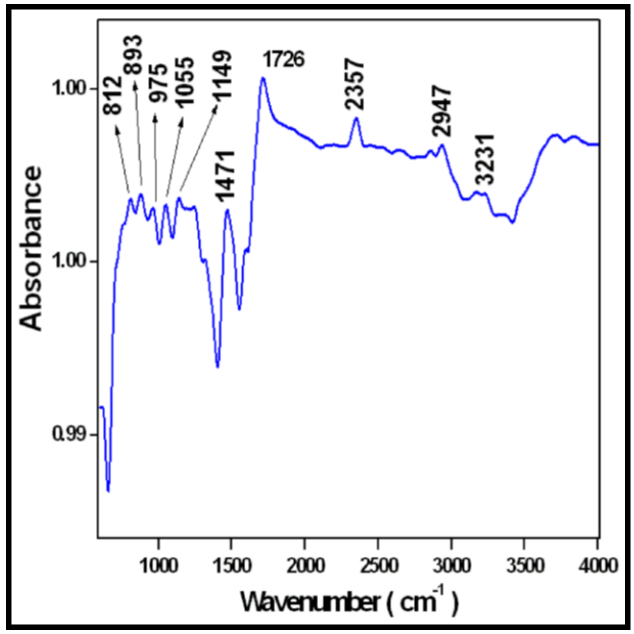

Figure 2: FT-IR spectrum of LA doped BTCA

III. Results and Discussion

Single crystal XRD

The cell parameters of pure and LA doped BTCA crystals have been determined by single crystal XRD technique using Enraf Nonius CAD4 X-ray diffractometer. The XRD data confirmed the orthorhombic crystal system of pure BTCA. The determined cell parameters of pure and LA doped BTCA crystals are tabulated in table 1. Though doping of LA did not affect the orthorhombic crystal system of BTCA, but the resulted change in cell parameter clearly indicates the incorporation of LA in BTCA crystal.

Table 1: Single crystal XRD data

Samples	**BTCA**	**LA doped BTCA**
Cell parameters (A^0)	a = 7.56 , b = 11.86 , c = 15.68	a = 5.76 , b = 6 , c = 12.3
Cell volume $(A^0)^3$	1374	425
Crystal System	Orthorhombic	Orthorhombic

Fourier transform infrared (FT-IR) analysis

The FT-IR spectrum of LA doped BTCA crystal shown in Fig. 2 has been recorded using the Bruker Alpha-ATR spectrophotometer in the range 600-4000 cm^{-1}. The characteristic vibrational frequencies of BTCA are reported in literature by Shahil Kirupavathy et. al. [6]. The identified functional groups in LA doped BTCA crystal are systematically assigned with corresponding wavenumber, discussed in table 2. The prominent shifts in the vibrational frequencies of BTCA indicate the incorporation of LA in BTCA crystal.

Table 2: FT-IR assignments of pure and LA doped BTCA crystal

Wavenumber (cm^{-1})		Assignments
BTCA [6]	LA doped BTCA	
789	812	C=S stretching
	893	CH_2 out of plane wagging
942	975	C-H stretching
1050	1055	C-N stretching
1110	1149	N-C-N stretching
1495	1471	COO^- stretching
1667	1726	C=O stretching
2387	2357	C-C stretching
2932	2947	C-H stretching
3228	3231	NH_2 stretching

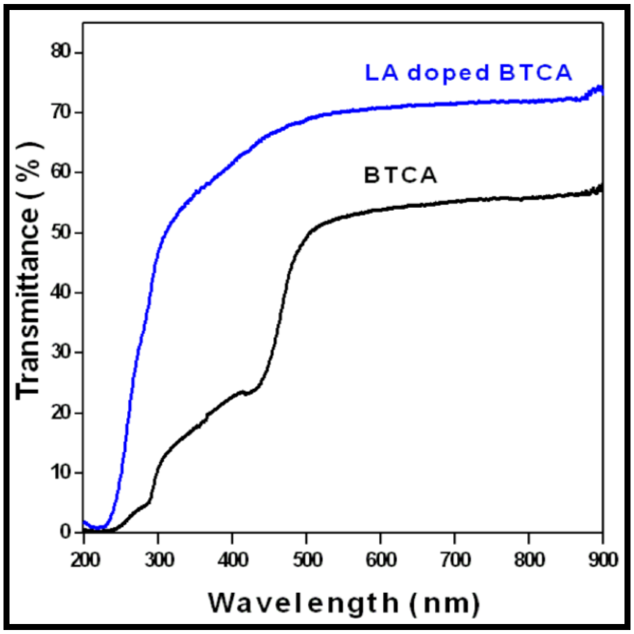

Figure 3: Transmittance spectrum

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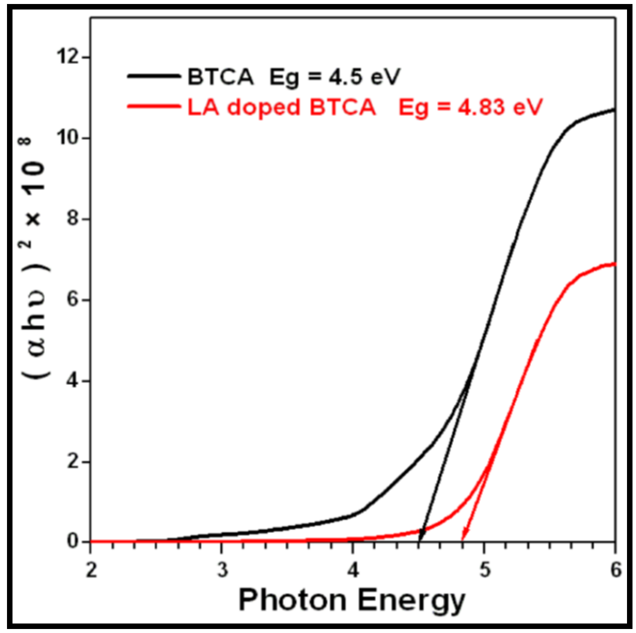

Figure 4: Tauc plot

UV-visible studies

The UV-visible studies of pure and LA doped BTCA crystals of thickness 1 mm were investigated using Shimadzu UV-2450 spectrophotometer in the range of 200-900 nm. The recorded transmittance spectra shown in Fig. 3 revealed that LA doped BTCA crystal has greater apex of optical transparency (70%) without any absorbance impede, as compared to pure BTCA. The transmittance efficiency of LA doped BTCA crystal is much higher in lower visible range from 300 to 450 nm offering wide transmission range. The high and large transmission of doped BTCA is offered by the effective (n→π) transitions and photoinduced effects observed in dopant LA [13].The LA doped BTCA crystal with improved optical transparency suggest its exclusive suitability for SHG transmission devices and NLO applications [14]. The transitory nature of electron in presence of optical field serves the evidence for energy band gap obeying the relation given as $\alpha = A\,(h\nu\text{-}Eg)^{1/2}$, were absorption coefficient $\alpha = 2.303 \log (1/T)/d$, hν is photon energy and Eg is energy band gap [15]. The energy band gap of pure and doped BTCA crystal was determined from the tauc extrapolation method depicted in Fig. 4. The band gap of doped BTCA is found to be 4.83 eV which is greater than pure BTCA. Thus LA doped BTCA with large optical band gap meets the demand of material imperative for UV tunable lasers [16].

SHG efficiency test

The powder SHG efficiency of pure and LA doped BTCA crystal has been determined using the Q switched Nd:YAG laser with operating wavelength of 1064 nm having pulse width of 8 ns and repetition rate of 10 Hz delivering the energy of $3mJpulse^{-1}$. The crystals were finely powdered and tightly packed in a microcapillary tube of uniform bore. The prepared samples of pure and doped BTCA were illuminated by the gaussian filtered beam of Nd:YAG laser. The emergence of bright green colour observed at the output of both the samples confirmed the effective SHG by grown crystals. The digital oscilloscope recorded the output voltage of 4 mV for pure BTCA and 16 mV for doped BTCA sample. The delocalization of pi electrons in presence of optical field and the photoinduced absorbance due to electron-phonon anharmonicities observed in dopant LA are the principle effects accountable for enhancing the second order susceptibility of doped BTCA crystal [13].The SHG efficiency of LA doped BTCA is 4 times that of pure BTCA which substantiates its potential suitability for frequency doubler and optical parametric oscillator devices [17].

Thermal studies

The thermal behavior of doped BTCA crystal has been investigated using the TQA-500 thermal analyzer in the homogeneous nitrogen atmosphere with a constant heating rate of 20^0C/min. The recorded TG-DTA curve of doped BTCA in the range of 30 to 400^0C is shown in Fig. 5. The thermal studies of pure BTCA are already reported in literature [11]. The TGA curve of doped BTCA revealed the two stage decomposition of compound. The slight decomposition at 140^0C might have occurred due to loss of water molecules in the crystal lattice. A major weight loss of doped BTCA occurs at 203^0C which further decomposes completely at 240^0C. The endothermic peak at 184^0C resembles the melting point of doped BTCA which is substantially less than BTCA due to unstable nature of dopant LA at higher temperature [10]. The doped BTCA undergoes to melt state at 240^0C which is also the final decomposition temperature of compound. The LA doped BTCA crystal shows significantly higher thermal decomposition temperature than several amino acid doped thiourea complex crystals [10, 16].

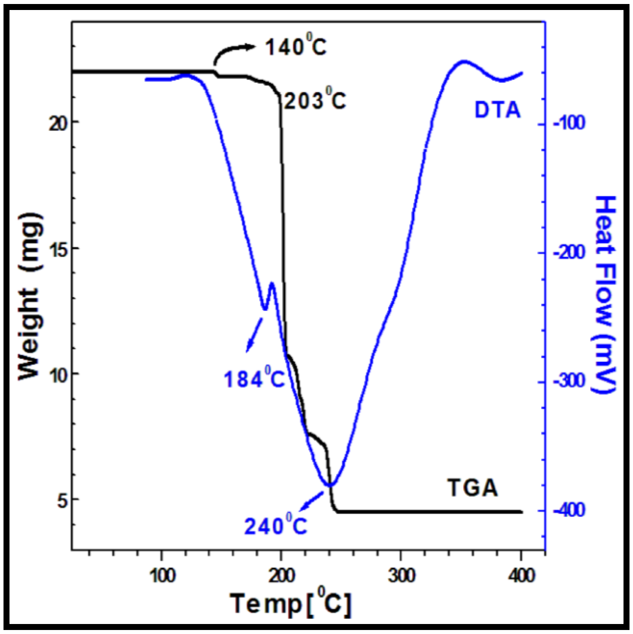

Figure 5: TG-DTA curve of LA doped BTCA

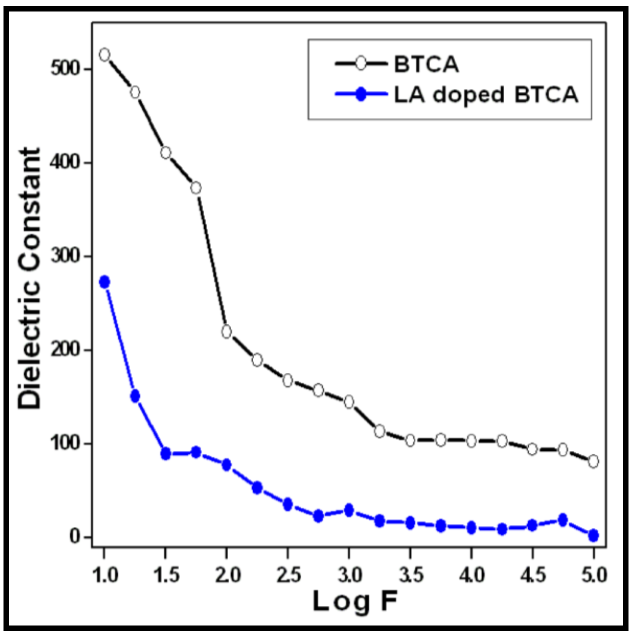

Figure 6: Dielectric constant vs. Log F

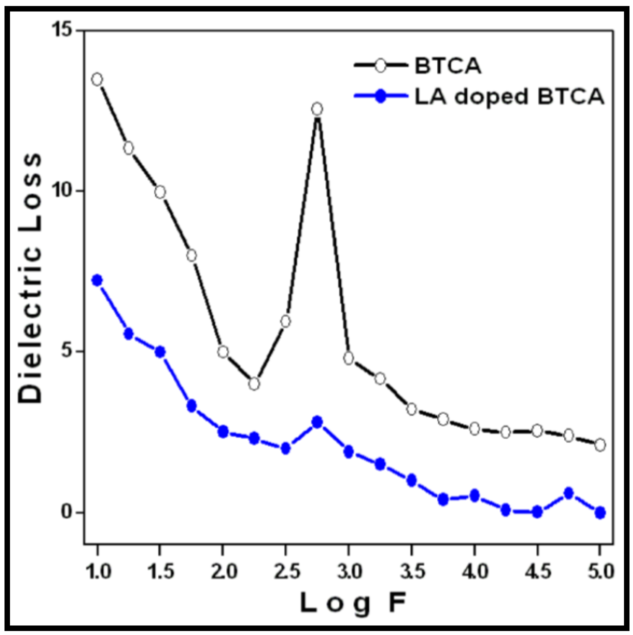

Figure 7: Dielectric loss vs. Log F

The dielectric properties of pure and doped BTCA were studies using the Gwinstek-819 LCR meter at room temperature. The frequency response of dielectric constant ($\varepsilon_r = Cd/\varepsilon_0 A$) of pure and doped BTCA crystal is shown in Fig. 6. The higher dielectric constant in lower frequency domain are attributed to dominance of polarization (electronic, ionic and space charge) effects while the suppression of these polarization effects at the higher frequencies confine to effectively lower values of dielectric constant [18]. The lower dielectric constant of doped BTCA crystal than pure suggests its potential candidature for microelectronics and photonics applications [18-19]. The lower dielectric constant of material serves good parameter for enhancing SHG coefficient as demonstrated by Millers rule [18]. The energy dissipation factor of material medium can be evaluated from the nature of dielectric loss, displayed in Fig. 7. The lower dielectric loss of doped BTCA crystal in high frequecy regime indicates its superior optical quality and reduced ratio of defects [20].

IV. Conclusion

The pure and LA doped BTCA crystal has been grown by slow solution evaporation technique. The single crystal XRD revealed that doping of LA offered change in cell parameters of BTCA without altering its orthorhombic crystal system. The prominent shifts in the vibrational frequencies of the identified functional groups confirmed the incorporation of LA in BTCA crystal. The doped BTCA crystal showed high optical transparency, large transmission and wide optical band gap (4.83 eV) than pure BTCA confirming its suitability for distinct optical applications. The thermal stability of doped BTCA crystal was ascertained from TG-DTA curve and it can be utilized for any application up to 184^0 C. The doping of LA favored lower dielectric constant and dielectric loss to BTCA imperative for microelectronics applications. The photoinduced effects in LA doped BTCA resulted enhancement in SHG efficiency which is 4 times of pure BTCA crystal. The doping of LA improved the optical, electrical and SHG efficiency of BTCA confirming its effective usability for NLO applications.

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References

[1] Moitra S., Bhattacharya S., Kar T., Ghosh A. Physica B 2008, 403, 3244-3247.
[2] Rajasekaran R., Ushasree P.M., Jayavel R., Ramasamy P. J. Cryst. Growth 2001, 229, 563-567.
[3] Anie Roshan S., Cyriac Joseph, Ittyachen M.A. Mater. Lett. 2001, 49, 299-302.
[4] Selvaraju K., Valluvan R., Kumararaman S. Mater. Lett. 2006, 60, 3130-3132.
[5] Selvaraju K., Valluvan R., Kumararaman S., Mater. Lett. 2007, 61, 751-753.
[6] Shahil Kirupavathy S., Stella Mary S., Srinivasan P., Vijayan N., Bhagavannarayana G., Gopalakrishnan R., J. Cryst. Growth 2007, 306, 102-110.
[7] Selvakumar S., Ravi Kumar S. M., Rajarajan K., Joseph Arul Pragasam A., Rajasekar S. A., Thamizharasan K., Sagayaraj P. Cryst. Growth Des. 2006, 6, 2607-2610.
[8] Ferdousi Akhtar, Jiban Podder J. Cryst. Process Technol. 2011, 1, 55-62.
[9] Dhumane N.R., Hussaini S.S., Dongre V.G., Ghugare P., Shirsat M.D. Appl. Phys. A 2009, 95, 727-732.
[10] Dhumane N.R., Hussaini S.S., Kunal Datta, Prasanta Ghosh, Shirsat M.D. Recnt. Res. Sci. Technol. 2010, 2, 30-34.
[11] Selvakumar S., Ravi Kumar S.M., Ginson P. Joseph, Rajarajan K., Madhavan J., Rajasekar S.A., Sagayaraj P. Mater. Chem. Phys. 2007, 103, 153-157.
[12] Ganesh V., Bhaskar Rao T., Kishan Rao K., Bhagavannarayana G., Shkir Mohd. Mater. Chem. Phys. 2012, 137, 276-281.
[13] Wojciechowski A., Ozga K., Reshak A. H., Miedzinski R., Kityk I. V., Berdowski J., Tylczyński Z. Mater. Lett. 2010, 64, 1957-1959.
[14] Alosious Gonsago C., Helen Merina Albert, Malliga P., Joseph Arul Pragasam A. Mater. Manufact. Process. 2012, 27, 355-359.
[15] Sabari Girisun T. C., Dhanuskodi S. Cryst. Res. Technol. 2009, 44, 1297-1302.
[16] Mohd Anis, Shaikh R.N., Shirsat M. D., Hussaini S.S. Opt. Laser Technol. 2014, 60, 124-129.
[17] Vivek P., Murugakoothan P. Opt. Laser Technol. 2013, 49, 288-295.
[18] Kannan V., Thirupugalmani K., Shanmugam G., Brahadeeswaran S. J. Therm. Anal. Calorim. DOI 10.1007/s10973-013-3269-y.
[19] Rajkumar M., Alfred Cecil Raj S., Renuga V. Mater. Manufact. Process. 2012, 27, 1217-1220.
[20] Shaikh R.N., Mohd Anis, Gambhire A. B., Shirsat M. D., Hussaini S.S. Mater. Res. Express. 2014, 1, 015016

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