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Growth, Optical, Thermal, Mechanical and Etching Studies on NLO Active Pure and L-Alanine Doped Single Crystals of Bis-Thiourea Cadmium Chloride

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ABSTRACT

The pure semiorganic nonlinear optical material Bis thiourea cadmium chloride (BTCC) and L-Alanine doped BTCC, were grown by slow evaporation technique at room temperature. The crystals obtained by the above technique were subjected to different characterization analysis. Unit cell parameters were evaluated by single crystal X-ray diffraction technique. The functional groups and optical behaviour of the crystals were identified from FTIR and UV-vis spectrum analysis. Micro hardness and thermal studies were also carried out on the samples respectively. The SHG efficiency of the grown crystals was measured through NLO studies.

***Keywords*:** Slow solvent evaporation technique; FTIR; NLO; microhardness and SHG.

1. Introduction

According to the idea of combining the inorganic with the asymmetric conjugate organic molecule [1], semiorganic materials have been attracting a great deal of attention in the NLO field, because such materials have the potential for combining the high optical nonlinearity and chemical flexibility of organics with temporal and thermal stabilities and excellent transmittance of inorganics. A number of semiorganic compounds were formed with thiourea, since it possesses high dipole moment [2-4], which are potentially useful materials for frequency doubling of the near IR laser radiation. Monaca et al. [5] have identified several salts of amino acids with better NLO properties than KDP. BTCC is a promising semiorganic NLO material for second-harmonic generation (SHG) [6-9]. BTCC is 110 times more nonlinear than quartz [10]. Xing et al. [9] have reported BTCC as an efficient semiorganic nonlinear optical material for SHG. Venkatramanan et al. [11] have reported that the BTCC crystals have the highest laser induced damage threshold values among the other solution grown NLO crystals. BTCC is 0.73 times more nonlinear than urea [12]. At higher frequencies BTCC has very low dielectric constant [13]. It also possesses high laser damage threshold and good mechanical properties [14, 15].

In the present investigation 1, 2,3mol% of L-Alanine was doped in BTCC and tested for SHG by Kurtz and Perry powder test. The efficiency was found to be higher in 1mol% than 2 and 3mol%. Since, 1mol% L-Alanine doped BTCC has already been investigated and reported [16], 2mol% L-Alanine doped BTCC has been taken for investigation.

2. Experimental

2.1 Crystal growth

Slow evaporation technique was employed for the growth of BTCC crystals. Single crystals of Bis thiourea cadmium chloride (BTCC) salt were synthesized by dissolving AR grade thiourea and cadmium chloride in the molar ratio 2:1 in deionized water. The required amount of cadmium chloride and thiourea was estimated according to the following reaction:

$$CdCl_2 + 2[CS(NH_2)_2] \rightarrow Cd[CS(NH_2)_2]_2Cl_2$$

The solution was heated and left for slow evaporation until the solvent completely dried and white crystalline salt was obtained. The salt was subjected to repeated recrystallization process. Saturated solution of BTCC was prepared in three different beakers and 1,2 and 3mol% L-Alanine was added in those three beakers. The salts were synthesized. The obtained salts were tested for SHG by Kurtz and Perry powder SHG test. The SHG efficiency of 1mol% L-Alanine doped BTCC was found to be higher than 2, 3mol%. Since, 1mol% L-Alanine doped BTCC has already been investigated and reported [16], 2mol% L-Alanine doped BTCC crystal was grown. The saturated solution of 2mol% L-Alanine doped BTCC was prepared at 38°C in constant temperature bath controlled to an accuracy of ± 0.01°C. The seeds were obtained from the same solution by slow evaporation. After a period of 30 days good quality, transparent crystals were harvested. The grown crystals are shown in Fig.1(a) and Fig.1(b).

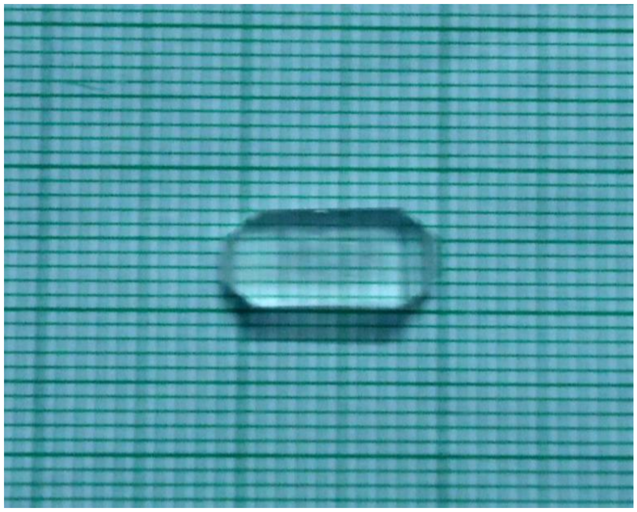

Fig. 1(a) **T**he Photograph of Pure BTCC crystal

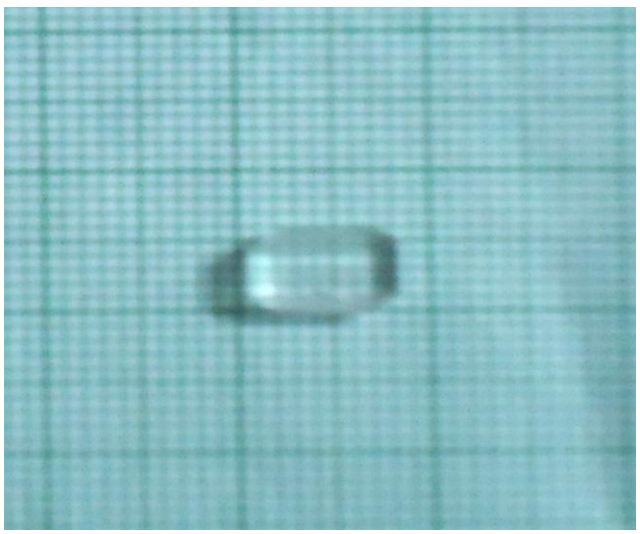

Fig. 1(b) The Photograph of L-Alanine doped BTCC crystal

3. Characterization

In order to estimate the crystal data of pure and L-Alanine doped BTCC crystals, the grown crystals were characterized by single crystal X-ray diffraction technique by using ENRAF NONIUS CAD4 diffractometer. To detect the presence of functional groups, the FTIR analysis was carried out using PERKIN ELMER

RX1 FTIR spectrophotometer by KBr pellet technique in the range 400-4000 cm^{-1}. The optical properties of the grown crystals were carried out by LAMBDA-35 UV-Vis spectrophotometer in the range 200-1200 nm. The melting point and weight loss of the grown crystals were determined by means of thermo gravimetric analysis (TGA) using TAQ-500 analyzer in the temperature range 25-400 °C. The second harmonic generation (SHG) conversion efficiency was measured by the Kurtz and Perry powder technique and the mechanical property of the crystals were studied by LEITZ microhardness tester.

3.1. Single crystal X-ray diffraction Analysis

To determine crystal structure and lattice parameter, the grown crystals were characterized by using ENRAF NONIUS CAD4 diffractometer. The observed values of the lattice parameters of pure and L-Alanine doped BTCC are shown in Table.1 which is in good agreement with the reported data [16].

Table – 1
Single-crystal XRD data of pure and L-Alanine doped BTCC crystals

Pure BTCC	**L-Alanine doped BTCC**
a = 5.813 A°	a = 5.81A°
b = 6.484A°	b = 6.481 A°
c = 13.108 A°	c = 13.125 A°
V= 493.81 $A^{\circ 3}$	V = 494.3 $A^{\circ 3}$
Orthorhombic	Orthorhombic
$\alpha = \beta = \gamma = 90^{\circ}$	
Space group- $Pmn2_1$	Space group- $Pmn2_1$

3.2 FTIR Analysis

To detect the different functional groups present in the compound of the grown crystals, the FTIR analysis was carried out using Perkin Elmer RX1 FTIR spectrophotometer by KBr pellet technique in the range 400-4000cm^{-1}. The spectrums of pure BTCC and 2mol% L-Alanine doped BTCC are shown in Fig.2(a) and Fig.2(b) respectively. The characteristic vibrational frequencies of the functional groups of pure and 2mol% L-Alanine doped BTCC are given in Table 2. In the FTIR spectrum of pure BTCC, the intensity 3387.70cm^{-1} is due to N-H stretching vibration of the NH_2 group of thiourea. The C=S stretching vibrations occur at 1616.62 and 711.96cm^{-1}. The peaks at 1491.01, 1434.20 and 1393.07cm^{-1} are due to HN_2 bending vibration. C-N vibration is confirmed by the peak at 1093.61cm^{-1}. The peak at 527.62cm^{-1} corresponds to N-C-N vibration. The similarity in the spectrum shows that both the crystals are not having water in their lattice. The presence of amino acid L-Alanine in the lattice of BTCC crystal is confirmed through the shift in the peak positions.

Table – 2
FTIR data comparison of pure and L-Alanine doped BTCC single crystals

Pure BTCC cm^{-1}	L-Alanine doped BTCC cm^{-1}	Assignment
3387.70	3386	N-H stretching
1616.62	1615.64	C=S stretching
1491.1	1496.82	NH_2 bending
1393.07	1391.88	NH_2 bending
1093.61	1093.11	C-N vibration
711.96	706.24	C=S stretching
527.62	530.74	N-C-N vibration

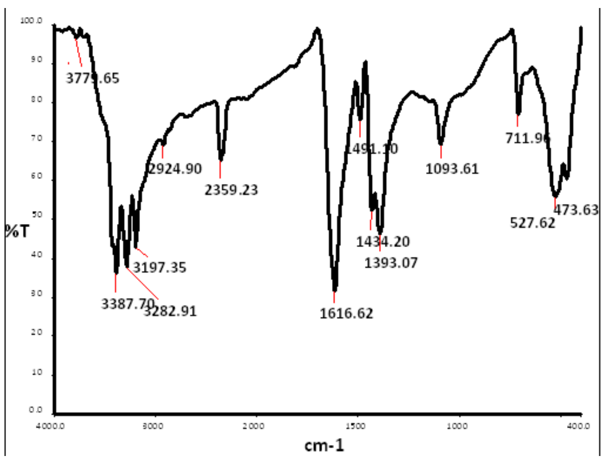

Fig. (2a) FTIR Spectrum of BTCC crystal

3.3. UV-visible spectral study

The UV-Vis spectrum analysis has been measured using LAMBDA-35 UV-Vis spectrophotometer. To find the transmission range of the grown crystals, the optical transmission spectrum was recorded for the wavelengths between 200 and 1100nm. The UV-vis spectrum gives limited information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electron in σ and π orbital from the ground state to higher energy states. The absorption spectra of pure and 2mol% L-Alanine doped BTCC is shown in Fig.3. The absorption spectra shows lower cutoff wavelength at around 290nm for L-Alanine doped BTCC and 300nm for pure BTCC.

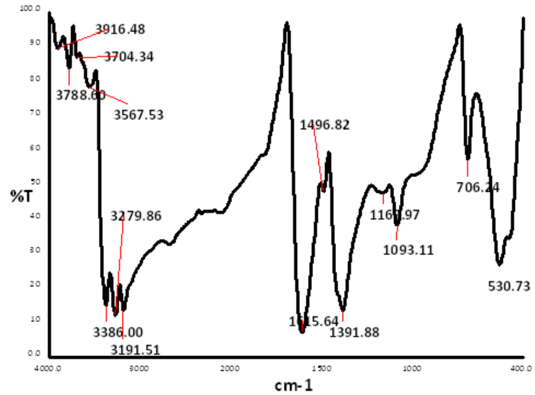

Fig. (2b) FTIR Spectrum of L-Alanine doped BTCC crystal

The transmittance is found to be maximum in the entire visible and infrared regions. When we consider the percentage of transmission, we observe that for pure BTCC crystal, the maximum value lies in the range of 70% and for L-Alanine doped BTCC 90% in the visible region. The data collected from the graph attest the usefulness of this material for optoelectronic applications and the second harmonic generation of the Nd:YAG laser and for the generation of the higher harmonics of the laser diodes.

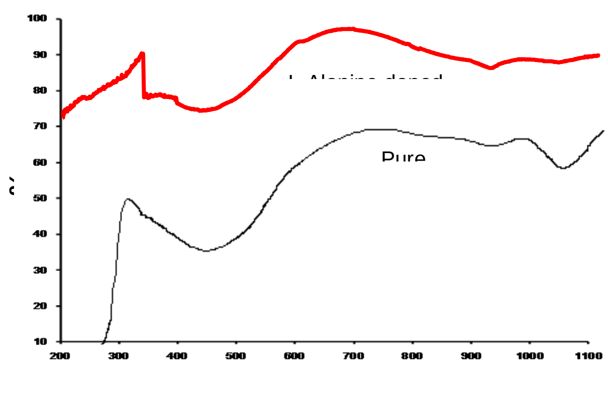

Fig. (3) UV-Vis spectrum of pure and L-Alanine doped BTCC crystals

3.4 Thermal analysis

The decomposition, phase transition, melting point and weight loss of the grown crystals were determined by means of thermo gravimetric analysis (TGA) by using TAQ-500 analyzer. The weight loss and thermal stability were determined at a heating rate of 25°C/min for temperature range 50 to 900°C in nitrogen inert atmosphere. The thermograms are shown in Fig.4(a) and Fig.4(b).

The TGA curve shows the first endothermic peak at 217.11°C and second peak at 276.14°C for L-Alanine doped BTCC crystal. This decomposition lead to a weight loss of about 28.90% which may be due to the liberation of volatile substances like sulphur oxide and amino acid L-Alanine[16]. In the case of pure BTCC crystal the endothermic peaks are at 215.24°C and 260.54°C with a weight loss of about 29.58%. There is no decomposition and phase transition up to the temperature 215.24°C in pure and 217.11°C in doped BTCC crystal. This ensures that the thermal stability of L-Alanine doped BTCC crystal is higher than pure BTCC crystal. In both the grown crystals there is no weight loss up to 100°C, indicating absence of water in the molecular structure of the grown crystals. This temperature range of the grown crystals, ensures the possibility of the crystals for NLO applications.

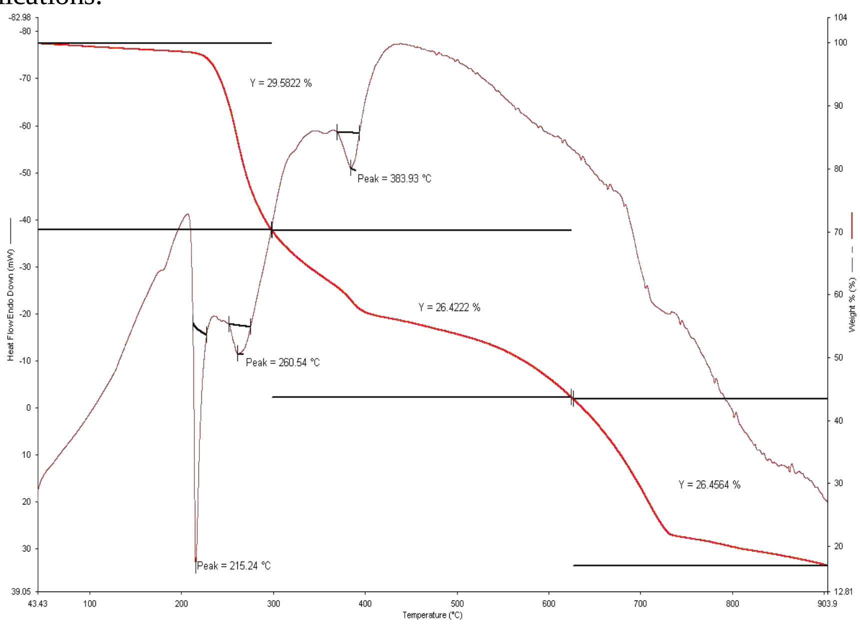

Fig. (4a) Thermogram of pure BTCC Crystal

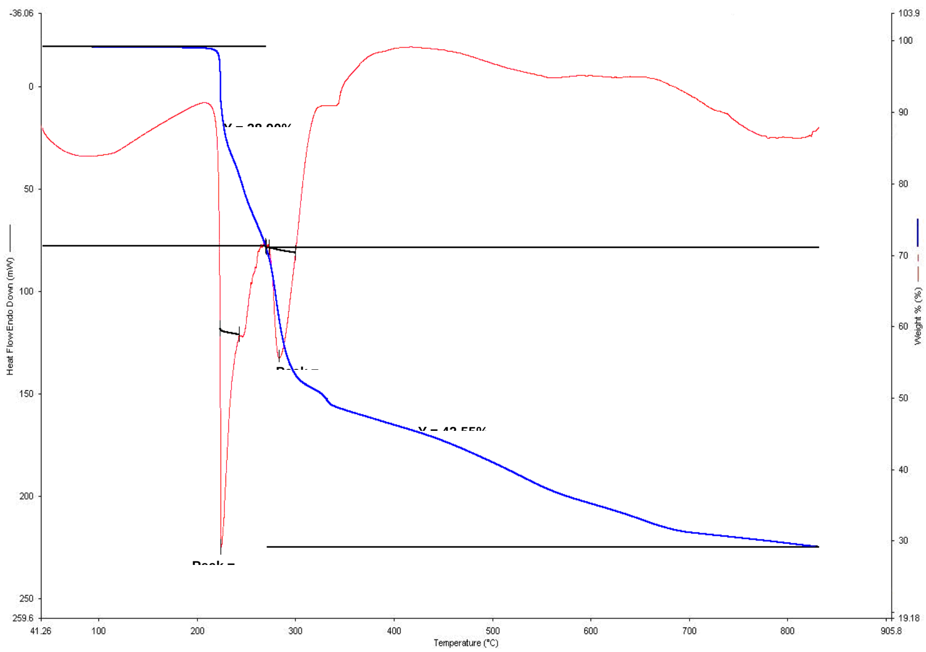

Fig (4b) Thermogram of L-alanine doped BTCC Crystal

3.5. Microhardness measurement

Hardness was measured using Leitz-Wetzler hardness tester. Indentations were made on the pure and L-Alanine doped BTCC crystals for different loads and indentation time given was 10s. The maximum indenter load applied was 100gm. Vickers hardness number was calculated and a graph has been plotted between the hardness values and the corresponding loads for the grown crystals as shown in Fig.5. From the results, it is observed that the hardness number increases as the load increases. Hardness begins to saturate (above 100gm) at higher concentration of impurity which may be due to the release of internal stresses generated locally by indentation [17]. The better mechanical property implies that the grown crystals are good engineering materials for device fabrication.

3.6. SHG efficiency measurement

The second harmonic generation (SHG) efficiency of the grown crystals was measured using the technique developed by Kurtz and Perry [19]. The crystal was ground into powder and densely packed in between two glass slides which act as the sample cell. An Nd:YAG laser beam of wavelength 1064nm was made to fall normally on the sample cell. The emission of green light confirmed the SHG of pure and L-Alanine doped BTCC crystals. The NLO efficiency was found to be 210mV and 230mV for pure and L-Alanine doped BTCC crystals. The SHG efficiency of

KDP was 21mV. The output voltage got for pure and L-Alanine doped BTCC crystals are 10 and 11 times higher than KDP. Thus the grown crystals are best suitable for NLO applications.

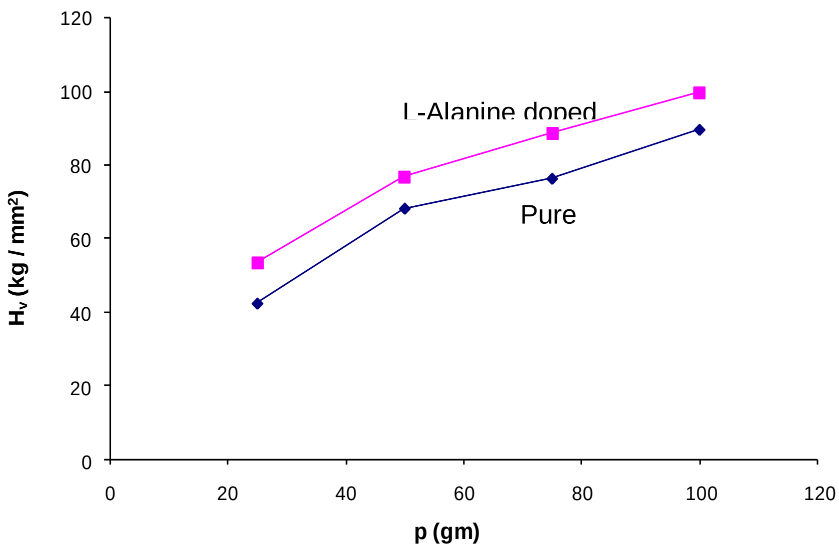

Fig. 5 Vickers Hardness Vs load for pure and L-Alanine doped BTCC Crystals

3.7. Etching Studies

The crystal defects were revealed using chemical etching. Etching studies on pure and L-Alanine doped BTCC crystals were carried out using water as etchant. Etch pits were observed on the (1 0 0) plane when etched with water for 5, 10 and 15 secs. The capability of revealing etch pits by a solvent on different faces depends on the crystallographic orientation and hence corresponds to the symmetry of the crystal face on which the pit is produced. The etching photographs of pure and L-Alanine doped BTCC crystals are shown in fig.6a, 6b, 6c and fig.6d, 6e, 6f. From the figures it is evident that when the crystals were etched for 10secs, well defined etch pits were observed rather than for 5 secs. Minimum patterns were observed for 15 secs etching time, which ensures the quality of the grown crystals.

5 secs

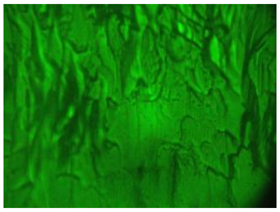

Fig.6a

10 secs

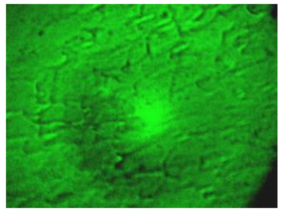

Fig.6b

15 secs

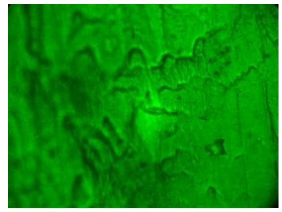

Fig.6c

Etching photographs of pure BTCC crystals

5 secs

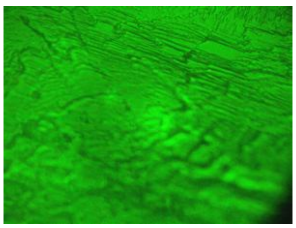

Fig.6d

10 secs

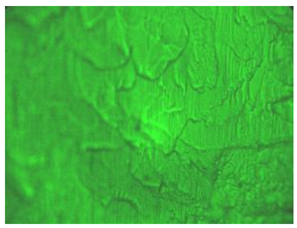

Fig.6e

15 secs

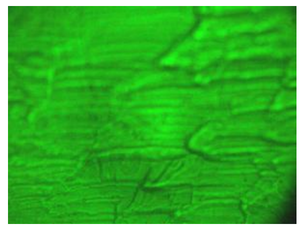

Fig.6f

Etching photographs of L-Alanine doped BTCC crystals

4. Conclusion

Pure and L-Alanine doped BTCC single crystals have been grown with reasonable growth rate along three crystallographic directions by solution growth method at room temperature. The lattice parameters have been found by single crystal X-ray diffraction technique. The FT-IR spectrum reveals the various functional groups present in the grown crystal. The optical absorption spectrum reveals that the crystals have wide optical window from 300nm to 1100nm. The crystals are transparent in the visible and near infrared spectral regions. Optical transmittance of the crystals is 70%. Thermo gravimetric analysis shows that the grown crystals are thermodynamically stable upto 215^{o}C. The Vicker's microhardness was calculated in order to understand the mechanical stability of the grown crystals. The SHG output voltage measured for pure and L-Alanine doped BTCC crystals are 10 and 11 times higher than KDP. Thus the grown crystals are best suitable for NLO applications. The etching studies showed that well defined etch pits were observed when the crystals were etched for 10 secs and minimum patterns were observed for 15 secs which ensures the quality of the grown crystals.

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