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Growth and characterization of nonlinear optical Crystal Bis thiourea cadmium chloride (BTCC) in presence of L-Alanine

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ABSTRACT

The present communication deals with growth and characterization of single crystal of Bis thiourea cadmium chloride (BTCC) doped with L-Alanine. L-Alanine doped single crystals of BTCC were grown by solvent evaporation method at constant temperature (36ºC). The grown crystals of L-Alanine doped BTCC exhibit significant SHG efficiency enhancement as compared to pure BTCC. Incorporation of L-Alanine in BTCC was estimated qualitatively by Fourier transformed infrared spectra. Lattice parameters were determined by single crystal X-ray diffraction. The influence of the organic impurity on optical and thermal properties has also been studied.

Keywords: Growth from solution, Amino acid, Non linear optical materials, crystal growth, SHG efficiency.

1. INTRODUCTION

In recent years there has been considerable interest in the synthesis of semi-organic NLO materials with excellent second order optical nonlinearities[1-7]. Semi organic nonlinear optical crystals combine good thermal and mechanical properties of inorganic with high optical nonlinearity of purely organic compound[8-10].

Bis thiourea cadmium chloride (BTCC) is a potential NLO material amongst the metal complexes of thiourea. BTCC is 0.73 times more nonlinear than urea[11]. In our earlier reported work we have shown that at higher frequencies BTCC has very low dielectric constant[12]. It also possesses high laser damage threshold and good mechanical properties[13-14]. The effects of several dopants on structural and physical properties of metal complexes of thiourea and KDP have been reported by our group. It is also reported in the literature that semiorganic nonlinear optical (NLO) crystals grown with amino acids possess the advantages of high optical nonlinearity. In present investigation L-Alanine was doped in BTCC to enhance the SHG efficiency. We have observed the enhancement in SHG efficiency of BTCC after addition of L-Alanine. The 1, 2 and 3mole% L-Alanine was

doped in BTCC and tested for SHG by Kurtz and Perry powder test. The higher enhancement was observed at 1mole% L-Alanine doped BTCC. Hence, 1mole% L-Alanine doped BTCC single crystal was grown by slow evaporation technique. The presence of various functional groups was confirmed by FTIR analysis. Presence of L-Alanine was confirmed by EDAX. The transparency of grown crystal was studied by UV-visible spectroscopy. The lattice parameters were measured by single crystal X-ray diffraction analysis. The thermal study was carried out by thermo gravimetric analysis (TGA).

2. EXPERIMENTAL

2.1. Synthesis

Bis thiourea cadmium chloride (BTCC) salt was synthesized by dissolving AR grade thiourea and cadmium chloride in the molar ratio 2:1 in deionized water according to following reaction,

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

The solution was slowly evaporated until 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 3mole% L-Alanine was added in these three beakers. The salts were synthesized. The obtained salts tested for SHG by Kurtz and Perry powder SHG test. The SHG efficiency of 1mole% L-Alanine doped BTCC was found to be higher than 2, 3mole% L-Alanine doped BTCC and pure BTCC. Hence 1mole% L-Alanine doped BTCC bulk crystal was grown.

2.2. Crystal Growth

The saturated solution of 1mole% L-Alanine doped BTCC was prepared at 36˚C in constant temperature bath controlled to an accuracy of ± 0.01˚C. The seeds were obtained from the same solution by slow evaporation. The obtained seed was employed for bulk growth of the crystal. After the period of 30 days good quality, transparent crystal was harvested.

3. CHARACTERIZATION

The SHG efficiency of synthesized compounds was measured by Kurtz and Perry powder SHG test at Indian Institute of Science, Bangalore. The grown crystal was characterized by various characterization techniques viz. single crystal X-ray diffraction analysis, FTIR, EDAX, UV-visible spectral study and thermal study by thermo gravimetric analysis (TGA).

4. RESULTS AND DISCUSSION

4.1. SHG Measurement

Current interest in quantum electronics is focused on finding materials, which have suitable non-linear optical properties so that it can be used as the active media in efficient second harmonic generators, tunable parametric oscillators and broad-band electro-optic modulators. The second harmonic generation (SHG) conversion efficiency of 1, 2, 3mole% L-Alanine doped BTCC and pure BTCC was measured by the Kurtz and Perry powder SHG test[15]. The fundamental beam of 1064 nm from Q switched Nd: YAG laser was used to test the Second Harmonic Generation (SHG) property of 1, 2 and 3mole% L-Alanine doped BTCC and pure BTCC. Pulse energy 3 mJ/pulse and pulse width 8ns and repetition rate 10 Hz was used. The photo multiplier tube (Hamahatsu R 2059) was used as detector. The input laser beam was passed through an IR detector and then directed on the microcrystalline powdered sample packed in a

capillary tube. The assembly of an oscilloscope and photodiode detector is employed to measure the light emitted by the sample. The SHG signal generated in the sample was confirmed from emission of green radiation from the sample. The SHG conversion efficiency of L-Alanine doped BTCC was found to be enhanced than that of pure BTCC. The optical signal generated from sample was converted in to electrical signal and measured on oscilloscope. The SHG conversion efficiency of 1mole% L-Alanine doped BTCC is found to be greater than pure BTCC and other molar concentrations of L-Alanine in BTCC.

4.2. Single crystal X-ray diffraction Analysis

To determine crystal structure and lattice parameter, grown crystal was characterize by single crystal X-ray diffraction technique by using Bruker axs (Kappa Apex2) diffractometer. Observed values of lattice parameters are a = 5.824A°, b = 6.483A°, c = 13.124A° with volume 495.50A°^{3} and $\alpha = \beta = \gamma = 90^\circ$. This confirms that the crystal belongs to orthorhombic system and space group $Pmn2_1$.

4.3. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR analysis was carried out using Perkin Elmer Spectrum FTIR spectrometer by KBr pallet technique in the range 450-4000cm^{-1} to detect the different functional present the compound of the grown crystal. The spectrums of pure BTCC and 1mole% L-Alanine doped BTCC are shown in figure 1 and figure 2 respectively. The characteristic vibrational frequencies of the functional groups of 1mole% L-Alanine doped BTCC have been compared with pure BTCC and thiourea[13-16]. The comparison is given in Table 1. From spectrum the high frequency N-H absorption band in the region 3100-3400 were not shifted to lower frequencies on formation of metal thiourea complex indicates that nitrogen to zinc bonds are absent and bonding must be between sulfur and zinc occur. The NH, C=S and N-C-N stretching vibrations were also seen. It is clearly evident from Table 1 that there is slight shift in absorption bands compared to pure BTCC. This shift may be due to doping of amino acid L-Alanine.

4.4 Energy dispersive analysis (EDAX)

Energy dispersive X-ray analysis is a useful tool for elemental analysis of the grown crystal. To confirm the presence of dopant in the grown crystal, EDAX analysis was carried out using JEOL-6360 scanning electron microscope. The recorded spectrum is shown in figure 3. The presence of L-Alanine in grown crystal was confirmed from EDAX spectrum.

4.5. UV-visible spectral study

The UV visible study of the grown crystal was carried out by Shimadzu UV 1600 UV visible spectrometer in a range 190-1100 nm. The absorption spectra of 1mole% L-Alanine doped BTCC is shown in figure 4. The window shown in figure 4 shows the absorption spectra of pure BTCC for comparison with L-Alanine doped BTCC. The absorption spectra shows lower cutoff wavelength at around 283nm for L-Alanine doped BTCC which is comparable to that of pure BTCC.

4.6 Thermo gravimetric analysis (TGA)

The decomposition, phase transition, melting point and weight loss of the grown

crystal were determined by means of thermo gravimetric analysis (TGA). The thermo gravimetric analysis of grown crystal was carried out by TA Q-500 analyzer in the temperature range 25-400˚C at a heating rate of 10˚C/min. the thermo gram is shown in figure 5. The TGA curve shows major decomposition between 218.46˚C and 273.59 ˚C (about 50.68%). This decomposition may be due to liberation of volatile substance sulfur oxide and amino acid L-Alanine. There is no decomposition and phase transition up to the temperature 218.46˚C. This ensures thermal stability of the compound up to temperature 218.46˚C. There is no weight loss up to 218.46˚C, indicates absence of water in the molecular structure of the grown crystal. There is no phase change till the melting of material; this increases the temperature range of grown crystal for possible NLO applications.

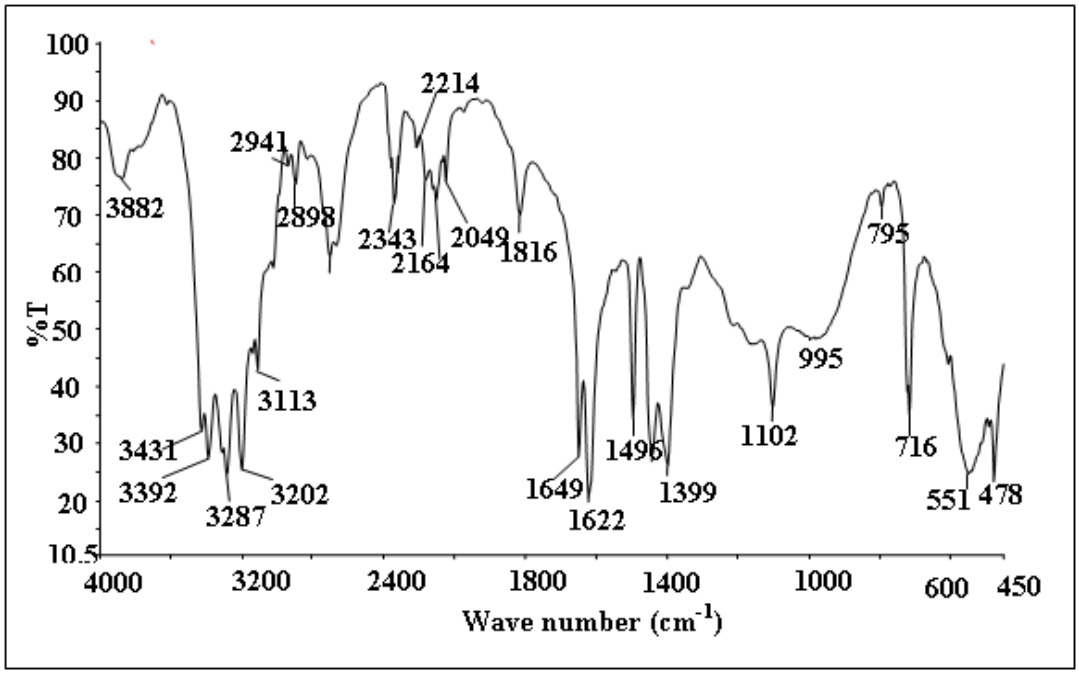

Figure 1: FTIR spectra of pure BTCC.

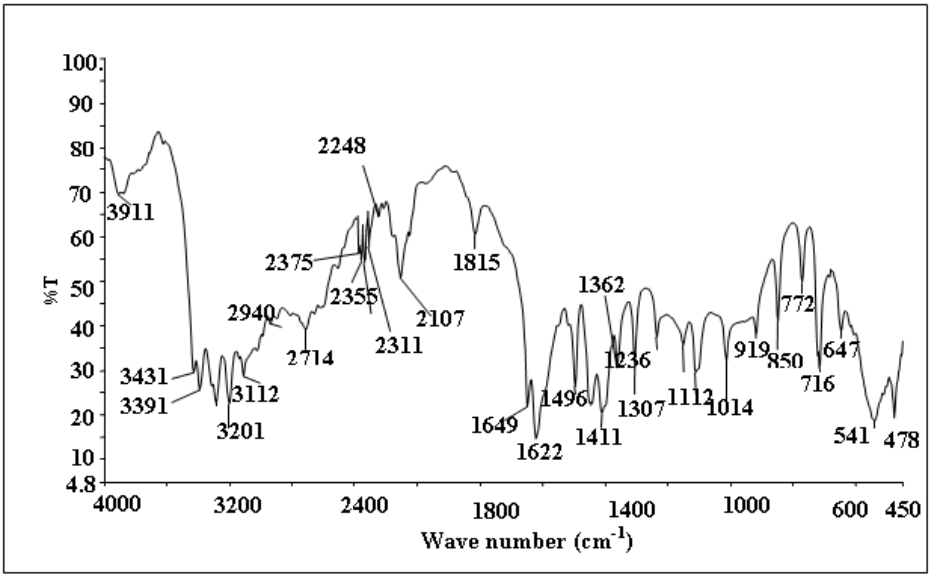

Figure 2: FTIR spectra of 1mole% L-Alanine doped BTCC.

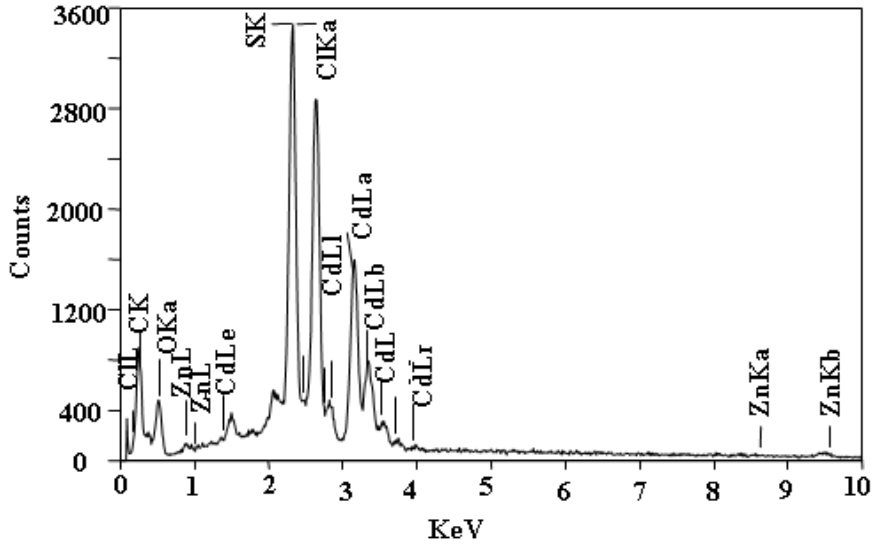

Figure 3: EDAX spectrum of 1mole% L-Alanine doped BTCC.

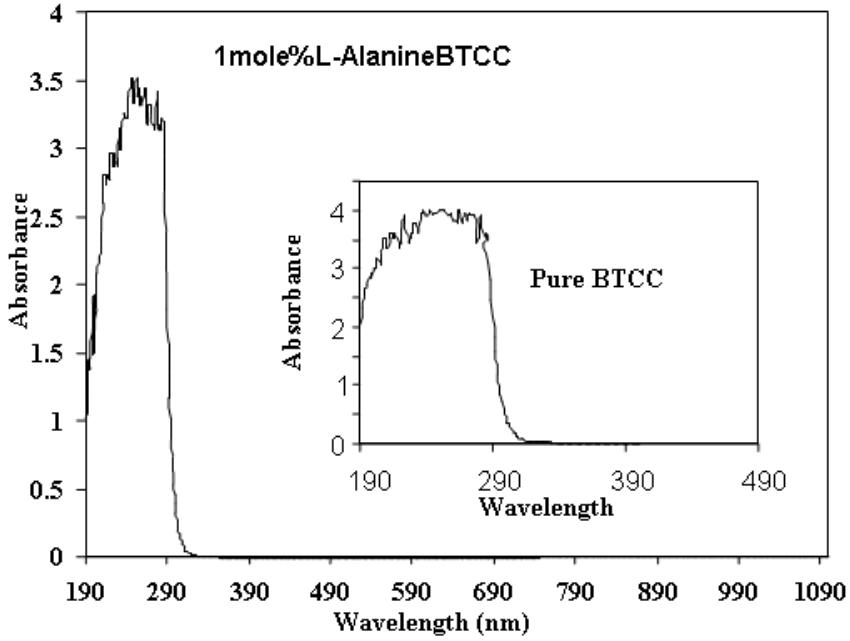

Figure 4: UV-visible spectrum of 1mole% L-Alanine doped BTCC.

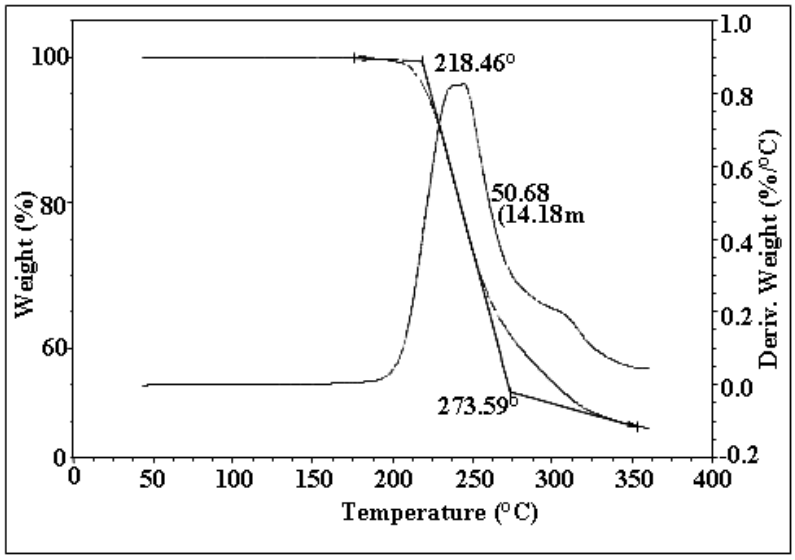

Figure 5: The TGA curve of 1mole% L-Alanine doped BTCC.

5. CONCLUSIONS

The following conclusions can be extracted from the results of the present study

- The 1mole% L-Alanine doped BTCC crystal was grown by low temperature solution growth, slow evaporation technique.
- The Kurtz and Perry powder SHG test shows higher enhancement for 1mole% L-Alanine doped BTCC than the other molar concentrations of L-Alanine.
- Single crystal X-ray diffraction analysis confirms orthorhombic structure of the grown crystal.
- The FTIR analysis confirmed the presence of different bonding and the co-ordination of sulfur and zinc.
- EDAX confirms the presence of L-Alanine in grown crystal.
- The UV-visible absorption spectra shows lower cutoff wavelength at around 283nm.
- Thermo gravimetric analysis (TGA) shows the grown crystal is thermally stable up to 218.46˚C.

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