



Investigation on the Physicochemical Properties of Non-Linear Optical Single Crystal: L-Cysteine Borate Decahydrate

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Abstract: A potentially useful semi-organic non-linear optical single crystal of L-cysteineborate decahydrate (LCBD) was synthesized and grown at room temperature by slow solvent evaporation method. The resulting crystals predominantly exhibit the needle morphology. The LCBD was subjected to single crystal X-ray diffraction analysis to identify the unit cell parameters. The transparency of the crystal was analyzed by UV-Visible spectrum. The presence of functional groups and coordination of L-cysteine and disodium tetraborate decahydrate were identified by FTIR study. Thermal stability of LCBD investigated by TG/DTA and DSC analyses confirms that the compound is stable up to 111°C. The second harmonic generation (SHG) efficiency was estimated by Kurtz and Perry powder technique and the study clearly suggests the influence of particle size on the SHG efficiency of LCBD.

Keywords: Solution growth, Non-linear optical material, X- ray analysis, FTIR, TG/DTA, DSC.

1. Introduction

The overwhelming success of molecular engineering in controlling NLO properties in the last decade has prompted better initiative in crystal engineering. The search for new, very efficient non-linear optical materials, for fast and optimum processing of optical signals has become very important, because of development of optical fiber communication, laser based imaging and remote sensing etc. [1]. Recently, variety of semi-organic crystals for nonlinear optical applications have been developed, among them the amino acids were found to have definite edge over others as they display special features of interest [2], such as (i) molecular chirality, which secures acentric crystallographic structures; (ii) absence of strongly conjugated bonds, leading to wide transparency ranges in the visible and UV spectral regions; (iii) Zwitterionic nature of the molecules, which favors favorable physicochemical stability.

In recent years, based on the above merits and after the discovery of promising NLO properties, L-cysteine salts have received much attention not only due to their unique properties but also for possible applications to novel photonic and optoelectronic devices. Nowadays, L-cysteine has been extensively studied because of the ability of its imidazole moiety to act as a proton donor, a proton acceptor, and a nucleophilic agent [3]. L-cysteine crystallizes in non-centrosymmetric space group making it a potential candidate for piezoelectric and non-linear applications. L-cysteine exist as a dipolar ion in solid state in which carboxyl group

is present as a carboxylate ion and amino group is present as ammonium ion. In addition, thiol group is present in aqueous solution of L-cysteine. Due to this dipolar nature, L-cysteine has a high melting point. Another added advantage of L-cysteine is the presence of chromophores namely amino group and carboxyl group which makes it transparent in the UV-Vis region. Thus more emphasis has been given by the scientists to develop non-linear optical crystals in L-cysteine analogs [4-8]. In the present investigation, we were reporting on the growth of L-cysteine borate decahydrate (LCBD) crystals. This report is focused on the growth of crystals of LCBD and to study linear and nonlinear optical and thermal properties. The SHG efficiency of LCBD was found out by Kurtz and Perry technique.

2. Experimental Procedure

LCBD crystals were grown from aqueous solution by slow solvent evaporation technique at room temperature. The starting materials were AR grade L-cysteine and disodium tetraborate decahydrate. The solution was prepared by dissolving 1 mol of L-cysteine and 2 mol disodium tetraborate decahydrate in 10 ml of deionized water. To achieve single crystal of good optical quality and relatively large size many growth attempts were made. Though the crystallization occurs at different pH values, we could get transparent good quality defect-free crystals for optimized pH= 2. The easiest method was to form tiny crystals by spontaneous nucleation; among them good quality seed crystals with perfect shapes and free from defects were chosen for growth experiment. The seed was suspended in the mother solution with nylon thread. By slow evaporation of the solvent, LCBD single crystal of size $20 \times 3 \times 2 \text{ mm}^3$ was growth in a period of 45-50 days.

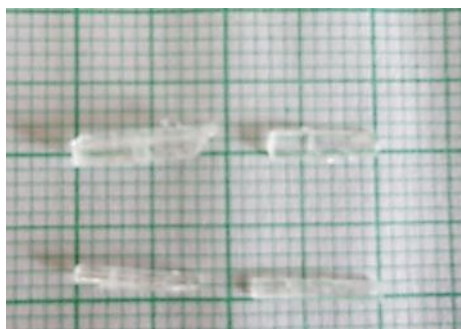


Fig. 1. Photograph of as grown LCBD crystal

3. Results and Discussions

3.1. Single crystal X-ray diffraction analysis

The LCBD single crystal was analyzed by single crystal X-ray diffraction method to determine the lattice parameters. The single crystal XRD data was recorded using ENRAF NONIUS CAD 4 diffractometer with MoK α radiation. It is observed that the grown crystal belongs to monoclinic system with space group P2₁ and the lattice parameter values were $a = 8.05 \text{ \AA}$, $b = 12.35 \text{ \AA}$, $c = 9.2 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$. The volume of the cell was $V = 914 \text{ \AA}^3$.

3.2. Linear and nonlinear optical properties

3.2.1 UV-Vis- NIR studies

The UV optical transmittance spectral analysis of LCBD single crystal was carried out between 200 to 1400 nm using Varien Carry 5E spectrophotometer which was shown in Fig.2. The transmittance spectrum depicts the transparency of the crystal was closer to 95% at 199.5 nm. But around 200 nm, there was a sharp decrease in transmittance due to absorbance leading to electronic excitation in this region. At the longer wavelength side, the crystal was highly transparent (nearly 100%) up to 1200 nm. Absence of absorption in this region between 300 and 1200 nm was an advantage, as it was the key requirement for materials having NLO properties. As a result, it can be used as a potential material for SHG in the visible region down to blue and violet light, which makes it suitable for laser frequency doubling and related optoelectronic application. The lower cut-off wavelength of the crystal was found to be 200 nm.

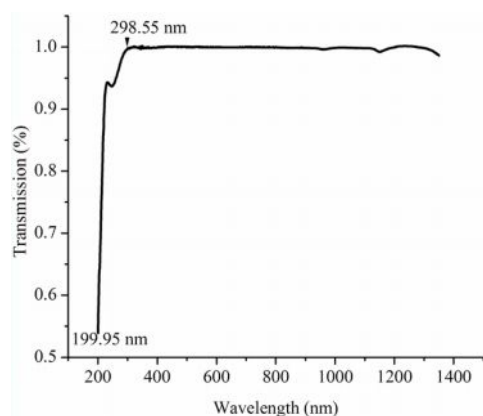


Fig.2. UV-Vis spectrum of the grown crystal

3.2.2 SHG efficiency measurement

The SHG efficiency was measured for the grown crystal using the standard Kurtz and Perry powder technique [9]. The fundamental beam of a Q-switched Nd:YAG laser with a wavelength of 1064 nm, input energy of 3.2 mJ, pulse duration of 8 ns, a repetition rate of 10 Hz and a spot size of 1 mm diameter was used. Powder was made from single crystals and then graded by the use of standard sieves to desired range of particle sizes from 50 to 150 μm . To make relevant comparison with known SHG materials, KDP was also powdered and sieved in to the same particle size range. The average particle size were filled air-tight in separate micro-capillary tubes of uniform bore of about 1.5 mm diameter to ensure uniform packing. The SHG output of 532 nm was emitted and collected by a photomultiplier tube (PMT) after being monochromated to collect only the 532 nm radiation. The optical signal incident on the PMT was converted into output voltage at the oscilloscope. The input energy incident on the capillary tube was selected to be 3.2 mJ, an energy level optimized not to cause any chemical decomposition of the sample. The results obtained by this method shows that the SHG efficiency of the LCBD sample was nearly 0.75 times more than that of KDP.

3.3 FTIR studies

Fourier transform infrared spectra of LCBD crystal was carried out using Bruker IFS 66V FTIR spectrophotometer and the spectrum was shown in Fig. 3. The vibration spectrum of a molecule generally consists of two major regions (i) Group frequency region (ii) Finger print region. Group frequencies are vibrations that are associated with certain structural units such as $-\text{CH}_3$, $-\text{NH}_2$, $-\text{C}\equiv\text{N}$ etc and appear fairly at a constant region in the spectrum. The molecules having similar groups show their vibration in the form of bands was called finger print region [10-11]. In the case of LCBD, CO_2 symmetric and asymmetric stretching modes of L-cysteine were assigned to the bands at 1568 and 1386 cm^{-1} , respectively. The bands at 1568, 1427 and 1386 cm^{-1} for L-cysteine were assigned to the CO_2^- asymmetric and symmetric stretching modes. The presence of these bands showed that the adsorbed L-cysteine was to be in its zwitterionic state. The presence of NH_3^+ group was in fact supported by the assigned band at 1634 cm^{-1} for L-cysteine. The bands at 1186 cm^{-1} for L-cysteine as well supported the presence of the NH_3^+ group. The B-O vibrations of borate have absorption bands at 781-1427 cm^{-1} [12-14]. The strong bands observed at 746 cm^{-1} and 1427 cm^{-1} have been assigned to ring B-O symmetric stretching vibration. The ring B-O asymmetric stretching vibrations appear at 1186 cm^{-1} and 1349 cm^{-1} with very strong intensity. The very strong peak at 1136 cm^{-1} has been attributed to B-O terminal symmetric stretching vibration. The B-O terminal asymmetric stretching vibration is observed at 1493 cm^{-1} . The peak at 3202 cm^{-1} has been assigned to OH stretching vibration.

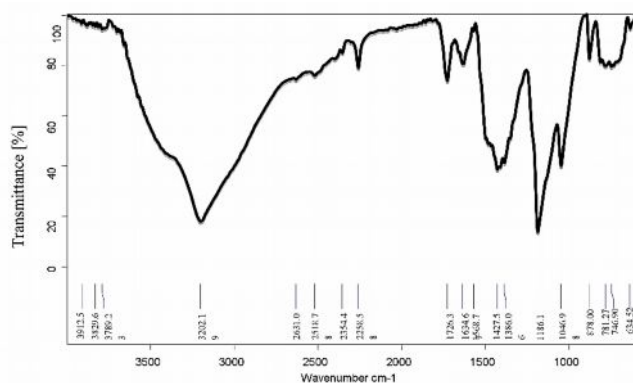


Fig.3. Infrared spectrum of LCBD crystal

3.4. Thermal analysis

3.4.1 TGA and DTA analysis

The TGA and DTA curves of LCBD single crystal were recorded between 20°C and 1000°C at a heating rate of 10°C/min in the nitrogen atmosphere using SDTQ600 V8 analyzer equipment. The TGA and DTA traces of LCBD were shown in Fig. 4. The TGA curve illustrates a consecutive weight losses starting at about 111.24°C. The weight loss of 32.20% corresponds to decomposition of the L-cysteine. It was followed by two more stages of weight losses between 158.59°C and 175.33°C, and the weight loss in these stages corresponds to 9.604%. There was a gradual and significant weight loss of about 8.285% as the temperature is increased beyond 217.92°C. The total weight loss was about 50.09% of the sample weight. As there was no weight loss below 111.24°C, the crystal was devoid of physically adsorbed water and water of crystallization. The TGA trace clearly indicates the thermal stability of the title compound as 111.24°C. The DTA trace depicts two exothermic peaks starting at about 116.82°C. It was exactly matching with the weight loss observed in TGA. Based on its exothermic nature, it is assigned to the decomposition of disodium tetraborate decahydrate ions. Hence, from this observation it can be clearly stated that the crystal retains its texture up to 111°C. Another peak was observed at 222.21°C may be attributed to volatilization of material. Prolonged heating up to 1000°C does not produce any significant exothermic or endothermic peaks in DTA curve. The DSC trace of LCBD crystal was recorded between 20°C and 1000°C at a heating rate of 10°C/min in the nitrogen atmosphere using SDTQ600 V8 analyzer equipment and it was shown in Fig. 5. The DSC trace indicates the origin of broad endotherm at 111°C. Since degradation of L-cysteine was to be an exothermic process, the endothermic nature of DSC trace was deliberately assigned to decomposition of disodium tetraborate decahydrate. The DSC analysis also confirms the absence of physically adsorbed water or water of crystallization. It was closely matching with TGA trace.

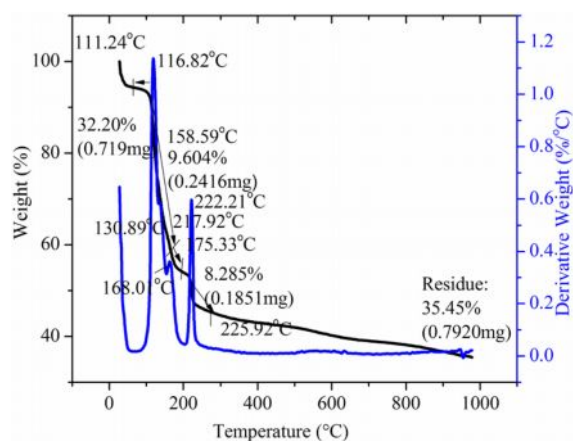


Fig.4. TG/DTA trace of LCBD single crystal

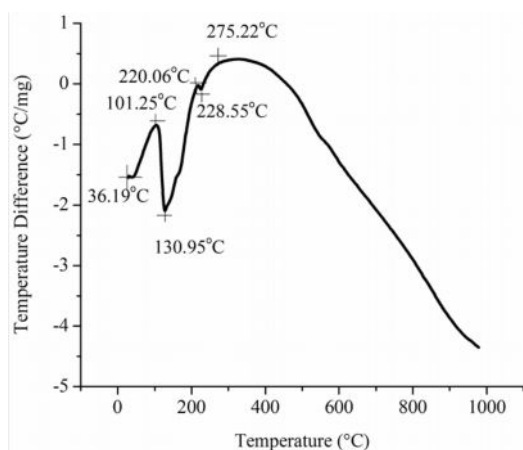


Fig.5. DSC trace of LCBD single crystal

4. Conclusion

We have successfully grown the crystals of LCBD of appreciable size by slow solvent evaporation technique. The crystal system was identified to be monoclinic from single-crystal X-ray diffractometry. LCBD has a wide transparency window from 300 to 1200 nm, which highlights their prospects of application as NLO materials. FTIR analysis confirms the presence of functional groups and coordination of LCBD single crystal. Thermal analysis clearly illustrates that the crystal undergoes decomposition above 111°C. NLO property was confirmed using Nd:YAG laser of wavelength 1064 nm and the efficiency was estimated to be 0.75 times higher than KDP.

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