GROWTH AND CHARACTERIZATION OF A SEMIORGANIC NLO MATERIAL: L-HISTIDINE BARIUM CHLORIDE DIHYDRATE

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Abstract

L-Histidine Barium Chloride dihydrate (LHBC), a semi organic nonlinear optical material was grown from aqueous solution by slow solvent evaporation method at room temperature. The LHBC crystals were characterized by X-ray powder diffraction analysis. The presence of functional groups was identified through Fourier Transform Infrared Spectroscopy. Thermogravimetric and Differential Thermal Analysis confirm that the crystal is stable up to 269oC. The mechanical properties of the grown crystals have been studied using Vickers microhardness test. The second harmonic generation behavior of LHBC crystal was tested by Kurtz-Perry powder technique.

Keywords: Crystal growth, X-ray diffraction, Optical material, Thermal studies, Nonlinear optics

INTRODUCTION

The overwhelming success of molecular engineering on controlling nonlinear optical (NLO) properties has attracted the attention of the researchers to search for a variety of new types of nonlinear optical materials [1] and to improve the NLO efficiency of the known materials. In the context of NLO, organic materials have advantages such as large NLO coefficients and structural diversity or flexibility, compared to the inorganic counterparts [2]. They also have some inherent drawbacks, for example, poor physico-chemical stability and low mechanical strength. As a result, the quest for new frequency conversion materials is presently concentrated on semi-organic crystals due to their large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [3–5]. Semi-organics include organic–inorganic salts and metal–organic coordination compounds [6]. Among these classes of materials, amino acids are interesting and useful materials for NLO applications. The salts of basic amino acid L-histidine gain much interest as promising nonlinear optical materials after the early works of Marcy et al., that the nonlinearity of L-histidine tetraflouroborate is much greater than that of potassium dihydrogen phosphate [7]. Due to its basic nature, L-histidine forms a number of salts with different organic and inorganic acids which have shown NLO properties. As a result, very good semiorganic nonlinear optical materials such as L-valine hydrochloride [8], L-arginine phosphate monohydrate (LAP) [9], L-histidine hydrochloride [10], L-alanine cadmium chloride [11] and L-valine cadmium chloride [12] are some of the good examples which proved very suitable materials for NLO applications. In the present investigation, the growth aspects of LHBC have been studied and crystals were grown by slow evaporation technique. Characterization studies such as single crystal XRD, FTIR, UV-VIS-NIR, TG/DTA, micro hardness and SHG studies have been carried out for the above crystal.

EXPERIMENTAL

Material synthesis

LHBC was synthesized from an aqueous solution of L-Histidine and Barium Chloride dihydrate in the equimolar ratio as per the reaction:

$$C_6H_9O_2N_3 + BaCl_2.2H_2O \rightarrow Ba\ (C_6H_9O_2N_3)\ Cl_2.2H_2O$$
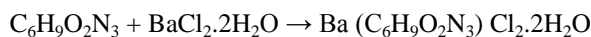
Growth of single crystals

Single crystal of L-histidine barium chloride dihydrate was grown from aqueous solution by slow solvent evaporation method at room temperature. The calculated amount of the salt was dissolved in the demonized water and stirred well using temperature controlled magnetic stirrer to yield a homogeneous mixture of solution. The solution was filtered to remove all suspended impurities using Whatman filter paper. Then the solution was allowed to evaporate at room temperature, which yield well defined single crystals of LHBC. The purity of the synthesized salt was increased by successive recrystallization processes. Good transparent crystals were harvested after a growth period of 20-25 days. The photograph of as-grown crystal is shown in Fig.1.
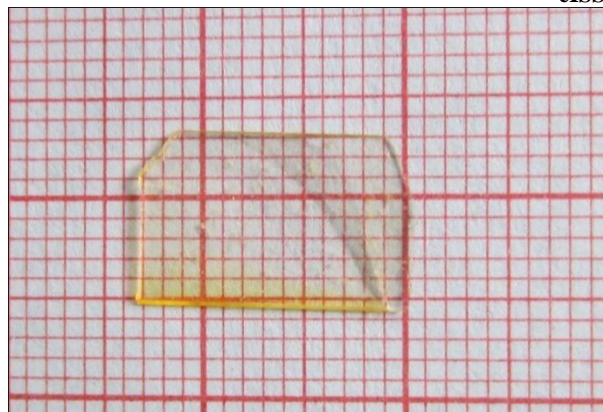
Figure 1: As-grown LHBC crystal

RESULTS AND DISCUSSION

Powder X-ray diffraction

The purified samples of grown crystals have been crushed to a uniform powder and subjected to a powder X-ray diffraction using a Bruker AXS D8 Advance powder X-ray Diffractometer. The K_α radiations (λ=1.5406 Å) from a copper target were used for the diffraction studies. The specimen was scanned in the reflection mode in the 2θ range 10°-70° with five decimal accuracy and the XRD pattern of the as grown crystal is shown in Fig. 2. The peaks were indexed using least square method. The well defined sharp peaks reveal the good crystalline nature of LHBC crystal. The powder XRD studies of LHBC suggest that the crystal is orthorhombic in structure with spacegroup $P2_12_12_1$. The calculated values of the lattice parameters are a=5.167 Å, b=7.378 Å, c=18.934 Å and the cell volume was found to be 721.81 $Å^3$.
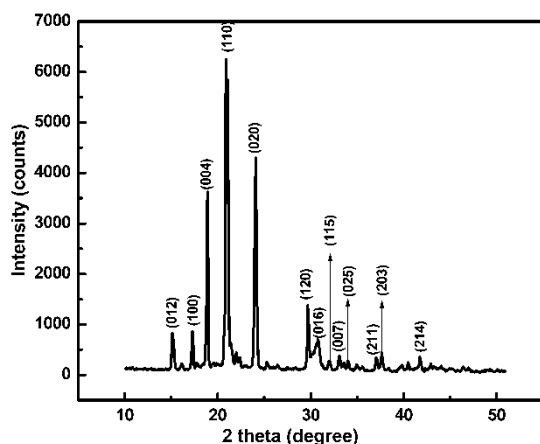

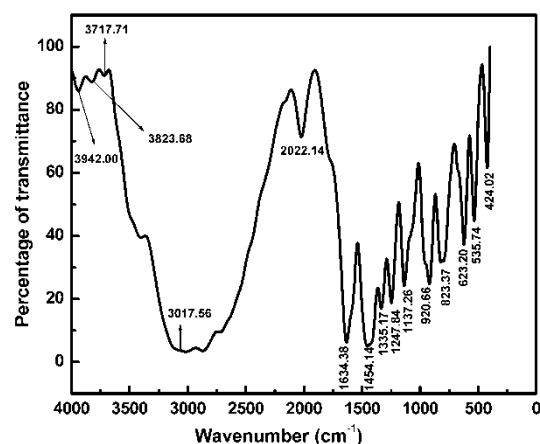**Figure 2: Powder XRD patterns of LHBC crystals**

Figure 3: FTIR spectrum of LHBC crystals

FTIR spectroscopic analysis

FTIR analysis was carried out to characterize the functional groups of the LHBC crystal molecules [13]. The FTIR spectrum was carried out using Perkin Elmer FTIR spectrometer by KBr pellet method in the range 4000-400cm^{-1}. Fig.3 gives the FTIR spectrum of as grown LHBC crystal. The presence of imidazole ring in the L-histidine molecule is indicated by the peak at 3017 cm^{-1} by the vibration of C-H stretch in the ring. The peak at 3717 cm^{-1} indicates its NH_2 stretch of the amine group of the L-histidine molecule. The peaks at 3942 cm^{-1}, 3823 cm^{-1}, 1634 cm^{-1}, 1454 cm^{-1} indicate the presence of hydrogen bonds with the electronegative atoms present in the molecule. The presence of the peak at 1335 cm^{-1} and 1247 cm^{-1} represent the C-O stretch of the carboxylic group in the L-histidine molecule. The band at 823 cm^{-1} and 623 cm^{-1} represent the organic halogen, namely $BaCl_2$ attached to the C-Cl stretch of the molecule. Thus the peak positions indicate the presence of the functional groups of LHBC. The strong peak intensities at 3017 cm^{-1}, 1634 cm^{-1}, 1454 cm^{-1}, 1335 cm^{-1} and 1247 cm^{-1} indicates that the concentration of the functional groups namely imidazole ring, OH group and the carboxylic group are more than any other groups present in the molecule. The broad spectrum of C-H stretch at 3017

cm^{-1}, O-H stretch at 1634 cm^{-1}, in plane O-H bend at 1451 cm^{-1} and O-H stretch at 3823 cm^{-1} indicate that the hydrogen bonds are formed because of the number of chemical environments. The narrow bands are due to the smaller number of chemical environments.

Optical transmittance studies

Nonlinear optical single crystals are mainly used in optical applications. The optical transmission range, transparency cut-off and the absorbance bands are the most important optical parameters for laser frequency conversion applications. The UV-VIS transmission spectrum of LHBC was recorded with Perkin Elmer Lamda 35 spectrophotometer in the range 190-1100 nm and the recorded spectrum is shown in Fig.4. The cut off wavelength of LHBC crystal is 215 nm. There is no remarkable absorption in the entire region of the spectra. The transmission in the ultraviolet region and IR region shows that these crystals are useful for the second harmonic generation of Nd: YAG laser.
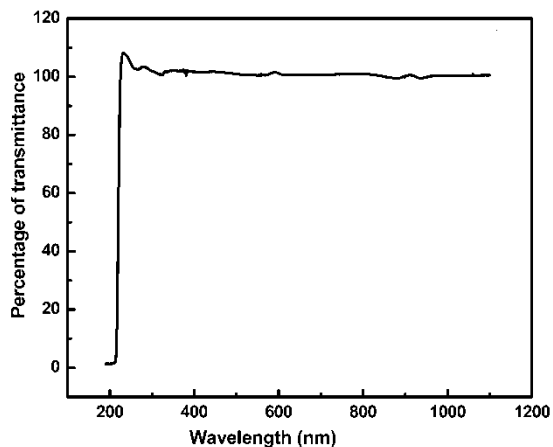

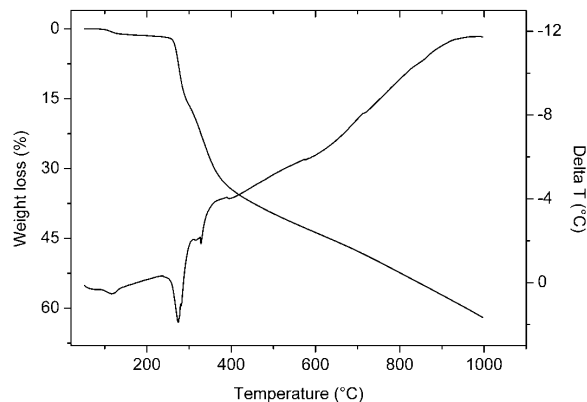**Figure 4: UV- Vis- NIR spectrum of LHBC crystals**

Figure 5: TG/DTA spectrum of LHBC crystals

Thermal analysis

Thermogram provides information about decomposition patterns of materials and weight loss [14]. The thermal stability of LHBC was studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) using Perkin Elmer, Diamond TG/DTA instrument between the temperatures 50˚C and 1100˚C at a heating rate of 10˚C/min under Nitrogen atmosphere. The LHBC sample weighing 18.518 mg is taken for the measurements. Fig.5. illustrates TG/DTA spectrum of LHBC. It is observed from the TGA that the grown crystal was thermally stable upto 269^0C. The low temperature of decomposition confirms the presence of water molecules in the grown crystal. There are gradual weight loss between 269^oC - 298^oC and 298^oC – 420^oC. It is seen that at different stages various gases like CO_2, NH_3, Cl, etc are liberated. Finally the resulting residue undergoes decomposition at 420^oC. In the DTA trace there was a sharp endotherm peak at 269^oC which is the melting point of the LHBC crystal. The minute endotherm is due to desorption of lattice entrapped water. The sharpness of this peak shows good degree of crystallinity of the sample [15]. Hence the present material may be a promising candidate for all types of nonlinear application.

Microhardness study

The micro hardness studies were carried out to determine the mechanical strength of the grown LHBC crystal using a Leitz Weitzler hardness tester fitted with a diamond indenter. The indentation marks were made on the surface of LHBC single crystal at room temperature by applying load of 25 to 50 g. The Vickers micro hardness number Hv of the crystal was calculated using the relation $Hv=1.8544P/d^2$ kg/mm^2 where, Hv is the Vickers micro hardness number in kg/mm^2, P is the applied load in kg and d is the average diagonal length of the indentation in mm [16]. A graph is drawn between the hardness values and corresponding loads is shown in fig.6. From the graph, the hardness values increases with increase in load up to 50 g. Beyond the load of 50 g cracking were developed on the crystal surface due to the release of internal stress generation locally by indentation.
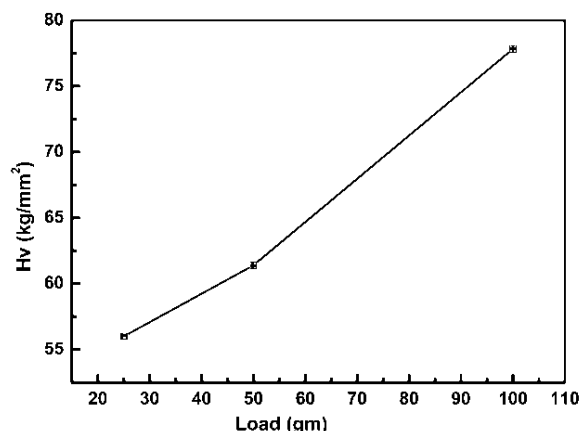
Figure 6: Graph of load (vs) Hv for LHBC crystal

Second Harmonic Generation measurements

The most widely used technique for confirming the SHG from second order NLO materials is the Kurtz Powder technique [17] to identify the materials with non- centrosymmetric crystal structures. A Q-switched Nd: YAG laser beam of wavelength 1064 nm, pulse width of 8ns and with a repetition rate of 10 Hz was used. The crystal was ground into fine powder and densely packed in a micro capillary tube. To make relevant comparisons with known SHG materials, KDP was also ground into fine powder. The second harmonic signal generated in the crystal was confirmed from the emission of green radiation by the crystal. The SHG conversion efficiency of LHBC is found to be about 0.8 times that of KDP.

CONCLUSIONS

Optical quality bulk single crystals of LHBC were grown by slow evaporation technique. Single crystal X-ray and powder diffraction confirms the unit cell parameters and LHBC crystal belong to orthorhombic crystal structure. The presence of various functional groups was confirmed by FTIR spectrum. Optical transmission studies showed that the crystal is transparent in the visible region with lower cut-off at 215 nm and hence it is suitable for frequency conversion applications. The decomposition temperature and percentage of weight loss of the material were found out from TG/DTA analyses. The degree of crystallinity and purity from a sharp endothermic peak was also confirmed. Vicker's microhardness was calculated in order to understand the mechanical stability of the grown crystals. The SHG efficiency measured by the Kurtz powder test was about 0.8 times that of potassium dihydrogen phosphate. Thus LHBC can act as a potential candidate for nonlinear optical applications.

ACKNOWLEDGEMENTS

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