Adv. Mater. App. 3 (2019) 16-21

L-Histidine cadmium bromide single crystal for photonic device fabrications

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Received 16 October 2019, Received in final form 11 November 2019, Accepted 15 November 2019

Abstract

A semi organic crystal L-Histidine cadmium bromide has been grown successfully by slow evaporation technique. The grown crystal has subjected to both single crystal and powder x-ray diffraction to identify the intense peaks on various planes. The calculated lattice parameter values are *a* = 14.62 Å, b = 5.43 Å, c = 11.09 Å and volume = 867 Å^3. FTIR spectrum confirms the presence of functional groups of the grown crystal. The optical absorption spectrum showed a cutoff wavelength at 250 nm for the L-Histidine cadmium bromide crystal. TGA studies result that the grown crystal can retain its texture up to 212° C. The micro hardness test confirms that the hardness of the crystal increases with the increase of load. The dielectric measurement of the crystal was studied as function of temperatures and it shows that decrease in dielectric constant with increase in higher frequency. FESEM micrograph shows the distribution of grains and the presence of microcrystals on the surface of the grown crystal. The second harmonic generation was confirmed by Kurtz powder method and it is found to be 0.9 times higher than that of KDP crystal.

Keywords: *Semi organic crystal, Second harmonic generation, dielectric properties, thermal property, FESEM.*

1. Introduction

Recently, a very new approach has been developed for obtaining new materials for non linear optics. The need for semi organic material is tremendously increasing because of their large nonlinearity, higher resistance and excellent mechanical hardness [1, 2] and its use in optoelectronic and photonic devices optical communications, optical data storage, optical computing and electro-optic shutters. Semi organic crystals uses are not only useful in electronic industry it is also useful in the field of Medicine. Semi organic crystal offers a variety of molecular structures by virtue of changes brought out in selection of metals, ligands. Semi organic crystals usually have higher chemical stability and mechanical strength compared to their inorganic compounds. Semi organic crystals are widely used in laser based imaging, high damage threshold, wide transparency range, excellent non non-linear optical coefficient, low angular sensitivity and remote switching.

L-Histidine and its family of crystals have been reported to be of very great interest for the nonlinear optical applications [3-5]. Cadmium bromide nanostructures are applied in solar cells, gas sensors, transparent electrodes and photodiodes, catalysts, photo catalysts and optoelectronic devices [6]. Hence L-arginine, L-histidine, L-threonium L-alanine and L-valine have been subjugated for the formation of salts with different inorganic acids. As a result very good semiorganic nonlinear optical materials such as L-valine hydrochloride, L-arginine phosphate monohydrate (LAP), L-histidine hydrochloride, L-alanine cadmium chloride, L-Histidine Cadmium Chloride and L-valine cadmium chloride are some of the good examples which proved very suitable materials for NLO applications.

In this paper Cadmium Bromide is combined with L-Histidine to form a new semi organic crystal L Histidine Cadmium Bromide (LHCdBr). This paper reports the synthesis, crystal growth and characterization of LHCdBr single crystal. It also presents the spectroscopic and physiochemical behavior of the grown material.

2. Materials and methods

2.1. Synthesis of LHCdBr single crystal

The materials were synthesized by taking L-Histidine and cadmium bromide in a 1:1 stochiometric ratio. The calculated amount of cadmium bromide was first dissolved in deionized water after deionization L-Histidine was then slowly added to the solution. In order to avoid co precipitation of multiple phases the mixture of the reactants had to be stirred well. The prepared solution was allowed to evaporate at room temperature. The purity of the synthesized crystal was further improved by successive recrystallization

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process. Thereby good quality of single crystal was obtained in the period of 14 days which is shown in Fig. 1.

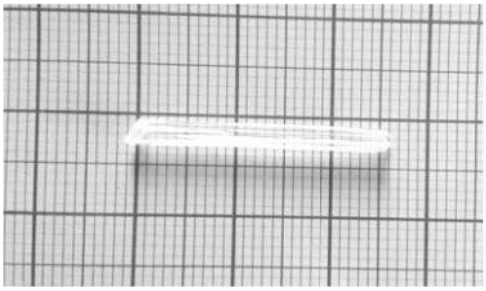

Fig. 1. *Grown crystal of LHCdBr*

2.3. Characterization

Single crystal XRD was recorded by Enraf Nonius CAD/MACH3 single crystal X-ray diffractometer. The powder XRD pattern of crystal was obtained using a BRUKER AXS D8 advance X-ray diffractometer with CuKα radiation (λ = 1.54). Fourier Transform Infrared Spectrometer (FTIR) analysis was carried out using PerkinElmer Spectrometer with the scan range of MIR 450-4000 cm^{-1}. The optical absorption and transmittance spectra were recorded using Lambda 35 UV–Visible spectrophotometer in the wavelength range of 190-700 nm. The dielectric studies of the crystal were analyzed out at room temperature using a TH 2816 A DIGITAL LCRZ METER in the frequency range of 50Hz–2MHz. The thermal analysis was carried out to find the weight loss of the title crystal using NETZSCH STA 449 F3. Field emission scanning electron microscopy (FESEM) image was recorded using Inspect F50 from FEI. The second harmonic generation (SHG) efficiency of the material was studied using Kurtz-Perry powder technique using Nd: YAG laser beam.

3. Results and discussions

3.1. Single crystal X-ray diffraction studies

From the XRD analysis, cell parameters were determined as a = 14.62 Å, b= 5.43 Å, c= 11.09 Å and volume V= 867 $Å^3$. From the study it was found that grown LHCdBr crystallized in Triclinic (P_1) system. When comparing the values with literature survey the obtained values were in very good agreement with the corresponding earlier reported value.

3.2. Powder X-ray diffraction studies

Powder x-ray diffraction study was used for the identification of crystallinity of the grown crystal. Fig. 2 represents the indexed powder diffractogram for the grown crystal L-Histidine cadmium bromide. The sharp intensity peaks found in the spectra shows good crystalline nature and purity of the grown crystal.

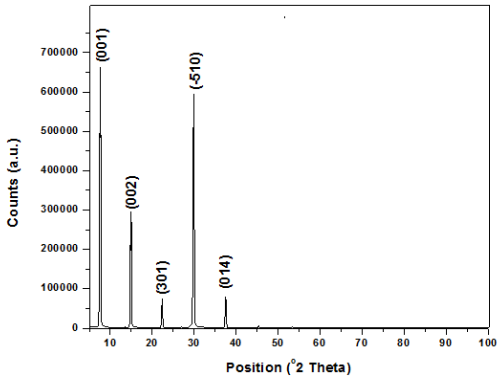

Fig. 2. *Powder X-ray diffraction pattern of LHCdBr*

3.3. FTIR Analysis

FTIR analysis was carried out to understand the chemical bonding and it also provides useful information regarding the molecular structure of the compound [7]. The FTIR spectrum of L-Histidine cadmium bromide was recorded in the wavelength range of 400-4000 cm^{-1}. The resulting spectrum is presented in Fig. 3. The C=O stretching vibration is found to be around 1750 cm^{-1}. The bond at 3446.79 is due to N-H stretching, which indicates the presence of amines and amides in the grown crystal. The peaks at 1403 and 1010 cm^{-1} represents the asymmetric and symmetric vibrations of N-C-N respectively. The N-H bond is present at 1631.78 cm^{-1}. The C=C stretching vibration peak shows around 2340 cm^{-1}. The C–H deformation appears at 622 cm^{-1} is due to out of plane bending vibrations. The symmetrical C-C stretching is found to be at 953 cm^{-1}. The shift in the positions of the characteristic peak confirms the formation of the grown crystal.

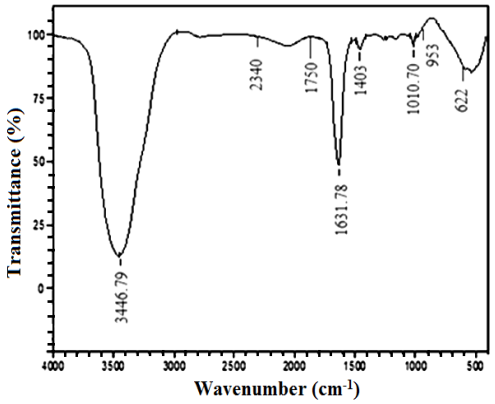

Fig. 3. *FTIR spectrum of LHCdBr crystal*

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3.4 Linear optical property

The crystal LHCdBr is well polished and the sample is dissolved in water to measure the absorption and transmission spectrum which is shown in Fig. 4 & 5. For optical fabrication, the crystal should be highly transparent over a considerable region of wavelength [8, 9]. Optical spectrum showed a cutoff wavelength at 315 nm. From the absorption spectrum, it is found that the crystal is transparent in the range 381-1100 nm without any absorption peak, which is an essential parameter of NLO crystals. Absence of absorption in the region 400-1100 nm is an advantage and it is the key requirement for materials exhibiting nonlinear optical (NLO) property. The band gap energy (E_g) is calculated using the formula as given below.

$$E_g = \frac{hc}{\lambda} \quad (1)$$

Where h-Planck's constant, c-velocity of light and λ is the wavelength of light used. The estimated E_g found to be 3.92 eV.

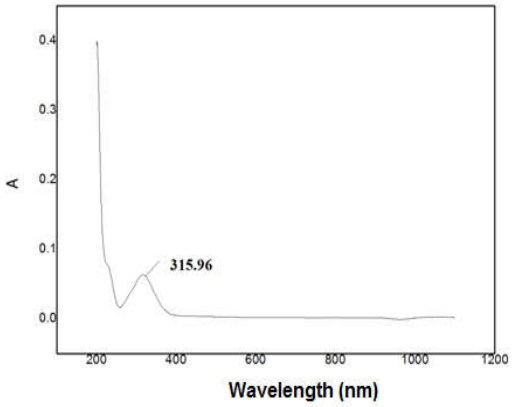

Fig. 4. *Absorption spectrum of LHCdBr*

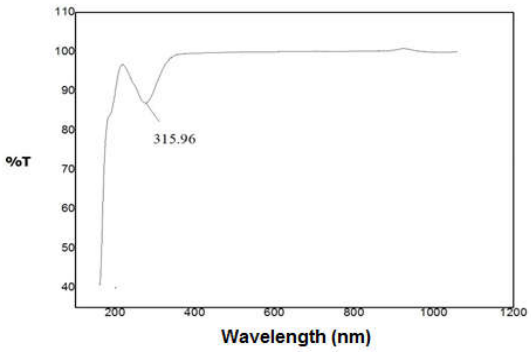

Fig. 5. *Transmission spectrum of LHCdBr*

Transmission spectra are very important for any NLO material because a nonlinear optical material can be of practical use only if it has wide transparency window. From the transmittance spectra, it is observed that the grown crystal have high transmittance in the entire visible and near IR region [10, 11]. The transparency is an added advantage for this crystal to be utilized in the field of optoelectronic devices.

3.5. Thermal analysis

The thermo gravimetric analysis of L-Histidine Cadmium Bromide crystal was carried out for the sample at a heating rate of 20 K min^{-1} in nitrogen atmosphere and the resultant spectrum is shown in Fig. 6. The TGA illustrates that there is no loss below 212°C, illustrating the absence of water in the crystal lattice [12]. The sharp weight loss starts at 212°C to 298°C without any intermediate stages, is assigned as melting point of the crystal. After that above 212° C the crystal sharply starts to decompose at 298°C. The sharpness of this peak shows the good degree of crystallinity and purity of the sample. Thus from the thermal studies, the crystal can retain its texture up to 212°C.

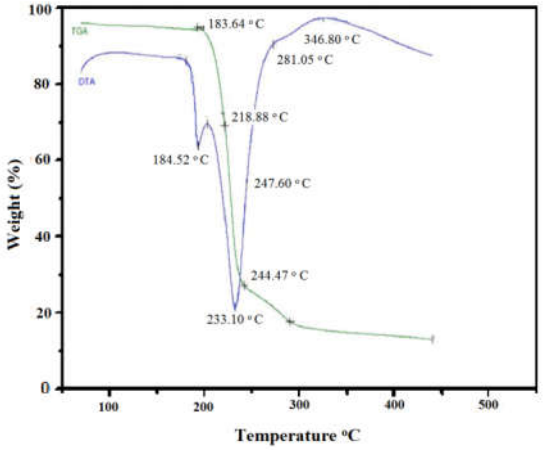

Fig. 6. *Thermal analysis of LHCdBr*

3.6 Micro Hardness Analysis

One of the methods to determine the mechanical behavior of the grown crystal is micro hardness test. It is correlated with other mechanical properties like elastic constants, yield strength and temperature of cracking [13]. The indentation marks were made on the surface of LHCdBr single crystal at room temperature by applying load of 25, 50 and 100 g. The Hv is found to be increase with increase in the load from 25 to 100 g and crack occurs at higher loads.

The Vickers micro hardness values were calculated from the standard formula [14]

$$Hv = 1.8544\ (P/d^2)\ kg/mm^2 \quad (2)$$

Where P is the applied load and d is the mean diagonal length of the indentation. The

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corresponding graph is shown in the Fig. 7, from which it is observed that the hardness increases with the increase of load up to 100g and crack occurs at that load.

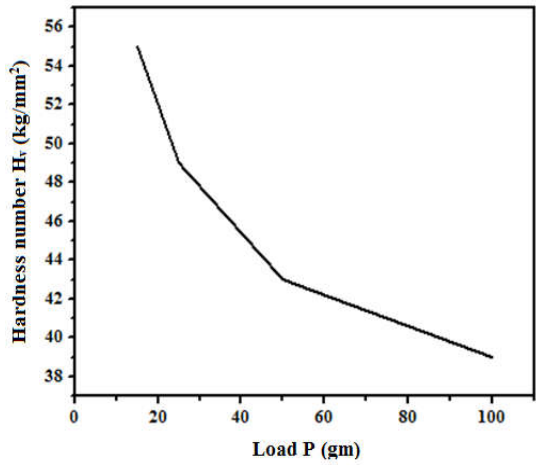

Fig. 7. *Relation between Vickers hardness number vs load*

According to the normal Indentation size effect (ISE), micro hardness of crystal decreases with increasing load and in Reverse indentation size effect (RISE) hardness increases with applied load. In our case, Hv increases with applied load [15, 16].

3.7. Dielectric studies

The variation of dielectric constant (ε) was studied as a function of frequency for the grown crystal at various temperatures and is shown in Fig. 8.

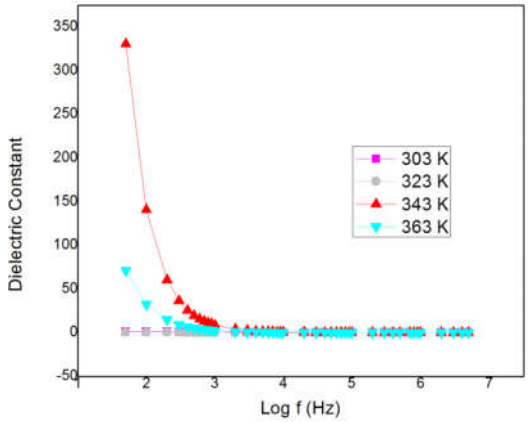

Fig. 8. *Variation of dielectric constant (ε) with applied frequency*

The dielectric constant is the measure of how easily a material is polarized in an external electric field [17]. In accordance with Miller rule, the lower value of dielectric constant at higher frequency is a suitable parameter for the enhancement of SHG coefficient.

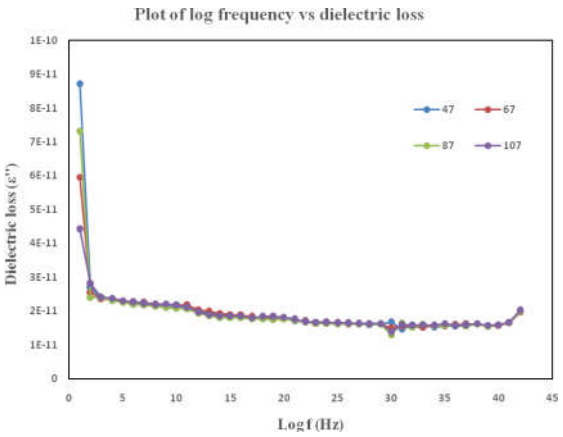

Fig. 9. *Variation of dielectric loss with applied frequency*

Fig. 9 shows the variation of dielectric loss with frequency. The crystal possesses enhanced optical quality with lesser defects and this parameter plays a vital role for the fabrication of nonlinear optical devices because of low dielectric loss with high frequency for the samples. Due to the impedance to the motion of charge carriers at the electrodes, space charge and macroscopic distortion results which might cause larger values of dielectric constant at lower frequencies [18]. As the frequency increases, the dielectric constant values are found to decrease exponentially and attain lower values [19].

3.8 FESEM Analysis

FESEM micrograph of L-Histidine cadmium bromide crystal is shown in Fig. 9.

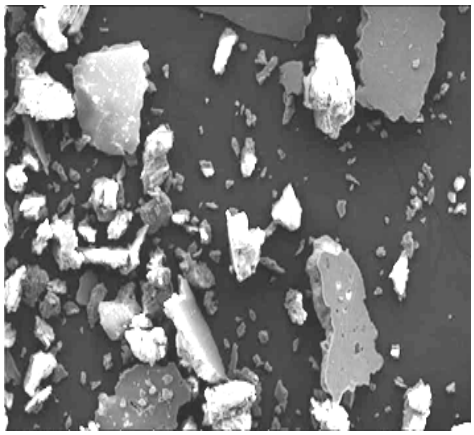

Fig. 10. *FESEM image of LHCdBr crystal*

The transparent regions of the crystal were cut into few mm for examining the surface of the crystal. It gives information about surface and the presence of imperfections in the crystal. Fig. 9

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clearly shows the grain distribution over the surface and a few micro crystals present on the surface of the grown crystal.

3.9 NLO Studies

The Kurtz powder technique is used to identify the materials with non-centrosymmetric crystal structures and widely used technique for confirming the SHG efficiency of NLO materials.

In order to confirm the NLO behavior of these material, powdered samples was subjected to Kurtz and Perry powder technique. The output power is found to be 0.9 times greater than that of KDP crystal.

4. Conclusions

A single crystal of L-Histidine cadmium bromide has been successfully grown using slow evaporation technique. From the single crystal and powder x-ray diffraction, the lattice parameter was calculated and found to be *a* = 14.62 Å, b = 5.43 Å, c = 11.09 Å and volume = 867 $Å^3$ and confirm the triclinic crystal structure of the LHCdBr crystal. The presence of functional groups of the grown crystal was confirmed using FTIR spectrum. The optical absorption spectrum showed a cutoff wavelength at 250 nm for the L-Histidine cadmium bromide crystal and the estimated band gap energy is about 3.92 eV. TGA studies resulted that the L-Histidine added cadmium bromide single crystal shows the enhanced melting point, 212°C. The micro hardness test of the grown crystal confirms increase in hardness of the crystal with the increase of load. The dielectric studies of the crystal represent that increase in dielectric constant with decrease in frequency. FESEM image of the LHCdBr crystal shows the distribution of small grains and the presence of microcrystals on the surface of the grown crystal. The second harmonic generation was studied using Kurtz powder method and is found to be 0.9 times larger than that of KDP crystal.

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