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Research Article

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Growth, thermal and mechanical characterizations of non linear optical L-arginine benzohydrazide single crystal

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ABSTRACT

Single crystals of L-Arginine Benzohydrazide (LABH) were grown by slow evaporation technique. Single crystal X-ray diffraction analysis reveals that the crystal belongs to orthorhombic crystal system with a=8.7740Å, b=10.4434Å and c=13.0843Å. Fourier Transform Infra-red analysis was carried out for the confirmation of functional group present in the grown crystal. The optical transmission study reveals the transparency of the crystal in the entire visible region and the cut off wavelength has been found to be 300 nm. Mechanical strength of the grown crystal was analyzed using Vickers microhardness tester and confirms that the grown crystal is a soft material. Nonlinear optical property of the crystal was confirmed by Kurtz Perry powder technique and it found that SHG efficiency is 1.9 times that of KDP.

Keywords: Solution growth, FTIR, Optical absorption, SHG, Mechanical hardness.

INTRODUCTION

Nonlinear optical materials are utmost currently used in building of inactive and active photo electronic devices [1, 2]. Frequency conversion devices also use nonlinear optical materials [3]. These applications are governed by various properties of the materials, such as transparency, stability etc. Among organic, semi organic and inorganic crystals, organic NLO crystals are abundantly used because they have high SHG efficiency and high optical threshold for laser power [4]. Even though many number of NLO crystals are grown, new NLO materials with different other properties are necessary for optoelectronic applications. Hence researchers are interested in growing new optical organic crystals which will be useful for many applications. Of these organic crystals, L-Arginine based crystals are deeply investigated because of its chirality, which induces as asymmetric molecular structure [5-7]. In our present work, L-Arginine Benzohydrazide single crystal is grown by slow solvent evaporation technique. The grown crystal is given for single crystal XRD, FTIR, UV-Vis spectral analysis; thermal, microhardness and NLO test.

EXPERIMENTAL SECTION

L-Arginine and Benzohydrazide (AR grade) are used as starting materials for growing LABH single crystals. L-Arginine and Benzohydrazide are dissolved separately in deionized water in the ratio 1:1 and are mixed together to prepare a supersaturated solution. This solution is filtered twice to ascertain the growth of pure crystals. Crystal growth process is carried out in an aqueous medium. The saturated solution is retained in an untouched condition and the beaker was covered with a polythene paper. A few holes are made on the polythene cover to enable slow evaporation. By adopting the solution growth method, single crystals of L-Arginine Benzohydrazide (LABH) were full-grown from the supersaturated solution at room temperature. The solution is

periodically inspected and after a month the crystal started growing. Further, the crystal is permitted to grow for another 20 days in order to obtain a nominal size suitable for characterization. The photograph of grown LABH crystal is shown in Figure 1.

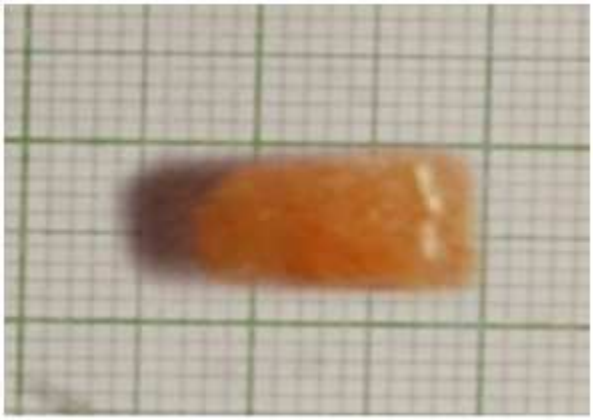

Figure 1. Photograph of LABH crystal

3. CHARACTERIZATION

3.1. SINGLE CRYSTAL XRD

Single crystal X-ray diffraction analysis for the grown crystal LABH has been carried out to categorize the cell parameters using an ENRAF NONIUS CAD 4 automatic X-ray diffractometer. From the XRD data, it is found that LABH belongs to the Orthorhombic system with a =8.7740 Å, b = 10.4434 Å and c=13.0843 Å, the space group being, P_{21} and the volume of the system is 1198.92 $Å^3$. The lattice parameter values for grown crystal LABH are in agreement with the reported work [8].

3.2. FTIR ANALYSIS

Fourier transform spectroscopy is a modest precise technique to resolve a complex wave into its frequency components. Fourier transform infrared (FTIR) has made the mid IR region more useful. The spectrum for LABH sample is recorded in the frequency range from 4000cm^{-1} to 400cm^{-1} and is shown in Figure 2. The C-H stretch of -CH2- groups produces the characteristic peak at 3028cm^{-1}. The broad band at 1644cm^{-1} can be assigned to C=O of Benzohydrazide. The sharp peak at 1446cm^{-1} is assigned to COO- symmetric stretching. The wave number associated with LABH crystal is tabulated in table 1.

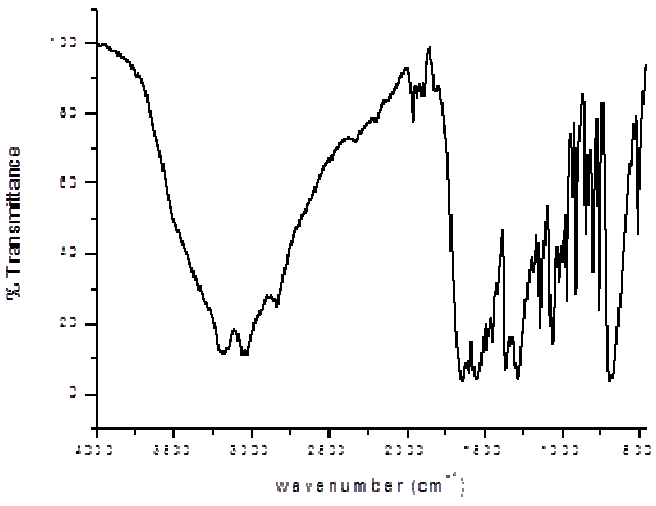

Figure 2. FTIR Spectrum of LABH crystal

Table 1. FTIR frequency assignment of LABH crystal

Wave number (cm^{-1})	Assignment
3181	NH2 stretching
3059	CH stretching
1644	C = O Stretching of Benzohydrazide
1446	C=O stretching of L-Arginine
1362	CH2 symmetric bending
1140	NH2 wagging
912	CH2 rocking
761	NH2 rocking
551	COO- in plane bending

3.3. UV-VIS ANALYISIS

In order to identify the usefulness of the grown crystal for nonlinear application in the visible and blue regions, UV-visible absorption study was performed. The UV-visible absorption spectrum was recorded for the grown crystal in the wavelength region 200−800 nm using a Varian Carry-5E UV−Vis Spectrophotometer. The recorded optical absorption spectrum of the sample is shown in Figure 3. From the absorption spectrum, it is observed that the optical absorption in the grown crystal is almost negligible in the UV and visible spectral regions with the lower cut off wavelength at around 300 nm. Minimum amount of optical absorption suggests that the LABH crystal is highly transparent in the UV–visible spectral region and is useful for nonlinear optical applications.Since wide optical window decides the properties of an NLO material, absorption spectrum wastaken for the sample LABH using spectrophotometer in the range 200-1200 nm. In all amino acids, the absorption of light in visible region is absent [9, 10].

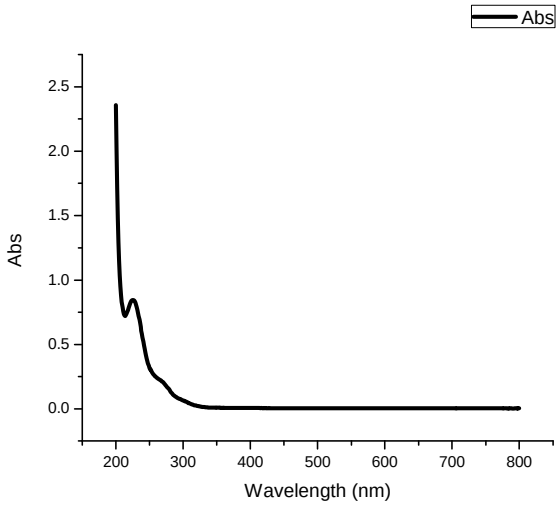

Figure 3. Optical absorption spectrum of LABH crystal

3.4. THERMAL ANALYSIS

The thermo gravimetric analysis of grown LABH crystal was performed in the temperature range of 20–1500^{o}C, using STA409C instrument, under nitrogen atmosphere and a heating rate 10^{o}C/min was maintained. The thermogram of LABH crystal is shown in Figure 4. It is observed from the thermogram that there are three stages of weight loss. The first weight loss is a sharp one starting at about 125^{o}C, which indicates the beginning of the decomposition with the evaporation of water moelcules. This is followed by a major weight loss (stage II) occurring between 230^{o}C and 300^{o}C. The weight loss at 230^{o}C is about 24.93% and hence the melting point of the grown sample LABH is 230˚C which is nothing but the decomposition temperature. The intense sharp weight loss (stage III) above 300^{o}C is assigned to the decomposition of remaining sample.

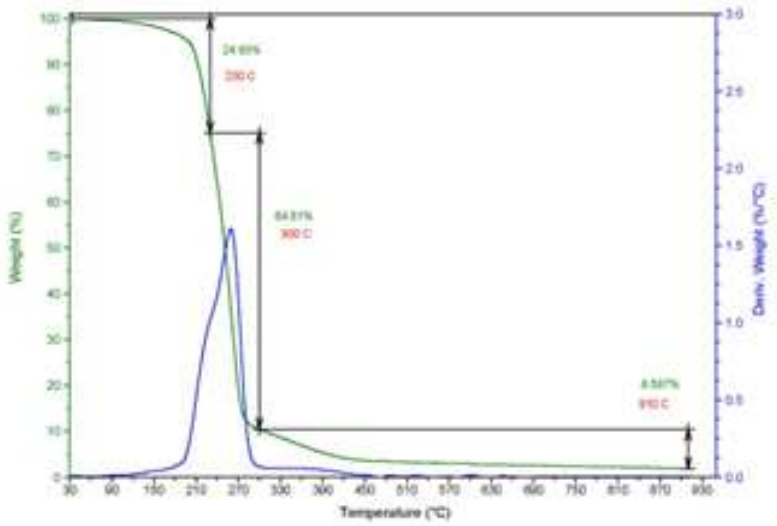

Figure 4. TG curve of LABH crystal

3.5. MICROHARDNESS MEASUREMENT

Hardness is a vital solid state property and plays a energetic role in fabricating optical devices and henceforth Vickers'smicro hardness measurement was carried out for L-Arginine Benzohydrazide (LABH) crystals to judge its mechanical strength. To evaluate the Vicker's hardness number, polished smooth surface of the grown crystals of L-Arginine Benzohydrazide were subjected to static indentation test at room temperature using Shimadzu HMV2 hardness tester fitted with Vicker's diamond pyramidal indenter with different loads like 25gms, 50gms, 100gms and 200gms. The Vicker's hardness number was calculated using the expression Hv = 1.8544 (P/ d^2). Where Hv is the Vicker's hardness number for a given load, P in gram and 'd' is the average diagonal length of the indentation in mm. The variation of vicker's hardness number against applied load is shown in Figure 5. This method is used in finding the resistance of the material against plastic deformation. It is found that for lesser loads, the hardness number is low and increases with increase in load. This can be attributed to the electrostatic attraction between the zwitterions present in the molecule. The relation between load (P) and diagonal length of indentation (d) is given by Mayer's law [11] which is represented as $P = a\ d^n$. Where a and n are constant for a particular material. The variation of log P with log d is shown in figure 6. The slope of the straight line gives the Mayer's index number or work hardening coeffiecient (n). The value of "n" for the grown crystal LABH is 3.19 which is greater than 1.6. According to Onitsch if n > 1.6 then they are soft materials [12]. Thus, it can be concluded that the grown crystal is a soft material.

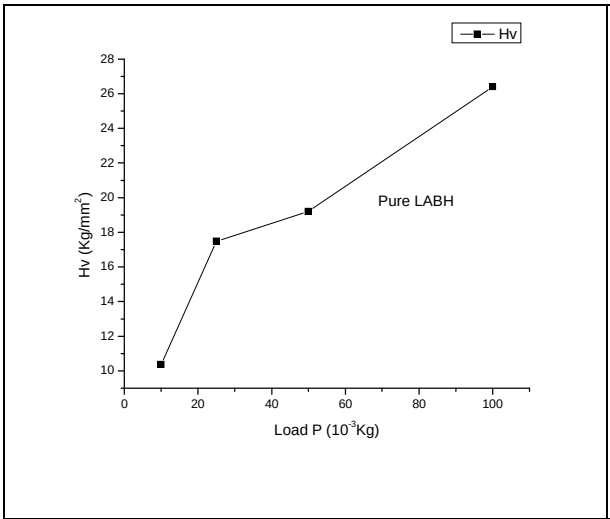

Figure 5. Plot of Hv vs P of LABH crystal

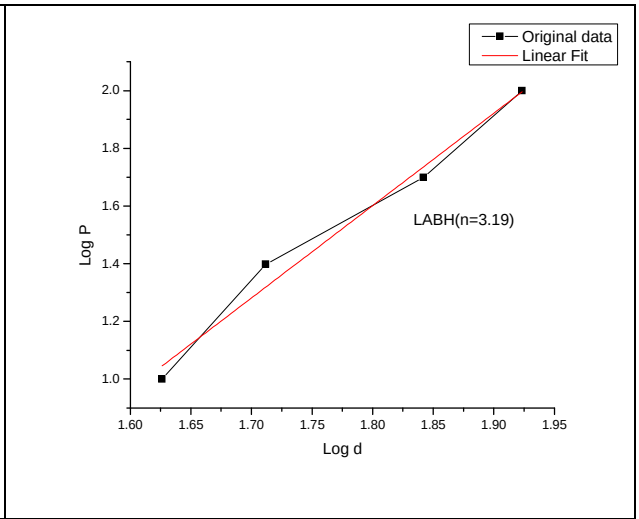

Figure 6. Plot of log P vs log d of LABH crystal

3.6. NLO STUDY

The Kurtz powder technique is the commonly used technique to confirm NLO property of the grown crystal [13, 14]. The powdered sample of LABH was illuminated by a laser of wavelength 1064nm. The emitted green radiation by the sample LABH shows the confirmation of second harmonic generation. The output is compared with KDP and it was found that the crystal LABH is 1.858 times KDP. Hence LABH is a confirmed NLO material.

CONCLUSION

A non linear optical single crystal L-Arginine Benzohydrazide (LABH) is grown by slow solvent evaporation method. Single crystal XRD method reveals the crystalline nature of the grown crystal and it is found that the grown crystal has orthorhombic crystal system. FTIR analysis confirms the presence of various functional groups present in the grown crystal. The lower cutoff frequency of 300nm is revealed by UV-VIS spectrum. Thermal analysis reveals the melting point of the grown sample LABH is 230˚C. Micro hardness measurement reveals the soft nature of the crystal and shows reverse ISE. SHG efficiency of the grown crystal is confirmed by Kurtz and Perry technique and is found to be nearly twice that of KDP.

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