GROWTH AND CHARACTERIZATION OF L-HISTIDINE BARIUM ACETATE NONLINEAR OPTICAL SINGLE CRYSTALS

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Abstract: *A variety of elementary analysis technique (XRD, FTIR, Raman, UV-Vis-NIR, PL, SHG, TG and DSC) are employed to characterize the structure, functional groups, optical, NLO and thermal properties. The single crystal XRD shows that the LHBA single crystallizes in orthorhombic system, with the space group of $P2_12_12_1$. The FTIR and Raman spectrum confirmed the presence of functional groups of the grown LHBA crystal. The UV-Vis spectrum shows that LHBA have very low absorbance in the entire visible region. The cutoff wavelength is at 205 nm and the NLO property is confirmed by SHG measurement. Fluorescence spectral studies were carried in the range of 100-800 nm for the grown crystal. Thermal strength of the grown crystal has been studied using thermo-gravimetric (TG) and differential scanning Calorimetric (DSC).*

Key Words: *NLO, solution growth, thermo-gravimetric (TG), UV-Vis-NIR, PL, SHG, DSC and FT-Raman.*

1. INDRODUCTION:

Over the past decade there has been a growing interest in the design and synthesis of new organic molecules with large molecular hyperpolarizability. Recent developments in the field of nonlinear optics (NLO) have pushed organic second order nonlinear optical material into practical applications such as high-speed information processing, optical communication and optical data storage. Among organic crystals, α - amino acids exhibit favourable features of molecular chirality and also possess wide transparency in the whole visible spectrum. L-histidine tetrafluoroborate, L-threonine, L-alanine are few such compounds reported earlier. L-histidine has been actively studied because of its ability of imidazole moiety to act as a proton donor and acceptor [1]. Acetate complexes of α–amino acids are reported for its potential second harmonic generation. Though, a work on the crystal structure of L-histidine acetate has only been reported earlier , to the best of the knowledge of the authors, there are no earlier reports on the bulk growth of L-histidine Barium acetate. In the present work, bulk and optical quality crystals were grown and its spectral, linear and nonlinear optical properties were investigated [2].

2. EXPERIMENTAL:

2.1. SYNTHESIS AND CRYSTAL GROWTH

The L – Histidine doped Barium Acetate materials were taken in equimolar ratio. In adduct is formed according to the following reaction.

$$C_6H_9N_3O_2 + \quad C_4H_6BaO_4 \rightarrow C_6H_9N_2O_2.C_4H_6BaO_4$$

The double distilled water and stirred at room temperature for 5 hrs to achieve the homogenous condition. The L-Histidine doped Barium Acetate material was synthesized by slow evaporation method tiny crystals also grown. The L-HBA material was purified by repeated recrystallization. After purification the solution was prepared for super saturation condition and filtered with whatmann filter paper. The crystal clear solution carefully transferred to 50 ml beaker and closed with pinholes plastic sheet for natural evaporation. After 4 weeks, optically clear crystal was harvested with good dimension 15mm x 5mm x 3mm. Good dimension crystals are very essential for device fabrications and optical applications. The grown crystal is shown in Fig. 1.

Fig. 1 Growth L-Histidine Barium Acetate crystal

3. RESULTS AND DISCUSSIONS:

3.1. Powder X-ray Diffraction

Powder X-ray diffraction study was performed for the powder form of good quality grown single crystal. The purified samples of grown LHBA crystals are crushed to a uniform powder and subjected to a powder X-ray diffraction using a Bruker D8 Advance powder X-ray diffractometer [3]. The Kα radiations (λ=1.5406 Å) from a copper target are used for the diffraction studies. The powdered sample is scanned in the range 10–90° at a scan rate of 2° /min. The well-defined sharp peaks reveal the good crystalline nature of LAAB crystals. The XRD pattern of the grown LHBA crystals is shown in Fig 2.

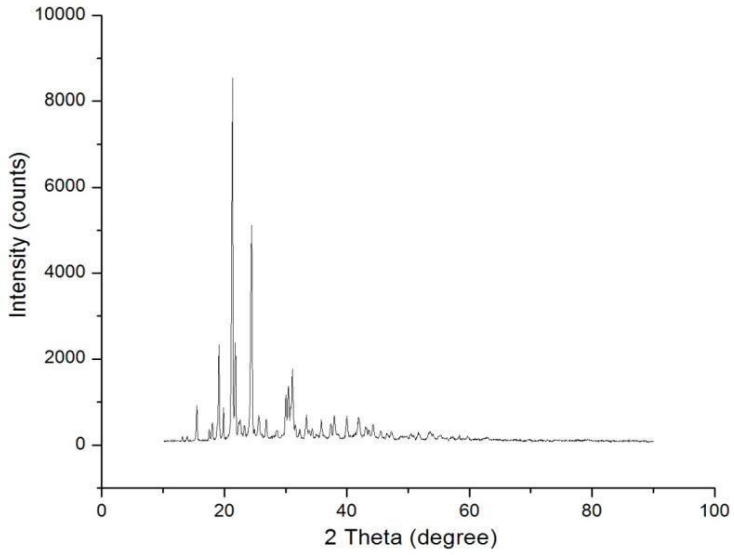


Fig.2 X-ray pattern of LHBA crystal

3.2. Single Crystal X-ray diffraction

The tiny crystal of L-Histidine Barium Acetate was subjected to single crystal X-ray diffraction analysis. Using the Bruker instrument the cell parameter and space group were found. The cell parameters of L-Histidine Barium Acetate crystal are a =20.79 Å, b = 6.19Å, c =4.83 Å, V = 621.57 $Å^3$; $\alpha = \beta = \gamma = 90^\circ$ and orthorhombic system with Space group of $P2_12_12_1$.The crystallographic data has good agreement with the reported values [4] .

3.3. Fourier Transform Infrared Spectroscopy

In the high energy region the peak at 3074 cm^{-1}, 2970 cm^{-1} could be attributed to the C-H stretching vibration. The peak at 2708 cm^{-1} is assigned to O-H stretching vibration. The peak at 1739 cm^{-1} is assigned to C=O stretching vibration. It is clearly seen that the existence of carboxylic acids (COOH) function groups [5]. The fact that some of the COOH groups are ionized implicates an appearance of the NH_3^+ group in Histidine molecule. The strong band 1631 cm^{-1} in the infrared spectrum is attributed to N–H bending vibration of NH_3^+ group. The peak at 1409 cm^{-1} is assigned to C–C stretching (in–ring) [6].

The peak at 1340 cm^{-1} is assigned to N–O symmetric stretch. The C-H Wagging vibration is assigned for the peak at 1247 cm^{-1} it's indicates the alkyl halide. Alkyl halide a compound with the type of formula RX, where R is an alkyl group and X is a halogen (X=F, Cl, Br, Ba &I). Ba is substituted group. The peak at 921 cm^{-1} is representing the O–H bending vibration. The peaks at 536 $cm^{-1}$and 623 cm^{-1} are assigned to C–Ba stretch; this stretching vibration also indicated alkyl halide. The FTIR spectrum shows in Fig.3

The observed peaks in the spectrum are assigned to their corresponding bonds and functional groups and tabulated in Table.1.

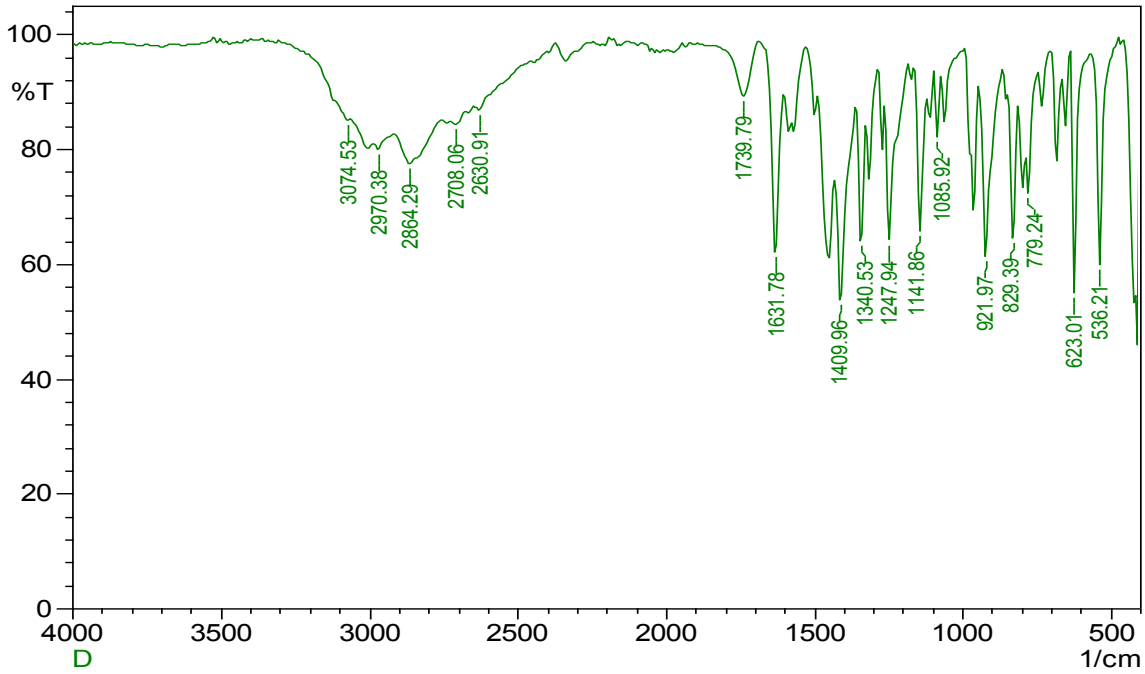


Fig.3 FTIR spectrum of LHBA crystal

Wavenumber (cm^{-1})	Assignments (Bond)
3074,2970	C–H stretching
2708	O–H stretching
1739	C=O stretching
1631	N–H bending
1409	C–C stretching (in–ring)
1340	N–O symmetric stretching
1247	C–H wagging (–CH_2X)
921	O–H bending
536, 623	C–Ba stretching

Table.1. Vibrational band assignments of LHBA crystal

3.4. FT - Raman Spectral analysis

The FT-Raman spectroscopes are effectively used to determine the molecular structure and the identification of the functional groups in the synthesized compound. The FT-Raman spectra of the grown crystal were recorded in the range 0 – 4000 cm^{-1}, using BRUKER: RFS 27 FT-Raman spectrometer and shown in figure.4.

In the FT-Raman spectra peaks around 3128 cm^{-1} is assigned to O-H stretching vibration. A sharp peak at 2968 cm^{-1} and 2894 cm^{-1} is assigned to C-H symmetric stretching vibration. In 1568 cm^{-1} its observed peak is assigned to N–O Asymmetric vibration, its indicate nitro compounds. The peak at 1406 cm^{-1} is assigned to C–H waging (–CH_2X) it indicates alkyl halides [7]. The peak at 1345 cm^{-1} is assigned to N–O symmetric stretching vibration. The peak at 1086 cm^{-1} is representing the C–O stretching vibration, and 973 cm^{-1} is representing the O–H stretching vibration then, these two stretching vibration its indicates carboxylic acids functional group present in the substance. The peaks at 653, cm^{-1}, 625 cm^{-1}, and 538 cm^{-1} are assigned to C–Ba stretch; this stretching vibration also indicated alkyl halide [8]. The strong and sharp peaks 168 cm^{-1},132 cm^{-1} and 103 cm^{-1} are assigned to Lattice vibrations in crystals.

The observed peaks in the spectrum of FT-IR and FT-Raman are assigned to their corresponding bonds and functional groups and tabulated in Table 2.

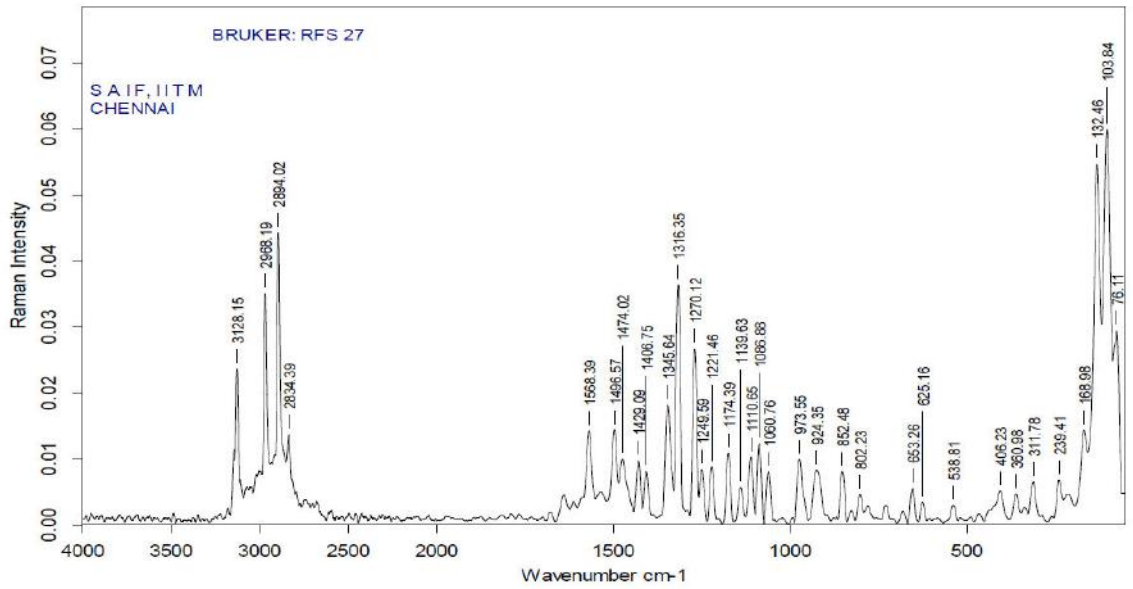


Fig.4. Raman spectrum of LHBA crystal

Wavenumber (cm^{-1})		Assignment (bond)	Functional group
FT-IR	**FT-Raman**		
–	3128	O–H stretching	carboxylic acids
3074,2970	2968, 2894	C–H stretching	aromatics
2708	–	O–H stretching	carboxylic acids
1739	–	C=O stretching	carboxylic acids
1631	–	N–H bending of NH_3^+ group.	amines
–	1568	N–O Asymmetric stretching	nitro compounds
1409	–	C–C stretching (in–ring)	aromatics
–	1496,1406	C–H waging (–CH_2X)	alkyl halides
1340	1345	N–O symmetric stretching	nitro compounds
1247	–	C–H wagging (–CH_2X)	alkyl halides
–	1086	C–O stretching	carboxylic acids
921	973	O–H stretching	carboxylic acids
623, 536	653, 625, 538	C–Ba stretching (RX)	alkyl halides
–	168, 132, 103	Lattice vibrations in crystals	–

Table.2. FT-IR and FT-Raman spectral assignments of LHSB

3.5. UV-Visible Spectral Studies of L-H Barium Acetate crystal

The grown crystal of LHBA was subjected to UV- absorption and transmittance spectra. The peak was absorbed in the range of 200 - 800 nm and shown in Fig.5. The grown crystal has highly transparent above the 205 nm also it is potential candidate for the optical applications [9].

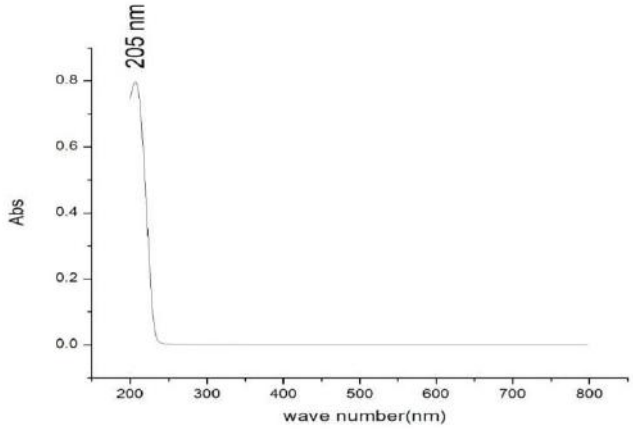


Fig.5. UV-VIS-NIR Spectrum of LHBA Crystals

3.6 Band Gap Energy

The energy band gap for a grown crystal was calculated using the Tauc equation

$$(\alpha h\nu) = A\,(h\nu - Eg)^{n.}$$

Where α is the absorption coefficient, h is the Plank's constant and ν is the frequency of incident photon, A is a constant. A plot of $(\alpha h\nu)^2$ Vs hν is shown in Fig.6 from the intercept of straight line on the energy axis, the band gap was found to be 5.4 eV. Large value of band gap indicates that the material is a good insulator and can provide large transmission invisible

Region [10].

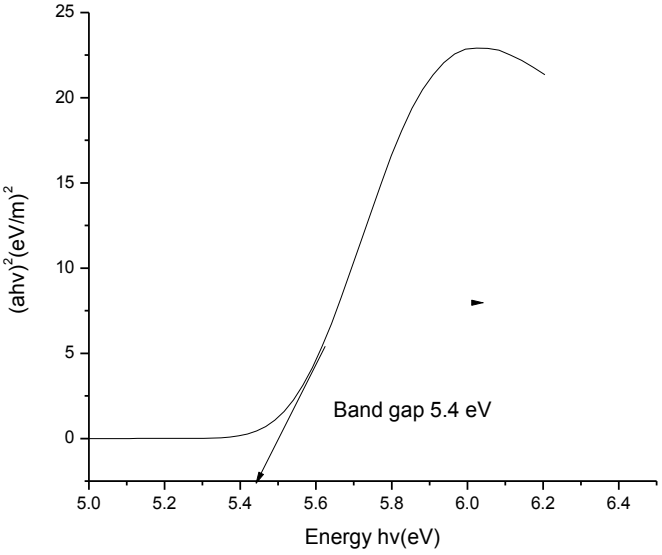


Fig.6. Band gap of LHBA crystals.

3.7. Photoluminescence Studies

The photoluminescence light from sample was measured at different wavelength and the emission was recorded for L-Histidine doped Barium Acetate crystal in the range of 200–800 nm with the excitation wavelength of 200 nm. The recorded spectrum of the sample is shown in the figure 7. The results show three emissions band a medium UV emission band at 208 nm, a strong blue band at 412 nm, and a red band at 619 nm [11]. From the results, it is confirmed that the grown. L-Histidine doped Barium Acetate crystal emits UV light, blue and red fluorescence light when they are excited with UV light of wavelength at 208 nm [12].

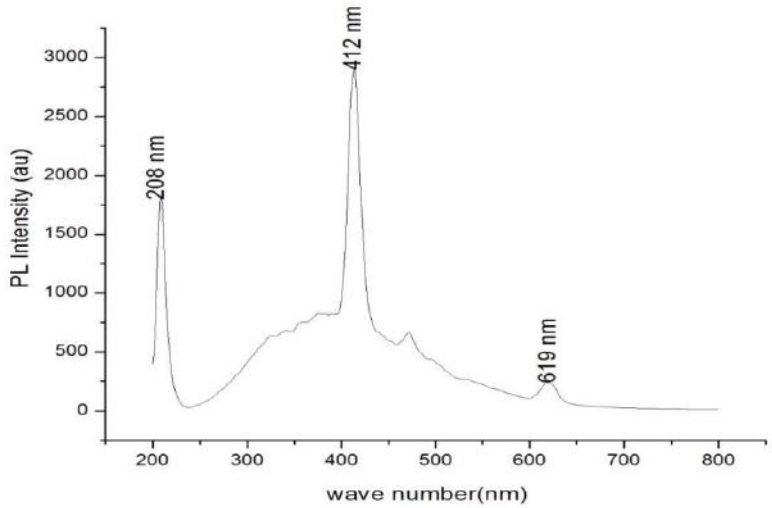


Fig.7. PL Emission of LHBA crystal

3.8. Thermo Gravimetric Analysis

The TGA trace shows, there is no weight loss below 270 ºC, hence the crystal is completely devoid of any entrapped solvent in the lattice of the crystal. The major weight loss occurs at three stages. First stage weight loss of about 15.84% (0.6115 mg) observed between 270 ºC to 284 ºC is due to the decomposition of L-Histidine. Second stage weight loss of about 22.35% (0.8627 mg) observed between 289.19 ºC to 390.5 ºC this is due to step by step decomposition and release of volatile substances in the Compound, probably ammonia and carbon dioxide [13]. The third stage gradual weight loss of about 20.52% (0.7922 mg) observed for wider range of temperature between 390.5 ºC to 800 ºC is due to the melting of Barium (714 ºC) . These three different stages weight loss indicates the decomposition of the substance. The final residue weight left was 41.30% (1.594 mg) after heating 800 ºC for LHBA crystal.

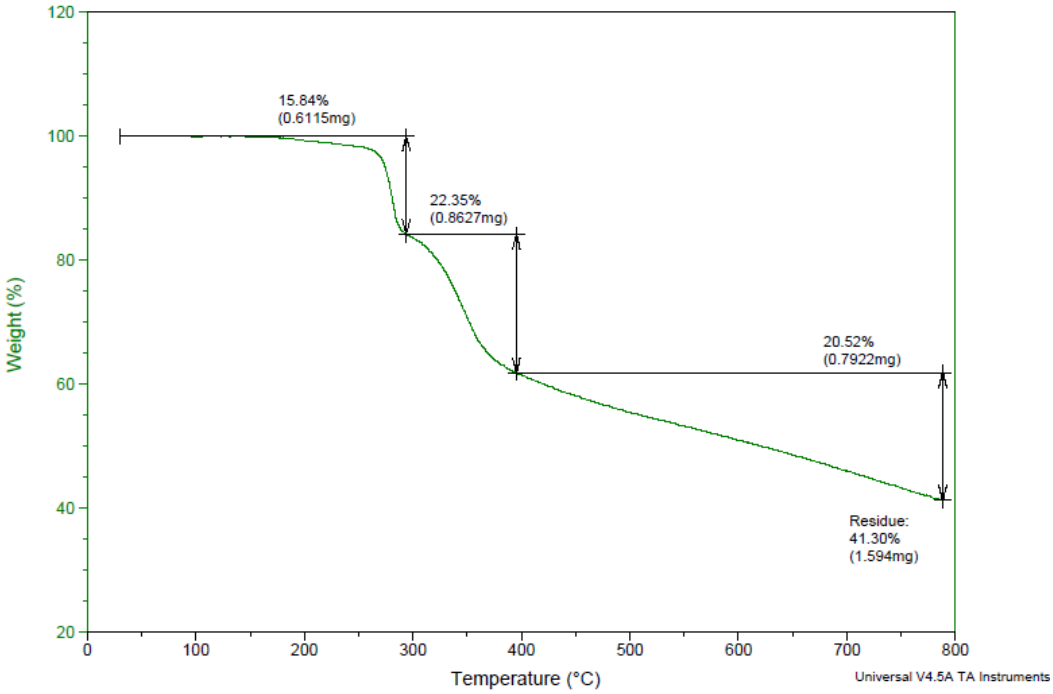
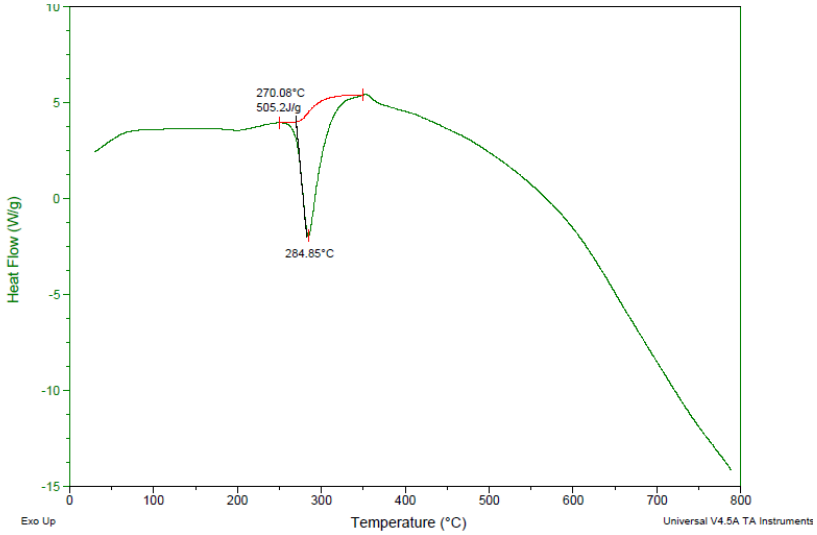


Fig. 8 TGA curve for LHBA crystals.

The DSC analysis of the grown crystal was carried out between 28 °C and 800 °C. There is a sharp endothermic peak starting at 270.08 °C which corresponds to the decomposition as observed in TGA analysis. Again it also confirms absence of melting and any entrapped solvent in the lattice [14]. DSC curve shows the sharp endothermic peak indicates the crystal has good crystallinity and decomposition point of as grown LHSB crystal is 284.85 ºC.



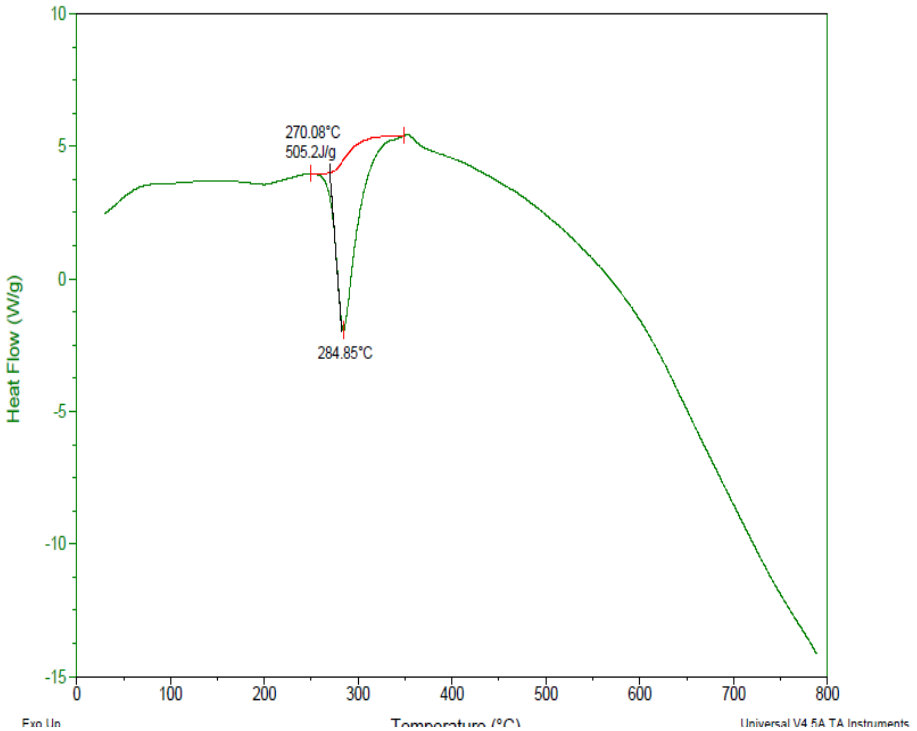


Fig.9. DSC curve for LHBA crystals

3.9. Second harmonic generation study

The relative second harmonic generation (SHG) efficiency was determined by modified Kurtz powder technique. It is an important and well accepted tool to evaluate the conversion efficiency of a nonlinear optical material. A Q-switched Nd:YAG laser operating at the fundamental wavelength of 1064 nm, generating about 11.4 mJ and pulse of width 8 ns with a repetition rate of 10Hz was used for the present experimentl study [15]. The input laser beam was passed through an IR reflector and then incident on the powdered form of the LHBA specimen, which was packed in a glass capillary tube. The output energy was detected by a photodiode detector integrated with oscilloscope assembly. Second harmonic signal was confirmed when the laser beam was passed through LHBA specimen. From this measurement the second harmonic signal of 0.0214 J were obtained from LHBA resepectively. It is observed that the SHG efficiency of the grown LHBA single crystal is 3 time that of the standard KDP crystal.

CONCLUSION:

The good optical quality single crystal of L-H Barium Acetate has been grown by slow evaporation solution growth technique (SESGT). The sharp and well defined Bragg's peaks of powder XRD pattern at specified 2θ angles shows the crystalline nature and purity of the crystal. The lattice parameters of L-Histidine Barium Acetate (LHBA) are determined by single crystal XRD. It belongs to orthorhombic crystal system with space group $P2_12_12_1$. The presence of functional groups was confirms by FTIR and FT- Raman analysis. The optical absorption studies confirmed that the LHBA crystal has good optical transmission in the complete UV region in the electromagnetic spectrum. The photo luminescence studies show the excitation of L-H Barium Acetate falls in blue and red fluorescence spectrum. The TGA measurement reveals that the crystal is thermally stable upto 284°C and there is no structural phase transition in low temperature region.

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