Growth and Characterization of L-Histidinium Ammonium Acetate Nonlinear Optical Single Crystal

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A semi organic L-histidinium ammonium acetate (L-HAA) single crystal has been grown by slow evaporation technique. Single crystal X-ray diffraction studies confirm the monoclinic crystal system. Vibrational spectroscopic studies confirm the various functional groups present in the crystal. The ultraviolet-visible spectrum analysis has been carried out and the optical band energy gap for a grown crystal is calculated to be 5.5 eV which indicates that the material is a good insulator and provides large transmission in visible region. Thermogravimetric-differential thermal analysis reveals that the material is thermally stable up to 273.02 °C. The second harmonic generation efficiency of L-HAA crystal is found to be 0.68 times lesser than that of KDP.

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1. Introduction

Nowadays nonlinear optical materials are having potential applications in the area of telecommunications and optical storage devices. Especially those materials, which can generate highly efficient second harmonic blue violet light by using laser diodes, are of great interest for wide variety of applications such as high-density data storage, under water communication, and medical diagnostics [1, 2]. Amino acids and their complexes belong to a family of organic materials that have enormous applications in the field of nonlinear optics (NLO). Amino acids are interesting materials for NLO applications as they contain a proton donor carboxyl acid COO- group and the proton acceptor amino NH^{3+} group. Amino acids such as L-histidine, L-alanine, and L-arginine, have shown promising results as efficient second harmonic generators and are being applied in devices such as optical parametric amplifiers.

In the present study, we have synthesized the L-HAA by conventional chemical reaction and then the single crystal has been grown by slow evaporation solution growth technique. The grown single crystal has been analyzed by different characterization studies like X-ray diffraction, vibrational, optical, thermal, and second harmonic generation.

2. Experimental procedure

2.1. Synthesis and crystal growth

The calculated amounts of the analytical reagent (AR) grade starting materials of L-HAA were taken in equal molar ratio and dissolved in double distilled water. The mixture was thoroughly stirred for about 5 h using a magnetic stirrer to ensure homogeneous concentration throughout the volume of the solution. The chemical reaction is given below

 $C_6H_7NO_2+C_2H_7NO_2 \rightarrow NH_4^++[C_6H_7NO_2]CH_3COO^-$

The saturated solution was filtered using the Whatmann filter paper. The filtered solution was taken in a beaker and covered with good quality perforated polythene cover to restrict the fast evaporation. Then the solution was kept at room temperature in a dust free compartment for slow evaporation. After the period of 28 days, colorless and optically transparent crystals of L-HAA with dimension $13 \times 8 \times 3$ mm³ were obtained. The grown crystal is shown in Fig. 1.



Fig. 1. Photograph of as grown LHAA crystal.

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3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

The grown crystal of L-HAA were subjected to single crystal X-ray diffraction studies using an ENRAF NONIUS CAD4-Fdiffractometer with Mo K_{α} radiation $(\lambda = 0.71073 \text{ Å})$ to determine the crystal structure. Single crystal X-ray diffraction analysis reveals that the crystal belongs to monoclinic system with space group of $P2_12_12_1$. The cell parameters of LHAA are calculated to be a = 5.22 Å, b = 7.47 Å, c = 9.55 Å, $\alpha = 90^{\circ}$, $\beta = 98.18^{\circ}$, $\gamma = 90^{\circ}$, and $V = 368 \text{ Å}^3$.

3.2. Powder X-ray diffraction analysis

Powder X-ray diffraction analysis of grown crystal has been carried out by using Bruker D8-Advance powder X-ray diffractometer with Cu K_{α} ($\lambda = 1.5418$ Å) line radiation, in the range of scanning angle from 10° to 80° of 2 theta. The recorded powder X-ray diffraction pattern is shown in Fig. 2. The prominent peaks in the powder X-ray diffraction confirm the crystalline nature of the grown crystal.



Fig. 2. Powder X-ray diffraction pattern of the LHAA.

3.3. FT-IR spectral analysis

The Fourier transform infrared (FT-IR) spectroscopy study is effectively used to identify the functional groups presents in the crystal. The FT-IR spectral analysis for the grown crystal has been recorded by using Perkin Elmer Spectrum one FT-IR spectrometer in the region $4000-400 \text{ cm}^{-1}$ using KBr pellet technique with a resolution of 4 cm⁻¹. The band intensities are expressed in transmittance (%). Figure 3 depicts the FT-IR spectrum of grown crystal. The peak at 3003 cm⁻¹ could be attributed to the CH stretching vibration. The peak at 2858 cm^{-1} is assigned to CH₂ stretching vibration. The peak at 2708 cm^{-1} is assigned to O–H stretching vibration. It is clearly seen that the existence of carboxylic acids (COOH) functional groups. The fact that some of the COOH groups are ionized implicates an appearance of the NH_3^+ group in histidine molecule. The strong band at 1629 cm⁻¹ in the infrared spectrum is attributed to N–H bending vibration of NH_3^+ group. The peak at 1411 cm⁻¹ is assigned to C–N stretching (in-ring). The strong band at 1568 cm⁻¹ in the infrared spectrum is attributed to asymmetric NH_3^+ group vibration. This peak is observed at 1577 cm⁻¹ in histidine [3]. The peak at 1411 cm⁻¹ is assigned to C–C stretching (in-ring). The peak at 1340 cm⁻¹ is assigned to CH₂ scissoring vibration. The C–H wagging vibration is assigned for the peak at 1247 cm⁻¹ which indicates the alkyl halide stretching vibration [4, 5].



Fig. 3. FT-IR spectrum of LHAA crystal.

3.4. FT-Raman spectral analysis

The FT-Raman spectroscopic analysis is 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 50–4000 cm⁻¹, using Bruker: RFS 27 FT-Raman spectrometer and shown in Fig. 4.



Fig. 4. Raman spectrum of LHAA crystal.

| Wave number $[cm^{-1}]$ | | Assignment description |
|-------------------------|-------------------------|--|
| $FT-IR [cm^{-1}]$ | FT -Raman $[cm^{-1}]$ | Assignment description |
| - | 3077 | O–H stretching |
| 3003, 2858 | 2999, 2930, 2888 | C–H stretching |
| 2708 | _ | O–H stretching |
| 1629 | _ | N–H bending of NH_3^+ group. |
| 1568 | 1595 | NH ₃ asymmetric stretching |
| 1450 | 1460 | C–N stretching mixed with C–C stretching |
| 1411 | 1409 | C–N stretching (in-ring) |
| _ | 1499, 1409 | C–H wagging $(-CH_2X)$ |
| 1340 | 1357 | CH_2 scissoring vibration |
| 1247 | 1237 | C–H wagging $(-CH_2X)$ |
| 1141 | 1144 | CH ₂ twist modes with mixing of CH and NH bending |
| — | 1111 | CH ₃ rocking |
| 962 | | $ m NH_3 \ rocking + CH \ bending$ |
| 921 | 918 | $ m C-N \ stretching + \ NH \ bending + \ C-C \ stretching$ |
| 621 | 649 | COO^- deformation |
| 536 | 529 | Ring deformation $+$ CN bending |
| — | 188,135,109 | Lattice vibrations in crystals |

Vibration band assignment of LHAA

In the FT-Raman spectra, peaks around 3077 cm^{-1} are assigned to O–H stretching vibration. Sharp peaks at 2999 cm^{-1} , 2930 cm^{-1} , and 2888 cm^{-1} are assigned to C-H symmetric stretching vibration. The peak observed at 1595 $\rm cm^{-1}$ is assigned to NH₃ asymmetric vibration. The peak at 1409 cm^{-1} is assigned to C–H wagging $(-CH_2X)$ which indicates alkyl halides. The peak at 1357 cm^{-1} is assigned to CH₂ scissoring vibration. The peak at 1111 $\rm cm^{-1}$ is attributed to $\rm CH_3$ rocking vibration, and the peak at 918 cm^{-1} is attributed to mixed vibration of C-N stretching and NH bending. These two stretching vibration indicates carboxylic acids functional group present in the substance. The strong and sharp peaks at 188 cm⁻¹, 135 cm⁻¹, and 109 cm⁻¹ are assigned to lattice vibrations in crystals [4, 5]. The other observed peaks in the spectrum of FT-IR and the FT-Raman are assigned to their corresponding bands and functional groups and are tabulated in Table I.

3.5. Ultraviolet-visible spectroscopic studies

The ultraviolet-visible spectrum analysis of the grown crystal was carried out in the wavelength range of 200–800 nm. The recorded absorption spectrum is shown in Fig. 5. The cut-off wavelength of LHAA crystal has been identified as 208 nm. It is observed that the wide range of optical transmission window occurs from 208 to 800 nm. There is no considerable absorption of light in the visible range of an electromagnetic spectrum which is an internal property of amino acids. Hence they can be used for fabrication of optical region. The optical band energy gap for a grown crystal was calculated using the Tauc equation $\alpha h\nu = A(h\nu - E_g)^n$ where α is the absorption coefficient, h is the Planck constant, ν is the frequency of incident photons, and A is a constant. The linear portion of the plot of $(\alpha h\nu)^2$ versus $h\nu$, when



TABLE I

Fig. 5. UV-visible spectrum of LHAA crystal.



Fig. 6. Band gap of LHAA crystal.

extrapolated to the energy axis, gives the band energy gap. A plot of $(\alpha h\nu)^2$ versus $h\nu$ is shown in Fig. 6. From the intercept of straight line on the energy axis, the band gap was found to be 5.5 eV. Large value of band gap indicates that the material is a good insulator and can provide large transmission in visible region [6–11].

3.6. Thermal analysis

In order to study the thermal stability of the grown crystal, thermogravimetric analysis (TGA) have been carried out using a SDT Q600 V20.9 Build 20 model thermal analyser in an inert nitrogen atmosphere. Powdered sample of about 3.6810 mg was used for the analysis in the temperature range of 28–800 °C with a heating rate of 20 °C/min. The TGA and differential scanning calorimetry (DSC) pattern recorded for the grown crystal LHAA as shown in Figs. 7 and 8, respectively. The TGA trace shows that there is no weight loss below 286.6 °C, 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 of weight loss of about 15.94%(0.4831 mg) is observed between $255.5 \,^{\circ}\text{C}$ and $286.6 \,^{\circ}\text{C}$ which is due to the decomposition of L-histidine. Second stage of weight loss of about 25.12% (0.767 mg), observed between 286.6 °C to 390.5 °C, is due to step by step decomposition and release of volatile substances in the compound, probably ammonia and carbon dioxide. The third stage gradual weight loss of about 20.12% (0.646 mg) observed for wider range of temperature between $390.5\,^{\circ}\text{C}$ to 800 °C is due to the decomposition of ammonium acetate. These three different stages of weight loss indicate the decomposition of the substance. The final residue weight left was 38.94% (1.189 mg) was found after heating to 800 °C. The DSC analysis of the grown crystal was carried out between 28 °C and 800 °C. There is a sharp endothermic peak starting from 273.02 °C to 291.38 °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. DSC curve shows the sharp endothermic peak that indicates that the crystal has good crystallinity and decomposition point of as grown LHAA crystal is 291.38 °C. The TGA-DSC result shows that the grown crystal is thermally stable up to 273.02 °C and establishes its suitability to withstand the high temperature for laser experiment carried out between $28 \,^{\circ}\text{C}$ and $800 \,^{\circ}\text{C}$ [9–13].

3.7. Second harmonic generation studies

In order to confirm the nonlinear optical property, powdered sample of LHAA was subjected to a Kurtz and Perry powder techniques, which remains as a powerful tool for initial screening of materials for SHG. A Q switched high energy Nd:YAG laser (QUANTA RAY Model LAB — 170-10) operating at the fundamental wavelength of 1064 nm with pulse width 8 ns and repetition rate of 10 Hz and input energy as 0.701 J was used. The NLO property of the sample was confirmed by the emission of bright green light with 2.903 mJ/pulse as



Fig. 7. TGA curves of LHAA crystal.



Fig. 8. DSC curves of LHAA crystal.

output with wavelength of 532 nm. The KDP sample was used as the reference material which gives a signal 9.0701 mJ/pulse for the same input energy. The efficiency of second harmonic generation of L-histidine ammonium acetate crystal was found to be 0.68 times lesser that of the reference material KDP. Thus LHAA crystal can be used as an effective candidate for nonlinear optical applications [14–18].

4. Conclusion

An organic nonlinear optical crystal of LHAA has been successfully grown from aqueous solution by slow evaporation technique at the room temperature. The crystalline nature of the grown crystal has been confirmed by powder X-ray diffraction. The single crystal X-ray diffraction study shows that the grown crystal belongs to monoclinic system with space group of $P2_12_12_1$. The different functional groups presented in the grown crystal have been identified by the Fourier transform infrared and Raman spectroscopy (FTIR). The UVvisible spectroscopic studies showed that the grown crystal was optically transparent in the entire visible region and the cut-off wavelength has been identified as 208 nm. Hence they can be used for fabrication of optoelectronic devices in visible region. The optical band energy gap (E_g) was found to be 5.5 eV from the Tauc relation. The TGA and DSC shows that the grown crystal is thermally stable up to 273.02 °C and establishes its suitability to withstand the high temperature for laser experiments. The SHG efficiency of the grown crystal was measured by the Kurtz and Perry powder techniques and its efficiency was found to be 0.68 times lesser than that of the reference material KDP. Thus LHAA crystal can be used as an effective candidate for non-linear optical applications.

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