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Research Paper

Crystallization and Characterization of L-Histidinium Succinate Monohydrate (LHS), A Novel Organic NLO Material

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L-histidinium succinate monohydrate (LHS), a novel organic nonlinear optical material has been successfully grown from aqueous solution by slow evaporation method. The crystal structure and unit cell parameters of the grown crystal have been measured by single crystal XRD which shows that the crystal belongs to orthorhombic system with the space group $P2_12_12_1$. The grown crystal was subjected to energy dispersive X-ray analysis (EDAX) for the identification of chemical composition of the material. The optical transmittance of the crystal was examined by UV-visible spectral study and it indicates that the crystal is highly transparent in the wavelength region 235-800 nm. The surface morphology of LHS crystal was studied HR-SEM analysis. The second harmonic generation of the grown crystal was tested by the powder technique of Kurtz and Perry. The thermal stability and purity of the compound was ascertained by DTA technique.

Key Words: Crystal Growth; XRD; EDAX; UV-Visible; HR-SEM; DTA

Introduction

In recent years, synthesis of novel nonlinear optical (NLO) materials has been given much importance due to their significant impact in various fields like waveguides, frequency conversion devices, optical switching, parametric oscillators etc. [1-3]. Organic nonlinear optical materials have been of particular interest since they have large optical susceptibilities, chemical flexibilities and rapid responses in electro-optic effect compared with the inorganic nonlinear materials. Organic NLO crystals find wide applications in laser technology, optical communications, optical data storage technology and optical information processing [4-6]. Among organic materials, amino acids are suitable materials for NLO applications, as they exhibit molecular chirality, absence of strongly conjugated bonds and zwitterionic nature of the molecule [7, 8]. The basic amino acid salt L-histidine can display high NLO property due to the presence of imidazole ring in addition to the amino carboxylate group.

The compounds of amino acid L-histidine with carboxylic acids have been explored much less. In order to grow new salts with better thermal and optical properties, the coordination of L-histidine with succinic acid has been synthesized. The present investigation deals with the growth and characterization of a novel organic nonlinear optical crystal of L-histidinium succinate monohydrate (LHS) grown by slow solvent evaporation method. The structure of the grown crystal was identified by single crystal XRD analysis. The chemical composition of the LHS was confirmed by EDAX analysis. The linear and nonlinear optical property of LHS was analyzed by UV-visible and SHG test. The surface morphology of the crystal was studied by HR-SEM analysis and the thermal behaviour was studied by DTA technique.

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Experimental

Good quality single crystal of L-histidinium succinate monohydrate (LHS) with the chemical formula $C_6H_{10}N_3O_2^+.C_4H_5O_4^-.H_2O$ was grown from aqueous solution by slow evaporation method at 32°C. Equimolar ratio of L-histidine (AR grade) and succinic acid (AR grade) were dissolved in double distilled water to prepare the aqueous solution of L-histidinium succinate monohydrate (LHS). The solution was stirred well for nearly 4 h using a magnetic stirrer to obtain a homogeneous mixture of the solution over the entire volume. To ensure high purity, the substance was purified by successive crystallization process using deionized water. By using synthesized salts, saturated solution was prepared at room temperature. In order to eliminate suspended impurities, the solution was filtered twice using micro-whatmann filter papers. Two drops of H_2O_2 were added to the saturated solution to restrain the growth of any microorganism [9]. The filtered solution was kept in a crystallizing vessel, covered with a perforated sheet and placed in a dust free atmosphere. Crystals obtained by spontaneous nucleation after the evaporation of solvent were used as seed crystals. A good quality single crystal of LHS was obtained in a period of 30 days and is shown in Fig. 1.

Fig. 1: Photograph of LHS crystal

Results and Discussions

Single Crystal XRD Study

The crystal structure and cell parameters of the grown crystal have been identified by single crystal X-ray diffraction analysis using BRUKER AXS kappa apex2 CCD diffractometer with MoKα radiation source of wavelength 0.71073 Å. The crystal structure and lattice parameters of LHS were calculated by least square refinement of 25 reflections in the range 20-30°. The X-ray crystallography data shows that the crystal belongs to orthorhombic system with the space group $P2_12_12_1$. It is well known that $P2_12_12_1$ is a noncentrosymmetric space group and hence satisfying one of the basic requirements for the nonlinear property of the LHS crystal. The observed lattice parameters are a = 8.31 Å, b = 8.82 Å, c = 19.45 Å, V = 1426 $Å^3$, Z = 4 and $\alpha = \beta = \gamma = 90^o$.

EDAX Analysis

Energy dispersive X-ray analysis (EDAX) is a micro-analytical tool, used to find the chemical composition of the grown crystal. In this study, the grown LHS crystal was subjected to EDAX analysis using the instrument FEI QUANTA 200F energy dispersive X-ray micro analyzer. Highly transparent region of the crystal was used for this analysis. A high-energy beam of charged particles such as electrons or protons, or a beam of X-rays, was made to fall onto the LHS sample. The number and energy of the X-rays emitted from the sample was measured by an energy-dispersive spectrometer. The recorded spectrum of LHS crystal is displayed in Fig. 2. The weight percentage (wt %) of C, N and O as obtained from EDAX analysis is compared with the theoretical values and are listed in Table 1.

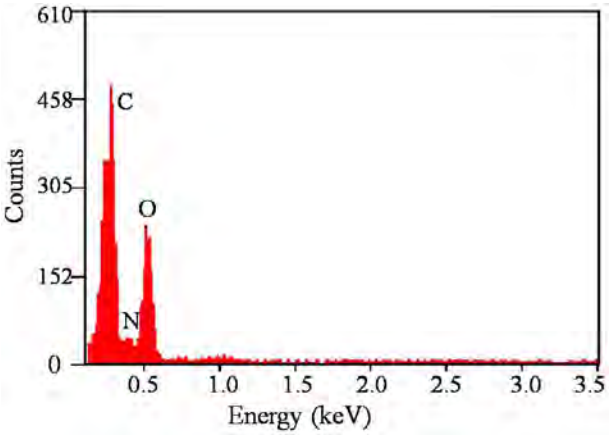

Fig. 2: EDAX spectrum of LHS

Table 1: EDAX quantification

Element	Wt (%) Experimental	Wt (%) Theoretical
Carbon	44.29	43.81
Nitrogen	15.74	15.33
Oxygen	39.97	40.86

Optical Transmittance Study

NLO materials should have good transparency window in the visible and UV regions to make use of them for frequency doubling process. The UV-visible transmittance spectrum was recorded for the LHS crystal in the wavelength region of 200-800 nm using a Varian Carry-5E UV-Vis Spectrophotometer. The optical transmittance spectrum of LHS is shown in Fig. 3. From the recorded spectrum, it is observed

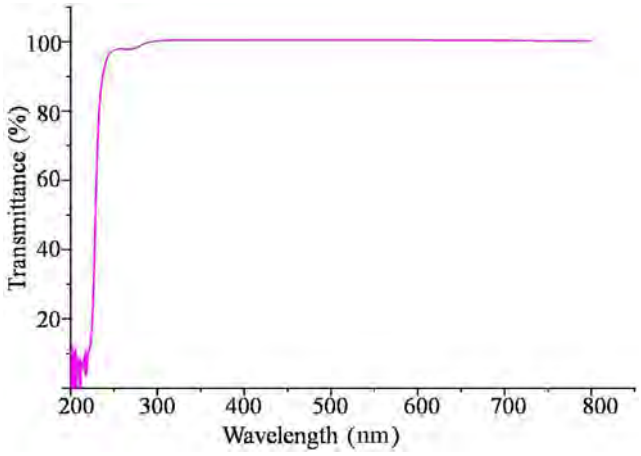

Fig. 3: Optical transmission spectrum of LHS

that the grown crystal is highly transparent in the UV and visible spectral regions with the lower cut off wavelength at 235 nm thereby confirming the advantages of the crystal for NLO applications [10].

Nonlinear Optical Property

A quantitative measurement of the SHG conversion efficiency of LHS crystal was carried out by Kurtz and Perry powder technique [11]. In this technique, the LHS sample was grounded into fine microcrystalline powder and densely packed between two transparent glass slides. A Q-switched Nd:YAG laser operating at 1064 nm, with an input power of 0.68 J and pulse width of 8 ns and 10 Hz pulse rate was allowed to pass through the sample cell. The output beam from the microcrystalline sample was filtered by an IR filter and then identified by a photomultiplier tube. The second harmonic generation of LHS was confirmed by the emission of green radiation (λ = 532 nm) from the sample. The second harmonic generation signal of 5.4 mJ has been obtained from LHS sample. But the standard KDP crystal emitted an SHG signal of 8.9 mJ for the same input energy. Thus, it has been observed that the SHG efficiency of the LHS crystal is 0.61 times that of the standard KDP crystal.

HR-SEM Analysis

The HR- SEM analysis is very useful to inspect the nature and surface morphology of the grown crystal. Highly transparent region of the crystal was used for the surface analysis. The SEM images of LHS crystal taken in two different magnifications are provided in Fig. 4. Fig. 4a shows the existence of evenly arranged closed packed layer on the surface of the crystal. It also shows step-like growth features, which can be assumed to be ridges. From Fig. 4a & b, it is noted that some precipitates are present over the surface. This may be due to temperature oscillations during the growth process and the presence of moisture.

Thermal Study

Differential thermal analysis (DTA) provides useful information regarding the water of crystallization and melting point of the compound [12]. The DTA analysis was carried using the instrument NETSZCH STA 409 C/CD under nitrogen atmosphere. The typical DTA curve of the LHS crystal is shown in Fig. 5. The plot shows a sharp endothermic peak at around 112°C which is ascribed to removal of weakly entrapped water. This is followed by another two consecutive endothermic peaks at around 147°C and 277°C which are ascribed to the partial disintegration and volatilization of the compound. Hence, the melting point of the compound is estimated to be 147°C.

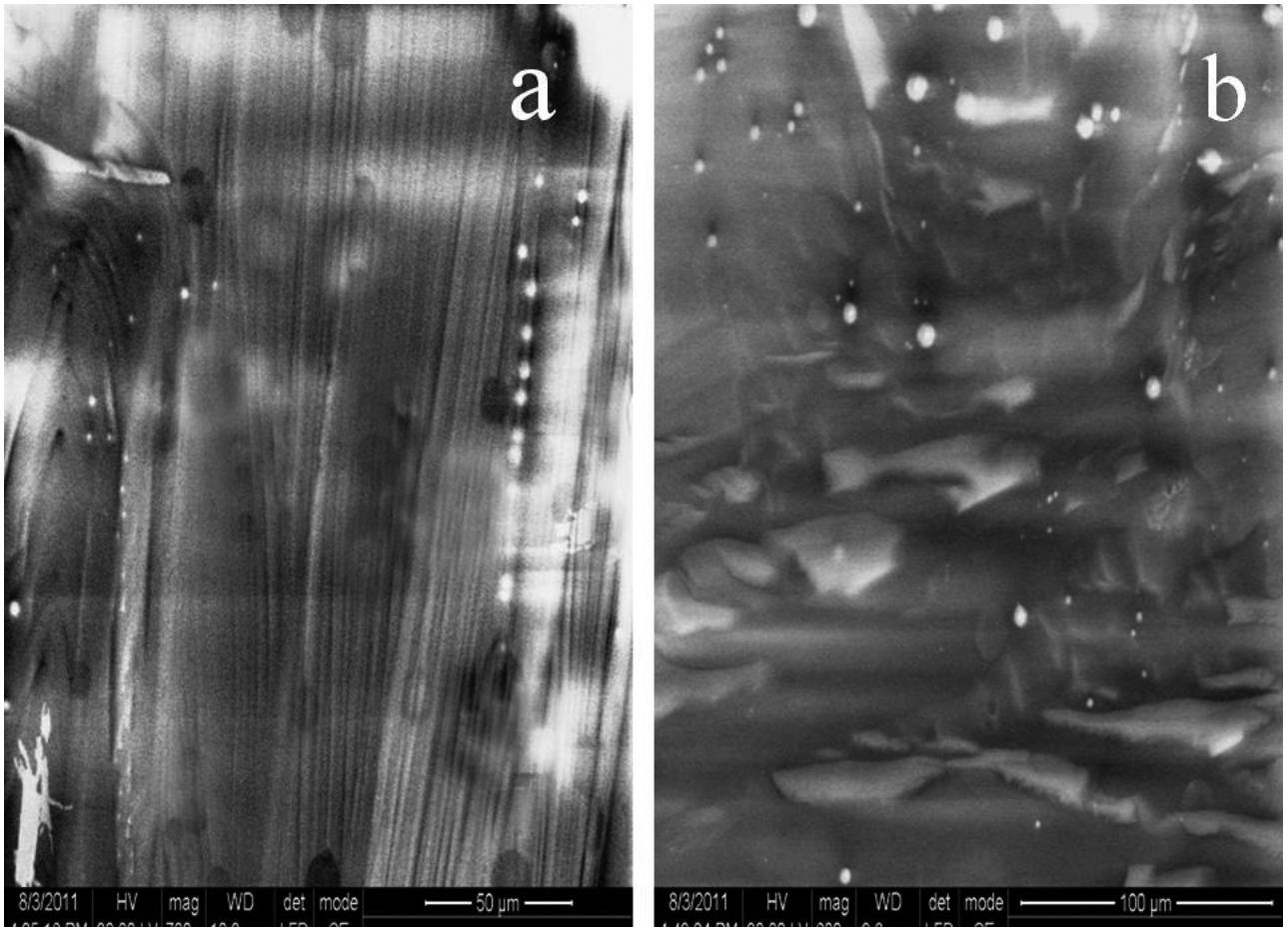

Fig. 4: SEM micrographs of LHS

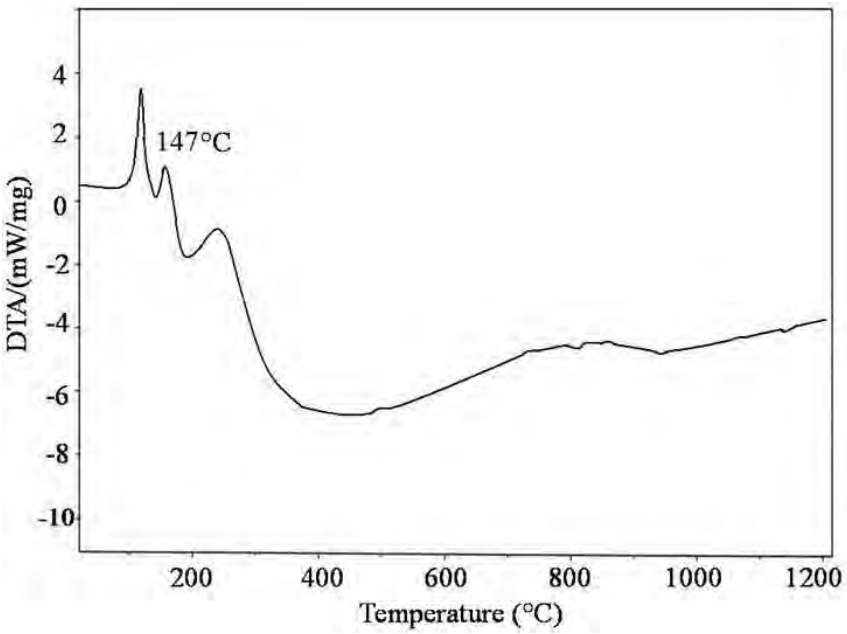

Fig. 5: DTA curve of LHS

Conclusion

Single crystal of L-histidinium succinate monohydrate (LHS) has been grown successfully by slow evaporation solution growth technique at room temperature. The lattice parameters and crystal structure were identified by single crystal XRD study. The chemical composition of the grown crystal was ascertained by EDAX analysis. The optical transmittance study reveals the transparency of the crystal which shows that the percentage of optical transmittance is much higher in the range 235 to 800 nm. The emission of SHG from LHS crystal is confirmed by Kurtz and Perry powder method. The HR-SEM analysis reveals the surface morphology of the LHS crystal. The thermal behaviour of the grown crystal was estimated by DTA technique. The above experimental results clearly show that the grown sample L-histidinium succinate crystal can be used as a potential material for NLO applications.

References

1. Ahmed AB, Elleuch N, Feki H, Abid Y and Minot C *Spectrochim Acta A* **79** (2011) 554
2. Gunasekaran S, Anand G, Arun Balaji R, Dhanalaksmi J and Kumaresan S *Pramana-J Phys* **75** (2010) 683
3. Alosious Gonsago C, Helen Merina Albert, Karthikeyan J and Sagayaraj and Joseph Arul Pragasam P *Mater Res Bull* **47** (2012) 1648
4. Janarthanan S, Kishore Kumar T, Pandi S and Prem Anand D *Indian J Pure Appl Phys* **47** (2009) 332
5. Selvarajan P, Glorium Arul Raj J and Perumal S *J Cryst Growth* **311** (2009) 3835
6. Moitra S and Kar T *Cryst Res Technol* **45** (2010) 70
7. Sathyalakshmi R, Kannan V, Bairava Ganesh R and Ramasamy P *Cryst Res Technol* **42** (2007) 78
8. Sun GH, Sun XT, Sun ZH, Wang XQ, Liu XJ, Zhang GH and Xu D *J Cryst Growth* **311** (2009) 3904
9. Joseph Arul Pragasam A, Selvakumar S, Thamizharasan K, Prem Anand D and Sagayaraj P *J Cryst Growth* **280** (2005) 2718
10. Thomas Prakash J and Kumararaman S *Mater Lett* **62** (2008) 4097
11. Kurtz SK and Perry TT *J Appl phys* **39** (1968) 3798
12. Thomas Joseph Prakash J, Vijayan N and Kumararaman S *Spectrochim Acta A* **71** (2008) 1250.