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Growth and characterization of L-Lysine adipate crystal

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ABSTRACT

Nonlinear optical crystals of L-Lysine adipate were grown by liquid diffusion method at room temperature. The lattice parameters were determined by single crystal X-ray diffraction analysis. Fourier Transform Infrared and Raman spectral studies were carried out to confirm functional groups present in the crystal. Optical property of crystal was examined by UV–vis–NIR studies. Molecular structure of grown crystal was established using ^{1}H NMR and ^{13}C NMR studies. Thermal stability and decomposition were analyzed using Thermo Gravimetric and Differential Thermal analysis. Second harmonic generation efficiency of crystal was determined by Kurtz Perry powder technique.

1. Introduction

Nonlinear optical (NLO) crystals have important applications in various optical devices. In nonlinear optics, frequency conversion is used as a suitable process for laser applications [1]. Inorganic nonlinear optical materials have good mechanical and thermal properties, but possess modest optical nonlinearity because of lack of extended electron delocalization [2,3]. Organic materials with NLO chromophores are positioned in a noncentrosymmetric way, thereby exhibiting excellent nonlinear activity compared to inorganic materials [4,5]. Different mixtures of amino acid and ionic salt have been investigated in the nonlinear optical field [6]. Since amino acid contain a proton donor carboxylic acid (COOH) and proton acceptor amino (NH_2) groups, they provide the ground state charge asymmetry for the molecule [7,8]. The literature studies indicate that amino acid impurities are capable of improving the material properties [9]. The vibrational spectra and SHG studies on L-Lysine with different acids have already been reported [10]. For the present investigation, L-Lysine adipate crystals are grown by liquid diffusion method. Since the structure of the crystal has already been reported by Sharma et al. [11], the characterization of L-Lysine adipate crystal is done here. The grown crystals are subjected to X-ray Diffraction analysis, Fourier Transform Infrared and Fourier Transform Raman spectroscopic analyses, UV–vis–NIR spectroscopy, Nuclear Magnetic Resonance spectroscopy, Thermal studies and Second Harmonic Generation efficiency.

2. Materials and methods

The liquid diffusion method is well suited for the growth of organic and protein crystals [12,13]. The concentrated solution of L-Lysine and adipic acid were prepared in a molar ratio of 1:1. This solution having a pH value of 4.1, was chosen as the first solvent. Acetonitrile was selected as the second solvent due to its good precipitating behavior and lesser density. When these two solvents were added together, an unmixed interface was formed between them. The acetonitrile diffused slowly into the concentrated solution of L-Lysine and adipic acid which resulted in the formation of L-Lysine adipate crystals in a period of one week. The photograph of grown L-Lysine adipate crystal is shown in Fig. 1.

3. Characterisation

Single crystal XRD study was carried out using Nonius CAD4/MACH 3 single crystal X–ray diffractometer with MoKα (λ=0.71069 Å) radiation. Fourier Transform Infrared spectrum was recorded by KBr pellet technique in SPECTROMRX1 FTIR spectrometer and FT Raman spectrum was recorded using BRUKER RFS 27 spectrometer to confirm the functional groups. The transparency was investigated by λ35 model PerkinElmer double beam UV–vis–NIR spectrometer in the range of 190–1100 nm. The ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature with D_2O as solvent in Bruker 300 MHz (ultrasheild)™ instrument (operated at 300 MHz for ^{1}H NMR and

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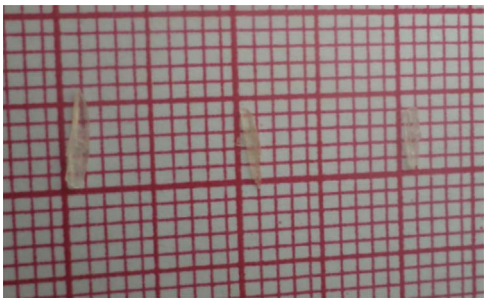

Fig. 1. Photograph of L-Lysine adipate crystal.

75 MHz for ^{13}C NMR) for the confirmation of molecular structure. TGA (Thermo Gravimetric Analysis) and DTA (Differential Thermal Analysis) were carried out under nitrogen atmosphere with a heating rate of 20 °C/min in the temperature range 30–1100 °C with SDT Q600 V20.9 Build 20. The powder technique of Kurtz and Perry was employed for SHG efficiency measurement. It was carried out using Q-switched mode locked Nd:YAG laser with first harmonic output at 1064 nm, with 1.9 mJ/pulse of input energy and 10 ns of pulse width at a repetition rate of 10 Hz.

4. Results and discussion

4.1. Single crystal X-ray diffraction analysis

The single crystal X-ray diffraction analysis was carried out to identify crystal system and estimate lattice parameter values. The observed values agree well with the reported values [11]. Table 1 shows the XRD data of L-Lysine adipate crystal.

4.2. FT-IR and FT-Raman spectral analyses

The functional group investigation of the crystal L-Lysine adipate was carried out by FTIR and FT Raman spectroscopy. Figs. 2 and 3 show the recorded FTIR and FT Raman spectra. The vibrational frequencies and their corresponding assignments were given in Table 2. The bands at 2941 cm^{-1} and 2930 cm^{-1} in FTIR and Raman spectra were attributed to the asymmetric stretching mode of CH_2 group [14]. The NH_3^+ asymmetric deformation was identified at 1636 cm^{-1} in IR and 1653 cm^{-1} in Raman spectrum [10]. The peaks at 1402 cm^{-1} and 1414 cm^{-1} were attributed to COO^- symmetric stretching vibration [15]. The Infra red band of CH_2 wagging was observed at 1237 cm^{-1}. The corresponding band in the Raman spectrum occurred at 1255 cm^{-1}. The C-H in plane deformation mode was assigned to the bands observed at 1062 cm^{-1} and 1084 cm^{-1}[16], while the C-C stretching vibration band appeared at 932 cm^{-1} and 933 cm^{-1} in IR and Raman spectra respectively [15]. The vibrations such as twisting and rocking of CH_2 and NH_3 were identified and given in Table 2. In Raman spectrum, the bands at lower wavenumbers 284 cm^{-1} and 71 cm^{-1} were assigned to lattice vibrations of L-Lysine adipate crystal.

Table 1
Lattice parameters of L-Lysine adipate crystal.

Lattice parameters	Observed values	Reported values[11]
a (Å)	10.612 (18)	10.532 (3)
b (Å)	7.385 (12)	7.283 (17)
c (Å)	10.701 (19)	10.599 (3)
α (°)	90	90
β (°)	113.32 (5)	113.358 (3)
γ (°)	90	90
Crystal system	Monoclinic	Monoclinic

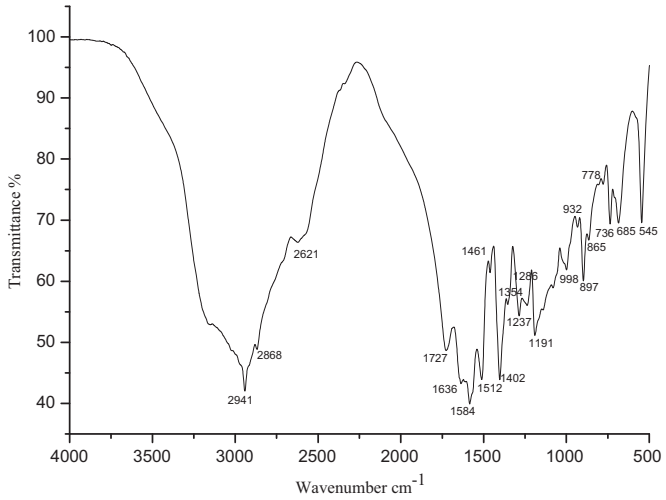

Fig. 2. FTIR Spectrum of L-Lysine adipate crystal.

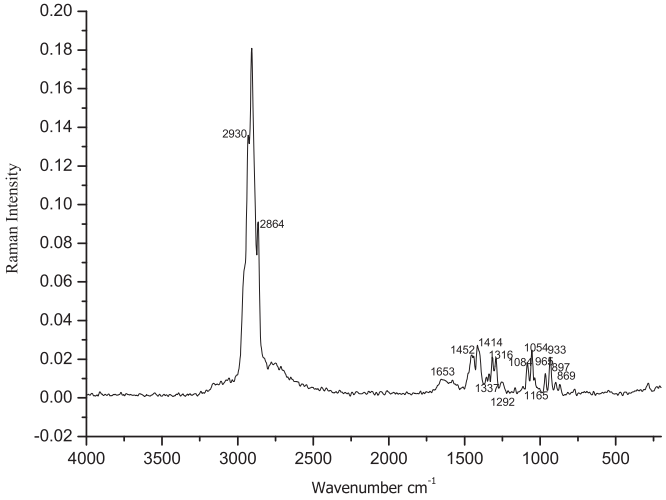

Fig. 3. FT Raman Spectrum of L-Lysine adipate crystal.

Table 2
Observed vibrational wavenumbers and their assignments.

Wavenumber cm^{-1}		Assignments
FTIR	FT- Raman	
2868	2864	CH_2 symmetric stretching
1461	1452	CH_2 scissoring
1354	1337	C-H bending
1286	1292	CH_2 twisting
1191	1165	NH_3^+ rocking
865	869	C-H in plane bending
736	724	C-OH stretching

4.3. Optical Transmission spectral study

For any NLO material, wide transparency in the UV–vis–NIR region is important. The UV–vis–NIR transmission spectrum of L-Lysine adipate crystal was recorded in the 190–1100 nm range (Fig. 4). The lower-cut off wavelength of the crystal occurs at 199 nm. The spectrum further exhibits a wide optical transmittance from 199 nm to 1100 nm. Moreover, the crystal shows good transparency in the entire Vis-NIR spectral region, making it a suitable material in the application of optoelectronics and SHG conversion.