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Crystal growth, solubility, structural, optical, thermal, mechanical and electrical studies of L-arginium adipate: An organic nonlinear optical material

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ABSTRACT

L-Arginium adipate (LAAD) single crystal has been grown by slow evaporation solvent technique at room temperature. The crystal structure and lattice parameters were determined for the grown crystal by single crystal X-ray diffraction studies. Single crystal X-ray diffraction analysis confirms the grown crystal has monoclinic crystal system with space group of $P2_1$. Fourier transform infra red (FTIR) spectroscopy and thermal analysis (DSC and TGA) were performed to study the molecular vibrations and thermal behaviour of the crystals, respectively. Powder X-ray diffraction analyses show the good crystalline nature. Mechanical characterization such as micro hardness studies on (1 0 0) plane were also carried out. Photoluminescence studies confirm the violet fluorescence emission peak at 400 nm. Linear optical study (UV–vis absorption) was determined by UV-Vis spectrophotometer. The dielectric constant, dielectric loss and ac conductivity of the compound were calculated at different temperatures and frequencies to analyze the electrical properties. Nonlinear optical property was discussed to confirm the SHG efficiency of the grown crystal.

1. Introduction

Organic materials have been of particular interest because the nonlinear optical response in this broad class of materials is microscopic in origin, offering an opportunity to use theoretical modelling coupled with synthetic flexibility to design and produce novel materials [1]. Amino acids are potential candidates for growth of nonlinear optical (NLO) single crystal. Since it has carboxyl group and amine group, these can form zwitterions when it is dissolved in its respective solvents and capable of forming salt with other counter ions of either organic or inorganic. There are numerous amino acid based NLO crystals have been reported and their properties were studied [2–4]. L-Arginine is one such important amino acid which gave large numbers of derivatives with its inorganic as well as organic compounds [5–7]. The adipic acid complexes of DL-arginine and L-arginine are made up of zwitterionic, singularly positively charged arginium ions and doubly negatively charged adipate ions, with a 2:1 stoichiometry. One of the two crystallographically independent arginium ions in the L-arginine complex has a conformation hitherto unobserved in crystal structures containing the amino acid. X-ray studies on crystalline complexes involving amino acids and peptides. XLII. Adipic acid complexes of L- and DL-arginine and supramolecular association in arginine–dicarboxylic acid complexes were reported by Roy et al. [8]. However, the properties like optical, thermal, mechanical, electrical and other structural characterization like powder X-ray diffraction study were unstudied. These properties and characterization should be precisely investigated in order to find the suitability of the crystal for its device fabrication. In the present investigation, single crystals have been grown from the super saturated solution by slow evaporation of solvent technique (SEST) using a suspended seed. In the present investigation a systematic study has been carried out on the growth of LAAD and the grown crystals have been subjected to various characterization studies.

2. Materials and methods

Crystals of the L-arginine complex were obtained by the diffusion of ethanol into an aqueous solution of L-arginine (Sigma) and

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adipic acid (AR, E-Merck) that were mixed in a 1:1 molar ratio. Platy and good quality colourless seed crystals were obtained by SEST method from a super saturated solution prepared from the synthesized salt. These seed crystals were used to study the various characterization of the present investigation. L-Arginine reacts with adipic acid as follows:

$$C_6H_{14}N_4O_2 + C_6H_{10}O_4 \rightarrow 2C_6H_{15}N_4O_2{\cdot}C_6H_8O_4$$

3. Characterization techniques

Single crystal XRD studies were carried out using Enraf Nonius CAD-4 single X-ray diffractometer to determine the lattice parameters and the space group. Powder X-ray diffraction patterns were recorded using a Philips X pert PRO X-ray diffractometer with Cu Kα (λ = 1.5418 Å) radiation. The FTIR spectra of grown crystals were recorded by KBr pellet technique using Perkin Elmer FTIR spectrometer in the range 4000–450 cm^{-1} with the resolution up to 1.0 cm^{-1}. The optical properties of the grown crystals were studied using the Perkin-Elmer Lambda 35 UV-Vis spectrometer in the wavelength region from 190 to 1100 nm. Fluorescence spectra were recorded with the help of Perkin Elmer LS45UV fluorescence spectrophotometer. The thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using STA 449F3 Jupiter at the heating rate of 10 K/min in inert nitrogen atmosphere ranging from 30 to 600 °C. Vicker's hardness studies have been carried out using the instrument Shimadzu HMV-2T. Vickers hardness tester fitted with a Vickers diamond quadrangular pyramidal indenter and attached to an incident light microscope, loads ranging from "10, 20, 30, 40, 50 g" were used for making indentation, keeping the time of indentation constant at 5 s. The dielectric study was carried out using the instrument, Agilent (Model 4284 A) LCR meter. Nonlinear optical properties were tested by Kurtz Perry powder technique [9].

4. Growth of single crystals

Seed crystals were obtained from the super saturated solution at constant temperature (30 °C) by SEST method. Due to slow evaporation of the solvent, spontaneous nucleation occurs and these are grown into crystals of few mm^3 size. Crystals with good habitual faces, transparency and less number of visible defects are selected as seed for growing bulk single crystals. A seed crystal was suspended in the super saturated solution contained beaker and kept in a constant temperature bath with accuracy of ±0.01 °C to maintain the growth solution at 30 °C. The beaker was covered separately by a perforated thin transparent sheet in order to enable the slow solvent evaporation. After a period of 29 days the seed crystals have grown to the dimension (12 mm × 10 mm × 12 mm) and the grown crystals were harvested carefully from the solution. The as grown crystal is shown in Fig. 1.

5. Results and discussion

5.1. Solubility studies

The solubility of LAAD was determined for six different temperatures namely 35, 40, 45, 50, 55 and 60 °C. A constant volume of 100 ml of saturated solution was used in this experiment. The measurement was performed dissolving the LAAD salt in water in an airtight container maintained at a constant temperature with continuous stirring. The solution was constantly stirred for 2 h using a magnetic stirrer for homogenization. The solubility of LAAD is shown in Fig. 2. It is seen from the figure that the LAAD has a positive gradient of solubility.

Fig. 1. Photographs of as grown single crystal of LAAD from the suspended seed.

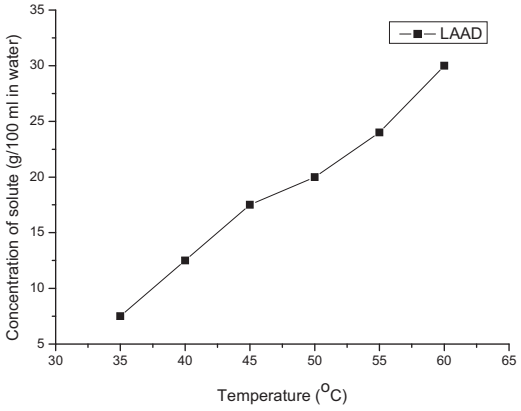

Fig. 2. Solubility curve of LAAD in water.

5.2. FTIR spectral analysis

Infrared spectra are an important record, which provide more information about the structure of a compound. In this technique almost all functional groups in a molecule absorb characteristically within definite range of frequency [10]. The absorption of IR radiation causes the various bands in a molecule to stretch and bend with respect to one another. The most important range (4000–450 cm−1) is of prime importance for the study of organic and semi-organic compounds by spectral analysis [11]. The FTIR spectrum of LAAD is shown in Fig. 3. The broad envelope between 2300 and 3750 cm^{-1} includes overlapping of stretching modes due to N—H and C—H. The aliphatic C—H stretching modes are resolved at 2905 cm^{-1} (asymmetric stretching mode). The symmetric stretching mode is less intense than the asymmetric stretching mode. Multiple fine structures at the lower energy mode of the envelope indicate strong hydrogen bonding interaction of —NH^{3+} group with —COO_1^- group in the crystal. The band at 2128 cm^{-1} is due to combination of asymmetrical —NH_3^+ bending (1639 cm^{-1}) and vibration and its torsional oscillation (543 cm^{-1}). The C=O stretch of —COO_1^- is observed at 1489 cm^{-1}. The peaks at 1165 and 1083 cm^{-1} are assigned to —COO^- vibrations. The peaks at