Synthesis, Growth, Spectroscopic and Thermal Studies of Organic Adduct of L-Alaninium Tartrate Single Crystal

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Organic non-linear optical materials are potential candidates for frequency mixing, electro-optic modulation, optical parametric oscillation optical by stability *etc*., due to the large optical non-linearity, low cutoff wavelength, short response time and high thresholds for laser power. In the present investigation, bulk crystal of L-alaninium tartrate, an organic adduct of L-tataric acid was grown by slow solvent evaporation technique. The grown crystal was subjected to single crystal X-ray diffractometry (XRD) to estimate the crystal structure and space group and its morphology was also studied. The optical property of the crystal was investigated using UV-vis-NIR. The functional groups were identified by the FTIR spectral analysis. The thermal stability of the crystal was estimated by TG/DTA.

Key Words: Organic material, Single crystal, Morphology, Non-linear optical, Optical properties, Thermal analysis.

INTRODUCTION

The search for suitable materials displaying excellent second-order non-linear optical (SONLO) properties is the focus of current research activity due to their potential applications in optoelectronics, telecommunication and optical storage devices. Materials with large second-order optical non-linearities, short transparency cut-off wavelengths and stable physico-chemical performances are needed to realize many of these applications[1].

In general, most of the organic molecules designed for non-linear optical (NLO) applications are the derivatives of an aromatic system substituted with donor and acceptor substituents. On the search for new NLO materials with better mechanical properties, researchers have mainly focused on the small organic molecules having a large dipole moment and with a chiral structure. Specifically, the combination of two simple organic molecules, one with a large dipole moment and the other, a chiral molecule with an acentrosymmetric crystal structure is an attractive strategy[2-4]. Generally, a salt is formed by an exchange of proton between a base and an acid. Tartaric acid forms a broad family of hydrogen-bonded crystals. In complexes of organic bases with tartaric acid, one or two protons can be transferred from the carboxylic groups of tartaric acid to form the monovalent (semi-tartrate) or divalent (tartrate) anions, respectively. Because of the ability of enhancing the

macroscopic non-linearity in a synergistic mode and initiating multidirectional hydrogen bonds, tartaric acid has been chosen to synthesize non-linear optical materials[3,5]. This opened the way for the resolution of compounds without basic properties with (+)-tartaric acid derivatives[2]. The structures of the tartaric acid complexes with amino acids have been studied for their interesting structural, spectroscopic and non-linear optical properties. Crystals of L-lysine-L-tartaric acid, L-alaninium tartrate, L-hystidinium-L-tartrate hemihydrate, *p*-nitroanilene-L-tartaric acid are the few examples for this class of materials[3,4]. In these complexes, the amino group abstracts one proton from tartaric acid and the cations and anions usually aggregate into separate alternating layers[6,7]. Because tartaric acid is a chiral molecule, materials exhibiting non-centrosymmetrical structures are easily obtained when tartaric acid combines with some organic base.

The present article deals with the growth and characterization of L-alaninium tartrate, which is a simple combination involving tartaric acid and amino acid organic systems. The crystal structure of L-alaninium tartrate (LAT) was solved by Rajagopal *et al.*[8]. In L-alaninium tartrate, the L-alanine molecule exists in the cationic form with positively charged amino group and uncharged carboxylic acid group. The tartaric acid molecule exists in the mono-ionized state. The structure is stabilized by three dimensional network of O–H···O and N–H···O hydrogen bonds (Fig. 1). The aggregation pattern observed in
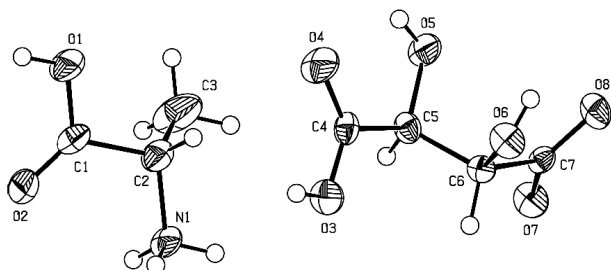
Fig. 1. ORTEP representation of L-alaninium tartrate molecule
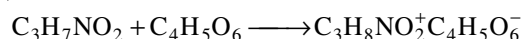

Fig. 2. Solubility curve of L-alaninium tartrate

the structure has striking similarities to those observed in other related amino acid-tartaric acid complexes, *e.g.*, sarcosinium tartrate[9] and L-prolinium tartrate[10].

In the present investigation, bulk single crystal of L-alaninium tartrate was grown by slow solvent evaporation technique. The grown crystal was subjected to single crystal X-ray diffractometry (XRD) to estimate the crystal structure, space group and morphology. The optical properties of the crystal were investigated using UV-vis-NIR and FT-IR spectroscopic techniques. The thermal analysis of the sample was carried out by TGA/DTA.

EXPERIMENTAL

Synthesis: L-Alaninium tartrate (LAT) was synthesized by dissolving one mole of L-alanine (Merck, purity 99 %) in double distilled water containing one mole of tartaric acid (SD fine chemicals, purity 99 %).

The reaction is as follows:

$$C_3H_7NO_2 + C_4H_5O_6 \longrightarrow C_3H_8NO_2^+ C_4H_5O_6^-$$

The synthesized salt was further purified by repeating the crystallization process at least thrice.

Solubility: The solubility of L-alaninium tartrate in double distilled water was measured at five different temperatures (30, 35, 40, 45 and 50 °C). The solubility data was determined by dissolving the synthesized salt of L-alaninium tartrate in 50 mL of double distilled water at a constant temperature with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The solubility curve for L-alaninium tartrate is shown in Fig. 2. The salt has a positive solubility coefficient in water. Since the solubility increases with temperature, the crystal can be conveniently grown by the method of temperature lowering or slow solvent evaporation.

Growth of L-alaninium tartrate single crystal by slow solvent evaporation method: The supersaturated solution of L-alaninium tartrate was prepared in accordance with the solubility data. Prior to the growth experiments, the preparation of seed crystal was done by spontaneous nucleation. The seeds were visible within a period of 5-7 days and, among them tiny crystals with perfect morphology and good optical grade were chosen as the seed to carry out the further growth experiments. The seed was kept immersed in the mother solution using a nylon thread. The content was kept in a 100 mL beaker and then covered with a perforated lid to encourage the evaporation of the solvent. Single crystal of L-alaninium tartrate was grown by slow solvent evaporation method (SSEM) at room tempe-
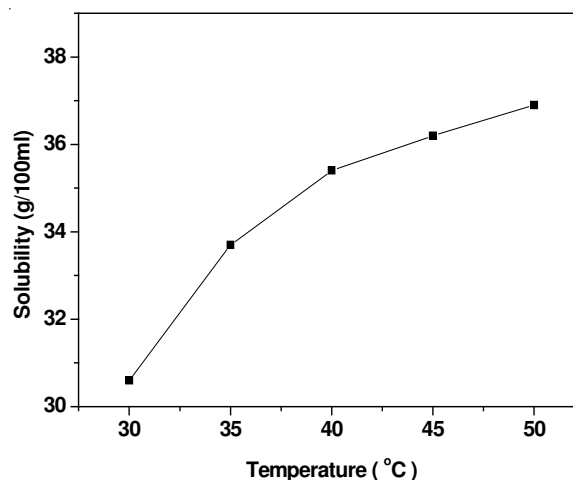
rature (30 °C). Crystals of dimension up to 14 mm × 4 mm × 2 mm were harvested after a period of 30 days. Fig. 3 shows the photograph of as grown crystal of L-alaninium tartrate. It is evident from the photograph that the crystal is highly transparent and free from visible inclusions. The morphology of L-alaninium tartrate establishes that there are eight developed faces, out of which the (0 2 3) and (0 1 $\bar{2}$) planes are more prominent. For each face, its parallel friedel plane is also present in the grown crystal and shown diagrammatically in Fig. 4.
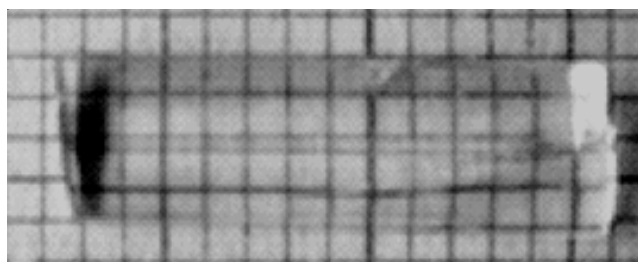

Fig. 3.   Photograph of slow solvent evaporation method grown L-alaninium tartrate single crystal
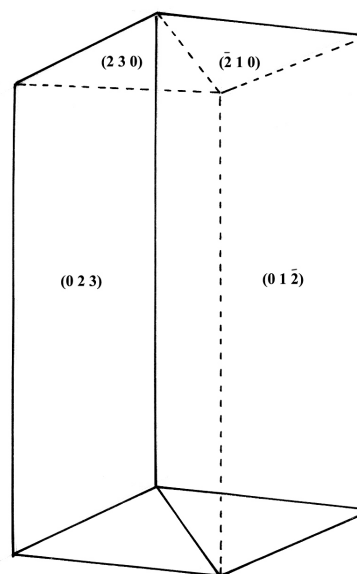

Fig. 4. Morphology of L-alaninium tartrate crystal

RESULTS AND DISCUSSION

Single crystal XRD analysis: Single crystal XRD data was collected using an automated diffractometer (Messrs Enraf Nonius). The structure of L-alaninium tartrate was solved by the direct method and refined by the full matrix least-square fit technique employing the SHELXL program. The single crystal XRD data of the as grown L-alaninium tartrate single crystal is presented. It is observed that L-alaninium tartrate crystallizes in monoclinic structure with space group of P2$_1$. The calculated lattice parameter values are: a = 5.144 Å, b = 13.720 Å and c = 7.475 Å, which are in good agreement with the reported values[8].

FT-IR analysis: The Fourier transform infrared analysis was carried out in 4000-500 cm^{-1} range by recording the spectrum using BRUKER IFS 66V FT-IR SPECTROMETER. The FT-IR spectrum of L-alaninium tartrate is shown in Fig. 5. The absorption band in the region 3400-2500 cm^{-1} is assigned to superimposed O-H and NH$_3^+$ stretching bands. The C=O stretch of COO$^-$ gives its peak at 1668 cm^{-1}, whereas the asymmetric NH bend of NH$_3^+$ shows its peak at 1640 cm^{-1}. The characteristic OH vibrations of tartaric acid alcoholic group and COOH group are seen to get overlapped with the NH vibrations of alanine. The characteristic CH vibrations of tartaric acid produce peaks at 2977 and 2960 cm^{-1}. The intense peaks at 2680 and 2714 cm^{-1} are due to hydrogen bonded OH groupings. The C=O stretch of tartaric acid gives a peak at 1730 cm^{-1}. The asymmetric and symmetric COO vibrations produce peaks at 1550 and 1416 cm^{-1}. The C-O stretching and OH deformation produce peaks at 1302, 1260 and 1210 cm^{-1}. The alcoholic C-O stretch is seen by the peak at 1060 cm^{-1}.
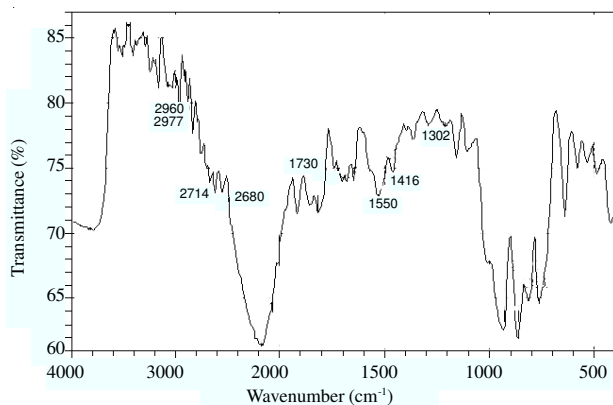

Fig. 5. FTIR spectrum of L-alaninium tartrate

UV-Vis-NIR spectral analysis: The optical absorption spectrum of L-alaninium tartrate crystal was recorded in the range 250-2000 nm using Varian Cary 5E spectrophotometer. The absorption spectrum (Fig. 6) for the sample indicates that the crystal has minimum absorbance in the region from 240-1850 nm without any absorption peaks, thus revealing the absence of any impurity in the grown crystal. It is evident from the absorption spectrum of L-alaninium tartrate crystal that it possesses a very low absorption in the entire visible region and near UV region. The crystal has its lower cut-off wavelength closer to 240 nm; which suggests that the crystal
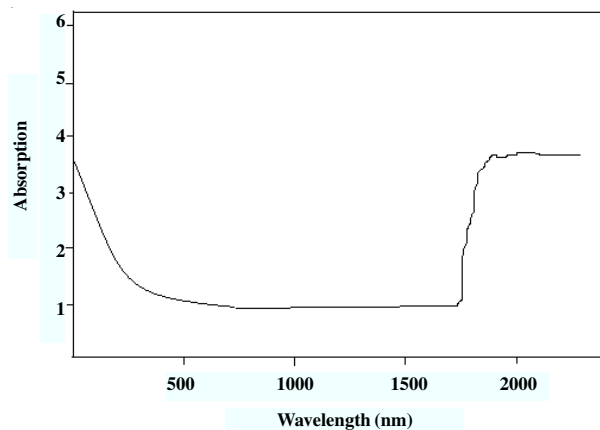

Fig. 6. UV-Vis-NIR spectrum of L-alaninium tartrate single crystal

posses good optical transparency for the second harmonic generation of Nd:YAG laser. The observed cut off wavelength is better than the other tartaric acid organic adducts such as hydroxyethylammonium L-tartrate monohydrate (335 nm), hydroxyethylammonium D-tartrate monohydrate (336 nm) and L-tartaric acid -nicotinamide (280 nm)[3,5].

In the present work, the absorption coefficient (α) of L-alaninium tartrate single crystal of thickness 2 mm was determined from optical transmittance measurements made at room temperature. The value of 'α' was estimated using the following expression:

$$\alpha = -\left(\frac{1}{t}\right)\ln(T)$$

where, T = transmittance and t = thickness of the specimen. These absorption coefficient values were used to determine optical energy gap. Using Tauc's relation a graph has been plotted to estimate the direct band gap value. Fig. 7 shows the plot of (αhν)^2 *versus* hν, where a is the optical absorption coefficient and hν is the energy of the incident photon. The energy gap (E$_{gd}$) is determined by extrapolating the straight line portion of the curve to (αhν)^2 = 0. From this drawing, the direct band gap (E$_{gd}$) is found to be 4.3 eV.
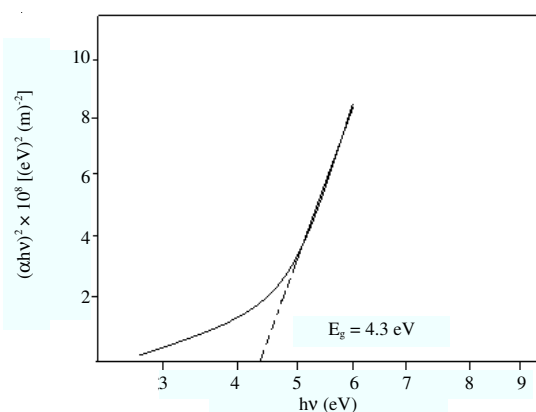

Fig. 7. Tauc's plot for L-alaninium tartrate single crystal

Thermal analysis: The TGA and DTA analysis of L-alaninium tartrate was carried between 28 and 1000 ℃ at a heating rate of 15 ℃/min using the instrument NETZSCH STA 409C. The TGA and DTA traces of L-alaninium tartrate are

shown in Fig. 8. There is a sharp weight loss starting at about 126 ºC, which is due to loss of water of crystallization. The total weight loss at this stage is equal to 4 % which corresponds to loss of one water molecule. This weight loss is followed by a major weight loss pattern between 231 and 270 ºC occurring in two stages. It is assigned to decomposition of the salt. In the DTA, a sharp endothermic peak is present at 118 ºC, which coincides with the first stage of weight loss in the TGA trace. There is also another sharp endothermic peak at 240 ºC, which corresponds to the second stage of weight loss in the TGA trace. Thus the thermal analysis proves that the decomposition of the compound is taking place in three different stages.
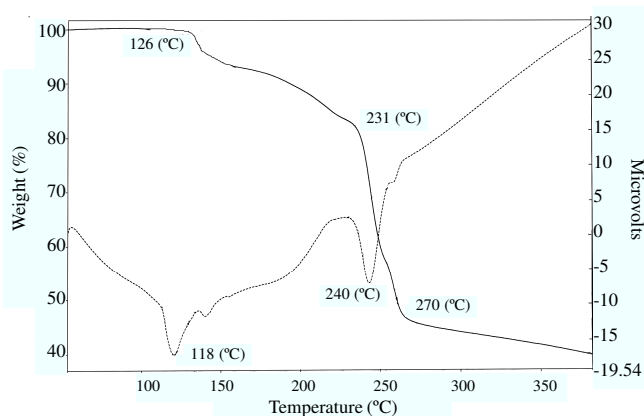

Fig. 8. TGA and DTA traces of L-alaninium tartrate single crystal

Conclusion

Relatively large size crystals of L-alaninium tartrate with good optical grade were conveniently grown by slow solvent evaporation technique. Single crystal XRD studies confirm the structure of the crystal as monoclinic crystal system with P2$_1$ space group. The presence of all the fundamental functional groups of the grown sample was confirmed by FT-IR analysis. L-alaninium tartrate has a wide absorption window from 240-2000 nm, which highlights its prospects of application as a non-linear opticalo material. Thermogravimetric analysis studies reveal the three stages of weight loss occurring in the sample and it further prove that it is thermally stable up to 126 ºC.

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