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Growth, structural, optical and thermal properties of an organic NLO material: L-Argininium hydrogen squarate

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ABSTRACT

L-Argininium hydrogen squarate (LAHS) is an organic nonlinear optical material grown by slow evaporation solution growth technique. The crystal structure was confirmed by single crystal X-ray diffraction analysis and the crystal system is identified as triclinic system. The thermal stability and decomposition process were studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The crystal is stable up to 238 °C. The optical transparency range and lower cut-off wavelength of grown crystal have been identified by UV–vis–NIR spectroscopy method. The existence of second harmonic generation (SHG) signal was observed using Nd:YAG laser with fundamental wavelength of 1064 nm. The SHG efficiency is compared with potassium di-hydrogen phosphate (KDP) and urea.

1. Introduction

In present day much attention is being paid on exploration of novel and good quality nonlinear optical (NLO) materials. These materials play vital role in industry which includes telecommunication, optoelectronics technology, optical data storage and signal processing [1–5]. As the amino acids have chiral symmetry and crystallize in non-centrosymmetric space groups, they are interesting and important materials for NLO applications. The amino acids with organic salts are capable materials for optical second harmonic generations. Organic NLO materials are superior to their inorganic counterparts due to high conversion efficiency for second harmonic generation and good transparency [6] in the visible region. The optical properties of amino acid crystals are increased by addition of organic acids because of their high range of transparency [7,8].

Amino acids are biologically important organic compounds contain proton accepting amino (NH_2) group and proton donating carboxyl (COOH) functional group in them. One such interesting amino acid is L-arginine ($C_6H_{14}N_4O_2$). It is widely found in animal sources, plant sources and biological substances. L-Arginine forms a number of complexes by reacting with organic acid and salts to produce a marvellous material for NLO applications.

Hydrogen bonding is one of the principal intermolecular interactions that frequently play key roles in molecular recognition and self-assembly as well as in crystal engineering research and has been used effectively to predict and design supramolecular assemblies in one, two and three dimensions [9]. Supramolecularly organized systems with a variety of novel features are widely generated through hydrogen-bonding. Hydrogen-bonded systems generated from organic cations and anions are of special interest since they are likely to show stronger hydrogen bonds than neutral molecules thus enabling the simple acid–base chemistry to tune the donor and acceptor properties of the counter ions [10]. Squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) which is popularly known as quadratic acid ($C_4H_2O_4$), is a white crystalline powder with highly acidic and chemically stable compound and it was first synthesized in 1959. Squaric acid was shown to be an unusually strong organic acid and one of the series of hydrogen-bonded ferroelectrics [11]. Squaric acid has been of much interest because of its cyclic structure and possible aromaticity.

Several basic aspects of the properties of squaric acid have been reported to assess its potentialities for NLO applications. In particular, squaric acid and several optically active amino acids co-crystallize under the form of non-centrosymmetric lattice that are expected to present large second-order susceptibilities [12]. The

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present work reports on the growth and characterization of squaric acid and amino acid based single crystal.

2. Experimental details

2.1. Synthesis and crystal growth

The title compound was grown from aqueous solution by slow evaporation solution growth technique. L-Arginine and squaric acid were taken in equimolar ratio and thoroughly dissolved in deionized water. The solution was stirred well for 6 h at room temperature using magnetic stirrer with 680 rpm to yield a homogenous mixture of solution. Then the saturated solution was filtered using Whatmann filter paper to eliminate unwanted impurities and transferred to a beaker. The beaker was covered with a perforated transparent polythene paper and kept at a dustless environment for slow evaporation. Good and transparent crystals were grown in a period of 3 weeks. The reaction involved in the process may be written as shown in Fig. 1.

2.2. Characterization

The grown LAHS crystal was subjected to various characterization techniques like single crystal X-ray diffraction, UV–vis–NIR, thermal analysis and nonlinear optical studies. In order to obtain the cell parameters and crystal data of LAHS crystal, X-ray diffraction studies were carried out using crystal diffractometer equipped with a CCD detector (Bruker Kappa APEX II ULTRA), a rotating anode (Bruker AXS, FR591) with MoKα radiation (λ = 0.71073 Å). The UV–vis–NIR optical absorption spectral analysis was carried out between 200 and 1100 nm, using Lambda 25 spectrophotometer. Thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) were carried out using SDT Q600 V8.3 Build 101 thermal analyzer instrument, ranging from room temperature to 1000 °C at the heating rate of 20 °C per minute under nitrogen atmosphere. The second harmonic generation efficiency was measured using Kurtz and Perry powder technique using Nd:YAG laser beam of energy 4.6 mJ/pulse.

3. Result and discussion

3.1. Crystal structure and X-ray diffraction analysis

The intensity data were collected at 296 K on a Bruker AXS Kappa APEX2 CCD Diffractometer [13] system using MoKα graphite monochromated radiation. The molecular structure of the LAHS crystal ($C_{10}H_{16}N_4O_6$) was refined by the least squares method using anisotropic thermal parameters: $R = 3\%$. The compound crystallizes in triclinic, $P1$. The parameter values calculated are $a = 5.0901(5)$ Å, $b = 8.2364(9)$ Å, $c = 14.7926(16)$ Å, and $Z = 2$. This value is in good agreement with earlier report [14] which was recorded at 292 K. The asymmetric unit of the title compound contains two 5-((amino(imino)methyl)amino)-2-amminopentanoate (C1–C6/O1/O2/N1–N4 and C11–C16/O7/O8/N5–N8) and two 2-hydroxy-3,4-dioxocyclobut-1-enolate (O3–O6/C7–C10 and O9–O12/C17–C20). The C—N bond distances of the NH_2 groups N1–C6 = 1.315(8) Å, N2–C6 = 1.315(9) Å, N5–C16 = 1.325(3) Å and N6–C16 = 1.310(1) Å, respectively, which is short for a C—N single bond 1.47 Å, but still not quite as contracted as one would expect for a fully established C=N double bond 1.27 Å. These bond length features are consistent with an imino resonance form as it commonly found for C—N single bonds involving sp^2 hybridized C and N atoms [15]. The bond distances C1–O1 = 1.256(3) Å, C1–O2 = 1.238(3) Å, C11–O7 = 1.237(1) Å, C11–O8 = 1.254(2) Å, C8–O4 = 1.230(9) Å, C9–O5 = 1.217(6) Å, C10–O6 = 1.249(1) Å, C17–O9 = 1.232(1) Å, C18–O10 = 1.214(8) Å and C19–O11 = 1.243(8) Å, respectively, clearly indicate the presence of C=O double bonds, including those also generated through resonance. The H atoms attached to the squaric groups (O6 and O11) are transferred to the basic centers N6 and N2 respectively, generating the iminium groups. Also the carboxylic H-atoms on O1 and O8 have been transferred to N4 and N8, respectively, to generate the common amino acid zwitterions.

The C=O double bonds generated through resonance in the squaric acid anion [C10=O6 (1.249(1) Å) in molecule A and C19=O11 (1.243(8) Å) in molecule B] are shorter than normal single C—O bond (1.426 Å) and slightly longer than normal double C=O bond (1.23 Å). Both molecules (A and B) are involved in inter and intra molecular N—H···O hydrogen bonds. Intramolecular C—H···O and N—H···O hydrogen bonds lead to the formation of a five-, six-, seven-, eight-, nine- and ten-membered ring motif S(5), S(6), S(7), S(8), S(9) and S(10), respectively [16]. The crystal structure of the compound is further stabilized by intermolecular C—H···O and N—H···O hydrogen bonds. The LAHS crystal data, experimental conditions and structural refinement parameters are presented in Table 1. The molecular structure, crystal packing and unit cell packing diagrams of LAHS are shown in Figs. 2–4, respectively.

For the title compound, data collection was done using the computer program APEX2 [13], cell refinement was done using the computer program APEX2/SAINT [13] and data reduction was done by using SAINT/XPREP [13]. The structure of the title compound was solved by using the computer program SIR92 [17] and refined using SHELXL-97 [18]. The molecular graphics were done using the computer programs ORTEP [19], Mercury [20] and PLATON [21]. All the H atoms were positioned geometrically and treated as riding on their parent atoms, with C—H = 0.98 Å (methine), and 0.97 Å (methylene), and refined using a riding model with $U_{iso}(H) = 1.2\,U_{eq}$ and $1.5\,U_{eq}$ (parent atom).

3.2. Thermal analysis

Thermogravimetric analysis is an analytical technique used to determine thermal stability and fraction of volatile compound of a crystal by monitoring the weight change that occurs as the crystal is heated. The TGA, DTA and DSC of LAHS crystal were carried between room temperature to 1000 °C at the heating rate of 20 °C per minute under nitrogen inert atmosphere. The resulting TGA/DTA and DSC curves are shown in Figs. 5 and 6, respectively.

The initial mass of the crystal subjected to analyses was 4.9670 mg and the final mass left out after the experiment was 5.163% of the initial mass. The TGA trace appears nearly straight

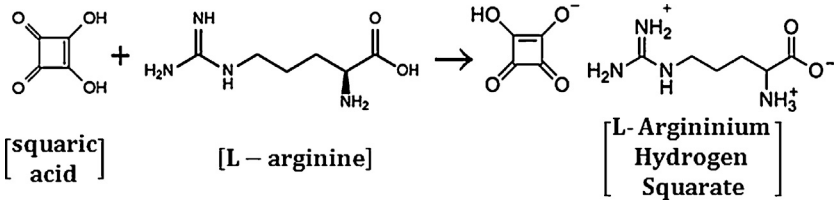

Fig. 1. Chemical reaction.