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Synthesis, growth and characterization of L-Phenylalaninium methanesulfonate nonlinear optical single crystal

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ABSTRACT

The titled compound, L-Phenylalaninium methanesulfonate (LPA-MS) was synthesized and grown into single crystals by slow solvent evaporation solution growth technique in aqueous solution containing equimolar concentrations of L-phenylalanine and methanesulfonic acid at room temperature. The grown crystals were subjected to single crystal X-ray diffraction studies. It crystallizes in the monoclinic crystal structure with P_{21} space group and the unit cell parameters are a = 5.312 (10) Å, b = 8.883 (2) Å and c = 25.830 (7) Å. The functional groups of the LPA-MS crystal were confirmed with FT-IR and FT-Raman analysis. The carbon-hydrogen skeleton was confirmed with ^{1}H NMR and ^{13}C NMR analysis. TG–DTG and DSC studies were carried out to determine the thermal stability of the crystals. The optical transparency ranges were studied through UV–vis–spectroscopy and the crystal was found to be transparent in the visible region. The second Harmonic generation (SHG) efficiency of the grown LPA-MS crystal was measured by the Kurtz–Perry powder technique. The dipolar nature of the L-phenylalaninium methanesulfonate and the presence of the intermolecular hydrogen bonding between the molecules are the vital factors responsible for the existence of SHG activity in the crystal.

1. Introduction

The crystal growth and analysis of novel non linear optical (NLO) materials have been strongly encouraged due to their extensive use in the field of optical communication, laser technology, optical computing, data storage, dynamic holography, harmonic generators, frequency mixing, and electro-optic switching [1,2]. Researcher has put great effort to develop high performance optoelectronic devices than the existing ones with higher efficiency with low costs. Varieties of materials including inorganic, organometallic, organic and polymeric materials have been studied for their NLO activity [3]. However, organic NLO materials are receiving major attention in nonlinear optics because, they have fast response, high NLO efficiency and high laser damage threshold compared to inorganic NLO materials [2]. The limitless architectural flexibility of the organic molecules gives tailor-made molecular engineering to find novel nonlinear optical materials with customized NLO properties [2]. Among the organic molecules, amino acids are playing vital role because of their specific features of interest such as molecular chirality, wide optical transparency window in the entire UV, Visible and NIR regions [4,5]. Many amino acids, individually and their complexes or salts with various compounds, are showing good second order nonlinearity because of the presence of chiral carbon atom, non-centrosymmetric crystal structure and the dipolar donor and acceptor groups that provide the ground state charge asymmetry of the molecule allows the intermolecular charge transfer possible [6]. In addition, these crystals can be easily grown using conventional slow evaporation technique (SET). By considering these aspects, several novel organic NLO materials with excellent properties have been developed and reported in the literature [7–10].

Among various amino acid investigated, L-phenylalanine is one of the essential amino acids used by the body to build neurotransmitters [11]. The single crystals of L-phenylalanine salts of various acids were investigated for NLO applications [12–14]. The crystal structures of LPA compounds involve alternating polar and non-polar zones that are stabilized by hydrogen bonds and Van der Waals interactions. Hence they are optically more nonlinear than inorganic materials [15]. The present work deals with the growth

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and crystal structure determination of a newly synthesized L-phenylalaninium methanesulfonate single crystal by slow solvent evaporation technique at room temperature. The structure of the grown crystal is analyzed by single crystal XRD, NMR, FT-IR, FT-Raman analysis. Further, systematic studies are carried out through UV–Visible absorption studies, thermal analysis and powder SHG for exploring the NLO applications of the crystal for the first time in literature.

2. Experimental

2.1. Material synthesis

The titled compound, LPA-MS, was synthesized from L-phenylalanine and methanesulfonic acid taken in the equimolar ratio (1:1) from aqueous solution. The precursor chemicals were dissolved in de-ionized water and stirred well using a magnetic stirrer for about 1 h. The reaction was preceded according to Scheme 1 at room temperature. The solvent was evaporated to obtain the LPA-MS as salt from the solution. The purity of the synthesized compound was improved by repeated re-crystallization process with water.

2.2. Solubility study

The solubility of LPA-MS was analyzed at temperature ranging between 30 and 50 °C in water. The solubility was determined by dissolving the LPA-MS salt in water taken in an air-tight container with continuous stirring. After attaining the saturation the concentration of the solute was estimated gravimetrically. This study shows that the solubility of LPA-MS increases with increase in temperature and the material has positive temperature coefficient of solubility.

2.3. Growth of single crystals

Slow evaporation solution growth method was used to grow the single crystals of the newly synthesized compound, LPA-MS. The saturated solution was prepared in accordance with solubility data and it was constantly stirred for about 3 h using a magnetic stirrer. It was then filtered and kept undisturbed for crystal growth. The grown crystal was harvested after a period of 12 days. A small single crystal with characteristic shape and size was used as a seed for bulk growth. Bulk crystal growth was attempted by submerged seed growth method by just immersing the seed inside the prepared supersaturated solution. The photograph of the as grown crystal is presented in Fig. 1a.

3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

The three dimensional X-ray intensity data were collected by employing single crystal X-ray diffraction measurement using ENRAF nonius CAD4 with graphite monochromatic MoKα radiation of wavelength 0.71073 Å at room temperature. A suitable good quality crystal was selected to subject X-ray diffraction and mounted perfectly on goniometer. Precise unit cell parameters were calculated by least square refinement with the setting angle of 25 well centered reflections using auto-indexing procedure [16]. The program SIR92 and SHELXL-97 were used to solve and refine the structure by full matrix least square refinement on F^2 respectively [17]. The h, k and l index ranges are $-6 \le h \le 6$, $-11 \le k \le 11$ and $-33 \le l \le 33$ respectively [18]. The positions of cation and anion were predicted by prominent peaks of calculated E-map. All the non-hydrogen atoms were refined isotropically monitored by anisotropic refinement [19]. The hydrogen atom attached with carboxyl oxygen atom was refined isotropically and all other hydrogen atoms were positioned in geometrically calculated position with riding model approximation [20,21].

Table 1 represents the crystallographic data and refinement parameter. From this table, it is clearly found that the compound was crystallized in orthorhombic spacegroup with Z = 4. The bond length and bond angle for crystal are listed in Table 2. The final atomic coordinates and isotropic displacement parameters of non-hydrogen atoms are listed in Table 3. The anisotropic thermal parameters for non-hydrogen atoms with their s.u,'s parentheses are shown in Table 4. Table 5 gives the isotropic thermal parameters of hydrogen atoms.

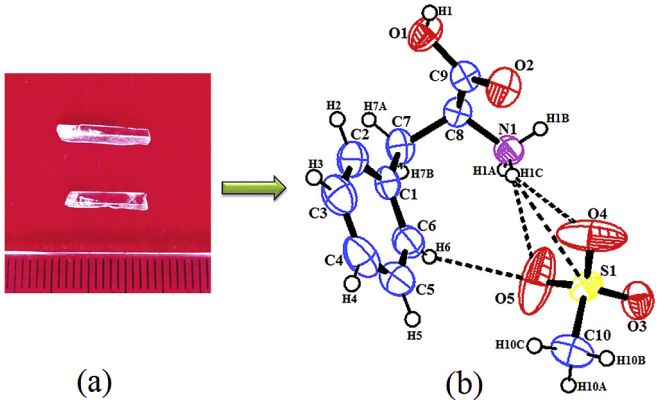
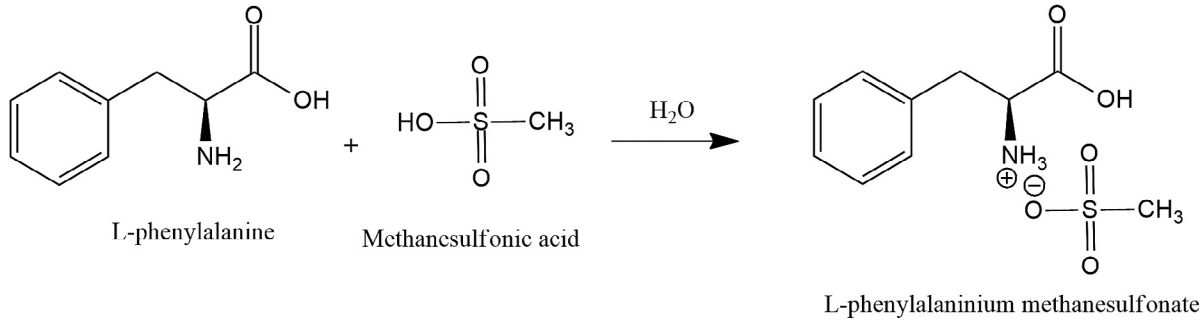


Fig. 1. (a) Photograph of grown LPA-MS single crystal (b) The molecular structure of LPA-MS with atomic numbering scheme.



Scheme 1. Reaction scheme of L-phenylalaninium methanesulfonate.