

Growth, thermal and optical studies of a new organic NLO material: L-methionine L-methioninium hydrogen maleate

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A new organic nonlinear optical crystal, L-methionine L-methioninium hydrogen maleate was crystallized from aqueous solution. Bulk crystals were grown using submerged seed solution method and characterized using single crystal X-ray diffraction. The thermal decomposition of the material was analyzed by thermogravimetric analysis. The various vibrational modes of the functional groups were identified by using Fourier transform infrared spectroscopy. Optical behavior such as transmission spectra and second harmonic generation efficiency were investigated to explore the nonlinear optical characteristics of the material. The second harmonic conversion efficiency is 90% of that of the standard potassium dihydrogen phosphate.

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1. Introduction

Organic and polymer second-order nonlinear optical(NLO) materials have been intensively studied in the past decade for their potential in high-speed electro-optic (EO) devices with very broad bandwidth (up to 200 GHz) and low driving voltages (<1 V)[1,2]. Among recently developed nonlinear crystals, organic molecular crystals stand out in view of their high nonlinearity and high laser damage threshold in the pulsed regime. The donor and acceptor groups provide the ground state charge asymmetry for the molecule, which is required for second order nonlinearity. In this context, amino acids are interesting materials for NLO applications as they contain a proton donor carboxylic acid (COOH) group and the proton acceptor amino (NH₂) group in them [3].

It will be useful to synthesize organic NLO materials and study their structural, thermal, optical and nonlinear properties. In our laboratory, a program has been launched to find new organic NLO materials especially from the amino acid family. Such work on L-Alaninium maleate [4], L-Prolinium tartrate [5], glycine nitrate [6], L-Cysteine tartrate, L-Histidine nitrate [7] and L-Tartaric acid [8] were recently reported from our laboratory. Presently, another new organic NLO material from the amino acid family viz., L-methionine L-methioninium hydrogen maleate (LMMM) was synthesized and bulk crystals were grown by submerged seed solution method. The single crystals were characterized using X-ray diffraction studies. In this article, the bulk growth of LMMM, thermal studies using TGA/DTA, optical studies using FTIR spectra, UV-Vis-NIR spectra and SHG studies of the powdered material are discussed. For large SHG coefficient, the molecule possess a powerful σ/π electron donor group, a powerful σ/π electron acceptor and a π -

conjugated polarizable bridge connecting donor and acceptor [9]. The π electrons present in the carboxylate group, carboxylic group and C=C group have a role in the nonlinear behavior of this material.

2. Experimental

2.1 Crystal growth

LMMM crystals were obtained by slow evaporation of an aqueous solution containing L-Methionine and maleic acid (Sd. fine, India) in the 2:1 ratio. Optically clear and well-shaped crystals suitable for usage as seed crystals were obtained in a period of few days. Bulk crystals were grown using the seeds in a saturated solution of LMMM in a crystallizer, using submerged-seed solution growth method. Transparent crystals of size: $13.0 \times 8.0 \times 5.0$ mm³ were obtained in a period of about four weeks (Fig. 1). The density of the crystal was determined as 1.42(3) gm /cm³ using the floatation method.



Fig. 1. Photograph of LMMM crystal.

2.2 Characterization

The grown crystals were subjected to single crystal X-ray diffraction using Nonius CAD-4/MACH 3 diffractometer, with MoK α radiation ($\lambda=0.71073$ Å). The cell data were obtained from the least-squares refinement of the setting angles of 25 reflections. The nonlinear optical conversion efficiency was tested using a modified setup of Kurtz and Perry [10]. A Q-switched Nd:YAG laser beam of wavelength 1064 nm was used with an input power of 10.5 mJ/pulse and pulse width of 10 ns, the repetition rate being 10 Hz. The crystals of LMMM were ground to a uniform particle size of about 125 – 150 μm and then packed in a capillary of uniform bore and exposed to laser radiations. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation ($\lambda = 532$ nm) from the crystal. The intensity of the green light was measured using a photomultiplier tube. The FTIR spectra of the sample were recorded in KBr phase in the frequency region of 400 – 4000 cm^{-1} using a Jasco Spectrometer (FTIR, model 410), at a resolution of 4 cm^{-1} and with a scanning speed of 2 mm/sec. Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out for the crystals, using a SDT Q600 V8-2 build 100 thermal analyzer. A powder sample was used for the analysis in the temperature range of 26 °C to 800 °C with a heating rate of 10 °C/min. The crucible used was of alumina (Al_2O_3), which served as a reference for the sample. The transmission spectrum was recorded using a VARIAN (Cary 500) UV-Vis-NIR spectrophotometer in the range of 200-1100 nm covering the entire near ultraviolet, visible and NIR regions.

3. Results and discussion

3.1 Single crystal X-ray diffraction studies

The single crystal studies revealed that LMMM crystallized in a non-centrosymmetric unit cell with the space group of P2₁. The crystallographic data are: $a = 12.981(8)$ Å, $b = 5.326(3)$ Å, $c = 15.124(9)$ Å, $\beta = 114.09(12)^\circ$, volume of the unit cell, $V = 954.6(10)$ Å³ and the number of molecules per unit cell, $Z=2$. The details of the structure elucidation are published elsewhere [11].

3.2 Second harmonic generation studies

While LMMM crystal gave a second harmonic signal of 300 mV, the standard KDP crystals gave a SHG signal of 330 mV/pulse for the same input energy. Higher efficiencies are expected to be achieved by optimizing the phase matching angle [12].

The level of SHG response of a given material is inherently dependent on the molecular and supramolecular nature of a given compound. The nature of the crystal packing, local crystal-field effects and intermolecular interactions highly influence the SHG effect [13]. On a molecular scale, the extent of charge transfer (CT) across

the NLO chromophore determines the level of SHG output, the greater the CT, the larger the SHG output. The presence of strong intermolecular interactions, such as hydrogen bonds, can extend this level of CT into the supramolecular realm, owing to their electrostatic and directed nature, thereby enhancing the SHG response [14, 15]. In LMMM, The maleate anion plays a vital role in hydrogen bonding with the amino acid residues. The methionine and methioninium residues are interlinked as dimer, by a strong asymmetric O-H...O hydrogen bond. The oxygen atoms of the maleate anions are involved in hydrogen bonding only with the amino nitrogen atoms of both methionine and methioninium residues. The amino nitrogen atom of the methioninium cation is involved in N-H...O type hydrogen bonds. The maleate anions are arranged as parallel arrays (Fig. 2) and the nearest separation between two maleate planes is 1.57 Å, which falls in the category of π - π stacking. But the mean inter planar spacing between the methionine molecules is 4.22 Å. The former distance is extremely short. Such parallel and close layer-like stacking is very favorable for the promotion of CT through the lattice. Thus, the large number of hydrogen bonds and the layer-like stacking of maleate anions enhance the SHG activity of this material [16].

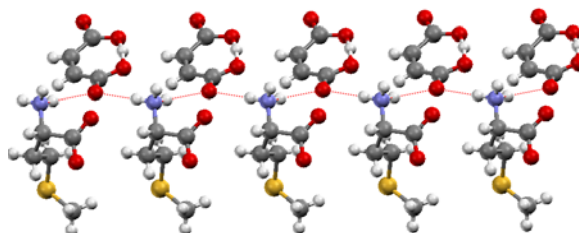


Fig. 2. A view of parallel stacking of maleate anion and the N-H...O hydrogen bonds (dashed lines) of methioninium residue running along the b-axis of the unit cell.

3.3 Thermal studies

The TGA/DTA curve is shown in Fig. 3. An endothermic peak observed at 122.27°C in the DTA corresponds to the melting point of the crystal. The possible decompositions are as follows. In the first stage of decomposition, maleic acid started to decompose and released two CO₂ molecules, one by one, between 150°C to 230°C. This accounts for the loss of weight of 21.2% of the substance. On further heating, the methionine residue started to decompose. The main ion fragment obtained from methionine [17] is represented by the side chain $\text{CH}_3\text{-S-CH}_2^+$. Other fragments are: $\text{CH}_2=\text{CH-CH}^+\text{-NH}_2$ obtained by the loss of CH_3SH (23.2 %) followed by the loss of amine fragments NH_3 , from the two residues (8.2%) released in the temperature range of 231°C to 350°C. On further heating, two CO₂ molecules got released gradually between 350°C to 460°C corresponding to a weight loss of 21.2%. The remaining molecules got evaporated in the temperature region of 461°C - 650°C.

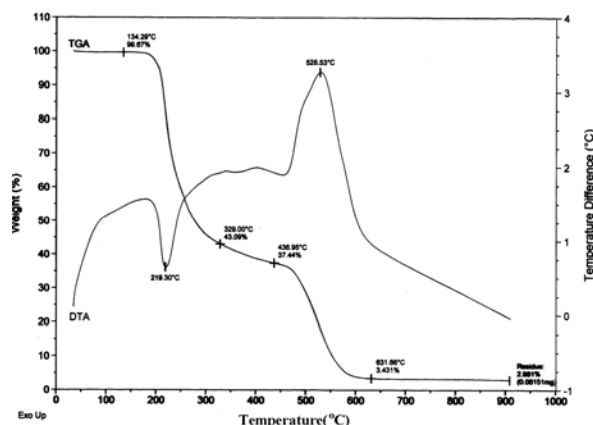


Fig. 3. TGA/DTA of LMMM.

3.4 FTIR and UV-Vis-NIR studies

The recorded FTIR spectra (Fig. 4) were compared with the standard spectra of the functional groups [18]. The asymmetric NH_3^+ stretching vibrations give rise to a band between 3150 cm^{-1} – 3000 cm^{-1} . The broad medium band at 2918 cm^{-1} established the existence of CH_2 -S asymmetric stretching. The strong bands at 1703 cm^{-1} and 1669 cm^{-1} occurred due to the symmetric stretching of C=O group. Similarly, a very strong peak occurred at 1572 cm^{-1} due to the COO^- asymmetric stretching. The stretching vibrations due to C-N (1066 cm^{-1}) and C-C-N (1114 cm^{-1}) are also observed. The twin peaks at 1195 cm^{-1} and 1182 cm^{-1} are assigned to C-O (H) stretching modes.

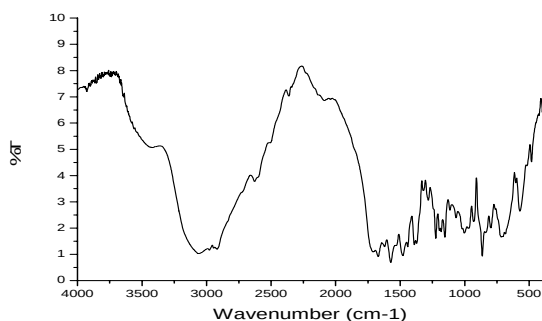


Fig. 4. FTIR spectra of LMMM.

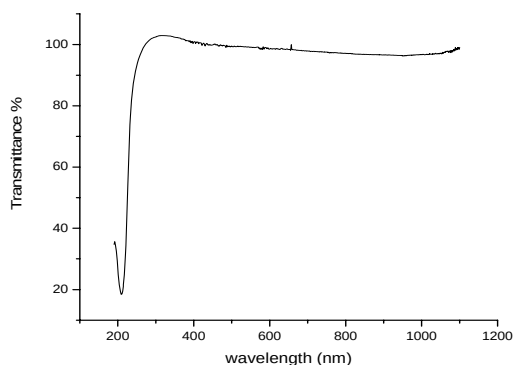


Fig. 5. Transmission spectrum of LMMM.

In the UV-Vis-NIR spectrum (Fig. 5), a strong absorption found at 220 nm is due to the $\pi\text{-}\pi^*$ transition and then there is no remarkable absorption in the entire region of the spectrum. Since the crystal is transparent in the region of $220 - 1200\text{ nm}$, this crystal is suitable for the second harmonic generation of YAG Nd: ($\lambda = 1064\text{ nm}$) laser.

4. Conclusions

A new NLO material from the amino acid family was successfully crystallized. The bulk crystals were grown using submerged-seed solution method. The identity of the material was confirmed using the single crystal X-ray diffraction data. TGA/DTA studies showed that the LMMM crystals are thermally stable without any phase transition upto the melting point (122.3°C). The modes of vibrations of the functional groups were identified using the FTIR spectra. UV-Vis-NIR study showed that the crystal is transparent for the fundamental and the second harmonic generation of Nd: YAG ($\lambda = 1064\text{ nm}$) laser. The SHG efficiency was measured using the Kurtz and Perry method and found to be about 90% of that of the standard KDP crystal. The above results viz., high melting point, transparency in the entire visible region and SHG efficiency showed that this material may have some NLO applications.

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