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Synthesis, crystal growth and physical characterizations of organic nonlinear optical crystal: Ammonium hydrogen L-malate

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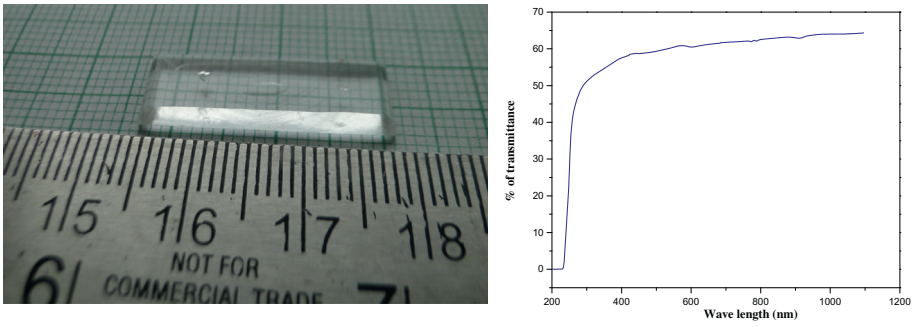
HIGHLIGHTS

- Bulk growth of ammonium hydrogen L-malate crystal in monoclinic system has been grown.
- Chemical structure of compound was established by FT-IR and NMR technique.
- The optical transmission spectrum of AHM crystal reveals 64% transmission in the entire visible region.
- The work hardening coefficient value of AHM is 4.04.
- The second harmonic efficiency of AHM was found to be 1.2 times that of KDP.

GRAPHICAL ABSTRACT



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ABSTRACT

An organic nonlinear optical crystal ammonium hydrogen L-malate (AHM) has been synthesized. Single crystals of AHM have successfully been grown by the slow evaporation solution method. Optically clear single crystals having dimensions up to $23 \times 9 \times 4$ mm^3 have been grown. Single crystal X-ray diffraction study confirms that the AHM crystallizes in orthorhombic crystal system with space group $P2_12_12_1$. The powder X-ray diffraction pattern of the grown crystal has been recorded. FT-IR spectrum was recorded to identify the various functional groups of AHM. The UV–vis–NIR transmission was analyzed for grown crystal. Thermal analysis was performed to find out thermal stability of the compound. Vickers microhardness measurements were carried and also work hardening coefficient has been found. The crystalline perfection of the grown crystal has been analyzed by HRXRD measurements. The second harmonic efficiency of AHM was found to be 1.2 times that of KDP.

Introduction

Nonlinear optical (NLO) materials play a major role in nonlinear optics and in particular they have a great impact on information technology and industrial applications. In the last decade, this effort has also brought its fruits in applied aspects of nonlinear optics. This can be essentially traced to the improvement of the performances of the NLO materials. The understanding of the nonlinear polarization mechanisms and their relation to the structural characteristics of the materials has been considerably improved. The new development of techniques for the fabrication and growth of artificial materials has dramatically contributed to this evolution. The aim is to develop materials presenting large nonlinearities and satisfying at the same time all the technological requirements for applications such as wide transparency range, fast response, and high damage threshold. But in addition to the processability, adaptability and interfacing with other materials improvements in nonlinear effects in devices, led the way to the

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study of new NLO effects and the introduction of new concepts. Optical solutions, optical switching and memory by NLO effects, which depend on light intensity, are expected to result in the realization of pivotal optical devices in optical fiber communication (OFC) and optical computing which make the maximum use of light characteristics such as parallel and spatial processing capabilities and high speed.

The current trend of research activities focuses much attention on materials suitable for displaying excellent second order nonlinear optical (SONLO) properties in view of their potential applications in optoelectronics, telecommunications and optical storage devices. Of particular interest are the materials which can generate highly efficient second harmonic blue–violet light by using laser diodes. Materials with large second-order optical nonlinearities, short transparency cutoff wavelengths and stable physico-chemical performances are needed in order to realize many of these applications [1–5]. In the recent past, extensive investigations are being carried out on organic nonlinear optical materials due to their high nonlinearity, variety of synthetical methods, and better laser damage resistance compared to their inorganic counterparts.

In general, most organic molecules designed for nonlinear applications are derivatives of an aromatic system substituted with donor and acceptor substituents. In this system, the conjugated π-bond enhances the polarizability of the molecule and the donor and acceptor groups contribute their own 'mesomeric moments', which give rise to a high nonlinear optical coefficient. On search for ultraviolet NLO materials with better mechanical properties, we focused attention on small organic molecules, 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. By linking the organic molecules through hydrogen bonds, we can obtain systems with NLO and strong mechanical property. Malic acid, as a chiral α-hydroxy dicarboxylic acid, plays a key role in metabolic pathways of plants and animals and is involved in many fundamental biochemical processes, e.g., the Krebs cycle [6,7] and it is a suitable building block in crystal engineering, being used to create two-dimensional anionic networks held together by hydrogen bonds [8–10]. The presence of complementary hydrogen-bonding sites implies that this optically active molecule ends to form 2D layers by bonding adjacent ions into chains (through head-to-tail O—H···O interactions) that are cross-linked via the hydroxyl group [11]. This tendency seems to be preserved in the presence of a variety of counter ions and because of its specific molecular chirality, its compound crystallizes into non-centro-symmetric structures described by space groups containing only rotation or/and screw axes [12]. Moreover, its chirality ensures the absence of a center of symmetry, essential for optical nonlinear second harmonic generation. Ammonium malate [13], racemic potassium malate [14], zinc malate, 1, 10-phenanthroline [15], cesium hydrogen malate monohydrate [16], strontium bis (hydrogen L-malate) hexahydrate [17], potassium hydrogen malate monohydrate [18], ammonium malate (racemic malic acid) [19] are the famous reported malic acid family crystals. The earlier report by Versichel et al. [20] dealt with the crystal structure of ammonium hydrogen L-malate. In the present investigation, structural, crystal growth, spectral, optical, thermal, mechanical, HRXRD and SHG efficiency of ammonium hydrogen L-malate have been reported.

Experimental procedure

Material synthesis, solubility and crystal growth

The commercially available ammonia and L-malic acid are used for the synthesis. AHM was synthesized by taking ammonia and L-malic acid in 1:1 equimolar ratio. Synthesis was carried out at room temperature using magnetic stirrer. A calculated amount of L-malic acid was dissolved in deionized water and then ammonia added. Its preparative temperature of the solution became 40 °C due to exothermic reaction. To make the solution homogeneous, it was continuously stirred for 6 h and filtered. This filtered solution was evaporated to dryness. The dried salt was collected and used for further growth of AHM crystal. The success of growing large and high-quality single crystals with low defect density is highly dependent on the purity of the starting materials. The synthesized material was purified by repeated recrystallization process. Fig. 1 represents the reaction scheme of the title compound.

The solubility of AHM in water was assessed by the function of temperature in the range 25–50 °C. The experiment was carried out in a constant temperature bath (CTB) with a cryostat facility. The concentration of the solute was determined gravimetrically. The solubility curve is shown in Fig. 2. Based on solubility data, the saturated solution was prepared by using synthesized salt at room temperature. The saturated solution is filtered by using Whatman filter paper. The filtered solution was taken into the 300 ml beaker, tightly covered with perforated sheets to control the rate of evaporation and kept in dust free environment. In order to improve the quality of the crystal further, we carried out the repeated recrystallization process. Optically transparent crystals of AHM have been grown in the period of 25 days by slow evaporation solution technique. The size of the grown crystal was up to $20 \times 9 \times 4\ mm^3$ and it is shown in Fig. 3.

Morphology of the grown crystals was identified by the single crystal X-ray diffraction studies (Bruker Kappa APEXII). It shows that the crystal has 9 developed faces out of which (0 0 1), (0 1 0) and (0 1 1) are prominent faces. The indexed morphology of AHM crystal is shown in Fig. 4.

Ammonia and L-malic acid used in the present study were bought from M/S. Merck and SPECTROCHEM (GR grade) India and the deionized water got from Millipore water purification unit. The resistivity of used deionized water is 18.2 MΩ cm.

Characterization studies

Ammonium hydrogen L-malate crystals have been subjected to various characterization studies to analyze structural, spectral, optical, thermal, mechanical, HRXRD and SHG efficiency studies.

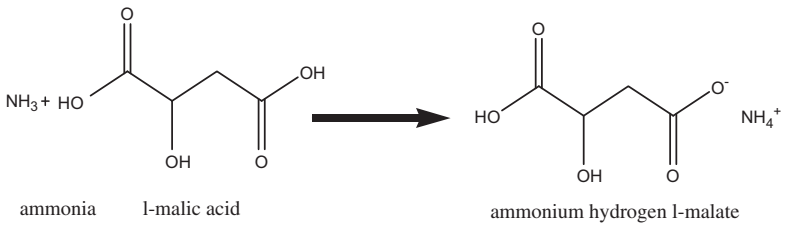

Fig. 1. Reaction scheme of AHM.