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.

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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 × 9 × 4 mm³ have been grown. Single crystal X-ray diffraction study confirms that the AHM crystallizes in orthorhombic crystal system with space group P2₁2₁2₁. 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
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 $20 	imes 9 	imes 4$ 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 APEXI1). It shows that the crystal has 9 developed faces out of which (001), (010) and (011) 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.
The Bruker kappa APEXII single crystal X-ray diffractometer with Mo Kα (λ = 0.71073 Å) was used to measure the cell parameters of AHM crystal. X-ray powder diffraction analysis of AHM crystal was carried out using RICH SEIFERT diffractometer with Cu Kα (λ = 1.5405 Å) radiation over the range 10–70° at a scanning rate 1°/min. The 1H and 13C NMR spectra of AHM were recorded in the range 400–4000 cm⁻¹ employing a JASCO FTIR 410 spectrometer by the KBr pellet method to study the functional groups in sample. Optical properties of the crystals were studied using a PerkinElmer Lambda 35 UV–vis–NIR spectrometer in the region 200–1100 nm. The thermal stability was identified by thermogravimetric (TG) and differential thermal analyses (DTA). Thermogravimetric and differential thermal analysis of AHM crystals were carried out between temperature range 35–300 °C in nitrogen atmosphere at heating rate of 10 °C/min using PerkinElmer Diamond TG/DTA instrument. Grown AHM crystals were subjected to indentation along their most plane surface using MATSUZAWA model MMT-X series microhardness tester fitted with diamond indenter. Load was varied from 1 to 100 g with dwell time of 5 s. The Vickers hardness number (VHN) was determined using the average length of the diagonals by using the relation \( H_V = 1.854 P/d^2 \) kg/mm², where \( d \) is average length of diagonals in mm and \( P \) is the indenter load in kg. Crystal-line perfection of the grown crystal was analyzed by high resolution X-ray diffraction measurement (HRXRD). The second harmonic generation efficiency of AHM has been analyzed by the Kurtz and Perry powder test using a Q-switched Nd: YAG laser with KDP as reference sample.

### Results and discussion

#### Single crystal and powder X-ray diffraction studies

The grown crystal AHM belongs to orthorhombic crystal system with P2₁2₁2₁ space group. The lattice parameters of AHM are \( a = 7.58 \AA, \ b = 10.56 \AA, \ c = 8.08 \AA \), \( V = 646.3 \AA^3 \). From Table 1 one can observe that the unit cell parameters are in very close agreement with the corresponding reported value [20]. X-ray powder diffraction was used to confirm the homogeneity of the sample and the crystallinity of the synthesized AHM crystal. The well-defined sharp peaks are indicating the good crystalline nature of the compound. The indexed powder XRD pattern of the grown crystal is shown in Fig. 5.

#### NMR spectral analysis

In the present investigation, the 1H and 13C NMR spectra were recorded to confirm the molecular structure. The NMR spectral
analysis is the important analytical technique used to the study of the structure of organic compounds. The spectrum is shown in Fig. 6a. An intense singlet peak was observed at δ = 4.70 ppm and is due to the presence of D₂O. The signals N—H and COOH protons do not show up due to fast deuterium exchange taking place in these two groups, with D₂O being used as the solvent. The CH₂ (a) protons of malate yielded their signals at 2.5 and 2.7 ppm and the CH (b) proton of same moiety showed its signal at 4.25 ppm. (a) protons of malate yielded their signals at 2.5 and 2.7 ppm and (b) protons of carboxylate functional group in malic acid.

The FT-IR spectral analysis

The room temperature Fourier Transform Infrared (FT-IR) spectrum of AHM was recorded in the region 400–4000 cm⁻¹ in order to analyze the synthesized compound qualitatively and the presence of functional groups in the molecule. The recorded FT-IR spectrum is shown in Fig. 7. In addition, the O—H stretching peak appears at 3459 cm⁻¹. The asymmetric stretch of N—H is assigned to the peak at 3190 cm⁻¹. The acid group carbonyl (C=O) stretching frequency appears at 1719 cm⁻¹. The asymmetric and symmetric modes of carboxylate anion (COO⁻) occur at 1563 and 1410 cm⁻¹ respectively. The CH₂ bending appears at 1281 cm⁻¹. The peaks at 1344 and 889 cm⁻¹ are attributed to the stretching of the O—H deformation. The peak at 972 cm⁻¹ is assigned to the C—C symmetric vibration. The peak at 650 cm⁻¹ is due to the C—H deformation. The observed vibrational frequencies and their assignments are listed in Table 2.

Optical transmittance spectrum

Transmittance spectrum was taken with 2 mm thickness of the sample. The recorded transmittance spectrum is shown in Fig. 8a. The lower cut off wave length is obtained at 232 nm and there is steady transmittance in the visible region. The transmittance of the AHM crystal is found to be 64% in the range between 240 nm and 1100 nm. The optical absorption coefficient (α) was calculated using the relation

$$\alpha = \frac{2.3036(1/T) / t}{\text{calculated weight loss}}$$

where T is the transmittance and t is thickness of the crystal.

Optical band gap (Eg) was evaluated from the transmission spectra and optical absorption coefficient (α) near the absorption edge is given by [21]:

$$h\nu/\alpha^{1/2} = A(h\nu - E_g)$$

where A is a constant, E_g the optical band gap, h the Planck constant and ν the frequency of the incident photons. The band gap of AHM crystal was estimated by plotting (hv/α)² versus hv as shown in Fig. 8b. As per Tauc’s idea [22], the optical band gap has been calculated from the extrapolation of linear part at absorption edge. The value of band gap was found to be 5.21 eV.

Thermal analysis

The thermal stability of AHM was studied by thermo gravimetric (TG) and differential thermal analysis (DTA). The AHM sample weighing 5.256 mg was analyzed and the thermogram is depicted in Fig. 9. The DTA curve indicates the same changes shown by TG curve. The TG curve shows single stage weight loss pattern when the material is heated from 35 to 280 °C. The first major weight loss occurs between the temperatures 150 and 270 °C with the elimination of 57.5% of the material into gaseous products. The weight loss is due to the loss of CO₂ and one molecule of ammonia (NH₃).

$$\text{C}_4\text{H}_8\text{NO}_5 \xrightarrow{150 \text{ to } 270 \text{ °C}} \text{CO}_2 \uparrow + \text{NH}_3 \uparrow + \text{hydrocarbons}$$

Experimental weight loss : 57.5%
Calculated weight loss : 63%

The weight loss in TGA curve matches with the endotherm in DTA curve. The endotherm at 193 °C suggests that the material melts and simultaneously decomposes. The structural and chemical stability of grown crystal can be considered as one of the strong reasons for possible selection of the material for applications.

Microhardness measurements

The structure and molecular composition of crystals greatly influence mechanical properties. In order to study the mechanical stability, the AHM single crystal was subjected to Vickers microhardness test. The indentations were carefully made on as grown crystal surface (010) with a dwell time of 5 s. The plot between hardness number (HV) and load (p) is shown in the Fig. 10a. It is observed that hardness number increases as load increases. This can
be described on the pattern of depth of penetration of the indenter. When load increases, a few surface layers are penetrated initially and then inner surface layers are penetrated by the indenter with increase in load. The measured hardness is a characteristic of these layers and the increase in hardness number is due to the overall effect on the surface and inner layers of the sample [23]. Beyond 100 g, significant cracks occurred around the indentation mark, which may be due to the release of internal stress generated locally by indentation. By plotting log P versus log d, the value of the work hardening coefficient ‘n’ was found and it is shown in Fig. 10b.

Table 2
FT-IR frequency assignments of AHM crystal.

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Assignments</th>
</tr>
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<tbody>
<tr>
<td>3459</td>
<td>O–H stretching</td>
</tr>
<tr>
<td>3190</td>
<td>Asymmetric stretching of N–H group</td>
</tr>
<tr>
<td>1719</td>
<td>C=O stretching frequency</td>
</tr>
<tr>
<td>1563</td>
<td>Asymmetric modes of carboxylate anion (COO(^{-}))</td>
</tr>
<tr>
<td>1410</td>
<td>Symmetric modes of carboxylate anion (COO(^{-}))</td>
</tr>
<tr>
<td>1281</td>
<td>CH(_2) bending vibration</td>
</tr>
<tr>
<td>1344 and 889</td>
<td>Stretching of the OH deformation</td>
</tr>
<tr>
<td>972</td>
<td>C–C symmetric vibration</td>
</tr>
<tr>
<td>650</td>
<td>C–H deformation</td>
</tr>
</tbody>
</table>

Fig. 6b. $^{13}$CNMR spectrum of AHM.

Fig. 7. FT-IR spectrum of AHM crystal.

Fig. 8a. UV–vis–NIR transmittance spectrum.
According to Onitsch, the value of $n$ is below 1.6 for hard materials and $n > 1.6$ for soft materials [24]. The work hardening coefficient value of AHM is 4.04. Hence, it is concluded that the grown AHM crystal is belongs to soft material category.

**High resolution X-ray diffraction analysis**

A multicrystal X-ray diffractometer designed and developed at National Physical Laboratory [25] has been used to study the crystalline perfection of the single crystal. The divergence of the X-ray beam emerging from a fine focus X-ray tube (Philips X-ray Generator; 0.4 mm, 8 mm; kW Mo) is first reduced by a long collimator fitted with a pair of fine slit assemblies. This collimated beam is diffracted twice by Bonsee Hart [26] type of monochromator crystals and thus the diffracted beam contains well-resolved Mo $K\alpha_1$ and Mo $K\alpha_2$ components. The Mo $K\alpha_1$ beam is isolated with the help of fine slit arrangement and allowed to further diffract from a third (111) Si monochromator crystal set in dispersive geometry (+, -, -). Due to dispersive configuration, though the lattice constant of the monochromator crystal and the specimen are different, the dispersion broadening in the diffraction curve of the specimen does not arise. Such an arrangement disperses the divergent part of the Mo $K\alpha_1$ beam from the Bragg diffraction peak and thereby gives a good collimated and monochromatic beam at the Bragg diffraction angle, which is used as incident or exploring beam for the specimen crystal. The dispersion phenomenon is well described by comparing the diffraction curves recorded in dispersive (+, -, -) and non-dispersive (+, -, +) configurations.

**Fig. 11.** Diffraction curve recorded for a typical AHM single crystal for (200) diffracting planes by employing the PAN analytical MRD diffractometer with Cu $K\alpha_1$ radiation.
Table 3
Comparison of malic acid based organic NLO crystal.

<table>
<thead>
<tr>
<th>Crystal name</th>
<th>SHG efficiency (KDP)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cesium hydrogen l-malate</td>
<td>2.5 times</td>
<td>[16]</td>
</tr>
<tr>
<td>Strontium bis (hydrogen l-malate)</td>
<td>3.4 times</td>
<td>[17]</td>
</tr>
<tr>
<td>Potassium hydrogen malate monohydrate</td>
<td>1.2 times</td>
<td>[18]</td>
</tr>
<tr>
<td>Ammonium malate [racemic malic acid]</td>
<td>2 times</td>
<td>[19]</td>
</tr>
<tr>
<td>Ammonium hydrogen l-malate</td>
<td>1.2 times</td>
<td>Present work</td>
</tr>
</tbody>
</table>

depicts that the crystalline perfection is fairly good. It may be mentioned here that such low angle boundaries could be detected in the diffraction curve only because of the high-resolution of the diffractometer used in the present investigations. Such defects may not influence much on the NLO properties. However, a quantitative analysis of such unavoidable defects is of great importance, particularly in case of phase matching applications as described in our recent article [29].

NLO property

The Kurtz–Perry powder technique remains an extremely valuable tool for initial screening of materials for second harmonic generation [30]. A laser beam of fundamental wavelength 1064 nm, 8 ns pulse width, with 10 Hz pulse rate was made to fall normally on the sample. The power of the incident beam was measured using a power meter. The green light was detected by a photomultiplier tube (Hamamatsu). KDP crystal was powdered to the identical size and was used as reference material in the SHG measurement. The SHG relative efficiency of AHM crystal was found to be 1.2 times that of KDP. The SHG values of some malic acid based organic NLO crystals are given in the Table 3.

Conclusion

Single crystals of ammonium hydrogen l-malate were grown from slow evaporation solution technique. Single crystal X-ray diffraction analysis revealed that the compound crystallizes in an orthorhombic system with non-centro symmetric space group P212121. The powder X-ray diffraction pattern of the grown crystal has been indexed. The modes of vibration of different functional groups present in the sample were identified by the FT-IR spectral analysis. The presence of carbons and protons was confirmed by 1H and 13C NMR analyses. The grown crystals are transparent in the entire visible region. From the TGA curve, it is seen that the material is stable up to 160 °C. Microhardness study revealed that the material belongs to soft material category. HRXRD analysis reveals that the grown crystal has reasonably good crystalline perfection. The relative second harmonic generation efficiency of AHM was 1.2 times that of KDP crystal.

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Reference