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Investigations on the Low Temperature Solution growth, etching, laser damage threshold, Photoluminescence, electrical characterization and nonlinear optical properties of organic material: Ammonium hydrogen L-malate

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ABSTRACT

Optically good quality bulk organic nonlinear optical crystal ammonium hydrogen L-malate (AHM) of crystal size 25 mm × 26 mm × 26 mm has been grown by slow cooling (Low Temperature Solution) method. The grown crystals were subjected to various characterization studies such as chemical etching, UV–vis spectrum, birefringence, laser damage threshold, Photoluminescence studies and second harmonic generation studies. The quality was ascertained by birefringence studies. Piezoelectric charge coefficients of the grown crystal have been determined. The dielectric constant, dielectric loss and ac conductivity of the compound were calculated at different temperatures and frequencies to analyze the electrical properties.

1. Introduction

The fast growing development of optical fiber communication systems has stimulated the search for highly nonlinear materials capable of fast and efficient processing of optical signals. Nonlinear crystals have proven to be interesting candidates for number of applications like second harmonic generation, frequency mixing, electro optic modulation, optical parametric oscillation, etc. [1]. The organic materials are the interesting materials for NLO and other photonic device applications [2]. Another advantage of organic materials is that they combine chemical functionality with their optical properties. Apart from exhibiting nonlinear optical properties, with the inherent charge electron transfer properties between donor and acceptor groups, one of these groups can in addition have redox or proton-transfer capability. Studying the effect of inter and intra-molecular processes directly or indirectly involved in NLO processes will be helpful to design novel crystals for the next generation of NLO devices. 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 p-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 hydroxy dicarboxylic acid, plays a key role in metabolic pathways of plants and animals and is involved in many fundamental biochemical processes [3,4] and it is a suitable building block in crystal engineering, being used to create two-dimensional anionic networks held together by hydrogen bonds [5–7]. Moreover, its chirality ensures the absence of a center of symmetry, essential for optical nonlinear second harmonic generation. Ammonium malate [8], racemic potassium malate [9], zinc malate, 1, 10-phenanthroline [10], cesium hydrogen malate monohydrate [11], strontium bis (hydrogen L-malate) hexahydrate [12], potassium hydrogen malate monohydrate [13], ammonium malate

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(racemic malic acid) [14] are the famous reported malic acid family crystals. The earlier reports were dealt crystal structure, single crystal XRD, FTIR, optical transmission, thermal analysis, microhardness and HRXRD studies [15,16]. In the present study, we report the investigation on the Low Temperature Solution growth by slow cooling method, etching, laser damage threshold, Photoluminescence, electrical characterization and nonlinear optical properties of ammonium hydrogen L-malate.

2. Experimental

2.1. Crystal growth

The procedure of synthesis of AHM was same in literature [16]. The growths of AHM single crystals were carried out by Low Temperature Solution growth technique by slow cooling method. According to the solubility data of AHM in deionized water, the saturated solution of AHM at 40 °C was prepared using recrystallised material. The solution was filtered to remove any insoluble impurities. We carefully ensured that the prepared solution was well within the metastable zone-width region. A constant temperature bath controlled at an accuracy of ± 0.01 °C was used for the Low Temperature Solution growth technique by slow cooling. Transparent and good quality seed crystals of size 5 mm × 4 mm × 3 mm obtained from slow evaporation technique were selected for the growth of bulk AHM single crystals by slow cooling method. The solution was maintained at 43 °C in constant temperature bath for 2 days before seeding. The cooling rate of 0.3 °C/d was employed throughout the growth period till the room temperature was reached. After the completion of the growth run, optically transparent crystal of size 25 mm × 26 mm × 26 mm was harvested (Fig. 1).

2.2. Material characterization techniques

The optical properties of the grown crystals were studied using the Perkin-Elmer Lambda 35 UV–Vis spectrometer in the wavelength region from 200 to 1100 nm. Fluorescence spectra were recorded with the help of Perkin Elmer LS45UV fluorescence spectrophotometer. The chemical etching analysis was carried out using an OLYMPUS U-TV0.5XC-3 optical microscope in the reflection mode. A Q-switched diode array side pumped Nd:YAG laser operating at 532 nm radiation was used for laser damage threshold measurement. The dielectric study was carried out using the instrument, Agilent (Model 4284 A) LCR meter. The piezoelectric studies were made using the piezometer system. A precision force generator applied a calibrated force (0.25 N), which generated a charge on the piezoelectric material under test. Nonlinear optical properties were tested by Kurtz Perry powder technique.

Fig. 1. Photograph of as grown single crystal of AHM from the slow cooling method.

3. Results and discussion

3.1. Optical studies

For optical application, the material considered must be transparent in the wavelength region of interest. The transparent behavior of AHM in the entire UV–vis region is clearly illustrated by its UV–vis spectrum shown in Fig. 2. The lower UV cut-off wavelength of the AHM single crystal is 230 nm. This indicates a single transition in near UV region of AHM. It has a good transparency more than 80%. The higher value in the percentage of transmission may be attributed to a reduced scattering from structural and crystallographic defects [17].

3.2. Chemical etching studies

The nonlinear efficiency of the NLO material mainly depends on the quality of the grown crystals because the segregated impurities and dislocations which occur during growth results in the distortion of the optical beam to be processed [18]. It is very essential to study the microstructural imperfections or crystal defects in the grown crystals [19]. The etching technique is the simplest characterization technique that can be best employed to study the defect structure of a single crystal [20]. However, the success of this technique lies in the efficiency of the chemical etchant to sense the dislocation sites selectively. Subsequently, etch pits are formed at the dislocation centers on those faces at which the additives are bound. The investigation of the morphology of surfaces of crystalline solids is of practical and general interest because many processes such as the growth of epitaxial films, catalytic reactions and nano manipulations are intimately connected with surfaces. In many cases cleavage faces are better than the surfaces prepared by cutting, abrasion and polishing because the latter techniques introduce defects and impurities in the surface layer [21]. Etching is an important tool for the identification of the crystal defects, which is able to develop some of the features such as growth hillocks, etch pits and grain boundaries on the crystal surface.

Etching study was made on the (0 1 0) plane of AHM crystal grown by slow cooling method (Fig. 3). AHM crystal was etched in water for 10 s. Water is a superior etching solution for revealing

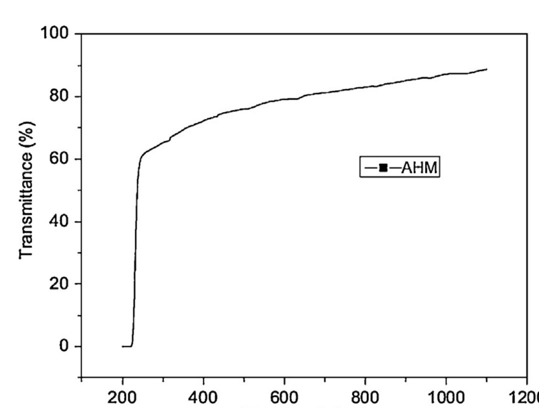

Fig. 2. Transmission spectra of AHM crystal.