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Crystal growth, structural, optical, thermal and dielectric properties of lithium hydrogen oxalate monohydrate single crystal

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ABSTRACT

The vibrational groups of the lithium hydrogen oxalate monohydrate have been investigated by FTIR and FT- Raman analyses. It has low absorbance in the UV-Vis-NIR region. The laser damage threshold study confirms that the material withstands upto 30 mJ with time of 7 s, after that circular dot damage is seen on the surface. The dark region of the surface damage spot occurs due to the thermal effects. The material is thermally stable upto 93 °C and there is no weight loss below this temperature. The dielectric studies were carried out at the frequency regions of 1 kHz–1 MHz and different temperatures from 40 °C to 80 °C. Semi-organic non-linear optical (NLO) single crystal lithium hydrogen oxalate monohydrate has been grown by slow evaporation solution growth technique. The Hirshfeld surface analysis was performed to understand the different intermolecular interactions in the title compound. The fingerprint plots contain the highest portion of H···O/O···H (48.3%) interactions.

1. Introduction

Different optoelectronic materials have motivated researchers to grow semi-organic single crystals for advanced high technology devices. In the recent years, second and third order nonlinear optical materials have evolved as one of the most interesting fields of research for various applications such as amplitude modulation, phase modulation, optical communication, optical electronics, optical data storage, laser frequency shifting, optical limiting, optical data processing and so on. The semi-organic crystals are combining the advantages of both organic and inorganic materials which have high thermal stability, large transmittance range, high laser damage threshold, mechanical strength and so on [1–5]. Lithium hydrogen oxalate monohydrate is one of the semi organic single crystals and crystallizes in triclinic crystal system with the space group P1. It owns strong pyroelectric, dielectric, piezoelectric, elastic and thermoelastic properties. Due to these promising properties, lithium hydrogen oxalate monohydrate crystal makes it a good candidate for image processing, ultrasonic transducers, impact detector and so on [6–9]. Lithium hydrogen oxalate monohydrate has asymmetric hydrogen bond chains along [101] plane [5,6]. There is increasing stress on the development of hydrogen bonds such as O–H···O, N–H···O and C–H···O, which are known to have specific effects on crystal packing modes. The hydrogen bonding materials have promising piezoelectrics and NLO properties [10,11]. The Hirshfeld surface (HS) analysis is a valuable tool for identifying intermolecular interactions and provides quantitative information about the intermolecular interactions maintaining a whole-of-molecule approach [12]. The photoinduced absorption is one of the important factors for increasing second and third order nonlinear optical susceptibility. This originates from the photoinduced electron–phonon anharmonicities [13,14]. Crystal growth is a non-equilibrium process and thus prone to defects incorporation during growth. Defects can be classified as point defects, linear defects, planar defects and volume defects. All these defects influence the quality of the crystal. Hence, evaluating defects provides elaborate information about the crystal quality and functional characteristics of the crystal. Analysis of defects in the crystals is crucial because present and future applications demand defects free single crystals [15–17]. In a previous paper we reported nucleation kinetics, crystal perfection, transmittance, photoconductivity properties of lithium hydrogen oxalate monohydrate crystal [9]. In this article the authors describe single crystal growth of lithium hydrogen oxalate monohydrate crystal by slow evaporation solution growth technique and their intermolecular interactions, FTIR, FT-Raman, optical band gap, thermal, laser damage threshold and dielectric properties.

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2. Experimental section

2.1. Crystal growth

Lithium hydrogen oxalate monohydrate crystal was grown by slow evaporation solution growth technique. To synthesize lithium hydrogen oxalate monohydrate, equimolar amount of lithium sulphate monohydrate and oxalic acid dihydrate were dissolved in deionized water with resistivity of 18.2 MΩ cm. Then, the solution was stirred well using a magnetic stirrer to ensure a homogeneous temperature and concentration throughout the entire volume of the solution. It was filtered using Whatman filter paper (Grade 1 with pore size of 11 μm) to remove impurities and transferred to beaker. According to the solubility data [9], the saturated solution was prepared (40 °C) and it was kept in constant temperature bath at 40 °C. After several days good quality crystals were harvested, which are shown in Fig. 1.

2.2. Characterization technique

The grown crystal was subjected to single crystal X-ray diffraction analysis to confirm the crystal structure by employing Bruker AXS Kappa APEX II CCD Diffractometer, equipped with graphite-monochromated MoKα radiation (λ = 0.7107 Å). Using XPERT-PRO X-ray diffractometer (λ = 1.5406 Å, CuKα radiation), the X-ray powder diffraction pattern was recorded for the finely powdered lithium hydrogen oxalate monohydrate. It was scanned for 2θ values from 10° to 80° at a rate of 2°/m and observed reflection peaks were indexed using the 'TWO THETA' refinement software. Hirshfeld surface and its two-dimensional fingerprint plots were determined using Crystal Explorer 3.1 [18] using crystallographic data. Crystallographic data is downloaded from CCDC and crystal structure was generated using Mercury 3.8 software (Fig. 2). FTIR spectrum of lithium hydrogen oxalate monohydrate crystal was recorded in the range between 4000 cm^{-1} and 500 cm^{-1} with Bruker alpha spectrometer using the attenuated total reflectance (ATR) mode. FT-Raman spectrum was carried out by BRUKER RFS 27 FT-Raman spectrophotometer in the spectral range between 4000 cm^{-1} and 100 cm^{-1} with resolution of 2 cm^{-1} using the Nd:YAG 1064 nm laser source. The TG/DTA was traced for the powdered lithium hydrogen oxalate monohydrate sample of weight 4.55 mg between 40 and 550 °C at a heating rate of 10 °C/min in nitrogen atmosphere using Perkin Elmer Diamond instrument. A Q-switched Nd:YAG laser of wavelength 532 nm, 7 ns pulse width and 10 Hz repetition was employed for the laser damage threshold studies (LDT). The lithium hydrogen oxalate monohydrate crystal was polished using its mother (lithium hydrogen oxalate monohydrate) solution and alumina powder to avoid impurities and imperfections on the crystal surface. Dielectric measurements were carried out using the Agilent Model 4284A LCR meter from 1 kHz to 1 MHz in the temperature range between 40 °C and 80 °C. Square shape crystal (2 mm thickness, 1 cm length and breadth) coated with silver paste on both sides for electrical contact was used.

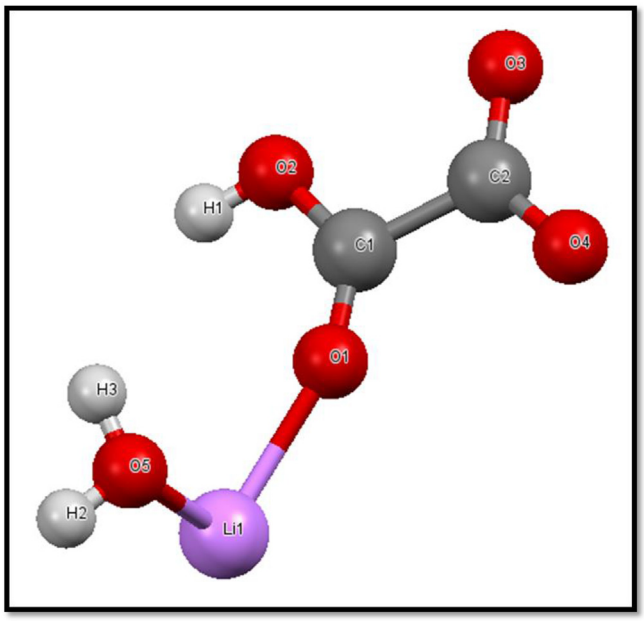

Fig. 2. An ORTEP view of the lithium hydrogen oxalate monohydrate structure: Atom numbering scheme (asymmetric unit).

3. Result and discussion

3.1. XRD analysis

The title compound crystallizes in the triclinic system with the space group P1 with lattice parameters a = 3.45 Å b = 5.09 Å, c = 6.14 Å and α = 78.47°,β = 84.84°, γ = 81.47° and V = 103 $Å^3$. The

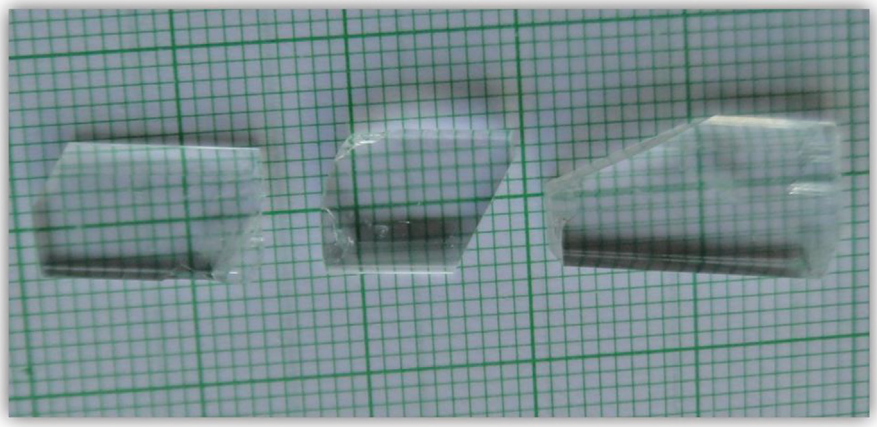

Fig. 1. As grown single crystals of lithium hydrogen oxalate monohydrate.