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Synthesis, crystal growth and structural characterization of lithium fumarate semi-organic single crystals

A. Arunkumar, P. Ramasamy *

Centre for Crystal Growth, SSN college of Engineering, Kalavakkam 603110, India

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ABSTRACT

Lithium fumarate was synthesized and single crystals have been grown by the slow evaporation method. The crystal structure of lithium fumarate has been determined by single crystal X-ray diffraction and it belongs to the monoclinic system. The thermal stability and melting point of the material of LF crystal have been investigated by means of thermogravimetric analysis and differential thermal analysis. The UV–vis–NIR transmittance spectrum was recorded in the range 200–1100 nm, to find the suitability of the single crystal for various optical applications. The mechanical stability of the crystal was analyzed by Vickers microhardness studies.

1. Introduction

Materials exhibiting large optical nonlinearity are of great interest for applications such as frequency conversion, telecommunication, optical computing, optical information processing and high optical disk data storage [1–3]. The common wisdom has been that an optical material should have a large charge transfer and the optical transparency with less dislocation density [4]. Organic materials show prominent properties due to their fast and large nonlinear response over a broad frequency range, inherent synthetic flexibility, and large optical damage threshold. However, organic materials may suffer from problems, such as volatility, low thermal stability, mechanical weakness, etc. Inorganic materials possess excellent mechanical and chemical properties but most of them show low nonlinear efficiency. The need for materials which combine large nonlinear optical characteristics with resistance to physical and chemical attack has led to the investigation of semi-organics [5–8]. Semi-organic materials have the potential for combining high optical nonlinearity and chemical flexibility of organics with the physical ruggedness of inorganics. The diversity of molecular structure gives an opportunity to tune the electronic properties and hence to exploit the linear and nonlinear optical properties. The advantages of semi-organic materials are that they can be grown from aqueous solution and form large three-dimensional crystals. The crystals can be easily cut and polished with specific phase-matching loci, acceptance angle, and the effective nonlinear coefficient for frequency doubling of 1064 nm. In the search for such systems that form cyclic motifs linked by intermolecular hydrogen bonds, we are focusing on the structural properties of molecular complex formed by fumaric acid. This paper reports the synthesis, structure, crystal growth and characterization studies of lithium fumarate (LF) single crystal.

2. Experimental

Synthesis and growth: In the present study, LF salt was synthesized using analar grade lithium hydroxide and fumaric acid in deionized water in a stoichiometric ratio of 1:1. The calculated amount of the lithium hydroxide was dissolved in the deionized water. Then fumaric acid was slowly added to the reaction. The resultant mixture was stirred well for three hours. The prepared solution was filtered by using Whatman filter paper into a beaker and covered with a good quality perforated cover. Finally, the prepared solution was kept in a constant temperature bath of accuracy ± 0.01 °C for the evaporation process. The purity of the synthesized salt was increased by recrystallizing three times. The period of growth ranged from 60 to 75 days. Photograph of grown lithium fumarate crystals is shown in Fig. 1(a). These crystals are non-hygroscopic and optically transparent in nature.

3. Results and discussion

Single crystal X-ray diffraction: The X-ray diffraction intensity data for LF were measured at 293 K using a Bruker AXS Kappa Apex II CCD diffractometer. The wavelength of the MoKα radiation (graphite monochromator) is 0.71073°. The intensity of 5208 reflections was

* Corresponding author. Tel.: +91 9283105760; fax: +91 44 27475166.
E-mail addresses: ramasamyp@ssn.edu.in, proframasamy@hotmail.com (P. Ramasamy).

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recorded in the range 2.59–27.47° of which 1170 unique reflections were recorded. The crystal structure was solved and refined by the SHELXS-97 program [9]. All non-hydrogen atoms of the molecule were located in the best E-map. Full-matrix least squares refinement was carried out using SHELXL97 and the final refinement cycles converged to an $R=0.0356$ and wR $(F2)=0.1097$ for intensity $I>2\,\sigma(I)$. The molecular structure of LF is shown in Fig. 1(b). The ORTEP drawing was performed with the ORTEP3 program [10]. The observed lattice parameter values are $a=0.85440(6)$ nm, $b=0.83608(5)$ nm, $c=0.78289(6)$ nm, $\alpha=90°$, $\beta=113.264(2)°$, $\gamma=90°$ and the volume of

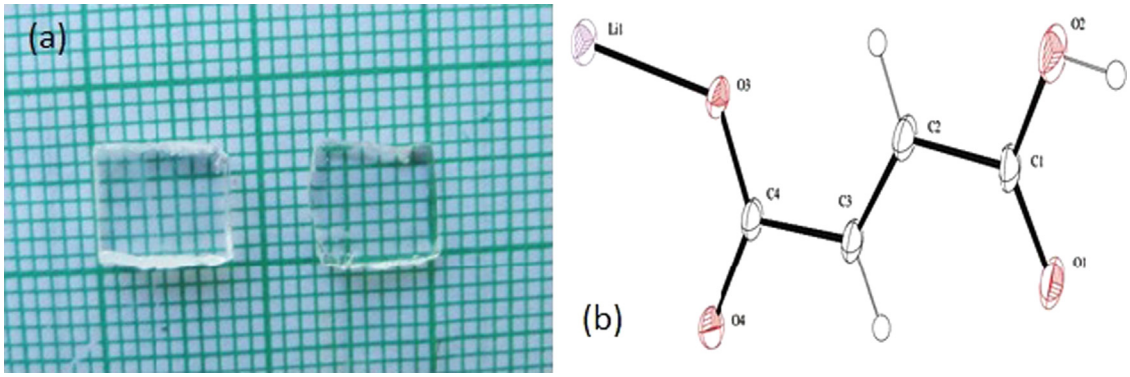

Fig. 1. (a) Photograph of grown crystal and (b) molecular structure of lithium fumarate.

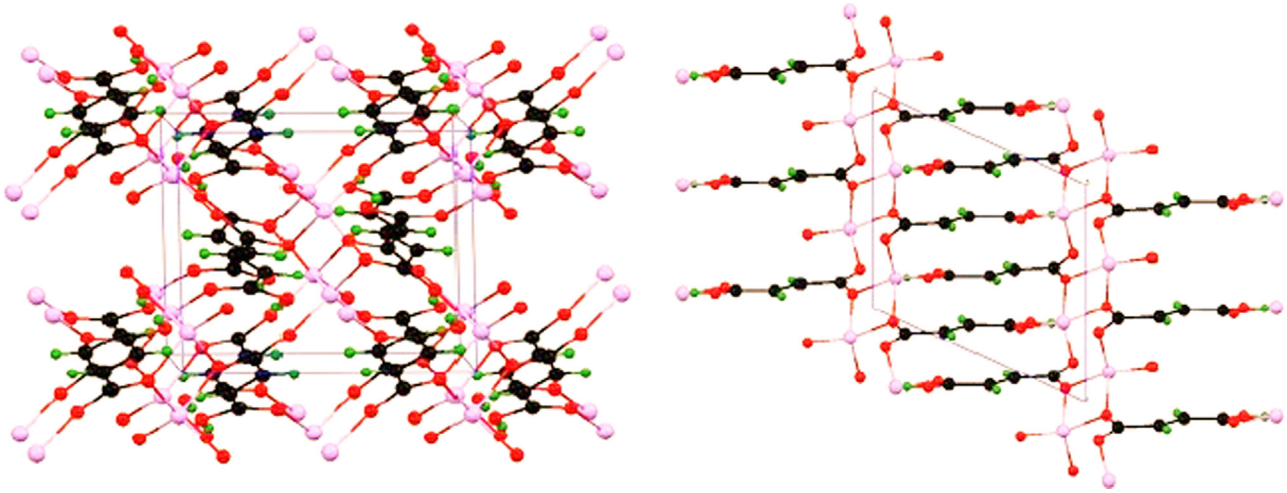

Fig. 2. Packing diagrams of lithium fumarate.

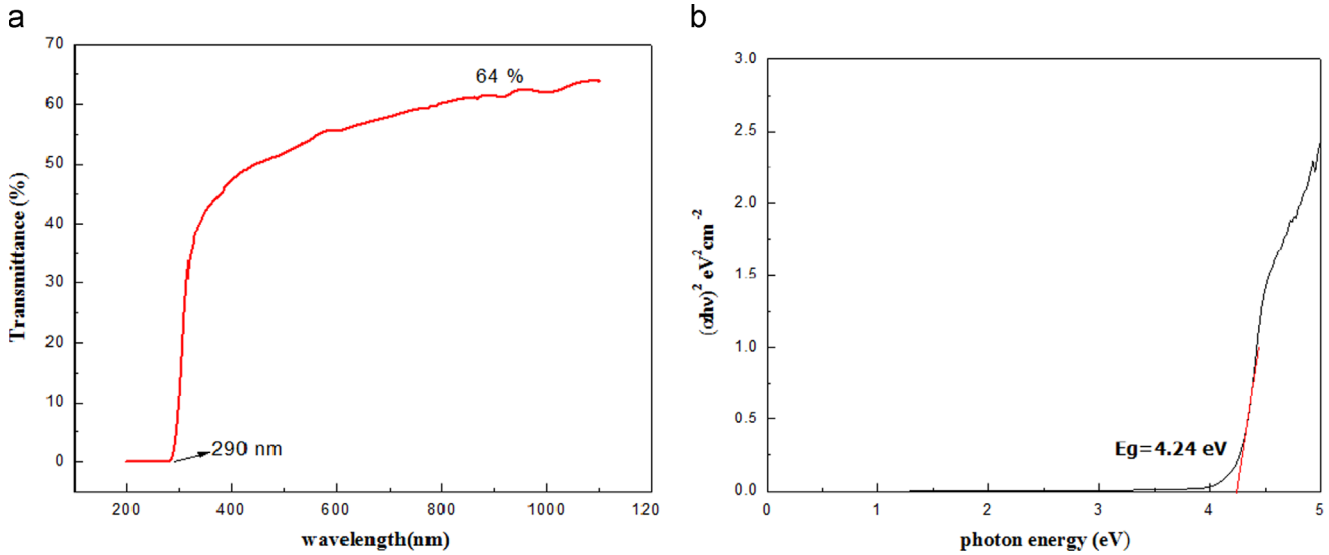

Fig. 3. (a) Transmittance and (b) optical bandgap spectrum of LF crystals.