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Growth and characterization of new semiorganic nonlinear optical and piezoelectric lithium sulfate monohydrate oxalate single crystals

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ABSTRACT

New semiorganic crystal of lithium sulfate monohydrate oxalate (LSO) for nonlinear application was synthesized by controlled slow evaporation method. The growth rate of various planes of the grown crystal was estimated by morphological study. Single crystal XRD analysis confirmed that the crystal belongs to triclinic lattice with space group P1. High transparency (~95%) with large band gap (4.57 eV) was analyzed by UV–vis studies. FTIR and Raman spectroscopy were used to identify various functional groups present in the LSO crystal. SHG efficiency was found to be equal to the KDP crystal. Thermal stability (up to 117.54 °C) and melting point (242 °C) of the crystal were studied by TG-DTA. In dielectric measurements, the value of dielectric constant decreases with increase in frequency. Hardness studies confirmed soft nature of crystals. The piezoelectric coefficient was found to be 6pC/N along [0 0 1].

1. Introduction

Non-linear optical (NLO) crystals have been found to have important applications in various optical devices. Frequency converter in the field of non-linear optics demands a novel material for laser application with good optical response and wide transparency in UV region. The low contribution of lattice ions in second harmonic generation (SHG) efficiency is counted in inorganic crystal, whereas delocalized π electrons are responsible for higher SHG efficiency in organic crystal [1,2]. By considering the above intuition, a new class of NLO materials has emerged in the form of semi-organic crystal with the combined effect of both inorganic and organic class to achieve a higher SHG efficiency. Many times, a single organic materials do not show any optical properties due to the centro-symmetric nature but the scenario changes when it combines with asymmetric inorganic materials. By combining the inorganic material with organic material, the performance of the optical devices was improved for tuning the range of frequencies in NLO application. On the basis of molecular packing, oxalic acid is known to crystallize in two forms viz., α (orthorhombic) and β (monoclinic). Both forms are centro-symmetric in nature and therefore the possibility of NLO activity is ruled out [3]. LSO semiorganic crystals were grown by slow evaporation method and which crystallized in triclinic system with non-centrosymmetric space group P1. The promising NLO activity and piezoelectric properties of LSO crystal makes it a suitable candidate for image processing, ultrasonic transducers, impact detector and position sensors [4,5]. The morphological studies based on Bravais–Friedel–Donnay–Harker (BFDH) law computed for the LSO crystal and were found to be relevant with the experimentally observed growth rate of the various planes present in the crystal [6]. The Vickers microhardness investigation has been carried out on the grown crystal. We have calculated the hardness number (H_v) and Meyer index (n) to understand the hardness of the material [7].

Pure and doped lithium sulfate monohydrate (LSMH) crystals have been grown by different techniques with promising piezoelectric, pyroelectric and NLO properties [8,9]. The property of Lithium ion (also known as hard acid), showing a higher charge density in comparison to all alkali metal and its ability to combine easily with organic and inorganic complexes [10] is being used in various semiorganic crystals. Many lithium sulfate materials such as Glycine lithium sulfate, Lithium sulfate admixtured L-alanine (LSLA), Ethylene Diamine Tetra Acetate doped lithium sulfate monohydrate were reported in the literature showing improved SHG efficiency [11–13]. In this class of materials, lithium sulfate monohydrate oxalate is found to be a promising crystal for the optical and piezoelectric applications. In the present work, we

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have synthesized LSO crystal for the first time and characterized the sample for their structural, optical, SHG, hardness as well as dielectric properties.

2. Experimental procedure

2.1. Crystal growth and characterization

Lithium sulfate monohydrate oxalate (LSO) crystals were grown by dissolving equimolar ratio of both lithium sulfate and oxalic acid in distilled water as a polar solvent. The whole solution was prepared by stirring for 4 h, using a magnetic stirrer to obtain a homogeneous mixture. The completely dissolved solution was filtered using filter paper to remove the suspended impurities and allowed to crystallize by slow evaporation of solvent. The solution was then kept in a constant temperature bath at 30 °C for slow evaporation. Well-defined transparent single crystals of LSO of dimensions 20 mm × 10 mm × 1 mm were grown in 25 days. Single crystal XRD of the LSO crystal (0.8 mm × 0.4 mm × 0.2 mm) was taken using an Oxford diffractometer (MoKα X-ray Source λ = 0.71073 Å). FT-IR spectra were recorded in the frequency range 400–4000 cm^{-1} with the Perkin Elmer Spectrum BX of 2 cm^{-1} resolution using KBr pellets. The UV–vis transmittance spectrum was recorded using a SHIMADZU UV-2501PC in the range 200–1100 nm. Thermal property of LSO crystal was investigated by thermogravimetric (TGA) and differential thermal analysis (DTA) using a Diamond Perkin Elmer system in the temperature range RT – 900 °C at a heating rate of 10 °C/min. SHG measurement was carried out by the Kurtz and Perry powder method. The Vicker's micro hardness tester was used to measure the variation of hardness with respect to the indented load for a fixed time of 10 s. Dielectric measurement was carried out by the impedance analyzer (Agilent E 4980A) in the frequency range 1 kHz-2 MHz at many temperatures between RT-145 °C. Piezoelectric analysis was carried out using Piezometer (PM 300 Piezotest) at a tapping frequency of 110 Hz with tapping force 0.25 N.

2.2. Morphological studies

Crystal morphology is an essential consideration in many applications like optimum packing, separation, pharmaceutical materials, etc [6]. The morphology of the grown crystal was solved by WinX-morph Software [14] and is shown in Fig. 1 along with photograph of LSO crystal. In the crystallization process Van der Walls intermolecular forces, solvent, additives and impurities directly affect the crystal morphology [6]. There are many approaches to predict the crystal morphology in the literature. According to the Gibbs theory, the shape of the crystal is developed to minimize the total surface free energy of crystal-medium interface. The Wulff's theorem states that the formation of a crystal faces are directly related to the surface energies of the faces to bind the crystal system at particular distances. BFDH law was used for simulation of crystal morphology in which surface energy concept is directly related to the interplanar distances d_{hkl}. Therefore, the rate of growth of the given hkl face is inversely proportional to the d_{hkl}. The morphological prediction by BFDH law is applicable in many cases, but sometime it also depends on the interfacial angles with adjacent planes. The modified formula for instantaneous growth rate of hkl face is shown below [15],

$$\frac{dl_{hkl}}{dt} = \frac{R_{h_1k_1l_1}\sin\gamma + R_{h_2k_2l_2}\sin\alpha + R_{hkl}\sin(\alpha+\gamma)}{\sin\alpha\sin\gamma}$$

where R_{hkl},$R_{h_1k_1l_1}$, $R_{h_2k_2l_2}$ are the normal growth rates of the hkl, $h_1k_1l_1$ and $h_2k_2l_2$ faces and its value according to BFDH law is equal to $1/d_{hkl}$, α and γ are the interfacial angles for given hkl plane. Theoretical morphology of the LSO crystal was deduced from the BFDH law and modified BFDH law. Table 1 summarizes the growth rate and morphological importance of the (0 0 1), $(0\bar{1}0)$ (1 0 0) and $(\bar{1}\bar{1}0)$ faces according to above relation. Morphological importance was deduced by both simple and modified BFDH laws. It has been found that the observed morphology of the grown crystal is closely matching with predictions of the simple BFDH law. Hence, it is concluded that the contributions of the growth rates of the adjacent planes in the growth rate of the LSO crystal plane negligible. The order of morphological importance of the LSO crystal by BFDH law directly reflects the corresponding area of the crystal faces.

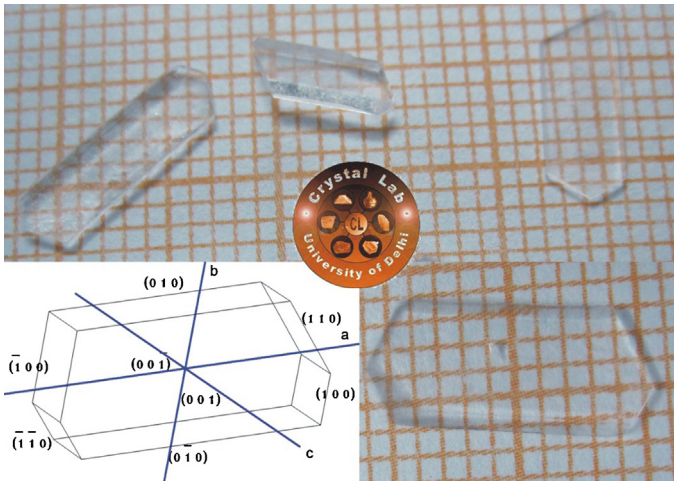

Fig. 1. Morphology of LSO single crystal and photograph of grown LSO crystals.

3. Result and discussion

3.1. XRD analysis

The powder X-ray diffraction studies of LSO crystal were carried out using Bruker D8 Advanced X-ray diffractometer with radiation of wavelength 1.5408 Å (CuKα) in the range of 10–80° at room temperature. The crushed powder sample of the LSO crystal was used for the X-ray diffraction experiment. Indexing of the Bragg peaks has been performed using FullProf software and the value of χ^2 was found to be 1.38 in rietveld refinement [16]. The sharp peak in the powder XRD data confirms the good crystallinity of the grown crystal (Fig. 2). The single crystal XRD data confirms the value of cell parameters of triclinic lattice as $a = 3.4014(4)$ Å, $b = 5.0397(9)$ Å, $c = 6.1204(11)$ Å, $\alpha = 78.620(15)°$, $\beta = 84.951(12)°$, $\gamma = 81.141(13)°$ and $V = 101.45(3)$ $Å^3$. The grown crystal belongs to non-centrosymmetric space group P1. These crystallographic parameters are compared with those of lithium oxalate monohydrate crystal [17]. It has been found that the inclusion of sulfate ion has brought about significant changes in cell parameters but the crystal system (triclinic lattice) and space group (P1) remain unchanged.

3.2. UV–vis transmission spectral analysis

High transmittance in the UV–vis region is significant for optoelectronic and laser threshold applications. The optical transmission spectrum of the grown crystal was recorded in the range from 200 nm to 1100 nm (Fig. 3). UV–vis spectra of the material revealed the information about electron excited from the valance band to conduction band. Transmission spectra have shown good transparency of about 95% in visible region, which is higher than other reported values for similar compounds e.g., ~60% in pure lithium sulfate crystal [8] and therefore it is more