



Bulk crystal growth, optical, mechanical and ferroelectric properties of new semiorganic nonlinear optical and piezoelectric Lithium nitrate monohydrate oxalate single crystal



Jyoti Dalal, Binay Kumar*

Department of Physics and Astrophysics, University of Delhi, Delhi 110007, India

ARTICLE INFO

Article history:

Received 7 November 2015
Received in revised form 19 November 2015
Accepted 20 November 2015
Available online 28 November 2015

Keywords:

Single crystal growth
Optical properties
Dielectric
Piezoelectricity
Ferroelectricity
Mechanical properties

ABSTRACT

New semiorganic nonlinear optical single crystals of Lithium nitrate oxalate monohydrate (LNO) were grown by slow evaporation solution technique. Single crystal X-ray diffraction study indicated that LNO crystal belongs to the triclinic system with space group P1. Various functional groups present in the material were identified by FTIR and Raman analysis. UV–vis study showed the high transparency of crystals with a wide band gap 5.01 eV. Various Optical constants i.e. Urbach energy (E_u), extinction coefficient (K), refractive index, optical conductivity, electric susceptibility with real and imaginary parts of dielectric constant were calculated using the transmittance data which have applications in optoelectronic devices. A sharp emission peak was found at 438 nm in photoluminescence measurement, which revealed suitability of crystal for fabricating violet lasers. In dielectric studies, a peak has been observed at 33 °C which is due to ferroelectric to paraelectric phase transition. Piezoelectric charge coefficients ($d_{33} = 9.2$ pC/N and g_{33}) have been calculated, which make it a suitable for piezoelectric devices applications. In ferroelectric studies, a saturated loop was found in which the values of coercive field and remnant polarization were found to be 2.18 kV/cm and 0.39 $\mu\text{C}/\text{cm}^2$, respectively. Thermal behavior was studied by TGA and DSC studies. The relative SHG efficiency of LNO was found to be 1.2 times that of KDP crystal. In microhardness study, Meyer's index value was found to be 1.78 which revealed its soft nature. These optical, dielectric, piezoelectric, ferroelectric, mechanical and non-linear optical properties of grown crystal establish the usefulness of this material for optoelectronics, non-volatile memory and piezoelectric devices applications.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Nonlinear optical (NLO) materials are of great interest for their potential applications such as frequency conversion, optical data storage technology, telecommunications, optical information processing and computing [1,2]. Organic materials have large non-linear susceptibilities, low thermal stability and mechanical weakness etc. due to weak Van der Waals and hydrogen bonds. While inorganic materials possess excellent mechanical strength and high degree of chemical inertness, however they have poor optical nonlinearity [3]. In organic nonlinear optical crystals, the external illumination by lasers of different wavelengths causes the changes in absorption spectra of material, which may occupy or depopulate the trapping molecular states. These photoinduced changes are due to the formation of polarized electron–phonon states and

may lead to an increase in the second-order non-linear optical susceptibility [4]. Triglycine selenate [5] and triglycine zinc chloride materials exhibit photoinduced changes in optical behavior which may be due to the large difference between their intermolecular and intramolecular chemical bonds. These photoinduced changes lead to the large number of defect levels within the energy band gap of material. A semiorganic material, formed by combining an organic and inorganic molecules, possesses promising NLO and mechanical properties [6,7]. In semiorganic crystals, among all alkali metal ions, Lithium ion has been used which has a higher charge density in comparison to other metal ions and it has ability to combine with organic and inorganic complexes [8]. Many lithium compounds have NLO activity, because according to PVLX bond theory, the Li–O bonds contribute to the crystal nonlinear optical tensors [9]. Among them, lithium iodate (LiIO_3) [10], lithium niobate (LiNbO_3) [11] and lithium nitrate based materials i.e. Glycine lithium nitrate [12] and Bisglycine lithium nitrate [6] have received attention due to their potential applications.

* Corresponding author.

E-mail address: b3kumar69@yahoo.co.in (B. Kumar).

Bisglycine lithium nitrate crystals exhibit luminescent and piezoelectric properties along with non-linear optical activity due to which they can be used in solid state laser sources, transducers and sensors. Glycine sodium nitrate compound is an interesting material which exhibit different kinds of photo-induced changes like photo-induced absorption, photoinduced electron–phonon anharmonicities etc. in optical behavior. These photo-induced changes, which are due to the difference between the inter-molecular and intra-molecular chemical bonds in the material can also change the non-linear effects [13]. Hydrogen bonding dynamics of Lithium Nitrate Trihydrate have also been reported [14]. In addition, organic hydrate crystals like L-lysine monohydrochloride dihydrate for nonlinear optics possess also promising elastooptical and electrooptical properties [15]. On the basis of molecular packing, oxalic acid crystallizes in two forms i.e. α (orthorhombic) and β (monoclinic) which are centrosymmetric in nature and hence they do not possess any NLO activity [16].

In addition to non-linear optical property, dielectric property of a material is an important parameter for device applications. For fabricating NLO devices, the material should have low dielectric constant, which means material supports an electrostatic field with minimal heat energy dissipation [17]. Thus a low dielectric materials have low power consumption and decrease R_c delay in microelectronics [18]. In the present investigation, we report synthesis, growth, optical, dielectric, piezoelectric, ferroelectric, mechanical and NLO properties of a new semiorganic crystal Lithium nitrate oxalate monohydrate for the first time. Due to good piezoelectric and ferroelectric behavior combined with good optical and low dielectric constant value, LNO crystals can be used in microelectronics, transducers and Optoelectronics devices.

2. Experiment details

2.1. Crystal growth

Lithium nitrate oxalate monohydrate was synthesized by taking Lithium nitrate (LiNO_3) and oxalic acid in the molar ratio of 1:1. The calculated amounts of these were dissolved in distilled water. The prepared solution was stirred well using a magnetic stirrer for 4 h to get a homogeneous mixture and kept in a constant temperature oil bath at 40 °C (accuracy of 0.01 °C). In a period of about 15 days, LNO transparent single crystals with sizes up to $25 \times 3 \times 2 \text{ mm}^3$ were obtained which are non-hygroscopic (Fig. 1).

2.2. Characterization techniques

Grown LNO single crystal was subjected to single crystal X-ray diffraction data analysis using an Oxford Diffractometer with Mo K_α radiation ($\lambda = 0.7107 \text{ \AA}$) to determine the unit cell dimensions. The obtained LNO single crystals were finely ground and subjected to powder X-ray diffraction analysis using Bruker, Discover D8 with graphite-monochromated Cu K_α radiation having wavelength, $\lambda = 1.5405 \text{ \AA}$. This powder XRD pattern obtained in the 2θ range of 5–70° with step size of 0.02° was further refined using checkcell software for indexing the peaks. To confirm various functional groups in grown crystal, Fourier transform infrared spectra were recorded using a Perkin Elmer FTIR spectrometer in the middle infrared region of 400–4000 cm^{-1} while Raman spectra were recorded at room temperature using a FT-Raman spectrophotometer with argon ion laser at 514.5 nm in the range 400–3000 cm^{-1} (spectral resolution = 0.1 cm^{-1}). For analyzing its optical properties, the absorption spectra (spectral resolution = 1 nm). were recorded in the region between 200 and 1100 nm using an evolution 300 spectrophotometer. During this analysis, baseline corrections were performed in order to get required material data only as

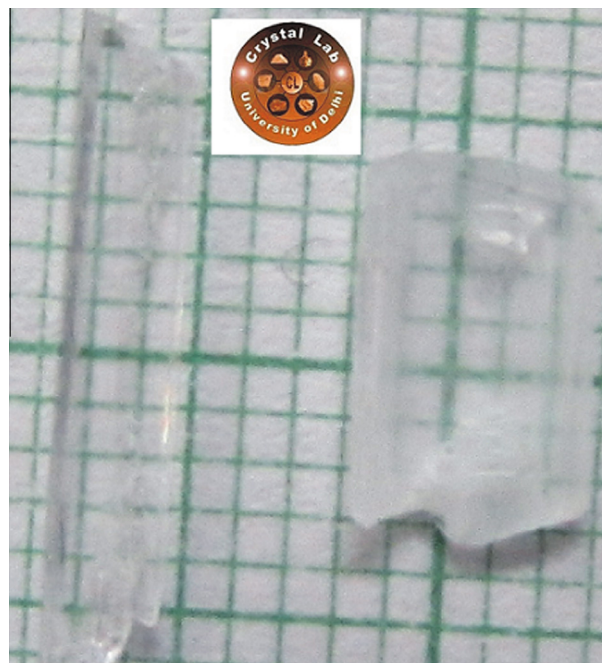


Fig. 1. Photographs of grown LNO crystal.

sample was taken in liquid form by dissolving in water solvent. Photoluminescence spectrum was recorded using Varian Cary Eclipse fluorescence spectrophotometer by exciting the crystal at 450 nm at room temperature. Using an Agilent E4980A LCR meter with a sample holder (Agilent Model 16048A), the dielectric measurements were taken at a heating rate of 0.25 °C min^{-1} . For piezoelectric property, firstly grown crystals were poled using a DC poling unit by immersing them in high-density silicon oil and then the piezoelectric charge coefficient (d_{33}) was measured using PM-300 piezometer system. For ferroelectricity, hysteresis loop was traced using an automatic P - E loop tracer. Hardness measurements were taken using a Vickers hardness tester fitted with a Vickers diamond pyramidal indenter, in which indentations were made for loads in the range 5–100 g for a dwell time of 10 s. Thermal analysis was carried out using a Diamond Perkin Elmer system in the temperature range RT–1000 °C at a heating rate of 10 °C/min in nitrogen atmosphere. In order to find NLO property, the grown crystal was subjected to second harmonic generation studies performed using Kurtz powder technique. In an experiment, grown crystals LON and KDP (taken as a reference), were ground into powdered form with uniform particle size of 63 μm , then packed in a microcapillary tube and finally a Q-switched Nd:YAG laser beam having wavelength 1064 nm was passed through these samples to determine second harmonic generation efficiency. Second harmonic signals were generated from the randomly oriented microcrystals, which were focused by a lens and then detected using a photomultiplier tube and then converted into electrical signal. The amplitude of converted electrical signal displayed on an oscilloscope indicates the SHG efficiency of the sample. The observed emission of green light having wavelength, $\lambda = 532 \text{ nm}$ confirmed the SHG property in the material.

3. Result and discussion

3.1. Single crystal data and PXRD analysis

Grown crystals were analyzed by single crystal X-ray diffraction studies using an Oxford Diffractometer with graphite

Download English Version:

<https://daneshyari.com/en/article/1493538>

Download Persian Version:

<https://daneshyari.com/article/1493538>

[Daneshyari.com](https://daneshyari.com)