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Structural, optical and dielectric studies of novel non-linear Bisglycine Lithium Nitrate piezoelectric single crystal

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ABSTRACT

The novel non-linear semiorganic Bisglycine Lithium Nitrate (BGLiN) single crystals were grown by slow evaporation technique. The structural analysis revealed that it belongs to non-centrosymmetric orthorhombic structure. The presence of various functional groups in the grown crystal was confirmed by FTIR and Raman analysis. Surface morphology of the grown crystal was studied by scanning electron microscopy. The optical studies show that crystal has good transmittance (more than 80%) in the entire visible region and a wide band gap (5.17 eV). The optical constants such as extinction coefficient (K), the reflectance (R) and refractive index (n) as a function of photon energy were calculated from the optical measurements. With the help of these optical constants the electric susceptibility (χ_c) and both the real (ε_r) and imaginary (ε_i) parts of the dielectric constants were also calculated which are required to develop optoelectronic devices. In photoluminescence studies, a broad emission band centered at 404 nm was found in addition to a small band at 352 nm. A broad transition (from 29 to 33 °C) was observed with low dielectric constant value. A high piezoelectric charge coefficient (d_{33}) of 14 pC/N was measured at room temperature which implies its usefulness for various sensor applications. The second harmonic generation efficiency of crystal was found to be 1.5 times to that of KDP. From thermo gravimetric analysis and differential thermal analysis, thermal stability and melting point (246 °C) were investigated. The dielectric behavior, optical characterization, piezoelectric behavior and the non-linear optical properties of the Bisglycine Lithium Nitrate single crystals were reported for the first time which established the usefulness of these crystals for various piezo- and opto-electronics applications.

1. Introduction

Recent advances in semiorganic nonlinear optical (NLO) materials have invoked a large revival of interest in this area of research on account of their widespread industrial potential applications in the field of optoelectronics, photonics, telecommunication, optical computing, optical storage and optical information process [1–5]. Pure organic materials have advantages like high NLO coefficient and flexibility [6] while inorganic counterpart has better strength and physic-chemical stability. A semiorganic material combines the favorable properties of both, resulting in a promising mechanical and NLO properties [7].

Amino-acid family single crystals have been established as highly feasible second-order NLO materials [8–10]. Efforts have been made to combine amino acids with interesting organic and inorganic materials as a substitute to the established inorganic materials like potassium dihydrogen phosphate (KDP), niobates and the borates for NLO applications [11,12]. Some crystals of amino acid complexes with inorganic salts show good physical properties. Glycine is one of the basic amino acid which does not possess any asymmetric carbon atom, making it optically inactive. However, it was reported that the crystals of glycine sodium nitrate [13], glycine silver nitrate [14], diglycine manganese chloride [15], triglycine sulphate [16], etc. exhibit ferroelectric properties. These crystals are used as infrared detectors, transducers and piezoelectric sensors. In addition, other glycine compounds like triglycine zinc chloride [17], glycine sodium nitrate [18] and triglycine selenate [19] are interesting materials for exhibiting different kinds of photo-induced changes in optical behavior due to the large difference between the inter-molecular and intra-molecular chemical bonds and hence also show non-linear effects [17–19]. These photo- induced processes, like photo-induced absorption, may be caused by formation of polarized electron–phonon states which further causes the effects described by second

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harmonic generation [17]. Several other glycine compounds showing non-linear optical properties have been reported [20–24].

Non-centrosymmetric structure has been reported in Bisglycine Lithium Nitrate crystal. Crystal structure refinement, FTIR, FT-Raman analysis and differential scanning calorimetric measurements (DSC) were also reported [25]. It is expected that the crystals having non-centrosymmetric structure will also exhibit SHG and piezoelectric effects. But there are no reports available so far on dielectric, piezoelectric, photoluminescence and NLO characterizations in Bisglycine Lithium Nitrate single crystals. In the present investigation, we have grown single crystals of Bisglycine Lithium Nitrate by solution method and have reported piezoelectric (d_{33} pC/N), SHG efficiency along with optical (photoluminescence, extinction coefficient, refractive index, etc), dielectric and structural characterizations in details.

2. Experiment details

2.1. Synthesis and crystal growth

Pure Bisglycine Lithium Nitrate was synthesized by taking high purity ($\geqslant$99%, Sigma–Aldrich) Glycine $(CH_2NH_2COOH)_3$ and Lithium Nitrate in the molar ratio of 2:1. Then the calculated amounts of glycine salt and Lithium Nitrate were slowly dissolved in the distilled water and the resultant mixture was stirred at 28 °C for 1 h. The prepared solution was filtered twice and kept in a constant temperature bath at 30 °C (temperature sensitivity 0.1 °C) which is free from thermal and mechanical jerks. Transparent colorless large single crystals of size 17 × 12 mm^2 across and 2 mm thick were obtained in about one month time. Photographs of grown crystal are shown in Fig. 1(a) (inset). Morphology of grown crystals showing generated crystal planes and directions was obtained using WinXMorph software and it is shown in Fig. 2(a).

2.2. Characterization techniques

The obtained single BGLiN crystals were finely ground and subjected to powder X-ray diffraction data analysis using Bruker, Discover D8 with Cu Kα radiation (λ = 1.5405 Å). The powder XRD pattern was obtained in the 2θ range of 5–70° with step size of 0.02°. These patterns were further refined by using the Fullprof software. FT-IR spectra of grown crystals were recorded with Perkin-Elmer spectrum BX spectrophotometer in the range of 400–4000 cm^{-1}. For optical analysis, absorption spectra of grown crystal were recorded at room temperature using an evolution 300 spectrophotometer in the region between 200 and 1100 nm. During this measurement, sample was dissolved in water so baseline corrections were done in order to get required material data only. Photoluminescence (PL) analysis was carried out using a Varian Cary Eclipse fluorescence spectrophotometer at room temperature with excitation wavelength of 262 nm. Dielectric measurements were carried out using a Novo control α-S high-resolution impedance analyzer (Agilent E4890A) in temperature ranging from 25 to 70 °C and frequency range from 20 Hz to 2 MHz. Piezoelectric coefficient of grown crystal was measured using PM-300 piezometer system. To find NLO property, the grown BGLiN crystal was subjected to second harmonic generation studies by the Kurtz powder technique. A Q-switched Nd:YAG laser beam of wavelength 1064 nm was passed through the sample to determine second harmonic generation efficiency. The second harmonic signals generated from the sample were focused by a lens and detected using a photomultiplier tube and then converted into electrical signal. The amplitude of converted electrical signal in volts displayed on an oscilloscope indicated the SHG efficiency of the sample. The observed emission of green light (λ = 532 nm) confirmed the SHG property in the material. Thermal studies of the sample were determined by thermo gravimetric (TGA) and differential thermal analysis (DTA) using a Diamond Perkin Elmer system in the temperature range 35–1000 °C at a heating rate of 10 °C/min in nitrogen atmosphere.

3. Result and discussion

3.1. PXRD analysis

Grown crystal of Bisglycine Lithium Nitrate was grounded and subjected to powder X-ray diffraction analysis with Cu Kα radiation of wavelength 1.5405 Å. Fig. 1(a) shows the XRD pattern of the BGLiN in the 2θ range of 5–70°. The powder XRD patterns were refined by Rietveld refinement using Fullprof software. The structural analysis reveals that it belongs to the non-centrosymmetric orthorhombic system with space group $Pca2_1$. In Fullprof software Dicvol PCR file was automatically generated in which indexed h, k, l and lattice parameters in refined form were also obtained. The resulting profile parameters as obtained after the refinement are Chi-Square (χ^2) = 3.60 and R-factors: R_B (Bragg factor) = 0.01076 and R–F factor = 0.06813 where χ^2 is the goodness of fit which has to be minimized, R_B (Bragg factor) = $100[\Sigma|I_{obs} - I_{calc}|/\Sigma|I_{obs}|]$ and R–F (Crystallographic factor) = $100[\Sigma|F_{obs} - F_{calc}|/\Sigma|F_{obs}|]$, where I_{obs} and I_{calc} are the observed and calculated integrated intensities and F is the structure factor. Pseudo–Voight function was used to model the Bragg peaks. The refined graph generated

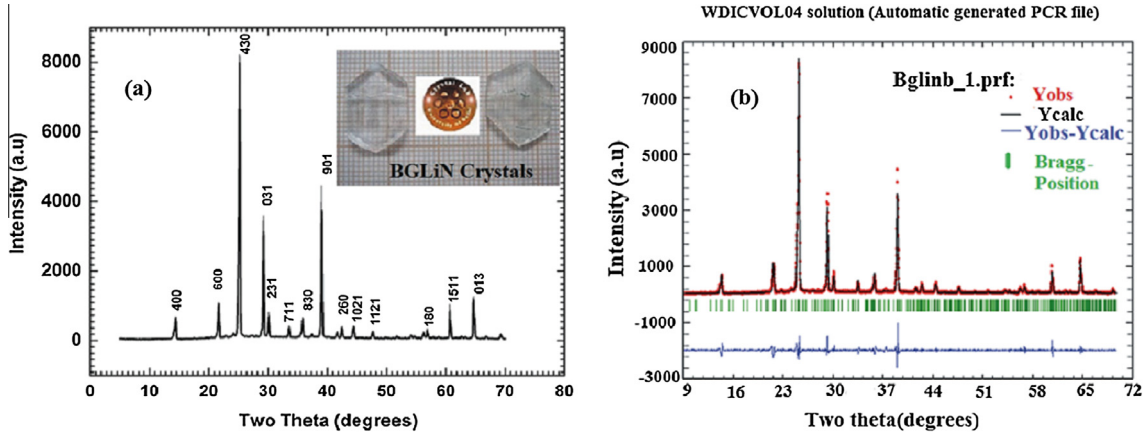

Fig. 1. (a) XRD pattern of BGLiN with photograph of crystals (inset). (b) Fullproof refinement of BGLiN XRD.