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Growth and design of novel nonlinear optical material (NLO) – Glycine barium nitrate potassium nitrate (GBNPN) crystal

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ABSTRACT

A potentially useful semi organic nonlinear optical (NLO) material – glycine with barium nitrate and potassium nitrate (GBNPN) has been synthesized by slow evaporation technique. Good transparent GBNPN crystals were obtained in a time span of 3 weeks. The grown crystals were characterized by single crystal/powder XRD, UV–vis–IR absorption, FTIR, thermal analysis and powder SHG measurements have been studied. The grown crystals were thermally stable up to 137.53 °C. The GBNPN crystal exhibits second harmonic generation efficiency of about 1.35 times than that of potassium di hydrogen phosphate (KDP). Mechanical properties such as micro hardness (H_v) and Mayer's index, n, have been carried out by indentation method. The refractive index (μ) has been measured by the Brewster's angle method.

1. Introduction

The search for new materials with high optical nonlinearity is a potential area for both academic and industrial purpose. These materials have attracted the interests of many theoretical and experimental researchers. In semi organic material, the organic ligand is ionically bonded with inorganic host therefore the semi organic crystals have higher mechanical strength and chemical stability [1]. Most of the organic NLO crystal usually have poor mechanical and thermal properties, and are susceptible for damage during the processing. Pure inorganic NLO material, Potassium di hydrogen phosphate (KDP) and its isomorphs are representative of hydrogen bonded materials which possess important piezoelectric, electro-optic and nonlinear optical properties with excellent mechanical and thermal properties, but possess relatively modest optical nonlinearity [2–4]. Hence it is appropriate to grow semi organic crystals which possess the aspects of organic and inorganic materials resulting in promising NLO properties. Many amino acids have already been reported to have NLO property [5]. L-Arginine phosphate is the first semi organic material discovered in 1983 [6].

In the present work, attempts have been made to crystallize and grow crystals of glycine with barium nitrate and potassium nitrate from aqueous solution at room temperature in the molecular ratio glycine:barium nitrate:potassium nitrate (1:1/4:3/4). Analytical reagent (AR) grade samples of glycine and barium nitrate and potassium nitrate were used to grow the crystals. Here we report the growth, design and characterization such as XRD, UV–vis–IR, FTIR, refractive index (μ), micro hardness, thermal analysis and SHG efficiency measurements.

2. Crystal growth

Glycine, an amino acid, was mixed with inorganic salts such as potassium nitrate and barium nitrate (E mark India) in aqueous solution in the ratio of (1:¼:¾) stirred continuously for 2 h to get a uniform solution. The saturated solution was filtered and allowed to evaporate at room temperature. Good transparent crystals of size 2.4 cm × 0.5 cm were obtained in a period of about 3 weeks as shown in Fig. 1.

The SEM photographs of the grown glycine barium nitrate potassium nitrate crystal are shown in Figs. 2 and 3, respectively. It is observed from the SEM photographs that glycine barium nitrate potassium nitrate crystal have cracks visible inclusions. Also SEM reveals the presence of crystalline islands in the sample.

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Table 1
Unit cell parameters of GBNPN crystal.

Parameter	*a*	*b*	*c*	Alpha	Beta	Gamma	Volume	System
Present study	7.032(2) Å	7.029(2) Å	5.473(40) Å	90.00(0)°	90.00(0)°	120.00(0)°	234(2) Å^3	Hexagonal

3. Results and discussion

The grown crystal has been subjected to single/powder XRD studies. The functional groups have been confirmed by FTIR. The optical behavior was analyzed by UV–vis–IR measurement. The NLO behavior was analyzed by a Q switched Nd-YAG laser. Mechanical strength and chemical stability have been confirmed from the micro hardness and DSC studies.

3.1. Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction analysis was carried out to determine the lattice parameters of GBNPN crystal using Four-circle Enraf Nonius CAD/MACH3 single crystal diffractometer instrument. The wavelength of X-ray used was 0.71073 Å [Target-Mo Kα]. 293 K temperature was maintained during the experiment. The reported values are given in Table 1.

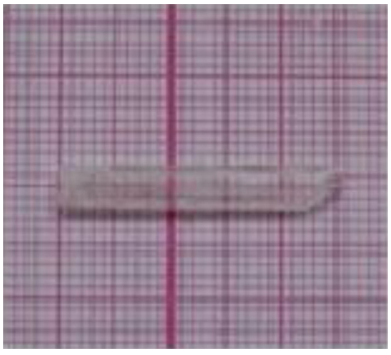

Fig. 1. GBNPN crystal.

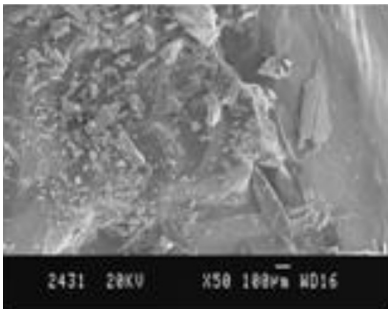

Fig. 2. SEM photograph (50×).

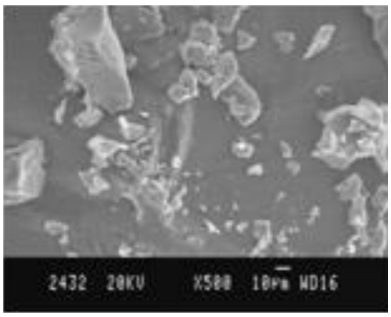

Fig. 3. SEM photograph (500×).

3.2. Powder X-ray diffraction

Powder X-ray diffraction studies were carried out to confirm the crystallinity using Rigaku-Miniflex II X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) in the range 0–100 °C in steps of 10 °C. The powder XRD pattern shown in Fig. 4 reflects the good crystallinity of the grown crystal.

3.3. FTIR spectral studies

The FTIR spectra of the GBNPN crystal was recorded in KBr phase in the frequency range 400–4000 cm^{-1} using FTIR-8400S spectrometer, SHIMADZU model under a resolution of 4 cm^{-1} and with the scanning speed of 2 mm/s. The recorded FTIR spectra shown in Fig. 5 were compared with standard spectra of functional group [7–9]. The tentative assignment is given in Table 2.

3.4. Powder second harmonic generation (SHG)

The nonlinear optical conversion efficiency has been carried out using Kurtz and Perry [10] instrument at Indian institute of science, Bangalore. The Nd:YAG laser beam of wavelength 1064 nm was used with an input power of 4.5 mJ/pulse, pulse width of 10 ns and repetition rate being 10 Hz.

The GBNPN crystal was grounded to a uniform particle size about 130–150 μm. Powder was packed in a capillary of uniform bore and exposed to laser radiation. A powder of KDP, with same

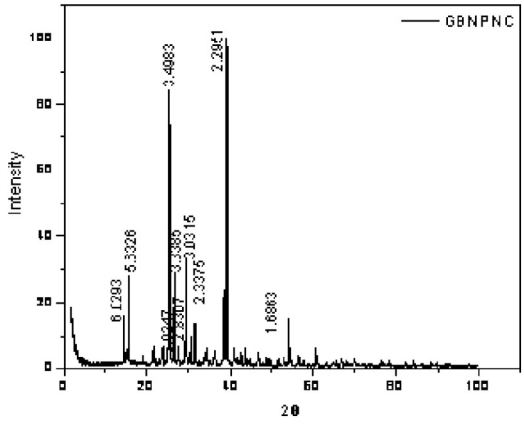

Fig. 4. Powder XRD pattern.

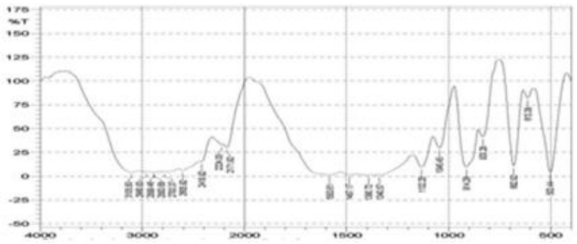

Fig. 5. The recorded FTIR spectra.