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Microhardness, chemical etching, SEM, AFM and SHG studies of novel nonlinear optical crystal – L-threonine formate

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ABSTRACT

The crystal L-threonine formate, an organic NLO crystal was synthesized from aqueous solution by slow evaporation technique. The grown crystal surface has been analyzed by scanning electron microscopy (SEM), chemical etching and atomic force microscopy (AFM). SEM analysis reveals pyramidal shaped minute crystallites on the growth surface. The etching study indicates the occurrence of etch pit patterns like striations and step like pattern. The mechanical properties of LTF crystals were evaluated by mechanical testing which reveals certain mechanical characteristics like elastic stiffness constant (C_{11}) and young's modulus (E). The Vickers and Knoop microhardness studies have been carried out on LTF crystals over a range of 10–50 g. Hardness anisotropy has been observed in accordance with the orientation of the crystal. AFM image shows major hillock on growth surface. The second harmonic generation (SHG) efficiency has been tested by the Kurtz powder technique using Nd:YAG laser and found to be about 1.21 times in comparison with standard potassium dihydrogen phosphate (KDP) crystals.

1. Introduction

Nonlinear optics has emerged as one of the most attractive fields of current research in view of its vital applications in areas of optical switching, optical data storage for the developing technologies in telecommunications and signal processing [1–3]. Applications, such as laser-based imaging, communication, remote sensing, require improved nonlinear optical materials to accomplish such conversions. These applications depend upon the various properties of the materials, such as transparency, birefringence, refractive index, dielectric constant and chemical stability. Second-order nonlinear optical (NLO) materials are much attracted because of their potential applications in the field of optoelectronics [4–7]. In recent years, organic molecular NLO materials have been intensely investigated due to their high nonlinearities, rapid response to electro-optic effect, as compared to inorganic NLO materials [8]. Recently, the amino acid crystals have been subjected to extensive investigations by several researchers owing to their high NLO properties. Amino acids are organic molecules that contain a carboxyl group (–COOH) as well as amino group ($-NH_2$). In the solid state, amino acids contain a protonated amino group (NH_3^+) and deprotonated carboxylic group as well as amino group (NH_2). This dipolar nature exhibits peculiar physical and chemical properties in amino acid which makes them an ideal candidate for NLO application. A series of amino acid compounds, such as L-arginine, L-histidine, L-threonine and glycine, have been grown for NLO applications [9–12].

The growth and characterization of nonlinear optical L-threonine single crystals have been reported by Ramesh Kumar et al. [13]. In this paper, we report on L-threonine formate (LTF), a new nonlinear optical crystal, for the first time in the literature. LTF belongs to tetragonal system and crystallizes in space group "$P4_1$" with cell parameters: $a = 7.86$ Å, $b = 7.86$ Å, $c = 11.07$ Å. In this present investigation, good quality and highly transparent single crystals of LTF have been grown from aqueous solution by the slow evaporation technique. Functional groups are identified by FTIR studies.

The surface features on the grown crystal have been investigated by employing atomic force microscopy (AFM) and scanning electron microscopy (SEM). Etching studies have been carried out to understand the growth mechanism and to assess the quality of grown crystals. Vickers and Knoop microhardness were carried out on LTF single crystals over a load range of 10–50 g. The Vickers (H_v) and Knoop (H_k) microhardness numbers for the above loads were found to be in the range of 61–115 kg mm^{-2} and 70–94 kg mm^{-2}, respectively.

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2. Experimental procedure

2.1. Material synthesis and growth

The title compound L-threonine formate (LTF) was synthesized by L-threonine (99% purity) and analar grade formic acid (98% purity) in the molar ratio 1:1 in triple distilled water. The purity of the synthesized salt was further increased by repeated recrystallization. The reaction of synthesis is depicted in Scheme 1.

$$C_4H_9NO_3 + CH_2O_2 \xrightarrow{-H_2O} C_5H_9NO_4$$

The solution is maintained at a temperature of 35° C. The stirring takes place for nearly 10 h. Then it is allowed to stand for 2 h. The solution is filtered using Whatman filter papers to remove any insoluble impurities. The filtered solution is transferred in borosil glass beaker and optimally closed using a perforated thin polythene sheet and was kept in a constant temperature bath equipped with EUROTHERM temperature controller of accuracy ±0.01 K. The temperature was maintained at 32 °C and solvent was evaporated slowly. Crystals grown by good quality appeared after a period of 16 days.

2.2. Characterization studies

The single crystal X-ray diffraction (XRD) analysis of LTF was carried out using a computer controlled Enraf Nonius CAD4-MV31 diffractometer and the unit cell dimensions and space group were determined. Fourier transform infrared (FTIR) spectrum was recorded by the KBr pellet technique using AVATAR 330 FTIR thermo Nicollet spectrometer for the range 500–4000 cm^{-1} to confirm the functional groups. The surface morphologies of the grown crystal has been investigated using F E I Quanta F E G high resolution scanning electron microscope operated at 30 kV with three modes of operation namely high vacuum (HV) mode for metallic samples, low vacuum (LV) mode and Environment scanning electron microscope (ESEM), for insulating, polymeric and ceramic samples, respectively. The resolution of the microscope is 12 nm gold particle separation on a carbon substrate with magnification from a minimum of 12× to greater than 100 000×.

Etch patterns were observed and photographed under a Carl Zeiss metallurgical microscope – (Axios Kop 40 MAT) provided by Clemex Vision PE software in reflected light. For etching purpose thin crystals of 5 mm thickness were cut from the grown crystal with the help of wet thread. To investigate the perfection of crystalline sample etching studies have been done using proper etchants, such as water, methanol and ethanol. The surface characteristics were studied with the aid of an AFM (Nano Surf Easy Scan 2, Switzerland) with a maximum XY-scan range of 70 μm.

The mechanical studies of L-threonine formate single crystals were made by Vickers and Knoop microhardness tests at room temperature. Crystals, free from cracks, with flat and smooth faces, were choosen for the static indentation tests. The crystal was mounted properly on the base of the microscope. Now, the selected faces were indented gently by loads varying from 10 to 50 g for a dwell period of 10 s using both Vickers diamond pyramid indenter and Knoop indenter attached to an incident ray research microscope (Mututoyo MH 112, Japan).The Vickers indented impressions were approximately square in shape. The length of the two diagonals was measured by a calibrated micrometer attached to the eyepiece of the microscope after unloading and the average was found out. For a particular load at least five well defined indentations were considered and the average of all the diagonals (d) was considered. The H_v was calculated using the standard formula:

$$H_v = 1.8544\,P/d^2, \quad (1)$$

where P is the applied load in kg, d is in mm and H_v is in kg mm^{-2}.

The Knoop indented impressions were approximately rhombohedral in shape. The average diagonal length (d) was considered for the calculation of the Knoop microhardness number (H_k) using the relation

$$H_k = 14.229P/d^2, \quad (2)$$

where P is the applied load in kg, d is in mm and H_k is in kg mm^{-2}.

Crack initiation and fragmentation become significant beyond 50 g of the applied load. So hardness test could not be carried out above this load. From Wooster's empirical relation [14],

$$c_{11} = H_v^{7/4}. \quad (3)$$

SHG studies were carried out using Q-switched Nd:YAG laser (1064 nm, Quanta Ray Series, USA) emitting a fundamental wavelength of 1064 nm.

3. Results and discussion

3.1. Single crystal X-ray diffraction

The single crystals were subjected to single crystal X-ray diffractometer with Mo radiation of wavelength λ = 0.71073 Å to determine the unit cell parameters and space group. LTF belongs to tetragonal system and crystallizes in space group "$P4_1$" with cell parameters a = 7.86 Å, b = 7.86 Å, c = 11.07 Å, $\alpha = \beta = \gamma = 90°$ and cell volume V = 684 $Å^3$.

3.2. FTIR analysis

Fig. 1 shows the FTIR spectrum of LTF. The peak at 2974.66 cm^{-1} shows a broad intense peak resulting from the hydrogen bonded symmetric and asymmetric stretching vibrations of the NH_3^+ group. The band at 1633.41 cm^{-1} was assigned to asymmetric bending of NH_3. The C=O stretch and OH bend of the COOH group observed at 1246.75 and 1347.03 cm^{-1} clearly indicates the unprotonation of carboxylic group in the L-threonine molecule. Rocking of the NH_3 structure was observed with wave numbers 1109.83 and 1184.08 cm^{-1}. The peak at 1040.41 cm^{-1} corresponds

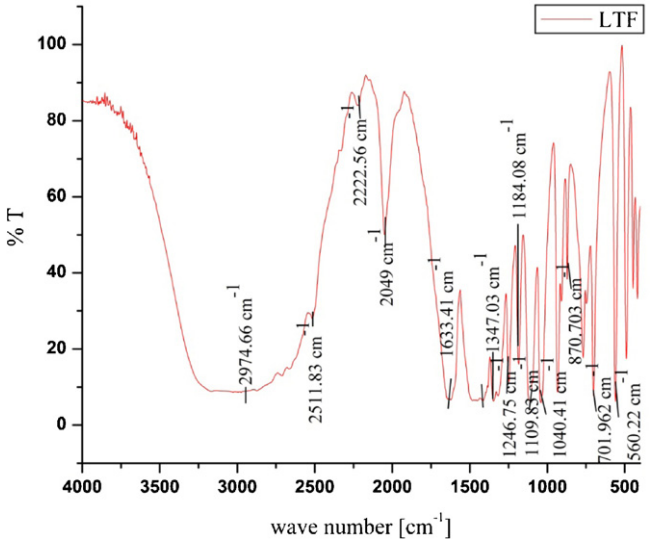

Fig. 1. FTIR spectrum of LTF single crystal.