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Characterization of L-threonine phthalate crystal for photonic and nonlinear optical applications

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ABSTRACT

L-Threonine phthalate (LTP) single crystal, an organic nonlinear optical material, has been synthesized and grown by slow evaporation technique at room temperature. The lattice parameters of the grown crystal have been determined using single crystal X-ray diffraction data. It crystallizes in the monoclinic system with space group C_2/c. The optical parameters: transmission range, extinction coefficient, refractive index and reflectance of the grown crystal were estimated from UV–vis–NIR spectral data. The steady-state photoluminescence spectra were recorded for L-threonine phthalate crystal at room temperature. The photoluminescence peaks show that the LTP crystal has strong ultraviolet and red emissions at 306 nm and 612 nm, respectively. The molecular weight of the new crystal has been ascertained from mass spectroscopic analysis to confirm the formation of the new crystal. The dielectric study of the sample was carried out in the frequency range from 50 Hz to 5 MHz. The mechanical properties of the grown crystal were analysed using Vickers microhardness tester. Since pure L-threonine is capable of generating second harmonic generation, phthalic acid doped L-threonine crystal is unable to generate second harmonic generation due to centrosymmetric nature. *Z*-scan technique was finally used to analyse third order NLO property.

1. Introduction

Nonlinear optics (NLO) is a field of current research because of its importance in providing the key functions of frequency conversion, optical switching, high-speed information processing, optical communication, light modulation, optical memory storage and opto-electronic applications. In recent years, organic nonlinear optical crystals have been studied in detail due to their high nonlinearities and rapid response in electro-optic modulation, frequency mixing, optical parametric oscillation, etc. [1,2]. The research on new organic nonlinear optical materials is attractive for their advantages over the inorganic nonlinear optical materials. In the field of nonlinear optical crystals, amino acids play a vital role. In general, amino acid single crystals have special features like wide transparency in UV as well as in visible region [3]. One of the main advantages of organic materials is that their structure can be modified to get the desired NLO properties. The origin of nonlinearity in organic NLO materials is due to the presence of delocalized π-electron connecting donor and acceptor groups, which enhance the necessary asymmetric polarizability. Organic crystals exhibit extremely large nonlinear optical coefficients, when compared with inorganic crystals [4]. Natural amino acids are, in general, exhibiting the nonlinear optical properties because they are characterized by chiral carbons, a proton – donating carboxyl ($COOH^-$) group and a proton – accepting amino (NH_2^+) group [5].

In the present investigation, we make an attempt to grow and characterize a new material L-threonine phthalate (LTP). LTP crystallizes in the monoclinic system with centrosymmetric space group C_2/c exhibiting third order nonlinear optical behaviour. LTP crystal can find wide applications in opto-electronics and photonics due to third order nonlinear optical behaviour. Hence, in the present study, single crystal XRD analysis, linear optical property, photoluminescence, mass spectral analysis, dielectric and microhardness studies and third order nonlinear optical property are reported to understand the characteristics of the grown crystal.

2. Results and discussion

2.1. Single crystal X-ray diffraction study

LTP crystal grown by solution growth technique was first subjected to single crystal XRD study using Nonius CAD4/MACH3 single

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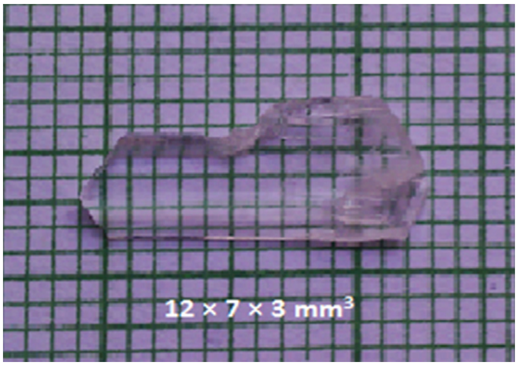

Fig. 1. As-grown LTP crystal.

crystal diffractometer to determine the cell parameters and space group. Fig. 1 shows the photograph of the as-grown LTP single crystal with dimensions of **12** × **7** × **3** mm^3.

Using XRD data provided by SHELEX program, the lattice parameters of LTP crystal were computed. From the results obtained, it is observed that the grown crystal belongs to monoclinic system with centrosymmetric space group C_2/c. The cell parameters determined from single crystal XRD analysis data are found to be a = 5.09 Å, b = 14.40 Å, c = 9.67 Å with $\alpha = \gamma = 90$, $\beta = 93.16$ and V = 709 $Å^3$. These cell parameters are different from those of L-threonine and anhydrous phthalic acid [6,7]. Since the grown material is centrosymmetric in nature, the basic requirement for exhibiting second order nonlinear behaviour is not fulfilled.

2.2. Linear optical properties

In order to explain the optical property of the L-threonine phthalate (LTP) single crystal, UV–vis–NIR transmittance and reflectance spectra were recorded in the range of 190–1900 nm, using Perkin Elmer lambda 35 UV–vis Spectrophotometer. The grown crystal of 2 mm thickness was used for recording the spectrum. From the spectrum, it is clear that the grown crystal has good transparency of about 99% with a lower cut-off wavelength at 300 nm. Due to wide transmission range of 309–1900 nm, the grown crystal can be used for fabricating NLO devices. The transmittance and corresponding reflectance spectra of LTP crystal are shown in Fig. 2. From the spectra, it is observed that the transmittance and reflectance are strongly dependent on applied wavelength.

It is noted that the high transmittance is due to the low reflectance of the crystal. The high transmittance, low reflectance and low refractive index of the material LTP over a wide range of wavelength suggest that the material LTP can be used as anti-reflection coating in solar thermal devices and nonlinear applications [8,9]. The optical constants such as refractive index and extinction coefficient of a material are the most important parameters of nonlinear optical crystal.

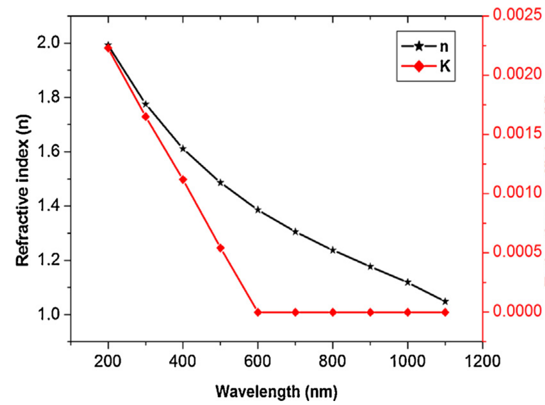

Fig. 3. Refractive index and extinction coefficient of LTP crystal.

The extinction coefficient (K) and refractive index (n) are expressed as,

$$K = \left(\frac{\lambda\alpha}{4\pi}\right) \quad (1)$$

and

$$n = \frac{-(T-2) \pm \sqrt{4-4T}}{T} \quad (2)$$

where λ is the wavelength of the incident radiation, α is the absorption coefficient and T is the transmittance of the crystal. The values of n and K were calculated and their dependence on wavelength is shown in Fig. 3.

From the figure, it is understood that the refractive index n decreases with increasing wavelength. The lower values of refractive index in the higher wavelength region suggest that the LTP crystal has wide transmission in the higher wavelength region. The extinction coefficient decreases abruptly up to 600 nm and almost zero at higher wavelengths. The extinction coefficient indicates the fraction of electromagnetic energy lost due to scattering and absorption [10]. The minimum value of extinction coefficient indicates that the energy lost due to scattering and absorption is negligibly small. Hence, the grown material shows wide transmission over the wavelength region 306–1100 nm required for device fabrications.

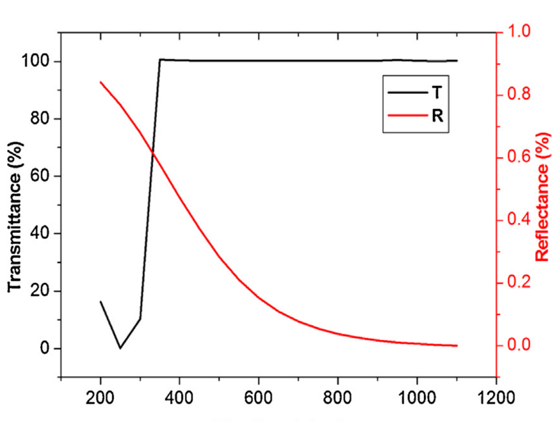

Fig. 2. Transmittance and reflectance spectra of LTP crystal.

2.3. Photoluminescence spectroscopy

Photoluminescence study is one of the standard techniques for characterizing single crystals to identify the various electronic energy levels due to excitation. The steady state photoluminescence spectra were recorded for LTP crystal using Cary 5E UV–vis–NIR spectrometer at room temperature. Photoluminescence in solids is the phenomenon in which electronic states of solids are excited by light of particular energy and the excitation energy is released as light. The photon energies reflect the variety of energy states that are present in the material.

Fig. 4 shows photoluminescence emission peaks recorded in the range of 250–900 nm for the excitation wavelength of 280 nm. There are five emission peaks observed at 306 nm, 340 nm, 415 nm, 612 nm and 680 nm, respectively. The highest emission peaks are observed at 306 nm and 612 nm, respectively. The lowest emission peaks are observed at 340 nm, 415 nm and 680 nm. The UV emission peak at 306 nm is due to the presence of electron donor group NH_2^+ and electron acceptor group $COOH^-$. The strong emission peak at