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Crystal Growth and Nonlinear Optical Properties of L-Tyrosine Doped Picrate (LTP) Single Crystal

D. Arthi[a*], D. Anbuselvi[a], J. Arul Martin Mani[a], D. Jayaraman[b], V. Joseph [a]

[a*]Department of Physics, Loyola College, Chennai, Tamil Nadu, India
[b]Department of Physics, Presidency College, Chennai, Tamil Nadu, India

Corresponding Author: arthi3010@gmail.com

Abstract - L-Tyrosine doped picrate single crystal was grown by slow evaporation solution growth techniques. The crystal system and lattice parameters were determined using single crystal XRD analysis. The transparent range of the grown material was studied using UV-vis-NIR spectral analysis and the optical band gap was evaluated from the absorption spectrum. The modes of vibrations of different molecular groups present in the sample were identified using FTIR spectral analysis. The Second Harmonic Generation efficiency (SHG) was evaluated experimentally to understand the NLO activity of the grown crystal. The solid state parameters such as Penn gap (E_P), Fermi Energy (E_F) and polarizability (α_p) were estimated using dielectric studies.

INTRODUCTION

The search for new materials with high optical nonlinearities is quite interesting because of their practical applications in harmonic generation, amplitude and phase modulation, laser technology, switching and other signal processing devices. Nonlinear optical (NLO) crystals find wide range of applications in the field of telecommunication for efficient signal processing and optical information storage devices. NLO crystals with high conversion efficiencies for second harmonic generation (SHG) and transparency in visible and ultraviolet ranges are required for various devices in the field of optoelectronics and photonics [1-3]. An optical material should have large charge transfer and wide optical transparency with less dislocation density for device fabrication [4]. In the recent past, amino-acid family single crystals are gaining importance as highly feasible second order NLO materials [5].In this paper, we report the growth of single crystal of L-tyrosine doped picrate (LTP) and its characterization using single crystal XRD study, UV-vis-NIR spectral study, FTIR spectroscopy and dielectric, and SHG measurement.

EXPERIMENTAL PROCEDURE

The material LTP was synthesised by dissolving the L-tyrosine and picric acid starting materials in mixed solvent according to stoichiometric ratio of 1:4.

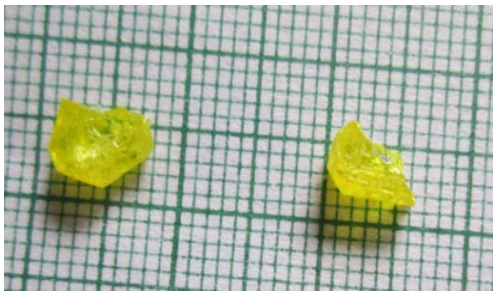

Figure1 Photograph of as-grown LTP crystal

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The solution was continuously stirred with a magnetic stirrer to ensure homogeneity of the solution. The solution was filtered and covered with a perforated lid and kept in a constant temperature bath. The slow evaporation gradually led to supersaturated condition for the nucleation of crystal phase resulting in the formation of tiny crystals of LTP in 10–15 days Fig.1. The dimensions of the grown LCDH are found to be
7 x 3x 2 mm^3.

RESULTS AND DISCUSSION

Single Crystal XRD Analysis

Single crystal XRD analysis was made using Four Circle EnrafNonius CAD4/MACH3 single crystal diffractrometer coupled with a computer program Well shaped, transparent, single crystals of LTP were selected for the study. Single crystal XRD analysis reveals that LTP crystal belongs to monoclinic system. The calculated unit cell parameters are found to be a = 10.01A˚, b = 11.13A˚, c = 21.36A˚ and $\alpha=\beta=\gamma=90^\circ$ and volume V= 2378 $Å^3$. The space group (C_2) is recognized as non-centrosymmetric which satisfies the condition for the material to exhibit NLO behaviour.

UV-VIS-NIR Spectrum Analysis

Figure 3 shows UV-VIS-NIR spectrum of LTP recorded in the wavelength range of 200 - 1100 nm. The material shows the transparent nature from 300 nm onwards, the lower cut-off wavelength beingnm. It is observed that thematerial can readily transmit the laser beam of wavelength 1064 nm for analysing the NLO activity of the crystal.

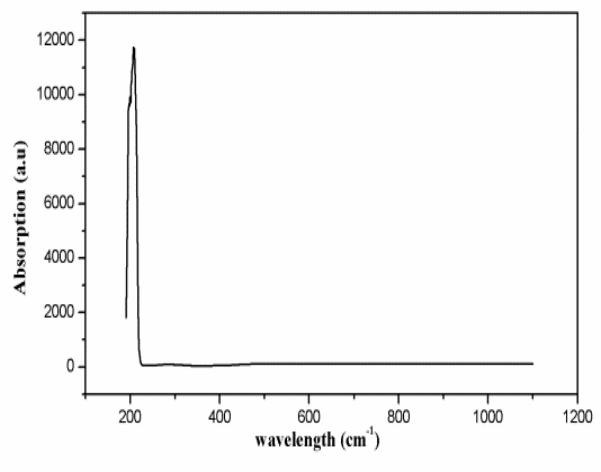

Figure 3 UV–vis–NIR spectrum of LTP crystal

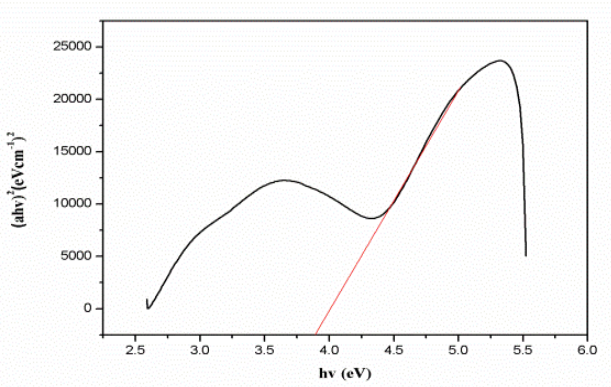

Figure 4 Tauc's plot of LTP crystal

Therefore, the material can be used for fabricating NLO devices. The energy band gap of the material has been estimated using the Tauc's [6] relation given by,

$$\alpha h\upsilon = A(h\upsilon - E_g)^n \qquad (1)$$

where α is the absorption coefficient, hν is the photon energy (eV) and E_g is the optical band gap (eV). The band gap was calculated from the plot of $(\alpha h\nu)^2$ versus hν as shown in Fig.5. The calculated band gap of LTP crystal was found to be 4.9eV. From the larger value of band gap it is concluded that LTP is a dielectric material suitable for induced polarisation when an intense radiation is incident on the material.

FTIR Spectral Analysis

Figure 5 presents the FTIR spectrum of LTP crystal recorded in the region 400-4000 cm^{-1}

The peaks at 3444-3381 cm^{-1} correspond to O-H stretching vibration. The absorption peak at 3063 cm^{-1} is assigned to presence of C-H aromatic ring. The C=C stretching vibration appears at 1567 $cm^{-1}$and the plane bending alkenes at 1352 cm^{-1}. The peak at 1250 cm^{-1} indicates presence of C-O stretching carboxylic acids. The absorption peak at 1026-1103 cm^{-1} indicates C-N stretching amines. The peak corresponding to 923 cm^{-1} indicates C-H bending alkenes and 782 cm^{-1} corresponding to C-H bending amides. The C-Cl stretching alkyl halides presence at 694 cm^{-1}.

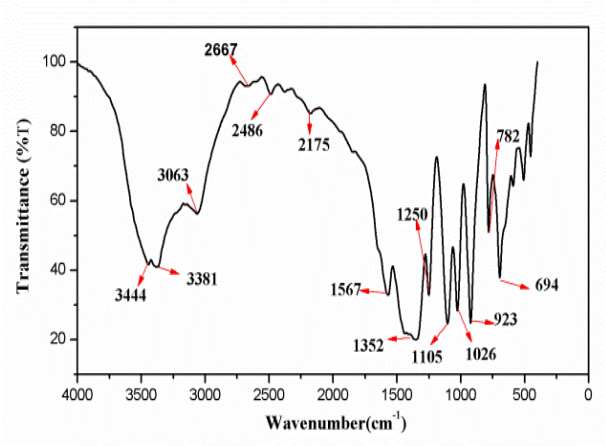

Figure 5 FTIR spectrum of LTP single crystal.

Dielectric Studies

The dielectric constant and dielectric loss were measured for the frequency range from 50 Hz to 5 MHz at various temperatures for the grown LTP crystal. Good quality crystal was selected for dielectric studies. The surface of the sample was coated with silver paste for good electrical contact. The dielectric constant and dielectric loss were calculated using the relations,

$$\varepsilon' = \frac{Cd}{A\varepsilon_o} \qquad (2)$$

and $\varepsilon'' = \varepsilon_r D$ (3)

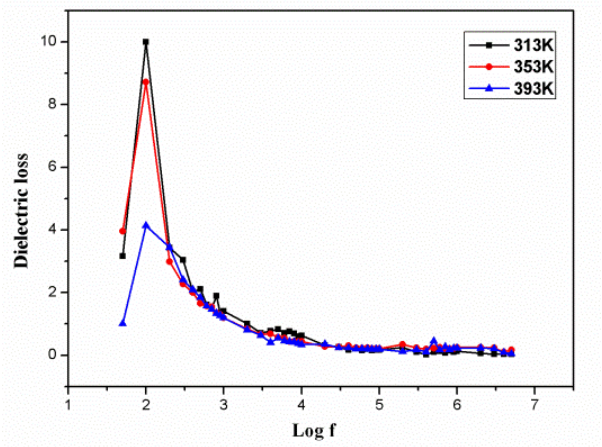

Fig.6 (a) Variation of dielectric constant of LTP as afunction of frequency at different temperatures where C is the capacitance, d is the thickness, A is the area of the crystal and D is the dissipation factor. The plots of dielectric constant and dielectric loss versus frequency are shown in Figs. 7(a) and 7(b) respectively at the temperatures 323 K, 373 K and 423 K. It is observed that the values of dielectric constant and dielectric loss are high in the lower frequency region. The large value of dielectric constant at low frequencies is due to the contributions from all the four polarizations, viz., electronic, ionic, dipolar and space-charge polarizations. The low values of dielectric constant and dielectric loss at high frequencies suggest that the grown crystal contains minimum density of defects with high optical quality. The variations of dielectric constant and dielectric loss with respect to temperature are found to be negligibly small.

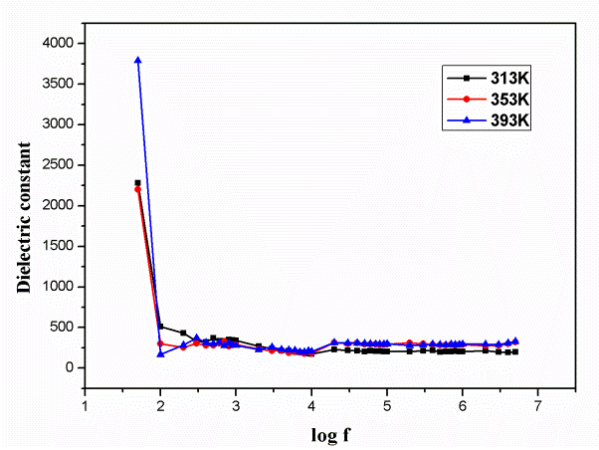

Fig.6(b) Variation of dielectric loss of LTP crystal afunction of frequency at different temperatures

SHG efficiency measurement using Solid state parameters

The dielectric measurement is a useful tool to calculate the polarizability of the medium for assessing SHG efficiency of the LTP crystal. The valance electron plasma energy is given by, where Z is the total number of valance electrons, M is the molecular weight and ρ is the density of LTP crystal. The dielectric constant at higher frequency is almost constant (ε_∞=62).The penn gap (E_p) and Fermi energy (E_F) were calculated using the following equations [7],

$$E_P = \frac{\hbar\omega_p}{(\varepsilon_\infty - 1)^{1/2}} \quad (5)$$

$$\hbar\omega_p = 28.8\left(\frac{Z\rho}{M}\right)^{1/2} \quad (4)$$

and

$$E_F = 0.2948\left(\hbar\omega_p\right)^{4/3} \quad (6)$$

The polarizability (α) of the grown material was calculated using the relation [15],

$$\alpha = \left[\frac{(\hbar\omega_p)^2 S_o}{(\hbar\omega_p)^2 S_0 + 3E_p{}^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^3 \quad (7)$$

where s_o is a constant for a particular material. S_0=1-$\left[\frac{E_P}{4E_F}\right] + \frac{1}{3}\left[\frac{E_P}{4E_F}\right]^2$ (8)

The value of α was also calculated using Clausius - Mosotti equation,

$$\alpha = \frac{3M}{4\pi\rho N_A}\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \quad (9)$$

Solid state Parameters	For LTP crystal	For KDP crystal
Plasma energy (eV)	38.44	17.33
Penn gap (eV)	4.69	2.39
Fermi energy (eV)	8.25	12.02
Polarizability by Penn gap (cm^3)	1.77×10^{-23}	2.14×10^{-23}
Polarizability by Clausius-Mosotti equation(cm^3)	1.94×10^{-23}	2.18×10^{-23}

where N_A is the Avogadro number. All the above fundamental parameters were calculated for KDP material also. Table 1 shows the fundamental parameters required for assessing SHG efficiency of LTP. The SHG efficiency depends upon the polarizability of the medium. The ratio of polarizability of LTP to that of KDP is calculated as 0.89 using plasma and this value is found to be in good agreement with the value (0.97) calculated using Clausius-Mosotti relation (Table 1).This theoretical prediction of SHG efficiency has been confirmed by Kurtz and Perry powder technique.

4. Conclusion

L-tyrosine doped picrate (LTP) crystal was grown by slow evaporation technique. From XRD data, it is observed that the grown crystal belongs to monoclinic system structure. The transparent range and the optical band gap of the crystal were evaluated using UV–vis-NIR spectrum. The functional groups of the grown crystal were identified using FTIR spectrum. Dielectric studies establish the dielectric behaviour of the grown material. Solid state parameters of such as Penn gap (E_P), Fermi Energy (E_F) and polarizability (α_p) were estimated using dielectric studies to assess the NLO activity of the grown material LTP. The SHG efficiency of the grown crystal LTP was found to be larger than that of KDP.

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