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Studies on growth and optical, structural, mechanical and photoconductivity of non-linear optical material L-threonine

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Abstract: L-threonine, one of the amino acid groups of materials, was grown as single crystal using slow evaporation technique. X-ray diffraction analysis revealed that the crystal belongs to orthorhombic structure with space group $P2_1\,2_1\,2_1$. The transmission range and the optical band gap were evaluated from UV-vis-NIR spectral analysis to study the optical behavior of the material. FTIR spectral studies were carried out to confirm the functional groups of L-threonine. The molecular structure of the material was analyzed using Nuclear Magnetic Resonance (NMR) studies. The microstructure of the crystal was studied using SEM-EDAX analysis. Microhardness measurement was made for the sample using Vickers hardness tester to discuss the mechanical properties of the grown sample. Photoconductivity study was carried out to analyze the response of the material to the incident visible light. Nonlinear optical (NLO) property was confirmed using Kurtz powder technique and the NLO efficiency was found to be 1.04 times that of KDP.
Keywords: Slow evaporation technique; FTIR spectral study; NMR Study; Non-linear optical material; Microhardness.

1.Introduction and Experimental

It is quite interesting to note that most of the amino acid crystals exhibit nonlinear optical (NLO) property. Nonlinear optical materials can find interesting applications including high speed optical communication, wireless optical communication, optical parallel information processing, optical disk data storage, laser fusion reactions, laser remote sensing, colour display, and medical diagnostics [1-3]. L-threonine ($C_4H_9NO_3$) crystal belongs to non-centrosymmetric orthorhombic system with space group $P2_12_12_1$ satisfying the fundamental criterion for NLO activity. The growth and characterization of L-threonine single crystal have been reported by Ramesh Kumar et al [4]. Nowadays amino acids are more suitable organic materials for nonlinear optical applications [5-8] because they possess dipolar nature due to the presence of protonated amino group (NH_3^+) and deprotonated carboxylic group (COO^-). L-threonine is an important amino acid material which shows higher SHG (Second Harmonic Generation) efficiency than other nonlinear amino acids. Even though L-threonine was grown and characterized already, NMR, SEM-EDAX, microhardness and photoconductivity studies were not studied.

Hence, in the present investigation, we report the important characterization studies: linear optical study, FTIR and NMR spectral studies, SEM–EDAX analysis, microhardness, photoconductivity and nonlinear

optical studies to analyze the transmission range, optical band gap, micro and macro structures, microhardness, photoconducting nature and nonlinear optical property of the grown crystal L-threonine.

L-threonine crystals were grown by slow evaporation technique. A saturated solution of L-threonine was prepared using the solubility data in water and the solution was well filtered with the help of a high quality filter paper. The vessel containing the solution was covered with a perforated cover for controlled evaporation. As slow evaporation took place, required supersaturation was gradually achieved to initiate nucleation followed by growth. The crystals were harvested after a period of 40 days. Fig.1 shows the as-grown L-threonine crystal with dimensions of 30×5×5 mm^3.The quality and the size of the crystal were improved by repeated crystallization process.

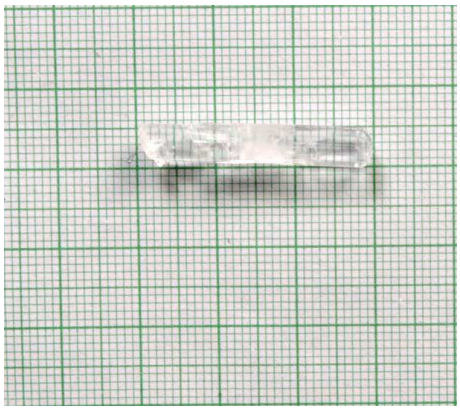

Fig.1 Photograph of the as grown L-threonine crystal

2. Results and Discussion

2.1 Single Crystal X-Ray Diffraction Analysis

Single crystal X-ray diffraction studies were carried out on the grown crystal using a computer - controlled ENRAF NONIUS CAD4 X- ray diffractometer to determine the lattice parameters and space group. The results obtained indicate that the crystal belongs to orthorhombic crystal system with space group $P2_12_12_1$ and the unit cell parameters are found to be a=5.15Å, b=7.75Å and c=13.66Å, $\alpha=\beta=\gamma=90^0$ and V=546$Å^3$. The space group suggests that the grown crystal is non - centrosymmetric which fulfills the fundamental criterion for the NLO activity of the material. XRD results are found to be in good agreement with the earlier reported values [9].

2.2 UV-vis-NIR Spectral Studies

The optical absorption spectrum of L-threonine crystal was recorded in the range of 200- 1100 nm using LAMBDA 35 UV-vis-NIR spectrometer to evaluate the transmission range and optical band gap of the material. This study was already reported [4]. The lower cut-off wavelength for the crystal is found to be 285.38 nm with transparent range in the region of 285.38 -1100 nm. This is the desirable property for second harmonic generation in the grown crystal.

The optical absorption coefficient (α) was calculated using the following relation,

$$\alpha = \frac{2.303 \log(1/T)}{d} \qquad (1)$$

where T is the transmittance and d is the thickness of the crystal.

The expression connecting the optical band gap (E_g), photon energy ($h\nu$) and absorption coefficient (α) is written as [10].

$$(\alpha h\nu)^2 = A (E_g - h\nu) \qquad (2)$$

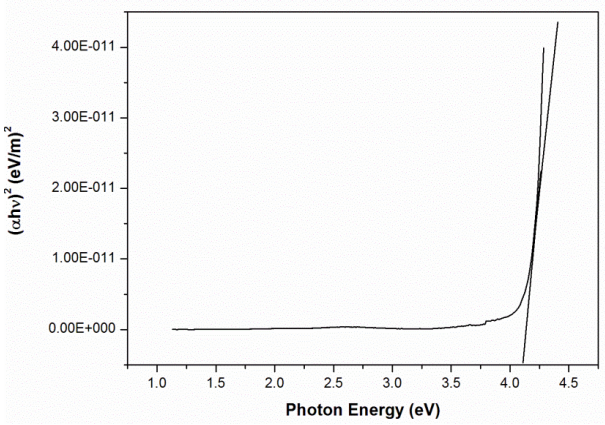

Fig. 2 Plot of $(\alpha h\nu)^2$ against photon energy

where A is a constant. The plot of $(\alpha h\nu)^2$ against $(h\nu)$ is shown in Fig.2 and E_g has been evaluated by the extrapolation of the linear part. The optical band gap is found to be 4.78 eV which confirms the wide transparency nature (300-1100 nm) and dielectric behavior of the material [11].

The wide optical band gap of the material shows that the material is dielectric in nature. The dielectric nature of the material really counts for the induced polarization in the material to exhibit NLO activity due to intense incident radiation on the material. This will result in the better conversion efficiency of the material L-threonine for second harmonic generation.

2.3 FTIR Spectral Studies

Fourier Transform Infrared (FTIR) spectrum of L-threonine crystal was recorded at room temperature in the wave number range of 450 - 4000 cm^{-1} using Perkin-Elmer spectrometer and KBr Pellet technique. Fig.3 shows the recorded FTIR spectrum of the grown crystal. The observed peaks are assigned as follows: The peak due to 3026 cm^{-1} corresponds to CH_3 asymmetric stretching vibrations. The peak at 2049 cm^{-1} represents N-H stretching vibrations. The band at 1625 cm^{-1} is due to C=O stretching vibrations. NH_3^+ asymmetric bending vibrations are assigned due to the peaks at 1455 and 1479 cm^{-1}. The bending vibrations of CH group are found corresponding to the peaks at 1246 and 1318 cm^{-1}. The peak at 1109 cm^{-1} is assigned to C-OH stretching modes of vibrations. The band at 931 cm^{-1} is associated with C-H stretching vibrations. The peak due to 907 cm^{-1} is related to stretching of CCN structure. The bonding of CO_2^- structure is observed at 767 cm^{-1}. FTIR spectral assignments thus reveal the amino acid characteristics of the grown material.

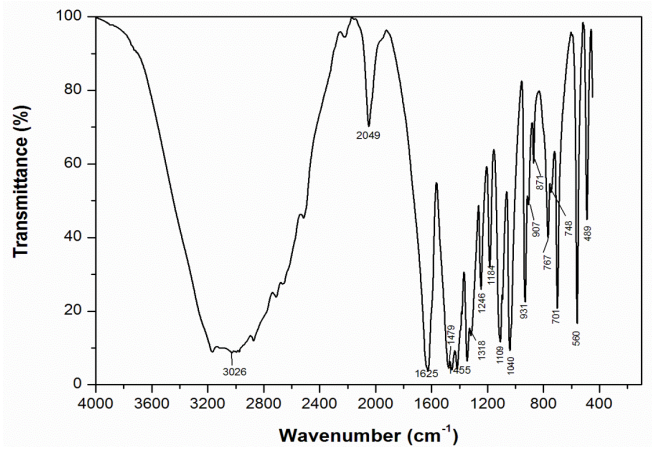

Fig.3 FTIR Spectrum of L-threonine crystal

2.4 NMR Spectral Studies

Nuclear Magnetic Resonance (NMR) is a very versatile technique in the identification of organic compounds. ^1H and ^{13}C NMR spectra of L-threonine were recorded using BRUKER AVANCE III NMR spectrometer. Fig.4 shows the ^1H NMR spectrum of L-threonine. The observed peak at δ=1.20 ppm corresponds

to the proton attached to methyl group of L-threonine. The ^{1}H NMR peak at δ=3.40 ppm is due to OH proton of L- threonine. The signal δ=4.70 ppm shows the proton attached to aromatic group of L-threonine. The present results are found to be in good agreement with the earlier reported predictions [12].

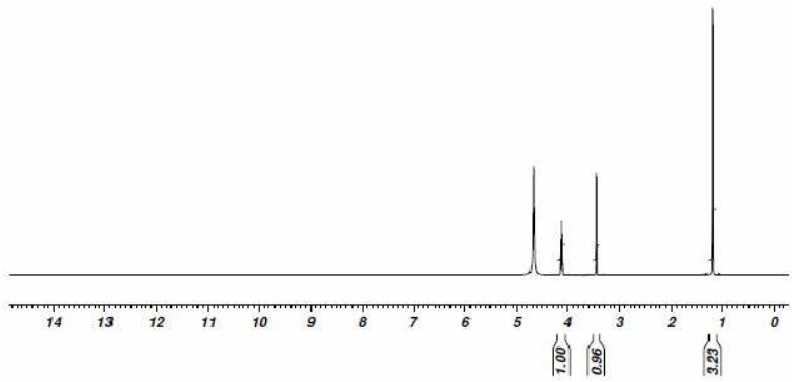

Fig. 4 ^{1}H NMR spectrum of L-threonine

13C NMR spectrum of L-threonine is shown in Fig.5. The signal at δ=19.407 ppm is assigned to the carbon associated with CH_2 group. The carbon attached to CH group is represented by the peak at δ=60.349 ppm. Finally, the peaks corresponding to δ=65.835 ppm and δ=172.745 ppm represent the type of carbons (C-O and C=O) present in the material.

The molecular structure of L-threonine is thus confirmed from ^{1}H NMR and ^{13}C NMR spectral studies.

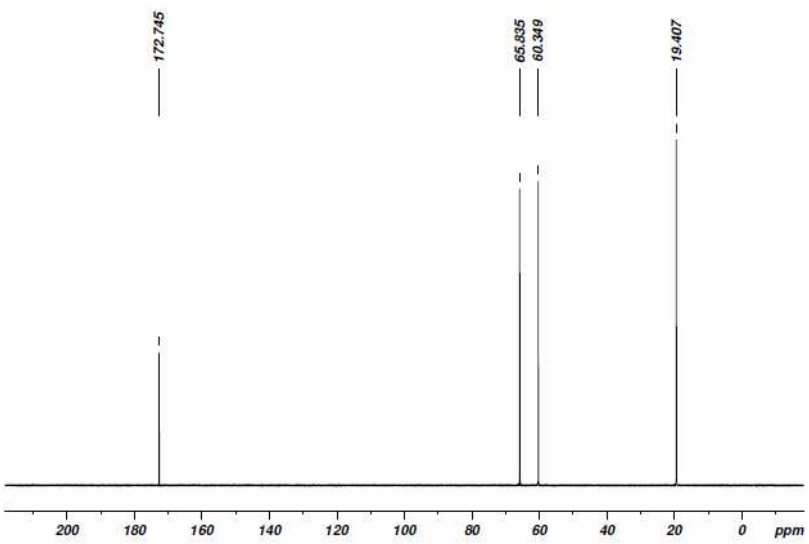

Fig. 5 ^{13}C NMR spectrum of L-threonine

2.5 SEM - EDAX Analysis

Figs.6 (a) and (b) show the microstructural SEM images of the grown crystal L-threonine recorded with resolutions 5μm and 10μm respectively. The images clearly reveal the layer-like pattern of atoms of different sizes which favours the adsorption layer growth mechanism introduced by Volmer [13]. According to Volmer, a molecule arriving at a crystal surface from the bulk of the supersaturated solution or supercooled melt loses a part of its latent heat. The molecules of this kind move along the surface and join together to form a two dimensional nucleus due to inelastic collisions. The transparent nature of the crystal is understood from the clear images of the atoms. The microstructural image of the crystal shows that the crystal contains minimum density of defects. From SEM analysis, the growth mechanism, the transparent nature, different components and the density of defects in the crystal are interpreted.

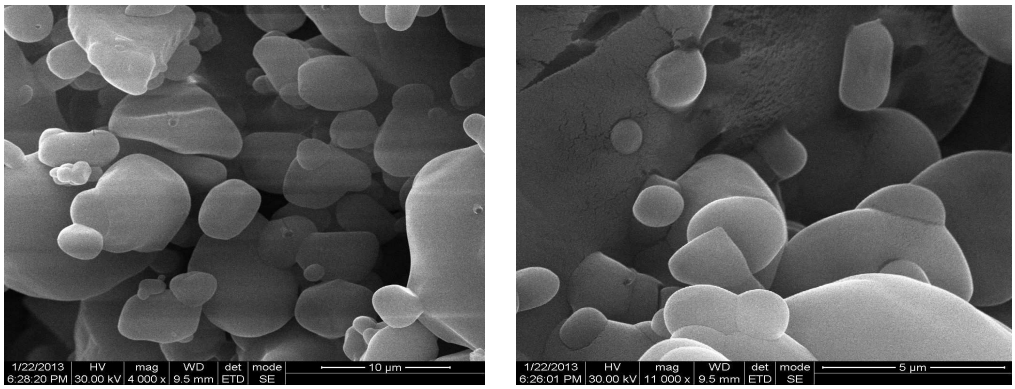

Fig. 6 (a) and (b) SEM images of L-threonine crystal with 5µm and 10µm resolutions

The presence of different components of the grown material is confirmed by EDAX analysis as shown in Fig.7.

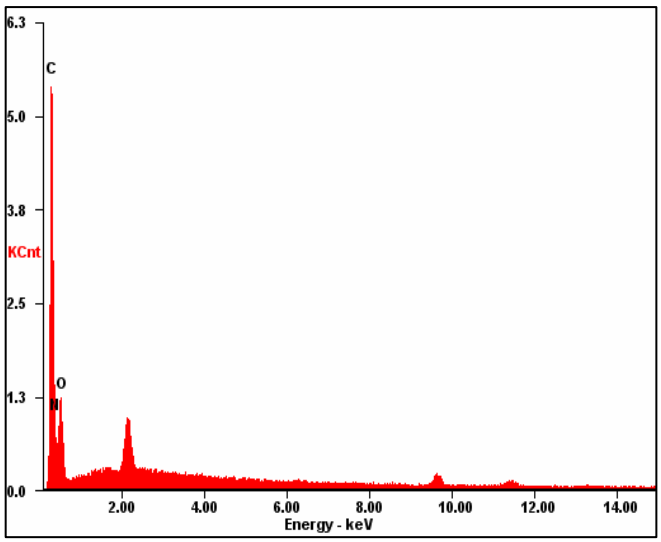

Fig. 7 EDAX pattern of L-threonine

2.6 Microhardness Studies

Hardness is an important mechanical property which correlates with other parameters such as hardness number, fracture toughness, brittleness index and yield strength. Vickers microhardness test was performed on L- threonine crystal using Vickers hardness tester fitted with a pyramidal indenter. Several indentations were made on the (100) face of the crystal for the various loads 25g,50g and 100g and the average diagonal length (d) was measured for each load. The hardness number was calculated using the relation,

$$H_v = \frac{1.8544\,P}{d^2}\ \text{kg/mm}^2 \qquad (3)$$

where P is the applied load in kg and d is the diagonal length in mm of the indentation impression. The variation of H_v as a function of applied load is shown in Fig.8. For loads beyond 100g, cracking begins to occur which may be due to the local stress generated by indentation. A plot of ln P versus ln d for the grown crystal is shown in Fig.9 which gives a straight line and its slope is equal to the work hardening index (n).The value of n is found to be 2.95.

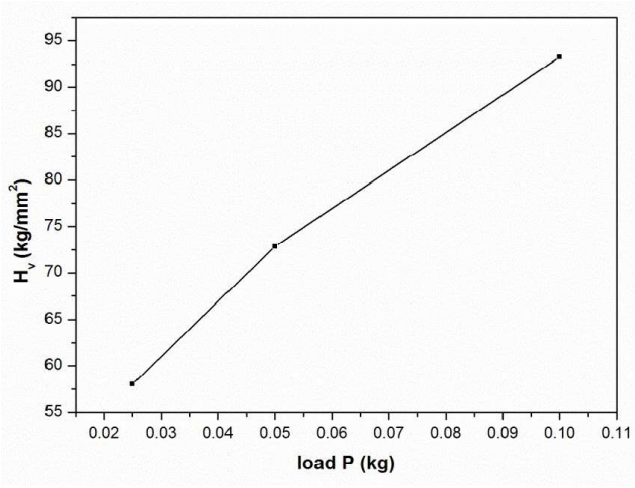

Fig. 8 Plot of H_v against load P

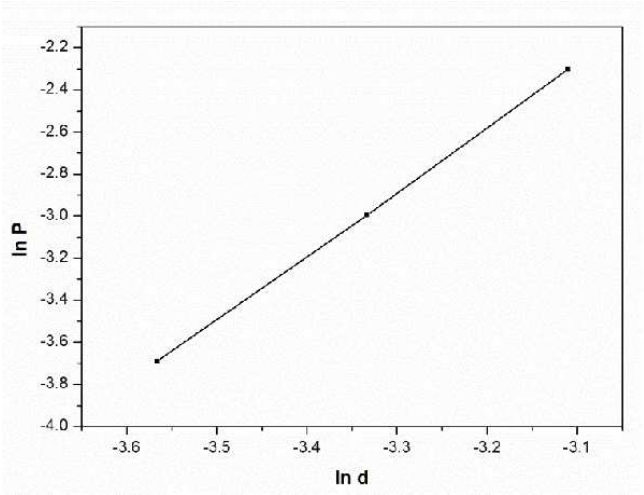

Fig. 9 Plot of ln P against ln d

According to Meyer's relation,

$$P = K_1 d^n \quad (4)$$

where, K_1 is the standard hardness value which can be found out from the plot of ln P against ln d. Since the material takes some time to revert to the elastic mode after every indentation, a correction x is applied to the d value and the Kick's law is modified as,

$$P = K_2 (d + x)^2 \quad (5)$$

where K_2 is another hardness parameter.

From equations (3) and (4),

$$d^{n/2} = \left[\frac{K_2}{K_1}\right]^{1/2} d + \left[\frac{K_2}{K_1}\right]^{1/2} x \quad (6)$$

The slope of $d^{n/2}$ versus d yields $\left[\frac{K_2}{K_1}\right]^{1/2}$ and the intercept is a measure of x .The fracture toughness (K_c) is given by

$$K_c = \frac{P}{\beta C^{3/2}} \quad (7)$$

where C is the crack length measured from the centre of the indentation mark to the crack tip, P is the maximum applied load and geometrical constant β = 7 for Vickers indenter. The brittleness index B is given by

$$B = \frac{H_v}{K_c} \quad (8)$$

The yield strength (σ_v) of the material can be found out using the relation,

$$\sigma_v = \frac{H_v}{2.9}\left[1 - (n-2)\right]\left[\frac{12.5(n-2)}{1-(n-2)}\right]^{n-2} \quad (9)$$

The load dependent hardness parameters n, K_1, K_2, fracture toughness (K_c), brittleness index (B) and yield strength (σ_v) were calculated for L-threonine crystal. According to Onitsch [14] if n>2, the microhardness value will increase with the increase of load.

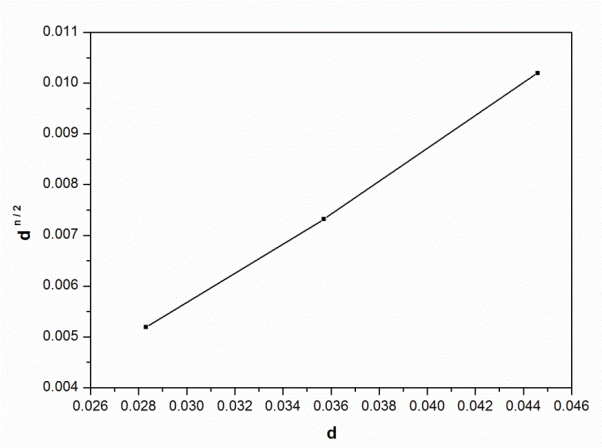

Fig. 10 Plot of $d^{n/2}$ against d

The increase of hardness with the load up to 100g suggests that the material is possessing sufficient mechanical strength to withstand the load up to 100g. The higher magnitude of mechanical parameters (K_1, K_2, H_v, K_c, B and σ_v) presented in Table 1 ensure the mechanical stability of the material required for device fabrications.

Table 1 Hardness parameters of L-threonine crystal

Parameters	**Values**
n	2.95
K_1 (kg/mm)	50.91
K_2 (kg/mm)	4.11
H_v (kg/mm^2)	93.27
K_c ($MNm^{-3/2}$)	0.3959
B ($m^{-1/2}$)	2.308×10^3
σ_v (G Pa)	2.85

2.7 Photoconductivity

Photoconductivity study was carried out at room temperature for L-threonine crystal using Keithley 6485 picoammeter. The dark current was recorded without exposing the sample to any radiation by increasing the field from 15V/cm to 100V/cm. The light from the halogen lamp (100W) was focussed on the sample and the photocurrent was measured for various fields. The plot of photocurrent and dark current as a function of the applied electric field is shown in Fig.13. It is observed from the plot that both dark current (I_d) and photocurrent (I_p) of the sample increase with the applied field up to 60V/cm and thereafter both the currents attain saturation. Since the photocurrent is larger than dark current up to a particular field, the material is said to possess positive photo response. The positive photo response of the material will be more useful for NLO applications [15].

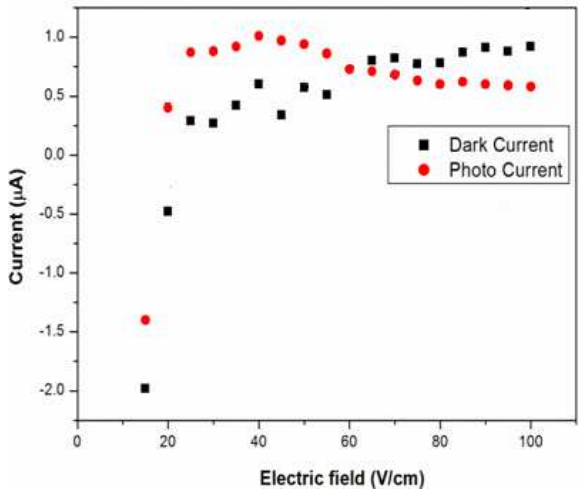

Fig. 11 Photocurrent and dark current as a function of applied electric field

2.8 Non Linear Optical Property

Kurtz and Perry powder technique was employed to confirm the nonlinear optical (NLO) property of L – threonine. In this method the material was powdered and filled in a micro - capillary tube of about 1.5 mm diameter. A Q - switched Nd : YAG laser source emitting a wavelength of 1064 nm with pulse width 8 ns was used to illuminate the sample. The emission of green radiation of wavelength 530 nm confirms the second harmonic generation by the crystal which is the characteristic of the nonlinear behaviour of the material. The input energy incident on the sample was 7.0 mJ / pulse and the corresponding output was measured as 7.2 mV. This output was compared with the output (6.9 mV) obtained for the standard material KDP. The SHG efficiency of L- threonine is thus found to be 1.04 times that of KDP. It is therefore concluded that L – threonine is a promising NLO material due to better linear and nonlinear optical properties of the material.

3. Conclusion

Optically good quality crystals of L-threonine were grown by slow solvent evaporation technique. From the XRD data, it is observed that L-threonine crystal belongs to orthorhombic system with space group $P2_12_12_1$. From the analyses of XRD and UV-vis-NIR spectrum, the material is found to possess the required transmission range and optical band gap with non–centrosymmetric space group for better SHG conversion efficiency. The functional groups of the grown crystal were identified using FTIR spectrum. The molecular and microstructures of the material were analyzed using NMR spectrum and SEM and EDAX images. The mechanical behavior of the material was discussed using Vickers hardness test. The photoconductivity study reveals the positive photo response of the material. The SHG efficiency of the material is found to be more than that of KDP. Therefore, L-threonine can be used for the fabrication of optical devices due to better linear and nonlinear optical properties and mechanical stability.

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