CRYSTAL GROWTH AND SOME OPTICAL AND ELECTRICAL STUDIES OF NLO L-THREONINE POTASSIUM IODIDE CRYSTAL

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Abstract:

A novel semi-organic NLO material L-Threonine Potassium Iodide (LTPI) has been synthesized by slow evaporation method. Single X-ray diffraction study shows that the grown crystal is orthorhombic structure with the noncentro symmetry space group $P2_12_12_1$. Powder XRD is also studied from which the sharp peak crystalline nature and hkl plane was identified. The FT-IR spectra are carried out for reveals various functional groups in the crystal have been derived. UV-vis-NIR studying has been performed within 200-1100 nm to determine the optical transparency of the grown LTPI crystal. The fluorescence spectra studies recorded of wavelength 300-700 nm and colour of emission, region reported. The molecular structure of grown LTPI crystal was verified by ^{1}H NMR analysis. The dielectric constant and dielectric loss of LTPI crystal was carried out as a function of frequency and the obtained result are discussed. Second harmonic generation efficiency of the grown sample was evaluating by Kurtz-Perry method, which yield an efficiency of 1.4 times better than KDP.

Keywords

Crystal growth, L-Threonine Potassium Iodide crystal, XRD, FT-IR, UV-vis-NIR, ^{1}H NMR, Dielectric, SHG studies.

1. Introduction

The optical material is technological powerful tools that laser generation typically advantage in Photonics and an electronics industry. L-Threonine is a secondary hydroxyl in polarisable with α amino acid unchanged side chain and chirallity [1].The important potential applications of the nonlinear crystal are optical parametric frequency conversion, electro-optic phase modulator, to generate switching and in amplitude modulation of other signal processing devices [2]. All this favourable property paved the way for the invention of new amino acid crystals such as L-Threonine and L-Alanine etc. Semi-organic compound shows the highest SHG efficient some over those other materials. In particular, the polar amino acid is an important material which shows higher NLO efficiency other than amino acids materials. L-Threonine was reported the carrier with very few more details [3]. The technologically importance of L-Threonine is relevantly present that derived material and also which shows

optical property greater than among related to KDP [4]. Here, this material reported the growth and investigation by many researchers [5]. In recent years, organic compound molecular nonlinear optical materials have been intensely investigative due to their high nonlinearities [6]. NLO materials Organic compound has attracted a great deals of attentions, as they have large optical susceptibilities and ultra speed response time and higher optical threshold gate for laser disc power as compared with other compound inorganic materials. For example, the Proton donor carboxylic -COO group and proton acceptor aminophylline NH_2. L-Threonine picrate and L-Threonine acetate showed very higher SHG efficiency [7]. L-Threonine is an important polarity amino acid and its dipole moment is nearby similar to water [8]. High power visible laser has been no ways, widely known various field such as the display, deep sea communication, bio photonics, optical storage, medicine, making and precision micro fabrications [9]. Intense Research in inorganic and organic on functionalized NLO optical materials play a crucially role because their bond strength, molecular interactions, east incorporating of Ionic etc [10].One of the major advantageous of organic material is that their structure can be modify with the proper doping to get the desired SHG properties [11].

In the present investigation focused mainly towards linearly and nonlinear optical performance of LTPI using single crystal XRD, powder XRD, FT-IR, UV-visible-NIR, ^{1}H NMR SHG[12].

2. Experimental procedures

L-Threonine potassium iodide crystals were synthesized by dissolving L-Threonine potassium iodide within molar ratio 1:1 in mixed with water solvent. The solution was stirred continuously, then filter in the prepare solution and fixed in grown of crystal by the slow evaporation method at room temperature. After about 25 days, good quality mono crystallomancy was harvested from the mother solution with the LTPI of dimensions of 0.27 x 0.27 x 0.3 mm^3.The grown crystals are found to be optically transparent an non-hygroscopic. Figure.1 shows the photographs of as grown LTPI crystal. The following chemical reaction for the synthesis of the material was expected to take place.

$$C_4H_9NO_3 + KI \rightarrow C_4H_9KNO_3^+ \ I^-$$

Fig.1. Photograph of as grown LTPI crystal

3. Characterization Techniques

The powder XRD data for the grown crystals were collected used to PANALYTICAL XPERT PRO X-Ray diffractometery with CuKα radiation. The wavelength of the radiation used was 1.5406 Å. The presence of functional groups and the bond assignments, nature of the bonds presently in the title materials were assessed by the FTIR spectral analysis using in PERKIN ELMER FTIR spectrophotometry. The optical characters of the sample were examined by subjects in to linear opticals analysis. The absorption and transmission spectrum were obtained within the wavelength range of 200 nm to 1100 nm with the help of PERKIN ELEMER LAMBDA 365 UV visible spectrometer. ^{1}H NMR Spectrum analyses of the LTPI grown crystal has been recorded with BRUKER AV-300 operating at 300 MH_Z. Dielectric analysis for LTPI was carried out using model PSM1735. The second Harmonic generation efficiency of LTPI crystals were tested by an AQ switched high energy Nd: YAG laser λ=1064 nm QUANTA RAY MODEL LAB-170-10 using a light source, with the input energy of 3.2 mJ, pulse width of 8ns and repetitions rate of 10Hz.

4. Results and Discussion

4.1 X-ray Powder Diffraction Studies

X-ray powder diffraction analysis of the grown sample was also carried out using PAN Anlytical XPert PRO powder diffractometery by scanning the powdered sample using CuKα radiation of the wavelengths λ=1.5418 nm over the range of 10-80º with a speed scan of 0.2/Sec, the results are plotted and shown in figure.2. From the powder XRD pattern the (h k l) and the correspondent d values were calculated then the lattice parameter values are obtained. The powder pattern was indexed used to the INDEXING software package [1].

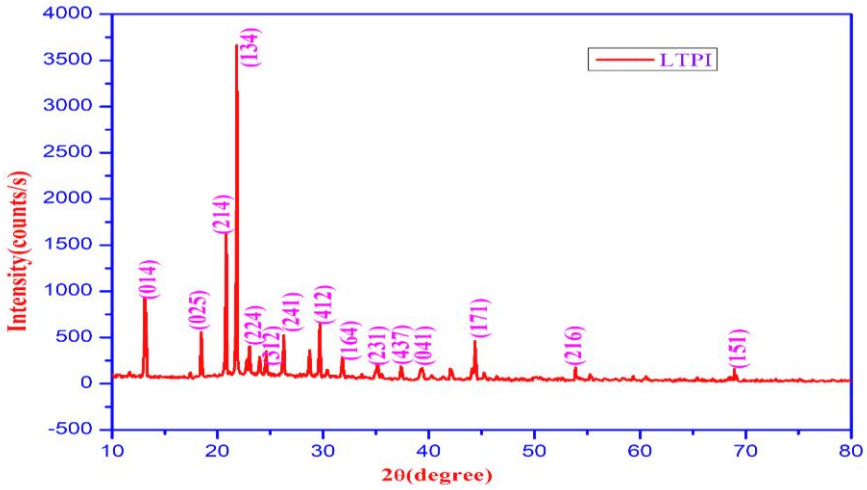

Fig.2. Powder X-rays diffraction pattern of LTPI crystal

4.2 FTIR studies

The FTIR spectrum is presented in figure.3.The frequency of various assignments has been listed in table.1. CH_2 scissoring vibrations are revealed due to the peak 1339 cm^{-1} [13]. The NH_3^+ group absorbed 1427 $cm^{-1}$and 1623 $cm^{-1}$and strong 1427 cm^{-1} and 1623 cm^{-1} strong symmetrical bending and weak asymmetrical bending. The peak at

2050 cm^{-1} and 2215 cm^{-1} due to asymmetrical NH_3^+ bending. The NH_3^+ bending observed at wave number 2511cm^{-1}. The peak observed strong NH_3^+ stretching band in the region at wave number 2714 cm^{-1}. The O-H stretching observed set 2876cm^{-1}. The sharp peak observed at 3175 cm^{-1} was assigned to N-H stretching of primary amino group in LTPI. The NH_3^+ group is nearly observed by 3724 $cm^{-1}$and 3893 cm^{-1}, which assigned NH_3^+ stretching bonds. The carboxylic groups and amine are coordination confirmed due to the presence of functional group in the FTIR spectra [11].

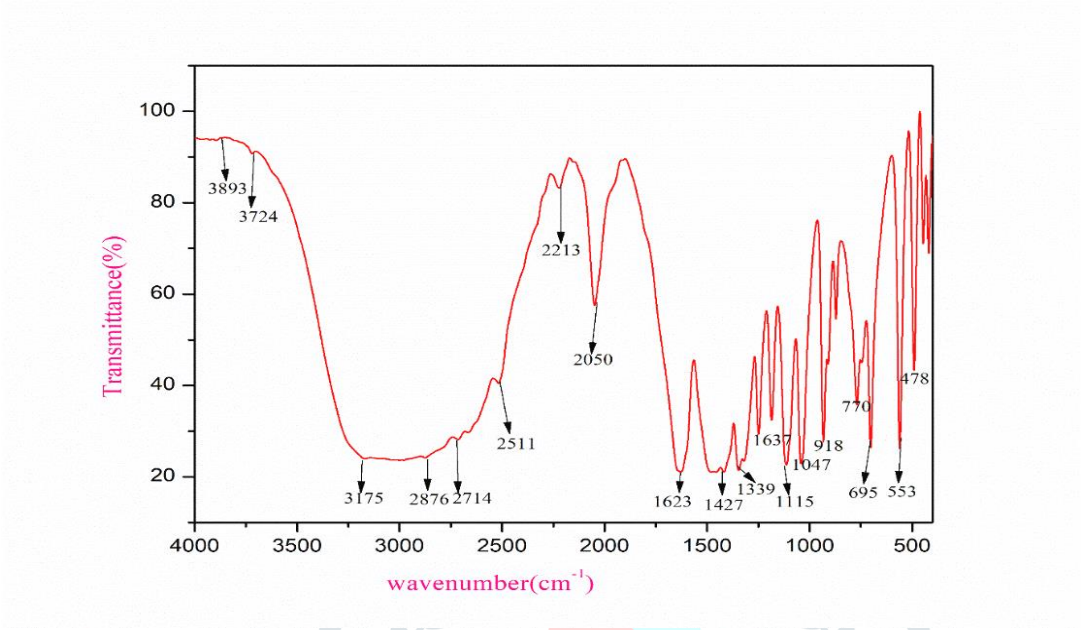

Fig 3. FT-IR spectrum of LTPI crystal

Table.1. FT- IR Assignments of LTPI crystal

wave number(cm^{-1})	Assignments
3893,3724	NH_3^+ stretching band
3175	N-H stretching
2876	O-H stretching
2714	strong NH_3^+ stretching band
2511	NH_3^+ bending
2213, 2050	asymmetrical NH_3^+ bending
1623	NH_3^+ week asymmetric bending
1427	strong symmetrical NH_3^+ banding
1339	CH_2 scissoring
1367	C-N stretching
1115	NH_3 rocking
1047	CH_2 wagging
918	CH_2 rocking
770	C-C stretching
695	KI mode

4.3 Optical studies

The UV-vis-NIR spectrum of LTPI was shown in fig.4 of thickness of the sample is 1.5cm.The cut off wave length was found to be lower than 275 nm. The cut off wavelength of LTPI was relatively lower compared with other standard organic NLO crystal; such good transparency of LTPI was highly useful for NLO application and optoelectronics. The wavelength of UV radiation causing electronic transition n-π^* at about 275nm depend orbital originally occupied. The transmittance measured T optical using absorption spectrum was calculated the coefficient α using the relation formula.

$$\alpha = \frac{2.3026}{t} \log (1/T)$$

Where, T is the transmittance and t are the thickness of the crystal. The optical absorptions coefficient α and opticals band gap E_g has been evaluates from the transmissions spectrum absorption edges as given by, $h\upsilon\alpha = A(h\upsilon - E_g)^{1/2}$, where E_g is the optical band gap, A is the constants h is the Plank constant is frequency of incident photons. The LTPI crystal band gap was estimating by plotting $\alpha h\upsilon^2$ versus hυ as shown Figure.5. The band width of LTPI crystals confirms the transmittance in the visible region and the opticals band gap was estimating by plotting $\alpha h\upsilon^2$ vs hυ. The plot was known as Tauc̀s plot from which the optical band gap was estimated and it was found to be 4.5 eV. Since the material possesses excellent qualities like lower cut-off wavelength 275 nm, LTPI crystal can be utilized as a potential material in the fabrications like LASER and LED [14].

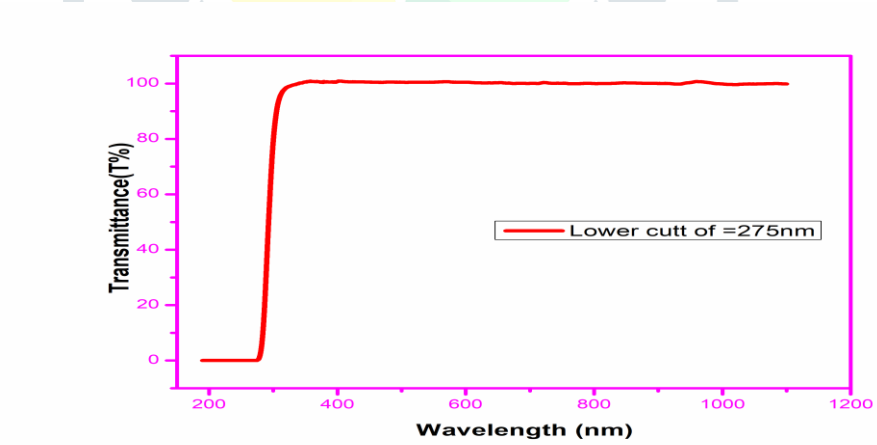

Fig.4.UV-vis-NIR transmittances spectrum of LTPI crystal

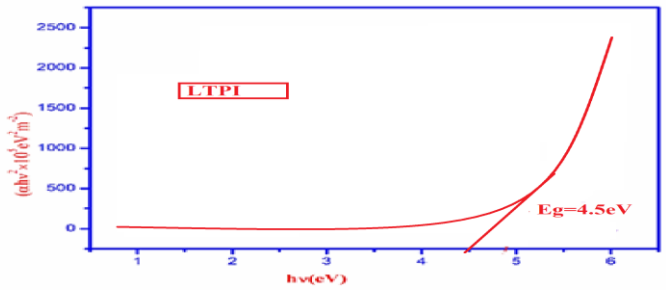

Fig.5. Tauc̓s plot $\alpha h\upsilon^2$ versus, hυ for LTPI crystal

4.4 ^{1}H NMR Studies

^{1}H NMR spectral analysis of the LTPI crystals was recorded and in the spectral peaks shown the figure.6. From the spectrum, the multiple peaks between δ=1.165 ppm and δ =1.187 ppm are attributed to C-H proton present in LTPI crystal. The presence of CH_3 proton group in LTPI is confirmed due to multiple peaks in the range between δ = 3.429 ppm and δ =3.445 ppm. The multiple triplex signals in the range between δ= 4.065 ppm and δ =4.086 ppm is due to hyperfine splitting of neighbouring CH_3 protons. The multiple triplex signals observed between δ =4.108 ppm and δ = 4.125 ppm for the high triplex value signal in the range between δ = 4.146 ppm and δ = 4.700 ppm in LTPI crystal are attributed to the presence of -CH proton next to the carboxylic acid. The high δ value of this triplet was due to the electron presence of withdrawing -COOH group and adjacent to the -CH carbon atom which, leads to the delocalization of polarization nature to account for the electrons [15].

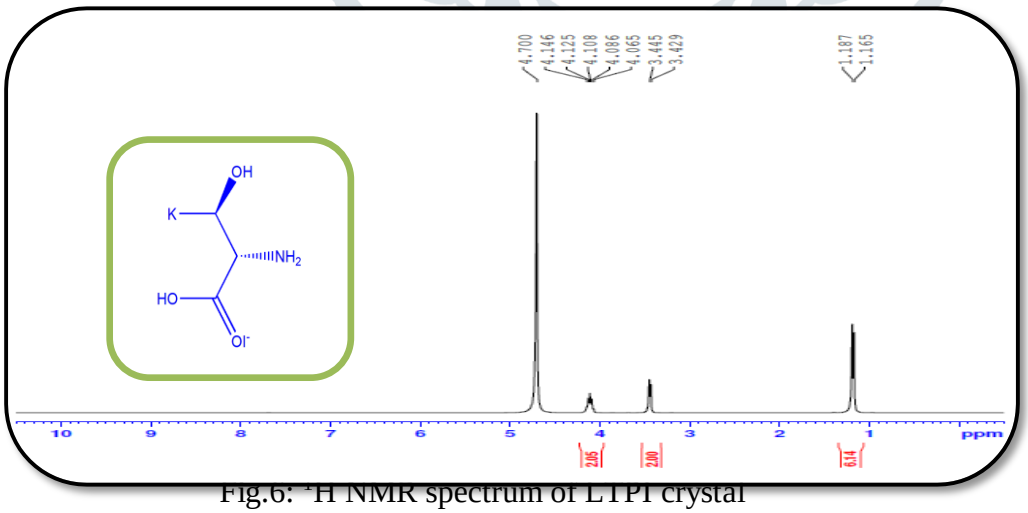

Fig.6: ^{1}H NMR spectrum of LTPI crystal

4.5 Dielectrics Studies

The dielectric loss and dielectric constant of the L-threonine potassium iodide (LTPI) crystals were calculated by using the following relation, $\varepsilon_r = \frac{cd}{\varepsilon o\ A}$ or ε = ε tan δ = $\frac{1}{WRC}$,where A is the area of the samples,ε_0 permittivity of free space c is the capacitance, d is the thickness of the sample. The low frequencies at a high value of dielectrics constant may be dues to the present in four polarization and its low value of high frequency

may be dues to the loss of polarization significantly in the fig.7.The dielectric loss with frequency variation was shown in figure.8. The frequency for low dielectric loss shows that its characteristics enhanced quality optical with defects laser [10].The dielectric ac conductivity was calculated using following formula, $\sigma_{ac} = \omega\varepsilon_0\varepsilon_r\tan\delta$, where ε_0 is the permittivity's of free space 8.85×10^{-12} F/m and $\omega = 2\pi f$ is angular frequency. The frequencies dependence of conductivity is presented in figure.9. σ_{ac} = sample investigated is shown, plot σ_{ac} versus frequency. It is from the evident of graph that conductivity increased with frequency [7]. The ac resistivity was calculated using the relations $A/2\pi fcd$, or $\sigma = 1/\rho$, frequencies of applied field are shown figure.10. An ac resistivity decreased as the frequency rapidly increased. According to Miller's rule, lower the value of dielectric constant at highest frequency is a suitable parameter for the enhancements of SHG coefficient.

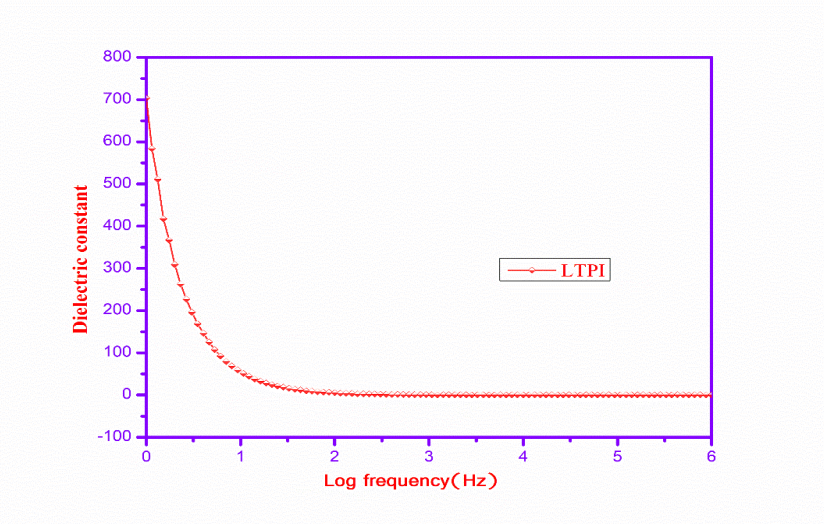

Fig.7.The plot of log frequency vs dielectric constant for LTPI crystal

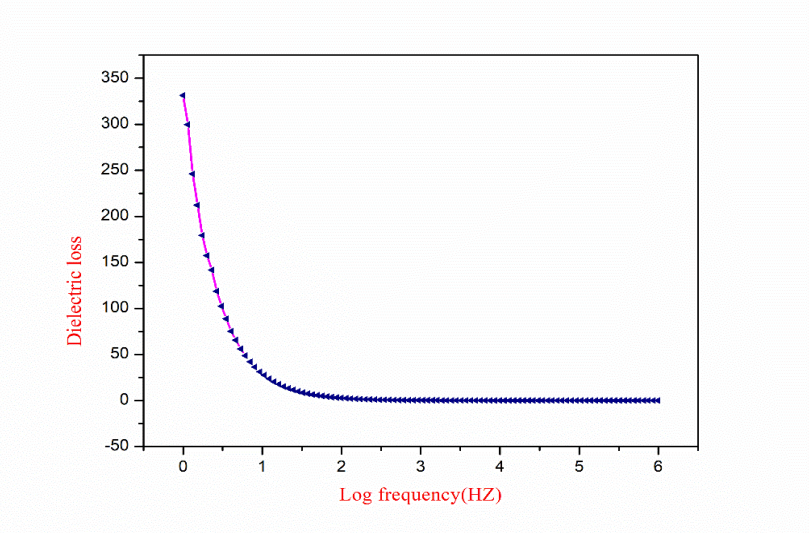

Fig.8.The plot log frequency vs dielectric loss for LTPI crystal

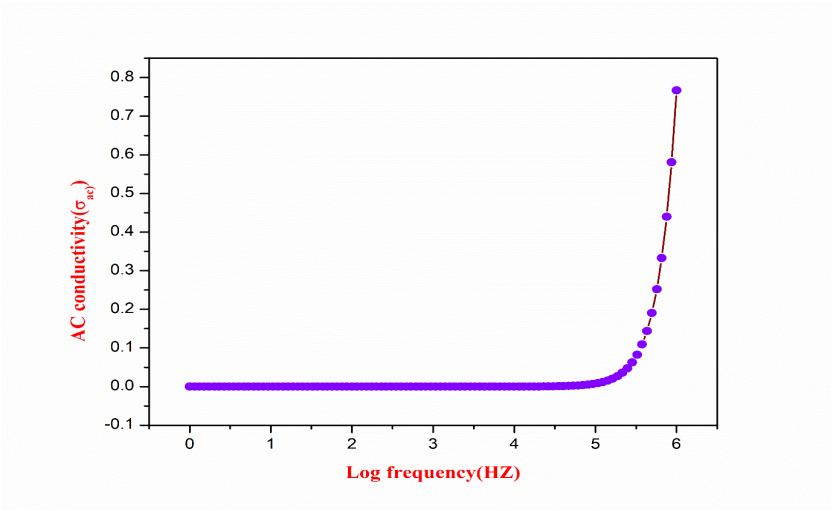

Fig.9.The curve of log frequency Vs ac conductivity of LTPI crystal

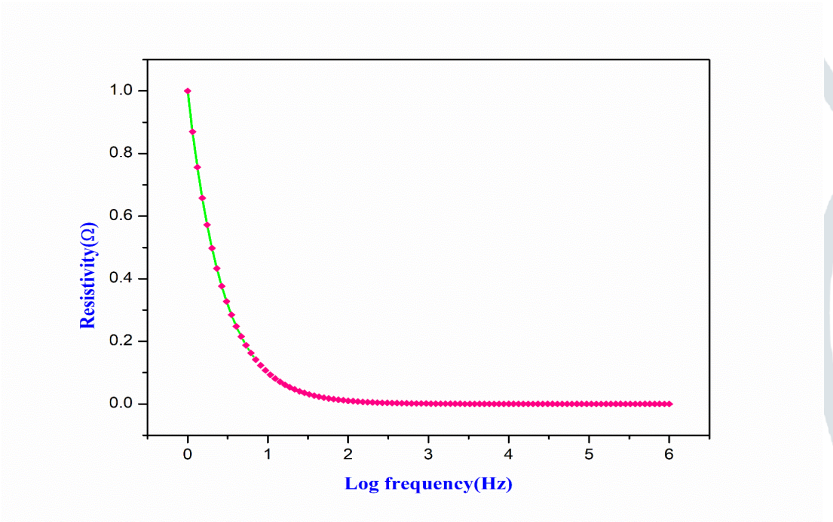

Fig.10.The curve of log frequency vs resistivity of LTPI crystal

4.6 NLO Studies

SHG Powder measurement was the crystallized sample confirms the SHG activities of LTPI crystal. The converter output was displayed on a digital storage oscilloscope. From the SHG efficiency obtained data the of LTPI samples was 1.4 time higher than that of potassium dihydrogen phosphate. This property of enhancing the frequency makes LTPI crystal can eligible candidate in doubling applications [16].

5 .Conclusion

Semi-organic crystal LTPI was grown by a slow solvent evaporation method at room temperature. Single crystal XRD confirms the orthorhombic crystal system and unit cell parameter with a non Centro symmetric space group. Powder XRD techniques identified the crystalline nature. The FTIR Spectra prove the presence of functional groups in LTPI crystal. The optical studies exhibit that the energy gap is about 4.5 eV. The transmission was lower cut off wavelengths 275 nm. ^{1}HNMR molecular structure was grown crystal studied. From the dielectric measurement it was founded that the high frequencies range increased and low dielectric value decreased . The second harmonics generation efficiency is due to powder sample of LTPI crystal which is 1.4 times higher than of KDP crystal. Among all the studies used in for the sample suitable at the fabrication of laser based device.

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