

# Growth and Some Characterization on L-Leucine Potassium Chloride NLO Crystals

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## Abstract

L-Leucine potassium chloride (LLPC) crystals have been synthesized and grown by most effective slow evaporation technique in water as the solvent. The single crystal XRD analysis shows that the grown crystal has monoclinic structure. The FT-IR spectroscopic studies reveal the various functional groups of the sample. The linear optical properties of the grown LLPC crystal were studied by recording the UV-Vis-NIR spectrum. The Vickers microhardness was determined by using a hardness tester at different applied loads. The crystal thermal stability was determined by TG-DTG analysis. The Second harmonic generation efficiency of the title material was tested using Kurtz and Perry experimental technique which reveals that L-Leucine potassium chloride crystal is the potential candidate for nonlinear optical applications. Third order NLO parameters like nonlinear absorption coefficient, refractive index nonlinear and nonlinear susceptibility of LLPC crystal are analysis by Z-scan method.

## Keywords

Crystal growth, XRD, FTIR, FL studies, Microhardness, TG-DTG studies, NLO study, Z-scan techniques.

## 1. Introduction

Nonlinear optical material has attracted the attention of the researchers for tailor device applications and other applications like optical switching, optical modulator, data storage device, telecommunications, optical information processing, and high density optical disk data storage [1]. In organic materials, the solids frameworks of conjugately  $\pi$  electrons along with weak Van der Waals and H bonds play a vital role of their NLO properties [2]. Some simple organics and inorganic

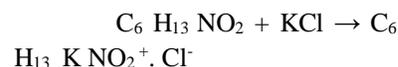
salts of amino acids appear to be promising materials for optical second harmonics generation [3]. One of the main advantages of organic materials is that their structures can be modified to get the desired NLO property [4]. Inorganic material like potassium dihydrogen orthophosphate remains the most widely used crystal for frequency conversion due to their modest nonlinearities [5]. In solid state, amino acids exist as zwitterions as they contain a proton donor carboxylic acid group COOH and a proton acceptor  $\text{NH}_2$

group [6] and L-Leucine is one of the amino acids and so its complexes are useful NLO materials. A number of complexes like L-Leucine picrate, L-Leucine nitrate and L-Leucine hydrobromide were reported in the literature [7, 11]. In the present communication we are reporting the growth of the semiorganic crystal of L-Leucine potassium chloride by solution grown method. Detailed studies on the structural, FT-IR, XRD, thermal, optical and mechanical, dielectric, FL, NLO properties of the grown crystals of LLPC are reported.

## 2. Experimental

### 2.1 Synthesis and crystal growth

L-Leucine and potassium chloride were taken in an equimolar ratio 1:1 with de-ionized water as the solvent. The reaction that takes place for synthesis of L-Leucine potassium chloride is as in the reaction formula



The calculated amount of L-Leucine and potassium chloride were dissolved in deionised water and the solution was stirred for three hours. The saturated solution was filtered and kept for solution evaporation. The colourless and transparent crystal

were harvested after the period 35 day. The photograph of the growth crystals of LLPC are shows

in figure 1.

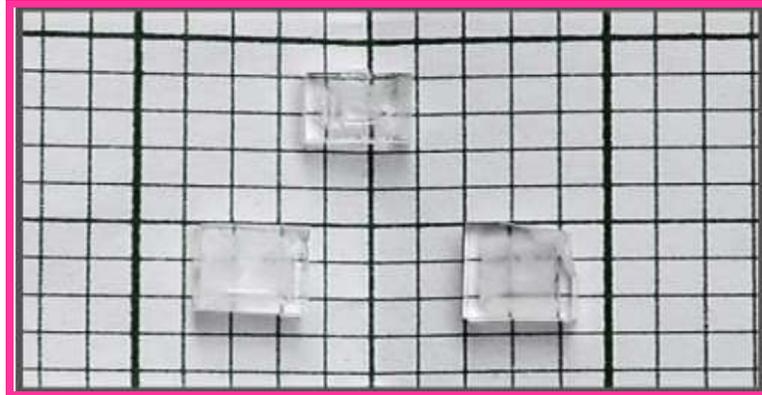


Fig.1The photograph of grown LLPC crystals

## 2.2 Characterization techniques

The radiation wavelength was 1.5406 Å. Single XRD details were collected used an ENRAFS NONIUS CAD4-MV31 single crystal X-ray diffractometry with MoK<sub>α</sub> (λ=0.71073 Å). The functional groups, present in the LLPC crystal and its bond nature with vibrational assignment were identified by the FTIR spectrum analysis used to PERKIN ELMER FTIR spectrophotometer. The thermal stability was analyzed by TG and DTG analysis in a closed chamber with controlled nitrogen flow atmosphere using NETZSCHT thermal analyser. Vickers microhardness test was carried out using SHIMADZU HMV Vickers hardness tester fitted with a diamond indenter. The SHG efficiencies of the growth crystals were analyzed using Nd: YAG lasers λ=1064 nm, QUANTA RAY MODELS LAB-170-10). Third order NLO parameters like nonlinear

absorption coefficient, refractive index nonlinear and nonlinear susceptibility of LLPC crystal are analysis by Z-scan method.

## 3. Results and Discussion

### 3.1 Single crystal XRD studies

The structure of the crystal has been identified by single XRD analysis data was been collected using an ENRAFNONIUS CAD4-MV31 X-ray diffractometry for single crystals with MoK<sub>α</sub> (λ=0.71073 Å). The single crystal XRD data reveals that LLPC crystals conforms to monoclinic structure with space group the obtained lattice parameter P2<sub>1</sub> are tabulated in the table1. The structural morphology of the LLPC crystals was indexed by a Winxmorph software program. The indexed morphology of LLPC of shown figure 2.

Crystal parameters	Values
Crystal system	Monoclinic
Space group	P2 <sub>1</sub>
a	9.412 (3) Å
b	12.721 (3) Å
c	8.945(3) Å
α	90°
β	102°
γ	90°
Unit Cell volume	1046.61(4) Å <sup>3</sup>
Z	2

Table 1: Single crystals XRD data for LLPC crystal



Fig.2. Indexed morphology of LLPC crystal

### 3.2. FT-IR spectral analysis

FT-IR analyses of LLPC crystal were recorded using Perkin Elmer spectrometer with KBr technique for the range 4000 - 400  $\text{cm}^{-1}$ . The functional group present in the crystals was identified by FTIR spectrum. FTIR spectrum is shown figure 3. The primary amine stretching bond is weak at 3420  $\text{cm}^{-1}$  and sharp peak observed at 3027  $\text{cm}^{-1}$  and there are attributed to OH and NH groups, stretching vibration are found. Peak found at 2669  $\text{cm}^{-1}$  and 2577  $\text{cm}^{-1}$  were corresponds to CH stretching vibration. C = C asymmetric stretching absorptions are identified around 1990  $\text{cm}^{-1}$ . A strong C = O

stretching absorptions is found at in 1726  $\text{cm}^{-1}$ . A varying vibration with reduced intensity is observed at 1675  $\text{cm}^{-1}$  which is attributing to  $\text{COO}^-$  symmetric stretching. A deformed  $\text{CH}_2$  and  $\text{CH}_3$  vibrations is found around 1489  $\text{cm}^{-1}$ . Some medium stretching vibration is observed around 1203  $\text{cm}^{-1}$ . Stretching vibrations of P-OH and S-OH are observes at 1024 and 817  $\text{cm}^{-1}$  respectively. A strong bending absorption is found around 588  $\text{cm}^{-1}$  which is belongs to C-H deformation vibration [12, 13]. The FTIR spectral assignments for the grown crystal of LLPC are provided in the table 2.

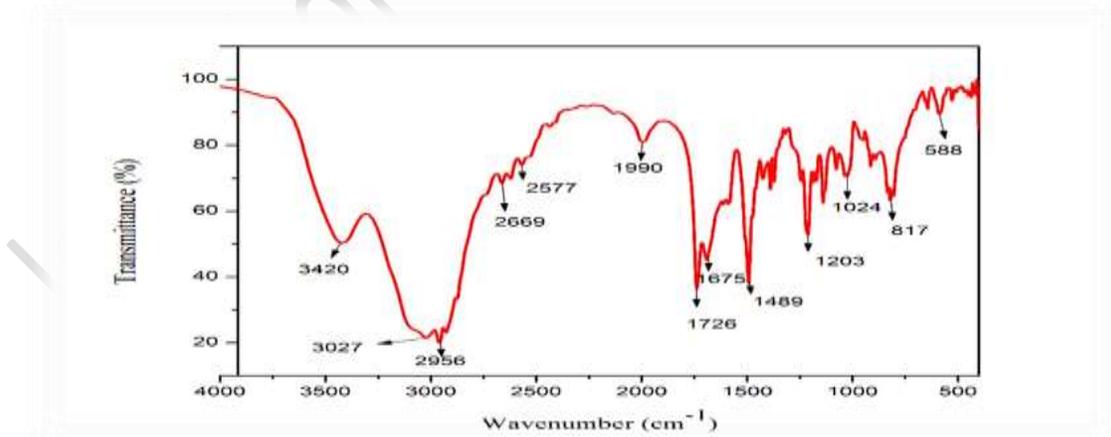


Fig.3. FT-IR Spectrum of LLPC crystal

Table 2: Spectral Assignments for LLPC crystal

Wave Number ( $\text{Cm}^{-1}$ )	Assignments
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3420	O-H Primary amines stretching
3027	N-H stretch
2956	CH Stretching vibration
2669,2557	CH stretching
1990	C=C asymmetric stretch
1726	C=O stretching
1675	COO <sup>-</sup> stretch
1489	CH <sub>2</sub> and CH <sub>3</sub> deformation
1203	O-C stretching
1024	P-OH stretching vibration
817	S-OH stretching vibration
588	C-H deformation

excitation is 240 nm. When UV

### 3.3 Fluorescence (FL) studies

Fluorescence spectrometer was used to record the FL spectrum the wavelength range 300-800 nm. The fluorescence emission spectrum is shown in the figure 4. The wavelength chosen for the

light used as the excitation light, electrons are excited from ground state to high state and due to this excitation, of visible light or UV light are emitted from the crystal. In the FL spectrum prominent peak at 478 nm corresponds to emission of blue light from the crystal. There is also a broaden peaks at 525 nm which corresponding to green light [14].

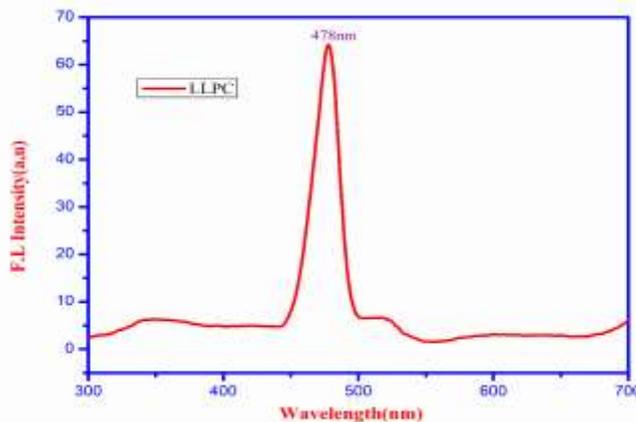


Fig.4. Fluorescence spectrum recorded emission of the LLPC Crystal

### 3.4 Micro hardness studies

The Vickers value of microhardness was estimates by SHIMADZU HMV microhardness tester. The mechanically stability of the growth crystals is checker by hardness tester. The load versus  $H_v$  gives the Vickers plot and it is shows in the figure 5 and from which it could be noticed that the material shows a linear increase in the hardness value on the application of increasing load. The increasing trend of microhardness within the applied load for the sample is due to reverse indentations size effects. The

plot of  $\log d$  versus  $\log P$  yields figure.6 straight line graph and from the slope the work hardening coefficient  $n$  and its was found to be 3.472 and it confirms LLPC the belongs to soft material. Elastic stiffness coefficient  $C_{11}$  gives the idea of tighten of bonding between neighboring atoms, which was calculate useful Wooster's empirical relation given by  $C_{11} = H_v^{7/4}$ . The variations of stiffness constants  $C_{11}$  with load is shown figure7. Another mechanical parameter viz., yield strength was calculated using relation  $\sigma_y = H_v/3$  where  $H_v$  is the microhardness number [15] and the variation of yield strength with

the applied load is also shown in figure7. From the results, it is observed that both stiffness constant and

yield strength increase with increase of applied load for LLPC crystal.

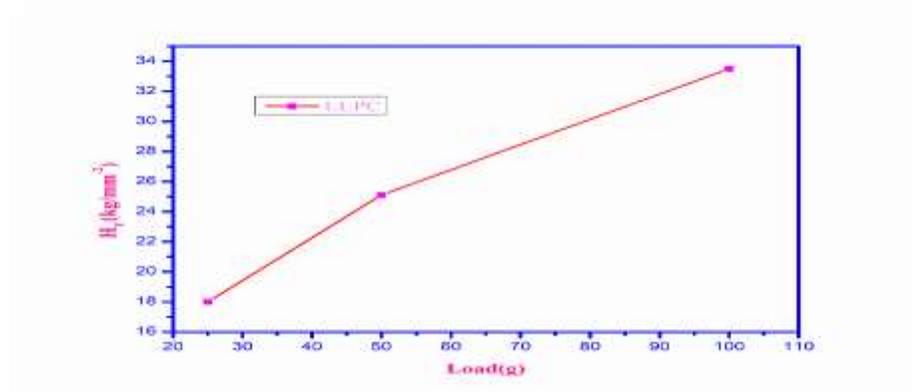


Fig.5. Variation of Vickers hardness of LLPC crystal versus of applied load

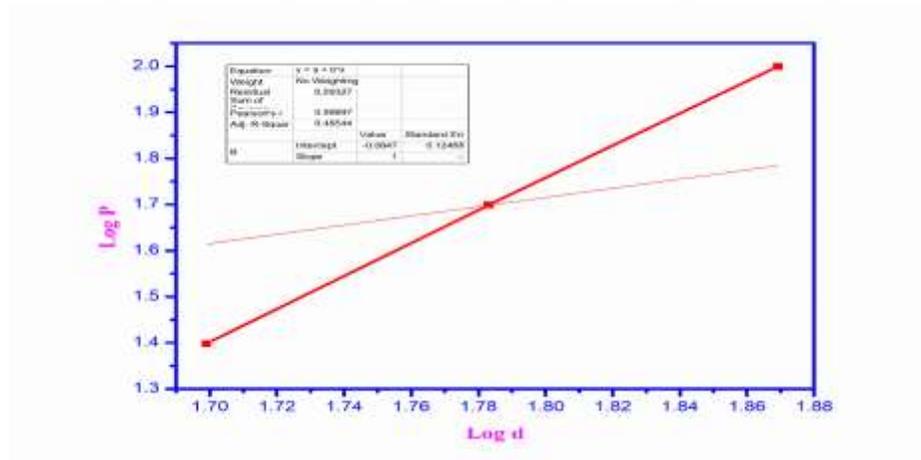


Fig.6.The curve of log d versus log p for LLPC crystal

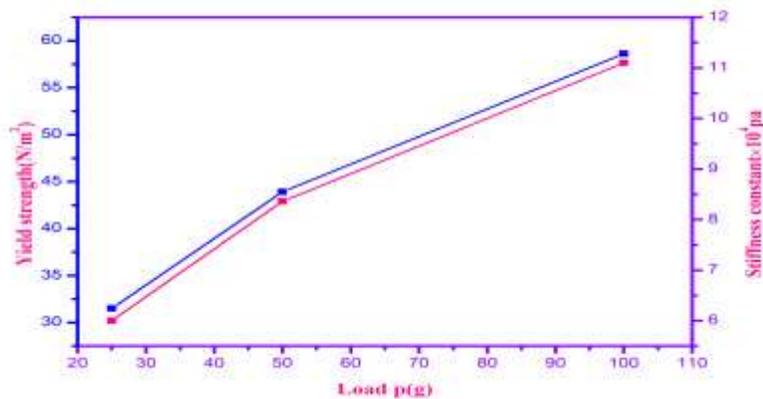


Fig.7.Variation of yield strength and stiffness constant vs applied load for LLPC crystal

### 3.5 Thermal analysis

TG-DTG analysis had carried using the NETZSCH thermal analyser. The sample was given heat treatment with the help of alumina crucible, in presence of nitrogen at a heating rate of 10k/min in the temperature range between 25°C to 1200°C. The TG/DTG thermo grams are shown in figure 8. From

the graph we could found that no weight loss up to 700 °C. It shows the sample high thermal stability of the crystal. The decomposition point of the grown LLPC crystal 911 °C. Beyond this temperature, the percentage of weight of the sample is found to be about 5%. Since the sample has high thermal stability, it can be used fabrication of NLO devices [16, 17]

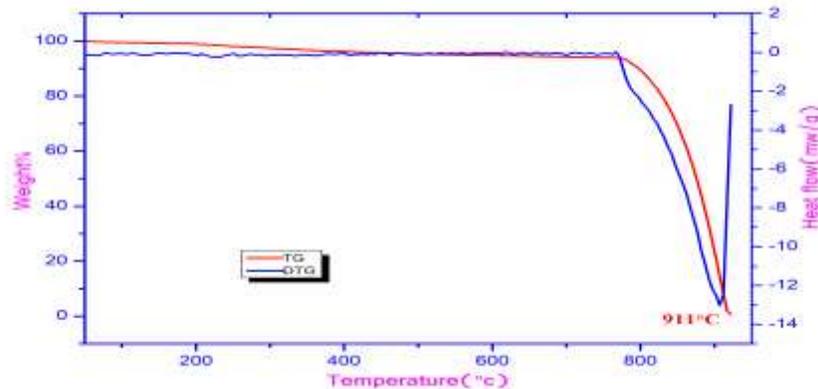


Fig.8.TG/ DTG plots for LLPC crystal

### 3.6 Second Harmonic Generation

The SHG efficiency of the growth crystals of LLPC was measurements by Kurtz Perry powders technique. Nd: YAG laser used as Q-switch with wavelength of 1064 nm with 8 ns pulse width with repetitions rates of 10 Hz was used. Here KDP crystal used as a reference material for measuring the SHG efficiency. The laser radiation was allowed to fall on the sample and emission of green laser radiation from the sample was observed. It is evident that the SHG sufficiency of LLPC. The SHG efficiency of LLPC crystal is 2.5 times that of the standard KDP sample [18].

### 3.7. Z-scan method

The third order NLO radiation is received from a bulk crystal in spite of interaction of higher energy laser gives the detailed knowledge of the nonlinear response of the crystal and it could be studied using Z-scan method [19,20].The importance NLO third order properties are nonlinear absorptions coefficient ( $\beta$ ), refractive index nonlinear ( $n_2$ ) and

nonlinear susceptibility of the crystal. The grown crystal of L-Leucine potassium chloride was subjected to He-Ne lasers of wavelengths 633 nm. Firstly the polished crystal of L-Leucine potassium chloride was emplaced at focus (at  $Z=0$ ) and the Gaussian filtered beam of the laser was focused on the crystals utilizing a convex lens. As the crystals are translated along the Z direction, the transmittance was measurement using a photo detector. The aperture was emplaced at face of the detector and in both open aperture (OA) and closed aperture (CA) modes; the transmittance was measure as the function of the distance (Z).The open aperture (OA) plot and closed aperture (CA) Z-scan plot for L-Leucine potassium chloride crystal are given in the figures 9 and 10. In the closed aperture Z-scan curve, it is seen that there is a prefocal maximum peak to post focal minimum valley and this corresponds to negative nonlinearity of the sample. This is due to self defocus nature of the sample.

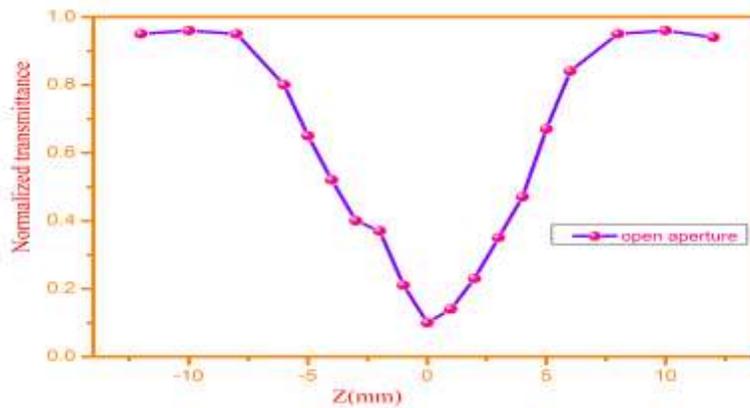


Fig.9. Open aperture of LLPC crystal Z-scan Plot

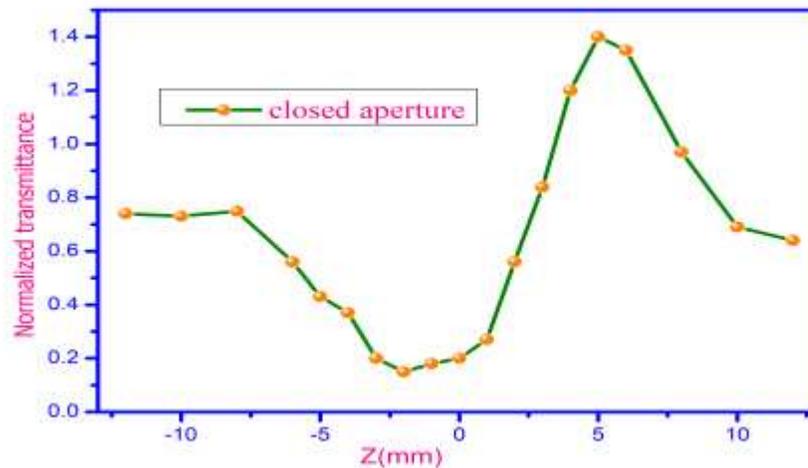


Fig.10. Closed aperture of LLPC crystal Z-scan plot

The refractive index nonlinear ( $n_2$ ) of L-Leucine potassium chloride crystal was determined using the following equation.

$$\eta_2 = \frac{Df}{(KI_0 L_{eff})}$$

where  $I_0$  is the intensities of the lasers beam at the focus and  $K = 2\pi/\lambda$   $\lambda$  is the wavelength of He: Ne laser beam.

The  $L_{eff}$  is the effective thickness can be calculated

the usage of the relation  $\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}}$

In which  $\Delta T$  is the peak value in the open aperture mode of Z scan curve. The value of  $\beta$  could be negatively for saturable absorptions and positively for two photon absorptions procedure. The real part

and imaginary a part of the third orders of nonlinear optical susceptibility ( $\chi^3$ ) may be determined via the following relations

$$\text{Real part of } \chi^3 = (10^4 \epsilon_0 c^2 \eta_0^2 \eta_2^2) / \pi \text{ (esu)}$$

$$\text{Imaginary part of } \chi^3 = (10^2 \epsilon_0 c^2 \eta_0^2 \lambda \beta) / 4\pi^2 \text{ (esu)}$$

$$\text{Absolute values of } \chi^3 = \{[\text{Real part of } \chi^3]^2 + \{[\text{Imaginary part of } \chi^3]^2\}^{1/2} \text{ (esu)}$$

Hence  $\epsilon_0$  is the permittivity vacuum,  $C$  is the light velocity,  $\eta_0$  is the linearity refractive index of the pattern and  $\eta_2$  is the nonlinearity refractive index of the pattern and  $\beta$  is the nonlinear absorptions coefficient of the pattern and nonlinear susceptibility of the grown L-Leucine potassium chloride crystal are provided in the table 3.

**Table3. The obtained Z-scan data for LLPC crystal**

Parameter	Value
Wavelength of laser beam	633 nm
laser Power	10 mW
Focal length of convex lens	7 cm
beam of aperture ( $\omega_a$ )	1 cm
radius of Aperture ( $r_a$ )	4 mm
Nonlinear absorption coefficient ( $\beta$ )	$2.345 \times 10^{-5}$ m/W
refractive index Nonlinear ( $n_2$ )	$1.152 \times 10^{-11}$ m <sup>2</sup> /W
Real part of nonlinear susceptibility $\chi^{(3)}$	$7.040 \times 10^{-9}$ esu
Imaginarey part of nonlinear susceptibility $\chi^{(3)}$	$1.519 \times 10^{-9}$ esu
nonlinear susceptibility $\chi^{(3)}$	$3.520 \times 10^{-6}$ esu

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### 3.8 Conclusion

Good quality semiorganic crystals of L-leucine potassium chloride (LLPC) successfully grown by slow solvent evaporation method. XRD analysis confirms the sample monoclinic structure of the crystal. The presence of functional groups are analysed . FL spectrum of the sample indicates that the sample gives out blue light. The mechanical parameters like hardness, work hardening coefficient, yields strengths and stiffness constants of LLPC crystal were evaluated and analyzed. TG-DTG analysis confirms high thermal stability of the crystal. The SHG efficiency of LLPC crystal was founded to be higher than that of KDP crystal. Third order NLO parameters like nonlinear absorptions coefficient, refractive index nonlinear and nonlinear susceptibility of LLPC crystal were determined by Z-scan method. The above studies confirms the LLPC crystal is a prominent NLO material for opto-electronic and laser applications.

### References

[1] Meera J, Nath, S.S.D., I. Hubert Joe Journal of physics and chemistry of solid 122(2018)

[2] M.Suresh, S.Asath Bahadur, S.Athimoolam, J.Mater. sci. Mater Electron, DOI10.1007/s10854-016-5572-4

[3] Mariusz K, Marachewka, Marek, Cent.Eur.J.Chem. 11(8).2013.12641277, DOI:10.2478/S11532-013-0259-7

[4] G. Bhagavannarayana, B. Riscob, Mohd. Shakir Materials chemistry and physics 126(2011)20-23

[5] P. Baskaran, M. Vimalan, P. Anandan, G. Bakiyaraj, K. Kirubavathi, SG. Praveen and K Selvaraju, Materials Research Express 3(2016) 035101

[6] Soma Adhikari, Tanusree kar. J. Cryst. Growth, 356(2012)4-9

[7] Soma Adhikari, Tanusree kar, Material Chemistry and Physics xxx(2014) 1-6

[8] P. Baskaran M. Vimalan P. Anandhan G. Bakiyaraj K. Kirubavathi K. Selvaraju, Journal of

Tibah University for science  
(2016),<http://dx.doi.org/10.1016/j.jtusci.2016.03.003>

[9] Sameh Guidara, Habib Feki, Younes Abid,  
Spectrochimica Acta partA: Molecular and  
Biomolecular Spectroscopy 115(2013) 437-444

[10] Soma Adhikari, Tanusree Kar ,Materials  
Research Bulletin 48(2013) 1612-1617

[11] R.M Silverstein G. clayton Bassler, Terence C.  
Morris Spectrometric identification of  
organic compounds, ISBN:9780471634041

[12] K. Mohana Priyadarshini, A. Chandramohan, G.  
AnandhaBabu, P. Ramasamy,  
Optik,125(2014)1390-1395

[13] K. Boopathi, S. Moorthy Babu, R. Jagan. P.  
Ramasamy Journal of physics and chemistry of  
Solid 111(2017)- 419-430

[14] Jagadeesh M.R, Suresh Kumar H.M, Ananda  
Kumari. R,Materials Science-Poland 33(3),  
2015, pp.529-536

[15] K. Kamatchi, P. Umarani, T. Radhakrishnan, C.  
Ramachandra Raja ,optick-International for  
light and Electron optics 172(2018)674-679

[16] P. Vasudevan, S. Gokul Raj, S. Sankar,  
Spectrochimica Acta Part A: Molecular and  
Biomolecular Spectroscopy 106 (2013) 210-215.

[17] S.K. Kurtz, T. T Perry. Apply Phy,39.3798.1968

[18]Prasad, A, Kalainathan, S,&  
Meenakshisundaram,S, 2016, Optik,vol.127,  
pp.6134-6149

[19]Sun, J, Ren, Q, Wang, XQ, Zhang, GH and Xu,  
D, 2009, Optics & Laser Technology,  
Vol, 41, pp. 209-212.

[20]Sutherland RL, 2003, Handbook of nonlinear  
optics, CRC press.