Growth and Some Physical Studies, NLO studies on L-Leucine Potassium Chloride Crystals

M. Kandasamy[1], S. Pari[2] G. Kanagan[2]

[1]Department of Physics, Govt. Arts College, Ariyalur
[2]Department of Physics, National College (Autonomous), Triuchirappalli

[*]Corresponding Author: mkandan2004@gmail.com

Abstract

L-Leucine potassium chloride (LLPC) crystals have been synthesized and grown by slow evaporation technique. The FT-IR spectroscopic studies reveal the various functional groups of the sample. The optical properties of the grown LLPC crystal were studied by recording the UV- Vis-NIR spectrum. The ^{1}H NMR spectrums are attributed to the presence of -CH proton next to the carboxylic acid. The crystal thermal stability was determined by TG-DTG analysis. Dielectric measurement was carried out as a function of frequency and results are discussed. 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.

Keywords

Crystal growth, Powder XRD, FTIR, UV, ^{1}HNMR, Dielectric studies, TG-DTG, NLO efficiency.

1. Introduction

Nonlinear opticals material grabbed the attentions of the researchers for tailored device applications and other applications are optical switching, optical modulator, data storage device, telecommunications, opticals information processing, and high density optical disk data storage[1]. In organic materials, the solids frame works of conjugately π 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 opticals second harmonic generation [3]. One of the main advantages of organics materials is that their structures

can be modifying to get a desirous 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 solids state, amino acid exist as zwitterions as they contain a proton donor carboxylic acid group COOH and a proton acceptor NH_2 group [6] and L-Leucine is one of the amino and so its complexes are useful NLO materials. Some of complexes like L-Leucinium picrate, L-Leucine nitrate and L-Leucine hydro bromide were reported in the literature [7, 11]. In the present communication, we are reported the growth of the semi organic crystal of L-Leucine potassium chloride by slow evaporation solution growth method. Detailed studies on the structural, FT-IR, XRD, ^1H NMR, thermal, optical and dielectric, 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

$$C_6H_{13}NO_2 + KCl \rightarrow C_6H_{13}K NO_2^{+}.Cl^{-}$$

The calculated amount of L-Leucine and potassium chloride were dissolved in deionised water and the solution was stirred for about three hours. The saturated solution was filtered and kept for solution slow evaporation. The colourless and transparency crystal were harvested after a period of 35 days. The photograph of the grown crystals of LLPC is shown in figure 1.

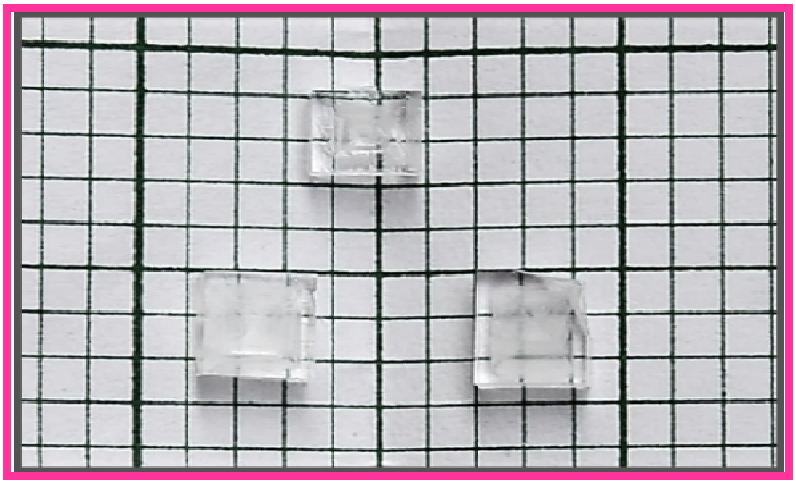

Fig.1The photograph of grown LLPC crystals

2.2 Characterization techniques

The powder XRD data of the LLPC crystal using collected PANALYTICAL XPERT PRO X-Ray diffractometery with CuK_α radiation. The functional groups, present in the LLPC crystal and its bond nature with vibrational assignment were identified from the FTIR spectrum used the model PERKIN ELMER FTIR spectrophotometer. The optical properties of the LLPC was analysed like the transmission spectrum of the LLPC recorded in the range of 190 nm to 1100 nm with help of PERKIN ELEMER LAMBDA 365 UV visible spectrometer. ^1H NMR spectrum analysis of the LLPC grown crystal was analysed with BRUKER AV-300 model. Dielectric analysis of LLPC crystal was obtained using an LCR meter. The thermal stability was analyzed by the TG and DTG analysis in a closed chamber with controlled nitrogen flow atmosphere within the range of 25°C to be 1200°C at a heating rate of 10°C /min, using NETZSCHT thermal analyser. The SHG efficiencies of the grown crystals were analyzed using Nd: YAG laser with λ=1064 nm, using the QUANTA RAY MODELS LAB-170 model.

3. Results and Discussion

3.1 Powder XRD studies

The powder XRD analysis was carried out using the PANALYTICAL XPERT PRO X-ray diffractometer with CuK_α (λ=1.5408 Å) radiation. The LLPC powder was scanned over the 2θ range of 10-80° at a rate of 1°/minutes. The powder XRD pattern of the grown crystal is shown figure 2. The sharp and well defined peaks confirmed the grown crystals are free from structurals grain boundaries and it is in the single crystal form [12, 13]. The powder pattern was indexed using the INDEXING software package.

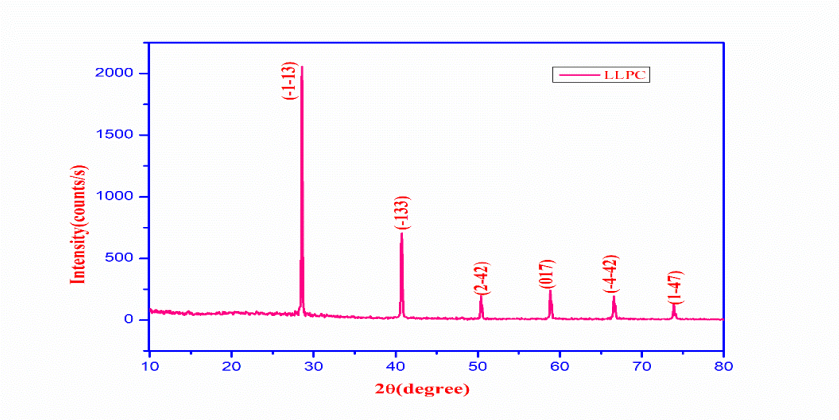

Fig.2. Powder X-ray diffraction pattern of LLPC crystal

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 cm^{-1}. The functional groups are presented in the crystal were identified by using FTIR spectrum and the spectrum is shown figure 3. The primary amine stretching bond is weak at 3420 cm^{-1} and sharp peak observed at 3027cm^{-1} and there are all attributed to OH and NH groups, strectching vibration are found. Peak found at 2669 cm^{-1} and 2577cm^{-1} were corresponds to CH stretching vibration. C = C asymmetric stretching absorptions are identified around 1990 cm^{-1}. A strong C = O stretching absorptions is found at in 1726 cm^{-1}. A varying vibration with reduced intensity is observed at 1675 cm^{-1} which is also attributed to COO^- symmetric stretching. A deformed CH_2 and CH_3 vibrations is found around 1489 cm^{-1}. Some medium stretching vibration is observed around 1203 cm^{-1}. Stretching vibrations of P-OH and S-OH are observes at 1024 and 817cm^{-1} respectively. A strong bending absorption is found at 588 cm^{-1} which is belongs to C-H deformation vibration [14, 15]. The FTIR spectral assignments for the grown crystal of LLPC are tabulated in the table 1.

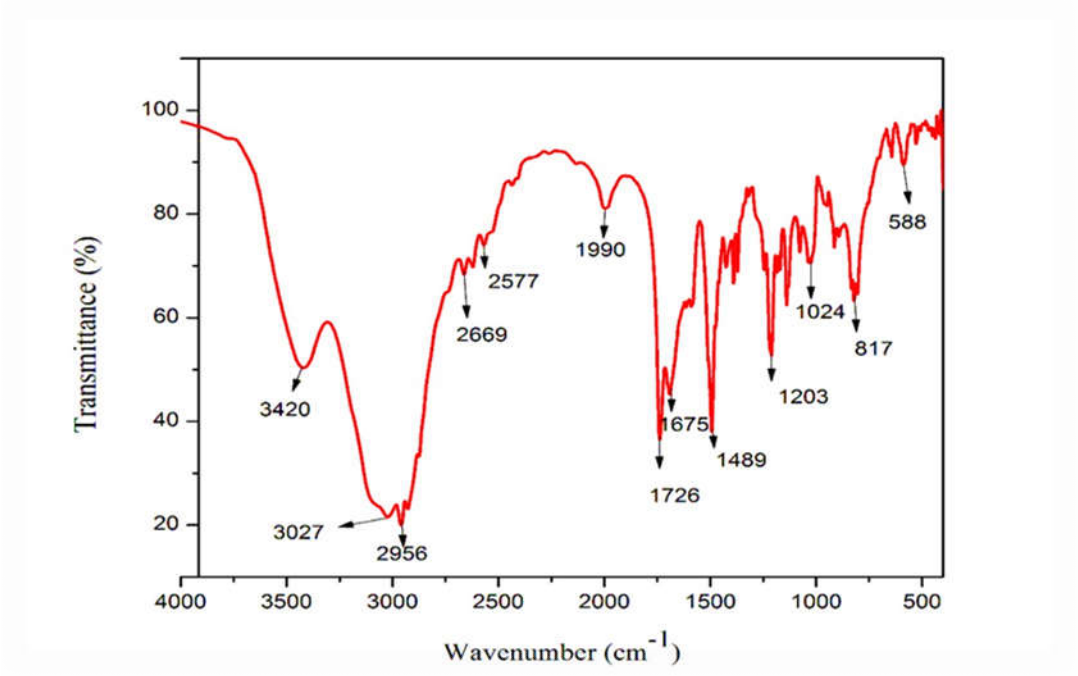

Fig.3. FT-IR Spectrum of LLPC crystal

Table 1: Spectral Assignments for LLPC crystal

Wave Number (Cm^{-1})	Assignments
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^- stretch
1489	CH_2 and CH_3 deformation
1203	O-C stretching
1024	P-OH stretching vibration
817	S-OH stretching vibration
588	C-H deformation

3.3. UV-Vis-NIR spectral analysis

The UV-vis-NIR spectrum was recorded is the range of 190 to1100 nm using Perkin Elmer Lambada365 spectrophotometer. The UV spectrum of LLPC is shown in figure 4, from the spectrum it is found that the transparency of LLPC crystal is in the visible region. Linear spectrum in the entire visible region of the LLPC crystal exhibits NLO property. The percentage of transmission is observed around 70%. The upper cut off wavelength was observed around at 280 nm, which makes the LLPC material a potential candidate for opto-electronic applications.

Optical band gap Absorption coefficient (α) of the LLPC sample from the relation determined $\alpha = \frac{2.3026}{t} \log (1/T)$

Where t-thickness of the LLPC crystal and T is the transmittance. The optical band gap of the LLPC crystal have been calculated from Tauc relation $h\alpha\upsilon = A(h\upsilon - E_g)^{1/2}$, where A is the constant, Eg is the opticals band gap, υ is frequencies of incident photon, h is the Planck's constant. From the Tauc plot, the opticals band gap of LLPC found to be 4.42 eV and is shown figure 5.

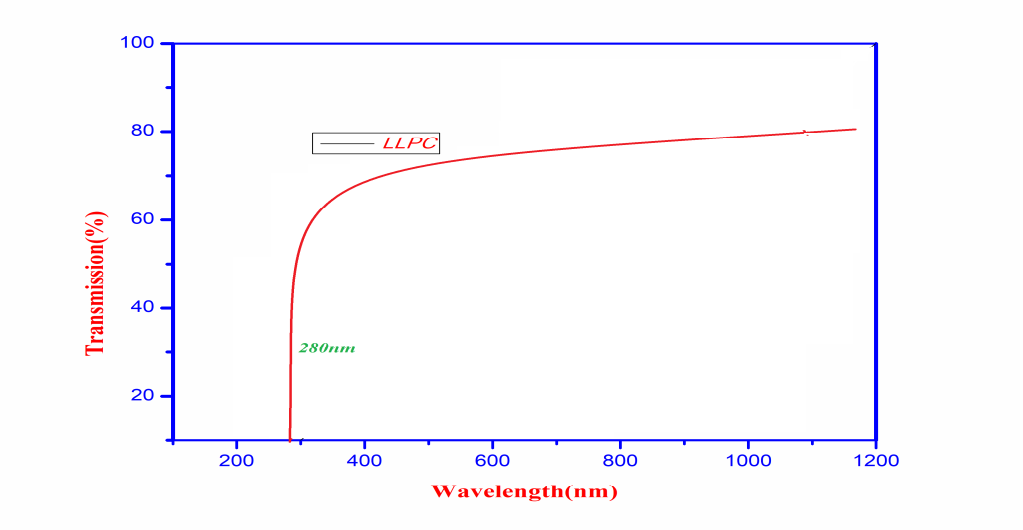

Fig.4. UV-vis-NIR transmittance spectrum of LLPC crystal

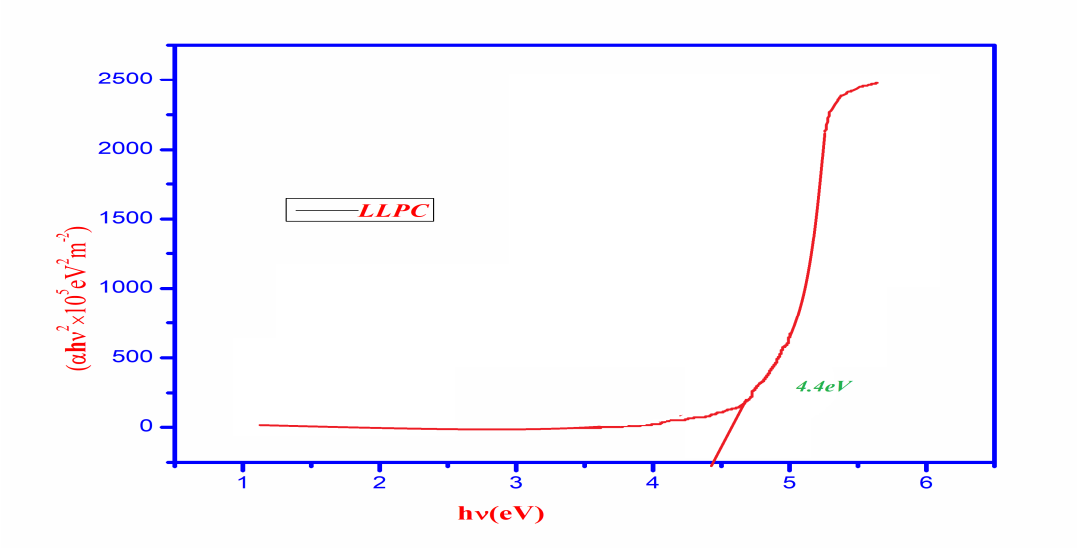

Fig.5. Tauc plot for L-Leucine potassium chloride crystal

3.4 ^{1}H NMR studies

^{1}H NMR spectral analysis of the LLPC crystal has been done with BRUKER AV-300 operating at 300MHz. The recorded ^{1}HNMR spectrum is shown in figure 6 and from the spectrum, the multiple peaks between δ=0.856 ppm and δ =0.868 ppm are confirmed as C-H proton presented in LLPC crystal. The presence of CH_3 proton group in L-Leucine potassium chloride is confirmed due to multiple peaks in the range between δ = 0.876 ppm and

δ = 0.887 ppm. Also, the multiple triplex signals in the range between δ= 1.621 ppm and δ =1.644 ppm is due to the hyperfine splitting of neighbouring CH_3 protons. The multiple triplex signals are observed between δ = 1.677 ppm and δ = 1.699 ppm and which δ = 1.717 ppm are attributed for the presence of -CH proton next to the carboxylic acid [16].

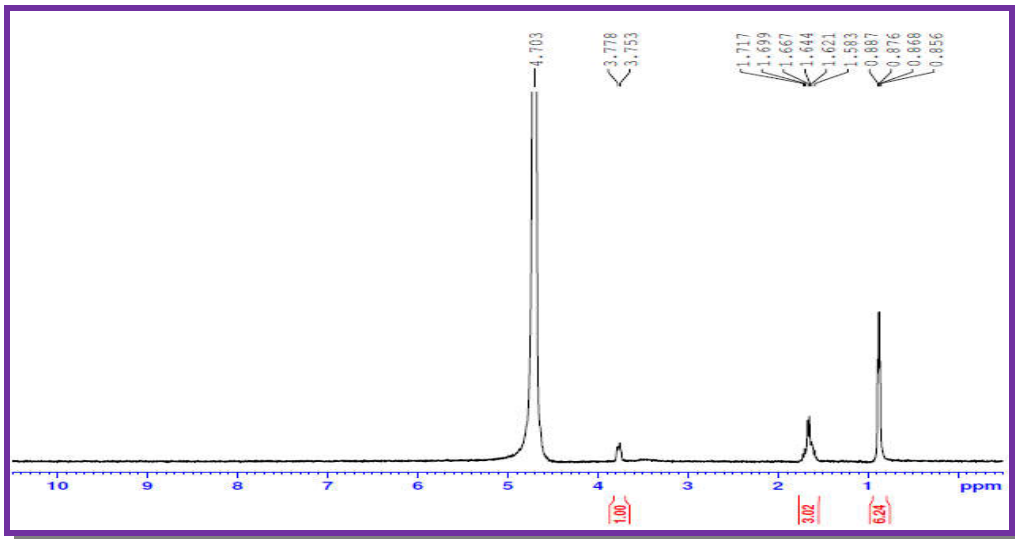

Fig.6.^{1}H NMR spectrum of LLPC crystal

3.5. Dielectric studies

Dielectric loss and dielectric constant value of the LLPC single crystal were carried out a using an LCR meter for different frequencies. The grown crystal LLPC of with thickness of 2mm kept was between the plates of a parallel plate capacitor for the measurement. The crystal faces were coated with silver paste for making good ohmic contact. The dielectric constant versus frequency for LLPC crystal is shown in the figure.7. From the graph, it is identified that dielectric constant decreases with increase of frequency. It is also noticed that the dielectric constant is nearly constant in the entire frequency range of 10^3 - 10^5 Hz. The plot of dielectric loss factor versus frequency for LLPC crystal is shown in the figure 8. The dielectric loss graphs also have shown that, loss decreases with increase of frequency. The decreasing graph of both reveals that of different types of polarizations like electronic, ionic and orientational and space charge polarizations [17].

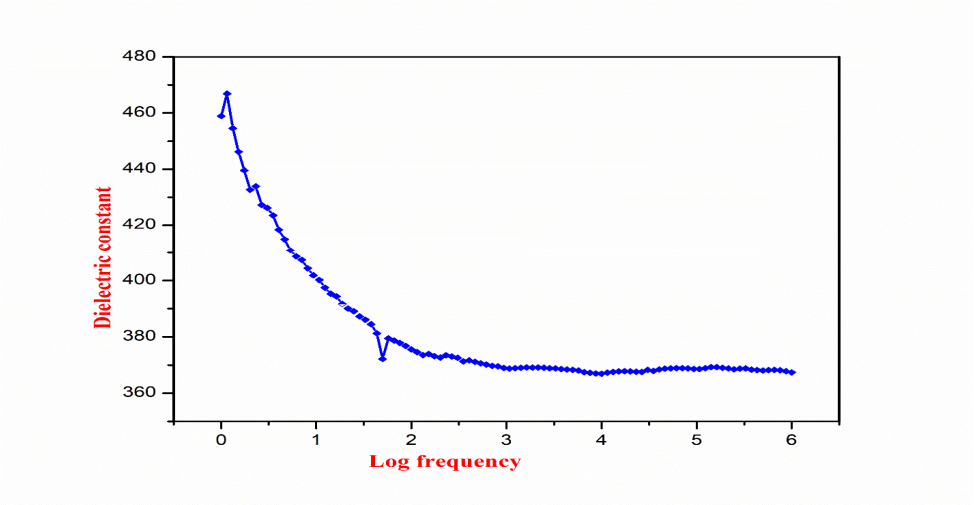

Fig.7. the plot of log frequency versus dielectric constant for LLPC crystal a temperature

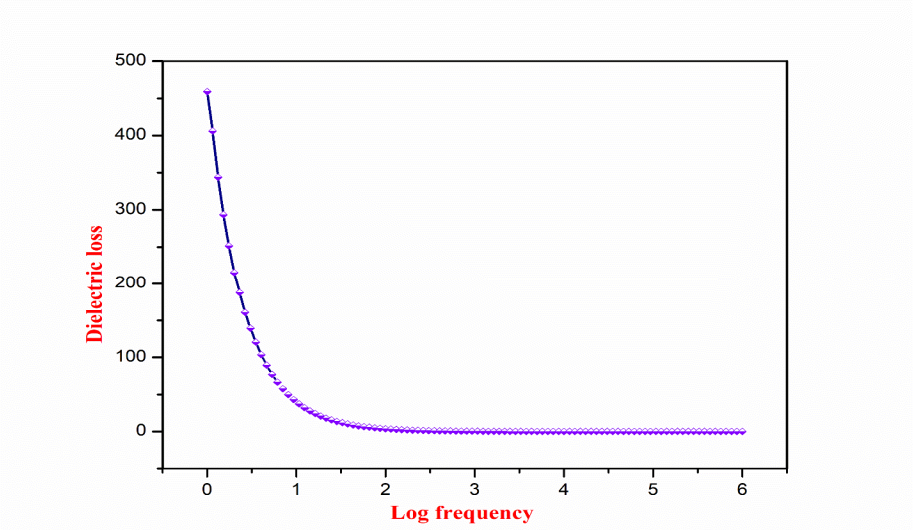

Fig.8.Plot of dielectric loss versus frequency for LLPC crystal at room temperature

3.6. Thermal analysis

TG-DTG analysis had carried using the NETZSCHT thermal analyser. The sample was given the 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 9. From the graph, we could found that no weight loss up to 700 ^{o}C and also shows the sample withstand high thermal stability of the crystal. The decomposition point of the

grown LLPC crystal measured at 911 ^{o}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 [18].

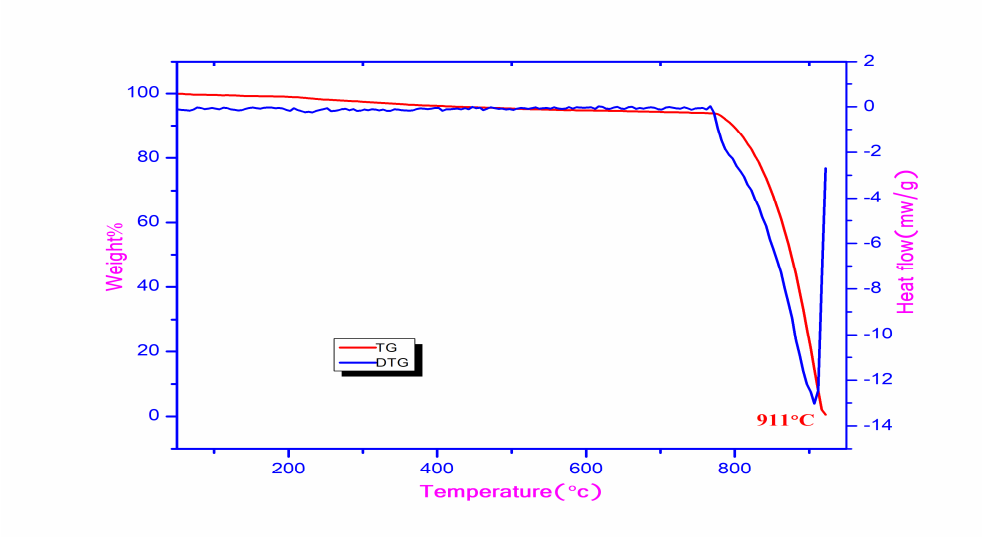

Fig.9.TG/ DTG plots for LLPC crystal

3.7. Second Harmonic Generation

The SHG efficiency of the growth crystals of LLPC was measurements by Kurtz Perry powder technique [18, 19]. Nd: YAG laser used as Q-switch with wavelength of 1064 nm with 8 ns pulse width with repetition rates of 10 Hz was used. Here KDP crystal used as a reference material for measuring the SHG efficiency. The laser radiation could fall on the sample and emission of green laser radiation from the sample was observed and also 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.

3.8 Conclusion

Good quality semiorganic crystals of L-leucine potassium chloride (LLPC) successfully grown by slow solvent evaporation method. The presence of functional groups is analyzed. The opticals band gap of LLPC crystal was founded to be 4.42 eV. The linear optical properties of the grown LLPC crystal were studied by recording the UV- Vis-NIR spectrum analyzed. The NMR spectrum confirms the grown crystal. 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. The dielectrics property of the samples was measured at different frequency and the electrical phenomena that are taking place in the sample were understood. The above studies confirm the LLPC crystal is a prominent NLO material for opto-electronic and laser applications.

Acknowledgment.

The authors are thankful to ACIC, St. Joseph's college Trichy and STIC, Cochin University, Cochin and Sastra University Thanjavur, SAIF, IIT Madras and NIT, Tiruchirappalli for providing the centres taken all of the studies and carried out the studies work successfully.

References

[1] Meera J, Nath, S.S.D., I. Hubert Joe Journal of physics and chemistry of solid 122(2018) 143-153

[2] M.Suresh, S.Asath Bahadur, S.Athimoolam, J.Mater. sci. Mater Electron, DOI10.1007/s 10854- 016-5572-4

[3] Mariusz K, Marachewka, Marek, Cent.Eur.J.Chem.11(8).2013.12641277, DOI:10.2478/S 11532- 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 ××× (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 part A: Molecular and Biomolecular Spectroscopy 115(2013) 437-444

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

[11]M.S. Dileepand, H.M.Suresh Kumar, Radiation Physics and Chemistry, https://doi.org/10.1016/j.radphyschem.2017.12.021

[12] T. Balakrishnan, S. Satheesh Kumar, K. Ramamurthi, S.Thamothran, Material chemistry and physics 2016, doi:10:1016/j.matchemphy.2016.10.036

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

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

[15] N. Pattanaboonmee, P. Ramasamy. P. Manyum Taylor Francis Ferroelectrics, 413: 96-107, 2011

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

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

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

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