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Growth and Characterization of L-alanine Potassium Nitrate Single Crystals for Nonlinear Optical Applications

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ABSTRACT

In this present work we have successfully grown L-alanine potassium nitrate (LAPN) single crystals by spontaneous nucleation solution growth method. The crystal structure and lattice parameters of the grown LAPN crystals have been determined using single crystal X-ray diffraction (SXRD) and powder X-ray diffraction (PXRD) techniques. The functional groups present in the grown crystals have been identified by means of Fourier transform infrared (FT-IR) analysis. Elemental analysis CHN was performed to confirm the inclusion of potassium nitrate into the crystal lattice of L-alanine. The UV-Vis-NIR study has been carried out within 200-2500 nm to determine the optical transparency and dielectric nature of the grown LAPN crystal. Second harmonic generation (SHG) efficiency of the grown samples were studied by Kurtz-Perry technique using Nd: YAG laser. The dielectric constant and dielectric loss of LAPN crystal was carried out as a function of frequency and the obtained results were discussed. The photoconductivity nature of the grown crystal was confirmed from photoconductivity analysis.

Keywords: A1. Crystal structure; A1. X-ray diffraction; B2. Nonlinear optic materials; B2. Dielectric Materials;

1. INTRODUCTION

Nonlinear optical (NLO) semi organic crystals are widely used for a variety of applications such as frequency conversion, optical switching, frequency doubling, and frequency tripling etc. In which a new frontier of science and technology is playing a key role in the emerging photonics and electro optics applications. Photonics crystals used in the application of photons for information and image processing and is trademarked to be the technology of the twenty-first century. These necessitate materials revealing second-order nonlinear optical effects and hence there is a great need for device quality single crystals [1-3]. In the last few decades, amino-acid based organic single crystals are gaining significance as highly possible second-order nonlinear optical materials. Huge efforts have been made to combine amino-acids with interesting inorganic materials to produce owing materials to challenge the traditional inorganic materials like niobates, borates and KDP [4-5]. In the contemporary world, the development of science in several areas has been accomplished through the growth of single crystals. Inorganic materials in combination with amino acids are extensively used in various device applications because of their higher nonlinear optical coefficient, which favors mechanical and thermal stability and a high degree of chemical inertness. In recent years, the researchers has been focused their search for new artificial nonlinear optical (NLO) materials in single crystal form which exhibiting high optical transparency, good physico-chemical properties, large laser damage threshold, and large second harmonic generation (SHG) efficiency [6-7]. Amino acids based organic materials are fascinating for nonlinear optical application as they contain proton donor carboxyl acid (COO) group and the proton acceptor amino (NH_2) group in them [8]. L-Alanine is an excellent organic nonlinear optical material under the amino acid category which is belongs to the orthorhombic crystal system with space group of P_{212121} and has a melting point of 297 °C. L-Alanine is one of the smallest chiral naturally occurring amino acid with a molecular weight of 89.09 [9-10]. In this present work describes the growth of L-alanine potassium nitrate (LAPN), which is found to have favourable properties for potential application in photonics and optoelectronics.

2. EXPERIMENTAL

2.1. Crystal growth

The raw materials L-alanine (99% Purity, Merck, India) and Potassium nitrate (99%, Merck, India) were mixed equimolar ratio 1:1 in a 250 ml glass beaker containing 100 ml deionised water at a pH of 5. The mixtures were stirred well continuously upto 6 h to get homogeneous transparent solution. The obtained saturated solution was filtered with a Whatman No1 filter sheet. The filtered solution was collected in a 500 ml crystallization dish. Then, the dish was closed with a Para film contains few pin holes and kept in vibration free clean crystal growth chamber and allowed for slow evaporation of solvent at an ambient temperature. The solution gets saturated with in few days and attains supersaturation in 12 days, after which small crystals were developed from nucleus and then they are allowed for further growth. Then the grown crystals were harvested in a growth period of 26 days. The grown crystals are shown in Fig. 1.

Fig.1 Photograph of the grown LAPN Single Crystals.

3. RESULTS AND DISCUSSION

3.1. Single crystal X-ray Diffraction analysis

Single crystal X-ray diffraction data were recorded using Enraf Nonius CAD4 X-ray Diffractometer with MoKα radiation (λ = 0.71073Å) to obtain the lattice parameters and space group. The single crystal X-ray diffraction data revealed that the grown LAPN crystal belongs to orthorhombic crystal system with space group $P2_12_12_1$. The space group indicates that the crystal is non centrosymmetric which is an elementary condition for

SHG applications. The lattice parameter values obtained for the grown LAPN crystal from single crystal X-ray diffraction analysis are a = 5.7686 Å, b = 6.0110 Å, c = 12.2901 Å and α = β = γ = 90° the unit cell volume, V = 426.16Å^3.

3.2. Powder X-ray diffraction analysis

Powder X-ray diffraction analysis of the powdered LAPN crystals were carried out using Bruker AXS D8 Advance X-ray diffractometer with Cu Kα radiation (λ=1.5406 Å) was scanned over a range 10˚–50˚at the scan rate of 1˚per min. The powder X-ray diffraction pattern of the grown LAPN crystal is depicted in Fig. 2. Powder X-ray diffraction study confirms that grown crystal crystallizes into the orthorhombic structure with space group $P2_12_12_1$. The peaks obtained from PXRD data confirm high crystalline nature of the grown LAPN crystal and the obtained peaks position are good matches with the data available in JCPDS Card No: 22-1532 [11-13]. Slight variations in the lattice parameter values show the role of dopant in the lattice of grown crystal, which is also confirmed by the slight shift observed in peaks.

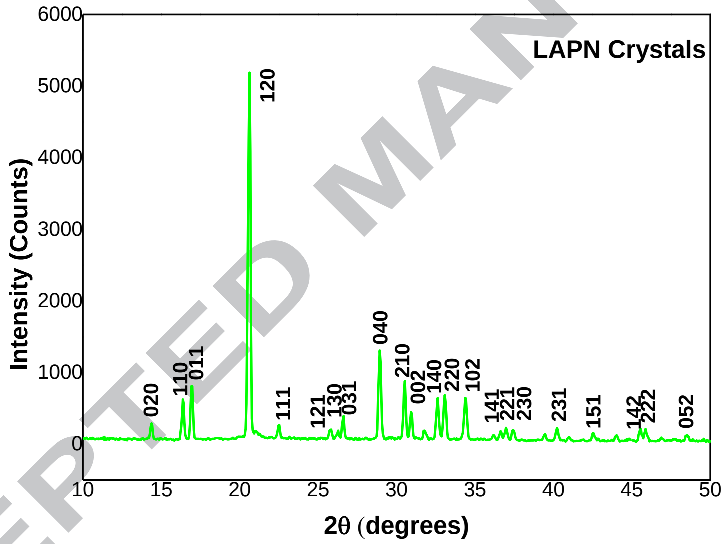

Fig. 2. PXRD pattern of the grown LASN crystal.

3.3. Elemental analysis

To ascertain the inclusion of potassium nitrate in to the grown LAPN crystal, CHN analysis was carried out on the sample. Carbon, Hydrogen, Nitrogen elemental analysis of the grown LAPN crystals were carried out using Elementar Vario EL III analyser. The result shows that the powdered LAPN sample contain Carbon = 39.42 (40.44) %, Hydrogen = 7.92 (7.92) %, and N = 15.64 (15.72) %. The obtained results of elemental analysis confirmed that the CHN analysis of the powdered LAPN sample shows good agreement with the theoretical values given in parenthesis [14].

3.4. FTIR analysis

The Fourier Transform Infrared (FTIR) spectrum of the grown LAPN crystal have been recorded in the frequency range 400-4000 cm^{-1} at room temperature by Perkin Elmer spectrometer using KBr pellet technique and is shown in Fig. 3

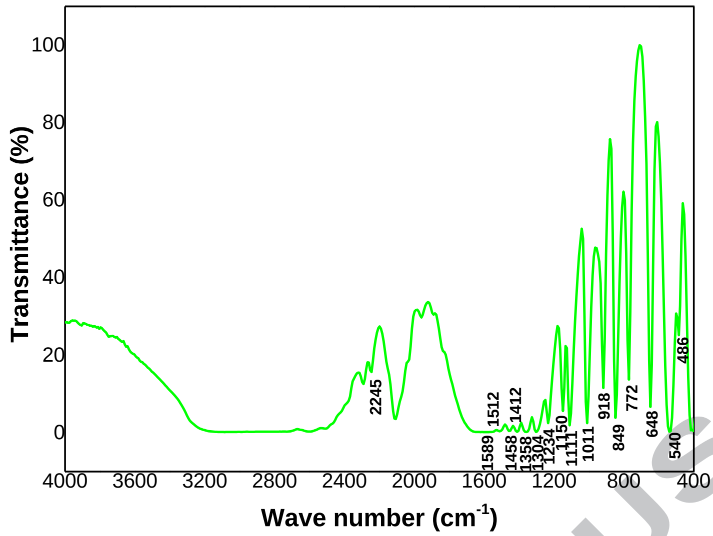

Fig. 3. FTIR spectrum of grown LAPN crystals.

The vibration peak at 2245 cm^{-1} is due to CH_3 stretching while the transmission peaks observed at 1589, 1512 cm^{-1}corresponds to the ammonium group (NH_3^+ bending). The peaks observed at 1458 cm^{-1} is corresponds to the asymmetric CH_3^+ bending. The peak observed at 1412 cm^{-1} is attributed to symmetric stretching of C-COO^-. The sharp peaks observed at 1358, 1111, 849 and 772 cm^{-1} are due to NO_3 stretching. C-H and N-H bending is observed at 1304 cm^{-1}. The band observed at 1234 and 1150 cm^{-1} are due to NH_3^+ rocking. The vibration peaks observed at 1011 and 918 cm^{-1} is attributed to overtone of torsional oscillation of NH_3^+. The COO- in plane deformation is attributed to the peak at 648 cm^{-1}. The vibration peak at 540 cm^{-1} is due to torsional oscillation of NH_3^+. The peak observed at 486 cm^{-1} is corresponds to the NH_3^+ in plane rocking. The presence of nitro groups in the obtained spectrum confirms the grown LAPN crystal. The presence of functional groups are in good agreement with the reported work [15]. The observed wavenumbers and the proposed band assignments of the FTIR spectrum of LAPN crystal are given in Table 1.

Table 1. Band assignments of LAPN crystal.

Wave number [cm^{-1}]	Band assignments
2245	CH_3 stretching
1589	NH_3^+ bending
1512	NH_3^+ bending
1458	asymmetric CH_3^+ bending
1412	symmetric stretching of C-COO^-
1358	NO_3 stretching
1304	C-H and N-H bending
1234	NH_3^+ rocking
1150	NH_3^+ rocking
1111	NO_3 stretching
1011	overtone of torsional oscillation of NH_3^+
918	overtone of torsional oscillation of NH_3^+
849	NO_3 stretching
772	NO_3 stretching
648	COO^- in plane deformation
540	torsional oscillation of NH_3^+
486	NH_3^+ in plane rocking

3.5. Optical transmission studies

The UV-Vis-NIR transmission spectrum of the grown LAPN crystal was recorded on a Varian (Model-Cary 5000) UV-Vis-NIR spectrophotometer between the wavelength range 200 and 2500 nm is shown in Fig. 4. The UV-Vis-NIR transmittance spectrum reveals that the grown crystal is transparent in the entire visible, NIR regions and has a lower cut-off wavelength of 272 nm. The bandgap energy of the grown crystal is 4.460 eV. It was calculated using Planck's energy equation ($E_g = \frac{hc}{\lambda_{min}}$ nm) with the data of lower cut-off wavelength. The value of bandgap energy reveals the dielectric nature of the material. This is one of the most essential property for photonics and electro-optic device materials [16].

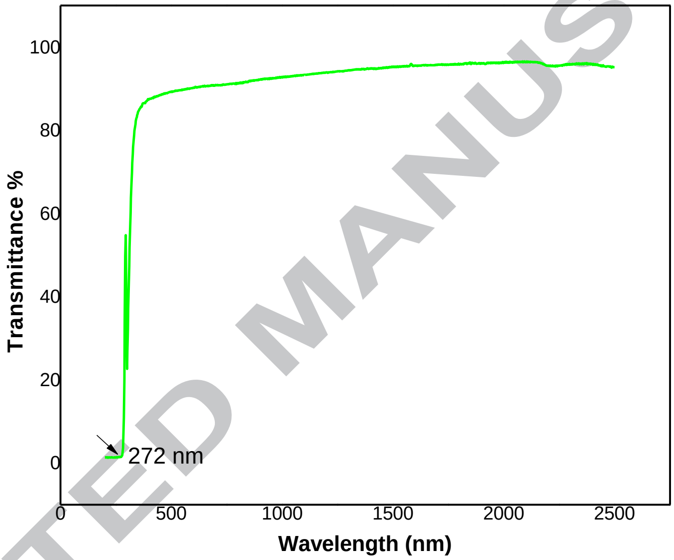

Fig. 4. UV-Vis-NIR spectrum of the grown LASN crystals.

3.6. Second Harmonic Generation Studies

The nonlinear optical efficiency of the grown LAPN crystal was analysed using the Kurtz-Perry powder technique [17]. The grown LAPN crystals were powdered into a uniform particle size of about 150 μm and then filled in a micro-capillary tube of constant bore. A Q-switched Nd: YAG laser beam with 1064 nm of wavelength, pulse energy of 1.2 mJ pulse and pulse width of 10 ns and repetition rate of 10 Hz was made to fall on the sample cell. The SHG behaviour was confirmed by the emission of green light (532 nm). The SHG efficiency of the grown LAPN crystal (35 mV) is found to be 1.25 times higher than that of reference material KDP (28 mV) crystal.

3.7. Dielectric studies

Dielectric measurements for a good quality LASN single crystal of thickness (d) 1mm was electrode on either side with a silver coating to make it behave like a parallel plate capacitor. The capacitance (C_{crys}) and dielectric loss (tan δ) were employed using the conventional parallel plate capacitor method with the frequency range 50 Hz to 5 MHz using a HIOCKI LCR HITESTER (Model 3532-50) instrument. The variation of dielectric constant (ε_r) versus log frequency and dielectric loss (ε') versus log frequency of the grown LAPN Single crystal are depicted in Fig. 5 (a) & (b).

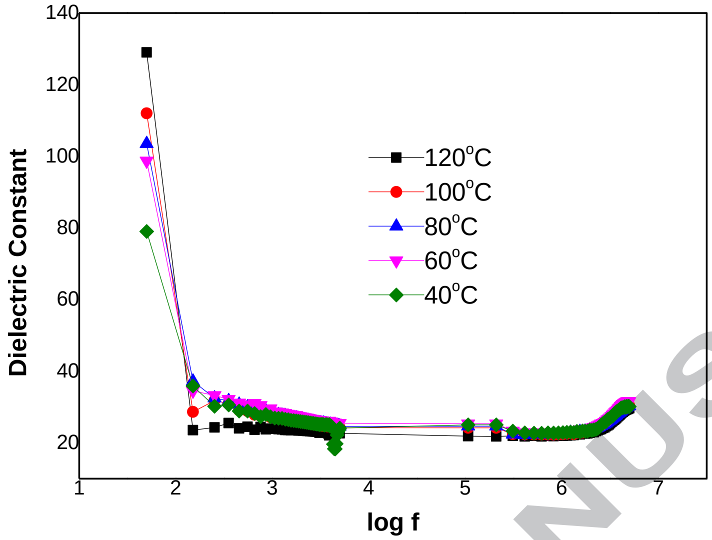

Fig. 5 (a). Plot between log f and dielectric constant

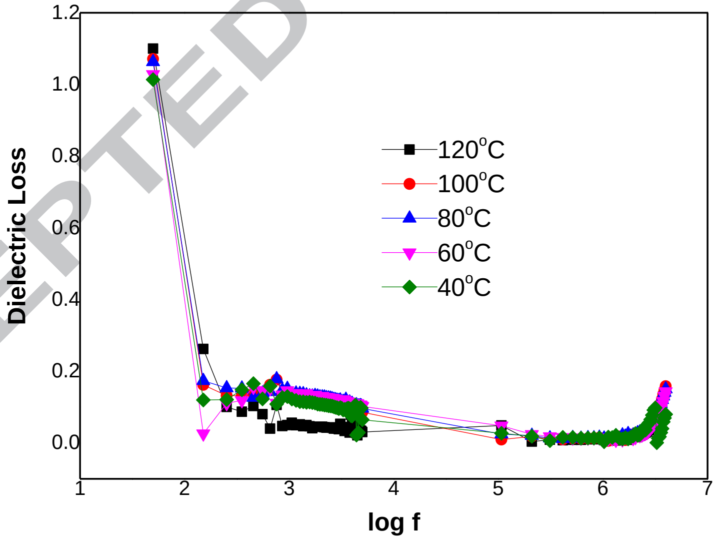

Fig. 5 (b) Plot between log f and dielectric loss

From the graph, it is observed that the dielectric constant and dielectric loss shows similar variation with frequency. It is observed at low frequency, dielectric constant and dielectric loss values are high. Then frequency increases, dielectric constant and dielectric loss decreases, lastly it becomes almost a constant at higher frequencies. The high value of dielectric constant at low frequency may be due to the contribution of four types of polarizations namely; space charge, electronic, dipolar and ionic polarization. The low value of dielectric constant at higher frequencies may be due to the loss of these four polarizations progressively. The very high dielectric constant at low frequency indicates the contribution of space charge polarization and it reveals the perfection of crystal [18-20]. At high frequencies low value of dielectric loss for the crystal possess good optical quality with lesser defects and this parameter is of extremely significant for photonics and NLO materials in their applications [21].

3.8. Photoconductivity study

The photoconductivity nature of the grown crystal was measured at room temperature using Keithley 6512 electrometer. The field dependent photoconductivity of grown crystal is depicted in Fig. 6. The crystal was covered with a black cloth and the dark current (Id) of the crystal was recorded with different applied input voltage which was increased from 1 to 10 V. Then sample was exposed to radiation from 100W halogen lamp containing iodine vapour and tungsten filament and its photocurrent (Ip) was recorded for the same input values of the applied voltage. From the figure, it is concluded that photocurrent is higher than that of the dark current for every applied electric field indicates, that the crystal has positive photoconductivity nature and this may be due to the increment in the number of charge carriers or their lifetime in the presence of radiation [22-23].

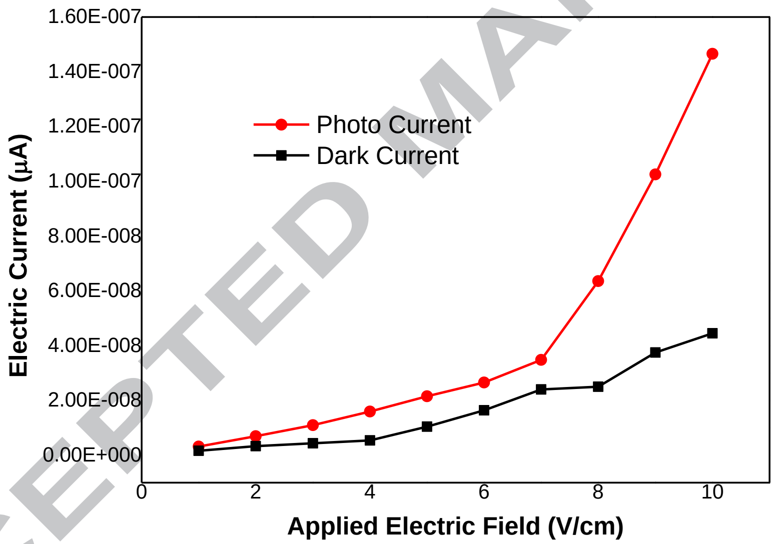

Fig. 6. Photoconductivity of grown LAPN crystal

4. CONCLUSIONS

Optical quality LAPN single crystals have been grown from aqueous solution by spontaneous nucleation solution growth method. The unit cell parameters have been determined by single crystal XRD analysis and they agree well with the reported values. The Powder XRD study confirms that the grown crystals crystallizes into the orthorhombic structure with space group $P2_12_12_1$, which makes it ideal for dielectric and NLO applications. FTIR analysis confirms the presence of functional group in the crystal. The UV–Visible–NIR transmission spectrum of LAPN crystals confirm wide transparent window in the entire UV, visible, NIR regions. It is a significant parameter for the materials having nonlinear optical properties. The powder SHG efficiency of the grown LAPN crystals was studied by Kurtz's and Perry powder method using Nd: YAG laser. It was found to be 1.25 times higher than that of reference material KDP. The dielectric constant and dielectric loss of grown crystal was carried out as a function of frequency and the results were discussed. The positive photoconducting nature of the grown LAPN crystal was confirmed from photoconductivity study. Thus the grown LAPN single crystals with noticeable optical, photoconductivity and dielectric properties shown its greatest reliability in designing components for optoelectronics, photonics convertors and nonlinear optical devices.

References

[1] M. Lydia Caroline, S. Vasudevan, Growth and characterization of an organic nonlinear optical material: L-alanine alaninium nitrate, *Mater. Lett.* 62 (2008) 2245.

[2] R. Mohan Kumar, D. RajanBabu, D. Jayaraman, R. Jayavel, K. Kitamura, Studies on the growth aspects of semi-organic L-alanine acetate: a promising NLO crystal, *J. Cryst. Growth* 275 (2005) 1935.

[3] D. Jaikumar, S. Kalainathan, G. Bhagavannarayana, Structural, spectral, thermal, dielectric, mechanical and optical properties of urea L-alanine acetate single crystals, *Physica B* 405 (2010) 2394.

[4] G. Marudhu, S. Krishnan, T. Thilak, P. Samuel, G. Vinitha and G. Pasupathi, Optical, thermal and mechanical studies on nonlinear optical material diglycine barium chloride monohydrate (DGBCM) single crystal, *J. Nonlinear Opt. Phys. Mater.* **22** (2013)1350043.

[5] X. Wang, D. Wang, H. Gao, Z. Yang, H. Cao, H. Yang, W. He, H. Wang, J. Gu and H. Hu, Third-order nonlinear optical properties of a novel series of D-π-A pyrene aldehyde derivatives, *J. Nonlinear Opt. Phys. Mater.* **25** (2016) 1650014.

[6] V.G. Pahurkar, Mohd Anis, M.I. Baig, S.P. Ramteke, B. Babu, G.G. Muley, Synchronized effect of Ca_2^+ ion doping concentration on structural, UV–vis and second harmonic generation efficiency of zinc thiourea chloride (ZTC) crystal: An interesting comparative study, *Optik* 142 (2017) 421-425.

[7] Duanliang Wang, Tingbin Li, Shenglai Wang, Jiyang Wang, Zhengping Wang, Jianxu Ding, Weidong Li, Chuanying Shen, Guangxia Liu, Pingping Huang, Effect of Fe^{3+} on third-order optical nonlinearity of KDP single crystals, *Cryst. Eng. Comm.* 18 (2016) 9292–9298.

[8] Y.B. Rasal, MohdAnis, M.D. Shirsat, S.S. Hussaini, Growth, structural, UV–visible, SHG, mechanical and dielectric studies of bis-thiourea zinc chloride doped KDP crystal for NLO device applications, *Mater. Res. Innov.* 21 (2017) 45–49.

[9] M.S. Kajamuhideen, K. Sethuraman, K. Ramamurthi, P. Ramasamy, Growth and physical characterization of organic nonlinear optical single crystal: N,N-diphenyl guanidinium formate, *Optics & Laser Tech.* 91 (2017) 159–165.

[10] M. Thangaraj, G. Ravi, T.C. Sabari Girisun, G. Vinitha, A. Loganathan, Ethylene diaminium di(4-nitrophenolate): A Third Order NLO Material for Optical Limiting Applications, *Spectrochim. Acta A* 138 (2014) 158–163.

[11] N. Elavarasu, P. Sathya, S. Pugazhendhi, N. Vijayan, K.K. Maurya, R. Gopalakrishnan, Evaluation of suitability of AMT single crystal for optical limiting applications by performing structural, dielectric, mechanical, optical and third order nonlinearity characterization studies, *Optics & Laser Tech.* 84(2016) 107–117.

[12] Sethuraman K, Ramesh Babu R, Gopalakrishnan R, Ramasamy P, “Synthesis, Growth, and Characterization of a NewSemiorganic Nonlinear Optical Crystal: L-Alanine Sodium Nitrate (LASN)”. *Crystal Growth Des.,* 8(6) (2008) 1863-1869.

[13] Vijayan N, Rajasekaran S, Bhagavannarayana G, Ramesh Babu R,Gopalakrishnan R, Palanichamy M, Ramasamy P, Growth and Characterization of Nonlinear Optical Amino Acid Single Crystal: L-Alanine, *Cryst. Growth Des.,* 6(11) (2006) 2441–2445.

[14] Nobuyasu Itoh, Ayako sato, Taichi Yamazaki, Masahiko Numata and Akiko Takatsu, *Analytical Sciences*, 29 (2013) 1209-1212.

[15] Lydia CM, Sankar R, Indirani RM, Vasudevan S, Growth, optical, thermal and dielectric studies of an amino acid organic nonlinear optical material: l-Alanine, *Materials Chem. Phys.*, 114 (2009) 490-494.

[16] Shanmugam Boomadevi, Krishnamoorthy Pandiyan, Second harmonic generation studies in L-alanine single crystals grown from solution, *Physica B* 432 (2014) 67–70.

[17] Kurtz SK, Perry TT,A Powder technique for the evaluation of nonlinear optical materials, *J. Appl. Phys.*, 39(1968) 3798-38l3.

[18] S.P. Ramteke, MohdAnis, M.I. Baig, V.G. Pahurkar, G.G. Muley, Optical and electrical analysis of Cu2+ ion doped zinc thiourea chloride (ZTC) crystal: An outstanding 30×24×04 mm^3 bulk monocrystal grown from pH controlled aqueous solution, *Optik* 137 (2017) 31–36

[19] S.M. Azhar, Mohd Anis, S.S. Hussaini, S. Kalainathan, M.D. Shirsat, G. Rabbani, Doping effect of l-cystine on structural, UV–visible, SHG efficiency, third order nonlinear optical, laser damage threshold and surface properties of cadmium thiourea acetate single crystal, Opt. Laser Technol. 87 (2017) 11–16.

[20] M. Anis, G.G. Muley, Single crystal growth and enhancing effect of glycine on characteristic properties of bis thiourea zinc acetate crystal, Phys Scr. 91 (2016) 85801–85808.

[21] Mohd Anis, G.G. Muley, M.I. Baig, S.S. Hussaini, M.D. Shirsat, Mater. Res. Innov. (2016), http://dx.doi.org/10.1080/14328917.2016.1265250.

[22] V. Joseph, S. Gunasekaran and V. Santhanam, Photoconductivity and dielectric studies of potassium pentaborate crystal (KB5), *Bull. Mater. Sci.,* 26 (2003) 383–386.

[23] C. Justin Raj, S. Dinakaran, S. Krishnan, B. Milton Boaz, R. Robert and S. Jerome Das: 'Studies on optical, mechanical and transport properties of NLO active L-alanine formate single crystal grown by modified Sankaranarayanan–Ramasamy (SR) method', Opt. Commun., 281 (2008) 2285–2290,

Highlights:

- Growth of L-alanine potassium nitrate (LAPN) is reported for the first time.
- Grown LAPN highly transparent in visible and NIR region.
- SHG efficiency of grown LLAPN crystal is 1.25 times that of reference KDP.
- The grown crystal exhibits a positive photoconductivity.
- Hence, title compound is suitable for photonics and optoelectronic applications.