Research Article **Available online www.ijsrr.org** **ISSN: 2279–0543**

International Journal of Scientific Research and Reviews

Growth and Characterization Studies of L-Alanine Potassium Iodide Single Crystal for NLO Applications

S. Sivasakthi[1*] and R. Suresh Babu[2]

[1,2]PG and Research Department of Physics, Muthurangam Government Arts College (A), Vellore-632 002. India. sivashakthi73@gmail.com[1*], rsb_7@yahoo.com[2]

ABSTRACT:

The homogeneous solution of L-Alanine Potassium Iodide (LAKI) was prepared for 1:1 ratio and good optical crystals were grown by slow evaporation method. The cell parameters were determined using single crystal X-ray diffraction studies and it shows the orthorhombic crystal with lattice parameters values of a = 5.82 Å, b = 6.60 Å, c = 12.40 Å and α = ɤ = β = 90º.The characteristics of the grown crystal were discussed in detail related to its cell parameters, optical, functional group analysis, thermal studies and SHG result with supporting evidence from various experiments. The presence of nitro groups in FTIR spectrum confirms the good formation of LAKI Compound. The efficiency of second harmonic generation of LAKI crystal was found to be 1.3 times greater than the reference material KDP.

KEYWORDS: LAKI, slow evaporation method, FTIR, SHG

***Corresponding Author**

S. Sivasakthi[1]

PG and Research Department of Physics,

Muthurangam Government Arts College (A),

Vellore-632 002. India

sivashakthi73@gmail.com

INTRODUCTION

In recent days, semiorganic non-linear optical (NLO) materials play a predominant role in the fabrication of various device applications. These semiorganic crystals were grown from the reactions of organic acids like L-histidine, L-alanine with different inorganic materials[1,2]. The metal coordination complexes of organic materials are another type of formation of semi-organic materials for various applications which leads to a wide range of electronic characteristics, mechanical hardness and thermal stability and on the other hand structural variety and the large polarizability[3]. The refractive indices of the crystal could also be tuned due to the exchangeability of metal and halogen species within anion[4,5]. Thus, they attract a lot of interest because of their applications such as electroluminescent and optoelectronic devices.

In addition, the proper combinations of inorganic with organic materials provide a potentially more efficient and stable NLO crystals which would leads to different second-order NLO properties such as switchable, multi-dimensional and tuneability of the optical as well as electronic properties of these materials[6]. Theses semi-organic materials provide enhancement of physicochemical stability, to break the centro symmetry in the crystal, to enhance the NLO intensity, to vary the hyper polarizability which was further used to change the electronic configuration of the materials.

In recent years, numerous investigations have been a carried out in order to understand the organic and inorganic complexes due to their optimized properties for NLO application like lasers, optical communications, frequency doublers, photoluminescence and data storage. However, lacks of investigations were done in the fabrication of L-Alanine Potassium Iodide (LAKI). This work mainly focuses on the synthesis of LAKI single crystal by slow evaporation method. The grown crystal was subjected to various characterizations such as single as well as powder X-ray diffraction, Fourier Transform Infrared (FTIR) spectroscopy, UV-Vis-NIR Spectroscopy, Thermo gravimetric analysis (TGA), Differential Scanning Calorimetery (DSC) and Second Harmonic Generation (SHG) and all the results were discussed in details.

EXPERIMENTAL DETAILS

LAKI crystal were characterized by structural characterization like powder XRD and single crystal XRD, Vibrational spectral analysis like FTIR, Optical characterization like Ultraviolet-Visible spectroscopic studies Thermal characterization like Thermo Gravimetric Analysis(TGA), Differential Scanning Calorimetry (DSC) and characterization of nonlinear optical properties

(SHG). The experimental details are discussed briefly in result and discussion part. The structure of L-Alanine is shown in Figure 1 and the Table 1 shows the various properties of L-Alanine and potassium iodide.

Table.1. Properties of L-Alanine and Potassium Iodide

Properties	L-Alanine	Potassium Iodide
Chemical formula	$C_3H_7NO_2$	KI
Molar mass	89.094 g·mol^{-1}	166.002 g·mol^{-1}
Appearance	white powder	white crystalline sol
Density	1.424 g/cm^3	3.12 g/cm^3
Melting point	258 °C	681°C
Solubility in water	167.2 g/L (25 °C)	128 g/ 100ml (16 °C

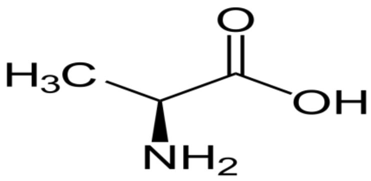

Figure 1. L-alanine structure.

Synthesis and Crystal Growth

The L- Alanine doped potassium iodide was synthesized by taking in equal molar ratio. The expected chemical reaction for this compound is

$$C_3H_7NO_2 + KI \longrightarrow K[C_3H_7NO_2]I$$

The calculated amount of L-alanine was first dissolved in distilled water and then known amount of potassium iodide was then added to the L-alanine solution after 5 hours of continuous stirring it achieve homogeneous solution. The saturated solution was filtered using Whatmann filter paper. The filtered solution was taken in a beaker and Covered with good quality perforated polythene cover to restrict the fast Evaporation it is kept at room temperature in a dust free compartment for Slow evaporation. The LAKI material was purified by repeated recrystallization process, after the period of 5 weeks, colourless and optically transparent crystals with dimension 15mm× 5mm×3mm to be obtain. Good dimension crystals are very essential for device fabrication and optical application. The LAKI crystal is succeeded. The grown crystal is shown in Figure 2.

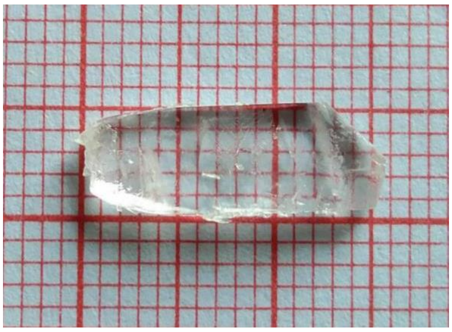

Figure 2. Photograph of grown LAKI crystal.

RESULT AND DISCUSSION

Powder x-ray diffraction

Powder X-ray diffraction analysis of grown crystal is crushed to a uniform powder and it has been carried out by using the Bruker D8Advanced powder X-ray diffractometer with Cu Kα (λ = 1.5418Å).

Figure 3 shows powder XRD pattern of LAKI single crystal recorded in the ranges from 10º to 90º 2θ which is synthesized using slow evaporation method. The prominent peaks in Figure 3 indicate the formation of good quality of LAKI single crystal which is matched well with the JCPDS card number 28-1508. Figure 3 shows the prominent peaks at 16.7^{o}, 20.69^{o}, 22.13^{o}, 25.58^{o}, 29.20^{o} and 36.26^{o} 2θ which are indexed as (011), (120), (040), (031) (040) and (120) plans respectively. However, the slight shift in PXRD peak position might be attributed to the substitution of potassium iodide into the L-alanine. The sharp and well Bragg's peaks at specified 2θ angle are directly related to its crystalline in nature and purity of crystal[7].

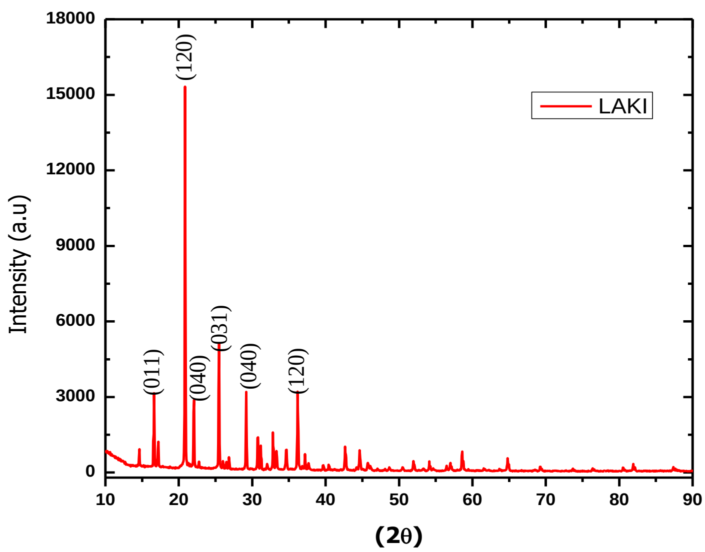

Figure 3. PXRD Pattern of LAKI Single Crystal

Single x-ray diffraction

The grown compound LAKI crystal is subjected to single crystal XRD using ENRAF NOUIUS CAD 4 diffractometer and the extracted lattice parameters are given in Table 2. It is observed that the LAKI crystalline belongs to Orthorhombic system with space group $P2_12_12_1$ [8,9].

Table 2. Lattice parameters of LAKI.

SAMPLE	LATTICE PARAMETER			VOLUME v(Å³)	α = ɤ = β	Structure
	a(Å)	b(Å)	c(Å)			
LAKI	5.82	6.06	12.40	437	90º=90º=90º	Orthorhombic

FTIR spectral studies

The FTIR spectroscopy studies are effectively used to identify the functional groups presents in the crystal. The FTIR spectral analysis for the grown crystal has been recorded in the range 400-4000 cm^{-1} Figure 4.

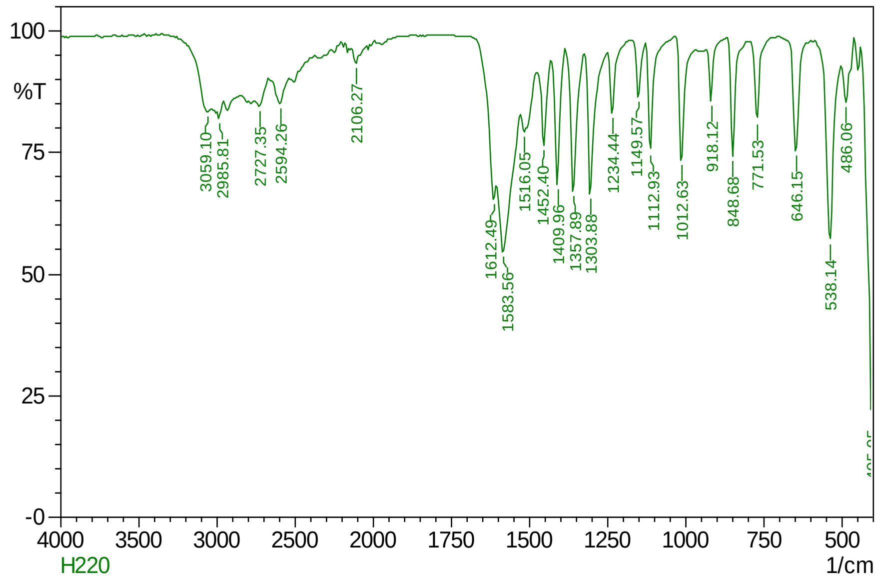

Figure 4. FTIR spectrum of LAKI crystal

Figure 4 shows the absorption peaks at 3059 cm^{-1} which indicates the presence of CH stretch. The peak at 2985 cm^{-1} is attributed to CH_3 symmetric stretching mode vibrations. The presence of peaks at 1234, 1303, 1357 cm^{-1} are due to C-O Stretch and O-H bend of the COOH group are Observed[10]. It is clearly seen that the existence of carboxylic (COOH) functional groups. The fact some of COOH groups are ionized implicates an appearance of the NH_3^+group in alanine molecule[11]. The presence of nitro groups in the spectrum confirms the LAKI Compound. The presence of iodine is realized by the peak at 538cm^{-1}. Other important functional groups are detailed in Table 3.

Table 3. FTIR Functional Group Assignments of the Grown LAKI Crystal

Wave number (cm^{-1})	Bond Assignments
3059	=C-H stretch
2985	O-H stretch
1583	NH_3^+ Stretch
1234	C-O-C Stretch
918	O-H Bend
538	C-I stretch
3059	=C-H stretch

UV-Vis spectral studies

UV-Vis spectrum of LAKI in Figure 5 shows the absorbance zone above 215 nm where a wide band completely transparent in all the visible range is observed using JASCO (V-670 PC) spectrophotometer. It is observed that the wide range of optical transmission window occurs from 208-800 nm. No considerable absorption of light in the visible range of an electromagnetic spectrum is an internal property of amino acids[12-14]. Hence then can be used for fabrication of optical region.

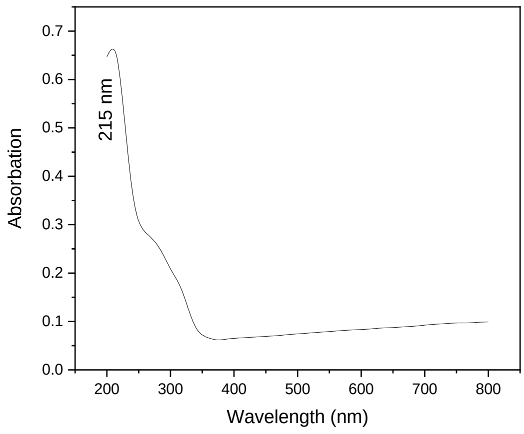

Figure 5. UV-Vis spectrum of LAKI crystal

Band gap energy

The energy band gap for a grown crystal was calculated using the Tauc equation.

$$\alpha h\nu = A\,(h\nu - E_g)^n$$

Where A is the optical constant, a is the absorption coefficient, Eg is the optical band gap, v is the frequency of incident photon. A plot of Absorbance versus hv (eV) shown in Figure 6. The band gap is estimated by Extrapolating graph, which turns out to be 4.9 eV. Large value of band gap indicates that the material is a good insulator and can provide large transmission in visible region.Thus optical Edge was analysed using tauc equation.

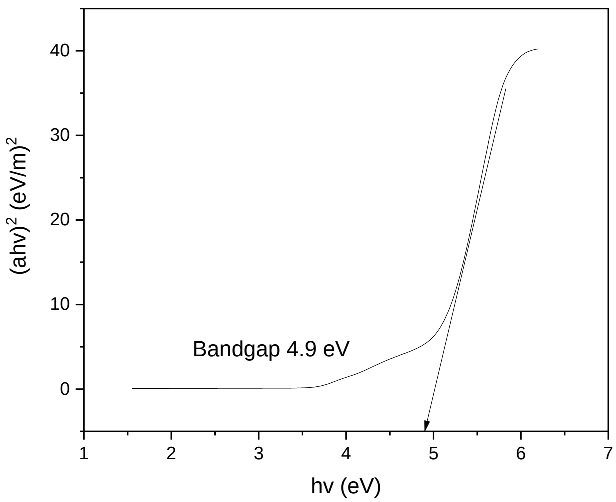

Figure 6. Band gap of LAKI crystal

Thermal gravimetric analysis

In order to study the thermal stability of the grown crystal, TGA has been carried out using a SDT Q600 V20.9 Build 20 model thermal analyzer in nitrogen atmosphere. The TGA was carried out for L-Alanine doped potassium iodide crystal in 28-800 ºC and is shown in Figure 7. The TGA trace shows, there is no weight loss below 276 ºC, hence the crystal is completely devoid of any entrapped solvent in the lattice of the crystal[15-17]. The major weight loss occurs at two stages the first weight loss of occurs at 28.16 % (0.5219 mg) observed between 265ºC to 285 ºC is due to the decomposition of L-Alanine and another weight loss found at 681ºC due to the decomposition of potassium iodide. Final residue weight left was 3.488 % (0.0646 mg).

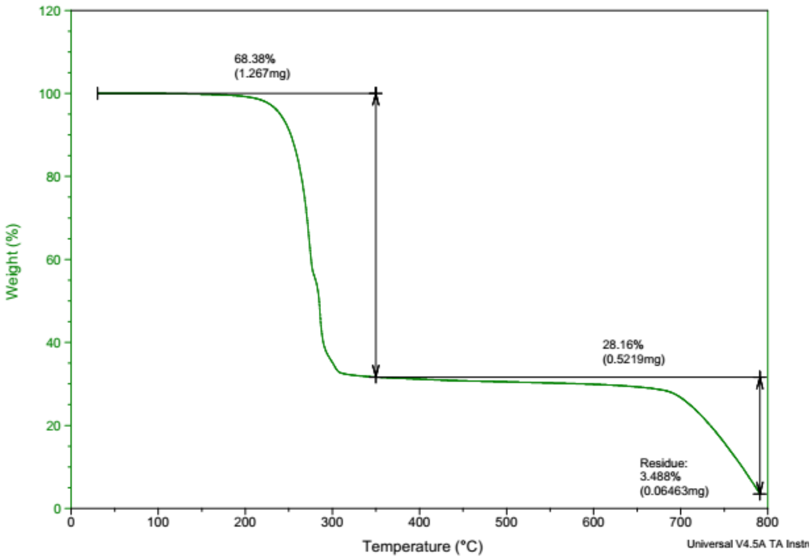

Figure 7. TGA curve for LAKI crystal

Differential Scanning Calorimetry

The DSC analysis of the grown crystal was carried out between 28 °C and 800 °C. There is a sharp endothermic peak found at 276 ºC and 681 ºC which corresponds to the decomposition as observed in TGA analysis. Again it also confirms absence of melting and any entrapped solvent in the lattice[18,19]. DSC curve shows the sharp endothermic peak indicates the crystal has good crystalllinity and decomposition point of as grown LHAA crystal is 276 ºC (see Figure 8).

The TGA-DSC result shows that the grown crystal is thermally stable up to 276 ºC and establishes its suitability to with stand the high temperature for laser experiments.

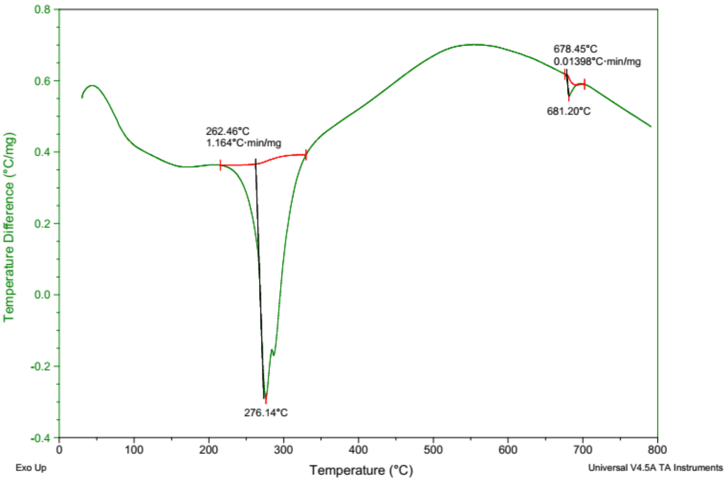

Figure 8. DSC curve for LAKI crystal

Second harmonic generation

In order to confirm the nonlinear optical property, powdered sample of LAKI was subjected to a Kurtz and Perry powder techniques, which remains a powerful tool for initial screening of materials for SHG. A Q switched High Energy Nd:YAG Laser (QUANTA RAY Model LAB – 170 - 10) operating at the fundamental wavelength of 1064 nm with pulse width 8 ns and repetition rate of 10 Hz and input energy as 0.701 J was used. The NLO property of the sample was confirmed by the sample was emission of bright green light as output with wavelength of 532 nm. The KDP sample was used as the reference material. The efficiency of second harmonic generation of L-Aalanine potassium iodide crystal was found to be 1.3 times greater than the reference material KDP[20]. Thus LAKI crystal can be used as an effective candidate for nonlinear optical applications.

CONCLUSION

A Semi organic nonlinear optical crystal of L-Alanine Potassium Iodide has been successfully grown from aqueous solution by slow evaporation technique at the room temperature. The crystalline nature of the grown crystal has been confirmed by powder X-ray diffraction. The single crystal X-ray diffraction study shows that the grown crystal belongs to orthorhombic system with space group of $P2_12_12_1$. The variation function groups are presented in the grown crystal has been identified by Fourier Transform Infrared spectroscopy (FTIR).The UV-Visible spectroscopic studies showed that the grown crystal was optically transparent in the entire visible region and the cut off wavelength has been identified as 215 nm. Hence they can be used for fabrication of optoelectronic devices in visible region. The optical band energy gap (E_g)

was found to be 4.9 eV from Tauc relation. The Thermo Gravimetric Analysis (TGA) and Differential Gravimetric Analysis (DTA) show that the grown crystal is thermally stable up to 276 ºC and establishes its suitability to withstand the high temperature for laser experiments. The SHG efficiency of the grown crystal was measured by Kurtz and Perry powder techniques and its efficiency was found to be 1.3 times greater than the reference material KDP. Thus LAKIS crystal can be used as an effective candidate for non-linear optical applications.

REFERENCES

1. Pratik M, Wankhade, Gajanan Muley G. Growth, morphology, optical, thermal, mechanical and electrical studies of a cesium chloride doped l-alanine single-crystal. Chinese Journal of Physics. 2017; 55: 2181-91.
2. Narmada Su et al. Comment on Synthesis, spectroscopic, optical and thermal properties of l-alanine ammonium chloride – A semi-organic crystal Optik- International Journal for Light and Electron Optics. 2014; 125: 6826–28.
3. Shanmugam P, Pari S, Selvarajan P. Growth, spectral, mechanical, thermal and dielectric studies of undoped and rhodamine-B doped l-alanine acetate crystals. Optik - International Journal for Light and Electron Optics. 2016; 127: 2764-70.
4. Benila B S, Bright K.C, Mary S et al.Optical, thermal and magnetic studies of pure and cobalt chloride doped L-alanine cadmium chloride. Journal of Magnetism and Magnetic Materials. 2017; 426: 390-95.
5. Kazuhiko Ishikawa, YukanaTerasawa, Masahito Tanaka and Toru Asahi Accurate measurement of the optical activity of alanine crystals and the determination of their absolute chirality. Journal of Physics and Chemistry of Solids. 2017;104: 257-66.
6. Sudhakar S, Dhondge, Jessie, Moses M et al. Physicochemical study of solute-solvent interactions of aqueous binary mixtures of l-alanine methyl ester hydrochloride and l-valine methyl ester hydrochloride at different temperatures: Volumetric and compressional study. The Journal of Chemical Thermodynamics. 2017; 105: 217-25.
7. Jayaprakash R N, and Sundaramoorthy P. Growth and characterization of l-alanine admixtured urea single crystal. Optik - International Journal for Light and Electron Optics. 2015;126: 3570-73.
8. Jothi Mani R, Selvarajan P, Alex Devadoss H and Shanth D. Second-order, third-order NLO and other properties of l-alanine crystals admixtured with perchloric acid (LAPA). Optik - International Journal for Light and Electron Optics. 2015; 126: 213-18.

9. Shanmugam Boomadevi, and Krishnamoorthy Pandiyan. Second-harmonic generation studies in l-alanine single crystals grown from solution. Physica B: Condensed Matter. 2014; 432: 67-70.
10. Thilak T, Basheer M, Ahamed, Marudhuand G, Vinitha G. Effect of KDP on the growth, thermal and optical properties of l-alanine single crystals. Arabian Journal of Chemistry. 2016; 9: 676-80.
11. Natarajan S, Moovendaran K, Mohan S et al. Unidirectional growth of l-alanine single crystal: NLO material from the amino acid family. Optik - International Journal for Light and Electron Optics. 2014; 125: 2503-08.
12. Bikshandarkoil R. Srinivasan. On the existence of l-alanine cadmium bromide. Spectro Chimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2013; 116: 639-41.
13. Jayaprakash R N and Sundaramoorthy P. Growth and characterization of l-alanine admixtured urea single crystal. Optik - International Journal for Light and Electron Optics. 2015; 126: 3570-73.
14. Lucia Rose A S J, Selvarajan P and Perumal S. Studies on growth and characterization of an NLO crystal L-alanine hydrogen chloride (LAHC). Materials Chemistry and Physics. 2011; 130: 950-55.
15. Sethuraman K, Ramesh Babu R, Gopalakrishnan R and Ramasamy P. Synthesis, Growth, and Characterization of a New Semiorganic Nonlinear Optical Crystal, L-Alanine Sodium Nitrate (LASN). Crystal Growth & Design. 8,2008; 8: 1863-69.
16. Lucia Rosea A S J, Selvarajanb P and Perumalc S. Studies on growth and characterization of an NLO crystal: L-alanine hydrogen chloride (LAHC). Materials Chemistry and Physics. 2011; 130 : 950 – 55.
17. Mohan Kumara R, RajanBabub D, Jayaraman D, Jayaveld R, Kitamuraa K Studies on the growth aspects of semi-organic L-alanine acetate: a promising NLO crystal. Journal of Crystal Growth. 2005; 275: 1935–39.
18. Ramachandra Raja C and Antony Joseph A. Crystal growth and characterization of new nonlinear optical single crystals of L-aluminum fumarate. Materials Letters. 2009; 63: 2507–09.
19. Vijayan N, Bhagavannarayana G, KMaurya K K, Sharma S N, Gopalakrishnan R, Jayabharathi J and Ramasamy P. Synthesis, growth of single crystals and their characterization: l-Alaninium maleate (LAM). Optik. 2012; 123: 604– 08.

20. Yasotha P, Thiagarajan R and Sagunthala P. Growth and characterization of potassium chloride and potassium iodide doped amino acid NLO single crystals. Journal of Non-Oxide Glasses. 2016; 8: 29-36.