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Synthesis growth and characterisation of l-alanine potassium nitrate –a potential non linear optical material

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ABSTRACT

A new semi organic nonlinear optical crystal, L-Alanine potassium nitrate has been synthesized and good optical quality single crystals were grown by slow evaporation technique. The growth conditions of the crystals are studied and the grown crystals are confirmed by powder X-ray diffraction studies. The grown crystal was characterized by using powderedXRD, FT-IR, UV–Vis–NIR, EDAX, and TG–DTA. The sharp peaks from powdered XRD spectrum shows high crystalinity of the grown crystal. The presence of various functional groups was confirmed by FT-IR spectroscopic technique. The UV–Vis–NIR spectrum indicates that the crystal has very good absorption in the entire visible and near IR region spectrum suggesting the suitability of the material for NLO applications. The decomposition temperatures and mass loss have been estimated from the thermo gravimetric analysis. The presence of potassium in the compound and composition of grown crystals was confirmed on the basis of energy dispersive analysis of X-ray (EDX).

Introduction

Organic crystals have been shown to have potential applications in nonlinear optics. Nonlinear optics (NLO) is at the forefront of current research because of its importance in providing the key functions of frequency shifting optical modulation, optical switching, optical logic, and optical memory for the emerging techniques in areas such as telecommunications, signal processing, and optical interconnections [4]. Organic materials have been of particular interest because the nonlinear optical response in this broad class of materials is microscopic in origin, offering an opportunity to use theoretical modeling coupled with synthetic flexibility to design and produce novel materials [8, 10 & 11]. Organic NLO materials have a very large nonlinear susceptibility, which are in many cases several orders of magnitude higher than that of inorganic crystals such as LiNbo3, KNbo3 and potassium dihydrogen phosphate (KDP).

Nonlinear optical materials (NLO) have proven to be an interesting candidate for a number of applications such as second harmonic generation, frequency mixing, elec-tro-optic modulation, etc. In recent years, organic NLO materials are attracting a great deal of attention for possi- ble use in optical devices because of their large optical nonlinearity, low cut-off wavelengths, short response time and high laser damage thresholds [1]. Considerable work has been done in order to understand the microscopic origin of nonlinear behavior of organic materials [2-5]. The NLO properties of large organic molecules and polymers have been the subject of extensive theoretical and experimental investigations during the past two decades and they have been investigated widely due to their high nonlinear optical properties, rapid response in electrooptic effect and large second- or third-order hyperpolar-izibilities compared to inorganic NLO materials [6]. Th- us, there is much impetus to design and understand organic compounds for SHG applications.

The present investigation deals with the growth of L-Alanine Potassiumnitrate (LAPN) an analog of L-Alanine single crystal by slow solvent evaporation technique. The grown crystal was subjected to powder XRD, FT-IR, UV–Vis–NIR, SEM, EDX, and TG-DTA.

Table 1. X-ray powder diffraction data of L-ALANINE crystal

Pos. [°2Th.]	d-spacing [Å]
16.5024	5.36745
17.0380	5.19988
20.8409	4.25884
22.6595	3.92098
26.7316	3.33221
28.8869	3.08831
30.5910	2.92004
32.7803	2.72985
33.2133	2.69524
34.5685	2.59262

Experimental methods

Synthesis and growth technique

The solution is prepared using L-Alanine and potassium nitrate in the molar ratio of 1:1. The pH of the solution was adjusted to 4.34 by adding 4 drops concentrated nitric acid. The above solution was filtered using the filter paper and transferred to a Petri dish. The Petri dish was covered with a filter paper with small hole, tied on top with rubber band to facilitate evaporation and crystal growth. After a period of 20 days, optically good quality single crystals are harvested.

Characterisation

Powdered X-ray Diffraction

Powder XRD patterns of the crystalline powder samples of L-Alanine and LAPN were recorded on a Rich-Seifert X-ray

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diffractometer using Bruker AXS D8 Advance Cu, Wavelength (1.5406 Å). The sample was scanned for a 2θ range of 10–80 ºC and at a scan speed of 2º C/minute.

The observed'd' values for different 2θvalues of the corresponding reflective planes for the crystal are given in Table 1. The results of well defined diffraction peaks at specific 2θ angles testimonies the crystalline nature and purity of the crystal.

Table 2. X-ray powder diffraction data of LAPN crystal

Pos. [°2Th.]	d-spacing [Å]
20.6939	4.28878
22.7997	3.89720
23.7177	3.74839
29.4699	3.02953
32.7353	2.73350
33.9723	2.63674
38.0759	2.36148
43.7481	2.06754
46.7812	1.94032
60.4808	1.52950

Fig 1. Powder XRD analysis of l-alanine

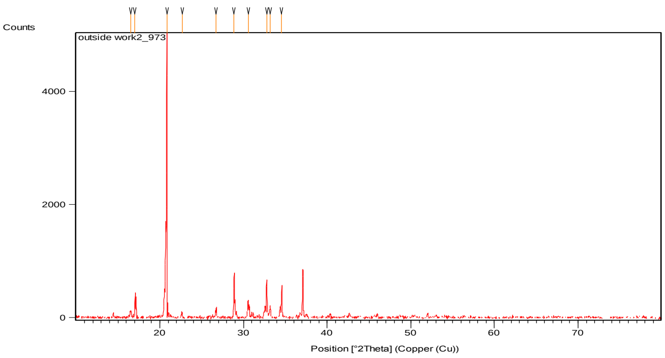
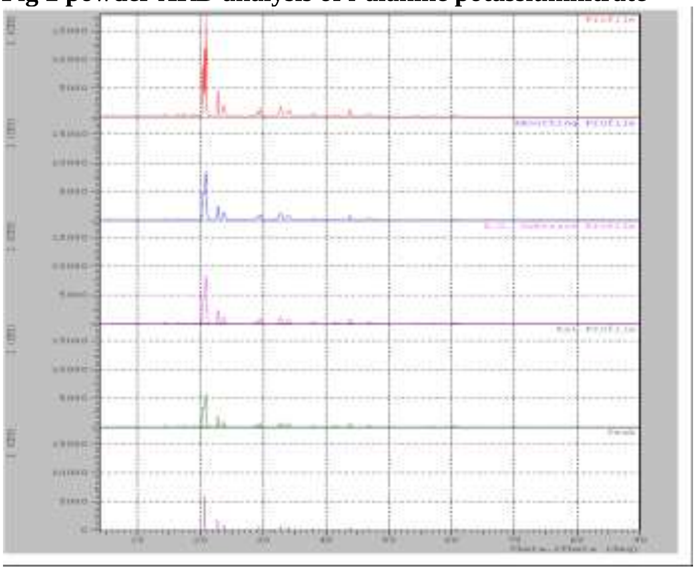


Fig 2 powder XRD analysis of l-alanine potassiumnitrate



FTIR studies

The infrared spectra of L-alanine and LAPN were obtained from potassium bromide pellets technique using MAKE–BRUKER Optic GmbH MODEL No-TENSOR 27 SOFTWARE-OPUS version 6.5 Spectrophotometer in the range of 4,000–400 cm-1.

The FTIR spectrum of L-Alaninepotassium nitrate reveals the following fetch.

The -NH3+ absorption, characteristic of amino acids, occurring in the range3130- 3100 cm-1 is more often shifted to lower wave number side due to the formation of amino salts, and in LAPN, it occurs at 3462 cm-1. 3381cm-1 with medium intensity refers to a primary amine free radical with N-H symmetric stretching mode of vibration 2604cm-1 with week band refers to overtones the formation of OH in-plane will be and C-O stretching vibration. From which we infer that band refers to carboxylic acid. 2110cm-1 with strong intensity band refers to NH_4 stretching which can be inferred as tertiary amine salt. 1411 cm-1 medium band refers to CH in-plane-bending.

Table 3. Comparison of FTIR spectra of L-Alanine and LAPN

Wave number/cm^{-1}		Assignments
L-ALANINE	LAPN	
3064.73	3462.18	N-H Stretching
2602.46	2592.97	O-H Stretching
2509.84	2592.97	C-H Stretching
2112.26	2067.57	Degenerative deformation of NH_3^+, Torsional vibration of NH_3^+
1618.34	1681.67	Asymmetric Stretching of CO_2^-
1510.81	1416.60	Symmetric Bending of NH_3^+
1110.00	1120.30	C-O Stretching,NH_3rocking
847.42	831.06	O-H out of plane deformation
771.85	775.74	CH_2 rocking
648.19	610.60	COO- plane deformation

Fig 3. FTIR Spectrum Of L-Alanine

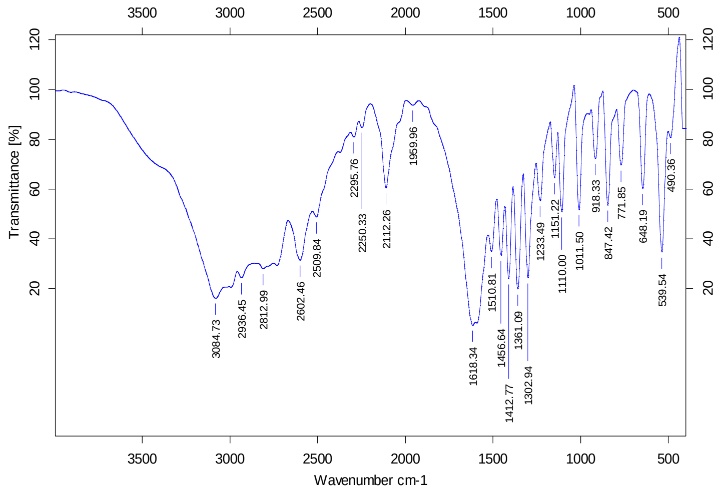
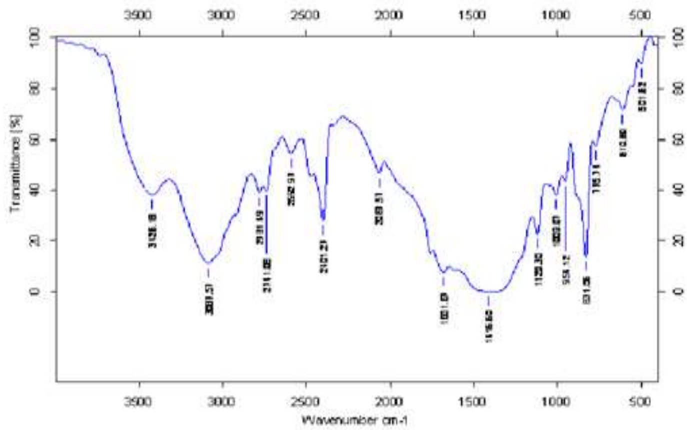


Fig 4. FTIR spectrum of l-alanine potassiumnitrate



UV-VIS Spectrophotometer

The UV-VIS-NIR spectra were recorded on a JascoV-630 spectrophotometer in the range of 200-1100 nm with scanning speed of 400 nm min-1.

The light of wavelength 300nm is absorbed. This is the cut of point. Then the crystal is highly transparent to the wave lengths above300 nm up to 1000nm. From this UV spectrum we infer that crystal may have NLO property.

Fig 5. UV-VIS-NIR spectrum of L-Alanine

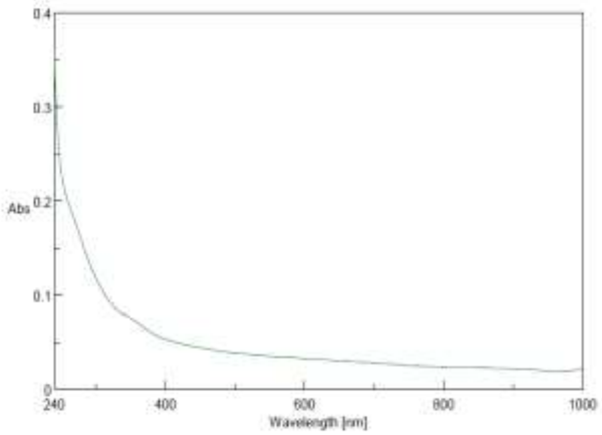
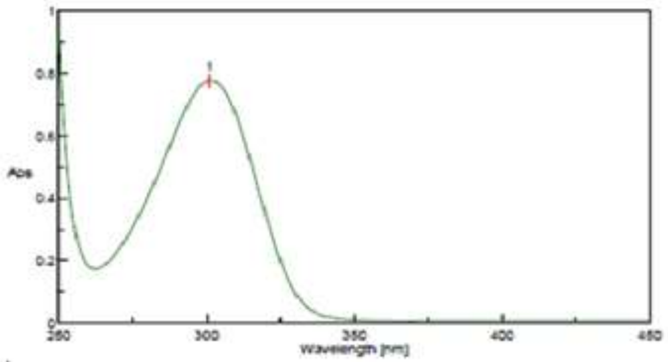


Fig 6. UV-VIS-NIR spectrum of L-Alanine Potassiumnitrate

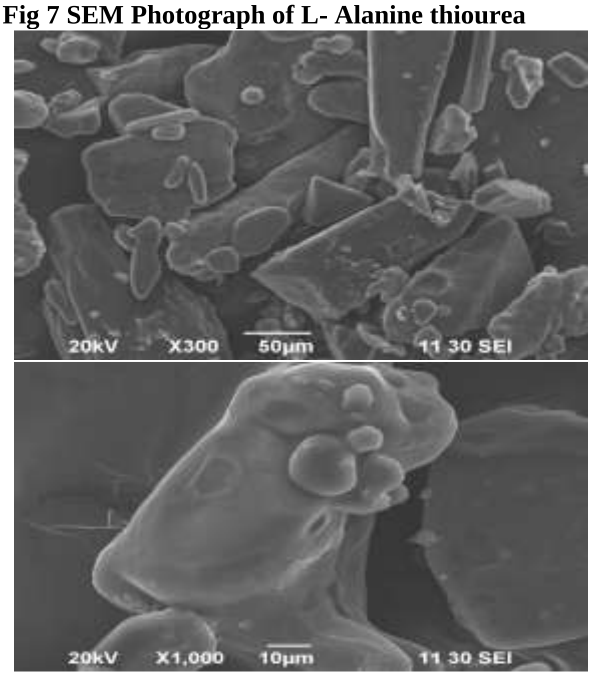


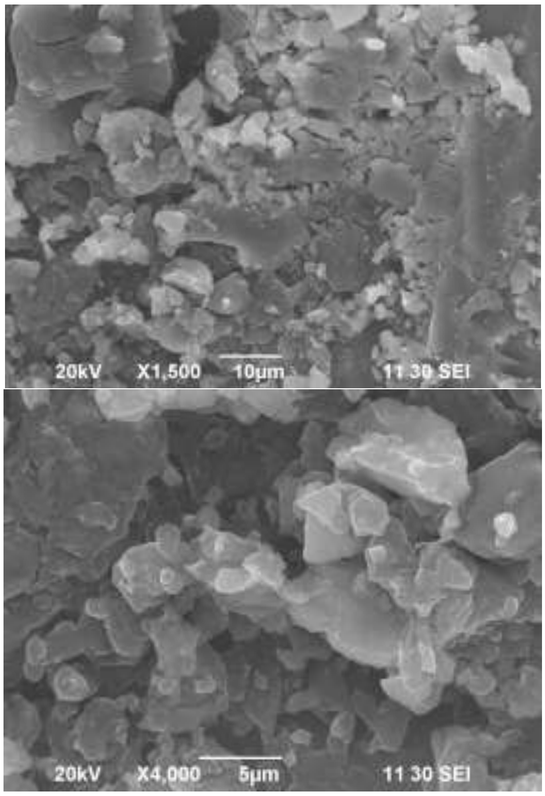
SEM

SEM analysis was carried out on a JSM 6360 JEOL/EO. The surface of the crystal was coated with a thin of carbon to make the sample conducting.

1. At a magnifications of 300 and at a scale of 50 micrometer we observe the crystals have smoothed surfaces.
2. At a magnifications of 1000 and 10 micrometer scale we can observe that the crystals have smoothed surfaces.
3. At a magnification of 1500 and at a scale of 10 micrometer.
4. At a magnifications of 4000 and at a scale of 5 micrometer.
5. At a magnification of 7500 and 2 micrometer scale we can observe that the crystals have an average thickness of 970.68nm.

Fig 7 SEM Photograph of L- Alanine thiourea





TG / DTA Studies

Differential Thermal analysis (DTA) and thermo gravimetric analysis (TG) were carried out simultaneously on a TA instruments SDTQ600 V 8.2.The sample was heated at a rate of 10oC min-1 in protected nitrogen gas flow and 10.6740mg of the sample was used to carry out the experiment.

There is a single major weight loss starting at about 212^0C. The decomposition completes at about 252^0C. The sharp endothermic peak in DTA at 143°C indicates the melting point of the crystal. There is no exothermic or endothermic peak below this endotherm. This illustrates the absence of any absorbed water in the crystal sample. It also shows the absence of any isomorphic transition. The sharpness of the peaks indicates a good degree of crystallinity of the sample.

In TGA the weight loss curve is observed starts at 212°C and ends at 252°C. This weight loss is due to the liberation. of volatile substances. The peak at 252ºC indicates a phase change from liquid to vapor state as evidence from the loss of weight in the TGA curve. The DSC, TGA analyses do not show any kind of phase transition of LAPN crystal.

Based on this result it is said that the compound can be used for NLO applications up to this temperature (143^0C). Also the thermal analysis of L-Alanine shows that it is thermally stable than the other members of amino acid family.

Fig.8.-TGA & DTA of L – Alanine

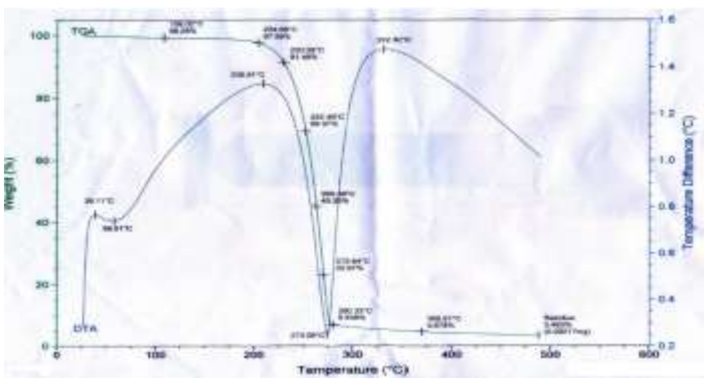
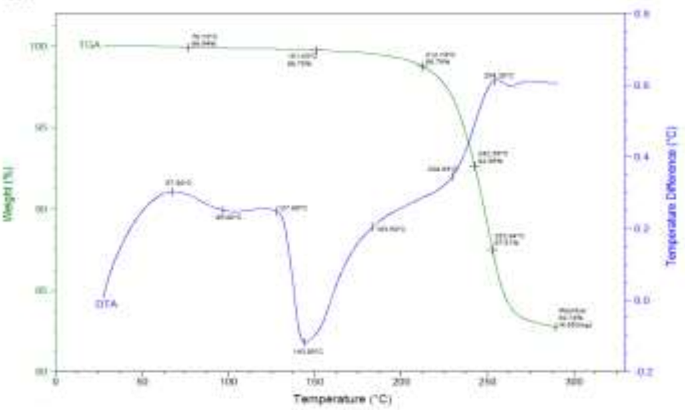


Fig.9.-TGA & DTA of L – alaninepotassium nitrate



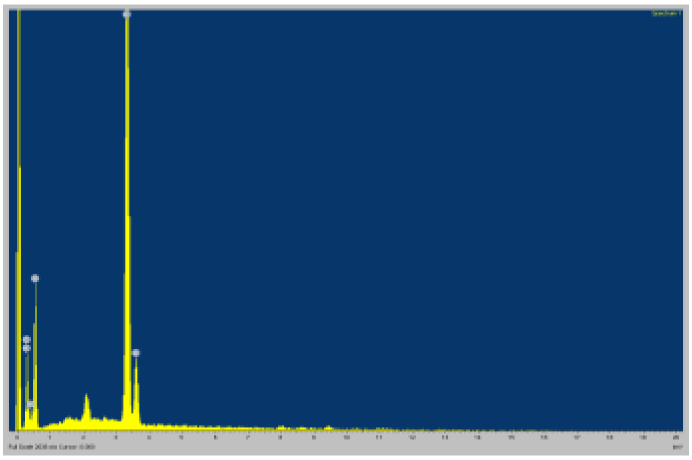
Energy Dispersive X-Ray Analysis

In order to confirm the presence of the elements of LAPN crystals, the sample of grown crystals were subjected to Energy Dispersive X-ray analysis using JEOL-6360 Scanning Electron Micro-scope. Figure 4 shows the EDX result of L- Alanine potassium nitrate crystals. Elements are identified and presented as atomic%. The presence of potassium in LAPN is confirmed by EDAX analysis.

Table 4. Energy dispersive x-ray analysis of lapn

Element	Spectral Type	Element/%	Atomic/%
C	ED	11.98	17.89
N	ED	16.14	20.67
O	ED	42.97	48.18
K	ED	28.90	13.26
Total	ED	100.00	100.00

Fig 10. Energy Dispersive X-Ray Analysis Of L-Alanine Potassium Nitrate



Conclusion

The seed crystals of L-Alanine Potassium nitrate crystals (LAPN) are grown from the solution prepared from the raw materials L-Alanine and Potassium nitrate. These crystals are characterized and the following results are obtained.

(1) The grown crystals are characterized by using powder XRD diffraction.

(2) From the FTIR spectrum we confirm the structure of the LAPN to have both the L-Alanine and Potassium nitrate molecules. These arrangements are in alternate layers in the crystal. This is evident from the non damage of L-Alanine structure.

(3) The UV-Vis spectrum establishes the good transmittance window and the lower cutoff are found to be as low as 300 nm, allowing for frequency conversion down to UV-region.

(4) The sharpness of the exothermic peak shows good degree of crystallinity of the grown crystals and indicates its suitability for application in lasers field.

(5) From the SEM analysis we conclude that the crystal surface is very smooth which shows that it can add more molecules to grow into a large crystal.

(6) EDX confirm the presence of the elements of LAPN.

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