

SYNTHESIS, GROWTH AND CHARACTERIZATION STUDIES OF SEMI ORGANIC NLO L-VALINE CALCIUM NITRATE AND L-VALINE POTASSIUM NITRATE SINGLE CRYSTALS

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ABSTRACT

These organic non-linear L-Valine potassium nitrate and L-Valine calcium nitrate crystals are grown at room temperature by slow evaporation techniques. The crystal structure was analyzed by powder X-ray method. The presence of a functional group can be identified by Fourier transform infrared spectrum (FT-IR). The second-order non-linear optical property is measured by the Kurtz powder technique. The optical behavior was analyzed by Ultraviolet –vis spectrum and found that the crystal is transparent in the region between the 200-1100nm.

Keywords: L-Valine, SHG, FT-IR. UV, EDAX

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INTRODUCTION

The NLO materials have great attention due to their application in optoelectronics and data storage technologies. organic crystal has low thermal and mechanical properties.¹ It's also has a low laser damage threshold and difficult to produce bulk size crystals. In inorganic, they have good thermal and mechanical properties but modest optical nonlinearities due to the shortage of extended π -electron delocalization.²⁻⁵ In semi-organic crystals, the organic ligands are stoichiometrically bound with the inorganic host. In recent years, semi-organic crystal has attracted great interest because they have high nonoptical linearity, chemical stability, good hardness and high resistance to laser-induced damage. L-Valine is an amino acid group that contain donate carboxylate group and accept amino acid group which gives non-centrosymmetric structures for crystals.⁶⁻¹⁵ This journal paper describes the synthesis of L-Valine Potassium nitrate and Calcium nitrate crystals. The grown crystal is characterized by X-Ray analysis, FTIR, Optical transmission spectra, SHG efficiency and EDAX.

EXPERIMENTAL

Synthesis and Crystal Growth

The commercially available material of L-valine, potassium nitrate and Calcium nitrate was received from Sisco Research Laboratories PVT. Ltd (India). This is a long recrystallization process and the available raw material is used one after purification. L-valine and potassium nitrate and L-Valine and Calcium nitrate is taken in a particular molar ratio and mixed in double-distilled water and stirred for 7hrs. The stirred solution was filtered to remove unwanted particles. Then the dissolved solution was transferred to a beaker. The beaker was covered by an aluminum sheet. Some holes were made on the aluminium sheet for evaporation at room temperature. The grown crystal of LVPN and LVCN was colorless and good transparent obtained in 3weeks.

Chemical Reactions

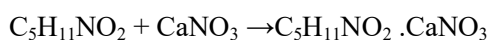
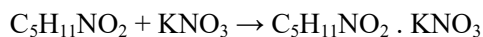




Fig.-1: L-Valine Calcium Nitrate and L-Valine Potassium Nitrate

RESULTS AND DISCUSSION

X-Ray Analysis

The grown crystal of L-Valine potassium nitrate and L-Valine Calcium nitrate were subjected to powder X-ray diffraction analysis to confirm the crystal structure and lattice parameter by using XPERT PRO diffraction meter. The Sample was scanned over the required range for 2θ values (10° - 50°). The Lattice values of L-Valine potassium nitrate is $a = 9.788 \text{ \AA}$, $b = 6.532 \text{ \AA}$ and $c = 12.00372 \text{ \AA}$ Cell vol= 436.11 \AA^3 . The lattice parameters for L-Valine Calcium nitrate is $a = 5.788 \text{ \AA}$, $b = 7.532 \text{ \AA}$ and $c = 10.00372 \text{ \AA}$ cellvol= 436.11 \AA^3 . The recorded spectrum of LVPN and LVCN is shown in Fig.-2.

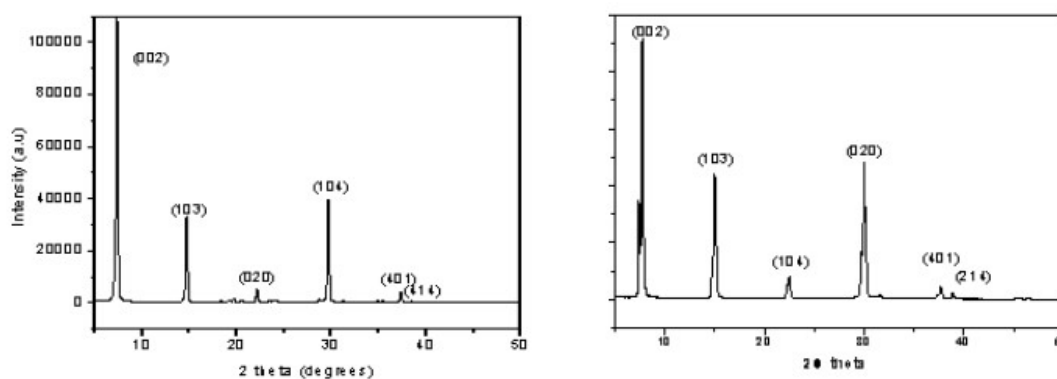


Fig.-2: XRD Pattern of L-Valine Potassium Nitrate and L-Valine Calcium Nitrate

The observed above result shows the grown crystal of L-Valine Potassium nitrate and L-Valine Calcium nitrate belongs to monoclinic.

FT-IR Spectral Analysis

The grown crystal of LVPN and LVCN were subject to FTIR analysis. It was recorded in the range of 400 - 4000 cm^{-1} employing a Perkin-Elmer spectrometer by the KBr pellet method. Figures-3 and 4 show the FTIR spectrum of crystal LVPN and LVCN. The vibrational frequency and their frequency assignment are presented in Table-1. The IR spectra of LVPN mainly arise due to internal vibration of functional groups NH_3^+ , CH , CH_3 and COOH . The sharp peak at 2966 is due to CH_2 vibration of amino acid. The absorption peak 2627 and 2100 is due to N-H-O valence stretching combination and Combination band of NH_3 bending vibrations. The absorption band at 1636 and 1500 corresponds to NH_3 asymmetric stretching and NH_3 symmetric stretching sharp peak at 3478 is due to H_2O asymmetric stretching. In LVCN, the peaks at 2960 , 2633 and 2367 are attributed to CH_2 symmetric stretching, N-H-O valence stretching combination and Overtones and combinations respectively. The peak at 2107 is due to NH_3^+ degenerative deformation and NH_3^+ torsion. The absorption band at 1636 and 1510 is due to NH_3 asymmetric stretching and symmetric stretching.

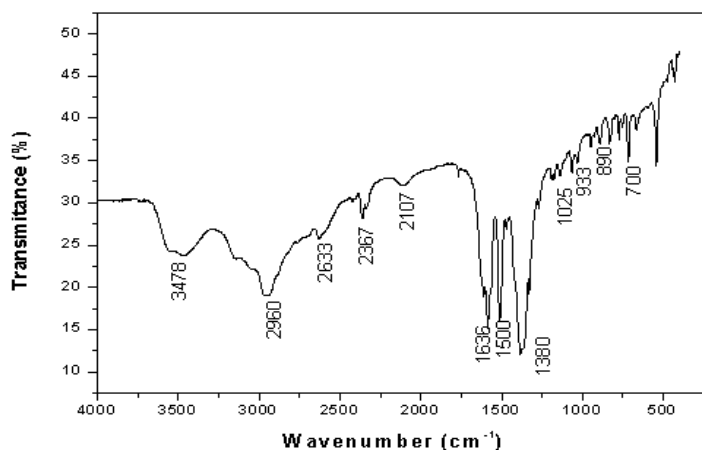


Fig.-3: FT-IR of of L-Valine with Calcium nitrate

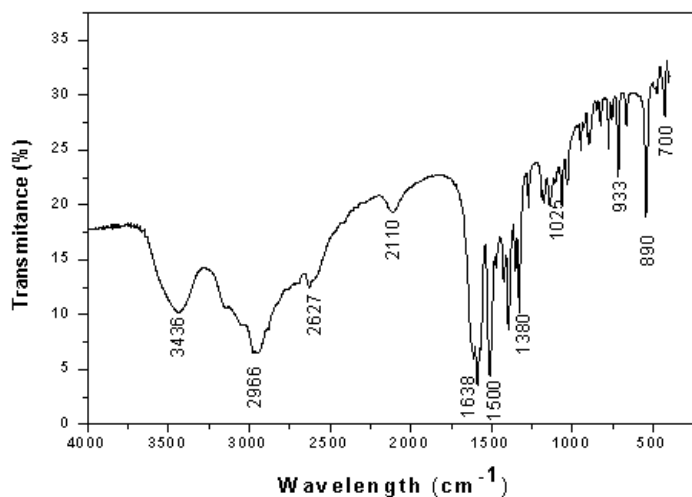


Fig.-4: FT-IR Analysis of L-Valine with Potassium Nitrate

Table-1: IR Frequencies of LVPN and LVCN

IR peak	Assignments	Frequencies cm ⁻¹	
		LVPN	LVCN
1	NH ₂ asymmetric stretching of Thiourea	3438	3478
2	CH ₂ symmetric stretching	2966	2960
3	N-H-O valence stretching combination	2627	2633
4	Combination band of NH ₃ bending vibrations	2110	2107
5	NH ₃ asymmetric stretching	1636	1632
6	NH ₃ symmetric stretching	1500	1510
7	C-O stretching	1380	1390
8	(CH ₃) ₂ symmetricstretching	1025	1030
9	C-CO symmetric stretching	933	955
10	C-C-N symmetric stretching	890	910

Optical Transmission Spectra

The transmittance range and cutoff wavelength are the most important parameter for optical application. The optical behavior of the crystal is studied using LAMBDA-35 spectrophotometer is shown in Figs.-5 and 6. The spectrum recorded in the range of 200nm-1100nm. The crystal has a lower cut-off wavelength

of 280 nm(LVPN) and 272 nm(LVCN). Optical transmittance of about 60% is observed for 1.5mm plates of L-Valine potassium nitrate and L-Valine Calcium nitrate crystals are adequately good for SHG.

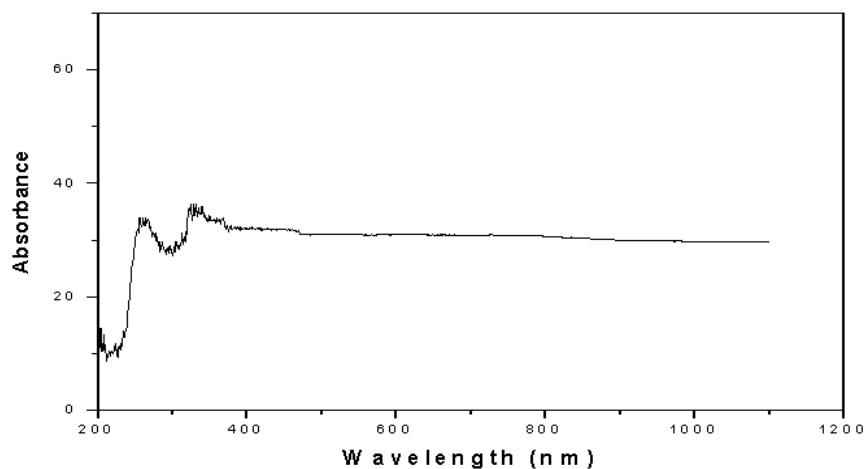


Fig.-5: UV for L-Valine with Calcium Nitrate

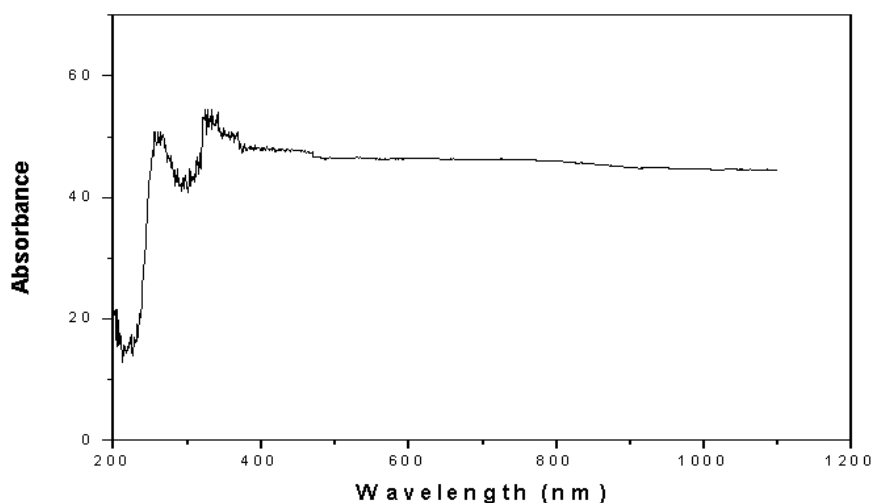


Fig.-6: UV for L-Valine with Potassium Nitrate

SHG Measurement

The second harmonic efficiency of the grown crystal LVPN and LVCN was performed by Kurtz and Perry powder SHG method. The sample could be compressed into uniform sized powdered and then the powdered crystal placed between two glass plates. The first harmonic radiation (1064 nm) of Q-switched Nd: YAG laser is allowed to fall on the sample with Pulse energy 4ml/pulse and width 6ns. The second harmonic signal in the grown crystal is confirmed by the emission of green radiation from the sample. In this experiment, potassium dihydrogen phosphate is used as reference material. The SHG efficiency of LVPN and LVCN was 0.6 and 0.5 times that of potassium dihydrogen phosphate (KDP).

Scanning Electron Microscope

Surface study of LVPN and LVCN is carried out through JSM 6360 JEOL/EO make. The utmost possible magnification in the apparatus is 3,00,000 times maximum with a resolution of 3 nm. The crystal surface with a skinny layer of carbon to make the sample conducting. Figures-7 and 8 show that the size of the crystals is 5 μm . It shows that the surface of the crystal is even and disorder free.

Table-2: SHG Efficiency of LVPN and LVCN

S. No.	Sample Name	Energy Output (milli joule)	Energy Input (joule)
1	L-valine+potassium nitrate	5.08	0.701
2	L-valine+Calcium nitrate	5.6	0.701
3	KDP (Reference)	8.91	0.701

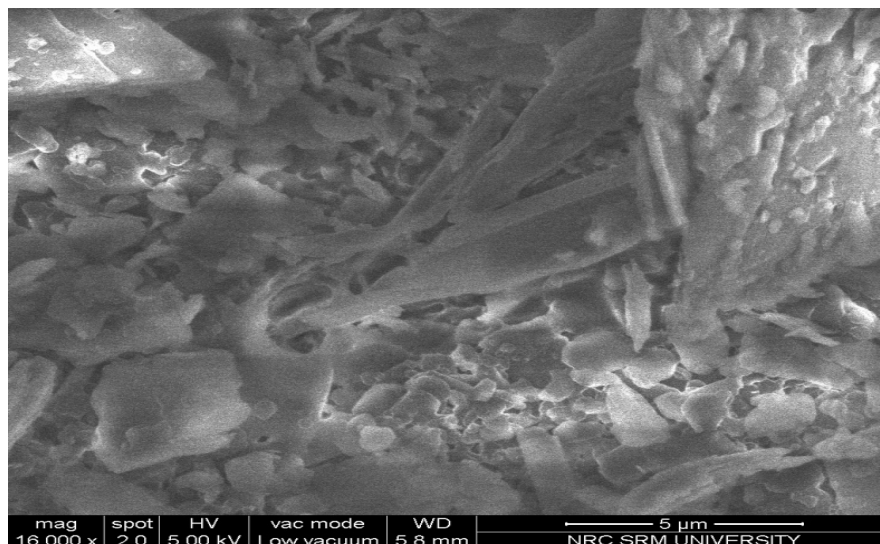


Fig.-7: SEM for L-Valine Potassium Nitrate

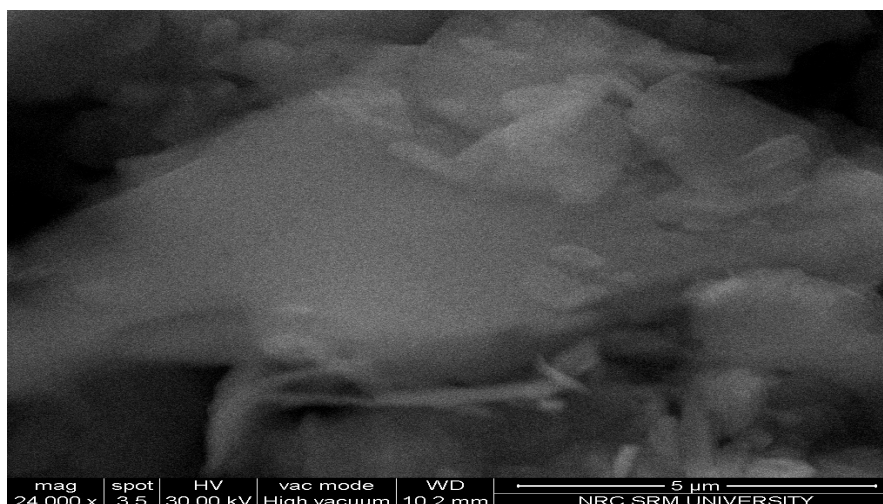


Fig.-8: SEM for L-Valine Calcium Nitrate Crystal

EDAX Analysis

The elements present in the grown crystal LVPN and LVCN was determined by using energy dispersive X-ray analysis (EDAX) measurements by using JEOL Model JED-2300 Energy Dispersive X-ray (EDAX). Microanalysis system attached to a JEOL JSM-6390LV scanning electron microscope (SEM) with a low vacuum solution of 4 nm. Figure-9 shows the EDAX spectrum of L-ValinePotassium nitrate which reveals the presence of .potassium and nitrogen. Figure-10 illustrates the EDAX spectrum of L-ValineCalcium nitrate which reveals the presence of Calcium and nitrogen.

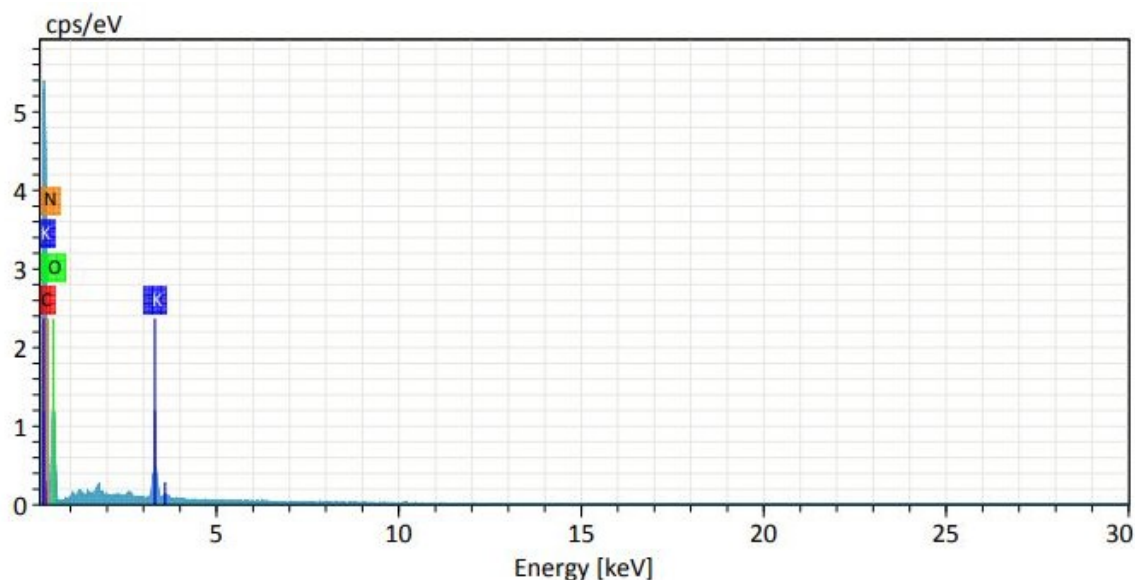


Fig.-9: EDAX for L-Valine Potassium Nitrate

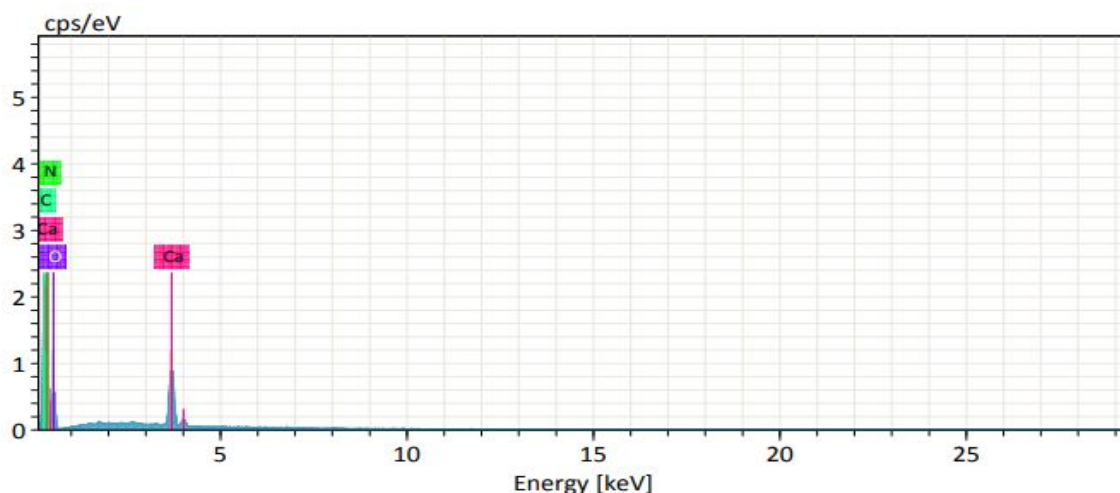


Fig.-10: EDAX for L-Valine Calcium Nitrate Crystal

CONCLUSION

By using slow evaporation technique to grow the Semiorganic crystals of L- Valine Potassium nitrate and Calcium nitrate at room temperature. The structure and lattice values can be measured from powder X-ray analysis. In the FTIR spectrum, the presence of various functional groups has been identified. The grown crystal has a good transmission window in the visible region between (270 and 280) to 1100 nm suitable for NLO applications. The SHG efficiency of the grown LVPN and LVCN crystal having 0.6 & 0.5times than that of KDP.

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