Growth And Characterization Of Semi-Organic NLO Material: L-Valine Potassium Nitrate And L-Valine Lithium Nitrate

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Abstract: Single crystals of semi organic non-linear L-Valine potassium nitrate and L-Valine lithium nitrate grown by slow evaporation method using water as a solvent. The L-Valine phase was confirmed by single crystal powder X-ray diffraction analysis. Presence of various functional groups of L-Valine was characterized by Fourier transform infra-red spectrum (FT-IR) and non-linear optical property is examined by Kurtz powder technique. The optical behavior was analysed by Ultra violet –vis spectrum and found that the crystal is transparent in the region between the 200-1100nm. Hence it may be very much useful for the second harmonic generation (SHG) applications. The crystal was thermally stable up to 215ºC (VPN) and 235ºC (VLN) as determined by DSC-TGA studies and mechanical stabilities of crystal have been confirmed by Vicker’s microhardness study. Dielectric constant was measured with various frequencies as a function of temperature.

Keywords: L-Valine, Second harmonic generation, Micro hardness, dielectric studies, thermal analysis

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I. Introduction

Second order non-linear optical (SONLO) materials have recently attracted much attention because of their potential applications in emerging optoelectronics technologies [1, 2]. Materials with large second order optical non-linearity, short transparency cutoff wavelengths, and stable physico-thermal performance are needed to realize many of these applications. The search for new frequency conversion materials over the past decade has concentrated primarily on organics. It has been demonstrated that organic crystals can have very large non-linear susceptibilities compared with inorganic crystals, but they used in low optical transparency, poor mechanical properties, low laser damage threshold, and the unable to produce and process large crystals [3, 4]. Purely inorganic nonlinear optical (NLO) materials typically have excellent mechanical and thermal properties with relatively modest optical nonlinearities because of the lack of extended \( \pi \)-electron delocalization. In semi-organics, polarizable organic molecules are stochiometrically bound within an organic host [5]. In recent years, the NLO properties of semi-organic complex products has attracted great interest because of these metal-organic complexes.

Here, L-valine is a branched chain amino acid, which has both a primary amino group and a primary carboxylate group. The carboxylate acid group donates its proton to the amino group. So in solid state, amino acid exists as zwitterions, which create hydrogen bonds, in the form of \( \text{N-H}^+-\text{O-C} \), which are very strong bonds. Hydrogen bonds have also been used in the possible generation of non Centro-symmetric structures, which is a prerequisite for an effective SHG crystal.

This paper describes the synthesis of crystal structure of L-valine potassium nitrate, L-Valine Lithium nitrate. The grown crystals were characterized by powder XRD, FTIR, optical transmission measurement, DSC–TGA, dielectric measurement, microhardness measurement and Kurtz and Perry powder SHG test was performed to confirm the second order nonlinearity of the grown crystal.

II. Experimental

Synthesis and crystal growth

L-valine, potassium nitrate and lithium nitrate was received from Sisco Research Laboratories PVT. Ltd (India). This is a long recrystallization processes and available raw material is used one after purification. L-valine and potassium nitrate is taken in a particular molar ratio and added 20 ml of double distilled water and stirring till dissolved the mixture. After dissolving the above mixture is transferred in to 100 ml beaker. The mixing solution kept in slow evaporation in beakers covered with aluminum foil sheet at room temperature. The L-Valine and lithium nitrate followed by the same procedure. Two grown crystal are colourless, good transparent crystals has obtained by 3 to 4 weeks

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Chemical reaction

\[
\begin{align*}
C_5H_{11}NO_2 + KNO_3 &\rightarrow C_5H_{11}NO_2 \cdot KNO_3 \\
C_5H_{11}NO_2 + Li(NO_3) &\rightarrow C_5H_{11}NO_2 \cdot Li(NO_3)
\end{align*}
\]

Fig.1 As grown the crystals of VPN and VLN

III. 3. Results And Discussions

3. 1.Powder X-ray diffraction

The grown single crystal of L-Valinepotassium nitrate and L-Valine Lithium nitrate has been subjected to powder X-ray diffraction. Powder form of the above mentioned crystal is taken for the analysis using XPERT PRO diffract meter. The indexed powder x-ray diffraction pattern of the grown crystal is presented in fig 2&3. The lattice parameters for L-Valine potassium nitrate obtained from the data of powder XRD pattern using UNITCELL software package are \(a = 9.788 \, \text{Å}, \, b = 6.532 \, \text{Å} \) and \(c = 12.00372 \, \text{Å}\). The lattice parameters for L-Valine Lithium nitrate obtained from the data of powder XRD pattern using UNITCELL software package are and \(a = 9.890 \, \text{Å}, \, b = 6.788 \, \text{Å} \) and \(c = 12.00222 \, \text{Å}\). Cellvol= 436.11Å\(^3\). The lattice parameters are found to be in good agreement with the literature.

Fig. 2 XRD pattern of L-Valine with Potassium nitrate
3.2. Optical transmission spectra

A transmission spectrum is very important for any NLO materials, because a nonlinear optical material can be of any practical use if it has a wide transparency window. In the present study, we have recorded the UV-Vis NIR transmission spectrum in the range of 200nm-1100nm is shown in fig 4&5 and the instrument used in the analysis is LAMBDA-35 UV-Vis spectrophotometer. From the spectrum, it is seen that the crystal has a lower cut-off wavelength of 272nm and 280nm (VPN). The spectrum further indicates that the crystal has a wide optical window from 272nm to 1100nm and 280nm to 1100 nm (VLN). The crystal is transparent in the visible and infrared spectral regions. Optical transmittance of about 100% is observed for 1.5mm plates of L-Valine potassium nitrate and L-Valine Lithium nitrate crystals is sufficiently good for SHG.
3.3. FTIR spectral analysis

The FTIR spectrum of VPN and VLN crystals were recorded in the range 400-4000cm<sup>-1</sup> employing a Perkin-Elmer spectrometer by KBr pellet method to study the metal organic coordination. Fig. 6&7 shows the recorded FTIR spectrum of the grown crystal of VPN and VLN. The vibrational frequency of various functional groups of VPN and VLN and the tentative frequency assignment are presented in table.
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From fig 9 DTA curve, it is observed that the material undergoes an irreversible exothermic transition at about 235°C where the decomposition starts, which indicate the material stable up to 235°C. The material is fully decomposed above 600°C. The sharpness of the exothermic peak shows good degree of crystallinity of the grown LVLN crystal. From TGA curve the weight loss curve is observed starts at 145°C and ends at 255°C. This weight loss is due to the liberation of volatile substances. The peak at 255°C indicates a phase change from liquid to vapor state as evidence from the loss of weight in the TGA curve.

![TGA/DTA Curve of L-Valine Potassium nitrate](image)

**Fig -8 TGA/DTA Curve of L-Valine Potassium nitrate**

![TGA/DTA Curve of L-Valine Lithium nitrate](image)

**Fig -9 TGA/DTA Curve of L-Valine Lithium nitrate**

### 3.6 Micro Hardness

The mechanical strength of the grown crystal was studied using HMV 2T, Vicker’s microhardness tester. Microhardness measurement is commonly used to determine the mechanical strength of the material which is related to bond strength and defect structure [11]. The static indentations were made on the surface of crystal by varying the load from 5-100g at room temperature. Vicker’s microhardness number was determined using $H_v=1.8544\frac{P}{d^2}\text{kg/mm}^2$. The variation of $H_v$ with the applied load $P$ is shown in Fig. 10. In our case, $H_v$ increases with load up to 75g and becomes load independent for $P_{75}$ g, which can be attributed to the work hardening of the surface and above 75g load significant cracking occurs, which may be due to the release of internal stresses generated with indentation. Finally the maximum value of hardness for LVPN&LVLN crystal at room temperature was found to be $72.4\text{ Kg/mm}^2$(LVPN) and $81.6\text{ Kg/mm}^2$(LVLN) for the load of 75g.
3.7 Dielectric Constant ($\varepsilon_r$)

The dielectric property of LVPN was studied at various temperatures using Agilent A 2484. The dielectric Constant ($\varepsilon_r$) of crystal was found by measuring the capacitance and dielectric loss, which is used to calculate the dielectric constant at various temperatures ranging between room temperature to 150ºC for three different frequencies (100Hz, 10KHz and 1MHz). From the figure the dielectric constant increased with increased the temperature. The current investigations showed that dielectric constant was observed maximum at 150ºC, since all types of polarization such as electronic, ionic, orientation and space charge polarizations occur at higher temperature. The variation of dielectric constant with temperature at three different frequencies like 100Hz, 10 KHz and 1 MHz is shown in Fig.12&13.
IV. Conclusion

Single crystals of L-valine potassium nitrate and L-valine lithium nitrate were successfully synthesized by solution growth technique. Its lattice dimensions have been determined from the powder X-ray diffraction analysis. The various functional groups have been identified from the Fourier transform infrared (FT-IR) analysis. The grown crystal has good transmission window in the visible region between (270 and 280) to 1100 nm, it is suitable for NLO applications. The thermal studies confirm that the crystal structure for LVPN and LVLN is stable up to 215°C & 235°C and indicate its suitability for application in lasers field. Microhardness value was calculated in order to understand the mechanical stability of the grown crystals. From the dielectric studies it is seen that the dielectric constant increased with increased temperature. The powder second harmonic generation efficiency measurement shows the grown VLN and VPN crystal having 0.5 and 0.6 times higher nonlinear optical efficiency than potassium dihydrogen phosphate.

Reference

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