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Growth and Characterization of Semi-Organic NLO Material: L-Valine Lithium Nitrate

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Abstract: Single crystals of semi organic non-linear 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 byKurtz 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 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,SHG ,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 π-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 carboxlate 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 $N\text{-}H^{+}\text{-}O\text{-}C$, 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 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 Procedure

L-valine and lithium nitrate was received from Sisco Research Laboratories PVT. Ltd (India).This is a the long recrystallization processes and available raw material is used one after purification. L-valine and Lithium 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 grown crystal are colourless, good transparent crystals has obtained by 3 to 4 weeks

Chemical reaction

$C_5H_{11}NO_2$ + Li $(NO_3)_2$------------------>$C_5H_{11}NO_2$ .Li$(NO_3)_2$

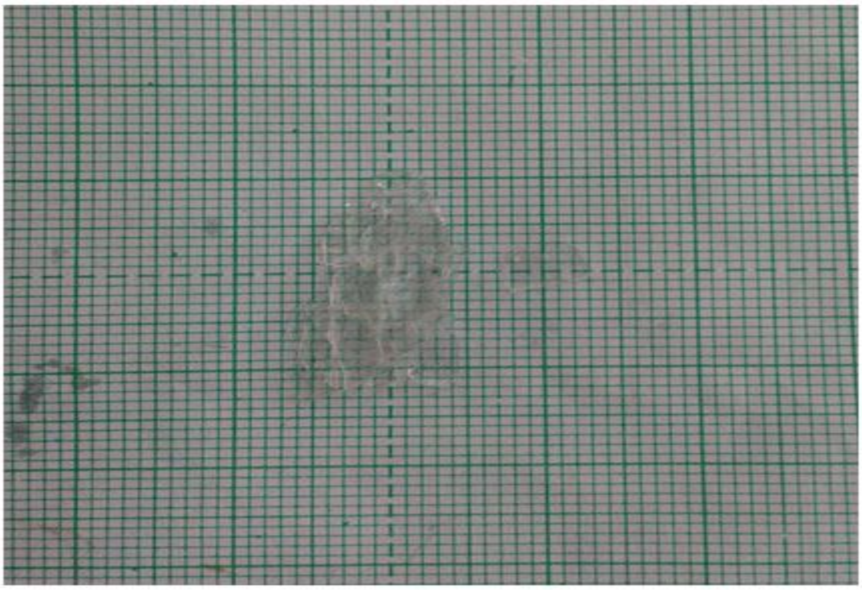

Fig.1 As grown the crystals of VLN

III. Results And Discussion

3. 1.Powder X-ray diffraction

The grown single crystal of 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. 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 Ǻ, b = 6.788 Ǻ and c = 12.00222ǺCell vol= 438 A^3 are found to be in good agreement with the literate.

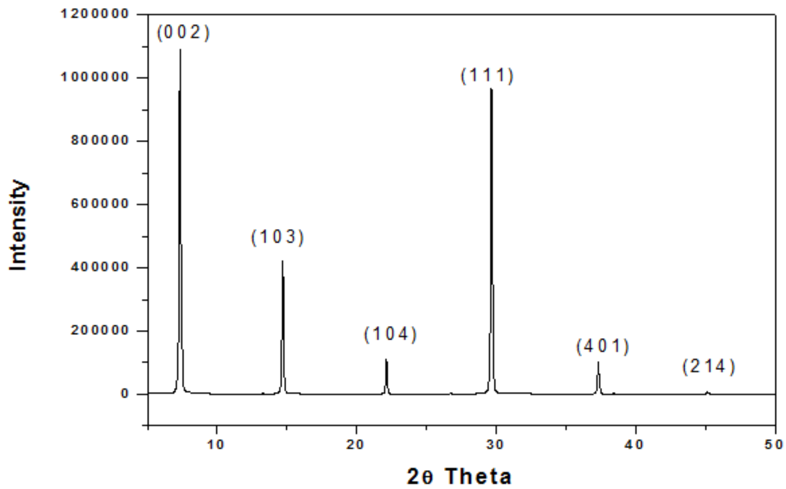

Fig. 2 XRD patteren L-Valine with Lithium nitrate

Table 1 for XRD Values of VLN crystal

Parameters(VLN)	Present study	Reported velues
A	9.890	9.9714
B	6.788	6.2930
C	12.002223	12.6480
V	438.00	434.22
System	Monoclinic	Monoclinic
Space group		P2

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 3 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-offwavelength of 280 nm(VLN). The spectrum further indicates that the crystal has a wide optical window from 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 and L-Valine Lithium nitrate crystals and is sufficiently good for SHG.

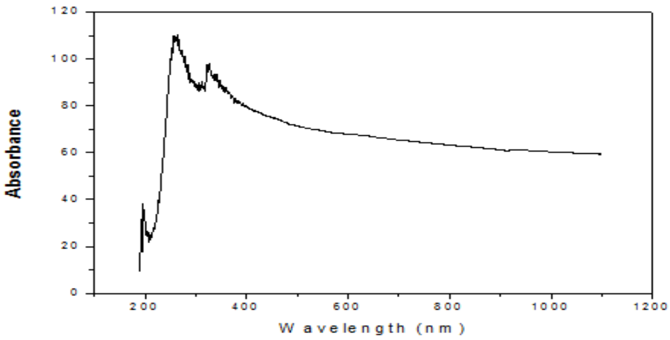

Fig. 3 UV spectrum for L-Valine with lithium nitrate

3.3. FTIR spectral analysis

The FTIR spectrum of VLN crystals were recorded in the range 400-4000cm-1 employing a Perkin-Elmer spectrometer by KBr pellet method to study the metal organic coordination. Fig.4 shows the recorded FTIR spectrum of the grown crystal of VLN. The vibrational frequency of various functional groups of VLN and the tentative frequency assignment are presented in table.

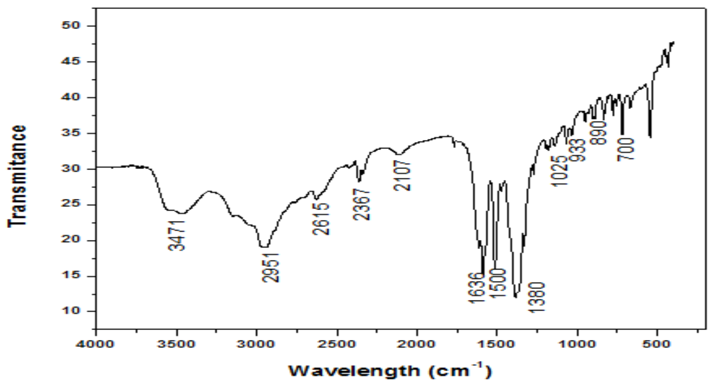

Fig. 4 FT-IR analysis of L-Valine with Lithium nitrate

Table: 2 IR frequencies of VLN

IR peak	Assignments	Frequencies
		VLN
1	CH_2 symmetric stretching	2951
2	N.H.O valance stretching	2615
3	NH_3 asymmetric stretching	1630
4	NH_3 symmetric stretching	1450
5	CH_3 symmetric stretching	1360
6	$(CH_3)_2$symmetricstretching	1000
7	C-C symmetric stretching	940
8	C-C-N symmetric stretching	870
9	CH_3 rocking	720

3.4. Second Harmonic Generation Test

The second harmonic generation (SHG) test on the VLN crystal was performed by Kurtz powder SHG method [18]. The powdered sample of crystal was illuminated using the fundamental beam of 1064 nm from Q-switched Nd:YAG laser. Pulse energy 4ml/pulse and pulse width of 6 ns and repetition rate of 10Hz were used. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation of wavelength 532 nm collected a monochromator after separating the 1064 nm pump beam with an IR-blocking filter. A photomultiplier tube is used as a detector. It is observed that the measured SHG efficiency of VLN crystal was 0.5 times times that of potassium dihydrogen phosphate (KDP).

Sl. No.	Code / Name of the Sample	Output Energy (milli joule)	Input Energy (joule)
1	L-valine+Lithium nitrate	4.54	0.701
2	**KDP (Reference)**	**8.91**	**0.701**

3.5 TGA and DTA analysis

To find the thermal characteristics of LVLN, differential analysis (DSC) and thermogravimetric analysis (TGA) were carried out simultaneously in a TA Instruments Q 600 SDT DSC: Simultaneous Thermal Analyzer. The sample was heated at a rate of 10ºC/min in protected nitrogen gas flow and 1.25 mg of the sample was taken to carry out the experiment. Fig.8 shows the thermograms illustrating simultaneously recorded TGA and DTA. From fig 5 DTA curve, it is observed that the material undergoes an irreversible exothermic transition at about **235ºC** where the decomposition starts, which indicate the material stable up to 235ºC. The material is fully decomposed above 600ºC. The sharpness of the exothermic peak shows good degree ofcrystallinity of the grown LVLN crystal. From TGA curve the weight loss curve is observed starts at 145ºC and ends at 255ºC. This weight loss is due to the liberation of volatile substances. The peak at 255ºC indicates a phase change from liquid to vapor state as evidence from the loss of weight in the TGA curve.

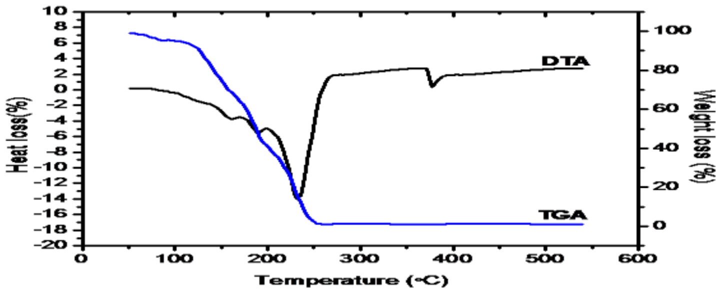

Fig -5 TGA/DTA Curve of L-Valine Lithium nitrate

3.6 Micro Hardness

The mechanical strength of the grown crystal was studied using HMV 2T, Vicker'smicrohardness 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'smicrohardness number was determined using H_v=1.8544 P/d^2kg/mm^2. The variation of H_v with the applied load P is shown in Fig. 6. In our case, Hv 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 LVLN crystal at room temperature was found to be 81.6 Kg/mm2(LVLN)for theload of 75g.

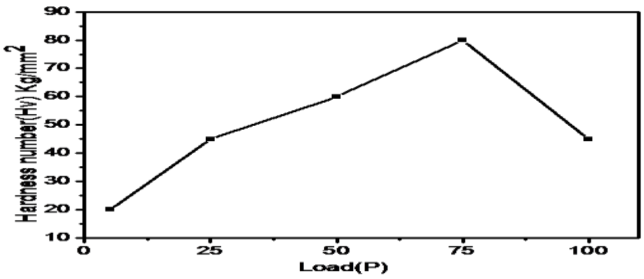

Fig -6 Micro hardness of L-Valine Lithium Nitrate crystal

3.7 Dielectric Constant (ε_r)

The dielectric property of LVLN was studied at various temperatures using Agilent A 2484. The dielectric Constant(**ε_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[7]. 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.7

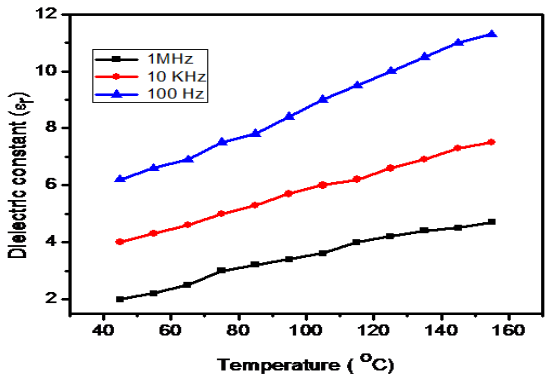

Fig.7 dieletric for L-valine lithium nitrate

IV. Conclusion

Single crystals of 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 transforminfra-red (FT-IR) analysis. The grown crystal has good transmission window in thevisible region between(270 and 280) to 1100 nm, it is suitable for NLO applications. The thermal studies confirm that the crystal structure for LVLN is stable up to 235ºC 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 thegrown VLN crystal having 0.5 times higher nonlinear optical efficiency than potassium dihydrogen phosphate.

Reference

[1]. Loiacono G M, Osborne W N. Crystal growth from solution using cylindricalseeds, Cryst J. Growth, 43(4), 1978, 401-405.
[2]. Kejalakshmy N, Srinivasan K. Growth,optical and electro-optical characterizations of potassium hydrogen phthalate crystals doped with Fe 3+ and Cr 3+ ions, Opt.Mater, 27(3), 2004, 389-394.
[3]. R.W. Boyd, Non Linear optics, Academic Press, San Diego, **1992**, 155.
[4]. B.E. Salch and M.C. Teich, Fundamentals of Photonics, Wiley, New York, **1991**, 113.
[5]. M.D. Agarwal, J. Choi, et al, Journal of crystal growth 1999, 179 204 .
[6]. W. kocehner, solid state laser engineering, 5th edition, Berlin Springer, 1999.
[7]. SK Kurtz and T.T. Perry, J. applied physics 1968, 39, 3798 .
[8]. Packiam Julius J, Joseph Arul Pragasam A, Selvakumar S, Sagayaraj P, J Cryst Growth,267 ,2004 619.
[9]. S. Natarajan, K. Ravikumar, S.S. Rajan, Z.Kristallogr., 168, 75 (1984).
[10]. P. Narayanan, S. Venkatraman, Z.Kristallogr., 142, 52 (1975).
[11]. K. Ravikumar, S.S. Rajan, Z.Kristallogr., 171, 201 (1985).
[12]. K. Ambujam, K. Rajarajan, S. Selvakumar, J. Madhavan, Gulam Mohamed andP. Sagayaraj, Opt. Mat. 29, 657 (2007).
[13]. J. Thomas Joseph Prakash, S. Kumararaman, Physica B: Condensed Matter, 403,3883 (2008)
[14]. Ra. Shanmugavadivu, G. Ravi and A. Nixon Azariah, J. Phy. and Chem. Solids67, 1858 (2006)
[15]. K. Ambujam, K. Rajarajan, S. Selvakumar, I. VethaPotheher, Ginson P. Josephand P. Sagayaraj, J. Cryst. Growth 286, 440 (2006)
[16]. G.AnandaBabu and P.Ramasamy,"Synthesis,Crystal growth and characterization of novelsemiorganicnon linear optical crystal:dichlorobis(1-proline)zinc(II)", Materials Chemistry andPhysics ,vol.113, no.23,pp.727-733 (2009).
[17]. T.U.Devi, N. Lawrence, R.RameshBabu and K.Ramamurthi, "Growth and characterization of 1-proline picrate single crystal: a promising NLO crystal", Journal of Crystal Growth, vol.310 no. 1, pp.116-123 (2008).

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