RJC
http://www.rasayanjournal.com

RASĀYAN *J. Chem.*
Vol.4, No.2 (2011), 320-326
ISSN: 0974-1496
CODEN: RJCABP

SYNTHESIS, GROWTH, SPECTROSCOPIC AND OPTICAL STUDIES OF A NEW SEMIORGANIC NONLINEAR OPTICAL CRYSTAL: L-VALINE POTASSIUM CHLORIDE

J.Chandrasekaran[1], P.Ilayabarathi[*,2] and P.Maadeswaran[3]

[1]Department of Physics, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore – 641 020, Tamil Nadu, India.

[*,2]Research and Development Center, Bharathiyar University, Coimbatore – 641 046, Tamil Nadu, India.

[3]Department of Physics, K S Rangasamy College of Technology, Tiruchengode – 637 215, Tamil Nadu, India

*E-mail: ilaya_pj@yahoo.co.in

ABSTRACT

A new semiorganic nonlinear optical crystal, L-Valine Potassium chloride (LVPC), has been synthesized and good optical quality single crystals (5×4×3mm^3) were grown by slow evaporation technique. The grown crystal was characterized by using FT-IR, UV-vis-NIR and DSC-TGA. 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 crystal was thermally stable up to 220ºC 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. The second harmonic generation behavior of LVPC crystal was tested by Kurtz–Perry powder technique.

Keywords: L-Valine potassium chloride, infrared spectrum, optical transmission spectrum, thermal analysis, dielectric measurement and SHG test.

INTRODUCTION

Developments of novel molecular and crystal design technique for assembling the materials are used for many device applications in the domain of opto-electronics and photonics[1]. In particular, semiorganic system provides many structure and bonding schemes for the molecular engineering of new materials. Semiorganic nonlinear optical (NLO) crystals are attracting a great deal of attention due to their high NLO coefficient, high damage threshold, high thermal stability and mechanical strength compared to organic NLO crystals. The crystal engineering of this nonlinear optical material is based on the anchorage of organic molecules exhibiting a large NLO efficiency on the amino acid groups[2]. Here, L-Valine is a branched chain amino acid, which has aliphatic non-polar side chain and has both a primary amino group and a primary carboxyl 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 N–H+–O–C, which are very strong bonds. Hydrogen bonds have also been used in the possible generation of non-centrosymmetric structures, which is a prerequisite for an effective SHG crystal[3]. In continuation of our work with examples of semiorganic NLO cryatsals are L-valine cadmium chloride monohydrate[4], L-valine L-valinium hydrochloride[5], L-Valine hydrochloride[6] and L-valine hydrobromide[7]. In the present paper reported the synthesis, growth and characterization of on L-valine (amino acid) and potassium chloride (inorganic compound) are reporting for the first time the synthesis of a new semiorganic nonlinear optical material L-valine potassium chloride (LVPC). The crystal was grown from its aqueous solution by slow evaporation method. The grown crystals were characterized by FT-IR, 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.

Synthesis and growth technique

The starting material was synthesized by taking L-Valine (Nice Chemie-AR grade) and Potassium chloride (Nice Chemie-AR grade) in a 1:1 stoichiometric ratio. The required amount of starting materials for the synthesis of L-valine potassium chloride (LVPC) crystal was calculated according to the following reaction:

$$C_5H_{11}NO_2 + KCl \rightarrow K.[C_5H_{11}NO_2].Cl \quad (1)$$

The calculated amount of potassium chloride was first dissolved in deionized water. L-Valine was then added to the solution. The solution was agitated with a magnetic stirring device for 8h continuously and filtered after complete dissolution of the starting materials. The prepared solution was allowed to dry at room temperature and the crystals were obtained by slow evaporation technique. The purity of the synthesized crystal was further improved by successive recrystallization process; thereby good optical qualities of single colorless crystals were obtained in 29 days which is shown in (Fig.1).

Characterization

The Fourier transform infrared spectrum was recorded by the KBr pellet technique using Thermo Nicolet, Avatar 370 Spectrophotometer to confirm the vibrational structure of the crystalline compound with range of wave number 4000-400 cm^{-1}. The thermal behavior of grown crystal was studied by using DSC-TGA instruments, Model: Q600 SDT and Q20 DSC instrument. The UV-vis-NIR spectrum was confirmed the optical absorption in the range 200–800nm using Varian, Cary 5000 instrument. The crystal was subjected to dielectric permittivity by using Agilent 4284 A Precision LCR meter. The mechanical property of the grown crystal was studied using HMV 2T microhardness tester. The powder technique of Kurtz and Perry confirms the NLO property of the grown crystal. The detailed discussions on the obtained results are presented in the following sections.

RESULTS AND DISCUSSIONS

FTIR absorption studies

The infrared spectra of LVPC were obtained from potassium bromide pellets technique using Thermo Nicolet, Avatar 370 Spectrophotometer to confirm the vibrational structure of the crystalline compound with range of wave number 4000-400 cm^{-1} and are shown in Fig.1. The IR spectra of LVPC mainly arise due to internal vibration of functional groups NH_3^+, CH, CH_3 and COOH. The absorptions of LVPC have been compared with those of the parent compound (L-valine)[8] in Table 1. The broad peak at 2945 cm^{-1} is due to the methylene symmetric stretching. The N-H--O valance stretching combination observed at 2626 cm^{-1}. The sharp peaks at 1579 and 1392 cm^{-1} are due to COO^- asymmetric and asymmetric stretching mode of vibrations. The deformation bands observed at 1509cm^{-1} is due to the protonated amino group NH_3^+. The C-C stretching modes are observed at 1179 and 1137 cm^{-1}.The sharp peak at 1064 cm^{-1} is due to C-C-N stretching mode[9]. The C-H out-of plane bending and C-CO deformation are observed at 714 and 542cm^{-1} respectively.

UV–vis–NIR Spectra

To find the optical absorption range of LVPC crystals, the UV–vis–NIR spectrum (Fig.3) was recorded using Varian, Cary 5000 spectrophotometer in the range at 200–800 nm with scanning speed of 200 nm/min. When the absorption is monitored from longer to shorter wavelengths, optical absorption with lower cut-off wavelength below 294nm for LVPC, which is sufficient for SHG laser radiation of 1064nm and the transmittance of the crystal, is about 90% in the entire visible and infrared region[10].

TGA and DSC analysis

To find the thermal characteristics of LVPC, differential Scanning calorimetry 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.4 shows the thermograms illustrating simultaneously recorded TGA and DSC. From DSC curve, it is observed that the material undergoes an irreversible exothermic transition at about 220ºC where the decomposition starts, which indicate the material stable up to 220ºC. The material is fully decomposed above 800ºC. The sharpness of the exothermic peak shows good degree of crystallinity of the grown LVPC crystal. From TGA curve the weight loss curve is observed starts at 175ºC and ends at 235ºC. This weight loss is due to the liberation of volatile substances. The peak at 235ºC 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 LVPC crystal[11].

Table-1: FTIR spectral band assignments of LVPC

Wavenumber (cm^{-1})		Assignments
L-valine[8]	LVPC	
2945	2945	CH_2 symmetric stretching
2629	2626	N-H..O.valance stretching combination
1585	1579	COO^- asymmetric stretching
1508	1509	NH_3^+symmetric deformation
1396	2392	COO^- symmetric stretching
1329	1325	C-O stretching
1179	1178	C-C stretching
1140	1137	C-C stretching
1065	1064	C-C-N streching
901	893	NH_3^+ rocking bending
716	714	C-H-out of plane bending
542	542	C-CO deformation
481	471	C-C deformation

Dielectric Constant (ε_r)

The dielectric property of LVPC 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.5.

Microhardness measurement

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 $Hv=1.8544\ P/d^2\ kg/mm^2$. The variation of Hv 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 $P \geq 75$ 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 LVPC crystal at room temperature was found to be $64.4kg/mm^2$ for the load of 75g.

Second harmonic generation efficiency (SHG)

The SHG efficiency of L-valine potassium chloride was measured by the powder technique of Kurtz and Perry[12]. The second harmonic output was generated by irradiating powder samples by a pulsed

laser beam. As a fundamental beam we used the output beam of Nd-YAG laser generating at λ = 1064nm with a pulse energy of 2.0 mJ per pulse. Generation of second harmonic beam was confirmed by the emission of green radiation (λ=532nm) from the sample. The output from the sample was filtered by an IR filter to eliminate the fundamental beam. The second harmonic beam was finally detected by a photomultiplier tube (PMT) and displayed on the oscilloscope (CRO). The second harmonic efficiency of L-valine potassium chloride is 0.32 times that of KDP.

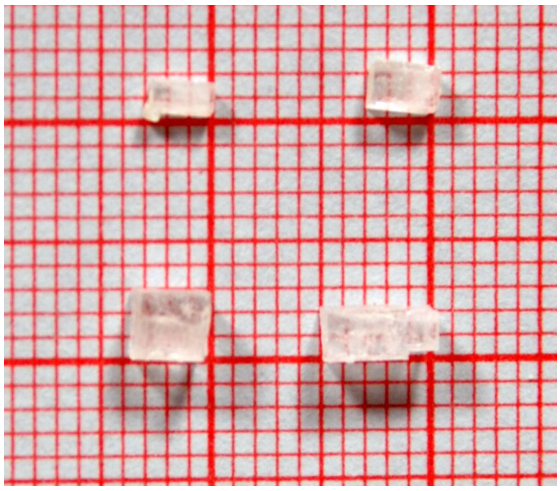

Fig.-1: As shown in LVPC Crystals

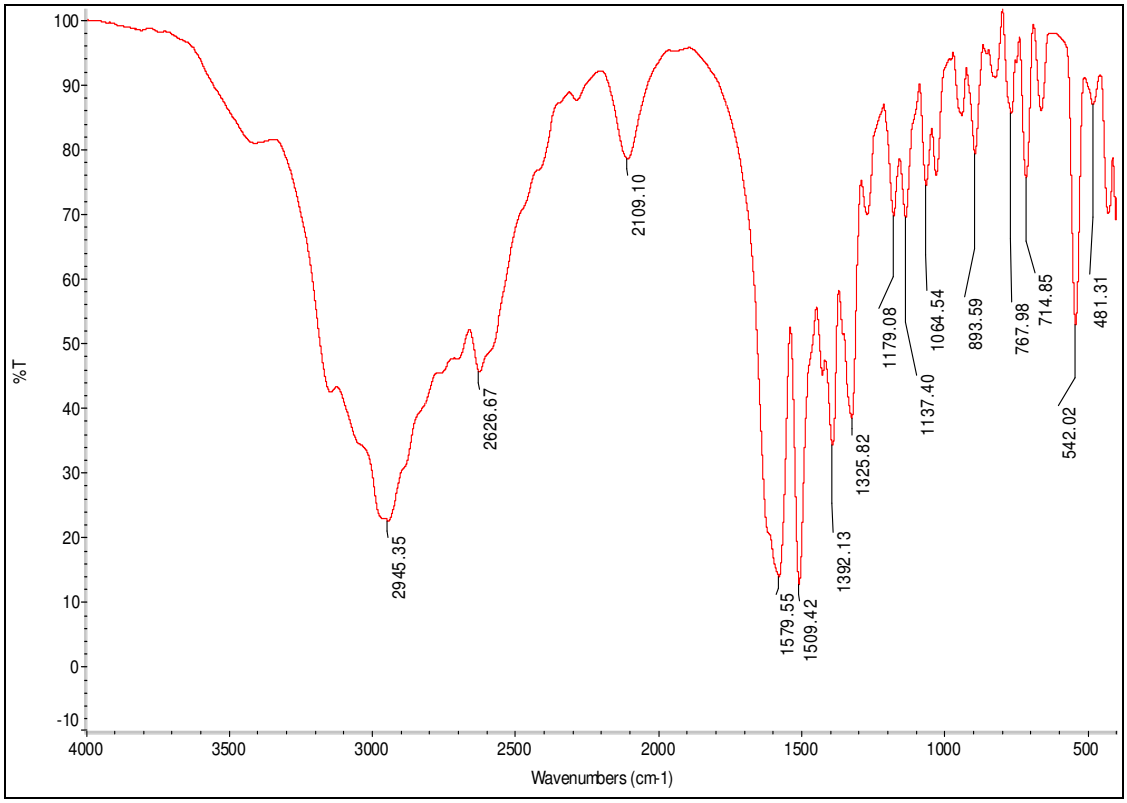

Fig.-2: FT-IR spectrum of LVPC crystal.

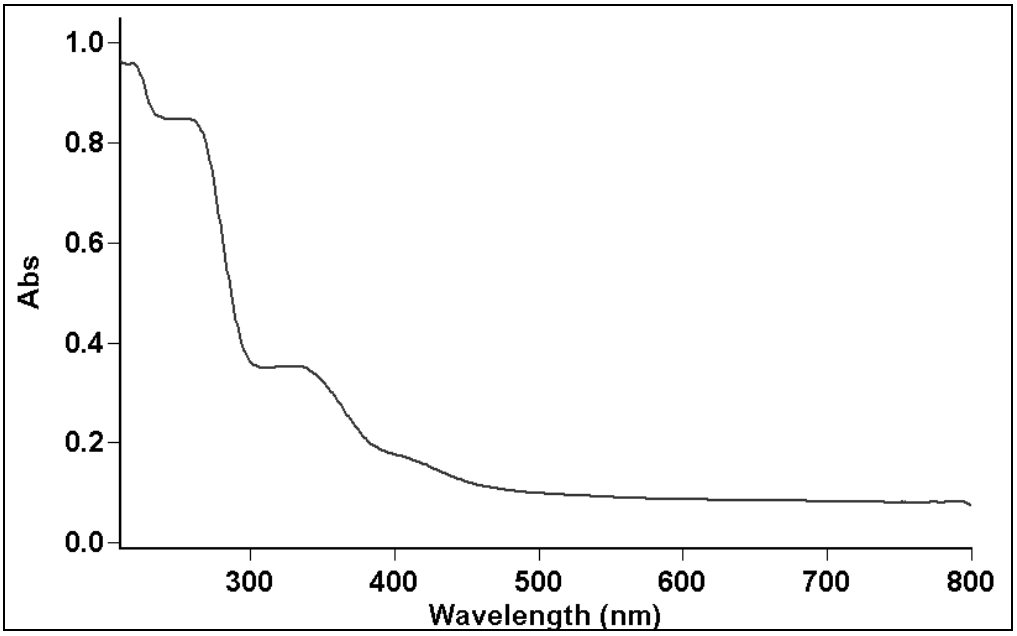

Fig.-3: Optical absorption spectrum of LVPC crystal

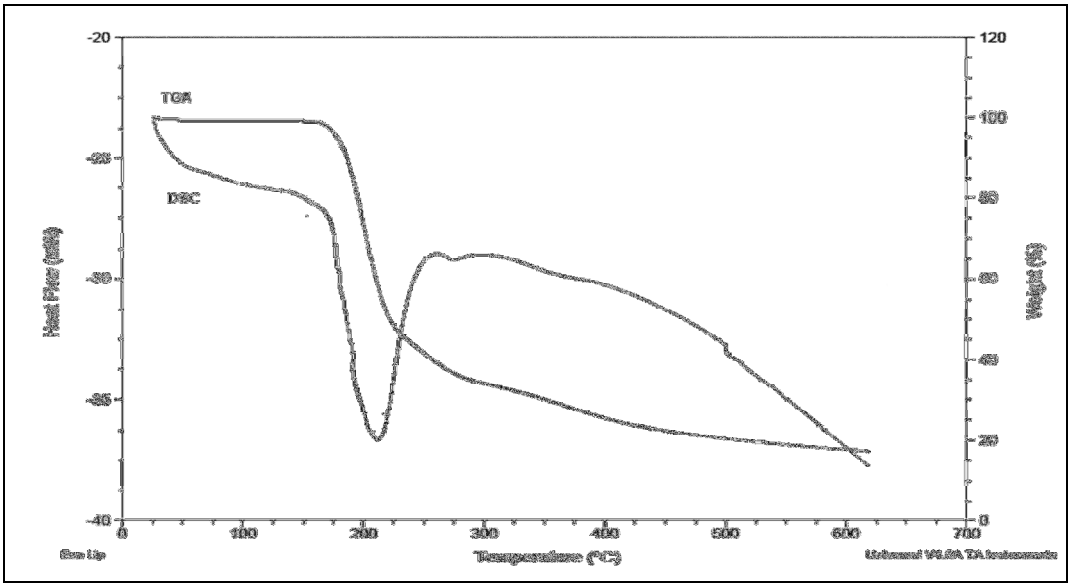

Fig.-4: TGA/DSC Curve of LVPC crystal

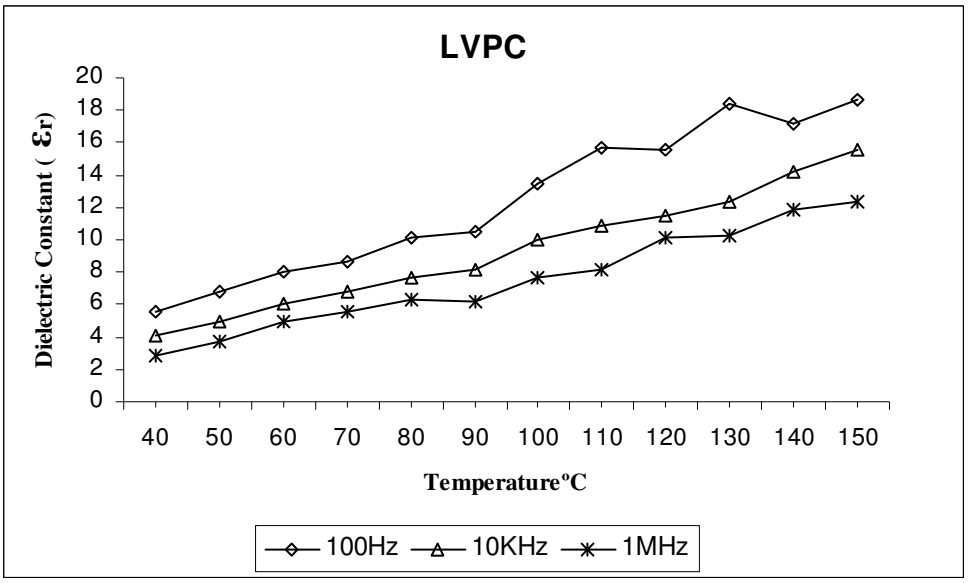

Fig.-5: Dielectric Constant of LVPC crystal

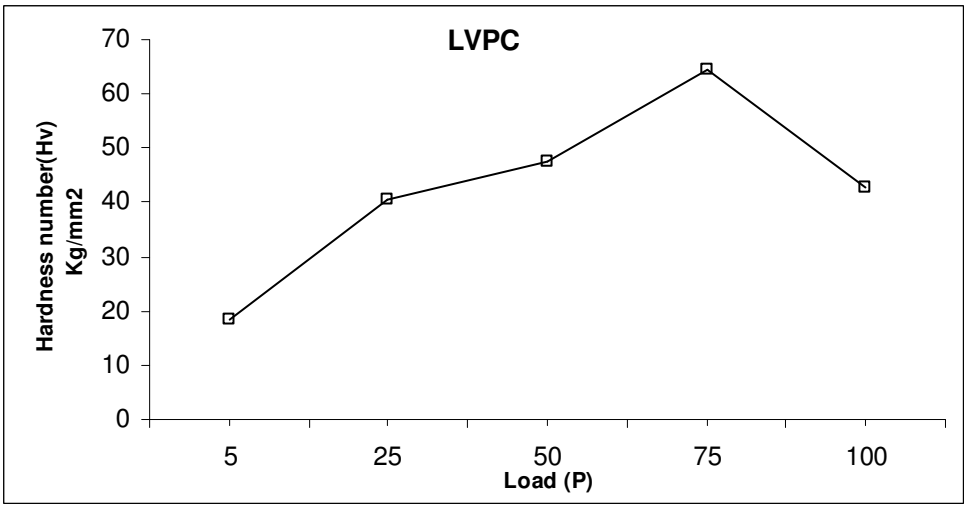

Fig.-6: Micro hardness of LVPC crystal

CONCLUSION

A potential semiorganic material for second-order NLO applications was synthesized and single crystals of L-valine potassium chloride have been grown by slow evaporation technique in mixed solvent of deionised water at room temperature. Vibrational frequencies were assigned from FT-IR spectral analysis, which confirm the presence of functional groups of the LVPC. The optical absorption study reveals the lower cut off wavelength of 294nm, thus, to as certain the fact that the crystal can be used for laser applications. The thermal studies confirm that the crystal structure is stable up to 220ºC 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 NLO behaviour of the LVPC crystal was observed by Kurtz–

Perry powder by the emission of green radiation. So LVPC could be a good candidate for the NLO applications.

ACKNOWLEDGMENTS

The authors thank to sophisticated analytical Instrumentation facility (STIC), Cochin. The authors are grateful to Prof.P.K.Das, IISc., Bangalore for extending the facilities to measure SHG efficiency. The authors thank to The Director and Principal, Mahendra Engineering College for Women, Thiruchengode for providing the Lab Facilities.

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[RJC-747/2011]