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Study of some amino acid based non-linear optical materials

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Non-linear optical (NLO) single crystals of L-valine l-valinium orthophosphate (LVP) and L-valine l-valinium nitrate (LVN) were grown by slow evaporation solution growth method using water as the solvent at room temperature. Purity of the crystals was increased by the method of recrystallization. The cell parameters of LVP and LVN were determined using single crystal X-ray diffraction technique. The grown crystals were characterized by measuring their thermal, optical and mechanical properties by Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TGA), Powder Second Harmonic Generation (SHG) efficiency, FTIR, UV-VIS NIR, damage threshold and microhardness measurements. The dielectric constant and dielectric loss of the crystals have been studied as a function of frequency at room temperature. Our studies showed that L-valine inorganic acids emerged as most promising NLO materials having SHG efficiency, mechanical and thermal stability greater than other semi-organic NLO materials.

Keywords: Slow evaporation technique, Recrystallization, DTA-TGA, Second harmonic generation, Microhardness

1 Introduction

Non-linear optics (NLO) is an innovative area of research and development which plays a key role in the field of optoelectronics and photonics[1]. The apparent development of semi-organic materials, where the organic ligand is ionically bonded with inorganic host refined the search of new materials with high optical nonlinearities which is an important area due to their optical applications such as optical communication, optical computing, optical information processing, optical disk data storage, laser fusion reaction, laser remote sensing, colour display, medical diagnostics, etc.[2]. Nonlinear optical (NLO) materials play a major role in non-linear optics and in particular they have a great impact on information technology and industrial applications. The new development technique for the fabrication and single crystal growth of nonlinear optical materials has dramatically contributed to this evolution. On account of the large flexibility for molecular design and higher nonlinear optical efficiency, there has been much progress in basic research on organic and semi-organic NLO materials. In this respect, amino acids are interesting materials for NLO applications[3-8]. The importance of amino acids for NLO application lies on the fact that almost all amino acids contain an asymmetric carbon atom and crystallize in non-centrosymmetric space group, except glycine. In solid state, amino acid contains a deprotonated carboxylic acid group (COO^-) and protonated amino group (NH^{3+}). The dipolar nature exhibits peculiar physical and chemical properties in amino acids, thus making them ideal candidates for NLO application. In the present paper, the synthesis and single crystal growth of L-valine inorganic acids followed by characterization by single crystal X-ray diffraction (XRD), DTA-TGA analysis, optical transmittance, second harmonic generation (SHG) efficiency test, dielectric behaviour, laser damage threshold and microhardness measurements, have been described.

2 Characteristic Parameters of NLO Crystal

Traditionally, the usefulness of a non-linear optical crystal has been evaluated in terms of materials parameters that are directly related to optical frequency conversion. These include (1) Conversion efficiency (2) Optical damage threshold (3) Birefringence (4) Dispersion (5) Optical transparency range (6) Optical homogeneity.

For fabrication of devices, little emphasis has been placed on the other characteristics such as (1) growth rate (2) morphology of crystals (3) mechanical strength (4) thermal stress resistance (5) coating and polishing. The parameter conversion efficiency and damage threshold are the most important parameters

of NLO crystal. The conversion efficiency of the second harmonic generation process is given by[9]:

$$\eta_{SHG}=(P_{2\omega}/P_{\omega})=2(\mu/\varepsilon_0)^{3/2}(\omega^2 d^2 l^2)/n^3 \sin^2(\Delta \mathbf{k} l/2)/(\Delta \mathbf{k} l/2)^2(P_{\omega}/A)$$

where d is the effective non-linear optical coefficients and **k** the wave vector. For a given material and a given frequency, the conversion efficiency is dependent on the square of the interaction length l, hence it is imperative that large crystals are needed. As a result of the interference from the input fundamental polarization wave and the driven harmonic polarization wave, the maximum useable length of the crystal is limited to a few microns. However, this problem could be circumvented by decreasing Δk to zero technically known as phase matching. In a chosen material and a selected interaction geometry, conversion efficiency can be further enhanced by increasing the power density (P_{ω}/A) of the input beam. This can be physically achieved by focusing the beam into the crystal, increasing the power densities to the tolerance limit, called the damage threshold. There are very few materials which satisfy most of these requirements. Hence, the search for new materials seems to be unending. Though other forms of materials like thin film polymers etc are also currently being explored, the discussion here in is limited to single crystals only.

3 Experimental Details

3.1 Material Preparation

L-valine l-valinium orthophosphate (LVP) was synthesized by the incorporation of L-valine (Hi-media) and orthophosphoric acid (Merck GR grade) in 2:1 stoichiometric ratio.

The expected chemical reaction for this compound is:

$$2(C_5H_{11}NO_2)+H_3PO_4 \rightarrow C_5H_{11}NO_2.C_5H_{12}NO_2^{+}H_2PO_4^{-}$$

L-valine l-valinium nitrate (LVN) was synthesized by taking l-valine (Hi-media) and nitric acid (Merck GR grade) in 2:1 stoichiometric ratio. An adduct LVN was formed according to the reaction:

$$2(C_5H_{11}NO_2)+HNO_3 \rightarrow C_5H_{11}NO_2.C_5H_{12}NO_2^{+}NO_3^{-}$$

The calculated amounts of the reactants in each of the reactions were thoroughly dissolved in double distilled water and stirred well for about 6 h using a magnetic stirrer to ensure homogenous temperature and concentration over the entire volume of the solutions. The solution was filtered using a Whatmann filter paper of pore size 11 μm, transformed to crystal growth vessels and crystallizations were allowed to take place by slow evaporation under room temperature. The purity of the synthesized salt was improved by successive recrystallization process. Transparent colourless crystals LVP and LVN were harvested in a period of 45 days and 60 days, respectively by slow evaporation and are shown in Fig. 1(a and b).

The chemical reactions for LVP and LVN are shown in Scheme 1 and Scheme 2, respectively.

3.2 Solubility

The solubility of LVP and LVN in double distilled water was determined as a function of temperature in the temperature range 30°-50°C. A plot of concentration (g/100 ml) and temperature (°C) is shown in Fig. 2.

4 Crystal Characteristics

4.1 Single Crystal X-ray Diffraction Analysis

Single crystal X-ray diffraction analysis had been carried out to determine the lattice parameters. The X-ray diffraction data were collected at room temperature using a computer-aided single crystal X-ray Diffractometer (make: ENRAF NONIUS). The preliminary cell parameters were obtained from the

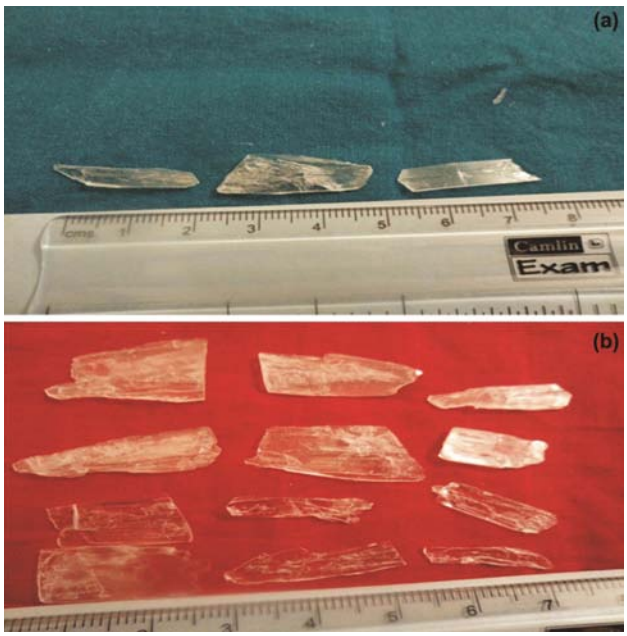
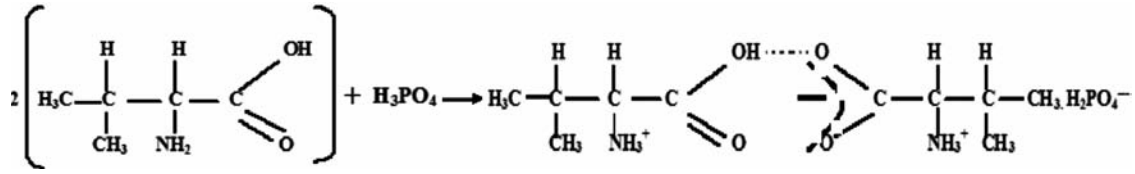
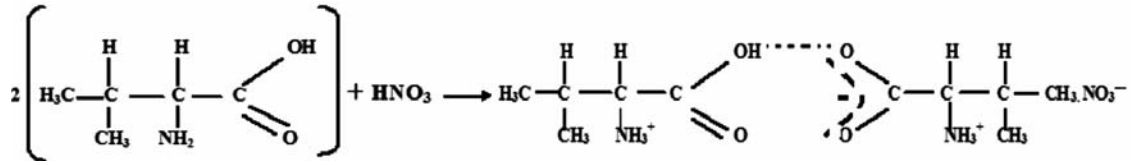


Fig. 1 — As grown single crystals of (a) LVP and (b) LVN



Scheme 1 — Reaction mechanism for LVP



Scheme 2 — Reaction mechanism for LVN

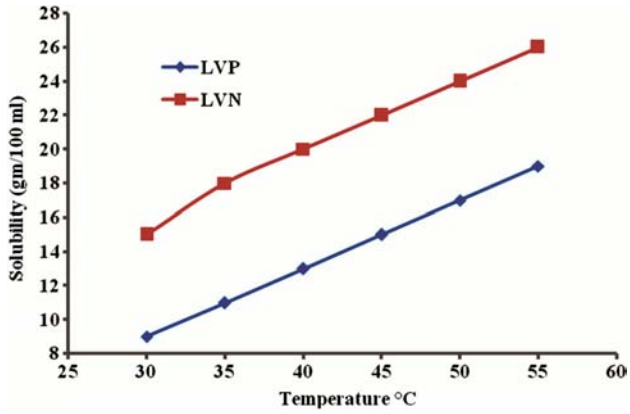


Fig. 2 — Variation of solubility with temperature for LVP and LVN crystals

Table 1 — Lattice parameter values of LVP and LVN crystals

Lattice parameters	LVP	LVN
a (A°)	9.670±0.012	5.256±0.006
b (A°)	5.249±0.006	9.75±0.02
c (A°)	12.064±0.014	11.98±0.02
α	90°	90°
β	90.81°	90°
γ	90°	90°
Volume *V* A°^{3}	612.32±0.18	613.9±0.2
Crystal system	monoclinic	orthorhombic
Space group	$P2_1$	$P2_12_12_1$

least-squares refinement of the setting angles of 36 reflections. The LVP crystallizes under monoclinic crystal system with a non-centrosymmetric space group $P2_1$ and LVN crystallizes under orthorhombic crystal system with a non-centrosymmetric space group $P2_12_12_1$. The cell parameters of L-valine l-valinium orthophosphate and L-valine l valinium nitrate are exemplified in Table 1.

4.2 FTIR Spectral Analysis

The Fourier transform infrared spectrums of LVP and LVN, as shown in Fig. 3(a and b), respectively, were recorded in the region between 400 cm^{-1} and 4000 cm^{-1} using PERKIN ELMER Fourier transform infrared spectrometer with the help of KBr pellets. The frequencies of the IR vibrations in LVP crystals were compared with the similar groups of L valine[10], L histidine diphosphate[11], L-arginine phosphate monohydrate[12] and that of LVN crystals were compared with the similar groups of L valine[13], L alanine alaninium nitrate[14] and L argininium dinitrate[15] and their tentative assignments are tabulated in Table 2. The existence of NH_3^+ and COO^- groups indicate that the grown crystals have zwitterionic nature.

4.3 DTA-TGA Analysis

Thermal analysis of materials gives useful information regarding the thermal stability of the material. Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) are of immense importance as far as the fabrication technology is concerned as they provide thermal stability for the material for fabrication where by a considerable amount of heat is generated during the cutting process. DTA and TGA analysis were carried out with the help of instrument TG/DTA 6200 thermal analyzer between 32°C to 800°C at a heating rate 20 °C/min in nitrogen atmosphere with ceramic crucible as the reference and the graph was plotted using PYRIS software. Figure 4 (a and b) show the thermograms illustrating simultaneously recorded TGA and DTA results of LVP and LVN, respectively.

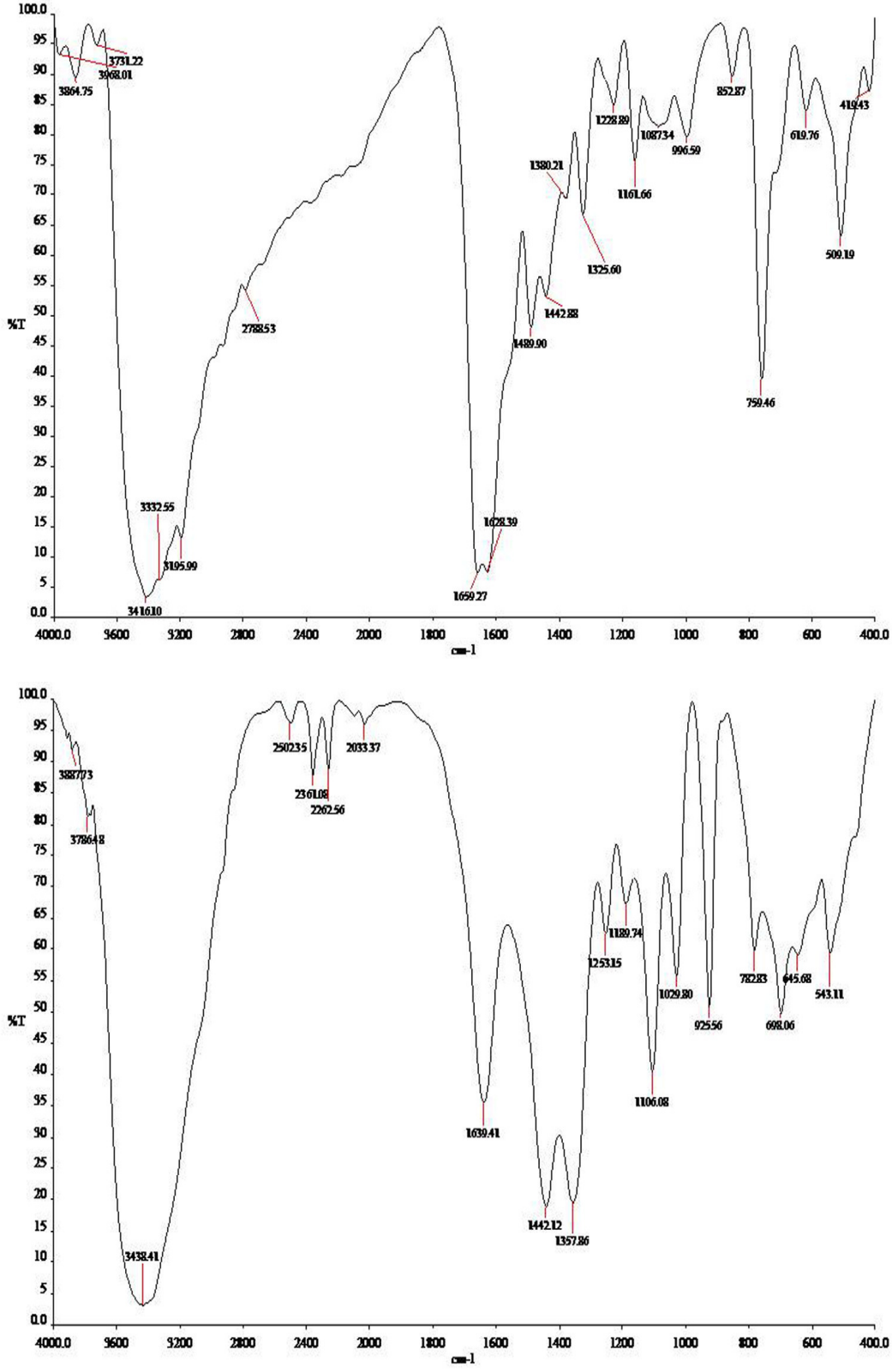


Fig. 3 — FTIR spectrum of (a) LVP and (b) LVN single crystals

Table 2 — Vibrational frequency assignments on LVP and LVN single crystals

LVP Wavenumber, cm^{-1}	Assignments	LVN Wavenumber, cm^{-1}	Assignments
537.51	$\nu_4(PO_4)$	645.68, 696.06	COO^- bending
582.25	O-H out of plane deformation	782.83	NH wagging
698.41	NH_2 wagging	925.56	NO_3^- vibration
767.52	COO-scissoring	1029.80	C-C stretching
976.07	H_2PO_4 stretching	1106.08, 1253.15	NO_3^- vibration
1024.30	P-OH deformation, C-N stretching	1189.74	NH_3^+ rocking
1106.31	$\nu_3(PO_4)$	1442.12	CH_2 bending
1269.55	P=O stretching	1639.41	NH_3^+ asymmetric bending
1402.43	COO^- symmetric stretching	2033.37	Hydrogen bonding of NH_3^+ and COOH groups
1450.09	ν_2 (H_2O)	2262.56	C-O-C stretching
1634.70	NH_3^+ degenerative deformation	2361.08	NH_3^+ symmetric stretching
2361.12	NH_3^+ symmetric stretching	3438.41	NH_2^+ symmetric stretching
3458.02	$\nu_3(H_2O)$	3786.48, 3887.73	Presence of H_2O molecule

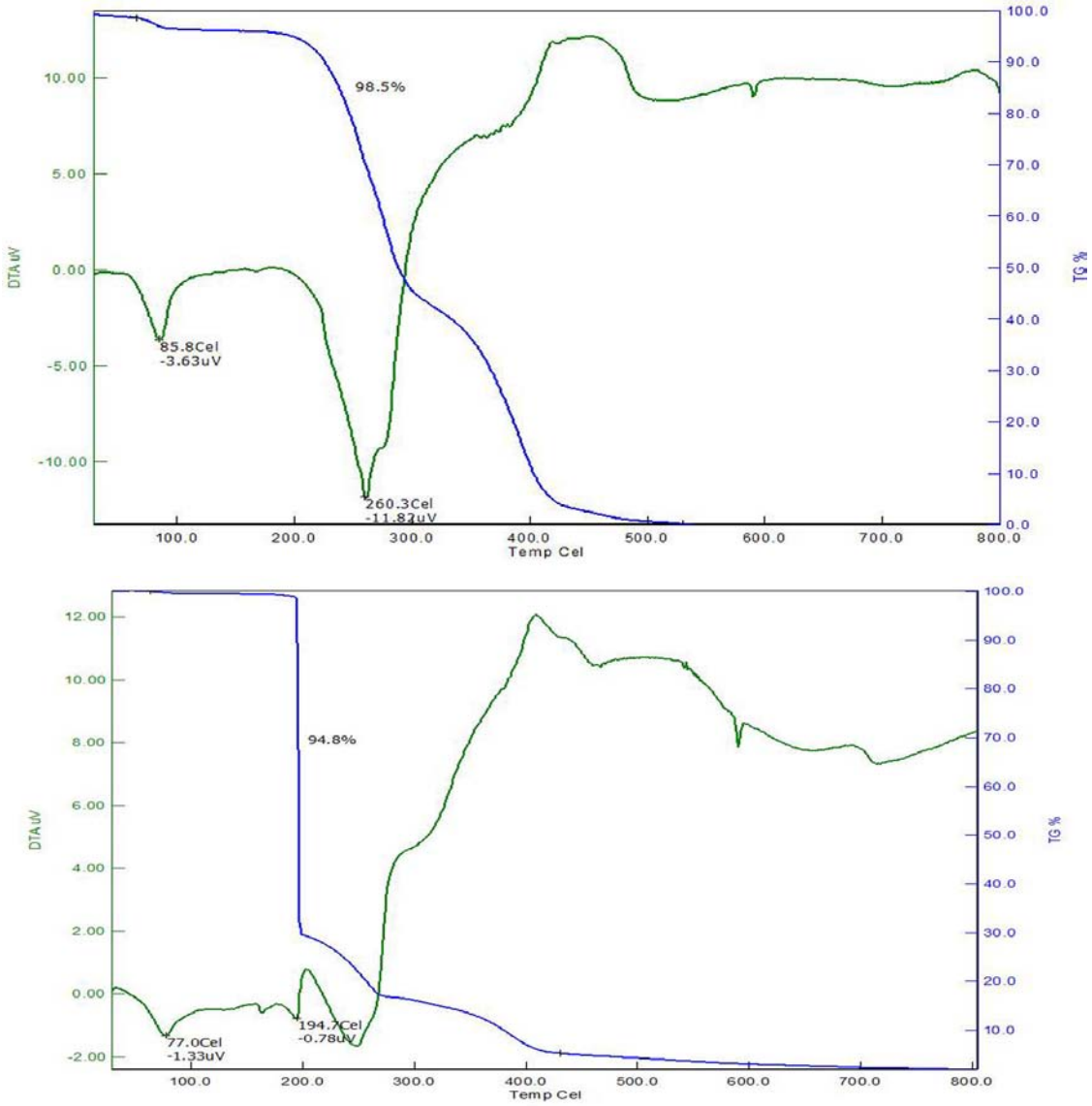


Fig. 4 — DTA-TGA thermogram of (a) LVP and (b) LVN single crystals

Table 3 — Values of different physical parameters of L-valine inorganic acids

Amino acid compounds	S.H.G w.r.t. KDP	S.H.G w.r.t. Urea	Laser damage threshold GW/cm^2	Optical transparency range nm	Cut-off wavelength nm	Forbidden energy bandgap E_g eV	Melting point °C	Mayer's index	Nature of crystal
LVP	0.602	0.596	0.85	200-1100	228	5.45	260.3	5.39	Soft
LVN	0.647	0.640	0.65	260-1100	260	4.78	194.7	6.29	soft

The DTA-TGA results of LVP and LVN show endothermic peaks around 100°C accompanied by weight loss in TG curve. These peaks correspond to the loss of water of crystallization in LVP and LVN crystals. The next endothermic peaks up to which the materials are stable correspond to the melting point of the compounds. DTA-TGA result shows that LVP and LVN decompose on melting. As a result the melt growth technique could not be used to grow bulk single crystal, so we have used a solution growth technique to grow single crystals of this material[16].

4.4 Optical Characterization

The grown crystals are characterized optically by measuring optical transparency range, damage threshold and second harmonic generation (SHG) efficiency. SHG efficiency was measured by powder method of Kurtz and Perry[17]. The second harmonic output was generated by irradiating powder samples by a pulsed laser beam. The source is Nd-YAG laser with a pulse width of 8ns and repetition rate of 10 Hz. The incident laser power was chosen as 0.68 J. The SHG was confirmed by the emission of green radiation (λ= 532 Å) which was finally detected by a photomultiplier tube (PMT) and displayed on the oscilloscope (CRO). The optical signal incident on the PMT was converted into voltage output at the CRO and its value was compared with the voltage output for a standard sample, potassium dihydrogen phosphate, KDP. Ratio between the two values gives the SHG efficiency of the experimental crystals considered here with respect to standard sample. Table 3 presents the values of SHG efficiency of LVP and LVN crystals wrt KDP and urea. The values of optical transparency range and damage threshold are also given in Table 3. The plots of optical absorbance and transmittance spectra are shown in Figs 5 and 6, respectively.

4.5 Microhardness Studies

Hardness is the resistance offered by a material to the motion of dislocation, deformation (or) damage under an applied stress[18]. During cutting and polishing

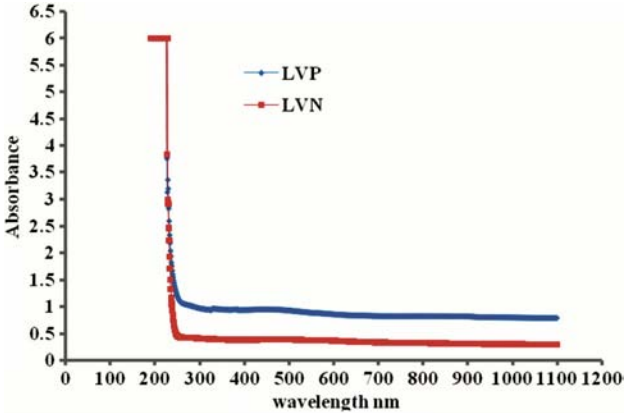


Fig. 5 — Plot of absorbance and wavelength of LVP and LVN crystals

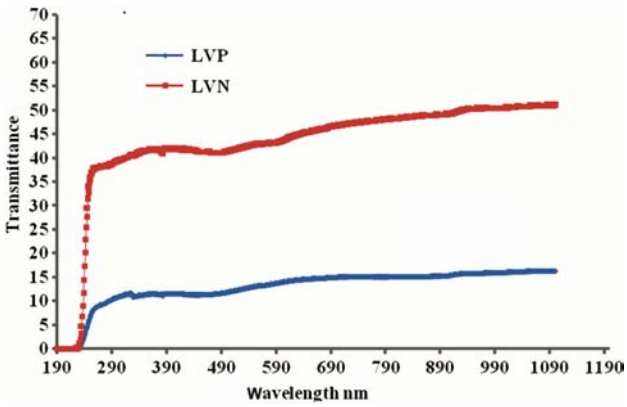


Fig. 6 — Plot of transmittance and wavelength of LVP and LVN crystals

of the crystals to make NLO devices, some mechanical stress is applied on the crystal. So it is necessary to know how much mechanical stress the crystals can withstand without any crack. The indentation hardness is measured as the ratio of the applied load to the projected area of indentation[19]. The microhardness studies were carried out on the flat surfaces of LVP and LVN crystals using SHIMADZU HMV-2T microhardness tester fitted with Vickers pyramidal indenter and attached to an optical microscope. Vickers microhardness values have been calculated using $H_v = 1.8544P/d^2$ kg/mm^2, where P is

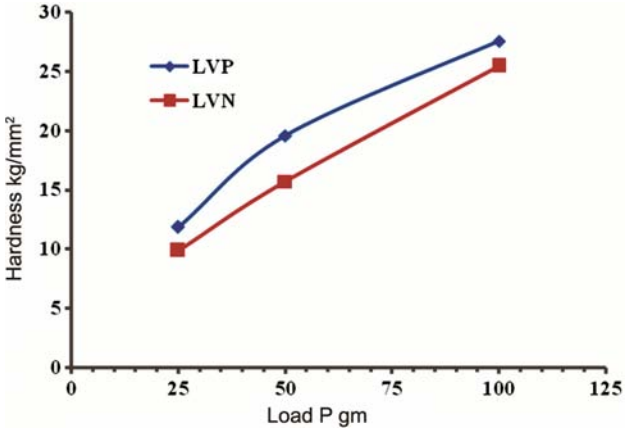


Fig. 7 — Variation of hardness and load of LVP and LVN crystals

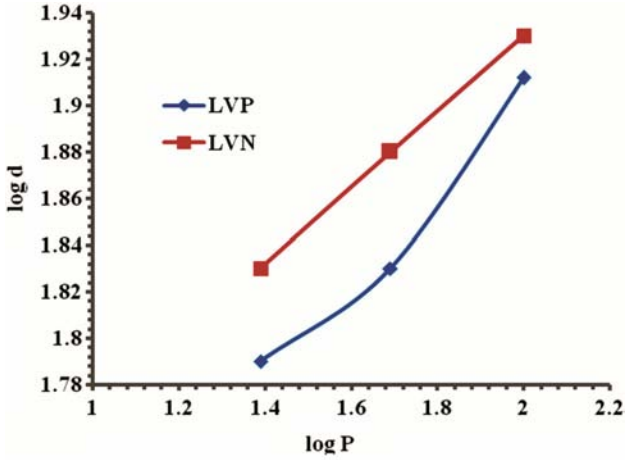


Fig. 8 — Plot of log *d* versus log *P* for LVP and LVN crystals

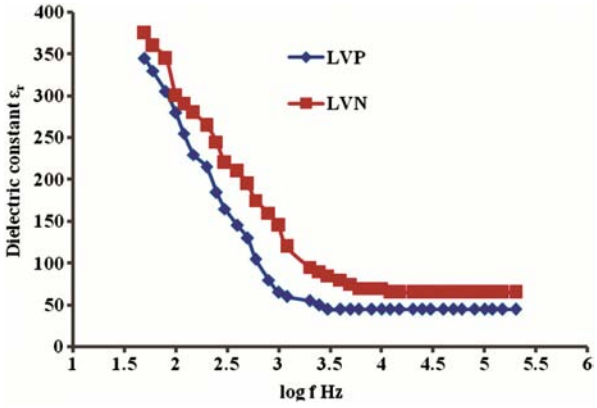


Fig. 9 — Plot of dielectric constant ε_r versus log *f* of LVP and LVN crystals

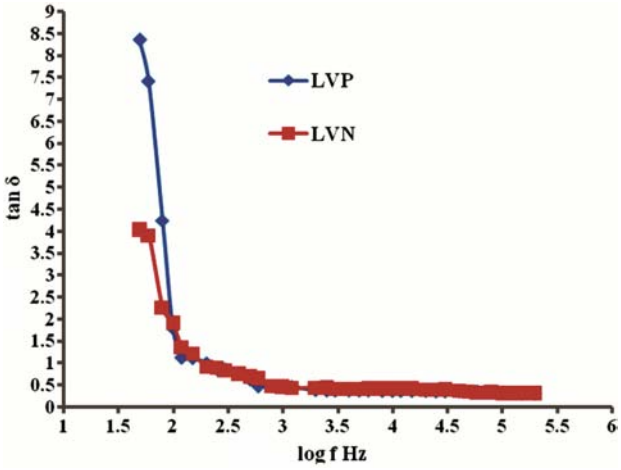


Fig. 10 — Variation of dielectric loss (tanδ) versus log *f* of LVP and LVN crystals

the applied load in kg and *d* is the mean diagonal length of the indenter impression. The hardness profile for various load are shown in Figs 7 and 8. From the hardness profile, it is observed that hardness value increases and then attains almost saturation with the increase in the applied load. At lower loads, the hardness decreases with load, which is attributed to the work hardening of the surface layers. The Mayer's index *n* has been calculated using the Mayer's law[20] $P = k_1 d^n$ (Fig. 8) and is exemplified in Table 3.

4.6 Dielectric Studies

The dielectric conductivity studies for the crystal were done with DIGITAL LCRZ METER, TH2816A in the range of frequencies 50 Hz-200 kHz. Silver paint was applied on both the faces to make a capacitor with the crystal as a dielectric material. The dielectric conductivity profiles are shown in Figs 9 and 10, both the crystals showed a normal dielectric behaviour and both dielectric constant and dielectric loss decrease with increase in frequency. The dielectric properties of the NLO materials are closely associated with the refractive index and related optical properties of the materials. The dielectric constant is calculated using the relation, $\varepsilon = cd/\varepsilon_0 A$, where *C* is the capacitance, *d* the thickness, *A* the area and ε_0 is the absolute permittivity [21]of the free space (8.854×10^{-12} F/m). The behaviour of low dielectric loss with high frequency for the samples suggest that the crystals possess enhanced optical quality with lesser defects and this parameter plays a vital role for the fabrication of non-linear optical devices[22,23].

5 Conclusions

Transparent crystals of L-valine l-valinium orthophosphate (LVP) and L-valine l-valinium nitrate (LVN) were grown using slow evaporation method

from saturated solution at room temperature. Grown crystals were characterized by X-ray diffraction and confirmed that the LVP and LVN crystals belong to monoclinic and orthorhombic system, respectively. The UV-Vis-NIR spectral studies confirm that the grown crystals have wider transparency range in the visible and UV spectral regions and the LVP and LVN crystals have lower cut-off at 228 and 260 nm, respectively. The good transparency shows that LVP and LVN crystals can be used for nonlinear optical applications. The modes of vibration of the molecules and the presence of functional groups were identified using FT-IR technique. The output SHG test proves that the LVP and LVN crystals are potential nonlinear optical materials.

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