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Growth And Characterisation Of Organic NLO Material: L-Isoleucine D-Valine Single Crystals.

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ABSTRACT

Single crystals of new organic nonlinear optical material L-Isoleucine D-Valine (LIDV) were grown by slow evaporation solution growth techniques at room temperature. Crystalline nature of the sample was confirmed by powder X-ray diffraction analysis. Functional groups present in the crystals were identified using FTIR and FTRAMAN analysis. TG-DTA studies were carried out and the thermal stability of the crystals were determined. Dielectric behavior of the system has been analyzed. Both dielectric constant and dielectric loss decreases with increasing frequency. The second harmonic generation behavior of the grown crystals was tested by Kurtz-Perry powder technique.

Keywords: LIDV, FT-IR, FT-Raman, Dielectric, UV, SHG.

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INTRODUCTION

Amino acids are the fundamental units of proteins and hence general reports on such systems, particularly in the understanding of crystal structures are available in the literature. Organic single crystals are known to exhibit comparable or even better NLO properties than known inorganic materials, especially second harmonic generation [1]. L-isoleucine D-valine is one of the organic single crystals extensively studied due to its high nonlinear and electro optic effects. Using aminoacids, difficult to grow large sized single crystals. The knowledge of intrinsic properties achievable in very pure and perfect crystals is important. Therefore we have carried out a program to grow single crystals of high purity and crystalline perfection. In order to preserve the single crystals for repeated use, the single crystals require a polymer coating for a prolonged life and protection of the surface for reproducible results [2]. Development of organic single crystals is one of the important emerging areas for optoelectronics and molecular engineering for advanced high-tech devices. The vibrational, structural and optical properties of aminoacids crystals have received much theoretical and experimental attention in the last years. There are many reasons for this, a detailed characterization of the interaction between polar and nonpolar molecules is fundamental for our understanding of biological functions. Raman polarizability tensor can give informations about the charge transfer mechanism and intermolecular interactions. Raman and infrared vibrational spectroscopies help in the understanding of the molecular conformation and the nature of hydrogen bonding in proteins as well as to provide an indirect way of estimating some thermodynamic parameters, such as enthalpy associated with the hydrogen bond in the crystals. Beyond many of those properties, Raman spectroscopy has also contributed both to characterize the vibrational modes of the aminoacids crystals [3] and to search for polymorphism. These subjects have attracted much interest in recent days due to their importance in crystal engineering and pharmacological industry. In particular, many studies focus on the understanding of the structures of aminoacids under high pressure conditions, as several works on glycine [4] L-alanine [5] L-serine [6] DL-serine and DL-valine [6,7] L-threonine [8] and taurine [9] have shown. However, the dynamic of NH_3 moiety which is related to hydrogen bonding, was investigated by Raman spectroscopy when aminoacid crystals are under high pressure only. For the past ten years aminoacids are playing a vital role in the nonlinear optical crystal growth. They individually exhibit nonlinear properties as they possess proton donor carboxyl acid (COO^-) and proton acceptor amino (NH_3^+) group also in solid state they exist as zwitterions.

In the present work L-isoleucine D-valine were grown by slow evaporation solution growth technique. The grown crystal was characterized by various characterization techniques such as XRD, FTIR, FTRaman, thermal, optical transmittance, dielectric and NLO measurements.

EXPERIMENTAL PROCEDURE

L-isoleucine D-valine single crystals were grown by slow evaporation solution growth technique at room temperature. L-isoleucine and D-valine were separately taken in equimolar ratio and thoroughly dissolved in double distilled water and stirred separately for half an hour. Then the solutions were mixed together and stirred well for about one day. The saturated solution was filtered using whatmann filter paper. The filtered solution was kept at undisturbed place for crystal growth. After one month optically good quality tiny single crystals were obtained and the photograph is shown in Fig.1

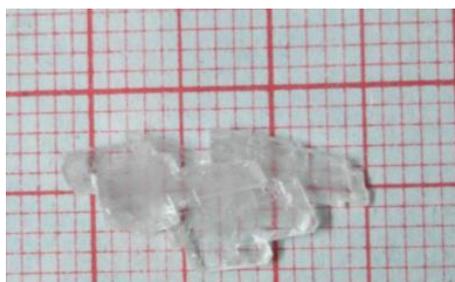
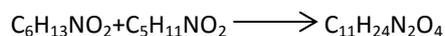


Fig.1

RESULTS AND DISCUSSION

POWDER X-RAY DIFFRACTION ANALYSIS

Finely crushed powder of L-isoleucine D-valine single crystals was subjected to powder X-ray diffraction analysis using RICH SIEFERT X-ray powder diffractometer. The sample was scanned over the range 10° to 50° at a scan rate of $2^{\circ}/\text{min}$. The recorded X-ray pattern of LIDV is shown in Fig 2. The LIDV crystal retained its monoclinic structure with lattice parameters $a= 5.2528 \text{ \AA}$, $b= 23.981 \text{ \AA}$, $c= 5.420 \text{ \AA}$, $\alpha=90$, $\beta= 110.420$, $\gamma= 90$ and space group $P2_1$ are tabulated in table.1.

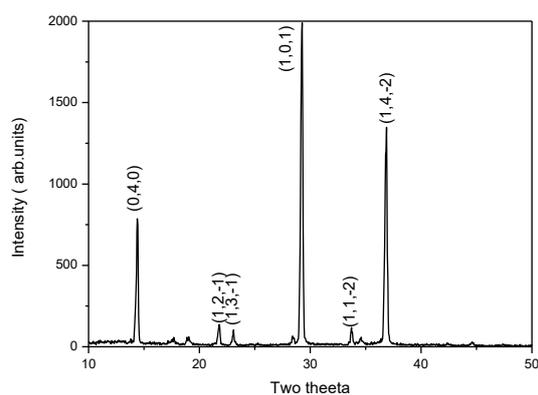


Fig.1 Powder diffraction pattern of LIDV

TABLE 1: Crystal data

Empirical formula	$C_{12}H_{20}N_2O_4$
Crystal System	Monoclinic
Space Group	$P2_1$
$a(\text{Å})$	5.2528
$b(\text{Å})$	23.981
$c(\text{Å})$	5.420
$\beta(\text{Deg})$	110.420
$V(\text{Å}^3)$	639.84

FT IR AND FT RAMAN ANALYSIS

The FT IR and FTRAMAN spectra of pure LIDV crystals were recorded on BRUKKER IFS FT-IR SPECTROMETER using KBr pellet in the range $4000-400 \text{ cm}^{-1}$ are shown in Fig.2 and 3. Among the 20 standard amino acids valine and leucine are the two most important aliphatic type amino acids molecules. Spectral assignments of FT-IR and FT RAMAN are tabulated in table.2. A broad band appears in the IR and RAMAN spectrum at 2965 cm^{-1} and 2956 cm^{-1} is due to asymmetric stretch of CH_2 group. There appears a peak at 2878 cm^{-1} in IR spectrum, at 2883 cm^{-1} in RAMAN spectrum in molecule due to asymmetric stretching of CH_2 group. In both spectrums, the band is seen at 1498 cm^{-1} and 1456 cm^{-1} respectively due to symmetry bending of CH_3 . In the IR and RAMAN spectrum of LIDV, band at 1330 cm^{-1} and 1326 cm^{-1} are assigned to C-C stretching. The correlative bands in IR spectrum are in well agreement with those in RAMAN spectrum. Similarly the bands 1265 cm^{-1} and 1261 cm^{-1} are assigned due to bending of CH vibrations. There are five bands in both spectrum of molecule at 1133 cm^{-1} , 1139 cm^{-1} , 1177 cm^{-1} , 1131 cm^{-1} , 1180 cm^{-1} are assigned. These bands are NH_3 rocking and bending of COH. Some additional IR and RAMAN peaks in molecule at 1031 cm^{-1} , 1026 cm^{-1} contributed by C-C stretching. The peaks 968 cm^{-1} , 944 cm^{-1} are contributed to C-N stretching. Bands are seen at 878 cm^{-1} , 831 cm^{-1} in IR and RAMAN spectra respectively are due to torsion of OH group. In LIDV molecule a peak appear in IR at 776 cm^{-1} and the corresponding RAMAN band is seen at 774 cm^{-1} due to C-C stretching with C-O bending. The peaks seen at 688 cm^{-1} , 685 cm^{-1} are due to bending of CO_2 . However in LIDV molecule peaks are observed at 535 cm^{-1} , 555 cm^{-1} are assigned as rocking of CO_2 . These values are agreed with reported values.

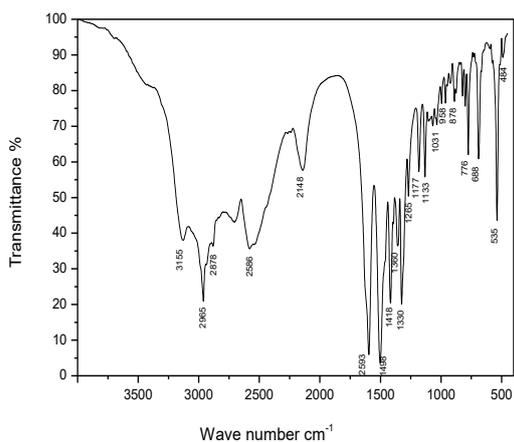


Fig.2 FT-IR spectrum of LIDV

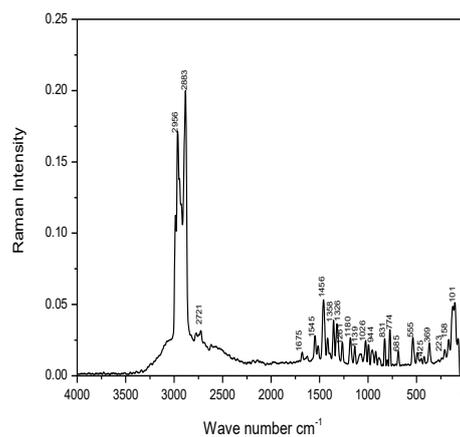


Fig.3 FT RAMAN spectrum of LIDV

TABLE 2: Spectral assignments of FT-IR and FT RAMAN studies

Wave number (cm ⁻¹)		Vibrational assignments
FT-IR	FT RAMAN	
2965	2596	N-H symmetric stretching of NH ₃ group
2878	2883	Asymmetric stretching of CH ₂ group
1586	1545	COO ⁻ asymmetric stretching
1498	1456	Symmetric bending of CH ₃
1330	1326	C-C stretching,rocking of CH,bending of CH ₃
1265	1261	Bending of C-H vibrations
1133	1139	NH ₃ rocking and bending of COH
1031	1026	C-C stretching bending vibrations of CH ₃
968	944	C-N stretching
878	831	Torsion of O-H group
776	774	C-O bending with C-C stretching
688	685	Bending of Co ₂
535	555	Rocking of Co ₂

THERMAL ANALYSIS

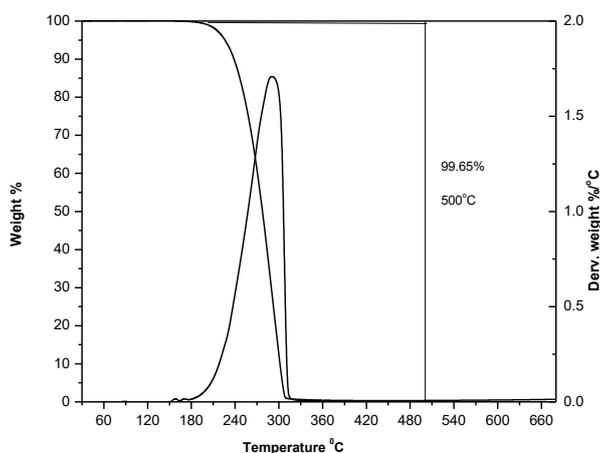


Fig.4 Thermogram of LIDV

The chemical decomposition, phase transition temperature, and the weight loss of the grown crystals were determined by thermogravimetric analysis. The Thermo Gravimetric Analysis (TGA) of LIDV was carried out by using in the Nitrogen atmosphere in the temperature range of 30°C-700°C at a heating rate of 20°C/min using TGA Q 500 instrument. The thermogram Fig.4 illustrates the absence of weight loss below 180°C, hence the crystal is completely free of any entrapped solvent in the lattice of the crystal. Hence it can be used for NLO applications upto 180°C. But from 180°C to 310°C there is a major weight loss 99.65% which may be due to decarboxylation. The DTA analysis shows a sharp endotherm at 270°C with the decomposition of LIDV.

DIELECTRIC STUDIES

The dielectric study was carried out using the instrument, HIOKI 3532-50 LCR HITESTER. Samples of known dimension were silver coated on the opposite faces and then placed between the two copper electrodes to form the parallel plate capacitor. The capacitance of the sample was noted for the applied frequency that varies from 50 Hz to 5 MHz at 40°C temperature. Fig.5(a) shows the plot of dielectric constant (ϵ_r) versus applied frequency for 40°C temperatures of LIDV. The applied frequency is represented by logarithmic values in the plot. The dielectric constant has high values in the lower frequency region and then it decreases with the applied frequency. The very high value of ϵ_r at low frequencies may be due to the presence of all four polarizations namely, space charge, orientational, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. Fig.5(b) represents the dielectric loss versus frequency of LIDV for at 40°C temperatures. The low dielectric loss at high frequency reveals the high optical quality of the crystal with lesser defects which is the desirable property for NLO applications.

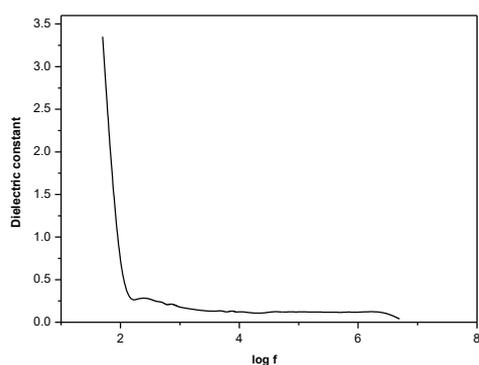


Fig.5 (a) Dielectric constant of LIDV

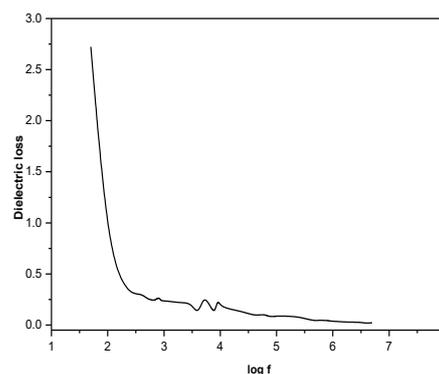


Fig. 5 (b) Dielectric loss of LIDV

NLO

The Second Harmonic Generation (SHG) test on the L-Isoleucine D-Valine crystal was performed by Kurtz powder SHG method. An Nd-YAG LASER with modulated radiation from 1064 nm was used as the optical source and pulse width of 8 ns. The powder SHG efficiency of L-Isoleucine D-Valine is found and comparable with KDP.

CONCLUSION

Single crystals of LIDV were grown by slow evaporation solution growth technique. Powder X- ray diffraction analysis revealed the crystal system and lattice parameters values. The calculated values are good in agreement with the reported values. The FTIR, FTRAMAN spectroscopic analysis confirmed the presence of various functional groups in the grown crystal. Thermal analysis carried out confirms that the crystal is thermally stable up to 180°C. Hence LIDV single crystals are suitable for frequency conversion photonic device applications. Dielectric behaviour of the system has been analysed. The powder SHG efficiency indicates that the crystal shows good efficiency.



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