

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Structural, Vibrational, Optical and Dielectric Studies on L-Isoleucine D-Norvaline.

P Geetha¹, SR Niranjana¹, S Pari², J Madhavan¹, and M Victor Antony Raj^{1*}.

¹Department of Physics, Loyola College, Chennai-34, Tamil Nadu, India.

²Department of Physics, National College, Trichy-1, Tamil Nadu, India.

ABSTRACT

Amino acids family crystals exhibit excellent nonlinear optical and electro optical properties. L-Isoleucine D-Norvaline single crystals belongs to the amino acid group and has been grown from aqueous solution by slow evaporation solution growth technique at room temperature. The crystals were obtained after a period of 45 days. The compound crystallizes in the noncentrosymmetric space group C_2 of the monoclinic system. Powder X-ray diffraction analysis revealed the crystallinity of the grown crystal. Infra-red and Raman spectroscopy techniques were used to elucidate the vibrational behaviour of chemical bond and its functional groups present in the compound. TGA was carried out to ascertain the thermal stability of the crystals. Optical absorption spectrum was recorded in the wavelength region of 200 nm to 1400 nm. The optical band gap of the grown crystal was found to be 4.78eV. The SHG efficiency of LIDNV crystals was examined by Kurtz powder method.

Keywords: LIDNV, SHG, UV-Vis and FT-IR, TGA.

**Corresponding author*

INTRODUCTION

Amino acids are the basic 'building blocks' that combine to form proteins and play an important physiological role in all life-forms. Amino acids can be used as models for the examination of the importance of intermolecular bonding in life processes. Recently, crystal structures of amino acids with strictly hydrophobic side chains, which are all divided into separate hydrophilic and hydrophobic layers. The layered build-up of the crystals is a consequence of the dual character of these molecules. The charged α -amino and α -carboxylate groups are engaged in hydrogen bonds with each other, while the side chains are distinctly hydrophobic and are involved in vanderwaals interactions only. To acquire accurate geometric information about the hydrogen-bonding network in this class of compounds and to construct a database for multivariate analysis of correlations between hydrogen bond parameters in identical hydrogen bonded frameworks [1]. Crystal growth of organic nonlinear materials has attracted much attention in recent years since they process very high nonlinear optical co-efficient compared to the more practical inorganic materials [2,3]. The preparation of more perfect single crystals of the required dimension is rather difficult in the case of organic crystals compared to the inorganic materials because the influence of organic solvents on the growth and habit of these highly polar organic materials is more significant [4]. Depending upon their chemical nature, solubility for a given material, polarity and other properties, organic solvents often yield crystals with different habits from needles to prismatic. It is known that the choice of solvent provides some control over crystal habit and this effect depends on the interaction of the surface of the crystal as it grows and the solvent molecules. Sometimes this is sufficient to result in the precipitation of a new crystalline phase [5]. The selection of potential solvents as growth mediums for the preparation of quality organic single crystals is therefore one of the essential criteria [6]. Norvaline and Norleucine have one hydrocarbon group longer and both possess the nor-prefix for historical reason, despite current conventional usage. In this paper, we report the growth and characterization studies of LIDNV single crystals. It belongs to the monoclinic crystal system with C_2 space group. The Solubility of the crystal was estimated at different temperature using deionized water as a solvent. The grown single crystals were characterized by various methods.

EXPERIMENTAL DETAILS

L-Isoleucine and D-Norvaline are taken in equimolar ratio were dissolved in double distilled water to prepare the aqueous solution of LIDNV. The reaction that takes place between L-Isoleucine and D- Norvaline is as follows.

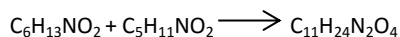


Fig.1 Photograph of grown LIDNV crystal

The growth rate of a crystal depends on its solubility and temperature. The solubility of LIDNV in the solvent of deionized water is determined using synthesized salt of LIDNV. L-Isoleucine and D-Norvaline were added in small amounts at successive stages. The addition of the salt and stirring were continued till a small amount of precipitate was formed, which confirmed the supersaturated condition. The solution is allowed to evaporate completely by warming the solution slightly above the room temperature. The spontaneous nucleation results in the formation of large number of crystals of microscopic dimension within 45 days. Good optical quality crystals, which were free from defects and inclusions, were selected for growing bulk crystals. Fig.1 shows the photograph of LIDNV single crystal grown from its aqueous solution by slow evaporation technique.

RESULTS AND DISCUSSION

X-RAY DIFFRACTION ANALYSIS

Powder X-ray diffraction pattern of the grown crystal was recorded from 10° to 60° . The resultant spectrum confirmed the crystalline nature of the sample. Fig.2 shows the powder XRD diffractogram for the grown LIDNV single crystal. The hkl planes of prominent peaks are indexed. It reveals that the structure of LIDNV belongs to monoclinic system with noncentro symmetric space group of C_2 . The lattice parameters of LIDNV is calculated from the powder XRD data and compared with reported values. The values are tabulated in table 1.

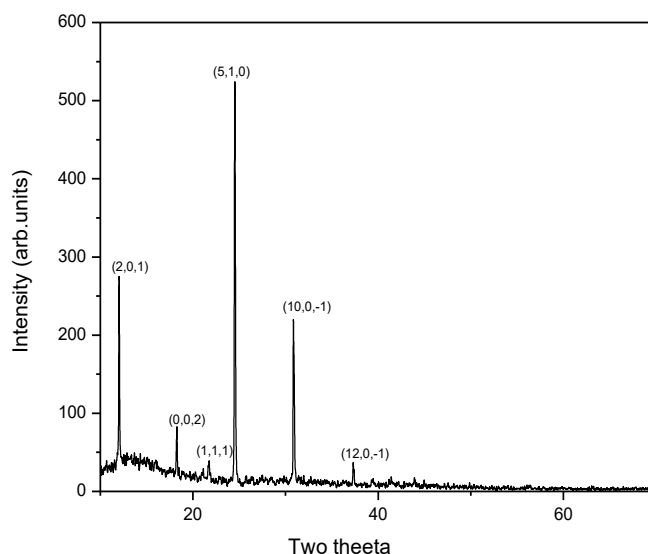


Fig.2 Powder diffraction pattern of LIDNV

TABLE 1: Crystal data

Empirical formula	$C_{11}H_{24}N_2O_4$
Crystal system	Monoclinic
Space group	C_2
a (Å)	29.0557
b (Å)	4.7551
c (Å)	9.9398
β (deg)	101.358
Volume	1346.41 \AA^3

FT-IR and RAMAN ANALYSIS

FT-IR spectroscopy is used as a tool to analyze the presence and confirmation of functional groups such as hydrogen bonds and ammonia group which play a very important role in crystallization and nonlinear optical performances. Fourier transforms infrared and FT Raman analysis of LIDNV single crystal was carried out between 4000 to 400 cm^{-1} . Fig 3. and Fig 4. Shows the resulting spectrum of that analysis in which functional groups present the molecules can be identified by stretching vibration. The presence of functional groups of the synthesized LIDNV crystal was confirmed and the assignment is identified by FT RAMAN spectrum and the assignments are tabulated in table.2. The region 3500 cm^{-1} - 2000 cm^{-1} , amino acids exhibit a great deal of hydrogen bonding as evidenced by the presence of many broad bands in their spectra, especially

in the region 3000 cm^{-1} - 2000 cm^{-1} . There is a characteristic bond at 2130 cm^{-1} which has been tentatively assigned to the N-H stretching in the group NH_3^+ . The broad and strong band 3404 cm^{-1} is assigned to NH_3^+ asymmetric stretching vibrations. The CH_3^+ asymmetric vibrations appear between 2965 cm^{-1} to 2960 cm^{-1} . The peaks at 2583 cm^{-1} and 2582 cm^{-1} due to CH symmetric stretching. The carboxylate ion group COO^- absorbs strongly at 1582 cm^{-1} . On the investigation of the absorption in medium wave number region, bonds corresponding to the C-O stretching at 1456 cm^{-1} , C-H deformation at 1344 cm^{-1} and NH_3 rocking at 1156 cm^{-1} are observed. There bands are all observed in the Raman spectrum with well agreement as expected. The vibrational band at 1037 cm^{-1} in IR spectrum and 1112 cm^{-1} in Raman spectrum are assigned to C-N symmetric stretching. Similarly the vibrational band 874 cm^{-1} in IR spectrum and 848 cm^{-1} in Raman spectrum are assigned to C-C-N symmetric stretching. The weak absorption at 554 cm^{-1} in IR and 563 cm^{-1} in RAMAN is due to the presence of COO^- wagging.

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

Wave number (cm^{-1})		Vibrational assignments
FT-IR	FT RAMAN	
3404	3395	NH_3 Stretching
2959	2965	CH_3 Asymmetric stretching
2582	2583	CH Symmetric stretching
1582	1535	COO^- Asymmetric stretching
1456	1438	C-O Stretching
1344	1302	CH Deformation
1156	1112	NH_3 Rocking
1037	1028	C-N Symmetric stretching
874	848	CCN Symmetric stretching
554	563	COO^- Wagging

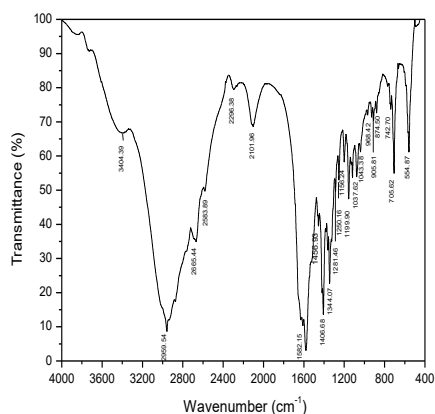


Fig.3 FT-IR Spectrum of LIDNV

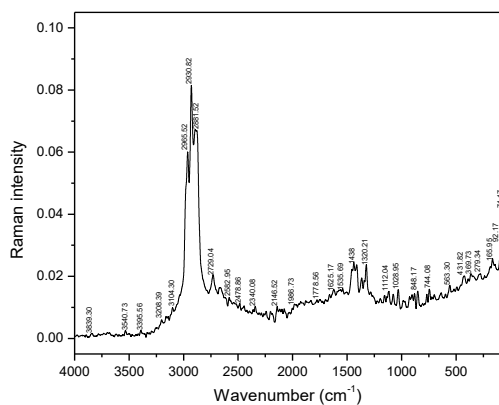


Fig.4 FT RAMAN Spectrum of LIDNV

THERMAL ANALYSIS

Thermo Gravimetric Analysis (TGA) of L-Isoleucine and D-Norvaline was carried out from room temperature to 400°C in Nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$ as shown in Fig.5. The compound begins to decompose at 175°C and complete decomposition take place at 272°C . There is only one exothermic peak at 272°C , which indicates that L-Isoleucine D-Norvaline decomposes completely at 272°C . Hence it can be used for NLO application upto 175°C . From 175°C to 285°C there is major weight loss 99.29 % which may be due to decarboxylation.

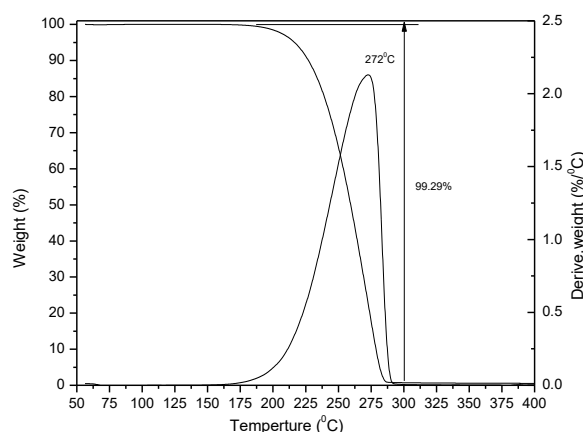


Fig.5 Thermo gram of LIDNV crystal

UV-Vis

UV-Vis spectrum gives information about the structure of the molecule because the absorption of UV and visible light involves promotion of electron in the σ and π orbital from the ground state of higher states. To determine the transmission range and hence to know the suitability of crystals for optical applications, the optical absorption spectral analysis of L-Isoleucine D-Norvaline was recorded between 200 nm and 1400 nm. The recorded absorption spectrum is shown in Fig.6. From the spectra it is evident that L-Isoleucine D-Norvaline crystal has UV cut off at 243 nm. To estimate the direct band gap value a graph has been plotted between photon energy and $(\alpha h\nu)^2$ where α is the absorption coefficient and $h\nu$ is the energy of the incident photon. From the Fig.7 the band gap energy is found to be 4.78eV. As the salt is colourless its absorption is nearly equal to zero in the entire region. This is the most desirable property of the crystals used for NLO application.

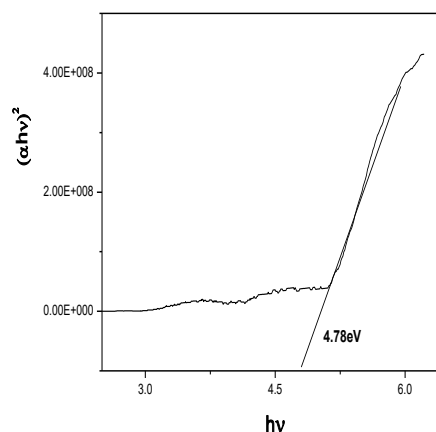
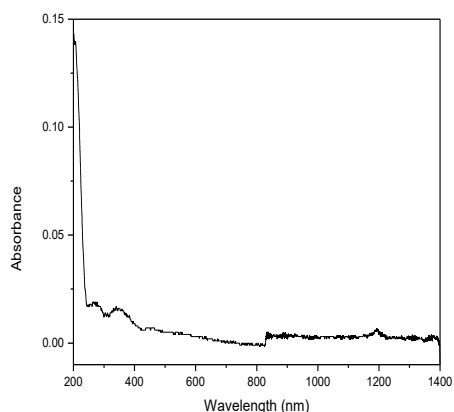


Fig.4 Optical absorption spectrum of LIDNV crystal Fig.5 Optical Band gap of LIDNV crystal

NLO

The NLO property of the crystal was confirmed by Kurtz and Perry technique to identify the materials with non-centro symmetric crystal structures. The fundamental beam of 1064 nm from Q switched Nd: YAG laser and 8ns pulse width used to test the second harmonic generation (SHG) property of the L-Isoleucine D-Norvaline crystals. A photo multiplier tube was used as detector. KDP sample was used as the reference material and the powder SHG efficiency of title single crystal was found is comparable with that of KDP.

CONCLUSION

In this paper, the synthesis and single crystal growth of LIDNV have been reported. The single crystals of LIDNV were grown by slow evaporation method. The unit cell parameters are calculated by powder XRD analysis and the result agree with reported values. XRD confirms crystalline nature. LIDNV crystal belongs to monoclinic system with the space group C_2 . FT-IR and Raman spectra are discussed to confirm the various functional groups in the grown crystal. From the thermal analysis, it is concluded that the grown crystal decomposes without melting at about 175°C. The TGA and DTA results show that the transformation is associated with the mass changes. The crystal is found to be an NLO material having a short cut-off wavelength within the UV region. The SHG of LIDNV is found to be comparable KDP, which shows that the crystal is a potential NLO material.

REFERENCES

- [1] B.Dalhus. &C.H. Gorbitz, (1996 a). Acta Cryst C52, 1761-1764.
- [2] A.F. Garito, K.D. Singer, Laser focus Fiberopt. Tech vol 18 (1982) 59
- [3] D.S. Chemla, J. Zyss (Eds), Nonlinear optical properties of organic molecules and crystals, Vol.1, Academic press, New York, 1987.
- [4] Y. Tanaka, M. Matsuoka, J. Crystal growth 99 (1990) 1130.
- [5] H.E. Buckley (Ed), Crystal growth, Wiley, New York, 1951.
- [6] J.N. Sherwood, pure Appl.opt.7(1998) 229.
- [7] U. Von Hundelshausen, Phys. Lett. A. 34, 7(1971).
- [8] C. Balarew and R.ouhlew, J. Solid state Chem.55. 1 (1984).
- [9] E.V. Kityl, B. Marciniak and A. Melfeh, J. Phys. D341 (2001).