Structural vibrational and thermal Studies on Amino acid Single Crystal: L-Isoleucine D-Alanine

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Abstract **- Single organic nonlinear optical material L-Isoleucine D-Alanine (LIDA) was successfully grown at room temperature from its aqueous solution by slow evaporation technique. Characterization of the crystals was made using powder X-ray diffraction. FT-IR and FT-RAMAN spectroscopic studies indicate the mode of vibrations of different molecular groups in crystals and confirm the protonation of the amino groups. The thermal behaviour of the grown crystal was also investigated by TGA and DTA. The dielectric constant, dielectric loss of the crystal was also studied as function of frequency and the results are discussed. The transparency of the crystal was checked by UV-study. The powder technique of Kurtz and Perry confirm the NLO property of the grown crystal.**

Keywords **- LIDA, Powder XRD, FTIR, TG-DTA.**

I. INTRODUCTION

In the modern world, the development of science in many areas has been achieved through the growth of single crystals. Crystal growth of organic materials has been recently attracting scientific attention in the search of new nonlinear optical materials. Many organic materials have been found to have greatly nonlinear or optoelectrical properties than inorganic substances [1, 2]. Nonlinear optical (NLO) materials are expected to play a major role in the technology of photonics including optical information processing [3]. Some organic compounds exhibit large NLO response, in many cases, order of magnitude larger than widely known inorganic materials. They also offer the flexibility of molecular design and the promise of virtually an unlimited number of crystalline structures. Amino acids are organic materials which can play a role in nonlinear optics as they contain proton carboxylic acid (COOH) group and the proton acceptor amino (NH_2) group. Considerable efforts have been made on the amino acid mixed complex crystals in order to make them suitable for device fabrications [4, 5]. L-Isoleucine is one of the protein genic amino acids that aids in the production of protein. It is a branched chain amino acid (BCAA) that is classified as a hydrophobic amino acid. One of its main benefits is increased strength and rapid muscle repair when combined with other amino acids. As it is an essential amino acid, it can only be obtained from dietary sources and supplements. It is also beneficial for children and teens that are in their growing years because it is vital for healthy growth. Other benefits of L-Isoleucine include normal blood sugar levels, increased production of haemoglobin, and formation of blood clots. Alanine is an efficient organic NLO compound under the amino acid category. It is the simplest amino acids with an asymmetric carbon atom. Alanine and DL-Alanine are the usually available forms of alanine. D-amino acids do not occur nature and are usually synthesized by manufacturers. The second harmonic generation (SHG) efficiency is about one-third that of potassium dihydrogen phosphate (KDP), the knowledge of studying the properties is very important since alanine can be considered as the fundamental building block of more complex amino acids.

In the present paper, we report the growth of organic materials of L-Isoleucine D-Alanine single crystals by slow evaporation method and its characterization. The tittle compound belongs to monoclinic crystal system with space group $P2_1$. The colourless grown single crystals were characterized by various methods. The NLO response and laser damage threshold were tested by using an Nd: YAG laser.

II. CRYSTAL GROWTH AND CHARACTERIZATION OF L-ISOLEUCINE D-ALANINE SYNTHESIS

L-Isoleucine D-Alanine single crystal was synthesized from L-Isoleucine and D-Alanine taken in the equimolar ratio. An adduct is formed according to the reaction

$$C_6H_{13}NO_2 + C_6H_7NO_2 \longrightarrow C_{12}H_{20}N_2O_4$$

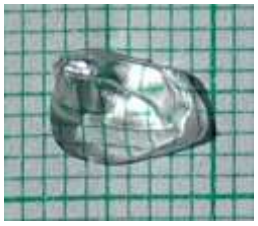

Fig.1 Photograph of the as grown single crystal of L-Isoleucine D-Alanine

The calculated amounts of the reactants were thoroughly dissolved in double distilled water and stirred well for 24 hours using a magnetic stirrer to obtain homogeneous mixture. The saturated solution was kept for a thirty days to evaporate the solvent slowly. Transparent crystals were obtained by evaporating the solvent at room temperature.

POWDER X-RAY DIFFRACTION ANALYSIS

The purified samples of the grown crystals have been crushed to a uniform fine powder and subjected to powder X-ray diffraction using a Rich Seifert powder X-ray diffractometer. The powder diffractogram of L-Isoleucine D-Alanine is shown in Fig 2. From the powder X-ray diffraction data, the lattice parameters and the volume have been calculated and are tabulated in table.1. It is confirmed that L-Isoleucine D-Alanine belongs to monoclinic crystal system with space group $P2_1$.

TABLE 1: Crystal data

Emprical formula	$C_{12}H_{20}N_2O_4$
Crystal Ssystem	Monoclinic
Space Group	$P2_1$
a(A°)	9.8944
b(A°)	4.7425
c(A°)	12.9045
β(Deg)	93.374
V(A°)	604.48

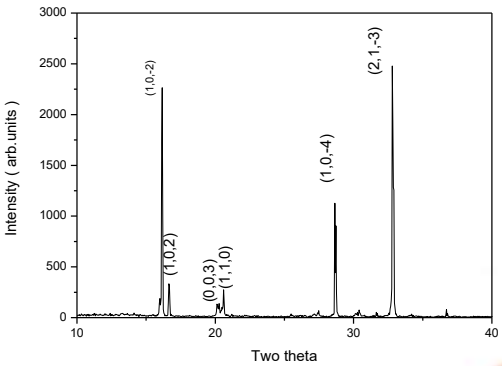

Fig: 2 Powder diffractogram of LIDA

FT-IR AND FT-RAMAN ANALYSIS

The spectrum was recorded using Perkin-Elmer 783 spectrophotometer between 4000 cm^{-1}- 400 cm^{-1} as shown in Fig.3 and Fig.4. The high wave number region consists of bands due to NH_3^+ and CH_2 stretching vibrations. The lower wave number region contains bands due to deformation vibrations of various groups. In the compound under study each of the N-H bonds of the NH_3^+ group is hydrogen bonded with the oxygen atoms of the nitrate ion and with the oxygen atom of the carboxylic group. The wave number of the CH_2 vibrational mode depends on its immediate environment. The stretching modes of the CH_2 group usually occur in the region 3100-2800 cm^{-1}. The peak appears at 3088 cm^{-1}, 2997 cm^{-1} for assigned in IR and RAMAN spectrum respectively due to NH stretching. The very strong band in the Raman spectrum at 2965 cm^{-1} is due to the symmetric stretching vibrations of the CH_2 group. In the present crystal, the strong absorption band at 2721 cm^{-1}, 2737 cm^{-1} in both spectrum are assigned to the symmetric stretching mode of COO^-. In amino acids containing the NH_3^+ group, the bending vibrational wave numbers are expected in the regions 1660 cm^{-1}-1610 cm^{-1} and 1550 cm^{-1}-1480 cm^{-1} [6]. In the crystal, the peak at 1620 in IR spectrum and 1602 cm^{-1} in RAMAN spectrum are assigned due to NH bending. The IR band at 1518 cm^{-1} and the band at 1504 cm^{-1} in the Raman spectrum is assigned to the CN asymmetric stretching mode of this group. The absorption bands arising from C-N stretching vibrations are observed in the wave number region 850-1150 cm^{-1} [7]. In the present crystal, C-N stretching vibrations are observed 1115 cm^{-1} in IR and RAMAN spectrum. The Aliphatic C-N vibrational bands have been identified at the peaks 1461 cm^{-1}, 1472 cm^{-1}. The IR and Raman bands at 920 cm^{-1} are assigned to C-C stretching vibrations. So these studies confirm that the crystals are non-Centro symmetry. The strong IR band at 849 cm^{-1} and strong band at 847cm^{-1} in Raman spectrum are due to CN stretching of NO_2 group. IR band at 763 cm^{-1} and Raman band at 766 cm^{-1} are assigned due to deformation mode of C-C-O group. In the L-Isoleucine D-Alanine crystal, CO_2 bendings are seen at 641 cm^{-1} and 653 cm^{-1} in IR and Raman respectively and the corresponding bands appear at 539 cm^{-1}, 531 cm^{-1} in IR and Raman spectrum are assigned to weak COO^- wagging.

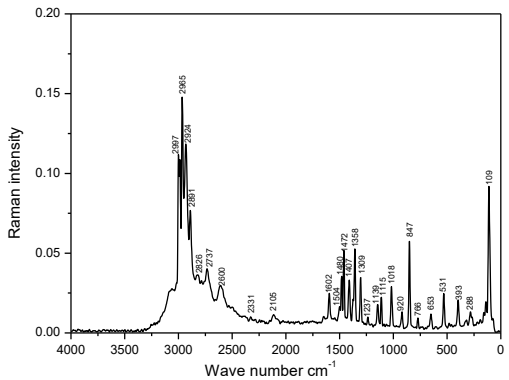

Fig. 3 FT-IR spectrum of LIDA

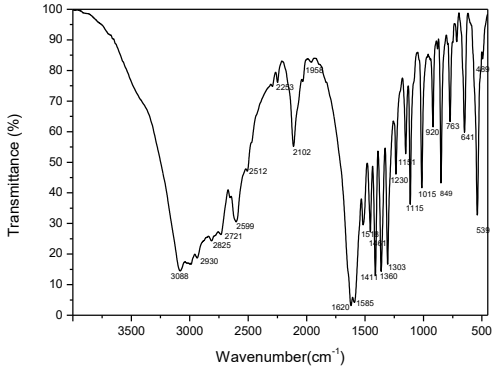

Fig.4 FT-RAMAN spectrum of LIDA

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

Wave number (cm^{-1})		Vibrational assignments
FT-IR	**FT-RAMAN**	
3088	2992	NH stretching in NH_3 group
1620	1602	NH bending
1518	1504	CN asymmetric stretching
1461	1472	Aliphatic CN vibration
1411	1407	COO^- symmetry stretching
1303	1309	CH_2 wagging
1151	1139	NH_3 rocking
1115	1115	C-N stretching
920	920	C-C stretching
763	766	C-C-O deformation

THERMAL STUDIES

Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) curves for L-Isoleucine D-Alanine were carried out in the temperature 30^0C - 680^0C at a heating rate of 200C/min using TGA Q500 instrument. The thermo gram Fig.4 illustrates the absence of weight loss below 180ºC, shows the crystal is completely free of any entrapped solvent in the lattice of the crystal. Hence it can be used for NLO applications up to 180ºC. From 180ºC to 270ºC, there is weight loss 27.8%. Two more stages were observed, the first one between 270°C to 285°C (8.26%) and the second one between 285°C to 650°C (54.61%). The DTA analysis show three sharp peaks matching with the TGA trace.

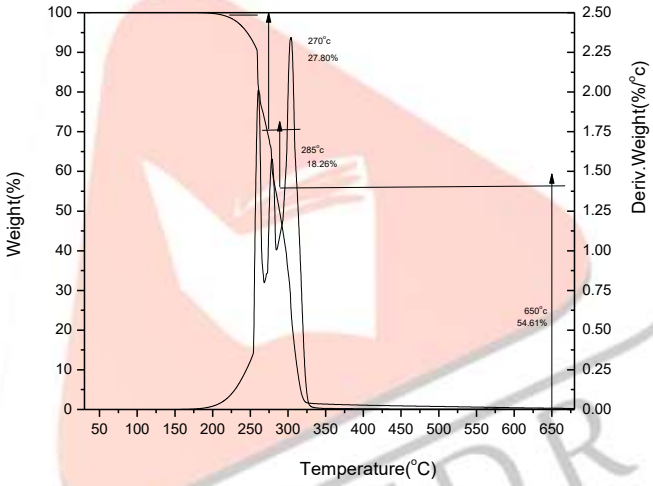

Fig.4 TGA-DTA curve of LIDA

DIELECTRIC STUDIES

The dielectric constant and dielectric loss of L-Isoleucine D-Alanine sample were measured using HIOKI 3532-50 LCR HITESTER in the frequency region 50 Hz to 5 MHz Fig.5 and Fig.6 shows the variations of dielectric constant and dielectric loss with log frequency at 40^0C. It is observed from the plots, that both the dielectric constant (ε^1) and the dielectric loss (D) are decreasing rapidly and get saturated at high frequencies. The low values of dielectric loss at high frequencies suggest that the crystal possess enhanced optical quality with low density of defect [8].

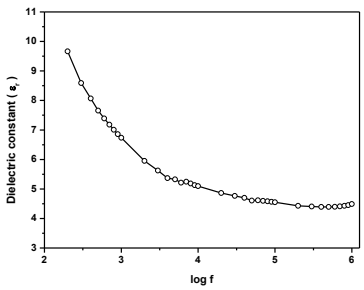

Fig.5. Dielectric constant of LIDA

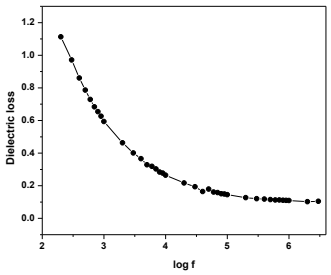

Fig.6. Dielectric loss of LIDA

UV-Vis

The UV- Vis spectral analysis was carried out between 400 nm and 1400 nm. The spectrum is shown in Fig .7 and Fig.8. As the powder is colourless, the analysis was carried in the near UV region. The absorbance is minimum in the visible region it is as an important requirement for NLO materials having non-linear optical applications [9]. From the absorpance spectrum, it was observed that LIDA crystal possess nearly zero, which is essential quality for Non-linear optical crystals. The optical cut off

wavelength was found to be 423 nm. In Fig.8 shows that band energy gap spectrum, plots between photon energy and $(\alpha h\nu)^2$. The band gap energy of LIDA was found to be 5.08 eV.

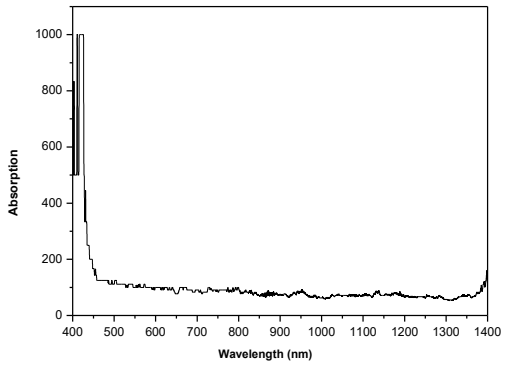

Fig.7 Optical absorbance of LIDA

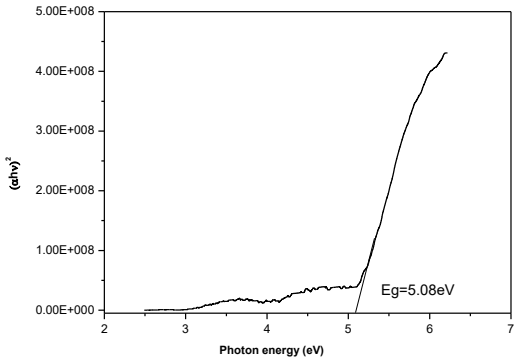

Fig.8 Energy band gap of LIDA

NLO

A Q-switched Nd: YAG laser (1064 nm) was used and the powder SHG studies of L-Isoleucine D-Alanine crystal were carried out by Kurtz powder technique. Intense green light has been observed. KDP sample was used as the reference material and the output power intensity of L-Isoleucine D-Alanine was comparable with the output power of KDP.

III. CONCLUSION

Single crystals of L-Isoleucine D-Alanine of appreciable size were grown by the slow evaporation method. The grown crystals were characterized by powder XRD. The FT-IR spectroscopic analysis confirms the molecular structure of the compound. From the TG-DTA studies establish that the compound undergoes no phase transition and is stable up to its melting point 180^0C. The dielectric studies prove that the sample has low dielectric constant and dielectric loss values at high frequency. The minimum absorption in the visible region is observed from the UV-Vis measurement. It is an important requirement for the materials having NLO properties. The laser damage threshold was measured and compared with that of standard KDP and other known organic single crystals. The SHG behaviour was tested by a Q switched Nd: YAG laser.

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