Synthesis, Structure, Crystal Growth and Characterization of an Organic Nonlinear Optical Single Crystal: L - Alanine L - Mandelic Acid

V. Sudarvizhi[1], A. Krishnaveni[2], T. Balakrishnan[1*]

[1]Crystal Growth Laboratory, PG & Research Department of Physics, Periyar E.V.R. College (Autonomous), Thiruchirapalli - 620 023, Tamil Nadu, India

[2]PG & Research Department of Zoology, National College, Thiruchirapalli – 620 001,Tamil Nadu, India

*Corresponding author's email: balacrystalgrowth@gmail.com

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ABSTRACT

L - alanine L - Mandelic acid [LALMA] single crystal was grown by slow evaporation technique at room temperature. The lattice parameters were assessed from single crystal X - ray diffraction analysis. The single crystal X - ray diffraction study proclaimed that the LALMA crystal crystallizes in monoclinic system and powder XRD analysis confirms the crystalline nature. FT - IR and FT - Raman spectral studies were carried out to confirm functional groups present in the crystal. Optical properties were analyzed using UV - Vis - NIR spectrum. Its lower cut off wavelength is 265 nm. The optical band gap of the crystal was calculated as 3.5eV. The photoluminescence spectrum exhibited two peaks (572 nm and 582 nm) due to the donation of protons from carboxylic acid to amino group.

Keywords: X-ray Diffraction; Spectral studies; Optical studies; Photoluminescence.

1 Introduction

Amino acid based organic crystals are fascinating for non linear optical application as they contain proton donor carboxyl acid (COO^-) group and the proton acceptor amino (NH_2) group [1]. L - alanine is one of the smallest chital naturally occurring amino acid its single crystal structure was reported by bernal [2]. L - alanine is forms number of complexes on reaction with mandelic acid. Diastereomer of alanine mandelic acid crystal were reported [3-5].Mandelic acid is an aromatic alpha hydroxyl acid with the molecular formula C_6H_5CH (OH) CO_2H. It has a long history of use in medicine as an antibacterial, particularly in the treatment of urinary tract infections. Recently single crystal structure, evaluation of charge assisted hydrogen bonds in L - (S) - Lysinium L - (S) - Mandelate dihydrate and L - (S) - alanine L - (S) - Mandelic acid complexes: Inputs from Hirshfeld surface, PIXEL energy and QTAIM analysis were reported by us [6]. In the present investigation we report the single crystal growth of L - alanine L - mandelic acid (LALMA), and detailed analysis of structural, spectral, optical.

2 Experimental Detail

2.1 Synthesis

Analytical grade starting materials L – alanine ($C_3H_7NO_2$) and L – mandelic acid (C_8 H_8O_3) were taken in 1:1 equimolar ratio. Calculated amount of salts were dissolved in double distilled water at room temperature. The prepared solution was left for evaporation to dryness at room temperature. The reaction mechanism of the synthesis is shown in scheme 1.

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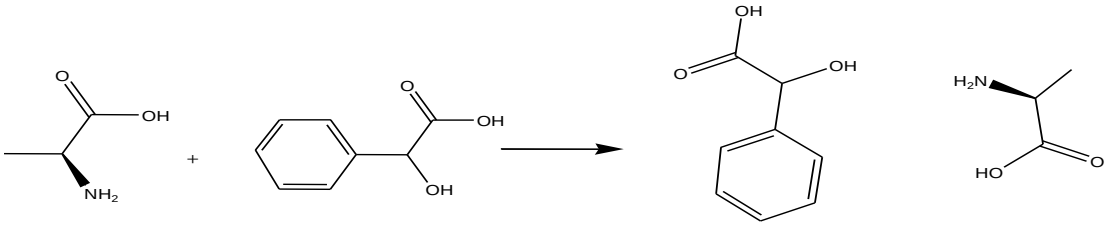

L - alanine L - mandelic acid L- alanine L- mandelic acid

Scheme1. The reaction mechanism involved in the synthesis of LALMA

2.2 Crystal growth

Saturated solution of about 25mL was prepared using the synthesized salt at room temperature. The solution was filtered with a Whatmann filter paper and optimally closed with perforated polythene sheet for controlled evaporation and kept in a vibration free area. Grown L - alanine L - Mandelic acid crystals of size 16 x 4 x 3 mm^3 are shown in Fig. 1

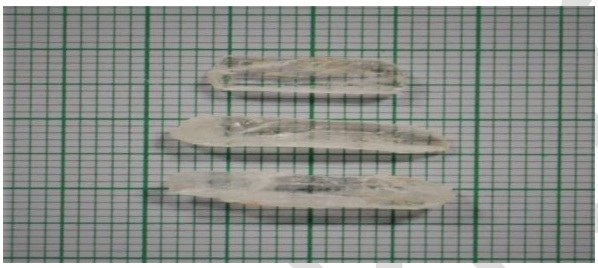

Fig 1: As grown crystals of LALMA

3 Result and Discussion

3.1 Single crystal X-ray diffraction

Single crystal X-ray diffraction analysis was carried out using Enraf Nonius-CAD4 diffractometer. A good transparent LALMA single crystal was subjected to single crystal XRD analysis to confirm the non - centro symmetric crystal structure and unit cell parameters. The grown LALMA crystal belongs to monoclinic crystal system with space group C_2. Lattice parameters values are compared with the reported values [4 - 6] and are presented in Table 1.

Table 1:Unit cell parameters of LALMA.

Cell parameters	**Reported work**		**Present work**
	S-S [4]	**D-DL [5]**	**L-L [6]**
Space group	**C_2**	**C_2**	**C_2**
a (A°)	17.795(4)	18.35	17.8364(13)A°
b (A°)	5.394(2)	5.53	5.4032(9)
c (A°)	12.431(2)	12.78	12.4447(11)

α (◦)	90°	90°	90°
β (◦)	100.659(10)	100	100.64
ν (◦)	90°	90°	90°
Volume (A°)^3	1172.7(5)	1276	1178.70(16)
Crystal system	Monoclinic	Monoclinic	Monoclinic

3.2 Powder X-ray diffraction analysis

The Freshly Crushed Powder of Lalma Have Been Characterized by Powder X-Ray Diffraction Analysis Using Bruker X-Ray Diffractometer with Cukα Radiation Of Λ = 1.5406 A° Was Scanned Over the Range 10 ° - 80 ° At the Scan Rate Of 1 ° Per Min. The Well-Defined Peaks at Specific 2θ Values Show High Crystalline Nature of The Grown Crystals. The Observed Xrd Pattern Were Indexed Using the Autox 93 Software Package Is Shown in Fig. 2.

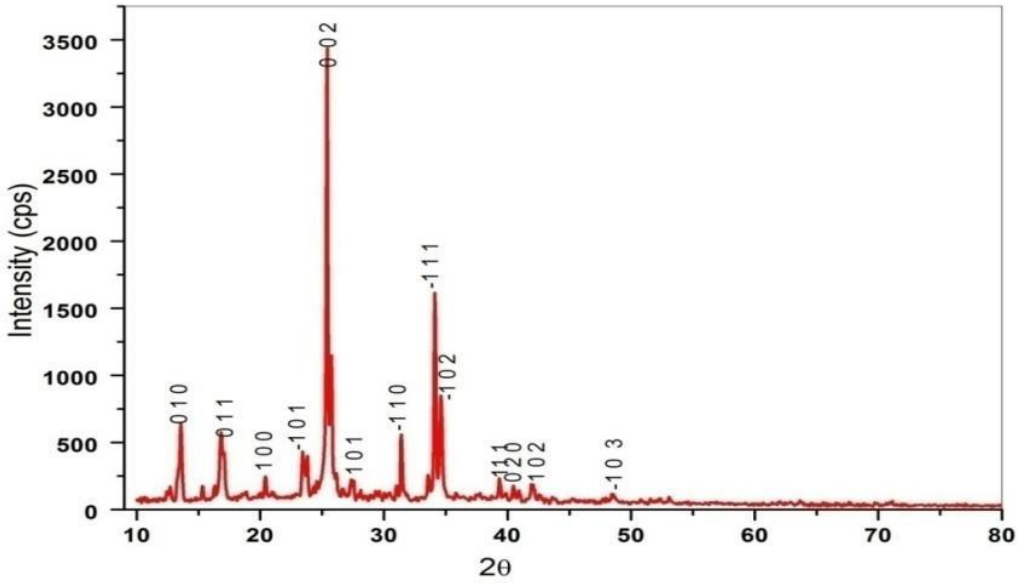

Fig 2: Powder X-ray diffraction pattern of LALMA.

3.3 FTIR and FT-Raman studies

Vibration spectral analysis gives some essential information about molecular structure, inter and intra molecular forces, crystalline environments, vibration interactions, distortion of molecules, hydrogen bonding isomerism, molecular rotations, etc [7]. FT - IR and FT - Raman spectrum was recorded by Perkin Elmer FT - IR spectrometer using KBr pellet technique in the range 400 - 4000 cm^{-1} and BRUKER KFS 27 FT - Raman spectrometer respectively in the wavelength range 50 - 4000 cm^{-1}. The recorded FTIR and FT-Raman spectrum LALMA is shown in Fig. 3 and Fig. 4 respectively.

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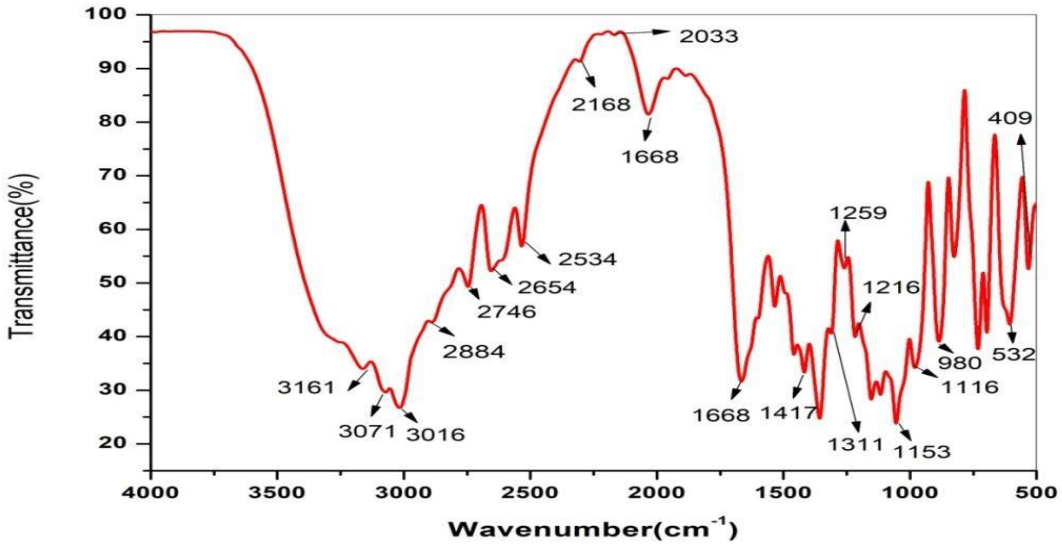

Fig 3: FT - IR spectra of LALMA crystal.

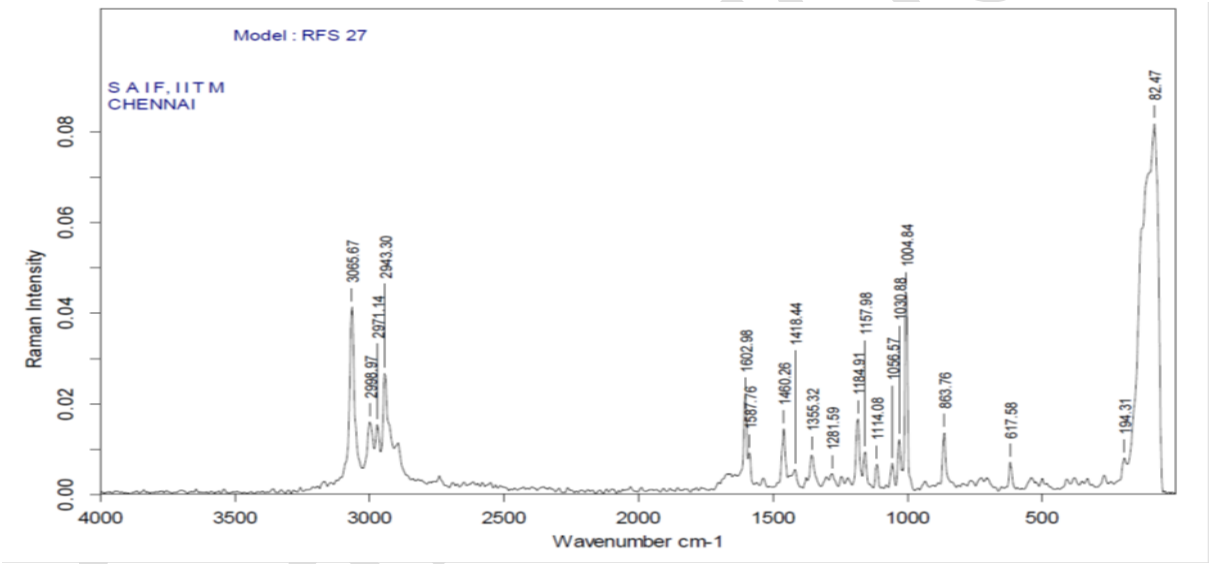

Fig 4: FT - Raman spectrum of LALMA.

Table 2: FT - IR and FT - Raman vibrational assignments of LALMA single crystal.

Wave number(cm^{-1})		**Band Assignments**
FTIR	FT-Raman	
3161	-	(NH_3^+) Symmetric stretching vibration
3071	3065	(NH_3^+) asymmetric stretching vibration
3016	-	(NH_3^+) Symmetric stretching
-	2998, 2971	CH_2 stretching
-	2943	C-H stretching
2889	-	C-H stretching
2746	-	Asymmetric NH_3^+ bending
2654	-	O-H stretching

2534	-	symmetric NH_3^+ bending
2168	-	Over tone combination
2033	-	Over tone and combination
1665	-	NH_3^+ deformation
-	1602	NH_3^+ asymmetric stretching
-	1587	NH_3^+ bending
1534	-	N-H in plane pending
1458	1460	C-NH stretching
1417	1418	COO^- symmetric stretching
1356	1355	O-H deformation
-	1281	NH_3^+ rocking
1259	-	C-O asymmetric stretching
1216	-	NH_3^+ rocking
-	1184	COO^- asymmetric stretching
1153	1157	COO^- asymmetric stretching
1116	1114	COO^- symmetric stretching
1054	1056	C-N asymmetric stretching
-	1030	$C-NH_2$ stretching
-	1004	$C-NH_2$ stretching
980	-	Torsional oscillation of NH_3^+
885	863	C-C-N asymmetric stretching
824	-	C-C-N symmetric stretching
731	-	COO^- deformation
696	-	COO^- scissoring
606	617	C-C-C out of plane bending
582	-	C-C-N deformation

The peak observed at 3071 cm^{-1} in infrared and 3065 cm^{-1} in Raman spectra are attributed to the NH_3^+ asymmetric stretching vibration of L - alanine ion. The IR band found at 1458 cm^{-1} and the corresponding Raman band at 1460 cm^{-1} is assigned to C-N-H stretching [2]. The symmetric stretching vibration of COO^- group is located at 1417 cm^{-1} in Infra-red spectrum and at 1418 cm^{-1} in Raman spectrum [2]. The peak observed at 1356 cm^{-1} in IR and 1355 cm^{-1} in Raman counterpart are attributed to O-H deformation vibration. The asymmetric mode of COO^- group is assigned to the wave numbers 1153 cm^{-1}, 1116 cm^{-1} in infrared spectrum and in Raman counterpart located at 1157, 1114 cm^{-1}respectively. The C - N asymmetric stretching vibration is due to bands positioned at 1054 cm^{-1} in IR and at 1056 cm^{-1} in Raman spectrum. The presence of symmetric stretching mode of C-C-N vibration appears at wave number 885 cm^{-1} in Infrared and at 863 cm^{-1} in Raman counterpart. The vibrational frequencies of LALMA with assignment are presented in Table.2

3.4 Optical transmission studies

The UV - Vis - NIR transmission spectrum (Fig.5) of the grown LALMA crystal was recorded on a Varian (model Carry 5000) UV - Vis - NIR spectrometer. The optical parameters such as the transmission, absorption band, cut off wavelength, band gap of the single crystal are determined to know the suitability of single crystals for NLO application LALMA crystal of thickness 2 mm was used to measure the transmittance and absorbance in the wavelength range (200 - 1000). The lower cut of wavelength of the crystal occurs at 247 nm. The transmittance percentage gradually increases from 300 nm and reaches 47%

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at 850 nm. The maximum percentage of transmission is observed between the wavelength region 850 nm and 1150 nm.

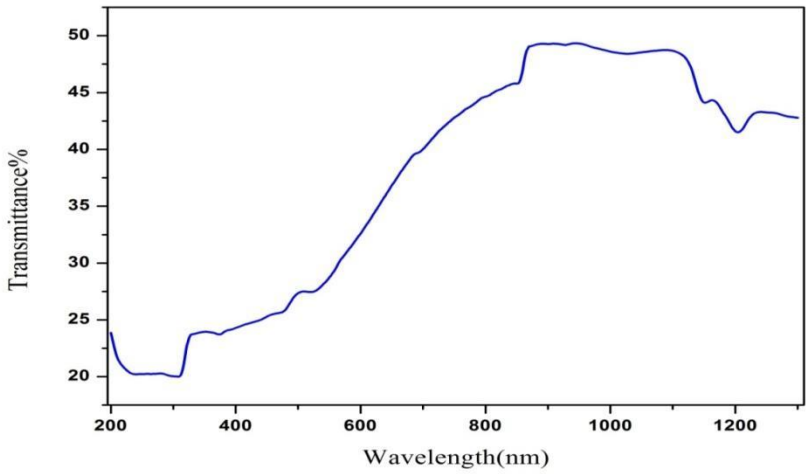

Fig 5: Transmittance spectrum of LALMA single crystal

UV - visible spectrum gives information about electronic transitions of the compound [8]. The optical electronic band gap (Eg) of the material is very closely related to the atomic and electronic band structures [9]. The optical absorption co-efficient (α) was calculated by using the equation,

$$\alpha = \frac{1}{t} log\ log\ (\frac{1}{T}) \quad \text{---------- (1)}$$

where, T is the transmittance t is the thickness of the crystal. The relation between the photon, energy and the optical absorption coefficient is $\alpha h\nu = B\ (\alpha h\nu - E_g)^{1/2}$,where E_g is energy gap. The band gap energy was estimated from plot (Fig.6) of the variation of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of L - alanine L - mandelic acid. The optical band gap of the LALMA crystal was calculated by extrapolating the linear part of the graph with the energy axis gives the value of E_g (3.5 eV).

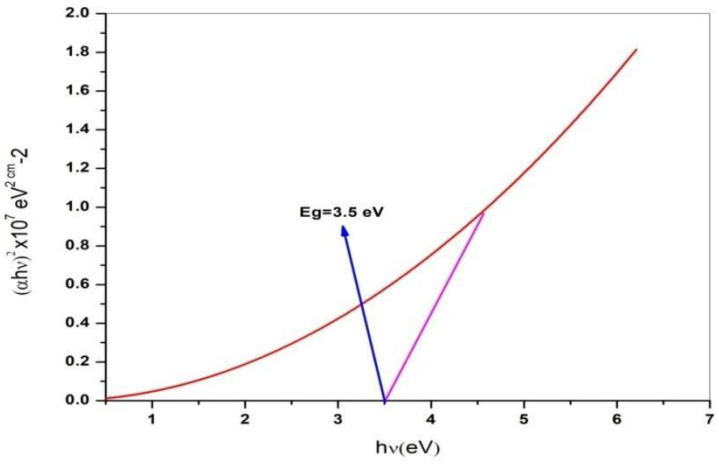

Fig 6: Plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for LALMA single crystal.

3.5 Photoluminescence study

Photoluminescence (PL) spectroscopy is the non-destructive test to characterize the defects, vacancies and other imperfections present in the grown crystal [10]. The photoluminescence spectrum of LALMA crystal was recorded using cary Eclipse fluorescence spectrometer fitted with 450 W high pressures Xenon Lamp as excitation source. The sample was excited at 265 nm and the recorded emission spectrum is shown in Figure.7.

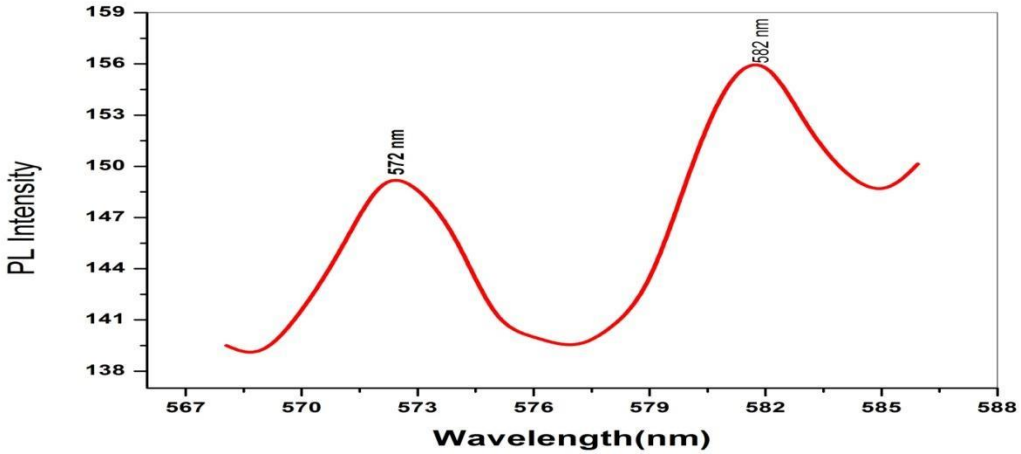

Fig 7: PL emission spectrum of LALMA single crystal.

Two sharp photoluminescence two emission peak is observed at 572 nm and 582 nm. The PL emission spectrum revealed that the LALMA crystal exhibits two fluorescence peaks at about 2.16 eV (572nm) and 2.13 eV (582 nm). It also revealed that LALMA crystals exhibit two emission peaks in the green region. The intensity is slowly reduced in the higher wavelength due to the presence of electrons donating protons from carboxylic acid to amino group in grown LALMA crystal. The strong broad Photoluminescence emission in the green region confirms the suitability of LALMA crystal for opto electronics and luminescence device.

4 Conclusion

LALMA single crystal of size 16 x 4 x 3 mm^3 was grown from double dissolved water by slow evaporation technique. The single crystal X-ray diffraction study confirmed that the LALMA grown crystal belongs to the monoclinic system with non - centrosymmetric space group C_2. The crystalline phase was confirmed by power XRD analysis. The UV lower cut off wavelength is found to be at 265 nm. The optical band gap determined as 3.5eV. FTIR and FT-Raman spectra revealed the presence of various functional groups. The photoluminescence study reveals two green emissions peaks at 572 nm and 582 nm.

5 Declarations

5.1 Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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