INVESTIGATION ON SYNTHESIS, GROWTH AND MULTI CHARACTER STUDIES OF LTMA SINGLE CRYSTAL

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Abstract. *The Novel L-Threonine Manganese Acetate (LTMA) single crystal was successfully grown by slow evaporation method at Room Temperature. LTMA crystal was characterized with single crystal XRD and powder XRD, EDAX, FTIR, UV-Vis-NIR, and MHD test. Single crystal XRD study was carried out to examine the crystal system and unit cell parameters. Powder XRD pattern confirm that there is change in the basic structure of material. The presence of Chemical composition used in the crystal was qualitatively confirmed by EDAX analysis. The functional groups in the crystal lattice, was qualitatively analyzed by FTIR spectrum. Optical property of the crystal was studied by UV-Vis-NIR, shows that LTMA crystal was well transparent in the range of 267-1100 nm and the energy band gap as 4.3eV. The Hardness of the LTMA crystal was studied by Vicker's Micro hardness analysis.*

Keywords: *Single crystal XRD study, Powder XRD study, Optical property, EDAX analysis, Mechanical property*

1. INTRODUCTION

In recent times, organic and inorganic materials are emerging out with desired properties for second harmonic generation as Non-linear optical materials. These materials have lot of uses in the field of photonics such as optical computing, optical communications, optical disk data storage, optical logic circuits, optical information processing, optical information processing, high - speed information processing, telecommunication, laser sensing and colour displays like LCD monitors. Like the semi organic crystals, amino acid based semi organic good optical and non-linear optical applications crystals were grown **[1-5]**. These single crystals can also be grown from aqueous solution for the enhanced hardness and the thermal stability. Later, L-Alanine, L-Proline, L-Valine, α-Histidine based semi organic crystals were invented **[6-13]**. In this plot form, pure L-Threonine single crystal and L-Threonine based semi organic crystals were carried out as L-Threonine Lithium Chloride (LTLC), L-Threonine Calcium Chloride (LTCC), L-Threonine Cadmium chloride (LTCC), L-Threonine Manganese chloride (LTMC) single crystals are grown and its characters also studied **[14-18]**. Then, L-Threonine sulfate crystals like lithium sulfate (LTLS), potassium sulfate (LTKS), zinc sulfate (LTZS) and copper sulfate (LTCS) single crystal and L-Threonine phosphate single crystal were grown and studied **[19-23]**. After, L-Threonine Cadmium Acetate (LTCA) and L-Threonine Zinc Acetate (LTZA) single crystals are grown **[24-25]**. In continues, in this work, the novel amino acid based semi-organic single crystal of pure L-Threonine Manganese Acetate (LTMA) was successfully grown by slow evaporation method. The various characterizations have been carried out and those properties are reported.

2. EXPERIMENTAL SECTION

2.1 Synthesis & Crystal Growth

L-Threonine Manganese acetate (LTMA) single crystal was successfully grown from aqueous solution in the equimolar ratio by slow evaporation method. L-Threonine and Manganese acetate tetra hydrate (Nice - AR grade) chemicals used to prepare 100 ml saturated solution at room temperature. After proper recrystallization process, solution was filtered into a beaker and it was covered with perforated plastic sheet and then housed in a dust free atmosphere so as to ensure solvent evaporation. After a period of 25 days, harvested single crystal of 11×3×2 mm^3 size LTMA was grown is shown in Fig. 1.

Chemical Formula

$$C_4H_9NO_3+(CH_3COO)_2Mn.4H_2O \rightarrow Mn[C_4H_9NO_3]^{+}\cdot 2(CH_3COO)^{-}+4H_2O\uparrow \quad (1)$$

Fig. 1 Photograph of as grown LTMA single crystal

3. RESULTS AND DISCUSSION

3.1 Single Crystal X – Ray Diffraction Analysis

The grown single crystal of LTMA was subjected to single crystal X-ray diffraction analysis to find the lattice parameters. Single crystal XRD analysis carried out using Nonius CAD4/MACH3 Single Crystal X-ray diffractometer with MoKα (α= 0.71073 Å) radiation revealed that like pure L-Threonine crystal, LTMA has Orthorhombic system with unit cell parameters were determined as shown in Table 1. Previous reports similar base material L-Threonine and Cadmium acetate doped L-Threonine single crystal results are compared in this table 1. This result proved that LTMA also satify the previous reports in this regard.

Table 1 Single Crystal XRD data of LTMA

Parameter	**LTMA [present]**	**Pure L-Threonine** [reported 14]	**LTCA** [reported 24]
a	5.106(19) Å	5:147 Å	5.131(1)Å
b	7.721(19) Å	7:733 Å	7.711(3)Å,
b	13.45(4) Å	13:610 Å	13.513(5)Å
α=β=γ	90°	90°	90°
Volume	530(4) $Å^3$	537:98 $Å^3$	534.6(3)Å
System	Orthorhombic	Orthorhombic	Orthorhombic

3.2 Powder X – ray diffraction analysis

The Powder X-ray diffraction pattern recorded for grown crystal by an X-ray diffractometer (Model JDX 8030) with CuKα (α = 1.5408 Å) radiation are shown in Fig.2. Miller indices estimated by powder V1.0 software along with 2 Theta values of LTMA crystal is given in table 2. The different peaks confirm the Powder XRD pattern L-Threonine Manganese Acetate single crystal. All the peaks differ from the peaks of pure L-Threonine single crystal [14].

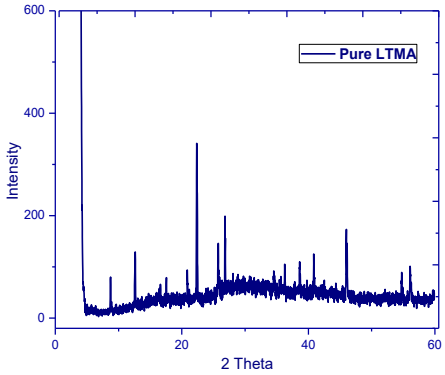

Fig. 2 Powder XRD pattern of LTMA single crystal

The first peak start at 3.93 degree and its plane calculated [111] and second maximum reaches as 345 a.u intensity in angle 22.2 degree, its plane calculated as [411]. The continual peaks reveals at the angles 25.6,26.6,36,38.4 and 44.9 in the repective peaks of plane 422,431, 444, 552 and 661. Fig.2 proved that the pure LTMA consist, number of different planes with different lattice points. It concluded that no one single element result as different peaks, therefore this material contain greater single element.

Table 2. 2θ Vs Intensity values LTMA crystal

2θ	**Intensity**	**hkl**
3.93	1178	111
12.5	134	211
17.6	100	222
22.2	345	411
25.6	154	422
26.6	203	431
36.0	108	444
38.4	113	552
44.9	176	661

3.3 Energy Dispersive analysis (EDAX)

Energy dispersive X-ray analysis (EDAX) used in conjunction mode and an important tool for confirming the element present in the crystal. Fig. 3 illustrates the EDAX spectrum of LTMA crystal under accelerated voltage 15.0 kV, magnification ×1000, working distance 15.1 mm using JEOL company (JSM-6701 F, SEM). The presence of Carbon, Nitrogen, Oxygen and Manganese in LTMA single crystal was determined. The spectrum of LTMA single

crystal was obtained as shown in Fig. 3. Due to the inclusion of acetic acid, Carbon & Oxygen has the maximum peaks. Manganese places are clearly displayed in EDAX Spectrum.

The percentage of elements was traced and showed that the compounds contained the elements as: Carbon, Nitrogen, Oxygen and Manganese. In Table 3, displays the weight, percentage of compound placed in crystal as experimental values. It proves the purity and exacts of the crystal.

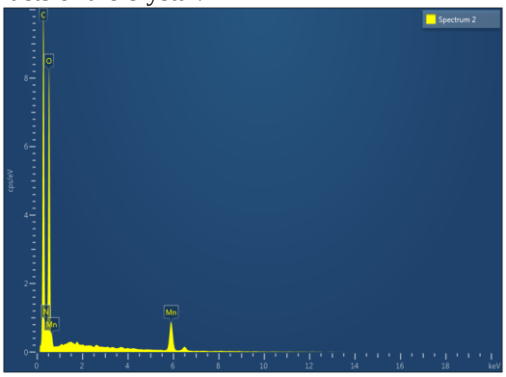

Fig. 3 EDAX spectrum of pure LTMA

Table 3 Experimented EDAX data of LTMA

Element	Line Type	Wt%	Atomic %
C	K series	41.51	49.7
N	K series	6.76	6.94
O	K series	46.79	42.06
Mn	K series	4.94	1.29
Total:		100	100

3.4 Fourier Transform Infra-Red analysis

The identification of functional groups was performed by Fourier Transform Infra-Red analysis (FTIR) spectroscopy. The FTIR spectrum of a compound provides more information than normally available electronic spectra. The presence or absence of absorption bands helps in predicting the presence of certain functional groups in the compound. To analyze the FTIR spectrum, accurate information about structure of L-Threonine and Manganese acetate is much essential. The FTIR spectra of pure LTMA crystal recorded by Perkin Elmer spectrometer in the frequency region of 400-4000 cm-1 using KBr pellet technique as shown in Fig.4. In order to do assignment, The FTIR frequencies of pure L-Threonine manganese acetate are tabulated below in Table 4. In order to do assignment, FTIR frequencies are tabulated in Table 4. The peak observed at 489 cm^{-1} is attributed to NH_3^+ bending. 560 cm^{-1}, 701 cm^{-1} and 769 cm^{-1} are COO^- rocking deformation, COO^- wagging vibration and COO^- bending respectively. 871 cm^{-1} and 932 cm^{-1} are C-C-N rocking and C-C rocking. 1040 cm^{-1}, 1113 cm^{-1} are C-N and NH_3^+ rocking and 1346 cm^{-1} was CH symmetric deformation. 1417 cm^{-1}, 1629 cm^{-1} are NH_3^+ symmetric and NH_3^+ asymmetric deformation respectively. The broad vibrational band observed at 3029 cm^{-1}, 3169 cm^{-1} is assigned to the NH_3^+ symmetric and NH_3^+ asymmetric stretching.

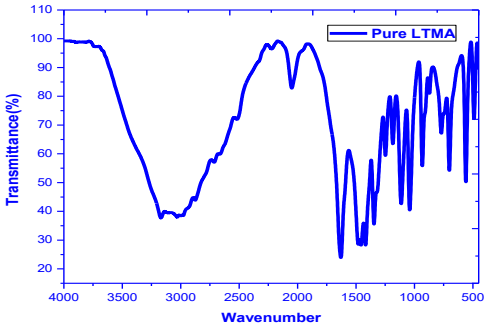

Fig.4: The FTIR spectra of LTMA

Table 4 The FTIR assignments of LTMA

Wavenumber (cm^{-1})		Assignments
Pure L-T [reported 24]	**LTMA** (Present work)	
3157	3169	NH_3^+ asymmetric
-	3029	NH_3^+ symmetric
1633	1629	NH_3^+ asymmetric deformation
1457	1417	NH_3^+ symmetric deformation
1342	1346	CH symmetric deformation
1112	1113	NH_3^+ Rocking
1037	1040	C-N Rocking
931	932	C-C Rocking
871	871	C-C-N Rocking
767	769	COO^- Bending
700	701	COO^- wagging vibration
559	560	COO^- Rocking Deformation
489	489	NH_3^+ Bending

3.5 Optical Studies

3.5.1 Transmittance Studies

The transmittance spectra of LTMA recorded in the range 190-1200 nm using Lambda 35 spectrometer. The Optical transmittance spectra of LTMA are shown in Fig.5. It reveals that there is no absorption peak in the range of 267 nm to 1100 nm. It can be seen from the transmission curve that below 300nm the transmittance of the

grown crystal LTMA slightly decreases. Variation in the transmittance may be due to the presence of manganese acetate. Very low absorbance in the entire visible region would be attributed to the delocalization of electronic cloud through charge transfer.

3.5.2 Absorption Studies

The absorption spectrum of grown crystal analyzed in the range 190-1200 nm. Fig.6 shown, there is no change from the transmittance spectra. The absence of absorption in the visible region clearly indicates that the grown crystal can be used for photonic applications. The absence of absorption spectrum concluded the good energy band gap value. By knowing optical constants of a material, examine the potential of the material for photonics applications. The optical absorption coefficient (α) calculated by the relation

$$\alpha = (1/t).\log(1/T) \quad (2)$$

Where, t is Thickness of the material and T is Transmittance.

The band gap of the crystal was estimated by Tauc's relation:

$$\alpha h\nu = A(h\nu - Eg)^n \quad (3)$$

Where, Eg is the optical bandgap of the crystal and A is a constant. So, the energy band gap of grown crystal was determined from the Fig. 7, as 4.3eV.

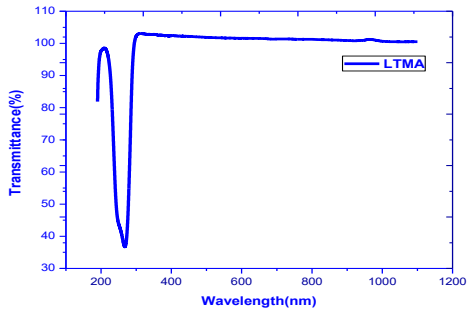

Fig. 5 UV transmittance spectrum of LTMA

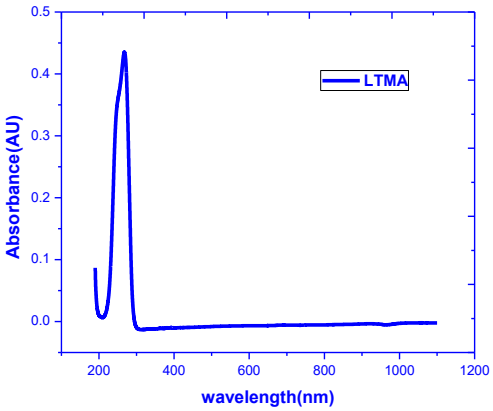

Fig. 6 UV Absorption spectrum of LTMA

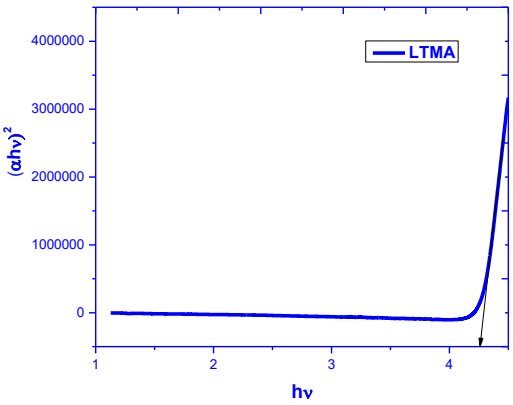

Fig. 7 Energy band gap of Pure LTMA crystal

3.6 Vicker's Micro Hardness Study (MHD)

The micro hardness study was carried out to determine the mechanical strength of the grown crystals using HMT 2T, SHIMADZU Vickers micro hardness tester. The indentation marks were made on the surface of the crystals at room temperature by applying load of 25gm, 50gm and 100gm. The H_v was found to increase with the increase in the load from 25 to 100g and crack occurred at higher loads as shown in Table 5. A graph (Fig. 8) has been plotted between H_v and applied load P. The Vickers micro hardness number H_v of the crystal was calculated using the relation

$$H_v = 1.8544\ P/d_2\ (kg/mm^2) \quad (4)$$

where, H_v is the Vickers hardness number in kg/mm^2, P is the applied load in kg and d is the average diagonal length of the indentation in mm. From the graph it can be observed that the hardness value increased up to 100g and the maximum hardness value was 80.5 kg/mm^2 at 100gm.

Table.5 Vickers Hardness Test data

Load P [gm]	Hardness [H_V]
25	37
50	50.8
100	80.5

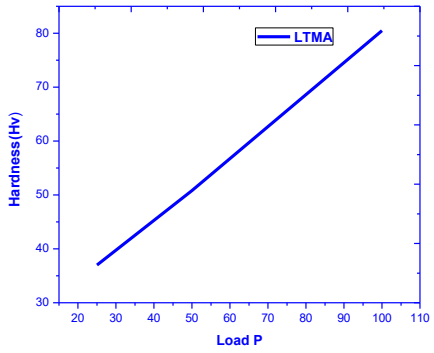

Fig. load P Vs hardness (H_V) of LTMA

4. CONCLUSIONS

Good quality single crystal of L-Threonine Manganese Acetate (LTMA) was grown in room Temperature by slow evaporation method. Structural characterization of the grown crystal was concluded as orthorhombic crystal system by single crystal and periodics of hkl planes analysed by powder X-ray diffraction studies, and the lattice parameters have been evaluated. Presence of Chemical compositions C, N, O and Mn in the grown mater was qualitatively confirmed by EDAX analysis. The functional groups in the crystal lattice, was analyzed by FTIR spectrum. The UV Transmittance & Absorption spectrum were plotted and energy band gap was determined as 4.3eV. The increasing Hardness nature of the LTMA crystal was obtained by Vicker's Micro hardness study. Thus the pure L-Threonine Manganese Acetate (LTMA) simgle crystal is a Multi character raw material.

5. REFERENCES

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