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Study on Growth, Structural, Optical and Mechanical nature of L-Threonine Manganese Acetate (LTMA) Single Crystal

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ABSTRACT

The Novel L-Threonine Manganese Acetate (LTMA) single crystal has been grown successfully by slow evaporation method at 300C. In order to determine the crystalline nature of the samples and cell parameters (a=5.106 Å, b= 7.721 Å, c=13.45 Å & α=β=γ=90°), Single crystal X-Ray Diffraction and Powder X-Ray Diffraction studies were carried out. The results confirm that drastic changes were observed in the structure of the material. The prominent peaks indicating the positions of the lattice points and crystal planes [111], [411], [422], [431], [444], [552] and [661]. EDAX analysis confirmed the presence of Chemical composition in the crystal. The active functional groups 3169cm-1, 3029 cm-1, 2200 cm-1 of the crystal points were analyzed by FTIR spectrum. Optical nature of the grown crystal obtained by UV-Vis-spectrometry, shows absorption 190nm to 1100nm, transparency in the range of 267-1100 nm and the energy band gap of 4.6eV. Hardness of the LTMA crystal was studied by Vicker's Micro hardness analyzer. The emission spectrum at 486nm of the grown crystal was determined by Photoluminescence study.

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

1. Introduction

In recent years, organic and inorganic materials are emerging out with desired properties for second harmonic generation as Non-linear optical materials. These materials have a 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 color displays like the LCD monitors. Similar to the semi organic crystals, amino acid based semi organic linear 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. Later on, L-Alanine, L-Proline, L-Valine, α-Histidine based semi organic crystals were invented [6-13]. In this plotform, 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) and L-Threonine Manganese chloride (LTMC) and single crystals were grown and their characteristics were studied [14-18]. Then, L-Threonine sulfate crystals like lithium sulfate (LTLS), potassium sulfate (LTKS), zinc sulfate (LTZS) and copper sulfate (LTCS) single crystals and L-Threonine phosphate single crystals were grown and studied [19-23]. Later on, L-Threonine Cadmium Acetate (LTCA) and L-Threonine Zinc Acetate (LTZA) single crystals were grown [24-25]. In this work, we have successfully grown L-Threonine Manganese Acetate (LTMA) single crystal and its activities were studied.

2. Materials and Methods

2.1 Synthesis

Growth of L-Threonine Manganese acetate (LTMA) single crystal was successfully done from aqueous solution in the equimolar ratio by slow evaporation method. 11.9 gm L-Threonine and 24.5 gm Manganese (II) acetate tetra hydrate (Nice - AR grade) were used to prepare 100 ml saturated solution at room temperature. After proper recrystallization process, solution was filtered and covered with perforated plastic sheet and then housed in a dust free atmosphere so as to ensure the solvent evaporation. After a period of 25 days, harvested single crystal of 11×3×2 mm3 size LTMA was grown as shown in Fig. 1.

The chemical formula for this process is given below

$$C_4H_9NO_3+(CH_3COO)_2Mn.4H_2O$$

$$\rightarrow Mn[C_4H_9NO_3]^+.2(CH_3COO)^-+4H_2O\uparrow \qquad (1)$$

Fig. 1 Photograph of the as grown pure LTMA

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3. Results and Discussion

3.1 Single Crystal X – Ray Diffraction studies

To analyze the crystal structure of the as grown LTMA single crystal Nonius CAD4/MACH3 Single Crystal X-ray diffractometer was used with MoKα (α= 0.71073 Å) as the source the data for L-Threonine crystal, L-Threonine Manganese Acetate (LTMA) was obtained as shown in Table 1. Comparison with previous works for similar materials (L-Threonine and Cadmium acetate doped L-Threonine single crystal) were reported in table 1. The data presented in Table 1 confirms that both the results are in good agreement with each other.

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
Space group	P_{212121}	P_{212121}	P_{212121}
System	Orthorhombic	Orthorhombic	Orthorhombic

3.2 Powder XRD Spectral studies

To study the lattice point and periodicity of the atoms, Powder XRD analysis was performed. The XRD pattern shows different peaks that reports the strength of atoms with compositions as shown in Fig.2. Miller indices assumed by powder V1.0 software as a function with 2 Theta values of LTMA crystal are presented in table 2. Different peaks confirm the Powder XRD pattern L-Threonine Manganese Acetate single crystal. The obtained result shows that all the peaks are different from that of the pure L-Threonine single crystal [14].

The first peak start at 3.93^0 and its corresponding plane as calculated is [111] whereas the second maximum coming at an angle of 22.2^0 with respective plane as [411]. The other peaks appearing at 25.6^0, 26.6^0, 36^0, 38.4^0 and 44.9^0 corresponding to [422], [431], [444], [552] and [661] planes respectively. Fig.2 proves that the pure LTMA consists of a number of different planes with different lattice points. It also clear that no other are appearing different from the above peaks, thus indicating that this material of mainly single crystal.

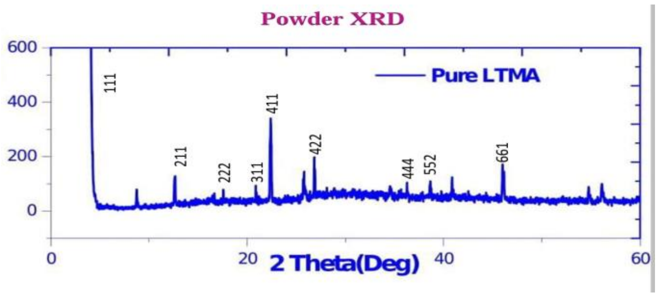


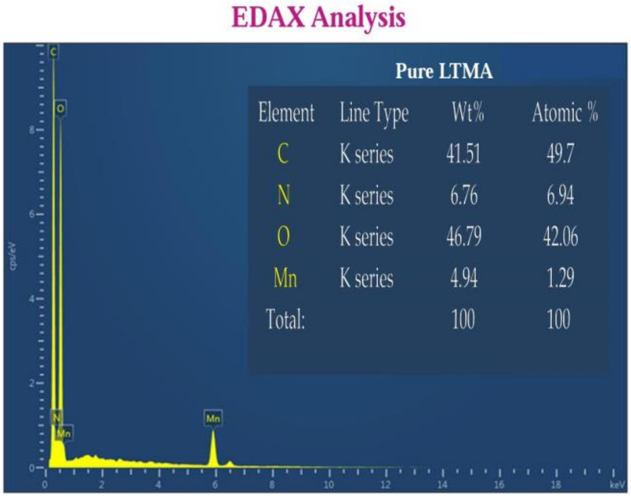
Fig. 2 Powder XRD pattern of pure LTMA single crystal

Table 2: 2θ vs Intensity of LTMA crystal XRD data

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) illustrates the EDAX spectrum of LTMA crystal using JEOL SEM (JSM-6701 F, SEM). The position of Carbon (C), Nitrogen (N), Oxygen (O) and Manganese (Mn) in LTMA single crystal was obtained as shown in Fig. 3. Due to the presence of acetic acid, Carbon and Oxygen has the maximum peaks. Manganese presence is clearly evident in EDAX Spectrum. The percentage of the elements recorded shows the samples are composed of Carbon (C), Nitrogen (N), Oxygen (O) and Manganese (Mn). The inset Table 3, that displays the weight and percentage of compound present in the samples. This confirms the phase and purity of the prepared crystals.



Pure 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

Fig. 3 EDAX Spectrum of pure LTMA single crystal

Table 3: EDAX data of LTMA

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3.4 Fourier Transform Infra-Red analysis (FTIR)

FTIR determines the bonding nature and necessary chain between the compositions. The possible formation of the functional groups that decide the position of atoms in the lattices, which implies structure and performance of the material as function of temperature (e.g the melting point). The FTIR spectrum determines the more internal efficiency of the material. The determination of presence/absence of the bands spectra helps to predict the functional groups in the compound. In FTIR study, the detailed information about the L-Threonine and Manganese II acetate in the form of vibrational bond in stretched modes and other related modes were identified. FTIR spectra of pure LTMA crystal obtained by Perkin Elmer device with frequency range of 400-4000 cm^{-1} using KBr pellet technique is shown in Fig.4. The FTIR frequencies of the pure L-Threonine and manganese acetate are tabulated below in Table 4. The peak observed at 489 cm^{-1} is attributed to NH_3^+ bending. whereas the other peaks at 560 cm^{-1}, 701 cm^{-1} and 769 cm^{-1} are the COO^- rocking deformation, COO^- wagging vibration and COO^- bending respectively. Peaks at 871 cm^{-1} and 932 cm^{-1} are C-C-N rocking and C-C rocking and the peaks at 1040 cm^{-1} and 1113 cm^{-1} are C-N and NH_3^+ rocking and the peak at 1346 cm^{-1} is attributed to CH symmetric deformation. The high frequency peaks at 1417 cm^{-1}, 1629 cm^{-1} are NH_3^+ symmetric and NH_3^+ asymmetric deformations respectively. The wide vibrational band region observed at 3029 cm^{-1}, 3169 cm^{-1} is known to be assigned to NH_3^+ symmetric and NH_3^+ asymmetric stretched modes.

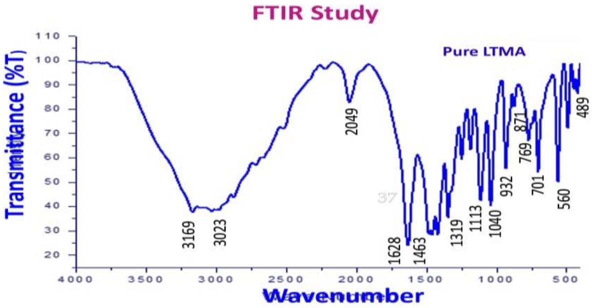

Fig.4 FTIR spectra of pure LTMA

Table 4 FTIR assignments of pure LTMA

Wavenumber (cm^{-1})		
Pure L-T [reported 24]	LTMA (Present work)	Assignments
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 spectrum of pure LTMA was collected in the range of 200-1100 nm using Lambda 35 spectrometer. The Optical transmittance spectra of LTMA are shown in Fig.5. It reveals that the clean absorption peak at 1200 nm. This can also confirm that the lower 300nm, transmittance LTMA slightly decreases. The change in the transmittance curve regions appears due to the presence of manganese II acetate. This results the absorption in entire transmittance curve that has been attributed to the delocalization of electronic cloud conventional diffusion of the Charged Carriers.

3.5.2 Absorption Studies

The aim of the absorption spectrum collected from grown crystal is, to determine the Energy band Gap. The absorption spectrum of the pure LTMA is plotted and shown in Fig.6. In the figure it is seen that there are no substantial changes in the transmittance spectra of the samples. The absence of the absorption spectrum clearly resulted that the grown material that has been used as the photonic devices. The absence of the absorption spectrum concluded the good energy band gap value 4.6 eV. By knowing the optical constants of a grown crystal, can help to determine the strength of the material for photonics devices. The UV-Visible absorption coefficient (α) can be calculated with the help of the following equation.

$$\alpha = 2.303/t \log_e(1/T) \tag{2}$$

Where, t - Thickness of the material, T - Transmittance.

The energy band gap of the material was calculated by Tauc's relation:

$$\alpha h\nu = A(h\nu - E_g)^n \tag{3}$$

Where, Eg - optical band gap of the pure LTMA and A is constant. So, the energy band gap of the grown crystal as determined from the Fig. 7, comes out to be 4.6eV.

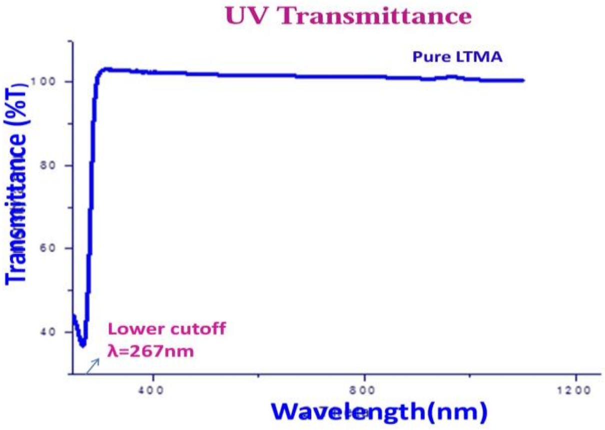

Fig. 5 UV transmittance spectrum of pure LTMA

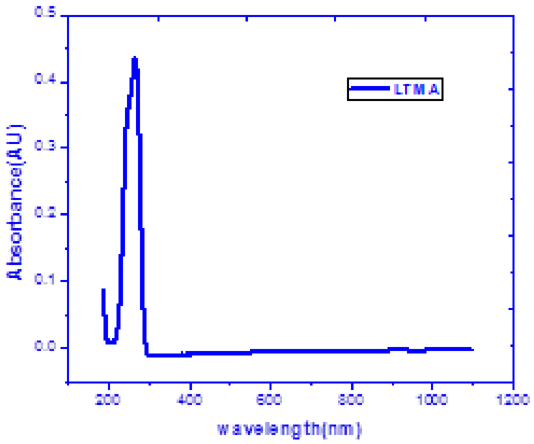

Fig. 6 UV Absorption spectrum of pure LTMA

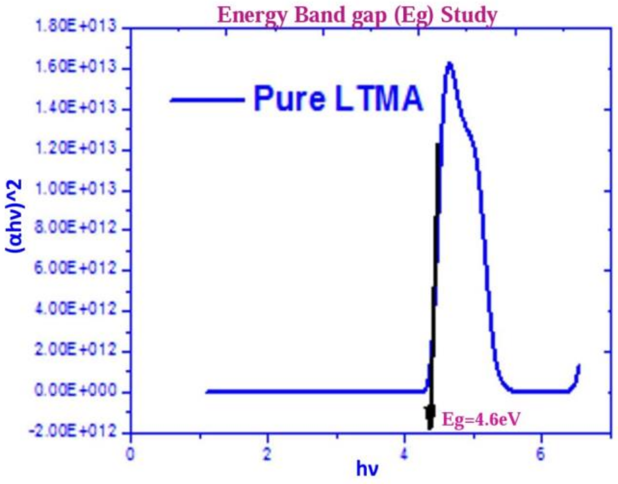

Fig. 7 Energy band gap of Pure LTMA crystal

3.6 Micro Hardness Study (MHD)

In order to study the micro hardness of the grown crystals, mechanical strength was measured using HMT 2T, SHIMADZU Vickers micro hardness tester. The indentation marks are shown on the surface of the crystal for different loads such as 25gm, 50gm and 100gm. The Hardness Number (H_v) has been determined with the increasing loads from 25gm to 100gm. The crack occurred at 50gm and 100gm as shown in Table 5. The MHD graph (Fig. 8) has been plotted between (H_v) with applied load (P). The Vickers micro hardness value H_v of the gown crystal was found out using the following formula.

$$H_v = 1.8544\ P/d^2\ (\mathrm{kg/mm^2}) \qquad (4)$$

Where, H_v is the Vickers hardness number with units of $\mathrm{kg/mm^2}$, P is the mechanical force with units of kg and d is the average diagonal length of the indentation with units in mm. The graph observed that the hardness number (H_v) was increased from 25gm up to 100gm and the maximum hardness of 80.5 $\mathrm{kg/mm^2}$, was attained for the 100gm mechanical force.

Table.5: Vickers Hardness Test data of pure LTMA

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

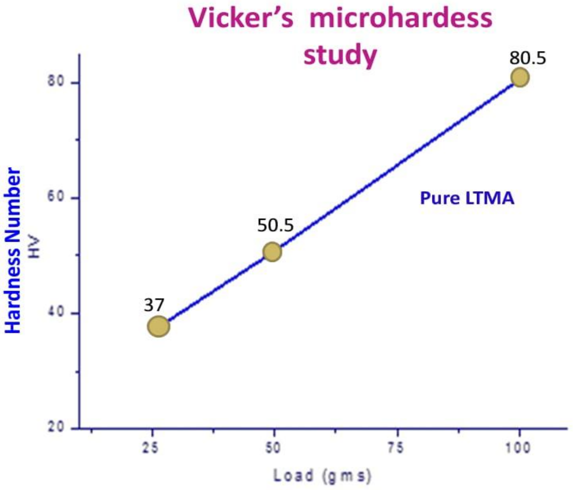

Fig.8 Load P vs Hardness (H_V) of pure LTMA

3.7 Photoluminescence Study (PL)

The grown crystal situated under PL Study, it (Fig.9) observes as the Emission spectrum around 450 nm and 486nm as respectively. The maximum peak of emission spectrum at 486.96 nm having the Photoluminescence intensity for pure LTMA single crystal is 28 a.m.u. Therefore this high intense pure LTMA may be used to optical electronic devices.

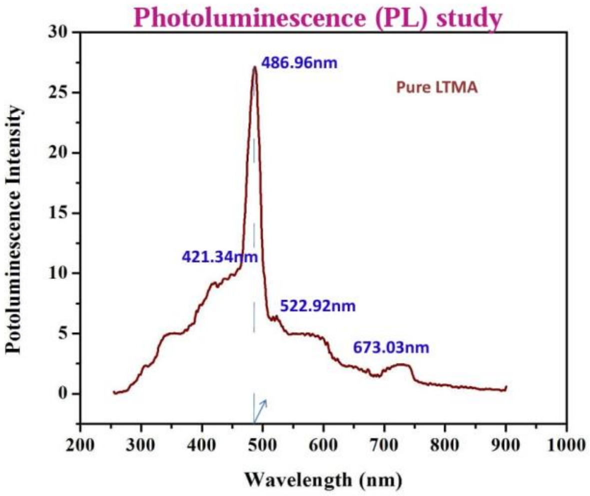

Fig. 9 PL spectrum of pure LTMA crystal

4. Conclusions

Good quality material of L-Threonine Manganese Acetate (LTMA) has been grown by slow evaporation method. Synthesis procedure of the pure LTMA successfully completed. Structural studies and crystalline nature of the pure LTMA determined with single crystal and powder X-ray diffraction studies respectively. Chemical composition was qualitatively confirmed by EDAX studies. The functional groups of L-Threonine Manganese Acetate (LTMA), was characterized by FTIR analysis. The UV Transmittance and absorption spectrum were plotted and energy band gap was determined as 4.6eV. The increasing Hardness of the LTMA crystal 30, 50.5 and 80.5 was determined for respective 25 gm, 50gm and 100gms load by Vicker's Micro hardness study. PL emission spectrum of Pure LTMA crystal was determined as 486.96 nm.

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