

Impact of Inner Dopants on Structural, Optical and Mechanical Properties of Unadulterated L-Threonine Manganese Acetate

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ABSTRACT

Equal molar ratio of L-Threonine and manganese acetate (LTMA) and 0.2 Molar mass of Zn^{2+} , Cd^{2+} and Pb^{2+} doped LTMA single crystals were grown with their aqueous solution using the slow evaporation technique. These crystals were subjected to various studies such that single crystal X-Ray Diffraction Volume = $530(4) \text{ \AA}^3$ increased upto $540.8(4) \text{ \AA}^3$, Powder X-Ray Diffraction, FTIR, UV-optical, Energy Dispersive and Microhardness studies. The cell length and interfacial angles $\alpha = \beta = \gamma = 90^\circ$ of the grown crystals were determined. EDAX study confirms the placing of dopant ions Zn^{2+} , Cd^{2+} and Pb^{2+} in the host material LTMA. FTIR analysis reported the functional group and UV-Vis analysis carried out the optical behavior of the crystals. UV-Vis absorption spectrum analysis determines the increasing energy band gap from 4.6eV to 6.5eV and transmittance spectrum determines the lower cutoff wavelength of the grown crystals as 267nm for pure LTMA and around 200nm for doped LTMA. Mechanical behaviors of the grown crystals have been studied by Vicker's Microhardness Study and their roughnesses are reported.

Keywords: Metallic Dopants, Single Crystal XRD, Powder XRD, EDAX, Microhardness MHD

1. Introduction

In the present era, solution growth has prominent effect to make in technical and scientific advancement. A single crystal is a well known periodic arranging of atoms in a three dimensional space with equally repeated rules. Single crystals are the fundamental building blocks for modern technology. The well preparation of single crystal has good properties in advantages and applications. So, the regularity and uniformity of the single crystals transmit electromagnetic waves without losses. Crystal growth has controlled phase transformation and implies important natures, properties and qualities in materials science. Significant properties of crystal growth technology develop many excellent crystals, in ever growing applications in lasers, optical communication and data storage technology and so many application crystals. Hence, single crystals are very important and essentiality for further research and technology. In beginning days, the crystal growth is faces very difficulties in selecting methods and compound for related work. At that time materials have the very nonlinearity natures in characterizations as well as applications. After, it was enabled for the commercial development of single crystals with promising nonlinear optical properties. In short durations, large size crystals are essential for device fabrication with several fast growth methods. The present day demand is for large and high quality NLO, ferroelectric, piezoelectric single crystals and magnetic materials with minimum defects [1, 2]. To growing any application crystal, microscopic and macroscopic homogeneity is improvement is very important property. The synthesis of lot of crystals is the complicated process to attaining notable technical applications in the synthesis,

growing process and analysis [3]. It has a connection between science and technology in making of regularly using device in the modern micro electronics industry. Most of the nonlinear optical crystals have proven as better single crystals to consist the applications such as nonlinear optical nature, frequency compiling, piezo electric modulation, optical statistic movements, optical disobedient etc. Due to the recent advancements of these nonlinear optical materials has good quality organic crystals are grown as excitement in the last decade. The crystal growth is an art of growing crystal based on scientific principles to facilitate high technology applications in lasers, semiconducting devices, computers, magnetic and optical devices and pharmaceuticals, among others and needs expertise in chemistry, physics, optics and crystallography [4-9]. The growth of single crystals is both scientifically and technologically important. In this regards, amino acid based single crystals are very successful material to competing the above task [10]. Researcher lot of works completed using the amino acids such as L-Alanine, L-Proline, L-Arginine, L-Histidine and L-Valine etc.. [11-15]. In recent, most of the exploration work has been done on the synthesizing and portrayal of semi natural crystal. Because of their wide optical applications, contrasted with different materials, amino corrosive blended natural crystal was intrigued to orchestrated. The search material has qualifies for the discovery of numerous natural NLO materials with high nonlinear natures and photonic applications. Authentically, it can utilize in uses of predominant quality precious stones. Like the semi natural precious stones, amino corrosive based semi natural gems were likewise has acceptable optical and non-direct optical natures. This

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single crystal can likewise be developed from watery answer for the improved hardness and the warm steadiness. In this reference, unadulterated L-Threonine single gem and L-Threonine based Lithium Chloride (LTLC), Calcium Chloride (LTCC), Cadmium chloride (LTCC), Manganese chloride (LTMC) single precious crystal are developed and its characters likewise examined [14-18]. Afterward, L-Threonine Sulfate crystal like Lithium Sulfate (LTLS), Potassium Sulfate (LTKS), Zinc Sulfate (LTZS) and Copper Sulfate (LTCS) single precious crystal are developed and considered [19-22]. At that point, L-Threonine Cadmium Acetate (LTCA) and L-Threonine Zinc Acetate (LTZA) single precious crystal are developed [23-24]. In proceeds, this work finished with development on unadulterated L-Threonine Manganese Acetate (LTMA) and the Zinc, Cadmium and Lead doped L-Threonine Manganese Acetate novel single crystals were effectively developed by slow evaporation method. The different portrayals have been done and those properties of both crystals were detailed.

2. Materials and Methods

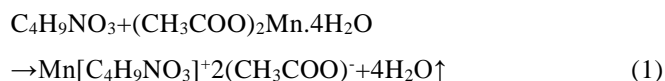
2.1. Synthesis

AR grade chemicals of L-Threonine and Manganese (II) acetate tetra hydrate in the ratio of 1:1 Molar ratio taken in 10ml distilled water and In continues, 0.2M of (AR grade) Zinc (II) acetate (ZnA), Cadmium (II) acetate (CdA) and Lead (II) acetate (PbA) added in 1:0.8 M ratio of L-Threonine and Manganese (II) Acetate solution taken in 10ml distilled water separately each with maintaining the molar ratio as 1:1. All the prepared saturated solutions was filtered and then housed in a dust free atmosphere. The pure LTMA Single crystal and Zn²⁺ doped LTMA, Cd²⁺ doped LTMA and Pb²⁺ doped LTMA single crystals were successfully grown at 30°C using with slow evaporation technique.

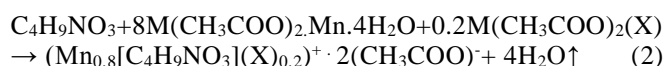
After a period of 25 days, harvested single crystals of 10×3×2 mm³ size pure LTMA single crystal, 10×4×2 mm³ size of Zn²⁺ doped LTMA, 10×3×2 mm³ size of Cd²⁺ doped LTMA and 10×3×2 mm³ size of Pb²⁺ doped LTMA were grown as shown in Figure 1.

The chemical formula for this process is given below:

Pure LTMA single crystal



0.2M (X)²⁺ doped LTMA single crystal



(Where X is substituted by Zn²⁺/ Cd²⁺/ Pb²⁺)



Fig 1 As grown (a) Pure LTMA (b) Zn²⁺ doped LTMA (c) Cd²⁺ doped LTMA (d) Pb²⁺ doped LTMA single crystals

3. Results and Discussion

This chapter deals with the characterization techniques of the single crystal. These techniques help to study the qualitative nature of the grown single crystal. It will also study the details or presence of chemicals and its activities and performance inside the material. This chapter will help to study the entire ability of the grown material. In general the characterization only exposes the exact nature and effective ability of the material. Based on the technical studies only to the material glittered in the using fields, such as mechanical, electrical and others. In fact, the grown crystal was succeeding by the way of full-fledged studies. Behaviors of a crystal very importantly with its qualitative chemical ratios, dimension, imperfections and the study of its electronic application, stable hardness (non-electrical), thermo gravimetric and lighting properties studies. Therefore, to find characterization, this grown pure LTMA and doped LTMA single crystal subjected to studied Single XRD study, Powder XRD study, Energy Dispersive X-ray Analysis (EDAX), Fourier transform infrared (FT-IR), UV-Visible absorbance spectral analysis, and etc.

In the present investigation, the grown crystals were subjected to crystallographic analysis like X-ray diffraction (XRD) study to determine the crystal system and its lattice parameters. The Energy Dispersive X-ray Analysis (EDAX) shows the presence of constituent elements. The functional groups and vibrational frequencies were identified using Fourier transform infrared (FT-IR) spectral analyses. The UV-Visible absorbance spectra were recorded to find out the cut-off wavelength and band gap between the compositions. The Photoluminescence and second harmonic generation nature of the crystal for NLO application are determined and Microhardness test was performed to evaluate the mechanical strength of the material.

3.1. Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction study has been completed for find the crystallinity and for determining the unit cell datas of the grown crystals. It proven as result that the all pure and doped single crystals become same orthorhombic crystal type and which categorized to non-

centro-symmetric. The unit cell parameters for pure LTMA and Zn²⁺-doped LTMA, Cd²⁺ doped LTMA and Pb²⁺ doped LTMA single crystals are given in Table 1. The volume of the pure LTMA become 530(4) Å³ and all the doped crystals were increased as 538 Å³ for Zn²⁺-doped LTMA, 540 Å³ for Cd²⁺ doped LTMA and 540.8(4) Å³ for Pb²⁺ doped LTMA.

Table 1; Lattice parameters of Pure LTMA and Zn²⁺, Cd²⁺ and Pb²⁺ doped LTMA Single crystals

Lattice parameters	Pure LTMA	Zn ²⁺ doped LTMA	Cd ²⁺ doped LTMA	Pb ²⁺ doped LTMA
a	5.106(19) Å	5.17 Å	5.14 Å	5.147(3) Å
b	7.721(19) Å	7.71 Å	7.72 Å	7.731(2) Å
b	13.45(4) Å	13.59 Å	13.60 Å	13.590(10) Å
α=β=γ	90°	90°	90°	90°
Volume	530(4) Å ³	538 Å ³	540 Å ³	540.8(4) Å ³
System	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	P ₂₁₂₁₂₁	P ₂₁₂₁₂₁	P ₂₁₂₁₂₁	P ₂₁₂₁₂₁

3.2. Powder XRD analysis

The Powder XRD pattern of pure LTMA and Zn²⁺, Cd²⁺ and Pb²⁺ doped LTMA Single crystals were plotted as shown in Fig. 2. All the doped Powder XRD patterns are clearly differs with different peaks reaction of dopants, the similarities and differences between the pure and doping crystals are well known in variations of patterns in Figure. 2. The inner reagent of Zinc (II) acetate (ZnA), Cadmium (II) acetate (CdA) and Lead (II) acetate (PbA) were well mixing with the Manganese (II) acetate (MnA) as 0.2 M and 0.8 M ratio. This perfect mixture results that without changing the pure LTMA crystal structure Orthorhombic crystal system and all the Zn²⁺ doped LTMA, Cd²⁺ doped LTMA and Pb²⁺ doped LTMA Single crystals also become as same Orthorhombic crystal system. The hkl planes of Pure LTMA and Zn²⁺, Cd²⁺ and Pb²⁺ doped LTMA single crystals with respective 2θ values are calculated tabulated in Table 3, 4 & Table 5.

Therefore, 0.2M dopant of Zn²⁺, Cd²⁺ and Pb²⁺ doped LTMA Single crystals, the first peak remains the same maximum peak level from pure LTMA is 1163 a.m.u and 1184 a.m.u, 1029 a.m.u & 1184 a.m.u for Zn²⁺ doped LTMA, Cd²⁺ doped LTMA and Pb²⁺ doped LTMA Single crystals respectively. Most of the peaks are differed with different 2θ values. Several peaks are repeated in different 2θ values.

3.3. EDAX analysis

Energy dispersive spectroscopy is a chemical microanalysis technique working in combination with Quanta 200 FEG scanning electron microscope (Figure 2.3). The interaction of the electron beam with a specimen in the scanning electron microscope produces many results, including X-rays. Some of the X-rays produced in this manner have wavelength and energies those are determine characteristics of the element of that specimen. It is a technique used to found the elemental composition of the sample. Elemental evaluation by the analytical microscopy may be accomplished with the help of analyzing the emitted radiation and result that those specific wavelengths are absorbed. All the crystals were subjected to energy dispersive

analysis. Elements are determined and displayed as atomic percentile. Energy achievements correspond to the related elements with positioning in pure and doped LTMA crystals is shown in the Fig. 3(a) and (b), (c), (d). In the EDAX analysis, it was observed that the presence of Mn²⁺ in pure LTMA single crystal and Mn²⁺. In doped LTMA single crystals all the dopant Zn²⁺, Cd²⁺ and Pb²⁺ are presents. The values of EDAX Spectra reported in Table.6, 7, 8 and 9.

Table.2; hkl planes of Pure LTMA single crystal

2θ	Intensity	hkl
20		
4.0	1163	111
8.8	93	211
12.5	134	222
17.6	100	411
22.2	345	422
25.6	154	431
26.6	203	444
36.0	108	552
38.4	113	661

Table.3 hkl planes of Zn²⁺ doped Pure LTMA single crystal

2θ	Intensity	Hkl
4.1	1184	111
12.6	100	211
17.6	160	220
19.6	173	221
20.6	384	301
21.0	199	311
22.6	147	222
25.6	151	302
28.0	108	321
29.0	182	322
31.0	139	402
34.0	104	422
36.0	95.9	432
38.8	78.8	521
41.8	104.5	532

Table.4 hkl planes of Cd²⁺ doped Pure LTMA single crystal

2θ	Intensity	hkl
4.1	1029	111
13.1	230	211
18.2	157.4	311
20.2	256.7	222
20.6	235.0	321
21.5	187.8	322
22.2	174.8	331
22.9	230.7	421
23.5	144.9	422
23.9	200.8	500
28.6	252.4	521
29.2	157.0	440
35.0	93.3	442
37.3	127.6	543
39.0	100	551

3.4. Fourier Transform Infra-Red analysis

The FTIR spectrum of Pure and doped LTMA crystals were obtained as shown in Fig. 4. The placing of NH₃³⁺ is clearly identified in the FT-IR spectrum by the wide intense with the respective data as 3169.25cm⁻¹ relating to

asymmetric vibration mode of NH₃⁺. The opposite symmetric vibration band lies as frequency of 3029.80 cm⁻¹. The both symmetric and asymmetric bending vibrations appear as 1417.94 cm⁻¹ and 1629.28 cm⁻¹. CH symmetric deformation appears in 1346.04cm⁻¹ respectively. NH₃⁺ Rocking, C-N Rocking, C-C Rocking and C-C-N Rocking appear in 1113.14cm⁻¹. 1040.72cm⁻¹, 932.53cm⁻¹ and 871.20cm⁻¹. 769.77 cm⁻¹ indicates COO⁻ Bending, 701.35 cm⁻¹ and 560.11cm⁻¹ indicates the COO⁻ wagging vibration and COO⁻ Rocking Deformation respectively. NH₃⁺ Bending appears at 489.82 cm⁻¹. The OCO rocking frequency found out at 445.18 cm⁻¹.

Table.5 hkl planes of Pb²⁺ doped Pure LTMA single 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

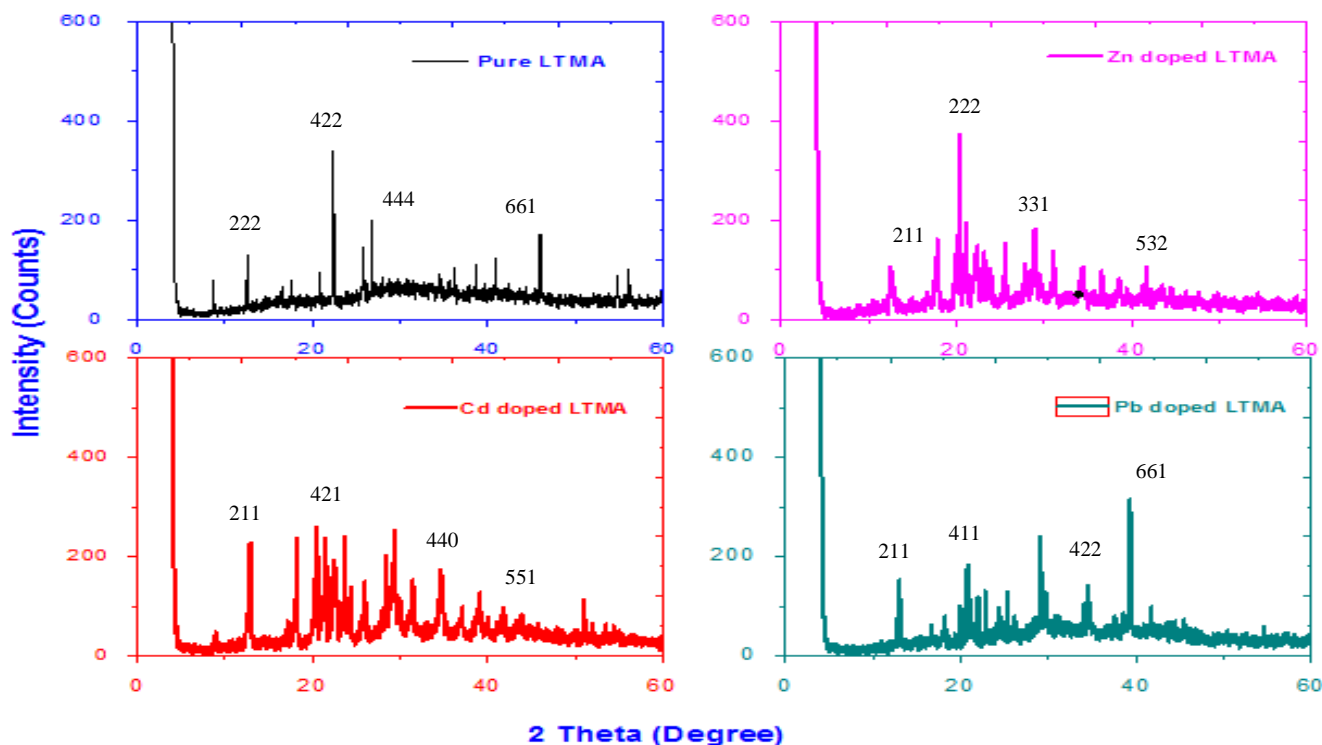


Fig. 2 XRD plotting of pure LTMA and Zn²⁺, Cd²⁺ and Pb²⁺ doped LTMA

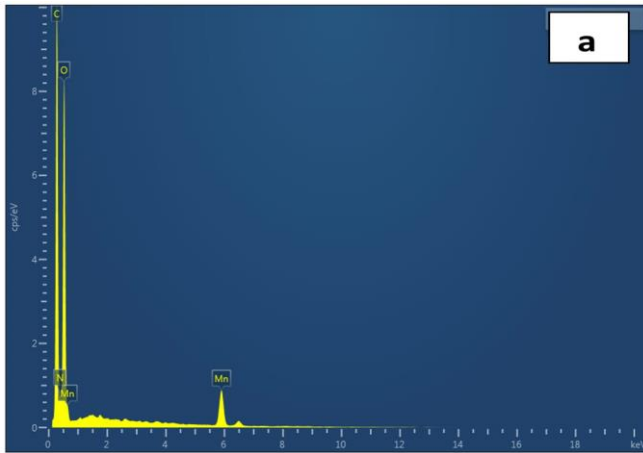


Fig. 3 Energy dispersive Spectra of (a) Pure LTMA

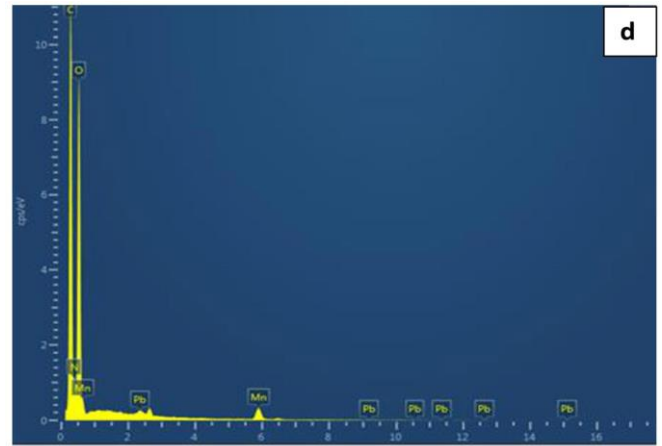


Fig. 6 Energy dispersive Spectra of (d) Pb²⁺ doped LTMA Single Crystal

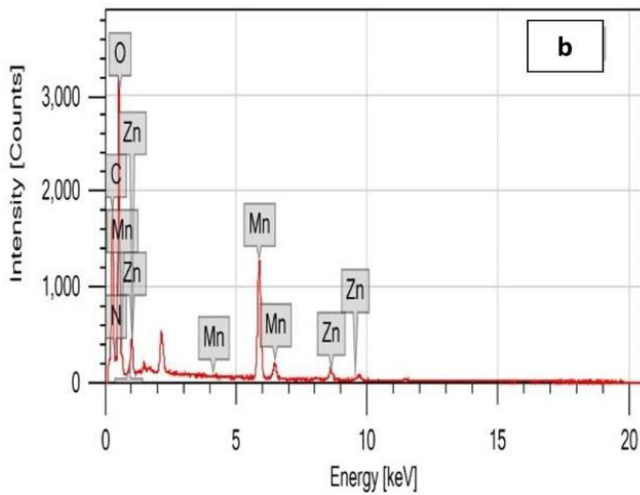


Fig. 4 Energy dispersive Spectra of (b) Zn²⁺ doped LTMA

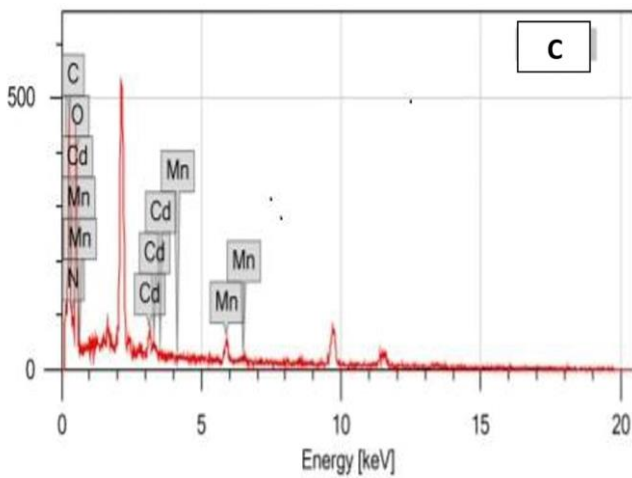


Fig. 5 Energy dispersive Spectra of (c) Cd²⁺ doped LTMA

Table.6 EDAX report of Pure LTMA

Element	Line Type	Wt%	Atomic %
Carbon	K	41.51	49.7
Nitrogen	K	6.76	6.94
Oxygen	K	46.79	42.06
Manganese	K	4.94	1.29
Total:		100	100

Table.7 EDAX report of (b) Zn²⁺ doped LTMA

Element	Line Type	Wt%	Atomic %
Carbon	K	36.47±0.19	51.73±0.26
Nitrogen	K	0.34±0.14	0.41±0.17
Oxygen	K	37.73±0.28 4	40.17±0.30
Manganese	K	21.24±0.22	6.59±0.07
Zinc	K	4.22±0.16	1.10±0.04
Total:		100	100

Table.8 EDAX report of Cd²⁺ doped LTMA

Element	Line Type	Wt%	Atomic %
Carbon	K	38.65	48.04
Nitrogen	K	7.75	8.26
Oxygen	K	45.04	42.03
Manganese	K	3.85	1.05
Cadmium	L	4.70	0.62
Total:		100	100

Table.9 EDAX report of Pb²⁺ doped LTMA

Element	Line Type	Wt%	Atomic %
Carbon	K	40.33	47.47
Nitrogen	K	9.14	9.22
Oxygen	K	48.55	42.9
Manganese	K	1.45	0.37
Lead	M	0.54	0.04
Total:		100	100

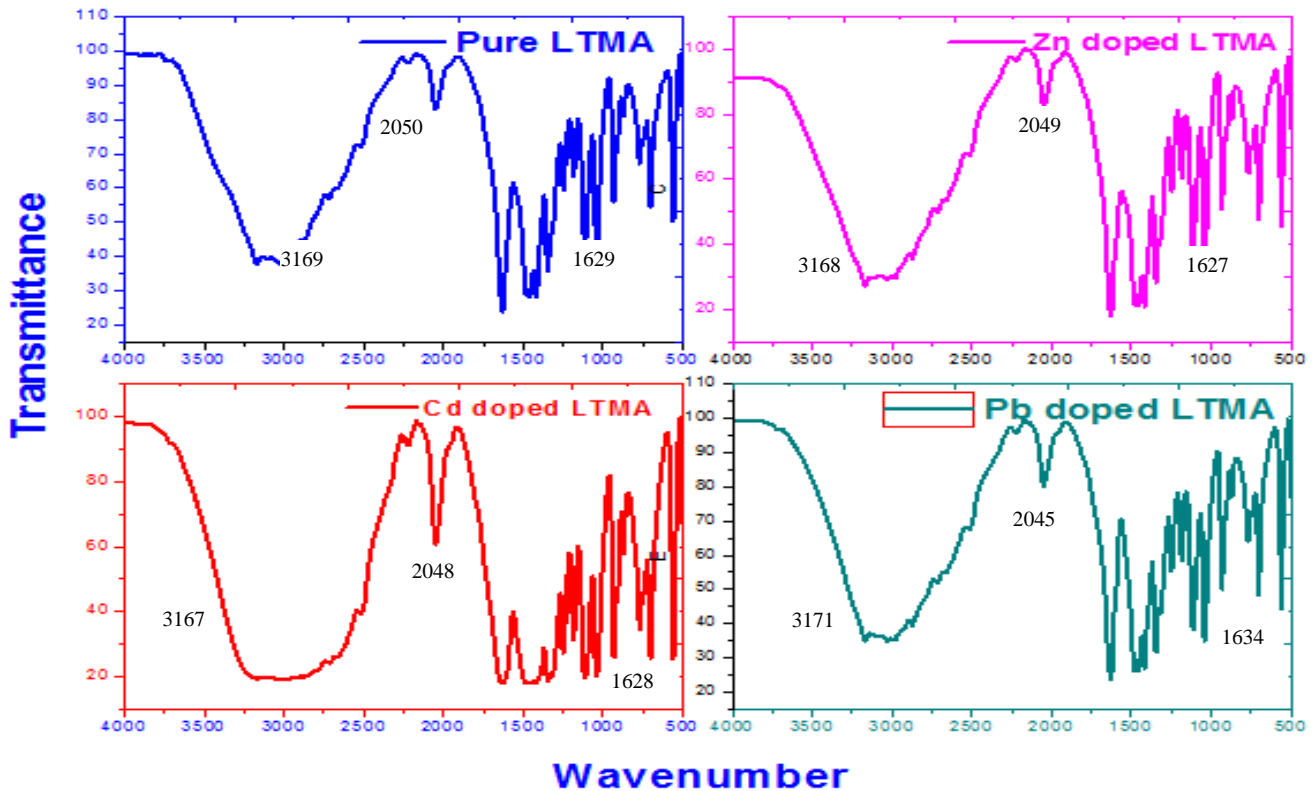


Fig. 7 FTIR Spectrum of Pure LTMA and Zn²⁺, Cd²⁺ and Pb²⁺ doped LTMA

3.5. Optical Studies:

3.5.1. UV- Absorption & Transmittance analysis

UV-Visible spectrum is the tracing of the penetration of the light beam when it passes through a powder or when getting reflection on sample surface. The optical transmission spectra are recorded for polished plates of grown crystals using VARIAN CARY 5E UV-Vis-NIR Spectrophotometer. The spectrophotometer makes the monochromatic beam which resolves radiation into its relating wavelengths, samples occupation and also detector which ensures the amount of beam transited on the sample. Two light sources are used to cover entire range of spectrum from 200-2500 nm. A straightened bandwidth was selected using with band pass filters. Then the radiation was repeatedly passed with the cells of the given phenomenon alternatively and respectively. This double beam process eliminates that the fluctuations on intensity of scattering radiation and solvent effects. The two rays were combined and differences in intensities of those two radiations are measured electrically. The displacement of the monochromator and the recorder were compiled and adjusted to that the recording the maximum effectual light

of appropriate radiation. The transmission study aimed to recording the insensible beam in terms of percentage of transmittance along with Y-axis and related the wavelength (nm) along X-axis. The UV-Visible spectrum implies that the information as the useful range of wavelength in which the NLO materials has been obtain. The recorded UV-transmittance plots of Pure and doped LTMA crystals were shown in Fig. 5. Observed transmittance spectrum is well cutoff for both pure and doped crystals which conclude as ignoring of NLO property material. UV absorption plot shows that the lower cut off λ 267 nm and around 200 nm for Pure and doped crystals respectively. The lower cut-off λ resulted that the very clear transparency, implies the use of material as electro optical devices, because the lower cutoff wavelength is 200nm and this character easily causes the NLO nature [25]. The energy band gap is calculated using the formula for pure crystal as 4.6eV and for the Zn²⁺, Cd²⁺ and Pb²⁺ doped crystal as 6.3eV, 6.45eV and 6.5eV as shown in fig 6.

$$E_g = 1240/\lambda \quad (3)$$

Table 10 FTIR Spectral Assignment of Pure LTMA and Zn²⁺, Cd²⁺ and Pb²⁺ doped LTMA Single Crystals

Wavenumber	Pure L-Threonine [Reported 14]	Pure LTMA	Zn ²⁺ doped LTMA	Cd ²⁺ doped LTMA	Pb ²⁺ doped LTMA	Assignment
-		3169.25	3168.09	3167.43	3171	NH ₃ ⁺ asymmetric stretching
-		3029.80	3028.32	3027.75	3028.16	NH ₃ ⁺ symmetric stretching
1625.99		1629.28	1627.65	1628.20	1634	NH ₃ ⁺ asymmetric deformation
1417		1417.94	1417.16	1417.01	1413	NH ₃ ⁺ symmetric deformation
1346.48		1346.04	1345.48	1345.17	1343	CH symmetric deformation
--		1113.14	1112.73	1112.90	1112	NH ₃ ⁺ Rocking
1040.52		1040.72	1040.89	1040.62	1051	C-N Rocking
931.50		932.53	932.33	932.31	921	C-C Rocking
871.09		871.20	870.76	870.92	871.29	C-C-N Rocking
767.90		769.77	769.12	769.20	769.05	COO ⁻ Bending
701.52		701.35	701.10	701.16	700	COO ⁻ wagging vibration
560.19 C		560.11	559.90	559.85	549	COO ⁻ Rocking Deformation
489.64		489.82	489.30	489.75	490.02	NH ₃ ⁺ Bending
-		445.18	444.79	445.36	445.89	In plan OCO Rocking

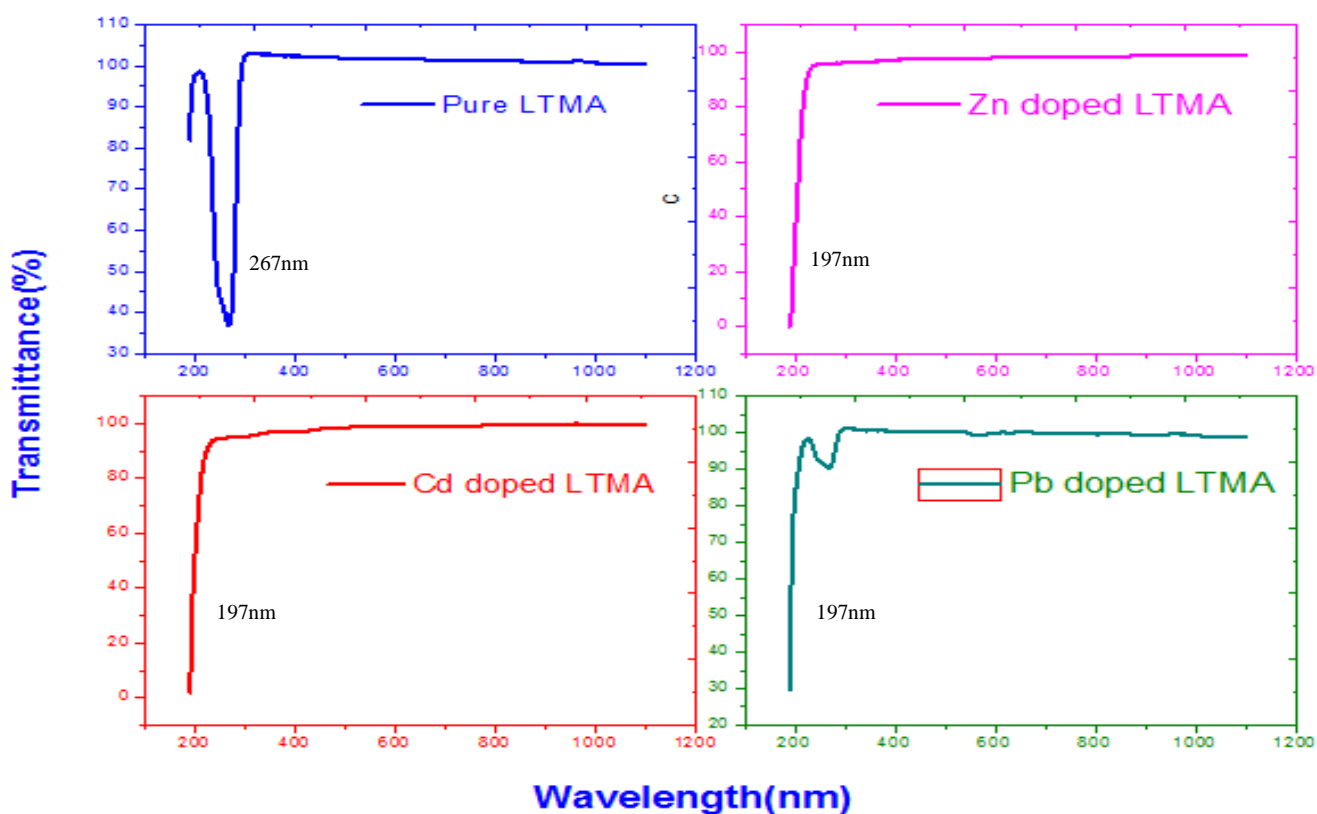


Fig. 8 The UV-Visible Transmittance Spectra of Pure and Zn²⁺, Cd²⁺ and Pb²⁺ doped LTMA

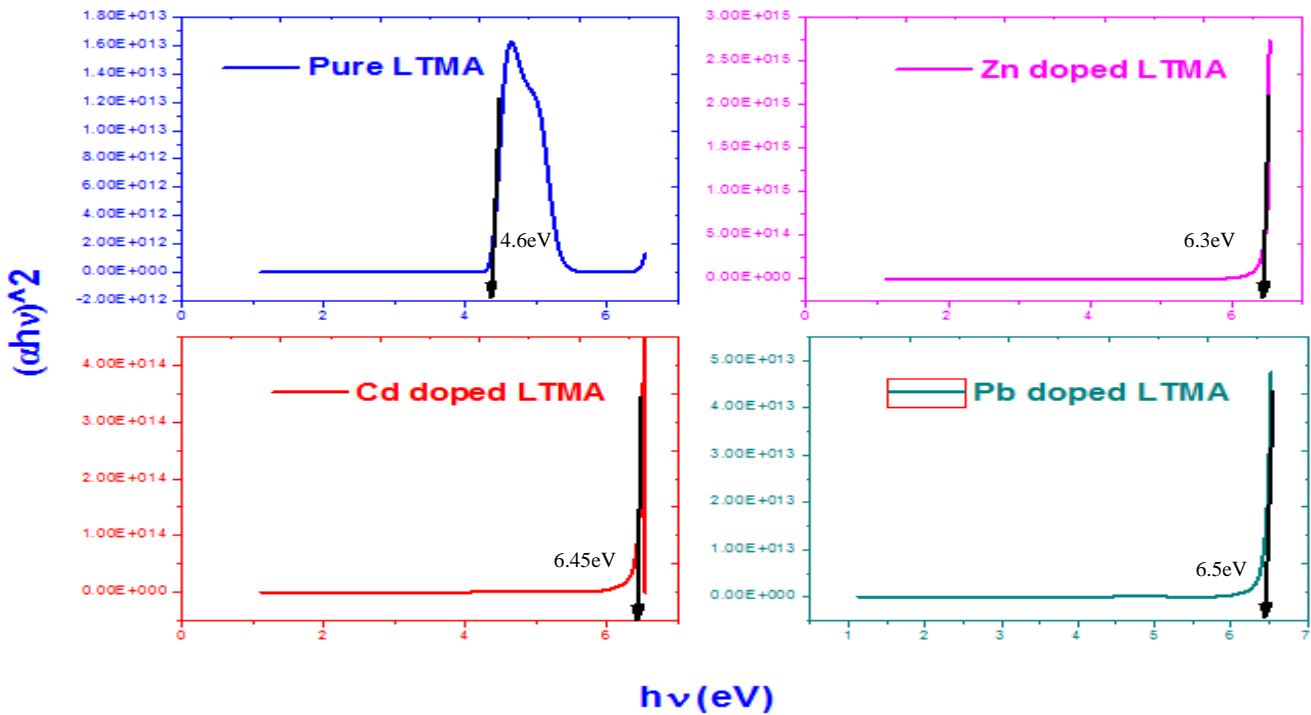


Fig. 9 Energy band gap Spectra of Pure and Zn²⁺, Cd²⁺ and Pb²⁺ doped LTMA

3.6 Vicker’s Microhardness Analysis

Microhardness study was obtained for determining the roughness of the all the grown crystals with HMT 2T, SHIMADZU. The indentation mark is determined on the all crystals at 30°C by applying load 25gm, 50gm and 100 gm. The hardness value H_v was determined as increases with the increase in mechanical stress applied from 25gm to 100 gm and crack resulted at higher loads. Vicker’s microhardness number H_v of the crystals was calculated using the following equation

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

Where, H_v - Vicker’s hardness number in kg/mm², P - mechanical stress and d - average diagonal distance of the indentation. From the graph, observed that the hardness value of all the doping crystals increased with small bends up to 100 gm. So, all the hardness numbers of Zn²⁺, Cd²⁺ and Pb²⁺ doped LTMA material increased and the datas are reported in Table 11.

Table 11 Hardness values of Pure LTMA and doped LTMA Single Crystals

Load (gm)	P	Hardness (H _v)			
		Pure LTMA	Zn ²⁺ doped LTMA	Cd ²⁺ doped LTMA	Pb ²⁺ doped LTMA
25	37	29.34	27.6	29.85	
50	50.8	40.8	30.2	49.65	
100	80.5	57.7	43.35	78.6	

3.7. Photoluminescence Study (PL)

The grown pure LTMA and 0.2M of Zn²⁺ doped LTMA, Cd²⁺ doped LTMA, Pb²⁺ doped LTMA crystals resulted that under situated to PL Study, it (Fig.10) reveals that the Emission spectrum at 486.96nm as respectively.

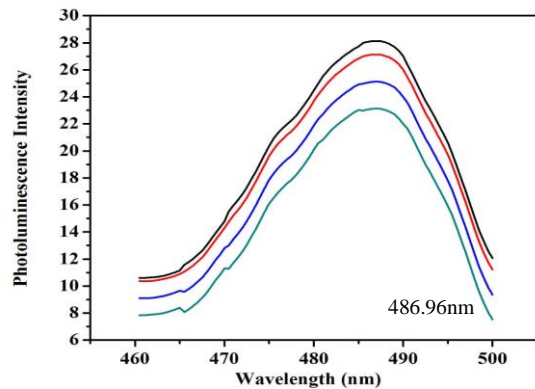


Fig. 10 PL spectrum of Pure and doped LTMA crystal.

4. Conclusions

Novel Single crystals of undoped and inner doped L-Threonine Manganese Acetate were effectively developed with spontaneous evaporation. Single precious crystal study examines structure of the all the crystals becomes

Orthorhombic and has bigger volume from 530\AA^3 to 540.8\AA^3 . The powder diffraction examinations were done the crystallinity contrasts between the unadulterated and inner doped LTMA single crystal. EDAX study affirmed the presence of the dopant Mn in Pure LTMA and Zn, Cd and Pb in doped Crystal. UV-study found the unadulterated and all the doped crystals have wide straightforwardness in entire noticeable area and utilizing with their vitality band holes 4.6eV and 6.3eV, 6.45eV and 6.5V were resolved. FTIR considers uncover that the nearness of utilitarian gatherings in the crystals. The enormous changes in mechanical quality of the pure and doped crystals were concentrated by Vicker's Micro hardness analyzer. PL emission spectrum wave length 486.96nm of Pure and doped LTMA crystal also determined

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