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Research Article

GROWTH AND CHARACTERIZATION OF MANGANESE DOPED AND UNDOPED CALCIUM OXALATE MONOHYDRATE CRYSTAL

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ABSTRACT

Urinary stone disease is one of the major diseases in the human history. The human urinary calculi are mainly formed from calcium oxalate, Struvite and uric acid crystals. It is important for the physician and surgeon to distinguish the two types of hydrates of calcium oxalate mainly mono and di-hydrate. Manganese doped Calcium Oxalate Monohydrate (MnCaOxM) crystals were grown by silica gel method. Manganese is a trace mineral that is present in tiny amounts in the body. It is found mostly in bones and blood clotting factors. It is also plays a role in fat and carbohydrate metabolism. Manganese is also necessary for normal brain and nerve function. The grown crystals were characterized by FTIR, FT-Raman XRD, SEM-EDX, TGA/DTA analysis and UV-Visible analysis.

INTRODUCTION

Calcium stones are most generally occurring form of nephrolithiasis or urinary stones, which is one of the oldest and common afflictions of humans. All over the world, 12% of the world population was suffering from such urinary stone problem due to global warming , life style and food habits(1). Not only humans, but animals and birds are also suffering from this urinary stone problem (2). Calcium oxalate may be found in the deposit from both acid and alkaline urines. Calcium Oxalate has low solubility in water and crystallizes in 3 hydrated form, Calcium Oxalate Monohydrate (COM), Calcium Oxalate Di-hydrate (COD) and Calcium Oxalate Tri-hydrate (COT) (3-5). Among these, COD and COT are difficult to form urinary stones because they are unstable and easy to eject from body along with the urine (6). However, COM is the most thermodynamically stable form of Calcium oxalate and occupies the biggest proportion of all the urinary stones (7-9). A number of foods particularly some fruits and vegetables contain oxalates, notable among these being rhubarb, spinach, sweet potatoes, and strawberries. Sometimes tiny stones may be flushed out of the body with urine without causing too much pain. Manganese is very important for the normal functioning of the brain and proper activity of our nervous system throughout the body. It is a powerful antioxidant.

Figure 1 a Growth of undoped CaOxM crystal

Figure 1 b Growth of undoped CaOxM crystal

Figure 1 c Growth of MnCaOxM crystal

Figure 1 d MnCaOxM crystal

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Manganese is an actual component of manganese super oxide dismutase enzyme. Gel method is the most powerful method and easily technique for growing urinary crystals (10). In the present work, manganese doped and undoped Calcium Oxalate Monohydrate crystals were grown in silica gel at ambient temperature and were characterized by FTIR, FT-Raman, XRD, SEM-EDX , TG/DTA analysis and UV-Visible analysis.

MATERIAL AND METHODS

The growth of manganese doped and undoped calcium oxalate monohydrate crystal was carried out in silica gel. All the chemicals used in this experiment are of AR grade. The borosilicate glass test tubes of 2.5cm diameter and 20cm length were used as crystallizing vessels. In a single diffusion gel method, gel was set by mixing sodium meta silicate solution of density 1.03g/cm^{-3} was adjusted to a PH of 6 by adding 5% glacial acetic acid (11). Calcium chloride (0.1M) and manganese chloride (0.001M) one of the reactants was incorporated inside the gel. After the gel was set an aqueous solution of oxalic acid solution was carefully poured along the walls of the tube with the help of pipette over the set gel, after the gel setting with few days white column of tiny crystals. The growth was completed within a period of 21 days were grown which are as shown in Fig 1(a) and 1(b).The harvested manganese doped and undoped crystals are as shown in Fig.1(c) and 1(d). The harvested crystals are characterised by FTIR, FT-Raman, XRD, SEM-EDX, TGA/DTA analysis and UV-Visible analysis.

Characterization Techniques

FTIR spectrum is recorded by KBr pellet method using Perkin Elmer FTIR spectrometer with the range 4000-400cm^{-1} is available at Centralised Instrumentation Science Laboratory, Department of Physics, St. Joseph College, Tiruchirappalli. Powder X-ray diffraction of the samples are carried out by EXPERT-PRO with CuKα radiation (λ=1.5418A^{o}) is available at Department of Physics, Alagappa University, Karaikkudi. The morphology of MnCaOxM crystal was studied by JEOL, JSM 6390 and the presence of elemental composition was calculated by OXFORD instruments, TINCA Pental FETX3 EDX method is available at Karunya University, Coimbatore. The TGA/DTA analysis obtained by NETZSCH STA 449F3 heating sample from room temperature to 600^{0}C in an atmosphere of nitrogen with heating rate of standard procedure. Absorption spectrum of undoped and doped MnCaOxM crystals were recorded using a UV-2400 PC Series UV-Visible spectrophotometer over the wavelength range 200nm to 900nm at Science Instrumentation Centre, Department of Physics, Standard Fire Rajarathnam Women's College, Sivakasi.

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy Analysis

The FTIR analysis is a technique that provides information about the chemical bonding or molecular structure of materials. The FTIR spectra of Manganese doped and undoped calcium oxalate monohydrate crystals as shown in fig2 (a) and 2(b). FTIR vibration assignments of Manganese doped and undoped calcium oxalate monohydrate crystals are tabulated in table.1.

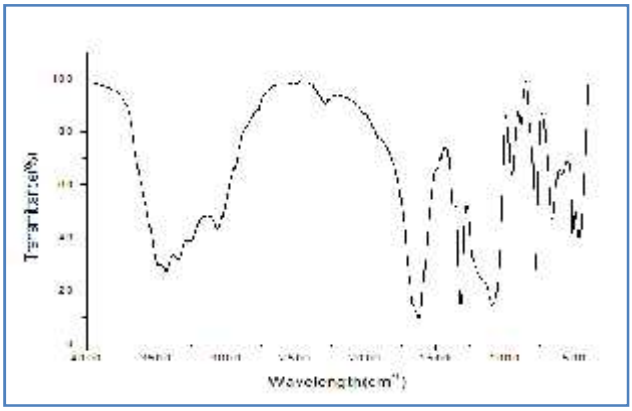

Figure 2 a FT-IR spectrum of undoped calcium oxalate monohydrate crystals

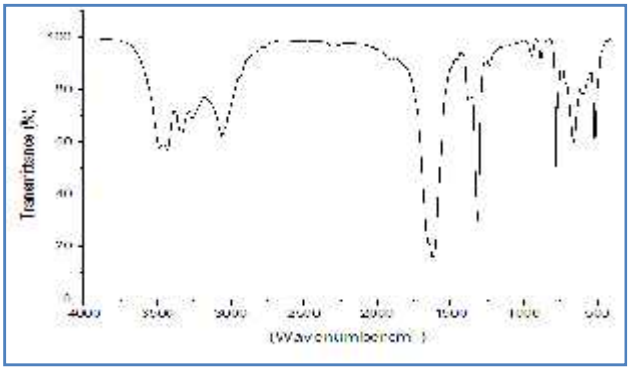

Figure 2 b FT-IR Spectrum of Manganese doped calcium oxalate monohydrate crystals

In FTIR spectrum, a strong band at 3433cm^{-1}, 3431cm^{-1} and 3063cm^{-1}, 3062cm^{-1} is due to asymmetric and symmetric OH stretching while an intense absorptions band at 3260cm^{-1} 3262cm^{-1} show inter molecular hydrogen bonded OH stretch. Intense absorption band at 1621cm^{-1} ,1622cm^{-1} and 1318cm^{-1} , 1318 cm^{-1} can be assigned to asymmetric and symmetric C=O stretching bands specific to the Calcium oxalate monohydrate. The sharp band at 885cm^{-1}, 885cm $^{-1}$ is due to C-C stretching vibrations which confirm the existence of oxalate group in Calcium oxalate monohydrate. The sharp peak at 781cm^{-1}, 781cm^{-1} is due to O-C=O and the wideband at 665cm^{-1} , 665cm^{-1} can be assigned to the bending modes of the water molecule.

Table 1 FTIR wave numbers and vibrations assignment of manganese doped and undoped calcium oxalate monohydrate crystals

Pure calcium oxalate wavenumber in cm^{-1}	Manganese doped calcium oxalate cm^{-1}	Vibrational band assignment
3431	3433	Asymmetric OH stretch
3063	3062	Symmetric OH stretch
3262	3260	Inter molecule H_2 bonded OH stretch
1621	1622	Asymmetric C=O stretch
1318	1318	Symmetric C=O stretch
1092	1097	Asymmetric C-O stretch
951	950	Symmetric C-O stretch
886	885	C-C stretch
781	781	O-C=O stretch
662	665	OH wagging
516	517	M-O bond

However, the peak at 517cm^{-1}, 518cm $^{-1}$ is assigned to the presence of metal-oxygen bond (11-14).

Thus FTIR reveals that the growth of COM crystals was due to the presence of O-H stretching, C=O, C-C, O-C=O and M=O bonds.

There are some additional peaks formed due to the process of doping some absorption peaks due to OH vibrations are changed because of the incorporation of dopant in the lattice. In the case of MnCaoxM crystals additional peaks are found at 1239cm^{-1} which are attributed to the C=O stretching. These peaks are found to be present in the spectrum of MnCaoxM confirms the presence of the element Manganese.

FT-Raman Analysis

FT- Raman spectra of the undoped and manganese doped calcium oxalate monohydrate crystals as shown in fig 3 (a) and (b). Table 2 shows the vibration assignment of undoped and manganese doped calcium oxalate monohydrate crystals.

Table 2 FT-Raman vibration assignment of undoped and manganese doped calcium oxalate monohydrate crystals

Pure calcium oxalate wave number in cm^{-1}	Manganese doped calcium oxalate cm^{-1}	Vibrational band assignment
3189	3193	OH stretching
3048	3102	OH stretching
2828	2822	CH_3 stretching
2721	2708	CH stretching
2223	2219	CH stretching
2181	2173	Stretching vibration of C-C
1895	1850	Stretching vibration of C-C
1722	1726	Stretching vibration of C-O
1628	1629	C-O stretching
1487	1486	Vibration of C-O
1461	1462	Vibration of C-O
892	894	C-C stretching
592	595	Phosphate bands
501	503	O-C-O in plane bending

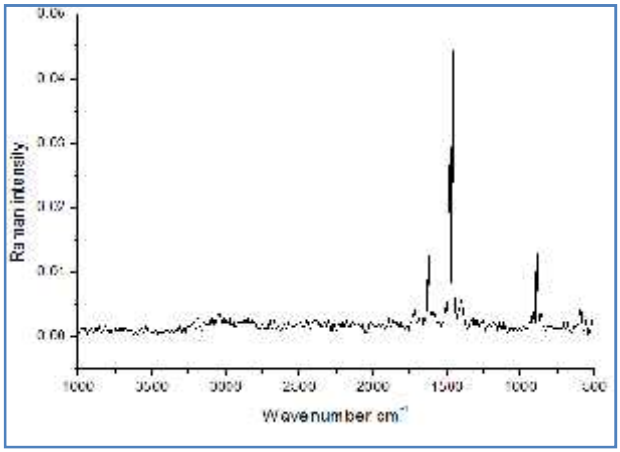

Figure 3 (a) FT-Raman analysis of undoped calcium oxalate monohydrate crystals.

The absorptions at 3189cm^{-1} , 3193cm^{-1} and 3048cm^{-1}, 3102cm^{-1} are due to O-H stretching. The sharp bands at 1461cm^{-1},1462cm^{-1} are due to C=O vibration and 1487cm^{-1},1486cm^{-1} are due to C-O symmetric stretching. The less intense1628cm^{-1}, 1629cm^{-1} band is due to the C-O asymmetric stretching and the 892cm^{-1}, 894cm^{-1} band due to C- C stretching. The weak bands around at 501cm-1, 503cm-1 are due to O-C-O plane bending of undoped and manganese doped calcium oxalate monohydrate (15, 16).

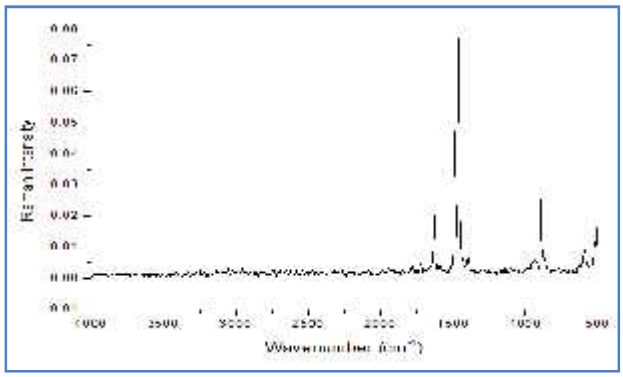

Figure 3 (b) FT-Raman analysis of manganese doped calcium oxalate monohydrate crystals.

XRD Analysis

The powder XRD pattern was recorded using diffractometer system =EXPERT-PRO X-ray diffractometer with CuKα radiation (λ =1.546A^0). The powder sample was scanned over the range 20^0 to 80^0 in at a rate of 1^0 per minute. The XRD analysis of the grown COM crystals was matched with the reported database using computer with PAN analytical software and result was matched with JCPDS File (14-0789) (17). The indexed powder data for the undoped and Manganese doped calcium oxalate monohydrate crystals are presented in table 2. From the collected XRD data, it is observed that from the cell parameters of both pure Calcium oxalate and Manganese doped Calcium oxalate belong to monoclinic system.

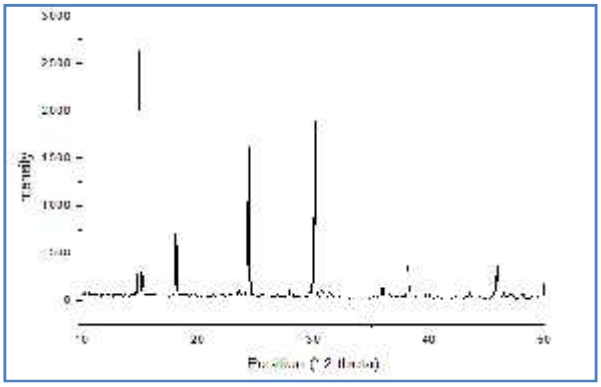

Figure 4 a X-ray diffraction analysis of undoped calcium oxalate monohydrate crystals

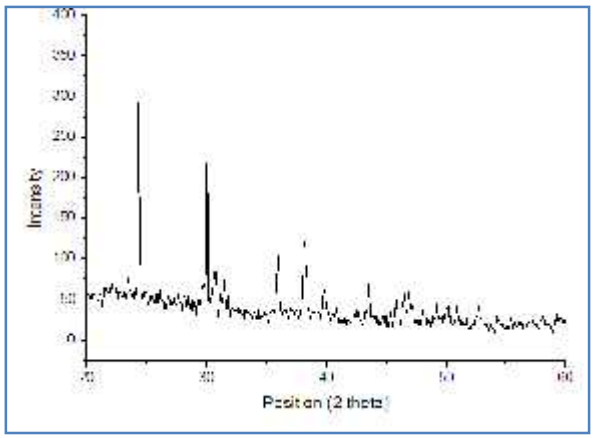

Figure 4 b X-ray diffraction analysis of manganese doped Calcium oxalate monohydrate crystals.

Table 3 (a) XRD analysis of undoped Calcium oxalate monohydrate crystals

Std value			Observed value			hkl value
2	I/I_0	d-space	2	I/I_0	d-space	
14.927	100	5.94	14.886	100	5.95	-101
15.290	60	5.79	15.259	19	5.80	011
23.516	40	3.78	23.527	11	3.78	-112
24.366	100	3.65	24.366	63	3.65	020
30.084	80	2.96	30.075	66	2.97	-202
31.440	40	2.84	31.679	14	2.82	121
35.965	20	2.49	35.943	16	2.49	211
37.136	20	2.41	37.297	2	2.41	-213
38.150	60	2.35	38.184	28	2.35	031
39.782	40	2.26	39.833	11	2.26	014
40.796	40	2.21	40.763	6	2.21	-204
43.560	60	2.07	43.588	10	2.07	123
45.837	60	1.97	45.855	14	1.97	-303
46.509	40	1.95	46.496	10	1.95	132
46.963	40	1.94	46.959	9	1.93	222
48.076	40	1.89	48.064	4	1.89	230

Table 3 b XRD analysis of manganese doped calcium oxalate monohydrate crystals

Observed value		Std value		Observed value	Std value d-spacing	hkl value
2	I/I_0	2	I/I_0			
14.828	100	14.92	100	5.97	5.93	-101
15.183	30	15.29	60	5.83	5.79	011
24.420	96	24.36	100	3.65	3.65	020
30.038	69	30.08	80	2.97	2.96	021
30.679	18	30.61	40	2.91	2.91	102
31.466	16	31.43	40	2.84	2.84	121
35.918	27	35.96	60	2.50	2.52	103
38.150	29	38.14	60	2.35	2.35	113
39.812	12	39.78	40	2.26	2.26	031
40.768	7	40.79	40	2.21	2.23	014
41.499	4	42.37	20	2.12	2.13	-132
43.559	11	43.55	60	2.07	2.07	123
45.792	15	45.83	60	1.98	1.99	024
46.790	6	46.96	40	1.94	1.95	114
49.213	6	49.32	6	1.84	1.89	230
50.126	6	50.28	4	1.81	1.81	-123
50.872	5	50.88	6	1.79	1.79	132

The peaks in the XRD patterns which were obtained in the present work are slightly shifted due to the addition of dopants which indicates that the dopants have entered into the lattice of the crystal. It is seen that the x-ray pattern is almost similar indicating the presence of Manganese has not affected the crystalline nature of the sample.

Scanning Electron Microscope and Energy Dispersive X-ray Analysis

The SEM studies of the crystal give valuable information about its internal structure. The morphology of the crystal was studied by Scanning Electron Microscope (SEM). Fig .5(a) and (b) shows a single monoclinic pyramidal morphology was observed (18).

Energy Dispersive X-ray Analysis

The elemental composition of the sample was identified using energy dispersive X-ray analysis. The manganese doped calcium oxalate crystals are as shown in Fig 6. The higher peaks of Ca, O and manganese show that these are more concentrated element in the fig 6(b).

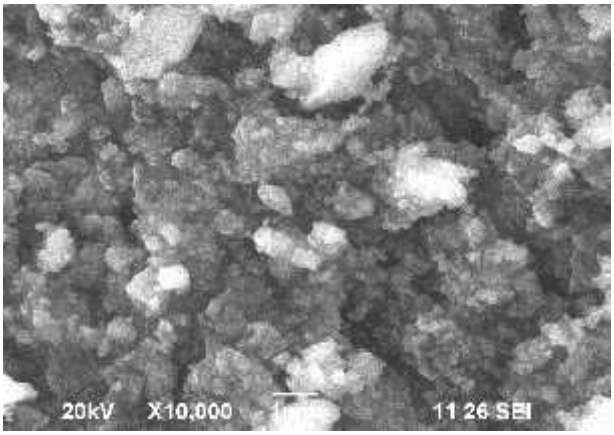

Figure 5 a SEM images of undoped calcium oxalate monohydrate crystals

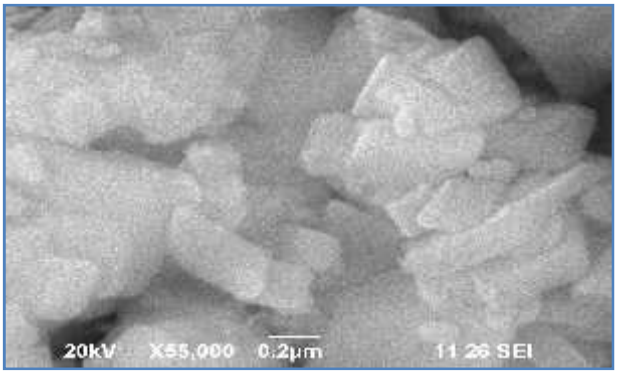

Figure 5 b SEM images of manganese doped calcium oxalate crystals

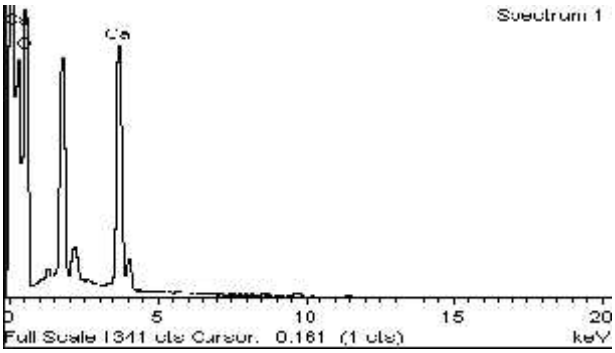

Figure 6 a EDX spectrum of undoped calcium oxalate monohydrate crystals

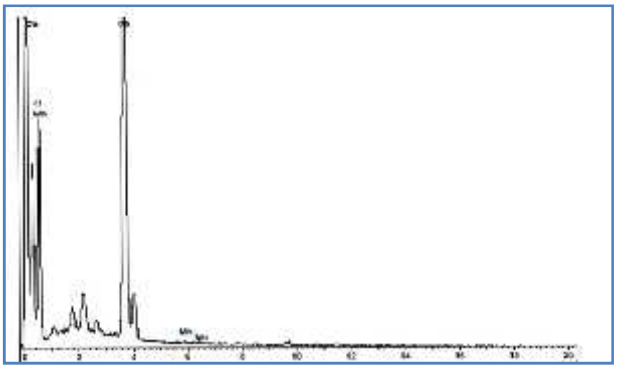

Figure 6 b EDX spectrum of manganese doped calcium oxalate monohydrate crystals

Table 4 a EDX analysis of undoped calcium oxalate monohydrate crystals

Element	Atomic weight%	Mass weight%
O	91.37	80.86
Ca	8.63	19.14
Total	**100**	**100**

Table4. b EDX analysis of manganese doped calcium oxalate monohydrate crystals

Element	Atomic weight%	Mass weight%
O	72.62	87.51
Ca	26.18	12.42
Mn	1.20	0.07
Total	**100**	**100**

Thermal analysis of pure and manganese doped calcium oxalate monohydrate crystals

TGA/DTA curves recorded for pure and manganese doped calcium oxalate monohydrate crystal as shown in fig 7(a), and 7(b). The loss of water crystallization in first step, carbon monoxide in second step, and carbon-di-oxide in third step. The undoped sample and manganese doped calcium oxalate monohydrate sample the weight loss occur in three stages.

In the first stage weight loss of about 3% occurs between 200^0C-140^0C which indicates the loss of water hydration. In the second stage weight loss about 15.15% occurred at temperature range between 140^0C-240^0C corresponding to dehydration of sample in first stage. In the third stage weight loss of 20% was observed 240^0C-510 ^{0}C the decomposition of calcium oxalate monohydrate with releasing of Co_2. It is observed that there are two endothermic peaks at 240^0C and 520^0C. The endothermic peak corresponds to formation of calcium oxalate monohydrate compound. The two exothermic peaks are observed 180^0C and 480^c C (19).

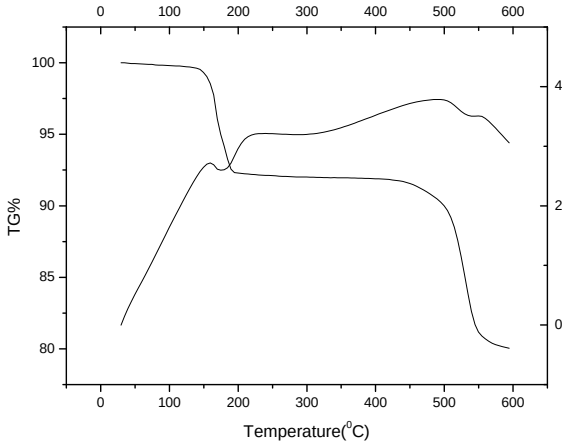

Figure 7 (a) Thermogram of the calcium oxalate monohydrate crystals

In the first stage weight loss of about 3% occurs between 20^0C-160^0C which indicates the loss of water hydration. In the second stage weight loss about 10% occurred at temperature range between 160^0C -240^0C corresponding to dehydration of sample in first stage. In the third stage weight loss of 18% was observed 400^0C-500^0C. The de composition of calcium oxalate monohydrate with releasing of Co_2. It is observed that there are two endothermic peaks at 220^0C and 480^0C. The endothermic peaks correspond to formation of calcium oxalate monohydrate compound. The two exothermic peaks are observed 180^0C and 520^0C. Thus there is a decrease in the peak temperature which indicates a reduced thermal stability of calcium oxalate monohydrate due to manganese doping.

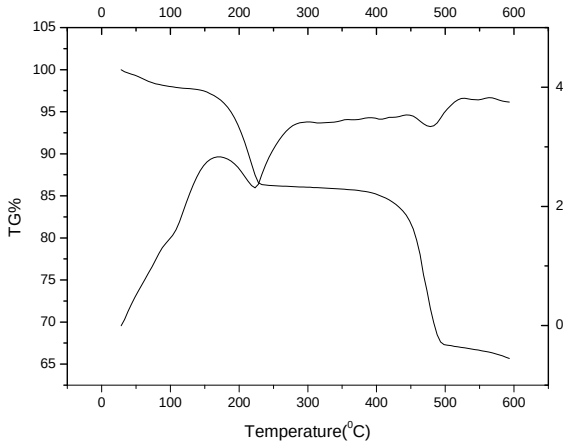

Figure 7 b Thermogram of the manganese doped calcium oxalate

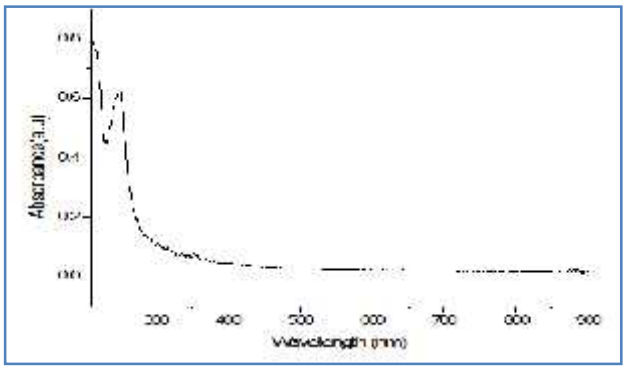

Figure 8 a UV-Visible analysis of undoped calcium oxalate monohydrate crystals

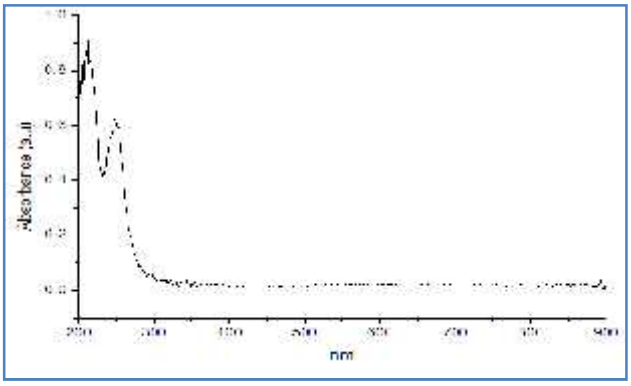

Figure 8 b UV-Visible analysis of manganese doped calcium oxalate crystals

UV-Visible Analysis

The recorded optical absorption spectra of the undoped and manganese doped calcium oxalate monohydrate crystals in the wavelength range 200-900 nm is shown in Fig. 7(a) and (b). It is inferred from the spectra that the grown crystals have low absorbance in the entire UV-Visible region considered and the cut off wavelength is around 246, 247 nm, closer to UV range.

The spectrum further indicates that the crystal has a wide optical transmission window range from 250nm. The presence of lower cut off wavelength and the wide optical transmission window range are the most desirous properties of materials possessing NLO activity (20).

CONCLUSION

Single diffusion gel method is suitable for manganese doped calcium oxalate monohydrate crystals. XRD data proves the crystalline of the samples. The presence of manganese in the grown crystals was identified by FTIR studies. The SEM image shows surface morphology of the crystals. The EDX confirmed the doping of manganese on calcium oxalate monohydrate. The thermal stability was studied by the TGA/DTA analysis. The optical properties were determined by UV-Visible analysis.

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