



GROWTH AND CHARACTERIZATION OF PURE AND BARIUM DOPED CALCIUM OXALATE MONOHYDRATE CRYSTALS

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ABSTRACT

Calcium stones are most commonly occurring form of nephrolithiasis or urinary stones, which is one of the oldest and common afflictions of humans. The usual components of urinary crystals such as brushite, struvite, Calcium oxalate monohydrate, hydroxyapatite, uric acid, and cystine etc. The calcium oxalate crystals were grown by single diffusion gel growth technique in sodium meta silicate gel. In the present work the growth and characterisation of pure and barium doped calcium oxalate monohydrate crystals. The grown crystals were characterized by FTIR, FT-Raman, XRD, SEM-EDX, TG/DTA analysis and UV-Visible analysis.

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INTRODUCTION

The formation of urinary calculi is known as nephrolithiasis, urinary calculi affected to many people in various age groups in this globe. A large number of people are affected from the due to urinary stones disease in different countries in the world. There are many areas of high incidence of urinary calculi which include British Isles, Scandinavian Countries, northern Australia, central Europe, and northern India, and Pakistan and Mediterranean countries (1-3). Calcium containing stones are the most common comprising about 75% of all urinary calculi which may be in the form of pure calcium oxalate (COM) or whewellite and calcium oxalate dehydrate (COD) or weddellite. Urolithiasis is a very painful disease that has afflicted a wide sector of human population since ancient times (4). Several reporters have attempted to grow Calcium oxalate monohydrate crystals by gel growth method (5). Many factors affect the growth of urinary calculi. Different mineral metabolisms are important role in the formation of urinary stones of calculi (6). COM is the most thermodynamically stable form of calcium oxalate and occupies in biggest proportion of all the urinary stones (7-8). In the present work, the in-vitro growth of pure Calcium oxalate monohydrate (CaOxM) and barium doped calcium oxalate monohydrate (BaCaOxM) crystal by single diffusion gel growth method in silica gel medium.

The harvested crystals are studied by FTIR, FT-Raman, XRD, SEM-EDX, TGA/DTA analysis and UV-Visible analysis.

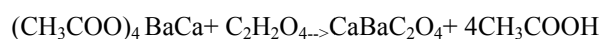
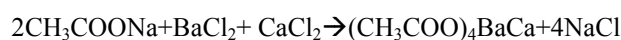
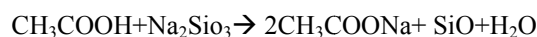
MATERIALS AND METHODS

Crystal growth

The single diffusion gel growth method was used to grow calcium oxalate monohydrate crystal. Distilled water and AR grade chemicals were used to grow the crystals.

The glass test tubes of 25mm diameter and 150 mm length were used as crystallizing vessels. Sodium meta silicate of 1.03 specific gravity was used to prepare gel. The sodium meta silicate solution was mixed with 5% acetic acid and PH is adjusted to 6. One of the reactant calcium chloride and barium chloride is incorporated inside the gel (9). After setting the gel, an aqueous solution of oxalic acid was slowly poured over it. Immediately a white column of tiny crystals were grown, which are shown in Fig1 (a), 1(b), 1(c), and 1(d).

The chemical reaction between calcium chloride and barium chloride and oxalic acid in gel medium resulted in the growth of Barium doped with Calcium oxalate monohydrate crystals.



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Fig. 1a Growth of pure CaOxM crystal



Fig. 1 b Growth of pure CaOxM crystal



Fig.1 c Growth of BaCaOxM crystal



Fig.1 d BaCaOxM crystal

Table.1 The optimum condition for the growth of barium calcium oxalate crystals

S. No	Parameters	Optimum Condition
1	Density of sodium meta silicate	1.03gm/cm ³
2	PH of gel	6
3	Concentration of CaCl ₂	1 Mole
4	Concentration of BaCl ₂	0.1Mole
5	Concentration of C ₂ H ₂ O ₄	1 Mole
6	Gel setting period	2 days
7	Gel aging	1 month
8	Period of growth	21 days
9	Temperature	Room temperature

Characterization Techniques

FTIR spectra is recorded by KBr pellet technique 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 CuK α radiation ($\lambda=1.5418\text{\AA}$) is available at Department of physics, Alagappa University, Karaikudi. The surface morphology of pure and Barium doped Calcium oxalate monohydrate crystal was studied by JEOL, JSM 6390 SEM 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°C in an atmosphere of nitrogen with heating rate of standard procedure. Absorption spectra of pure and Barium Calcium oxalate monohydrate crystals were recorded using a UV-2400 PC Series UV-Visible spectrophotometer wavelength range 200nm to 900nm at Science Instrumentation centre, Department of Physics, standard Fire Rajarathnam Women’s College, Sivakasi. FT-Raman spectra were recorded in the range of 4000cm⁻¹ to 400cm⁻¹ using BRUCKER, Model RFS 27. FT-Raman spectrometer which is available at Sophisticated Analytical Instrument Facility (SAIF), Indian Institute of Technology(IIT), Chennai, Tamilnadu, South India.

RESULTS AND DISCUSSION

The single diffusion gel growth technique is found to be simple method to grow pure and barium doped with Calcium oxalate monohydrate crystals.

FT-IR analysis on pure and doped with calcium oxalate monohydrate crystal analysis

The FTIR spectra of pure and barium doped with calcium oxalate monohydrate crystal as shown in Fig 2 (a) and 2(b) FT-IR assignments of pure and barium doped calcium oxalate monohydrate crystals are listed in table 2.

Table.2 FTIR wave numbers and vibrations assignments of barium doped calcium oxalate monohydrate crystals

Pure calcium oxalate monohydrate wave number in cm ⁻¹	Barium doped calcium oxalate monohydrate wave number in cm ⁻¹	Vibration band assignments
3431	3423	Asymmetric OH stretch
3063	3058	Symmetric OH stretch
3262	3256	Inter molecule H ₂ bonded OH stretch
1621	1620	Asymmetric C=O stretch
1318	1323	Symmetric C=O stretch
1092	1098	Asymmetric C-O stretch
951	950	Symmetric C-O stretch
886	888	C-C stretch
781	786	O-C=O stretch
662	663	OH wagging
516	520	M-O bond

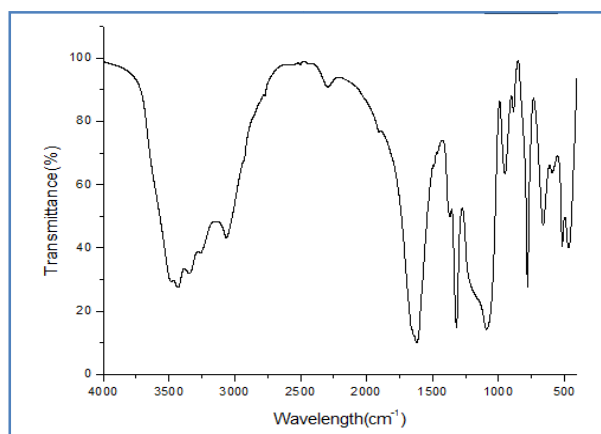


Fig.2 a FT-IR spectrum of pure Calcium oxalate monohydrate crystals

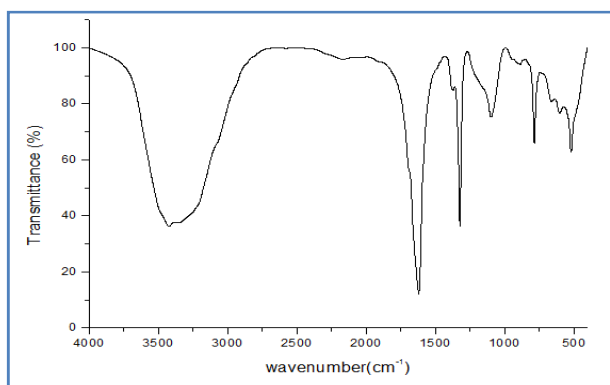


Fig 2 b FT-IR spectrum of Barium doped Calcium oxalate monohydrate crystals.

The absorption peaks at 3431cm^{-1} , 3423cm^{-1} , 3063cm^{-1} , 3058cm^{-1} are due to O-H stretching vibration respectively. 1621cm^{-1} , 1620cm^{-1} , 1323cm^{-1} , 1318cm^{-1} and 1098cm^{-1} , 1092cm^{-1} are due to C=O stretching vibrations. 951cm^{-1} and 950cm^{-1} are due to symmetric C-O stretching vibration. 888cm^{-1} , 886cm^{-1} and 786cm^{-1} , 781cm^{-1} are due to C-C and O-C=O stretching. 520cm^{-1} and 516cm^{-1} is due to presence of metal-oxygen bond (10).

The barium doped with calcium oxalate monohydrate crystals is more when compared to pure calcium oxalate monohydrate crystals with slight change in frequencies and intensities.

Powder X-ray Diffraction analysis

The powder XRD pattern was recorded using diffractometer system= EXPERT PRO X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.5418\text{\AA}$). The powder sample was scanned over the range 10° to 60° in a rate 1° per minute.

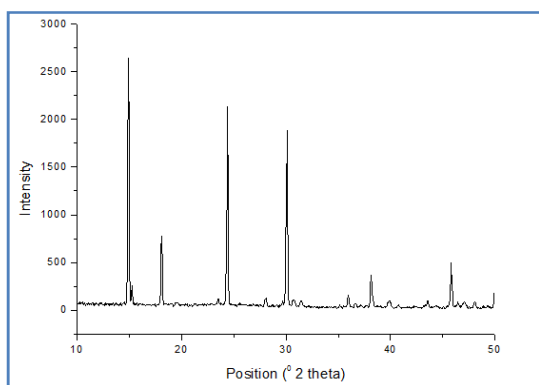


Fig. 3 a X-ray diffraction analysis of pure Calcium oxalate monohydrate crystals

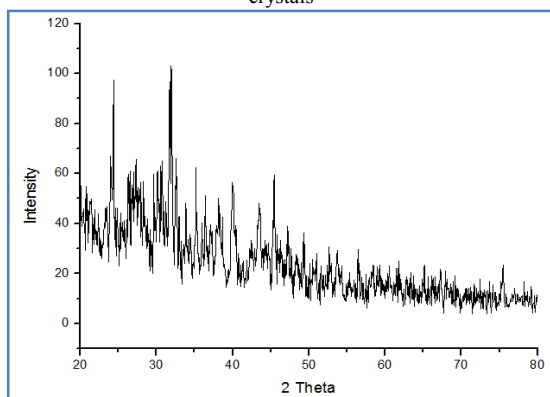


Fig. 3 b X-ray diffraction analysis of barium doped calcium oxalate monohydrate crystals

Table 3a XRD analysis of pure Calcium oxalate monohydrate crystals

Std value			Observed value			hkl value
2θ	I/I_0	d-space	2θ	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 barium doped calcium oxalate monohydrate crystals

Std value			Observed value			hkl value
2θ	I/I_0	d-space	2θ	I/I_0	d-space	
14.927	100	5.93	14.903	100	5.93	-101
19.579	40	4.48	19.799	60.34	4.52	101
24.365	70	3.62	24.366	92.99	3.65	020
29.679	40	2.96	29.994	48.84	2.96	112
31.439	40	2.84	31.839	91.99	2.84	121
35.964	60	2.52	35.216	53.59	2.52	103
38.348	60	2.38	38.215	40.42	2.38	031
39.964	20	2.26	39.943	55.64	2.26	130
43.558	60	2.09	43.499	44.87	2.09	123
45.837	60	1.99	45.428	65.80	1.99	024
49.302	6	1.84	49.275	32.55	1.84	-510
53.747	2	1.70	53.905	11.78	1.70	240

The powder XRD pattern of pure and barium doped calcium oxalate monohydrate crystals as shown in fig 4 (a) and (b) table 4 and 5 gives the data. The data confirm the presence of calcium oxalate monohydrate crystal in the form of whewellite CaOx vide JCPDS card (14-0789) (11). The results confirm the purity and crystalline nature form. The calcium oxalate monohydrate crystal system is monoclinic. The lattice parameters of the calcium oxalate monohydrate crystal is $a=6.30$, $b=7.287$ and $c=9.96$ respectively.

The samples are highly crystalline in nature. From the collected XRD data, it is observed that from the cell parameters of both pure calcium oxalate and barium doped calcium oxalate monohydrate crystal belong to monoclinic system. The peaks in the XRD patterns, which were obtained 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 barium has not affected the crystalline nature of the sample.

FT-Raman spectral analysis of pure and barium doped calcium oxalate monohydrate crystals

FT- Raman spectra of the pure and barium doped calcium oxalate monohydrate crystals as shown in fig 5 (a) and (b). Table 4 shows the vibration assignment of pure and barium doped calcium oxalate monohydrate crystals.

Table .4 Vibrational band assignment of pure and barium doped calcium oxalate monohydrate crystals

Pure calcium oxalate monohydrate wavenumber in cm^{-1}	Barium doped calcium oxalate monohydrate wavenumber in 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 asymmetric stretching
1487	1486	C-O symmetric stretching
1461	1462	Vibration of C-O
892	895	C-C stretching
592	598	Phosphate bands
501	505	O-C-O in plane bending

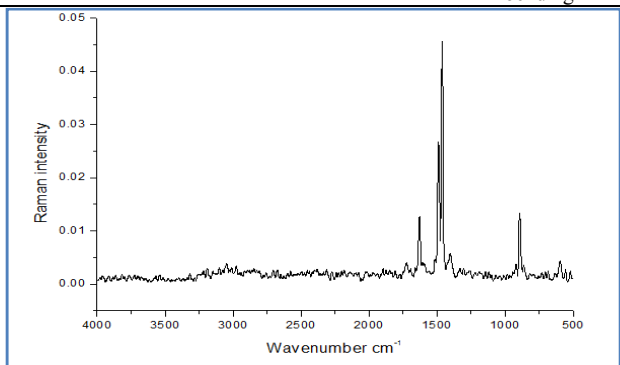


Fig. 4 a FT-Raman analysis of pure calcium oxalate monohydrate crystals.

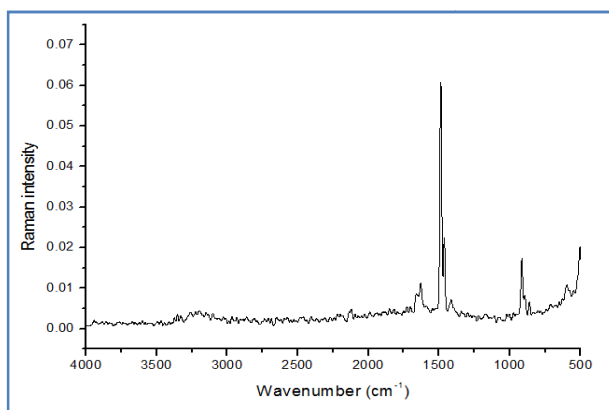


Fig. 4 b FT-Raman analysis of barium doped calcium oxalate monohydrate crystals.

The spectrum of calcium oxalate monohydrate crystal shows O-H stretching vibration between 3189cm^{-1} , 3223cm^{-1} and 3048cm^{-1} , 3102cm^{-1} . The sharp bands at 1461cm^{-1} , 1486cm^{-1} and 1487cm^{-1} , 1486cm^{-1} are due to the C=O vibration and C-O symmetric stretching of pure and barium doped calcium oxalate monohydrate crystals. The less intense 1628cm^{-1} and 1629cm^{-1} band due to the C-O asymmetric stretching and the 893cm^{-1} , 863cm^{-1} band due to the O-C-O plane bending of calcium oxalate monohydrate and barium doped calcium oxalate monohydrate(12).

Scanning Electron Microscope (SEM)-Energy Dispersive X-ray analysis

The morphology of the pure and barium doped calcium oxalate monohydrate crystal was studied by EDX. Fig 5(a) and (b) shows the SEM images shows of pure and barium doped calcium oxalate monohydrate crystals. The growth of calcium oxalate monohydrate crystals were obtained in different morphologies such as monoclinic, prismatic, hexagonal prismatic plate like shape (13).

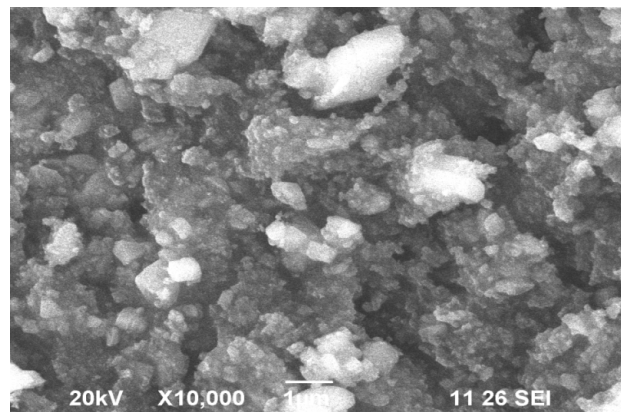


Fig. 5 a SEM images of pure calcium oxalate monohydrate crystals

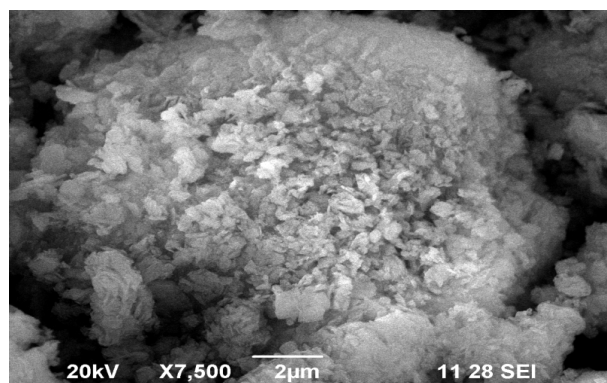


Fig. 5 b SEM images of barium calcium oxalate monohydrate crystals

The barium doped calcium oxalate monohydrate crystal is spherulitic morphology is appeared (14).

It was found that, the structure of the grown crystals does not affect the morphology of the crystals by doping. The presence of Ca and Barium quantitative elemental analysis were performed on the applications of EDX spectra of pure and doped calcium oxalate monohydrate crystals as shown in fig.6 (a) and (b).

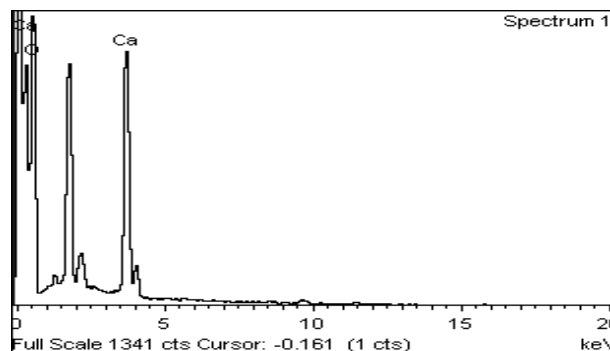


Fig. 6 a EDX spectrum of pure calcium oxalate monohydrate crystals

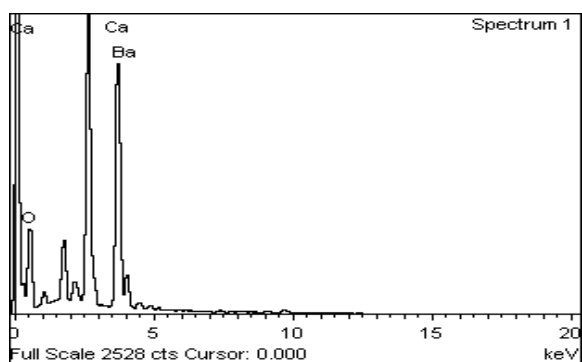


Fig. 6 b EDX spectrum of barium doped calcium oxalate monohydrate crystals.

Table 5 a EDX analysis of pure calcium oxalate monohydrate crystals

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

Table 5 b EDX analysis of barium doped calcium oxalate monohydrate crystals

Element	Atomic weight%	Weight %
O	82.38	63.32
Ca	17.03	32.80
Ba	0.59	3.89
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 fig7.(a), and 7.(b). The loss of water crystallization in first step, carbon monoxide in second step, and carbon-di-oxide in third step. In pure 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 20°C-140°C which indicates the loss of water hydration. In the second stage weight loss about 15.15% occurred at temperature range between 140°C-240°C corresponding to dehydration of sample in first stage.

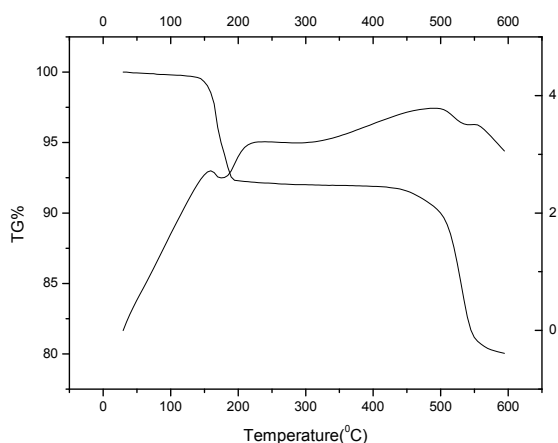


Fig. 7 a Thermogram of the calcium oxalate monohydrate crystals

In the third stage weight loss of 20% was observed 240°C-510°C the decomposition of calcium oxalate monohydrate with releasing of CO₂. It is observed that there are two endothermic peaks at 240°C and 520°C. The endothermic peak corresponds to formation of calcium oxalate monohydrate compound. The two exothermic peaks are observed 180°C and 480°C(15).

In the first stage weight loss of about 3% occurs between 20°C-140°C which indicates the loss of water hydration. In the second stage weight loss about 6% occurred at temperature range between 120°C -200°C corresponding to dehydration of sample in first stage. In the third stage weight loss of 19% was observed 200°C-300°C. In the fourth stage weight loss of about 10% was observed 440°C-520°C the decomposition of calcium oxalate monohydrate with releasing of again CO₂. In the fifth stage weight loss of about 3% was observed 520°C-560°C. The de composition of calcium oxalate monohydrate with releasing of CO₂. It is observed that there are two endothermic peaks at 220°C and 480°C. The endothermic peaks correspond to formation of calcium oxalate monohydrate compound. The two exothermic peaks are observed 180°C and 520°C. Thus there is a decrease in the peak temperature which indicates a reduced thermal stability of Calcium oxalate monohydrate due to barium doping.

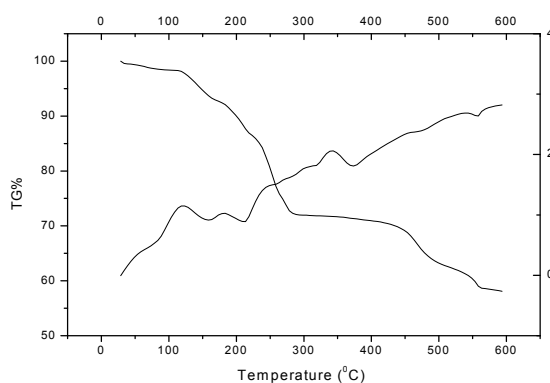


Fig. 7 b Thermogram of the barium doped calcium oxalate monohydrate crystals

UV-Visible analysis

Optical absorption spectra was recorded on a UV-2400 PC series UV-Visible spectrophotometer with performing wavelength ranging from 200nm to 900nm as shown in fig 7(a) and 7 (b).

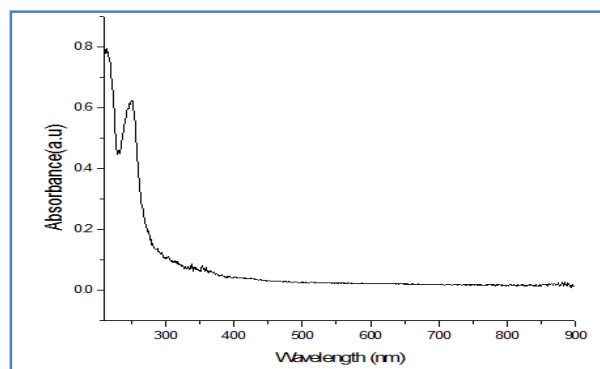


Fig 7 a UV-Visible analysis of pure calcium oxalate monohydrate crystals.

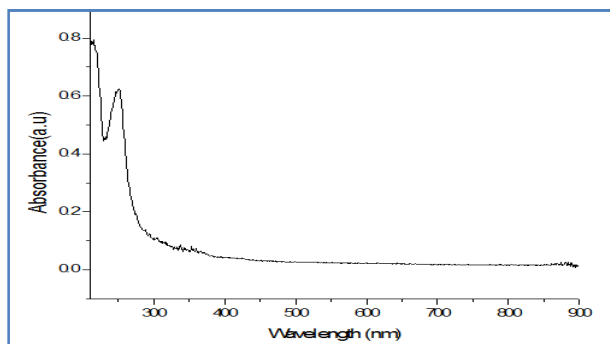


Fig.7 b UV-Visible analysis of barium doped calcium oxalate monohydrate crystals

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 of pure calcium oxalate monohydrate is 247 and barium doped calcium oxalate monohydrate cut off wavelength is 246nm closer to UV range from 200-900 nm. The presence of lower cut off wavelength and the optical transmission window range are the most desirous properties of materials possessing NLO activity (16).

CONCLUSION

The pure and barium doped calcium oxalate monohydrate crystals were grown using silica gel method. FTIR and FT-Raman results confirmed the presence of functional groups of pure and barium doped calcium oxalate monohydrate crystal. The XRD data proves the crystalline of the samples. The SEM image shows surface morphology of the crystals. The EDX confirmed the doping of barium on calcium oxalate. The thermal stability was studied by the TGA/DTA analysis. The optical properties were determined by UV-Visible analysis.

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