ISSN NO. 2320-5407

Journal Homepage: - www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

Article DOI:10.21474/IJAR01/4307
DOI URL: http://dx.doi.org/10.21474/IJAR01/4307

RESEARCH ARTICLE

GROWTH, STRUCTURAL, MORPHOLOGICAL AND OPTICAL CHARACTERIZATIONS OF PURE AND CADMIUM DOPED CALCIUM OXALATE MONOHYDRATE CRYSTALS

R. Selvaraju and S. Sulochana
Engineering Physics, FEAT, Annamalai University, Annamalai Nagar.

Manuscript Info

Manuscript History

Received: 20 March 2017
Final Accepted: 25 April 2017
Published: May 2017

Key words:-
Caox, FTIR, XRD, SEM-EDX, and UV-Visible.

Abstract

The human urinary calculi are mainly formed from Calcium Oxalate Monohydrate (COM), Magnesium Ammonium Phosphate Hexahydrate (MAPH) and Uric acid crystals. It is mainly classified into two types of hydrates, Calcium Oxalate Monohydrate (whewellite) and Calcium Oxalate Dehydrate (weddelite). The pure calcium oxalate monohydrate and cadmium doped Calcium Oxalate Monohydrate (CdCaoxM) crystals are grown by single diffusion gel growth method. The grown crystals are characterized by FTIR, FT-Raman, XRD, SEM-EDX and UV-Visible analysis.

Introduction:-

The formation of urinary calculi is known as nephrolithiasis. Urinary calculi affected too many people in various age groups. In this world, urinary calculi are one of the most hazardous and painful existing urological disorder causing threats to the global population. (1,2). Calcium containing stones are the most common comprising about 75% of all urinary calculi which may be in the form of pure calcium oxalate (50%) or calcium phosphate (5%) and a mixture of both (45%). Calcium oxalate stones are found in two different varieties, Calcium Oxalate Monohydrate (COM) or whewellite and Calcium Oxalate Dehydrate (COD) or weddelitte. Many factors affect the growth of urinary calculi. Investigation of the urinary stones showed large number of trace elements including Cd, Pb, Zn, Mg, Sr, Cr, Mn, Ni, Cu, Co, Au, Ti, Bi, etc., along with the main constituents (3). Urinary calcium excretion is influenced by dietary intake of calcium, sodium, protein, carbohydrates, alcohol and potassium (4). The case of insufficient intake of water or due to the decreased rate of excretion, the crystallogenic substances in the urine can be concentrated, leading to crystal formation. A change in the pH value in the urine can lead to the crystal growth (5, 6). Humans are exposed to cadmium is if no use to the human body and is toxic even at low levels. The negative effects of cadmium is of no use to the human body and numerous and can impact nearly all systems in the body, including cardiovascular reproductive, the kidneys, eyes and even the brain. The size and morphology of the stones were examined using optical microscopy, while their component and crystalline phases were determined by Fourier Transform Infrared spectroscopy, Ultraviolet spectroscopy and X-ray powder diffraction (7). The scanning electron microscopic studies help in understanding the surface morphology and ultra structure of the calculi (8). In-vitro growth of calcium oxalate monohydrate crystal by single diffusion gel growth method in silica gel medium. The harvested crystals are characterized by Fourier Transform Infrared spectroscopy, X-ray diffraction, thermal analysis and the effect of aqueous extracts of Tribulus terrestris are studied on the inhibition growth of crystals in vitro and may be useful in prevention and cure of this crystal induce ailments(9). In the present paper is to report the growth of pure calcium oxalate monohydrate and cadmium doped calcium oxalate monohydrate crystals in silica gel method. The harvested crystals are characterized by FTIR, FT-Raman, XRD, SEM-EDX and UV-visible analysis.

Corresponding Author:-R. Selvaraju.
Address**:**-Engineering Physics, FEAT, Annamalai University, Annamalai Nagar.

Materials and Methods:-

Crystal Growth:-

The growth of pure calcium oxalate monohydrate and cadmium doped 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 (10). Calcium chloride and cadmium chloride one of the reactants was incorporated inside the gel. After the gel was set an aqueous solution of oxalic acid was slowly added over the gel and the experiments were conducted at room temperature. Within a day, a white column of tiny crystals were formed. The growth was completed within a period of 21 days were grown which are as shown in Fig 1(a) and 1(b). The growth and harvested cadmium doped calcium oxalate monohydrate crystals are as shown in Fig. 2(a) and 2(b).

Different parameters such as concentration of reactants, pH of gel, impurities in the solvent, gel setting time, etc, have considerable effect on growth rates.

Table 1:- The optimum condition for the growth of pure and cadmium doped calcium oxalate monohydrate crystal.

S. No	Parameter	Optimum condition
1	Density of sodium meta silicate	1.03gm/cm^{-3}
2	pH of gel	6
3	Concentration of $CaCl_2$	1 M
4	Concentration of $CdCl_2$	0.01M
5	Concentration of $C_2H_2O_4$	1 M
6	Gel setting period	2 days
7	Gel aging	1 month
8	Period of growth	21 days
9	Temperature	Room temperature

Fig. 1. (a). Growth of pure CaOxM crystal

Fig. 1.(b). The harevested pure CaOxM crystal

Fig.2. (a) Growth of CdCaoxM crystal

Fig. 2:-(b) The harvested CdCaoxM crystal .

Characterization Techniques:-

FTIR spectrum is recorded by KBr pellet technique using Perkin Elmer FTIR spectrometer with the range 400-4000cm^{-1} is available at Centralised Instrumentation Science Laboratory, Department of Physics, St. Joseph College, Tiruchirappalli. FT-Raman spectra were recorded in the range of 4000cm^{-1} to 100cm^{-1} using BRUCKER, Model RFS27. FT-Raman spectrum which are available at Sophisticated Analytical Instrument Facility (SAIF). Indian Institute of Technology (IIT), Chennai, Tamilnadu, South India. 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 pure calcium oxalate monohydrate and cadmium 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. Absorption spectra of pure calcium oxalate monohydrate and cadmium doped calcium oxalate monohydrate 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:-

The pure calcium oxalate monohydrate and cadmium doped calcium oxalate monohydrate crystals were grown by single diffusion gel growth technique and the harvested crystals are analyzed by FTIR, FT-Raman, XRD, SEM-EDX and UV-Visible analysis are studied.

Fourier Transform Infrared Spectroscopy:-

The FTIR spectra of pure calcium oxalate monohydrate and cadmium doped calcium oxalate monohydrate crystals were as shown in Fig 3(a) and 3(b). The vibrational modes of pure calcium oxalate monohydrate and cadmium doped calcium oxalate monohydrate are presented in Table 2. In FTIR spectra, a strong band at 3431 cm^{-1}, 3433cm^{-1} and 3061cm^{-1}, 3063cm^{-1} is due to asymmetric and symmetric OH stretching while an intense absorptions band at 3261cm^{-1}, 3259cm^{-1} show intermolecular hydrogen bonded OH stretch. Intense absorption band at 1621 cm^{-1} ,1616cm^{-1} and 1318cm^{-1}, 1319cm^{-1} can be assigned to asymmetric and symmetric C=O stretching bands specific to the calcium oxalate monohydrate. The sharp band at 886cm^{-1}, 885cm^{-1} is due to C-C stretching vibrations which confirm the existence of oxalate group in calcium oxalate monohydrate. The sharp peaks at 781cm^{-1} ,781cm^{-1} is due to O-C=O and the wideband at 665cm^{-1} , 662cm^{-1} can be assigned to the bending modes of the water molecule. However, the peak at 518cm^{-1} and 516$cm^{-1}$is assigned to the presence of metal-oxygen bond (10). Thus FTIR reveals that the growth of calcium oxalate monohydrate crystals was due to the presence of O-H stretching, C=O, C-C, O-C=O and M=O bonds.

Fig 3:- (a). FT-IR spectrum of pure calcium oxalate monohydrate crystal.

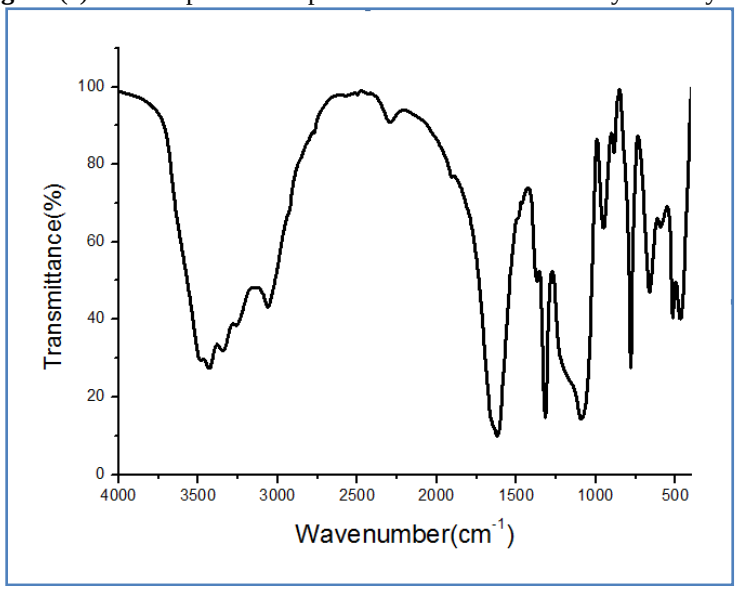


Fig. 3:- (b). FT-IR spectrum of cadmium doped calcium oxalate monohydrate crystal.

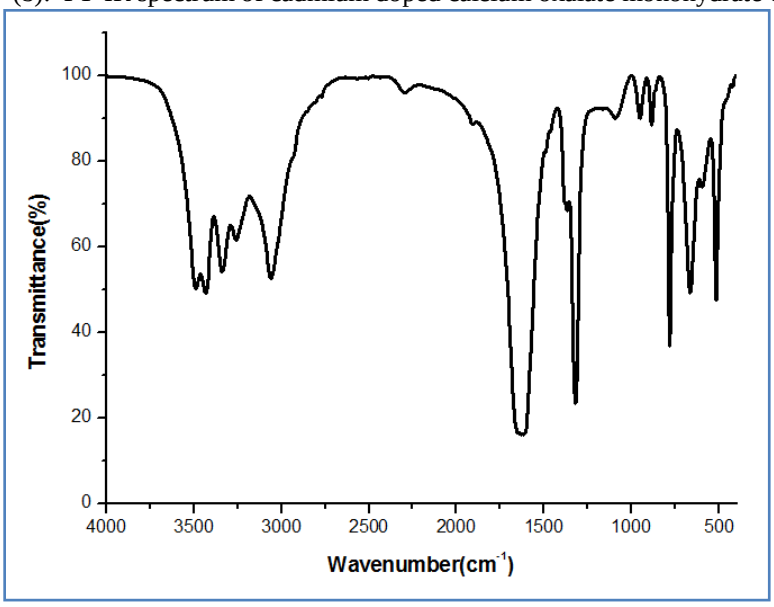


Table 2:- FTIR wave numbers and tentative assignment of pure calcium oxalate monohydrate and cadmium doped calcium oxalate monohydrate crystal.

Pure calcium oxalate monohydrate wavenumber cm^{-1}	Cadmium doped calcium oxalate monohydrate wavenumber cm^{-1}	Tentative band Assignment
3431	3433	Asymmetric OH stretch
3063	3061	Symmetric OH stretch
3262	3259	Inter molecule H_2 bonded OH stretch
1621	1616	Asymmetric C=O stretch
1318	1319	Symmetric C=O stretch
1092	1092	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	518	M-O bond

These peaks are found to be present in the spectrum of cadmium doped calcium oxalate monohydrate crystals confirms the presence of the element cadmium.

Fourier Transform Raman studies:-

FT-Raman spectra of the pure calcium oxalate and cadmium doped calcium oxalate monohydrate crystals as shown in Fig 4(a) and 4(b) and Table 3 shows the vibration assignment of pure calcium oxalate monohydrate and cadmium doped calcium oxalate monohydrate crystals.

Table 3:-Vibration band assignment of pure calcium oxalate monohydrate and cadmium doped calcium oxalate monohydrate crystal.

Pure calcium oxalate monohydrate wave number in cm^{-1}	Cadmium doped calcium oxalate monohydrate wave number in cm^{-1}	Vibration band assignment
3088	3058	OH stretching
3048	-	OH stretching
2828	-	CH_3 stretching

2721	-	C-H stretching
2223	-	C-H stretching vibration
2181	-	Stretching vibration of C-C
1895	1813	Stretching vibration of C-C
1722	1727	Stretching vibration of C-O
1628	1629	C-O asymmetric stretching
1487	1488	Vibration of C-O
1461	1462	Vibration of C-O
-	1395	O-C-O stretching mode
938	918	PO_4^3 bending
894	892	C-C Stretching
595	592	Phosphate bands
502	501	O-C-O in plane bending

The spectra of pure calcium oxalate monohydrate and cadmium doped calcium oxalate monohydrate crystal shows O-H stretching vibration between 3088cm^{-1} and 3058cm^{-1}, 3048 cm^{-1}.The sharp bands at 1461cm^{-1}, 1462cm^{-1} and 1487cm^{-1}, 1488cm^{-1} are due to the C=O vibration and C-O symmetric stretching of pure calcium oxalate monohydrate and cadmium doped calcium oxalate monohydrate crystals. The less intense 1628cm^{-1} and 1629cm^{-1} band due to the C-O asymmetric stretching and the 892cm^{-1}, 894cm^{-1} band due to the O-C-O plane bending of pure calcium oxalate monohydrate and cadmium doped calcium oxalate monohydrate(11).

Fig. 4:- (a). FT-Raman spectrum of pure calcium oxalate monohydrate crystal.

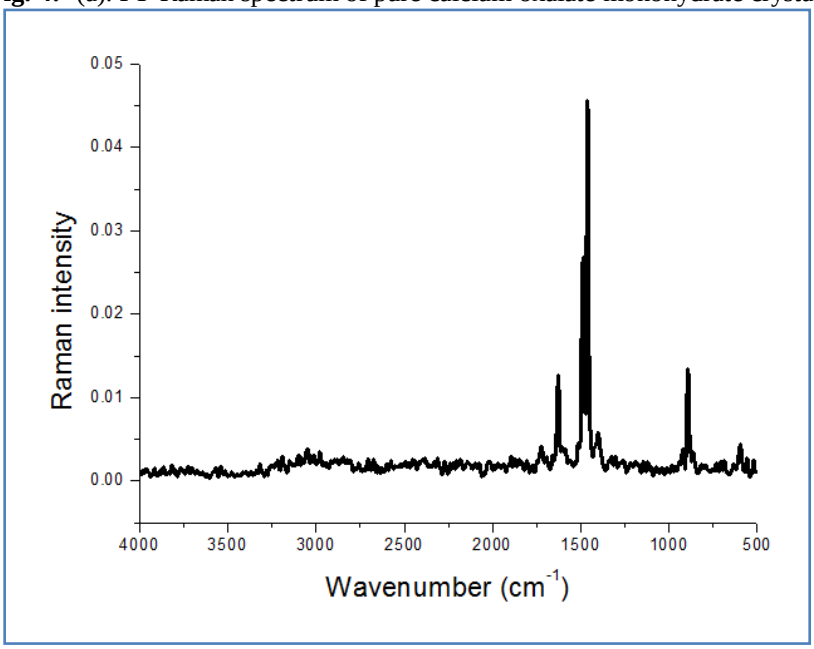
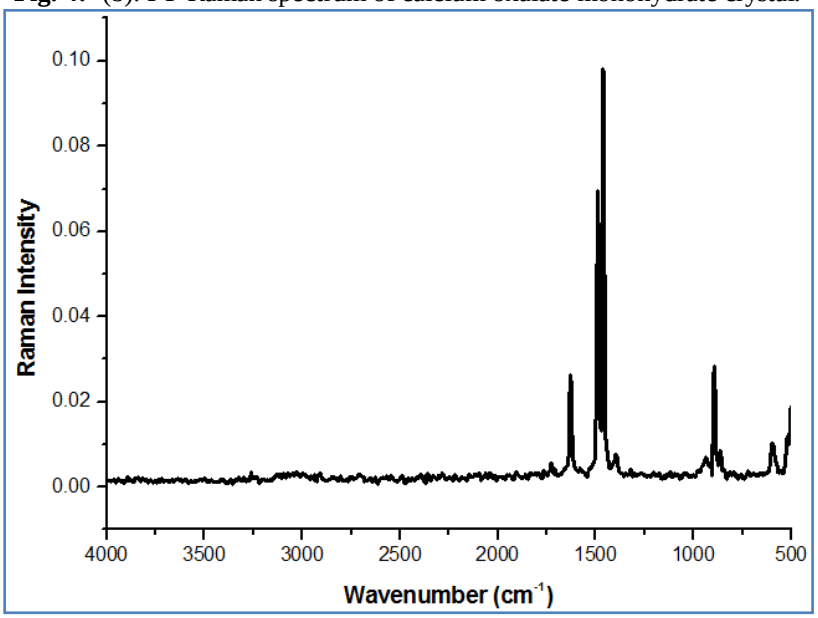


Fig. 4:- (b). FT-Raman spectrum of calcium oxalate monohydrate crystal.



X-ray diffraction Analysis:-

The powder XRD pattern was recorded using diffractometer system=XPERT-PRO X-ray diffractometer with CuKα radiation (λ =11.546A^0). The powder sample was scanned over the range 10^0 to 60^0 in at a rate of 1^0 per minute. Fig 5(a) and 5(b) shows that the pure calcium oxalate and cadmium doped calcium oxalate monohydrate crystals.

The powder XRD analysis of the grown calcium oxalate monohydrate crystals was matched with the reported database using computer with PAN analytical software and result was matched with JCPDS File (14-0789) (12). The indexed powder data for the pure calcium oxalate and cadmium doped calcium oxalate monohydrate crystals are presented in Table.4 and 5. From the XRD data, it is observed that from the cell parameters of both pure calcium oxalate monohydrate and cadmium doped calcium oxalate monohydrate crystals belong to monoclinic system.

Fig. 5:- (a) X-ray diffraction analysis of pure calcium oxalate monohydrate crystal.

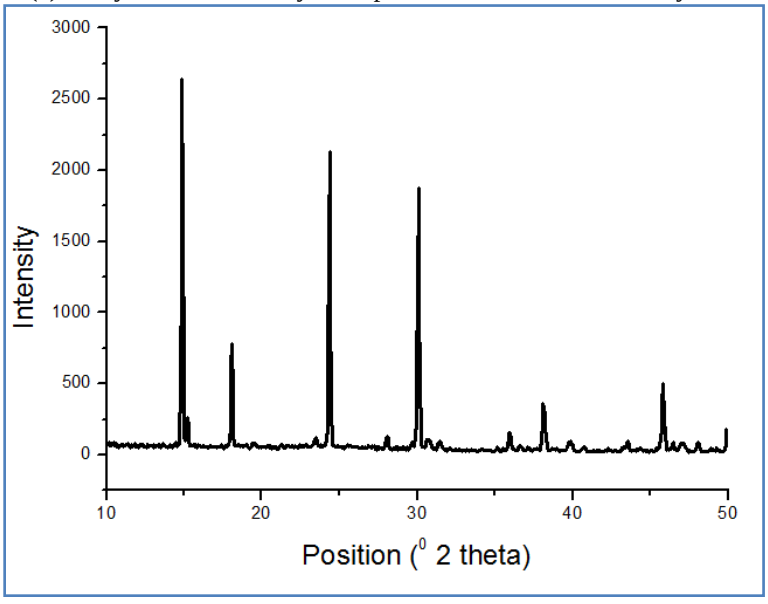


Fig 5:- (b). X-ray diffraction analysis of cadmium doped calcium oxalate monohydrate crystal.

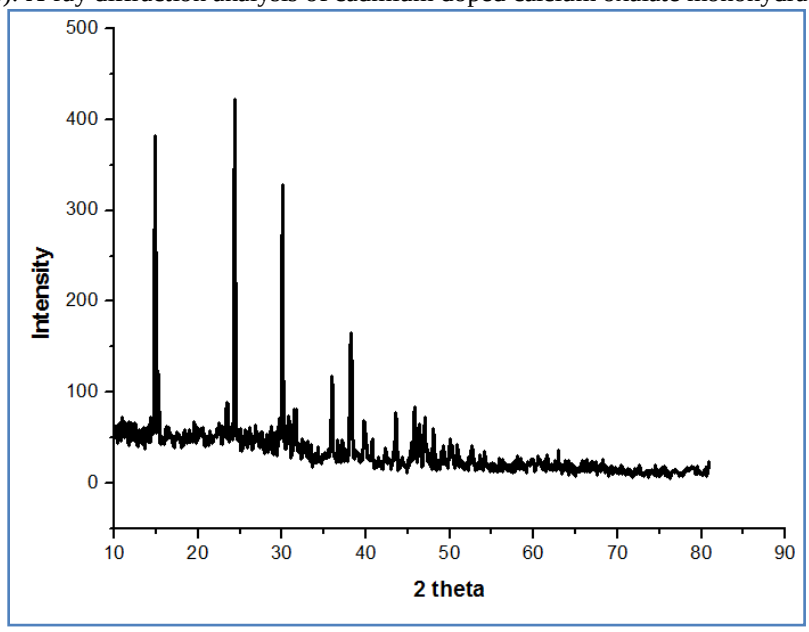


Table 4:- X-ray diffraction analysis of pure calcium oxalate monohydrate crystal.

Standard value			Observed value			hkl value
2θ	I/I_0	**d-space**	2θ	I/I_0	**d-space**	
14.927	100	5.93	14.875	100	5.95	-101
15.290	60	5.79	15.233	9	5.81	011
19.579	40	4.53	19.588	2	4.53	101
23.515	40	3.78	23.480	3	3.78	-112
24.365	98	3.65	24.364	81	3.65	020
30.083	80	2.96	30.073	70	2.97	-202
31.439	40	2.84	31.419	2	2.83	121
35.964	60	2.49	35.954	5	2.49	211
36.663	20	2.44	36.629	2	2.45	-213
38.148	60	2.35	38.156	2	2.35	031
40.795	40	2.26	40.749	` 1	2.21	-204
43.558.	60	2.07	43.563	3	2.07	123
45.835	60	1.97	45.836	17	1.97	-303
46.308	10	1.95	46.446	2	1.95	132
47.199	10	1.92	47.096	2	1.92	222
48.086	40	1.89	48.081	2	1.89	230

Table 5:-X-ray diffraction analysis of cadmium doped calcium oxalate monohydrate crystal.

Standard value			Observed value			hkl value
2θ	I/I_0	**d-space**	2θ	I/I_0	**d- space**	
14.927	100	5.93	14.895	95	5.94	-101
15.290	60	6.79	15.257	25	5.80	011
18.585	20	3.77	23.475	16	3.78	-112
24.365	100	3.65	24.377	100	3.65	020
30.083	80	2.97	30.086	75	2.97	-202
30.611	40	2.90	30.768	12	2.90	013
31.449	40	2.93	31.550	12	2.83	121
35.964	60	2.49	35.970	24	2.49	211
36.663	20	2.41	36.648	7	2.42	-123

38.158	60	2.38	38.197	35	2.35	113
39.780	40	2.26	39.768	12	2.26	014
40.795	40	2.21	40.769	7	2.21	-204
42.379	20	2.13	42.413	3	2.13	-132
43.558	60	2.07	43.596	14	2.09	-301
45.835	60	1.99	45.830	15	1.97	024
46.306	10	1.97	46.439	7	1.95	-303
46.966	40	1.93	46.958	9	1.93	310
48.074	40	1.89	48.033	5	1.89	230

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 cadmium has not affected the crystalline nature of the sample.

Scanning Electron Microscopy –EDX Analysis:-

The morphology of the pure calcium oxalate monohydrate and cadmium doped calcium oxalate monohydrate crystals were studied by SEM. Fig .6(a) and 6(b)shows the scanning electron microscope images of pure and cadmium doped calcium oxalate monohydrate crystals. The grown crystals are obtained in different morphologies such as monoclinic, prismatic, and hexagonal prismatic and plate like shape (13).

Fig. 6:- (a) SEM images of pure calcium oxalate monohydrate crystal.

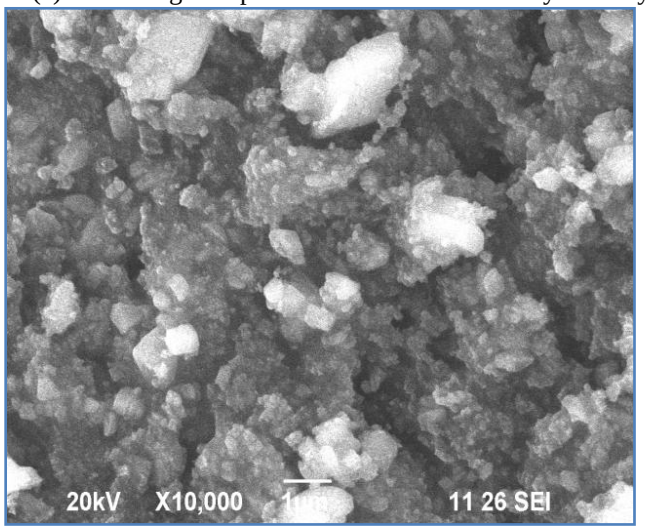
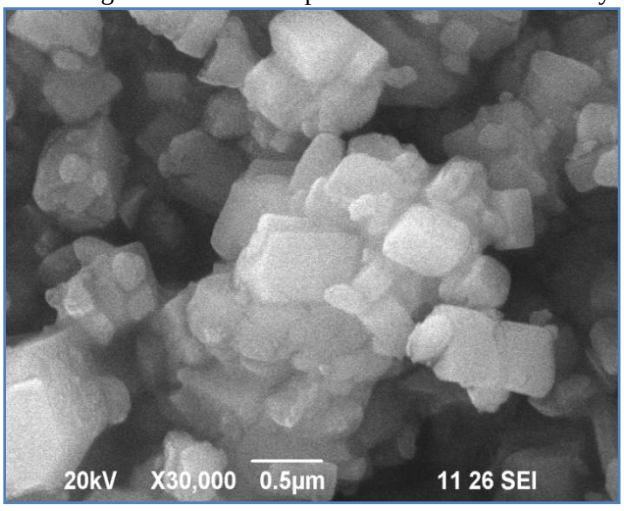


Fig.6:- (b). SEM images of cadmium doped calcium oxalate monohydrate crystal.



It was found that the structure of the grown crystals does not affect the morphology of the crystals by doping.

The presences of pure calcium and cadmium quantitative elemental analysis were performed on the application of energy dispersive X-ray analysis. The energy dispersive x-ray analysis of pure calcium oxalate monohydrate and cadmium doped calcium oxalate monohydrate crystal as shown in Fig.7 (a) and 7(b).

Fig. 7:-(a). EDX spectrum of pure calcium oxalate monohydrate crystal.

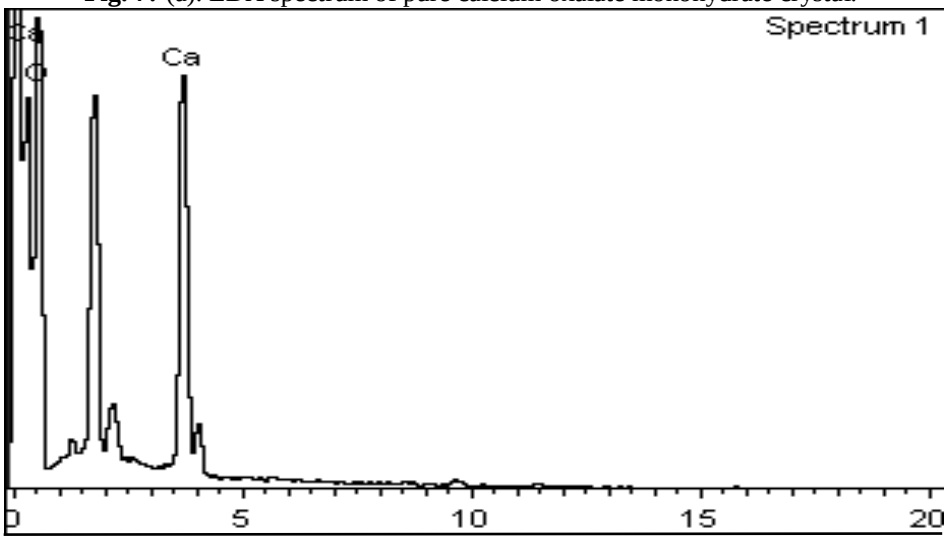


Table 6:- (a) EDX analysis of pure calcium oxalate monohydrate crystal.

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

The atomic percentage of present element oxygen, calcium was found to be 91.37% 8.63% are present (14).

Fig. 7:- (b) EDX analysis of cadmium doped calcium oxalate monohydrate crystal.

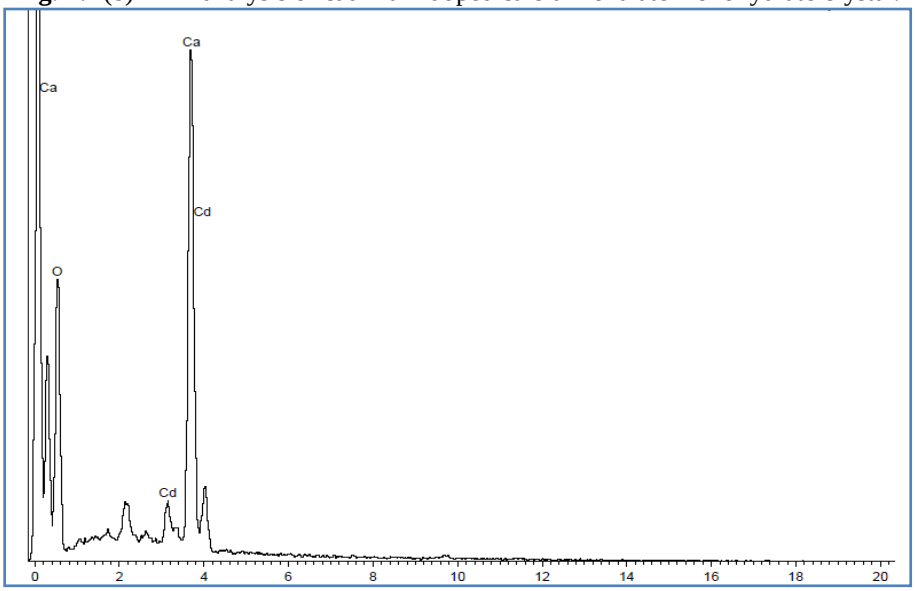


Table 6:- (b). EDX analysis of cadmium doped calcium oxalate monohydrate crystal.

Element	Atomic weight%	Mass weight%
O	86.50	65.92
Ca	12.59	25.34
Cd	0.91	5.14
Total	100	100

The atomic percentage of present element oxygen, calcium, and cadmium was found to be 86.50% 12.59 % and 0.91% are present (14).

UV-Visible Analysis:-

Optical absorption spectrum was recorded on a UV-2400 PC Series UV-Visible spectrophotometer with performing wavelength ranging from 200nm to 900 nm as shown in Fig. 7(a) and 7(b). It is inferred from the spectra, that the grown pure calcium oxalate monohydrate and doped calcium oxalate monohydrate crystals have low absorbance in the entire UV-Visible region considered and the cut off wavelengths are around 249nm and 247nm, closer to UV range from 247-900nm. The presence of lower cut off wavelength and the wide optical transmission window range are the most desirous properties of materials possessing NLO activity (15).

Fig 7:- (a) UV-Visible analysis of pure calcium oxalate monohydrate crystal.

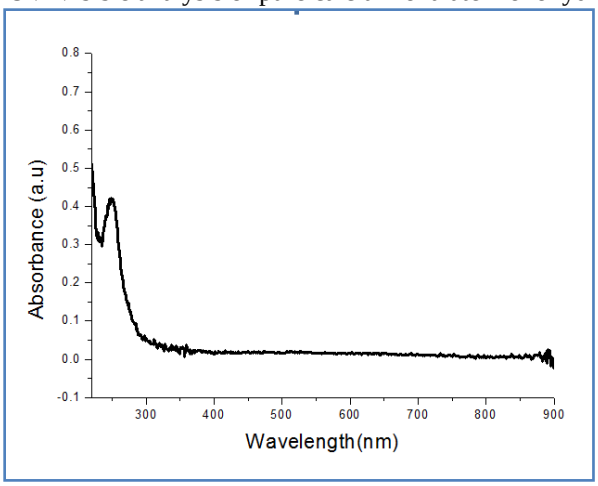
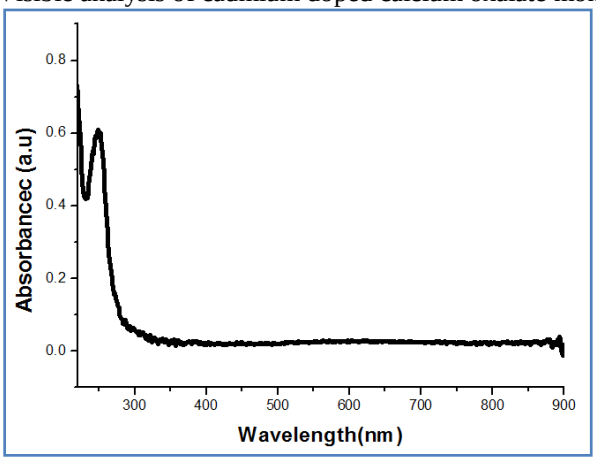


Fig. 7:- (b). UV-Visible analysis of cadmium doped calcium oxalate monohydrate crystal.



Conclusion:-

Gel growth technique is used to grown urinary type of crystals. FTIR spectrum was recorded and the functional group frequencies of pure calcium oxalate monohydrate and doped calcium oxalate monohydrate and cadmium doped calcium oxalate monohydrate crystal were analyzed. The functional groups are identified by FT-Raman

spectra of pure calcium oxalate monohydrate and cadmium doped calcium oxalate monohydrate crystals. Powder XRD data confirms the crystal structure of the pure calcium oxalate and cadmium doped calcium oxalate monohydrate crystals. SEM images shows the crystals are grown by monoclinic, prismatic, and hexagonal prismatic and plate like shape. The incorporation of cadmium in the crystals of calcium oxalate monohydrate has been confirmed by energy dispersive X-ray analysis. The optical properties were determined by UV-Visible analysis.

References:-

1. Vladimir Uvarov, Inna Popov, Nandhakishore shapur et al., 'X-ray diffraction and SEM study of kidney stones in Israel'. Quantitative analysis crystallite size determine and statistical characterization, Environ. Geo.chem. Health, 2011, (33), 613-622.
2. Mohamed Ali, N. Arunainambi Raj, S. Kalainathan, & P. Palnichamy, 'Micro hardness and acoustic behavior of Calcium Oxalate urinary stone'. Material Letters, 2008, (62), 2351-2354.
3. Moroz, T.N. Palchik, N.A. Dar, A.V, 'Micro elemental and mineral compositions of pathogenic bio mineral concernments: SRXFA, X-ray powder diffraction and vibration spectroscopy data'. Nuclear instruments and methods in physics Research section A: Accelerators, Spectrometers, Detectors and associated equipment, 2009, (603), 141-143.
4. Singh R, P Gawr SS White DJ and Nancollas GH, Surface effects in the crystal growth of calcium oxalate monohydrate'. Collid and interface science, 1987,118, 379-386.
5. Suresh, P. Kanchana, G. Sundaramoorthi, 'Growth and characterization studies of MnHP single crystal in silica gel Medium'. Journal of Minerals Materials Characterization Engineering, 2009, (8), 349-357.
6. Achillesa W, Feritag R,Kiss B,Ridemiller , 'Qualification of crystal growth of calcium oxalate in gel and its modification by urinary constituents in a new flow model of crystallization'. J Urol. 1995, (154), 1552-1156.
7. Kalkura SN, Vaidyan VK, Kanakavel M, Ramasamy P. 'Crystallization of Uric acid'. J. Cryst Growth.1993, (132), 617-620.
8. G. Madhurambal, N. Prabha, S.P. Lakshmi S. C. Mojumdar, 'Thermal, UV, FTIR and XRD studies of urinary stones'. J. Therm Anal Calorim .2013, (112), 1067-1075.
9. Eascolar E & Ballanato 'Analysis of feline urinary calculi and urethral plugs by infrared spectroscopy and scanning electron microscopy'. J Vet. Rec. 2003, (152), 625-628.
10. R. Selvaraju and S. Sulochana, 'In-vitro Growth and Inhibition Studies of Tribulus Terrestris on Calcium Oxalate Monohydrate Crystals'.International Journal of science and Research, *2016, 5(6), 83-87.*
11. D.Valarmathi, Leela Abhram, & S. Gunasekaran, 'Growth and characterization of agar gel Brushite crystals'. Indian Journal of Pure and Applied Physics, 2010, (48), 36-38.
12. Selvaraju R, A Raja, G Thiruppathi, 'Chemical composition and binary mixture of human urinary stones using FT-Raman spectroscopy method**',** Spectrochimica Acta Part A: Molecular and Bio-Molecular spectroscopy. 2013, (114), 650-657.
13. V.B. Suryawanshi, R.T. Chaudhari, 'Growth and study of micro- crystalline *Calcium Oxalate Monohydrate Crystals by agar gel system', Archi* of Phy. Res, 2014, 5(2), 38-44.
14. V.B. Suryawanshi and R.T. Chaudhari, 'Effect of neutral gel on nucleation and growth of urinary calcium oxalate monohydrate crystals in agar gel'. Archieves of Physics Research.2015, (1), 7-12.
15. Mary Freeda, R. Krishna Priya, T.H. Freeda and S. Mary Delphine, Crystallization and characterization of mixed crystals of strontium calcium barium tartrate'. Archievees of Applied Science Research, 2012, 4(1), 128-136.