iJRASET
International Journal For Research in Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 5 **Issue:** VI **Month of publication:** June 2017

DOI:

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Volume 5 Issue VI, June 2017
ISSN: 2321-9653
International Journal for Research in Applied Science & Engineering Technology (IJRASET)

Crystal Growth, Functional, Thermal and Optical Characterizations of Pure and Cobalt Doped Calcium Oxalate Monohydrate Crystals by Single Diffusion Gel Method

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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. Of course the calcium oxalate is one of the principle components of urinary stones. It is found in three different types of forms. They are calcium oxalate monohydrate (com), calcium oxalate di-hydrate (cod) and calcium oxalate tri-hydrate (cot), however majority of com or cod. Most calcium stones are formed when the calcium combines with oxalates. The pure and cobalt doped calcium oxalate monohydrate crystals were grown by single diffusion gel growth technique. A white column of tiny crystals are formed. The crystals were investigated by ft-raman, tga/dta and uv-visible analysis. The presence of functional group has been confirmed by ft-raman analysis. The tga/dta shows the thermal properties of the crystal. The optical nature of the grown crystal is analysed using the uv-visible spectrum.***
Keywords: calcium, cobalt, ft-raman, tga/dta analysis.

I. INTRODUCTION

Nephrolithiasis is common affecting up to 10% of the population at some point during their lifetime (1). Calcium containing stones are the most commonly occurring to an extent of 75-90% followed by magnesium ammonium phosphate(struvite) to an extent of 10-15%, uric acid 3-10% and cystine 0.5%-1%(2). Calcium oxalate stones are found in two different varieties, calcium oxalate monohydrate (COM) of whewellite and calcium oxalate dehydrate (COD) or weddellite, and calcium the thermodynamically most stable form is observed more frequently in clinical stones than COD and it has a greater affinity for renal tubular cells, thus responsible for the formation of stones in the kidney(3). Among this calcium oxalate monohydrate crystals are in monoclinic, prismatic, hexagonal form, while COD in tetragonal bipyramid or weddellite and COT in triclinic or needle shape (4). The presence of functional groups and phase of the urinary stones were analysed using X-ray diffraction (XRD), Fourier Transform infrared and Fourier Raman infrared spectroscopy(5). Growth and characterization of calcium oxalate monohydrate crystals by gel technique and the harvested crystals are analysed by FTIR, XRD and thermal analysis (6). As cobalt is widely dispersed in the environment humans may be exposed to it by breathing air, drinking water and eating food that contains cobalt. Cobalt is beneficial for humans because it is a part of vitaminB12 which is essential for human health. In the present paper is to report the growth of pure calcium oxalate and cobalt doped calcium oxalate monohydrate crystals in silica gel method. The harvested crystals are analysed by FT-Raman, TGA/DTA and UV-Visible analysis.

II. MATERIALS AND METHODS

A. Crystal Growth

The growth of pure calcium oxalate monohydrate and cobalt 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 (7). Calcium chloride and cobalt 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 cobalt doped

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Volume 5 Issue VI, June 2017
ISSN: 2321-9653
International Journal for Research in Applied Science & Engineering Technology (IJRASET)

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 cobalt 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 $CoCl_2$	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 harvested pure CaOxM crystal

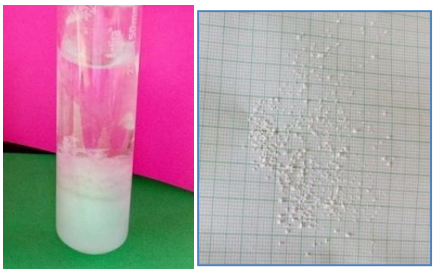
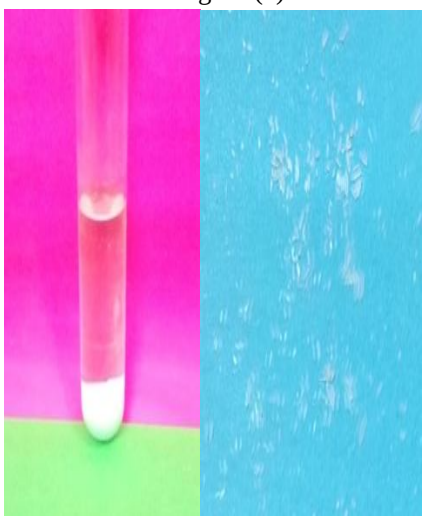


Fig.2. (a) Growth of CoCaoxM crystal

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



B. Characterization Techniques

FT-Raman spectrum which are available at Sophisticated Analytical Instrument Facility (SAIF), Indian Institute of technology (IIT), Chennai, Tamilnadu, South India. Absorption spectra of pure calcium oxalate monohydrate and cobalt doped calcium oxalate monohydrate crystals were recorded using a UV-2400 PC series UV-Visible spectrometer over the wavelength range 200nm to 900nm at science Instrumentation Centre, department of Physics, Standard fire Rajarathnams Women's college, sivakasi. 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.

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Volume 5 Issue VI, June 2017
ISSN: 2321-9653
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III. RESULTS AND DISCUSSION

The pure calcium oxalate monohydrate and cobalt doped calcium oxalate monohydrate crystals were grown by single diffusion gel growth technique and the harvested crystals are analysed by FT-Raman, TGA/DTA and UV-Visible analysis.

A. Fourier Transform Raman analysis

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

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

Pure calcium oxalate monohydrate wave number in cm^{-1}	Cobalt doped calcium oxalate monohydrate wave number in cm^{-1}	Vibration band assignment
3088	3063	OH stretching
3048	-	OH stretching
2828	2849	CH_3 stretching
2721	2782	C-H stretching
2223	2280	C-H stretching vibration
2181	2138	Stretching vibration of C-C
1895	-	Stretching vibration of C-C
1722	1723	Stretching vibration of C-O
1628	1682	C-O asymmetric stretching
1487	1488	Vibration of C-O
1461	1462	Vibration of C-O
894	894	C-C Stretching
595	594	Phosphate bands
502	502	O-C-O in plane bending

The spectra of pure calcium oxalate monohydrate and cobalt doped calcium oxalate monohydrate crystal shows O-H stretching vibration between 3088cm^{-1} and 3063cm^{-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 cobalt doped calcium oxalate monohydrate crystals. The less intense 1628cm^{-1} and 1682cm^{-1} band due to the C-O asymmetric stretching and the 894cm^{-1} band due to the C-C plane bending of pure calcium oxalate monohydrate and cobalt doped calcium oxalate monohydrate(8).

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

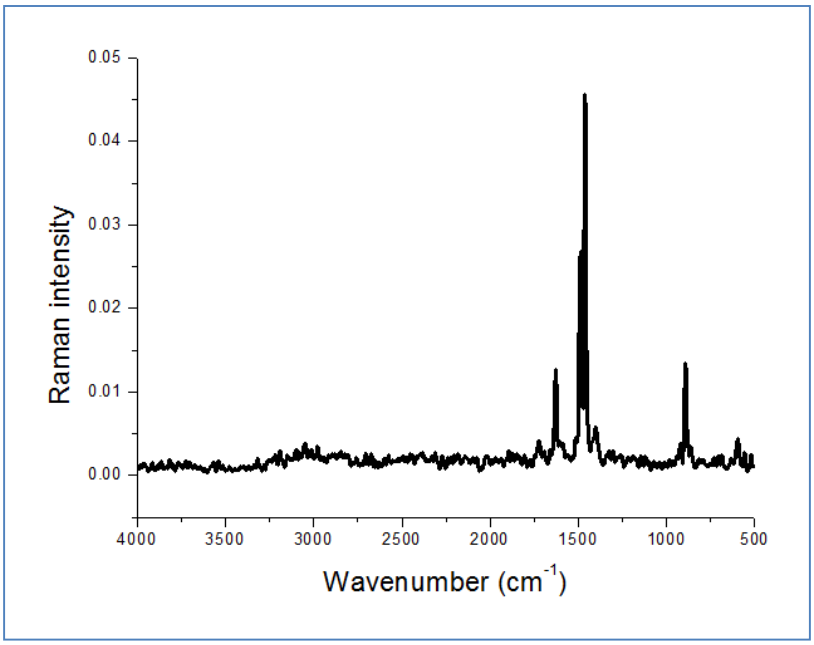
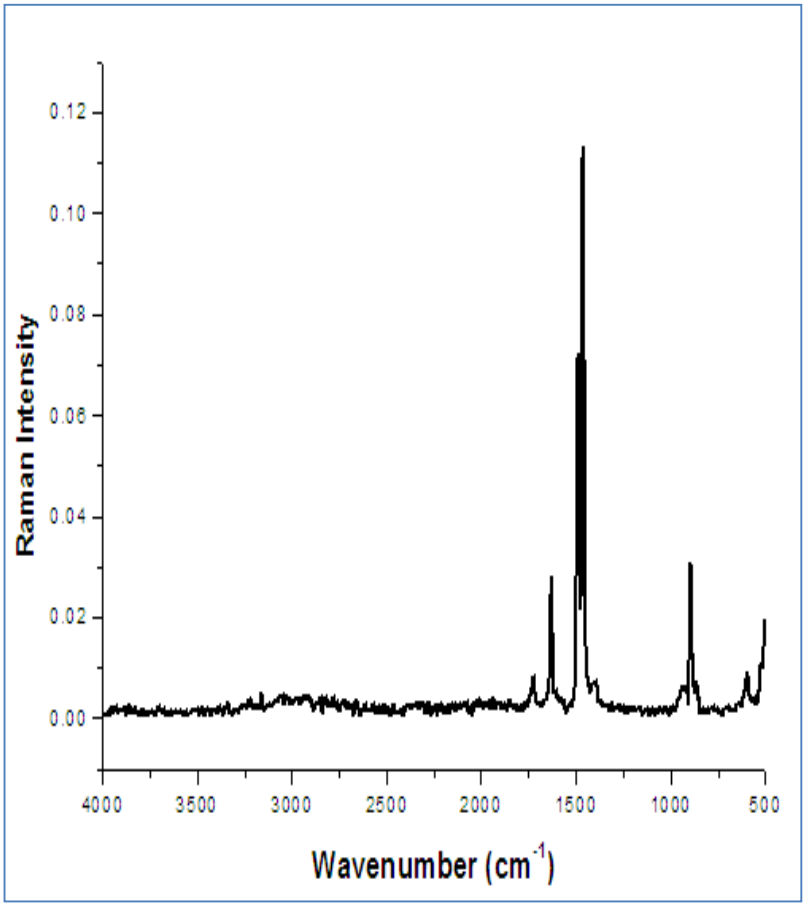


Fig. 3:- (b). FT-Raman spectrum of cobalt doped calcium oxalate monohydrate crystal.



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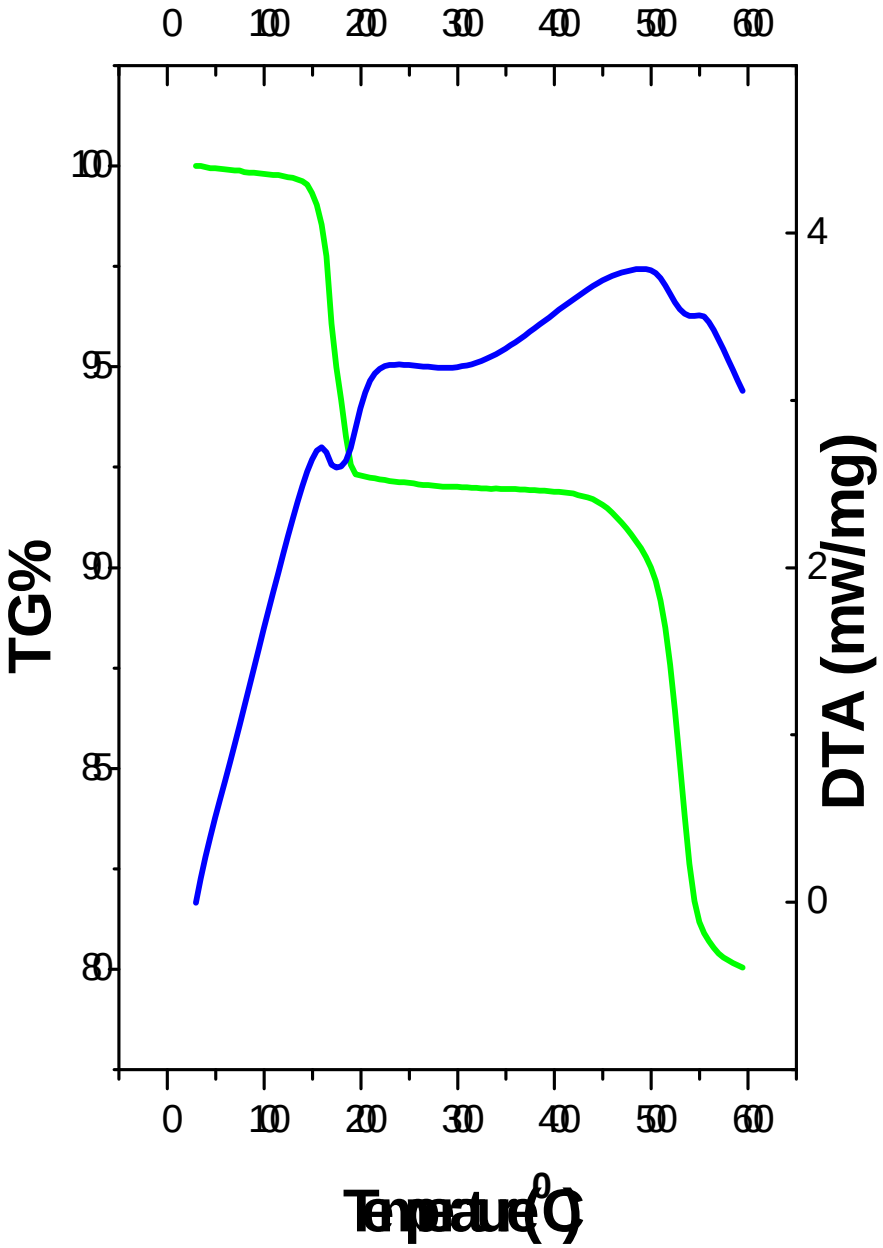
B. Thermal analysis of pure and cobalt doped calcium oxalate monohydrate crystals

TGA/DTA curves recorded for pure and cobalt doped calcium oxalate monohydrate crystal as shown in Fig 4(a) and 4(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 cobalt doped calcium oxalate monohydrate sample the weight loss occur in three stages.

Fig. 4(a)Thermogram of pure calcium oxalate monohydrate crystals



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ISSN: 2321-9653
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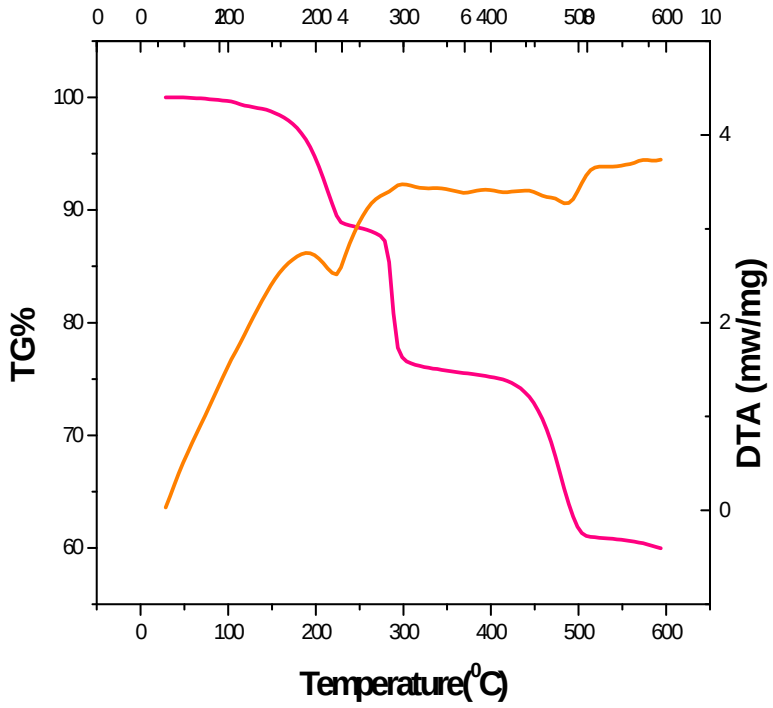
Fig 4(b) Thermogram of cobalt doped calcium oxalate monohydrate crystals



In the first stage weight loss of about 3% occurs between 30^0C-140^0C which indicates the loss of water hydration. In the second stage weight loss of 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-510^0C 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 corresponds to formation of calcium oxalate monohydrate compound. The mass loss corresponds well with the DTA results by the appearance of an endothermic peak at 220^0C and thus there is an increase in the peak temperature which indicates the thermal stability of calcium oxalate monohydrate crystals (9).

In the first stage weight loss of about 2% occurs between 30^0C-140^0C which indicates the loss of water hydration. In the second stage weight loss about 12% occurred at temperature range between 140^0C-240^0C corresponding to dehydration of sample in first stage. In the third stage weight loss of 4% was observed 380^0C-440^0C composition of calcium oxalate monohydrate with releasing of CO_2. In the fourth stage weight loss about 17% was observed between 440^0C-520^0C. The mass loss corresponds well with the DTA results by the appearance of an endothermic peak at 225^0C and thus there is an increase in the peak temperature which indicates the improved thermal stability of cobalt doped calcium oxalate monohydrate crystals.

C. UV-Visible Analysis

The optical properties of a material are important, as they provide information on the electronic band structure, localized state and types of optical transitions. 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. 5(a) and 5(b). It is inferred from the spectra, that the grown pure calcium oxalate monohydrate and cobalt doped calcium oxalate monohydrate crystals have low absorbance in the entire UV-Visible region considered and the cut off wavelengths are around 249nm and 245nm, closer to UV range from 245-900nm. The presence of lower cut off wavelength and the wide optical transmission window range are the most desirous properties of materials possessing NLO activity (10).

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ISSN: 2321-9653
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Fig 5. (a) UV-Visible analysis of pure calcium oxalate monohydrate crystal.

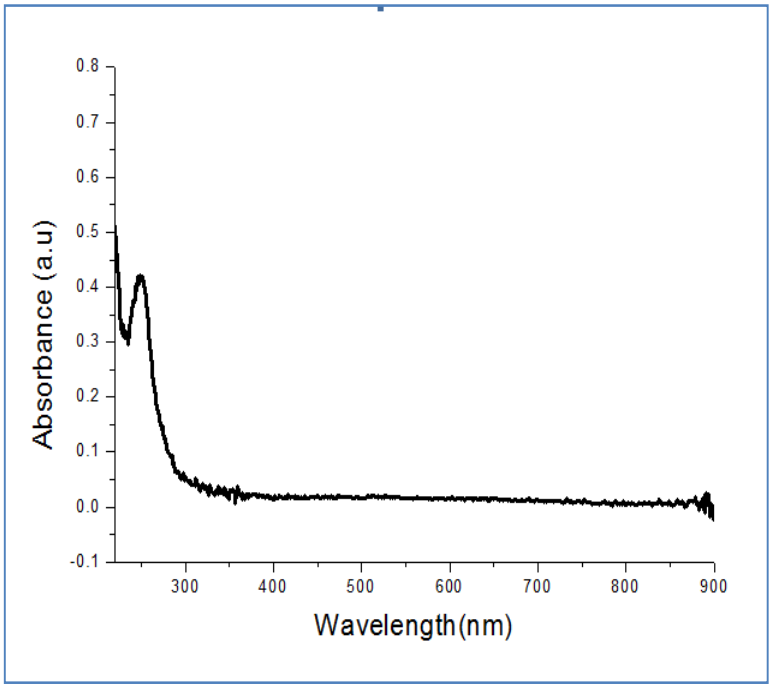
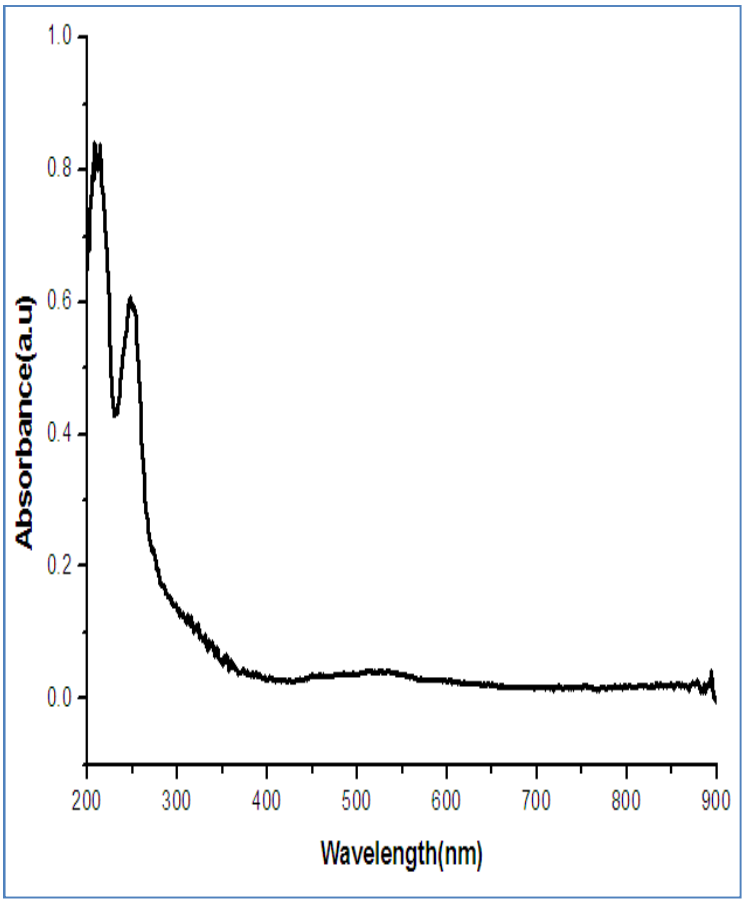


Fig 5 .(b) UV-Visible analysis of cobalt doped calcium oxalate monohydrate crystal.



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IV. CONCLUSION

Single diffusion gel growth technique is used to grown urinary type of crystals. FT-Raman spectrum was recorded and the functional group frequencies of pure calcium oxalate and cobalt doped calcium oxalate monohydrate crystals were analysed. The cut off wavelengths were determined by pure and cobalt doped calcium oxalate monohydrate crystals. The TGA/DTA was analyzed by pure calcium oxalate and cobalt doped calcium oxalate monohydrate crystals.

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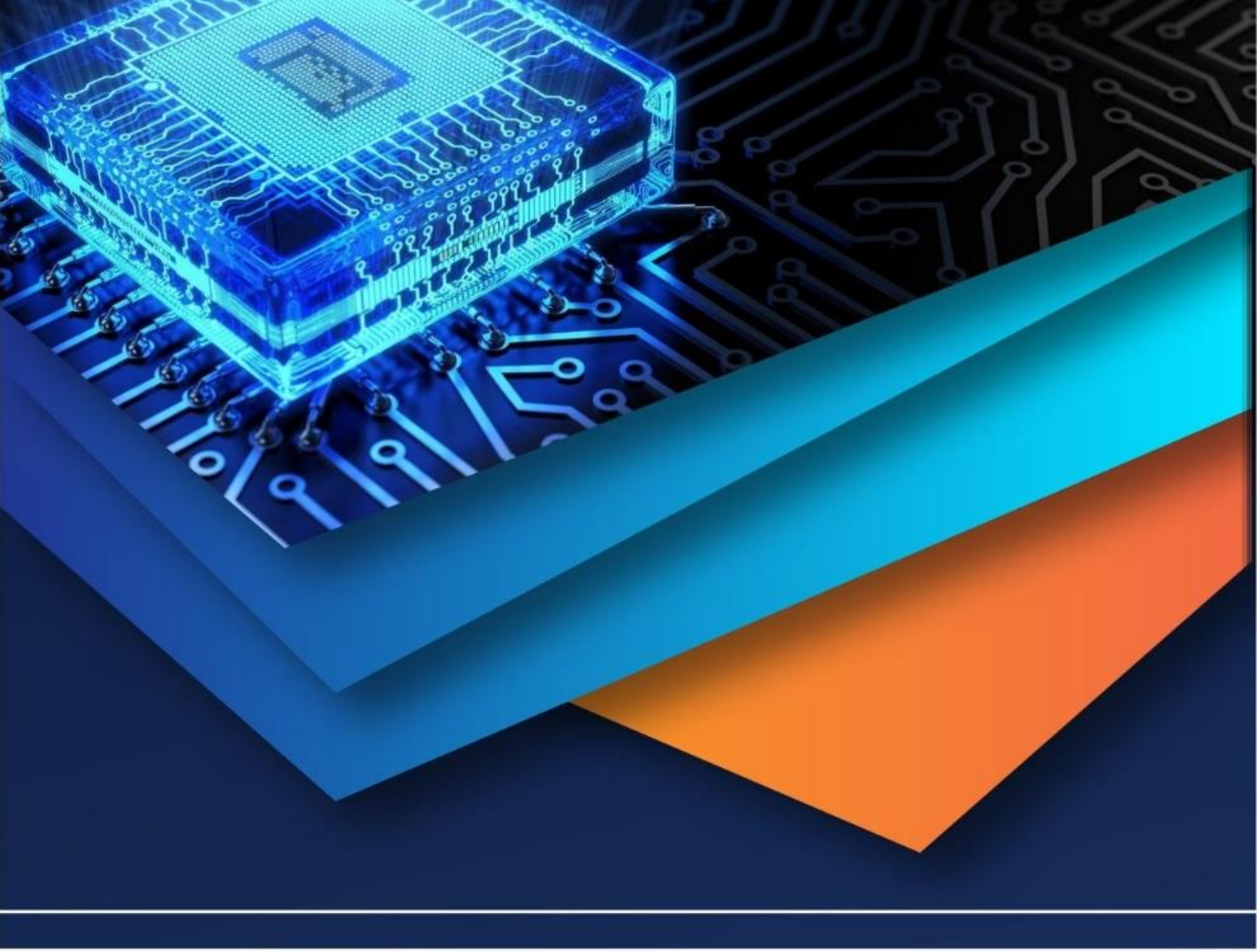

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