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Growth and Spectral Investigation on Pure Calcium Phosphate Doped With (Copper and Magnesium) Crystals

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ABSTRACT

Calcium stones are most commonly occurring form of cholelithiasis or gallbladder stones most one of the oldest and common afflictions of humans. Calcium phosphate is dissolved minerals in causes of renal to gallbladder stone in both human and animals. Of course, the calcium phosphate is one of the components of gallbladder. Calcium phosphate doped with (Cu and Mg) are crystals are grown by sol-gel method. In the present work the growth and characterization of pure and doped with (Cu and Mg) crystals. The grown crystals were characterization by FT-IR, SEM-EDX and TG/DTA analysis.

Keywords: Calcium phosphate, FT-IR, SEM-EDX and TG/DTA

I. INTRODUCTION

Bio crystallization are most useful important phenomenon in which crystal growth of specific biomaterial compounds like minerals and elements occur in body of living organisms. [Kamal H et al., 2015]. The body fluid contains different levels to higher amount minerals and elements at various levels of saturation in calcium phosphate are most important role in human beings and vertebrate [Gunawan et al., 2013]. In many minerals is dissolved form in human body. It is helpful for the growth of human bones and teeth. Biomineralization involves the controlled deposition and regulated growth materials in biological system [Bachhave et al.,2014]. The crystal growth of organic and inorganic micro and macromolecules such as proteins, nucleic acid and complex of compounds are reported many others. The present work growth and spectral investigation on calcium phosphate doped with (copper and magnesium). Spectral studies like that FT-IR, SEM-EDX and TGA/DTA are used. The results are discussed.

Table 1.1. The optimum condition for the growth of calcium phosphate doped with (Cu and Mg) crystals

Parameter	**Optimum Condition**		
	Calcium phosphate	**Copper calcium phosphate**	**Magnesium calcium phosphate**
Density of sodium meta silicate	1.05gm/cm^{-3}	1.05gm/cm^{-3}	1.05gm/cm^{-3}
PH of gel	6	6	6
Concentration $CaCl_2$	1 Mole	0.01 Mole	0.01Mole
Gel setting period	2days	2days	2days
Gel aging	1month	1month	1month
Period of growth	21 days	21 days	21 days
Temperature	Room Temperature	Room Temperature	Room Temperature

Calcium Phosphate crystal growth

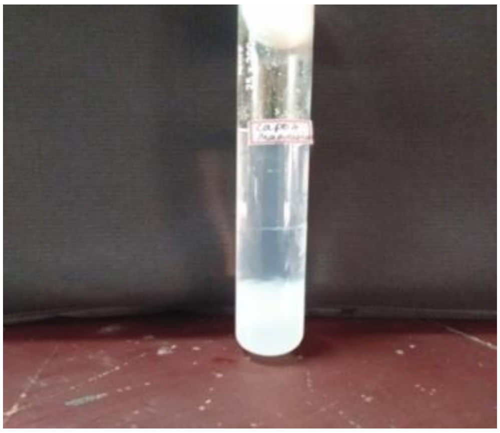

Fig.1a Growth of pure CaP crystal

Fig.1b Harvested crystals for CaP crystal

$$3CaCl_2 + 2H_3PO_4 \rightarrow Ca_3(PO_4) + 6HCl$$

Copper calcium phosphate crystal growth

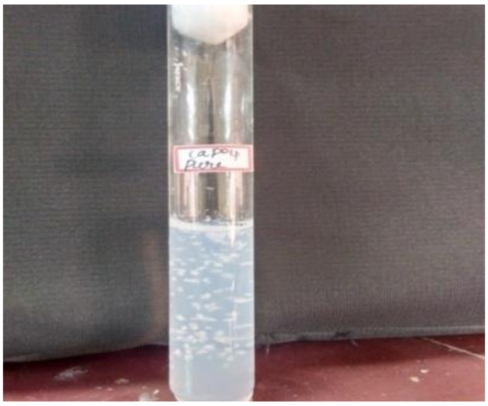

Fig. 2a Growth of CuCaP crystal

Fig.2b Harvested of CuCaP crystal

$2CH_3COOH + Na_2SiO_3 \rightarrow 2CH_3COONa \downarrow + SiO_2 + H_2O$

$4CH_3COONa + CaCl_2 + CuCl_2 \rightarrow (CH_3COO)_4CuCa \downarrow + 4NaCl$

$3(CH_3COO)_4CuCa + 4H_3PO_4 \rightarrow (CuCa)_3(PO_4)_4 \downarrow + 12CH_3COOH$

Magnesium calcium phosphate crystal growth

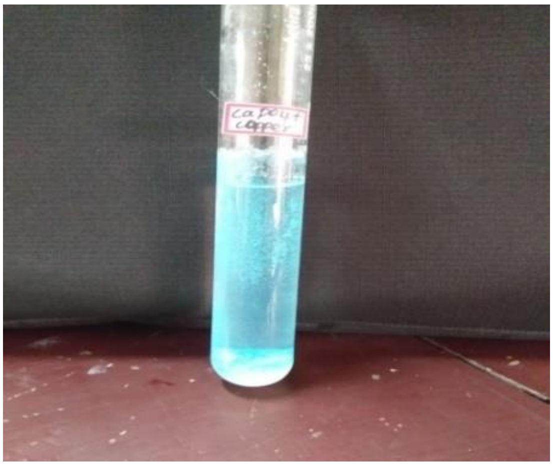

Fig.3a Growth of MgCaP crystal

Fig.3b Harvested crystal for MgCaP crystal

$2CH_3COOH + Na_2SiO_3 \rightarrow 2CH_3COONa \downarrow + SiO_2 + H_2O$

$4CH_3COONa + CaCl_2 + MgCl_2 \rightarrow (CH_3COO)_4MgCa \downarrow + 4NaCl$

$3(CH_3COO)_4MgCa + 4H_3PO_4 \rightarrow (MgCa)_3(PO_4)_4 \downarrow + 12CH_3COOH$

The table 1.1 shows that optimum condition crystal growth in calcium phosphate with doped copper and magnesium as per the standard procedure is followed. The reaction of crystal growth calcium phosphate, copper calcium phosphate and magnesium calcium phosphate are solved. The growth and harvested crystals are shown in Fig 1a, 1b, 2a, 2b and 3a, 3b.

II. MATERIALS AND METHODS

The single diffusion gel growth of pure calcium phosphate doped with (Copper and Magnesium) crystals. 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, copper chloride and magnesium chloride is incorporated inside the gel. After setting the gel, an aqueous solution of orthophosphoric acid was slowly poured over it. Two or three days a white column of tiny crystals were grown, which are shown in Fig1(a), 1(b), 2(a), and 2(b), and 3(a), 3(b). The chemical reaction between calcium chloride, copper chloride, magnesium chloride and orthophospharic acid in gel medium of calcium phosphate doped with (Cu and Mg) crystals. After 21 days harvested crystal for further analysis.

Characterization Techniques

FT- IR spectra is recorded by KBr pellet technique using Perkin Elmer FT-IR spectrometer with the range 4000-400cm is available at Centralized Instrumentation Science Laboratory, Department of Physics, St. Joseph college, Thriuchirapalli. The surface morphology of pure calcium phosphate doped with (Cu and Mg) crystals was studied by JEOL-SEM-5610 SEM and the presence of elemental composition was calculated by OXFORD instruments. This facilities available at Centralized instrumentation and service laboratory, Department of Physics, Annamalai University, Chidambaram, Tamilnadu and South

India. The TG/DTA analysis obtained by NETZSCH STA449F3 heating sample from room temperature 1000ºC in an atmosphere of nitrogen with heating rate standard procedure. Available at Centralized instrumentation and service laboratory, Department of Physics, Annamalai University, Chidambaram, Tamilnadu and South India.

III. RESULT AND DISCUSSION

The harvested crystals calcium phosphate doped with copper and magnesium are studied by FT-IR, SEM-EDX and TG/DTA method. FT-IR spectrum calcium phosphate, copper calcium phosphate crystal and magnesium calcium phosphate crystal (CuCaP and MgCaP) confirmed the presences of the functional groups are identified. The SEM images show surface morphology of the crystals. The EDX spectrum shows the elemental status is identified confirmed the copper calcium phosphate and magnesium calcium phosphate crystal (CuCaP and MgCaP). The TGA/DTA studies thermal stability of the calcium phosphate, doped with copper and magnesium.

1. FT-IR studies

The FT-IR spectrum is calcium phosphate crystals as shown in Fig. 4, Copper calcium phosphate crystal as shown in Fig 5 and Magnesium calcium phosphate crystal as shown in Fig 6. FT-IR assignments of calcium phosphate doped with (Cu and Mg) crystals are noted in table 1.2.

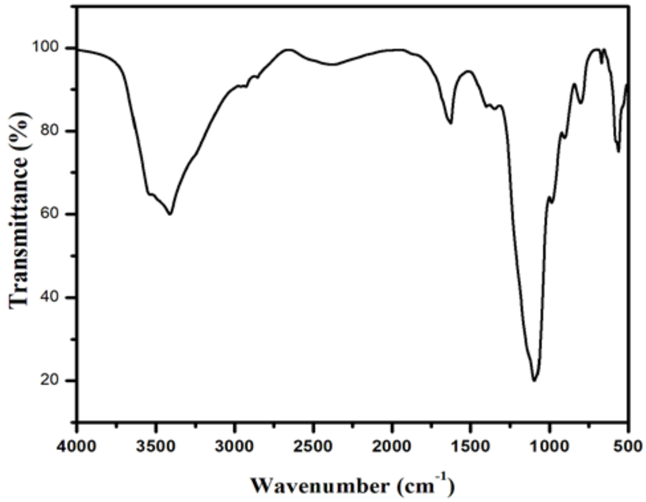

Fig .4 FT-IR spectrum studies on calcium phosphate crystal

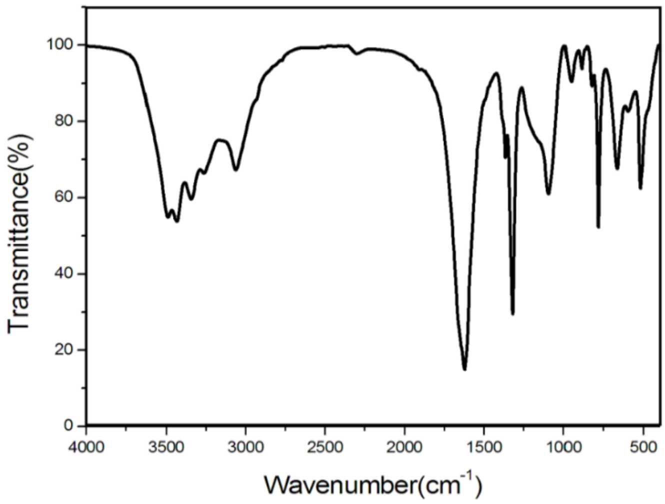

Fig.5 FT-IR spectrum studies on copper calcium phosphate crystal

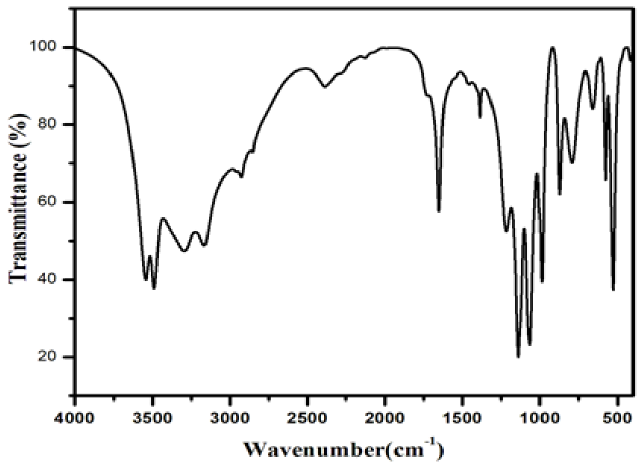

Fig .6 FT-IR spectrum studies on magnesium calcium phosphate crystal

Table 1.2

FT-IR absorption frequencies (cm^{-1}) intensity estimate along with tentative assignment for pure calcium phosphate doped with metals (Cu and Mg) crystals

Pure calcium phosphate	Copper calcium phosphate crystal	Magnesium calcium phosphate crystal	Assignments
3485	3411	3543	OH stretching
3276	3384	3490	OH symmetric and asymmetric stretching
2652	2625	2657	CH_2 symmetric and asymmetric stretching
1649	1647	1655	H-O-H symmetric vibration
1401	1486	1450	C-O asymmetric stretching
1132	1156	1184	P=O stretching vibration
1068	1096	1063	P=O bending vibration
999	803	987	P-O –P vibration
887	870	874	P-O asymmetric stretching vibrations
509	569	528	Metal-oxygen bond
406	469	477	Phosphate bond

The Table1.2 and Fig 4, 5 and 6 are shows. The peaks at 3485 cm^{-1} 3411 cm^{-1} and 3543 cm^{-1}due to intermolecular OH stretching vibration respectively. 3276 cm^{-1}, 3384 cm^{-1} and 3490 cm^{-1}, is the peak appearing OH symmetric and asymmetric. 2652 cm^{-1}, 2625 cm^{-1}, and 2657 cm^{-1}, is CH_2 symmetric and asymmetric stretching. 1649 cm^{-1}, 1647 cm^{-1} and 1655 cm^{-1}, is also attributed to bending vibration of water molecule H-O-H and 1401 cm^{-1}, 1486 cm^{-1}, 1450cm^{-1} are C-O Stretching vibration are observed. 1132 cm^{-1} 1156 cm^{-1}, and 1184 cm^{-1} is exceptional to P=O associated stretching vibration. 1068 cm^{-1}, 1096 cm^{-1}, 1063 cm^{-1} P=O bending vibration. The peaks are 999 cm^{-1}, 803 cm^{-1} and 987 cm^{-1} P-O-P asymmetric stretching vibration. 887 cm^{-1},870 cm^{-1} and 874 cm^{-1} C= C asymmetric stretching vibrations. 509 cm^{-1}, 569 cm^{-1} and 528 cm^{-1} is Metal-oxygen bond. Phosphate bond are observed in 406cm^{-1}, 469cm^{-1} and 477cm^{-1} [Brajendra Singh *et al.,* 2015, Haixia Niu et al., 2006 and Goalian *et al.,* 2011].

SEM-EDX Studies

Calcium phosphate harvested crystals are studied by the scanning electron microscope with EDX method. The Fig 7 shows the square and rectangular shape is observed. Shape and Morphology are present [Sekar and Suguna 2011].

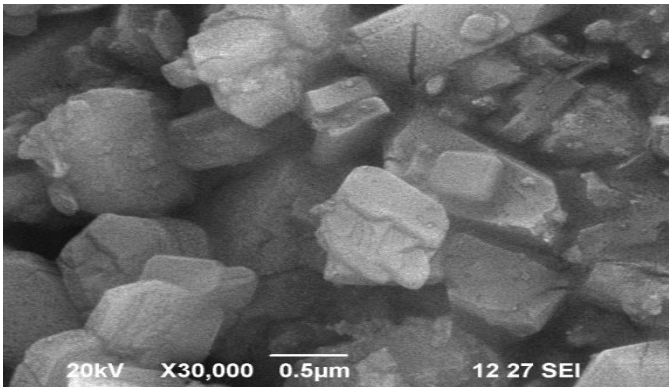

Fig. 7 SEM of calcium phosphate crystal

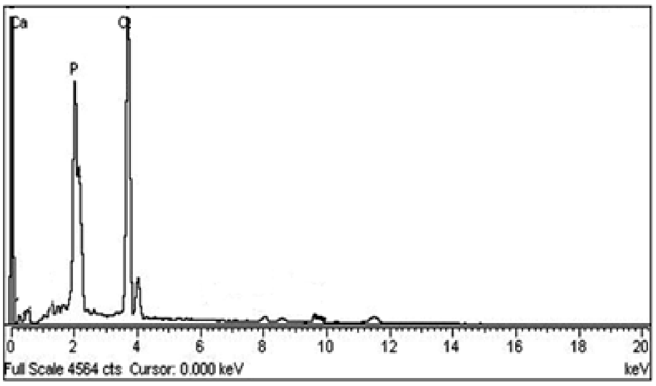

Fig. 7a EDX spectrum of calcium phosphate crystal

Table-1.3

The elemental concentration of calcium phosphate crystal by SEM-EDX method

Elements	**Weight %**
Ca	40.36
P	17.4
O	42.60

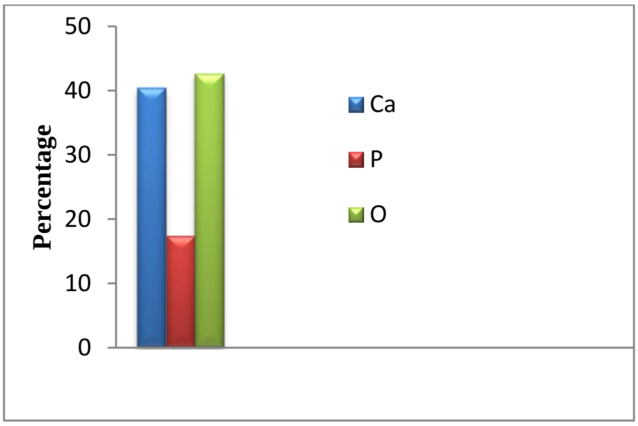

Fig.7 b. The relative distribution of calcium phosphate crystal

Table 1.3 and Fig 9b EDX studies is calcium phosphate crystal. The table 1.3 shows. The revealed that Ca is 40.36%, P is 17.4% and O is 42.60% present in calcium phosphate crystal. The structure and element variation are found. [Raynaud et al., 2002].

Copper calcium phosphate crystal

Copper calcium phosphate harvested crystals are studied by the scanning electron microscope with EDX method. The Fig 8 shows the needle shape shape is observed. Shape and Morphology are present [Zeljko Radovanovic et al., 2018

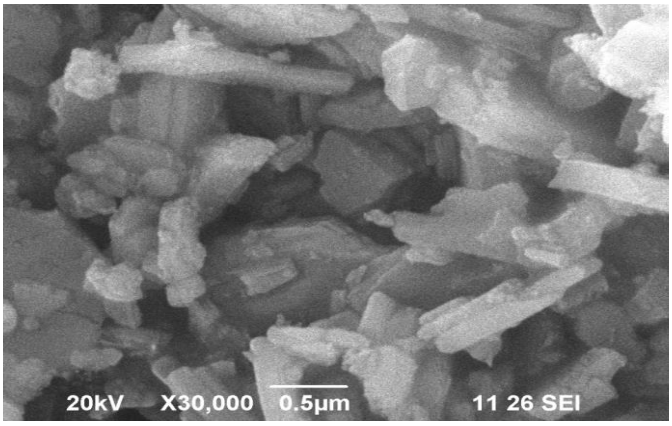

Fig. 8 SEM of copper calcium phosphate crystal

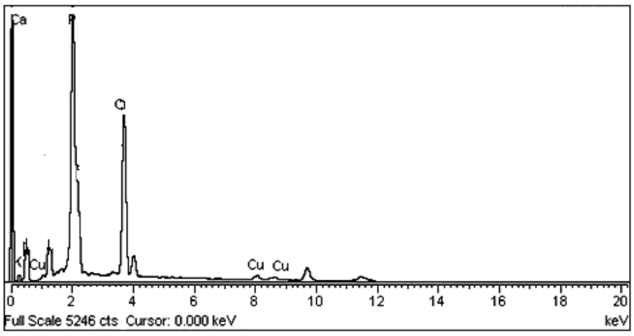

Fig. 8a EDX spectrum of copper calcium phosphate crystal

Table-1.4

The elemental concentration of copper calcium phosphate crystal by SEM-EDX method

Elements	**Mass %**
Ca	36.94
P	36.84
O	18.92
Cu	7.40

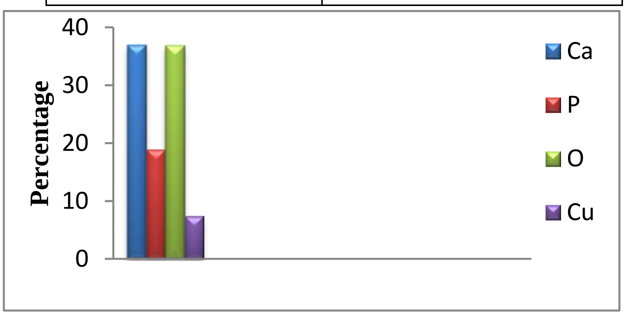

Fig.8 b The relative distribution of copper calcium phosphate crystal

Table 1.4 and Fig 10b EDX studies is copper calcium phosphate crystal. The table 1.4 shows. The values revealed that Ca is 36.94%, P is 36.84, O is the 18.92% and Cu is 7.40% present in copper calcium phosphate crystal. The structure and element variation are found.

Magnesium calcium phosphate crystal

Magnesium calcium phosphate harvested crystals are studied by the scanning electron microscope with EDX method. The Fig 9 shows the irregular shape is observed. Shape and Morphology is present [Mostafa Shahrezaee, et al., 2017].

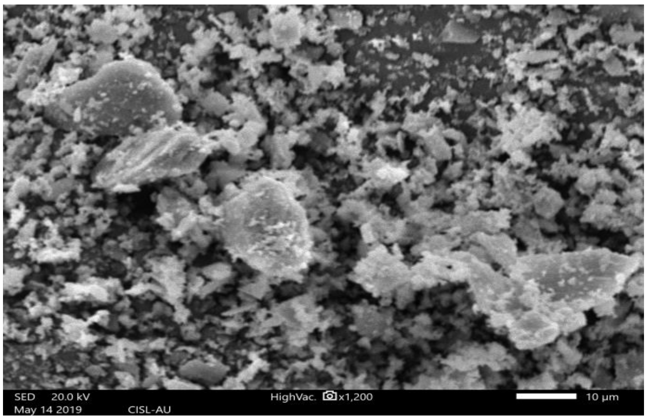

Fig .9 SEM of magnesium calcium phosphate crystal

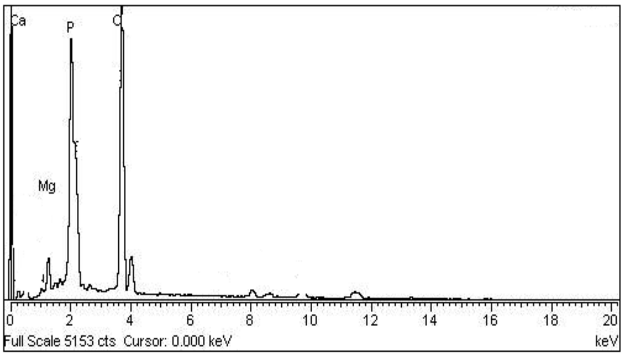

Fig. 9a EDX spectrum of magnesium calcium phosphate crystal

Table-1.5

The elemental concentration of magnesium calcium phosphate crystal by SEM-EDX method

Elements	Mass %
Ca	37.56
P	30.43
O	33.21
Mg	5.90

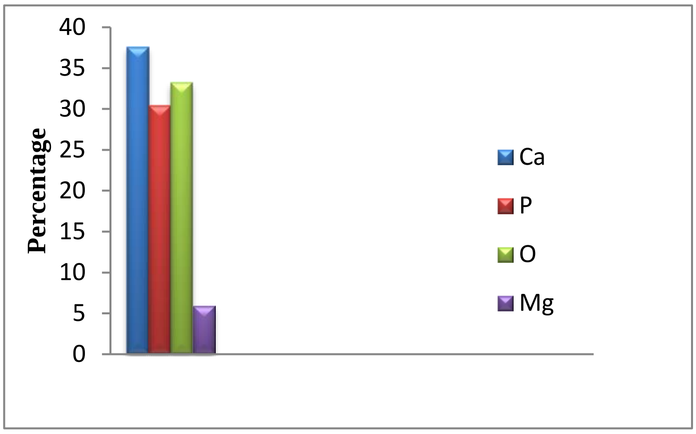

Fig.9b The relative distribution of magnesium calcium phosphate crystal

Table1.5 and Fig 9a EDX studies are magnesium calcium phosphate crystal. The table 1.5 shows. The values revealed that Ca is 37.56%, P is 30.43%, O is 33.21% and Mg is 5.90% present in magnesium calcium phosphate crystal. The structure and element variation are found.

TG/DTA Studies

Calcium phosphate crystal

Thermo gravimetric analysis and differential thermal analysis (TGA-DTA) of gallbladder stone type of crystals with their thermal properties of calcium phosphate doped with (Cu, and Mg) crystals are studied through TGA/DTA analysis. The thermo gravimetric analysis of gallbladder stone type of crystals is shown in Fig 10.

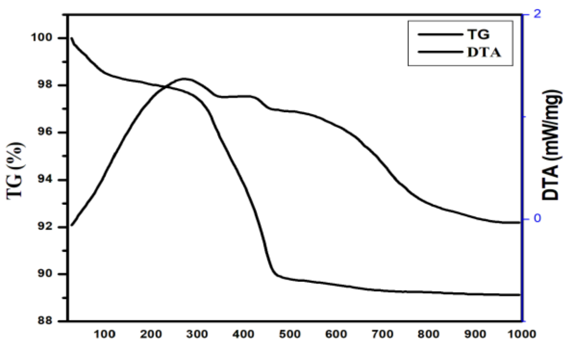

Fig.10 TGA-DTA spectrum of calcium phosphate crystal

Table-1.6. Thermo gravimetric analysis of calcium phosphate crystal

Name of the samples	Stage-I			Stage-II			Stage-III			Stage-IV		
	T_i^0C	T_f^0C	Mass (%)	T_i^0 C	T_f^0 C	Mass (%)	T_i^0 C	T_f^0 C	Mass (%)	T_i^0 C	T_f^0 C	Mass (%)
calcium phosphate crystal	28	68	5	68	363	36	363	573	46	573	738	50

T_i = Initial temperature

T_f =Final temperature

Fig 10 and Table 1.6 shows (TGA/DTA) curve of calcium phosphate crystal In the first stage 5% mass loss occurs between 28°C-68ºC which is indicate the elimination of water molecule. In the second stage 36% mass loss occurs between 68ºC-363°C losing crystalline water immediately associated water molecule completely removed at 363°C and becomes anhydrous subsequently when the temperature is further increased 363ºC-573ºC at mass loss 46% of the sample remaining stable. In the fourth stage weight loss about 50% was observed between 573 °C-738 °C. The mass loss corresponding well with the DTA results by the appearance of an exothermic peak at 245 °C and thus there is an increase in the peak temperature which indicates the improved thermal stability of pure calcium phosphate. Thus there is an increase in the peak temperature which indicates the improved thermal stability of calcium phosphate crystal [Sibel Ataol *et al.,* 2015].

Copper calcium phosphate crystal

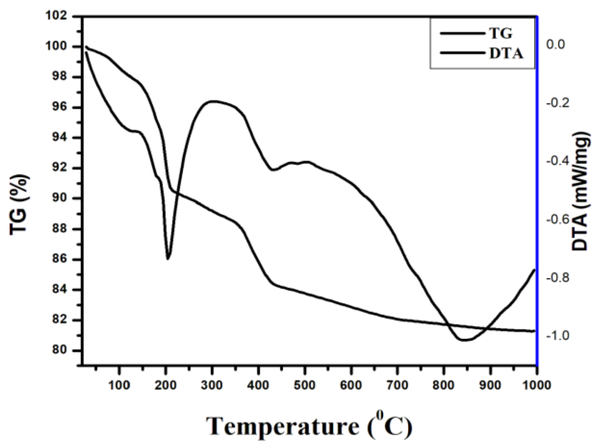

Fig .11 TGA-DTA spectrum of copper calcium phosphate crystal

Table 1.7. TGA/DTA analysis of copper calcium phosphate crystal

Name of the samples	Stage-I			Stage-II			Stage-III			Stage-IV		
	T_i^0 C	T_f^0 C	Mass (%)	T_i^0 C	T_f^0 C	Mass (%)	T_i^0 C	T_f^0 C	Mass (%)	T_i^0 C	T_f^0 C	Mass (%)
copper calcium phosphate crystal	28	249	10	249	364	12	364	469	16	469	639	19

T_i = Initial temperature

T_f =Final temperature

Fig. 11 and Table. 1.7 shows (TGA/DTA) curve of copper calcium phosphate crystal In the first stage 10% mass loss occurs between 28°C-249ºC which is indicate the elimination of water molecule. In the second stage 12% mass loss occurs between 249ºC-364°C losing crystalline water immediately associated water molecule completely removed at 364°C and becomes anhydrous subsequently when the temperature is further increased 364ºC-469ºC at mass loss 16% of the sample remaining stable. The fourth stage is 469ºC-639ºC at mass loss 19%. The mass loss corresponding well with the DTA results by the appearance of an endothermic peak at 200 °C and thus there is an increase in the peak temperature which indicates the improved thermal stability of copper calcium phosphate. Thus there is an increase in the peak temperature which indicates the improved thermal stability of calcium phosphate crystal [Quasim et al., 2009].

Magnesium calcium phosphate crystal

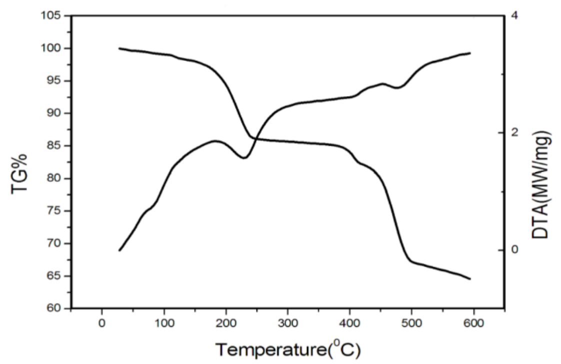

Fig. 12 TGA-DTA spectrum of magnesium calcium phosphate crystal

Table 1.8. TGA-DTA spectrum of magnesium calcium phosphate crystal

Name of the samples	Stage-I			Stage-II			Stage-III			Stage-IV		
	Ti⁰ C	Tf⁰ C	Mass (%)	Ti⁰ C	Tf⁰ C	Mass (%)	Ti⁰ C	Tf⁰ C	Mass (%)	Ti⁰ C	Tf⁰ C	Mass (%)
magnesium calcium phosphate crystal	40	150	3	150	240	10	240	370	4	370	460	16

T_i = Initial temperature

T_f =Final temperature

Fig 12 and Table1.8 shows (TGA/DTA) curve of magnesium calcium phosphate crystal In the first stage 3% mass loss occurs between 28°C-150ºC which is indicate the elimination of water molecule. In the second stage 10% mass loss occurs between 150ºC-240°C losing crystalline water immediately associated water molecule completely removed at 240°C and becomes anhydrous subsequently when the temperature is further increased 240ºC-370ºC at mass loss 4% of the sample and fourth mass loss 16% occurs between 370ºC-460ºC remaining stable. Thus there is an increase in the peak temperature which indicates the improved thermal stability of Magnesium calcium phosphate crystal. The mass loss corresponding well with the DTA results by the appearance of an endothermic peak at 225 °C and thus there is an increase in the peak temperature which indicates the improved thermal stability of magnesium calcium phosphate. Thus there is an increase in the peak temperature which indicates the improved thermal stability of calcium phosphate crystal [Toibah, et al., 2012]

IV.CONCLUSION

The analysis of gallstone type crystals are such as calcium phosphate doped with copper calcium phosphate and magnesium calcium phosphate. FT-IR methods. All the functional groups of the chemical constituents are studied infrared region 400cm^{-1}-4000cm^{-1}. The tentative assignments for FT-IR absorption peaks are tabulated in pure calcium phosphate doped with (Cu and Mg) samples. From the results, the following chemical compounds frequencies are observed C=O stretching, O-H stretching, C-H bonding, C=C stretching, C=N stretching and M=O bond. The functional groups are studied. XRD studies are carried out to analyze the crystalline nature present in gallstone type crystal samples. The observed values 2θ, d spacing and intensity are compared JCPDS data are used in identification crystalline nature surface morphological are identified with SEM. The elemental composition is determined by EDX method. Thermal properties of gallstone type crystal by TGA-DTA analysis. In the present study has been carried out in order to find the mass loss occurs in different stages. The mass losses of all gallstone type crystals are conformed and the results are discussed.

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