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X-ray powder diffraction, thermal analysis and IR studies of zinc ammonium phosphate hexahydrate

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Zinc Ammonium Phosphate Hexahydrate (ZAPH) crystals are grown by slow evaporation. These crystals are characterized by powder X-ray diffraction, TG-DTA and IR studies. The power diffraction pattern of ZAPH indicates the orthorhombic crystal structure analogous to struvite. TG-DTA analysis suggests loss of water of hydration ($6H_2O$) between 103 and 500°C. Later the substance melts and only Zn remains around 1000°C. Infra Red spectrum is characteristic of H_2O, PO_4^{3-} and NH_4^+ ions.

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1. Introduction

The mineralizations of calcified tissues in biological systems are comprises of two phases: organic and inorganic or mineral phases. The inorganic phase consists of one or more types of phosphate minerals depending on the nature of calcification (e.g. normal as in bones and teeth or abnormal/ pathological as in dental calculi and urinary stones). More than 99% of the human urinary stones are composed of crystalline substances. These substances are calcium carbonate, calcium phosphate, calcium oxalate, ammonium magnesium phosphate (struvite), uric acid, urates of ammonium, sodium, potassium, calcium and magnesium, hippuric acid, cystine, cholesterol, xanthine and bilirubin. Struvite ($MgNH_4PO_4.6H_2O$) the bio-mineral is a constituent of renal and vesical calculi. A series of orthorhombic struvite analogues ($MM`PO_4.6H_2O$ with M= Mg, Zn, Cd, M`= K, Tl, NH_4 and Rb) have been reported earlier due to biomedical importance of these crystals [1-6]. The present investigations are undertaken to present comprehensive view of powder X-ray pattern, thermal analysis and vibrational modes of Zinc Ammonium Phosphate Hexahydrate (ZAPH) with struvite analogues.

2. Experimental

ZAPH single crystals are grown by slow evaporation at room temperatures from the aqueous equi-molar solutions of ammonium dihydrogen phosphate and zinc sulphate. Good tabular crystals of size ~ 5mm, with well developed (001) faces, are grown in about a fortnight. Powder X-ray diffraction study is carried out with a Rigagu-Rint 2000 X-ray diffractometer using Ni filtered CuKα radiation. The thermal dehydration processes are studied using TGDTA ULVAC 2000S up to a temperature of 1000˚C at a heating rate of 10˚C per minute in air. IR Spectrum of crystalline powder in KBr was recorded on Sp3-300 Pye Unicam IR spectrophotometer in 400 to 4000 cm^{-1} region.

3. Results and discussion

3.1 X-ray powder diffraction

XRD pattern of the ZAPH crystal is shown in Fig. 1. The crystals can be indexed as orthorhombic. The cell parameters are evaluated using Crystal Utility Program assembled by Nakamuta [7].

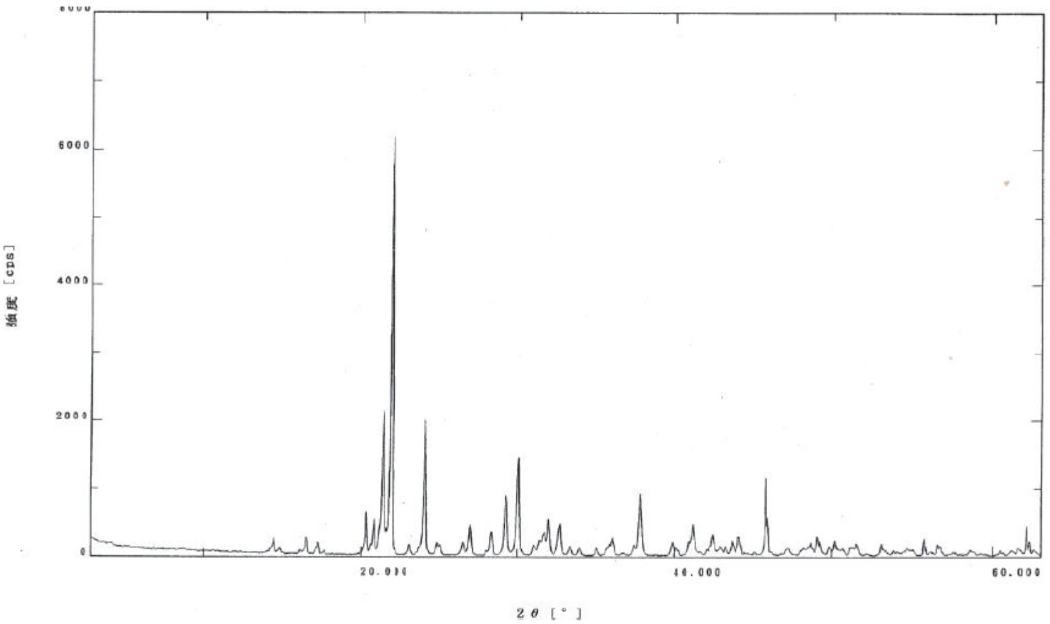

Fig. 1. X-ray diffraction pattern of ZAPH.

The cell parameters are a = 6.1459, b = 12.6759 and c = 20.1950 Å.

The experimental and calculated results are given in Table 1.

Table 1. Experimental and calculated data of ZAPH.

d-spacing obs. (Å)	d (calc.)/Å	Intensity (obs)	Indices			2 Theta obs.	2 Theta calc.
			h	k	l		
10.0975	10.0975	2	0	2	0	8.75	8.75
6.1459	6.1459	4	1	0	0	14.40	14.40
5.3681	5.3681	6	0	2	2	16.50	16.50
5.1363	5.0487	4	0	4	0	17.25	17.55
4.3710	4.4121	12	1	0	2	20.30	20.11
4.2670	4.2731	9	1	3	1	20.80	20.77
4.1487	4.1357	40	0	1	3	21.40	21.47
4.0551	4.0430	100	1	2	2	21.90	21.97
3.8471	3.8484	4	0	5	1	23.10	23.09
3.6973	3.6901	38	1	3	2	24.05	24.10
3.5659	3.5787	4	0	3	3	24.95	24.86
3.3607	3.3658	4	0	6	0	26.50	26.46
3.3056	3.2916	10	1	2	3	26.95	27.07
3.1509	3.1690	8	0	0	4	28.30	28.13
3.0507	3.0380	20	2	1	0	29.25	29.37
2.9713	2.9727	28	0	6	2	30.05	30.03
2.8778	2.8752	2	1	6	1	31.05	31.08
2.8466	2.8638	4	2	2	1	31.40	31.20
2.8246	2.8166	5	1	0	4	31.65	31.74
2.7945	2.7955	7	2	3	0	32.00	31.99
2.7404	2.7395	10	2	1	2	32.65	32.66
2.6844	2.6841	4	0	4	4	33.35	33.35
2.6384	2.6372	2	1	5	3	33.95	33.96
2.5580	2.5579	2	1	7	1	35.05	35.05
2.4927	2.4932	6	0	5	4	36.00	35.99

d-spacing obs. (Å)	d (calc.)/Å	Intensity (obs)	Indices			2 Theta obs.	2 Theta calc.
			h	k	l		
2.4435	2.4456	2	2	5	0	36.75	36.72
2.3750	2.3725	18	0	3	5	37.85	37.89
2.2576	2.2656	4	0	4	5	39.90	39.75
2.1893	2.1911	10	1	8	2	41.20	41.16
2.1277	2.1258	6	1	4	5	42.45	42.49
2.0496	2.0486	6	3	0	0	44.15	44.17
2.0065	2.0077	2	3	2	0	45.15	45.12
1.9754	1.9745	18	0	8	4	45.90	45.92
1.9240	1.9242	2	0	10	2	47.20	47.19
1.8864	1.8861	2	1	9	3	48.20	48.21
1.8700	1.8720	4	0	5	6	48.65	48.59
1.8522	1.8577	6	1	4	6	49.15	48.99
1.8158	1.8170	4	0	11	1	50.20	50.17
1.7991	1.8036	2	0	1	7	50.70	50.56
1.7714	1.7710	4	2	8	3	51.55	51.56
1.7509	1.7500	2	3	6	0	52.20	52.23
1.7233	1.7204	4	3	0	4	53.10	53.19
1.6766	1.6770	2	3	5	3	54.70	54.69
1.6682	1.6683	2	0	12	1	55.00	54.99
1.6475	1.6458	4	2	4	6	55.75	55.81
1.6221	1.6232	4	1	12	0	56.70	56.66
1.6002	1.5987	2	2	5	6	57.55	57.61
1.5715	1.5724	2	1	12	2	58.70	58.66
1.5571	1.5555	2	2	1	7	59.30	59.36
1.5290	1.5295	2	2	11	2	60.50	60.48
1.5132	1.5129	2	3	9	0	61.20	61.21
1.5043	1.5061	2	1	13	0	61.60	61.52
1.4923	1.4921	6	1	9	6	62.15	62.16

The unit cell size of zinc struvite (ZAPH) is in between that of the magnesium struvite (MAPH) and cadmium struvite (CAPH). The crystallographic data of struvite and the analogues are given in Table 2. In struvite analogues $MM`PO_4.6H_2O$ the cell parameters are similar with change of $M` = K^+, Tl^+, Cs^+, Rb^+$ and NH_4^+ whereas the cell parameter deviation is more with change of M = Mg^{2+}, Zn^{2+} and Cd^{2+}. The deviation of cell parameters might be due to the difference of ionic radii of Mg^{2+} (0.72 Å), Zn^{2+} (0.74 Å) and Cd^{2+}(0.95 Å).

Table 2. Crystallographic data of struvite analogous.

Compound	a (Å)	b (Å)	c (Å)	Ionic radius (Å)	Reference
$MgNH_4PO_4{\times}6H_2O$	6.95	11.21	6.14	1.48 ($M^{'}$)	[3]
$MgKPO_4{\times}6H_2O$	6.87	11.09	6.16	1.33 ($M^{'}$)	[3]
$MgTlPO_4{\times}6H_2O$	6.861	11.35	3.135	1.44 ($M^{'}$)	[3]
$MgRbPO_4{\times}6H_2O$	6.852	11.27	6.177	1.48 ($M^{'}$)	[3]
$ZnKPO_4{\times}6H_2O$	5.964	12.495	5.808	0.74 (M)	[5]
$MgNH_4PO_4{\times}6H_2O$	6.941	11.199	6.137	0.72 (M)	[2]
$ZnNH_4PO_4{\times}6H_2O$	6.146	12.676	20.195	0.74 (M)	Present work
$CdNH_4PO_4{\times}6H_2O$	13.882	12.249	11.395	0.95 (M)	[6]

$M^{'} = NH_4^+, K^+, Tl^+, Rb^+$, $M = Mg^{2+}, Zn^{2+}, Cd^{2+}$

3.2 TG-DTA analysis

TG-DTA curves of ZAPH crystal are shown in Fig. 2. The TG analysis shows that between 103°C and 500°C the weight loss is 25%. This indicates dehydration. The strong endothermic peaks in DTA curve around 147°C with the associated shoulders indicate the stepwise removal of water during this temperature range. There is another endothermic peak around 630^{o}C in DTA curve indicating melting of substance. This is associated with a loss of weight of about 28% in TG curve (upto 630^{o}C) and further weight loss about 15% losses up to 1000^{o}C. These weight losses are due to dissociation of the substance and evaporation of phosphate and ammonia respectively. The final loss of weight in TG curve (about 43%) indicates only the presence of zinc. The behavior is similar to the TG-DTA curves of struvite and CAPH. Dehydration starts around 116^{o}C for struvite [8] and 113^{o}C for CAPH [6] and in the present investigation around 103^{o}C. The exothermic reaction ends at 665^{o}C for struvite, 740^{o}C for CAPH whereas ZAPH at 755^{o}C.

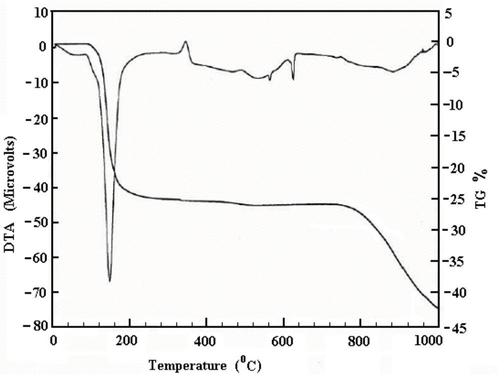

Fig. 2. TG-DTA curve of ZAPH.

3.3 Infra red spectrum

IR spectra of ZAPH are shown in Figs. 3 and 4.

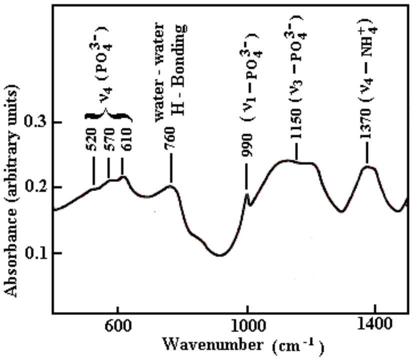

Fig. 3. Infra red spectrum of ZAPH in the region 400 -1500 cm^{-1}.

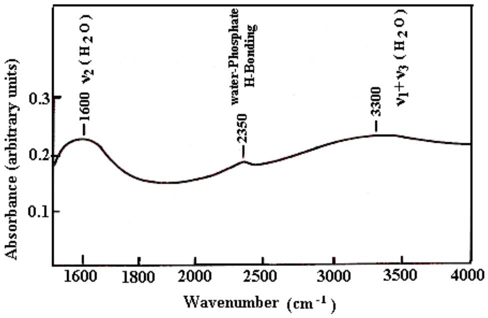

Fig. 4. Infra red spectrum of ZAPH in the region 1500 - 4000 cm^{-1}.

Water molecule possesses three modes of fundamental vibrations ν_1, ν_2, and ν_3. All these modes are infrared active and in vapour phase occur at 3652(ν_1), 1595(ν_2) and 3765(ν_3) cm^{-1}. They show shifts in liquid and solid phases. In general, their positions in liquid phase are 3219, 1645 and 3405 cm^{-1} whereas in solid phase they are 3200, 1640 and 3400 cm^{-1} respectively. Such shifts are characteristic of hydrogen bonding in liquid and solid phases [9]. In the present investigation two broad bands are observed at 3300 and 1600 cm^{-1}. Of these, the band at 1600 cm^{-1} is attributed to the H-O-H bending mode (ν_2) and the other band at 3300 cm^{-1} is assigned to ν_1 and ν_3 mode.

The bands observed in the region 1400 to 400 cm^{-1} are characteristic of phosphate ion PO_4^{3-}. The phosphate ion in free-state exists in tetrahedral symmetry. In ideal case phosphate ion exhibits four fundamental modes of vibrations at 1082 (ν_3), 980 (ν_1), 515 (ν_4), and 363 (ν_2) cm^{-1}. Of these ν_1 is non-degenerate, ν_2 is doubly degenerate, whereas ν_3 and ν_4 are triply degenerate. The ν_3 and ν_4 vibrations alone are infrared active. In general in most of the cases phosphate ion is distorted from the ideal tetrahedral symmetry. This removes the degeneracy of the infrared active vibrations (ν_3 and ν_4) also allows the non active vibrations ν_1 and ν_2 to absorb energy in the infrared region. In the present study the band observed at 990 cm^{-1} is attributed to ν_1 mode. The broad band observed at 1150 cm^{-1} with shoulders is assigned to ν_3 mode. The band consisting of three components at 520, 570 and 610 cm^{-1} is assigned to triply degenerate mode ν_4. The band observed at 760 cm^{-1} is attributed to water-water H-bonding.

For NH_4^+ ion, the triply degenerate ν_3 vibration in the region 3350-3050 cm^{-1} and is generally observed by the water bands also. The triply degenerate ν_4 band occur around 1400 cm^{-1} and is characteristic diagnostic absorption. In the present investigation the band at 1370 cm^{-1} is attributed to the triply degenerate ν_4 mode of NH_4^+ ion. Similar observations are reported in literature and the splittings are attributed to the active rotation of the ammonium group about its three axes [3]. The band observed at 2350 cm^{-1} is assigned to water-phosphate H-bonding.

4. Conclusions

The struvite analogues offer a unique opportunity to study the effect of ionic size on a family of hydrated phosphates. Powder X-ray studies of the ZAPH crystals suggest that they belong to the orthorhombic system and the cell parameters are evaluated. Differential thermal analysis ascertains the presence of six molecules of water of hydration $6H_2O$. In IR spectrum, the splitting of the ν_3 asymmetric stretch absorption band which occurs near 1000 cm^{-1} is a quantitative measure of the deviation of the PO_4^{3-} group from ideal tetrahedral symmetry. This ν_3 band is triply degenerate if the tetrahedron is perfect and the degeneracy will lift if the tetrahedron is distorted. Distortion of the PO_4^{3-} tetrahedron will also cause the infrared-inactive ν_1 symmetric stretch to appear weakly in the IR spectra.

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