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## Structural and Spectral Studies of $\text{ZnKPO}_4 \cdot 6\text{H}_2\text{O}$ Crystals

Zinc Potassium Phosphate Hexahydrate (ZPPH) is analogous to naturally occurring struvite. ZPPH crystals are grown by slow evaporation technique. These crystals are characterised by x-ray and infrared studies. Powder x-ray pattern indicates the orthorhombic crystal structure analogous to struvite with unit cell parameters  $a = 5.964$ ,  $b = 5.808$  and  $c = 12.495 \text{ \AA}$ . Infrared spectrum is characteristic of  $\text{H}_2\text{O}$  and  $\text{PO}_4^{3-}$  radicals.

Keywords: powder x-ray, IR, orthorhombic, zinc potassium phosphate hexahydrate (ZPPH), cell parameters

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### 1. Introduction

A number of investigations have been carried out on struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ), a constituent of renal and vesical calculi. It was thoroughly investigated by mineralogists, chemists and physicians, who studied it from different points of view and described many physical and chemical properties due to biomedical importance of these crystals. The system belongs to orthorhombic space group  $\text{Pmn}2_1$  with two molecules in unit cell. The Mg sites are octahedrally coordinated by six water molecules (ABBONA and BOISTELLE (1979)). Many authors have studied struvite analogues ( $\text{MgMPO}_4 \cdot 6\text{H}_2\text{O}$ , with  $M = \text{K}, \text{Tl}, \text{NH}_4$  and  $\text{Rb}$ ). In terms of increasing size of  $M$ , the end members are  $\text{K}^+$  salt and the two equally sized  $\text{Rb}^+$  or  $\text{NH}_4^+$  salts (BANKS et. al. (1975), WHITAKER and JEFFERY (1970), MATHEWE and SCHROEDER (1979)).  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$  is analogue of struvite. The present investigation is carried out on Zinc Potassium Phosphate Hexahydrate (ZPPH) with a view to ascertain the structure as analogous to naturally occurring struvite.

### 2. Experimental

ZPPH single crystals are grown by slow evaporation at ordinary temperatures from the aqueous equi-molar solutions of potassium dihydrogen phosphate and zinc sulphate. Good tabular crystals with well developed (001) faces grow in about ten days. The size is about  $2 \times 5 \times 10 \text{ mm}$ . This type of morphology has been reported earlier (ABBONA and BOISTELLE (1979)). Powder x-ray diffraction studies are carried with a JEOL x-ray diffractometer using Ni filtered  $\text{CuK}\alpha$  radiation. Vibrational spectrum of crystalline powder in KBr is recorded on Sp3-300 Py-Unicam IR spectrometer in  $400\text{--}4000 \text{ cm}^{-1}$  region.

### 3. Results and Discussion

#### X-ray diffraction studies

Powder x-ray diffraction pattern of the ZPPH crystal (Figure 1) has given the strong evidence of the elements Zn, K, P, O and H. The experimental data is tabulated in Table. 1

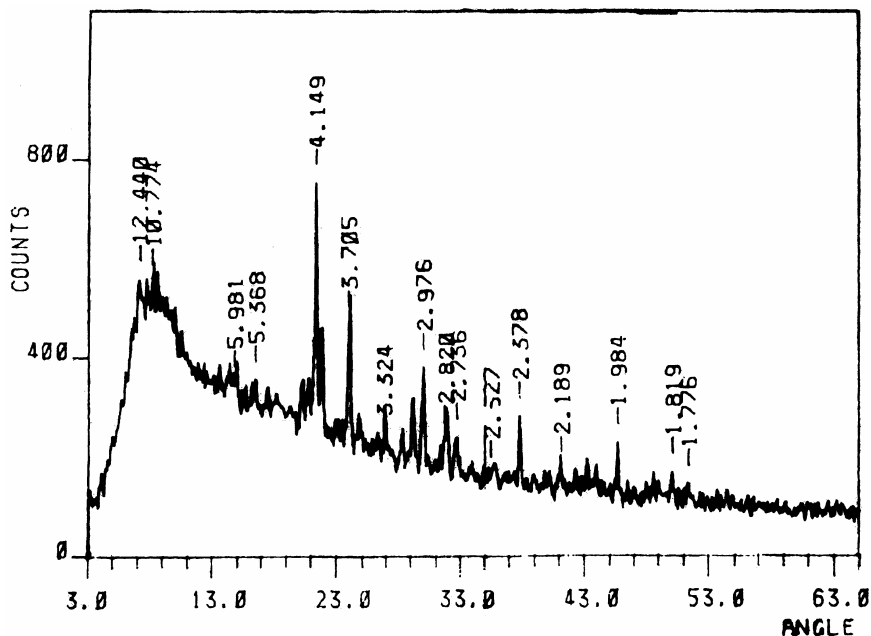


Fig. 1: Powder x-ray patter of the ZPPH crystal

The lattice parameters are evaluated by using Crystal Utility Program developed by NAKAMUTA (1991). The lattice parameters are  $a = 5.964$ ,  $b = 5.808$  and  $c = 12.495$  Å. The reported values of cell parameters for MPPH (MATHEW and SCHROEDER (1979)) are  $a = 6.873$ ,  $b = 6.160$  and  $c = 11.087$  Å. The deviation of cell parameters is due to the difference of ionic radii of  $Mg^{2+}(0.64)$  and  $Zn^{2+}(0.74)$ . These values are in good agreement with other reported cell parameters of the struvite analogues.

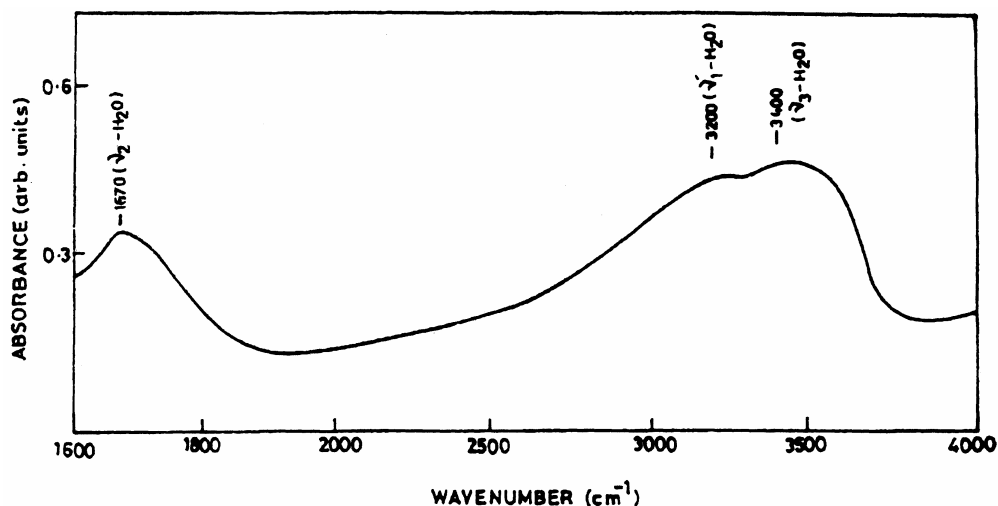
#### Infra Red Spectrum

The IR spectra of water molecule possesses three modes of fundamental vibrations  $\nu_1, \nu_2, \nu_3$ . All these modes are infrared active and in vapour phase occur at  $3652$  ( $\nu_1$ ),  $1595$  ( $\nu_2$ ) and  $3765$  ( $\nu_3$ )  $cm^{-1}$ . They show shifts in liquid and solid phases (HUNT and SALISBERY (1970)). 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. The IR spectrum (Figure 2) exhibits three bands characteristic of water molecule at  $1670$ ,  $3200$ ,  $3400$   $cm^{-1}$ . These are attributed to the fundamental vibrations  $\nu_2$  (bending mode),  $\nu_1$  (symmetric stretch) and  $\nu_3$  (asymmetric stretch) respectively. The band observed at  $750$   $cm^{-1}$  is assigned to water-water H-bonding (BANKS et al. (1975)). The bands observed in the region  $1400-400$   $cm^{-1}$  are characteristic of

phosphate ion  $\text{PO}_4^{3-}$ . The phosphate ion in free state exists in tetrahedral ( $T_d$ ) symmetry. In ideal case phosphate ion exhibits four fundamental modes of vibrations at 1082 ( $\nu_3$ ), 980 ( $\nu_1$ ), 515 ( $\nu_4$ ) and 363 ( $\nu_2$ )  $\text{cm}^{-1}$  (HERZBERG (1962)). Of these  $\nu_1$  is non-degenerate,  $\nu_2$  is doubly degenerate, whereas  $\nu_3$  and  $\nu_4$  are triply degenerate. The  $\nu_3$  and  $\nu_4$  vibrations alone are infrared active. In general, in most of the cases, phosphate ion is distorted from the ideal  $T_d$  symmetry. This removes the degeneracy of the infrared active vibrations ( $\nu_3$  and  $\nu_4$ ) and also allows the non-active vibrations  $\nu_1$  and  $\nu_2$  to absorb energy in the infrared region.

Table 1: Experimental and calculated data of ZPPH crystal

d-spacing ( $\text{\AA}$ )		Int. obs	Indices h k l	2Theta (Deg)	
obs.	calc.			obs.	calc.
12.440	12.513	515	0 1 0	7.10	7.06
10.774		544		8.20	
5.981	6.257	357	0 2 0	14.80	14.14
5.368	5.382	329	1 1 0	16.50	16.46
4.149	4.160	443	1 0 1	21.40	21.34
3.705	3.947	354	1 1 1	24.00	22.51
3.324	3.388	238	0 3 1	26.80	26.29
2.976	2.981	267	2 0 0	30.00	29.95
2.820	2.829	245	0 2 1	31.70	31.60
2.736	2.751	206	0 1 4	32.70	32.52
2.527	2.557	168	1 2 1	35.50	35.08
2.378	2.382	190	0 2 3	37.80	37.73
2.189	2.157	161	2 0 4	41.20	41.84
1.984	1.974	149	2 2 2	45.70	45.94
1.819	1.819	133	2 1 5	50.10	50.11
1.776	1.766	128	1 3 2	51.40	51.71

Fig. 2: IR spectrum of ZPPH crystal in the region 1600-4000  $\text{cm}^{-1}$

In the present case, the bands corresponding to  $\nu_1$  and  $\nu_2$  modes are also observed at 990 and 450  $\text{cm}^{-1}$  in addition to the infrared active  $\nu_3$  and  $\nu_4$  modes around 1100 and 600  $\text{cm}^{-1}$ .  $\nu_3$  and  $\nu_4$  modes consist of three components each (Figure 3). This clearly indicates the deviation of the ideal  $T_d$  symmetry of the  $\text{PO}_4^{3-}$  ion in this crystal.

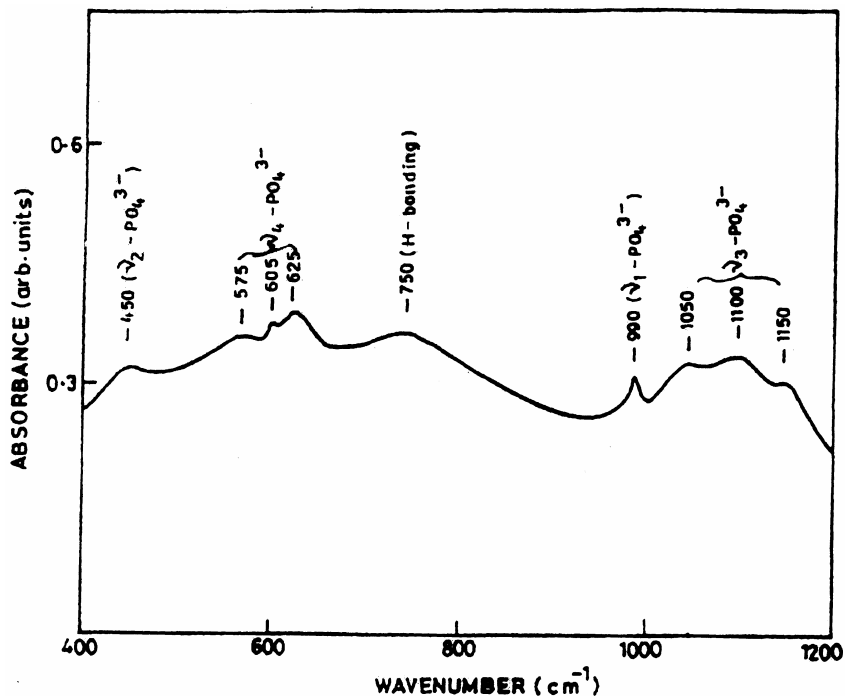


Fig. 3: IR spectrum of ZPPH crystal in the region 400-1200  $\text{cm}^{-1}$

#### 4. Conclusions

From the powder x-ray data the cell parameters are evaluated. Crystal structure is orthorhombic with unit cell  $Z=2$ , which is also a analogue to struvite. The unit cell volume of the crystal is reduced when compared to that of MPPH. Infra Red spectrum exhibits the presence of water and phosphate radicals. For  $\text{PO}_4^{3-}$  ion, distorted  $T_d$  symmetry is indicated. Hydrogen bonding is indicated by shifts of the  $\text{H}_2\text{O}$  vibrational modes. The splitting of absorption band due to  $\nu_3$  asymmetric stretch is a quantitative measure of the deviation of  $\text{PO}_4^{3-}$  group from ideal  $T_d$  symmetry. From the IR spectra of MPPH (BANKS et. al., (1975)) and ZPPH the splittings are observed to be in the order of 55  $\text{cm}^{-1}$  and 100  $\text{cm}^{-1}$  respectively. This indicates that the distortion of  $\text{PO}_4^{3-}$  group in ZPPH is larger. The deviation of sharp  $\nu_2$  band of water in solid phase from that of the liquid phase is a measure of the strength of the hydrogen bonding in solid phase. The deviation is more in ZPPH indicating relatively strong hydrogen bonding.

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