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| <i>Cryst. Res. Technol.</i> | <b>34</b> | 1999 | 7 | 911–914 |
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R. V. S. S. N. RAVIKUMAR, A. V. CHANDRASEKHAR, S. N. RAO, N. MADHU,  
B. J. REDDY, Y. P. REDDY

Chemical Physics and Spectroscopy Laboratories, S.V. University, Tirupati - 517 502, India

## Orthorhombic Site Symmetry of $\text{Cr}^{3+}$ in $\text{ZnNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ Crystals

Spectroscopic investigations of  $\text{Cr}^{3+}$  doped ZAPH are carried out. From the nature of optical absorption bands and their splittings at the liquid nitrogen temperature, the site symmetry of the  $\text{Cr}^{3+}$  in ZAPH is attributed to orthorhombic distortion.

Keywords: Chromium, orthorhombic symmetry, optical absorption spectra, Zinc Ammonium phosphate hexahydrate (ZAPH)

### 1. Introduction

Struvite is a biomineral which occurs in human urinary sediments and vesical and renal calculi. It is also present in soils as a reaction product from phosphate fertilizers. Whitaker and JEFFERY (1970), ABONA and BOISTELLE (1979) reported the crystal structure of Magnesium Ammonium Phosphate Hexahydrate ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) which is generally called struvite. It belongs to the orthorhombic space group  $\text{Pmn}2_1$ , with two molecules in unit cell. Zinc ammonium Phosphate Hexahydrate ( $\text{ZnNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) hereafter called ZAPH is analogous to struvite. In this crystal,  $\text{Zn}^{2+}$  is octahedrally coordinated by six water molecules and dopants replace  $\text{Zn}^{2+}$ . Due to the biological importance, detailed spectroscopic investigations are made on struvite and its analogues for their characterization.

PREM, CHAND and AGARWAL (1991) from their EPR investigations suggested tetragonal distortion for vanadyl ion and orthorhombic distortion for manganese ion in the present host. Ravikumar et al (1996) reported the near octahedral symmetry for  $\text{Co}^{2+}$  ion and  $\text{Ni}^{2+}$  ion in the host. In the case of  $\text{Co}^{2+}$  spin-orbit interaction was also reported. However no optical absorption studies on  $\text{Cr}^{3+}$  doped zinc struvite have been reported in literature. Therefore the authors have undertaken the optical absorption studies of  $\text{Cr}^{3+}$  in ZAPH crystal with a view to study the distortion in site symmetry and splittings of the energy levels.

### 2. Experimental technique

The single crystals of ZAPH are grown by the slow evaporation technique at the laboratory temperature from an aqueous equimolar solution of ammonium dihydrogen phosphate and zinc sulphate. Good crystals of ZAPH grow in about a fortnight. The  $\text{Cr}^{3+}$  doped crystals are grown by adding 0.1 mole weight of chromium sulphate to the growth solution. Optical absorption spectra at laboratory and liquid nitrogen temperatures are recorded using 2 mm thick crystals on Hitachi U-3400 spectrophotometer in UV-VIS-NIR region.

### 3. Theory

The chromium ion,  $\text{Cr}^{3+}$  ( $d^3$ ) gives rise to the free ion terms  ${}^4\text{F}$ ,  ${}^4\text{P}$ ,  ${}^2\text{G}$  and several other doublet states, of which  ${}^4\text{F}$  is the ground state. In octahedrally coordinated system in the

weak fields,  $^4F$  splits as  $^4A_2(F)$ ,  $^4T_2(F)$  and  $^4T_1(F)$  whereas  $^4P$  transforms as  $^4T_1(P)$ . In the doublet states,  $^2G$  splits as  $^2A_1(G)$ ,  $^2E_g(G)$ ,  $^2T_1(G)$  and  $^2T_2(G)$  and  $^2H$  splits as  $^2E_g(H)$ ,  $^2T_1(H)$  and  $^2T_2(H)$ . The weak field terms  $^4A_2(F)$ ,  $^2E_g(G)$ ,  $^2T_1(G)$  and  $^2T_2(G)$  correspond to the lowest strong field configuration  $t_{2g}^3$ . The ground state is  $^4A_2(F)$  at all strengths of the crystal field. Thus only three spin allowed transitions arise from  $^4A_2(F)$  to  $^4T_2(F)$ ,  $^4T_1(F)$  and  $^4T_1(P)$  states in addition to several spin forbidden transitions. If the symmetry is lowered the degeneracy will be removed and more number of absorption bands observed.

#### 4. Results and Discussion

Optical absorption spectra of Cr<sup>3+</sup>:ZAPH at the room temperature (RT) and the liquid nitrogen temperature (LNT) are shown in Figure 1. The RT spectrum exhibits two strong bands at 597 and 426 nm and four weak bands at 710, 680, 350 and 326 nm. At LNT the bands at 597 and 680 nm split into three components each: 567, 590, 610 nm and 680, 683, 690 nm respectively whereas the higher wavelength side band at 710 nm splits into two components: 707 and 710 nm. The bands on the lower wavelength side (350 and 326 nm) are too weak to be observed at LNT.

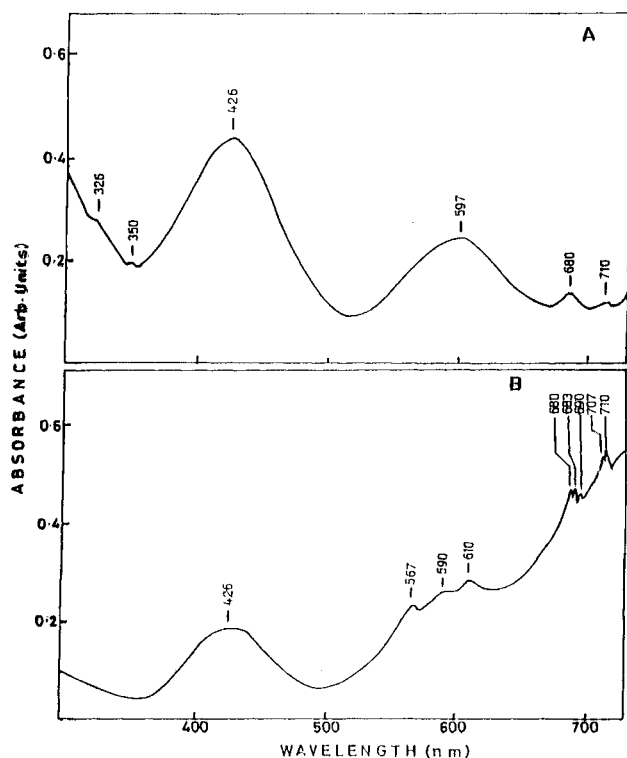


Fig. 1: Absorption spectra of Cr<sup>3+</sup> doped ZAPH (A:RT, B:LNT)

The broad bands observed at RT at 597 and 426 nm are attributed to the spin allowed transitions  $^4A_2(F) \rightarrow ^4T_2(F)$  and  $^4A_2(F) \rightarrow ^4T_1(F)$  respectively. The band position ( $\nu_1 = 16746 \text{ cm}^{-1}$ ) corresponding to the transition  $^4A_2(F) \rightarrow ^4T_2(F)$  gives the 10 Dq value. The wavenumber of the band corresponding to  $^4A_2(F) \rightarrow ^4T_1(F)$  is  $23468 \text{ cm}^{-1}$  ( $\nu_2$ ). Using the following formula (PERUMA REDDY, 1969):  $B = (2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2) / (15\nu_2 - 27\nu_1)$ , the value

of B is evaluated and found to be  $673 \text{ cm}^{-1}$ . The other weak bands at 710, 680, 350 and 326 nm are attributed, with the help of Tanabe-Sugano diagram (1954), to the spin forbidden transitions from  ${}^4A_{2g}(F)$  to  ${}^2E_g(G)$ ,  ${}^2T_{1g}(G)$ ,  ${}^2T_{2g}(H)$  and  ${}^2A_{1g}(G)$  respectively. The  ${}^4A_{2g}$ ,  ${}^2E_g$  and  ${}^2T_{1g}$  terms result from the same configuration  $t_{2g}^3$ . The bands corresponding to an electron jump between these states, arising from the same configuration, are expected to be sharp. Therefore the assignments of the sharp bands observed at 710 and 680 nm to the transitions  ${}^4A_{2g}(F) \rightarrow {}^2E_g(G)$  and  ${}^4A_{2g}(F) \rightarrow {}^2T_{1g}(G)$  are in tune with the theoretical prediction. Based on the above assignments the TANABE-SUGANO matrices (1954) for different values of Dq, B and C are solved and the following values give good agreement between the calculated and observed band positions : Dq = 1675, B = 675 and C = 3035  $\text{cm}^{-1}$ .

The band head data along with their assignments are presented in Table 1

| Transition from ${}^4A_{2g}$ | Observed band position<br>Wavelength (nm) | Wavenumber ( $\text{cm}^{-1}$ ) | Calculated<br>Wavenumber ( $\text{cm}^{-1}$ ) |
|------------------------------|---|---------------------------------|---|
| ${}^2E_g(G)$                 | 710                                       | 14081                           | 14084   |
| ${}^2T_{1g}(G)$              | 680                                       | 14702                           | 14682   |
| ${}^4T_{1g}(F)$              | 597                                       | 16746                           | 16750   |
| ${}^4T_{2g}(F)$              | 426                                       | 23468                           | 23487   |
| ${}^2A_{1g}(G)$              | 350                                       | 28563                           | 28555   |
| ${}^2T_{2g}(H)$              | 326                                       | 30666                           | 30699   |

Table 1: Observed and calculated band positions for (RT)  $\text{Cr}^{3+}$ :ZAPH

## 5. Conclusions

The optical absorption bands at the RT are characteristic of  $\text{Cr}^{3+}$  in the near octahedral symmetry. In the LNT spectrum these bands exhibit splittings. The band associated with the  ${}^2E_g(G)$  level splits into two components (710 and 707 nm) and those bands associated with  ${}^2T_{1g}(G)$  and  ${}^4T_{2g}(F)$  levels split into three components each (690, 683 and 680 nm ; 610, 590 and 567 nm).

The  ${}^2E_g$  level does not split in trigonal distortion. But it splits in tetragonal or orthorhombic distortions. Since the band associated with  ${}^2E_g$  level exhibits splitting, the distortion can be either tetragonal or orthorhombic.

The  $T_{1g}$  or  $T_{2g}$  levels split into two components each in tetragonal and three components each in orthorhombic distortion. Since in the present case the band associated with  ${}^2T_{1g}$  and  ${}^4T_{2g}$  levels split into three components each the distortion is ascribed to the orthorhombic type.

### Acknowledgments

One of the authors (Ravikumar) is thankful to CSIR New Delhi for award of Research Associateship.

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*Authors' address:*

R. V. S. S. N. RAVIKUMAR, A. V. CHANDRASEKHAR  
S. N. RAO, N. MADHU, B. J. REDDY, Y. P. REDDY  
Chemical Physics and Spectroscopy Laboratories  
S.V. University  
Tirupati - 517 502  
India