

# Magnetic and thermodynamic studies of new lamellar structure $\text{Mn}_{0.5}\text{Co}_{0.5}\text{NH}_4\text{PO}_4 \cdot 2\text{H}_2\text{O}$

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$\text{Mn}_{0.5}\text{Co}_{0.5}\text{NH}_4\text{PO}_4 \cdot 2\text{H}_2\text{O}$  has been synthesized at room temperature by coprecipitation method. The structure was determined on X-ray powder diffraction data leading to a crystallization in the space group  $\text{Pmn}2_1$  with cell parameters  $a = 5.568 \pm 0.011 \text{ \AA}$ ,  $b = 6.158 \pm 0.008 \text{ \AA}$  and  $c = 19.38 \pm 0.04 \text{ \AA}$ . TG-DTA curves, suggest the loss of water hydration ( $2 \text{ H}_2\text{O}$ ). The IR spectrum is characteristic of  $\text{H}_2\text{O}$ ,  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  radicals. The magnetic study confirms the presence of two ions  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$  with ratio  $\frac{1}{2} - \frac{1}{2}$  and exhibits an antiferromagnetic compoment.

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## 1. Introduction

Struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) is known as a bio-mineral. It is a constituent of renal and vesical calculi. Due to biomedical importance of these crystals, several investigations have been undertaken by different searchers [1]. The system is orthorhombic (space group  $\text{Pmn}2_1$ ) with two molecules in the unit cell. The Mg ions are octahedrally coordinated [2,3]. Analogue compounds  $\text{NiNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  [4] and  $\text{CoNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  [5] were synthesized and reported as isomorphous to struvite structure. The well known series of compounds  $\text{M}^I\text{M}^{II}\text{PO}_4 \cdot \text{H}_2\text{O}$  ( $\text{M}^I = \text{NH}_4, \text{K}$ ;  $\text{M}^{II} = \text{Cd}, \text{Co}, \text{Fe}, \text{Mg}, \text{Mn}$  and  $\text{Ni}$ ) are related to the ditmarite  $\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O}$  [6].

## 2. Experimental

### 2.1. Synthesis

An extensive investigation of reactions in aqueous solution for the  $[\text{Mn}^{2+}\text{-Co}^{2+}/\text{PO}_4^{3-}/\text{NH}_4\text{OH}]$  system was carried out. The  $\text{Mn}_{0.5}\text{Co}_{0.5}\text{NH}_4\text{PO}_4 \cdot 2\text{H}_2\text{O}$  was synthesized by direct reaction between cobalt sulfate ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ), ( $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ ) and ammonium hydrogenophosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ). The reaction was performed at room temperature by dissolving each of the precursors in distilled water with the desired ratio. The formation of the precipitate was obtained by the slow addition of mixed manganese-cobalt sulfate to the aqueous solution of

ammonium hydrogenophosphate at a constant pH (pH = 8.70) and with rapid stirring. A permanent control of the pH by the  $\text{NH}_4\text{OH}$  (3N) is necessary. After filtering and washing several times with the distilled water then finally with acetone, the homogeneous powder with small grains was obtained.

### 2.2. Characterizations

The XRD spectrum was recorded using Philips PW 1710 diffractometer. The phase has been identified on the basis of a comparison with the data reported in the ICDD (International Center for Diffraction Data) tables.

IR spectrum was recorded on a UNICAM spectrometer using dry KBr pellet containing 2% of the sample.

The water content was obtained from the combined thermogravimetric analysis and differential thermal analysis (TGA and TDA). This study was carried out under nitrogen atmosphere on a (SETERAM) at a heating rate of  $10^\circ\text{C}/\text{min}$ .

The magnetic susceptibility was measured on polycrystalline samples between 4.5 and 300K using a DSM8 magnetometer under magnetic field of 0.1T.

Heat capacity measurements between 1.6 and 40 K, were performed on a calorimeter provided of a screen adiabatic (IPCMS-GMI, Strasbourg - France).

### 3. Results and discussion

#### 3.1. X-ray diffraction study

Powder X-ray diffraction pattern of the MnCoAPH sample is shown in Fig. 1.

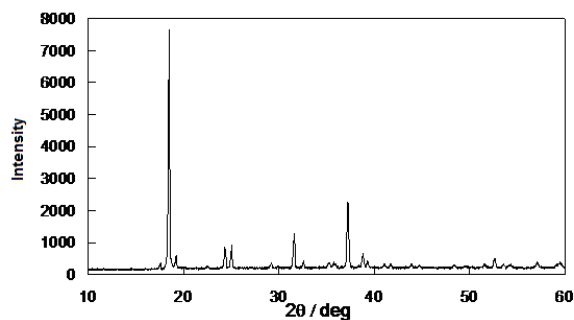


Fig. 1. XRD Pattern of  $\text{Mn}_{0.5}\text{Co}_{0.5}\text{NH}_4\text{PO}_4 \cdot 2\text{H}_2\text{O}$ .

The parameters refinement using the TREOR program gives a new crystallographic structure data leading to a crystallization in the space group  $\text{Pmn}2_1$  with cell parameters  $a = 5.568 \pm 0.011 \text{ \AA}$ ,  $b = 6.158 \pm 0.008 \text{ \AA}$  and  $c = 19.38 \pm 0.04 \text{ \AA}$ .

In Table 1, we compare our result to compounds already studied  $\text{NH}_4\text{CoPO}_4 \cdot 6\text{H}_2\text{O}$  [5] and  $\text{NH}_4\text{MnPO}_4 \cdot 1\text{H}_2\text{O}$  [7].

Table 1. Cell parameters of  $\text{NH}_4\text{CoPO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{NH}_4\text{MnPO}_4 \cdot 1\text{H}_2\text{O}$ .

Compound	$\text{NH}_4\text{CoPO}_4 \cdot 6\text{H}_2\text{O}$	$\text{NH}_4\text{MnPO}_4 \cdot 1\text{H}_2\text{O}$
a (Å)	6.9403(2)	5.731(1)
b (Å)	6.1457(2)	8.817(1)
c (Å)	11.9190(1)	4.9883(6)
G.S.	$\text{Pmn}2_1$	$\text{Pmn}2_1$
Ref	5	7

We observe that the XRD pattern of  $\text{Mn}_{0.5}\text{Co}_{0.5}\text{NH}_4\text{PO}_4 \cdot 2\text{H}_2\text{O}$  has a great similarity to the pattern of  $\text{NH}_4\text{CoPO}_4 \cdot 6\text{H}_2\text{O}$ . However, the comparison between the cell parameters shows that there is a slight decrease in a and b parameters and a doubling of the parameter c. This result shows that the compound  $\text{Mn}_{0.5}\text{Co}_{0.5}\text{NH}_4\text{PO}_4 \cdot 2\text{H}_2\text{O}$  has a superstructure than  $\text{NH}_4\text{CoPO}_4 \cdot 6\text{H}_2\text{O}$  and exhibits a lamellar structure.

#### 3.2. TG-DTA studies

Figs. 2a and 2b show the TG-DTG and TG-DTA curves obtained by speed heating of  $10^\circ\text{C min}^{-1}$ . The thermal decomposition of this compound exhibits two steps of mass losses.

However, this sample presents the property of absorbing moisture from the air between the room temperature and  $140^\circ\text{C}$ . This little hygroscopic behavior is

confirmed by the presence of two peaks at  $40$  and  $93^\circ\text{C}$  in DTG curve with a percentage of water adsorption closely  $2\%$ . This result shows that this compound presents a porous surface. TG-DTG curve of MnCoAPH compound is shown in Fig. 2a which shows that between  $140^\circ\text{C}$  and  $700^\circ\text{C}$  the weight loss is about  $25.7\%$  which is close to that calculated in theory ( $26.2\%$ ), This indicates the loss of water of hydration ( $2\text{H}_2\text{O}$ ) and one ammonia.

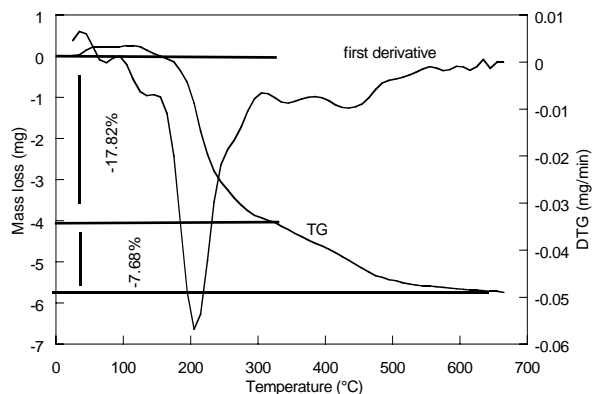
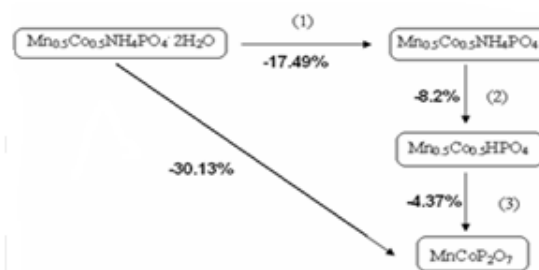


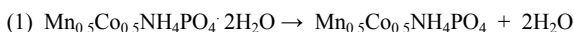
Fig. 2a. TGA curve of sample prepared at room temperature  $m = 22.5 \text{ mg}$ ; heating rate  $10^\circ\text{C} \cdot \text{min}^{-1}$

To understand these thermal transformations, and account for the number of moles of intercalated species, the thermogravimetric analysis on the prepared sample allows the clarification of the decomposition steps.

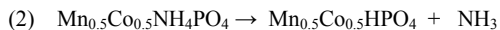
A continuous weight loss of  $17.82\%$  starting about  $160^\circ\text{C}$  and a sudden weight of  $7.68\%$  around  $450^\circ\text{C}$ . By attributing the first weight loss mainly to the removal of the water and the second of one of the completion of the  $\text{Mn}_{0.5}\text{Co}_{0.5}\text{NH}_4\text{PO}_4 - \text{Mn}_{0.5}\text{Co}_{0.5}\text{HPO}_4$  phase transition, the weight percentage of water was calculated from the total weight loss recorded in TGA after taking into account the hydration of  $\text{Mn}_{0.5}\text{Co}_{0.5}\text{NH}_4\text{PO}_4 \cdot 2\text{H}_2\text{O}$ . This result is in good agreement with theoretical calculation made on the decomposition of  $\text{Mn}_{0.5}\text{Co}_{0.5}\text{NH}_4\text{PO}_4 \cdot 2\text{H}_2\text{O}$  as the organization chart below shows



During the heating,  $\text{Mn}_{0.5}\text{Co}_{0.5}\text{NH}_4\text{PO}_4 \cdot 2\text{H}_2\text{O}$  sample may undergo several types of transformation. Firstly, thermal decomposition of the hydrate crystal involves the evolution of crystallization water and formation of anhydrous salt in a crystalline or amorphous state.



Secondary, the decomposition of the ammonium complex leads to the formation of gaseous ammonia and an hydrogenophosphate salt



According to the thermogramme TG -DTA coupled (Figure 2b), we observe, as generally for this type of compounds, the departure of the water molecules, then the departure of the ammonium molecule and intermolecular dehydrations of anions (polycondensation).

Taking into account of the absence of the exothermic peak for temperature lower than 700 °C and the loss of total mass which is far from 30 %, we confirm that the reaction (3) which suggests that rearrangement of the hydrogenophosphate anion with the waste of remaining water and formation of diphosphate end product did not take place.

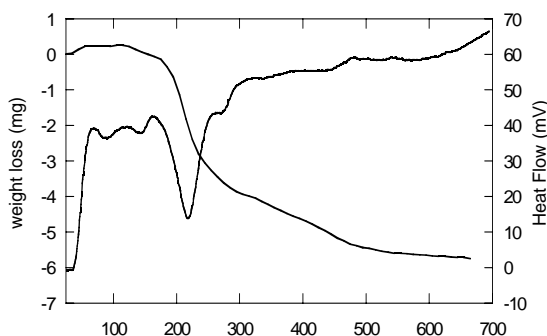
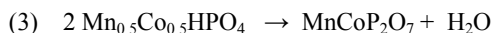


Fig. 2b. TG-DTA curves of sample prepared at room temperature  $m=22,5$  mg; heating rate  $10^\circ\text{C} \cdot \text{min}^{-1}$ .

### 3. 3. Infra red spectrum

The FTIR spectrum of the MnCoAPH is shown in Fig. 3. It presents two broad bands at 3411 and 1644  $\text{cm}^{-1}$  along with a shoulder at 3200  $\text{cm}^{-1}$ . Of these, the band at 1644  $\text{cm}^{-1}$  is attributed to the H-O-H bending mode ( $\nu_2$ ) and the others at 3411 and 3200  $\text{cm}^{-1}$  are assigned to  $\nu_3$  (asymmetric stretch) and  $\nu_1$  (symmetric stretch) respectively.

The bands observed in the region 1400 – 400  $\text{cm}^{-1}$  are characteristic of phosphate ion  $\text{PO}_4^{3-}$ . In the present study, the band observed at 933  $\text{cm}^{-1}$  is attributed to  $\nu_1$  mode. The bands consisting of three components at 1100, 1044 and 933  $\text{cm}^{-1}$  are assigned to triply degenerate  $\nu_3$  mode. So, the vibrations at 622 and 555  $\text{cm}^{-1}$  are linked to  $\nu_4$  mode. The band observed at 755  $\text{cm}^{-1}$  is attributed to the wagging vibration N-H [8-11].

In  $\text{NH}_4^+$  ion, the triply degenerate  $\nu_3$  vibration occurs in the region 3350-3050  $\text{cm}^{-1}$  and is generally obscured by the water bands. The triply degenerate  $\nu_4$  band occurs

around 1400  $\text{cm}^{-1}$  and is characteristic to diagnostic absorption. In the present investigation, the band at 1466 and 1433  $\text{cm}^{-1}$  are attributed to the triply degenerate  $\nu_4$  mode of  $\text{NH}_4^+$  ion. According to the presence of three peaks of triply degenerate  $\nu_3$  mode; the tetrahedra  $\text{PO}_4$  are not regular in this structure. Similar observations are reported in the literature and the splittings are attributed to the active rotation of the ammonium group about its three fold axis [12]. The structure of MnCoAPH keep the same morphology as  $\text{CoNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  compound, but the local structure of different polyhedral are surely distorted. This distortion is due to the difference of ionic radii of  $\text{Mn}^{2+}$  (0.80 Å) and  $\text{Co}^{2+}$  (0.74 Å).

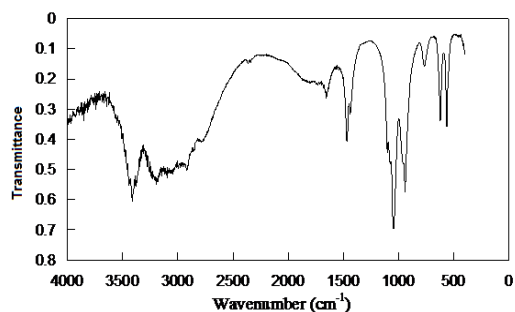


Fig. 3. IRTF spectrum of  $\text{Mn}_{0.5}\text{Co}_{0.5}\text{NH}_4\text{PO}_4 \cdot 2\text{H}_2\text{O}$ .

### 3. 4. Magnetic study

The evolution of molar magnetic susceptibility and the product  $\chi_m \cdot T$  versus temperature for  $\text{Mn}_{0.5}\text{Co}_{0.5}\text{NH}_4\text{PO}_4 \cdot 2\text{H}_2\text{O}$  are shown in Fig. 4a.

Magnetic susceptibility  $\chi_m$  decreases rapidly to a minimum value of 0.016 emu / mol at 293K and  $\chi_m \cdot T$  aims towards 0 at low temperatures indicating that the compound is an antiferromagnetic one.

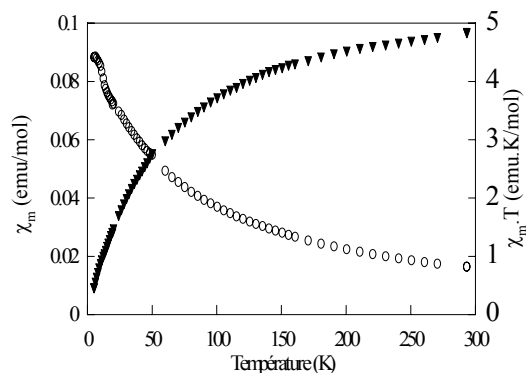


Fig. 4a. Thermal evolution of the susceptibility  $\chi_m$  (circle) and  $\chi_m \cdot T$  (triangle) of  $\text{Mn}_{0.5}\text{Co}_{0.5}\text{NH}_4\text{PO}_4 \cdot 2\text{H}_2\text{O}$ .

The variation of  $\chi_m^{-1}$  versus temperature follows at  $T > 50\text{K}$  a Curie-Weiss law:

$$\chi_m^{-1} = \frac{T - \theta_p}{C_m} = 11,2904 + 0,20748T \text{ with } C_m = 4.82$$

uem.K / mol ( $\mu_{\text{eff}} = 6.20 \mu_B$ ).

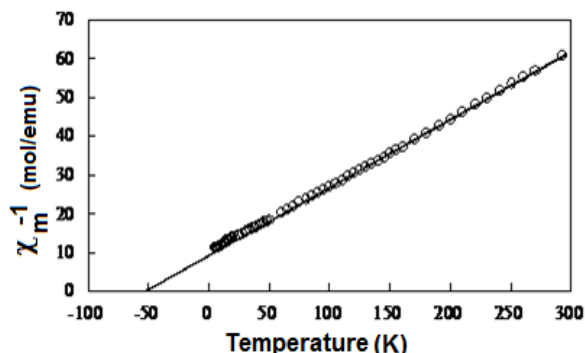


Fig. 4.  $\chi_m^{-1}$  thermal evolution of  $Mn_{0.5}Co_{0.5}NH_4PO_4 \cdot 2H_2O$ .

The negative value of the paramagnetic temperature  $\theta_p$  shows that the interactions are antiferromagnetic. In this context and as expected, the approximation of ions carrying magnetic moments and the substitution of  $Co^{2+}$  ( $S=3/2$ ) ions by  $Mn^{2+}$  ( $S = 5/2$ ) ions (spin stronger) has intensified the antiferromagnetic interactions. This explains the high value of  $\theta_p = -50$  K. The magnetic study confirms the presence of two ions  $Co^{2+}$  and  $Mn^{2+}$  with ratio  $1/2-1/2$ .

### 3-5. Specific heat

A preliminary study of specific heat of  $Mn_{0.5}Co_{0.5}NH_4PO_4 \cdot 2H_2O$  sample between 1.5 and 40 K is reported in Fig. 5. After subtraction of the lattice contribution  $C_p(\text{lat}) = a.T^3$  ( $a = 3.210^{-4}$ ), we obtain the residual specific heat  $C_m$  which is due to the magnetic interaction. The shape of  $C_m$  is not of  $\lambda$  type characteristic of long-range order. The maximum observed around 11.22 K is probably due to the low dimensionality of the structure. This proves that the magnetic interactions between  $Mn^{2+}$  and  $Co^{2+}$  are in the plane (a, c) then 2D dimensionality.

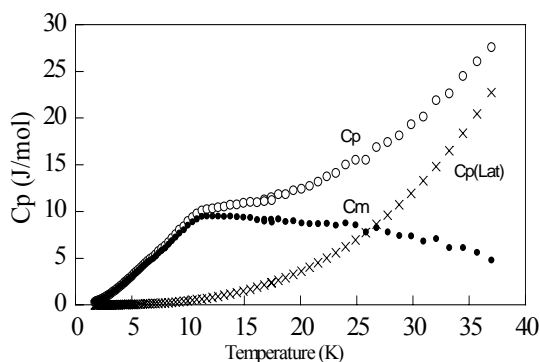


Fig. 5. Specific heat of  $Mn_{0.5}Co_{0.5}NH_4PO_4 \cdot 2H_2O$ .

## 4. Conclusion

In this work, we have stabilized  $Mn_{0.5}Co_{0.5}NH_4PO_4 \cdot 2H_2O$  and we have discussed their thermodynamic measurements. Powder X-ray study suggests that the structure belongs to orthorhombic system. TG-DTA indicates the presence of two water molecules. Infra Red spectrum exhibits the presence of water, phosphate and ammonium radicals. The structure of  $MnCoAPH$  keeps the same morphology as  $CoNH_4PO_4 \cdot 6H_2O$  compound, but the local structure of different polyhedral are surely distorted. The magnetic study shows a 2D antiferromagnetic behavior and confirms the presence of two ions  $Co^{2+}$  and  $Mn^{2+}$  with ratio  $1/2 - 1/2$ .

## References

- [1] P. W. Anton Perera, Zhi-Ying Han, Ying-Xu Chen, Wei-Xiang Wu, Biomedical and environmental sciences **20**, 343 (2007).
- [2] A. Whitaker, J. W. Jeffery, Acta Cryst. B **26**, 1429 (1970).
- [3] G. Ferrarais, M. Franchini-Angela, Acta Cryst. **B29**, 859 (1973).
- [4] A. Göni, J. L. Pizarro, L. M. Lezama, G. E. Barberis, M. I. Arriotua, T. Rojo, J. Mater. Chem., **6**, 421 (1996).
- [5] M. Touaiher, M. Bettach, K. Benkhoulja, M. Zahir, M. A. G. Aranda, S. Bruque, Ann. Chim. Sci. Mat. **26**(3), 49 (2001).
- [6] D. Tranqui, A. Durif, J.-C. Guitel, M. T. Averbuch-Pouchot, Bull. Soc. Fr. Miner. Cristallogr. **91**, 10 (1968).
- [7] M. Touaiher, K. Rissouli, K. Benkhoulja, M. Taibi, J. Aride A. Derory J. P. Lambour, M. Drillon, Phys. Chem. News **2**, 101(2001).
- [8] V. G. Koleva Spectrochimica Acta PartA **621**, 196 (2005).
- [9] V. G. Koleva Spectrochimica Acta Part A66413 (2007).
- [10] C. K. Chauhan, K. C. Joseph, B. B Parekh, M. Joshi, Indian J. of pure and App. Phys., **46**, 507(2008).
- [11] C. Danvirutai, P. Noisong S. Youngme J. Therm. Anal. Calorim. **100**, 117 (2010).
- [12] E. Banks, R. Chianelli, K Korenstein, Inorg. Chem. **14**, 1634 (1975).

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