

NEW PYROPHOSPHATES $M^I M^{III} P_2 O_7$

M. GABELICA-ROBERT and P. TARTE

University of Liège, Institute of Chemistry, Sart-Tilman, B-4000 Liège 1 (Belgium)

ABSTRACT

A number of new pyrophosphates $M^I M^{III} P_2 O_7$ ($M^I = Na, K, Rb, Cs, Tl, Ag$; $M^{III} = Al, Cr, Ga, Fe, In, Y$ and some R.E.) have been synthesized and investigated by x-ray diffractometry and vibrational spectroscopy. According to their vibrational spectra, they may be distributed into three structural families; these results are confirmed by the diffractograms which have been indexed for all the compounds.

These structural families are apparently determined by the nature of the monovalent cation: $M^I = Na, Ag$ or $M^I = K, Rb, Cs, Tl$, except for the Y and R.E. compounds whose structure depends on the size of both M^I and M^{III} cations.

INTRODUCTION

A small number of $M^I M^{III} P_2 O_7$ compounds is known at present. The following were synthesized by Gamondes et al. (ref. 1); their x-ray powder patterns show they belong to two different structural types:

type I : $KAlP_2 O_7$, $KFeP_2 O_7$ and I- $NaFeP_2 O_7$ (low temperature form)

type II : $NaAlP_2 O_7$ and II- $NaFeP_2 O_7$ (high temperature form)

Both types of compounds crystallize in the monoclinic $P2_1/c$ space group with $Z = 4$. The structure of $KAlP_2 O_7$ and II- $NaFeP_2 O_7$ are representative of the two families; they have been investigated by Nam Ng and Calvo (ref. 2) and by Gabelica, Goreaud, Labbé and Raveau (ref. 3) respectively. These structures are rather different.

Our purpose was to synthesize other $M^I M^{III} P_2 O_7$ compounds and to search for possible analogies with the former structural types.

RESULTS

The compounds have been prepared by classical solid state reactions, at temperatures ranging from 700 to 900°C, depending on the nature of the cations.

The x-ray diffractograms are very complex, according to the monoclinic symmetry of most of the compounds; moreover, an indexation by comparison is not obvious because of large variations of peak intensities when changing the ca-

tions, especially M^I . So, we preferred IR spectroscopy for the identification of the compounds ; indeed, IR spectra allow the detection of impurities such as metaphosphates appearing when the synthesis leads to a mixture of different phosphates ; we can also decide if two compounds are isostructural or not because the IR spectra are characteristic of each structural type, at least in the region of the vibrations of the P_2O_7 group. A similar behaviour is observed in the Raman spectra. Fig. 1 shows the IR spectra of K- and NaFeP₂O₇ which are characteristic of the type I and II structures respectively.

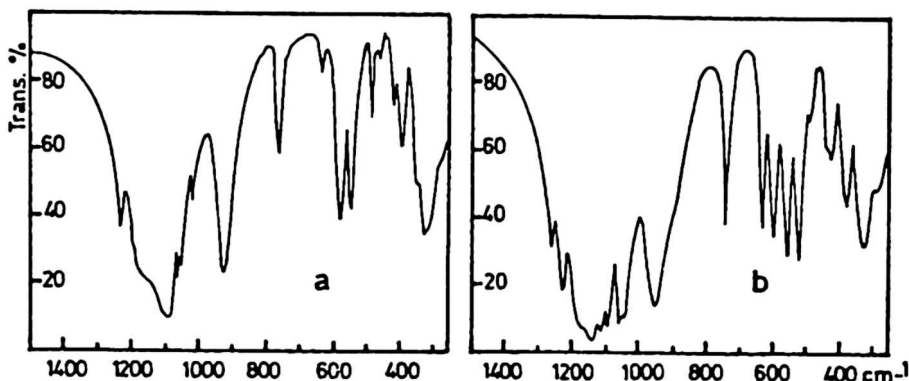


Fig. 1. IR spectra of KFeP₂O₇ (a) and NaFeP₂O₇ (b), representing the type I and II structures.

Table 1 summarizes the results of the IR and x-ray investigations. They show the existence of three structural types : types I and II refer to the group of compounds isostructural with KAlP₂O₇ and II-NaFeP₂O₇ respectively ; the compounds of type III form a new group and their diffractograms have been indexed in the orthorhombic system, by using an indexation program which was set up according to ref. 4.

The unit cell parameters and their standard deviations were deduced and refined from d values (between 15 and 25) through a conventional least-square procedure. They are listed in Table 2 for the Na and Ag compounds and in Table 3 for the K, Rb, Cs and Tl compounds.

No systematic synthesis has been tried at this time for the R.E. compounds, except with $M^I = K$; the synthesis of KREP₂O₇ with a rare earth larger than Dy leads to a mixture of phosphates, but it seems that the replacement of K by a larger monovalent cation gives phases having the same structure than KAlP₂O₇.

These results show that the existence of a compound and its structure depend on the ratio of the ionic radii $r_{M^I}/r_{M^{III}}$.

TABLE 1 : Structural types of the $M^I M^{III} P_2 O_7$ pyrophosphates

M^{III}	M^I	Na	Ag	K	Tl	Rb	Cs
Al		II		I	I	I	
Cr		II ^{**}	II	I ^{**}	I	I	
Ga		II	II	I	I	I	
Fe		II	II	I	I	I	I
In		II	II	I	I	I	I

Lu				I			
Yb				I			
Tm				I			
Er				III			
Y				III	I	I	I
Ho				III			
Dy				III		I	
Gd							I

** These compounds have been mentioned by Gamondes et al (ref. 5)

TABLE 2 : Unit cell parameters of the type $II-M^I M^{III} P_2 O_7$ compounds

Compounds	a (Å)	b (Å)	c (Å)	β (°)	References
$Na M^{III} P_2 O_7$					
$M^{III} = Al$	7.197(2)	7.695(2)	9.312(2)	111.73(2)	1
Cr	7.192(4)	7.698(5)	9.308(5)	111.722(1)	**
Ga	7.280(4)	7.841(4)	9.468(8)	111.757(1)	**
Fe	7.269(3)	7.831(3)	9.464(5)	112.036(1)	**
	7.326(2)	7.902(2)	9.573(2)	111.813(1)	1
	7.3244(13)	7.9045(7)	9.5745(15)	111.858(13)	3
	7.321(3)	7.900(4)	9.569(5)	111.824(1)	**
In	7.486(8)	8.182(7)	9.823(9)	112.205(1)	**
$Ag M^{III} P_2 O_7$					
$M^{III} = Cr$	7.302(5)	7.932(5)	9.483(5)	111.804(1)	**
Ga	7.299(8)	7.921(10)	9.458(10)	112.182(1)	**
Fe	7.335(4)	7.998(4)	9.575(5)	111.862(1)	**
In	7.490(10)	8.267(13)	9.833(11)	112.117(1)	**

** : This work.

Phase transition in $NaFeP_2 O_7$

We tried to synthesize the low temperature form of $NaFeP_2 O_7$ mentioned by Gamondes et al (ref. 1, 5) by

- . crystallisation of the corresponding glass at 500°C
- . cation exchange between $KFeP_2 O_7$ and $NaNO_3$ at 300°C
- . heating up to 500°C of $NaFeP_2 O_7 \cdot xH_2 O$ ($x=2,5$) precipitated from an aqueous solution.

Each of these methods, working at lower temperatures than the transition one (about 750°C) mentioned in ref. 5 leads to the high temperature phase of $NaFeP_2 O_7$

TABLE 3 : Unit cell parameters of the $M^{III}P_2O_7$ compounds having the type I or III structure

Compounds	a (Å)	b (Å)	c (Å)	β (°)	References
Rb $M^{III}P_2O_7$					(²) this work
$M^{III}=Al$	7.448(4)	9.616(6)	8.108(5)	105.972(1)	*
Cr	7.478(4)	9.891(5)	8.227(4)	105.976(1)	*
Ga	7.453(6)	9.802(6)	8.229(4)	105.886(1)	*
Fe	7.495(4)	9.972(6)	8.278(4)	105.760(1)	*
In	7.539(4)	10.402(6)	8.482(5)	105.423(1)	*
Y	7.705(3)	10.947(5)	8.662(3)	105.364(1)	*
Dy	7.700(3)	11.001(6)	8.676(4)	105.296(1)	*
Tl $M^{III}P_2O_7$					
$M^{III}=Al$	7.468(2)	9.639(3)	8.106(4)	105.978(1)	*
Cr	7.483(2)	9.891(2)	8.208(2)	105.927(1)	*
Ga	7.469(4)	9.822(5)	8.212(4)	105.822(1)	*
Fe	7.513(4)	9.987(5)	8.259(4)	105.822(1)	*
In	7.545(3)	10.384(4)	8.455(4)	105.569(1)	*
Y	7.703(4)	10.932(4)	8.636(5)	105.587(1)	*
Cs $M^{III}P_2O_7$					
$M^{III}=Fe$	7.693(6)	9.959(9)	8.391(5)	104.863(1)	*
In	7.739(4)	10.322(8)	8.586(6)	104.743(1)	*
Y	7.897(4)	10.904(6)	8.758(4)	104.207(1)	*
Gd	7.920(3)	11.072(5)	8.824(3)	104.098(1)	*
K $M^{III}P_2O_7$ (type I)					
$M^{III}=Al$	7.308(8)	9.662(6)	8.025(4)	106.69(8)	2
	7.329(2)	9.654(2)	8.045(2)	106.93(2)	1
	7.326(4)	9.647(6)	8.036(5)	106.858(1)	*
Cr	7.337(5)	9.892(9)	8.151(6)	106.532(1)	*
Ga	7.311(8)	9.816(8)	8.131(14)	106.505(1)	*
Fe	7.362(2)	10.005(2)	8.207(2)	106.44(2)	1
	7.339(5)	9.996(6)	8.176(10)	106.294(1)	*
In	7.408(6)	10.376(18)	8.383(8)	106.301(1)	*
Lu	7.545(4)	10.776(4)	8.537(4)	106.654(1)	*
Yb	7.535(4)	10.819(7)	8.542(6)	106.667(1)	*
Tm	7.534(4)	10.855(6)	8.561(4)	106.803(1)	*
K $M^{III}P_2C_7$ (type III)					
$M^{III}=Er$	9.198(8)	12.209(8)	5.698(5)		*
Y	9.216(8)	12.244(8)	5.712(5)		*
Ho	9.215(3)	12.242(3)	5.717(2)		*
Dy	9.487(3)	12.764(4)	5.478(3)		*

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REFERENCES

- 1 J.P. Gamondes, F. d'Yvoire and A. Boullé, C.R. Acad. Sci. Paris, 272C(1971), 49-52.
- 2 H. Nam Ng and C. Calvo, Can. J. Chem., 51(1973), 2613-2620.
- 3 M. Gabelica-Robert, M. Goreaud, Ph. Labbé and B. Raveau, J. Solid State Chem., submitted for publication.
- 4 J.W. Visser, J. Applied Crystall., 2(1969), 89-95.
- 5 J.P. Gamondes, F. d'Yvoire and A. Boullé, C.R. Acad. Sci. Paris, 269C(1969), 1532-1535.