

# Diphosphate structures related to the dichromate or thortveitite type

A. Boukhari

Laboratoire de Chimie du Solide Appliquée, Département de Chimie, Faculté des Sciences, Rabat (Morocco)

## Abstract

The diphosphate structures  $A_2P_2O_7$  contain  $P_2O_7$  anions which show an eclipsed (dichromate-type) or staggered (thortveitite-type) spatial conformation. The first class is related to large ions A(II) ( $A \equiv Ca, Sr, Ba, Cd, Pb$ ), while the second family includes small cations ( $A \equiv Mg, Mn, Fe, Co, Ni, Cu, Zn$ ). In the mixed phosphates  $(A,B)_2P_2O_7$ , where A and B are bivalent ions, the type of structure is generally controlled by the largest cation.

## 1. Introduction

Compounds with the formula  $R_2M_2O_7$  show a small number of groups of related structures [1, 2]. The size of the  $R^{n+}$  and  $M^{(7-n)+}$  cations plays an important role in determining the type of crystalline structure. Thus, when the ionic radius of M is greater than about 0.5 Å, the observed structure types are pyrochlore [3] or weberite [4]. In this case the framework is built of interconnected  $MO_6$  octahedra. However, if the ionic radius of M is less than 0.5 Å, two types of structures are known: the dichromate [5] and the thortveitite type [6, 7]. These compounds have been obtained with phosphorus, vanadium, silicon and chromium in their highest oxidation state [8–13]. They are characterized by isolated  $M_2O_7$  groups made of two  $MO_4$  tetrahedra sharing one corner.

The crystal structures of the diphosphates  $A_2P_2O_7$ , where A is a divalent cation, have been widely studied. The structure of materials with  $A \equiv$  alkaline earth (Ca, Sr, Ba), Pb, Cd contains an eclipsed conformation of  $P_2O_7$  anions [14–22] and is called dichromate (D) type. The second family corresponds to structures with bivalent metallic ions of small size ( $A \equiv Mg, Mn, Fe, Co, Ni, Cu, Zn$ ) where the  $P_2O_7$  ions have a staggered conformation [23–36]. Figure 1 shows the two spatial (eclipsed and staggered) geometries of  $P_2O_7$  anions. The  $Cd_2P_2O_7$  phosphate with the dichromate structure is the limit between the two families of dichromate and thortveitite type.

The size of A and B in  $(A,B)_2P_2O_7$  compounds, where A and B are bivalent ions, plays a determining role in the  $P_2O_7$  conformation. Therefore the following mixed compounds  $(A,B)_2P_2O_7$  could be prepared.

(1) A and B are large ions; the parent  $A_2P_2O_7$  and  $B_2P_2O_7$  diphosphate structures are related to the dichromate family ( $A, B \equiv Ca, Sr, Ba, Pb, Cd$ ).

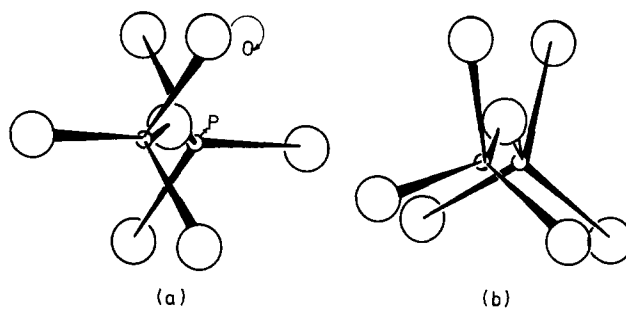


Fig. 1. (a) Eclipsed and (b) staggered conformation in dichromate- and thortveitite-type structures respectively.

(2) A and B have a small size ( $A, B \equiv Mg, Mn, Fe, Co, Ni, Cu, Zn$ ); the  $A_2P_2O_7$  and  $B_2P_2O_7$  frameworks contain a staggered  $P_2O_7$  conformation of the thortveitite type.

(3) A is large ( $A \equiv Ca, Sr, Ba, Pb, Cd$ ) and B is a small cation ( $B \equiv Mg, Mn, Fe, Co, Ni, Cu, Zn$ ); the parent phosphates  $A_2P_2O_7$  and  $B_2P_2O_7$  belong to the dichromate and thortveitite type respectively.

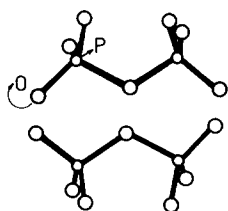
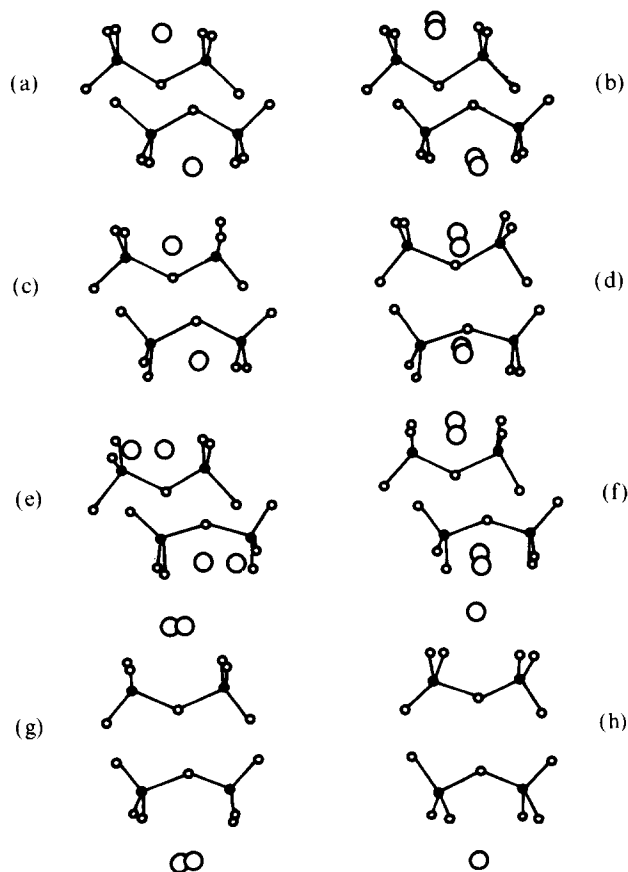
Our work deals with  $A_2P_2O_7$  and  $(A,B)_2P_2O_7$  single-crystal structures related to the dichromate or thortveitite type and the influence of the cations A and B on the mixed frameworks with staggered or eclipsed  $P_2O_7$  groups.

## 2. $A_2P_2O_7$ phosphates

### 2.1. Dichromate-related structures

The term “dichromate” results from the alkaline dichromate structure  $K_2Cr_2O_7$  characterized by the eclipsed conformation of  $Cr_2O_7$  [5].

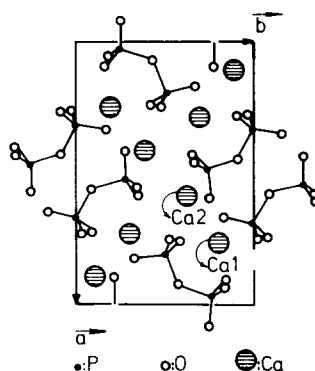
The structures of  $A_2P_2O_7$  phosphates of this family are made of basic units formed by two  $P_2O_7$  groups related by an inversion or pseudoinversion centre of

Fig. 2.  $(P_2O_7)_2$  basic unit in dichromate structures.Fig. 3.  $(P_2O_7)_2$  basic units observed in some diphosphate and dichromate structures of dichromate type.

symmetry. The two bridging oxygen atoms of the P–O–P links in the  $P_2O_7$  groups are arranged in such a way as to obtain a close packing of them (Fig. 2).

Figure 3 shows the  $P_2O_7$  units in some diphosphate and dichromate structures. The expansion of the basic units forms a zigzag infinite chain in the lattice (see *e.g.* Fig. 9). Figure 4 gives the projection on the (001) plane of  $\alpha$ - $Ca_2P_2O_7$ , which is a common structure for several diphosphates of the dichromate type [14], as we establish below.

Table 1 lists the allotropic forms and crystallographic data of diphosphates of the dichromate type. The P–O–P angle values of  $P_2O_7$  groups in dichromate diphosphates  $A_2P_2O_7$  ( $A \equiv Ca, Sr, Ba, Pb, Cd$ ) range from  $128^\circ$  to  $138^\circ$ .

Fig. 4. Structure of  $\alpha$ - $Ca_2P_2O_7$  projected on (001) plane with Ca(1) and Ca(2) sites.

## 2.2. Thortveitite type

The structure of the mineral thortveitite,  $(Sc,Y)_2Si_2O_7$ , was determined by Zachariassen in the 1930s [7] and later refined by Cruickshank *et al.* [6]. The lattice is formed by isolated sheets of  $Si_2O_7$  anions parallel to the (001) plane. The scandium and yttrium cations are located between two adjacent sheets of  $(Si_2O_7)^{6-}$ . The Si–O–Si angle value is  $180^\circ$  for the staggered  $Si_2O_7^{6-}$  group.

Among the condensed diphosphates, several  $A_2P_2O_7$  diphosphates ( $A \equiv Mg, Mn, Fe, Co, Ni, Cu, Zn$ ) crystallize with the thortveitite-type structure. They exhibit high temperature crystallographic forms except for  $A \equiv Mn, Fe, Co$ .

The crystallographic data of  $A_2P_2O_7$  phosphates with the thortveitite structure are listed in Table 2. The P–O–P angle values range from  $137^\circ$  to  $180^\circ$  (high symmetry).

## 3. $(A,B)_2P_2O_7$ diphosphates; A, B divalent cations

$(A,B)_2P_2O_7$  crystal structures are less well known than their parent diphosphates  $A_2P_2O_7$  and  $B_2P_2O_7$ , where A and B are divalent ions. As reported above, the size of A and B has an important effect on the nature of the  $P_2O_7$  conformation (staggered or eclipsed) in the lattice. Three possibilities can be discussed.

### 3.1. $(A,B)_2P_2O_7$ crystal structures; $A_2(B_2)P_2O_7$ of dichromate type

The mixed  $(A,B)_2P_2O_7$  diphosphates of this family, reported with solved crystal structures, to our knowledge are  $PbBaP_2O_7$  [37],  $CdBaP_2O_7$  [38],  $Cd_{1.25}Ca_{0.75}P_2O_7$  and  $CdSrP_2O_7$  [39–41]. The two last compounds have been found as a particular composition in the solid solutions  $Cd_{2-x}Ca_xP_2O_7$  and  $Cd_{2-x}Sr_xP_2O_7$  respectively ( $0 \leq x \leq 2$ ) and have been characterized by powder diffraction methods [39]. The

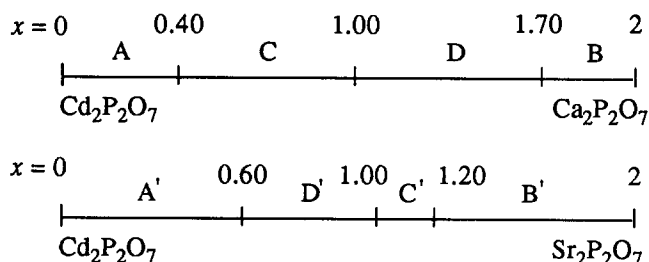
TABLE 1. Allotropic forms and crystallographic data of diphosphates  $A_2P_2O_7$  of dichromate type

A	Allotropic form	Space group; Z	Coordination number	P-O-P angle (deg)	Reference(s)
Ca	$\gamma$	—	—	—	14, 15
	$\beta^a$	$P4_1; 8$	7, 8, 9	130.5 137.8	
	$\alpha$	$P2_1/n; 4$	8	131 128	
Sr	$\beta^a$	$P4_1; 8$	7, 8, 9	128 131	16–18
	$\alpha^b$	$Pbnm; 4$	9	133.5	
Ba	$\delta$	$P6_3-3$	—	—	19
	$\alpha^b$	$Pbnm; 4$	—	—	
Cd		$P1; 2$	5, 6	131.3	21
Pb		$P1; 4$	8, 9	130 132	20

<sup>a, b</sup>Isotypical structures.

structures of  $PbBaP_2O_7$  and  $CdBaP_2O_7$  have been determined on single crystals. The former is isostructural with  $\alpha-Ca_2P_2O_7$ .

X-ray diffraction analysis on powders of several compositions of the solid solution  $Cd_{2-x}M_xP_2O_7$  ( $M \equiv Ca, Sr$ ) with  $0 \leq x \leq 2$  shows different domains as indicated below



where A and A' are solid solutions isotypical with  $Cd_2P_2O_7$ , B and B' are solid solutions isotypical with  $\alpha-Ca_2P_2O_7$  and  $\alpha-Sr_2P_2O_7$  respectively, C and C' are solid solutions isotypical with  $Cd_{1.25}Ca_{0.75}P_2O_7$  and  $CdSrP_2O_7$  respectively and D and D' are mixtures of phases of adjacent domains C, B and A', C' respectively.

### 3.1.1. $M \equiv Ca$

Compounds of domains A ( $0 \leq x \leq 0.40$ ) and B ( $1.70 \leq x \leq 2$ ) are isomorphous to  $Cd_2P_2O_7$  and  $\alpha-Ca_2P_2O_7$  respectively. Compounds with composition between 0.40 and 1.00 (domain C) show a solid solution of new phases of which the structure has been solved on a single crystal [40].

The evolution of density with the composition of domains A, B and C is presented in Fig. 5. A decrease

in the density is seen as  $Cd^{2+}$  ions are replaced by  $Ca^{2+}$  atoms.

### 3.1.2. $M \equiv Sr$

Domains A' and B' correspond to solid solutions isostructural with  $Cd_2P_2O_7$  and  $\alpha-Sr_2P_2O_7$  respectively. The  $CdSrP_2O_7$  ( $x = 1$ ) structure solved on a single crystal is isomorphous to  $\alpha-Ca_2P_2O_7$ . The variation in cell parameter values with the composition of domain B' is shown in Fig. 6.

Diphosphates synthesized in  $Cd_{2-x}Sr_xP_2O_7$  solid solutions ( $0 \leq x \leq 2$ ) are closely related to the dichromate type as  $Cd_2P_2O_7$  and  $Sr_2P_2O_7$ .

### 3.2. $(A,B)_2P_2O_7$ diphosphates; $A_2P_2O_7/B_2P_2O_7$ of dichromate/thortveitite type

This subsection deals with diphosphates  $(A,B)_2P_2O_7$  where the pair  $A_2P_2O_7/B_2P_2O_7$  corresponds to the dichromate/thortveitite type respectively.

Mixed structures of this type which have been determined using single-crystal data are as follows.

(1)  $SrNiP_2O_7$  [42],  $CaCoP_2O_7$  [43],  $BaCoP_2O_7$ ,  $Ba-NiP_2O_7$  [44],  $PbCoP_2O_7$  [38],  $SrCoP_2O_7$  and  $BaCuP_2O_7$  [45]: these were found in the dichromate family with eclipsed  $P_2O_7$  anions. Cations A of large size ( $A \equiv Ca, Sr, Ba, Cd, Pb$ ) control the type of structure obtained.

(2)  $CaCuP_2O_7$ ,  $SrCuP_2O_7$  [46, 47] and  $CdCuP_2O_7$  [48]: these structures are built of staggered  $P_2O_7$  anions and are related to the thortveitite class. However, the first two compounds are isomorphous to  $\alpha-Ca_2P_2O_7$ , while the last structure is characterized by mixed Cd-Cu sites (0.50:0.50). They are the first diphosphates which show that  $Cu^{2+}$ , smaller in size than  $A^{2+}$

TABLE 2. Allotropic forms and crystallographic data of diphosphates  $A_2P_2O_7$  of thortveitite type

A	Allotropic form	Space group; Z	Coordination number	P–O–P angle (deg)	Reference(s)
Mg	$\alpha^b$	$B2_1/c$ ; 8	5, 6	144	26–28
	$\beta^a$	$C2/m$ ; 2	6	180	
Mn	$\alpha$	$C2/m$ ; 2	6	180	34
Fe		$C1$ ; 2	6	180	35, 36
Co	$\beta$	$B2_1/c$ ; 8	5, 6	143.1	23
Ni	$\alpha^b$	$B2_1/c$ ; 8	5, 6	137	29–31
	$\beta^a$	$C2/m$ ; 2	6	180	
	$\gamma$	—; 8	—	180	
	$\sigma$	$P2_1/a$ ; 2	6	180	
Cu	$\alpha$	$C2/c$ ; 4	5	157	24, 25
	$\beta^a$	$C2/m$ ; 2	6	180	
Zn	$\alpha$	$I2/c$ ; 12	5, 6	139	32, 33
	$\beta^a$	$C2/m$ ; 2	6	180	

<sup>a, b</sup>Isotypical structures.

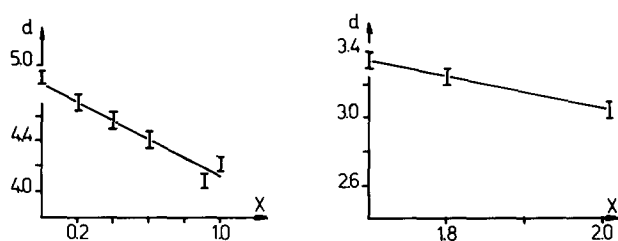


Fig. 5. Density variation with composition for domains A ( $0 \leq x \leq 0.40$ ), C ( $0.40 < x < 1.00$ ) and B ( $1.70 \leq x \leq 2$ ) of  $Cd_{2-x}Ca_xP_2O_7$  solid solution.

(A  $\equiv$  Ca, Sr, Cd), has influenced the framework, resulting in the thortveitite type, despite the expectation that larger  $A^{2+}$  ions should dominate the selection of the dichromate structure.

$(Cd_{0.5}Cu_{0.5})_2P_2O_7$  is a particular composition of the solid solution  $Cd_{2-x}Cu_xP_2O_7$ ,  $0 \leq x \leq 2$ . Two domains, A ( $0 \leq x \leq 0.40$ ) and B ( $1.60 \leq x \leq 2$ ), have been observed. The phases of domain A are isomorphous to  $Cd_2P_2O_7$ . Those of domain B have X-ray spectra similar to those of  $\alpha$ - or  $\beta$ - $Cu_2P_2O_7$  [48]. A linear variation in unit cell parameters is observed in domain A with changing Cd:Cu ratio. An increase in  $x$  leads to a decrease in the volume of the unit cell.

The diphosphates  $SrCuP_2O_7$ ,  $CaCuP_2O_7$ ,  $SrCdP_2O_7$ ,  $BaPbP_2O_7$  and  $PbCoP_2O_7$ , solved on single crystals and which are isomorphous to  $\alpha$ - $Ca_2P_2O_7$ , have the large ions located at Ca(1) sites, while the small atoms are

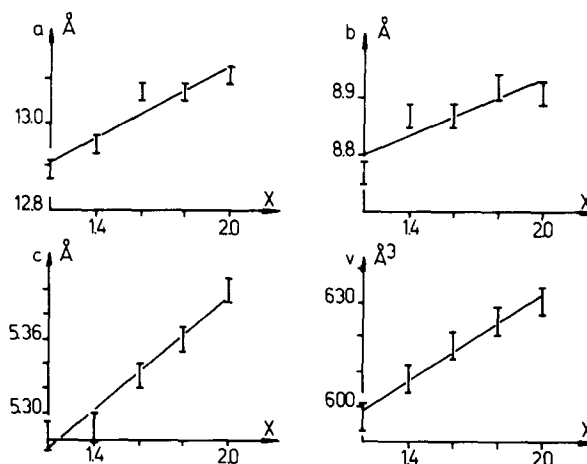


Fig. 6. Variation with  $x$  of the unit cell parameters in domain B' of  $Cd_{2-x}Sr_xP_2O_7$  solid solution.

inserted at the Ca(2) sites in the lattice. This distribution could be associated with the size of the Ca(1) sites, where the more voluminous cations such as calcium ( $CaCuP_2O_7$ ), strontium ( $SrCuP_2O_7$ ,  $SrCdP_2O_7$ ), barium ( $BaPbP_2O_7$ ) or lead ( $PbCoP_2O_7$ ) are found.

Figure 7 reports the variation in the P–O–P angle of the  $P_2O_7$  groups vs. the mean radius  $r((r_A + r_B)/2)$  of  $ABP_2O_7$  phosphates isotypical with  $\alpha$ - $Ca_2P_2O_7$ . Values of  $r_A$  and  $r_B$  are taken from Shannon's data [49]. Oxygen coordinations of A and B are those observed in these structures. We observe an increase and linear variation in the P–O–P angle with an increase in  $r$ .

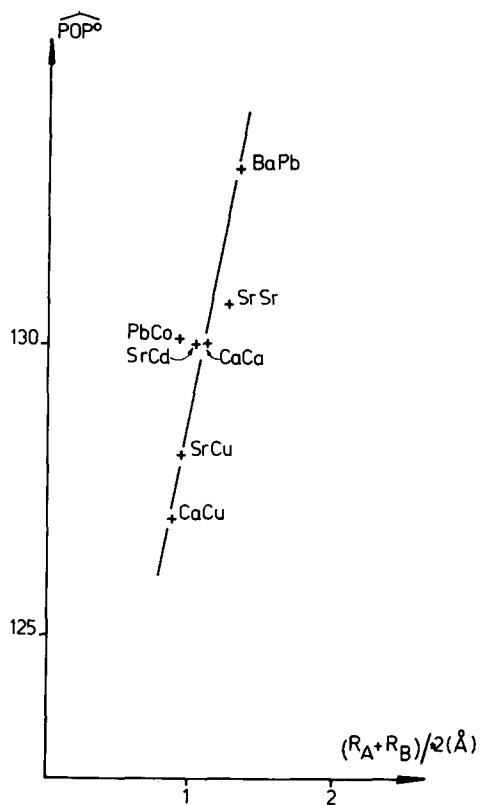


Fig. 7. P–O–P angle vs. mean radius  $r$  of  $ABP_2O_7$  phosphates isotypical with  $\alpha$ - $Ca_2P_2O_7$ , where A and B are bivalent ions.

Small values are obtained with copper diphosphates, showing a strong deformation of  $P_2O_7$  anions with the staggered conformation.

### 3.3. $(A,B)_2P_2O_7$ ; $A_2(B_2)P_2O_7$ of thortveitite type

Moqine and coworkers have synthesized and characterized powders of solid solutions  $Mg_{2-x}Cu_xP_2O_7$ ,  $0 \leq x \leq 2$  [46, 50]. They have obtained a continuous domain between  $x = 0.05$  and 1.94 isomorphous to  $\beta$ - $Cu_2P_2O_7$  (or  $\beta$ - $Mg_2P_2O_7$ ). The two  $\beta$  forms are isotypical.  $(Mg,Cu)_2P_2O_7$   $\alpha$ - $\beta$  transition temperatures were determined using the differential thermal analysis technique. The  $\beta$ - $Mg_2P_2O_7$  form has been obtained at room temperature with about 2.5%  $Cu^{2+}$  ions in  $\alpha$ - $Mg_2P_2O_7$ , while  $\beta$ - $Cu_2P_2O_7$  was stabilized with about 3%  $Mg^{2+}$  ions in  $\alpha$ - $Cu_2P_2O_7$ . The increase in the  $\alpha$ - $\beta$  transition temperature in solid solution is about 20 K ( $\alpha,\beta$ - $Mg_2P_2O_7$ ) and 16 K ( $\alpha,\beta$ - $Cu_2P_2O_7$ ) with 1%  $Cu^{2+}$  ( $Mg_2P_2O_7$ ) and 1%  $Mg^{2+}$  ( $Cu_2P_2O_7$ ) respectively.

Similar results have been observed with  $Cu_{2-x}A_xP_2O_7$  solid solutions ( $A \equiv Fe, Co, Ni$ ;  $0 \leq x \leq 2$ ), where the  $\beta$ - $Cu_2P_2O_7$  form was stabilized with the substitution of a small amount of copper by A ions [51].

No details of single-crystal data are known for  $(A,B)_2P_2O_7$  diphosphates of the thortveitite type. We have developed in our laboratory a systematic synthesis

of mixed diphosphates with small ions ( $A, B \equiv Mg, Mn, Fe, Co, Ni, Cu, Zn$ ). Thus  $CuFeP_2O_7$ ,  $MnCuP_2O_7$  and  $NiCuP_2O_7$  single crystals have been obtained.

## 4. Other diphosphate structures

Diphosphates other than  $(A,B)_2P_2O_7$  seen above are known to have eclipsed  $P_2O_7$  units. These compounds could be associated with the dichromate family. The structures of  $Na_{7.39}Ni_{4.24}(P_2O_7)_4$ ,  $Na_{7.13}Mg_{4.36}(P_2O_7)_4$ ,  $Na_2CuP_2O_7$  (two forms, I and II) [52] and  $Na_2CoP_2O_7$  (two forms, I and II) [53] have been solved using single crystals.

### 4.1. $Na_{7.39}Ni_{4.24}(P_2O_7)_4$ and $Na_{7.13}Mg_{4.36}(P_2O_7)_4$ diphosphates

Isostructural (Na,Ni) and (Na,Mg) structures have been determined on single crystals [52]. The solid state structures are characterized by mixed  $NiO_6$  ( $MgO_6$ ) and  $PO_4$  polyhedra which delimit large tunnels where  $Na^+$  ions are located. Both structures contain  $(P_2O_7)_2$  basic units found in the dichromate type. These diphosphates could be classified in the dichromate family.

### 4.2. $Na_2CuP_2O_7$ structures

$Na_2CuP_2O_7$  diphosphate exists in two allotropic solid state forms, I and II. The structures of the two forms, determined on single crystals, show eclipsed  $P_2O_7$  groups associated in pairs as has been seen above in the dichromate type.

$Na_2CuP_2O_7$ (I) is closely related to  $\alpha$ - $Ca_2P_2O_7$ . The cell parameters are

$$\begin{aligned} Na_2CuP_2O_7(I): \quad P2_1/n, \quad a &= 13.494(3) \text{ \AA}, \\ &b = 8.823(3) \text{ \AA}, \quad c = 5.108(2) \text{ \AA}, \\ &\beta = 92.77(3)^\circ \end{aligned}$$

$$\begin{aligned} \alpha\text{-}Ca_2P_2O_7: \quad P2_1/n, \quad a &= 12.66(1) \text{ \AA}, \quad b = 8.542(8) \text{ \AA}, \\ &c = 5.315(5) \text{ \AA}, \quad \beta = 90.3(1)^\circ \end{aligned}$$

The  $Na^+$  ions are inserted at Ca(1) and Ca(2) sites of the calcium diphosphates; however, the  $Cu^{2+}$  ions are located between two equivalent and adjacent  $P_2O_7$  groups along the  $c$ -axis (Fig. 8). Figure 9 shows  $P_2O_7$  chains linked together with  $Cu^{2+}$  ions along the [001] axis in the  $Na_2CuP_2O_7$ (I) structure.

### 4.3. $Na_2CoP_2O_7$

The crystal structures of two allotropic forms, (I, II) of  $Na_2CoP_2O_7$  have been obtained [53]. Structures of the form I can be described as a framework composed of mixed  $CoO_6$  and  $PO_4$  polyhedra creating tunnels parallel to the [001] direction. The  $Na^+$  ions are located in these tunnels. The four independent  $P_2O_7$  groups

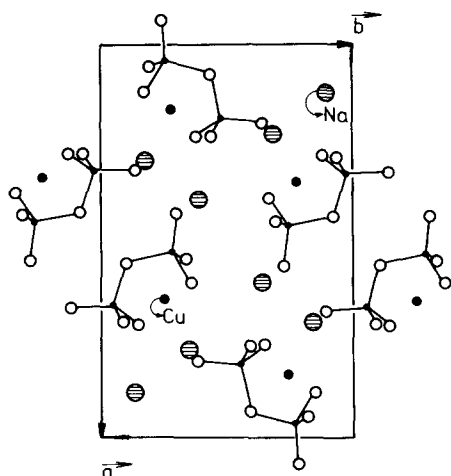


Fig. 8. Structure of  $\text{Na}_2\text{CuP}_2\text{O}_7(\text{I})$  projected on (001) plane.

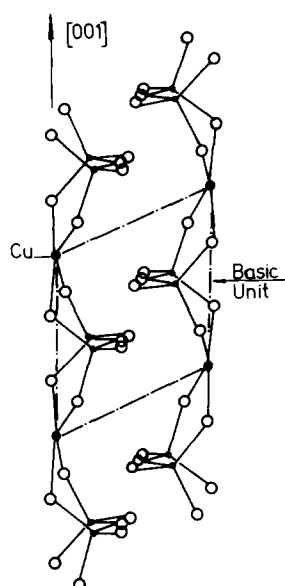


Fig. 9.  $(\text{CuP}_2\text{O}_7)^{2-}$  infinite chains of  $\text{P}_2\text{O}_7$  groups along [001].

exist in a quasi-eclipsed conformation and are arranged in groups of two to form the basic units determined in dichromate structures. The form I of  $\text{Na}_2\text{CoP}_2\text{O}_7$  belongs to the dichromate class of  $\text{P}_2\text{O}_7$  complexes.

The form II structure is characterized by layers of mixed  $\text{CoO}_4$  and  $\text{PO}_4$  tetrahedra alternating with layers of  $\text{Na}^+$  ions.  $\text{P}_2\text{O}_7$  exists in the eclipsed conformation and the framework shows no pairing of  $\text{P}_2\text{O}_7$  groups. The structure is not of the dichromate family despite the eclipsed conformation of the  $\text{P}_2\text{O}_7$  anion.

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