

# Crystal chemistry of $\text{Cd}_2\text{P}_2\text{O}_7\text{-A}_2\text{P}_2\text{O}_7$ phosphates; $\text{A} \equiv \text{Sr, Pb, Mg, Co and Ni}$

A. Alaoui El Belghiti and A. Boukhari

Laboratoire de Chimie du Solide Appliquée, Département de Chimie, Faculté des Sciences, Université Mohammed V, Avenue Ibn Batouta, Rabat (Morocco)

E. M. Holt

Department of Chemistry, Oklahoma State University, Stillwater, OK 74078 (USA)

## Abstract

Domains of composition of  $\text{Cd}_{2-x}\text{A}_x\text{P}_2\text{O}_7$ ,  $0 \leq x \leq 2$ ,  $\text{A} \equiv \text{Sr, Mg, and Ni}$ , have been established by powder diffraction methods. Solid solutions have been found near  $\text{Cd}_2\text{P}_2\text{O}_7$  and  $\text{A}_2\text{P}_2\text{O}_7$ ,  $\text{A} \equiv \text{Sr, Mg and Ni}$ . New phases have been identified using single-crystal X-ray diffraction. The mixed diphosphates  $\text{CdPbP}_2\text{O}_7$  and  $\text{CdCoP}_2\text{O}_7$  crystallize in the triclinic space group  $P\bar{1}$ ;  $\text{CdSrP}_2\text{O}_7$  crystallizes in the monoclinic space group  $P2_1/c$ . The diphosphates  $\text{CdSrP}_2\text{O}_7$  and  $\text{CdCoP}_2\text{O}_7$  are isostructural with  $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$  and  $\text{Cd}_2\text{P}_2\text{O}_7$  respectively. All the phosphate structures obtained in this work are closely related to the dichromate type.

## 1. Introduction

The diphosphates with bivalent cations  $\text{A}_2\text{P}_2\text{O}_7$  are characterized by the existence of two types of structures. The first group ( $\text{A} \equiv \text{Mg, Mn, Fe, Co, Ni, Cu}$  and  $\text{Zn}$ ) [1–13] is of the thortveitite type [14] in which  $\text{P}_2\text{O}_7^{4-}$  exhibits a staggered conformation. The thortveitite  $\text{Sc}_2\text{Si}_2\text{O}_7$  was investigated by Zachariasen in 1930. He pointed out that the  $\text{Si-O-Si}$  link in the  $\text{Si}_2\text{O}_7^{6-}$  pyrosilicate anion is linear. The second group ( $\text{A} \equiv \text{Cd, Ca, Sr, Ba and Pb}$ ) [15–23] is of the dichromate type with an eclipsed  $\text{P}_2\text{O}_7^{4-}$  conformation. The potassium dichromate structure  $\text{K}_2\text{Cr}_2\text{O}_7$  was resolved by Brandon *et al.* [24] in 1967.

Diphosphate structures of the type  $\text{A}^{\text{II}}\text{B}^{\text{II}}\text{P}_2\text{O}_7$  are less well known. Only  $\text{SrNiP}_2\text{O}_7$  [25],  $\text{CaCoP}_2\text{O}_7$  [26],  $\text{BaCoP}_2\text{O}_7$ ,  $\text{BaNiP}_2\text{O}_7$  [27],  $\text{BaCuP}_2\text{O}_7$  [28],  $\text{PbCoP}_2\text{O}_7$ ,  $\text{PbBaP}_2\text{O}_7$  [29] were found to be in the dichromate family;  $\text{CuFeP}_2\text{O}_7$  [29],  $\text{CaCuP}_2\text{O}_7$  [30],  $\text{SrCuP}_2\text{O}_7$  [31] are of the thortveitite type.

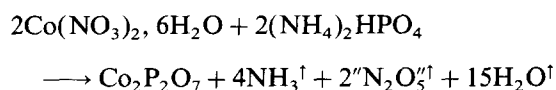
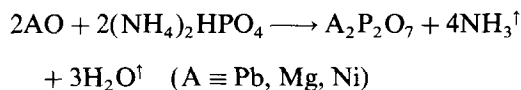
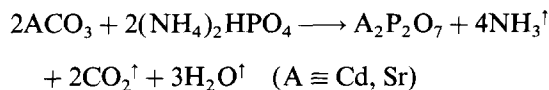
The solid solutions  $\text{Cd}_{2-x}\text{A}_x\text{P}_2\text{O}_7$ ,  $0 \leq x \leq 2$ ,  $\text{A} \equiv \text{Ca}$  and  $\text{Cu}$ , have been synthesized as powder [32, 33]. Solid solutions have been found near  $\text{Cd}_2\text{P}_2\text{O}_7$  and  $\text{A}_2\text{P}_2\text{O}_7$ . The  $\text{Cd}_2\text{P}_2\text{O}_7\text{-Ca}_2\text{P}_2\text{O}_7$  system presents three solid solutions. The compositions of the first domain ( $0 \leq x \leq 0.40$ ) are isostructural with  $\text{Cd}_2\text{P}_2\text{O}_7$ , and the compositions of the second ( $0.40 < x \leq 1.00$ ) have the same monoclinic space group as  $(\text{Cd}_{0.625}\text{Ca}_{0.375})_2\text{P}_2\text{O}_7$ , while the compounds of the third ( $1.70 \leq x \leq 2$ ) are isostructural with  $\beta\text{-Ca}_2\text{P}_2\text{O}_7$  [32]. However, when  $\text{A} \equiv \text{Cu}$ , two solid solutions ( $0 \leq x \leq 0.40$ ,  $1.60 \leq x \leq 2$ ) have been identified to be respectively isostructural with

$\text{Cd}_2\text{P}_2\text{O}_7$  and  $\beta\text{-Cu}_2\text{P}_2\text{O}_7$  diphosphates [33]. New phases have been identified by single-crystal X-ray diffraction which previously did not identify diphosphates:  $(\text{Cd}_{0.625}\text{Ca}_{0.375})_2\text{P}_2\text{O}_7$  [32],  $\text{CdSrP}_2\text{O}_7$ ,  $\text{CdBaP}_2\text{O}_7$  [34] and  $(\text{Cd}_{0.5}\text{Cu}_{0.5})_2\text{P}_2\text{O}_7$  [33].  $\text{Cd-Ca}$  and  $\text{Cd-Cu}$  mixed sites have been obtained in  $(\text{Cd}_{0.625}\text{Ca}_{0.375})_2\text{P}_2\text{O}_7$  and  $(\text{Cd}_{0.5}\text{Cu}_{0.5})_2\text{P}_2\text{O}_7$  phosphates;  $\text{CdSrP}_2\text{O}_7$  is of the  $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$  type [17]. All these phosphates possess a dichromate-type structure except for  $(\text{Cd}_{0.5}\text{Cu}_{0.5})_2\text{P}_2\text{O}_7$ .

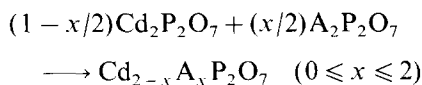
The present work deals with crystal chemistry results of  $\text{Cd}_2\text{P}_2\text{O}_7\text{-A}_2\text{P}_2\text{O}_7$  systems where  $\text{A} \equiv \text{Sr, Pb, Mg, Co and Ni}$ .

## 2. Experimental details

The starting materials  $\text{Cd}_2\text{P}_2\text{O}_7$  and  $\text{A}_2\text{P}_2\text{O}_7$  were synthesized by grinding together stoichiometric amounts of  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{AO}$ ,  $\text{ACO}_3$  or  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{A} \equiv \text{Sr, Pb, Mg and Ni}$ , and heating them progressively to 1173 K with intermittent regrinding, according to the following equations:



Diphosphates with compositions  $Cd_{2-x}A_xP_2O_7$  ( $0 \leq x \leq 2$ ) have been obtained by heating mixtures of  $Cd_2P_2O_7$  and  $A_2P_2O_7$  to 873 K and then to 1173 K according to the equation



Polycrystalline samples were characterized using a CGR (Theta 60) powder diffractometer with  $Cu K\alpha_1$  ( $\lambda = 1.54051 \text{ \AA}$ ).  $D$  spacing values have been calibrated using silicon as an internal standard. Unit cell parameters for the solid solutions have been refined using least-squares techniques. The density has been determined experimentally using a pycnometer in diethylorthophthalate at ambient temperatures.

Single crystals of  $(Cd, A)_2P_2O_7$  have been prepared by fusion in the presence of excess  $P_2O_5$  with the molar ratio  $(Cd, A)_2P_2O_7:P_2O_5 = 0.88$ ,  $A \equiv Sr, Pb$  and  $Co$ .

Crystals of  $(Cd, A)_2P_2O_7$  were mounted on a Syntex P3 automated diffractometer. Unit cell dimensions were determined by least-squares refinement of the best angular alignment procedures [35].

### 3. Crystal chemistry

#### 3.1. $Cd_2P_2O_7-Sr_2P_2O_7$ system

Powder diffraction analysis of mixed diphosphates  $Cd_{2-x}Sr_xP_2O_7$ ,  $0 \leq x \leq 2$ , reveals the existence of solid solutions A ( $0 \leq x \leq 0.60$ ), B ( $1.00 \leq x < 1.20$ ) and C ( $1.20 \leq x \leq 2$ ). The other domains are mixtures of parent compounds.

##### 3.1.1. Domain A: $0 \leq x \leq 0.60$

The solid solution obtained between  $x = 0$  and  $x = 0.60$  is isostructural with  $Cd_2P_2O_7$ . Figure 1 shows the variation in the unit cell volume of this solid solution. As  $Cd^{2+}$  is replaced by increasing amounts of  $Sr^{2+}$  ions, the larger ionic radius of  $Sr^{2+}$  is reflected in the increased cell volume.

##### 3.1.2. Domain B: $1.00 \leq x < 1.20$

The compounds of this domain are isostructural with  $CdSrP_2O_7$  which is isostructural to  $\alpha-Ca_2P_2O_7$  [34].

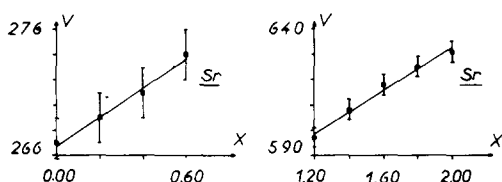


Fig. 1. Variation in unit cell volume (cubic ångströms) of the solid solutions  $Cd_{2-x}Sr_xP_2O_7$  in domains A ( $0 \leq x \leq 0.60$ ) and C ( $1.20 \leq x \leq 2$ ).

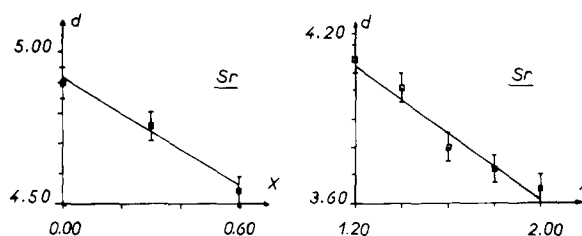


Fig. 2. Variation in density of  $Cd_{2-x}Sr_xP_2O_7$  compounds in domains A ( $0 \leq x \leq 0.60$ ) and C ( $1.20 \leq x \leq 2$ ).

The powder spectra of materials within this domain exhibit only a very small change in the cell dimensions with a change in the composition  $x$ .

##### 3.1.3. Domain C: $1.20 \leq x \leq 2$

X-ray spectra of compositions in the domain C are similar to that of  $\alpha-Sr_2P_2O_7$ . The linear variation in the cell volume is shown in Fig. 1.

Figure 2 reflects the decrease in density in domains A and C with increase in  $x$ . The mixture of B and C domains around the composition 1.20 could not be observed by the X-ray diffraction technique because  $\alpha-Ca_2P_2O_7$  (domain B) and  $\alpha-Sr_2P_2O_7$  (domain C) structures are closely related [17, 20].

The domain of the solid solution  $Cd_{2-x}Ca_xP_2O_7$  ( $0 \leq x \leq 1.00$ ) as reported below, is larger than that observed with  $Cd_{2-x}Sr_xP_2O_7$  ( $0 \leq x \leq 0.60$ ) and the domain ( $1.70 \leq x \leq 2$ ) of  $Cd_{2-x}Ca_xP_2O_7$  is narrower than that of  $Cd_{2-x}Sr_xP_2O_7$  ( $1.20 \leq x \leq 2$ ).

#### 3.2. $Cd_2P_2O_7-Ni_2P_2O_7$ system

The results of X-ray spectrum suggested that the system  $Cd_2P_2O_7-Ni_2P_2O_7$  has only two solid solutions. Compositions of the first solid solution ( $0 \leq x \leq 0.60$ ) are isostructural with  $Cd_2P_2O_7$ . The compositions of the second domain ( $1.60 \leq x \leq 2$ ) are similar to  $\alpha$ - or  $\beta$ - $Ni_2P_2O_7$ . The two allotropes  $\alpha$ - and  $\beta$ - $Ni_2P_2O_7$  are very closely related. The  $\beta \rightarrow \alpha$  transition (843 K) is accompanied by doubling of the  $a$  and  $c$  cell parameters [8, 9]:

$$\beta-Ni_2P_2O_7 (C2/m) \quad a = 6.501 \text{ \AA} \quad b = 8.239 \text{ \AA}$$

$$c = 4.48 \text{ \AA} \quad \beta = 104.14^\circ$$

$$\alpha-Ni_2P_2O_7 (B2_1/c) \quad a = 13.093 \text{ \AA} \quad b = 8.275 \text{ \AA}$$

$$c = 8.975 \text{ \AA} \quad \beta = 104.94^\circ$$

Thus, the powder X-ray diffraction results have been indexed in the  $B2_1/c$  space group.

Figure 3 presents the linear variation in unit cell volume in both domains. Figure 4 shows the decrease in density with increasing  $x$ .

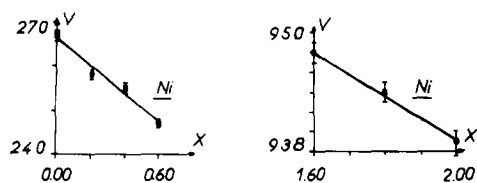


Fig. 3. Variation in unit cell volume (cubic Ångströms) of the solid solutions  $Cd_{2-x}Ni_xP_2O_7$ ,  $0 \leq x \leq 0.60$  and  $1.60 \leq x \leq 2$ .

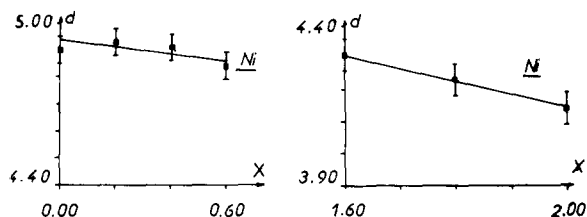


Fig. 4. Variation in density in domains of compositions  $Cd_{2-x}Ni_xP_2O_7$ ,  $0 \leq x \leq 0.60$  and  $1.60 \leq x \leq 2$ .

### 3.3. $Cd_2P_2O_7-Mg_2P_2O_7$ system

The identification of the compounds of the  $Cd_2P_2O_7-Mg_2P_2O_7$  system reveals two solid solutions. The domain of compositions ranging between  $x = 0$  and  $x = 0.40$  is isostructural with  $Cd_2P_2O_7$ . The X-ray spectra of the compounds belonging to the other domain ( $1.20 \leq x \leq 2$ ) are similar to that of  $\alpha$ - or  $\beta$ - $Mg_2P_2O_7$  which could not be identified with the X-ray technique as mentioned above for  $\alpha$ - or  $\beta$ - $Ni_2P_2O_7$ . The  $\alpha$  forms ( $\beta$  forms) of  $Ni_2P_2O_7$  and  $Mg_2P_2O_7$  are isomorphous [1, 2].

The linear evolution of the density of this domain can be observed in Fig. 5.

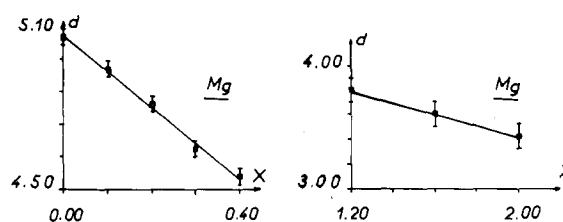


Fig. 5. Variation in density of  $Cd_{2-x}Mg_xP_2O_7$ ,  $0 \leq x \leq 0.40$  and  $1.20 \leq x \leq 2$ .

### 3.4. $Cd_2P_2O_7-A_2P_2O_7$ system, $A \equiv Co, Pb$

Only single crystals were prepared in this system having a composition specified by  $x = 1$ :  $CdCoP_2O_7$  and  $CdPbP_2O_7$  diphosphates. Single-crystal data are reported in Table 1.

## 4. Crystal structure results

Table 1 gives the cell parameters and space group of  $(Cd, A)_2P_2O_7$  single crystals,  $A \equiv Ca, Sr, Ba, Pb, Co$  and  $Cu$ , identified in  $Cd_2P_2O_7-A_2P_2O_7$  phosphates. Table 2 presents the cation coordination, average Cd-O, A-O and P-O bonds distances and P-O-P angles for dichromate or thortveitite-type structure.

The P-O-P angles range between  $130(9)^\circ$  ( $CdSrP_2O_7$ ) and  $134(7)^\circ$  ( $CdCoP_2O_7$ ) for the dichromate family.

In the phases  $(Cd, A)_2P_2O_7$ ;  $A \equiv Ca, Sr, Ba, Pb, Co$  and  $Cu$ , the cation  $Cd^{2+}$  is coordinated to five ( $CdSrP_2O_7, CdCoP_2O_7$ ) and six oxygen atoms ( $(Cd_{0.625}Ca_{0.375})_2P_2O_7, CdBaP_2O_7, (Cd_{0.5}Cu_{0.5})_2P_2O_7$ ). However, the cations  $Ba^{2+}$  ( $CdBaP_2O_7$ ),  $Ca^{2+}$  ( $(Cd_{0.625}Ca_{0.375})_2P_2O_7$ ) and  $Sr^{2+}$  ( $CdSrP_2O_7$ ),  $Co^{2+}$  ( $CdCoP_2O_7$ ) and  $Cu^{2+}$  ( $(Cd_{0.5}Cu_{0.5})_2P_2O_7$ ) exhibit

TABLE 1. The unit cell parameters and space groups of  $CdAP_2O_7$ ,  $A \equiv Ca, Sr, Ba, Pb, Co$  and  $Cu$

Diphosphate	Space group	Cell parameters (Å) and angle (deg)		Unit cell volume (Å <sup>3</sup> )
$Cd_{1.25}Ca_{0.75}P_2O_7$	$P\bar{1}$	$a = 15.477(5)$ $c = 6.667(2)$	$b = 7.222(2)$ $\alpha = 122.93(2)$	266.5(1)
$CdSrP_2O_7$	$P2_1/n$	$a = 5.414(1)$ $c = 12.878(5)$	$b = 8.615(3)$ $\beta = 90.01(3)$	600.6(4)
$CdBaP_2O_7$	$P\bar{1}$	$a = 5.641(1)$ $c = 7.624(2)$	$b = 7.038(2)$ $\alpha = 78.55(2)$	296.2(2)
$CdPbP_2O_7$	$P\bar{1}$	$a = 8.902(4)$ $c = 6.728(4)$	$b = 6.741(2)$ $\alpha = 86.58(4)$	275.1(2)
$CdCoP_2O_7$	$P\bar{1}$	$\beta = 131.51(3)$ $a = 6.522(2)$ $c = 6.422(2)$	$\gamma = 74.46(3)$ $b = 6.587(2)$ $\alpha = 83.28(3)$	251.4(1)
$CdCuP_2O_7$	$P1$	$\beta = 81.72(2)$ $a = 5.516(4)$ $c = 5.504(3)$	$\gamma = 67.34(2)$ $b = 4.504(2)$ $\alpha = 99.65(3)$	127.8(1)
		$\beta = 103.70(6)$	$\gamma = 99.79(5)$	

TABLE 2. Cation coordination with bond lengths and P-O-P angle in  $(Cd, A)_2P_2O_7$  dichromate (D) or thortveitite-type (T) structure

Diphosphate	Coordination		Mean bond values			P-O-P angle (deg)	Type of structure
	Cd	A	$\langle Cd-O \rangle$	$\langle A-O \rangle$	$\langle P-O \rangle$		
$Cd_{1.25}Ca_{0.75}P_2O_7$	6,8 <sup>a</sup>	8	2.305(9)	2.538(10)	1.534(11) 1.539(10)	132.4(10)	D
$CdSrP_2O_7$	5	8	2.29(1)	2.635(1)	1.53(2)	130.0(9)	D
$CdBaP_2O_7$	6	9	2.34(1)	2.86(1)	1.54(1)	132.2(8)	D
$CdPbP_2O_7$	6	7	2.29(2)	2.52(3)	1.55(2) 1.53(2)	132.0(1)	D
$CdCoP_2O_7$	5	6	2.28(1)	2.16(1)	1.53(1) 1.55(1)	134.0(7)	D
$CdCuP_2O_7$	6 <sup>a</sup>	6 <sup>a</sup>	2.22(4) 2.25(4)	2.22(4) 2.25(4)	1.53(4) 1.57(4)	142.0(2)	T

<sup>a</sup>Cd-Ca: mixed site coordination. Cd-Cu: mixed site coordination.

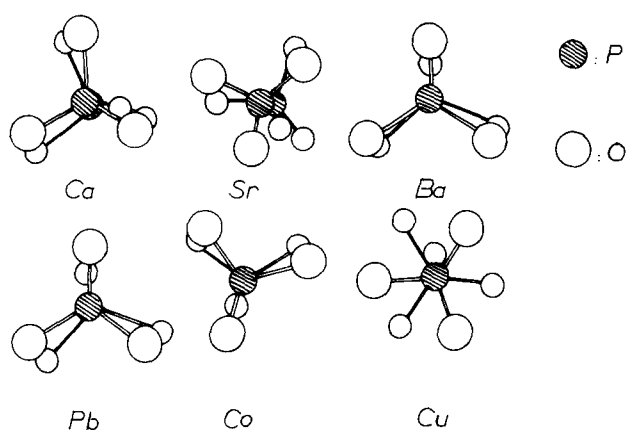


Fig. 6. Staggered and eclipsed conformations of  $P_2O_7$  in  $CdAP_2O_7$ ,  $A \equiv Ca, Sr, Ba, Pb, Co$  and  $Cu$ .

respectively ninefold, eightfold and sixfold oxygen coordination in these diphosphate structures.

Figure 6 shows the staggered and eclipsed conformations of the  $P_2O_7$  group observed in the phosphates with different crystal structures obtained in this work.

Generally, the  $P_2O_7$  conformation in the mixed diphosphates  $(A, B)_2P_2O_7$  follows the parent structure of the biggest cation A or B (dichromate type). This was observed in  $(Cd, A)_2P_2O_7$  with  $A \equiv Ca, Sr, Ba, Pb$  and  $Co$ , except for  $(Cd_{0.5}Cu_{0.5})_2P_2O_7$  phosphate where  $P_2O_7$  groups have a staggered conformation related to the thortveitite-type structure as observed in the  $Cu_2P_2O_7$  framework (Table 2).

More structural details on diphosphates reported in this paper will be published elsewhere.

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