

## Synthesis and Characterization of New Copper (II) Mixed Diphosphates $(M, Cu)_2P_2O_7$ with $M = Mg, Ca, Sr, \text{ and } Ba$

A. BOUKHARI,<sup>1</sup> A. MOQINE, AND S. FLANDROIS\*

*Laboratoire de Chimie du Solide Appliquée, Département de Chimie, Faculté des Sciences, Rabat, Morocco; and \*Centre de Recherche Paul Pascal du CNRS, Domaine Universitaire de Bordeaux I, 33405 Talence, France*

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We have obtained at 1173 K new diphosphates  $(M, Cu)_2P_2O_7$  with  $M = Mg, Ca, Sr, \text{ and } Ba$ . The  $\beta$ -forms of  $Mg_2P_2O_7$  and  $Cu_2P_2O_7$  appear with a small quantity of  $Cu^{2+}$  and  $Mg^{2+}$  ions in their structure, respectively. The solid-solution  $\beta$ - $Mg_{2-x}Cu_xP_2O_7$  ( $0.04 \leq x \leq 1.94$ ) at 298 K is continuous and isomorphous to  $\beta$ - $Mg_2P_2O_7$  and  $\beta$ - $Cu_2P_2O_7$ ; its limits were evaluated with DTA and X-ray techniques. Only three new phases  $CaCuP_2O_7$ ,  $SrCuP_2O_7$ , and  $BaCuP_2O_7$  were isolated in the  $(A, Cu) P_2O_7$  systems,  $A = Ca, Sr, \text{ and } Ba$ . The two former are isomorphous to  $\alpha$ - $Ca_2P_2O_7$ , while the X-ray spectrum of the latter is similar to that of  $BaCoP_2O_7$  and  $BaNiP_2O_7$ . © 1990 Academic Press, Inc.

### Introduction

Divalent metal ion diphosphates are characterized by mixed octahedral and tetrahedral frameworks. They can be divided into two series. The first one is formed by cations of small radii (Mg, Mn, Co, Ni, Cu, and Zn) (1-13) and diphosphates of this class have structures closely related to that of thortveitite (14). The second series are those diphosphates of alkaline earth (Ca, Sr, and Ba) which seem to have too large atoms to stabilize the thortveitite lattice (15-18). The  $Cd_2P_2O_7$  compound is the upper limit of the thortveitite-like structure and the lower limit of the alkaline earth class (19).

However, not many studies have been reported on mixed alkaline earth and transition metal diphosphates. The compounds

$CaMgP_2O_7$ ,  $SrMgP_2O_7$ ,  $SrZnP_2O_7$ ,  $BaMgP_2O_7$ , and  $BaZnP_2O_7$  have been obtained and investigated for their luminescence properties (20-26). Recently, the diphosphates  $BaNiP_2O_7$  and  $BaCoP_2O_7$  have been mentioned by Riou *et al.* (27).

This paper deals with chemical studies and characterization of new phases of copper (II)-mixed diphosphates  $(M, Cu)_2P_2O_7$ , where  $M = Mg, Ca, Sr, \text{ and } Ba$ , with large radii, except for Mg. Their cell parameter values are discussed in comparison with other compounds of these systems.

### Experimental

The solid-solutions  $M_{2-x}Cu_xP_2O_7$  (MCuss) with  $M = Mg, Ca, Sr, \text{ and } Ba$  ( $0 \leq x \leq 2$ ) were prepared at 1173 K from powder starting materials  $M_2P_2O_7$  and  $Cu_2P_2O_7$  which are obtained by two processes: the dry and wet methods.

<sup>1</sup> To whom correspondence should be addressed.

**Dry method.** Stoichiometric amounts of diammonium phosphate  $(\text{NH}_4)_2\text{HPO}_4$  and oxide  $(\text{MgO}, \text{CuO})$  or carbonate  $(\text{CaCO}_3, \text{SrCO}_3, \text{BaCO}_3)$  were mixed, ground in a mortar, and then heated slowly to 1173 K in an alumina crucible. Several heatings of pressed pellets were used to obtain pure powders.

**Wet method.** The starting diphosphates could be prepared also by precipitation from an aqueous solution  $\text{Na}_4\text{P}_2\text{O}_7$  with an excess of metal nitrate or chloride. The precipitate was filtered, washed with cold water, and then fired at 1173 K.

All samples were identified with X-ray diffraction (XRD) on a diffractometer (CGR, Theta 60) using  $\text{CuK}\alpha_1$  radiation, filtered by a monochromator.

Measurements of the magnetic susceptibility of  $\text{CaCuP}_2\text{O}_7$  (CaCu),  $\text{SrCuP}_2\text{O}_7$  (SrCu), and  $\text{BaCuP}_2\text{O}_7$  (BaCu) were carried out on powder samples using the Faraday technique between 4.2 and 300 K.

## Results and Discussion

### $\text{Mg}_{2-x}\text{Cu}_x\text{P}_2\text{O}_7$ Solid-Solution ( $0 \leq x \leq 2$ )

The XRD pattern analysis of MgCuss shows the existence of the  $\beta$ -forms of  $\text{Mg}_2\text{P}_2\text{O}_7$  and  $\text{Cu}_2\text{P}_2\text{O}_7$  with small substitution of  $\text{Mg}^{2+}$  and  $\text{Cu}^{2+}$  in both diphosphates by  $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$ , respectively.

Figure 1 gives the evolution of  $\alpha$ - $\beta$  polymorphism, determined by DTA (micro ATD, Setaram M5), with the composition  $x$  of MgCuss. We observe in this figure a continuous solid-solution  $\beta$ - $(\text{Mg}, \text{Cu})_2\text{P}_2\text{O}_7$  between  $x = 0.04$  and 1.94 at 298 K. These values were deduced by extrapolation, at this temperature, of experimental data (temperature, composition) close to  $\text{Mg}_2\text{P}_2\text{O}_7$  ( $x = 0$ ) and  $\text{Cu}_2\text{P}_2\text{O}_7$  ( $x = 2$ ). These limits are in good agreement with those determined by X-ray diffraction ( $x = 0.05$  and 1.94).

The XRD patterns of  $\alpha$ - and  $\beta$ - $\text{Cu}_2\text{P}_2\text{O}_7$  are very similar and only the (11 $\bar{3}$ ) and (221) peaks, observed in  $\alpha$ -form, allow dis-

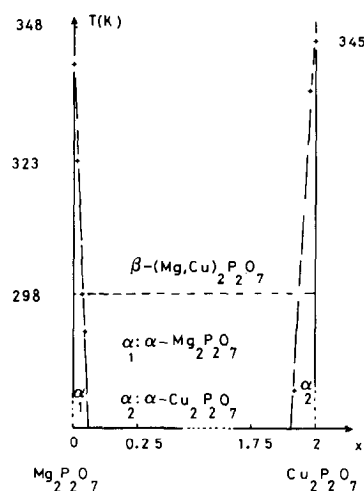


FIG. 1. Variation of  $\alpha$ - $\beta$  transition temperature with the composition  $x$  determined by DTA of MgCuss.

tinguishing between them inspite of their weak intensities; they disappear for  $x \leq 1.94$ .

The  $\alpha$ - $\beta$  transition temperature decreases with the increased concentration of  $\text{Cu}^{2+}$  in the  $\text{Mg}_2\text{P}_2\text{O}_7$  lattice, like the behavior of  $\text{Mg}^{2+}$  in  $\text{Cu}_2\text{P}_2\text{O}_7$ . The decreasing values of transition temperature are 20 K ( $\alpha$ - $\beta$ - $\text{Mg}_2\text{P}_2\text{O}_7$ ) and 16 K ( $\alpha$ - $\beta$ - $\text{Cu}_2\text{P}_2\text{O}_7$ ) with 1% of  $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$ , respectively, in the lattice of  $\text{Mg}_2\text{P}_2\text{O}_7$  and  $\text{Cu}_2\text{P}_2\text{O}_7$  phosphates. These values could be used to estimate the effect of  $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$  on the transition temperature.

The parameter values of the monoclinic cell ( $C2/m$ ) of  $\beta$ - $(\text{Mg}, \text{Cu})_2\text{P}_2\text{O}_7$  are collected in Table 1. Figure 2 gives their linear variation with  $x$  ( $0.04 \leq x \leq 1.94$ ), where the cell data of  $\beta$ - $\text{Mg}_2\text{P}_2\text{O}_7$  and  $\beta$ - $\text{Cu}_2\text{P}_2\text{O}_7$  compounds are added. The  $a$ ,  $c$ , and  $\beta$  values increase, whereas  $b$  decreases with the composition of the  $\beta$ -MgCuss.

### $\text{ACuP}_2\text{O}_7$ Compounds ( $A = \text{Ca}, \text{Sr}, \text{and Ba}$ )

Only  $\text{CaCuP}_2\text{O}_7$ ,  $\text{SrCuP}_2\text{O}_7$ , and  $\text{BaCuP}_2\text{O}_7$  (BaCu) diphosphates were isolated in

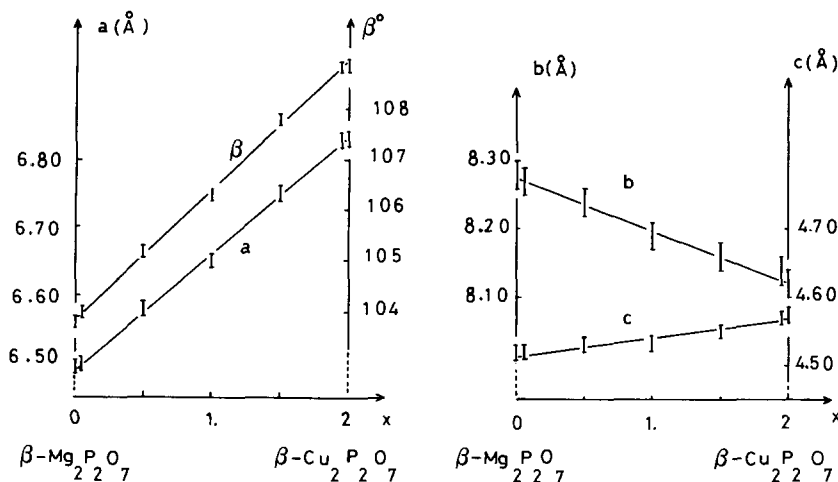


FIG. 2. Dependence of the monoclinic cell parameters ( $C2/m$ ) of  $\beta\text{-Mg}_{2-x}\text{Cu}_x\text{P}_2\text{O}_7$  phases against  $x$  (data of  $\beta\text{-Mg}_2\text{P}_2\text{O}_7$  and  $\beta\text{-Cu}_2\text{P}_2\text{O}_7$  are added).

$\text{A}_2\text{P}_2\text{O}_7\text{-Cu}_2\text{P}_2\text{O}_7$  systems,  $A = \text{Ca}, \text{Sr},$  and  $\text{Ba}$ .

The XRD patterns of  $\text{CaCu}$  and  $\text{SrCu}$  are similar to that of  $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$  (17); they are isomorphous to this phosphate. Lately, we have prepared good crystals of  $\text{SrCu}$  by a flux method, and Weissenberg photographs confirmed this isomorphism. On the other hand, there is a similarity between XRD spectra of  $\text{BaCu}$ ,  $\text{BaNi}$ , and  $\text{BaCo}$  reported by Riou *et al.* (27). These authors have indicated the existence of dimeric groups of co-

balt ions resulting from two edge-sharing irregular  $\text{MO}_6$  octahedra ( $M = \text{Co}, \text{Ni}$ ). However, our magnetic measurements on powder samples of  $\text{BaCu}$  diphosphate show no maximum on the  $\chi_M = f(T)$  curve (Fig. 3a); thus, it is not in favor of  $\text{Cu-Cu}$  dimers

TABLE I  
CELL PARAMETER DATA OF  $\beta\text{-(Mg,Cu)}_2\text{P}_2\text{O}_7$   
DIPHOSPHATES

$x$	$a \pm 0.01 \text{ \AA}$	$b \pm 0.02 \text{ \AA}$	$c \pm 0.01 \text{ \AA}$	$\beta \pm 0.1^\circ$	$v \pm 2 \text{ \AA}^3$
0. <sup>a</sup>	6.49	8.28	4.52	103.8	236
0.05	6.50	8.27	4.52	104.0	236
0.50	6.58	8.24	4.53	105.2	237
1.00	6.65	8.19	4.53	106.3	237
1.50	6.75	8.16	4.55	107.8	239
1.94	6.83	8.13	4.57	108.8	240
2. <sup>b</sup>	6.83	8.12	4.58	108.85	240

<sup>a</sup> Data from Ref. (2).

<sup>b</sup> Data from Ref. (7).

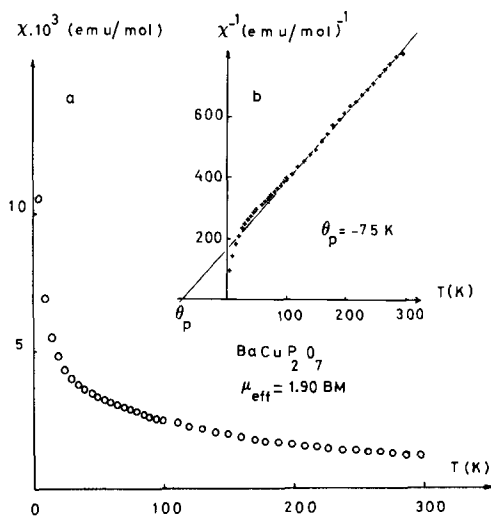


FIG. 3. Temperature dependence of the magnetic susceptibility  $\chi$  (a) and its reciprocal  $\chi^{-1}$  (b) for  $\text{BaCuP}_2\text{O}_7$ .

TABLE II  
CELL PARAMETER VALUES OF  $A_2P_2O_7$  AND  $ACuP_2O_7$  COMPOUNDS ( $A = Ca$  AND  $Sr$ )

Compound	$a \pm 0.02 \text{ \AA}$	$b \pm 0.02 \text{ \AA}$	$c \pm 0.01 \text{ \AA}$	$\beta \pm 0.1^\circ$	$V \pm 3 \text{ \AA}^3$	$\langle r \rangle \text{ \AA}$	Ref.
$\alpha\text{-Sr}_2P_2O_7^a$	13.10	8.91	5.40	90	630	1.28	(16)
$\alpha\text{-Ca}_2P_2O_7^b$	12.66	8.54	5.32	90.3	575	1.12	(17)
$SrCuP_2O_7^b$	12.46	8.13	5.37	90.6	544	0.99	(c)
$CaCuP_2O_7^b$	12.36	8.05	5.22	90.8	519	0.925	(c)

<sup>a</sup> Spacegroup  $Pbnm$ .

<sup>b</sup> Spacegroup  $P2_1/n$ .

<sup>c</sup> This work.

TABLE III  
INTERPLANER DISTANCE VALUES OF  $ACuP_2O_7$  WITH  $A = Ca, Sr (P2_1/n)$  AND  $Ba$

CaCuP <sub>2</sub> O <sub>7</sub>						SrCuP <sub>2</sub> O <sub>7</sub>						BaCuP <sub>2</sub> O <sub>7</sub>	
<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> <sup>calcd</sup>	<i>d</i> <sup>obsd</sup>	<i>I/I</i> <sub>0</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> <sup>calcd</sup>	<i>d</i> <sup>obsd</sup>	<i>I/I</i> <sub>0</sub>	<i>d</i> <sup>obsd</sup>	<i>I/I</i> <sub>0</sub>
1	1	0	6.75	6.75	20	1	1	0	6.81	6.83	10	7.4	6
2	0	0	6.18	6.18	<5	2	0	0	6.23	6.24	10	5.80	7
{	2	1	0	4.90	40	{	1	0	1	4.95	5	4.61	6
	1	0	1	4.83			2	1	0	4.94		4.41	13
	1	0	1	4.78	35		1	0	1	4.91		4.35	7
	0	1	1	4.38	5		0	1	1	4.48	5	4.13	6
	0	2	0	4.03	10		0	2	0	4.07	10	4.00	6
	1	2	0	3.83	10		1	2	0	3.86	<5	3.85	5
	3	1	0	3.67	15		3	1	0	3.70	<5	3.78	12
{	2	1	1	3.59	<5	{	2	1	1	3.65	10	3.68	6
	2	1	1	3.55			2	1	1	3.62		3.62	13
	2	2	0	3.37	15		2	2	0	3.40	<5	3.55	100
	3	0	1	3.26	100		3	0	1	3.30	100	3.30	12
{	3	0	1	3.21	80	{	3	0	1	3.27	75	3.05	25
	0	2	1	3.19			0	2	1	3.24		3.25	75
{	1	2	1	3.09	30	{	1	2	1	3.14	20	2.952	51
	4	0	0	3.09			1	2	1	3.13		3.13	20
	1	2	1	3.08			4	0	0	3.11		2.916	8
	3	1	1	3.02	10	{	3	1	1	3.06	60	2.818	13
	3	1	1	2.98	60		3	1	1	3.03		3.04	60
{	4	1	0	2.884	30	{	4	1	0	2.909	45	2.689	9
	3	2	0	2.879			3	2	0	2.905		2.906	45
	2	2	1	2.823	25		2	1	1	2.868	45	2.525	8
{	1	3	0	2.622	90	{	0	0	2	2.685	65	2.506	12
	0	0	2	2.610			1	3	0	2.648		2.650	40
	4	1	1	2.539	40	{	4	1	1	2.568	25	2.424	18
	0	1	2	2.483	<5		3	2	1	2.563		2.563	25
{	4	2	0	2.451	20	{	0	1	2	2.549	15	2.244	7
	1	1	2	2.440			3	2	1	2.547		2.545	15
	2	0	2	2.392	10		4	1	1	2.547		2.209	4
{	0	3	1	2.386	10	{	1	1	2	2.503	5	2.164	7
	5	1	0	2.363			2	0	2	2.475		2.478	5
	2	1	2	2.314	10		4	2	0	2.472		2.128	7
												2.043	10

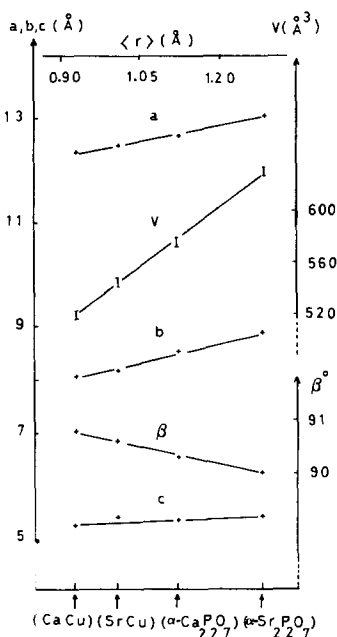


FIG. 4. Evolution of cell data of  $\alpha$ - $A_2P_2O_7$  and (ACu) compounds ( $A = \text{Ca}$  and  $\text{Sr}$ ) with the average radii  $\langle r \rangle$ .

in the lattice. Recently, we have obtained crystals of this phosphate and the structure study is in progress.

The crystalline structures of  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$  and  $\alpha$ - $\text{Sr}_2\text{P}_2\text{O}_7$  were determined by Calvo (17) and Hagman et al. (16), respectively. Weak distortions of  $\text{P}_2\text{O}_7^{4-}$  anions and small displacements of  $\text{Ca}^{2+}$ , in comparison to the  $\alpha$ - $\text{Sr}_2\text{P}_2\text{O}_7$  lattice, reduce the cell symmetry from the  $Pbnm$  spacegroup ( $\alpha$ - $\text{Sr}_2\text{P}_2\text{O}_7$ ) to the subgroup  $P2_1/n(\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7)$  (17).

Table II gives the crystallographic data of the monoclinic cell of CaCu and SrCu related to  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$  and  $\alpha$ - $\text{Sr}_2\text{P}_2\text{O}_7$ . Table III reports the interplanar distance values of CaCu, SrCu and BaCu compounds.

Figure 4 shows the cell parameter variation of CaCu, SrCu, and  $\alpha$ -forms of  $\text{Ca}_2\text{P}_2\text{O}_7$  and  $\text{Sr}_2\text{P}_2\text{O}_7$  phosphates with the mean radii  $\langle r \rangle$  of cations in the lattice.  $\langle r \rangle$  values are calculated taking into account the oxygen

atoms around ( $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Cu}^{2+}$ ) cations in the structure. The coordination numbers of  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  ions are respectively 8 and 9 in  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$  and  $\alpha$ - $\text{Sr}_2\text{P}_2\text{O}_7$  lattices (17, 16). Thus, the same oxygen neighborhood observed for  $\text{Ca}^{2+}$  in  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$  was taken for  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  in the mixed phosphate  $\text{CaCuP}_2\text{O}_7$  and  $\text{SrCuP}_2\text{O}_7$  due to their isomorphism. A maximum six-coordinated copper was adopted for  $\text{Cu}^{2+}$ . All radii ion values are from Shannon and Prewitt's data (28).

The variation of the cell parameters with  $\langle r \rangle$  for CaCu, SrCu,  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$ , and  $\alpha$ - $\text{Sr}_2\text{P}_2\text{O}_7$  represented in Fig. 4 indicated a regular variation from  $\alpha$ - $\text{Sr}_2\text{P}_2\text{O}_7$  to CaCu  $\text{P}_2\text{O}_7$ . The decrease of  $\langle r \rangle$  induces lattice deformations which could be evaluated with the  $\beta$  angle, ranging from  $90^\circ$  ( $\alpha$ - $\text{Sr}_2\text{P}_2\text{O}_7$ ) to  $90.8^\circ$  ( $\text{CaCuP}_2\text{O}_7$ ).

Magnetic susceptibility measurements carried out on powder samples of CaCu and SrCu show a Curie-Weiss behavior with a very small Curie-Weiss temperature ( $\theta_0 \approx -6$  K), which means quasi-isolated mag-

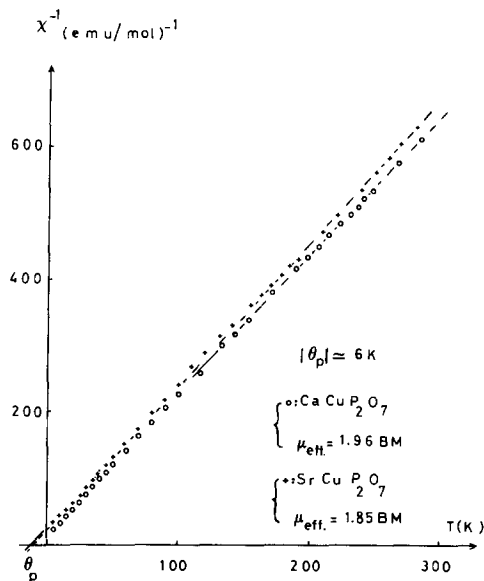


FIG. 5. Temperature dependence of the reciprocal magnetic susceptibility for ACu diphosphates,  $A = \text{Ca}$  and  $\text{Sr}$ .

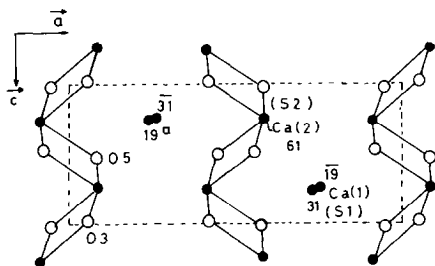


FIG. 6. Partial projection on (010) plane of  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$  showing calcium chains of S2 sites. S1 positions of Ca(1) are isolated in the lattice. Only the copper- and oxygen-bridged ions are reported (values are from Ref. (17)). *a*, this number indicates the  $y \cdot 10^2$  value along  $\vec{b}$ -axis.

netic sites (Fig. 5). This behavior could be explained on account of  $\text{Cu}^{2+}$  distribution in the lattice. In fact, we have seen above an isomorphism between  $\text{CaCu}$ ,  $\text{SrCu}$ , and  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$  compounds. The  $\text{Ca}^{2+}$  ions occupy two independent crystallographic sites of the spacegroup  $P2_1/n$  of  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$  cell, labeled S1 (Ca1) and S2 (Ca2), respectively (17). The S2 positions form an infinite chain along the  $\vec{c}$ -axis, while the sites S1 are isolated in the structure (Fig. 6).

The Curie-Weiss law observed with  $\text{CaCu}$  and  $\text{SrCu}$  compounds, not consistent with the occupancy of sites S2 by  $\text{Cu}^{2+}$ , confirms, otherwise, the presence of these ions in sites S1.  $\text{Ca}^{2+}$  ( $\text{CaCu}$ ) or  $\text{Sr}^{2+}$  ( $\text{SrCu}$ ) are located in sites S2.

## Conclusion

In this paper we have developed the crystalline chemistry of copper (II)-mixed diphosphates ( $M, \text{Cu}$ ) $_2\text{P}_2\text{O}_7$ ,  $M = \text{Mg}, \text{Ca}, \text{Sr}$ , and  $\text{Ba}$ .

The  $\beta$ -forms of  $\text{Mg}_2\text{P}_2\text{O}_7$  and  $\text{Cu}_2\text{P}_2\text{O}_7$  appear with small quantities of  $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$  in their lattice, respectively. The  $\beta$ - $\text{MgCuSS}$  is continuous between  $x = 0.04$  and  $1.94$  at  $298 \text{ K}$ . Only three phases  $\text{CaCuP}_2\text{O}_7$ ,  $\text{SrCuP}_2\text{O}_7$ , and  $\text{BaCuP}_2\text{O}_7$  are existing in ( $A, \text{Cu}$ ) $_2\text{P}_2\text{O}_7$  systems,  $A = \text{Ca}, \text{Sr}$ , and  $\text{Ba}$ . The two former are isomorphous to  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$ ,

the structure study of the latter is in progress.

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