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Crystal Chemistry of $Cd_{2-x}Ca_xP_2O_7$, $0 \le x \le 2$ and the Structure Analysis of $Cd_{1.25}Ca_{0.75}P_2O_7$*

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The system, $Cd_{2-x}Ca_xP_2O_7$, $0 \le x \le 2$, has been prepared in powder form at 1173 K and found to exist in four domains, A, B, C, and D. The materials of these domains have been identified by powder diffraction methods. A crystal of $Cd_{1.25}Ca_{0.75}P_2O_7$ ($Cd_{2-x}Ca_xP_2O_7$, $x = 0.75$) has been isolated in domain B ($0.4 \le x \le 1.00$) which has not been previously identified and structurally determined by single crystal X-ray diffraction. This phase crystallizes in the triclinic space group $P1$ bar with $a = 15.477(5)$, $b = 7.222(2)$, $c = 6.667(2)$ Å, $\alpha = 122.93(2)$, $\beta = 154.78(9)$, $\gamma = 60.68(2)°$, and $Z = 2$. A final least squares refinement yielded $R = 5.4\%$ for 1531 observed reflections. The solid state structure is of the dichromate family, containing isolated and eclipsed $P_2O_7^{4-}$ groups which form columns parallel to the c axis of the triclinic cell. A Cd^{2+} ion with sixfold coordination to oxygen [Cd–O av. 2.30(3) Å] and a mixed Cd^{2+}/Ca^{2+} site [eightfold oxygen coordination, M–O, 2.54(4) Å] are located between these columns. © 1993 Academic Press, Inc.

Introduction

Two types of structures are found for solid state diphosphates. In $A_2P_2O_7$ where A is a bivalent cation, the types are thortveitite and dichromate (*1*). The anionic groups, $P_2O_7^{4-}$ are in staggered conformation in thortveitite structures and eclipsed in dichromates (*1*). Divalent alkaline diphosphates ($A_2P_2O_7$) have received wide attention in the literature. Mg^{2+}(*2–4*), Ca^{2+} (*5, 6*). Sr^{2+} (*7–9*) and Ba^{2+} (*10*) diphosphates are known to exist in at least two phases whose structures or isostructural relationships have been established by single crystal or powder X-ray diffraction. Structural information for divalent transition metals have also been reported [Co^{2+} (*11*), Cu^{2+} (*12, 13*), Ni^{2+} (*14–16*), Zn^{2+} (*3, 17*), Mn^{2+} (*18*), and Cd^{2+} (*19, 20*)]. $Pb_2P_2O_7$ is also known (*21*).

Mixed metal diphosphates (AMP_2O_7, A is an alkaline earth cation, M is a transition metal) are less well known. $BaCoP_2O_7$, $BaNiP_2O_7$, and $CaCoP_2O_7$ have been examined by single crystal X-ray analysis (*22, 23*). $BaCoP_2O_7$ and $BaNiP_2O_7$ are isostructural and, along with $CaCoP_2O_7$, crystallize in a triclinic unit cell. $SrMgP_2O_7$, $SrCuP_2O_7$, and $CaCuP_2O_7$ (*5, 24*) have been identified as isomorphous with $\alpha Ca_2P_2O_7$ (monoclinic, space group $P2_1/n$). The crystal chemistry of the system, $Cd_{2-x}Ca_xP_2O_7$, $0 \le x \le 2$ (*25*) has been investigated and we have determined the single crystal X-ray structure of $Cd_{1.25}Ca_{0.75}P_2O_7$ in order to better understand the structural chemistry of this mixed alkaline earth-transition metal diphosphate.

Experimental

Materials in powder form have been synthesized according to the equation:

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TABLE I

CRYSTAL DATA FOR $Cd_{1.25}Ca_{0.75}P_2O_7$

Formula	$Cd_{1.25}Ca_{0.75}P_2O_7$
M_r	344.5
a	15.477(5) Å
b	7.222(2)
c	6.667(2)
a	122.93(2)°
b	154.78(9)
g	60.68(2)
V	266.5(1) Å^3
$F(000)$	322
μMoKα	63.35 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	4.292 g cm^{-3}
Z	2
Space group	$P1$ bar
Obs. refl.	1531
Octants meas.	$\pm h, k, \pm l$
R/R_ω	5.4/8.2%
G.O.F.	0.66

$$(1 - x/2)Cd_2P_2O_7 + (x/2)Ca_2P_2O_7 \rightarrow Cd_{2-x}Ca_xP_2O_7, \quad 0 \leq x \leq 2$$

by grinding together a mixture of starting materials (stoichiometric amounts) heating the resulting mixture to 873 K, followed by successive regrinding and heating to 1173 K over a period of 72 hr. Diphosphates, $Cd_2P_2O_7$, and $Ca_2P_2O_7$ have been obtained by heating a mixture of the appropriate carbonate and $(NH_4)_2HPO_4$ slowly to 1173 K according to the equation:

$$2MCO_3 + 2(NH_4)_2HPO_4 \rightarrow M_2P_2O_7 + 4NH_3\uparrow + 3H_2O\uparrow + 2CO_2\uparrow, \quad M = \text{Cd, Ca.}$$

Single crystals of the solid solution $Cd_{2-x}Ca_xP_2O_7$ have been prepared by fusion in the presence of excess P_2O_5 [(moles $CdCuP_2O_7$)/(moles P_2O_5) = 0.89]. A mixture of materials was heated slowly to liquidity at 1373 K. This product was then cooled slowly (4 K hr^{-1}) to 1173 K and then at a rate of 10 K hr^{-1} to 473 K. Below this temperature, the oven was turned off and cooling allowed to continue to room temperature. Experimental densities were determined by pycnometry in diethylorthophthalate at ambient temperature. Analysis of the X-ray powder patterns was carried out using a CGR (Theta 60) diffractometer with monochromated CuKα_1 radiation (1.5405 Å). Spectra were calibrated by the addition of Si or NaCl as an internal standard.

A crystal of $Cd_{1.25}Ca_{0.75}P_2O_7$ (dimensions 0.15 × 0.15 × 0.15 mm) was mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table I) were determined by least squares refinement of the best angular positions for fifteen independent reflections ($2\theta > 15°$) during normal alignment procedures. Data (1571 independent points after removal of redundant data) were collected at room temperature using a variable scan rate, a θ–2θ scan mode and a scan width of 1.2°. The intensities of three standard reflections were remeasured after every 97 reflections. As the intensities of these reflections showed less than 5% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization, and background effects. Observed reflections [1531 points ($I > 3.0\sigma(I)$)] were used for solution and refinement. Direct methods (*26*) permitted location of the heavy atom positions. A cycle of least-squares refinement followed by a difference Fourier synthesis allowed location of the $P_2O_7^{-4}$ groups. Initially cadmium and calcium atoms were each placed in general and full occupancy positions. However, the isotropic thermal parameter for calcium was observed to be negative, leading to the conclusion that this site was a mixed Ca/Cd site. Refinement of partial occupancy factors for this position led to 25% Cd/75% Ca occupancy and a final stoichiometry of $Cd_{1.25}Ca_{0.75}P_2O_7$. An attempt to resolve the disorder by refinement in the accentric cell produced no resolution of the disorder. The unit cell thus contains two full occupancy cadmium positions, two 75% Ca/25% Cd sites and two $P_2O_7^{4-}$ groups. Final refinement (*27*) of scale factor, positional and isotropic thermal parameters was carried out

TABLE II

DENSITY AS A FUNCTION OF x IN DOMAINS A, B AND D OF $Cd_{2-x}Ca_xP_2O_7$

	Domain A			Domain B			Domain D		
x	0.00	0.20	0.40	0.60	0.75	1.00	1.70	1.80	2.00
$\rho_{exp} \pm 0.05$ g/cm^3	4.90	4.71	4.58	4.46	4.23	4.07	3.35	3.39	3.12
ρ_{calc} g/cm^3	4.97	4.72	4.54	4.42	4.29	4.06	3.40	3.31	3.13

to convergence in the centric cell. Final cycles of least squares refinement were completed with anisotropic thermal parameters. [function minimized, $\Sigma(|F_0| - |F_c|)^2$] leading to a final agreement factor. $R = 5.4\%$. [$R = (\Sigma\, \omega||F_0| - |F_c||/\Sigma\, \omega|F_0|) \times 100$]. Scattering factors were taken from Cromer and Mann (*28*). Anomalous dispersion corrections were made for Cd and Ca (*29*). In the final stages of refinement a weight of $1/\sigma(F)2$ was used ($R_\omega = 8.2\%$).

Discussion

The powder X-ray diffraction analysis of the $Cd_{2-x}Ca_xP_2O_7$ solid solution, $0 \leq x \leq 2$, shows the existence of four domains depending upon the value of x. Domain A, ($0.00 \leq x \leq 0.40$) corresponds to a solid solution isostructural with $Cd_2P_2O_7$ and domain D, ($1.70 \leq x \leq 2.00$) to a solid solution of type β-$Ca_2P_2O_7$. However, domain B, ($0.4 \leq x \leq 1.00$), corresponds to a new and previously unknown phase. Domain C ($1.00 \leq x \leq 1.70$) consists of a mixture of the phases of the nearest domains, B and D. Table II shows that the variation of density (g cm^{-3}) with x is linear in each of the domains A, B and D.

Domain A ($0.00 \leq x \leq 0.40$, Isostructural with $Cd_2P_2O_7$)

Table III summarizes the cell dimensions of the triclinic cell as a function of stoichiometry within this domain. Cell dimensions reported have been arrived at by least squares refinement of the two theta positions observed in powder spectra. As Cd^{2+} is replaced by increasing amounts of Ca^{2+} ion, the larger ionic radius of Ca^{2+} is reflected in the increased cell volume.

Domain B ($0.4 \leq x \leq 1.00$)

A solid solution of a previously unknown phase was obtained between $x = 0.4$ and $x = 1.0$. The powder patterns of domains A and B are very similar. It was not possible to distinguish a mixed zone in the vicinity of $x = 0.4$ from analysis of X-ray powder diffraction spectra. The powder pattern of the material within domain B showed only a small variation in cell dimensions. The unit cell dimensions determined during the single crystal X-ray study of $Cd_{1.25}Ca_{0.75}P_2O_7$ permitted indexing of the powder patterns of this domain. A view of $Cd_{1.25}Ca_{0.75}P_2O_7$ is shown in Fig. 1, based on the positional parameters of Table IV. Bond angles and distances are listed in Table V.

$P_2O_7^{4-}$ groups exist in groups of two, related by a center of inversion, which form columns parallel to the c axis of the cell. The cations, Cd^{2+} and Ca^{2+}, lie between

TABLE III

UNIT CELL DIMENSIONS OF $Cd_{2-x}Ca_xP_2O_7$, WITHIN DOMAIN A, $0.00 \leq x \leq 0.40$

x	a	b	c	α	β	γ	V
0.00	6.60	6.78	6.63	95.8	97.7	65.0	267
0.10	6.61	6.77	6.63	95.3	97.4	65.0	266
0.20	6.64	6.73	6.64	94.1	97.1	65.6	269
0.40	6.68	6.72	6.68	94.1	97.2	65.0	270

Note. a, b, and c (± 0.01) in Å; α, β, and γ (± 0.1) in degrees; and $V(\pm 2)$ in Å^3.

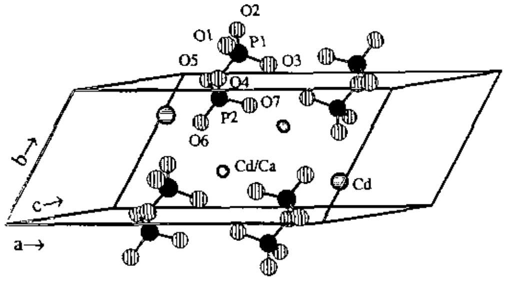

FIG. 1. View of the unit cell of $Cd_{1.25}Ca_{0.75}P_2O_7$.

these columns. Cadmium atoms in general positions show six fold coordination; Cd–O range 2.272–2.344 Å (Cd–O average 2.30(3) Å). This is consistent with the observed averages, 2.31(2) and 2.39(2) Å for six coordinate cadmium in $Cd_2P_2O_7$ (*19*) and $CdSrP_2O_7$ (*30*), respectively. in the mixed cd : Ca site, coordination is eightfold with average M–O distance, 2.54(4) Å. Eight coordinated calcium atoms show average Ca–O distances of 2.52(1) and 2.534 Å in α- and β-$Ca_2P_2O_7$ (*5, 6*). However, eight coordinated cadmium atoms have not been observed in mixed alkaline earth/transition metal phosphates.

In $P_2O_7^{4-}$ groups the average P–O distance is 1.536(10) Å with $P–O_{terminal}$ distances (average 1.513(14) Å) shorter than $P–O_{bridging}$ bonds (average 1.606(18) Å). $P_2O_7^{4-}$ groups show eclipsed conformation. The P–O–P angle of 132.4(10)° is normal whereas, the angles about the phosphorous atoms show distortion from idealized tetrahedral geometry. [O–P(1)–O range 105.0–114.5° and O–P(2) range 102.6–115.2°].

TABLE IV

POSITIONAL PARAMETERS FOR $Cd_{1.25}Ca_{0.75}P_2O_7$

Atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$	U_{eq}[a]
Cd	0.1491(1)	−0.2587(1)	−1.5720(2)	64(3)
Ca1/Cd	0.3778(3)	0.3126(3)	0.3039(6)	
P1	0.3521(2)	0.2304(3)	−0.3266(6)	14(6)
P2	0.1314(3)	−0.1915(3)	−1.0627(6)	11(6)
O1	0.4347(8)	0.3459(8)	0.0953(19)	3(2)
O2	0.1908(8)	0.3604(9)	−0.7039(20)	7(2)
O3	0.5124(8)	0.1645(9)	−0.1808(20)	8(2)
O4	0.2421(7)	0.0163(8)	−0.5982(18)	5(2)
O5	−0.0796(8)	−0.1078(9)	−1.5084(19)	4(2)
O6	0.1333(7)	−0.3655(8)	−1.0002(18)	4(2)
O7	0.2560(8)	−0.2428(8)	−1.0141(18)	6(2)

[a] $U_{eq} = \frac{1}{3} \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

TABLE V

BOND ANGLES (°) AND DISTANCES (Å) FOR $Cd_{1.25}Ca_{0.75}P_2O_7$

Cd. . .O7	2.275(14)	Cd/Ca. . .O1	2.357(17)
Cd. . .$O6^{i}$	2.309(14)	Cd/Ca. . .$O3^{v}$	2.480(14)
Cd. . .$O2^{ii}$	2.327(5)	Cd/Ca. . .$O1^{vi}$	2.406(5)
Cd. . .$O3^{iii}$	2.302(6)	Cd/Ca. . .$O7^{vii}$	2.457(6)
Cd. . .$O2^{iv}$	2.344(7)	Cd/Ca. . .$O6^{viii}$	2.543(14)
Cd. . .$O5^{iv}$	2.272(5)	Cd/Ca. . .$O2^{v}$	2.698(6)
		Cd/Ca. . .$O5^{v}$	2.342(8)
		Cd/Ca. . .$O3^{vii}$	3.025(8)
P1–O1	1.493(12)	P2–O4	1.625(6)
P1–O2	1.533(8)	P2–O5	1.523(4)
P1–O3	1.520(14)	P2–O6	1.505(12)
P1–O4	1.588(9)	P2–O7	1.502(15)
O1–P1–O2	114.5(5)	P1–O4–P2	132.4(10)
O1–P1–O3	114.1(5)	O4–P2–O5	104.5(3)
O1–P1–O4	105.0(7)	O4–P2–O6	102.6(6)
O2–P1–O3	106.7(8)	O4–P2–O7	106.3(5)
O2–P1–O4	106.5(4)	O5–P2–O6	114.0(6)
O3–P1–O4	109.8(5)	O5–P2–O7	112.8(8)
		O6–P2–O7	115.2(5)

Note. $^{i} = x, y, -1.0 + z$; $^{ii} = x, -1.0 + y, -1.0 + z$; $^{iii} = 1.0 - x, -y, -1.0 - z$; $^{iv} = -x, -y, -3.0 - z$; $^{v} = x, y, 1.0 + z$; $^{vi} = 1.0 - x, 1.0 - y, 1.0 - z$; $^{vii} = 1.0 - x, -y, -z$; and $^{viii} = x, 1.0 + y, 1.0 + z$.

The phosphorous–oxygen bonds form PO_4 tetrahedra which are comparable to those observed in the diphosphates of cadmium and of calcium (*5, 6, 19, 20*). The orientation of these tetrahedra in eclipsed conformation within $P_2O_7^{4-}$ groups and the organization of $P_2O_7^{4-}$ groups about a center of symmetry (Fig. 2) with bridging oxygen atoms directed towards each other, classifies the structure of $Cd_{1.25}Ca_{0.75}P_2O_7$ as of the dichromate type.

Domain D (1.70 ≤ x ≤ 2.00, Isostructural with β-$Ca_2P_2O_7$)

The powder spectrum of materials within this domain shows only a very small change in the cell dimensions with a change in composition (x).

The system, $Cd_{2-x}Ca_xP_2O_7$, $0 \le x \le 2$, thus exists in four phases which are composed of solid solutions based on $Cd_2P_2O_7$ and β-$Ca_2P_2O_7$ as well as a previously unknown phase typified by $Cd_{1.25}Ca_{0.75}P_2O_7$.

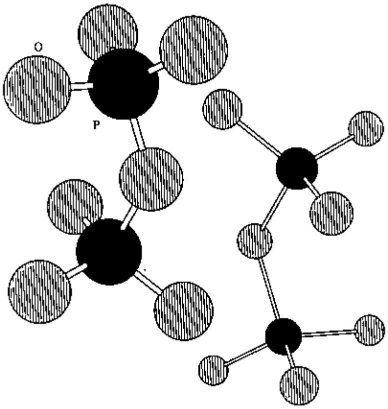

FIG. 2. Orientation of $P_2O_7^{4-}$ about a center of inversion in $Cd_{2-x}Ca_xP_2O_7$.

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References

1. I. D. BROWN AND C. CALVO, *J. Solid State Chem.* **1,** 173 (1970).
2. C. CALVO, *Acta Crystallogr.* **23,** 289 (1967).
3. C. CALVO, *Can. J. Chem.* **43,** 1139 (1965).
4. K. LUKASZEWICZ, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **XV,** 2, 53 (1967).
5. C. CALVO, *Inorg. Chem.* **7,** 1345 (1968).
6. N. C. WEBB, *Acta Crystallogr.* **21,** 942 (1966).
7. J-C. GRENIER AND R. MASSE, *Bull. Soc. Fr. Minéral. Crystallogr.* **XC,** 285 (1967).
8. L-O. HAGMAN, I. JANSSON, AND C. MAGNELI, *Acta Chem. Scand.* **22,** 1419 (1968).
9. C. W. W. HOFFMAN, AND R. W. MOONEY, *J. Electrochem. Soc.* **107,** 854 (1960).
10. M. C. MORRIS, H. F. MCMURDIE, E. H. EVANS, B. PARETZKIN, J. H. DEGROOT, C. R. HUBBARD, AND S. J. CARMEL (eds.), *Nat. Bur. Stand. U.S. Monogr. 25,* **16** 19 (1979).
11. N. KRISHNAMACHARI AND C. CALVO, *Acta Crystallogr. Sect. B* **28,** 2883 (1972).
12. B. E. ROBERTSON AND C. CALVO, *Acta Crystallogr.* **22,** 665 (1967).
13. B. E. ROBERTSON AND C. CALVO, *Can. J. Chem.* **46,** 605 (1968).
14. K. LUKASZEWICZ, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.* **XV** 2, 47 (1967).
15. K. PIETRASZKO AND K. LUKASZEWICZ, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.* **XV** 4, 183 (1968).
16. R. MASSE, J. C. GUITEL, AND A. DURIF, *Mat. Res. Bull.* **14,** 337 (1979).
17. B. E. ROBERTSON AND C. CALVO, *J. Solid State Chem.* **1,** 120 (1970).
18. T. STEFANIDIS AND A. G. NORD, *Acta Crystallogr. Sect. C* **40,** 1995 (1984).
19. C. CALVO AND P. K. L. AU, *Can. J. Chem.* **47,** 3409 (1969).
20. M. C. MORRIS, H. F. MCMURDIE, E. H. EVANS, B. PARETZKIN, J. H. DEGROOT, C. R. HUBBARD, AND S. J. CARMEL (Eds.), *Nat. Bur. Stand. U.S. Monogr. 25* **16,** 26 (1979).
21. D. F. MULLICA, H. O. PERKINS, D. A. GROSSIE, L. A. BOATNER, AND B. C. SALES, *J. Solid State Chem.* **62,** 371 (1986).
22. D. RIOU, P. LABBE, AND M. GOREAUD, *C. R. Acad. Sci. Paris* **307,** 903 (1988).
23. D. RIOU, P. LABBE, AND M. GOREAUD, *C. R. Acad. Sci. Paris* **307,** 1751 (1988).
24. A. BOUKHARI, A. MOQINE, AND S. FLANDROIS, *J. Solid State Chem.* **87,** 251 (1990).
25. A. ALAOUI EL BELGHITI, Thèse du troisieme cycle, Laboratoire de Chimie du Solide Appliquée, Université Mohammed V, Avenue Ibn Batouta, Rabat, Maroc (1990).
26. P. MAIN, S. J. FISKE, S. E. HULL, L. LESSINGER, G. GERMAIN, J. P. DECLERQ, AND M. M. WOOLFSON, University of York, England (1980).
27. J. M. STEWART, Ed., The XRAY System, Version of 1980, Technical Report TR446 of the Computer Center, University of Maryland, College Park, MD.
28. D. T. CROMER AND I. B. MANN, *Acta Crystallogr. Sect. A* **24,** 321 (1968).
29. International Tables for X-Ray Crystallography Vol. IV. Birmingham: Kynoch Press (Present distributor Kluwer Academic Publishers, Dordrecht.) (1974).
30. A. ALAOUI EL BELGHITI, A. BOUKHARI, AND E. M. HOLT, *Acta Crystallogr. Sect. C* **47,** 473 (1991).