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## The Crystal Structure of Cadmium Sodium Orthophosphate $\text{Cd}_4\text{Na}(\text{PO}_4)_3$

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### Abstract

The structure of  $\text{Cd}_4\text{Na}(\text{PO}_4)_3$  has been refined with 3900 diffractometer data to  $R = 0.058$ . The space group is  $Pnma$  with  $a = 6.670$  (2),  $b = 15.10$  (3),  $c = 10.04$  (2) Å,  $Z = 4$ . The network can be described as a three-dimensional lattice made up of isolated  $\text{PO}_4$  tetrahedra linked together by Cd and Na atoms.

### Introduction

The need for new materials having structures able to contain optically active ions by appropriate substitutions, as well as their capacity to provide fast-alkali-ion transport for use as solid electrolytes, has been the main reason for work carried out on a number of orthovanadates and phosphates. As has been shown (Hagenmuller & Van Gool, 1978) fast-ion transport can take place in skeleton structures consisting of rigid three-dimensional covalent networks with voids containing sites only partially occupied by alkali ions. Appropriate structures seem to be, in particular, those having strongly covalent tetrahedra such as  $\text{SiO}_4^{4-}$ ,  $\text{PO}_4^{3-}$  or  $\text{VO}_4^{3-}$ . Several of these compounds have already been studied (Draï, Olazcuaga & Le Flem, 1974; Vlasse, Salmon & Parent, 1976; Salmon, Parent, Le Flem & Vlasse, 1976; Olazcuaga, Vlasse & Le Flem, 1977). In the study of the systems  $\text{CdO}-\text{Na}_2\text{O}-\text{X}_2\text{O}_5$  ( $X = \text{P}, \text{V}$ ), two new phases have been prepared:  $\text{Cd}_4\text{Na}(\text{PO}_4)_3$  and  $\text{Cd}_4\text{Na}(\text{VO}_4)_3$ . To investigate the possibilities of these materials as host structures for optically active ions and as starting materials for fast-ion transport, a structural determination was necessary. The work on the phase  $\text{Cd}_4\text{Na}(\text{VO}_4)_3$  has been reported (Ben Amara, Vlasse, Olazcuaga & Le Flem, 1978), while the present paper gives that for  $\text{Cd}_4\text{Na}(\text{PO}_4)_3$ .

### Experimental

#### Preparation

The orthophosphate  $\text{Cd}_4\text{Na}(\text{PO}_4)_3$  was obtained when a stoichiometric mixture of  $\text{NaPO}_3$ ,  $\text{CdO}$  and

$\text{V}_2\text{O}_5$  was allowed to react in a sealed gold tube heated first at 723 K for 15 h and then at 923 K for 48 h. The product is a white non-hygroscopic powder. Single crystals were prepared by heating 5 g of this powder (in a Pt boat) at 1373 K for 2 h and then cooling at  $10 \text{ K h}^{-1}$  to 773 K.

#### Single-crystal diffraction data

Weissenberg and precession photographs indicate the Laue symmetry  $mmm$ . The systematic extinctions ( $hk0: h = 2n$  and  $0kl: k + l = 2n$ ) are consistent with  $Pnma$  or  $Pn2_1a$ . The cell dimensions obtained from powder diffraction data are:  $a = 6.670$  (2),  $b = 15.10$  (3),  $c = 10.04$  (2) Å, where the reported errors represent the e.s.d.'s. There are four  $\text{Cd}_4\text{Na}(\text{PO}_4)_3$  formula units per unit cell [ $d_x = 4.92$  (5),  $d_c = 4.97 \text{ Mg m}^{-3}$ ].

A single crystal in the form of a parallelepiped  $0.11 \times 0.11 \times 0.06 \text{ mm}$  was mounted along **b**. The intensities were measured on an Enraf–Nonius CD-3 three-circle automatic diffractometer with Mo  $K$  radiation ( $\lambda = 0.70942 \text{ Å}$ ), a pyrolytic graphite monochromator (002), and a  $4^\circ$  take-off angle. A scintillation counter and a  $\theta/2\theta$  multiple-scanning technique with a scan rate of  $10^\circ (2\theta) \text{ min}^{-1}$  were used. The background was taken at each end of the scan range for a time equal to the actual scan time. Three control reflexions measured for each batch of 50 reflexions showed a random fluctuation of about 5%. 4500 independent reflexions were measured up to  $\theta_{\text{max}} = 60^\circ$ ; 3900 of these had  $I > 3\sigma(I)$ , where  $\sigma(I) = (\text{total counts} + \text{background counts})^{1/2}$  and were considered to be observed. These intensities were corrected for Lorentz and polarization effects, but not for absorption. For  $\lambda(\text{Mo } K\alpha)$ ,  $\mu = 9.45 \text{ mm}^{-1}$  and  $\mu r_{\text{max}} = 0.52$ .

#### Structure determination

The structure was solved from a Patterson synthesis in  $Pnma$ . The Na and O atoms were located from a difference synthesis. Full-matrix least-squares refinement (Busing, Martin & Levy, 1962) with isotropic temperature factors led to  $R = 9.3\%$ . A similar refinement was carried out for  $Pn2_1a$  resulting in  $R = 8.6\%$ ,

Table 1. Atomic coordinates ( $\times 10^4$ ) for  $\text{Cd}_4\text{Na}(\text{PO}_4)_3$  with e.s.d.'s in parentheses

	x	y	z
Cd(1)	3354 (1)	3910 (1)	3382 (1)
Cd(2)	1436 (1)	5939 (1)	4391 (1)
Na	4503 (5)	$\frac{3}{4}$	2850 (4)
P(1)	73 (5)	$\frac{1}{4}$	4143 (3)
P(2)	1507 (3)	5679 (1)	1329 (2)
O(1)	9764 (7)	6029 (5)	446 (5)
O(2)	3230 (7)	5457 (3)	318 (5)
O(3)	2161 (8)	6420 (4)	2282 (5)
O(4)	974 (8)	4855 (4)	2160 (5)
O(5)	9237 (13)	1652 (4)	3536 (6)
O(6)	9390 (13)	$\frac{1}{4}$	5595 (8)
O(7)	2391 (16)	$\frac{1}{4}$	3995 (13)

but the Hamilton (1965) statistical test indicates that  $Pnma$  can be accepted at a 99.5% confidence level. Furthermore, high correlations exist between atoms related by the mirror plane when refined separately in  $Pn2_1a$ . Anisotropic refinement in  $Pnma$  led to a final  $R$  ( $\sum |F_o| - |F_c| / \sum |F_o|$ ) of 0.058, with a data-to-parameter ratio of 40. A final ( $F_o - F_c$ ) synthesis confirmed the structure and the space group  $Pnma$ .

$\sum w(|F_o| - |F_c|)^2$  was minimized with  $w = 1$  for all reflexions. The final value of the scale factor  $k$  was 2.98 ( $F_o = kF_c$ ). The form factors of Na, Cd, P and O were taken from McMaster, Kerr del Grande, Mallet & Hubbel (1969).

The final positional parameters are given in Table 1. Table 2 contains the interatomic distances.\*

## Results and discussion

A projection of the structure on the (100) plane is given in Fig. 1. The structure of  $\text{Cd}_4\text{Na}(\text{PO}_4)_3$  can be

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34362 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

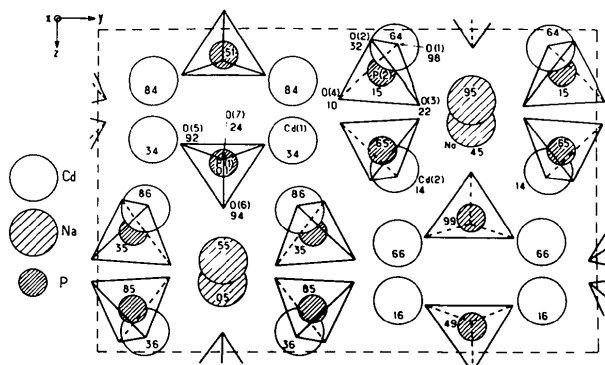


Fig. 1. Projection of the structure on the (100) plane.

Table 2. Interatomic distances (Å) for  $\text{Cd}_4\text{Na}(\text{PO}_4)_3$  with e.s.d.'s in parentheses

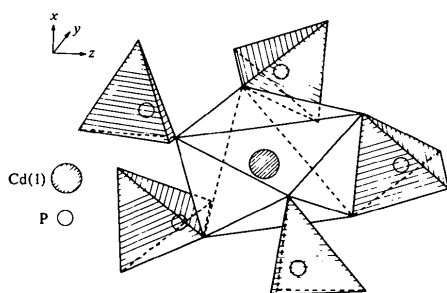
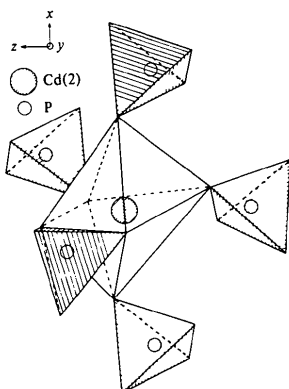
$\text{Cd}(1^a)\text{—O}(1^b)$	2.424 (6)	$\text{Cd}(2^a)\text{—O}(1^c)$	2.230 (6)
$\text{Cd}(1^a)\text{—O}(2^c)$	2.410 (5)	$\text{Cd}(2^a)\text{—O}(2^a)$	2.277 (5)
$\text{Cd}(1^a)\text{—O}(4^a)$	2.462 (6)	$\text{Cd}(2^a)\text{—O}(2^c)$	2.316 (5)
$\text{Cd}(1^a)\text{—O}(4^d)$	2.320 (6)	$\text{Cd}(2^a)\text{—O}(3^a)$	2.290 (5)
$\text{Cd}(1^a)\text{—O}(5^c)$	2.186 (7)	$\text{Cd}(2^a)\text{—O}(5^h)$	2.386 (7)
$\text{Cd}(1^a)\text{—O}(7^a)$	2.308 (8)	$\text{Cd}(2^a)\text{—O}(6^h)$	2.421 (6)
$\langle \text{Cd}(1)\text{—O} \rangle$	2.352	$\langle \text{Cd}(2)\text{—O} \rangle$	2.320
$\text{P}(1^a)\text{—O}(5^f)$	1.524 (7)	$\text{P}(2^a)\text{—O}(1^i)$	1.554 (6)
$\text{P}(1^a)\text{—O}(5^j)$	1.524 (7)	$\text{P}(2^a)\text{—O}(2^a)$	1.569 (5)
$\text{P}(1^a)\text{—O}(6^f)$	1.527 (6)	$\text{P}(2^a)\text{—O}(3^a)$	1.536 (6)
$\text{P}(1^a)\text{—O}(7^a)$	1.553 (8)	$\text{P}(2^a)\text{—O}(4^a)$	1.540 (6)
$\langle \text{P}(1)\text{—O} \rangle$	1.532	$\langle \text{P}(2)\text{—O} \rangle$	1.549
$\text{Cd}(1^a)\text{—P}(1^a)$	3.147 (2)	$\text{Na}^a\text{—O}(1^k)$	2.809 (6)
$\text{Cd}(2^a)\text{—P}(1^h)$	2.955 (2)	$\text{Na}^a\text{—O}(1^k)$	2.809 (6)
$\text{Cd}(1^a)\text{—P}(2^c)$	3.024 (2)	$\text{Na}^a\text{—O}(3^a)$	2.329 (6)
$\text{Cd}(2^a)\text{—P}(2^a)$	3.100 (2)	$\text{Na}^a\text{—O}(3^d)$	2.413 (6)
$\text{Cd}(2^a)\text{—Na}^a$	3.483 (3)	$\text{Na}^a\text{—O}(3^f)$	2.329 (6)
		$\text{Na}^a\text{—O}(3^m)$	2.413 (6)
		$\text{Na}^a\text{—O}(6^p)$	2.382 (6)
		$\text{Na}^a\text{—O}(6^h)$	3.030 (6)
		$\langle \text{Na—O} \rangle$	2.564
$\text{O}(1^a)\text{—O}(2^a)$	2.471 (7)	$\text{O}(3^a)\text{—O}(4^a)$	2.496 (8)
$\text{O}(1^a)\text{—O}(3^a)$	2.927 (8)	$\text{O}(3^a)\text{—O}(6^h)$	2.876 (8)
$\text{O}(1^a)\text{—O}(3^a)$	2.510 (8)	$\text{O}(4^a)\text{—O}(5^j)$	2.903 (9)
$\text{O}(1^a)\text{—O}(4^a)$	2.599 (8)	$\text{O}(5^a)\text{—O}(5^a)$	2.560 (14)
$\text{O}(1^a)\text{—O}(4^a)$	2.978 (8)	$\text{O}(5^a)\text{—O}(6^a)$	2.434 (9)
$\text{O}(2^a)\text{—O}(2^a)$	2.809 (9)	$\text{O}(5^a)\text{—O}(7^a)$	2.505 (11)
$\text{O}(2^a)\text{—O}(3^a)$	2.552 (7)	$\text{O}(6^a)\text{—O}(7^a)$	2.566 (10)
$\text{O}(2^a)\text{—O}(4^a)$	2.552 (7)	$\langle \text{O—O} \rangle$	2.674
$\text{O}(2^a)\text{—O}(5^a)$	3.052 (8)		

## Symmetry code

(a) $x, y, z$	(j) $x - 1, \frac{1}{2} - y, z$
(b) $\frac{3}{2} - x, 1 - y, \frac{1}{2} + z$	(k) $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} - z$
(c) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$	(l) $x, \frac{3}{2} - y, z$
(d) $\frac{1}{2} + x, y, \frac{1}{2} - z$	(m) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} - z$
(e) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$	(n) $1 + x, y, z$
(f) $x - \frac{1}{2}, y, \frac{1}{2} + z$	(o) $1 - x, 1 - y, \bar{z}$
(g) $x - \frac{1}{2}, y, \frac{1}{2} - z$	(p) $\frac{3}{2} - x, \frac{1}{2} + y, z - \frac{1}{2}$
(h) $1 - x, \frac{1}{2} + y, 1 - z$	(q) $x, \frac{1}{2} - y, z$
(i) $x - 1, y, z$	

described as a three-dimensional network of isolated  $\text{PO}_4$  tetrahedra linked together by the Cd and Na atoms. The Cd(1) and Cd(2) atoms occupy distorted octahedral sites (Figs. 2 and 3). Each Cd octahedron is bound to four  $\text{PO}_4$  tetrahedra sharing a common corner and to one tetrahedron by a common edge. Na is found in an eightfold coordinated site in the form of a trigonal and a tetragonal pyramid nested one inside the other sharing a common vertex (Fig. 4). This type of coordination for Na has never been observed before in similar compounds.

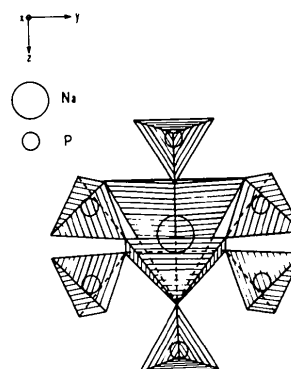
A comparison of the structure of  $\text{Cd}_4\text{Na}(\text{PO}_4)_3$  with those of  $\text{Cd}_4\text{Na}(\text{VO}_4)_3$  (Ben Amara, Vlasse, Olazcuaga & Le Flem, 1978) and  $\text{Cd}_4\text{K}(\text{VO}_4)_3$  (Holt, Drai, Olazcuaga & Vlasse, 1977) shows that  $\text{Cd}_4\text{Na}(\text{PO}_4)_3$

Fig. 2. Polyhedral environment of Cd(1) in  $\text{Cd}_4\text{Na}(\text{PO}_4)_3$ .Fig. 3. Polyhedral environment of Cd(2) in  $\text{Cd}_4\text{Na}(\text{PO}_4)_3$ .

differs greatly from the other two. This difference arises from the greater covalency of the  $\text{PO}_4$  tetrahedron, corroborated by some close intertetrahedral O—O distances [ $\text{O}(1^a)\text{—O}(4^o) = 2.978$ ;  $\text{O}(2^a)\text{—O}(2^o) = 2.809$  and  $\text{O}(3^a)\text{—O}(6^h) = 2.876$  Å].

The  $\text{P}(1)\text{—O}$  and  $\text{P}(2)\text{—O}$  tetrahedral distances give an average of 1.532 and 1.549 Å respectively. These are comparable with the  $\text{P—O}$  average distance of 1.495 Å found in  $\text{Na}_{4.5}\text{Yb}_{1.5}(\text{PO}_4)_3$  (Salmon, Parent, Vlasse & Le Flem, 1979). The minimum, maximum and average tetrahedral O—P—O angles are respectively:  $\text{O—P}(1)\text{—O} = 105.82, 114.34$  and  $109.48^\circ$ ;  $\text{O—P}(2)\text{—O} = 104.56, 114.27$  and  $109.47^\circ$ .

The  $\text{Cd—O}$  distances for Cd(1) and Cd(2) of 2.352 and 2.320 Å respectively are much closer to those found in the interstitial voids of the  $\text{Cd}_4\text{K}(\text{VO}_4)_3$  framework (2.334 and 2.446 Å) than to the  $\text{Cd—O}$  distances

Fig. 4. Coordination polyhedron of Na in  $\text{Cd}_4\text{Na}(\text{PO}_4)_3$ .

in the polyhedral cluster  $\text{Cd}_2(\text{VO}_4)_3^{5-}$  (2.276 and 2.224 Å). We can conclude then that the Cd atoms in  $\text{Cd}_4\text{Na}(\text{PO}_4)_3$  indeed occupy interstitial sites.

The covalent character of this structure with its interstitial sites occupied by divalent or monovalent cations should make it a possible candidate for fast-ion transport, as well as a good host structure for optically active ions. This work is now in progress.

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