

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

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### Abstract

The structure of  $\text{Cd}_4\text{Na}(\text{VO}_4)_3$  has been refined with 1241 diffractometer data to  $R = 0.049$ . The space group is  $Pn2_1a$  with  $a = 9.820$  (8),  $b = 7.040$  (5),  $c = 5.360$  (5) Å and  $Z = 4(\text{Cd}_{4/3}\text{Na}_{1/3}\text{VO}_4)$ . The three-dimensional framework is made up of chains of edge-sharing  $\text{CdO}_6$  octahedra linked by  $\text{VO}_4$  tetrahedra sharing common corners. An interstitial void is partially occupied by Na and Cd atoms.

### Introduction

The work reported here was motivated by several factors. The first is the need for new materials able to contain optically active ions by appropriate substitutions. The second is the interest in solid electrolytes with fast-alkali-ion transport. As shown by a number of workers (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. In particular, appropriate structures seem to be those having strongly covalent tetrahedra such as  $\text{SiO}_4^{4-}$ ,  $\text{PO}_4^{3-}$  or  $\text{VO}_4^{3-}$ . For these reasons several orthovanadates have been studied (Draï, Olazcuaga & Le Flem, 1974; Vlasse, Salmon & Parent, 1976; Salmon, Parent, Le Flem & Vlasse, 1976; Olazcuaga, Vlasse & Le Flem, 1977). The study of the system  $\text{CdO}-\text{Na}_2\text{O}-\text{X}_2\text{O}_5$  ( $X = \text{P}, \text{V}$ ) has led to two new phases:  $\text{Cd}_4\text{Na}(\text{PO}_4)_3$  and  $\text{Cd}_4\text{Na}(\text{VO}_4)_3$ , both with unknown structures. Since the interpretation of both optical and fast-ion transport properties requires a detailed knowledge of the structures, we decided to carry out the structural determination of  $\text{Cd}_4\text{Na}(\text{VO}_4)_3$ .

### Experimental

#### Preparation

$\text{Cd}_4\text{Na}(\text{VO}_4)_3$  was obtained by reacting a stoichiometric mixture of  $\text{NaVO}_3$ ,  $\text{CdO}$  and  $\text{V}_2\text{O}_5$  in a sealed

gold tube, heated first at 773 K for 15 h and then at 1073 K for 48 h.

Single crystals were prepared by heating 5 g of the vanadate (in a Pt boat) to 1173 K for 2 h and then cooling the molten liquid at  $10 \text{ K h}^{-1}$  to 773 K.

#### Single-crystal diffraction data

The zero- and upper-layer Weissenberg and precession photographs indicate Laue symmetry  $mmm$ . The systematic extinctions ( $hk0: h = 2n$ , and  $0kl: k + l = 2n$ ) are consistent with space groups  $Pnma$  and  $Pn2_1a$ . The cell dimensions obtained from powder diffraction data are  $a = 9.820$  (8),  $b = 7.040$  (5) and  $c = 5.360$  (5) Å, where the reported errors represent the standard deviations. A comparison of the cell parameters with some of the olivine-group compounds ( $\text{CaMgSiO}_4$  for example) indicated that the formula of  $\text{Cd}_4\text{Na}(\text{VO}_4)_3$  can be expressed as  $\text{Cd}_{1/3}\text{Na}_{1/3}\text{VO}_4$ . There are four  $\text{Cd}_{4/3}\text{Na}_{1/3}\text{VO}_4$  formula units per unit cell [ $d_x = 4.80$  (5),  $d_c = 4.84 \text{ Mg m}^{-3}$ ].

A single crystal in the form of a parallelepiped  $0.14 \times 0.10 \times 0.08 \text{ mm}$  was mounted about  $a$ . The intensities were measured on an Enraf–Nonius CD-3 three-circle automatic diffractometer with Mo  $K\alpha$  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 every batch of 50 reflexions showed a random fluctuation of about 4%. 1287 independent reflexions were measured up to  $\theta_{\text{max}} = 45^\circ$ ; 1241 had  $I > 2\sigma(I)$ , 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  $\lambda(\text{Mo } K\alpha)$ ,  $\mu = 10.5 \text{ mm}^{-1}$  and  $\mu r_{\text{max}} = 0.78$ .

#### Determination and refinement of the structure

The structure was solved from a Patterson synthesis in space group  $Pn2_1a$ . One V and four O atoms were

located from a difference synthesis. At this point it was noticed that the electron count of a position thought to be occupied by either Na or Cd did not correspond to a full occupation of the site by one or other of the atoms. On the contrary, it seemed to be compatible with a site occupancy of  $\frac{1}{3}$ Na and  $\frac{2}{3}$ Cd. This is in agreement with the proposed stoichiometry  $\text{Cd}_4\text{Na}(\text{VO}_4)_3$  or  $\text{Cd}_{1/3}\text{Na}_{1/3}\square_{1/3}\text{CdVO}_4$ . Full-matrix least-squares refinement (Busing, Martin & Levy, 1962) with anisotropic temperature factors led to an  $R$  ( $\sum |F_o| - |F_c| / \sum |F_o|$ ) of 0.049, with a data-to-parameter ratio of 20. A final ( $F_o - F_c$ ) synthesis confirmed the proposed solution and the assumed space group  $Pn2_1a$ .

The function  $\sum w(|F_o| - |F_c|)^2$  was minimized with  $w$  taken as unity for all reflexions. An overall scale factor was used with a final value of 10.43 ( $F_o = kF_c$ ). The form factors of  $\text{Na}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{V}^{5+}$  and  $\text{O}^{2-}$  were taken from McMaster, Kerr del Grande, Mallet &

Hubbel (1969), with the real and imaginary anomalous-dispersion terms given by Cromer (1965).

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

## Results and discussion

Projections of the structure on (001) are shown in Figs. 1 and 2. Although a metric relationship can be found between some members of the olivine group

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33972 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

	<i>x</i>	<i>y</i>	<i>z</i>
Na/Cd	3539 (2)	2713 (14)	9957 (3)
Cd	12 (2)	200 (5)	9 (1)
V	1809 (1)	2679 (11)	4928 (2)
O(1)	1152 (22)	884 (30)	3344 (27)
O(2)	1189 (17)	4705 (25)	3575 (24)
O(3)	3584 (6)	2748 (35)	4413 (15)
O(4)	1308 (7)	2726 (40)	8022 (11)

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

V(a)—Cd(a)	3.621 (3)	V(a)—O(1)(a)	1.654 (9)
V(a)—Cd(c)	3.591 (3)	V(a)—O(2)(a)	1.712 (9)
V(a)—Cd(d)	3.598 (3)	V(a)—O(3)(a)	1.766 (9)
V(a)—Na/Cd(a)	3.186 (5)	V(a)—O(4a)	1.730 (9)
V(a)—Na/Cd(c)	3.560 (5)	$\langle \text{V—O} \rangle$	1.716 (9)
Cd(a)—O(1)(a)	2.163 (9)	Na/Cd(a)—O(1)(c)	2.413 (1)
Cd(a)—O(2)(e)	2.281 (8)	Na/Cd(a)—O(2)(f)	2.259 (8)
Cd(a)—O(3)(f)	2.232 (7)	Na/Cd(a)—O(3)(k)	2.389 (7)
Cd(a)—O(3)(g)	2.297 (7)	Na/Cd(a)—O(4)(a)	2.424 (7)
Cd(a)—O(4)(h)	2.432 (7)	$\langle \text{Na/Cd—O} \rangle$	2.371 (8)
Cd(a)—O(4)(i)	2.414 (7)		
$\langle \text{Cd—O} \rangle$	2.303 (8)		
O(1)(a)—O(2)(a)	2.693 (12)	O(2)(a)—O(3)(a)	2.763 (10)
O(1)(a)—O(3)(a)	2.785 (11)	O(2)(a)—O(4)(a)	2.764 (10)
O(1)(a)—O(4)(a)	2.827 (11)	O(2)(a)—O(3)(l)	3.100 (10)
O(1)(a)—O(2)(e)	2.950 (12)	O(3)(a)—O(4)(a)	2.956 (9)
O(1)(a)—O(3)(f)	3.063 (12)	$\langle \text{O—O} \rangle$	2.878 (10)

### Symmetry code

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

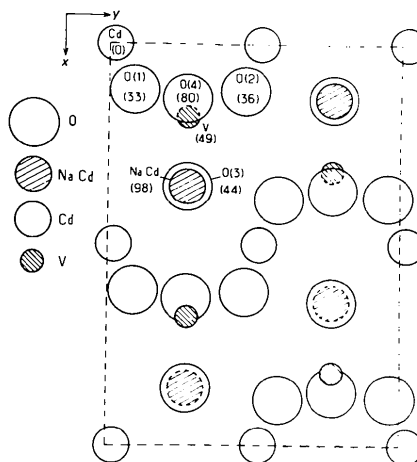


Fig. 1. Projection of the structure on the (001) plane.

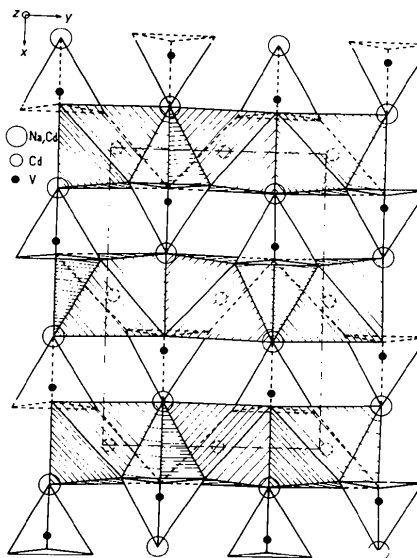


Fig. 2. The  $\text{Cd}_4\text{Na}(\text{VO}_4)_3$  lattice shown on the (001) plane. Full lines indicate tetrahedra pointing up and dashed lines tetrahedra pointing down.

( $CaMgSiO_4$  for example) and  $Cd_4Na(VO_4)_3$ , no direct structural relation could be established between them.

The structure of  $Cd_4Na(VO_4)_3$  can be described as a three-dimensional framework formed by  $CdO_6$  octahedra and  $VO_4$  tetrahedra. The  $CdO_6$  octahedra share edges giving infinite chains running along  $[010]$ . These chains are arranged in parallel planes normal to  $[100]$  and are linked together by the  $VO_4$  tetrahedra sharing common corners (Figs. 2 and 3). This three-dimensional framework leaves a number of interstitial voids, one of which is partially occupied by  $\frac{1}{3}Na$  and  $\frac{1}{3}Cd$  atoms in a deformed tetrahedral environment (Fig. 3).

Although both  $Cd_4Na(VO_4)_3$  and  $Cd_4K(VO_4)_3$  have framework structures consisting of  $CdO_6$  octahedra and  $VO_4$  tetrahedra, their actual structures are quite different. This difference arises mainly from the disparity between the ionic radii of the alkali ions [ $r(IV)_K = 1.38$ ,  $r(IV)_{Na} = 1.02$  Å] (Shannon & Prewitt, 1969). The much smaller  $Na^+$  ion could not be accommodated in the large interstitial voids of the  $Cd_4K(VO_4)_3$  structure (Holt, Draï, Olazcuaga & Vlasse, 1977).

The average V—O distance of 1.716 (9) Å found in the  $VO_4$  tetrahedron is comparable to those found in  $Cd_4K(VO_4)_3$  ( $\langle V-O \rangle = 1.677$  to 1.734 Å) and

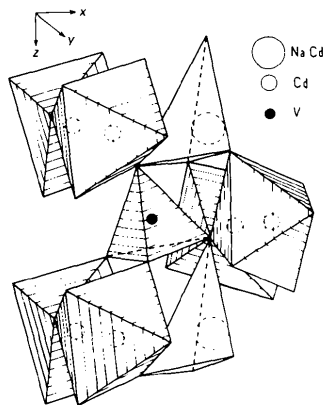


Fig. 3. A fragment of the  $Cd_4Na(VO_4)_3$  structure showing the immediate environment of the  $VO_4$  tetrahedron.

$LaNa_3(VO_4)_2$  (Vlasse, Salmon & Parent, 1976) ( $\langle V-O \rangle = 1.673$  to 1.726 Å). The average Cd—O distance of 2.303 (8) Å is much closer to the distances found in the polyhedral cluster  $Cd_2(VO_4)_3^{2-}$  of  $Cd_4K(VO_4)_3$  (2.276 and 2.224 Å) than the Cd—O distances (2.334 and 2.446 Å) found in the interstitial voids of the  $Cd_4K(VO_4)_3$  framework. This shorter Cd—O distance indicates more covalent character for the Cd—O bond.

All O—O distances are normal with an average of 2.878 Å. The minimum, maximum and average tetrahedral O—V—O angles are 105.20, 115.46 and 109.35° respectively.

According to the criteria established by Goodenough, Hong & Kafalas (1976), the structure of  $Cd_4Na(VO_4)_3$  having a covalent framework character and partially occupied interstitial sites should be a good candidate for Na fast-ion transport. This work is now in progress.

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