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Sodium calcium orthovanadate, $NaCa_4(VO_4)_3$

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Single crystals of sodium tetracalcium trivanadium dodecaoxide were prepared by melting a powder sample of $NaCa_4(VO_4)_3$ at 1673 K, followed by slow cooling to room temperature. The compound crystallizes in the *Pnma* space group and is isostructural with the mineral silicocarnotite, $Ca_5(PO_4)_2SiO_4$. The structure is composed of isolated VO_4 tetrahedra linked by sodium and calcium cations disordered over eight- and seven-coordinated sites.

Comment

Many different structures have been observed for orthovanadates with the $AB_4(VO_4)_3$ stoichiometry (A = Li, Na, K and Rb, and B = Ca, Mg and Cd). In the $ACd_4(VO_4)_3$ series, three different structural types are observed. The structure of $LiCd_4(VO_4)_3$ (Gaudin *et al.*, 2004) is a modulated variant of the Na_2CrO_4 type (Nimmo, 1981), $NaCd_4(VO_4)_3$ crystallizes with the maricite structure (Abrahams *et al.*, 1983), and $KCd_4(VO_4)_3$ (Eddahby *et al.*, 1997) and $RbCd_4(VO_4)_3$ (Mueller-Buschbaum & Mertens, 1997) adopt the scheelite structure. With increasing size of the A cation, its coordination number increases from 4 to 6 with associated structural changes. Moreover, disorder is often observed between the A and B cations. In the incommensurate structure of $LiCd_4(VO_4)_3$, or $(Li_{\frac{1}{3}}Cd_{\frac{1}{3}}\square_{\frac{1}{3}})CdVO_4$ (□ = vacancy), the Li/Cd disorder induces strong steric strains in the tetrahedral sites and a strong modulation of their occupancies (Gaudin *et al.*, 2004, 2005). In $NaCd_4(VO_4)_3$, or $(Na_{\frac{1}{3}}Cd_{\frac{1}{3}}\square_{\frac{1}{3}})CdVO_4$, an Na/Ca/vacancy disorder is observed in strongly distorted tetrahedral sites derived from an octahedral site (Le Page & Donnay, 1977). In $KCd_4(VO_4)_3$ (Eddahby *et al.*, 1997) and $RbCd_4(VO_4)_3$ (Mueller-Buschbaum & Mertens, 1997), all sites are fully occupied, but slight Cd/alkali mixing is observed in some sites. In the $AMg_4(VO_4)_3$ series, only $LiMg_4(VO_4)_3$ (Tyutyunnik *et al.*, 2004) and $NaMg_4(VO_4)_3$ (Murashova *et al.*, 1988) have been observed, and both crystallize with the same structure, different from those of the Cd analogues. No A/Mg disorder is observed in these structures; the Mg atoms occupy octahedral sites and the alkali cations occupy sites with eightfold coordination. For the $ACa_4(VO_4)_3$ series, only $NaCa_4(VO_4)_3$ has been reported (Krasnenko *et al.*, 1987) but without detailed structural data. Its structure has now been determined and is described here. $NaCa_4(VO_4)_3$ is isostructural with the mineral siliocarnotite, $Ca_5(PO_4)_2SiO_4$ (Dickens *et al.*, 1971), and is the first example of an orthovanadate adopting this structure type.

The $NaCa_4(VO_4)_3$ structure (Fig. 1 and Table 1) is very similar to those of $Ca_3Y_2(SiO_4)_3$ (Yamane *et al.*, 1997) and $NaCd_4(PO_4)_3$ (Ben Amara *et al.*, 1979), with a silicocarnotite-type structure. The structure can be described as a three-dimensional network of isolated VO_4 tetrahedra linked by calcium and sodium cations. The Ca and Na cations are randomly distributed over three distinct crystallographic positions, Ca1/Na1, Ca2/Na2 and Ca3/Na3, coordinated to seven, eight and seven O atoms, respectively.

The VO_4 tetrahedra are almost regular, with mean V1—O and V2—O distances of 1.707 and 1.704 Å, respectively, in good agreement with the Shannon (1976) radii. The bond-valence sums, equal to 5.18 and 5.23 for atoms V1 and V2, respectively (Brown, 1996), are close to the +5 oxidation state expected for vanadium. The Ca1/Na1 and Ca3/Na3 sites are occupied by 77 and 80% Ca, and 23 and 20% Na, respectively. The Na/Ca—O distances range from 2.2724 (14) to 2.6834 (19) Å and are consistent with the Shannon radii [$r(Ca^{2+})$ = 1.06 Å and $r(Na^+)$ = 1.12 Å for a coordination number of 7]. The bond-valence sums are 1.97, 1.84, 1.26 and 1.18 for atoms Ca1, Ca3, Na1 and Na3, respectively. By comparison with the expected values of +2 and +1, these bond-valence sums show that sites 1 and 3 are more favorable for Ca^{2+} than Na^+ ions, since the Na^+ ions are overbonded. In contrast, one would expect site 2 to be more favorable for Na^+ ions, as suggested by the bond-valence sums of 1.68 for Ca2 and 1.08 for Na2. The Ca2/Na2—O distances range from 2.4365 (18) to 2.780 (3) Å and are longer than for the two other Ca/Na sites. Surprisingly, the Na2/Ca2 ratio of 0.14 is smaller than those for the two other sites, *viz*. 0.31 for Na1/Ca1 and 0.26 for Na3/Ca3. In the case of the isotypic compound $NaCd_4(PO_4)_3$ (Ben Amara *et al.*, 1979), no Cd/Na disorder has

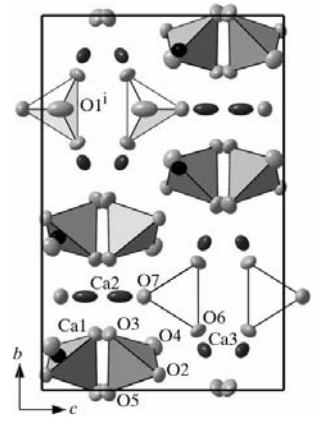

Figure 1
A view of the structure of $NaCa_4(VO_4)_3$ along the a axis. The VO_4 tetrahedra are drawn in grey and white for V1 and V2, respectively. Displacement ellipsoids are shown at the 90% probability level. [Symmetry code: (i) $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$.]

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been observed. The Na atoms occupy the crystallographic site corresponding to the Ca2/Na2 site of the title compound where the coordination number is the highest. The disorder between Ca and Na over the three sites can be attributed to their close ionic radii and, moreover, calcium, unlike cadmium, is often observed with a high coordination number.

Experimental

$NaCa_4(VO_4)_3$ was obtained by the solid-state reaction of a stoichiometric mixture of Na_2CO_3, $CaCO_3$ and V_2O_5. The reagents were ground in an agate mortar and placed in a platinum crucible. The temperature was raised slowly to 873 K in an oxygen flow and maintained for 12 h to decompose the carbonates. A second heat treatment at 1123 K for 48 h with intermediate grindings was needed to ensure a total reaction. The purity of the powder product was confirmed by powder X-ray diffraction. Single crystals of $NaCa_4(VO_4)_3$ were obtained by heating the powder (1 g) at 1673 K in a platinum crucible in air for 1 h, followed by slow cooling at a rate of 10 K h^{-1} to 1473 K and at 20 K h^{-1} to ambient temperature. A product consisting of the major phase $NaCa_4(VO_4)_3$ and two impurities, *viz*. $NaCaVO_4$ and $Ca_3(VO_4)_2$, was recovered. Electron microprobe quantitative analyses revealed the presence of these impurities and confirmed the stoichiometry of the $NaCa_4(VO_4)_3$ crystals. No impurities were observed in the powder of $NaCa_4(VO_4)_3$ before crystallization.

Crystal data

$NaCa_4(VO_4)_3$
$M_r = 528.1$
Orthorhombic, *Pnma*
$a = 6.7703$ (10) Å
$b = 16.0954$ (11) Å
$c = 10.3136$ (5) Å
$V = 1123.88$ (19) Å^3
$Z = 4$
$D_x = 3.120$ (1) Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 236 reflections
$\theta = 5$–35°
$\mu = 4.37$ mm^{-1}
$T = 295$ K
Block, colorless
0.09 × 0.07 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω frames scans
Absorption correction: Gaussian (*JANA2000*; Petricek & Dusek, 2000)
$T_{min} = 0.643$, $T_{max} = 0.795$
25346 measured reflections

2433 independent reflections
1927 reflections with $I > 2\sigma(I)$
$R_{int} = 0.088$
$\theta_{max} = 35.0°$
$h = -10 \rightarrow 10$
$k = -25 \rightarrow 25$
$l = -16 \rightarrow 16$

Table 1

Selected interatomic distances (Å).

Ca1/Na1—O2^{i}	2.3292 (14)	Ca3/Na3—O2	2.3561 (13)
Ca1/Na1—O2^{ii}	2.3451 (15)	Ca3/Na3—O4	2.6834 (19)
Ca1/Na1—O3	2.4701 (13)	Ca3/Na3—O5^{vi}	2.4418 (19)
Ca1/Na1—O4^{iii}	2.3075 (15)	Ca3/Na3—O5^{vii}	2.5410 (19)
Ca1/Na1—O5	2.676 (2)	Ca3/Na3—O6	2.567 (2)
Ca1/Na1—O6^{i}	2.5041 (13)	Ca3/Na3—O6^{viii}	2.2724 (14)
Ca1/Na1—O7^{i}	2.5633 (6)	V1—O2	1.7116 (13)
Ca2/Na2—O3	2.4365 (18)	V1—O3	1.7059 (15)
Ca2/Na2—O3^{iv}	2.5081 (19)	V1—O4	1.7017 (17)
Ca2/Na2—O3^{v}	2.4365 (18)	V1—O5	1.7097 (19)
Ca2/Na2—O4^{iv}	2.5768 (18)	V2—O1	1.683 (3)
Ca2/Na2—O7	2.641 (2)	V2—O6	1.7117 (16)
Ca2/Na2—O7^{i}	2.780 (3)	V2—O7	1.708 (2)
Ca3/Na3—O1	2.5168 (13)		

Symmetry codes: (i) $+x+\frac{1}{2}, y, -z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, -y, +z-\frac{1}{2}$; (iii) $+x-\frac{1}{2}, y, -z+\frac{1}{2}$; (iv) $+x-\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (v) $x, -y+\frac{1}{2}, z$; (vi) $-x+1, -y, -z+1$; (vii) $-x+\frac{1}{2}, -y, +z+\frac{1}{2}$; (viii) $+x+\frac{1}{2}, y, -z+\frac{3}{2}$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.083$
$S = 1.16$
2433 reflections
99 parameters

Weighting scheme based on measured s.u.'s
$w = 1/[\sigma^2(I) + 0.0016I^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.89$ e Å^{-3}
$\Delta\rho_{min} = -0.57$ e Å^{-3}

An initial model with sites 1 and 3 fully occupied by Ca atoms and site 2 by Na atoms gave a reliability index *R* of 6.2% (*wR* = 14.9%) and a non-positive definite value for the Na2 atomic displacement parameter. The disordering of Na and Ca over the three cation positions led to the best result. In a first step, only constraints of fully occupied sites were used, and the chemical formula calculated from the refined Na and Ca site occupancies was found to be equal to the expected $NaCa_4(VO_4)_3$ composition. Then, in the final step, the total Ca and Na contents were fixed to match this ideal stoichiometry.

Data collection: *COLLECT* (Nonius, 2004); cell refinement: *EVALCCD* (Duisenberg *et al.*, 2003); data reduction: *JANA2000* (Petricek & Dusek, 2000); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *JANA2000*; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *JANA2000*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1070). Services for accessing these data are described at the back of the journal.

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