

NaCa₄Nb₅O₁₇: a layered perovskite *A_nB_nO_{3n+2}* compound

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Sodium tetracalcium pentaniobium heptadecaoxide, NaCa₄Nb₅O₁₇, corresponds to the $n = 5$ term of the homologous *A_nB_nO_{3n+2}* family of structures composed of *ABX₃* perovskite layers. The structure consists of perovskite-type blocks of $n = 5$ layers of NbO₆ octahedra, separated by an interblock region. Successive blocks along the *b* axis are displaced by $\frac{1}{2}\mathbf{c}$ with respect to each other. The deformation of the NbO₆ octahedra is a minimum at the middle of each block, and increases along the direction of the *b* axis to a maximum at each end of the block. Ca and Na share the same intrablock sites, coordinated by 12 O atoms, whereas only Ca atoms are found in the interblock cavities, at sites with different coordination geometries.

Comment

Compounds of the series *A_nB_nO_{3n+2}* (where *A* is Ca, La or Sr, and *B* is Ti or Nb), with $n = 4, 4.5, 5, 6$ and 7 , have attracted attention because of their interesting physical properties and their flexibility in accommodating various compositions (Lichtenberg *et al.*, 2001). The structure of these compounds is derived from the *ABX₃* perovskite, in which *BX₆* octahedra share corners and *A* cations lie in the *X* cavities. For any value of n , the ideal structure of the corresponding compound can be interpreted in terms of blocks formed by *BO₆* octahedra; the blocks are stacked along the $[110]_p$ direction of the ideal perovskite structure. The periodicity along the stacking direction (conventionally labelled as the *b* axis) contains two blocks of n octahedral layers, so that its magnitude depends on the composition and is, to a first approximation, given by $b \simeq (n+1)2^{1/2}a_p$ ($a_p = 3.933$ Å; Levin & Bendersky, 1999). The other two cell vectors, usually defined as $a = [100]_p$ ($a = 3.93$ Å) and $c = [0\bar{1}1]_p$ ($c = 5.6$ Å), span the $(011)_p$ blocks of octahedra. This setting of the orthorhombic cell parameters is generally used for the structural description of the family.

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Consecutive blocks of octahedra are shifted with respect to each other by the vector $\frac{1}{2}(\mathbf{a}+\mathbf{c})$, leaving interlayer regions where octahedra do not share two O atoms. Note that the ideal perovskite structure corresponds to the limiting value $n = \infty$, *i.e.* with a single infinitely thick slab of octahedra. On the other hand, $n = 4$ is the lower limit, due to valence considerations. Intermediate integral values of n correspond to equally thick sequences of blocks, but non-integer values are also possible and correspond to sequences of octahedra-based blocks with alternating numbers of layers, *e.g.* $n = 4.5$ corresponds to alternating blocks of four and five layers.

A general description and symmetry classification of this type of structure has been reported by Levin & Bendersky (1999). Based on the tilts of the octahedra (Glazer, 1972), they present a scheme relating the stacking sequence and octahedral tilts to the symmetry of *A_nB_nO_{3n+2}* structures. The review contains references to 40 compounds, six of which correspond to compositions with $n = 5$. More recently, Levin *et al.* (2000) published a transmission electron microscopy study of the Sr_{*n*}(Nb,Ti)_{*n*}O_{3*n*+2} series, with $n = 4, 4.5, 5, 6$ and 7 . They reported the existence of commensurate→incommensurate phase transitions for members with $n = 4, 5, 6$ and 7 , with modulation vectors close to $\frac{1}{2}\mathbf{a}^*$. A lock-in phase to $\frac{1}{2}\mathbf{a}^*$ was only confirmed for the compound with $n = 5$. However, phases with a cell parameter $a \simeq 2a_p$ (7.7 Å) are very common, as reported in the review by Lichtenberg *et al.* (2001), and result from the presence of an alternating tilt of the octahedra around the *b* axis.

A different approach for describing this family of compounds has been proposed by Elcoro *et al.* (2001). Based on the superspace formalism, they describe many known phases of the Sr_{*n*}(Nb,Ti)_{*n*}O_{3*n*+2} series as modulated structures, with a composition-dependent primary modulation wave-vector $\mathbf{q} = \gamma\mathbf{b}^*$ [$\gamma = 1/(1+n)$] and step-like occupational modulation functions. In this way, the introduction of the composition variable n within the 'structural parameter' \mathbf{q} leads to a unique structural model with a unique superspace group. The efficacy of this method was tested by comparing the symmetry reported for members of this family with the resulting space groups derived from the superspace model; even the case of symmetry breaking due to the phase transitions present in many compounds can be taken into account with this method.

With the aim of testing the superspace method described above, we have prepared new compounds of the *A_nB_nO_{3n+2}* family. In this paper, we report the structure of a system with mixed Ca/Na composition for the *A* cations and with *B* = Nb. The first studies on Ca-based compounds of this series were carried out by Nanot *et al.* (1979, 1981, 1986). For the compounds (La₄Ca)Ti₅O₁₇, (Nb₄Ca)Ti₅O₁₇ and Ca₅(Nb₄-Ti)O₁₇, despite the apparent orthorhombic symmetry (*C*222₁) observed on precession photographs, they proposed a monoclinic cell with similar *a* and *c* axes, but with $b' = \frac{1}{2}(b-a)$ and with *P*2₁/*b* or *P*2₁ as possible space groups; the apparent orthorhombic symmetry was attributed to systematic pseudo-merohedral twinning of the crystals. For all three compounds, a cell parameter $a = 2a_p$ was reported. In the present case,

$\text{NaCa}_4\text{Nb}_5\text{O}_{17}$, we confirm a monoclinic cell and $P2_1/b$ as space group.

A projection of the structure of $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ is shown in Fig. 1. Owing to the monoclinic distortion, successive slabs of octahedra stacked along the b -axis direction are shifted by $\frac{1}{2}c$. The shift transforms to $\frac{1}{2}(\mathbf{a}+\mathbf{c})$ when the parameters of the C -centred orthorhombic cell are used. Thus, the packing of the blocks does in fact correspond to that expected for a structural motif composed of an odd number of layers of octahedra. Similar packing is found in $\text{Sr}_5\text{TiNb}_4\text{O}_{17}$ (Drews *et al.*, 1996) and $\text{Sr}_5\text{Nb}_5\text{O}_{17}$ (Schmalle *et al.*, 1995; Abrahams *et al.*, 1998). The structure has a pseudo-lattice translation of $\frac{1}{2}\mathbf{a}$ for the heavy atoms, which is broken by differing tilts of the oxygen octahedra; successive octahedra along the a axis exhibit tilts around \mathbf{b} in antiphase; that is, consecutive octahedra along the a axis are successively tilted clockwise and anticlockwise. This fact, and the weakness of the superlattice reflections with $k = 2n + 1$, permits a description of this phase as a modulation with wavevector $\mathbf{q} = \frac{1}{2}\mathbf{a}^*$ (lock-in phase) of a hypothetical higher-temperature phase (incommensurate phase). Such a phase transition has been reported for other compounds (Levin *et al.*, 2000) experiencing the sequence of symmetries $Immm \rightarrow Pmnn \rightarrow Inc \rightarrow P112_1/b$, with the final structure being associated with an a^+b or a^+c tilt of the untilted high-temperature $Immm$ structure.

The distorted octahedra in $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ have Nb—O distances within two different ranges (Table 1). The shortest and longest distances for octahedra in the middle of the block (Nb1 and Nb2) span the range 1.965 (2)–1.990 (2) Å. For the next layer of octahedra outward from the centre, the distances range from 1.843 (2) to 2.164 (2) Å, and for the octahedra at the edges of the blocks, the distances range from 1.798 (2) to 2.259 (2) Å. Thus, the distortion of the octahedra clearly increases from the centres to the edges of the slabs. The Ca atoms located in the O-bounded cavities between octahedra are arranged in columns along the a axis and exhibit two different coordination environments. Atoms Ca1 and Ca2 are

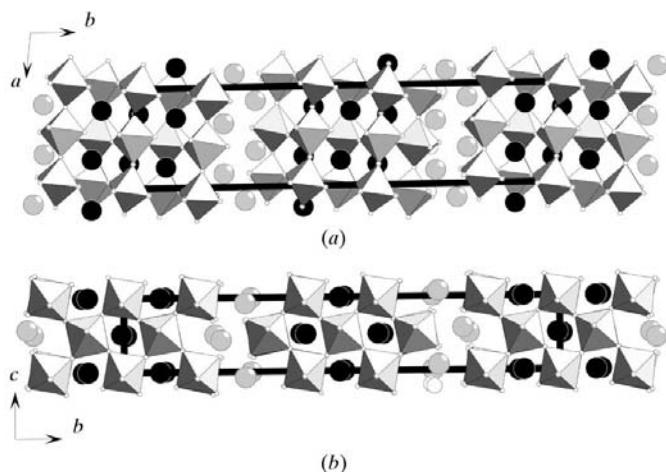


Figure 1
Projections of the structure of $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ along (a) the [001] and (b) the [100] direction.

in the inter-block region, in sites fully occupied by Ca; Ca1 is coordinated to seven O atoms, with distances ranging from 2.303 (2) to 2.529 (2) Å, and Ca2 is coordinated to 6+3 O atoms, at distances in the range 2.398 (2)–3.277 (2) Å, with a break at 2.643 (2) Å. Atoms Ca3, Ca4 and Ca5, embedded in the blocks, are 12-coordinate, with Ca—O distances ranging from 2.343 (2) to 3.348 (2) Å.

Refinement of the occupancy factors of the Ca/Na atoms shows that the Na atoms are located inside the slabs. This preference is in accord with the charge distribution in the structure. The interslab regions have an excess of O atoms and so full occupancy of Ca favours local electroneutrality. A random distribution of the Na atoms at the sites inside the slabs would correspond to occupancy factors of $\frac{2}{3}$ and $\frac{1}{3}$ for Ca and Na, respectively. But, according to the refined values, the Ca sites in the middle of the blocks (Ca3 type) have a higher proportion of Ca [0.747 (3)], while those closer to the edges have Ca fractions of 0.796 (4) (Ca4) and 0.457 (4) (Ca5). A similar distribution has been reported for $\text{Nd}_4\text{Ca}_2\text{Ti}_6\text{O}_{20}$ (Nanot *et al.*, 1976), in which Ca atoms replace Nd preferentially on sites away from the interblock regions.

Experimental

Single crystals of $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ were isolated by heating a mixture corresponding to the composition $\text{Na}_2\text{Ca}_4\text{Nb}_6\text{O}_{20}$ under oxygen at 1753 K. $\text{Na}_2\text{Ca}_4\text{Nb}_6\text{O}_{20}$ was initially prepared by firing an appropriate stoichiometric mixture of Na_2CO_3 , CaCO_3 and Nb_2O_5 . The sample was mixed in an agate mortar and heated in an alumina crucible at 1223 K for 24 h, and, in a final step, at 1473 K for 24 h. The preparations were carried out under a flow of oxygen.

Crystal data

$\text{NaCa}_4\text{Nb}_5\text{O}_{17}$
 $M_r = 919.82$
Monoclinic, $P2_1/b$
 $a = 7.710$ (2) Å
 $b = 32.350$ (5) Å
 $c = 5.4838$ (6) Å
 $\gamma = 96.820$ (13)°
 $V = 1358.0$ (4) Å³
 $Z = 4$

$D_x = 4.499$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 9.1$ – 29.6°
 $\mu = 5.74$ mm⁻¹
 $T = 293$ (2) K
Parallelepiped, colourless
0.21 × 0.08 × 0.05 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: Gaussian [PLATON (Spek, 1990) and WinGX (Farrugia, 1999)]
 $T_{\min} = 0.599$, $T_{\max} = 0.759$
17 947 measured reflections
8692 independent reflections

6585 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$
 $\theta_{\max} = 40^\circ$
 $h = -13 \rightarrow 13$
 $k = -58 \rightarrow 58$
 $l = 0 \rightarrow 9$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
 $R(F) = 0.028$
 $wR(F^2) = 0.071$
 $S = 1.06$
8692 reflections
252 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 1.0534P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.032$

$\Delta\rho_{\max} = 2.123$ e Å⁻³
[at (0.5188, 0.0165, 0.0006),
0.54 Å from Nb2]
 $\Delta\rho_{\min} = -2.234$ e Å⁻³
[at (-0.0029, 0.08794),
0.66 Å from Nb1]
Extinction correction: SHELXL97 (Sheldrick, 1997)
Extinction coefficient: 0.00168 (6)

Table 1
Selected interatomic distances (Å).

Nb1—O2	1.966 (2)	Ca2—O14 ⁱ	2.506 (2)
Nb1—O1	1.976 (2)	Ca2—O13 ⁱ	2.6428 (18)
Nb1—O3	1.9849 (19)	Ca2—O10	2.989 (2)
Nb2—O5	1.965 (2)	Ca2—O9	3.094 (2)
Nb2—O1	1.987 (2)	Ca2—O17 ^v	3.277 (2)
Nb2—O4	1.9895 (19)	Ca3—O1 ⁱ	2.366 (2)
Nb3—O9	1.843 (2)	Ca3—O5 ^{vi}	2.367 (2)
Nb3—O8 ⁱ	1.8963 (18)	Ca3—O2 ^{vii}	2.383 (2)
Nb3—O6 ⁱⁱ	1.984 (3)	Ca3—O7	2.4050 (17)
Nb3—O7	1.997 (2)	Ca3—O4	2.644 (2)
Nb3—O3	2.100 (2)	Ca3—O3	2.644 (2)
Nb3—O2 ⁱ	2.151 (2)	Ca3—O5 ⁱ	2.659 (2)
Nb4—O10	1.850 (2)	Ca3—O2 ⁱ	2.678 (2)
Nb4—O11 ⁱ	1.8863 (18)	Ca3—O6 ^{viii}	2.9577 (19)
Nb4—O6	1.978 (3)	Ca3—O1	3.157 (2)
Nb4—O7	2.013 (2)	Ca3—O4 ^{viii}	3.304 (2)
Nb4—O4	2.114 (2)	Ca3—O3 ^{ix}	3.318 (2)
Nb4—O5 ⁱ	2.164 (2)	Ca4—O7 ^x	2.3904 (17)
Nb5—O15	1.8401 (19)	Ca4—O4	2.408 (2)
Nb5—O14	1.841 (2)	Ca4—O3	2.427 (2)
Nb5—O12 ⁱⁱ	1.998 (2)	Ca4—O13	2.4319 (17)
Nb5—O13	2.000 (2)	Ca4—O11	2.497 (2)
Nb5—O8	2.1197 (19)	Ca4—O9	2.532 (2)
Nb5—O9	2.227 (2)	Ca4—O8	2.552 (2)
Nb6—O17	1.798 (2)	Ca4—O10	2.559 (2)
Nb6—O16	1.8660 (19)	Ca4—O7	3.1835 (17)
Nb6—O12	1.980 (2)	Ca4—O1	3.2138 (18)
Nb6—O13	2.022 (2)	Ca4—O5	3.332 (2)
Nb6—O11	2.1540 (19)	Ca4—O2	3.348 (2)
Nb6—O10	2.259 (2)	Ca5—O11	2.320 (2)
Ca1—O17 ⁱ	2.303 (2)	Ca5—O8 ^{iv}	2.343 (2)
Ca1—O14 ⁱⁱⁱ	2.365 (2)	Ca5—O6	2.3661 (19)
Ca1—O15 ^{iv}	2.445 (2)	Ca5—O1 ^{vi}	2.5527 (18)
Ca1—O15 ^v	2.454 (2)	Ca5—O4	2.752 (2)
Ca1—O14 ^v	2.455 (2)	Ca5—O2 ^{iv}	2.756 (2)
Ca1—O16	2.472 (2)	Ca5—O3 ^{iv}	2.756 (2)
Ca1—O12	2.5287 (18)	Ca5—O5	2.764 (2)
Ca2—O17 ⁱ	2.398 (2)	Ca5—O12	2.8192 (18)
Ca2—O15	2.398 (2)	Ca5—O6 ^x	3.1205 (19)
Ca2—O16 ^v	2.414 (2)	Ca5—O9 ^{iv}	3.265 (2)
Ca2—O16	2.446 (2)	Ca5—O10	3.304 (2)

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

The diffraction patterns from precession photographs show weak (hkl) $h = 2n + 1$ layers and an apparent orthorhombic symmetry. With reference to the orthorhombic cell ($a = 7.710$, $b = 64.24$ and $c = 5.4838$ Å), the systematic absences observed were those of C -centring, including $k = 2n + 1$ for $(0k0)$. Such a lattice type has been registered for compounds with $n = 4$ and 6, but the tilt pattern expected in the present case, with an odd number of octahedra-based layers per block, points to a P -type orthorhombic or monoclinic space group (Levin & Bendersky, 1999). However, attempts to find a solution in space group $C222_1$ failed. Using the direct methods routines of *SHELXS97* (Sheldrick, 1997), a solution was found and refined in both $P2_1$ and $P2_1/b$, with the lattice constants given in the *Crystal data* table above (an unconventional setting is used to permit facile comparisons with other previously published work). The choice of this monoclinic cell assumes a pseudo-merohedral twinned crystal with perfect superposition of both lattices (note that the monoclinic angle is almost 90° in the C -centred cell) and a twin law given by a binary axis about the $[100]$ direct lattice direction, relating (hkl) and

($h, -(h+k), -l$) reflection pairs from each twin. The violation of the systematic absences for the b -glide plane was assumed to be due to the twinning, so the centrosymmetric space group was chosen. In fact, only reflections of type $(hk0)$ $h = \text{odd}$ and $k = \text{odd}$ were observed to violate the b -glide extinctions and correspond to reflections (odd, even, 0) of the second twin component. Using the twin model and with all A sites fully occupied by Ca atoms, the refinement converged to $R = 0.057$ (all atoms anisotropic); at this point, some Ca atoms showed large atomic displacements. A model containing Na and Ca atoms was employed, constraining the population factors to the given composition and keeping the anisotropic displacements equal for all Ca/Na sites during the refinement. Near the end of the refinement, the occupancy factors for the Ca atoms in the interlayer regions were close to 1 and they were fixed to that value in the final cycles. The final population parameter for the twin was 0.5559 (9).

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *STRUPLO84* (Fischer, 1985).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1002). Services for accessing these data are described at the back of the journal.

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