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A Ruddlesden–Popper-type layered perovskite, $Na_2Ca_2Nb_4O_{13}$

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Abstract

Single crystals of disodium dicalcium tetraniobium tridecaoxide, $Na_2Ca_2Nb_4O_{13}$, were grown by the flux method. The structure was determined in space group $Bb2_1m$. Perovskite-type layers with the formula $[(Ca_2Na)Nb_4O_{13}]^-$ are concatenated by Na^+ cations near the interlayer, forming a Ruddlesden–Popper-type structure. The interlayer structure, composed of Na and O atoms, can be regarded as a rocksalt-type. NbO_6 octahedra are tilted about [010] and [001]. The off-centre displacement of Nb atoms suggests a ferroelectric nature along [010], with a calculated magnitude of polarization of 0.12 C m^{-2}.

Comment

The Dion–Jacobson series of layered perovskite-type compounds can be formulated as $M^+\cdot[Ca_2Na_{n-3}Nb_nO_{3n+1}]^-$, where M represents Li, Na, K, Rb, Cs, NH_4 or Tl (Dion *et al.*, 1981, 1986; Jacobson *et al.*, 1985). Despite their importance in applications utilizing physical and chemical properties, such as luminescence, non-linear optical properties, intercalation and fast ionic conduction through the interlayer, the structural details of the series have not been well understood, except for $CsCa_2Nb_3O_{10}$ (Dion *et al.*, 1984). This paper deals with the structure of $Na_2Ca_2Nb_4O_{13}$, which corresponds to $n = 4$ and M = Na in the above formula.

The structure, shown in Fig. 1, has orthorhombic symmetry with space group $Bb2_1m$, and is basically categorized as a Ruddlesden–Popper-type layered perovskite (Ruddlesden & Popper, 1957). The thickness of the layer can be characterized by the four corner-sharing NbO_6 octahedra. The stacking mode of the perovskite-type layers is different from that of the Dion–Jacobson series compound with M = K (Jacobson *et al.*, 1985).

There are two symmetrically independent 12-fold coordinated sites, Ca1 (= Na1) and Ca2 (= Na2), in the perovskite-type layer. Na atoms slightly prefer the inner sites (Na1) of the layer to the outer ones (Na2), which is favourable for reducing the net charge of the perovskite-type unit $[(Ca_xNa_{1-x})NbO_3]^{x+}$ constituting the inner part of the layer.

The displacements of the Nb atoms from the respective geometrical centres of their coordination octahedra have noticeable components of about 0.1 Å along [010] and much more along [001]. The components along [001] and the negligibly small components along [100] cancel each other within a layer because of the symmetry requirement, while those along [010] do not, giving rise to a net polarization along [010] in the crystal. The calculated polarization was 0.12 C m^{-2}, which corresponds to approximately half the value for the tetragonal $BaTiO_3$ at room temperature. The crystal is potentially ferroelectric, in contrast to the antiferroelectric $NaNbO_3$ (Sakowski-Cowley *et al.*, 1969). The tilting angles of the $Nb1O_6$ octahedra constituting the inner part of the perovskite-type layer are 10 and 11° about [010] and [001], respectively. Those of the $Nb2O_6$ octahedra constituting the outer part of the layer are 9 and 4° about [010] and [001], respectively. No tilts are allowed about [100] because of the symmetry requirement.

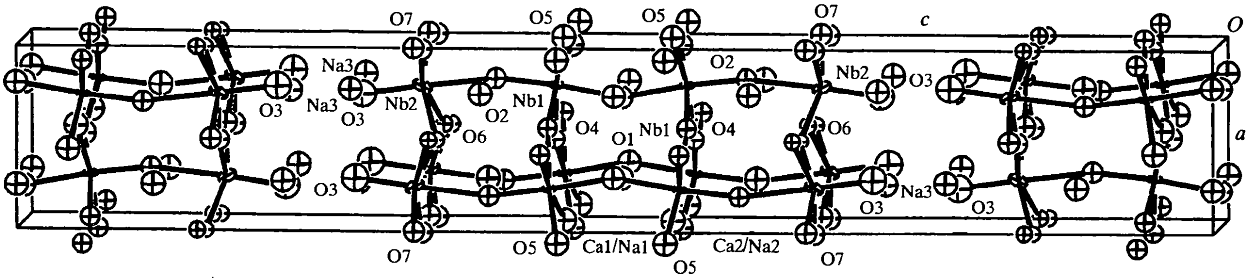

Fig. 1. *ORTEP* (Johnson, 1970) drawing of the orthorhombic $Bb2_1m$ structure of $Na_2Ca_2Nb_4O_{13}$. Displacement ellipsoids are drawn at the 90% probability level.

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Sato *et al.* (1993) conducted a Rietveld study on a tetragonal *I4/mmm* structure of $Na_2Ca_2Nb_4O_{13}$, dehydrated from $Na_2Ca_2Nb_4O_{13}\cdot1.7H_2O$, which was obtained by ion exchange of $RbNaCa_2Nb_4O_{13}$. Apart from the tilting and distortion of the octahedra in the perovskite-type layer, which was assumed to be ideal in their study, there is a striking difference compared with the present structure regarding the coordination of Na atoms (Na3) connecting neighbouring layers. In the present structure, each Na3 atom of a layer is linked to the adjacent layer *via* a short Na3—O3 bond nearly parallel to [001], as shown in Fig. 2. The disposition of Na3 and O3 atoms near the interlayer can be considered as a rocksalt-type single-unit layer, which is characteristic of the Ruddlesden–Popper-type layered perovskites. The Na3 atom is surrounded by nine O atoms, of which eight belong to the same layer, with distances in the range 2.63 (4)–3.30 (4) Å, while the ninth belongs to the adjacent layer, with the shortest distance of 2.20 (2) Å. On the other hand, the corresponding Na atoms in the structure described by Sato *et al.* (1993) reside almost at the middle position of the interlayer, being coordinated tetrahedrally to two O atoms belonging to one layer and to two from the other layer; the distance of the four Na—O bonds of the NaO_4 tetrahedron is reported as 2.26 (3) Å. The difference in coordination of Na atoms near the interlayer is reflected in the slightly shorter *c* length of the present crystal [36.15 (1) Å] compared with that of the crystal analysed by Sato *et al.* (1993) [36.937 (2) Å].

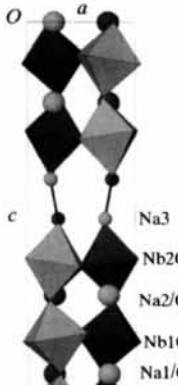

Fig. 2. Polyhedral drawing of the orthorhombic $Bb2_1m$ structure of $Na_2Ca_2Nb_4O_{13}$. The interlayer bonding between Na3 and the O atoms is shown by solid lines.

From the above results, there are presumably two kinds of $Na_2Ca_2Nb_4O_{13}$ crystals at room temperature with different structures, and consequently different *c* lengths, namely, one synthesized through the anhydrous flux growth route and the other synthesized through the ion-exchange and dehydration route. It should be noted that the presence of a polymorph for $Na_2Ca_2Nb_4O_{13}$ with slightly different *c* lengths at room temperature was also inferred by Dion *et al.* (1986). We observed a linear increase of about 0.25 Å for the *c* length of the present crystal when it was left under ambient conditions for six months. This suggests that the present crystal is unstable under ambient conditions. Two interpretations are possible to explain the *c*-length increase; one is a gradual reconstruction of the interlayer structure to provide the tetrahedral coordination for Na3 atoms, and the other is a gradual intercalation of some chemical species such as H_2O through the interlayer. The latter may be accompanied by a resultant change of the coordination of Na atoms near the interlayer. A detailed study of this time-dependent structural change of the compound is in progress.

Experimental

Crystals of the title compound were grown by cooling a mixture of Na_2CO_3, $CaCO_3$ and Nb_2O_5 with Na_2SO_4 flux from 1373 K at a rate of 5 K h^{-1}. The composition was confirmed by EPMA and ICP analyses. Details of the growth experiment are given by Oishi *et al.* (1998). Transparent crystals were grown with habit planes parallel to {001}.

Crystal data

$Ca_2Na_2Nb_4O_{13}$
$M_r = 705.75$
Orthorhombic
$Bb2_1m$
$a = 5.474\ (3)$ Å
$b = 5.510\ (3)$ Å
$c = 36.150\ (10)$ Å
$V = 1090.3\ (9)$ Å^3
$Z = 4$
$D_x = 4.299$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 5$–$11°$
$\mu = 5.19$ mm^{-1}
$T = 293$ K
Rectangular
$0.13 \times 0.09 \times 0.02$ mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{min} = 0.642$, $T_{max} = 0.897$
4390 measured reflections
1361 independent reflections

669 reflections with $I > 3\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 45°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 71$
6 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.044$
$wR = 0.026$
$S = 1.993$
669 reflections
58 parameters
Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{\text{max}} = 0.001$
$\Delta\rho_{\text{max}} = 2.078$ e Å^{-3}
$\Delta\rho_{\text{min}} = -2.06$ e Å^{-3}
Extinction correction: Gaussian (Becker & Coppens, 1974)
Extinction coefficient: $1.5(3) \times 10^2$
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Nb1	0.2623 (15)	0	0.05497 (5)	0.0054 (8)
Nb2	0.2517 (14)	0.9897 (13)	0.16809 (4)	0.0091 (7)
Ca1	0.244 (5)	0.507 (5)	0	0.018 (2)
Na1	0.244 (5)	0.507 (5)	0	0.018 (2)
Ca2	0.250 (4)	0.4738 (19)	0.11318 (12)	0.0192 (12)
Na2	0.250 (4)	0.4738 (19)	0.11318 (12)	0.0192 (12)
Na3	0.276 (5)	0.498 (11)	0.2216 (4)	0.019 (6)
O1	0.197 (3)	0.036 (5)	0	0.018 (6)
O2	0.2997 (18)	0.024 (3)	0.1056 (4)	0.014 (3)
O3	0.207 (2)	0.010 (6)	0.2177 (4)	0.025 (4)
O4	0.051 (3)	0.308 (3)	0.0586 (5)	0.012 (3)
O5	0.458 (4)	0.713 (4)	0.0457 (5)	0.019 (4)
O6	0.979 (4)	0.236 (4)	0.1532 (4)	0.009 (3)
O7	0.525 (4)	0.773 (4)	0.1651 (5)	0.015 (4)

† Site occupancy = 0.63 (3). ‡ Site occupancy = 0.37 (3). § Site occupancy = 0.69 (3). ¶ Site occupancy = 0.31 (3). †† Site occupancy = 0.50.

Table 2. *Selected bond lengths (Å)*

Nb1—O1	2.029 (5)	Ca1—O5$^{\text{x}}$	2.83 (3)
Nb1—O2	1.846 (15)	Ca2—O2	2.51 (2)
Nb1—O4	2.058 (17)	Ca2—O4	2.43 (2)
Nb1—O5$^{\text{i}}$	1.94 (2)	Ca2—O5	3.00 (2)
Nb1—O4$^{\text{ii}}$	2.019 (18)	Ca2—O7	2.92 (2)
Nb1—O5$^{\text{iii}}$	1.96 (2)	Ca2—O6$^{\text{xi}}$	2.45 (2)
Nb2—O7	1.92 (2)	Ca2—O2$^{\text{v}}$	3.06 (2)
Nb2—O6$^{\text{iv}}$	2.09 (2)	Ca2—O2$^{\text{viii}}$	3.03 (2)
Nb2—O2$^{\text{v}}$	2.282 (15)	Ca2—O4$^{\text{viii}}$	3.16 (2)
Nb2—O3$^{\text{v}}$	1.813 (15)	Ca2—O5$^{\text{iii}}$	3.25 (2)
Nb2—O6$^{\text{vi}}$	1.96 (2)	Ca2—O7$^{\text{iii}}$	2.50 (2)
Nb2—O7$^{\text{vi}}$	1.99 (2)	Ca2—O2$^{\text{vi}}$	2.50 (2)
Ca1—O1	2.61 (4)	Ca2—O6$^{\text{vi}}$	2.40 (2)
Ca1—O4	2.61 (2)	Na3—O3	2.72 (7)
Ca1—O5	2.32 (3)	Na3—O7	2.89 (4)
Ca1—O1$^{\text{v}}$	2.93 (4)	Na3—O6$^{\text{xi}}$	3.29 (4)
Ca1—O4$^{\text{vii}}$	2.61 (2)	Na3—O3$^{\text{v}}$	2.85 (7)
Ca1—O5$^{\text{vii}}$	2.32 (3)	Na3—O3$^{\text{viii}}$	2.65 (3)
Ca1—O1$^{\text{viii}}$	2.42 (3)	Na3—O7$^{\text{iii}}$	2.63 (4)
Ca1—O4$^{\text{viii}}$	3.14 (3)	Na3—O3$^{\text{vi}}$	2.83 (3)
Ca1—O5$^{\text{iii}}$	2.83 (3)	Na3—O6$^{\text{vi}}$	3.13 (4)
Ca1—O1$^{\text{vi}}$	3.06 (3)	Na3—O3$^{\text{xii}}$	2.20 (2)
Ca1—O4$^{\text{ix}}$	3.14 (3)		

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

The crystal has a body-centred pseudo-tetragonal unit cell with dimensions of approximately 3.9 × 3.9 × 36 Å^3 (Chiba *et al.*, 1998). The space group of the aristotype is *I*4/*mmm*. The presence of several weak superstructure reflections at room temperature suggested a B-centred orthorhombic symmetry with the *a* and *b* axes lying along the [110] directions of the pseudo-tetragonal cell. Here, the *c* axis was chosen in accordance with the aristotype. The space group was restricted to *B*222, *B*22$_1$2, *Bb*2$_1$*m*, *Bbm*2 and *Bbmm* from the systematic absences of reflections. Because of the long *c* axis of the crystal, for Mo *Kα* radiation it was difficult to determine uniquely the scan width of the $\omega/2\theta$ scan appropriate for all reflections to be measured. Therefore, the intensity data were first taken with a scan width chosen to be optimal for reflections not near the *c** axis. Then the backgrounds of the reflections near the *c** axis were checked carefully, and the intensities of the reflections with high or uneven backgrounds were re-collected by choosing narrower scan widths after scanning their profiles. Neither a decay of the standard reflections nor a significant increase of the *c* length was observed during the 14-day data collection. The aristotype structure was solved by direct methods. Various hettotype models were then examined, based on all the orthorhombic B-centred space groups mentioned above, taking into consideration the tilt and distortion of NbO$_6$ octahedra. All the models, except for *Bb*2$_1$*m*, were discarded because of problems encountered during the course of refinement procedures, such as convergence problems, unreasonable magnitudes of the isotropic displacement parameters of some constituent atoms, or unreasonable distortion of some NbO$_6$ octahedra. No such problems were found in the refinement based on *Bb*2$_1$*m*. The *y* value of Nb1 was fixed at 0 to define the origin. The non-centrosymmetric nature of the crystal was confirmed from the shifts of Nb2 atoms along **b** with respect to Nb1.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *Xtal*3.4 (Hall *et al.*, 1995). Data reduction: *Xtal*3.4. Program(s) used to solve structure: *Xtal*3.4. Program(s) used to refine structure: *Xtal*3.4. Molecular graphics: *ORTEP* (Johnson, 1970) and *ATOMS* (Dowty, 1995). Software used to prepare material for publication: *Xtal*3.4.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1080). Services for accessing these data are described at the back of the journal.

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Pentabarium tetraantimonide, β-Ba_5Sb_4: a more symmetrical arrangement for the Ba_5Sb_4 compound

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Abstract

Ba_5Sb_4 crystallizes in the orthorhombic space group *Cmca* and is isostructural with Eu_5As_4 reported in the *Ccmb* alternate setting. β-Ba_5Sb_4 is a new arrangement which is more symmetrical than α-Ba_5Sb_4 [Brechtel, Cordier & Schäfer (1981). *Z. Naturforsch. Teil B*, **36**, 1341–1342; *Pnma*, isostructural with Sm_5Ge_4]. The structure contains two anionic moieties, *i.e.* Sb_2^{4-} dumbbells [Sb—Sb 2.886 (3) Å] and Sb^{3-}. The Sb1 atom (Sb^{3-}) lies inside a monocapped distorted trigonal prism (6 × Ba1 and 1 × Ba2). The Sb2 atom, which forms the Sb_2^{4-} dumbbell, sits inside a tricapped trigonal prism (6 × Ba1, 2 × Ba2 and 1 × Sb2).

Comment

The structure of Ba_5Sb_4 has been determined in the centrosymmetric space group *Cmca* (No. 64) and is isostructural with Eu_5As_4 (Wang *et al.*, 1978). We designate this the β form with respect to the form reported by Brechtel *et al.* (1981) in the *Pnma* space group, which results from a distortion of the *Cmca* structure. The two space groups *Pnma* and *Cmca* frequently occur in the R_5P_4 family (R = rare earth; P = Si, Ge, Rh); Eu_5As_4 crystallizes in the *Cmca* space group, while Gd_5Si_4 (Iglesias & Steinfink, 1972), Sm_5Ge_4 (Smith *et al.*, 1967) and Pu_5Rh_4 (Cromer, 1977) crystallize in *Pnma*. It is obvious that the two structural forms are closely related. Atomic positions (X,Y,Z) in the *Cmca* cell can be obtained from those (x,y,z) in the *Pnma* structure by the transformation: $X = y - \frac{1}{4}$, $Y = -x - \frac{1}{4}$, $Z = z + \frac{1}{2}$.

The orthorhombic *Pnma* structure of α-Ba_5Sb_4 [a = 9.012 (3), b = 17.823 (6) and c = 9.041 (3) Å] contains atoms Ba(1), Ba(2) and Sb(1) at 8*d* special positions, and Ba(3), Sb(2) and Sb(3) at 4*c* special positions.

Owing to the presence of supplementary twofold axes in the *Cmca* space group, the transformation of atomic positions from *Pnma* into *Cmca* evidently results in some extremely short interatomic distances (in the order of 0.4 Å). The number of independent atoms is then reduced by one third (four in *Cmca* instead of six in *Pnma*). Merging the two 8*d* positions [Ba(1) and Ba(2)], and the two 4*c* positions [Sb(2) and Sb(3)] of the *Pnma* structure gives 16*g* and 8*f* atomic positions, respectively, for Ba1 and Sb2 in the *Cmca* structure; Ba(3) (4*c*) and Sb(1) (8*d*) are transformed into Ba2 (4*a*) and Sb1 (8*d*). Then, in the *Cmca* structure, there are two independent Sb (Sb1 and Sb2) and two independent Ba (Ba1 and Ba2) atoms.

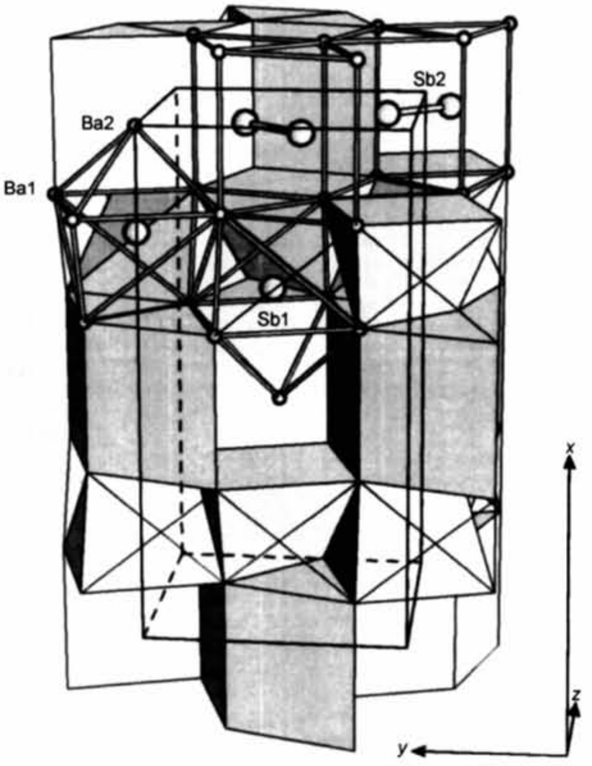

Fig. 1. Representation of the unit cell of β-Ba_5Sb_4. The Sb^{3-} and Sb_2^{4-} anionic moieties are shown inside their barium coordination prisms. The Ba atoms lie at the corners of the polyhedra.

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