

Refinement

Refinement on F^2

$$R[F^2 > 2\sigma(F^2)] = 0.049$$

$$wR(F^2) = 0.130$$

$$S = 0.952$$

1533 reflections

44 parameters

$$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 5.547 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -3.847 \text{ e } \text{\AA}^{-3}$$

Extinction correction:

SHELXL97 (Sheldrick,

1997a)

Extinction coefficient:

$$2.1(7) \times 10^{-4}$$

Scattering factors from

International Tables for
Crystallography (Vol. C)Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. University of Cambridge, England.Sheldrick, G. M. (1997a). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.Sheldrick, G. M. (1997b). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.Sportouch, S., Belin, C. & Tillard-Charbonnel, M. (1994). *Acta Cryst.* **C50**, 1861–1862.Tillard, M., Monconduit, L., Traber, B. & Belin, C. (1999). *Acta Cryst.* **C55**, 833–835.Wang, Y., Calvert, L. D., Smart, M. L. & Taylor, J. B. (1980). *Acta Cryst.* **B36**, 131–133.Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Ba1	0.22205 (19)	3/4	0.37368 (9)	0.0111 (3)
Ba2	0.25836 (13)	0.95429 (8)	0.63202 (6)	0.0113 (2)
Ta	0.66206 (12)	3/4	0.54470 (6)	0.0067 (2)
As1	0.2338 (2)	0.44439 (14)	0.38341 (11)	0.0122 (3)
As2	0.2240 (3)	3/4	0.13505 (15)	0.0104 (4)
O	0.386 (2)	3/4	0.5541 (10)	0.008 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Ba1—O	2.669 (14)	Ba2—As1 ^{iv}	3.316 (2)
Ba1—As2	3.216 (3)	Ba2—As1 ⁱⁱⁱ	3.390 (2)
Ba1—As2 ⁱ	3.350 (3)	Ba2—As1 ^v	3.422 (2)
Ba1—As2 ⁱⁱ	3.376 (3)	Ba2—As1 ^{vi}	3.537 (2)
Ba1—As1 (×2)	3.3920 (17)	Ta—O	1.861 (14)
Ba2—O	2.640 (7)	Ta—As2 ⁱⁱ (×2)	2.458 (2)
Ba2—As2 ⁱⁱⁱ	3.2812 (11)	Ta—As1 ^v	2.4647 (16)
O—Ta—As2 ⁱⁱ	103.7 (4)	Ta—O—Ba2	110.6 (3)
O—Ta—As1 ^v	104.87 (19)	Ba2 ^{vi} —O—Ba2	118.2 (5)
As2 ⁱⁱ —Ta—As1 ^v	109.83 (5)	Ta—O—Ba1	110.5 (6)
As1 ^v —Ta—As1 ^{vi}	121.97 (8)	Ba2—O—Ba1	103.2 (3)

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

In the final difference Fourier map, the highest electron-density peak was found 0.8 \AA from the Ta atom and the deepest hole was found 0.9 \AA from the Ba1 atom.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: local program. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a). Molecular graphics: *ATOMS* (Dowty, 1993) and *ORTEPII* (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1254). Services for accessing these data are described at the back of the journal.

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Na₂Ca₃Ta₂O₉ with a simple stacking of oxygen triangular nets

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Abstract

The crystal structure of the title quaternary oxide, disodium tricalcium ditantalum nonaoxide, has a distorted simple hexagonal packing of the O atoms. The Na, Ca and Ta atoms are positioned in oxygen trigonal prisms. Two oxygen prisms containing Ta atoms constitute face-sharing prisms of [Ta₂O₉]⁸⁻.

Comment

The crystal structure of oxides has traditionally been described with closest packing of the oxide ions, such as hexagonal closest packing (*ab*), cubic closest packing (*abc*) and their combinations. The structure of the new compound Na₂Ca₃Ta₂O₉ is, however, based on a simple stacking of oxygen triangular nets with *aaa*. All other metal atoms occupy the trigonal prism sites in the sequence –Na–Ta–Ta–Na–(vacant)–Ca1–Ca2–Ca1–(vacant)– along the *c* axis (Table 1). As shown in Fig. 1, the triangles of O atoms twist a little and expand or shrink depending on the other atoms in the prisms. Trigonal prismatic coordinations along the *c* axis can be seen in detail in Fig. 2.

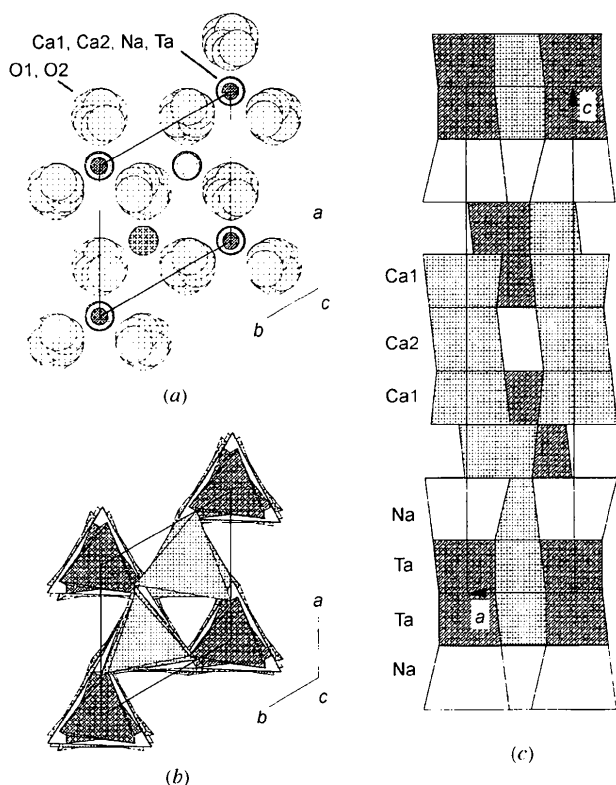


Fig. 1. The structure of $\text{Na}_2\text{Ca}_3\text{Ta}_2\text{O}_9$, showing (a) atoms as spheres projected along the c axis, (b) the oxygen polyhedra along the c axis, and (c) the oxygen polyhedra along the b axis.

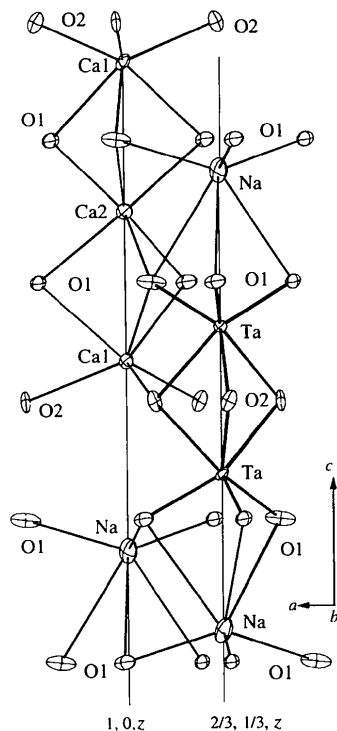


Fig. 2. The structure of trigonal prismatic coordinations along the c axis in $\text{Na}_2\text{Ca}_3\text{Ta}_2\text{O}_9$, showing 50% probability displacement ellipsoids.

Two oxygen trigonal prisms containing Ta atoms share one face and consist of $[\text{Ta}_2\text{O}_9]^{8-}$. The interatomic distances between Ta and O atoms are 2.133 (7) Å ($\times 3$) for shared O atoms (Ta—O2), and 1.907 (7) Å ($\times 3$) for unshared O atoms (Ta—O1). These values are consistent with those observed for Ta—O distances in two face-sharing $[\text{Ta}_2\text{O}_9]^{8-}$ octahedra in $\text{Mg}_4\text{Ta}_2\text{O}_9$ and $\text{Mg}_2\text{NiTa}_2\text{O}_9$ (Halle & Müller-Buschbaum, 1988), and $\text{Ba}_3\text{SrTa}_2\text{O}_9$ (Zandbergen & Ijdo, 1983), where the interatomic distances between Ta atoms in the octahedra and the shared O atoms are in the range 2.12–2.13 Å, and between Ta atoms and the unshared O atoms are in the range 1.89–1.91 Å. The Ta—Ta distance in the two face-sharing trigonal prisms is 3.0490 (9) Å, which is slightly longer than the Ta—Ta distances (2.95–3.02 Å) reported in the two face-sharing octahedra.

The Na atom is situated in a highly distorted O1 trigonal prism, with Na—O1 distances of 2.343 (8) ($\times 3$) and 2.848 (8) Å ($\times 3$), being distant from the Ta and Na atoms in the neighbouring prisms and close to the vacant prism. The presence of Na atoms occupying the oxygen trigonal prism sites has also been reported for $\text{Ba}_3\text{NaTaO}_6$ (Na—O 2.45 Å; Wehrum & Hoppe, 1992), and $\text{NaCa}_3\text{IrO}_6$ and $\text{NaCa}_3\text{RuO}_6$ (Na—O 2.33–2.34 Å; Claridge *et al.*, 1997).

The Ca1 atom is located in an oxygen trigonal prism and near the vacant prism. The Ca1—O2 and Ca1—O1 distances are 2.287 (6) and 2.443 (7) Å, respectively. The Ca2 atom is coordinated by six O1 atoms at the same distance of 2.350 (6) Å, which agrees well with the Ca—O distance [2.35 Å ($\times 6$)] of the trigonal prism in $\text{Mg}_3\text{Ca}(\text{CO}_3)_4$ (Graf & Bradley, 1962).

Experimental

Na_2CO_3 (extra pure grade, Wako Pure Chemical Industries Ltd), CaCO_3 (99.99% purity, Rare Metallic Co. Ltd) and Ta_2O_5 (99.99% purity, Rare Metallic Co. Ltd) were weighed to give a 3:1:1 Na—Ca—Ta atomic ratio. The powders were mixed in an agate mortar and then pressed into a pellet. The pellet was heated at 1273 K for 1 h in air on a Pt plate. After heating, the sample was cooled to 1073 K at a rate of 3 K h^{-1} . Below this temperature, the sample was cooled in the furnace by shutting off the electric power. The sample obtained consisted of two phases, $\text{Na}_2\text{Ca}_3\text{Ta}_2\text{O}_9$ and Na_3TaO_4 . The extra amount of Na reacted with the Pt plate and formed Na_2PtO_3 . Colourless transparent platelet single crystals of $\text{Na}_2\text{Ca}_3\text{Ta}_2\text{O}_9$ were picked up from the two-phase mixture. The Na—Ca—Ta atomic ratio obtained by semi-quantitative energy dispersive X-ray analysis (EDAX Kevex) on a scanning electron microscope (Hitachi X-60) was 2.0:3.1:1.8, which is close to the ideal ratio of 2:3:2. EDAX analysis did not detect any other impurity elements.

Crystal data

$\text{Na}_2\text{Ca}_3\text{Ta}_2\text{O}_9$
 $M_r = 672.12$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Hexagonal

R32
 $a = 5.6969$ (6) Å
 $c = 23.523$ (3) Å
 $V = 661.15$ (13) Å³
 $Z = 3$
 $D_x = 5.064$ Mg m⁻³
 D_m not measured

Cell parameters from 1199

reflections
 $\theta = 1.00$ – 27.49°
 $\mu = 26.678$ mm⁻¹
 $T = 293$ (2) K
 Platelet
 $0.13 \times 0.10 \times 0.03$ mm
 Colourless

Data collection

Bruker SMART1000 CCD
 area-detector diffractometer
 ω scans
 Absorption correction:
 analytical face-indexed
 $T_{\min} = 0.071$, $T_{\max} = 0.512$

1452 measured reflections
 348 independent reflections
 $R_{\text{int}} = 0.069$
 $\theta_{\text{max}} = 27.49^\circ$
 $h = -7 \rightarrow 7$
 $k = -7 \rightarrow 4$
 $l = -30 \rightarrow 27$
 Intensity decay: 0.14%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.057$
 $S = 1.187$
 348 reflections
 28 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0095P)^2 + 20.9824P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.343$ e Å⁻³
 $\Delta\rho_{\text{min}} = -2.097$ e Å⁻³

Extinction correction:
SHELXL97 (Sheldrick, 1997)
 Extinction coefficient:
 0.0025 (3)
 Scattering factors from
International Tables for Crystallography (Vol. C)
 Racemic twinning:
SHELXL97
 Fractional contribution:
 0.51 (6)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j$$

	x	y	z	U_{eq}
O1	0.0534 (15)	0.3162 (15)	0.1040 (2)	0.0149 (14)
O2	0.2617 (18)	0	0	0.0135 (19)
Ta	0	0	0.064809 (17)	0.0067 (2)
Na	0	0	0.2020 (2)	0.0170 (11)
Ca1	0	0	0.36845 (9)	0.0086 (5)
Ca2	0	0	1/2	0.0104 (6)

Table 2. Selected geometric parameters (Å, °)

Ta—O1 ⁱ (×3)	1.907 (7)	Na—O1 ^v (×3)	2.848 (8)
Ta—O2 ⁱ (×3)	2.133 (7)	Ca1—O2 ^{vi} (×3)	2.287 (6)
Ta—Ta ⁱⁱ	3.0490 (9)	Ca1—O1 ^{vii} (×3)	2.443 (7)
Ta—Na	3.227 (6)	Ca1—Ca2	3.094 (2)
Ta—Ca1 ⁱⁱⁱ	3.3624 (6)	Ca2—O1 ^{viii} (×6)	2.350 (6)
Na—O1 ^{iv} (×3)	2.343 (8)		
O1—Ta—O1 ⁱ	98.6 (2)	O2 ^{vi} —Ca1—O2 ^{vi}	107.72 (9)
O1—Ta—O2 ⁱ	137.0 (2)	O2 ^{vi} —Ca1—O1 ^{xii}	62.71 (16)
O1 ⁱ —Ta—O2 ⁱ	124.3 (2)	O2 ^{xii} —Ca1—O1 ^{xii}	127.1 (3)
O1 ^v —Ta—O2 ⁱ	75.0 (3)	O2 ^{xiii} —Ca1—O1 ^{xiii}	125.0 (2)
O2 ⁱ —Ta—O2 ^v	74.5 (3)	O1 ^{xiii} —Ca1—O1 ^{vii}	80.8 (2)
O1 ^{iv} —Na—O1 ^{ix}	112.75 (16)	O1 ^{viii} —Ca2—O1 ^{xiii}	118.6 (4)
O1 ^{iv} —Na—O1 ^v	126.45 (17)	O1 ^{viii} —Ca2—O1 ^{vii}	150.6 (4)
O1 ^{ix} —Na—O1 ^v	70.7 (2)	O1 ^{xiii} —Ca2—O1 ^{vii}	84.8 (2)
O1 ^x —Na—O1 ^v	113.8 (3)	O1 ^{vii} —Ca2—O1 ^{xiv}	80.3 (3)
O1 ^v —Na—O1 ⁱ	61.1 (2)		

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

Since the Flack parameter (Flack, 1983) was refined to about 0.4 for both configurations of the absolute structure, we used the racemic twin instruction at the final refinement of the structure parameters with *SHELXL97* (Sheldrick, 1997). The refined fractional contribution parameter was 0.51 (6).

Data collection: *SMART* (Bruker, 1997a). Cell refinement: *SMART*. Data reduction: *XPREP* (Bruker, 1997b). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL97*. Molecular graphics: *ATOMS* (Dowty, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1255). Services for accessing these data are described at the back of the journal.

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An extreme case of ZnO₆ octahedral distortion in trizinc tris(selenite) hydrate, Zn₃(SeO₃)₃·H₂O

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Abstract

Trizinc tris[trioxoselenate(IV)] hydrate, Zn₃(SeO₃)₃·H₂O, is built up from ZnO₆ octahedra [$d_{\text{av}}(\text{Zn—O}) =$