591 reflections
50 parameters
H atoms not located
$w = 1/[\sigma^2(F_o^2) + (0.1209P)^2 + 188.5222P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* $(\mathring{A}^2)$

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

	x	y	z	U_{eq}
V1†	1/4	1/4	1/4	0.006 (3)
Mo	0.13794 (3)	0.24552 (4)	0.13794 (3)	0.0313 (6)
O1	0.0989 (3)	0.1830 (2)	0.1830 (2)	0.0278 (16)
O2	0.2100 (2)	0.2100 (2)	0.2100 (2)	0.012 (2)
O3	0.1169 (3)	0.3009 (2)	0.1991 (2)	0.0244 (15)
O4	0.0860 (2)	0.2591 (3)	0.0860 (2)	0.0372 (18)
Rb1‡	0	0.2061 (3)	0	0.0678 (19)
Rb2§	0.1498 (2)	0.8502 (2)	1/2	0.065 (2)
Rb3¶	0	0	0	0.070
Rb4††	0	1/2	0	0.070
OW1‡‡	0.2427 (5)	0.2573 (5)	0	0.016 (4)
OW2	0	0.1271 (5)	0.1271 (5)	0.068 (4)
OW3	0	0.3366 (18)	0	0.138 (12)
OW4§§	0.0735 (13)	0.4265 (13)	0.0735 (13)	0.15 (3)

† Site occupancy = 0.62 (3). ‡ Site occupancy = 0.698 (12). § Site occupancy = 0.363 (9). ¶ Site occupancy = 0.11 (2). †† Site occupancy = 0.07 (2). ‡‡ Site occupancy = 0.50. §§ Site occupancy = 0.74 (8).

All metal atoms and the O atoms in the Keggin-type cluster were refined with anisotropic displacement parameters using a 'rigid-bond' restraint to U_{ij} of two bonded atoms (Rollett, 1970), implemented as the *DELU* instruction in *SHELXL97* (Sheldrick, 1997). All water O atoms were refined isotropically. OW1 was originally located at the 24d position but was split to a half-occupied 48h position. OW2 and OW3 are fully occupied, while the occupancy of OW4 decreased significantly during the refinement. Rb3 and Rb4 are located in large voids at 4a and 4b. The isotropic displacement parameters U_{iso} of Rb3 and Rb4 were fixed to 0.07 and the occupancy was refined for both atoms. The largest residual densities are located at 1.9 Å from Rb4 and 0.5 Å from OW1.

Data collection: *EXPOSE* (Stoe, 1997). Cell refinement: *PIRUM* (Version 930101; Werner, 1969). Data reduction: *INTEGRATE* (Stoe, 1997). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97*. Molecular graphics: *DIAMOND* (Bergerhoff, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1070). Services for accessing these data are described at the back of the journal.

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Ba3TaAs3O displaying the distorted tetrahedral TaAs3O6− anion

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Abstract

The orthorhombic cell of tribarium tantalum arsenate, Ba_3TaAs_3O, contains pseudo-tetrahedral $TaAs_3O^{6-}$ anions surrounded by Ba^{2+} cations. This forms a three-dimensional network of interconnected trigonal prisms. The compound is isostructural with Ba_3NbAs_3O and Eu_3TaAs_3O.

Comment

The quaternary phase Ba_3TaAs_3O (orthorhombic *Pnma*) is isostructural with the compounds Ba_3NbAs_3O (Monconduit *et al.*, 1999) and Eu_3TaAs_3O (Wang *et al.*, 1980). The unit cell contains four $TaAs_3O^{6-}$ anions stacked above each other along **b**, with their Ta—O bonds parallel to the *a* axis. The As atoms, with surrounding Ba atoms, form the base of a pseudo-trigonal prism centered by the Ta—O bond. The anionic $TaAs_3O^{6-}$ unit, with 32 valence electrons, is isoelectronic with more or less distorted tetrahedral ML_4^{n-} an-
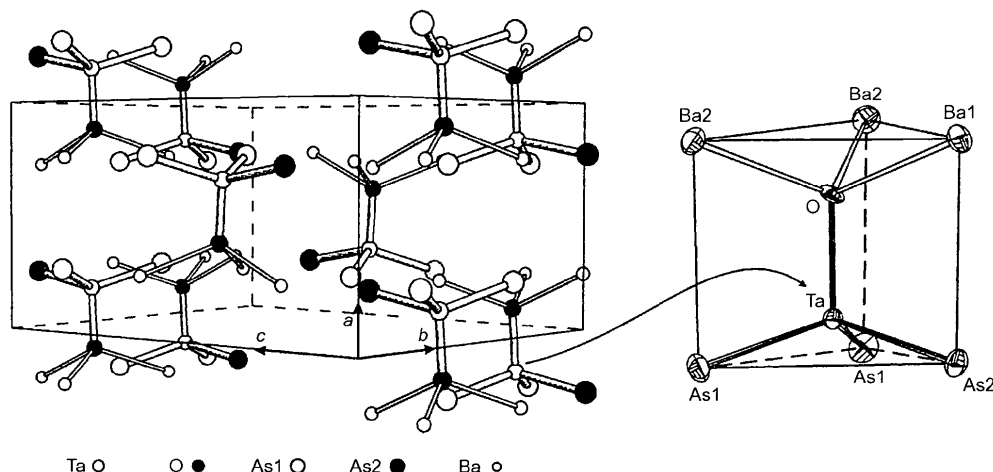
Fig. 1. Representation of the orthorhombic unit cell of Ba_3TaAs_3O. The $TaAs_3O^{6-}$ anion is shown inside the pseudo-trigonal prism formed by As and Ba atoms around the Ta—O bond.

ions such as $InTe_4^{5-}$ (Sportouch *et al.*, 1994), ClO_4^-, PO_4^{3-}, SO_4^{2-}, $S_2O_3^{2-}$, $Sb_2O_3^{4-}$ (Tillard *et al.*, 1999) and $NbAs_3O^{6-}$. In the present compound, distortion of the $TaAs_3O^{6-}$ anion from C_{3v} geometry is quantified by two As—Ta—As angles of 109.83 (5)° and one of 121.97 (8)°, and is comparable to that observed in Eu_3TaAs_3O [two As—Ta—As angles of 109.14 (4)° and one of 124.11 (7)°]. For comparison, in the $NbAs_3O^{6-}$ anion (Ba_3NbAs_3O), two As—Nb—As angles are of 109.64 (4)° and the other is of 122.14 (6)°. The Ta—O bond length of 1.86 (1) Å in Ba_3TaAs_3O [1.87 (1) Å in Eu_3TaAs_3O] is shorter than the Pauling single-bond covalent radii of the elements (2.08 Å). Similar to Nb—O, Raman spectroscopy indicates that the Ta—O bond has no double-bond character. In the Raman spectrum recorded at room temperature, the ν_s(Ta—O) frequency at $645\,cm^{-1}$ is found at nearly the same position as the ν_s(Nb—O) frequency and the very sharp principal line observed at $256\,cm^{-1}$ is assigned to symmetric ν_s(Ta—As) stretching. The Ta—As bonds [2.458 (2) and 2.464 (2) Å (×2)] compare well with corresponding Ta—As bonds in Eu_3TaAs_3O [2.439 (2) and 2.458 (1) Å (×2)] and Nb—As bonds in Ba_3NbAs_3O [2.459 (2) and 2.464 (1) Å (×2)].

Experimental

With the aim of obtaining the quaternary phase Ba_3TaAs_3O, BaO, As, Ta and Ba (ratio 1:3:1:2) were inserted in a tantalum reactor weld-sealed under argon. The tantalum reactor was protected in an inox container also weld-sealed under argon. The mixture was heated to 1323 K ($50\,K\,h^{-1}$) for 10 h, maintained at 1173 K for 100 h and finally cooled at a rate of $150\,K\,h^{-1}$. The product of the reaction was quite homogeneous, had a metallic luster and was very air sensitive. Elemental analyses (SEM) of several small crushed pieces

confirmed the presence of Ba, Ta and As in the atomic ratio 3:1:3. Crystalline pieces were selected under a microscope inside a glove-box filled with purified argon. Crystallographic parameters were first determined by oscillation and Weissenberg techniques. The best diffracting crystal was used for accurate determination of the cell parameters. A single crystal (<1 mm) was sealed in a Lindemann glass capillary under dry argon and analyzed at room temperature using confocal laser Raman microspectrometry (Dhamelincourt *et al.*, 1993) with a Labram–Dilor spectrometer. The BX40 microscope objectives, which are high numerical aperture (NA) optics, are able to focus the laser beam (He/Ne: 632.817 nm, 20 mW) into a very small volume and to collect, under a wide angle, the light scattered by this volume.

Crystal data

Ba_3TaAs_3O	Mo $K\alpha$ radiation
$M_r = 833.73$	$\lambda = 0.71069$ Å
Orthorhombic	Cell parameters from 25
$Pnma$	reflections
$a = 6.722\,(2)$ Å	$\theta = 11.06{-}18.45°$
$b = 11.088\,(2)$ Å	$\mu = 32.197\,mm^{-1}$
$c = 13.475\,(4)$ Å	$T = 293\,(2)$ K
$V = 1004.3\,(5)$ Å^3	Parallelepiped
$Z = 4$	$0.20 \times 0.08 \times 0.07$ mm
$D_x = 5.514$ Mg m^{-3}	Silver metallic luster
D_m not measured	

Data collection

Enraf–Nonius CAD-4	$\theta_{max} = 29.96°$
diffractometer	$h = 0 \rightarrow 9$
$\omega{-}\theta$ scans	$k = 0 \rightarrow 15$
Absorption correction:	$l = 0 \rightarrow 18$
numerical (*SHELX*76;	3 standard reflections
Sheldrick, 1976)	every 100 reflections
$T_{min} = 0.279$, $T_{max} = 0.469$	intensity decay: <3%
1533 measured reflections	
1533 independent reflections	
957 reflections with	
$I > 2\sigma(I)$	

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

$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 5.547$ e Å^{-3}

$\Delta\rho_{min} = -3.847$ e Å^{-3}

Extinction correction:
SHELXL97 (Sheldrick, 1997a)

Extinction coefficient:
2.1 (7) × 10^{-4}

Scattering factors from
International Tables for Crystallography (Vol. C)

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

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

	x	y	z	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 (Å, °)*

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^{Vii}	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 Å from the Ta atom and the deepest hole was found 0.9 Å 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 *ORTEP*II (Johnson, 1976).

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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.