The Cu $K\alpha$ radiation was selected by means of a graphite monochromator. A system of diverging, anti-scattering and receiving slits of 0.5, 0.5° and 0.15 mm, respectively, was used; one Soller slit was positioned on the incident beam before the divergent slit, and one was placed on the diffracted beam before the monochromator. The pattern was collected with 35 kV tube voltage and 180 mA tube current in step-scan mode (step width 0.03°, counting time 1 s per step). The electron-diffraction patterns were studied with a JEOL JEM-2000EX microscope (Electron Microscope Laboratory, Tohoku University) operating at 200 kV. Fine powder specimens for electron microscopic observations were prepared by crushing the sintered products in an agate mortar. They were then mounted on colloidal film meshes.

In the *ab initio* structure determination, the following programs were used: *ITO* (Visser, 1969) for the automatic indexing procedure, *EXTRA* (Altomare, Burla, Cascarano *et al.*, 1994) for the full-profile peak decomposition and for extraction of the squared structure-factor moduli ($|F|^2$), the atomic positions were obtained by the direct-methods program *SIRPOW.92* (Altomare, Burla, Camalli *et al.*, 1994), and the profile refinement, by the Rietveld method, was performed using *RIETAN94* (Kim & Izumi, 1994). Selected bond lengths and angles were calculated using *ORFFEPPC* (Busing *et al.*, 1964), and the crystal structure information was converted into a standard format by *STRUCTURE TIDY* (Parthé & Gelato, 1984; Gelato & Parthé, 1987).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1030). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 17–19

$BaNb_{4-x}Ti_xO_6$ ($x = 0.53$)

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(*Received 4 March 1998; accepted 17 August 1998*)

Abstract

The title compound, barium niobium titanium oxide, is isostructural with $BaNb_4O_6$, *i.e.* it contains alternating NbO and perovskite-type single slabs. The NbO slabs can alternatively be described as layers of Nb_6O_{12} clusters, condensed *via* corner sharing among the central Nb_6 octahedra.

Comment

A number of compounds with Nb_6O_{12} clusters have been synthesized in the K–, Sr–, Ba– and Eu–Nb–O systems (Köhler *et al.*, 1992). These clusters can be discrete, or condensed *via* corner sharing among the central Nb_6 octahedra. Dimers have been found in $K_4Al_2Nb_{11}O_{21}$ (Köhler *et al.*, 1989), infinite chains in $BaNb_5O_8$ (Zubkov, Perelyaev, Berger, Kontsevaya *et al.*, 1990), layers in $BaNb_4O_6$ (Zubkov, Perelyaev, Berger, Voronin *et al.*, 1990; Svensson *et al.*, 1991) and three-dimensional condensation in NbO (Brauer, 1941; Schäfer & Schnering, 1964). The compounds with chains or layers of condensed Nb_6O_{12} clusters can be described as intergrowth structures between NbO and $BaNbO_3$. Those with alternating layers of NbO and perovskite form a homologous series of the form $Ba_nNb_{3m+n}O_{3m+3n}$ (n = width of the perovskite-type slab and m = width of the NbO slab); these

Acta Crystallographica Section C
ISSN 0108-2701 © 1999

compounds all exhibit metal-like conductivity (Köhler *et al.*, 1992). Very often it is possible to change the electrical properties of a compound by heterovalent doping. Recently, we reported a study of the influence of replacing the d^5 metal Nb with the d^4 metal Ti in $Ba_2Nb_{5-x}Ti_xO_9$ (Svensson *et al.*, 1997). We report here a single-crystal study of $BaNb_{4-x}Ti_xO_6$, with x = 0.53 (2).

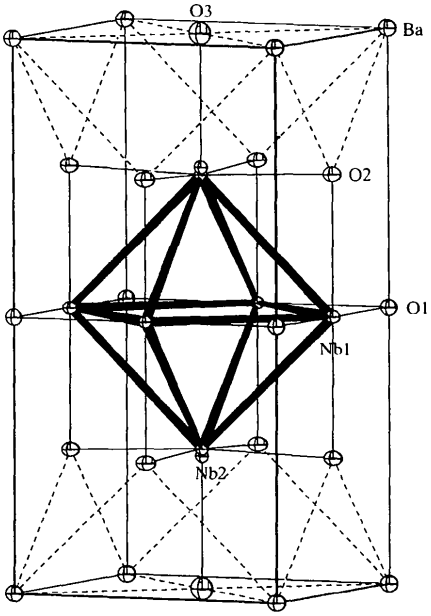

Fig. 1. *DIAMOND* (Bergerhoff, 1996) plot showing the unit cell of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

The structure of $BaNb_{3.47}Ti_{0.53}O_6$ can be described as an intergrowth between NbO-type and perovskite-type slabs, both one unit wide. The NbO slab can alternatively be described as a two-dimensional net of Nb_6O_{12} clusters, condensed *via* corner sharing among the Nb_6 octahedra. As in the NbO structure, the Nb1/Ti1 atoms have a planar fourfold coordination of O atoms and an eightfold coordination of Nb1,2/Ti1,2 atoms, forming a tetragonal prism. The Nb2/Ti2 atoms completing the $(Nb/Ti)_6$ octahedron in the NbO slab are 4+1-coordinated by O atoms, forming a square pyramid, and four-coordinated by Nb/Ti atoms, as in a discrete Nb_6O_{12} cluster. The Nb2/Ti2 atoms are shared with the perovskite slab, and within the perovskite slab, atoms O2 and O3 form a slightly distorted cubo-octahedron around the Ba atoms.

All interatomic distances are slightly shorter in the title compound than in $BaNb_4O_6$, except two that involve Ti2. The interatomic Nb1—*M* distance is longer when *M* = Ti2 [Nb1—Ti2 2.98 (4) Å] than when *M* = Nb2 [Nb1—Nb2 2.907 (4) Å]. This implies that the Ti2—O3 bond [1.97 (5) Å] is shorter than the Nb2—O3 bond [2.077 (6) Å]. Ti—Nb bonding is thus weaker than Nb—Nb bonding, whereas the Ti—O bonds are stronger than the Nb—O bonds. This is in agreement with the smaller radius of the Ti^{4+} ion (0.605 Å; Shannon, 1976) compared with that of the Nb^{4+} ion (0.64 Å; Shannon 1976).

The preference of the Ti atoms for the Nb2 position can be understood from a comparison of the structures of NbO (Brauer, 1941) and ordered TiO (Watanabe *et al.*, 1970). Both have rock-salt-type structures, with 25 and 12% anion and cation vacancies, respectively. In NbO, every atom is four-coordinated (square planar), while in TiO, only 20% are square planar and 80% are five-coordinated. A cluster description of TiO, like that of NbO, reveals the presence of Ti_6O_{12} clusters condensed along one dimension (Simon, 1981), not three. Band-structure calculations (Burdett & Hughbanks, 1984) have shown that the NbO structure is preferred for d^3 and TiO for d^2. In $BaNb_{3.47}Ti_{0.53}O_6$, Ti therefore prefers the Nb2 position, coordinated by five O atoms as in TiO, over the four-coordinated Nb1 position. An alternative approach to the preference of the Ti ions is that O is a hard base. Ti is a harder acid than Nb (Pearson, 1988) and should therefore prefer sites with higher O-coordination, such as the Nb2 position.

Experimental

Powders of Nb_2O_5, Nb, Ti (all *p.a.*, *ex* Merck) and $Ba_5Nb_4O_{15}$ [presynthesized from $BaCO_3$ (*p.a.*, *ex* Merck) and Nb_2O_5], were mixed according to the composition $BaNb_3TiO_6$. A pellet of the mixture in an Nb ampoule, sealed under argon, was heated at 1873 K for 6 h, after which the furnace was turned off. Electron-dispersive microanalysis (LINK AN 10000) in a scanning electron microscope (JEOL JSM-820) showed the metal composition to be Ba:Nb:Ti = 20.9 (5):69.1 (1):10.0 (2)%, corresponding to x = 0.50. Transmission electron microscopy studies (JEOL JEM 2000 FX) showed no indications of structural disorder. This indicates that the Ti atoms are statistically distributed over the Nb positions in the structure.

Crystal data

$BaNb_{3.47}O_6Ti_{0.53}$
M_r = 581.12
Tetragonal
$P4/mmm$
a = 4.1662 (3) Å
c = 8.2085 (7) Å
V = 142.48 (2) Å^3
Z = 1
D_x = 6.773 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 20 reflections
θ = 7.0–10.2°
μ = 14.251 mm^{-1}
T = 293 (2) K
Prism
0.05 × 0.04 × 0.03 mm
Black

Data collection

Stoe AED-4 diffractometer
$\omega/2\theta$ scans

$R_{\rm int}$ = 0.049
$\theta_{\rm max}$ = 30°

Absorption correction:
empirical *via* ψ scans
(North *et al.*, 1968)
$T_{\min} = 0.520$, $T_{\max} = 0.644$
837 measured reflections
163 independent reflections
144 reflections with
$I > 2\sigma(I)$

$h = -5 \rightarrow 5$
$k = -5 \rightarrow 5$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 90 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.027$
$S = 1.185$
163 reflections
21 parameters
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.848$ e Å^{-3}
$\Delta\rho_{\min} = -0.785$ e Å^{-3}
Extinction correction:
*SHELXL*93
Extinction coefficient:
0.0154 (10)
Scattering factors from
International Tables for Crystallography (Vol. C)

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

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

	Occupancy	x	y	z	$U_{\rm eq}$
Ba	1	0	0	0	0.0066 (2)
Nb1	0.957 (8)	0	1/2	1/2	0.0041 (2)
Ti1	0.043 (8)	0	1/2	1/2	0.0041 (2)
Nb2	0.776 (8)	1/2	1/2	0.2530 (8)	0.0037 (5)
Ti2	0.224 (8)	1/2	1/2	0.240 (6)	0.0037 (5)
O1	1	0	0	1/2	0.0058 (13)
O2	1	1/2	0	0.2437 (5)	0.0068 (6)
O3	1	1/2	1/2	0	0.011 (2)

Table 2. *Selected bond distances (Å)*

Ba—O2	2.888 (3)	Ti1—Nb2	2.907 (4)
Ba—O3	2.9459 (2)	Ti1—Ti1$^{\rm ii}$	2.9459 (2)
Nb1—O1	2.0831 (1)	Nb2—O3	2.077 (6)
Nb1—O2$^{\rm i}$	2.104 (4)	Nb2—O2	2.0845 (3)
Nb1—Nb2	2.907 (4)	Ti2—O3	1.97 (5)
Nb1—Nb1$^{\rm ii}$	2.9459 (2)	Ti2—O2	2.0834 (8)
Nb1—Ti1$^{\rm ii}$	2.9459 (2)	Ti2—Ti1$^{\rm iii}$	2.98 (4)
Ti1—O1	2.0831 (1)	Ti2—Nb1$^{\rm iii}$	2.98 (4)
Ti1—O2$^{\rm i}$	2.104 (4)		

Symmetry codes: (i) $y, 1 - x, z$; (ii) $-y, x, 1 - z$; (iii) $1 - y, 1 + x, 1 - z$.

Occupancy factors were constrained to add up to 1.0 for the Nb/Ti sites. Both Nb/Ti sites were refined with equal anisotropic displacement parameters (ADP) as an extra constraint, with ADP(Ti1) = ADP(Nb1) and ADP(Ti2) = ADP(Nb2). Nb2 and Ti2 were refined with individual z coordinates. The low ratio of reflections to parameters is not serious, since we wished to refine composition (occupancies at Nb/Ti sites) and ADP's for all atoms. It is possible that the extinction correction could have been omitted in order to reduce the number of parameters, but it seems to be significant.

Data collection: *DIF*4 (Stoe & Cie, 1991*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1991*b*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *DIAMOND* (Bergerhoff, 1996).

This work was supported by a grant from the Swedish Natural Science Research Council.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1024). Services for accessing these data are described at the back of the journal.

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