Table 2. *Selected geometric parameters (Å, °)*

Rb-atom coordination			
Rb(1)—O(1^{i}) × 2	3.000 (4)	Rb(2)—O(1^{iv})	3.070 (5)
Rb(1)—O(2^{i}) × 2	3.222 (5)	Rb(2)—O(1^{v})	3.140 (5)
Rb(1)—O(2^{ii}) × 2	3.241 (4)	Rb(2)—O(1^{vi})	2.874 (5)
Rb(1)—O(3^{ii}) × 2	2.964 (3)	Rb(2)—O(2^{vii})	3.060 (4)
Rb(1)—O(4^{iii}) × 2	2.815 (4)	Rb(2)—O(3)	3.040 (5)
Average	3.048	Rb(2)—O(3^{iv})	3.125 (5)
		Rb(2)—O(3^{viii})	2.909 (4)
		Rb(2)—O(4)	3.179 (4)
		Rb(2)—O(4^{v})	3.080 (5)
		Rb(2)—O(4^{ix})	3.390 (5)
		Average	3.087
SeO_4 ion			
Se—O(1)	1.618 (4)	O(1)···O(2)	2.629 (5)
Se—O(2)	1.680 (4)	O(1)···O(3)	2.685 (5)
Se—O(3)	1.622 (4)	O(1)···O(4)	2.698 (5)
Se—O(4)	1.619 (4)	O(2)···O(3)	2.620 (5)
Average	1.635	O(2)···O(4)	2.669 (5)
		O(3)···O(4)	2.698 (5)
		Average	2.667
O(1)—Se—O(2)	105.7 (2)	O(2)—Se—O(4)	108.0 (2)
O(1)—Se—O(3)	111.9 (2)	O(3)—Se—O(4)	112.7 (2)
O(1)—Se—O(4)	112.9 (2)	Average	109.4
O(2)—Se—O(3)	105.0 (2)		
Hydrogen bridge			
O(2)···O(2^{x})	2.473 (4)	O(2)···H^{xi}	1.39 (2)
O(2)—H^{iii}	1.08 (2)	H···H^{xii}	0.34 (3)
O(2^{iii})—H···O(2^{xi})	173 (2)	Se—O(2)···H^{xi}	103.4 (6)
Se—O(2)—H^{iii}	110.1 (8)		

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

All reflections could be indexed in space group *A*2/*a*. The principle design of HRPD is described elsewhere (Ibberson, David & Knight, 1992). The refinement was carried out using *TF*12*LS* (Mark 4.12), a program based on the Cambridge Crystallography Subroutine Library (David, Ibberson & Matthewman, 1992). Initial structural parameters were taken from Makarova, Verin & Shchagina (1986).

The authors are grateful to A. Bohn for the sample preparation.

Lists of intensity data and complete geometry, together with a plot of observed, calculated and difference profiles, have been deposited with the IUCr (Reference: JZ1057). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Baranov, A. I., Makarova, I. P., Muradyan, L. A., Tregubchenko, A. V., Shuvalov, L. A. & Simonov, V. I. (1987). *Sov. Phys. Crystallogr.* **32**, 400–407.

Belushkin, A. V., Ibberson, R. M. & Shuvalov, L. A. (1993). *Crystallogr. Rep.* **38**, 322–325.

Bohn, A., Melzer, R., Sonntag, R., Lechner, R. E., Schuck, G. & Langer, K. (1995). *Solid State Ionics*, **77**, 111–117.

David, W. I. F., Ibberson, R. M. & Matthewman, J. C. (1992). Report RAL-92-032. Rutherford Appleton Laboratory, Chilton, England.

Gesi, K. (1980). *J. Phys. Soc. Jpn*, **48**, 886–889.

Ibberson, R. M., David, W. I. F. & Knight, K. S. (1992). Report RAL-92-31. Rutherford Appleton Laboratory, Chilton, England.

Ichikawa, M., Gustafsson, T. & Olovsson, I. (1992). *Acta Cryst.* C**48**, 603–607.

Makarova, I. P., Verin, I. A. & Shchagina, N. M. (1986). *Sov. Phys. Crystallogr.* **31**, 105–106.

Noda, Y., Kasatani, K., Watanabe, Y. & Terauchi, H. (1992). *J. Phys. Soc. Jpn*, **61**, 905–915.

Noda, Y., Uchiyama, S., Kafuku, K., Kasatani, H. & Terauchi, H. (1990). *J. Phys. Soc. Jpn*, **59**, 2804–2810.

Thomas, J. O. (1992). *Proton Conductors*, edited by P. Colomban, pp. 79–89. Cambridge University Press.

Acta Cryst. (1996). C**52**, 1063–1065

$CsLaNb_2O_7$

N. Kumada,[a] N. Kinomura[a] and A. W. Sleight[b]

[a]*Faculty of Engineering, Yamanashi University, Miyamae-cho 7, Kofu 400, Japan, and* [b]*Department of Chemistry, Oregon State University, Corvallis, OR 97331-4003, USA*

(*Received 14 July 1995; accepted 21 November 1995*)

Abstract

The title compound, caesium lanthanum diniobium heptaoxide, belongs to the $ARNb_2O_7$ (A = K, Rb, Cs; R = La, Nd) family of compounds and crystallizes as a layered structure in which the Cs^+ ions are located in the interlayer gap formed by double perovskite $LaNb_2O_7$ layers. The single-crystal X-ray refinement of the structure of $CsLaNb_2O_7$ reported here is the first for a member of this family.

Comment

The alkali metal–rare earth niobium oxides $ARNb_2O_7$ (A = Na, K, Rb, Cs; R = La, Nd) have layer structures formed from double perovskite layers of composition RNb_2O_7 (Dion, Ganne & Tournoux, 1986; Gopalakrishnan, Bhat & Raveau, 1987). This family of compounds is divided into two groups by a difference in the conformation of adjacent perovskite layers; for A = Na and K adjacent layers are staggered, while for A = Rb and Cs they are eclipsed. The lattice parameters for $CsLaNb_2O_7$ [a = 3.908 (1), c = 11.160 (4) Å] agree well with the values determined from X-ray powder diffraction data [a = 3.905 (2), c = 11.185 (6) Å; Gopalakrishnan *et al.*, 1987].

Recently, the crystal structures of $KLaNb_2O_7$ (Sato, Abo, Jin & Ohta, 1992) and $RbLaNb_2O_7$ (Armstrong & Anderson, 1994) were refined by the Rietveld method, and were found to have a supercell. The present study shows that $CsLaNb_2O_7$ has no supercell. The lattice parameters of $KLaNb_2O_7$ [a = 3.9060 (1), b = 21.6030 (7), c = 3.8879 (1) Å] are related to those of

$CsLaNb_2O_7$ by $a_K \simeq a_{Cs}$, $b_K \simeq 2c_{Cs}$ and $c_K \simeq a_{Cs}$. The lattice parameters of $RbLaNb_2O_7$ [a = 5.4941 (4), b = 21.9901 (6) and c = 5.4925 (4) Å] are related to those of $CsLaNb_2O_7$ by $a_{Rb} \simeq \sqrt{2}(a_{Cs} + b_{Cs})/2$, $b_{Rb} \simeq 2c_{Cs}$ and $c_{Rb} \simeq \sqrt{2}(a_{Cs} + b_{Cs})/2$.

The Nb atom in the NbO_6 octahedron is displaced towards the interlayer gap, as observed in $KLaNb_2O_7$ and $RbLaNb_2O_7$, and the short Nb—O(2) distance [1.736 (7) Å] is intermediate between the Nb—O distances of 1.695 (19) Å in $KLaNb_2O_7$ and 1.774 (7) Å in $RbLaNb_2O_7$.

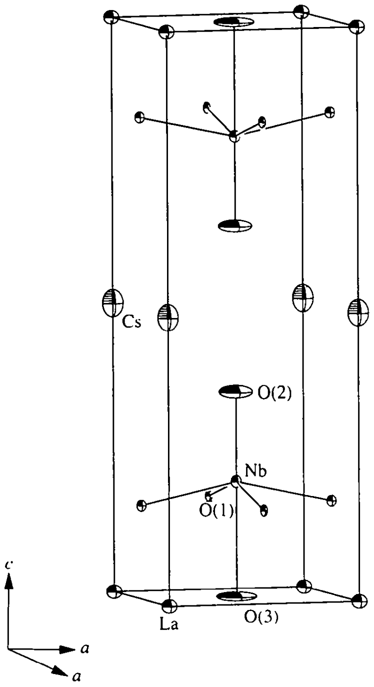

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the structure of $CsLaNb_2O_7$. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Transparent plate-like single crystals of $CsLaNb_2O_7$ were prepared by heating a mixture of Cs_2CO_3, La_2O_3 and Nb_2O_5 with a molar ratio of 4:1:2 at 1273 K.

Crystal data

$CsLaNb_2O_7$
M_r = 569.62
Tetragonal
$P4/mmm$
a = 3.908 (1) Å
c = 11.160 (4) Å
V = 170.4 (1) Å^3
Z = 1
D_x = 5.55 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 22 reflections
θ = 10.5–21.4°
μ = 14.57 mm^{-1}
T = 296 K
Plate
0.15 × 0.15 × 0.03 mm
Colorless

Data collection

Rigaku AFC-7R diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical, based on the six crystal faces
$T_{\min}$ = 0.182, $T_{\max}$ = 0.645
2934 measured reflections
450 independent reflections
426 observed reflections [$I > 3.0\sigma(I)$]

$R_{\rm int}$ = 0.039
$\theta_{\max}$ = 45°
$h = -6 \rightarrow 6$
$k = -6 \rightarrow 6$
$l = -20 \rightarrow 20$
3 standard reflections monitored every 300 reflections
intensity decay: 1.60%

Refinement

Refinement on F
R = 0.026
wR = 0.031
S = 1.79
426 reflections
18 parameters
Unit weights
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 3.30 e Å^{-3} [at O(3)]
$\Delta\rho_{\min}$ = −3.34 e Å^{-3} (at La)

Extinction correction: Coppens & Hamilton (1970)
Extinction coefficient: 2.23 × 10^{-6}
Atomic scattering factors from Cromer & Waber (1974)

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

$$B_{\rm eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
La	0	0	0	0.678 (4)
Cs	0	0	1/2	1.668 (8)
Nb	1/2	1/2	0.20139 (5)	0.396 (4)
O(1)	0	1/2	0.1634 (6)	1.82 (9)
O(2)	1/2	1/2	0.3569 (6)	2.64 (8)
O(3)	1/2	1/2	0	3.6 (1)

Table 2. *Selected geometric parameters (Å, °)*

NbO$_6$ octahedron			
Nb—O(1) × 4	1.999 (1)	O(1)···O(1$^{\rm i}$) × 4	2.763 (1)
Nb—O(2)	1.736 (7)	O(1)···O(2) × 4	2.912 (7)
Nb—O(3)	2.248 (1)	O(1)···O(3) × 4	2.672 (4)
O(1)—Nb(1)—O(1')	87.42 (7)	O(1)—Nb(1)—O(2)	102.3 (2)
O(1)—Nb(1)—O(3)	77.7 (2)	O(2)—Nb(1)—O(3)	180.0
La—O(1) × 8	2.672 (4)	La—O(3) × 4	2.763 (1)
Cs—O(2) × 8	3.191 (4)		

Symmetry code: (i) $1 - y, x, z$.

An absorption correction was applied using *TEXSAN* (Molecular Structure Corporation, 1993). The method is based on the analytical method proposed by de Meulenaer & Tompa (1965).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS*. Program(s) used to solve structure: *DIRDIF*92 *(PATTY)* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: OH1090). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Armstrong, A. R. & Anderson, P. A. (1994). *Inorg. Chem.* **33**, 4366–4369.

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.

Coppens, P. & Hamilton, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A, pp. 72–98. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Dion, M., Ganne, M. & Tournoux, M. (1986). *Rev. Chim. Miner.* **23**, 61–69.

Gopalakrishnan, J., Bhat, V. & Raveau, B. (1987). *Mater. Res. Bull.* **22**, 413–417.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.

Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Sato, M., Abo, J., Jin, T. & Ohta, M. (1992). *Solid State Ionics*, **51**, 85–89.

Acta Cryst. (1996). C**52**, 1065–1067

$\mathrm{Re_4S_4Te_4}$

Vladimir E. Fedorov,[a] Yuri V. Mironov,[a] Vladimir P. Fedin,[b] Hideo Imoto[b] and Taro Saito[b]

[a]*Institute of Inorganic Chemistry, Russian Academy of Sciences, pr. Lavrentyeva 3, 630090, Novosibirsk, Russia, and* [b]*Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan. E-mail: taro@chem.s.u-tokyo.ac.jp*

(*Received 5 June 1995; accepted 12 December 1995*)

Abstract

The structure of the tetrahedral cluster compound tetrarhenium tetrasulfide tetratelluride, $\mathrm{Re_4S_4Te_4}$, has been determined using X-ray diffraction data collected on a single crystal grown by the high-temperature reaction of stoichiometric amounts of rhenium and sulfur in molten tellurium. The compound contains tetrahedral $\mathrm{Re_4}$ clusters with S atoms capping each of the four faces; the Te atoms bridge the $[\mathrm{Re_4S_4}]$ units to form a three-dimensional structure.

Comment

Chalcogenides of rhenium are of fundamental interest because of their significance as catalysts, their material properties and their occurrence as minerals (Halbert, Ho, Stiefel, Chianelli & Daage, 1991; Korzhinsky, Tkachenko, Shmulovich, Taran & Steinberg, 1994). All structurally characterized chalcogenides of rhenium are cluster compounds. The participation of Re atoms in the formation of metal–metal bonds results in the formation of $\mathrm{Re_4}$ parallelograms in $\mathrm{ReS_2}$ and $\mathrm{ReSe_2}$ (Murray, Kelty, Chianelli & Day, 1994; Wildervanch & Jellinek, 1971) or $\mathrm{Re_6}$ octahedra in $\mathrm{Re_6Te_{15}}$ (Klaiber, Petter & Hullinger, 1983). It is conceivable that the amorphous compound $\mathrm{Re_2S_7}$ also contains $\mathrm{Re_4}$ cluster fragments (Müller, Krickemeyer, Bögge, Ratajczak & Armatage, 1994). Recently, we prepared the first non-molecular tetrahedral cluster compound of rhenium, $\mathrm{Re_4S_4Te_4}$, and also partly substituted phases such as $\mathrm{Re}_{4-x}\mathrm{Mo}_x\mathrm{S_4Te_4}$ and $\mathrm{Re_3MoS}_{4-y}\mathrm{Se}_y\mathrm{Te_4}$ (Fedorov, Mironov, Fedin & Mironov, 1994). The structure of $\mathrm{Re_4S_4Te_4}$ was determined by the Rietveld method from powder diffraction data. Reported in this communication are the preparation and determination of the structure of single crystals of the title compound. These crystals can be obtained by the high-temperature reaction of a stoichiometric powder mixture of rhenium and sulfur in molten tellurium. Using a large excess of tellurium does not cause substitution of sulfur by tellurium, and the product of the reaction has the composition $\mathrm{Re_4S_4Te_4}$.

The $\mathrm{Re_4S_4Te_4}$ structure is characterized by the presence of tetrahedral $\mathrm{Re_4}$ clusters with an Re—Re distance of 2.785 (3) Å, similar to the Re—Re distances in the molecular tetrahedral cluster compounds of $\mathrm{Re^{IV}}$, $[\mathrm{Re_4S_4(CN)_{12}}]^{4-}$ (Laing, Kiernan & Griffith, 1977) and $[\mathrm{Re_4S_4(S_3)_6}]^{4-}$ (Müller, Krickemeyer & Bögge, 1986). Each triangular face of the regular $\mathrm{Re_4}$ tetrahedron is capped symmetrically by triply bridging sulfide ions with an Re—S distance of 2.337 (10) Å. Each Re atom is further coordinated by three bridging Te atoms at a distance of 2.790 (2) Å.

This structure is isotypic with those of the chalcogeno halides of niobium and molybdenum, $M_4Y_4X_4$ (M = Nb, Mo; Y = S, Se; X = Cl, Br, I) (Fedorov, Evstaf'ev, Kirik & Mishchenko, 1981; Perrin, Chevrel & Sergent, 1975). These structures have been described as an NaCl-type arrangement of M_4Y_4 clusters and tetrahedral X_4 fragments. In $\mathrm{Re_4S_4Te_4}$, the Te—Te distance within a $\mathrm{Te_4}$ tetrahedron is 3.62 Å with the centre of the $\mathrm{Te_4}$ tetrahedron at $(\frac{1}{2},0,0)$. The structure can also be envisaged as a zinc-blende-type arrangement of $\mathrm{Re_4S_4}$ clusters and $\mathrm{Te_4}$ tetrahedra. In this description, the $\mathrm{Te_4}$ tetrahedron is centred at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and the Te—Te distance

Acta Crystallographica Section C
ISSN 0108-2701 ©1996