REGULAR STRUCTURAL PAPERS

Structure of a New Siliconiobate $K_{6.5}Ca_{0.75}Nb_{14}Si_4O_{47}$

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Abstract

A new siliconiobate, potassium calcium siliconiobate, $K_{6.5}Ca_{0.75}Nb_{14}Si_4O_{47}$, has been isolated which is isotypic with the oxide $Ba_{6+x}Nb_{14}Si_4O_{47}$ [Evans & Katz (1973). *J. Solid State Chem.* **8**, 150–158]. Its host lattice consists of an intergrowth of two structural types, $K_3Nb_8O_{21}$ [Groult, Chailleux, Choisnet & Raveau (1976). *J. Solid State Chem.* **19**, 235–244] and $Ba_3Nb_6Si_4O_{26}$ [Shannon & Katz (1970). *Acta Cryst.* B26, 105–109]. In this cage structure, the K and Ca atoms are distributed over two kinds of sites which are characterized by fifteen- and twelvefold coordination, respectively.

Comment

Colorless single crystals of the title compound were isolated from a mixture with nominal composition $K_4Nb_5PO_{17}$ which was heated at 1273 K for six months in an evacuated silica ampoule. The composition $K_{6.5}Ca_{0.75}Nb_{14}Si_4O_{47}$ was confirmed by microprobe analysis and structure refinement.

This oxide is isotypic with the oxide $Ba_{6+x}Nb_{14}Si_4$-O_{47} (Evans & Katz, 1973), *i.e.* its framework (Fig. 1) consists of an intergrowth of pure octahedral layers $[Nb_8O_{21}]_\infty$ forming the structure of $K_3Nb_8O_{21}$ (Groult, Chailleux, Choisnet & Raveau, 1976), and $[Nb_6Si_4O_{26}]_\infty$ layers corresponding to the structure of $K_6Nb_6Si_4O_{26}$ (Choisnet, N'Guyen, Groult & Raveau, 1976). It differs from $Ba_{6+x}Nb_{14}Si_4O_{47}$ in that the niobium does not exhibit mixed valency but is pentavalent. The unit cell is similar to that of $K_8Ta_{14}Si_4O_{47}$ (Birkett, Wiseman & Goodenough, 1981). The geometries of the NbO_6 octahedra and SiO_4 tetrahedra are very similar in both compounds. In the cages, one type of site (A in Fig. 1) has a twelvefold coordination, *i.e.* surrounded by 3×2 NbO_6 octahedra and is fully occupied by K atoms as in $Ba_{6+x}Nb_{14}Si_4O_{47}$. The second site (B) which has a

fifteenfold coordination, *i.e.* surrounded by 3×2 octahedra and two P_2O_7 groups, is only partially occupied by K and Ca atoms statistically distributed at random.

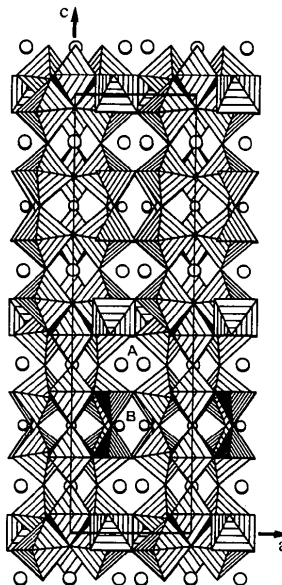Fig. 1. Arrangement of NbO_6 octahedra and SiO_4 tetrahedra in $K_{6.5}Ca_{0.75}Nb_{14}Si_4O_{47}$.

Experimental

Crystal data

$K_{6.5}Ca_{0.75}Nb_{14}Si_4O_{47}$	$\lambda = 0.71073$ Å
$M_r = 2449.22$	Cell parameters from 25
Hexagonal	reflections
$P6_3/mcm$	$\theta = 18$–$22°$
$a = 9.046$ (1) Å	$\mu = 4.765$ mm^{-1}
$c = 27.883$ (1) Å	$T = 294$ K
$V = 1976.2$ (4) Å^3	Stick
$Z = 2$	$0.1136 \times 0.0727 \times$
$D_x = 4.11$ Mg m^{-3}	0.0318 mm
Mo $K\alpha$ radiation	Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer	1175 observed reflections $[I > 3\sigma(I)]$
Bisect scans	$\theta_{max} = 45°$
Absorption correction: analytical	$h = 0 \rightarrow 18$
	$k = 0 \rightarrow 18$
$T_{min} = 0.7359$, $T_{max} = 0.8601$	$l = 0 \rightarrow 55$
	3 standard reflections
6180 measured reflections	frequency: 50 min
6180 independent reflections	intensity variation: <0.1%

Refinement

Refinement on F	
Final $R = 0.028$	$\Delta\rho_{max} = 1.8$ e Å^{-3}

$wR = 0.027$
$S = 1.004$
1175 reflections
71 parameters
$w = F\sin(\theta/\lambda)$
$(\Delta/\sigma)_{max} = 0.004$

$\Delta\rho_{min} = -1.1$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Nb(1)	0.24520(7)	0.0	0.04437(2)	0.579(9)
Nb(2)	0.23777(6)	0.0	0.18222(2)	0.715(8)
Nb(3)	1/3	2/3	0.0	0.79(1)
Si	1/3	2/3	0.19176(7)	0.37(2)
K(1)	0.5924(2)	0.0	0.10739(6)	1.29(3)
K/Ca	0.6018(6)	0.0	0.25	1.15(9)
O(1)	0.2172(5)	0.0	0.1106(2)	0.89(9)
O(2)	0.2752(8)	0.0	0.25	0.9(1)
O(3)	0.1973(5)	0.0	0.5328(2)	0.69(9)
O(4)	0.1744(5)	0.0	0.6862(2)	0.55(8)
O(5)	1/3	2/3	0.25	1.4(1)
O(6)	0.1817(4)	0.4856(4)	0.1731(1)	0.74(6)
O(7)	0.1684(4)	0.4815(4)	0.4584(1)	0.88(6)

Table 2. *Distances* (Å) *angles* (°) *in the* NbO_6SiO_4 *and* BiO_4 *polyhedra and main* K—O *and* K/Ca—O *distances* (Å)

The Nb—O(i) or Si—O(i) are on the diagonal, above it are the O(i)—O(j) distances and under it are O(i)—Nb—O(j) or O(i)—P—O(j) angles.

Nb(1)	O(1)	O(3^i)	O(3^{ii})	O(3^{iii})	O(7^{iv})	O(7^v)
O(1)	1.863(5)	4.001(8)	2.872(5)	2.872(5)	2.846(6)	2.846(6)
O(3^i)	160.8(2)	2.194(5)	2.554(8)	2.554(8)	3.051(6)	3.051(6)
O(3^{ii})	93.9(2)	73.7(2)	2.062(1)	3.09(1)	2.723(5)	3.946(8)
O(3^{iii})	93.9(2)	73.7(2)	97.1(2)	2.062(2)	3.946(8)	2.723(5)
O(7^{iv})	98.0(2)	95.9(2)	86.5(2)	167.3(2)	1.908(4)	2.638(7)
O(7^v)	98.0(2)	95.9(2)	167.3(2)	86.5(2)	87.5(2)	1.908(4)

Nb(2)	O(1)	O(2)	O(4^{ii})	O(4^{iii})	O(6^{vi})	O(6^{vii})
O(1)	2.006(5)	3.923(8)	2.774(6)	2.774(6)	2.766(6)	2.766(6)
O(2)	175.2(3)	1.920(2)	2.815(6)	2.815(6)	2.791(5)	2.791(5)
O(4^{ii})	89.5(2)	93.9(2)	1.932(1)	2.733(8)	2.807(5)	3.957(8)
O(4^{iii})	89.5(2)	93.9(2)	90.0(3)	1.932(1)	3.957(8)	2.807(5)
O(6^{vi})	86.6(2)	90.0(2)	90.3(2)	176.1(2)	2.027(4)	2.847(8)
O(6^{vii})	86.6(2)	90.0(2)	176.1(2)	90.3(2)	89.2(2)	2.027(4)

Nb(3)	O(7^i)	O(7^{viii})	O(7^{ix})	O(7^x)	O(7^{xi})	O(7^{ii})
O(7^i)	1.969(4)	2.756(7)	2.756(7)	3.925(8)	2.970(7)	2.663(7)
O(7^{viii})	88.9(2)	1.969(4)	2.756(7)	2.663(7)	3.925(8)	2.970(7)
O(7^{ix})	88.9(2)	88.9(2)	1.969(4)	2.970(7)	2.663(7)	3.925(8)
O(7^x)	170.8(2)	85.1(2)	97.9(2)	1.969(4)	2.756(7)	2.756(7)
O(7^{xi})	97.9(2)	170.8(2)	85.1(2)	88.9(2)	1.969(4)	2.756(7)
O(7^{ii})	85.1(2)	97.9(2)	170.8(2)	88.9(2)	88.9(2)	1.969(4)

Si	O(5)	O(6)	O(6^{xiii})	O(6^{xiv})
O(5)	1.624(2)	2.629(3)	2.629(3)	2.629(3)
O(6)	108.8(1)	1.608(4)	2.637(7)	2.637(7)
O(6^{xiii})	108.8(1)	110.1(1)	1.608(4)	2.637(7)
O(6^{xiv})	108.8(1)	110.1(1)	110.1(1)	1.608(4)

K(1)—O(1^{xv})	3.197(2)	K/Ca—O(2)	2.956(1)
K(1)—O(1^{xvi})	3.197(2)	K/Ca—O(2^v)	3.194(5)
K(1)—O(3^{xvii})	2.819(6)	K/Ca—O(2^{vii})	3.194(5)
K(1)—O(4^{xviii})	3.046(5)	K/Ca—O(4^{xiii})	2.695(7)
K(1)—O(6^{vi})	3.079(4)	K/Ca—O(4^{viii})	2.695(7)
K(1)—O(6^{ii})	2.930(4)	K/Ca—O(5^v)	2.769(2)
K(1)—O(6^{iii})	2.930(4)	K/Ca—O(5^{vii})	2.769(2)
K(1)—O(6^{viii})	3.079(4)	K/Ca—O(6^{iv})	3.256(4)
K(1)—O(7^{ii})	3.154(4)	K/Ca—O(6^{iii})	3.182(5)
K(1)—O(7^v)	2.867(4)	K/Ca—O(6^{viii})	3.182(5)
K(1)—O(7^i)	2.867(4)	K/Ca—O(6^{vii})	3.256(4)
K(1)—O(7^x)	3.154(4)	K/Ca—O(6^{iv})	3.182(5)
		K/Ca—O(6^i)	3.182(5)
		K/Ca—O(6^x)	3.256(4)

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

Calculations were performed on a MicroVAX II computer using the *SDP* system (B. A. Frenz & Associates, Inc., 1982). The θ-scan width was $(1.00 + 0.35 \tan\theta)°$ with a ω–4/3θ scan. The figure was drawn using *STRUPLO84* (Fischer, 1985).

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55663 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1008]

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Redetermination of the Structure of α-Tetraphosphorus Trisulfide Diiodide at 180 K

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Abstract

Redetermination of the structure of the title compound from data collected at 180 K gives considerably improved precision. The two independent molecules in the asymmetric unit are practically identical and have essentially C_2 symmetry unaffected by crystal packing. The greatest difference between the two molecules is in the 'book angles' between the fused five-membered rings; this is in accordance with chemical-shift variations observed in ^{31}P NMR spectra for this and related compounds.