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The Potassium Niobyl Cyclotetrasilicate $K_2(NbO)_2Si_4O_{12}$

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The single-phase compound $K_2(NbO)_2Si_4O_{12}$ was prepared by solid-state reaction. It crystallizes in the tetragonal system, space group *P4bm* with $a = 8.7404(8)$ Å and $c = 8.136(1)$ Å, $Z = 2$. The structure was determined from 484 reflections collected with a Nonius CAD4 diffractometer with Mo$K\alpha$ radiation. The final R index and weighted R_w index are 0.021 and 0.022, respectively. This framework structure is built up from chains of corner-shared NbO_6 octahedra running parallel to the four-fold axes and linked together by four-membered Si_4O_{12} single rings. This structure is very similar to that of $K_4(ScOH)_2Si_4O_{12}$. © 1992 Academic Press, Inc.

Introduction

Among three-dimensional skeleton structure types offering interesting possibilities for fast alkali-ion mobility, Nasicon (*1*), whose framework is built up from MO_6 octahedra and XO_4 tetrahedra, has been extensively studied. In an attempt to find similar materials with both octahedra and tetrahedra, we have extended our investigations to other systems: A_2O–M_2O_5–SiO_2 (A = alkali metal and M = Sb, Nb, Ta). This paper reports the preparation and crystal structure determination of a new potassium niobyl silicate: $K_2(NbO)_2Si_4O_{12}$.

Experimental

Single crystals of $K_2(NbO)_2Si_4O_{12}$ were grown from mixtures of KNO_3, Nb_2O_5, and SiO_2 (all GR grade, Merck). The chemicals were weighed out in a 2 : 1 : 6 mole ratio and the mixture was heated in air, in a platinum crucible, first at 773 K for 6 hr to decompose the KNO_3 and then at 1423 K to complete the reaction. The crystals obtained are colorless rectangular platelets with large (001) faces. Their chemical analysis, conducted with an electron microprobe, leads to an atomic K to Nb and Si ratio of 1 : 1 : 2. Single crystal X-ray study indicates that the compound is of tetragonal symmetry. The cell parameters (Table I) were refined by a least-squares procedure from powder diffraction data collected with an INEL curved multidetector, using a 0.2 mm capillary and Cu$K\alpha_1$ radiation (λ = 1.54059 Å; silicon as standard). The powder pattern (Table II) includes observed and calculated interplanar distances of the reflection planes along with the intensities calculated from the LAZY–PULVERIX program (*2*). Intensity data were collected with a Nonius CAD4

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TABLE I

CRYSTALLOGRAPHIC AND EXPERIMENTAL DATA

Formula weight	600.4
Space group	*P*4*bm*
a(Å)	8.7404(8)
c(Å)	8.136(1)
V(Å^3)	621.5(2)
Z	2
D_{calc} (g cm^{-3})	3.225
μ(Mo$K\alpha$)(cm^{-1})	29.4
Crystal size (mm)	$0.20 \times 0.15 \times 0.02$
Radiation (Å)	Mo$K\alpha$, $\lambda = 0.71069$
Scan mode	ω
Scan angle (°)	$\Delta\omega = 1.0 + 0.35 \tan \theta$
Recording angular range (θ°)	1.5–35.0
Number of independent data observed with $\sigma(I)/I < 0.33$ (used in refinements)	484
Number of variables (isotropic temperature factors)	33
$R = \Sigma (\|\|Fo\| - \|Fc\|\|)/\Sigma\|Fo\|$	0.025
$R_w = [\Sigma w(\|Fo\| - \|Fc\|)^2/\Sigma w Fo^2]^{1/2}$, with $w = 1/(1 + [(F_{obs} - F_{av})/F_{max}]^2$	0.026
Number of variables (anisotropic temperature factors for Nb, K, and Si atoms)	44
$R =$	0.021
$R_w =$	0.022
Extinction parameter refined $g =$	$9.4(7) \times 10^{-7}$

TABLE II

$K_2(NbO)_2Si_4O_{12}$: X-RAY POWDER DIFFRACTION DATA

h	k	l	d_{obs}(Å)	d_{calc}(Å)	I/I_o	h	k	l	d_{obs}(Å)	d_{calc}(Å)	I/I_o
0	0	1	8.134	8.136	4	4	1	0	2.120	2.120	16
1	1	0	6.175	6.180	83	4	0	1	2.112	2.110	2
1	1	1	4.909	4.921	4	3	2	2	2.082	2.082	2
2	0	0	4.359	4.370	90	4	1	1	2.052	2.051	6
0	0	2	4.061	4.068	93	0	0	4	2.034	2.034	32
2	1	0	3.903	3.909	32	4	2	0	1.955	1.954	47
2	0	1	3.843	3.850	9	3	1	3)		1.936	7
								)	1.933		
2	1	1	3.521	3.523	66	1	1	4)		1.932	15
1	1	2	3.396	3.398	52	4	0	2	1.924	1.925	14
2	2	0	3.091	3.090	48	2	0	4	1.844	1.844	15
2	0	2	2.982	2.978	86	3	3	2	1.838	1.838	12
2	2	1	2.889	2.889	2	3	2	3	1.807	1.807	5
2	1	2	2.821	2.819	60	4	2	2	1.762	1.762	36
3	1	0	2.766	2.764	100	5	1	0	1.714	1.714	28
0	0	3	2.713	2.712	3	4	0	3)		1.701	4
								)	1.699		
1	1	3	2.484	2.483	3	2	2	4)		1.699	16
2	2	2	2.462	2.461	12	5	1	1	1.678	1.677	2
3	2	0	2.425	2.424	3	3	3	3	1.640	1.640	3
3	2	1	2.324	2.323	4	3	1	4	1.638	1.638	29
2	0	3	2.305	2.304	3	5	2	1	1.591	1.592	4
3	1	2	2.286	2.286	17	5	1	2	1.579	1.580	30
4	0	0	2.186	2.185	4	4	4	0	1.545	1.545	18

diffractometer operating under the conditions given in Table I. For the data reduction, structure solution, and refinement, the MOLEN program chain (1990 version) of Enraf–Nonius (*3*) was used.

Structure Determination

An examination of the intensity data showed the systematic absences characteristic of space groups *P*4/*mbm*, *P*4*bm*, and $P\bar{4}b2$: $k = 2n + 1$ for $0kl$ reflections. The structural determination was first conducted in the centrosymmetric group *P*4/*mbm*. A Patterson map was used to elucidate the initial position of the heavy atom Nb, with the remaining atoms being found from successive difference Fourier maps. Refinement was carried out by the full-matrix least-squares method. The positional parameters of the eight unique atoms, the anisotropic (for Nb, K, and Si atoms) and isotropic (for oxygen atoms) temperature factors were refined to $R = 0.099$ and $R_w = 0.123$. At the completion of the refinement two oxygen atoms located on the four-fold axis, as is the Nb atom, exhibited anomalously large temperature factors (~4 Å^2). Similar results were observed when the structure was refined in the acentric $P\bar{4}b2$ space group ($R = 0.094$ and $R_w = 0.122$) probably due to the fact that the change from *P*4/*mbm* to $P\bar{4}b2$ leads to the same equivalent positions for atoms on the four-fold axis. The conversion was then made from *P*4/*mbm* to *P*4*bm* with use of prime and non-prime numbers for pairs of unique atoms corresponding to a single independent position when the *P*4/*mbm* space group is used. The z coordinate for O(2) was held invariant in order to define the origin. After some refinement

TABLE III

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	Position	x	y	z	$B(\text{Å}^2)^a$
Nb(1)	2*a*	0.0	0.0	0.2160(2)	0.580(6)
Nb(1′)	2*a*	0.0	0.0	0.7194(2)	0.542(6)
K	4*c*	0.3226(1)	0.8226(1)	0.9919(3)	1.28(2)
Si(1)	4*c*	0.1242(2)	0.6242(2)	0.3015(2)	0.50(2)
Si(1′)	4*c*	0.1240(2)	0.6240(2)	0.6938(2)	0.47(2)
O(1)	8*d*	0.4251(4)	0.2882(4)	0.2330(4)	0.81(5)*
O(1′)	8*d*	0.4219(5)	0.2892(5)	0.7654(5)	1.02(6)*
O(2)	2*a*	0.0	0.0	0.0	0.96(9)*
O(3)	2*a*	0.0	0.0	0.5010(9)	0.97(9)*
O(4)	4*c*	0.1200(4)	0.6200(4)	0.4968(9)	1.34(7)*
O(5)	2*b*	0.5	0.0	0.228(1)	1.2(1)*
O(5′)	2*b*	0.5	0.0	0.7628(8)	0.8(1)*

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb(1)	0.0071(1)	U_{11}	0.0079(2)	0	0	0
Nb(1′)	0.0064(1)	U_{11}	0.0079(2)	0	0	0
K	0.0180(4)	U_{11}	0.0124(6)	−0.0034(5)	0.0005(5)	U_{13}
Si(1)	0.0076(4)	U_{11}	0.0039(6)	0.0007(7)	0.0004(5)	U_{13}
Si(1′)	0.0071(4)	U_{11}	0.0036(7)	−0.0001(6)	−0.0003(5)	U_{13}

Note. The form of the anisotropic thermal parameter is

$$\exp[2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})].$$

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as

$$B_{\text{eq}} = 4/3 \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j.$$

cycles the R and R_w indices are drastically reduced to 0.025 and 0.026, respectively, and the temperature factors of the oxygen atoms mentioned above are lowered to more classical values (see Table III). At this level empirical absorption corrections were applied to the data with use of program DIFABS (*4*). Table I indicates the main results of the final refinements, which include corrections for secondary extinction and take anomalous dispersion into account. In order to keep a data to parameter ratio higher than 10 : 1, anisotropic temperature factors were not assigned to all atoms but to Nb, K, and Si atoms only. It must be mentioned that a refinement of the enantiomorph did not give a significantly different R value. The final Fourier difference map is featureless with maxima and minima in the range ±0.8 e Å^{-3}.

Table III presents the final atomic coordinates and thermal parameters (structure factor tables will be sent upon request).

Description of the Structure

The structure, depicted as a polyhedral representation in Fig. 1, may be described as consisting of chains of corner-shared NbO_6 octahedra running parallel to the four-fold axes. The chains are coupled together by four-membered Si_4O_{12} rings so that each octahedron shares four corners with four SiO_4 tetahedra belonging to four different Si_4O_{12} rings (Fig. 2). In the Si_4O_{12} ring each of the eight outwardly pointing vertices (O(1) or O(1′)) joins with one NbO_6 octahedron so that each Si_4O_{12} ring links four different chains, thus giving a three-dimensional network. This arrangement delimits channels which extend through the structure in the [001] direction and wherein potassium atoms are situated.

A list of bond distances and bond angles along with their standard deviations is given for $K_2(NbO)_2Si_4O_{12}$ in Table IV. The NbO_6 octahedra are almost regular with O–O distances ranging from 2.73(1) to 2.93(1) Å for the $Nb(1)O_6$ octahedron and from 2.74(2) to 2.91(1) Å for the $Nb(1')O_6$ octahedron.

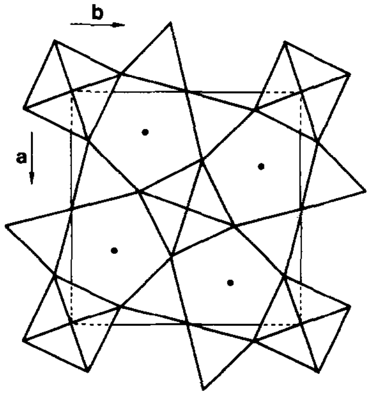

FIG. 1. $K_2(NbO)_2Si_4O_{12}$: [001] view of the structure.

TABLE IV

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR THE COORDINATION POLYHEDRA

Coordination of the potassium atom

K–O(1) (2×)	2.937(6)
K–O(1) (2×)	3.106(6)
K–O(1′) (2×)	2.837(7)
K–O(1′) (2×)	3.056(7)
K–O(2) (2×)	3.219(1)
K–O(5)	2.92(1)
K–O(5′)	2.878(6)

$Nb(1)O_6$ octahedron

Nb(1)	O(1)	O(1)	O(1)	O(1)	O(2)	O(3)
O(1)	1.968(6)	2.777(9)	3.93(1)	2.777(9)	2.73(1)	2.93(1)
O(1)	89.72(2)	1.968(6)	2.777(9)	3.93(1)	2.73(1)	2.93(1)
O(1)	171.9(3)	89.72(2)	1.968(6)	2.777(9)	2.73(1)	2.93(1)
O(1)	89.72(2)	171.9(3)	89.72(2)	1.968(6)	2.73(1)	2.93(1)
O(2)	94.0(2)	94.0(2)	94.0(2)	94.0(2)	1.76(2)	4.07(3)
O(3)	86.0(2)	86.0(2)	86.0(2)	86.0(2)	180	2.32(2)

$Nb(1')O_6$ octahedron

Nb(1′)	O(1′)	O(1′)	O(1′)	O(1′)	O(2)	O(3)
O(1′)	2.000(8)	2.78(1)	3.94(1)	2.78(1)	2.74(2)	2.91(1)
O(1′)	87.99(6)	2.000(8)	2.78(1)	3.94(1)	2.74(2)	2.91(1)
O(1′)	158.4(3)	87.99(6)	2.000(8)	2.78(1)	2.74(2)	2.91(1)
O(1′)	87.99(6)	158.4(3)	87.99(6)	2.000(8)	2.74(2)	2.91(1)
O(2)	79.2(2)	79.2(2)	79.2(2)	79.2(2)	2.28(2)	4.07(3)
O(3)	100.8(2)	100.8(2)	100.8(2)	100.8(2)	180	1.78(2)

$Si(1)O_4$ tetrahedron

Si(1)	O(1)	O(1)	O(4)	O(5)
O(1)	1.597(6)	2.64(1)	2.631(8)	2.603(6)
O(1)	111.2(5)	1.597(6)	2.631(8)	2.603(6)
O(4)	111.3(3)	111.3(3)	1.59(1)	2.64(1)
O(5)	106.7(3)	106.7(3)	109.3(5)	1.647(5)

$Si(1')O_4$ tetrahedron

Si(1′)	O(1′)	O(1′)	O(4)	O(5′)
O(1′)	1.608(8)	2.61(2)	2.665(9)	2.619(8)
O(1′)	108.4(5)	1.608(8)	2.665(9)	2.619(8)
O(4)	112.1(3)	112.1(3)	1.604(9)	2.62(1)
O(5′)	107.8(3)	107.8(3)	108.4(3)	1.632(4)

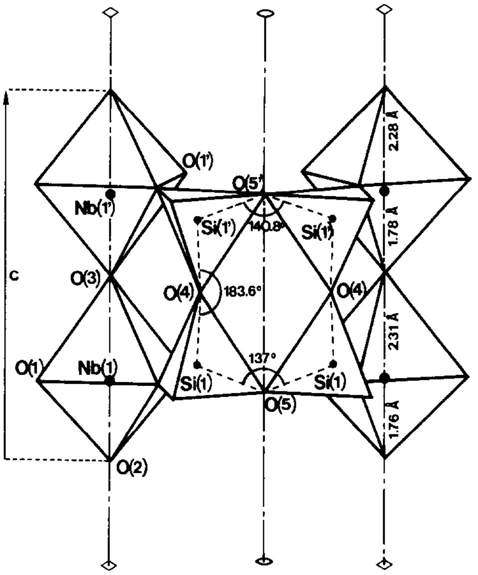

FIG. 2. Perspective [110] view of the Si_4O_{12} ring with two of its four adjacent chains of NbO_6 octahedra.

Within these octahedra the Nb atoms are displaced from the center by about 0.28 Å for Nb(1) and 0.25 Å for Nb(1′), thus leading to alternatively short and long Nb–O distances along the four-fold axis (Nb(1)–O(2) = 1.76(2) Å, Nb(1)–O(3) = 2.32(2) Å, Nb(1′)–O(3) = 1.78(2) Å, and Nb(1′)–O(2) = 2.28(2) Å). It must be pointed out that this sequence of Nb–O distances along the four-fold axis cannot occur when *P*4/*mbm* and $P\bar{4}b2$ space groups are used for the structural determination. In the NbO_6 octahedra the four remaining Nb–O distances are equivalent (Nb(1)–O(1) = 1.968(6) Å and Nb(1′)–O(1′) = 2.000(8) Å). The coordination polyhedra around Nb atoms are very similar to those observed around Ti atoms in the well-known potassium titanyl phosphate $KTiOPO_4$ (5).

The SiO_4 tetrahedra are almost regular with Si–O distances ranging from 1.59(1) to 1.647(5) Å for the $Si(1)O_4$ tetrahedron and from 1.604(9) to 1.632(4) Å for the $Si(1')O_4$ tetrahedron. Within the Si_4O_{12} ring the four silicon atoms and the four bridging oxygen atoms all lie on a mirror plane, two of these latter bridging oxygen atoms (O(5) and O(5′)) being situated on the binary axis. Moreover the Si(1)–O(4)–Si(1′) angle is close to 180° (183.6(3)°). The four-membered Si_4O_{12} ring can then be described as the association through a mirror plane of two Si_2O_7 groups in an eclipsed configuration (Fig. 2). The symmetry of the Si_4O_{12} ring is in fact very close to *mmm* and the acentric character of the structure, i.e., the change from *P4/mbm* to *P4bm*, is mainly due, as previously mentioned, to the sequence of Nb–O distances along the four-fold axis.

The $[(NbO)_2Si_4O_{12}{}^{2-}]_n$ framework is very similar to the $[(ScOH)_2Si_4O_{12}{}^{4-}]_n$ framework already observed in $K_4(ScOH)_2Si_4O_{12}$ (*6*). One can observe that in this latter compound there are twice as many potassium atoms per formula unit as in the title one; vacant sites, which could allow fast potassium ion mobility, are then available within the $[(NbO)_2Si_4O_{12}{}^{2-}]_n$ framework.

Preliminary second harmonic generation tests, performed on a polycrystalline sample of $K_2(NbO)_2Si_4O_{12}$ with use of the 1.06-μm line of a YAG:Nd laser, have confirmed subsequently that the structure is non-centrosymmetric. Ion exchange, dielectric, and non-linear optical properties of the title compound are presently being investigated (*7*, *8*).

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