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$Rb_4(Si,Nb)_2Nb_{35}O_{70}$: a new phase containing isolated Nb_6O_{12} clusters

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Abstract

Golden plate-like crystals of $Rb_4(Si,Nb)_2Nb_{35}O_{70}$ were prepared by heating a mixture of Rb_2CO_3, Nb_2O_5 and NbO (2:2:3) in a quartz ampoule at 1100 °C. The incorporated silicon originates from the container material. $Rb_4(Si,Nb)_2Nb_{35}O_{70}$ crystallizes in $P\bar{3}$ with $a = 782.1(2)$ pm, $c = 2651.3(8)$ pm and $Z = 1$ (four-circle diffractometer Syntex $P\bar{1}$, 2063 I_0 (hkl), Mo Kα, $R_w = 0.10$). The structure consists of slabs similar to those found in the structures of $Ba_3(Si,Nb)_2Nb_{20.8}O_{44}$ and $Na_3Al_2Nb_{34}O_{64}$, and can be described in terms of a common close packing of oxygen and rubidium atoms together with Nb_6 octahedra. Characteristic building units of the new structure type are isolated Nb_6O_{12} clusters, NbO_6 octahedra and SiO_4 tetrahedra. Slabs occur in which three NbO_6 octahedra share edges forming Nb_3O_{13} units with long Nb–Nb distances (306 and 335 pm) indicating weak and no Nb–Nb bonds, respectively, to be present. The Nb_6O_{12} clusters exhibit M–M bonding with short distances $d_{Nb-Nb} = 279$–284 pm.

1. Introduction

In the last few years many reduced oxoniobates containing isolated or condensed Nb_6O_{12} clusters [1–25] have been synthesized and the number is still growing. An extensive comparison of the so far known compounds is given in refs. 26 and 27. The structures of these compounds can be described in terms of a common close packing of oxygen atoms, Nb_6 octahedra and large countercations, such as the higher homologues of the alkaline, earth alkaline or rare earth (lanthanum, praseodymium, neodymium) metals. Depending on the stacking of the sheets the countercations are cuboctahedrally or close-hexagonally surrounded by 12 oxygen atoms. There is a size limitation for the countercations filling the cavities that are built from oxygen atoms and Nb_6 octahedra. For example, $BaNb_4O_6$ [21, 23] has been prepared but the corresponding compound $SrNb_4O_6$ has not yet been synthesized. However, some structure types seem to be rather insensitive to the size of the countercation, *e.g.* MNb_8O_{14} (M ≡ K, Sr, Ba, La) [7, 10, 17] and $M_2Nb_5O_9$ (M ≡ K, Sr, Ba) [12, 16, 23].

Highly reduced alkali metal oxoniobates exhibiting metal–metal bonded arrays have been found so far only with sodium or potassium and it seemed

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promising to look for comparable phases with the larger homologues caesium and rubidium. All experiments with caesium have failed [28], but we have found a new reduced oxoniobate containing Nb_6O_{12} clusters and rubidium on which we report here.

2. Experimental details

2.1. *Preparation and characterization*

$Rb_4(Si,Nb)_2Nb_{35}O_{70}$ was prepared by heating a mixture of Rb_2CO_3 (Morthon–Thiokol) and Nb_2O_5 (Merck) in a 1:1 ratio for 1 day at 900 °C under vacuum until gas evolution ceased. This product was then heated under argon together with NbO (Johnson–Matthey) in a 2:3 mixture (pressed to a pellet and brought into a quartz ampoule) for 11 days at 1100 °C. The ampoule was cooled slowly. The pellet was partially molten and embedded into the ampoule wall.

The product consisted of very thin golden plate-like crystals with a hexagonal habit which formed conglomerates. An energy-dispersive X-ray analysis showed only the presence of niobium and rubidium. Silicon could not be detected because its Kα and Kβ peaks (1745 eV and 1838 eV respectively) are hidden by the intense Lα peak of rubidium (1700 eV). $Rb_4(Si,Nb)_2Nb_{35}O_{70}$ is stable against mineral acids, and impurities could therefore be removed by washing the sample with concentrated HCl.

The powder diagram (Stoe STADIP powder diffractometer, position-sensitive detector) of the HCl-treated platelets showed only a few impurity lines besides the lines of $Rb_4(Si,Nb)_2Nb_{35}O_{70}$. The title compound is described by the following characteristic lines at the resolution for Cu Kα_1 radiation (calculated d values (pm), intensities in parentheses): 2651.3(100), 1325.7(12), 883.8(26), 656.2(21), 603.2(22), 537.6(56), 473.7(37), 417.5(33), 370.1(24), 336.8(32), 330.6(57), 328.1(45), 316.2(73), 314.7(80), 301.6(24), 297.7(42), 292.8(88), 285.4(11), 270.1(23), 254.8(56), 251.4(49), 245.9(87), 241.0(27), 238.8(28), 221.5(40), 212.1(46), 202.6(85), 201.1(14), 193.2(29), 184.2(65), 183.7(10), 183.5(18), 178.8(20), 168.3(19), 167.3(42), 152.2(38), 147.8(83), 145.5(16), 144.9(10), 126.0(21), 120.5(12), 119.4(11). The refinement of the lattice constants resulted in $a = 782.1(2)$ pm and $c = 2651.3(8)$ pm.

2.2. *Structure analysis*

Precession photographs (($hk0$) and (hkl)) of a single crystal of $Rb_4(Si,Nb)_2Nb_{35}O_{70}$ look very similar to the corresponding ones observed for single crystals of $M(Si,Nb)Nb_{10}O_{19}$ and $M_3Al_2Nb_{34}O_{64}$ (M ≡ Na, K) [7, 26]. This indicates that a comparable structure set-up with close-packed layers of oxygen atoms and Nb_6 units is present. The different length of the c axis in $Rb_4(Si,Nb)_2Nb_{35}O_{70}$ compared with $Na_3Al_2Nb_{34}O_{64}$ is due to the different stacking of the close-packed layers.

The general quality of the single crystals was poor, but with one out of a number of tested single crystals which seemed to be the best (Table

TABLE 1

Summary of single-crystal data and X-ray intensity collection for $Rb_4(Si,Nb)_2Nb_{35}O_{70}$

Formula	$Rb_4(Si_{1.68}Nb_{0.32})Nb_{35}O_{70}$
Molar weight	4782.2 Da
Lattice constants[a]	$a = 782.1(2)$ pm, $c = 2651.3(8)$ pm[a]
Space group	$P\bar{3}$, $Z = 1$
d_{calc}	5.65 g cm^{-3}
μ(Mo Kα) λ	97.37 cm^{-1}, 71.069 pm
Dimensions of the single crystal	$0.3 \times 0.2 \times 0.02$ mm^3
Data collection	Four-circle diffractometer Syntex $P\bar{1}$ graphite monochromator, scintillation counter
Range of data, method	$2° \leqslant 2\theta \leqslant 55°$, ω scan
Scan speed	Variable depending on I
Number of reflections	2631
Independent reflections	2063 of 2189 with $F \geqslant 3\sigma(F)$
Absorption correction	Ψ scan with 11 reflections
Refinement	SHELX-76 full matrix, least squares
Number of parameters	116
R (aniso)	10.8%
R_ω (aniso)	10.1%

[a] From powder diffractometer data.

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen, F.R.G., on quoting the depository number CSD-55798, the names of the authors, and the journal citation.

1) the structure analysis could be carried out. The structure was solved via Fourier syntheses using a set of starting parameters calculated from the positional parameters for the structure $Na_3Al_2Nb_{34}O_{64}$ [5] in which similar sheets of oxygen atoms and Nb_6 units occur. The refined positional parameters and displacement factors are listed in Tables 2 and 3. It is remarkable that the displacement factors of O(5) and O(10) show relatively large values of 390 pm^2 and 294 pm^2 respectively. This is due to the partial occupation of the neighbouring positions of silicon and Nb(6) (see discussion). According to the short distance $d_{Si-Nb(6)} = 155$ pm these positions cannot be simultaneously occupied. A similar situation is found in $Na(Si,Nb)Nb_{10}O_{19}$. Consequently the occupation factors were restricted to a sum of 1.0. Fourier syntheses at the last state revealed non-spherical electron density around O(5) and O(10). Therefore a new structure refinement was carried out assuming the presence of split positions for these atoms by coupling the occupation factors for the split pairs with the corresponding factors of silicon and Nb(6). The parameters of the refined split positions for O(5) and O(10) are shown in Table 4.

3. Discussion of the crystal structure

The new structure of $Rb_4(Si,Nb)_2Nb_{35}O_{70}$ consists of layers containing O atoms (type ω), O and Rb atoms (α) and O atoms and Nb_6 Units (β)

TABLE 2

Positional parameters, site occupation factors k, U_{equi} values of the anisotropic and U_{iso} values of the isotropic displacement factors (pm^2) for $Rb_4(Si,Nb)_2Nb_{35}O_{70}$

Atom	Site	x	y	z	$U_{iso/equi}$	k
Nb(1)	6g	0.2176(3)	0.1960(3)	0.95617(8)	137(8)	1
Nb(2)	6g	0.1153(3)	0.4701(3)	0.22811(8)	136(8)	1
Nb(3)	6g	0.4506(3)	0.1393(3)	0.68386(8)	138(8)	1
Nb(4)	2d	1/3	2/3	0.0404(1)	171(9)	1
Nb(5)	6g	0.0855(3)	0.4715	0.86867(9)	219(9)	1
Nb(6)	2d	2/3	1/3	0.234(1)	280(53)	0.159(8)
Nb(7)	2c	0	0	0.3128(1)	160(9)	1
Nb(8)	6g	0.3929(3)	0.1261(3)	0.40720(8)	162(8)	1
Nb(9)	1b	0	0	1/2	194(14)	1
Rb(1)	2c	0	0	0.1783(1)	210(11)	1
Rb(2)	2d	2/3	1/3	0.5365(2)	289(12)	1
Si	2d	2/3	1/3	0.2924(5)	161(31)	0.841(8)
O(1)	6g	0.260(2)	0.429(2)	−0.0004(5)	106(30)	1
O(2)	6g	0.395(2)	0.904(2)	0.0856(5)	96(29)	1
O(3)	6g	−0.207(2)	0.028(2)	0.0890(6)	146(31)	1
O(4)	2d	2/3	1/3	0.0912(9)	77(44)	1
O(5)	6g	−0.287(3)	0.568(3)	0.1739(8)	390(46)	1
O(6)	6g	0.124(2)	0.691(2)	0.1803(7)	254(38)	1
O(7)	6g	0.150(2)	0.919(2)	0.2712(6)	155(33)	1
O(8)	6g	−0.108(2)	0.479(2)	0.2735(6)	152(32)	1
O(9)	6g	−0.167(2)	0.063(2)	0.3548(6)	144(32)	1
O(10)	2d	2/3	1/3	0.358(1)	291(60)	1
O(11)	6g	0.093(2)	0.461(2)	0.3626(7)	222(36)	1
O(12)	6g	0.497(2)	0.390(2)	0.4330(6)	168(33)	1
O(13)	6g	0.013(2)	0.223(2)	0.4548(6)	181(33)	1

Standard deviations are given in parentheses.

which are stacked in hexagonal or cubic manner (see Fig. 1). Interatomic distances are given in Tables 5 and 6. The two different common close-packed layers of six oxygen atoms and one Nb_6 unit (β) are surrounded by the neighbouring sheets ((ω, ω) or (ω, α) respectively) in a cubic manner resulting in $[Nb_6O_{12}{}^{i}]O_6{}^{a}$ clusters. The central part of the unit cell represents the complete structure of $Ba_3Si_2Nb_{20.8}O_{44}$ [1] with M≡Ba instead of M≡Rb. It is enhanced by a bar in Fig. 1. The upper and lower part of the unit cell is also found to be part of an already known structure, namely $Na_3Al_2Nb_{34}O_{64}$ [5].

Between the common close-packed layers containing Nb_6O_{12} clusters additional Nb atoms (Nb(6) and Nb(7)) are located in octahedral holes and Si atoms in tetrahedral holes. As mentioned above, the neighbouring positions of silicon and Nb(6) reveal a special situation. Because of the too short Nb(6)–Si distance ($d_{Nb(6)-Si} = 155$ pm) an alternating occupation (k(Si):k(Nb(6)) = 0.84:0.16) was obvious. This results in split positions for

TABLE 3

U_{ij} values[a] of the anisotropic displacement factors (pm^2) for $Rb_4(Si,Nb)_2Nb_{35}O_{70}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb(1)	144(10)	145(10)	127(10)	76(8)	−17(8)	−13(8)
Nb(2)	123(10)	139(10)	134(10)	57(8)	−5(8)	3(8)
Nb(3)	146(10)	152(10)	113(10)	72(9)	−5(8)	−7(8)
Nb(4)	186(11)	U_{11}	142(17)	$U_{11}/2$	0	0
Nb(5)	262(12)	228(12)	144(11)	105(10)	−4(9)	22(9)
Nb(6)	221(65)	U_{11}	400(88)	$U_{11}/2$	0	0
Nb(7)	178(11)	U_{11}	122(17)	$U_{11}/2$	0	0
Nb(8)	186(11)	187(11)	119(10)	99(9)	5(8)	2(8)
Nb(9)	201(16)	U_{11}	178(26)	$U_{11}/2$	0	0
Rb(1)	211(13)	U_{11}	207(20)	$U_{11}/2$	0	0
Rb(2)	301(15)	U_{11}	265(23)	$U_{11}/2$	0	0
Si	217(39)	U_{11}	48(50)	$U_{11}/2$	0	0

The positions of oxygen atoms have been refined isotropically.
Standard deviations are given in parentheses.
[a] The U_{ij} are defined for $\exp[-2\pi^2(U_{11}h^2a^{*2}+\ldots+2U_{23}klb^*c^*)]$.

TABLE 4

Positional parameters, site occupation factors k and isotropic displacement factors (pm^2) of the oxygen split positions in $Rb_4(Si,Nb)_2Nb_{35}O_{70}$

Atom	Site	x	y	z	U_{iso}	k
O(5)	6g	−0.284(4)	0.568(4)	0.172(1)	388(64)	0.841(8)
O(5a)	6g	−0.300(9)	0.570(9)	0.181(6)	264(105)	0.841(8)
O(10)	2d	2/3	1/3	0.356(1)	225(73)	0.159(8)
O(10a)	2d	2/3	1/3	0.374(7)	352(106)	0.159(8)

Standard deviations are given in parentheses.

the surrounding oxygen atoms O(5) and O(10). In the case of occupation of the silicon position the O(10) atom is closer to this position for electrostatic reasons than in the case of non-occupation. O(5) behaves in the same way with respect to the position of Nb(6). The displacement factor of O(8) that is shared between SiO_4 tetrahedra and Nb_6 octahedra is of a normal size, 153 pm^2. Obviously the rigid bond of O(8) to the Nb_6 octahedron (type O^i) prevents an observable split position for this atom.

Nb(5) and Nb(8) atoms occupy three of the seven octahedral holes within one (α, ω) slab in such a way that the NbO_6 octahedra share three edges forming Nb_3O_{13} units. Comparable units are well known from reduced molybdates, *e.g.* $Zn_2Mo_3O_8$ [29], or halides such as Nb_3Br_8 [30], in which short M–M distances indicate metal–metal bonding within the M_3 triangle. Owing to the rather long distances $d_{Nb(5)-Nb(5)} = 306$ pm within the Nb_3 triangle in this structure there is probably only weak metal–metal bonding. The Nb(8)–Nb(8) distances are even larger ($d_{Nb(8)-Nb(8)} = 335$ pm).

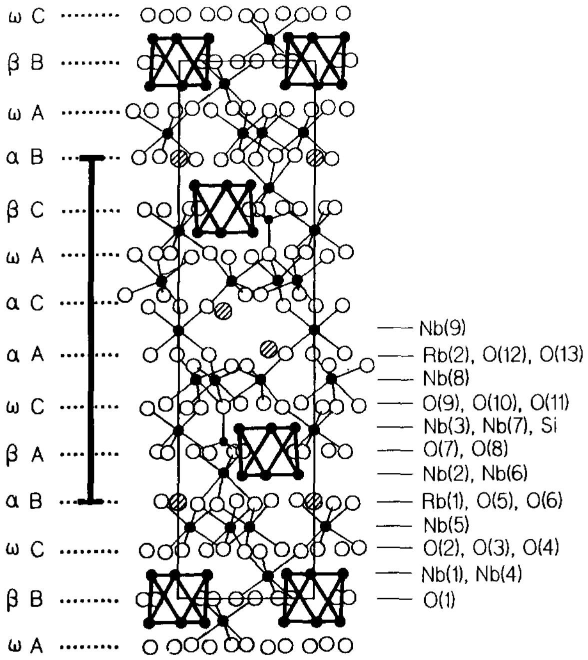

Fig. 1. Projection of the crystal structure of $Rb_4(Si,Nb)_2Nb_{35}O_{70}$ along [1 0 0]: ○, O atoms; ●, rubidium atoms. Nb_6 octahedra, NbO_6 octahedra and SiO_4 tetrahedra are graphically emphasized. That part of the structure which corresponds to the unit cell of $Ba_3(Si,Nb)_2Nb_{20.8}O_{44}$ is indicated by a bar.

The rubidium atoms are surrounded by 12 oxygen atoms, each in a cubic close-packed environment for Rb(1) and a hexagonal close-packed environment for Rb(2) respectively.

Between the two central layers of oxygen and rubidium atoms (type α) only one Nb(9) atom provides weak bonding between the slabs which explains the easy cleavability of the plate-like crystals. The distances within the octahedron around Nb(9) are very large ($d_{Nb(9)-O(13)} = 208$ pm (six times) and $d_{O(13)-O(13)} \approx 294$ pm (twelve times)). A similar situation is found in the structure of $Ba_3Si_2Nb_{20.8}O_{44}$ where the corresponding Nb(5)–O(7) and O(7)–O(7) distances are 208 pm and 295 pm respectively.

Motifs of the mutual adjunction [31] together with bond order sums [32] are listed in Table 7. An assignment of oxidation numbers to the atoms on the basis of bond order sums can be made, but for mixed-valence oxides containing Nb_6O_{12} clusters it needs special care as a certain hierarchy of the bond strengths is reflected by large deviations from expected values (see ref. 5).

The structure of $Rb_4(Si,Nb)_2Nb_{35}O_{70}$ contains two different Nb_6O_{12} clusters with average distances $d_{Nb-Nb} = 282$ pm. The bond order sum $\Sigma s_i(\text{Nb(1)–O}) = 3.03$ is much higher than the average bond order sum 2.71 for Nb(2) and Nb(3), thus suggesting different numbers of electrons in M–M

TABLE 5

Important interatomic distances in $Rb_4(Si_{1.68}Nb_{0.32})Nb_{35}O_{70}$ (pm)

Nb(1)–O(1)	203.9(15)		Nb(6)–O(8)	186.9(21)	3×
O(3)	204.5(13)		O(5)	231.6(30)	3×
O(3)	208.6(17)		Nb(7)–O(7)	193.1(19)	3×
O(1)	212.3(12)		O(9)	196.1(18)	3×
O(2)	221.6(17)		Nb(8)–O(13)	180.5(19)	
Nb(1)	281.3(3)	2×	O(12)	190.6(12)	
Nb(1)	283.5(4)	2×	O(12)	192.4(15)	
Nb(2)–O(7)	209.3(18)		O(11)	201.1(15)	
O(6)	210.6(15)		O(9)	201.4(16)	
O(6)	211.3(20)		O(10)	233.5(17)	
O(8)	215.1(18)		Nb(9)–O(13)	207.8(18)	6×
O(5)	231.1(24)		Rb(1)–O(7)	293.1(17)	3×
Nb(2)	282.0(3)	2×	O(3)	293.4(17)	3×
Nb(3)	283.8(3)		O(5)	298.1(17)	3×
Nb(3)	284.3(3)		O(6)	302.5(22)	3×
Nb(3)–O(11)	204.2(18)		Rb(2)–O(13)	311.0(13)	3×
O(7)	212.6(18)		O(12)	312.3(20)	3×
O(8)	213.1(3)		O(12)	317.5(17)	3×
O(11)	214.0(19)		O(11)	319.9(17)	3×
O(9)	222.7(13)		Si–O(8)	162.6(14)	3×
Nb(3)	279.0(3)	2×	O(10)	173.5(33)	
Nb(4)–O(1)	197.0(15)	3×	(Si–Nb(6)	155.0(31)[a]	
O(2)	205.3(15)	3×			
Nb(5)–O(6)	197.4(16)				
O(2)	199.5(13)				
O(3)	201.6(18)				
O(5)	204.4(18)				
O(4)	206.3(12)				
O(5)	208.5(24)				

Standard deviations are given in parentheses.

[a] Hypothetical distance for simultaneous occupation.

TABLE 6

Selected interatomic distances (pm) with regard to the split positions in $Rb_4(Si,Nb)_2Nb_{35}O_{70}$

Nb(6)–O(8)	186(2)	3×	O(5a)–Nb(5)	211(11)	
O(5a)	223(12)	3×	Nb(2)	212(12)	
Si–O(8)	163(2)		Nb(6)	223(12)	
O(10)	169(4)	3×	Nb(5)	227(12)	
O(5)–Nb(5)	204(3)		Rb(1)	229(6)	
Nb(5)	223(1)		O(10)–Si	169(4)	
Nb(2)	235(3)		Nb(8)	236(2)	3×
Rb(1)	298(2)		O(10a)–Nb(8)	213(8)	3×

Standard deviations are given in parentheses.

bonding states. In $Na_3Al_2Nb_{34}O_{64}$ with its two different Nb_6O_{12} clusters, not only the average distances d_{Nb-Nb} (≈ 282 pm) but also the bond order sums (≈ 2.95) for the niobium cluster atoms are nearly the same.

TABLE 7

Motifs of mutual adjunction [31] and bond order sums [32] Σs_i in $Rb_4(Si_{1.68}Nb_{0.32})Nb_{35}O_{70}$

Atom[a]	6O(1)^{i}	6O(2)^{a}	6O(3)^{i}	2O(4)$^{-}$	6O(5)^{a}	6O(6)^{i}	6O(7)^{i}	6O(8)^{i}	6O(9)^{a}	2O(10)$^{-}$	6O(11)^{i}	6O(12)$^{-}$	6O(13)$^{-}$	CN	Σs_i
6Nb(1)	2/2	1/1	2/2	–	–	–	–	–	–	–	–	–	–	5	3.03
6Nb(2)	–	–	–	–	1/1	2/2	1/1	1/1	–	–	–	–	–	5	2.64
6Nb(3)	–	–	–	–	–	–	1/1	1/1	1/1	–	2/2	–	–	5	2.78
2Nb(4)	3/1	3/1	–	–	–	–	–	–	–	–	–	–	–	6	4.60
6Nb(5)	–	1/1	1/1	1/3	2/2	1/1	–	–	–	–	–	–	–	6	4.38
2Nb(6)	–	–	–	–	3/1	–	–	3/1	–	–	–	–	–	6	4.65
2Nb(7)	–	–	–	–	–	–	3/1	–	3/1	–	–	–	–	6	5.46
6Nb(8)	–	–	–	–	–	–	–	–	1/1	1/3	1/1	2/2	1/1	6	5.15
1Nb(9)	–	–	–	–	–	–	–	–	–	–	–	–	6/1	6	3.82
2Rb(1)	–	–	3/1	–	3/1	3/1	3/1	–	–	–	–	–	–	12	1.80
2Rb(2)	–	–	–	–	–	–	–	–	–	–	3/1	6/2	3/1	12	1.09
2Si	–	–	–	–	–	–	–	3/1	–	1/1	–	–	–	4	3.72
Cn	3	3	4	3	5	4	4	4	3	4	4	4	3		
Σs_i	2.12	1.92	2.23	1.99	1.86*	2.14	2.28	2.09*	2.06	1.72*	2.08	2.16	2.07		

CN, coordination number.

[a] For the notation of the O atoms see ref. 33.

*Calculated assuming a ratio Si:Nb(6) = 1.68:0.32 and taking the split positions of O(5) and O(10) into account.

A more detailed analysis shows that the bond order sums of the O^i atoms (notation according to ref. 33) are somewhat higher than the expected value 2.0 whereas the O^a atoms exhibit lower values. The bond order sum for O(10) is 1.72 when its split position is taken into account. In comparable systems these deviations from expected values are discussed in terms of a higher bond strength within the Nb_6O_{12} clusters compared with the bond strength within NbO_6 octahedra or other M–O bonds (see ref. 5).

The bond order sum for silicon is 3.7 which is comparable with the value found for silicon in $Na(Si,Nb)Nb_{10}O_{19}$ and the normal oxidation state +4 is clearly indicated. In contrast, the assignment of an oxidation state for the octahedrally surrounded Nb atoms is rather ambiguous. Nb(9) which is located between the two central layers (type α) has a bond order sum of 3.86 and it is safe to assume the oxidation state +4. Nearly the same value is obtained for the corresponding atom Nb(5) in $Ba_3Si_2Nb_{20.8}O_{44}$ and therefore the oxidation number should not be +5 as assigned by Evans and Katz [1]. The oxidation state +5 is obvious for Nb(8) and Nb(7) for which too high bond order sums of 5.15 and 5.46 have been calculated. The value 5.46 for Nb(8) results from very short distances to O(12) (180.5 pm) and to O(13) (190.6 and 192.4 pm). As these oxygen atoms belong to the central (α, α) slab in which they are very weakly bonded to the rubidium and Nb(9) atoms respectively, they must form a strong bond to Nb(8). Taking into account the special bonding situation in the neighbourhood of the Nb_6O_{12} clusters [5], Nb(4) and Nb(6) with bond order sums of 4.60 and 4.65 respectively could still be +5. Problems occur for Nb(5) whose bond order sum is 4.36, thus leaving a clear assignment of an oxidation state open.

Finally, the problems with bond order summations in such structures become evident with the rubidium atoms. In contrast to a cuboctahedral void, which is much too small for Rb(1) exhibiting a bond order sum of 1.8, the hole with the hexagonal close-packed coordination can accommodate up to the size of rubidium by enlargement, yielding a bond order sum of 1.1 for Rb(2).

Under the assumption that all niobium atoms with the exception of Nb(9) have an oxidation number +5, the ionic limit

$$Rb_4{}^{+}Si_{1.68}{}^{4+}Nb_{0.32}{}^{5+}Nb_1{}^{4+}Nb_{16}{}^{5+}(Nb_6)_3O_{70}{}^{2-}$$

leads to a charge of $70\cdot2-(4\cdot1+1.68\cdot4+0.32\cdot5+1\cdot4+16\cdot5)=+43.68$ which has to be compensated by the 18 niobium cluster atoms. Thus the average number of electrons available for metal–metal bonding for the two different Nb_6O_{12} clusters is $(18\cdot5-43.68)/3\approx15.5$ which would thus be the highest so far observed in oxoniobates. The Nb–Nb distances within the clusters range between 279 and 284 pm and this distortion is relatively large compared with the same kind of clusters in other structures but the mean distance $d_{Nb-Nb}=282.3$ pm is similar to what has usually been found in reduced oxoniobates with 13, 14 or 15 valence electrons in N–N bonds of the Nb_6O_{12} cluster [4, 5, 7–10, 17]. In contrast to corresponding halides where a significant correlation between the number of valence electrons and

Nb–Nb distances within the Nb_6X_{12} clusters ($X \equiv Cl$, Br) is observed, this is not the case for Nb_6O_{12} clusters (see Table 6). A possible difference in average Nb–Nb bond lengths due to variations of the number of valence electrons is possibly hidden by matrix effects.

Molecular orbital calculations [34] have shown that a cluster of the M_6X_{12} type can contain a maximum of 16 valence electrons in M–M bonding states but then strong M–O anti-bonding states are already filled. The "magic" number of 14 valence electrons is often found in such oxoniobates with only bonding states of the M_6X_{12} clusters being filled. Therefore a description in the ionic limit

$$Rb_4{}^{+}Si_{1.68}{}^{4+}Nb_{0.32}{}^{5+}Nb_1{}^{4+}Nb_{10}{}^{5+}[Nb(5)_6{}^{5+}(Nb_6)_3{}^{16+}\cdot 4.5e^{-}]O_{70}{}^{2-}$$

is more adequate, where the Nb_6O_{12} clusters contain a minimum of 14 electrons and the remaining 4.5 valence electrons are distributed over the three Nb_6O_{12} clusters and the Nb_3O_{13} units. In this case the low bond order sum of 4.36 for Nb(5) would indicate that an intermediate oxidation state between +4 and +5 for Nb(5) is reasonable and weak Nb–Nb bonding in the $(Nb(5))_3$ units is present.

References

1 D. M. Evans and L. Katz, *J. Solid State Chem.*, *6* (1973) 459.
2 B. O. Marinder, *Chim. Scripta*, *11* (1977) 97.
3 J. Köhler and A. Simon, *Angew. Chem.*, *98* (1986) 1011; *Angew. Chem. Int. Ed. Engl.*, *25* (1986) 996.
4 R. Burnus, J. Köhler and A. Simon, *Z. Naturforsch.*, *426* (1987) 536.
5 J. Köhler and A. Simon, *Z. anorg. allg. Chem.*, *553* (1987) 106.
6 S. J. Hibble, A. K. Cheetham and D. E. Cox, *Inorg. Chem.*, *26* (1987) 2389.
7 J. Köhler, A. Simon, S. J. Hibble and A. K. Cheetham, *J. Less-Common Met.*, *142* (1988) 123.
8 J. Köhler, G. Miller and A. Simon, *Z. anorg. allg. Chem.*, *568* (1989) 8.
9 J. Köhler and A. Simon, *Z. anorg. allg. Chem.*, *572* (1989) 7.
10 S. J. Hibble, A. K. Cheetham, J. Köhler and A. Simon, *J. Less-Common Met.*, *154* (1989) 271.
11 A. Simon, J. Köhler, R. Tischtau and G. Miller, *Angew. Chem.*, *101* (1989) 1695; *Angew. Chem., Int. Ed. Engl.*, *28* (1989) 1662.
12 G. Svensson, *Mater. Res. Bull.*, *23* (1988) 437.
13 G. Svensson, *J. Solid State Ionics*, *32-33* (1989) 126.
14 G. Svensson, *Chem. Commun., Univ. Stockholm 3* (1989) 1.
15 G. Svensson, *Acta Chem. Scand.*, *44* (1990) 222.
16 C. E. Michelson, P. E. Rauch and F. J. DiSalvo, *Mater Res. Bull.*, *25* (1990) 971.
17 J. Köhler, R. Tischtau and A. Simon, *J. Chem. Soc., Dalton Trans.*, (1991) 829.
18 G. Svensson, *J. Solid State Chem.*, *90* (1991) 249.
19 G. Svensson, *Microsc. Microanal. Microstruct.*, *1* (1990) 343.
20 V. G. Zubkov, V. A. Perelyayev, I. F. Berger, I. A. Kontzevaya, O. B. Makarova, S. A. Turshevskii, V. A. Gubanov, V. I. Voronin, A. V. Mirmelstein and A. E. Karkin, *Sverkhprovodimost': Fiz., Khim., Tekhnol.*, *3* (1990) 2121.
21 V. G. Zubkov, V. A. Perelyayev, I. F. Berger, V. I. Voronin, I. A. Kontzevaya and G. P. Shveikin, *Dokl. Akad. Nauk. SSSR, Kristallogr.*, *312* (3) (1990) 615.
22 V. G. Zubkov, V. A. Perelyayev, D. G. Kellermann, V. E. Stapsev, V. P. Lyankina, I. A. Kontzeva, O. B. Makarova and G. P. Sveikin, *Dokl. Akad. Nauk. SSSR*, *313* (1991) 2.

23 G. Svensson, J. Köhler, A. Simon, *J. Less-Common Met.*, *176* (1991) 123–132.

24 S. A. Davydov, B. N. Goschchitskii, E. A. Karkin, A. V. Mirmelstein, V. I. Voronin, V. D. Parkhomenko, V. G. Zubkov, V. A. Perelyayev, I. F. Berger and I. A. Kontzevaya, *Int. J. Mod. Phys. B*, *4* (1990) 1531.

25 K. B. Kersting and W. Jeitschko, *J. Solid State Chem.*, *93* (1991) 350.

26 R. Tischtau, *Dissertation*, Stuttgart University, 1991.

27 J. Köhler, G. Svensson and A. Simon, to be submitted to *Angew. Chem.*

28 J. Köhler, S. J. Hibble and A. Simon, unpublished results.

29 R. E. McCarley, *Philos. Trans. R. Soc. London, Ser. A*, *308* (1982) 141.

30 A. Simon and H. G. v. Schnering, *J. Less-Common Met.*, *11* (1966) 31.

31 R. Hoppe, *Angew. Chem.*, *92* (1980) 25; *Angew. Chem., Int. Ed. Engl.*, *19* (1980) 110.

32 I. D. Brown and D. Altermatt, *Acta Crystallogr. B*, *41* (1985) 244.

33 H. Schäfer and H. G. Schnering, *Angew. Chem.*, *76* (1964) 833.

34 F. A. Cotton and T. E. Haas, *Inorg. Chem.*, *3* (1964) 10.