

Supporting Information

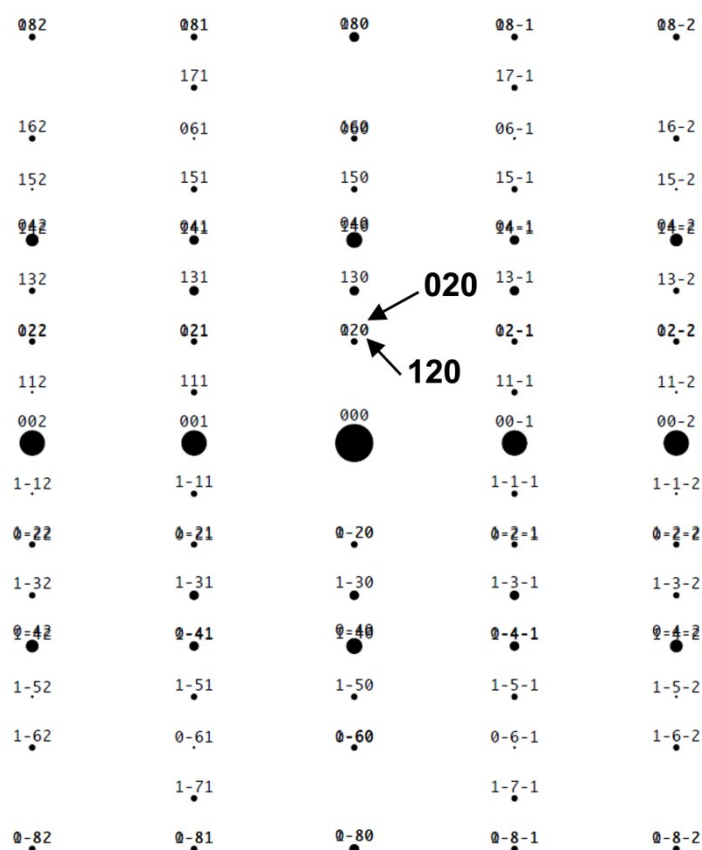


Fig. S1. Calculated selected area electron diffraction pattern of the [100] zone, using the final model as input. Overlap occurs at $k=2n$ positions of the reflections of [100] and neighboring zones because of the small reciprocal a^* distance. All reflections with $k=2n+1$ do not belong to the [100] zone itself, but are also visible here for the same reason as the overlapping $k=2n$ reflections.

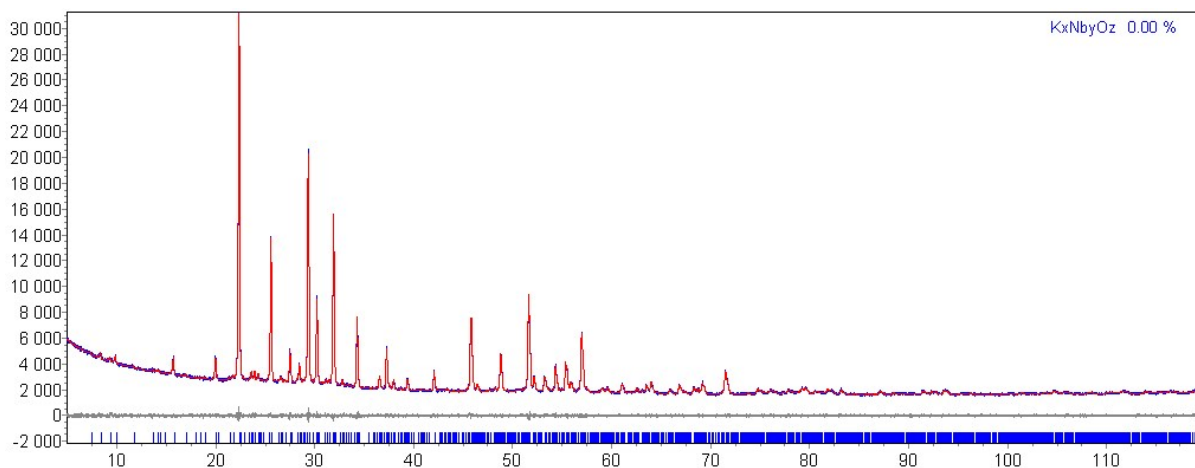


Fig. S2. Le Bail decomposition of PXRD profile (see description in the text). Experimental, calculated and difference curves are drawn with solid blue, red and grey lines, Bragg positions are marked with vertical blue bars.

Table S1

Atomic coordinates for $K_{6.4}Nb_{28.2}Ta_{8.1}O_{94}$ (S.G. *Pbam*, $a = 37.461$ Å, $b = 12.471$ Å, $c = 3.954$ Å) as derived from transmission electron microscopy.

Atom	Wyckoff			
	position	x/a	y/b	z/c
K1	2d	0.0000	0.5000	0.5000
K2°	4h	0.0558	0.2000	0.5000
K3	4h	0.1654	0.0126	0.5000
K4°	4h	0.2312	0.3207	0.5000
K5*	4h	0.95892	0.11645	0.5000
K6*	4h	0.71216	0.89315	0.5000
K7*	4h	0.62966	0.11454	0.5000
Nb1/Ta1	4g	0.9290	0.5563	0.0000
Nb2/Ta2	4g	0.8925	0.3166	0.0000
Nb3/Ta3	4g	0.9786	0.2908	0.0000
Nb4/Ta4	4g	0.8982	0.0586	0.0000
Nb5/Ta5	2a	0.0000	0.0000	0.0000
Nb6/Ta6	4g	0.8576	0.7781	0.0000
Nb7/Ta7	4g	0.2338	0.0665	0.0000
Nb8/Ta8	4g	0.1756	0.4907	0.0000
Nb9/Ta9	4g	0.1947	0.7633	0.0000
O1	4g	0.0920	0.2850	0.0000

O2	4g	0.9767	0.6228	0.0000
O3	4g	0.0582	0.5982	0.0000
O4	4g	0.8805	0.5120	0.0000
O5	4g	0.0695	0.8119	0.0000
O6	4g	0.8809	0.9144	0.0000
O7	4g	0.5022	0.3433	0.0000
O8	4g	0.9452	0.9801	0.0000
O9	4g	0.1884	0.1227	0.0000
O10	4g	0.2064	0.9144	0.0000
O11	4g	0.1404	0.8426	0.0000
O12	4g	0.1681	0.6383	0.0000
O13	4g	0.1738	0.3319	0.0000
O14	4g	0.2260	0.4681	0.0000
O15	4g	0.2458	0.7130	0.0000
O16	4h	0.8524	0.7908	0.5000
O17	4h	0.9268	0.5566	0.5000
O18	4h	0.8804	0.3572	0.5000
O19	4h	0.9711	0.2678	0.5000
O20	4h	0.9050	0.0665	0.5000
O21	2b	0.0000	0.0000	0.5000
O23	4h	0.2352	0.0798	0.5000
O24	4h	0.1685	0.4763	0.5000
O25	4h	0.1847	0.7781	0.5000

[°] K^+ in pentagonal channels, positions partially occupied by $Nb(Ta)^{5+}$

* K^+ in trigonal channels, occupation lower than 1

Table S2

Crystal data from refinement against combined X ray and neutron powder diffraction data.

$K_{6.4}Nb_{28.2}Ta_{8.1}O_{94}$	$\beta = 90^\circ$
$M_r = 5822.65$	$\gamma = 90^\circ$
Orthorhombic, <i>Pbam</i>	$V = 1850.54(63) \text{ \AA}^3$
$a = 37.4676(90) \text{ \AA}$	$Z = 1$
$b = 12.4934(30) \text{ \AA}$	neutron radiation, $\lambda = 1.594 \text{ \AA}$
$c = 3.95333(15) \text{ \AA}$	$D_x, \text{ g cm}^{-3} = 5.228$
$\alpha = 90^\circ$	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
K1/Nb1	0.449 (4)	0.344 (13)	0.5	2.42 (2)*	0.1486(55)/0.0132(55)
K2/Nb2	0.059 (2)	0.170 (6)	0.5	2.42 (2)*	0.7279(71)/0.2813(71)
K3	0.167 (3)	0.003 (8)	0.5	2.42 (2)*	0.4351(92)
K4/Nb4	0.226 (3)	0.332 (8)	0.5	2.42 (2)*	0.2884(92)/0.2804(90)
Nb1/Ta1	0.9300 (18)	0.573 (5)	0	2.42 (2)*	0.669(13)/0.331(13)
Nb2	0.8898 (12)	0.323 (3)	0	2.42 (2)*	1.0
Nb3/Ta3	0.9765 (16)	0.297 (6)	0	2.42 (2)*	0.776(13)/0.224(13)
Nb4/Ta4	0.903 (2)	0.067 (5)	0	2.42 (2)*	0.697(12)/0.303(12)
Nb5/Ta5	0	0	0	2.42 (2)*	0.604(17)/0.396(17)
Nb6/Ta6	0.8574 (19)	0.792 (6)	0	2.42 (2)*	0.670(10)/0.330(10)
Nb7/Ta7	0.2354 (19)	0.072 (5)	0	2.42 (2)*	0.705(13)/0.295(13)
Nb8/Ta8	0.1677 (12)	0.495 (4)	0	2.42 (2)*	0.639(11)/0.361(11)
Nb9/Ta9	0.1911 (18)	0.791 (6)	0	2.42 (2)*	0.714(35)/0.286(35)
O1	0.0970 (12)	0.291 (2)	0	2.42 (2)*	1.0
O2	0.9817 (7)	0.6092 (16)	0	2.42 (2)*	1.0
O3	0.0559 (5)	0.5794 (18)	0	2.42 (2)*	1.0
O4	0.8822 (5)	0.5011 (14)	0	2.42 (2)*	1.0
O5	0.0719 (5)	0.7850 (16)	0	2.42 (2)*	1.0
O6	0.8805 (7)	0.9275 (18)	0	2.42 (2)*	1.0
O7	0	0.160 (3)	0	2.42 (2)*	1.0
O8	0.9493 (6)	0.991 (2)	0	2.42 (2)*	1.0
O9	0.1918 (5)	0.1454 (16)	0	2.42 (2)*	1.0
O10	0.2071 (7)	0.934 (2)	0	2.42 (2)*	1.0
O11	0.1407 (6)	0.843 (2)	0	2.42 (2)*	1.0
O12	0.1666 (5)	0.6483 (15)	0	2.42 (2)*	1.0
O13	0.1687 (5)	0.3438 (15)	0	2.42 (2)*	1.0
O14	0.2195 (6)	0.4914 (19)	0	2.42 (2)*	1.0
O15	0.2629 (7)	0.207 (4)	0	2.42 (2)*	1.0

O16	0.8595 (12)	0.788 (3)	0.5	2.42 (2)*	1.0
O17	0.9297 (9)	0.578 (3)	0.5	2.42 (2)*	1.0
O18	0.8922 (11)	0.324 (5)	0.5	2.42 (2)*	1.0
O19	0.9774 (7)	0.3100 (15)	0.5	2.42 (2)*	1.0
O20	0.9001 (5)	0.0617 (19)	0.5	2.42 (2)*	1.0
O21	0	0	0.5	2.42 (2)*	1.0
O23	0.2374 (8)	0.074 (4)	0.5	2.42 (2)*	1.0
O24	0.1703 (7)	0.488 (2)	0.5	2.42 (2)*	1.0
O25	0.1918 (9)	0.784 (2)	0.5	2.42 (2)*	1.0
