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The Crystal Structure of $NaNb_{13}O_{33}$ and the Geometrical Principles of the Homologous Series $NaM_{3n+1}O_{8n+1}$

STEN ANDERSSON

Research Institute of National Defence, Dept. 4, Stockholm 80, and Institute of Inorganic Chemistry, University of Stockholm, Stockholm, Sweden

The ternary oxide $NaNb_{13}O_{33}$ is monoclinic, space group $C2/m$, with the unit-cell dimensions:
$a = 22.40$ Å, $b = 3.834$ Å, $c = 15.37$ Å, $\beta = 91.47°$
Its crystal structure has been determined, using single-crystal methods. The niobium atoms are in octahedral coordination while the sodium atom is in a planar, almost square coordination. From the atomic arrangement of the oxide, a homologous series can be proposed with the general formula $NaM_{3n+1}O_{8n+1}$, $NaNb_{13}O_{33}$ being the member for $n = 4$.

Two new oxides were identified some time ago in Na_2O—Nb_2O_5 system by Reisman *et al.*[1] A crystal structure determination has now been carried out of one of these phases, and the composition shown to be slightly different from that proposed by Reisman *et al.* The formula thus derived, $NaNb_{13}O_{33}$, will be used for the sake of simplicity in the following text to designate this compound.

EXPERIMENTAL

Pure α-Nb_2O_5 was obtained in a way described earlier.[2] $NaNbO_3$ was made by mixing α-Nb_2O_5 and Na_2CO_3 of high purity and heating for two days at 1100°C. Different compositions around the mole ratio $Na_2O \cdot 14Nb_2O_5$ were obtained by mixing $NaNbO_3$ and α-Nb_2O_5. The samples were sealed in platinum capsules and heated at 1100°C for a week. Guinier powder patterns confirmed the presence of a phase different from α-Nb_2O_5. The complete phase analysis of the system $NaNbO_3$—Nb_2O_5, performed at elevated temperatures at 1 atm. as well as at several thousand atm. in supercritical water, will soon be published.[3] The indexed Guinier powder pattern of $NaNb_{13}O_{33}$ will also be given in that publication.

Rod-formed, colourless crystals were obtained from a sample which had been melted and then heated at 1000°C for a few days. The intensities were recorded for the $h0l$, $h1l$ and $h2l$ levels with copper radiation using Weissenberg methods and the multiple-film technique. The dimensions of the rod-like crystal were $0.01 \times 0.02 \times 0.2$ mm³. Due to the very small crystal used no absorption corrections were considered necessary. In the early stage of the refinement of the structure, an overall temperature factor of $B = 0.7$ Å was derived. The Nb^{5+} scattering curve used was derived from the tables

of Thomas and Umeda.[4] For Na^+ and O^{2-} the scattering curves given by Freeman [5] and Suzuki [6] were used.

The unit-cell dimensions were found to be:

$a = 22.40$ Å, $b = 3.834$ Å, $c = 15.37$ Å, $\beta = 91.47°$

The observed density as obtained by Reisman, Holtzberg and Banks is 4.40. With 2 formula units of $NaNb_{13}O_{33}$ in the unit cell, the calculated density is 4.42.

STRUCTURE DETERMINATION

The systematic absences, hkl with $h + k \neq 2n$, gave the space group alternatives $C2$, Cm or $C2/m$. The $h0l$ and $h2l$, with due regard for observational errors and for the effects of thermal motion, were found to be identical. All the atoms were therefore assumed to be situated in two planes normal to the y-axis and $b/2$ apart, making $C2/m$ a probable space group.

A simple orthogonal sub-cell with strong similarities to the Nb_3O_7F structure [7] could be recognized in the reciprocal lattice. From the index relations, the vector relationships between the true cell and the sub-cell were found to be:

$$\mathbf{a} = \mathbf{a}_{Nb_3O_7F} + 2\ \mathbf{c}_{Nb_3O_7F}$$
$$\mathbf{b} = \mathbf{b}_{Nb_3OF_7}$$
$$\mathbf{c} = -0.3\ \mathbf{a}_{Nb_3O_7F} + 3.5\ \mathbf{c}_{Nb_3O_7F}$$

Table 1. Atomic coordinates and temperature factors with standard deviations for $NaNb_{13}O_{33}$.

Space group $C2/m$ $(0,0,0;\frac{1}{2},\frac{1}{2},0)$ +

Atom	Point position	x	y	z	B
2 Na	2(*d*)	0	$\frac{1}{2}$	$\frac{1}{2}$	3.15 ± 0.80
2 Nb_1	2(*a*)	0	0	0	1.66 ± 0.12
4 Nb_2	4(*i*)	0.0709 ± 0.0002	0	0.2283 ± 0.0002	1.20 ± 0.08
4 Nb_3	4(*i*)	0.2255 ± 0.0002	0	0.1362 ± 0.0002	0.84 ± 0.07
4 Nb_4	4(*i*)	0.1557 ± 0.0002	0	0.9022 ± 0.0002	1.02 ± 0.07
4 Nb_5	4(*i*)	0.1370 ± 0.0002	0	0.4682 ± 0.0002	0.91 ± 0.07
4 Nb_6	4(*i*)	0.2936 ± 0.0002	0	0.3745 ± 0.0002	0.91 ± 0.07
4 Nb_7	4(*i*)	0.0864 ± 0.0002	0	0.6739 ± 0.0002	0.83 ± 0.07
2 O_1	2(*b*)	0	$\frac{1}{2}$	0	2.1 ± 1.1
4 O_2	4(*i*)	0.083 ± 0.001	0	0.949 ± 0.002	1.5 ± 0.7
4 O_3	4(*i*)	0.322 ± 0.001	0	0.097 ± 0.002	1.0 ± 0.6
4 O_4	4(*i*)	0.251 ± 0.001	0	0.862 ± 0.002	1.5 ± 0.7
4 O_5	4(*i*)	0.153 ± 0.001	0	0.196 ± 0.002	2.0 ± 0.8
4 O_6	4(*i*)	0.429 ± 0.002	0	0.755 ± 0.002	2.7 ± 0.9
4 O_7	4(*i*)	0.194 ± 0.001	0	0.030 ± 0.002	1.1 ± 0.9
4 O_8	4(*i*)	0.035 ± 0.002	0	0.117 ± 0.002	2.8 ± 0.9
4 O_9	4(*i*)	0.127 ± 0.001	0	0.789 ± 0.002	1.0 ± 0.6
4 O_{10}	4(*i*)	0.270 ± 0.001	0	0.268 ± 0.002	1.0 ± 0.7
4 O_{11}	4(*i*)	0.101 ± 0.001	0	0.365 ± 0.002	1.0 ± 0.7
4 O_{12}	4(*i*)	0.013 ± 0.001	0	0.708 ± 0.002	0.6 ± 0.6
4 O_{13}	4(*i*)	0.391 ± 0.001	0	0.339 ± 0.002	2.0 ± 0.8
4 O_{14}	4(*i*)	0.181 ± 0.001	0	0.612 ± 0.002	1.4 ± 0.7
4 O_{15}	4(*i*)	0.222 ± 0.001	0	0.432 ± 0.002	0.8 ± 0.6
4 O_{16}	4(*i*)	0.349 ± 0.001	0	0.507 ± 0.002	1.6 ± 0.7
4 O_{17}	4(*i*)	0.072 ± 0.001	0	0.545 ± 0.002	1.6 ± 0.7

From this expression an idealized structure was obtained by methods that are discussed elsewhere.[8] This structure was of the composition $NaNb_{13}O_{33}$ in concordance with the formula suggested by the density data and rather close to the composition $Na_2O{\cdot}14Nb_2O_5$, which originally was given by Reisman *et al.* for this compound. As the ideal structure showed up to have some similarities with the structure of $Ti_2Nb_{10}O_{29}$[9] which is discussed below, distortions were thus introduced into the ideal structure according to the structure of $Ti_2Nb_{10}O_{29}$. The first set of structure factors gave reasonable agreement and an electron density projection on to (010) could be calculated using 90 of the 230 observed, independent reflections. The atomic parameters derived gave a very good overall improvement and after three F_o-F_c Fourier projections the discrepancy factor had dropped to 17.3 %, calculated for all the observed *h*0*l* reflections.

Assuming *C*2/*m* to be the correct space group the *h*0*l* and *h*1*l* data were finally used in the refinement, which was done by means of ten least-squares cycles, using the Åsbrink-Brändén program written for the Swedish computer FACIT.[10] The least-squares procedure brought down the *R*-factor to 9.1 %. Atomic coordinates and temperature factors with standard deviations are given in Table 1. The weight analysis for the last cycle of refinement is given in Table 2.

Table 2. Weight analysis used in the last cycle of the refinement of $NaNb_{13}O_{33}$. w = weighting factor. $\Delta = ||F_o|-|F_c||$

Interval sin Θ	$w\,\Delta^2$	Number of independent reflections	Interval F_o	$w\,\Delta^2$	Number of independent reflections
0.00–0.45	0.95	133	0– 40	0.49	6
0.45–0.57	0.90	79	40– 80	0.65	132
0.57–0.66	1.25	44	80–120	1.00	114
0.66–0.72	1.06	36	120–160	1.10	67
0.72–0.78	0.87	39	160 -200	1.41	38
0.78–0.83	0.81	42	200–240	1.81	17
0.83–0.87	1.24	27	240–280	1.33	16
0.87–0.91	1.20	36	280–320	1.56	17
0.91–0.95	0.54	10	320–360	0.62	14
0.95–0.98	1.99	4	360–400	1.21	31

DESCRIPTION OF THE STRUCTURE

The crystal structure of $NaNb_{13}O_{33}$ is shown in Fig. 1. The structure is built up of NbO_6 octahedra having corners and edges in common. The Nb–O distances vary between 1.71 and 2.40 Å. The shortest O–O distance is 2.62 Å and this corresponds to an edge which is common to two octahedra. The sodium atoms have an environment of four oxygens lying in one plane with the four Na–O distances of 2.60 Å. They approximately form a square (3.48 Å × 3.83 Å). This is a rare coordination for sodium, but has nevertheless been observed

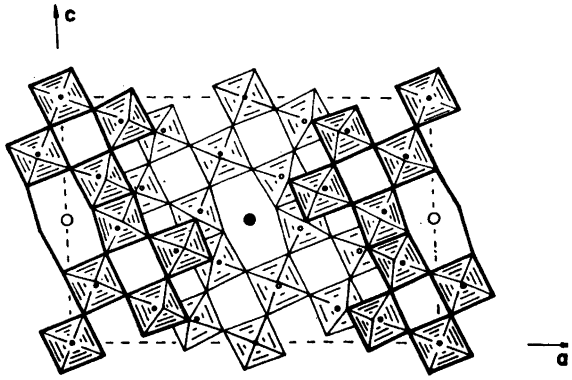

Fig. 1. The crystal structure of $NaNb_{13}O_{33}$. The niobium atoms are the smaller, and sodium the larger circles.

earlier in sodium titanium dioxide bronze and also to some extent, in sodium hexatitanate.[8]

The complex octahedral arrangement of the structure is better understood if it is compared with the structures of the mixed titanium niobium oxides determined by Wadsley.[9,11] Wadsley found, from the structures of $TiNb_2O_7$ and $Ti_2Nb_{10}O_{29}$, these oxides to be members of a series $M_{3n}O_{8n-3}$. The parent structure of this homologous series was at that time a hypothetical arrangement of octahedra with the composition M_3O_8. In Fig. 2 it is shown, according

Table 3. Interatomic distances in $NaNb_{13}O_{33}$.

Distance	Å	σ Å	Mean value Å	Distance	Å	σ Å	Mean value Å
2 Nb_1-O_1	1.917	0.00		Nb_5-O_{11}	1.76	0.03	
2 Nb_1-O_2	2.04	0.03	1.97	Nb_5-O_{14}	2.39	0.03	
2 Nb_1-O_8	1.94	0.04		Nb_5-O_{15}	2.00	0.03	2.00
				2 Nb_5-O_{16}	1.98	0.02	
Nb_2-O_5	1.92	0.04		Nb_5-O_{17}	1.90	0.03	
2 Nb_2-O_6	1.93	0.02					
Nb_2-O_8	1.87	0.04	2.00	Nb_6-O_{10}	1.71	0.03	
Nb_2-O_{11}	2.19	0.03		Nb_6-O_{13}	2.26	0.04	
Nb_2-O_{12}	2.14	0.03		2 Nb_6-O_{14}	2.01	0.02	2.03
				Nb_6-O_{15}	1.85	0.03	
Nb_3-O_3	2.26	0.03		Nb_6-O_{16}	2.36	0.03	
2 Nb_3-O_4	1.99	0.02					
Nb_3-O_5	1.89	0.04	2.02	Nb_7-O_9	1.97	0.03	
Nb_3-O_7	1.76	0.03		Nb_7-O_{12}	1.74	0.03	
Nb_3-O_{10}	2.23	0.03		2 Nb_7-O_{13}	1.99	0.02	2.01
				Nb_7-O_{14}	2.35	0.03	
Nb_4-O_2	1.80	0.03		Nb_7-O_{17}	2.00	0.03	
2 Nb_4-O_3	1.98	0.02					
Nb_4-O_4	2.24	0.03	1.99	4 Na $-O_{17}$	2.59	0.04	
Nb_4-O_7	2.12	0.03					
Nb_4-O_9	1.84	0.03					

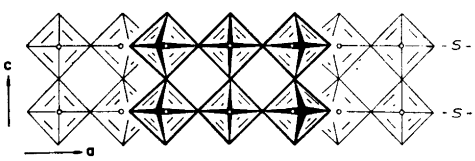

Fig. 2. The Nb_3O_7F structure described by means of Wadsley's S-units.

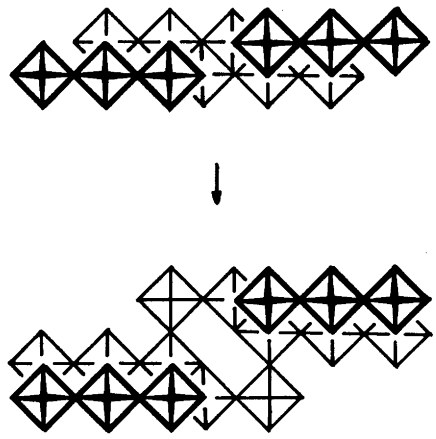

Fig. 3. The shear plane of the homologous series $M_{3n}O_{8n-3}$ as compared with the shear plane of $NaM_{3n+1}O_{8n+1}$.

to Wadsley, how this parent structure is built up of so-called S-units. Blocks of the ReO_3-structure type, three octahedra in width, are fused together by means of octahedra sharing edges and a hypothetical structure of the formula M_3O_8 is found. A compound with the composition Nb_3O_7F has now been found to have this actual structure.[7] Different members in Wadsley's series $M_{3n}O_{8n-3}$ are then obtained if shear planes are introduced into the M_3O_8 structure. The shear planes always run parallel to the S-unit in the $M_{3n}O_{8n-3}$ series. The

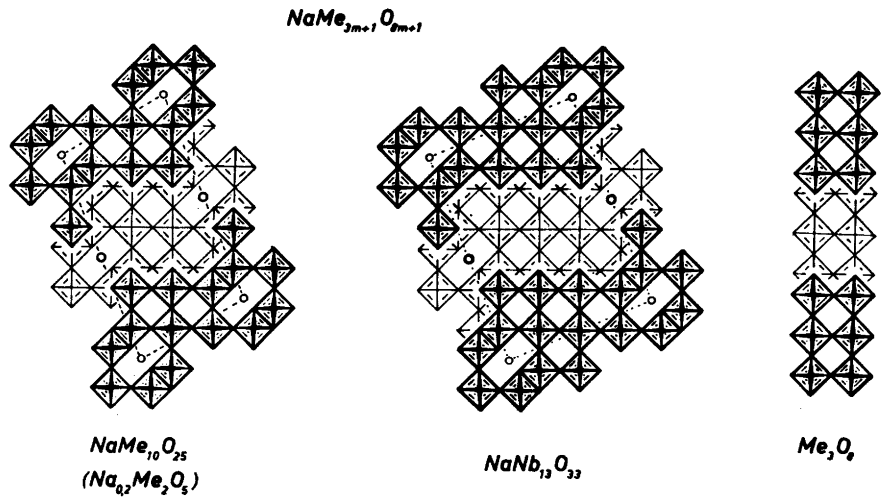

Fig. 4. The homologous series $NaM_{3n+1}O_{8n+1}$ with the members $n = 3$ ($NaM_{10}O_{25}$, hypothetical), $n = 4$ ($NaNb_{13}O_{33}$) and $n = \infty$ (Nb_3O_7F).

are, however, here interrupted in a regular way in order to form holes or tunnels for the sodium atoms. In this way a shear plane is formed parallel to the *a*-direction, which contains the sodium atoms. This new shear plane can be derived from the shear plane of the series $M_{3n}O_{8n-3}$ by means of a simple shift, which is demonstrated in Fig. 3. The shift forms a hole or tunnel in the lattice, which in $NaNb_{13}O_{33}$ is occupied by the sodium atoms. This shear plane is *not parallel* to the S-units, but nevertheless, different ternary oxides can now be proposed as demonstrated in Fig. 4. This is done by means of either M_3O_8 structure is also the basic unit in the $NaNb_{13}O_{33}$ structure. The S-units expanding or compressing the space between the shear planes and fitting parts of the M_3O_8 structure type between them. When there are four S-units between the shear planes (or sodium atoms) the structure of $NaNb_{13}O_{33}$ is formed. The S-units are interrupted so that they contain 13 Nb-octahedra. When there are three S-units between the shear planes, a hypothetical structure of the chemical formula $NaM_{10}O_{25}$ ($Na_{0.2}Nb_2O_5$) is obtained. The S-units are now interrupted so that they contain 10 Nb octahedra. This could very well be the structure for an alkali metal niobium pentoxide bronze.

The above discussion leads to a homologous series with the general formula $NaM_{3n+1}O_{8n+1}$. $NaNb_{13}O_{33}$ then corresponds to $n = 4$, the hypothetical $NaM_{10}O_{25}$ corresponds to $n = 3$ and Nb_3O_7F corresponds to $n = \infty$.

The similarities between the series $NaM_{3n+1}O_{8n+1}$ and Wadsley's $M_{3n}O_{8n-3}$ are demonstrated in Fig. 5 where one block of $NaNb_{13}O_{33}$ is com-

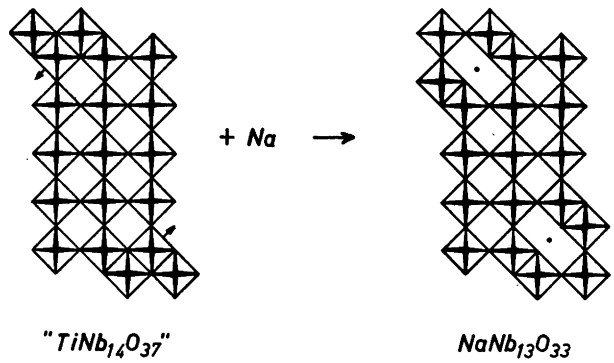

Fig. 5. One block of the $NaNb_{13}O_{33}$ structure compared with a corresponding block from the homologous series $M_{3n}O_{8n-3}$. If one octahedron in the "$TiNb_{14}O_{37}$" structure is shifted along one octahedron edge in the direction of the arrow in the figure, the hypothetical $NaNb_{13}O_{33}$ is obtained.

pared with a corresponding block in the hypothetical "$TiNb_{14}O_{37}$". In the same way the $TiNb_2O_7$ and $Ti_2Nb_{10}O_{29}$ structures are related to the hypothetical NaM_7O_{17} and $NaM_{10}O_{25}$. In general it can be said as a geometrical conclusion that when a sodium atom enters a lattice of a $M_{3n}O_{8n-3}$-series type compound, a lattice of the $NaM_{3n+1}O_{8n+1}$-series type can be formed.

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REFERENCES

1. Reisman, A., Holtzberg, F. and Banks, E. *J. Am. Chem. Soc.* **80** (1958) 37.
2. Andersson, S. and Åström, A. *Acta Chem. Scand.* **18** (1964) 2233.
3. Andersson, S. *To be published.*
4. Thomas, L. H. and Umeda, K. *J. Chem. Phys.* **26** (1957) 293.
5. Freeman, A. J. *Acta Cryst.* **12** (1959) 261.
6. Suzuki, T. *Acta Cryst.* **13** (1960) 279.
7. Andersson, S. *Acta Chem. Scand.* **18** (1964) 2339.
8. Andersson, S. and Wadsley, A. D. *Acta Cryst.* **15** (1962) 194.
9. Wadsley, A. D. *Acta Cryst.* **14** (1961) 664.
10. Åsbrink, S. and Brändén, C.-I. *List of Crystallographic Computer Programs* (1962). Accession number 6023.
11. Wadsley, A. D. *Acta Cryst.* **14** (1961) 660.

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