

## On the Crystal Structures of Some Phases in the $\text{Al}_2\text{O}_3\text{-Nb}_2\text{O}_5$ -System

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A phase analysis of the  $\text{Al}_2\text{O}_3\text{-Nb}_2\text{O}_5$ -system has been performed in the composition range  $1 > x_{\text{Nb}_2\text{O}_5} > \frac{1}{2}$  at temperatures between 1100°C and 1500°C. Besides the previously known phases  $\text{AlNb}_{11}\text{O}_{29}$  and  $\text{Al}_4\text{Nb}_{24\frac{1}{2}}\text{O}_{62}$ , a new phase “ $(\text{Al,Nb})\text{O}_{2.283}$ ”, probably  $\text{Al}_4\text{Nb}_{62\frac{1}{2}}\text{O}_{132}$ , has been observed.

Two previously unknown phases in the  $\text{Al}_2\text{O}_3\text{-Nb}_2\text{O}_5$ -system,  $\text{Al}_2\text{O}_3 \cdot 9\text{Nb}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3 \cdot 25\text{Nb}_2\text{O}_5$ , have been reported by Layden.<sup>1</sup> The first oxide was thought to correspond to  $\text{NbO}_{2.40}$ ,<sup>2</sup> which was later shown to consist of two forms of  $\text{Nb}_{12}\text{O}_{29}$ ,<sup>3,4</sup> and the second oxide to  $\text{Nb}_{11}\text{O}_{27}$ .<sup>2</sup> Roth, Wadsley and Gatehouse<sup>5</sup> have pointed out that  $\text{AlNb}_{11}\text{O}_{29}$  is isostructural with the corresponding phase in the  $\text{TiO}_2\text{-Nb}_2\text{O}_5$ -system. Waring and Roth<sup>6</sup> agree with the above authors on the correspondence between  $\text{Al}_2\text{O}_3 \cdot 25\text{Nb}_2\text{O}_5$  and  $\text{Nb}_{11}\text{O}_{27}$ . Gruehn and Schäfer<sup>7</sup> have suggested the formulae  $(\text{Al,Nb})\text{O}_{2.417}$ , (corresponding to the monoclinic form of  $\text{Nb}_{12}\text{O}_{29}$ )<sup>4</sup> for  $\text{Al}_2\text{O}_3 \cdot 9\text{Nb}_2\text{O}_5$  and  $(\text{Al,Nb})\text{O}_{2.467}$  (corresponding to the lower limit,  $\text{NbO}_{2.467}$ , of  $\text{Nb}_{25}\text{O}_{62}$ <sup>15</sup>) for  $\text{Al}_2\text{O}_3 \cdot 25\text{Nb}_2\text{O}_5$ . In order to ascertain the proposed phase composition a reinvestigation of the  $\text{Nb}_2\text{O}_5$ -rich part of the  $\text{Al}_2\text{O}_3\text{-Nb}_2\text{O}_5$ -system has been performed.

### | EXPERIMENTAL

Mixtures of high purity  $\text{Al}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  were melted at about 1500°C. Some of the melted samples were tempered at various temperatures in the range 1250–1500°C for 1–11 days. Other intimate mixtures were tempered under the same conditions but without first being melted. The samples were quenched and investigated with Guinier and Weissenberg methods. Experimental data obtained from the phase analysis are given in Table 1. In several samples more than two phases occur, indicating either that equilibrium is not reached or that small amounts of neighbouring phases are formed during the quenching. The densities were determined from the apparent loss of weight in benzene.

Table 1. Experimental data from the phase analysis of samples  $(\text{Al,Nb})\text{O}_x$  with  $2.3 < x < 2.5$ . Reflexions from the following phases were found in Guinier photographs of the quenched samples:

Phase 1 =  $\text{H-Nb}_2\text{O}_5$ ; 2 = " $(\text{Al,Nb})\text{O}_{2.483}$ "; 3 =  $\text{Al}_2\text{Nb}_{24\frac{1}{2}}\text{O}_{62}$ ; 4 =  $\text{AlNb}_{11}\text{O}_{29}$ ; 5 =  $\text{AlNbO}_4$ .

Molar ratio $\text{Al}_2\text{O}_3/\text{Nb}_2\text{O}_5$	Heat treatment	Phases found
1/40	melted	1, 2, 3, 4
1/40	melted and tempered at 1400°C for 4 d	1, 3
1/25	melted	1, 2, 3, 4
1/25	melted and tempered at 1400°C for 3 d	3.
1/21	melted	1, <sup>a</sup> 2, <sup>a</sup> 3, 4 <sup>a</sup>
1/21	melted and tempered at 1400°C for 4 d	3, 4 <sup>a</sup>
1/21	tempered at 1400°C for 1 d	3, 4 <sup>a</sup>
1/11	melted and tempered at 1400°C for 1 d	3, 4
1/11	tempered at 1400°C for 1 d	3, 4
1/9	melted	3, <sup>a</sup> 4
1/9	melted and tempered at 1100°C for 11 d	4
1/8.5	tempered at 1400°C for 1 d	4
1/5	melted	4, 5

<sup>a</sup> very little.

#### RESULTS OF THE X-RAY STUDIES

A comparison of Guinier and single crystal data shows that there is no doubt that  $\text{AlNb}_{11}\text{O}_{29}$  and  $\text{Al}_2\text{Nb}_{24\frac{1}{2}}\text{O}_{62}$  are isostructural with  $\text{Nb}_{12}\text{O}_{29}(\text{mon})^4$  and  $\text{TiNb}_{24}\text{O}_{62}$ ,<sup>8</sup> respectively.  $d$ -Values for the two Al-Nb-oxides agree with those given by Layden<sup>1</sup> for  $\text{Al}_2\text{O}_3 \cdot 9\text{Nb}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3 \cdot 25\text{Nb}_2\text{O}_5$ . Crystallographic

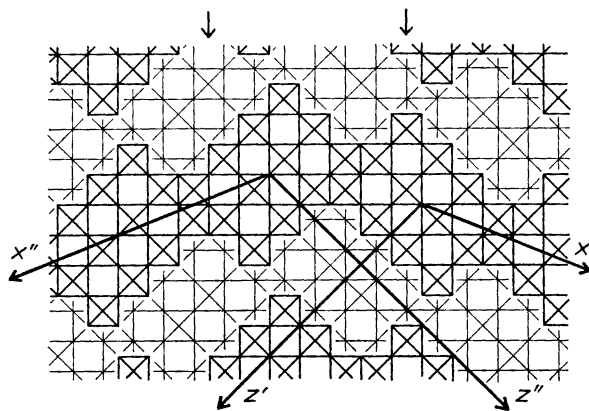


Fig. 1. Idealized projection on the  $xz$ -plane showing a plausible mode of twinning of two  $\text{AlNb}_{11}\text{O}_{29}$  crystals along their  $20\bar{1}$  planes. Heavy squares with diagonals indicate  $\text{MeO}_6$ -octahedra ( $\text{Me}=\text{Nb}$  or  $\text{Al}$ ) in  $y=0$  and fine squares with diagonals those in  $y=\frac{1}{2}$ . The axial directions of the two crystals are indicated (cf. the idealized picture of  $\text{Nb}_{12}\text{O}_{29}(\text{mon})^4$ ). The two small arrows indicate the positions of two planes, parallel to  $20\bar{1}$ , delimiting those parts of the structure common to both crystals.

data for the two compounds and powder pattern data, refined using a computer program written by Lindqvist,<sup>9</sup> are given in Tables 2 and 3.

All crystals of  $\text{AlNb}_{11}\text{O}_{29}$  hitherto investigated show the same kind of twinning. Examination of the reciprocal lattice of such a twinned crystal shows two lattices with their  $a^*$ -axes mutually inclined at an angle of very close to  $90^\circ$  but with their  $b^*$ -axes and  $20\bar{1}$  directions in common. The crystals must thus be twinned along the  $20\bar{1}$  planes with their  $c$ -axes inclined at an angle of very close to  $90^\circ$ . A plausible ideal mode of twinning of two  $\text{AlNb}_{11}\text{O}_{29}$ -crystals is shown in Fig. 1.

In addition to the powder patterns of  $H\text{-Nb}_2\text{O}_5$ ,  $\text{Al}_2\text{Nb}_{24\frac{1}{2}}\text{O}_{62}$ , and  $\text{AlNb}_{11}\text{O}_{29}$ , lines corresponding to a new phase were observed in Guinier photographs of melted, but not tempered, samples with  $x_{\text{Nb}_2\text{O}_5} > 0.95$ . Weissenberg photographs  $h0l$ - $h2l$  for a single crystal found in one of these samples indicated the presence of a phase isostructural with  $\text{NbO}_{2.483}$ .<sup>10</sup> The new phase should therefore be “ $(\text{Al,Nb})\text{O}_{2.483}$ ”. No analysis has, however, yet been carried out to ascertain its composition. A phase with this composition has been predicted by Gruehn.<sup>11</sup>

Table 2. Crystallographic data for  $\text{AlNb}_{11}\text{O}_{29}$ .

Unit cell dimensions:  $a = (31.14 \pm 0.02)$  Å;  $b = (3.813 \pm 0.002)$  Å;  $c = (20.55 \pm 0.02)$  Å;  $\beta = (113.26 \pm 0.04)^\circ$ .

Systematically absent reflexions:  $hkl$  with  $k+l=\text{odd}$   
 $h0l$  with  $h=\text{odd}$ .

Possible space groups: No. 15  $A2/a$  and No. 9  $Aa$ .

$\rho_{\text{calc}} = 4.49$  g  $\text{cm}^{-3}$ ;  $\rho_{\text{obs}} = (4.47 \pm 0.02)$  g  $\text{cm}^{-3}$ .

$Z = 4$ .

Powder pattern data.  $\text{CuK}\alpha_1$  radiation.  $\lambda(\text{CuK}\alpha_1) = 1.5405$  Å.

$I$ obs	$\sin^2\theta \times 10^5$ obs	$d$ obs	$h$ $k$ $l$	$\sin^2\theta \times 10^5$ calc	$d$ calc
vw	290	14.30	2 0 0	290	14.30
vw	611	9.85	2 0 $\bar{2}$	608	9.87
vw	665	9.44	0 0 2	666	9.44
vw	1161	7.149	4 0 0	1160	7.152
m	2257	5.127	2 0 $\bar{4}$	2258	5.126
vw	2427	4.944	4 0 $\bar{4}$	2434	4.937
m	2609	4.769	6 0 0	2610	4.768
vw	3639	4.038	2 0 4	3646	4.033
vvst	4244	3.739	0 1 1	4246	3.738
vw	4307	3.712	6 0 2	4316	3.708
w	4358	3.690	2 1 $\bar{1}$	4363	3.688
vst	4644	3.574	8 0 0	4639	3.576
vw	4707	3.550	2 1 1	4710	3.549
vst	5074	3.420	4 0 $\bar{6}$	5067	3.422
vw	5204	3.377	4 0 4	5209	3.375
vw	5238	3.366	2 0 $\bar{6}$	5238	3.366
m	5341	3.333	2 1 $\bar{3}$	5347	3.331
vw	5472	3.293	6 0 $\bar{6}$	5477	3.291
vw	5576	3.262	0 1 3	5577	3.262
vw	5750	3.212	4 1 1	5753	3.211
vw	6458	3.031	10 0 4	6442	3.035
vw	7245	2.862	10 0 0	7249	2.861

Table 3. Crystallographic data for  $\text{Al}_2\text{Nb}_{244}\text{O}_{62}$ .

Unit cell dimensions:  $a=(29.78 \pm 0.02)$  Å;  $b=(3.818 \pm 0.002)$  Å;  $c=(21.10 \pm 0.02)$  Å;  $\beta=(94.94 \pm 0.04)^\circ$ .

Systematically absent reflexions:  $hkl$  with  $h+k=\text{odd}$ .

Possible space groups: No. 12  $C2/m$ , No. 8  $Cm$ , and No. 5  $C2$ .

$\rho_{\text{calc}}=4.56 \text{ g cm}^{-3}$ ;  $\rho_{\text{obs}}=(4.52 \pm 0.02) \text{ g cm}^{-3}$ .

$Z=2$ .

Powder pattern data.  $\text{CuK}\alpha_1$  radiation.  $\lambda(\text{CuK}\alpha_1)=1.5405$  Å.

<i>I</i> obs	$\sin^2\theta \times 10^5$ obs	<i>d</i> obs	<i>h</i> <i>k</i> <i>l</i>	$\sin^2\theta \times 10^5$ calc	<i>d</i> calc
vw	269	14.85	2 0 0	269	14.82
vw	534	10.54	0 0 2	537	10.51
vw	739	8.96	2 0 2	741	8.95
vw	1073	7.44	4 0 0	1078	7.42
vw	1274	6.82	4 0 1	1278	6.81
vwv	2141	5.264	0 0 4	2147	5.257
m	2657	4.725	6 0 1	2658	4.725
w	4129	3.791	1 1 0	4137	3.787
w	4280	3.723	1 1 1	4288	3.720
vvst	4583	3.598	8 0 1	4578	3.600
vw	4660	3.568	3 1 0	4676	3.562
vvst	4905	3.478	2 0 $\bar{6}$	4904	3.478
vwv	5124	3.403	8 0 2	5111	3.407
			8 0 $\bar{3}$	5127	3.402
st	5288	3.349	1 1 $\bar{3}$	5296	3.347
			2 0 6	5297	3.347
vw	5500	3.284	4 0 $\bar{6}$	5516	3.280
w	5748	3.213	5 1 0	5754	3.211
vwv	5957	3.156	5 1 1	5971	3.152
vwv	6275	3.075	6 0 5	6272	3.076
vwv	6296	3.070	4 0 6	6302	3.068
vwv	6619	2.994	3 1 4	6627	2.992
vwv	6738	2.967	10 0 0	6738	2.967
w	7042	2.903	10 0 1	7036	2.904
st	7412	2.829	1 1 $\bar{5}$	7410	2.830

Since the formula  $\text{Nb}_{53}\text{O}_{132}$  has been proposed for the compound  $\text{NbO}_{2.483}$ ,<sup>10</sup> “(Al,Nb) $\text{O}_{2.483}$ ” may be given the corresponding formula  $\text{Al}_2\text{Nb}_{524}\text{O}_{132}$ . The following unit cell dimensions have been obtained from Weissenberg photographs:

$$a=63 \text{ Å}; b=3.8 \text{ Å}; c=21 \text{ Å}; \beta=95^\circ$$

Attempts to prepare this phase in a pure state have so far not been successful.

#### DISCUSSION

It is of interest to compare the phase relations in the  $\text{Al}_2\text{O}_3$ -system with those of the rather well known  $\text{TiO}_2\text{-Nb}_2\text{O}_5$ -<sup>8,12-14</sup> and  $\text{NbO}_2\text{-Nb}_2\text{O}_5$ -systems.<sup>2-4,10,15,16</sup> Both systems contain the phases  $(\text{Me,Nb})_{25}\text{O}_{62}$  (Me=Ti, Nb<sup>IV</sup> or Al) and  $(\text{Me,Nb})\text{O}_{2.483}$ , but the existence of a stability interval for

"(Al,Nb)O<sub>2.483</sub>" has not yet been proved. For Me=Ti,<sup>12,13</sup> Nb(IV),<sup>3,4</sup> Ga, Fe(III), and Ni<sup>14</sup> the oxide (Me,Nb)<sub>12</sub>O<sub>29</sub> exists in two modifications, one monoclinic and one orthorhombic, the former observed at low temperatures ( $\leq 1100-1200^\circ\text{C}$ ) and the latter at high ( $\leq 1100-1200^\circ\text{C}$ )<sup>14,16</sup>. No compound AlNb<sub>11</sub>O<sub>29</sub>(o-rh) has been found in the Al<sub>2</sub>O<sub>3</sub>-Nb<sub>2</sub>O<sub>5</sub>-system. The monoclinic oxide AlNb<sub>11</sub>O<sub>29</sub> seems to be stable up to its melting point, *i.e.* at temperatures at which the orthorhombic modifications are stable in the other five systems.

Remarkable is the discrepancy between the crystallographic compositions AlNb<sub>11</sub>O<sub>29</sub> (Al<sub>2</sub>O<sub>3</sub>/Nb<sub>2</sub>O<sub>5</sub>=1/11) and Al<sub>4</sub>Nb<sub>24½</sub>O<sub>62</sub> (Al<sub>2</sub>O<sub>3</sub>/Nb<sub>2</sub>O<sub>5</sub>=1/49) and the compositions of the corresponding one-phase samples where Al<sub>2</sub>O<sub>3</sub>/Nb<sub>2</sub>O<sub>5</sub>=1/9 and 1/25, respectively, which agree with the data observed by Layden.<sup>1</sup> The reason for this discrepancy is not yet clearly understood, but an analogous phenomenon is, however, discussed for NbO<sub>2.483</sub>.<sup>10</sup> The composition Al<sub>2</sub>O<sub>3</sub>/Nb<sub>2</sub>O<sub>5</sub>=1/25 yields a metal/oxygen molar ratio equal to 2.462 which is in good agreement with the value 2.467 given by Gruehn and Schäfer.<sup>7</sup>

Investigations of the related systems, ZnO-Nb<sub>2</sub>O<sub>5</sub>, NiO-Nb<sub>2</sub>O<sub>5</sub>, and ZrO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub>, are being conducted in order to examine the effect of the ionic radius, electronegativity, and ionic charge of the Me-ion on the formation of Nb<sub>2</sub>O<sub>5</sub>-rich (Me,Nb)O<sub>x</sub>-phases.

*Acknowledgements.* The author wishes to thank Professor A. Magnéli, Professor G. Lundgren and Dr. R. Gruehn for many valuable discussions in connection with this work.

This investigation forms part of a research programme supported by the *Swedish Natural Science Research Council*.

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Received September 27, 1968.