Note on the Phase Composition of the $MgO—Nb_2O_5$ System

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In recent years, the crystal structures of some niobium-rich binary oxide phases have been studied at this department.[1,2] The existence of an orthorhombic phase with the formula $(Mg,Nb)O_{2.417}$, reported by Gruehn and Schäfer,[3] suggested that a study of the phase composition of the $MgO-Nb_2O_5$ system might prove interesting and an investigation of the niobium-rich half of this system has therefore been performed.

Intimate mixtures of high purity MgO and Nb_2O_5 were pressed into small tablets. The samples were either melted and quenched (I), melted, tempered, and quenched (II), or tempered and quenched without previous melting (III).

Table 1. Experimental data from the preparation of phases in the $MgO-Nb_2O_5$ system. The phases found in the different samples are denoted: $Me_{12}O_{29}$(mon) = $Mg_{2/3}Nb_{11\,1/3}O_{29}$(mon), $Me_{12}O_{29}$(o-rh) = $Mg_{2/3}Nb_{11\,1/3}O_{29}$(o-rh), H-Nb_2O_5 and $MgNb_2O_6$.[4]

Mg/Nb molar ratio	Method	Tempered °C	Tempered time, h	Phases found
1/34	I			$Me_{12}O_{29}$(mon) + H-Nb_2O_5
	II	1350	12	$Me_{12}O_{29}$(o-rh) + H-Nb_2O_5
	III	1375	24	$Me_{12}O_{29}$(o-rh) + H-Nb_2O_5
1/17	I			$Me_{12}O_{29}$(mon) + H-Nb_2O_5 [a]
	II	1350	12	$Me_{12}O_{29}$(o-rh) + H-Nb_2O_5 [a]
	III	1375	24	$Me_{12}O_{29}$(o-rh) + H-Nb_2O_5 [a]
1/3	II	1350	12	$Me_{12}O_{29}$(o-rh) + $MgNb_2O_6$

[a] Traces.

Table 2. Crystallographic data for $Mg_{2/3}Nb_{11\,1/3}O_{29}$(mon). Unit cell dimensions: $a = 31.24 \pm 0.01$ Å; $b = 3.832 \pm 0.001$ Å; $c = 20.67 \pm 0.01$ Å and $\beta = 113.11 \pm 0.005°$. Powder pattern data. $CuK\alpha_1$ radiation. $\lambda(CuK\alpha_1) = 1.54051$ Å.

I obs	$\sin^2\theta \times 10^5$ obs	d obs	$h\,k\,l$	$\sin^2\theta \times 10^5$ calc	d calc
w	604	9.911	$2\,0\,\bar{2}$	603	9.920
vvw	659	9.488	$0\,0\,2$	657	9.506
w	1143	7.205	$4\,0\,\bar{2}$	1124	7.265
			$4\,0\,0$	1150	7.183
m	2236	5.151	$2\,0\,\bar{4}$	2232	5.156
m	2585	4.791	$6\,0\,0$	2587	4.789
vs	4209	3.754	$0\,1\,1$	4205	3.756
w	4310	3.710	$2\,1\,\bar{1}$	4321	3.705
s	4597	3.592	$8\,0\,0$	4599	3.592
vvw	4670	3.564	$2\,1\,1$	4663	3.576
s	5017	3.439	$4\,0\,\bar{6}$	5012	3.440
vvw	5166	3.389	$2\,0\,\bar{6}$	5173	3.386
w	5266	3.357	$2\,1\,\bar{3}$	5293	3.348
vvw	5673	3.234	$4\,1\,1$	5695	3.228
vw	6431	3.037	$8\,0\,\bar{6}$	6416	3.041
vvw	7197	2.871	$10\,0\,0$	7186	2.872
s	7587	2.796	$2\,1\,\bar{5}$	7579	2.798
			$4\,1\,\bar{5}$	7588	2.796
m	8098	2.707	$8\,1\,\bar{1}$	8121	2.703
vvw	8919	2.579	$4\,0\,\bar{8}$	8926	2.578

Table 3. Crystallographic data for $Mg_{2/3}Nb_{11\frac{1}{3}}O_{29}$(o-rh). Unit cell dimensions: $a = 28.74 \pm 0.01$ Å; $b = 3.832 \pm 0.001$ Å; $c = 20.65 \pm 0.01$ Å. Powder pattern data. $CuK\alpha_1$ radiation. $\lambda(CuK\alpha_1) = 1.54051$ Å.

I obs	$\sin^2\theta \times 10^5$ obs	*d* obs	*h k l*	$\sin^2\theta \times 10^5$ calc	*d* calc
w	638	9.643	1 0 2	628	9.717
w	1164	7.139	4 0 0	1149	7.184
w	1191	7.058	3 0 2	1203	7.023
s	2227	5.161	0 0 4	2226	5.163
vvw	2305	5.073	1 0 4	2298	5.081
vvs	4189	3.763	0 1 1	4179	3.768
vvs	4259	3.732	1 1 1	4251	3.736
w	4469	3.644	2 1 1	4466	3.645
vs	4604	3.590	8 0 0	4598	3.592
vvw	4827	3.506	3 1 1	4825	3.506
vs	5017	3.439	0 0 6	5008	3.442
s	5080	3.417	1 0 6	5080	3.417
w	5283	3.351	0 1 3	5291	3.349
vw	5356	3.328	1 1 1	5363	3.326
vvw	5658	3.238	3 0 6	5655	3.239
s	6820	2.949	8 0 4	6823	2.949
vvw	7177	2.875	10 0 0	7183	2.874
s	7596	2.795	6 0 6	7594	2.795
w	7703	2.775	7 1 1	7699	2.776
vvw	7871	2.745	6 1 3	7877	2.744
w	8166	2.695	3 1 5	8164	2.696
w	8530	2.637	7 0 6	8528	2.638

Guinier photographs of all samples were taken using $Pb(NO_3)_2$ or KCl as internal standards. The results of the phase analysis are given in Table 1. The unit cell dimensions of the phases found were calculated on a IBM 360/65 computer using a computer program written by Lindquist and Wengelin.[5]

In the composition range investigated, two intermediate phases with the composition $2MgO.17Nb_2O_5$ were found. One of the oxides has orthorhombic symmetry and is identical with the phase reported by Gruehn and Schäfer,[3] while the other has monoclinic symmetry. An investigation of the powder patterns of these phases showed them to be isostructural with the $Ti_2Nb_{10}O_{29}$(o-rh) and $Ti_2Nb_{10}O_{29}$(mon) phases reported by Wadsley.[6] They must therefore have the formulae $Mg_{2/3}Nb_{11\frac{1}{3}}O_{29}$ (o-rh) and $Mg_{2/3}Nb_{11\frac{1}{3}}O_{29}$(mon), respectively. Crystallographic data for the two Mg-Nb-oxides are given in Tables 2 and 3.

A comparison between the $MgO-Nb_2O$-system and the $ZnO-Nb_2O_5$ system[2] showed almost complete agreement within the composition range investigated at temperatures over 1050°C. The orthorhombic form of $Mg_{2/3}Nb_{11\frac{1}{3}}O_{29}$ appears to be stable below its melting point down to about 1050°C, while its monoclinic counterpart is metastable within this temperature range. The formation of metastable $Mg_{2/3}Nb_{11\frac{1}{3}}O_{29}$ in quenched melts also agrees with corresponding observations in other oxide systems, *e.g.* $Ti_2Nb_{10}O_{29}$(mon) and $Nb^{IV}{}_2Nb^{V}{}_{10}O_{29}$(mon).[7]

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