Note on the Phase Composition of the ZnO-Nb_2O_5 System

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In their investigation of the Nb_2O_5-rich part of the ZnO-Nb_2O_5-system Waring and Roth [1] found the previously unknown phase $Zn_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$* thought to be isostructural with $Ti_2Nb_{10}O_{29}$(mon).[2] In order to ascertain whether or not this phase, like $Ti_2Nb_{10}O_{29}$,[2] existed also in an orthorhombic form, a reinvestigation of the Nb_2O_5-rich part of the system was performed.

* The formula has, by mistake, been written as $ZnNb_{11}O_{29}$ in the text of their paper.

Intimate mixtures of high purity ZnO and Nb_2O_5 were pressed into small tablets. The samples were either melted and quenched, melted, tempered and quenched, or tempered and quenched without first being melted.

Guinier photographs of all samples were taken using $Pb(NO_3)_2$ or KCl as internal standards. Weissenberg photographs *h0l-h2l* of single crystals found in the melted samples made the indexing of the powder patterns possible. The unit cell dimensions and their standard deviations were calculated on a SAAB D21 computer using a program written by Lindqvist.[3] The densities were calculated from the apparent loss of weight of the crystals in benzene.

In the composition range investigated, the following phases were observed: H-Nb_2O_5, $Zn_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$ (mon), $Zn_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$ (o-rh) and $ZnNb_2O_6$.[4] In samples tempered at 950–1000°C without previous melting only H-Nb_2O_5 and $ZnNb_2O_6$ were found, while in those tempered at 1050°C for 4 weeks a mixture of the two forms of $Zn_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$ was observed. Melted and

Table 1. Crystallographic data for $Zn_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$ (mon).

Unit cell dimensions: $a = (31.19 \pm 0.02)$ Å; $b = (3.829 \pm 0.002)$ Å; $c = (20.67 \pm 0.01)$ Å; $\beta = (112.9 \pm 0.1)°$.
Systematically absent reflexions: hkl with $k+l$ = odd, $h0l$ with h = odd.
Possible space groups: No. 15 $A2/a$ and No. 9 Aa.
$\varrho_{calc} = 4.56$ g cm^{-3}; $\varrho_{obs} = (4.51 \pm 0.02)$ g cm^{-3}.
$Z = 4$.
Powder pattern data. Cu$K\alpha_1$ radiation. λ(Cu$K\alpha_1$) = 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
w	603	9.919	$2\,0\,\bar{2}$	604	9.911
m	1145	7.198	$4\,0\,0$	1150	7.183
s	2225	5.164	$2\,0\,\bar{4}$	2231	5.157
s	2586	4.790	$6\,0\,0$	2588	4.788
vvs	4215	3.752	$0\,1\,1$	4211	3.754
w	4322	3.705	$2\,1\,\bar{1}$	4329	3.702
vs	4600	3.591	$8\,0\,0$	4602	3.591
vvw	4668	3.565	$2\,1\,1$	4667	3.565
s	5006	3.443	$4\,0\,\bar{6}$	5016	3.439
w	5163	3.390	$2\,0\,\bar{6}$	5168	3.388
s	5294	3.348	$2\,1\,\bar{3}$	5301	3.345
m	5443	3.302	$6\,0\,\bar{6}$	5439	3.303
m	5707	3.224	$4\,1\,1$	5699	3.227
vw	7184	2.874	$10\,0\,0$	7190	2.873
vw	7304	2.850	$6\,1\,1$	7307	2.850
vs	7588	2.796	$2\,1\,\bar{5}$	7582	2.797
			$4\,1\,\bar{5}$	7599	2.794

Table 2. Crystallographic data for $Zn_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$(o-rh).

Unit cell dimensions: $a = (28.71 \pm 0.02)$ Å; $b = (3.826 \pm 0.002)$ Å; $c = (20.66 \pm 0.01)$ Å.
Systematically absent reflexions: hkl with $k+l =$ odd, $h0l$ with $h =$ odd.
Possible space groups: No. 63 *Amma*, No. 40 *Am2a* and No. 36 $A2_1ma$.
$\varrho_{calc} = 4.57$ g cm^{-3}; $\varrho_{obs} = (4.52 \pm 0.02)$ g cm^{-3}.
$Z = 4$.
Powder pattern data. Cu$K\alpha_1$ radiation. λ(Cu$K\alpha_1$) = 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
m	286	14.40	2 0 0	288	14.35
vvw	555	10.34	0 0 2	556	10.33
s	626	9.735	1 0 2	628	9.720
s	1146	7.195	4 0 0	1152	7.176
vs	2219	5.171	0 0 4	2224	5.165
vw	2291	5.089	1 0 4	2296	5.083
vs	2585	4.791	6 0 0	2591	4.785
vvs	4184	3.766	0 1 1	4191	3.763
vvs	4256	3.734	1 1 1	4263	3.731
vvs	4605	3.589	8 0 0	4606	3.589
w	4835	3.503	3 1 1	4839	3.502
vvs	4995	3.446	0 0 6	5004	3.443
vs	5070	3.421	1 0 6	5076	3.419
vs	5293	3.348	0 1 3	5303	3.345
vw	5364	3.326	1 1 3	5375	3.322
vw	5641	3.243	3 0 6	5652	3.240
vvw	5739	3.215	7 0 4	5751	3.212
w	6820	2.949	8 0 4	6830	2.947
m	7191	2.872	10 0 0	7197	2.871
vvs	7597	2.795	1 1 5	7599	2.794
s	7723	2.772	7 1 1	7718	2.773

quenched samples always contained $Zn_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$ (mon) and traces of its orthorhombic dimorph. In all samples tempered at temperatures above 1100°C, only the orthorhombic $Zn_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$ was observed. Tempering of melted samples at the same temperature led to the transformation of the monoclinic modification to the orthorhombic.

Weissenberg photographs of the two forms of $Zn_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$ show an almost complete agreement with the corresponding photographs of $Nb_{12}O_{29}$(mon) [5] and (mon) [5] $Nb_{12}O_{29}$(o-rh),[6] leaving no doubt that these compounds are isostructural with $Zn_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$ (mon) and $Zn_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$ (o-rh). Crystallographic data for the two Zn-Nb-oxides are given in Tables 1 and 2.

The formation of the metastable $Zn_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$(mon) from quenched melts agrees with observations made on the TiO_2-Nb_2O_5 system discussed by Gruehn.[7] In this system, as well as in the NbO_2-Nb_2O_5 system and in the system investigated, $(Me,Nb)_{12}O_{29}$(o-rh) (Me = Nb(IV), Ti, or Zn) seems to be stable at temperatures above 1050−1150°C and $(Me,Nb)_{12}O_{29}$(mon) is observed at temperatures below this approximate value (*cf.* Gruehn [7]).

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