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Phase Analysis Studies on the $NaNbO_3$-Nb_2O_5, NaF-Nb_2O_5, and $NaNbO_3$-Nb_2O_5-H_2O Systems

STEN ANDERSSON

Research Institute of National Defence, Dept. 4, Stockholm 80, Sweden

$NaNb_3O_8$ and $NaNb_{13}O_{33}$ were prepared at 1100–1200°C in the system $NaNbO_3$–Nb_2O_5. $Na_2Nb_2O_5F_2$, $NaNb_2O_5F$, and $NaNb_6O_{15}F$ were found in the NaF–Nb_2O_5 system at 800–1000°C. $Na_2Nb_4O_{11}$ and $NaNb_6O_{15}(OH)$ were identified in the $NaNbO_3$–Nb_2O_5–H_2O system at 500–700°C and 2000 atm. H–Nb_2O_5 was transformed to N–Nb_2O_5 in supercritical water at 900°C and 2000 atm.

Indexed powder patterns are given.

The substitution of F^- for O^{2-} in pentavalent niobium oxide has been shown to occur through the synthesis and crystal structure determination of a number of new compounds, *viz.* Nb_3O_7F, $Nb_5O_{12}F$, $Nb_{17}O_{42}F$, and $Nb_{31}O_{77}F$.[1-3] In order to learn to which extent F^- and also OH^- can substitute for O^{2-} in ternary pentavalent niobium oxides, systematic phase analyses of the systems $NaNbO_3$–Nb_2O_5–H_2O and NaF–Nb_2O_5 were carried out. Phase studies on the dry system $NaNbO_3$–Nb_2O_5 were also performed for comparison.

EXPERIMENTAL

The system $NaNbO_3$–Nb_2O_5 was studied in a way described earlier.[4] Preparations with water in the system were carried out in Nimonic 115 vessels. The samples were kept in sealed platinum or gold capsules, which had been cleaned with boiling concentrated nitric acid. 50–100 mg of the oxides were mixed with 10–30 mg of water. The pressure was controlled with a needle valve and a high pressure gauge. The temperatures used varied between 500 and 900°C and the pressure normally applied was 2000 atm. The heating time was usually 3–6 days. The NaF–Nb_2O_5 system was studied by heating mixtures of NaF and Nb_2O_5 in sealed platinum capsules at temperatures between 800 and 1000°C for 1–3 days. The samples were examined by X-ray powder photographs obtained with a Guinier focusing camera of 80 mm diameter, using monochromatized Cu$K\alpha$ radiation. Single crystal photographs were taken of all the compounds reported here. The powder patterns given below were indexed with the guidance of the single crystal data.

RESULTS OF THE PHASE ANALYSES

In the dry system, $NaNbO_3$—Nb_2O_5, investigated at 1100—1200°C, only two phases were found, *viz.* $NaNb_3O_8$ and $NaNb_{13}O_{33}$. The structure of the $NaNb_3O_8$ phase [5] has some similarities with that of the tetragonal potassium tungsten bronze compound.[6] The *b*-axis of $NaNb_3O_8$ (37.10 Å) corresponds to a three doubling of one of the tetragonal axes. The detailed structure of the $NaNb_{13}O_{33}$ compound has been reported earlier.[4] The indexed Guinier X-ray powder patterns of the two oxides $NaNb_3O_8$ and $NaNb_{13}O_{33}$ are given in Tables 1 and 2.

$NaNb_3O_8$ and $NaNb_{13}O_{33}$ were not formed in the system $NaNbO_3$—Nb_2O_5—H_2O. Instead two different compounds were identified, *viz.* $Na_2Nb_4O_{11}$ and $NaNb_6O_{15}OH$. The composition $Na_2Nb_4O_{11}$ was derived from the starting composition, from the observed density and also from a preliminary structure determination.[7] Wether OH^- actually substitutes for O^{2-} in $Na_2Nb_4O_{11}$, to give a composition $Na_{2-x}Nb_4O_{11-x}(OH)_x$, has not been investigated. However, the good agreement between the observed and calculated densities indicates that x should be rather small, if any such substitution had occurred. The composition of the second compound, $NaNb_6O_{15}OH$, was derived by the structure determination of the isomorphous $NaNb_6O_{15}F$.[8] $NaNb_6O_{15}OH$ coexisted with H—Nb_2O_5 at intermediate compositions at 500—700°C. At temperatures above 850°C, H—Nb_2O_5 transformed into N—Nb_2O_5 in the presence of a

Table 1. Guinier powder data of $NaNb_3O_8$.

I	$\sin^2\theta_{obs}$	*hkl*	$\sin^2\theta_{calc}$
vw	0.00426	110	0.00431
w	0.00559	120	0.00560
vw	0.00692	040	0.00690
vw	0.01074	140	0.01077
vw	0.01464	150	0.01465
vw	0.01587	210	0.01594
w	0.01939	230	0.01938
		160	0.01939
vw	0.02234	240	0.02240
w	0.03101	260	0.03102
vw	0.03519	310	0.03531
vw	0.03657	320	0.03660
		270	0.03662
vst	0.03794	001	0.03794
w	0.03876	330	0.03876
		190	0.03879
w	0.04315	0 10 0	0.04310
vw	0.04353	121	0.04354
vw	0.04477	041	0.04484
vw	0.04560	350	0.04566
st	0.05039	360	0.05040
		290	0.05041
vvw	0.05389	211	0.05388
vvw	0.05609	1,11,0	0.05603
v	0.05728	231	0.05732
		161	0.05733

Table 2. Guinier powder data of $NaNb_{13}O_{33}$.

I	$\sin^2\theta_{obs}$	*hkl*	$\sin^2\theta_{calc}$
w	0.00476	200	0.00473
vw	0.00710	$20\bar{1}$	0.00707
vw	0.00744	201	0.00742
w	0.01520	202	0.01514
vvw	0.01895	400	0.01893
st	0.02110	$40\bar{1}$	0.02109
m	0.02790	203	0.02789
vst	0.04159	110	0.04155
w	0.04397	$11\bar{1}$	0.04397
vst	0.04565	204	0.04566
vst	0.05157	$60\bar{2}$	0.05158
w	0.05322	$31\bar{1}$	0.05327
vw	0.05367	311	0.05377
w	0.06160	312	0.06159
w	0.06672	$20\bar{5}$	0.06670
vw	0.06988	510	0.06993
m	0.07194	$51\bar{1}$	0.07203
m	0.07438	313	0.07443
st	0.16145	020	0.16144

few weight percent water. The crystal structure of N—Nb_2O_5 has recently been determined.[9]

The indexed X-ray Guinier powder patterns of $Na_2Nb_4O_{11}$, $NaNb_6O_{15}OH$, and N—Nb_2O_5 are given in Tables 3, 4, and 5.

Table 3. Guinier powder data of $Na_2Nb_4O_{11}$.

I	$\sin^2\theta_{obs}$	hkl	$\sin^2\theta_{calc}$
st	0.01590	002	0.01585
m	0.02185	200	0.02191
st	0.02242	11$\bar{1}$	0.02246
w	0.02732	20$\bar{2}$	0.02734
w	0.02761	111	0.02767
w	0.04811	202	0.04817
w	0.04895	11$\bar{3}$	0.04895
vst	0.06339	004	0.06339
vst	0.06520	310	0.06492
		31$\bar{2}$	0.06515
st	0.06647	021	0.06647
st	0.07670	311	0.07669
m	0.07716	31$\bar{3}$	0.07715
st	0.07837	022	0.07836
vw	0.08983	22$\bar{2}$	0.08985
w	0.09627	312	0.09637
vw	0.09708	31$\bar{4}$	0.09708
w	0.09812	023	0.09816

Table 4. Guinier powder data of $NaNb_6O_{15}OH$.

I	$\sin^2\theta_{obs}$	hkl	$\sin^2\theta_{calc}$
w	0.00849	011	0.00844
vvw	0.02283	020	0.02287
w	0.03030	013	0.03025
vst	0.03794	100	0.03792
m	0.04369	004	0.04362
w	0.04631	111	0.04636
vvw	0.04889	102	0.04882
st	0.05418	031	0.05419
vvw	0.06067	120	0.06079
st	0.06653	024	0.06649
w	0.06810	113	0.06817
vvw	0.07161	122	0.07169
m	0.07382	015	0.07387
m	0.07590	033	0.07599
m	0.08165	104	0.08154
st	0.09199	131	0.09211
m	0.10450	124	0.10443

Table 5. Guinier powder data of N—Nb_2O_5.

I	$\sin^2\theta_{obs}$	hkl	$\sin^2\theta_{calc}$
w	0.00292	001	0.00288
w	0.00315	20$\bar{1}$	0.00318
w	0.01147	002	0.01151
w	0.01213	40$\bar{1}$	0.01214
vw	0.01274	40$\bar{2}$	0.01274
m	0.02585	003	0.02591
m	0.02633	60$\bar{2}$	0.02631
vst	0.04156	110	0.04154
m	0.04234	11$\bar{1}$	0.04241
vst	0.04607	004	0.04606
vvst	0.04676	111	0.04644
		80$\bar{3}$	0.04683
		31$\bar{1}$	0.04704
w	0.04852	80$\bar{2}$	0.04856
vw	0.05069	80$\bar{4}$	0.05086
vw	0.05423	601	0.05393
w	0.05710	112	0.05709
w	0.05883	51$\bar{2}$	0.05889
vw	0.06130	11$\bar{3}$	0.06141
vw	0.06996	60$\bar{6}$	0.07007
w	0.07200	005	0.07198
m	0.07353	113	0.07350
		100$\bar{4}$	0.07371
		100$\bar{3}$	0.07371
st	0.07680	80$\bar{6}$	0.07620
		71$\bar{2}$	0.07681

In the $NaF-Nb_2O_5$ system three compounds were identified, *viz.* $Na_2Na_2O_5F_2$, $NaNb_2O_5F$, and $NaNb_6O_{15}F$. The compositions given here were deduced from structural considerations and also from density measurements. The X-ray data of $Na_2Nb_2O_5F_2$ had strong subcell features, the substructure being of the pyrochlore structure type. The unit cell given in Table 9 is ob-

Table 6. Guinier powder data of $Na_2Nb_2O_5F_2$.

I	$\sin^2\theta_{obs}$	I	$\sin^2\theta_{obs}$
st	0.01408	vw	0.05001
m	0.01617	m	0.05883
m	0.02134	vst	0.06418
vw	0.03025	vw	0.06452
w	0.04264	vvw	0.07135
vw	0.04469	m	0.08555

Table 7. Guinier powder data of $NaNb_2O_5F$.

I	$\sin^2\theta_{obs}$	hkl	$\sin^2\theta_{calc}$
vw	0.00780	110	0.00777
w	0.01944	210	0.01944
w	0.03112	220	0.03110
vst	0.03821	001	0.03817
m	0.03889	310	0.03887
st	0.05061	320	0.05053
vw	0.05763	211	0.05761
st	0.06613	410	0.06608
vw	0.06921	221	0.06927
m	0.06991	330	0.06997
m	0.07700	311	0.07704
w	0.07770	420	0.07774
st	0.08869	321	0.08870

Table 8. Guinier powder data of $NaNb_6O_{15}F$.

I	$\sin^2\theta_{obs}$	hkl	$\sin^2\theta_{calc}$
w	0.00844	011	0.00845
vvw	0.02283	020	0.02284
w	0.03036	013	0.03035
vst	0.03804	100	0.03803
m	0.04379	004	0.04381
w	0.04647	111	0.04648
vvw	0.04892	102	0.04898
st	0.05415	031	0.05414
vvw	0.06088	120	0.06087
st	0.06657	024	0.06665
w	0.06835	113	0.06832
vvw	0.07181	122	0.07183
m	0.07412	015	0.07416
m	0.07603	033	0.07604
m	0.08184	104	0.08184
st	0.09213	131	0.09217
m	0.10466	124	0.10468

tained from single crystal data. As the powder pattern showed considerable line splitting, it was not indexed completely and is given here only for identification purposes. The structure of $NaNb_2O_5F$ is of the tetragonal potassium bronze structure type.[6] The detailed structure of the $NaNb_6O_{15}F$ compound has been reported in an earlier publication.[8]

The Guinier X-ray powder patterns of the three compounds $Na_2Nb_2O_5F_2$, $NaNb_2O_5F$, and $NaNb_6O_{15}F$ are given in Tables 6, 7, and 8.

Table 9. Crystallographic constants and approximate temperatures of preparation for the various compounds.

Space group	$NaNb_3O_8$ *Pba2* or *Pbam*	$NaNb_{13}O_{33}$ *C2/m*	$Na_2Nb_2O_5F_2$ *C2/c* or *Cc*	$NaNb_2O_5F$ *P4/mbm*	$NaNb_5O_{15}F$ *Amm 2*	$Na_2Nb_4O_{11}$ *C2/c*	$NaNb_5O_{15}OH$ *Amm 2*	N−Nb_2O_5 *C2/m*
a Å	12.372	22.40	12.91	12.355	3.949	10.840	3.955	28.51
b Å	37.10	3.834	7.45	—	10.192	6.162	10.186	3.830
c Å	3.954	15.37	18.24	3.943	14.721	12.745	14.753	17.48
β	—	91.47	90.0	—	—	106.22	—	120.80
d_{obs}	4.62	4.40	4.00	—	—	4.75	4.67	—
d_{calc}	4.72	4.42	4.18	4.25	4.70	4.82	4.68	4.31
°C	1100−1200	1100−1200	800−900	800−900	900−1000	500−700	500−700	850−920

DISCUSSION

Crystallographic constants and approximate temperatures of preparation for the various compounds are given in Table 9. A general observation in the chemistry of the mixed niobium oxides is that a normal reaction temperature is around 1100—1200°C. The presence of fluorine in form of NbO_2F[1-3] or NaF and H_2O in the supercritical state lowers the reaction temperature with several hundred degrees centigrade. Different reaction mechanisms can be proposed and will shortly be published in a forthcoming paper.

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