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THE PHASE DIAGRAMS OF Na_2O AND K_2O WITH Nb_2O_5 AND THE TERNARY SYSTEM Nb_2O_5–Na_2O–Yb_2O_3 *

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ABSTRACT

The Nb_2O_5–Na_2O and Nb_2O_5–K_2O systems were re-investigated between 50 and 100 mol% Nb_2O_5 by thermal analysis, dilatometry and X-ray techniques. Five compounds were found in the investigated region of the first system: $NaNbO_3$, $Na_2Nb_4O_{11}$, $Na_{1\pm x}Nb_{3\pm x}O_{8\pm 2x}$, $NaNb_7O_{18}$ and $NaNb_{13}O_{33}$. $NaNbO_3$ melts congruently, $Na_2Nb_4O_{11}$ decomposes peritectoidally and the three others decompose peritectically. $NaNb_{13}O_{33}$, $NaNb_7O_{18}$ and $Na_{1\pm x}Nb_{3\pm x}O_{8\pm 2x}$ are high temperature compounds. The system Nb_2O_5–K_2O contains eight compounds in the investigated region: $KNbO_3$, $K_4Nb_6O_{17}$, $K_{5.75}Nb_{10.85}O_{30}$, $K_3Nb_7O_{19}$, KNb_3O_8, $K_2Nb_8O_{21}$, KNb_7O_{18} and $KNb_{13}O_{33}$. $K_4Nb_6O_{17}$ melts congruently, all the others decompose peritectically or peritectoidally. Linear thermal expansion coefficients between 350 and 1250 K are given for the sodium and potassium niobates. Two isothermal sections of the ternary oxide system Nb_2O_5–Na_2O–Yb_2O_3 were studied at 1273 and 1523 K. No ternary oxide was detected.

INTRODUCTION

Compounds with unusual electric, magnetic and optical properties were observed in mixtures of the alkali metal oxides with niobium(V) and tantalum(V) oxide. To exploit these materials technologically, methods for the growth of single crystals had to be developed and conditions for producing materials with reproducible compositions had to be determined. This was not simple because some of these compounds have broad homogeneity ranges [1]. New interesting materials may be prepared by partial replacement of the alkali metal with niobium or tantalum ions. However, a knowledge of the binary and ternary phase diagram enables these problems to be resolved. The published phase equilibria of the Nb_2O_5–$NaNbO_3$ and Nb_2O_5–$KNbO_3$ systems are not in agreement. Therefore we re-investigated these oxide systems because the constituent binary phase diagrams are needed for the analysis of X-ray and thermal data in ternary oxide systems.

* Dedicated to Professor H.J. Seifert on the occasion of his 60th birthday.

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We began the search for ternary oxide compounds with the Nb_2O_5–Na_2O–Yb_2O_3 system.

EXPERIMENTAL

The samples were prepared by powder synthesis from the starting materials: Na_2CO_3, K_2CO_3 (Merck, suprapur), Nb_2O_5 (H.C. Starck, ceramic grade) and Yb_2O_3 (Auer Remy, 99.9%). The reaction products were identified by X-ray powder methods. Phase relations were determined with differential thermal analysis (DTA), differential scanning calorimetry (DSC), dilatometry and high-temperature X-ray techniques.

The powders were mixed in steps of 2–5 mol% and the mixtures were annealed in platinum crucibles for periods of between one week and three months. All samples were subjected to thermal and X-ray experiments. For the DTA and DSC experiments, we used a Dupont 990 thermal analyser with a heating rate of 5 or 10 K min^{-1}. The X-ray diffraction data of the powders were obtained with a Guinier-4 (Enraf–Nonius) camera or a diffractometer (Stoe Automated Powder Diffraction System) using Cu $K\alpha_1$ radiation. High temperature X-ray data were collected using a Simon–Guinier camera (radiation Cu $K\alpha_1$). In these experiments a heating rate of 5 K h^{-1} was used.

THE Nb_2O_5–$NaNbO_3$ SYSTEM

Between 1958 and 1974, a number of papers were published which attempted to establish the phase relations of this system. Figure 1 shows the composition and homogeneity ranges of the reported compounds.

The phase diagram of the Nb_2O_5–$NaNbO_3$ system obtained in the present investigation is shown in Fig. 2: the results of the preceding single-crystal, powder diffraction measurements and the thermal analysis data were considered in the construction of the equilibrium lines.

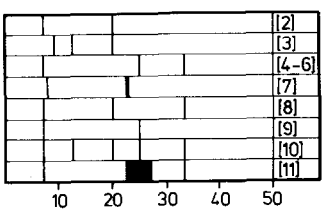

Fig. 1. Composition of previously reported compounds in the system Nb_2O_5–$NaNbO_3$.

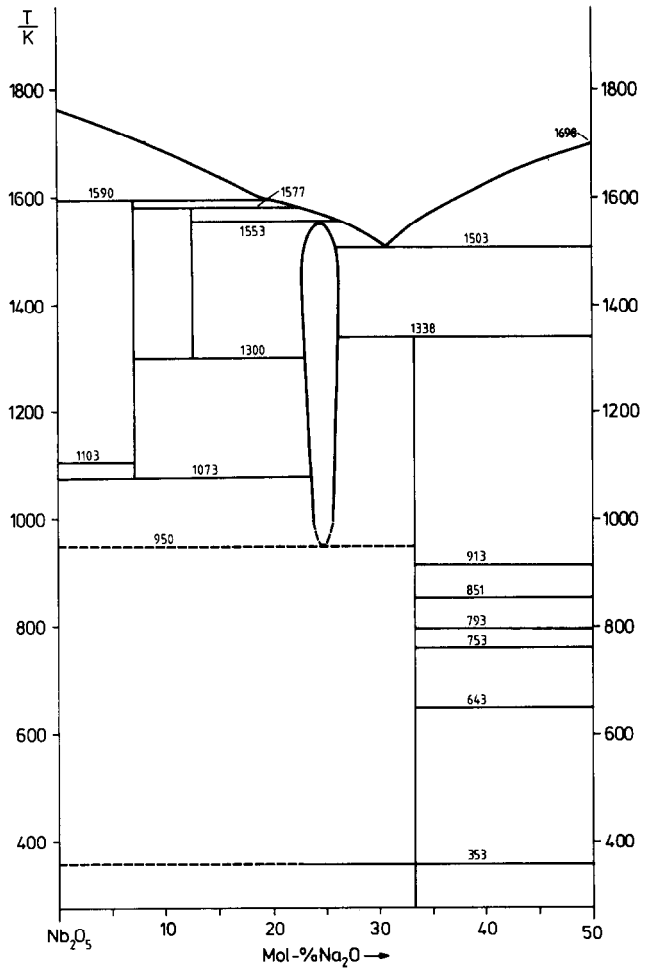

Fig. 2. $T-x$ diagram of the system Nb_2O_5–$NaNbO_3$.

In the composition range up to 50 mol% Na_2O, the five intermediate compounds, $NaNb_{13}O_{33}$, $NaNb_7O_{18}$, $Na_{1\pm x}Nb_{3\pm x}O_{8\pm 2x}$, $Na_2Nb_4O_{11}$ and $NaNbO_3$, were identified by their X-ray patterns.

The existence of $NaNb_{13}O_{33}$ was first demonstrated by Reisman et al. [2] and confirmed by several other authors. The temperature of the peritectic equilibrium Nb_2O_5 + melt → $NaNb_{13}O_{33}$ was 1590 K. The phase decomposes into the eutectoid Nb_2O_5 + $Na_{1\pm x}Nb_{3\pm x}O_{8\pm 2x}$ at 1073 K. $NaNb_7O_{18}$, observed for the first time by Shafer and Roy [3], is formed in the peritectic reaction $NaNb_{13}O_{33}$ + melt → $NaNb_7O_{18}$ at 1577 K and decomposes into the eutectoid $NaNb_{13}O_{33}$ + $Na_{1\pm x}Nb_{3\pm x}O_{8\pm 2x}$ at 1300 K. Due to the small temperature interval over which this compound is stable, it was not observed in most of the previous publications.

The peritectic formation of $Na_{1\pm x}Nb_{3\pm x}O_{8\pm 2x}$ occurs at 1553 K from melt + $NaNb_7O_{18}$. The homogeneity limits of this compound are 23.5 and

25.5 mol% Na_2O at 1273 K. The width of the homogeneity region increases with temperature [11,13]. $Na_{1\pm x}Nb_{3\pm x}O_{8\pm 2x}$ decomposes into the eutectoid $Nb_2O_5 + Na_2Nb_4O_{11}$ at around 950 K. These three compounds are high temperature compounds. However, once formed, they exist in a metastable state at room temperature. The reported lower decomposition temperatures correspond to the temperatures above which they were formed following extensive periods of annealing.

$Na_2Nb_4O_{11}$ is formed peritectoidally at 1338 K and undergoes a previously unreported transformation at 353 K.

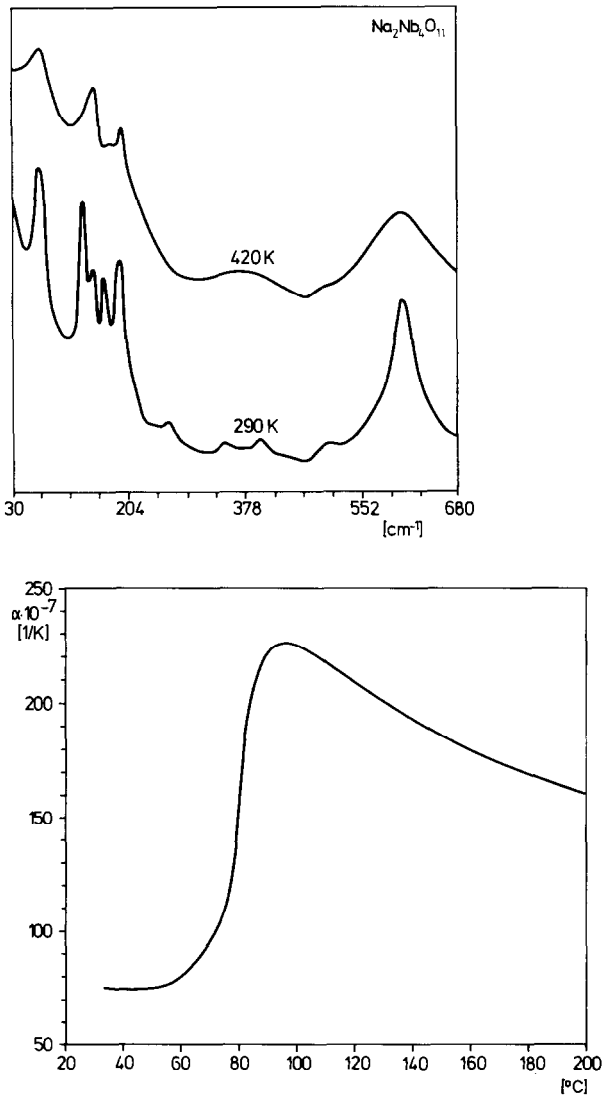

Fig. 3. The phase transition of the compound $Na_2Nb_4O_{11}$: upper, Raman spectra at 290 and 420 K; lower, linear thermal expansion coefficient curve (303–473 K).

TABLE 1

Lattice constants of the intermediate compounds in the system Nb_2O_5–$NaNbO_3$ (in parentheses, quenched from this annealing temperature; $T = 298$ K, slowly cooled to room temperature; s.g., space group)

Compound	Reference	This work
$NaNb_{13}O_{33}$	[5]	
(1273 K)	s.g. $C2/m$	
	$a = 2240$ pm	$a = 2240.0(4)$ pm
	$b = 383.4$ pm	$b = 382.86(6)$ pm
	$c = 1537$ pm	$c = 1536.3(3)$ pm
	$\beta = 91.47°$	$\beta = 91.36(1)°$
$NaNb_7O_{18}$	[12]	
(1423 K)	s.g. $Immm$	
	$a = 1428.4$ pm	$a = 1429.5(2)$ pm
	$b = 2622.4$ pm	$b = 2621.8(6)$ pm
	$c = 384.16$ pm	$c = 384.23(7)$ pm
$Na_{1\pm x}Nb_{3\pm x}O_{8\pm 2x}$	[13]	
(1273 K)	s.g. $Pba2$	
	$a = 1236.4$ pm	$a = 1237.1(2)$ pm
	$b = 3699.2$ pm	$b = 3737.0(8)$ pm
	$c = 395.5$ pm	$c = 395.54(6)$ pm
L-$Na_2Nb_4O_{11}$	[6]	
(298 K)	s.g. $C2/c$	
	$a = 1084.0$ pm	$a = 1084.5(2)$
	$b = 616.2$ pm	$b = 616.6(2)$
	$c = 1274.5$ pm	$c = 1278.9(6)$
	$\beta = 106.22°$	$\beta = 106.21(3)°$
H-$Na_2Nb_4O_{11}$		Monoclinic
(481 K)		$a = 1033.5(4)$ pm
		$b = 617.2(2)$ pm
		$c = 1459(1)$ pm
		$\beta = 108.25(5)°$

Figure 3a shows the Raman spectra of the low (298 K) and high (423 K) temperature forms of this compound and Fig. 3b shows the curve for a dilatometric experiment between 303 and 473 K. The high temperature modification could not be quenched; its structure probably has monoclinic symmetry.

The temperatures of the phase transitions of $NaNbO_3$ agree with the literature data [14–16].

The lattice parameters of the compounds are listed in Table 1. The observed d and θ values of the high temperature modification of $Na_2Nb_4O_{11}$ are given in Table 2. The linear thermal expansion coefficients, α, of polycrystalline $NaNb_{13}O_{33}$, $Na_{1\pm x}Nb_{3\pm x}O_{8\pm 2x}$, $Na_2Nb_4O_{11}$ and $NaNbO_3$ are given in Table 3.

THE Nb_2O_5–$KNbO_5$ SYSTEM

A literature survey of the compounds found in the system Nb_2O_5–$KNbO_3$ is given in Fig. 4. The phase diagram shown in Fig. 5 is based on these data and on the new results obtained in the course of this investigation.

Eight compounds, including three stable only at elevated temperatures, were observed. $KNb_{13}O_{33}$ is formed at 1273 K from Nb_2O_5 and $K_2Nb_8O_{21}$. The peritectical decomposition into Nb_2O_5 and KNb_7O_{18} occurs at around 1623 K. Deviating from our recent results [22], the high temperature compound KNb_7O_{18} is formed at 1473 K from $KNb_{13}O_{33}$ and $K_2Nb_8O_{21}$, with a small homogeneity range of around 1 mol%. It decomposes peritectically at 1563 K. $K_2Nb_8O_{21}$ is stable above 750 K, decomposes peritectically (1541 K) and has a homogeneity range of around three mol%. R.S. Roth et al. [11] suggested the space groups $Pmam$, $P2_1am$ or $Pma2$ for $K_2Nb_8O_{21}$. Our second harmonic generation measurements revealed the absence of a

TABLE 2

d and θ values of the high temperature modification of $Na_2Nb_4O_{11}$ at $T = 481$ K

d_{obs} (pm)	$2\theta_{obs}$ (deg) [a]	h	k	l	Int. [b]	$\delta(2\theta)$ (deg) [c]
615.69	14.374	0	1	0	vs	−0.035
516.76	17.144	−2	0	1	vs	0.016
464.50	19.090	1	1	1	vw	0.020
305.84	29.174	2	1	2	vs	0.018
301.77	29.577	0	1	4	vs	−0.028
277.25	32.260	0	0	5	vs	0.019
258.18	34.715	−4	0	2	vw	0.007
247.14	36.319	1	0	5	w	−0.007
203.99	44.370	0	3	1	vw	0.112
203.38	44.510	−5	0	1	vw	−0.007
202.34	44.750	2	1	5	vw	−0.016
196.28	46.212	−3	2	5	w	0.001
192.28	47.231	−4	2	0	m	0.056
179.54	50.810	2	1	6	s	0.032
172.32	53.103	3	2	4	w	0.024
170.58	53.687	−3	1	8	s	−0.094
165.07	55.629	0	3	5	vw	−0.037
154.75	59.703	−3	1	9	w	−0.022
154.28	59.901	0	4	0	vw	−0.005
152.78	60.553	4	2	4	vw	−0.022
152.41	60.712	1	4	0	w	−0.003
150.46	61.584	−1	4	2	vw	0.026
148.79	62.355	−6	2	4	w	−0.014
145.23	64.059	−5	0	9	vw	0.011
131.15	71.933	−3	2	10	vw	−0.010

[a] Wavelength: Cu $K\alpha_1$.

[b] vw, very weak; w, weak; m, medium; s, strong; vs, very strong.

[c] $\delta(2\theta) = 2\theta_{calc} - 2\theta_{obs}$.

TABLE 3

Linear thermal expansion coefficient, α, of the compounds in the system Nb_2O_5–$NaNbO_3$

Temp. (K)	α (10^{-6} K^{-1})	Temp. (K)	α (10^{-6} K^{-1})	Temp. (K)	α (10^{-6} K^{-1})
$NaNb_{13}O_{33}$ (7.14 mol% Na_2O)					
350	1.93	750	1.22	1150	1.51
400	1.43	800	1.31	1200	1.47
450	1.23	850	1.38	1250	1.32
500	1.06	900	1.45	1300	0.94
550	1.04	950	1.47	1350	0.13
600	1.01	1000	1.46	1400	−1.88
650	1.05	1050	1.49	1450	−8.67
700	1.12	1100	1.50		
$Na_{1\pm x}Nb_{3\pm x}O_{8\pm 2x}$ (25 mol% Na_2O)					
350	4.68	750	8.76	1150	8.50
400	6.44	800	8.71	1200	8.30
450	7.61	850	8.71	1250	7.99
500	8.08	900	8.84	1300	7.47
550	8.42	950	8.81	1350	6.70
600	8.59	1000	8.74	1400	5.36
650	8.71	1050	8.69		
700	8.76	1100	8.61		
$Na_2Nb_4O_{11}$ (33.33 mol% Na_2O)					
350	2.57	700	6.48	1050	7.52
400	3.96	750	6.66	1100	7.17
450	4.77	800	6.85	1150	6.13
500	5.24	850	7.03	1200	3.28
550	5.65	900	7.19	1250	−3.37
600	5.97	950	7.34	1300	−1.32
650	6.23	1000	7.52	1350	0.65
$NaNbO_3$ (50 mol% Na_2O)					
350	8.65	750	12.18	1150	14.15
400	8.69	800	12.83	1200	13.87
450	8.94	850	13.60	1250	13.37
500	9.15	900	14.14	1300	12.65
550	9.71	950	14.42	1350	11.62
600	10.38	1000	14.46	1400	10.33
650	10.64	1050	14.40		
700	11.58	1100	14.29		

symmetry centre. The compound crystallizes in the non-centrosymmetric space group *P*mam. Three further compounds are observed at lower temperatures. All decompose peritectically: KNb_3O_8 at 1498 K, $K_3Nb_7O_{19}$ at 1467 K and $K_{5.75}Nb_{10.85}O_{30}$ at 1438 K. KNb_3O_8 and $K_3Nb_7O_{19}$ transform at 1273 and 377 K, respectively, into their high temperature modifications. The homogeneity range of $K_{5.75}Nb_{10.85}O_{30}$ is about 1.5 mol%. The hygroscopic

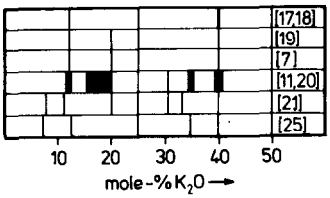

Fig. 4. Composition of previously reported compounds in the system Nb_2O_5–$KNbO_3$.

$K_4Nb_6O_{17}$ melts congruently at 1450 K. The temperature and composition of the $K_4Nb_6O_{17} + KNbO_3$ eutectic were determined as 1331 K and 37.5 mol% K_2O. $KNbO_3$ is formed in a peritectic reaction at 1349 K and undergoes two phase transitions. The phase transition temperatures of 489 and 694 K correspond well with values measured by other authors [23–25].

Table 4 lists the lattice parameters of the compounds. The linear thermal expansion coefficients, α, of the polycrystalline substances, $KNb_{13}O_{33}$, KNb_7O_{18}, $K_2Nb_8O_{21}$, KNb_3O_8, $K_3Nb_7O_{19}$, $K_{5.75}Nb_{10.85}O_{30}$, $K_4Nb_6O_{17}$ and $KNbO_3$, are given in Table 5.

THE TERNARY SYSTEM Nb_2O_5–Na_2O–Yb_2O_3

In systems of rare earth oxides with alkali metal niobates, tantalates and vanadates, quaternary compounds have been found: e.g. $K_2RENb_5O_{15}$

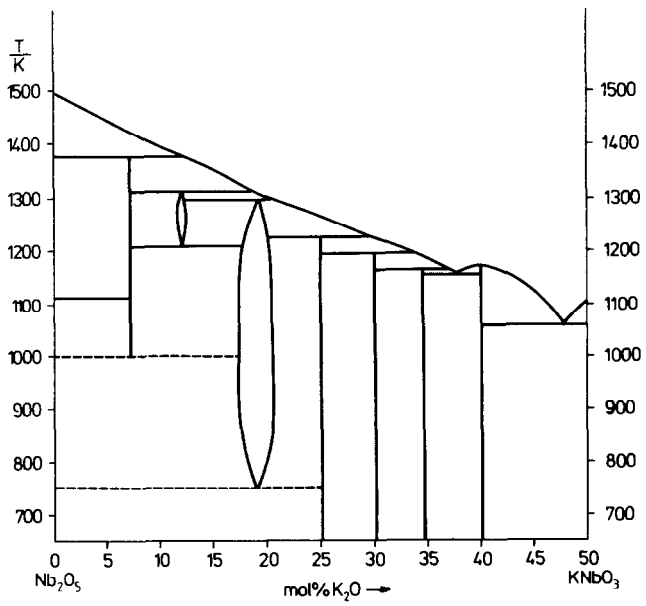

Fig. 5. T–x diagram of the system Nb_2O_5–$KNbO_3$.

TABLE 4

Lattice constants of compounds in the system Nb_2O_5–$KNbO_3$ (in parentheses, quenched from this temperature; $T = 298$ K, slowly cooled to ambient temperature; s.g., space group)

Compound	Reference	This work
$KNb_{13}O_{33}$	[25]	
(1373 K)	s.g. $C2/m$	
	$a = 2247.9(3)$ pm	$a = 2250.7(8)$ pm
	$b = 383.70(5)$ pm	$b = 383.4(2)$ pm
	$c = 1534.7(2)$ pm	$c = 1533.3(8)$ pm
	$\beta = 91.07(2)°$	$\beta = 90.97(5)°$
KNb_7O_{18}	[11]	
(1473 K)	s.g. $P42_12$ or $P42_1m$	
	$a = 2751.8(4)$ pm	$a = 2730.6(7)$ pm
	$c = 396.87(3)$ pm	$c = 396.1(1)$ pm
$K_2Nb_8O_{21}$	[11]	
(1273 K)	s.g. $Pmam$, $P2_1am$ or $Pma2$	s.g. $Pmam$
	$a = 3755.8$–3763.6 pm	$a = 3750.9(3)$ pm
	$b = 1251.9$–1254.5 pm	$b = 1249.4(2)$ pm
	$c = 395.2$–395.7 pm	$c = 397.0(1)$ pm
L-KNb_3O_8	[25,26]	
(298 K)	s.g. $Amam$	
	$a = 891.86(4)$ pm	$a = 891.9(1)$ pm
	$b = 2120.6(1)$ pm	$b = 2121.0(6)$ pm
	$c = 380.53(1)$ pm	$c = 380.57(5)$ pm
H-KNb_3O_8	[25]	
(1275 K)	Tetragonal	
	$a = 1251.18(5)$ pm	$a = 1250.7(1)$ pm
	$c = 396.63(3)$ pm	$c = 396.15(4)$ pm
L-$K_3Nb_7O_{19}$	[27,28]	
(298 K)	s.g. $P\bar{1}$	
	$a = 1412.82(9)$ pm	$a = 1419.0(4)$ pm
	$b = 993.69(9)$ pm	$b = 997.4(4)$ pm
	$c = 645.53(6)$ pm	$c = 647.8(2)$ pm
	$\alpha = 106.44(1)°$	$\alpha = 106.48(2)°$
	$\beta = 95.856(6)°$	$\beta = 95.63(2)°$
	$\gamma = 97.30(1)°$	$\gamma = 97.61(2)°$
$K_{5.75}Nb_{10.85}O_{30}$	[11,25]	
(298 K)	s.g. $P4/mbm$	
	$a = 1257.88(3)$ pm	
	$c = 398.33(1)$ pm	
$K_4Nb_6O_{17}$	[25]	
(298 K)	s.g. $Pmnb$ or $P2_1nb$	Not indexed on the basis of literature data
	$a = 781.6(6)$ pm	
	$b = 3312(3)$ pm	
	$c = 648.0(3)$ pm	

TABLE 5

Linear thermal expansion coefficients, α, of the compounds in the system Nb_2O_5–$KNbO_3$

Temp. (K)	α (10^{-6} K^{-1})	Temp. (K)	α (10^{-6} K^{-1})	Temp. (K)	α (10^{-6} K^{-1})
$KNb_{13}O_{33}$ (7.14 mol% K_2O)					
350	0.85	750	1.63	1150	1.91
400	1.25	800	1.73	1200	1.62
450	1.37	850	1.85	1250	1.20
500	1.39	900	1.95	1300	0.57
550	1.38	950	1.99	1350	−0.30
600	1.41	1000	2.03	1400	−1.95
650	1.46	1050	2.07	1450	−6.13
700	1.54	1100	2.02		
$K_2Nb_8O_{21}$ (20 mol% K_2O)					
350	4.15	750	4.73	1150	4.96
400	4.23	800	4.80	1200	4.69
450	4.36	850	4.88	1250	4.16
500	4.41	900	4.96	1300	3.36
550	4.49	950	5.01	1350	1.82
600	4.56	1000	5.05	1400	−5.17
650	4.62	1050	5.06		
700	4.68	1100	5.04		
KNb_3O_8 (25 mol% K_2O)					
350	6.21	750	6.18	1150	6.37
400	6.02	800	6.20	1200	6.40
450	6.06	850	6.23	1250	6.42
500	6.06	900	6.26	1300	6.25
550	6.06	950	6.30	1350	5.59
600	6.08	1000	6.33	1400	1.51
650	6.10	1050	6.36		
700	6.14	1100	6.36		
$K_3Nb_7O_{19}$ (30 mol% K_2O)					
350	−0.58	700	0.63	1050	2.14
400	−4.18	750	0.96	1100	2.14
450	−2.61	800	1.27	1150	2.13
500	−1.58	850	1.52	1200	2.02
550	−0.77	900	1.74	1250	1.80
600	−0.19	950	1.93	1300	1.27
650	0.24	1000	2.06		
$K_{5.75}Nb_{10.85}O_{30}$ (34.64 mol% K_2O)					
350	3.90	700	6.45	1050	6.76
400	4.66	750	6.61	1100	5.82
450	5.26	800	6.80	1150	3.76
500	5.57	850	6.95	1200	0.09
550	5.91	900	7.06	1250	−5.23
600	6.09	950	7.10		
650	6.28	1000	7.06		

TABLE 5 (continued)

Temp. (K)	α (10^{-6} K^{-1})	Temp. (K)	α (10^{-6} K^{-1})	Temp. (K)	α (10^{-6} K^{-1})
$K_4Nb_6O_{17}$ (40 mol% K_2O)					
350	2.73	650	5.92	950	6.97
400	4.23	700	6.11	1000	7.14
450	4.80	750	6.31	1050	7.27
500	5.17	800	6.50	1100	7.34
550	5.49	850	6.67	1150	7.29
600	5.71	900	6.82	1200	6.86
$KNbO_3$ (50 mol% K_2O)					
350	5.06	650	4.67	950	5.48
400	4.99	700	3.62	1000	5.79
450	4.96	750	3.95	1050	6.08
500	4.85	800	4.36	1100	6.23
550	5.10	850	4.75		
600	5.13	900	5.13		

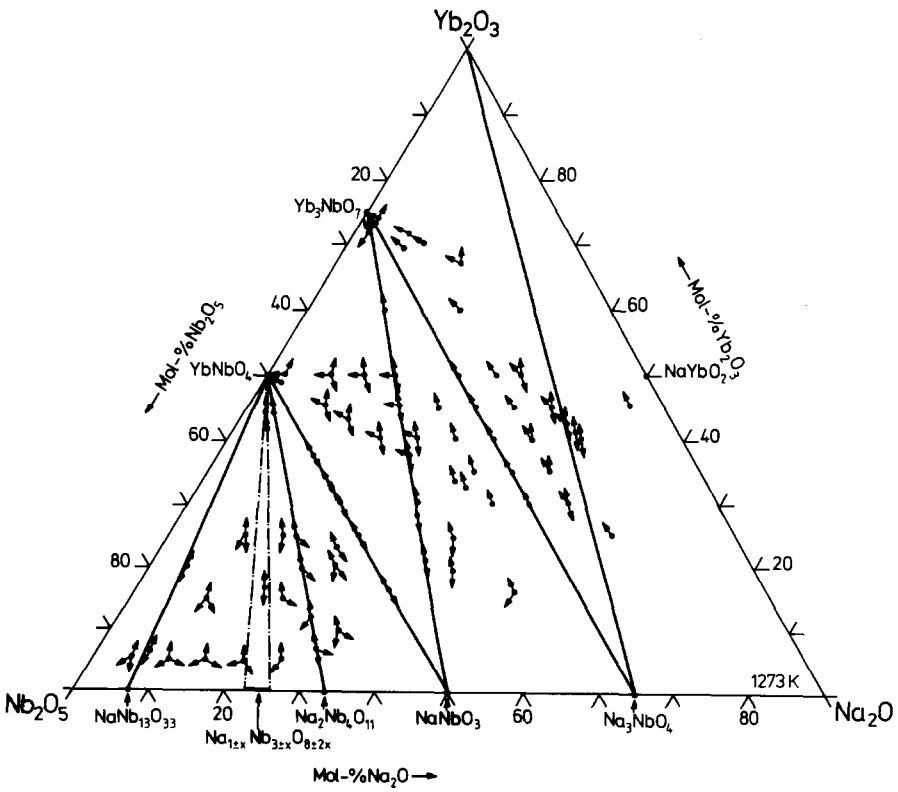

Fig. 6. The system Nb_2O_5–Na_2O–Yb_2O_3 (isothermic section at 1273 K).

(RE = Y–Ho) [29], $Na_2Sc_2V_2O_9$, $Na_3La_8V_3O_{21}$ [30], $Na_2LaNb_5O_{15}$ [31] and $NaYNb_2O_7$ [32].

While searching for new ternary oxide compounds, phase relations in the ternary system Nb_2O_5–Na_2O–Yb_2O_3 at 1273 and 1523 K were determined.

Results

The isothermal section at 1273 K is given in Fig. 6. The arrows point to those substances of the binaries which were identified by X-ray methods in the ternary mixtures. No ternary compound exists in the system Nb_2O_5–Na_2O–Yb_2O_3 at 1273 and 1523 K.

Characteristic of phase relations of this system is the dominating influence of $YbNbO_4$ which appears in most of the phase equilibria.

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REFERENCES

1 A. Räuber, in E. Kaldis (Ed.), Current Topics in Material Science, Vol. 1, North-Holland, Amsterdam, 1978.
2 A. Reisman, F. Holtzberg and E. Banks, J. Am. Chem. Soc., 80 (1958) 37.
3 M.W. Shafer and R. Roy, J. Am. Ceram. Soc., 42 (1959) 482.
4 S. Andersson, Acta Crystallogr., 16 (1963) A21.
5 S. Andersson, Acta Chem. Scand., 19 (1965) 1401.
6 S. Andersson, Acta Chem. Scand., 21 (1967) 1777.
7 C.D. Whiston and A.J. Smith, Acta Crystallogr., 19 (1965) 169.
8 H. Brusset, H. Gillier-Pandraud and J.-P. Belle, Bull. Soc. Chim. Fr., (1967) 2784.
9 Y. Bouillaud, Bull. Soc. Chim. Fr., (1968) 112.
10 P. Appendino, Ann. Chim. (Rome), 63 (1973) 547.
11 R.S. Roth, H.S. Parker, W.S. Brower and D.B. Minor, NASA Techn. Report CR 134599, 1974.
12 B.-O. Marinder and M. Sundberg, Acta Crystallogr., B40 (1984) 82.
13 D.C. Craig and N.C. Stephenson, J. Solid State Chem., 3 (1971) 89.
14 A. Avogadro, G. Bonera, F. Borsa and A. Rigamonti, Phys. Rev., B9 (1974) 3905.
15 H.D. Megav, Ferroelectr., 7 (1974) 87.
16 O.A. Zhelnova, O.E. Fesenko and V.G. Smotrakov, Sov. Phys. Solid State, 28 (1986) 144.
17 A. Reisman and F. Holtzberg, J. Am. Chem. Soc., 77 (1955) 2115.
18 A.I. Manakov, O.A. Esin and B.M. Lepinskikh, Russ. J. Inorg. Chem., 7 (1962) 169.
19 J.E. Guerchais, Bull. Soc. Chim. Fr., (1962) 103.
20 R.S. Roth, W.S. Brower, H.S. Parker, D.B. Minor and J.L. Waring, NASA Techn. Report CR 134869, 1975.
21 P. Appendino, M. Montorsi and M. Vallino, Ann. Chim. (Rome), 66 (1976) 417.

22 R. Blachnik and E. Irle, J. Therm. Anal., 35 (1989) 609.
23 A.W. Hewat, J. Phys. C: Solid State Phys., 6 (1973) 2559.
24 M.D. Fontana and G.E. Kugel, Jpn. J. Appl. Phys., 24 Supplem. 24-2 (1985) 223.
25 M. Lundberg and M. Sundberg, J. Solid State Chem., 63 (1986) 216.
26 K. Nassau, J.W. Shiever and J.L. Bernstein, J. Electrochem. Soc., 116 (1969) 348.
27 M. Gasperin, Acta Crystallogr., B38 (1982) 2024.
28 M. Sundberg and M. Lundberg, Acta Crystallogr., B43 (1987) 238.
29 B.A. Scott, E.A. Giess, G. Burns and D.F. O'Kane, Mat. Res. Bull., 3 (1968) 831.
30 M.Ya. Khodos and A.A. Fotiev, Russ. J. Inorg. Chem., 32 (1987) 1776.
31 I.G. Ismailzade, Soviet Phys.-Cryst., 8 (1963) 351.
32 V.S. Chincholkar, J. Inorg. Nucl. Chem., 34 (1972) 2973.