JOURNAL OF SOLID STATE CHEMISTRY 2, 250–261 (1970)

The System Niobium Pentoxide-Phosphorus Pentoxide

ERNEST M. LEVIN AND ROBERT S. ROTH

National Bureau of Standards, Washington, D.C. 20234

Received January 15, 1970

A partial phase diagram of the system Nb_2O_5–P_2O_5 has been determined experimentally, using the quenching technique and identifying the phases by X-ray powder diffractometry. The major phase, $NbPO_5$, has a melting point above 1650°C. It transforms at about 1253°C from a low-temperature, tetragonal phase to a high-temperature, monoclinic phase, isostructural with $TaPO_5$. The $9Nb_2O_5 \cdot P_2O_5$ phase shows a limited solid solution range and melts incongruently at 1435°C. The eutectic between 9:1 and $NbPO_5$ is at 1365°C and 67 mole % Nb_2O_5. At 96.4 mole % Nb_2O_5 another phase was found, stable between ~1340 and 1420°C and isostructural with the 9:1 phase. A new monoclinic phase, "22:1" *ss* was found, with a limited stability field in both temperature and composition. It is most likely composed of 3 × 3 and 3 × 4 ReO_6-type blocks of octahedrally oxygen-coordinated niobium. In the subsystem $NbPO_5$–P_2O_5 liquidus values could not be determined even in sealed Pt tubes because of reactivity and high vapor pressure of P_2O_5. One compound was identified of probable composition $Nb_2O_5 \cdot 2P_2O_5$, with pseudocubic symmetry and melting incongruently at about 1025°C. X-ray powder diffraction data and unit cell dimensions are listed for the phases.

I. Introduction

Although no previous phase diagram for the system Nb_2O_5–P_2O_5 was found in the literature, a number of investigators have prepared niobium phosphate compounds by wet and by solid state reactions and have studied them by chemical analysis, by single crystal and powder X-ray diffraction, and by infra red absorption. The compound $Nb_2O_5 \cdot P_2O_5$ has been most extensively studied: first by Hahn in 1951 (*1*) followed by Kurbatov and Demenov (*2*), Haider (*3, 4*), Brown and Hummel (*5*), and finally by Longo and Kierkegaard in 1966 (*6*). Another compound composition unequivocally established is $9Nb_2O_5 \cdot P_2O_5$. Waring and Roth (*7*) presented the indexed powder data in 1964, and Roth et al. (*8*) determined the structure by single crystal analysis in 1965. Haider (*4*) who has made the most complete study to date on the niobium phosphates also reported the compound $Nb_2O_5 \cdot 2P_2O_5$. Two other reported compounds whose existence have not been verified in the present study are $2Nb_2O_5{:}P_2O_5$ (*2, 9*) and $3Nb_2O_5{:}5P_2O_5$ (*10*).

In addition to clarifying some of the inconsistencies in the reported data, we had two other objectives. One was to determine if liquid immiscibility existed in phosphate systems, although subsequent to the start of the experimental work, it was concluded that immiscibility in binary phosphate systems was either non existent or very rare (*11*). The second objective was to apply the *block principle* of multiphase formation as developed by Roth and Wadsley (*12*, Part IV) to the niobium phosphate system.

II. Sample Preparation and Test Methods

Starting materials for the preparation of mixtures consisted of high purity niobium pentoxide and a commercial preparation of *nitrogen-coated* P_2O_5, which consisted of agglomerates of hexagonal crystalline phosphorus anhydride coated with an ammonium polyphosphate. The Nb_2O_5 was part of the same batch used in previous studies of the systems Nb_2O_5–B_2O_3 (*13*) and Nb_2O_5–GeO_2 (*14*), with a reported melting point of 1485°C. It contained the following impurities when examined by the general qualitative spectrochemical method: Si—less than 0.1%; Fe, Sn, Ti—0.001–0.01%; Ca, Mg—0.0001–0.001%; Cu—? Spectrographic analysis of the P_2O_5 showed: Ba, Fe, Mg—less than 0.001%.

Calculated amounts of Nb_2O_5 and P_2O_5 sufficient to yield 5-g batches, on an ignited basis, were weighed into plastic containers and blended with a high-speed mechanical mixer. As the coated P_2O_5 was relatively nonhygroscopic, it could be conveniently and accurately weighed.

The mixtures were formed into disks 16 mm in diameter by pressing in a mold at approximately 20,000 psi. The disks were placed in covered platinum crucibles and heated slowly (1°/min) to the calcining temperature. The fired disks were ground in an agate mortar, remixed, pressed, and given a second heat treatment at a higher temperature. The complete process of grinding, pressing, and heating was repeated a third time. Temperatures of the three calcinations (10-hr durations) for mixtures containing 50 mole % P_2O_5 and greater were 300, 400, and 600°C. Mixtures higher in niobia than 50 mole % were calcined for 5 hr at 600, 800, and 1000°C, respectively.

The formulated compositions were analyzed for ignition loss and niobia by the Analytical Chemistry Division of the National Bureau of Standards. Except for the two compositions richest in P_2O_5, analyzed values were within 1 mole % of the formulated ones. The following compositions were formulated from Nb_2O_5 and one of the analyzed mixtures: 97.5% Nb_2O_5, 96.4% Nb_2O_5, and 92.5% Nb_2O_5 (see Table I and footnotes 8 and 9). For verification of the existence of solid solution in the $9Nb_2O_5 \cdot P_2O_5$ compound the 92.5% Nb_2O_5 compositions was formulated from two different mixtures (see Table I).

The quenching technique was used to obtain subsolidus and liquidus data on samples sealed in Pt tubes. Quenched samples were examined with the binocular and polarizing microscopes and by X-ray powder diffractometry (Ni-filtered CuKα radiation, $\lambda = 1.54050$ Å) using a high-angle Geiger-counter diffractometer. The technique of sample preparation as well as the apparatus and method have been described in previous publications (*14*). Some solidus and liquidus values were obtained also by differential thermal analysis using a commercial DTA apparatus.

Temperatures were measured with a Pt vs 90Pt:10Rh calibrated thermocouple wire and are given on the International Practical Temperature Scale of 1968 (*15*). During the course of the experiments the thermocouple was checked against the melting point of gold (1064.4°C) and of barium disilicate (1422°C).

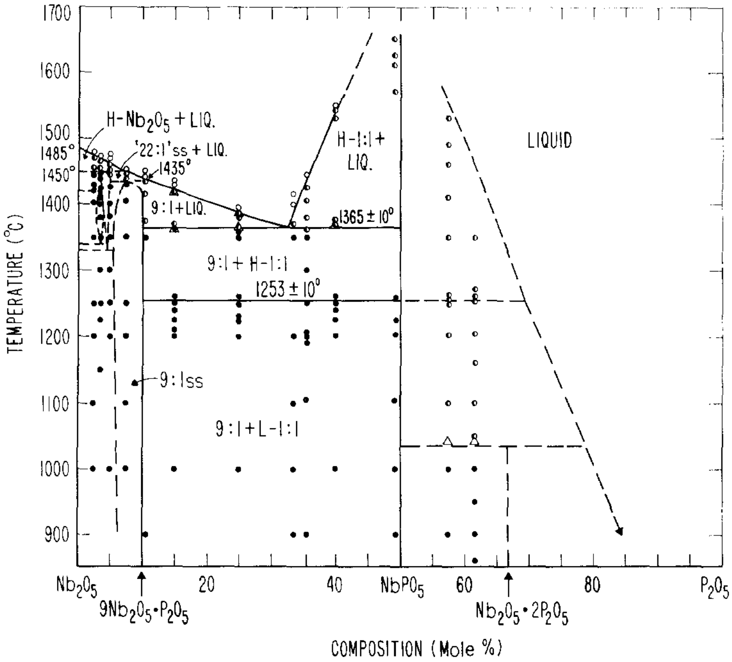

FIG. 1. Partial phase equilibrium diagram for the system Nb_2O_5–P_2O_5.

●—no melting; ◐—partial melting; ○—complete melting. △—Solidus and/or liquidus determined by DTA.

L-1:1 = low-temp. polymorph of $NbPO_5$; H-1:1 = high temp. polymorph of $NbPO_5$ (isostructural with $TaPO_5$); 9:1 (*ss*) = $9Nb_2O_5 \cdot P_2O_5$ (solid solution); '22:1' *ss* = $22Nb_2O_5 \cdot P_2O_5$ solid solution.

TABLE 1

Experimental Data[1] for Compositions in the Binary System Nb_2O_5-P_2O_5

Composition[2]		Heat Treatment[3]		Results	
Nb_2O_5 Mol %	P_2O_5 Mol %	Temp °C	Time hrs	Physical Observation	X-Ray Diffraction Analyses[4]
38.6	61.4	900	166	no melting	1:2 + L-1:1 + [?]
		1000	95	no melting	1:2 + L-1:1
		1255	2.3	some melting	L-1:1 + H-1:1(tr)
		1349	1	considerable melting	H-1:1
42.6	57.4	1000	95	no melting	1:2 + [?] + L-1:1
		1251	2	some melting	L-1:1 + [?]
		1257	4	some melting	L-1:1 + H-1:1 + [?]
		1529	1	considerable melting	H-1:1
50.7	49.3	900	166	no melting	L-1:1
		1225	4.5	no melting	L-1:1 + 9:1
		1258	3	no melting	H-1:1 + 9:1
		1650	0.5	some melting	H-1:1 + [L-Nb_2O_5][5]
60.0	40.0	1000	5	no melting	L-1:1 + 9:1
		1250	22	no melting	L-1:1 + 9:1
		1260	17	no melting	L-1:1 + 9:1 + H-1:1
		1371	2	slight melting	H-1:1 + 9:1
		1544	0.75	nearly melted	-
		1550	1.75	melted	[H-1:1]
64.5	35.5	900	15	no melting	H-1:1[6] + 9:1
		1104	1	no melting	L-1:1 + 9:1 + H-1:1(tr)
		1360	1	slight melting	H-1:1 + 9:1
		1426	1	nearly melted	H-1:1 + [L-Nb_2O_5]
		1446	1	melted	[H-1:1 + 9:1]
66.4	33.6	900	166	no melting	L-1:1 + 9:1
		1349	1.5	no melting	H-1:1 + 9:1
		1369	1.5	considerable melting	H-1:1 + [L-Nb_2O_5 + 9:1]
		1401	1.5	melted	[H-1:1 + L-Nb_2O_5]
75.0	25.0	1000	5	no melting	9:1 + L-1:1
		1248	3	no melting	9:1 + L-1:1
		1261	20	no melting	9:1 + H-1:1 + L-1:1
		1261	20		9:1 + L-1:1 + H-1:1(tr)[7]
		1229	20		

TABLE 1 (continued)

		1360	2	no melting	9:1 + H-1:1
		1365	2	slight melting	9:1 + [H-1:1]
		1384	2	nearly melted	-
		1391	2	melted	glass hump
85.0	15.0	1000	5	no melting	9:1 + L-1:1
		1261	20	no melting	9:1 + H-1:1
		1364	2.5	no melting	9:1 + H-1:1
		1370	2	some melting	9:1 + H-1:1
		1423	3	considerable melting	9:1
		1429	3	melted	[9:1]
89.5	10.5	900	166	no melting	9:1
		1416	2	some melting	9:1
		1435	2	considerable melting	9:1 + [L-Nb_2O_5]
		1440	16	melted	[9:1 + L-Nb_2O_5]
92.5[8]	7.5[8]	1000	70	no melting	9:1 ss
		1250	114	no melting	9:1 ss
		1430	3	no melting	9:1 ss
		1450	1	melted	[9:1 ss + L-Nb_2O_5]
92.5[9]	7.5[9]	1200	20	no melting	9:1 ss
		1445	35	almost melted	'22:1' ss + [9:1 ss + L-Nb_2O_5]
95.0	5.0	1000	5	no melting	9:1 ss + H-Nb_2O_5
		1305	22	no melting	9:1 ss + H-Nb_2O_5
		1350	90	no melting	9:1 ss + '22:1' ss
		1425	67	no melting	9:1 ss + '22:1' ss
		1459	1	considerable melting	['22:1' ss] + H-Nb_2O_5
		1470	1	melted	['22:1' ss]
96.4	3.6[9]	1250	144	no melting	H-Nb_2O_5 + 9:1 ss
		1350	90	no melting	'9:1' ss[10]
		1411	21	no melting	'9:1' ss[10]
		1424	70	no melting	'22:1' ss
		1424 1299	70 88		9:1 ss[11] + H-Nb_2O_5
		1443	23	no melting	'22:1' ss + H-Nb_2O_5
		1443 1380	23 18		'9:1' ss[12]
		1448	4	no melting	'22:1' ss + H-Nb_2O_5
		1455	3.5	some melting	'22:1' ss + H-Nb_2O_5

TABLE 1 (continued)

		1465	2	nearly melted	['22:1' ss] + H-Nb_2O_5
		1470	1.5	melted	[L-Nb_2O_5]
97.5[9]	2.5[9]	1000	70	no melting	9:1 ss + H-Nb_2O_5
		1350	90	no melting	'9:1' ss + H-Nb_2O_5
		1403	19	no melting	'9:1' ss + H-Nb_2O_5
		1421	4	no melting	'9:1' ss + H-Nb_2O_5 + 22:1 (?)
		1428	19	no melting	'22:1' ss + H-Nb_2O_5
		1428	19		
		1250	144		H-Nb_2O_5 + 9:1 ss[13]
		1444	4	no melting	H-Nb_2O_5 + '22:1' ss
		1454	1.5	slight melting	H-Nb_2O_5 + '22:1' ss
		1470	2	considerable melting	[L-Nb_2O_5] + H-Nb_2O_5
		1477	1	melted	[L-Nb_2O_5]

---

[1] Only definitive data are given; figure 1 shows all of the heat treatments.

[2] Except as stated otherwise, analyzed value for Nb_2O_5; P_2O_5, by difference.

[3] Specimens quenched in sealed Pt tubes.

[4] Phases are listed in order of amount present at room temperature and are designated by the numerical ratios of Nb_2O_5 to P_2O_5. Phases not necessarily present at the elevated temperature are enclosed in brackets.

[5] Low Nb_2O_5 crystallizes from quenched liquid.

[6] H-1:1 is formed metastably.

[7] Shows reversibility between H-1:1 and L-1:1.

[8] Formulated from Nb_2O_5 and the analyzed composition: 64.5 Nb_2O_5:35.5 P_2O_5

[9] Formulated from Nb_2O_5 and the analyzed composition: 89.5 Nb_2O_5:10.5 P_2O_5

[10] Isostructural with phase at 9:1 composition.

[11] Shows reversibility between '22:1' ss and 9:1 ss + H-Nb_2O_5 (Point (b), Fig. 2).

[12] Shows reversibility between '22:1' ss + H-Nb_2O_5 and '9:1' ss (Point (a), Fig. 2).

[13] Shows reversibility between '22:1' ss + H-Nb_2O_5 and 9:1 ss + H-Nb_2O_5 (Point (c), Fig. 2)

III. Results and Discussion

3.1. Phase Diagram

The partial phase diagram for the system Nb_2O_5–P_2O_5 as determined in sealed Pt tubes is shown in Fig. 1. Table I lists the compositions studied, the important heat treatments, and the phases identified by X-ray analysis. The outstanding feature is the compound $NbPO_5$, with a melting point greater than 1650°C. However, this compound when heated in air by induction to 1650°C completely volatilized. The system shows no indication of liquid immiscibility, and three incongruently melting solid solution phases appear in the niobium-rich portion: 9:1 *ss*, '22:1' *ss*, and '9:1' ss (Fig. 2).

Experimental difficulties were encountered in all regions except that between $NbPO_5$ and $9Nb_2O_5 \cdot P_2O_5$. Compositions rich in P_2O_5 hydrated rapidly at low temperatures, and at high temperatures they

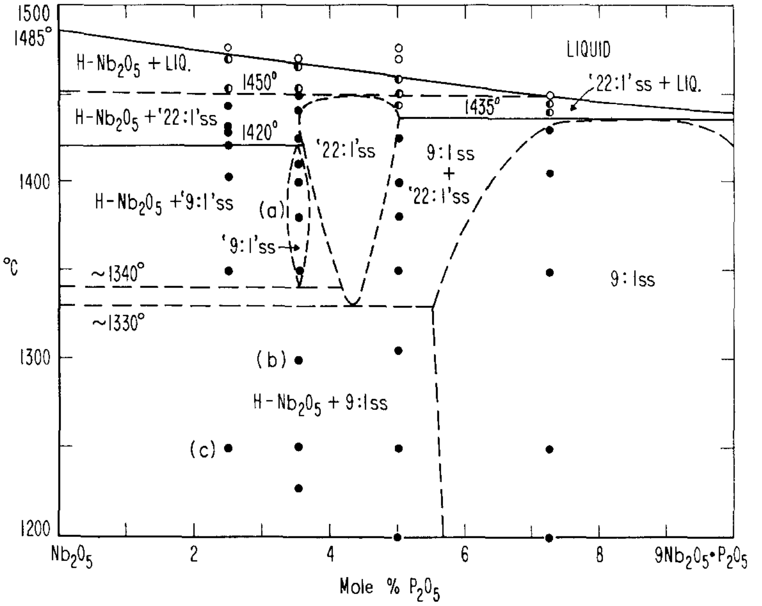

FIG. 2. Phase equilibrium diagram of the subsystem Nb_2O_5–$9Nb_2O_5 \cdot P_2O_5$, enlarged.

●—no melting; ◑—partial melting; ○—complete melting.

9:1 *ss* = $9Nb_2O_5 \cdot P_2O_5$ solid solution; '9:1' *ss* = phase isostructural with 9:1 *ss* phase; '22:1' *ss* = $22Nb_2O_5 \cdot P_2O_5$ solid solution. (a), (b), (c) = reversibility experiments (see Table I and text).

lost P_2O_5 by volatilization. The phase designated '9:1' *ss*, at about 3.6 mole % P_2O_5, was stable over only 80°C and was isostructural with 9:1 *ss* of the nominal composition. However, no differences in any of the X-ray powder patterns were detected between the two phases. The width of the 9:1 *ss* phase (about 4.5 mole %) was determined from the single-phase compositional region and not by change in X-ray *d* spacings. As noted by Roth et al. (*8*), the size of the tetrahedral atom in PNb_9O_{25} (9:1) is not significantly different from the one in the high temperature form of Nb_2O_5. In the latter case the tetrahedral atom is Nb instead of P. Accordingly, it is not unexpected that the substitution of Nb for P in the 9:1 solid-solution phases is not reflected in a detectable change in the unit cell dimensions.

Several reversibility experiments were tried in order to verify the stability relations of the '9:1' *ss* and the '22:1' *ss* phases. Thus the composition 3.6 mole % P_2O_5 (Fig. 2) heated at 1443° for 2 hr formed the '22:1' phase. On reheating at 1380°C for 18 hr [point (a)], single phase '9:1' *ss* was obtained. Another sample of the same composition showing single phase '22:1' *ss*, when heated at 1299°C for 88 hr [point (b)] yielded the 9:1 *ss* phase and H–Nb_2O_5. Likewise, a sample of composition 2.5 mole % P_2O_5 showing '22:1' *ss* and H-Nb_2O_5 phases after heating at 1428°C for 19 hr yielded 9:1 *ss* and H–Nb_2O_5 upon reheating at 1250°C for 114 hr [point (c)].

Kurbatov and Demenov in 1956 (*2*) reported the compound $2Nb_2O_5 \cdot P_2O_5$, and Shtin (*9*) in his study of niobium phosphates and their hydrates reported the dehydration of $2Nb_2O_5 \cdot P_2O_5 \cdot H_2O$ at 980°C to give $2Nb_2O_5 \cdot P_2O_5 + H_2O$. He presented an unindexed X-ray powder pattern, which the present authors find to be a mixture of several phases. Haider in 1964 (*4*) found by X-ray examination that specimens with compositions near the molar ratio of $2Nb_2O_5$ to P_2O_5 were comprised of mixtures of $NbPO_5$ and Nb_2O_5. Figure 1 shows that the composition $2Nb_2O_5:P_2O_5$ is located in a two phase equilibrium region consisting of $NbPO_5$ and $9Nb_2O_5 \cdot P_2O_5$ (not Nb_2O_5).

3.2. Compounds in the System

$Nb_2O_5 \cdot 2P_2O_5$ ($Nb_2P_4O_{15}$). Haider (*4*) prepared the compound by precipitation methods and by reaction of Nb_2O_5 with ammonium phosphate or phosphoric acid at high temperature. He indexed the X-ray diffraction pattern on the basis of a cubic cell, and the compound was found to be *isomorphous* with zirconium pyrophosphate (ZrP_2O_7) by comparison with the X-ray data of Levi and Peyronel

TABLE II

COMPOUNDS IN THE SYSTEM Nb_2O_5–P_2O_5

Compound	Reference	Unit Cell Dimensions[a]				XR Density	Structure
		a	b	c	β		
		A	A	A		g cm^{-3}	
$Nb_2P_4O_{15}$ (1:2)	Haider (1963)	8.073 ± 0.005				3.462 ($Z = 2$)	$(ZrP_2O_7)_4$ pseudocubic
	Levin & Roth (1969)	8.066					
L-$NbPO_5$ (1:1)	Haider (1963)	6.394		4.103		4.032 ($Z = 2$)	NbO_6+ PO_4
	Longo & Kierkegaard (1966)	6.3873 ± 0.001		4.1037 ± 0.0008		4.044	
	Levin & Roth (1969)	6.382 ± 0.001		4.101 ± 0.001		4.053	
H-$NbPO_5$	Levin & Roth (1969)	11.257 ± 0.002	5.276 ± 0.001	6.606 ± 0.001	90°17′ ± 1′	3.452 ($Z = 4$)	
$TaPO_5$	Levin & Roth (1969)	11.272 ± 0.001	5.281 ± 0.001	6.621 ± 0.001	90°13′ ± 1′	4.920	
Nb_9PO_{25} (9:1)	Waring & Roth (1964)	15.60		3.828			
	Roth, Wadsley, & Andersson (1965)	15.60		3.828		4.52 ($Z = 2$)	NbO_6 blocks 3 × 3 × ∞
	Levin & Roth (1969)	15.638 ± 0.001		3.827 ± 0.001		4.496	
$Nb_{44}P_2O_{115}$ (22:1)	Levin & Roth (1969)	22.238 ± 0.006	3.827 ± 0.001	25.91 ± 0.01	93°7′ ± 2′	4.516 ($Z = 1$)	NbO_6 blocks 3 × 3 × ∞ 3 × 4 × ∞
Nb_2O_5 $(NbNb_{27}O_{70})$	Gatehouse & Wadsley (1964)	21.16	3.822	19.35	119°50′	4.55 ($Z = 14$)	NbO_6 blocks 3 × 4 × ∞ 3 × 5 × ∞

---

[a] In the present work unit cell values and their standard errors were determined by a least-squares calculation made on the Nat. Bur. Stand. electronic computer according to a program developed by H. T. Evans, Jr., D. E. Appleman, and D. S. Handwerker, Least-squares refinement of crystal unit cells with powder diffraction data by an automatic computer indexing method; presented at *Amer.* Crystal Assoc. Annual Meeting, Cambridge, Mass., 1963; Program 42–43. Lattice constant errors are based on the least-squares refinement of the variance-covariance matrix derived from the unweighted $\Delta\theta$ residuals.

[b] Approximate cell unit after J. G. Allpress, C.S.I.R.O., Melbourne, Australia.

(*16*) as well as with those of a freshly prepared sample of ZrP_2O_7. Haider noted that the contents of a unit cell of niobium pyrophosphate ($Nb_4P_8O_{30}$) contains two more oxygen atoms than that of zirconium pyrophosphate ($Zr_4P_8O_{28}$). He suggested the possibility of the presence of tetravalent niobium forming the isostructural compound NbP_2O_7. The present study does not confirm the cubic symmetry of the compound either by the X-ray data or by microscopic examination. However, the X-ray data could be indexed on the basis of a pseudocubic cell, with $a = 8.066$ Å, very close to the 8.073 Å value given by Haider (Table II). Table III lists the X-ray powder data.

Seifer and Tananaev (*10*) reported preparation of $3Nb_2O_5 \cdot 5P_2O_5$ by solution methods. Their identification was solely by chemical analysis, and attempts by the present authors to duplicate their procedure were unsuccessful.

$Nb_2O_5 \cdot P_2O_5$ ($NbPO_5$). Hahn in 1951 (*1*) was the first one to prepare a stable niobium phosphate compound of this composition, and he reported an unindexed X-ray powder pattern. Haider (*4*) established the tetragonal unit cell for low $NbPO_5$ (L–$NbPO_5$) and showed that this was the phase obtained by Hahn. Longo and Kiekegaard (*6*) determined the crystal structure. A comparison of the unit cell dimensions obtained by the various investigators is given in Table II.

TABLE III

X-RAY POWDER DIFFRACTION DATA[a] FOR $Nb_2O_5 \cdot 2P_2O_5$ (CuKα radiation $\lambda = 1.54050$ Å)

hkl[b]	*d*(*A*)	*I*/*I*$_0$(%)
111	4.662	23
	4.316	5
200	4.035	100
210	3.606	35
211	3.294	31
220	2.850	36
300	2.687	3
311	2.431	43
222	2.329	10
320	2.237	4
400	2.016	5
410	1.9568	5
411	1.9019	4
331	1.8503	11
420	1.8040	19
421	1.7602	3
422	1.6461	14
511	1.5520	18

[a] Obtained in dry mount. Sample first heated to 600°C for 10 hr.

[b] Based on pseudocubic unit cell: $a = 8.066$ Å.

Haider also reported that at 1070°C $Nb_2O_5 \cdot 2P_2O_5$ lost P_2O_5 by volatilization yielding $NbPO_5$ structurally identical to $TaPO_5$ rather than to the normal tetragonal $NbPO_5$. On further heating to 1250°C, the $TaPO_5$ form of $NbPO_5$ changed to the tetragonal form. In the present work the high form of $NbPO_5$(H–$NbPO_5$) has been indexed[1] on the basis of a monoclinic unit cell.

Tantulum phosphate ($TaPO_5$) was made by melting together high purity Ta_2O_5 in an excess of KH_2PO_4, leaching the product in water, and heating the remaining residue in air at 1503°C. High Nb_2O_5 and $TaPO_5$ are isostructural, as seen by a comparison of the X-ray powder patterns given in Table IV, thus confirming Haider's observation. However, contrary to his findings, the present work showed that tetragonal $NbPO_5$ is the stable low-temperature form, and monoclinic $NbPO_5$ ($TaPO_5$ type) is the stable high-temperature form.

Brown and Hummel (*5*) in 1965 found that $NbPO_5$ underwent an irreversible transformation at 985 ± 25°C, and they listed the X-ray powder data for α and β forms. Inspection of their data shows that the α form was probably mostly $Nb_2O_5 \cdot 2P_2O_5$ and that the β form was a mixture of low $NbPO_5$ and $9Nb_2O_5 \cdot P_2O_5$. Apparently, in the preparation of $NbPO_5$ from the Nb_2O_5 and $NH_4H_2PO_4$ starting materials, $Nb_2O_5 \cdot 2P_2O_5$ was formed at low temperature. With subsequent heating at about 1000°C, the mixture lost P_2O_5 by volatilization, and the average composition moved into the two-phase region of $NbPO_5$ and $9Nb_2O_5 \cdot P_2O_5$.

The powder diffraction file (*17*) contains four patterns of $NbPO_5$: two by Brown and Hummel (card Nos. 19-868 and 19-869), one by Hahn (No. 5-0427), and one by Longo and Kierkegaard (No. 19-866). All but the last pattern should be discarded.

$9Nb_2O_5 \cdot P_2O_5$ (Nb_9PO_{25}). This tetragonal phase was first indexed by Waring and Roth (*7*) who discovered other isostructural phases of the type ANb_9O_{25} and ATa_9O_{25}, where A is one or another of the small pentavalent ions As, V, and P. The phases are apparently isostructural with $Ta_2O_5 \cdot 2Nb_2O_5$. The crystal structure of Nb_9PO_{25} was

---

[1] John G. Allpress, CSIRO, University of Melbourne, Australia, determined the approx unit cell by using electron diffraction techniques.

TABLE 4

X-Ray Powder Diffraction Data for Isostructural Compounds H-$NbPO_5$ and $TaPO_5$ (CuKα radiation λ = 1.54050Å).

H-$NbPO_5$ (1570°/1hr)					$TaPO_5$ (1503°/2hr)			
$2\theta_{calc}$	$2\theta_{obs}$	I/Io	d(A)	hkl[a]	d(A)	I/Io	$2\theta_{obs}$	$2\theta_{calc}$
15.51	15.50	14	5.71	$10\bar{1}$	5.72	13	15.48	15.48
15.58	15.60	19	5.68	101	5.70	24	15.54	15.53
15.73	15.75	56	5.62	200	5.63	49	15.74	15.71
20.77	20.74	59	4.28	201	4.29	56	20.72	20.72
21.54	21.54	100	4.122	011	4.130	100	21.50	21.51
22.98	22.99	89	3.865	111	3.875	53	22.93	22.94
--	--	--	--	210	3.857	23	23.04	23.06
26.74	26.78	65	3.326	$21\bar{1}$	3.331	56	26.74	26.71
26.83	26.83	67	3.320	211	--	--	--	--
27.25	27.27	30	3.267	$30\bar{1}$	3.272	16	27.23	27.22
27.37	27.35	25	3.258	301	3.263	14	27.31	27.31
--	--	--	-	102	3.173	5	28.10	28.10
31.31	31.32	9	2.854	$20\bar{2}$	2.859	8	31.26	31.26
31.45	31.47	11	2.840	202	2.850	10	31.36	31.36
31.77	31.78	7	2.813	400	--	--	--	--
32.18	32.21	20	2.777	$31\bar{1}$	2.780	20	32.17	32.15
32.29	32.30	19	2.769	311	2.773	19	32.25	32.23
32.91	32.94	49	2.717	$11\bar{2}$	--	--	--	--
32.98	32.98	52	2.714	112	2.720	53	32.90	32.90
33.96	33.96	40	2.638	020	2.639	29	33.94	33.92
34.55	34.54	11	2.595	$40\bar{1}$	2.595	17	34.53	34.52
34.68	34.67	12	2.585	401	2.590	21	34.61	34.61
35.73	35.74	11	2.510	$21\bar{2}$	2.514	12	35.69	35.68
35.86	35.82	10	2.505	212	2.509	14	35.76	35.77
36.15	36.14	39	2.483	410	2.486	48	36.10	36.10
37.63	37.65	7	2.387	220	2.391	15	37.58	37.59
40.08	40.10	6	2.248	$22\bar{1}$	2.250	14	40.04	40.04
				221	2.246	10	40.11	40.08
41.72	41.72	8	2.163	$10\bar{3}$	2.167	14	41.64	41.63
--	--	--	--	103	2.164	14	41.70	41.70
--	--	--	--	022	2.064	5	43.83	43.82

TABLE 4 (continued)

				12$\bar{2}$	2.032	10	44.56	44.57
44.68	44.67	14	2.027	122	2.030	6	44.60	44.61
46.85	46.85	14	1.9376	22$\bar{2}$	1.9391	8	46.81	46.79
46.96	46.95	15	1.9337	222	1.9364	14	46.88	46.87
48.80	48.79	12	1.8650	50$\bar{2}$	1.8671	9	48.73	48.74
49.04	49.06	15	1.8553	502	1.8603	10	48.92	48.93
49.23	49.21	14	1.8500	42$\bar{1}$	1.8522	14	49.15	49.18
49.33	49.34	10	1.8454	421	1.8486	16	49.25	49.25
50.41	50.41	17	1.8088	32$\bar{2}$	1.8111	17	50.34	50.35
50.55	50.55	22	1.8041	322	1.8071	22	50.46	50.45
50.97	50.94	20	1.7912	31$\bar{3}$	1.7932	18	50.88	50.89
51.18	51.18	19	1.7834	313	1.7879	22	51.04	51.05
51.67	51.68	16	1.7673	610	1.7698	12	51.60	51.60
53.56	53.54	8	1.7102	61$\bar{1}$	1.7120	8	53.48	53.50
53.70	53.70	15	1.7055	611	1.7084	11	53.60	53.60
53.90	53.89	16	1.6999	031	1.7014	14	53.84	53.85
				13$\bar{1}$				
54.58	54.60	11	1.6795	131	1.6809	8	54.55	54.58
54.84	54.86	24	1.6721	12$\bar{3}$	1.6749	25	54.76	54.75
--	--		--	123				
--	-	-	--	004	1.6554	4	55.46	55.47
56.21	56.20	6	1.6354	10$\bar{4}$	--	--	--	--
				60$\bar{2}$				
--		--	--	104	1.6370	6	56.14	56.15
--	--	--	--	23$\bar{1}$	1.6300	8	56.40	56.44
56.54	56.54	11	1.6263	231	1.6285	10	56.46	56.47
59.00	59.00	6	1.5643	70$\bar{1}$	1.5652	8	58.96	58.93
59.11	59.13	9	1.5611	701	1.5643	10	59.00	59.04

[a] Based on monoclinic cell: For H-Nb_2O_5, a = 11.257, b = 5.276, c = 6.606Å, β = 90°17';
For $TaPO_5$, a = 11.272, b = 5.281, c = 6.621Å, β = 90°13'
(See Table 2, footnote a).

determined by Roth et al. (*8*). The unit cell dimensions determined in the present work agree with those of Waring and Roth (Table II). As noted earlier, no variation in unit cell dimensions with composition were detected for the 9:1 *ss* and '9:1' *ss* phases.

$22Nb_2O_5 \cdot P_2O_5$ ($Nb_{44}P_2O_{115}$). This phase was indexed[2] on the basis of a monoclinic unit cell (Table V).

---

[2] John G. Allpress, CSIRO, University of Melbourne, Australia, determined the approx unit cell by using electron diffraction and lattice image techniques.

TABLE V

X-RAY POWDER DIFFRACTION DATA FOR $22Nb_2O_5 \cdot P_2O_5$[a]
(CuKα radiationλ = 1.54050 Å)

hkl[b]	$d(A)$	$I/I_0(\%)$	$2\theta_{obsd}$	$2\theta_{calcd}$
002	12.95	7	6.82	6.83
200	11.10	6	7.95	7.96
400	5.56	6	15.93	15.95
402	5.003	12	17.71	17.71
$\bar{2}05$	4.789	20	18.51	18.50
111	3.728	44	23.85	23.85
$\bar{1}12$	3.630	8	24.50	24.50
$\bar{2}07$	3.560	49	24.98	24.95
602	3.506	76	25.38	25.37
$\bar{1}13$	3.446	12	25.68	25.67
311	3.358	34	26.52	26.51
$\bar{1}14$	3.270	9	27.25	27.24
604	3.145	9	28.38	28.41
407	3.001	11	29.75	29.73
511	2.868	24	31.16	31.14
$\bar{1}16$	2.853	41	31.33	31.34
513	2.720	17	32.90	32.91
$\bar{3}16$	2.703	17	33.11	33.12
804	2.501	16	35.87	35.86
118	2.444	9	36.74	36.74
711	2.421	5	37.10	37.09
318	2.316	46	38.86	38.88
10,0,4	2.067	24	43.76	43.78
$\bar{4},0,12$	2.049	34	44.16	44.19
020	1.914	100	47.46	47.47
$\overline{12},0,3$	1.830	13	49.80	49.79

[a] Heat treatment 1424°C for 70 hr for composition $96.4Nb_2O_5:3.6P_2O_5$.

[b] Based on monoclinic cell: $a = 22.238$, $b = 3.827$, $c = 25.91$ Å, $\beta = 93°7'$ (see Table II, footnote *a*).

3.3. The Block Principle in Niobate Structures

Magneli (*18*) introduced the concept of homologous series of transition metal oxides in his study of slightly reduced molybdenum and tungsten oxides. Roth and Wadsley (*12*) extended and applied this concept to homologous series of compound formation in niobate systems containing an additional small highly charged cation, such as Ti, P, W. The structures all contain niobium in octahedral coordination with oxygen atoms. The octahedra form blocks (ReO_3 type) with finite numbers of octahedra in two dimensions but with infinite numbers in the third. The blocks condense upon themselves by edge-sharing with other blocks at different levels along the short axis, in such a way that tetrahedral holes are formed at the block junction. These tetrahedral holes may or may not be partially filled with atoms such as Ti, Nb, P, W.

Several of the compounds in the Nb_2O_5–P_2O_5 system illustrate the block principle. The structure of the compound Nb_9PO_{25} was predicted from these crystallochemical principles and was verified and refined by Fourier and least-squares single-crystal analyses (*8*). It contains blocks of $[NbO_6]$ octahedra, 3 octahedra wide, three long and infinite in the third dimension. These blocks are joined to similar blocks at 1/2 *c* by sharing octahedral edges, and some of the tetrahedral positions at the junctions are occupied by phosphorus atoms. This compound may be represented by the general structural formula $B_{nm+1}O_{3nm-(n+m)+4}$ [(*12*), Part IV (Table 2, p. 46)], in which n and m represent the number of octahedra in the width and length of a block, respectively. For the 3 × 3 block, as in Nb_9PO_{25}, the formula reduces to $B_{10}O_{25}$ or $(B, B_9)O_{25}$ with one of the ten cations in tetrahedral coordination.

A limiting structure represented by the above general formula would occur for blocks of single octahedra, in which case both n and m would be one. The structural formula reduces to B_2O_5 (B, BO_5) which corresponds to the compound $NbPO_5$. This compound contains chains of corner-shared $[NbO_6]$ octahedra running parallel to the tetragonal *c* axis. Tetrahedra of $[PO_4]$ link the chains together to give a three-dimensional network (*6*).

The crystal structure of high Nb_2O_5 was determined by Gatehouse and Wadsley (*19*). It contains 14 molecules to the unit cell, and one of the 28 niobium atoms is in tetrahedral coordination. The structure consists of two sets of octahedral blocks. At one level these blocks are 3 octahedra wide by 5 long and form slabs running through the structure by edge sharing on both sides. At the other level isolated 3 × 4 blocks join the slabs of 3 × 5 blocks by edge sharing, to form tetrahedral holes, which are partially filled with niobium atoms. The two sizes of blocks complicate the derivation of the general expression for the structural formula, which becomes the sum of the appropriate formulas for the two levels. The same general expression given above can be used to calculate the particular formula for the 3 × 4 block level, yielding $B_{13}O_{33}$. However, a different formula must be used for the level of 3 × 5 blocks, because they are joined together at the same level. The general formula [(*12*), Part IV (Table 2, p. 46)] is $B_{nm}O_{3nm-(n+m)}$, which reduces to $B_{15}O_{37}$. Combining the two simplified formulas gives $B_{28}O_{70}$ (e.g., $Nb,Nb_{27}O_{70}$).

Roth et al. (*8*) discuss the possible substitution of P for Nb in the high niobia structure. If the one tetrahedrally coordinated niobium atom out of the 28 niobium atoms in the unit cell can be replaced by P, they reasoned that a solid solution might exist "between Nb_2O_5 and some hitherto unsuspected phase $PNb_{27}O_{70}$, with the same structure and essentially identical unit cell dimensions." It was for this reason that the 27:1 molar ratio of Nb_2O_5: P_2O_5 was studied. This composition (3.6 mole % P_2O_5, Fig. 2) produced the "9:1" *ss* phase. Although there might be some question as to the existence of this phase on the equilibrium diagram, there is no doubt of a two-phase region between H-Nb_2O_5 and the phase. The surprising fact is that phosphorous does not substitute for tetrahedrally coordinated niobium in Nb_2O_5 (as predicted) but rather niobium substitutes for tetrahedrally coordinated phosphous in Nb_9PO_{25}, as discussed earlier.

The phase designated as $22Nb_2O_5 \cdot P_2O_5$, examined by Allpress[2] gave an electron lattice image pattern showing it to consist of an intergrowth of isolated 3 × 3 and 3 × 4 blocks. Therefore, the same general structural formula $B_{nm+1}O_{3nm-(n+m)+4}$ can be applied twice. For the 3 × 3 blocks, the formula reduces to $B_{10}O_{25}$; for the 3 × 4 blocks, to $B_{13}O_{33}$. Thus the structural formula for the compound is $B_{10}O_{25} + B_{13}O_{33} = B_{23}O_{58}$. The idealized structure consists of a block of corner-sharing octahedra three wide by three long and infinite in the third direction, joined by tetrahedrally coordinated P atoms to identical blocks, forming slabs through the structure. This structural element is identical to that of Nb_9PO_{25}. The other structural element is similar except that the blocks are 3 × 4 and that tetrahedral positions are occupied with Nb rather than P. The two structural elements alternate in a regular sequence. Theoretical unit cell dimensions from the idealized structure are as follows, in good agreement with the experimental values given in Table II: $a = 22.0$ Å, $b = 3.8$ Å, $c = 25.9$ Å, $\beta = 93.4°$, $Z = 2$. However, whereas the theoretical unit cell contents is $B_{46}O_{116}$, the actual atom composition is $B_{46}O_{115}$ ($Nb_{44}P_2O_{115}$).

Although the explanation for this oxygen shortage is unknown, two other similar cases in the niobates have been reported. The compound designated $9Nb_2O_5 \cdot GeO_2$ [7], apparently isostructural with $9Nb_2O_5 \cdot P_2O_5$, shows an oxygen deficiency between the structural formula and the atomic formula. A similar discrepancy exists in the solid solution region between $8Nb_2O_5 \cdot WO_3$ and $6Nb_2O_5 \cdot WO_3$ in the system Nb_2O_5–WO_3 [(*12*), Part I]. Neutron diffraction techniques, which might be able to locate oxygen vacancies in a large unit cell, could possibly be used to resolve the structure for these cases.

References

1. R. B. Hahn, Phosphates of niobium and tantalum, *J. Amer. Chem. Soc.* **73**, 5091–3 (1951).

2. D. I. Kurbatov and N. V. Demenov, *Zh. Priklad Khim.* **29**, 1747 (1956); *Engl. transl., J. Appl. Chem. U.S.S.R.* 1877 (1956).

3. S. Z. Haider, *Anal. Chim. Acta* **24**, 250 (1961).

4. S. Z. Haider, Niobium and tantalum phosphates, *Proc. Pak. Acad. Sci.* **1**, 19–28 (1964).

5. J. J. Brown and F. A. Hummel, Reactions between ZnO and selected oxides of elements of groups IV and V, *Trans. Brit. Ceram. Soc.* **64**, 419–437 (1965).

6. John M. Longo and Peder Kierkegaard, The crystal structure of $NbOPO_4$, *Acta Chim. Scand.* **20**, 72–78 (1966).

7. J. L. Waring and R. S. Roth, Tetragonal phases of the general type $10M_2O_5 \cdot 90M'_2O_5$ apparently isostructural with $Ta_2O_5 \cdot 2Nb_2O_5$, *Acta Crystallogr.* **17**, Part 4, 455–6 (1964).

8. R. S. Roth, A. D. Wadsley, and S. Andersson, The crystal structure of PNb_9O_{25},($P_2O_5 \cdot 9Nb_2O_5$), *Acta Crystallogr.* **18**, Part 4, 643–7 (1965).

9. A. P. Shtin, Niobium phosphates and their hydrates, *Izv. Sib. Otd. Akad. Nauk S.S.S.R.* No. 3, 68–74 (1961).

10. G. S. Seifer and I. V. Tananaev, Normal orthophosphates of niobium and tantalum, *Zh. Neorg. Khim.* **8**, 63–65 (1963); Engl. transl., Russ J. Inorg. Chem. 30–32 (1963).

11. E. M. Levin, Structural interpretation of immiscibility in oxide systems: IV. Occurrence, extent and temperature of the monotectic, *J. Amer. Ceram. Soc.* **50**, 29–38 (1967).

12. R. S. Roth and A. D. Wadsley, Multiple phase formation in the binary system Nb_2O_5–WO_3. I. Preparation and identification of phases, *Acta Crystallogr.* **19**, 25–32 (1965); IV. The Block principle, *Acta Crystallogr.* **19**, 42–47 (1965).

13. E. M. Levin, Phase equilibria in the system niobium pentoxide-boric oxide, *J. Res. Nat. Bur. Stand. Sect. A* **70**, 11–16 (1966).

14. E. M. Levin, Phase equilibria in the system niobium pentoxide-germanium dioxide, *J. Res. Nat. Bur. Stand. Sect. A* **70**, 5–10 (1966).

15. The international practical temperature scale of 1968, *Metrologia* **5**, 35–44 (1969).

16. G. R. Levi and G. Peyronel, Crystalographic structure of the isomorphous group (Si^{4+}, Ti^{4+}, Zr^{4+}, Sn^{4+}, Hf^{4+}) P_2O_7, *Z. Kristallogr.* **92A**, 190–209 (1935).

17. Powder Diffraction File, Diffraction Data Dept., ASTM Bldg. 1916 Race St., Philadelphia, Pa. 19103.

18. A. Magnélli, Structures of the ReO_3 type with recurrent dislocations of atoms: Homologous Series of molybdenum and tungsten oxides, *Acta Crystallogr.* **6**, 495–500 (1953).

19. B. M. Gatehouse and A. D. Wadsley, The crystal structure of the high-temperature form of niobium pentoxide, *Acta Crystallogr.* **17**, 1545–1554 (1964).