JOURNAL OF RESEARCH of the National Bureau of Standards — A. Physics and Chemistry
Vol. 70A, No. 1, January–February 1966

Phase Equilibria in the System Niobium Pentoxide—Germanium Dioxide

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(October 11, 1965)

The phase equilibrium diagram for the system $Nb_2O_5-GeO_2$ has been determined experimentally, using the quenching technique and examining the samples by optical microscopy and x-ray powder diffractometry. The system contains one compound, $9Nb_2O_5 \cdot GeO_2$, which melts incongruently at 1420 °C. A eutectic between this compound and GeO_2 is located at about 97 mol percent GeO_2 and 1090 °C. The system does not show liquid immiscibility, and it is concluded that the ionic field strength limit for two-liquid separation in the series of glass formers occurs with the Nb^{+5} cation.

Key Words: Germanium dioxide, immiscibility, niobium pentoxide, phase equilibria.

1. Introduction

Liquid immiscibility in binary oxide systems appears to be confined to the glass forming systems. In a systematic search for the principles underlying two-liquid formation it is necessary to examine the effect of different glass-forming cations, e.g., B^{+3}, Ge^{+4}, Si^{+4}, and also of different modifier cations, i.e., with varying charges and ionic radii. Many binary phase diagrams of glass formers with modifier oxides from Groups I and II of the Periodic Table have been reported [1].[1] Only a few systems with modifier oxides from Groups III and IV have been reported. Two pertinent systems from Group V have been published: $Nb_2O_5-SiO_2$ [2] and $Nb_2O_5-V_2O_5$ [3]. Finally, in Group VI, phase relationships in the system $WO_3-B_2O_3$ [4] have been established.

Determination of the phase diagrams of Nb_2O_5 with B_2O_3, GeO_2, and P_2O_5 has been undertaken in order to complete the study of the effect of a cation of high charge (Nb^{+5}) on immiscibility in a series of glass formers. This paper, therefore, reports the phase equilibrium relations in the $Nb_2O_5-GeO_2$ system and its bearing on immiscibility.

2. Sample Preparation and Test Methods

Starting materials for the preparation of mixtures consisted of high purity niobium pentoxide and electronic grade germanium dioxide, designated by the manufacturers as over 99.7 percent and 99.9+ percent pure, respectively. The Nb_2O_5 contained the following impurities when examined by the general qualitative spectrochemical method: Si—less than 0.1 percent; Fe, Sn, Ti—0.001 to 0.01 percent; Ca, Mg—0.0001 to 0.001 percent, Cu—? Spectrographic analysis of the GeO_2 showed: Si—0.001 to 0.01 percent; Ca, Mg—0.0001 to 0.001 percent; Cu—less than 0.0001 percent, Ag, Al, Fe—?

Calculated amounts of Nb_2O_5 and GeO_2 sufficient to yield 4-g batches, on an ignited basis, were weighed into plastic containers and blended with a high-speed mechanical mixer. The mixtures were formed into discs 16 mm in diameter by pressing in a mold at approximately 20,000 lb/in^2. The disks were placed in covered platinum crucibles and calcined in air at 800 °C for 15 hr, using an electrically heated furnace. The fired disks were ground in an agate mortar, remixed, pressed, and given a second heat treatment at about 900 °C for 12 hr. The complete process of grinding and pressing was repeated a third time, and the specimens were heated in the range of 900 to 1000 °C for 12 hr. Formulated compositions were used in constructing the phase diagram. Analyses of two small samples for Nb_2O_5 only, by the Analytical Chemistry Division, were about 0.75 percent low.

The quenching technique was used to obtain subsolidus and liquidus data on samples sealed in Pt tubes. Constant temperature control of the quenching furnace to within ±2 °C was achieved with a self-adjusting a-c bridge-type controller. Quenched samples were examined with the binocular and polarizing microscopes and by x-ray powder diffractometry (Ni-filtered CuK_α radiation) 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 [5].

The solidus value was deduced from observation of the first temperature at which the sample showed slumping, coupled with x-ray evidence that one of the phases was disappearing. The liquidus temperature was indicated by the formation of a concave meniscus, coupled with microscopic evidence of a quenched glass (for several compositions rich in GeO_2) or x-ray evidence of large amounts of low-temperature niobia-type phases. The polarizing microscope was of limited value in the latter case.

Temperatures were measured with a Pt versus 90 Pt:10 Rh thermocouple which was taken from lengths of thermocouple wire which originally had been calibrated by the temperature physics section.

[1] Figures in brackets indicate the literature references at the end of this paper.

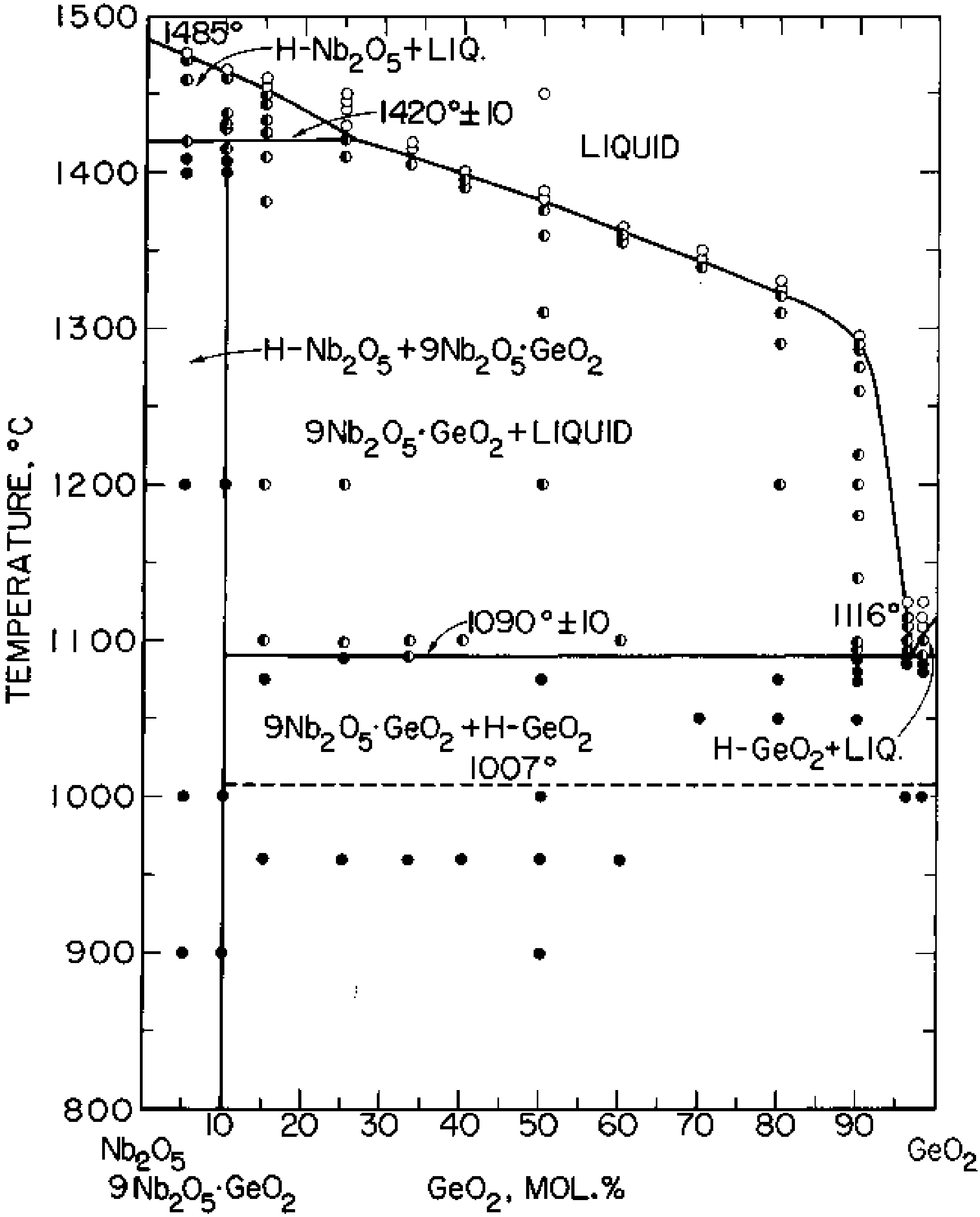

FIGURE 1. *Phase equilibrium diagram for the system* $Nb_2O_5-GeO_2$.
●—No melting; ◐—partial melting; ○—complete melting.
H—Nb_2O_5—High-temperature form of Nb_2O_5.
H—GeO_2—Quartz form of GeO_2.

Temperatures are given on the International Practical Temperature Scale of 1961. During the course of the experiments the thermocouple was checked against the melting points of gold (1063 °C) and of barium disilicate (1420 °C). The overall maximum uncertainty of the temperature values reported herein is estimated to be within ± 10 °C.

3. Results and Discussions

3.1. Nb_2O_5 and GeO_2 Components

No quenching experiments were made with the components, as they were the same materials that had been used previously in phase equilibirum studies originating in this laboratory [3, 6, 7].

The Nb_2O_5 used as starting material gave an x-ray pattern of poorly crystalline low-Nb_2O_5 [8]. The so-called high temperature, monoclinic form [9] was the only stable modification encountered in the present work. This finding agrees with that reported in studies of other binary phase diagrams [9, 10].

The GeO_2 used as starting material was the high-temperature (quartz form) polymorph, and it was the only form detected throughout the experiments. In pure GeO_2 the transition from the low to the high form is given at 1007 °C [11], and the phase diagram is constructed on the assumption of no solid solubility of niobia in germania.

3.2. Phase Diagram

Figure 1 shows the phase diagram for the system. Table 1 lists the compositions studied, the important heat treatments, and the phases identified, as well as the indices for several quenched phases. The system is characterized by one eutectic point at about 97.0 mole percent, GeO_2 (3.0% Nb_2O_5) and 1090 °C and by one peritectic point at about 25 percent GeO_2 (75% Nb_2O_5) and 1420 °C. The latter temperature corresponds to the incongruent melting point of $9Nb_2O_5 \cdot GeO_2$, the only binary compound found in the system.

TABLE 1. *Experimental data [1] for compositions in the binary system* $Nb_2O_5-GeO_2$

Composition		Heat treatment [2]		Results		Notes
Nb_2O_5	GeO_2	Temp.	Time	Physical observation	X-ray diffraction analyses [3]	
Mole %	*Mole %*	°C	*Hours*			
2.0	98.0	1000	12	No melting.	$GeO_2 + 9Nb_2O_5 \cdot GeO_2$	
		1080	1	No melting.	$GeO_2 + 9Nb_2O_5 \cdot GeO_2$	
		1084	1.25	No melting.	$GeO_2 + 9Nb_2O_5 \cdot GeO_2$	
		1090	1.25	Start of melting.	$GeO_2 + 9Nb_2O_5 \cdot GeO_2$	Solidus.
		1100	1	Considerable melting.	$GeO_2 + [9Nb_2O_5 \cdot GeO_2]$	
		1109	16	Complete melting.	Glass + $[9Nb_2O_5 \cdot GeO_2]$	
		1114	2	Complete melting.	Glass + $[9Nb_2O_5 \cdot GeO_2]$	N_D = 1.613 (25°).
4.0	96.0	1000	12	No melting.	$GeO_2 + 9Nb_2O_5 \cdot GeO_2$	
		1086	1.25	No melting.	$GeO_2 + 9Nb_2O_5 \cdot GeO_2$	
		1089	1.5	No melting.	$GeO_2 + Nb_2O_5 \cdot GeO_2$	
		1098	1	Partial melting.	$[GeO_2] + 9Nb_2O_5 \cdot GeO_2$	
		1099	1.5	Considerable melting.	$9Nb_2O_5 \cdot GeO_2 + [GeO_2]$	
		1109	1.5	Complete melting.	Glass + $[9Nb_2O_5 \cdot GeO_2]$	N_D = 1.616 (25°)
10.0	90.0	1050	15	No melting.	$GeO_2 + 9Nb_2O_5 \cdot GeO_2$	
		1075	67.5	No melting.	$GeO_2 + 9Nb_2O_5 \cdot GeO_2$	1098°/18 hr starting material.
		1088	18	No melting.	$GeO_2 + 9Nb_2O_5 \cdot GeO_2$	
		1095	2	Start of melting.	$9Nb_2O_5 \cdot GeO_2 + GeO_2$	
		1098	18	Partial melting.	$9Nb_2O_5 \cdot GeO_2$ + glass	
		1200	2	Partial melting.	$9Nb_2O_5 \cdot GeO_2$ + glass	
		1275	1.5	Considerable melting.	$9Nb_2O_5 \cdot GeO_2$ + glass	
		1287	2	Almost melted.	$9Nb_2O_5 \cdot GeO_2$ + glass	N_D = 1.711 (25°).
		1291	2	Almost melted.		
		1295	1.75	Complete melting.	$[L-Nb_2O_5]$ + glass	N_D = 1.729 (25°).
20.0	80.0	1050	15	No melting.	$GeO_2 + 9Nb_2O_5 \cdot GeO_2$	
		1075	67.5	No melting.	$GeO_2 + 9Nb_2O_5 \cdot GeO_2$	
		1200	5	Partial melting.	GeO_2 + glass	
		1310	1.5	Considerable melting.	$9Nb_2O_5 \cdot GeO_2 + [L-Nb_2O_5]$	N_D = 1.771 (25°).
		1320	1	Almost melted.	$9Nb_2O_5 \cdot GeO_2 + [L-Nb_2O_5]$	
		1325	1	Complete melting.		N_D ~ 1.84.
		1330	2	Complete melting.	$[L-Nb_2O_5]$	
30.0	70.0	1050	15	No melting.	$GeO_2 + 9Nb_2O_5 \cdot GeO_2$	
		1339	1.5	Considerable melting.	$9Nb_2O_5 \cdot GeO_2 + [L-Nb_2O_5]$	
		1344	2	Complete melting.	$[L-Nb_2O_5]$	
40.0	60.0	960	2.5	No melting.	$9Nb_2O_5 \cdot GeO_2 + GeO_2$	
		1100	15	Partial melting.	$9Nb_2O_5 \cdot GeO_2$ + glass	
		1355	1.5	Considerable melting.	$9Nb_2O_5 \cdot GeO_2 + [L-Nb_2O_5]$	
		1360	2	Almost melted.	$[L-Nb_2O_5] + 9Nb_2O_5 \cdot GeO_2$	
		1365	1.25	Complete melting.	$[L-Nb_2O_5]$	

Table 1. *Experimental data*[1] *for compositions in the binary system* $Nb_2O_5-GeO_2$ — Continued

Composition		Heat treatment[2]		Results		Notes
Nb_2O_5	GeO_2	Temp.	Time	Physical observation	X-ray diffraction analyses[3]	
Mole %	*Mole %*	°C	*Hours*			
50.0	50.0	900	1.75	No melting.	$GeO_2 + 9Nb_2O_5 \cdot GeO_2 + [Nb_2O_5]$	
		960	456	No melting.	$9Nb_2O_5 \cdot GeO_2 + GeO_2$	$L-GeO_2$ not formed.
		1000	1.75	No melting.	$9Nb_2O_5 \cdot GeO_2 + GeO_2$	
		1075	144	No melting.	$9Nb_2O_5 \cdot GeO_2 + GeO_2$	
		1200	5	Partial melting.	$9Nb_2O_5 \cdot GeO_2$	
		1375	1.5	Considerable melting.	$9Nb_2O_5 \cdot GeO_2 + [L-Nb_2O_5]$	
		1379	1.5	Almost melted.	$[L-Nb_2O_5] + 9Nb_2O_5 \cdot GeO_2$	
		1383	1.5	Complete melting.	$[L-Nb_2O_5]$	
		1450	2	Complete melting.	$[L-Nb_2O_5]$	
60.0	40.0	960	2.5	No melting.	$9Nb_2O_5 \cdot GeO_2 + GeO_2$	
		1100	15	Just melting.	$9Nb_2O_5 \cdot GeO_2$	
		1390	1.5	Considerable melting.	$9Nb_2O_5 \cdot GeO_2 + [L-Nb_2O_5]$	
		1395	2	Almost melted.	$[L-Nb_2O_5] + 9Nb_2O_5 \cdot GeO_2$	
		1400	1.5	Complete melting.	$[L-Nb_2O_5]$	
66.7	33.3	960	2.5	No melting.	$9Nb_2O_5 \cdot GeO_2 + GeO_2$	
		1090	18	Start of melting.	$9Nb_2O_5 \cdot GeO_2$	At solidus.
		1100	15	Slight melting.	$9Nb_2O_5 \cdot GeO_2$ + glass	
		1405	1	Considerable melting.	$9Nb_2O_5 \cdot GeO_2 + [L-Nb_2O_5]$	
		1414	1	Complete melting.	$[L-Nb_2O_5] + 9Nb_2O_5 \cdot GeO_2$	
75.0	25.0	960	2.5	No melting.	$9Nb_2O_5 \cdot GeO_2 + GeO_2$	
		1090	15	No melting.	$9Nb_2O_5 \cdot GeO_2 + GeO_2$	
		1098	18	Slight melting.	$9Nb_2O_5 \cdot GeO_2$	
		1200	5	Some melting.	$9Nb_2O_5 \cdot GeO_2$	
		1410	1.1	Partial melting.	$9Nb_2O_5 \cdot GeO_2$	
		1421	2	Considerable melting.	$9Nb_2O_5 \cdot GeO_2 + [L-Nb_2O_5]$	
		1450	1.25	Complete melting.	$[L-Nb_2O_5] + [9Nb_2O_5 \cdot GeO_2]$	
		1458	3.5	Complete melting.	$[L-Nb_2O_5]$	
85.0	15.0	960	2.5	No melting.	$9Nb_2O_5 \cdot GeO_2 + GeO_2$	
		1075	144	No melting.	$9Nb_2O_5 \cdot GeO_2 + GeO_2$	
		1100	16	Slight melting.	$9Nb_2O_5 \cdot GeO_2$ + glass	
		1200	5	Slight melting.	$9Nb_2O_5 \cdot GeO_2$	
		1409	65	Partial melting.	$9Nb_2O_5 \cdot GeO_2$	
		1427	1.5	Partial melting.	$9Nb_2O_5 \cdot GeO_2$	
		1433	9	Partial melting.	$[9Nb_2O_5 \cdot GeO_2] + H-Nb_2O_5$	Decomp. $9Nb_2O_5 \cdot GeO_2$.
		1442	3	Considerable melting.	$[9Nb_2O_5 \cdot GeO_2] + H-Nb_2O_5 + [L-Nb_2O_5]$	
		1450	1.5	Considerable melting.	$[9Nb_2O_5 \cdot GeO_2] + H-Nb_2O_5 + [L-Nb_2O_5]$	
		1455	2	Complete melting.	$[L-Nb_2O_5]$	
90.0	10.0	900	12	No melting.	$Nb_2O_5 + 9Nb_2O_5 \cdot GeO_2$	Nonequilibrium.
		1000	12	No melting.	$9Nb_2O_5 \cdot GeO_2 + H-Nb_2O_5$	Nonequilibrium.
		1200	5	No melting.	$9Nb_2O_5 \cdot GeO_2$	Single phase.
		1401	2	No melting.	$9Nb_2O_5 \cdot GeO_2$	
		1409	1.75	No melting.	$9Nb_2O_5 \cdot GeO_2$	
		1415	2	Slight slumping.	$9Nb_2O_5 \cdot GeO_2 + H-Nb_2O_5$	At decomp. $9Nb_2O_5 \cdot GeO_2$.
		1427	2	Partial melting.	$H-Nb_2O_5 + [9Nb_2O_5 \cdot GeO_2]$	
		1460	1.5	Considerable melting.	$[9Nb_2O_5 \cdot GeO_2] + H-Nb_2O_5 + [L-Nb_2O_5]$	
		1465	1.5	Complete melting.	$[L-Nb_2O_5]$	
95.0	5.0	900	12	No melting.	$Nb_2O_5 + 9Nb_2O_5 \cdot GeO_2 + [GeO_2]$	Nonequilibrium.
		1000	12	No melting.	$Nb_2O_5 + 9Nb_2O_5 \cdot GeO_2 + [GeO_2]$	Nonequilibrium.
		1200	5	No melting.	$H-Nb_2O_5 + 9Nb_2O_5 \cdot GeO_2$	
		1400	1.5	No melting.	$H-Nb_2O_5 + 9Nb_2O_5 \cdot GeO_2$	
		1409	2.75	No melting.	$H-Nb_2O_5 + 9Nb_2O_5 \cdot GeO_2$	
		1421	2	Slight melting.	$H-Nb_2O_5 + 9Nb_2O_5 \cdot GeO_2$	At decomp. $9Nb_2O_5 \cdot GeO_2$.
		1459	1.5	Slight melting.	$H-Nb_2O_5 + [9Nb_2O_5 \cdot GeO_2]$	
		1472	1.5	Considerable melting.	$H-Nb_2O_5 + [9Nb_2O_5 \cdot GeO_2] + [L-Nb_2O_5]$	
		1476	1.5	Complete melting.	$[L-Nb_2O_5] + [H-Nb_2O_5]$	

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

[2] Specimens quenched in sealed Pt tubes.

[3] Phases identified are listed in order of amount present at room temperature. Brackets enclose phases not necessarily present at the elevated temperature or not believed to be in final equilibrium. Only the high-temperature, hexagonal (quartz form) of GeO_2(H-GeO_2) was observed in these experiments. $H-Nb_2O_5$ and $L-Nb_2O_5$ refer to high and low temperature forms, respectively. Glass identified as a broad diffuse band in 18° to 28° — 2θ range.

[4] This phase quenched from the liquid indexes on a hexagonal unit cell basis (table 2).

[5] This phase quenched from the liquid indexes on a pseudo-orthorhombic basis (table 2).

3.3. Compound $9Nb_2O_5 \cdot GeO_2$

This compound was reported by Waring and Roth [12] to be a tetragonal phase conforming to the general type $10M_2O_5 \cdot 90M'_2O_5$ apparently isostructural with $Ta_2O_5 \cdot 2Nb_2O_5$. The existence of this phase and the unit cell dimensions[2] were verified in the present study. The phase formed readily throughout the system at temperatures above 1000 °C. Decomposition of the phase above the incongruent melting point (1420 °C) was sluggish. For example, a sample of composition 85 percent Nb_2O_5 heated at 1433 °C for 9 hr (table 1) still showed a considerable proportion of the compound.

In the eight reported isostructural compounds [12] of the general type $10M_2O_5 \cdot 90M'_2O_5$, Ge^{+4} is the only

[2] $a = 15.70$ Å, $c = 3.817$ Å.

cation not pentavalent. It would be instructive for crystal chemical reasons to know if the compound composition were indeed exactly $9Nb_2O_5 \cdot GeO_2$. Results of the present study are consistent with the 9:1 ratio and indicate no solid solution region. However, limitations in the sensitivity of microscopic and x-ray detection of homogeneity preclude an unequivocal statement of the compound composition. For example, the ratio $10Nb_2O_5 \cdot GeO_2$ contains 90.9 mole percent Nb_2O_5, and would not be distinguishable from the 9:1 composition.

3.4. Metastable Phases Quenched From Liquid

Two metastable low niobia-like phases were obtained from quenched liquids (see table 1, footnotes d and e, and table 2). Samples of composition 50 Nb_2O_5:50 GeO_2 and richer in niobia when quenched from the liquid gave a phase that could be partially indexed on the basis of low-Ta_2O_5 [13]. The several unindexed peaks (table 2), however, indicate that this cell is at best a subcell of low-Nb_2O_5. The pseudo-orthorhombic cell has unit cell dimensions: $a=6.17$ Å, $b=3.64$ Å, and $c=3.92$ Å.

Samples in the composition range $30Nb_2O_5$:$70GeO_2$ to $10Nb_2O_5$:$90GeO_2$ quenched from the liquid to give a phase that could be indexed on a hexagonal unit cell basis: $a=3.60$ Å, $c=3.90$ Å, $c/a=1.088$. In table 2 the coincidence of orthorhombic indices as related to the hexagonal indices is indicated. Thus, the orthorhombic (110) and (200) become the hexagonal (100), etc.

Quenches from the liquid of samples of composition $40Nb_2O_5$:$60GeO_2$, intermediate between the composition ranges for the two metastable phases, showed both phases (table 1). It should be noted, however, that no detectable change in unit cell dimensions with changing composition was noted for either metastable phase. Furthermore, as some GeO_2-rich glass was present in the quenched specimens, the exact composition limits of the metastable phases cannot be specified.

3.5. Application to Liquid Immiscibility Theory

From the standpoint of liquid immiscibility considerations, this system is noteworthy because of the absence of expected immiscibility. It is instructive to consider the following binary systems of Nb_2O_5 with the glass formers: B_2O_3, SiO_2, and GeO_2.

The $Nb_2O_5-B_2O_3$ [14] and $Nb_2O_5-SiO_2$ [2] systems have large regions of immiscibility, whereas the $Nb_2O_5-GeO_2$ system shows complete miscibility. In the hexavalent group of modifier cations, only the $WO_3-B_2O_3$ system has been reported [4]; and this system does not exhibit liquid immiscibility. The ionic field strength[3] (i.f.s.) of Nb^{+5} is greater than that of Ge^{+4}, slightly greater than that of B^{+3}, and less than that of Si^{+4}; the i.f.s. of W^{+6} is considerably greater than that of B^{+3}, Ge^{+4}, and Si^{+4}.

From the above information on immiscibility in oxide systems and i.f.s. of the modifier cations it may be concluded that the existence of immiscibility, per se, is not directly related to the extent of immiscibility. Whereas structural considerations determine the

[3] e.g., calculated as $\frac{Z}{(R_c+1.40)^2}$, where Z is the cationic charge and R_c and 1.40 are the ionic radii of the cation and oxygen, respectively.

TABLE 2. *X-ray diffraction powder data for metastable low niobia-type phases quenched from liquid* (CuK_α *radiation*)

$50Nb_2O_5$:$50GeO_2$ (quenched from 1450 °C/2hr)					$20Nb_2O_5$:$80GeO_2$ (quenched from 1330 °C/2hr)				
hkl[1]	d	I/I_0	$1/d^2_{obs}$	$1/d^2_{calc}$	hkl[2]	d	I/I_0	$1/d^2_{obs}$	$1/d^2_{calc}$
	5.18	8	0.0373						
001	3.922	100	.0650	0.0650	001	3.912	93	0.0653	0.0653
110	3.136	94	.1017	.1017	100	3.114	100	.1031	.1031
200	3.084	63	.1052	.1051					
	2.731	4	.1341						
111	2.449	45	.1667	.1667	101	2.437	43	.1684	.1684
201	2.425	25	.1701						
	2.116	7	.2234						
	2.010	8	.2475						
002	1.9604	25	.2602	.2602	002	1.9568	18	.2612	.2612
020	1.8212	11	.3015	.3016	110	1.7987	18	.3091	.3093
310	1.7908	20	.3118	.3118					
112	1.6625	15	.3618	.3618	102	1.6562	18	.3645	.3644
021	1.6570	14	.3642	.3666					
202	1.6537	14	.3657	.3653					
311	1.6297	10	.3765	.3769	111	1.6339	15	.3746	.3746
220	1.5690	7	.4062	.4067	200	1.5570	7	.4125	.4125
400	1.5436	4	.4197	.4203					
221	1.4576	7	.4708	.4717					
022	[3]1.3358	4	.5605	.5618					
312	[3]1.3214	5	.5727	.5720					

[1] Indices determined by analogy to low Ta_2O_5 [13], but refer only to a pseudocell as several peaks cannot be indexed. Unit cell dimensions of the pseudocell are: $a=6.17$ Å, $b=3.64$ Å, $c=3.92$ Å.
[2] Hexagonal unit cell dimensions: $a=3.59_6$ Å, $c=3.91_3$ Å, $c/a=1.088$.
[3] Broad peak.

extent of the immiscible region [15], i.f.s. relationships between the glass-forming cation and the modifier cation largely govern the presence or absence of immiscibility. Just as the differences in i.f.s. between the modifier cation with oxygen and the glass-forming cation with oxygen can be too large to produce immiscibility, they may also be too small. The maximum i.f.s. difference occurs in the series of glass formers with Ba^{+2}, and the minimum occurs with Nb^{+5}. It may also be concluded that none of the hexavalent ions, e.g., Mo^{+6}, Te^{+6}, Cr^{+6}, will show immiscibility phenomenon. These principles will be elaborated in future publications [16].

4. Summary

The phase equilibrium diagram for the system $Nb_2O_5-GeO_2$ has been constructed from "quenching" data on 13 selected compositions. Solidus and liquidus values were determined by examination of the samples with the binocular and polarizing microscopes and x-ray powder diffractometry.

The system was found to contain: one compound, $9Nb_2O_5 \cdot GeO_2$, melting incongruently at 1420 °C; one eutectic point between GeO_2 and the compound, located at about 97 mole percent GeO_2 and 1090 °C; and one peritectic point at about 25 mole percent GeO_2 and 1420 °C.

Although the 9:1 ratio of oxides in the $9Nb_2O_5 \cdot GeO_2$ compound is consistent with the results, various limitations in the experimental method preclude an unequivocal statement as to the exactness of this ratio.

Two metastable low niobia-type phases were obtained from quenched liquids. A quenched liquid of composition $50Nb_2O_5:50GeO_2$ gave an x-ray powder pattern that could be partially indexed on a subcell of low Nb_2O_5. It had pseudo-orthorhombic unit cell dimensions of $a=6.17$ Å, $b=3.64$ Å, $c=3.92$ Å. The pattern of quenched liquid of composition $20Nb_2O_5:80GeO_2$ was indexed on a hexagonal unit cell basis: $a=3.59_8$ Å, $c=3.91_3$ Å.

Application of the results to liquid immiscibility theory leads one to the conclusion that a cation may have too strong an ionic field strength, as well as one that is too weak, to produce two-liquid separation. Furthermore, the limiting maximum occurs in the series of Nb_2O_5 with the glass formers, as B_2O_3 and SiO_2 both show large regions of immiscibility.

The author expresses his sincere appreciation to Robert S. Roth who aided in the interpretation of the x-ray data.

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(Paper 70A1–381)