CANADA

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II.   THE BINARY SYSTEM CaO-Nb_2O_5

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MINES BRANCH

RESEARCH REPORT

R 101

Price 25 cents.

JULY 27, 1962

FOREWORD

This report contains the reprints
of two papers recently published in the Journal
of the American Ceramic Society. Since both
papers are short and are on related topics, it
has been decided to combine them into one
report rather than to issue them individually.

The Binary System Nb_2O_5–SiO_2

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The binary system Nb_2O_5–SiO_2 has been shown to include an extensive two-liquid region over the range 5 to 80% Nb_2O_5. The minimum temperature of the two-liquid area is 1695°C. A eutectic composition occurs at 95% Nb_2O_5 and 1448°C. and another at approximately 5% Nb_2O_5 and 1695°C. The experimental results were obtained by the cone-fusion method.

I. Introduction

ARISING from the discovery near Oka, Quebec, of the mineral niocalite,[1] which is essentially a calcium niobium silicate, an investigation of the ternary system CaO–Nb_2O_5–SiO_2 has been conducted. A preliminary publication of the results obtained for this system has been made,[2] and a further publication is proposed. Of the three binary systems comprising the boundaries of the main ternary system, viz., CaO–SiO_2, CaO–Nb_2O_5, and Nb_2O_5–SiO_2, the first mentioned is well established,[3] and no further investigation of it was considered to be necessary in this study. A preliminary publication of work on the system CaO–Nb_2O_5 has already been made,[4] and a final publication is in course of preparation. The binary system Nb_2O_5–SiO_2 forms the subject of the present paper.

II. Experimental

(1) Materials

The niobium pentoxide used in this work was high-purity material supplied by the Fansteel Metallurgical Corporation, North Chicago, Illinois, and was stated to contain 99%+ of Nb_2O_5.

The silica was prepared from Baker's Analyzed Reagent silicic acid powder. This material was treated for a week with cold, concentrated hydrochloric acid to remove any iron impurity and was then thoroughly washed with distilled water, dried, and heated in a muffle furnace to 1500°C to

dehydrate it. The product was then ground to a fine powder and used as such.

(2) Procedures

Four-gram mixtures of appropriate proportions of the well-blended constituent oxides were heated in platinum crucibles in a small furnace, preheated to 1650°C, and fired with a propane-oxygen mixture. The temperature employed in preparing most of the compositions was 1700°C. The crucible was kept in the furnace at this temperature for 40 to 45 minutes and was then water-quenched. At the high-niobia end of the composition range, the mixtures melted within a few minutes. At the high-silica end of the range, the products were not completely molten, but were obtained as semivitrified lumps. These lumps were crushed to fine powders and reheated to 1715°C. Over a wide range of compositions, the quenched product exhibited a very obvious two-liquid appearance. The mixtures were carefully removed from the crucibles, crushed, and used for the melting-point determinations by the cone-fusion method.

The reasons for choosing the cone-fusion method for these melting-point determinations, in preference to the quenching method as developed by the Geophysical Laboratory, Washington, D. C., were twofold:

(a) At the high-niobia end of the system, where the temperatures involved are well within the range of the quenching method, it is virtually impossible to quench the melt without immediate devitrification.

(b) In those parts of the system where satisfactory quenching can be achieved, i.e., in the medium- to high-silica regions, the temperatures involved, 1700°C or higher, are inconveniently high for the operation of the quenching equipment available.

Since these difficulties occur at the two ends of the system, it was considered to be generally more convenient to use the cone-fusion method throughout the work.

Several cones (three at least), each 10 to 15 mg in weight, were made from each composition, using 10% aqueous polyvinyl alcohol solution as binder. This binder burned out readily when the cones were heated without interfering with the results. The cones were mounted on a small piece of 80Pt20Rh foil, which was placed on an alumina plaque that could be slid easily into a suitable furnace. For temperatures up to 1600°C, a small platinum-wound alumina tube furnace was used, the temperatures being measured by means of a Pt–Pt10Rh thermocouple and recorded on a Leeds and Northrup Speedomax recorder. For temperatures above 1600°C, a gas microfurnace having an alumina muffle tube was used, with the temperatures being observed by means of a Leeds and Northrup optical pyrometer. No emissivity corrections were made.

Temperatures in all cases were recorded on the 1948 International Temperature Scale. The optical pyrometer used for the measurements at the highest temperatures was calibrated at the melting point of pure platinum and was found to register correctly within the limits of observation, which are considered to be ±2°C. The Pt–PtRh thermocouple used with the recorder for the measurements at the lower temperatures was calibrated at the melting points of gold, palladium, and pseudowollastonite, as recorded on the 1948 International Temperature Scale. The thermoelectromotive forces in these calibrations were measured on a

[1] (a) E. H. Nickel, "Niocalite—A New Calcium Niobium Silicate Mineral," Am. Mineralogist, 41 [9/10] 785–86 (1956); Ceram. Abstr., 1957, June, p. 150h.

(b) E. H. Nickel, J. F. Rowland, and J. A. Maxwell, "Composition and Crystallography of Niocalite," Can. Mineralogist, 6 [2] 264–72 (1958).

[2] N. F. H. Bright, "High Temperature Inorganic Reactions," Chem. in Can., 11 [5] 30–34 (1959).

[3] E. M. Levin, H. F. McMurdie, and F. P. Hall, Phase Diagrams for Ceramists, Fig. 49, p. 48. The American Ceramic Society, Inc., Columbus, Ohio, 1956. 286 pp.

[4] J. F. Rowland, N. F. H. Bright, and Arnout Jongejan, "Crystallography of Compounds in the Calcium Oxide–Niobium Pentoxide System," Proc. Conf. Ind. Appl. X-Ray Anal., 7th, Denver, 1958, pp. 97–106; published by the University of Denver, Denver, Colo.
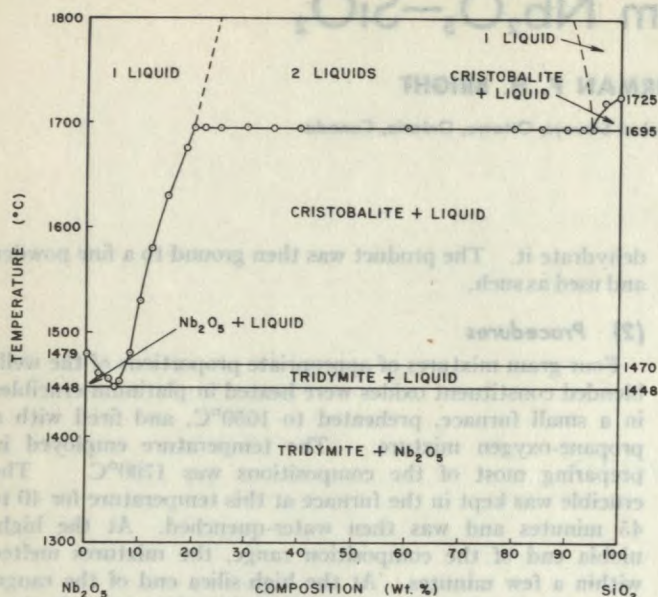
Fig. 1. The system Nb_2O_5–SiO_2.

Fig. 2. Coarse two-liquid texture in the system Nb_2O_5–SiO_2. Compositions are: (*upper left*) 80% Nb_2O_5, (*upper right*) 60% Nb_2O_5, (*lower left*) 40% Nb_2O_5, and (*lower right*) 20% Nb_2O_5.

standard potentiometer, and the temperatures calculated therefrom agreed with the recorder readings also to within ±2°C. It is therefore felt that the actual temperature measurements throughout the range encountered within this investigation carried an error of not more than ±2°C, although, as mentioned elsewhere, the reproducibility of the results was not as good as this owing to difficulties of observation of the melting phenomena.

The cones were observed continuously while being heated, and the temperatures at which changes of configuration occurred, as well as the temperatures of complete slumping of the cones, were noted. The latter were taken as the melting points of the compositions concerned. With the highly siliceous compositions, the cones tended to yield very viscous melts and the temperature of complete melting was correspondingly difficult to observe. In the case of the cones of high niobia content, there was a tendency for the first liquid to drain away quickly and creep over the edge of the platinum foil; to overcome this behavior, the flat foil was replaced by a small 60Pt40Rh dish. After the melting-point determination had been made, the molten product was cooled rapidly to room temperature and examined by X-ray diffraction.

(3) Results

The experimental observations are detailed in Table I* and are shown graphically in Fig. 1. The crystalline phases observed as a result of the X-ray diffraction examinations are also indicated in this phase diagram.

The main difficulty encountered during the course of this work was the reluctance of the silica-rich cones to melt sharply. Owing to the high viscosity of the melts containing 80 to 95% silica, the separation of the material into two liquids was much less readily observable in the case of the cone melts than it was in the case of the crucible melts.

Rather remarkable coarse two-liquid textures were observed in a number of the crucible melts. Separation on a macroscale into two phases, readily visible to the unaided eye, was

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* Table I has been deposited as Document No. 7087 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.
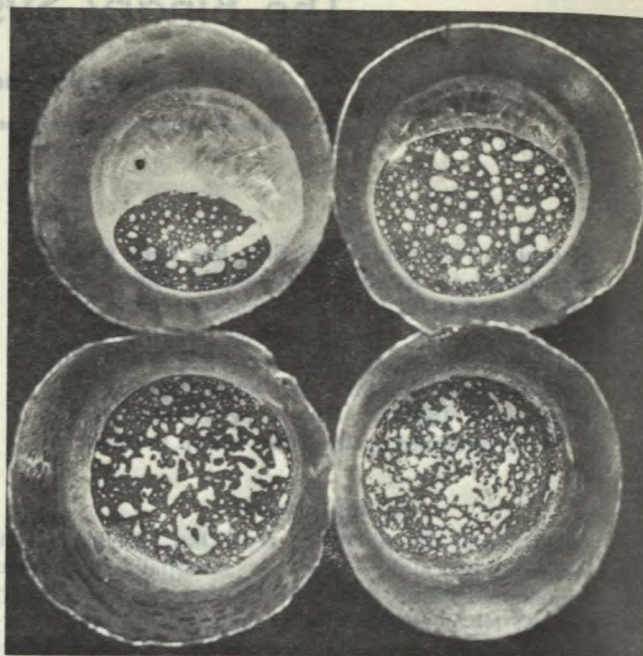
frequently seen on removal of the crucibles from the melting furnace. The niobia-rich liquid crystallized to a buff-yellow crystalline mass, whereas the silica-rich liquid formed a dark-blue glass showing inclusions of droplets of the niobia-rich material. Figure 2 is a photograph showing the contents of four crucibles after three fusions at 1725°C. The four compositions are in the two-liquid area of the binary system Nb_2O_5–SiO_2.

In the two-liquid region, the cone melt, on quenching, gave a blue glass from the silica-rich compositions and a buff-colored crystalline product from the niobia-rich compositions; the X-ray diffraction pattern showed Nb_2O_5 as the only crystalline phase present. At the 5/95 (Nb_2O_5/SiO_2) composition, the glass was almost colorless, with only a faint bluish tinge being observable in a few places in the product. This point was taken as the silica-rich limit of the two-liquid zone. The 3/97 and 0/100 compositions gave colorless glasses only on quenching the cone melt.

It was observed from the spread of the experimental results on the three or more cones tested for each composition that the values became progressively more scattered as the amount of silica in the composition increased. This was due largely to the difficulty of defining the end point of the melting process precisely in those samples which yielded a very viscous melt. The results shown in Table I indicate that, at the Nb_2O_5 end of the system, the spread was ±2°C, whereas at the SiO_2 end the spread was ±10°C. The experimental points plotted in Fig. 1 are mean values of the various determinations involved.

Attempts were made to determine the composition of the two liquids by chemical analysis of the quenched crucible melts. No concordant results, however, could be obtained, partly because of the difficulty of analyzing such a mixture and partly because of the fact that it was not possible to ensure that the solidified material from one liquid phase was free of contamination by solidified material from the other liquid phase.

In conclusion, it may be stated that the most noteworthy feature of this binary system is the very extensive two-liquid region which can, under suitable conditions, be observed on a macroscale with the unaided eye.

The Binary System CaO–Nb₂O₅

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The binary system CaO–Nb₂O₅ has been shown to include three compounds: CaO·Nb₂O₅, which melts congruently at 1560°C; 2CaO·Nb₂O₅, which melts congruently at 1576°C; and 3CaO–Nb₂O₅, which melts incongruently at 1560°C. Three eutectic compositions occur at 6% CaO (1362°C), 23% CaO (1492°C), and 34% CaO (1535°C). These results were obtained by the cone-fusion technique. The compound 3CaO–Nb₂O₅ has been shown to exist in two forms: type I, face-centered cubic with $a = 7.978$ A, having a superlattice with $a = 23.934$ A, and type II, orthorhombic (pseudotetragonal, distorted cubic) with $a = 11.51$ A, $b = 11.10$ A, $c = 15.98$ A, having a pseudocell with $a = 5.754$ A, $b = 5.551$ A, and $c = 7.990$ A. The conditions controlling the formation of these two forms were not determinable from the experiments conducted.

I. Introduction

THE discovery of the niobium-bearing mineral niocalite,[1] which was shown to be essentially a calcium niobium silicate, has prompted the investigation of the ternary system CaO–Nb₂O₅–SiO₂ by phase equilibrium methods. A preliminary publication of the results has already been made,[2]

and work is still in progress to produce a finalized phase diagram of this system. Of the three binary systems which form the boundaries of this ternary system, the system CaO–SiO₂ is well established and the system Nb₂O₅–SiO₂ has been made the subject of a recent publication[3]; the system CaO–Nb₂O₅ forms the subject of the present paper, which represents the completion of the work reported in a preliminary publication.[4]

The existence of three calcium niobates was reported briefly many years ago by Holmquist,[5] by Joly,[6] and by Larsson.[7]

[1] (a) E. H. Nickel, "Niocalite—A New Calcium Niobium Silicate Mineral," *Am. Mineralogist*, 41 [9/10] 785–86 (1956); *Ceram. Abstr.*, 1957, June, p. 150h.

(b) E. H. Nickel, J. F. Rowland, and J. A. Maxwell, "Composition and Crystallography of Niocalite," *Can. Mineralogist*, 6 [2] 264–72 (1958).

[2] N. F. H. Bright, "High Temperature Inorganic Reactions," *Chem. in Can.*, 11 [5] 30–34 (1959).

[3] M. Ibrahim and N. F. H. Bright, "The Binary System Nb₂O₅–SiO₂," *J. Am. Ceram. Soc.*, 45 [5] 221–22 (1962).

[4] J. F. Rowland, N. F. H. Bright, and Arnout Jongejan, "Crystallography of Compounds in the Calcium Oxide–Niobium Pentoxide System," *Proc. Conf. Ind. Appl. X-Ray Anal.*, 7th, Denver, 1958, pp. 97–106; published by the University of Denver, Denver, Colo.

[5] (a) P. J. Holmquist, "Synthetische Studien über die Perowskit- und Pyrochlormineralien," *Bull. Geol. Inst. Univ. Uppsala*, 3 [5] 181–268 (1896–97).

(b) P. J. Holmquist, "Synthetische Studien über die Perowskit-und Pyrochlormineralien," *Z. anorg. Chem.*, 18, 84–85 (1898).

[6] (a) A. Joly, "Recherches sur les composés du niobium et du tantale," *Ann. Scient. École Norm. Supérieure de Paris*, [Ser. 2], 6, 125–86 (1877).

(b) A. Joly, "Recherches sur les niobates et les tantalates," *Compt. rend.*, 81, 267–69 (1875).

[7] A. Larsson, "Untersuchungen über Niob," *Z. anorg. Chem.*, 12, 188–207 (1896).

These compounds and their properties, as reported at the time of their discovery, are as follows:

(1) $CaO \cdot Nb_2O_5$, or $Ca(NbO_3)_2$: Tabular crystals having a specific gravity variously given as 4.12 and 4.484.

(2) $2CaO \cdot Nb_2O_5$, or $Ca_2Nb_2O_7$: Colorless, prismatic crystals, rhombic needles, or plates, also stated to have a specific gravity of 4.484.

(3) $3CaO \cdot Nb_2O_5$, or $Ca_3(NbO_4)_2$: No details given.

These materials were made by the reaction of either niobium pentoxide or a sodium niobate with calcium chloride, carbonate, or sulfate followed by acid leaching of the product to yield a calcium niobate residue.

Two types of calcium niobates occurring as natural minerals have been reported: (1) a hydrated niobate, $CaO \cdot Nb_2O_5 \cdot 2H_2O$, known as ellsworthite[x] and (2) the mononiobate, $CaO \cdot Nb_2O_5$, with extensive substitution, known as fersmite.[9] Ellsworthite is not relevant to the present study, but fersmite is similar to one of the compounds synthesized in the writers' earlier work[4] and further reported on in the present paper.

The fragmentary information available on this binary system made it desirable to verify the existence of the reported calcium niobates, to study their crystallography and other properties, and to determine the liquidus curve for this binary system to make possible the compilation of the complete ternary phase diagram of the system $CaO–Nb_2O_5–SiO_2$.

II. Experimental

(1) Materials

The niobium pentoxide used in this work was supplied by the Fansteel Metallurgical Corporation, North Chicago, Illinois, and was stated to be 99%+ pure. A semiquantitative spectrographic analysis showed the presence of the following impurities: Zr 0.08, Ta < 0.01, Ti 0.002, Fe 0.03, Si 0.04, Mg 0.005, Al 0.004, and Mn < 0.001%.

The calcium carbonate used as the source of CaO in this work was Baker Analyzed cp reagent (low in alkalis). The theoretical CaO content was found to be applicable to this material within the limits of experimental error.

(2) Procedures

(A) *Preparation of Mixtures:* Mixtures of calcium carbonate and niobium pentoxide in sufficient quantity to yield about 4 g of the required product were prepared by intimate blending of the constituent materials. These mixtures were fired in platinum crucibles to 1000°C, thereby decomposing the carbonate and inducing a certain amount of sintering of the oxides produced. The sintered products were crushed and blended and then heated in platinum crucibles in a small furnace (fired with a propane gas/oxygen mixture) that had been preheated to 1650°C. The temperature employed in preparing most of these compositions was 1700°C.

Mixtures containing up to 42% CaO melted under these conditions; mixtures containing higher proportions of CaO merely sintered. The molten products were cooled and then crushed in preparation for the melting-point determinations. In those cases where only partial melting had occurred, the products were several times crushed, reblended, and refired to 1700°C to achieve completeness of reaction and uniformity of product.

(B) *Cone-Fusion Work:* The cone-fusion method of determining the melting points of the compositions was chosen in preference to the quenching method since it was found to be impossible to prepare glasses in the system $CaO–Nb_2O_5$, the products devitrifying immediately and completely, even on rapid quenching.

Several cones, 10 to 15 mg in weight, were made from each composition, using 10% aqueous polyvinyl alcohol solution as binder. This binder burned out readily when the cones were heated without interfering with the results.

The cones were mounted on a small piece of 80Pt20Rh foil which was placed on an alumina plaque capable of being slid easily into a furnace tube. For temperatures up to 1600°C, a small platinum-wound alumina tube furnace was used, the temperatures being measured by means of a Pt–Pt10Rh thermocouple and recorded on a Leeds and Northrup Speedomax recorder. For temperatures in the range 1600° to 1800°C, a gas-fired microfurnace having a high-fired alumina muffle tube was used. For temperatures in excess of 1800°C, the alumina muffle was replaced by a similar stabilized zirconia muffle. For the higher-temperature experiments, the 80Pt20Rh foil was replaced by a small 60Pt40Rh dish, and for the experiments involving temperatures in excess of 1800°C, a small thoria plaque was used to support the cone. No reaction between the cone and the thoria plaque was observable.

The cones were observed continuously while they were being heated, and the temperatures at which changes of configuration occurred, as well as the temperature of complete slumping of the cones, were noted. The latter was taken as the liquidus temperature of the composition concerned. The temperatures were observed by means of a Leeds and Northrup optical pyrometer. No emissivity corrections were made.

Temperatures in all cases were recorded on the 1948 International Temperature Scale. The optical pyrometer used at the higher temperatures was calibrated at the melting point of pure platinum (1769°C) and was found to register correctly within the limits of observation, which were considered to be ±2°C. The Pt–Pt10Rh thermocouple used with the recorder for the measurements at the lower temperatures was calibrated at the melting points of gold, palladium, and pseudowollastonite, as recorded on the 1948 International Temperature Scale. The thermoelectromotive force in these calibrations was measured on a standard potentiometer; the temperatures calculated therefrom agreed with the recorder readings, also to within ±2°C.

It is therefore felt that the precision of the actual temperature measurements throughout the range encountered in the present investigation was within ±2°C. However, the absolute accuracy of the measurements did not lie within these limits, since it was shown, in the writers' study of the ternary system $CaO–Nb_2O_5–SiO_2$, that at those compositions for which cone-fusion and quenching methods could be used for the determination of the liquidus temperature, the correlation between the temperatures determined by the two methods was rather poor. The cone-fusion method gave substantially lower temperatures; in some cases the discrepancy was in excess of 20°C. At eutectic and congruent compound compositions in the system $CaO–Nb_2O_5$ minimum discrepancies between the cone-fusion data and the true liquidus temperatures are to be expected.

(C) *X-Ray Diffraction Work:* The various crystalline phases encountered in the course of this study were examined by means of X-ray diffraction and in some cases were also observed with the petrographic microscope. Powder diffraction patterns were obtained with Debye-Scherrer cameras 114.6 mm in diameter and filtered copper and cobalt radiations. Single-crystal films were obtained with a Weissenberg camera and with a Buerger precision camera using molybdenum and copper radiations. Correlations of the powder data with the single-crystal data permitted the determina-

[x] T. L. Walker and A. L. Parsons, "Ellsworthite and Associated Minerals from Hybla, Ontario," *Univ. Toronto Studies, Geol. Ser.,* 16, 13–20 (1923).

[9] (a) E. M. Bonstedt-Kupletskaya and T. A. Burova, "Fersmite, A New Calcium Niobate from Pegmatites of the Vishnevye Mountains, Central Urals," *Compt. rend. acad. sci. U.R.S.S.,* 52, 69–71 (1946) (in English); see also *Am. Mineralogist,* 32 [5/6] 373 (1947) (abstract).

(b) A. G. Zhabin, V. B. Alexandrov, and T. A. Burova, "New Data on Fersmite," *Proc. All-Soviet Mineralogical Soc.,* 40 [3] 70–80 (1961).

Table I. Liquidus Determinations of CaO-Nb₂O₅ Compositions

Composition (wt %)		Liquidus temp. (°C)	Composition (wt %)		Liquidus temp. (°C)
CaO	Nb₂O₅		CaO	Nb₂O₅	
0	100	1479	28	72	1562
2	98	1435	29.7	70.3	1576
4	96	1378	32	68	1550
6	94	1362	33	67	1540
7	93	1368	34	66	1535
8	92	1380	35	65	1540
10	90	1410	36	64	1548
12	88	1440	38	62	1574
14	86	1485	38.8	61.2	1580
16	84	1532	40	60	1615
17.4	82.6	1560	42	58	1675
18.5	81.5	1535	44	56	1745
20	80	1510	46	54	1800
22	78	1500	48	52	1835
23	77	1492	50	50	1880
24	76	1496	53	47	1895
25	75	1510	55	45	1940
26	74	1522	(100	0	~2570) (Published data)*

* See footnote 15.

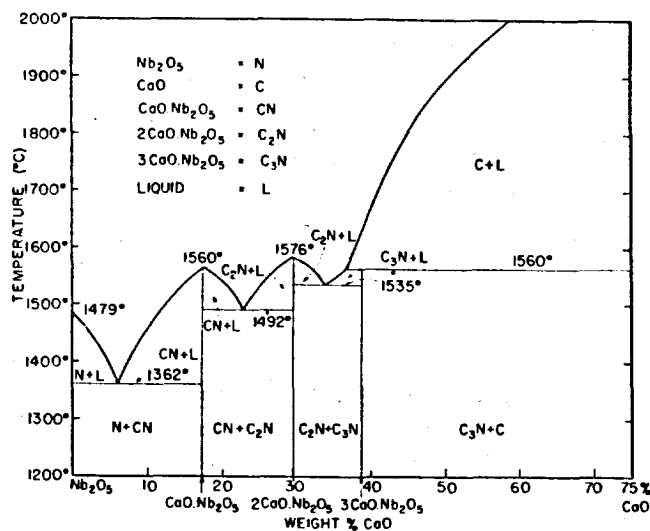Fig. 1. Phase diagram of the system CaO–Nb₂O₅.

tion of the space group, cell dimensions, and cell content and the indexing of the powder diffraction pattern for each compound. The petrographic microscope examinations are described fully in the writers' earlier paper.[4]

(3) Results

The results obtained by the cone-fusion method for the liquidus temperatures of the various compositions are given in Table I, and the liquidus data and the results of the phase identification by X-ray diffraction are shown in Fig. 1. Compositions representing definite compounds and also those corresponding to eutectic points are listed in Table II with their melting points and the nature of their melting behavior. Some of the optical and other physical properties of the various compounds encountered in this system are given in Table III.

In Fig. 1 it has been found convenient to abbreviate CaO as C and Nb₂O₅ as N; the three binary compounds in this system therefore are denoted by CN, C₂N, and C₃N respectively. In Fig. 1 the compositions have been plotted from 0% CaO/100% Nb₂O₅ to 55% CaO/45% Nb₂O₅ only, since the region from 55 to 100% CaO was beyond the scope of the equipment used.

The liquidus curve for this system and the temperatures and compositions of both the eutectics and the peritectic point are also shown. The curve is considered to be at the probable location of the true liquidus curve. Comparison of the data

Table II. Melting Data for Compounds and Eutectic Compositions in the System CaO–Nb₂O₅

Composition (wt %)	Melting point (°C)	Remarks
100 Nb₂O₅	1479	Congruent
6 CaO/94 Nb₂O₅	1362	Eutectic 1
17.4 CaO/82.6 Nb₂O₅, i.e., CN composition	1560	Congruent
23 CaO/77 Nb₂O₅	1492	Eutectic 2
29.7 CaO/70.3 Nb₂O₅, i.e., C₂N composition	1576	Congruent
34 CaO/66 Nb₂O₅	1535	Eutectic 3
38.8 CaO/61.2 Nb₂O₅, i.e., C₃N composition	1560	Incongruent
100 CaO	~2570 (Published data)*	Congruent

* See footnote 15.

in Table I with the curve in Fig. 1 shows that there is a variable discrepancy between the true liquidus and many of the cone-fusion temperatures in the sense that the latter are lower than the former. This discrepancy is at a minimum at compound and eutectic compositions.

The melting point of pure niobia was found to be 1479°C by the technique used in the present work. This temperature is somewhat lower than the temperature of 1491° ± 2°C

Table III. Physical Properties of Compounds in the System CaO–Nb₂O₅

Compound	Optical properties					Crystal system and habit	Specific gravity
	Indices of refraction			Optical sign	2V		
	α	β	γ				
Nb₂O₅	(Very high indices)						
CaO·Nb₂O₅ (synthetic)	2.07	2.10	2.19	(+ ve)	62°	Orthorhombic; flattened prisms	4.72
Fersmite (natural CaO·Nb₂O₅)	About 2			(+ ve)	43°–46°	Orthorhombic	
2CaO·Nb₂O₅	1.97	2.16	2.17	(– ve)	30°	Monoclinic; thin plates, twinned; cleavage (100)	4.39
3CaO·Nb₂O₅	2.2 approx.					Cubic,* face centered; low birefringence to isotropic	4.23

* Approximately cubic; see discussion in text.

given by Holtzberg, Reisman, Berry, and Berkenblit[10] and significantly lower than the temperature of 1500°C given by Roth[11] and by Roth and Coughanour.[12] Roth and Waring[13] have more recently quoted a temperature of 1487°C.

The information used in the identification by X-ray diffraction of the various phases encountered in this work was as follows: (a) For Nb_2O_5, the adequate published data in the literature[14] were used; (b) for $CaO \cdot Nb_2O_5$ and $2CaO \cdot Nb_2O_5$, the data given in the writers' earlier publication[4] were used; and (c) for $3CaO \cdot Nb_2O_5$, as was mentioned in that publication, the data then available were merely preliminary; the more recent data obtained are discussed in the following section.

III. Discussion of X-Ray Data for $3CaO \cdot Nb_2O_5$

The X-ray diffraction data obtained from single-crystal and powder films of $3CaO \cdot Nb_2O_5$ can be tentatively interpreted in the following way. The atoms of this compound appear to be arranged with a perovskite-type structure, and distortion of the lattice from cubic symmetry occurs in various amounts. Two types of $3CaO \cdot Nb_2O_5$ have been distinguished: type I, which is cubic (no distortion), and type II, which is orthorhombic (pseudotetragonal, distorted cubic). Type II includes all the noncubic varieties, the distortion being of the same manner in all cases but to different degrees. The data included in this report refer to material displaying maximum distortion.

Type I $3CaO \cdot Nb_2O_5$ is face-centered cubic with the unit-cell dimension $a = 7.978$ A plus a face-centered cubic superlattice with a unit-cell dimension $a = 23.934$ A, which value is three times that of the smaller cell. The smaller cell indexes completely the strong lines of the powder diffraction pattern, and the larger cell satisfies the vast majority of the faint lines, in addition to the strong lines. This interpretation is a modification of that reported previously for $3CaO \cdot Nb_2O_5$.[4]

Type II $3CaO \cdot Nb_2O_5$ is orthorhombic (pseudotetragonal and pseudocubic) with unit-cell dimensions $a = 11.51$ A, $b = 11.10$ A, and $c = 15.98$ A. A pseudocell with each unit-cell dimension being one half the foregoing values, i.e., $a = 5.754$ A, $b = 5.551$ A, and $c = 7.990$ A, indexes all but a few faint lines of the powder diffraction pattern, and the larger cell may represent a superlattice such as occurs in type I. The stronger lines of the powder diffraction pattern can be correlated with those of the undistorted face-centered cubic cell of type I ($a = 7.978$ A) and the weaker lines with those of a primitive cubic cell having the same unit-cell dimension. The orthorhombic cell orientation used is not in the standard $c < a < b$ setting but in one which illustrates the pseudotetragonal nature of the lattice.

The powder diffraction data for $3CaO \cdot Nb_2O_5$, type I and type II, are given in Tables IV and V, respectively. Only those spacings required for indexing the measured diffractions are included in the calculated d values.

The measured specific gravity of $3CaO \cdot Nb_2O_5$ (not separated into types I and II), using a pycnometer and carbon tetrachloride, is 4.23. The unit-cell contents for each of the

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Table IV. Powder Diffraction Data for $3CaO \cdot Nb_2O_5$, Type I (Cubic)*

Intensity	d (meas.) (A)	$1/d^2$ (meas.)	$1/d^2$ (calc.)	(hkl) Small cell	(hkl) Large cell
4	13.92	0.0052	0.0052		111
2	8.48	.0139	.0140		220
1	7.23	.0191	.0192		311
1	6.89	.0210	.0210		222
1	4.87	.0422	.0419		422
4	4.60	.0473	.0471	111	511
2	4.22	.0561	.0559		440
8	3.99	.0629	.0628	200	600
1	3.80	.0692	.0698		620
1/2	3.60	.0773	.0768		622
1	3.440	.0845	.0838		444
1	3.352	.0890	.0891		711
2	3.304	.0916	.0908		640
1	3.196	.0979	.0978		642
1	3.122	.1026	.1030		731
10	2.820	.1257	.1257	220	822
2	2.786	.1289	.1309		751
1	2.611	.1467	.1466		842
2	2.508	.1590	.1589		931
2	2.404	.1730	.1728	311	933
1	2.380	.1765	.1746		10.0.0
1	2.298	.1894	.1885	222	10.2.2
2	2.227	.2016	.2025		10.4.0
1	2.154	.2154	.2147		11.1.1
1	2.110	.2246	.2234		880
1	2.088	.2295	.2304		10.4.4
1	2.024	.2400	.2444		10.6.2
7	1.994	.2515	.2514	400	12.0.0
1	1.936	.2668	.2654		12.2.2
1	1.919	.2716	.2706		11.5.3
1	1.868	.2867	.2863		12.4.2
2	1.829	.2989	.2985	331	13.1.1
1	1.802	.3078	.3072		12.4.4
5	1.782	.3147	.3142	420	12.6.0
1	1.761	.3225	.3212		12.6.2
1	1.709	.3424	.3422		14.0.0
3	1.642	.3709	.3701		14.4.0
6	1.627	.3778	.3771	422	14.4.2
2	1.618	.3820	.3823		13.7.1
etc.	etc.	etc.	etc.	etc.	etc.

* Small cell, $a = 7.978$ A; large cell (superlattice), $a = 23.934$ A. The intensities were estimated visually, with strongest line as 10.

lattices described in the foregoing are given below. The calculated specific gravity for undistorted cubic type I is 4.26, and the space group to which both lattices of type I belong is probably $Fm3m$. The smaller orthorhombic cell of type II satisfies the requirements of space group $Cccm$, but the space group for the larger orthorhombic cell is indeterminate.

The smaller cubic cell of type I contains 3 molecules of $3CaO \cdot Nb_2O_5$; its formula is therefore $Ca_9Nb_6O_{24}$. The larger cell, referred to as a superlattice, contains 81 molecules of $3CaO \cdot Nb_2O_5$.

The larger orthorhombic cell of type II contains 12 molecules of $3CaO \cdot Nb_2O_5$; its formula is therefore $Ca_{36}Nb_{24}O_{96}$ and is equivalent to four of the small cubic cells of type I. This relation is to be expected from the fact that the orthorhombic cell dimensions are in the approximate ratio of $\sqrt{2}$, $\sqrt{2}$, and 2 to the undistorted cubic cell dimension. The smaller orthorhombic pseudocell contains one eighth the number of molecules in the larger cell, i.e., $1\frac{1}{2}$ molecules of $3CaO \cdot Nb_2O_5$; its formula is therefore $Ca_{4.5}Nb_3O_{12}$.

A rearrangement of the formulas given in the foregoing will show a possible relation of the structure of this compound to that of perovskite, calcium titanate ($CaTiO_3$). A pseudocubic form of perovskite, with the unit-cell dimension variously reported as $a = 7.644$ A and 7.660 A, contains 8 molecules of $CaTiO_3$, i.e., $Ca_8Ti_8O_{24}$. If the cell content of

Table V. Powder Diffraction Data for 3CaO·Nb₂O₅, Type II (Orthorhombic)*

Intensity	d (meas.) (A)	1/d² (meas.)	1/d² (calc.)	(hkl) Large cell	(hkl) Small cell
2	4.67	0.0459	0.0459	202	101
2	4.56	.0481	.0481	022	011
5	4.00	.0626	.0626	004, 220	002, 110
½	3.69	.0734	.0736	213	
1	3.58	.0782	.0783	114, 222	111
1	3.129	.1022	.1032	303	
½	3.088	.1049	.1043	321	
3	2.884	.1202	.1208	400	200
10	2.824	.1254	.1253	224	112
3	2.779	.1295	.1298	040	020
½	2.704	.1367	.1365	402	201
½	2.558	.1528	.1532	420	210
1	2.500	.1600	.1600	240	120
1	2.436	.1684	.1689	422	211
2 br	2.394	.1745	.1734	026	013
			.1756	242	121
½	2.336	.1832	.1834	404	202
½	2.281	.1921	.1924	044	022
½	2.246	.1983	.1983	325	
2	2.217	.2035	.2036	226, 334	113
1	2.156	.2152	.2159	424	212
½	2.125	.2214	.2215	136	
			.2226	244	122
8	1.996	.2510	.2506	008, 440	004, 220
1	1.953	.2621	.2618	406, 530	203
1	1.939	.2661	.2663	118, 442	221
½	1.890	.2798	.2808	208	104
½	1.844	.2940	.2942	426	213
2	1.813	.3042	.3042	620	310
3	1.788	.3127	.3132	228, 444	114, 222
2	1.767	.3202	.3199	622	311
			.3222	260	130
½	1.723	.3369	.3379	262	131
5	1.651	.3667	.3669	624	312
3	1.643	.3706	.3714	408	204
3	1.620	.3810	.3804	048	024
6	1.613	.3842	.3849	264	132
etc.	etc.	etc.	etc.	etc.	etc.

* Large cell, $a = 11.51$ A, $b = 11.10$ A. $c = 15.98$ A; small cell (pseudocell), $a = 5.754$ A, $b = 5.551$ A, $c = 7.990$ A. The intensities were estimated visually, with strongest line as 10.

br = broad.

the smaller cubic cell of 3CaO·Nb₂O₅ type I ($a = 7.978$ A) is expressed as Ca₈(Nb₆Ca)O₂₄, a similarity becomes apparent. For this correlation the following assumptions are made: (a) The oxygen atoms of the calcium niobate occupy the same positions as the oxygen atoms of perovskite, (b) as many calcium atoms of the calcium niobate as possible occupy the same positions as the calcium atoms of perovskite, and (c) all the niobium atoms and the remaining calcium atoms of the calcium niobate occupy the same positions as the titanium atoms of perovskite, the deficiency in atoms available for these sites resulting in some vacancies.

It is possible, therefore, to represent this cell content in the following ways: $3(3CaO \cdot Nb_2O_5) \equiv Ca_9Nb_6O_{24} \equiv Ca_8(Nb_6Ca\square)O_{24} \equiv 8(CaNb'O_3)$, where $\square$ = vacancy and $Nb' = Nb_{0.75} + Ca_{0.125} + \square_{0.125}$. The larger cubic cell ($a = 23.934$ A) can, in the same way, be represented as containing 216 molecules of CaNb'O₃ and the larger and smaller orthorhombic cells of type II as 32(CaNb'O₃) and 4(CaNb'O₃), respectively.

The evident similarity of the powder diffraction patterns of 3CaO·Nb₂O₅ and CaTiO₃ first suggested the possibility of a similarity in the structure of these two compounds. The correlation given in the foregoing followed logically from the evidence obtained during the X-ray diffraction study. The mode of distortion present in 3CaO·Nb₂O₅ has not hitherto been reported as occurring in CaTiO₃, and its occurrence is thus probably due to a mechanism different from that operating in perovskite. It is possible that the cubic 3CaO··

Nb₂O₅ type I represents a random arrangement of the 6 niobium atoms plus 1 calcium atom plus 1 vacancy over the 8 available sites (occupied by titanium in CaTiO₃), whereas the orthorhombic 3CaO·Nb₂O₅ type II may represent an ordering of these atoms, resulting in the lower symmetry.

IV. Discussion of Phase Equilibrium Work

The system CaO–Nb₂O₅ appears to be straightforward and to present no feature of particular interest up to a composition containing about 36% CaO (see Table II). The values reported in that table are in good accord with the preliminary data presented in the earlier publication.[4]

No difficulty was experienced in conducting, in the platinum-wound alumina tube furnace referred to earlier, tests on compositions containing up to 36% CaO. The melting of the eutectics was very sharp, and the liquids produced were extremely fluid. Observe that the compounds CaO··Nb₂O₅ and 2CaO·Nb₂O₅ exhibited congruent melting points.

The compound 3CaO·Nb₂O₅, on the other hand, exhibited an incongruent melting point. A composition containing 36% CaO melted at 1548°C. However, with the composition corresponding exactly to the compound 3CaO·Nb₂O₅, namely 38.8% CaO, melting started at about 1560°C and the first liquid ran out from the cone. When the sample holder was redesigned so as to retain this liquid, the remaining solid dissolved in the liquid and melting was complete at 1580°C. This temperature was reproduced accurately on several occasions and has been taken as the liquidus temperature for 3CaO·Nb₂O₅, the incongruent melting point being 1560°C. Thus, it is considered that the compound 3CaO·Nb₂O₅ is formed by a peritectic reaction between lime and a liquid slightly richer in niobia than 3CaO·Nb₂O₅.

If, after heating a cone of the composition 3CaO·Nb₂O₅, the product is quenched, some 2CaO·Nb₂O₅ is found to be present on examination by X-ray diffraction. This behavior is attributed to incompleteness of the foregoing peritectic reaction; i.e., some of the liquid richer in Nb₂O₅ becomes solidified before it has had an adequate time to react completely with the lime.

No compound richer in lime than 3CaO·Nb₂O₅ was found, nor was any 2CaO·Nb₂O₅ ever obtained as a reaction product from any sample richer in lime than 3CaO·Nb₂O₅. This is considered to demonstrate that 3CaO·Nb₂O₅ is the most lime-rich compound possible in this system.

When samples richer in lime than corresponds to the formula 3CaO·Nb₂O₅ were examined by X-ray diffraction, it became possible to detect free lime as the second phase when the composition 50% CaO/50% Nb₂O₅ was reached. However, by testing for free base, using universal indicator paper, it was found possible to demonstrate the presence of free CaO as the second phase in compositions as low in CaO as 42% CaO/58% Nb₂O₅, even though the amount of lime was insufficient to be detectable by X-ray diffraction. The compounds CaO·Nb₂O₅ and 2CaO·Nb₂O₅ were shown to have an absolutely neutral reaction in water, whereas 3CaO·Nb₂O₅ was found to yield a pH in water of not higher than 8.0. It should be mentioned that the detection by X-ray diffraction of free CaO in the presence of much 3CaO·Nb₂O₅ is not easy because of the near coincidence of the stronger lines of the CaO pattern and those of 3CaO·Nb₂O₅; hence, one has to rely on comparatively weak CaO lines, thus making the level of detection of this compound by this means rather unfavorable. With the compositions of highest CaO content studied, much free lime was detected in the quenched product after melting, even by X-ray diffraction techniques.

The compound 3CaO·Nb₂O₅, in addition to exhibiting the incongruent melting phenomenon, has also been shown to possess at least two different, although related, crystal forms, already discussed. No attempt has been made to specify the conditions under which these forms are produced, nor was any evidence available from the powder data obtained on samples prepared at various compositions and tempera-

tures which could be systematically correlated with the conditions controlling the occurrence of either form. Hence, no account has been taken of this polymorphic behavior in drawing up the CaO–Nb₂O₅ phase diagram. Where 3CaO·Nb₂O₅ is indicated as being one of the crystalline phases present, it can be either type I or type II or both. The X-ray data were used merely as a means of identifying the chemical nature of the phase(s) present.

It is considered to be probable that the liquidus curve of the high-lime end of the system will proceed in an unbroken curve from the highest point observed, 1940°C (for a composition containing 55% CaO), up to 2570°C, the published melting point for 100% CaO.[15] The equipment available did not permit this region of the system to be studied conveniently, but it has been demonstrated that no further lime-rich compound can be expected to occur. It must be pointed out that, in the course of this work, no attempt has been made to investigate possible low-temperature polymorphs or phases whose equilibrium regions do not reach the liquidus curve, other than to point out the two modifications of the compound 3CaO·Nb₂O₅. Hence, no such polymorphs or phases appear in Fig. 1.

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