

PHASE EQUILIBRIA IN THE SYSTEM CaO-TiO_2 ^{1,2}

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A phase equilibrium diagram has been determined for the system CaO-TiO_2 . Two compounds exist: CaO-TiO_2 and $3\text{CaO} \cdot 2\text{TiO}_2$, the former corresponding to the mineral perovskite. CaO-TiO_2 melts congruently and forms a eutectic with TiO_2 at 1460° at 83 wt. % TiO_2 . $3\text{CaO} \cdot 2\text{TiO}_2$ melts incongruently at 1750° to give a liquid containing 42 wt. % of TiO_2 in equilibrium with CaTiO_3 . The eutectic between $\text{Ca}_3\text{Ti}_2\text{O}_7$ and CaO is at 1695° and 39 wt. % TiO_2 .

Introduction and Previous Investigation

A recent study of phase equilibria in the system $\text{CaO-TiO}_2\text{-SiO}_2$ in this Laboratory³ emphasized the need for the establishment of a consistent phase diagram for the binary system CaO-TiO_2 . Phase equilibria in this system have been studied by several investigators, but an unequivocal representation of the phase relationships is not available. Three partially complete phase diagrams of the system have been published. The diagrams of van Wartenberg, *et al.*,⁴ Umezu and Kakiuchi,⁵ and Fukushima⁶ are shown in Fig. 1. The work of the first was done by observing the melting of cones and only the liquidus curve was presented. This study suggested the existence of the compounds $3\text{CaO} \cdot \text{TiO}_2$ and $2\text{CaO} \cdot \text{TiO}_2$ in addition to the 1:1 mole ratio compound. Umezu and Kakiuchi⁵ studied the system under reducing conditions in a graphite furnace and used both thermal analysis and melting techniques. Fukushima's study of a portion of the system ($\text{CaTiO}_3\text{-TiO}_2$) was based on quenching studies only. The form of the diagram from CaTiO_3 to TiO_2 is in general agreement although temperatures given for the eutectic range from 1400 to 1437° . It is plain from the figure that the main source of confusion in the system is in the region from CaO to CaTiO_3 . This situation is further complicated by the solid state reactions reported by Tanaka,⁷ Parga-Pondel and Bergt,⁸ Ershov⁹ and Fisk.¹⁰ A summary of these workers' conclusions is shown in Table I. The obvious disagreement in regard to the composition, number and stability of the compounds in this system needs clarification. The present investigation may serve to clarify some of the discrepancies. In this regard considerable care has been taken to ensure the reproducibility of the data by using several different techniques with emphasis on the attempt to extend the advantages of the

(1) Paper presented at the Annual Meeting of the American Ceramic Society, April 28, 1953.

(2) This paper is based on a part of a dissertation entitled, "Phase Equilibria in the System $\text{CaO-TiO}_2\text{-SiO}_2$ " submitted by R. C. DeVries in partial fulfillment of the requirements for the degree of Doctor of Philosophy at The Pennsylvania State University, August, 1953.

(3) R. C. DeVries, R. Roy, and E. F. Osborn, *J. Am. Cer. Soc.*, in press.

(4) H. van Wartenberg, H. J. Reusch and E. Saran, *Z. anorg. Chem.*, **230**, 257 (1937).

(5) S. Umezu and F. Kakiuchi, *Nippon Kogyo Kwai*, **45**, 866 (1930).

(6) M. Fukushima, *Kinzoku no Kenkyu*, Tokyo, **11**, 590 (1934).

(7) Y. Tanaka, *J. Chem. Soc. Japan*, **61**, 345 (1940).

(8) I. Parga-Pondel and K. Bergt, *Anal. soc. espan. fis. quim.*, **31**, 623 (1933); *Cer. Abs.*, **13** [5] 131 (1934).

(9) L. D. Ershov, *Gosudarst. Vsesoyuz. Inst. Proektirovaniyu Predpriyatii i Nauchno-Issledovatel. Rabote; Tsement., Prom. Giprotsement Trudy*, **1**, 5 (1940).

(10) H. C. Fisk, *J. Am. Cer. Soc.*, **34**, 9 (1951).

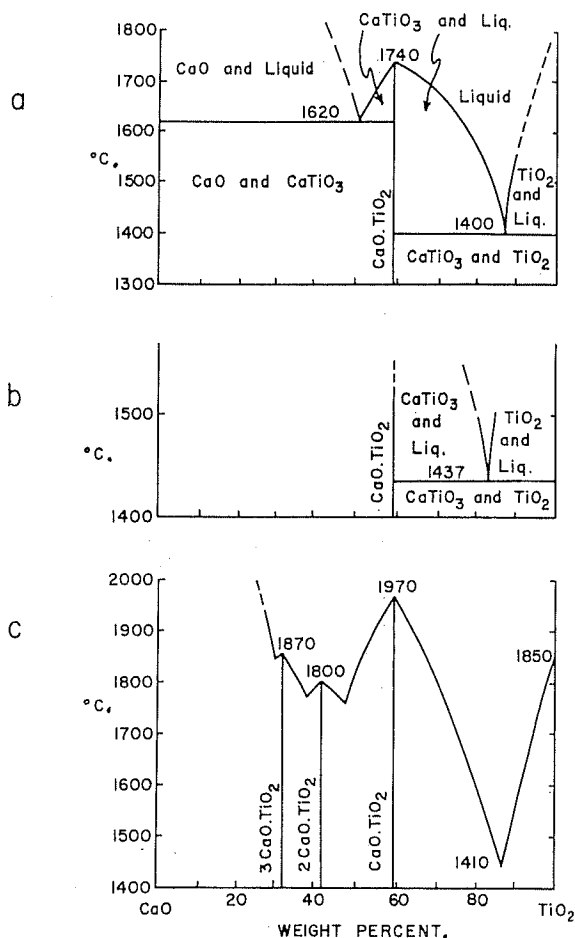


Fig. 1.—Previous versions of the system CaO-TiO_2 : a, Umezu and Kakiuchi⁵; b, Fukushima⁶; converted from the original version in terms of CaTiO_3 and TiO_2 by the present authors; c, v. Wartenberg, *et al.*⁴

quenching method to as high temperatures as possible in this system.

Experimental Procedure

The mixtures to be studied were made from reagent grade chemicals which were thoroughly mixed and then sintered in platinum crucibles at 1300° for at least 48 hours with intermediate crushing and mixing at 12-hour intervals.

Quenching, thermal analysis and pellet-melting methods were used. Quenching runs on the sintered mixtures were made using conventional quenching techniques in a platinum-wound tube type furnace for temperatures up to 1600° .¹¹

(11) This technique was originally described by Shepherd, Rankin and Wright¹² and has been redescribed in many papers from the Geophysical Laboratory of The Carnegie Institution of Washington and this laboratory.

(12) E. S. Shepherd, G. A. Rankin and F. E. Wright, *Am. J. Sci.*, **28**, 293 (1909).

TABLE I

SUMMARY OF PREVIOUS STUDIES IN THE SYSTEM CaO-TiO₂

Investigator	Compounds (mole ratio) (CaO:TiO ₂)	Remarks
van Wartenberg, <i>et al.</i> , ⁴	1:1, 3:1, 2:1	Phase diagram, liquidus curve only; m.p. CaTiO ₃ , 1970°
Umezumi and Kakiuchi ⁵	1:1	Phase diagram; m.p. CaTiO ₃ , 1740°
Fukushima ⁶	1:1	Phase diagram; (CaTiO ₃ -TiO ₂)
Tanaka ⁷	1:1	Solid solution of CaO in CaTiO ₃
Parga-Pondel and Bergt ⁸	1:1, 3:1	CaTiO ₃ stable up to 1300°, 3CaO-TiO ₂ forms at 1400°
Ershov ⁹	1:1, 3:2	
Fisk ¹⁰	1:1, 3:2	

A strip furnace of the type described by Roberts and Morey¹³ was used for quenching experiments up to 1860° (by using 60Pt40Rh strips). An oxy-hydrogen flame was used for melting pressed pellets of the mixtures. Temperatures were measured by means of calibrated 90Pt10Rh thermocouples in the tube furnaces and by an optical pyrometer on the strip furnace and pellet runs. The reproducibility of temperatures recorded with methods using thermocouples is 3°; for the optical pyrometer measurements, about ±10°. The accuracy of both types of measurements as referred to absolute temperature scales has been discussed in another paper.¹⁴

To determine the first appearance of liquid (solidus) by both the strip furnace and tube furnace quenching methods a sample is heated to successively higher temperatures until evidence of liquid formation can be detected by binocular microscope observation after quenching. The final disappearance of crystals (liquidus) as determined on the strip furnace is based on the interpretation of a characteristic appearance, namely, complete flow of the sample with no visible mounds of unmelted material remaining. This condition cannot be determined as precisely as the solidus since a "mush" of crystals and liquid may exhibit the same characteristics.

The temperature of the first appearance of liquid as determined from heating pellets in the oxy-hydrogen flame was not as reproducible as on the strip furnace because of the inherent inaccuracies of the method. The temperature interpreted as the liquidus (sudden very rapid flow) was remarkably reproducible (±15°) and consistent for a series of mixtures, considering the nature of this technique. Here, too, a few crystals may be present in the liquid in which case the liquidus temperatures would be low.

Due to the difficulties frequently encountered in differential thermal analysis (*e.g.*, stray A.C. e.m.f. due probably to thermionic emission or conduction) at high temperatures, only thermal analysis runs were made. The calibrated Pt10Rh thermocouple was surrounded by the mixture in a 1-ml. platinum crucible. A motor-driven variac was used for heating the same type of tube furnaces used for quenching. By this method runs as high as 1720° have been made. Heating rates of 8-9° per minute were most satisfactory. The temperatures of the heat effects (taken as the initial break of the curve) are reproducible to ±5°, and they agreed well with the temperatures found by the quenching method. There was no evidence for appreciable supercooling in the melts.

The phases were identified both optically and by X-ray methods. The high indices of refraction of the crystalline phases forming in this system and the non-quenchability of the liquids (to a glass) seriously limit the use of the former method for detecting and identifying primary phases. The physical aspects of the formation of liquid can be ob-

served optically, and therefore the first appearance of liquid can be determined by binocular observation alone. Solid immersion media (2.2-2.5) were used to enable examination of some of the quenched runs by means of transmitted light.

A GE XRD-3 diffractometer was used for all the spacing measurements and for most of the identification. In favorable cases measurements are reproducible to ±0.01 2θ on this instrument with the methods used. Copper radiation filtered through nickel was used. Calibration was made against the quartz peaks at 50.186 and 26.664° (2θ).

Results of Investigation

The results of quenching runs, thermal analyses and pellet-melting are presented in Table II. The proposed phase diagram is shown in Fig. 2.

TABLE II

SUMMARY OF RUNS ON MIXTURES IN THE SYSTEM CaO-TiO₂

Composition (wt. %)		Time, hr.	Temp., °C.	Phases present ^c
CaO	TiO ₂			
85.0	15.0	0.05	1710 ^a	Liq, xl
		0.05	1680 ^a	Xl
		0.25	1605	CaO, Ca ₃ Ti ₂ O ₇
		48.0	1300	CaO, Ca ₃ Ti ₂ O ₇
67.8	32.2		1860 ± 4 ^{b,4}	Liq
		0.05	1860 ^a	Liq
		0.05	1835 ^a	Liq, CaO
		0.05	1700 ^a	Liq, xl
		0.05	1675 ^a	Xl
			1670 ^b	First app. of liq.
		1.0	1600	Ca ₃ Ti ₂ O ₇ , CaO
		0.6	1501	Ca ₃ Ti ₂ O ₇ , CaO
63.0	37.0	48.0	1300	Ca ₃ Ti ₂ O ₇ , CaO
			1800 ^{b,3}	Liq
		0.05	1795 ^a	Liq
			1725 ^{b,4}	First app. of liq.
		0.05	1715 ^a	Liq, xl
			1698	Heat effect—ther- mal analysis
		0.05	1690 ^a	Xl
		48.0	1300	Ca ₃ Ti ₂ O ₇ , CaO
58.4	41.6	0.05	1805 ^a	Liq
		0.05	1770 ^a	Liq, xl
		0.05	1760 ^a	Liq, Ca ₃ Ti ₂ O ₇
			1748 ^{b,3}	Liq
		0.05	1700 ^a	Liq, xl
		0.05	1680 ^a	Xl
			1678 ± 9 ^{b,3}	First app. of liq.
		1.0	1600	Ca ₃ Ti ₂ O ₇ , CaO
55.0	45.0	2.0	1500	Ca ₃ Ti ₂ O ₇ , CaO
		48.0	1300	Ca ₃ Ti ₂ O ₇ , CaO
		0.05	1865 ^a	Liq
			1753 ± 8 ^{b,3}	First app. of liq.
		0.05	1720 ^a	Liq, Ca ₃ Ti ₂ O ₇
		0.05	1695 ^a	Liq, xl
		0.05	1675 ^a	Xl
		48.0	1400	Ca ₃ Ti ₂ O ₇ , CaO
51.29	48.71		1878 ± 15 ^{b,3}	Liq
		0.05	1765 ^a	Liq, xl
		0.05	1745 ^a	Xl
		0.05	1720 ^a	Xl
		0.5	1600	Ca ₃ Ti ₂ O ₇
		72.0	1539	Ca ₃ Ti ₂ O ₇
		48.0	1300	Ca ₃ Ti ₂ O ₇

(13) H. S. Roberts and G. S. Morey, *Rev. Sci. Instr.*, **1**, 576 (1930).(14) R. C. DeVries, R. Roy and E. F. Osborn, *Trans. Brit. Cer. Soc.*, Sept. (1954).

TABLE II (Continued)

Composition CaO (wt. %) TiO ₂	Time, hr.	Temp., °C.	Phases present ^c
48.65 51.35		1932 ± 15 ^{b,3}	Liq
	0.05	1800 ^a	Liq, xl
	0.05	1775 ^a	Liq, xl
	0.05	1750 ^a	Xl
	0.05	1725 ^a	Xl
	0.05	1695 ^a	Xl
	0.05	1650 ^a	Xl
	0.25	1605	Ca ₃ Ti ₂ O ₇ , CaTiO ₃
	140.0	1546	Ca ₃ Ti ₂ O ₇ , CaTiO ₃
46.0 54.0		1950 ± 10 ^{b,3}	Liq
	0.05	1800 ^a	Liq, xl
	0.05	1765 ^a	Liq, xl
	0.05	1735 ^a	Xl
	0.05	1685 ^a	Xl
	12.0	1594	Ca ₃ Ti ₂ O ₇ , CaTiO ₃
	72.0	1539	Ca ₃ Ti ₂ O ₇ , CaTiO ₃
	72.0	1300	Ca ₃ Ti ₂ O ₇ , CaTiO ₃
43.6 56.4		1980 ^{b,2}	Liq (very little liq, up to this temp.)
	0.05	1790 ^a	Liq, xl
	0.05	1770 ^a	Liq, xl
	0.05	1735	Xl
	0.05	1700	Xl
	0.05	1650	Xl
	0.25	1605	CaTiO ₃ , Ca ₃ Ti ₂ O ₇
	140.0	1546	CaTiO ₃ , Ca ₃ Ti ₂ O ₇
41.2 58.8		1954 ± 18 ^{b,4}	Liq
	72.0	1539	CaTiO ₃
30.0 70.0		1853 ± 25 ^{b,2}	Liq
		1460 ²	Heat effect (ther- mal analysis)
20.0 80.0	0.05	1645 ^a	Liq
	0.05	1595 ^a	Liq, xl
	1.5	1501	Liq, TiO ₂ , CaTiO ₃ (?)
		1469	Heat effect (ther- mal analysis)
	1.0	1468	Liq, xl
	1.5	1456	Xl
15.0 85.0	0.05	1595 ^a	Liq
	0.05	1545 ^a	Liq, xl
	1.0	1524	Liq, TiO ₂
	0.5	1465	Liq, xl
		1462	Heat effect (ther- mal analysis)
	4.0	1457	Xl
10.0 90.0	0.05	1690 ^a	Liq
	0.05	1645 ^a	Liq, xl
	0.25	1464	Liq, xl
	0.5	1458	Xl
		1456	Heat effect (ther- mal analysis)

^a Strip furnace runs. ^b Pellet melts; superscript number = number of determinations; temperature and σ are result of statistical treatment of these determinations. All other runs made in Pt-wound quench furnaces. ^c Phases present at temperature indicated; at room temperature "liq" = liquid crystallized during quenching as observed under the microscope; xl = crystals.

CaTiO₃-TiO₂.—The eutectic temperature between perovskite (CaTiO₃) and rutile (TiO₂) was found to be 1460 ± 5° by both thermal analysis

and quenching techniques. Since the liquids forming in this system are extremely fluid, their first appearance is very easy to detect by noting the wetting of the platinum envelope. The quenching method does not allow for positive identification of the primary phases since all mixtures quenched from above the temperature of the eutectic contain the two crystalline phases, perovskite and rutile, at room temperature. The composition of the eutectic agrees within the limits of experimental error with Fukusima's value of 17% CaO.

The melting point of perovskite, 1970°, is that given by van Wartenberg, *et al.*⁴ The average temperature (four determinations) determined in the present investigation for this point was 1954 ± 18°. Quenching molten pellets resulted in a product that had low, often wavy birefringence, a refractive index of about 2.35, and often displayed alternating isotropic and anisotropic bands. This last feature may be the result of a rapid inversion not inhibited by quenching.

CaTiO₃-CaO.—The portion of the diagram from CaTiO₃ to CaO received the main emphasis of the study and was investigated above 1300°. Our interpretation of the data is in agreement with Ershov⁹ and Fisk,¹⁰ namely, that the 3:2 mole ratio composition was found to be the only other binary compound besides perovskite (CaTiO₃) existing in the system. All mixtures higher in CaO than the 3:2 mole ratio, contain only 3CaO·2TiO₂ and CaO. The 3:2 composition melts incongruently to CaTiO₃ and liquid (about 42% TiO₂) at 1750 ± 10°. The eutectic between 3CaO·2TiO₂ and CaO has the composition, 39% TiO₂, and the temperature, 1695 ± 5°.

From Table III the similarity of the powder diffraction patterns of CaO·TiO₂ and 3CaO·2TiO₂ will be easily seen. It should be noted that the latter compound has reflections overlapping those of each perovskite line. The question to be decided is whether the composition 3CaO·2TiO₂ does in fact represent a unique compound or whether it is the limit of solid solution of excess CaO in CaTiO₃. (A third possibility which may be nearest the truth is a combination of the above two, resulting in the existence of both unique compounds and some solid solution in each.) The latest analysis of the mineral perovskite structure by Murdoch¹⁵ gives a pseudocubic unit cell with $a_0 = 15.26$ Å. Examples are well known of solid solution of various ions in compounds with the perovskite structure resulting in the increase or decrease of the extent of "distortion" from the ideal cubic arrangement. The problem at hand was therefore to distinguish between the case where new diffraction lines due to a new compound appear when compositions are varied from 50 to 60 mole per cent. CaO, and that in which the perovskite pattern (with the superstructure and distortion already present) is altered continuously by the entry of excess Ca²⁺ ions. Increasing the complication is the very likely fact that perovskite itself may have a high-temperature form (which admits more or less Ca²⁺ than the low form) and the fact that the extent of solid solution may increase appreciably with temperature. If this were the case,

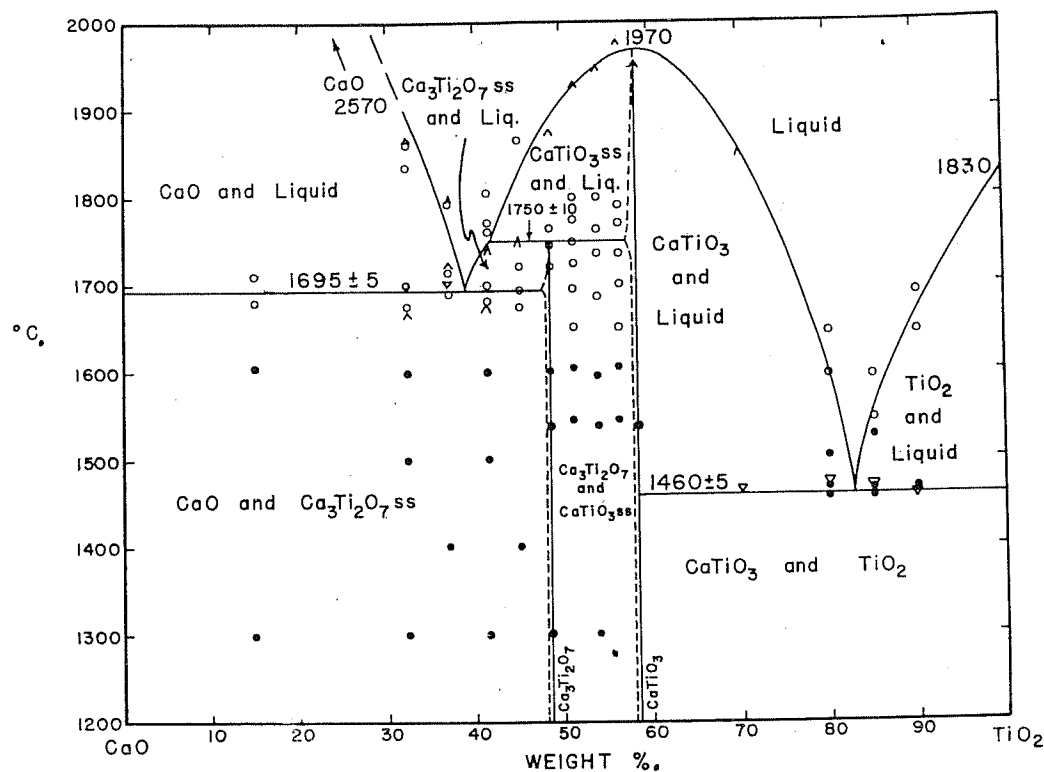


Fig. 2.—Proposed phase diagram for the system CaO-TiO_2 : solid dots, conventional quenching runs; open circles, strip furnace runs; Δ (at apex), pellet melting runs; ∇ (at lower apex), thermal analysis runs; ss, solid solution.

(and as has been shown by DeVries and Roy¹⁶ for other systems involving CaTiO_3 , high-temperature forms may remain "quenched in") the problem takes on major proportions.

TABLE III
INTERPLANAR SPACINGS FOR COMPOUNDS IN THE SYSTEM
 CaO-TiO_2

d $3\text{CaO} \cdot 2\text{TiO}_2$	I/I_0	d $\text{CaO} \cdot \text{TiO}_2$	I/I_0
9.77	41	3.83	12
4.887	65	3.43	3
3.762	12	2.708	100
2.730	100	2.417	2b ^a
2.710	76	2.362	2b
2.481	6	2.304	8
2.254	7	2.219	9
2.080	18	2.201	7b
1.9509	65	2.122	5b
1.9141	53	2.049	3b
1.8860	20	1.9141	64
1.5826	26	1.8579	6
1.5679	20	1.7142	5
1.3912	6	1.6922	2
1.3662	12	1.6779	6
1.3423	6	1.5655	23
1.2303	5	1.5583	26
1.2119	5	1.3524	17
		1.2094	7b
		1.1013	2b

^a b = broad.

The experimental work done in addition to identification powder patterns was as follows: powder

(16) R. C. DeVries and R. Roy, paper presented at the Annual Meeting of the American Ceramic Society, April, 1954.

X-ray diffraction patterns were run at a rate of $1/5^\circ$ 2θ per min. on a series of samples of the two "compounds" prepared under various conditions especially as quenched from different temperatures. Mechanical mixtures were also made of these two compounds and their patterns run. The same slowly scanned patterns were then also obtained for the significant runs made on compositions between 50 and 60 mole per cent. TiO_2 . Some idea of the type of data obtained is conveyed through Fig. 3. Our interpretation of all the data leads to the conclusion that a definite compound with the composition $3\text{CaO} \cdot 2\text{TiO}_2$ exists, but that both this phase and $\text{CaO} \cdot \text{TiO}_2$ may admit some excess CaO into their structures. The determination of the extent of this solid solution with any degree of reliability in these structures and especially as a function of temperature was considered to be a minor consideration not justifying the great deal of work necessary. A reflection near 4.9 \AA . in the powder pattern of $3\text{CaO} \cdot 2\text{TiO}_2$ appears at first to be convincing evidence of the uniqueness of this composition. However, 4.91 also corresponds to the basal spacing of $\text{Ca}(\text{OH})_2$, and Fisk¹⁰ had claimed that $3\text{CaO} \cdot 2\text{TiO}_2$ was "hydraulic." We refluxed the compound with water for a period of 24 hours at 100° and could find no evidence of any change of pattern. Moreover, there is also a weak line at 9.8 \AA . of which the 4.9 \AA . line is the second order, and it is unlikely that single crystal studies of $\text{Ca}(\text{OH})_2$ would have missed such an obvious feature. Furthermore, the other strong reflections of $\text{Ca}(\text{OH})_2$ are absent (at least in their proper intensity ratios). Careful study of the spacings also showed that the spacing associated with $3\text{CaO} \cdot 2\text{TiO}_2$ compound was 4.89 as com-

pared with 4.92 for $\text{Ca}(\text{OH})_2$; and it was actually possible to show the existence of both reflections in mixtures containing more CaO than the $3\text{CaO} \cdot 2\text{TiO}_2$ ratio which had hydrated in the atmosphere. It will also be seen from Fig. 3 that in addition to the fact that compositions between 50 and 60 mole per cent. CaO yield patterns which are essentially superpositions of the CaTiO_3 and $3\text{CaO} \cdot 2\text{TiO}_2$ patterns, there is in some cases a systematic shift in both patterns. It is felt that the inconsistent results obtained were due to inability to retain the high temperature structure by sufficiently rapid quenching in all cases. A definite shift has been noted in several patterns leading to the qualitative representation shown in Fig. 2 in which some solid solution is shown in each compound toward the CaO end with the extent of solid solution decreasing at lower temperatures. No quantitative values can be ascribed to the extent of solid solution but it would appear to be less than 2-3 wt. per cent. in each case. Thus the X-ray diffraction data, though not straightforward, confirm the thermal data regarding the presence of the compound $3\text{CaO} \cdot 2\text{TiO}_2$.

Optical examination of these end members and mixtures although performed under unfavorable conditions due to their high indices of refraction provided confirmatory evidence for this interpretation. When mounted in solid immersion media of index 2.3, both phases can be detected in the mixtures ($3\text{CaO} \cdot 2\text{TiO}_2$ as birefringent, subhedral laths less than 2.3; CaTiO_3 as isotropic, or nearly isotropic anhedral to rounded grains of index greater than 2.3). This is in agreement with Fisk's¹⁰ data on the refractive indices.

Quench runs of the $3\text{CaO} \cdot 2\text{TiO}_2$ composition from all temperatures have the same pattern, and microscopic examination fails to show any other phase. All mixtures higher in CaO than the $3\text{CaO} \cdot$

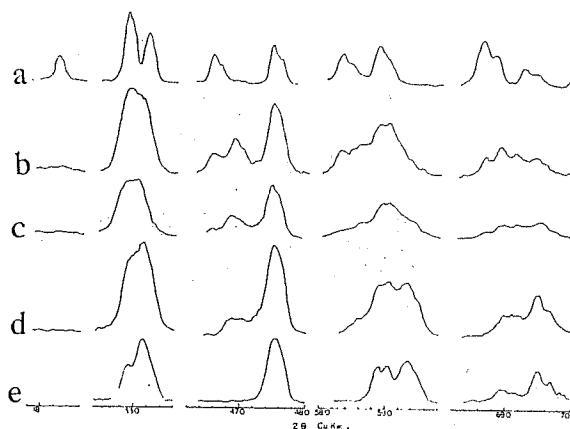


Fig. 3.—X-Ray diffractometer patterns of a series of mixtures from $\text{Ca}_3\text{Ti}_2\text{O}_7$ to CaTiO_3 (after melting and quenching) illustrating difficulties in interpretation of these data; composition of mixtures in weight %, CaO/TiO_2 : a, 51.29/48.71 ($\text{Ca}_3\text{Ti}_2\text{O}_7$); b, 48.65/51.35; c, 46.00/54.00; d, 43.60/56.40; e, 41.24/58.76 (CaTiO_3). Each subdivision, 0.2° 2θ $\text{Cu K}\alpha$.

2TiO_2 composition contain $3\text{CaO} \cdot 2\text{TiO}_2$ in the same form as the pure compound as determined by both X-ray and microscopic methods.

This interpretation of the data is seen to agree with most of the more recent work such as that of Ershov⁹ and Fisk¹⁰ and explain some aspects of the earlier work. Failure to retain high temperature phases on quenching to room temperature and the similarities between the two binary compounds would appear to explain some of the discrepancies.

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CHEMORHEOLOGY OF SOME SPECIALLY PREPARED SILICONE RUBBERS

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Contribution from the Frick Chemical Laboratory, Princeton University, Princeton, N. J.

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Specially prepared silicone rubbers were formulated from octamethylcyclotetrasiloxane, cross-linking agent and catalyst. These rubbers were extremely labile as evidenced by stress relaxation measurements. The lability could be overcome by tying up the acid catalyst with water vapor or pyridine.

Introduction

Ring siloxanes such as octamethylcyclotetrasiloxane $[(\text{CH}_3)_2\text{SiO}]_4$ may be catalytically transformed into long chains by shaking with a small quantity of sulfuric acid.^{1,2}

It was desired to prepare films of lightly cross-linked silicone rubber directly from octamethylcyclotetrasiloxane by incorporation of a cross-linking agent and a catalyst. The catalyst was based on sulfuric acid, but since sulfuric acid is not soluble

in the silicones in the desired concentration range, a means was found to incorporate this catalyst without separation into two phases. The cross-linking agent was added to prevent thermoplastic flow.

Once these films were prepared, they were found to be highly labile because the presence of catalyst caused continual interchange of the SiO bonds. These interchanges were manifest by a loss of weight in the samples if they were not kept in closed containers. This undoubtedly was due to the formation of volatile ring siloxanes.

The great lability of the rubber films prepared in this way was also manifest by the extremely rapid

(1) W. Patnode and D. F. Wilcock, *J. Am. Chem. Soc.*, **68**, 358 (1946).

(2) A. V. Tobolsky, F. Leonard and G. P. Roeser, *J. Polymer Sci.*, **3**, 604 (1948).