

Phase Equilibrium Relations in the Systems Lime-Titania and Zirconia-Titania

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The systems CaO-TiO_2 and $\text{ZrO}_2\text{-TiO}_2$ were studied by means of solid-state reactions and by the observation of fusion characteristics. The existence of two binary compounds in the CaO-TiO_2 system was confirmed. One compound was found to exist in the $\text{ZrO}_2\text{-TiO}_2$ system. This compound, $\text{ZrO}_2\text{-TiO}_2$, has been found to have orthorhombic symmetry with the following parameters at room temperature: $a=4.806$ Å, $b=5.032$ Å, $c=5.447$ Å. Solid-solution development was observed in the $\text{ZrO}_2\text{-TiO}_2$ system, but not in the CaO-TiO_2 system. From the data obtained, an equilibrium diagram is suggested for each system.

I. Introduction

A study of phase relationships in the systems CaO-TiO_2 and $\text{ZrO}_2\text{-TiO}_2$ has been conducted as a part of a program of fundamental studies of ceramic dielectrics.¹ Both of these systems have been investigated by previous workers. The results of these investigations were rather divergent, however, so it was considered essential that the systems be reinvestigated.

The number of compounds proposed for the CaO-TiO_2 system has varied from one [1]² to three [2]. Some previous studies of the $\text{ZrO}_2\text{-TiO}_2$ system [3, 4] have indicated the absence of any compounds in the system and the presence of partial solid solutions. The possibility of the stabilization of the tetragonal form of ZrO_2 by TiO_2 has also been suggested [5]. Brown and Duwez [6] from X-ray and thermal-expansion measurements proposed a phase diagram indicating the compound $\text{ZrO}_2\text{-TiO}_2$. Their diagram, although not supported by fusion-point data, is similar to the one determined in the present investigation.

The determination of the melting points of the compounds, and of the solidus and liquidus temperatures at various points across the two systems, have supplied data from which a revised equilibrium diagram has been constructed for the systems CaO-TiO_2 and $\text{ZrO}_2\text{-TiO}_2$.

2. Sample Preparation and Test Methods

The following materials were used as the source of components in the samples for this study: CaO —Eimer Amend Co. reagent-grade calcium carbonate of 99.5-percent purity; ZrO_2 —dense ZrO_2 of nominal 99-percent purity, obtained from the Titanium Alloy Manufacturing Co.; TiO_2 —highly purified titania of purity over 99.9-percent, obtained from the Titanium Division of the National Lead Co.

Calculations of weight composition were made to ± 0.01 percent, no correction being made for the percentage purity of the raw materials.

The components, in sufficient quantities to give a 10-g sample, were weighed to the nearest milligram. They were then mixed with a binder of either a 5-percent soluble-starch solution or a saturated solution of paraffin in carbon tetrachloride, and 1-in.-diam disks were formed at a pressure of 5,000 lb/in.². The pressed samples were fired for 4 hr at 1,200° C on platinum foil in an air atmosphere, using an electrically heated furnace wound with 80 Pt-20 Rh wire. The disks were cooled and then ground, repressed, and refired for 4 hr at 1,350° C, again under oxidizing conditions. X-ray examination of the samples showed, after these two heat treatments, that the solid-phase reactions were essentially complete with the exception of the formation of $3\text{CaO}\cdot 2\text{TiO}_2$. The composition representing this compound was a mixture of CaO and CaO-TiO_2 after these two calcinations. However, upon heating to 1,500° C, or higher, the reaction to form the compound $3\text{CaO}\cdot 2\text{TiO}_2$ took place quite readily.

Following this preliminary heat treatment the disks were ground, remixed with starch-solution binder, and disks about $\frac{1}{4}$ in. high were formed at 15,000 lb/in.² in a $\frac{1}{2}$ -in.-diam mold. From these disks, the specimens for solidus and liquidus determinations were ground in the form of small four-sided pyramids, grooved on each side [7]. The tests were conducted in a thoria resistor-type furnace [8, 9]. The specimens were placed in the furnace on a disk of a platinum-rhodium alloy for temperatures below 1,900° C. For temperatures higher than this value, the samples were placed on an iridium disk. The metal disk was on a support of ThO_2 . The heating rate during the tests was about 4 deg C/min until the solidus temperature was approached, when it was reduced to about 2 deg C/min, or less. There was an oxidizing atmosphere in the furnace at all times. The temperature and fusion characteristics of the specimens were observed with an optical pyrometer calibrated at the National Bureau of Standards. In the determination of the solidus and liquidus temperatures, the first sign of liquid formation, rounding of the corners of the test pyramid, was recorded as the solidus temperature. The

¹ This study was sponsored by the Office of Ordnance Research, Department of the Army.

² Figures in brackets indicate literature references at the end of this paper.

temperature of complete melting, as arrived at by observations through the optical pyrometer and by visual inspection of the cooled specimen, was recorded as the liquidus temperature. In all cases, several tests had to be made to determine these two values.

The determination of such temperatures is subject to a number of sources of error. Among these are the slight deviations from blackbody conditions, the introduction of small quantities of impurities into the specimens in the forming and grinding operations, the possibility of reduction of TiO_2 at high temperatures, and the inherent difficulty in the visual determination of the solidus and liquidus temperatures. In the present study, care was taken to keep each of these possible errors to a minimum. It is believed that the temperatures as recorded are accurate to $\pm 10^\circ \text{C}$.

After the fused specimens had cooled, they were analyzed either petrographically or by means of X-ray powder patterns, using a high-angle recording spectrometer, and $\text{Cu K}\alpha$ radiation. All X-ray data are reported as observed, uncorrected for temperature or adsorption characteristics. Similar analyses were performed on specimens that had been quenched from temperatures up to $1,600^\circ \text{C}$.

3. The CaO-TiO_2 System

A considerable amount of work has been done on this system by previous investigators. The results, however, have been in rather serious disagreement, and the present study was undertaken to determine the correct equilibrium relations.

Tanaka [1] decided that there is only one compound, $\text{CaO}\cdot\text{TiO}_2$, in the system and that CaO forms solid solutions with this compound. Hedvall and Anderson [10], by means of X-ray studies of samples fired to a maximum temperature of $1,135^\circ \text{C}$,

also concluded that $\text{CaO}\cdot\text{TiO}_2$ is the only compound in the system. H. von Wartenberg, et al. [2] published a liquidus curve for the system which indicated the existence of three congruently melting compounds, $3\text{CaO}\cdot\text{TiO}_2$, $2\text{CaO}\cdot\text{TiO}_2$, and $\text{CaO}\cdot\text{TiO}_2$. Several other investigators [11-15] have indicated that the compounds existing in the system are $3\text{CaO}\cdot 2\text{TiO}_2$ and $\text{CaO}\cdot\text{TiO}_2$. De Vries, et al. [15] proposed a diagram similar to the one here determined.

The equilibrium diagram resulting from the present study is shown in figure 1. The fusion-behavior data from which the diagram is constructed are given in table 1. It is seen that there are two compounds in the system. These are $\text{CaO}\cdot\text{TiO}_2$ (perovskite), which melts congruently at about $1,915^\circ \text{C}$, and $3\text{CaO}\cdot 2\text{TiO}_2$, which melts incongruently at about $1,750^\circ \text{C}$. It should be noted that the compound $3\text{CaO}\cdot 2\text{TiO}_2$ does not form readily at temperatures below $1,500^\circ \text{C}$. This may explain why it was not noted by some other investigators. The X-ray powder diffraction pattern for the compound $3\text{CaO}\cdot 2\text{TiO}_2$ is given in table 2, but attempts to index this pattern have not, as yet, been successful.

The absence of solid solutions in the diagram should be noted. There is considerable overlapping of some peaks in the diffraction patterns of the compounds $\text{CaO}\cdot\text{TiO}_2$ and $3\text{CaO}\cdot 2\text{TiO}_2$. This fact makes it rather difficult to unambiguously establish solid-solution relationships by X-ray methods. This difficulty is not present in the petrographic method of analysis, however, as their optical properties differ rather widely. Perovskite has very low birefringence and an index of refraction of about 2.38. The optical properties of the compound $3\text{CaO}\cdot 2\text{TiO}_2$ may be tabulated as follows: Optical

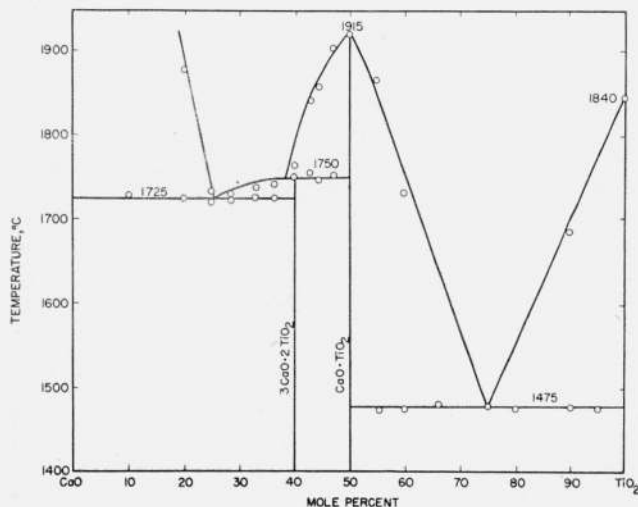


FIGURE 1. Suggested equilibrium diagram for the system CaO-TiO_2 .

TABLE 1. Fusion characteristics of compositions in the CaO-TiO_2 system

Composition				Results of heating		Results of petrographic or X-ray examination (specimens examined were not quenched and the phases observed may not be those in equilibrium at the liquidus)
Mole		Weight		Solidus	Liquidus	
CaO	TiO ₂	CaO	TiO ₂			
<i>w</i> %	<i>t</i> %	<i>w</i> %	<i>t</i> %	<i>° C</i>	<i>° C</i>	
4.76	95.24	3.39	96.61	1,470	-----	$\text{CaO}\cdot\text{TiO}_2 + \text{TiO}_2$.
10.00	90.00	7.23	92.77	1,470	1,680	Do.
20.00	80.00	14.93	85.07	1,470	-----	Do.
25.00	75.00	18.96	81.04	1,475	-----	Do.
33.33	66.67	25.98	74.02	1,475	-----	Do.
40.00	60.00	31.88	68.12	1,470	1,730	Do.
44.44	55.56	35.96	64.04	1,470	1,850	Do.
50.00	50.00	41.24	58.76	1,915	1,915	$\text{CaO}\cdot\text{TiO}_2$.
53.00	47.00	44.18	55.82	1,750	>1,900	$\text{CaO}\cdot\text{TiO}_2 + 3\text{CaO}\cdot 2\text{TiO}_2$.
55.56	44.44	46.73	53.27	1,745	1,855	Do.
57.00	43.00	48.20	51.80	1,755	1,840	Do.
60.00	40.00	51.28	48.72	1,755	1,765	$3\text{CaO}\cdot 2\text{TiO}_2$.
63.64	36.36	55.12	44.88	1,725	1,740	$3\text{CaO}\cdot 2\text{TiO}_2 + \text{CaO}$.
66.67	33.33	58.39	41.61	1,725	1,735	Do.
71.43	28.57	63.70	36.30	1,720	1,725	Do.
75.00	25.00	67.81	32.19	1,720	1,720	Do.
80.00	20.00	73.73	26.27	1,725	1,879	Do.
90.00	10.00	86.33	13.67	1,725	-----	Do.

character—biaxial (—), $2V \approx 80^\circ$; approximate indices of refraction— $\alpha=2.16$, $\beta=2.20$, $\gamma=2.22$. These values are in good agreement with those in the partial list of optical properties given by Fisk [14].

TABLE 2. X-ray powder diffraction pattern for the compound $3\text{CaO} \cdot 2\text{TiO}_2$

2 θ	<i>d</i>	R. I. ^a	2 θ	<i>d</i>	R. I. ^a
6.53	13.5	1.4	77.41	1.23	0.8
9.08	9.7	29	77.93	1.22	1.5
13.04	6.8	0.3	78.37	1.22	2.3
18.19	4.9	53	78.78	1.21	1.4
19.63	4.5	2.0	79.00	1.21	0.6
23.63	3.76	1.2	83.72	1.154	.5
26.98	3.30	0.5	85.97	1.129	.8
32.74	2.73	23	86.21	1.127	1.4
32.82	2.73	12	86.57	1.123	0.3
33.05	2.71	10	87.64	1.112	.6
34.36	2.61	0.6	88.94	1.099	.6
36.22	2.48	1.1	90.41	1.085	.2
36.82	2.44	0.8	94.40	1.049	.3
37.08	2.42	.6	96.07	1.036	1.4
37.37	2.40	.5	96.90	1.029	0.9
37.96	2.37	.5	97.34	1.026	.9
38.32	2.35	.3	97.42	1.025	.6
39.61	2.27	.5	101.92	0.9917	1.5
39.95	2.25	1.7	104.32	.9753	10.9
40.63	2.25	1.2	104.86	.9718	0.6
42.58	2.12	0.3	107.09	.9576	.3
43.44	2.08	3.5	107.75	.9536	.5
43.93	2.06	0.5	108.77	.9475	.3
45.03	2.01	.6	113.66	.9202	.8
46.52	1.95	100	114.14	.9177	1.1
47.41	1.92	4.2	114.75	.9145	1.1
48.18	1.89	2.2	115.24	.9121	1.2
50.32	1.81	0.6	115.40	.9112	0.8
51.17	1.78	.9	116.98	.9035	.9
52.67	1.74	.5	117.21	.9021	1.7
53.61	1.71	.5	120.60	.8867	.6
55.36	1.66	.6	122.02	.8806	1.2
56.56	1.63	6	124.80	.8692	0.6
58.23	1.58	6	127.23	.8598	.8
58.80	1.57	4.2	128.17	.8564	1.1
63.69	1.46	0.6	128.86	.8539	0.6
64.82	1.44	1.4	132.14	.8427	.8
67.12	1.39	5	138.84	.8228	1.4
68.61	1.37	2.2	139.45	.8211	0.8
69.24	1.36	1.1	140.00	.8197	.6
69.35	1.35	1.5	141.02	.8171	.6
69.91	1.34	0.8	142.79	.8127	3.4
74.23	1.28	.8	146.38	.8046	0.8
76.85	1.24	.8	148.58	.8001	2.2

^a R. I. is the intensity of diffraction peaks relative to the strongest peak.

4. The $\text{ZrO}_2\text{-TiO}_2$ System

A liquidus curve for this system was published by von Wartenberg and Gurr [16]. They showed a eutectic point at about 80 mole percent TiO_2 and $1,760^\circ\text{C}$. This is in exact agreement with the eutectic determined in the present work. Büssem, Schusterius, and Ungewiss [3] in an X-ray study of the system noted solid-solution development but no compound formation. Sowman and Andrews [4] published a phase diagram for the system $\text{ZrO}_2\text{-TiO}_2$. Their diagram was one of partial solid solution with no compounds present. They located the eutectic at 45 to 50 weight percent TiO_2 and $1,600^\circ\text{C}$. This diagram is not in agreement with the one determined in the present work. Later work by Sowman [5] on the $\text{ZrO}_2\text{-TiO}_2$ system indicated to him that the 1:1 composition, after heat treatment, consists of either a distorted form of tetragonal ZrO_2 or a new compound. Recently, Brown and Duwez [6] proposed a diagram indicating the existence of the compound $\text{ZrO}_2 \cdot \text{TiO}_2$. Their diagram is quite similar to the one determined at the Bureau.

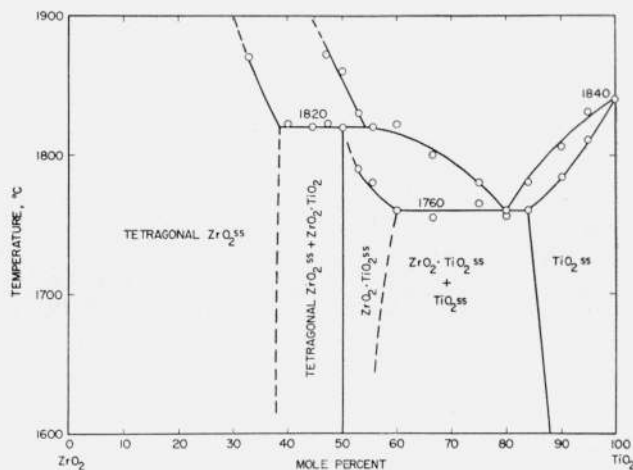


FIGURE 2. Suggested equilibrium diagram for the system $\text{ZrO}_2\text{-TiO}_2$.

The equilibrium diagram for the $\text{ZrO}_2\text{-TiO}_2$ system, as determined in the present study, is shown in figure 2, and the fusion behavior—data from which the diagram was constructed are listed in table 3. It is seen that the compound $\text{ZrO}_2 \cdot \text{TiO}_2$ melts incongruently at about $1,820^\circ\text{C}$. The eutectic point for the system is located at about 80 mole percent TiO_2 and $1,760^\circ\text{C}$. Rather extensive solid-solution development is noted at the higher temperatures.

No attempt was made in this study to work out thoroughly the lower-temperature relationships in this system. Some observations on quenched specimens and slowly cooled specimens did, however, yield some information on this part of the system. X-ray analyses of specimens quenched from $1,500^\circ\text{C}$ indicated that at this temperature about 12 percent of ZrO_2 will dissolve in TiO_2 . This is in good agreement with the value given by Büssem, et al. (3).

TABLE 3. Fusion characteristics of compositions in the $\text{ZrO}_2\text{-TiO}_2$ system

Compositions				Results of heating		Results of petrographic or X-ray examination (specimens examined were not quenched and the phases observed may not be those in equilibrium at the liquidus)
Mole		Weight		Solidus	Liquidus	
ZrO_2	TiO_2	ZrO_2	TiO_2			
%	%	%	%	$^\circ\text{C}$	$^\circ\text{C}$	
90.00	10.00	93.28	6.72	---	---	Monoclinic ZrO_2 ss. Monoclinic ZrO_2 ss+ $\text{ZrO}_2 \cdot \text{TiO}_2$.
75.00	25.00	82.23	17.77	>1,900	---	
66.67	33.33	75.51	24.49	1,845	---	Do.
60.00	40.00	69.81	30.19	1,825	---	Do.
55.56	44.44	65.84	34.16	1,820	---	Do.
52.94	47.06	63.44	36.56	1,825	1,870	Do.
50.00	50.00	60.71	39.29	1,820	1,860	$\text{ZrO}_2 \cdot \text{TiO}_2$.
47.06	52.94	57.82	42.18	1,790	1,835	$\text{ZrO}_2 \cdot \text{TiO}_2 + \text{TiO}_2$ ss.
44.44	55.56	55.23	44.77	1,775	1,820	Do.
40.00	60.00	50.69	49.31	1,760	1,825	Do.
33.33	66.67	43.54	56.46	1,755	1,800	Do.
25.00	75.00	33.95	66.05	1,765	1,780	Do.
20.00	80.00	27.83	72.17	1,755	1,760	Do.
16.67	83.33	23.57	76.43	1,760	1,780	Do.
10.00	90.00	14.63	85.37	1,785	1,805	TiO_2 ss.
5.00	95.00	7.51	92.49	1,810	1,830	Do.

The mole composition $2\text{ZrO}_2:3\text{TiO}_2$, when quenched from $1,460^\circ\text{C}$, had only a small percentage of TiO_2 in it, and the parameters of the $\text{ZrO}_2\cdot\text{TiO}_2$ had changed, indicating some solid solution at this temperature. No solid solution of TiO_2 in $\text{ZrO}_2\cdot\text{TiO}_2$ could be detected in slowly cooled samples.

Diffraction patterns of specimens high in ZrO_2 content indicated that TiO_2 is soluble in monoclinic ZrO_2 to the extent of 10 to 15 weight percent at room temperature. The ZrO_2 diffraction peaks in such samples had shifted to higher angles, indicating a smaller unit cell than that for pure ZrO_2 . This result is at variance with the findings of Brown and Duwez [6], who stated that the solubility of titania in monoclinic ZrO_2 is probably very small.

5. The Compound $\text{ZrO}_2\cdot\text{TiO}_2$

In view of the disagreement between the present authors and some previous workers concerning the existence of the compound $\text{ZrO}_2\cdot\text{TiO}_2$, some discussion of its properties is in order. First of all, it was noted that the 1:1 mixture formed a single phase when fired at $1,250^\circ\text{C}$ for a sufficiently long period of time, or when fired at higher temperatures for shorter periods of time. There is a superficial resemblance between the X-ray pattern of this material and that of tetragonal ZrO_2 . However, the pattern of the 1:1 fired mixture contained so many excess lines that it could not be indexed on the basis of tetragonal symmetry. The patterns are compared in figure 3. It is evident that these patterns are for two entirely different materials.

Further, it was found that the 1:1 composition, when fused and cooled relatively slowly, gave crystals large enough for petrographic examination. Such examination showed the material to consist of a single crystalline phase having the following properties: Biaxial (-), $2V \approx 80^\circ$; approximate indices of refraction— $\alpha=2.33$, $\beta=2.38$, $\gamma=2.41$.

These properties are not compatible with tetragonal symmetry. It therefore must be assumed that the 1:1 mixture does not form stabilized tetragonal ZrO_2 , but does form a distinct compound. It is to be noted that the X-ray pattern for the heated 1:1 mixture is indexed on the basis of orthorhombic symmetry. The indexed pattern is listed in table 4. The indexing of the powder pattern of $\text{ZrO}_2\cdot\text{TiO}_2$ was facilitated by the similarity of this pattern to that of tetragonal ZrO_2 . It was noted that the 002/200 doublet of tetragonal ZrO_2 was split into three peaks, indicating a lower symmetry for $\text{ZrO}_2\cdot\text{TiO}_2$. When this triplet was assigned values of 002/020/200, the pattern was easily indexed and proved the compound $\text{ZrO}_2\cdot\text{TiO}_2$ to have orthorhombic symmetry.

The theoretical possibility of the formation of the compound $\text{ZrO}_2\cdot\text{TiO}_2$ may be realized by noting the work of Dietzal and Tober [17]. They state that the tendency for compound formation between two oxides is dependent upon the relative difference in the field strengths of the two components involved. The field strength may be represented as being proportional to the quantity z/a^2 , where z is the charge on the cation, and a is the distance between the cation and anion. They noted that for most binary oxide systems $\Delta(z/a^2)$ should be at least 0.30 in order that compound formation may occur.

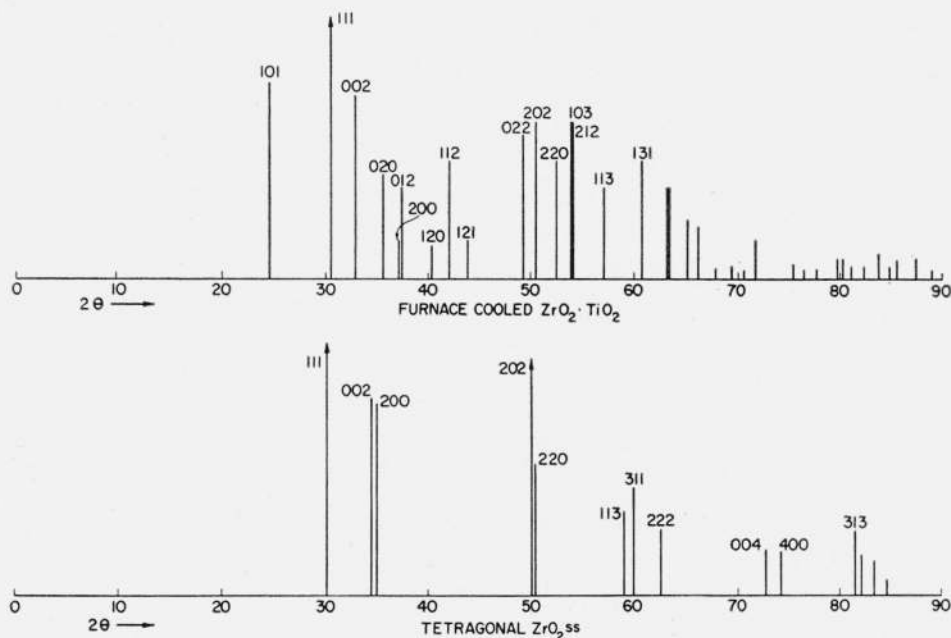


FIGURE 3. X-ray diffraction patterns for $\text{ZrO}_2\cdot\text{TiO}_2$ and tetragonal ZrO_2 .

TABLE 4. X-ray diffraction patterns of the compound $ZrO_2 \cdot TiO_2$

Specimen slowly cooled from 1,550° C to room temperature				Specimen quenched from 1,550° C			
<i>hkl</i>	1/d ² obs.	1/d ² calc.	R. I. ^a	<i>hkl</i>	1/d ² obs.	1/d ² calc.	R. I. ^a
101	0.077	0.077	15	101	0.077	0.077	19
111	.117	.117	100	111	.116	.116	100
002	.135	.135	14	002	.133	.133	16
020	.158	.158	8	020	.158	.158	9
200	.173	.173	3	012	.173	.173	11
012	.174	.174	7	200	.173	.174	7
120	.201	.201	2.5	120	.201	.201	3
112	.218	.218	9	112	.216	.216	10
121	.235	.235	3	121	.235	.235	3
022	.293	.293	11	022	.291	.291	9
202	.308	.308	12	202	.307	.307	9
220	.331	.331	9	220	.332	.331	14
103	.347	.347	12	103	.343	.343	10
212	.348	.348	12	212	.346	.346	10
113	.386	.386	7	113	.382	.382	8
131	.433	.432	9	131	.432	.432	10
311	.463	.463	7	311	.462	.463	4
222	.465	.466	7	222	.465	.464	7
032	.490	.490	4.5	032	.489	.488	4
123	.505	.505	4	123	.501	.501	4
302	.525	.525	0.5				
320	.547	.547	1	320	.549	.548	0.5
312	.564	.564	0.5	014	.572	.572	3.5
014	.519	.579	3	321	.582	.581	.5
040	.632	.632	1	040	.632	.632	1
223	.647	.635	0.5				
033	.664	.663	.5	303	.689	.689	1.5
232	.693	.693	1.5	400	.693	.694	2
133	.7019	.7020	1.5	133	.6975	.6978	1.5
204	.7127	.7126	1	141	.7072	.7081	1
410	.7319	.7323	1	313	.7288	.7291	1
214	.7516	.7519	2	330	.7452	.7455	3
042	.7644	.7666	1	042	.7642	.7646	1
331	.7787	.7788	1.5	331	.7783	.7787	2
240	.8052	.8050	1.5	240	.8049	.8049	1
402	.8266	.8276	0.5	233	.8278	.8281	0.5
420	.8507	.8508	.5	223	.8473	.8475	1.5
412	.8692	.8671	2	224	.8655	.8636	0.5
224	.8855	.8704	1	412	.8655	.8663	1
421	.8855	.8845	1	105	.8751	.8751	1
105	.9402	.9398	1	034	.8878	.8875	0.5
242	.9786	.9784	1	242	.9379	.9380	1
143	.9848	.9856	1	143	.9743	.9743	1
422	1.0140	1.0158	0.5	422	.9848	.9847	1
150	1.0311	1.0305	1	413	1.0331	1.0330	2
125	1.0436	1.0438	1.5	333	1.0444	1.0445	0.5
430	1.0489	1.0482	1.5				
151	1.0652	1.0642	1	234	1.0615	1.0610	2
234	1.0683	1.0680	1	151	1.0634	1.0633	1.5
511	1.1551	1.1557	1	342	1.1552	1.1548	1
432	1.1829	1.1830	1	511	1.1568	1.1568	1
502	1.2201	1.2174	1	432	1.1812	1.1820	1
404	1.2319	1.2323	1	305	1.2220	1.2220	1
305	1.2524	1.2528	1				
016	1.2591	1.2568	1	016	1.2378	1.2371	0.5
414	1.2706	1.2716	1	414	1.2650	1.2656	1
343	1.3259	1.3245	1	252	1.3001	1.2932	0.5
244	1.3443	1.3442	1	343	1.3212	1.3212	1
441	1.3604	1.3583	0.5				
235	1.3773	1.3711	.5	325	1.3800	1.3798	1
350	1.3898	1.3900	1				
351	1.4101	1.4106	1	351	1.4109	1.4102	1.5
513	1.4255	1.4253	1	513	1.4229	1.4229	0.5
531	1.4706	1.4716	1	530	1.4288	1.4393	.5
054	1.5263	1.5264	1	531	1.4726	1.4725	.5
				145	1.5071	1.5065	1
				054	1.5195	1.5190	1
				344	1.5534	1.5540	0.5
				434	1.5821	1.5813	.5

^a R. I. is the intensity of diffraction peaks relative to the strongest peak.

Further, if compound formation does take place when $\Delta(z/a^2)$ is less than 0.30, the compound must have an incongruent melting point. Furthermore, they indicate that $\Delta(z/a^2)$ for the $ZrO_2 \cdot TiO_2$ system is equal to 0.30. Thus, we see that the compound $ZrO_2 \cdot TiO_2$ is a possible occurrence according to this scheme, and that, if formed, it should have incongru-

ent melting characteristics. This is exactly the situation observed in the present study.

The compound when cooled slowly from a temperature of 1,200° to 1,600° C to room temperature has the following parameters: $a=4.806\text{Å}$, $b=5.032\text{Å}$, $c=5.447\text{Å}$. If the compound is quenched from 1,200° to 1,500° C, the c -axis is found to have a larger value, whereas the a - and b -axes remain essentially the same. The parameters of the quenched compound are: $a=4.802\text{Å}$, $b=5.034\text{Å}$, $c=5.483\text{Å}$. If the compound is quenched from 800° C, the parameters are the same as those in the slowly cooled specimen. These results seem to indicate the existence of two polymorphic forms of $ZrO_2 \cdot TiO_2$, with the transition temperature between 800° and 1,200° C.

The only extinction rules which are observed for the low temperature form of $ZrO_2 \cdot TiO_2$ are as follows; $h00$, $h=2n$; $0k0$, $k=2n$; $00l$, $l=2n$. From these it must be concluded that this compound has a primitive lattice rather than a face-centered lattice, as is the case in the tetragonal, cubic, and monoclinic forms of ZrO_2 . The high-temperature form of $ZrO_2 \cdot TiO_2$ seems to have the additional extinction rule of: $h0l$, $h+l=2n$. This indicates that the high-temperature form of $ZrO_2 \cdot TiO_2$ has a different symmetry than the low-temperature form.

6. Summary

The systems $CaO \cdot TiO_2$ and $ZrO_2 \cdot TiO_2$ were studied by observing solid-state reactions and fusion characteristics. The existence of two compounds in the $CaO \cdot TiO_2$ system was confirmed. They are $CaO \cdot TiO_2$, which melts congruently at about 1,915° C, and $3CaO \cdot 2TiO_2$, which melts incongruently at about 1,750° C. The two eutectic points were located as follows: 75 mole percent TiO_2 and 1,475° C, and about 23 mole percent TiO_2 and 1,725° C. No solid-solution formation was noted in this system.

One compound, $ZrO_2 \cdot TiO_2$, was found to occur in the $ZrO_2 \cdot TiO_2$ system. This compound melts incongruently at about 1,820° C. The eutectic point for the system was located at about 80 mole percent TiO_2 and 1,760° C. Partial solid-solution development was noted in this system.

The X-ray powder diffraction pattern of the compound $ZrO_2 \cdot TiO_2$ was indexed on the basis of orthorhombic symmetry.

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