Revision of the Phase Equilibrium Diagram of the Binary System Calcia-Titania, Showing the Compound Ca$_4$Ti$_3$O$_{10}$

Robert S. Roth

The compound Ca$_4$Ti$_3$O$_{10}$ has been found to be a stable phase in the system CaO-TiO$_2$. It melts incongruently at about 1755±10° C, presumably to CaTiO$_3$ plus liquid. This compound is shown in a revision of the phase diagram for the system CaO-TiO$_2$.

1. Introduction

Phase equilibrium diagrams for the system CaO-TiO$_2$ were published almost simultaneously by Coughanour, Roth, and DeProsse [1] [1] and by De-Vries, Roy, and Osborn [2]. The diagrams are very similar, both showing the existence of two compounds, CaTiO$_3$ and Ca$_3$Ti$_2$O$_7$. DeVries et al. [2], discussed the reactions between the two compounds and, on the basis of some changes in the X-ray patterns of the mixtures, concluded that a small amount of solid solution existed in both compounds. They published an X-ray pattern of Ca$_3$Ti$_2$O$_7$ which was quite similar to that reported by Fisk [3] for the same compound. Coughanour, Roth, and DeProsse [1] did not find solid solution between the two compounds but reported an X-ray pattern for Ca$_3$Ti$_2$O$_7$ which contained many more lines than those of the other publications.

Ruddlesden and Popper [4] studied the compound Sr$_3$Ti$_2$O$_7$ and have indicated it to be body centered tetragonal with $a=3.90$ A and $c=20.38$ A. They have also found a compound Sr$_2$TiO$_4$ [5] which contains alternate layers of perovskite and SrO, and have proposed that Sr$_3$Ti$_2$O$_7$ contains double perovskite layers interleaved with one SrO layer.

2. X-Ray Diffraction Data

The X-ray pattern previously published by Coughanour, Roth, and DeProsse [1] for Ca$_3$Ti$_2$O$_7$ can be partially accounted for on the basis of a body centered tetragonal cell with $a=3.832$ A and $c=19.505$ A. The pattern published by DeVries, Roy, and Osborn [2], which contains fewer lines, can be almost completely accounted for by a body centered tetragonal unit cell with $a=3.8$ A and $c=19.5$ A. These values correspond to double perovskite layers interleaved with CaO layers.

In the SrO-TiO$_2$ system Ruddlesden and Popper [4] predicted the possible existence of phases with triple or quadruple perovskite layers interleaved with SrO layers. They found some evidence for a compound Sr$_4$Ti$_3$O$_{10}$, which is also body centered tetragonal, with $a=3.90$ A and $c=28.1$ A, and contains triple perovskite layers.

Many of the extra lines in the pattern of Coughanour, Roth, and DeProsse [1] [2] can be accounted

for by assuming a mixture of two body centered tetragonal compounds, Ca$_3$Ti$_2$O$_7$ and Ca$_4$Ti$_3$O$_{10}$, the latter having a c-axis of 27.147 A. In the present study the two compounds have been isolated and the partially indexed X-ray patterns of both compounds are shown in tables 1 and 2. Although these two

TABLE 1. *X-ray diffraction powder pattern for the compound* Ca$_3$Ti$_2$O$_7$ *(CuK$_{\alpha 1}$ radiation)*

Fisk	DeVries, Roy, Osborn	Present work				hkl
d	d	d_{obs}	I/I_0	$1/d^2_{obs}$	$1/d^2_{cal}$ a	
------	9.77	9.73	b 100	0.0106	0.0105	002
(4.88)	4.887	4.873	b 100	.0421	.0421	004
------	3.762	3.762	8	.0707	.0707	101
------	------	3.302	3	.0907	.0918	103
------	------	------	------	------	.0946	006
------	2.730	2.733	100	.1339	.1338	105
2.70	2.710	2.708	66	.1364	.1362	110
------	------	------	------	------	.1467	112
2.51	2.481	2.478	7	.1629	------	------
------	------	2.439	b 5	.1681	.1682	008
------	------	------	------	------	.1783	114
2.19	{ 2.254	2.255	11	.1967	.1969	107
	2.080	2.081	23	.2308	.2308	116
1.93	1.9509	1.9505	b 100	.2629	.2629	0-0-10
1.91	1.9141	1.9159	27	.2724	.2724	200
------	1.8860	1.8871	14	.2808	.2810	109
------	------	------	------	------	.2829	202
------	------	------	------	------	.3044	118
------	------	1.7836	6	.3143	.3145	204
------	------	1.7363	3	.3317	------	------
------	------	1.7080	3	.3428	.3432	211
------	------	1.6581	4	.3637	.3642	213
------	------	------	------	------	.3671	206
------	------	1.6258	b 37	.3783	.3785	0-0-12
------	------	------	------	------	.3862	1-0-11
1.57	{ 1.5826	1.5831	38	.3990	3991	1-1-10
	1.5679	1.5690	27	.4062	.4062	215
------	------	------	------	------	0.4406	208
------	------	1.4598	4	0.4693	.4693	217
------	------	------	------	------	.5123	1-0-13
------	------	------	------	------	.5147	1-1-12
------	1.3912	1.3933	b 32	.5151	.5152	0-0-14
1.358	1.3662	1.3667	14	.5354	.5353	2-0-10
------	1.3539	1.3539	10	.5455	.5448	220
------	1.3423	1.3444	5	.5533	.5534	219
------	------	------	------	------	.5554	222
------	------	------	------	------	.5869	224
------	------	------	------	------	.6156	301
------	------	------	------	------	.6366	303
------	------	------	------	------	.6395	226
------	------	1.2394	5	------	.6509	2-0-12
------	------	------	------	------	.6514	1-1-14
------	1.2303	1.2318	5	.6591	{ .6586	2-1-11
					.6595	1-0-15
------	------	1.2191	b 15	.6729	.6729	0-0-16
------	------	------	------	------	.6787	305
1.210	1.2119	1.2109	4	.6819	.6811	310
------	------	------	------	------	.6916	312
------	------	------	------	------	.7131	228
------	------	------	------	------	.7231	314
------	------	------	------	------	.7417	307
------	------	------	------	------	.7757	316
------	------	------	------	------	.7847	2-1-13

See footnotes at end of table.

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[1] Figures in brackets indicate literature references at the end of this paper.
[2] This pattern is represented in the ASTM index of X-ray diffraction powder patterns by card No. 6-0698. As this pattern is a mixture of two compounds it should be eliminated and replaced by the two patterns listed in this paper.

Fisk	DeVries, Roy, Osborn	Present work				hkl
d	d	d_{obs}	I/I_0	$1/d^2_{obs}$	$1/d^2_{cal}$[a]	
------	-------	1.1234	2	.7924	.7876	2·0·14
------	-------	1.1124	4	.8081	.8077	2·2·10
------	-------	------	------	------	.8091	1·1·16
------	-------	------	------	------	.8259	309
------	-------	1.0995	4	.8272	.8277	1·0·17
------	-------	------	------	------	.8493	318
------	-------	------	------	------	.8516	0·0·18
------	-------	------	------	------	.8880	321
------	-------	1.0559	9	.8969	------	------
------	-------	------	------	------	.9090	323
------	-------	------	------	------	.9233	2·2·12
------	-------	------	------	------	.9310	3·0·11
------	-------	------	------	------	.9319	2·1·15
------	-------	1.0292	6	.9441	.9439	3·1·10
------	-------	------	------	------	.9453	2·0·16
1.021	-------	1.0251	4	.9516	.9511	325
------	-------	------	------	------	.9878	1·1·18
------	-------	------	------	------	1.0142	327
------	-------	0.99168	10	1.0168	1.0170	1·0·19
------	-------	.97534	[b] 71	1.0512	1.0514	0·0·20
------	-------	------	------	------	1.0572	3·0·13
------	-------	------	------	------	1.0596	3·1·12
------	-------	------	------	------	1.0600	2·2·14
------	-------	.95764	2	1.0904	1.0897	400
------	-------	------	------	------	1.0983	329
------	-------	.95359	3	1.0997	1.1002	2·1·17
------	-------	------	------	------	1.1002	402
------	-------	------	------	------	1.1241	2·0·18
------	-------	------	------	------	1.1317	404
------	-------	------	------	------	1.1604	411
------	-------	------	------	------	1.1814	413
------	-------	------	------	------	1.1843	406
------	-------	0.91768	7	1.1875	1.1876	1·1·20
------	-------	------	------	------	1.1962	3·1·14
------	-------	------	------	------	1.2034	3·2·11
------	-------	.91125	5	1.2043	1.2044	·0·15
------	-------	------	------	------	1.2177	2·2·16
------	-------	------	------	------	1.2235	415
------	-------	.90346	6	1.2251	1.2259	330
------	-------	.90236	11	1.2281	1.2273	1·0·21
------	-------	------	------	------	1.2364	332
------	-------	------	------	------	1.2579	408
------	-------	------	------	------	1.2680	334
------	-------	.88673	[b] 43	1.2718	1.2722	0·0·22
------	-------	------	------	------	1.2866	417
------	-------	.88058	8	1.2896	1.2894	2·1·19
------	-------	------	------	------	1.3205	336
------	-------	.86915	4	1.3238	1.3238	2·0·20
------	-------	------	------	------	1.3296	3·2·13
------	-------	.85982	5	1.3526	1.3525	4·0·10
------	-------	------	------	------	1.3540	3·1·16
------	-------	------	------	------	1.3621	420
------	-------	------	------	------	1.3707	419
------	-------	.85388	4	1.3715	1.3726	3·0·17
------	-------	------	------	------	1.3726	422
------	-------	------	------	------	1.3919	2·1·20
------	-------	------	------	------	1.3941	338
------	-------	------	------	------	1.3965	2·2·18
------	-------	------	------	------	1.4042	424
------	-------	.84268	5	1.4082	1.4084	1·1·22
------	-------	------	------	------	1.4567	426
------	-------	------	------	------	1.4586	1·0·23
------	-------	------	------	------	1.4682	4·0·12
------	-------	------	------	------	1.4758	4·1·11
------	-------	------	------	------	1.4768	3·2·15
------	-------	0.81968	4	1.4884	1.4887	3·3·10
------	-------	.81272	[b] 22	1.5140	1.5140	0·0·24
------	-------	------	------	------	1.5303	428
------	-------	------	------	------	1.5327	3·1·18
------	-------	.80463	5	1.5446	1.5446	2·0·22
------	-------	------	------	------	1.5618	3·0·19
------	-------	------	------	------	1.5962	2·2·20

[a] The $1/d^2$ values have been calculated on the basis of a tetragonal unit cell with a=3.832A, c=19.505A.
[b] These (ool) peaks are probably abnormally strong due to preferred orientation.

TABLE 2. *X-ray diffraction powder pattern for the compound* $Ca_4Ti_3O_{10}$ (CuK$_{\alpha1}$ *radiation*)

d_{obs}	I/I_0	$1/d^2_{obs}$	$1/d^2_{cal}$ [a]	hkl
13.5	6	0.0055	0.0054	002
6.78	7	.0217	.0217	004
4.525	11	.0488	.0489	006
3.795	9	.0694	.0696	101
-----	----	-----	.0805	103
-----	----	-----	.0868	008
3.337	5	.0898	-----	---
-----	----	-----	.1022	105
2.725	100	.1347	.1348	107
2.718	100	.1353	.1357	0·0·10
2.706	46	.1365	.1365	110
-----	----	-----	.1420	112
-----	----	-----	.1582	114
2.422	8	.1705	-----	----
2.367	4	.1785	.1782	109
-----	----	-----	.1854	116
2.283	3	.1919	-----	----
-----	----	-----	.1954	0·0·12
2.212	4	.2044	-----	----
2.116	10	.2234	.2234	118
2.075	3	.2323	.2325	1·0·11
1.939	33	.2660	.2660	0·0·14
1.915	65	.2726	.2722	1·1·10
			.2731	200
-----	----	-----	.2785	202
1.874	3	.2848	-----	----
-----	----	-----	.2948	204
1.832	7	.2979	.2976	1·0·13
1.764	6	.3214	.3219	206
-----	----	-----	0.3319	1·1·12
1.713	4	0.3409	.3427	211
-----	----	-----	.3474	0·0·16
-----	----	-----	.3535	213
1.664	5	.3612	.3599	208
-----	----	-----	.3736	1·0·15
-----	----	-----	.3753	215
1.576	15	.4028	.4025	1·1·14
-----	----	-----	.4078	217
1.565	40	.4085	.4088	2·0·10
-----	----	-----	.4396	0·0·18
-----	----	-----	.4512	219
-----	----	-----	.4604	1·0·17
-----	----	-----	.4685	2·0·12
-----	----	-----	.4839	1·1·16
1.405	4	.5067	.5055	2·1·11
1.362	21	.5388	.5390	2·0·14
-----	----	-----	.5428	0·0·20
1.351	9	.5477	.5461	220
1.326	4	(b)	(b)	
1.323	5	(b)	(b)	
1.256	4	(b)	(b)	
1.224	4	(b)	(b)	
1.213	12	(b)	(b)	
1.109	7	(b)	(b)	
1.087	3	(b)	(b)	
1.052	3	(b)	(b)	
1.044	3	(b)	(b)	
1.028	8	(b)	(b)	
1.026	9	(b)	(b)	
1.023	10	(b)	(b)	

[a] The $1/d^2$ values have been calculated on the basis of a tetragonal unit cell with a=3.827A and c=27.147A.
[b] Due to the very large unit cell, no attempt was made to index the rest of this pattern.

patterns can be almost completely accounted for on the basis of two tetragonal unit cells, there are still some very small peaks which cannot be indexed on this basis. It seems possible that these calcia-titania compounds are not completely isostructural with the corresponding strontia-titania compounds. It is possible that these compounds have lower symmetry, just as $CaTiO_3$ has a lower symmetry than $SrTiO_3$.

DeVries, Roy, and Osborn [2] have published parts of X-ray diffraction patterns of a series of mixtures
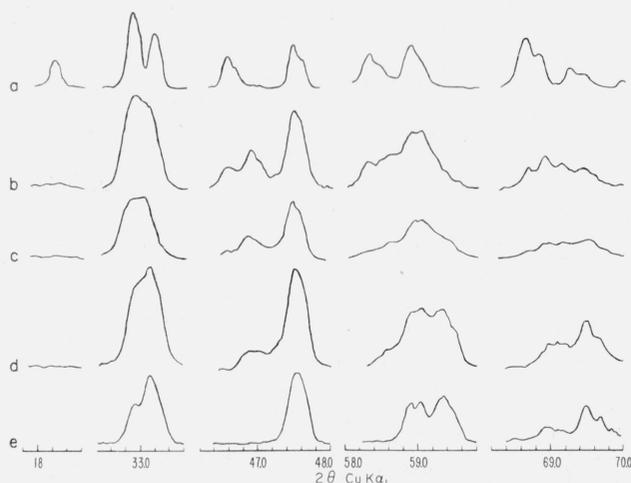
FIGURE 1. *X-ray diffractometer patterns of a series of mixtures from $Ca_3Ti_2O_7$ to $CaTiO_3$ (after melting and quenching).*

Taken from DeVries, Roy, and Osborn [2].

a=51.29/48.71 wt. % CaO/TiO_2 ($Ca_3Ti_2O_7$)
b=48.65/51.35 wt. % CaO/TiO_2
c=46.00/54.00 wt. % CaO/TiO_2
d=48.60/56.40 wt. % CaO/TiO_2
e=41.24/58.76 wt. % CaO/TiO_2 ($CaTiO_3$)
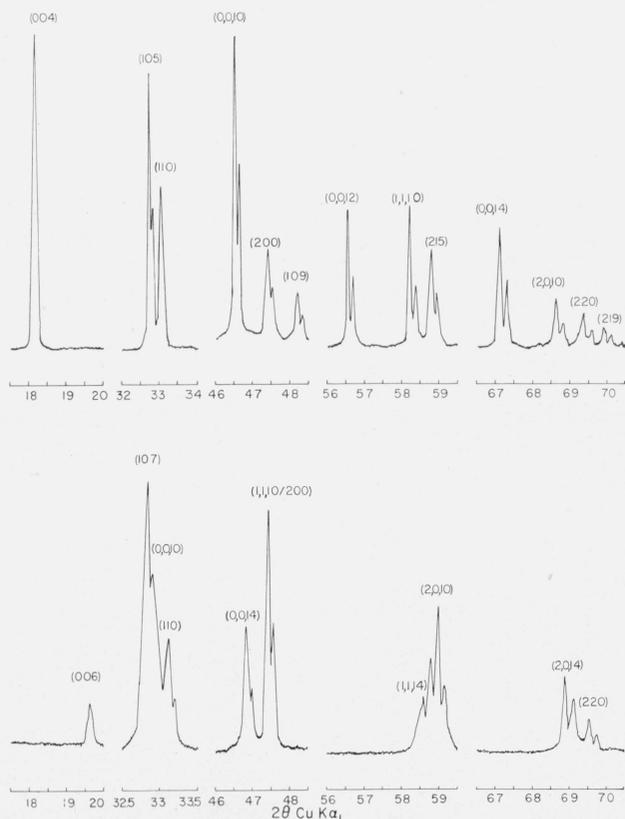
FIGURE 2. *X-ray diffraction patterns, from the present work, of the two compounds $Ca_3Ti_2O_7$ (above) and $Ca_4Ti_3O_{10}$ (below) covering essentially the same part of the diffraction spectra as figure 1.*

from $Ca_3Ti_2O_7$ to $CaTiO_3$ after melting and quenching. Part a (of fig. 3, ref. [2] reproduced here as fig. 1) represents a portion of the pattern of $Ca_3Ti_2O_7$ and part e that of $CaTiO_3$. Figure 2 shows essentially the same portions of the X-ray patterns of the two compounds $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$, as found in the present work. Although all of the patterns in figure 1 are very poorly resolved it can be seen in part b that there are three peaks in the region of 46 to 48°2θ. The composition of this mixture is very close to $4CaO:3TiO_2$ and this pattern represents the compound $Ca_4Ti_3O_{10}$ with a small amount of $Ca_3Ti_2O_7$. Parts c and d are mixtures of $CaTiO_3$ and $Ca_4Ti_3O_{10}$ and both show the center of the three peaks at $47°\,2θ$, while this peak is eliminated in part a, $Ca_3Ti_2O_7$. These published X-ray diagrams support the theory of an intermediate compound ($Ca_4Ti_3O_{10}$) much better than the theory of solid solution proposed by the authors of the published patterns.

3. Experimental Procedures

It might be thought possible that $Ca_4Ti_3O_{10}$ is only a metastable compound having no true equilibrium position in the CaO-TiO_2 phase diagram. If such were the case, an equi-molar mixture of preformed $CaTiO_3$ and $Ca_3Ti_2O_7$ would not form the $Ca_4Ti_3O_{10}$ phase upon heating. Such an equi-molar mixture was prepared, using the same raw materials as in the previous study (Coughanour, Roth, and DeProsse [1]). The specimen was heated in a conventional Pt-wound quench furnace to 1,650° C, held for 2 hr, and quenched in air. The compound $Ca_4Ti_3O_{10}$ was the only product identified in this specimen. It must therefore be concluded that the compound $Ca_4Ti_3O_{10}$ is the equilibrium product of the composition $4CaO:3TiO_2$, at least at 1,650° C.

From the data of Coughanour, Roth, and DeProsse [1] as well as that of DeVries, Roy, and Osborn [2], it can be seen that the compound $Ca_4Ti_3O_{10}$ can not melt congruently. It must either dissociate before melting or else melt incongruently at a temperature somewhat higher than the incongruent melting point of $Ca_3Ti_2O_7$, given in both papers as 1,750° C.

Specimens with a calcia-titania ratio of 4:3 were pressed into pellets, calcined in a conventional Pt-wound furnace at 1,250° C, ground, repressed, and reheated to 1,600° C and slow-cooled. They showed only the compound $Ca_4Ti_3O_{10}$. Specimens were then ground and placed in a Pt envelope, heated in the Pt-wound quench furnace, and quenched into water from temperatures of 1,500° C, 1,550° C, 1,600° C and 1,650° C. All of these quenched specimens still showed only the compound $Ca_4Ti_3O_{10}$. Specimens were then heated and quenched in a graphite susceptor induction furnace, from temperatures of 1,700° C and 1,725° C. These two specimens also showed only the compound $Ca_4Ti_3O_{10}$. One more specimen was placed in a smooth Pt tube, so that the temperature could be read more precisely with an optical pyrometer, heated to 1,745° C and quenched. This specimen still showed only $Ca_4Ti_3O_{10}$. As the reported solidus for $Ca_3Ti_2O_7$ is 1,750°
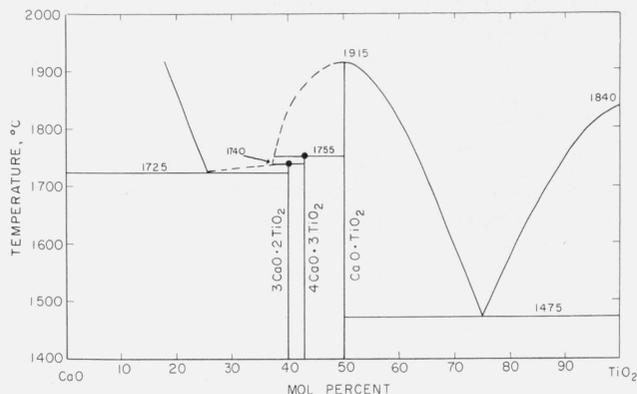
FIGURE 3. *Revised phase equilibrium diagram of the system* CaO-TiO₂, *showing the compound* Ca₃Ti₂O₇ *melting incongruently at 1,740° C and the compound* Ca₄Ti₃O₁₀ *melting incongruently at 1,755° C.*

(After Coughanour, Roth, and DeProsse [1]).

◓ Solidus temperatures determined in the present study.

C, it must be assumed that $Ca_4Ti_3O_{10}$ either does not dissociate to two solids, or that such dissociation cannot be quenched.

In order to check the solidus temperatures of the two compounds $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$, fragments of the two materials, previously heated to 1,650° C for 2 hr, were set side by side on an iridium button in the graphite induction furnace. The $Ca_3Ti_2O_7$ specimen definitely began melting before the $Ca_4Ti_3O_{10}$ specimen. However, the fluid liquid quickly spread over the iridium button, obscuring the results of melting of the second specimen. As it appeared that the iridium button was hotter than the inside of the graphite crucible, a new experiment was performed utilizing only an iridium crucible with an iridium button inside. Using a flat button and a cover on the crucible and sighting through a hole in the cover, perfect black-body conditions were obtained and the specimen could not be seen. By utilizing a concave button and no cover, the specimen could be watched during the whole experiment. The temperature of the solid specimen at beginning of melting appeared 25° to 30° C cooler than the true temperature, but the liquid formed appeared to show the true temperature. The solidus temperature for $Ca_3Ti_2O_7$ was found to be 1,740° C and that of $Ca_4Ti_3O_{10}$ was 1,755° C. These results were rechecked by again heating fragments in the iridium crucible using a flat button and the crucible cover. The $Ca_3Ti_2O_7$ specimen when heated to 1,740° C

showed a rounding of the corners and a small amount of crystal growth on the iridium button. The $Ca_4Ti_3O_{10}$ specimen showed no sign of melting at this temperature but did show some melting when heated to 1,755° C.

These measurements have been used to revise the phase diagram of the binary system CaO–TiO₂ first proposed by Coughanour, Roth, and DeProsse [1].[3] The revised diagram is shown in figure 3.

4. Summary

The compound $Ca_4Ti_3O_{10}$ has been shown to exist as a stable phase in the system CaO–TiO₂. Both compounds are pseudo-tetragonal with only a few weak lines indicating a departure from tetragonality. The c–axis$=19.505$ A for $Ca_3Ti_2O_7$ and 27.147 A for $Ca_4Ti_3O_{10}$. The dimensions indicate that $Ca_3Ti_2O_7$ has double perovskite layers interleaved with CaO, while $Ca_4Ti_3O_{10}$ has triple perovskite layers interleaved with CaO. The new compound, $Ca_4Ti_3O_{10}$, has been found to melt incongruently at about 1,755° C, while the incongruent melting point of $Ca_3Ti_2O_7$ has been shown to be about 1,740° C. The revised phase diagram for the system CaO–TiO₂ is presented.

5. References

[1] L. W. Coughanour, R. S. Roth, and V. A. DeProsse, J. Research NBS **52,** 37 (1954) RP2470.
[2] R. C. DeVries, R. Roy, and E. F. Osborn, J. Phys. Chem. **58,** 1069 (1954).
[3] H. G. Fisk, Jr., J. Am. Ceram. Soc. **34,** 9 (1951).
[4] S. N. Ruddlesden and P. Popper, Acta Cryst. **11,** 54 (1958).
[5] S. N. Ruddlesden and P. Popper, Acta Cryst. **10,** 538 (1957).

[3] The two previously published diagrams of Coughanour et al. [1] and DeVries et al. [2] disagree on the temperatures of the melting point of CaTiO₃ (1,915° C and 1,970° C) and on the temperature of the eutectic between CaO and Ca₃Ti₂O₇ (1,725° C and 1,695° C). No attempt has been made in the present study to reconcile these two discrepancies.

WASHINGTON, August 4, 1958.