Identification of Binary Compounds in the System Ce_2O_3–WO_3

M. YOSHIMURA,* F. SIBIEUDE, A. ROUANET, AND M. FOEX

*Laboratoire des Ultra-Refractaires du C.N.R.S., Odeillo,
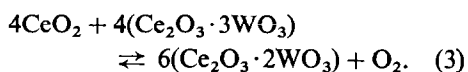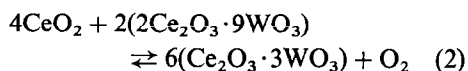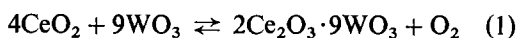66120 Font-Romeu, France*

The systems CeO_2–Ce_2O_3–WO_3 and Ce_2O_3–WO_3–W are studied at high temperature. Six compounds were found as stable phases in the system Ce_2O_3–WO_3. The compound $3Ce_2O_3 \cdot WO_3$ has a fluoritelike cubic structure of $a_0 = 11.040$ Å and forms solid solutions with constituent oxides or CeO_2. The compound $3Ce_2O_3 \cdot 2WO_3$, which seems to be isostructural with $3La_2O_3 \cdot 2WO_3$, is stable only in the temperature range, $1545 \sim 1730°C$. The compound $Ce_2O_3 \cdot WO_3$, which has a monoclinic structure, transforms reversibly at $1360°C$ to a tetragonal structure with the cell parameters $a_0 = 5.469$ Å, $c_0 = 8.790$ Å. The compound $Ce_2O_3 \cdot 2WO_3$ identified to be monoclinic, also has a reversible transformation at $1105°C$. Its high-temperature phase has a cubic cell with the cell parameter $a = 7.046$ Å. As is well known, $Ce_2O_3 \cdot 3WO_3$ appeared to have similar high-temperature behavior to $La_2O_3 \cdot 3WO_3$. The compound $2Ce_2O_3 \cdot 9WO_3$, whose structure could not be analyzed, melts congruently at $1026°C$.

Introduction

Several previous researches on compound formations in R_2O_3–WO_3 systems have been done. Ivanova et al. (*1*) reported compounds of the molar ratio, $La_2O_3/WO_3 = 3/1$, $3/2$, $1/1$, $1/2$, and $1/3$ in the system La_2O_3–WO_3. Rode and Karpov (*2*) found the following compounds in the system Nd_2O_3–WO_3, $Nd_2O_3/WO_3 = 3/1$, $2/1$, $4/3$, $1/1$, $1/2$, and $1/3$. Chang et al. (*3*) reported $3/1$, $7/4$, $1/1$, $1/2$, and $1/3$ compounds as the stable phases in the system Sm_2O_3–WO_3. Recently, McCarthy et al. (*4*) prepared and identified many compounds: $R_2O_3/WO_3 = 3/1$ (La $\sim$ Lu, Y), $5/2$ (Gd $\sim$ Ho, Y), $7/4$ (Nd $\sim$ Lu, Y), $1/1$ (Nd $\sim$ Lu, Y), $1/2$ (Pr $\sim$ Gd except Tb), and $1/3$ (La $\sim$ Lu, Y).

The system based upon Ce_2O_3 is difficult because of the instability of Ce_2O_3. Since free Ce_2O_3 reoxidizes to CeO_x or CeO_2 during heating or cooling processes even in very lightly oxidizing atmospheres (*5*), one must

study at least on the ternary system CeO_2–Ce_2O_3–WO_3. Borchardt (*6*) stated that $Ce_2O_3 \cdot 3WO_3$ was only one compound which was produced by the reaction between CeO_2 and WO_3 in air. However, we studied this system up to $1400°C$ (*7*) and found that a new compound $2Ce_2O_3 \cdot 9WO_3$ was also prepared in addition to $Ce_2O_3 \cdot 3WO_3$ from CeO_2 and WO_3 in air without particular difficulties, and that $Ce_2O_3 \cdot 2WO_3$ was also prepared in an argon atmosphere ($pO_2 \sim 10^{-5}$ atm). These three compounds are stable phases in the system Ce_2O_3–WO_3 and their preparations are shown by following equilibrium equations:

$$4CeO_2 + 9WO_3 \rightleftarrows 2Ce_2O_3 \cdot 9WO_3 + O_2 \quad (1)$$

$$4CeO_2 + 2(2Ce_2O_3 \cdot 9WO_3) \\ \rightleftarrows 6(Ce_2O_3 \cdot 3WO_3) + O_2 \quad (2)$$

$$4CeO_2 + 4(Ce_2O_3 \cdot 3WO_3) \\ \rightleftarrows 6(Ce_2O_3 \cdot 2WO_3) + O_2. \quad (3)$$

Therefore, the phase relation varies with temperatures and partial oxygen pressures. For example, at $850°C$, $2Ce_2O_3 \cdot 9WO_3$ is only one stable phase under 1 atm of oxygen,

$2Ce_2O_3 \cdot 9WO_3$ and $Ce_2O_3 \cdot 3WO_3$ are stable in air ($pO_2 = 0.21$ atm) and then $2Ce_2O_3 \cdot 9WO_3$, $Ce_2O_3 \cdot 3WO_3$, and $Ce_2O_3 \cdot 2WO_3$ are stable in argon ($pO_2 = 10^{-5}$ atm). Only these three compounds were stable in the conditions of temperatures up to 1400°C and of oxygen pressures above 10^{-5} atm. Brixner et al. (8) prepared $Ce_2O_3 \cdot WO_3$ in a platinum capsule, and Klevtsov et al. (9) obtained $Ce_2O_3 \cdot 2WO_3$ by a hydrothermal method. In any case, it is necessary to use higher temperatures than 1400°C and/or lower oxygen pressures than 10^{-5} atm for studying phase equilibria in the system Ce_2O_3–WO_3.

In this study, we used a cofusion method (10) of oxide mixtures using a solar furnace of 2 kW with a vertical axis for preparing reaction products. According to this method, oxide mixtures were heated and fused only in a few seconds and formed small balls of molten oxides on a water-cooled metal support. Then, they were cooled rapidly by removing the focus of the solar furnace. The advantages of this method are: (1) Reaction rates are very rapid because of liquid state reactions at high temperatures; (2) contaminations from containers are negligible; (3) homogeneous products can be obtained easily; (4) atmospheres during preparations can be controlled; (5) heating and cooling rates are very rapid. Advantages 4 and 5 are preferable for the system based on cerium oxides, which are very unstable. For the purpose of studies at high temperatures *in situ* of every phase, high-temperature X-ray methods were employed. Furthermore, we always compared the products based on cerium with those based on La_2O_3 and Nd_2O_3 by the same methods in order to ascertain whether or not Ce^{3+} was present in our products.

We could find and identify the following compounds as stable phases in the system Ce_2O_3–WO_3: $Ce_2O_3/WO_3 = 3/1$, $3/2$, $1/1$, $1/2$, $1/3$, and $2/9$. In this report, their identifications and high-temperature behaviors are described. The subsolidus phase relation is also discussed for the ternary system CeO_2–Ce_2O_3–WO_3. The compound $3Ce_2O_3 \cdot 2WO_3$ and the high-temperature phase of $Ce_2O_3 \cdot 2WO_3$ are reported for the first time.

Experimental

Starting materials were high-purity CeO_2 (99.9%, Ugine–Kuhlmann), WO_3(99.9%, Ugine–Carbone Ltd.), and W (99.9% Koch–Light Laboratory Ltd.). Oxides with bulk compositions of 0, 10, 15, 17.5, 18.18, 19, 20, 25, 30, 33.33, 40, 45, 50, 55, 60, 65, 66.67, 70, 75, 80, 85, 90, 95, and 100 mol% Ce_2O_4 ($= 2CeO_2$) were weighed and mixed thoroughly in a mortar. To reduce CeO_2 to Ce_2O_3, the bulk mixtures where WO_3 was replaced by metallic W partially or completely were also prepared in cerium-rich samples.
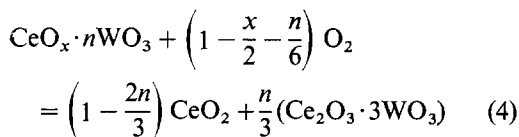
Mixtures were fused by a cofusion method (10) with a solar furnace on a water-cooled metal support under atmospheres of flowing air, 550 mm Hg argon with 7 ppm oxygen, and 300 mm Hg hydrogen, for $10 \sim 20$ sec. In the cases of cofusions under controlled atmospheres, samples were covered by a Pyrex balloon. Fused samples of small balls with $7 \sim 8$ mm diameters were quenched by removing them from the focus of the solar furnace. The balls were turned off and remelted by the same procedure. Reactions between oxides, or oxide and W-metal, were accomplished by this procedure. The difference in cofusion times, 10 sec (twice), 30 sec (twice), and 10 sec (six times), gave no effect for the products. A "splat cooling method" by a mechanical hammer on molten balls (11) was also employed. Cooling rates were supposed to be $\sim 10^2$°K/sec for the normal quenching and $\sim 10^5$°K/sec for the splat cooling.

Phases were identified by X-ray powder diffraction methods with a Philips diffractometer using Ni-filtered Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å). The diffraction patterns were calibrated with NaCl ($a_0 = 5.6402$ Å at 26°C) or W ($a_0 = 3.16516$ Å at 25°C) as an internal standard. To observe high-temperature behaviors *in situ*, high-temperature X-ray methods were also performed with platinum or rhenium strip heaters in air or helium atmospheres. The apparatus and experimental procedures have been described in detail elsewhere (12).

Ordinary solid-state reaction methods for compacted bulk mixtures and annealing methods at temperatures up to 1400°C were

also employed for several samples. These procedures have been reported previously (7).

The oxygen contents of the products were checked by the weight gain with reoxidation on reheating at 1000°C in air. This reoxidation is described by the following equation since CeO_2 and $Ce_2O_3 \cdot 3WO_3$ coexist at the equilibrium state at 1000°C in air ($pO_2 = 0.21$ atm), as described later in this report,

$$CeO_x \cdot nWO_3 + \left(1 - \frac{x}{2} - \frac{n}{6}\right) O_2$$

$$= \left(1 - \frac{2n}{3}\right) CeO_2 + \frac{n}{3}(Ce_2O_3 \cdot 3WO_3) \quad (4)$$

were, $1.5 < x < 2$ and $0 < n < 1.5$.

Results and Discussions

1. Deviations of Compositions

As described above, the samples were prepared at very high temperatures, in general above 2000°C. The deviations of bulk compositions should be considered to be caused by vaporizations of constituent oxides, particularly WO_3. Preliminary studies, however, demonstrated that repeating cofusion treatments, at least up to four times, gave no detectable effects in X-ray studies even in the cases of $Ce_2O_3 \cdot 3WO_3$ and $2Ce_2O_3 \cdot 9WO_3$, which have low melting temperatures (below 1100°C). In addition, the cofusion products of $3La_2O_3 \cdot WO_3$ with different fusion times, for 20 sec, 1 min, 3 min, and even 10 min had the same cell parameters, though vaporizations could obviously be observed. It will show that apparent vaporization rates are almost the same by chance for CeO_2 or La_2O_3 and WO_3 from these compounds These results indicate that the cation ratios in the samples were scarcely varied by the experimental procedure used. It should be noted that heating times were very short, only 30 sec at maximum, and that the vaporization rates were very different between free oxides and their compounds. The vaporization rate of WO_3 was 10^6 times lower from $3R_2O_3 \cdot WO_3$ than from free WO_3 (13).

On the other hand, the bulk contents of oxygen in the products that have bulk compositions of more than 33.33 mol% Ce_2O_4

were increased by repeated cofusion treatments in argon atmospheres. That is, the products that contain $Ce_2O_3 \cdot WO_3$, $3Ce_2O_3 \cdot 2WO_3$, $3Ce_2O_3 \cdot WO_3$ and Ce_2O_3 have a tendency to reoxidize in proportion to the amount of impurity oxygen in the atmospheres. Thus, the products were more reoxidized in the flowing argon atmosphere than in 550 mm Hg of the same argon atmosphere, so it was necessary to quench in order to prevent any reoxidation during the cooling process.

The valence states were considered fundamentally to be Ce^{3+} and W^{6+} in every compound identified in this work. The trivalent cerium ion had been confirmed in $2Ce_2O_3 \cdot 9WO_3$, $Ce_2O_3 \cdot 3WO_3$, and $Ce_2O_3 \cdot 2WO_3$ by magnetic measurements (7). The colors of all cerium tungstates were yellow or brown, which is characteristic of the Ce^{3+} ion. All lanthanum tungstates were white, and all neodymium tungstates were purple in the products prepared by the same experimental procedures as cerium tungstates. These results indicate the valence states of R^{3+} and W^{6+}. No rare-earth tungstates based upon W^{5+} or W^{4+}, except "bronze," have been found yet. This does not, however, rule out the possibility of the little nonstoichiometry caused by other valences, especially in the cases of $Ce_2O_3 \cdot WO_3$ and $3Ce_2O_3 \cdot WO_3$, which would form solid solutions.

2. Identification and High-Temperature Properties

We could identify six cerium tungstates; $3Ce_2O_3 \cdot WO_3$, $3Ce_2O_3 \cdot 2WO_3$, $Ce_2O_3 \cdot WO_3$, $Ce_2O_3 \cdot 2WO_3$, $Ce_2O_3 \cdot 3WO_3$, and $2Ce_2O_3 \cdot 9WO_3$, in the pseudobinary system Ce_2O_3–WO_3. This system resembles the system based upon La_2O_3 rather than Nd_2O_3, where $2Nd_2O_3 \cdot WO_3$ or $4Nd_2O_3 \cdot 3WO_3$ and $7Nd_2O_3 \cdot 4WO_3$ were reported instead of $3Nd_2O_3 \cdot 2WO_3$ (2, 4).

The results obtained in this work are summarized in Table I. Identification and high-temperature properties of every phase are as follows.

2a. $3Ce_2O_3 \cdot WO_3$ (Ce_6WO_{12}). It is well known that $3R_2O_3 \cdot WO_3$ has a fluorite-related structure; however, the true crystal structure

TABLE I

PHASES IDENTIFIED IN THE SYSTEM Ce_2O_3–WO_3

	$3Ce_2O_3 \cdot WO_3$	$3Ce_2O_3 \cdot 2WO_3$	α-$Ce_2O_3 \cdot WO_3$	β-$Ce_2O_3 \cdot WO_3$	α-$Ce_2O_3 \cdot 2WO_3$	β-$Ce_2O_3 \cdot 2WO_3$	$Ce_2O_3 \cdot 3WO_3$	$2Ce_2O_3 \cdot 9WO_3$
Composition	$Ce_6WO_{11.923}$[a]	Not determined	$Ce_2WO_{5.93}$[a]		$Ce_2W_{1.99}O_{8.97}$[b]		$Ce_2W_{2.96}O_{11.88}$[b]	$Ce_4W_{8.88}O_{32.65}$[b]
Crystal structure	Cubic	Unknown	Monoclinic	Tetragonal	Monoclinic	Cubic	Monoclinic	Unknown
Cell parameter (Å) at RT	$a = 11.040$	Unknown	$a = 5.570^c$ $b = 11.524$ $c = 15.947$ $\beta = 91.83°$	$a = 5.469$ $c = 8.790$	$a = 7.690$ $b = 9.925$ $c = 9.261$ $\beta = 107.5°$	$a = 7.046$	$a = 7.828^d$ $b = 11.738$ $c = 11.604$ $\beta = 109.5°$	Unknown
Color	Brown	Brown	Brown	Brown	Orange yellow	Orange yellow	Yellow	Brown yellow
Transition temperature (°C)	No transition	No transition[e]	1360		1105 ± 10^f		1005 ± 10^f	No transition
Melting temperature (°C)	~2030 congruent	~1730 incongruent		1545 incongruent		1395 ± 10 congruent[f]	1070 ± 10 incongruent[f]	1026 ± 10 congruent[f]

[a] From weight gain.

[b] From chemical analysis; see Ref. (7).

[c] After Brixner et al., see Ref. (8).

[d] After Brixner et al., see Ref. (26).

[e] This phase decomposes into $Ce_2O_3 \cdot WO_3$ and $3Ce_2O_3 \cdot WO_3$ below 1545°C.

[f] Determined by DTA, see Ref. (7).

has not been determined yet, particularly for the compounds based on La $\sim$ Sm. Chang and Phillips (14) reported that La_6WO_{12} and Sm_6WO_{12} had a fcc cell of disordered pyrochlore-type or ordered defect fluorite-type with cell parameters of 11.18 and 10.80 Å, respectively. Trunov et al. (15) indexed the powder data for Nd_6WO_{12} and Sm_6WO_{12} based upon pseudo-tetragonal cells with $a_0 = 5.470$ Å, $c_0 = 5.442$ Å and $a_0 = 5.412$ Å, $c_0 = 5.405$ Å. Foex (16) stated that La_6WO_{12}, Pr_6WO_{12}, Nd_6WO_{12}, and Sm_6WO_{12} had pseudo-cubic cells with $a_0 = 11.18$, 11.00, 10.94, and 10.84 Å, respectively. McCarthy et al. (4) studied all R_6WO_{12} and reported that La_6WO_{12} had a fcc cell with $a_0 = 11.182$ Å, Pr_6WO_{12} had a fluorite cell with $a_0 = 5.486$ Å, and Nd_6WO_{12} had a pseudo-tetragonal cell with $a_0 = 5.467$ Å and $c_0 = 5.446$ Å. They also prepared "Ce_6WO_{12}" by a solid-state reaction between CeO_2 and WO_3 at 1400°C in a purified argon atmosphere, and stated that it had a pseudo-cubic cell with $a_0 = 5.518$ Å. However, they could not index three weak extra lines observed. It is probable that their "Ce_6WO_{12}" was a solid solution with CeO_2 from the results obtained in present work. These inconsistencies seen in R_6WO_{12} appear to be caused by the different thermal histories in their preparations. There are two possibilities of "ordering" in the compounds R_6WO_{12} by cation sublattice and anion sublattice. Since the cation diffusion is very slow and the anion diffusion is very rapid in fluorite-related lattices, as is well known, a change in heat treatment will bring about a great influence on the type of "ordering" in each sublattice. We observed that Nd_6WO_{12} would change the structure by different heat treatments. That is, the cofusion gave a cubic fluorite phase with $a_0 = 5.467$ Å, but broadenings in diffraction lines were observed by annealing at 1400°C for 10 days. A so-called pseudo-tetragonal phase was obtained by a solid-state reaction at the same condition. These results indicate that the experimental conditions used in previous studies, 1400°C for 10 days at maximum, would be insufficient to establish an "equilibrium state." Further studies on R_6WO_{12} are in progress.

In the case of cerium, there is a more complicated problem: Ce_6WO_{12} would make solid solutions with CeO_2 and/or CeO_x. In fact, the solid solution phase based upon Ce_6WO_{12} was found in the cofusion products with wide bulk compositions, 40 $\sim$ 95 mol% Ce_2O_4 in the present work. The cell parameters varied between 11.09 and 10.86 Å. The cofusion of the bulk mixture of Ce_2O_4, 75 mol%, and WO_3, 25 mol%, always gave products consisting of three phases; i.e., $3Ce_2O_3 \cdot WO_3$ (S.S.) with $a = 10.890$ Å, $Ce_2O_3 \cdot WO_3$ and CeO_2 (S.S.) with $a = 5.414$ Å in air, $3Ce_2O_3 \cdot WO_3$ (S.S.) with $a = 11.031$ Å, $3Ce_2O_3 \cdot 2WO_3$ and $Ce_2O_3 \cdot WO_3$ in argon, $3Ce_2O_3 \cdot WO_3$ (S.S.) with $a = 11.074$ Å, Ce_2O_3 and W in hydrogen. The cofusion in argon of the mixture of Ce_2O_4, 75 mol%, and W, 25 mol%, whose bulk composition is equivalent to $3Ce_2O_3 \cdot WO_3$, gave a $3Ce_2O_3 \cdot WO_3$ solid solution phase with $a = 11.039$ Å slightly contaminated by $3Ce_2O_3 \cdot 2WO_3$. The weight gain on reheating this product indicated that the reduction of CeO_2 was not completed by the presence of impurity oxygens in the argon atmosphere. Excess CeO_2 would form a solid solution with $3Ce_2O_3 \cdot WO_3$.

The single phase of $3Ce_2O_3 \cdot WO_3$ could be obtained by three repeats of the cofusion in argon of the initial mixture of $6CeO_{2-x} + W$. The bulk composition of this single phase was determined to be $Ce_6WO_{11.923}$ from the weight gain on reoxidation according to Eq. (4).

The X-ray powder data are shown in Table II. Those for $3La_2O_3 \cdot WO_3$, which was prepared by the same procedure as $3Ce_2O_3 \cdot WO_3$, are also shown for comparison. They have similar weak superstructure lines which could be well indexed based upon a cubic cell with the double parameter of the fluorite cell, but not the same. In the case of $3La_2O_3 \cdot WO_3$, all superstructure lines are able to be classified into C-type bcc and into fcc; that is, (211), (411/330), (332), (510/431), (611/532), (541), and (631) belong to the former, and (111), (200), (311), (422), and (511/333) belong to the latter.

The recent detail work (17) demonstrated that $3La_2O_3 \cdot WO_3$ has a C-type bcc symmetry, and that it is stable only at high temperatures (above 1740°C). Below this temperature, it changed to the $5La_2O_3 \cdot 2WO_3$ phase, which

TABLE II

X-Ray Powder Diffraction Data for $3Ce_2O_3 \cdot WO_3$ and $3La_2O_3 \cdot WO_3$

h k l	$3Ce_2O_3 \cdot WO_3$[a]			$3La_2O_3 \cdot WO_3$[b]		
	I/I_0	d_{obsd}	d_{calc}	I/I_0	d_{obsd}	d_{calc}
1 1 1	1	6.362	6.374	2	6.454	6.454
2 0 0			5.520	1	5.595	5.590
2 1 1	2	4.506	4.507	2	4.566	4.564
3 1 1	1	3.249	3.329	2	3.367	3.371
2 2 2	100	3.187	3.187	100	3.229	3.227
4 0 0	40	2.761	2.760	32	2.796	2.795
4 1 1/3 3 0			2.602	1	2.635	2.635
3 3 1			2.533	1	2.551	2.565
4 2 1	2	2.409	2.409			2.440
3 3 2			2.354	1	2.381	2.383
4 2 2	2	2.252	2.253	2	2.281	2.282
5 1 0/4 3 1	2	2.166	2.165	3	2.192	2.192
5 1 1/3 3 3	1	2.124	2.125	2	2.152	2.151
5 2 0/4 3 2	2	2.050	2.050			2.076
4 4 0	50	1.9517	1.9516	50	1.9762	1.9762
6 1 1/5 3 2	2	1.7903	1.7909	1	1.8139	1.8135
5 4 1	1	1.7030	1.7035	1	1.7241	1.7250
6 2 2	35	1.6642	1.6643	36	1.6853	1.6853
6 3 1	2	1.6274	1.6278	2	1.6510	1.6483
4 4 4	12	1.5931	1.5935	12	1.6138	1.6136

[a] $a = 11.040$.
[b] $a = 11.179$.

has a pyrochlorelike fcc symmetry. According to an ordering in the cation sublattice, this compound would be written as,

$$La_2(La_{2/3}W_{1/3})_2O_7. \qquad (5)$$
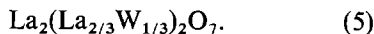
Thus, the fcc superstructure lines observed in $3La_2O_3 \cdot WO_3$ prepared by cofusion methods seems to be brought about by a cation ordering during a cooling process.

It is probable that $3Ce_2O_3 \cdot WO_3$ is also a high-temperature phase that has the same symmetry as $3La_2O_3 \cdot WO_3$. One can see similar C-type superstructure lines in $3Ce_2O_3 \cdot WO_3$. In the case of $3Ce_2O_3 \cdot WO_3$, it is noteworthy that the superstructure lines classified into neither bcc nor fcc, as (421) and (520/432) have been observed. It may indicate more complicated ordering in the cerium system than in the lanthanum system at lower temperatures. It is quite reasonable

that Ce^{3+} (or La^{3+}) and W^{6+} would order at low temperatures because the differences in their valences and sizes are greater than those between Ce^{3+} and Zr^{4+}, which give an ordered pyrochlore $Ce_2Zr_2O_7$ (18). However, the rare-earth tungstates that do not have the cation ratio 2/2 as a typical pyrochlore could not take the ideal pyrochlore symmetry. If a cation ordering like that in Eq. (5) were assumed, it would not be surprising that $Ce^{3+}-W^{6+}$ and $La^{3+}-W^{6+}$ showed different ordering symmetries. Similar complicated orderings were supposed for an intermediate compound, $La_2(LaCe_{1/2}W_{1/2})O_7$ (19), where (421), (520/432), and (630/542) belonging to a primitive cubic symmetry also were observed.

Unfortunately, we could not anneal $3Ce_2O_3 \cdot WO_3$ without any reoxidations. Thus, we cannot discuss the fluorite-related cerium tungstates further. Here, we wish to note that $3Ce_2O_3 \cdot WO_3$ would show C-type bcc superstructure lines and that it would have the possibilities of some orderings at lower temperatures. The structure analysis for single crystals or neutron diffraction studies are expected.

2b. $3Ce_2O_3 \cdot 2WO_3$ ($Ce_6W_2O_{15}$). This compound was found for the first time in the present work. It always coexisted with the $3Ce_2O_3 \cdot WO_3$ phase or the $3Ce_2O_3 \cdot WO_3$ and Ce_2O_3 phases in the products after cofusion. Attempts to prepare the single phase by cofusion methods on appropriate mixtures of $CeO_2 + WO_2 + W$ were unsuccessful.

The X-ray powder data shown in Table III are almost identical to the data for $3La_2O_3 \cdot 2WO_3$ identified by Ivanova et al. (1). Our data for $3La_2O_3 \cdot 2WO_3$ were obtained by the cofusion of the mixture $3La_2O_3 + 2WO_3$ in air, showed more diffractions, and were in good agreement with those for $3Ce_2O_3 \cdot 2WO_3$. However, we are unable to index these powder data by a normal trial-and-error method.

By the high-temperature X-ray methods, the $3CeO_3 \cdot 2WO_3$ phase in the cofusion products disappeared by reheating and decomposed to $3Ce_2O_3 \cdot WO_3$ phase and $Ce_2O_3 \cdot WO_3$ phase, which has a phase transition at 1360°C, as described in the next section. That is, reheating of cofusion products of Ce_2O_3 60

TABLE III

X-RAY POWDER DIFFRACTION DATA FOR $3Ce_2O_3 \cdot 2WO_3$ AND $3La_2O_3 \cdot 2WO_3$

$3Ce_2O_3 \cdot 2WO_3$		$3La_2O_3 \cdot 2WO_3$		$3La_2O_3 \cdot 2WO_3{}^a$	
d_{obsd}	I/I_0	d_{obsd}	I/I_0	d_{obsd}	I
		4.462	4		
3.779	13	3.806	23		
3.742	5	3.770	6	3.77	$1 \sim 2$
3.607	8	3.639	24		
3.191^b	60	3.208	51	3.20	5
3.136	10	3.157	19		
3.081	100	3.108	100	3.09	8
2.962	22	2.980	41	2.96	$4 \sim 5$
2.860	6	2.888	13		
		2.797	4	2.78	1
2.669	6	2.696	4	2.69	1
2.576	10	2.600	20	2.59	3
		2.577	4		
		2.471	2		
2.413	5	2.430	13	2.43	$2 \sim 3$
2.332	3	2.348	5	2.33	0.5
		2.305	2		
		2.277	3		
		2.249	3		
2.202	31	2.227	27	2.20	5
2.153	8	2.166	10	2.16	4
		2.121	2		
		2.101	4		
2.057	5	2.075	13	2.07	4
		2.026	2		
1.972	3	1.982	6	1.973	4
1.907	13	1.924	25	1.918	5
1.869	7	1.883	12	1.878	4
		1.838	2		
1.803	7	1.819	16	1.810	3
1.767	8	1.785	13	1.779	4
1.749	3	1.762	8	1.758	4
1.730	8	1.743	12	1.740	5
1.681	3	1.694	14	1.692	4
1.624	5	1.640	6	1.637	$2 \sim 3$
1.602	7	1.616	9	1.611	$3 \sim 4$
		1.603	2		
1.565	8	1.582	34	1.577	5
		1.553	3		

^{a} After Ivanova et al., see Ref. (*1*).

^{b} Overrapped by diffraction peak of (111) of $3Ce_2O_3 \cdot WO_3$ s.s.

mol% ($\equiv 3Ce_2O_3 \cdot 2WO_3$) at 1200 or 1300°C immediately showed that the two phases consisted of $3Ce_2O_3 \cdot WO_3$ and α-$Ce_2O_3 \cdot WO_3$,

which changed to β-$Ce_2O_3 \cdot WO_3$ at temperatures above 1360°C, as seen in Fig. 1. Similar behaviors could be observed for the sample of Ce_2O_3, 65 mol% (Fig. 2). A fusion has been observed at 1545°C, and then the diffraction peaks of $Ce_2O_3 \cdot WO_3$ disappeared. $3Ce_2O_3 \cdot 2WO_3$ appears to be prepared above this temperature by the reaction between $3Ce_2O_3 \cdot WO_3$ and liquid phase because the preparation of $3Ce_2O_3 \cdot 2WO_2$ was always accompanied by a fusion at 1545°C. This reaction was so slow that $3Ce_2O_3 \cdot 2WO_3$ could not be prepared at 1550°C for 10 min. Figure 2 demonstrates that a long heating above 1545°C was necessary to produce $3Ce_2O_3 \cdot 2WO_3$.

In contrast with the decomposition of $3Ce_2O_3 \cdot 2WO_3$, which was very rapid on reheating, the decomposition on cooling was slow. That is, $3Ce_2O_3 \cdot 2WO_3$, which was once prepared at temperatures higher than 1545°C, stayed in a metastable phase at lower temperatures (up to room temperature). Figure 2 shows that the decomposition of $3Ce_2O_3 \cdot 2WO_3$ on cooling began after 40 min at 1410°C. It also indicates that the equilibrium

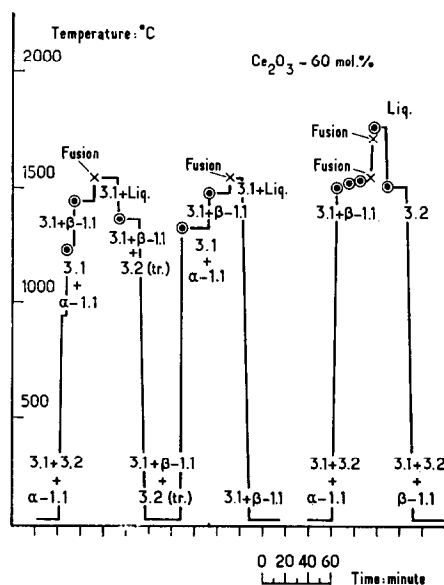FIG. 1. Schematic illustration of the results of high-temperature X-ray for the sample of Ce_2O_3, 60 mol% (= $3Ce_2O_3 \cdot 2WO_3$). 3:1 = $3Ce_2O_3 \cdot WO_3$; 3:2 = $3Ce_2O_3 \cdot 2WO_3$; 1:1 = $Ce_2O_3 \cdot WO_3$; liq. = liquid phase; tr. = trace.
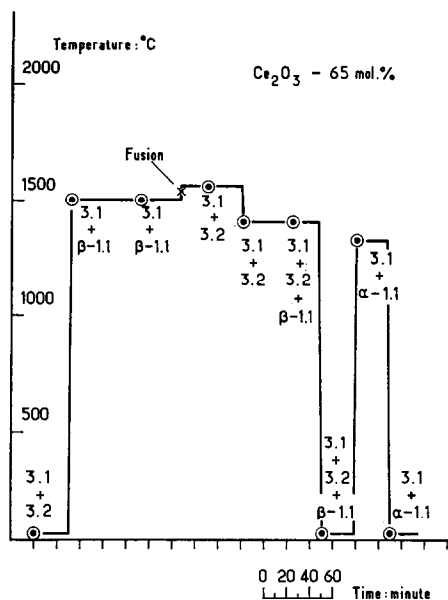
FIG. 2. Schematic illustration of the results of high-temperature X-ray for the sample of Ce_2O_3, 65 mol%.

phases at 1565°C would be $3Ce_2O_3 \cdot WO_3$ + $3Ce_2O_3 \cdot 2WO_3$ for the composition of Ce_2O_3 65 mol%. The $3Ce_2O_3 \cdot 2WO_3$ compound seemed to melt incongruently at ~1730°C. At 1770°C, no solid phases could be found by X-ray diffraction.

Although we could not obtain the single phase of $3Ce_2O_3 \cdot 2WO_3$, it can be concluded that this phase is a stable phase within the limited temperature region of 1545 ~ 1730°C, as described above.

Ivanova et al. (1) reported that $3La_2O_3 \cdot 2WO_3$ had a large solid-state region, i.e., 54 ~ 60 mol% La_2O_3. It seemed that $3Ce_2O_3 \cdot 2WO_3$ did not form solid solutions, because the d-values observed in diffraction patterns for any products with different bulk compositions did not change. By the way, we did not observe the apparent differences in powder patterns of $3La_2O_3 \cdot 2WO_3$ between room temperature and a high temperature (up to 1565°C) in contrast to the results reported by Ivanova et al., where two reversible transition points, 630 and 930°C, were reported without X-ray data for every form except the lowest form.

2c. $Ce_2O_3 \cdot WO_3$ (Ce_2WO_6). Brixner et al.

(8) recently prepared $Ce_2O_3 \cdot WO_3$ for the first time by a symproportionation according to $6CeO_2 + W + 2WO_3 \rightarrow 3Ce_2WO_6$ in a sealed platinum capsule and reported that it was monoclinic with the cell parameters of $a_0 = 5.570$ Å, $b_0 = 11.524$ Å, $c_0 = 15.947$ Å, and $\beta = 91.83°$, which was isostructural with other R_2WO_6 compounds ($R = Pr \sim Ho$). Here we call this phase an α-form. However, we found a $Ce_2O_3 \cdot WO_3$ phase which had another structure (β-form) in the products prepared by cofusion methods in all atmospheres used. The diffraction data of this phase could be indexed based upon a tetragonal cell

TABLE IV

X-Ray Powder Diffraction Data for the High-Temperature Phase of $Ce_2O_3 \cdot WO_3$, β-Form, at Room Temperature

	Sample 1[a]			Sample 2[b]		
$h\,k\,l$	I/I_0	d_{obsd}	d_{calc}	I/I_0	d_{obsd}	d_{calc}
1 0 1				10	4.625	4.644
0 0 2	17	4.409	4.411	80[d]	4.394	4.395
1 1 0	25	3.855	3.854	20	3.863	3.867
1 1 1	63	3.531	3.532	13	3.535	3.540
1 0 2	7	3.428	3.429	7	3.417	3.426
0 0 3	23	2.941	2.941	100[d]	2.930	2.930
1 1 2	100	2.905	2.903	40	2.907	2.903
2 0 0	49[c]	2.725[c]	2.726	36	2.734	2.735
1 0 3	11	2.589	2.588	10	2.584	2.583
0 0 4	8	2.205	2.206	47[d]	2.201	2.198
1 0 4				7	2.026	2.039
2 0 3	26	2.000	1.999	27	2.001	1.999
2 2 0	34[c]	1.926[c]	1.927	20	1.935	1.934
2 1 3	10	1.879	1.877	7	1.878	1.878
2 0 4	10	1.716	1.715			
3 1 1	6	1.692	1.692			
1 0 5	9	1.679	1.679			
3 1 2	21	1.607	1.606			
	tetragonal			tetragonal		
	$a = 5.451$ Å			$a = 5.469$ Å		
	$c = 8.823$ Å			$c = 8.790$ Å		
	$V = 262.1$ Å³			$V = 262.9$ Å³		

[a] In cofusion products coexisted with $3Ce_2O_3 \cdot WO_3$ s.s.

[b] Single phase in high-temperature X-ray studies.

[c] Overrapped by diffraction peaks of $3Ce_2O_3 \cdot WO_3$ s.s.

[d] Orientation along (00l) axis.

with cell parameters of $a_0 = 5.451$ Å and $c_0 = 8.823$ Å, as shown in Table IV. The attempts to prepare the single phase of β-form by cofusion methods of appropriate mixtures of $CeO_2 + WO_3 + W$ were unsuccessful. The fused products showed more complex diffraction patterns, γ-form,[1] which are identical to those of $La_2O_3 \cdot WO_3$ reported by Ivanova et al. (1) as given in Table V. Polymorphisms in $R_2O_3 \cdot WO_3$ at high temperature have not been studied yet, so we studied $Ce_2O_3 \cdot WO_3$ in detail in comparison with $La_2O_3 \cdot WO_3$ and $Nd_2O_3 \cdot WO_3$ by cofusion methods, solid-state reactions, and high-temperature X-ray methods. The results will be seen in another report (20). Here we report mainly for the polymorphism of $Ce_2O_3 \cdot WO_3$.

Two repeats of cofusion with grinding of the initial mixture of Ce_2O_4 (50 mol%) + WO_3 (25 mol%) + W (25 mol%) in argon atmosphere gave the γ-form. The bulk oxygen content of this product was determined to be $Ce_2WO_{5.93}$.

By the high-temperature X-ray studies, as given partly in Figs. 1 and 2, heating of the γ-form in a purified helium atmosphere at 1200°C gave the α-form and at 1400°C gave the β-form. This transition between the α-form and β-form was reversible at 1360°C, but sluggish. Thus, the β-form was easily brought about at room temperature by a rapid cooling. The β-form seemed to melt incongruently at 1545°C. The γ-form could not be observed by the high-temperature X-ray studies in any temperatures. These results lead to the conclusion that the α-form is a low-temperature phase, the β-form is a high-temperature phase, and the γ-form is a metastable phase.

X-ray powder data for the β-form observed in high-temperature X-ray studies were slightly different from those found in cofusion products, as shown in Table IV. They indicate that this compound may make solid solutions. X-ray diffraction patterns sometimes showed an orientation along the (00l) axis as seen in Table IV. The β-form, which has a tetragonal structure, has not been found in any $R_2O_3 \cdot WO_3$ compounds yet, but we also could find that this is a stable phase at high temperatures

[1] Sometimes γ-form + β-form.

TABLE V

X-Ray Powder Diffraction Data for γ-Form of $Ce_2O_3 \cdot WO_3$ and $La_2O_3 \cdot WO_3$

$Ce_2O_3 \cdot WO_3$		$La_2O_3 \cdot WO_3$		$La_2O_3 \cdot WO_3$[a]	
I/I_0	d	I/I_0	d	I/I_0	d
9	4.364	19	4.407		
5	4.024	7	4.037		
7	3.778	3	3.806		
10	3.728	17	3.756		
12	3.684	22	3.706		
8	3.577	12	3.606		
		3	3.542		
12	3.458	33	3.480	4	3.45
6	3.377	9	3.405		
58	3.316	81	3.330	3 ∼ 4	3.31
4	3.271	5	3.288		
45	3.177	41	3.198		
19	3.149	31	3.180	4	3.16
100	3.073	100	3.091	3	3.09
57	3.023	77	3.040	3	3.03
10	2.997	26	3.013		
35	2.937	52	2.956	3	2.95
29	2.809	57	2.829	3	2.82
7	2.773				
14	2.727	21	2.778		
14	2.699	20	2.720	2	2.70
26	2.667	34	2.680		
14	2.582	23	2.602	5	2.59
5	2.559	6	2.554		
5	2.527	8	2.540		
9	2.513	15	2.525		
7	2.478	6	2.489	0.5	2.49
10	2.459	9	2.475		
6	2.390				
7	2.376	13	2.393	1	2.40
3	2.348	6	2.364		
3	2.260	7	2.271	0.5	2.28
12	2.202	4	2.231		
9	2.189	15	2.204	2	2.20
11	2.180	13	2.192		
7	2.144	7	2.160	2	2.16

[a] After Ivanova et al., see Ref. (1).

(above 1440°C) in $La_2O_3 \cdot WO_3$ and $Nd_2O_3 \cdot WO_3$. This phase could be quenched by the "splat cooling" methods and on the strip heater of high-temperature X-ray. The phase transitions, $\alpha \leftrightarrow \beta$ in $Nd_2O_3 \cdot WO_3$ and $\gamma \leftrightarrow \beta$

in $La_2O_3 \cdot WO_3$ were reversible at 1460 and 1440°C, respectively. The X-ray data for the γ-form of $La_2O_3 \cdot WO_3$ prepared by annealing at 1400°C for 27 hr after cofusions are also given in Table V.

2d. $Ce_2O_3 \cdot 2WO_3$ ($Ce_2W_2O_9$). This compound has been studied by several researchers. Klevtsov et al. (9) and Borisov et al. (21) tried to prepare single crystals of $R_2O_3 \cdot 2WO_3$ ($R = $ Ce, Pr, Nd), and performed a partial structure analysis on $Pr_2O_3 \cdot 2WO_3$. They reported that these three compounds have the same monoclinic structure of the space group $P2_1/C$. McCarthy et al. (4) found that this phase was stable in the systems with Pr_2O_3, Nd_2O_3, Sm_2O_3, Eu_2O_3, and Gd_2O_3. This monoclinic $Ce_2O_3 \cdot 2WO_3$ was found in the products prepared by the cofusion methods.

Ivanova et al. (1) found $La_2O_3 \cdot 2WO_3$, whose structure was not known. We also obtained this compound by the cofusion method. These X-ray data, however, could not be indexed. It is also observed that $R_2O_3 \cdot 2WO_3$ has phase transitions at high temperature, i.e., 1075°C for $La_2O_3 \cdot 2WO_3$ (1), 1105°C for $Ce_2O_3 \cdot 2WO_3$ (7), and 438 and 1248°C for $Nd_2O_3 \cdot 2WO_3$ (2). The phase transition of $Sm_2O_3 \cdot 2WO_3$ has been reported (3). However, the crystal structure of high-temperature phases of them has not been reported yet.

In this study, we could obtain the high-temperature phase of $Ce_2O_3 \cdot 2WO_3$ both by a splat-cooling method and high-temperature X-ray methods. The X-ray powder data, Table VI, were well indexed based upon a cubic cell with the parameter of $a_0 = 7.046$ Å. This phase is isostructural with that of $La_2O_3 \cdot 2MoO_3$ reported by Alekseev et al. (22). It was also found in this work that the high-temperature phases of $La_2O_3 \cdot 2WO_3$ and $Nd_2O_3 \cdot 2WO_3$ were identical to that of $Ce_2O_3 \cdot 2WO_3$. Since the phase transition of $R_2O_3 \cdot 2WO_3$ is reversible and very rapid, one cannot obtain the high-temperature phases by normal quenching methods. It should be noted that $La_2O_3 \cdot 2WO_3$ was the low-temperature phase in the products even by the splat cooling. Detailed results on the polymorphism of $R_2O_3 \cdot 2WO_3$ will be described elsewhere.

TABLE VI

X-Ray Powder Diffraction Data for β-$Ce_2O_3 \cdot 2WO_3{}^a$ at Room Temperature

$h\,k\,l$	I/I_0	d_{obsd}	d_{calc}
1 1 1	12	4.071	4.068
2 0 0	16	3.524	3.523
2 1 0	100	3.150	3.151
2 1 1	46	2.877	2.877
2 2 0			2.491
3 0 0	5	2.348	2.349
3 1 0	3	2.228	2.228
3 1 1	9	2.126	2.125
2 2 2			2.034
3 2 0	5	1.9537	1.9542
3 2 1	39	1.8835	1.8831
4 0 0	6	1.7592	1.7615
4 1 0	9	1.7080	1.7089
3 3 0	4	1.6623	1.6608
3 3 1	7	1.6174	1.6165

Primitive cubic
$a = 7.046$ Å

^{a} This phase was obtained by a "splat cooling."

2e. $Ce_2O_3 \cdot 3WO_3$ ($Ce_2W_3O_{12}$, $Ce_2(WO_4)_3$). This compound is well known, and its structure was analyzed by Nelson and McKee (23). It has a monoclinic cell with the space group $C2/c$, which is common to many $R_2O_3 \cdot 3WO_3$ ($R = $ La ~ Dy). $Ce_2O_3 \cdot 3WO_3$ was believed to be a stable compound in air (6). Recently, it was demonstrated that this compound decomposed into $2Ce_2O_3 \cdot 9WO_3$ and CeO_2 at temperatures below 800°C in air ($pO_2 = $ 0.21 atm) and below 847°C in oxygen ($pO_2 = $ 1 atm) (7).

Nassau et al. (24) indicated the possibility of the phase transition at 970°C for $Ce_2O_3 \cdot 3WO_3$ from DTA measurements as well as for other $R_2O_3 \cdot 3WO_3$ ($R = $ La ~ Gd). We also observed an endothermic effect in the DTA curves at 1005°C on heating and an exothermic one on cooling (7). More recently, Brixner et al. (25), however, concluded that no phase transitions existed in the compounds $R_2O_3 \cdot 3WO_3$ ($R = $ Ce ~ Eu) and that only $La_2O_3 \cdot 3WO_3$ transformed at 897°C.

We reexamined $Ce_2O_3 \cdot 3WO_3$ and $La_2O_3 \cdot 3WO_3$ by the high-temperature X-ray method.

These results indicated that powder patterns, which changed slightly from those at room temperature, were identical for two compounds at higher temperatures than "transition points" reported, as seen in Table VII. The diffraction pattern of structure "D" stated by Nassau et al. (24) could not be observed at any temperatures near room temperature (~1060°C), though it was found that $La_2O_3 \cdot 3WO_3$ melted incongruently and gave some additional diffraction peaks based upon $La_2O_3 \cdot 2WO_3$, which was the high-

temperature phase above its transition temperature, ~1040°C. We could not obtain any phases other than the monoclinic phase at room temperature even by a splat-cooling method for $Ce_2O_3 \cdot 3WO_3$ and $La_2O_3 \cdot 3WO_3$.

Since the phase transition, even if it existed, would only show a small change in the crystal structure, as observed previously (24). Further studies for single crystals at high temperatures are expected.

2f. $2Ce_2O_3 \cdot 9WO_3$ ($Ce_4W_9O_{33}$). This phase was found recently as a stable phase in the

TABLE VII

X-RAY POWDER DIFFRACTION DATA FOR $Ce_2O_3 \cdot 3WO_3$ AND $La_2O_3 \cdot 3WO_3$ AT HIGH TEMPERATURE

$La_2O_3 \cdot 3WO_3$ (at 1040°C)[a]		$Ce_2O_3 \cdot 3WO_3$ (at 1010°C)[a]		$Ce_2O_3 \cdot 3WO_3$ (at RT)		
d	I/I_0	d	I/I_0	d	I/I_0	$h\,k\,l$
6.24	10			6.25	6	1 1 0, 1 1 $\bar{1}$
5.69	14			5.48	13	0 0 2
5.31	7			5.19	4	0 2 1
4.94	8			4.87	26	1 1 1, 1 1 $\bar{2}$
				4.01	3	0 2 2
3.711	8	3.712	5	3.639	26	1 1 $\bar{3}$
3.469	8	3.502	3	3.457	6	1 3 0, 1 3 $\bar{1}$
		3.258	19	3.261	100	2 2 $\bar{1}$
3.251	20	3.188	24	3.151	19	1 3 1, 1 3 $\bar{2}$
3.214	100	3.163	100	3.098	74	0 2 3
3.013	61	2.993	14	2.934	47	0 4 0
				2.795	7	2 2 $\bar{3}$
2.816	4	2.742	5	2.735	12	0 0 4, 1 3 $\bar{3}$, 1 3 2
2.715	59	2.695	45	2.684	24	2 0 $\bar{4}$
2.658	4			2.661	22	2 0 2
				2.417	5	3 1 $\bar{3}$, 3 1 0
				2.291	4	0 4 3, 1 1 $\bar{3}$
2.353	3			2.236	5	1 5 0, 1 5 $\bar{1}$
				2.204	5	3 1 $\bar{4}$
2.201	2			2.164	5	1 5 $\bar{2}$, 1 5 1
2.056	7	2.036	2	1.999	7	1 5 2, 1 3 $\bar{3}$, 0 4 4
2.003	16	2.004	41	1.975	35	2 4 4, 3 1 $\bar{3}$
1.970	10			1.956	18	0 6 0, 4 0 $\bar{2}$
				1.905	15	2 0 4, 1 1 $\bar{6}$
1.896	16	1.879	12	1.830	11	0 6 2, 4 0 0, 0 0 6
1.774	34	1.773	11	1.750	14	2 6 $\bar{1}$
		1.761	5	1.729	16	1 3 5, 0 6 3
				1.661	13	4 2 1
1.653	7	1.651	21	1.655	12	4 2 $\bar{3}$
1.639	28	1.625	18	1.629	10	4 4 2
1.596	5			1.589	7	2 2 5, 2 2 $\bar{7}$

[a] These data have not been indexed yet.

system Ce_2O_3–WO_3 (7). It was also reported that it had no phase transition up to the congruent melting temperature of 1026°C. The X-ray powder data reported have not been indexed yet. This phase was found in the products of both solid-state reactions and cofusions in air and argon atmospheres. This phase coexisted with WO_3 in products whose bulk compositions were $0 \sim 17.50$ Ce_2O_4 mol% and coexisted with $Ce_2O_3 \cdot 3WO_3$ in the composition range $19.00 \sim 25.00$ Ce_2O_4 mol%. The stoichiometric composition of this phase was between 17.5 and 19.0 Ce_2O_3 mol%. We could not determine it more precisely; therefore, the possibility that the true stoichiometry would not be 2/9 (18.18 Ce_2O_3 mol%) but 3/13 (18.45 Ce_2O_3 mol%), etc., could not be neglected. This phase appeared not to have solid solution regions because the d-values observed were unchanged in any cases.

Although this phase has not been reported in other R_2O_3 systems, we also could confirm that it was a stable phase in the system R_2O_3–WO_3 for La_2O_3, Pr_2O_3, and Nd_2O_3 both by solid-state reaction and cofusion methods. In the systems based on Sm_2O_3 and Y_2O_3, this phase did not exist. Thus, the mixture oxides with the bulk composition of $2R_2O_3 \cdot 9WO_3$ yielded the products of two-phases which consisted of WO_3 and $Sm_2O_3 \cdot 3WO_3$ or $Y_2O_3 \cdot 3WO_3$.

2g. Other compounds. Ostertag (26) reported a cubic tungsten bronze, $Ce_{0.10}WO_3$, which contains W^{5+}. This phase was also prepared when $Ce_2O_3 \cdot 2WO_3$ or $Ce_2O_3 \cdot 3WO_3$ was heated on strip heaters of tungsten in a helium atmosphere at temperatures above 1000°C. This phase appeared to be produced by the reaction between cerium tungstates and tungsten metal and vaporized at temperatures higher than 1200°C. This phase, which is not a phase in the "Join" Ce_2O_3–WO_3, was not studied in detail. It is probable that this phase is a stable phase in the ternary system Ce_2O_3–WO_3–W. McCarthy et al. (27) reported that Eu_xWO_3 with $x = 0.07 \sim 0.15$ was one of the equilibrium phases in the system Eu_2O_3–WO_3–W.

Timchenko et al. (28) and Kharachenko et al. (29) obtained single crystals of $2R_2O_3 \cdot 3WO_3$ (R = La, Pr, Nd) by hydrothermal or flux techniques. They have not been prepared by solid-state reactions of the appropriate oxide mixtures (1, 2). We observed this phase neither in the system Ce_2O_3–WO_3 nor in the systems La_2O_3, Nd_2O_3–WO_3. This phase, which has been prepared only as single crystals, may be metastable.

3. Phase Relations in the System CeO_2–Ce_2O_3–WO_2

The previous study (7) on the system CeO_2–Ce_2O_3–WO_3 in the ranges of oxygen pressures of $1 \sim 10^{-5}$ atm and temperatures of $RT \sim 1400$°C showed that only $Ce_2O_3 \cdot 2WO_3$, $Ce_2O_3 \cdot 3WO_3$, and $2Ce_2O_3 \cdot 9WO_3$ were prepared and that excess cerium oxide was CeO_2, which was stable under these experimental conditions. The preparations of these phases were shown by equilibrium reactions such as Eqs. (1)–Eq. (3). According to the "phase rule," three phases can coexist at a fixed oxygen pressure only at a certain
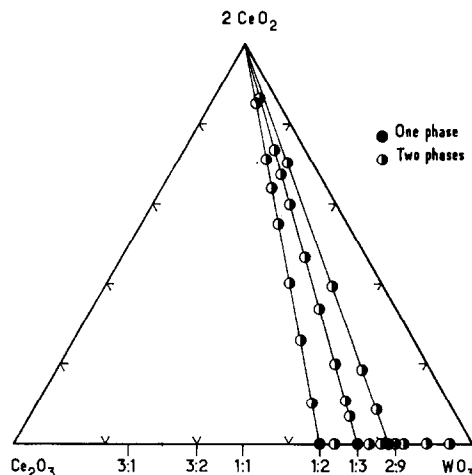

FIG. 3. Subsolidus phase equilibria in the system CeO_2–Ce_2O_3–WO_3 at 700–1000°C in several atmospheres. In oxygen ($pO_2 = 1$ atm): $T < 889$°C, "Join" CeO_2–$2Ce_2O_3 \cdot 9WO_3$ and "Join" $2Ce_2O_3 \cdot 9WO_3$–WO_3; $T > 889$°C, "Join" CeO_2–$Ce_2O_3 \cdot 3WO_3$ and "Join" $Ce_2O_3 \cdot 3WO_3$–WO_3. In air ($pO_2 = 0.21$ atm): $T < 830$°C, "Join" CeO_2–$2Ce_2O_3 \cdot 9WO_3$ and "Join" $2Ce_2O_3 \cdot 9WO_3$–WO_3; $T > 830$°C, "Join" CeO_2–$Ce_2O_3 \cdot 3WO_3$ and "Join" $Ce_2O_3 \cdot 3WO_3$–WO_3. In argon ($pO_2 = 10^{-5}$ atm): $T < 790$°C, "Join" CeO_2–$Ce_2O_3 \cdot 3WO_3$ and "Join" $Ce_2O_3 \cdot 3WO_3$–WO_3; $T > 790$°C, "Join" CeO_2–$Ce_2O_3 \cdot 2WO_3$ and "Join" $Ce_2O_3 \cdot 2WO_3$–WO_3.

temperature in the ternary system M–M'–O (M, M', metal; O, oxygen). At the other temperatures, two phases coexist at equilibrium states at a fixed oxygen pressure. In fact, the reaction products in the previous study consisted generally of two phases: two cerium tungstates or one cerium tungstate and CeO_2, as given in Ref. (7). Thus, the phase relations can be shown by two "Joins" which vary with temperatures and oxygen pressures, as shown in Fig. 3. Here we have used the equilibrium at 1000°C in air for the determination of oxygen contents in the cofusion products by the weight gain on reheating according to Eq. (4).

The results in Fig. 3 also indicate that the equilibrium oxygen pressures for reaction (2) are 1 atm at 889°C and 0.21 atm at 830°C, and for reaction (3) 10^{-5} atm at 790°C. These will be the first results where the actual equilibrium oxygen pressures for reactions related to ternary oxides of cerium have been determined. It was expected that equilibrium pressure would be lower than these values at higher temperatures as used in this work. $Ce_2O_3 \cdot 2WO_3$ was prepared by cofusion methods even in air ($pO_2 = 0.18$ atm).[2] It indicates that the equilibrium pressure for reaction (3) would be lower than 0.18 atm at temperatures above 2000°C. However, it should be noted that each phase was prepared from "liquids" in this work. The equilibria are not the same for liquid phases and solid phases. In addition, CeO_2 was no longer stable in the experimental conditions used here and changed to intermediate phases, CeO_x. The compounds CeO_2 and/or CeO_x can form solid solutions with $3Ce_2O_3 \cdot WO_3$ and also may be with $Ce_2O_3 \cdot WO_3$. Thus, we cannot apply Eq. (3) directly for the results obtained here, and we cannot present the preparations of $3Ce_2O_3 \cdot WO_3$, $3Ce_2O_3 \cdot 2WO_3$, and $Ce_2O_3 \cdot WO_3$ by the equilibrium equations. The solid solutions can change their compositions according to temperatures and oxygen pressures. These changes were so rapid that we observed some reoxidations or phase

[2] This study has been done in "Laboratoire des Ultra-Refractaires" which is at the altitude of 1600 m, where the atmospheric pressure is not 760 mm Hg but 640 mm Hg.

changes even during quenching of the products containing Ce_2O_3, $3Ce_2O_3 \cdot WO_3$, and $Ce_2O_3 \cdot WO_3$ as described before. This instability makes the phase study on the system CeO_2–Ce_2O_3–WO_3 very difficult, particularly in the domain bounded by CeO_2–Ce_2O_3–$Ce_2O_3 \cdot 2WO_3$. The cofusion products in this domain consisted generally of three phases or two phases containing solid solutions. It indicates that the phase relations in this domain would no longer be shown by simple "Joins" as seen in Fig. 3. We are continuing the studies in this domain in comparison with the system CeO_2–La_2O_3–WO_3.

On the other hand, the ternary system Ce_2O_3–WO_3–W seemed to be more simple except the domain near the "Join" WO_3–W, because the formation of solid solutions between cerium tungstates and tungsten metal is not expected; this is similar to the results for the system Sm_2O_3–WO_3–W (3). In fact, the cofusion products where excess tungsten metal coexisted were generally three phases, i.e., W metal and two cerium tungstates, which correspond to the bulk composition. These results are similar to those in the system Sm_2O_3–WO_3–W.

Acknowledgments

References

1. M. M. IVANOVA, G. M. BALAGINA, AND E. YA. RODE, Izv. Akad. Nauk. SSSR, Neorg. Mater. 6, 914 (1970).
2. E. YA. RODE AND V. N. KARPOV, Izv. Akad. Nauk. SSSR, Neorg. Mater. 2, 683 (1968).
3. L. L. Y. CHANG, M. G. SCROGER, AND B. PHILLIPS, J. Inorg. Nucl. Chem. 28, 1179 (1966).
4. G. J. MCCARTHY, R. D. FISCHER, G. G. JOHNSON, JR., AND C. E. GOODEN, NBS Special Publication 364, p. 397 (1972).
5. T. SATA AND M. YOSHIMURA, Yogyo Kyokai-shi (J. Ceram. Soc. Japan) 76, 30 (1968).
6. H. J. BORCHARDT, J. Chem. Phys. 39, 504 (1963).
7. M. YOSHIMURA, T. SATA, AND T. NAKAMURA, Nippon Kagaku Kai-shi (J. Chem. Soc. Japan) 2287 (1973).

8. L. H. Brixner, A. W. Sleight, and C. M. Foris, *J. Solid State Chem.* **7**, 418 (1973).

9. P. V. Klevtsov, L. Yu. Kharachenko, and R. F. Klevtsova, *Dokl. Akad. Nauk. SSSR* **176**, 575 (1967).

10. M. Foex and J. P. Traverse, *Rev. Int. Hautes Tempér. Réfract.* **3**, 429 (1966).

11. A. Rouanet, F. Sibieude, and M. Faure, *J. Phys. (E)*, in press.

12. M. Foex and J. P. Traverse, *Bull. Soc. Fr. Miner. Cristall.* **89**, 184 (1966).

13. J. Millet, G. Benezech, J. Dubois, P. Canale, and G. Provost, *Rev. Int. Hautes Tempér. et Réfract.* **8**, 277 (1971).

14. L. L. Y. Chang and B. Phillips, *Inorg. Chem.* **3**, 1792 (1964).

15. V. K. Trunov, G. I. Tyushevskaya, and N. S. Afonskii, *Zh. Neorg. Khim.* **13**, 936 (1968).

16. M. Foex, *Bull. Soc. Chim. Fr.* 3696 (1967).

17. M. Yoshimura, A. Rouanet, F. Sibieude, and M. Foex, to appear.

18. M. Yoshimura and T. Sata, *Bull. Tokyo Inst. Tech.* **108**, 25 (1972).

19. M. Yoshimura and J. F. Baumard, *Mater. Res. Bull.*, in press.

20. M. Yoshimura, A. Rouanet, F. Sibieude, and M. Foex, *C.R. Acad. Sci. (Paris)* **279C**, 863 (1974).

21. S. V. Borisov and R. F. Klevtsove, *Kristallografiya* **15**, 38 (1970).

22. F. P. Alekseev, E. Get'man, G. G. Koshcheev, and M. V. Mokhosoev, *Zh. Neorg. Khim.* **14**, 1560 (1969).

23. J. B. Nelson and J. H. McKee, *Nature (London)* **158**, 753 (1946).

24. K. Nassau, H. J. Levinstein, and G. M. Loiacono, *J. Phys. Chem. Solids* **26**, 1805 (1965).

25. L. H. Brixner and A. W. Sleight, *Mat. Res. Bull.* **8**, 1269 (1973).

26. W. Ostertag, *Inorg. Chem.* **5**, 758 (1965).

27. G. J. McCarthy, R. D. Fischer, and J. Sanzgiri, *J. Solid State Chem.* **5**, 200 (1972).

28. T. I. Timchenko, L. V. Petushkova, E. A. Pobedinskaya, and A. V. Pashkova, *Dokl. Akad. Nauk. SSSR* **185**, 573 (1969).

29. L. Yu. Kharachenko, T. M. Polyanskaya, and P. V. Klevtsov, *Izv. Akad. Nauk. SSSR, Neorg. Mater.* **6**, 1720 (1970).