

# Preparation and Structure of Cerium Titanates Ce<sub>2</sub>TiO<sub>5</sub>, Ce<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, and Ce<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub>

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Compounds Ce<sub>2</sub>TiO<sub>5</sub>, Ce<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, and Ce<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub> were prepared by heating appropriate mixtures of solids containing Ce<sup>4+</sup> and Ti<sup>3+</sup> or Ti which were placed in a platinum–silica–ampoule combination at  $T = 1250^\circ\text{C}$  (3d) under vacuum. The new compounds were characterized by powder patterns. We obtained Ce<sub>2</sub>TiO<sub>5</sub> which is isotypic to La<sub>2</sub>TiO<sub>5</sub> and crystallizes in the Y<sub>2</sub>TiO<sub>5</sub>-type (space group *Pnma*) with  $a = 10.877(6)$  Å,  $b = 3.893(1)$  Å,  $c = 11.389(8)$  Å,  $Z = 4$ . Ce<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> is isotypic to La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and crystallizes in the monoclinic Ca<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> type (space group *P 2<sub>1</sub>*) with  $a = 7.776(6)$  Å,  $b = 5.515(4)$  Å,  $c = 12.999(6)$  Å,  $\beta = 98.36(5)$ ,  $Z = 4$ . The compound Ce<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub> crystallizes orthorhombic with  $a = 14.082(4)$  Å,  $b = 35.419(8)$  Å,  $c = 14.516(4)$  Å,  $Z = 16$ . The new cerium titanate Ce<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub> is isotypic to Nd<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub> (space group *Fddd* (No. 70)) which represents a novel type of structure. © 1994 Academic Press, Inc.

## 1. INTRODUCTION

In the past 30 years rare-earth titanates have become one of the best investigated rare-earth compounds. Meanwhile there exist a great number of well-known and also well-characterized compounds. The number of publications on their preparation, structure, thermodynamics, and magnetic and electronic properties is impressive. Table 1 provides an overview.

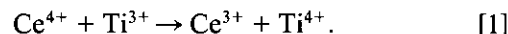
However, there are only a few investigations on systems RE/Ti/O (RE = rare-earth element) dealing with the preparation of compounds containing RE = Ce<sup>3+</sup>. And often the expressions used, such as “. . .RE = La–Lu. . .” were not followed by any substantial description on the preparation or characterization of the Ce(III) compound, respectively (1–4).

## 2. SYNTHESIS AND STRUCTURAL CHARACTERIZATION

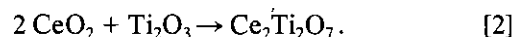
It is indeed difficult to prepare Ce(III) compounds at high temperatures. This is because of the preference of the Ce(IV) oxidation state contrary to the other rare-earth elements. Ce(III) compounds generally tend to form the thermodynamically very stable CeO<sub>2</sub> when heated in the

presence of oxidizing agents or even gaseous oxygen from the air. CeO<sub>2</sub> once isolated is unreactive even in a finely spread form and does not tend to form polynary compounds. The one known exception representing the Ce(IV) oxidation state is the compound CeTi<sub>2</sub>O<sub>6</sub>, which is reported to be stable between 1300 and 1350°C (5–8).

For preparing ternary compounds in systems Ce/Ti/O we therefore did not start in the common way using oxides in oxidation states RE<sup>3+</sup>/Ti<sup>4+</sup>, but tried to enter via the solid state reaction Eq. [1] into systems Ce<sup>3+</sup>/Ti<sup>4+</sup>/O by starting with compounds containing Ce<sup>4+</sup> and Ti<sup>3+</sup>:



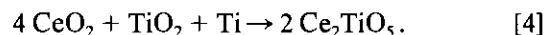
The synthesis of the compound Ce<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (9) could work by following the reaction



The unknown compound Ce<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub> might be synthesized in the same manner:



Analogously, the also unknown compound Ce<sub>2</sub>TiO<sub>5</sub> should be preparable:



### 2.1 Preparation of Ce<sub>2</sub>TiO<sub>5</sub>

To synthesize Ce<sub>2</sub>TiO<sub>5</sub> according to Eq. [4], CeO<sub>2</sub> prepared in the manner mentioned later (cf. Section 3.1) was mixed with TiO<sub>2</sub> (anatase modification, Fluka purum >99%) and powdered titanium metal.

Then the mixture was placed in a platinum ampoule. After sealing the surrounding silica ampoule (see Section 3.2 for further information) and heating (3d, 1200–1250°C) we found a reddish-brown colored product which was indicated by Guinier techniques to be Ce<sub>2</sub>TiO<sub>5</sub> (sometimes

TABLE 1  
Publications on Rare-Earth Titanates RE<sub>2</sub>TiO<sub>5</sub>, RE<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>,  
and RE<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub>

Subject	Compounds		
	RE <sub>2</sub> TiO <sub>5</sub>	RE <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	RE <sub>4</sub> Ti <sub>9</sub> O <sub>24</sub>
Preparation	[16, 26, 27, 28, 29, 30, 31, 32]		
	[10, 33, 34, 35]	[9, 12, 18, 33]	[13, 34, 36, 37]
	[37, 38, 39, 40]	[34, 37, 39, 41]	[42, 43, 44, 45]
	[43, 46, 47, 48]	[42, 43, 46, 49]	
	[50]	[51, 52, 53, 54]	
		[55, 56]	
Structure	[26, 36, 49, 53, 57, 58, 59, 60]		
	[2, 10, 38, 40]	[11, 12, 18, 54]	[13]
	[47, 61]	[61, 62, 63, 64]	
High-temperature- and High-pressure-modifications	[39, 62, 65, 66]		
	[38, 40, 61]	[51, 61]	
		[40, 67]	
	[35, 68]	[68, 69]	
Chemical and thermodynamical behavior	[5, 7, 21, 46, 70, 71, 72, 73]		
	[2, 38, 39, 61, 74]	[39, 61, 63, 64, 74]	
	[28, 37, 42, 63, 64, 65, 66, 75, 76, 77, 78, 79]		
		[56]	
Physical properties		[43, 80, 81]	
	[2, 37]	[37, 41, 52, 82]	[37]
		[55]	

with very small amounts of CeO<sub>2</sub>). CeTiO<sub>5</sub> is isotypic to La<sub>2</sub>TiO<sub>5</sub> (10) and crystallizes in the Y<sub>2</sub>TiO<sub>5</sub> type (space group *Pnma*) with  $a = 10.877(6)$  Å,  $b = 3.893(1)$  Å,  $c = 11.389(8)$  Å,  $Z = 4$ . Tables 2 and 3 show the lattice constants of Ce<sub>2</sub>TiO<sub>5</sub>, in comparison to the other rare-earth titanates RE<sub>2</sub>TiO<sub>5</sub>.

## 2.2. Preparation of Ce<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>

Ce<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> was prepared in an analogous procedure to Ce<sub>2</sub>TiO<sub>5</sub> following Eq. [2]. A mixture (2 : 1) of CeO<sub>2</sub> (cf. 3.1) and commercially available Ti<sub>2</sub>O<sub>3</sub> (Johnson Matthey, >99%) was homogenized and tempered (3 d, 1200°C) in the same way as described below (cf. Section 3.2), where CeO<sub>2</sub> was used as the carrier of Ce<sup>4+</sup> and Ti<sub>2</sub>O<sub>3</sub> as the Ti<sup>3+</sup> carrier.

The products we obtained were reddish-brown powders. According to Guinier data the products proved to be Ce<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> which was in general monophasic (in some cases we found small traces of CeO<sub>2</sub>). Ce<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, which is isotypic to La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (11, 12), crystallizes in the monoclinic Ca<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> type (space group *P* 2<sub>1</sub>) with  $a = 7.776(6)$  Å,  $b = 5.515(4)$  Å,  $c = 12.999(6)$  Å,  $\beta = 98.36(5)$ ,  $Z = 4$ .

Lattice constants of Ce<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> are compared with the other rare-earth titanates RE<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> in Table 4.

## 2.3. Preparation of Ce<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub>

Ce<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub> can be prepared, similarly to Ce<sub>2</sub>TiO<sub>5</sub> and Ce<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, using CeO<sub>2</sub> (cf. 3.1), commercially available TiO<sub>2</sub> (anatase modification, Fluka >99%), and Ti<sub>2</sub>O<sub>3</sub> (Johnson Matthey, >99%) according to Eq. [3]. Mixtures of CeO<sub>2</sub>, Ti<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> (4 : 2 : 5) were homogenized, sealed in silica ampoules (cf. Section 3.2), and heated (1250°C; 3 d).

The products obtained were chestnut colored and found to be Ce<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub> by using Guinier techniques. Similar to the above-mentioned synthesis of Ce<sub>2</sub>TiO<sub>5</sub> and Ce<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, in some cases traces of CeO<sub>2</sub> were obtained. We presume that this is due to an incomplete reaction of the mixtures or the presence of traces of oxidizing agents. Ce<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub> is isotypic to Nd<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub> and crystallizes in the orthorhombic space group *Fddd* (No. 70) with  $a = 14.082(4)$  Å,  $b = 35.419(8)$  Å,  $c = 14.516(4)$  Å,  $Z = 16$ . The very complicated structure of Nd<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub> was recently published and described elsewhere (13, 14).

Table 5 gives a comparison of the lattice constants of the rare-earth titanates RE<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub> (RE = La, Ce, Pr, Nd).

## 2.4. Indexing and Refinement of the Lattice Constants

The lattice constants derived from Guinier data were obtained from powders of the cerium titanates mixed with

TABLE 2  
Crystallographic Data of Compounds RE<sub>2</sub>TiO<sub>5</sub>  
(RE = La–Tb): Y<sub>2</sub>TiO<sub>5</sub> Type

Compound	Y <sub>2</sub> TiO <sub>5</sub> type ( <i>Pnma</i> , $Z = 4$ )				Reference
	$a$ (Å)	$b$ (Å)	$c$ (Å)	Vol. (Å <sup>3</sup> )	
La <sub>2</sub> TiO <sub>5</sub>	10.97	3.937	11.37	491.1	(10, 37, 83)
Ce <sub>2</sub> TiO <sub>5</sub>	10.877(6)	3.893(1)	11.389(8)	482.6(5)	This work
Pr <sub>2</sub> TiO <sub>5</sub>	10.776	3.855	11.396	473.4	(84)
Nd <sub>2</sub> TiO <sub>5</sub>	10.720	3.840	11.361	467.7	(47)
Sm <sub>2</sub> TiO <sub>5</sub>	10.59	3.792	11.35	455.8	(33)
Eu <sub>2</sub> TiO <sub>5</sub>	—	—	—	—	—
Gd <sub>2</sub> TiO <sub>5</sub> <sup>a</sup>	10.48	3.76	11.33	446.5	(17, 75)
Tb <sub>2</sub> TiO <sub>5</sub> <sup>a</sup>	10.426	3.855	11.32	455.0	(66, 84)
Y <sub>2</sub> TiO <sub>5</sub>	10.35	3.70	11.25	430.8	(17)

<sup>a</sup> Low-temperature modification.

TABLE 3  
Crystallographic Data of Compounds RE<sub>2</sub>TiO<sub>5</sub> (RE = Gd–Lu)

Compound	(Possible space groups; <i>P6/3mmc</i> , <i>P6<sub>3</sub>mc</i> , <i>P6<sub>2</sub>c</i> )			CaF <sub>2</sub> type ( <i>Fm3m</i> )	
	<i>a</i> (Å)	<i>c</i> (Å)	Reference	<i>a</i> (Å)	Reference
Gd <sub>2</sub> TiO <sub>5</sub> <sup>a</sup>	3.683	11.995	(75)		
	3.672	10.907	(74)		
Tb <sub>2</sub> TiO <sub>5</sub> <sup>a</sup>	3.9475	11.895	(66, 84)		
Dy <sub>2</sub> TiO <sub>5</sub> <sup>b</sup>	3.632	11.837	(58, 74)		
Ho <sub>2</sub> TiO <sub>5</sub>	3.616	11.89	(61)		
Er <sub>2</sub> TiO <sub>5</sub>				5.132	(2, 38, 63, 65)
Tm <sub>2</sub> TiO <sub>5</sub>				5.12	(79)
Yb <sub>2</sub> TiO <sub>5</sub>				5.094	(2, 38)
Lu <sub>2</sub> TiO <sub>5</sub>				5.081	(2, 38, 64)

<sup>a</sup> High-temperature modification.

<sup>b</sup> Single crystals of Dy<sub>2</sub>TiO<sub>5</sub> were obtained using CO<sub>2</sub> laser techniques.

The metastable compound crystallizes cubic (*a* = 10.3189 Å). The metal positions are similar to the pyrochlore type but with distorted and partially occupied cation sites. While heating this modification (*T* < 1400°C) it transforms to the hexagonal high-temperature modification of Dy<sub>2</sub>TiO<sub>5</sub> (40).

low quartz as an internal standard. The indexing of the reflexes of Ce<sub>2</sub>TiO<sub>5</sub>, Ce<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, and Ce<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub> was carried out analogously to the corresponding isotopic lanthanum compounds (La<sub>2</sub>TiO<sub>5</sub> and La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>) and the isotopic neo-

dymium compound (Nd<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub>), respectively. Calculations for the refinement of the lattice constants were carried out with the program SOS (15) using the least-squares-fit method. The lattice constants are listed in Tables 2, 4, and 5. Tables 6, 7, and 8 include the indexed Guinier data of the compounds Ce<sub>2</sub>TiO<sub>5</sub>, Ce<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, and Ce<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub>.

### 2.5. Structure of Ce<sub>2</sub>TiO<sub>5</sub>

The rare-earth compounds RE<sub>2</sub>TiO<sub>5</sub> form different structures depending on the radii of the rare-earth cations. While compounds RE<sub>2</sub>TiO<sub>5</sub> with RE = La–Dy crystallize in the orthorhombic Y<sub>2</sub>TiO<sub>5</sub> type (space group *Pnma*) (10, 16, 17), the compounds with RE = Sm–Ho prefer the hexagonal high-temperature form. Rare-earth titanates RE<sub>2</sub>TiO<sub>5</sub> with RE = Er–Lu crystallize in the cubic CaF<sub>2</sub> type, as was indicated by their powder diffractograms.

The titanium atoms are coordinated by oxygen-forming trigonal bipyramids, which are connected over the top and bottom to build infinite polyhedra chains (10).

### 2.6. Structure of Ce<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>

Compounds RE<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> with radii quotients of the cations  $r_{Ln^{3+}}/r_{Ti^{4+}} \geq 1.5$ , i.e., RE = La–Nd, prefer the monoclinic La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> type (space group *P2<sub>1</sub>*) (11, 12, 18), which

TABLE 4  
Crystallographic Data of Compounds RE<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (RE = La–Lu)

Compound	<i>a</i> (Å)	Ca <sub>2</sub> Nb <sub>2</sub> O <sub>7</sub> type ( <i>P2<sub>1</sub></i> , <i>Z</i> = 4)			Reference	Pyrochlore type ( <i>Fd3m</i> , <i>Z</i> = 8)	
		<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)		<i>a</i> (Å)	Reference
La <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub> <sup>a</sup>	7.80	5.546	13.011	98.6	(11, 53)		
Ce <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub> <sup>b</sup>	7.776(6)	5.515(4)	12.999(6)	98.36(5)	This work		
	7.74	5.50	12.99	98.6	(9)		
Pr <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	7.723	5.482	12.989	98.48	(49)		
Nd <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub> <sup>c</sup>	7.68	5.46	12.99	98.5	(53)		
Sm <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub> <sup>d</sup>	7.61	5.42	12.98	98.4	(85)	10.211	(41)
Eu <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>						10.192	(41)
Gd <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>						10.171	(41)
Tb <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>						10.148	(41)
Dy <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>						10.119	(41)
Ho <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>						10.095	(41)
Er <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>						10.069	(41, 59)
Tm <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>						10.050	(41)
Yb <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>						10.028	(41)
Lu <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>						10.011	(41)

<sup>a</sup> There is a high-temperature modification (above 1053 K) (62).

<sup>b</sup> The preparation of Ce<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> via reduction of a CeO<sub>2</sub>/TiO<sub>2</sub> (1 : 1) mixture with H<sub>2</sub> is described, but without any lattice constants (5).

<sup>c</sup> There is a publication on a monoclinic (*P2<sub>1</sub>*) modification with a doubled *c*-axis (12).

<sup>d</sup> The Ca<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> type is only available under high-pressure conditions (*p* = 54 kbar, 1390°C) (67).

TABLE 5  
Crystallographic Data of Compounds RE<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub>  
(RE = La, Ce, Pr, Nd)

Compound	RE <sub>4</sub> Ti <sub>9</sub> O <sub>24</sub> ( <i>Fddd</i> , <i>Z</i> = 16)				Reference
	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )	
La <sub>4</sub> Ti <sub>9</sub> O <sub>24</sub>	6.54	6.71	9.79	429.6	(42)
	14.142	35.50	14.578	7318.8	(36)
Ce <sub>4</sub> Ti <sub>9</sub> O <sub>24</sub>	14.082(4)	35.419(8)	14.516(4)	7240.3(34)	This work
Pr <sub>4</sub> Ti <sub>9</sub> O <sub>24</sub>	14.025	35.35	14.507	7192.3	(36)
Nd <sub>4</sub> Ti <sub>9</sub> O <sub>24</sub>	13.991	35.29	14.478	7148.4	(36)
	13.991	35.289	14.479	7148.7	(44)
	13.9926(11)	35.2844(21)	14.4676(17)	7142.95	(13)

is isotopic to Ca<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub>. Under high-pressure conditions Sm<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> crystallizes in the same structure. Compounds RE<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> with RE = Sm–Lu, which have cationic radii quotients  $1.22 \geq r_{Ln^{3+}}/r_{Ti^{4+}} \leq 1.5$ , crystallize in the cubic pyrochlore structure (19–21).

### 2.7. Structure of Ce<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub>

Ce<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub> which is isotopic to Nd<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub> crystallizes in the orthorhombic space group *Fddd* (No. 70). The structure of Nd<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub> could be solved by using single crystals prepared via chemical vapor transport with Cl<sub>2</sub> as transport agent. The very complicated structure can be described by building units of TiO<sub>6</sub> octahedra connected in a three-dimensional framework with distorted REO<sub>8</sub> square antiprisms and REO<sub>6</sub> octahedra (13, 14).

TABLE 6  
Guinier Data of Ce<sub>2</sub>Ti<sub>5</sub>O<sub>7</sub>; CuKα<sub>1</sub> Radiation  
(λ = 1.54051 Å)

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> <sub>cal</sub> (Å)	<i>d</i> <sub>obs</sub> (Å)	<i>I</i> <sub>c</sub>
1	0	1	7.8660	7.88	21
2	0	1	4.9077	4.91	9
2	0	2	3.9330	3.93	1
0	1	1	3.6837	3.67	3
1	0	3	3.5843	3.59	19
2	1	0	3.1656	3.17	100
2	0	3	3.1129	3.11	72
3	0	2	3.0584	3.06	8
0	1	3	2.7179	2.72	33
1	1	3	2.6369	2.64	11
3	1	2	2.4050	2.40	8
3	1	3	2.1747	2.17	9
4	1	2	2.0759	2.08	3
0	2	0	1.9465	1.95	21
4	1	3	1.9224	1.92	44

### 3. EXPERIMENTAL

#### 3.1. Preparation of CeO<sub>2</sub>

For the preparation of the cerium titanates Ce<sub>2</sub>TiO<sub>5</sub>, Ce<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, and Ce<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub> we used CeO<sub>2</sub> which was prepared by heating (800°C, 4 hr) commercially available Ce<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> · 9 H<sub>2</sub>O (Johnson Matthey, puriss. 99.9%) as the starting material in air:

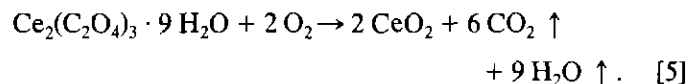


TABLE 7  
Guinier Data of Ce<sub>2</sub>Ti<sub>5</sub>O<sub>7</sub>; CuKα<sub>1</sub> Radiation  
(λ = 1.54051 Å)

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> <sub>cal</sub> (Å)	<i>d</i> <sub>obs</sub> (Å)	<i>I</i> <sub>c</sub>
0	1	2	4.1865	4.19	42
1	1	2	3.8329	3.83	0
0	1	3	3.3848	3.38	9
0	0	4	3.2152	3.21	40
2	1	1	3.1525	3.15	28
1	0	4	3.1331	3.12	8
2	0	3	3.0956	3.09	11
1	1	3	2.9748	2.97	100
0	1	4	2.7777	2.78	24
0	2	0	2.7578	2.75	35
2	1	3	2.6995	2.70	51
2	0	4	2.6651	2.67	20
2	2	1	2.1770	2.18	21
0	0	6	2.1435	2.14	6
2	1	5	2.1214	2.12	13
0	2	4	2.0933	2.09	30
2	2	3	2.0592	2.06	16
2	0	6	2.0002	2.00	6
3	1	3	1.9396	1.94	39
2	2	4	1.9164	1.92	20
0	2	5	1.8810	1.88	17

TABLE 8  
Guinier Data of  $Ce_4Ti_9O_{24}$ ;  $CuK\alpha_1$  Radiation  
( $\lambda = 1.54051 \text{ \AA}$ )

$h$	$k$	$l$	$d_{cal} (\text{\AA})$	$d_{obs} (\text{\AA})$	$I_0$
0	2	2	6.7174	6.73	42
2	2	0	6.5446	6.55	5
1	5	1	5.8008	5.81	46
2	0	2	5.0553	5.05	13
2	6	0	4.5242	4.53	32
0	8	0	4.4266	4.42	22
2	4	2	4.3900	4.39	70
3	3	1	4.1785	4.18	3
3	5	1	3.7795	3.78	4
0	4	4	3.3603	3.36	100
2	8	2	3.3303	3.33	24
4	4	0	3.2723	3.27	64
3	3	3	3.2407	3.24	13
2	10	0	3.1639	3.16	48
4	2	2	3.1191	3.12	21
3	5	3	3.0432	3.04	15
1	9	3	2.9833	2.98	48
3	9	1	2.9528	2.95	29
3	7	3	2.7905	2.79	13
5	1	1	2.7528	2.75	5
1	11	3	2.6333	2.63	8
3	11	1	2.6119	2.61	6
2	12	2	2.5486	2.55	21
4	0	4	2.3978	2.40	45
2	10	4	2.3851	2.39	7
4	10	2	2.3613	2.36	6
1	9	5	2.3051	2.31	17
0	12	4	2.2900	2.29	16

The product was of a light yellow color. This color is significant for  $CeO_2$  powders containing less than 0.001% of praseodymium oxide (22).

### 3.2. Heating and Sealing Procedure

The mixtures of the starting compounds used to obtain cerium titanates were placed under argon atmosphere into platinum ampoules which had been sealed before at one end. The open end of the platinum ampoule was closed by gently pressing with a plier. The platinum ampoules prepared in this way were placed into silica ampoules and sealed under dynamic vacuum.

Then the silica-platinum ampoule combination could be heated in a silicon-carbide oven.

We recommend this procedure instead of taking only platinum ampoules because of the better reuse of the platinum ampoules. Using only silica ampoules would cause a reaction with the ampoule material at the temperatures used and will result in heavy damage to the ampoule.

### 4. CHEMICAL TRANSPORT OF $Ce_2TiO_5$ , $Ce_2Ti_2O_7$ , and $Ce_4Ti_9O_{24}$

As cerium titanates containing Ce(III) are sensitive to oxidation, experiments with oxidizing transport agents as the commonly used  $Cl_2$  were not started. Instead we tried to carry out a chemical vapor transport (23–25) by using gaseous HCl as transport agent.

The powdery cerium titanates  $Ce_2TiO_5$ ,  $Ce_2Ti_2O_7$ , and  $Ce_4Ti_9O_{24}$  were placed under argon atmosphere in silica ampoules. Then the silica ampoules were evacuated, heated under dynamic vacuum (2 hr at 200–300°C for removing traces of water), filled with gaseous HCl ( $p(HCl)$ , 298 K = 1 atm), and finally sealed.

Experiments on the chemical vapor phase transport of the cerium titanates  $Ce_2TiO_5$ ,  $Ce_2Ti_2O_7$ , and  $Ce_4Ti_9O_{24}$  were carried out at different temperatures with different temperature gradients (between 1050 and 900°C with  $\Delta T$  varying between 50 and 150°C).

In not a single case we observed a transport through the gas phase by the resulting deposition at the less hot zone. The starting compounds did not decompose but remained stable against HCl as rare-earth titanates  $Ce_2TiO_5$ ,  $Ce_2Ti_2O_7$ , and  $Ce_4Ti_9O_{24}$ , respectively.

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