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STRUCTURES AND STABILITIES OF TRIVALENT AND TETRAVALENT  
RARE EARTH IONS IN SEVENFOLD AND EIGHTFOLD COORDINATION  
IN FLUORITE-RELATED COMPLEX OXIDES

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objective of our actinide chemistry research program is to characterize structural, spectroscopic, and thermodynamic properties of tetravalent lanthanide and actinide ions, especially when an isostructural class of compounds is available. Examples of such isostructural classes of compounds are the dioxides, tetrafluorides, and perovskites  $BaMO_3$ . Table II orders lanthanide and actinide ions by their aqueous  $M^{4+}/M^{3+}$  reduction potentials, with most stable 4+ ions at left and least stable 4+ ions at right [1]. Since the actinide ions  $Am^{4+}$ ,  $Cm^{4+}$ ,  $Bk^{4+}$ , and  $Cf^{4+}$  are produced only under strongly oxidizing conditions, and have oxidation-reduction potentials (Table II) and ionic radii (Table III) [3] comparable to those of the lanthanide ions  $Ce^{4+}$ ,  $Pr^{4+}$ , and  $Tb^{4+}$ , it is appropriate to search for and to study additional classes of compounds with 3+ or 4+ lanthanide ions as models for or in parallel with the similar 3+ or 4+ actinide ions.

Table IV shows the most common structural classes of lanthanide and actinide complex oxides. It is striking that almost all of these compounds have the lanthanide or actinide ion in coordination number 6. There are a few complex oxides with coordination number 8, related to the fluorite ( $CaF_2$ ) structure, some of which are listed near the bottom of Table IV.

The fluorite structure is exhibited by all lanthanide (Ce, Pr, Tb) and actinide (Th through Cf) dioxides. Studies of  $CeO_2$ ,  $UO_2$ , and  $PuO_2$  have shown these oxides to be inert to chemical attack and stable toward reduction and radiation damage. Fluorite-related phases in the form of stabilized zirconia [4] (cubic  $MO_{2-x}$  with M coordination number 8) or titanate ceramics [5] (pyrochlore  $CaMTi_2O_{7-x}$  with M coordination number 8 or zirconolite  $CaMTi_2O_{7-x}$  with M

Table II. Aqueous  $M^{4+}/M^{3+}$  reduction potentials of the lanthanides and actinides. The elements with most stable +4 ions appear at left; those with the least stable 4+ ions appear at right.

	← Stable 4+ State					----	Stable 3+ State →					
M	Th	U	Np	Pu	Bk	Ce	Am	Tb	Pr	Nd	Dy	
$M^{4+}/M^{3+} E^\circ(aq)$	-3.7	-0.52	+0.179	+1.01	+1.67	+1.72	+2.62	+3.1	+3.2	+4.9	+5.7	
Uncertainty	0.5	0.05	0.005	0.01	0.07	0.05	0.09	0.2	0.5	0.5	1.0	

Table III. Ionic Radii (in Å) for Selected 3+ and 4+ Ions with Coordination Number 8

Element	Radius ( $M^{3+}$ ) <sup>a</sup>	Radius ( $M^{4+}$ ) <sup>a</sup>
Y	1.019	
La	1.16	
Ce	1.143	0.97
Pr	1.126	0.96
Nd	1.109	
Tb	1.040	0.88
Th		1.05
U	1.15	1.00
Np	1.13	0.98
Pu	1.12	0.96
Am	1.09	0.95
Cm	1.08	0.95
Bk	1.07	0.93
Cf	1.06	0.92
Zr		0.84

<sup>a</sup> Ionic radii were taken from Shannon [3].

coordination number 7) have been of considerable interest as nuclear waste disposal hosts for 4+ actinide ions. These materials are also (to different degrees) chemically inert toward leaching and stable with respect to radiation damage [6,7].

Rare-earth ( $M^{3+}$ ) pyrochlores  $M_2Ti_2O_7$  ( $M = Sm-Lu, Y$ ) and  $M_2Zr_2O_7$  ( $M = La-Gd$ ) have been thoroughly characterized [8]. It seemed reasonable that the two  $M^{3+}$  (ionic radii 1.1 Å) ions could be replaced by a pair of large  $M^{2+}$  ( $Ca^{2+}$ , CN 8 ionic radius 1.12 Å) and  $M^{4+}$  ( $Ce^{4+}$ , CN 8 ionic radius 0.97 Å) ions to form "ordered pyrochlores". A model is the known oxide  $CaZrTi_2O_7$  (often referred to as zirconolite), a set of fluorite-related structures [9] that can incorporate lanthanide(III) or actinide(IV) ions in seven- or eight-fold coordination. Lanthanide and actinide ionic radii shown in Table III indicate that the large +4 ions may form "ordered pyrochlores" [10] and that smaller +4 ions may adopt the zirconolite structure. The only "ordered pyrochlores" that have been reported are  $CaCeTi_2O_7$ ,  $CdCeTi_2O_7$  [11],  $CaUTi_2O_7$  [12], and  $CaPuTi_2O_7$  [13]. As Table II shows,  $Ce^{4+}$  and  $U^{4+}$  are moderately stable with respect to  $Ce^{3+}$  and  $U^{3+}$ ; in oxides these ions are very stable with respect to reduction (in fact,  $U^{4+}$  oxides

Table IV. Lanthanide and Actinide Coordination in Complex Oxides

Coordination Number (CN) and Geometry	Structure Type	Extended Structure	Examples [usually Ln(IV) or An(VI)]
CN 6: Compressed octahedra (two short An-O "axial" bonds and four long An-O "equatorial" bonds)	$K_2NiF_4$ (layered perovskite)	Layers of $AnO_6$ octahedra sharing vertices along equatorial planes	$K_2UO_4$ $Cs_2PuO_4$ $BaUO_4$
	Rutile	Chains of edge-sharing $AnO_6$ octahedra	$MgUO_4$
CN 6: Octahedron (ideal or slightly distorted)	Closest-packed oxygen layers	$AnO_6$ octahedra sharing <b>no</b> vertices	Ln(IV): $Li_8CeO_6$ An(IV): $Li_8AmO_6$ An(V): $Li_7NpO_6$ An(VI): $Li_6UO_6$ An(VII): $Li_5PuO_6$
	Perovskite or ordered perovskite	$AnO_6$ octahedra sharing <b>all</b> vertices	Ln(III): $LaTiO_3$ An(III): $AmScO_3$ Ln(IV): $SrTbO_3$ An(IV): $BaUO_3$ An(V): $KUO_3$ An(VI): $Ca_3UO_6$ An(VII): $Ba_2NaNpO_6$
CN 6: Elongated octahedron (two long An-O "axial" bonds and four short An-O "equatorial" bonds)	Ordered NaCl	Chains of vertex-sharing $AnO_6$ octahedra	Ln(III): $NaNdO_2$ Ln(IV): $Na_2PrO_3$ $Li_4NpO_5$ $\beta-Na_4UO_5$
CN 8: Cubic (ideal or compressed along a body diagonal)	Distorted $CaF_2$ (fluorite)	Vertex-sharing $AnO_8$ cubes	An(VI): $CaUO_4$ An(VI): $Rb_2U_2O_7$ An(IV): $CaUTi_2O_7$
CN 8: Interpenetrating distorted tetrahedra	Zircon		An(IV): $USiO_4$

can easily be further oxidized). One objective of this study was therefore to attempt to prepare  $\text{CaPrTi}_2\text{O}_7$  and  $\text{CaTbTi}_2\text{O}_7$ , compounds containing the rather unstable  $\text{Pr}^{4+}$  and  $\text{Tb}^{4+}$  ions. The other objective was to compare the structural and bonding of complex oxides that have  $\text{M}^{4+}$  in eightfold and sevenfold coordination with complex oxides that have  $\text{M}^{4+}$  in the more common sixfold coordination.

## EXPERIMENTAL

Syntheses of Ti-containing oxides were carried out by a modified citrate method, similar to that used for  $\text{BaTiO}_3$  [14] and recently for  $\text{Tb}_2\text{Ti}_2\text{O}_7$  [15]. A stock solution of  $\text{Ti}^{3+}$ , Fisher Scientific SO-T-43 "Titanous Chloride Solution 20% Stabilized", was assayed gravimetrically by weighing aliquots, precipitating titanium quantitatively with  $\text{NH}_3(\text{aq})$ , centrifuging, washing, and calcining to  $\text{TiO}_2$ . The solution assay was 5.57 mass per cent Ti. For each preparation, 5.00 ml of this solution was pipetted into two 40-ml centrifuge cones, precipitated quantitatively with  $\text{NH}_3(\text{aq})$ , and centrifuged and washed twice to free it of excess chloride. The hydroxide precipitate (which had air-oxidized from violet  $\text{Ti}^{3+}$  to white  $\text{TiO}^{2+}$ ) was then converted to a sirupy gel by heating in a hot-water bath with 9 g citric acid in ca. 60 ml  $\text{H}_2\text{O}$  for several hours. Weighed amounts of calcined  $\text{CaCO}_3$  and the appropriate lanthanide compound ( $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ ,  $\text{PrO}_2$ ,  $\text{Pr}_6\text{O}_{11}$ , or  $\text{Tb}_{11}\text{O}_{20}$  (other oxides or nitrates of known lanthanide content could have been selected to achieve desired product stoichiometry) were dissolved in dilute nitric acid and mixed thoroughly with the Ti-containing gel. The resulting solutions were evaporated slowly on a hot plate and then calcined to 500 °C in loosely-covered glass beakers. [CAUTION: Citrate decomposition takes place by air combustion, observed sometimes as red-hot burning particles within the beakers. Gradual heating and small samples prevented any overheating, but this procedure should be carried out only on a small scale with appropriate protective equipment.] Bulk samples were thoroughly ground in an agate ball mill for 30 minutes, then calcined in flowing oxygen to 900 °C, pelletized with a hydraulic pellet press, and then calcined in oxygen to 1150 °C or 1350 °C.

Following cooling of the black products, X-ray powder diffraction capillaries were prepared and diffraction patterns were obtained in 57.3-mm diameter Debye-Scherrer cameras with Kodak No-Screen (NS-392) film. 200-mg samples of the same products were heated in a Mettler TA-2 thermal analyzer in flowing air, then reheated in 10%  $\text{H}_2$  - 90% Ar. X-ray diffraction films were read, corrected for film shrinkage by conventional techniques, and indexed as fluorite, perovskite, pyrochlore, and/or zirconolite. Lattice parameters were determined by least-squares reduction with correction for sample absorption [16].

One preparation of  $\text{CaUTi}_2\text{O}_7$  was attempted by dissolving a weighed amount of  $\text{UCl}_4$  in a small excess of dilute hydrochloric acid and proceeding as above, except that, after heating to 500 °C in air, the mixture was calcined to 900 °C for 72 hours in flowing  $\text{N}_2$  in an attempt to prevent its oxidation to hexavalent uranium.

$\text{CaCeZr}_2\text{O}_7$  and  $\text{CaPrZr}_2\text{O}_7$  syntheses were attempted as described above, except that the source of Zr was a reagent labeled " $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ". Since the label had no further analytical information, its Zr content was assayed as 39.2 mass per cent Zr by calcination to  $\text{ZrO}_2$  at 800 °C;  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  would have 34.21 mass per cent Zr.

## RESULTS

Even though each nitrate-citrate preparation mixture was first decomposed by heating to 500 °C, it lost considerable additional weight on heating in the thermal analysis (TGA) apparatus from 500 to 820 °C (Table V). No further weight loss was noted to 1150 °C, nor was there any subsequent weight gain upon slow cooling. When each TGA sample was then reheated in flowing 10% H<sub>2</sub>-90% Ar, CaCeTi<sub>2</sub>O<sub>7</sub> lost weight in two equal steps between 670-770 °C and 850-920 °C that corresponded to an overall change from CaCeTi<sub>2</sub>O<sub>7</sub> to CaCeTi<sub>2</sub>O<sub>6.5</sub>; the Pr and Tb preparations sustained no further weight losses. The colors of the products were as follows: CaCeTi<sub>2</sub>O<sub>7</sub> mustard yellow before the TGA H<sub>2</sub> reduction, "CaPrTi<sub>2</sub>O<sub>7</sub>" pale green before and after the TGA H<sub>2</sub> reduction, CaTbTi<sub>2</sub>O<sub>7-x</sub> white before and cream-colored after TGA reduction, CaCeZr<sub>2</sub>O<sub>7</sub> white before TGA reduction, and "CaPrZr<sub>2</sub>O<sub>7</sub>" pale tan before and after the TGA H<sub>2</sub> reduction. (CaCeZr<sub>2</sub>O<sub>7</sub> was not heated in a reducing atmosphere.) From the TGA results and colors we infer that these products contained Ce<sup>4+</sup>, Pr<sup>3+</sup>, and Tb<sup>3+</sup> when heated in the oxidizing atmosphere, and Ce<sup>3+</sup>, Pr<sup>3+</sup>, and Tb<sup>3+</sup> when heated in the reducing atmosphere. The TGA results and colors of the Pr and Tb preparations following heating in oxygen were surprising, since it is reasonable to expect that they would be mixed-valent or tetravalent compounds under oxidizing conditions.

Mustard-yellow CaCe<sup>VIII</sup>Ti<sub>2</sub>O<sub>7</sub> is a pyrochlore,  $a = 10.142(4)$  Å, with Ce<sup>4+</sup> much more easily reducible than in the perovskite BaCe<sup>VI</sup>O<sub>3</sub>. (Superscript Roman numerals refer to coordination numbers, e.g. Ce<sup>VIII</sup> means CN 8.) As seen in Table VI, the lattice parameter found in this research is significantly smaller than that found earlier [11]. By contrast, a preparation with the stoichiometry CaPrTi<sub>2</sub>O<sub>7-x</sub> is a two-phase mixture of perovskite CaTiO<sub>3</sub> and a presumably Pr<sup>3+</sup> pyrochlore Pr<sup>VIII</sup><sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. [The rare earth pyrochlores M<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> have been reported only for M = Sm through Lu so that this phase may be a solid solution such as (Ca,Pr)<sub>2</sub>Ti<sub>2</sub>O<sub>7-x</sub>.] White CaTbTi<sub>2</sub>O<sub>7-x</sub> appears to be a Tb<sup>3+</sup> pyrochlore,  $a = 10.149(2)$  Å, related to the recently-studied Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [12]. It is surprising that the lattice parameters of Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and CaTbTi<sub>2</sub>O<sub>7-x</sub> are nearly identical (Table VI). Since "CaPrTi<sub>2</sub>O<sub>7-x</sub>" is a two-phase mixture, preparations with the stoichiometry CaCeZr<sub>2</sub>O<sub>7</sub> and CaPrZr<sub>2</sub>O<sub>7-x</sub> were made in the hope that the larger B-site Zr<sup>4+</sup> would enhance the stability of Ce<sup>4+</sup>, Pr<sup>3+</sup>, or Pr<sup>4+</sup> in the A sites, since, for example, the rare earth pyrochlores M<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> are known for M = La through Tb. White CaCeZr<sub>2</sub>O<sub>7</sub> is a pyrochlore,  $a = 10.524(1)$  Å; several unindexable lines were also present (not CaZrO<sub>3</sub>, ZrO<sub>2</sub>, or zirconolite). The CaPrZr<sub>2</sub>O<sub>7</sub> preparation also appeared to yield a two-phase mixture, perovskite CaZrO<sub>3</sub> and pyrochlore Pr<sup>VIII</sup><sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>. A neutron powder diffraction

Table V. Thermogravimetric results on Ln<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> preparations, showing thermogravimetric reduction temperatures of Ln<sup>4+</sup> to Ln<sup>3+</sup> in 10% H<sub>2</sub> - 90% Ar.

CeO <sub>2</sub> (white)	No reduction to 1000 °C
PrO <sub>2-x</sub> (black)	500-600 °C (green after reduction)
TbO <sub>2-x</sub> (dark brown)	440-560 °C (white after reduction)
BaCeO <sub>3</sub> (white)	No reduction to 1150°C
BaPrO <sub>3</sub> (brown)	800-1000 °C (pale green after reduction)
BaTbO <sub>3</sub> (yellow)	570-820 °C (white after reduction)
CaCeTi <sub>2</sub> O <sub>7</sub> (yellow)	670-770 °C, 850-920 °C (two steps)
CaPrTi <sub>2</sub> O <sub>7-x</sub> (pale green)	No weight loss to 1150 °C
CaTbTi <sub>2</sub> O <sub>7-x</sub> (white)	No weight loss to 1150 °C (cream after reduction)

Table VI. Crystallographic results (pyrochlore lattice parameters) on  $\text{CaMTi}_2\text{O}_7$  and  $\text{Ln}_2\text{Zr}_2\text{O}_7$  preparations

<u>Compound</u>	<u>Literature (Å)</u>	<u>This Research (Å)</u>
$\text{CaCeTi}_2\text{O}_7$	fcc, a = 10.211(2) [6]	fcc, a = 10.142(4)
$\text{CaPrTi}_2\text{O}_{7-x}$	Not reported	$\text{CaTiO}_3$ (perovskite)+ $\text{Pr}_2\text{Ti}_2\text{O}_7(?)$ (pyrochlore)
$\text{Tb}_2\text{Ti}_2\text{O}_7$	fcc, a = 10.1516(2) [9]	Not prepared
$\text{CaTbTi}_2\text{O}_{7-x}$	Not reported	fcc, a = 10.149(2)
$\text{CaUTi}_2\text{O}_7$	fcc, a = 10.1579(5) [7]	Not prepared
$\text{CaPuTi}_2\text{O}_7$	fcc, a = 10.132 [8]	Not prepared
$\text{CaCeZr}_2\text{O}_7$	Not reported	fcc; a = 10.524(1)
$\text{CaPrZr}_2\text{O}_7$	Not reported	$\text{CaZrO}_3$ (perovskite)+ $\text{Pr}_2\text{Zr}_2\text{O}_7(?)$ (pyrochlore)

investigation of " $\text{CaPrTi}_2\text{O}_{7-x}$ " and " $\text{CaPrZr}_2\text{O}_{7-x}$ " is in progress to ascertain the site occupancy of all phases found in these preparations.

The uranium preparation " $\text{CaUTi}_2\text{O}_7$ " was black after heating to 900 °C in  $\text{N}_2$ . Its powder pattern was not identifiable. It lost further mass (14.2 %) upon TGA heating in  $\text{O}_2$ . The product was yellow (indicative of  $\text{UO}_2^{2+}$ ) and its powder pattern had changed but was still not identifiable. The black material thus had not fully decomposed. A completely anaerobic preparation (from  $\text{CaO} + \text{UO}_2 + 2 \text{TiO}_2$  in a sealed tube) would have been preferable.

## CONCLUSIONS

Fluorite-related ordered pyrochlore complex oxides  $\text{A}^{4+}\text{A}'^{3+}\text{B}_2\text{O}_{7-x}$  are not suitable for stabilization of 4+ lanthanides but they do appear to stabilize 3+ lanthanides. The oxygen content and oxidation-reduction behavior of  $\text{CaUTi}_2\text{O}_7$  and  $\text{CaPuTi}_2\text{O}_7$  deserve further study. The compound  $\text{CaAmTi}_2\text{O}_{7-x}$  is expected to be an  $\text{Am}^{3+}$  pyrochlore.

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