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New Actinide Matrix with Pyrochlore Structure

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A search for optimal forms of the immobilization of high level radioactive wastes (HLW) has been conducted in various countries for more than forty years. Recently, the disposal of high-actinide wastes acquired a great significance. This is related to the development of methods for HLW separation into fractions and the subsequent immobilization in optimal matrices. The actinide content in the long-lived fraction may reach $10 n$ %. The actinide-bearing residues are also produced during weapons-grade plutonium conversion.

Promising host materials for actinides are pyrochlore-type compounds [1]. In the USA, a host material composed of a pyrochlore-type phase (80–90 vol %), rutile, and brannerite (5–10 vol % each) has been designed to immobilize 17 t of excess Pu [2]. The host material is based on a phase of nominal composition $CaUTi_2O_7$ with Pu and neutron absorbers (Gd, Hf) that inhibit any chain reaction in the preserving material.

The problem of optimal host material for plutonium immobilization has not been conclusively solved. Pyrochlore-type gadolinium zirconate ($Gd_2Zr_2O_7$), whose chemical durability and radiation stability are significantly higher than those of titanate pyrochlores, has been proposed for this purpose [3]. The series of pyrochlore phases, which can serve as possible host materials for actinides, should be extended in order to immobilize the partitioned wastes with more complex composition. In addition to plutonium, the host material must have a high capacity with respect to other actinides (U, Np, Am) and associated Zr and REE. This work presents the results of a study of new crystalline pyrochlore-structured host materials for actinides.

The pyrochlore lattice (space group $Fd3m$, $Z = 8$) is a double-edged fluorite cell, in which half of the cubes lack two diagonal anions [4]. As a result, the phase stoichiometry transforms from $^{VIII}A_4^{IV}X_8$ (four-fold fluorite formula) to $^{VIII}A_2^{VI}B_2^{IV}O_6^{IV}X$, and coordination numbers (CN) of ions are described by relationships AO_6X_2, BO_6, OA_2B_2, and XA_4. A and B are cations in two different structural sites, and X is an additional anion. Oxygen anions are located in apices of the octahedron. They also occupy six of eight apices of the polyhedron with CN = 8. The other two apices are occupied by X anions. The occurrence of two different cationic positions results in a higher ordering of the pyrochlore structure as compared to fluorite structure. More than 500 pyrochlore-type phases, including actinide-bearing varieties, have been synthesized [1–3, 5–10]. Natural pyrochlores consist of tantalite–niobate varieties and often contain high U, Ti, Ca, and REE concentrations.

Structural and chemical features of the pyrochlore-type compounds are interrelated [5–10]. It has been established that the phases with ideal formula $(A^{3+})_2(B^{4+})_2O_7$ have a pyrochlore structure if the $R_A : R_B$ ratio is 1.46–1.80 [9] or 1.46–1.78 [10]. Here, R_A and R_B are ionic radii in A and B sites, respectively. On this basis, one can determine the elements with CN = 8 capable of forming the pyrochlore-type phases with a certain octahedral ion. The relationship between ionic sizes in different sites affects compositional variations of pyrochlores, including possible host materials for the HLW. We studied pyrochlores containing actinides, REE, and Zr. Specific attention has been given to compounds with the perfect stoichiometry $^{VIII}(CaA^{4+})^{VI}(B^{4+})_2O_7$, where A^{4+} = Ce, Th, or U, and B^{4+} = Ti and (or) Zr.

The charge was prepared from oxides, which were ground in an agate mortar to 20–30 μm in size. The powder was pressed at 200–400 MPa into a cylindrical pellet 12–20 mm in diameter and 4–5 mm in height. The pellet was placed into alundum-made crucible and sintered at 1500–1550°C for 6–10 h. The Ce-pyrochlore was synthesized at 1300–1350°C for 5–50 h in a pure oxygen medium. The latter provided element transformation into the tetravalent state required to form pyrochlore. In some cases, the sample was repeatedly ground and heated to accelerate synthesis. The attainment of equilibrium in the system was established by the stable phase composition of the sample with an increase of the run duration. The obtained ceramic was

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Table 1. Phase compositions of the samples and pyrochlore formulas

Calculated composition of charge	Constituent phases	Pyrochlore formula, SEM/EDS data
$CaUTi_2O_7$	Pyr > Br	$Ca_{1.06}U_{0.72}Ti_{2.22}O_{6.94}$
$CaCeTi_2O_7$	Pyr > Pe > Ox	$Ca_{1.03}Ce_{0.99}Ti_{1.98}O_{6.98}$
$Gd_2Ti_2O_7$	Pyr	$Gd_{2.04}Ti_{1.96}O_{6.98}$
$CaThZr_2O_7$	Pyr > Pe ~ Ox	$Ca_{0.91}Th_{0.84}Zr_{2.25}O_{7.09}$
$CaUZr_2O_7$	Ox	No pyrochlore
$(Ca_{0.5}GdTh_{0.5})Zr_2O_7$	Pyr $\gg$ Ox	$(Ca_{0.44}GdTh_{0.42})Zr_{2.13}O_{7.05}$
$(Ca_{0.5}GdU_{0.5})Zr_2O_7$	Ox	No pyrochlore
$(Ca_{0.5}GdTh_{0.5})(ZrTi)O_7$	Pyr $\gg$ Ox	$(Ca_{0.47}Gd_{0.95}Th_{0.40})(Zr_{1.29}Ti_{0.89})O_{7.05}$
$(Ca_{0.5}GdU_{0.5})(ZrTi)O_7$	Pyr > Ox	$(Ca_{0.62}Gd_{0.97}U_{0.23})(Zr_{0.84}Ti_{1.34})O_{6.90}$

Note: (Pyr) pyrochlore, (Br) brannerite, (Pe) perovskite, (Ox) oxide with a fluorite-type lattice.

examined with X-ray diffraction, scanning microscopy, and transmission electron microscopy.

Nine samples with pyrochlore formulas and different patterns of site occupation were studied. Most of them contain pyrochlore as a main or single phase. It occurs in all titanate ceramics (Table 1). Two titanate samples contain brannerite, perovskite, and fluorite-type oxide. In the zirconate host material, pyrochlore was found only in the Th-bearing samples. Perovskite-type and fluorite-type phases were also found there. The Th substitution by U leads to the formation of fluorite-type oxide rather than pyrochlore. The mixed titanate–zirconate ceramics are dominated by pyrochlore with a subordinate amount of fluorite-type oxide.

Actual pyrochlore compositions in samples fall off from perfect stoichiometry. The major difference is a Ca excess as compared to actinides or Ce (Table 1). The lowest atomic ratio of these elements was found in the Ce-pyrochlore synthesized at 1350°C. It increases in the phases prepared at 1500–1550°C and reaches a maximum value in U-bearing pyrochlores. Probably, the occupation of sites with CN = 8 by Ca^{2+} ions rather than tetravalent actinides or Ce, especially at high temperature, is preferable.

We first determined the compositions of most pyrochlores except those produced in the Cd–Ti–O and Ca–U–Ti–O systems. These phases are not highlighted in the X-ray databases. The interplanar spacing d_{222} of the Ce-pyrochlore ($Ca_{1.03}Ce_{0.99}Ti_{1.98}O_{6.98}$) is 0.2930 nm, corresponding to a unit cell dimension of 1.015 nm. Its X-ray diffraction data are most similar to $Tb_2Ti_2O_7$ (card JCPDS #23-565 in the PDF-2 database). Other pyrochlores have the following formulae: $Ca_{0.91}Th_{0.84}Zr_{2.25}O_{7.09}$; $(Ca_{0.44}GdTh_{0.42})Zr_{2.13}O_{7.05}$; $(Ca_{0.47}Gd_{0.95}Th_{0.4})(Zr_{1.29}Ti_{0.89})O_{7.05}$; и $(Ca_{0.62}Gd_{0.97}U_{0.23})(Zr_{0.84}Ti_{1.34})O_{6.9}$.

All of these phases are characterized by a shortage of cations in the eight-coordinated sites. Probably, some portion of the Zr^{4+} ions can also occupy the sites with CN = 8. Unit cell dimensions for these pyrochlores

are 1.23, 1.21, 1.04, and 1.02 nm, respectively, which correlate with the radii of dominating cations.

The pyrochlore structure becomes unstable as a result of the Th substitution by U in the zirconate phases with perfect formulas $CaThZr_2O_7$ and $(Ca_{0.5}GdTh_{0.5})Zr_2O_7$. This is probably related to the fact that the U^{4+} radius (0.100 nm) is smaller than the Th^{4+} radius (0.105 nm). As a result, the ratio of ionic radii for cations in the ^{VIII}[A] and ^{VI}[B] sites decreases and falls beyond the range typical of pyrochlore-type phases. The partial substitution of Zr^{4+} (0.072 nm) by smaller Ti^{4+} (0.061 nm) in the octahedral sites leads to an increase of this ratio, thus providing stability of the pyrochlore structure for phases with ideal stoichiometry $(CaU)(ZrTi)O_7$ and $(Ca_{0.5}GdU_{0.5})(ZrTi)O_7$.

Let us analyze the formation conditions of the pyrochlore lattice for the phases $A_2B_2O_7$ and $(CaA)B_2O_7$, where A is lanthanides or tri- and tetravalent actinides. Among the titanates, this structure is typical of the middle and heavy lanthanides with a small ionic size (Table 2). For germanates (radius of the $^{VI}Ge^{4+}$ ion is smaller than that of Ti^{4+} and reaches up to 0.053 nm), such a structure was obtained for the yttrium group phases under a pressure of 6 GPa [12]. Among hafnates and zirconates, the pyrochlore lattice is typical of the largest lanthanides (La to Gd). Gd and Sm occupy a specific position in this series (Table 2). Zirconate phases with both pyrochlore- and fluorite-type structures were obtained for these elements [10]. The boundary between these modifications runs along 1600 and 2000°C. The pyrochlore-type plumbates are absent due to the excessively large radius of the $^{VI}Pb^{4+}$ ion (0.078 nm). Oxides with a fluorite-type lattice, where REE^{3+} and Pb^{4+} occupy the same sites with CN = 8, are formed instead.

Thus, ionic radii in the six-coordinated site of the lanthanide-bearing pyrochlore-type phases may range between 0.061 nm (Ti^{4+}) and 0.072 nm (Zr^{4+}). The optimal ionic radius is probably located in the middle of this range. For example, Sn can form pyrochlore-type phases with practically all of the lanthanides [7]. It should be noted that Tc^{4+} (0.065 nm) can also be

Table 2. Possible pyrochlore-type phases of REE and actinides (An) with nominal stoichiometry: $^{VIII}REE_2\ ^{VI}B_2O_7$, $^{VIII}An_2\ ^{VI}B_2O_7$, and $^{VIII}(CaAn^{4+})^{VI}B_2^{4+}O_7$

$A^{VIII} = (REE)^{3+}$	Ti^{4+} (0.061 nm)	Sn^{4+} (0.069 nm)	Hf^{4+} (0.071 nm)	Zr^{4+} (0.072 nm)	$A^{VIII} = An^{3+}$ $Ca^{2+} + (An, Ce)^{4+}$
La^{3+} (0.116 nm)	–	+	+	+	
Ce^{3+} (0.114)	–	+	+	+	
Pr^{3+} (0.113)	–	+	+	+	
Nd^{3+} (0.111)	–	+	+	+	Pu^{3+} (0.110)
Pm^{3+} (0.109)	–	+	+	+	Am^{3+} (0.109)
Sm^{3+} (0.108)	+	+	+	±	Ca + Th (0.1085)
Eu^{3+} (0.107)	+	+	+	±	Cm^{3+} (0.108)
Gd^{3+} (0.105)	+	+	+	±	Ca + U (0.106)
	+	+	+	±	Ca + Np (0.105)
Tb^{3+} (0.104)	+	+	+	–	Ca + Ce (0.1045)
	+	+	+	–	
Dy^{3+} (0.103)	+	+	–	–	
Y^{3+} (0.102)	+	+	–	–	
Ho^{3+} (0.102)	+	+	–	–	
Er^{3+} (0.100)	+	+	–	–	
Tm^{3+} (0.099)	+	+	–	–	
Yb^{3+} (0.099)	+	+	–	–	
Lu^{3+} (0.098)	+	–	–	–	

Note: (+) Pyrochlore structure is stable, (–) pyrochlore structure is unstable; (±) structural varieties both of pyrochlore and fluorite types are possible. Ionic radii were taken from [11].

accommodated in the octahedral sites of the pyrochlore lattice. Its long-lived isotope ^{99}Tc ($t_{1/2} > 2 \cdot 10^5$ yr) produced by ^{235}U fission in the nuclear reactor is also ecologically dangerous.

Existing data on the stability of REE-bearing pyrochlores make it possible to evaluate the stability of similar actinide-bearing phases. Ionic radii of Pu^{3+}, Am^3, and Cm^{3+} are close to the radii of Nd^{3+}, Pm^{3+}, and Sm^{3+}. Therefore, actinide compounds can form the pyrochlore structure with the same ion in the octahedral sites as in the REE phases (Table 2). The occurrence of at least four such compounds for Cm and three compounds each of Am and Pu can be suggested. Unlike Cm^{3+}, titanate phases of Pu^{3+} and Am^{3+}, similar to LREE, are crystallized in monoclinic syngony. This is probably related to the fact that their trivalent cations have larger radii than those required for the formation of the pyrochlore-type lattice. In spite of the absence of a cubic lattice for $Pu_2Ti_2O_7$ and $Am_2Ti_2O_7$, pyrochlore-type titanates with significant Pu and Am contents were obtained [13]. In these phases, the lanthanide ions with smaller radii stabilize the pyrochlore lattice. In particular, the $Gd_2Ti_2O_7$-based pyrochlore solid solution incorporates up to 16 mol % $Pu_2Ti_2O_7$. The lanthanide ion radius inversely correlates with the plutonium end member content in pyrochlore to 22% (for $Er_2Ti_2O_7$) and 33% (for $Lu_2Ti_2O_7$). The higher Am content

(61 mol %) was found in the pyrochlore $(Er, Am)_2Ti_2O_7$. The partial substitution of Ti^{4+} ions in the octahedral sites by the larger Hf^{4+} or Zr^{4+} ions will probably lead to the same result, i.e., stabilization of the pyrochlore structure for the $Pu_2(Ti, Hf, Zr)_2O$ phase.

Actinides can be present in crystalline phases in various valence states [1, 9, 10, 14]. In the samples produced at 1200–1600°C in an air or inert argon medium, they normally have a charge of 3+ (Cm, Am) or 4+ (U, Np). Depending on synthesis conditions, plutonium may occur as either Pu^{4+} (in air) or Pu^{3+} (in inert or reducing media). Similar behavior is characteristic of Ce [10, 14]. But Pu is more stable in the tetravalent state, whereas Ce is more stable in the trivalent state. Only a small portion of actinides may occur in the tetravalent form in $A_2B_2O_7$ pyrochlores, e.g., in the phase $(Pu_{2-x}^{3+}Pu_x^{4+})(Hf, Zr)_2O_{7+x}$ [9]. The solubility of tetravalent actinides in the pyrochlore lattice can be increased by the incorporation of a charge compensator such as Ca^{2+}. This is observed in compounds, where trivalent ions are replaced by a pair of di- and tetravalent cations according to the scheme: $2REE^{3+} = Ca^{2+} + Ce^{4+}$ (U^{4+}, Th^{4+}, Np^{4+}, Pu^{4+}). The comparison of radii of these ionic pairs and REE suggests the existence of several pyrochlore-type phases of tetravalent actinides and cerium. The average radius of pairs ($Ca^{2+} + U^{4+}$) and

$(Ca^{2+} + Np^{4+})$ is close to the ionic radius of Gd^{3+}. Pm^{3+} or Sm^{3+} is the counterpart of the Ca^{2+}–Th^{4+} pair, whereas Tb^{3+} is the counterpart for pairs with Ce^{4+} or Pu^{4+} (Table 2).

Pyrochlore with a composition close to $CaUTi_2O_7$ has been obtained experimentally [15]. $Ca(Pu, U, Zr)Ti_2O_7$ and $Ca(Np, Zr)Ti_2O_7$ containing up to 45 wt % PuO_2 and NpO_2 were also synthesized [1]. Stannate pyrochlores with the general formula $(Ca^{2+}An^{4+})(Sn^{4+})_2O_7$ and a ratio of ionic radii in two different structural sites ranging between 1.55 and 1.60 are typical of both lanthanide and actinide varieties.

Data on the compositional and structural correlation must be taken into account to choose the optimal host material for actinide-bearing wastes, especially of complex compositions. The radii of ions in the octahedral sites of the pyrochlore lattice for the phases with REE and trivalent actinides may range between 0.055 and 0.075 nm. Ti^{4+}, Sn^{4+}, Hf^{4+}, and Zr^{4+} satisfy these conditions. Tetravalent actinides will fill eight-coordinated structural sites with simultaneous incorporation of Ca^{2+} cations.

We have synthesized new actinide (Th, U) and cerium pyrochlore phases. As compared to perfect formulas, they are characterized by Ca excess with respect to Ce and actinides. The increase of this ratio with temperature is in good agreement with previously obtained data. The lowest value (1.08) was found in the phases produced at 1250°C [15]. This ratio raises to 1.30 in the pyrochlores prepared at 1350°C [3].

Tc^{4+} with radius 0.065 nm is among other elements that can be located in the octahedral sites of the pyrochlore lattice. Its long-lived isotope ^{99}Tc is produced during [235]U fission. Due to its high hazard, it also should be fixed in stable matrices like pyrochlore.

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