HOST PHASES FOR ACTINIDES AND LONG-LIVED FISSION PRODUCTS TRANSMUTATION/IMMOBILISATION

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Abstract

Transmutation of long-lived actinides and fission products incorporated into solid form under neutron flux is one of ways to reduce significantly their amounts. Phases with pyrochlore structure are of special interest among these matrices. We have analysed formation of this structure for $A_2B^{4+}_2O_7$ and $(CaA)B^{4+}_2O_7$ type compounds, where A = lanthanides, tri- and tetravalent actinides, and B = Ti, Tc, Sn, Zr, Hf. In the lanthanide-bearing pyrochlores, the ionic radii in the six-coordinated site may range between 0.061 nm (Ti^{4+}) and 0.072 nm (Zr^{4+}). Tc^{4+} (r_{VI} = 0.065 nm) can also be accommodated in the octahedral sites of the pyrochlore lattice. For actinides with the same ion dimension as for REEs the pyrochlore structure can be formed. The occurrence of at least four such compounds for Cm and three compounds each of Am and Pu was suggested. To increase significantly tetravalent actinide solubility in the lattice simultaneous incorporation of a charge-compensating ion, such as Ca^{2+}, is required.

Introduction

A search for optimal high level waste (HLW) immobilisation forms has been ongoing in the USA, Australia, Russia, France, UK for more than forty years. [1-3] Actinides are the most troublesome constituent of HLW due to their long half-lives ($2.44 \cdot 10^4$, $2.14 \cdot 10^6$ and $4.32 \cdot 10^2$ years for ^{239}Pu, ^{237}Np and ^{241}Am, respectively), radiation and chemical toxicity. Actinide separation, as specific waste stream of HLW for immobilisation in a stable form, has been proposed as a way of insuring that these actinides are not released to the biosphere. In Russia this process is under implementation at PA "Mayak". [4] Moreover, actinide-bearing residues are produced by weapons plutonium conversion and some solid waste incineration.

Two main routes for long-lived actinides and fission products utilisation exist – immobilisation into durable matrices followed by disposal deeply in the Earth interior or transmuation ("burning") in reactors. Both methods need special materials (waste forms of matrix) in which radionuclides should be incorporated. Desired properties of the matrix are: [5-7] (1) a low neutron absorption cross-section, (2) chemical compatibility with the reactor coolant and fuel, (3) resistance to radiation, (4) high melting point and good thermal conductivity, (5) appropriate physical-mechanical properties: density, strength. Metal and ceramic materials have been considered for this application. [5,6] For example ceramic materials include cubic zirconia (ZrO_2) stabilised in the fluorite structure by additions of CaO, Y_2O_3 MgO or MgO, and spinels $MgAl_2O_4$.

Conventional fabrication processes for waste forms and inert matrix oxide fuels include both dry powder operations and wet processes such as co-precipitation or sol-gel reactions. [7-8] There has been some experience with infiltration of a nitrate solution or oxides of transuranics into inert ceramic particles, followed by calcinations/denitration and sintering. [9]

Promising host phases for plutonium and the other actinides are pyrochlore-structured compounds. [8] In the USA a waste form composed of a pyrochlore-type phase (80-90 vol.%), and 5-10% each of rutile, and brannerite (UTi_2O_6) has been designed. [9] The pyrochlore phase can accommodate both Pu and neutron absorbers (Gd, Hf). One difficulty with the titanate pyrochlore has been a concern for its amorphisation due to alpha-decay events damage. At typical waste loadings (10 wt% Pu-239), this material will become amorphous in less than 800 years of storage/disposal. [10] Numerous investigations were conducted throughout the world to optimise the formulation of Pu-bearing host phases. The REE zirconate pyrochlore exhibits remarkable radiation stability. It will not become amorphous for millions of years, and is chemically durable. [11] In order to immobilise the partitioned waste with complex compositions, additional investigations on the host choice have been required. Host phases for the long-lived fraction of HLW have to be high capable of incorporating both actinides (U, Np, Pu, Am, Cm) and zirconium and rare earth elements (REE). In this paper some new crystalline pyrochlore-structured actinide phases have been synthesised and characterised.

Previous data on actinide pyrochlores stability

The pyrochlore lattice is isometric (*Fd3m*, *Z*=8) with a cell parameter, *a*, that is twice that of the equivalent fluorite structure. [12-13] One-eight of anions are missing. As a result, the stoichiometry transforms from $^{VIII}A_4^{IV}O_8$ (four fluorite molecules) to $^{VIII}A_2^{VI}B_2^{IV}O_6^{IV}X$. Co-ordination numbers (CN) of ions are indicated by the Roman numerals with the following co-ordination geometries: AO_6X_2, BO_6, OA_2B_2 and XA_4, where "A" and "B" are cations in two different structural sites and "X" is an additional anion. Oxygen anions are located at vertices of B-site octahedra and occupy six of the eight apices of a distorted cubic polyhedron with CN = 8. The other two apices of the "cube" are occupied

by "X" anions. Due to occurrence of two different cationic positions the pyrochlore structure is ordered, as compared to the disordered A- and B-site in the fluorite structure. To date more than 500 synthetic pyrochlores including actinide varieties have been synthesised. [13-18] Natural pyrochlores are tantalite-niobate varieties and they often contain high U, Ti, Ca, and REE concentrations. [19,20]

The structure of pyrochlore depends in a sensitive way on composition of the A– and B-site. [11-17] Phases with the ideal formula $A^{3+}_2B^{4+}_2O_7$ have pyrochlore structure if $R_A:R_B$ ratio ranges between 1.46 and 1.80. Here R_A and R_B are average ionic radii in "A" and "B" sites, respectively. On this basis, for any octahedrally coordinated ion in combination with a specific A-site cation (CN = 8) one may predict whether the pyrochlore structure will form. Some compounds exist for which stability of either pyrochlore or fluorite structure depends on temperature. For example, the pyrochlore to fluorite transformation for $Gd_2Zr_2O_7$ occurs at temperature 1 550-1 600°C. [21] Connection between ionic sizes in different sites affects possible compositional variations of pyrochlores, particularly for those that are possible actinide waste hosts. In the paper new pyrochlore-type phases containing actinides, REEs, and zirconium have been studied. Specific attention was focused on compounds $^{VIII}(CaA^{4+})^{VI}B^{4+}_2O_7$, where A^{4+} = Ce, Th, U; and B^{4+} = Ti and/or Zr.

Experimental

Samples with pyrochlore stoichiometry and different schemes for the occupation of the A- and B-sites were synthesised (Table 1). Batches were prepared from oxides milled in an agate mortar to 20-30 μm in size. Powders were compacted under pressure of 200-400 MPa in cylindrical pellets 12-20 mm in diameter and 4-5 mm in height. These pellets were placed in alumina-made crucibles and sintered at 1 500-1 550°C for 6-10 hours. Ce-pyrochlores were synthesised at 1 300-1 350°C for 5-50 hours in pure oxygen medium. The latter transformed cerium to tetravalent state required to form a pyrochlore. In some cases to get better homogenisation once-sintered samples were re-milled and heated again. Evidence for equilibrium in the systems was established by unchanging phase composition of the samples at longer test durations (up to 20 hours). The ceramics produced were examined by X-ray diffraction (XRD) using a DRON-4 (Russian model) and X'pert MPD (Phillips Co.) diffractometers (Cu K_α radiation), scanning electron microscopy with energy dispersive system (SEM/EDS) using a JSM-5300+Link ISIS unit, and transmission electron microscopy (TEM) using a JEM-100c unit equipped with a KEVEX-5100 analyser.

Results

In most of the samples pyrochlore was found to be a major phase (Table 1, Figure 1). Pyrochlore is present in all of the titanate ceramics. Brannerite, perovskite, and fluorite-type oxide also occurred in the samples. Zirconate pyrochlore formed in the samples containing Th. Substitution of U for Th and Ca for Sr yielded a fluorite-type oxide rather than pyrochlore. In the titanate-zirconate ceramics, pyrochlore is the major phase and cubic oxide is minor phase (5-30 vol.%). Pyrochlore compositions do not exhibit perfect stoichiometry (Table 1). This is one explanation for the presence of additional minor phases in the samples (5-10% each of brannerite, perovskite, and fluorite-structured oxide).

Data on $CaUTi_2O_7$ and $CaCeTi_2O_7$ pyrochlores were published earlier. [22,23] The interplanar spacing for d_{222} of the $Ca_{1.03}Ce_{0.99}Ti_{1.98}O_{6.98}$ is 0.2930 nm (unit cell dimension of 1.015 nm), which is close to $Tb_2Ti_2O_7$. Other phases have formulae: $Ca_{0.91}Th_{0.84}Zr_{2.25}O_{7.09}$, $(Ca_{0.44}GdTh_{0.42})Zr_{2.13}O_{7.05}$, $Ca_{0.92}Th_{0.92}Sn_2Fe_{0.08}O_{6.96}$, $(Ca_{0.47}Gd_{0.95}Th_{0.4})(Zr_{1.29}Ti_{0.89})O_{7.05}$, and $(Ca_{0.62}Gd_{0.97}U_{0.23})(Zr_{0.84}Ti_{1.34})O_{6.90}$. The most typical feature of these samples is some deficiency in the A-site cations with eight co-ordination. Probably, some fraction of the Zr^{4+} ions can occupy this site.

Table 1. **Chemical and phase compositions of the samples and calculated pyrochlore formulae**

Target composition	Phases identified	Pyrochlore formulae, SEM/EDS data
$CaUTi_2O_7$	pyrochlore > brannerite	$Ca_{1.06}U_{0.72}Ti_{2.22}O_{6.94}$
$CaCeTi_2O_7$	pyrochlore > perovskite > FSO	$Ca_{1.03}Ce_{0.99}Ti_{1.98}O_{6.98}$
$CaThSn_2O_7$	pyrochlore >> FSO	$Ca_{0.92}Th_{0.92}Sn_{2.00}(Fe_{0.08})*O_{6.96}$
$CaThZr_2O_7$	pyrochlore > perovskite ~ FSO	$Ca_{0.91}Th_{0.84}Zr_{2.25}O_{7.09}$
$CaUZr_2O_7$	FSO	–
$SrThZr_2O_7$	perovskite > FSO	–
$SrThSn_2O_7$	FSO > perovskite	–
$(Ca_{0.5}GdTh_{0.5})Zr_2O_7$	pyrochlore >> FSO	$(Ca_{0.44}GdTh_{0.42})Zr_{2.13}O_{7.05}$
$(Ca_{0.5}GdU_{0.5})Zr_2O_7$	FSO	–
$(Ca_{0.5}GdTh_{0.5})(ZrTi)O_7$	pyrochlore >> FSO	$(Ca_{0.47}Gd_{0.95}Th_{0.40})(Zr_{1.29}Ti_{0.89})O_{7.05}$
$(Ca_{0.5}GdU_{0.5})(ZrTi)O_7$	pyrochlore > FSO	$(Ca_{0.62}Gd_{0.97}U_{0.23})(Zr_{0.84}Ti_{1.34})O_{6.90}$

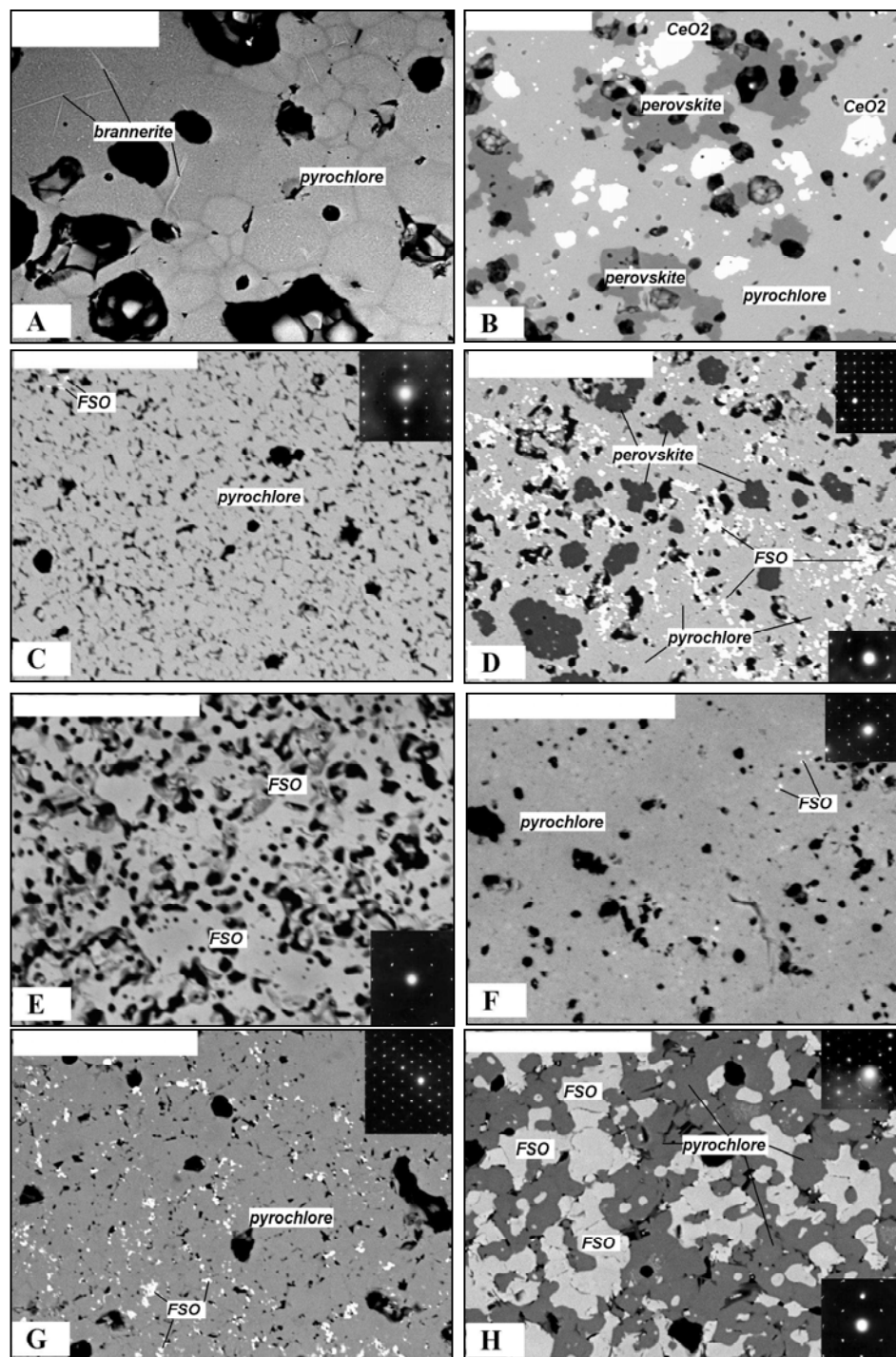FSO – fluorite-structured oxide.   * – due to contamination of batch with iron during the milling.

Substitution of U for Th and Ca for Sr in phases $CaThZr_2O_7$, $(Ca_{0.5}GdTh_{0.5})Zr_2O_7$, and $CaUSn_2O_7$ makes pyrochlore structure instable. This is probably because U^{4+} or Ca^{2+} radii (0.100 and 0.112 nm) are less than those of Th^{4+} or Sr^{2+} (0.105 and 0.126 nm). As a result the ratio of ionic radii for cations in the $^{VIII}[A]$ and $^{VI}[B]$ sites decreases and falles outside of the range typical of pyrochlore-type structures. Partial substitution of smaller Ti^{4+} (0.061 nm) for Zr^{4+} (0.072 nm) in the octahedral sites may lead to an increase in this ratio; thus, providing for the stability of the pyrochlore structure for the phases with ideal stoichiometry: $(CaU)(ZrTi)O_7$ and $(Ca_{0.5}GdU_{0.5})(ZrTi)O_7$.

Discussion

We have analysed conditions that lead to formation of the pyrochlore structure for $A_2B_2O_7$ and $(CaA)B_2O_7$, where A = lanthanides or tri- and tetravalent actinides, compositions. Among the titanates this structure is typical of intermediate and heavy lanthanides with small ionic radii (Table 2). For germanates (radius of $^{VI}Ge^{4+}$ ion is smaller than Ti^{4+} and equal to 0.053 nm) the pyrochlore structure was obtained for phases of the small REEs (Y group) only and under very high pressure (6 GPa). [24] Among hafnates and zirconates pyrochlore lattice is typical of the largest lanthanides from La to Gd. Gd, Eu, and Sm take up in this row a specific position (Table 2). For these elements both pyrochlore- and fluorite-structured phases with the same composition were obtained. [18] The temperature boundary between these structural varieties occurs between 1 600 and 2 300°C. Pyrochlore-structure plumbates do not occur due to large radius of $^{VI}Pb^{4+}$ ion (0.078 nm). Oxides with fluorite lattice, where REE^{3+} and Pb^{4+} occupy the same sites with CN = 8, are formed instead of pyrochlore.

Thus, for the lanthanide-bearing pyrochlore-type structures, the ionic radii in the six-coordinated site may range between 0.061 nm (Ti^{4+}) and 0.072 nm (Zr^{4+}). The optimum ionic radius is in the middle part of this range. For example, tin can form pyrochlore-type phases with almost all of the lanthanides. [15] Tc^{4+} (r = 0.065 nm) takes an intermediate position between Ti^{4+} (r = 0.061 nm) and Sn^{4+} (r = 0.069 nm) and, therefore, can also be accommodated inth the octahedral sites of pyrochlore lattice. This may be important for immobilisation of long-lived ^{99}Tc ($T_{1/2}$ = 2.13·10^5 years), which is ecologically dangerous product of ^{235}U fission in the nuclear reactor. Existing data on rare earth pyrochlores provides evaluation of stability for similar actinide-bearing phases. Ionic radii of Pu^{3+}, Am^{3+}, and Cm^{3+} are close to radii of Nd^{3+}, Pm^{3+}, and Sm^{3+}. Therefore, for actinide compounds with the same ion in the octahedral sites as for REEs phases the pyrochlore structure can be formed (Table 2). The occurrence of at least four such compounds for curium and three compounds each of americium and plutonium can be suggested (Table 2).

Figure 1. **SEM images of the ceramics with nominal stoichiometry: $CaUTi_2O_7$ (A, see Table 1), $CaCeTi_2O_7$ (B), $CaThSn_2O_7$ (C), $CaThZr_2O_7$ (D), $CaUZr_2O_7$ (E), $(Ca_{0.5}GdTh_{0.5})Zr_2O_7$ (F), $(Ca_{0.5}GdTh_{0.5})(ZrTi)O_7$ (G), and $(Ca_{0.5}GdU_{0.5})(ZrTi)O_7$ (H). Scale bars are equal to 50 μm**

Insets: electron diffraction patterns for pyrochlore-type (top) or fluorite (bottom) lattice.

Unlike Cm^{3+}-titanate, phases of Pu^{3+} and Am^{3+}, as well as of the light REEs (from La to Nd), form monoclinic ($P2_1$) or orthorhombic ($Pna2_1$) structures. This is probably due to larger ionic radii of their trivalent cations than is required to form pyrochlore type lattice. In spite of absence of a cubic lattice for $Pu_2Ti_2O_7$ and $Am_2Ti_2O_7$, pyrochlore-structured titanates with significant Pu and Am contents have been previously obtained. [25] In these phases the lanthanide ions with smaller radii stabilise pyrochlore structure. In particular, $Gd_2Ti_2O_7$-based pyrochlore solid solution has been established to incorporate up to 16 mol.% $Pu_2Ti_2O_7$. As radius of lanthanide ion decreases, the content of the plutonium pyrochlore end-member increases to 22 mol. % for $Er_2Ti_2O_7$ and 33 mol.% for $Lu_2Ti_2O_7$. Americium content in the pyrochlore $(Er,Am)_2Ti_2O_7$ was found to be 61 mol. %. [25] Replacement of some of Ti^{4+} ions in the octahedral sites by larger Hf^{4+} or Zr^{4+} ions will lead to the same result: stabilisation of the pyrochlore structure for phase with $Pu_2(Ti,Hf,Zr)_2O_7$ composition. [17]

Actinides can be present in waste (and crystalline phases) in various valence states [7,8,17,18,27]. In the samples produced at 1 200-1 600°C in air or inert argon medium, actinides normally have a formal charge 3+ (Cm, Am) or 4+ (U, Np). Plutonium may occur as either Pu^{4+} (in air) or Pu^{3+} (in inert or reducing gas media). Similar behaviour is characteristic of Ce. [23,27] The difference between Pu and Ce is the higher stability of tetravalent state for Pu and trivalent state for Ce. Small fraction of the total actinide content may be incorporated into $A_2B_2O_7$ pyrochlores in the tetravalent form as, for example, in the phase $(Pu^{3+}_{2-x}Pu^{4+}_x)(Hf,Zr)_2O_{7+x}$ [17] To increase tetravalent actinide solubility in the pyrochlore structure, simultaneous incorporation of a charge compensating cation, such as Ca^{2+}, is required. This leads to compounds for which trivalent ions are replaced by pair of di- and tetravalent cations according to the scheme: $2REE^{3+} = Ca^{2+}+Ce^{4+}$ (U^{4+}, Th^{4+}, Np^{4+}, Pu^{4+}).

Table 2. **Possible pyrochlore-type structure for phases of REEs and actinides (An) with nominal stoichiometry:** $^{VIII}REE_2{}^{VI}B_2O_7$, $^{VIII}An_2{}^{VI}B_2O_7$, and $^{VIII}(CaAn^{4+})^{VI}B^{4+}{}_2O_7$

$A^{VIII} = REE^{3+}$	Ti^{4+} (0,061 nm)	Sn^{4+} (0,069 nm)	Hf^{4+} (0,071 nm)	Zr^{4+} (0,072 nm)	$A^{VIII} = An^{3+}$, $Ca^{2+}+(An,Ce)^{4+}$
	-	-	-	-	Sr+Th (0,116)
La^{3+} (0,116 nm)	-	+	+	+	
Ce^{3+} (0,114 nm)	-	+	+	+	
Pr^{3+} (0,113 nm)	-	+	+	+	
Nd^{3+} (0,111 nm)	-	+	+	+	Pu^{3+} (0,110)
Pm^{3+} (0,109 nm)	-	+	+	+	Am^{3+} (0,109)
Sm^{3+} (0,108 nm)	+	+	+	±	Ca+Th (0,1085)
Eu^{3+} (0,107 nm)	+	+	+	±	Cm^{3+} (0,108)
Gd^{3+} (0,105 nm)	+	+	+	±	Ca+U (0,106)
	+	+	+	±	Ca +Np (0,105)
Tb^{3+} (0,104 nm)	+	+	+	-	Ca+Ce (0,1045)
	+	+	+	-	Ca+Pu (0,104)
Dy^{3+} (0,103 nm)	+	+	-	-	
Y^{3+} (0,102 nm)	+	+	-	-	
Ho^{3+} (0,102 nm)	+	+	-	-	
Er^{3+} (0,100 nm)	+	+	-	-	
Tm^{3+} (0,099 nm)	+	+	-	-	
Yb^{3+} (0,099 nm)	+	+	-	-	
Lu^{3+} (0,098 nm)	+	-	-	-	

(+) pyrochlore structure is stable;
(-) instable;
(±) structure varieties both of pyrochlore and fluorite types are possible.
Ionic radii of the cations were taken from ref. [26].

Average radii of pairs ($Ca^{2+}+U^{4+}$) and ($Ca^{2+}+Np^{4+}$) are close to ionic radius of Gd^{3+}. For the Ca^{2+}-Th^{4+} pair such an analog is Pm^{3+} or Sm^{3+} and for the pairs with Ce^{4+} or Pu^{4+} - Tb^{3+} (Table 2). We suggest, based on comparison of radii of the ionic pairs and REEs, that phases of tetravalent actinides and cerium with pyrochlore structure may form. Pyrochlores with a composition close to $CaCeTi_2O_7$ and $CaUTi_2O_7$ have been obtained experimentally. [22,23] Pyrochlores $Ca(Pu,U,Zr)Ti_2O_7$ and $Ca(Np,Zr)Ti_2O_7$ containing up to 45 wt.% PuO_2 and NpO_2 have also been synthesised. [8] Stannate pyrochlores with formula ($REE_2/Ca^{2+}An^{4+})Sn^{4+}_2O_7$ and ratio of ionic radii in two different structural sites ranged between 1.55 and 1.60 are typical of lanthanide [15] and actinide varieties as well. We have also produced Ca-Th-Sn-pyrochlore (Table 1). Data on the correlation between composition and structure in the pyrochlore group must be considered in designing an actinide host phase, especially in the case of complex waste stream compositions. Radii of ions in the octahedral sites of the pyrochlore structure for the phases with REEs and trivalent actinides may range between 0.055 and 0.075 nm. This condition corresponds to radii of Ti^{4+}, Sn^{4+}, Hf^{4+}, and Zr^{4+} ions. Tetravalent actinides can easily occupy the eight-coordinated A-sites at simultaneous incorporation of Ca^{2+} as charge compensators.

Conclusions

Transmutation of long-lived actinides and fission products by neutron flux is suggested now as promising way to reduce significantly their amounts. The other way is immobilisation of the nuclides in durable matrices for further ultimate disposal in the Earth. Among the materials suggested as the host phases oxides with fluorite structure (stabilized ZrO_2) are of special interest. Pyrochlore phases with formula $^{VIII}A_2{}^{VI}B_2O_6X$ (X – additional anion in specific position, usually O^{2-}) and fluorite-derived structure (space group $Fd3m$) are also promising hosts for this goals. In this structure two cation's structural sites are present allowing simultaneous incorporation both of large actinides and REEs in the eight-coordinated [A] sites and smaller fission products and Zr in the six-coordinated [B] positions.

We have analysed the conditions of formation of the pyrochlore structure for the $A_2B^{4+}_2O_7$ and $(CaA)B^{4+}_2O_7$ compounds, where A = lanthanides, tri- and tetravalent actinides, and B = Ti, Sn, Zr, Hf. In the lanthanide-bearing pyrochlores, the ionic radii in the six-coordinated site may range between 0.061 nm (Ti^{4+}) and 0.072 nm (Zr^{4+}). Tin can form pyrochlore-type phases with almost all of the lanthanides. Tc^{4+} (r_{VI} = 0.065 nm) takes an intermediate value between Ti^{4+} (r = 0.061 nm) and Sn^{4+} (r = 0.069 nm) and, therefore, can also be accommodated in the octahedral sites of the pyrochlore lattice. Ionic radii of Pu^{3+}, Am^{3+}, and Cm^{3+} are close to radii of Nd^{3+}, Pm^{3+}, and Sm^{3+}. For actinides with the same ion dimension as for REEs the pyrochlore structure can be formed. The occurrence of at least four such compounds for Cm and three compounds each of Am and Pu was suggested. To increase tetravalent actinide solubility simultaneous incorporation of a charge-compensating ion, such as Ca^{2+}, is required. Trivalent ions are replaced by pair of di- and tetravalent cations according to the scheme: $2REE^{3+}$ = $Ca^{2+}+Ce^{4+}$ (U^{4+}, Th^{4+}, Np^{4+}, Pu^{4+}). Average radii of pairs ($Ca^{2+}+U^{4+}$) and ($Ca^{2+}+Np^{4+}$) are close to the ionic radius of Gd^{3+}. For the Ca^{2+}-Th^{4+} pair such an analog is Pm^{3+} or Sm^{3+} and for the pairs with Ce^{4+} or Pu^{4+} - Tb^{3+}. Stannate pyrochlores with formula ($REE_2/Ca^{2+}An^{4+})Sn^{4+}_2O_7$ and ratio of ionic radii in two different structural sites ranged between 1.55 and 1.60 are typical of lanthanide and actinide varieties as well.

New actinide (Th, U) and cerium pyrochlore phases have been synthesised by cold pressing and sintering. In most of the samples pyrochlore was found to be a major phase. Pyrochlore is present in all of the titanate ceramics. Brannerite, perovskite, and fluorite-type oxide also occurred in the samples. Zirconate pyrochlore formed in samples containing Th. Substitution of U for Th and Ca for Sr yielded a fluorite-type oxide or perovskite rather than pyrochlore. This is probably because U^{4+} and Ca^{2+} radii are less than those of Th^{4+} and Sr^{2+}. As a result the ratio of ionic radii for cations in the ^{VIII}[A] and ^{VI}[B] sites is lower and outside of the range typical of pyrochlore-type structures. Partial

substitution of smaller Ti^{4+} (0.061 nm) for Zr^{4+} (0.072 nm) in the octahedral sites may lead to an increase in this ratio; thus, providing for the stability of the pyrochlore structure for the phases with ideal stoichiometry: $(CaU)(ZrTi)O_7$ and $(Ca_{0.5}GdU_{0.5})(ZrTi)O_7$. In the titanate-zirconate ceramics, pyrochlore is the major phase and cubic oxide is minor phase (5-30 vol.%). The measured pyrochlore compositions do not exhibit perfect stoichiometry. This is explanation for the presence of additional minor phases in the samples (5-10% each of brannerite, perovskite, and fluorite-structured oxide).

Compositions of the most of pyrochlores, except those produced in the system Ca-U-Ti-O and Ca-Ce-Ti-O have been established for the first time. Diffraction data on these phases in databases are also absent. The interplanar spacing for d_{222} of the Ce-pyrochlore $Ca_{1.03}Ce_{0.99}Ti_{1.98}O_{6.98}$ is 0.2930 nm corresponding to unit cell dimension of 1.015 nm, which is close to $Tb_2Ti_2O_7$ (#23-565). The other phases have formulae: $Ca_{0.91}Th_{0.84}Zr_{2.25}O_{7.09}$, $(Ca_{0.44}GdTh_{0.42})Zr_{2.13}O_{7.05}$, $Ca_{0.92}Th_{0.92}Sn_{2.00}Fe_{0.08}O_{6.96}$, $(Ca_{0.47}Gd_{0.95}Th_{0.40})(Zr_{1.29}Ti_{0.89})O_{7.05}$, and $(Ca_{0.62}Gd_{0.97}U_{0.23})(Zr_{0.84}Ti_{1.34})O_{6.90}$. Typical feature of these samples is deficiency in A-site cations in the eight-coordinated sites. Probably, some fraction of the Zr^{4+} ions can also occupy this site.

Considering ability of the pyrochlore-structure phases to accommodate high amounts of tri- and tetravalent actinides and some long-lived fission products, their resistance to radiation and hot water attack, the phases may be suggested as appropriate hosts for utilisation of the dangerous radionuclides.

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