Actinide Complex Oxides

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Muratite–Pyrochlore Series: A Family of Complex Oxides with Nanoscale Pyrochlore Clusters**

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One of the most important problems related to the use of nuclear energy and the advanced nuclear fuel cycle is immobilization of plutonium and minor actinides, as well as of rare earth fractions and corrosion products present in high-level radioactive waste (HLW).[1] The most enduring proposal was made by Ringwood et al.,[2] who invented Synroc, a polyphase waste form consisting of titanates. In Synroc, actinides are incorporated mainly in pyrochlore and zirconolite, two closely related complex oxides based on 3D frameworks of TiO_6 octahedra.[3] In 1982, Morgan and Ryerson[4] identified another titanate phase, a synthetic analogue of muratite,[5] in a titanate ceramic containing HLW imitators produced at the Savannah River nuclear plant in the USA. In 1997, Laverov et al.[6a] identified muratite in a Synroc matrix with imitators of HLRWs from PO Mayak, a radiochemical facility for production and reprocessing of nuclear fuel in the Russian Federation. Five volume percent of this phase accumulated about 40% of the total uranium present in the sample, and this led to detailed investigations of the chemistry and properties of muratite, in particular, its chemical durability and radiation resistance.[6] However, structural mechanisms of incorporation of actinides into muratite remained unknown up to date. Here we report results of structural investigations on one of muratite varieties that provide direct evidence for existence of a family of complex Ti-based oxides consisting of nanoscale pyrochlore clusters connected through muratite-related structural units.

The structure of muratite, $(Y,Na)_6(Zn,Fe)_5Ti_{12}O_{29}(O,F)_{10}F_4$,[5b] is based on a nanoporous 3D framework consisting of polymerized α-Keggin $[Zn^{[4]}Ti^{[6]}{}_{12}O_{40}]^{30-}$ clusters with T_d symmetry (Figure 1a). Polymerization of Keggin units results in creation of two types of voids that can be characterized as a truncated tetrahedron 3^46^4 (Figure 1b) and cubooctahedron 4^66^8 (Figure 1c). In terms of nodal representation, the Keggin cluster can be characterized as a 3^84^6 cubooctahedron (Figure 1a). The framework accommodates a complex fluorite-like substructure of Y, Fe, and Na cations and O^{2-} and F^- anions. Muratite (as well as pyrochlore) can also be considered as a $3\times3\times3$ anion-deficient fluorite structure with ordered arrangement of cations. By analogy, pyrochlore has a $2\times2\times2$ fluorite superstructure (Figure 2).

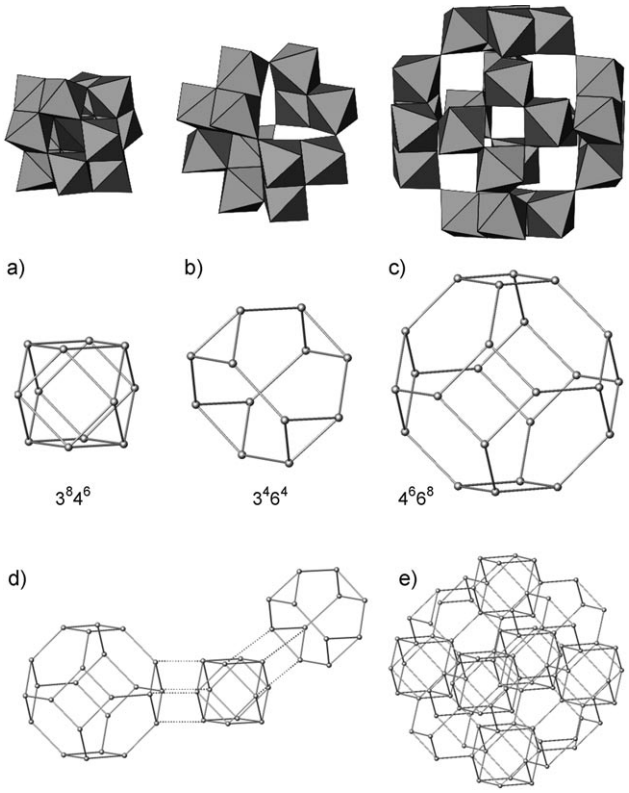

Figure 1. Basic polyhedral units making up the octahedral framework in the structure of natural muratite: cubooctahedron 3^84^6 (a), truncated tetrahedron 3^46^4 (b), cubooctahedron 4^66^8 (c), their linkage mode (d), and the resulting 3D network (e). In a–c), light gray and dark gray polyhedra are TiO_6 octahedra and ZnO_4 tetrahedra, respectively.

Transmission electron microscopy studies[6b] identified synthetic muratite varieties with $3\times3\times3$, $5\times5\times5$, $7\times7\times7$, and $8\times8\times8$ cubic supercells referred to as Mu-3, Mu-5, Mu-7 and Mu-8, phases. In muratite ceramic, typical grains contain

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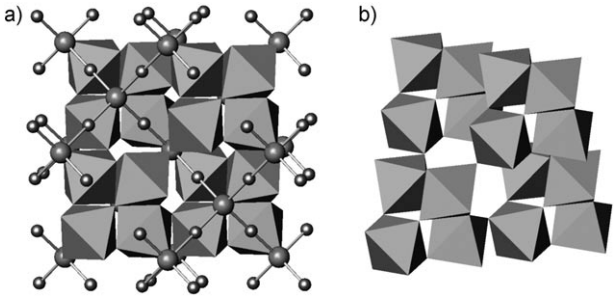

Figure 2. Structure of pyrochlore $A_2B_2O_6O'$ shown as consisting of an octahedral $[B_2O_6]$ framework (light brown) and a $[A_2O']$ framework of corner-sharing oxo-centered $O'A_4$ tetrahedra (O' and A atoms are shown as large and small circles, respectively) (a), and the unit-cell portion of the octahedral framework (b).

pyrochlore and Mu-5 at the core surrounded by Mu-8 and Mu-3 (Figure 3).[6i] In the current work, we studied a sample of murataite ceramic consisting of zoned crystals with Mu-5 as

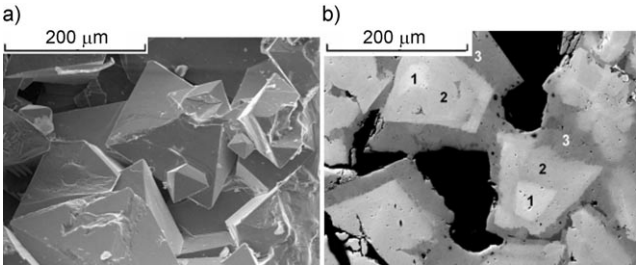

Figure 3. SEM images of octahedral murataite crystals and their cross section. 1–3: murataite Mu-5, Mu-8, and Mu-3 varieties with ThO_2 contents of 12.6, 10.9, and 5.1 wt%, respectively.

a major grain component. Solution of its crystal structure revealed an unusually complex octahedral framework with cavities occupied by non-octahedral cations and "additional" O atoms. The framework consists of cubic pyrochlore clusters with a diameter of 1.5 nm. These clusters represent pyrochlore cubic unit cells (Figure 2b) and are arranged within the Mu-5 cubic unit cell in a 3D chessboardlike fashion (Figure 4a). The pyrochlore clusters are formed by $Ti1O_6$ and $Ti4O_6$ octahedra and are linked through $Ti3O_6$ octahedra (Figure 4b). The $Ti2O_6$ and $Ti5O_6$ octahedra form a framework (Figure 4c,d) based on two polyhedral units derived from the structure of murataite Mu-3: a truncated tetrahedron 3^46^4 (Figure 1b) formed by Ti2 and cubooctahedron 4^66^8 (Figure 1c) formed by Ti5 atoms (Figure 5). In contrast to the structure of murataite Mu-3, 3^46^4 and 4^66^8 units do not share hexagonal faces, but unite through linkage of a triangular face of 3^46^4 and a hexagonal face of 4^66^8 to form a truncated pyramid $3^43^61^1$ (Figure 5b). The basic polyhedral units 3^46^4 and 4^66^8 in Mu-5 are geometrically identical to those observed in Mu-3. In contrast to Mu-3, the structure of Mu-5 contains no Keggin polyanionic clusters. In the structure of Mu-5, the subframework of linked pyrochlore clusters and the subframework of murataite-like units communicate by sharing those

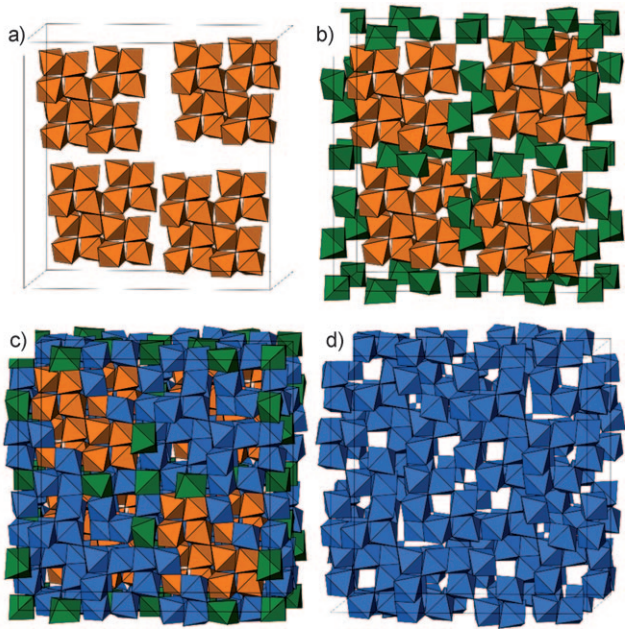

Figure 4. Octahedral framework in the structure of Mu-5: arrangement of pyrochlore clusters formed by corner sharing of $Ti1O_6$ and $Ti4O_6$ octahedra (a), linkage of pyrochlore clusters by $Ti3O_6$ octahedra (b), whole framework as combination of linked pyrochlore clusters and murataite-like framework formed by $Ti2O_6$ and $Ti5O_6$ octahedra (c), and murataite-like framework (d).

corners of TiO_6 octahedra which are not involved in the subframework constructions.

The stoichiometry of the octahedral framework is rather complex and has no analogues among known octahedral frameworks. Its formula can be written as $[(Ti,Zr)_{29}O_{86}]^{56-}$. The Mn and M cations as well as O' atoms not linked to the Ti sites form a fluorite-type substructure with each O' atom being at the center of $O'A_4$ oxo-centered tetrahedron, similar to the situation observed in pyrochlore and other fluorite-related framework materials. Taking into consideration this substructure, a general structural formula of Mu-5 can be written as $Mn_8M_{59}O_{39}[(Ti,Zr)_{29}O_{86}]_2$.

As seen from Figure 4, the whole framework of the Mu-5 structure contains modules of essentially pyrochlore (Figure 4b) and murataite Mu-3 (Figure 4d) structures, as originally proposed by Urusov et al.[6f,h] Pyrochlore is a $2\times2\times2$ fluorite superstructure, and murataite a $3\times3\times3$ fluorite superstructure. Their isometric combination results in the $(2n+3m)\times(2n+3m)\times(2n+3m)$ superstructures, of which $5\times5\times5$ ($n=1$, $m=1$), $7\times7\times7$ ($n=2$, $m=1$), and $8\times8\times8$ ($n=1$, $m=2$) superstructures are the first and simplest members of the polysomatic series. Indeed, the structure of Mu-5 described here is a combination of single pyrochlore unit cells with recombined murataite framework and thus is a rare case of a 3D polysomatic structure[7] constructed from two parent frameworks.

As mentioned above, pyrochlore is one of the most promising hosts for actinide immobilization in terms of actinide load, radiation resistance, and chemical durability. The current study reveals that the murataite–pyrochlore polysomatic series is based on incorporation of high-actinide

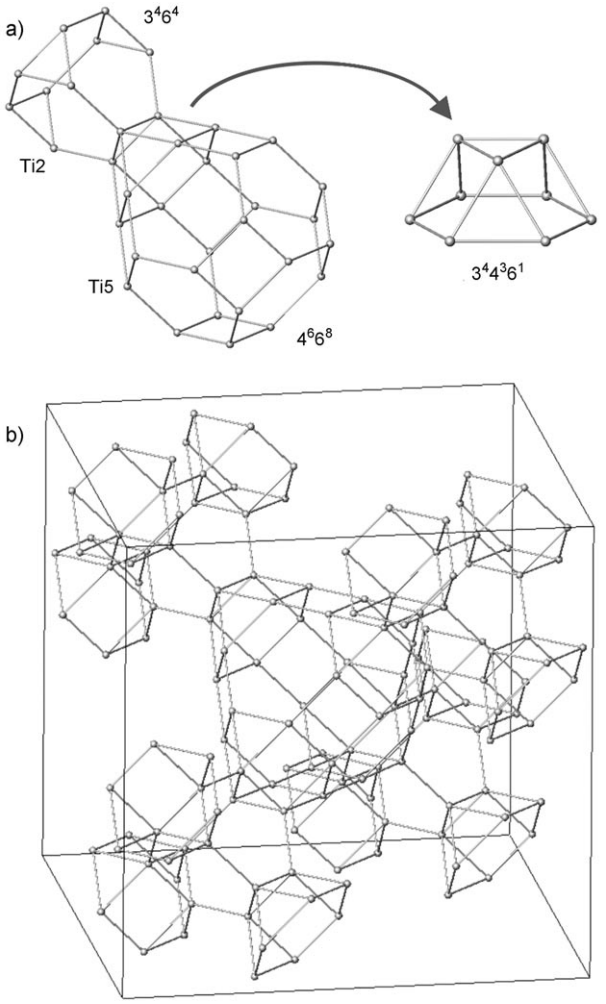

Figure 5. Description of the murataite-like subframework in the structure of Mu-5: linkage of the 3^46^4 and 4^66^8 units through a trigonal face of the former and a hexagonal face of the latter results in formation of $3^43^61^1$ unit (a); nodal representation of murataite-like subframework (b).

pyrochlore nanoclusters into modified murataite-like frameworks with cavities that may accommodate not only actinides but also Mn, Fe, Al, Ca, Sr, Na, and other cations present in HLWs as admixtures and corrosion products. In this context, complex oxides from the murataite–pyrochlore series may be viewed as a complex form of waste and probably the most elaborate family of complex oxides tuned at nanoscale dimensions known to date.

Experimental Section

In a typical synthesis of murataite ceramics, the initial mixture contained (in wt%): 55 TiO_2, 10 MnO, 10 CaO, 5 Al_2O_3, 5 Fe_2O_3, 5 ZrO_2, and 10 AnO_2 (An = Th, U, Np, Pu). The ceramic was obtained by cold compaction combined with sintering at 1100–1300 °C, by melting in an electric furnace at 1500 °C with subsequent cooling to room temperature, or by induction melting in a cold crucible (IMCC) at 1600 °C. Chemical composition of the Mu-5 sample used in this study was determined by energy-dispersive X-ray spectroscopic analysis to be $Ca_{3.17}Mn_{1.39}U_{0.92}Zr_{0.79}Ti_{8.57}Fe_{0.30}Al_{0.34}O_{26.09}$. Single-crystal X-ray diffraction data for Mu-5 were collected at 293 K on a Bruker APEX II charge-coupled device (CCD) diffractometer: cubic, $F\bar{4}3m$, $a = 24.564(7)$ Å, $V = 14822(7)$ Å^3, $\rho_{calcd} = 4.98$ g cm^{-3}, $\mu = 14.797$ mm^{-1}, $2\theta_{max} = 56°$, $\lambda = 0.71073$ Å; total reflections 41848; unique reflections 1762 [$R_{int} = 0.0470$]; R_1 [$I > 2\sigma(I)$] = 0.074, $wR_2 = 0.231$; GOF = 0.936. The model accounted for racemic twinning (Flack parameter 0.45(3)). Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-422137. The crystal chemical formula derived from structure refinement and determined on the basis of site-scattering power of cation sites (see Supporting Information) is $Ca_{24.47}Mn_{21.97}U_{7.71}Al_{2.46}Ti_{59.84}Zr_{8.56}O_{172}$, which is in reasonable agreement with the formula derived from electron microprobe analysis.

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