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Novel Open-Framework Material: Cerium Oxyfluoride with CeO_6F_2 Dodecahedron

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Both natural and synthetic zeolites and molecule sieves have found extensive applications as sorbents, ion-exchangers, and catalysts.[1,2] Attempts to synthesize novel open-framework materials with new framework atoms, basic unit structural types, and channel structures beyond conventional aluminosilicate zeolites have led to extensive research. Aluminophosphate,[3] gallophosphate,[4] zincophosphate,[5] cobalt[6] phosphate, titanosilicate,[7] and germanium oxide[8] have been prepared. Meanwhile, coordination polyhedra such as trigonal pyramids or octahedra are also shown to exist in structures of them. The recent expansion of the fluoride synthetic method in hydrothermal systems opened the new path to molecular sieves with novel structures,[9] for example, ZrPOF-*n*,[10,11] ULM-*n*,[12,13] and TREN-GaPO,[14] in the structures of which fluoride atom serves as a terminal or bridge group. However, no open-framework materials incorporating lanthanide or actinide elements had been obtained, until O'Hare et al.[15] reported the first open-framework actinide oxyfluoride MUF-1 last year. To our knowledge it is the only reported example of open-framework materials constructed from actinide oxyfluoride so far.

Metal oxyfluorides, due to their intriguing properties such as superconductivity,[16] attracted exploratory syntheses. Hydrothermal methods have proved to be invaluable for the synthesis of almost all kinds of recently important materials such as superionic conductors,[17] magnetic materials,[18] and metal glycolates,[19] in particular microporous and mesoporous molecular sieves.[20,21] In the present work, a novel open-framework lanthanide material, cerium oxyfluoride, has been hydrothermally crystallized. In the structure of the compound, a cerium-

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Table 1. Atomic Coordinates and B_{eq} for YU-1

atom	*x*	*y*	*z*	occ	B_{eq}
Ce(1)	0.60948(3)	0.46401(3)	0.99860(3)	1.0000	0.923(5)
F(1)	0.7138(3)	0.6142(3)	0.0646(4)	1.0000	1.46(7)
F(2)	0.6102(3)	0.4527(3)	0.1997(4)	1.0000	1.62(7)
O(1)	0.5490(3)	0.5511(3)	0.9285(4)	1.0000	0.65(5)
O(2)	0.7521(4)	0.4555(4)	0.0387(5)	1.0000	1.59(9)
O(3)	0.5031(4)	0.3771(3)	0.8363(4)	1.0000	1.37(7)
N(1)	0.7497(5)	0.6402(5)	0.3246(6)	1.0000	2.0(1)
N(2)	0	0	0	0.1667	2.3(2)

centered dodecahedron (CeO_6F_2) as a new lanthanide-containing basic building unit is incorporated into the framework. Six CeO_6F_2 dodecahedra link to form a three-ring possessing an octahedral $Ce_6O_{24}F_{12}$ cage, and connect to one another via bridging oxygen atoms to give rise to a three-dimensional channel system with an eight-ring pore opening. The inner surface of the channels covered with terminal fluorine atoms of the framework forms the unique shape of the pore openings. At the intersections of the channels, there are large supercages with the longest body diagonal of 17 Å.

Our new cerium oxyfluoride is denoted as YU-1 (Yamanashi University Number 1). YU-1 with a formula of $H_{25.5}(NH_4)_{10.5}Ce_9O_{27}F_{18}$ was synthesized using a starting composition of 1.0 $Ce(SO_4)_2$/0.5 H_3PO_4/1.5 $H_2N(CH_2)_2NH_2$/4.0 NH_4F/150 H_2O. This mixture was heated at 160−180 °C for 3−8 days in Teflon-lined stainless steel autoclaves. The crystalline product was filtered and washed with deionized water and ethanol and then dried in air at ambient temperature. YU-1 was prepared in a yield of 20−30%. This preparation also gave crystals of a new open-framework cerium phosphate fluoride.[22] Although many reaction variations have been attempted, the optimum reaction conditions for the preparation of YU-1 have not yet been discovered. However, the amounts of the cerium source and the acidity of the system were found to be the dominant synthetic factors. Thermal analysis of YU-1 with minor cerium phosphate fluoride indicated that YU-1 could be stable up to ∼400 °C.

A transparent tetrahedral crystal with approximate dimensions of $0.12 \times 0.12 \times 0.12$ mm^3 was selected for single-crystal X-ray analysis.[23] The result indicates that YU-1 crystallizes in the trigonal system space group $R\bar{3}$ (No. 148) with $a = 15.252(8)$ Å, $c = 10.749(4)$ Å, and $Z = 3$. The coordinates and temperature factors for YU-1 are listed in Table 1.

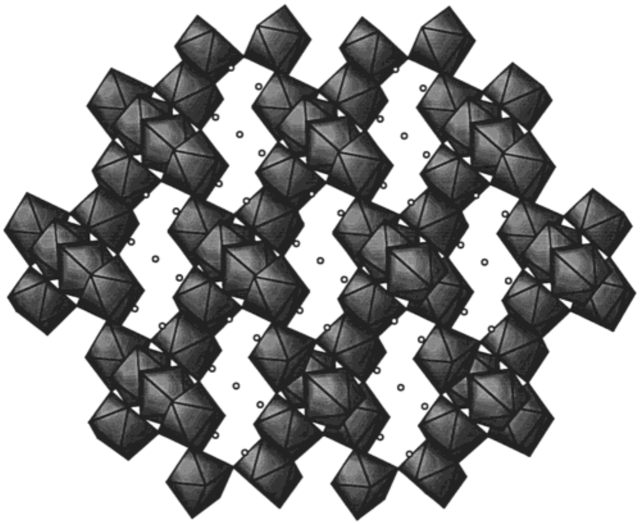

Figure 1. Framework of the YU-1 showing the hexagonal arrangement of the octahedral cages and locations of NH_4^+ cations.

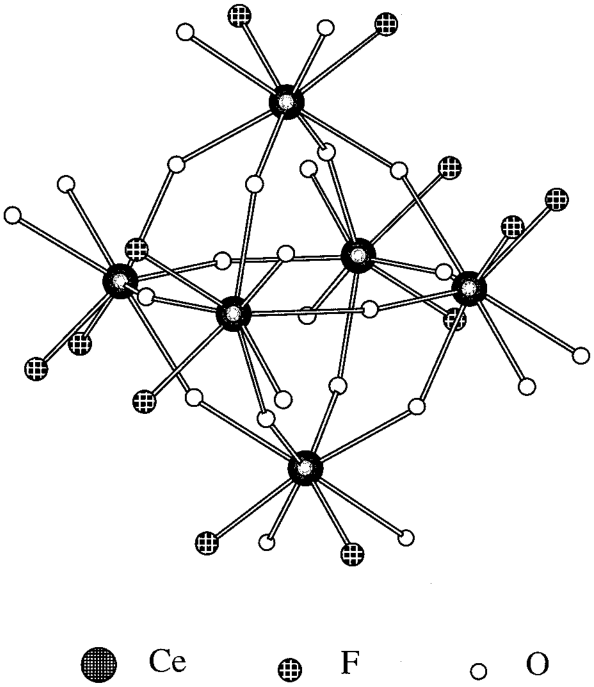

Figure 2. Octahedral cage formed with CeO_6F_2 dodecahedra.

The framework can be described as a hexagonal arrangement of octahedral cages connected by bridging oxygen atoms (Figure 1). This kind of octahedral cage has never been found in previous structure types of microporous materials (Figure 2). Each octahedral cage is formed by six corner-sharing cerium-centered CeO_6F_2 dodecahedra, and through linkage of this manner a great deal of three-rings with the pore opening of 2.9 Å from O to O are formed. The sizes of pores and cages are indicated by the distances between the centers of corresponding oxygen or fluoride atoms. Although the octahedral cage is made up of dodecahedra with large volume, it has a large body diagonal of 5.8 Å from O to O because of the relatively long Ce−O bond length (∼2.4 Å). The octahedral cages connect each other by sharing edges of the dodecahedra to give rise to a framework structure with one three-dimensional channel system. The channel system passes through the opposite faces of the supercage in the $[3\bar{3}\bar{1}]$, $[\bar{3}31]$, and [301] directions, and has the elliptical eight-ring windows with O- - -O

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(22) The novel open-framework cerium phosphate fluoride, $(NH_4)[Ce^{IV}F_2(PO_4)]$, crystallizes in the monoclinic space group $P2_1/m$ (no. 11), with $a = 6.660(2)$, $b = 5.875(2)$, $c = 7.177(3)$ Å, $\beta = 114.31(2)°$, and $V = 255.9(2)$ Å^3 ($R = 0.039$ and $R_w = 0.047$). In this compound, the cerium-centered polyhedra CeO_4F_4 link via a common edge containing two fluoride atoms to form the corrugated one-dimensional chains along the *b* axis of the structure, which are further connected by PO_4 tetrahedra to give rise to an open-framework structure with a three-dimensional channel system. NH_4^+ cations are accommodated at the intersection of the channels.

(23) Crystal structure data were collected on a transparent tetrahedral crystal with approximate dimensions of $0.12 \times 0.12 \times 0.12$ mm^3 using molybdenum Kα radiation ($\lambda = 0.71069$ Å, graphite monochromator). The space group $R\bar{3}$ could be assigned uniquely after a careful inspection of all reciprocal lattice points for which $2\theta < 90°$. 3971 of the total 4257 collected reflections were unique. The final cycle of full-matrix least-squares refinement was based on 2466 observed reflections ($I > 3.00\sigma(I)$) and 67 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.045$ and $R_w = 0.051$. Hydrogen atoms were added to balance the negative charges of the framework.

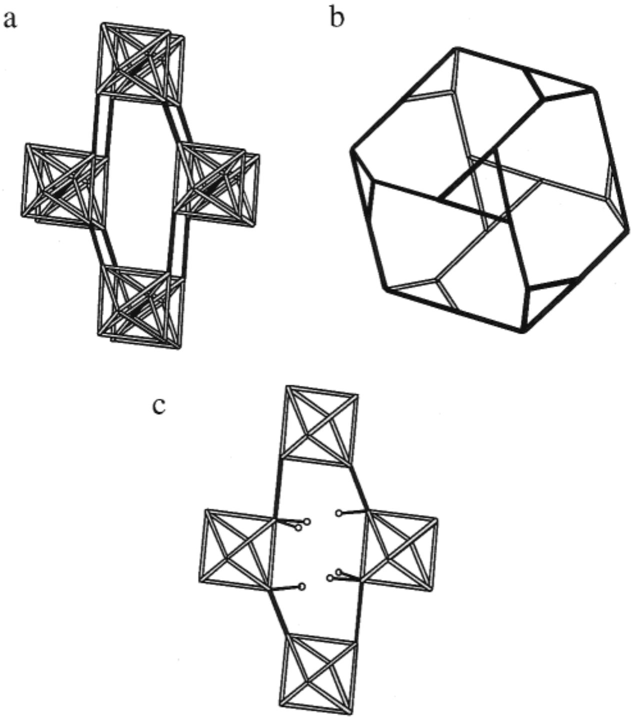

Figure 3. (a) Framework topology of the large supercage of the structure. (b) Interface of the large supercage. (c) Channel system with elliptical eight-ring view along the [3$\bar{3}\bar{1}$] direction. The nodes represent dodecahedral cerium atoms, the unfilled in (a) and (c) circles represent F atoms, and the gray and black sticks represent the connections of dodecahedral cerium atoms through single and double bridges, respectively.

distance varied between 6.3 and 9.7 Å and F- - -F distance varied between 3.7 and 4.4 Å as shown in Figure 3a and c. At the intersection of these channel systems, there are large supercages (Figure 3) with the body diagonal of 13−17 Å from O to O. NH_4^+ cations are accommodated in the channels to balance the framework negative charge (Figure 1). Ethylenediamine was not incorporated in the structure, which was further confirmed by CHN elemental analysis and infrared spectroscopy (IR) of the mixed product (YU-1 with minor cerium phosphate fluoride). In the reported open-framework uranium oxyfluoride MUF-1,[15] fluorines serve as both bridged and terminal atoms, whereas all the fluoride atoms of YU-1 are terminal and point to the interspace of the channels. It is suggested that NH_4^+ cations as well as terminal fluorides might have an effect on the shape-direction of the windows.

In summary, a novel open-framework cerium oxyfluoride has been hydrothermally synthesized and further reveals the great value of the hydrothermal method for material preparation. In addition, its new structural type and some potential properties inspire us to explore open-framework metal oxyfluorides. We are currently investigating the synthetic conditions to separate a pure phase of the title compound and the preparations of organically templated cerium materials, which would open up many intriguing possibilities in new open-framework materials synthetic chemistry.

Supporting Information Available: Structure factors (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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