Synthesis and Characterization of the First Organically Templated Layered Cerium Phosphate Fluoride: $[(CH_2)_2(NH_3)_2]_{0.5}[Ce^{IV}F_3(HPO_4)]$

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(Received January 9, 2004; CL-040041)

A novel organically templated layered cerium phosphate fluoride $[(CH_2)_2(NH_3)_2]_{0.5}[Ce^{IV}F_3(HPO_4)]$ has been synthesized by hydrothermal synthesis technology, and characterized by means of single-crystal X-ray diffraction. Its unique layered structure is based on a network of novel CeO_3F_5 polyhedral and PO_4 tetrahedral. The $[NH_3(CH_2)_2NH_3]^+$ cations contact with the adjacent layers via hydrogen bonds to compensate the negative charge of the inorganic framework.

Lanthanide materials with potential applications as ion exchanger, moisture sensor, fluorescence material, and ion conductor, have attracted considerable research attentions.[1] Synthesis of novel lanthanide materials with layered or open- framework structures is of great interest because the high coordination numbers, variety coordination geometries, and existence of mutable oxidation states of lanthanide elements would give new materials with novel framework architectures, and some potential properties such as catalysis, ion exchange, intercalation, and magnetism as well.[2]

Hydrothermal methods have proved to be invaluable for the synthesis of almost all kinds of recently important materials,[3] in particular layered and porous materials with novel structural architectures.[4] Synthesis of lanthanide materials by using soft chemistry method including hydrothermal method was stared early.[5] However, these syntheses were limited to some known phases. In our recent research, by using F^- ion mineralizer and organic template two novel open-framework cerium materials, cerium oxyfluoride[6] and cerium phosphate fluoride,[7] and an organically templated layered cerium phosphate–hydrogen sulfate[8] have been successfully synthesized under hydrothermal conditions. Additionally, J. Rocha et al. reported a microporous cerium silicate.[9] In the present work, a novel organically templated layered cerium phosphate fluoride, $[(CH_2)_2(NH_3)_2]_{0.5}$-$[Ce^{IV}F_3(HPO_4)]$, has been hydrothermally crystallized. Its unique layered structure possesses cerium-centered polyhedral CeO_3F_5 as a new basic building unit. The protonated ethylenediammonium are located between adjacent layers and are connected with them via hydrogen bonds to compensate the negative charge of the inorganic framework.

The title compound was synthesized hydrothermally from a starting mixture of 1.0 $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 4H_2O$/ $3.6H_3PO_4$/2.6 $H_2N(CH_2)_2NH_2$/10 HF/220 H_2O. This mixture was sealed in Teflon-lined stainless steel autoclaves and heated at 160 °C for 3 days. The cream color crystalline product was filtered and washed with deionized water, and then dried in air at ambient temperature. As the acidity of the reaction system is always the dominant factor for product crystallization, in this synthesis we tried to use a relatively high acidity and low synthesis temperature, so as to stabilize the protonated organic amine and further incorporate it into the structure of the product. ICP analysis gave the Ce/P ratio of 1.00:1.01, and no S was found in the product. Elemental analysis indicated that the C, N, and H contents are 3.72%, 4.38%, and 1.91%, corresponding to a molar ratio C:N:H = 1.00:1.01:6.11, which is in good agreement with the calculated value from the compound formula. Energy dispersive X-ray spectrometer (EDX) analysis of the compound indicated the existence of the framework fluoride atoms, and the result is coincident with the structure formula $[(CH_2)_2(NH_3)_2]_{0.5}$-$[Ce^{IV}F_3(HPO_4)]$.

A cream color prismatic crystal with approximate dimensions of 0.20 × 0.20 × 0.10 mm was selected for single-crystal X-ray analysis.[10] The result indicates that this compound crystallizes in the triclinic system, space group $P1$ (No. 1) with the cell parameters of $a = 6.248(2)$ Å, $b = 7.079(2)$ Å, $c = 8.794(3)$ Å, $\alpha = 103.92(2)°$, $\beta = 100.84(2)°$, $\gamma = 110.28(2)°$, $V = 338.0(2)$ Å^3, $Z = 2$.

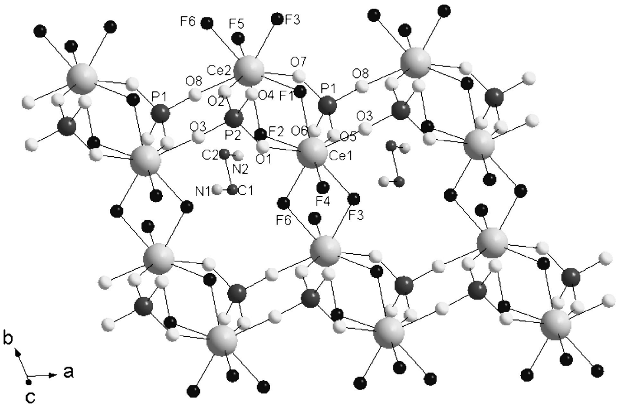

Figure 1. Stick-and-ball representation of the layer structure with atoms labeled.

The structure of this crystal consists of macroanionic $[CeF_3(HPO_4)]^-$ layers and interlamella diprotonated ethylene–diammonium cations. The macroanionic $[CeF_3(HPO_4)]^-$ layer is formed by cerium-centered polyhedral CeO_3F_5 and phosphorus-centered tetrahedral PO_4 (Figure 1). The cerium-centered CeO_3F_5 polyhedron is a novel basic building unit formed by the cerium atom coordinated to three oxygen atoms and five fluorine atoms, which is different from the other three new cerium-centered basic building units, CeO_6F_2,[6] CeO_4F_4,[7] CeO_9,[8] formed in open-framework and layered structures that we recently reported. Along the b-axis of the structure, CeO_3F_5 polyhedra are connected with each other via Ce_2F_2 rings to give the corrugated chains (Figure 2). Each PO_4 group shares its oxygen corners with three CeO_3F_5 polyhedra and leave the forth oxygen as –OH group to link up the chains of cerium-centered polyhedra and form the 2-D layers (Figure 1). The macroanionic layers were separated by organic diprotonated ethylenediaminum cations. In the planes vertical to the *c*-axis, there is six-ring window contains four CeO_3F_5 polyhedra and two PO_4 tetrahedra with the polyhedron arrangement as –Ce–Ce–P–Ce–Ce–P– and has diagonal varied between 3.86 and 7.08 Å (Figure 1), which is similar to that of six-ring channels of $(NH_4)[Ce^{IV}F_2(PO_4)]$.[7] Ethylenediaminium cations are located near the six-ring windows to balance the framework negative charge and direct the windows structure.

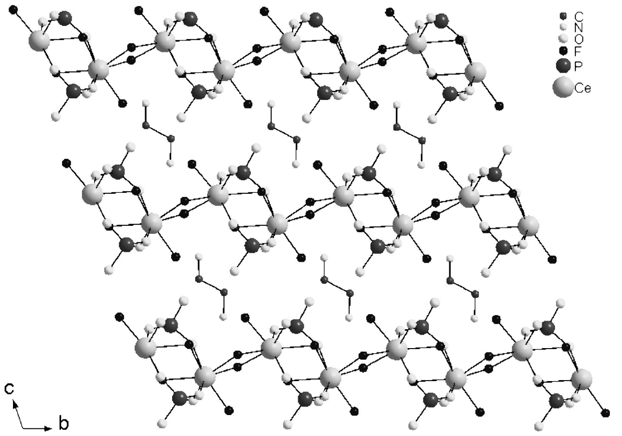

Figure 2. Stick-and-ball representation of the title compound showing arrangement of organic template between the adjacent layers.

The Ce–O distances vary in the range from 2.208 to 2.35 Å, which is comparable with the range of 2.188–2.407 Å for cerium atoms coordinated by eight oxygen atoms in $Ce^{IV}OSO_4(H_2O)$.[11] The average Ce–F bond length of 2.300 Å is coincident with that observed in $NH_4CeF_7(H_2O)$.[12] The average P–O distance of 1.537 Å is a little longer than 1.53 Å observed in calcium–cerium phosphate, $Ca_{19}Ce^{IV}(PO_4)_{14}$.[13] The organic template is connected with the inorganic layers through hydrogen bonds. N(1) and N(2) are involved in hydrogen bonds with framework terminal F(4) and F(5) with $N(1)\equiv F(5) = 2.934(3)$ Å and $N(2)\equiv F(4) = 2.909(3)$ Å, respectively.

Differential thermal analysis and thermogravimetric analysis of this compound shows that the template ethylenediamine decomposed endothermically at 265 °C, which gives rise to a marked weight loss. Then the title compound undergoes complicated oxidization decomposition at 300–800 °C and converts into a crystalline phase of $CePO_4$ at higher temperature.[14] The total weight loss is ca. 27.14% which agrees well with the calculated result (27.46%) according to Eq 1:

$$[(CH_2)_2(NH_3)_2]_{0.5}[Ce^{IV}F_3(HPO_4)] + 1.25O_2 \rightarrow$$
$$CO_2\uparrow + NH_3\uparrow + 1.5F_2\uparrow + 0.5H_2O\uparrow + CePO_4 \qquad (1)$$

In summary, a novel organically templated layered cerium phosphate fluoride has been synthesized under hydrothermal conditions. This work indicates that the higher acidity of the synthesis system might be a dominant factor that influences the incorporation of organic amine template into the structure, and further reveals the possibility of formation of organically templated layered or open-framework materials with wide topological range based on novel units. By proper controlling of organic templates and reaction conditions the syntheses of other novel lanthanide materials are very possible. Moreover, with $[(CH_2)_2(NH_3)_2]^{2+}$ cations located in the interspace of the layers, the title compound might have interesting ion-exchange properties.

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10 All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo Kα radiation. The space group was determined to be *P*1 (No. 1). Of the 10144 reflections which were collected, 5072 were unique; equivalent reflections were merged. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement on *F* was based on 4566 observed reflections ($I > 3.00\sigma(I)$) and 199 variable parameters and converged (largest parameter shift was 0.02 times its esd) with unweighted and weighted agreement factors of $R = 0.024$, $R_w = 0.021$. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-227968. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).
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Published on the web (Advance View) March 20, 2004; DOI 10.1246/cl.2004.458