Chemistry Letters Vol.33, No.9 (2004)

A Novel Open-framework Cerium Sulfate Hydrate: Synthesis and Characterization

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(Received July 5, 2004; CL-040790)

A novel open-framework cerium sulfate hydrate $[Ce^{III}(SO_4)_{1.5}(HSO_4)_{0.5}]\cdot 0.5H_3O$ has been synthesized hydrothermally, and characterized by single-crystal XRD, SEM, SQUID, and elemental analysis. In its structure, the CeO_7 polyhedra and SO_4 tetrahedra are connected via corner sharing in a strictly alternate manner to form an open-framework structure with a one-dimensional eight-membered ring channel system along the *b* axis. Protonated H_2O molecules are accommodated in the channels.

Cerium materials, owing to the potential applications as ion exchanger, moisture sensor, fluorescence material, and ion conductor, have attracted considerable research attentions.[1] Synthesis of novel cerium materials with layered or open-framework structures is of great interest because that the high coordination numbers, variety coordination geometries, and existence of mutable oxidation states of cerium element would give new materials with novel framework architectures and some potential properties.[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 cerium materials by using soft chemistry method including hydrothermal method was started early.[5] However, these syntheses were limited to some known phases. In our recent research, by using F^- ion mineralizer and organic templates two novel open-framework cerium materials, cerium oxyfluoride[6] and cerium phosphate fluoride,[7] and two novel organically templated layered cerium materials, cerium phosphate-hydrogen sulfate[8] and cerium phosphate fluoride[9] have been successfully synthesized under hydrothermal conditions. Additionally, J. Rocha et al. reported a microporous cerium silicate.[10] In the present work, a novel three dimensional open-framework cerium sulfate hydrate, $[Ce^{III}(SO_4)_{1.5}(HSO_4)_{0.5}]\cdot 0.5H_3O$, has been hydrothermally crystallized. Its unique open-framework structure possesses Ce^{III}-centered polyhedral CeO_7 as a new basic building unit, which is connected with SO_4 tetrahedra in a strictly alternate manner to form an eight-membered ring channel system and several kinds of four-membered windows. The H_2O molecules are accommodated in the interspaces of the four-ring windows as well as that of the eight-membered ring channels to direct the window formation.

The title compound was synthesized hydrothermally from a starting mixture of 1.0 $Ce(SO_4)_2\cdot 2(NH_4)_2SO_4\cdot 4H_2O/2.8\ H_3PO_4/3.6\ H_2SO_4/2.6\ H_2N(CH_2)_2OH/140\ H_2O$. This mixture was subsequently sealed in Teflon-lined stainless steel autoclaves and heated at 110 °C for 4–7 days. The big yellow crystalline product was recovered by filtering and washing with deionized water, and then dried in air at ambient temperature. EDX analysis gave the Ce/S ratio of 1:2, and no P and F was found to exist in the product. This is in good agreement with the calculated value from the compound formula. The result is coincident with the structure formula $[Ce^{III}(SO_4)_{1.5}(HSO_4)_{0.5}]\cdot 0.5H_3O$.

A yellow prismatic crystal with approximate dimensions of $0.77 \times 0.28 \times 0.12$ mm was selected for single-crystal X-ray analysis.[11] The result indicates this compound crystallizes in the monoclinic system, space group *Pm* (No. 6) with the cell parameters of $a = 7.095(5)$ Å, $b = 5.423(4)$ Å, $c = 9.240(7)$ Å, $\beta = 98.73(3)^\circ$, $V = 351.4(4)$ Å^3, $Z = 2$.

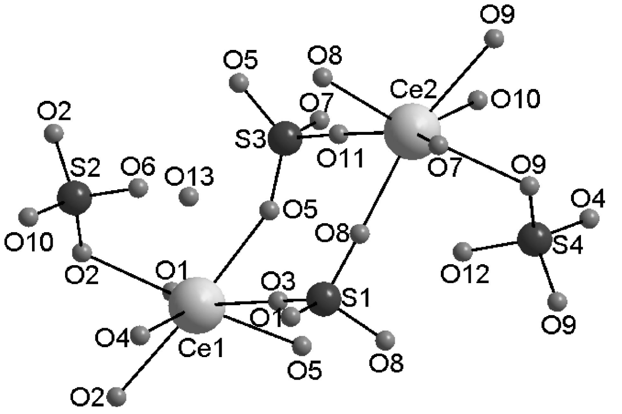

Figure 1. Stick-and-ball representation of the asymmetric unit of the title compound with atoms labeled.

The complex atomic crystal structure consists of two cerium sites, four sulfate groups, and water molecules, which performs several structural functions (Figure 1). Both of the two cerium sites are occupied by Ce^{III} with identical coordination numbers (CN = 7). This cerium-centered CeO_7 polyhedron is a new type of basic building unit followed the other four cerium-centered basic building units, CeO_6F_2,[6] CeO_4F_4,[7] CeO_3F_5,[9] CeO_9,[8] which we recently reported in synthesis of open-framework and layered cerium materials. The CeO_7 polyhedra share all their oxygen corners with seven SO_4 tetrahedra. While as for the four SO_4 tetrahedra, two of them are surrounded by four CeO_7 polyhedra, and the other two are connected with only three CeO_7 polyhedra leaving the terminal oxygen as S–OH and S=O, respectively. In connectivity term, the framework structure could be written as $\{[CeO_{7/2}]_2[SO_{4/2}]_2[SO_{3/2}O][SO_{3/2}OH]\}^-$. This connectivity results in an open-framework structure with strictly alternate CeO_7 and SO_4, and an eight-membered ring channel system along [010] direction and several kinds of four-membered windows along three of the axes (Figure 2). The acid reaction system made H_2O protonated and located in the channel system to balance the framework negative charge. Notably, different from the cerium materials we synthesized before, in which cerium-cen-

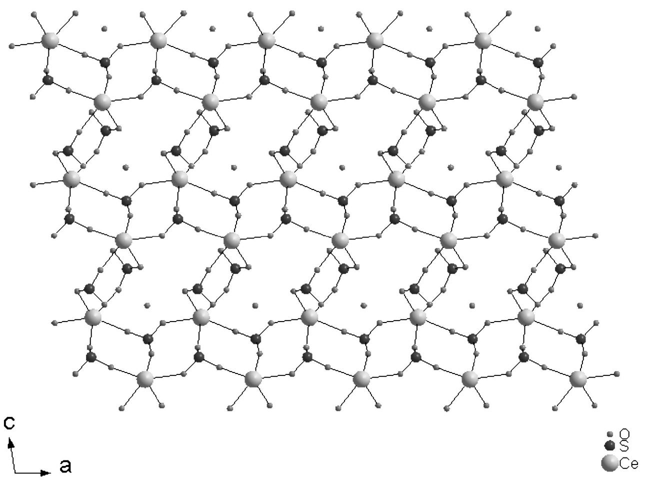

Figure 2. Stick-and-ball representation of the title compound showing the eight-membered ring channel system and four-membered windows along the [010] direction, with H_2O molecules inside the channel system.

tered polyhedra have a tendency to link with each other, while in the title compound, CeO_7 polyhedra bare separated by SO_4 groups in a strictly alternate manner. This is a typical linkage of polyhedra observed in traditional microporous zeolites and aluminophosphates.

The Ce–O distances vary in the range from 2.355 to 2.558 Å, which is comparable with the range of 2.27–2.55 Å for cerium atoms with mixed valence in reported cerium sulfate hydrate.[12] The bridge S–O distances are in the range from 1.432 to 1.498 Å, and the terminal S–O namely S(2)–O(6) and S(4)–O(12) have distances of 1.416 and 1.531 Å respectively, which could be considered as S=O and S–OH correspondingly. These distances are comparable with those observed in cerium phosphate hydrogensulfate.[8]

Magnetic susceptibility measurement indicated that the compound is paramagnetic and displays Curie–Weiss behavior in higher temperature range, having Curie constant of $C = 0.76\,\text{emu}\,\text{K}^{-1}\,\text{mol}^{-1}$ and a Weiss constant of $\theta = -110\,\text{K}$, which corresponds to the effective magnetic moments of $\mu_{\text{eff}} = 2.47\,\text{BM}$. This value is consistent with the experiential ($\mu_{\text{exp}} = 2.40\,\text{BM}$) and the calculated ($\mu_{\text{cal}} = 2.54\,\text{BM}$) data for a system consisting of isolated high-spin Ce^{3+},[13] therefore, the cerium of the compound is considered as Ce^{3+}.

In summary, a novel open-framework cerium sulfate hydrate has been prepared from hydrothermal system. The alternately arranged CeO_7 and SO_4 are connected to form a 3-D framework with eight-membered channel system. This work further revealed the possibility of forming open-framework cerium materials under hydrothermal conditions.

D. Wang thanks the "Century Program or Hundreds-Talent Program" of Chinese Academy of Sciences, and R. Yu thanks the Foundation of University of Science & Technology Beijing (Grant No.: 20040214890) for financial support. This work was partly supported by National Natural Science Foundation of China (NSFC) (Grant No.: 59704008 and 20221603), and the Ministry of Science and Technology P. R. China (Grant No.: 2003AA322070 and 2001BA310A08).

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11 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 *Pm* (No. 6). Of the 6138 reflections which were collected, 3069 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 2653 observed reflections ($I > 3.00\sigma(I)$) and 127 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of $R = 0.056$, $R_w = 0.064$. Crystallographic data reported in this paper have been deposited with Fachinformationszentrum Karlsruhe as supplementary publication no. CSD-414161. Copies of the data can be obtained free of charge via www.fiz-informationsdienste.de/en/DB/icsd/ (or from the Fachinformationszentrum Karlsruhe, Informationsdienste, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen Germany; or crysdata@fiz-karlsruhe.de).

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Published on the web (Advance View) August 14, 2004; DOI 10.1246/cl.2004.1186