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Synthesis of a new open framework cerium silicate and its structure determination by single crystal X-ray diffraction†

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Hydrothermal synthesis of a new open framework cerium silicate and its structure determination by single crystal X-ray diffraction are reported.

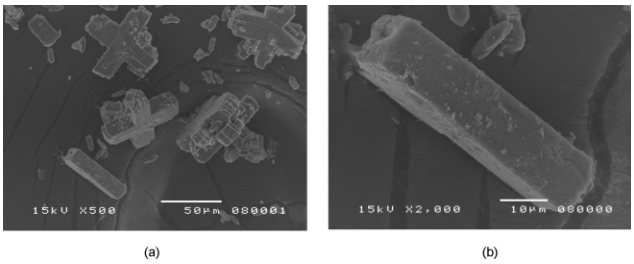
Open framework mixed octahedral- and tetrahedral-metal oxides may find applications in catalysis, ion exchange, adsorption and optoelectronic devices distinct from those of zeolites and other tetrahedral frameworks.[1–3] As a result, considerable research effort in the last decade has been devoted to synthesizing and elucidating the structure of such frameworks.

The first microporous cerium silicate, AV-5, has been reported by Rocha and coworkers.[4] Its potential for use in optoelectronics has also been discussed. AV-5 is analogous to AV-1, a synthetic analogue of the rare sodium yttrium silicate mineral montregianite ($Na_4K_2Y_2Si_{16}O_{38}\cdot10H_2O$) with replacement of [$YO_6$] octahedra with [$CeO_6$] octahedra. The [$CeO_6$] octahedra are isolated from each other, and connected with [$NaO_4(H_2O)_2$] octahedra. The ability to control the ratio of Ce^{III}/Ce^{IV} present in AV-5 was achieved by framework oxidation/reduction. Correspondingly, the ability to tune the adsorption properties of AV-5 as well as its luminescence properties was also suggested. As the Ce^{IV} content increases, less extra-framework cations are required to balance the charge of the anionic framework, thus potentially changing the adsorption characteristics of the material.

In this paper, we report the synthesis and crystal structure of a new open framework cerium silicate with a chemical composition of [$Na_{4.8}Ce_2Si_{12}O_{30}\cdot4H_2O$].

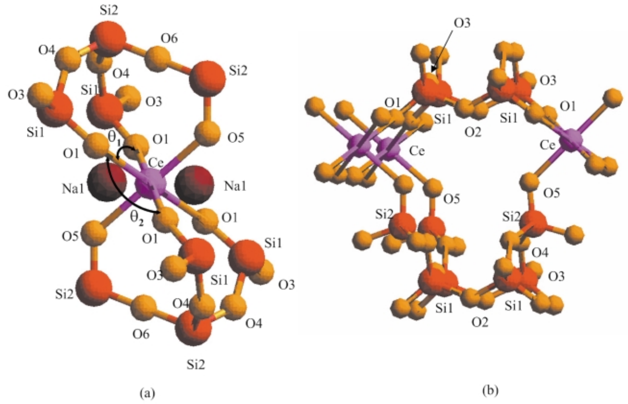
In a typical synthesis, the molar composition of the mother solution for the cerium silicate was 1 CeO_2 : 10 SiO_2 : 18 NaOH : 675 H_2O. Sodium hydroxide (3.67 g) was dissolved in de-ionized water (97.39 g). Cerium sulfate (2.99 g, $Ce(SO_4)_2$ 99%, Aldrich) was added under stirring, and followed by immediate addition of 2.5 g of sulfuric acid (96%, Fisher Scientific). The mixture was stirred for 1 hour to completely dissolve cerium sulfate. A sodium silicate solution (20 g, 27% SiO_2, 14% NaOH, 59% H_2O, Aldrich) was mixed with the above solution and stirred for 1 hour. The resulting yellowish solution was then introduced into a stainless steel autoclave (Parr) and hydrothermally crystallized at 200 °C with varying crystallization times (typically 1–3 d). After the autoclave was cooled to room temperature, the product was washed with de-ionized water until neutral pH, and dried at 85 °C overnight. SEM images of the material are shown in Fig. 1. Most of the cerium silicate crystals are twinned in the form of a cross-shaped crystal. For the purpose of single crystal X-ray study, a long non-twinned crystal of cerium silicate, like the one shown in Fig. 1(b), was chosen.‡

The crystal structure of the cerium silicate consists of [SiO_4] tetrahedra, [CeO_6] octahedra, [$NaO_4(H_2O)_2$] octahedra, sodium cations and additional water molecules within the pores of distorted double eight-membered rings. Fig. 2 shows two clusters belonging to the cerium silicate structure: (a) isolated [CeO_6] octahedra, and (b) distorted double eight-membered rings. The silicon atoms exist in two different environments as shown in Fig. 2. One (Si1) is coordinated to the planar oxygen (O1) while the other (Si2) is coordinated to the apical oxygen (O5) of [CeO_6] octahedron. One Si2 is connected to two Si1's by two O4 oxygen atoms, forming a four-membered ring arrangement with the cerium atom as shown in Fig. 2(a). The other two oxygen atoms for Si1 are O3 (forming an Si1–O3–Si1 linkage) and O2 (forming an Si1–O2–Si1 linkage), while for Si2 there is O6 (forming an Si1–O3–Si1 linkage). The reported bond angle of Si1–O3–Si1 (180°) is probably an outcome of averaging alternate arrangements of O6. The cerium silicate contains isolated [CeO_6] octahedra. Two of the four planar oxygen atoms (O1) are coordinated to Na1 on each side of the [CeO_6] octahedra. This causes the O1–Ce–O1 angle facing Na1 (θ_1) to be smaller than 90° (84.21°), while O1–Ce–O1 facing the 8MR (θ_2) is larger than 90° (95.79°) (see Fig. 2(a)). The Na1 is six-coordinated with four framework oxygens and two oxygens of water molecules to form [$NaO_4(H_2O)_2$] octahedra. Na1 has a bond valence of 0.836(16) calculated using the empirical bond valence model.[5] These [$NaO_4(H_2O)_2$] octahedra are similar to those found in AV-5.[4] Bond lengths of the four symmetry-related Na1–O1 and Na1–Ow1 are 2.496(6) Å, and 2.684(15) Å, respectively. [$NaO_4(H_2O)_2$] octahedra interconnect with [CeO_6] octahedra along the *a*-direction by edge-sharing. Planes of [CeO_6] octahedra are on either [0 2 4] or [0 −2 4]. We



(a) (b)

Fig. 1 Scanning electron microscope images of as-synthesized cerium silicate.



(a) (b)

Fig. 2 Representative clusters of the cerium silicate framework: (a) the isolated [CeO_6] octahedron and (b) the double eight-membered rings consisting of [CeO_6] octahedra and [SiO_4] tetrahedra.

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† Electronic supplementary information (ESI) available: powder XRD patterns, TG data. See http://www.rsc.org/suppdata/cc/b2/b206738m/

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assigned Na2 in the distorted 8MR. Na2 is seven-coordinated with five framework oxygens and two oxygens from water molecules, having a bond valence[5] of 0.767(22). This sodium site was identified based on X-ray data and coordination considerations along with the information from the chemical analysis data (Na content) and the thermogravimetric analysis data (water content). The long Na–O distances (2.980(11) Å with O4, 2.804(9) Å with O5) may be partially reconciled by considering the higher coordination (seven) of Na2. In addition, because of the partial occupancy of the Na2 position (70%), the O5 position may vary depending on whether the corresponding Na2 site is occupied or not. This scenario, which is supported by the large ADP values of O5, will result in the reported average Na2–O5 distance being larger than the actual one. Fig. 3 shows the structure as viewed down the crystallographic *a*-direction. The structure consists of distorted 8MR units of [SiO_4] tetrahedra and [CeO_6] octahedra. The eight-membered rings form a straight channel along the [100] direction. Six-membered rings run along the *b*-direction, consisting of four [SiO_4] tetrahedra and two [CeO_6] octahedra. Na1 cations sit in the middle of the six-membered rings and coordinate to the framework oxygen and the oxygen of water molecules.

The powder X-ray diffraction pattern of the as-synthesized cerium silicate along with the simulated pattern based on the structure solved by single crystal X-ray diffraction is supplied as ESI.† There is good agreement that suggests that the single crystal analyzed is representative of the synthesized powder material. The difference in intensities is probably due to a preferred orientation effect. The cerium silicate was found to be thermally stable up to 500 °C (see XRD data provided as ESI†).

Thermogravimetric analysis data (given as ESI†) are consistent with the proposed structure of the cerium silicate. The dehydration is essentially complete at 400–450 °C, and the total mass loss is 5.9%. Two stages of dehydration occur, between 20–90 °C due to the loss of the adsorbed water on the surface (0.4%), and between 90–350 °C due to the loss of the water in the pores (5.5%), which agrees well with 5.6% of water based on the structure solution.

With a chemical composition of [$Na_{4.8}Ce_2Si_{12}O_{30}\cdot 4H_2O$] and assuming all the cerium being Ce^{IV} in the cerium silicate, −0.8 *e*/unit cell are missing for satisfying charge balance, while assuming cerium is present only as Ce^{III}, there is an excess of −1.2 *e*/unit cell. This implies that some of the cerium atoms might be present as Ce^{III} and some as Ce^{IV}.[4] At this moment we cannot determine the amount of Ce^{III}/Ce^{IV} in the sample as we may also have disordered sodium ions, or protons coordinated to the framework, to water molecules and to defects in the framework.[6] Chemical analysis (ICP-OES) showed 0.18 Ce/Si and 0.36 Na/Si ratios, which agrees with the structure solution. Further investigation on the ion exchange and catalytic properties is in progress.

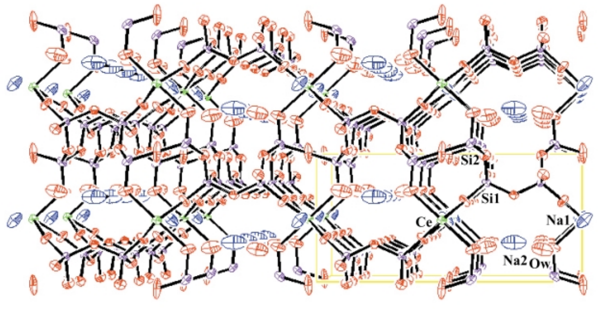

Fig. 3 The structure of the cerium silicate viewed along the [100] direction. Figure was made using Ortep-III for Windows.[9]

To our knowledge, the material reported here is the second synthetic microporous cerium silicate and unlike the first one reported by Rocha *et al.*[4] it does not have a natural counterpart.

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Notes and references

‡ Crystal data for the cerium silicate: $Na_{4.8}Ce_2Si_{12}O_{30}\cdot 4H_2O$, orthorhombic, space group *Pmna*, a = 7.3093(4) Å, b = 7.1350(4) Å, c = 14.9713(9) Å, U = 780.78(8) Å^3, Z = 1, atoms in asymmetric unit 12. Single crystal X-ray diffraction data (4.22–25.03°) were collected using a Nonius Kappa CCD diffractometer and graphite monochromated MoK_α radiation (λ = 0.71073 Å), yielding 749 unique reflections; μ = 35.33 cm^{-1}. Data were collected at 23 ± 2 °C and corrected for Lorentz and polarization effects. No corrections were made for absorption effects that are largely taken care of by the scaling of multiple measurements. All of the data were included in the refinement. The structure was solved by direct methods (in *Pmna* space group) and difference Fourier techniques and refined by full-matrix least-squares. Refinements were based on F^2 and computations were performed using SHELXS-86 for solution,[7] and SHELXL-97 for refinement (R = 0.0473, R_w = 0.1201).[8] All of the non-hydrogen atoms were refined anisotropically. One of the two sodium ions (Na2) has partial occupancy and on refinement it converged to 70%. The hydrogen atoms on the water molecules were not included in the calculations. The final agreement factors reported are based on the reflections with $I \geq 2\sigma_I$. CCDC 190099. See http://www.rsc.org/suppdata/cc/b2/b206738m/ for crystallographic files in CIF or other electronic format.

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