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$Na_3TbSi_3O_9\cdot3H_2O$: A New Luminescent Microporous Terbium(III) Silicate Containing Helical *Sechser* Silicate Chains and 9-Ring Channels

Guangmei Wang,[†] Jiyang Li,[†] Jihong Yu,*[,†] Peng Chen,[†] Qinhe Pan,[†] Hongwei Song,[‡] and Ruren Xu[†]

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P.R. China, and Key Laboratory of Excited-State Physics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, P.R. China

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Microporous silicates hosting lanthanide elements have attracted considerable attention because such materials have high thermal stability, uniform microporosity, and a tunable optical property that may have many important applications.[1−21] A number of lanthanide silicates were prepared under high-temperature and high-pressure hydrothermal conditions to search for fast alkali ion conductors.[1,5−7] Recently, luminescent microporous lanthanide silicate materials containing stoichiometric amounts of lanthanide (Ln) in the framework have been successfully prepared under mild hydrothermal conditions at 200−230 °C in the presence of alkali metal cations.[17] Rocha and co-workers reported AV-5 (Ln = Ce)[11] and AV-9 (Ln = Eu, Tb, Er)[12,18] that are synthetic analogues of mineral montregianite and AV-20 (Ln = Eu, Tb, Sm, and Ce) that is closely related to hydrated calcium silicate minerals, known as tobermorites.[16] Tsapatsis and co-workers reported $Na_{4.8}Ce_2Si_{12}O_{30}\cdot4H_2O$,[13] which is closely related to mineral sanzhinite.[17] The structures of microporous lanthanide silicates are typically built up from Ln-centered polyhedra (LnO_6 or LnO_7) and SiO_4 tetrahedra. Up to now, the largest pore opening occurring in these structures is limited to 8-rings.

This paper presents a novel luminescent microporous terbium silicate $Na_3TbSi_3O_9\cdot3H_2O$ (denoted TbSiO-CJ1; CJ stands for China Jilin University) crystallized in the enantiomorphic space group $P2_12_12_1$. Strikingly, its structure is featured by a Λ-$Co(en)_3^{3+}$-like chiral unit of $[TbSi_6O_9]$ and contains helical *sechser* silicate chains and 9-ring channels. Such structural features are particularly rare in microporous silicates.

TbSiO-CJ1 was prepared by the mild hydrothermal reaction (see Synthesis and Characterization) of a mixture of fumed silica, $Tb(NO_3)_3\cdot nH_2O$, NaOH, and water in a 1.0:0.12:8.46:58 molar ratio at 230 °C for 6 days in a Teflon-lined stainless-steel autoclave.

Single-crystal structural analysis reveals that TbSiO-CJ1 is composed of a macroanionic $[TbSi_3O_9]^{3-}$ framework. The Na^+ ions residing in the channels compensate the negative charge of the inorganic framework. Each asymmetric unit contains one crystallographically distinct Tb atom, three crystallographically distinct Si atoms, Na atoms, and water molecules, respectively (Figure 1). Of the three distinct Na atoms, the Na(3) atom is disordered over two sites. The Tb(1) atom shares six oxygen atoms with adjacent Si atoms, forming a slightly distorted TbO_6 octahedron. The Tb−O bond lengths are in the range of 2.270(3)−2.332(3) Å, and the O−Tb−O bond angles are in the range of 83.99(10)−174.75(11)°. All Si atoms are tetrahedrally coordinated to O atoms, forming two Si−O−Si bonds and two Si−O−Tb bonds. The observed Si−O bond lengths of 1.600(3)−1.670(3) Å and O−Si−O bond angles of 101.38(17)−116.39(17)° are typical values for silicate materials.[24] The Na(1) atom and Na(2) and Na(3)/Na(3′) atoms are six- and five-coordinated, respectively, to O atoms of the framework and extra-framework water molecules. The Na−O distances range from 2.19(3) to 2.99(11) Å.

The linkages of TbO_6 octahedra and SiO_4 tetrahedra via vertex oxygen atoms result in a three-dimensional (3D) open framework of TbSiO-CJ1 (Figure 2a). It contains 9-ring channels along the [100] direction delimited by four TbO_6 octahedra and five SiO_4 tetrahedra with a free aperture of 3.0 × 7.1 Å. Its structure is featured by a Λ-$Co(en)_3^{3+}$-like chiral unit of $[TbSi_6O_9]$ (Figure 2b). Interestingly, the connection of SiO_4 tetrahedra results in an infinite left-handed helical silicate chain with a period of six tetrahedra following the 2_1 screw axis running along the *a*-axis (Figure 2c). According to the classification of Liebau, this type of single chain is called an "unbranched *sechser* single chain" and

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* To whom correspondence should be addressed. Fax: +86-431-5168608. E-mail: jihong@jlu.edu.cn.

[†] Jilin University.

[‡] Chinese Academy of Sciences.

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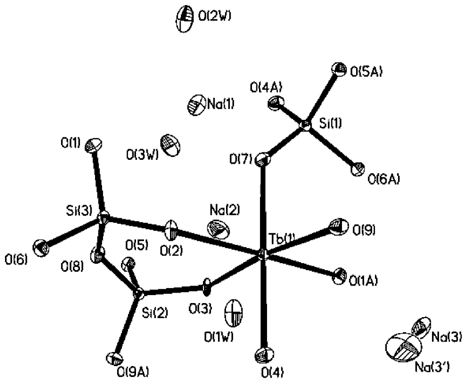

Figure 1. Thermal ellipsoid plot (50%) of TbSiO-CJ1.

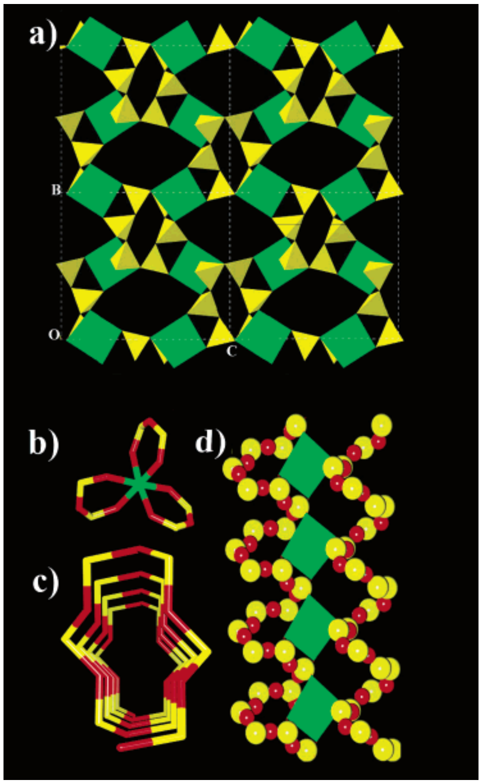

Figure 2. (a) Polyhedral view of the open-framework structure of TbSiO-CJ1 along the [100] direction, showing the 9-ring channels (H_2O and Na^+ are omitted for clarity). (b) the Λ-$Co(en)_3^{3+}$-like chiral unit of $[TbSi_6O_9]$. (c) The left-handed helical *sechser* silicate chain following the 2_1 screw axis running along the [100] direction. (d) Neighboring helical silicate chains connected by TbO_6 octahedra to form the 3D open framework of TbSiO-CJ1 (color code: Tb, green; Si, yellow; O, red).

can be described by the following structural formula: $[^6Si_6O_{18}]$. A prominent feature of this helical chain lies in its small pitch of approximately 7.02 Å and low stretching factor of $f_s = 0.45$, which is much smaller than those of other reported helical silicate chains, such as stokesite[23] ($f_s = 0.72$), AV-10[24] ($f_s = 0.73$), and $Cs_2SnSi_3O_9$[25] ($f_s = 0.74$). The helical silicate chain has been found in minerals and synthetic stannosilicates, however, it rarely occurs in the structures of microporous lanthanide silicates.

Neighboring helical *sechser* silicate chains are connected by TbO_6 octahedra (Figure 2d) to form the 3D open framework of TbSiO-CJ1. The Na(1), Na(2), O(1w), and O(2w) reside in the 9-ring channels along the [100] direction. The $Na(3)^+$ ions are enclosed in the spiral silicate chains, and the O(3w) atoms locate near the spiral silicate chains. There exist hydrogen bonds between the water molecules and hydrogen bonds between the water molecules and the framework oxygen atoms. The O⋯O distances are in the range of 2.676(5)−2.794(5) Å, and the O⋯H⋯O angles are in the range of 158(6)−177(8)°.

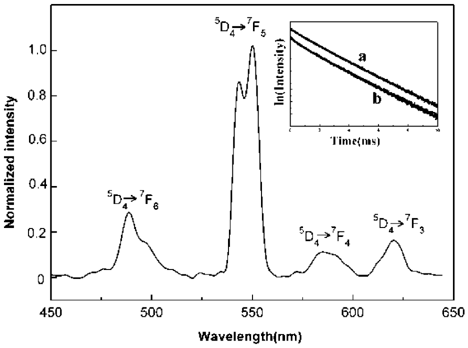

Figure 3. Room-temperature emission spectrum of TbSiO-CJ1. The inset is the room-temperature $^5D_4$ decay curves detected within the $^5D_4 \rightarrow {}^7F_5$ region (*a*, 551 nm; *b*, 543 nm) and excited at 266 nm.

Figure 3 shows the room temperature (RT) photoluminescence spectrum of TbSiO-CJ1, excited at 325 nm. It shows several lines between 480 and 650 nm, which are associated with the $^5D_4 \rightarrow {}^7F_J$ ($J = 3-6$) transitions of Tb^{3+} ions. Among them, the green $^5D_4 \rightarrow {}^7F_5$ transitions at 543 and 550 nm are the strongest, whereas the luminescence from higher excited states (e.g., $^5D_3$) is not detectable, implying very efficient nonradiative relaxation to the $^5D_4$ level. The room-temperature fluorescence decay curves (in natural log scale) of the $^5D_4 \rightarrow {}^7F_5$ transitions for TbSiO-CJ1, excited at 266 nm, are well-fitted by a single-exponential function, yielding a lifetime value of 3.11 ms. This suggests the presence of a single Tb^{3+} environment in agreement with the single-crystal structure of TbSiO-CJ1.

In summary, a new terbium silicate $Na_3TbSi_3O_9 \cdot 3H_2O$ (TbSiO-CJ1) has been synthesized under mild hydrothermal conditions. Differently from the known dense phase terbium silicate $Na_3TbSi_3O_9$[26] with a similar chemical composition, TbSiO-CJ1 is a new microporous compound and its structure consists of helical *sechser* silicate chains which are connected by TbO_6 octahedra to form a 3D open framework containing 9-ring channels along the [100] direction. Among the known microporous framework structures, channels bound by even-numbered rings are frequently encountered, such as 6-, 8-, 10-, and 12-rings, while channels bound by odd-numbered rings are rare with the exception of the more frequent 5-rings in zeolites.[27] A few zeotype materials, such as LOV, VSV, RSN, and STT structure types,[28] and a vanadium silicate VSH-12[29] have been known to possess 9-ring channels. TbSiO-CJ1 is the first microporous lanthanide silicate

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containing 9-rings with a free aperture of 3.1 × 7.0 Å. Our preliminary studies reveal that the Na^+ ions in the structures can be exchanged by other ions such as NH_4^+, K^+, Li^+, and so forth. Lanthanide silicates containing Ce, Eu, Er, Sm, and so forth with a structure analogous to TbSiO-CJ1 could also be prepared. Further investigation on their properties such as ion-exchange capacity, adsorption ability, and ionic conductivity is underway.

Synthesis and Characterization. In a typical hydrothermal preparation of TbSiO-CJ1, $Tb(NO_3)_3 \cdot nH_2O$ (0.24 g, 0.60 mmol) was dissolved in distilled water (5.19 mL), and then fumed silica (0.3 g, 5 mmol) and NaOH (1.692 g, 42.3 mmol) were subsequently added with continuous stirring. A homogeneous gel (pH ∼13) was formed after stirring for another 1 h and then was sealed in a Teflon-lined stainless steel autoclave (15 mL) and heated at 230 °C for 6 days under the static condition. The resulting colorless single crystals in the shape of a prism accompanied by the impurity phase of $Na_3TbSi_3O_9$[26] in the shape of polyhedron were isolated by filtration, washed with deionized water, and dried in the air. A batch of single crystals of TbSiO-CJ1 was manually selected under optical microscope for single-crystal X-ray diffraction analysis and other characterizations. The phase purity of selected TbSiO-CJ1 was confirmed by its X-ray powder diffraction pattern, which is consistent with the simulated one on the basis of single-crystal structural analysis (Supporting Information, Figure S1).

X-ray powder diffraction data were collected on a Siemens D5005 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Inductively coupled plasma (ICP) analysis performed on a Perkin-Elmer Optima 3300 DV ICP instrument gave Na, 13.66; Tb, 31.12; and Si, 16.67 wt % (calcd Na, 13.52; Tb, 31.15; and Si, 16.46 wt %). The emission spectra at room temperature were measured by a LabRam Raman spectrometer (Jobin-Yvon Co., France). A 325-nm continuous He−Cd laser was used as the excitation source. In the measurements of the fluorescent dynamics of Tb^{3+}, a 266-nm light generated from the fourth harmonic generator pumped by the pulsed Nd:YAG laser was used as the general excitation source. The spectra and dynamics were recorded by a Spex 1403 spectrometer, a photomultiplier, and a boxcar integrator and processed by a computer.

Structural Determination. Structural analysis of a single crystal (0.10 × 0.10 × 0.05 mm^3) was performed with a Siemens SMART CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were collected at a temperature of 20 ± 2 °C. Data processing was accomplished with the SAINT processing program.[30] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL97.[31] Tb, Si, Na, and O atoms were easily located, and then H atoms associated with water were found in the Fourier maps. The non-hydrogen atoms were refined anisotropically.

Crystal data for TbSiO-CJ1: $Na_3TbSi_3O_9 \cdot 3H_2O$, $M = 510.21$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 7.0280(14)$, $b = 11.757(2)$, $c = 13.503(3)$ Å, $U = 1115.8(4)$ $Å^3$, $Z = 4$, 10 911 reflections measured, 2544 unique ($R_{int} = 0.0255$). The final wR_2 (all data) was 0.0420, and R_1 ($I > 2\sigma(I)$) was 0.0168. The flack parameter was 0.422(10). CSD-416648 and Supporting Information contain the supplementary crystallographic data for this paper.

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Supporting Information Available: Simulated and experimental power XRD patterns and tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for TbSiO-CJ1 (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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