High-Temperature, High-Pressure Hydrothermal Synthesis, Crystal Structure, and Luminescence Properties of $Cs_3EuSi_6O_{15}$, a New Europium(III) Silicate with a Three-Dimensional Framework Structure

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The crystal structure and luminescence properties of hydrothermally grown crystals of $Cs_3EuSi_6O_{15}$ are reported. The structure consists of loop-branched vierer double chains of silicate with four-, six-, and eight-membered rings, which are connected via 10-membered rings at their interfaces to form a 3-D silicate framework. The six-coordinate europium atoms are located at sites between six-membered silicate rings. This Cs, Eu silicate is the second example of 3-D silicate framework with Si:O = 2:5, which contains only tertiary [SiO_4] tetrahedra. The sharp peaks in the emission spectrum are assigned, and the lifetime measurements confirm the presence of one local Eu^{3+} environment. Crystal data: monoclinic, space group $P2_1/n$, $a = 7.1664(1)$ Å, $b = 28.4756(6)$ Å, $c = 8.5418(2)$ Å, $\beta = 104.976(1)°$, $V = 1683.89(7)$ Å^3, and $Z = 4$.

Introduction

Aluminosilicates with 3-D open framework structures are of considerable technological importance as catalysts, ion-exchange solids, and molecular sieves. Recently, much work has focused on the synthesis of microporous silicate framework solids containing metals in different coordination geometries.[1] A large number of hydrothermally synthesized silicates of transition metals,[2−8] main group elements,[9−12] uranium,[13−18] and lanthanide elements[19−24] have been reported. They have shown a rich structural chemistry and interesting physical and chemical properties. Most of these silicates were synthesized with alkali metal cations in a Teflon-lined autoclave under mild hydrothermal conditions at 180−240 °C. A niobium and a uranium silicate have also been synthesized by using organic ammonium cations as structure-directing agents.[7,13] We have also synthesized a number of new silicates of transition metals,[8] indium,[11,12] and uranium[16−18] by high-temperature, high-pressure hydrothermal reactions at 500−600 °C in gold ampules. Compounds that were synthesized under high-*T*/high-*P* hydrothermal conditions generally have more compact structures as compared to those from mild hydrothermal reactions. The high-*T*/high-*P* synthetic route also facilitates crystal growth of dehydrated phases and may produce new compounds, which are distinct from those by mild or moderate-condition hydrothermal method. For example, the anhydrous uranyl silicate $Cs_2(UO_2)(Si_2O_6)$,[17] which was prepared at 550 °C and ∼110 MPa, adopts a structure analogous to that of hydrate phase $Cs_2(UO_2)(Si_2O_6)\cdot 0.5H_2O$, which was prepared at 230 °C.[14] The structure of the anhydrous vanadyl silicate $Cs_2VOSi_6O_{14}$[25] is considerably different from that of the hydrous compound $Cs_2VOSi_6O_{14}\cdot 3H_2O$.[3] Metal silicates with

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novel structures and unusual oxidation states have also been synthesized by the high-*T*/high-*P* route. For example, the structure of $Rb_3In(H_2O)Si_5O_{13}$ consists of five-membered rings of corner-sharing SiO_4 tetrahedra connected via corner sharing to four adjacent five-membered rings to form a 3-D silicate framework which belongs to the $CdSO_4$ topological type.[12] We have synthesized the first pentavalent-uranium silicate, although the U^{5+} valence state is considered unstable in aqueous solutions.[18]

Recently, we have extended the exploratory synthetic, structural, and property studies to the class of lanthanide silicates because lanthanide complexes exhibit interesting luminescence properties.[26−28] A good number of lanthanide silicates (denoted as AV-n) have already been synthesized under mild hydrothermal conditions by Rocha and co-workers.[19−21] Embedding lanthanide ions in the silicate frameworks is a new approach for preparing luminescent microporous materials, which contain a stoichiometric amount of lanthanide ions. A number of lanthanide silicates were also synthesized under high-*T*/high-*P* hydrothermal conditions by Haile et al. to search for fast alkali ion conductors.[23,24] The present paper presents the crystal structure and luminescence properties of hydrothermally grown crystals of $Cs_3EuSi_6O_{15}$ (denoted as **1**). To our knowledge, **1** is the second example of 3-D silicate framework with Si:O = 2:5, which contains only tertiary [SiO_4] tetrahedra.

Experimental Section

Synthesis. The hydrothermal reactions were carried out under autogenous pressure in gold ampules contained in a Leco Tem-Pres autoclave, where pressure was provided by water. The degree of filling of the autoclave by water at room temperature was 55%. A reaction mixture of 406 μL of 5.74 M $CsOH_{(aq)}$, 0.0410 g of Eu_2O_3 (Cerac, 99.9%), and 0.0896 g of SiO_2 (Alfa Aesar, 99.995%) (molar ratio Cs:Eu:Si = 10:1:6) in a 5.8 cm long gold ampule (inside diameter = 4.85 mm) was heated at 600 °C for 3 d. The pressure was estimated to be 170 MPa according to the pressure−temperature diagram of pure water. The autoclave was then cooled to 330 °C at 5 °C/h followed by fast cooling to room temperature by removing the autoclave from the furnace. The product was filtered off, washed with water, rinsed with ethanol, and dried at ambient temperature. The reaction produced colorless plate crystals of **1** as the major product and unidentified polycrystalline solid, as indicated by powder X-ray diffraction. EDX analysis of several plate crystals confirmed the presence of Cs, Eu, and Si. A crystal was selected for structure determination by single-crystal X-ray diffraction. Powder X-ray data were collected on a Shimadzu XRD-6000 automated powder diffractometer with Cu Kα radiation equipped with a scintillation detector. The plate crystals were manually separated from the powder to give a pure sample of **1** as judged by visual microscopic examination and by comparison of the X-ray powder pattern to the pattern simulated from the atomic coordinates derived from single-crystal study. The yield of **1** was 32% based on europium. The sample was used for luminescence properties study. Thermogravimetric analysis and infrared spectroscopy (KBr method) did not reveal any lattice water or hydroxyl group in the sample.

Single-Crystal X-ray Diffraction. A suitable crystal of **1** with dimensions 0.06 × 0.07 × 0.25 mm^3 was selected for indexing and intensity data collection on a Siemens SMART CCD diffractometer equipped with a normal focus, 3-kW sealed tube X-ray source. Intensity data were collected at room temperature in 1271 frames with ω scans (width 0.30° per frame). The program SADABS was used for the absorption correction (T(min/max) = 0.457/0.529). The structure was solved by direct methods and difference Fourier syntheses. The Cs(1) atom exhibited a very large U_{33} value and a large residual electron density near the Cs atom, indicating that Cs(1) is positionally disordered. A difference Fourier synthesis based on the atomic coordinates of Eu, Si, O, and the other Cs atoms revealed two nonequivalent Cs atoms having the same site occupancy. The distance between the two sites is very short (0.54 Å), precluding simultaneous Cs occupancy of these sites. Therefore, the structure was refined with two Cs(1) atoms each having a site occupancy of 0.5. The final cycles of least-squares refinement included atomic coordinates and anisotropic thermal parameters for all atoms, $\Delta\rho_{max,min} = 2.27, -1.10$ e Å^{-3}. The largest residual electron density in the final difference Fourier maps was at 2.47 Å from Cs(1). All calculations were performed using the SHELXTL Version 5.1 software package.[29]

Photoluminescence Measurements. Ten crystals of **1** each having about the same dimensions as those of the crystal for single-crystal X-ray diffraction were contained in a glass capillary for luminescence study. A laser beam at 532 nm, which corresponds to the Eu^{3+} excitation to the $^5D_1$ state, from a diode laser was employed as the light source to light up the sample for recording the emission spectra. The emission was collected by an f/1 focal lens and imaged onto a monochromator (Acton Research Corp. SP308) attached with an intensified charge-coupled device (ICCD, Roper Scientific PI-MAX 1024RB) detector. To reduce the interference of laser light scattering, a 532 nm Notch filter was inserted in front of the monochromator. The typical emission spectrum was recorded at 15 mW and at 10-min data acquisition time. This apparatus was also used for the measurements of photoluminescence lifetime except that the detector and the excitation light source were, respectively, replaced by a high-sensitivity photomultiplier tube (Thorn EMI 9558QB) and a pulsed 532 nm Nd:YAG (Spectra Physics INDI-40-10) laser beam at 10 mJ/pulse. The photoluminescence temporal waveform (i.e., the photoluminescence decay curve) was acquired with 1000 laser-shot-averaging in a 350 MHz high-frequency digital oscilloscope (LeCroy LT262) when the monochromator moves to the specific emission wavelength. Excitation spectrum was recorded on a powder sample at room temperature using a PTI QuantaMaster C-60 spectrofluorometer.

Results and Discussion

Structure. The crystallographic data are given in Table 1, and selected bond lengths are given in Table 2. As shown in Figure 1, the structure of **1** is constructed from the following structural elements: 6 SiO_4 tetrahedra, 1 EuO_6 octahedron, and 4 Cs sites. All atoms are at general positions.

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Table 1. Crystallographic Data for $Cs_3EuSi_6O_{15}$

formula	$Cs_3EuSi_6O_{15}$
a/Å	7.1664(1)
b/Å	28.4756(6)
c/Å	8.5418(2)
β/deg	104.976(1)
V/Å^3	1683.89(7)
Z	4
formula weight	959.23
space group	$P2_1/n$
T, °C	23
λ(Mo Kα), Å	0.71073
D_{calc}, g cm^{-3}	3.784
μ(Mo Kα), cm^{-1}	106.2
R_1[a]	0.0289
wR_2[b]	0.0697

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2(F_c)^2]/3$, where $a = 0.0368$ and $b = 0$.

Table 2. Selected Bond Lengths (Å) for $Cs_3EuSi_6O_{15}$

Eu(1)−O(3)	2.325(4)	Eu(1)−O(5)	2.289(4)
Eu(1)−O(8)	2.266(3)	Eu(1)−O(11)	2.302(4)
Eu(1)−O(13)	2.306(4)	Eu(1)−O(15)	2.337(4)
Si(1)−O(1)	1.627(4)	Si(1)−O(2)	1.609(4)
Si(1)−O(3)	1.577(3)	Si(1)−O(4)	1.635(4)
Si(2)−O(4)	1.624(4)	Si(2)−O(5)	1.561(4)
Si(2)−O(6)	1.626(4)	Si(2)−O(7)	1.643(4)
Si(3)−O(7)	1.647(3)	Si(3)−O(8)	1.560(3)
Si(3)−O(9)	1.643(4)	Si(3)−O(10)	1.625(4)
Si(4)−O(9)	1.642(4)	Si(4)−O(10)	1.636(4)
Si(4)−O(11)	1.573(3)	Si(4)−O(12)	1.610(4)
Si(5)−O(6)	1.617(4)	Si(5)−O(12)	1.616(4)
Si(5)−O(13)	1.562(4)	Si(5)−O(14)	1.644(4)
Si(6)−O(1)	1.629(4)	Si(6)−O(2)	1.613(4)
Si(6)−O(14)	1.646(4)	Si(6)−O(15)	1.562(3)

The observed Si−O bond lengths (1.560−1.647 Å, average 1.614 Å) and O−Si−O bond angles (102.8−115.8°) are typical values and are within the normal range.[30] Each SiO_4 tetrahedron shares three of its four oxygen corners with a corner of a neighboring SiO_4 group to form 4-, 6-, and 8-rings. The fourth corner remains unshared, being bonded to Eu and Cs atoms as well. The $Si-O_{term}$ bond length is shorter than the $Si-O_{br}$ distances. The EuO_6 octahedron is quite regular with the Eu−O bond lengths in the range from 2.266 to 2.337 Å. The bond-valence sum for Eu(1) is 3.23,[31] indicating that the europium atom is trivalent. Each EuO_6 octahedron shares its six corners with six different SiO_4 tetrahedra. Cs(1) is disordered over two sites with equal site occupancy, and the other two Cs sites are fully occupied. Based on the maximum cation−anion distance by Donnay and Allmann,[32] a limit of 3.70 Å was set for Cs−O interactions, which gives the following coordination numbers: Cs(1), CN = 9; Cs(1A), CN = 5 + 1, the first number referring to the number of neighboring atoms at shorter distances; Cs(2), CN = 11; Cs(3), CN = 11.

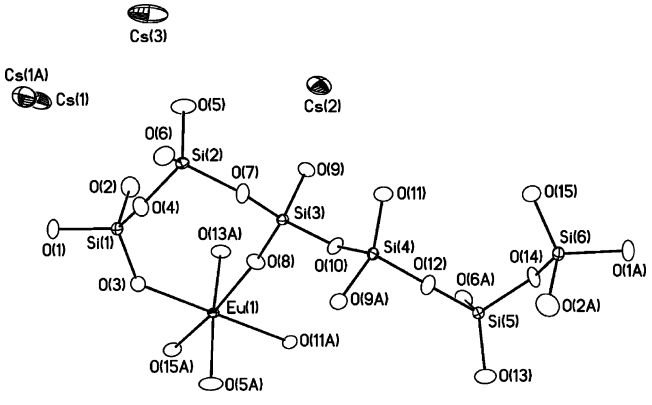

Figure 1. Building units of **1** showing the atom labeling scheme. Thermal ellipsoids are shown at 50% probability.

As shown in Figure 2, the 3-D framework structure of **1** consists of 4-, 6-, and 8-ring channels along the *a*-axis and 5- and 6-ring channels along the *c*-axis. The silicate framework of **1** consists of loop-branched vierer double chains with four-, six-, and eight-membered rings extending parallel to the *c*-axis. Adjacent double chains come together to form 10-membered rings at their interface so that a 3-D architecture is generated (Figure 3). Europium atoms are located at sites between six-membered silicate rings in the 6-ring channels, and each Eu^{3+} ion is bonded to three oxygen atoms of a ring and three more oxygens belonging to an adjacent ring. Cs(1) and Cs(1A) are located between two double chains. Cs(2) is at the center of the 10-membered ring at the interface. Cs(3) is located between two double chains and alternates along the *c*-axis with Eu atom.

There are a number of related $A_nLnSi_6O_{15}$ (A = alkali metal) compounds in the literature. Their structures have been found to contain 0-D double rings, 1-D double chains where the single rings or chains are linked via all tetrahedra, or 2-D single layers. The double-chain and single-layer structures are the most common. In synthetic $K_2CeSi_6O_{15}$, a 3-D framework has been found that contains only tertiary tetrahedra Q^3.[33] The structure can also be understood in terms of (Si_6O_{13}) layers, containing 6- and 10-membered rings, that are linked together by bridging O atoms to form the 3-D silicate anion. To our knowledge, this K, Ce silicate and compound **1** are the only two silicates with Si:O = 2:5 known to have interrupted frameworks of tertiary SiO_4 tetrahedra. Recently, a europium silicate, $Na_3EuSi_6O_{15}\cdot 2H_2O$, with the same framework stoichiometry but different structure was reported.[34] Its structure consists of undulated silicate layers containing five- and eight-membered rings. Adjacent layers are connected by Eu^{3+} ions through coordinative interactions to the terminal SiO_4 oxygen atoms to form a 3-D network.

Photoluminescence Studies. Figure 4 shows the room-temperature (RT) emission spectrum of **1**. The RT excitation spectrum of **1** from 350 to 550 nm is shown in the inset of Figure 4. The excitation lines are assigned to the Eu^{3+} intra-4f^6 transitions including the $^5D \leftarrow {}^7F$, $^5L \leftarrow {}^7F$, and $^5G \leftarrow {}^7F$ transitions. The RT emission spectra recorded at 532 and 466 nm (not shown) are very similar and show a number of lines between 575 and 720 nm. These lines are ascribed to the transitions between the first excited $^5D_0$ state and the $^7F_{0-4}$ Stark levels of the fundamental Eu^{3+} septet. Because only a single sharp line is observed in the region for $^5D_0 \rightarrow {}^7F_0$ transition, this indicates the presence of one Eu^{3+}-local environment. The emission from excited levels above the

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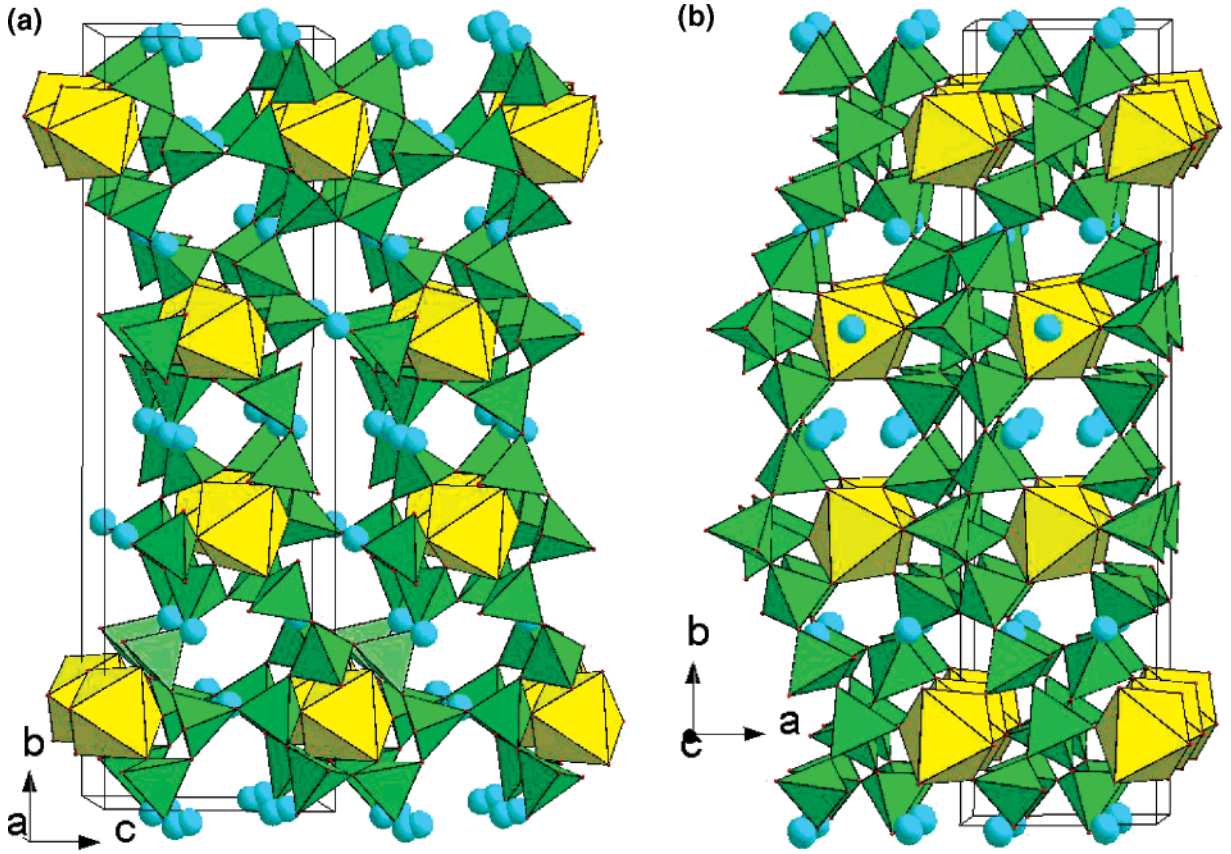

Figure 2. (a) Structure of **1** viewed along the *a*-axis. The yellow and green polyhedra represent EuO_6 octahedra and SiO_4 tetrahedra, respectively. Blue circles represent Cs atoms. (b) Structure of **1** viewed along the *c*-axis.

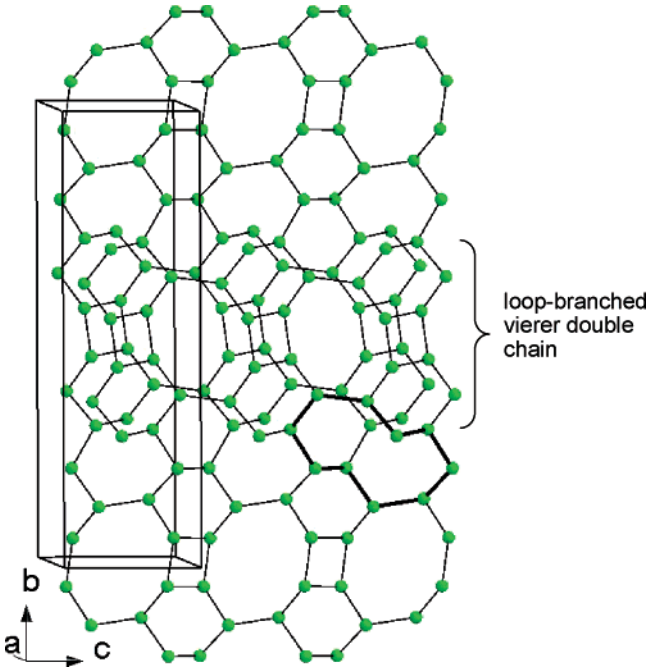

Figure 3. Silicate framework of **1** viewed along the *a*-axis to show the connectivity between adjacent loop-branched vierer double chains. One of the 10-membered rings at the interface is highlighted by thick lines. In this simplified schematic diagram, a tetrahedral Si atom is located at the intersection of the lines, as oxygen bridges are made by corner-sharing from the vertices of the tetrahedron.

$^5D_0$ such as $^5D_2$ and $^5D_1$ was not observed due to very efficient nonradiative relaxations to the $^5D_0$ level. This phenomenon is evidenced by the fact that the emission spectrum of pumping 466 nm is almost identical to Figure 4.

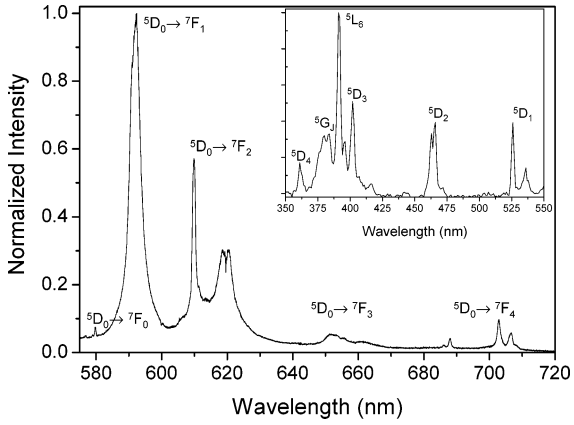

Figure 4. Room-temperature emission spectrum of **1** excited at 532 nm. The inset shows the excitation spectrum detected within the $^7F_1$ manifold (594 nm).

The $^5D_0 \rightarrow {}^7F_{0,3}$ transitions are allowed due to the ligand field effects, and the $^5D_0 \rightarrow {}^7F_1$ transitions around 594 nm have magnetic dipole (MD) character. On the other hand, the $^5D_0 \rightarrow {}^7F_{2,4}$ transitions in the 605−625 and 685−710 nm regions have electric dipole (ED) character and are allowed if the Eu^{3+} site lacks a center of symmetry. The integrated intensities of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions are almost the same, and this indicates that the local symmetry of the Eu^{3+} site does not have an inversion center.[35] Because the $^5D_0 \rightarrow {}^7F_2$ ED transition is hypersensitive to the nature of the Eu^{3+}−ligand surroundings, the nearly equal integrated intensities of the two transitions, $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$, also

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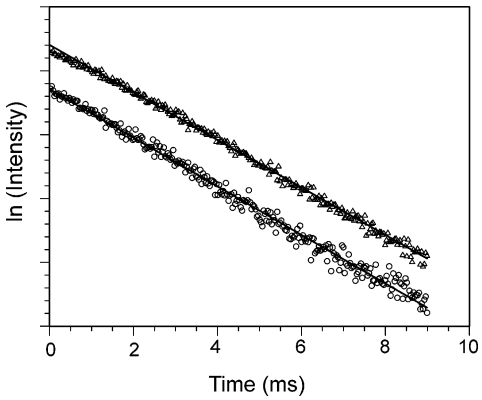

Figure 5. Room-temperature $^5D_0$ decay curves detected within the $^5D_0 \rightarrow {}^7F_1$ (△) and $^5D_0 \rightarrow {}^7F_2$ (○) regions and excited at 532 nm. The straight lines represent the best fit ($r^2 = 0.99$) to the data considering a single decay behavior.

imply that the EuO_6 octahedron is not strongly distorted. This result is consistent with the crystallographic results that the EuO_6 octahedron is quite regular with the Eu−O bond lengths between 2.27 and 2.34 Å and O−Eu−O bond angles between 84.4° and 97.3°.

As shown in Figure 5, the room-temperature $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ decay curves (in natural log scale) excited at 532 nm are well fitted by a single-exponential function, yielding lifetime values of 5.45 ± 0.01 ms, which is typical for anhydrous inorganic Eu^{3+} crystals. The lifetime measurements confirm the presence of one local Eu^{3+} environment.

In conclusion, the synthesis and crystal structure of a new europium silicate have been reported. It is a new member of open-framework lanthanide silicates, which contain stoichiometric amounts of lanthanides ions. The structure of **1** consists of loop-branched vierer double silica chains with four-, six-, and eight-membered rings, which are connected to form 10-membered rings at their interfaces so that a 3-D architecture is generated. It adopts a new type of structure and is the second example of 3-D silicate framework with Si:O = 2:5, which contains only tertiary [SiO_4] tetrahedra. The luminescence properties of **1** have also been reported. The sharp lines in the emission spectrum are assigned. The conclusions drawn from the relative intensities of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions and the lifetime measurements are consistent with the crystallographic results. Further research to synthesize new lanthanide silicates and mixed-metal silicates, particularly those belonging to the 3d−4f systems, are in progress.

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Supporting Information Available: Crystallographic data for **1** in CIF format, X-ray powder patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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