Inorg. Chem. **2008**, *47*, 1910−1912

Inorganic Chemistry
Communication

$Rb_2REGaSi_4O_{12}$ (RE = Y, Eu, Gd, Tb): Luminescent Mixed-Anion Double Layer Silicates Containing Chains of Edge-Sharing REO_7 Pentagonal Bipyramids

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Received December 18, 2007

Four new rare earth gallosilicates, $Rb_2REGaSi_4O_{12}$ (RE = Y, Eu, Gd, and Tb, denoted as REGS-1), have been synthesized under high-temperature, high-pressure hydrothermal conditions and characterized by single-crystal X-ray diffraction. They are the first examples of rare earth gallosilicates that contain individually occupied tetrahedral Ga^{3+} and Si^{4+} centers. The unique structure is formed of two 1D and one 2D substructural units: unbranched achter single chains which are seldom observed in silicates, the $PaCl_5$-type infinite chains formed of edge-sharing REO_7 petagonal bipyramids and the unprecedented mixed-anion double layers with the composition $[GaSi_4O_{12}]$. The photoluminescence properties of EuGS-1 and TbGS-1 have been studied. The Y^{3+} ion in YGS-1 can be partially replaced by Eu^{3+} and Tb^{3+} to yield luminescent materials.

The synthesis of microporous solids with extended inorganic framework topologies and varied chemical compositions has attracted much attention because of the continuing demand for these materials in a wide variety of applications.[1] Such materials include mainly zeolites, aluminophosphate- and silicoaluminophosphate-based molecular sieves with frameworks built of silicon, and aluminum and/or phosphorus oxide tetrahedra. The substitution of Al with Ga in known aluminosilicate frameworks has been extensively studied.[2] A gallosilicate having no counterpart among the aluminosilicates has also been synthesized.[3] In contrast to the substitutional compounds, heterometal gallosilicates with each metal occupying an individual site are rather limited. Only two piezoelectric materials, $Sr_3TaGa_3Si_2O_{14}$ and $La_3Ga_5SiO_{14}$, were previously documented.[4,5] In the latter, the first member in the lanthanide gallosilicate system, still the tetrahedral Ga^{3+} and Si^{4+} sites are mixed and indistinguishable. Herein, we report four new heterometal gallosilicates, $Rb_2REGaSi_4O_{12}$ (designated as REGS-1 with RE = Y, Eu, Gd, and Tb), obtained from hydrothermal reactions under the conditions of 600 °C and 170 MPa. These materials adopt a prototype framework topology and are the first examples of rare earth gallosilicates that contain individually occupied pentagonal bipyramidal RE^{3+} and tetrahedral Ga^{3+} and Si^{4+} centers. In addition, they are of great interest as host materials for other lanthanide ions to fine-tune desired photoluminescence properties.

A reaction mixture of 208 μL of RbOH(aq) (50 wt %), 33 mg of Ga_2O_3, 62 mg of Eu_2O_3, and 85 mg of SiO_2 in the molar ratio Rb:Ga:Eu:Si = 5:1:1:4 was sealed in a 4.2 cm long gold ampule (i.d. = 4.85 mm), which was contained in an autoclave and counterpressured with water at a fill level of 55%. The autoclave was heated at 600 °C for 36 h, cooled to 350 at 5 $°C \cdot h^{-1}$, and then rapidly cooled to room temperature (RT) by turning off the power of the tube furnace. The pressure at 600 °C was estimated to be 170 MPa according to the pressure−temperature diagram for pure water. The reaction yielded colorless columnar crystals of EuGS-1 as the major product, which was accompanied by a slight amount of unknown powder. The same reaction conditions, with Eu_2O_3 being replaced by Y_2O_3 or Gd_2O_3, produced colorless lamellar crystals of YGS-1 or GdGS-1 as major products. In an attempt to prepare the Tb analogue by using Tb_4O_7 as the metal source with the molar ratio Rb:

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10.1021/ic7024445 CCC: $40.75

Ga:Tb:Si = 8:1.5:1:4, we obtained colorless crystals of TbGS-1 along with some unidentified powder. The yields of these four materials were estimated to be 62, 50, 81, and 36%, respectively, based on Y_2O_3, Eu_2O_3, Gd_2O_3, and Tb_4O_7. Suitable crystals were selected for structure determination by single-crystal X-ray diffraction from which the chemical formula was determined to be $Rb_2REGaSi_4O_{12}$ (RE = Y, Eu, Gd, and Tb).[6] The Er compound was synthesized as a minor product according to powder X-ray diffraction. Compounds containing other rare earth metals have not been prepared.

The crystals of EuGS-1 and TbGS-1 were manually separated from the side products to give pure samples as judged by visual microscopic examination and powder X-ray diffraction (Figure S1). The samples were used for photoluminescence measurements. The Y^{3+} ion in YGS-1 can be partially replaced by Eu^{3+} and Tb^{3+} to form crystals of $Rb_2Y_{0.89}Eu_{0.11}GaSi_4O_{12}$ and $Rb_2Y_{0.94}Tb_{0.06}GaSi_4O_{12}$, respectively, as indicated by single-crystal X-ray diffraction. X-ray powder diffraction data were collected on a Shimadzu XRD-6000 powder diffractometer with Cu Kα radiation. Several crystals of EuGS-1 were contained in a glass capillary for luminescence study at RT. A laser beam at 473 nm from a diode laser was employed as the light source. The emission was collected by an *f*/l focal lens and imaged onto a monochromator attached with a charge-coupled device detector. This setup was also used for the measurements of emission radiative lifetime except that the detector and the excitation light source were, respectively, replaced by a photomultiplier tube and a tunable pulsed Nd:YAG laser and a pumped dye laser. Solid-state PL studies of TbGS-1 were performed on a powder sample at RT. PL spectra were measured on a Hitachi F-4500 FL spectrophotometer equipped with a Xe lamp as the light source.

The four compounds are isostructural, and therefore, only the structure of EuGS-1 is discussed. The structure is constructed by the following structural elements: 2 Rb sites, 1 EuO_7 pentagonal bipyramid, 1 GaO_4 tetrahedron, and 4 SiO_4 tetrahedra. All atoms are in general positions. The structure consists of unbranched single chains of corner-sharing SiO_4 tetrahedra in a period of eight along the *c* axis. The observed Si−O bond lengths and O−Si−O and $Si-O_{br}-Si$ bond angles are typical values within the normal range.[7] The stretching factor, f_s, which is defined by $f_s = I_{chain}/l_T \times P$, where I_{chain} is the length of identity period, l_T is the length of tetrahedron edge (2.70 Å), and *P* is the periodicity of the chain, is equal to 0.69.[7] The shrinkage of the chain is most pronounced for chains with an even number of tetrahedra in the repeat unit. For example, the indium silicate $K_5In_3Si_7O_{21}$ consists of single siebener chains with $f_s = 0.89$.[8] The 24er single chain in $Na_{24}Y_8Si_{24}O_{72}$ is extremely folded with $f_s = 0.23$.[9] As shown in Figure 1a, adjacent silicate chains are linked via corner-sharing by GaO_4 tetrahedra to form a mixed-anion layer. Each GaO_4 tetrahedron shares its corners with three SiO_4 tetrahedra within a layer and one SiO_4 tetrahedron in a neighboring layer such that hybrid double layers of tetrahedra with the composition $[GaSi_4O_{12}]$ in the *bc* plane are formed.

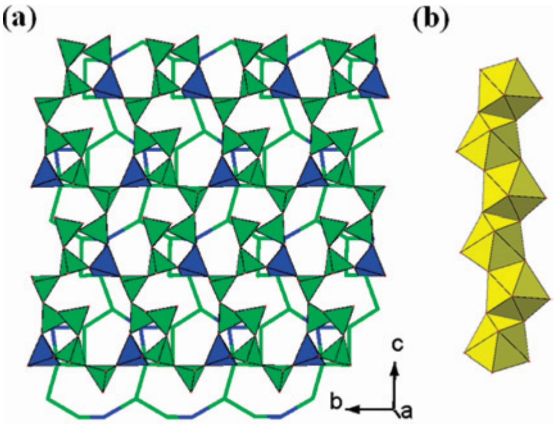

Figure 1. (a) Section of a mixed-anion double layer in EuGS-1. The green and blue tetrahedra represent SiO_4 and GaO_4 units, respectively. For clarity, one layer is shown in simplified representation in which a tetrahedral atom is located at the intersection of the lines, as oxygen bridges are made by corner-sharing from the vertices of the tetrahedra. (b) Section of an infinite chain formed of edge-sharing EuO_7 pentagonal bipyramids.

The rare earth ions are 7-fold coordinated in the 3+ oxidation state as indicated by bond valence calculations,[10] and each REO_7 unit approximates to a pentagonal bipyramid. Eu(1) is axially bonded to two oxygen atoms at 2.261 and 2.282 Å with an O−Eu−O bond angle of 178.7°. Each axial O atom is also bonded to a Si atom. Equatorially, Eu(1) is bonded to five oxygen atoms, four of which bond to Si atoms, with Eu−O bond lengths ranging from 2.303 to 2.542 Å, whereas the fifth oxygen bonds to one Si and one Ga atom (Eu−O = 2.720 Å). The five equatorial atoms are nearly coplanar. As shown in Figure 1b, the EuO_7 polyhedra share two equatorial edges to form linear chains with the composition $EuO_{2/1}O_{4/2}O_{1/1}$ (i.e., EuO_5). The chain is similar to that in $PaCl_5$, except that the dihedral angle between the equatorial planes of adjacent EuO_7 polyhedra in EuGS-1 is 27.6°, and all of the equatorial Cl atoms in a chain in $PaCl_5$ are coplanar.[11] Each EuO_7 polyhedron shares an edge with one SiO_4 tetrahedron and corners with one GaO_4 and five SiO_4 to form a 3D framework containing two types of six-ring channels along the *b* axis (Figure 2). The 8-fold coordinated Rb^+ cations are located at sites between adjacent six-memebered rings on the periphery of the channels.

A good number of lanthanide silicates, which were prepared under mild hydrothermal conditions at 200–230 °C,

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(6) Crystallographic data for EuGS-1: crystal of dimensions 0.05 × 0.06 × 0.25 mm, monoclinic, space group $I2/a$, $M_r = 696.98$, and $a = 22.555(2)$ Å, $b = 7.3428(7)$ Å, $c = 14.929(1)$ Å, $\beta = 90.137(2)°$, $V = 2472.4(4)$ Å^3, $Z = 8$, $d_{calcd} = 3.745$ g cm^{-3}, μ(Mo Kα) = 15.476 cm^{-1}. A total of 8587 reflections were measured at 294 K, which gave 3067 independent reflections with $R_{int} = 0.0249$. $R1 = 0.0293$ and $wR2 = 0.0786$ for 2802 reflections with $I > 2\sigma(I)$ and 181 parameters. Crystallographic data for the REGS-1 materials are summarized in Table S1, selected bond lengths and bond angles are given in Table S2. The unit cell dimensions for GdGS-1 and TbGS-1 are smaller because of lanthanide contraction.

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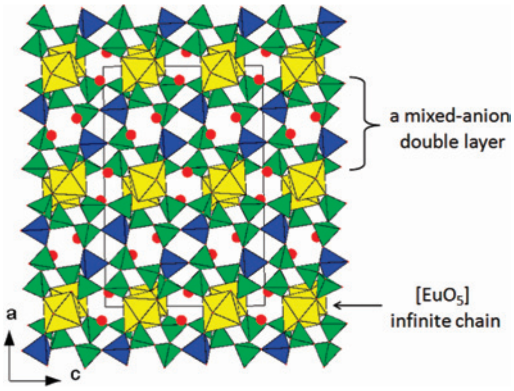

Figure 2. Structure of EuGS-1 viewed along the *b* axis. The yellow, blue, and green polyhedra represent EuO_7 pentagonal bipyramids, GaO_4 tetrahedra, and SiO_4 tetrahedra, respectively. Red circles are Rb^+ cations.

have been reported.[12] Most of them contain discrete Ln-centered polyhedra (LnO_6 or LnO_7). To our knowledge, $Na_{1.08}K_{0.5}Ln_{1.14}Si_3O_{8.5}\cdot 1.78H_2O$ (designated as AV-20, Ln = Eu, Tb, Sm, Ce) are the only known lanthanide silicates which also contain $PaCl_5$-type $[LnO_5]$ chains.[13] A small number of metal silicates contain silicate anions which can be regarded as a product of the condensation of two single layers. These double layer silicates are called diphyllosilicates. For example, monteregianite is a lanthanide diphyllosilicate.[14] Mixed-anion diphyllosilicates are extremely rare.[15,16] The double layer found in REGS-1 has not been observed in any diphyllosilicates. The structure is novel in terms of the $PaCl_5$-type $[REO_5]$ chains and mixed-anion double layers. An organically templated open framework uranyl silicate, which has some structural similarities with REGS-1, was reported.[17] The structure of the uranium compound contains silicate double layers which are connected by $PaCl_5$-type uranate chains formed of UO_3F_4 pentagonal bipyramids.

Compounds EuGS-1 and TbGS-1 and the mixed-metal materials $Rb_2Y_{1-x}Eu_xGaSi_4O_{12}$ and $Rb_2Y_{1-x}Tb_xGaSi_4O_{12}$ showed red and green photoluminescence, respectively, when irradiated with UV radiation. The RT emission spectrum recorded at 473 nm ($^5D_2 \leftarrow {}^7F_0$) excitation exhibits a number of lines between 570 to 700 nm (Figure S2). These lines are ascribed to emission from the first excited $^5D_0$ state to the $^7F_{0-4}$ Stark levels of the fundamental Eu^{3+} septet. The presence of one $^5D_0 \rightarrow {}^7F_0$ line indicates the existence of one Eu^{3+} local environment, and this is consistent with the crystallographic results. The integrated intensity of the $^5D_0 \rightarrow {}^7F_1$ lines is a little higher than that of the $^5D_0 \rightarrow {}^7F_2$ lines, indicating that the deviation from inversion symmetry for the Eu^{3+} ion is small. The decay curves of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions at 473 nm excitation are well fitted by a single exponential function, yielding lifetime values of about 2.9 ms, which confirms the presence of one local Eu^{3+} environment. The lifetime is shorter than the value (5.45 ms) in $Cs_3EuSi_6O_{15}$.[18] The shorter emission lifetime implies a larger electronic transition dipole moment in EuGS-1 than in $Cs_3EuSi_6O_{15}$. However, it should be noted that the concentration quenching of Eu^{3+} could also contribute to the shorter lifetime for EuGS-1 because the structure contains chains formed of edge-sharing EuO_7 pentagonal bipyramids. The emission lines in the RT emission spectrum of TbGS-1 are assigned to the $^5D_4 \rightarrow {}^7F_{6-3}$ transitions. The green $^5D_4 \rightarrow {}^7F_5$ transitions at 541 and 549 nm are intense, whereas the $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_4$, and $^5D_4 \rightarrow {}^7F_3$ transitions are made up of several unresolved weak peaks (Figure S3).

In summary, four new rare earth gallosilicates $Rb_2REGaSi_4O_{12}$ (RE = Y, Eu, Gd, and Tb) have been synthesized under high-temperature, high-pressure hydrothermal conditions. They are the first examples of rare earth gallosilicates that contain an individually occupied RE^{3+} ion site and tetrahedral Ga^{3+} and Si^{4+} centers in the 3D framework. The unique structure contains two 1D and one 2D substructural units: unbranched achter single chains which are seldom observed in silicates, the $PaCl_5$-type infinite chains formed of edge-sharing REO_7 pentagonal bipyramids, and the unprecedented mixed-anion double layers $[GaSi_4O_{12}]$ wherein the Rb^+ cations are encapsulated. The Y^{3+} ion in YGS-1 can be partially replaced to yield luminescent $Rb_2Y_{1-x}RE_xGaSi_4O_{12}$ (RE = Eu, Tb) materials. The structure may allow the simultaneous incorporation of a second (or even a third) type of lanthanide ion in the framework and, therefore, the fine-tuning of their photoluminescence properties. Further work on this theme is in progress.

Acknowledgment. We thank the National Science Council for financial support, and Prof. B.-C. Chang at National Central University for PL measurements.

Supporting Information Available: X-ray crystallographic information files (CIF), tables of crystallographic data and selected bond lengths for REGS-1; calculated and observed power XRD patterns for REGS-1, room-temperature emission spectrum and decay curves of EuGS-1; room-temperature emission spectrum and excitation spectrum of TbGS-1. This material is available free of charge via the Internet at http://pubs.acs.org.

IC7024445

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