



Chiral microporous rare-earth silico-germanates: Synthesis, structure and photoluminescence properties

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ABSTRACT

The first examples of chiral microporous rare-earth silico-germanates were obtained by isomorphous substitution of Si^{4+} by Ge^{4+} in small-pore $\text{Na}_3[\text{RESi}_3\text{O}_9]\cdot 3\text{H}_2\text{O}$ ($\text{RE} = \text{Y}^{3+}, \text{Eu}^{3+}$), using hydrothermal synthesis. Single-crystal X-ray diffraction and ^{29}Si solid-state NMR clearly demonstrate the framework insertion of Ge^{4+} , with preference for two of the three crystallographic T^{4+} sites.

The isomorphous Ge^{4+} for Si^{4+} substitution originates a dispersion of the RE^{3+} environments, resulting in multiple and broader Eu^{3+} emission lines. Despite these, the main photoluminescence properties of pure Si- and Ge,Si-materials are very similar. A particularly intriguing feature is the detection, in both cases, of quasi-enantiomeric domains by selective excitation at 12 K.

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1. Introduction

Microporous lanthanide silicates, reminiscent of zeolites (pure microporous aluminosilicates built from tetrahedral units), combine microporosity and optical properties. They are built from tetrahedral SiO_4 and polyhedral LnO_n ($n \geq 6$) building blocks and exhibit a rich structural chemistry and interesting physical and chemical properties. Most of these compounds are prepared under mild hydrothermal conditions (150–240 °C) in Teflon-lined autoclaves [1–19], by flux-growth techniques [20–22], and high temperature (above 500 °C) and high autogenous pressures [23,24]. The aim of many of these reports is the engineering of photoluminescent trivalent lanthanide (Ln^{3+}) centers into such materials. In this context, the proof of concept was presented with microporous materials containing Ce^{3+} (AV-5) [1], Eu^{3+} and Tb^{3+} (AV-9) [2] and with structures related to the structure of mineral monteregianite, which photoluminescence in the visible region upon UV irradiation. AV-9 materials containing, respectively, Er^{3+} and Tb^{3+} have also been used to demonstrate the infrared luminescence and X-ray scintillation capabilities of such porous materials [6]. The simultaneous incorporation of different Ln^{3+} ions (plus Y^{3+} , for ion dilution) in the structures of certain lanthanide silicates improves and fine-tunes their photoluminescence properties by minimizing the quenching concentration, adjusting the excitation wavelength, and taking advantage of the energy transfer between Ln^{3+} pairs, such as Ce^{3+} – Tb^{3+} and Gd^{3+} – $\text{Tb}^{3+}/\text{Eu}^{3+}$ [13,14,25–28].

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The potential applications of porous and layered lanthanide silicates in medical diagnosis, particularly in dual optical imaging and magnetic resonance imaging (MRI), constitute a very attractive field of future development [7,12,29,30].

Germanium has been extensively used to replace silicon in zeolite materials, yielding silico-aluminogermanates by isomorphous substitution and/or new pure GeO_2 and mixed $(\text{Ge,Si})\text{O}_2$ zeolites, depending essentially on the symmetry requirements of their tetrahedral double four-ring (D4R) units (Ref. [31] and references therein). Recently, Sastre and Corma calculated the equilibrium angles for Si–O–Si, Ge–O–Si, and Ge–O–Ge with values of 157.7°, 137.8°, and 133.3°, respectively, predicting the feasibility of several structures as pure silicate/germanate zeolites [32]. Ge^{4+} and Si^{4+} have the same valence shell electronic structure, similar ionization energies and electronegativities. Being larger than Si^{4+} , in germanates Ge^{4+} adopts coordination numbers of 5 and 6, besides 4, due to the intrinsic longer M–O bond length (by about 0.15 Å) and shorter M–O–M angles [32].

In contrast to microporous rare-earth silicates, essentially no work is available on the microporous germanium analogues. Only a few pure lanthanide germanate compounds were structurally characterized, namely $\text{Eu}_2\text{Ge}_2\text{O}_7$ [33], and NaEuGeO_4 [34], while a single paper on KEuGe_2O_6 reports on photoluminescence properties [35]. We have previously reported on $\text{Na}_3[\text{RESi}_3\text{O}_9]\cdot 3\text{H}_2\text{O}$ ($\text{RE} = \text{Y}, \text{Eu}, \text{Tb}, \text{Er}, \text{Ce}$), an unprecedented chiral, photoluminescent microporous silicate system containing Ln^{3+} ions, for which it was shown that Eu^{3+} photoluminescence spectroscopy, with excitation by unpolarized light in the absence of an external magnetic field, is able to identify enantiomeric domains [8,36]. Here, we wish to report the synthesis and structural characterization of a similar system,

$\text{Na}_3[(\text{Y},\text{Eu})(\text{Si},\text{Ge})_3\text{O}_9]\cdot 3\text{H}_2\text{O}$, exhibiting isomorphous substitution of Si^{4+} by Ge^{4+} , and assess to what extent this substitution influences the photoluminescence properties.

2. Experimental

2.1. Synthesis

The syntheses of rare-earth mixed silico-germanates and pure silicate were carried out in Teflon-lined autoclaves, under static hydrothermal conditions, in ovens preheated at 150 and 230 °C. The rare-earth nitrate solutions (0.4 M) were prepared by dissolving the corresponding rare-earth oxides (99.99% purity) in diluted nitric acid under heating. In all syntheses, the autoclaves were removed and quenched in cold water after an appropriate time. The obtained microcrystalline powders were filtered off, washed at room temperature with distilled water, and dried at 80 °C.

The following compounds were prepared: $\text{Na}_3[(\text{Y}_{0.7}\text{Eu}_{0.3})\text{Si}_3\text{O}_9]\cdot 3\text{H}_2\text{O}$, **1**; $\text{Na}_3[\text{YSi}_3\text{O}_9]\cdot 3\text{H}_2\text{O}$, **2**; $\text{Na}_3[(\text{Y}_{0.75}\text{Eu}_{0.25})\text{Si}_{2.5}\text{Ge}_{0.5}\text{O}_9]\cdot 3\text{H}_2\text{O}$, **3**; $\text{Na}_3[(\text{Y}_{0.75}\text{Eu}_{0.25})\text{Si}_2\text{GeO}_9]\cdot 3\text{H}_2\text{O}$, **4**; $\text{Na}_3[(\text{Y}_{0.75}\text{Eu}_{0.25})\text{SiGe}_2\text{O}_9]\cdot 3\text{H}_2\text{O}$, **5**; $\text{Na}_3[\text{YSi}_2\text{GeO}_9]\cdot 3\text{H}_2\text{O}$, **6**; $\text{Na}_3[\text{YSiGe}_2\text{O}_9]\cdot 3\text{H}_2\text{O}$, **7**. The chemical composition of samples was ascertained by EDS (considering a standard error of ca. 20%) and single crystal X-ray studies.

The purely siliceous powdered samples **1** and **2** were prepared using the procedure previously reported, autoclaving the starting gels at 150 °C for 13 days [8]. Single crystals of $\text{Na}_3[(\text{Y}_{0.7}\text{Eu}_{0.3})\text{Si}_3\text{O}_9]\cdot 3\text{H}_2\text{O}$, **1b**, were obtained reacting at 230 °C for 5 days an identical starting composition. The resulting sample contains small amounts of $\text{H}_{0.5}\text{Na}_{2.5}[(\text{Y}_{0.7}\text{Eu}_{0.3})\text{Si}_3\text{O}_9]\cdot 3\text{H}_2\text{O}$ and dense $\text{Na}_3[(\text{Y}_{0.7}\text{Eu}_{0.3})\text{Si}_3\text{O}_9]$ [8].

2.1.1. Typical synthesis of $\text{Na}_3[(\text{Y}_{0.75}\text{Eu}_{0.25})\text{Si}_{2.5}\text{Ge}_{0.5}\text{O}_9]\cdot 3\text{H}_2\text{O}$, **3**

An alkaline solution was made by mixing 3.27 g sodium silicate solution (27% m/m SiO_2 , 8% m/m Na_2O , Merck), 60.03 g H_2O and 14.05 g NaOH (Panreac). An amount of 4.75 g GeO_2 (99.99%) was added to the previous alkaline solution under stirring. After complete dissolution of GeO_2 , a mixture of 12.25 mL $\text{Y}(\text{NO}_3)_3$ and 5.25 mL $\text{Eu}(\text{NO}_3)_3$ 0.4 M was added to this solution and stirred thoroughly. The gel, with composition 2.97 Na_2O : 0.755 SiO_2 : 0.245 GeO_2 : 0.0408 Y_2O_3 : 0.0175 Eu_2O_3 : 55.5- H_2O , was reacted in autoclaves (volume 150 cm^3) for 10 days at 150 °C. The resulting sample, mostly composed by single crystals of **3**, also contains unidentified colloidal particles easily removed by washing several times with fresh water. Compounds **4–7** were prepared in a similar way, adjusting the Si, Ge, Y and Eu contents. Single crystals of **4** and **5** were also obtained, but compounds **6** and **7** are powdered materials. In contrast with the pure siliceous form, for which the content of the final product is quantitative in terms of the Eu introduced in the gel, for the mixed Si/Ge materials we noticed a reduction of the introduced Eu on the final product: Eu/(Y + Eu) ratio around 0.3 and 0.25 in the gel and in the final product, respectively. Also the insertion of Ge is not quantitative, for Ge/(Si + Ge) ratios of 0.25, 0.5 and 0.75 on the starting gel we estimate, respectively, 0.17, 0.33 and 0.66 in the final products.

2.2. Techniques

The morphology of the samples was analyzed on a Hitachi SU-70 scanning electron microscope. EDS was carried out using an EDS Römteck System with an attached polymeric window.

^{29}Si magic angle spinning (MAS) NMR spectra were recorded at 79.49 MHz on a (9.4 T) Bruker Avance III 400 spectrometer, using 40° pulses, spinning rates of 5 kHz and 60 s recycle delays. ^1H - ^{29}Si cross-polarization (CP) MAS NMR spectra were recorded

with 5.0 μs ^1H 90° pulses, 8 ms contact time and 1 s recycle delays. Chemical shifts are quoted in parts per million from TMS.

Photoluminescence measurements were recorded on a Fluorolog[®]-3 Model FL3-2T with double excitation spectrometer (Triax 320), fitted with a 1200 grooves/mm grating blazed at 330 nm, and a single-emission spectrometer (Triax 320), fitted with a 1200 grooves/mm grating blazed at 500 nm, coupled to R928P photomultiplier. The excitation sources used were a 450 W Xe arc lamp and a pulsed Xe-Hg lamp, for the steady-state and time-resolved measurements, respectively. The excitation spectra were corrected from 240 to 600 nm for the spectral distribution of the lamp intensity using a photodiode reference detector. Emission and excitation spectra were also corrected for the spectral response of the monochromators and the detector, using typical correction spectra provided by the manufacturer. The measurements at low temperature were performed using a He closed-cycle cryostat. Time-resolved measurements were carried out using a 1934D3 phosphorimeter coupled to the Fluorolog[®]-3 and a Xe-Hg flash lamp (6 μs /pulse half width and 20–30 μs tail) was used as excitation source.

Very small single crystals of compounds $\text{Na}_3[(\text{Eu}_{0.3}\text{Y}_{0.7})\text{Si}_3\text{O}_9]\cdot 3\text{H}_2\text{O}$ (**1**), $\text{Na}_3[(\text{Eu}_{0.25}\text{Y}_{0.75})\text{Si}_2\text{GeO}_9]\cdot 3\text{H}_2\text{O}$ (**4**) and $\text{Na}_3[(\text{Eu}_{0.25}\text{Y}_{0.75})\text{SiGe}_2\text{O}_9]\cdot 3\text{H}_2\text{O}$ (**5**) were directly harvested from the reaction vessel and immersed in highly viscous FOMBLIN Y perfluoropolyether vacuum oil (LVAC 140/13) purchased from Sigma-Aldrich. After careful inspection and selection, suitable single-crystals of each material were mounted on Hampton Research CryoLoops [37] with the help of a Stemi 2000 stereomicroscope equipped with Carl Zeiss lenses. Data were collected at 150(2) K on a Bruker X8 Kappa APEX II charge-coupled device (CCD) area-detector diffractometer (MoK_α graphite-monochromated radiation, $\lambda = 0.71073$ Å) controlled by the APEX2 software package [38], and equipped with an Oxford Cryosystems Series 700 cryostream monitored remotely using the software interface Cryopad [39]. Images were processed using the software package SAINT+ [40], and data were corrected for absorption by the multi-scan semi-empirical method implemented in SADABS [41].

The crystal structures were solved using the Patterson synthesis algorithm implemented in SHELXS-97 [42,43], which allowed the immediate location of most of the atoms composing the asymmetric unit, in particular the rare-earth (RE^{3+}) metal centers and the mixed-sites $\text{Si}^{4+}/\text{Ge}^{4+}$. All remaining non-hydrogen atoms were located from difference Fourier maps calculated from successive full-matrix least squares refinement cycles on F^2 using SHELXL-97 [42,44]. All non-hydrogen atoms were successfully refined using anisotropic displacement parameters.

Concerning the occupancy of the heavy sites, all structures are much disordered: the crystallographically independent RE^{3+} site may be occupied by Y^{3+} or Eu^{3+} , while the three tetrahedral sites may contain Si^{4+} or Ge^{4+} (in the case of compounds **4** and **5**). The occupancy of each site was obtained from unrestrained refinement with complementary rates of occupancy for each $\text{Y}^{3+}/\text{Eu}^{3+}$ or $\text{Si}^{4+}/\text{Ge}^{4+}$ pair. Upon full least-squares convergence the respective site occupancies were fixed to give the molecular formulae quoted above for each material.

Hydrogen atoms associated with the three crystallographic independent water molecules of crystallization were clearly visible as distortions of the electronic cloud observed from difference Fourier maps. These atoms were included in the structural model with the O–H and H...H distances restrained to 0.95(1) and 1.55(1) Å, respectively, in order to ensure chemically reasonable geometries for the solvent moieties. In addition, their isotropic thermal displacements parameters (U_{iso}) were fixed at $1.5 \times U_{\text{eq}}$ of the oxygen atom to which they are attached.

As found for the materials we have previously reported [8], during the refinement stage, crystals of **1**, **4** and **5** produced strong

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