Optical Detection of Solid-State Chiral Structures with Unpolarized Light and in the Absence of External Fields**

Duarte Ananias, Filipe A. Almeida Paz, Luís D. Carlos, Carlos F. G. C. Geraldes, and João Rocha*
Zeolites are microporous aluminosilicate materials of considerable industrial importance because they are excellent molecular sieves, ion exchangers, and heterogeneous catalysts. With the advent of the nanotechnology era, and increasing interest in the use of molecular sieves for device applications, novel zeolite-type materials containing stoichiometric amounts of lanthanide (Ln) metals that exhibit photoluminescence and magnetic properties have been investigated.[1–3] Herein we report the remarkable framework of Na₃[(Y,Ln)Si₃O₉]·3H₂O (Ln = Eu, Tb, Er, Ce), an unprecedented chiral, photoluminescent, and microporous Ln-silicate system. Only two zeolite-type silicates exhibit chiral polymorphism, namely zeolite beta and ETS-10, but neither of these materials is photoluminescent.[4,5] The crystal structure of Na₃[(Y,Ln)Si₃O₉]·3H₂O materials displays (Si₃O₉)ₖ chiral spirals interconnected by [(Y,Ln)O₆] octahedra, and it exhibits a statistical excess of one enantiomer over the other. For the first time, we show that Eu³⁺ photoluminescence spectroscopy with excitation by unpolarized light in the absence of an external magnetic field is able to identify, and possibly quantify, enantiomeric domains in chiral frameworks. This enantioselectivity phenomenon may be of importance in the context of fundamental interactions between light and condensed matter.

Although conventional zeolites are built up of tetrahedral [SiO₄] and [AlO₄] units, microporous silicates whose frameworks contain transition-metal heteropolyhedra have been known since the early 1990s.[1–3] The most prominent member of this family is titanosilicate ETS-10, which contains [TiO₆] and [SiO₄] units.[5] The constituent elements of heteropolyhedral silicates have been recently extended to lanthanides, and it exhibits a statistical excess of one enantiomer over the other. For the first time, we show that Eu³⁺ photoluminescence spectroscopy with excitation by unpolarized light in the absence of an external magnetic field is able to identify, and possibly quantify, enantiomeric domains in chiral frameworks. This enantioselectivity phenomenon may be of importance in the context of fundamental interactions between light and condensed matter.

Previously, chirality involving lanthanide complexes has been sensed by magnetochiral dichroism (MChD)⁶–⁷ and circular dichroism (CD) methods, such as Ln-centered absorption, ligand absorption, and Ln-centered circularly polarized luminescence (CPL).[⁸,⁹] Whereas CPL measures the difference in emission intensity between left and right circularly polarized light, MChD evaluates the difference in luminescence intensity in the directions parallel and antiparallel to an externally applied magnetic field using unpolarized light (e.g., from a Hg-discharge lamp). Enantiodiscrimination typically uses the magnetic dipole-allowed Eu(5D0→7F₅), Tb(5D₄→7F₄), and Yb(5F₇→5F₃) transitions in CPL experiments, whereas in MChD the 5D₀→7F₁₃ transitions are employed.[⁶–⁹]

The solids described herein were obtained as byproducts in the hydrothermal synthesis of dense Na₃[LnSi₃O₉] phosphors.[¹⁰–¹²] Crystals suitable for single-crystal X-ray diffraction were prepared for small-pore materials Na₃[(Y₀.₉₉₅Eu₀.₀⁰₅)Si₃O₉]·3H₂O (1a) and Na₃[(Y₀.₉₈₆Er₀.₀₁₄)Si₃O₉]·3H₂O (1b). Isostructural Na₃[(Y₀.₉₄Te₀.₀₆)Si₃O₉]·3H₂O (1c) and Na₃[(Y₀.₉₄Tb₀.₀₆)Si₃O₉]·3H₂O (1d) were also synthesized as powders and used in the photoluminescence studies. These solids are chiral orthorhombic phases exhibiting a statistical enantiomeric excess (see the Supporting Information). A second type of smaller, monoclinic, centrosymmetric crystals which often cocrystallize with 1, namely, H₀.₅Na₂.₅[(Y₀.₉₉₅Er₀.₀⁰₅)Si₃O₉]·3H₂O (2), were manually harvested and analyzed on a rotating-anode diffractometer.

The structure of dense Na₃[LnSi₃O₉] is constructed from complex double spiral chains (Si₉O₂₇)ₖ with a period of 15.14 Å, which connect isolated [LnO₆] octahedra.[¹⁰] The chiral (1) and centrosymmetric (2) materials share a common type of (Si₉O₂₇)ₖ chain (Figure 1b and Supporting Information) running along the [100] direction (period of one a-axis length, ca. 6.97 Å). Although the (Si₉O₂₇)ₖ chains are different they are both built up of triortho groups Si₁₀O₁₈ and the latter chain readily transforms into the former on calcining solids 1 and 2 at 800°C. We speculate that the Si₁₀O₁₈ group is the structural motif that first forms in the gel and templates the synthesis of the three phases. The silicon oxide chains not only connect individual [LnO₆] octahedra but they also isolate them, at minimal Ln···Ln distances of about 6.32 and 5.88 Å in 1 and 2, respectively (Figure 1 and Supporting Information). Such separation of the optically active centers is important because it effectively avoids self-quenching.

Although the (Si₉O₂₇)ₖ structural motif is similar for both 1 and 2, the way it is linked to the metal centers is different. Consider the first coordination sphere of the [(Y,Ln)O₆] distorted octahedra (see the Supporting Information), whereas in 1 chelation of the metal center by three SiO₂ moieties ultimately leads to a chiral structure, in 2 one of the chelate rings is broken. As a result, the small-pore structure of the former contains one-dimensional mixed 8-ring channels along the [100] direction, which have a cross section of about 2.₀ × 4.₀ Å (Figure 1a) and host Na⁺ ions and hydrogen-bonded water molecules, whereas the comparatively dense framework of the latter has 6-ring tunnels housing Na⁺ and H⁺ ions and water molecules (see the Supporting Information).
Excitation and emission spectra of 1d were recorded at room temperature and 10 K (Supporting Information). In the excitation spectra, the sharp lines between 280 and 500 nm are assigned to $7F_6 \rightarrow 5D_4$, $5L_10$, $5G_6 \rightarrow 3$, $5H_7 \rightarrow 4$, and $5F_5$, intraconfigurational forbidden $4f^8 \rightarrow 4f^8$ transitions of Tb$^{3+}$. The broad band between 250 and 280 nm is ascribed to the spin-forbidden (high-spin, HS) interconfigurational $4f^8 \rightarrow 4f^75d^1$ transition of Tb$^{3+}$ (see reference [13] and references therein). This type of spin-forbidden fd band may be observed for (heavy) Ln$^{3+}$ ions with more than seven $4f$ electrons at an energy lower than that of spin-allowed (low-spin, LS) fd transitions. The broad band at about 236 nm is assigned to the spin-allowed (LS) interconfigurational fd transition of Tb$^{3+}$. The emission spectra of 1d, excited at 265 nm, show a series of sharp lines between 475 and 700 nm, assigned to the $5D_4 \rightarrow 7F_J$ ($J=6–1$) transitions of Tb$^{3+}$ (see the Supporting Information). The same emission is obtained with excitation at the intra-$5D_3$ (377 nm) line.

The excitation spectra of 1c recorded at room temperature and 10 K (Figure 2) display a series of sharp lines assigned to $^7F_{5,6} \rightarrow D_{4,5}$, $^1I_{10}$, $^5L_6$, $^5G_6 \rightarrow 7$, and $^5F_{1,3}$ Eu$^{3+}$ intra-4f transitions. The faint broad band ($4f^5 \rightarrow 4f^75d^1$) at high energy is probably the beginning of the spin-allowed, interconfigurational fd Eu$^{3+}$ transition band, which normally appears at higher energy than the equivalent Tb$^{3+}$ band. At 10 K the spectrum exhibits an additional broad band that peaks at 264.5 nm and is attributed to ligand-to-Eu$^{3+}$ charge transfer (CT). The energy (4.69 eV) and full-width at half-maximum (0.58 eV) of the CT band are in the range of values reported for many structures containing Eu$^{3+}$.\[14\]

The sharp lines of the emission spectra (Figure 3) are assigned to transitions between the first excited nondegenerate $5D_0$ state and the $7F_J$ levels of the fundamental Eu$^{3+}$ septet. Local-field splitting of the $5F_{1,2}$ levels into three and five Stark components (inset in Figure 3, green line) supports the presence of a single low-symmetry Eu$^{3+}$ environment, as indicated by the crystal structure. Surprisingly, when the sample is excited at the CT band (265 nm) the number of $F_{1,2}$ Stark components doubles (inset in Figure 3, magenta line). We note that this is only observed between 10 and about 120 K, the temperature range in which the CT band is also detected (despite the fact that the X-ray data, collected at 100 K, call for the presence of a single Eu$^{3+}$ site).

Because the $5D_0 \rightarrow 7F_0$ line is very faint, we did not draw any conclusions from its evolution when the excitation wavelength was varied from the CT to the intra-4f lines. The relative intensities of the two main $5D_0 \rightarrow 7F_2$ Stark components depend on the particular sample studied (see the Supporting Information). This observation constitutes first (though not unequivocal) evidence for the presence of two enantiomers in 1c. Moreover, the enantioselective detection of Eu$^{3+}$-containing molecular compounds by CPL and MChD has been found to be much more sensitive in the magnetic dipole-allowed $5D_0 \rightarrow 7F_1$ transition than in the induced electric-dipole $5D_0 \rightarrow 7F_2$ transition. In 1c we observe maximum splittings of the $5D_0 \rightarrow 7F_1$ transition of 172 and...
95 cm⁻¹, respectively for excitation at the CT band and intra-
4f⁰ lines (inset in Figure 3). For the Dₓ → F₂ transition the
maximum splittings are 373 and 310 cm⁻¹, respectively, for
the same excitations. Thus, the maximum splitting difference
is significantly larger for the Dₓ → F₁ transition (77 cm⁻¹,
compared with 63 cm⁻¹ for the other transitions).

Measurements of Dₓ lifetimes for Naₓ-
[(Yₓ₋Euₓ)SiₓO₃]·3H₂O (a = 0.2, 0.3; see the Supporting
Information) clearly support this conclusion. In all measure-
ments, the Dₓ decay curves are well fitted by a single
exponential (Supporting Information). At 10 K the two
samples display a similar lifetime (1.59 ± 0.01 ms) for
excitation in the Dₓ level (526 nm) and detection in the
strongest F₁ Stark component (608.5 nm). However, excita-
tion in the CT band leads to different lifetimes. Whereas the
sample with a = 0.2 has the same lifetime for the two main F₂
Stark components at 607.8 and 609.1 nm ((1.48 ± 0.01) ms),
that with a = 0.3 displays different lifetimes of (1.39 ± 0.01)
and (1.54 ± 0.01) ms for detection at these wavelengths,
respectively.

We now try to rationalize the unusual detection of
enantiomeric domains by photoluminescence spectroscopy
in all the syntheses, autoclaves were removed and quenched in cold
water after an appropriate time. The obtained microcrystalline
powders were filtered, washed at room temperature with distilled
water, and dried at 100°C.

Typical synthesis of single crystals of 1a: An alkaline solution
was made by mixing sodium silicate solution (6.83 g, 27 wt % SiO₂,
8 wt % Na₂O, Merck), H₂O (10.07 g), and NaOH (6.59 g, Panreac).
A mixture of YCl₃·6H₂O (1.05 g, Aldrich), TbCl₃·6H₂O (0.058 g,
Aldrich), EuCl₃·6H₂O (0.035 g, Aldrich), and CeCl₃·7H₂O (0.050 g,
Aldrich) in H₂O (10.0 g) was added to this solution, and the
solution was stirred thoroughly. The gel, with composition
2.97Na₂O·1.00SiO₂·0.075Y₂O₃·0.0201Tb₂O₃·0.0014Eu₂O₃·0.0014
Ce₂O₃·36.3H₂O, was heated in autoclaves (volume 37 cm³) for 8 d at
230°C. The resulting sample also contained single crystals of 2 and
dense Naₓ[(Yₓ₋Euₓ)SiₓO₃]·3H₂O (Supporting Informa-
tion).[11–12] Typical synthesis of single crystals of 2: An alkaline solution
was made by mixing sodium silicate solution (7.91 g, 27 wt % SiO₂,
8 wt % Na₂O, Merck), H₂O (12.20 g), and NaOH (7.72 g, Panreac).
A mixture of YCl₃·6H₂O (1.293 g, Aldrich) and ErCl₃·6H₂O (0.008 g,
Aldrich) in H₂O (10.0 g) was added to this solution and the solution
was stirred thoroughly. The gel, with composition
3.00Na₂O·1.00SiO₂·0.060Y₂O₃·0.0003Er₂O₃·34.7H₂O, was heated in
autoclaves (volume 42 cm³) for 5 d at 230°C. The resulting sample
also contained small amounts of 1b and dense
Naₓ[(Yₓ₋Euₓ)SiₓO₃]·3H₂O.[11–12] Ultrasonication of a water suspension of
the material disperses the crystals of 2. Unlike the dense material
[10–12] and 1b crystals, crystals of 2 remain in the aqueous
phase and are easily isolated.

Pure samples of 1c and 1d were prepared from a similar initial
gel by introducing the desired Yₓ⁺ and Eu³⁺ or Tb³⁺ contents and heating
for 13 d at 150°C (see the Supporting Information).

The chemical composition of the samples was ascertained by
energy-dispersive X-ray spectroscopy. Thermogravimetry
confirmed that materials 1 and 2 contain three water molecules per formula unit.

Further details on the crystal structure investigations may be
obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggen-
stein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata＠fiz-karlsruhe.de), on quoting the depository numbers
CSD-415853 ([1a], -415852 ([1b], and -415852 ([2). See also the
Supporting Information.

Experimental Section

The syntheses of rare-earth-metal silicates were carried out in teflon-
lined autoclaves under static hydrothermal conditions in
oven preheated to 150–230°C. All lanthanide salts were of 99.9% purity.

Crystal data for 1a: H₂O₄Er₂O₃Na₂O₂O₂Si₁₀Y₁₀₃, M = 1785.47,
orthorhombic, space group P2₁2₁2₁, Z = 1, a = 6.9724(14),
b = 11.6872(2), c = 13.404(3) Å, V = 1092.2(4) Å³, μ(MoKα) =
5.864 mm⁻¹, ρ(calc) = 2.715 g·cm⁻³. Of a total of 5575 reflections
collected, 2408 were independent (Rint = 0.0525). Crystal size 0.08 ×
0.07 × 0.04 mm. Final R1 = 0.0288 [I > 2σ(I)] and wR2 = 0.0650
(all data).

Crystal data for 1b: H₂O₄Er₂O₃Na₂O₂O₂Si₁₀Y₁₀₃, M = 1762.36,
orthorhombic, space group P2₁2₁2₁, Z = 1, a = 9.6910(14), b = 11.669(2), c =
13.375(3) Å, V = 1086.4(4) Å³, μ(MoKα) = 5.892 mm⁻¹, ρ(calc) =
2.694 g·cm⁻³. Of a total of 9102 reflections collected, 2226 were
independent (Rint = 0.0453). Crystal size 0.10 × 0.09 × 0.06 mm. Final
R1 = 0.0268 [I > 2σ(I)] and wR2 = 0.0566 (all data).

Crystal data for 2: H₂O₄Er₃O₃Na₂O₂O₂Si₁₀Y₁₀₃, M = 1718.40, mono-
clinic, space group P2₁/n, Z = 1, a = 9.0734(4), b = 8.8283(4), c =
12.963(5) Å, β = 107.687(2)°, V = 988.87(7) Å³, μ(MoKα) =
13.675 mm⁻¹, ρ(calc) = 2.886 g·cm⁻³. Of a total of 2571 reflections
collected, 990 were independent (Rint = 0.1025). Crystal size 0.05 ×
0.05 × 0.11 mm. Final R1 = 0.0832 [I > 2σ(I)] and wR2 = 0.2030
(all data).

Photoluminescence measurements were performed on a Fluoro-
log-3 Model FL3-2T with double excitation spectrometer (Trixia
320), fitted with a 1200-groves·mm⁻¹ grating blazed at 330 mm, and a
single emission spectrometer (Trixia 320), fitted with a 1200-groe-
es·mm⁻¹ grating blazed at 500 mm, coupled to an R928P photo-
multiplier. The excitation source was a 450-W xenon lamp. Excitation

spectra were corrected from 240 to 600 nm for the spectral distribution of the lamp intensity by using a photodiode reference detector. Emission and excitation spectra, recorded between 10 K and room temperature in 20–30-K steps by using a closed-cycle He cryostat, were also corrected for the spectral response of the monochromators and the detector by using typical correction spectra provided by the manufacturer. Time-resolved measurements were carried out with a 1934D3 phosphorimeter coupled to the Fluorolog-3 and a Xe–Hg flash lamp (6 μs/pulse half width and tail of 20–30 μs) was used as excitation source.

Received: July 17, 2006  
Revised: September 11, 2006  
Published online: October 19, 2006

Keywords: hydrothermal synthesis · lanthanides · luminescence · microporous materials · silicates