Luminescent Hybrid Material Based on a Clay Mineral

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Clay minerals, and within these, the smectite group, including the hectorites in focus, possess layered structures, in which interlayer chemistry may be applied to functionalize them optically. While luminescence from organic dyes has previously been described in the structurally closely related montmorillonites, attempts to obtain luminescence from occluded rare earths is not known to exhibit significant efficiency. This may in part be due to the presence of significant amounts of iron, but is mostly due to the inherent presence of water and structural OH groups. In the present paper, attempts to screen Tb^{3+} from disadvantageous matrix interactions by generating complexes with 2,2′-bypyridine within the interlayers are described, which eventually yield a 12-fold increase in emission intensity on complexation or about 20% in quantum efficiency, respectively. Even very low levels of iron impurities appear to still be a delimiting factor with regard to optical efficiency. However, if these can be avoided, the distinctly two-dimensional morphological features of of the hectorites or other clay minerals may be exploited toward new interesting optical applications.

Introduction

Lanthanide ions, especially Eu^{3+} and Tb^{3+}, have in the past been demonstrated to afford efficient luminescence on doping into porous matrixes, such as sol−gel materials and zeolites.[1,2] However, a principal bottleneck of merely rare earth doped host−guest systems, for, e.g., photoluminescence (PL) driven light-generating purposes, is the weak absorption of the rare earth ions above 250 nm, caused by the forbidden nature of the f−f transitions. Furthermore, water is encountered in most of these matrixes, leading to disadvantageous deactivation of the excited states via high-energy vibrations. If the emissive states are energetically allocated below approximately 30 000 cm^{-1}, the quantum yields will thus increasingly be reduced, eventually reaching values below, e.g., 10% for aqueous Tb^{3+} and below 1% for Eu^{3+}.[3] Last, but not least, in the case of Eu^{3+}, immediate interaction of the ion with matrix oxygens generates a O → Eu charge transfer state (CT), which may extend into the near UV and can cause radiationless return to the ground state. These shortcomings are known to be circumvented successfully by the coordination of shielding ligands to the encapsulated rare earth ions. Bidentate aromatic organic ligands are particularly useful, as they contribute to the absorptivity and can act as "antennas" to the rare earth ion's luminescence as well. This process is well documented and proceeds along the following successive steps:[4,5] (1) singlet−singlet absorption of the ligand ($^1S_0 \rightarrow {}^1S^*$, $\pi-\pi$ in nature); (2) intersystem crossing (ISC, $^1S^* \rightarrow {}^3T$, promoted by the spin−orbit coupling due to the Tb^{3+} ion); (3) (exchange resonance driven) energy transfer ligand (^3T) → Tb^{3+} ($^5D_4$).

In addition to this "local" intramolecular luminescence mechanism of the complexes, communication, i.e., energy transfer or migration, between structurally differing rare earth ions within the matrixes plays an important role. In structurally isotropic zeolites (e.g., cubic zeolite X) and random sol−gel matrixes, energy transfer will essentially be a three-dimensional process, while a confinement to two dimensions may be expected in layered structures; see, e.g., layered double hydroxides.[6] Hectorite rather than other minerals of the smectite group was chosen as the layered substrate because it could be obtained with comparably low $Fe^{2+/3+}$ content, a factor which is often essential in the interpretation of luminescence and optical data,[7] especially if bipyridines are involved (see below).

Structurally, hectorites are characterized by alternating stacks of complex layers, composed of complex sheets, and variable interlayers. The complex layers, also referred to as the "TOT" layers, consist of two sheets of tetrahedral SiO_4,

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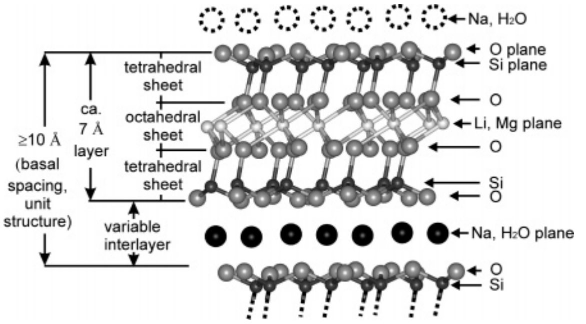

Figure 1. Sketch of the hectorite structure. Nomenclature according to Bailey.[8]

which are enveloping one $(Mg,Li)(O,F)_6$ plane. The interlayers, thus sandwiched between such TOT layers, contain mobile and thus exchangeable Na^+ ions in addition to variable amounts of water. Furthermore, the fluoride ions of the octaherdral sheets may be replaced by OH^- ions (see Figure 1 and ref 8). Hectorites, just like the structurally related, but more widely used montmorillonites, serve (among many other purposes) technical purposes as fillers in polymers or rheological additives in coating−film formulations,[9] and are therefore of applicatory interest in rendering such systems optically active as well.

2,2′-Bipyridine (bipy) was initially chosen as a ligand because its terbium and other rare earth complexes are known to show luminescence[10] and, due to an envisaged planar arrangement of a $Tb(bipy)_2^{3+}$ species, additionally anchored to atoms of sandwiching oxygen planes. However, such an arrangement remains hypothetical at this stage, as the stoichiometry and spectroscopic properties found on complexation suggest that $Tb(bipy)_3^{3+}$ entities prevail. It is more than likely that the Tb^{3+} coordination number is higher than 6, as coordination numbers of up to 12 have been found for bipyridine dominated rare earth complexes.[11] It should be mentioned here that previous investigations on $[Ru(bipy)_3]^{2+}$ in hectorite show the tris-ligated structure of the cation to be maintained as well.[12] However, an alignment of luminescent complexes[13] and, more recently, optical interactions between rare earth ions and organic sensitizers in bentonite[14] and within montmorillonite interlayers[15] have also been proposed. $[Ru(bipy)_3]^{2+}$ has furthermore served as a photoprobe in hectorites and laponites, respectively.[16]

Experimental Section

Materials Composition. Carbon analyses were carried out using a C-analyzer with IR-detection unit (ELTRA, Germany). Differential thermal analysis (DTA)/differential thermogravimetric (DTG) measurements were conducted from 20 to 1000 °C with a Netzsch (Germany) STA 409 C/CD at a heating rate of 10 K/min in Al_2O_3 crucibles in synthetic air. Tb was determined by dissolving the materials in nitric acid, followed by precipitation with excess oxalic acid. The precipitate was filtered off, washed thoroughly, and redissolved in sulfuric acid, from which it could be determined titrimetrically with $KMnO_4$. In the hectorite composite, Tb^{3+} was additionally monitored with energy-dispersive X-ray (EDX) spectrometry.

Lanthanoid salts and bipyridine were purchased from Aldrich and used without further purification. Deionized water was used in all syntheses.

The hectorite (Laporte Ltd., Great Britain) was used without further treatment, the water content was determined from DTG, and the composition was measured using EDX/ZAF ($Na_{0.36}Li_{0.2}Mg_{2.72}Si_4O_{10}(OH)_2$, see above). In addition to the specified matrix elements, 0.01 mol % iron was detected. Infrared spectra were recorded in pressed KBr disks on a Perkin-Elmer Spectrum One Fourier transform infrared spectrometer. X-ray diffraction powder measurements were conducted with Cu Kα radiation (Philips powder diffractometer).

Complex Syntheses. *$Tb(bipy)_2(NO_3)_3$.* A 3 mmol sample of bipy was dissolved in 20 mL of ethanol, followed by dropwise addition of 1 mmol of $Tb(NO_3)_3$ (2 mL 0.5 *m* aqueous solution, pH 6.0). The mixture was cooled to 4 °C for 48 h, after which colorless crystals were isolated, washed with cold ethanol, and dried in a vacuum (10^{-3} mbar) at room temperature. The composition of the complex was identified on the basis of carbon analysis, DTG, and IR. Theory etically for $Tb(bipy)_2(NO_3)_3$: C 36.54%; found: 35.81. No weight loss was detectable below 300 °C in DTA, and H−O vibrations were absent in the IR.

$Tb(bipy)_2Cl_3(H_2O)_n$ Used For Spectroscopic Comparison. The material was obtained by titration of a freshly prepared precipitate of $Tb(OH)_3$ (0.084 g, 0.4 mmol) with approximately 5 *m* HCl to give a neutral solution of $TbCl_3$. To this solution ethanol was added to give a total volume of 10 mL. An excess quantity of 2,2′-bipyridine (0.1872 g, 1.2 mmol) was dissolved in another 10 mL of ethanol, after which both solutions were unified. The pH of the solution was maintained at 7. After 30 min a precipitate had formed, which was filtered off and dried for 10 h at 60 °C in a drying chamber. Intense green emission was observed under UV irradiation. The product obtained in this manner was not single phase and was thus only used as an aid in assigning bipyridine modes in the IR spectrum, because the pure complex, $Tb(bipy)_2(NO_3)_3$ (s.a.), had nitrate vibrations in critical regions. Analytically found: C 33.05%, Tb 24.2%, H_2O 5.71% (DTG); theoretically for, e.g., $Tb(bipy)_2Cl_3(H_2O)_4$: C 36.97%, Tb 24.9%, H_2O 5.55%).

Hectorite Ion Exchange. A 1 g sample of the matrix hectorite was exchanged at room temperature with 5 mL of a 0.5 mol/L solution of $Tb(NO_3)_3$ at pH 5 by stirring over 10 h. The pH was controlled continously during the exchange. The solution was then centrifuged and the solid was washed with ethanol. Drying took place at 40 °C for 24 h in a vacuum.

Gas-Phase Loading with Bipyridine. Excess 2,2′-bipyridine (500 mg) was added to Tb^{3+}-exchanged hectorite under vacuum conditions (10^{-2} mbar). The starting materials were hermetically sealed in a glass ampule and treated at 80 °C over 50 h. After breaking the ampule, the resulting powder was repeatedly washed with ethanol and dried again in a vacuum drying chamber at 40 °C.

The composition of the complex containing hectorite was determined as $Tb_{0.2}Mg_{2.7}Si_4O_{10}(OH)_2(bipy)_{0.48}(H_2O)_{1.5}$. Theory: Tb

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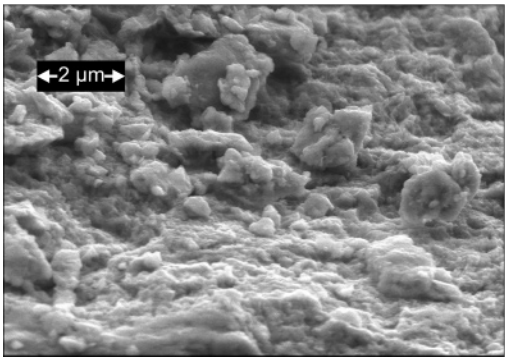

Figure 2. SEM image of the hectorite used in the present investigation.

7.1%, found 7.23%; C 12.87%, 12.9% (DTG); H_2O 6.02%, 6.1% (DTG).

Spectroscopic Characterization. Emission and excitation spectra of the solids were recorded at an angle of incidence of ca. 50° using a praying mantis type of setup to allow horizontal sample positioning without a cover. Reflectance spectra were obtained using an integrating sphere with a diameter of 70 mm and 10 mm port openings versus commercial white and black references (Labsphere) and $BaSO_4$, respectively. Two Acton 300 Monochromators of 300 mm focal length were thus synchronously scanned. The intensity of the 450 W Xe source was detected with an Acton P2 photomultiplier tube; the gratings had 1200 grooves mm^{-1}. The excitation spectra were corrected for the lamp and spectrometer profiles against Lumogen Red doped PMMA powders (doping level 50 ppm), whose quantum yield was taken as a constant 42%. Additional verification of the quantum yields below 320 nm was acquired by measurements vs $BaMgAl_{10}O_{17}$:Eu (BAM). Reference Lumogen Red and BAM were generously provided by BASF, Ludwigshafen (Germany), and Philips Laboratories, Aachen (Germany), respectively. Lifetimes were measured with an Edinburgh Instruments FL 920 lifetime spectrometer (single photon counting) equipped with a Edinburgh Instruments μF900 flash lamp and a Hamamatsu extended red sensitivity photomultiplier tube. Prior to sample measurements, the lifetime of commercial green emitting $LaPO_4$:Ce,Tb (Nichia) with a quantum yield of 89% at 254 nm excitation was measured to be 2.886 ± 0.003 ms.

Results and Discusson

The hectorite used ("Laponite", Laporte; see also Figure 2; composition according to supplier was $Na_{0.36}Li_{0.2}Mg_{2.72}Si_4O_{10}(OH)_2$, additionally containing three interlayer H_2O as determined by DTG) was subjected to an aqueous ion exchange with Tb^{3+} and subsequently loaded with bipy using a gas-phase-loading scheme in static vacuum, similar to the loading of zeolites with organic ligands.[17] High loading levels could only be obtained using comparably concentrated Tb^{3+} solutions of approximately 2 mol/L, after drying at 120 °C, eventually giving a composition of $Tb_{0.2}Mg_{2.7}Si_4O_{10}(OH)_2(H_2O)_{1.5}$ (Tb−hect). In this formula, it was assumed that all of the Na^+, but also the Li^+ of the octahedral sheets, was exchanged; however, some uncertainty remains in the total stoichiometry because the amount of Mg^{2+} was not reproducably determined with sufficient precision to exclude the loss of some Mg instead of Li or Na. The as-obtained hectorite had a lattice spacing of 14.33 Å, while the ion exchange with Tb^{3+} caused an expansion to 14.97 Å in the hydrated state due to the higher H_2O-coordination capacity of the Tb^{3+} ion compared to Na^+ (see Figure 3). Both of these data are still in a range characteristic for smectites and, within these, the hectorites in particular.[9] In comparison, the stepwise increase of hydration of the hectorites is known to cause basal plane distances of 10.0, 12.4, 15.6, and 18.8 Å, corresponding to zero, one, two, and three layers of water molecules.[18] The relatively high Tb^{3+} content after ion exchange, along with the appreciable loss in Li^+ from the octahedral sheets, and eventually also the Tb:bipy ratio of 1:2.4 (see below) indicate that, next to the interlayers, some of the Tb^{3+} has penetrated the octahedral sheets as well. It should be noted that the incorporation of trivalent Eu^{3+} and Cm^{3+} ions into octahedral sheets of synthetic hectorites during a dedicated synthesis has recently been supported by means of EXAFS analysis.[19] Considering the above-mentioned aspects, the approximate overall composition may be rewritten as $[Tb_{0.16}(H_2O)_{1.5}]^{inter}[Mg_{2.7}Tb_{0.04}]^{octahedral}[Si_4O_{10}(OH)_2]^{tetrahedral}$.

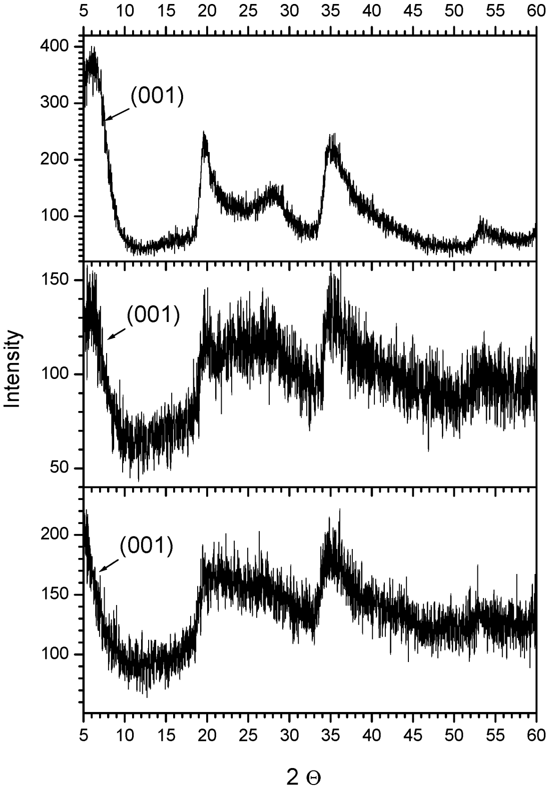

Figure 3. X-ray diffraction pattern of the hectorites (Cu Kα). Bottom: $Tb_{0.2}Mg_{2.7}Si_4O_{10}(OH)_2(bipy)_{0.48}(H_2O)_{1.5}$ after loading with bipyridine. Middle: Tb^{3+} ion exchanged $Tb_{0.2}Mg_{2.7}Si_4O_{10}(OH)_2(H_2O)_{1.5}$. Top: as-supplied $(Na_{0.36}Li_{0.2}Mg_{2.72}Si_4O_{10}(OH)_2$. Only the basal reflections were used to calculate the interlayer spacings.

Subsequent gas-phase loading with bipy leads to the formation of the complex within the interlayers. Due to instrumental restrictions, the lowest X-ray reflection could not be monitored completely, but it unambigously shows that the vertical lattice constant assumes a value in excess of 17.34 Å. Since the TOT layer thickness amounts to ap-

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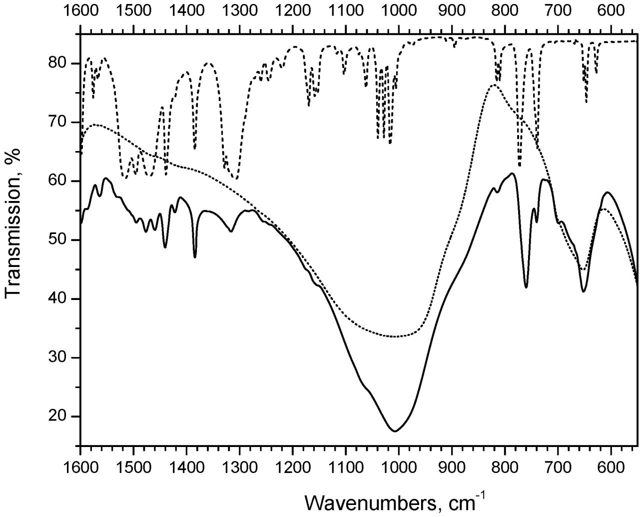

Figure 4. Infrared spectra of ion exchanged and gas-phase-loaded $Tb_{0.2}Mg_{2.7}Si_4O_{10}(OH)_2(bipy)_{0.48}(H_2O)_{1.5}$ (bottom, solid line); $(Na_{0.36}Li_{0.2}Mg_{2.72}Si_4O_{10}(OH)_2$, hectorite as purchased (center, dotted line); and free complex $Tb(bipy)_2(NO_3)_3$ (top, dashed line).

proximately 7 Å,[9] the interlayer sheet now assumes a thickness of more than 10.34 Å, sufficient to accommodate a complete $Tb(bipy)_3{}^{3+}$ cation, while a planar $Tb(bipy)_2{}^{3+}$ cation would demand less than 4 Å. The projected area consumed by a $Tb(bipy)_3{}^{3+}$ cation requires at least ≈80 Å^2, while the hectorite unit cell base with $a = 5.25$ and $b = 9.18$ offers a free area of about 50 Å^2. Thus, at a composition of $Tb_{0.2}Mg_{2.7}Si_4O_{10}(OH)_2(bipy)_{0.48}(H_2O)_{1.5}$ ($Tb(bipy)_3$−hect) the interlayer's area coverage amounts to approximately 30%. This description is reflected in the infrared spectra (Figure 4); no absorption bands of free bipy ligand are observed (expected 1416, 1454 C=N; 1558, 1579 C=C).

In anhydrous $Tb(NO_3)_3(bipy)_2$, all nitrate ligands bond to the metal center in a chelating fashion, leading to a coordination number of 10 of the Tb^{3+} ion.[20] A comparison of $TbCl_3(bipy)_2(H_2O)_n$, $TbBr_3(bipy)_2(H_2O)_n$,[21] $Eu(NO_3)_3(H_2O)_5$,[22] $Tb(NO_3)_3(bipy)_2$, and pure bipyridine reveals four NO_3 modes (1518 cm^{-1}, 1472 cm^{-1}, 1308 cm^{-1}, and, with less confidence due to overlap with bipyridine vibrations, a weak shoulder at 745 cm[23]). The coordination of bipyridine in both $Tb(NO_3)_3(bipy)_2$ and $Tb(bipy)_3$−hect is evident from the absence of several prominent vibrations of free bipyridine or their shift, respectively. In accord with coordination, ring modes involving −C=N− stretch character are blue-shifted (in cm^{-1}: 1438, 1495, and doublets at 1567/1576 and 1598/1605) in comparison to free bipyridine. The appearance of the doublets is a consequence of the higher number of bonds in the $Tb(bipy)_2{}^{3+}$ and $Tb(bipy)_3{}^{3+}$ units, each of which in principle requires an additional vibration. The increased number of vibrations is also in accord with the proposed noncentrosymmetric structure in the hectorite.

Further support is gained from the optical spectra as reproduced in Figure 5. Depicted are excitation and emission spectra of the free complex $Tb(bipy)_2(NO_3)_3$, Tb^{3+}-doped hectorite, and the material after gas-phase loading, $Tb(bipy)_3$−hect. Although the emission spectra appear comparable qualitatively, apart from the drastic intensity changes, it is recognized that the ($^5D_4 \rightarrow {}^7F_5$)/($^5D_4 \rightarrow {}^7F_6$) emission ratios are occasionally interpreted in terms of local symmetry.[24] While this is probably not conclusive by itself, it may be pointed out that the intensity ratios of the magnetic dipole transitions $^5D_4 \rightarrow {}^7F_5$ over (forced) electric dipole $^5D_4 \rightarrow {}^7F_6$ increase in the series $Tb(bipy)_2(NO_3)_3$ (2.02; 542 nm/491 nm), $Tb(bipy)_3$−hect (2.5; 544 nm/490 nm), and Tb-doped hectorite (2.67; 544 nm/489 nm), thus indicating the highest deviation from centrosymmetry for pure Tb^{3+} in the matrix and the highest symmetry for $Tb(bipy)_2(NO_3)_3$.[25] The excitation of the pure Tb^{3+} ion in the hectorite is very low over the monitored spectral range. A weak feature at 230 nm is ascribed to an f−d excitation band. Considering the allowed nature of this band, it is concluded that the hectorite matrix obscures and prevents efficient excitation at this wavelength. As opposed to that, introduction of the bipy into either complex or hectorite leads to strong excitability at approximately 330 and 340 nm in the hectorite, respectively. The apparent lower intensity of hectorite imbedded complex species is understood in terms of a lower number of absorbing species per volume. In support of the screening of Tb^{3+} by the bipyridine ligands, we have determined the quantum yield of $Tb(bipy)_3$−hect to amount to 19.8% at 340 nm excitation with a monoexponential decay of 0.981 ± 0.003 ms, which is an appreciable value considering the high-energy, deactivating −OH vibrations present in this hybrid material. Nevertheless, comparing the data with the quantum yields and lifetimes measured for the anhydrous $Tb(bipy)_2(NO_3)_3$ (>90%, 1.446 ± 0.006 ms), a quantum yield of

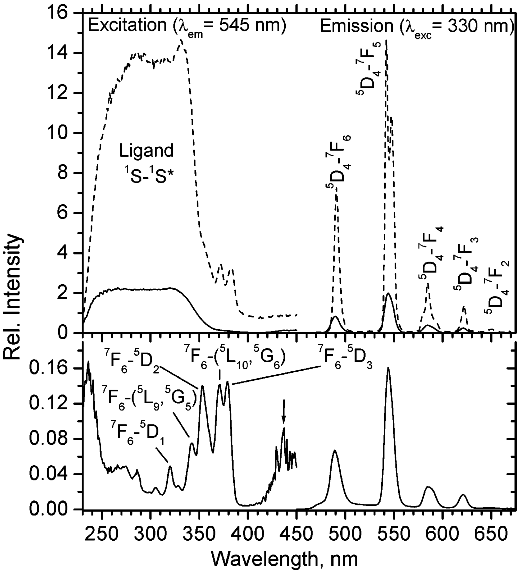

Figure 5. Excitation and emission spectra of $Tb_{0.2}Mg_{2.7}Si_4O_{10}(OH)_2(bipy)_{0.48}(H_2O)_{1.5}$ (top, solid line), free $Tb(bipy)_2(NO_3)_3$ (top, dashed line), and $Tb_{0.2}Mg_{2.7}Si_4O_{10}(OH)_2(H_2O)_{1.5}$ (bottom). Note that the intensities of Tb−hectorite are reduced by a factor of ≈100. The arrow indicates an artifact due to the correction procedure.

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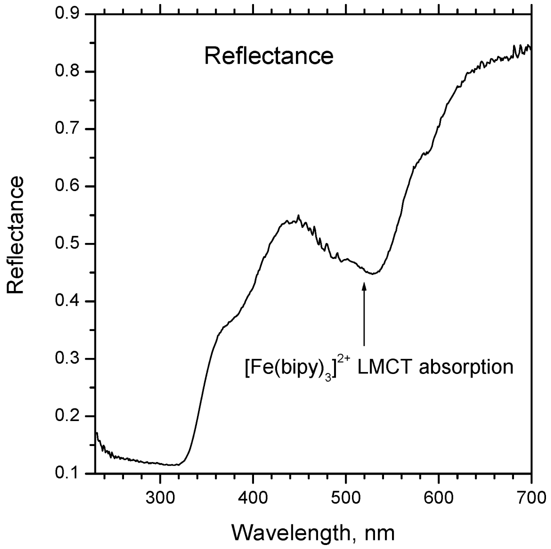

Figure 6. Reflectance spectrum of $Tb_{0.2}Mg_{2.7}Si_4O_{10}(OH)_2(bipy)_{0.48}(H_2O)_{1.5}$, indicating the $Fe^{2+/3+}$ impurities of the native hectorite.

approximately 60% might be expected. However, inspection of the reflectance spectra at approximately 530 nm leads to the conclusion that the hectorite still contains Fe^{2+}, which undergoes a strong ligand to metal charge transfer (LMCT) transition at 520 nm (Figure 6).[26] Next to reabsorption of Tb^{3+}-related emissions, which will already diminish the quantum yield by about a factor of 2, it is conceivable that the Fe^{2+} additionally provides quenching channels accessed via $Tb^{3+} \rightarrow Fe^{2+}$ energy transfer.

Conclusion

In summary, hectorites have been demonstrated to exhibit appreciable luminescence efficiencies on incorporation of Tb^{3+} ions, which, however, have to be shielded and sensitized, respectively, with suitable organic ligands. As such, bipyridine was utilized, and was incorporated via the gas phase, most likely forming a tris-ligated Tb^{3+} species, possibly with additionally coordinating water. The formation of the complexes is accompanied by a swelling of the interlayer spaces to values in excess of 17 Å. In order to arrive at high luminescence efficiencies within this scheme, residue iron has to be abolished or avoided. Due to its structural anisotropy and rheological, i.e., layer-forming, properties, an interesting hybrid material for several optical applications may thus be obtained.

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