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# Energy transfer in luminescent Tb- and Eu-containing layered double hydroxides

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**The synthesis of new Tb- and Eu-containing LDH-based luminescent hybrid materials with quantum yields up to 45% is described; energy transfer studies in corresponding mixed $Tb^{3+}/Eu^{3+}$ systems revealed highly efficient ligand→$Tb^{3+}/Eu^{3+}$ and $Tb^{3+}$→$Eu^{3+}$ communication channels.**

The development of new methods for the synthesis of stable and inexpensive luminescent materials for optical applications is a central problem in modern materials science. The main requirements for such materials are high quantum efficiencies, the repeatability of synthetic procedures and the stability of light output. Organic complexes of rare earth elements fulfill many of these requirements and are used in optical applications. Moreover, the incorporation of highly efficient rare-earth based luminescent molecules into optically transparent solid matrices holds the promise of novel hybrid materials combining the chemical and mechanical stability of the solid state with optical features typical of molecular complexes. As recent examples, luminescent materials based on mesoporous molecular sieves, zeolites and polymers can be quoted.[1–3]

We studied the intercalation of lanthanide picolinate [pyridine-2-carboxylate, (pic)] complexes $Tb(pic)_4^-$ and $Eu(pic)_4^-$ into a layered double hydroxide matrix. Layered double hydroxides (LDHs) are hydrotalcite-like layered compounds with the general formula $M_{1-x}^{2+}M_x^{3+}(OH)_2[(anion^{n-})_{x/n}{\cdot}mH_2O]$. The LDH structure consists of positively charged hydroxide layers $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}$ bonded to negatively charged anions, which occupy interlayer spaces.[4] The structure of LDH provides high mobility of anions between rigid hydroxide layers, allowing them to exchange without rearrangement of hydroxide layers. Compared to zeolites, sol–gel matrices and mesoporous silica, the use of LDHs makes it possible to control the amount of anions in the interlayer space by varying the $M^{2+}:M^{3+}$ ratio at the synthetic stage.[5] In addition, the use of this system provides a unique opportunity of studying the energy transfer efficiency depending on interlanthanide distance. Actually, a homogeneous distribution of molecules between the layers and a change in complex content allows us to adjust the RE–RE distance in a wide range. According to published data,[6] one of the most promising systems for energy transfer studies is a mixture of terbium and europium picolinates due to the presence of efficient europium–oxygen energy transfer in the UV region of spectra, followed by the relaxation of an excited state with energy dissipation decreasing overall light emission intensity. Thus, $Mg_nAl(OH)_{2n+2}[Ln(pic)_4{\cdot}mH_2O]$ samples with different terbium to europium ratios (Ln = Tb, Eu, $Tb_{0.98}Eu_{0.02}$, $Tb_{0.9}Eu_{0.1}$, $Tb_{0.5}Eu_{0.5}$) were synthesised.

The samples of MgAl LDHs in carbonate form were obtained by co-precipitation of magnesium and aluminium nitrates ($Mg^{2+}:Al^{3+}$ = 2:1, 3:1, 4:1, 6:1, 9:1 or 12:1) with a mixture of NaOH and $Na_2CO_3$ at pH 10.0±0.1:[7]

$$(1-x)Mg^{2+} + xAl^{3+} + 2OH^- + (x/2)CO_3^{2-} + mH_2O \rightarrow Mg_{1-x}Al_x(OH)_2[(CO_3^{2-})_{x/2}{\cdot}mH_2O].$$

**Table 1** X-ray diffraction and elemental analysis data for $Mg_nAl$_Tb(pic) composites.

| Sample | Unit cell parameter $c$/Å | Interlayer spacing/Å ($d_{003}$ – 4.8 Å) | Content |  | Tb:pic ratio | Calculated distances Ln–Ln/Å |
|---|---|---|---|---|---|---|
|  |  |  | Tb (wt.%) | C (wt.%) |  |  |
| $Mg_2Al$_Tbpic | 40.41±0.01 | 8.67±0.003 | 21.4 | 28.5 | 1:2.94 | 7.36±0.06 |
| $Mg_3Al$_Tbpic | 40.35±0.01 | 8.65±0.003 | 19.4 | 22.3 | 1:2.54 | 8.23±0.07 |
| $Mg_4Al$_Tbpic | 36.62±0.01 | 7.41±0.005 | 17.8 | 20.6 | 1:2.56 | 8.37±0.08 |
| $Mg_6Al$_Tbpic | 24.55±0.03 | 3.38±0.012 | 17.2 | 17.8 | 1:2.28 | 10.84±0.11 |
| $Mg_9Al$_Tbpic | 23.38±0.04 | 2.99±0.023 | 15.0 | 13.4 | 1:1.97 | 11.67±0.22 |
| $Mg_{12}Al$_Tbpic | 23.12±0.03 | 2.91±0.017 | 13.2 | 13.5 | 1:2.27 | 12.32±0.25 |

To enhance the crystallinity of LDHs, the samples were aged at 80 °C for 4 days. The terbium and europium complexes were intercalated using the Chibwe procedure.[8] Carbonate LDHs were annealed at 550 °C to get rid of $H_2O$ and $CO_2$. The 'layered double oxides' obtained were impregnated with the anionic complexes Ln(pic)$_4^-$ (Ln = Tb, Eu, $Tb_{0.98}Eu_{0.02}$, $Tb_{0.9}Eu_{0.1}$, $Tb_{0.5}Eu_{0.5}$) at 60 °C for 12 h. The resulting compounds were designated as $Mg_nAl$_Ln(pic), where $n$ is the Mg:Al ratio and Ln = Tb, Eu, $Tb_{0.98}Eu_{0.02}$, $Tb_{0.9}Eu_{0.1}$, $Tb_{0.5}Eu_{0.5}$.

X-ray powder diffraction of the samples indicates a stepwise decrease of the parameter of the LDH structure with decreasing aluminium content of the matrix irrespectively of complex chemical composition [data for $Mg_nAl$_Tb(pic) samples are presented in Table 1]. High interplanar distances (8–9 Å) were observed in $Mg_nAl$_Ln(pic) ($n$ = 2, 3 or 4) systems, whereas the distances of about 3 Å were found for $n$ = 6, 9 or 12. It is evident that LDHs with high charges of the layers have the closest packing of anions, while at lower anion contents, the anions are arranged more freely providing a minimal interlayer distance. Indeed, calculations show that the first samples have the Ln–Ln distances of 7.36, 8.23 and 8.37 Å, respectively (Table 1). However, according to crystallographic data for Na[Tb(pic)$_4$], the diameter of the spherical Ln(pic)$_4^-$ complex is ~9 Å, *i.e.*, exceeds the calculated values. Thus, steric hindrances result in the change of the geometry and stability constants of the complex leading to the exchange of a picolinate ligand for the OH group or the bonding of the complex to the oxygen of the layers. This statement is also supported by the experimental Ln:pic ratio of ~3, which was determined by elemental analysis (Table 1). At the same time, the $Mg_nAl$_Ln(pic) samples ($n$ = 6, 9 or 12) show a Ln:pic ratio of ~2, which points to the formation of roughly linear molecules. This agrees with the formation of the Ln(pic)$_2$(O$_{\text{layer}}$)$_2$ complex with the Ln–O$_{\text{layer}}$ bond.

The optical properties of the samples are in good agreement with this spatial model and were previously reported.[9] Their reflection spectra [calculated using commercial black (coal) and white ($BaSO_4$) standards] exhibit two broad minima at 240–280 and 320–360 nm, which arise from excitation of the π-electrons of the aromatic ring. Besides the reflection minimum matches well the maximum in the excitation spectrum and corresponds to excitation transfer to the lanthanide atom. The emission spectra for an excitation wavelength of 254 nm (mercury lamp emission maximum) were measured with an ARC SpectraPro-300i spectrometer. Emission spectra were normalised to the emission intensity of narrow-band luminescent terbium ($LaPO_4$:Ce,Tb, NP220) and europium ($Y_2O_3$:Eu, U744) standards. In case of $Mg_nAl$_Ln(pic) samples, where Ln = $Tb_{0.98}Eu_{0.02}$, $Tb_{0.9}Eu_{0.1}$, $Tb_{0.5}Eu_{0.5}$, the normalization was performed to the overall emission intensity of an NP220:U744 mixture with the ratio corresponding to the Tb:Eu ratio in the sample. The quantum efficiencies for the excitation wavelength of 254 nm were calculated from normalised emission spectra using reflection and quantum yield values of corresponding NP220:U744 mixtures as standards.[10] The resulting quantum efficiencies as a function of Tb:Eu ratio and the overall charge of the layers are presented in Figure 1. Note that the quantum yields for terbium-containing samples are high (30–50%) and comparable with the intensities of free molecular complexes, which gives rise to the possibility of their application in optics. The dependence of quantum efficiency on the content of the intercalated complex indicates a step corresponding to the change in the symmetry of the complex and proves the coordination of rare earth ions to the layers.

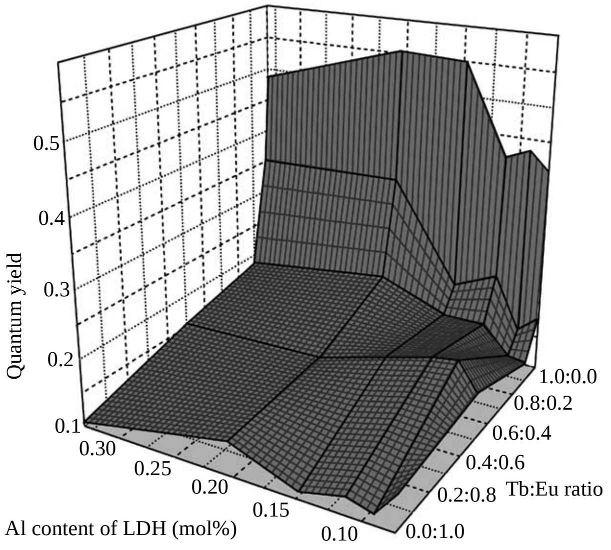

**Figure 1** Quantum efficiencies of Tb- and Eu-containing layered double hydroxides as a function of Tb:Eu ratio and aluminium concentration in LDHs.

At the same time, the replacement of Tb atoms by Eu results in a halved overall luminescence intensity at the excitation wavelength of 254 nm already after replacing 2% terbium complexes in LDH for europium [$Mg_nAl$_$Tb_{0.98}Eu_{0.02}$(pic) samples]. Obviously, very efficient intra- and intermolecular communication channels such as ligand→$Tb^{3+}$/$Eu^{3+}$ and $Tb^{3+}$→$Eu^{3+}$ occurred. Probably, UV irradiation of the system leads to the excitation of ligand electrons to the π-orbital and subsequent ligand→central atom energy transfer. Then, the energy transfer $Tb^{3+}$→$Eu^{3+}$ takes place due to a high lifetime of the $Tb^{3+}$ excited state.

Thus, we prepared new LDH-based luminescent hybrid materials with high quantum yields. The Coulomb interactions between LDH layers and complexes lead to a change of the structure depending on the charge of the hydroxide matrix. Energy transfer studies in corresponding mixed $Tb^{3+}$/$Eu^{3+}$ systems revealed ligand→$Tb^{3+}$/$Eu^{3+}$ and $Tb^{3+}$→$Eu^{3+}$ communication channels; in the case of $Eu^{3+}$, additionally lattice→Eu CT states appear to participate.

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