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Energy transfer in europium and terbium compounds formed with $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ and $[\text{Cr}_{0.1}\text{Al}_{0.9}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ heteropolyanions

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Abstract

The new compounds $\text{Ln}[\text{M}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ ($\text{Ln} = \text{Tb}, \text{Eu}$ and $\text{M} = \text{Al}, \text{Cr}$) were synthesized and their luminescence properties analysed and discussed. Results show that there is a very efficient energy transfer from Eu^{3+} (Tb^{3+}) to Cr^{3+} ions in $\text{Eu}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ and $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$. The transfer strongly quenches Eu^{3+} (Tb^{3+}) luminescence and greatly shortens the lifetimes of the radiative levels. By using selective excitation at low temperature, the transfer mechanisms are investigated and models are presented. Based on the above model, a rate of ET $k_C = 1.33 \times 10^6 \text{ s}^{-1}$ from Tb^{3+} to Cr^{3+} ions in $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ at 12 K is obtained.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In previous papers, we have reported structural and luminescent properties of lanthanide compounds formed with heteropolyanions with Anderson's structure: $[\text{TeMo}_6\text{O}_{24}]^{6-}$ and $[\text{IMo}_6\text{O}_{24}]^{5-}$ [1, 2]. It seems interesting to expand this study to compounds with such structure to reveal possible trends in luminescence properties in relation with the lanthanide-ion coordination. With this goal, europium and terbium compounds formed with $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ and $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ anionic groupings having a similar Anderson structure [3] were investigated. The results obtained show that compounds formed with $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ polyanions are interesting systems in which to study energy transfer (ET) between transition and lanthanide metals.

The ET process has now been being investigated for over half a century [4–6]. It occurs via exchange interaction or electric multipolar interaction, when the donor emission spectrum

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overlaps the acceptor absorption spectrum. One excellent example of ET between transition and lanthanide metals is provided by the system $\text{MnF}_2:\text{Eu}$, where high efficiency of ET from Mn^{2+} to Eu^{3+} ions induces a bright Eu^{3+} luminescence [7, 8]. The mechanism of ET between d and f ions is also used to enhance the emission of Nd^{3+} ions in $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Nd}$, Cr and $\text{Gd}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}:\text{Nd}$, Cr laser crystals [9, 10]. However, studies of ET between d and f ions usually focus on the process from d ions to f ions; few data can be found in the literature for the opposite process, which of course is also very important. In addition, for pure compounds (especially pure molecular compounds) of transition and lanthanide metals, reports on ET are very limited. The aim of this paper is to study the ET from lanthanide ions (Eu^{3+} and Tb^{3+}) to the transition metal ion (Cr^{3+}) and its dependence on concentration and sample temperature in compounds with heteropolyanions. To our best knowledge, it is the first report on the ET between d ions and f ions in this kind of system.

We present here an ET study involving europium and terbium compounds formed with $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ and $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ heteropolyanions. In $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ and $\text{Eu}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$, an efficient ET to Cr^{3+} ions strongly quenches the luminescence of Eu^{3+} (Tb^{3+}) ions and greatly shortens the lifetimes of the radiative levels. The temperature dependence on the ET efficiency as well as that on the transfer mechanisms are investigated and analysed.

2. Experimental details

$(\text{NH}_4)_3[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot n\text{H}_2\text{O}$ and $(\text{NH}_4)_3[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot n\text{H}_2\text{O}$ compounds were synthesized as described earlier [11] and purified by recrystallization from aqueous solutions. Crystalline compounds of trivalent Eu and Tb formed with $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ and $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ heteropolyanions were synthesized from $\text{Ln}(\text{NO}_3)_3$ and $(\text{NH}_4)_3[\text{M}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}, \text{Tb}$; $\text{M} = \text{Al}, \text{Cr}$) mixed solutions. Compounds containing fractional amounts of Cr/Al and Eu have also been prepared for behaviour comparison.

The samarium compound formed with $(\text{NH}_4)_3[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot n\text{H}_2\text{O}$ was first studied within the lanthanide series. According to single-crystal x-ray diffraction data, its stoichiometric composition is $\text{Sm}[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$. Identical XRD spectra recorded for europium and terbium compounds prepared for this study show that they are all isostructural and can be ascribed to the same composition: $\text{Ln}[\text{M}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}, \text{Tb}$; $\text{M} = \text{Al}, \text{Cr}$).

Samples were placed in a circulating liquid-helium optical cryostat (Oxford International) with a temperature-regulated gas system allowing the temperature to be varied between 10 and 300 K. Excitation spectra were recorded using laser radiations from coumarin 480 and rhodamine 610 dyes pumped by the third and the second harmonics of $\text{YAG}:\text{Nd}^{3+}$ ($\lambda = 1.06 \mu\text{m}$, pulse duration 10 ns, with a repetition rate of 30 Hz) respectively. The emission spectra were recorded with a Jobin-Yvon HR-1000 monochromator equipped with a Hamamatsu R374 photomultiplier. The output was analysed by a Stanford SR-510 lock-in amplifier and stored in computer memories. The luminescent decay profiles were recorded with a Lecroy 9350M oscilloscope (500 MHz) interfaced with a computer.

3. Results and discussion

3.1. $\text{Tb}[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ compound

Under selective excitation to the $^5\text{D}_4$ level of Tb^{3+} at 486.5 nm, $\text{Tb}[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ shows an intense green emission at 12 K (figure 1(a)). The emission spectrum consists of several

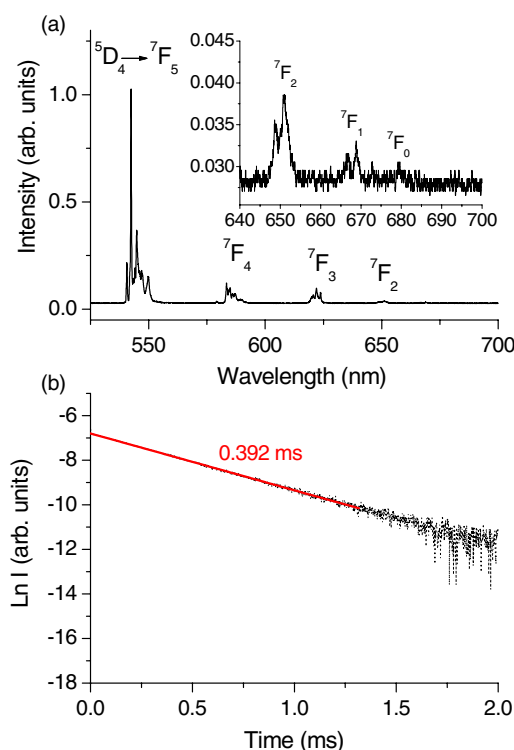


Figure 1. (a) The emission spectrum of Tb[Al(OH)₆Mo₆O₁₈]·11H₂O under selective excitation to the ⁵D₄ level of Tb³⁺ ions at 12 K, $\lambda_{ex} = 486.5$ nm. The inset shows the ⁵D₄ → ⁷F_{0–2} emissions. (b) The decay curve for ⁵D₄ → ⁷F₅ emission under 486.5 nm excitation at 12 K, $\lambda_{em} = 542.4$ nm (dotted curve). The lifetime value is obtained by fitting the decay with a single-exponential function.

groups of lines attributed to ⁵D₄ → ⁷F_J ($J = 0–5$) transitions. Compared to the strongest ⁵D₄ → ⁷F₅ emission, the intensities of the other transitions are much weaker, especially for ⁵D₄ → ⁷F_{2,1,0} (a different scale is used for inset of figure 1(a)). Figure 1 shows three peaks for the transition ⁵D₄ → ⁷F₁, which is consistent with the local C₁ symmetry of the Tb³⁺-ion environment in the crystal.

In polytungstate compounds, terbium luminescence was reported to be quenched via ET from Tb³⁺ excited levels to the W⁶⁺ grouping [12]. The W⁶⁺ ions develop a strong short-range potential to attract electrons from their oxygen environment for reduction. The electron transfer populates the charge transfer state, W⁶⁺ → W⁵⁺. The same factor leads to the quenching of Tb³⁺ luminescence in iso-polymolybdate solutions, which was studied in [13]. However, when aluminium is added to the composition, the compound Tb[Al(OH)₆Mo₆O₁₈]·11H₂O shows a quite strong Tb³⁺ emission (figure 1(a)). A possible reason is that the position of the charge transfer state Mo⁶⁺–Mo⁵⁺ in this system is located much higher in energy than the emitting ⁵D₄ level in Tb³⁺ ions measured at 20 555 cm^{–1} (486.5 nm), so the energy cannot be transferred non-radiatively from the Tb³⁺ excited level to the Mo⁶⁺ charge transfer state. Accordingly, the fluorescence decay of the ⁵D₄ → ⁷F₅ transition in Tb[Al(OH)₆Mo₆O₁₈]·11H₂O excited resonantly shows a pure exponential feature both at 12 K and at 300 K. Linear fitting of the decay profile (the solid curve in figure 1(b)) provides a lifetime equal to 0.392 ms for the ⁵D₄ level at 12 K. At 300 K the value becomes 0.37 ms due to the increase in efficiency of the non-radiative transition.

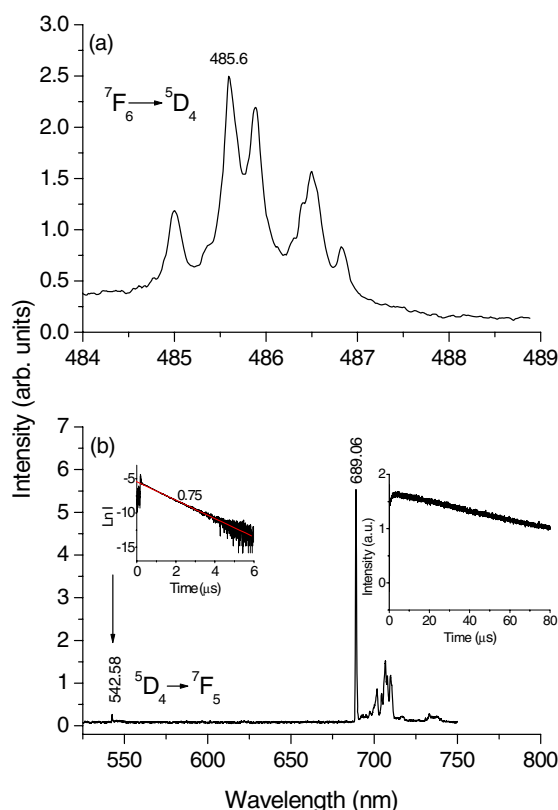


Figure 2. (a) The excitation spectrum of $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ at 12 K, $\lambda_{em} = 542.58$ nm. (b) The emission spectrum of $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ under selective excitation to the $^5\text{D}_4$ level of Tb^{3+} ions at 12 K, $\lambda_{ex} = 485.6$ nm. The left inset shows the decay curve for $^5\text{D}_4 \rightarrow ^7\text{F}_5$ emission with 485.6 nm excitation at 12 K, $\lambda_{em} = 542.58$ nm. The lifetime value is obtained by fitting the decay with a single-exponential function. The right inset is the decay profile of the R line (689.06 nm) of Cr^{3+} under selective excitation to the $^5\text{D}_4$ level of Tb^{3+} ions at 12 K, $\lambda_{ex} = 485.6$ nm.

3.2. Energy transfer in $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ compound

For the compound formed with chromium, $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$, the excitation spectrum at 12 K of $^5\text{D}_4 \rightarrow ^7\text{F}_5(\text{Tb}^{3+})$ emission at 542.58 nm is shown in figure 2(a) in the energy region of $^7\text{F}_6 \rightarrow ^5\text{D}_4$. The spectrum is composed of five peaks with the strongest one at 485.6 nm, as well as some smaller peaks detected as shoulders. Unlike $\text{Tb}[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$, the chromium compound $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ shows only a very weak luminescence under selective excitation at $\lambda_{ex} = 485.6$ nm at 12 K (figure 2(b)) and even the strongest transition, $^5\text{D}_4 \rightarrow ^7\text{F}_5$ in Tb^{3+} ions, provides here only weak peaks. In addition, the lifetime of the $^5\text{D}_4$ level is shortened to a value of 0.75 μs , less than 2/1000 of that observed in $\text{Tb}[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$. Simultaneously, the Cr^{3+} luminescence appears in the region of 700 nm under selective excitation to the $^5\text{D}_4$ level in Tb^{3+} ions, and its decay profile shows clearly a rise time corresponding to the lifetime of $^5\text{D}_4$ level in Tb^{3+} (the right inset of figure 2(b)). All data obtained are providing evidence that a rather effective ET from Tb^{3+} to Cr^{3+} takes place in $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$, resulting in a drastic Tb^{3+} luminescence quenching.

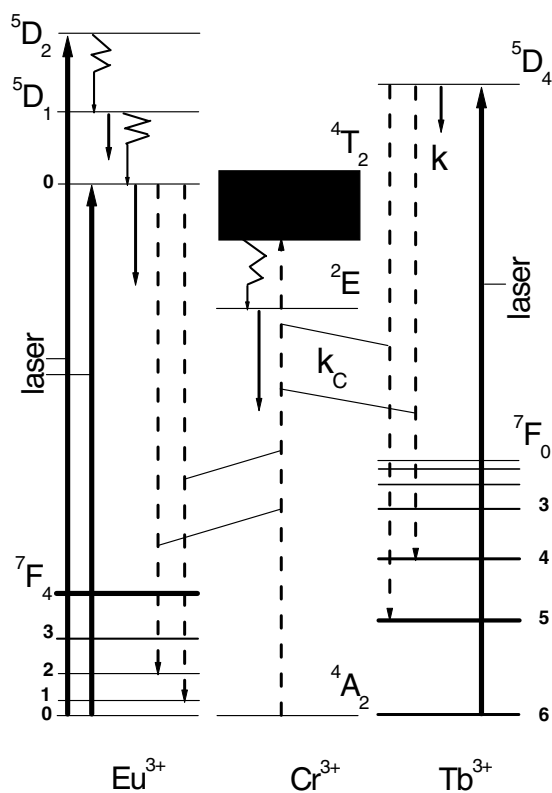
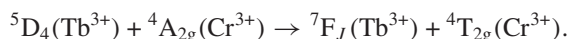


Figure 3. Models of ET in $\text{Eu}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ and $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$. Thick lines represent transitions induced by the laser light absorption, thin lines represent fluorescence transitions and the dashed lines represent cross-relaxation mechanisms.

In the compound investigated, $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$, Cr^{3+} ions are in an octahedral field induced by the oxygen atoms in the neighbouring arrangement. According to the spectral and energy level structure for Cr^{3+} and Tb^{3+} ions, ET in the $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ system occurs via the following cross-relaxation process (figure 3):



Since the transitions ${}^5\text{D}_4 \rightarrow {}^7\text{F}_J$ in Tb^{3+} and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ in Cr^{3+} are both forced electric dipole allowed and the spectral overlap is nearly optimal, this ET is very efficient. Using the lifetime values of the ${}^5\text{D}_4$ level in Tb^{3+} ions in $\text{Tb}[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ (0.392 ms) and in $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ (0.75 μs) at 12 K, one can calculate the ET rate k_C from the equation $k = k_C + k'$ (figure 3). Here $k = 1/0.75 \mu\text{s}^{-1}$ is the decay rate of the ${}^5\text{D}_4$ level in Tb^{3+} ions in $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ while $k' = 1/0.392 \text{ ms}^{-1}$, in $\text{Tb}[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$. The k_C -value obtained equals $1.33 \times 10^6 \text{ s}^{-1}$, really a very large transfer rate.

The emission spectrum presented in figure 2(b) is typical for Cr^{3+} ions in octahedral field symmetry. The intense sharp peak at 689.06 nm is the well-known R line originating in the ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$ transition; the weaker lines on the lower-energy side are the sidebands of the R line. Due to the low sample temperature (12 K), the population of the higher ${}^2\text{E}_g$ sub-level cannot be achieved and only one R line appears in the spectrum. From the spectrum, we can also learn that ${}^2\text{E}_g$ is the lowest excited-state level of Cr^{3+} ions in $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$.

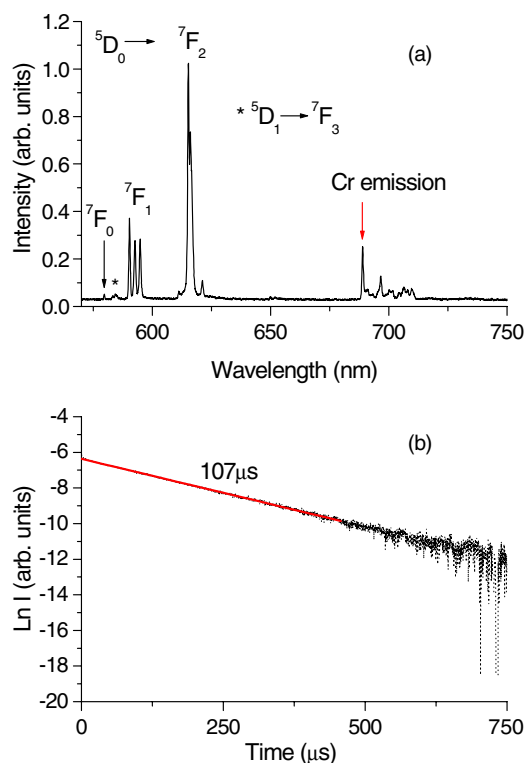


Figure 4. (a) The emission spectrum of $\text{Eu}[\text{Cr}_{0.1}\text{Al}_{0.9}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$ under 355 nm excitation at 12 K. (b) The decay curve for ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ emission under 355 nm excitation at 12 K, $\lambda_{em} = 615.26$ nm (dotted line). The lifetime value is obtained by fitting the decay with a single-exponential function.

3.3. Energy transfer in $\text{Eu}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$ compound

Similar results are obtained for the europium compound $\text{Eu}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$. Powder x-ray analysis showed that it is isostructural with $\text{Sm}[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$, where Sm^{3+} has C_1 symmetry. Figure 4(a) presents the emission spectrum of the mixed chromium/aluminium compound $\text{Eu}[\text{Cr}_{0.1}\text{Al}_{0.9}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$ under 355 nm excitation at 12 K. As expected, the spectrum is composed of emission lines originating from both Eu^{3+} and Cr^{3+} ions. The emission of Cr^{3+} ions is centred around 700 nm and overlaps the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transition lines in Eu^{3+} ions. The other emission lines of Eu^{3+} are well separated from that of Cr^{3+} ions, so the assignments given in the figure can be easily achieved. Apart from the Eu^{3+} intense emission originating from the ${}^5\text{D}_0$ level, weaker ${}^5\text{D}_1 \rightarrow {}^7\text{F}_3$ emissions (584.3 nm) are also recorded. The peak numbers for ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{0-2}$ transitions are 1, 3 and 5 (four lines and a shoulder) respectively, confirming again only one site of C_1 symmetry for Eu^{3+} ions in $\text{Eu}[\text{Cr}_{0.1}\text{Al}_{0.9}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$. Similarly to the case for the Eu^{3+} ion in $\text{X}_1\text{-Y}_2\text{SiO}_5:\text{Eu}^{3+}$ [14] where it has the same C_1 symmetry, the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ emission is very weak. From the peak positions for ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{0-2}$, one can easily deduce the Stark levels of ${}^7\text{F}_{0-2}$ and ${}^5\text{D}_0$, as presented in table 1. It should also be pointed out that two other mixed phases, probably resulting from the distortion of Eu^{3+} surroundings, were detected but at a very weak level (which can only be recorded under selective excitation), which is difficult to avoid when powder samples are considered.

Table 1. Some of the experimental energy levels of the Eu^{3+} ion in $\text{Eu}[\text{Cr}_{0.1}\text{Al}_{0.9}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$.

$2S + 1L_J$ level	Energy (cm^{-1})
${}^7\text{F}_0$	0
${}^7\text{F}_1$	310
	377
	440
${}^7\text{F}_2$	887
	997
	1018
	1031
	1151
${}^5\text{D}_0$	17250

The fluorescence decay profile of the 615.2 nm emission (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$) of Eu^{3+} ions in the mixed compound $\text{Eu}[\text{Cr}_{0.1}\text{Al}_{0.9}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$ at 12 K shows a pure exponential decay under 355 nm excitation with a lifetime of 107 μs for the ${}^5\text{D}_0$ radiative level (figure 4(b)). This value is much smaller than the one measured for the pure aluminium compound $\text{Eu}[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$ (234 μs), showing that an ET should occur between Cr^{3+} and Eu^{3+} ions.

For the mixed compound $\text{Eu}[\text{Cr}_{0.1}\text{Al}_{0.9}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$, it is interesting to compare the two emission spectra of Eu^{3+} ions obtained respectively for non-selective excitation at 355 nm and selective excitation to the ${}^5\text{D}_0$ (579.72 nm) level of Eu^{3+} ions (figure 5(a) where the spectra are normalized for the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition of Eu^{3+}). Figure 5(a) shows that selective excitation in the ${}^5\text{D}_0(\text{Eu}^{3+})$ level induces more Cr^{3+} emission. This can be explained as follows: the direct excitation of Cr^{3+} by the 579.72 nm radiation, together with the ET from Eu^{3+} to Cr^{3+} , results in an enhanced relative emission intensity of Cr^{3+} as compared with 355 nm excitation.

The concentration dependence of the emission spectra of $\text{Eu}[\text{Cr}_x\text{Al}_{1-x}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$ under 355 nm excitation at 12 K confirms again the ET from Eu^{3+} to Cr^{3+} . The result is shown in figure 5(b). For comparison, the two spectra were normalized for the R line of Cr^{3+} . With increasing Cr^{3+} concentration and accordingly increasing interaction between Eu^{3+} and Cr^{3+} , more energy was transferred from the Eu^{3+} to the Cr^{3+} ions, leading to a relatively weak Eu^{3+} emission in $\text{Eu}[\text{Cr}_{0.5}\text{Al}_{0.5}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$ compared to that in $\text{Eu}[\text{Cr}_{0.1}\text{Al}_{0.9}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$.

For stoichiometric Eu and Cr compounds $\text{Eu}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$, the emission spectra change substantially because of the more active $\text{Eu} \rightarrow \text{Cr}$ ET (figure 6). At 12 K and under selective excitation to the ${}^5\text{D}_0$ level of Eu^{3+} ions at 579.72 nm, the hypersensitive transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ of Eu^{3+} ions produces several weak peaks with the strongest one located at 615.2 nm. The fluorescence decay profile for the emission at 615.2 nm is also single exponential and provides a value of 1.3 μs for the lifetime of the ${}^5\text{D}_0$ level (see the inset of figure 6). This value is much smaller than the value of 107 μs measured for the mixed compound $\text{Eu}[\text{Cr}_{0.1}\text{Al}_{0.9}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$ and 234 μs measured for $\text{Eu}[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$. The acceptor concentration is responsible of this variation in the ET efficiency: higher Cr^{3+} concentration results in weaker Eu^{3+} luminescence and shorter lifetime. As expected, the temperature also affects the ET efficiency: the Eu^{3+} luminescence becomes weak when temperature increases. In figure 6, at 98 K, we can still notice a residue of Eu^{3+} emission (denoted by an arrow), but at room temperature (RT), it is hard to distinguish it.

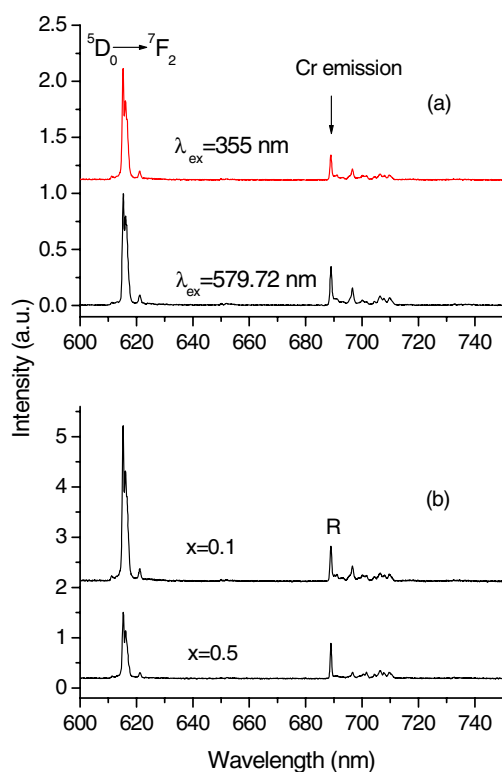


Figure 5. (a) Emission spectra of $\text{Eu}[\text{Cr}_{0.1}\text{Al}_{0.9}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$ at 12 K under 355 nm excitation and selective excitation to the $^5\text{D}_0$ level of Eu^{3+} ions at 17250 cm^{-1} (579.72 nm). (b) The concentration dependence of the emission spectra of $\text{Eu}[\text{Cr}_x\text{Al}_{1-x}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$ under 355 nm excitation at 12 K.

The Cr^{3+} ions show intense luminescence in $\text{Eu}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$, and similarly to the Eu^{3+} -ion behaviour, the emission spectrum changes markedly with temperature. At 12 K, the emission spectrum originates from the lowest excited-state level $^2\text{E}_g$ and consists of R lines and their sidebands with the R1 line dominant. When the temperature is increased up to 98 K, the higher sub-level of $^2\text{E}_g$ is more populated, leading to a more intense R2 line. At RT, the spectrum changes drastically: the R1 and R2 lines have comparable intensity and a new strong broad emission appears in the region of the R lines. This new broad band is attributed to the transition $^4\text{T}_{2g} \rightarrow ^4\text{A}_{2g}$. From the Tanabe–Sugano diagram for the d^3 configuration [15], we know that the $^4\text{T}_{2g}$ energy level position depends strongly on the crystal field intensity: for a low crystal field interaction, the $^4\text{T}_{2g}$ level is the lowest excited state, while at higher crystal field, the lowest excited state is assigned as $^2\text{E}_g$. In section 3.1, we pointed out that in $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$, the lowest excited state is $^2\text{E}_g$, and only the emission from the $^2\text{E}_g$ level is detected at low temperature. However, at RT, figure 6 tells us that $^4\text{T}_{2g}$ is thermally populated and emission originates from there. Since according to the spin selection rule, the $^4\text{T}_{2g} \rightarrow ^4\text{A}_{2g}$ transition probability is larger than that of the $^2\text{E}_g \rightarrow ^4\text{A}_{2g}$ transition, one can understand that the $^4\text{T}_{2g}$ emission will dominate at high temperature.

Figure 7(a) provides direct evidence of the ET from Eu^{3+} to Cr^{3+} ions in $\text{Eu}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 11\text{H}_2\text{O}$. Monitoring the Cr^{3+} emission at 689.33 nm, one finds a narrow excitation peak at 464.8 nm that corresponds to the $^7\text{F}_0 \rightarrow ^5\text{D}_2$ absorption transition in the Eu^{3+}

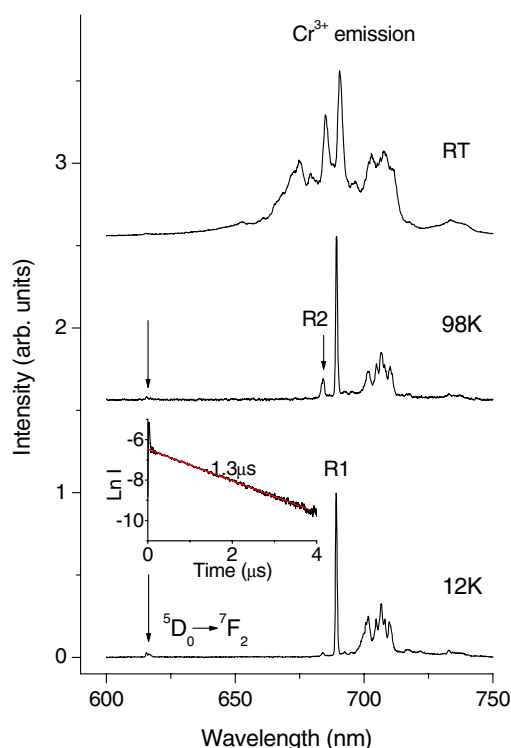
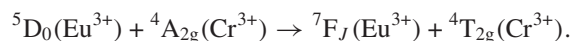


Figure 6. Emission spectra of $\text{Eu}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ under selective excitation to the $^5\text{D}_0$ level of Eu^{3+} ions at 12, 98 K and RT, $\lambda_{ex} = 579.72$ nm. The inset shows the decay curve for $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission under 579.72 nm excitation at 12 K, $\lambda_{em} = 615.2$ nm. The lifetime value is obtained by fitting the decay with a single-exponential function.

ion. This means that exciting Eu^{3+} ions can produce the emission of Cr^{3+} . If the $^5\text{D}_2$ level of Eu^{3+} ions at $21\,515\text{ cm}^{-1}$ (464.8 nm) is selectively excited in $\text{Eu}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ at 12 K, a quite different spectrum from that of $\text{Eu}[\text{Cr}_{0.1}\text{Al}_{0.9}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ (figure 4(a)) is obtained (figure 7(b)). The differences reside mainly in two aspects:

- (i) Cr^{3+} emission is dominant in the former compound;
- (ii) the emissions originating from $^5\text{D}_1$ and $^5\text{D}_0$ levels of Eu^{3+} ions have comparable intensity in $\text{Eu}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ (see the inset of figure 7(b)), while in the mixed Cr, Al compound $\text{Eu}[\text{Cr}_{0.1}\text{Al}_{0.9}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$, the $^5\text{D}_1$ emission is very weak compared to that of $^5\text{D}_0$.

From these experimental features, we can draw the conclusion that the ET occurs mainly from the $^5\text{D}_0$ level of Eu^{3+} ions to Cr^{3+} ions in $\text{Eu}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$. After resonant excitation to the $^5\text{D}_2$ level of Eu^{3+} , the ions relax non-radiatively to the lower $^5\text{D}_1$ level and from there, only a small proportion of the ions relax radiatively, while the majority populate the $^5\text{D}_0$ level non-radiatively. Then according to the ET depicted in figure 3, the nearby Cr^{3+} ions can be excited through the following cross-relaxation process leading to Cr^{3+} emission:



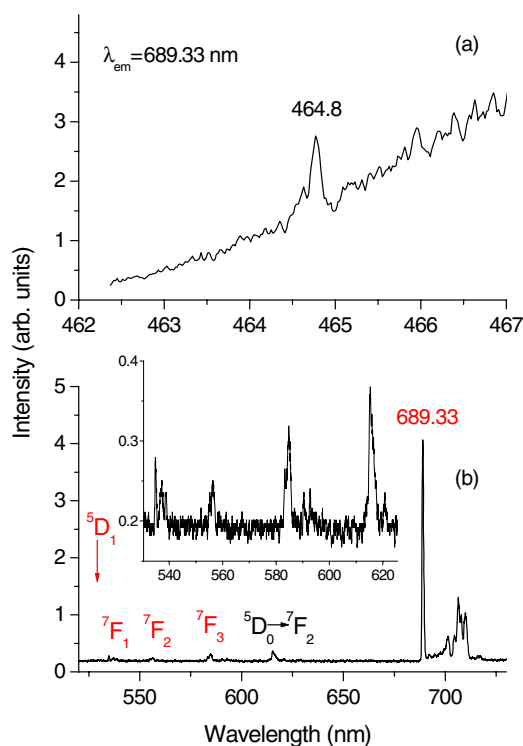
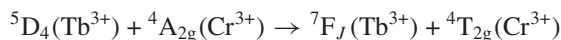


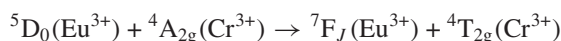
Figure 7. (a) The excitation spectrum of $\text{Eu}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ at 12 K, $\lambda_{em} = 689.33$ nm. (b) The emission spectrum of $\text{Eu}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ under selective excitation to the $^5\text{D}_2$ level of Eu^{3+} ions at 12 K, $\lambda_{ex} = 464.8$ nm. The inset shows the $^5\text{D}_1 \rightarrow ^7\text{F}_{1-3}$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emissions.

4. Conclusions

New europium and terbium compounds formed with $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ and $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ polyanions have been synthesized and a systematic spectroscopic study in the visible region has been performed. The luminescence of Tb^{3+} in the compound formed with $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ is surprisingly intense, in spite of the strong quenching effect of ET to the Mo^{6+} – Mo^{5+} charge transfer state that one could expect from the literature. In $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ and $\text{Eu}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$, there is a very efficient ET from Eu^{3+} (Tb^{3+}) to Cr^{3+} ions that strongly quenches their luminescence and greatly shortens the radiative level lifetime. The transfer mechanisms involve the following cross-relaxations:



in $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ and



in $\text{Eu}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ respectively. Based on the above model, a rate of ET of $k_C = 1.33 \times 10^6 \text{ s}^{-1}$ from Tb^{3+} to Cr^{3+} ions in $\text{Tb}[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ at 12 K can be obtained.

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