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Variation of the Eu^{II} Emission Wavelength by Substitution of Fluoride by Hydride in Fluorite-Type Compounds EuH_xF_{2-x} ($0.20 \leq x \leq 0.67$)

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Ⓢ *Supporting Information*

ABSTRACT: Mixed-hydride fluorides EuH_xF_{2-x} were prepared by the solid-state reaction of EuF_2 and EuH_2 under hydrogen gas pressure in an autoclave. Eu^{II} luminescence is observed for $0.20 \leq x \leq 0.67$, while pure EuF_2 does not show any emission. The energy of the emission depends strongly on the degree of substitution x. For low hydride contents, yellow emission is observed, whereas higher hydride contents lead to red emission. The red shift is attributed to the nephelauxetic effect of the hydride anion. Remarkably, limited concentration quenching is observed in EuH_xF_{2-x} ($0.20 \leq x \leq 0.67$). This observation is explained by suppression of long-range energy migration due to disorder in the local environment of Eu^{2+} in the mixed H/F crystals. The strong x dependence of the luminescence maxima proves hydride−fluoride substitution to be a valuable tool to tune the emission wavelength of Eu^{II}-containing phosphors.

Because of the parity-allowed electric-dipole transition $4f^65d-4f^7$ and the high emission intensities, Eu^{II} plays an important role in the production of phosphors for light-emitting devices. Because the outer-shell 5d electrons interact with the ligands, the emission energies show a strong dependence on the chemical environment.[1] For oxides and halides, usually blue or green emission is observed.[2] For instance, the optical properties of Eu(II)-doped fluorite-type compounds have been studied extensively[3−7] and those compounds typically emit in the blue region.[7] In EuF_2, there are two broad absorption bands in the UV, but no emission is observed.[3,8] In contrast to fluorides, hydrides as host lattices have been considered only recently.[9,10] It was shown that the strong nephelauxetic effect and the large crystal-field strength of the hydride ligand lead to a significant red shift in the emission energies of Eu^{II}. Because the ionic radii of the rather hard fluoride anion and the soft and polarizable hydride may be similar in many compounds,[11,12] the formation of a solid solution series is sometimes observed.[13] However, hydride−fluoride mixed crystals have never been considered as host lattices for Eu^{II} luminescence before but could serve as interesting host lattices because of the huge differences in polarizability and therefore in their nephelauxetic effects. This allows the design of host lattices with emissions over a wide spectral range. Within our present study, we have chosen the system EuH_2-EuF_2 as a model system and observed for the first time Eu^{2+} emission from a mixed-hydride fluoride compound. EuF_2 crystallizes in the cubic fluorite structure type, and EuH_xF_{2-x} with $x < 0.8$ was shown to form a solid solution series in the fluorite structure type.[14] Pure EuH_2, in contrast, crystallizes in the orthorhombic $PbCl_2$ structure type (*Pnma*).[15]

The mixed crystals were synthesized from EuH_2 and EuF_2 and characterized by powder X-ray diffraction (see the Supporting Information, SI). In good agreement with ref 14, the lattice parameter a of about 584 pm did not show a significant change for different x values (maximum effect of 0.4 pm; for a complete list of lattice constants, see the SI). The colors of the samples varied from light yellow for EuF_2 and fluoride-rich samples to darker yellow and dark red/brown for large x (≥ 0.67). Luminescence emission and excitation spectra were measured at room temperature for all samples (for details, see the SI). Luminescence emission and excitation spectra of EuH_xF_{2-x} are shown in Figures 1 and 2.

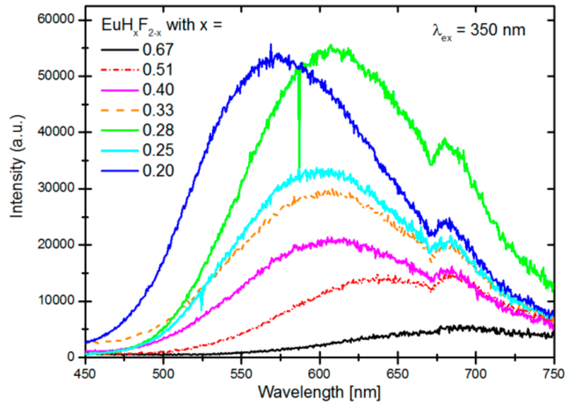

Figure 1. Luminescence emission spectra of EuH_xF_{2-x} at 293 K. All spectra were measured under the same instrumental conditions under 350 nm excitation.

For EuH_xF_{2-x}, a broad-band emission is observed, which we assign to the parity-allowed electric-dipole transition between the $4f^65d$ and $4f^7$ levels of Eu^{2+}. It is clearly visible that the emission maximum shifts to higher energies for increasing fluoride content. The sample with $x = 0.67$ shows only a weak emission in the red, whereas the samples with higher fluoride content show stronger emissions in the orange and yellow color region.

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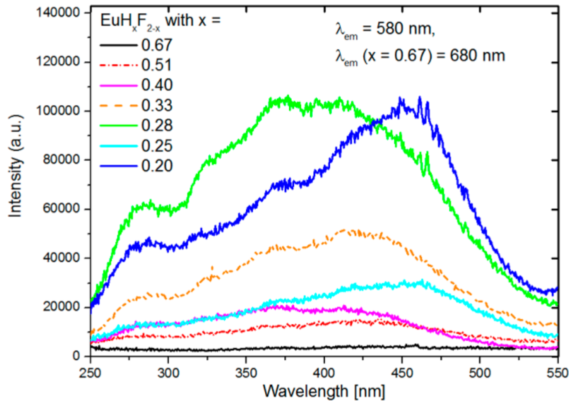

Figure 2. Luminescence excitation spectra of EuH$_x$F$_{2-x}$ at 293 K for 580 nm emission ($x < 0.67$) or 680 nm emission ($x = 0.67$).

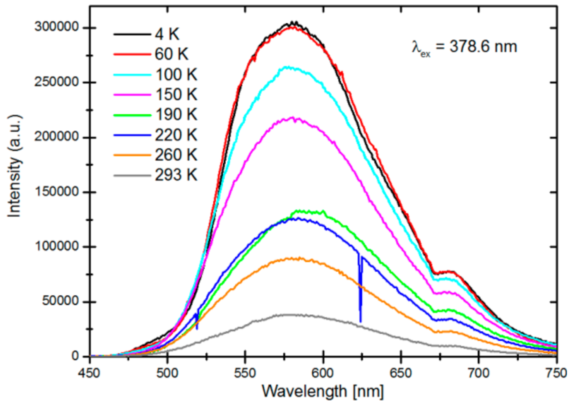

Figure 3. Temperature-dependent luminescence emission spectra of EuH$_{0.28}$F$_{1.72}$.

Substitution of the strongly polarizable hydride anion by the less polarizable fluoride anion leads to a significant shift in the emission wavelengths. This is in good agreement with our previous observation of a strong nephelauxetic effect and a large crystal-field splitting and therefore a large shift of the barycenter of the Eu^{2+} 5d levels in hydride host lattices compared to the corresponding isostructural fluoride compound.[10] The observation of a second maximum above 700 nm might be an instrumental artifact due to variations in the detector response and monochromator throughput in this spectral range. Samples with $x = 0.67$ only show a very weak emission, and pure EuF$_2$ does not show a broad-band emission at all. In the case of large hydride contents, the extremely weak emission can be explained by the rather small band gaps (dark-red to brown samples) and quenching may occur because of thermally activated photoionization from the 5d state to the conduction band.

The hydride content x and approximate emission maximum are given in Table 1.

Table 1. Maximum of the Eu^{2+} 4f^{6}5d Emission in EuH$_x$F$_{2-x}$[a]

x	$\lambda_{\text{em-max}}$	x	$\lambda_{\text{em-max}}$
0.10	no emission	0.40	605
0.20	570	0.51	636
0.25	595	0.67	685
0.28	605	>0.67	no emission
0.33	605		

[a] The values of x are according to the initial weights and were rounded to two internal decimal places (see the SI for a complete list of x values).

Temperature quenching is observed for the Eu^{2+} emission. As an example, the temperature-dependent behavior of the luminescence is shown for EuH$_{0.28}$F$_{1.72}$. The sample shows a bright-yellow luminescence with an emission maximum at approximately 600 nm. With decreasing temperature, the emission intensities increase significantly; see Figure 3.

Emission intensities at low temperature are almost 10 times higher than those at room temperature. For low temperatures, a lifetime of about 480 ns was obtained. This value is slightly shorter than that expected for decay times of Eu^{2+} emission at around 600 nm.[16] However, it was shown before that the lifetimes of Eu^{2+} in hydride host lattices are somewhat shorter than expected[10] because of the higher refractive index of hydride.[17] An increase of the refractive index leads to a strong increase of the radiative decay rate. Assuming the refractive index of mixed-hydride fluorides to be larger than the typical values observed for oxide host lattices, its change can explain the observation of shorter radiative decay times. The temperature dependencies of the emission intensities and lifetimes are shown in Figure 4.

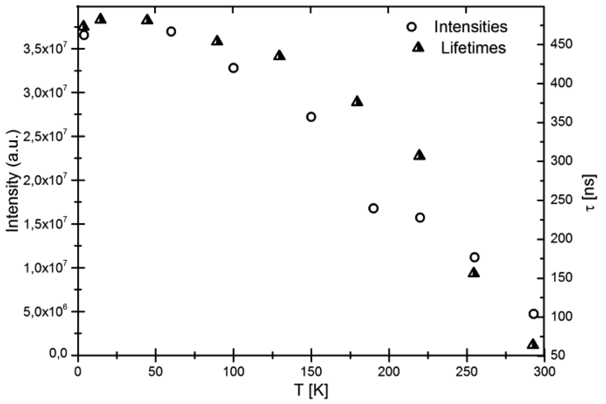

Figure 4. Temperature dependence of the emission intensities and decay times of Eu$_{0.28}$F$_{1.72}$: excitation at 376.8 nm and emission at 570 nm. Temperature quenching occurs at approximately 200 K.

The temperature dependencies of the emission intensities and lifetimes are similar and show an increase of about a factor 10 at low temperatures compared to room temperature. The similarity is consistent with a shortening of the lifetime due to thermal quenching.

In many cases, solid-state luminescent materials suffer from strong concentration quenching in fully concentrated systems except for materials in which the distance between the luminescent ions is too large for energy transfer (e.g., elpasolites,[18] some coordination polymers, and metal–organic frameworks[19]). Interestingly, only limited concentration quenching is observed in EuH$_x$F$_{2-x}$ ($0.20 \leq x \leq 0.67$), a fully concentrated Eu^{2+} composition. An explanation for this observation is that energy migration over large distances is hampered by disorder in the F/H coordination of Eu^{2+} ions. The strong influence of the hydrogen coordination (shifting the 4f^{6}5d state to lower energies) will result in a variation of the position of the 5d level for Eu^{2+} ions with different numbers of coordinating F$^-$ and H$^-$ ligands. Energy transfer between neighboring Eu^{2+} ions becomes unidirectional: energy transfer to Eu^{2+} ions for which the 4f^{6}5d state is at lower energies. Back transfer to Eu^{2+}

ions with higher energy $4f^65d$ states is a thermally activated process, and this barrier will hamper long-range energy transfer to quenching centers. In EuF_2, the coordination of all Eu^{2+} is the same (eight fluorine atoms), and efficient energy migration over the Eu^{2+} sublattice to traps/quenching centers leads to concentration quenching.

The decay curves observed for the Eu^{2+} emission in the mixed H/F compounds show a long component, typical of the radiative decay rate for Eu^{2+}, and a faster component, which can be assigned to emission from Eu^{2+} suffering from partial quenching due to single-step energy transfer or energy migration to quenching sites. The relative intensities for the fast and slow components vary with temperature. Around 10 K, the biexponential fit gives a 10 times higher initial intensity for the fast decay. The ratio increases at higher temperatures, possibly because of more efficient thermally activated concentration quenching. A detailed analysis of the decay curves is outside the scope of this report, and the biexponential fits used are not sufficient to capture the variation in the decay rates for Eu^{2+} ions with different local surroundings.

For the first time, Eu^{2+} luminescence has been observed in hydride−fluoride host lattices. Broad-band emission is assigned to the parity-allowed electric-dipole transition between the $4f^65d$ and $4f^7$ levels of Eu^{2+}. Because of the large difference in the polarizability of the hydride and fluoride anions and the resulting difference in the strength of the nephelauxetic effect, a large shift in the emission energies is observed for higher hydride concentrations. Because of the small nephelauxetic effect in (ionic) fluoride host lattices, the barycenter of the Eu^{2+} 5d state is located at high energies.[20] The strong nephelauxetic effect of the hydride ligand then leads to a lowering of the barycenter and a red shift of the emission. The present study shows that a partial substitution of fluoride by hydride has a strong effect on the emission energy and allows for the design of phosphors with varying emission wavelengths of almost any desired color.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, Rietveld refinement, and a detailed list of lattice constants and decay times. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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