



# Energy transfer between different $\text{Eu}^{2+}$ ions in the white phosphor $\text{Ba}_7\text{F}_{12}\text{Cl}_2:\text{Eu}^{2+}$

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## ABSTRACT

We have studied in detail the emission spectra of the white phosphor  $\text{Ba}_7\text{F}_{12}\text{Cl}_2:\text{Eu}^{2+}$  as a function of Europium content, excitation wavelength and temperature. The change of the emission spectrum with excitation wavelength shows a systematic shift in the CIE chromaticity diagram from warm white upon excitation in the near UV (370 nm) to cold white upon excitation at shorter wavelengths. The observed intensity changes with europium concentration confirm that energy transfer takes place, which is both concentration and temperature dependent. Temperature and sample dependent lifetime studies show that the observed lifetimes do not change within experimental error between dilute and concentrated Eu-doped samples, and they remain constant between 5 K and room temperature. The second observation confirms the previous results that the thermal quenching of the white emission occurs at high temperature (200 °C). The combination of all observations suggests that the energy transfer takes place first between the normal  $4f^6 5d^1$  states of the Eu ions located on the 3 different crystallographic sites of Ba, and is followed by subsequent relaxation to anomalous emission states whose emission lifetimes remain constant with sample concentration and temperature from 5 K to 300 K.

## 1. Introduction

Alkaline earth fluorohalides have been studied extensively for a variety of properties [1–10]. The most prominent members have the PbFCl (matlockite structure) with tetragonal symmetry. Matlockite based compounds doped with rare earth ions are used as storage phosphors for imaging with  $\text{BaFBr}:\text{Eu}^{2+}$  [1], data storage in  $\text{Sm}^{2+}$ -doped mixed crystals by optical hole burning [2] or in  $\text{BaFCl}$  nanocrystals by deep UV illumination [3].  $\text{Sm}^{2+}$  doped  $\text{BaFCl}$  is also a good pressure sensor [4]. Biodegradable coated  $\text{SrFCl}:\text{Nd}^{3+}$  nanoparticles were recently presented for biomedical applications (phototheranostics) [5].  $\text{SrFCl}$  nanoparticles co-doped with  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  allow to detect ionizing radiation by upconversion luminescence [6], and also for thermometry [7].

The detailed study of the  $\text{BaF}_2\text{--BaCl}_2$  phase diagram [8] revealed the formation of 2 new compounds:  $\text{Ba}_{12}\text{F}_{19}\text{Cl}_5$  [9] and  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$  [10]. While the structure of the first one appears so far to be unique, other compounds with the structure of  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$  have been reported, such as the hydrides  $\text{M}_7\text{F}_{12}\text{H}_2$  with  $\text{M} = \text{Sr}$  and  $\text{Ca}$  [11,12]. Note that for the hydrides, the compounds  $\text{Ba}_2\text{H}_3\text{Cl}$  and  $\text{Ca}_2\text{H}_3\text{Br}$  have also been reported [12,13]. Recently, fluoride-rich  $\text{BaF}_2\text{--BaCl}_2$  mixtures have been shown to be efficient catalysts for the preparation of vinylidene fluoride [14],

and new studies of the synthesis and structure of these compounds have been presented [15–17].

Europium-doped  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$  is a new single compound tunable white phosphor under near UV excitation, which allows for a good color rendering index [18]. The great advantage of this phosphor is that it is a single compound which allows to obtain emissions from warm white to cold white and blue, and does not necessitate to blend different phosphors to obtain the desired white color coordinates. Further, its synthesis is quite simple, either by solid state reaction of  $\text{BaCl}_2$  and  $\text{BaF}_2$  or  $\text{BaFCl}$  and  $\text{BaF}_2$ , or alternatively from  $\text{BaF}_2$  with some alkali chloride as chloride source and reaction flux. This compound is also thermally stable up to 850 °C, and the Eu emission is quenched at 200 °C. The white emission observed is the result of the superposition of the emission of three different  $\text{Eu}^{2+}$  ions located on the three different Ba lattice sites available in this structure (see Figure S1). The emission color of this phosphor can be tuned either by shifting the excitation wavelength (see below), by chemical modifications (partial cationic or anionic substitution), and also be the  $\text{Eu}^{2+}$  concentration [18]. Several previous studies [eg. 19–21] have investigated the energy transfer between  $\text{Eu}^{2+}$  ions on different sites in the host crystal. In  $\text{La}_{2.5}\text{Ca}_{1.5}\text{Si}_{12}\text{O}_{4.5}\text{N}_{16.5}$ , the emission color arising from the superposition of 2 emission bands shifts

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from blue-green for dilute to orange for highly Eu-concentrated samples [19]. In  $\text{Ba}_4\text{Gd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2\text{:Eu}^{2+}$  [20], two overlapping  $\text{Eu}^{2+}$  emission bands at ca 460 and 560 nm are observed. The lifetimes of these two emissions are 0.46 and 1.28  $\mu\text{s}$  respectively for dilute samples. While the lifetime of the 560 nm emission does not depend on the  $\text{Eu}^{2+}$  concentration, the lifetime of the 460 nm emission is found to decrease significantly with increasing  $\text{Eu}^{2+}$  content. A similar behavior was also observed for  $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$  [21].

In order to improve our fundamental understanding of the emission processes in  $\text{Ba}_7\text{F}_{12}\text{Cl}_2\text{:Eu}^{2+}$ , we have studied a series of samples with varying Eu content to investigate the energy transfer processes between Eu ions in this material.

## 2. Experimental

### 2.1. Sample preparation

The samples were prepared using a mixture of lithium-potassium chlorides as flux. Typically, about 10g of  $\text{BaF}_2$  were mixed with 0.42g  $\text{LiCl}$  and 0.72g  $\text{KCl}$  and a small amount of  $\text{EuF}_2$  (eg 0.152g for a nominal Eu content of 1.4%) and put into a glassy carbon crucible. This mixture was heated to ca 300 °C under vacuum to remove residual water, and then further up to 950 °C under nitrogen atmosphere, and finally cooled slowly (14 h) to 750 °C, before switching of the furnace to bring it back to room temperature. The nominal concentration of  $\text{Eu}^{2+}$  with respect to  $\text{Ba}^{2+}$  ranged from 0.015% to 3.7% (see tables S1 and S2 for examples of reaction mixtures and the list of all samples which were prepared). We have shown previously [22] using single crystal x-ray diffraction that under these conditions,  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$  is obtained in the ordered modification with space group P-6. A representative single crystal sample gave the lattice parameters  $a = 10.6274(14)$  and  $c = 4.1719(6)$  Å, in agreement with the previously reported single crystal structure data [10].

$\text{Ba}_7\text{F}_{12}\text{Cl}_2$  crystallizes as needles [10,18,22] which were mechanically separated under a polarizing microscope from the solid mass for the spectroscopic studies. This procedure allows to obtain phase pure samples, as there are no other birefringent crystals ( $\text{BaF}_2$  and alkali halides as well as  $\text{LiBaF}_3$  are cubic) in the solid mass. These manually selected crystals were placed in 1 mm diameter quartz capillaries for the spectroscopic studies. Fig. 1 shows a typical sample under white light and 254 nm excitation.

### 2.2. Spectroscopic experiments

Luminescence experiments were performed using a Fluorolog F3-22 instrument in conjunction with a Janis closed cycle cryostat for temperature dependent measurements.

Time-resolved experiments were performed using 355 nm excitation

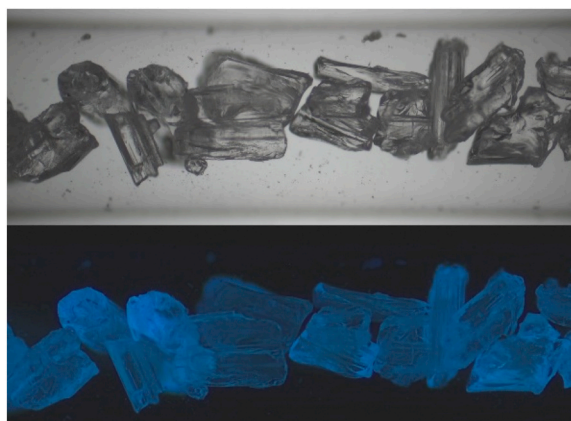


Fig. 1. Microscope picture of  $\text{Ba}_7\text{F}_{12}\text{Cl}_2\text{:Eu}^{2+}$  crystals under white and 254 nm excitation. The diameter of the quartz tube is 1 mm.

from a Quantel Q-switched Nd-YAG laser and also using 266 nm excitation from a CNI MPL-F 266 nm 10 mW laser. The emitted light was collected with a Spex 270 monochromator equipped with both a CCD camera as well as with a PM connected to a Tectronix TDS540 Oscilloscope. The whole set-up is run with a home-built program.

## 3. Results and discussion

Fig. 2 presents the intensity normalized emission spectra as a function of excitation wavelength at room temperature. These spectra reveal the presence of 3 superimposed emission bands centered at about 430, 480 and 570 nm. The blue emission is favored under far UV excitation, as can be seen also in Fig. 1 under 254 nm excitation. The host crystal  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$  presents 3 different  $\text{Ba}^{2+}$  sites which can be occupied by  $\text{Eu}^{2+}$ . Each site has a coordination number of 9, one with 9 fluoride ions atoms, and the 2 others with 7 fluoride ions and 2 chloride atoms (see figure S1).

As each emission band has a different excitation spectrum (10 K excitation spectra were shown in figure S6 of ref [18]), shifting the excitation wavelength results in different relative emission intensities. Figure S2 presents room temperature excitation spectra of the 0.015% Eu-doped sample observed at various emission wavelengths which show a systematic red shift of the excitation wavelength with increasing emission wavelength. This then tunes the emission color as shown in Fig. 3. Increasing the excitation energy leads to a blue shift of the emission, going thus from a warm white to a cold white and finally blue emission (see also Figs. 1 and 2). In the compound  $\text{Ba}_3\text{Sc}(\text{BO}_3)_3$ , there are 4 different Ba lattice sites. When doped with  $\text{Eu}^{2+}$ , orange emission light is observed, and at 78 K, the emission band can be fitted with 4 gaussians peaking at 474, 566, 724 and 786 nm [23]. Similarly to the results reported here, exciting at different wavelengths results in different emission spectra of  $\text{Ba}_3\text{Sc}(\text{BO}_3)_3\text{:Eu}^{2+}$  [23].

## 4. Effect of concentration

Fig. 4 compares the room temperature emission spectra of dilute (0.1%) and concentrated (3.7%) Europium-doped  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ , excited at different wavelength between 275 and 380 nm.

This figure shows that in the dilute sample, the emission is dominated by a strong emission band at 430 nm, while the spectrum becomes much broader for the concentrated sample, with an increasing intensity of the orange band at ca 570 nm. It is also interesting to note that the emission intensity between 470 and 570 nm becomes stronger in the more europium concentrated samples. This trend is illustrated for the entire series of samples studied in figure S3. These observations suggest that energy transfer does indeed take place from the high energy emission (430 and 480 nm) to the lower energy (570 nm) emission. It is however important to note that the highest energy band is not completely quenched even in the most concentrated sample at room

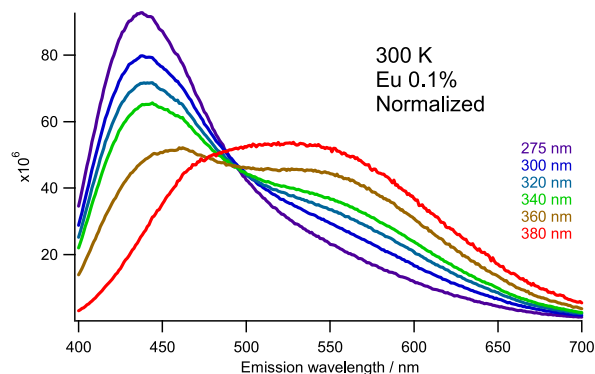
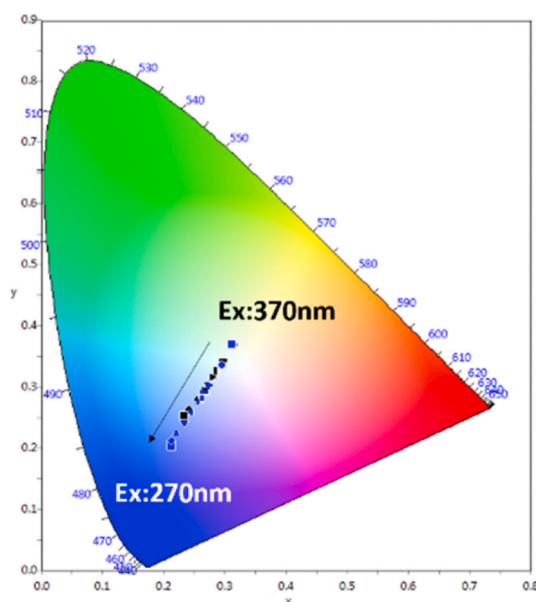


Fig. 2. Intensity normalized emission spectra as a function of excitation wavelength at room temperature for  $\text{Ba}_7\text{F}_{12}\text{Cl}_2\text{:0.1\%Eu}$ .



**Fig. 3.** Evolution of color coordinates of the room temperature emission spectra of  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ : 3.7%Eu in black and  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ : 0.6%Eu in blue as a function of excitation wavelength.

temperature.

In the blue phosphor  $\text{La}_{3-x}\text{Si}_8\text{N}_{11}\text{O}_4:\text{xEu}^{2+}$  [24], the maximum of the emission peak is red-shifted from 481 to 513 nm as the  $\text{Eu}^{2+}$  content increases from  $x = 0.002$  to  $x = 0.3$ . In this compound,  $\text{Eu}^{2+}$  is located on the 2 different La lattice sites, and the observed emission is a superposition of 2 broad emission bands. The red shift corresponds to an increased relative intensity of the lower energy component with increasing  $\text{Eu}^{2+}$  concentration.

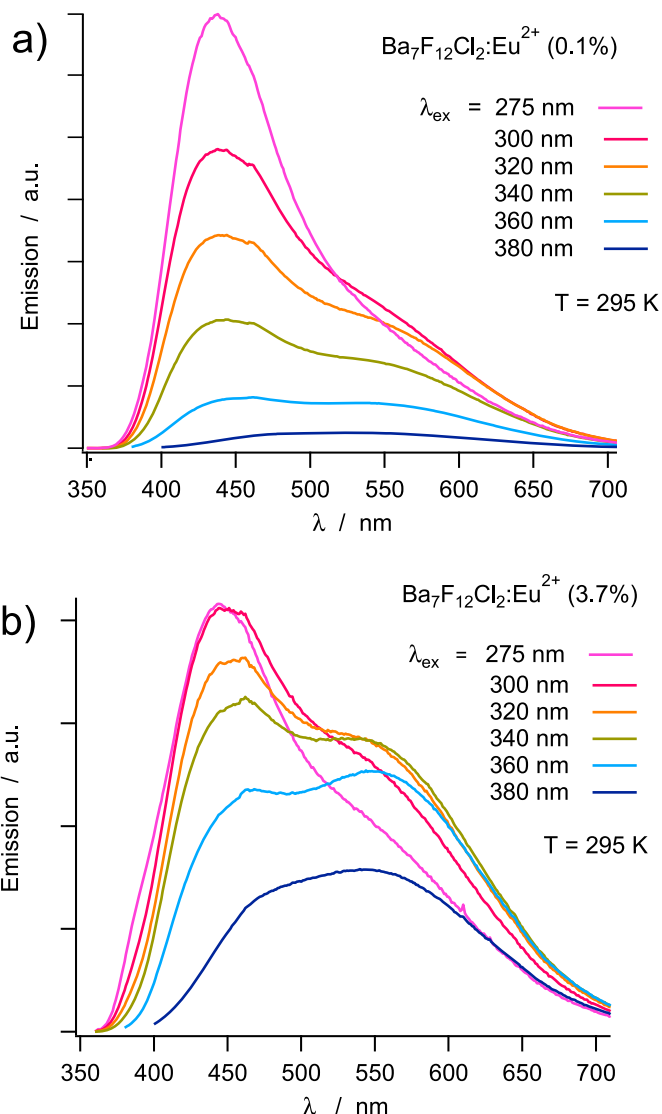
## 5. Effect of temperature

Fig. 5 shows the effect of temperature on the emission spectrum of  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ : 0.9%Eu excited at 320 nm. With increasing temperature, the band positions shift to form a more compact and less resolved emission spectrum, with the “blue” maximum shifting from 435 to 450 nm, and the shoulder at 600 nm going to about 580 nm (“orange” emission). The strongest shift appears for the intermediate band observed at 525 nm at 5 K (“green” emission) shifting to about 480 nm at room temperature (see Fig. 5).

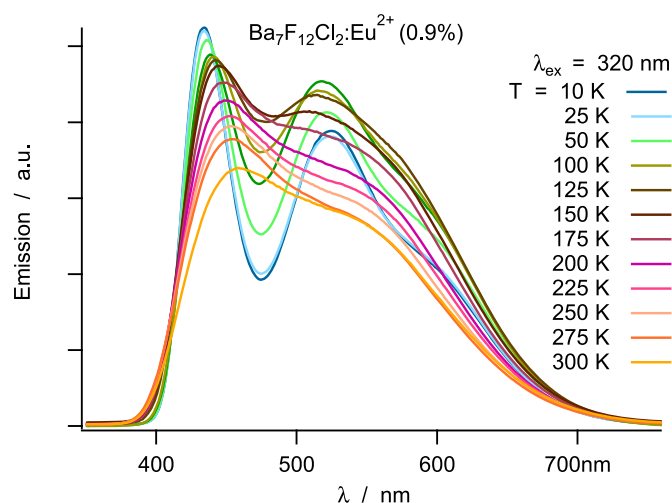
This behavior was analyzed more quantitatively by fitting these emission spectra for a dilute, intermediate and concentrated Eu samples as the sum of three Gaussians, yielding the results shown in Fig. 6 below for the emission spectra measured at 10 K with different excitation energies. Figure S4 shows an example of a fitted spectrum.

With 355 nm, the orange emission dominates for all 3 samples, as both other bands are barely excited at this wavelength. For excitations between 300 and 340 nm, it appears that the relative intensity of the blue component is reduced with increasing Eu content, suggesting the presence of energy transfer (from the “blue” to the “orange” emissions). It is interesting to note that the relative intensity of the green component remains more or less constant for different  $\text{Eu}^{2+}$  concentrations at a given wavelength. Note that this behavior is by far not as pronounced as the one which has been observed previously for  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$  where the relative intensity of the “blue” emission with respect to the “green” emission decreases from about 50% for 0.1% nominal Eu content to less than 10% for 2% Eu [19].

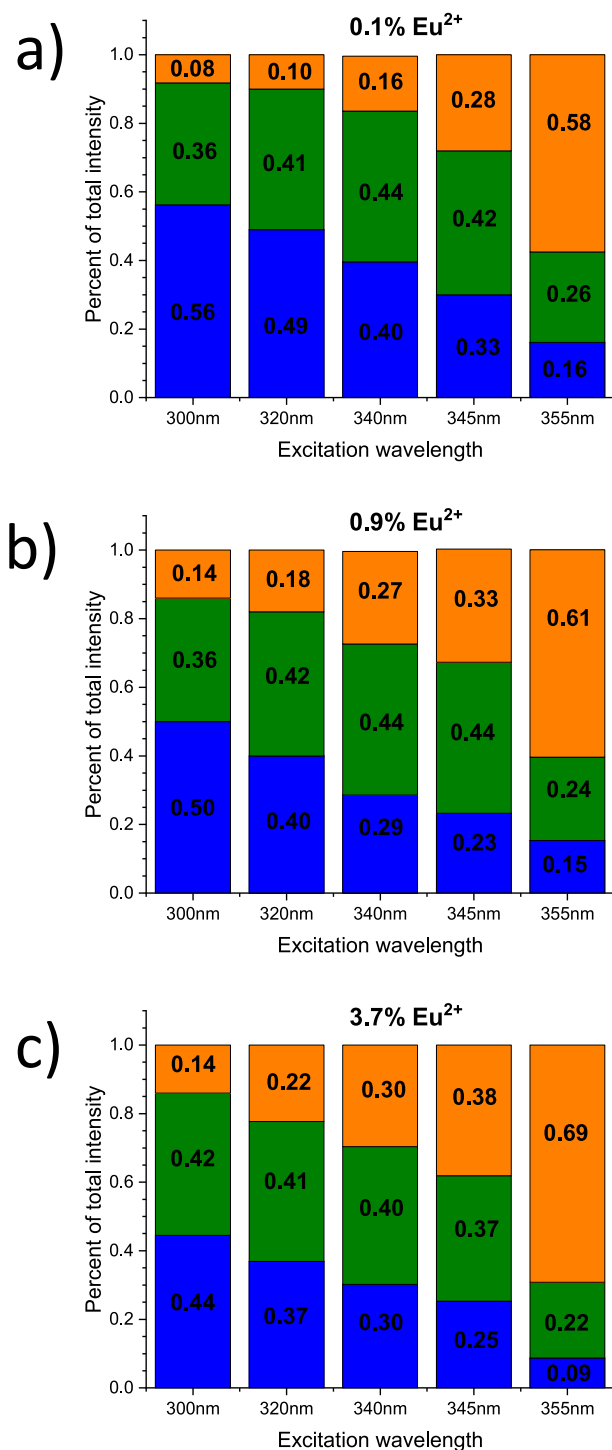
In the next step, we have analyzed the temperature evolution of these relative intensities, and the results are shown in Fig. 7 for  $\lambda_{\text{ex}} = 320$  nm. It can be seen from the results that the fractions of the “blue” and



**Fig. 4.** Room temperature emission spectra excited at different wavelengths for a)  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ : 0.1%Eu and b)  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ : 3.7%Eu.

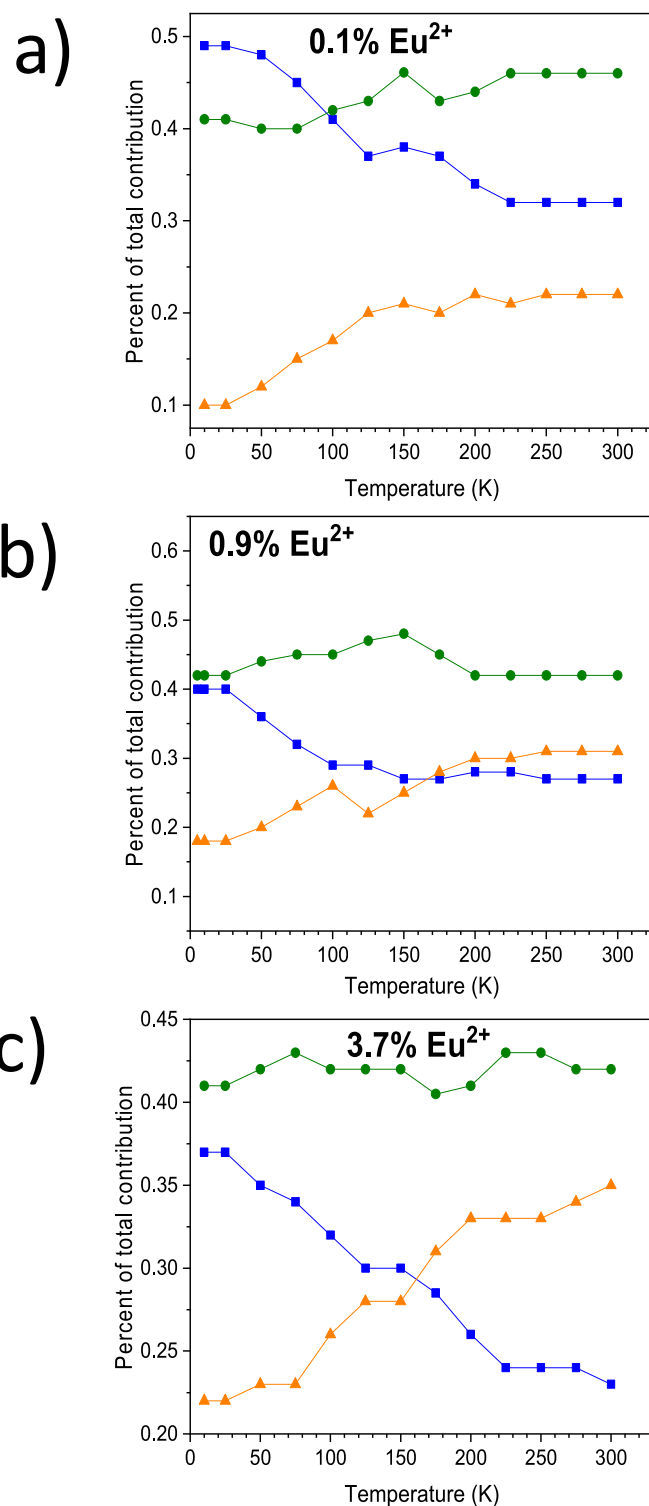


**Fig. 5.** Temperature dependent emission spectra of  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ : 0.9%Eu excited at 320 nm.



**Fig. 6.** Comparison of relative intensities of the 3 components (fitted using Gaussians) of the emission spectra of Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub>: x% Eu with a) x = 0.1, b) x = 0.9 and c) x = 3.7 at 10 K.

“orange” emission changes depending on the temperature which means that the energy transfer processes between these different Europium sites depends also on the temperature. As shown above, at 10 K, the higher the doping Eu concentration, the higher the fraction of orange emission is observed. Increasing the temperature, the fraction of the orange component increases for the three samples and reaches a plateau situated at ~56–60% of the total emission for the two more dilute samples. This plateau is reached at ~200K for 0.1% Eu<sup>2+</sup> and for 0.9% Eu<sup>2+</sup>. This reveals an efficient energy transfer from the “blue” to the



**Fig. 7.** Temperature dependence of the relative emission intensity excited at 320 nm of the three emission bands for Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub>: x% Eu with a) x = 0.1, b) x = 0.9 and c) x = 3.7.

“orange” emission which depends both on Eu concentration and on temperature (see Fig. 7).

## 6. Time dependent experiments

The emission lifetimes were then measured both as a function of temperature and emission wavelength for the samples with nominal Eu

concentrations of 0.1, 0.9 and 3.7%, using an excitation of 355 nm, and also at 266 nm in one case.

All decay curves were fitted with a mono-exponential decay function. Typical experimental decay curves are shown in Figure S5. The decay time curves measured at short wavelengths (e.g. 415 nm, 440 nm) can be fitted to a single exponential function with a standard deviation of below 1%. The decay time curves measured at longer wavelengths (e.g. 580 nm, 620 nm), on the other hand, are not quite single exponential, reflecting the superposition of different emissions as well as the energy transfer. The single lifetimes thus obtained increase continuously from about 0.7 to 0.8  $\mu$ s below 450 nm to more than 2  $\mu$ s around 600 nm at 5 K, as shown in Fig. 8. This trend of increasing lifetime with increasing emission wavelength has also been observed for other  $\text{Eu}^{2+}$  phosphors, such as in  $\text{Ba}_4\text{Gd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2\text{:Eu}^{2+}$  [20] with a lifetime of 0.46  $\mu$ s at 450 nm and of 1.28  $\mu$ s at 580 nm.

Within experimental error, the different lifetimes are identical for dilute and concentrated Eu-doped samples at 5 K. Further, these lifetimes remain practically unchanged at room temperature. This confirms on one side the high thermal quenching temperature (above 200 °C) of the Eu emission which was observed previously [18]. On the other side, this result is surprising, as the measured lifetimes do not appear to reflect the energy transfer inferred from the intensity changes which are clearly observed. In previous studies of the energy transfer between 2 different Europium ions on two different lattice sites [20,21], both the emission intensity and lifetime as a function of Eu content were perfectly correlated. This is not the case here.

The presence of energy transfer is also observed from the initial rise of the emission intensity as shown in Fig. 9. The time constant of this rise increases with increasing emission wavelength (from 415 nm to 620 nm), however with our set-up, it could not be quantified accurately.

These apparent conflicting results from intensity and lifetimes can be explained in the following way. It is well known that  $\text{Eu}^{2+}$  can present both “normal” and “anomalous” emissions [25]. The “anomalous” emissions are characterized by.

- an abnormally large Stokes shift and width of the band
- a wavelength of emission which is not consistent with the wavelength anticipated from the properties of the compound
- an anomalous decay time and thermal quenching behavior

For  $\text{BaF}_2$ , P. Dorenbos [25] indicates a normal emission observed at 403 nm, and an anomalous emission at 590 nm. The compound  $\text{Ba}_{12}\text{F}_{19}\text{Cl}_5$  has two Ba sites with a similar coordination of 7 fluoride and

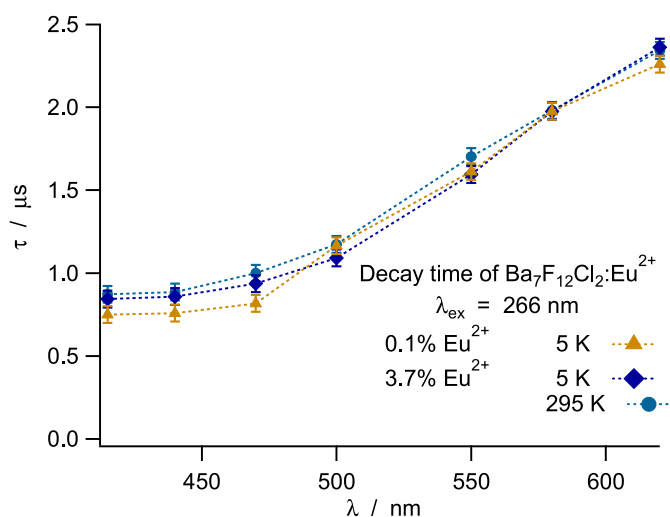


Fig. 8. Evolution of mono-exponential decay times as a function of emission wavelength at 5 K and 295 K for  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ : 3.7% Eu and at 5 K for  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ : 0.1% Eu.

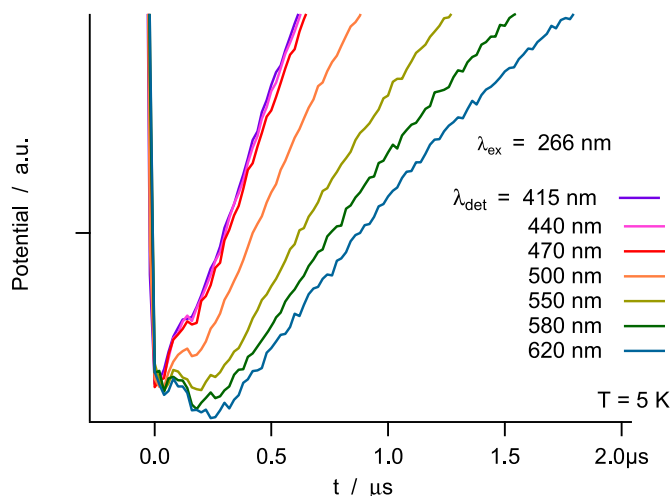


Fig. 9. Zoom on the first data points obtained in the time dependent experiments for  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ : 0.1% Eu at 5 K with 266 nm excitation for different emission wavelength.

2 chloride ions as in  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ , plus one additional site with 4 chloride ions and 5 fluoride ions [9], and in  $\text{BaFCl}$  there are 4 fluoride and 5 chloride ions in the first coordination sphere of Ba. The emission spectrum of Eu-doped  $\text{Ba}_{12}\text{F}_{19}\text{Cl}_5$  presents a broad band centered at 440 nm ( $22'700\text{ cm}^{-1}$ ) which can be decomposed into 3 Gaussian components [26], and in Eu-doped  $\text{BaFCl}$ , the single  $fd$  emission band is observed around 380 nm, in addition to sharp  $ff$  bands around 360 nm [26]. These blue and near UV emissions are thus normal europium emissions. Following the arguments of P. Dorenbos [25], the red-shifted emissions observed in Eu-doped  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$  are therefore very likely to be anomalous emissions.

The scheme below (Fig. 10) illustrates qualitatively our model.

Upon excitation, the normal 5d states of the 3 different sites occupied by Eu in  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$  are excited. These relax to the “anomalous states” which yield the observed emission spectrum.

When the europium concentration is changed, energy transfer takes place between the 5d states, which then relax to the anomalous states. This model explains the observation of different relative intensities, but similar emission lifetimes for the series of samples studies.

Another observation supports this model (see Figure S6). The emission spectrum of the sample with 3.7% Eu excited with 266 nm at 5 K present some very weak  $ff$  emission bands at 364, 368 and 372 nm which can be assigned to the  $^6\text{P}_J - ^8\text{S}_{7/2}$  transition of  $\text{Eu}^{2+}$  with  $J = 7/2$  and  $5/2$ . These bands are only observed if the lowest  $4f^6 5d^1$  state of  $\text{Eu}^{2+}$  is

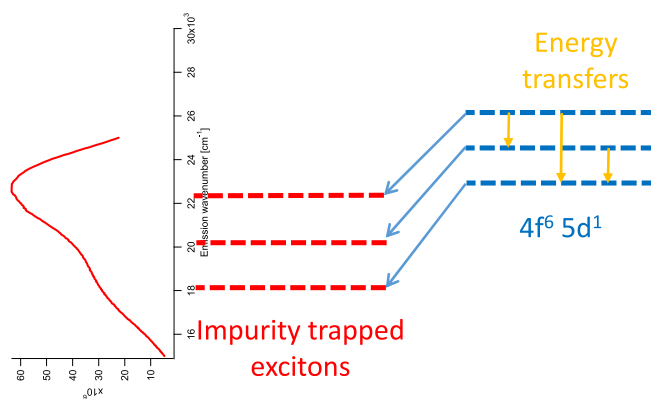


Fig. 10. Proposed approximate energy level scheme for the normal and anomalous energy levels corresponding to the three different sites of Eu in  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$  and emission spectrum of  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ :1%Eu.



higher in energy, as otherwise the *fd* emission would completely mask them. Thus, the corresponding normal Eu *fd* emission would be expected around 380 nm as in BaFCl. This low temperature emission spectrum further shows sharp emission bands at ca 690, 615 and 630 nm which are typical for Eu<sup>3+</sup>. In this sample with relatively high Eu concentration (3.7%), it is possible that some Eu ions have been oxidized to the 3<sup>+</sup> state. Note that the model of anomalous emission also involves photo-oxidation to form an impurity trapped exciton [25].

Recently, the optical properties of the structurally related Eu<sup>2+</sup>-doped Ca<sub>7</sub>H<sub>12</sub>Cl<sub>2</sub> and Sr<sub>7</sub>H<sub>12</sub>Cl<sub>2</sub> have been presented [27]. The emission in these compounds is yellow and orange-red. This red shift of the emission was explained by the strong polarizability of the hydride anion and the resulting strong nephelauxetic effect, or alternatively by impurity trapped exciton states. Our results presented above tend to favor the second possibility.

## 7. Conclusions

The emission spectrum of the single compound white phosphor Ba<sub>7</sub>F<sub>12</sub>Cl<sub>2</sub>:Eu<sup>2+</sup> is the result of the superposition of three emission bands. Europium ions replacing Barium ions on the three different crystallographic sites are at the origin of this emission. The change of the emission spectrum with excitation wavelength shows a systematic shift in the CIE chromaticity diagram from warm white when excited in the near UV (370 nm) to cold white when excited at shorter wavelengths. Excitation above 350 nm generates almost perfect white emission.

With increasing Europium doping, the relative intensity of the blue emission band decreases, and the intensity of the orange component increases, confirming that energy transfer takes place. Note that this energy transfer is both concentration and temperature dependent. In the phosphors Ba<sub>4</sub>Gd<sub>3</sub>Na<sub>3</sub>(PO<sub>4</sub>)<sub>6</sub>F<sub>2</sub>:Eu<sup>2+</sup> [20] and La<sub>3</sub>Si<sub>8</sub>N<sub>11</sub>O<sub>4</sub>:Eu<sup>2+</sup> [24], the energy transfer was found to be a dipole-dipole process. This is probably also the case here, as Eu<sup>2+</sup> has dipole allowed *fd* transitions.

Temperature and sample dependent lifetime studies show that the emission lifetime (fitted using a single exponential) increases with increasing emission wavelength. Further, the observed lifetimes do not change within experimental error between dilute and concentrated Eu-doped samples, and they remain constant between 5 K and room temperature. This second observation confirms the previous results that the thermal quenching of this white emission is at high temperature (200 °C).

The combination of all observations suggest that the energy transfer appears to take place first between the normal 4f<sup>6</sup> d<sup>1</sup> states of the Eu ions located on the 3 different crystallographic sites of Ba, and is followed by subsequent relaxation to anomalous emission states whose emission lifetimes remain constant with sample concentration and temperature from 5 K to 300 K.

## Credit

Caroline Hasler: Investigation, Validation, Visualization. Andreas Hauser: Supervision, Investigation, Methodology, Validation, Writing – review & editing. Jacob Olchowka: Formal analysis, Visualization, Writing – review & editing. Hans Hagemann: Conceptualization, Methodology, Supervision, Validation, Writing – original draft.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jlumin.2020.117866>.

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