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Observation of multiple sites for trivalent europium ions in SrAl_2O_4

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ABSTRACT

We have measured room temperature and low temperature luminescence spectra of Eu³⁺ in $\text{SrAl}_2\text{O}_4\text{:Eu}^{3+/2+}$. The powder samples were synthesized in reducing atmosphere above 1200 °C, cooled down to room temperature in the same atmosphere, and heated again to 750 °C in air. The analysis of the emission spectra of Eu³⁺ showed the presence of multiple sites for this ion, revealing that many different charge compensating defects are located in close vicinity to the europium ions. These defects can be positioned in each of the two void sites identified in the crystal structure of SrAl_2O_4 . Lifetime measurements reveal the presence of very short-lived excited Eu³⁺ species with lifetimes around 0.7 μs, in addition to species with lifetimes around 1.6 ms. These very short lifetimes are postulated to be related to intervalence charge transfer with few remaining divalent Eu²⁺ ions which had not been oxidized by the thermal treatment in air. This type of intervalence charge transfer between divalent to the trivalent rare earth ion could be crucially associated to processes involved in the afterglow of the persistent phosphor $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+},\text{Dy}^{3+}$.

1. Introduction

Persistent luminescence [1–7] and optically stimulated luminescence phosphors [8] require the trapping of excitations which are subsequently released either thermally or under optical irradiation. SrAl_2O_4 co-doped with Eu²⁺ and Dy³⁺ is an excellent persistent phosphor, and numerous papers have been devoted to elucidate the origin of the persistent luminescence in this material [1–4]. It has been shown previously [1–6] that the co-doping with Dy³⁺ improves dramatically the afterglow performance. Very recently, Joos et al. [6] demonstrated that Dy³⁺ acts as an electron trap in these persistent phosphors and gets reduced to Dy²⁺. Considering the ionic radii, it is generally assumed that Dy³⁺ replaces Sr²⁺ in SrAl_2O_4 . There are 2 different sites for Sr in SrAl_2O_4 [9], but there can also be charge compensating defects in the close vicinity of the trivalent rare earth ion, which thus lead to a variety of different surroundings. In a previous study, we have addressed the luminescence of SrAl_2O_4 doped only with Dy³⁺ in the absence or presence of boron [10]. This study revealed the presence of defects and confirmed indeed that there are more than 2 different surroundings observed for Dy³⁺ in SrAl_2O_4 . Further, local distortions in the presence

of boron could be observed.

In this work, we address the luminescent behavior of Eu³⁺ in SrAl_2O_4 in detail. The europium-doped strontium aluminate persistent phosphors are typically prepared using the trivalent Eu³⁺ as dopant which is then reduced at high temperatures (above 1100 °C) in a forming gas atmosphere. This process can leave some unreduced Eu³⁺ which can also act as electron trap for the excited Eu²⁺ ions in a similar way as Dy³⁺ does. In order to elucidate the local structures of Eu³⁺ in SrAl_2O_4 , we have oxidized $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$ samples (prepared previously above 1200 °C in reducing atmosphere) by heating them in air up to 750 °C. This temperature is just above the temperature of the phase transition from the monoclinic to the hexagonal structure [11]. In addition, high temperature conductivity measurements have been reported for SrAl_2O_4 [12]. At 1000 °C, the conductivity is approximately equal to 10⁶ S/cm with an activation energy of ca 150 kJ/mol (700–1000 °C). Hence, at 750 °C the mobility of oxygen ions in strontium aluminates is negligible and the Eu³⁺ ions may be in a “frozen” environment which corresponds to the environment of Eu²⁺ after charge transfer to Dy³⁺ in the afterglow process.

The emission properties of Eu³⁺ have been extensively studied [13],

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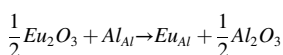
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as the intense red intra-configurational $^5D_0 \rightarrow ^7F_J$ transitions allow to probe the local symmetry experienced by the Eu^{3+} ion in the host material.

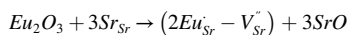
2. Background

The doping of SA with Eu^{3+} has been studied experimentally and theoretically by dos Santos et al. [14]. These authors considered theoretically the following substitution reactions:

Substitution at the Al site:

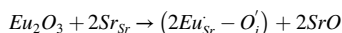


Substitution at the Sr site (compensation by Sr vacancy):



Substitution at the Sr site (compensation by $\text{Sr}^{2+}/\text{Al}^{3+}$ substitution).

Substitution at the Sr site (compensation by O^{2-} interstitial):



Substitution at the Sr site (compensation by Al^{3+} vacancy).

The lowest-energy charge compensation mechanism involves substitution at the Sr site with oxygen interstitial compensation. The authors calculated for this process 6 situations with two Eu ions located in 2 of the 4 Sr sites of the unit cell. The extensive literature for rare-earth doped CaF_2 supports this result, as tetragonal and trigonal charge compensations with interstitial fluoride ions are commonly observed [15,16]. We have explored this situation further as follows:

The analysis of the crystal structure of SrAl_2O_4 reported in Ref. [9] shows that there are two different voids labelled V1 and V2. There are three voids (V1) located at 294.6, 297.2 and 308.1 pm from the strontium atom on site 2, and three voids (V2) located at 278.0, 279.8 and 333.8 pm from the strontium atom on site 1. The fractional coordinates are (−0.019, 0.163, 0.682) and (0.506, 0.315, 0.313) for V1 and V2 respectively.

If strontium is replaced by a trivalent ion such as Eu^{3+} and Dy^{3+} , the excess positive charge can be compensated by a negative charge located in these voids. This excess charge can be for instance a single electron (F-center), or an interstitial OH^- , O^- , or O^{2-} (which would compensated the charge of two trivalent ions). The presence of an interstitial compensation negative ion/charge on these void sites is expected to have a strong impact on the crystal field of the dopant trivalent rare earth ion, as it adds formally a ligand into the coordination sphere.

3. Experimental

Eu(II) doped SrAl_2O_4 was prepared by high temperature solid state reaction starting from Al_2O_3 , SrCO_3 and a rare earth oxide [17], including high temperature annealing in a reducing atmosphere for 4 h. The phase purity was checked using X-ray powder diffraction (a PANalytical X'Pert PRO θ -2 θ scan system with a Johansson monochromator and an X'Celerator linear detector) and revealed no secondary phase for the Eu(II) -doped sample. Heating these samples (prepared without boron oxide) to 750 °C in air leads to the oxidation of Eu(II) and their color turns from yellow to white.

Emission spectra of Europium (III/II) doped SrAl_2O_4 were measured at room temperature and 11 K with a FT-Spectrometer (Bruker, IFS66v/S), excited with a quadrupled Nd:YAG Laser (266 nm) with 10 mW output power. Further emission spectra were acquired at 3 K with a home-made setup. The light source was a Quantel Q-switched Nd:YAG Laser with a repetitions rate of 10 Hz connected to an OPO which allows to finely tune the excitation wavelength. The luminescence was detected with a SPEX 270MX monochromator equipped with a CCD camera. The sample was cooled using a Janis closed cycle cryostat. Lifetimes at 3 K were measured using a gated CCD camera (Andor, i-star). Excitation

spectra were acquired at 8 K using a Jobin Yvon 3–22 Fluorolog instrument equipped with a second Janis closed cycle cryostat for low temperature experiments.

4. Results and discussion

As noted previously [17] $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ samples co-doped with boron did not show significant oxidation of the Europium ions upon heating in air to 750 °C, i.e. above the monoclinic to hexagonal phase transition in SrAl_2O_4 [11]. This behavior may be associated to the improved crystallization of the boron-doped samples. In Ref. [17], the crystallite size of boron-doped SrAl_2O_4 (as estimated from the Scherrer equation) was about twice the size compared to samples without boron prepared with the same reaction protocol. Fig. 2 compares the room temperature emission spectra (excited at 463 nm) of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ (in blue) and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{B}^{3+}$ (in red) samples which were heated in air to 750 °C. The boron containing sample still presents a strong Eu^{2+} emission at 520 nm under this excitation which is at the very edge of the Eu^{2+} absorption band [18,19], while it is completely suppressed for the sample without boron under these conditions (blue trace in Fig. 2). Several lines corresponding to the Eu^{3+} emission are seen for both samples.

It is important to note that the sample without boron still contains some Eu^{2+} after the heat treatment in air. An emission spectrum excited at 362 nm (where Eu^{2+} absorbs strongly [18,19]) shows the Eu^{2+} emission at 520 nm (Figure S1), however its intensity is similar to the intensity of the Eu^{3+} emission bands. Considering that the absorption for Eu^{2+} is a f - d transition, in contrast to Eu^{3+} which is excited by a forbidden f - f absorption, it appears that the relative concentration $\text{Eu}^{2+}/\text{Eu}^{3+}$ is very small (less than 1% considering the emission lifetimes of about 1 μs for Eu^{2+} [17] and 1 ms for Eu^{3+} (see below). SrAl_2O_4 ceramics with nominal composition $\text{Sr}_{(1-x-y)}\text{Al}_{1.94}\text{B}_{0.06}\text{O}_4:\text{Eu}_x\text{Dy}_y$ ($x = 0.001, 0.01, y = 0.001, 0.005, 0.01$) were prepared in with the laser sintering technique using a CO_2 laser [20]. These samples showed under 365 nm the typical Eu^{2+} emission at 512 nm, and under 280 nm excitation additionally weak bands around 610 nm from the $^5D_0 \rightarrow ^7F_2$ emission of Eu^{3+} [20]. The ratio between Eu^{2+} and Eu^{3+} can be quantified using XANES measurements around the Eu LIII edge. XANES measurements by Dutczak et al. [21] show the typical Eu^{2+} peaks at 6973.9 eV for SrAl_2O_4 and 6973.9 eV for $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ prepared with 5% H_2 :95% N_2 , but only a very weak signal at about 7–8 eV higher energy which would be typical for Eu^{3+} . The XANES data reported in Ref. [20] for the laser annealed sample showed in contrast a shoulder at around 6974 eV for Eu^{2+} and a strong peak at 6983 eV for Eu^{3+} . In our case the situation is similar to these laser annealed samples since upon heating in air, the powders changed from yellow to white, i.e. the intensity of the f - d absorptions of Eu^{2+} was strongly reduced. Further, as shown in the paper, the emission lifetimes are typically in the range of ms, so no significant quenching due to non-radiative intervalence charge transfer (IVCT) transitions as reported in Ref. [22] takes place.

Fig. 3 together with Figures S2 and S3 present the low temperature excitation and emission spectrum of Eu^{3+} in SrAl_2O_4 which show the typical sharp bands expected for Eu^{3+} (5D_2 21,500, 5L_6 25,400, 5G_6 26,700, 5H_6 31,500 cm^{-1}).

In the far UV region, a broad band is observed around 250 nm in the excitation spectrum. This has been assigned previously to an oxygen to europium charge transfer band [23]. The position of this band is also a measure of the separation between the valence band and the fundamental level of Eu^{2+} in SrAl_2O_4 [24]. Around 578 nm, the transition $^5D_0 \rightarrow ^7F_0$ is observed in both excitation and emission spectra, which is allowed by the selection rules for the non-centrosymmetric site symmetry of both Sr sites in the crystal [9]. It is interesting to note that this band has not been observed for boron and lithium co-doped SrAl_2O_4 : Eu^{3+} samples prepared in air at 1200 °C [25]. In Ref. [25], it was noted that the relative intensity of the $^5D_0 \rightarrow ^7F_1$ band around 590 nm (induced magnetic dipole transition) and $^5D_0 \rightarrow ^7F_2$ band around 612 nm (induced electric dipole transition) was changed upon boron doping, indicating

the presence of boron in rather close vicinity to the Eu^{3+} ions. It is important to note here that in this study, the samples were not exposed to a reducing atmosphere, but rather to mildly oxidizing conditions. This observation is also in agreement with our previous study on Dy^{3+} -doped SrAl_2O_4 in the presence of boron [10].

The spectroscopy of Eu^{3+} in SrAl_2O_4 has been studied experimentally and theoretically more recently [14]. In this paper, 2 bands for the transition $^5\text{D}_0\text{--}^7\text{F}_0$ are observed at 575 and 576 nm respectively and assigned to Eu^{3+} on the 2 different Sr sites in the crystal. Comparing their computed and experimental spectra at low temperature, the different components of the $^5\text{D}_0\text{--}^7\text{F}_1$ band and $^5\text{D}_0\text{--}^7\text{F}_2$ band were assigned to each species.

While measuring the room temperature emission spectra of our samples, it appeared that the shape of the $^5\text{D}_0\text{--}^7\text{F}_2$ bands changed significantly upon small changes of the excitation wavelength (see Figure S4). In order to achieve a more selective excitation, we have recorded the emission spectra of the $^5\text{D}_0\text{--}^7\text{F}_{0,1}$ bands at 3 K by exciting the $^7\text{F}_0\text{--}^5\text{D}_2$ band around 460 nm in small steps (see Fig. 4).

As the $^5\text{D}_0\text{--}^7\text{F}_0$ transition is non-degenerate, a different band is expected for each different site. In contrast to the previous results [14], Fig. 4 reveals that there are more than just 2 different Eu^{3+} sites. While 2 bands at 575 and 576 nm were reported [14], we observed that the different bands range from 574 to 579 nm, i.e. a much longer wavelength range. The changes of the $^5\text{D}_0\text{--}^7\text{F}_0$ emission upon slightly different excitation wavelengths are also to different structures of the $^5\text{D}_0\text{--}^7\text{F}_1$ transitions as shown in Fig. 4, as well as for the other transitions which are presented in Figure S5, revealing indeed a variety of different environments for the Eu^{3+} ions in SrAl_2O_4 .

488 nm laser excitation at room temperature (see Figure S6) reveals quite sharp $^5\text{D}_1\text{--}^7\text{F}_0$ emission bands, in contrast to the rather broad shape of the $^7\text{F}_0\text{--}^5\text{D}_0$ emission band, highlighting again that this band is inhomogeneously broadened [26,27].

Another significant feature is the relatively large spread of the $^5\text{D}_0\text{--}^7\text{F}_1$ transitions. For instance, in the orange trace in Fig. 4, there is at 579 nm the single band with a shoulder corresponding to the $^5\text{D}_0\text{--}^7\text{F}_0$ transition and 3 quite distinct $^5\text{D}_0\text{--}^7\text{F}_1$ transitions observed at 587, 592 and 597 nm respectively. Considering that the site symmetry of both Sr ions is C_3 in the high temperature phase of SrAl_2O_4 and that the room temperature monoclinic $\text{P}2_1$ phase is a maximal subgroup of $\text{P}6_3$, one could suspect that in the monoclinic phase, the local surroundings of the Sr ions are not so far from a trigonal symmetry. In trigonal symmetry, the $^5\text{D}_0\text{--}^7\text{F}_1$ band is split into 2 components, and if the distortion from this symmetry is not too large, the splitting of the degenerate sublevel is expected to be rather small. This corresponds to the reported assignments (580.7, 589.3, 590.5 nm for one site and 583.4, 590.1 and 591.1 nm for the other site) [14]. In contrast, 3 quite distinct bands are observed as shown in Fig. 4, indicating that in this case, the symmetry is far from C_3 and very likely associated with an oxygen defect located on one of the two vacancy sites in SrAl_2O_4 (see Fig. 1).

Further informations were obtained from lifetime measurements. The measurement of the lifetime, as a function of the emission wavelength showed two different lifetimes: a long lifetime of approximately 1.6 ms, which corresponds to a typical value of Eu^{3+} emission lifetime in the literature [4]. The other lifetime is around three orders of magnitude faster (ca 0.7 μs). Fig. 5 shows the time-gated emission spectrum observed 5 μs after the excitation pulse at 463.4 nm (top), as well as the one observed 2 ms after this pulse (bottom). While the second spectrum resembles the one observed under cw-excitation at 266 nm, the first one is quite different and much broader in the $^5\text{D}_0\text{--}^7\text{F}_2$ region between 16,000 and 16,500 cm^{-1} .

It is shown (Figure S1) that there is a small residual population of Eu^{2+} in our oxidized sample. At 463.4 nm, this population can in principle also be excited, however the corresponding emission intensity is too weak to be observed in the blue trace in Fig. 2. Another possibility is the inter-valence charge transfer between Eu^{2+} and Eu^{3+} which has recently been reported [22]. If one considers a pair of differently

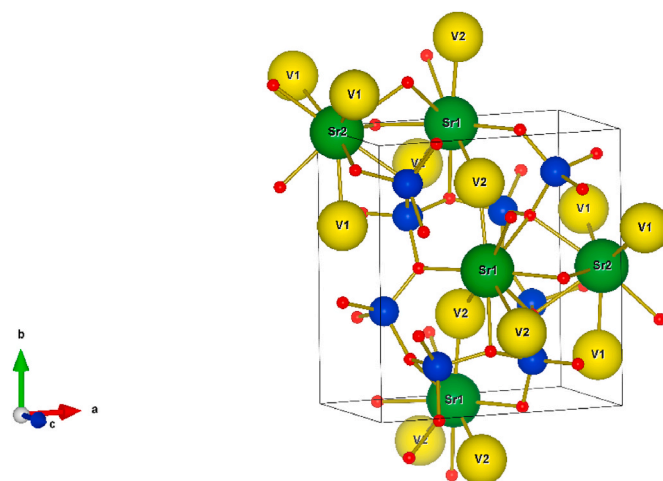


Fig. 1. Crystal structure of SrAl_2O_4 and location of the two different voids labelled V1 and V2.

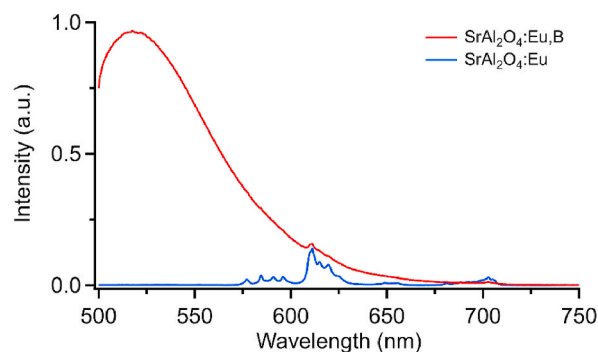


Fig. 2. Room temperature emission spectra excited at 463 nm of $\text{SrAl}_2\text{O}_4\text{:Eu,B}$ (in red) and $\text{SrAl}_2\text{O}_4\text{:Eu}$ (in blue) after heating in air to 750 °C.

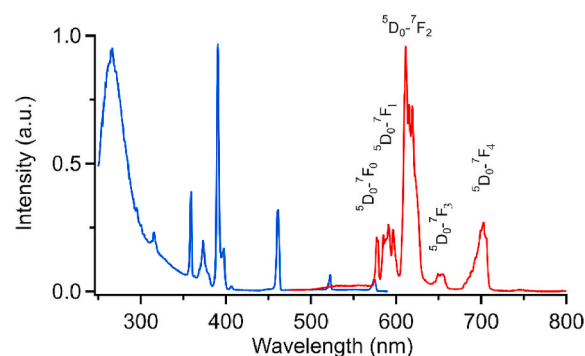


Fig. 3. Excitation (monitored at 612 nm) and emission spectra (excited at 395 nm) of Eu^{3+} in $\text{SrAl}_2\text{O}_4\text{:Eu}$ at 5 K.

charged ions on adjacent Sr1 and Sr2 sites, one could have a fast charge transfer equilibrium of the type: $\text{Eu}^{2+} + \text{Eu}^{3+} \leftrightarrow \text{Eu}^{3+} + \text{Eu}^{2+}$, i.e. the valence of the Eu ions switches rapidly (ns time scale or faster?). The lifetime of 0.8 μs corresponds to the lifetime of the blue emitting Eu^{2+} ion [19] at 3 K, and this is in fact the shortest radiative lifetime available for Eu at this temperature, as the lifetime of the green emitting Eu^{2+} was found to be 1.2 μs [19].

5. Conclusions

The spectra reported in this work indicate that trivalent Eu^{3+} (and by

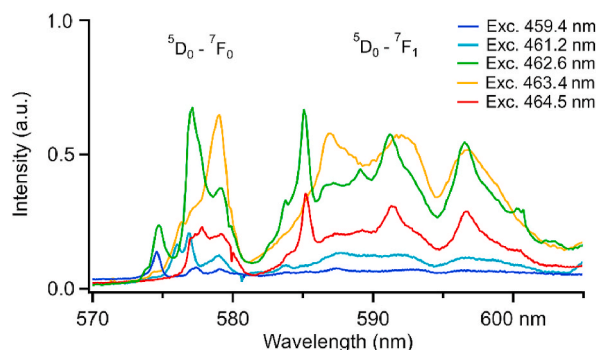


Fig. 4. Emission spectra at 3 K excited around 460 nm using the OPO pumped at 355 nm.

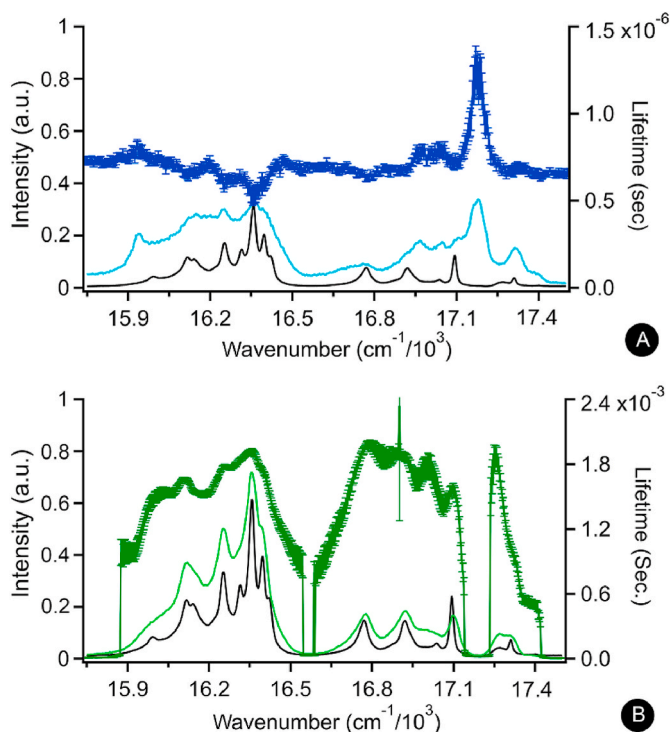


Fig. 5. 3 K Time-gated emission spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ excited at 463.4 nm. The black trace is a reference cw emission spectrum excited at 266 nm measured at 12 K: A. Light blue: emission spectrum, 5 μs after excitation at 463.4 nm (exposure time: 1 μs); blue: lifetime (spectral dependent); B. light green: emission spectrum, 2 ms after excitation at 463.4 nm (exposure time: 50 ms); green: lifetime (spectral dependent).

extension also other trivalent rare earth ions, in particular Dy^{3+}) in SrAl_2O_4 are associated with a multitude of different charge compensating (oxygen?) defects. Different sites were also observed for Dy^{3+} in SrAl_2O_4 [10]. EPR studies of $\text{Sr}_x\text{Al}_2\text{O}_4$ ($x = 0.99, 1.0, 1.01$) with or without Dy^{3+} revealed a variety of signals corresponding to different defects [28] present in these samples. The large spread of the $^5\text{D}_0 - ^7\text{F}_1$ emission bands indicates that these defects are most probably in the first coordination sphere induced by a charge compensating defect in one of the voids in the structure which lead thus to significant distortions from the idealized trigonal symmetry observed in the high temperature phase of SrAl_2O_4 . Dysprosium ions in strontium aluminate can act as trap states in the persistent phosphor SrAl_2O_4 by charge transfer from Eu^{2+} (in the excited state) to Dy^{3+} [6]. The diversity of surroundings experienced by the trivalent rare earth ion which is demonstrated in this work for Eu^{3+} is thus also associated with the large energy distribution of trap states in

the persistent phosphor. The observation of very short lifetimes (around 0.7 μs) for Eu^{3+} is possibly a direct proof that there is indeed a charge transfer from Eu^{2+} to Eu^{3+} , which results then in a much shorter emission lifetime.

Credit author statement

Jakob Bierwagen: Investigation, Methodology, Formal analysis, Visualization. Teresa Delgado: Validation, Writing - Review & Editing. Jafar Afshani: Validation, Visualization. Songhak Yoon: Resources, Methodology. Nando Gartmann: Resources. Bernhard Walfort: Resources, Formal analysis, Writing - Review & Editing, Project administration. 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.2021.118348>.

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