

## Photoluminescence

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## Underestimated Color Centers: Defects as Useful Reducing Agents in Lanthanide-Activated Luminescent Materials

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**Abstract:** Inorganic hosts, such as  $\text{SrB}_4\text{O}_7$  or certain nitrides, intrinsically stabilize  $\text{Eu}^{2+}$  even when the dopant is an  $\text{Eu}^{3+}$ -based precursor and reducing conditions are not employed in the synthesis. Although this concept is well known in the synthesis of phosphorescent materials, the mechanistic details are scarcely understood. Herein, we demonstrate that trapped charge carriers, such as color centers, can also act as redox partners to stabilize certain oxidation states of activators.  $\text{Eu}$ -activated  $\text{CsMgCl}_3$  and  $\text{CsMgBr}_3$  are used as examples. Upon doping with  $\text{EuCl}_3$  and in the absence of reducing conditions during the synthesis, dominant cyan or green luminescence from  $\text{Eu}^{2+}$  ions was observed. Photoluminescence spectroscopy at 10 K revealed that the reduction is correlated to color centers localized at defects. Although defects are typically undesired in phosphors, we have shown that their role may be underestimated and they could be used on purpose in the preparation of selected inorganic phosphors.

Lanthanides are promising activators for novel phosphors in solid-state lighting,<sup>[1]</sup> medical imaging,<sup>[2]</sup> as well as up-<sup>[3]</sup> and down-conversion processes<sup>[4]</sup> for photovoltaics. They are most stable in their trivalent oxidation state with a partially occupied  $4f^n$  shell ( $n=0$  for  $\text{La}^{3+}$  to  $n=14$  for  $\text{Lu}^{3+}$ ). For the majority of those ions, their optical properties in the UV and visible range are dominated by narrow and parity-forbidden intraconfigurational  $4f^n \leftrightarrow 4f^n$  transitions. Their wavelengths of the emitted light related to those transitions is characteristic for a given lanthanide ion and almost independent from the surrounding host environment, which

is a result of the low spatial extension and thus, shielded nature of the  $4f$  orbitals. In addition, the parity-forbidden nature of those electronic transitions gives rise to very low absorption cross sections.

A promising alternative to overcome those drawbacks are electric-dipole allowed interconfigurational  $4f^{n-1}5d \leftrightarrow 4f^n$  transitions with characteristically broad emission bands. In addition to  $\text{Ce}^{3+}$  and  $\text{Pr}^{3+}$  which are able to show this type of transition in the visible and UV range<sup>[5]</sup> respectively, the optical spectra of divalent lanthanides are also dominated by this type of transition. The higher spatial extension of the  $5d$  orbitals and higher degree of overlap with the orbitals of the surrounding ligand field allows both the absorption and emission wavelengths connected to  $4f^{n-1}5d^1 \leftrightarrow 4f^n$  transitions to be tailored by the specific design of both the extent of polarizability and coordination symmetry of the surrounding ligand field.<sup>[6]</sup>

Chemically, the stabilization of divalent lanthanides in inorganic host compounds is still a challenging task for most of these species and limits potential application areas.<sup>[6]</sup> The most prominent representative among the divalent lanthanides for current applications is certainly  $\text{Eu}^{2+}$  ( $4f^7$ ).<sup>[1,7]</sup> This fact is easily understandable by its comparably low reduction potential ( $E^0(\text{Eu}^{3+}/\text{Eu}^{2+}) = -0.35$  V in aqueous solution)<sup>[8]</sup> allowing the stabilization of  $\text{Eu}^{2+}$  in many inorganic bulk and nanocrystalline compounds combined with a relative ease in synthesis compared to the other lanthanide ions.<sup>[6,8,9]</sup> Among the possible ways to prepare both purely  $\text{Eu}^{2+}$ -based or  $\text{Eu}^{2+}$ -activated solid compounds from the more stable  $\text{Eu}^{3+}$ -based precursors are, for example, the reduction with  $\text{H}_2$  gas at elevated temperatures ( $> 400^\circ\text{C}$ ),<sup>[10]</sup> but also with  $\text{LiH}$ <sup>[11]</sup> or liquefied  $\text{NH}_3$ .<sup>[12]</sup> In addition to the explicit reduction of  $\text{Eu}^{3+}$ -based starting materials, several compounds containing polarizable anions with appreciable covalent bonding character, such as iodides,<sup>[13,14]</sup> hydrides,<sup>[15]</sup> heavy chalcogenides,<sup>[16]</sup> and nitrides,<sup>[1,17]</sup> readily stabilize  $\text{Eu}^{2+}$ , sometimes even upon use of  $\text{Eu}^{3+}$ -based starting materials. Among them, especially the class of  $\text{Eu}^{2+}$ -activated nitride-based phosphors with their related narrow-band red emission has emerged to a promising class of inorganic materials that play a dominant role for phosphor-converted white-light-emitting diodes (pc-wLEDs).<sup>[1,18]</sup> The stability of  $\text{Eu}^{2+}$  in the previously mentioned classes of compounds is chemically intuitively evident by means of Pearson's hard and soft acid and base (HSAB) principle. Moreover, these anions are generally oxidizable and it is thus also mechanistically clear how  $\text{Eu}^{3+}$  ions can be readily reduced in those compounds even without explicit reducing conditions during the synthesis at high temperatures as elemental by-products stemming from the anions can also be formed then.

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An alternative prominent compound in the field of luminescence spectroscopy that is known to stabilize  $\text{Eu}^{2+}$  even upon explicit doping with  $\text{Eu}^{3+}$  and without any reducing synthesis conditions is  $\text{SrB}_4\text{O}_7$ .<sup>[19]</sup> Its intrinsic reducing action has also been demonstrated on other trivalent luminescent activators with much lower reduction potentials. As such, it fully stabilizes  $\text{Yb}^{2+}$ ,<sup>[20]</sup>  $\text{Sm}^{2+}$ ,<sup>[21]</sup>  $\text{Tm}^{2+}$ ,<sup>[22]</sup>  $\text{Nd}^{2+}$ ,<sup>[23]</sup> or more exotic ions, such as  $\text{Bi}^{2+}$ <sup>[24]</sup> even when synthesized in air. Unlike the host compounds with oxidizable soft anions, the tetrahedral  $[\text{BO}_4]^{5-}$  units present in the crystal structure of  $\text{SrB}_4\text{O}_7$  cannot be further oxidized. Although it appears thermodynamically reasonable that the  $[\text{BO}_4]^{5-}$  units as soft Lewis bases may rather stabilize  $\text{Eu}^{2+}$ , the mechanism of the inherent reduction is still under debate. It was speculated that the intrinsic reducing action of  $\text{SrB}_4\text{O}_7$  stems from potential charge-compensating defects present in  $\text{SrB}_4\text{O}_7$  that allow reduction of the trivalent activators.<sup>[25]</sup> Alternatively, a potential impact of the rigid network built up by the composing  $[\text{BO}_4]^{5-}$  units was also anticipated,<sup>[26]</sup> and it could be shown that this is clearly related to a long-range ordered crystalline structure of the host material.<sup>[27]</sup>

Since then, other borates,<sup>[28]</sup> aluminates<sup>[29]</sup> or silicates<sup>[30]</sup> have also been demonstrated to show these inherent reducing effects despite similarly lacking the possibility for additional oxidation of the respective complex anions. Dorenbos finally indicated that the redox stability of a given oxidation state of a lanthanide ion in an inorganic host should depend on the relative position between the ground state of the incorporated activator within the band gap and the Fermi level of the inorganic host material.<sup>[25]</sup> In contrast, to our knowledge, no explicit proof or any clear indication of the redox-related action of defects on activators that would mechanistically explain the intrinsic reducing action of host materials has been given to date.

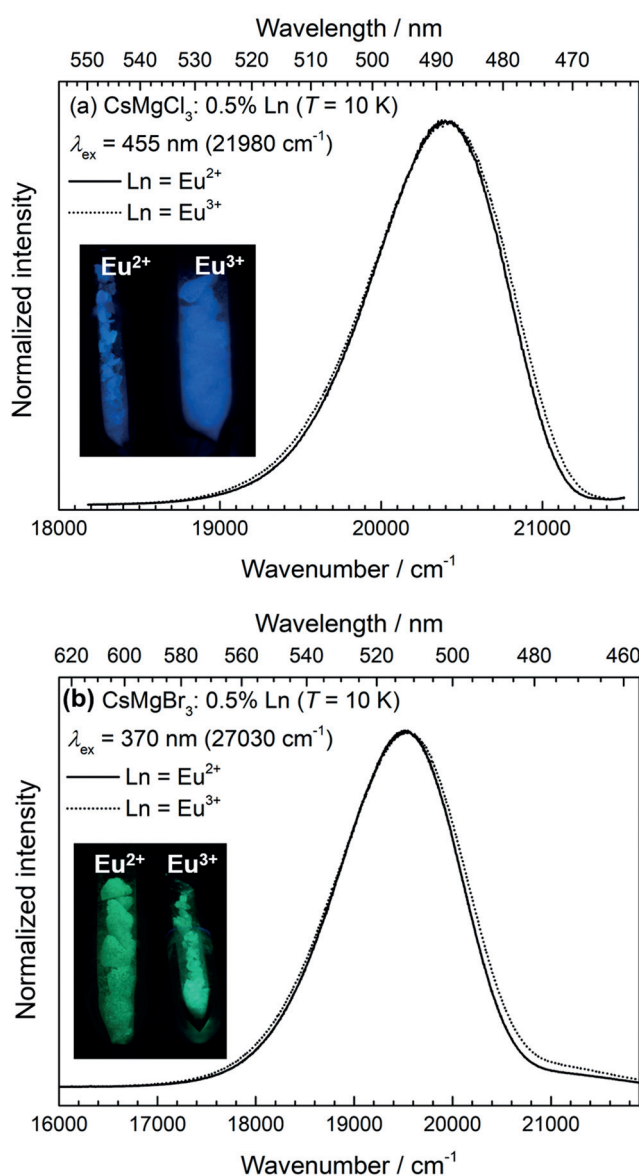
Mostly, defects are considered undesirable in phosphors as they can act as trapping sites for charge carriers and thereby diminish the luminescence efficiency or completely quench it.<sup>[31]</sup> In fact, this particular, apparently undesirable feature of defects has found a useful application in the field of persistent phosphors.<sup>[32]</sup> However, a role as redox-active centers to help stabilize luminescent dopants in a desirable oxidation state could prove to be a beneficial alternative concept for a simple chemical access to new phosphors.

Luminescence spectroscopy is a simple and yet very powerful method to elucidate such details since defects that are generated during synthesis or due to doping can also occasionally show UV or visible luminescence. One of the most prominent candidates of luminescent defects are color centers ( $F$  centers), which are localized electrons in anion vacancies. They are particularly well studied in halides and have been investigated in much detail by both optical spectroscopy and magnetic resonance.<sup>[33,34]</sup> Their role was especially acknowledged and anticipated in the performance of X-ray-storage phosphors, such as  $\text{BaFBr}:\text{Eu}^{2+}$ ,<sup>[35]</sup> or in investigations of optical absorption spectra of divalent lanthanides by  $\gamma$ -irradiation or heating in Ca vapor of (trivalent) rare-earth activated  $\text{CaF}_2$ .<sup>[36]</sup> The interest in the optical properties of similar defects has experienced a renaissance in the nitrogen vacancy ( $NV$ ) centers in diamond<sup>[37]</sup> that

prove to be interesting for quantum information technology,<sup>[38]</sup> electric<sup>[39]</sup> and magnetic field sensing,<sup>[40]</sup> or remote thermometry.<sup>[41]</sup>

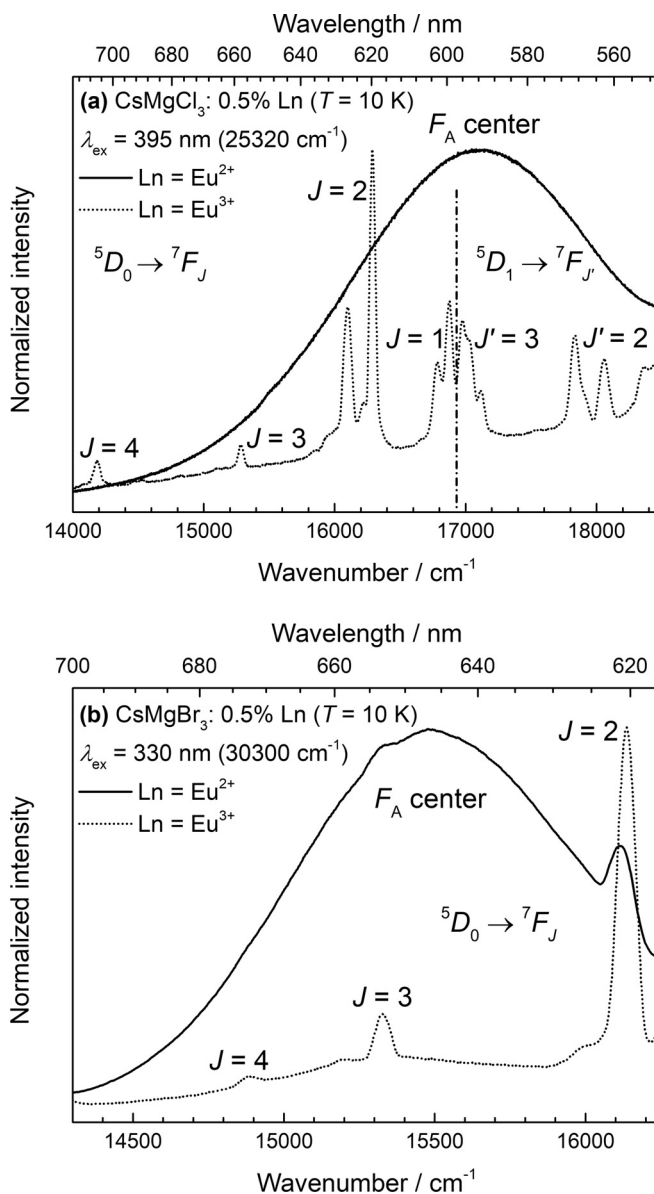
Throughout our studies on  $\text{Eu}^{2+}$ -activated  $\text{CsMgX}_3$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ),<sup>[42]</sup> we also observed intense intrinsic host-based luminescence that could be assigned to the presence of impurity-localized self-trapped excitons (IL-STEs) in those compounds.<sup>[43]</sup> STEs are commonly encountered in both halidoperovskites and other halides, especially if the band gap is successively lowered and they obtain more semiconducting character. The recently most prominent representatives in that field are various ternary cesium lead and tin halides that show strong intrinsic (self-trapped) exciton luminescence both in nanocrystals and bulk.<sup>[44]</sup>  $\text{CsMgX}_3$  ( $X = \text{Cl}, \text{Br}$ ) crystallizes in a hexagonal  $\text{CsNiCl}_3$  crystal structure type and could be synthesized in pure manner under exclusion of air (see Supporting Information for more details).<sup>[45]</sup> The hexagonal crystal structure imposes a pseudo one-dimensionality of the face-sharing  $[\text{MgX}_6]^{4-}$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) octahedra along the  $c$  axis.<sup>[45]</sup> This structural feature strongly favors polaron formation and self-trapping of excitons within these chains,<sup>[46]</sup> as already studied very thoroughly for the isotypically crystallizing compound  $\text{CsCdBr}_3$ .<sup>[47]</sup> The mismatch in ionic radii between  $\text{Eu}^{2+}$  ( $r(\text{Eu}^{2+}) = 1.17 \text{ \AA}$ ) and  $\text{Mg}^{2+}$  ( $r(\text{Mg}^{2+}) = 0.72 \text{ \AA}$ ) in six-fold coordination<sup>[48]</sup> additionally favors exciton localization at the  $\text{Eu}^{2+}$  impurities based on the very strong induced distortion as was also demonstrated by us earlier, both by a thermally activated energy transfer from the IL-STEs to the  $\text{Eu}^{2+}$  ions and analysis of the decay kinetics of the IL-STEs.<sup>[43]</sup>

Impurity localization of STEs should also allow an interaction of one of the charge carriers with the Eu impurities dependent on their oxidation state. Upon doping of  $\text{CsMgCl}_3$  and  $\text{CsMgBr}_3$  with 0.5 mol %  $\text{EuCl}_2$  and  $\text{EuBr}_2$  (see Supporting Information for details on the synthesis), respectively, the incorporated  $\text{Eu}^{2+}$  ions can potentially act as hole traps thus forming intermediate  $\text{Eu}^{3+}$  ions. Correspondingly, the  $\text{Eu}^{2+}$ -IL-STE entity can be chemically envisioned as a " $\text{Eu}^{3+} + e^-$ " Frenkel-type exciton. Next to the expected dominant  $\text{Eu}^{2+}$ -related broad emission from the electronic  $4f^65d^1 \rightarrow 4f^7$  transition in either the cyan ( $\text{CsMgCl}_3:\text{Eu}^{2+}$ ) or green ( $\text{CsMgBr}_3:\text{Eu}^{2+}$ ) spectral range (see Figure 1, solid lines), an additional broad emission band in the red spectral range is observable at sufficiently low temperatures (in this case, at  $T = 10 \text{ K}$ , see Figure 2, solid lines). At room temperature, this emission is effectively thermally quenched in both halide hosts. In the case of  $\text{CsMgCl}_3$ , the red emission band has a maximum at around 580 nm ( $E_{\text{em}} = 17240 \text{ cm}^{-1}$ ), which becomes slightly redshifted in the case of  $\text{CsMgBr}_3$  with a wavelength of 650 nm ( $E_{\text{em}} = 15380 \text{ cm}^{-1}$ ). Both the width of the emission bands ( $> 2000 \text{ cm}^{-1}$ ) and their position in the red to near-infrared range also agree with the established features of  $F$  centers in binary alkali halides.<sup>[33]</sup> As such, the broad band is interpreted as an activator-perturbed  $2p^1(^2P) \rightarrow 1s^1(^2S)$  hydrogen-like transition. An additional indication for the assignment of the red emission band to an activator-localized  $F_A$  center is the parallel observation of  $\text{Eu}^{3+}$ -related narrow  $4f^6(^3D_{0,1}) \rightarrow 4f^6(^7F_{J=0...6})$  transitions upon excitation in the UV range (see Figures S3.(a) and S4.(a), Supporting



**Figure 1.** Photoluminescence emission spectra of a) CsMgCl<sub>3</sub>: 0.5% Ln and b) CsMgBr<sub>3</sub>: 0.5% Ln (Eu<sup>2+</sup>, solid line; Eu<sup>3+</sup>, dotted line) acquired at 10 K showing the 4f<sup>6</sup>5d<sup>1</sup>→4f<sup>7</sup> emission transition of Eu<sup>2+</sup>. Excitation wavelengths are specified in the graphs. Insets: photographs of the visible photoluminescence of the respective Eu<sup>2+</sup>- and Eu<sup>3+</sup>-activated samples upon UV irradiation at room temperature.

Information). Monitoring of the narrow Eu<sup>3+</sup>-related emission, however, only affords broad excitation bands that are similar to those of Eu<sup>2+</sup> instead (see Figures S3.(b) and S4.(b)). This observation shows that the Eu<sup>3+</sup>-related luminescence have not been formed which is as result of the oxidation of the divalent EuCl<sub>2</sub> or EuBr<sub>2</sub> salts employed during the synthesis of the doped halidoperovskites, which should otherwise lead to the observation of Eu<sup>3+</sup>-related narrow 4f<sup>6</sup>→4f<sup>6</sup> excitation transitions. Thus, the observed luminescence of Eu<sup>3+</sup> is intrinsically related to the presence of Eu<sup>2+</sup> ions, which is already a strong indication for the anticipated charge carrier trapping mechanism explained above. In the case of CsMgBr<sub>3</sub>: 0.5% Eu<sup>2+</sup>, the excitation



**Figure 2.** Photoluminescence emission spectra of a) CsMgCl<sub>3</sub>: 0.5% Ln and b) CsMgBr<sub>3</sub>: 0.5% Ln (Ln = Eu<sup>2+</sup>, solid line; Ln = Eu<sup>3+</sup>, dotted line) acquired at 10 K. Excitation wavelengths are specified in the graphs.

spectrum upon monitoring both the F<sub>A</sub> center emission or a separate Eu<sup>3+</sup>-related emission additionally shows three well separated UV transitions at around 300 nm (see Figure S4). Their appearance can be understood on the basis of the 1s<sup>1</sup>(<sup>2</sup>S)→2p<sup>1</sup>(<sup>2</sup>P) transition of the F<sub>A</sub> center. The low C<sub>2v</sub> site symmetry of the anion sites in CsMgBr<sub>3</sub><sup>[45]</sup> (probably even lowered by the presence of the Eu impurities) will completely remove the three-fold orbital degeneracy of the <sup>2</sup>P term and thereby leads to the observation of three separate excitation bands. In the case of CsMgCl<sub>3</sub>: 0.5% Eu<sup>2+</sup>, these bands are expected to be located farther in the UV range (λ < 240 nm) based on the higher ionicity of the host compound and was thus not accessible by the spectroscopic equipment employed. Finally, the decay times of the anticipated F<sub>A</sub> center-based

emission bands are also in the range of 0.1 ms, which is expected for defects (Figure S5).

The redox couple  $\text{Eu}^{2+}/\text{Eu}^{3+}$  also allows a reversion of the selective charge carrier trapping mechanism. Selective doping of  $\text{CsMgCl}_3$  and  $\text{CsMgBr}_3$  with 0.5 mol %  $\text{EuCl}_3$  ( $\text{EuBr}_3$  is not stable at ambient conditions) as a source for  $\text{Eu}^{3+}$  impurities and no reductive conditions during synthesis yet leads to an observation of strong  $\text{Eu}^{2+}$ -related cyan or green emission from the resulting halides (see Figure 1). This clearly demonstrates the intrinsic reductive ability of the hosts on intentionally incorporated  $\text{Eu}^{3+}$  ions. To rule out a potential thermally induced reduction of  $\text{EuCl}_3$  during synthesis,  $\text{CsMgBr}_3$  was also doped with  $\text{Eu}_2\text{O}_3$  and reduction to  $\text{Eu}^{2+}$  was still recorded (Figure S6). Similar observations in  $\text{CsCdBr}_3$  were already reported earlier,<sup>[49]</sup> but have remained hitherto fully unexplained.

According to the charge carrier trapping mechanism,  $\text{Eu}^{3+}$  ions should in turn act as potential electron scavengers. Indeed, dominant  $\text{Eu}^{2+}$ -related luminescence is observed in that case (see Figure 1, solid lines). In exact agreement with those expectations, the luminescence spectra at 10 K reveal that the broad red emission band, which had been observed in the intentionally  $\text{Eu}^{2+}$ -activated samples, now vanishes (see Figure 2, dashed lines) while luminescence of residual non-reduced  $\text{Eu}^{3+}$  is observable in that case. This is clear evidence for the reductive action of impurity-localized  $F_A$  centers. Although the spectra depicted in Figure 1 were acquired at 10 K for the sake of appreciable luminescence intensity, the intrinsic reducing ability of  $\text{CsMgCl}_3$  and  $\text{CsMgBr}_3$  on  $\text{Eu}^{3+}$  ions to form  $\text{Eu}^{2+}$  is even possible at room temperature (see inset photographs in Figure 1). As such, the  $\text{Eu}^{3+}$ -IL-STE entity now more resembles a “ $\text{Eu}^{2+} + \text{h}^+$ ” Frenkel-type exciton.

These findings are a first step towards a microscopically mechanistic and experimentally supported explanation for the intrinsic reductive action of selected inorganic host materials, such as  $\text{SrB}_4\text{O}_7$  on activators. Strong evidence for the presence of trapped electrons was given by combined thermoluminescence and electron paramagnetic resonance studies in the borate  $\text{Zn}_4\text{B}_6\text{O}_{13}$ .<sup>[50]</sup> Not only is this relevant from a fundamental perspective. It also opens up a strategy to make use of either intrinsically present or dopant-induced trapped charge carriers and defects as redox partners in solids for the synthesis of potential phosphors on the basis of reduced activators, such as the divalent lanthanides, without the necessity of employing challenging reducing conditions in the preparation. Photoluminescence spectroscopy is both simple and valuable to elucidate those mechanistic features. In particular, the present study also demonstrates that it is worthwhile investigating a wider spectral range, especially in the red and near infrared range for a mechanistic investigation of the redox-related action of inorganic host materials. In particular, color centers tend to show emission in that lower energetic regime and can thus be easily identified by careful control experiments next to other techniques, such as magnetic resonance.

## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** color centers · defects · europium · photoluminescence · reduction

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