

Green Luminescence of Divalent Europium in the Hydride Chloride EuHCl

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Dedicated to Professor Arndt Simon on the Occasion of His 75th Birthday

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Abstract. Luminescence properties of divalent europium in the mixed-anion hydride chloride EuHCl were studied for the first time. Olive-green single crystals of EuHCl (PbFCl-type structure: tetragonal, $P4/nmm$, $a = 406.58(3)$ pm, $c = 693.12(5)$ pm, $cla = 1.705$, $Z = 2$) resulted from the reaction of elemental europium (Eu), sodium hydride (NaH) and sodium chloride (NaCl), while powder samples were prepared from the binary components europium dihydride (EuH₂) and dichloride (EuCl₂). Low temperature X-ray powder diffraction proved the absence of phase transitions for $12(2)$ K $\leq T \leq 295(2)$ K. Bright green emission was observed under UV-excitation and assigned to the

$4f^65d^1-4f^7$ transition of divalent europium. Temperature-dependent luminescence absorption and emission, as well as lifetime measurements were carried out on single crystal and powder samples. Surprisingly, only limited concentration quenching was found. Additionally, two emission bands (485 and 510 nm) are observed, whose intensity ratio depends strongly on temperature. In order to explain this behavior for a single Eu²⁺ site, we suggest either a dynamical Jahn–Teller effect in the excited 5d¹ state or emission from both a 4f⁶5d¹ state and a trapped exciton state.

Introduction

For applications as phosphors, luminescent materials showing high quantum efficiencies are essential. Since divalent europium often shows the parity-allowed 4f–5d transition and therefore high emission intensities, it is of great interest in the

production of lighting devices.^[1] Even though luminescence of divalent europium in different host lattices has been studied extensively and a large collection of Eu²⁺ luminescence properties exists,^[2,3] studies of the Eu²⁺ luminescence in hydrides and mixed-anion compounds containing the hydride anion are scarce. However, such studies might be interesting because the Eu²⁺ 4f–5d transition depends strongly on the coordination sphere and the crystal-field strength, and the use of hydride is known to have a large influence on the emission energies.^[4] Lately, Eu²⁺ luminescence was studied in europium(II) hydride fluorides.^[5] However, no studies of Eu²⁺-luminescence properties in mixed-anion hydride chlorides have been carried out so far. Several hydride chlorides with divalent europium as well as with the alkaline-earth metals, such as Eu₂H₃Cl,^[6] EuHCl,^[7] AEHCl ($AE = Ca, Sr$ and Ba),^[8] Sr₇H₁₂Cl₂,^[9] and Ba₂H₃Cl^[10] are known. In order to study the luminescence properties of divalent europium in a mixed-anion hydride chloride, we have chosen the well-known EuHCl, which crystallizes in the PbFCl-type structure (tetragonal, space group: $P4/nmm$)^[11] and shows very weak antiferromagnetic interactions at low temperatures.^[7] Luminescence of Eu²⁺-doped materials crystallizing with the PbFCl-type structure, mainly BaFX:Eu²⁺ ($X = Cl$ and Br),^[12] has attracted much interest, especially in the field of storage phosphors, but fluoride was never substituted by hydride during these investigations.

Results and Discussion

EuHCl crystallizes as olive-green square platelets with PbFCl- (= matlockite-) type structure in the tetragonal space

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group type $P4/nmm$ (no. 129, Table 1 and Table 2). The crystallographically unique Eu^{2+} cations are coordinated by four hydride and five chloride anions building a square antiprism that is capped by one of the five chloride anions. There are two different Eu–Cl distances, four shorter ones with 305 pm from the Eu^{2+} cations to the four Cl^- anions of the square and one slightly larger distance with 308 pm to the capping Cl^- anion. The H^- anions are coordinated tetrahedrally by the Eu^{2+} cations and the Cl^- anions are surrounded by five Eu^{2+} cations forming a quadratic pyramid. From this point of view the matlockite-type structure of EuHCl can be formulated as $\infty\{(\text{Eu}^{2+})(\text{H}^-)_{4/4}(\text{Cl}^-)_{5/5}\}$. On the other hand H^- -centered $(\text{Eu}^{2+})_4$ tetrahedra are present, which share four edges according to $\infty\{[(\text{H}^-)(\text{Eu}^{2+})_{4/4}]^+\}$ (see Table 3 for H–Eu distances and Eu–H–Eu angles, which are in the typical range for europium with coordination number nine.^[14,15]). These cationic layers are held together and charge-balanced by double layers of Cl^- anions which are half as dense. The coordination of the different ions can be seen in Figure 1 that shows the crystal structure of EuHCl . Selected interatomic distances in the crystal structure of EuHCl are listed in Table 3.

Table 1. Crystal data and structure refinement of EuHCl .

| Chemical formula | EuHCl |
|---|-------------------------------|
| Space group type | $P4/nmm$ (no. 129) |
| Crystal system | tetragonal |
| a /pm | 406.58(3) |
| b /pm | 693.12(5) |
| c/a | 1.705 |
| Z | 2 |
| ρ_{calc} /g·cm ⁻³ | 5.461 |
| Molar volume, V_m /cm ⁻³ ·mol ⁻¹ | 34.50 |
| Diffractometer | κ -CCD (Bruker-Nonius) |
| $F(000)$ | 162 |
| Range in $\pm h, \pm k, \pm l$ | 7, 7, 12 |
| μ /mm ⁻¹ | 28.07 |
| Total number of reflections | 4682 |
| Number of unique reflections | 254 |
| $R_{\text{int}}, R_{\sigma}$ | 0.083, 0.020 |
| Structure solution and refinement | SHELX-97 ^[13] |
| R_1, wR_2 | 0.027, 0.071 |
| Goodness of Fit | 1.102 |
| Residual electron densities /e ⁻ Å ⁻³ | 2.03, -1.89 |
| CSD number | 428162 |

Table 2. Fractional atomic coordinates, anisotropic and equivalent isotropic displacement parameters for EuHCl ($U_{22} = U_{11}$ and $U_{12} = U_{13} = U_{23} = 0$ for all atoms due to the space group symmetry).

| Atom | Site | x/a | y/b | z/c | U_{11} /pm ² | U_{33} /pm ² | U_{eq}^{a} /pm ² |
|------|------|-------|-------|------------|---------------------------|---------------------------|---|
| Eu | 2c | 1/4 | 1/4 | 0.20363(4) | 109(2) | 127(2) | 115(2) |
| H | 2a | 3/4 | 1/4 | 0 | – | – | 532 ^b |
| Cl | 2c | 1/4 | 1/4 | 0.6485(3) | 156(4) | 145(7) | 152(3) |

a) $U_{\text{eq}} = 1/3(U_{11} + U_{22} + U_{33})$, b) The isotropic displacement factor of the hydrogen atom was constrained by a factor of 3.5 to the equivalent displacement factor of chlorine as the last non-metal atom being unconstrained.

According to Rietveld analysis based on X-ray diffraction data powder samples consist of EuHCl (93.5(3) wt.-%) and secondary phases Eu_2O_3 (4.5(3) wt.-%) and EuH_2 (1.9(1) wt.-%). The impurity phases are not expected to disturb

Table 3. Selected interatomic distances (d /pm) and angles (\angle /°) in the crystal structure of EuHCl (estimated standard uncertainties 0.1 and 0.2 pm for Eu–Cl and Eu–Cl', respectively, and < 0.1 for all other values).

| | | | |
|--------|------------|---------|------------|
| Eu–H | 247.5 (4×) | Eu⋯Eu | 402.9 (4×) |
| Eu–Cl | 305.2 (4×) | Eu⋯Eu | 406.6 (4×) |
| Eu–Cl' | 308.3 (1×) | Eu–H–Eu | 109.0 (4×) |
| H⋯H | 287.5 (4×) | Eu–H–Eu | 110.5 (2×) |

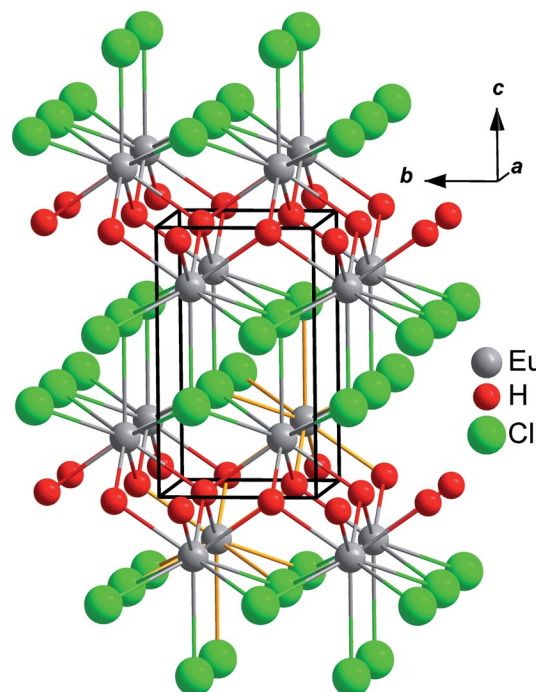


Figure 1. View at the crystal structure of EuHCl approximately along [100].

the luminescence measurements. Refinement of the lattice parameters yielded $a = 406.45(4)$ and $692.37(9)$ pm for EuHCl , in good agreement with single crystal data (Table 1). The microstructural parameters of EuHCl , $L_{\text{Vol-IB}} = 245(17)$ nm and $L_{\text{Vol-FWHM}} = 326(21)$ nm as well as a microstrain ϵ_0 of 0.011(1) were obtained. Cooling to 12(2) K leads to a decrease in the unit cell volume by 1% without any sign of a phase transition (Supporting Information).

EuHCl shows a bright light green emission under UV light (Figure 2). At room temperature, a broad-band emission as it is typical for a d–f transition with a maximum at around 510 nm is observed (Figure 3 and Figure 4). For comparison, the emission maxima of EuFCl ^[16] and EuFBr ^[17] are known to be 417 nm and 393 nm, respectively. Thus, the substitution of fluoride by hydride leads to a red shift of the emission of about 100 nm. This can be explained by the strong nephelauxetic effect of the hydride ligand,^[14,51] which leads to a shift of the barycenter of the Eu^{2+} 5d levels to lower energies.

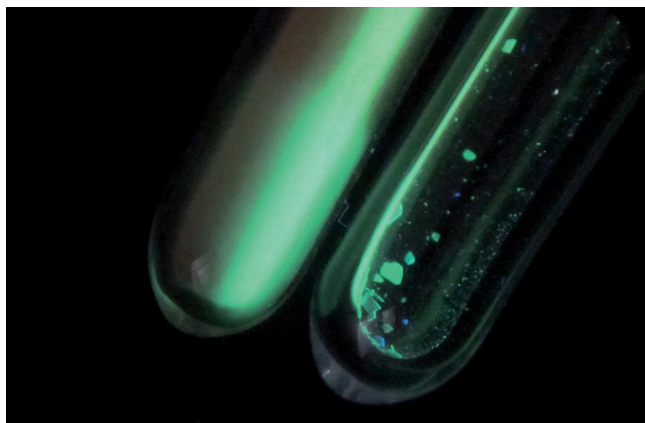


Figure 2. EuHCl powder (left) and single crystals (right) under UV light.

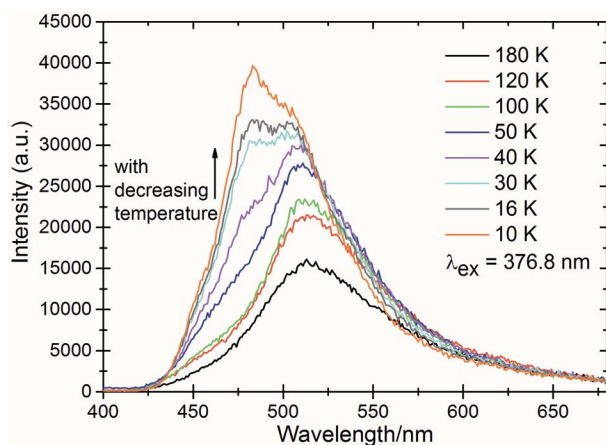


Figure 3. Temperature-dependent emission spectra of EuHCl single crystals (excitation at $\lambda = 376.8$ nm).

As is often observed, the emission intensities increase with decreasing temperature (Figure 3). However, below approximately 50 K a blue shift of the emission band and a second peak maximum at approximately 485 nm are observed. This behavior is found in the spectra of both the single crystals as well as the powder samples.

Since both emission maxima are obtained under the same excitation wavelength and only one crystallographic lattice site (2c) exists for Eu^{2+} (Table 2), the existence of two different luminescence centers is unlikely. Two distinct crystallographic sites might arise in case of a phase transformation of EuHCl from the tetragonal matlockite-type structure of PbFCl e.g. into the orthorhombic cotunnite-type structure of PbCl_2 as already observed for LaSeCl ,^[18] LaTeCl and CeTeCl .^[19] Such a phase transition could be ruled out for EuHCl by X-ray powder diffraction for temperatures $12(2) \text{ K} \leq T \leq 295(2) \text{ K}$ (vide supra and Supporting Information). The observation of temperature-dependent emission maxima for one luminescence center has previously been observed for systems where a Jahn–Teller distortion lifts the degeneracy (e. g. s^2 cations such as Sb^{3+} ,^[20] where a dynamical Jahn–Teller effect leads to a distortion of the adiabatic potential energy surface of the excited state).

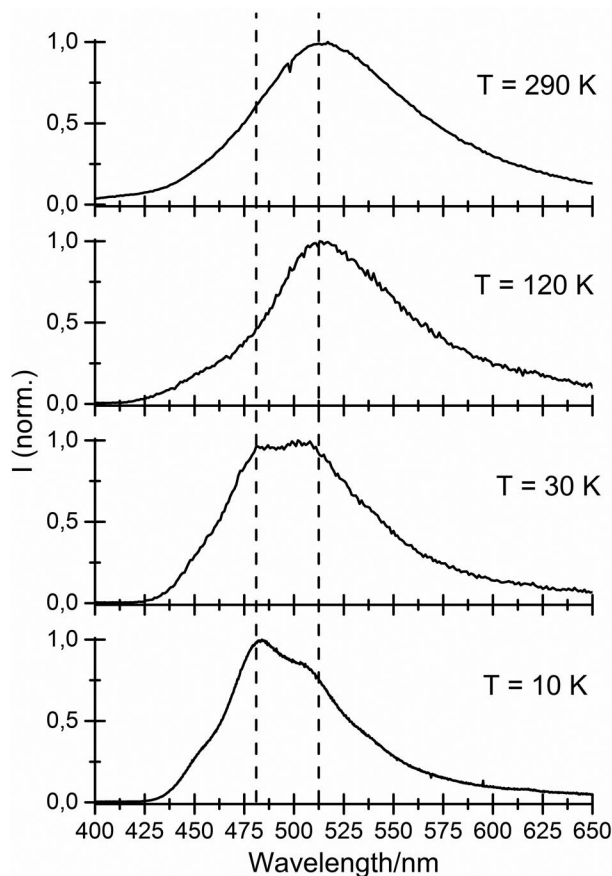


Figure 4. Emission spectra of the EuHCl single crystals at different temperatures (excitation at $\lambda = 376.8$ nm).

Also in d^1 systems such as $\text{Al}_2\text{O}_3:\text{Ti}^{3+}$ ^[21] Jahn–Teller distortion of the ground and excited state has been reported, leading to spectra different from those predicted by the crystal-field theory. For $4f5d$ states of lanthanides a Jahn–Teller distortion has been suggested, with a small (75 cm^{-1}) Jahn–Teller stabilization energy.^[22] Normalized emission spectra of the single crystals for different temperatures are shown in Figure 4.

We propose that due to the considerably stronger nephelauxetic effect of hydride compared to fluoride anions, a shortening of the interatomic Eu–H distances as well as an elongation of the Eu–Cl distances in the excited $\text{Eu}^{2+} 5d^1$ state might be energetically favored giving rise to a Jahn–Teller distortion in the $5d$ state. Although a redshifted emission from a distorted in $4f^65d^1$ state has been suggested for Eu^{2+} ,^[23] convincing experimental evidence for emission from a Jahn–Teller distorted $4f^65d^1$ state is still lacking, making the Jahn–Teller explanation for the observation of two Eu^{2+} emission bands speculative.

Alternatively, a single Eu^{2+} center may give rise to two emission bands due to the presence of two almost resonant excited states. In addition to ‘normal’ $4f-5d$ emission also anomalous Eu^{2+} emission can be observed from a europium trapped exciton state. There are a few examples where the two states are very close in energy but due to the difference in relaxation (parabola off-set in the configurational coordinate diagram) the emission maxima are at different wave-

lengths.^[24,25] A temperature induced cross-over from ‘normal’ to ‘anomalous’ Eu^{2+} emission has been previously observed, with both emissions present in an intermediate temperature regime, giving rise to two emission bands for a single Eu^{2+} site. Further research is required to distinguish between different possible explanations for the two emission bands. The shoulder around 450 nm in the emission spectra (Figure 4) probably belongs to Eu_4OCl_6 .^[26,27] This compound often occurs during synthesis in very small quantities not detectable by X-ray diffraction, but visible in the emission spectra.

Schematic configurational coordinate diagrams for the above mentioned possibilities are given in the Supporting Information.

The excitation spectra of EuHCl single crystals are shown in Figure 5 for the emissions at 485 and 510 nm. The radiative lifetime of the Eu^{2+} emission in the single crystals is about 250 ns at room temperature for the emission at 510 nm and 450 ns for the 510 nm emission at 10 K, respectively. Interestingly enough, even though EuHCl is a fully-concentrated system, the bulk samples show a really bright emission and only limited concentration quenching seems to take place. Based on the lifetime, a quantum yield of 30–50% can be estimated since the radiative lifetime for 500 nm Eu^{2+} emission in a host with a relatively large refractive index is typically 500–750 ns.^[4] Such limited concentration quenching has previously also been observed for Eu_4OCl_6 .^[27] The absence of concentration quenching in fully concentrated systems is usually only observed for solid-state materials, where energy transfer is hampered by the large distance between the activator ions^[28] or in low dimensional systems.^[29,30] However, in EuHCl the shortest $\text{Eu}\cdots\text{Eu}$ separations are 403 and 407 pm between and within the europium layers perpendicular to crystallographic c (Figure 1), which are not especially large interatomic distances. Thus, the PbFCl -type structure seems to be a good candidate for avoiding pronounced concentration-quenching effects.

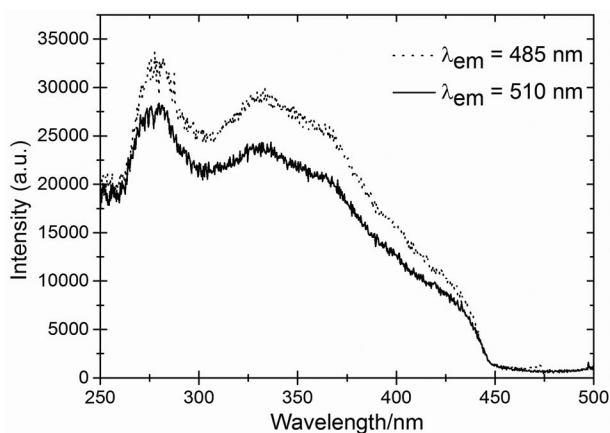


Figure 5. Excitation spectra of EuHCl single crystals at 10 K (emission at $\lambda = 485$ and 510 nm).

Conclusions

Eu^{2+} emission was studied in a mixed-anion hydride chloride system. The efficient green broad-band emission of PbFCl -

type EuHCl was assigned to the transition between the Eu^{2+} $4f^65d^1$ and $4f^7$ levels, which is both parity- and dipole-allowed. A red shift of the emission compared to the isostructural fluoride derivatives EuFCl and EuFBr is observed and is explained by the strong nephelauxetic effect of the hydride anions. The observation of two emission bands for a single Eu^{2+} site is unexpected. Possible explanations are a Jahn–Teller distortion or a close proximity in energy for the $4f^65d^1$ state and the Eu-trapped exciton state. Surprisingly, only limited concentration quenching was observed. The present results help understanding the luminescence properties of mixed-anion hydride systems and might encourage further studies on other mixed-anion hydride halides.

Experimental Section

Sample Preparation

Due to air- and moisture-sensitivity of EuHCl , all product samples were handled in an argon-filled glove box (M. Braun, Garching, Germany). Olive-green single crystals of EuHCl emerged from the reaction of europium powder (Eu: ChemPur, 99.9%), sodium hydride (NaH: Aldrich, 95%) and sodium chloride (NaCl: Merck, 99.99%) in a molar ratio of 1:1:1. The starting material mixtures were filled into niobium capsules that were arc-welded under helium atmosphere. The niobium capsules were sealed into evacuated fused silica ampoules and these reaction containers were heated to 900 °C within 7 h. This temperature was held constant for 13 h, then the furnace was turned off and allowed to cool down to room temperature. Alternatively, powder samples of EuHCl were prepared via the solid-state reaction of europium dihydride (EuH_2) and europium dichloride (EuCl_2 ; Sigma–Aldrich, 99.99%) at 480 °C under 120 bar hydrogen pressure (H_2 : Praxair, 99.9%) in an autoclave (hydrogen resistant Nicrofer® 5219 alloy, Inconel 718, reaction time: 5 d). EuH_2 was obtained via hydrogenation of surface-cleaned europium metal (Alfa Aesar, 99.9%) at 300 °C and 50 bar hydrogen gas pressure in an autoclave (vide supra).

X-ray Single Crystal and Powder Diffraction

Single-crystal intensity data from X-ray diffraction were collected at room temperature by using a κ -CCD diffractometer (Bruker-Nonius, Delft, Netherlands) with graphite-monochromatized $\text{Mo-K}\alpha$ radiation ($\lambda = 71.07$ pm). The structure solution and parameter refinement (full-matrix least-squares against F^2) were carried out with the SHELX-97^[13] software package. Numerical absorption correction using the program HABITUS^[31] was applied. The structure was solved by direct methods with anisotropic displacement factors for both non-hydrogen atoms. The corresponding results can be found in Table 1. Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-428162. X-ray powder diffraction data were collected with a Bruker D8 Advance with a Lynxeye detector, focusing Bragg–Brentano geometry and a fine focus X-ray tube ($\text{Cu-K}\alpha_{1,2}$ radiation) in the diffraction range $10 \leq 2\theta \leq 110^\circ$ and a data collection time of 60 minutes. Due to moisture- and air- sensitivity, the samples were enclosed between kapton foils in apiezon grease. Low temperature X-ray powder diffraction data down to 12(2) K for a sample enclosed between aluminium foils under vacuum were collected on a Huber

Günier G670 camera with image plate system using Cu- $K_{\alpha 1}$ radiation. The crystal structure was refined using TOPAS 4.2 (Bruker AXS, Karlsruhe, Germany)^[32] and the fundamental parameter approach.^[33] The instrumental function was determined empirically by means of a reference scan of LaB₆.

Luminescence Measurements

Due to moisture- and air-sensitivity, all EuHCl samples were enclosed in sealed silica tubes of 0.5–1.0 cm diameter for all photoluminescence measurements. Photoluminescence emission and absorption spectra were measured on an Edinburgh Instruments FLS920 spectrofluorometer. A 450 W xenon lamp and a ps 376.8 nm Edinburgh pulsed diode LASER were used for sample excitation, a double monochromator according to Czerny-Turner (300 mm focal length) for the excitation beam, a monochromator (500 nm focal length) and a photomultiplier tube R928P (Hamamatsu) for UV/Vis detection. For UV/Vis detection of the decay curves, a Hamamatsu H7422–02 photomultiplier tube was used. Low-temperature measurements were carried out using an Oxford liquid helium coldfinger cryostat. Samples were attached to the coldfinger using high-purity silver paint in order to facilitate heat transfer. Spectra were corrected for lamp intensity and photomultiplier sensitivity. Luminescence decay curves were recorded under pulsed excitation with an Edinburgh 376.8 nm pulsed diode laser with approx. 65 ps pulses. A single exponential function was used for analysis of the luminescence decay curves and the small deviation from single exponential (fast initial decay) within the higher temperature range was neglected. The presence of small amounts of EuH₂,^[34] Eu₂O₃,^[35] Eu₄OCl₆,^[26] or Eu₂H₃Cl^[6] in the powder samples could not be completely excluded. We have taken care not to use samples containing Eu₄OCl₆ for our luminescence measurements, since this europium(II) oxide chloride is known to emit in the blue.^[27] Errors due to the presence of small amounts of EuH₂ or Eu₂O₃ are not expected, since EuH₂ does not emit owing to its small band gap and Eu₂O₃ is known to show only a weak emission in the red at 616 nm.^[36] A comparison of the powder spectra with those of the single crystals showed the aforementioned small impurities in the powder samples.

Supporting Information (see footnote on the first page of this article): Schematic configurational coordinate diagrams for the above mentioned possibilities.

Acknowledgments

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