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Novel and Easy Access to Highly Luminescent Eu and Tb Doped Ultrasmall CaF₂, SrF₂ and BaF₂ Nanoparticles – Structure and Luminescence

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Abstract

A universal fast and easy access at room temperature to transparent sols of nanoscopic Eu^{3+} and Tb^{3+} doped CaF_2 , SrF_2 and BaF_2 particles via the fluorolytic sol-gel synthesis route in is presented. Monodisperse quasi-spherical nanoparticles with sizes of 3–20 nm are obtained with up to 40% rare earth doping showing red or green luminescence. Beginning luminescence quenching effects are only observed for the highest content, which demonstrates the unique and outstanding properties of these materials. From CaF_2 :Eu10 via SrF_2 :Eu10 to BaF_2 :Eu10 a steady increase of luminescence intensity and lifetime occurs by a factor of ≈ 2 , photoluminescence quantum yield increases by 29 to 35% due to lower phonon energy of the matrix.

The fast formation process of the particles within fractions of seconds is clearly visualized by exploiting appropriate luminescence processes during the synthesis. Multiply doped particles are also available by this method. Fine tuning of luminescence properties is achieved by variation of the Ca-to-Sr ratio. Co-doping with Ce³⁺ and Tb³⁺ results in a huge increase (>50 times) of the green luminescence intensity due to energy transfer Ce³⁺ \rightarrow Tb³⁺. In this case, the luminescence intensity is higher for the CaF₂ than for SrF₂, due to lower spatial distance of the rare earth ions.

1 Introduction

Luminescence materials based on rare earth ions have gained increasing interest in the last 20 years. Alkaline earth metal fluorides are excellent host materials for rare earth metal ions. CaF₂, SrF₂ and BaF₂ form solid solutions Ca/Sr/Ba_{1-x}Ln_xF_{2+x} ($x = 0...\approx 0.45$, Ln = Y, La...Lu) with a fluorite crystal structure over a broad range up to 40–50 mol% of rare earth doping.¹ The charge compensating additional fluoride ions are situated in the octahedral holes of the fluorite structure and form different types of defect clusters.²⁻⁴ Such rare earth doped alkaline earth metal fluorides raised strong interest in many different areas of application such as surface coatings,⁵ dental applications⁶, biolabelling⁷⁻⁹, lamps, displays¹⁰ and photovoltaic devices¹¹. Their outstanding luminescence properties are caused by their low phonon energies, compared to oxidic matrices, which minimizes non-radiative relaxations.¹² The phonon energies have been determined to e.g. 466 cm⁻¹ for CaF₂, 366 cm⁻¹ for SrF₂, and 319 cm⁻¹ for BaF₂ in contrast to NaYF₄, which is 350 cm⁻¹. ^{13, 14} The latter compound exists in two different crystal structures α and β . β -NaYF₄ is the currently most used matrix for photon upconversion systems, basically

because of its high quantum efficiency.¹⁵⁻¹⁷ Recently it was found that rare earth doped CaF₂ could be equally efficient like NaYF₄, and in some cases even better.¹⁸ Furthermore, alkaline earth metal fluoride matrices have distinct advantages with respect to NaYF₄. Thus, the separation of other rare earth metals from the commercial yttrium precursors required for NaYF₄ synthesis is costly and elaborate. The presence of other rare earth metals as matrix impurities should be absolutely avoided, because they can cause an unwanted change in the colour and efficiency of the luminescence, especially in photon upconversion systems.¹⁹ Rare earth free matrices like CaF₂ and SrF₂ elegantly avoid this challenge.

There are several reports about the synthesis and characterization of rare earth metal doped CaF_2 and SrF_2 nanoparticles,^{5-11, 18, 20, 21} but only a few for or BaF_2 .²²⁻²⁵ The latter has been reported to notoriously result in larger particles and to possess a higher tendency to form agglomerates. A universal method capable of synthesizing all three compounds under equal conditions is still missing.

It is often stated that luminescence yields and lifetimes should increase from CaF_2 to BaF_2 matrix.^{16, 17} Surprisingly, there is no direct experimental proof for this claim. So far, only one group reported on the synthesis and luminescence quantum yields of doped particles from all three matrices.²⁶ Mudring and co-workers used CaF_2 , SrF_2 and BaF_2 from a synthesis in ionic liquids co-doped with Gd^{3+} and Eu^{3+} for *quantum splitting*. The group reported an increase of the quantum yield from CaF_2 to SrF_2 , but then a decrease for the BaF_2 matrix. It shall be kept in mind that this is a multiple centre energy transfer process, and therefore, the observed trends may deviate from single centre luminescence.

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Another important aspect influencing the luminescence properties of rare earth doped alkaline earth metal fluoride nanoparticles is the use of additives during the synthesis. In general, every nanoparticle in colloidal solution needs some kind of stabilization. In the ideal case, the solvent is already sufficient. But often additives are necessary for the stabilization of the particles, in order to make them compatible for other applications, as has been shown e.g. for MgF₂ and AlF₃ nanoparticles in transparent acrylate composites.^{27, 28} It is known that the emission lines of Eu³⁺ are hypersensitive to the local surrounding.²⁹ Hence, in nanoparticles, which possess a large surface area, the additives should influence the luminescence.^{8, 30, 31}

In this work, we present a universal fast and easy access to transparent sols of highly luminescent nanoscopic rare earth doped CaF₂, SrF₂ and BaF₂ particles via the fluorolytic sol-gel synthesis route with rare earth contents up to 40%. The focus is set on SrF₂ systems. Not only is the synthesis of singly doped particles possible at room temperature, but also of systems containing more than two metal cations. Litre amounts of colloidal solutions are available, resulting in several hundred grams of materials after spray drying. This is an important premise for any further application. The synthesis yields fully transparent colloidal solutions, i.e. sols, for which no further purification, centrifugation or redispersion step is necessary.

Methanol and ethylene glycol are applied as solvents. Both solvents have advantages for different applications or analytical investigations. Methanol has a low boiling point (65°C), which is required for dip coating processes, and it makes TEM measurements more convenient, but the synthesis requires additives for stabilization of the particles. In ethylene glycol, no additional stabilizer is needed, which would influence the luminescence properties.

Luminescence lifetime and intensity tuning of Eu^{3+} and Tb^{3+} doped CaF_2 , SrF_2 and BaF_2 particles is presented. Fine tuning is achieved by adjusting the Ca/Sr ratio in doped (Ca,Sr)F₂ solid solutions. The capability of energy transfer between the rare earth ions on multiply doped systems is demonstrated for sensitization of the green luminescence of Tb^{3+} by co-doping with Ce^{3+} . This allows directly following the particle formation optically during the synthesis process.

2 **Experimental**

2.1 Sample Synthesis

2.1.1 Chemicals

Europium oxide (Eu₂O₃, 99.9%, Sigma Aldrich), terbium oxide (Tb₂O₃, 99.9%, Sigma Aldrich), erbium oxide (Er₂O₃, 99.9%, Sigma Aldrich), ytterbium oxide (Yb₂O₃, 99.9%, Sigma Aldrich), calcium lactate hydrate (Ca(OLac)₂·5H₂O, AppliChem, OLac⁻ = CH₃CHOHCOO⁻), strontium lactate (Sr(OLac)₂·*x*H₂O, 98%, Dr. Paul Lohmann), aluminium isopropoxide (Al(OCH(CH₃)₂)₃), 98% Sigma Aldrich), ethylene glycol (99% Sigma Aldrich) and dehydrated methanol (99.8% Sigma Aldrich) were used. Trifluoroacetic acid (TFA) was obtained from Roth and Fluka Analytical.

Barium lactate (Ba(OLac)₂·xH₂O) was synthesized by dissolving barium carbonate in aqueous lactic acid followed by evaporation of the solvent. Calcium and barium lactate were dehydrated in vacuum for 5 h at 120°C. Rare earth metal acetates $RE(OAc)_3$ were obtained by reflux of the respective rare earth metal oxides with 12 equivalents of 50% aqueous acetic acid. The products were dried under vacuum for 3 h at 150 °C to obtain the water-free salts. Remaining water in Ca, Sr and Ba lactates was analysed by thermogravimetry (Ca 0.2; Sr 0.8; Ba 0.9).

HF gas bottle was obtained from Solvay Fluor. Methanolic HF solution was formed by dissolution of HF gas in water-free methanol provided in a FEP bottle using argon as carrier gas. The bottle was furnished with a Teflon screw cap with three openings for handling under argon. Tubes were made of stainless steel and PTFE. The HF gas bottle was heated up to 60°C to ensure a steady flow of HF. The FEP bottle containing the methanol was cooled with ice. The final HF solution in methanol was stored under argon and the concentration was determined by titration with NaOH using phenolphthalein as indicator.

CAUTION! HF is a hazardous agent and has to be used under restricted conditions only.

2.1.2 Labelling shortcuts

The rare earth-doped strontium fluoride particles will be henceforth labelled as $AEF_2:REx$ (AE = Ca, Sr, Ba; RE = Y, La...Lu; x = amount of rare earth doping in mol% referring to the total metal amount). Hence, SrF_2:Eu10 = Sr_{0.9}Eu_{0.1}F_{2.1}, CaF_2:Tb20 = Ca_{0.8}Tb_{0.2}F_{2.2}, SrF_2:Ce5,Tb10 = Sr_{0.85}Ce_{0.05}Tb_{0.10}F_{2.15}, SrF₂:Yb10,Er2 = Sr_{0.88}Yb_{0.10}Er_{0.02}F_{2.12} etc. For the compounds containing both Ca and Sr, a parameter $\chi_C \sim$ "Ca fraction of alkaline earth metal content" is defined as $\chi_C = \frac{n_{Ca}}{(n_{Ca} + n_{Sr})}$. For undoped Ca_xSr_{1-x}F₂, it is $\chi_C = x$. For the shortcuts, exact composition and χ_C values of the rare earth doped (Ca,Sr)F₂ samples cf. SI Table S1.

2.1.3 Sol-Gel Synthesis (1) (in ethylene glycol, no additives)

The preparation is described exemplarily for the synthesis of 20 mL of 0.2 M SrF₂:Eu10: $Eu(OAc)_3$ (131.6 mg, 0.40 mmol) and Sr(OLac)₂·0.8H₂O (785.5 mg, 3.60 mmol) were dissolved in

20 mL *ethylene glycol*. Then, 0.51 mL (4.20 mmol) of a methanolic HF solution (16.38 M) was added under vigorous stirring. After some minutes a transparent sol was received.

In the case of BaF_2 , either 15 mol% of $Al(O'Pr)_3$ or 5 mol% of benzoic acid are added directly after fluorination.

2.1.4 Sol-Gel Synthesis (2) (in methanol, additive Al(OⁱPr)₃)

The preparation is described exemplarily for the synthesis of 20 mL of 0.2 M SrF₂:Eu10: Eu(OAc)₃ (131.6 mg, 0.40 mmol) and Sr(OLac)₂·0.8H₂O (785.5 mg, 3.60 mmol) were dissolved in 20 mL *methanol* by addition of TFA (0.1 mL \approx 13 µmol). Then 0.51 mL (4.20 mmol) of a methanolic HF solution (16.38 M) was added under vigorous stirring, resulting in the formation of a turbid sol. Al(O'Pr)₃ (12.3 mg, 60 µmol =15 mol% ref. to Sr+Eu) was added, and the mixture was stirred overnight. A transparent sol was received in the course of one day.

2.1.5 Post-treatment

Some samples from synthesis 2 were dried in vacuum and annealed in an open porcelain crucible at 400°C for 3 h or at 700°C for 2 h (heating rate 10 K/min).

2.2 Characterization

2.2.1 XRD

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X-ray diffractograms of powders were obtained with a Seiffert 3003TT diffractometer (Seiffert & Co. Freiberg, Germany, Bragg-Brentano geometry) using Cu K α (1.542 Å) radiation. The 2 ϑ step width was 0.05°. Peak maxima and widths were recalculated to Cu K α_1 (1.5406 Å) using Rachinger correction. The size of the coherent scattering region was calculated using the Debye-Scherrer equation.

2.2.2 NMR

Both ¹⁹F MAS and static NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (Larmor frequency: $v_{19F} = 376.4$ MHz) using a 2.5mm double-bearing magic angle spinning (MAS) probe (Bruker Biospin) for MAS experiments and a 4 mm probe for static experiments. ¹⁹F MAS NMR spectra were made with a $\pi/2$ pulse duration of 3.6 µs, a spectrum width of 400 kHz, a recycle delay of 5 s and accumulation number of 64. Static ¹⁹F spectra were recorded with 1024 accumulations and a 90 ° pulse length of 4 µs. ¹⁹F chemical shifts are referenced to CCl₃F. Existent background signals of ¹⁹F were suppressed with the application of a phase- cycled depth pulse sequence according to Cory and Ritchey. ³²

2.2.3 Dynamic light scattering (DLS)

DLS measurements were performed by using a Malvern Zetasizer Nano ZS instrument.

2.2.4 Transmission electron microscopy (TEM)

TEM analysis has been carried out using a Philips CM200 LaB_6 microscope operating at 200 kV. Sols were diluted with methanol to a concentration of 10^{-4} M prior to the measurement. A few drops of the solution containing the nanoparticles were deposited on a carbon-coated copper grid and left to dry for 1 hour prior to the inspection.

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2.3 Luminescence measurements

Luminescence emission and excitation spectra as well as lifetimes were recorded with a FluoroMax-4P from Horiba Jobin Yvon in 10 mm quartz cells. Luminescence lifetimes were recorded in a single photon counting mode using the TCSPC accessory with a collecting time up to 88 ms.

Fitting the luminescence lifetimes with a single monoexponential decay was not possible. This is typical for nanoparticles, because luminescence centres in the middle or near the surface of the particle have significantly different decay behaviour.^{33, 34} Instead, lifetimes t_1 were fitted using a q-exponential function $A_0e_q(-t/t_1)$ with $e_q(x) = [1 + (1 - q)x]^{1/(1-q)}$. This function is a stretched exponential function, which is capable to fit the luminescence decay of statistically distributed lifetimes. The parameter q represents the degree of asymmetry or skewness of the distribution of lifetimes. q was allowed to fit between 1.01 ... 1.30. Higher values than 1.30 have no physical sense, and for $q \rightarrow 1$ this function approaches the normal exponential function e^x .

Absorption spectra were obtained on a Specord 210 PLUS from Analytik Jena in 10 and 50 mm quartz cells. Because of the high optical transparency of the suspensions, the determination of relative photoluminescence quantum yields Φ_{PL} employing organic dyes with a known Φ_{PL} as standards is a viable approach^{35, 36} and was performed here with Coumarin 102 in ethanol ($\Phi_{PL} = 0.76$), quinine sulphate in 0.105 M HClO₄ ($\Phi_{PL} = 0.61$) and terphenyl in cyclohexane ($\Phi_{PL} = 0.93$) as the standards for the Eu-, Tb- and Ce/Tb-doped particles, respectively.^{37, 38} The uncertainty of measurement amounts to ±10%.

3 Results and discussion

3.1 Structure and morphology of singly doped SrF₂ particles

The synthesis of 0.2 M sols of Eu and Tb doped SrF_2 sols in ethylene glycol or methanol is straightforward. Transparent and water-clear sols are obtained at room temperature, and batches of up to several litres can be prepared easily (Figure 1). Sols in ethylene glycol become transparent nearly immediately, sols in methanol only cleared off after one day, when 15 mol% of $Al(O'Pr)_3$ were added after fluorination. Under excitation with a handheld UV lamp (366 mm), these sols show red (Eu³⁺) or green (Tb³⁺) luminescence. The formation of the particles during the fluorination is very fast, and takes place within fractions of seconds (see Section 4 for further details).

Dynamic light scattering (DLS) measurements of the transparent sols revealed particle sizes of \approx 3 nm for the low doping range, i.e., 1-2 mol% of Eu³⁺ and Tb³⁺, while higher amounts of doping (15 mol%) lead to an increase in size of up to 24 nm (Figure 2C and SI Table S2).



Figure 1. Photographs of 0.2 M sol. Left column: SrF_2 :Tb10 +15% Al(O'Pr)₃ in methanol (200 ml batch). Right column: SrF_2 :Eu10 in ethylene glycol (500 ml batch). Upper row: room light, lower row: excited at 366 nm with a UV lamp.



Figure 2. TEM and EDX investigations of (A) SrF_2 :Eu10 and (B) SrF_2 :Tb10 (methanol +15 mol% Al(O'Pr)₃). (C) DLS of 0.2 M SrF_2 :Eu10 and SrF_2 :Tb10 in methanol +15 mol% Al(O'Pr)₃ (sy1) and in ethylene glycol without additive (sy2). (D) High resolution TEM image of SrF_2 :Eu10 (methanol +15 mol% Al(O'Pr)₃). The intense EDX peak at 8 keV is due to the copper grid sample holder.

Figure 2A and B show the TEM images of the as-synthesized SrF_2 :Eu10 and SrF_2 :Tb10 from methanol (synthesis 2). All particles have a regular, elliptical shape and a monodisperse size of about 5–6 nm (Figure 2D). The obtained results correlate with the DLS measurement of SrF_2 :Tb10 (5 nm). The apparent particle size of 24 nm for SrF_2 :Eu10 could thus be due to small agglomerates formed in the sol, which cannot be resolved by DLS. Additional EDX analysis of the particles confirmed the SrF_2 scaffold and Eu^{3+} doping, in line with results by XRD. EDX also shows that Al and O stemming from the stabilizer $Al(O/Pr)_3$ used are still present. This fact clearly is a hint for the presence of Al species on the particles.

Powder diffractograms of the dried sols of SrF_2 :Eu10 prepared by synthesis 2 in methanol with and without $Al(O^{i}Pr)_3$ as an additive annealed at different temperatures (dried powders) show the typical reflections of nanoscaled cubic SrF_2 (cf. SI Figure S1). All diffractograms can be assigned to the cubic space group ($Fm\overline{3}m$). Successful introduction of Eu³⁺ into the SrF_2 lattice changes the cubic lattice parameter from 5.80 Å for pure SrF_2 to 5.77 Å for SrF_2 :Eu10. This proves the formation of the solid solution $Sr_{0.9}Eu_{0.1}F_{2.1}$. In the case of Eu^{3+} and Tb^{3+} doped CaF_2 nanoparticles the lattice parameter increases.¹²

The average crystallite diameter of pure SrF_2 (synthesis 2) annealed at 400°C for 3 h is 59 nm. The samples with 10 mol% of Eu^{3+} exhibit consistently smaller crystallite sizes, namely 20 nm (400°C) and 33 nm (700°C) for SrF_2 :Eu10 + 15% Al(OⁱPr)₃. This reduction in crystallite size can be due to the dopant limiting the crystal growth during the calcination, or may be also caused by the stabilizer Al(OⁱPr)₃ forming a thin layer of hydrolysed species like Al(OH)₃, AlO(OH) and Al₂O₃ on the particle surface. Such surface species have a different phase structure than the cubic SrF_2 :Eu10, hindering the thermally induced crystal growth of the cubic phase. To assess whether one of the processes can be ruled out, a sample of SrF_2 :Eu10 was synthesized without Al(OⁱPr)₃, and then annealed for 2 h at 700°C. The size was determined to 36 nm only, which is significantly smaller than the 59 nm for pure SrF_2 under the same conditions. This suggests that the major effect stems from doping with rare earth metals.

Surprisingly, no reflections of crystalline aluminium compounds are seen in the powder XRD even after annealing at 700°C, although 15 mol% Al species are present. Hence, ¹⁹F MAS NMR was used to characterise those Al species in a pure SrF_2 xerogel (SI Figure S2). Besides the expected ¹⁹F signal of SrF_2 at \approx -88 ppm, two additional broad signals at -146 and -160 ppm are found. These signals can be assigned to different local coordination geometries [AlF_nO_{6-n}] in fluorinated alumina. The signal at -146 ppm hints at n = 2-3 and the signal at -160 ppm at $n = 4-5.^{39}$ These NMR results support the above interpretation that chemical surface reactions between Al(O'Pr)₃ and fluorine indeed take place on the surface of the SrF_2 nanoparticles. These surface modifications presumably prevent agglomeration of the particles in the sol. In case of absence of Al(O'Pr)₃, no such shielding is possible, resulting in less stable suspensions and turbid sols.

The different agglomeration behaviour of the nanoparticles in methanol and ethylene glycol can be attributed to the different properties of the solvents. Ethylene glycol can act as a bidentate ligand, and thus, it will be stronger bound to the particle surface than methanol. Additionally, it is much more hydrophilic than methanol ($pK_{ow} = -0.74$ for methanol, -1.36 for ethylene glycol). Hence, the remaining water in the solvent is better solvated, and is therefore less reactive towards the particle surface. Both effects successfully stabilize the particles in ethylene glycol without any further additives.

3.2 Luminescence of singly doped SrF₂ in different solvents

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In methanol and ethylene glycol, the transparent sols of SrF₂:Tb10 and SrF₂:Eu10 display a bright green and red luminescence, respectively (Figure 1). Although 366 nm is not the ideal excitation wavelength, a strong luminescence can be observed with the naked eye. The PL emission spectra are shown in Figure 3 (for excitation spectra cf. SI Figure S3).



Figure 3. Luminescence emission spectra of 0.2 M sols (A) SrF₂:Eu10 (λ_{ex} = 393 nm) and (B) SrF₂:Tb10 (λ_{ex} = 350 nm). *Red line*: in ethylene glycol without additives, *black line*: in methanol with 15 mol% aluminium isopropoxide.

The emission bands of Eu³⁺ (Figure 3A) can be assigned to the transitions ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ (578 nm), ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ (590 nm, **T1**), ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (611 nm, **T2**), ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ (647 nm) and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ (698 nm). In particular, the Eu³⁺ doped SrF₂ nanoparticles prepared by synthesis 1 and synthesis 2 show significantly different intensity ratios of transitions **T1** and **T2**. For the sol prepared without additives, the intensity of **T2** is less prominent than for the sol prepared with 15 mol% Al(O*i*Pr)₃.

The hypersensitive transition **T2** is only allowed, when the local symmetry of Eu^{3+} has no inversion centre.²⁹ The higher the deviation from centrosymmetry is, the higher is **T2**'s intensity. When placed on a regular Sr²⁺ lattice site, Eu^{3+} has an inversion symmetry (coordination [EuF₈] in a cube), which would increase transition **T1**. For synthesis 1 (no additive) showing a rather weak **T2** band, only a small fraction of Eu^{3+} is thus presumably located in square-antiprismatic coordination in defect clusters^{3, 4} or close to the surface of the particle, in surroundings deviating from inversion symmetry, giving rise to **T2** emission.

When an additive such as $Al(O^{i}Pr)_{3}$ is present, partially or fully hydrolysed Al species are present at the particles surface (cf. ¹⁹F NMR in SI Figure S2), distorting the symmetry of more Eu³⁺ species in the outer particle area, leading to increased contributions from Eu³⁺ ions being located in non-inversion sites, and hence the **T2** emission drastically increases. A similar effect was observed for Eu³⁺ doped CaF₂ by different groups.^{8, 12, 30} In the latter studies, higher **T2** intensities resulted, because of a thin SiO₂ shell or strongly adsorbed carboxylic acids on the surface of the nanoparticles.

The emission spectra of Tb³⁺ (Figure 3B) do not show such an effect. The spectrum consists of the typical emissions ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ (488 nm), ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ (541 nm), ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$ (581 nm) and ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$ (620 nm). For this samples a slightly higher intensity for the SrF₂:Tb10 prepared by synthesis 2 can be found for all transitions. Since Tb³⁺ does not shown any hypersensitive, intense transitions, the intensity ratio of the emission lines does not depend on sample composition.

3.3 Tuning luminescence properties

The synthesis in ethylene glycol does not require the addition of further stabilizers. Therefore, this system is very suitable to investigate the influence of different variations on the

luminescence properties, and was applied for the further luminescence investigations. Especially the influence of additives their selves is investigated, but also the influences of the matrix composition and the dopant concentration. This creates a tool for tuning luminescence properties directly.

3.3.1 Effect of additives

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A wide variety of additives is often used either in the synthesis of nanoparticles, or as posttreatment to make them compatible to further applications.^{8, 9, 27, 28, 30} The emission spectra of Eu^{3+} in Figure 3A show significant differences between the particles with and without $Al(O'Pr)_3$. The use of additives is not limited to $Al(O'Pr)_3$. Typical additives are citric acid, benzoic acid (BA), phenylphosphonic acid (PPA), tetramethyl orthosilicate (TMOS), aluminium isopropoxide $Al(O'Pr)_3$ and titanium isopropoxide $Ti(O'Pr)_4$. To clarify the influence of such additives on the luminescence properties, a sol of pure SrF_2 :Eu10 in ethylene glycol was used. Then the different additives were added, stirred for several days, and the effect on the luminescence was investigated.

Figure 4 shows the emission spectra of neat SrF₂:Eu10 and of the modified sols. For the luminescence lifetimes and **T1**:**T2** intensity ratios cf. SI Table S3. The additives TMOS (e), Al(OⁱPr)₃ (f) and Ti(OⁱPr)₄ (g) all entail a relative increase of transition **T2** (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, 615 nm) with respect to **T1** (${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, 590 nm), which is attributed to the above mentioned binding of (partially) hydrolysed metal alkoxides to the surface, disturbing the local symmetry of Eu³⁺. The strongest increase of **T2** was found for Al(OⁱPr)₃. This spectrum fully resembles that of the synthesis in methanol with Al(OⁱPr)₃. TMOS and Ti(OⁱPr)₄ do not increase the transition **T2** so much. Obviously, they do not bind so strongly to the particles surface, and hence, do not cause a strong disturbance of the local symmetry of Eu³⁺.²⁹



Figure 4. Luminescence emission spectra of 0.2 M SrF₂:Eu10 sols in ethylene glycol with different additives (15 mol%). (a) pure, (b) citric acid, (c) benzoic acid, (d) phenylphosphonic acid, (e) tetramethyl orthosilicate, (f) aluminium isopropoxide, (g) titanium isopropoxide. (λ_{ex} =393 nm) **T1**: ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, **T2**: ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$.

The addition of citric and benzoic acids to the pure SrF_2 :Eu10 nanoparticles has no measurable effect on the luminescence lifetime (cf. SI Table S3). The addition of phenylphosphonic acid or TMOS leads to an increase of the lifetime, $Al(O'Pr)_3$ and $Ti(O'Pr)_4$ to its decrease.

The strong decrease of the luminescence lifetime for Al(O^{*i*}Pr)₃ correlates with the strong increase in **T2**, and the largest asymmetry parameter among the decay fits (cf. SI Table S3). Most probably, hydrolysed Al species bind more strongly to the particles surface than in the case of Si or Ti species. It is known that such partially hydrolysed and fluorinated aluminium alkoxides contain a certain amount of strongly bound alcohol molecules.^{40, 41} Therefore, an effective coupling between the Eu³⁺ centres and the OH group occurs via Al–O clusters, which seems to be much stronger than just by normal solvation of particle surface by the solvent. This effect, which also prevents the formation of agglomerates, amplifies non-radiative relaxation processes, and hence, significantly decreases the luminescence lifetimes.

Contrary, for TMOS the luminescence lifetime increases, although the intensity of the **T2** emission also increases. Most probably, the hydrolysed Si species, i.e. SiO_2 , contain no OH groups, or are not so strongly bound to the particle surface. Thus, non-radiative relaxation into the solvent's OH groups is hindered, resulting in longer lifetimes of the excited state.

3.3.2 Effect of doping rates

It could be expected that the luminescence intensity increases with increasing concentration of luminescence centres, namely Eu^{3+} and Tb^{3+} ions. In contrast, it is often observed that the luminescence intensity decreases above a critical concentration, which is mostly around 10...20%. This is caused by quenching effects due to cross relaxation between neighbouring rare earth ions. This strongly depends on the synthesis route and the distribution of the rare earth ions in the matrix.

For the new synthesis developed here, this was studied by synthesizing a series of SrF_2 nanoparticles containing up to 40 mol% of Eu^{3+} or Tb^{3+} . Clear sols are obtained even with high doping rates (Figure 5 (left)). With increasing contents of rare earth ions, the particle size slightly decreases for Eu^{3+} and slightly increases for Tb^{3+} (Figure 5 (right) and SI Table S4).



Figure 5. Left: Picture of a series of SrF_2 : EuX with X = 0, 0.1, 0.2, 1, 5, 10, 20, 30, 40 (from left to right). (A) at visible light, (B) excited at 366 nm with an UV lamp. Right: DLS particle size of these samples.

The corresponding luminescence spectra and intensities for the Eu³⁺ series are given in Figure 6A. Emission bands are the same as described before (cf. Figure 3A). An increase of the Eu³⁺ content leads to a steady increase in luminescence intensity. Until 10 mol% of doping, the correlation is nearly linear. At Eu³⁺ contents of 20 mol% and higher, the correlation deviates from linearity, most likely because of the local proximity of the Eu³⁺ ions in the matrix, increasing the possibility of cross relaxation. It is important to note that despite a flattening of the correlation, no actual quenching, i.e., a reduction in luminescence yield was found.

This impressively demonstrates the adventure brought about by the new synthesis approach employed here. Menon et al. investigated Eu^{3+} doped CaF_2 particles and already obtained a deviation from the linear increase at 5 mol% of doping and the onset of saturation for doping rates between 15 and 20 mol% ⁸ which cannot be found for our sample till 40 mol% of doping. Additionally, Wang et al. recognized a considerable *decrease* of the luminescence intensity for doping concentrations above 15 mol% for Eu^{3+} doped CaF_2 .⁴²



Figure 6. Luminescence emission spectra of 0.2 M sols SrF_2 :LnX in ethylene glycol with X = 0...40. (A) Ln = Eu (λ_{ex} =393 nm), (B) Ln = Tb (λ_{ex} =350 nm). Inset: integrated emission intensity, solid line: linear fit for the data points with $X \le 10$.

The behaviour of the corresponding Tb³⁺ compounds is slightly different (Figure 6B). Here, a nearly linear correlation is observed until 30 mol% of Tb³⁺. At 40 mol%, then indeed quenching of the luminescence is observed. This correlates with a sudden drop of the luminescence lifetime from 3.43 to 2.41 ms (SI Table S4). Obviously, non-radiative relaxation processes start to increase very rapidly for the Tb³⁺ system above a content of 30 mol%. This is probably caused by a larger difference of the ionic radii of matrix and dopant (Sr²⁺ 1.40 Å; Eu³⁺ 1.206 Å; Tb³⁺ 1.180 Å; all c.n. 8).⁴³ The larger difference between r(Sr²⁺) and r(Tb³⁺) may cause problems in forming proper solid solutions for higher doping ratios and increase the creation of Tb rich domains.

The high intrinsic luminescence intensity and the lack of actual quenching effects favour these particles for many potential applications. The new synthesis route suppresses the formation of rare earth clusters in the matrix and provides a good distribution of the rare earth metal ions in the matrix.

3.3.3 Effect of matrix composition – CaF₂, SrF₂ and BaF₂

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 CaF_2 , SrF_2 and BaF_2 are all suitable matrices for rare earth doping. Synthesizing doped CaF_2 and SrF_2 particles is straightforward, but BaF_2 is more challenging. Applying the new developed route, transparent sols of BaF_2 :Eu10 were obtained, but only with the use of the additives aluminium isopropoxide or benzoic acid. To ensure the comparability between the three systems, CaF_2 :Eu10 and SrF_2 :Eu10 were synthesized with the same additives, although they are not required to obtain transparent sols.

PL emission spectra of these sols are shown in Figure 7. Indeed, the emission intensity increases distinctly from CaF_2 to BaF_2 , as expected from theory. The luminescence intensity of BaF_2 :Eu10

is nearly twice as high as that of CaF_2 :Eu10. As already observed before (cf. Figure 4), the hypersensitive transition **T2** is more intense than **T1** in the case of aluminium isopropoxide (Figure 7A), but the opposite is true for benzoic acid (Figure 7B). These spectra again reveal the tremendous impact of different additives on the luminescence spectra of the Eu³⁺ doped compounds.



Figure 7. Comparison of the luminescence emission spectra of 0.2 M sols CaF₂:Eu10, SrF₂:Eu10 and BaF₂:Eu10 with 15 mol% of aluminium isopropoxide (A) or 5 mol% of benzoic acid (B) as additive. **T1**: ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, **T2**: ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$.

Luminescence lifetimes (Figure 9A and SI Table S5) steadily increase from CaF_2 to BaF_2 . The lifetimes are systematically longer for the series with benzoic acid as additive. This is in perfect agreement with results shown before (cf. Figure 4 and SI Table S3). Furthermore, the increase in PLQY upon going from the SrF_2 to the BaF_2 matrix is rather pronounced (Table 1). These results indicate, that the increase in luminescence intensity is mainly caused by the reduction of phonon energy, which leads to a suppression of non-radiative relaxation of the excited states into lattice vibrations.

Fine tuning of the luminescence lifetime can be achieved by using the solid solution $Ca_xSr_{1-x}F_2$ as host matrix. To prove the statistic distribution of alkaline earth metal ions through the particle, and hence, the existence of solid solutions, a series of $Ca_xSr_{1-x}F_2$ with $x = 0.1 \dots 0.9$ was synthesized and investigated by static ¹⁹F solid state NMR. Due to the mobility of the particles in the solvent, isotropic liquid-like NMR spectra are obtained (Figure 8). The observed five different signals correspond to the possible coordination spheres [FCa_nSr_{4-n}] (n = 0, 1, 2, 3, 4), and moreover, their intensity follows a binomial distribution. These results fit the simulated ¹⁹F spectra for such solid solutions using the superposition model (cf. SI Figure S4).⁴⁴ Thus, it is clearly shown that the synthesized phases are solid solutions with a purely statistical distribution of the cations Ca and Sr. No Ca or Sr rich domains are present. This is in full accordance to spectra of these compounds synthesized via growth of single crystals or mechanochemical synthesis.^{45, 46} It can be assumed that in the synthesis of rare earth doped particles analogue solid solutions are formed.³



Figure 8. ¹⁹F NMR spectra of 0.2 M sols $Ca_xSr_{1-x}F_2$ (x = 0.1...0.9) sols in ethylene glycol. Dashed lines: chemical shifts for pure CaF_2 and SrF_2 particles.

Then, a series of $Ca_xSr_{1-x}F_2$:Eu10 was synthesized for fine tuning of luminescence lifetimes and intensities (cf. SI Table S1). As expected, the luminescence lifetime increases monotonously from CaF_2 :Eu10 to SrF_2 :Eu10 (Figure 9B and SI Table S6). The highest luminescence intensity should be expected for the compound with the highest Sr content. Surprisingly, the compounds with $\chi_c = 0.056...0.500$, i.e. $Ca_{0.1}Sr_{0.9}F_2$:Eu10 to $Ca_{0.5}Sr_{0.5}F_2$:Eu10, express higher luminescence intensities than SrF_2 :Eu10 (Figure 9C). The highest total intensity is found for $Ca_{0.25}Sr_{0.75}F_2$:Eu10, and the largest deviation from the expected intensity is found for $Ca_{0.5}Sr_{0.5}F_2$:Eu10 (see the residual line in Figure 9C). This result is surprising on the first glance. The absorption of Eu³⁺ at 393 nm is highest for the mixed matrices (cf. SI Figure S5). This transition is structure sensitive and strongly depends on the local symmetry of the ion. A non-symmetric surrounding increases the absorption coefficient, resulting in more intense emission intensities of $Ca_{0.25}Sr_{0.75}F_2$:Eu10 and $Ca_{0.25}Sr_{0.75}F_2$:Eu10. Measurements of the quantum yield support this interpretation. The quantum yield strictly increases from CaF_2 :Eu10 via $Ca_{0.25}Sr_{0.75}F_2$:Eu10 (Table 1), and does not correlate with the emission intensity. As expected, the quantum yield is highest for SrF_2 :Eu10.



Figure 9. (A) PL lifetimes of CaF₂:Eu10, SrF₂:Eu10 and BaF₂:Eu10 (additives: 5BA ~ 5% benzoic acid, 15Al ~ 15% Al($O^{i}Pr$)₃). (B) PL lifetimes of Ca_xSr_{1-x}F₂:*RE*10 (*RE* = Eu, Tb). (C) PL intensity of Ca_xSr_{1-x}F₂:*RE*10 (*RE* = Eu, Tb). For exact composition cf. SI Table S1.

Sample	λ _{ex} (nm)	QY (%)		
CaF ₂ :Eu10 +5%BA	393	29.4		
SrF2:Eu10 +5%BA	393	29.8		
BaF ₂ :Eu10 +5%BA	393	34.6		
CaF ₂ :Eu10	393	24.7		
Ca0.25Sr0.75F2:Eu10 (*)	393	26.9		
SrF2:Eu10	393	27.3		
CaF ₂ :Tb10	350	76.5		
SrF2:Tb10	350	79.2		
SrF ₂ :Ce5,Tb10	310	79.7		

Table 1. Photoluminescence quantum yields (QY) of different Eu and Tb doped nanoparticles (0.2 M sol in ethylene glycol). BA ~ benzoic acid. λ_{ex} ~ excitation wavelength.

(*) See experimental part for exact composition.

In contrast, the $Ca_xSr_{1-x}F_2$:Tb10 compounds exhibit the expected monotonous increase in luminescence intensity from CaF_2 :Tb10 to SrF_2 :Tb10 (Figure 9C). The absorption transition of Tb³⁺ at 350 nm is not structure sensitive, and hence, "normal" behaviour is observed. The quantum yields of these samples are high (above 70%), and SrF_2 :Tb10 has a higher yield than CaF_2 :Tb10 (Table 1). The main reason for the qualitative difference between Eu^{3+} and Tb^{3+} compounds is the fact that the Eu^{3+} ion is hypersensitive to structural changes in its surrounding, while the Tb^{3+} ion is not. Interestingly, the luminescence increase from CaF_2 to SrF_2 matrix is similar for both rare earth ions, it reaches $\approx 35\%$.

3.4 Luminescence sensitization in Ce³⁺-Tb³⁺ co-doped particles

Energy transfer processes between different rare earth ions are important for further tuning of the luminescence properties of rare earth doped nanoparticles. Co-doping with Ce^{3+} strongly increases the light efficiency of the green emission of Tb^{3+} . It serves as a model system here, which also allows comparing energy transfer processes in the different matrices CaF_2 and SrF_2 .

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The Ce³⁺ ion is acts as sensitizer excited via the $4f({}^{2}F_{5/2}) \rightarrow 5d$ level transition, which is parity allowed and possesses very high oscillator strength.⁴⁷⁻⁵⁰ The absorbed energy is then transferred to Tb³⁺, and hence, the luminescence intensity can be increased by more than one order of magnitude (Figure 10).



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Figure 10. Luminescence sensitization. Left: schematic representation of the energy transfer between Ce³⁺ and Tb³⁺. Right: Pictures of (A) CaF₂:Ce5,Tb10 and (B) CaF₂:Tb10 under different excitation (upper 366 nm, lower 254 nm).

CaF₂:Ce5,Tb10 and SrF₂:Ce5,Tb10 were both synthesized as transparent sols in ethylene glycol. Luminescence excitation and emission spectra are shown in Figure 11. The excitation spectra for both compounds are almost identical in the region between 330 and 400 nm. In this region, electrons are excited from the ground state into higher 4*f* states of Tb³⁺. In the region between 260 and 320 nm, the excitation spectra of both compounds are different. Here, the electrons are excited from the ground state into the empty 5*d* orbital of Ce³⁺. The 5*d* orbitals undergo crystal field splitting due to the surrounding matrix. This splitting is slightly different for both matrices.

The emission spectra are qualitatively similar, regardless of the matrix (CaF₂ or SrF₂), and regardless of the excited ion (Ce³⁺ or Tb³⁺), but the emission intensity greatly depends on the excited ion (Table 2). For CaF₂:Ce5,Tb10, the luminescence intensity is increased 62-fold when Ce³⁺ is excited instead of Tb³⁺. For SrF₂:Ce5,Tb10 the increase is still 54-fold. Obviously, the emission for CaF₂:Ce5,Tb10 is slightly more effective than for SrF₂:Ce5,Tb10 (excitation of Ce³⁺ in both cases). This fact is in contrast to the point that the SrF₂ matrix has lower phonon energy. Less radiation free relaxations, and hence, a higher emission intensity is expected for SrF₂:Ce5,Tb10. As expected, luminescence lifetimes are longer for the SrF₂ matrix than for the CaF₂ matrix (Table 2). The energy transfer from Ce³⁺ to Tb³⁺ is much faster than the lifetime of the visible emission of Tb³⁺. The total lifetime increases by \approx 5%, when Ce³⁺ is excited instead of Tb³⁺.



Figure 11. Luminescence spectra of 0.2 M sols CaF₂:Ce5,Tb10 and SrF₂:Ce5,Tb10. Left: Excitation spectra (λ_{em} = 542 nm). Right: Emission spectra at different excitation wavelengths, Inset: Integrated emission intensity. QY: quantum yield.

Table 2. Luminescence	properties	of CaF_2 and	d SrF ₂	co-doped	with	Ce ³⁺	and	Tb ³⁺	$(t_1 =$	lifetime	and	$q_1 =$
asymmetry parameter).												

Sample	Luminesce $\lambda_{em} = 1$	Luminescence intensity ratio		
	$Ce^{3+} \rightarrow Tb^{3+}$	Tb ³⁺ direct	$\frac{\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}}{\text{Tb}^{3+} \text{ direct}}$	
CaF2:Ce5,Tb10	$\lambda_{ex} = 282 \text{ nm}$ $t_1 \ 3.34 \text{ ms}$ $q_1 \ 1.079$	$\lambda_{ex} = 350 \text{ nm}$ $t_1 \ 3.21 \text{ ms}$ $q_1 \ 1.080$	62	
SrF ₂ :Ce5,Tb10	$\lambda_{ex} = 301 \text{ nm}$ $t_1 4.29 \text{ ms}$ $q_1 1.079$	$\lambda_{ex} = 350 \text{ nm}$ $t_1 4.04 \text{ ms}$ $q_1 1.083$	54	

To explain the higher amplification for the CaF_2 matrix, another effect should be taken into account. The distance between two cation sites in the undoped CaF_2 lattice is ≈ 386 pm, in the SrF_2 lattice it is ≈ 410 pm. Most probably, the shorter spatial distance between Ce^{3+} and Tb^{3+} allows a more effective energy transfer. This would explain why the CaF_2 matrix shows higher emission enhancement by co-doping with Ce^{3+} .

The QY for the excitation of Ce³⁺ in SrF₂:Ce5,Tb10 is 79.7% (cf. Table 1). This is nearly the same as the 79.2% for the direct excitation of Tb³⁺ in SrF₂:Tb10. Thus, the energy transfer between Ce³⁺ and Tb³⁺ is very effective and reaches a QY of \approx 100%. In fact, Ce³⁺ is the inorganic pendent to antenna ligands, which are frequently used to increase luminescence efficiencies of Eu³⁺ or Tb³⁺.⁵¹ Contrary to organic ligands, the Ce³⁺ withstands high energy density of the excitation source without decomposing.

4 Illustration of particle growth

The energy transfer between Ce^{3+} and Tb^{3+} can be used to illustrate the formation process of these nanoparticles via sol-gel synthesis. In a precursor solution containing $Sr(OLac)_2$, $Ce(OAc)_3$ and $Tb(OAc)_3$, the spatial distance between Ce^{3+} and Tb^{3+} is too large for an energy transfer. When the solution is fluorinated, particles of SrF_2 :Ce5,Tb10 are formed, the distance between

Ce³⁺ and Tb³⁺ drastically decreases, and hence, an energy transfer between Ce³⁺ and Tb³⁺ is possible. When the reaction mixture is illuminated at 254 nm, the precursor solution shows no visible luminescence, but the nanoparticles do. Hence, the formation of the nanoparticles during the fluorolytic sol-gel synthesis can be directly illustrated during the synthesis process in an easy way (Figure 12).

Start	1 s	2 s	3 s	4 s
5 s	6 s	7 s	8 s	9 s
10 s	11 s	12 s	13 s	30 s

Figure 12. Fluorination of a solution of 85% Sr(OLac)₂, 5% Ce(OAc)₃ and 10% Tb(OAc)₃ (sum conc. 0.2 mol/l) with 2.15 eq of HF/MeOH within 30 sec under illumination at 254 nm. The addition of HF starts at 1 sec and ends at 25 sec. The formed SrF₂:Ce5,Tb10 nanoparticles show bright green luminescence.

This experiment gives two-fold insights into this system. First, it shows that the rare earth metal ions are well distributed within the matrix. Second, it illustrates how fast the nanoparticles are formed during synthesis, i.e. the first nanoparticles are already formed immediately after addition of the first drop of HF after 1 s, as it can be seen by the green luminescence. With every further drop, more and more nanoparticles are formed, resulting in an increase of the luminescence intensity (until 30 s). After addition of all HF, the luminescence reaches its maximum. This clearly demonstrates, how fast HF is reacting with the precursors to form nanoparticles, and that particle formation is already finished with the addition of the last drops of HF.

5 Conclusions

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The fluorolytic sol-gel synthesis has proven to be a universal tool to synthesize transparent sols of rare earth containing alkaline earth metal nanoparticles at room temperature in a fast and straightforward way. A universal access to all three of CaF₂, SrF₂ and BaF₂ and solid solutions of them became available for the first time now. Methanol and ethylene glycol can be both used as solvents, having advantages for different applications.

The method is not limited to two metal ions, e.g. Ca_{0.5}Sr_{0.5}F₂, Ca_{0.9}Eu_{0.1}F_{2.1} or Sr_{0.8}Tb_{0.2}F_{2.2}, but also quaternary fluorides like Ca_{0.2}Sr_{0.7}Eu_{0.1}F_{2.1} or Sr_{0.85}Ce_{0.05}Tb_{0.10}F_{2.15} were successfully synthesized. In principle, it should also be possible to prepare nanoparticles with even more cations. Such multiply doped systems are of interest for tuning the luminescence emission colour by adjusting

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the ratio of various different rare earth ions. In addition, syntheses of batches up to 1 liter scale and more are also easily possible. Nanoparticles are formed instantly on the addition of HF. This is directly visualized through the sudden occurrence of energy transfer processes in Ce³⁺-Tb³⁺ co-doped samples during the synthesis.

In these new materials, the rare earth ions are very homogeneously distributed throughout the matrix even for highly doped systems. Therefore, high luminescence intensities are achieved without significant quenching effects even for 30% rare earth content and more. This is a new and promising result, and a big step forward towards higher light efficiency. Luminescence intensities, lifetimes and quantum yields of the rare earth ions steadily increase from CaF_2 via SrF_2 to BaF_2 . This was proven for the first time experimentally. Fine-tuning of luminescence properties is possible by variation of the Ca content in solid solutions $Ca_xSr_{1-x}F_2$ (x = 0...1) as matrix.

The study of energy the transfer $Ce^{3+} \rightarrow Tb^{3+}$ shows interesting results for both matrices CaF_2 and SrF_2 . The emission intensity of Tb^{3+} increases more than 50 times, because of the large absorption coefficient of Ce^{3+} similar to an organic antenna ligand. Although the lifetimes of the excited states are by $\approx 25\%$ longer for the SrF_2 matrix, the energy transfer seems to be more effective for the CaF_2 matrix, resulting in slightly higher emission intensity. This result is in strong contrast to the luminescence of singly doped systems, where SrF_2 is more efficient. This demonstrates clearly that not only the lifetimes of the excited states are important, but also the spatial difference between the two rare earth ions, which is shorter for CaF_2 than for SrF_2 .

Thus, it cannot be stated in general, which of the matrices CaF_2 and SrF_2 is the most suitable host for luminescence applications, but it depends on the exact system and the processes involved.

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