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## Facile preparation of quantum cutting $GdF_3$ : $Eu^{3+}$ nanoparticles from ionic liquids<sup>†</sup>

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Microwave reaction of  $Ln(OAc)_3 \cdot xH_2O$ , Ln = Gd, Eu; OAc = acetate) with and in the ionic liquid  $[C_4mim][BF_4]$  ( $C_4mim = 1$ -butyl-3-methylimidazolium) allows the fast and efficient synthesis of small, uniform, oxygen-free lanthanide nanofluorides with excellent photophysical behaviour. For  $GdF_3 : Eu^{3+}$  nanoparticles a quantum efficiency of up to 145% was determined.

Energy-efficient lighting is a prevailing topic. It is estimated that remarkable amounts electricity can be saved when more energy-efficient light sources are used.<sup>1</sup> Various countries have already or are currently planning to ban conventional incandescent lamps,<sup>2</sup> which suffer from a poor luminous efficiency since most of the energy is converted to heat, and have them replaced by more environmentally benign light sources such as compact fluorescent lamps (CFLs) or light emitting diodes (LEDs). Although the use of LEDs seems to be the most environmentally benign way of lightning, white emitting LEDs still suffer from a poor color rendering index (CRI) and a comparatively low luminous intensity (especially when a good CRI is attempted). At the moment they cannot completely replace conventional light bulbs in many applications and CFLs are currently the most prevalent replacements. In commercially available CFLs a mercury discharge is used to produce UV (ultraviolet) light ( $\lambda_{max} = 254$  nm) which is converted by phosphors on the inner side of the light tube to visible light. The use of mercury has several major drawbacks. The most important ones being the environmental safety and health issues that have to be considered during manufacturing and at the end-of-life of such fluorescent tubes. Many consumers today are unaware of the potential risks of CFLs. Furthermore, mercury based fluorescent light tubes need about 1-3 min of start-up time until they reach their full light power as mercury in the tube has to be heated and evaporated first. Thus, they are not suited for use in combination with motion sensors. An alternative is the replacement of mercury by noble gases such as xenon in CFLs. The Xe dimer discharge results in a broad UV emission with a maximum at 172 nm. However, the discharge efficiency is lower compared to that of mercury. In addition, conversion of the yet shorter wavelength radiation to visible light results in an even larger energy loss compared to Hg based CFLs. In order to make xenon-based

CFLs competitive, a quantum yield of the used phosphors of larger than 100% needs to be achieved. The conversion of a UV or VUV (vacuum ultraviolet) photon into more than one photon of lower energy was first reported in 1974 for  $YF_3$ :  $Pr^3$ and YF<sub>3</sub>:Tm.<sup>4</sup> LiGdF<sub>4</sub>:Eu and GdF<sub>3</sub>:Eu were the first materials that yielded a high photon output in the visible region of light.<sup>5</sup> In order to use such compounds in CFLs the materials need not only to have an excellent photophysical performance, it is also desired that they have a uniform and small particle size in order to minimize stray light. Unfortunately, the preparation of lanthanide fluoride nanoparticles is not an easy task and only a few reports have appeared in the literature so far. Well-established methods for the synthesis of lanthanide fluoride nanoparticles are hydrothermal,<sup>6</sup> sonochemistry-assisted,<sup>7</sup> microemulsion<sup>8</sup> and solution-phase<sup>9</sup> synthesis routes. However, to the best of our knowledge, oxygen-free nanoparticles with a size below 8 nm have not been obtained using these time-consuming methods. Indeed, special care has to be taken to avoid the formation of oxides and oxide-fluorides because even oxygen impurities can lead to nonradiative relaxation via europium-oxygen charge transfer states followed by emission from these levels. Here we report a fast and efficient synthesis route to oxygen-free, single phase doped lanthanide nanofluorides with good quantum cutting behaviour by microwave treatment of simple lanthanide precursors  $(Ln(OAc)_3 xH_2O, OAc = acetate)$  in the task-specific ionic liquid  $[C_4mim][BF_4]$  ( $C_4mim = 1$ -butyl-3methylimidazolium). The optical properties of the obtained GdF<sub>4</sub>: Eu<sup>3+</sup> nanofluorides with different active ion concentrations (0.5, 5, 10 mol% of Eu<sup>3+</sup>) were investigated with respect to their potential as quantum cutting phosphors as well as the physicooptical properties of pure EuF<sub>3</sub>.

The concept of task-specific ionic liquids (TSILs), hence, room temperature molten salts designed to fulfil a certain application, was developed some time ago and has found its application mainly in separations (especially CO<sub>2</sub> capture), organic synthesis and catalysis.<sup>10</sup> However, the concept has been neglected for applications in materials synthesis although the advantages of ionic liquids in this area<sup>11</sup> have been realized. Here we employ [C4mim][BF4] as a task-specific ionic liquid. During synthesis [C<sub>4</sub>mim][BF<sub>4</sub>] acts both as a reaction medium and reaction partner. It is well-known that thermal decomposition as well as hydrolysis of [BF<sub>4</sub>]-containing ionic liquids leads to the release of fluoride. This circumstance has turned out to be a nuisance for organic synthesis and catalysis<sup>12</sup> but becomes extremely helpful for the microwave synthesis of fluoridic nanomaterials. As a heating source a single mode microwave (CEM, Discover. USA) operating at a frequency of 2455 MHz was used. One of the key advantages

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**Fig. 1** TEM micrographs of representative samples of  $GdF_3$ :  $Eu^{3+}$  with 5% (left) and 10% (right) doping.

of ILs in microwave synthesis is the presence of large ions with high polarizability and conductivity which renders them highly susceptible to microwaves, leading to large heating rates which results in a high formation rate of nuclei favouring nanoparticle formation.<sup>13</sup> Fig. 1 shows TEM (transmission electron microscopy) photos of typical GdF<sub>3</sub>: Eu<sup>3+</sup> samples. Analysis of the particle size distribution yields a range between 2 and 9.5 nm and an average particle size of about 6 nm.

The excitation spectra of GdF<sub>3</sub>: Eu<sup>3+</sup> with 0.5, 5, 10 mol% europium and of pure EuF<sub>3</sub> were measured at room and liquid nitrogen temperature (Fig. 2 and ESI†). Monitoring the emission at 592 nm ( ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition of Eu<sup>3+</sup> ion) leads to a series of narrow absorption lines related to the f–f transitions of Eu<sup>3+</sup> in the case of EuF<sub>3</sub> and features characteristic for Gd<sup>3+</sup> and Eu<sup>3+</sup> for GdF<sub>3</sub>: Eu<sup>3+</sup>.

The emission spectra of typical samples (Fig. 3) recorded at room and low temperature under direct excitation of the  ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$  transition of the Eu<sup>3+</sup> ion ( $\lambda_{ex} = 393$  nm) show transitions from the  ${}^{5}D_{0}$  excited state to the  ${}^{7}F_{J}$  (J = 1, 2, 3, 4) ground states of the Eu<sup>3+</sup> ion.

The point symmetry of the Eu<sup>3+</sup> crystal sites estimated by the relative intensity of the magnetic dipole  ${}^5D_0 \rightarrow {}^7F_1$  and electric dipole  ${}^5D_0 \rightarrow {}^7F_2$  transitions is in agreement with the YF<sub>3</sub> type of structure of EuF<sub>3</sub> (and GdF<sub>3</sub>).<sup>14</sup> In addition to pure EuF<sub>3</sub>, the profiles of the fluorescence spectra of GdF<sub>3</sub> doped with Eu<sup>3+</sup> also show emission transitions from higher localized excited states, the most intensive corresponding to  ${}^5D_1 \rightarrow {}^7F_2$  ones at 554 nm. In neat EuF<sub>3</sub> these transitions are quenched by cross-relaxation and ion-ion interaction. The decay times of all studied nanocrystals were measured at low and room temperature using two different excitation energies (393 and 275 nm). The decay curve for the  ${}^5D_0$  level



Fig. 2 Excitation spectra of  $EuF_3$  (a) and  $GdF_3:Eu^{3+}$  5% (b), emission recorded at 592 nm.



Fig. 3 Emission spectra of  $EuF_3$  and  $GdF_3$ :  $Eu^{3+}$  0.5% excited at 393 nm at 77 K. For other doping concentrations see ESI.<sup>†</sup>

 $({}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition) could be fitted with a single exponential function. For EuF<sub>3</sub> the decay times are strongly temperature dependent, they are equal to 0.7 and 1.4 ms at RT and 77 K, respectively. The decay times for the diluted samples increased dramatically (~10 ms) and became nearly temperature independent (see ESI†).

In GdF<sub>3</sub>: Eu<sup>3+</sup> downconversion occurs upon excitation at the  ${}^{6}G_{J}$  levels of a  $Gd^{3+}$  ion and two subsequent energy transfer processes: first cross-relaxation  $Gd^{3+} {}^{6}G_{J}$ ,  $Eu^{3+} {}^{7}F_{1} \rightarrow$  $Gd^{3+} {}^{6}P_{J}$ ,  $Eu^{3+} {}^{5}D_{0}$  (thermally activated) yields one photon from the  ${}^{5}D_{0} \rightarrow {}^{7}F_{I}$  transition and secondly the Gd<sup>3+</sup> ion in the  ${}^{6}P_{I}$  state transfers the remaining excitation energy to a high-energy state of another Eu<sup>3+</sup> ion through migration via the Gd<sup>3+</sup> sublattice. After fast nonradiative relaxation from this high excited state to the  ${}^{5}D_{J}$  levels, a second visible photon is emitted due to the  ${}^{5}D_{0,1,2,3} \rightarrow {}^{7}F_{J}$  transition with a normal branching ratio (for the energy scheme see Fig. 4).<sup>3</sup> Consequently, a substantial increase in the relative intensity of the  ${}^{5}D_{0}$  emission is expected if quantum cutting through this two-step energy transfer occurs. When exiting into the  ${}^{6}P_{J}$ ,  ${}^{6}I_{J}$ or  ${}^{6}D_{I}$  levels, a single energy transfer step to Eu<sup>3+</sup> occurs and the normal branching ratio for the  $Eu^{3+} {}^5D_I$  emission is observed. Thus, the occurrence of quantum cutting can be confirmed by comparing the emission spectra for excitation into the  ${}^{6}G_{I}$  levels (~200 nm) and the  ${}^{6}P_{I}$  levels  $(\sim 305 \text{ nm}) \text{ of } \text{Gd}^{3+}$ .



Fig. 4 Experimentally determined energy scheme of  $GdF_3$ : Eu (a) and downconversion pathways in  $GdF_3$ : Eu (b).





**Fig. 5** Emission spectra of  $GdF_3$ :  $Eu^{3+}$  10% and 5% nanocrystals upon excitation into the  ${}^6P_J$  and  ${}^6G_J$   $Gd^{3+}$  levels recorded at RT. The spectra were normalized for  ${}^5D_1 \rightarrow {}^7F_J$  emission.

Fig. 5 presents the emission spectra of 5 and 10 mol% Eu<sup>3+</sup>-doped samples excited by high energy synchrotron radiation. Due to the quantum cutting effect the ratio of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{I}/{}^{5}D_{1} \rightarrow {}^{7}F_{I}$  peaks increases by a factor of up to 1.5. Judging from the intensity ratios the cross-relaxation probability is  $\sim 25\%$  for the 10 mol% Eu<sup>3+</sup>-doped sample and  $\sim 45\%$  for the 5% mol Eu<sup>3+</sup>-doped sample, yielding a quantum efficiency of about 125% and 145%, respectively. These values are astonishingly high when taking the extremely small particle size into account. While in the bulk materials a quantum yield close to the theoretical maximum of 200% can be observed ( $\sim 170\%$ for GdF<sub>3</sub>: Eu<sup>3+</sup>),<sup>5</sup> with smaller particle size and rising surface area a drastic reduction of the quantum yield due to surface quenching is expected. Maybe for this reason and the experimental difficulties in synthesizing uniform LnF3 particles, almost no reports on quantum cutters on the nanoscale exist. However, for GdF<sub>3</sub>: Eu<sup>3+</sup> nanorods of substantially larger size than our particles (length 60-200 nm, diameter 18-20 nm) a quantum vield close to the bulk material has been suggested.<sup>15</sup>

In conclusion, in this work we describe a fast and facile access to pure, oxygen free, small size ( $\sim 6$  nm), polycrystalline GdF<sub>3</sub>: Eu<sup>3+</sup> nanoparticles *via* microwave synthesis. Here, the ionic liquid not only serves as the synthesis medium but also as a fluoride source, hence, the reaction partner. Quantum yields as high as 145% can be obtained which renders these materials of great interest for optical applications.

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