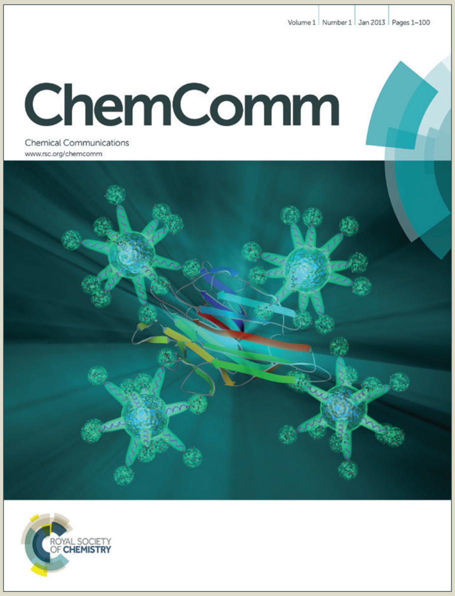
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

A novel approach to optically active ion doped luminescent materials via electron beam evaporation into ionic liquids

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

K. Richter[#,a], C. Lorbeer [#,a] and A.-V. Mudring[a,b*]

A novel approach to luminescent materials via electron-beam evaporation into ionic liquids is presented which even allows to dope host lattices with ions that have a strong size mismatch. To prove this, MgF_2 nanoparticles doped with Eu^{3+} were fabricated. The obtained nanoparticles feature an unusually high luminescence lifetime and the obtained material shows a high potential for application.

Metal ion doped fluorides find wide applications in optical and photonic technologies such as storage phosphors, solid-state lasers, dosimeters, scintillators and thermoluminescent materials[1-8] as they are excellent host materials for optical active ion centers because of their large band gaps and their low phonon energies. In particular, cheap, non-rare earth based host matrices such as alkaline earth fluorides[9] are of special interest since rare earths are considered critical materials. When doping with optical centers such as rare earth ions materials for advanced applications such as scintillation[4], upconversion[10,11] and quantum cutting,[12] can be realised. The (crystal) structure of the host lattice and distribution of the dopant ion among the surrounding lattice determines the optical properties particularly in case of nanoparticles. Via novel synthetic methods involving different techniques of dopant ion incorporation it is possible to yield new materials with astounding properties.[13]

For that reason, we developed a novel method to optically ion doped luminescent materials via electron beam evaporation into ionic liquids. Ionic liquids (ILs) are an innovative class of solvents and have received substantial attention in the recent years. They can exhibit unusual solvent properties such as a low vapour pressure, wide liquidus ranges, high thermal stabilities, wide electrochemical windows which are advantageous for a large number of applications.[14] In the last decade, ILs have received considerable attention as a reaction medium for the preparation and stabilization of nanomaterials because they can act as a structure-directing agent and stabilize particles by steric and electrostatic interaction.[15,16] Especially because of their negligible vapor pressure, ILs appear as favourable media for vacuum experiments and applications.[17]

So far, physical vapor deposition and electron beam evaporation has been used for thin film preparation. Kawano et al. reported the preparation of luminescent rare earth ions-doped CaF_2 and MgF_2 films by simultaneous evaporation of lanthanide fluorides and alkaline earth fluorides.[1] Undoped MgF_2 nanoparticles have been prepared by sol-gel methods,[18] microwave[19] or ultrasound-assisted methods[20]. Conversely, the synthesis by chemical routes implies the use of fluorinated salts, fluorinated organic precursors[21-24] or the additional use of hydrofluoric acid.[25]

Recently, we developed a synthesis procedure for metal, metal-oxide[26] alloy,[27] and rare earth fluoride nanoparticles[28] under high vacuum via thermal evaporation into ILs modifying the original SMAD (solvated metal atom dispersion) technique.[29-31] By replacing the conventional solvents and stabilizing agents, which typically exhibit high vapour pressures, with ILs with negligible vapour pressure, it is possible to evaporate materials at ambient temperatures into a liquid substrate. Here we describe an easy, environmentally friendly access to small, luminescent Eu^{3+} doped MgF_2 nanoparticles by simple electron beam co-evaporation of bulk EuF_3 and MgF_2 into an ionic liquid using a SMAD setup which was also used for physical vapour deposition recently.[26] The electron beam evaporation setup used herein principally consists of a source of electrons which are accelerated and focused by a magnetic field onto a crucible containing the evaporant. The electron beam bombardment heats the sample by transfer of kinetic energy. One advantage of the e-beam system is the fact, that high power densities up to 10 kW/cm^2 can be applied in order to achieve high evaporation temperatures and high evaporation rates. In detail, the e-beam is emitted from a tungsten filament and accelerated and focused by an electric and magnetic field. The focused beam melts the sample in a small spot. In order to prevent overheating of the evaporant, the crucible is cooled with water. The e-beam spot can be focused with a shield cage and the therein applied potential. The material is evaporated and condenses onto the ionic liquid film which is contained on the inner surface of a rotating flask surrounding the evaporation source. The principle of the e-beam evaporation and pictures of the set-up are shown in figure 1.

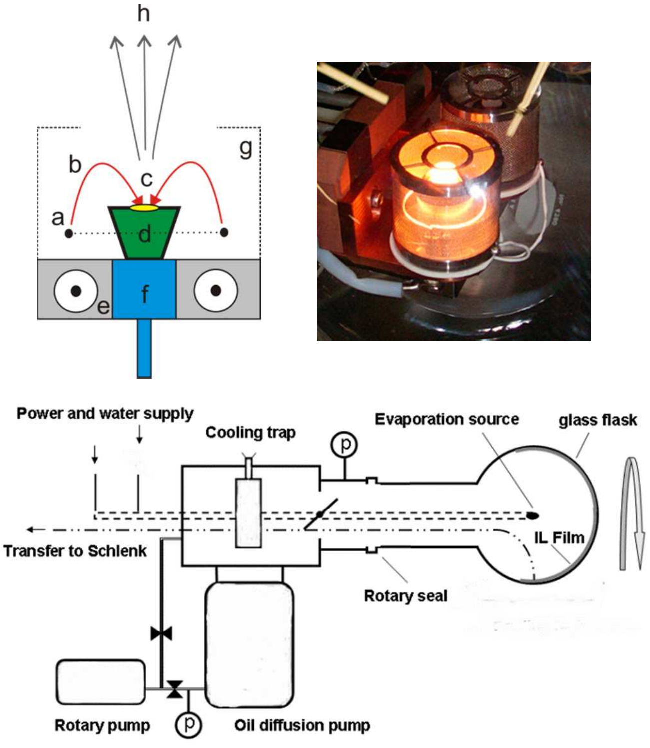


Figure 1. Electron beam evaporation set-up. Upper left corner: working principle of the e-beam gun as an evaporation source: a) tungsten filament, b) electron beam, c) heating spot, d) crucible with sample, e) magnetic field lines, f) cooling head, g) shield cage for focusing the e-beam spot, h) material vapour. Upper right corner: Photograph of the crucible during evaporation. Below: Schematic diagram of the SMAD set-up. For experimental details see ESI.

The IL 1-butyl-3-methylimidazolium tetrafluoroborate [C_1C_4im][BF_4] was used because of prior excellent results in the synthesis of nanoscale metal fluorides[33] and its superior stabilizing properties against metal nanoparticle precipitation[26]. In order to show the intriguing performance of the method presented herein, doping of MgF_2 with Eu^{3+} as the optical center was used. Eu^{3+} and Mg^{2+} have a large difference in their ion radii which typically hampers doping. However, doping inexpensive, cheap and abundant fluoride host matrices such as alkali earth fluorides is strongly preferred over the use of precious rare earth fluorides since they are considered critical materials. In a typical experiment, 40 ml of [C_1C_4im][BF_4] was placed in the glass bulb of the reactor. A mixture of 1800 mg MgF_2 (ABCR, 99.99 %) and 200 mg EuF_3 (ABCR 99.95 %; REO) was grinded under inert atmosphere and placed in a Fabmate® crucible (Kurt-Lesker company, England) for electron-beam evaporation. After evaporation the as-prepared particles were precipitated from the ionic liquid by adding a dichloromethane/methanol mixture.

The powder X-Ray diffraction pattern of the particles prepared by electron beam evaporation reveals tetragonal rutile-type MgF_2.[32] No additional reflections belonging to a distinct phase of undoped EuF_3 or another impurity could be observed. For comparison, MgF_2:Eu^{3+} particles synthesized in a microwave reaction as described are displayed.[33]

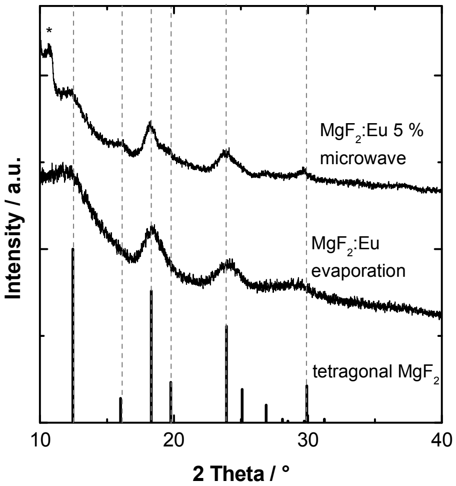


Figure 2. Powder X-ray diffraction pattern of MgF_2:Eu^{3+} synthesized with different methods (microwave vs. electron beam evaporation). For comparison, the database pattern of tetragonal MgF_2 is shown (ICSD 394, space group P 4_2/mnm). The asterisk denotes a reflection originating from the instrument.

During synthesis, a dopant concentration of about 5 % was envisioned (see ESI). However, corresponding to ICP measurements an actual concentration of 2.77 w% or 1.17 mol% was found for the Eu^{3+} ion in the sample prepared by e-beam evaporation. The different evaporation rate of neat MgF_2 and EuF_3 under electron beam irradiation leads to the diminished molar concentration. By proper adjustment of the starting materials' ratio, the obtained concentration can be controlled. Figure 3 shows the transmission electron micrograph of the precipitated and washed Eu^{3+} doped MgF_2 particles. After removal of the stabilizing IL, the particles form larger aggregates on the TEM grid which makes an exact size distribution difficult. However, it is clear that these aggregates consist of smaller, unsymmetrically particles with a diameter between 8 nm and 14 nm.

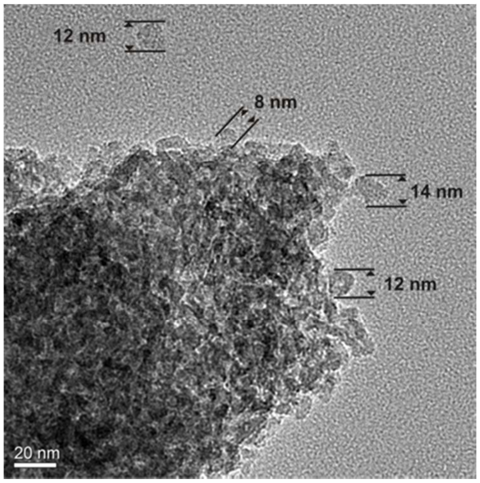


Figure 3. Transmission electron micrograph of $MgF_2:Eu^{3+}$ particles synthesized via electron beam evaporation.

The photoluminescence excitation spectra of the synthesized powdered material (Figure 4) show the typical Eu^{3+} f-f lines corresponding to $^7F_{0,1} \rightarrow {}^5D_1$, $^5D_2$, $^5L_6$, $^5G_{2\text{-}6}$, $^5D_4$, $^5H_4$ transitions. In neither case any oxygen impurities can be traced (as would become visible by a broad and significant Eu-O charge transfer band around 250 nm).

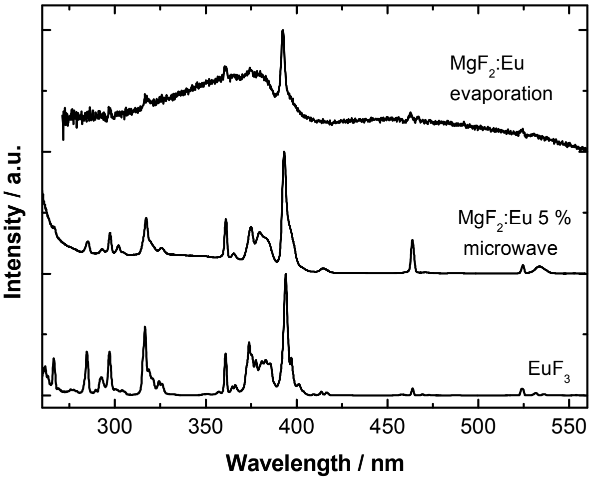


Figure 4. Comparison of the room temperature excitation spectra (λ_{em}= 611 nm) of the synthesized MgF_2:Eu particles (microwave vs. electron beam evaporation) and bulk EuF_3 used as the starting material.

The particles show orange-red emission originating from the optical center Eu^{3+}. The emission spectra are displayed in figure 5. The emission arises from the Eu^{3+} $^5D_0 \rightarrow {}^7F_{0\text{-}4}$ f-f transitions. The symmetry of the Eu^{3+} ion incorporated in the MgF_2 host material is different from the Eu^{3+} in the starting material EuF_3 as can be judged by the so-called asymmetry ratio of the $^5D_0 \rightarrow {}^7F_1$ transition (592 nm) with respect to the $^5D_0 \rightarrow {}^7F_2$ (611 nm) transition. Indeed, the emission is similar to previously obtained Eu^{3+} emission in other nanoscale alkali earth fluorides including CaF_2, SrF_2 and BaF_2 which further proves the incorporation of the Eu^{3+} ion into the lattice and that a (close to) octahedral site symmetry was achieved.[34] Noticeably, the nanoscale size of the particles leads to several slightly different Eu^{3+} coordination and thus symmetry environments yielding a much broader emission spectrum and a less resolved crystal field fine structure[35] in comparison to the bulky starting material EuF_3.

The luminescent lifetimes of the Eu^{3+} emission were determined for the material prepared via electron beam evaporation, via microwave and for the starting material EuF_3. Herein, the material prepared via electron beam evaporation shows the longest luminescence lifetime of the $^5D_0 \rightarrow {}^7F_2$ transition excited at λ_{ex}= 393 nm and monitored at λ_{em}= 612 nm.

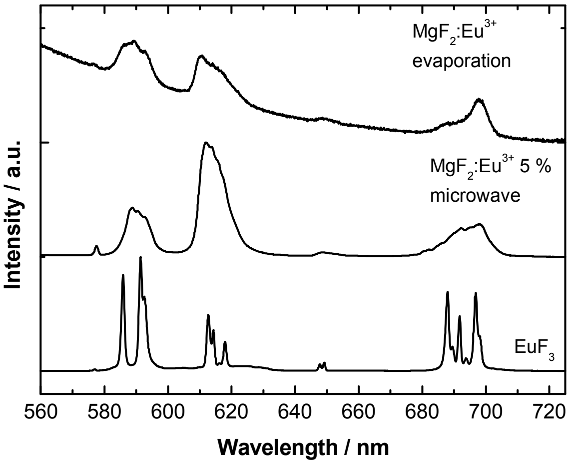


Figure 5. Room temperature emission spectra (λ_{ex}= 393 nm) of the synthesized MgF_2:Eu particles and the starting material EuF_3 for comparison.

Table 2. Average luminescent lifetimes of the Eu^{3+} emission (λ_{ex}= 393 nm, λ_{em}= 612 nm) of the $MgF_2:Eu^{3+}$ particles synthesized with different methods in comparison with the analog luminescent lifetime $\bar{\tau}$ of the EuF_3 starting material.

Material / Composition	$\bar{\tau}$
EuF_3 (pure)	2.1 ms
MgF_2:Eu by electron beam evaporation	2.6 ms
MgF_2:Eu 5 % by microwave	1.5 ms

In summary, crystalline Eu^{3+} doped MgF_2 nanoparticles with a size between 8 nm and 14 nm have been synthesized via simultaneously e-beam evaporation of neat MgF_2 and EuF_3 into the ionic liquid $[C_1C_4im][BF_4]$. The particles show a bright orange-red luminescence and further no impurities from oxygen could be detected. The incorporation of the Eu^{3+} ion into the MgF_2 host lattice was confirmed by luminescence spectroscopy. The quantum yield of the particles prepared via e-beam evaporation has been determined to be 3.7 % which is in good agreement with an optical material purely relying on the intraconfigurational f-f emission of Eu^{3+} in an insulating nanoscale material such as MgF_2.

The luminescent lifetime of the nanoparticles is with 2.6 ms the longest compared with particles obtained from other preparation methods. This also confirms the promising properties of the synthesis method presented herein.

Acknowledgement

This work is supported in part by the Critical Materials Institute, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office.

Notes and references

[#] These authors contributed equally.

[a] Inorganic Chemistry III- Materials Engineering and Characterization, Ruhr-Universität Bochum, Universitätsstr. 150, 44801 Bochum, Germany. E-mail: anja.mudring@rub.de

[b] Department of Materials Science and Engineering, Iowa State University and Critical Materials Institute, Ames Laboratory (DOE), Ames, IA 50010, USA. E-mail: mudring@iastate.edu

Electronic Supplementary Information (ESI) available: Experimental and instrumental details, synthesis of ionic liquids used. See DOI: 10.1039/c000000x/

1 B.-C. Hong and K. Kawano, *J. Alloys Compd.* 2006, **408–412**, 838–841.
2 P. F. Moulton, A. Mooradian and T. B. Reed, *Opt. Lett.* 1978, **3**, 164-166.
3 L.G. Jacobsohn, A.L. Roy, C.L. McPherson, C.J. Kucera, L.C. Oliveira, E.G. Yukihara and J. Ballato, *Optical Materials*, 2013, **35**, 2461–2464.
4 W.Chen, S. L. Westcott, S. Wang, and Y. Liu, *J. Appl. Phys.* 2008, **103**, 113103.
5 M. Secu, S. Jipa, C. E. Secu, T. Zaharescu, R. Georgescu and M. Cutrubinis, p hys. stat. sol. (b), 2008, **245(1)**, 159–162.
6 J. W. Stouwdam and F. C. J. M. van Veggel, *Nano Lett*., **2002**, 2, 733; R. Yan and Y. Li, *Adv. Funct. Mater*., **2005**, 15, 763.
7 M. M. Lezhnina, T. Jüstel, H. Kätker, D. U. Wiechert and U. H. Kynast, *Adv. Funct. Mater.*, **2006**, 16, 935; R. Chai, H. Lian, C. Li, Z. Cheng, Z. Hou, S. Huang and J. Lin, *J. Phys. Chem. C*, **2009**, 113, 8070; S. Sivakumar, J. C. Boyer, E. Bovero, F. van Veggel and C. J. M. Frank, *J. Mater. Chem*., **2009**, 19, 2392; X. Zhou, S. Li, X. Chen, Q. Zhu, Z. Wang and J. Zhang, *J. Nanosci. Nanotechnol*., **2008**, 8, 1392.
8 G. Blasse and B.C. Grabmaier, *Luminescent Materials*, **1994**, Springer–Verlag, Berlin, Heidelberg.
9 C. Lorbeer, J. Cybinska and E. Zych, A.-V. Mudring, *Opt. Mater.,* 2011, ***34***, 336.
10 S. Fischer, J. C. Goldschmidt, P. Löper, G. H. Bauer, R. Brüggemann, K. Krämer, D. Biner, M. Hermle, and S. W. Glunz1, J. Appl. Phys. 2010, **108**, 044912.
11 K. W. Krämer, D. Biner, G. Frei, H. U. Güdel, M. P. Hehlen and S. R. Lüthi,| *Chem. Mater.* 2004**, 16**, 1244-1251.
12 C. Lorbeer, J. Cybinska and A.-V. Mudring, *J. Mater. Chem. C*, 2014, **2**, 1862.
13 P. L. Archer, S. A. Santangelo, D. R. Gamelin, *Nano Lett.* 2007, **7**, 1037.
14 N. V. Plechkova and K.R. Seddon, *Chem. Soc. Rev*., 2008, **37**, 123.
15 M. Antonietti, D. Kuang, B. Smarsly and Y. Zhou, *Angew. Chem., Int. Ed.*, 2004, **43**, 4988; A. Taubert, A. Uhlmann, A. Heddrich and K. Kirchhoff, *Inorg. Chem*., 2008, **47**, 10758; K.-S. Kim, S. Choi, J.-H. Cha, S.-H. Yeon and H. Lee, *J. Mater. Chem*., 2006, **16**, 1315; N. von Prondzinski, A. Babai, A.-V. Mudring and K. Merz, *Z. Anorg. Allg. Chem*., 2007, **633**, 1490.
16 J. Dupont and J. D. Scholten, *Chem. Soc. Rev*., 2010, **39**, 1780.
17 S. Kuwabata, T. Torimoto, A. Imanishi, T. Tsuda, *Electrochemistry*, 2012, **80**, 498503; S. Kuwabata, T. Tsuda and T. Torimoto, *J. Phys. Chem. Lett*., 2010, **1**, 3177.
18 S. Bas, U. Chatterjee and M. D. Soucek, J. *Appl. Polym. Sci. Vol.* 2012, **126**, 998–1007.
19 Z. Quan, P. Yang, C. Li, J. Yang, D. Yang, Y. Jin, H. Lian, H. Li, J. Lin, *J. Phys. Chem. C,* 2009, **113***,* 4018–4025.
20 J. Lellouche, A. Friedman, J.-P. Lellouche, A. Gedanken and E. Banin, Nanomedicine, *Nanotechnology, Biology and Medicine*, 2012, **8**, 702; M. Eshed, J. Lellouche, E. Banin and A. Gedanken, *J. Mater. Chem. B,* 2013, **1**, 3985.
21 S. Fujihara, M. Tada and T. Kimura, *J. Sol–Gel Sci. Technol*., 2000, **19**, 311.
22 M. Tada, S. Fujihara and T. Kimura, *J. Mater. Res.,* 1999, **14**, 1610.
23 S. Fujihara, Y. Kadota and T. Kimura*, J. Sol–Gel Sci. Technol*., 2002, **24**, 147.
24 S. Fujihara, H. Naito and T. Kimura, *Thin Solid Films*, 2001, **389**, 227.
25 I. M. Thomas, *Appl. Opt.*, 1988, **27**, 3356.
26 K. Richter, A. Birkner and A.-V. Mudring, *Angew. Chem. Int. Ed.,* 2010, **49**, 2431-2435; K. Richter, P. S. Campbell, T. Baecker, A. Schimitzek, D. Yaprak and A.-V. Mudring, *Physica Status Solidi B: Basic Solid State Physics*, 2013, **250**, 1152.
27 D. König, K. Richter, A. Siegel, A.-V. Mudring and A. Ludwig, *Adv. Funct. Mater.* 2014, **24**, 2049–2056.
28 N. von Prondzinski, J. Cybinska and A.-V. Mudring, *Chem. Commun*., 2010, **46**, 4393.
29 S. B. Kalidindi and B. R. Jagirdar, *J. Phys. Chem. C*, 2008, **112**, 4042; S. Cingarapu, Z. Yang, C. M. Sorensen and K. J. Klabunde, *Chem. Mater*., 2009, **21**, 1248.30
30 P. L. Timms, Angew. Chem., 1975, **87**, 295; U. Zenneck, Angew. Chem., 1990, **102**, 171; P. D. Hooker and K. J. Klabunde, Chem. Mater., 1993, **5**, 1089; K. J. Klabunde, P. L. Timms, P. S. Skell and S. Ittel, Inorg. Synth., 1979, **19**, 59; P. L. Arnold, F. G. N. Cloke, P. B. Hitchcock and J. F. Nixon, J. Am. Chem. Soc., 1996, **118**, 7630.
31 P. D. Hooker and P. L. Timms, J. Chem. Soc. 1988, **158**; P. Hooker, B. J. Tan, K. J. Klabunde and S. Suib, *Chem. Mater*., 1991, **3**, 947.
32 *Acta Crystal. B* 1976, **32**, 2200.
33 C. Lorbeer, J. Cybinska, A.-V. Mudring, *Chem. Commun.*, 2010, **46**, 571.
34 C. Lorbeer, F. Behrends, J. Cybinska, H. Eckert, A.-V. Mudring, *submitted*.
35 V. Sudarsan, F. C. J. M. van Veggel, R. A. Herring, M. Raudsepp, *J. Mater. Chem*., 2005, **15**, 1332.