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Rare earth doped core-shell particles as phosphor for warm-white light-emitting diodes

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Light-emitting diodes (LEDs) are efficient, energy-saving light sources. Unfortunately, designing phosphors for LEDs that emit warm white light is not straightforward. We solvothermally prepared rare earth doped alkaline earth sulfides with a core-shell structure in order to obtain a physical separation between different dopants (europium and cerium). Cathodoluminescence of a single phosphor particle in an electron microscope proves simultaneous Eu^{2+} and Ce^{3+} broad band emission. The emission color can be tuned by variation of the composition, core size and shell thickness. Upon excitation of $SrS:Eu^{2+}$-$SrS:Ce^{3+}$ core-shell structures at 430nm, white light emission with good color rendering and a color temperature around 3000K is obtained.

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White light-emitting diodes (LEDs) are highly eco-friendly light sources, with a much lower energy consumption than incandescent or even fluorescent lamps [1,2]. The development of white LEDs embarked with the combination of a blue-emitting LED and a yellow phosphor ($Y_3Al_5O_{12}$:Ce) [3]. Although this simple approach using only one phosphor material is robust and straightforward, YAG:Ce lacks a significant output in the green and red region of the visible spectrum, leading to a relatively poor color rendering. Furthermore, warm white LEDs cannot be prepared in this way [3].

There are two pathways to improve the color rendering of a phosphor converted white LED: (1) the combination of two or more phosphor materials [4,5] and (2) a single phosphor with a broad emission spectrum. The first method allows color temperature tuning but the main disadvantages are the necessity for a homogeneous and reproducible phosphor mixture and the often different thermal behavior of the phosphors. For the second method, a broad emission spectrum can be obtained when multiple lattice sites are available for the dopants or by using different dopant ions in a single host. A broad band emission of the phosphor materials is favorable for achieving a high color rendering index (CRI). Also a good overlap of the phosphor's excitation spectrum and the LED's emission spectrum is required. Finally, to prevent saturation in high flux devices, fast decay times are necessary [6]. These requirements favor the broad band emitting rare earth ions (e.g. Ce^{3+} and Eu^{2+}) over ions like Eu^{3+}, Tb^{3+} and Mn^{2+}.

Although in recent years considerable attention was devoted to the development of Eu^{2+} and Ce^{3+} doped (oxy)nitride phosphors [7-9], rare earth doped alkaline earth sulfides are still valuable candidates for wavelength conversion of LEDs for lighting applications [10]. A disadvantage, however, is their limited stability against moist air, but this can be efficiently improved by covering the phosphor's surface with a protective coating [11].

By doping these sulfides with Eu^{2+} or Ce^{3+} ions, the luminescence can be varied over a wide wavelength range (Fig. 1), with a higher emission energy for Ce^{3+} compared to Eu^{2+}, when doped in the same host [12]. For example, SrS:Eu^{2+}[1%] has an emission peak at 620 nm, with a full-width-half-max (FWHM) of about 80 nm and SrS:Ce^{3+} peaks at 500 nm with a FWHM of 105 nm. This implies that broad (and potentially white) emission might simply be obtained by doping with Eu^{2+} and Ce^{3+} simultaneously. Unfortunately, codoped samples do not show any Ce^{3+} emission due to energy transfer from Ce^{3+} to Eu^{2+} (Fig. 1 (b)) [13]. This problem can be solved by physically separating both types of dopants. This separation is achieved in the present work by the synthesis of SrS:Eu-SrS:Ce core-shell particles. In the present work we report on particles with a core and a shell consisting of SrS:Eu and SrS:Ce, respectively. With this configuration, one reduces the fraction of the blue-green emission of Ce^{3+} being absorbed by the Eu^{2+} doped phosphor. Many variations of this core-shell system can be thought of, using different hosts and/or dopants. Therefore, this work presents a generic method to obtain physical separation between different dopants in the same, or compositionally similar, host matrices.

The SrS:Eu-SrS:Ce core-shell particles were prepared with a solvothermal synthesis method [14]. The starting materials were anhydrous $SrCl_2$ (99.5% Alfa Aesar), dried $EuCl_3 \cdot nH_2O$ (99.9%), $CeCl_3 \cdot nH_2O$ (99.9% Alfa Aesar) and sulfur powder. Ethylenediamine ($C_2H_8N_2$, 99% Alfa Aesar) was used as solvent.

To prepare the cores, $SrCl_2$ and an appropriate amount of $EuCl_3$ and sulfur powder (in 15% excess) were added into a Teflon-lined autoclave (Autoclave France Eze Seal) and cooled ethylenediamine was added. The autoclave was maintained at 200°C for 18 h and then naturally cooled to room temperature. A synthesis temperature of 200°C gives a good compromise between the size of the crystallites and the yield of the product. After cooling down, the solvent was separated from the reaction product, which precipitated at the bottom of the Teflon-lined autoclave. The unreacted chlorides and sulfur in the autoclave were removed by washing the reaction product with absolute ethanol. Subsequently, these cores were introduced again in the Teflon-lined autoclave together with $SrCl_2$, $CeCl_3$ and sulfur powder (in 15% excess) and a similar synthesis and separation method was used.

The photoluminescence of the particles was studied with a fluorescence spectrometer (FS920, Edinburgh Instruments). Cathodoluminescence (CL) was performed in a scanning electron microscope (SEM, FEI Quanta 200), using a fiber coupled QE65000 spectrometer (Ocean Optics).

The emission spectrum of core-shell $SrS:Eu^{2+}$-$SrS:Ce^{3+}$ particles covers the entire visible spectrum as it combines the orange-red emission of $SrS:Eu^{2+}$ and the bluish-green emission of $SrS:Ce^{3+}$ (Fig. 1). To obtain white light with a specific color temperature, several approaches can be used, such as a variation of the dopant concentration, different core-shell geometries or a change in the chemical composition of the host matrices. More specifically, an increase in the Ce^{3+} concentration in SrS leads to a red-shift of the Ce^{3+} emission [3]. The relative contribution by core and shell to the combined emission spectrum can be changed by tuning the diameter of the core and the thickness of the shell. The emission of $SrS:Eu^{2+}$ can be red-shifted when substituting Sr by Ca [15,16]. Fig. 2 shows the influence of the $SrS:Ce^{3+}$ shell thickness, while keeping the diameter of the cores fixed. Increasing the shell thickness clearly intensifies the emission in the short wavelength range. In this work, low dopant concentrations were used to reduce the effects of thermal quenching (see below). The associated relatively low absorption of the excitation light did not allow determining the quantum efficiency of the luminescent particles in a sufficiently accurate way. Nevertheless, growing shells composed of $SrS:Ce^{3+}$ around $SrS:Eu^{2+}$ core particles led to similar integrated PL intensities compared to the core particles.

The excitation spectra of the core-shell particles are displayed in Fig. 3. When monitored at an emission wavelength of 480 nm, the typical $SrS:Ce^{3+}$ excitation spectrum is obtained (with relatively narrow bands at 282 nm and 430 nm). For the red part of the emission spectrum, we find an excitation spectrum which is characteristic for $SrS:Eu^{2+}$, with a similar host-related band at 280 nm and a very broad excitation band in the blue-green part of the spectrum. Interestingly, the optimal excitation wavelength coincides for both core and shell material at about 430 nm, allowing efficient pumping by common, deep-blue to violet LEDs. By comparing the excitation spectra for Eu^{2+} in SrS:Eu particles and in core-shell $SrS:Eu^{2+}$-$SrS:Ce^{3+}$ particles (Fig. 3), one can observe the effect of a partial absorption of the blue-green Ce^{3+} emission generated in the shell by Eu^{2+} luminescent centers in the core. This leads to an enhanced excitation for Eu^{2+} in the 400 to 450nm range.

The photoluminescence results alone are not sufficient to prove that core-shell structures were effectively obtained, as opposed to a mere physical mixture of SrS:Eu and SrS:Ce particles. Therefore, the emission spectrum of single particles was evaluated by SEM-CL (cathodoluminescence spectroscopy in a scanning electron microscope) [17]. A representative ensemble of about 85 particles is shown in Fig. 4(a), along with the corresponding CL emission spectrum (Fig 4(b)). The average size of the particles is 2.06 µm (σ = 0.30µm), which is in the same order as the penetration depth of electrons at 10 to 25 keV as used in SEM. Consequently, the internal structure of these luminescent particles can be probed by performing CL at different electron energies. For the ensemble, the double CL emission band from Ce^{3+} and the Eu^{2+} emission at 610nm is seen. For the area shown in Fig. 4(a), the CL emission spectrum was then mapped in a 128 by 100 grid. The barycenter of the emission spectrum at each point is shown in Fig. 4(c) for the case of 25keV electrons. The emission of all particles lies well in between the values one would expect for particles consisting only of $SrS:Ce^{3+}$ or $SrS:Eu^{2+}$, with an average of 568nm (σ = 7nm) for the barycentric emission wavelength for the ensemble shown in Fig. 4(a). Although this narrow distribution is already a strong indication of a core-shell structure for all particles, this can further be proven by changing the accelerating voltage and thus altering the penetration depth of the beam. Upon increasing the acceleration voltage from 10 to 25keV, a red-shift of the spectrum due to the increased contribution of the core to the emission (being composed of $SrS:Eu^{2+}$) is expected. This is indeed observed for both the ensemble (Fig. 4(b)) and at the level of individual particles (Fig. 4(d)).

If this core-shell structure is used, it is possible to obtain a broad emission spectrum which can yield white light emission upon proper choice of dopants, hosts and the core-shell geometry. For example, when exciting the core-shell particles shown in Fig. 2 (with the thickest shell) at 430nm, the emission spectrum corresponds to a color temperature of 3200K (CRI = 85), albeit with a large deviation from the black body locus (duv = 0.019). By allowing some leakage of the excitation light, one obtains pure white light with a color temperature of 3400K (CRI = 90, duv = 0). The set of particles shown in Fig.4 has a color temperature of 2800K (CRI = 85) under excitation at 430nm.

In Ref. 9 six main requirements for conversion phosphors were discerned, against which phosphor compositions should be evaluated, dealing with i) the shape and position of the emission bands, ii) the excitation wavelength and efficiency, iii) the saturation behavior for high excitation intensities, iv) the quantum efficiency, v) the thermal quenching behavior and finally vi) the stability. The proposed core-shell concept features a broad (and tunable) emission covering the entire visible spectrum, which can be efficiently excited by violet-to-blue LEDs due to the strong 4f-5d absorption in Ce^{3+} and Eu^{2+}. Because of the short decay times of Ce^{3+} and Eu^{2+}, conversion saturation is not an issue. The quantum efficiency of Eu^{2+} in $Ca_{1-x}Sr_xS$ was reported to be as high as 80% [15], provided the dopant concentration can be kept low enough. Furthermore, Eu-doped binary sulfides have already been used as conversion phosphors for LEDs [10]. Similarly, the thermal quenching behavior is strongly influenced by the dopant concentration [15]. For a specific set of SrS:Eu[0.1%]-SrS:Ce[0.25%] core-shell particles, the total emission intensity dropped by 40% at

400K, compared to room temperature along with a color shift due to the slightly different thermal quenching behavior for the Ce^{3+} and the Eu^{2+} emission. This relatively strong thermal quenching behavior is typical for (bulk) rare earth doped SrS, not only for the solvothermally prepared particles[10,15]. Ways to improve the thermal quenching behavior are currently being investigated. Finally, the stability of the core-shell particles under ambient conditions (temperature and humidity) is good, although this can considerably be enhanced by a conformal protective coating [11].

In this work we proposed a generic method to obtain white emitting phosphors, based on the physical separation of Ce^{3+} and Eu^{2+} dopant ions in a core-shell structure. They can efficiently be excited in the violet to blue part of the emission spectrum, allowing the use as color conversion phosphor in white LEDs. By modifying the chemical and structural composition of the core-shell structure, it is possible to obtain white light emission of variable color temperature, while maintaining a good color rendering, due to the broadness of the Ce^{3+} and Eu^{2+} emission bands. Finally, the relatively narrow size distribution of the phosphor particles is an advantage for color reproducibility of phosphor coated LEDs.

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FIG. 1: Photoluminescence emission spectra at an excitation wavelength of 410 nm of **(a)** SrS:Ce^{3+}, **(b)** SrS:Eu^{2+},Ce^{3+} , **(c)** SrS:Eu^{2+} particles and **(d)** SrS:Eu^{2+}-SrS:Ce^{3+} core-shell particles.

FIG. 2: Photoluminescence emission spectra at an excitation wavelength of 410 nm of core-shell particles SrS:Eu(1%)-SrS:Ce(1%) with different core-shell thickness ratios. The average size of the core-shell particles, as determined by SEM, is **(a)** 2.5µm, **(b)** 3.5µm and **(c)** 5.0µm, using cores with an average size of 1.25µm.

FIG. 3: Excitation spectra of core-shell particles SrS:Eu (0.1%)-SrS:Ce(0.25%) at an emission of 480 nm (dotted line) and at 620 nm (full line). The excitation spectrum, monitored at 620nm, for SrS:Eu (core) particles is shown for comparison (dashed line).

FIG. 4: SEM-CL results on SrS:Eu-SrS:Ce core-shell particles. **(a)** Secondary electron image of an ensemble of particles. **(b)** CL spectrum of the same ensemble at 10 and 25keV. **(c)** Barycentric emission wavelength at 10 keV. **(d)** Shift of the barycentric emission wavelength upon changing the excitation voltage from 10 keV to 25 keV.

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Fig.1

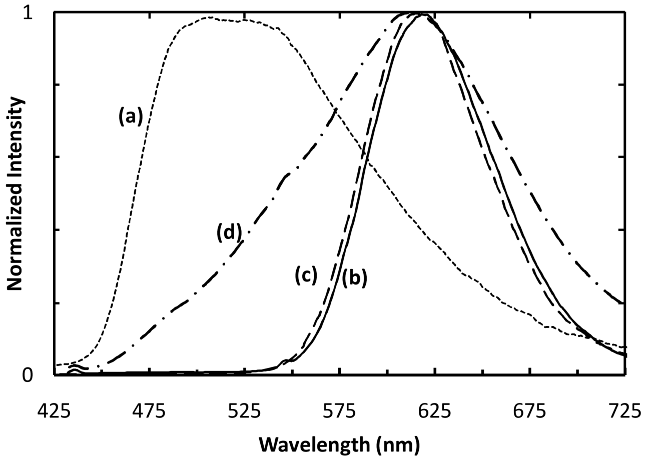


Fig.2

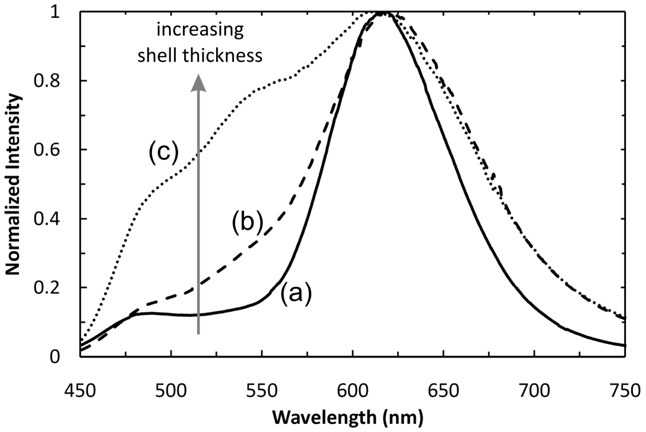


Fig.3

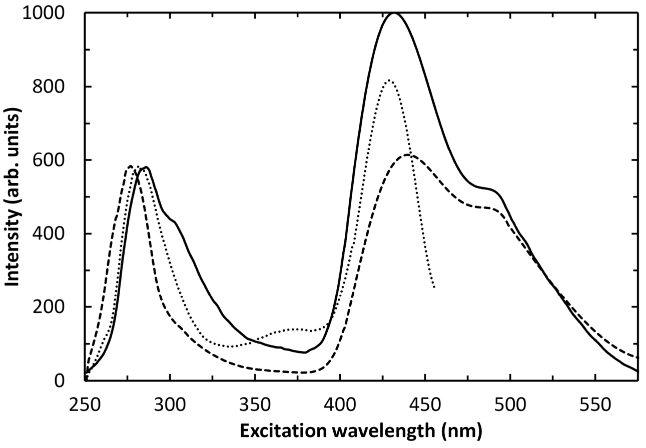
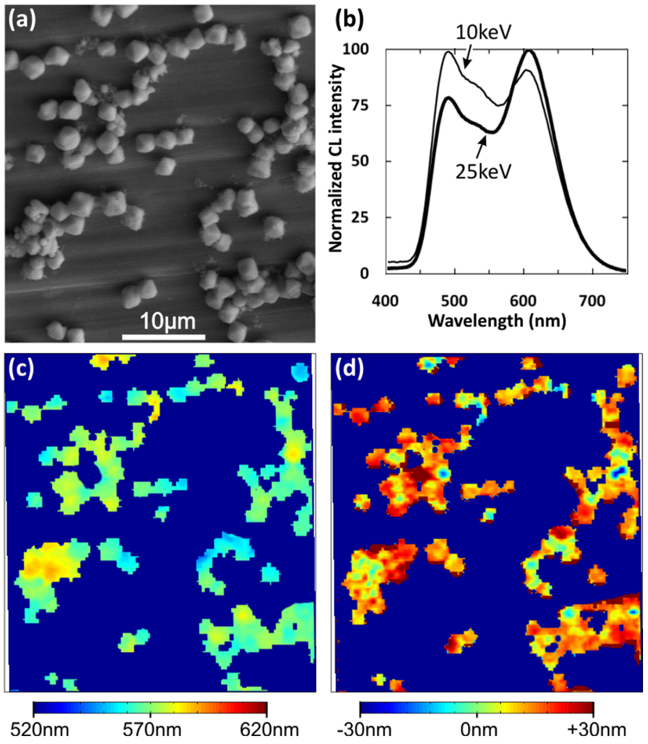


Fig. 4.


(a)
10µm
(b)
10keV
25keV
Normalized CL intensity
100
75
50
25
0
400
500
600
700
Wavelength (nm)
(c)
(d)
520nm
570nm
620nm
-30nm
0nm
+30nm