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Amorphous $Si_3B_3N_7$ Ceramic as a Versatile Host for Inorganic Phosphor Activators

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Among the inorganic phosphors used in advanced lighting technologies, rare-earth doped nitridosilicates have attracted significant attention because they exhibit superior photoluminescence properties in connection with high thermal, chemical, and mechanical stabilities. All of these materials are crystalline, which imposes substantial limitations in discovering new phosphors, since the activators to be included in the host matrix need to comply closely with the respective lattice sites, at least with respect to charge and size. As an approach to overcome such implications, an amorphous matrix, namely $Si_3B_3N_7$, is suggested as a universal nitride-based host accessible to (co)dope various activators, e.g., Eu^{2+}, Ce^{3+} and Tb^{3+}. Unlike crystalline phosphors, in the amorphous $Si_3B_3N_7$ matrix, activator ions do not replace any atom from the random network host; instead, they act as network modifiers. The synthesis of this new class of amorphous phosphors is based on a precursor route, enabling high purities, and avoiding harsh temperature treatments.

1. Introduction

In comparison with the conventional lighting technologies, e.g. incandescent and fluorescent lamps, LED-based solid state lighting devices provide remarkable improvements in terms of durability, compactness, designability, environmental friendliness and, most importantly, energy efficiency.[1–6] In this recent lighting technology, wavelength conversion phosphors play a crucial role, and great efforts have been made to explore new phosphors with improved overall performance. Luminescent materials described up to now are mainly based on crystalline matrices, where photoluminescence is achieved by replacing suitable ions of the crystalline host with luminescent ones, commonly Eu^{2+}, Ce^{3+} or Tb^{3+}, which are called activators. The chemical and crystal chemical properties of the activator ions, in particular size and charge, must correspond to those of the cations to be substituted in the host lattice. Obviously, these requirements impose limitations in identifying suitable combinations of crystalline hosts and activator ions. As another disadvantage, previously described luminescent materials are commonly produced via solid state reactions at high temperatures requiring long reaction times, including repeated grinding and heating cycles.[3,7]

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Among those phosphors considered for applications are rare-earth doped nitridosilicate based materials, which exhibit superior chemical, thermal, and radiation stability compared to oxide, sulphide and halide based phosphors or combinations thereof.[8–15] In particular, the luminescent properties of rare earth ions, which emit radiation via 5d→4f transitions, such as Eu^{2+} and Ce^{3+}, are dramatically affected by the large covalency of N^{3-} ions. As a result, the centres of gravity of the 5d levels are shifted to positions lower in energy (nephelauxetic effect),[16] leading to longer wavelength emission bands, providing a red component needed for the fabrication of white-LEDs.

With the aim of circumventing the drawbacks mentioned inherent to doped crystalline luminescent materials, and at the same time keeping the advantages of high thermal and radiation stability of nitridosilicates, and also of nitrogen ions as coordinating ligands, we have developed the novel approach of using nitride based inorganic random networks as hosts, for which the cationic network sites are not accessible to the rare earth activator elements because of incompatible size and bonding properties. Instead, the activator elements act as network modifiers, with the far reaching consequence that activators of any size and charge can be easily incorporated in quite variable concentrations. We regard the further options of co-doping two or more activators and sensitizers into the same matrix as a substantial advantage over the conventional approaches based on crystalline materials. Here, we report on the realization of such an innovative concept, and present a novel family of phosphors based on a highly durable amorphous $Si_3B_3N_7$[17,18] matrix doped with rare earth elements.[19]

In order to demonstrate the versatility of amorphous $Si_3B_3N_7$ as a host matrix, Eu^{2+}, Ce^{3+} and Tb^{3+} and combinations thereof have been included as activators. The new materials have been synthesized along a sol-gel process in the ammono system.[20]

2. Results and Discussion

Tri(chlorosilylamino)dichloroborane (TADB, $Cl_3Si\text{-}NH\text{-}BCl_2$) serves as a single source precursor.[17,18,21] It is subjected to ammonolysis and polycondensation with liquid ammonia, in which europium metal is dissolved, or rare earth metal complexes, i.e. $RE[N(Si(CH_3)_3)_2]_3$, where RE = Eu, Ce and Tb, are

suspended. Subsequent pyrolysis of the polymeric intermediates yields the desired inorganic phosphors.

As-synthesized rare earth (co)doped $Si_3B_3N_7$ ceramic powders are air-stable and X-ray amorphous (Supporting Information, Figure S1). They show similar structural fingerprints, like B-N and Si-N vibrations in the FT-IR spectra (Supporting Information, Figure S2), and high temperature stability (Supporting Information, Figure S3), as the undoped amorphous $Si_3B_3N_7$ network.[17] The bulk composition of the Eu^{2+}, Ce^{3+} and Tb^{3+} (co)doped ceramic powders corresponds to $Si_3B_3N_7$ with Eu, Ce and Tb contents, ranging from 0.3 to 11.4 weight percent, within the error limits of the elemental analysis (Supporting Information, Table S1).

Photoluminescence spectra of the Eu^{2+} doped amorphous $Si_3B_3N_7$ phosphors are presented in **Figure 1**a. These samples have a broad absorption band between 250 and 480 nm peaking between 340 and 365 nm. Furthermore, they show a broad emission band between 540 and 640 nm, depending on the doping concentration of Eu^{2+} ions, and an increasing full width at half maximum (FWHM) from 150 nm for 0.5 % (wt) to 190 nm for 11.4 % (wt) europium. When the europium concentration is raised, the maximum of the broad band shifts towards the red region of the spectrum, accompanied by a decrease in its intensity (Figure 1a and 1d). We associate shifting the emission maximum (also called red shift) values to energy transfer followed by reabsorption and reemission processes between two neighboring luminescent active centers,[23] a process that is gaining probability with increasing Eu^{2+} content.

Also for Ce^{3+} doped amorphous $Si_3B_3N_7$ ceramics, there is a strong excitation band at around 365 nm (Figure 1b). The excitation peak at 310 nm, emerging at significantly lower cerium content, is due to the amorphous $Si_3B_3N_7$ host matrix.[22] The respective emission spectra are characterized by broad bands of around 190 nm of FWHM values, with peak maxima varying from 520 to 580 nm, depending on the cerium concentration. An increase in cerium content causes a slight red shift in the emission.

Tb^{3+} doped $Si_3B_3N_7$ ceramics absorb strongly between 240 and 340 nm (**Figure 2**a). The Tb^{3+} emission lines at 480, 544, 580 and 620 nm are narrow, which is typical for the $^5D_4 \rightarrow {}^7F_j$ transitions of Tb^{3+} ions. These emission lines are dominating, particularly the one at 544 nm ($^5D_4 \rightarrow {}^7F_5$ transition), when the sample is excited between 250 and 290 nm, resulting in an intense green emission (Figure 2b). The line emissions from

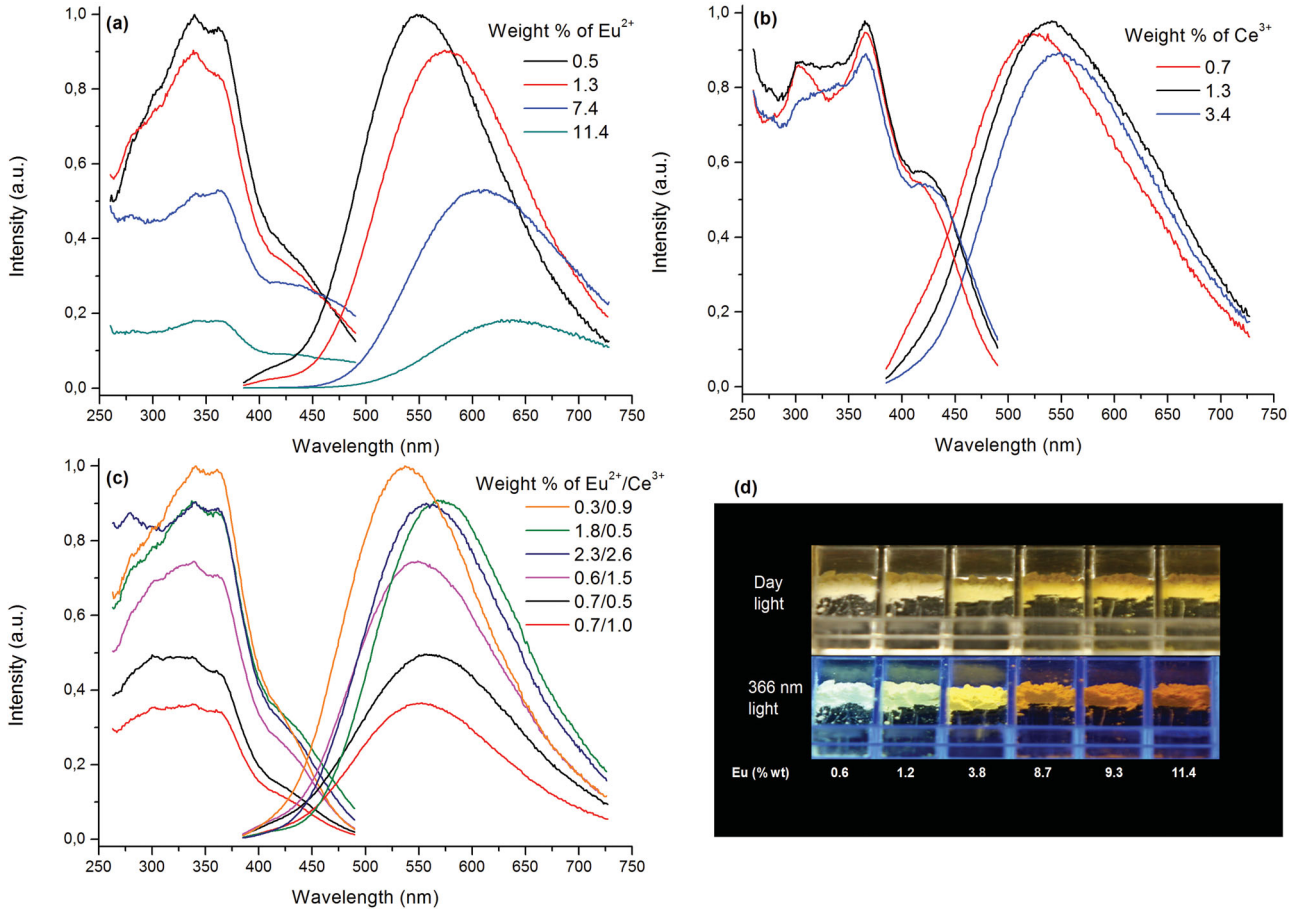

Figure 1. Photoluminescence spectra of a) Eu^{2+} doped, b) Ce^{3+} doped and c) Eu^{2+}/Ce^{3+} codoped amorphous $Si_3B_3N_7$ ceramics with varying rare earth content (in weight percent). d) Photograph of Eu^{2+} doped $Si_3B_3N_7$ ceramics with different Eu^{2+} content under day light and 366 nm excitation light in the dark.

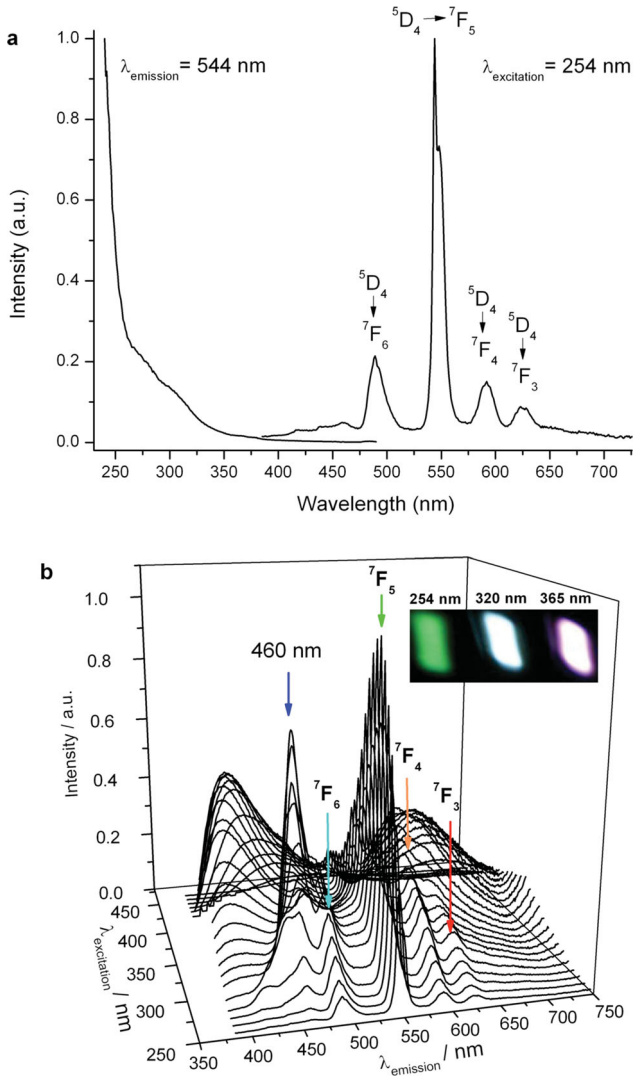

Figure 2. a) 2D and b) 3D photoluminescence spectra of Tb^{3+} doped amorphous $Si_3B_3N_7$ ceramic. The tuning of the emission color via excitation wavelength is depicted with the inset in (b).

the $^5D_3$ level of Tb^{3+} are commonly of weak or insignificant intensity in such a low concentration of Tb (Table S1), and we regard clustering of Tb^{3+} ions within the $Si_3B_3N_7$ matrix a possible explanation for such emissions (Figure 2).[24] When the sample is excited between 290 and 340 nm, an additional emission appears at 460 nm, intrinsic for the $Si_3B_3N_7$ matrix.[22] Combination of this blue emission with the line emissions produces intense white light. On the other hand, exciting the sample with 340 nm or higher wavelengths induces a violet emission only, intrinsic for the $Si_3B_3N_7$ matrix.[22]

The Ce^{3+} and Eu^{2+} codoped $Si_3B_3N_7$ phosphors have strong and broad absorption bands with maxima between 300 and 370 nm, and emit between 525 and 575 nm with FWHM values ranging between 155 and 180 nm, depending on the concentrations of the rare earth ions (Figure 1c). For those Ce^{3+} and Eu^{2+} codoped samples, where the Eu^{2+} content exceeds the Ce^{3+} concentration, the emission maximum is shifted towards the red region of the spectrum, while for a reverse ratio of Eu^{2+}/Ce^{3+} a shift towards the blue region of the spectrum is observed. **Figure 3** compares the photoluminescence spectra of Tb^{3+} and Ce^{3+} codoped samples with the singly Tb^{3+} or Ce^{3+} doped ones. The codoped sample shows both, absorptions and emissions, due to Ce^{3+} and Tb^{3+} ions superimposed.

Photoluminescence investigations of the rare earth (co) doped $Si_3B_3N_7$ phosphors have revealed that the rare earth elements are present in their trivalent states, except for europium, which is always in the divalent state. Accordingly, broad emission bands result from 5d→4f transitions for Ce^{3+} and Eu^{2+} (co) doped, and narrow 4f→4f emission lines for Tb^{3+} (co)doped, $Si_3B_3N_7$ phosphors in the visible region of the spectrum. While the transitions between well shielded 4f-related states are but little affected by variations of the crystal field, the local environment has a dramatic effect on the luminescence of Ce^{3+} and Eu^{2+} ions resulting from the respective d→f transitions.[25]

Compared to crystalline nitridosilicate-type host lattices, the presence of covalent B-N bonds in $Si_3B_3N_7$ further reduces the effective charge of nitrogen due to back donation of electron density to adjacent boron atoms. The resulting smaller ligand field splitting causes shifts of both the d → f absorption and emission of the activator ions to shorter wavelengths. To illustrate, Eu^{2+} doped amorphous $Si_3B_3N_7$ phosphors show maximal emission at 550 nm, whereas Eu^{2+} doped crystalline $M_2Si_5N_8$ (M = Ca, Sr and Ba)[9] phosphors emit in the orange-to-red region of the spectrum.

Interestingly, the Eu^{2+} and Ce^{3+} (co)doped $Si_3B_3N_7$ phosphors absorb best at 365 nm, which corresponds to the maximum emission of pure GaN LEDs. The new phosphors emit broadly, covering a large window in the visible region of the spectrum, and are emitting already warm white light when excited with 365 nm light. Therefore, they are good candidates for down-converting near-UV light as provided by GaN LEDs into visible light, which is regarded the future of the solid state lighting technology. The large FWHM values, i.e. between 150 and 190 nm, of Eu^{2+} and Ce^{3+} (co)doped amorphous $Si_3B_3N_7$ phosphors can be understood in terms of inhomogeneous line broadening caused by the amorphous host. This results in better color rendering properties compared to a conventional YAG:Ce^{3+} yellow phosphor with a maximal FWHM of 130 nm.[3]

The novel phosphors based on a $Si_3B_3N_7$ random network show substantial advantages over the crystalline ones. First of all, all starting materials can be easily and efficiently purified via either distillation (TADB, hexane and europium metal) or sublimation techniques ($RE[N(Si(CH_3)_3)_2]_3$, where RE = Ce, Eu and Tb), and the contamination level in the final product can be kept at an extremely low level, which is crucial for optimal luminescent performance. Since the production method of the new phosphors is based on a reaction in liquid phases (ammono sol-gel process), highly homogeneous distributions of the activator ions in the final ceramic matrix can be realized. In contrast, the crystalline phosphors are prepared via solid state reactions, where it is difficult to suppress contamination and which include tedious handling and intermediate grinding steps, and more critically, long reaction times at high temperatures, sometimes even applying high pressure. For the $Si_3B_3N_7$ based phosphors, however, pyrolysis of the polymeric intermediate at 1200 °C for 3 hours is already sufficient to

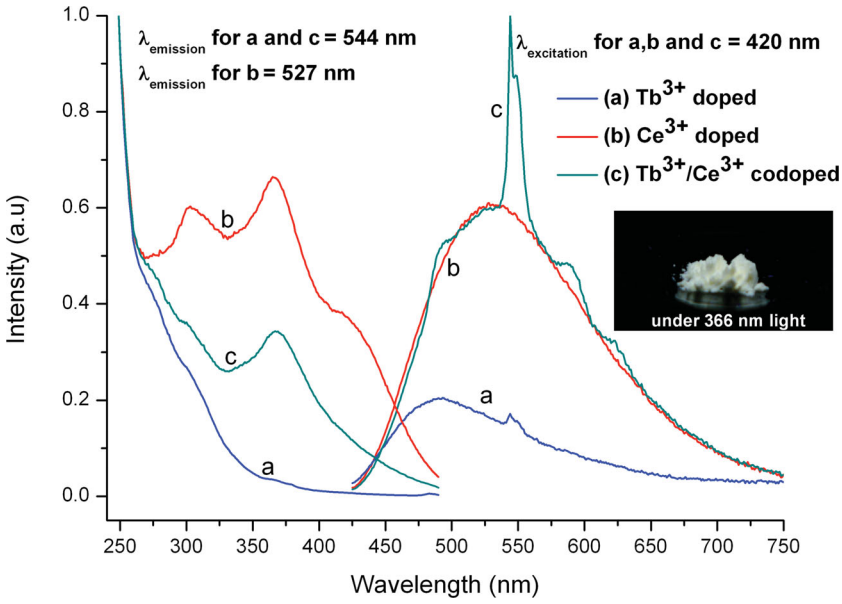

Figure 3. Photoluminescence spectra of Ce^{3+}/Tb^{3+} codoped amorphous $Si_3B_3N_7$ ceramic. (a) represents the excitation (at 544 nm emission) and emission (at 420 nm excitation) spectra of Tb^{3+} doped, (b) the excitation (at 527 nm emission) and emission (at 420 nm excitation) spectra of Ce^{3+} doped, and (c) the excitation (at 544 nm emission) and emission (at 420 nm excitation) spectra of Ce^{3+}/Tb^{3+} codoped amorphous $Si_3B_3N_7$ phosphors. The inset picture shows the Ce^{3+}/Tb^{3+} codoped amorphous $Si_3B_3N_7$ under 366 nm light in the dark.

obtain the desired products. Moreover, any unreacted chemicals (excess NH_3, hexane) and side-products (NH_4Cl) can easily be recycled or removed, providing environmental and economical benefits. As another beneficial feature of the amorphous phosphors, more than one type of activator ions can be simultaneously incorporated into the amorphous $Si_3B_3N_7$ host, without needing to worry about any lattice symmetry, or size and charge of the ions. As a remarkable result, the emission color can be tuned by codoping various activator and sensitizer ions, and fabricating a white-LED by employing only *one* primary emitter supplied with one phosphor is rendered possible. Last but not least, the intermediate polymeric stage brings the advantage in further processing that the intermediate rare earth doped polyborosilazanes may be directly coated on a LED and then pyrolysed, for example by laser beam heating, without requiring any additional resin coating.

3. Conclusions

With rare earth doped amorphous $Si_3B_3N_7$ ceramics, we present a new class of nitride based inorganic phosphors, along with its basic spectroscopic characterization. We have demonstrated in this study that amorphous $Si_3B_3N_7$ ceramic can indeed host various activator ions, e.g. providing new Eu^{2+} and Ce^{3+} (co)doped amorphous $Si_3B_3N_7$ phosphors featuring advantageous photoluminescence properties, e.g. they can be excited efficiently between 340 and 365 nm and have a broad emission band centered around 550 nm. Thus, Eu^{2+} and Ce^{3+} (co)doped amorphous $Si_3B_3N_7$ ceramics are very promising candidates as luminescent materials to be used in white LEDs based on GaN primary emitters.

4. Experimental Section

Synthesis of Eu^{2+}, Ce^{3+}, and Tb^{3+} (Co)doped Amorphous $Si_3B_3N_7$ Phosphors: All reactions were carried out under an inert atmosphere (argon) in rigorously dried reaction apparatus and solvents. The phosphors based on amorphous $Si_3B_3N_7$ ceramics were prepared by following the conventional synthesis method for the amorphous $Si_3B_3N_7$ ceramic from the single source precursor molecule, tri(chlorosilylamino)dichloroborane (TADB), with some minor modifications. TADB was synthesized according to the literature via a two-step reaction.[17] TADB was reacted, under a slow argon flow and at intense string, with liquid ammonia (99.999%, Westfalen AG, Münster, Germany) at −76 °C (in a dry ice and ethanol mixture), in which activators were included. In case of Eu^{2+}, europium metal was dissolved in liquid ammonia. Alternatively, commercially available $Eu[N(Si(CH_3)_3)_2]_3$ has been used as a europium source. Since cerium and terbium metals are not soluble in liquid ammonia, $Ce[N(Si(CH_3)_3)_2]_3$ and $Tb[N(Si(CH_3)_3)_2]_3$ were used for Ce^{3+} and Tb^{3+} doping, respectively. Hexane was added as a co-solvent in order to enhance mixing during the reaction, warranting an optimal homogeneous distribution of the rare earth ions in the final ceramic.

In a typical synthesis, around 50 mL liquid ammonia was condensed on 0.051 g freshly distilled europium metal at −76 °C (dry ice and ethanol mixture) in a three-neck flask, resulting in a dark blue solution. About 125 mL freshly distilled hexane, which is immiscible with liquid ammonia, was added into the flask. A solution of 5 mL TADB in 25 mL hexane was added dropwise into the flask containing the mixture of liquid ammonia and hexane under a slow argon flow. After the reaction was completed, the flask was allowed to reach room temperature under strong stirring. Subsequently, hexane was removed under vacuum into a cold trap. The solid residue consists of NH_4Cl and partially crosslinked polyborosilazane. The NH_4Cl salt was sublimed off at 210 °C under vacuum ($P \approx 10^{-3}$ mbar). Almost salt-free as-obtained rare-earth doped polyborosilazane was loaded into a dried BN crucible in an argon filled glove-box (MB 200B, M.Braun GmbH, Garching, Germany) and then heated to 900 °C (warmed to 300 °C with 100 °C/h rate, kept at this temperature for 3 h, then heated to 900 °C with 100 °C/h rate, dwelled at 900 °C for 3 h and cooled to room temperature with the same rate) under ammonia flow inside a quartz tube in a horizontal furnace. Finally, the obtained ceramic material was calcined in a flow of N_2 or N_2 (95 %) / H_2 (5 %) at 1200 °C, from room temperature to 1200 °C with 10 °C/min rate, dwelled at 1200 °C for 3 h and cooled to room temperature with 10 °C/min rate (Carbolite STF 15/50, Carbolite, Hope Walley, UK).

Photoluminescence Measurements: Photoluminescence spectra were recorded using a Fluorolog-3 Model FL3-22 spectrometer (Horiba Jovin Yvon, Bensheim, Germany) equipped with a 450-W xenon light source, two double grating monochromators in the excitation and emission paths in an "L" configuration (Czerny Turner design), a T-box sample compartment module with a flat sample holder and a front face emission collector, and a photomultiplier detector (room temperature R928P detector). A black anodized aluminum sample holder was used, in which powder samples were fixed in a space of $12 \times 6 \times 1.6$ mm^3 with the help of 0.2 mm thick suprasil glass. The excitation and emission spectra were recorded in the range between 260–490 nm and 385–750 nm, respectively. The excitation and emission slit widths were adjusted between 0.55 and 0.68 nm in order not to exceed the linear range of the R928P detector, that is 2.10^6 counts per second. In order to avoid second-order peaks in the emission spectra, a 385 nm cut-off filter was used. All emission spectra were corrected with regard to detector

sensitivity and all excitation spectra were corrected with regard to the intensity of xenon lamp. Data acquisition and analysis were performed by the software FluorEssence, created by Horiba Jobin Yvon.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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