Inorg. Chem. **2007**, *46*, 7235–7237

Inorganic Chemistry
Communication

Efficient X-ray Generation of Sm^{2+} in Nanocrystalline BaFCl/Sm^{3+}: a *Photoluminescent* X-ray Storage Phosphor

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Received December 21, 2006

Efficient X-ray generation of relatively stable Sm^{2+} centers is observed in nanocrystalline Sm^{3+}-activated BaFCl, as prepared by a one-step wet chemical reaction. The conversion efficiency is ≈50 000 times higher than that in microcrystalline BaFCl/Sm^{3+} prepared at 900 °C. The Sm^{2+} centers, and hence the radiation dose, can be directly monitored by the narrow photoexcited ^5D_J–^7F_J f–f luminescence lines. The relatively high efficiency of Sm^{2+} generation appears to be directly linked to the particle size.

X-ray storage phosphors are materials capable of recording an image created by the absorption of X-ray radiation; electronic and structural changes occur upon exposure to ionizing radiation. The mechanism is usually based on the capture of radiation-generated electrons and holes in traps. After *photostimulation* (usually in the red) electron−hole recombination occurs, yielding visible light (usually in the blue) proportional to the dose of ionizing radiation.[1−5] The best-known phosphor is BaF(Br_x,I_{1-x})/Eu^{2+} with a small fraction ($1 - x$) of iodide.[1] Upon exposure to ionizing radiation, electron−hole pairs are created. It is thought that F and Br vacancies act as the electron traps, leading to the formation of F centers.[1−3] Upon excitation of the F centers at 2.1 or 2.5 eV for the F(Br^-) and F(F^-) centers, respectively, the electrons recombine with the holes and transfer excitation energy to the activator, Eu^{2+}, yielding broad $4f^65d \rightarrow 4f^7$ emission at about 390 nm. The main commercial applications of X-ray storage phosphors are in the field of computed radiography[4] because the sensitivity exceeds that of a conventional scintillator−screen system by at least an order of magnitude[2] and in dosimetry of ionizing radiation.[5] Notwithstanding their recent success, currently available X-ray storage phosphors still suffer from some disadvantages, including rapid erasure of the information upon exposure to ambient light, fading as a result of spontaneous or thermally induced electron−hole recombinations and the limited signal-to-noise ratio in the readout process.[1−5]

More importantly, there is a prevailing effort to improve the resolution and sensitivity of storage phosphors. The latter is of high importance in preventive health-care measures such as breast-screening programs, where it is most desirable to reduce the applied X-ray dose by at least an order of magnitude.[6,7] Higher efficiency storage phosphors, applied to imaging plates, may enable such a reduction.

We have recently discovered that *nanocrystalline* Sm^{3+}-activated BaFCl displays efficient X-ray generation of Sm^{2+} and hence may have some potential as a directly *photoexcitable* (photoluminescent) storage phosphor.[8]

The preparation of nanocrystalline BaFCl/Sm^{3+} is based on the reaction of two aqueous solutions. Hydrated barium chloride, $BaCl_2{\cdot}2H_2O$, and samarium chloride, $SmCl_3{\cdot}6H_2O$ (0.5 mol %), salts were added to water and dissolved under stirring to prepare a solution with a $BaCl_2$ concentration of 0.4 mol/L. The solution was kept at room temperature (20−25 °C). Then the same volume of an aqueous solution of ammonium hydrogen difluoride, $NH_4F{\cdot}HF$, with a concentration of 0.2 M was added to the solution under vigorous stirring. The obtained nanocrystalline precipitate was separated from the solution by centrifugation and subsequent decanting of the nascent solution and then dried at a temperature of 70 °C. The process yields nanocrystalline powder of the Sm^{3+}-activated BaFCl phosphor with the space group $P4/nmm$ (D_{4h}^7) as verified by powder X-ray diffraction. There is no reducing agent in the solution, and thus it is safe to assume that the Sm is introduced into the lattice in the 3+ oxidation state. However, a large fraction of the Sm^{3+} ions will remain in the nascent solution, and hence the 0.5% is a *nominal* concentration only.

From powder diffraction, the main crystal grain size of the phosphor was estimated to be ∼150 nm. This is in good

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(1) von Seggern, H. *Braz. J. Phys.* **1999**, *29*, 254.
(2) Schweizer, S. *Phys. Status Solidi A* **2001**, *187*, 335.
(3) Takahashi, K. *J. Lumin.* **2002**, *100*, 307.
(4) Rowlands, J. A. *Phys. Med. Biol.* **2002**, *47*, R123.
(5) Bøtter-Jensen, L.; McKeever, S. W. S.; Wintle, A. G. *Optically stimulated luminescence dosimetry*; Elsevier: Amsterdam, The Netherlands, 2003.
(6) Heyes, G. J.; Mill, A. J.; Charles, M. W. *Br. J. Radiol.* **2006**, *79*, 195.
(7) Berrington de González, A.; Darby, S. *Lancet* **2004**, *363*, 345.
(8) Riesen, H.; Kaczmarek, W. A. International PCT application PCT/AU2005/001905, International Publication Number WO 2006/063409.

10.1021/ic062455g CCC: $37.00

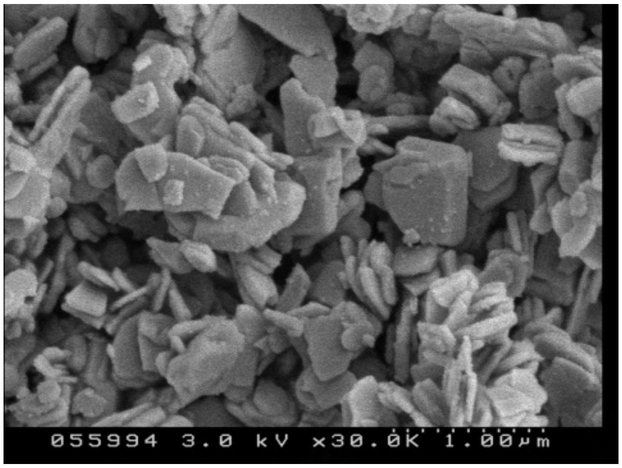

Figure 1. SEM picture of the nanocrystalline BaFCl/Sm^{3+} X-ray storage phosphor as prepared by the method described in the text.

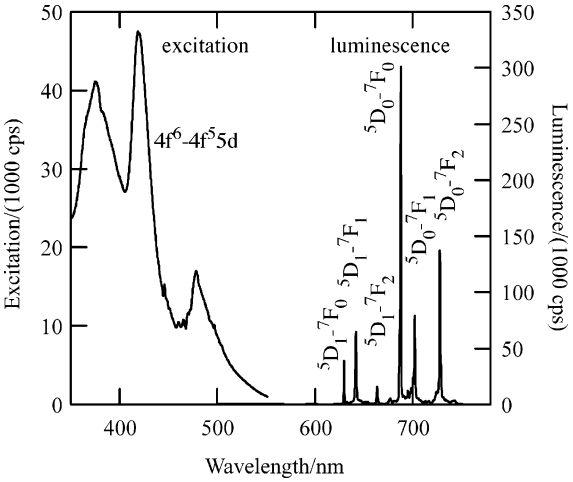

Figure 2. Room-temperature excitation and luminescence spectra of nanocrystalline BaFCl/Sm^{3+} after exposure to ~100 mGy of 8 keV Cu Kα radiation. Initial and final electronic terms for the Sm^{2+}-based transitions are indicated. The excitation spectrum was measured by monitoring the luminescence line at 688 nm. The luminescence spectrum was excited at 420 nm. Spectra were measured on a Horiba Jobin-Yvon Spex Fluoromax-3 fluorometer.

agreement with size distributions seen in scanning electron microscopy (SEM) pictures (see Figure 1).

By analyzing SEM pictures, we get an average particle size of $300 \times 200 \times 70$ nm^3.

Figure 2 shows the room-temperature excitation and luminescence spectra of a sample of nanocrystalline BaFCl/Sm^{3+} after exposure to ~100 mGy of 8 keV Cu Kα radiation. Both spectra are clearly due to Sm^{2+} centers: the narrow emission lines are readily assigned to $^5D_J \rightarrow {}^7F_J$ transitions within the f-electron system, and the broader absorption transitions in the near-UV region are due to $4f^6 \rightarrow 4f^55d$ excitations. Transitions are labeled with their initial and final electronic states. We stress here that none of the Sm^{2+} transitions are present in freshly prepared, nonirradiated samples (see Figures 3b and 4).

It has been documented before that Sm^{3+} in BaFCl can be reduced to Sm^{2+} by X-rays.[9] However, compared with

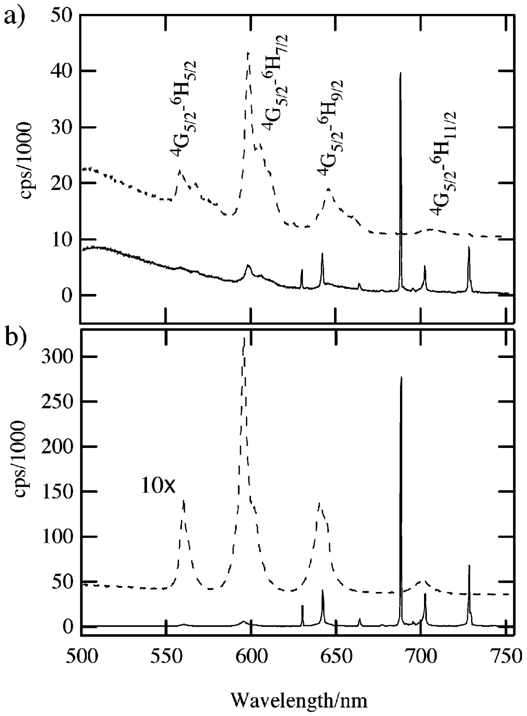

Figure 3. X-ray responses of (a) sintered microcrystalline BaFCl/Sm^{3+} (0.5 mol %) and (b) nanocrystalline BaFCl/Sm^{3+} (nominal 0.5 mol %) as prepared by wet chemistry. The dashed (401 ± 2 nm excitation) and solid (415 ± 2 nm excitation) lines show the luminescence spectra before and after irradiation. Samples were exposed in a powder X-ray diffractometer (40 kV, 25 mA, Cu anode) for (a) 63 600 s and (b) 5 s. The Sm^{3+} transitions are assigned in the upper panel.

bulk crystalline BaFCl/Sm^{3+}, the nanoparticles prepared in this work exhibit a $Sm^{3+} \rightarrow Sm^{2+}$ conversion efficiency that is many orders of magnitude higher.

Figure 3 compares the efficiency of X-ray generation of Sm^{2+} in nanocrystalline BaFCl/Sm^{3+}, as prepared by wet chemistry described in this work, with that of microcrystalline BaFCl/Sm^{3+}, as prepared by sintering of $BaCl_2$, BaF_2, and SmF_3 for 6 h at 900 °C. The $Sm^{3+} \rightarrow Sm^{2+}$ conversion efficiency is ca. 50 000 times higher in the nanocrystalline sample. This significantly higher efficiency may be associated with a high number of defects in the nanoncrystalline particles because of the much larger surface-to-volume ratio. Figure 3 also shows the luminescence spectra of the unexposed samples, and the lines can be assigned to the $^4G_{5/2} \rightarrow {}^6H_{5/2,7/2,9/2,11/2}$ transitions of Sm^{3+}. This confirms that Sm is incorporated into the lattice in the 3+ oxidation state.

Figure 4 shows the luminescence spectra of the nanocrystalline BaFCl/Sm^{3+} before and after X-ray exposure in the region of the $^4G_{5/2} \rightarrow {}^6H_{5/2,7/2}$ transitions in more detail.

A slight reduction of the intensity of the Sm^{3+} lines is observed while a dramatic increase of the Sm^{2+} lines occurs. This behavior can be rationalized by the fact that at 401 nm (as well as at 415 nm) the Sm^{2+} ions are excited via a parity-allowed f−d transition whereas the Sm^{3+} ions are excited by a parity-forbidden f−f transition. Hence, the intensities are not a reflection of the concentrations of the two oxidation states, and only a fraction of the Sm^{3+} centers yields stable Sm^{2+} centers upon exposure to X-rays. Moreover, it is likely

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(9) Qin, W.; Jang, K.; Cho, H.; Chung, Y.; Park, S.; Lee, Y.-I.; Kim, Ch. *J. Korean Phys. Soc.* **2004**, *45*, 512.

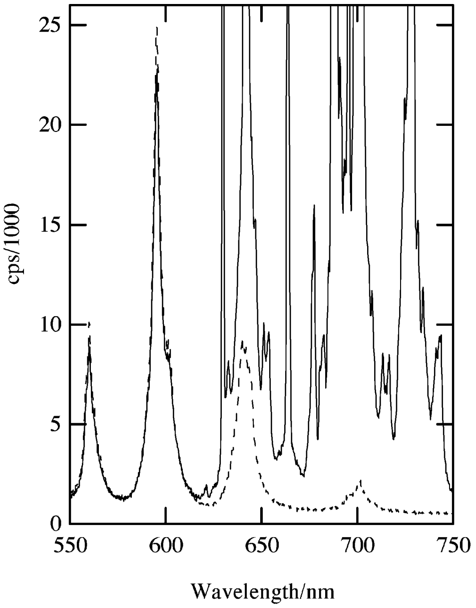

Figure 4. Comparison of the $^4G_{5/2}-^6H_{5/2,7/2}$ luminescence spectra excited at 401 nm with a bandpass of 4 nm of nanocrystalline BaFCl/Sm^{3+} as prepared by wet chemistry before (dashed line) and after 3 min of exposure (solid line) to X-ray (40 kV, 25 mA Cu anode) radiation.

that some of the Sm^{3+} emission is due to impurities that do not undergo X-ray reduction.

Figure 5 shows the dependence of the intensity of the $^5D_0 \rightarrow ^7F_0$ emission line on cumulative exposure to 44 keV Tb γ-ray radiation. The luminescence was excited with 0.5 mW of 473 nm light from a diode-pumped solid-state laser. This figure illustrates the sensitivity of the nanocrystalline BaFCl/Sm^{3+} phosphor and the near linearity for radiation exposures up to 400 μGy.

The X-ray-induced Sm^{2+} traps are relatively stable and are not erased under ambient light conditions or under irradiation with low-powered lasers. However, exposure to >20 W/cm^2 of 488 nm Ar^+ laser light results in relatively rapid (reversible) erasure. For example, a 10 min exposure of a X-ray-saturated sample to 30 W/cm^2 of 488 nm Ar^+ laser light results in erasure of 82% of the Sm^{2+} centers. After the erasure, the material retains its sensitivity to X-rays. We note here that the mechanism of Sm^{2+} photoionization in crystals of BaFCl/Sm^{2+} has been studied previously by hole-burning spectroscopy.[10] The present storage phosphor is readout by *direct photoexcitation* in contrast to *photostimulation*, as is the case for currently applied phosphors. This enables multiple readouts of the latent information because the Sm^{2+} traps are relatively stable, potentially yielding better signal-to-noise ratios in computed radiography. We note here that the readout technology for the present storage phosphor has to be adapted to the relatively long excited-state lifetime of the $^5D_0$ state (ca. 2 ms), and the conventionally used "flying spot" method is inadequate. However, we have successfully conducted preliminary imaging experiments, using standard oral examination doses.

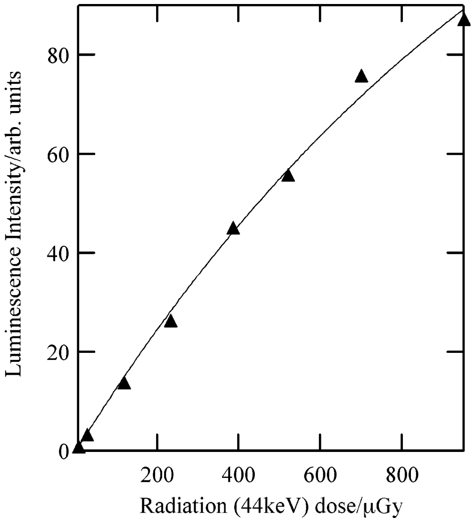

Figure 5. Dependence of the luminescence intensity of the $^5D_0-^7F_0$ Sm^{2+} f−f transition as a function of cumulative irradiation of nanocrystalline BaFCl/Sm^{3+} by 44 keV Tb γ-ray radiation. The luminescence was excited by 0.5 mW of 473 nm light of a diode-pumped solid-state laser (spot size ≈250 μm).

The present phosphor can be used in personal radiation monitoring,[5] allowing a nondestructive readout of the accumulated dose of ionizing radiation (see Figure 5). Optimization of the particle size and its distribution may result in even higher quantum efficiencies.

Acknowledgment. We thank the Australian Research Council and UNSW for financial support of this project.

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(10) Winnacker, A.; Shelby, R. M.; Macfarlane, R. M. *Opt. Lett.* **1985**, *10*, 350.