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Microcharacterization of Core Shell Nanocrystallites.

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The development of novel technologies based on nanostructured materials is facilitated by advanced microscopy and microanalysis techniques which provide spatially resolved high sensitivity information about the structure, composition and properties of materials. BaFCl:Sm^{3+} is a photoluminescent storage phosphor for ionising radiation [1,2]. The mechanism is based on the reduction of Sm^{3+} to Sm^{2+} by F-centres and/or free electrons that are created upon exposure to ionising radiation in the BaFCl host. Recently, we have significantly improved the efficiency of this class of storage phosphors by optimizing the preparation of core-shell nanoparticles comprising of a BaFCl core and a BaFCl:Sm^{3+} shell using a co-precipitation method[3]. The $Sm^{3+} \rightarrow Sm^{2+}$ conversion efficiency of these nanoparticles is more than four orders of magnitude greater than that of conventional high temperature (HT) sintered microcrystals.

The nanocrystallites have been characterized with complementary SEM and TEM microanalytical techniques as well as Photoluminescence (PL), and high resolution powder X-ray diffraction techniques which indicate average crystallite size of ~160 nm consistent with electron microscopy. In particular Cathodoluminescence (CL) microanalysis provides information about the optical properties and defect microstructure of luminescent materials and is ideal for investigating the useful properties of these efficient nano-phosphors[3]. The CL data were collected in a JEOL 7001F FESEM equipped with a Gatan XiCLone CL system. Fig 1 (a) shows typical CL spectra from microcrystalline, nanocrystalline and x-ray irradiated nanocrystalline BaFCl:Sm^{3+}. Major $^4G_J \rightarrow {}^6H_J$ (Sm^{3+}) and $^5D_J \rightarrow {}^7F_J$ (Sm^{2+}) transitions are identified. In all spectra a broad emission centered at ~380nm is observed (not shown) and is associated with defects in the BaFCl host lattice. There are significant differences in the $^4G_J \rightarrow {}^6H_J$ (Sm^{3+}) emission lines between the two materials, indicating significantly different local environments for the Sm^{3+} ions. After ionizing radiation, there is a net increase in Sm^{2+} associated CL emission which is consistent with PL data. It is also noted that after reduction to Sm^{2+} by ionizing radiation the resulting $^5D_J \rightarrow {}^7F_J$ (Sm^{2+}) emission lines coincide for both materials.

Fig 2 shows typical monochromatic cathodoluminescence images from the <100nm thick platelet nanocrystals in comparison with the >μm diameter microcrystals demonstrating the local variations in concentration of associated defect centers which have also been investigated using hyperspectral CL techniques. The sensitivity of CL microanalysis to dopants is typically several orders of magnitude better than x-ray microanalysis. In situ cathodobleaching properties of the HT sintered and nanocrystalline samples have also been investigated (and compared with photobleaching data). These extremely efficient and stable nano-phosphors are ideal for small probe applications for example in medical/ dental radiography, nuclear reactors, etc.

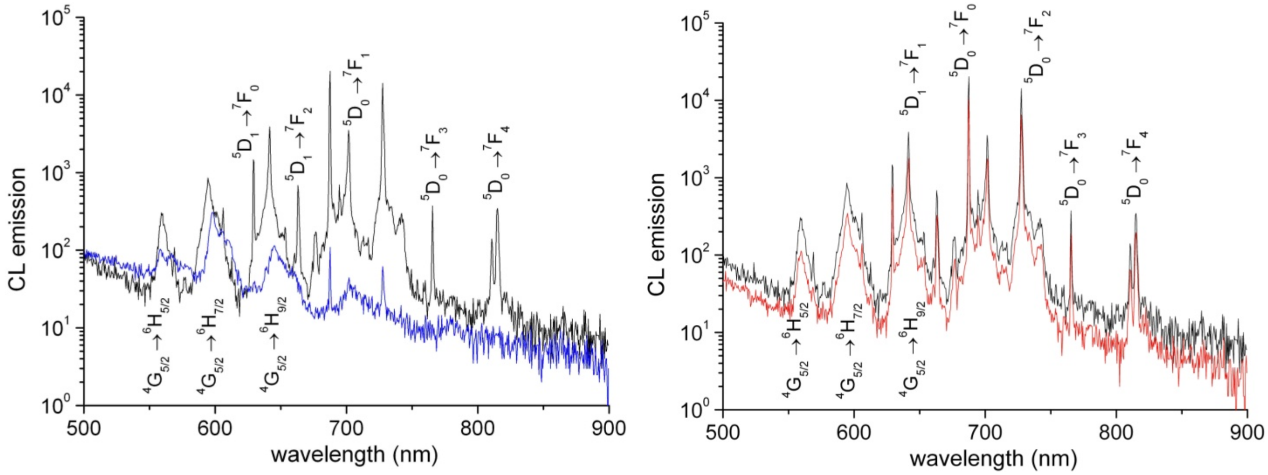
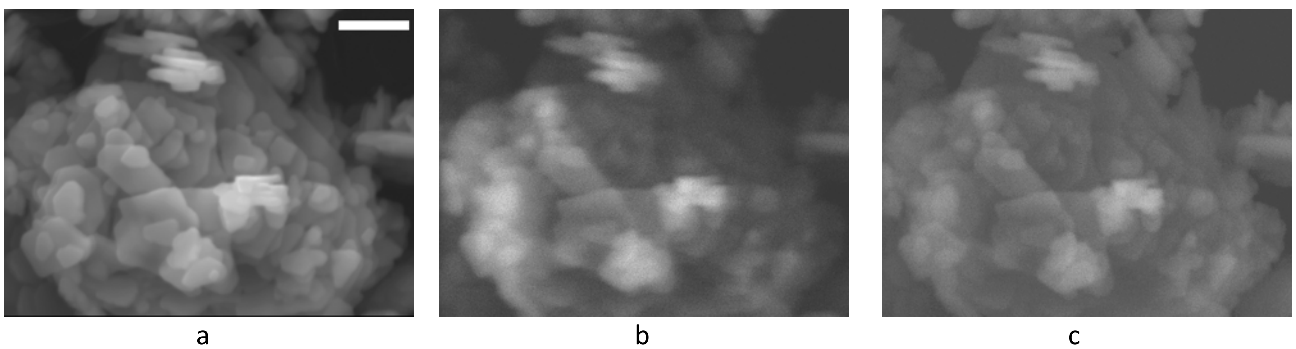


Fig. 1. Cathodoluminescence spectra obtained from at 15 keV, 3 nA, from a HT sintered BaFCl:Sm^{3+} (blue line), nanocrystalline BaFCl:Sm^{3+} (black line) and following X-ray dose of 50 mGy (red line). Major $^4G_J \rightarrow {}^6H_J$ (Sm^{3+}) and $^5D_J \rightarrow {}^7F_J$ (Sm^{2+}) transitions are shown.



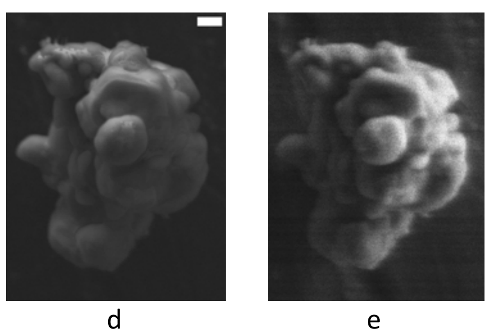


Fig. 2 (a)SEI and corresponding (b) 690nm (c) 350nm monochromatic CL images of nanocrystalline BaFCl:Sm^{3+} (d) SEI and corresponding (e) 690nm monochromatic CL image of HT sintered BaFCl:Sm^{3+} CL imaging shows the local distribution of defects and dopants in the crystallites.
(**scale bars ≡ 1 μm**).

References

[1] H. Riesen, W.A. Kaczmarek, Inorg. Chem. 46 (2007) 7235-7237.
[2] H. Riesen, W.A. Kaczmarek, Radiation storage phosphor & applications, International PCT Application, WO2006063409-A1, 16 Dec. 2005.
[3] Yacobi, B.G., & Holt, D.B. (1990) Cathodoluminescence Microscopy of Inorganic Solids. Plenum Press, New York.
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