



Experiment title: ***In Situ* detection of Ce oxidation state in YAG nanoparticles by high resolution XANES**

Experiment number:
MA-3672

Beamline: BM16	Date of experiment: from: 15 November 2017 to: 21 November 2017	Date of report: 14 February 2018
Shifts: 18	Local contact(s): Denis Testemale and Jean-Louis Hazemann, BM16 (FAME-UHD)	<i>Received at ESRF:</i>
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Context: Commercial wLEDs are composed of blue InGaN diodes and micron-sized $Y_3Al_5O_{12}$ doped with 1 mol.% Ce^{3+} (YAG:Ce) phosphors inserted in an epoxy or silicone dome. The use of micron-sized phosphors and their encapsulation in resins induce reduced efficiency and limited ageing properties. To overcome these drawbacks the idea is to use YAG:Ce nanoparticles (50 to 100 nm in size) that will decrease light scattering and allow a binder-free shaping. However, the oxidation of luminescent Ce^{3+} into non-luminescent Ce^{4+} is a common process in nanocrystals as it is often favored by the wet chemical methods used to produce nanoparticles and, moreover, it is promoted at the particle surface [1]. The presence of Ce^{4+} ions, even at low concentration, is highly detrimental for the photoluminescence (PL) properties as Ce^{4+} acts as a PL quencher, favoring non-radiative processes (PL poison), and should thus be absolutely avoided.

The aim of these high-resolution XANES experiments was to follow the oxidation state of Ce in nano-YAG samples both post-synthesis and *in situ* in order to determine the best experimental conditions ensuring cerium in its 3+ oxidation state.

Experimental: The oxidation state of Ce in nanocrystals of Ce-doped $Y_3Al_5O_{12}$ (YAG:Ce) was examined using high-resolution XANES experiments at the L_3 edge of Ce (5.723 keV), both on already-synthesized nanopowders and during the solvothermal synthesis in the FAME high T-P autoclave [2]. The *in situ* experiments were performed in a vitreous carbon cell into which the precursors dissolved in 1,4-butanediol were introduced between two pistons equipped with Viton seals. The typical external pressure applied was 200 bars. Numerous synthesis parameters (temperature, precursor concentration, annealing post-treatment) were explored with the goal of determining the best synthesis parameters leading to the formation of YAG:Ce nanocrystals with minimal Ce^{4+} concentration. For each synthesis the Ce^{3+}/Ce^{4+} ratio was determined and quantified using standards (CeO_2 nanopowder for Ce^{4+} and $Ce(\text{acetate})_3$ dissolved in 1,4-butanediol for Ce^{3+}). In addition to studying nano-YAG:Ce, we examined the oxidation state of cerium in nano- $Gd_3Sc_2Al_3O_{12}$ (GSAG), another very promising phosphor [3].

A total of 4 *in situ* (in autoclave) and 16 *ex situ* (on powder) experiments were performed. The high sensitivity of the BM16 (FAME-UHD) was necessary to observe the Ce signal, especially during the *in situ* experiments for which the Ce concentration was very low (10^{-3} mol/L). This low concentration is mandatory as Ce^{3+} ions, doping ions responsible for photoluminescent (PL) properties, must be diluted in the matrix to avoid PL quenching through energy transfers between near neighbors Ce cations (1 mol% in YAG, i.e. $Y_{2.97}Ce_{0.03}Al_5O_{12}$). Moreover the YAG precursor concentration should be kept low to control the nucleation and growth of nano-YAG:Ce and obtain nanocrystals in the 50-100 nm range.

Results: The oxidation state of cerium ions during the nano-YAG:Ce synthesis was successfully detected, even considering the low Ce concentration and could be quantified using standard references for Ce^{4+} and Ce^{3+} . The *in situ* detection of cerium oxidation state as a function of the synthesis temperature shows that the oxidation of Ce^{3+} into Ce^{4+} occurs at temperatures higher than 300°C and that the proportion of Ce^{4+} increases as the synthesis temperature increases (**Figure 1a**). These results are

consistent with our *in situ* Raman observations performed on the same system and under the same operating conditions. Indeed, Raman spectroscopy evidenced the dehydration of the solvent (1,4-butanediol) above 300°C. This water departure probably creates an oxidizing environment that induces cerium oxydation. The presence of Ce⁴⁺ is detected whatever the nanocrystal size, which tends to indicate that the oxidation occurs during the synthesis process and not afterwards at the surface of the particles. We show that a post-annealing treatment at 1600°C under vacuum allows the reduction of all Ce⁴⁺ into Ce³⁺ but also induce an unwanted particle sintering as observed by Scanning Electron Microscopy. Interestingly, Ce-doped GSAG nanopowder exhibits only Ce in its 3+ state (**Figure 1b**). We believe the presence of Sc³⁺ creates a more reducing environment and favors the preservation of the 3+ oxidation state of cerium ions. This result opens the door to new garnet-type nanophosphor engineering.

Conclusions & perspectives: This set of experiments enabled **for the first time** to quantify *in situ* the Ce³⁺/Ce⁴⁺ in YAG:Ce nanocrystals during their nucleation and growth in high T-P autoclave. It reveals that, although high-temperature high-pressure process is efficient to produce well-crystallized nanocrystals with a controlled size as we recently published [4, 5], it favors the oxidation of cerium at high temperature. Further experiments in reducing atmosphere should be performed to preserve the cerium ions in their 3+ oxidation state. Moreover, the results obtained on GSAG:Ce pave the way to new nanophosphor engineering.

References cited:

[1] T.S. Wu et al., *Chem. Comm.* (2016), [2] Testemale D. et al. (2005) *Rev. Sci. Instrum.* 76, 043905-043909, [3] L. Devys, G. Dantelle et al. *J. Lumin.* (2017), [4] G. Dantelle et al. *Thin Solid Films* (2017), [5] G. Dantelle et al. *SPIE Proceedings* (2018)

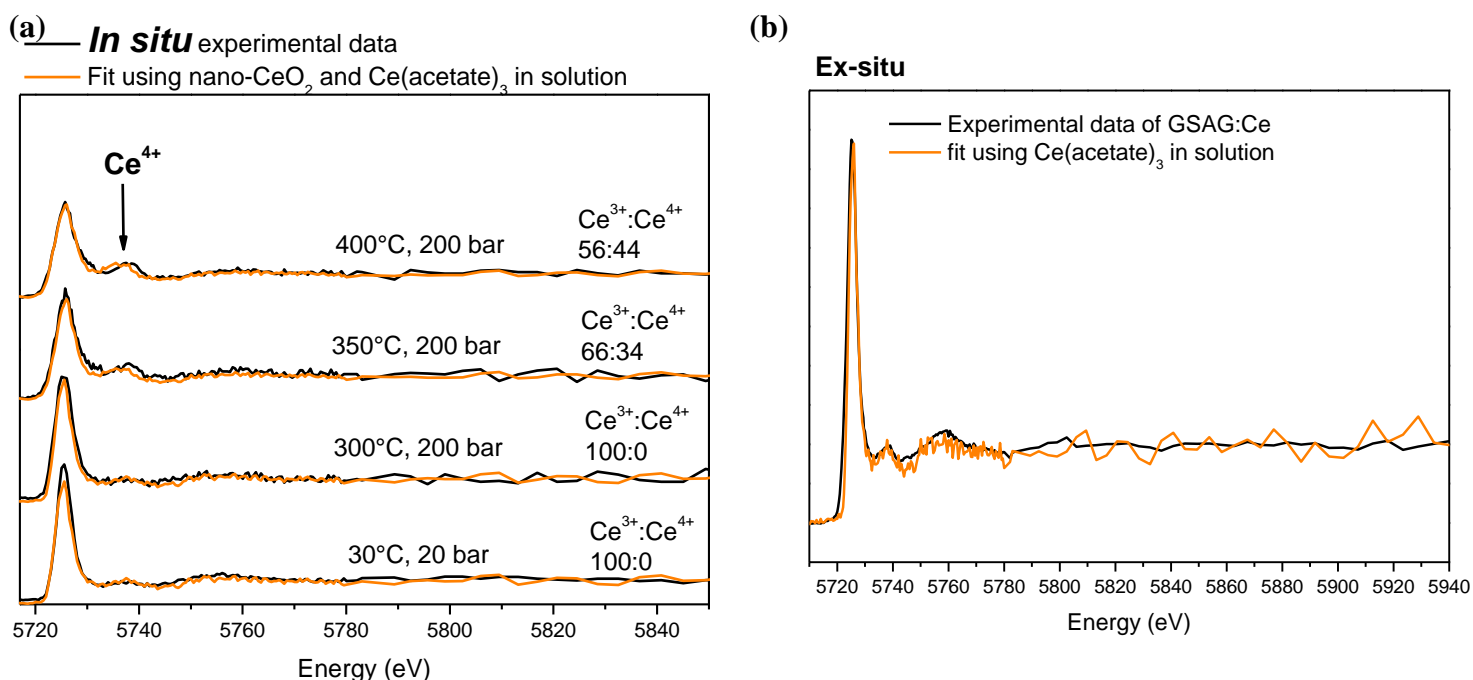


Figure 1: (a) Experimental XANES spectra recorded during the solvothermal synthesis of nano-YAG:Ce under various temperature conditions and the corresponding fits obtained using nano-CeO₂ and Ce(acetate)₃ in butanediol as standards for Ce³⁺ and Ce⁴⁺ respectively. The quantification of Ce³⁺/Ce⁴⁺, indicated just above each spectrum, shows that the oxidation of Ce³⁺ is favored above 300°C. (b) Experimental XANES spectrum of GSAG:Ce nanopowder and its corresponding fit using Ce(acetate)₃ in solution as a standard show clearly that Ce is only in its 3+ oxidation state.