



Experiment title: *In Situ detection of Ce oxidation state in garnet-type nanocrystals by high resolution*

Experiment number:
MA-4275

Beamline: BM16	Date of experiment: from: 3 october 2018 to: 8 Octobre 2018	Date of report: 14 February 2020
Shifts: 18	Local contact(s): Denis Testemale and Jean-Louis Hazemann, BM16 (FAME-UHD)	<i>Received at ESRF:</i>
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Context: Nano-sized $Y_3Al_5O_{12}$ doped Ce^{3+} (YAG:Ce) have attracted a great interest for a use as nanophosphors in white LEDs, with the aim of reducing the back-scattering induced by micron-sized YAG in commercial LEDs. We developed an original solvothermal method using high pressure and high temperature, allowing to produce nanocrystals with a high crystal quality [1,2]. However, using *in situ* high-resolution XANES experiments at the L_3 edge of Ce (5.723 keV) on the BM16 beamline at the ESRF, we showed the luminescent Ce^{3+} ions are partially oxidized into Ce^{4+} , reducing the photoluminescence of our nanocrystals [1]. The aim of these high-resolution XANES experiments was to find new experimental conditions (addition of reducing agent, bubbling of a reducing gas) of the solvothermal synthesis conditions to prevent Ce^{3+} oxidation up synthesis of YAG:Ce nanocrystals.

In addition, we studied Ce-doped garnet-type single-crystals containing additional codoping ions. These single-crystals have strong applications as scintillators. It has proved that, for scintillation properties, the presence of Ce^{4+} ions is more favorable. The idea was to codope Ce-doped $Gd_3Al_2Ga_3O_{12}$ and $Lu_3Al_5O_{12}$ single-crystals with Mg^{2+} and Li^+ ions, which could act as charge compensators and promote the oxidation of cerium. The high-resolution XANES experiments were performed to determine the $Ce^{3+}:Ce^{4+}$ ratio in these single-crystals.

Experimental: The oxidation state of Ce in nanocrystals of Ce-doped $Y_3Al_5O_{12}$ (YAG:Ce) and in other garnet-type single-crystals was examined using high-resolution XANES experiments at the L_3 edge of Ce (5.723 keV). A total of 18 *ex situ* (on powder) experiments were performed. The high sensitivity of the BM16 (FAME-UHD) was necessary to quantify accurately the $Ce^{3+}:Ce^{4+}$ ratio in the samples. The low doping concentration (<0.5 mol.%) 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. $Y_{2.97}Ce_{0.03}Al_5O_{12}$).

Results: The oxidation state of cerium ions during the nano-YAG:Ce synthesis was successfully modified by bubbling a gas in the precursor solution, prior to solvothermal synthesis. Indeed, when bubbling a reducing gas (Ar/H₂), the $Ce^{3+}:Ce^{4+}$ ratio is of 71:29 whereas when bubbling O₂, it is 64:36 (**Figure 1**). These key results are reported in a paper, submitted at the end of January [3].

In addition, on single-crystals, we showed that Ce^{3+},Mg^{2+} -codoped compounds ($Gd_3Al_2Ga_3O_{12}$), the proportion $Ce^{3+}:Ce^{4+}$ is 75:25, whereas with no codopant (Ce^{3+} -doped $Gd_3Al_2Ga_3O_{12}$ and $Lu_3Al_5O_{12}$) only Ce^{3+} is present. The reason for this difference is the presence of Mg^{2+} ions which play the role of charge compensators. These results are reported in a publication [4].

Conclusions & perspectives:

Regarding nano-YAG:Ce, we proved, for the first time, that it is possible to modify the $Ce^{3+}:Ce^{4+}$ ratio in the nanocrystals by bubbling a gas in the precursor solution. In addition, this bubbling induces heterogeneous nucleation of YAG:Ce nanocrystals, leading to a size increase of these nanocrystals [3].

Regarding $\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ and $\text{Lu}_3\text{Al}_5\text{O}_{12}$ single-crystals, we showed that, when adding codoping ions such as Li^+ and Mg^{2+} , the cerium oxidation was modified through charge compensation: in codoped crystals, the proportion of Ce^{4+} is increased, explaining their better performances in scintillation, where Ce^{4+} is favorable than Ce^{3+} [4].

References cited:

[1] G. Dantelle et al. *RSC Advances* (2018) [2] Testemale D. et al. (2005) *Rev. Sci. Instrum.* 76, 043905-043909, [3] A. Cantarano et al [4] G. Dantelle et al. *Physica Status Solidi B: Basic Solid State Physics* (2019)

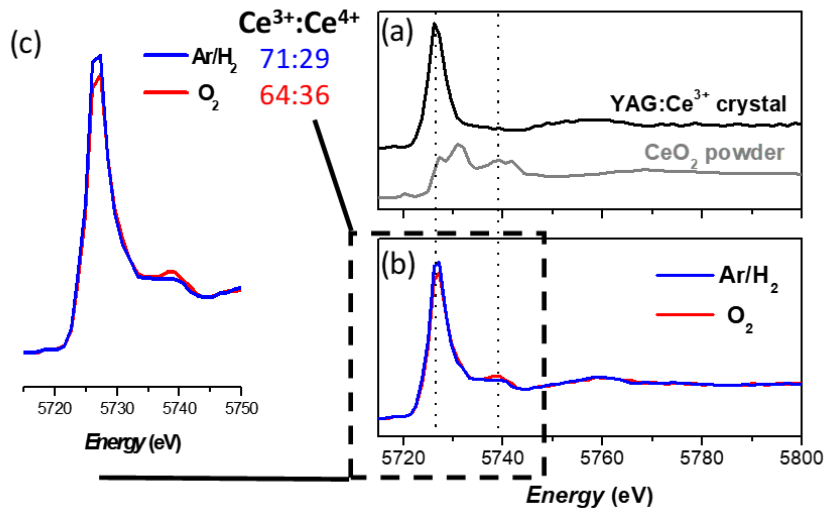


Figure 1: (a) XANES spectra of the standards used for the linear combination (b) XANES spectra of the nanophosphors obtained after Ar/H₂ or O₂ gas bubbling. (c) Zoom on the peaks characteristics of Ce³⁺ absorption (at 5725 eV) and of Ce⁴⁺ absorption (at 5738 eV). The Ce³⁺:Ce⁴⁺ ratio is indicated for each sample.