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|   | <b>Experiment title:</b><br>Ce in aluminosilicate optical fiber preforms: in situ determination of the effect of temperature and glass composition on the redox | <b>Experiment number:</b><br><b>MA-3203</b> |
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## Report:

In order to quantitatively estimate the valence states of Ce ions in silica-based optical fibres and to correlate the  $\text{Ce}^{3+}/\text{Ce}_{\text{tot}}$  ratio with the observed luminescence properties, we collected XAS data in fluorescence mode at the Ce LIII edge for Si-based optical fibre preforms and alkali-silicate/aluminosilicate glasses.

Some of the samples have been analysed “in-situ” at high temperature. Indeed, for high-temperature XANES, the samples have been loaded, in a microfurnace, as  $\mu\text{m}$ -powders in a 0.5-mm hole of a Pt-Ir10 % heating wire.

We were able to assess the changes of Ce valence in function of chemical composition, dopant level, synthesis conditions and temperatures.

### XAS Ce LIII-edge: measurements at room temperature (RT).

All measurements were done in the energy range: 5600 eV till  $k=10\text{\AA}^{-1}$  (6100 eV). Calibration of the energy was carried out by collecting a Cr foil (5989 eV) each day. Two model compounds were measured both in transmission and fluorescence mode: Ce(III)-pyrochlore and  $\text{CeO}_2$ . Si-based optical fibre preforms had different synthesis conditions (done in different atmosphere: He,  $\text{O}_2$ ,  $\text{N}_2$ ) and contained different amounts of Al.

The collection of XAS spectra at high temperatures (HT) for three Si-based optical fibre preforms was not carried out as initially planned, because the measurements were extremely long, and the signal/noise ratio not good enough. Indeed, extremely HTs were required to get a homogeneous melt for pure Si fibers, and together with the low absorber dilution ( $\sim 0.1$  mol% Ce), for a single sample we spent almost 6 hours attaining poor quality spectra. Thus, Si-based optical fibre preforms were studied only at RT.

Samples for XAS measurements were prepared as finely ground powder sputtered onto a kapton tape. XAS data were recorded in a step-scan mode with an average energy step of 0.30 eV in the main edge region and counting 10 s per point; the average of three-six spectra was taken.

Ce LIII-edge XANES analysis allowed the estimation of the  $\text{Ce}^{3+}/\text{Ce}_{\text{tot}}$  ratio in the investigated optical fibre preforms. Moreover, it was possible understanding the effect of Al presence or of the synthesis conditions ( $\text{O}_2$  atmosphere or not) on Ce redox state (Fig. 1).

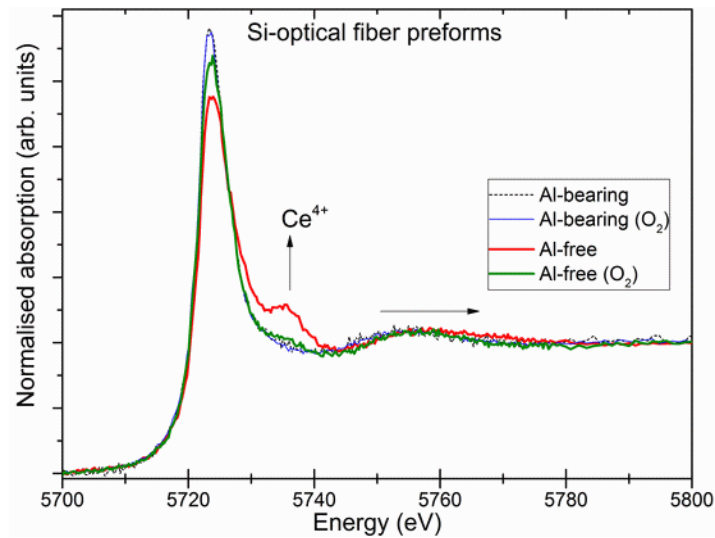


Figure 1- Normalised XAS spectra at the Ce  $L_{III}$ -edge for some Si-based optical fiber preforms. Variation of the  $Ce^{3+}$  and  $Ce^{4+}$  contributions were observed depending on chemistry and synthesis conditions.

#### XAS Ce $L_{III}$ -edge: measurements at RT, high temperatures in air (HT), and at HT under Ar flux.

A set of alkali- silicate/aluminosilicate glasses ( $\sim 0.36$  mol%  $CeO_2$ ) were studied both at RT and HT in order to verify the redox kinetic for different temperatures or different synthesis conditions. In particular, Na-silicate glasses, with three different amounts of  $Al_2O_3$ , were chosen in order to assess the influence of Al presence (as well as amount) on Ce redox properties.

Finely ground powder was loaded in a 0.5-mm hole of a Pt-Ir10 % heating wire of a microfurnace already used for in situ XANES high temperature study [e.g. 1-3]. First of all, XAS spectra were collected at room temperature (Fig. 2). Then, the powder was heated up ( $\sim 1500^\circ C$ ) in order to obtain a homogeneous melt. After 5 minutes, XAS spectra were acquired. Other measurements were done at HT and under Ar flux for different dwell times (5', 10' and 15') in order to follow the redox kinetic in slightly reducing conditions.

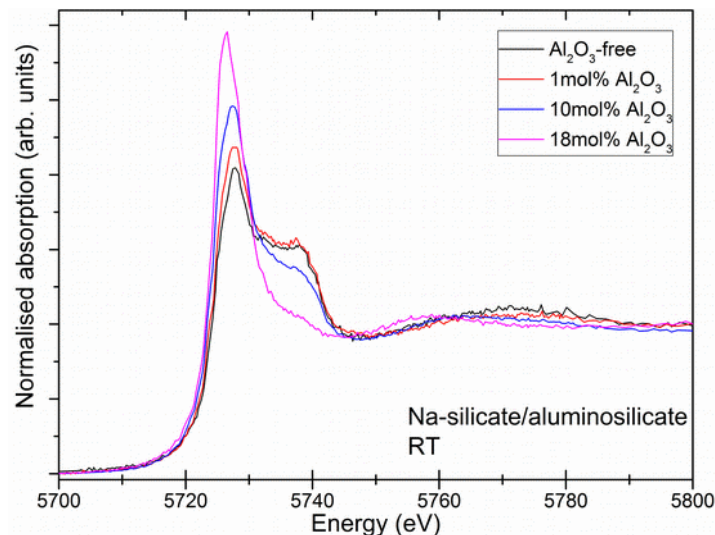


Figure 2- Normalised XAS spectra at the Ce  $L_{III}$ -edge for some silicate/aluminosilicate glasses. A systematic variation of the  $Ce^{3+}$  and  $Ce^{4+}$  contributions was observed depending on Al content.

Thanks to these results, we will be able to estimate the absorption cross-section of  $Ce^{4+}$  at 260 nm, to deepen our understanding on the role of Ce ions in the photo- and radio-darkening mechanisms involved in optical fibers [4] and to improve our knowledge on the synthesis conditions.

The preliminary results will be presented at the 12<sup>th</sup> Pacific Rim Conference on Ceramic and Glass Technology including Glass & GOMD Annual Meeting, May 21-26, 2017 in Waikoloa, Hawaii, USA.

REF: Cochain et al. 2009 *J Phys: Conf Series*190; Neuville et al. 2014 *Rev.Min.Geo.*78; Cicconi et al. 2015 *AmericMin*100; Luppi et al., *Opt. Lett.* 2016