



	Experiment title: Understanding the role of Ce in hydrogen peroxide dissociation by HERFD-XANES and RIXS	Experiment number: MA 3049
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Report:

In this experiment we followed in-situ the modification of different Ce-doped bioactive glasses during the reaction with hydrogen peroxide, by means of HERFD-XANES at Ce L₃ edge.

The experiment was based on some previous studies on cerium-doped glasses, which showed that the incorporation of cerium oxide at low concentration is effective in reducing H₂O₂ concentration in solution, adding a catalase mimetic activity to the materials [1]. The aim of the present experiment was to investigate the evolution of the Ce electronic structure during the reaction with hydrogen peroxide, for different glass composition (i.e. different environment around cerium) and different concentration of H₂O₂. This information is expected to be useful to elucidate the mechanism of reaction, necessary to understand and optimize the functionality of the material.

The samples belong to three different families of bioglasses: 45S5 Hench glasses, with a molar composition of (46.2-x)% SiO₂ 24.3% Na₂O 26.9%CaO 2.6% P₂O₅ x% CeO₂; Kokubo glasses, with a molar composition of (50-x)% SiO₂ 24.3% Na₂O 25% CaO 25% x% CeO₂; Mesoporous BioGlasses (MBG), 75.8% SiO₂ 14.2% CaO 4.7% P₂O₅ 5.3% CeO₂. While the former two were prepared by conventional melt-quenching methods, the latter was prepared by evaporation induced self-assembly method, which confers a mesoporous structure to the glass, leading to materials with a much higher surface to volume ratio compared to the ones obtained by melt-quenching. In order to investigate also the possible influence of the initial oxidation state of cerium ions inside the glass, we prepared also a MBG glass which was thermally treated in controlled atmosphere after preparation. All of the samples were milled and sieved to obtain glass powders with size < 50 μm. In addition, two reference samples, CeO₂, Ce(NO₃)₃, were also measured.

Two different experimental setups were used to measure the glasses during reaction with the solution of H₂O and H₂O₂: a liquid jet setup with 45 ml of powdered samples, and a second setup, in which the samples in forms of pellets were soaked with a few drops of solution every 15 minutes. The results obtained using the two setups were found to be comparable. Beam-induced modifications of the Ce oxidation state were

observed to be negligible in the liquid jet setup, while they were minimized by moving the sample under the beam in the pellet setup.

Fig. 1 a reports the Ce L₃ edge HERFD-XANES spectra for all of the glasses before the reaction, along with the reference samples. Cerium ions are present in both the 3+ and 4+ oxidation states in all of the glasses. The samples prepared by melt-quenching show a higher Ce³⁺ concentration than the MBG ones. The thermal treatment performed on the MBG sample lead to a higher concentration of Ce⁴⁺ ions inside the glass matrix. Fig. 1b shows the evolution of HERFD-XANES spectra during the reaction of 5.3% CeO₂ doped Hensch glass with a 0.1 M solution of H₂O₂ (liquid jet setup). The spectral modifications in the energy regions evidenced by the arrows, indicate an increase of the Ce⁴⁺ concentration with reaction time. The inset shows a magnified pre-edge region, where it is possible to resolve two different peaks, one related to the electronic configuration of Ce³⁺ (at lower energies) and one related mainly to Ce⁴⁺. The evolution of the pre-edge region with reaction time is compatible with the evolution of the near-edge region. Expectedly, an increase of H₂O₂ concentration to 10 M in the solution, leads to a faster modification of the Ce oxidation state at the early stages of reaction (cfr Fig. 1b and 1c), while a steady state is reached after approximately one hour.

For all of the measured samples, the reaction leads to an increase of Ce⁴⁺ concentration with time (fig 2a reports the case of the MBG glass), with the spectral modifications being more pronounced in samples with a higher Ce⁴⁺ concentration (see for example the two different MBG samples in Fig. 2a and 2b).

Further analysis is required in order to understand the evolution of the electronic structure of cerium ions inside the material. This requires the identification of all the spectral features present in the acquired HERFD-XANES spectra. The correlation between the evolution of the electronic structure of the different samples and the corresponding efficiency for H₂O₂ dissociation is expected to be of help for the identification of the catalytically active cerium oxide phases within the investigated materials. This will in turn lead to the possibility of designing of materials with optimized catalase mimetic activity and minimized cerium concentration.

[1] V. Nicolini et al., J. Phys. Chem. B 2015, 119, 4009–4019.

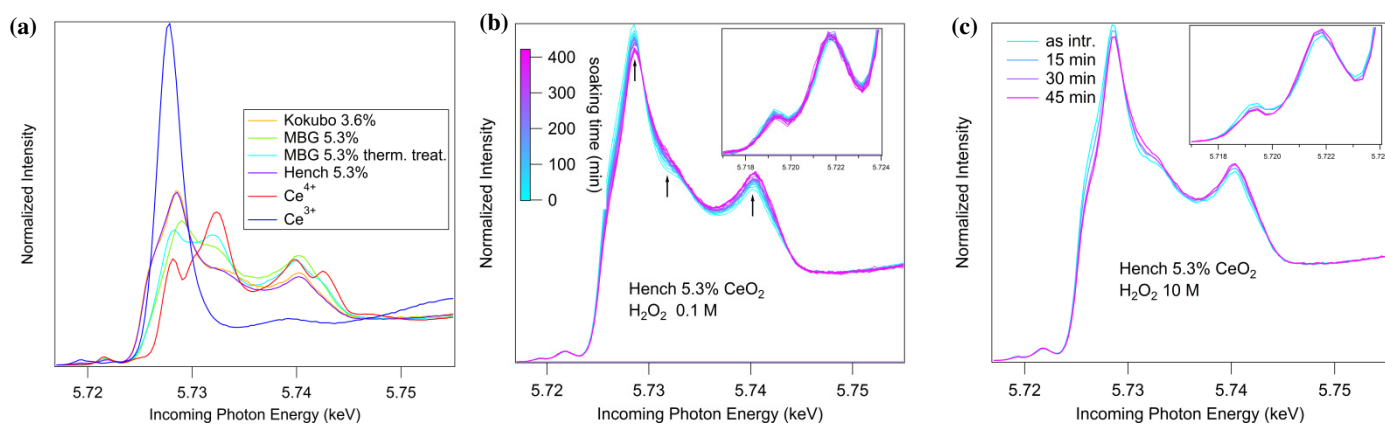


Fig. 1: Ce L₃-edge HERFD-XANES of (a) the different glass samples and of the reference Ce³⁺ and Ce⁴⁺ samples, (b) 5.3% CeO₂ doped Hensch glass soaked in a 0.1 M solution of H₂O₂ in liquid jet setup, (c) 5.3% doped Hensch glass in a 10 M H₂O₂ solution in pellet setup. The inset shows the zoomed pre-edge region.

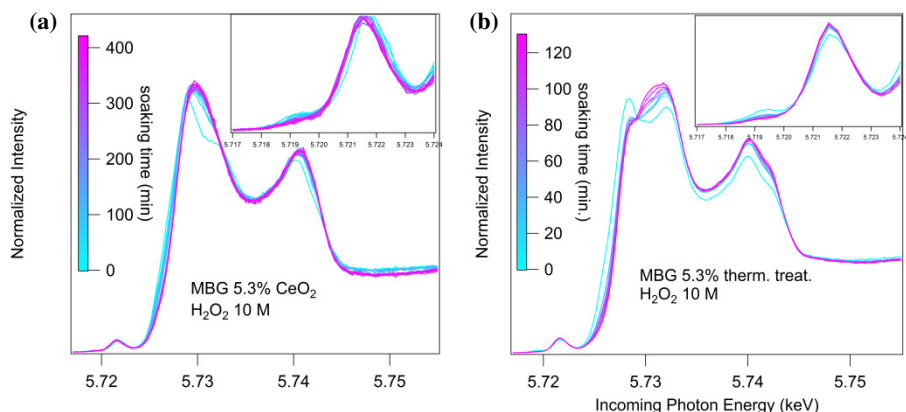


Fig. 2: Ce L₃-edge HERFD-XANES of (a) 5.3% CeO₂ doped MBG glass soaked in a 10 M solution of H₂O₂ (liquid jet setup), (b) 5.3% CeO₂ doped MBG glass with thermal treatment soaked in a 10 M solution (pellet setup). The inset shows the pre-edge region.