



	Experiment title: Local structural and chemical environment of cerium in bioactive glasses additivated with cerium oxide	Experiment number: MA 2353
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Report:

In this experiment we investigated the chemical and structural environment of cerium incorporated in Hench bioactive glasses by means of Ce K-edge x-ray absorption measurements, in the near edge and extended energy ranges.

The experiment was based on previous studies of cerium-doped glasses, which showed that the incorporation of cerium oxide at low concentration in bioactive glasses is effective in reducing H₂O₂ concentration in solution, showing a good catalase mimetic activity [1]. The aim of the present experiment was to provide a description of the local atomic environment of Ce in these materials at different Ce concentration, at different compositions and for different soaking times. This information is expected to be useful to understand the functionality of the material and to provide a valuable input for the modelization of the system, in turn extremely important for a rational design and optimization of the material.

The bioactive glass samples, with the nominal molar composition of 45S5 Hench glasses, (46.2-x)% SiO₂ 24.3% Na₂O 26.9%CaO 2.6% P₂O₅ x% CeO₂, were prepared by conventional melt quenching methods, and subsequently milled and sieved to obtain glass powders with particle size in the 250–500 μm range.

Three kinds of samples were investigated, namely a set of three “as quenched” (AQ) Hench glasses containing different amounts (molar concentration of 5.3%, 3.6% and 1.2%) of cerium oxide; two sets of 5.3% doped Hench glasses soaked for different times, up to 7 days, in 1M and 0.1M H₂O₂ solutions and an AQ 3.6% cerium-doped Kokubo glass, a bioactive glass with molar composition very close to Hench glasses, which does not contain P₂O₅. In addition, three reference samples, CeO₂, Ce(NO₃)₃ and CePO₄, were also measured. All of the data were collected at nitrogen temperature, in transmission mode.

The overall quality of the data can be seen in Fig. a and 1b. The XANES spectra in Fig1a show that the local atomic neighbourhood in AQ Hench glasses differs from both CeO₂ and Ce(NO₃)₃, reference samples in which Ce is in the 4+ and 3+ oxidation state, respectively.

The preliminary results of a first shell (Ce-O) analysis, carried out in the 2÷7 Å⁻¹ k and 1÷3 Å R range are reported in Fig.1 and 2. Fig.1c reports the Fourier transform of the χ(k) of the three AQ Hench glasses. The fit curves (in red) are in good agreement with the data. Fig. d shows the behaviour of the measured Ce-O distance with increasing cerium oxide concentration. A contraction of the Ce-O distance compared to the CeO₂ bulk value is evident, while for the different doping levels the values are the same within the errors.

Similar results were obtained on the two series of Hench glasses soaked in H₂O₂. Fig.2a and 2b show good quality first-shell fits for the 1M (a) and 0.1M (b) series, while Fig.2c shows the behaviour of the Ce-O

distance with soaking time. A contraction of the Ce-O distance with respect to bulk CeO₂ is evident, but also in this case it is not possible to clearly detect modifications of the distance with soaking time.

The data analysis is still in progress. The next steps include a fitting of the data collected from Kokubo glass, to tell if the Ce local atomic environment is different in the presence and in the absence of phosphorous in the glass matrix. A second shell fit of the Hensch glasses (extending the k and the R range), will be also tried in order to test the possibility of having information on the second coordination shell.

[1] V. Nicolini, E. Gambuzzi, G. Malavasi, L. Menabue, M. C. Menziani, G. Lusvardi, A. Pedone, F. Benedetti, P. Luches, S. D'Addato, S. Valeri, *J. Phys. Chem. B* **119**, 4009 (2015).

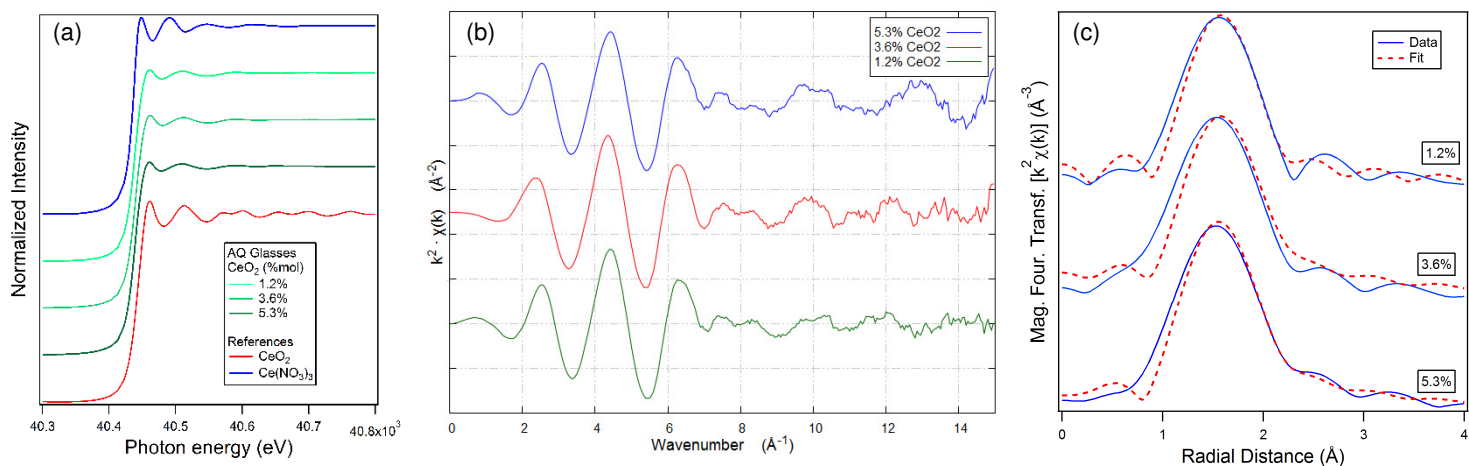


Fig. 1: (a) XANES, (b) $k^2\chi(k)$, and (c) modulus of the Fourier transforms of $k^2\chi(k)$ and fit of the three AQ Hensch glasses with a molar concentration of CeO₂ of 5.3%, 3.6% and 1.2%. (d) Behaviour of the measured Ce-O distance with increasing cerium oxide concentration.

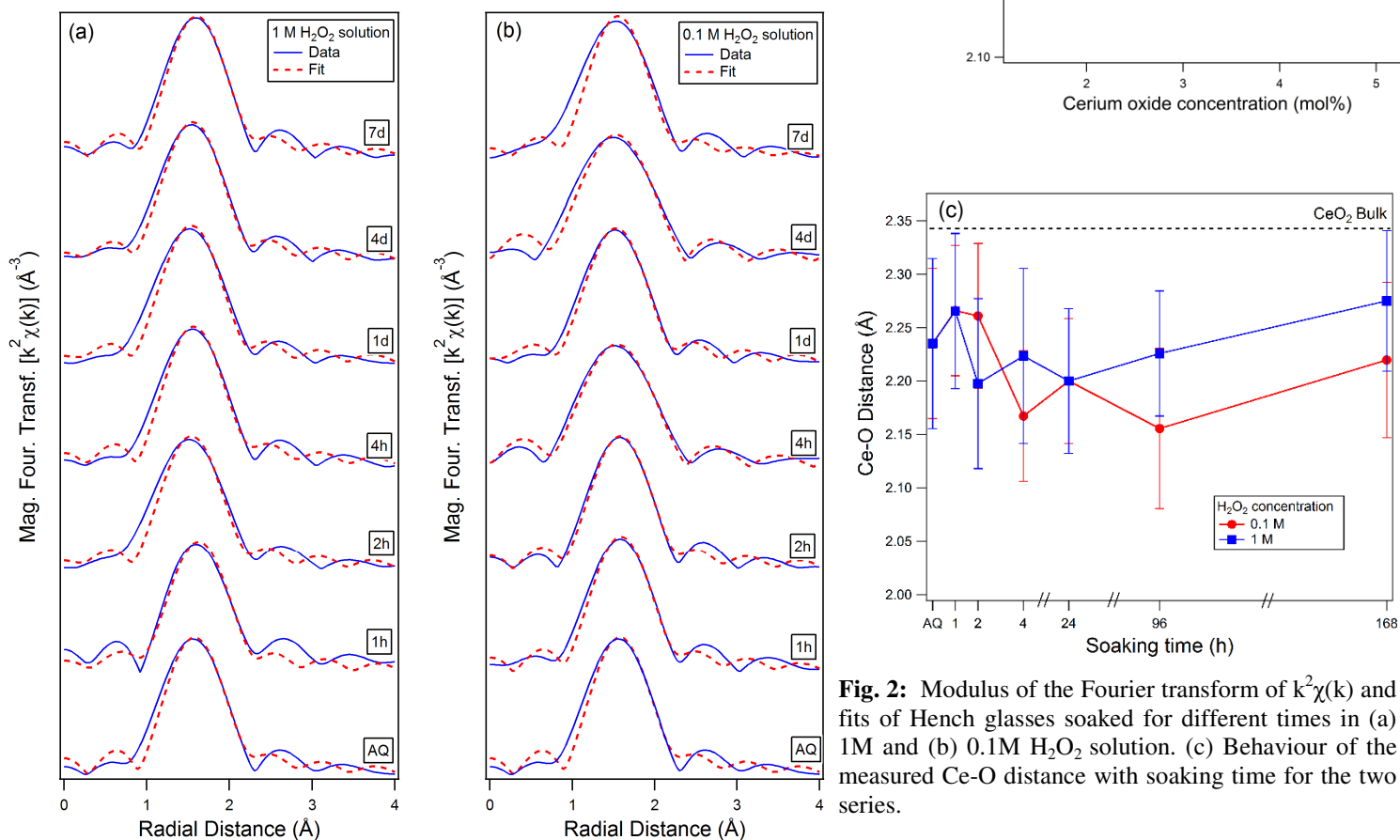


Fig. 2: Modulus of the Fourier transform of $k^2\chi(k)$ and fits of Hensch glasses soaked for different times in (a) 1M and (b) 0.1M H₂O₂ solution. (c) Behaviour of the measured Ce-O distance with soaking time for the two series.