



	Experiment title: EXAFS study of copper state in Cu-alkali ion-exchanged soda-lime glass	Experiment number: CH1106
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Report:

The aim of this experiment was to determine the local rearrangement of copper ions introduced in a silicate glass matrix via copper-alkali ion-exchange process. The process is realized by immersing silicate glass slides in eutectic molten salt baths containing copper ions, that penetrate several microns into the glass, interdiffusing with the outgoing alkali ions of the matrix. The optical and luminescence properties of copper in glass depend on the copper state within the glass, namely, Cu(+), Cu(2+) or metallic Cu in the form of nanoclusters. In this framework, the nature of the local environment of the doping metal is a central issue for the understanding of both the exchange and the aggregation processes. The samples were prepared by varying the glass type (soda-lime or BK7), the exchange bath (CuSO₄:Na₂SO₄ or CuSO₄:K₂SO₄), the temperature of the bath and time of the exchange process. In this way, we have studied how different conditions of preparation affect the ions diffusion into the glass, whereas different local rearrangement around the copper atoms are expected. EXAFS measurements were performed at copper K-edge in X-ray fluorescence yield detection due to the sample dilution. The analysis was performed on 13 samples, plus copper and copper oxides standards. EXAFS analysis shows that copper atoms coordinate 2 to 3 oxygens, at a distance varying from 1.84 to 1.91 Å, confirming that most of the copper is in the Cu(+) state of valence. However, the Cu—O bond length turns out to be significantly shorter than the Na—O separation in soda-lime glasses (2.30 Å), indicating that the exchange process does not take place as a simple ion substitution in the sites made available by the alkali species in the glass. Several open questions arise concerning the copper behavior inside the glass upon ion-exchange. The copper diffusion presents non-Fickian shapes, critically depending on both glass and bath compositions as well as on the process parameters. It has been suggested that Cu(2+) diffuses directly from the bath in the very first exchanged region following erfc-like profiles, while the much more mobile species Cu(+) migrates up to the highest depth values with Gaussian-like profiles, determining the waveguiding properties. ReEXAFS measurements, performed on some of the samples, have partially confirmed this behavior, but the investigation of the very first superficial layer (50 nm) deserves further experiments. Moreover, recent photoluminescence studies suggest a possible role of distortion of Cu(+) sites.

Publications [1] S. Padovani et al., "Local rearrangement of copper in silicate glasses after Cu-alkali ion-exchange: an EXAFS study", to be submitted to Eur. Phys. J. B