	Experiment title: *Cu-alkali ion-exchange in silicate glasses: depth dependence of the Cu state by ReflEXAFS measurements*	**Experiment number**: 08-01-604
Beamline: BM08	**Date of experiment**: from: 19 september 2002 to: 23 september 2002	**Date of report**: 12 april 2003
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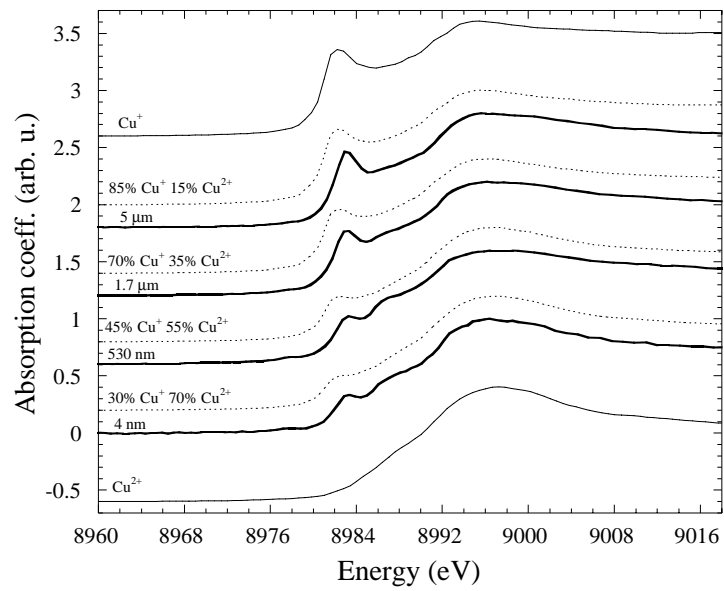F. Gonella*, E. Cattaruzza*, INFM, Physical Chemistry Dept., University of Venice, Italy

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Report:

Metal-alkali ion-exchange in glass process has been widely used to dope silicate glasses. The process is performed by immersing silicate glass slides in a molten salt bath containing the dopant ions, which replace alkali ions of the glass matrix. Ion-exchange with copper is important for the blue-green luminescence properties of copper-doped glasses, useful for laser technology, as well as for the third-order nonlinear optical features of copper nanoclusters in glass. The former property is due to the presence of copper ions dispersed in the glass matrix in the Cu(+) state of valence, and the latter to the formation of Cu metallic nanoclusters. In this framework, the oxidation state and the distribution of copper inside the treated glass is a central issue for both the understanding of the incorporation process and for application purposes.

Cu-alkali ion-exchange in silicate glasses gives rise to a peculiar copper distribution, with the presence of both the Cu(2+) and Cu(+) states. In this experiment, x-ray absorption near-edge spectroscopy in reflection mode was performed on soda-lime and Schott BK7 glasses after Cu-alkali ion-exchange. Glass slides wer immersed in a molten eutectic bath of $CuSO_4:Na_2SO_4$ (54:46 mol%) at 545 °C for 10 minutes. X-ray absorption spectroscopy was performed at liquid nitrogen temperature, for the Cu K-edge (8979 eV). The flux on the sample was of the order of 1×10^{10} photons s^{-1}. Due to the low Cu concentration in the samples (1-5×10^{21} atoms/cm^3), the x-ray absorption spectra were collected in fluorescence mode, by a high-purity element Ge detector. Measurements were taken for different beam incidence angle values, ranging (with respect to the sample surface) from 0.1 to 7.5 degrees, corresponding to a probed depth from about 3 nm to 10 μm, respectively. Using reflection configuration, it was possible to obtain detailed information on the state of copper in different ion-exchanged regions. In the figure, the x-ray absorption near-edge structure (XANES) spectra are reported for a soda-lime sample, collected at different incidence angles, together with standard spectra from copper ions in glass with different oxidation states, Cu(+) and Cu(2+). The spectra were simulated using the absorption expectd for silica layers doped with different relative concentrations of the two copper species (see figure). Taking into account the beam degradation with the depth, the experimental results were used to determine the copper behavior in terms of different diffusion regimes for the mono and divalent copper ions. XANES performed in reflection mode indicates that the Cu(2+)/Cu(+) ratio is strongly depth-dependent, suggesting that the relative presence of the two species throughout the exchanged region is governed by their different diffusion regimes, while the local composition and the overall local copper concentration play a minor role (F. Gonella, E. Cattaruzza, A. Quaranta, S. Padovani, C. Sada, C. Maurizio, F. D'Acapito, "Depth-selective XANES study of copper state in Cu-alkali ion-exchanged glasses", and "Copper diffusion regimes in Cu-alkali ion-exchanged glasses", both in preparation).

Cu K-edge absorption coefficient spectra collected at different incidence angle (solid line) and compared to that of copper in glass with state of valence (1+) and (2+), respectively indicated as Cu(+) and Cu(2+). Together with the experimental data, the simulation of spectra are also reported (dashed lines). The simulation is made by a linear combination of Cu(+) and Cu(2+).