


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## Copper diffusion in ion-exchanged soda-lime glass

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**ABSTRACT** Cu-alkali ion exchange in silicate glasses gives rise to a peculiar copper distribution, with the presence of both the  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  oxidation states. Grazing incidence X-ray absorption near-edge structure spectroscopy and secondary ion mass spectrometry were performed on different ion-exchanged samples. The results show that the  $\text{Cu}^{2+}/\text{Cu}^+$  ratio is strongly depth-dependent. The relative presence of the two species throughout the exchanged region turns out to be governed by their different diffusion regimes, while the chemistry of the redox process is shown to play a minor role. A phenomenological model is proposed to describe the diffusion process.

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### 1 Introduction

Metal-alkali ion exchange in glass has been widely used to dope silicate glasses [1]. The process is realized 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 has in particular attracted new attention for the blue-green luminescence properties of copper-doped glasses [2, 3], useful for laser technology, as well as for the third-order nonlinear optical features of copper nanoclusters in glass [4–6]. The former property is due to the copper ions dispersed in the glass matrix in the  $\text{Cu}^+$  oxidation state [7], while the latter to the formation of Cu metallic nanoclusters. In this framework, the knowledge of the distribution of copper oxidation states inside the treated glass is a central issue for both the understanding of the incorporation process and for application purposes. At present, only a few studies have been dedicated to ion exchange with copper [8–12], and several open questions yet remain concerning the copper behavior inside the glass upon ion exchange. Because of the possible presence of different oxidation states, namely,  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Cu}^0$ , copper distribution within the matrix follows a rather complex behavior [11], critically depending on both glass and bath composition as well as on the process parameters. In this work, X-ray ab-

sorption fine structure (XAFS) spectroscopy in grazing incidence mode and secondary ion mass spectrometry (SIMS) were performed on soda-lime glasses after Cu-alkali ion exchange. The combined use of these analytical tools allowed us to define an exhaustive picture of the microscopic structure reached after the doping process. In particular, XAFS spectroscopy provides detailed depth-dependent information on the local structure, allowing to relate the observed copper distribution features to the local composition and structure [13]. A phenomenological model of the diffusion process was developed to account for the anomalous distribution of the copper species outlined by the experimental analysis techniques.

### 2 Experimental

Ion exchange was realized by immersing commercial soda-lime (wt. % 69.6  $\text{SiO}_2$ , 15.2  $\text{Na}_2\text{O}$ , 1.1  $\text{K}_2\text{O}$ , 6.5  $\text{CaO}$ , 5.1  $\text{MgO}$ , 1.8  $\text{Al}_2\text{O}_3$ , 0.4  $\text{SO}_3$ , 0.2  $\text{TiO}_2$  and 0.1 traces) glass slides in a molten salt bath of  $\text{CuSO}_4:\text{Na}_2\text{SO}_4$  (54:46 mol %); the process was carried out at 545 °C for 10 minutes.

X-ray absorption spectroscopy was performed for the Cu *K*-edge (8979 eV), on the Italian beamline GILDA of the European Synchrotron Radiation Facility (ESRF), with a bending magnet device source. The sagittally focusing monochromator [14], used in the so-called dynamical focusing mode, was equipped with two Si(311) crystals. Harmonic rejection was achieved by using two Pd coated mirrors with an energy cutoff at about 21 keV. The X-ray absorption spectra were collected at room temperature in fluorescence mode, by a high-purity 13-element Ge detector. Using XAFS in grazing incidence [15] configuration, one can select the probed depth by varying the incidence angle of the incoming beam. X-ray absorption near-edge structure (XANES) spectra were simulated as a linear combination of the standard spectra for  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  in soda lime glass [16], to obtain the information on the oxidation state of copper in different ion-exchanged regions. Extended X-ray absorption fine structure (EXAFS) region of the X-ray absorption coefficient was analyzed to have information about the local environment of copper ions, in term of interatomic distances, coordination numbers and Debye–Waller factors. To select the thickness of the probed region, measurements were taken for different beam incidence angles, ranging from 0.13 to 3.5 degrees

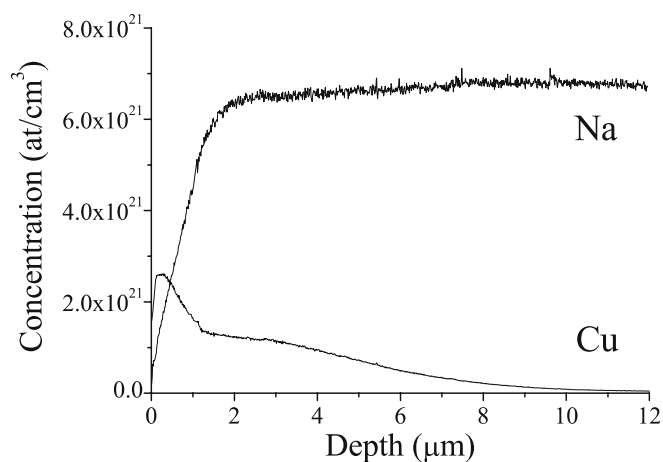
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(with respect to the sample surface), corresponding to an attenuation length from about 4 nm to 5  $\mu\text{m}$ , respectively. The attenuation lengths were calculated following the data tables [17]. As a standard reference, X-ray absorption spectra in transmission mode were recorded for  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  crystalline powders, and for  $\text{Cu}$  bulk. EXAFS (extended X-ray absorption fine structure) data processing was carried out by Fourier filtering and multi-parameter fit in the R-space. Theoretical scattering amplitude and phase were generated by FEFF code [18] and the multi-electron amplitude reduction factor  $S_0^2$  in standard EXAFS formula was fixed to the value obtained from standards spectra ( $S_0^2 = 0.8 \pm 0.1$  for both  $\text{CuO}$  and  $\text{Cu}_2\text{O}$ ). Copper and alkali ion concentration profiles were determined by secondary ion mass spectrometry using an IMS-4f CAMECA spectrometer, equipped with a normal incidence electron gun to compensate the surface charge build-up while profiling insulating samples. We used a 14.5 keV  $\text{Cs}^+$  primary beam and negative secondary ion detection (rastered area:  $125 \times 125 \mu\text{m}^2$ ). The absolute values of concentrations were determined by Rutherford backscattering spectrometry (RBS) measurements.

### 3 Results

Concentration profiles from SIMS data are shown in Fig. 1 for a typical soda-lime doped sample, processed under the conditions described above. For a soda-lime matrix, the exchange takes place between copper and sodium (see Fig. 1). An accumulation of copper in the region near the surface is evident, giving rise to copper distribution profiles that cannot be described by the usual phenomenology for the diffusion of a single ion species. Previous studies evidenced that the resulting profiles are given by the contribution of both  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  species [11, 19, 20]. In particular, it has been suggested that  $\text{Cu}^{2+}$  diffuses directly from the bath in the very first exchanged region following an erfc profile, while the much more mobile  $\text{Cu}^+$  species is distributed throughout the whole exchanged region, with a gaussian shape [11, 19, 20].

Previous XAFS studies [21–23] showed that copper ions in ion-exchanged soda-lime glass are mostly in the  $\text{Cu}^+$  state,

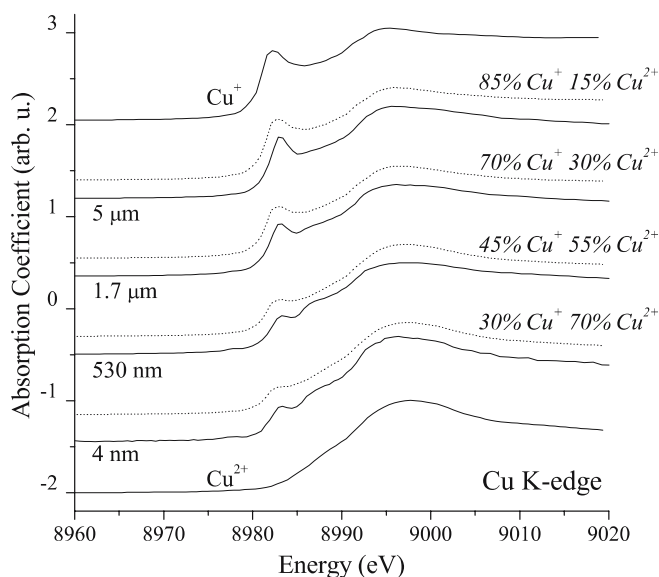


**FIGURE 1** SIMS in-depth concentration profile of ion species taking part to ion exchange in soda lime glass. Exchange was performed in  $\text{CuSO}_4:\text{Na}_2\text{SO}_4$  bath at 545 °C for 10 min

but this result does not distinguish the possible different location of the copper ion species within the doped layer, since data are integrated over the whole ion-exchanged layer. In order to quantitatively determine the relative amount of the two oxidation states for copper at different depths, and thus to test the validity of the assumption about the location of the two copper species, the  $\text{Cu}^+/\text{Cu}^{2+}$  ratio values were determined as a function of the depth from the collected X-ray absorption near-edge structure (XANES) data. In Fig. 2, the XANES spectra are reported, collected for different incidence angles, together with standard spectra for  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  polycrystalline samples. In Fig. 2, the spectra obtained for incidence angles ranging from 0.13 deg to 3.5 deg, corresponding to attenuation lengths of 4 nm to 5  $\mu\text{m}$ , respectively, are shown together with the simulations (dotted lines). The  $\text{Cu}^+/\text{Cu}^{2+}$  ratio varies from 30:70 at the surface up to 85:15 in the case of the spectrum collected at 3.5 deg of incidence (5  $\mu\text{m}$  of attenuation length).

The local order was investigated, in terms of coordination number, interatomic distances and Debye–Waller factors, by EXAFS analysis. The moduli of the EXAFS Fourier transform (FT) with the relative fits are reported in Fig. 3 for  $\text{Cu}$   $K$ -edge. Transformations were performed in the interval  $k = 3\text{--}9.5 \text{ \AA}^{-1}$  with a  $k^3$ -weight. The interatomic distances, coordination numbers and Debye–Waller factors, as obtained by the fitting procedure, are reported in Table 1, together with the data for reference standards.

The moduli of EXAFS FTs exhibit, for all the samples, only one peak that can be ascribed to copper coordination with oxygen atoms. No second shell correlation is suggested between alkali and copper ions, as already found in other investigation [15, 16, 21–23]. In the ion-exchanged samples,  $\text{Cu}$  atoms are expected to locate in the  $\text{Na}^+$  sites, bound to non-bridging O atoms after the substitution in the glass matrix. Nevertheless, the  $\text{Cu}\text{--O}$  bond length, which varies from



**FIGURE 2**  $\text{Cu}$   $K$ -edge absorption spectra collected for different incidence angles (solid lines), together with spectra of copper in glass with oxidation state (+1) and (+2), indicated as  $\text{Cu}^+$  and  $\text{Cu}^{2+}$ . The simulated spectra are also reported (dotted lines). Respective attenuation lengths are also indicated









