Oxidation state of sulfur, iron and tin at the surface of float glasses

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Abstract. Sulfur is an important element of glasses, not because of its amount, always very low (less than 0.4 % in weight of SO\(_3\)), but because of its role since it actively participates to the refinement process and, combined to other elements, it can be responsible for the coloration of the glass. Iron is also of a major importance in most of the glasses. In the case of the float glass, the two faces, because of the fabrication process, are different in terms of composition (presence of Sn for one face) and also in terms of oxidation state of these minority elements (Fe, Sn, S). There should be a subtle interplay between the concentrations and the oxidation states of these different minority elements, and anyway these variations occur over a thickness of the order of few micrometers below the surface.

Using the high intensity and the focusing properties (3 x 3 \(\mu\)m\(^2\)) of the x-ray beam from the Lucia beamline, we have therefore studied the speciation of iron and sulfur near the face of a float glass in relation with the behavior of tin. This has been obtained by combining elemental x-ray fluorescence cartography and x-ray micro-absorption at the different K-edges.

1. Introduction

The manufacturing of glass by means a float bath in a reductive atmosphere causes the glass to present a reduced skin\(^1\), which is less basic and more viscous than the bulk and may result in a surface roughening. The present work aims at analyzing the concentration profiles and the oxidation states of minority components, i.e. Sn, Fe and S, in the very near vicinity of the surface (a few micrometers) by microspectroscopy. These parameters are hardly accessible by other techniques. Analyses were done in the following way: first a cartography of all the elements of interest has been obtained, including a region from the surface to about 40 micrometers into the bulk. The evolution of the concentration of each element can be extracted from these mappings. Then, X-ray Absorption Spectroscopy has been performed at the three K-edges in order to extract informations on the electronic state of each element as a function of the distance from the surface.

2. Results

2.1. Cartographies

Experiments have been conducted on the Lucia beamline installed at this time on the Swiss Light Source (Villigen, Switzerland). The spot size was typically 3 x 3 \(\mu\)m\(^2\) at all energies of interest. Samples are float glass pieces, stuck together by the face called ‘Sn’ because it was in contact with the tin bath of the float process, or the face called ‘A’ because it was facing the atmosphere. A careful polishing of this cut was then done in order to have a very flat surface for the cartography experiments. In order to avoid any artefact from the self-absorption of the fluorescence signal, the common surface of the glass has been set horizontal, and this common surface can be precisely localized by the study of the silicon mapping whose concentration versus the distance from the surface must be constant. The present work only shows the main results concerning the 10 mm thick sample.
Figure 1. Cartographies of Si, Sn, Fe and S (from left to right) across the ‘Sn’ surface of a 10 mm thick glass.

The silicon and iron maps (figure 1) have been obtained with an incident energy of 7130 eV, the tin map has been made at 3990 eV in order to avoid the contribution of calcium present in the glass, and the sulfur one has been recorded at 2500 eV in order to maximize the fluorescence signal.

The vertical line profiles of the cartographies (figure 2), averaged over the whole width of the image, give the evolution of the concentration of each element as a function of the distance from the surface.

Figure 2. The concentration of the different elements as deduced from vertical line profiles of Fig. 1.

The dashed area at the center, which has a width of about 5 micrometers, corresponds to the dead zone filled with the glue which holds the two ‘Sn’ faces together. We can make the following observations:

- the concentration of Sn decreases strongly from the surface, in line with the glass preparation method. We find, around 10 microns from the surface, a ‘bump’ in the Sn concentration which has already be observed by SIMS and EPMA, and which is also associated to a change in the Sn valence from Sn²⁺ (near the surface), to mostly Sn⁴⁺ (away from the surface) 1,2.
- the iron concentration presents a dip at about the same position that the Sn bump 2.
- the sulfur concentration increases in the same domain.

Far away from the surface, all these concentrations will keep a stable value of the order of the one reached at 40 μm.

2.2. Evolution of the valence state of each element.
XAS experiment have then been recorded at several location away from the surface, scanning the sample position vertically by steps of about 2 μm.

2.2.1 Sulfur. This element presents in the near edge spectrum several features characteristic of the various oxidation states, which can easily be calibrated from model compounds. Some of the XANES spectra are shown in figure 3. Going away from the surface, we see that the component at 2473 eV decreases while the peak at about 2482 eV, characteristic of S\(^{6+}\), increases strongly. A careful comparison with model compounds (pure sulfur and ZnS) indicates that this 2473 eV component originates from S\(^{2-}\).

![Figure 3. K-edge XANES spectra of sulfur at various distances from the surface](image)

![Figure 4. Relative amount of 6+ and 2- valence of sulfur as a function of the surface distance.](image)

All these spectra have been modelled by a sum of four lorentzian (at 2473.2, 2477.4, 2481.6 and 2497 eV, the origin of the peak at 2477.4 eV being still an open question) superimposed to an arctg function centered at 2486 eV. We therefore can extract the relative amount of 2- and 6+ components of sulfur as a function of the distance from the glass surface. The results are shown in figure 4. The evolution appear in line with what was generally expected, that is to say that sulfur is essentially 6+ in the bulk although a strong 2- component is present near the surface.

2.2.2 Iron. The same XAS methodology has been applied for iron at the K-edge. Figure 5 shows the results for three different distances from the surface. The insert gives a more detailed view of the so-call characteristic pre-peaks. As already proved by several studies, the first shape resonance which in the present case is around 7185 eV, is a good signature of the local order around the iron \(^3\).

![Figure 5. Fe XANES spectra at different distances from the surface. In insert, an expanded view of the pre-edge peaks.](image)

In our case, the stability of this resonance indicates that the local order around the iron atoms remains the same whatever the distance from the surface. On the contrary, the changes observed on the main ‘white line’ at 7130 eV indicates that the medium to long range order might vary, although
quantitative information cannot be extracted from these changes. In the insert, the pre-peak structure shows a definite evolution which can be analyzed as a variation of the relative amount of Fe$^{2+}$ and Fe$^{3+}$ as a function of the distance. We have then analyzed quantitatively the pre-peaks on a now classical way: the background is modelled by an arctg function, and two Voigt functions simulate the two pre-peak components. The width and the shape of these Voigts have been kept constant, while their position and amplitude were the free parameters of the fits. Actually, the energy position of the peaks do not move from one fit to another (7113.1 and 7114.8 eV) while their amplitude ratio gives the relative amount of Fe$^{3+}$/Fe$^{2+}$. We obtain the values of 1.8, 1.1 and 1.9 for distances from the surface of 4, 10 and 22 micrometers respectively. The more reduced state of iron around 10 μm is associated with the so-called tin hump where Sn$^{4+}$ dominates.

2.2.3. Tin. The evolution of the near edge spectra is shown in Fig.6. The spectra are very similar, nevertheless we observe a shift (labelled ΔE in the figure) towards higher energies, when we go into the bulk of the glass. This shift is in line with an evolution of the Sn valence from 2+ to 4+ as shown in model compounds and assuming that the structural disorder smooths the differences of the spectra of SnO$_2$ and SnO around 3960 eV (the spectra at the surface corresponding to the 2+ type). The transition between the two states appears (blue line) at about 10 μm from the surface, but, as the overall shape of the near edge structure, there is no obvious change of the local structure around the tin atoms.

Figure 6. Sn XANES spectra at different distances from the surface, showing the energy shift ΔE related to an increase of the Sn valence from 2+ to 4+.

3. Conclusion
All these results can be gathered as the following: other techniques have already shown the evolution of the Sn concentration as a function of the depth into the glass, with a bump at about 10 μm and a change from 2+ to 4+. This behavior is well obtained on the cartography and XAS experiments looking at the Sn L absorption edge (figures 2 and 6). It has been argued that this valence change could be induced by a charge transfer from the sulfur atoms. This may be the case since the spectroscopic results show that, near the surface, the sulfur evolves from 6+ (bulk) to 2− where the tin is oxidized into Sn$^{4+}$. Iron could also play a role in the charge balance since, around 10 μm where exists the Sn bump and the change in the Sn valence, we find that Fe presents a definite increase in its 2+ component. A complete discussion should also involve the relative Sn/Fe/S concentrations.

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