Surface Analysis of Oxide Glass Surfaces : the Relationship between Atomic Charges and XPS Chemical Shifts

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The aim of this work was to get a better understanding of the O 1s binding energies E_b(O1s) in complex glasses of interest in nuclear waste storage in relationship with the mean charge on the oxygen atoms, relevant to acidic/basic properties of the glass. Three different glasses were considered : an aluminum borosilicate, a lanthanum aluminosilicate and a calcium aluminosilicate. The O1s binding energies were measured for each glass, along with individual simple oxides. The oxygen charges were estimated by an empirical method based on the electronegativity equalization principle. We show that for the first two glasses, the O 1s binding energy shift is driven by the changes in the oxygen charge induced by mixing the oxides to obtain the glass. For the latter glass however, Madelung effects are of prime importance and the E_b(O1s) value of the glass cannot be predicted from the values in the individual oxides.

I - Introduction

Complex oxide glasses attract much attention because of their applications, especially in the field of nuclear waste storage. Their surface has a very important role, as these materials have to be very resistant towards aqueous alteration. X-ray photoelectron spectroscopy (XPS) is well suited to study the surface alteration of glasses [1]. Besides quantitative analysis, a good understanding of the O 1s binding energy shifts in these materials could be very useful. Indeed in any oxide material, the O 1s binding energy carries information on the electron density on the oxygen atoms, hence on the optical basicity, which is used also as a measure of acidic/basic properties of oxides [2].

Several attempts have been made in the literature to use the O1s binding energy as a fingerprint of the ionicity/covalency of oxides (with one type of cation). For example, Noller et al plotted the O1s binding energy of selected oxides as a function of the oxygen Pauling charge, and proposed to use the O 1s binding energy as a fingerprint of the ionicity/covalency or basicity/acidity of oxides, the covalency/acidity increasing with the O 1s binding energy [3]. A correlation between the O 1s binding energy, as measured by XPS, and the calculated optical basicity has been obtained for simple oxides with cations P, Si, Al, Mg and Na, with a decrease of the O1s binding energy when basicity increases [4]. Such an approach has been more recently extended to binary tellurium oxide glasses, in which increasing content of alkali-oxides from Li_2O to Cs_2O were added, so as to increase the basicity. As with simple oxides, the O1s binding energy decreases when the optical basicity increases [5]. Even more recently, a similar behavior has been observed in boron oxide glasses, with increasing contents of Sb_2O_3 [6].

A simple phenomenological rule is widely used to predict the evolution of covalency / ionicity in mixed oxides (e.g. with several types of cations), compared to the simple oxides (one type of cation), as well as to interpret the XPS binding energy shifts in terms of charge transfer [7]. This rule states as follows. Considering the mixing of two oxides (A_mO_n and M_xO_y) to form a complex mixed oxide ($A_zM_sO_t$), the cation (A) of the more ionic metal oxide (e.g. A_mO_n) is expected to become even more ionic after formation of the complex oxide, whereas the cation (M) of the more covalent oxide (M_xO_y) should experience a corresponding increase in covalency. In other terms, this means that the charge on the A cation is expected to be larger in the mixed oxide than in the A_mO_n oxide, while the charge on the M cation is expected to be smaller than in the M_xO_y oxide, the charge on oxygen having an intermediate value. We have tested recently the validity of this simple rule and its application to XPS of mixed oxides with a prototypical system : crystalline zircon $ZrSiO_4$ and simple oxides ZrO_2 and SiO_2, by using the atomic charges extracted from an ab initio electronic structure calculation [8]. The purpose of the present work was to test this rule with complex silicate glasses. For such amorphous materials, electronic structure calculations are not easily available, so that the atomic charges have been in a first approximation obtained by an empirical method based on the electronegativity equalization principle [9].

Three different glasses were considered : a borosilicate labelled SiBNaZrO, and two aluminosilicates labelled SiAlLaO [1] and SiAlCaO. For each glass, the O1s binding energy was measured, and compared to its values in the simple oxides (SiO_2, Al_2O_3, ...). The results are discussed in terms of the dependence of binding energy shifts on atomic charges, and also on the Madelung contribution.

II – Experimental

All glass samples were polished monoliths. Before loading into ultra-high vacuum, they were ultrasonically cleaned in ethanol. Some of them were heated in air at 400°C to minimize the carbon contamination of the surface. The nominal molar concentrations were:

SiBNaZrO : 67% SiO_2 – 18% B_2O_3 – 13% Na_2O – 2% ZrO_2

SiAlLaO : 60% SiO_2 – 20% Al_2O_3 – 20% La_2O_3

SiAlCaO : 60% SiO_2 – 10% Al_2O_3 – 30% CaO

The reference simple oxides SiO_2, ZrO_2, Na_2O, B_2O_3, Al_2O_3, La_2O_3 and CaO were those powders used for the elaboration of glasses. These powders were heated in air so as to decrease the hydroxyl content as much as possible, and pressed into indium foil.

The XPS analyses were performed in a VG ESCALAB Mark II. X-ray photoelectron spectra were produced using a non-monochromatized X-ray source ($h\nu = 1486.6$ eV) and an hemispherical analyzer fitted with a five-channeltron multidetection. Calibration of the spectrometer was such that the Ag $3d_{5/2}$ line had a binding energy of 368.35 eV and a FWHM of 0.85 eV, with a 20 eV pass energy. Drift of the electron binding energy due to the surface charging effect was calibrated by utilizing the C1s peak of contamination carbon, for which the C1s photoelectron line was set at 284.6 eV, as in ref [8].

Survey spectra were recorded for the 0 to 1250 eV region to determine the elements present in the sample and to check for surface contamination. Then the O1s photoelectron lines were recorded. The O1s binding energies appearing in the plots of figure 1 are those measured in the present work at the maximum of the peaks, except for the CaO sample. Indeed in this latter case, as the hydroxyl component of the O1s photoelectron line was too intense to allow determination of the binding energy of pure CaO, we have used the value given in ref [10].

III - Deriving atomic charges from the electronegativity equilization principle

The atomic charges have been in a first approximation estimated by the electronegativity equalization principle [9]. Initially established for liquids, this model does not take into account the structure, but only the composition, with P_i the stoichiometric coefficient of element i. The electronegativity χ_i of an element i is defined as the opposite of the chemical potential μ_i. For an element i embedded in a condensed phase, the electronegativity χ_i can be written as $\chi_i = \chi_i^* + k\sqrt{\chi_i^*}\,q_i$, where χ_i^* is the electronegativity of the neutral isolated atom and q_i the partial charge of the element i in the solid. The term $k\sqrt{\chi_i^*}$ represents the hardness of element i, i.e. the resistance of the chemical potential to adding/removing an electron. At the thermodynamic equilibrium, all electronegativities χ_i are equal to an average electronegativity denoted $\bar{\chi} = \frac{\sum_i P_i \sqrt{\chi_i^*}}{\sum_i \frac{P_i}{\sqrt{\chi_i^*}}}$. Then the partial charges can all be calculated by the following equation $q_i = \frac{\bar{\chi} - \chi_i^*}{k\sqrt{\chi_i^*}}$. The atomic charges on oxygen q_O in the plots of figure 1 were estimated in this way by using the Allred-Rochow electronegativities [9]. These charges depend on the k constant, which is usually taken equal to 1.36 [9]. These charges should not be considered as absolute values, but simply as relative values. It must be emphasized that this way of calculating the atomic charges completely neglects the structure, and one must be aware that this can be a possible limitation of the approach.

IV- Discussion

Figure 1 shows the variation of the O1s binding energy $E_b(O1s)$ as a function of atomic charge on oxygen q_O, for the three glasses under study, along with the corresponding individual oxides. When considering the simple oxides, the plots show an overall increase of $E_b(O1s)$ when $|q_O|$ decreases, that is to say, when $\bar{\chi}$ increases, or when the ionicity / basicity decreases. However the relationship is far from being linear, so that a universal linear relationship between q_O and $E_b(O1s)$, as suggested by Noller et al [3], does not seem to be valid. This is because one has to take into account the Madelung contribution (which is also an initial state contribution) and the extra-atomic relaxation energy contribution (final state contribution), when comparing very different oxides.

However, in our previous work on the system SiO_2-ZrO_2-$ZrSiO_4$ [8], the changes in the atomic charges were the most important effect driving the binding energy shifts. More precisely, a linear relationship was obtained when plotting the O 1s binding energy of the three oxides as a function of the oxygen charge, not because the Madelung and relaxation corrections were negligible, but because they were compensating each other. We have also checked that in this case the atomic charges evaluated by the electronegativity equalization principle varied in the same way as those calculated by the ab initio density functional theory (DFT) method.

When mixing three simple oxides to obtain a glass, if the change of atomic charges would be the driving effect to explain the binding energy shifts, then one would expect the [q_O, $E_b(O1s)$] point to lie inside the triangle built by linking together the points of the individual oxides. This is indeed what is obtained with the borosilicate SiBNaZrO glass (the ZrO_2 concentration is so small that the [q_O, $E_b(O1s)$] point lies inside the triangle of the three main oxides, figure 1a), and with the SiAlLaO aluminosilicate glass (figure 1b). However, with the SiAlCaO glass, the [q_O, BE(O1s)] point lies outside the triangle of the simple oxides (figure 1c). This behavior has to be related to a particularity of CaO, which is a highly ionic alkaline-earth oxide of the series MgO, CaO, SrO and BaO. Pacchioni et al [11] have shown that in these oxides, ab initio electronic structure calculations indicated a decrease of the ionicity along the series (MgO being the more ionic oxide), although the electronegativity criterion would predict the contrary, as the cation electronegativity decreases along the series Mg, Ca, Sr, Ba. This is an effect of stabilization of the solid lattice by a strong Madelung potential. The decrease of $E_b(O1s)$ along the series MgO, CaO, SrO, BaO experimentally observed [11] is not due to an increase of ionicity, but, again, to a strong Madelung field effect. In this case, the

E_b(O1s) shifts cannot be explained simply by a change in the oxygen charge, and Madelung effects cannot be neglected. Then the E_b(O1s) value in the SiAlCaO glass cannot be predicted from the values in the individual oxides.

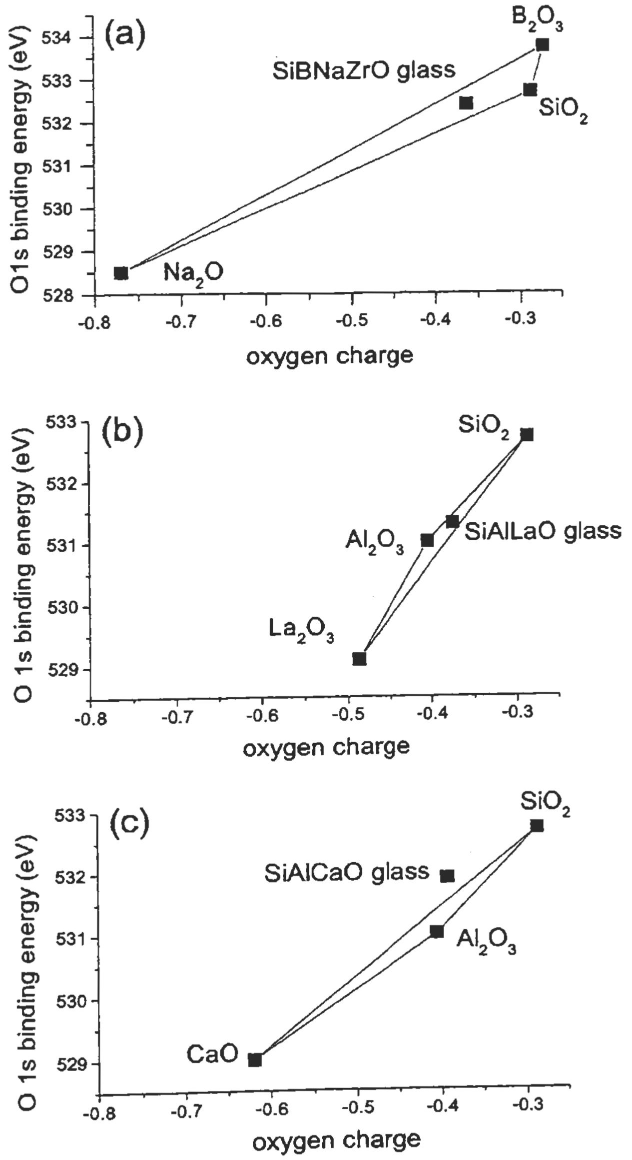

Figure 1. Measured O 1s binding energy as a function of the oxygen charge estimated from the electronegativity equalization principle (see text) for (a) the borosilicate glass SiBNaZrO ; (b) the lanthanum aluminosilicate glasss SiAlLaO ; (c) the calcium aluminosilicate glass SiAlCaO, and the individual oxides. For CaO, the E_b(O1s) value is taken from ref [10].

IV Conclusion

The aim of the paper was to get a better understanding of the binding energy shifts of the oxygen 1s photoelectron lines in three different glasses by comparing the E_b(O1s) values in the glass to their values in the individual oxides.

In the borosilicate glass and the lanthanum aluminosilicate glass, the E_b(O1s) values can be explained by the dominant effect of the change in the oxygen charge, as predicted by the empirical method of electronegativity equalization. However for the calcium aluminosilicate glass, Madelung effects are of prime importance, so that the E_b(O1s) cannot be explained simply by the change in the oxygen charges estimated from our empirical method. A careful study of the binding energy shifts of both oxygen and cation core levels in glasses based on SiAlCaO, taking into account also extraatomic relaxation corrections, will be detailed more extensively in a forthcoming paper [12].

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