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1. Introduction

Using XPS as the principal investigative tool, we are examining bonding properties of selected metal oxides added to silicate glass. In this paper, we examine the simple sodium silicates $(\text{Na}_2\text{O})_x(\text{SiO}_2)_{1-x}$ and $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ into which we add varying amounts of CaO. It has been generally accepted that the addition of Na_2O to SiO_2 breaks the Si-O-Si linkages (bridging bonds), replacing them with nonbridging oxygen bonds of the type Si-O^{-Na} Na⁺O-Si. Earlier studies [1,2] have shown that these nonbridging bonds could be readily monitored by examining binding energy shifts at the O 1s core level.

In this paper we extend the results of Ref. [1] to include an examination of CaO in sodium silicate glass. In addition, we present results of a theoretical cluster calculation for the sodium silicates to examine electronic states in the valence band region.

2. Experimental

The samples of sodium trisilicate glasses containing CaO were prepared by melting appropriate amounts of CaO with powdered $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ glass. To minimize the compositional variation of the sample, a large batch of sodium trisilicate glass was prepared and then used to prepare the calcium glasses. The glasses were melted in air at 1300°C in platinum crucibles. The samples were crushed and remelted several times to ensure homogeneity. X-ray powder diffraction patterns were taken for several randomly selected samples to check for the presence of crystalline phases and none could be detected. After preparation, samples were stored in a dessicator. Prior to use, they were ground on dry emory paper to the appropriate shape for insertion into the XPS spectrometer. After insertion, the glass surface was scraped with an alumina rod to eliminate the contaminated layer that had been exposed to air.

3. O 1s: Sodium Silicate

Figure 1 shows the O 1s spectra for amorphous SiO_2 and for several $(\text{Na}_2\text{O})_x(\text{SiO}_2)_{1-x}$ glasses. A number of Na Auger lines also appear in the spectra

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of Fig. 1. With the addition of Na_2O , a new peak appears on the low-binding-energy side of the O 1s peak. This peak scales with sodium concentration, as expected (since one Na atom is associated with each non-bridging oxygen site).

If all Na_2O added to $(\text{Na}_2\text{O})_x(\text{SiO}_2)_{1-x}$ glasses simply breaks bridging (O_I) bonds, then we expect [1] the concentration of bridging oxygen, O_I and non-bridging oxygen, O_{II} sites (scaled to Si concentration) to behave as

$$\frac{\text{O}_I}{\text{Si}} = \frac{2-3x}{1-x} \quad (1)$$

$$\frac{\text{O}_{II}}{\text{Si}} = \frac{2x}{1-x} \quad (2)$$

The total oxygen concentration is

$$\frac{\text{O}_T}{\text{Si}} = \frac{\text{O}_I}{\text{Si}} + \frac{\text{O}_{II}}{\text{Si}} = \frac{2-x}{1-x} \quad (3)$$

In order to test this model prediction, in Ref. [1], the two components of the O 1s line were fitted to Gaussian functions to determine relative intensities (as well as peak positions). A single scaling parameter was required. In this paper, we discuss an alternate analysis procedure (and find that we get essentially the same results as Ref. [1]). Our procedure here is to consider one sample to be a standard and measure the intensities and peak positions relative to this standard. For this analysis, all spectra are normalized to a Si 2s core line (operationally, the spectra for all samples are first scaled so that the Si 2s line always has the same integrated intensity). Assuming our standard sample has concentration x_0 , we measure the intensity ratio $R_1(x)$ for sample x by zeroing out the O_I peak in the (normalized) difference

$$\left(\frac{\text{O}_I}{\text{Si}}\right)_x - R_1(x) \left(\frac{\text{O}_I}{\text{Si}}\right)_{x_0} = 0 \quad (4)$$

Similarly, $R_2(x)$ is measured by zeroing the O_{II} peak:

$$\left(\frac{\text{O}_{II}}{\text{Si}}\right)_x - R_2(x) \left(\frac{\text{O}_{II}}{\text{Si}}\right)_{x_0} = 0 \quad (5)$$

For this analysis the $x = 0.22$ glass was chosen to be the standard.

Using Eqs. (1) - (5) we have, for the $x_0 = 0.22$ standard,

$$\left(\frac{\text{O}_I}{\text{Si}}\right)_x = R_1(x) \left(\frac{\text{O}_I}{\text{Si}}\right)_{x_0} = 1.72 R_1(x) \quad (6)$$

$$\left(\frac{\text{O}_{II}}{\text{Si}}\right)_x = 0.56 R_2(x) \quad (7)$$

and

$$\left(\frac{\text{O}_T}{\text{Si}}\right)_x = 1.72 R_1(x) + 0.56 R_2(x) \quad (8)$$

Thus, relative to the $x_0 = 0.22$ standard glass, Eqs. (6) and (7) give the experimental intensities for the O_I and O_{II} components of the O 1s line for the $(\text{Na}_2\text{O})_x(\text{SiO}_2)_{1-x}$ glass series.

Figure 2 shows the results of the intensity measurements using this ratio measurement technique. The solid lines are the theoretical expressions of Eqs. (1) - (3). The concentration ratio of bridging oxygen to Si, i.e., O_I/Si is, of

course, equal to 2 at $x = 0$ (SiO_2) and falls to zero at $x = 0.67$ where all oxygens of the matrix should appear in nonbridging (O_{II}) sites. If the model predictions hold for all x up to 0.67, then the glass will consist solely of SiO_4^{4-} ionic units, each bonded to 4 Na atoms and, of course, $\text{O}_{\text{II}}/\text{Si} = 4$.

A check on experimental consistency is provided with the curve for $\text{O}_\text{T}/\text{Si}$, the total oxygen concentration. The measurement ($\text{O}_\text{T}/\text{Si}$), the sum of the O_I and O_{II} components, is in reasonable agreement with the theoretical expression [Eq. (3)]. Independent measurement of O_T using the integrated total O 1s line gives results essentially identical to those shown in Fig. 2. For the components O_I and O_{II} , however, agreement between experiment and the simple model predictions is good for small x (see also Ref. 1) but is increasingly less satisfactory as more Na_2O is added. It may be that for Na_2O rich glasses, some Na_2O does not simply react with the silicate matrix, as proposed, to produce non-bridging bonds. However, the discrepancy may occur as a consequence of the fact that, for high x , the samples are extremely hygroscopic. Furthermore, if the glass surface is washed with water, Na is preferentially and rapidly removed [3] apparently leaving behind SiO_2 . Also, if the glass surface is exposed to a humid environment, Na migrates to the sample surface [3]. Thus, water apparently interacts with Na rich glasses, probably to (initially) release Na ions and O_{II} oxygens from the matrix. Thus, if water is absorbed by the sample during or subsequent to preparation, a reduction of the expected O_{II} content might occur. Since spectra are acquired in high vacuum, excess water will probably be removed during measurement (so O_T would not be anomalous). However, the glass structure would be changed with O_{II} 's removed from nonbridging sites. Then (as seen in Fig. 2) the measured O_{II} should fall below the model prediction and the apparent O_I concentration should fall above the theoretical line, as observed.

4. O 1s: CaO in Sodium Silicate

It is clear that Na_2O , when added to SiO_2 , disrupts bridging oxygen bonds and produces non-bridging sites although some discrepancy from simple model predictions occurs for large alkali concentrations. We now examine the effect of CaO on the silicate glass structure. Suitable glasses of the form $(\text{SiO}_2)_{1-x}(\text{CaO})_x$ cannot readily be prepared [4], so we systematically examine glasses of composition $(0.25 \text{ Na}_2\text{O} + 0.75 \text{ SiO}_2)_{1-x}(\text{CaO})_x$ where x is varied between 0 and 0.25. If CaO interacts with the glass like Na_2O , then we should expect each added CaO unit to produce two O_{II} sites while destroying one O_I site. However, Ca is a divalent ion so that it must bridge two O_{II} -type oxygens:

For the O 1s analysis to be meaningful, it is necessary that O_I and O_{II} sites have sufficiently different binding energies to be resolved in XPS. The sites were clearly resolved for the sodium glass and, fortunately, appear to be comparably resolved for the CaO glasses. We use an analysis similar to that described in Sec. 3 with the $\text{Na}_2\text{O} + 3\text{SiO}_2$ glass as standard, i.e., we examine the series $(0.25 \text{ Na}_2\text{O} + 0.75 \text{ SiO}_2)_{1-x}(\text{CaO})_x$ with the standard being $x = 0$. As in Sec. 3, we count the expected O_I and O_{II} sites and scale them to the Si concentration to obtain

$$\left(\frac{\text{O}_\text{I}}{\text{Si}}\right)_x = \frac{1.667 - 3x}{1 - x}, \quad (9)$$

$$\left(\frac{O_{II}}{Si}\right)_x = \frac{2x + 0.667}{1 - x}, \text{ and} \quad (10)$$

$$\left(\frac{O_{tot}}{Si}\right)_x = \frac{2.333 - x}{1 - x}, \quad (11)$$

valid if the simple model holds. Proceeding as done in Eqs. (4) - (8) we obtain for $x_0 = 0$,

$$\left(\frac{O_I}{Si}\right)_x = \left(\frac{1.667 - 3x_0}{1 - x_0}\right) R_1(x) = 1.667 R_1(x) \quad (12)$$

$$\left(\frac{O_{II}}{Si}\right)_x = \left(\frac{2x_0 + 0.667}{1 - x_0}\right) R_2(x) = 0.667 R_2(x) \quad (13)$$

$$\left(\frac{O_{tot}}{Si}\right)_x = 1.667 R_1(x) + 0.667 R_2(x), \quad (14)$$

where, again, $R_1(x)$ and $R_2(x)$ are the intensities of the O_I and O_{II} component lines measured relative to the standard.

Figure 3 shows the theoretical (solid lines) results [Eqs. (9) - (11)] plotted with the measured O_I and O_{II} concentrations [Eqs. (12) - (14)]. Like the Na-silicate results, agreement between theory and experiment is good but the CaO does not produce as many O_{II} sites as are predicted in the simple theory. It seems unlikely that excess water incorporated into the glass would be responsible for the observed deviation. Both H_2O uptake and modification of surface composition appear to be small for the $(0.25 Na_2O \bullet 0.75 SiO_2)_{1-x}(CaO)_x$ glasses when exposed to water [5]. Also, Fig. 3 shows that the measured O_{total} is in agreement with the model prediction indicating that the glass does not hold excess water (during the measurements). Rather, it would appear that some CaO is unreacted or that bonding of the form,

must be taking place. That is, clustered CaO rich regions, suggestive of early stages of phase separation, may be bound into the silicate network.

It is not entirely clear where the O 1s peak of clustered CaO would appear in an XPS spectrum relative to the O_I and O_{II} peaks of the glass. However, if the Ca 2p peaks of XPS spectra for CaO are aligned with the corresponding Ca 2p peaks of the glass spectrum, we find that the O 1s of CaO is located centrally between the O_I and O_{II} . Thus, we may assume that the O 1s of unreacted CaO would be approximately equally divided between O_I and O_{II} .

We represent the glass as

where z represents the fraction of reacted CaO. Again, utilizing the simple model, (equally dividing the unreacted fraction) we count the bridging and non-bridging sites to obtain

$$\frac{O_I}{Si} = \frac{1.667 - (1 + 2z)x}{1 - x} \quad (15)$$

$$\frac{O_{II}}{Si} = \frac{0.667 + 2zx}{1-x} \quad (16)$$

The dashed lines in Fig. 3 are plots of Eqs. (15) and (16) for $z = 0.80$. Thus, the data of Fig. 3 are consistent with the interpretation that 80% of the added CaO produces non-bridging sites in accordance with the simple model. It appears that the same fraction of CaO is "reacted" for all CaO concentrations in the sodium-trisilicate glass.

5. Core Level Shifts

Bonding information can be inferred from chemical shifts, or changes in the absolute binding energies of electron core levels that result from changes in the chemical makeup of a material. A quantitative interpretation of the chemical shifts is not straightforward. Difficulties can be encountered with determination of relaxation effects [6] and with establishing the zero of energy [7]. Nonetheless, relative binding energy changes of the various energy levels in a multicomponent system can provide insight regarding charge distribution in the material. Some relative shifts for a series of sodium silicates are reported in Ref. [1]. Shifts for decomposed components of the O 1s line in several silicate and phosphate glasses are reported by Brückner et al. [2].

Our results for the $(Na_2O)_x(SiO_2)_{1-x}$ and the $(0.25 Na_2O \bullet 0.75 SiO_2)_{1-x}(CaO)_x$ glasses are summarized in Figs. 4 and 5. In this display, we (arbitrarily) assume that the valence band edge (nearest E_F) undergoes no chemical shift as the sample composition is changed. Furthermore, only the slopes of these displayed curves are relevant since all binding energies were measured relative to a reference (sodium disilicate) sample and some curves have been offset in the figure. For the Ca glass series, $(0.25 Na_2O \bullet 0.75 SiO_2)_{1-y}(CaO)_y$, we plot the shift (to decreasing binding energy) as a function of y . In order to facilitate a direct comparison of the Na glass and Ca glass results, we have plotted the Na glasses' vs. y using the similar form $(0.25 Na_2O \bullet 0.75 SiO_2)_{1-y}(Na_2O)_y$. In this way, we directly compare the effect of one molecule of CaO on the matrix glass to the corresponding effect of one molecule of Na_2O on the glass. (Measurements for the Na series span a wider composition range.) We notice that systematic changes for the two glass series are remarkably similar suggesting that each Ca^{2+} ion behaves much like two Na^+ ions in the glass. (Although Ca-O bonds are apparently stronger [8].) If relaxation effects are small or slowly varying with composition, then a core level shift to decreasing binding energy implies that increased charge appears on the atom in question. Given the energy level reference scheme we have used for Figs. 4 and 5, we expect, for increasing Na or Ca content, that charge migrates to the Si atoms and, to a smaller degree, to the bridging oxygens while very little change would be expected at Na or non-bridging oxygen sites.

Si undergoes the largest shift (to decreasing binding energy). This effect may be largely attributable to those Si atoms that bond to non-bridging oxygens. The Si atom, at the center of a tetrahedron of oxygens, senses the presence of an adjacent non-bridging oxygen. The electron contributed (ionically) by the sodium (or calcium) to the non-bridging oxygen apparently enables that oxygen to somewhat relax its attractive potential to the Si atom (and to a lesser extent, the other oxygens in the tetrahedron) [1]. This "electron relaxation" effect to the Si atom was also found in preliminary theoretical cluster calculations. Calculated effective charges associated with the different atomic sites are: $O_I - 7.55 e^-$, $O_{II} - 7.69 e^-$, $Si_I - 0.92 e^-$, $Si_{II} - 1.00 e^-$, $Na - 0.15 e^-$, where Si_I refers to a Si atom at the center of a tetrahedron of bridging oxygens and Si_{II} is at the

center of an oxygen tetrahedron, one atom of which is non-bridging. This charge analysis indicates that Na is highly ionic, almost totally surrendering its one valence electron. The Si and O atoms are also highly ionic. Si gives up approximately three electrons while each O atom acquires ~ 1.6 . Both O_{II} and Si_{II} are more negatively charged than are the corresponding O_I and Si_I in agreement with experiment. We point out, however, that the calculations are preliminary and are somewhat dependent on the choice of structural parameters for the model cluster.

For three samples core level energies were measured relative to Au 4f lines of a gold film vapor deposited on the samples. A thick gold covering was used and the sample was lightly scraped after film deposition to reveal some of the substrate. Using this calibration procedure, we find for both the Na and Ca glasses, that the slopes of the lines in Figs. 4 and 5 are somewhat too high. For the sodium silicate series, the magnitude of the slopes (of decreasing binding energy) $\Delta(BE)/\Delta y$ should be reduced by about 0.88 eV per unit value of y . This reference scheme would not alter the arguments cited above regarding charge distribution. For the Au referenced Ca glass, however, a somewhat larger slope correction (1.4 eV per unit of y) is needed. In this case, charge would still migrate to Si (with added Ca) but would shift away from the oxygen sites as well as the Na and Ca sites.

6. Valence Band Structure

The valence bands contain those electrons most directly involved in chemical bonding. Thus, a detailed examination of the valence states and observation of systematic changes resulting from composition variations should provide insights into microstructure and bonding properties. For SiO_2 , a number of calculations and analyses of valence band data (including UPS, XPS, SXS, and optical measurements) appear in the literature [9]. These studies generally support the view - that the valence band is composed of different regions containing electron states with identifiable character. Predominately, O 2p, Si 3s, and Si 3p states are involved. The lowest lying states (~ 10 eV binding energy) are Si 3s. The Si 3p's are dominant in the mid-region (~ 7 eV) and the O 2p's produce the dominant peak nearest to the Fermi level. The correspondence between XPS and most density of states calculations is generally not very close, apparently because experimental excitation probabilities vary significantly for the different electron states. Roughly consistent with observation, Scofield's [10] atomic calculations of XPS intensities show that Si 3s should be about four times more intense than the O 2p.

In Ref. [1] it was pointed out that addition of Na_2O to SiO_2 produces significant changes in the valence band structure. Similar to the core level O 1s peak, the O 2s is also split with Na_2O addition. Valence spectra for a series of glasses are shown in Fig. 6. These spectra are scaled to a common silicon line so, with increasing x , we see a substantial growth of the valence band intensity since the O/Si ratio increases. Most of the intensity increase occurs near the band gap in the vicinity of the O 2p contribution that was identified in SiO_2 . In SiO_2 , of course, all oxygens are in the bridging configuration whereas, in the alkali silicates, the bridging concentration is reduced (relative to the Si concentration) while the O_{II} concentration grows directly with Na addition. Thus, the changes observed in Fig. 6 should largely be attributable to O 2p electron states associated with the non-bridging oxygen atoms.

In this paper we make a first step in theoretically addressing changes in valence band structure with Na_2O addition with resort to a suitable cluster calculation. The cluster contains 162 atoms in a random network. Embedded in this large cluster is one added "molecule" of Na_2O arranged to produce two non-bridging oxygen sites. The separation of the Na atom and O_{II} site is 2.35 Å (further details of the model calculation will be presented elsewhere). The total effective charge about a given atom can be calculated using the Mullikan analysis scheme. Also, the local density of states (LDOS) appropriate to a given atom can be obtained. Our procedure is to calculate LDOS spectra and appropriately combine them to produce a simulation of the various sodium silicates. For this purpose we confine our attention to three LDOS calculations representing O_{I} and O_{II} sites as well as a silicon atom bonded to three bridging oxygens and one non-bridging oxygen. (We assume that changes in the Si LDOS that result from changes in the number of O_{I} or O_{II} bonded neighbors will be much smaller than the LDOS differences between the O_{I} and O_{II} sites themselves.) The LDOS for Na was ignored since the calculation shows Na to be very ionic with nearly complete charge transfer away from the Na atom. For SiO_2 , the simulation is the sum of 2 O_{I} and 1 Si LDOS. For $(\text{Na}_2\text{O})_{0.33}(\text{SiO}_2)_{0.67}$, there is one O_{II} per tetrahedral unit and our simulation requires 1 Si, 1 O_{II} , and 3/2 O_{I} (i.e., 3 O_{I} 's each shared by 2 Si atoms). Similarly, for $(\text{Na}_2\text{O})_{0.5}(\text{SiO}_2)_{0.5}$, we need 1 Si, 1 O_{I} , and 2 O_{II} . For the (idealized) $(\text{Na}_2\text{O})_{0.67}(\text{SiO}_2)_{0.33}$, we use 1 Si and 4 O_{II} 's. Figure 7 shows the results of these simulations. (The data have been convoluted with a 0.8 eV FWHM Gaussian to simulate instrument broadening.) Like the data of Fig. 6, these spectra are effectively normalized to correspond to a fixed Si concentration. A number of features in these calculated spectra can be found in the data of Fig. 6. The calculated non-bridging oxygen is shifted by 1.6 eV to lower binding energy to be compared with an experimental shift at the O 2s level of 2.2 eV. Consistent with experiment, the O_{I} peak decreases and the O_{II} peak increases in intensity with x. In the valence band region, the total intensity increases dramatically (since the O/Si ratio increases from 2 to 4) with the growth occurring near the valence band edge. Again, this is consistent with experiment (also see Fig. 5 of Ref. [1]).

7. Conclusions

This paper shows that CaO added to silicate glasses behaves much like Na_2O in converting bridging oxygen sites to non-bridging sites. Good correspondence with model predictions was obtained but deviations were still sufficiently large to warrant attention. We speculate that some CaO may remain unreacted or that small scale phase separation may occur. XPS core level shifts were monitored and possible charge transfer effects were considered. Preliminary theoretical calculations utilizing a molecular cluster approach were presented. XPS spectra for various glass compositions were simulated by appropriately combining local densities of states calculated for individual atoms. Dominant spectral features observed experimentally were found in the simulations. In conjunction with experiments, more carefully refined calculations will be subsequently examined.

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Figure Captions

1. The O 1s XPS spectra for SiO_2 and several sodium silicate glasses. The low binding energy component of the O 1s peak corresponds to non-bridging oxygens.
2. Intensities of the bridging (open circles) and non-bridging (closed circles) O 1s core lines plotted vs. Na_2O concentration for a series of $(\text{Na}_2\text{O})_x(\text{SiO}_2)_{1-x}$ glasses. The squares measure the total O 1s intensity.
3. Intensities of the bridging and non-bridging O 1s core lines plotted vs. CaO concentration for a series of $(0.25 \text{ Na}_2\text{O} \bullet 0.75 \text{ SiO}_2)_{1-x}(\text{CaO})_x$ glasses. The solid line is predicted by theory. The dashed line is the theoretical result assuming 80% of CaO is reacted.
4. XPS core level shifts as a function of Na_2O concentration in a series of sodium silicate glasses. All spectra are referenced to the low binding energy edge of the valence band. The glass is represented as $(0.25 \text{ Na}_2\text{O} \bullet 0.75 \text{ SiO}_2)_{1-x}(\text{Na}_2\text{O})_x$ for ease of comparison with a corresponding Ca glass series (Fig. 5).
5. XPS core level shifts as a function of CaO concentration in a series of sodium silicate glasses containing CaO (see also Fig. 4).
6. XPS spectra (within 40 eV of the Fermi level) for SiO_2 and for the $x = 0.25$ and 0.42 glasses of the series $(\text{Na}_2\text{O})_x(\text{SiO}_2)_{1-x}$.
7. Approximate electron densities of states from theoretical cluster calculations represently (a) SiO_2 , (b) $\text{Na}_2\text{O} \bullet 2\text{SiO}_2$, (c) $\text{Na}_2\text{O} \bullet \text{SiO}_2$, and (d) $2\text{Na}_2\text{O} \bullet \text{SiO}_2$.

Fig. 1.

Fig. 2.

Fig. 3.

, Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.