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ABSTRACT

X-ray photoelectron spectroscopy (XPS) and extended x-ray absorption fine structure (EXAFS) studies have been undertaken on sodium disilicate glasses containing varying amounts of Fe_2O_3 and UO_2. The XPS results enable one to distinguish the different bonding characteristics of iron and uranium in these glasses. A three dimensional model for the iron coordination in the sodium disilicate glass is inferred from the combined XPS and EXAFS results.

INTRODUCTION

The silicate glasses have remarkably high solubility for numerous metal oxides from all regions of the periodic table. This universality is particularly important for waste disposal since many active nuclear species with great variation in atomic number must be stored. Because of the long-term requirement of the storage glasses, fundamental information relating to the bonding properties of metal oxides in the glass is of major importance. Such fundamental information can provide useful input into evaluating the confinement integrity of the glass storage concept. Using two relatively new experimental techniques, XPS (x-ray photoelectron spectroscopy) and EXAFS (extended x-ray absorption fine structure) we have undertaken a study of the bonding properties of metal oxides in silicate glasses. Since iron is the most widely

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investigated transition metal solute in glasses, the iron-glasses should be good materials for initial study to determine if additional bonding information can be obtained. A preliminary study of the bonding properties of uranium oxides in sodium disilicate glasses is also reported.

The coordination of Fe^{3+} in sodium silicate glasses has been studied extensively by many investigators using various experimental techniques. Coordinations have been inferred from optical absorption, electron spin resonance (ESR), and Mössbauer measurements. For these amorphous materials, however, it is difficult to uniquely determine the coordination of the Fe^{3+} site. To illustrate, Bamford (1) concluded that the optical absorption of iron in silicate glasses resulted from Fe^{3+} in octahedral symmetry. Steele and Douglas (2), however, suggested that tetrahedral coordination of Fe^{3+} is most consistent with the optical data. ESR experiments on Fe^{3+} in silicate glasses were reported by Sands (3) and Castuer et al. (4) but they were unable to discern the Fe^{3+} coordination. Kurkjian and Sigety (5) concluded from the combined results of optical and paramagnetic resonance experiments that Fe^{3+} is predominantly tetrahedrally coordinated. Pargamin et al. (6) performed Mössbauer effect measurements on Fe_2O_3 in sodium and calcium silicate glasses. Based on the comparison of isomer shifts and quadrupole splittings of Fe^{3+} ions in the glasses and in crystals, they concluded that the ferric ions are tetrahedrally coordinated in the sodium silicate glass. On the other hand, Bhat et al. (7) concluded, from their Mössbauer data, that the Fe^{3+} ion is octahedrally coordinated.

Using Mössbauer spectroscopy, one can clearly distinguish between Fe^{2+} and Fe^{3+} ions in glass but discriminating between tetrahedral and octahedral Fe^{3+} coordinations is much less definitive. As indicated above, there is also uncertainty in the interpretation of both optical data and ESR data when used to infer the Fe^{3+} coordination. Loveridge and Parke (8) gave a clear account of some of the difficulties involved in fitting ESR data to a spin Hamiltonian to obtain the coordination of Fe^{3+} in glasses.

An examination of the literature thus indicates that, while many experiments have been reported for iron dissolved in sodium silicate glasses, the coordination of the Fe^{3+} ion in these glasses is still not clearly established.

Unlike the iron glasses, published information on uranium glasses is very sparse. Uranium dioxide was an important coloring agent for glasses in the 1930's. Because of its radioactivity, it is no longer being used in commercial application. The hexavalent uranium, in dilute quantity, imparts a yellow-green color to transmitted light associated with a strong absorption band centered at

420 nm. Melting under reducing conditions gives a proportion of the uranium in the +4 state. Depending on the amount of U^{+4} ion in the glass, the color may go from yellow-brown through grey to green. The detailed absorption spectra of U^{+4} and U^{+6} in glasses have been established by Weyl (9) and by Smith and Cohen (10). Kroger et al. (11) studied the fluorescence of U^{+6} ion in glasses and suggested that the fluorescence is associated with the formation of a uranyl group. Very little information (or speculation) is available regarding the coordination of uranium in silicate glasses.

EXPERIMENTAL

The iron and uranium containing glasses were prepared by melting appropriate amounts of Fe_2O_3 and UO_2 with powdered $Na_2O \cdot 2SiO_2$ glass. To minimize the compositional variation of the samples, a large batch of sodium disilicate glass was prepared and then used to prepare the iron and uranium glasses. The iron glasses containing from 5 to 30 mole percent of Fe_2O_3 were melted in air or flowing oxygen at 1100°C in platinum crucibles. Two series of uranium glasses, containing 10, 20, and 30 mole percent of uranium dioxide, were prepared. One series of uranium glasses was melted in air at 1085°C and another was melted in vacuum in a temperature range from 1100 to 1400°C. It was found that, at 1400°C in 10^{-6} torr vacuum, UO_2 and SiO_2 were vaporized and deposited on the platinum cover plate of the crucible. No deposit was found if the melting was done at temperatures below 1200°C. X-ray powder diffraction patterns were taken for all the samples to check for the presence of crystalline phases. Except for the vacuum melted uranium glasses, no crystalline phase could be detected in any of the samples. Very weak powder patterns of uranium dioxide are observed in all the vacuum melted uranium glasses indicating incomplete dissolution of UO_2 in the sodium disilicate glasses. After preparation samples were stored in a dissicator placed in an oxygen-restricted glove box environment. Prior to use they were ground on dry emory paper to the appropriate shape for insertion into the XPS spectrometer. After insertion into the spectrometer, the glass surface was scraped with an alumina rod to eliminate the contaminated surface layer that had been exposed to air.

XPS data were taken on a Hewlett-Packard 5950A spectrometer equipped with an on-line minicomputer supplied by Nicollett Instruments, Inc. Computer controlled data acquisition and manipulation is essential for the analysis presented here. Different spectral regions are acquired "concurrently" with computer control of the data acquisition. Two (or more) spectral regions are concurrently obtained by recording the individual scans of different regions in alternate sequence. This mode of operation eliminates the concern for time dependent variations in spectrometer signal intensity and preserves the correct relative intensities of all measured spectral features.

The EXAFS experiments, for the Fe K-absorption edge, were carried out in air at room temperature utilizing an in-laboratory apparatus (12). Detailed information regarding the EXAFS spectrometer construction and operation and data handling techniques can be found in Ref. 12. Using this spectrometer, a suitably high precision spectrum can be obtained for an iron glass sample in a 10 to 15 hour run.

In addition to the sodium disilicate glasses (containing Fe_2O_3) EXAFS studies were also performed on lithium and potassium disilicate glasses (containing Fe_2O_3) and for sodium disilicate glass (containing Fe_2O_3) with germanium substituted for the silicon. The purpose of substituting Li and K for Na, and Ge for Si, is to obtain a better understanding of the iron environment and coordination. Each of the different atomic species has a characteristic "backscattering amplitude" which affects the EXAFS spectrum thus providing a means for identifying the atomic species which have short range order relative to the iron atom.

RESULTS AND DISCUSSION

Based on a detailed x-ray diffraction study, B.E. Warren (13) proposed a model for the structure of sodium silicate glass. The proposed structure is a continuous network of SiO_4 tetrahedra with the sodium ions fitting in a random manner in the large holes. Because of the extra oxygen atoms introduced with the Na_2O, not all of the oxygens are joined to two silicon atoms as they are in SiO_2. Some of the oxygen atoms are bonded to only one silicon atom. These are usually termed "nonbridging" oxygens; and those linking two silicons are termed "bridging" oxygens. As Na_2O is added to the SiO_2 matrix, the number of nonbridging oxygen atoms should appear in direct proportion to the number of sodium atoms added. Since the bonding of the bridging and nonbridging oxygen atoms is markedly different, the local charge distributions, and hence the XPS binding energies of the oxygen core levels for

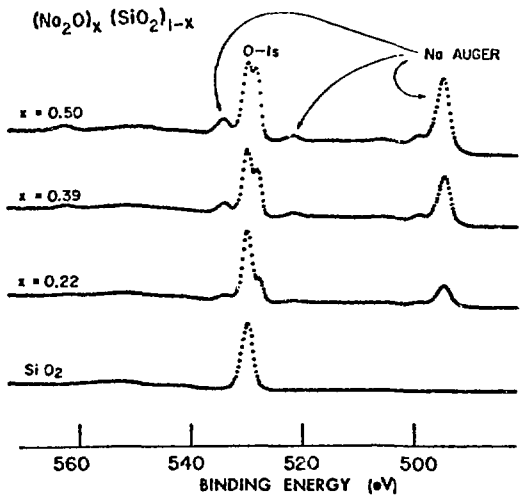

Fig. 1. The O 1s XPS spectra for SiO_2 and several $(Na_2O)_x(SiO_2)_{1-x}$ glasses. The low binding energy component of the O 1s peak, which scales with sodium concentration, is a measure of the nonbridging oxygen.

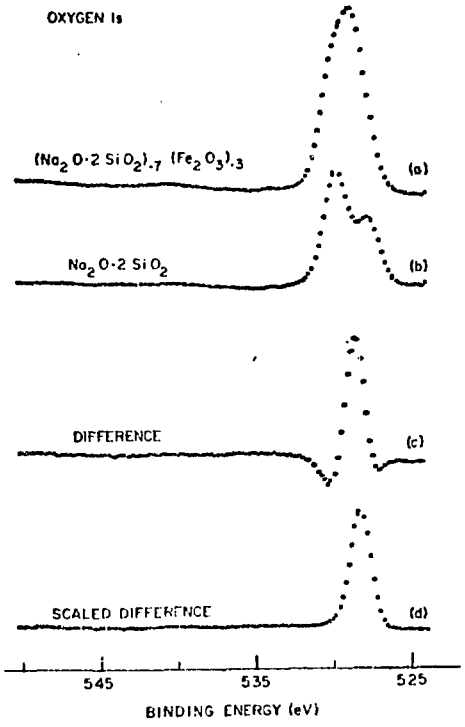

Fig. 2. O 1s lines for $(Na_2O \cdot 2SiO_2)_{0.7}(Fe_2O_3)_{0.3}$ and $Na_2O \cdot 2SiO_2$ (curves a and b, respectively); difference (residual) between experimental lines (curve c); weighted difference between experimental lines (curve d) -- see text.

the bridging and nonbridging oxygen atoms, should be different. The binding energy shift between the bridging and nonbridging sites was demonstrated in a systematic XPS study of Na_2O in silicate glasses (14). The effect is shown in Figure 1 where the O 1s spectra for SiO_2 and for several $(Na_2O)_x(SiO_2)_{1-x}$ glasses are presented (14). With the addition of Na_2O to SiO_2, a new peak (the nonbridging oxygen) appears on the low-binding-energy side of the O 1s peak. This peak scales with sodium concentration (which is measured by the nearby Na Auger peak), as could be expected if the Na_2O were entering the lattice of SiO_2 in the manner suggested by Warren.

When Fe_2O_3 is dissolved into sodium disilicate glass, matrix oxygen bonds are disrupted, apparently to permit the Fe^{3+} ion to bond to three oxygens of the glass matrix. Figure 2(a) shows the measured O 1s line for the iron glass; and figure 2(b) shows the O 1s levels for the sodium disilicate glass (15). Subtracting the sodium disilicate contribution from the iron glass spectrum, we obtain the difference or residual spectrum shown in Fig. 2(c). To visualize the significance of the residual result, it is useful to consider a simple mixture of Fe_2O_3 and $Na_2O \cdot 2SiO_2$. If Fig. 2(a) were the O 1s mixture spectrum, then the residual, Fig. 2(c), should be a simple, nearly Gaussian line corresponding to the O 1s line of Fe_2O_3. However, in Fe_2O_3, only 1.5 oxygens are associated with each iron atom. If Fe chooses to bond to more than 1.5 oxygens, then the associated oxygen must be obtained from the $Na_2O \cdot 2SiO_2$ matrix to which Fe_2O_3 was added. In this case, if one were to subtract out the $Na_2O \cdot 2SiO_2$ XPS contribution from the total $(Na_2O \cdot 2SiO_2)_{0.7}(Fe_2O_3)_{0.3}$ XPS spectrum to recover the O 1s associated with the Fe atoms, then the $Na_2O \cdot 2SiO_2$ part must be scaled to account for the loss of the matrix oxygens; i.e., those oxygens which now bond to the Fe's. Without the scaling, too much $Na_2O.2SiO_2$ will be subtracted out and one will obtain an "overshoot" spectrum such as seen in Fig. 2(c). These results clearly

indicate that with the addition of Fe_2O_3 to $Na_2O{\cdot}2SiO_2$, the O 1s bonds of the starting matrix are destroyed and new sites associated with Fe-O bonds are produced. To obtain a simple nearly Gaussian line shape [Fig. 2(d)] by subtraction of curve b from curve a, curve be must be scaled by a factor whose magnitude implies that for each added molecule of Fe_2O_3, three oxygen bonds of the disilicate matrix are broken and replaced by bonds to the iron atoms. Figure 3 shows the residual spectra for three samples of $(Na_2O{\cdot}2SiO_2)_{1-x}(Fe_2O_3)_x$ that have mole fractions x = 0.3 (curve a), x = 0.1 (curve b) and x = 0.05 (curve c) of Fe_2O_3. The characteristic shape of the residual spectra is preserved for all samples.

The EXAFS experiments on sodium-iron-silicates show that at least two atomic sites (or species) are contributing to the measured EXAFS spectrum $\chi(k)$. One "backscatterer" is clearly oxygen (established with the XPS study). In order to identify the second backscatterer, EXAFS experiments were conducted on Li, Na and K disilicate glasses and Na silicate glasses containing Ge substituted for Si. These different atoms have characteristic backscattering amplitudes and should generate very different EXAFS spectra. It was found, however, that all of the spectra were essentially identical and apparently resulted from first and second near neighbor oxygen shells surrounding the Fe atoms. $\chi(k)$ vs k spectra for Fe

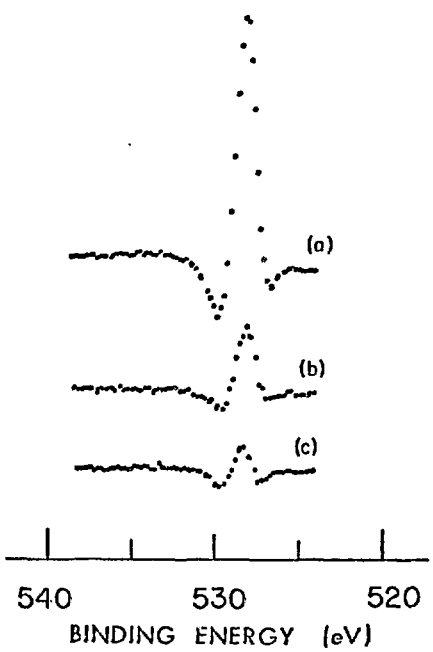

Fig. 3. O 1s residuals for three $(Na_2O{\cdot}2SiO_2)_{1-x}(Fe_2O_3)_x$ glasses with x = 0.3 (a), x = 0.1 (b), and x = 0.05 (c).

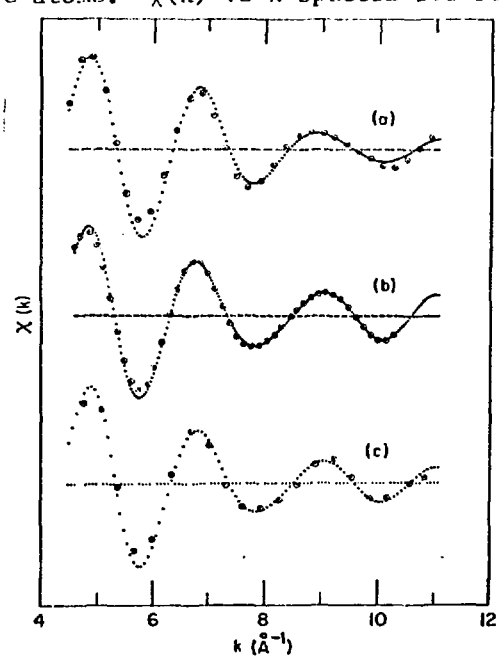

Fig. 4 EXAFS measurements of $\chi(k)$ vs k for three alkali silicate glasses.

in $(Li_2O{\cdot}2SiO_2)_{0.7}(Fe_2O_3)_{0.3}$, $(Na_2O{\cdot}2SiO_2)_{0.7}(Fe_2O_3)_{0.3}$ and $(K_2O{\cdot}2SiO_2)_{0.8}(Fe_2O_3)_{0.2}$ are shown in curves (a), (b), and (c), respectively of Fig. 4. The circled points in Fig. 4 are experimental results and the dotted curves are computer simulations of the data based on the standard EXAFS formula (Ref. 12) utilizing equal numbers of oxygen atoms in the first and second shells surrounding the absorbing Fe atom. The distance between the iron atom and the first oxygen shell is 1.85 Å and the Fe-O distance of the second oxygen shell is 2.40 Å.

The combined XPS and EXAFS results suggest that the Fe^{3+} ions in sodium silicate glass are coordinated with six oxygen atoms but are bonded to only three of them. These results do not substantiate the proposed tetrahedrally coordinated oxygen model inferred from ESR and Mössbauer experiments. One possible model that is consistent with all known data is illustrated in Fig. 5. Three oxygen atoms, with Fe-O distance of 1.85 Å, lie in a plane containing the Fe atom and three other oxygen atoms lie in a perpendicular plane at 2.40 Å from Fe. This coordination produces C_{2v} symmetry at the Fe site.

When UO_2 is dissolved into sodium disilicate glass, with the sample melting done in air or flowing oxygen, we find that essentially all uranium appears in the hexavalent state. If the melting is conducted in vacuum, the majority of the uranium ions are in the tetravalent state. Because of the existence of weak UO_2 powder patterns in the vacuum melted samples, however, it is not clear what

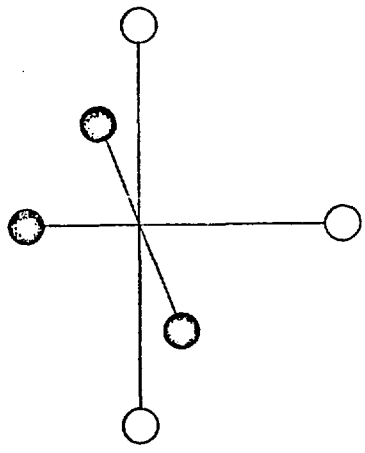

Fig. 5. A possible structural model for the bonding of Fe in iron-sodium-silicate glasses.

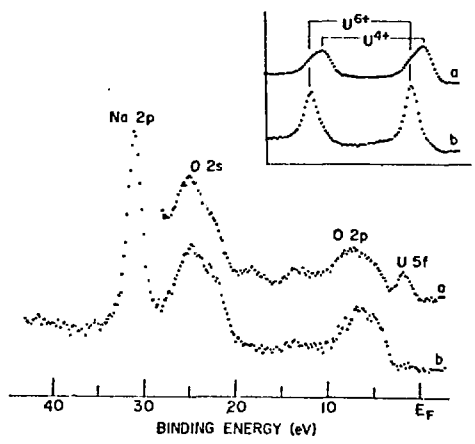

Fig. 6. XPS data near the Fermi level E_F for uranium sodium disilicate glasses nominally containing 20 mole percent UO_2. (See text for details.)

fraction of the U^{+4} ions is dissolved in the glass and what fraction is in undissolved UO_2. XPS results are shown in Fig. 6. The peak near the valence band edge [see curves (a)-vacuum meet sample] is a measure of the occupancy of localized 5f electrons (uranium ions in the +4 ionization state). No 5f occupancy appears in the air melt sample [curves (b)] nor in a glass sample prepared with UO_3, indicating that for these glasses, the uranium ions are in the +6 oxidation state (16). Similar conclusions for the valence state of uranium in the glasses can be drawn by examining the 4f core levels. The core levels for uranium in the +6 ionization state are shifted to higher binding energy than are the core levels for the +4 state (see insert of Fig. 6). The following discussion pertains only to the hexavalent uranium glasses.

The behavior of UO_2 (air melted) or UO_3 in silicate glass appears to be dramatically different from the behavior of Fe_2O_3 dissolved in the glass. Figure 7a shows the XPS O 1s levels for a sample of $(Na_2O{\cdot}2SiO_2)_{0.7}(UO_3)_{0.3}$ (15). Subtracting the $Na_2O{\cdot}2SiO_2$ contribution (curve b) from the uranium glass spectrum, we obtain the residual spectrum shown in curve c. Unlike the iron glasses, the simple difference lineshape cannot be improved by altering the relative scaling of the $(Na_2O{\cdot}2SiO_2)$ before subtraction from $(Na_2O{\cdot}2SiO_2)_{0.7}(UO_3)_{0.3}$. Thus, no bond alteration in the matrix sodium disilicate can be detected when UO_3 is added. It may be that molecular units of UO_3 are retained in open regions of the glass matrix without forming strong molecular orbitals between the matrix and the uranium oxide. Similar conclusions can be drawn from analysis of the residual spectrum in the valence band region. Figure 8a shows the uranium sodium disilicate glass within 40 eV of the Fermi energy. Figure 8b shows the sodium disilicate glass spectrum in the same energy region. The residual spectrum is shown in Fig. 8c. In Fig. 9 the residual spectrum is compared with an independently measured spectrum of γ-UO3.

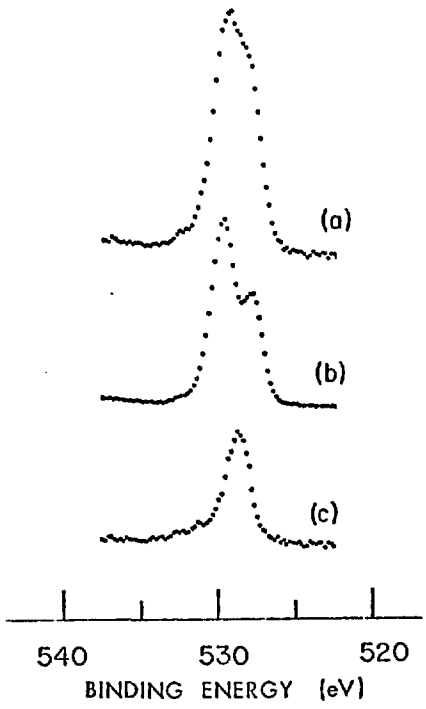

Fig. 7. O 1s lines for $(Na_2O{\cdot}2SiO_2)_{0.7}(UO_3)_{0.3}$ and $Na_2O{\cdot}2SiO_2$ (curves a and b, respectively); difference (residual) between experimental lines (curve c).

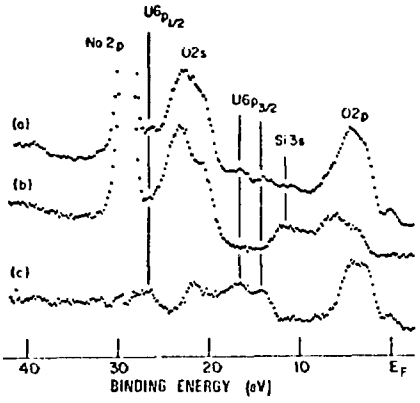

Fig. 8. XPS spectra near E_F for $(Na_2O{\cdot}2SiO_2)_{0.7}(UO_3)_{0.3}$ and $Na_2O{\cdot}2SiO_2$ (curves a and b, respectively); difference (residual) between experimental lines (curve c).

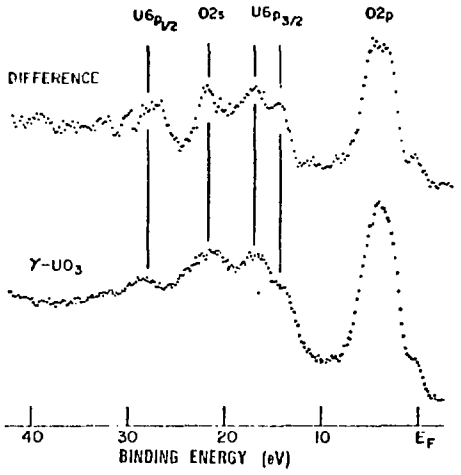

Fig. 9. The residual of Fig. 8 compared with the spectrum of γ-UO_3.

These spectra are remarkably similar. The positions of the various core levels fall at the same energy and the crystal field splitting of the U $6p_{3/2}$ level, characteristic of many hexavalent uranium compounds (17), is almost identical for the two curves. These results suggest that essentially unreacted UO_3 is contained in the sodium disilicate glass matrix. It seems unlikely that the uranium glass is a macroscopically phase separated mixture of UO_3 and $Na_2O{\cdot}2SiO_2$ since the glass does not have the milky appearance characteristic of phase separated glasses.

A two phase model would be consistent with the XPS data if the UO_3 phase regions were sufficiently small such that light scattering was small but sufficiently large so that linear -U-O-U-O- chains could exist. These chains produce an axial field at the uranium site that splits the $6p_{3/2}$ level. UO_3 is not stable at the melting temperature of the glass, but it may be formed in the cooling down phase of the glass preparation.

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