



The effect of uranium oxide additions on the structure of alkali borosilicate glasses



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ABSTRACT

The effect of uranium on glass structure is of interest in the context both of geological and nuclear waste glasses. In this study, solid state Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) spectroscopy was used to establish the effect of UO_3 on the bulk structure of mixed alkali borosilicate glass. The effects of increasing UO_3 content on boron co-ordination, alkali co-ordination and network polymerisation, determined using MAS-NMR, show that UO_3 acts essentially as an intermediate within the glass, occupying sites in the interstices of the glass network related to the alkali channels. This requires little structural rearrangement of the glass and so allows for the high solubility of UO_3 . It is shown that each mole of UO_3 requires 2 moles of alkali for charge balance. ^7Li MAS-NMR spectra indicate that with the addition of UO_3 the structural role of Li changes.

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1. Introduction

In most high level nuclear waste streams derived from the PUREX process only a small fraction of UO_3 is present which does not cause significant changes to glass structure or properties. However, some legacy higher activity wastes in the UK are rich in U and other transition metals. The effective immobilisation of these wastes in a durable glass matrix is of importance due to the long half-life of uranium (^{238}U ca. 4.5×10^9 years) and high solubility of UO_2^{2+} in ground waters. The large proportion of UO_3 present in the waste (ca. 18 wt.%) means that high uranium loadings have to be achieved in the glass to make vitrification a realistic option. At these high concentrations (ca. 5 mol%) UO_3 may have a significant effect on glass structure and properties. It is important to understand any such changes.

The aspects of the structural chemistry of uranium in glass have been previously studied with various motivations: understanding geological science [1], production of vitreous nuclear fuel rods [2,3]; attractive glass ware (a bright yellow glass with a green fluorescence under UV light) [4], and vitrification of nuclear waste [5,6].

Previous workers have shown that uranium can exist in the oxidation states U^{6+} , U^{5+} , and U^{4+} in alkali borosilicate and silicate glasses. Under standard melting conditions (i.e. air) the majority (>90%) is reported to occur U^{6+} with a small amount of U^{5+} ; U^{4+} is not observed except under strongly reducing conditions ($P_{\text{O}_2} \approx 10^{-8}$ – 10^{-12} atm. [1]). The U^{6+} present has been shown to exist in the form of the uranyl species

UO_2^{2+} with an additional 4 or 5 equatorial oxygens co-ordinating to the uranium cation [1,5].

The uranyl species is a large, but low charge, oxycation and it has been suggested that it enters a glass structure in a similar fashion to network modifiers. XAS data presented by Greaves et al. [5] suggested that the uranyl species were present in channels, akin to the alkali channels postulated in the modified random network theory [7] and this was taken to indicate a modifier type role. Dominé and Velde [8] suggested two different mechanisms, one in which uranium acted as a network modifier, the other in which uranium was complexed with alkalis (i.e. as an intermediate), it was suggested that U^{6+} was more likely present in the former. Farges [1] suggested that the uranyl species bonds to non-bridging oxygens (NBOs) within a silicate glass indicating an intermediate type role, with alkali ions acting as charge compensators. A neutron and X-ray scattering study on iron phosphate glasses by Badyal et al. [9] showed that there was very little change in the bulk structure of the glass with UO_x additions. They concluded that the U^{6+} occupies interstitial sites in an otherwise relatively undisturbed glass structure. Dietzel's rules on glass networks would suggest that U^{6+} acts as an intermediate due to the field strength, F , values ($F = Z/d^2$ where Z is the ionic valence and d the oxygen bond length) [10].

Burns et al. [11] report the structure of many uranyl compounds derived from XAS and X-ray diffraction. In the majority of these structures the uranyl ion is co-ordinated by four, five or six anions in square, pentagonal or hexagonal bipyramidal arrangements respectively. This structural motif has been observed in glasses with axial uranyl ($\text{U}=\text{O}$) distances of ca. 1.8 Å, and 4–6 equatorial oxygen ions at longer U–O distances of ca. 2.2 Å [1]. In many U^{6+} bearing minerals the uranyl species often form layered structures (e.g. $\text{Na}_2\text{U}_2\text{O}_7$). It has been suggested that such layered structural motifs are also present within glasses [5]. A

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Table 1

Analysed glass compositions (ICP and XRF). All compositions are expressed on a molar basis (uncertainty in measured composition is $\pm 0.02\%$).

Sample	SiO ₂	B ₂ O ₃	Na ₂ O	Li ₂ O	UO ₃
U-0	61.65	15.88	10.37	12.10	0.00
U-1	62.62	15.32	10.39	11.56	0.11
U-2	60.80	15.87	10.01	12.80	0.52
U-3	60.32	16.72	9.97	12.01	0.99
U-4	58.39	17.53	10.48	11.76	1.84
U-5	56.94	16.74	9.20	12.30	4.83

similar concept was suggested by Knapp et al. [12] where, again, EXAFS results suggested uranyl clustering within a sodium silicate glass.

It has also been proposed that the redox state of uranium has a strong effect on the solubility of UO_x in oxide glasses. Under reducing conditions ca. 10 wt.% UO_x will dissolve in a borosilicate glass, while >40 wt.% will dissolve under an atmosphere of air [13]. More generally UO_x is known to have low solubility in high silica (highly polymerised) glasses and this is believed to be due to the lack of alkali ions that would provide charge balancing [1]. Thus, the solubility of UO_x in (boro)silicate melts is thought to be enhanced by high oxygen anion activities (i.e. increased NBOs and NFOs).

Understanding all these effects is vital to ensuring the long term immobilisation of UK nuclear wastes with significant UO_x content, including some intermediate level wastes derived from degraded Magnox fuel [14]. Therefore, this paper presents the results of a solid state Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) spectroscopic investigation supported by bond valence calculations, XAS and TEM into the structure–property relationships of an alkali borosilicate glass with UO₃ additions. We will show that under these conditions UO₃ acts essentially as an intermediate within the glass.

2. Experimental

All glasses were prepared from a [61.5 mol% SiO₂]-[16.0 mol% B₂O₃]-[10.0 mol% Na₂O]-[12.5 mol% Li₂O] base-glass frit ball milled with measured additions of up to 4.8 mol% UO₃. Nominal compositions were batched to span the uranium concentration range of interest, with the UO₃ concentration increasing by a factor of approximately two in sequence. The batches were then melted in silica crucibles at 1100 °C. The glasses were annealed at 550 °C and slow cooled (nominally at 1 °C min⁻¹) to room temperature. The base glass composition used was similar to that employed at the Sellafield site in the vitrification of UK HLW. Due to the radiological hazards of handling uranium particulates, the preparation of these glasses was undertaken using a purpose developed laboratory at the University of Sheffield. Glass compositions were analysed by XRF and ICP-AES (see Table 1); analysed compositions are used for all data analyses.

MAS-NMR spectra were collected in conjunction with the EPSRC MAS-NMR service at Durham University. The spectra were obtained using a Varian Unity Inova spectrometer operating at 59.56 MHz for ²⁹Si, 79.31 MHz for ²³Na, 96.19 MHz for ¹¹B, and 116.52 MHz for ⁷Li. A 5 mm (rotor o.d.) probe was used for the ²³Na, ¹¹B and ⁷Li measurements and a 7.5 mm probe was used for the ²⁹Si. All the spectra were obtained using a pulse-acquire experiment. For the quadrupolar

Table 2

Bond lengths (Å) and bond valences for a selection of cations. Bond length (d_{iO}) calculated as sum of ionic radii. r_{iO} (used to calculate v_{iO}) values taken from Breese and O'Keefe [21].

Cation	d_{iO}	v_{iO}	Cation	d_{iO}	v_{iO}
^{IV} Si ⁴⁺	1.62	1.01	^V Na ⁺	2.38	0.21
^{III} B ³⁺	1.37	1.00	^{IV} Li ⁺	1.95	0.27
^{IV} B ³⁺	1.47	0.77			

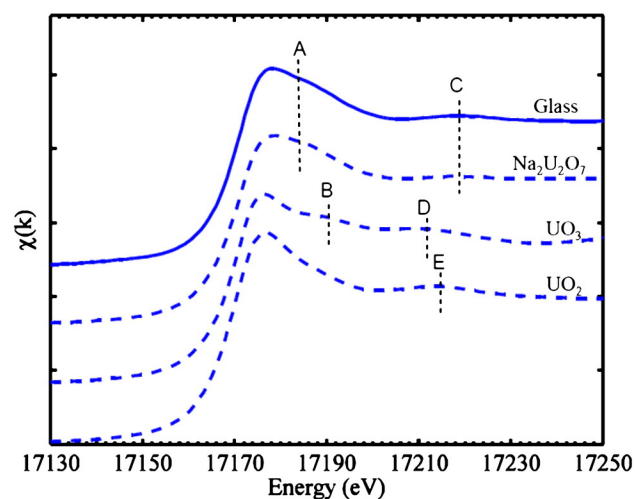


Fig. 1. XANES data for glasses showing similarity between glass U L₃ – XANES of glass containing (4.83 mol% UO₃) and Na₂U₂O₇.

nuclei a pulse angle of approximately 22° was used with a 90° pulse for the silicon. The recycle delays were 300 s for ²⁹Si, 1 s for ²³Na, 1 s for ⁷Li, and 2 s for ¹¹B. The sample spin-rate was approximately 8 kHz for the ²³Na, ¹¹B and ⁷Li measurements and 5 kHz for the ²⁹Si. Spectral referencing was with respect to 1 M NaCl, 1 M LiCl, BF₃/OEt₂ or tetramethylsilane. Fitting of data was carried out using DMfit [15].

Fitting of the ¹¹B spectra was carried out using 4 peaks. Two pseudo-Voigt peaks (factor = 0.5) were used to represent 4-coordinated boron (^{IV}B) peak; with the amplitude, position and width being allowed to refine. The two 3-coordinated boron (^{III}B) peaks were fitted using Q_{MAS} 1/2 curves with amplitude, position, EM (apodisation of the theoretical lineshape), and η_Q (quadrupolar frequency) being allowed to refine. The asymmetry parameter of the curves (η_Q) was fixed at 0.28. η_Q measures the deviation from local cylindrical symmetry [16]. Starting values were taken from the work of Rodderick et al. and Parkinson et al. [17–19] who obtained their parameters on very similar glasses to those used in this work. ^{IV}B values were corrected with the resolved ^{III}B fraction being increased by 4%.

X-ray Absorption Spectroscopy (XAS) data show characteristic features indicative of the environment and oxidation state of the absorber element. For this work data were collected using beamline X23A2 of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), USA. This beamline uses an upward reflecting Si (311) monochromator of a fixed exit Golovchenko–Cowan design. Here the L₃-edge of U was used (17.167 keV). All samples were in the form of powders (sieved to <52 μm) which were attached to layers of adhesive tape (for highly absorbing standards boron nitride was intimately mixed to reduce X-ray absorption). Samples were visually checked for inhomogeneities prior to data acquisition. The thickness of each sample was tuned to give an optimum absorbance and edge step. Each glass sample was scanned at least twice and the data combined. Alongside glass samples, crystalline standards were examined (usually with a single scan). XAS data were processed and normalised using the freeware program Athena [20].

TEM was carried out using a FEI CM200 FEG-TEM operating at 197 kV and fitted with a Gatan Imaging filter (GIF 200). Samples were prepared by crushing small fragments of glasses with analytical grade ethanol using a mortar and pestle. A drop of the suspension was pipetted onto a holey carbon film supported by a copper grid (200 mesh).

Bond valence (BV) calculations have been used in this work to provide an insight to the validity of certain structural arrangements

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