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Effect of minor additions on structure and volatilization loss in simulated nuclear borosilicate glasses

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Abstract

Structural and thermal properties are reported for a range of caesium oxide-containing alkali borosilicate glasses, of the form $x\mathrm{Cs_2O}(100 - x)\mathrm{ZMW}$ ($0 < x < 10$), where ZMW represents a variety of simulated base-glasses. Glass densities increase and glass transition temperatures decrease with increase in caesium oxide concentration. Mass-loss from the melt is found to depend on composition in the same manner as the fraction of silicon Q^3 units, resolved from ^{29}Si MAS NMR, and is related to the presence of danburite medium-range order units, resolved from ^{11}B MAS NMR. Volatilization is shown to occur even in the absence of caesium oxide and the mixed alkali borosilicate composition of the volatile species, evolved from the melt at high temperature, is independent of the starting composition of the glass.

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1. Introduction

The efficient processing, immobilization and long-term storage of high level nuclear waste (HLW) is currently one of the most significant problems associated with the use of nuclear power as a serious replacement for fossil fuel-based energy production [1,2]. Of the many possible immobilization methods, vitrification of the waste using a mixed-alkali borosilicate glass waste form (MW), of composition 10.29 mol% $\mathrm{Li_2O}$, 10.53 mol% $\mathrm{Na_2O}$, 18.57 mol% $\mathrm{B_2O_3}$, 60.61 mol% $\mathrm{SiO_2}$, is currently the preferred technique for HLW in the UK [3–5]. A significant problem associated with the process of HLW vitrification is the evolution of a volatile species at the glass melt stage. Although the volatile species is known to be caesium-containing [6–10], its overall composition and the structural conditions affecting its formation have still to be fully established. We have sought to identify those structural changes which occur in the solid glass when caesium oxide is added to a variety of simulated waste-forms and attempt to relate these to the measured volatilization losses from the melt.

Many studies have been made of borosilicate glasses using NMR, Raman spectroscopy and various thermal analysis techniques [11–28] including a study of caesium oxide-doped MW [29]. These have all focussed on changes in the structure of the borate and silicate glass networks, as a function of alkali content, which lead to changes in density and thermal behavior.Structural studies, using ^{11}B, ^{29}Si and ^{17}O magic angle spinning nuclear magnetic resonance (MAS NMR), have led to widely accepted models for both the borate and borosilicate systems [11–13]. The addition of a glass modifier to a borate glass network initially converts trigonal planar, three-coordinated boron in [$\mathrm{BO_3}$]

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units (B_3) to tetrahedral, four-coordinated boron in $[BO_4]^-$ units (B_4). At higher modifier concentrations, B_4 are replaced by B_3^-, i.e., trigonal planar borons, with one non-bridging oxygen (NBO) [13,30–36]. The trend in the fraction of four-coordinated boron (N_4) differs between the borate and borosilicate glass systems, although both are non-linear in nature. The most accurate N_4 model to date for the borosilicate glass system is that of Dell et al. [13], although recently ^{11}B MAS NMR measurements have shown deviations from this model for $R > 0.5$, where R is the ratio of free alkali oxide to boron oxide content. ^{29}Si MAS NMR of borosilicate glasses has enabled the identification of the Q^n fractions (n denoting the number of bridging oxygens). Most commonly these are observed as Q^4, Q^3 and $Q^4(B)$ units, where (B) indicates 3Si + 1B or 2Si + 2B next nearest neighbors [37]. Q^2 sites are only possible when there is sufficient alkali oxide associated with the silicate network that the ratio of alkali oxide to silica exceeds 1:2. The number of non-bridging oxygens per silicon (NBO/Si), i.e., Q^3 fraction, was predicted

$$\mathrm{NBO/Si} = Q^3(\text{predicted}) = \frac{2 \times (\Sigma\text{mol\% } M_2O - \Sigma\text{mol\% } X_2O_3 - N_4 \times \text{mol\% } B_2O_3)}{\text{mol\% } SiO_2} \quad (1)$$

In this work, M_2O refers to modifiers Li_2O, Na_2O, Cs_2O and MgO, while X_2O_3 refers to intermediates Al_2O_3 and La_2O_3. Eq. (1) assumes that the trivalent cations form species of the type $[XO_n]^-$, where n is effectively four directly bonded oxygens for X = Al, B and 6–7 (including non-bonded) oxygens for La. The use of Eq. (1) is based on the assumption that $\mathrm{NBO/Si} \equiv Q^3$ for these glasses. The Dell model for speciation in borosilicate glasses [13] predicts that only Q^4 and Q^3 are present for the value of K ($= [SiO_2]/[B_2O_3] = 3.2$) and the ranges of R ($= ([M_2O] - [Al_2O_3, La_2O_3] + [MgO])/[B_2O_3]$) covered by these glass compositions. Previous work on related systems shows that this is true to even higher values of R than expected from the model [15].

Continuing from our previous study on Cs_2O additions to MW [29] we report the effect, on structure and volatilization, of the introduction of other oxide components of significance. These are Al_2O_3, La_2O_3 and MgO, in quantities which reflect their occurrence in HLW, outlined in Section 2.1 and Table 1. In the previous study [29], it was found that there was a correlation between mass-loss from the melt and the fraction of Q^3 units resolved from ^{29}Si MAS NMR. The latter depends on the structural role of the additional oxide, i.e., Al_2O_3, La_2O_3 or MgO, and how it affects the distribution of modifier cations between the borate and silicate network polyhedra. ^{11}B and ^{29}Si MAS NMR have been used in this current study to determine the speciation of the borate and silicate glass networks and their relationship with caesium volatility, from mass-loss measurements.

2. Experimental

2.1. Sample preparation

Four mixed-alkali borosilicate glass systems; Cs(AlMW), Cs(LaMW), Cs(MgMW) and Cs(Mg′MW), were made at compositions: $x Cs_2O(100 - x)ZMW$, ($0 < x < 10$) where ZMW represents a variety of simulated base-glasses to which Cs_2O is added (Table 1). These four base-glasses are modifications of the base-glass composition (MW) used by BNFL Ltd. for HLW vitrification, with a further oxide (Z) added, in a quantity realistic to that found in HLW. These additional oxides (and their initial molar quantities, y, before the addition of caesium oxide) are: Al_2O_3 (0.95 mol%), La_2O_3 (1.68 mol%) and MgO (2.55 and 10.2 mol%). MW is scaled down proportionally in the form $y[Al_2O_3, La_2O_3, MgO](100 - y)MW$ to form the new base-glasses to which caesium oxide is then added.

For each mixed-alkali borosilicate system, 100 g batches were made with the appropriate reagent grade lithium carbonate (99.9%), sodium carbonate (99.95%), caesium carbonate (99.99%), aluminium oxide (99.9%), lanthanum oxide (99.99%), magnesium oxide (99.9%), sodium tetraborate (99.5%) and Wacomsil© quartz (99.9%) with 0.1 mol% iron (III) oxide (99.5%) added to reduce ^{29}Si MAS NMR T_1 relaxation times. Samples were mixed on rollers for 24 h before being transferred to 90% Pt/10% Rh crucibles and heated to between 1350 and 1400 °C (depending on composition) for 20 min before being cast into de-ionized water to form a frit. Samples were then re-melted at the same temperature and cast. Samples were analyzed by X-ray diffraction to confirm their amorphous character.

For use in volatilization measurements caesium-containing reedmergnerite and danburite samples were made to the compositions outlined in Table 2, using the appropriate

Table 1
Starting compositions of the borosilicate glass systems

System	SiO_2 (mol%)	B_2O_3 (mol%)	Na_2O (mol%)	Li_2O(mol%)	Al_2O_3, La_2O_3, MgO (mol%)	Fe_2O_3 (mol%)	R
MW	60.61	18.57	10.53	10.29	–	0.1	1.12
Cs(AlMW)	60.03	18.39	10.43	10.19	0.95	0.1	1.07
Cs(LaMW)	59.59	18.26	10.35	10.12	1.68	0.1	1.03
Cs(MgMW)	59.06	18.10	10.26	10.03	2.55	0.1	1.26
Cs(Mg′MW)	54.43	16.68	9.46	9.24	10.20	0.1	1.73

N.B. $K = 3.2$ for all compositions.