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Quantitative measurement of Q^3 species in silicate and borosilicate glasses using Raman spectroscopy

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Abstract

Raman spectroscopy has been used to measure the fraction of tetrahedral silicate units connected at three corners into the network (Q^3) in binary lithium silicate glasses and also in the more complex borosilicate glasses used for waste immobilization. Agreement within experimental error was obtained with ^{29}Si MAS NMR measurements of the same samples. Raman provides an alternative method of structural determination for silicon-containing glasses with a high content of paramagnetic species where NMR loses resolution. Analysis was performed on borosilicate glasses containing up to 11.98 mol% Fe_2O_3 and the Q^3 values obtained by Raman spectroscopy agree within error with the published ^{29}Si NMR results from borosilicate glasses containing the equivalent quantity of Al_2O_3.

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1. Introduction

Silicate glasses have a wide variety of industrial uses – particularly borosilicates, with their relatively low melting points and high chemical durability. Because of this technological importance, these glasses have long been the subject of structural studies, using a range of techniques, including ^{29}Si and ^{11}B MAS NMR and Raman spectroscopy. ^{29}Si MAS NMR, which has been used on a variety of silicate systems [1–4] can provide a quantitative measure of the fraction of different silicon Q^n units present, where n is the number of bridging oxygens (BO) on the tetrahedral unit. More recently, Raman spectroscopy has been used to study glasses [5–7] allowing the short-range order (SRO) and medium-range order (MRO) structural units present to be inferred. For borosilicate glasses, Raman spectroscopy has been able to show the presence of MRO structures, such as reedmergnerite and danburite units [8,9], as well as SRO Q^n silicon units [3,4].

One of the important applications for borosilicate glasses is their use in the immobilization, by vitrification, of high level nuclear waste (HLW) [10] which contains a large number of oxides, including paramagnetic oxides which can make NMR uninformative. In performing NMR experiments on ^{29}Si, it is common to add small quantities of paramagnetic oxides (usually of the order of 0.1 mol% Fe_2O_3 or MnO) in order to reduce the spin-lattice relaxation time, T_1, and hence reduce the experiment acquisition time needed for good signal-to-noise. Such concentrations of paramagnetic species do

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not have any significant effect on lineshape. However, glass which is fully loaded with HLW will contain several percent of paramagnetic metal oxides and, at these levels, the variation in local fields due to the unpaired electron spins produces sufficient broadening of NMR lines that different contributions cannot be resolved and some may even be unobservable [11]. Raman spectroscopy is not affected by the presence of paramagnetic species and therefore it would be a very useful tool for quantitative measurement of structural fractions, such as Q^n and N_4 (the fraction of boron atoms which are 4-coordinated) in systems where NMR is impracticable. Traditionally, the use of Raman spectroscopy as a quantitative technique has been limited because of a number of problems. The most challenging of these is to relate peak intensity to the concentration of absorbing unit, because different units can have different oscillator strengths. A second problem often encountered is that of background correction of a spectrum, although a solution to this problem is described by Mysen [6].

Two types of silica-containing glass systems were studied in order to test the possible quantitative use of Raman spectroscopy. The first was a binary lithium silicate system, for which a detailed NMR study has recently been presented [12]. The second type was a range of modified mixed-alkali borosilicate glasses, simulating the vitrification of HLW. On both systems, ^{29}Si MAS NMR was possible and was used to obtain values of Q^3 to compare with those obtained from Raman spectroscopy. It has been demonstrated that the Q^3 fraction in the borosilicate glasses is a determining factor controlling corrosion resistance [13] and volatilization from the melt [14]. Theoretical values of the fraction of Q^3 units for the borosilicate systems in this study were calculated using Eq. (1),

$$\mathrm{NBO/Si} = Q^3(\mathrm{predicted}) = \frac{2 \times (\sum \mathrm{mol\%M_{2/z}O} - \sum \mathrm{mol\%X_2O_3} - N_4 \times \mathrm{mol\%\ B_2O_3})}{\mathrm{mol\%SiO_2}}. \quad (1)$$

In this work, $M_{2/z}O$ refers to modifiers Na_2O, Li_2O, Cs_2O, MgO, FeO whilst X_2O_3 refers to intermediates Al_2O_3, Fe_2O_3 and La_2O_3. Eq. (1) assumes that the trivalent cations form species of the type $[MO_n]^-$, where n is effectively four directly bonded oxygens for M = Al, Fe, B and 6–7 (including non-bonded) oxygens for La. The use of Eq. (1) is based on the assumption that, in this R range, B_3 are converted to B_4 only and that $\mathrm{NBO/Si} \equiv Q^3$ for these glasses. Feil and Feller [15], using the Dell model for speciation in borosilicate glasses [16], predicted that only Q^4 and Q^3 are present for this value of $K(=[SiO_2]/[B_2O_3] = 3.2)$ and the ranges of $R(= [M_2O]/[B_2O_3])$ 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 [17,14].

Three further borosilicate glasses, with high (>1 mol%) Fe_2O_3 contents, and hence unsuitable for NMR, were then used to test the procedure.

2. Experimental

2.1. Sample preparation

Lithium silicate glasses were made from reagent grade silica and lithium carbonate as reported in [12]. Appropriate amounts of the batch compounds were thoroughly mixed in a platinum crucible and the resulting mixture was heated in the range 1300–1400 °C until a clear, colorless melt was produced (after approximately 20 min). Samples were cooled, weighed, reheated for several minutes, and subsequently quenched either by dipping the crucible in an ice–water bath (only for the sample with 37.5 mol% Li_2O) or through the use of a roller-quencher [18] producing a cooling rate of about 10^5 K/s.

Four mixed-alkali borosilicate glass systems (CsAlMW, CsLaMW, CsMgMW and CsMg′MW) were made at compositions: $x\mathrm{Cs_2O}(100-x)\mathrm{ZMW}$, $(0 < x < 10)$ where ZMW represents a variety of simulated base-glasses to which caesium oxide 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 representative of 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 $y[\mathrm{Al_2O_3, La_2O_3, MgO}](100-y)\mathrm{MW}$ to form the new base-glasses to which caesium oxide is then added.

For each system, 100 g batches were made with the appropriate reagent grade lithium carbonate (99.9%), sodium carbonate (99.95%), caesium carbonate (99.99%), aluminum 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 °C and 1400 °C (depending on composition) for 20 min before being cast into de-ionised water to form a frit. The glasses were then re-melted at the same temperature and cast. Samples were analyzed by X-ray diffraction to confirm their amorphous character.