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Quantitative measurement of Q³ 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 (Q³) in binary lithium silicate glasses and also in the more complex borosilicate glasses used for waste immobilization. Agreement within experimental error was obtained with ²⁹Si 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% Fe₂O₃ and the Q³ values obtained by Raman spectroscopy agree within error with the published ²⁹Si NMR results from borosilicate glasses containing the equivalent quantity of Al₂O₃.

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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 ²⁹Si and ¹¹B MAS NMR and Raman spectroscopy. ²⁹Si 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 Qⁿ 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 Qⁿ 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 ²⁹Si, it is common to add small quantities of paramagnetic oxides (usually of the order of 0.1 mol% Fe₂O₃ 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),

$$\text{NBO/Si} = Q^3(\text{predicted}) = \frac{2 \times (\sum \text{mol}\% \text{M}_{2/z}\text{O} - \sum \text{mol}\% \text{X}_2\text{O}_3 - N_4 \times \text{mol}\% \text{B}_2\text{O}_3)}{\text{mol}\% \text{SiO}_2} \quad (1)$$

In this work, $\text{M}_{2/z}\text{O}$ 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 $[\text{MO}_n]^-$, where n is effectively four directly bonded oxygens for $\text{M} = \text{Al}$, 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 $\text{NBO/Si} \equiv Q^3$ for these glasses. Feil and Feller [15], using the Dell model for specification in borosilicate glasses [16], predicted that only Q^4 and Q^3 are present for this value of $K(=[\text{SiO}_2]/[\text{B}_2\text{O}_3] = 3.2)$ and the ranges of $R(=[\text{M}_2\text{O}]/[\text{B}_2\text{O}_3])$ 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: $x\text{Cs}_2\text{O}(100-x)\text{ZMW}$, ($0 < x < 10$) 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 $y[\text{Al}_2\text{O}_3, \text{La}_2\text{O}_3, \text{MgO}](100-y)\text{MW}$ 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.

Table 1
Nominal compositions for the base compositions of each of the borosilicate glass systems used in the study

System	SiO ₂ (mol%)	B ₂ O ₃ (mol%)	Na ₂ O (mol%)	Li ₂ O (mol%)	Al ₂ O ₃ , La ₂ O ₃ , MgO (mol%)	Fe ₂ O ₃ (mol%)	R	[Fe ³⁺]/[Fe ²⁺] [19]
MW	60.61	18.57	10.53	10.29	–	–	1.12	–
AlMW	60.03	18.39	10.43	10.19	0.95	0.1	1.07	–
LaMW	59.59	18.26	10.35	10.12	1.68	0.1	1.12	–
MgMW	59.06	18.10	10.26	10.03	2.55	0.1	1.12	–
Mg'MW	54.43	16.68	9.46	9.24	10.20	0.1	1.12	–
Fe2MW	59.10	18.1	10.31	10.07	–	2.42	1.08	3.5
Fe9MW	54.70	16.77	9.55	9.32	–	9.66	0.79	6.1
Fe12MW	53.34	16.34	9.28	9.06	–	11.98	0.65	7.3

FeMW samples were made by Duddridge [19].

Three Fe₂O₃-mixed-alkali borosilicate glass samples, of nominal composition $y[Fe_2O_3](100-y)MW$, prepared in a previous study [19], were used to test the effectiveness of measuring Q³ with Raman spectroscopy in situations where ²⁹Si MAS NMR is impossible because of the high quantities of paramagnetic iron(III) species present. These glasses had been made in an identical fashion to the four mixed-alkali borosilicate systems described above.

2.2. Nuclear magnetic resonance

²⁹Si MAS NMR was carried out on the lithium silicate and borosilicate glasses using a CMX Infinity 360 NMR spectrometer operating at 71.54 MHz with a 6 mm Otsuka probe spinning at ~6 kHz. For the lithium silicate glasses, spectra were obtained with a single pulse-acquire pulse sequence using a pulse length of 1.2 μs (~π/6), and a recycle delay of 120 s. This delay was found to be sufficient to ensure relaxation, and hence quantitative spectra, in spite of the absence of paramagnetic additions. Typically

500–600 scans were acquired and a line broadening of 50 Hz applied prior to Fourier transformation. For the borosilicate glasses a 2 μs pulse width (30° tip angle) and

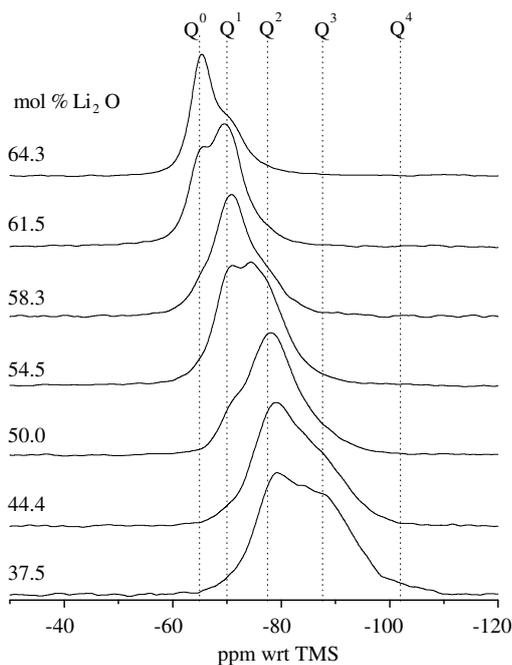


Fig. 1. ²⁹Si MAS NMR spectra for the lithium silicate system.

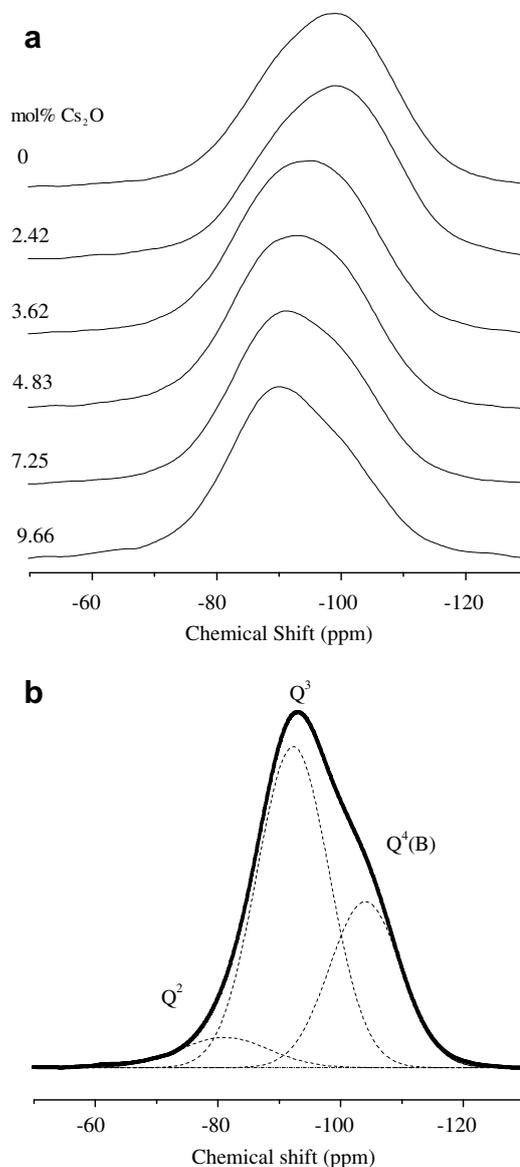


Fig. 2. (a) Typical ²⁹Si MAS NMR spectrum (CsAlMW system); (b) typical peak fit for an alkali borosilicate glass ²⁹Si MAS NMR spectrum (9.66 mol% Cs₂O).

5 s pulse delay were used with ~ 1000 acquisitions and a line broadening of 50 Hz. All samples were referenced to tetramethylsilane (TMS) at 0 ppm.

2.3. Raman spectroscopy

Raman spectra were obtained on all glasses using a Renishaw Invia Raman spectrometer equipped with a 20 mW argon laser operating at 514 nm. Measurements reported here were performed at room temperature, with 10 mW incident laser power and a x50 objective, across the range 100–3200 cm^{-1} . The spectrometer resolution was approximately 2 cm^{-1} .

3. Results

3.1. ^{29}Si MAS NMR spectra

For the lithium silicate glasses, only the main peaks are shown for clarity in Fig. 1 but the spinning sidebands were included in the peak fitting process [12]. Gaussian line-shapes were used to fit the contributions from Q^4 , Q^3 and Q^2 , however, the peaks from Q^1 and Q^0 were significantly narrower and a better fit was obtained using a pseudo-Voigt function with a 66% Lorentzian contribution.

For the borosilicate glasses, the ^{29}Si MAS NMR spectra (Fig. 2(a)) were fitted in most cases with two Gaussian

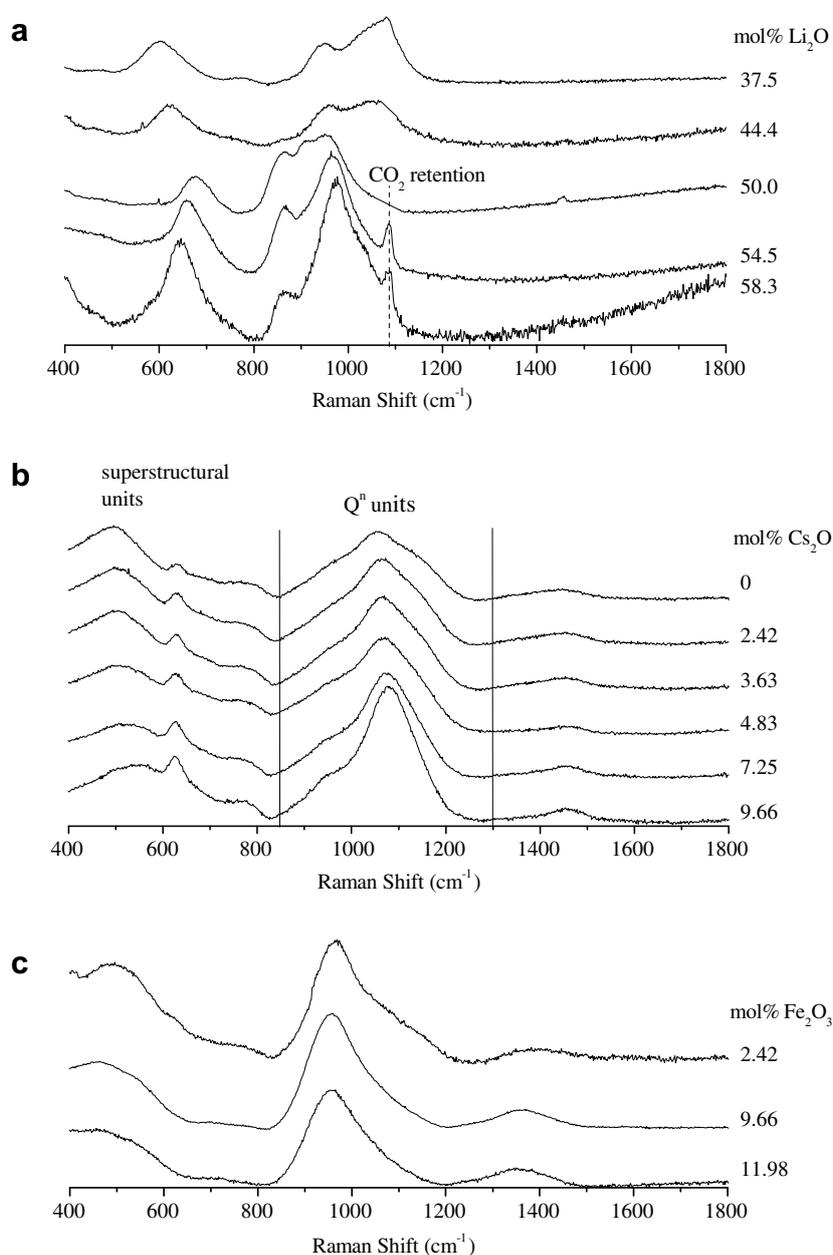


Fig. 3. Raman spectra for: (a) the lithium silicate glasses, (b) the alkali borosilicate glasses (CsAIMW), (c) for the FeMW glasses.

lines: one Q^3 peak and one $Q^4(B)$ peak, representing silicon atoms with predominantly two Si and two B next nearest neighbors [20]. Contributions from Q^2 units were negligible for all but typically the highest Cs_2O contents and the high MgO content system. Fig. 2(b) shows a fit for a borosilicate glass with 9.66 mol% Cs_2O , where the best fit requires a Q^2 fraction of 6%.

3.2. Raman spectra – Band assignments and resolved species fractions

The background for each Raman spectrum was subtracted by fitting an exponential curve to the data in a technique adapted from Mysen [6]. The corrected spectrum was then fitted with Gaussian peaks which were assigned to individual vibrations according to the literature.

Peaks were found from lithium silicate glass Raman spectra (Fig. 3(a)) at approximately 850 cm^{-1} (Q^2), 950 cm^{-1} (Q^2), 1000 cm^{-1} (Q^3), 1050 cm^{-1} (Q^3), 1080 cm^{-1} (Q^3) and 1150 cm^{-1} (Q^4) with the possible assignments (indicated in brackets) according to [7,21,22]. A typical fit is shown in Fig. 4(a). In Fig. 3(a), the sharp feature near 1070 cm^{-1} for the Raman spectra of the 54.5 mol% and 58.3 mol% compositions, is due to the retention of CO_2 formed during the manufacturing process.

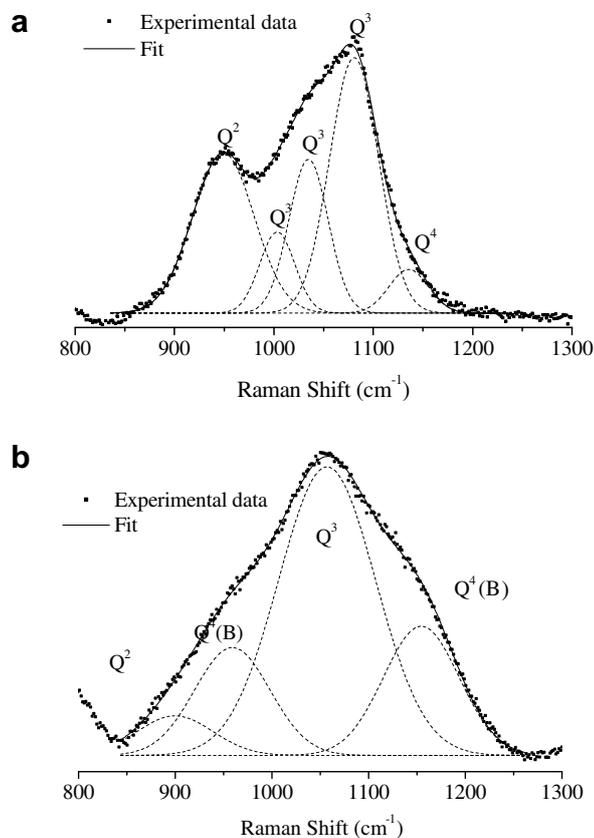


Fig. 4. Typical peak fit for the silicon Q^n region of the Raman spectra from: (a) the lithium silicate (37.5 mol%) glass, (b) the 0 mol% Cs_2O AIMW borosilicate glass.

The spectra for the borosilicate glass systems (Fig. 3(b) and (c)) can be clearly divided into two regions. The first, from 400 to 850 cm^{-1} , includes the vibrational modes of the two medium-range order superstructures, reedmergnerite $[BSi_3O_8]^-$ and danburite $[B_2Si_2O_8]^{2-}$. The second region, from 850 to 1250 cm^{-1} , includes peaks from silicon Q^n vibrational modes and it is this region which is of interest in this study. Peaks originating from vibrations arising solely from SRO units involving B are not resolvable. Peak fitting of the data in the Q^n region used four Gaussian peaks at approximately 925 cm^{-1} , 970 cm^{-1} , 1065 cm^{-1} and 1150 cm^{-1} (Fig. 4(b)). Peak half-widths for all but the peak at $\sim 1065\text{ cm}^{-1}$ (assigned as the central Q^3 peak [7,22]) were accepted as being realistic when between 60 and 80 cm^{-1} . Previous work [7] suggested that the peak at 925 cm^{-1} is due to a vibrational mode of the Q^2 unit. However, it should be noted that the fraction of the Q^2 units resolved in the ^{29}Si MAS NMR data is generally negligible, except for the highest caesium oxide content in the borosilicate glasses and the high MgO content system. The peak at approximately 1060 cm^{-1} has been assigned to the Q^3 vibrational unit, with the remaining peaks at 970 cm^{-1} and 1150 cm^{-1} to $Q^4(B)$ groups. Direct comparison of peak positions between the silicate and borosilicate glass systems was not made due to differences of assignment arising from the literature for the two systems. The Raman spectra from the iron oxide-containing borosilicate glasses are shown in Fig. 3(c) and were fitted in an identical manner to that described above.

For all the Raman spectra, Q^3 fractions were obtained by summing the areas of all the resolved Q^3 peaks and dividing by the total peak area in the range 850 – 1250 cm^{-1} . These fractions are then compared with those obtained by ^{29}Si MAS NMR in Figs. 5 and 6. This approach uses the assumption that the oscillator strengths for the different Q^n units are equal.

4. Discussion

The ^{29}Si MAS NMR spectra from the lithium silicate samples have been discussed in detail elsewhere [12]. The

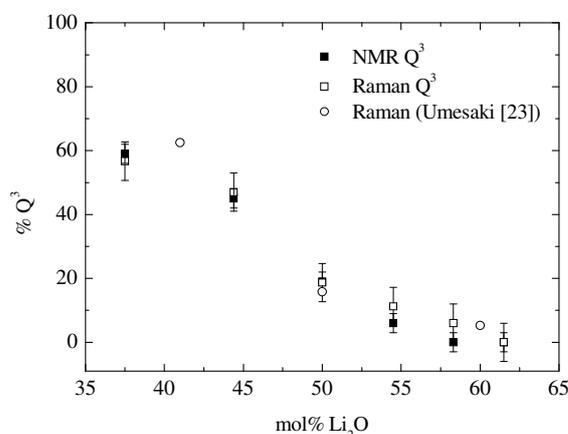


Fig. 5. Resolved Q^3 fractions measured from ^{29}Si MAS NMR and Raman spectroscopy for the lithium silicate system.

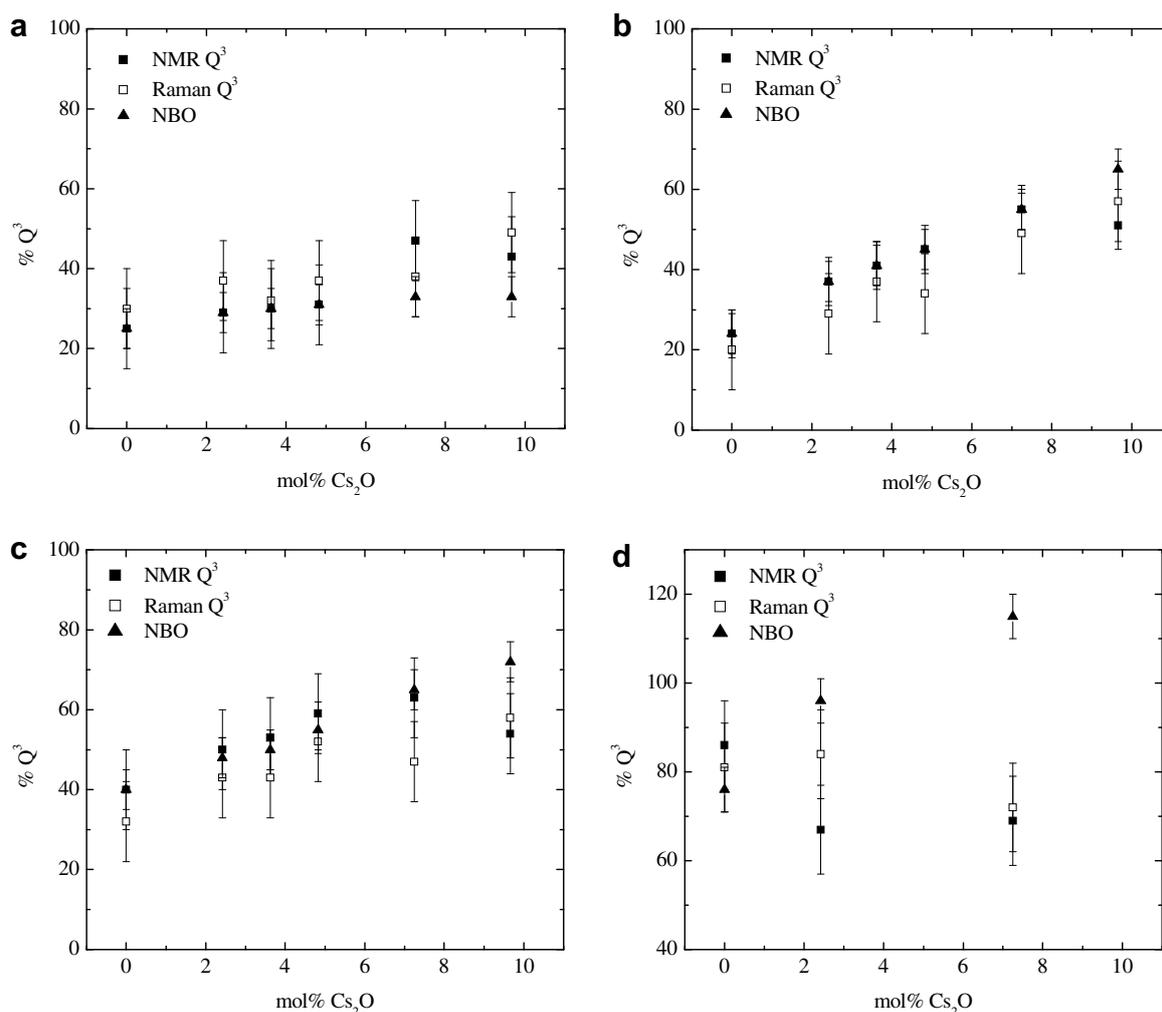


Fig. 6. Resolved Q^3 fractions from ^{29}Si MAS NMR and Raman spectroscopy for: (a) the CsAlMW system, (b) the CsLaMW system, (c) the CsMgMW system, (d) the CsMg'MW system.

Q^n fractions obtained agree with earlier (low mol% Li_2O) results from Dupree et al. [2] and Maekawa et al. [4], and with Raman results from Umesaki et al. [23] which cover a similar composition range. The Q^n distribution can be described as a disproportionated binary, where some Q^n is converted as: $2Q^n \rightarrow Q^{n+1} + Q^{n-1}$. In Fig. 5, the Q^3 fractions for the lithium silicate glasses are plotted for both the NMR data obtained previously [12] and for the Raman data from the current study. The Q^3 values from Umesaki et al. [23] are also shown.

For the four modified mixed-alkali borosilicate glass systems, the trend is for the Q^3 fraction to increase with caesium oxide concentration, when $Q^4(\text{B})$ groups are converted to Q^3 units. Relatively small additions of aluminum, lanthanum and magnesium oxides to the CsMW system alter the Q^3 fraction significantly for compositions of identical caesium oxide content, with Al_2O_3 and La_2O_3 effectively behaving as network intermediates, whilst MgO behaves as a modifier. This behavior is discussed in more detail in [24]. In Fig. 6, the Raman- Q^3 values are compared with those obtained from ^{29}Si MAS NMR and also with

the values predicted by Eq. (1). These agree within experimental error ($\pm 10\%$) for all of the systems, except the high MgO system, where the modifier content is sufficiently large that significant amounts of Q^2 species are generated.

Values of the Q^3 fractions obtained by peak fitting of the Raman spectra from the three iron-containing mixed-alkali borosilicate glasses are plotted against R in Fig. 7. When calculating R , assumptions are made about the structural role of the iron oxide added to these glasses. This requires knowledge of the oxidation state of the iron ions in the glass. It is well known that the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio depends on glass composition, as well as the temperature and atmosphere during melting. Mössbauer measurements on these glasses give the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios listed in Table 1 [19]. It is generally accepted that Fe^{2+} behaves as a modifier in glass, whilst Fe^{3+} forms $[\text{FeO}_4]^-$ network polyhedra, which require charge balancing M^+ ions, as is the case for Al^{3+} ions. In Fig. 7, the data points plotted for the iron-containing glasses have R values calculated using the oxidation ratio from the Mössbauer measurements such that $R = (\text{M}_2\text{O} + \text{FeO} - \text{Fe}_2\text{O}_3)/\text{B}_2\text{O}_3$. The line drawn in

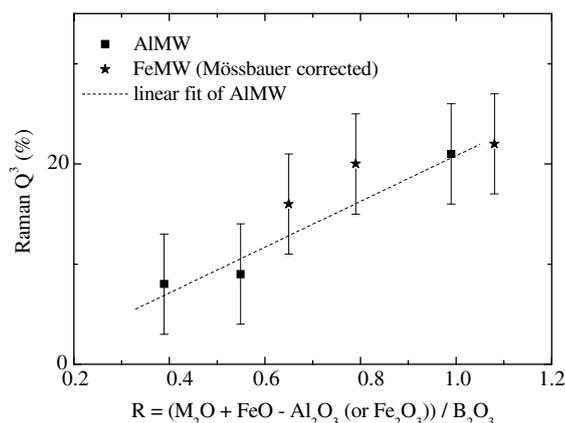


Fig. 7. Resolved Q^3 fractions from Raman spectroscopy for the FeMW glass system, compared with predicted NBO/Si for the AIMW system. The dotted line is a linear least squares fit to the AIMW data.

Fig. 7 is the linear least squares fit to the AIMW system. The Raman data from the FeMW system are within experimental error of this line.

5. Conclusions

Quantitative Raman spectroscopy has enabled the Q^3 fraction to be measured for both lithium silicate and complex borosilicate glass systems and shows agreement within 10% of values found from ^{29}Si MAS NMR and predicted from theory. For the iron-containing borosilicate glasses compositions, where ^{29}Si MAS NMR was not possible, Raman spectroscopy has been used to measure the fraction of Q^3 , giving values which are consistent with ^{29}Si MAS NMR measurements on the equivalent, but non-paramagnetic, alumina-containing borosilicate glass systems. The implication of these findings confirm results from Umesaki [25] that the oscillator strengths for the silicon species resolved from the Raman spectra are sufficiently similar that the relative intensities can be used in a quantitative procedure.

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