Observation of a stuffed unmodified network in beryllium silicate glasses with multinuclear NMR spectroscopy

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The structure of $BeO-SiO_2$ glasses with up to 20 mol % BeO has been studied with [9]Be and ^{29}Si NMR spectroscopic techniques. The NMR results are consistent with a glass structure consisting of nanoclusters of corner-shared BeO_4 tetrahedra that occupy the interstices of an unmodified and highly strained corner-shared SiO_4 network. The complete absence of nonbridging oxygens in these glasses contradicts the conventional wisdom of oxide glass structures based on the modified random-network-type models. This structure type may have important implications in understanding and designing glasses with unusual properties.

Silicate glasses are important technological materials that have found widespread use in our lives.[1] These are also classic materials from which the modern concepts of atomic structure of glass originated.[2] Vitreous silica is structurally an archetypal example of a continuous random network made of corner-sharing SiO_4 tetrahedra.[3] The complete connectivity of the structure is believed to be responsible for the high glass-transition temperature, viscosity, and chemical durability that are characteristic of silica.[4] The addition of network-modifying alkali and/or alkaline-earth ions to SiO_2 breaks up the connectivity of the corner-linked SiO_4 tetrahedra with the creation of non-bridging oxygens (NBO) that are linked to only one Si atom. Progressive "depolymerization" and weakening of the network with increasing concentration of network-modifying cations results in rapid and abrupt changes in physical properties including viscosity, diffusivity, thermal expansivity, and chemical durability.[4–8] In simple alkali or alkaline-earth silicate glasses, each alkali atom introduces one NBO while each alkaline-earth atom introduces two NBOs. This structural change for an alkaline-earth silicate glass can be schematically represented with the reaction

$$Si\text{-}\text{\O}\text{-}Si + RO = 2[Si-O^-] + R^{2+},$$
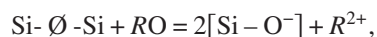
where $\text{\O}$ and O^- represent bridging (BO) and non-bridging oxygen, respectively, and R^{2+} represents an alkaline-earth ion.[5–8] Therefore, the relative concentrations of BO and NBO in a simple silicate glass are completely determined by its chemical composition.[8] This structural model has indeed been confirmed by detailed high-resolution ^{29}Si NMR and Raman spectroscopic studies on a wide range of binary alkali and alkaline-earth silicate glasses.[5,7–9]

However, such structural studies have never been extended in the past to binary $BeO-SiO_2$ glasses primarily because of the difficulty in melting these compositions related to the high liquidus temperatures in excess of 1700 °C associated with this system.[10] This is unfortunate since chemically Be^{2+} is found to be a rather unique cation with

the highest field strength (charge-to-radius ratio) and electronegativity among all alkaline-earth and alkali ions.[11] Be^{2+} is also characterized by a small electronic polarizability, comparable to that characteristic of network-forming cations such as B^{3+} and Si^{4+}.[12] Unlike other alkaline earths, Be is always found to be fourfold coordinated to oxygen in crystalline oxides and to form regular BeO_4 tetrahedra with $Be-O$ distances ranging between ~1.65 and 1.75 Å and intratetrahedral $O-Be-O$ angles of ~110°.[13–15] Crystalline BeO itself is characterized by unique properties such as unusually high thermal conductivity and refractoriness.[10] Beryllium aluminosilicate glasses have been reported to have high elastic modulii and strong chemical and thermal shock resistance.[16] This unusual coordination chemistry of Be and the associated physico-chemical properties of Be compounds make the structural study of binary $BeO-SiO_2$ glasses a compelling case. In this regard, [9]Be and ^{29}Si NMR spectroscopy are ideal for investigating the short-range structural characteristics of these glasses.

All glasses were prepared in $2-5$ g batches by the conventional melt quenching method. The batch materials used in glass melting were ultrahigh-purity silica (99.999%) and BeO (99.99%). The batch materials were handled inside a glove box to avoid any physical contact with BeO, which is known to be highly toxic and carcinogenic when inhaled. Mixed batches were contained in 80% Pt–20% Rh crucibles and were melted at 1800 °C for 4 h in a furnace (Deltech DT-33-CVT-912) in air. These melts were cooled in air and the resulting glasses were finely crushed and remelted for another 4 h at 1800 °C to ensure chemical homogeneity and finally quenched in water. All glass samples were completely colorless and did not show any visual indication of phase separation. All ^{29}Si and [9]Be MAS NMR spectra were obtained with a Bruker Avance 500 spectrometer equipped with a widebore ultrashield 11.75 T magnet. For ^{29}Si MAS NMR, a 7 mm Bruker CPMAS probe and a zirconia rotor with KelF cap were used. The [9]Be MAS NMR data were collected with a 4 mm Bruker CPMAS probe and a zirconia rotor with a KelF cap. The [29]Si chemical shifts are refer-
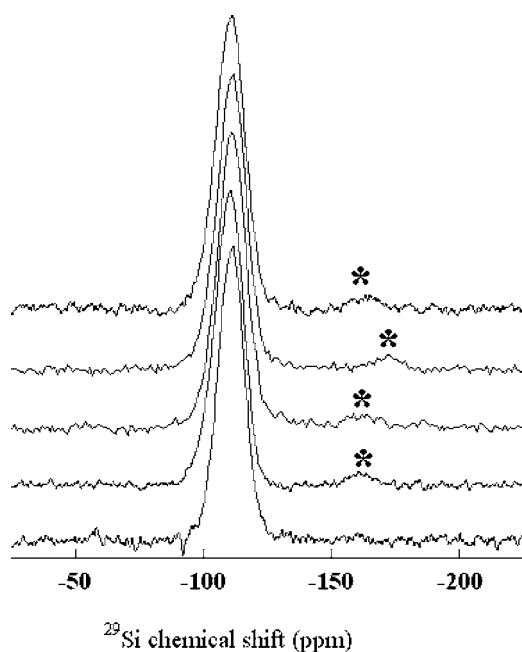
FIG. 1. ^{29}Si MAS NMR spectra of pure silica and Be-silicate glasses. The spectra from bottom to top are in the order of increasing BeO content: 0, 5, 10, 15, and 20 mol % BeO. The asterisks denote spinning sidebands. Spectra were collected under the following conditions: Larmor frequency: 99.34 MHz; pulse length: 2 μs (45° tip angle); recycle delay: 60 s; spinning rate: 5–6 kHz; number of transients averaged: 1500–2500.

enced to tetramethylsilane (TMS). The ^{9}Be chemical shifts are reported with respect to crystalline Be_2SiO_4, which has been used as a secondary standard ($\sim$−2.7 ppm from the primary standard of 0.1 M aqueous $BeSO_4$).

The ^{29}Si magic-angle-spinning (MAS) NMR spectra of the four Be-silicate glass compositions containing 5–20 mol % BeO consist of a single symmetric Gaussian peak centered at −111 ppm (Fig. 1). The position and width of this ^{29}Si MAS NMR isotropic peak do not appreciably change as a function of chemical composition and are nearly identical to those that are characteristic of pure silica glass (Fig. 1). The ^{29}Si isotropic chemical shifts for SiO_4 tetrahedra with one or more NBOs are found to be in the range of −60 to −100 ppm in a wide range of silicate crystals and glasses and are therefore significantly deshielded from the value of $\sim$−111 ppm observed here.[17] Therefore, the ^{29}Si MAS NMR spectra in Fig. 1 unambiguously indicate that no significant amount of NBOs is being created in the structure of these glasses even on addition of up to 20 mol % BeO. Thus the silicate framework in these glasses consists solely of SiO_4 tetrahedra with all bridging oxygens, i.e., Q^4 species. This result is remarkable considering the fact that in binary silicate glasses with 20 mol % alkali, or alkaline-earth, oxide, the NBO/Si ratio is expected and has been observed to be $\sim$0.5.[5]

A careful look at the ^{29}Si MAS NMR spectra reveals the presence of one set of spinning sidebands centered at $\sim$−160 ppm in the spectra of all Be-silicate glasses, while no such sidebands are present in the spectrum of the pure SiO_2 glass (Fig. 1). The occurrence of spinning sidebands on one
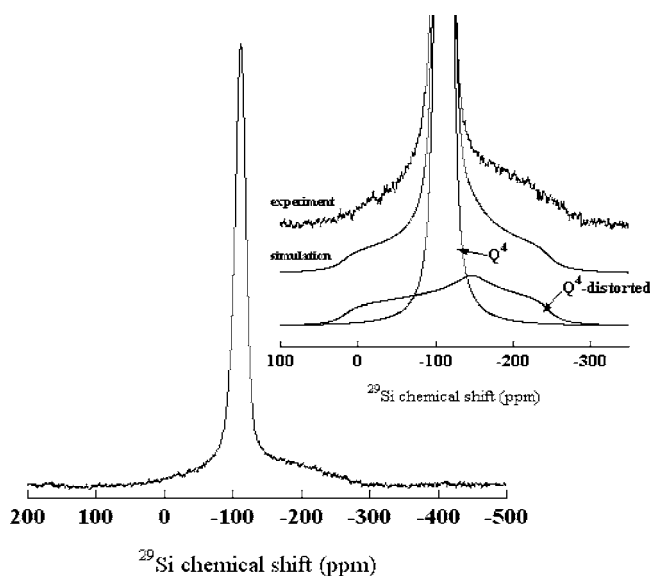

FIG. 2. ^{29}Si static NMR spectrum of 15% BeO–85% SiO_2 glass. The spectrum was collected under the following conditions: Larmor frequency: 99.34 MHz; pulse length: 4 μs (90° tip angle); recycle delay: 60 s; number of transients averaged: 11 400. Inset shows the same experimental spectrum magnified by a factor of 5 to emphasize the broad component with large CSA. The corresponding simulated spectrum is shown below along with the individual simulation components corresponding to regular and distorted Q^4 species.

side of the ^{29}Si MAS NMR isotropic line shape is indicative of the presence of significant chemical shift anisotropy (CSA) associated with a fraction of ^{29}Si nuclides in the Be-silicate glasses. This CSA becomes more apparent in the ^{29}Si static (nonspinning) spectra of these glasses, an example of which is shown in Fig. 2 for a glass with 15 mol % BeO. The ^{29}Si static NMR line shape consists of a narrow Gaussian component centered at $\sim$−111 ppm and a very broad component centered at $\sim$−146 ppm that spans a range of nearly 300 ppm (Fig. 2). The narrow component is similar to the static ^{29}Si spectrum of pure silica and corresponds to Si sites with local cubic symmetry as normally expected in the case of undistorted Q^4 tetrahedra. The broad component must then originate from Q^4 tetrahedra that are distorted such that the local cubic symmetry at the Si site is destroyed. The static ^{29}Si line shape can be simulated well with a narrow Gaussian component at −110.5 ppm and a broad component with an isotropic chemical shift of $\sim$−115 ppm and a large CSA of $\sim$140 ppm (Fig. 2). The asymmetry parameter η for this broad component is found to be $\sim$0.7. Although the severe broadening resulting from glassy disorder does not allow a highly accurate simulation of the static ^{29}Si line shape, the isotropic chemical shift values for both components are well within the chemical shift range characteristic of Q^4 species.[17] The integrated areas under these two components indicate that $\sim$30% of the Q^4 sites in this glass are characterized by large CSA and hence are distorted.

The ^{9}Be MAS NMR spectra of the four Be-silicate glasses are shown in Fig. 3. For a quadrupolar nuclide such as ^{9}Be with spin=$\frac{3}{2}$, these spectra correspond to the central transition line shape. All spectra consist of an intense narrow
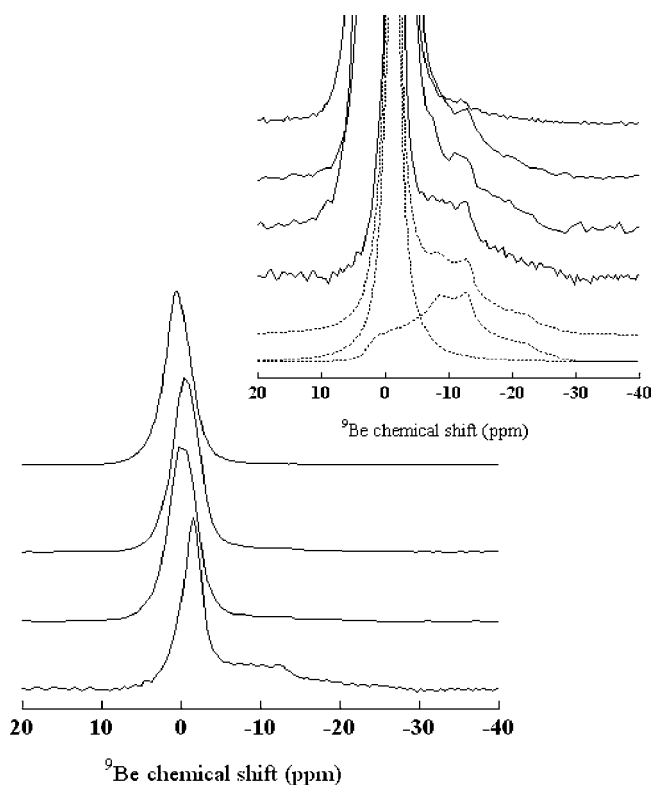
FIG. 3. ^{9}Be MAS NMR spectra of Be-silicate glasses. The spectra from bottom to top are in the order of increasing BeO content: 5, 10, 15, and 20 mol % BeO. Spectra were collected under the following conditions: Larmor frequency: 70.28 MHz; pulse length: 4 μs (90° tip angle); recycle delay: 5 s; spinning rate: 10 kHz; number of transients averaged: 3000–7000. Inset shows magnified versions of the same set of experimental spectra (solid lines), revealing the compositional dependence of the component with large Cq. The magnification factors are 1 for the bottom-most spectrum and 5 for all other spectra. The simulated ^{9}Be MAS NMR spectrum for the glass with 5% BeO is shown at the bottom of the inset along with the individual simulation components (dashed lines).

symmetric peak near $\sim$0 ppm and another broad component centered at $\sim$−10 ppm. The central transition peak position in quadrupolar nuclides is typically affected by the isotropic chemical shift and the second-order quadrupolar shift, the latter being nonzero when the nuclide is in a site with non-cubic local symmetry.[18,19] Be in crystalline silicate, alumino-silicate, and germanate phases is always found to be tetrahe-drally coordinated to four oxygen atoms.[13–15] The ^{9}Be MAS NMR spectra of these phases are typically narrow symmetric line shapes indicating that the quadrupolar effect is very small due to the regularity of the BeO$_4$ tetrahedra, small quadrupole moment (5×10^{-30} m^2) of ^{9}Be and its small chemical shift range.[13,14,18–20] The chemical shift of the intense peak in the ^{9}Be MAS NMR spectra of these glasses is very similar to that in the case of crystalline Be$_2$SiO$_4$ where all Be atoms are tetrahedrally coordinated, indicating that most of the Be atoms in these glasses are also in tetrahedral coordination. The relative intensity of the broad component centered at −10 ppm in the ^{9}Be MAS NMR spectra of these glasses decreases rapidly with increasing concentration of Be (Fig. 3). The line shapes of all of these ^{9}Be MAS NMR
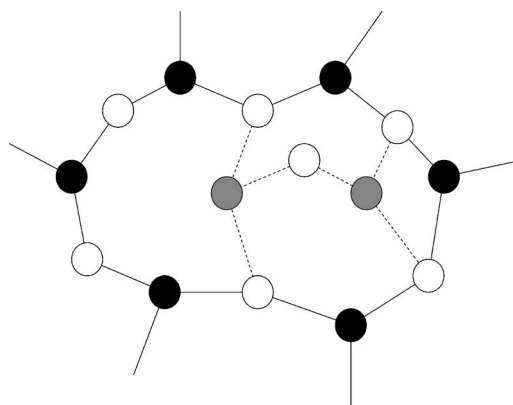

FIG. 4. A two-dimensional schematic representation of a stuffed unmodified —Si–O–Si— network with Be atoms occupying the interstices and forming Be–O–Be and Be–O–Si$_2$ linkages. The black and gray filled circles represent Si and Be atoms, respectively, and O atoms are represented by open circles. The Si and Be atoms, although fourfold-coordinated to oxygen in reality, are shown to be threefold-coordinated for the sake of clarity in a two-dimensional representation. The fourth oxygen can be imagined to be out of the plane of drawing.

spectra can be simulated well with a Lorentzian peak centered at $\sim$0 ppm and a second-order quadrupolar line shape with an isotropic chemical shift of +3.3 ppm, a quadrupolar coupling constant Cq=1.5 MHz, and an asymmetry parameter η=0.7 (Fig. 3). The chemical shift of the narrow, Lorentzian peak increases from −1.3 to +0.66 ppm with increasing Be content in these glasses, from 5 to 20 mol % BeO. On the other hand, the chemical shift and the quadrupolar parameters for the broad component are found to be nearly independent of glass composition. The isotropic chemical shifts for the two Be sites in these glasses are well within the range for fourfold-coordinated Be.[20] Therefore, it is most likely that the Be sites with large Cq represent extremely distorted tetrahedral environments in these glasses. The integrated peak areas indicate that the relative fraction of the Be sites with large Cq decreases from being $\sim$35% in the glass with 5 mol % BeO to $\sim$8% in the glasses with 10–15 mol % BeO and finally to <1% in the glass with 20 mol % BeO.

These multinuclear NMR data bring out a unique short- and intermediate- range structural picture for binary Be-silicate glasses. The lack of any detectable fraction of NBO and of any high-coordinated Si atoms in the ^{29}Si MAS NMR spectra implies the existence of Be–O–Be bonds which would result in the formation of Be-rich nanoclusters in the glass structure. These nanoclusters will occupy the interstices or voids of an unmodified —Si–O–Si— network (Fig. 4). Such a stuffing of the silicate network without the formation of NBOs is expected to result in significant strain. The presence of such a strained silicate network is corroborated by the ^{29}Si static NMR results, which indicate that a large fraction of the Q^4 tetrahedra are indeed significantly distorted in these glasses. Furthermore, it is likely that the Be atoms in the interfacial region between the Be-rich nanoclusters and the silicate network may form Be–O–Si$_2$ linkages involving BOs (Fig. 4). These Be atoms are expected to form signifi-

cantly distorted BeO_4 tetrahedra. The relative fraction of these "interfacial" Be atoms would decrease with increasing Be concentration in the glass structure, which results in increasing size and decreasing surface-to-volume ratio of the Be nanoclusters. This structural scenario is consistent with (a) the assignment of the minor component with large Cq in the [9]Be MAS NMR spectra to Be atoms in distorted BeO_4 environments and (b) the rapid drop in the relative fraction of this component with increasing Be concentration (Fig. 3). The formation of Be−O−Be bonds and Be-rich nanoclusters is expected to eventually give rise to phase separation with increasing Be concentration in this glass-forming system. A strong tendency of phase separation has indeed been observed in the glass with 20 mol % BeO, when the melt is cooled in air. The unusual structure of these glasses provides the unique opportunity of fabricating chemically and thermally resistant, insulating glassy materials with high thermal conductivity in the event that the Be-rich regions with Be−O−Be bonds retain the unusual properties of crystalline BeO and form percolating clusters.

In summary, we have studied the structure of $BeO-SiO_2$ glasses with ^{29}Si and [9]Be NMR spectroscopy. The spectroscopic data indicate that the Si−O network remains nearly intact on addition of up to 20 mol % BeO and no evidence of the formation of any nonbridging oxygen is found. The Be atoms are tetrahedrally coordinated in the structure, possibly occupying the interstices of the Si−O network, in which case the BeO_4 tetrahedra may share oxygen with Si−O−Si bridging oxygens forming threefold-coordinated oxygens in the structure. The resulting stuffed unmodified network may have interesting physico-chemical properties that warrant future study. Such network-forming behavior of an alkaline-earth cation is novel and unprecedented in simple oxide glasses.

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