

Structural Characteristics of Novel Ca–Mg Orthosilicate and Suborthosilicate Glasses: Results from ^{29}Si and ^{17}O NMR Spectroscopy

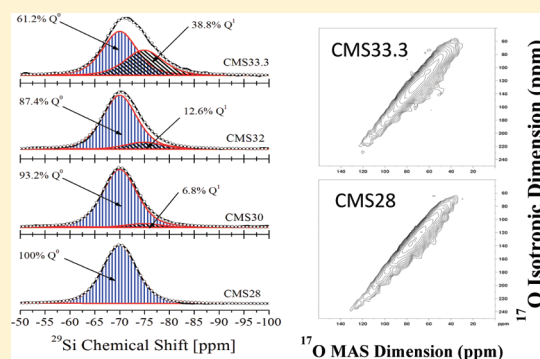
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ABSTRACT: The structural characteristics of novel alkaline-earth suborthosilicate glasses along the compositional join $(1 - x) - (\text{Ca}_{0.5}\text{Mg}_{0.5}\text{O}) - x\text{SiO}_2$ with $0.28 \leq x \leq 0.33$ are investigated using high resolution ^{29}Si and ^{17}O nuclear magnetic resonance spectroscopy. The structures of these glasses consist of isolated Q^0 and Q^1 anionic species and Mg^{2+} and Ca^{2+} counteranions that are held together by Coulombic interactions. The concentration of the Q^1 species rapidly decreases with decreasing SiO_2 content and becomes undetectable in the glass with $x = 28$ mol %. The compositional variation of the physical properties of these glasses such as glass transition temperature and density can be attributed to the Q-speciation in the structure. The NBOs are associated with a random distribution of the alkaline-earth cations in their nearest neighbor coordination shell. The resulting random packing of dissimilar Ca-NBO and Mg-NBO coordination polyhedra may give rise to structural and topological frustration responsible for the unusual glass-forming ability of these suborthosilicate liquids with extremely low SiO_2 contents. Finally, the composition and the formation of Q^1 species necessitate the formation of free O^{2-} ions in the structure of these glasses that are only bonded to Mg^{2+} and Ca^{2+} cations. The ^{17}O NMR results presented in this study allow for direct observation of such oxygen species.



INTRODUCTION

Silicate glasses are of wide-ranging technological importance with their extensive use spanning the range of products as mundane as bottles and windows to those as advanced as optical fibers, lasers, flat-panel display substrates, and hosts for solidification and sequestering of radioactive waste.¹ The fundamental understanding of these materials and formulation of accurate predictive models for the compositional dependence of physicochemical properties require detailed knowledge of their atomic structure. The short- and intermediate-range structural characteristics of silicate glasses have been studied extensively in past decades with a variety of experimental techniques.² Silica (SiO_2) is the archetypal glass former with a structure that can be described as a fully connected network of corner-sharing SiO_4 tetrahedra. Therefore, the oxygen atoms are two-coordinated in Si–O–Si linkages that are designated as bridging oxygen (BO). Addition of network-modifying alkali or alkaline-earth cations results in the gradual depolymerization of the silica network with the formation of nonbridging oxygen atoms (NBO) that are linked to only one Si atom forming Si–O–M linkages where M represents a modifying cation. The structure of a silicate glass is conveniently described in terms of Q^n species, where $0 \leq n \leq 4$ represents the number of bridging oxygens (BO) per SiO_4 tetrahedra. By increasing the modifier cation content and thus lowering the silica content, one can

reach orthosilicate compositions in crystalline silicates with 33.33 mol % SiO_2 such as the forsterite polymorph of Mg_2SiO_4 where extreme depolymerization is obtained and only Q^0 species, i.e., isolated SiO_4 tetrahedra, exist in the structure. Although glass formation in binary alkali and alkaline-earth silicates becomes increasingly difficult with decreasing SiO_2 concentration, it was demonstrated in the literature that container-less levitation and rapid melt quenching technique can produce binary orthosilicate glasses in the MgO – SiO_2 system.³ At this extremely depolymerized silicate composition the glass structure is expected to consist solely of isolated SiO_4 tetrahedra, i.e., $(\text{SiO}_4)^{4-}$ anions like their crystalline counterparts. However, recent structural studies of vitreous Mg_2SiO_4 using Raman spectroscopy, ^{29}Si nuclear magnetic resonance (NMR) spectroscopy, as well as X-ray and neutron scattering methods have demonstrated that besides the Q^0 species a substantial concentration ($\sim 40\%$) of Si atoms are present as Q^1 species, i.e., $(\text{Si}_2\text{O}_7)^{6-}$ anions in the glass structure.^{4–8} The presence of Q^1 species in vitreous Mg_2SiO_4 implies the formation of “free” oxygen ions that are not bonded to any Si atom in the glass structure. The free oxygens are released from

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Table 1. Nominal and Analyzed Chemical Compositions of CMS Glasses

sample name	nominal composition mol %			analyzed composition mol %		
	CaO	MgO	SiO ₂	CaO	MgO	SiO ₂
CMS33.3	33.35	33.35	33.33	32.9 ± 0.3	33.5 ± 0.5	33.6 ± 0.1
CMS32	34	34	32	33.5 ± 0.2	33.6 ± 0.4	32.8 ± 0.1
CMS30	35	35	30	34.6 ± 0.2	35.5 ± 0.3	30.8 ± 0.1
CMS28	36	36	28	35.7 ± 0.3	36.5 ± 0.4	28.6 ± 0.3

the SiO₄ tetrahedra via the Q-species disproportionation reaction: $2Q^0 = 2Q^1 + O^{2-}$. These free oxygens bond only to Mg²⁺ ions in the glass structure, and they are known to be present in the high pressure crystalline polymorph of Mg₂SiO₄, wadsleyite.⁹ The orthosilicate composition was known to be the low-silica limit of glass formation in silicates until very recently; we reported glass formation in the CaO–MgO–SiO₂ system with even lower nominal SiO₂ content than orthosilicates (27 mol % ≤ SiO₂ ≤ 33.33 mol %). These novel “sub-orthosilicate” glasses were synthesized for the very first time using the aerodynamic levitation/CO₂ laser melting technique and were characterized using Raman spectroscopy.¹⁰ These Raman spectroscopic results, when taken together with those from semiempirical molecular orbital calculation, indicated that the concentration of Q¹ species monotonically decreased with decreasing SiO₂ content and became undetectable in glasses with less than 30 mol % SiO₂. These glasses were characterized by isolated negatively charged “tetrahedral” SiO₄⁴⁻ and free O²⁻ anions with M²⁺ (M = Mg, Ca) as the counterions, held together by pure Coulombic (ionic) interactions. However, the lack of knowledge regarding the relative Raman scattering cross sections of Q⁰ and Q¹ species in these glasses did not allow quantitative characterization of the Q-speciation that is crucial to understand the effect of structure on their physical properties. Moreover, the nearest neighbor coordination environments around NBO and free oxygen atoms and the spatial distribution of the modifier cations that are the major chemical constituents of these glasses remain unknown. Here we report the results of density, glass transition temperature *T_g*, and ²⁹Si and ¹⁷O NMR spectroscopic studies of the atomic structures of these suborthosilicate glasses. Quantitative Q-speciation and oxygen coordination environments in the glass structure, as determined from the ²⁹Si magic-angle-spinning (MAS) and ¹⁷O MAS and triple-quantum (3Q) MAS NMR spectra, are used to build a model of the compositional evolution of the structure and its relation to density and glass transition process in these novel glasses.

EXPERIMENTAL SECTION

Synthesis and Characterization. The details of the synthesis of these glasses have been described in a recent publication by us;¹⁰ hence, only the salient points are mentioned here. The starting chemicals for syntheses of these glasses were reagent grade SiO₂ (99.999%), MgO (99.95%), and CaO (99.95%), all purchased from Alfa Aesar. The oxides were dried in a furnace at ~700 K for 24 h and were batched to prepare nominal compositions (1 – *x*)(Ca,Mg)O – *x*SiO₂ with *x* = 0.333, 0.32, 0.30, and 0.28. For the sake of brevity these nominal compositions are denoted in the subsequent discussion as CMS33.33, CMS32, CMS30, and CMS28, respectively. The vitrification of these oxide mixtures was achieved by CO₂ laser melting under aerodynamic levitation.¹⁰ The final step of the synthesis involved heating and melting of the levitated samples followed by rapid quenching via sudden

shutdown of the CO₂ laser that resulted in spherical, colorless, and transparent beads of about 1–1.5 mm in diameter. Powder X-ray diffraction measurements indicated these samples to be X-ray amorphous. Corresponding samples with ¹⁷O isotopic enrichment were prepared for ¹⁷O NMR spectroscopic studies using 100% ¹⁷O-enriched SiO₂ as a reagent. The latter was synthesized by hydrolyzing SiCl₄ with 100% enriched H₂¹⁷O.¹¹

The chemical compositions of all glasses were analyzed with standard electron probe microanalysis (EPMA) technique (CAMECA SX-100). The results of the chemical analyses are shown in Table 1. All glasses were found to be chemically homogeneous over length scales of a few μm, the latter being limited by the resolution of the EPMA technique. The glass transition temperature *T_g* of all samples was determined to ±1 K by differential scanning calorimetry (SETSYS Evolution TGA-DTA/DSC) using a heating rate of 10 K/min, and density was determined by the Archimedes method using toluene as the immersion medium. The *T_g* and the density values of these glasses are listed in Table 2.

Table 2. Density, Glass Transition Temperature, and Relative Fractions of Q⁰ and Q¹ Species in CMS Glasses

sample name	density (g cm ⁻³)	<i>T_g</i> (±1 K)	% Q ⁰	% Q ¹
CMS33.3	2.923 ± 0.007	1025	61.2	38.8
CMS32	2.943 ± 0.007	1023	87.4	12.6
CMS30	2.947 ± 0.007	1018	93.2	6.8
CMS28	2.959 ± 0.007	1016	100	0

NMR Spectroscopy. The ²⁹Si and ¹⁷O NMR spectra of all glass samples were collected using Bruker CP MAS probes and a Bruker Avance 500 spectrometer operating at the Larmor frequencies of 99.3 and 67.8 MHz for ²⁹Si and ¹⁷O, respectively. A 7 mm probe was used for ²⁹Si MAS NMR experiments. The samples in the form of spherical beads were spun in ZrO₂ rotors at 5 kHz without further crushing. One-pulse ²⁹Si MAS spectra were collected using a radio frequency (rf) pulse of duration 3.5 μs (corresponding to a 60° tip angle) and a recycle delay of 60 s. Approximately 4000 free induction decays (FIDs) were averaged to obtain each spectrum. Chemical shifts for all ²⁹Si spectra are referenced in parts per million relative to tetramethylsilane (TMS). ¹⁷O MAS and 3QMAS NMR experiments were carried out in a 4 mm Bruker CP MAS probe. Samples in the form of spherical beads were spun in ZrO₂ rotors at 14–15 kHz without further crushing. One-pulse ¹⁷O MAS spectra were collected using 0.3 μs excitation pulse (solids π/12) and a recycle delay of 2 s. Approximately 4000–8000 free induction decays (FIDs) were averaged to obtain each ¹⁷O MAS spectrum. ¹⁷O 3QMAS NMR spectra were collected for CMS33.33 and CMS28 glass samples using a 3-pulse zero quantum filtered pulse sequence. The high power excitation and conversion pulse lengths were optimized to 5.0 and 1.5 μs, respectively. The length for the π/2 selective pulse was 25 μs. 3QMAS data were typically collected using 700

acquisitions with a recycle delay of 5 s at each of the 48 t_1 slices. These slices were spaced in increments of half rotor cycle of 35.7 μ s. The ^{17}O 3QMAS spectra were processed and shear transformed using the Bruker TopSpin software. The ^{17}O NMR chemical shifts are externally referenced to H_2O .

RESULTS AND DISCUSSION

The ^{29}Si MAS NMR spectra of all glasses are shown in Figure 1. The spinning sidebands are outside the chemical shift range

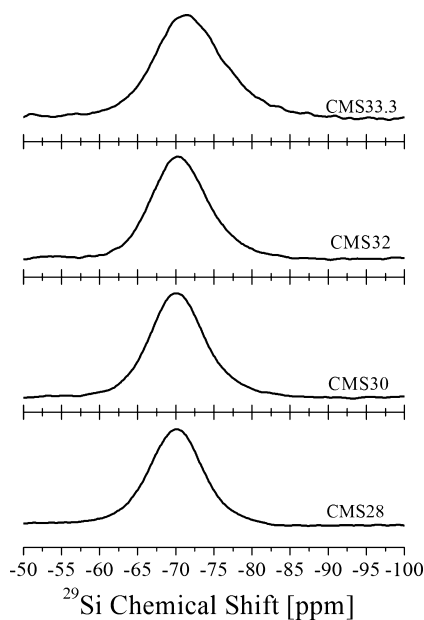


Figure 1. ^{29}Si MAS NMR spectra of CMS glasses. Sample designations are alongside the spectra.

displayed in Figure 1, and their intensities are practically negligible compared to the isotropic peak in these spectra. It is evident from Figure 1 that the center of gravity of the isotropic peak in these ^{29}Si MAS NMR spectra systematically shifts from near -70 ppm to near -75 ppm as the SiO_2 content increases from the lowest to the highest value. Moreover, the ^{29}Si MAS NMR line shape becomes increasingly asymmetric with a tail toward lower chemical shifts with increasing SiO_2 content. The ^{29}Si MAS NMR spectrum of CMS28 glass shows a symmetric Gaussian line shape centered at -70 ppm indicating the presence of only Q^0 species in this glass. This result is consistent with the Raman spectrum of this glass reported by us in a recent study that indicated complete absence of the bending modes corresponding to Si-O-Si linkages in the structure.¹⁰ The SiO_4 tetrahedral unit is topologically rather rigid, and the corresponding Si-O bond lengths and intratetrahedral O-Si-O bond angles are practically independent of composition in a wide range of silicates. Consequently, it is reasonable to assume that the isotropic chemical shift δ_{iso} and the width of the ^{29}Si MAS NMR line shape corresponding to the isolated SiO_4 tetrahedra, i.e., the Q^0 species, remain unchanged over the limited composition range covered by these CMS glasses. In that case the simulation of the ^{29}Si MAS NMR spectra of CMS30, CMS32, and CMS33.3 glasses requires the presence of a second Gaussian line shape centered at -74.8 ppm (Figure 2). Previous studies in the literature have shown that this ^{29}Si δ_{iso} is characteristic of Q^1 species in Mg_2SiO_4 glass structure.^{5,6} Therefore, the ^{29}Si δ_{iso} values

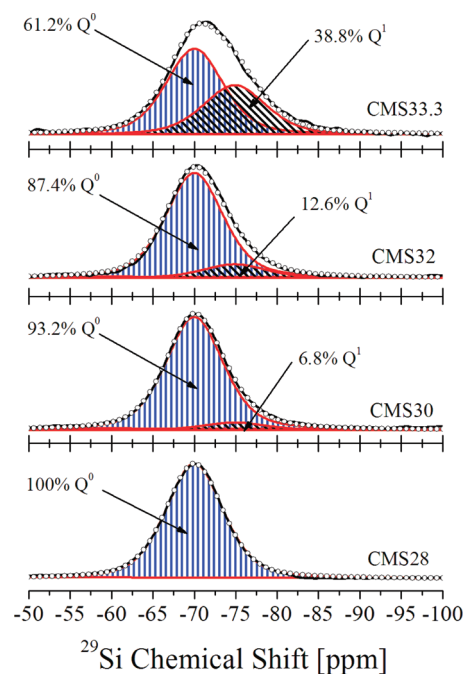


Figure 2. Simulation of the ^{29}Si MAS NMR spectra in Figure 1. The black solid line represents the raw ^{29}Si MAS NMR spectra, while the open circles represent the overall fit. The individual simulation components corresponding to the Q^0 and Q^1 species are shown with vertical blue lines and tilted black lines, respectively.

corresponding to the Q^0 and Q^1 species have been kept constant at -70 and -74.8 ppm, respectively, in all ^{29}Si NMR line shape simulations (Figure 2). Moreover, the corresponding full width at half-maximum (fwhm) for these two peaks are kept constrained to 8 ppm for the Q^0 and 9 ppm for the Q^1 species in all simulations. The corresponding peak areas in these constrained and self-consistent simulations yield the relative fractions of the Q^0 and Q^1 species in these glasses that are listed in Table 2, and their compositional evolution is shown in Figure 3a. It is clear that the relative fraction of the Q^1 species in these glasses decreases monotonically with decreasing SiO_2 content. A closer look at the data shows an abrupt drop in the concentration of the Q^1 species from $\sim 39\%$ in the CMS33.33 glass to 12.6% in the CMS32 glass and subsequently a linear drop to 0% in the CMS28 glass (Figure 3a). This result is corroborated by the compositional variation in the relative intensity of the 700 cm^{-1} band corresponding to the Si-O-Si bending mode of the Q^1 species in the Raman spectra of these glasses reported in a previous study.¹⁰ The intensity variation of this Raman band closely mimics that of the Q^1 species concentration as obtained in this study from the simulations of the ^{29}Si MAS NMR spectra (Figure 3b).

The presence of the Q^1 species in the structure of these glasses implies their formation via the following speciation reaction: $2\text{Q}^0 = 2\text{Q}^1 + \text{O}^{2-}$. The “free” O^{2-} ion is only bonded to the M^{2+} cations in the glass structure. The compositional variation of the Q^1 species concentration indicates that the release of the O^{2-} ion due to the condensation of Q^0 species into Q^1 species becomes increasingly less favorable with decreasing SiO_2 content in these glasses. This trend is consistent with the fact that the stoichiometry itself demands the presence of free oxygens in the structure of the suborthosilicate compositions with less than 33.33 mol % SiO_2 that are not formed via the above-mentioned Q -species

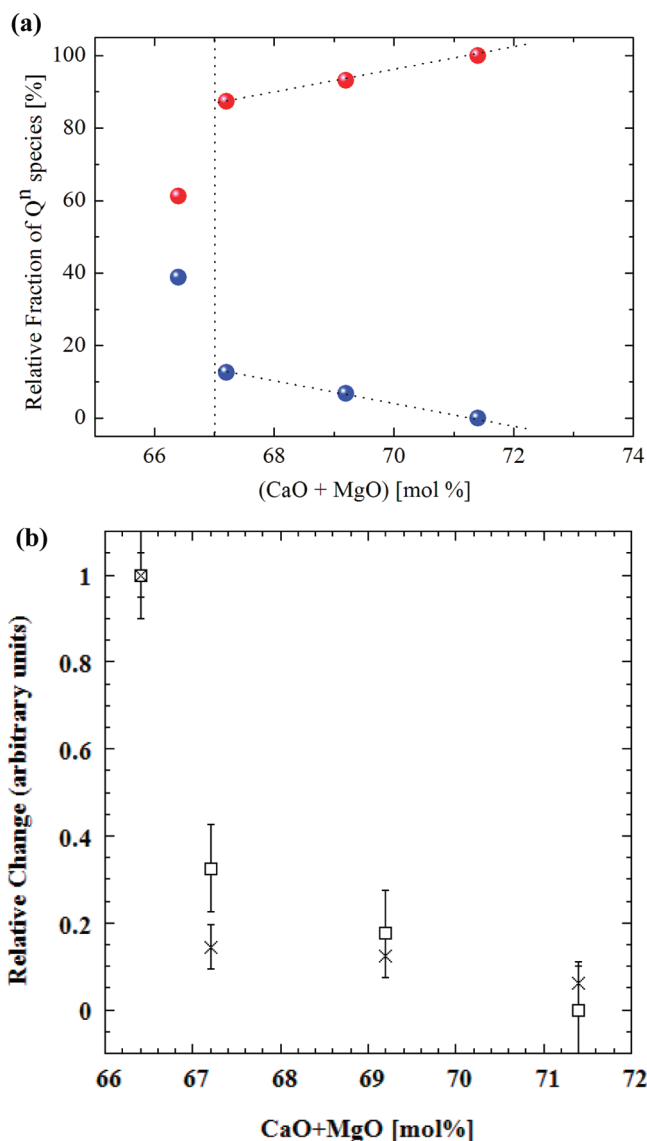


Figure 3. (a) Compositional dependence of the relative populations of Q^0 (red symbols) and Q^1 (blue symbols) species in CMS glasses. (b) Comparison of changes in Q^1 population from ^{29}Si NMR (squares) and the relative intensity of the Raman band at $\sim 700\text{ cm}^{-1}$ (crosses). Both data sets are normalized to the corresponding values in the CMS33 glass for the sake of comparison.

disproportionation reaction. A comparison between the compositional variation of the free oxygen concentration in these glasses as expected from stoichiometry and as calculated from the experimentally determined Q^1 species concentration is shown in Figure 4. It is evident from Figure 4 that the experimental values for the free oxygen concentrations in all glasses except for the CMS28 composition are somewhat greater than those expected from the stoichiometry, thus implying the presence of an excess of free oxygen present in their structure.

^{17}O NMR spectroscopic measurements were carried out on the isotopically enriched samples in order to investigate the coordination environment of the NBOs, to directly observe the free O^{2-} ions and to determine the extent of mixing between Mg^{2+} and Ca^{2+} cations in the glass structure. The ^{17}O MAS NMR spectra of all four CMS glasses are shown in Figure 5. These spectra are all characterized by a line shape that appears

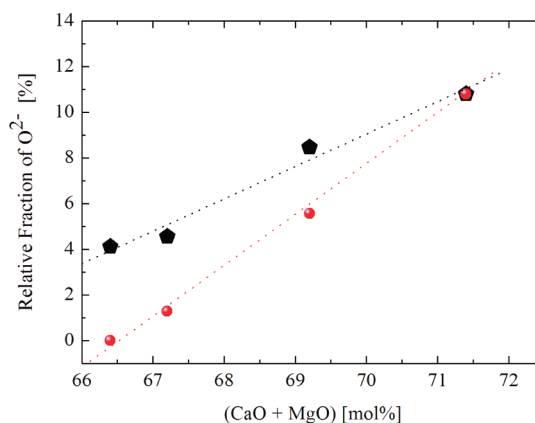


Figure 4. Concentration of free oxygen [O^{2-}] relative to the total number of oxygen atoms, as expected from the glass compositions (red symbols). Black symbols take into account the creation of excess free oxygen due to $Q^0 \rightarrow Q^1$ conversion (see text for details).

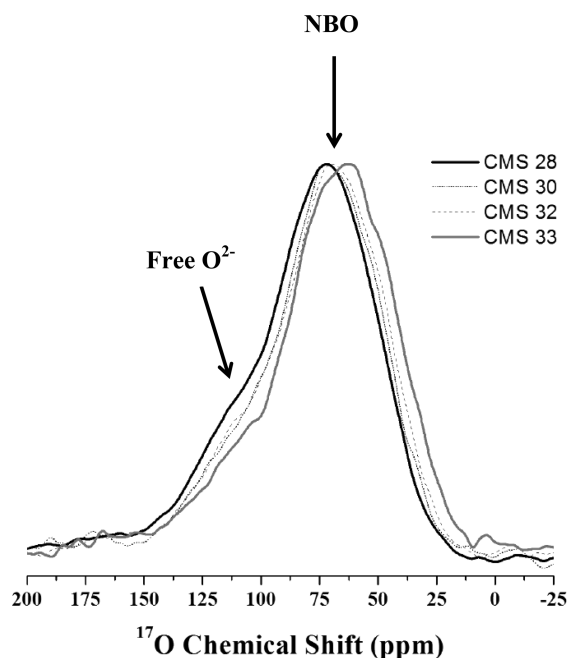


Figure 5. ^{17}O MAS NMR spectra of CMS glasses. Solid black, dotted, dashed, and solid gray lines correspond to CMS28, CMS30, CMS32, and CMS33.33 glass samples, respectively.

to have a main peak at $\sim 65\text{--}70\text{ ppm}$ with a shoulder at $\sim 110\text{ ppm}$. The relative frequency of the main peak is characteristic of NBO sites in Ca,Mg-silicate glasses as reported in the literature.^{12–15} Previous ^{17}O NMR studies of silicate glasses have indicated that the ^{17}O MAS NMR line shapes for the NBO sites are dominated by chemical shift distribution and not by the second-order quadrupolar effect.¹⁵ The ^{17}O 3QMAS spectra of the CMS28 and CMS33.33 glasses (Figure 6) clearly show that the signal is spread along a diagonal ridge implying that the ^{17}O NMR line shape is indeed dominated by chemical shift distribution. Therefore, the shoulder at $\sim 110\text{ ppm}$ in the ^{17}O MAS spectra in Figure 5 likely corresponds to a second oxygen environment. This hypothesis is supported by the total isotropic projections of the ^{17}O 3QMAS NMR spectra of these glasses (Figure 7) that are free of quadrupolar broadening effects and yet show similar features as in the MAS spectra. Simulation of the ^{17}O MAS NMR spectra with simple Gaussian

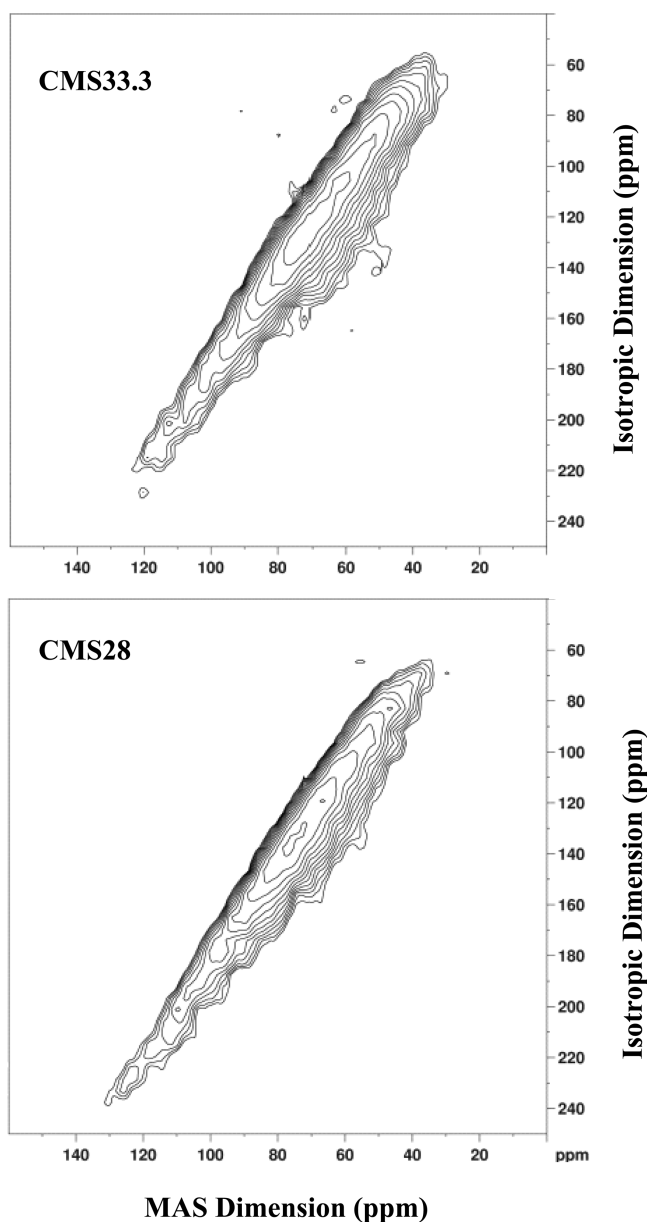


Figure 6. ^{17}O 3QMAS NMR spectra of CMS28 and CMS33.33 glasses. There are 12 linearly spaced contours from 5% to 95% intensity.

line shapes indicates that the relative fraction of this second oxygen environment progressively increases from $\sim 5\%$ in the CMS33.33 glass to $\sim 10\%$ in the CMS28 glass. These relative fractions are similar to those expected for the concentration of free O^{2-} ions in these glasses (see Figure 4). Therefore, it is reasonable to speculate that the shoulder at 110 ppm corresponds to free O^{2-} ions in the structures of these glasses. This assignment is also consistent with the fact that the chemical shift value of 110 ppm is intermediate between the chemical shifts of 38 to 47 ppm and 294 ppm, respectively, for $\text{Mg}-\text{O}-\text{Mg}$ and $\text{Ca}-\text{O}-\text{Ca}$ oxygen sites in the wadsleyite polymorph of Mg_2SiO_4 and in crystalline end member compositions MgO and CaO .^{16,17} However, it should be noted that a ^{17}O NMR chemical shift of 110 ppm is also characteristic of NBO sites in Ca,Mg-silicate glasses that are associated with 3 Ca nearest neighbors.¹⁵ Therefore, an unequivocal assignment of this spectral feature requires further

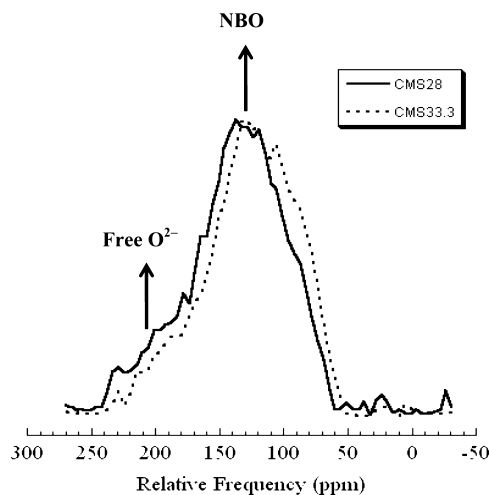


Figure 7. Total isotropic projections of the ^{17}O 3QMAS NMR spectra of CMS28 (—) and CMS33.33 (---) glasses in Figure 6.

consideration of structural models of these suborthosilicate glasses.

Previous ^{17}O NMR studies of Ca,Mg-silicate glasses have adopted a model for the NBO environments where each NBO is bonded to a total of 3 alkaline-earth cations (i.e., Ca^{2+} and Mg^{2+}) besides the Si. This model is based on bond valence arguments as well as on the consideration of the structures of a wide range of crystalline Ca,Mg-silicates.¹⁵ Therefore, the NBOs in Ca,Mg-silicate glasses can be associated with 3 Mg, 2Mg + 1Ca, 1Mg + 2Ca, and 3Ca nearest neighbors, and their characteristic ^{17}O chemical shift ranges are 25–50, 50–75, 75–100, and 100–125 ppm, respectively.¹⁵ This entire chemical shift range is covered in the MAS dimension by the diagonal ridge in the ^{17}O 3QMAS NMR spectra of the CMS28 and CMS33.33 glasses (Figure 6). The intensity maximum in these spectra is located near a chemical shift of ~ 70 ppm in the MAS dimension indicating that on an average the NBOs in these suborthosilicate glasses are associated with 1.5Mg and 1.5Ca, and therefore, the Ca^{2+} and Mg^{2+} ions are not spatially clustered in the glass structure. Since the signal in the MAS dimension extends from ~ 30 to ~ 125 ppm, the distribution of the cations around NBOs is likely to be random and not homogeneous. However, both the ^{17}O MAS and 3QMAS isotropic projection spectra (Figures 5 and 7) of these glasses display an asymmetric shoulder that cannot be explained by a random distribution of Ca^{2+} and Mg^{2+} ions around the NBOs, and the presence of another type of oxygen site besides the NBOs needs to be invoked. Therefore, when taken together, these structural and ^{17}O MAS and 3QMAS NMR line shape based arguments lend support to the above-mentioned assignment of the shoulder at ~ 110 ppm in the spectra in Figure 5 to free O^{2-} ions in these glasses.

The ^{29}Si and ^{17}O NMR spectroscopic results presented here indicate that the structure of these orthosilicate and suborthosilicate glasses consists of SiO_4^{4-} and $\text{Si}_2\text{O}_7^{6-}$ anions with Mg^{2+} and Ca^{2+} as the counterions that are held together primarily by Coulombic interaction. The Ca^{2+} and Mg^{2+} ions are randomly distributed in the nearest neighbor coordination shell of the NBOs. The crystalline Ca–Mg silicates near the orthosilicate composition are typically characterized by Ca^{2+} (Mg^{2+}) ions that are 6–8 (4–6) coordinated to oxygen atoms. The larger average coordination number of Ca^{2+} ions compared to that of Mg^{2+} ions is consistent with the larger ionic radius of

the former (1.00–1.12 Å) compared to that of the latter (0.57–0.72 Å). Similar Ca-NBO and Mg-NBO coordination polyhedra are also expected to be present in the structure of the CMS glasses studied here. It is likely that the structural and topological frustration resulting from packing of spatially randomly distributed dissimilar Ca-NBO and Mg-NBO coordination polyhedra may be responsible for the unusual glass forming ability of the corresponding liquids in this extremely SiO₂-deficient composition range.

The structural relaxation process associated with glass transition in typical silicate liquids (e.g., with ≥ 50 mol % SiO₂) is believed to be controlled by Si–O bond breaking that results in Q-species exchange.² Although this scenario may be partially valid for the orthosilicate glasses with Q⁰ and Q¹ species in a $\sim 60:40$ ratio, it would be less so for suborthosilicate compositions where the concentration of the Q¹ species decreases with decreasing SiO₂ content and the structure consists primarily of isolated Q⁰ species. Instead, structural relaxation in the latter compositions is likely to be more and more dominated by Ca/Mg–O bond breaking and diffusion of alkaline-earth cations and SiO₄⁴⁻ (Q⁰) anions. This hypothesis would predict a lowering of T_g in these glasses with increasing alkaline-earth oxide concentration that would mirror the decrease in the concentration of the Q¹ species. On the other hand, the packing of Ca²⁺ and Mg²⁺ ions around the Q¹ species would be somewhat less efficient compared to that around the highly symmetric Q⁰ species due to the presence of the bridging oxygen in the Q¹ species that is not shared by the alkaline-earth cations. Consequently, one would expect that the densities of these glasses would increase with increasing alkaline-earth oxide concentration and the compositional dependence would be the inverse of that of the concentration of Q¹ species. The compositional variation in T_g and density of these glasses are shown in Figure 8. It is clear that the decrease

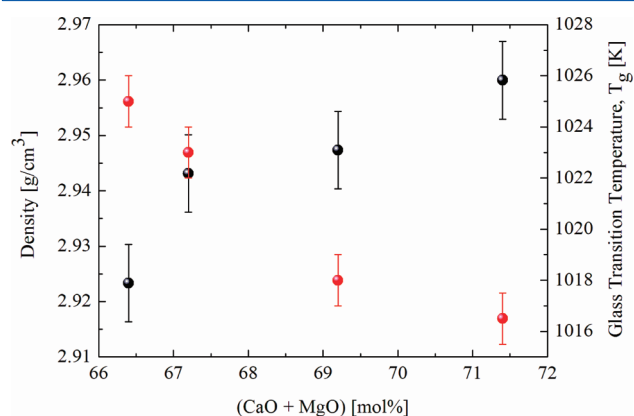


Figure 8. Density (black symbols) and T_g (red symbols) of the CMS glasses.

in T_g and increase in density with increasing alkaline-earth oxide concentration are significantly more rapid near the orthosilicate composition and show the above-mentioned trends with respect to the compositional variation of the Q¹ species concentration (see Figure 3).

SUMMARY

The structural attributes of Ca,Mg suborthosilicate glasses with SiO₂ contents ranging between 33.3 and 28 mol % have been investigated using ²⁹Si and ¹⁷O NMR spectroscopy. The ²⁹Si

MAS NMR results suggest that the structures of these glasses consist of Q⁰ and Q¹ species. The concentration of the Q¹ species drops abruptly from $\sim 39\%$ in the CMS33.33 glass to 12.6% in the CMS32 glass, and a further decrease in SiO₂ content results in a linear drop to 0% in the CMS28 glass. This composition dependence of Q¹ species concentration is closely related to that of the T_g and atomic packing in these glasses. The presence of the Q¹ species in the structure of these glasses implies the concomitant formation of “free” O²⁻ ions via the following speciation reaction: $2Q^0 = 2Q^1 + O^{2-}$. The free O²⁻ ion is only bonded to the Ca²⁺ and Mg²⁺ cations in the glass structure and is characterized by a ¹⁷O NMR chemical shift of ~ 110 ppm. The concentration of these free oxygens increases with decreasing SiO₂ content in these glasses. ¹⁷O MAS and 3QMAS spectra indicate that the Ca²⁺ and Mg²⁺ cations are randomly distributed in the nearest neighbor coordination shell of the NBOs of the Q⁰ and Q¹ species. The unusual glass forming ability of these extremely SiO₂-deficient liquids is likely related to the structural and topological frustration associated with the random packing of dissimilar Ca-NBO and Mg-NBO coordination polyhedra.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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