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Chemical order in mixed-cation silicate glasses and melts

Sung Keun Lee,* Bjorn O. Mysen, and George D. Cody
Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd., Washington, DC 20015

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Cation ordering in covalent oxide glasses and melts profoundly affects the macroscopic properties, such as viscosity, diffusivity, and thermodynamic potentials. It is commonly assumed that in glasses and melts nonframework cations such as Na^+, Ca^{2+}, and Ba^{2+} distribute randomly around nonbridging oxygen (NBO). Several macroscopic studies on the melting of silicates and thermodynamic data have suggested that a possible nonrandomness may exist among cations around NBO in mixed-cation silicate glasses. Here, we report unambiguous experimental evidence of chemical ordering of nonframework cations and demonstrate a clear preference for certain types of cation-NBO complexes in mixed-cation silicate glasses using ^{17}O magic angle spinning (MAS) and multiple quantum MAS NMR. Particularly, complete bonding preference and cation ordering occurs in Ba-Mg silicate glasses ($BaMgSi_2O_6$) glass in such a way that nonbridging oxygen either only has Ba^{2+} as a nearest neighbor (Ba-NBO) or exists as a complex containing one Ba^+ and two Mg^{2+} as nearest neighbors while no detectable fraction of Mg-NBO is observed. Ba-Na silicate glasses, on the other hand, show a wide distribution of configurations for two types of cations around NBO, forming Ba- and Na-NBO as well as substantial intensity of mixed NBO peaks, which indicates a prevalence of dissimilar pairs around NBO or a stronger preference to Ba-O-$^{[4]}$Si over Na-O-$^{[4]}$Si. The present results, combined with the previous results on Na-Ca silicate glasses, highlight the tendency for chemical ordering upon cation mixing in oxide glasses and may provide an atomistic explanation for diffusivity anomalies as well as activity-composition relationship of silicate melts.

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I. INTRODUCTION

Traditional views of covalent oxide glasses and melts hold that framework units (e.g., silicon tetrahedra, $^{[4]}$Si, $^{[4]}$Al, and $^{[3]}$B) are polymerized to form bridging oxygen (BO) such as $^{[4]}$Si-O-$^{[4]}$Si, $^{[4]}$Si-O-$^{[4]}$Al, and $^{[3]}$B-O-$^{[3]}$B. Network-modifying cations perturb such frameworks, necessitating the formation of nonbridging oxygen (NBO) coordinated by framework $^{[4]}$Si and alkali or alkaline-earth elements (e.g., Na-O-$^{[4]}$Si and Ba-O-$^{[4]}$Si). In spite of extensive efforts to quantify the degree of randomness among these framework units (e.g., Refs. 1–4) and network-modifying cations (e.g., Refs. 5–7), the nature of cation distribution has remained uncertain for several decades primarily because of a lack of direct experimental evidence of atomic-scale disorder.[8] In the case of mixed-cation silicate glasses, model systems for magmatic melts and relevant to other technologically important glasses, a quantitative assessment of disorder is particularly challenging.[9] Previously reported schemes for disorder in mixed-cation silicate glasses and melts have included clustering of cations,[10] random distributions with[6] or without segregation of NBO's,[11–13] and chemical order favoring dissimilar types of cation pairs.[13,14] These disparate results likely stem from the model dependence of the analyses due to the lack of resolution available in conventionally employed spectroscopic and scattering methods. Quantification of the atomic disorder in mixed-cation silicate glasses provides an explanation for the "mixed-cation effect," where mobility of a cation significantly decreases by the presence of other cations species (e.g., Refs. 6, 15, and 16). Furthermore, ordering associated with intermixing among cations results in a variation of configurational thermodynamic properties of melts, including silicate activity, which governs the melting relations and compositions of magmas in equilibrium with mantle rock.[17–19] Previous experiments on melting of peridotite (the primary constituents of Earth's mantle (Ref. 20) as well as chemical composition of mantle xenoliths[21] suggest apparent negative deviation of silica activity from ideal solution although satisfactory physical explanation for this phenomena has not yet been made.

We approach the problem of assessing cation ordering by analyzing the atomic configurations around NBO in selected mixed cation silicate glasses using ^{17}O magic angle spinning (MAS) NMR and triple quantum (3Q) MAS NMR (e.g., Refs. 3 and 22–24). We find that Ba-Na silicate glasses are ideal for studying cation mixing in silicate glasses due to the moderate difference in ionic radii and charge (Na^+:1.02 Å, Ba^{2+}:1.35 Å), which leads to one of the largest chemical shift differences in Na-NBO (Na-O-$^{[4]}$Si, isotropic chemical shift of about 40 ppm for Na disilicates glass) and Ba-NBO (Ba-O-$^{[4]}$Si, from 159 to 169 ppm for NBOs in crystalline $BaSiO_3$).[9,25,26] This allows us to clearly determine the extent of ordering. Ba-Mg silicate glasses are analogues to the common Ca-Mg glasses,[27] but have larger chemical shift dispersion between NBOs due to their larger ionic radii difference (Mg^{2+}:0.72 Å, Ba^{2+}:1.35 Å).[22] We also quantify the extent of disorder among network modifying cations by introducing one order parameter, degree of cation distribution (Q_m), and finally discuss the effect of disorder and macroscopic properties including diffusivity.

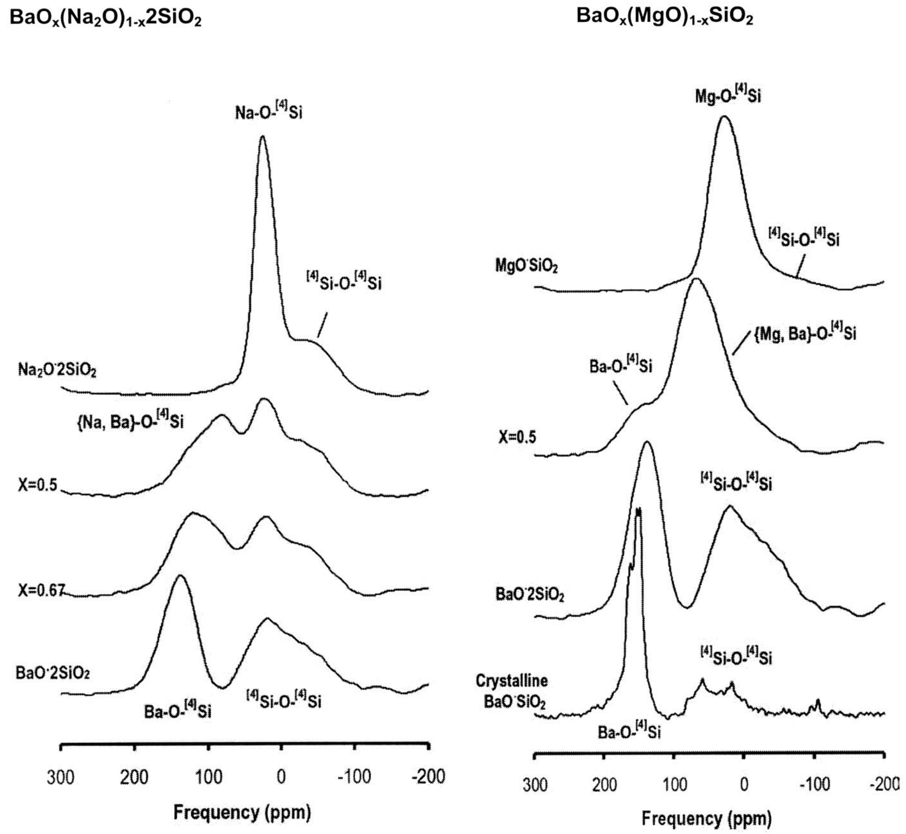

FIG. 1. ^{17}O MAS spectra for Ba-Na $[BaO_x(Na_2O)_{1-x}2SiO_2]$ and Ba-Mg silicate glasses $[BaO_x(MgO)_{1-x}SiO_2]$ at 7.1 T with varying $X_{BaO}=BaO/[BaO+Na_2O\ (or\ MgO)]$.

II. EXPERIMENTAL PROCEDURES

A. Sample preparation

Mixed cation silicate glasses $[BaO_x(Na_2O)_{1-x}2SiO_2$ and $BaO_x(MgO)_{1-x}SiO_2]$ with varying $X_{BaO}=BaO/[BaO+Na_2O$ (or MgO)] were synthesized from 20% ^{17}O-enriched SiO_2 and alkali and alkaline-earth carbonate (e.g., Na_2CO_3 and $BaCO_3$). About 0.2% of Gd_2O_3 was added to reduce spin lattice relaxation time. The mixtures were fused for an hour at between 1100 and 1650 °C (depending on the liquidus temperature after decarbonation) and then quenched. $BaSiO_3$ is not a good glass former, and thus ^{17}O-enriched $BaSiO_3$ crystals were synthesized as a reference to peak positions for NBO and BO in 3QMAS NMR spectra. Negligible weight loss is observed in synthesis.

B. NMR spectroscopy

^{17}O MAS spectra were collected on a CMX infinity 300 spectrometer (7.1 T) at a Larmor frequency of 40.7 MHz with a 5-mm zirconia rotor. Recycle delays for ^{17}O MAS NMR are 1 s with radio frequency pulse lengths of about 0.38–0.4 μs, which is about a 15° tip angle for the central transition in solids. In the 3QMAS NMR experiment at 7.1 T, the FAM- (fast-amplitude-modulation-) based shifted-echo pulse sequence,[28–30] comprising two hard pulses of duration 5.75 μs and 1.2 μs, a selective pulse with duration of 15–20 μs, and an echo time of 0.545 ms, was used after optimization of pulse lengths to ensure maximum intensity. A sample spinning speed of 11–12 kHz was used. Recycle delays ranged from 1 to 4 s depending on the spin lattice relaxation time. The spectra were referenced to external tap water.

III. RESULTS

Figure 1 presents ^{17}O MAS NMR spectra of the mixed-cation silicate glasses, revealing bridging oxygen ($^{[4]}$Si-O-$^{[4]}$Si) and several types of nonbridging oxygens, including Na-NBO, Ba-NBO, and Mg-NBO as well as mixed NBO's of {Na,Ba}-O-$^{[4]}$Si and {Ba-Mg}-O-$^{[4]}$Si. Na-NBO is more shielded and presents a narrower chemical shift distribution than Ba-NBO. The peak width of pure end member NBO peak is mainly related to multiple configurations around NBO's and appears to increase from Na to Ca to Ba-NBO.[9] The substantial intensity of mixed NBO peaks observed in both systems also demonstrates extensive mixing among cations. Intermediate composition glasses exhibit a wide distribution in the chemical shift of total NBO's spanning from pure Na-NBO to Ba-NBO. The mean peak position of the mixed NBO peak ({Na,Ba}-O-$^{[4]}$Si) increases with Ba content. These results show that this system exhibits neither a complete preference for Na-Ba pairs (as would be revealed by the absence of end-member NBO peaks) nor a clustering of similar types of cations, which would not allow larger fractions of mixed peak. The intensity of the pure Na-O-$^{[4]}$Si peak in Ba-Na silicate glasses decreases with Ba and is weak at $X_{BaO}=0.67$ (Na/Ba$=$1), which may suggest a preference of NBOs for Ba or chemical ordering favoring {Na,Ba}-O-$^{[4]}$Si (see discussion). The BO peak is less affected by the cation type, indicating stronger interaction of

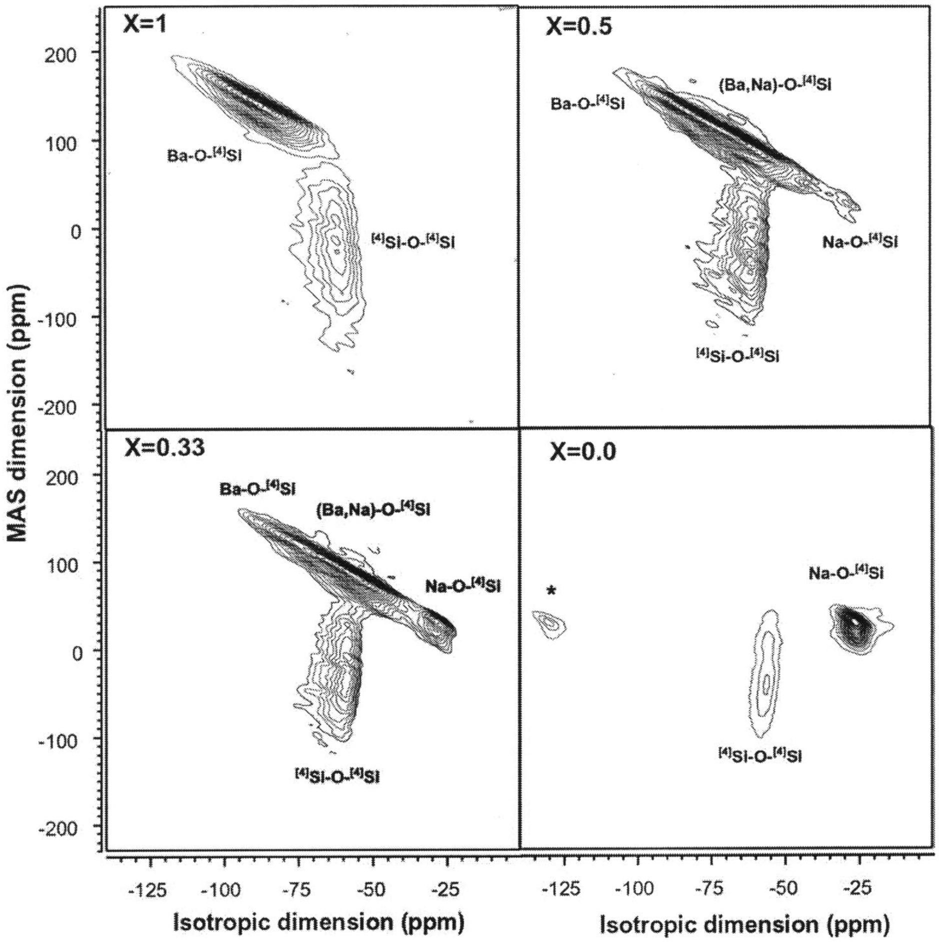

FIG. 2. ^{17}O 3QMAS NMR spectra for the Ba-Na $[\mathrm{BaO}_x(\mathrm{Na_2O})_{1-x}2\mathrm{SiO_2}]$ silicate glasses at 7.1 T with varying $X_{\mathrm{BaO}}=\mathrm{BaO}/[\mathrm{BaO}+\mathrm{Na_2O}$ (or MgO)]. Contour lines for end members are drawn from 3% to 98% of the relative intensity with a 5% increment and 8% to 98% for the intermediate compositions. The asterisk (*) denotes spinning side band.

network-modifying cations with NBO than with BO.

The ^{17}O MAS NMR spectrum for the Ba-Mg glasses differs enormously from that of the Ba-Na silicate glasses. The Mg-O-$^{[4]}$Si peak is wider than that of Na-O-$^{[4]}$Si partly because the increased cation field strength of Mg^{2+} increases the configurational disorder around the NBO and partly because this site has larger quadrupolar coupling constant (C_q, a structurally relevant NMR parameter) of about 2.8 MHz compared with about 2 MHz for Na-NBO.[25] The Mg-O-$^{[4]}$Si peak overlaps the BO peak in pure $\mathrm{MgSiO_3}$ glass. The peak width differences due to different C_q for the two peaks[25] allow us to assign the narrow and broad components as Mg-O-$^{[4]}$Si and BO, respectively. The peak near 150 ppm is assigned to Ba-O-$^{[4]}$Si by comparison with crystalline $\mathrm{BaSiO_3}$ and Ba disilicate glasses (BS12) (recall that $\mathrm{BaSiO_3}$ is not a good glass former). The {Ba,Mg}-O-$^{[4]}$Si in the mixed composition exhibits a chemical shift range intermediate from the end members, suggesting possible chemical order. Peak overlap between Na-NBO (and Mg-NBO) and $^{[4]}$Si-O-$^{[4]}$Si, in addition to several mixed-cation peaks in the one dimensional (1D) ^{17}O MAS NMR spectra, hampers quantification of disorder. The two-dimensional ^{17}O 3QMAS NMR spectra, however, can yield better resolution among peaks by removing residual quadrupolar broadening.[2,4,24]

Figure 2 presents the ^{17}O 3QMAS NMR spectra of Ba-Na glasses. Each type of BO and NBO is resolved as compared with the 1D MAS spectra. The isotropic chemical shift (^{17}O δ_{iso}) and P_q of Na-O-$^{[4]}$Si (39 ppm and 2.2 MHz) appears independent of the concentration of charge-modifying cations (X_{BaO}) and has a narrower chemical shift dispersion in 3QMAS dimension than Ba-NBO (δ_{iso} and C_q of about 151 ppm and 1.63 MHz, respectively). For the quadrupolar coupling product P_q [equal to $C_q\ (1+\eta^2/3)^{1/2}$, where $0 \leqslant \eta \leqslant 1$ is the quadrupolar asymmetry parameter] and isotropic chemical shift (δ_{iso}), mean values were estimated for each NBO and BO from the positions of the mixed peaks and from the centers of gravity for the end-member peaks. The position maxima of mixed NBO peaks exhibit significant variation with Ba content, consistent with MAS data. These mixed NBO peaks for intermediate composition glasses are due to the contribution from several NBO components surrounded by a varying number of Na and Ba (see discussion). The ^{17}O δ_{iso} of these mixed peaks increases with increasing Ba content from about 95 ppm (P_q of 1.6 MHz, $X_{\mathrm{BaO}}=0.33$) to about 128 ppm (P_q of 1.8 MHz, $X_{\mathrm{BaO}}=0.5$). ^{17}O δ_{iso} of $^{[4]}$Si-O-$^{[4]}$Si varies from about 52 (± 1) ppm for sodium disilicates glasses (NS12) to 62 (± 3) ppm for BS12, with nearly constant P_q of about 4.8 (± 0.2) MHz as shown in the shift of peak positions in 2D spectra (Fig. 2), demonstrating that network-modifying cations also interact with BO. The considerable range and intensity of mixed peaks confirms the preference for dissimilar pairs {Ba,Na}-O-$^{[4]}$Si.

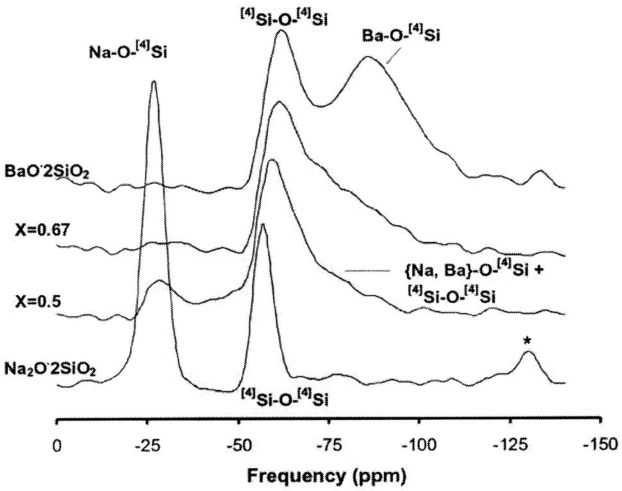

FIG. 3. Isotropic projection of ^{17}O 3QMAS spectra for Ba-Na silicate at 7.1 T with varying $X_{\mathrm{BaO}} = \mathrm{BaO}/(\mathrm{BaO}+\mathrm{Na_2O})$. The asterisk (*) denotes spinning side band.

Figure 3 also shows isotropic projection of the ^{17}O 3QMAS NMR spectra of Ba-Na glasses.

Figure 4 presents the ^{17}O 3QMAS NMR spectra of Ba-Mg silicate glasses revealing Mg-O-$^{[4]}$Si and BO peaks are well separated in pure $\mathrm{MgSiO_3}$ glass [Fig. 4(A)]. The ^{17}O 3QMAS NMR spectrum for crystalline $\mathrm{BaSiO_3}$ reveals two NBO peaks as well as a BO peak that has a peak position near that of BS12 [Fig. 4(B)]. The $\mathrm{BaMgSi_2O_6}$ glass reveals two NBO peaks assigned to Ba-O-$^{[4]}$Si and mixed {Ba,Mg}-O-$^{[4]}$Si. Note that there is negligible Mg-O-$^{[4]}$Si in the $\mathrm{BaMgSi_2O_6}$ glass [Fig. 4(C) where two spectra in Fig. 4(A) are superposed for comparison]. Figure 5 presents the isotropic projections for the ^{17}O 3QMAS NMR spectra of $\mathrm{MgSiO_3}$ and $\mathrm{BaMgSi_2O_6}$ glasses, which confirms the absence of Mg-O-$^{[4]}$Si. This result demonstrates the strong chemical preferences in mixed-cation glasses forming exclusively Ba-NBO in mixed cation silicate glasses. Highly probable configurations of network-modifying cations around NBO in mixed Ba-Mg silicate glasses are {2 Ba, 1 Mg} and {1 Ba and 2 Mg}. If we consider the compositional constraints (1:1 mixing of Ba and Mg) as well as significant fraction of Ba-O-$^{[4]}$Si in the absence of Mg-O-$^{[4]}$Si, the mixed NBO peak may consist mostly of Ba^{2}Mg-O-$^{[4]}$Si (two Mg and 1 Ba around NBO). ^{17}O δ_{iso} and P_{q} of Mg-O-$^{[4]}$Si are 49.2 ppm and 2.8 MHz, respectively, and those of BO peaks are 57.7 ppm and 4.9 MHz. These parameters for Ba^{2}Mg-O-$^{[4]}$Si obtained from peak maxima are 107.2 ppm and 1.98 MHz.

These NMR data reveal an onset of cation ordering around NBO's in Ba-Mg silicate glasses, forming mainly Ba^{2}Mg-O-$^{[4]}$Si, as opposed to multiple mixed peaks and end members as is observed in Ba-Na (Fig. 2) and Na-Ca silicate glasses.[9] Figures 4 and 5 provide unambiguous evidence of the preferential formation of Ba-NBO over Mg-NBO. Another aspect of the ^{17}O 3QMAS NMR spectra for Ba-Mg silicate glasses is that the BO peak position in $\mathrm{BaMgSi_2O_6}$ glass is similar to those in crystalline $\mathrm{BaSiO_3}$ and in BS12 but not in the case of pure $\mathrm{MgSiO_3}$ [Fig. 4(C)]. This demonstrates that $^{[4]}$Si-O-$^{[4]}$Si is clearly perturbed by network-modifying cations and BO shows a preference (or affinity) for Ba over Mg.

IV. DISCUSSION

The present results, combined with the previous results on Na-Ca silicate glasses,[9] highlight the tendency for chemical ordering upon cation mixing in oxide glasses. Quantification of the extent of disorder can be derived through analysis of oxygen site populations contributing to each NBO peak. Populations of Na-O-$^{[4]}$Si are well constrained due to distinct and narrow chemical shift ranges and thus we fit each ^{17}O MAS NMR spectrum with the assumption of a single BO site and four NBO sites (^{4}Na, ^{2}Na^{1}Ba, ^{1}Na^{2}Ba, and ^{3}Ba). A detailed methodology for obtaining fractions of NBO has been discussed previously.[9] The choice of types of NBO peaks is somewhat arbitrary (e.g., the existence of a ^{3}Na^{1}Ba NBO peak or number of Na neighbors for end members), but regardless of this complexity, the purpose of this procedure is to determine the Na-O-$^{[4]}$Si fraction and compare it with the predictions from modeling (see below). Each of the NBO's is assumed to be a Gaussian function whose width and peak positions are further assumed to be invariant with X_{BaO}. Due to the peak overlap among mixed peaks and Ba-NBO, the simultaneous fitting results for these peaks may be model dependent. However, the fraction of Na-O-$^{[4]}$Si is well constrained due to its narrow chemical shift ranges, making the results based on Na-NBO is robust.[9] Figure 6 shows the fitting results of ^{17}O MAS NMR spectrum for $X_{\mathrm{BaO}}=0$ and 0.5 glasses as examples.

Figure 7(A) presents the extent of disorder (and degree of cation distribution, Q_{m}) among network-modifying cations in mixed cation (M-N) silicate glasses as a function of composition, where M and N denote network-modifying cations. Here Q_{m} is defined as follows:

$$Q_{\mathrm{m}} = 1 - \exp(2W/kT_{\mathrm{f}}) \quad \text{if } 2W \leqslant 0, \tag{1a}$$

$$Q_{\mathrm{m}} = 1 - \exp(-2W/kT_{\mathrm{f}}), \quad \text{if } 2W > 0, \tag{1b}$$

where $2W$ defines the lattice energy difference of $[M\text{-}M] + [N\text{-}N] = 2[M\text{-}N]$. Here, M-M refers to a next-nearest M-M pair. T_{f} and k are fictive temperature (in kelvin, glass transition temperature of a system that varies with cooling rate) and the Boltzmann constant, respectively. The Q_{m} is thus expected to vary from one extreme case of clustering (or phase separation among cations, $Q_{\mathrm{m}}=-1$) through complete random distributions ($Q_{\mathrm{m}}=0$), to the other extreme of chemical order where M-N pairs are favored around NBO ($Q_{\mathrm{m}}=1$). The fraction of N-O-$^{[4]}$Si can be expressed as follows from a quasichemical approximation,[4] considering the probability of finding N around an N-N pair:

$$P_{\text{N-O-Si}} = X_N (1 - T X_M)^2, \tag{2}$$

where

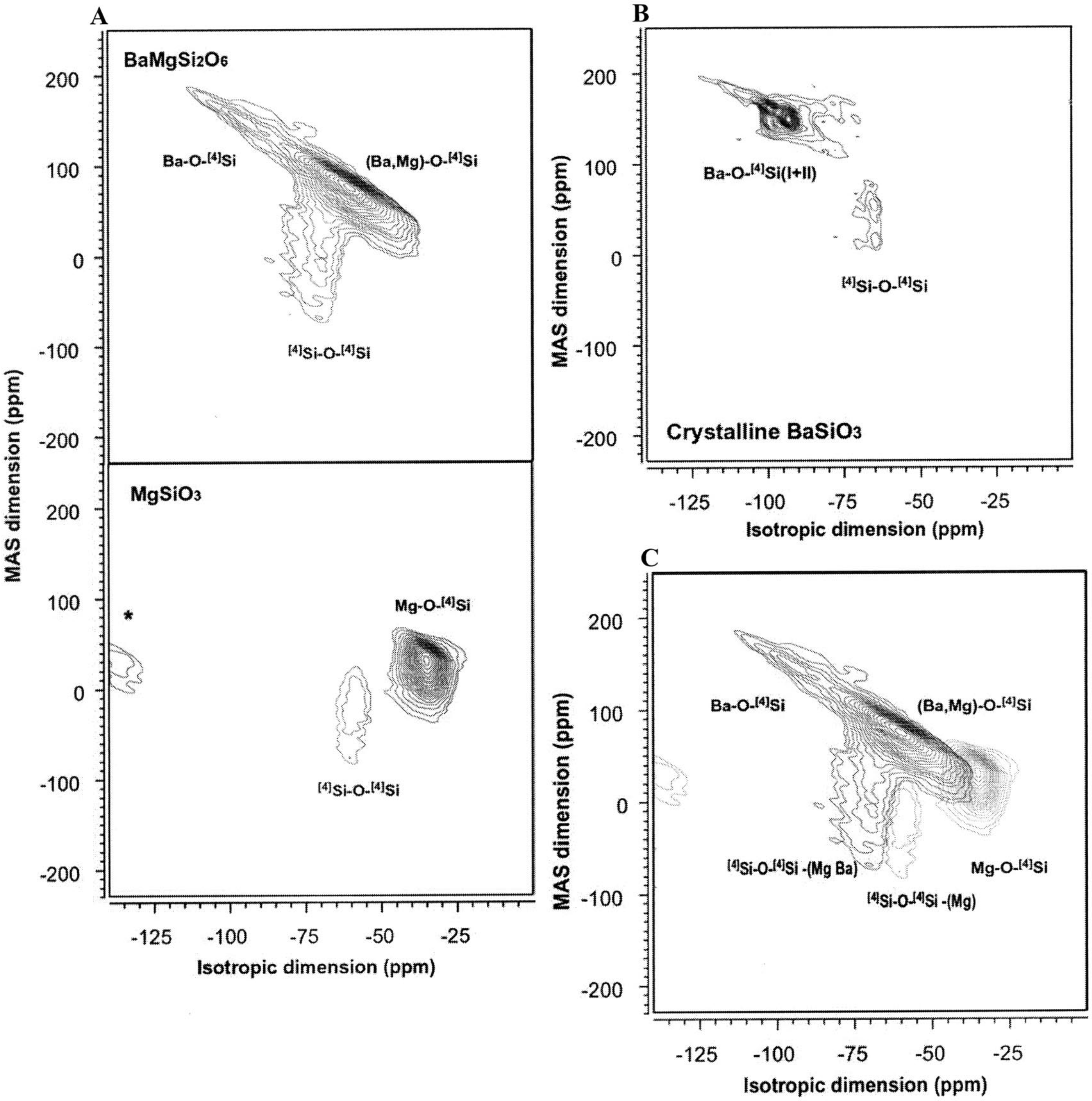

FIG. 4. ^{17}O 3QMAS NMR spectra for the Ba-Mg silicate glasses $[\mathrm{BaO}_x(\mathrm{MgO})_{1-x}\mathrm{SiO}_2]$. Contour lines are drawn from 8% to 98% of the relative intensity with a 5% increment and an added line at 5%.

$$X_N = N/(N+M), \quad T = \frac{2}{(\beta+1)}, \quad \beta = \sqrt{1-4X_A X_B Q_\mathrm{m}}.$$

The fraction of N-O-$^{[4]}$Si (e.g., Na-O-$^{[4]}$Si) decreases with increasing fraction of M (here, Ca and Ba) and is much less than would be predicted by a random distribution of cations. This indicates a prevalence of dissimilar pairs M-N around NBO or a preference for M-O-Si. In Ba-Na silicate glasses, the fraction of Na-O-$^{[4]}$Si is less than that observed for Na-Ca silicate glasses, suggesting that Ba-Na silicate glasses exhibits a stronger prevalence of chemical order (larger Q_m) than Na-Ca glass, or a stronger preference to Ba-O-$^{[4]}$Si over Ca-O-$^{[4]}$Si. Because the fraction of Na-NBO in Na-Ca silicate glasses is less than the prediction from long-range order (LRO) in M-N mixing, it is also probable that NBO's prefer Ca to Na. Here, LRO in the cation distribution refers to the situation where the N-M-N-M pair distribution extends beyond nearest-neighbor interactions and N-O-Si fraction can be expressed as $1-3X_M$. The Ba-Mg system reveals clear evidence of chemical ordering of cations around NBO's as well as a strong preference toward Ba-O-$^{[4]}$Si.

Na-K silicate glasses are particularly interesting mainly because of their pronounced mixed cation effect as well as geophysical relevance. Previous studies of the Na-K glass have suggested that the network-modifying cations are randomly distributed [Fig. 7(a)].[12] The analysis of this system can be model dependent due to moderate peak overlap among Na- and K-NBO.[26] K-Mg silicate glasses do show a signature of cation ordering, with a moderate preference for Mg^{2+} by NBO's.[13] Taken all together these results reveal a hierarchy in the NBO preference for various network-modifying cations, resulting from the competition between steric (ionic radius) and electrostatic (charge) effects of the cation. When mixing high- and low-field-strength cations (e.g., Mg^{2+} and K^+, respectively), it appears that the high-field-strength cation (Mg^{2+}) is consistently favored at the

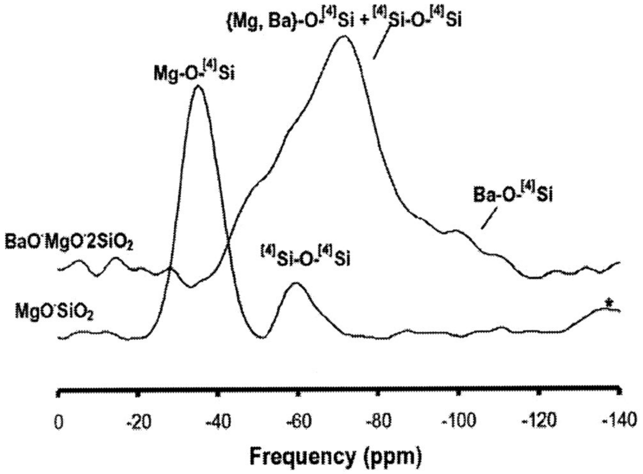

FIG. 5. Isotropic projection of ^{17}O 3QMAS spectra for Ba-Mg silicate at 7.1 T. The asterisk (*) denotes spinning side band.

NBO's. On the other hand, when a pair of cations with identical charge but different ionic radii is mixed, the steric effect predominates, favoring the larger cation (e.g., Ba^{2+}, low cation field strength) to occupy both BO and NBO. As manifested in Ba- (or Ca-) Na and Ba-Mg silicate glasses as well as the previously studied K-Mg system,[13] it is possible that the onset of chemical ordering upon cation mixing appears when the difference of the ionic radii (r) exceeds a threshold (e.g., $\Delta r > 0.3$ Å). It should be also noted that intermediate structural arrangement of glasses[31] affected by the difference in coordination number (CN) of each cation as well as total concentration of SiO_2 (i.e., total alkali and alkaline-earth fraction) may contribute the preference and ordering of these cations.

Cation ordering has a significant influence on the macroscopic properties of melts and glasses. For instance, the diffusivities of both smaller and larger cations in mixed silicate decrease with increasing degree of chemical order (increasing Q_m). Figure 7(B) illustrates how the extent of intermixing among cations may affect the diffusivity of smaller cations (N, e.g., Mg and Na) as a function of composition. Diffusivity is calculated considering only thermally activated jump processes. It is further assumed that the total activation energy of the jump processes from i (N or M) to i (E_{ii}) and i to j (E_{ij}) are scaled to the fractions of the i-j and i-i bonds obtained from quasichemical approximations,[1–4] respectively. It should also be noted that there are other cooperative processes as well as long-range ionic diffusion contributing to total diffusivity,[32] which are not considered in this model. The expression for the diffusivity of N is given as follows:

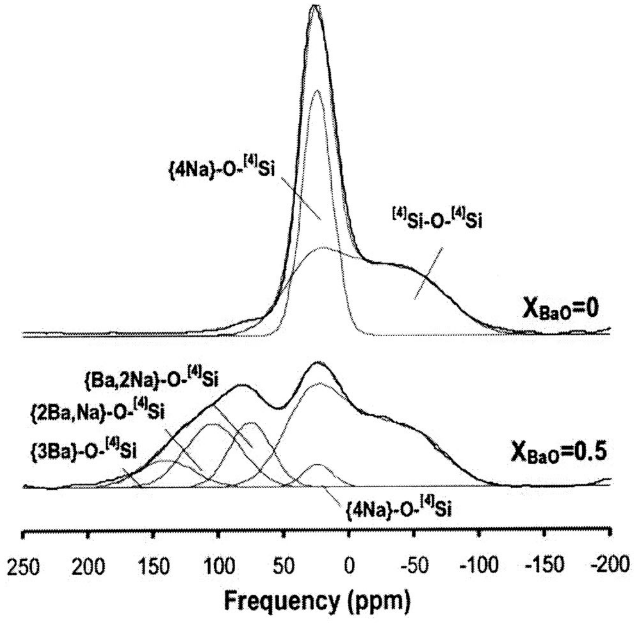

FIG. 6. Fitting results of ^{17}O MAS NMR spectrum for $X_{BaO}=0$ and 0.5 glasses. Thick and thin lines show the experimental and fitting results, respectively. The nonsymmetric peak shape of BO due to second-order quadrupolar broadening was simulated with three Gaussian functions (Ref. 9).

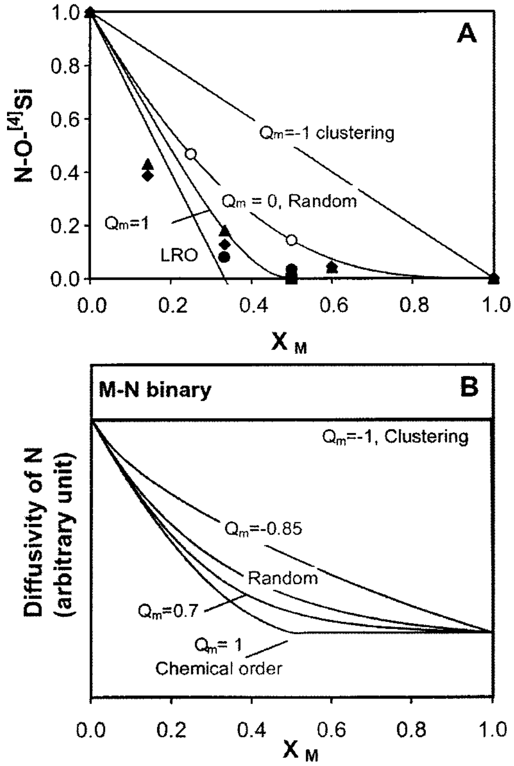

FIG. 7. (A) The extent of disorder in mixed-cation, M-N silicate glasses with composition (X_M) and (B) the effect of disorder on the diffusivity of N with X_M. Solid circles and square denote the fractions of Na-O-$^{[4]}$Si for Na-Ba silicates and Mg-O-$^{[4]}$Si for Mg-Ba silicate glasses, respectively. Diamonds (from ^{17}O MAS) and triangles (from 3QMAS NMR) denote the Na-NBO fraction for Na-Ca silicate glasses. Open circles refer to coordination-number-adjusted fraction of Na-O-$^{[4]}$Si for the Na-K system; here the fraction of previous Na-NBO for the Na-K system (Ref. 12) is normalized by dividing the Na-O-$^{[4]}$Si by the mole fraction of X_{Na}. This allows direct comparison among the systems with different coordination numbers of network-modifying cations. The activation energy ratio and temperature for the calculations (E_{NN}/E_{NM}) are 0.33 and 750 K, respectively.

$$D_N = D_0^* \exp\{[2X_M E_{NM} + (\beta+1-2X_M)E_{NN}]/(\beta+1)kT\}, \tag{3}$$

where D_0 is the preexponential factor and the other variables have been defined previously. The diffusivity of N is predicted to decrease both with increasing fraction of M and the degree of disorder from clustering of similar types of cations ($Q_\mathrm{m} = -1$) to complete order. The diffusivity of M (larger cation) also shows similar behavior while the relative diffusivity difference between cations varies with relative magnitudes of activation energy barriers (e.g., E_{ij}/E_{ji}). This behavior stems from a site mismatch energy difference among each distinct cation site and therefore the addition of one type of cation inhibits the diffusivity of the other cations by an increased activation energy barrier from the original site to a site previously occupied by a dissimilar cation.[15] The probability of the next-nearest neighbor being occupied by a different cation is directly related to the degree of cation order (Q_m). In a random distribution of network-modifying cations, the diffusivity is lower than with clustering, with a negative deviation from linearity, which confirms that the mixed-cation effect is also prominent in a random distribution of cations (e.g., Ref. 33). The smaller diffusivity of Na in Na-Ca as compared to Na-K silicate glasses is likely due to the higher chemical order (larger Q_m) of the former.[34]

Finally, chemical ordering also controls silica activity in melts. The present results showing a preference to dissimilar pairs of network-modifying cations indicate that there will be a reduction in the activity coefficient of silica in multicomponent melts.[35] Taken together with additional chemical ordering among framework units ($^{[4]}$Si and $^{[4]}$Al),[2–4,35] these results provide an atomistic explanation of silica activity in melts in equilibrium with mantle mineral assemblages.

The results and methodology given here provide insight into glass and melt structures and modify the classic view of glass structures of random distribution of network-modifying cations around NBO by introducing Q_m. These methods can be applied to explore the effect of pressure and temperature on the cation ordering to gain further insight into a molecular origin of the properties of glasses and the corresponding melts.[3]

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*Electronic address: s.lee@gl.ciw.edu

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