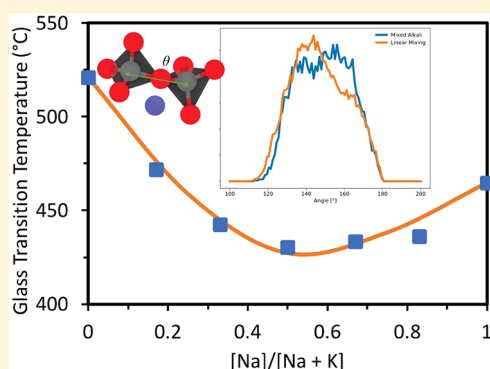


1 Topological Origins of the Mixed Alkali Effect in Glass

2 Collin J. Wilkinson,[†] Arron R. Potter,[‡] Rebecca S. Welch,[¶] Caio Bragatto,[¶] Qiuju Zheng,[§]3 Mathieu Bauchy,^{||} Mario Affatigato,[¶] Steven A. Feller,[¶] and John C. Mauro^{*,†,||}4 [†]Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, United States6 [‡]Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180, United States7 [¶]Department of Physics, Coe College, Cedar Rapids, Iowa 52402, United States8 [§]School of Materials Science and Engineering, Qilu University of Technology, Jinan, 250353, China9 ^{||}Department of Civil and Environmental Engineering, University of California, Los Angeles, California 90095, United States

ABSTRACT: The mixed alkali effect, the deviation from expected linear property changes when alkalis are mixed in a glass, remains a point of contention in the glass community. While several earlier models have been proposed to explain mixed alkali effects on ionic motion, models based on or containing discussion of structural aspects of mixed-alkali glasses remain rare by comparison. However, the transition-range viscosity depression effect is many orders in magnitude for mixed-alkali glasses, and the original observation of the effect (then known as the Thermometer Effect) was of the highly anomalous temperature dependence of stress and structural relaxation time constants. With this in mind, a new structural model based on topological constraint theory is proposed herein which elucidates the origin of the mixed alkali effect as a consequence of network strain due to differing cation radii. Discussion of literature models and data alongside new molecular dynamics simulations and experimental data are presented in support of the model, with good agreement.



25 ■ INTRODUCTION

The mixed alkali effect (MAE) was originally discovered in 1883 by Weber¹ as part of his investigation of the Thermometer Effect, wherein a glass containing significant content of more than one alkali modifier undergoes unusually fast low-temperature relaxation, altering the calibration of a thermometer composed of such glass.^{1–3} The MAE manifests as a nonadditivity of many glass properties as the ratio of one alkali to the other changes and appears in a wide variety of properties. Furthermore, one glass system may exhibit the MAE for some property but another system may not, e.g., glass transition temperature (T_g) in silicates (significant effects)^{4–8} and borates (lesser effects).^{9–11}

Since its discovery, several models have been proposed to describe the MAE, to varying degrees of success. In many cases, models predicated purely on electrical properties fail to accurately predict changes in mechanical or thermal properties.¹¹

Major MAE Phenomena. As noted above, the mixed alkali effect was first observed experimentally in the unusually fast relaxation of thermometer glass.^{1–3,12} Since then, other mechanical and thermomechanical glass properties have also been found to exhibit a mixed alkali effect. One of the largest of these is found in the transformation-range viscosities of silicate glasses, which can be represented by their accordingly depressed glass transition temperatures (T_g).^{4–8,13–16} Internal

friction also shows a significant mixed-alkali effect, exhibiting large peaks associated with coordinated rearrangement of alkali ions in mixed-alkali glasses, which correlates in magnitude with the slower ion diffusivity and maximizes where diffusivities are equal.^{10,11,17,18}

Mixed-alkali glasses also show some deviations in other mechanical properties.^{10,11} Of particular modern importance due to the recent popularity of ion-exchanged glass products (some, e.g.,^{19,20} even utilizing ion exchange to examine the MAE itself), the hardness of mixed-alkali glasses has been shown to exhibit a moderate positive MAE.^{11,21,22}

Although the original observation of the MAE was thermomechanical, the effect is now perhaps best known for its orders-of-magnitude changes in DC electrical conductivity and ionic diffusivity.^{10,11} Jain et al.^{23,24} found that the activation energy for DC electrical conduction increases in mixed-alkali silicate glasses by almost a factor of 2; this leads to correspondingly large effects in the conductivities themselves, an effect noted across multiple glass systems.^{10,11,23–25} The MAE in conductivity diminishes with temperature and frequency of the applied field, however, suggesting that local

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72 motion is uninhibited but long-range motion is more difficult
73 in these systems.^{9–11,26}

74 The diffusivities of alkali ions exhibit a “crossover”, a
75 common occurrence in mixed-alkali glasses where the majority
76 ion may limit the diffusivity of the minority ion, drastically
77 reducing its mobility.^{10,11,23–25,27–29} Notably, cesium is a large
78 ion for which diffusion is rather difficult, yet there exists a
79 composition range in which the minority sodium ions are the
80 slower-diffusing cation species.²³ Day and Isard both also note
81 that the dielectric constant and loss are both significantly
82 diminished, in accordance with diminishing alkali mobili-
83 ties.^{10,11}

84 **Recent Experimental Results.** Greaves and Ngai³⁰ found via
85 X-ray absorption fine structure (XAFS) experiments that
86 alkalis in mixed-alkali silicate glasses do exhibit a tendency
87 toward local clustering, but those clusters generally appear to
88 be well-mixed in composition. They also suggest that alkali–
89 alkali interactions likely occur indirectly through differing
90 structural effects of each alkali.³⁰

91 Swenson et al.³¹ and Swenson and Adams³² conducted
92 neutron and X-ray diffraction experiments on mixed-alkali
93 phosphate glasses and used reverse Monte Carlo analysis to
94 determine the structure of those glasses. Glass structure *local* to
95 the alkali ions was largely unchanged between mixed- and
96 single-alkali glasses and alkalis were found to have mixed
97 randomly, supporting the conclusions of Greaves and
98 Ngai.^{30–32}

99 The far-infrared (FIR) spectroscopy of Kamitsos et al.³³
100 revealed that structural peaks associated with alkali-oxygen
101 bonds are shifted in mixed-alkali borate glasses relative to those
102 in single-alkali borate glasses. Large ion peaks decreased in
103 wavenumber and small ion peaks increased, suggesting that
104 small ion bonding is strengthened in mixed-alkali glasses. Large
105 ion bonding, by contrast, is weakened. Importantly, this study
106 found that the FIR spectra for mixed-alkali borate could not be
107 reproduced by any linear combination of single-alkali spectra.³³

108 Sen et al.³⁴ noted that ⁷Li and ²³Na spin–lattice relaxation
109 times (T_1) reach their minimum value at much higher
110 temperatures for mixed-alkali silicate glasses than for single-
111 alkali silicate glasses. They suggest that this is due to a smaller
112 effective number of hopping sites through which to diffuse.
113 This also increases the high-energy cutoff for the percolation
114 process responsible for DC conductivity.³⁴

115 Tomozawa and co-workers^{19,20,35} found that mixed alkali
116 glasses have large, negative enthalpies of mixing, which may be
117 explained by strong alkali–alkali interactions and local
118 ordering. This is consistent with the observed radius effects.
119 Stress formed in ion-exchanged glass alters this enthalpy of
120 mixing,³⁵ and may induce ordering in the glass.^{19,20} The
121 addition of alumina to mixed-alkali glasses effectively reduces
122 the prevalence of alkali–alkali interactions since alkalis are
123 “consumed” by charge compensating aluminum ions.²⁰

124 **Recent Computational Results.** Habasaki and Ngai³⁶
125 performed molecular dynamics simulations of mixed-alkali
126 silicates. It was shown that for a short time after a site is
127 vacated, alkali ions of one type do not enter the sites of the
128 other until sufficient relaxation has taken place. This work
129 found that stress from mismatched sites causes depressed ionic
130 conductivity in mixed-alkali glasses and results in greater
131 coupling of ionic motion behavior to the network for mixed-
132 versus single-alkali glasses. The study also noted that
133 cooperative jumps of more than one alkali ion were made
134 more difficult in mixed-alkali glasses.³⁶

Huang and Cormack^{37–39} performed molecular dynamics 135
on sodium, potassium, and sodium–potassium silicate glasses. 136
Their radial distribution functions show good agreement with 137
literature values and note alkali clustering with random mixing 138
of alkalis in accordance with the later experiments of Greaves 139
and Ngai.³⁰ They found that small ions bind more tightly, 140
though the majority ions exert some degree of control over the 141
glass structure. However, the overall site distributions for each 142
alkali in mixed-alkali glasses are narrower than in single-alkali 143
glasses, and their reported Si–O–Si bond angle distributions 144
exhibit significant bimodality compared to an expected additive 145
relation in mixed-alkali glasses. They argue that these results 146
support a conclusion later backed experimentally by Greaves 147
and Ngai; namely, that the MAE is largely structural in 148
origin.^{30,37–39} Yu et al. further confirmed the structural origins 149
of the MAE by performing molecular dynamics simulations of 150
mixed-alkali silicates as well, showing significant stress on the 151
constituent alkali ions (see the following section).⁴⁰ 152

Theoretical Models. Yu et al.⁴⁰ proposed local instabilities 153
as a possible origin of the MAE *vis-à-vis* the thermometer effect 154
and showed via molecular dynamics simulations a compressive 155
stress exerted by the glass network on the alkali contained 156
within.⁴¹ Taking into account the relatively high deformability 157
of the oxygen ion electron cloud discussed by Anderson and 158
Stuart,⁴² the presence of nontrivial structural deformation as a 159
result seems quite plausible. 160

This is supported by LaCourse,⁴³ who suggested that mixed- 161
alkali Si–O–Si bonds would be under strain, and again 162
considering the deformability of the oxygen electron cloud, this 163
deformation would increase in mixed-alkali glasses.^{29,42,43} 164
LaCourse also argued that ionic conductivity is well-modeled 165
by weak electrolyte and interstitial pair mechanisms. LaCourse 166
claimed a structural origin of the MAE in that ion motion is 167
site-specific, rather than path-specific, arguing that alkali ions 168
form their own environments and find it highly difficult to hop 169
to other alkali sites (“defect formation”).⁴³ 170

Bunde⁴⁴ and Ingram^{3,45} both build on a theory similar to 171
that of LaCourse. The dynamic structure model considers that 172
alkalis have individualized sites which relax to suit their 173
inhabitants. When the alkali leaves the site, the site retains 174
“memory” of that ion, making it difficult for ions of the other 175
type to hop into it. This means pathways for ion diffusion are 176
limited to sites of that ion type, and are dependent on 177
relaxation of those sites in order to form new diffusion 178
pathways.^{3,44,45} So-called “mixed defects”, an alkali sitting in an 179
unlike site, are increasingly less likely to form with increasing 180
size ratio, consistent with experiment.³ 181

For further information on the subject beyond the largely 182
modern scope of the preceding discussion, the reader is urged 183
to consult one of many other works which have also conducted 184
thorough review of the subject.^{2,3,10,11,35,43–47} 185

Stress and strain in the network forms a common thread 186
through much of the modern experimental and computational 187
literature and many recent theoretical models either rest upon 188
or predict such phenomena. This has been shown to have 189
significant effects on macroscopic glass properties in recent 190
work. Herein a theoretical model is proposed based on the 191
strained topological constraint model of Potter et al. and 192
quantitative results discussed.⁴⁸ 193

Background. Topological Constraint Theory. Topological 194
constraint theory^{49–51} has been employed to solve many 195
problems in the field of theoretical glass design.^{51–55} It has 196
successfully predicted the compositional dependence of 197

Vickers hardness,^{21,56–58} fragility, changes in heat capacity at the glass transition, and glass transition temperature (T_g).^{21,56–59} Using the energy landscape approach of Naumis and the Adam–Gibbs model,⁶⁰ Mauro et al. showed that the ratio of two glasses' configurational entropies S_c is equal to the ratio of their topological degrees of freedom f per atom as follows:^{53,54}

$$\frac{S_c[T_g(x_r), x_r]}{S_c[T_g(x), x]} = \frac{f[T_g(x_r), x_r]}{f[T_g(x), x]} \quad (1)$$

where x is some glass composition and the subscript r denotes a reference value. f is given by

$$f = d - n \quad (2)$$

where d is the dimensionality of the network and n is the number of constraints per atom. Since the systems in question are macro-scale oxide glasses, d is simply 3. As shown by Mauro and Gupta:^{53,54}

$$\frac{S_c[T_g(x_r), x_r]}{S_c[T_g(x), x]} = \frac{T_g(x)}{T_g(x_r)} \quad (3)$$

and hence, given the average number of constraints per atom (n), T_g may be expressed as

$$T_g(x) = \frac{(d - n[T_g(x_r), x_r])T_g(x_r)}{d - n[T_g(x), x]} \quad (4)$$

There are three types of constraints considered in this work.

- α : linear bond stretching constraints associated with N–O bonds in oxide glasses, where N is some network former
- β : angular bond bending constraints associated with the O–N–O bond angle
- γ : the angular bond bending constraint associated with the N–O–N bond angle

α and β constraints govern the shape of the rigid glass former polyhedra (e.g., SiO_2 tetrahedra), leaving the γ constraints to govern the coupling of those polyhedra. The onset temperature of a constraint is the characteristic temperature describing the floppy-to-rigid transition of that constraint. The γ constraint in silicate systems is of particular interest at low temperatures (up to and including the glass transition) due to its relatively low onset temperature, and is the primary focus of this study.^{48,51,53,54,61,62}

When the topologically predicted T_g would dip below the onset temperature, of the γ constraint (T_γ), as in high alkali-content silicate glasses, or rise above the formation temperature of the β constraint (T_β), as in lithium borates, the actual T_g becomes fixed at the onset temperature of the constraint.^{51,53,54,61,62} Potter et al. described the origin of the effect of water on T_g in silicate glasses using an extension of this model,⁴⁸ suggesting that the energy of a given constraint may be described by the following:

$$U_c = \frac{3}{2}k_B T_c \quad (5)$$

where U_c is the constraint potential energy of an associated constraint type c , T_c is the onset temperature for that constraint, and k_B is Boltzmann's constant. This constraint energy may be weakened or strengthened by interaction with

the local environment (e.g., by strain due to interstitial species).⁴⁸

MODEL

Under the Gupta-Cooper theory, alkali ions are usually considered to simply fill interstitial space between rigid polyhedra and convert bridging oxygens to nonbridging oxygens; this is assumed to be the case throughout this work.^{52,63} Any stress on the network from alkali must therefore act on the γ constraint, since α and β constraints only affect the geometry of individual polyhedra and not the interpolyhedra couplings. To analyze the change in the γ constraint, a silicate glass composition is utilized which has a predicted T_g below T_γ , thus ensuring $T_g = T_\gamma$ as per ref 48.

T_γ lies between 450 and 500 °C in binary silicate glasses, depending on which alkali modifier is present.⁴⁸ If internal stresses act on the γ constraint, a corresponding change in the T_g is expected in these alkali silicates, whereas if no internal stresses arise from the mixing of alkali (or for compositions not dominated by T_γ), T_g will not drop below T_γ .⁴⁸ This explains the minimal T_g MAE for low alkali-content silicate glasses found by Shelby.⁷ Equation 5 is used with both T_γ and eq 6 to express the strain energy per atom required for a depression in T_γ :

$$U_\epsilon = U_{\gamma 0} - U_\gamma = \frac{3}{2}k_B[T_{\gamma 0} - T_\gamma] \quad (6)$$

where $U_{\gamma 0}$ and $T_{\gamma 0}$ are the energy and onset temperature, respectively, of the unstrained γ constraint in the pure glass former and U_γ and T_γ are the energy and onset temperature, respectively, of the strained γ constraint in the modified glass. From above, since the predicted T_g for all glasses examined herein would be below T_γ , $T_g = T_\gamma$, and therefore

$$U_\epsilon = \frac{3}{2}k_B[T_{\gamma 0} - T_g] \quad (7)$$

A number of previous models have suggested that glass networks conform to the alkali species contained.^{3,30,42,43,46,47,64–67} It is suggested here that each alkali prefers some preferential distribution of angles between tetrahedron on the network and different species introduce strain due to the competing distributions. Considering that alkalies are located predominantly interstitially, it becomes clear that any strain from alkalies must occur in the γ constraint; that is, only the angle distribution between connected silica polyhedra should change. When this additional strain energy is modeled simplistically as spring-like, the onset temperature of the γ constraint is lowered according to the following relationship:

$$U_{\gamma 0} = U_\gamma + U_\epsilon = \frac{3}{2}k_B T_\gamma + \frac{1}{2}k(\Delta\theta)^2 \quad (8)$$

where k is the spring constant and $\Delta\theta$ is the change in the γ constraint angle.

METHODS

Experimental Section. Binary and ternary sodium–potassium silicate glasses were synthesized with nominal compositions $0.30(y\text{Na}_2\text{O} + [1 - y]\text{K}_2\text{O}) \cdot 0.70\text{SiO}_2$. Reagent-grade powders of sodium carbonate, potassium carbonate, and silica were thoroughly mixed in platinum crucibles in stoichiometric amounts. Samples were then melted in a preheated electric muffle furnace for 15 min at 1500 °C.

Postmelt weight loss was measured on an analytical balance after cooling. The melt was reheated at the original melt temperature for 5 min and then rapidly quenched via a twin-roller quench method to ensure homogeneity. The weight losses of all glasses were found to be in good agreement with prediction.

Quenched samples were then immediately powdered and analyzed in a PerkinElmer Diamond differential scanning calorimeter (DSC) using the following procedure:

1. Hold at 350 °C for 1 min.
2. Heat at 10 °C per minute to 590 °C.
3. Hold at 590 °C for 1 min.
4. Cool at 10 °C per minute to 350 °C.
5. Hold at 350 °C for 1 min.
6. Heat at 10 °C per minute to 590 °C.
7. Hold at 590 °C for 1 min.
8. Cool at 10 °C per minute to 350 °C.

This procedure was used to guarantee identical thermal treatments among samples and remove any internal stress remaining after the quench. Reported values were obtained from the second heating curve. Glass transition temperatures were determined using the onset method and are precise to 3 °C.

Computational. Molecular dynamics simulations were carried out using potentials from Wang et al.⁶⁸ using canonical ensembles of 3000 atoms with the composition $0.3[y\text{Na}_2\text{O} + (1 - y)\text{K}_2\text{O}] \cdot 0.7\text{SiO}_2$. Compositions with $y = 1$, $y = 0.75$, $y = 0.5$, $y = 0.25$, and $y = 0$ were tested. Atoms were randomly distributed in a box, the volume of which was fixed to correspond to the room-temperature density of the glass being tested.^{69–71} For intermediate compositions an additive density relation was used, as density has been shown to be relatively insensitive to mixed-alkali effects.^{7,10,11} Timesteps of 1 were used and long-range Coulombic interactions were computed using the Ewald method. Glass melts were initially held at a temperature of 3000 °C for 1000 ps, then quenched from 3000 to 2000 °C instantaneously in the *NVT* ensemble and allowed to equilibrate for a further 1000 ps as an *NPT* ensemble. Melts were then quenched to form glasses at a fixed rate of 1 K/ps to 300 K in the *NPT* ensemble. The final result is shown in Figure 1.

The strain in the Si–O–Si bond angle was calculated by subtracting the expected additive distribution from the real distributions found in simulation. The resulting distributions were smoothed using high-order polynomial fits, and the minimum and maximum were determined. The difference between the two was taken to be the angular strain. Angle distributions are shown in Figures 2 and 3.

RESULTS

Results from the experimental work are in good agreement with those from the literature and are shown in Table 1. Small deviations from the literature of less than 5 °C are reasonable, since different measurement apparatus (for example, Shelby used dilatometry and Poole used fiber-elongation viscometry) or thermal scan rates (Moynihan used a DSC scan rate of 20 °C per minute) are known to affect T_g . In accordance with literature results, the maximum deviation from additivity occurs when alkali are present in nearly equal amounts.^{5–8}

Atomic positions and molecular structures from molecular dynamics were recorded for a 10 ps increment at room temperature for each glass studied. Using atomic positions, Si–

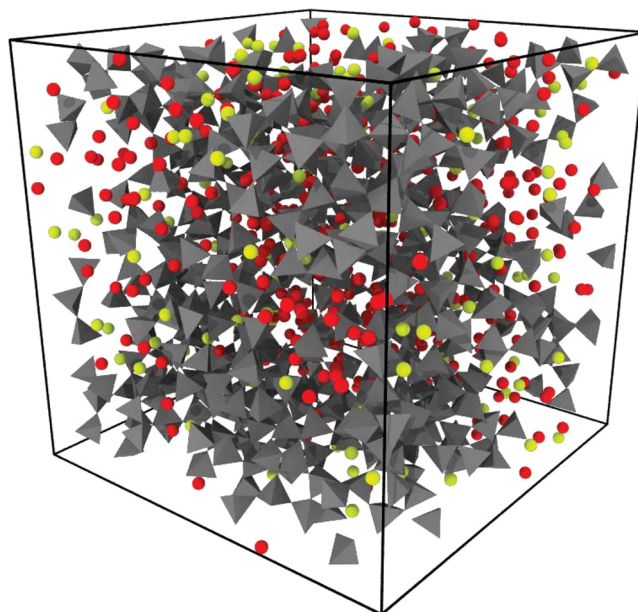


Figure 1. A simulated sodium–potassium silicate glass shown after quench ($y = 0.5$). Yellow and red atoms are sodium and potassium, respectively; silica tetrahedra are shown in gray.

O bond lengths (α constraint) and O–Si–O bonding angles (β constraint) were calculated. The respective distributions of the α and β constraints were observed to be identical across compositions, as shown in Figure 2. Si–O–Si bond angles (γ constraints) were also calculated, and display significant bimodality when compared with the additive distribution, as shown in Figure 3. These results are in excellent agreement with similar simulations performed by Huang et al., who reported an even greater degree of bimodality using a slower quench rate.^{37–39} This may also suggest that glasses with lower fictive temperatures may show the MAE to a greater extent, a conclusion also supported by the work of Soules and Busbey.

DISCUSSION

It is proposed that strain in the γ constraint is the major cause for deviations from additivity observed in macroscopic properties of mixed-alkali glasses. This strain has previously been shown to manifest itself experimentally as a drop in T_g in the T_g -dominated region.⁴⁸ The presence of network strain has been inferred experimentally from present DSC results and literature T_g values, and computationally from molecular dynamics simulations showing γ constraint angle distributions that are quite bimodal compared to the additive distribution, in agreement with Huang and Cormack.^{37–39} Constant α and β constraint values found in these simulations suggest that the altered γ constraint angle distributions must be due to strain in that constraint; this seems reasonable, as the γ constraint forms below T_g and is less able to relax due to the high viscosity in its formation range. The extent of bimodality has also been found to be roughly proportional to the degree of mixing in the samples.

Simulations indicate that alkali are distributed identically throughout the network regardless of the degree of mixing, as shown in Figure 4. However, considering the angular strain present in the network, it appears that each alkali species is able to “customize” its local environment to its particular size and shape. This suggests that the preferred site of one alkali

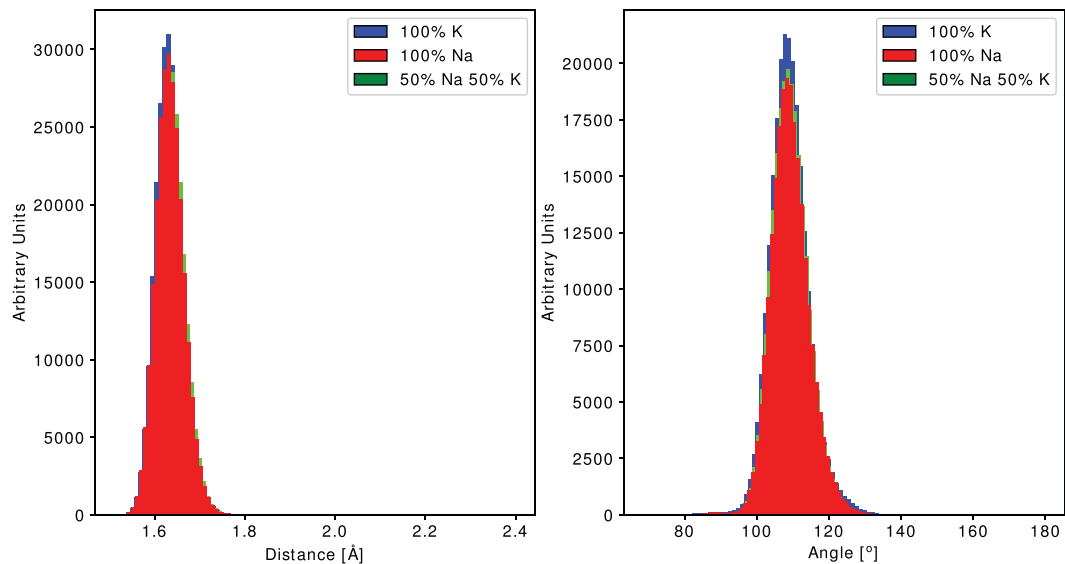


Figure 2. Left: Distribution of Si–O bond lengths (α constraint). Right: Distribution of O–Si–O bonding angles (β constraint).

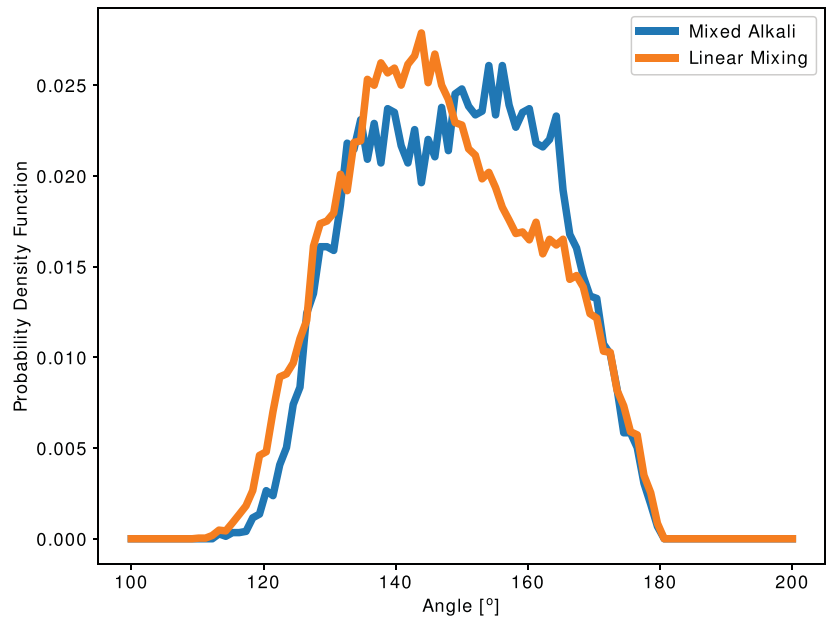


Figure 3. Expected (additive) and observed angle distributions for a simulated $0.3[y\text{Na}_2\text{O} + (1 - y)\text{K}_2\text{O}]\cdot 0.7\text{SiO}_2$ glass with $y = 0.5$. This same angle distribution disparity is also seen in simulations of other mixed alkali glasses.

Table 1. Experimental T_g for Synthesized Compositions Given in $^{\circ}\text{C}^a$

y	T_g ($^{\circ}\text{C}$)	Δ ($^{\circ}\text{C}$)
0	521	0
0.17	472	−40
0.33	442	−60
0.5	430	−63
0.67	433	−50
0.83	436	−38
1	465	0

^a Δ refers to the difference between the T_g which would be expected from additive mixing and that observed experimentally.

Here, it is considered that the reduced potential energy of the γ constraint is largely retained in the system as spring potential energy. Using this approximation, topological constraint theory and MD simulation data have been used to calculate an effective spring constant for the γ constraint. Using the average shift of bond angles from MD and the deviation of experimentally measured depressed glass transition temperatures from theoretical additive values at $y = 0.09$, a spring constant of $\frac{k}{k_b} \approx 0.52$ was obtained using an empirical fit. This empirical spring constant allows for the calculation of the predicted T_g of the tested systems, which shows excellent agreement with experimental data as seen in Figure 5.

Yu et al.^{40,41} found that alkali in simulated mixed-alkali silicate glasses experience significant stress from the surrounding network. The network therefore must experience a corresponding stress and resulting strain, distorting the

species puts the neighboring sites containing other alkali species under stress, and vice versa. This is in agreement with the experimental results of Greaves and Ngai.³⁰

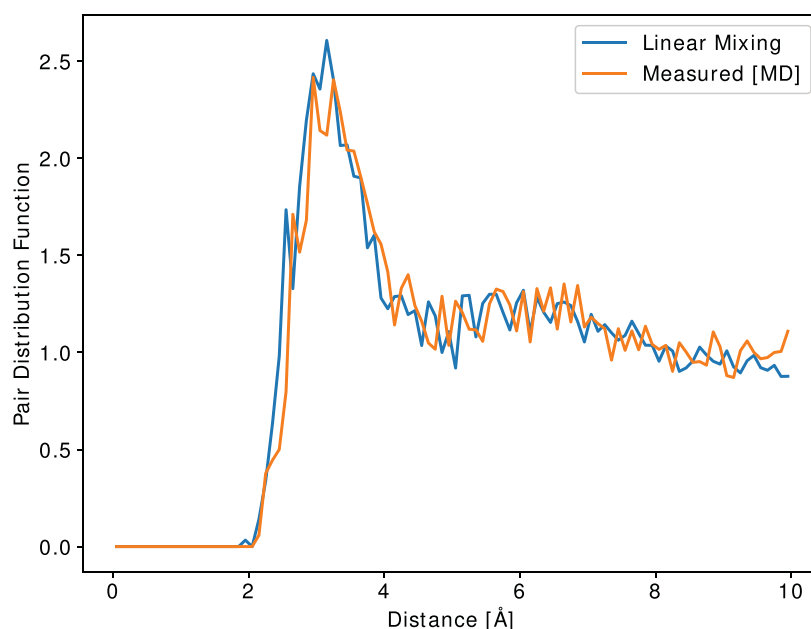


Figure 4. Alkali-alkali partial radial distribution functions (RDF) of a theoretical additive potassium-sodium silicate glass (the average RDF of two simulated binary glasses) and that of a simulated mixed-alkali glass.

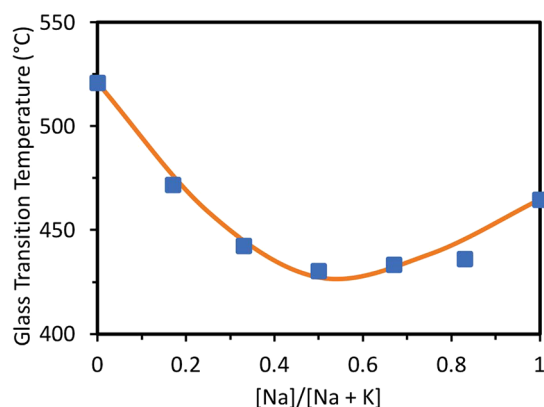


Figure 5. T_g versus sodium ion fraction for sodium-potassium silicates containing 30 mol % alkali. The orange line is the prediction from the shift in the angles calculated from simulations using $\frac{k}{k_B} = 0.09$ K and the points are present data from DSC measurements (error bars for experimental data are smaller than the points).

CONCLUSION

During quench, mixed-alkali glass interstices relax to better conform to the residing alkali. Interstices containing mismatched alkali species relax toward different ultimate structures, however, and the competition between these interstices results in stress on the network as observed in simulations by Yu et al.^{40,41} and predicted by ionic motion-based theoretical models.^{3,43,45} The network strain model described herein has been shown to have excellent quantitative agreement with experimental T_g and good qualitative agreement with a number of observations and models for the mixed-alkali effect.

The compositional dependence of constraint energies as a result of network strain as introduced by Potter et al.⁴⁸ is proposed as the mechanism responsible for the mixed alkali effect. New results for mixed-alkali silicate glass transition temperatures have been presented, as well as molecular dynamics simulations showing uniform alkali distributions, unmodified α and β constraints, and bimodal γ constraint distributions for mixed-alkali silicates as compared with binary alkali silicate glasses, all in good agreement with literature.^{30,37–39} Finally, experimental observations of the mixed alkali effect in the glass transition temperature have been explicated quantitatively in terms of a topological model with strained Si–O–Si bond angles.

The implications of this model on ionic conductivity are currently under investigation.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jcm426@psu.edu.

ORCID

Qiuju Zheng: 0000-0003-3785-1709

Mathieu Bauchy: 0000-0003-4600-0631

John C. Mauro: 0000-0002-4319-3530

Notes

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network, as observed in the presently reported bimodal (strained) γ constraint distribution. During quench, alkali-containing interstices relax to the minimal energy state for that alkali, but since the alkali distribution in mixed-alkali glasses is uniform (as shown by ref 30 and in Figure 4), nearby interstices containing alkali of different species relax in competition, resulting in strain on the network as inferred from^{40,41} above. This strain lowers the energy of the corresponding γ constraint and is analogous to that from molecular H₂O in hydrated glass as per ref 48 which showed that constraint energies are not constant throughout the entire composition range, resulting in the alteration of T_g and therefore T_g . The negative enthalpies of mixing observed by Lezzi and Tomozawa^{19,20} are well-explained by the competitive relaxation and opposing stresses described above, which results in an indirect attractive interaction and increased relaxation driving force for $T_f - T > 0$, as found by Yu et al.^{40,41}

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