INTRODUCTION

The mixed-alkali effect (MAE) is responsible for unexpected physical phenomena such as the “thermometer effect:” wherein soda-potash-lime silicate thermometers exhibit substantial structural relaxation following common laboratory temperature changes, that is, from boiling water to ice, which led the zero mark to be shifted in some cases by more than one degree Celsius (compared to single-alkali glasses showing only a tenth of degree rise).\(^1,2\) The MAE is typified by a deviation from linearity or the law of additivity (sometimes called Vegard’s law) for a property with respect to the molar ratio of two or more different alkalis, generally formulated as \(A/(A + B)\).\(^2,4\) Exploited since at least the 1820s for the enhanced chemical durability it imparts,\(^1\) the MAE has been the topic of numerous investigations. Nonetheless, a single atomistic model capable of predicting all observed physical phenomena of the MAE remains elusive.

Both static and dynamic properties exhibit the MAE, for example: ionic conductivity, elastic modulus, hardness, chemical durability, viscosity, thermal expansion, density, molar volume, and refractive index.\(^3,4\) The departure can be significant for dynamic properties, as is the case for ionic conductivity, where an increase of five orders of magnitude is possible, or it can be only slight (\(\leq \pm 10\%\)) such as for static properties like the density, molar volume, and refractive index. The deviations in mechanical properties and thermal expansion are generally of intermediate strength (MAE \(\leq \pm 20\%\)), perhaps reflecting that these macroscopic properties are combinations of static properties and dynamic processes.

Due to the strength of the departure from linearity in ionic conductivity, the following experimental and theoretical investigations focus on ionic transport in glass when attempting to evaluate and understand the effect of glass composition on the MAE. The magnitude of the MAE is positively correlated with the difference in size between the two alkalis (or, for
ions of differing valences, the difference in field strength), and also with the total amount of modifier in the glass.\textsuperscript{1,5-9} One common mechanistic explanation proposes that when a cation enters the empty, recently vacated site of a differently sized cation, more energy is required for the glass network to rearrange and accommodate the electrostatic field of the new foreign cation.\textsuperscript{10,11} It is thought that more opportunities for different cations to become trapped in ill-fitting configurations lead to a stronger MAE,\textsuperscript{12} thus, glass series with highly conducting single-alkali endmember compositions are expected to have generally larger deviations from linearity. Thus, generally glasses with more modifier and higher conductivity have stronger MAE.\textsuperscript{5,13,14} As Wright and Shelby\textsuperscript{14} point out, percolating ion channels, that is, phase separation, must form in order for the MAE to manifest in ionic conduction (<5 mol\% total alkali results in a maximum in the conductivity ($\sigma$), rather than a minimum).

Some axiomatic models of the MAE evaluate the importance of ion-ion interactions, for example, by the direct blocking of preferred ion channels by the frozen cation (called low-dimensional migration pathways in the random distribution model) or by the formation of immobile interstitial mixed-alkali pairs.\textsuperscript{15-20} One of the more recent papers uses MD simulations to demonstrate that the weak electrolyte assumption (that due to necessary ion-ion interactions only a small number of total ions are mobile) is not necessary to explain how the conductivity drastically decreases in the dilute foreign alkali region (only 1\%-2\% of other type cation) since the partial blockade of ion channels hinders mobility at a much larger distance than its nearest neighbor radius.\textsuperscript{17} On the other hand, the dynamic structure model (DSM) focusses on the interaction between the ions and the network, that is, how the mobile cations actively change the local structure of the glass (even below $T_g$) and how the time and energy required for relaxation leads to reduced ion conduction.\textsuperscript{21,22}

Interestingly, the same mechanism is thought to be valid whether the ion “hopping” occurs at dc or far-IR frequencies.\textsuperscript{23-25} Several papers have formalized this idea and added extra energy terms for changes in structural units\textsuperscript{15} or elastic strain energy.\textsuperscript{5,26} Although differing models have different mechanisms, many agree that as temperature increases, the magnitude of the MAE decreases, as the energy differences between cation sites become less important.\textsuperscript{20}

The authors have also searched for the structural origins of the MAE, sometimes finding that the single-alkali local structure is retained in the presence of the second ion,\textsuperscript{5,27,28} yet for other compositions, the modifier–oxide and former–oxide bond distances, amount of disorder and even cation coordination numbers depend on the alkali ratio.\textsuperscript{10,15,29,30} The local structural differences created by the additional types of cations are thought to result in increased structural heterogeneity,\textsuperscript{29} resulting in relaxation processes occurring at more than one rate and therefore via several processes. Structural effects may cause the reduction in unoccupied free volume observed in mixed-alkali glasses, where generally the minimum molar volume correlates with the maximum energy barrier for dynamic processes.\textsuperscript{5,31,32} Indeed, Dietzel argues that cations with different coordination numbers can in fact encourage better packing.\textsuperscript{8} One MD study proposes that even at low temperatures immediately near $T_g$ the mismatched cation and site produce local regions of compression and tension, which neutralize each other and relax stresses,\textsuperscript{33} as is observed phenomenologically even well below $T_g$ in the “thermometer effect.”

Many glass formers exhibit the MAE: phosphates, borates, germanates, aluminosilicates, and silicates are all known to deviate from the rule of mixtures,\textsuperscript{2,3} and it has also been shown that the MAE extends to other types of cations such as alkaline earth ions\textsuperscript{34} and perhaps even transition metals, like Ag$^+$ and Ti$^7$, as well\textsuperscript{2} (thus sometimes the more general term “mixed-mobile ion effect” is used\textsuperscript{35}). Even anions such as fluorine and chlorine have been known to interact with the MAE,\textsuperscript{35} or result in the mixed-anion (or mixed-former) effect, which generally has deviations in the opposite direction to the typical MAE.\textsuperscript{36}

Recently, ionic glasses have gained renewed interest as a distinct class of glasses as their existence challenges conventional glass formation theory.\textsuperscript{37} Due to their enhanced electrical conduction,\textsuperscript{38} unique relaxation and mechanical properties,\textsuperscript{39,40} and their ability to be compositionally tuned,\textsuperscript{41} ionic glasses are likely to be interesting for applications as well, in addition to their being of fundamental interest. Ionic glasses have been loosely defined as compositions with more modifier than former (so called invert glasses\textsuperscript{42}), where rather than the conventional, percolating 3d network, the glass is composed of small, individual, highly charged oxoanions, such as pyro- and orthophosphates ($P_2O_7^{4-}$ and $PO_4^{3-}$, respectively) compensated by newly important cross-linking cations. Although the MAE is well-known in network glasses with a sufficient amount of modifier (>10 mol\%),\textsuperscript{3} it is not known whether the same physical rules which govern the MAE hold when ionic interactions, rather than a phase-separated percolating covalent network and ion channels, dominate the structure.

In this study, we compare two glass families expected to have a high amount of ionic bonding: aluminofluorophosphate (FP) and aluminosulfatefluorophosphate (FPS) glasses. We also look at the MAE for two different cation pairs, Li–Na and K–Na, making a total of four glass series: two FP series: 70MPO$_3$–10M$_2$O–20AlF$_3$ (M = Li, Na) and 70MPO$_3$–10M$_2$O–20AlF$_3$ (M = K, Na), and two FPS series: 60MPO$_3$–20M$_2$SO$_4$–20AlF$_3$ (M = Li, Na) and 60MPO$_3$–20M$_2$SO$_4$–20AlF$_3$ (M = K, Na). We have chosen the alkali concentration per total atoms (M$^+$/atoms) to be constant for all compositions, as this is often a significant factor in determining ionic conduction, which is known to be correlated with the MAE. We chose two mixed-alkali series of each glass family, Li–Na and Na–K, to evaluate the importance of
cation size difference and to have multiple series to draw conclusions from. Between the two glass families, that is, with and without $\text{SO}_4^{2-}$, we compare the magnitude of the MAE and position of the maximum alkali molar fraction (defined as $[M]/[M + M']$). Both fluorine and $\text{SO}_4^{2-}$ bond more ionically, and as such enhance ionic conductivity by loosening the initial structure and reducing the binding energy between the charge carriers and glass matrix. Thus, from the high $\sigma$, we may expect the MAE to be large for dynamic properties in both series, however, especially so in sulfate-containing systems. Similarly, since hardness involves plasticity, it is expected to also have large deviations from linearity. Other properties, such as $T_g$, density and elastic moduli, which have smaller MAEs in general, are more difficult to predict.

2 | EXPERIMENTAL METHODS

2.1 | Sample preparation

In this study, we followed the glass formulation and melting protocols of previous reports on poly-anionic glasses of the FP(S) type. Two groups of phosphate glasses were investigated in the present study: aluminofluorophosphate (FP) and aluminosulfofluorophosphate (FPS) glasses, where each group contains two series of phosphate glasses, one Li–Na and one K–Na. Nominal molar compositions of FP glasses were $70\text{MPO}_3–10\text{M}_2\text{O}–20\text{AlF}_3$ ($M = \text{Li, Na}$) and $70\text{MPO}_3–10\text{M}_2\text{O}–20\text{AlF}_3$ ($M = \text{K, Na}$). Nominal molar compositions of FPS glasses were $60\text{MPO}_3–20\text{M}_2\text{SO}_4–20\text{AlF}_3$ ($M = \text{Li, Na}$) and $60\text{MPO}_3–20\text{M}_2\text{SO}_4–20\text{AlF}_3$ ($M = \text{K, Na}$). Before any glass melting, all reagents were dried at $95\degree\text{C}$ for at least 3 hours, and sometimes left overnight to dry; this was done not only to remove water for weighing but also because fluorine is known to react with water and leave the glass melt as HF gas. Batches of 80 g using raw materials of at least 97% purity ($\text{LiPO}_3$, $\text{KPO}_3$, $\text{NaPO}_3$, $\text{Na}_2\text{CO}_3$, $\text{Li}_2\text{CO}_3$, $\text{K}_2\text{CO}_3$, $\text{Na}_2\text{SO}_4$, $\text{Li}_2\text{SO}_4$, $\text{K}_2\text{SO}_4$, and $\text{AlF}_3$) were mixed in desired ratios and melted in Pt crucibles in a muffle furnace at $800\degree\text{C}–1100\degree\text{C}$ for 1.5 hours (melting temperatures and alkali molar ratios of $[\text{Li}]/[\text{Na} + \text{Li}]$ and $[\text{K}]/[\text{Na} + \text{K}]$ ratios are given in Table 1). The melting was all done in the same furnace and within 2 weeks of each other for each series.

During melting, the main difference was that the melting temperature of lithium-containing phosphate glasses was higher than the potassium-containing phosphate glasses. After melting, the melts of FP glasses were poured into a preheated graphite moulds and then annealed at $310\degree\text{C} – 390\degree\text{C}$ for 3 hours before cooling to room temperature. Among the FP glasses, only the pure lithium FP glass was prepared through rapid quenching by pouring the melt onto cold copper plate and immediate pressing with another copper stamp. Because of their poor glass forming ability, all FPS glasses were obtained by quenching. Subsequently, annealing of these

| Series                      | [Li]/[Na + Li] ratios or [K]/[Na + K] ratios | Synthesis condition (°C) | Annealing condition (°C) |
|-----------------------------|---------------------------------------------|---------------------------|--------------------------|
| Li–Na FP glasses            |                                             |                           |                          |
| [Li]/[Na + Li] = 0          | 850°C 40 min                                | 350°C 3 h                 |                          |
| [Li]/[Na + Li] = 0.25       | 850°C 30 min 900°C 1 h                      | 370°C 3 h                 |                          |
| [Li]/[Na + Li] = 0.5        | 850°C 30 min 900°C 1 h                      | 370°C 3 h                 |                          |
| [Li]/[Na + Li] = 0.75       | 850°C 30 min 900°C 1 h                      | 370°C 3 h                 |                          |
| [Li]/[Na + Li] = 1          | 950°C 30 min 1000°C 1 h                     | 380°C 3 h                 |                          |
| K–Na FP glasses            |                                             |                           |                          |
| [K]/[Na + K] = 0            | 850°C 40 min                                | 350°C 3 h                 |                          |
| [K]/[Na + K] = 0.25         | 800°C 40 min                                | 340°C 3 h                 |                          |
| [K]/[Na + K] = 0.5          | 800°C 40 min                                | 340°C 3 h                 |                          |
| [K]/[Na + K] = 0.75         | 800°C 40 min                                | 340°C 3 h                 |                          |
| [K]/[Na + K] = 1            | 750°C 40 min                                | 310°C 3 h                 |                          |

| Li–Na FPS glasses           |                                             |                           |                          |
| [Li]/[Na + Li] = 0          | 850°C 30 min 900°C 1 h                      | 370°C 3 h                 |                          |
| [Li]/[Na + Li] = 0.25       | 950°C 1 h 1000°C 30 min                    | 380°C 3 h                 |                          |
| [Li]/[Na + Li] = 0.5        | 950°C 1 h 1000°C 1 h                       | 380°C 3 h                 |                          |
| [Li]/[Na + Li] = 0.75       | 1000°C 1 h 1050°C 30 min                   | 390°C 3 h                 |                          |
| [Li]/[Na + Li] = 1          | 1000°C 1 h 1100°C 30 min                   | 390°C 3 h                 |                          |

| K–Na FPS glasses           |                                             |                           |                          |
| [K]/[Na + K] = 0            | 850°C 30 min 900°C 1 h                      | 370°C 3 h                 |                          |
| [K]/[Na + K] = 0.25         | 850°C 30 min 900°C 1 h                      | 370°C 3 h                 |                          |
| [K]/[Na + K] = 0.5          | 850°C 30 min 900°C 1 h                      | 370°C 3 h                 |                          |
| [K]/[Na + K] = 0.75         | 950°C 1 h 1000°C 30 min                    | 380°C 3 h                 |                          |
| [K]/[Na + K] = 1            | 1000°C 1 h 1050°C 30 min                   | 380°C 3 h                 |                          |

| Li–Na FPS glasses           |                                             |                           |                          |
| [Li]/[Na + Li] = 0          | 850°C 30 min 900°C 1 h                      | 370°C 3 h                 |                          |
| [Li]/[Na + Li] = 0.25       | 850°C 30 min 900°C 1 h                      | 370°C 3 h                 |                          |
| [Li]/[Na + Li] = 0.5        | 850°C 30 min 900°C 1 h                      | 370°C 3 h                 |                          |
| [Li]/[Na + Li] = 0.75       | 950°C 1 h 1000°C 30 min                    | 380°C 3 h                 |                          |
| [Li]/[Na + Li] = 1          | 1000°C 1 h 1050°C 30 min                   | 380°C 3 h                 |                          |

| K–Na FPS glasses           |                                             |                           |                          |
| [K]/[Na + K] = 0            | 850°C 30 min 900°C 1 h                      | 370°C 3 h                 |                          |
| [K]/[Na + K] = 0.25         | 850°C 30 min 900°C 1 h                      | 370°C 3 h                 |                          |
| [K]/[Na + K] = 0.5          | 850°C 30 min 900°C 1 h                      | 370°C 3 h                 |                          |
| [K]/[Na + K] = 0.75         | 950°C 1 h 1000°C 30 min                    | 380°C 3 h                 |                          |
| [K]/[Na + K] = 1            | 1000°C 1 h 1050°C 30 min                   | 380°C 3 h                 |                          |

TABLE 1 Compositions and melting conditions of FP and FPS glasses
quenching samples followed the same procedure as casting samples. After annealing, the glass samples which were obtained through casting were cut down to thicknesses of 1 and 2 mm, then two parallel sides were polished (using a final grit of 2400 sandpaper) for further spectroscopic and mechanical analyses. For the quenched samples of FPS glasses and pure lithium FP glass, the obtained plates were polished directly without further cutting.

The introduction of AlF$_3$ and Al$_2$O$_3$ decreased the glasses’ vulnerability to water attack, thus, only the high potassium content FPS glasses showed any signs of degradation, for example, a white cloudy surface. The FPS [K]/[Na + K] = 0.75 and 1 samples surfaces became cloudy over time and needed to be repolished before further measurements. Since the cloudy layer was removed successfully, we do not believe water to be a major contributor to the results.

### 2.2 Analysis of the glass compositions

Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX, JSM-7001F) was carried out on the samples at 15 to 20 keV. Before the measurements, each sample was mounted in epoxy resin and polished to a relatively flat surface for analysis. Then all specimens were coated with carbon on the surface to make the specimens conductive. We measured three points for each sample to analyze the real composition. Unfortunately, EDX is not the most suitable technique for light elements such as lithium (unmeasurable by this technique) nor fluorine and aluminum, which would be expected to have the highest error. Accurate fluorine content analysis is a continued problem in glass science: fluorine is known to have large errors in EDX analyses (both because aluminum is over-represented and the detection limit of fluorine appears to be greater than 2 mol%).\(^47\) In previously measured samples, we found the measured fluorine content to vary by up to 5 mol% for the same sample, likely depending on the efficacy of the carbon coating.

The compositional analysis results are shown in Tables 2 and 3 for the Li–Na and K–Na FP series respectively, and in Tables 4 and 5 for the Li–Na and K–Na FPS series, respectively. As expected, there was significant fluorine loss due to HF gas being formed and evaporated, especially in the sulfate-containing compositions which required higher melting temperatures and/or longer melting times (see Table 1). Nonetheless, the [F]/[Al] content remains relatively constant throughout each individual series (70NaPO$_3$–10Na$_2$O–20AlF$_3$, or 0Li in Table 2 being an exception), and therefore, in our opinion, the fluorine loss is consistent and our reported compositions are acceptable for comparing the MAE between each series.

In Tables 2-5, the M$_2$O, P$_2$O$_5$, Al, and SO$_3$ ratios are also consistent: [Na]/[former] or [Na]/[Na + K] is considered to be equivalent to the M$_2$O content for the lithium- and potassium-containing series, respectively, while [AlF$_3$ + AlO$_3$/2] is simply equal to the atom% of Al measured by EDX (we do not accurately know the chemical environment of Al). We believe the limitations of EDX to preclude highly accurate quantification of oxygen and fluorine, so we have excluded those values when calculating M$_2$O, P$_2$O$_5$, Al, and SO$_3$ ratios in Table 2-5. Two compositions do not have consistent element ratios: the high Li-containing of the Li–Na FPS series lost a significant amount of sulfate (Table 4). Higher melting temperatures were needed for samples containing Li, thus, we are not surprised that some chemical components were lost during melting. Interestingly, studies have shown that alkali sulfates can undergo both vaporization and decomposition from both the solid and molten forms, and the dominant process depends on the alkali: higher field strength cations shift the equilibrium toward decomposition.\(^48,49\) Thus, we conclude that higher melting temperatures greatly exacerbated the decomposition of Li$_2$SO$_4$ from our glass melts. Since it is uniquely possible that molecular K$_2$SO$_4$ can leave the glass, this may be the reason for lower sulfate and [K]/[K + Na] for high K$_2$SO$_4$ compositions in Table 5.

Generally, the alkali ratio, for example, [K]/[K + Na], follows the expected trends (however, in the case of Li-containing glasses, only [Na]/[former] could be calculated in Tables 2 and 4). There are some differences between the nominal alkali molar ratio and the analyzed one, however, we do not know the amount of lithium, only the [Na]/[former], and so we have decided to use the nominal alkali ratios for the remainder of the investigation.
Finally, in Tables 2-5, the average error refers to the precision error of replicate measurements: generally, it was 0.2-0.5 at% for all elements with [Al] having the smallest error and [O] having the largest error. In most cases, the propagated error was < 1 mol%, but in four compositions, one replicate of the set had a higher than expected [O], leading to a 3 mol% error for some of the reported elements. Although the absolute precision error for these measurements was consistent with the others, elements with low concentrations, such as fluorine, had larger relative errors.

2.3 | Density measurements

The glass density was measured at room temperature with the Archimedes method using ethanol as the immersion liquid. Each sample was measured three times. The accuracy of the measurements was approximately ±0.001 g/cm³.

2.4 | Mechanical properties

2.4.1 | Sonography

The elastic properties of FP and FPS glasses were determined by ultrasonic echography on polished glasses samples. The longitudinal $C_L$ and transversal $C_T$ sound velocities were recorded at frequencies of 8-12 MHz with an Echometer 1077 (Karl Deutsch GmbH & Co. KG). Different coupling liquids were required to measure $C_L$ (gel) and $C_T$ (honey). Each sample was tested three times. It was difficult to obtain a stable $C_T$ signal on some samples.
where the thickness was less than 1 mm, and those samples required several measurements.

2.4.2 | Nano-indentation

Nano-indentation measurements were taken through instrumented indentation (G200, Agilent Inc) on polished samples, under ambient air and constant humidity (~35%) conditions. Due to the low hardness of phosphate glasses, we used lowest force available (98.12 mN) for the measurements. Each sample was indented 20 times. The K–Na FPS glasses readily absorb water because of the high humidity. In order to obtain accurate results, we measured this series two times; before the second measurements, we repolished the surface of the high-K specimens. A high-resolution microscope (Smart Proof 5, Zeiss) was used to capture the images of sample surface after nano-indentation experiments. The size of each indentation was determined by the software Image-J. We repeated the indentation size measurements of the Li–Na series by Image-J for the purpose of getting reliable data; the results were similar between the two replicates.

2.5 | Impedance spectroscopy

Well-polished glass samples with a flat surface of roughly 1-2 cm² (area was measured three times for each sample by Image-J) and a thickness of around 1 mm were prepared for impedance spectroscopy by sputtering a thin gold layer on both sides. The impedance measurements were performed on a Novocontrol Alpha-A spectrometer paired with a Novotherm Temperature Control System. The frequency range covered was from 10⁻¹ to 10⁷ Hz and temperatures from 50°C to 250°C with intervals of 50°C were measured. Any problems with the data collection, such as observation of two half circles during the measurement, were solved by washing. Any problems with the data collection, such as observation of two half circles during the measurement, were solved by washing with acetone as well as repolishing with 2400 grit sandpaper. It is suspected that glue from previous measurements or surface roughness caused this issue.

The resistance under direct current (\(R_{\text{DC}}\)) was determined as the right end of the half circle of the Nyquist plot (ie, a plot of the real and imaginary part of the impedance: \(Z'\) vs \(Z''\)). The conductivity (\(\sigma\)) was calculated as:

\[
\sigma = \frac{1}{R_{\text{DC}}} \frac{l}{A}
\]

where \(l\) is the thickness of the sample and \(A\) is the area of the sample.

The temperature dependency of the ionic conductivity was described by the Arrhenius relation:

\[
\sigma T = \sigma_0 \exp \left( -\frac{E_a}{K_B T} \right),
\]

where \(\sigma_0\) is the prefactor, \(K_B\) is the Boltzmann constant and \(E_a\) is the activation energy of the ionic conductivity.

2.6 | Glass transition temperature

Glass transition temperatures (\(T_g\)) were measured by differential scanning calorimetry (Netzch STA 449 F3 Jupiter); all measurements were performed using Al pans under a controlled N₂ atmosphere (flow rate = 20 mL/min) at a heating rate of 20 K/min up to 450°C. The midpoint temperature of the endothermic event was taken to be the \(T_g\) value, however, no difference in the reported trends was observed when the onset temperature was used instead (only a shift in the value by 5°C-10°C).

3 | RESULTS

In this study, we often discuss the magnitude or strength of the MAE for a given compositional series. Conceptually, it is the maximum difference between the experimental data and the ideal additivity line drawn between the endmember compositions. For a given alkali ratio, \(x\), we can calculate the ideal property value, \(P_{[x]}^{\text{add}}\), using the properties of the endmembers, \(P[0]\) and \(P[1]\), using the law of additivity (or Vegard’s law):

\[
P_{[x]}^{\text{add}} = xP[0] + (1 - x)P[1].
\]

Now the % deviation from linearity can be quantified for each experimental value \(P[x]\):

\[
\%\text{deviation} = 100\frac{P[x] - P_{[x]}^{\text{add}}}{P_{[x]}^{\text{add}}}. \tag{2}
\]

In the following Figures, the maximum deviation for each property was calculated using Equations 1 and 2, and the exact value can be found under each Figure. This allows us to semiquantitatively discuss differences in the magnitude of the MAE, however, the lines drawn on the Figures are simple second-order polynomial fits of the experimental data; they are only guides for the eyes to allow the reader to quickly observe the direction and magnitude of the MAE.

3.1 | Density and molar volume

There is some debate whether density should follow a linear relationship with composition for even a single-alkali glass: in glasses, most properties do not actually follow the rule of mixtures, and density is often no different. However, several authors found a linear change in density and that it should follow Vegard’s law. The values of and trends
in the density (Figure 1A) are similar for the mixed Li–Na FP (shown in black) and FPS (red) series. Other studies of the MAE have reported small deviations from linearity for density, ≤ ±5%, thus, the positive deviations here are normal. The densities of the mixed K–Na FP and FPS series (Figure 1B) also show very similar behaviors; it is interesting that both series show a decrease in density despite increasing K₂O content.

To gain more information about the glasses’ packing densities, which greatly influence mechanical properties, the molar volume, \( V_m \), was calculated using the compositions determined from EDX in Section 2.2. The molar volume of Li–Na FP and FPS series (Figure 1C) shows different trends, as the FPS series trendline is translated downwards and has a much clearer MAE. Unfortunately, based on the EDX results, the high Li-containing samples have less sulfate than the other glasses in the Li–Na FPS series, and thus we would expect additional sulfate to decrease the \( V_m \) more, and make the trend more linear, so it is difficult to comment on the MAE of the Li–Na \( V_m \).

The decrease in density with increasing K₂O content results in a large increase in molar volume as sodium is replaced with potassium in both the K–Na FP and FPS series (Figure 1D). Once again, the FPS series has significantly lower molar volume than the corresponding FP series; although the sulfate content is more constant in the K–Na

**FIGURE 1** Comparison of density and molar volume for mixed Li–Na and K–Na FP (black) and FPS (red) series. Lines are second-order polynomial fits and guides to the eye only. A, Density of mixed Li–Na FP and FPS series; maximum deviation from linearity is 0.03 g/cm³ (1%) and 0.07 g/cm³ (3%) for FP and FPS series, respectively. B, Density of mixed K–Na FP and FPS series; maximum deviation from linearity is 0.02 g/cm³ (0.8%) and 0.03 g/cm³ (1.1%) for FP and FPS series, respectively. C, \( V_m \) of mixed Li–Na FP and FPS series. Line represents ideal additivity. Maximum deviation from linearity is −1.13 cm³/mol (−4%) and −0.9 g/cm³ (−3%) for FP and FPS series, respectively. D, \( V_m \) of mixed K–Na FP and FPS series. Line represents ideal additivity. Maximum deviation from linearity is −0.13 cm³/mol (−0.3%) and −0.6 g/cm³ (−2%) for FP and FPS series, respectively. Maximum % deviation is calculated using Equations 1 and 2 in Section 3. [Color figure can be viewed at wileyonlinelibrary.com]
FPS series, the difference between the FP and FPS series is highest for the K endmember. Finally, the $V_m$ for the FPS series has a small negative deviation, which may be significant over such a large range of $V_m$ values (from 33-45 cm$^3$/mol). Overall, sulfate reduces the $V_m$ significantly; the MAE is small for the static properties measured, and may be larger for the FPS series.

### 3.2 Ionic conductivity

Comparison of conductivity as function of temperature between the FP and FPS series (Figure 2A,B vs Figure 2C,D, respectively) shows that the addition of sulfate increased the conductivity of Na$^+$ significantly, from $10^{-9}$ in Figure 2A ($x = 0$) to $10^{-7}$ in Figure 2C ($x = 0$). Interestingly, we do not see the same jump in the conductivity of the lithium endmember upon sulfate addition (perhaps reflecting less sulfate in these compositions). Furthermore, sulfate content shows minimal effects on the conductivity of the K endmember of the FP vs FPS series.

The MAE is known to manifest most strongly in ionic conductivity (several orders of magnitude decrease for mixed vs single cation composition). As expected, the conductivity decreases with cation mixing in both the Li–Na FP and FPS series. In the FP series, there is a three to seven orders of magnitude decrease for the respective Na- or Li-only endmember, while the FPS series shows roughly a $10^{-4}$ decrease for the mixed compositions compared to either the Li- or Na-only conductivity. The conductivity is so low for the mixed K–Na series that our instrument is incapable of measuring the conductivity reliably at low temperatures; thus, many points at
50°C, 75°C, and 100°C are missing from Figure 2B,D. If we compare the conductivity at 125°C in the K–Na FP and FPS series it can be seen that both show roughly a $10^{-2}$ decrease in ionic conductivity compared to the pure K endmember. The main difference is that the minimum is much more asymmetric and shifted toward the less mobile ion. All four series follow expected trends: the MAE decreases as temperature increases, and the minimum in $\sigma$ shifts toward the less mobile cation.

The Arrhenius plots of the Li–Na FP and FPS series can be found in Figure 3A,B and C,D respectively. All of the $Z'$ vs $Z''$ plots were fit well with single semicircles. Despite choosing the glass series to have similar [Na]/[atom] ratios, addition of sulfate is expected to make the glass generally more conductive. Indeed, the activation energies of the Li–Na FP and FPS series plotted in Figure 4A show that sulfate increases the conductivity and MAE. The FPS series has lower $E_a$ for the single-alkali endmembers compared with the corresponding compositions in the FP series; conversely, the mixed-alkali FPS compositions have higher $E_a$ than the FP mixed compositions, revealing that sulfate increases the MAE.

The $E_a$ for the K–Na FP and FPS series in Figure 4B follows a different trend than that of the Li–Na series; here the sulfate does not increase the conductivity for the pure potassium FPS endmember composition. Moreover, unlike the Li–Na series, the MAE is equal or even less pronounced for the FPS series compared with the FP series for the K–Na...
mixture. Finally, all four series have their maximum in $E_a$ shifted toward the less mobile ion.

### 3.3 HARDNESS

The manifestation of the MAE in mechanical properties is substantially less studied than that in ionic conductivity; likely due to the much larger deviation from linearity in $\sigma$, but also in part because the underlying physical mechanism understood to affect the conductivity is more difficult to apply to mechanical properties. The MAE in ionic conduction can be easily rationalized in terms of foreign ions blocking the preferred ion channels and/or extra energy required for the structural relaxation of newly occupied cation sites. This model translates well to the MAE in hardness, where reduced plasticity or slippage along the ion channels in mixed-alkali systems results in less permanent deformation. Specifically, other investigations observed less pileup at the indent edge for mixed-alkali compositions. Hardness depends on both plastic flow and densification, however, the MAE in hardness has been found to still be present despite having a linear trend in packing density (and therefore likely densification ratio), emphasizing the importance of structural heterogeneity and superstructural cohesion. Our $V_m$ trends for both the expected and analyzed compositions do not have a large MAE present (Figure 1C,D), thus, we also believe our MAE in hardness to mainly be the result of plastic flow reduction.

In the case of our glass systems, the presence of sulfate decreases hardness for the FPS Na-endmember in Figure 5A,B ($x = 0$ for both Figures), while having little effect on the FPS Li-endmember. Nonetheless, the mixed Li–Na FPS series have a markedly increased MAE compared to the FP series. In the case of the FPS K endmember (Figure 5B), sulfate addition appears to make the glass much softer compared to the FP K endmember composition. The MAE is not discernible in the hardness of the K–Na FP series in Figure 5B, however, the trend is mostly linear, reflecting that perhaps there is not a large reduction in plastic flow for these mixed compositions. On the other hand, the K–Na FPS series exhibits a much larger MAE than the FP series. Overall, it appears that for the both alkali mixtures (Li–Na and K–Na) the addition of sulfate greatly decreases the hardness of the single-alkali compositions and the presence of more than one type of cation “returns” the hardness to a value equal to that of a FP composition without sulfate. Since the deviation from linearity is heavily dependent on the endmember compositions, this produces a markedly stronger MAE in the FPS glasses.

### 3.4 Elastic moduli

Figure 6A-D and Figure 7A-D display the four elastic moduli: Young's modulus, Poisson ratio, bulk modulus, and shear modulus ($E$, $\nu$, $K$, and $G$, respectively) of the FP and FPS series for both Li–Na and K–Na mixtures. The most striking result is simply that the MAE for all elastic moduli (except the bulk modulus) is much more pronounced in the FPS series compared to the FP series. The deviations from linearity in elastic moduli found in literature are generally small, roughly ±10% of the ideal mixture value. In a comparison of Li–Na in silicate, phosphate and borate glasses, the bulk modulus had the least

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**FIGURE 4** A, Activation energy of mixed Li–Na FP (black) and FPS (red) series. Maximum deviation from linearity is 0.32 eV (31%) and 0.42 eV (64%) for FP and FPS series, respectively. B, Activation energy of mixed K–Na FP (black) and FPS (red) series. Maximum deviation from linearity is 0.48 eV (37%) and 0.37 eV (45%) for FP and FPS series, respectively. Lines are second-order polynomial fits and guides to the eye only. Maximum % deviation is calculated using Equations 1 and 2 in Section 3 [Color figure can be viewed at wileyonlinelibrary.com]
clear deviation (it was sometimes positive and sometimes negative), while the shear modulus had the largest, clearly positive, MAE. This agrees perfectly with the trends in the FP series (black line), with the largest negative deviation from additivity being in bulk modulus (Li–Na) with the deviation sometimes also being positive (Figure 7A,B). Moreover, the largest positive deviation for the FP series is in the shear modulus (K–Na) in Figure 7D. Finally, unlike the ionic conductivity, the maximum deviation is generally shifted toward the more mobile ion, especially in $E$ and $G$.

The MAE in the FPS series follows similar trends, it appears in similar directions, but the magnitude is markedly higher with the average deviation being 20%-30% and the maximum MAE in $G$ for the K–Na FPS series is 66%. The addition of sulfate in the single-alkali case results in a lowered $E$ and $G$, while it has the opposite effect on $\nu$ and $K$ (the bulk modulus of the FPS Li-endmember being the only exception). Although all elastic moduli are related to the bond dissociation energy of the material through the bond strength and bond density, the Poisson ratio and bulk modulus have been found to be more strongly correlated to molar volume and packing density.\textsuperscript{57,58} In the case of Young’s and shear moduli, the bond strength or bonding type, such as directional vs ionic bonding is expected to be more strongly determinant. Since sulfate lowers network connectivity and increases the packing density, as seen from the lower molar volume for FPS glasses in Figure 1C,D, it follows that $\nu$ and $K$ would increase, while $E$ and $G$ would decrease with its addition. Like in the ionic conductivity, the difference between the single-alkali endmember with and without sulfate enhances the magnitude of the MAE. Once again, it appears the presence of the MAE “returns” the mechanical properties of the FPS mixed compositions to those of the corresponding FP glasses. Nonetheless, the mechanical properties of the mixed-alkali FPS glasses are still often above or below the values for the FP glasses, perhaps indicating a further effect.

### 3.5 Glass transition temperature

Due to their interesting electrical and mechanical properties, we also wanted to investigate the thermal properties of these mixed-alkali series. The thermal behavior of mixed-alkali glasses has been debated, with several authors reporting no significant deviation from additivity in heat capacity or structural relaxation data\textsuperscript{59-61} or, in the case of Shelby, pointing out that similar nonlinear behaviors occur in mixed-former glasses without any alkali added.\textsuperscript{62} Nonetheless, those authors\textsuperscript{59-62} and others\textsuperscript{63,64} have reported a significant deviation in $T_g$ values for mixed-alkali glasses, and many older papers discuss a decrease of one to two orders of magnitude in viscosity.\textsuperscript{4,65} In contrast to structural studies which report only linear changes in the structure of mixed-alkali glasses,\textsuperscript{5,27,28} this substantial decrease in $T_g$ has been related to an increase in the number of NBOs and a change in the coordination number of the cations\textsuperscript{63,66}—clear structural modifications that might be expected to have manifestations in the relaxation behavior.

![Figure 5](wileyonlinelibrary.com)
Consequently, to properly investigate this question for these glasses, more in-depth thermal behavior measurements and structural studies would be required.

Therefore, for this investigation, we wish to comment only on how the $T_g$ changes as function of sulfate content, that is, by comparing FP and FPS, for the two alkali mixtures Li–Na and K–Na. In both Figure 8A,B the $T_g$ of the sulfate-containing endmember compositions are higher than those of the FP endmember compositions (high-Li FPS is an exception again; likely due to lower sulfate content, see Table 4), and like the other properties (ionic conductivity, elastic moduli and hardness), this leads to a larger MAE for the mixed FPS compositions. This is especially clear in Figure 8B, where K–Na FP (black) has a diminished MAE, while equal parts K–Na FPS (red) has a much larger negative deviation. It is striking that the sulfate addition increases the $T_g$, despite lowering the energy of many of the dynamic processes, yet since the deviation in $T_g$ is negative, this allows the FPS series again to have a larger MAE than the FP series. It suggests that the underlying cause of the MAE trends in the other dynamic properties is the same for the thermal properties.

4 | DISCUSSION

As glass scientists, we are always looking to relate physical properties to glass structure. In our FP and FPS series, despite having the same mixture of cations, the magnitude...
and “shape” of the MAE differs between glass formers, and we therefore know that the interaction between ion and glass network plays an inherent role in the MAE. Many glass formers exhibit the MAE: phosphates, borates, germanates, aluminosilicates, and silicates are all known to deviate from the rule of mixtures. However, the magnitude and exact manifestation of the MAE depends on the glass former; for example the coordination change in germanates produces a much different trend than silicates.\textsuperscript{5} Comparative studies of the MAE in silicates and aluminosilicates have suggested that the reduced number of NBOs following aluminum addition is responsible for a higher MAE,\textsuperscript{15,67} and that this results in a reduction in the required configurational changes (i.e., increased cooperativity) and lower activation energies for ion migration.\textsuperscript{15} On the other hand, the introduction of Al\textsubscript{2}O\textsubscript{3} into phosphate glass drastically decreases the MAE of ionic conduction until it nearly disappears, yet the conductivity of the single-alkali glasses remains mostly unaffected.\textsuperscript{68}

The molecular structures of the current glass systems, sodium aluminofluorophosphate and sulfoaluminofluorophosphate, have been investigated by us and others.\textsuperscript{69-71} We note that when fluorine is added as AlF\textsubscript{3}, it is exclusively bonded to the network through Al–F and P–F bonds without
any Na-F moieties; thus, fluorine is not expected to contribute significantly to the ion conduction. Although the Al$_2$O$_3$ to AlF$_3$ ratios have some variation between glass series (Tables 2-5), we believe Al–O–P bonding to be as important as Al–F bonding in determining the glass behavior. The two glass families, 70MPO$_3$–10M$_2$O–20AlF$_3$ and 60MPO$_3$–20M$_2$SO$_4$–20AlF$_3$, have only small differences in the [Al]/[P] ratio (~15%), and the [M]/[atom] ratio is nearly equal across all compositions (generally the number of charge carriers or cations, M, per atom is correlated with ionic conductivity). Therefore, the differences in the MAE between the two families should mostly be the result of sulfate replacing phosphate: a purely ionic anion replacing an anion capable of forming a conventional directional glass network.

SO$_4^{2-}$ largely does not interact with the phosphate network; instead it remains as pseudo-Q$^0$ units interacting with the glass structure through cations only. SO$_4^{2-}$ is known to remain as an isolated ion without creating any bridging oxide bonds to the glass network, as such it results in a large number of nonbridging oxygens in the network, and ionic conductivity has been shown to be proportional to the concentration of SO$_4^{2-}$. Interestingly, sulfate has a very similar ionic volume and polarizability to PO$_4^{3-}$, perhaps allowing the two anions to mix well and preventing large-scale phase separation, that is, formation of sulfate-rich and phosphate-rich regions, from occurring.

Thus, since we know the sulfate forms a more ionic structure, akin to “interacting balls of charge,” we understand the reason why the FPS series has lower molar volume and higher packing density compared to the FP series (Section 3.1). For the same reason, that is, the added ionic bonding, we can rationalize the higher conductivity or lower $E_a$ (Section 3.2) observed for single-alkali endmembers of the FPS series. Consequently, the generally higher MAE in the ionic conductivity for the FPS series can be explained mostly by the endmembers having substantially higher conductivity or lower $E_a$. A similar line of thinking could also be applied to those properties involving plastic flow (such as hardness), or even infinitesimal mechanical perturbations, that is, the elastic moduli (possibly due to the relationship with $V_m$ and packing density). In almost all properties the MAE in the FPS series results in moduli that are equal or greater/lesser (depending on the direction of the MAE) to those of the corresponding FP series; it appears as though the MAE nullifies the contribution of the sulfate to the glass property, or in some cases reverses the effect of sulfate addition to obtain said greater/lesser values.

Although discussions about the MAE often focus on ionic conductivity, we wish to focus more on the uniquely large MAE in the mechanical properties of our glass series. The following discussion focuses on the reduced ion mobility in the ion channels of mixed-alkali glasses, which result in reduced plasticity and higher resistance to shear forces or “slippage along the lines of NBO atoms.” Furthermore, ionic migration is believed to help relax applied stresses. Overall, this leads to mixed-alkali compositions having less ductility, which is clear in Figure 9, which relates the shear to bulk modulus ratio ($G/K$) to fracture behavior. Specifically, it demonstrates that only single-alkali FPS compositions

**Figure 8** A, Glass transition temperature (measured by DSC) for mixed Li–Na FP (black) and FPS (red) series. Maximum deviation from linearity is −36°C (−10%) and −47°C (−13%) for FP and FPS series, respectively. B, Glass transition temperature for mixed K–Na FP (black) and FPS (red) series. Maximum deviation from linearity is −25°C (−8%) and −44°C (−12%) for FP and FPS series, respectively. Lines are second-order polynomial fits and guides to the eye only. Maximum % deviation is calculated using Equations 1 and 2 in Section 3 [Color figure can be viewed at wileyonlinelibrary.com]
have ductile behavior \((G/K\text{ ratio} < 0.43)\), while all other glass compositions, including mixed-alkali FPS compositions, have brittle behavior \((G/K\text{ ratio} > 0.43)\).

The difference in fracture behavior highlights the unique plasticity mechanism present in the FPS endmembers. We believe it to be a result of the extra degrees of freedom possessed by the sulfate anion. Figure 10A,B show a schematic representation of the structure wherein the sulfate can freely rotate in single-alkali glasses, while Figure 10C demonstrates that in a mixed-alkali structure rotational freedom is impeded by the neighboring interstices being occupied by two types of cations. In Figure 10 we have chosen to represent sulfate rotation, but this is likely the least important degree of freedom with respect to the mechanical properties, it is simply the easiest to visualize in two dimensions.

As discussed earlier, the crisscrossing of two different types of ion channels leads to reduced plasticity which immobilizes the sulfate and removes its added degrees of freedom. This helps explain why the endmember FPS compositions have substantially lower \(E_a\) and lower hardness compared to both the endmember FP compositions and the mixed-alkali FPS compositions. Similarly, this effect would result in a generally stronger MAE for the FPS series over the FP series. Thus, we may conclude that if a glass composition has higher plasticity in the network or anionic portion of the glass, it will likely also have a larger deviation from linearity in its mechanical properties; the reduction in plasticity of the modifiers is transferred to all of the other glass components. However, this is only relevant if some of the other glass components are mobile in the first place. On the other hand, the restrictions on the alkali mobility created by the aluminophosphate network may be a requirement as well: in order to produce this immobilization, the cations must have a stationary network to become trapped against. This immobilization effect is perhaps difficult to observe in other glasses since as the network percolation decreases, that is, more mobile \(\text{PO}_4^{3-}\) and \(\text{P}_2\text{O}_7^{4-}\) groups are formed, there is a concomitant increase in the number of modifying cations. Indeed, the MAE is known to increase when more NBOs are formed. Thus, one normally cannot deconvolute these two factors, and a case where a network-forming anion can be traded for a nonnetworking forming anion (such as here) is required.

The MAE can be related to plastic flow, but its manifestation in elastic or static properties is generally weaker; the substantially larger MAE for the elastic moduli of the FPS series (Figures 6 and 7) compared to the FP series is unexpected, and is the most challenging to understand. We might expect the static properties and/or bonding of the network structure to adapt to the presence of more than one type of modifier.

In our case, there is only a slight increase in the MAE of density and \(V_m\) for the FPS series compared to the FP

![FIGURE 9](https://example.com)  
**FIGURE 9** Fracture behavior as correlated with shear/bulk moduli ratio. A \((G/K\text{ ratio} < 0.43)\) indicates intrinsic plasticity as observed in metallic glasses, while most oxide glasses have a \((G/K\text{ ratio} > 0.43)\) and possess brittle fracture behavior. [Color figure can be viewed at wileyonlinelibrary.com]
series (the high Li content compositions for the Li–Na FPS are ignored). It is common to report large deviations from linearity for dynamic properties without any similar trends in static properties; so much so, that Dietzel\textsuperscript{8} wrote an entire paper on the subject. He used a simple spring and ball model to demonstrate that dynamic properties can change greatly, while density remains relatively constant: he posits that the more covalent bond of the smaller radius cation becomes shorter, while that of the larger cation increases in length. The summation of the shortening and lengthening of the two different M\textsuperscript{+}∙∙O\textsuperscript{−} bonds leads to nearly zero change in density for the mixed-alkali compositions.

Perhaps this strengthening of Li\textsuperscript{+}∙∙O\textsuperscript{−} or Na\textsuperscript{+}∙∙O\textsuperscript{−} bonds in Li–Na or K–Na FPS glasses has a disproportionally large effect on the mechanical properties, while the weakening of the more ionic (Na\textsuperscript{+} or K\textsuperscript{+}) M\textsuperscript{+}∙∙O\textsuperscript{−} bond is less vital. Elastic moduli which depend on network connectivity, that is, bond constraints, will generally equate one ionic bond with another of less equal strength, a small decrease in covalency is negligible. However, as bonds approach more directionality, a small increase in covalency results in a disproportionally large increase in mobility restriction. We would expect these types of changes to influence the elastic part, that is, the bottom, of a potential well and may be responsible for the MAE in elastic properties in general.

Even if Dietzel's and others supposition that some M\textsuperscript{+}∙∙O\textsuperscript{−} bonds lengthen and others shorten is correct,\textsuperscript{8} we are still left with the question of why the MAE is much stronger for the elastic properties in the FPS series. Perhaps the mobility of sulfate helps each cation find its preferred site, and this allows the MAE in dynamic and mechanical properties to be stronger. The sulfate may allow ionic preferences to play more of a role, and permit this bond lengthening and shortening to occur to a greater extent throughout the glass structure.

To further answer this question, we look to the unified site relaxation model\textsuperscript{23,73} to explain how the elastic part of a potential well can be affected by the MAE. The model assumes that an effective potential has two components: a site-specific potential and a Coulomb “cage.” An ion hop from one site to another “like” site still includes an energy term for rearrangement, but the energy mismatch is low, yet in the case of an ion hop from one site to a different site, the mismatch energy is even higher (due to difference in site-specific potential). The mismatch determines the success rate of the ion hops, with the hop frequency being observed as the intensity of the mechanical loss peaks. In Figure 11, we extend a similar line of thinking to the sulfate anion: we imagine that in single-alkali compositions the potential well for sulfate mobility is roughly equivalent in all directions (represented by a 8-pointed star in Figure 11A,B). However, in Figure 11C, when more than one type of alkali is present, there is a large energy mismatch between the potential wells of the different sulfate configurations, preventing its rotation. Importantly, the depth and shape of the energy wells for the sulfate are greatly affected by the presence of two different ions, affecting the elastic moduli as well.

Although there are clearer correlations between mechanical properties and ionic conductivity (ie, strain energy), the connection between viscosity and ionic conductivity is less established: both are both dynamic properties, but as stated before, several authors believe the MAE to be only unique to ion transport properties, and not thermal properties.\textsuperscript{59,60,62} Thus, it is not immediately clear how the electrical, mechanical, and thermal trends are related for the MAE. However, if one reconsiders the “thermometer effect,” where structural relaxation is observed to happen at temperatures much below \(T_g\), MD simulation results have suggested that cation mixing makes local compressive and tensile stresses which encourage structural rearrangements.\textsuperscript{33} Then, based on the \(T_g\) trends (Figure 8) we can conclude that mixed FPS glasses will contain higher stresses than their single-alkali FPS counterparts, which allows structural relaxation associated with the \(T_g\) to occur at lower temperatures. Similarly, single-alkali FPS glasses will have the lowest stresses of all glasses studied, and
have the highest $T_g$. We believe that the hindered structural rearrangement of the sulfate anion may magnify the compression and tension; these higher compressive and tensile stresses appear to be correlated with reduced ionic mobility as well as stiffer, harder, and more brittle (Figure 9) material behavior. Finally, this interpretation is also in-line with our explanation of the MAE in elastic properties: the mismatched cationic site potentials which create the stresses also hinder the extra degrees of freedom of the sulfate as shown in Figure 11. Thus, we believe the temperature or energy at which the structural relaxation occurs to have a correlation with the MAE observed in mechanical and ion transport properties.

5 | CONCLUSION

When the MAE in aluminofluorophosphate (FP) and aluminosulfofluorophosphate (FPS) glasses was compared, it was found that the deviation from additivity was almost always larger for the sulfate-containing glasses. This was rationalized in terms of the increased ionicity and degrees of freedom introduced from the sulfate anion, which is not able to bond to the aluminophosphate backbone. The increased mobility may be responsible for the lower molar volume of the FPS compositions; however, no large differences between the MAE of static properties in FP and FPS glasses were observed.

Nonetheless, the other properties studied made it clear that in glasses with larger amounts of plasticity, such as those including sulfate, the MAE is stronger. For the single-alkali FPS compositions, these extra degrees of freedom manifest as higher conductivity, lower $E_a$ and hardness, decreased shear and Young’s moduli and increased Poisson’s ratio. Since the endmember compositions of the FPS series are significantly different to those of the FP series, this results in a magnified MAE. In almost all of the properties examined, the mixed compositions of the FPS series have properties at least equal to those of the corresponding FP series, indicating that the mobility of the sulfate is nullified by the MAE. This is relatively easy to reconcile with the general understanding of the origins of the MAE, where ion hopping, plasticity, and/or slippage is reduced along ion pathways translates to immobilizing the sulfate ion as well.

However, it becomes harder when attempting to understand the MAE in elastic moduli; instead the cumulative potential energy well (Coulombic interaction and site-specific energy) of the sulfate anion demonstrates that the elastic minimum of a rotation can also be affected by the presence of a second cation. The thermal trends confirm the magnified mismatch in potential wells of the cations, manifested by regions of higher compressive and tensile stresses, and a larger negative deviation from additivity in $T_g$ for the FPS series.

Overall, the replacement of a network-forming phosphate tetrahedra by a pseudo $Q^0$ sulfate ion, incapable of bonding to the aluminophosphate backbone, creates a unique situation where the influence of the amount of NBOs and ionic bonding can be separated. Since the extra degrees of freedom imparted by the ionicity of the sulfate are grossly hindered by the already present MAE, the MAE strength increases, but at the same time, the already present MAE necessitates a relatively immobile and constrained glass network.

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