



# Correlation Between Ionic Mobility and Plastic Flow Events in NaPO<sub>3</sub>-NaCl-Na<sub>2</sub>SO<sub>4</sub> Glasses

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We report on the evolution of the mechanical and electrical properties of sodium metaphosphate glasses with addition of sodium sulfate or sodium chloride. The addition of these two sodium salts converts the medium-range order of our glasses from 2D phosphate chains to a mixed 1D + 2D network similar to ionic glasses, while the short-range order of the phosphate units remains unaffected. Replacing the phosphate units by chloride ion monotonically decreases the glass transition temperature, but enhances the Young's modulus and moderately increases the ionic conductivity. On the other hand, the sulfate group decreases the glass transition temperature as well, though the Young's modulus remains constant, while the ionic conductivity strongly increases. The changes in conductivity are related to the enhancement of the ionic mobility in these glasses, which in turn affect the size and distribution of the plastic events taking place during indentation-driven deformation.

**Keywords:** phosphate glasses, nanoindentation, shear transformation zones, impedance spectroscopy, ionic mobility

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## INTRODUCTION

Unlike silicate and borosilicate glasses, phosphate glasses are mainly explored for specialty applications, such as laser gain media, hermetic seals, nuclear waste immobilization, and biomaterials (Brow, 2000). Another potential application is their use as solid electrolytes for ion-conducting solid state batteries (Jun et al., 1990; Kim et al., 2015) due to their high ionic conductivity at room temperature ranging from 10<sup>-5</sup> to 10<sup>-3</sup> S.cm<sup>-1</sup> (Martin and Angell, 1986). For the latter, it has been observed that further significant enhancement can be achieved by the dissolution of ionic salts such as halides, sulfides, and sulfates into the glassy matrix (Martin, 1991). However, the mechanism of incorporation is not the same for all salts; usually sulfide and fluoride salts depolymerize the phosphate chain backbone by reacting with the bridging oxygens to form chain terminating P-F or P-S bonds (Brow et al., 1992; Cutroni et al., 1992; Saunders et al., 1996; Kartini et al., 2004), while the other halides and sulfates occupy the interstitial spaces in-between the phosphate chains, increasing the inter-chain spacing and keeping the short-range structure largely untouched (Malugani et al., 1982; Scotti et al., 1992; Kartini et al., 2002; Da et al., 2011; Sirotkin et al., 2012; Kabi and Ghosh, 2014; Möncke et al., 2014; Thieme et al., 2015; Le et al., 2017). Therefore, sulfate/halide-phosphate glassy systems are convenient model systems to study

how changes in the bonding and geometry of the first coordination shell of the modifier ions impact the ensemble's properties.

Selecting the  $\text{NaPO}_3\text{-NaCl-Na}_2\text{SO}_4$  ternary system is convenient since both the  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  anions occupy the free volume available between the phosphate chains as they are incorporated into the glass network, while leaving the phosphate chains largely intact. These glasses also allow for a comparison between the behavior of  $\text{Na}^+$  cations when only coordinated by non-bridging oxygens or when in a mixed halide and oxyanion environment, thus providing an interesting control group to whether the mechanical and electrical properties are more sensitive to changes in the overall packing density (where both the  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  should behave similarly, when taking their respective sizes into account) or to the chemistry of the anions coordinating the cationic modifier (where the  $\text{NaPO}_3$  and the sulfate bearing glasses should be comparable, while the sodium chloride glasses should behave differently).

## MATERIALS AND METHODS

Glasses with nominal compositions of  $(100-x)\text{NaPO}_3\text{-}x\text{NaCl}$  and  $(100-x)\text{NaPO}_3\text{-(}x/2\text{)Na}_2\text{SO}_4$  with  $x = 0, 10, 20, 30, 40, 50$  were prepared from mixtures of reagent grade  $(\text{NH}_4)_2\text{HPO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{NaCl}$  (Sigma Aldrich, purity > 99%) in the appropriate proportions. The powder mixtures were homogenized in a mortar and melted in  $\text{Al}_2\text{O}_3$  crucibles for 1 h at 1,000 K. Melt droplets were splat-quenched between two stainless steel plates and several disks of about 1 mm thickness and 10 mm diameter were produced from each glass melt. The resulting quenched glasses were homogeneous, colorless, and transparent, with the exception of the  $50\text{NaPO}_3\text{-}50\text{NaCl}$  sample, which fully crystallized during casting. The density  $\rho$  of the as-prepared glasses was determined by the Archimedes' method in distilled water and via He pycnometry (Quantachrome Ultrapyc 1200e, Anton Paar GmbH). The glass transition temperature  $T_g$  was determined from the onset of the endothermic event observed in the differential scanning calorimetry (DSC, Netzsch STA 499F1). All DSC measurements were performed in a flowing  $\text{N}_2$  atmosphere at a constant heating rate of 20 K/min using powdered samples of 20 mg mounted in platinum crucibles. Except for the thermal analysis, all experiments were carried out in laboratory air under ambient conditions.

The elastic properties were analyzed using a piezoelectric transducer operating at frequencies of 8 to 12 MHz (Echometer 1077, Karl Deutsch GmbH & Co KG). Values of the longitudinal  $c_L$  and transversal  $c_T$  sound wave velocities were derived from the corresponding sound wave propagation times and the exact thickness of the co-planar, optically-polished glass plates. On that basis the shear  $G$ , bulk  $K$ , and Young's moduli  $E$  as well as the Poisson's ratio  $\nu$  were calculated by means of the following equations:

$$G = \rho c_T^2 \quad (1)$$

$$K = \rho \left( c_L^2 - \frac{4}{3} c_T^2 \right) \quad (2)$$

$$E = \rho \left[ \frac{3c_L^2 - 4c_T^2}{(c_L/c_T)^2 - 1} \right] \quad (3)$$

$$\nu = \frac{c_L^2 - 2c_T^2}{2(c_L^2 - c_T^2)} \quad (4)$$

The mechanical properties were further analyzed through instrumented indentation testing using a nanoindenter (G200, Agilent Inc.), equipped with a three-sided Berkovich diamond indenter tip (Synton-MDP Inc.), and operating in the continuous stiffness measurement mode (CSM). The tip area function and instruments frame compliance were calibrated prior to the first experiments on a fused silica reference glass sample of known elastic properties (Corning Code 7980, Corning Inc.). On every glass specimen, 15 indentations with a maximum penetration depth of  $h = 2 \mu\text{m}$  were created at a constant strain-rate of  $\dot{\epsilon} = 0.05 \text{ s}^{-1}$  (defined as the loading rate  $dP/dt$  divided by the actual load  $P$ ). The load-displacement curves recorded by the nanoindenter were subsequently analyzed following the method proposed by Oliver and Pharr (1992), where the hardness  $H$  is estimated from the load divided by the projected contact area of the indenter tip  $A_c$ :

$$H = \frac{P}{A_c} \quad (5)$$

and the values of  $E$  are derived from the combined elastic response of the diamond indenter used ( $E_i = 1,141 \text{ GPa}$ ,  $\nu_i = 0.07$ ) and the material tested (Johnson, 1985):

$$E = (1 - \nu^2) \left[ \frac{1}{E_r} - \frac{1 - \nu_i^2}{E_i} \right]^{-1} \quad (6)$$

with the reduced elastic modulus  $E_r$  (Pharr et al., 1992):

$$E_r = \frac{S}{2} \sqrt{\frac{\pi}{A_c}} \quad (7)$$

Here, the parameter  $S$  denotes the contact stiffness as determined from the slope of the load-displacement curve at the onset of unloading. By operating in the CSM mode, the contact stiffness (or harmonic stiffness) can be recorded also during the monotonic load increase, which allows for the parallel determination of  $E$  and  $H$  as a function of the indenter displacement (Li and Bhushan, 2002; Pharr et al., 2009). For this purpose, the continuously increasing load-displacement signal was superimposed by a small oscillation of the indenter tip ( $f = 45 \text{ Hz}$ ,  $\Delta h = 2 \text{ nm}$ ). The values of  $E$  and  $H$  were finally averaged between the upper 10% and lower 20% of each indentation depth profile.

The strain-rate sensitivity  $m$  was analyzed in nanoindentation strain-rate jump test, as described in detail elsewhere (Limbach et al., 2014). On each glass specimen, ten strain-rate jump tests with strain-rates of 0.05; 0.007; and  $0.001 \text{ s}^{-1}$  (in descending order) were performed, and the values of  $m$  were derived from

the slope of the logarithmic plot of the hardness against the indentation strain-rate  $\dot{\epsilon}_i$  [defined as the displacement rate  $dh/dt$  divided by the total penetration depth (Shen et al., 2012)]:

$$m = \frac{\partial \ln H}{\partial \ln \dot{\epsilon}_i} \quad (8)$$

where  $\dot{\epsilon}_i = \dot{\epsilon}/2$  for materials with a depth-independent hardness value (Lucas and Oliver, 1999). The thermal drift rates are below  $0.05 \text{ s}^{-1}$  for the nanoindentation experiments. To avoid possible interactions between the residual stress fields, adjacent indentations were spaced by distances of  $50 \mu\text{m}$  (Hay, 2009).

A structural analysis was carried out by Raman spectroscopy. Raman spectra were collected in the range of  $150$  to  $1,300 \text{ cm}^{-1}$ , using a  $488 \text{ nm}$  Ar-laser as excitation source (Renishaw in Via Raman microscope). Each spectra was averaged over 20 consecutive measurements, corrected for baseline and thermal population (Shuker and Gammon, 1970) and normalized by the intensity of the peak at  $\sim 1,140 \text{ cm}^{-1}$ .

The ionic conductivity was analyzed by impedance spectroscopy (Novocontrol Alpha-A analyzer and a Novotherm Temperature Control System), in the frequency range from  $10^{-1}$  to  $10^6 \text{ Hz}$  and at temperatures between  $303$  and  $423 \text{ K}$ . A thin gold layer was deposited on the surface of each sample by means of a sputtering system (Anatech Hummer 10.2), operating for  $300 \text{ s}$  at an average current of  $20 \text{ mA}$ . In order to extract the glass properties from the experimental data, the setup was modeled with a single parallel RC element representing the bulk glass as an ideal solid electrolyte (Hodge et al., 1976; Almond and West, 1983) in series with a constant-phase element (CPE) representing the gold electrodes (Barsoukov and Macdonald, 2005). The total impedance of this circuit is given by Barsoukov and Macdonald (2005), Lvovich (2012):

$$\begin{aligned} Z^*(\omega) &= Z' + i \cdot Z'' \\ &= Z_{RC}^* + Z_{CPE}^* = \frac{R - i \cdot \omega \cdot R^2 \cdot C}{1 + (\omega \cdot R \cdot C)^2} + \frac{1}{Q \cdot (i \cdot \omega)^\alpha} \end{aligned} \quad (9)$$

where  $i$  is the imaginary number,  $\omega = 2\pi f$  is the angular frequency,  $R$  and  $C$  are the parameters of the RC element, and  $Q$  and  $\alpha$  are the CPE parameters. From Equation (9), the dc conductivity  $\sigma_{dc}$  of each sample can be evaluated by:

$$\sigma_{dc} = \frac{1}{R} \cdot \frac{l}{A} \quad (10)$$

where  $l$  and  $A$  are the sample thickness and area, respectively. The temperature dependence of the conductivity is given by the Arrhenius-scaling of both the number of effective charge carriers  $n(T)$  and the frequency of successful atomic hops  $\Gamma(T)$  (Tuller et al., 1980; Hairetdinov et al., 1994; Rodrigues et al., 2011):

$$\sigma_{dc} \cdot T = \sigma_0 \cdot \exp\left(-\frac{E_\sigma}{RT}\right) \quad (11)$$

$$n(T) = n_c \cdot \exp\left(-\frac{E_n}{2 \cdot R \cdot T}\right) \quad (12)$$

$$\Gamma(T) = \Gamma_0 \cdot \exp\left(-\frac{E_m}{R \cdot T}\right) \quad (13)$$

where  $\sigma_0$  is the conductivity pre-exponential term,  $n_c$  is the number density of ions,  $\Gamma_0$  is the attempt frequency,  $R$  is the universal gas constant, and the parameters  $E_\sigma$ ,  $E_n$ , and  $E_m$  are the activation energies of conductivity, charge carrier creation, and mobility, respectively. The activation energies are related via the following equation (Souquet, 1981; Ngai and Moynihan, 1998; Bandara and Mellander, 2011; Rodrigues et al., 2019):

$$E_\sigma = E_m + \frac{E_n}{2} \quad (14)$$

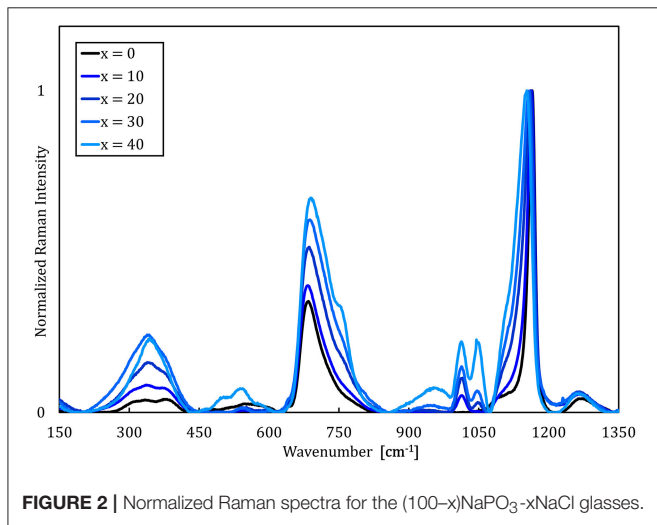
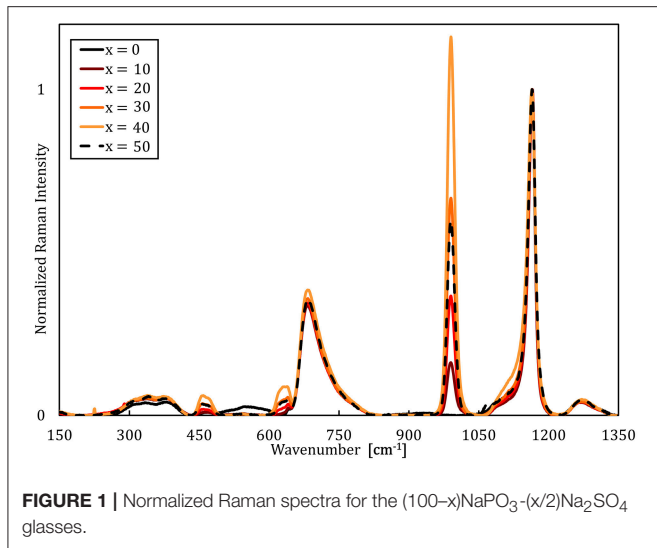
## RESULTS

### Raman Spectroscopy

Raman spectra of the  $\text{NaPO}_3$ - $\text{Na}_2\text{SO}_4$  and  $\text{NaPO}_3$ - $\text{NaCl}$  glasses (Figures 1, 2, respectively) show that the phosphate network is generally unaffected by the addition of  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$ , as the main features at approximately  $680$  and  $1,140 \text{ cm}^{-1}$  [associated with the symmetric stretching modes  $\nu_s(\text{P-O-P})$  and  $\nu_s(\text{PO}_2)$  of  $\text{Q}^2$  species, respectively (Hudgens et al., 1998; Velli et al., 2005; Konidakis et al., 2011)], remain relatively unchanged. In the Raman spectra of the  $\text{NaPO}_3$ - $\text{Na}_2\text{SO}_4$  glasses in Figure 1, the appearance of a peak at  $\sim 1,000 \text{ cm}^{-1}$  is assigned to the symmetric stretching  $\nu_s(\text{SO}_4^{2-})$  (Da et al., 2011; Thieme et al., 2015) and it increases in intensity with increasing  $\text{Na}_2\text{SO}_4$  concentration. The spectra of the  $\text{NaPO}_3$ - $\text{NaCl}$  glasses (Figure 2) are more complex. A slight shift of the  $\nu_s(\text{Q}^2)$  to lower wavenumbers is observed with increasing  $\text{NaCl}$  content, in conjunction with the appearance of shoulders at  $\sim 1,100$  and  $\sim 750 \text{ cm}^{-1}$ , consistent with the phosphorus tetrahedron and bridging oxygen symmetric stretching vibrations of the  $\text{Q}^1$  unit (Da et al., 2011; Thieme et al., 2015; Kapoor et al., 2017). The vibrations at  $\sim 1,000$  and  $1,050 \text{ cm}^{-1}$  can be assigned to chain-terminating  $\text{Q}^1$  units (Brow et al., 1995; Brow, 2000; Da et al., 2011), while the broad envelope centered at around  $340 \text{ cm}^{-1}$  is due to network bending vibrations (Brow et al., 1995; Hudgens et al., 1998; Velli et al., 2005). These observations indicate that the addition of  $\text{NaCl}$  progressively depolymerizes the glass network, forming shorter phosphate chains, which is in accordance with previous observations from MD simulations of  $\text{LiPO}_3$ - $\text{LiCl}$  glasses (Rao and Seshasayee, 2004). However, earlier studies have revealed that metaphosphate glasses are in general characterized by low degrees of network polymerization, with the reported average chain size of  $\text{NaPO}_3$  glasses ranging from 3.5 to 9 phosphate units (Westman and Gartaganis, 1957; Brow, 2000). Considering that the  $\text{NaPO}_3$  glass presently investigated already consists of relatively small chains, the effect of depolymerisation is assumed to be of secondary importance.

### Thermal and Mechanical Characterization

Selected physical properties of the  $\text{NaPO}_3$ - $\text{Na}_2\text{SO}_4$  and  $\text{NaPO}_3$ - $\text{NaCl}$  glasses examined in this study are listed in Tables 1, 2,



respectively. As expected, the addition of Na<sub>2</sub>SO<sub>4</sub> and NaCl leads to a decrease in both the glass transition temperature (Figure 3) and molar volume, illustrating the overall weakening of the glass network and the more efficient packing due to the presence of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> groups occupying the interstitial spaces in-between the phosphate chains, similar to the effect of AgI in AgPO<sub>3</sub> glasses (Novita et al., 2009; Rodrigues and Wondraczek, 2013; Limbach et al., 2014). The mechanical properties show very different compositional trends (Figures 4, 5): the addition of Na<sub>2</sub>SO<sub>4</sub> leads to a slight decrease of the Young's modulus, while the strain-rate sensitivity and Poisson's ratio remain almost constant; on the other hand, the addition of NaCl induces a significant increase in the Young's modulus, while the strain-rate sensitivity decreases and the Poisson's ratio remains almost the same within the limits of error.

According to the elastic models of glass-forming liquids (Dyre, 2006), the instantaneous elastic properties measured at laboratory time-scales can be used as probes for the individual

TABLE 1 | Physical properties of the (100-x)NaPO<sub>3</sub>-(x/2)Na<sub>2</sub>SO<sub>4</sub> glasses.

Sample	T <sub>g</sub> [K]	ρ [g.cm <sup>-3</sup> ]	V <sub>m</sub> [cm <sup>3</sup> .mol <sup>-1</sup> ]	G [GPa]	K [GPa]	ν	E [GPa] <sup>a</sup>	E [GPa] <sup>b</sup>	H [GPa]	m
NaPO <sub>3</sub>	560 ± 3	2.52 ± 0.01 <sup>c</sup>	40.5 ± 0.2	14.3 ± 0.1 <sup>d</sup>	29.4 ± 0.5 <sup>d</sup>	0.290 ± 0.007 <sup>d</sup>	36.9 ± 0.7 <sup>d</sup>	36.9 ± 0.4	2.25 ± 0.06	0.0400 ± 0.0001
90NaPO <sub>3</sub> -5Na <sub>2</sub> SO <sub>4</sub>	551 ± 3	2.4853 ± 0.0005 <sup>e</sup>	41.87 ± 0.01	13.7 ± 0.1	29.1 ± 0.5	0.296 ± 0.007	35.5 ± 0.6	36.6 ± 0.3	2.25 ± 0.03	0.0386 ± 0.0002
80NaPO <sub>3</sub> -10Na <sub>2</sub> SO <sub>4</sub>	556 ± 3	2.4843 ± 0.0005 <sup>e</sup>	42.83 ± 0.01	13.2 ± 0.1	28.7 ± 0.5	0.300 ± 0.007	34.4 ± 0.6	35.1 ± 0.3	2.11 ± 0.03	0.0397 ± 0.0005
70NaPO <sub>3</sub> -15Na <sub>2</sub> SO <sub>4</sub>	549 ± 3	2.4842 ± 0.0005 <sup>e</sup>	43.89 ± 0.01	13 ± 0.1 <sup>f</sup>	28.2 ± 0.5 <sup>f</sup>	-	-	33.8 ± 0.3	1.99 ± 0.03	0.0381 ± 0.0002
60NaPO <sub>3</sub> -20Na <sub>2</sub> SO <sub>4</sub>	549 ± 3	2.5020 ± 0.0004 <sup>e</sup>	44.76 ± 0.01	12.8 ± 0.1	29.1 ± 0.5	0.309 ± 0.007	33.5 ± 0.5	34.0 ± 0.3	2.04 ± 0.03	0.038 ± 0.001
50NaPO <sub>3</sub> -25Na <sub>2</sub> SO <sub>4</sub>	546 ± 3	2.51 ± 0.01 <sup>c</sup>	45.9 ± 0.2	13.5 ± 0.1	29.3 ± 0.4	0.299 ± 0.006	35.2 ± 0.5	33.9 ± 0.3	2.02 ± 0.03	0.03880 ± 0.00003

<sup>a</sup> Values of E determined by ultrasonic echography.

<sup>b</sup> Values of E analyzed through nanoindentation. Note, that for the glasses where no Poisson's ratio could be detected by ultrasonic echography, a value of ν = 0.3 was used to calculate the Young's modulus from the reduced elastic modulus  $E_r = \left[ \frac{1-\nu^2}{E} + \frac{1-\nu^2}{E_i} \right]^{-1}$ , where  $E_i = 1,141$  GPa and  $\nu_i = 0.07$  are the elastic constants of the Berkovich diamond indenter tip used.

<sup>c</sup> Values of ρ as determined via the Archimedes method.

<sup>d</sup> Values of G, K, ν and E are taken from Le et al. (2017).

<sup>e</sup> Values of ρ as determined by means He pycnometry.

<sup>f</sup> Values of G and K are estimated from the values of E as determined by nanoindentation and ν = 0.3, using the following relations:  $G = \frac{E}{2(1+\nu)}$  and  $K = \frac{E}{3(1-2\nu)}$ , respectively.

TABLE 2 | Physical properties of the (100-x)NaPO<sub>3</sub>-xNaCl glasses.

Sample	T <sub>g</sub> [K]	ρ [g·cm <sup>-3</sup> ]	V <sub>m</sub> [cm <sup>3</sup> ·mol <sup>-1</sup> ]	G [GPa]	K [GPa]	ν	E [GPa] <sup>a</sup>	E [GPa] <sup>b</sup>	H [GPa]	m
NaPO <sub>3</sub>	560 ± 3	2.52 ± 0.01 <sup>c</sup>	40.5 ± 0.2	14.3 ± 0.1 <sup>d</sup>	29.4 ± 0.5 <sup>d</sup>	0.290 ± 0.007 <sup>d</sup>	36.9 ± 0.7 <sup>d</sup>	36.9 ± 0.4	2.25 ± 0.06	0.0400 ± 0.0001
90NaPO <sub>3</sub> -10NaCl	562 ± 3	2.5045 ± 0.0005 <sup>e</sup>	38.97 ± 0.01	15.0 ± 0.1 <sup>f</sup>	32.4 ± 0.5 <sup>f</sup>	-	-	38.9 ± 0.5	2.47 ± 0.06	0.0381 ± 0.0004
80NaPO <sub>3</sub> -20NaCl	551 ± 3	2.5051 ± 0.0005 <sup>e</sup>	37.23 ± 0.01	15.1 ± 0.1	31.9 ± 0.5	0.296 ± 0.007	39.1 ± 0.6	42.7 ± 0.5	2.90 ± 0.06	0.033 ± 0.001
70NaPO <sub>3</sub> -30NaCl	537 ± 3	2.4967 ± 0.0005 <sup>e</sup>	35.61 ± 0.01	16.2 ± 0.1	33.5 ± 0.6	0.286 ± 0.007	43.1 ± 0.8	45.5 ± 0.5	3.05 ± 0.06	0.029 ± 0.002
60NaPO <sub>3</sub> -40NaCl	545 ± 3	2.4916 ± 0.0005 <sup>e</sup>	33.94 ± 0.01	15.6 ± 0.1	33.5 ± 0.6	0.298 ± 0.008	40.6 ± 0.7	45.6 ± 0.5	3.06 ± 0.06	0.027 ± 0.002

<sup>a</sup> Values of E determined by ultrasonic echography.

<sup>b</sup> Values of E analyzed through nanoindentation. Note, that for the glasses where no Poisson's ratio could be detected by ultrasonic echography, a value of ν = 0.3 was used to calculate the Young's modulus from the reduced elastic modulus  $E_r = \left[ \frac{1-\nu^2}{E} + \frac{1-\nu^2}{E_t} \right]^{-1}$ , where  $E_t = 1,141$  GPa and  $\nu_t = 0.07$  are the elastic constants of the Berkovich diamond indenter tip used.

<sup>c</sup> Values of ρ as determined via the Archimedes method.

<sup>d</sup> Values of G, K, ν and E are taken from Le et al. (2017).

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<sup>f</sup> Values of G and K are estimated from the values of E as determined by nanoindentation and ν = 0.3, using the following relations:  $G = \frac{E}{2(1+\nu)}$  and  $K = \frac{E}{3(1-2\nu)}$ , respectively.

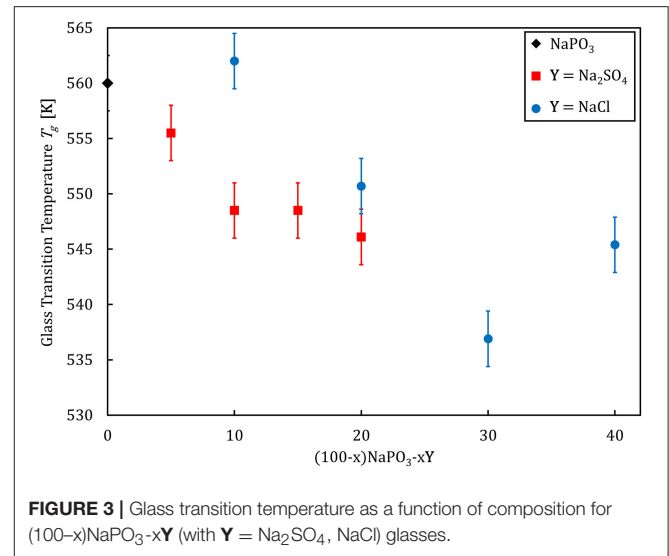
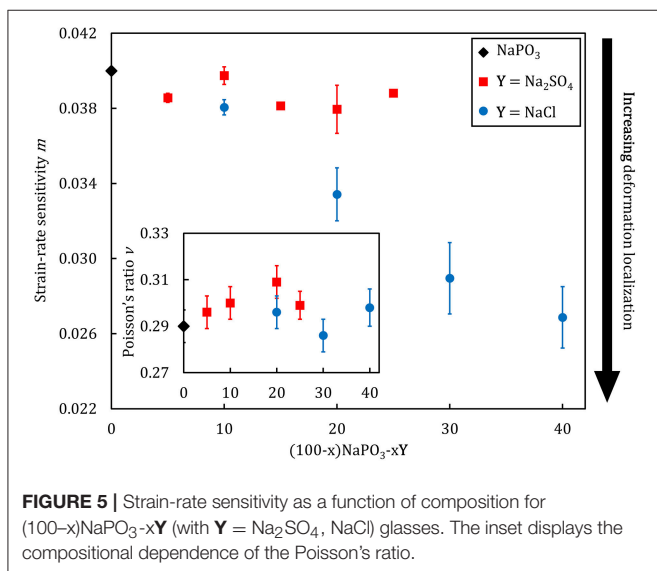
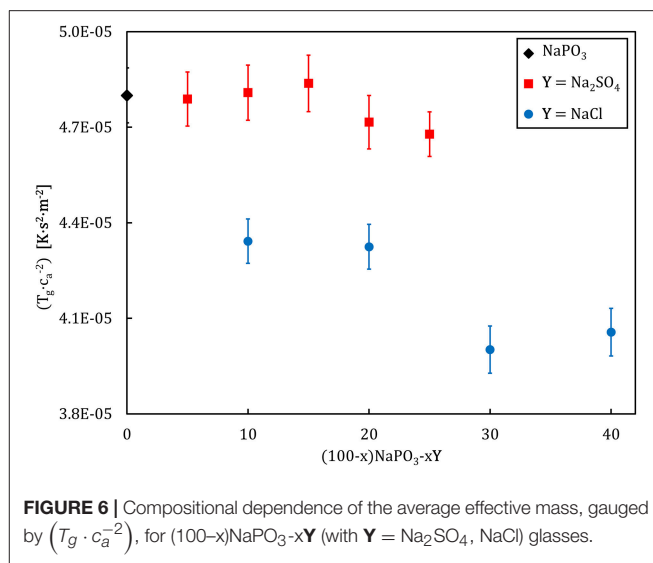
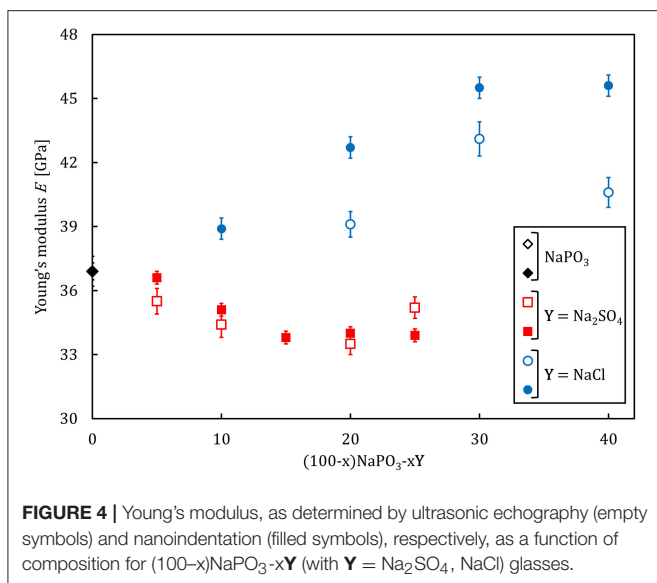


FIGURE 3 | Glass transition temperature as a function of composition for (100-x)NaPO<sub>3</sub>-xY (with Y = Na<sub>2</sub>SO<sub>4</sub>, NaCl) glasses.

“flow events” and molecular rearrangements which undergo some sort of transition through an energy barrier. The most classic of such relations is given by the Maxwell relation  $\tau = \eta \cdot G$ , which links the macroscopic shear modulus to the microscopic relaxation time  $\tau$  through the shear viscosity  $\eta$  (Perez, 1994). In a more refined sense the same arguments are used when calculating the elastic constants in MD simulation boxes from the derivative of the energy landscape as a function of strain (Pedone et al., 2008a,b; Jabraoui et al., 2016). Drawing parallels between “traditional” glass systems and simple Lennard-Jones glass models, Heuer and Spiess argued that the glass transition should be given by:

$$T_g = k_g \cdot \bar{M}_e \cdot c_a^2 \quad (15)$$

where  $k_g$  is a constant ( $\sim 0.014$  for glassy noble gases and  $\sim 0.011$  for “traditional” glassy systems),  $\bar{M}_e$  is the average effective mass, and  $c_a$  is the acoustic sound velocity, defined as the square on the ratio between the bulk modulus and the density  $c_a \equiv \sqrt{\frac{K}{\rho}}$  (Heuer and Spiess, 1994). With glass transition temperature and the acoustic sound velocity as easily accessible parameters, Equation (15) provides a convenient route to study the mechanism governing the glass transition. The proportionality constant includes information regarding the “elementary unit” undergoing an activated transition, which enables the whole system to evolve from a frozen-in state toward a supercooled liquid. Figure 6 illustrates the compositional dependence of the calculated average effective mass, expressed as the factor  $(T_g \cdot c_a^{-2})$ . The average effective mass remains upon the addition of Na<sub>2</sub>SO<sub>4</sub>, but it decreases when NaCl is added. This result suggests that the “elementary unit” in NaPO<sub>3</sub>-Na<sub>2</sub>SO<sub>4</sub> glasses remains largely unchanged when the phosphate groups are substituted by sulfate groups, as the molar mass of a PO<sub>4</sub><sup>3-</sup> and a SO<sub>4</sub><sup>2-</sup> tetrahedra are very similar (94.93 g·mol<sup>-1</sup> as compared to 96.03 g·mol<sup>-1</sup>). On the other hand, the average effective mass



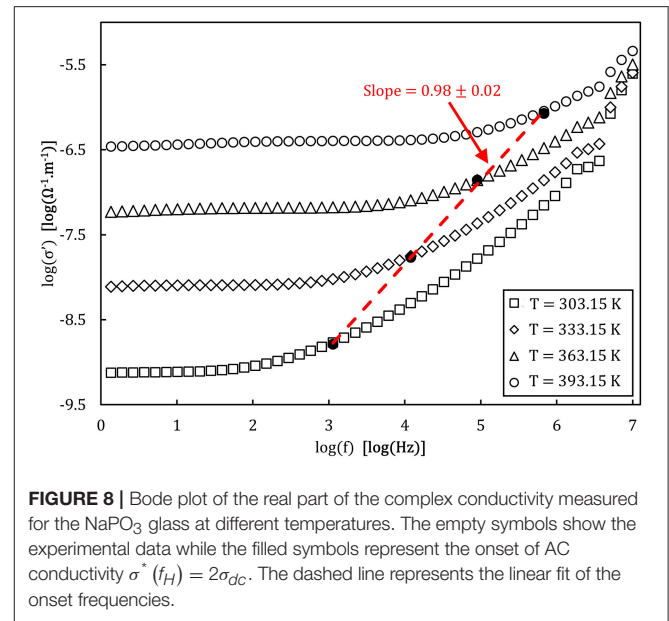
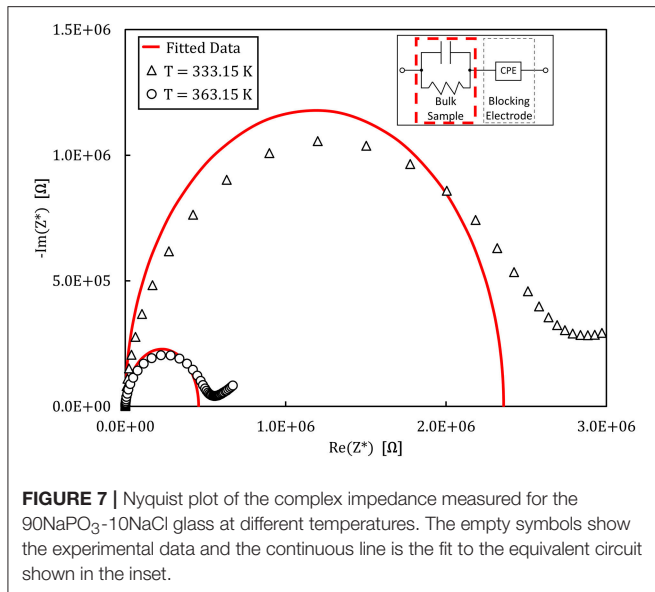
decreases with NaCl addition due to the much smaller mass of the chloride ions ( $35.45 \text{ g}\cdot\text{mol}^{-1}$ ).

The values of the Poisson's ratio and strain-rate sensitivity corroborate this interpretation. The Poisson's ratio, defined as the negative of the ratio between the transverse contraction strain and the longitudinal extension strain along the loading axis, is directly linked to the structural arrangements at short- and medium-range length scales in glasses, as evident from its interrelation to the packing density and network dimensionality (Rouxel, 2006, 2007; Rouxel et al., 2008a,b; Greaves et al., 2011). As our structural analysis have demonstrated, the phosphate network characteristic remains largely unchanged upon the addition of increasing amounts of  $\text{Na}_2\text{SO}_4$  and NaCl salts. Accordingly, the overall network dimensionality also remains constant, as it is roughly composed of spherical elements ( $\text{Na}^+$ ,

$\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  ions) packed around short phosphate chains. This is consistent with the observed relative invariance of the Poisson's ratio (Figure 5), where values of 0.3 are expected for glasses with a mixed 1D + 2D network structure (Rouxel, 2007). The slightly higher values of the Poisson's ratio which we observe for the sulfate-substituted glasses might originate from the significantly higher polarizability of the sulfate ion, leading to lower local order, and therefore, decreased structural dimensionality. For metallic glasses, the strain-rate sensitivity is an indicator for the tendency toward a localization of the plastic flow, and lower values are in general associated with more heterogeneous, localized plastic flow events (Spaepen, 1977; Limbach et al., 2017). This is consistent with the experimental data from Figures 5, 6, demonstrating that the plastic flow event distribution and average effective mass remains constant for the  $\text{NaPO}_3$ - $\text{Na}_2\text{SO}_4$  glasses, while the incrementally lower average effective mass in the  $\text{NaPO}_3$ - $\text{NaCl}$  glasses lead to a stronger localization of the plastic flow. Structural heterogeneities at short- and medium-range length scales are thought to be characteristic of the glassy state (Queiroz and Sestak, 2010; Hong et al., 2011), and their presence is an important factor controlling the mechanical properties of MD simulations (Tsamados et al., 2009; Rodney et al., 2011; Mantsi et al., 2012), colloidal glasses (Kawasaki et al., 2007; Schall et al., 2007; Rahmani et al., 2014; Varnik et al., 2014), metallic glasses (Fan et al., 2014; Hufnagel et al., 2016), and oxide glasses (Limbach et al., 2015; Benzine et al., 2018).

## Impedance Spectroscopy

An example of the Nyquist plots graphed from the experimental impedance analysis of the  $90\text{NaPO}_3$ - $10\text{NaCl}$  glass is presented in Figure 7. The graph displays the temperature dependence of the semicircles, together with the fits from the model Equation (9). Figure 8 shows the real part of the complex conductivity as a function of frequency for the  $\text{NaPO}_3$  glass at four different



temperatures. It also illustrates that our glasses obey the Nernst-Einstein relation (Sidebottom, 2009; Bandara and Mellander, 2011; Sangoro and Kremer, 2012):

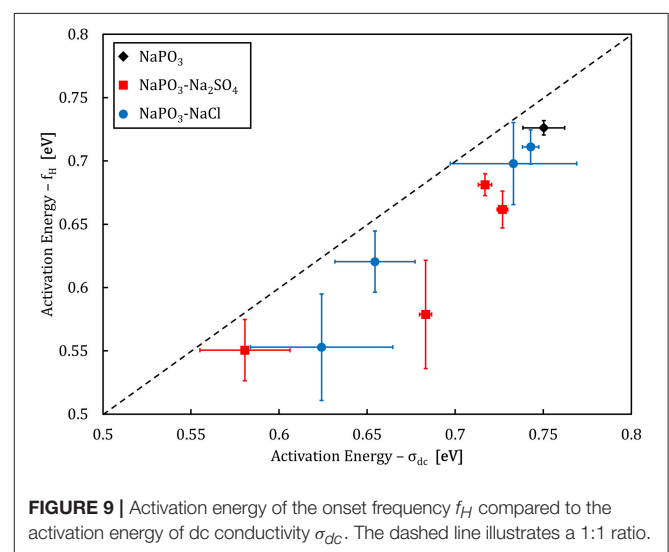
$$\sigma_{dc} = \frac{n(T) \cdot \lambda^2 \cdot e^2 \cdot \Gamma(T)}{g' \cdot k \cdot H_R} \quad (16)$$

where  $\lambda$  is a characteristic length so that  $\lambda^2$  is approximately equal to the mean square displacement,  $e$  is the elementary charge (Bhattacharya and Ghosh, 2004),  $g'$  is a geometric factor,  $k$  is Boltzmann's constant, and  $n(T)$  and  $\Gamma(T)$  are given by Equations (12,13), respectively. Since  $f_H$ , as defined by the Jonscher power-law,  $\sigma^*(f_H) = 2\sigma_{dc}$  (Almond et al., 1983, 1984; Popov et al., 2012; Singh et al., 2016), is directly related to the timescales of ionic hopping (Marple et al., 2018),  $\Gamma(T)$  equals  $f_H(T)$  and therefore Equation (16) can be rewritten as:

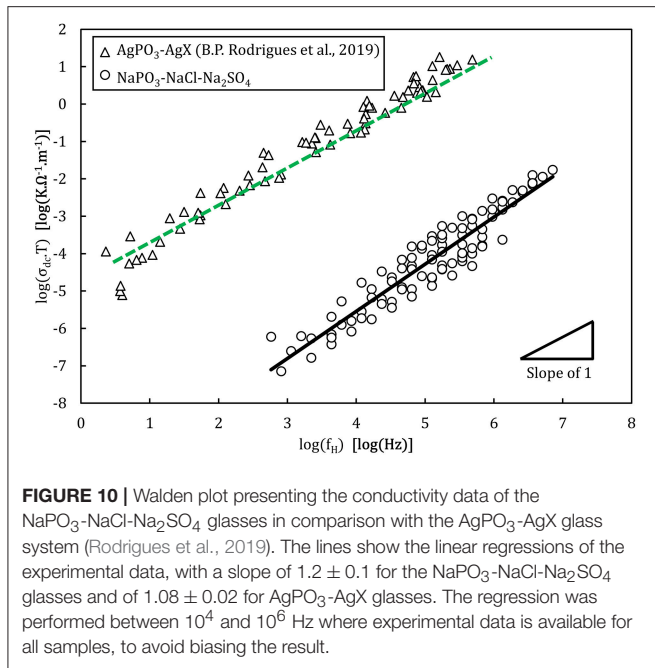
$$\log(\sigma_{dc}) = \log\left(\frac{n(T) \cdot \lambda^2 \cdot e^2}{g' \cdot k \cdot H_R}\right) + \log(f_H) \quad (17)$$

From which the linear relation between  $\log(\sigma_{dc})$  and  $\log(f_H)$  with a slope of unity is recovered.

Analysis of the activation energies show that for these glasses,  $E_n \ll E_m < E_\sigma$  as can be seen in **Figure 9**, and thus the ionic conductivity is determined mainly by the ionic mobility. More specifically, the mobility of the sodium cation, as previous studies have shown that for sulfate- and chloride-containing alkali metaphosphate glasses the contributions of the anions is negligible (Sokolov et al., 2003; Bhide and Hariharan, 2007; Rao et al., 2009; Hraiech and Ferid, 2013). Despite that, charge carrier formation does play a non-negligible role in this glass system, as illustrated by the Walden plot of the conductivity data in **Figure 10**, where it is clear that the NaPO<sub>3</sub>-NaCl-Na<sub>2</sub>SO<sub>4</sub> glasses show a broad distribution, covering over two



orders of magnitude along the  $\log(\sigma_{dc} \cdot T)$  axis for each measured frequency, suggesting that the addition of sodium chloride and sodium sulfate enhances the number of effective charge carriers. However, calculation of the number of charge carriers  $n(T)$  at 323 K from experimental activation energy values shows that both sodium salts seem to have the inverse effect: when considering the end-members of our compositions, the number density of charge carriers decreases non-linearly from  $6.3 \times 10^{21}$  ions.cm<sup>-3</sup> for NaPO<sub>3</sub> to  $5.0 \times 10^{21}$  ions.cm<sup>-3</sup> for 60NaPO<sub>3</sub>-40NaCl and to  $4.6 \times 10^{21}$  ions.cm<sup>-3</sup> for 50NaPO<sub>3</sub>-25Na<sub>2</sub>SO<sub>4</sub>, respectively. Normalizing these numbers by the sodium number density derived from experimental density data, the ratio of charge carriers to the total sodium ion density decreases from 0.42 for NaPO<sub>3</sub> to 0.28 for 60NaPO<sub>3</sub>-40NaCl and to 0.34 for 50NaPO<sub>3</sub>-25Na<sub>2</sub>SO<sub>4</sub>, respectively. This result, in conjunction

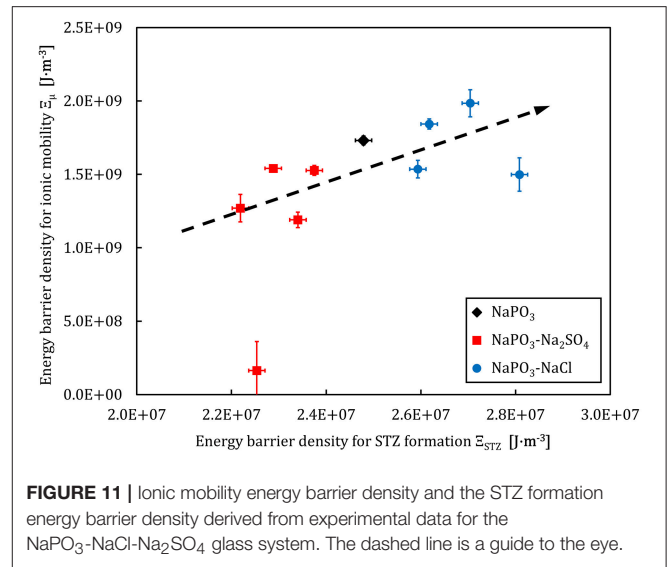


**FIGURE 10** | Walden plot presenting the conductivity data of the  $\text{NaPO}_3\text{-NaCl-Na}_2\text{SO}_4$  glasses in comparison with the  $\text{AgPO}_3\text{-AgX}$  glass system (Rodrigues et al., 2019). The lines show the linear regressions of the experimental data, with a slope of  $1.2 \pm 0.1$  for the  $\text{NaPO}_3\text{-NaCl-Na}_2\text{SO}_4$  glasses and of  $1.08 \pm 0.02$  for  $\text{AgPO}_3\text{-AgX}$  glasses. The regression was performed between  $10^4$  and  $10^6$  Hz where experimental data is available for all samples, to avoid biasing the result.

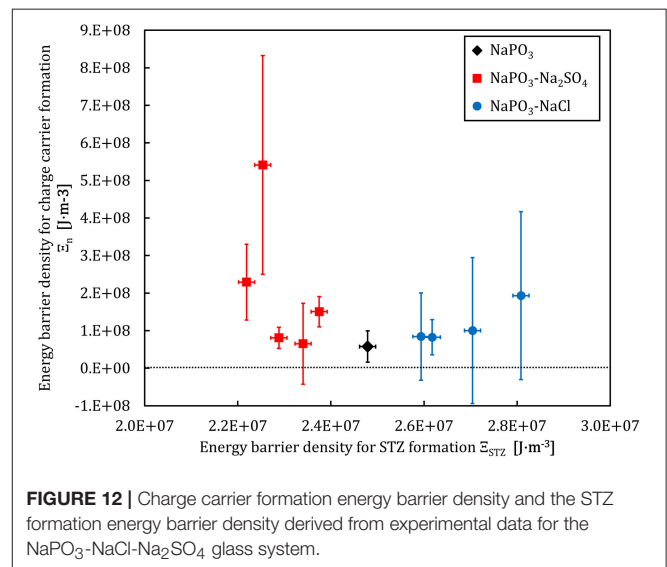
with the fact that the linear regression of the  $\text{NaPO}_3\text{-NaCl-Na}_2\text{SO}_4$  data in the Walden plot is significantly higher than one, indicates that both the average distance between ions and the Haven ratio (Rodrigues et al., 2019) exhibit non-trivial compositional and/or temperature dependences. Moreover, this also implies that the improved ionic conductivity is based on an even stronger increase in ionic mobility, as it has to compensate the parallel reduction in the number of charge carriers. Referring again to the end-members of the two glass series, the experimental data shows that the addition of NaCl causes an increase of about one order of magnitude in the ionic mobility, while the addition of  $\text{Na}_2\text{SO}_4$  results in an enhancement of approximately three orders of magnitude (see inset in Figure 14).

## DISCUSSION

Some of the terminology used to discuss the mechanical properties in this report originates from the concept of shear-transformation zones (STZ), i.e., the cooperative rearrangement of a group of atoms. While STZs are mostly used to describe the fundamental processes governing the plasticity of metallic glasses, the STZ theory has also been used to describe general glassy dynamics (Bouchbinder and Langer, 2009a,b,c, 2011). By definition, STZs are localized flow events marking the irreversible transition between the inherent structures of the energy landscape as the glassy system is subjected to mechanical stress or strain (Bouchbinder and Langer, 2011). Therefore, it is possible to draw a parallel between the atomic motion during plastic deformation and ionic conductivity, since both result from the activation of extremely localized, atomic-level rearrangements by external stimuli. While the atomic motion



**FIGURE 11** | Ionic mobility energy barrier density and the STZ formation energy barrier density derived from experimental data for the  $\text{NaPO}_3\text{-NaCl-Na}_2\text{SO}_4$  glass system. The dashed line is a guide to the eye.



**FIGURE 12** | Charge carrier formation energy barrier density and the STZ formation energy barrier density derived from experimental data for the  $\text{NaPO}_3\text{-NaCl-Na}_2\text{SO}_4$  glass system.

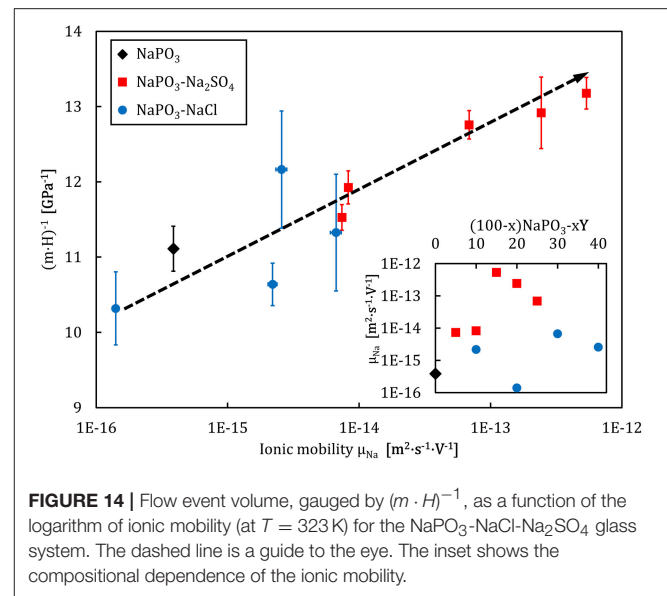
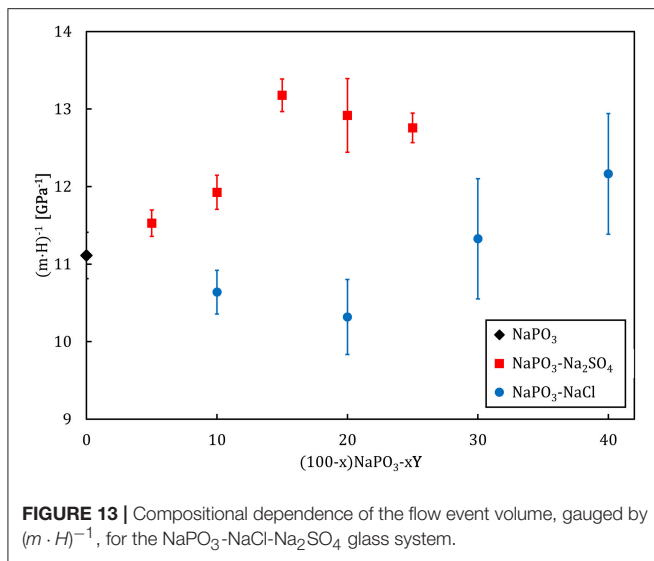
related to a STZ originates from the stress gradient and the strain bias, the ionic jumps which manifest in the electric conductivity are driven by the applied voltage.

The energy barrier density (in  $\text{J}\cdot\text{m}^{-3}$ ), which determines the STZ formation is given by Liu et al. (2010):

$$\Xi_{STZ} = \frac{8}{\pi^2} \cdot G \cdot \gamma_c^2 \cdot \xi \quad (18)$$

where  $\gamma_c = 0.0267$  and  $\xi = 3$  are constants from the cooperative shear model (Johnson and Samwer, 2005). The Figures 11, 12 show a comparison between the energy barrier density for STZ formation and the barrier densities for ionic mobility  $\Xi_{\mu}$  and charge carrier formation  $\Xi_n$ , respectively. Interestingly, the energy barrier densities for mobility and STZ formation scale linearly for the  $\text{NaPO}_3\text{-Na}_2\text{SO}_4\text{-NaCl}$  system, while the relations





between the energy density barrier of charge carrier formation and STZ formation depend on the added salt: the  $\text{NaPO}_3\text{-NaCl}$  glasses follow a positive linear trend, while the  $\text{NaPO}_3\text{-Na}_2\text{SO}_4$  glasses show a broad distribution of ionic mobility energy barriers within a somewhat narrow distribution of STZ energy barrier densities. These results suggest that the plastic deformation in  $\text{NaPO}_3\text{-NaCl}$  glasses is strongly coupled to the motion of the sodium cations, while the  $\text{NaPO}_3\text{-Na}_2\text{SO}_4$  glasses deform in a more homogeneous way, requiring the rearrangement of the sulfate and phosphate groups that are part of the glass network. In conjunction with the data from **Figures 5, 6**, we obtain a consistent picture of how the addition of NaCl shifts the structural units responsible for plastic deformation from the covalently-bonded phosphate network to the strongly ionic interchain  $\text{Na}^+\text{-Cl}^-$  “tissue.” The addition of sodium sulfate, on the other hand, barely affects the average effective mass of the “elementary unit” (**Figure 6**) and its distribution (**Figure 5**). The strongly changing ionic mobility energy barrier density in relation to the relatively constant SZT formation energy barrier density suggests a larger degree of cooperative motion involved in the diffusion of sodium ions, which is consistent with our impedance measurements.

Considering the growing influence of the sodium cation and its environment on the mechanical properties, we arrive at the conclusion that ionic glasses with 1D + 2D mixed networks are created upon the progressive addition of  $\text{Na}_2\text{SO}_4$  and NaCl, where the respective constituents can be approximated as quasi-spheres that interact mainly via electrostatic forces. As opposite to traditional oxide glasses with covalent network structures, these electrostatic forces are longer ranging and less directional. This in turn allows us to interpret the indentation deformation of the  $\text{NaPO}_3\text{-Na}_2\text{SO}_4\text{-NaCl}$  glasses in analogy to the mechanical behavior of metallic glasses and charged colloidal suspensions, which are characterized by spherical structural units, arranged as densely packed clusters bound via long-range, non-directional forces (Tokuyama, 1998; Pan et al., 2008; Varnik et al., 2014; Ma,

2015). The indentation deformation in such systems typically comprise the activation of flow units involving a collection of simultaneously operating STZs (Limbach et al., 2017). The volume of these flow units can be estimated by Pan et al. (2008):

$$\Omega = \frac{k \cdot T}{C' \cdot m \cdot H} \quad (19)$$

where  $C'$  is a constant related to the cooperative shear model (Johnson and Samwer, 2005). Since all experiments were performed under isothermal conditions, the factor  $(k \cdot T)/C'$  is constant for all glasses and consequently, we can utilize the factor  $(m \cdot H)^{-1}$  as a measure for the compositional dependence of the volume of the flow units (**Figure 13**). As  $\text{Na}_2\text{SO}_4$  is added, an increase in  $(m \cdot H)^{-1}$  is observed. On the other hand, NaCl incorporation initially results in a decrease of  $(m \cdot H)^{-1}$  down to a minimum at  $x = 20$ . Further addition of NaCl causes  $(m \cdot H)^{-1}$  to rapidly increase.

The effect of sulfate addition follows the slight decrease in the average effective mass of each “elementary unit” of plastic flow (**Figure 6**) as the deformation homogeneity remains constant, as reflected by the marginal changes in the strain-rate sensitivity of the  $\text{NaPO}_3\text{-Na}_2\text{SO}_4$  glasses (**Figure 5**). However, the addition of NaCl illustrates the more complex scenario of the changing topological structures controlling the plastic deformation. Starting from  $\text{NaPO}_3$ , the addition of NaCl continuously increases the mobility of the phosphate chains. This is accompanied by a decreasing volume of the flow events and a lower strain-rate sensitivity, which indicates that the plastic deformation becomes more and more localized around the most mobile phosphate chains. At  $\sim 20 \text{ mol\%}$  NaCl, the interchain  $\text{Na}^+\text{-Cl}^-$  “tissue” reaches a critical threshold and starts to concentrate the flow events, causing the phosphate chains to stop being the controlling factor. Further, addition of NaCl continuously decreases the glass transition temperature and the

strain-rate sensitivity but increases the volume of the flow units since the fraction of the ionic interchain “tissue” also increases. Analogous behavior can be found on several physical properties of inorganic glass systems with marked compositional-dependent transitions in the glass topology (Vaills et al., 2005; Micoulaut and Phillips, 2007; Micoulaut, 2008), e.g., in  $(100-x)\text{AgPO}_3-x\text{AgI}$  system at  $x \sim 20$  (Micoulaut et al., 2009; Novita et al., 2009).

The dependence of the volume of flow events on interactions beyond the short-range scale is exemplified in the direct correlation to the effective ionic mobility (calculated for  $T = 323\text{ K}$ ), illustrated in **Figure 14**. The ionic mobility contains information on the correlated motion of ions through the Haven ratio (Murch, 1982; Murch and Dyre, 1989), which the Impedance analysis suggests exhibits a non-trivial compositional dependence (**Figure 10**). These results relate back to the increased tendency for a localization of the plastic deformation upon the addition of NaCl (**Figure 5**), reflecting the smaller STZ volumes and lower ionic mobility in relation to the sodium metaphosphate. On the other hand, the addition of  $\text{Na}_2\text{SO}_4$  strongly increases the ionic mobility, leading to larger STZ volumes but no change in the localization of deformation, also in line with recent results from Raman measurements of the Boson peak in indented  $\text{SiO}_2$  (Benzine et al., 2018).

## CONCLUSIONS

In this work we have shown an interesting correlation between the atomic motions governing the ionic conductivity and the plastic deformation in sodium metaphosphate glasses containing sodium sulfate and sodium chloride, respectively. In summary, the structure and physical properties of melt-quenched  $\text{NaPO}_3\text{-NaCl-Na}_2\text{SO}_4$  glasses were characterized. The addition of sulfate and halide salts was found to maintain the phosphate network largely untouched, while the coordination sphere around the  $\text{Na}^+$  cations changes, whereas the medium-range order evolves from 2D phosphate chains to a heterogeneous 1D + 2D mixed network. The addition of NaCl enhances the Young's modulus

and results in a stronger localization of the plastic flow, while the addition of  $\text{Na}_2\text{SO}_4$  on the other hand, keeps the Young's modulus and the homogeneity of the plastic flow events basically constant. Due to the similar atomic masses of the  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  tetrahedra, the average effective mass of the “elementary unit” remains constant as well. Impedance measurements show a moderate increase in ionic conductivity as a result of the enhanced mobility of the  $\text{Na}^+$  cation, while the number density of charge carriers decreases with the addition of the two sodium salts. We observed a smaller STZ volume in glasses with less mobile ions and a more localized deformation, whereas higher ionic mobilities at similar localization degrees imply a larger STZ volume. This reflects in lower average effective masses for the elementary units of deformation, as the plastic flow events are concentrated in a smaller volume and become more dependent on the movement of the lighter ions. A higher  $\text{Na}^+$  mobility increases the average displacement of the ions, leading to stronger cooperative motions, and a larger volume of the flow units.

## DATA AVAILABILITY

The datasets generated for this study are available on request to the corresponding author.

## AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

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**Conflict of Interest Statement:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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