Mixed-cation Li_xAg_{1-x}PO₃ glasses studied by ⁶Li, ⁷Li, and ¹⁰⁹Ag stimulated-echo NMR spectroscopy

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We show that NMR stimulated-echo experiments provide detailed information about the jump dynamics of each of the ionic species in mixed mobile ion glasses. The potential of this technique is exploited to measure two-time correlation functions of the lithium and silver ionic hopping motions in $Li_xAg_{1-x}PO_3$ glasses. Comparison of stimulated-echo decays from ⁶Li or ⁷Li NMR with that from ¹⁰⁹Ag NMR shows that the residence times at the ionic sites are significantly longer for the respective minority component than for the majority component at both ends of the composition range, while lithium and silver ions exhibit similar jump rates for x = 0.5. Substitution of silver by lithium results in a strong and continuous slowdown of the silver ionic jumps, whereas the lithium ionic jumps show a weaker dependence on the glass composition. In the vicinity of the conductivity minimum, the activation energies obtained from the stimulated-echo studies for both lithium and silver ionic jumps are significantly smaller than that obtained from the dc conductivity. This suggests that mixing of cation species promotes differences between short-range and long-range ionic motions. For all studied glass compositions and for both lithium and silver, we can rule out the existence of a significant fraction of truly immobile cations. However, broad distributions of jump rates lead to strongly nonexponential correlation functions of the ionic hopping motion. Interestingly, the correlation functions become more and more exponential when the observed cation species is successively replaced by the unobserved cation species. The present results suggest that dynamical heterogeneities and correlations of ionic motions, which involve like and unlike ions and length scales of several interatomic distances, are important aspects of ion dynamics in mixed mobile ion glasses.

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I. INTRODUCTION

Ion conducting melts, glasses, or crystals reveal a nonmonotonous variation of their dynamical properties when the mobile ion species is successively replaced by larger or smaller mobile ions.^{1–3} In most studies of this mixed mobile ion effect (MME), the mobile ionic species were alkali ions, so that this phenomenon is also known as the mixed-alkali effect (MAE). While the MME is accompanied by local structural changes, the global network structure is not affected.^{3,4} The MME is considered to be a promising testing ground to understand the complexities of ion conduction in solids.⁵ Puzzling manifestations of the MME were observed early on⁶ and explored in more detail in now-classical studies of mechanical absorption,^{7,8} electrical conduction,^{9,10} and tracer diffusion.^{11,12} The macroscopic observations include the so-called vulnerability;¹³ that is, a dramatic conductivity reduction when single-cation glasses are weakly doped with foreign cations.^{7,10}

The interplay between local structure and ion transport in mixed mobile ion glasses was the focus of numerous theoretical studies. A variety of interactions was suggested to be at the origin of the MME, including, on the one hand, the "direct" Coulombic¹⁴ or dipolar¹⁵ interactions among like and unlike mobile ions or, on the other hand, more indirect lattice-mediated interactions between them. The latter can be further classified as leading to quasistatic "mesh-size" effects¹⁶ or to temporal^{5,17} as well as permanent¹⁸ adaptations of sites to a specific mobile ion species. As explored in various computer simulations, these concepts can result in the existence of preferred ionic pathways, to enhanced jumps back to preferred sites,¹⁹ and to effects of cooperativity blocking.^{20,21} To enable site-mismatch adaptation even in the glassy state, a concerted, isochoric hopping of small and large ions was envisaged.^{22,23}

While many macroscopic features of the MME could convincingly be captured by these concepts, there is no general consensus regarding the type of interaction that dominates the MME in glassy materials. This is partly due to a lack of experimental data providing information about the ion dynamics directly at the microscopic level, for systems such as the cation mixed-phosphate glass $Li_x Ag_{1-x} PO_3$. Here, the ionic radius mismatch between Ag⁺ and Li⁺, r_{Ag}/r_{Li} , is about 1.5 and, thus, intermediate between that of the Li-Na and of the Li-K couples, which were intensively studied in the past using macroscopic techniques.⁸ The overall dc conductivity of $Li_x Ag_{1-x} PO_3$ glasses exhibits a pronounced minimum at a LiPO₃ fraction of $x \approx 0.8$.²⁴ However, the respective contributions of the mobile species are impossible to infer from conductivity measurements. Also, the commonly employed radiotracer diffusion method is not feasible for a separate mapping of the lithium and silver ionic mobilities. While ¹¹⁰Ag is an often-used isotope to study the MME,²⁵ no suitable radiotracer exists for lithium. As a macroscopic technique, tracer-diffusion measurements would hardly provide local dynamical information anyway.

Owing to its isotope selectivity, NMR spectroscopy allows one to separately assess the microscopic dynamics of the ionic species in mixed mobile ion glasses. In previous works, NMR spin-lattice-relaxation analysis was used to investigate the MME.^{26,27} However, the potential of stimulated-echo studies, which enable straightforward measurement of microscopic ionic hopping correlation functions,^{28,29} has not yet been explored. Here, we exploit the fact that ⁶Li, ⁷Li, and ¹⁰⁹Ag NMR stimulated-echo spectroscopies provide detailed insights into the lithium and silver ion dynamics in Li_xAg_{1-x}PO₃ glasses. These NMR techniques were already successfully employed to study the mobile ion dynamics in pure LiPO₃³⁰ and AgPO₃³¹ glasses.

II. THEORETICAL ASPECTS

NMR studies of ion dynamics in solid-state electrolytes exploit the fact that it is often possible to ascribe an inherent resonance frequency to each ionic site.^{28,29} In glasses, diverse local environments lead to distinguishable values so that jumps between the ionic sites render the resonance frequency of a nucleus time dependent. Different properties of the local environments determine the observed frequency shift ω with respect to the Larmor frequency ω_0 for different probe nuclei. For ⁶Li (I = 1) and ⁷Li ($I = \frac{3}{2}$), the interaction between the electric quadrupole moment of the nucleus and the electric field gradient at the nuclear site dominates the value of ω . For ¹⁰⁹Ag ($I = \frac{1}{2}$), the frequency shift, the chemical shift, is determined by the magnetic shielding of the static magnetic field at the nuclear site.

⁶Li, ⁷Li, and ¹⁰⁹Ag NMR stimulated-echo experiments provide detailed insights into slow ionic hopping motions in solids.^{28–41} Specifically, correlation times in the range $\tau \approx 10 \ \mu s$ to 1 s are accessible. In these experiments, three pulses divide the experimental time into two short evolution times $t_p \ll \tau$ that are separated by a much longer mixing time t_m .^{42,43} While the spins are labeled according to their NMR frequencies during the evolution times, ion dynamics may change the value of ω during the intermediate mixing time. Using appropriate pulse lengths and phases, the pulse sequence generates a stimulated echo. Measurement of the echo height for various t_m and constant t_p provides access to correlation functions of the ionic jump motion. In particular, it is possible to correlate the respective resonance frequencies during the two evolution periods according to^{28,29,32}

$$F_2(t_m) \propto \langle \sin[\omega(0)t_p] \sin[\omega(t_m)t_p] \rangle. \tag{1}$$

Here, the brackets $\langle \cdots \rangle$ denote the ensemble average. In addition to ion dynamics, further effects can lead to a decay of the stimulated echo in experimental practice. In Sec. IV, we will show that, despite these effects, stimulated-echo spectroscopy provides access to hopping correlation functions, which allow for a straightforward microscopic interpretation.

For most solid electrolytes, $F_2(t_m)$ does not exhibit single exponential behavior, but it can rather be described by a Kohlrausch-Williams-Watts (KWW) function:

$$F_2(t_m) = (1 - C) \exp\left[-\left(\frac{t_m}{\tau_K}\right)^{\beta_K}\right] + C.$$
 (2)

Then, τ_K and β_K are measures for the time scale and the stretching of the decay, respectively. From these fit parameters, the mean correlation time of the ionic jump motion, $\langle \tau \rangle$, can be obtained according to

$$\langle \tau \rangle = \frac{\tau_K}{\beta_K} \Gamma\left(\frac{1}{\beta_K}\right),$$
 (3)

where $\Gamma(x)$ denotes the Gamma function.

III. EXPERIMENT

Detailed information about the sample preparation and the setups of the ⁶Li and ¹⁰⁹Ag NMR experiments can be found in previous publications.^{30,31,34,37,44-46} Briefly, we worked at Larmor frequencies of 23.3³¹ or 28.0 MHz³⁷ in ¹⁰⁹Ag NMR and at Larmor frequencies of 44.1³⁰ or 46.1 MHz⁴⁶ in ⁶Li NMR. For both these nuclei, an evolution time of $t_p = 100 \ \mu s$ was used. The ⁷Li NMR experiments were performed at a Larmor frequency of 116.6 MHz using a TecMag console and a home-built probe. The duration of the 90° pulses was 2.1 μs . For ⁷Li, an evolution time of $t_p = 15 \ \mu s$ was utilized.

To improve the signal-to-noise ratio in ⁶Li and ¹⁰⁹Ag NMR, $Li_r Ag_{1-r} PO_3$ glasses were prepared using isotopically enriched Li₂CO₃ (95% ⁶Li, ISOTEC, Inc.) and AgNO₃ (99% ¹⁰⁹Ag, STB isotopes). Here, we compare results for the glass compositions x = 0.20, 0.50, and 0.75 with previous findings for $x = 0.0 (\text{AgPO}_3)^{31}$ and $x = 1.0 (\text{LiPO}_3)^{30}$ For x = 0.20and x = 0.50, we prepared samples with maximum possible (95%) ⁶Li enrichment. For materials with higher lithium concentration, however, maximum isotopic enrichment strongly enhances spin diffusion, which interferes with the observation of slow lithium dynamics in ⁶Li stimulated-echo experiments; see Sec. IV. Therefore, 50% ⁶Li enrichment was used for the Li_{0.75}Ag_{0.25}PO₃ glass, which proved a good compromise between sufficient signal-to-noise ratio and acceptable spin diffusion contribution in our previous work on LiPO₃ glass.³⁰ The metaphosphate glass composition of all samples was checked using ³¹P magic angle spinning (MAS) NMR.³⁰

IV. DATA ANALYSIS

In stimulated-echo experiments, the echo intensity I_2 can diminish not only due to ionic jumps, but also due to spin-lattice relaxation and spin diffusion; that is, a transfer of magnetization as a consequence of flip-flop processes of the spins. Moreover, in general, the stimulated-echo decays depend on the length of the evolution time t_p . To consider these effects, we write

$$I_2(t_m, t_p) \propto F_2(t_m, t_p) S(t_m, t_p) R(t_m).$$
(4)

Here, *S* and *R* are the decays due to spin diffusion and spinlattice relaxation, respectively. For the studied $\text{Li}_x \text{Ag}_{1-x} \text{PO}_3$



FIG. 1. (Color online) Decays of the ⁶Li stimulated-echo intensity $I_2(t_m, t_p)$ of Li_{0.5}Ag_{0.5}PO₃ glass for various temperatures and an evolution time $t_p = 100 \ \mu$ s. The lines are KWW fits.

glasses and temperatures, ⁶Li and ¹⁰⁹Ag spin-lattice relaxation measurements show that the relaxation is too slow to lead to a substantial damping of the stimulated echo and, hence, $R(t_m) \approx 1$. Spin diffusion is usually negligible in ¹⁰⁹Ag NMR stimulated-echo investigations of solidstate electrolytes, 31, 34-38, 47, 48 in harmony with the present results; see below. However, this effect needs to be considered when analyzing ⁶Li NMR stimulated echoes.^{28–30} This difference occurs because ¹⁰⁹Ag has a smaller gyromagnetic ratio than ⁶Li and, thus, the former nucleus exhibits much smaller homonuclear dipolar interactions, which mediate spin diffusion. However, it was shown for LiPO₃ glass that, although both ion dynamics and spin diffusion contribute to the ⁶Li NMR stimulated-echo decays, their effects can be successfully separated on the basis of temperature-dependent measurements.³⁰ For ⁷Li, both spin-lattice relaxation and spin diffusion may affect the stimulated-echo decays at low temperatures. Therefore, we restrict our analysis to ⁷Li data obtained at sufficiently high temperatures.

To determine whether a separation of contributions from ion dynamics and spin diffusion to ⁶Li stimulated-echo decays is also possible for the mixed-cation glasses of the present study, we show the echo intensity $I_2(t_m, t_p = 100 \ \mu s)$ for Li_{0.5}Ag_{0.5}PO₃ glass in Fig. 1. Evidently, the thermally induced shift of the curves ceases at low temperatures. Moreover, the curves become more exponential when the temperature is decreased. These effects show that, upon cooling, more and more of the decay due to ionic jump motion is cut off by the more exponential decay due to spin diffusion. For a quantitative analysis, we fit the data to Eq. (2). The temperature dependence of the resulting fitting parameters τ_K and β_K is displayed in Fig. 2. We see that, below about 290 K, the fit parameters are independent of temperature, indicating that the stimulated-echo decays are governed by temperature-independent spin diffusion rather than temperature-dependent ion dynamics. When we determine $S(t_m, t_p)$ from these data at low temperatures, we can remove the effect of spin diffusion upon the data at higher temperatures. Specifically, following previous work³⁰ and dividing the experimental data $I_2(t_m, t_p)$ by $S(t_m, t_p)$, we obtain the correlation functions $F_2(t_m, t_p)$, which directly reflect the ionic hopping motion. In Table I, we compile the parameters τ_K and β_K describing the decay due to spin diffusion in the studied $Li_x Ag_{1-x} PO_3$ glasses. They indicate that spin diffusion



FIG. 2. (Color online) Temperature dependence of the parameters (a) τ_K and (b) β_K , as obtained from KWW fits of the ⁶Li stimulated-echo intensity $I_2(t_m, t_p)$ of Li_{0.5}Ag_{0.5}PO₃ glass. Results for $t_p = 100 \ \mu s$ and $t_p = 300 \ \mu s$ are compared. For the shorter evolution time, the horizontal dashed lines mark the temperature-independent values of the parameters, which originate from spin diffusion at sufficiently low temperatures.

slows down when diluting ⁶Li and, hence, reducing the Li-Li homonuclear dipolar interactions, as expected. Throughout Sec. V, we show ⁶Li NMR correlation functions, which were corrected for spin diffusion using these parameters.

In general, NMR correlation functions can depend on the length of the evolution time t_p ; see Eq. (1). However, for various silver and lithium-ion conductors, including silver and lithium phosphate glasses,^{30,34,35,38} it was found that $F_2(t_m)$ hardly depends on the evolution time in a wide range of values. Then, $F_2(t_m)$ measures the probability that an ion still or again occupies the initial site in the glassy matrix after a time t_m . Such an interpretation will be possible if the time dependence of the resonance frequency of a nucleus results exclusively from the hopping motion of the corresponding ion (i.e., if the dynamics of other ions has no effect).²⁹ In ¹⁰⁹Ag NMR, this condition is usually met when recording stimulated-echo decays for $t_p = 100 \ \mu s.^{31,34,38}$ Therefore, we use this evolution time in the present ¹⁰⁹Ag NMR stimulated-echo experiments.

TABLE I. Parameters describing the spin-diffusion decay $S(t_m, t_p = 100 \ \mu \text{s})$ in Li_xAg_{1-x}PO₃ glasses. The data (*) for x = 1.00 were reported in previous work on an LiPO₃ glass.³⁰

x	$ au_{K}(\mathbf{s})$	β_K	⁶ Li Enrichment
0.20	2.80	0.80	95%
0.50	1.00	0.75	95%
0.75	0.85	0.85	50%
1.00*	0.37	0.90	50%

To check to what extent ⁶Li NMR correlation functions of $Li_rAg_{1-r}PO_3$ glasses depend on the length of the evolution time, we compare results obtained for x = 0.5 using evolution times $t_p = 100 \ \mu s$ and $t_p = 300 \ \mu s$. In Fig. 2, we contrast τ_K and β_K resulting from KWW fits of $I_2(t_m, t_p = 300 \ \mu s)$ with the above discussed values from $I_2(t_m, t_p = 100 \ \mu s)$. It is evident that the fit parameters hardly depend on the evolution time, in particular at high temperatures, where the decays are governed by lithium-ion dynamics. Therefore, we apply an evolution time $t_p = 100 \ \mu s$ in the following ⁶Li NMR stimulated-echo experiments on $Li_x Ag_{1-x} PO_3$ glasses, ensuring that an interpretation of the decays in terms of ionic jump correlation functions is possible. Since ⁷Li exhibits a larger quadrupole moment and, thus, broader spectra than ⁶Li, comparable phases ωt_p are achieved when applying shorter evolution times for the former nucleus. We use $t_p = 15 \ \mu s$, which proved a suitable value in previous ⁷Li NMR stimulatedecho studies.²⁸

V. RESULTS

Figure 3 shows results from ⁶Li and ¹⁰⁹Ag stimulatedecho experiments on $Li_{0.50}Ag_{0.50}PO_3$ glass. As discussed in Sec. IV, the decays map out the correlation functions of the lithium and silver ionic hopping motions. For both ionic species, the time scale of the correlation loss strongly increases



FIG. 3. (Color online) Correlation functions $F_2(t_m)$ from (top) ⁶Li NMR and (bottom) ¹⁰⁹Ag NMR stimulated-echo experiments on Li_{0.50}Ag_{0.50}PO₃ glass. For both nuclei, the data are compared with that for the corresponding single-cation glasses, LiPO₃³⁰ and AgPO₃,³¹ respectively. An evolution time of $t_p = 100 \ \mu s$ was used in all measurements. The dashed and solid lines are KWW fits (C = 0).



FIG. 4. (Color online) Correlation functions $F_2(t_m)$ from ⁶Li and ¹⁰⁹Ag NMR stimulated-echo experiments on Li_{0.20}Ag_{0.80}PO₃ glass at T = 320 K. The lines are KWW fits (C = 0).

upon cooling, while the data yield no evidence for a temperature dependence of the pronounced stretching of the decays, indicating that time-temperature superposition is obeyed to a good approximation in the studied temperature range. In addition, comparison of the data for both nuclei reveals that lithium and silver ionic jump dynamics occur on comparable time scales in $\text{Li}_{0.50}\text{Ag}_{0.50}\text{PO}_3$ glass. Contrasting the present findings with that for the corresponding single-cation glasses, LiPO₃ and AgPO₃,^{30,31} two observations are striking: First, the silver and the lithium ionic hopping motions are considerably slower in the mixed-cation glass, reflecting the MME. Second, the nonexponentiality of the ionic jump correlation functions is reduced when mixing the ionic species.

In Fig. 4, we present $F_2(t_m)$ from ⁶Li and ¹⁰⁹Ag NMR stimulated-echo experiments on Li_{0.20}Ag_{0.80}PO₃ glass at T = 320 K. For this asymmetric mixture of lithium and silver ions, we see that the hopping motions of the ionic species do not occur on the same time scale, but rather the jump dynamics of the lithium ions (i.e., of the minority component) is significantly slower than that of the silver ions (i.e., of the majority component). An analogous behavior is observed for the ⁶Li, ⁷Li, and ¹⁰⁹Ag NMR correlation functions of Li_{0.75}Ag_{0.25}PO₃ glass; see Fig. 5. Again, the majority component, in this case the lithium ions, exhibits



FIG. 5. (Color online) Correlation functions $F_2(t_m)$ from ⁶Li, ⁷Li, and ¹⁰⁹Ag NMR stimulated-echo experiments on Li_{0.75}Ag_{0.25}PO₃ glass at T = 360 K (or T = 364 K for ⁷Li). The lines are KWW fits (C = 0).

faster jump dynamics than the minority component, although the difference is less pronounced than for x = 0.20. Thus, both ionic species escape from their initial sites at comparable times in the symmetric mixture of lithium and silver ions, x = 0.50, while diverse jump rates of the ionic species exist in the studied asymmetric mixtures. Furthermore, it is evident in Figs. 3–5 that, in general, the ionic species of a mixed-cation glass show hopping correlation functions with different nonexponentialities. This discrepancy is particularly prominent for x = 0.20; see Fig. 4. Clearly, the stretching is more pronounced for silver ions than for lithium ions in this glass. Finally, we observe small residual correlations ($C \le 0.1$) at long mixing times t_m , indicating that a substantial fraction of truly immobile lithium or silver ions does not exist for the studied glass compositions and temperatures.

When comparing the ⁶Li and ⁷Li data for x = 0.75 in Fig. 5, it is evident that both correlation functions decay on a similar time scale, while the stretching is more pronounced for ⁶Li than for ⁷Li. The former finding indicates that our results on the lithium ionic jump rates are independent of the probe nucleus used. This finding is in harmony with previous conductivity⁴⁹ and NMR relaxometry⁵⁰ measurements. These experiments on lithium borate glasses demonstrated that a ⁶Li vs. ⁷Li isotope effect leading to significant variations of conductivity or spin-lattice relaxation times could not be found. However, it is clear that, in a glassy matrix, the mass difference of the two stable lithium isotopes should affect their respective vibrational frequencies. Such a mixed-isotope effect was considered long ago. 15,51 Via its impact on the distribution of transition rates among different ion sites this could lead to differences in the shape of the corresponding correlation functions.⁵²

Whether these effects are sufficient to fully account for the different degrees of stretching as seen for the two lithium isotopes in Fig. 5 is not clear. This is because further NMR-specific effects need to be kept in mind: In ⁶Li and ⁷Li NMR, Li-Li dipolar interactions cannot be neglected completely so that the resonance frequency of a nucleus changes not only when the corresponding ion jumps to a new site, but it also fluctuates when neighboring lithium ions are redistributed.²⁹ As a consequence, there may be single-particle and multiparticle contributions to the decays of the measured correlation functions. The importance of these contributions depends on the relative strengths of the quadrupolar and dipolar interactions, which differ for ⁶Li and ⁷Li, and, in general, single-particle and multiparticle correlation functions should exhibit different stretching. Therefore, the different degrees of nonexponentiality of the ⁶Li and ⁷Li NMR correlation functions may also result from the effect that single-particle and multiparticle effects come along with diverse stretching and contribute differently to the respective data.

KWW fits enable quantitative analysis of the lithium and silver ionic jump dynamics. Free fits do not yield evidence for a systematic temperature dependence of the stretching parameter β_K , consistent with the results of visual inspection of the data (see Fig. 3), but they can lead to substantial scattering of the values. Therefore, we performed a second round of fitting keeping β_K fixed at the average value for a given glass composition. The fit parameters τ_K and β_K resulting from the latter approach were used to calculate



FIG. 6. (Color online) (a) Temperature dependence of the mean correlation times $\langle \tau \rangle$ describing lithium and silver jump dynamics in Li_xAg_{1-x}PO₃ glasses, respectively. The glass compositions *x* are indicated. The lines are fits to an Arrhenius law. (b) Temperatures *T* at which the mean correlation times of lithium and silver dynamics amount to $\langle \tau \rangle = 1$ s as a function of the composition.

mean correlation times according to Eq. (3). In Fig. 6(a), we compile the temperature-dependent mean correlation times $\langle \tau \rangle$ of the lithium and silver ionic hopping motions in all studied $Li_x Ag_{1-x} PO_3$ glasses. The analysis confirms that the ion dynamics is considerably faster in the single-cation glasses LiPO₃ and AgPO₃ than in the mixed-cation glasses and that both ionic species exhibit similar jump rates in the symmetric mixture, x = 0.50. Furthermore, we see that a reduction of the silver content results in a continuous slowdown of the silver ionic jumps, while such a continuous composition dependence does not exist for the lithium ionic jumps. Specifically, the mean correlation time of the lithium dynamics increases when the lithium fraction decreases from x = 1.0 to x = 0.50, while further replacement of lithium ions by silver ions does not result in a further slowdown of the lithium dynamics, as can be inferred from the results for x = 0.20.

To study the dependence of the ionic hopping motion on the glass composition in more detail, we determine the temperatures at which the ionic species show jump dynamics characterized by $\langle \tau \rangle = 1$ s. In Fig. 6(b), this temperature is a maximum at $x \approx 0.50$ for the lithium ions, while a linear dependence on the composition is evident for the silver ions.



FIG. 7. (Color online) Characteristics of lithium and silver jump dynamics in $\text{Li}_x \text{Ag}_{1-x} \text{PO}_3$ glasses as a function of glass composition. (a) Activation energies E_a of the hopping motion. The results from our NMR stimulated-echo experiments are compared with E_{dc} from present (star) and previous²⁴ (lines) measurements of the dc conductivity. The error bars of the NMR data amount to ± 0.1 eV. (b) Stretching parameters $\beta_{\rm K}$ of the ionic jump correlation functions. The errors are less than ± 0.05 .

The temperature dependence of $\langle \tau \rangle$ is described by an Arrhenius law for the studied $Li_xAg_{1-x}PO_3$ glasses. The corresponding activation energies E_a are displayed in Fig. 7(a). We see that the silver ionic jumps show higher activation energies in the mixed-cation glasses than in the single-cation glass, in harmony with slower ion dynamics in AgPO₃, see Fig. 6(b). As for the lithium ionic hopping motion, the activation energies do not show a clear composition dependence, but large error bars of up to ± 0.1 eV hamper a more detailed discussion. Nevertheless, the ⁶Li, ⁷Li, and ¹⁰⁹Ag data for x = 0.75 consistently reveal an interesting effect. For this composition, the activation energies of lithium and silver ionic jump dynamics, which amount to ca. 0.62 and 0.85 eV, respectively, are substantially smaller than the value of about $E_{\rm dc} = 1.0 \text{ eV}$ found in previous²⁴ and present measurements of the dc conductivity. These pronounced discrepancies imply that short-range dynamics, as observed in NMR, and longrange dynamics, as probed in conductivity studies, show a different temperature dependence. Such a difference was not observed in previous studies on single-cation glasses,^{28,29} suggesting that this effect is typical of "mixed glasses."

Figure 4(b) shows the stretching parameters β_K of the lithium and silver ionic correlation functions as a function of the composition. We see that, for both ionic species, the stretching parameter increases when the relative concentration

of a cation species decreases. In particular, the value of β_K is higher in the mixed-cation glasses; that is, lithium and silver ionic relaxations become more exponential upon mixing of the ionic species. Moreover, it is evident that silver relaxation is more nonexponential than lithium relaxation in the symmetric mixture x = 0.5. Consistently, the correlation functions of AgPO₃ glass are more stretched than that of LiPO₃ glass.

VI. DISCUSSION

For the studied $\text{Li}_x \text{Ag}_{1-x} \text{PO}_3$ glasses, ⁶Li, ⁷Li, and ¹⁰⁹Ag NMR stimulated-echo experiments indicated that the jump motion of both lithium and silver ions is slower in the mixed-cation glasses than in the corresponding single-cation glasses. Hence, the MME can be observed not only on a macroscopic level (e.g., via conductivities or diffusivities), but also on a microscopic level. While the correlation functions of lithium and silver jump dynamics are characterized by similar mean correlation times for the symmetric mixture (x = 0.50), the dynamics of the respective majority component is faster than that of the minority component for the asymmetric glass compositions. The silver ionic jumps continuously slow down when the silver content is reduced in the studied composition range. The lithium ionic hopping motion is most sluggish for a 50:50 mixture of lithium and silver ions, but the dependence of the ionic jump dynamics on the glass composition is substantially weaker for lithium than for silver. These findings imply that the difference in the ionic radii plays a role for the effect of cation mixing on the ionic hopping motion. Consistently, stronger effects on the dc conductivity of Li-Ag tellurite oxide glasses were found when lithium ions replace silver ions than in the opposite case.⁵³ For the glass compositions and temperatures studied in the present work, the decays of the correlation functions of lithium and silver jump dynamics rule out that a substantial fraction of immobile ions exists on the time scale covered by the stimulated-echo experiments (i.e., the one set by the reported mean ion-hopping correlation times). In contrast, by analyzing electric conductivity spectra of Li-Na borate glasses, previous work argued that the effective number of mobile ions is strongly reduced in mixed-alkali glasses.⁵⁴ Further comments on this issue may be found in Ref. 3.

When comparing present and previous findings relating to the MME, it is important to consider that, usually, smaller ions are more mobile than larger ions, whereas, in our case, the larger silver ions show faster dynamics than the smaller lithium ions. Like NMR, radiotracer diffusion experiments allow one to separately analyze the dynamical behavior of the mobile ion species in mixed-cation glasses. Both methods provide access to microscopic dynamics and macroscopic transport, respectively. For Na-Rb borate glasses, a tracer diffusion study reported that dilution of the larger rubidium ions results in a strong and continuous decrease of their diffusivity, while the dependence of the diffusivity of the smaller sodium ions on the glass composition is weaker and levels off at sufficiently small sodium content.¹² Furthermore, the diffusivity of the respective majority component was found to be higher than that of the minority component at both ends of the composition range. Qualitatively, these findings for the diffusivity are consistent with our results for the composition-dependent lithium and silver ionic jump rates. Differences result, for example, because the macroscopic transport is slowest on the small-ion–rich side for Li-Ag mixtures and on the large-ion–rich side for Na-Rb mixtures. The diffusivity data together with findings for the internal friction, including the vulnerability, were rationalized assuming that the fraction of vacant ionic sites is small.^{13,55} Such small concentrations of vacant ionic sites were indeed found in molecular dynamics simulations of glassy ion conductors.^{19,56–58}

Previous ⁷Li and ²³Na NMR spin-lattice relaxation studies on various mixed-cation silicate glasses reported that the energy barriers become higher and the lithium and sodium dynamics become slower when mixing two kinds of mobile ions,^{26,27} consistent with the present results. For most singlecation glasses, spin-lattice relaxation analysis yields activation energies E_a that differ substantially from E_{dc} ,^{28,59} while $E_a \approx$ $E_{\rm dc}$ is usually observed in stimulated-echo approaches.^{28,29} unlike spin-lattice relaxation Moreover, analysis, stimulated-echo experiments enable direct measurement of the correlation functions of ion jump dynamics. Relating to the activation energies obtained from our ⁶Li, ⁷Li, and ¹⁰⁹Ag NMR stimulated-echo decays on $Li_x Ag_{1-x} PO_3$ glasses, two effects are conspicuous: First, comparison of Figs. 6 and 7 reveals that, for the activation energies, the dependence on the glass composition differs somewhat from that of the mean correlation times, indicating that the residence times of the ions at their sites do depend not only on local energy barriers, but also on other factors. Second, the present values of E_a are significantly smaller than E_{dc} (Ref. 24) for compositions in the vicinity of the conductivity minimum at x = 0.8. Hence, in contrast to findings for LiPO₃³⁰ and AgPO₃³¹ glasses, for such glass compositions, stimulated-echo experiments do not probe the decisive step of macroscopic charge transport; that is, a mixing of mobile ion species enhances differences between short-range and long-range dynamics.

Interestingly, we observed that the NMR correlation functions of a mobile ion species become more and more exponential when this species is successively substituted by the other mobile ion species. In particular, we found that the ¹⁰⁹Ag and ⁶Li NMR correlation functions are less stretched in the studied mixed-cation glasses than in the corresponding single-cation glasses. The microscopic origin of the nonexponentiality of NMR two-time correlation functions for ion jump dynamics can be determined based on NMR three-time correlation functions.²⁸ Recently, analysis of ¹⁰⁹Ag and ⁶Li NMR threetime correlation functions of Li_{0.5}Ag_{0.5}PO₃ glass indicated that the nonexponentiality is largely due to an existence of a broad distributions of jump rates,²⁹ consistent with findings for various glassy and crystalline solid-state electrolytes featuring a single mobile ion species.^{35–37} Hence, the present results imply that the rate distributions governing the jumps of a mobile ion species become narrower when this species is replaced by another mobile ion species. However, the behavior may be different above and below T_g . For example, a photoncorrelation spectroscopy study on lithium-sodium phosphate glasses concluded that a mixing of cations increases the heterogeneity at $T > T_g$,⁶⁰ different from our findings at $T < T_g$.

Recent studies agree upon the relevance of structural aspects for the MME. Specifically, there is evidence that

the sites in the glassy matrix are favorable for one type of ion, but unfavorable for the other type of ion, leading to the existence of preferential pathways for each kind of mobile ions.⁵ Therefore, it may be asked whether independent ionic jumps in preferential pathways are sufficient for a complete understanding of the dynamical behavior of mixed-cation glasses. Our findings relating to the dependence of the activation energy and the nonexponentiality of ion jump dynamics on the glass composition are difficult to explain within such a scenario. Specifically, mixing may be expected to lead to additional energetic disorder and, thus, to broader rate distributions, at variance with less-stretched correlation functions in the mixed-cation glasses. Moreover, such a model does not explain that the composition dependence of the activation energy is different for lithium and silver ions. In the literature, it was argued that a mixing of mobile ion species in a mixed-cation glass resembles a reduction of the concentration of mobile ions in a single-cation glass.⁶¹ In particular, both changes were expected to reduce many-particle correlations and nonexponentiality when preferential pathways exit, consistent with the present composition dependence of the stretching parameter β_K .

Overall, this leads us to conclude that single-particle dynamics among preferred ionic sites is not sufficient to describe ion transport in mixed-cation glasses. Rather, we propose that it is important to include mutual exchange between the two types of ions, the existence of broad distributions of jump rates, and correlations of ionic motions, which involve both ion species. The relevance of these effects differs for microscopic and macroscopic dynamics, as indicated by the difference of the respective activation energies. Therefore, one may speculate that less mobile ions effectively block the dynamics of like and unlike ions on length scales of several interatomic distances and, thus, suppress effective relaxation pathways and delay the charge transport, while the ions may still explore their local environments. Mutual exchange between the ionic species and cooperative dynamics, including direct and indirect dynamical couplings of unlike ions, was already used to explain various experimental observations relating to the MME.^{22,23,62} For example, cooperative motions in common conduction pathways were found to be of particular importance for Na-Ag phosphate glasses.⁶³ In molecular dynamics simulation work on the mixed-cation effect in silicate glasses,^{19–21} cooperative motions of like and unlike ions were reported and a blockage of cooperativity^{20,21} due to less mobile particles was discussed.

VII. CONCLUSION

NMR stimulated-echo experiments have proven a versatile tool to measure correlation functions of the lithium and silver ionic jump dynamics in mixed-cation glasses and, hence, to provide microscopic insights into the nature of the MME. For $Li_x Ag_{1-x}PO_3$ glasses, cation mixing more strongly affects the jump rates of the larger silver ions than those of the smaller lithium ions. For both kinds of mobile ions, the correlation functions become more exponential when diluting the observed species by the other species. Moreover, the activation energies of the microscopic lithium and silver motions become smaller than that of the macroscopic transport upon mixing of the cationic species. The present observations imply that dynamical heterogeneities and correlations on length scales of several interatomic distances, which involve both kinds of mobile ions, are important aspects of ion dynamics in mixed-cation glasses and, hence, these effects need to be considered in theories of the MME.

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