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NMR and conductivity studies of the mixed glass former effect in lithium borophosphate glasses

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Alkali ion charge transport has been studied in a series of mixed glass former lithium borophosphate glasses of composition 0.33Li2O + 0.67[xB2O3 + (1 – x)P2O5]. The entire concentration range, 0.0 ≤ x ≤ 1.0, from pure glassy Li2P2O11 to pure glassy Li2B2O7 has been examined while keeping the molar fraction of Li2O constant. Electrical conductivity measurements and nuclear magnetic resonance techniques such as spin relaxometry, line shape analysis, and stimulated-echo spectroscopy were used to examine the temperature and frequency dependence of the Li+ ion motion over wide ranges of time scale and temperature. By accurately determining motional time scales and activation energies over the entire composition range the ion dynamics and the charge transport are found to be fastest if the borate and the phosphate fractions are similar. The nonlinear variation of the charge conduction, the most notable feature of the mixed glass former effect, is discussed in terms of the composition dependence of network former units which determine the local glass structure.

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I. INTRODUCTION

Amorphous solids with their wide glass forming ranges offer excellent opportunities for optimizing the physical properties of glass by continuously adjusting the chemical compositions, in both organic and inorganic materials. Well known examples where specific material characteristics and properties can be tailored and combined include non-crystalline polymer blends and polymer-plasticizer systems1 as well as multi-component glassy pharmaceuticals.2 Amorphous solid electrolytes constitute yet another active research area in which component mixing can have profound, often nonlinear, effects on ionic transport and many other properties.3 A famous example is the mixed cation effect in which combining melts containing two different alkali species results in glasses with an ionic conductivity that is often several orders of magnitude lower than either of the single-species glasses with the same total ion concentration.4, 5 A generally accepted framework for the theoretical explanation of this century-old mixed-alkali effect6,7 has emerged only recently.8

With a perspective on battery applications,9 it is of course more interesting to identify materials for which glass component mixing leads to an enhancement rather than to a reduction of the ionic conductivity and other charge transport characteristics. In this context, mixed matrix glasses of the type yM2O + (1 – y)(xA + (1 – x)B), where A and B are glass formers which feature only a single type of mobile alkali ion M, are particularly interesting. Here, the relative content y of alkali oxide, i.e., of the network modifier, is kept fixed while the composition x of the glass former species is varied, typically between 0 and 1. The components A ≠ B can be as diverse as SiO2, GeO2, BO1/2 (B2O3), and PO1/2 (P2O5), etc., or their sulfide analogs, such as SiS2, and GeS2, etc. Some glasses of this type were studied some time ago.10,11 Only recently, more of them have come under scientific scrutiny to specifically examine the role that mixed glass formers have upon glass structure and properties.12–15

Remarkably, some systems, e.g., with M = Na, A = B2O3, B = 2SiO2, exhibit a reduced conductivity at intermediate compositions x, while others, e.g., M = Na, A = B2O3, B = P2O5, exhibit an enhanced ion conductivity upon mixing. The existence of a positive as well as of a negative mixed glass former effect (MGFE) and the availability of numerous suitable network former components should allow one to distinguish purely chemical phenomena from the physical principles governing the nonlinear compositional effects. This opens the venue to a microscopic understanding of the properties of this interesting class of materials.

In fact, encouraging conceptual steps in this direction have been undertaken recently.16,17 These studies have pursued the goal of rationalizing the compositional dependence of the activation energies hindering ion transport in terms of the structural subunits present in these mixed network glasses. Such an approach is facilitated considerably by knowledge regarding the speciation of the various subunits that could be mapped out for a few ternary MGFE systems by virtue of nuclear magnetic resonance (NMR)18 spectroscopy as well as by vibrational spectroscopy19 and other structural probes.20,21

So far, charge transport in MGFE glasses has been explored mainly using impedance spectroscopy and tracer diffusion techniques.22 It is the purpose of the current work to obtain insight into the dynamics of 0.33Li2O + 0.67[xB2O3 + (1 – x)P2O5] mixed network former glasses by combining conductivity spectroscopy with various 7Li NMR techniques
to examine the mobile ion motions directly. In an effort to investigate the Li\(^{+}\) ion conduction process over a wide dynamic range of about six decades in time, we have combined spin-lattice relaxometry with line shape analyses as well as stimulated-echo spectroscopy.

II. THEORETICAL ASPECTS

NMR studies often exploit the dominating precession frequency \(\omega_0\) that depends on the local environment of the observed spins. The translational hopping motion of mobile ions among various sites renders \(\omega_0\) time and temperature dependent and therefore the motional time scale of the mobile ions becomes accessible. For the quadrupolar nucleus \(^7\text{Li}\) \((I = 3/2)\) the secular first-order quadrupolar Hamiltonian is given by

\[
\hat{H}_Q = \frac{1}{6} \omega_0 [3\hat{I}_x \hat{I}_z - I(I + 1)]
\]

(1a)

and

\[
\omega_0 = \frac{1}{2} \delta_Q (3 \cos^2 \theta_Q - 1 - \eta_Q \sin^2 \theta_Q \cos 2\phi_Q).
\]

(1b)

Here \(\delta_Q = \frac{3e^2 Q}{2I}\) designates the anisotropy parameter for nuclei with spin quantum number \(I = 3/2\) and \(\eta_Q\) denotes the asymmetry parameter. The angles \(\theta_Q\) and \(\phi_Q\) define the orientation of the principal axis system of the electric field gradient (EFG) tensor with respect to a laboratory frame wherein the external static magnetic field is directed along the \(z\)-axis. For an \(I = 3/2\) nucleus, the line shapes corresponding to the allowed non-central transitions, i.e., the ones for which \(m = +3/2 \Leftrightarrow m = +1/2\) and \(m = -1/2 \Leftrightarrow m = -3/2\), with \(m\) denoting the magnetic quantum number, can be calculated from Eq. (1b). While typical powder patterns are expected for polycrystalline samples which yield \(\delta_Q\) and \(\eta_Q\), the structural disorder in glasses causes a broad range of EFGs and this disorder is observed in the spectrum of the matrix. The central transition \((m = +1/2 \Leftrightarrow m = -1/2)\) remains unaffected by the quadrupolar interactions in the limit of first-order perturbation theory.

A. Solid echoes

Solid-echo NMR spectra of \(^7\text{Li}\) nuclei can be generated with the two-pulse sequence \(X_{90^\circ} - t_p - Y_{64^\circ} - I_0\) and a Fourier transformation of the time domain signal starting from the echo maximum. Here, \(t_p\) designates the evolution time which also defines the expected position of the signal maximum in the acquisition time \(t_0\). From a straightforward density matrix calculation using the Hamiltonian in Eq. (1a), for \(I = 3/2\), one expects spectra reflecting the three transitions described above: A central line with intensity \(I_C\) whose width predominantly reflects the dipolar interaction strength and two broad satellite lines with intensity \(I_S\) whose shape is dominated by quadrupolar effects. When the flip angle of the second pulse in the sequence given above is chosen to be \(64^\circ\), the solid echo approximately reproduces the theoretically expected intensity ratio, \(I_C/I_S = 2/3\), that can be generated from a free induction decay.\(^{23}\) At higher temperatures where successful ionic jump motions become more prevalent, the effect on the line shape depends significantly on the characteristic time scale \(\tau\) of the precession frequency changes with respect to the spectral dispersion \(\Delta\omega_{Q,D}\). Here, we use the indices \(Q\) and \(D\) to indicate the quadrupolar and the dipolar interactions, respectively. At sufficiently low temperatures where the hopping motion is much slower than the inverse linewidth, \(\tau \gg \Delta\omega_{Q,D}^{-1}\), the line shape is not affected by the ionic motion. The observed “rigid-lattice” spectrum in glasses can then often be described by a superposition of broad and narrow Gaussian line shapes, which reflect the quadrupolar and the dipolar broadened satellite and central transitions, respectively. With rising temperature, the motional correlation times shorten, reaching \(\tau \approx \Delta\omega_{Q,D}^{-1}\), and motional narrowing of the respective spectral contribution sets in at a temperature \(T_{\text{onset}}\). From \(T_{\text{onset}}\) of the central transition, Waugh and Fedin obtained a rough estimate of the ionic motion activation energy,\(^{24}\)

\[
\Delta E_a (\text{meV}) = 1.62 \times T_{\text{onset}} (\text{K})
\]

(2)

At much higher temperatures, at which the inverse motional correlation times are larger than the spectral dispersion, the spin environment appears averaged on the experimental time scale and the observed narrow line is then best described by a Lorentzian shape.

If a broad distribution of correlation times \(G(\tau)\) is present, as is found in many glasses,\(^{25-29}\) Eq. (2) is prone to underestimating the activation energy because motional narrowing takes place over a wide temperature range and \(T_{\text{onset}}\) only accounts for the fastest ions.

To resolve this problem, a powerful method for determining \(G(\tau)\) has been described in detail for \(^2\text{H}-\text{NMR}\)\(^{30,31}\) and has also been applied to lithium NMR.\(^{32-34}\) Briefly, a broad distribution \(G(\tau)\) gives rise to the appearance of both motional narrowing as well as broad, “slow” contributions in the spectra which are commonly called “two-phase” spectra. Starting from a superposition of weighted contributions, the temperature dependent \(^7\text{Li}\) spectra \(S(\omega,T)\) are usually written to consist of three parts,

\[
S(\omega,T) = S_C(\omega) \int_{\ln(\tau_Q)}^{\infty} g(\ln \tau) d \ln(\tau) + S_{Q,C}(\omega) \int_{\ln(\tau_Q)}^{\infty} g(\ln \tau) d \ln(\tau)
\]

\[
+ S_L(\omega) \int_{-\infty}^{\ln(\tau_Q)} g(\ln \tau) d \ln(\tau).
\]

(3)

Here, the time scales \(\tau^{*}_{Q,D}\) divide the ions into rapidly and slowly moving fractions. They are related to the second moments \(M_2\) or the standard deviations \(\sigma_{Q,D}\) of the rigid lattice spectrum via \(\tau^{*}_{Q,D} = 1/M_{2,Q,D} = 1/\sigma_{Q,D}\). The prefactors \(S_C(\omega), S_{Q,C}(\omega),\) and \(S_L(\omega)\) correspond to the normalized spectral intensities for the satellites, the central line, and the narrowed Lorentzian line shape, respectively. The two former ones, \(S_C\) and \(S_{Q,C}\), account for slow and the latter, \(S_L\), for fast motions. The first two integrals in Eq. (3) represent the temperature dependent weighting factor \(W_Q(T)\) and \(W_D(T)\), respectively. When the Arrhenius law

\[
\tau = \tau_0 \exp \left( \frac{-\Delta E_a}{k_B T} \right)
\]

(4)

holds for a thermally activated ionic jump motion, varying the temperature allows one to extract the underlying distribution
of activation energies (DAE) $g(\Delta E)$. As $g(\Delta E)$ represents a property of the rigid glassy matrix, we assume it to be temperature independent. With $g(\Delta E) d\Delta E = g(\text{ln} r) d\text{ln} r$ and the validity of an Arrhenius law assumed, one obtains $g(\text{ln} r) = k_B T \cdot g(\Delta E)$. If we furthermore assume $g(\Delta E)$ to be a Gaussian with a mean value $\Delta E_m$ and a second moment $\sigma_{\Delta E}^2$, the weighting factor is

$$W_Q(T) = S_5 \int_{\Delta E_m}^{\infty} g(\Delta E) d\Delta E = S_5 \left[ \frac{1}{2} - \frac{1}{2} \text{erf} \left( \frac{\Delta E^*(T) - \Delta E_m}{\sqrt{2} \sigma_{\Delta E}} \right) \right].$$

Here, erf($x$) denotes the error function and $\Delta E^*(T)$ is obtained from the derivative of the weighting factor with respect to temperature according to

$$\frac{dW_{Q,D}}{dT} = -S_5 k_B \ln \left( \frac{\tau_{P,Q}}{\tau_0} \right) g(\Delta E).$$

In the following, we focus on $W_Q$ and emphasize that the multi-particle nature of the dipolar interaction is hampering a straightforward interpretation of $W_D$.

### B. Stimulated echoes

Stimulated-echo experiments allow one to study the ion dynamics in the ultra-slow regime, i.e., at temperatures at which correlation times $\tau_c$ range from milliseconds to seconds. In our measurements, we apply the Jeener-Broekaert sequence$^{35} X_{90°} - t_p - X_{45°} - t_m - X_{45°} - t_p$ that has been used previously to study atom and ion dynamics.$^{32,36,37}$ During the evolution time $t_p$, the spins with their quadrupolar perturbed NMR frequency gain a phase label according to their specific charge or EFG environment. For pure quadrupolar perturbation, a spin-alignment state is created with the second pulse and the labeling is stored during the subsequent mixing time $t_m$. Following the last pulse, a spin echo is observed at a rephasing time near or equal to $t_p$. The signal amplitude yields information about the loss of phase correlation during $t_m$. More precisely, the two-time phase correlation function

$$F_2(t_p, t_m) = \frac{9}{20} \left[ \sin[\omega(t_m) t_p] \sin[\omega(t_m) t_p] \right]$$

is probed. In Eq. (7) the brackets $\langle \cdots \rangle$ denote an ensemble average. In the limit of sufficiently small evolution times, $F_2(t_p, t_m)$ probes the probability that an ion still or again occupies the same site after as before the mixing time. The decay of the echo signal with respect to $t_m$ is then interpreted to be due to the motion of the spin carrying ions that come along with changes of the dominating quadrupolar precession frequency. However, this simple interpretation is only possible if frequency changes of another origin can be neglected,$^{32,40}$ e.g., if dipolar correlations are kept small by sufficiently short evolution times. In experimental practice, further effects, such as spin relaxation and spin diffusion, can lead to a premotional decay of the echo, and can lead to be taken into account. The relaxation time $T_{1Q}$ of the spin-alignment state can be estimated from separate measurements of the spin-lattice relaxation time $T_1$, which for slow motions, $\omega_L \tau \gg 1$, and in polycrystalline samples is related to $T_{1Q}$ according to $T_{1Q} = 25k_B \beta_0$. Spin diffusion leads to magnetization transfer via a flip-flop process among the spins. This process is caused by dipolar interactions that are quite effective in the glasses studied here due to the large gyromagnetic ratio of the $^7$Li nuclei and can lead to a substantial damping of the echo amplitude at long times and low temperatures when the ion dynamics become slow.

The decay of the experimentally accessible stimulated-echo signal can usually be well described by a suitably adapted Kohlrausch function

$$I_2(t_p, t_m) \propto \exp \left[ -\left( \frac{t_m}{\tau_c} \right)^\beta \right] S(t_p, t_m) R(t_m).$$

Here, $\beta$ quantifies the non-exponentiality of the hopping correlation function that is observed for most solid electrolytes.$^{25} S(t_p, \text{ta})$ and $R(t_m)$ account for the effects of spin diffusion and of spin relaxation, respectively.

### C. Spin-lattice relaxation

Information regarding the dynamics on the time scale of nanoseconds, i.e., on the order of the inverse Larmor frequency is gained by performing spin relaxation experiments. While the measurement of spin-lattice relaxation times $T_1$ is straightforward, for an accurate interpretation of such experiments several aspects have to be considered. For $I = 3/2$, a slightly non-exponential relaxation is generally expected at low temperatures. The relaxation rate $1/T_1$ for an isotropic motional process at sufficiently low temperatures and caused by a fluctuating quadrupolar interaction is customarily related to the spectral density $J_2(\text{mos}) = 2 \tau_c/[1 + (\text{mos} \tau_c)^2]$ at multiples of the Larmor frequency,$^{33,44}$

$$\frac{1}{T_1} = K_Q \left[ J_1(\omega_L) + 4J_2(2\omega_L) \right].$$

Here, $K_Q = \frac{1}{\sqrt{3}} \delta^2(1 + \eta^2/3)$ is a metric of the quadrupolar coupling. In the presence of a broad distribution of correlation times $G(\tau)$, fluctuations of the magnetic field or the EFG at the spin site are effective on a wide range of rates. In our studies, we use the Cole-Davidson (CD) spectral density$^{25}$

$$J_{\text{CD}} = \frac{2 \sin[\beta_\text{CD} \arctan(\omega_{\text{CD}})]}{\omega[1 + (\omega_{\text{CD}})^2]^{3/2}},$$

which has proven effective in describing the spin-lattice relaxation times near the $T_1$ minimum. Under these circumstances, Eq. (9) describes an asymmetric curve on an inverse temperature scale. For high temperatures, $\omega_L \tau_{\text{CD}} \ll 1$, the relaxation rate $1/T_1$ follows the same activation energy $\Delta E_a$ as $\tau_{\text{CD}}$. In Eq. (10), the distribution parameter $\beta_{\text{CD}}$ describes the change of slope in the low-temperature regime $\omega_L \tau_{\text{CD}} \gg 1$ as compared to $\Delta E_a$. The parameter $\beta_{\text{CD}}$ is related to the stretching parameter of Eq. (8), although only numerical conversions exist.$^{35}$
III. EXPERIMENTAL DETAILS

A series of mixed lithium borophosphate glasses of composition $0.33\text{Li}_2\text{O} + 0.67\text{xB}_2\text{O}_3 + (1-x)\text{P}_2\text{O}_5$ was prepared from lithium carbonate (Li$_2$CO$_3$, Fisher Scientific, 99.8%), boric acid (H$_3$BO$_3$, Fisher Scientific, 99.7%), and di-ammonium hydrogen phosphate [(NH$_4$)$_2$HPO$_4$, Fisher Scientific, 99.7%]. The powders were pre-dried, mixed, and ground in the desired molar ratios. The mixtures were degassed and melted within platinum crucibles, which were introduced for 60 min into a furnace pre-heated to around 1300 K. The mixtures were stirred frequently to ensure homogeneity and to remove CO$_2$, NH$_3$, and H$_2$O. Because we have found that these glasses are slightly hygroscopic, afterwards the bubble-free glasses were quenched to room temperature, brought inside a high-quality glove box, $<5$ ppm O$_2$ and H$_2$O, and were remelted for 15 min in a furnace hermetically connected to the side of a nitrogen filled glove box. Following this second melting, the melts were quenched to $\sim$500 K into pre-heated sample molds and were annealed about 5 to 10 K below their glass transition temperature, $T_g$, for around 30 min and then cooled slowly, $\sim$5 K/min, to room temperature. Weight losses incurred during this procedure were generally found to be within 1% to 2%. All samples were kept in closed jars inside the glove box. For the NMR experiments, the glassy specimens were ground to fine powders and filled into quartz glass tubes which were then flame sealed under vacuum.

NMR measurements at Larmor frequencies of 117 and 150 MHz were performed using home-built spectrometers. For experiments below room temperature and up to 435 K, a cryostat from Oxford Instruments and a home-built probe were employed. For temperatures up to 890 K, a furnace was utilized which has been described elsewhere.$^{46}$ The temperature stability was about $\pm$0.2 K in each case. The duration of the 180$^\circ$ radio-frequency pulses ranged from 5 to 7 $\mu$s. Additional static $^7$Li NMR spectra were obtained at 77.8 MHz on a 4.7 T magnet operated with a Bruker DSX-400 spectrometer. Single-pulse spectra were obtained with 20$^\circ$ pulses of 2 $\mu$s length and relaxation delays of 120 s were used. These measurements were done in 20 K steps within a temperature range of 200–500 K.

Spin-lattice relaxation times were measured at 117 and 150 MHz using an inversion recovery pulse sequence combined with a solid echo for detection in order to circumvent the receiver’s dead time. These experiments were conducted at temperatures from 158 up to 454 K at 117 MHz and from 300 to 890 K at 150 MHz. A recovery time of about 4$T_1$ was inserted prior to each experiment. At temperatures below 280 K, the spin relaxation measurements were preceded by a saturation sequence.

The interpulse delay for the acquisition of solid-echo spectra was chosen to be $\Delta = 20$ $\mu$s. To minimize spectral noise, we performed an apodization of the recorded time signal with a Gaussian function before Fourier transformation. The phasing of all spectra was tuned by a first-order phase correction to minimize the dispersive part of the spectrum. For the spin-alignment experiments, the evolution times were set to 20 $\mu$s which is short enough to sufficiently separate the quadrupolar from the dipolar contributions in the time domain signal. The latter contribution produces a spectral pedestal at the quadrupolar echo maximum which amounts to less than 10% of the total echo amplitude. Experiments above the respective $T_g$ were performed carefully and checked in each single measurement against the occurrence of crystallization, which would manifest itself in substantially longer relaxation times in repeat experiments at lower temperatures.

Electrical conductivity measurements were carried out using a Novocontrol impedance spectrometer using a setup described previously.$^{47}$ Samples were measured within the frequency range $10^{-2}$–$10^6$ Hz, between 200 and 550 K at an applied voltage of 20 mV on polished samples of 1 to 2 mm thickness and $\sim$20 mm diameter. To improve the contact to the electrodes, the sample surfaces were covered with a layer of gold by radio-frequency sputtering using an Anatech Hummer V sputtering device inside the glove box. Temperatures were controlled within $\pm$0.2 K and samples were equilibrated for 30 min at each temperature.

IV. RESULTS AND ANALYSES

A. Electrical conductivity spectra

Figure 1 shows a typical conductivity spectrum over the temperature range considered for the $x = 0.5$ sample; results for all of the other glass compositions were found to be qualitatively similar. The sigma isotherms show the typical behavior of ion conducting glasses for which the electronic conductivity is essentially zero. The slopes observed in the low-frequency ranges at higher temperatures arise from electrode polarization effects. Towards higher frequency, the typical dc plateaus are observed which convert to the dispersive region towards yet higher frequencies. For all of the samples, $\sigma_{dc}$ was found to follow an Arrhenius temperature dependence, see however Ref. 47. The corresponding activation energies are summarized in Sec. VA2.

B. $^7$Li-NMR spectra

In Fig. 2, we present static $^7$Li single-pulse spectra of the central $-1/2$ ↔ $+1/2$ transition in the temperature range

![FIG. 1. Double-logarithmic representation of the electrical conductivity $\sigma(\nu)$ of a 0.33Li$_2$O + 0.67[0.5B$_2$O$_3$ + 0.5P$_2$O$_5$] glass as measured from 200 to 540 K in steps of 20 K. At high temperatures and low frequencies the data are affected by space charge (electrode polarization) effects.](image-url)
200 K < T < 500 K for x = 0.0, 0.5, and 1.0 glasses. For example, for the sample with x = 0.5, the central transition exhibits a Gaussian shape at low temperatures with a full width at half maximum of $\Delta \nu \approx 5$ kHz. With increasing temperature, the absorption line narrows continuously and indicates motional narrowing. At intermediate temperatures, the line shape can be described by a superposition of a Gaussian and a Lorentzian function, whereas at high temperatures only a narrow Lorentzian line remains. From Fig. 2, it can be seen that for the x = 0.5 glass, motional narrowing sets in at a temperature that is lower than $T_{\text{onset}}$ for the other two samples.

In Fig. 3, the linewidths are plotted against temperature for the x = 0.0, 0.3, 0.5, 0.7, and 1.0 glasses. For the binary glasses at the borate (x = 1.0) and phosphate (x = 0.0) limits, motional narrowing is observed at substantially higher temperatures, $T_{\text{onset}} \approx 329$ K and 345 K, respectively, than for intermediate compositions, e.g., $T_{\text{onset}} \approx 283$ K for x = 0.5. To highlight the observed x-dependence, we employed a parabolic fit to the inflection points in $\Delta \nu (T)$ and included the results for x = 0.1, 0.2, 0.4, 0.6, 0.8, and 0.9 (which are not shown in Fig. 3).

In Fig. 3, the line-width data are shifted vertically for display purposes only. It should be noted that the low-temperature linewidths, which are dominated by the homonuclear $^7$Li-$^7$Li magnetic dipole-dipole couplings, increase with x from $\Delta \nu \approx 3.9$ kHz for x = 0.0 up to 6.4 kHz for x = 1.0. We ascribe this broadening to the increase of the Li number density with increasing x and thus to stronger dipolar interactions towards the borate-rich side of the concentration range. Figure 4 shows a plot of the central line’s second moment $M_2 = \Delta \nu^2/(8 \ln 2)$, valid for a Gaussian line shape, as a function of the Li ion concentration $N_V$. Here $N_V$ was calculated from the molar volumes which in turn were deduced from experimentally determined densities. $M_2$ depends approximately linearly on $N_V$, see Fig. 4, as expected theoretically for a random Li ion distribution.49

For the x = 0.5 sample Fig. 5 shows a $^7$Li NMR spectrum at 280 K that also includes the satellite contributions. To describe the line shape quantitatively, we split the normalized spectral area into three contributions, as suggested by Eq. (3). Explicitly, we use a superposition of two Gaussian and one Lorentzian functions,

$$S(\omega) = \frac{A_Q}{\sigma Q \sqrt{2\pi}} \exp\left(-\frac{(\omega - \omega_0, Q)^2}{2\sigma^2_Q}\right) + \frac{A_D}{\sigma_D \sqrt{2\pi}} \times \exp\left(-\frac{(\omega - \omega_0, D)^2}{2\sigma^2_D}\right) + \frac{A_L}{\pi} \frac{\gamma L}{(\omega - \omega_0, L)^2 + \gamma^2 L}.$$  

(11)

FIG. 2. Static single-pulse $^7$Li-NMR spectra of 0.33Li$_2$O + 0.67[B$_2$O$_3$ + (1 – x)P$_2$O$_5$] with x = 0.0, 0.5, and 1.0 showing a narrowing of the central line with increasing temperature. The spectra in each frame were recorded for temperatures ranging from 200 K (spectra at bottom) to 500 K (spectra at top) in steps of 20 K.

FIG. 3. Full width at half maximum of the central line read out from the spectra exemplified in Fig. 2 and from corresponding data for 0.33Li$_2$O + 0.67[B$_2$O$_3$ + (1 – x)P$_2$O$_5$] with x = 0.3 and 0.7. The linewidths were shifted vertically by $x \times 10$ kHz to avoid overlap. The dashed line shows a parabolic fit through the temperature dependent inflection points in $\Delta \nu (T)$ for all sample compositions. This includes data for x = 0.1, 0.2, 0.4, 0.6, 0.8, and 0.9 which are not shown here.

FIG. 4. The dipolar second moments $M_2(^7$Li-$^7$Li) calculated from the full widths at half maximum are plotted as a function of the lithium ion number density $N_V$ in the glasses under study. $N_V$ steadily increases with x. The approximately linear dependence is consistent with a spatially random distribution of Li ions. The line is drawn to guide the eye.
decrease continuously with increasing temperature. The solid line represents a solid-echo spectrum of 0.33Li2O + 0.67[0.5B2O3 + 0.5P2O5] recorded at 280 K with an inter-pulse delay \( \Delta \) of 20 \( \mu \)s. The other lines reflect the various contributions of a combined fit to the spectrum. The shaded area and the red dashed-dotted line refer to Gaussian functions, whereas the blue dashed line corresponds to a Lorentzian contribution. See Eq. (3) and text for details. Frame (a) provides an overall view of the spectrum. In frame (b) the satellite contributions are magnified fivefold.

Here, the first two terms represent the satellite and the central transitions of the slowly moving ions whereas the last term accounts for the fraction of fast ions, with \( \gamma_L \) parameterizing the width of the latter spectral contribution. Each term is weighted with an appropriate amplitude \( A_{Q,D,L} \). The designations “slow” and “fast” refer to the appropriate reference time scale \( \tau_{Q,D}^\ast \). Equation (11) provides an excellent description of our spectra at all temperatures if we constrain \( \omega_{0,Q,D} \) and \( \omega_{0,L} \) to the values obtained from the spectra acquired at the lowest and highest temperatures, respectively. For the compositions \( x = 0.3 \) to 1.0, the Gaussian width of the satellites is about \( 2\pi \times 32 \) kHz. For the \( x = 0.0 \) glass, we find a much smaller width of \( \sigma_Q = 2\pi \times 22 \) kHz.

From best fits to Eq. (11), we calculated the weighting factors \( W_{Q,D} = A_{Q,D}/(A_Q + A_D + A_L) \), the temperature dependence of which is described by Eq. (5). We furthermore define the temperature \( T_{\text{max},Q,D} \) that marks the most probable energy barrier via

\[
\Delta E_m = k_B T_{\text{max},Q} \ln(\tau_Q^\ast/\tau_{0,Q}).
\]

The temperature dependence of the Gaussian contributions \( W_Q \) and \( W_D \) is shown in Fig. 6(a). As expected, \( W_Q \) and \( W_D \) decrease continuously with increasing temperature. These parameters account for the fraction of spins (or Li ions) that move slowly with respect to the time scale \( \tau_Q^\ast \) and \( \tau_D^\ast \), respectively. The fraction \( W_D \), relating to the central line, decays within a temperature range of about 150 K, whereas for the satellite contributions \( W_Q \) a much wider range of more than 300 K is observed. This indicates that there is a major difference between the narrowing of the quadrupolar satellites and of the dipolar broadened central line which arises not solely because of the difference in \( \tau_Q^\ast \) versus \( \tau_D^\ast \). In other words, the same motional process affects the two contributions in a substantially different fashion. The central line reflects a multiparticle interaction and therefore not only the motion of an observed spin itself but also the motion of adjacent ions leads to an averaging of the local frequency at the spin site.

From fits using Eq. (5), we obtained the first derivatives of the weighting factors, see Fig. 6(b). For these fits, we have taken \( \Delta E_a \) as the mean activation energy and the Arrhenius prefactor \( \tau_0 \) from Table I. For a more detailed description of how these parameters were determined for the \( x = 0.5 \) glass, see Sec. V A. Clearly, the satellites yield a distribution with a much higher maximum temperature \( T_{\text{max},Q} = (440 \pm 18) \) K than for the central line for which \( T_{\text{max},D} = (374 \pm 6) \) K. Keeping in mind the above argument of a more effective averaging of dipolar broadenings, this finding of vastly different \( T_{\text{max}} \) values is not surprising. With \( \sigma_Q = 2\pi \times 32 \) kHz and \( \sigma_D = 2\pi \times 2.1 \) kHz, the maximum temperatures correspond to characteristic time scales of \( \tau_Q^\ast \sim 5 \mu s \) and \( \tau_D^\ast \sim 76 \mu s \), respectively.

The weighting factors \( W_Q \) evaluated for different compositions \( x \) are compared in Fig. 7. Here, for clarity, we again shifted the data vertically according to their \( x \)-dependence. The binary glasses, \( x = 0.0 \) and \( x = 1.0 \), exhibit higher \( T_{\text{max},Q} \) values than the ternary glass with \( x \sim 0.5 \). The lines in this plot were calculated using Eq. (5) in conjunction with the

\[
\begin{align*}
\Delta E_a &= E_a(1 - x)P_2O_5 + E_a xP_2O_5 + E_a(1 - x)B_2O_3, \\
T_{\text{max},Q} &= T_{\text{max},Q} (1 - x)P_2O_5 + T_{\text{max},Q} xP_2O_5 + T_{\text{max},Q} (1 - x)B_2O_3, \\
\tau_0 &= \tau_0(1 - x)P_2O_5 + \tau_0 xP_2O_5 + \tau_0 (1 - x)B_2O_3.
\end{align*}
\]

\[
\begin{array}{cccc}
\text{TABLE I.} & \text{Compilation of various parameters determined for the 0.33Li_2O} \\
& \text{+ 0.67[0.5B_2O_3 + 0.5P_2O_5] glasses via the NMR techniques used in this work.} \\
x & \Delta E_a (eV) & \tau_0 (s) & \sigma_{\Delta E} (eV) \\
\hline
0.0 & 1.07 \pm 0.09 & 1 \times 10^{-16} & 0.14 \pm 0.02 \\
0.3 & 0.88 \pm 0.09 & 4 \times 10^{-16} & 0.20 \pm 0.05 \\
0.5 & 0.74 \pm 0.05 & 3 \times 10^{-14} & 0.18 \pm 0.05 \\
0.7 & 0.75 \pm 0.09 & 1 \times 10^{-13} & 0.2 \pm 0.1 \\
1.0 & 0.88 \pm 0.09 & 1 \times 10^{-14} & 0.2 \pm 0.1 \\
\end{array}
\]
Arrhenius parameters and energy widths $\sigma_{\Delta E}$ given in Table I and describe the experimental data very well.

C. Dynamics probed by two-time correlation functions

$^7$Li stimulated-echo experiments have been performed to study the ion dynamics in the low-temperature, slow-motion, regime. In Fig. 8(a), we present the normalized echo intensities for $x = 0.5$ at temperatures ranging from $T = 158$ K to $T = 387$ K. To describe our data, we use Eq. (8) and account for the decay of the spin-alignment state by an exponential function with a time constant $(8/25) \times T$ as motivated in Ref. 41. A decay (presumably due to spin diffusion with $T_{SD} \sim 0.7$ s) is indicated by the dashed line. Normalized stimulated-echo intensities of 0.33Li$_2$O + 0.35Li$^+$ + 0.5P$_2$O$_5$ at $T = 348$ K. The lines are fits to the data using Eq. (8). A non-monotonic evolution of the decay times as a function of the concentration $x$ is evident.

For Eq. (8), we obtain stretching parameters $\beta = 0.5, 0.35, 0.28, 0.38$, and 0.41 for $x = 0.0, 0.3, 0.5, 0.7$, and 1.0, respectively. For $T \geq 330$ K, the mutual differences between these parameters for different $x$ values are similar to the ones given here.

Below $\sim 330$ K, the decays of the correlation functions do not slow down as much as observed at higher temperatures, but become substantially more exponential indicating a non-negligible effect of spin diffusion that ultimately masks the decay due to ionic jump motions. To account for this premature decay of $F_2$, we determine the time constants $T_{SD}$ and stretching parameters $\beta_{SD}$ for spin diffusion from measurements at low temperatures. We find mean $T_{SD}$ of the order of seconds and $\beta_{SD} \sim 0.6 \pm 0.1$ without any evident composition ($x$) dependence.

Figure 8(b) depicts normalized echo intensities recorded for all of the glasses at $348$ K. In these glasses, $F_2$ decays to zero at long $t_m$ as expected by the stretched exponential function in Eq. (8). From this we find that the Li$^+$ ion dynamics are more than one order of magnitude faster in the $x = 0.5$ glass than either for the $x = 0.0$ or for the $x = 1.0$ glass. The decays of the $F_2$ functions are all strongly non-exponential indicating that the underlying distributions of correlation times are broad. From Fig. 8(b) one recognizes that the response of the $x = 0.5$ glass is the most stretched, in accord with the expectation that in this sample the largest diversity of network former environments should be present. From fits using Eq. (8), we find almost constant $T_{SD}$ values and a slight decrease for larger $t_p$ (not shown). The latter arises from the growing dipolar contribution, thereby hampering a simple interpretation of the decay time.

D. Spin relaxation measurements

In Fig. 9, the measured spin-lattice relaxation times are summarized for sample compositions $x = 0.0, 0.3, 0.5,$ and

![Image](https://via.placeholder.com/150)
Above 300 K, we observe single exponential magnetization recovery curves \( M(t) \propto \exp[-(t/T_1)^{\beta}] \) with \( \beta = 0 \) and below 300 K slight deviations from exponential magnetization recovery occur. At the lowest investigated temperatures, fits using the given Kohlrausch function yield \( \mu = 0.04 \), except for \( x = 0 \) where \( \mu = 0.16 \) below 200 K. In Fig. 9, we present the mean relaxation times, taken over the distribution underlying the Kohlrausch function, \( \langle T_1 \rangle = T_1 (1 - \mu)^{-1} \Gamma[1 - \mu] \), with \( \Gamma \) denoting Euler’s Gamma function. At the low temperature end, the spin-lattice relaxation times become almost temperature independent and samples with increasing boron content exhibit shorter \( T_1 \) as documented in the inset of Fig. 9.

With increasing temperature, \( T_1 \) becomes significantly shorter until at values of \( \langle T_1 \rangle \approx 0.1 \) s we find minima at 775, 676, and 752 K for \( x = 0.0, 0.3, \) and 0.5, respectively.\(^{51} \) For \( x = 0 \) this minimum occurs at temperatures substantially higher than the glass transition temperature, whereas in the \( x = 0.3 \) and 0.5 samples, the temperature of the minimum appears to coincide roughly with \( T_g \). Unfortunately, for the modestly conducting oxide glasses under study, it is not possible for the Larmor frequencies used here to detect a \( T_1 \) minimum below \( T_g \) for any of the glasses. A straightforward quantitative analysis of the data in Fig. 9 on the basis of Eq. (9) in conjunction with a single suitable spectral density seems therefore not to be appropriate: For all the glasses except the one with \( x = 0.0 \), the \( T_1 \) values measured on the different two sides of the minimum, at low and high temperatures, refer to two different physical states. The high-temperature side refers to the supercooled melt while the low-temperature side refers to the glassy state. These different states can be expected to be associated with different activation energies and spectral densities.\(^{52} \) Therefore, we chose to estimate the width parameter of the latter using the following procedure: For Cole-Davidson spectral densities, cf. Eq. (10), we expect an asymmetrically shaped minimum with a “reduced” slope \( \beta_{CD} \Delta E_a \) in the low-temperature regime, \( \omega_1 \tau \gg 1 \), as compared to the behavior in the high-temperature limit, \( \omega_1 \tau \ll 1 \), where the magnitude of the slope is simply \( \Delta E_a \). However, since the high-temperature regime does not occur in the glassy state, but rather above \( T_g \) in the (supercooled) liquid, it is not possible to obtain \( \Delta E_a \) by analyzing the \( T_1 \) data in that regime. Therefore, for a determination of \( \Delta E_a \) we have to resort to the various echo techniques that were applied below \( T_g \). For \( x = 0.5 \) the corresponding Arrhenius plot (see Fig. 10, below) is presented and discussed in detail in Sec. V A 1. From these data and those of other concentrations \( x_{CD} \) was evaluated via the Arrhenius relation, Eq. (4), yielding \( \tau_0 \) and \( \Delta E_a \) as summarized in Table I. Use of these activation energies together with the “reduced” ones as obtained from fitting \( T_1 \) in the slow-motion regime yields the distribution parameter \( \beta_{CD} = 0.28 \pm 0.11 \) for \( x = 0.5 \). For the curve shown in Fig. 9 we set \( \delta_1 \tau = 86 \) kHz as the anisotropy parameter for \( x = 0.5 \). The curve describes the data even above \( T_g \) into the supercooled liquid state with only slight deviations. According to Eqs. (9) and (10), the condition for the \( T_1 \) minimum becomes \( \omega_1 \tau_{CD} < 1 \), which means \( \tau_{CD} = 2.0 \) ns at 752 K for \( x = 0.5 \). The corresponding analysis yields \( \beta_{CD} = 0.43 \pm 0.13, \delta_1 \tau = 83 \) kHz, and \( \tau_{CD} = 1.4 \) ns for \( x = 0.0 \) and \( \beta_{CD} = 0.30 \pm 0.06, \delta_1 \tau = 82 \) kHz, and \( \tau_{CD} = 1.6 \) ns for \( x = 0.3 \). The relatively good agreement between experimental data and calculated \( T_1 \) curve, even above \( T_g \), suggests that the activation energy is not altered dramatically while passing through \( T_g \). This is not entirely unexpected for the decoupled ion conductors we deal with in the present investigation.\(^{52} \)
Spin-spin relaxation times $T_2$ have been measured using a solid-echo pulse sequence in the temperature range from $T = 158$ K up to 890 K. We find a $T_2$ minimum at $T = 424$ K for $x = 0.5$ (not shown). At this temperature, the correlation time is of the order of the inverse satellite linewidth, i.e., $\sigma_Q \tau \sim 1$. Here, $\sigma_Q$ represents the quadrupolar linewidth parameter of the rigid lattice spectrum and $\tau$ is the correlation time of the fluctuations determining the temperature at which the $T_2$ minimum is observed. We obtain $\tau \sim 5 \, \mu s$ (for $x = 0.0$ an analogous analysis yields $\tau = 7 \, \mu s$).

V. DISCUSSION

A. Time scales, activation energies, and their distribution

1. Time scales for $x = 0.5$

Using various NMR techniques and from conductivity experiments, we collected time constants $\tau_c$ over a wide dynamic range from nanoseconds to milliseconds and present them on an inverse temperature scale for $x = 0.5$ in Fig. 10. This figure includes time constants obtained from two-time correlation functions, cf. Fig. 8(a), from the minima of the spin-lattice relaxation times $T_1$ and of the spin-spin relaxation times $T_2$, see Sec. IV D, as well as from the maximum of $dW_Q(T)/dT$, see Fig. 6(b). Applying the Arrhenius law, Eq. (4), to the data shown for $T > 310$ K in Fig. 10 then yields an activation energy $\Delta E_a = 0.74$ eV and a pre-exponential factor $\tau_0 = 3 \times 10^{-14}$ s for the ion hopping in $0.33\text{Li}_2\text{O} + 0.67[0.5\text{B}_2\text{O}_3 + (1 - x)\text{P}_2\text{O}_5]$ as included in Table I. At temperatures below 310 K, the time constants obtained from the $F_2$ measurements deviate significantly from an Arrhenius behavior, possibly indicating the contribution from a second process. Spin-lattice relaxation times are always at least 100 times longer than the time constants measured via stimulated echoes. Since we are mainly interested in ion hopping times, we restricted our analysis to temperatures higher than 310 K.

Apparently, the determination of correlation times from high-field $T_1$ measurements of the $x = 0.5$ glass requires experiments above its calorimetric glass transition temperature, $T_g \sim 732$ K. Since $T_g$ usually corresponds to a structural matrix relaxation time of the order of 100 s, whereas at the $T_1$ minimum the correlation time for the ion motion is close to 1 ns, the two time scales are well separated from each other. Hence, near $T_g$ the $\text{Li}^+$ ions can be considered to be fully decoupled from the motion of the underlying network structure, a situation that is common for fast ion conducting glasses. Nevertheless, the situation remains that above $T_g$ the mobile $\text{Li}^+$ ions are conducting within a slowly and viscously relaxing matrix and as such, the dynamics of the $\text{Li}^+$ ion motion will reflect, however limited, this motion. In measurements of the ionic conductivity of such glasses above $T_g$, this is observed as a higher and temperature dependent activation energy. The higher activation is thought to arise from the conduction process now encountering the added temperature dependent structural relaxation of the viscous liquid network. See, for example, Ref. 53.

From the electrical conductivity $\sigma'(\nu)$ of $0.33\text{Li}_2\text{O} + 0.67[0.5\text{B}_2\text{O}_3 + 0.5\text{P}_2\text{O}_5]$ a conductivity relaxation time,54

$$\tau_\sigma = \varepsilon_0\varepsilon_\infty/\sigma_{dc},$$

was extracted and the results are included in Fig. 10. Here $\varepsilon_0$ is the permittivity of free space and $\varepsilon_\infty$ is the high-frequency dielectric constant (8.7 for $x = 0.5$). The time constants $\tau_\sigma$ thus obtained are in good agreement with those determined from the various NMR techniques.

2. Compositional dependence

To delineate the compositional dependence of the time scales, in Fig. 11 we plot the dc-conductivities, the correlation rates from $F_2$, and the spin-lattice relaxation rates versus the boron-oxide content for various temperatures. Obviously, $\sigma_{dc}$ is proportional to the thermally induced hopping rate $\tau_c^{-1}$ measured by NMR. A similar argument applies to the spin-lattice relaxation time below its minimum which, according to Eqs. (9) and (10), yields $\tau_1 \propto \tau_c^{1/2}$. Furthermore, it is clearly seen that all experimental methods reveal an enhanced ion mobility between $x = 0.4$ and 0.5 demonstrating the MGFE. Creating a hybrid matrix seems to enable the ions to perform a faster motion through the glass. Furthermore, in the $0.33\text{Li}_2\text{O} + 0.67\text{P}_2\text{O}_5$ glass, the matrix hinders the ion motion, i.e., having a higher activation energy, substantially more than in the borate glass. Evidently, the anionic metaphosphate groups form deeper Coulomb traps compared to the anionic BO$_4$ groups in the borate glass system.

Figure 12 depicts the activation energies $\Delta E_a$ obtained via the different techniques and demonstrates that
consistent results are obtained within the experimental uncertainties. Clearly, all data display the MGFE, i.e., reduced activation energies in the mixed systems, exhibiting a minimum near $x = 0.5$. Only the activation energies estimated from the temperature $T_{\text{onset}}$, at which motional narrowing of the spectra sets in, cf. Eq. (2) due to Waugh and Fedin,24 yields consistently smaller activation energies, nevertheless exhibiting the same compositional trend as the other data in Fig. 12.

### 3. Distribution of activation energies

As illustrated in Fig. 6 for $x = 0.5$, distributions of activation energies, $g(\Delta E)$, can be evaluated from detailed line shape analyses. Furthermore, $g(\Delta E)$ is accessible from an appropriate scaling of spin-lattice relaxation times $T_1$ as follows:45 We start from a superposition of spectral densities, yielding the relaxation rate, cf. Eq. (9),

$$\frac{\omega_n}{T_1} = K_Q \int_0^\infty G(\tau) \left[ \frac{\omega_n \tau}{1 + \omega_n^2 \tau^2} + \frac{4 \omega_n \tau}{1 + 4 \omega_n^2 \tau^2} \right] d\tau. \quad (14)$$

We use the Arrhenius law to connect $G(\tau) = k_B T / \tau \cdot g(\Delta E)$ to the DAE and, if $g(\Delta E)$ is broad enough to consider it as constant regarding the integration, Eq. (14) reduces to

$$g(\Delta E) \approx \frac{2 \omega_n}{3 \pi K_Q T_1 k_B T}. \quad (15)$$

Since the temperature is related to the energy scale by $\Delta E = -\ln(\omega_n T_0) k_B T$, cf. Eq. (12), appropriate scaling of $T_1$ can be used to determine $\tau_0$ as given in Table I. Applying the scaling procedure suggested by Eq. (15) for $x = 0.0, 0.3, 0.5, 0.7$, and 1.0 yields the results shown in Fig. 13. The DAE obtained at different Larmor frequencies are seen to fit together nicely if we set the coupling constant to $K_Q = (1400 \pm 400)$ kHz$^2$. The DAE evaluated from $dW_Q(T)/dT$, cf. Sec. IV B, are included as solid lines in Fig. 13 as well. The DAE from both methods of determination are seen to be compatible with each other, within the sometimes considerable experimental uncertainty. Only for the $x = 0.0$ glass are the scaled $T_1$ data peaked at a slightly lower mean activation energy as compared to the one yielded by $dW_Q(T)/dT$. Shifting the data by an offset of $x$, as done in Fig. 13, we again find a clear depiction of the MGFE as one tracks the evolution of the DAE maxima.

The widths of the DAE shown in Fig. 13 are fairly large, nearly 20% of the average. In view of the considerable uncertainty in determining the detailed shape of these DAE, however, we refrain from discussing any possible $x$-dependence of their widths, $\sigma_{\Delta E}$, beyond stating that the $x = 0$ glass exhibits the narrowest distribution. Based upon recent studies it might be expected that a 20% width of the average results in significant deviations from Arrhenius behavior in various Li$^+$ transport coefficients. However, such deviations be noticeable in an Arrhenius plot only at relatively low temperatures.47 We are in the process of measuring the Li$^+$ ion conductivity of these glasses to lower temperatures to examine their DAE in detail.

### B. Correlation of transport with the composition dependence of glass structure

In the present section we will discuss the compositional changes of the Li$^+$ transport in terms of the $x$-dependence of the local structural building blocks. An excellent review of the structures of these and related glasses in relation to the MGFE is available, see also Ref. 56. Therefore, here we will focus on the most important structural changes that are occurring for the present glass system. These changes concern those structures in which mobile Li$^+$ ions are involved. We will begin with the structures of the binary lithium phosphate...
glasses and consider the effect of $B_2O_3$ additions, small $x$, to this glass, then progress to glasses rich in $B_2O_3$, large $x$, and finally to pure binary lithium borate glasses.

By analogy with sodium phosphate glasses a $0.33Li_2O + 0.67P_2O_5$ glass is known to consist of two network forming units (NFUs), the so-called $P^{(3)}$ and $P^{(2)}$ structures. Here the superscript refers to the number of bridging oxygens (BOs) on the central P atom, possessing no or one formal negative charge, respectively. Overall charge balance with the Li$^+$ ions requires that the fraction of $P^{(2)}$ of the singly negatively charged $P^{(2)}$ NFUs in these binary glasses is $\{P^{(2)}\} = (2 \times 0.33)/(2 \times 0.67) = 0.5$. Hence in the absence of other P groups, the fraction of the electrically neutral metaphosphate, $P^{(3)}$, groups is $\{P^{(3)}\} = 1 - \{P^{(2)}\} = 0.5$.

As $P_2O_5$ is substituted by $B_2O_3$, $x > 0$, it was found that all of the added B is incorporated into the glass in the form of $B^{(4)}$ units even though the base binary glass $0.33Li_2O + 0.67B_2O_3$ ($x = 1$) is found to consist of $\sim 45\%$ $B^{(4)}$ units, $\sim 45\%$ $B^{(3)}$, and $\sim 10\%$ $B^{(2)}$. The formation of $B^{(4)}$ units in the ternary glasses can be thought to arise from the reaction of a neutral $B^{(3)}$ unit with a $P^{(2)}$ unit. In a shorthand notation which also indicates the charge states ($q = 0$ and $1 -$) of the NFUs this disproportionation reaction can be written as:

$$ (B^{(3)})^0 + (P^{(2)})^{1-} \rightarrow (B^{(4)})^{1-} + (P^{(3)})^0. \quad (16) $$

Hence, with increasing borate content up to $x \sim 0.5$, anionic $P^{(2)}$ units are formally being replaced by anionic $B^{(4)}$ units. A recent model enables one to compute the compositional evolution of the various NFU fractions in mixed matrix glasses.

A comparison of the $x$-dependence of the activation energies (Fig. 12) with that of the formally charged NFUs (i.e., $B^{(4)}$ and $P^{(2)}$, see Fig. 14) reveals a striking similarity. A related observation was made for the sodium borophosphate glass system $0.4Na_2O + 0.6[xB_2O_3 + (1-x)P_2O_5]$: It was shown that the macroscopic ionic conductivities as well as the microscopic characteristic lengths of charge transport in these glasses follow the same compositional dependence as the concentration of four-coordinated boron atoms. In fact, evidenced by experimental data from $^{31}P$ and $^{11}B$ NMR as well as from XPS and vibrational spectroscopy a correlation similar to that shown in Fig. 14 has been found most recently for the present glass system, see Ref. 48.

Bond valence considerations indicate further that the formal charges in Eq. (16) are in reality re-distributed within the $B–O–P$ linkages so that Eq. (16) must be considered a simplification only for book-keeping purposes. As discussed in detail elsewhere, the formal charge associated with a $B^{(4)}$ unit linked to four $P^{(3)}$ species is dispersed over the four non-bridging O atoms of the latter. Hence, with increasing borate content, the mobile Li$^+$ ions bound to discrete non-bridging oxygens on the $P^{(2)}$ units are successively replaced by mobile lithium ions bound to the more widely dispersed charges on the $P^{(3)}$ units linked to the $B^{(4)}$ species, and are thus trapped less effectively. As the borate concentration increases beyond $x = 0.4$, the $B–O–P$ linkages are successively replaced by $B^{(4)}–O–B^{(3)}$ linkages, increasing the anionic character of the $B^{(4)}$ units, and of the bridging oxygen atoms associated with them.

The close correspondence between the ion transport properties and the pattern seen in Fig. 14 suggests that ionic mobility is related to the extent in delocalization $d$ defined in Ref. 17 as the magnitude of the charge state, $q|d|$, of a given NFU divided by the number of oxygen atoms (bridging or non-bridging) over which the charge is spread. Thus, $d$ is $1/4$ for $B^{(4)}$ and $1/2$ for $P^{(2)}$. As explained above, $d$ is also $1/4$ for a $B^{(4)}$ species involved in four $B–O–P^{(3)}$ linkages, as its charge is effectively delocalized upon the four P-bound non-bridging oxygen atoms. Thus, within the composition range $0 \leq x \leq 0.4$ there is a successive change from $d = 1/2$ to $d = 1/4$, whereas at higher borate content $d$ remains at an approximately constant value of $1/4$. The results of the present study show that a larger degree of charge dispersal (via $B^{(4)}–O–P^{(3)}$ linkages at low $x$ values and via $B^{(4)}–O–B^{(3)}$ linkages at high $x$ values) appear to be favorable for ion transport, by diminishing Coulombic forces between the mobile Li$^+$ ions and the oxygens which now possess significantly less than a full negative charge.

VI. SUMMARY AND CONCLUSIONS

In the present article we applied conductivity spectroscopy as well as various NMR techniques with the goal to obtain a more complete understanding of the ion dynamics in mixed matrix ionic glasses of the general composition $0.33Li_2O + 0.67[xB_2O_3 + (1-x)P_2O_5]$. From temperature dependent measurements of electrical conductivity, from analyses of the dipolar and quadrupolar $^7Li$ line shapes, from spin-relaxation measurements, and from stimulated-echo
experiments we collected motional correlation times over wide spectral and temperature ranges. While keeping the Li⁺ fraction fixed, we find clear indications for an enhanced ion mobility at roughly equimolar concentrations x of the network formers from all these techniques. The MGFE is thus borne out by considering the data from all applied techniques and the results all agree with each other well. The mean activation energies ΔEa obtained on the basis of these data exhibit a shallow minimum near x ∼ 0.5. Evidence for wide distributions of activation energies or motional time scales was also obtained. Expressed in terms of ΔEa, the full width at half maximum of the distribution g(ΔEa) is about 0.2ΔEa for x > 0.

The maximum of the Li⁺ conductivity at intermediate concentrations was rationalized in terms of how the abundance of various structural units varies with the borate fraction x. The increase in ion conductivity for increasing x < 0.5 was attributed to an increase of the number of the low charge density B⁴ groups at the expense of P⁵ groups, and hence the fraction of Li⁺ ions bound to the P⁵ units which favor cation trapping decreases with decreasing x. For x > 0.5 the avoidance of electrostatically unfavorable B⁴–O–B⁴ linkages results primarily in the replacement of uncharged P³ groups by uncharged B⁵ groups, so the overall trapping ability ceases to change much with composition, in harmony with the present experimental findings.

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