

Communication: Conductivity enhancement in plastic-crystalline solid-state electrolytes

K. Geirhos, P. Lunkenheimer,^{a)} M. Michl, D. Reuter, and A. Loidl

Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, 86159 Augsburg, Germany

(Received 7 July 2015; accepted 14 August 2015; published online 25 August 2015)

Finding new ionic conductors that enable significant advancements in the development of energy-storage devices is a challenging goal of current material science. Aside of material classes as ionic liquids or amorphous ion conductors, the so-called plastic crystals (PCs) have been shown to be good candidates combining high conductivity and favorable mechanical properties. PCs are formed by molecules whose orientational degrees of freedom still fluctuate despite the material exhibits a well-defined crystalline lattice. In the present work, we show that the conductivity of Li^+ ions in succinonitrile, the most prominent molecular PC electrolyte, can be enhanced by several decades when replacing part of the molecules in the crystalline lattice by larger ones. Dielectric spectroscopy reveals that this is accompanied by a stronger coupling of ionic and reorientational motions. These findings, which can be understood in terms of an optimized “revolving door” mechanism, open a new path towards the development of better solid-state electrolytes. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4929554>]

Ionic conductors are essential for a number of applications, including energy-storage and energy-conversion devices as batteries, fuel cells, supercapacitors, and solar cells. The most natural choice for such materials seems to be liquids that act as solvents for ionic species as Li^+ or Na^+ and provide a highly mobile host system enabling fast ionic motions. Indeed, even in modern electrochemical devices as, e.g., the Li-ion battery, liquid electrolytes are still commonly used. Nevertheless, various strategies are pursued to achieve further advances in electrolyte technology. One is the development of superior liquid materials, the most prominent current example being the so-called ionic liquids.¹ An alternative approach is the use of *solid* materials with high ionic conductivity, thus avoiding the common shortcomings of liquid electrolytes, e.g., leakage and flammability. Materials with special crystal structures allowing for sizable ionic diffusion, at least at high temperatures, are known long since (e.g., β -alumina²). Amorphous solids are another interesting option, e.g., polymers as polyethylene oxide.^{3,4} The most recent development are plastic crystals (PCs), some of which have been shown to reach technically relevant conductivity values of $>10^{-4} \Omega^{-1} \text{cm}^{-1}$ around room temperature when ions are added.^{5–11}

In plastic crystals, the centers of mass of the molecules are fixed on a crystalline lattice with translational symmetry. However, their orientational degrees of freedom more or less freely fluctuate at high temperatures and often show glassy freezing at low temperatures.¹² The molecules of most PCs have roughly globular shape and relatively weak mutual interactions, providing little hindrance for reorientational processes. This often leads to high plasticity, thus explaining the term “plastic crystal.” This plasticity can be beneficial for application, enabling adaption to mechanical stresses. Ionic

charge transport in PCs is often thought to be directly coupled to these reorientational motions via a “revolving door” or “paddle wheel” mechanism.^{6,9,13–15} The reorientations may generate transient free volume within the lattice enabling ionic motion. Various types of defects in the PC phase were also considered to explain the high ionic mobility.^{6,7,11,16–19} Two classes of ionically conducting PCs are known, “classical” PCs consisting of a single neutral molecular species^{7,10,11} and ionic PCs, composed of at least two types of ions^{5,6,8,9,13,16,18} (some of the latter in fact can be regarded as ionic liquids if considering the usual definition of this material class¹ comprising a melting point of less than 100 °C). In addition to the charge transport of the dopant ions like Li^+ or Na^+ , which is prerequisite for many electrochemical applications, ionic PCs can also exhibit some self-diffusion of the ions constituting the host material,^{6,18} which may hamper their applicability.

The best known ionically conducting, but non-ionic PC is succinonitrile (SN), $\text{C}_2\text{H}_4(\text{CN})_2$. In two pioneering works by Long *et al.*¹⁰ and Alarco *et al.*,⁷ it was demonstrated that the conductivity of SN around room-temperature reaches values up to 10^{-3} – $10^{-2} \Omega^{-1} \text{cm}^{-1}$ when adding ions by admixing several percent of selected salts like LiTFSI (lithium bis-trifluoromethanesulphonimide). Even pure SN exhibits non-negligible ionic conductivity, most likely due to small amounts of impurities.^{10,20} A lot of effort has been made to optimize the conductivity in SN by varying the type and amount of added salt^{7,10,11,21} and SN also was suggested to be used in composites with polymer electrolytes, leading to an enhanced conductivity.^{22,23}

The plastic phase of SN is limited to a rather small temperature range of about 235–330 K. In contrast to many other PCs,¹² it is difficult to supercool and at $T < 235$ K, the material transfers into an orientationally ordered crystal. However, the addition of the related molecular compound glutaronitrile

^{a)}Electronic mail: peter.lunkenheimer@physik.uni-augsburg.de

(GN), $C_3H_6(CN)_2$ strongly extends the plastic-crystalline region, enabling the transition into a so-called glassy crystal.^{20,24} The glassy freezing of the orientational degrees of freedom in this system was investigated in detail.^{20,24} In the present work, we report that, unexpectedly, the addition of GN to SN doped with Li salt leads to a marked enhancement of the ionic conductivity by up to three decades. In contrast to varying the added ionic compound,^{7,10,11,21} the partial substitution of the PC molecules also seems to be a promising approach to optimize plastic-crystalline solid-state electrolytes.

SN and GN with purities >99% were purchased from Arcos Organics. $LiPF_6$ (purity 99.99%) was obtained from Sigma-Aldrich. Appropriate amounts of GN (liquid at room temperature) and $LiPF_6$ powder were added to SN powder.²⁴ For low x , the mixtures were slightly heated to achieve complete dissolution. The samples were characterized by differential scanning calorimetry (DSC) (see the supplementary material²⁵). The dielectric measurements were performed using a frequency-response analyzer (Novocontrol Alpha-analyzer). The sample materials were filled into parallel-plate capacitors with plate distances of 0.1 mm. For cooling and heating of the samples, a N_2 -gas cryostat was used. The measurements for $x \leq 0.4$ were done under heating. To avoid ambiguities arising from the complex succession of different phases known to occur at higher SN concentrations under heating,²⁴ the measurements for $x = 0.8$ were done under cooling (see also the supplementary material²⁵).

To check for the influence of GN on the ionic conductivity, we investigated several $SN_{1-x}GN_x$ mixtures with x between 0 and 0.8. As conducting ion we used Li^+ , introduced into the mixtures by adding 1% $LiPF_6$, a commonly used salt for electrolytes. In contrast to salts as $LiTFSI$, its anion has no dipolar moment, which facilitates the interpretation of dielectric-spectroscopy results. In the supplementary material,²⁵ DSC measurements are provided revealing the melting points and other transitions in the investigated mixtures. The dc conductivity and the relaxation times characterizing the reorientational motions in the SN-GN mixtures were determined from dielectric measurements. A typical example is presented in Fig. 1 for $SN_{0.6}GN_{0.4}$ showing the frequency and temperature-dependent dielectric loss ϵ'' . The two dominating microscopic processes in conducting PCs, ionic charge transport and molecular reorientation, are nicely revealed by the red and blue/green regions of this plot, respectively. Via the relation $\epsilon''_{dc} = \sigma_{dc}/(\epsilon_0\omega)$ (ϵ_0 is the permittivity of free space and $\omega = 2\pi\nu$), the ionic dc conductivity of the sample leads to the low-frequency divergence of $\epsilon''(\nu)$ observed at the higher temperatures. The blue and green curves, revealing loss peaks, signify a typical relaxational process.^{20,24} Its continuous shift to lower frequencies with decreasing temperature mirrors the glassy freezing of the orientational degrees of freedom as also observed for the ion-free $SN_{1-x}GN_x$ mixtures.^{20,24} At the lowest temperatures, indications for a faster, secondary relaxation process are found. For the ion-free system, it was treated in detail in Ref. 20.

Figure 2(a) shows the frequency-dependent dielectric constant ϵ' as measured at various temperatures. The step-like decrease observed at high frequencies for 149–188 K arises from the molecular reorientations. In contrast to the nominally

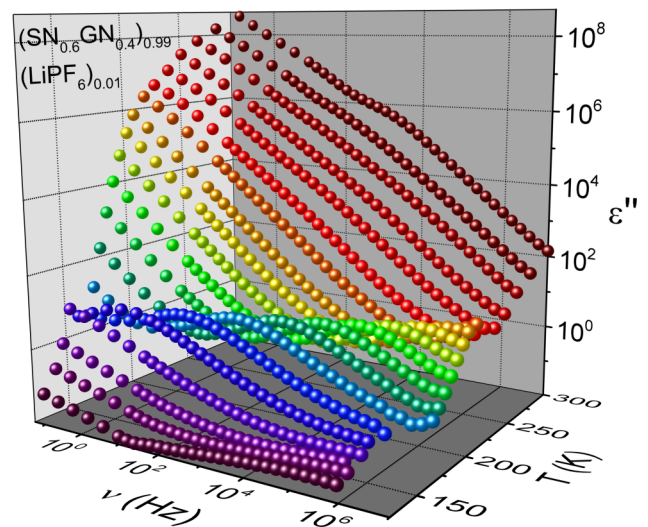


FIG. 1. Dielectric loss spectra revealing the two microscopic processes in plastic crystals. The figure shows spectra for $SN_{1-x}GN_x$ mixtures with 1% $LiPF_6$ and $x = 0.4$ as measured at different temperatures. While the red curves are dominated by ionic charge transport, the blue and green curves signify molecular reorientation processes.

ion-free SN-GN system,^{20,24} the addition of 1% Li salt leads to a huge increase of $\epsilon'(\nu)$ at low frequencies, reaching values of up to 10^8 . This finding can be ascribed to electrode polarization or blocking electrodes and is a typical phenomenon of ionic conductors.²⁶ It arises from the simple fact that the ions cannot penetrate into the metallic capacitor plates.

The intrinsic dc conductivity of the sample corresponds to a plateau in $\sigma'(\nu)$ [Fig. 2(b)]. The electrode blocking causes the observed reduction of σ' at low frequencies, which is most pronounced at the highest temperatures due to the high ionic mobility. The electrode effects in this system seem to occur in two successive steps, leading to an s-shaped curvature in the spectra at low frequencies and high temperatures. Similar behavior is often found in ionic conductors investigated in a sufficiently broad frequency/temperature range and possible microscopic origins were discussed, e.g., in Ref. 26. In Ref. 27, similar effects, observed in SN doped with Li salts, were interpreted as indications for an intrinsic relaxation process arising from the trans-gauche isomerism of the SN molecules. As this led to unrealistically high relaxation strengths of the order of 10^6 , to us, electrode polarization seems the most likely explanation.

Accounting for the different contributions discussed above, simultaneous fits of the spectra of ϵ' and ϵ'' were performed (lines in Fig. 2). The blocking electrodes were modelled by two distributed RC circuits, connected in series to the bulk contribution.²⁶ For the dc conductivity σ_{dc} , a term $\epsilon''_{dc} = \sigma_{dc}/(\epsilon_0\omega)$ was introduced. The relaxations were fitted by the empirical Cole-Davidson function (main relaxation) or the Cole-Cole function (secondary relaxation), a common approach in glass physics.^{12,28} Overall, the achieved fits are excellent, except for small deviations around the minimum in $\epsilon''(\nu)$ at the left wing of the main relaxation peak [Fig. 2(c)]. In Ref. 20, these deviations, also seen in the ion-free system, were discussed in terms of possible ac conductivity or an additional relaxation process, which, however, is out of the scope of the

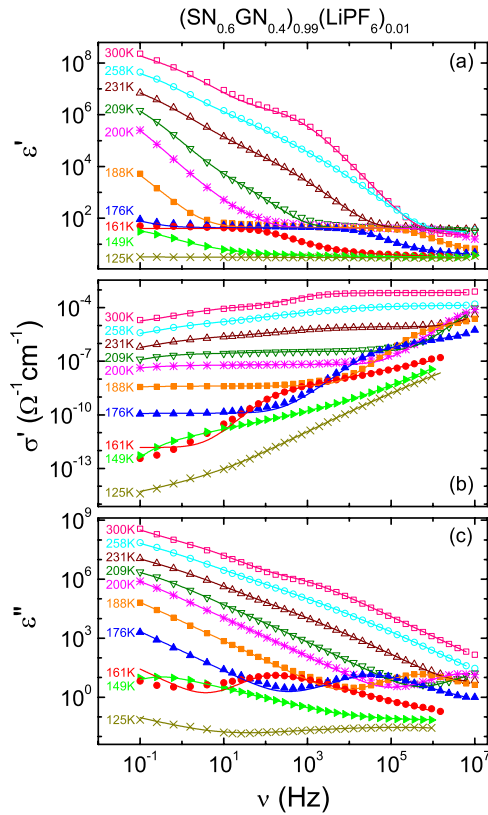


FIG. 2. Typical dielectric and conductivity spectra of a $\text{SN}_{1-x}\text{GN}_x$ mixture with 1% LiPF_6 . Spectra of the dielectric constant (a), conductivity (b), and loss (c) are shown for $x = 0.4$ and various temperatures. The lines in (a) and (c) are fits assuming two distributed RC circuits to account for the blocking electrodes, a dc-conductivity contribution, and two relaxation functions for the reorientational motions as explained in the text. The lines in (b) are calculated from the fit curves in (c) via $\sigma' = \epsilon'' \epsilon_0 \omega$.

present work. The determination of σ_{dc} at low temperatures is hampered by this effect, and thus, only data at $T > 170$ K are used for the further evaluation. The other investigated SN-GN mixtures showed qualitatively similar spectra as in Figs. 1 and 2.

Figure 3 shows the temperature dependence of the two most important parameters, dc resistivity $\rho_{dc} = 1/\sigma_{dc}$ (left scale) and reorientational relaxation time τ (right scale) as determined from the spectra. The data are provided in Arrhenius representation for pure SN and three SN-GN mixtures. To enable a comparison, the ρ_{dc} and τ ordinates are scaled to achieve the same number of decades per scale unit. Starting values of the ordinates were chosen to make the ρ_{dc} and τ curves match at the highest investigated temperatures. Without GN addition [Fig. 3(a)], charge transport and reorientational motions are clearly decoupled: While ρ_{dc} follows thermally activated behavior, $\rho_{dc} \propto \exp[E/(k_B T)]$, $\tau(T)$ can be better described by the empirical Vogel-Fulcher-Tammann (VFT) law known from glass physics,²⁸ usually written in the modified form,²⁹

$$\tau = \tau_0 \exp \left[\frac{DT_{VF}}{T - T_{VF}} \right]. \quad (1)$$

Here, D is the so-called strength parameter,²⁹ τ_0 an inverse attempt frequency, and T_{VF} is the Vogel-Fulcher temperature,

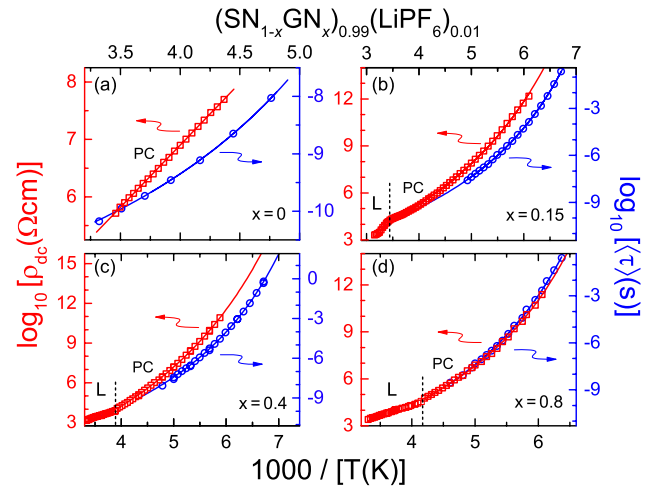


FIG. 3. Temperature dependence of the ionic and reorientational dynamics in $\text{SN}_{1-x}\text{GN}_x$ mixtures with 1% LiPF_6 . The dc resistivity (squares, left scale) and reorientational relaxation times (circles, right scale) as deduced from the dielectric spectra are shown in Arrhenius representation. (The provided average relaxation times $\langle \tau \rangle$ were determined from the parameters of the Cole-Davidson function.^{20,24} For $x = 0$, the τ data represent the behavior for SN without LiPF_6 .) Data for pure SN (a) and three SN-GN mixtures (b)-(d) are shown. In each frame, the left and right ordinates were scaled to achieve the same number of decades per scale unit. Obviously, GN addition increases the coupling of the translational ionic and reorientational molecular motions. The solid lines are fits with the VFT law. For $x = 0$, $\sigma_{dc}(T)$ could be fitted by an Arrhenius law. The vertical dashed lines indicate the melting points, in reasonable agreement with the DSC measurements provided in the supplementary material.²⁵

where τ diverges. For $x > 0$, VFT behavior is also found for the resistivity. For the highest concentration, $x = 0.8$, the $\tau(T)$ and $\rho(T)$ curves can perfectly be scaled onto each other [Fig. 3(d)]. Overall, the addition of GN to SN seems to increase the coupling of the translational ionic and reorientational molecular motions. To understand this finding, it seems reasonable to assume that reorientations of the bulkier, more stretched GN molecules expand the lattice and are more effective in opening paths for translational motions of the ions. For high GN concentrations, sufficient numbers of these highly effective “revolving doors” are available and this mechanism seems to dominate the ionic charge transport (however, pure GN cannot be used as it has no plastic phase^{20,24}). Alternatively, a more defect-dominated mechanism also seems possible as, of course, admixing GN implies an increase of the defect concentration.

It should be noted that for ion-free samples, it was shown that, between about 70% and 90% GN contents, a supercooled liquid phase can also be prepared.²⁴ Thus, one may argue that the samples investigated here could be partly mixed phases, which may especially apply for $x = 0.8$. However, as shown in the supplementary material,²⁵ the two phases exhibit significantly different relaxation times (and, thus, glass temperatures).²⁴ If indeed a phase mixture would be present in our samples, two different glass transitions should be detected in the DSC results and two relaxation peaks should show up in the loss spectra, which is not the case. However, small residual amounts of the liquid phase cannot be fully excluded.

We want to also note that for $x = 0.4$, in the whole temperature range, the ionic conductivity is several decades

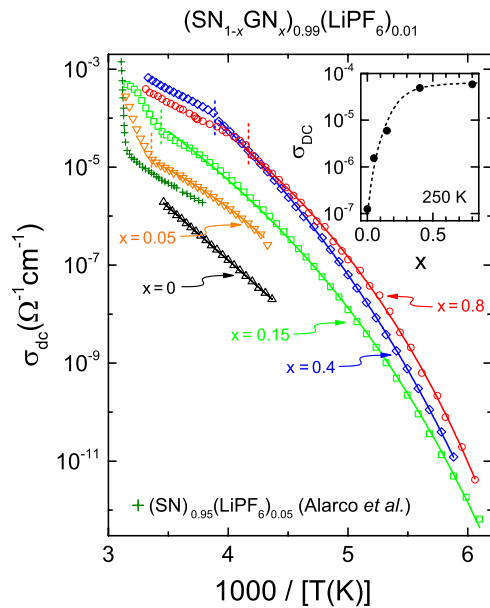


FIG. 4. Influence of GN content on the temperature-dependent ionic conductivity in $\text{SN}_{1-x}\text{GN}_x$ mixtures with 1% LiPF_6 . The dc conductivity is shown in Arrhenius representation for all investigated mixtures. The solid lines are fits with the VFT equation, Eq. (1), modified for the conductivity: $\sigma_{\text{dc}} = \sigma_0 \exp[-DT_{\text{VF}}/(T - T_{\text{VF}})]$. The vertical dashed lines indicate the melting points (cf. DSC measurements in the supplementary material²⁵). The plusses show the results for pure SN, doped with 5% LiPF_6 as published in Ref. 7. The inset shows the dependence of σ_{dc} in the plastic phase on SN concentration. Obviously, adding GN strongly enhances the ionic conductivity of plastic-crystalline SN.

higher than for the corresponding sample without LiPF_6 , reported in Ref. 20 and no conductivity anomalies show up for this and the other GN concentrations (except at the melting point) (Figs. 3 and 4). This makes it unlikely that part of the salt precipitates at low temperatures.

Does the rising importance of the revolving door mechanism when GN is added also lead to more effective charge transport, reflected in an increase of conductivity? This is clarified in Fig. 4, comparing the dc conductivities of the investigated mixtures. Indeed, a huge increase of σ_{dc} is found: Even for the smallest GN concentration of only 0.05 (inverted triangles), it becomes enhanced by more than one order of magnitude compared to pure SN (upright triangles, see also inset of Fig. 4, where $\sigma_{\text{dc}}(x)$ at 250 K is shown). Despite the salt concentration is only 1%, the conductivity of this mixture exceeds that of pure SN with 5% LiPF_6 as reported in Ref. 7 (plusses in Fig. 4). Obviously, 5% GN addition leads to a marked improvement of ionic mobility. This generates a stronger increase of conductivity than the fivefold enlargement of the ion density when adding 5% LiPF_6 to pure SN (plusses in Fig. 4) instead of 1% (upright triangles). Moreover, Fig. 4 demonstrates that, when adding larger amounts of GN, the conductivity of SN even can be improved by up to three decades. Saturation of $\sigma_{\text{dc}}(x)$ is approached above $x \approx 0.4$ (inset of Fig. 4).

Overall, our detailed dielectric investigations reveal a marked increase of ionic conductivity when GN is added to the prominent solid-state electrolyte SN, which is accompanied by a stronger coupling of molecular reorientation and ionic translation. It seems that an effective revolving-door mech-

anism achieved by adding the larger GN molecules to SN is the key to considerably enhance ionic mobility and, thus, conductivity. However, the role of possible defect mechanisms and of the trans-gauche isomerism of the involved molecules remains to be clarified. It should be noted that the melting point of $\text{SN}_{1-x}\text{GN}_x$ mixtures decreases with GN concentration.^{20,24} Therefore only for $x = 0.05$, the samples are in the PC state at room temperature. While it was not the aim of the present work to find a new PC ionic conductor optimized for application, our findings demonstrate a new path to a considerable conductivity enhancement in PCs. To find solid-state electrolytes, optimally suited for application, performing further experimental work following this path, e.g., by varying the added salt and exploring the feasibility for other PCs, seems a promising approach.

This work was supported by the Deutsche Forschungsgemeinschaft via Research Unit FOR1394.

- ¹M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, and B. Scrosati, *Nat. Mater.* **8**, 621–629 (2009).
- ²Y. F. Y. Yao and J. T. Kummer, *J. Inorg. Nucl. Chem.* **29**, 2453–2475 (1967).
- ³F. Croce, G. B. Appetecchi, L. Persi, and B. Scrosati, *Nature (London)* **394**, 456–458 (1998).
- ⁴C. Do, P. Lunkenheimer, D. Diddens, M. Götz, M. Weiß, A. Loidl, X.-G. Sun, J. Allgaier, and M. Ohl, *Phys. Rev. Lett.* **111**, 018301 (2013).
- ⁵D. R. MacFarlane, J. Huang, and M. Forsyth, *Nature* **402**, 792–794 (1999).
- ⁶D. R. MacFarlane and M. Forsyth, *Adv. Mater.* **13**, 957–966 (2001).
- ⁷P. J. Alarco, Y. Abu-Lebdeh, A. Abouimrane, and M. Armand, *Nat. Mater.* **3**, 476–481 (2004).
- ⁸J. M. Pringle, *Phys. Chem. Chem. Phys.* **15**, 1339–1351 (2013).
- ⁹E. I. Cooper and C. Angell, *Solid State Ionics* **18-19**, 570–576 (1986).
- ¹⁰S. Long, D. R. MacFarlane, and M. Forsyth, *Solid State Ionics* **161**, 105–112 (2003).
- ¹¹D. Hwang, D. Y. Kim, S. M. Jo, V. Armel, D. R. MacFarlane, D. Kim, and S. Y. Jang, *Sci. Rep.* **3**, 3520 (2013).
- ¹²R. Brand, P. Lunkenheimer, and A. Loidl, *J. Chem. Phys.* **116**, 10386–10401 (2002).
- ¹³L. Nilsson, J. O. Thomas, and B. C. Tofield, *J. Phys. C: Solid State Phys.* **13**, 6441–6451 (1980).
- ¹⁴R. Aronsson, B. Jansson, H. Knape, A. Lundén, L. Nilsson, C.-A. Sjöblom, and L. Torell, *J. Phys. Colloq.* **41**, 35–37 (1980).
- ¹⁵L. Börjesson and L. M. Torell, *Phys. Rev. B* **32**, 2471–2477 (2013).
- ¹⁶Y. Abu-Lebdeh, P.-J. Alarco, and M. Armand, *Angew. Chem., Int. Ed.* **42**, 4499–4501 (2003).
- ¹⁷J. Huang, A. Hill, M. Forsyth, D. R. MacFarlane, and A. Hollenkamp, *Solid State Ionics* **177**, 2569–2573 (2006).
- ¹⁸J. M. Pringle, P. C. Howlett, D. R. MacFarlane, and M. Forsyth, *J. Mater. Chem.* **20**, 2056–2062 (2010).
- ¹⁹S. Das and A. J. Bhattacharyya, *J. Phys. Chem. Lett.* **3**, 3550–3554 (2012).
- ²⁰Th. Bauer, M. Köhler, P. Lunkenheimer, A. Loidl, and C. A. Angell, *J. Chem. Phys.* **133**, 144509 (2010).
- ²¹S. Long, D. R. MacFarlane, and M. Forsyth, *Solid State Ionics* **175**, 733–738 (2004).
- ²²L. Z. Fan, Y. S. Hu, A. J. Bhattacharyya, and J. Maier, *Adv. Funct. Mater.* **17**, 2800–2807 (2007).
- ²³M. Patel and A. J. Bhattacharyya, *Electrochem. Commun.* **10**, 1912–1915 (2008).
- ²⁴M. Götz, Th. Bauer, P. Lunkenheimer, and A. Loidl, *J. Chem. Phys.* **140**, 094504 (2014).
- ²⁵See supplementary material at <http://dx.doi.org/10.1063/1.4929554> for DSC results and information on the different phases for $x = 0.8$.
- ²⁶S. Emmert, M. Wolf, R. Gulich, S. Krohns, P. Lunkenheimer, and A. Loidl, *Eur. Phys. J. B* **83**, 157–165 (2011).
- ²⁷S. Das and A. J. Bhattacharyya, *J. Phys. Chem. B* **115**, 2148–2154 (2011).
- ²⁸P. Lunkenheimer, U. Schneider, R. Brand, and A. Loidl, *Contemp. Phys.* **41**, 15–36 (2000).
- ²⁹C. A. Angell, “Strong and fragile liquids,” in *Relaxations in Complex Systems*, edited by K. L. Ngai and G. B. Wright (NRL, Washington, DC, 1985), pp. 3–11.