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Ion dynamics in mixed alkali glasses

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To study the ion dynamics in an amorphous mixed alkali system, frequency-dependent conductivities of $0.3[xLi_2O\cdot(1-x)Na_2O]\cdot 0.7B_2O_3$ glasses have been measured by impedance spectroscopy in a wide temperature range. The conductivities show a transition from their dc values into a dispersive regime where they increase continuously with frequency, tending towards a linear frequency dependence at sufficiently low temperatures. In addition to the "classical" mixed alkali effect, *i.e.* the occurrence of a minimum in the dc conductivity, we also observe the following new mixed alkali effect. In contrast to conductivity spectra of single cation glasses which follow the time-temperature superposition principle, featuring a temperature-invariant shape, the shapes of the conductivity spectra of the mixed alkali glasses studied here are found to change with temperature. To explain the effect, we suggest differently activated mobilities of the two different ionic species. The spectra are discussed in the framework of the concept of mismatch and relaxation (CMR).

Introduction

Mixed cation effects and in particular mixed alkali effects belong to the most challenging research topics in solid state science. Mixed cation effects occur in glassy (and in some crystalline) ion-conducting systems where the *relative* cation contents are changed while the *overall* cation content remains constant. Understanding such effects is not only of scientific interest, but is also important for many industrial applications which focus on mixed cation glasses. Mixed alkali effects have been found, *e.g.*, in ionic diffusivities and dc conductivities, in conductivity spectra, in mechanical loss spectra, and also in non-transport quantities like the glass transition temperature.[1–3]

One classical mixed alkali effect is the existence of a crossover point of diffusivities where the diffusion coefficients of both cationic species become equal. Usually, the crossover occurs at a glass composition with comparable amounts of dissimilar cations. On either side of the diffusivity crossover, ionic transport is dominated by the more mobile species. Therefore, the dc conductivity, which reflects long-range ionic transport, features a minimum close to the crossover point. In iso-frequency representations of the conductivity, the mixed alkali effect is known to become less pronounced with both increasing frequency and increasing temperature.

As pointed out by Roling *et al.*, mixed alkali effects are also found in the shapes of frequency-dependent conductivities.[4] While in the low-frequency limit the conductivity is independent of frequency, its value being the dc conductivity σ_{dc}, there is a substantial increase above a characteristic onset frequency, ν_0. According to ref. 4, the transition from the dc regime into the dispersive regime is more gradual in mixed alkali than in single alkali glasses, corresponding to a considerably higher static dielectric constant. The effect is also observed in this study.

Another mixed alkali effect, which consists of a violation of the time–temperature superposition principle, is for the first time reported in this contribution. To appreciate the effect, it is useful to consider single cation glasses first. Their conductivity spectra usually follow the time-temperature superposition principle. The principle states that the shape of the conductivity isotherms of a given glass does not change with temperature.[5] If it is valid, ionic conductivities measured at different temperatures can be collapsed on a single "master curve". In many glasses, this is achieved by plotting $\sigma(\nu)/\sigma_{dc}$ *versus* $\nu/(\sigma_{dc}T)$ in a log–log fashion. This particular kind of scaling was first suggested for amorphous semiconductors by Summerfield and Butcher.[6] Later, it was shown to be valid for many ion-conducting glasses as well.[7]

An example is given in Fig. 1. Conductivity isotherms of glassy $B_2O_3\cdot 0.56Li_2O\cdot 0.45LiBr$ which we have measured recently are presented in Fig. 1a, their shape being typical of most single cation glasses. It should be noted that the 148 K isotherm still shows the transition into the dc plateau, the conductivity still being caused by activated hopping processes. The results presented in Fig. 1 are in agreement with the following properties of conductivity spectra of glasses that are well known from impedance spectroscopy.

At sufficiently low frequencies ν, ionic conductivities of glasses, $\sigma(\nu)$, *roughly* follow the Jonscher power law,[8] $\sigma(\nu)\approx\sigma_{dc}(1+(\nu/\nu_0)^p)$. Reported values of the exponent p typically range from 0.5 to 0.7. However, with increasing frequency and/or decreasing temperature the Jonscher power law becomes more and more inappropriate. In fact, the apparent exponent is found to vary with the ratio $\sigma(\nu)/\sigma_{dc}$, increasing gradually and tending towards unity for large values of $\sigma(\nu)/\sigma_{dc}$, then corresponding to a nearly frequency-independent dielectric loss.[9]

Fig. 1b shows the master curve constructed from the data of Fig. 1a by means of the Summerfield scaling procedure.[6] For reasons of clarity only three isotherms are included in the scaled representation, although all other isotherms also fall on the master curve. The validity of the time-temperature superposition principle implies that the same transport mechanism operates at different temperatures. More specifically, the validity of the Summerfield scaling implies that the characteristic onset frequency ν_0 and the macroscopic coefficient of self-diffusion, which is proportional to $\sigma_{dc}T$ because

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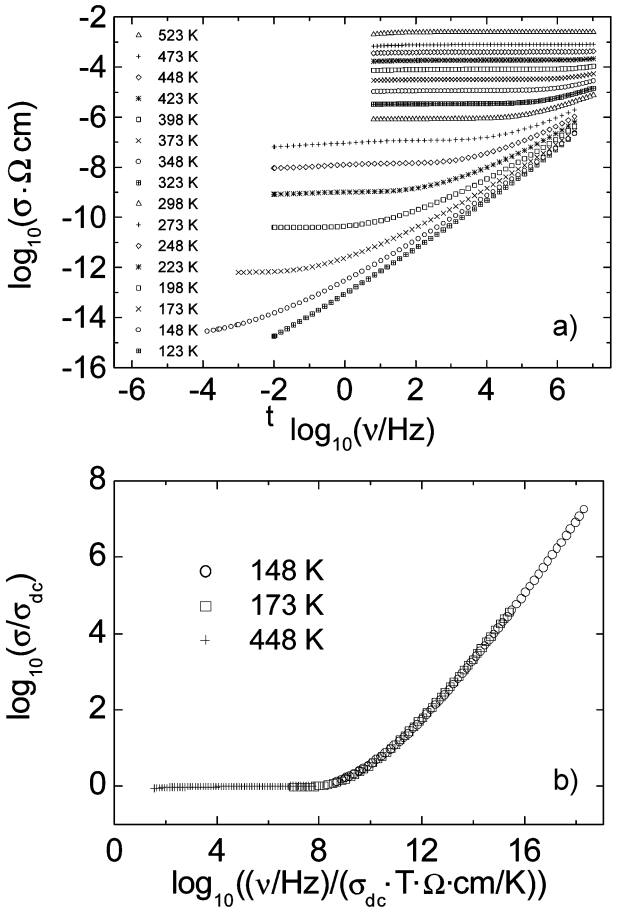

Fig. 1 Conductivity spectra of glassy $B_2O_3{\cdot}0.56Li_2O{\cdot}0.45LiBr$: (a) experimental spectra, (b) master curve representation.

of the Nernst–Einstein relation, increase with temperature at the same rate.

In this paper, we present conductivity spectra of glasses of composition $0.3[xLi_2O{\cdot}(1-x)Na_2O]{\cdot}0.7B_2O_3$ with x ranging from zero to one in steps of 0.2. The transition regime, where the onset of the dispersion is observed, will be considered in particular. In this regime, the spectral shape is analysed including its variations with both composition and temperature. The occurring effects are then quantified and discussed in the framework of the concept of mismatch and relaxation (CMR).[10]

Experimental

For the preparation of the mixed Li/Na glasses, dry mixtures of stoichiometric amounts of Na_2CO_3, Li_2CO_3 and B_2O_3 powders were melted in a platinum crucible at 1000 °C for 2 h. The melt was then poured into a graphite mould. The samples were removed from the mould, annealed for 2 h at 20 K below their respective glass transition temperatures and then cooled to ambient temperature at a rate of 0.5 K min^{-1}. The glass plates thus obtained showed no internal stress. Cylindrical samples were then drilled from the glass plates, and their front surfaces were polished. The samples were of 28 mm diameter and approximately 1 mm thickness. Silver/platinum electrodes were sputtered onto their front surfaces.

Conductivity spectra were measured with a Novocontrol impedance spectrometer covering a frequency range from 10^{-4} Hz to 6 MHz. The conductivities and frequencies attained are much lower than those accessible in conventional impedance spectroscopy. The upper temperature limit was 573 K.

Results

Fig. 2a shows the dc conductivity, σ_{dc}, of glassy $0.3[xLi_2O{\cdot}(1-x)Na_2O]{\cdot}0.7B_2O_3$ at 323 K as a function of composition. The lowest dc conductivity in this glass system occurs at 40% lithium ion content. Between the two binary end-members, the difference in σ_{dc} is only a factor of ten. At $x = 0.4$, however, the dc conductivity is about four to five orders of magnitude lower than σ_{dc} of either binary glass. The minimum in the dc conductivity corresponds to a maximum in the activation energy of $\sigma_{dc}T$ as determined from the Arrhenius equation, see Fig. 2b.

In Fig. 3 we present frequency-dependent conductivities of glassy $0.3\,[xLi_2O{\cdot}(1-x)Na_2O]{\cdot}0.7\,B_2O_3$ measured for different x at a fixed temperature, *viz.* 323 K. In order to compare the shapes of the spectra, all data are presented in a normalised fashion. To make the spectra coincide at high frequencies we have, besides the Summerfield scaling, also used a scaling factor f, which is however close to unity for all compositions. The spectra of Fig. 3 corroborate the trend already reported in ref. 4. Starting with the binary sodium borate glass where $x = 0$, the transition into the dispersive regime becomes more and more gradual with increasing x until the composition $x = 0.4$ is reached. With further increase of x, the transition becomes less gradual again. Finally, the conductivity spectrum of the binary lithium borate glass coincides with the spectrum of the binary sodium borate glass.

Fig. 4a and Fig. 4b are scaled representations of several conductivity isotherms of the binary glass $0.3Na_2O{\cdot}0.7B_2O_3$ and of the ternary glass $0.18Li_2O{\cdot}0.12Na_2O{\cdot}0.7B_2O_3$, respectively. In both cases, the Summerfield scaling has been applied. Comparing Fig. 4a and Fig. 4b, we encounter both similarities and differences.

The two glasses agree in displaying a first derivative, $\partial\log(\sigma(\nu))/\partial\log(\nu)$, that increases with frequency, tending towards unity. This is also well in line with the shapes of conductivity spectra of many other solid electrolytes such as the one of glassy $B_2O_3{\cdot}0.56Li_2O{\cdot}0.45LiBr$, *cf.* Fig. 1.

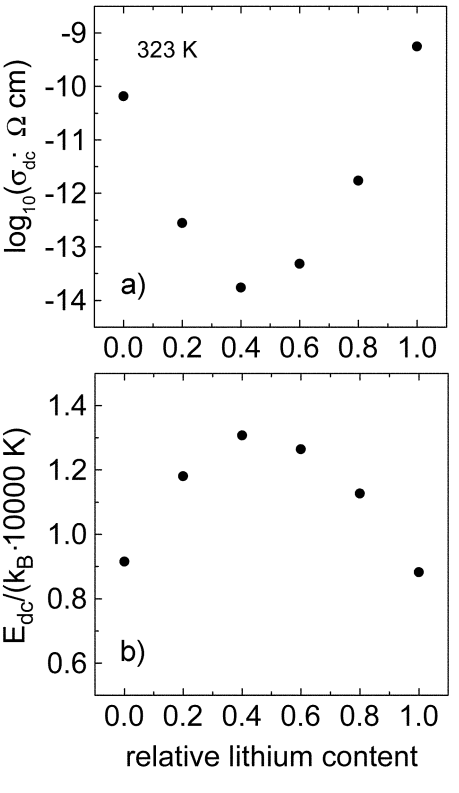

Fig. 2 (a) dc conductivity of $0.3[xLi_2O{\cdot}(1-x)Na_2O]{\cdot}0.7B_2O_3$ glasses at 323 K, (b) activation energy of the dc conductivity.

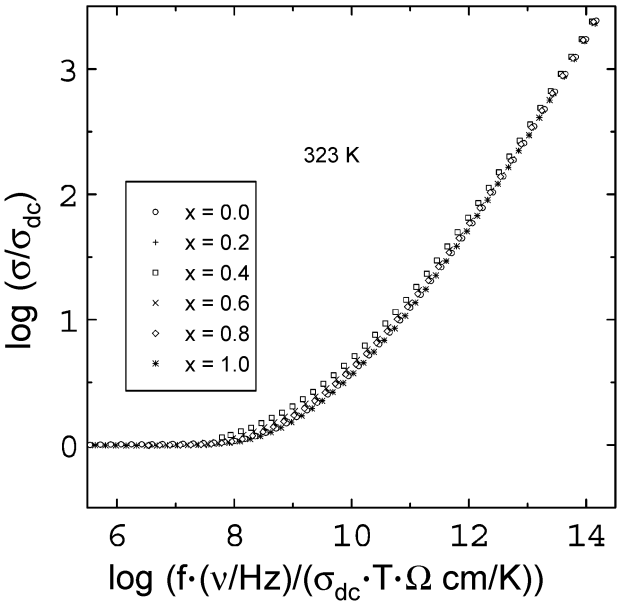

Fig. 3 Scaled conductivity spectra of $0.3[xLi_2O{\cdot}(1-x)Na_2O]{\cdot}0.7B_2O_3$ glasses at 323 K.

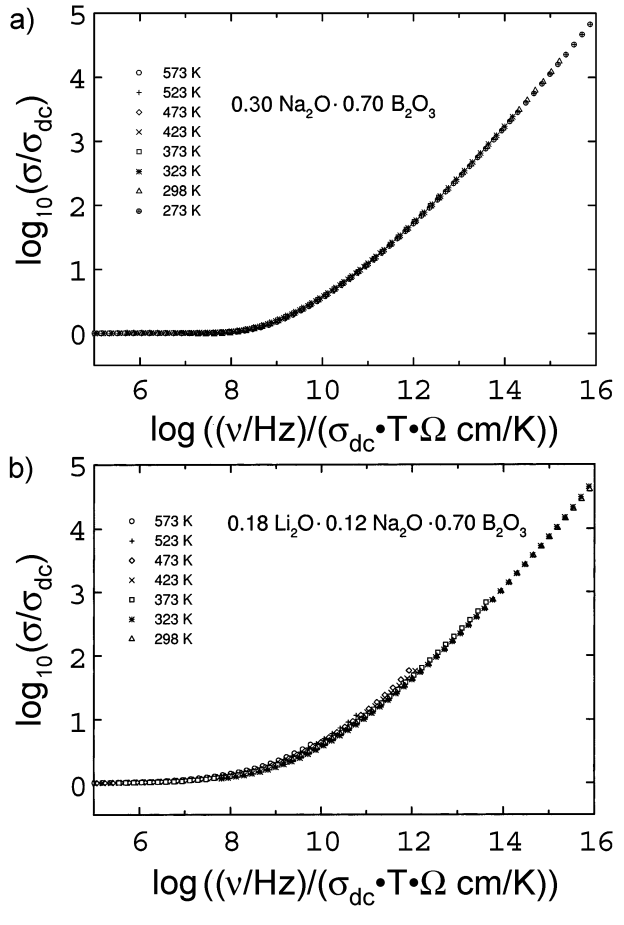

Fig. 4 Scaled conductivity spectra of glassy (a) $0.3Na_2O{\cdot}0.7B_2O_3$ and (b) $0.18Li_2O{\cdot}0.12Na_2O{\cdot}0.7B_2O_3$.

On the other hand, the two glasses differ regarding the preservation of the shape of their conductivity spectra when the temperature is changed. For the single cation glass $0.3Na_2O{\cdot}0.7B_2O_3$, the shape turns out to be temperature-invariant, resulting in a single master curve in the scaled representation, see Fig. 4a. As in $B_2O_3{\cdot}0.56Li_2O{\cdot}0.45LiBr$, see Fig. 1, the time–temperature superposition principle and the Summerfield scaling are again found to be valid.

In contrast to Fig. 4a, we see in Fig. 4b that different isotherms of the mixed alkali glass do not collapse to a single master curve. Obviously, the shape of the conductivity spectra is temperature-dependent. In the following section, this effect will be discussed in more detail.

Discussion

We have reported on two mixed alkali effects, concerning changes in the shapes of frequency-dependent conductivities that occur along with variations of composition and temperature, respectively. In the following, these effects will be quantified by application of a one-parameter procedure that has been established recently, within the framework of the concept of mismatch and relaxation (CMR) model. Since, at the same time, the CMR is also able to provide a guideline for an interpretation of the ion dynamics, a brief outline is given of this particular model concept.

Conductivity spectra of glassy and crystalline electrolytes have often been described by Ngai's coupling concept[11] and by the jump relaxation model.[12] However, these models fail to reproduce the transition from a Jonscher-type power-law behaviour[8] into a nearly-constant-loss behaviour[9] which is experimentally well validated. The latter transition is, however, reproduced within the CMR, which differs from the jump relaxation model by the inclusion of a second rate equation. In the following, we only mention the basic assumptions of the model and then use it for reproducing and parameterising the experimental spectra.

The central idea of the CMR is the following. A mismatch is created by each hop of a mobile ion. The system then tends to reduce the mismatch, which can be done by a backward hop of the ion itself ("single-particle route") or by rearrangement of its neighbourhood ("many-particle route"). The first rate equation claims that the rates of relaxation along the two routes are always proportional to each other. The second rate equation exploits the fact that the mobile neighbours are of the same kind as the "central" ion. The rate of relaxation on the "many-particle route" is thus again related to single-particle functions such as the velocity autocorrelation function. The latter are then obtainable from the two equations in a self-consistent fashion. Local mismatch is, however, not only *reduced* by the rearrangement of the neighbourhood, but at the same time also progressively *shielded*. An empirical parameter K is introduced to quantify the time dependence of the shielding effect. More details are given in ref. 10.

The parameter K turns out to modify the shape of the conductivity spectra, increasing values of K resulting in a more gradual onset of the dispersion.

In most single cation glasses and also in many crystals the value of K is found to be close to 2.0. Such an example is given in Fig. 5 where the experimental conductivity master curve of glassy $0.3Na_2O{\cdot}0.7B_2O_3$ is compared with the corresponding CMR master curve. The two master curves are found to be in excellent agreement. The same holds true for glassy $0.3Li_2O{\cdot}0.7B_2O_3$, because the conductivity spectra of the two binary borate glasses have almost the same shape, *cf.* Fig. 3.

As shown in Fig. 3, the shapes of the mixed alkali conductivity spectra strongly vary with composition. In order to quantify this effect, we have determined the values of the parameter K needed to obtain excellent fits to the experimental spectra. The results are displayed in Fig. 6. Evidently, the parameter K shows a pronounced mixed alkali effect with a maximum at $x = 0.4$. The maximum of K, the minimum in the dc conductivity and the maximum in the corresponding activation energy thus all occur at the same composition, *cf.* Fig. 2.

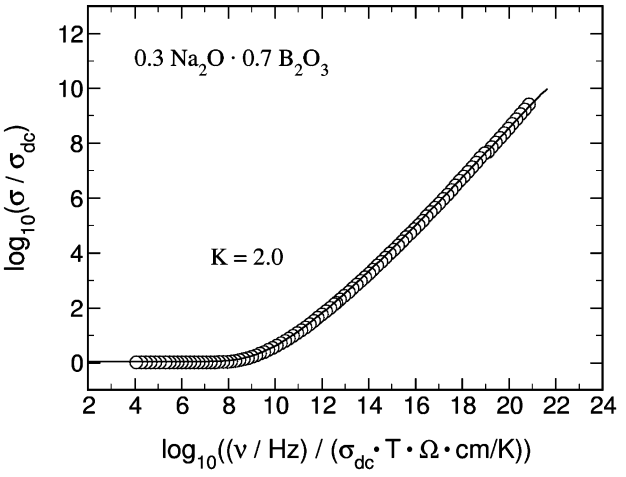

Fig. 5 Experimental master curve of glassy $0.3Na_2O{\cdot}0.7B_2O_3$ in comparison with a master curve resulting from the CMR model.

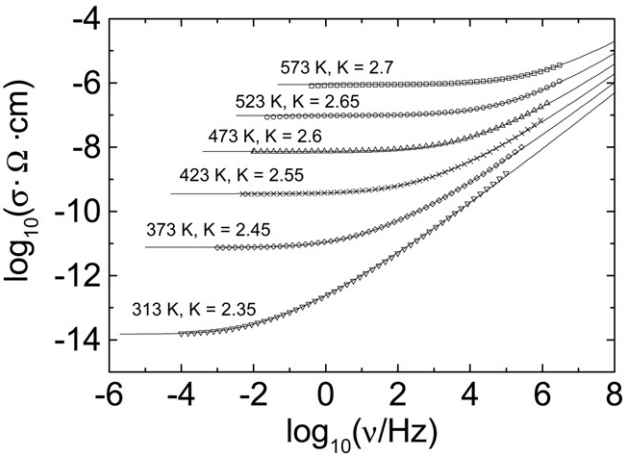

Fig. 7 Experimental conductivity spectra of glassy $0.18\ Li_2O{\cdot}0.12Na_2O{\cdot}0.7B_2O_3$ at various temperatures and fits based on the CMR model. The value of the parameter K increases with temperature.

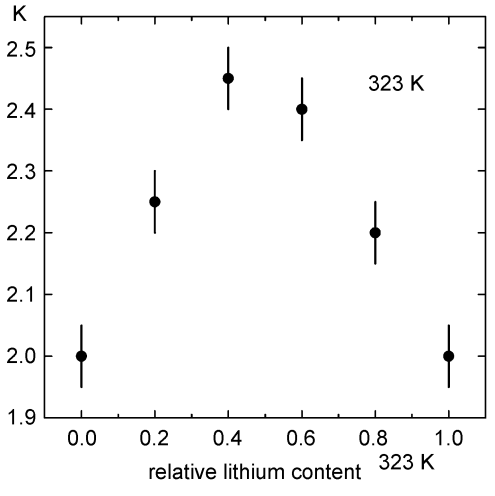

Fig. 6 K-parameter values resulting from fits of the CMR model to conductivity spectra of $0.3[xLi_2O{\cdot}(1-x)Na_2O]{\cdot}0.7B_2O_3$ glasses at 323 K.

The parameter K appears to be linked to the effective number density of mobile ions. The smaller the number density, the higher is the value of K. Accordingly, spectra of glasses and crystals with small concentrations of mobile cations are reproduced by model spectra with larger K values than glasses and crystals with high cation contents. In a mixed alkali glass system such as $0.3\ [xLi_2O{\cdot}(1-x)Na_2O]{\cdot}0.7B_2O_3$, however, the total number of cations remains constant for all glass compositions. Nevertheless, Fig. 6 suggests that the effective number of mobile ions should be strongly reduced in a mixed alkali glass as compared to the binary glasses. This can be understood in the framework of the dynamic structure model (DSM) developed by Bunde *et al.*.[13] In the DSM, each cation species creates its own chemical environment when a solid glass is formed from a melt. Therefore, a Li site in a glass differs from a Na site. As each cation species prefers to migrate *via* pathways of sites adjusted to its own requirements, the ionic mobility is drastically reduced if the pathways of the respective species interfere with each other. This picture readily explains the strong reduction of the effective number of mobile ions in mixed alkali glasses.

In the following, we consider the temperature dependence of the conductivity spectra. As discussed in the previous section, the shape of the conductivity spectra of the single cation glasses does not change with temperature, see Figs. 1b and 4a. In terms of the CMR, the observed validity of the time-temperature superposition principle means that temperature variations affect the ion dynamics only by changing the rates of the hopping processes, while the mechanism and the number of ions involved remain unchanged.

The conductivity spectra of the mixed alkali glasses which do not collapse on a master curve, see Fig. 4b, can also be described by the CMR, at least formally. The experimental spectra of glassy $0.18Li_2O{\cdot}0.12Na_2O{\cdot}0.7B_2O_3$ are presented in Fig. 7 along with curves obtained by the CMR. In contrast to the single cation glasses where a constant K value of 2.0 has been used to describe *all* conductivity isotherms, the value of K is found to *increase with temperature* in the mixed alkali glasses. The higher the temperature, the more gradual is the transition from the dc plateau into the dispersive regime. This violation of the time-temperature superposition principle is a new kind of mixed alkali effect. The reason why the effect was not detected in a previous study on the same glass system[4] has to be seen in more limited ranges in frequency and temperature.

An explanation of the temperature-dependent shape of the mixed alkali conductivity spectra may be provided by the assumption of differently activated mobilities of the two different ionic species. As mentioned earlier, ionic transport is dominated by the more mobile ionic species. This applies on either side of the diffusion crossover point.[14] However, there is a lack of radiotracer experiments concerning the temperature dependences of the respective mobilities in mixed alkali glasses. *A priori*, of course, there is no reason why the different cation species should have identical activation energies of their mobilities.

Let us, therefore, in the following, assume that, in a given mixed alkali glass, the mobilities of the two species are slightly differently activated. In a simplified approach we also assume that each of the two species contributes separately to the overall conductivity. The total conductivity spectrum is then easily constructed at each temperature by adding the individual spectra of both species. It turns out that even if the individual spectra follow the time–temperature superposition principle, the shape of the total spectra will be temperature dependent. This is in agreement with the actual experimental findings.

If the mobilities of the two cation species were Arrhenius activated, but with different activation energies, the sum of these two contributions should deviate from the Arrhenius law which is usually used to describe the temperature dependence

of $\sigma_{dc}T$. Instead of a straight line one would expect a slightly concave curve. We have, therefore, carefully checked the validity of the Arrhenius law for the experimental dc conductivities of our mixed alkali glasses. We find the experimental data basically well described by an Arrhenius law. However, very small deviations from a straight line are detectable at our lowest and highest temperatures. Similar deviations have been reported by Mehrer *et al.*,[14] Namikawa[15] and Jain *et al.*[16] Nevertheless, dc conductivity measurements over an even larger temperature range are desirable to make any further conclusions. Apart from this, temperature dependent tracer measurements would surely shed light on the temperature dependence of ionic mobilities in mixed alkali glasses.

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