Nonuniversal Features of the ac Conductivity in Ion Conducting Glasses

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Recently, Sidebottom [Phys. Rev. Lett. **82**, 3653 (1999)] proposed a new scaling approach for the conductivity spectra of ion conducting glasses. This approach is based on the condition that the shape of the spectra is universal. In this Letter, we show that this condition is generally not fulfilled, but that the shape depends on the glass composition. In single alkali glasses, the frequency dependence of the conductivity varies with the alkali oxide content. Furthermore, the mixing of dissimilar alkali ions leads to pronounced changes in the shape of the conductivity spectra.

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Structurally disordered solid electrolytes show a strikingly similar dispersion of the electrical ac conductivity [1,2]. Usually, the frequency- and temperature-dependent conductivity spectra obey the time-temperature superposition principle. This means that, for a given material, the conductivity isotherms can be collapsed to a master curve upon appropriate scaling of the conductivity and frequency axes. The master curves of different solids have very similar shapes.

Finding an explanation for this high degree of universality is still one of the major challenges in solid state physics. On the other hand, the high degree of universality suggests that the ac conductivity contains only little information on microscopic details of the conduction process [3,4]. Therefore, in order to extract such information from the experimental data, it seems important to perform systematic studies on nonuniversal features of the ac conductivity. In this Letter, this is done for ion conducting glasses by analyzing the scaling properties of high-resolution and high-precision conductivity spectra.

Scaling methods for the analysis of the ac conductivity of ion conducting glasses were first used by Taylor [5–7] and by Isard [8]. They found the conductivity master curves of different glasses to be closely similar. In 1991, Kahnt [9] compared the master curves of a variety of silicate, borosilicate, and germanate glasses. He did not notice any difference in shape between different master curves and thus concluded that the shape is independent of the ionic concentrations and of the glassy structures. In 1997, Roling *et al.* [10] analyzed the scaling properties of the conductivity spectra of sodium borate glasses containing different amounts of sodium oxide. They observed that the master curves of different glasses could be collapsed by scaling the frequency axis with the self-diffusion coefficient of the sodium ions. However, as shown by Roling in a subsequent paper [11], the superposition of the master curves is not exact, but there are small differences in shape between the master curves.

Recently, Sidebottom [12] demonstrated that the master curves of different sodium germanate glasses cannot be superimposed by scaling the frequency axis with the self-diffusion coefficient of the sodium ions. He attributed this to changes in the "ion hopping length" with changing alkali oxide content of the glasses. Therefore, he proposed a new scaling approach which uses the dielectric relaxation strength $\Delta\varepsilon = \varepsilon'(0) - \varepsilon'(\infty)$ as a scaling parameter for the frequency axis. Here, $\varepsilon'(\infty)$ denotes the high-frequency dielectric constant which is due to vibrational and electronic polarizations.

Subsequently, Schroder and Dyre [13] proved that the temperature-dependent conductivity spectra of a given glass can then be superimposed onto a master curve upon application of Sidebottom's scaling approach *if* the shape of these spectra does not depend on temperature. Consequently, the master curves of different glasses thus obtained will then superimpose *if* these master curves are identical in shape.

In this Letter, we show that the latter condition is generally not fulfilled. In single alkali glasses, the shapes of the conductivity spectra depend on the alkali oxide content as well as on the nature of the network former. Furthermore, there are pronounced differences in shape between the conductivity spectra of single and mixed alkali glasses. Owing to these differences in shape, the master curves of different glasses can generally not be superimposed by using Sidebottom's scaling approach. Consequently, we use a modified version of this scaling approach to detect and to analyze the differences in shape.

In the following, we reexamine the conductivity data of single and mixed alkali borate glasses [10,11,14] and of sodium germanate glasses [15]. Additionally, we have performed frequency- and temperature-dependent conductivity measurements on a $0.40\text{Na}_2\text{O} \cdot 0.60\text{GeO}_2$ glass. This glass was prepared by the same method as used for the germanate glasses with lower sodium oxide contents (see Ref. [15]).

It is well known that, for a given ion conducting glass and a given temperature, the real part of the ac conductivity, $\sigma'(\nu)$, is frequency independent below a characteristic crossover frequency. In this frequency range, $\sigma'(\nu)$ is identical to the dc conductivity σ_{dc}. Above the crossover frequency, $\sigma'(\nu)$ increases with frequency.

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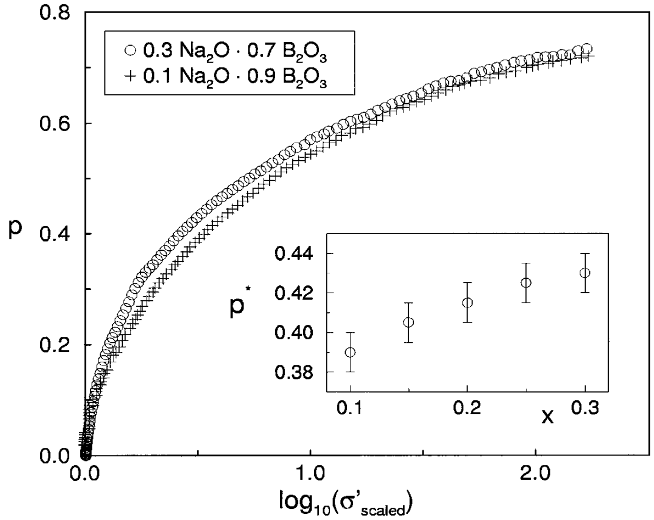

FIG. 1. Plot of the apparent exponent $p = \Delta\log\sigma'/\Delta\log\nu$ versus the scaled conductivity $\sigma'_{\rm scaled}(\nu) = \sigma'(\nu)/\sigma_{\rm dc}$ for two sodium borate glasses containing different amounts of sodium oxide. Inset: Dependence of the apparent exponent $p^* = p(\log\sigma'_{\rm scaled} = 0.5)$ on the sodium oxide content x of the borate glasses.

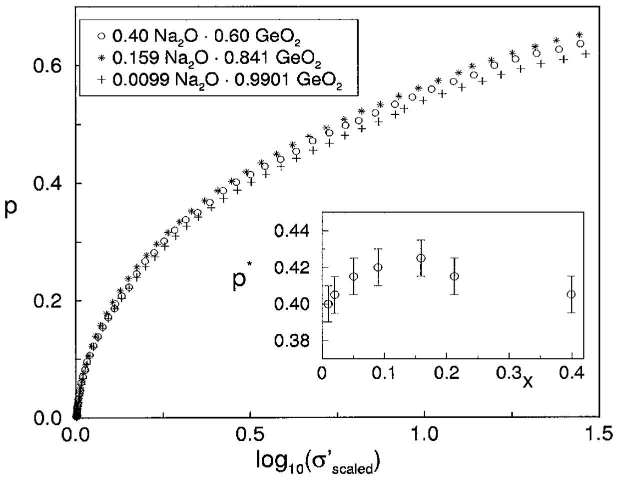

FIG. 2. Plot of the apparent exponent $p = \Delta\log\sigma'/\Delta\log\nu$ versus the scaled conductivity $\sigma'_{\rm scaled}(\nu) = \sigma'(\nu)/\sigma_{\rm dc}$ for sodium germanate glasses containing different amounts of sodium oxide. Inset: Dependence of the apparent exponent $p^* = p(\log\sigma'_{\rm scaled} = 0.5)$ on the sodium oxide content x of the germanate glasses.

In Fig. 1, the apparent exponent of double-logarithmic spectra of $\sigma'(\nu)$, $p = \Delta\log\sigma'/\Delta\log\nu$, is plotted versus the scaled conductivity $\sigma'_{\rm scaled}(\nu) = \sigma'(\nu)/\sigma_{\rm dc}$ for two sodium borate glasses of compositions $0.3{\rm Na_2O}\cdot 0.7{\rm B_2O_3}$ and $0.1{\rm Na_2O}\cdot 0.9{\rm B_2O_3}$. This type of plot was first used by Dyre and co-workers [13,16] for analyzing the shapes of model spectra. For each of our glasses, we first generate a conductivity master curve by plotting $\sigma'_{\rm scaled}$ versus $\nu/(\sigma_{\rm dc}T)$ [10,11,14,15]. Then we determine $p = \Delta\log\sigma'/\Delta\log\nu = \Delta\log\sigma'_{\rm scaled}/\Delta\log(\nu/\sigma_{\rm dc}T)$ numerically. The existence of a conductivity master curve implies that p is a temperature-independent function of $\sigma'_{\rm scaled}$. However, the $p(\sigma'_{\rm scaled})$ curves of the two sodium borate glasses with different sodium oxide contents can clearly be distinguished. For the $0.1{\rm Na_2O}\cdot 0.9{\rm B_2O_3}$ glass, the transition from the dc conductivity to the dispersive conductivity is more gradual than for the $0.3{\rm Na_2O}\cdot 0.7{\rm B_2O_3}$ glass. On the other hand, at higher frequencies and values of p above 0.7, the $p(\sigma'_{\rm scaled})$ curves seem to converge. The differences between the $p(\sigma'_{\rm scaled})$ curves are most pronounced around $\log\sigma'_{\rm scaled} = 0.5$. In the inset of Fig. 1, the apparent exponent $p^* = p(\log\sigma'_{\rm scaled} = 0.5)$ is plotted versus the sodium oxide content x of our borate glasses. The error of p^* is estimated to be around 0.01. As seen from the inset, p^* increases continuously with the sodium oxide content.

In Fig. 2, the same method of analysis is applied to sodium germanate glasses of compositions $x{\rm Na_2O}\cdot(1-x){\rm GeO_2}$ with $x = 0.0099$, 0.159, and 0.40. Here, the differences in shape between the conductivity spectra of different glasses are less pronounced than in the case of the sodium borate glasses. In the inset of Fig. 2, $p^* = p(\log\sigma'_{\rm scaled} = 0.5)$ is plotted versus the sodium oxide content x. Clearly, the dependence of p^* on x is distinct from that of the borate glasses. At low values of x up to $x = 0.159$, p^* increases with x. Above $x = 0.159$, p^* seems to decrease with x. However, taking into account the experimental error, the existence of a maximum of p^* around $x = 0.159$ is uncertain.

In Fig. 3, the $p(\sigma'_{\rm scaled})$ curve of the single alkali glass $0.3{\rm Na_2O}\cdot 0.7{\rm B_2O_3}$ is compared to that of the mixed alkali glass $0.3(0.6{\rm Na_2O}\cdot 0.4{\rm Li_2O})\cdot 0.7{\rm B_2O_3}$. For the mixed alkali glass, the transition from the dc conductivity to the dispersive conductivity is more gradual than for the single alkali glass. Note that the difference between the $p(\sigma'_{\rm scaled})$ curves is larger than in the case of the two sodium borate glasses containing 30 mol % and 10 mol % Na$_2$O.

In the following, we will demonstrate the application of a modified version of the Sidebottom scaling as an alternative and very sensitive method to detect and analyze the differences in shape between the spectra of various glasses. In this modified version, we replace $\Delta\varepsilon$ by $\varepsilon''_{\rm max}$. $\varepsilon''_{\rm max}$ is the maximum value of the imaginary part of the dielectric function, $\varepsilon''(\nu) = [\sigma'(\nu) - \sigma_{\rm dc}]/(2\pi\nu\varepsilon_0)$. Here, ε_0 denotes the permittivity of free space. For all of our glasses, the function $\varepsilon''(\nu)$ was obtained by a Kramers-Kronig transformation of $\varepsilon'(\nu)$. $\varepsilon''_{\rm max}$ could be determined more accurately than $\Delta\varepsilon$, since the determination of $\varepsilon''_{\rm max}$ is less affected by electrode polarization effects that the determination of $\Delta\varepsilon$.

It is now easy to show that this modified version of the Sidebottom scaling would then result in a common conductivity master curve for different glasses *if* the shapes of these master curves were identical, i.e., *if* the scaled

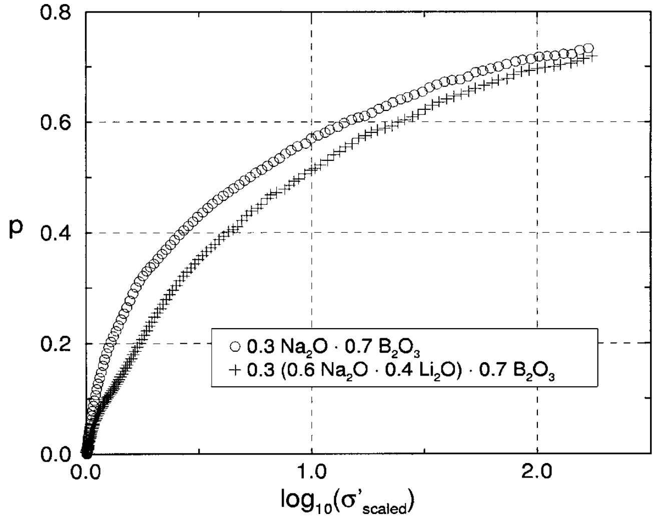

FIG. 3. Plot of the apparent exponent $p = \Delta \log \sigma' / \Delta \log \nu$ versus the scaled conductivity $\sigma'_{\text{scaled}}(\nu) = \sigma'(\nu)/\sigma_{\text{dc}}$ for one single alkali and one mixed alkali borate glass.

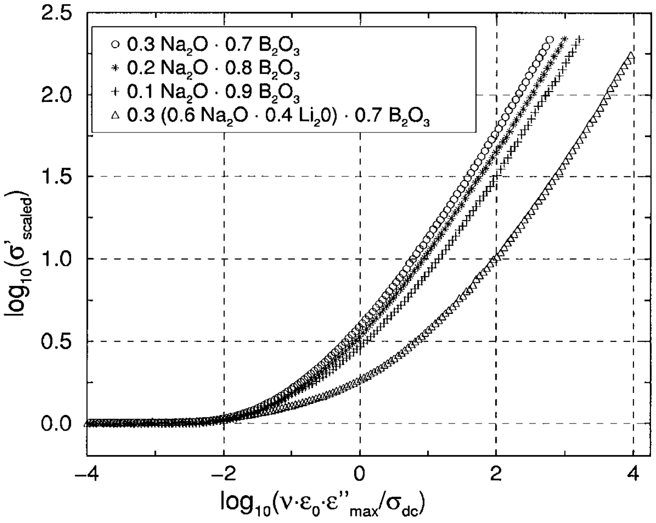

FIG. 4. Conductivity spectra of three sodium borate glasses and one mixed sodium-lithium borate glass scaled according to a modified version of Sidebottom's approach.

conductivity σ'_{scaled} was a temperature- and composition-independent function F of a scaled frequency $\nu/\nu_{\max}$:

$$\frac{\sigma'(\nu)}{\sigma_{\text{dc}}} = F\left(\frac{\nu}{\nu_{\max}}\right). \tag{1}$$

Here, $\nu_{\max}$ denotes the frequency of the $\varepsilon''(\nu)$ maximum. If Eq. (1) is valid, we may write the following for $\varepsilon''_{\max} = \varepsilon''(\nu_{\max})$:

$$\varepsilon''_{\max} = \frac{\sigma'(\nu_{\max}) - \sigma_{\text{dc}}}{2\pi \nu_{\max} \varepsilon_0} = \frac{[F(1) - 1]\sigma_{\text{dc}}}{2\pi \nu_{\max} \varepsilon_0}. \tag{2}$$

From this equation it follows that

$$\frac{\sigma_{\text{dc}}}{2\pi \nu_{\max} \varepsilon''_{\max} \varepsilon_0} = \frac{1}{F(1) - 1}, \tag{3}$$

i.e., the quantity $\sigma_{\text{dc}}/(2\pi \nu_{\max} \varepsilon''_{\max} \varepsilon_0)$ is independent of temperature and composition.

In Fig. 4, we apply the modified Sidebottom scaling to the conductivity data of the $x\text{Na}_2\text{O} \cdot (1 - x)\text{B}_2\text{O}_3$ glasses with $x = 0.1$, 0.2, 0.3 and to the conductivity data of the mixed alkali glass $0.3(0.6\text{Na}_2\text{O} \cdot 0.4\text{Li}_2\text{O}) \cdot 0.7\text{B}_2\text{O}_3$. While the conductivity isotherms of a given glass are superimposed onto a master curve, the master curves of different glasses do not collapse. With decreasing sodium oxide content, the master curves are shifted to higher values on the scaled frequency axis. This effect reflects the continuous change in the spectral shape with decreasing sodium oxide content as shown in Fig. 1. The experimental error of the position of the master curves on the $\log(\nu \varepsilon_0 \varepsilon''_{\max}/\sigma_{\text{dc}})$ axis is estimated to be around 0.05. Clearly, the shift between the master curves of the sodium borate glasses lies outside this error range.

The positions of the master curves of the single alkali glass $0.3\text{Na}_2\text{O} \cdot 0.7\text{B}_2\text{O}_3$ and of the mixed alkali glass $0.3(0.6\text{Na}_2\text{O} \cdot 0.4\text{Li}_2\text{O}) \cdot 0.7\text{B}_2\text{O}_3$ on the $\nu \varepsilon_0 \varepsilon''_{\max}/\sigma_{\text{dc}}$ axis differ enormously reflecting the pronounced difference in shape between these master curves (see Fig. 3).

In Fig. 5 the modified Sidebottom scaling is applied to the conductivity data of $x\text{Na}_2\text{O} \cdot (1 - x)\text{GeO}_2$ glasses with $x = 0.0099$, 0.159, and 0.40. Again, the composition dependence of the position of the master curves on the scaled frequency axis reflects the composition dependence of p^* as shown in Fig. 2. The comparison of Figs. 4 and 5 confirms that the dependence of the spectral shape on the sodium oxide content is clearly different in borate and germanate glasses.

We would like to emphasize that the composition dependence of the shape of the conductivity spectra we have analyzed here is *not* the main reason for the strong composition dependence of the width of electrical modulus peaks

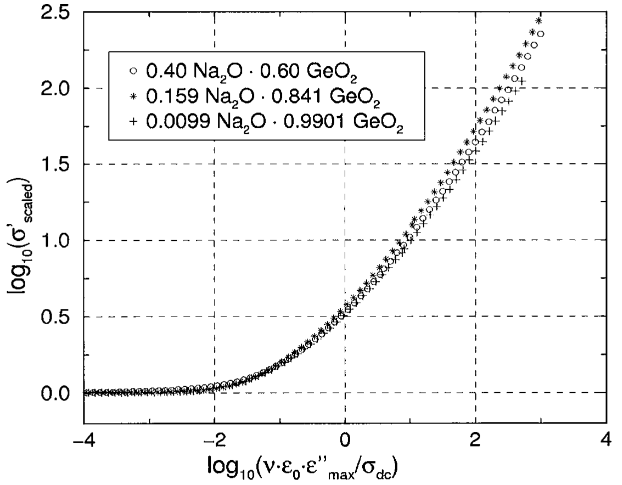

FIG. 5. Conductivity spectra of three sodium germanate glasses scaled according to a modified version of Sidebottom's approach.

[17–20]. As has been shown by several authors [21–23], the strong composition dependence of this width is mainly caused by the influence of $\varepsilon'(\infty)$ on the shape of the modulus peak.

Finally we would like to discuss what causes the changes in the shape of the conductivity spectra of single alkali glasses with increasing alkali content. Possible reasons are the increasing strength of the Coulombic interactions between the alkali ions on the one hand and structural changes on the other hand. As shown by Maass *et al.* [24,25], the frequency-dependent conductivity of interacting particles in disordered landscapes is influenced considerably by the strength of the repulsive interactions. Recently, Sidebottom [26] demonstrated that, in ion conducting crystals, the shape of the conductivity spectra depends strongly on the "local dimensionality" of the diffusion pathways. Our results from germanate glasses suggest that the "germanate anomaly" [27–31] influences the shape of the conductivity spectra of these glasses. At alkali oxide contents below approximately 15 mol %, the connectivity of the network increases with the alkali oxide content since GeO_4 units are converted into GeO_6 units. Above approximately 15 mol %, the network depolymerizes upon addition of alkali oxide due to the formation of nonbridging oxygens. A similar anomaly is found in borate glasses but it occurs at higher alkali oxide contents between 25 and 30 mol % [32]. These different structural features could be responsible for the different composition dependences of the spectral shapes we observe for germanate and borate glasses.

Owing to the limited amount of experimental data analyzed so far, this interpretation is, of course, rather speculative. Clearly, there is a need for a comprehensive analysis of these nonuniversal features in the ac conductivity spectra of various ion conducting glasses with different network structures.

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