Scaling behaviour in the frequency dependent conductivity of mixed alkali glasses

A. R. Kulkarni, Peter Lunkenheimer, Alois Loidl

Kulkarni, A. R., Peter Lunkenheimer, and Alois Loidl. 1998. “Scaling behaviour in the frequency dependent conductivity of mixed alkali glasses.” *Solid State Ionics* 112 (1-2): 69–74. https://doi.org/10.1016/S0167-2738(98)00210-0.

Scaling behaviour in the frequency dependent conductivity of mixed alkali glasses

A.R. Kulkarni*, P. Lunkenheimer, A. Loidl

Institute of Physics, Experimentalphysik V, Universität Augsburg, D-86135, Germany

1. Introduction

Ionically conducting glasses have gained importance in recent years for two reasons. First due to their technological applications for example in microbatteries, sensors and smart windows [1–3]. The second reason is the fundamental interest in the study of the mechanism of ion transport in glasses [4,5]. A large number of glass forming systems has been investigated over a wide range of compositions with respect to transport related properties such as the conductivity σ and its dependence on temperature, frequency, concentration, diffusivity and relaxations both electrical and mechanical. An excellent account of the experimental observations of electrical relaxations in ion conducting glasses has been published recently [6]. Ion dynamics is mostly studied by analyzing data from experimental techniques such as ac conductivity, nuclear magnetic resonance, quasi-elastic neutron and light scattering [7]. Among these techniques, ac conductivity measurements are widely used and the data are usually analyzed in terms of conductivity relaxations. In many ionic glasses the shape of the spectra are unaffected when parameters as for example the composition and the temperature

---

*Corresponding author. Present address: Dept. Met. Eng. and Mat. Sci., Indian Inst. of Technology, Bombay, Mumbai 400076, India. Tel.: +91 22 576 7636; fax: +91 22 578 3480; e-mail: ajit.@met.iitb.ernet.in

are varied. On the other hand, the dc conductivity and the onset frequency of the dispersion changes in characteristic fashion and leads to scaling laws. The first universality was suggested by Jonscher and was called Universal Dielectric Response (UDR) [8]. In later years this term has been modified to Universal Dynamic Response to include both conducting and dielectric behavior [9].

During the past few years the scaling behavior of $\sigma(\nu)$ has been investigated in several glasses. Kahnt [10] examined the scaling of a large number of structurally different oxide glasses and showed that all the $\sigma(\nu)$ curves could be overlapped resulting into a single curve. The power-law exponent in these glasses varied between 0.67 ± 0.05. Elliot [11] reviewed the frequency-dependent conductivity of ionically and electronically conducting glasses and observed that although the ac conductivity could be scaled in both types of glasses, the response varied significantly in either systems. Lee et al. [12,13] reported a new universality based on a power-law analysis of the ac conductivity over a wide range of temperatures. They claimed that although the power-law dispersion exhibited by $\sigma(\nu)$ can be scaled to a master curve, it appears to fail at low temperatures. This behavior was found for a few materials and termed second universality [12]. Similar behavior was reported for phosphate glasses, including a mixed alkali composition and ion-conducting polymers [14,15]. Recently Macdonald [16] applied a complex-non-linear-least-squares method to evaluate previously published data [11] but did not observe this new-universality casting doubt about this analysis. Finally, Roling et al. [17] have reported a new scaling function of the frequency dependent conductivity of disordered materials. These authors have shown that at high temperatures the ac conductivity of sodium borate glasses can be scaled by the dc conductivity which led to the conclusion that the ionic relaxations are both temperature and composition independent. Comparing this scaling with the modulus formalism they have shown that it may be more meaningful to discuss conductivity relaxations in terms of the log–log dependence of the conductivity on frequency since it takes into account the mobility and the number density of charge carriers.

Recently, for the first time, we have reported the mixed alkali effect (MAE) in the ac conductivity of the ternary $x\mathrm{LiF}–(80-x)\mathrm{KF}–0.2\mathrm{Al(PO_3)_3}$ glasses, by analyzing our data using the universal dynamic response [18]. The power-law exponent s was found to be dependent both on composition and temperature. In this article, we investigate scaling in the mixed alkali system and compare it with a single alkali system at high temperatures only. The motivation is to study changes in scaling functions for glasses containing two species of conducting cations, to collect additional experimental evidence regarding ion dynamics in mixed alkali glasses and to evaluate whether the proposed scaling functions for the frequency dependent conductivity are also adequate to explain the shapes of the conductivity spectra of mixed alkali glasses. For a proper comparison with the reported data we have employed a commonly used frequency range (20 Hz–1 MHz). We have shown that two scaling functions, each corresponding to the dominant charge carriers below and above the minimum in conductivity, are needed to explain the frequency dependent conductivity of the mixed alkali glasses.

2. Experimental procedure

Starting materials, LiF, KF and $\mathrm{Al(PO_3)_3}$ mixed in appropriate proportion (each glass weighing about 10 g) were melted in a covered platinum crucible at a temperature of 1100–1200 K for 5 min. The melts were cast between two brass plates which were pre-heated to 473 K to avoid thermal stress induced shattering of the samples, and the 3 cm × 1.5 cm × 0.5 cm rectangular blocks were annealed for 12 h before slowly cooling to room temperature. Glass transition temperatures were recorded on 10 mg samples in sealed aluminum pans using a Perkin Elmer DSC-2 differential scanning calorimeter at a heating rate of 10 K per min. For conductivity measurements, silver paste was applied on the parallel faces of the samples. The ac electrical conductivity was determined using computer controlled facilities. An HP 4284 impedance/gain phase analyzer scanned the frequency from 20 Hz to 1 MHz. The data was recorded in the temperature range 323 K–523 K and the temperature was controlled within ±0.5 K.

3. Results and discussion

We have analyzed the frequency dependence of conductivity for all the glasses as isotherms in log–log plots. A representative plot, for composition G6 (see Table 1) is shown in Fig. 1. It may be pointed out that, although the data were recorded over 323 K–523 K, only few temperature scans are included in the plot for clarity. The dynamic conductivity showed a typical behavior: a frequency-independent plateau and a power-law increase at high frequencies. The solid lines are fits to the data using the sum of a power-law and the dc conductivity σ_{dc}. At this juncture it is appropriate to mention that we have considered only the real part of the complex conductivity. The same power-law will follow for the

Table 1
Composition and electrical properties of LiF–KF–Al$(PO_3)_3$ glasses

	LiF	KF (mol %)	Al(PO_3)	ΔE (Kcal mol^{-1})	σ_{dc} 473 K (Ω^{-1} cm^{-1})	log A (Ω^{-1} cm^{-1})
G1	0	80	20	19.11	1.60×10^{-7}	2.05
G2	10	70	20	22.83	2.25×10^{-8}	2.92
G3	20	60	20	24.43	4.97×10^{-9}	3.01
G4	30	50	20	25.96	1.46×10^{-9}	3.18
G5	40	40	20	23.44	4.04×10^{-9}	2.46
G6	50	30	20	23.24	1.99×10^{-8}	3.06
G7	60	20	20	20.96	2.09×10^{-7}	3.02
G8	70	10	20	15.89	3.33×10^{-6}	1.88
G9	80	0	20	13.37	4.64×10^{-5}	1.86

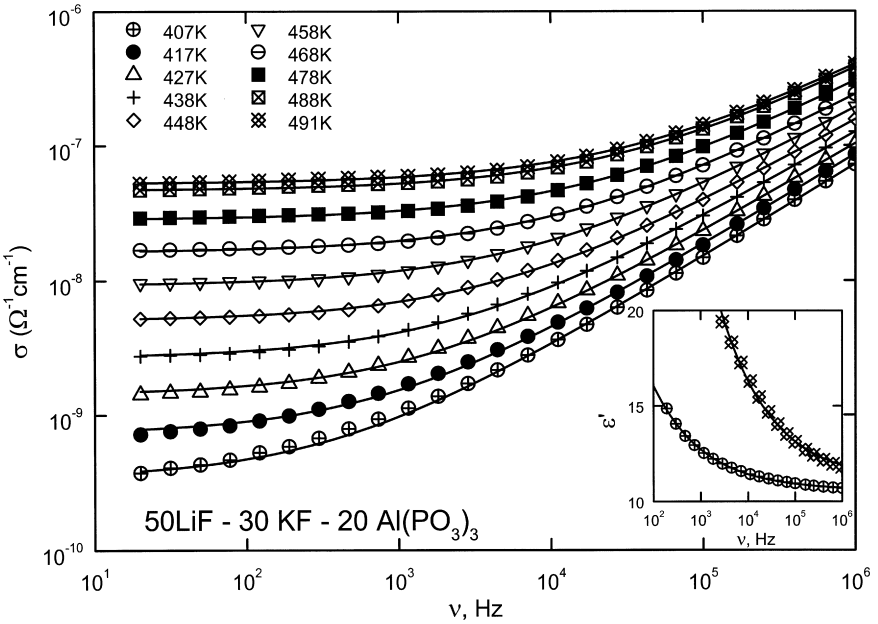

Fig. 1. A representative plot of the variation of the ac conductivity with frequency over the temperature range 407–491 K. The sample composition is 50 LiF–30 KF–20 Al$(PO_3)_3$. The lines are fits to the data with the sum of a power-law and σ_{dc}. The inset shows the variation of the real part of the dielectric constant with frequency for the lowest (407 K) and the highest (491 K) temperature. The lines are the fits to the data with a sum of power-law and ε_∞. The dielectric data below 100 Hz, due to electrode polarisation, are not included in the inset.

imaginary part of the complex conductivity also [8,9]. For the real part of the dielectric constant (ε') the power-law leads to a ω^{s-1} behaviour with an additional ε_∞ contribution. The inset to Fig. 1 shows the power-law fit with ε_∞ contribution to the real part of the dielectric constant at the lowest and the highest temperatures. The data fits well with same parameters as observed with real part of the conductivity. The fits have been obtained with ε_∞ as the only free parameter. The power-law exponent s was found to be temperature dependent as observed earlier [11,13] and varied between 0.70 and 0.59 in the temperature range 407–491 K. The dc conductivity, obtained from fits to the experimental data as a function of temperature, showed Arrhenius behavior obeying the relationship $\sigma_{\mathrm{dc}} = A \exp(-\Delta E/kT)$, where A is the pre-exponential factor, ΔE is the activation energy and k is the Boltzmann constant. In this investigation we have restricted our discussion to high temperature data only. The values of the dc conductivity at 473 K and activation energies obtained from a fit using the Arrhenius-law are given in Table 1. It may be noted that the dc conductivity goes through a minimum for glass G4, corresponding to a maximum in the activation energy. This confirms that we have observed the MAE in the dc conductivity.

Let us now turn our attention to the matter of scaling this frequency dependent conductivity. In Fig. 2 we show the normalization of $\sigma(\nu,T)$ for the data of Fig. 1. The data have been normalized with respect to the dc conductivity and the measurement temperature, plotting $\sigma'/\sigma_{\mathrm{dc}}$ vs $\nu/(\sigma_{\mathrm{dc}}T)$. The data for all temperatures collapsed into a single curve, indicating that the relaxation is temperature independent as observed previously for oxide glasses and amorphous semiconductors [10,11,17]. All nine compositions in the present systems (Table 1) could be normalized as described above.

To explore the possibility of scaling mixed alkali glasses, let us represent the glass system as xLiF–$(80-x)$KF–20Al$(PO_3)_3$ containing two mobile species, Li^+ and K^+. While the concentration of both these species is varying the total concentration of the mobile ions is held constant at 80 mol%. In Fig. 3a we plot the temperature independent master curves for all the compositions simultaneously. It may be noted that all the curves do not collapse into a single curve. In order to scale the data for different compositions we adopt the scaling of Roling et al.

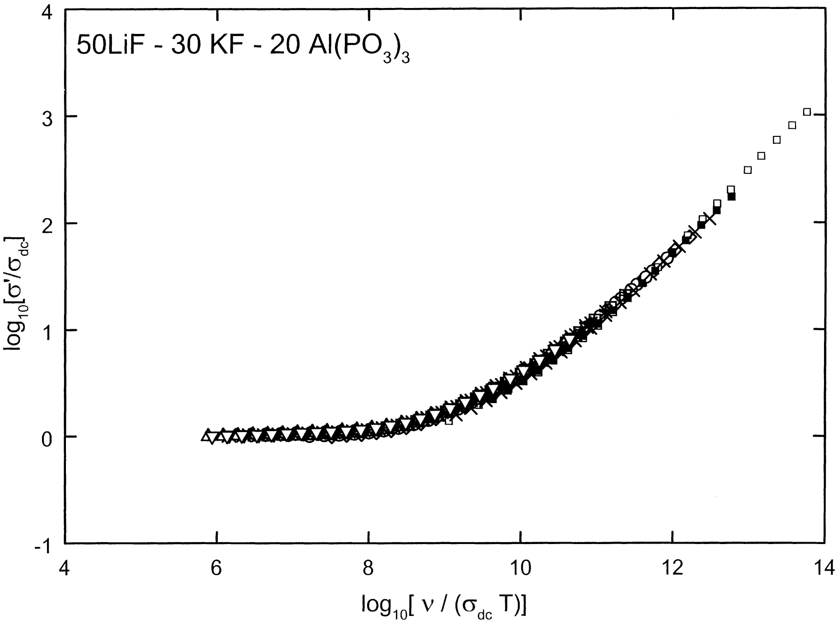

Fig. 2. Master curve for the data in Fig. 1. Note collaps of the data into a single curve in the temperature range 407–491 K.

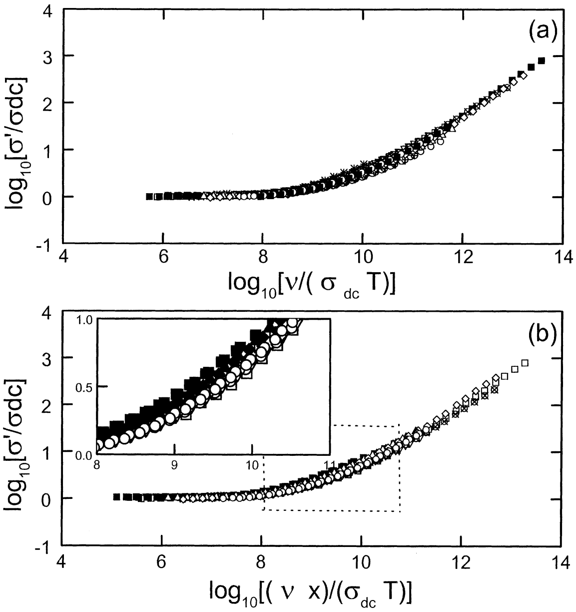

Fig. 3. (a) Individual master curves, for all the nine compositions in the present systems. Note the non-overlapping nature of these curves. (b) Master curves obtained by normalizing the frequency data in (a) by x, in the x LiF–$(80-x)$KF–20Al$(PO_3)_3$ glasses. The separation into two sets of master curves with filled and open symbols is clearly seen.

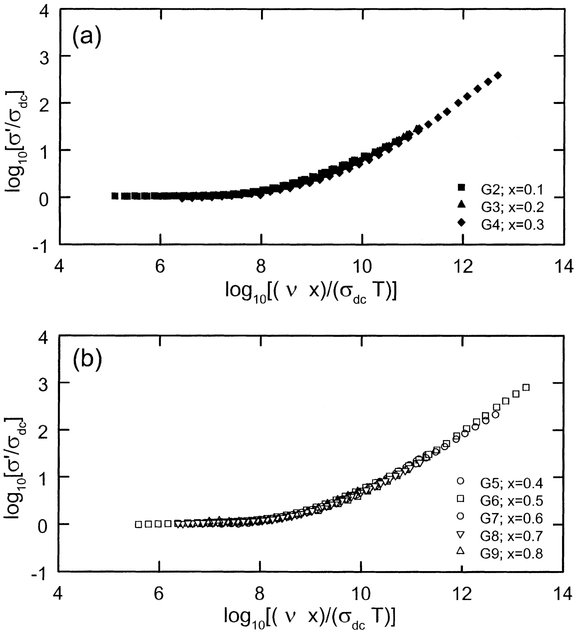

Fig. 4. (a) Master curve indicating temperature and composition independent relaxation for dominant K^+ region. (b) Scaling for the dominant Li^+ region.

[17] and use the concentration of LiF as an additional scaling factor for the frequency axis. The result of this normalization is shown in Fig. 3b. It is evident that again all curves fail to overlap into a single curve. Therefore, at first glance, it appears that the scaling method predicted to be universal [17] may not apply to mixed alkali glasses. However, a closer look at the figure reveals that the composition master curve has in fact split into two sets of superimposed curves. The filled symbols correspond to one set of compositions and the open symbols correspond to another. This is clearly shown in the inset which shows the enlarged view of the area marked by the dotted lines. The data sets pertaining to each of these scaled regions were separated and are shown in Fig. 4 a and b. It is interesting to note that one set of master curve corresponds to compositions G1–G4 ($x = 0$ to 0.4; Fig. 4a) and the other set of curves to the compositions G5–G9 ($x = 0.5$–0.8; Fig. 4b). A close examination of the table shows that these two regions are located on either side of the mixed alkali composition where the minimum in conductivity was observed. This indicates that there are two distinct scales on either side of the minimum. In addition, the scaling in this mixed alkali system is not a simple sum of these two functions.

Recalling the procedure of Roling et al. [17] and assuming that the number density of charge carriers is proportional to its concentration the scaling function can be written as

$$[\sigma'/\sigma_{dc}] = F[\nu/(\mu_{dc}.T)]$$

where σ' is the real part of the frequency dependent conductivity and μ_{dc} is the dc mobility. This holds good for both, the potassium ion dominant compositions before the cross-over and also to the lithium ion dominant compositions after the cross-over.

Measurements of transport numbers and self diffusion coefficients in mixed alkali glasses reveal a ‘mobility crossover’ where the conductivity reaches a minimum and the dc mobility of both cations is identical [1]. In the present case for small x the K^+ ions are dominant initially and in this region the mobility does not change with compositions. As KF is progressively replaced by LiF a mobility crossover takes place at the composition with minimum conductivity. Finally, for large x the Li^+ ions become dominant and the mobility assumes another composition independent value. A mobile ion crossover was reported for mixed cation and anion conducting glasses from conductivity and glass transition temperatures [19,20]. This supports our assertion that in each of these dominant cation regions the ion dynamics is independent of both temperature and composition and leads to a separate scaling function. The difference in the two scaling functions may also be explained on the basis of the dynamic structure model [21] which predicts the MAE as a relaxation process in which the amorphous backbone adjusts itself depending on the dominant cations and substantiates our arguments on the use of two scales to explain the frequency dependent conductivity. It will be interesting to investigate this scaling feature in the other mixed mobile glasses, for example, those containing an anion and a cation (say Li^+/Na^+ and F^-/Cl^-) and also with two different anions (say Cl^- and F^-), before generalizing the scaling behavior of the mixed mobile glasses.

In conclusion, we have shown that the scaling function proposed by Roling et al. [17] which explains the dynamics in ion conducting glasses can be applied to a mixed alkali glass. However, depending on the dominant charge carries two functions are needed to explain the frequency dependent conductivity to be temperature and concentration independent. This behavior is consistent with the dynamic structure model of glasses.

Acknowledgements

One of us (ARK) is grateful to Alexander Von Humboldt Foundation for fellowship to carry out the present work.

References

[1] C.A. Angell, Chem. Rev. 90 (1990) 523.
[2] M.D. Ingram, Phys. Chem. Glasses 28 (1987) 215.
[3] C.A. Angell, Ann. Rev. Phys. Chem. 43 (1992) 693.
[4] M.D. Ingram, P. Mass, A. Bunde, Ber. Bunsenges. Phys. Chem. 95 (1991) 1002.
[5] K. Funke, R. Hoppe, Solid State Ionics. 40–41 (1990) 200.
[6] K.L. Ngai, J. Non-cryst. Solids. 203 (1996) 232.
[7] D. Brinkmann, Progr. NMR Spectrosc. 24 (1992) 527.
[8] A.K. Jonscher, Nature 256 (1975) 566.
[9] A.K. Jonscher, in: Universal Relaxation Law, Chelsea Dielectric Press, London, 1996, Ch. 1.
[10] H. Kahnt, Ber. Bunsenges. Physik. Chem. 95 (1991) 1021.
[11] S.R. Elliott, Solid State Ionics 70–71 (1994) 27.
[12] W. Lee, J. Liu, A.S. Nowick, Phys. Rev. Lett. 67 (1991) 1559.
[13] A.S. Nowick, B.S. Lim, A.V. Vaysleyb, J. Non-Cryst. Solids 172–174 (1994) 1243.
[14] D.L. Sidebottom, P.F. Green, R.K. Brow, Phys. Rev. Lett. 74 (1995) 5068.
[15] D.L. Sidebottom, P.F. Green, R.K. Brow, J. Non-cryst. Solids 203 (1996) 300.
[16] J.R. Macdonald, J. Non-Cryst. Solids 210 (1997) 70.
[17] B. Roling, A. Happe, K. Funke, M.D. Ingram, Phys. Rev. Lett. 78 (1997) 2160.
[18] A.R. Kulkarni, P. Lunkenheimer, A. Loidl, J. Non-Cryst. Solids (submitted).
[19] D.L. Sidebottom, P.F. Brow, R.K. Green, J. Non-Cryst. Solids 222 (1997) 354.
[20] A.R. Kulkarni, C.A. Angell, J. Non-Cryst. Solids 99 (1988) 195.
[21] P. Mass, A. Bunde, M.D. Ingram, Phys. Rev Lett. 68 (1992) 3064.