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Mixed alkali effect in the ac conductivity of glasses

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Abstract

The ac electrical conductivity of mixed alkali LiF-KF-Al(PO₃)₃ glasses has been investigated using the complex conductivity formalism. For the first time, a mixed alkali effect has been detected in the ac conductivity of glasses which also exhibit the classical mixed alkali effect in the dc conductivity. The observed conductivity relaxations have been analyzed using three and four parameter functions. Jonscher's universal dielectric response yields the best description of the experimental data. ©2000 Elsevier Science S.A. All rights reserved.

1. Introduction

The mixed alkali effect (MAE) refers to the non-linear variations of physical properties of glasses. The most celebrated case is the so-called 'mixed alkali' effect in which mixing of two alkali oxide glasses (silicate, borate, phosphate etc.) of comparable dc conductivities, results in a glass with a dc conductivity orders of magnitude lower than either of the binary end-member glasses [1–3]. Depending on composition both, the activation energy and the exponential factor go through a maximum though the activation energy is known to be a dominant factor. In recent years MAE was found in mixed crystals (β -alumina) [4], cation and anion (Li⁺ and F[−]) conducting glasses [5,6] and also for glasses containing two glass formers (P₂O₅-B₂O₃) [7]. A new term 'Mixed Mobile Ion (MMI)' effect was suggested to include all these variations [2]. Although, this effect is known for a long time there is no acceptable theory to explain physical origins of this effect and only limited work has been reported on the frequency dependence of conductivity (ion dynamics) in mixed alkali glasses. Moynihan [8] reported that, in the hydrate melts, the dc conductivity is a strong function of concentration and temperature, while the ac conductivity is a linear function of concentration. The disappearance of the mixed alkali effect at high frequencies, was also predicted by the dynamic structure model [9] in agreement with re-

ported data [10,11]. Recently, Hunt [12] applied the theory of percolative transport to the MAE and predicted a disappearance of MAE when temperature or frequency is raised. To the best of our knowledge, there are no reports on how the ac conductivity varies with composition in ion conducting glasses with two different types of mobile charge carriers.

In this paper, we investigate the variation of ac conductivity of mixed alkali glasses and for the first time provide evidence for a mixed alkali effect in the ac conductivity of glasses which exhibit MAE in the dc conductivity. We extract the ac conductivity from the complex conductivity and compare the composition variation of both the ac and the dc conductivity. For a proper comparison with reported data we have chosen the commonly used frequency range. 20 Hz–1 MHz. The comparison is, therefore, unaffected by the so-called window effect [13]. We have also analyzed our data within the framework of the widely used modulus formalism to provide a direct comparison of our data with that reported in the literature.

The ac electrical data, in principle, can be analyzed in terms of complex modulus, conductivity, admittance or complex dielectric constant. Ionically conducting glasses have been studied using both modulus and power-law formalisms although the use of the former is quite widespread. In recent years, there has been a debate regarding the most appropriate formalism to explain ac conductivity/relaxation in glasses [14–16]. Recently, Roling et al. [17] have shown that it may be more meaningful to discuss conductivity relaxations in terms of the log–log dependence of the

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Table 1
Composition and electrical properties of LiF-KF-Al(PO₃)₃ glasses

	LiF	KF	Al(PO ₃) ₃	$\Delta E(\text{Kcal mol}^{-1})$	$\sigma_{\text{dc}} 473 \text{ K } (\Omega \text{ cm})^{-1}$	$\log A (\Omega \text{ cm})^{-1}$
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

conductivity on frequency since it takes into account the mobility and the number density of charge carriers. It was shown by Jonscher [18] that the ac conductivity can be parameterised using so-called Universal Dielectric Response (UDR)

$$\sigma(\omega) = \sigma_{\text{dc}} + \sigma_0 \omega^s \quad (1)$$

where σ_{dc} is the dc (or frequency independent) conductivity, σ_0 is a temperature dependent parameter and s lies in the range $0 < s < 1$. In this investigation, we analyze our data primarily using the complex conductivity formalism but also show the results of an evaluation of the electric modulus. Previously the ac conductivity of MAE glasses has been analyzed using Eq. (1). However, no clear trends could be established for the composition variation or the exponent s . Jain and Mundy [19] analyzed the conductivity of three alkali triborate glasses. The exponent was found to depend on temperature and no composition correlation emerged. A lack of dependence of s on x was also reported in the MAE system in Li₂O-Na₂O-P₂O₅ [7,20]. Here s remained constant ($= 0.45$) within experimental errors.

There are some reports, on conductivity relaxation and its dependence on composition (including MAE glasses), using the complex modulus formalism. The variation of the stretched exponential parameter β_{KWW} with composition forms the main basis of these studies. A maximum in β with composition in a mixed alkali glass series was explained by Ngai et al. using the coupling model [21]. However, Tomozawa et al. [22] found a maximum in β only for high concentrations of alkali ions while at lower concentrations β showed a minimum. The former was attributed to the failure of the stretched exponential function to describe the experimental data at low frequencies for high alkali containing glasses. From above discussions, it is quite clear that there are no definite correlations and explanations for these discrepancies. A detailed analysis of relaxation in MAE systems is therefore necessary to resolve this issue. The present investigation is an attempt in this direction.

High ionic conductivity has been reported in LiF-Al(PO₃)₃ glasses which are predominantly lithium ion conductors [5]. In the present work, we have studied ternary LiF-KF-Al(PO₃)₃ glasses. We have examined dc and ac conductivities of these glasses, as KF is progressively added

to replace LiF in 80LiF-20Al(PO₃)₃ glass. The motivation has been to see a mixed alkali effect in both dc and hitherto unreported ac conductivity as mobile lithium and potassium ions interfere with one another.

2. Experimental

Nine glasses, whose batch compositions are given in Table 1, were melted in a covered platinum crucible, at 1100–1200 K for 5 min, cast into rectangular blocks, and annealed near T_g before slowly cooling to room temperature. The frequency dependent conductivity was measured in a temperature range 223–523 K and over a frequency range 20–10⁶ Hz using a Hewlett Packard HP 4284 impedance analyzer, and the automatic data acquisition system developed in the laboratory. The electrodes were conducting silver paste.

3. Results and discussion

We have analyzed the frequency dependence of conductivity for all the glasses as isotherms in the log–log plots. At very low temperatures, only ac conductivity was observed. As the temperature was increased, the dynamic conductivity showed a typical behavior: a frequency independent plateau and a power-law increase at high frequencies. The dc conductivity (σ_{dc}), obtained at various temperatures by fitting Eq. (1) to the experimental data, showed Arrhenius behavior of conductivity obeying the relationship $\sigma_{\text{dc}} = A \exp(-\Delta E/kT)$, where A is the pre-exponential factor, ΔE the activation energy and k is the Boltzmann constant. The exponent s was found to be temperature dependent as observed previously [13,23]. 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 seeing how the ac conductivity varies with composition for these glasses

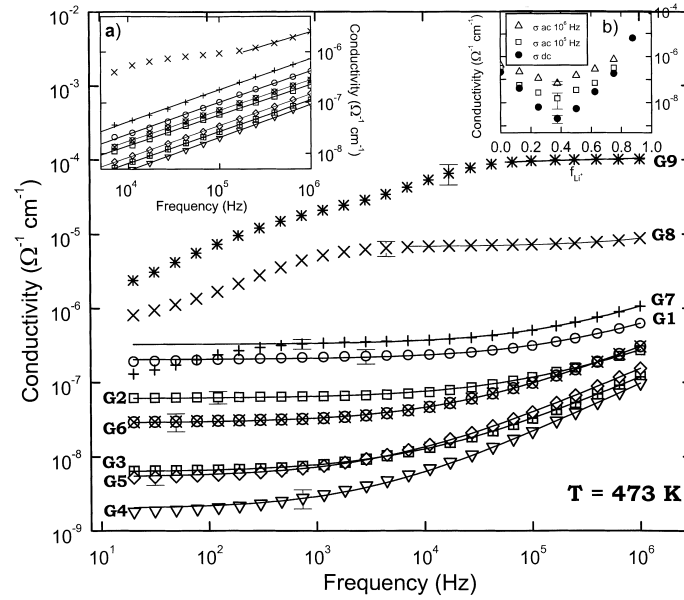


Fig. 1. Double logarithmic plots of the frequency dependent conductivity for LiF-KF-Al(PO₃)₃ glasses at 473 K. The solid lines are fits to Eq. (1). The insets to the figure show (a) the frequency variation of the ac conductivity (the lines are linear fit to the data) and (b) the variation of the ac and the dc conductivity with composition.

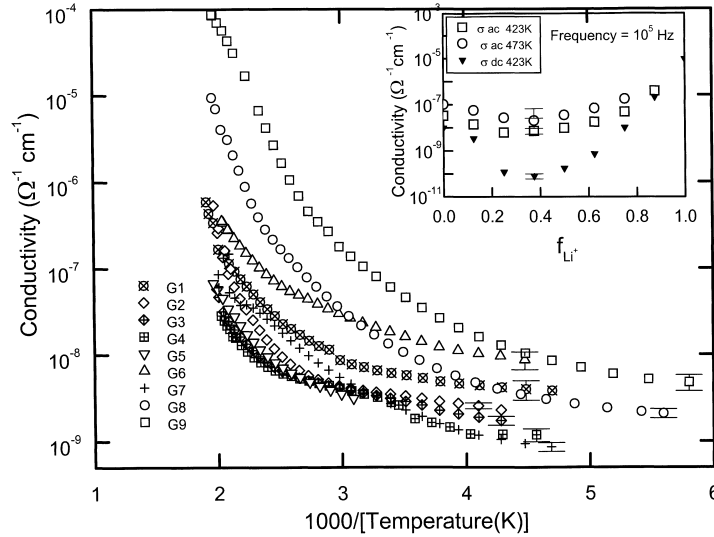


Fig. 2. Isochronal diagram of the ac conductivity σ_{ac} , plotted in Arrhenius coordinates for all compositions in the LiF-KF-Al(PO₃)₃ system, at 10⁵ Hz. The inset to the figure shows the variation of the ac conductivity at 423 and 473 K with composition. Values of dc conductivity at 473 K are included for comparison.

at a fixed temperature. Fig. 1 shows double logarithmic plots of the real part of the complex conductivity σ' at 473 K. The plateau of σ' spread over several decades in the medium frequency range corresponds to the dc conductivity. The rapid fall of the conductivity at low frequencies, for compositions G8 and G9, is the well-known electrode polarization phenomenon. All the glasses showed typical power-law behavior. Again the dc conductivities were extracted by fitting Eq. (1) to the real part of complex conductivity. In the Inset b to Fig. 1, we show the variation of the dc conductivity (473 K) and the ac conductivities,

at 10⁵ and 10⁶ Hz (after subtracting the dc conductivity) with the lithium-cation mole fraction defined by the ratio $f_{Li^+} = \text{mol LiF/mol(LiF + KF)}$. It is interesting to note that the ac conductivity also goes through a minimum at the same composition and in the same manner as does the dc conductivity. Although, the magnitude of the effect seems to decrease with frequency, it nevertheless is significant and indeed the ac conductivity exhibits a MAE. In the inset a to Fig. 1, we have plotted variation the ac conductivity ($\sigma' - \sigma_{dc}$) with applied frequency. For all the compositions the conductivity varies linearly with frequency, over 2.5

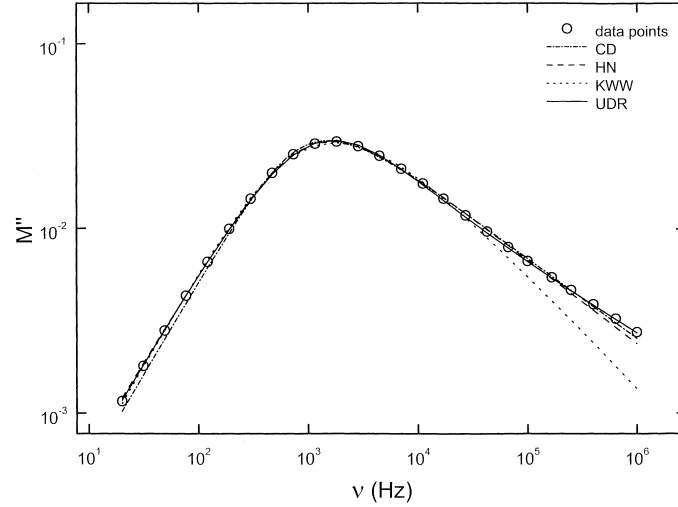


Fig. 3. Modulus spectrum for a representative mixed alkali composition [60LiF-20KF-20Al(PO₃)₃] of the present system. Four functions, Cole–Davidson, Kohlrausch–Williams–Watt, Havriliak–Negami and UDR are fitted to the data. The UDR shows the best fit to modulus data for this composition.

decades, except for the compositions with high dc conductivity. In this case, the linear variation is seen only over a decade. The value of exponent s , determined over a decade will exhibit significant error. These are not considered in the composition dependence of s .

In order to explore this effect further, we have studied the temperature dependence of the ac conductivity. The ac conductivity was defined at 10^5 Hz by $\sigma_{ac} = \sigma(10^5 \text{ Hz}) - \sigma_{dc}$ as reported earlier by Sidebottom et al. [23]. In Fig. 2, an Arrhenius representation of the ac conductivity (defined above) is depicted for all mixed alkali compositions. At high temperatures, compositions with high conductivity, G8 and G9, show Arrhenius behavior and at low temperatures the ac conductivity shows only a weak temperature dependence. In the inset, the variation of $\sigma_{ac}(10^5 \text{ Hz})$ with composition at 423 and 473 K is compared with σ_{dc} at 473 K. Again the ac conductivity shows a minimum with composition confirming observation in Fig. 1. This is a decisive result that we are indeed observing a MAE in the ac conductivity. It is also evident from Figs. 1 and 2 that the MAE in the ac conductivity is present at different frequencies at a fixed temperature and also at a fixed frequency (10^5 Hz) and two different temperatures with significant depth. In both cases, the depth decreases with increasing temperature or frequencies. This is in contrast to the reported linear variation of the ac conductivity [8] and is a new result.

Finally, we show some results from an analysis of our data within the modulus formalism. A typical modulus spectrum for one of the compositions (close to minimum conductivity) is shown in Fig. 3. It may be noted that the spectrum is slightly asymmetric suggesting a stretching behavior for the mixed alkali composition. In order to get a proper description of the relaxation, we have fitted the data with three commonly used phenomenological functions namely, the three parameter Cole–Davidson (CD) and Kohlrausch–Williams–Watts (KWW) functions, and the four

parameter Havriliak–Negami (HN). The fits with these functions are shown as lines in Fig. 3. In addition, we show a fit using Jonscher's four-parameter expression for the complex conductivity, Eq. (1) and $\sigma'' = \sigma' \cdot \tan(s\pi/2) + e_{\infty}e_0/2\pi\nu$ [24] which has been converted to the modulus data. It may be noted that the modulus fit obtained from the complex conductivity parameters gives the best description of the experimental data followed by the four parameter HN function. The three parameter functions, CD and KWW, fail to explain the low and high frequency deviations, respectively. This is in disagreement with the observation of Moynihan [14,25] whose analysis shows KWW as the best function to describe relaxation phenomena in glasses in the range $10^{-2} < \omega\tau < 10^2$. A detailed analysis of our data using above fitting functions, over the entire frequency range, will be published elsewhere [26]. The fitting parameters, β_{CD} , β_{KWW} , s and β_{HN} , obtained at 473 K, are plotted with composition in Fig. 4. Within experimental errors the trend in s with compositions shows a maximum for G4, where both

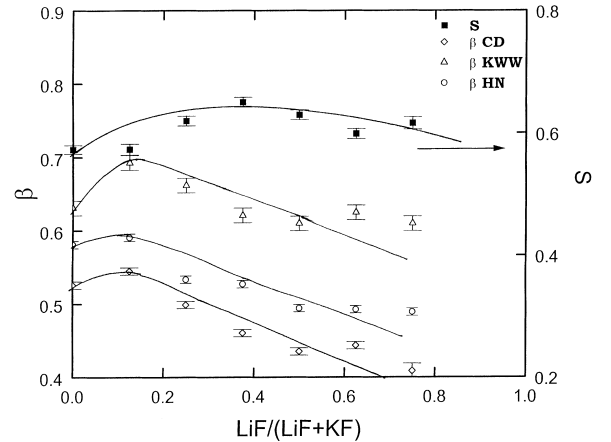


Fig. 4. Compositional variation of relaxation parameters, β_{CD} , β_{KWW} , β_{HN} and power law exponent s at 473 K.

ac and dc conductivity show a minimum, while the other three functions show a maximum for G2 and then a monotonic drop in the value of relaxation parameters. This is in contrast to the observation in $\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{P}_2\text{O}_5$ glasses [20] where s remained constant. This leads us to conclude, that a comparison of the composition variation of relaxation parameters in MAE, obtained from KWW analysis in previously reported data with our data is not straightforward. In the present glassy system, fits with Jonscher's expression gives best description of the relaxation and the composition dependence of the relaxation parameter s shows a maximum for the same composition where the ac conductivity goes through a minimum. This result also reinforces the recent arguments about the usefulness of the UDR formalisms to explain ion dynamics in fast ion conducting glasses [17].

4. Conclusions

In conclusion, we have shown that the celebrated mixed alkali effect which is well documented for the dc conductivity of glasses also occurs in the ac conductivity. The complex conductivity formalism gives the best description of the electrical relaxation. The maximum in the exponent s occurs for the same composition where ac conductivity shows a minimum.

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