IONIC CONDUCTIVITY and RELAXATIONS IN Li AND (Li AND K) FLUOROPHOSPHATE GLASSES

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ABSTRACT

Fluorophosphate glasses in the system LiF-KF-$Al(PO_3)_3$ were synthesized and the glass-transition temperature, dc conductivity and electrical relaxations were studied. The conductivity spectrum of the 0.8 LiF-0.2$Al(PO_3)_3$ glass was recorded at room temperature covering 17 decades in frequency. A maximum conductivity of 38 (Ω^{-1} cm^{-1}) at 3.4 x 10^{13} Hz agreed with the theoretically predicted value. For mixed cation glasses, the frequency dependent conductivity was measured in the frequency range 20 Hz to 2 GHz and at temperatures 100 K $\leq$ T $\leq$ 523 K. While the dc conductivity showed a characteristic minimum with composition, the ac conductivity also exhibited the mixed alkali effect. The data recorded at room temperature supported the existence of two relaxation processes: the Jonscher's universal dielectric response at low frequency and a high-frequency process characterized by a power-law exponent larger than unity.

INTRODUCTION

Ionic conductivity and electrical relaxations in fast ion conducting glasses have been intensely investigated in recent years [1-3]. Ion dynamics is usually investigated from electrical conductivity relaxations represented by the ac

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conductivity from near zero frequency (dc) to the far or mid infrared spectrum to which relaxations of the ion and network motions contribute. Many models have been proposed in recent years to explain the data below 10^6 Hz, but only limited data are available in the range 10^6 to 10^{10} Hz. Wong and Angell [4] were the first to construct a complete spectrum for a sodium silicate glass by interpolating conductivity data recorded below 10^6 Hz and the far infrared measurements and predicted that in the GHz range the conductivity will be proportional to $\nu^{1.0}$. Cole et. al [5] measured the conductivity for the same composition and observed $\nu^{1.0}$ behavior in the GHz range. Recently, Funke and co-workers reported a complete spectrum for glasses [6-9] from 1 Hz to 10^{14} Hz and observed $\nu^{1.0}$ and $\nu^{1.3}$ behavior at higher frequencies. The former universality was explained using Jonscher's universality [10] while the latter was debated [11]. However, the experimental observations agree with both the jump relaxation model [12] and the coupling model [13,14]. Recently Ngai et al [15] reported the physical origins of these $\nu^{1.0}$ and $\nu^{1.3}$ contributions to the conductivity spectrum. Above conclusions were arrived at after analyzing data over wide frequency and temperature range [16]. In this paper, the conductivity spectrum at room temperature over 17 decades of frequency has been reported for a lithium fluorophosphate glass and discuss different contributions to hopping conductivity.

Although the mixed alkali effect in the dc conductivity has been known for a long time, there is no acceptable theory to explain the physical origins of this effect and only limited work has been reported on the dynamics of the ionic conductivity in mixed alkali glasses [17,18,19]. The major finding has been a disappearance of mixed alkali effect when temperature or frequency is raised. Our results show that the mixed alkali effect is present in the ac conductivity too [20].

In the present work, we have studied ternary LiF-KF-$Al(PO_3)_3$ glasses. We have examined the dc and ac conductivities of these glasses, as KF is progressively added to replace LiF in 80LiF-20$Al(PO_3)_3$ glass. The ac conductivity was measured over a wide range of temperature (100 - 523K) and frequency (1mHz - 150 THz). The aim was to investigate relaxations in a wide frequency range and to compare the high frequency conductivity with theoretical predictions.

EXPERIMENTAL

Starting materials, LiF, KF and 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 1100-1200K for 5 minutes. The melts were cast between two brass plates which were preheated to 473K to avoid thermal stress induced shattering of the samples, and the 3 cm x 1.5 cm x 0.5 cm rectangular blocks were annealed for 12 hours before slowly cooling to room temperature. The nominal compositions for the glasses are given in Table I. 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 10K per minute.

For conductivity measurements, silver paste was applied on the parallel surfaces of the glass. The ac electrical conductivity was determined using computer controlled facilities. An HP4284 impedance/gain phase analyzer scanned the frequency from 20 Hz to 1 MHz at temperatures from 100K - 523K. A binary composition was investigated over a broad band of frequency from 1mHz to 150 THz employing various techniques. For the radio frequency experiments a reflectometric technique was employed. The microwave data were recorded in reflection using coaxial lines. Above 60 GHz, a quasioptical technique [21] was used with an experimental arrangement similar to a Mach-Zehnder interferometer. Reflection was used in the infrared (FIR, MIR, and NIR). The reflection data were converted to dielectric data using Kramers-Kronig relations. A complete conductivity spectrum was constructed by combining the impedance measurements at low frequencies and the dielectric data obtained at high frequencies.

RESULTS AND DISCUSSION

Figure 1 shows log σ - log ν plots for the binary composition at various temperatures and in the frequency range 1 Hz to 2 GHz. 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 following the so-called Universal Dielectric Response (UDR) [10]

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

Where σ_{dc} is the dc (or frequency independent) conductivity, σ_0 is a temperature dependent parameter and s lies in the range $0 < s < 1$. The dc conductivity (σ_{dc}) was obtained at various temperatures by fitting eq (1) to the experimental data. The exponent s varied from 1 at very low temperatures to 0.6 at higher temperatures. This is in agreement with the new universality reported by Lee et

al. [22]. The rapid fall of the conductivity at low frequencies and higher temperatures is the well-known electrode polarization phenomenon (blocking electrodes) and is observed for all compositions.

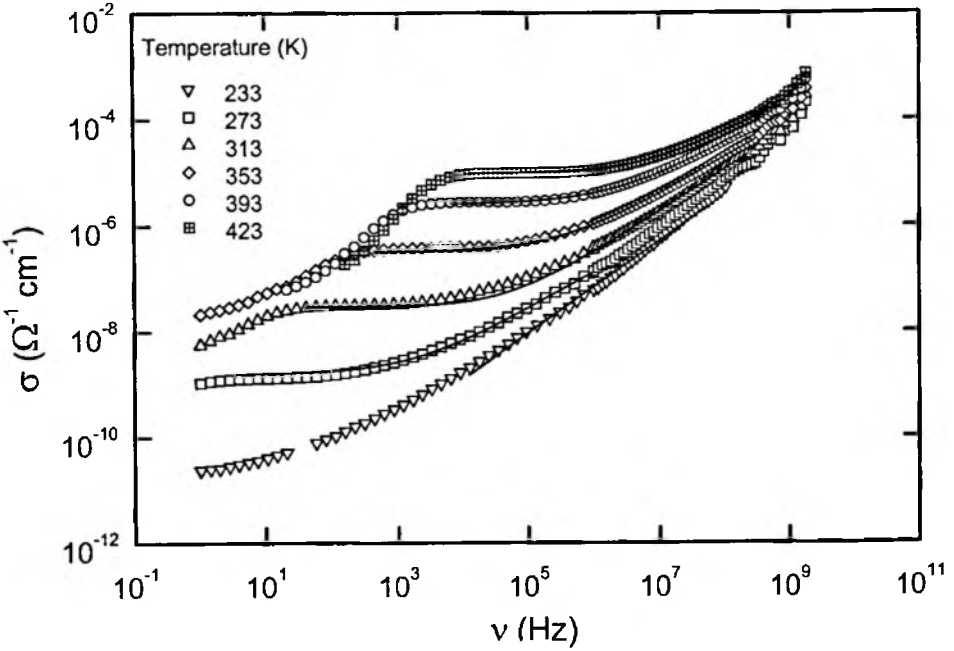

Figure 1: Conductivity spectra of the $80LiF\text{-}20Al(PO_3)_3$ glass recorded at various temperatures shown in the legend. The dc conductivity was obtained by fitting eq (1) to the data. The fits are shown by solid lines through the data points.

Figure 2 shows the variation of the dc conductivity with inverse temperature for all glass compositions studied. The value of dc conductivity at 473K, and the activation energy obtained by fitting Arrehenius euation to the data are given in Table I. Both conductivity and T_g exhibit minima with composition variation in this system. Figure 3 shows the variation of σ_{dc} at 473K, the ac conductivities (473K) at 10^5 Hz and 10^6 Hz (after subtracting the dc conductivity) with the lithium-cation mole fraction defined by the ratio f_{Li+} = mol LiF/mol(LiF+KF). The ac conductivity shows a minimum at the same composition and in the same manner, as does the dc conductivity. This confirms that we have observed the mixed alkali effect in both the dc and hitherto unreported ac conductivity of ion conducting glasses. This is reported for the first time by us and the details are published elsewhere [20].

Table 1: Composition and the physical properties of LiF-KF-Al $(PO_3)_3$ glasses

	LiF	KF	$Al(PO_3)_3$	Tg	$\Delta E\ \sigma$	σ_{dc} 473K	log A	$\Delta E\ \tau$
	(mole %)			(K)	(Kcal/mol)	(Ω^{-1} cm^{-1})	(Ω^{-1} cm^{-1})	(Kcal/mol)
G1	0	80	20	566	19.11	1.60×10^{-7}	2.05	19.15
G2	10	70	20	536	22.83	2.25×10^{-8}	2.92	22.81
G3	20	60	20	542	24.43	4.97×10^{-9}	3.01	26.55
G4	30	50	20	540	25.96	1.46×10^{-9}	3.18	29.12
G5	40	40	20	542	23.44	4.04×10^{-9}	2.46	25.44
G6	50	30	20	558	23.24	1.99×10^{-8}	3.06	24.73
G7	60	20	20	565	20.96	2.09×10^{-7}	3.02	21.03
G8	70	10	20	578	15.89	3.33×10^{-6}	1.88	17.02
G9	80	0	20	593	13.37	4.64×10^{-5}	1.86	13.13

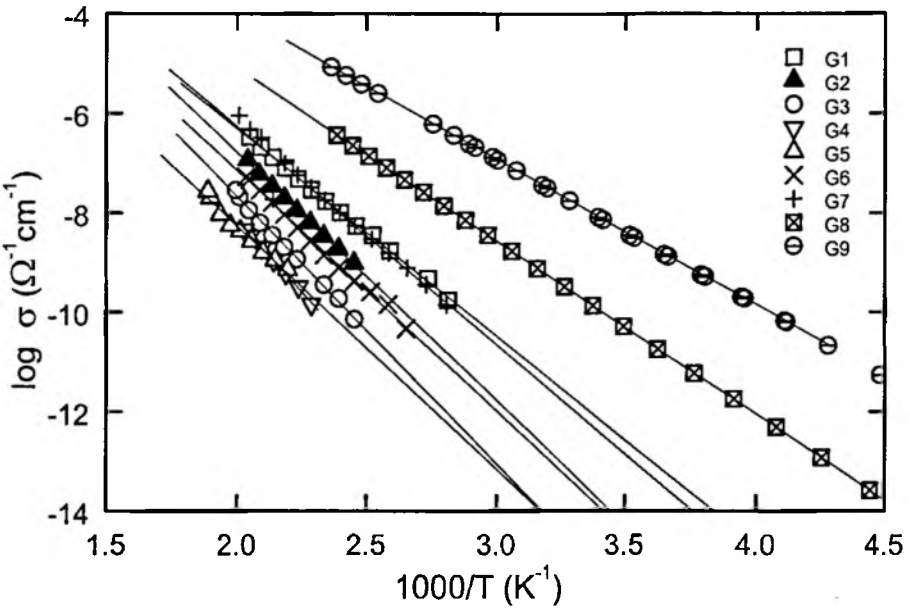

Figure 2: Arrhenius plot of the dc conductivity of LiF-KF-Al $(PO_3)_3$ glasses specified in the legend.

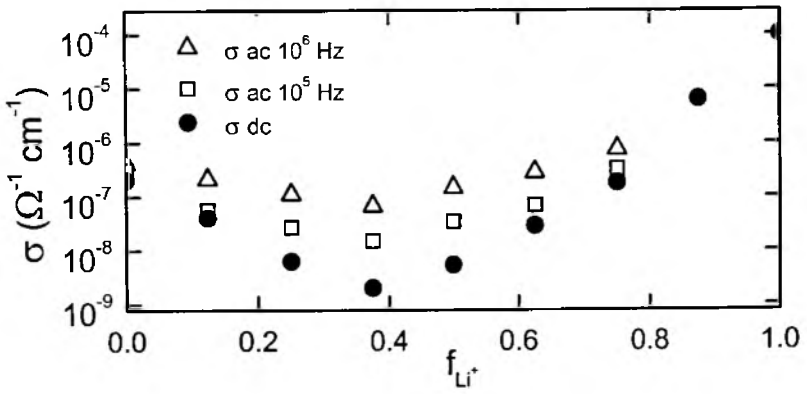

Figure 3: Dependence on lithium mole fraction of the dc and the ac conductivity at 473K. Note the minima in both the dc and the ac conductivities.

Additional dynamic characteristics of the ion motion have been studied by analyzing the ac data in the modulus formalism. Figure 4 shows the frequency dependence of the imaginary part of the complex electrical modulus at various temperatures for 60LiF-20KF-20Al$(PO_3)_3$ glass. The height of the M″ curves is independent of temperature, which implies that the relative permittivity is independent of temperature. It may be noted that the electrical relaxations are asymmetric, implying that as for the most glasses the relaxation is non-exponential.

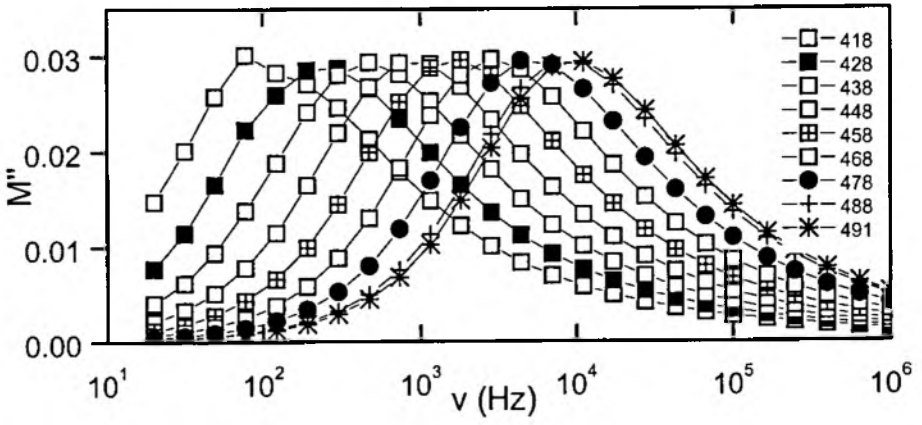

Figure 4: Imaginary part of electrical modulus, M″, versus frequency for 60LiF-20KF-20Al$(PO_3)_3$ glass. The numbers in the legend indicate temperatures in K. The lines through the data points are for visual clarity.

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) [23] and Kohlrausch-Williams-Watts (KWW) [24] functions, and the four parameter Havriliak-Negami (HN) [25]. The fits with these functions are shown as lines in Figure 5, where data at only 453 K are shown for analysis. In addition, we show a fit using Jonscher's four-parameter expression for the complex conductivity, eq (1) and $\sigma'' = \sigma' \tan(s\pi/2) + e_\infty e_0 2\pi\nu$ [26] which was converted to the modulus data.

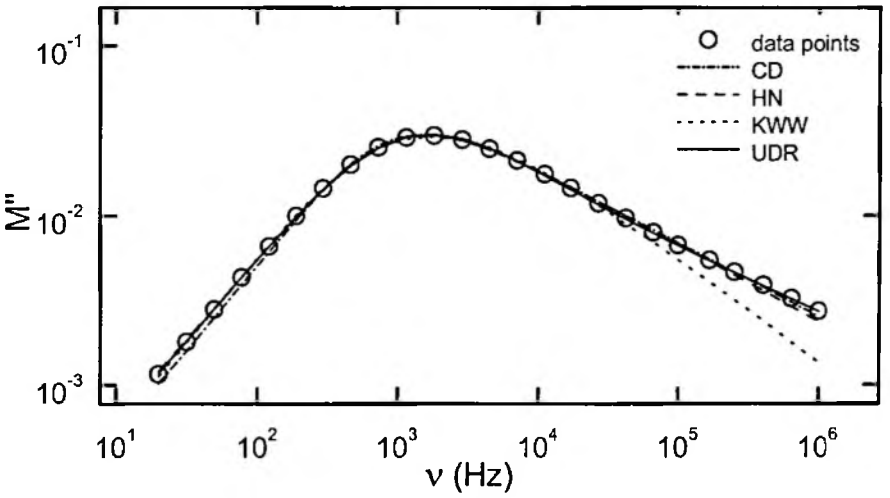

Figure 5: Modulus spectrum for a representative mixed alkali composition [60LiF-20KF-20Al$(PO_3)_3$] of the present system. Four functions, Cole-Davidson, Kohlrausch-Williams-Watt, Havriliak-Negami and UDR are fitted to the data.

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 does not agree with the observation of Moynihan [27,28] 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 [29]. The spectra for all the compositions at various temperatures were fitted with Jonscher's four parameter function. The relaxation times at each temperature and for each composition were

determined in the vicinity of the modulus peak. The relaxation times followed the Arrhenius relation. The values of the activation energies are compared with those obtained from the conductivity data in Table I. Both activation energies matched within experimental errors and suggesting that the same process is responsible for ionic conductivity and relaxation. In the present case the process is hopping of the mobile ions in the disordered solids.

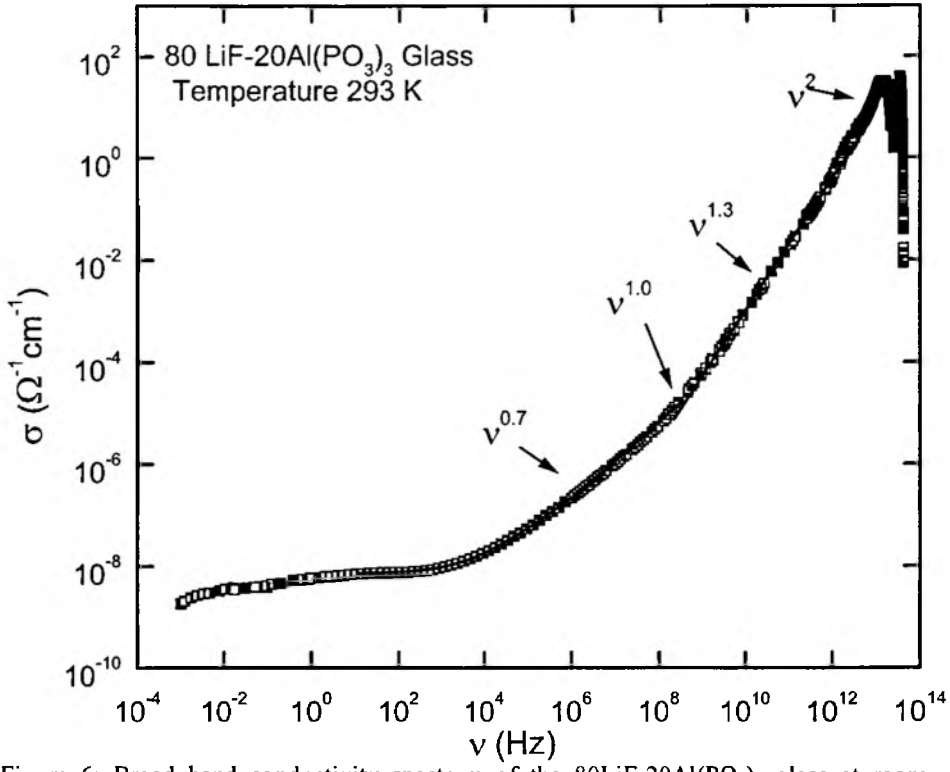

Figure 6: Broad band conductivity spectrum of the 80LiF-20Al$(PO_3)_3$ glass at room temperature. The infrared reflection data were converted into dielectric data using Kramers-Kronig relations and then into conductivity data.

The broad band spectrum of 80LiF-20Al$(PO_3)_3$ glass at room temperature recorded over a frequency range from 1mHz to 150 THz. The spectrum is a true representation of all the dynamical features of disordered solids. In the low frequency region three different processes are distinctly visible. The electrode polarization at very low frequencies, the frequency independent plateau (dc conductivity), and the power-law dispersion. Above this range, conductivity

increases continuously up to infrared frequencies. It may be noted in Figure 6 that at room temperature we are able to see all the features. The exponents for the processes identified are depicted in Figure 6. As expected, the power-law fits up to $10^{6.5}$ Hz yield the exponent s = 0.7. At higher frequencies, and in the range from $10^{8.5}$ - 10^{12} Hz, the conductivity increases even steeper with $\nu^{1.3}$. Presumably, the superposition of these two contributions leads to the $\nu^{1.0}$ contribution being observed in a relatively narrow frequency window ($10^{6.5}$ to $10^{8.5}$). Beyond 10^{12} Hz, resonant absorption by quasi lattice modes with a stronger frequency dependence, $\sigma \propto \nu^2$ becomes significant. In this frequency range, the dispersive part of the spectrum merges into the high-frequency part of the spectrum and the conductivity is dominated by vibrational motions. The first conductivity maximum is very broad and often termed "Boson peak". In other words, at these frequencies we observe deviations of the experimental data from straightness. These are due to an additional process (vibrational motion, in this case) showing ν^2 dependence. These are usually interpreted as the low-frequency flank of the lowest-lying vibrational mode. It has also been reported that this contribution to the conductivity can be extrapolated to lower-frequencies and subtracted from the experimentally observed data. Such a procedure results in a high temperature plateau for fast ion glasses [7] in agreement with the jump relaxation model and the coupling model [13-15].

All the frequency dependencies observed for the present glass i. e. $\nu^{0.7}$, $\nu^{1.0}$, $\nu^{1.3}$, and ν^2 are consistent with the previous reports [6-9, 16]. The origins of the first three of these relaxations have been assigned to Jonscher's universality, vibrational part of the ion motion, and the frequency dependent susceptibility on the low frequency side of the Boson peak, respectively [15]. An important point to be noted is that we have been able to identify these contributions to ionic relaxations at room temperature unlike others that have studied the spectrum at higher temperatures. Also our data corroborate the arguments about the universality of the $\nu^{1.3}$ dependence in disordered solids.

Finally, we discuss the theoretical limit of conductivity achievable. While discussing the conjecture regarding $\nu^{1.0}$, Wong and Angell [4] also proposed that the far infrared conductivity will be the effective maximum value for the dc conductivity in the glass-melt system and predicted it to be 10 (Ω^{-1} cm^{-1}) at 10^{12} Hz. In the present case the conductivity, 4 (Ω^{-1} cm^{-1}) observed at room temperature and at 10^{12} Hz is in close agreement with the above-predicted value, although the highest value, 38 (Ω^{-1} cm^{-1}) is observed at 3.4 x 10^{13} Hz. The latter value agrees well with conductivity, 30 (Ω^{-1} cm^{-1}) for lithium borate systems at

3.4×10^{13} Hz.

CONCLUSION

We have shown that the LiF-KF-$Al(PO_3)_3$ glasses show mixed alkali effect in both the ac and the dc conductivity. The dynamic conductivity of these lithium fluorophosphate glasses shows universal features, with $\nu^{0.7}$, $\nu^{1.0}$ and $\nu^{1.3}$ behavior. The highest room temperature conductivity, (38 Ω^{-1} cm^{-1}) at 3.4×10^{14} Hz agrees with the theoretically predicted values.

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