AC conductivity of some alkali borosilicate glasses

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Abstract. The frequency-dependent complex impedance of some alkali borosilicate glasses xNa_2O–$(54.5 - x)B_2O_3$–$45\ SiO_2$–$0.5CuO$ ($4.5 \leqslant x \leqslant 19.5$ mol%) was measured from 5 Hz to 500 kHz in the temperature range between 250 and 600 °C. The results show that the conductivity increases with increasing temperature over two linear parts characterized by two different activation energies. It is also shown that the temperature and frequency dependence of the electric modulus give a single relaxation peak. The temperature full width at half-maximum (FWHM) of M'' increases with increase in alkali ion content while the frequency FWHM of M'' remains unchanged with temperature. The frequency dependence of the AC conductivity in such glasses is found to obey Jonscher's relation. The temperature dependence of both the DC conductivity σ_0 and the hopping rate ω_p, are the same within experimental error.

1. Introduction

Much attention in the literature has been given to ion movement relaxation in glasses. It was noticed that the dielectric relaxation in glass is related to the migration of alkali ions in the glass network. Therefore, the complex impedance spectrum gives important information about the mechanism of ion movement in glasses.

Investigation of the electrical behaviour of alkali borosilicate glasses has been reported [1–5]. However, most studies have concentrated on DC measurements [1–3], and the study of the dielectric relaxation processes has attracted little attention in such glasses [4, 5].

The present paper is an expansion of our previous work [1] to investigate the dependence of the conductivity and electric modulus of some sodium borosilicate glasses on frequency and temperature.

2. Experimental procedure

2.1. Sample preparation

The glass samples xNa_2O–$(54.5 - x)B_2O_3$–$45SiO_2$–$0.5CuO$ were prepared from reagent-grade chemicals. The values of x range between 4.5 mol% (glass G1) to 19.5 mol% (glass G6). The compositions of the glasses studied are listed in table 1. Na_2CO_3, H_3BO_3, $CuCO_3.Cu(OH)_2.H_2O$ and acid-washed quartz sand were mixed together and melted using a platinum crucible in an electric furnace for about 2 h at temperatures ranging from 1250 to 1350 °C depending on the glass composition. Homogenized melts were poured into pre-heated steel moulds. The glasses were annealed at about 450 °C and allowed to cool to room temperature with a rate of 60 °C h^{-1}. The samples were stored under vacuum until use.

Table 1. The compositions of the studied glasses, and their conductivities σ' measured at 20 kHz and 450 °C and activation energies ± 0.03 eV.

Glass	Glass composition (mol%)				σ' 450 °C (Ω^{-1} cm^{-1})	E_1 (eV)	E_2 (eV)
	SiO$_2$	B$_2$O$_3$	Na$_2$O	CuO			
G1	45	50	4.5	0.5	5.715×10^{-9}	1.414	—
G2	45	48	6.5	0.5	1.416×10^{-8}	1.353	0.852
G3	45	46	8.5	0.5	4.764×10^{-8}	1.22	0.764
G4	45	44	10.5	0.5	9.863×10^{-8}	1.088	0.686
G5	45	40	14.5	0.5	5.662×10^{-7}	0.969	0.647
G6	45	35	19.5	0.5	2.965×10^{-6}	0.882	0.563

2.2. AC conductivity measurements

For AC measurements, samples were prepared in the form of discs of diameter 1 cm and thickness ranging between 0.1 and 0.25 cm. The parallel surfaces of the samples were coated with graphite as electrodes. AC conductivity measurements were made over the temperature range from 250 to 600 °C. Complex impedance measurements were made in the frequency range from 5 Hz to 500 kHz using a calibrated Tesla BM 507 impedance meter; two terminal electrodes of the sample cells were made from silver and electrically shielded to minimize the external noise and stray impedance. The error in the absolute value of the complex impedance was less than 5% and the error in its phase was 1°. A thermocouple, which was kept near the sample, was used to control the temperature within the experimental accuracy of ± 1 °C.

The complex impedance Z^* is related to the complex conductivity σ^* by the following equations:

$$Z^* = Z' - iZ'' \tag{1}$$

$$\sigma^* = (d/s)(Z^*)^{-1} = \sigma' + i\sigma'' \tag{2}$$

where s is the electrode area and d is the sample thickness.

3. Results and discussion

The temperature dependence of the real part σ' of the complex conductivity for glasses G1–G6 measured at constant frequency of 20 kHz is given in figure 1. This figure shows that the conductivity in the studied glasses obeys the Arrhenius relation

$$\sigma' = \sigma'_{01} \exp(E_1/kT) + \sigma'_{02} \exp(E_2/kT) \tag{3}$$

where σ'_{01} and σ'_{02} are constants, k is Boltzmann's constant, T is the absolute temperature, and E_1 and E_2 are the activation energies for high- and low-temperature regions, respectively. The values of the activation energies were calculated and are listed in table 1. In previous work [1] the temperature dependence of the DC conductivity for the same glasses G1–G6 were measured. A straight line with one slope, i.e. a single activation energy, over the temperature range for each glass was found. Figure 2 represents the temperature dependence of σ' for the glass containing 20% alkali oxide (as in the example) at different fixed frequencies. The solid line represents the DC conductivity σ_{dc} and corresponds to an activation energy $E_{dc} = 0.84$ eV [1]. The AC conductivity σ_{ac} again exhibits two regions. In the high-temperature region, σ_{ac} tends to σ_{dc} at all frequencies. However, at
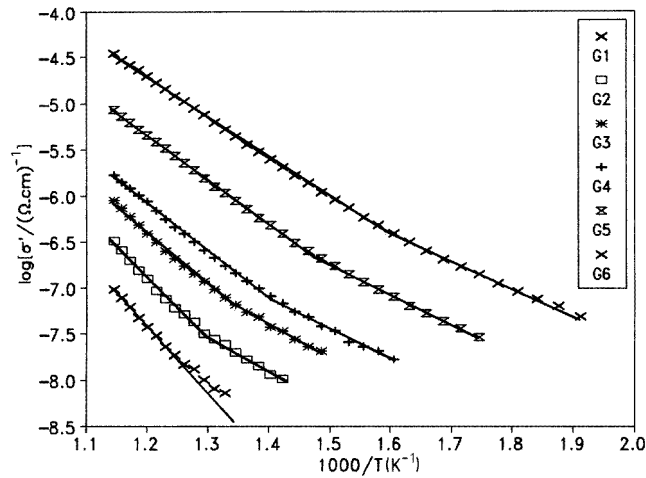
Figure 1. The temperature dependence of the conductivity (real part) σ' for glasses G1–G6 at 20 kHz.
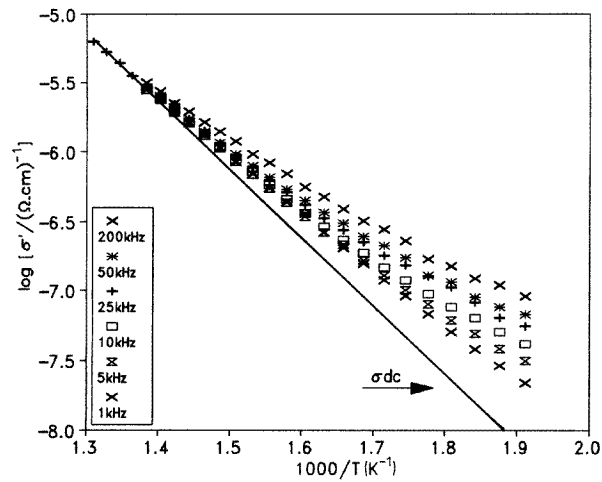
Figure 2. The temperature dependence of the conductivity (real part) σ' for glass G6 at different frequencies: ——, from [1].

low temperatures, σ_{ac} is frequency dependent, with different slopes. Also, σ_{ac} is higher than σ_{dc} and the activation energy decreases with increasing applied frequency. Therefore, the results obtained in figures 1 and 2 indicate that there are two distinct contributions to the conduction observed in these glasses, which gives rise to the two activation energies E_1 and E_2. It has been proposed that the variations in the conductivity and the activation energy are related to the ease with which the mobile ions can jump from one site to the next through the glass network [6]. This leads us to assume that, in the high-temperature region (corresponding to E_1), the effect of thermal agitation is predominant, where the ion has sufficient energy to jump from its site to the next but loses this energy by collision with the other ions surrounding the next site. Therefore, the conductivity is not affected by the frequency in this region. However, in the low-temperature region the energy loss

by collision should be small and the effect of frequency is predominant. In this case, the probability that the ion makes jumps increases with increasing frequency and therefore it can easily move within the network [7]. This causes an increase in the conductivity and a decrease in the activation energy E_2 (see figure 2).
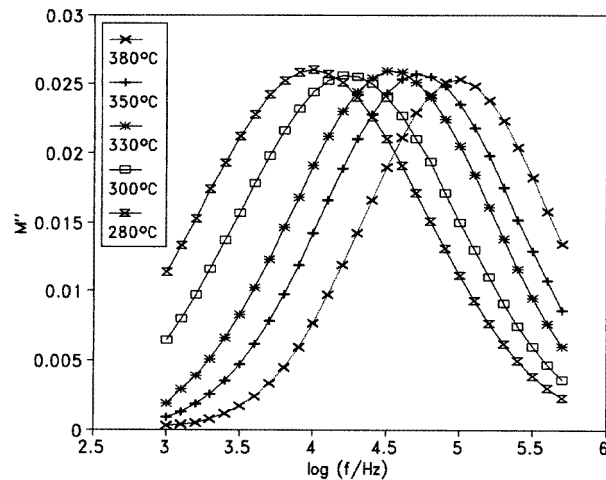
The electrical relaxation in ionic glasses can be described by the complex electric modulus M^*, which is related to the complex impedance Z^* by the formula

$$M^* = M' + iM'' = \omega\epsilon_0 Z^* \tag{4}$$

where $\omega(= 2\pi f)$ is the angular frequency and ϵ_0 is the vacuum permittivity [8, 9].
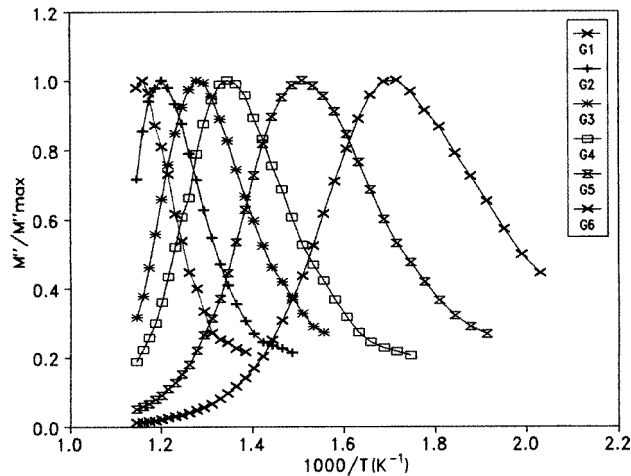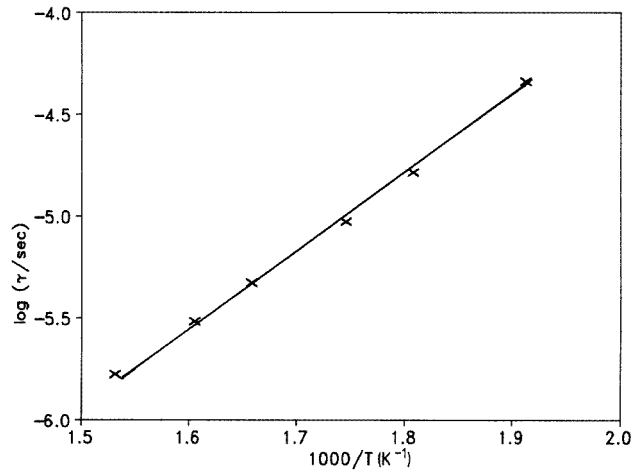

**Figure 3.** The effect of temperature on the normalized modulus for glasses G1–G6 at 20 kHz.

Figure 4. The imaginary modulus as a function of frequency for glass G6 at different temperatures.

Figure 3 shows the effect of the temperature on the normalized modulus M''/M''_{max} for glasses G1–G6 measured at a constant frequency of 20 kHz. It is obvious that the shape

Figure 5. The temperature dependence of the conductivity relaxation time τ for the glass containing 20% alkali oxide. τ is calculated according to equation (5).

of the spectrum seems to be the same (single relaxation peak). The broad relaxation of all peaks was found to have a Gaussian distribution. In addition, M''_{max} is shifted towards a lower temperature with increasing alkali ion content. It is observed from figure 3 that the full width at half-maximum FWHM of the normalized modulus increases with increase in the alkali ion content. This indicates that the distribution of the relaxation times may be associated with the alkali ion relaxation processes in the glass network. This behaviour is in agreement with that previously reported by Almond and West [10]. They suggested that the breadth of the electrical relaxation peak is a sensitive function of the concentration of mobile charge carriers. As the concentration of the mobile ions increases, and consequently the ion–ion distance decreases, the M'' peak becomes wider [11–13].
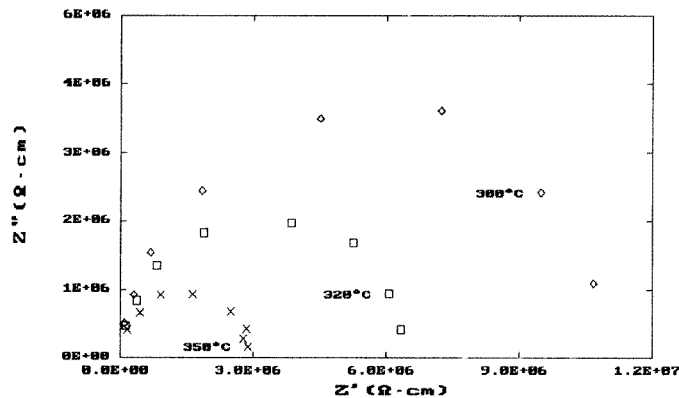
Figure 6. Typical impedance plane diagram for the glass containing 20% alkali oxide.

For an ideal solid electrolyte the plot of M'' against frequency has single Debye peaks, whose maxima are given by $\omega_{max}\tau = 1$. The existence of a distribution of relaxation times is indicated by broadening of the M'' spectrum [14]. The imaginary part M'' measured at

several temperatures for the glass containing 20% alkali oxide is plotted against frequency in figure 4. From this figure, it is obvious that the shape of the spectrum is temperature independent. The FWHM is greater than the ideal Debye FWHM of 1.14 decades. Also, the peak frequency f_{max} of the M'' spectra shifted towards a higher frequency with increasing temperature. From the peak frequency, the temperature dependence of the conductivity relaxation time τ which corresponds to $1/f_{max}$ can be expressed as [7]

$$\tau = \tau_0 \exp(E/kT). \tag{5}$$

Figure 5 shows the Arrhenius temperature dependence of the conductivity relaxation time τ with an activation energy of 0.81 eV. This value is in good agreement with the activation energy of σ_{dc}, within experimental error. This indicates that ionic migration is responsible for both the observed DC conductivity and the modulus spectrum. Similar behaviour was proposed by Smedley and Angell [15] and observed by Chowdari and Akhter [16] for other glass systems.

Plots of Z'' against Z' (Cole–Cole plots) for the glass containing 20% alkali oxide (again as an example) at three different temperatures are given in figure 6. It is seen that, as the temperature is increased, all depressed semicircles shifted to higher frequencies and their sizes also decreased. These depressed semicircles arise from ionic migration in the glass matrix and are due to the distribution of relaxation times [17]. The intercept of the arcs with the real axis gives the true bulk resistance excluding electrode polarization.

Table 2. Some physical parameters of the glass containing 20% alkali oxide.

T (K)	$\sigma_0 T$ (Ω^{-1} cm^{-1} K)	ω_p (s^{-1})	AT (Ω^{-1} cm^{-1} K)	k' (Ω^{-1} cm^{-1} s^{-1} K)
723	0.0294	2.089×10^6	1.734×10^{-6}	1.445×10^{-8}
673	0.0104	6.457×10^5	1.343×10^{-6}	1.622×10^{-8}
623	5.546×10^{-3}	1.995×10^5	8.091×10^{-7}	1.479×10^{-8}
573	7.047×10^{-4}	4.677×10^4	5.152×10^{-7}	1.445×10^{-8}
523	1.409×10^{-4}	1.047×10^4	2.877×10^{-7}	1.349×10^{-8}
473	4.624×10^{-5}	4.677×10^3	1.607×10^{-7}	1×10^{-8}

Figure 7 shows the variation in the conductivity σ' with frequency at six different temperatures for the glass containing 20% alkali oxide. It is found that the values of σ' obey Jonscher's universal relation [18]

$$\sigma'(\omega) = \sigma_0 + A\omega^n \tag{6}$$

where σ_0 is the DC conductivity and can be evaluated at each temperature from the conductivity plateau. As the temperature decreases, the conductivity plateau moves to lower frequencies until it disappears at about 200 °C. At high frequencies and low temperatures the weakly temperature-dependent parameters A and n ($0 \leqslant n \leqslant 1$) give rise to the dispersion region. In this region the observed conductivity is attributed to the bulk property [19]. Similar behaviour was observed for other glass systems [19, 20] and this is typical of ionic conductors [21]. Other glass compositions also showed similar behaviours.

From the frequency dependence of conductivity (figure 7), the parameter n (see equation (6)) is found to be temperature independent ($n = 0.67$) over the temperature range studied. This behaviour has been previously reported for many glass systems [22–24]. In fact, there is a contradiction in the literature about the behaviour of the parameter n with the temperature. Some workers [25, 26] stated that n increases with decreasing temperature. On
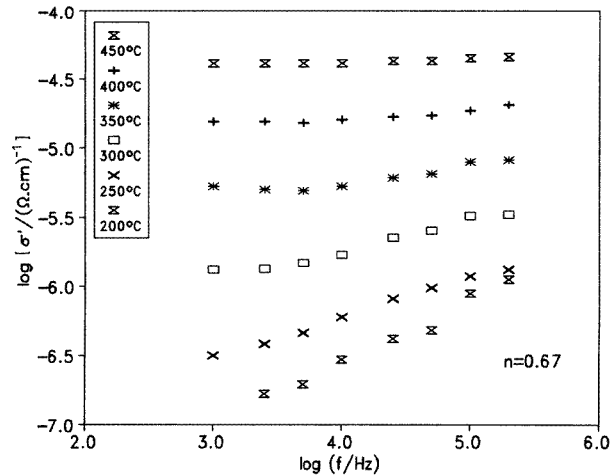
Figure 7. The frequency dependence of the conductivity (real part) σ' for glass G6 at different temperatures.

the other hand, Lee *et al* [27] show that in alkali silicate glasses the parameter n takes a constant value at high temperatures and it increases towards the limit of unity with decreasing temperature. However, Jain and Mundy [20] determined the values of n for many germanate and borate glasses. They found that n does not show any simple behaviour with temperature. Therefore, any interpretation concerning the general behaviour of the parameter n with temperature is very difficult. As previously reported [24], one can conclude that the parameter n may depend on the glass composition and the limit of temperature measurements.
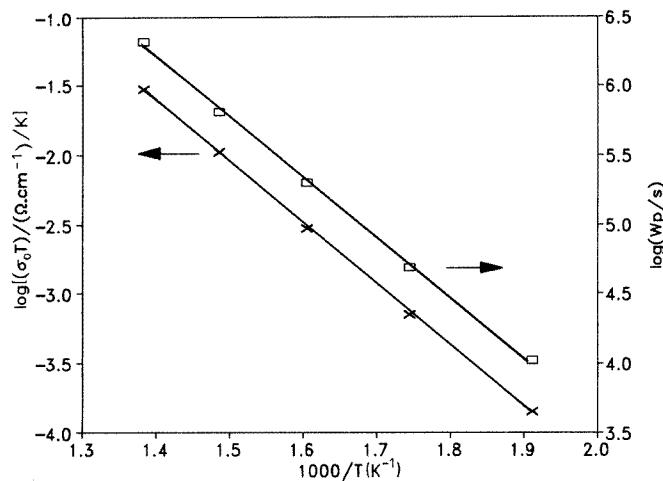
Figure 8. The temperature dependence of ω_p and $\sigma_0 T$ for the glass containing 20% alkali oxide.

According to Almond *et al* [28], the hopping rate ω_p is given by the relation

$$\omega_p = (\sigma_0/A)^{1/n}. \tag{7}$$

It is found that ω_p increases with increasing conductivity and shifted to higher frequencies with increasing temperature, as illustrated in table 2. Figure 8 shows the temperature

dependences of ω_p and $\sigma_0 T$. It is apparent that the values of activation energies of ω_p and $\sigma_0 T$ are nearly the same, within experimental error, 0.865 eV and 0.837 eV, respectively. The mobile ion concentration factor $k' = \sigma_0 T/\omega_p$ is calculated and listed in table 2. It is found that k' is nearly constant with temperature over the temperature range studied. This indicates that the mobile ion concentration in these glasses is not thermally activated.

4. Conclusions

From the previous results and discussion the following points can be made.

(1) There are two contributions to the AC conductivity at high and low temperatures characterized by two activation energies.

(2) The electric modulus spectrum indicates that a distribution of the relaxation times may be associated with the alkali ion relaxation processes in the glass matrix.

(3) The parameter n is temperature independent over the temperature range studied.

(4) The hopping rate is thermally activated with the same activation energy as for the DC conductivity. However, the mobile ion concentration is found to be independent of temperature over the temperature range studied.

Acknowledgment

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