

# Evidence from infrared spectroscopy of structural relaxation during field assisted and chemically driven ion exchange in soda–lime–silica glasses

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Evidence is provided by infrared reflectance spectroscopy of structural relaxation occurring in ion exchanged surface layers in commercial soda–lime–silica glasses. Monovalent cations ( $K^+$ ,  $Ag^+$  and  $Li^+$ ) are introduced from molten nitrate baths both by simple diffusion and with the assistance of externally applied electric fields. In the case of  $K^+$  ions, a highly resistive layer is created and is characterised by impedance spectroscopy. The mid infrared spectra provide information on changes in the silicate network: they show that the introduction of  $Li^+$  and  $Ag^+$  leads to a disproportionation reaction with conversion of  $Q_3$  into  $Q_2$  and  $Q_4$  species. In contrast, the introduction of  $K^+$  ions leads to the opposite (i.e. comproportionation) reaction, where  $Q_2$  and  $Q_4$  are converted into  $Q_3$  units. These processes are chemically driven; they are impeded, e.g. by the build up of internal pressures accompanying the introduction of the larger  $K^+$  ion. The results provide direct evidence for cation-induced relaxations in the glass network (CAIRON).

Ion exchange has been used for many years to increase the strength of glass<sup>(1,2)</sup> and to alter its optical properties for a range of technical applications.<sup>(3)</sup> More recently, a question has arisen concerning the structural changes that may occur in glass as a consequence of such ion exchange. An issue is how far such changes occur below  $T_g$  and how they may influence ion mobilities, and may therefore control the processes of ion exchange.<sup>(4–10)</sup>

The phenomenon that has previously received attention in our own laboratories<sup>(9)</sup> involves the replacement of  $Na^+$  by  $K^+$  ions in soda–lime–silica (commercial float)

glass by ion exchange in molten  $KNO_3$  baths at temperatures below  $T_g$ . This process is usually carried out in the temperature range 420–480°C, with the aim of building up an internal pressure that increases the tensile strength of the glass. Figure 1 shows experimental diffusion and stress profiles obtained by Bradshaw & Taylor.<sup>(11)</sup> The shape of the concentration profile was interpreted in terms of Fick's law with a composition independent interdiffusion coefficient,  $D_{Na/K}$ . The loss of stress close to the surface was attributed to some kind of relaxation process.

The apparent simplicity of the diffusion behaviour obscures a surprising degree of complexity. Thus, if thermodynamic non-ideality is ignored, one can express the interdiffusion coefficients,  $D^*$ , of ions A and

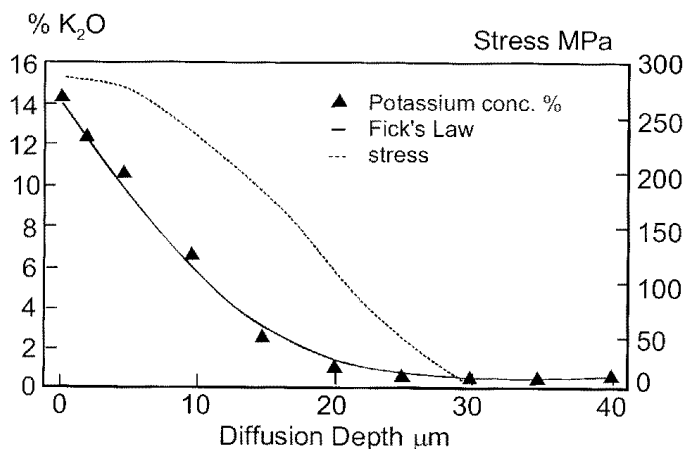


Figure 1. Potassium diffusion profile (solid line) and induced compressive stress (dotted line) in commercial soda–lime–silica (float) glass, after exposure to molten  $KNO_3$  for 6 h at 425°C. The  $K_2O$  concentration is given as a weight percentage. The data are from Bradshaw & Taylor<sup>(11)</sup>

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B in terms of the corresponding self diffusion coefficients,  $D_A$  and  $D_B$ , by the Nernst-Planck equation

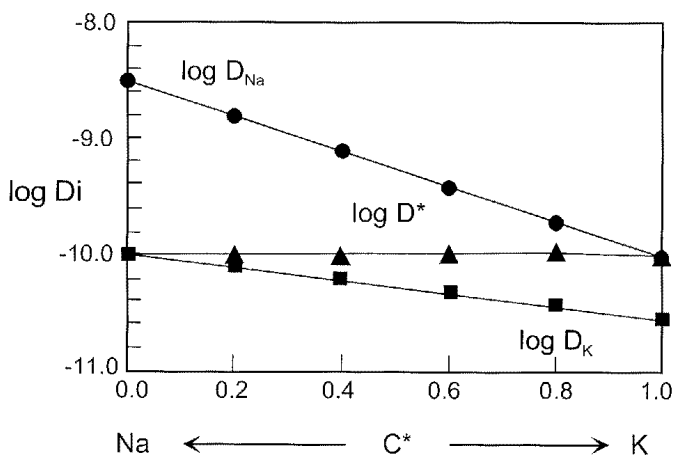
$$D^* = D_A D_B / (x_A D_A + x_B D_B) \quad (1)$$

where  $x_A$  and  $x_B$  are the cation fractions of A and B, respectively.

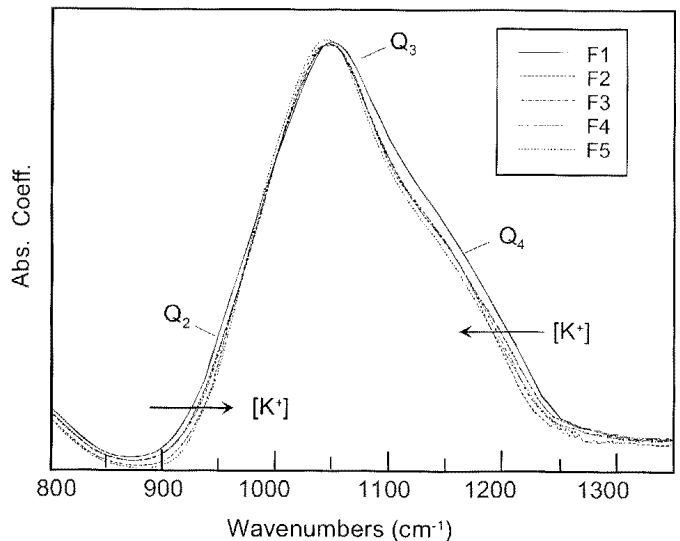
In the limits where  $x_A$  and  $x_B$  are tending to unity, the values of  $D^*$  become  $D_B$  and  $D_A$ , respectively. In other words, the mobility of the minority cation controls the interdiffusion process.  $D^*$  can remain constant and independent of composition, either when  $D_A$  and  $D_B$  are equal and constant (i.e. there really are no mixed cation effects), or when  $D_B$ , for example is very small (and nearly constant) and  $D_A$  is much larger and is highly composition dependent.

This latter behaviour<sup>(8-10)</sup> is often encountered when  $K^+$  ions replace  $Na^+$  ions in soda-lime-silica glass. Figure 2 shows this schematically. Within the ion exchanged layer and moving towards the surface, the  $Na^+$  ion mobility (self diffusivity) decreases progressively with the decreasing concentration of  $Na^+$  ions (just as it does in normal melt grown mixed cation glasses<sup>(12,13)</sup>). On the other hand, and again moving towards the glass surface, the  $K^+$  ion mobility does not increase with increasing  $K^+$  ion concentration. It remains much smaller than the corresponding mobility of  $K^+$  ions in melt grown soda-lime-silica glasses. What is missing from Figure 2, therefore, is the familiar 'crossover of mobilities', which is normally taken to be the defining characteristic of the mixed alkali effect.<sup>(12,13)</sup> It has been suggested<sup>(9)</sup> that this ion exchanged system exhibits an 'anomalous' mixed alkali effect.

However, in one important respect, the ion exchanged glass does resemble melt grown mixed cation soda-lime-silica glasses: namely, that the structure of the silicate framework changes in response to the changing cation population. Figure 3 shows how the mid-infrared spectra, obtained by specular reflectance from the surface layers (approximately 1  $\mu m$  in depth) of synthetic 'float' glasses, change with changing proportions of  $Na^+$  and  $K^+$  ions. The result of progressively replacing  $Na^+$  by  $K^+$  is a progressive narrowing



**Figure 2.** Schematic plot showing how a constant interdiffusion coefficient,  $D^*$ , may correspond to variable self diffusion coefficients,  $D_{Na}$  and  $D_K$ , when  $Na^+$  ions are replaced by  $K^+$  ions in the surface of glass. The values of  $D^*$  are calculated from  $D_{Na}$  and  $D_K$  via the Nernst-Planck equation (see text).  $C^*$  represents the proportion of  $Na$  replaced by  $K$



**Figure 3.** Mid infrared spectra from melt grown mixed cation ( $Na^+/K^+$ ) float glasses, for F1=3%, F2=25%, F3=50%, F4=75%, F5=97%  $K^+$ , respectively, expressed in terms of total (monovalent) cation content. Q-numbers refer to silicate speciation (see text)

of the main band that is centred at  $1050\text{ cm}^{-1}$ , and this narrowing has been attributed<sup>(9)</sup> to a comproportionation reaction



where the Q-values refer to the number of bridging oxygens (BOs) attached to any Si atom. Note that in this (reversible) reaction, negative charge is conserved (two on the  $Q_2$  unit and one each on the two  $Q_3$  units) and so no oxide ions leave or enter the glass during the ion exchange process. All that happens is that the introduction of potassium leads to a more uniform and chemically homogeneous glass structure. The key result, reported earlier,<sup>(9)</sup> and to be confirmed in this investigation, is that this spectroscopic (and structural) narrowing occurs in soda-lime-silica glasses ion exchanged even far below  $T_g$ .

This possibly unexpected result poses several questions including: (i) 'how and why' such structural relaxations occur in glass, and (ii) whether such relaxations actually facilitate or hinder the movements of ions. The present paper addresses these issues, first by employing field assisted ion exchange,<sup>(14-16)</sup> in order to bring these processes about at much lower temperatures, and second by examining what changes occur when other cations ( $Ag^+$  and  $Li^+$ ) are introduced into these glasses. The emphasis in the present paper is placed on these changes in glass structure. A following paper<sup>(17)</sup> will deal in more detail with the electrochemical aspects of field assisted ion exchange.

## Experimental

Infrared spectroscopic data<sup>(9)</sup> for thermally exchanged ( $K^+$  for  $Na^+$ ) float glass are presented here along with corresponding data for field assisted ion exchange ( $K^+$ ,  $Ag^+$  and  $Li^+$ , all for  $Na^+$ ) in soft soda glass tubes. The float glass was kindly supplied in the form of glass discs by Pilkington,<sup>(9)</sup> while the soda glass tubes were obtained from the glass blowing workshop. Prior to ion exchange, the float glass samples were polished, top and bottom, to remove any gradients in chemical

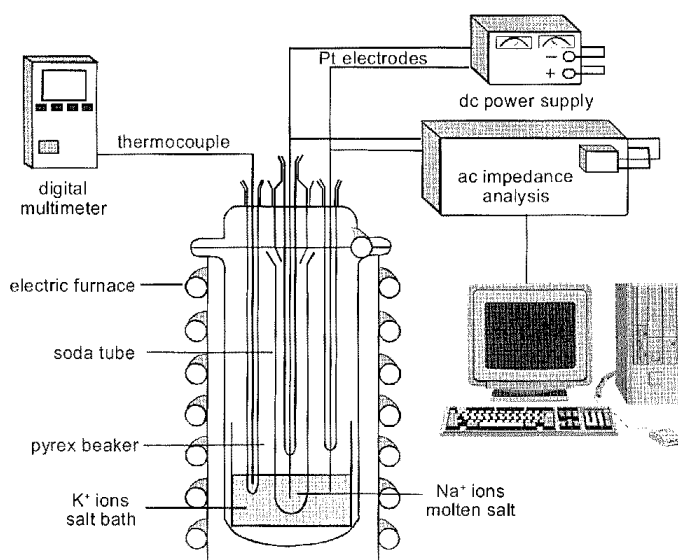
**Table 1.** Compositions (in mol%) of relevant soda-lime-silica glasses

Oxide component	Pilkington float glass <sup>9,11</sup>	Soft glass tubing
SiO <sub>2</sub>	71.78	71.62
Na <sub>2</sub> O	12.44	14.02
CaO	8.76	6.19
K <sub>2</sub> O	0.38	1.03
MgO	5.88	4.82
BaO	none	1.50
Al <sub>2</sub> O <sub>3</sub>	0.58	1.49
Fe <sub>2</sub> O <sub>3</sub>	0.04	0.02
ΣO <sub>2</sub>	0.14	0.22

composition (e.g. in tin oxide) introduced during the manufacturing process. The respective molar compositions are given in Table 1. These compositions are similar, and both are described here as 'soda-lime-silica' glasses. The float glass is somewhat richer in CaO and MgO, but slightly poorer in Na<sub>2</sub>O and K<sub>2</sub>O.

Figure 4 shows the apparatus used for field assisted ion exchange. For K<sup>+</sup> ion insertion experiments, the anodic electrolyte (anolyte) was typically a mixture of KNO<sub>3</sub> and KNO<sub>2</sub> (7:1 by weight), which melted at approx. 313°C, and was contained in a pyrex beaker that was enclosed within an outer pyrex tube, which in turn was placed inside a vertical tube furnace. For Ag<sup>+</sup> and Li<sup>+</sup> ion insertions, AgNO<sub>3</sub> and LiNO<sub>3</sub> melts were employed. The corresponding catholyte was a 50:50 mixture (by weight) of NaNO<sub>3</sub> and NaNO<sub>2</sub>, melting at 220°C, which was contained inside the soda glass tube and was used for all field assisted diffusion experiments. In all experiments, the area of glass tube exposed to anolyte was approximately 9.9 cm<sup>2</sup>.

At intervals during dc electrolysis (more complete details are given elsewhere<sup>(17,18)</sup>), impedance spectra were determined *in situ* using a Solartron Schlumberger 1260 Impedance Analyser, and were interpreted in a conventional manner, see for example Garcia *et al.*<sup>(20)</sup> After completion of electrolysis, the glass tube was removed from the molten salt bath, intact if possible, and was sectioned for electron microprobe analysis on a Cameca SX51 instrument, equipped with four wavelength dispersive spectrometers for chemical analysis.



**Figure 4.** The electrochemical apparatus used for performing field assisted ion exchange in 'soft' soda lime-silica glass tubes, showing facility for *in situ* impedance analysis

Samples of curved glass, taken from the outer surface of the glass tube, were examined by infrared reflectance spectroscopy at the NHRF in Athens in the frequency range 30–5000 cm<sup>-1</sup>, using a Fourier transform vacuum spectrometer (Bruker 113v), with an 11° off normal specular reflectance attachment and a high reflectivity Al mirror as reference. Each reflectivity spectrum results from the average of 200 scans. The wavenumber accuracy is better than 0.05 cm<sup>-1</sup>, and the estimated experimental error in infrared absorption is less than 0.5%. The data were analysed and interpreted using established methods, see for example Kamitsos.<sup>(19)</sup> The observed spectral changes (see Figures 3, 7 and 8) are significantly larger than the estimated experimental error.

## Results

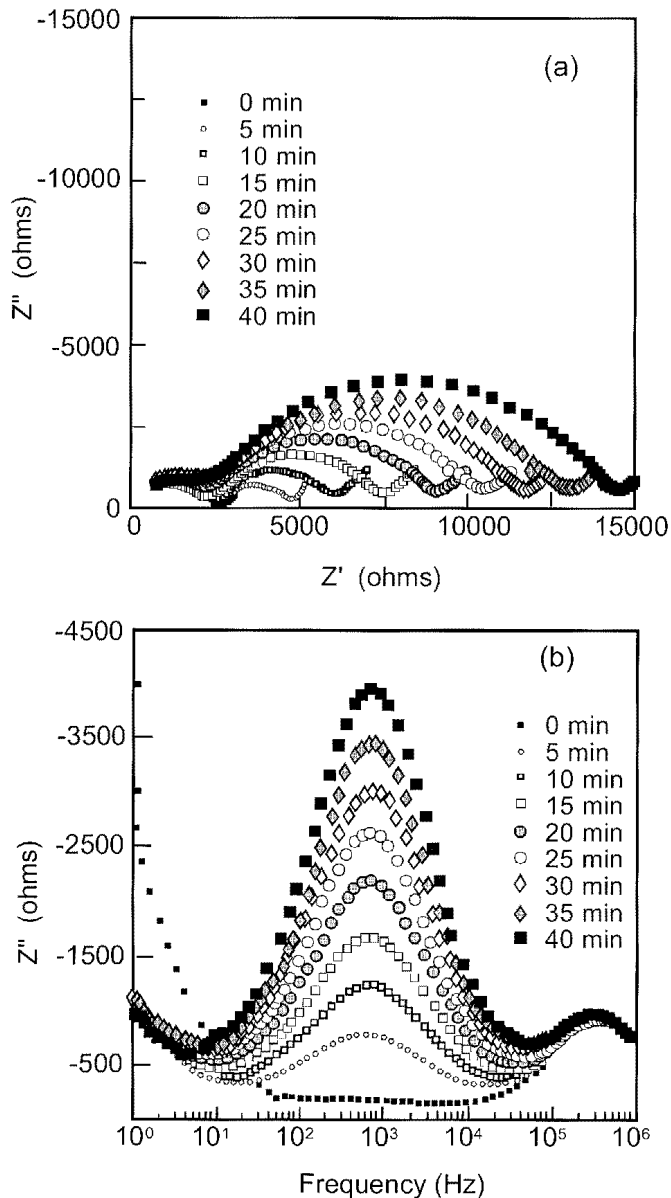
### Field assisted migration of K<sup>+</sup> ions

Figure 5 shows impedance data, presented both as complex plane diagrams (plots of Z'' versus Z') and as 'loss spectra', i.e. where the imaginary part of the impedance, Z'', is plotted as a function of log frequency. These data were collected at five minute intervals when a current of 5 mA was passed in the electrolysis cell at a temperature of 320°C, for a total of 40 min.

Figure 5(a) shows very clearly that the simplest equivalent circuit for the ion exchanged glass contains two parallel RC elements placed in series, see Garcia *et al.*<sup>(20)</sup> for a discussion of this procedure. The first RC element gives rise to a 'semicircle' that is almost unaffected by the electrolysis and represents the properties of the original Na<sup>+</sup> ion containing glass. The second gives rise to a 'semicircle' that grows in size throughout the period of electrolysis, and represents the changes occurring in the ion exchanged layer. Figure 5(b) shows that that this build up of resistance cannot be attributed to changes in local resistivity, since the frequency of this second Z'' peak remains constant. In fact, the build up of resistance represents the increasing thickness of the ion exchanged layer, see also Ohta *et al.*<sup>(14)</sup>

Figure (6) shows K concentration profiles for various 'constant Faraday' experiments, where the same quantity of electricity (24C=2.49×10<sup>-4</sup> mol) has been passed at differing currents (expressed on the figure in mA) for the appropriate periods of time. Two points may be noted. First, a sharp boundary exists between the K rich layer and the underlying base glass. Second, the thickness of the exchanged layer (22.5 μm) is independent of the current. This suggests that field assisted ion exchange may be regarded as a 'faradaic' process, in the sense that chemical change depends only on the quantity of electricity passed, while the K<sup>+</sup> ions are being inserted into the glass on a 'one for one' basis in place of the Na<sup>+</sup> ions.

An elementary calculation provides support for this simple picture. Based on the glass composition (see Table 1), its density (2.50 g cm<sup>-3</sup>), and the area of glass exposed to molten KNO<sub>3</sub> (9.9 cm<sup>2</sup>), one can calculate that K<sup>+</sup> ions will occupy a layer of glass 21.8 μm deep, assuming that all the Na<sup>+</sup> ions are swept out before them. This value is so close to the actual thickness of the K rich layer as indicated by epma, that one has to

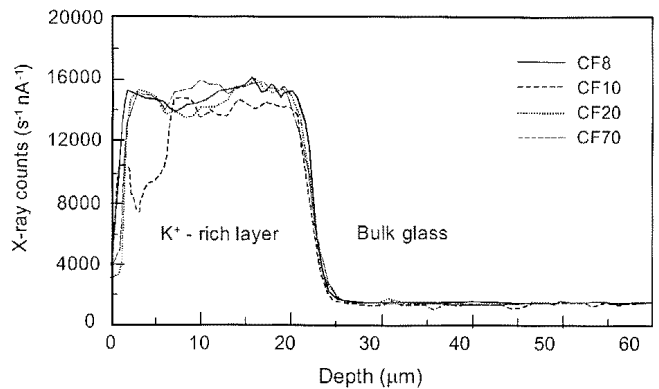


**Figure 5.** Impedance data accumulated at 5 min intervals, during field assisted ion exchange of  $K^+$  for  $Na^+$  at a current of 5 mA, at 320°C. (a) shows the data in the conventional complex plane representation; (b) shows the frequency dependent spectra obtained from the imaginary component,  $Z''$

conclude that all (or nearly all) of the  $Na^+$  ions are being replaced by  $K^+$ .

The outcome is consistent also with the information contained in Figure 5(b). Here we note that the frequency shift in the  $Z''$  spectra points to the inserted  $K^+$  ions being approximately 1000 times less mobile than  $Na^+$  ions in the base glass. This means that they will always tend to 'lag behind' the displaced  $Na^+$  ions, which explains why such a sharp boundary is observed. The key result, however, in the present context is that  $K^+$  ions can be inserted into a soda-lime-silica glass in relatively short times, and at temperatures far below  $T_g$ .

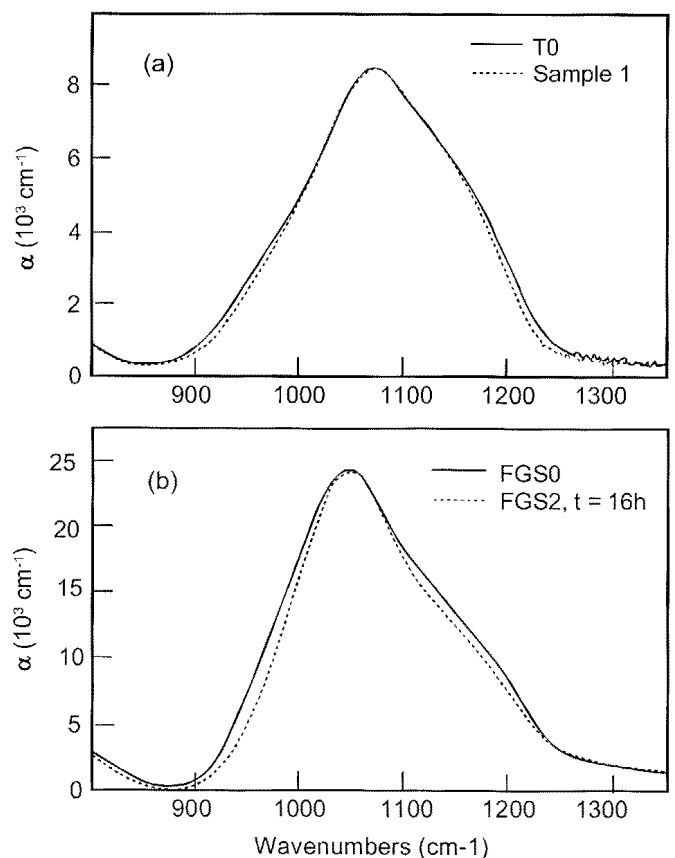
Figure 7(a) shows the mid infrared band obtained by specular reflectance for: (i) a pristine soda glass tube, and (ii) a tube electrolysed at 350°C for 20 min, at 20 mA. These conditions of electrolysis imply that there is again an ion exchanged layer some 20  $\mu m$  deep. The infrared spectrum provides structural information about the outer regions of this layer, some 1–2  $\mu m$  deep.



**Figure 6.** Potassium concentration profiles (given in arbitrary units of x-ray counts per unit electron beam current) for various 'constant Faraday' (CF) experiments ( $2.49 \times 10^{-4}$  mol electricity passed). The currents employed (in mA) are given in the figure

The changes occurring as a result of electrolysis may be compared with those in Figure 3 for the previously investigated synthetic float glasses, and with those in Figure 7(b) for actual float glasses (i) before ion exchange, and (ii) after exposure to molten  $KNO_3$  for 16h at 475°C, as reported in our earlier paper.<sup>(9)</sup>

A clear result emerges. The spectrum of the glass subjected to field assisted ion exchange has indeed narrowed somewhat in comparison to the pristine specimen, but the narrowing is much less than for the sample that was chemically exchanged at a much higher temperature. It seems reasonable to conclude, therefore, that while the comproportionation Reac-



**Figure 7.** Mid infrared spectra of the outer surface ( $\sim 1 \mu m$  deep) of: (a) a 'soft' soda-lime-silica tube in pristine condition (T0) and after being subjected to field assisted ion exchange in molten  $KNO_3$  at 20 mA for 20 min at 350°C (sample 1); and (b) a commercial 'float' glass sample in pristine condition (solid line) and after soaking in molten  $KNO_3$  for 16 h at 475°C (dashed line)

tion (2), does occur at 350°C, it is less important than it is at 475°C.

#### Field assisted migration of $\text{Ag}^+$ and $\text{Li}^+$ ions

It was not found possible to monitor the build up of highly resistive layers during the entry of  $\text{Ag}^+$  and  $\text{Li}^+$  ions into glass by impedance spectroscopy, since no second 'semicircle' appeared during these experiments. The indications<sup>(17)</sup> are that even at 260°C the mobility of  $\text{Ag}^+$  ions within the surface layers is comparable to that of  $\text{Na}^+$  ions, and that  $\text{Li}^+$  ions are actually more mobile than the  $\text{Na}^+$  ions they displace.

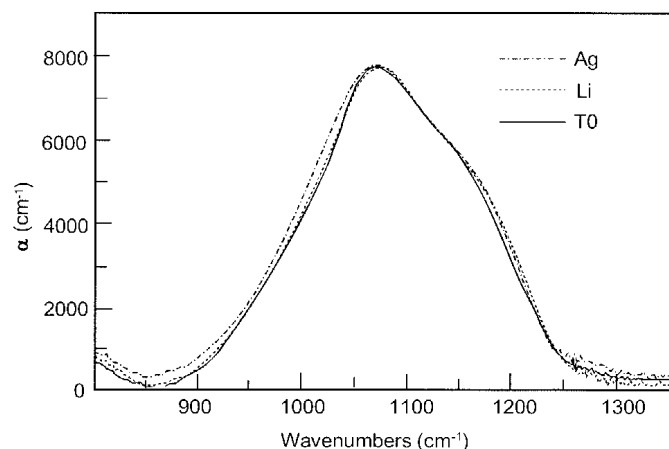
Figure 8 shows the mid infrared band for soda glass tubes: (i) in a pristine condition; (ii) after electrolysis in molten  $\text{AgNO}_3$  at 260°C at 30 mA for 40 min; and (iii) after electrolysis in molten  $\text{LiNO}_3$  at 260°C at 5 mA for 30 min. The calculated penetration depths, assuming one for one exchange as for  $\text{K}^+$  ions, are 72 and 8  $\mu\text{m}$ , respectively. In fact, the actual penetration depths are 90 and 260  $\mu\text{m}$ . Under these conditions, thermally driven diffusion is apparently very important.

Nevertheless, and perhaps as a consequence of this, the spectral changes are highly significant. After insertion of either of these cations, the spectra are appreciably wider than that of the pristine glass. The conclusion is that the reverse of Reaction (2) is occurring, i.e. that the glass structure is becoming less rather than more homogeneous.<sup>(4-7)</sup> Moreover, these changes are occurring far below  $T_g$ .

#### Discussion

Both electrochemical and the spectroscopic aspects of ion exchange are critically dependent on the nature of the foreign cation being introduced into the glass structure. In the electrochemical context, the key factor appears to be the size of the incoming cation. Based on recently published activation volumes for the ion transport process in glass,<sup>(21)</sup> one can assign 'effective' molar volumes to  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Ag}^+$  and  $\text{K}^+$  ions of 1.5, 3.5–4.0, 3.0–5.0 and 6.0  $\text{cm}^3\text{mol}^{-1}$ , respectively. A smaller ion, or one that is similar in size to the  $\text{Na}^+$  ion, can apparently enter the glass quite easily. However, a larger cation can be significantly impeded.

This is not an obvious or predictable result. Thus, a



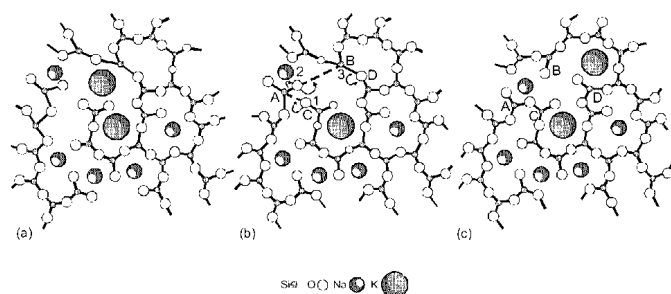
**Figure 8.** Mid infrared spectra for the outer surface ( $\sim 1 \mu\text{m}$  deep) of a 'soft' soda-lime-silica glass tube in pristine condition ( $T_0$ ) and after ion exchanges involving  $\text{Li}^+$  ions (at 5 mA at 260°C for 30 min) and  $\text{Ag}^+$  ions (at 30 mA at 260°C for 40 min), respectively

recent interpretation of mixed cation effects in glass based on molecular dynamics (MD) calculations<sup>(22)</sup> indicates that a significant mismatch energy (see also papers on the dynamic structure model<sup>(23,24)</sup>) exists, even when small cations such as  $\text{Li}^+$  enter sites vacated by larger alkali ions. The effect of such a mismatch should be to slow down the entry of  $\text{Li}^+$  ions into any 'foreign' glass, but this is not the case in the present instance. The reason for such an important discrepancy between theory and experiment needs to be established, but it seems it may lie in the nature of the structural changes being indicated by infrared spectroscopy.

In an earlier publication,<sup>(9)</sup> some of us have attributed the comproportionation reaction, that accompanies  $\text{K}^+$  ion exchange, to cation induced relaxations of the network (CAIRON) as illustrated here in Figure 9. The key point is that a concerted migration of electron pairs occurs within a localised region of the silicate network, and allows for a limited displacement of nonbridging oxygens (nBOs), which in turn enables neighbouring  $\text{K}^+$  ions to move further apart. We suggest that this effect is 'chemical' rather than 'mechanical' in origin. We argue, therefore, that the structural rearrangement does not occur in response to local pressures being generated in the surface layers. Indeed, the expected response of a silicate system to a pressure increase, both as found experimentally<sup>(25)</sup> and as 'predicted' by molecular dynamics calculations,<sup>(26)</sup> is for the anions in the network to disproportionate, making the cations move even closer together.

The contradiction disappears, however, if we identify the driving force of CAIRON as the differing chemical affinities of various cations for nBOs. The more 'acidic' the cation, the greater is the affinity. Elsewhere, Duffy *et al.*<sup>(27)</sup> have shown that, despite their size differences,  $\text{Li}^+$  and  $\text{Ag}^+$  ions show rather similar acidic properties. So, it is not surprising, therefore, that they each seek out and may even create cation environments rich in nBOs. This process has already been shown to happen in earlier ion exchange experiments involving  $\text{Ag}^+$  ions.<sup>(4-7)</sup>

However, another paradox remains. Elsewhere, Dubiel *et al.*<sup>(10)</sup> have shown that the conductivities of  $\text{K}^+$  for  $\text{Na}^+$  exchanged glasses do not attain the same conductivity as the equivalent melt grown glasses, even when this exchange has taken place somewhat above



**Figure 9.** A schematic showing how CAIRON facilitates the comproportionation reaction ( $Q_2 + Q_2 = 2Q_3$ ), which occurs when  $\text{K}^+$  ions replace  $\text{Na}^+$  ions in the surface layers of silicate glass. Note that curly arrows reveal the movement of electron pairs, while the dashed line indicates the formation of new Si-O bond. A, B, C and D identify particular Si atoms. One  $\text{K}^+$  ion is removed from (b) to make it easier to see the bond rearrangements

the glass transition temperature. We are thus confronted with two apparently contradictory facts: (i) as revealed by the ionic conductivity, structural relaxation is slow even above  $T_g$ ; and (ii) as revealed by infrared spectroscopy, network rearrangement may occur even far below  $T_g$ .

The paradox disappears if it is recognised that two separate processes are involved. First, there is the ‘conductivity relaxation’, which according to Kirchheim’s ideas<sup>(28)</sup> would involve an increase in network ‘mesh size’. In the context of the newly revisited dynamic structure model,<sup>(24)</sup> and of a new interpretation of high-pressure data and the related activation volumes,<sup>(21)</sup> an alternative explanation emerges. This involves the opening up of ‘good’ K ion sites, which must remain empty long enough for  $K^+$  ions to hop into them. To facilitate the formation of such empty K sites, the melt (or glass) must first expand – but it will not be driven to expand until such sites begin to emerge. In effect, each process will wait for the other one to happen. The result is that both processes will occur very slowly. It is worth recalling, in this context, that Huang *et al*<sup>(29)</sup> had earlier described an ‘anomalous’ expansion, which occurs in sodium triborate melts, even far above  $T_g$ . Such volume effects exert a lasting effect on the glass conductivity.

Second, there is the network isomerisation reaction, which depends as indicated in Figure 9, on electron pair migrations occurring within the  $\sigma$ – $\pi$  bonded structure of the silicate network. These processes benefit from being cooperative in nature, although free volume will certainly disappear when  $Na^+$  is being replaced by larger  $K^+$  ions and this will slow things down. Otherwise, this process should be relatively fast, as seems to be the case where  $Ag^+$  or  $Li^+$  ions are concerned.

Since viscous flow is not directly involved in the isomerisation reaction (although the converse of this statement is probably not true), the reaction may represent a localised ‘ratchet’ process of the kind proposed earlier by Greaves & Ngai.<sup>(30)</sup> We suggest that the kinetics of the redistribution of electron density within the network structure is crucial to this phenomenon, and may also be involved in mixed cation effects in glass, generally.

In conclusion, ion exchange processes reveal a wide range of complexities involving ion–network interaction in glass. The process of ion exchange may be either slow or fast, and the kinetics of structural relaxation may be important both above and below the glass transition temperature. The impact of these latter ‘kinetic’ factors on the ion transport mechanism

is such that the behaviour of ion exchanged glasses differs significantly from that of melt grown materials. These differences in glass behaviour may indeed have led earlier workers to think of the ‘disappearance of the mixed alkali effect’ in some systems; the reality is not so simple.

### Acknowledgements

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