1. Introduction

The motion of ions during heating of glass samples is conveniently examined using the newly reported technique of thermal relaxation ion electro-spectroscopy (TRIES).1) In TRIES, the motion of ions that have non-equilibrium distributions arising from built-in concentration gradients and electric fields is used to generate either a potential difference between externally applied electrodes, or a current in the circuit joining the electrodes. The potential difference or current are then recorded while the sample is subjected to a temperature ramp. This technique has recently been used to examine the activation energy for the diffusion of silver3) and many different metal ions in soda-lime glass.

In this study we apply the technique to examine the diffusion of copper in glass, which, like silver is of interest in the creation of in-glass optical and electronic devices. Although silver is well known as an ion of interest for these applications, copper poses some interesting opportunities and raises some scientific questions as, unlike silver, it has potential for both monovalent and divalent ions.

In this study, we prepare samples of copper diffused soda-lime glass by applying a potential difference between evaporated copper electrodes while the sample is heated. We examine the effect of pre-diffusing the samples with potassium ions in order to assess whether there are interactions between the potassium and the copper of the type already found for silver3) such interactions may affect the ability to diffuse copper into samples which have been pre-diffused with potassium to thermally toughen the glass. We will examine the evidence for aggregation of the copper and the presence of divalent as well as monovalent ions by examining diffusion-depth profiles with cross sectional scanning electron microscopy (SEM) using energy dispersive analysis of x-rays.

2. Experimental

Soda-lime silicate glass samples 1.9 mm thick were cut into 15 mm × 20 mm squares and cleaned with detergent and then washed with ethanol. To diffuse potassium ions into the glass, potassium nitrate, KNO₃ (Sigma-Aldrich, Inc.) was placed on the samples and melted to cover the surface by heating in an oven (B. & L. Tetlow Melbourne Australia) and maintaining the temperature at 450 °C for 25 h. After the annealing process, KNO₃ was removed from the glass surface by dissolving in water. After washing and drying, Cu was deposited onto both samples with and without pre-diffused potassium by vacuum evaporation. The samples were treated in the setup of Fig. 1.

To diffuse the samples with Cu, a voltage of 1,500 V was applied, providing a field strength in the sample of 789 V/mm. All samples for TRIES measurement were treated for 10 min then cooled down to room temperature. And for diffusion profile measurement using Energy Dispersive X-ray Spectroscopy (EDS) analysis in the Phenom XL® (Phenom-World B.V.) SEM, they were
treated for 1 h. Electrical resistance was measured during the field-assisted diffusion process using a TENMA® model 72-9405 resistance meter during application of the voltage. The resistance for 1500 V applied was found to lie in the range from 20 GΩ to 1 MΩ. The electrical conductivity of the glass samples undergoing diffusion at various temperatures was calculated from the applied voltage, the measured resistance, the sample thickness and the contact area of the electrode covering the entire face of the sample. The resistance of potassium pre-diffused samples decreased less rapidly with temperature than the resistance of samples without potassium. Therefore, a higher temperature of 250 °C was used for potassium diffused samples to give an initial resistance in the same range as the samples without potassium diffused at 220 °C.

After DC application, the samples were allowed to cool down to room temperature before the TRIES measurement began as shown in Fig. 2. A sample is put on a Cu plate (10 cm × 10 cm × 0.5 cm) which is connected to a multimeter (Agilent 34461A) to the negative line then another Cu plate (5 cm × 5 cm × 0.5 cm) which is connected to positive line is placed on the sample. The sample is heated up from room temperature to 600 °C at a rate of 250 °C per hour while measuring either voltage generated by the sample or the resistance of the sample. Different samples prepared under the same conditions were used for the voltage and the resistance measurement.

A Phenom XL® scanning electron microscope was used for imaging using a backscattered electron detector as well as for EDS elemental profiling as a function of depth. The operating voltage for all measurements was 15 kV. For depth profiling, the cross-sectional glass samples were fractured by propagating cracks from a scratch. EDS measurements were integrated for 0.5 s at each of 512 locations. Give imaging conditions and EDS conditions, voltage detectors etc.

The EDS depth profiles after preparation with electric field assisted diffusion for copper, sodium, potassium, calcium and silicon were measured on near the positive side of the sample cross section and after thermal cycling for the TRIES measurements were made near the both positive and negative sides. The ion concentration changes were found to be too small after 10 min DC application was found to be too small for EDS measurement, therefore, 1 h of DC applied voltage was used prepare samples for depth profiling.

### 3. Results

Depth profiles are shown as atomic ratios of each species relative to silicon, which is assumed to provide a non-diffusing reference atom. Using Si in this way, it is easier to observe net depletion or accumulation of the other atom types.

The atomic composition of the glass is shown in Table 1.

![Fig. 1. The configuration used for DC voltage application to the samples. (a) is the soda-lime glass with Cu electrodes as both electrodes. (b) is the same as (a) with prior potassium diffusion.](image1.png)

![Fig. 2. Configuration used for the TRIES measurements. (a) Soda lime glass prepared with Cu diffusion. (b) Potassium diffused glass with subsequent Cu diffusion. M indicates the multimeter for measuring voltage, current or resistance.](image2.png)

| Table 1. The atomic composition of the soda-lime glass |
|----------------------------------|
| Elements | O | Si | Na | Mg | Ca | Al |
| Composition (atomic %) | 71.9 | 13.5 | 9.6 | 2.7 | 1.2 | 1.2 |
3.1 Potassium depth profile in baked samples

Figure 3(a) shows the depth profile near the surface for reference samples containing a potassium layer prepared by holding the sample at 450°C for 25 h with a molten KNO₃ layer on the top surface. The counts for Na, K, Ca, Al, Mg, Si and O were taken as a ratio with the silicon counts. Silicon was used as a reference atom as it is likely to maintain a constant concentration in the glass as it is the network forming element. The Na and K profiles appear symmetrical about a horizontal line, indicating that some surface sodium was replaced by potassium supplied from the molten KNO₃, with the total alkali ion content remaining constant in the ion exchange region. Figure 3(b) shows the profile for the glass as received.3)–5)

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3.2 The Cu profile resulting from the application of DC voltage in samples without potassium

Figures 4(a) and 4(b) show the results of EDS analysis and corresponding SEM images in backscattered electrons near the positive electrode side after field-assisted diffusion of Cu into samples without potassium held at various temperatures. A voltage of 1,500 V was applied for 60 min to the samples. Using EDS analysis, the samples without potassium show no Cu diffusion at 170°C, however when the temperature is raised further, the copper starts to diffuse.6) At temperatures of 195°C sodium shows a strong depletion area7)–10) to a depth of 2 μm and the curve shows the formation of a maximum in sodium content, followed by a minimum and another maximum. After the application of voltage, the evaporated Cu film could not easily be removed by mechanical polishing, showing that the copper film was well bonded to the surface and there was no longer a distinct interface with the copper. This type of “anodic bonding” has previously been reported for an Al film on glass.11,12)

3.3 The Cu profile resulting from the application of DC voltage in samples with potassium

When diffusion of copper into samples containing pre-diffused potassium was attempted under the same conditions, much higher temperatures were required to achieve a current in the circuit containing the electrodes, indicating that diffusion of copper was impeded by the potassium content. The diffusion profiles in the potassium-containing samples were obtained at higher temperatures as shown in Figs. 4(c) and 4(d). Oscillatory variations of composition with depth are clearly visible in EDS analysis and are also clearly seen in the backscattered electron image. When the sample contains both sodium and potassium, the two alkali ions seem to move together, both being displaced by the incoming copper ions and the interaction between them seems to be less important than the interaction with copper.

3.4 TRIES measurement and activation energies for diffusion

The results of TRIES measurements conducted on soda lime glass without any treatment and on samples pre-diffused with potassium are shown in Fig. 5(a). In both curves, voltage appears from 350°C. The voltage for the sample without potassium appeared in the range from 350 to 470°C, higher than for the K diffused sample then the K diffused sample shows a higher voltage at 580°C then falls again.1) These two regions show suppression of voltage which corresponds to three peaks in the subtraction spectrum. The TRIES measurement shows that the sample with diffused potassium shows diffusion at a higher temperature than the untreated sample. This may be because the treated sample has been subjected to an anneal at 450°C, so any effects at lower temperature would be removed. The measurement shows that some motion of ions does occur in soda lime glass at these temperatures.3) The treatment with potassium creates a concentration gradient which acts as a driving force for diffusion of the ions, so it is not surprising that the diffused sample shows an effect at temperatures above the treatment temperature.

TRIES measurements using Cu diffused samples with and without potassium are shown in Fig. 5(b). The TRIES
Fig. 4. EDS analysis of soda-lime glass samples previously subjected to field assisted diffusion using 1,500 V for 1 h. Left panels show the atomic ratios relative to silicon. Copper is green, potassium is red and sodium is indigo. The right panels show the corresponding backscattered electron images with the analysis line shown as a dashed line (a) diffusion of Cu into a sample without potassium at 170 °C showing no diffusion (b) diffusion of Cu into a sample without potassium at 195 °C showing a maximum in the sodium content beneath the surface and two maxima in the calcium content and (c) diffusion of Cu into a sample with potassium at 245 °C showing a depletion of both Na and K in the Cu diffused region (d) diffusion of Cu into a sample with potassium at 270 °C, showing a maximum in calcium content near the surface, while the sodium and potassium are driven more deeply. The Cu has become a minority species in the surface layer.
measurement of the Cu diffused samples shows that the diffusion starts at a relatively low temperature. This may be because the built-in electric fields created in the diffusion process assist the diffusion. It also shows that the potassium impedes the copper diffusion as shown by the difference curves. The low temperature response near 200 °C is eliminated and the high temperature response near 350 °C is greatly reduced.

The sample without potassium produced voltages of more than 1,000 mV during the TRIES study. The K diffused sample also shows almost the same voltage. However, the rise of voltage is slower than for the sample without K.

The results for Ag with potassium and without potassium are shown in Fig. 5(c). The potassium sample shows a large voltage reduction.

The differences of those two curves are shown in Fig. 5(d). The result shows three peaks at 220, 350 and 550 °C respectively.

The activation energy calculated from TRIES measurement using Arrhenius plots obtained by plotting the TRIES voltage on a log scale as a function of 1/T in Fig. 6. The slope gives the activation energy and the voltage intercept gives the pre-exponential factor known as the attempt frequency and R² fitting values are shown in Table 2. The data shows that potassium-diffused samples have a higher
activation energy. The Meyer-Neldel correlation rule states that the attempt frequency for an activated process described by the Arrhenius relation is correlated with the activation energy when some change is made to the system. There are two different Meyer-Neldel slopes when the logarithm of the attempt frequency is plotted against the activation energy (Fig. 6), indicating different activation fields for copper ion diffusion and diffusion in soda-lime glass where NBO diffusion also contributes, which has a different phonon spectrum for its activation. The R2 fitting values for both soda lime and Cu slopes are shown in Table 3. Both R2 values were calculated to pass through the position coordinate of \((x, y) = (0, 1)\) because one of the MNR parameters is unity, which gives the point \((0, 1)\).

### Table 2. Results for activation energy, attempt frequency and the temperature range used in their calculation from TRIES measurements and coefficient of determination \((R^2)\) for the fitting. All data are for 10 min DC voltage application

| Elements       | Soda lime | Soda lime (K) | Cu | Cu (K) |
|----------------|-----------|---------------|----|--------|
| Activation energy (eV) | 1.16 | 1.48 | 1.07 | 1.13 |
| Attempt frequency (Hz)     | \(3.4 \times 10^{10}\) | \(1.0 \times 10^{12}\) | \(1.23 \times 10^{13}\) | \(4.03 \times 10^{12}\) |
| Temperature range (°C)    | 375–426 | 327–453 | 189–243 | 146–191 |
| Coefficient of determination \((R^2)\) | 0.979 | 0.989 | 0.995 | 0.997 |

### Table 3. Result of coefficient of determination \((R^2)\) for the fitting for MNR

| Elements       | Soda lime | Cu |
|----------------|-----------|----|
| Coefficient of determination \((R^2)\) | 0.990 | 0.994 |

3.5 Depth profiles after annealing of copper diffused samples

Diffusion depth profiles of samples without pre-diffused potassium that had been diffused with copper using 1500 V for 1 h are shown in Fig. 7 (anode side) and Fig. 8 (cathode side), before and after heating to 400, 500 and 600 °C. The sodium depletion area is shown for the sample after copper diffusion in Fig. 7(a). After 400 °C, there is no significant change [Fig. 7(b)] but after a 500 °C anneal, Cu starts diffusing by thermal diffusion.\(^{13–16}\) Ca also starts moving at the temperature [Fig. 7(c)]. At 600 °C a clear border line appears between copper, and sodium, calcium and silicon at 7 μm [Fig. 7(d)]. It appears that Cu is pushing sodium and calcium towards the cathode side.

On the cathode side, the ion distribution does not show significant change until 600 °C [Fig. 8(d)]. At 600 °C, Cu diffused to 15 μm which is attributed to thermal diffusion.

4. Discussion

The main findings of this work are summarized here. We find copper diffusion into soda-lime glass is increased...
by electric field assistance so that useful concentrations of copper can be injected in a surface layer. By annealing the copper diffused glass at higher temperatures than used for the diffusion process, a relatively uniform concentration of copper can be achieved in the surface layer, with potential application to optical devices. We have applied energy dispersive analysis of X-rays (EDS) and the TRIES technique to the study of copper diffusion in soda-lime glass. EDS analysis of cross sections of the glass shows the effect of potassium on the diffusion of copper and the interactions between the various ions in the glass.

The TRIES technique has allowed us to evaluate the Arrhenius parameters (activation energy and attempt frequency) on the diffusion of ions and in particular the effect of potassium ions on the diffusion of copper. We found that potassium impedes the diffusion of copper using both techniques. Potassium may impede the diffusion of copper through its effect on sodium diffusion in the effect known as the "mixed alkali effect". We also find that the Meyer-Neldel rule shows that the diffusion of copper is fundamentally different to the diffusion of the ions in soda-lime glass in that the diffusion on the non-bridging oxygen contributes to the diffusion in pure soda lime glass, while the diffusion of copper is similar to the diffusion of many other ions in soda-lime glass.17-20 In another study of the diffusion of eleven different metal ions, copper obeys the same Meyer-Neldel rule as the other ten metal ions, but different to the rule for soda-lime glass. This is attributed to the different thermal excitation of cation motion in glass than applies to the silicate backbone that governs the diffusion of the non-bridging oxygen ions in pure soda-lime glass.

Our study reveals that interactions take place between copper, sodium, potassium and calcium ions. These interactions are manifested in the diffusion profiles. For example, "waves" or multiple local maxima in alkali and Ca ion concentration are caused by the interaction of these ions with the Cu ion as it diffuses into the glass under the influence of the electric field. There appear to be strong interactions between Cu and the alkali (Na, K) and Ca ions. There are also strong interactions between the alkali and calcium ions that cause the formation of local maxima in the alkali ions in separate locations from the maxima in calcium ions. The interaction between the two alkali ions Na and K is less strong, as both tend to move together in their response to the other ions (Cu and Ca). The copper "repulsion" experienced by all other ions may arise from the effect of the copper ion to limit the ease of diffusion of other ion species by creating a "roadblock" effect.

5. Conclusion

We have demonstrated the usefulness of the TRIES method by applying it to the study of the field assisted diffusion of copper in soda-lime glass. The combination of the TRIES technique with EDS analysis of diffusion profiles is especially informative. The findings concerning copper diffusion are several. First, electric field assistance enables injection of copper ions into soda-lime glass at a lower temperature than possible with thermal diffusion alone. Second, copper diffusion in soda-lime glass obeys...
the same Meyer-Neldel rule relating the activation energy to the attempt frequency in the Arrhenius relation as other metals, but the ion motion in pure soda-lime glass obeys a different rule, possibly because non-bridging oxygen contributes to the ion motion in glass. Third, we find potassium impedes the diffusion of copper ions into glass. Fourth, we find strong interactions between copper ions and the native alkali (Na, K) and Ca ions in glass, leading to local maxima in ion concentrations. There are also interactions between the alkali ions and calcium ions. However, the interactions between the two alkali ions appear weak, allowing the two ions to diffuse together in response to the other ions. Finally, we find that thermal anneal of copper diffused glass leads to a uniform copper-rich layer of potential use in copper optical devices.

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