

ON THE CHANGE OF THERMAL PARAMETERS IN A GLASS DURING A Na/Tl ION-EXCHANGE-CHARACTERIZED BY DTA MEASUREMENTS

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The Na/Tl exchange is investigated in two silicate glasses ($\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ and crown-flint “KF3”) by estimation of concentration or refractive index profiles, resp. ($c_{\text{Tl}}(x)$ or $n(x)$). The forms of the profiles are discussed in connection with changes of the glass transition temperature T_g owing to an increase of Tl_2O contents, determined by DTA on homogeneous glass samples. During the Na/Tl exchange the local and temporal enlargement of the Tl_2O content causes a drastic decrease of $T_g(x, t)$ values and of the viscosity $\eta(x, t)$, which yields a remarkable acceleration of the Na/Tl interdiffusion.

Ion-exchange in optical glasses is the most favourable process for generation of gradient-index materials [1]. Glasses with definite gradients of refractive index are useful both for optics of image (geometrical optics) and for integrated micro-optics (wave optics). The glass, which contains commonly alkali ions (Na^+ , K^+), will be contacted with an appropriate salt melt enriched of monovalent cations with a high electronic polarizability (Ag^+ , Tl^+). In the glass network structure only the monovalent ions have a sufficiently high mobility for exchange out of the bulk of the glass.

A schematic representation of the experimental arrangement is given in Fig. 1. Usually the ion-exchange is carried out at temperatures $T \lesssim T_g$ (T_g : glass transition temperature).

At the surface of the glass, the ion-exchange is governed by the equilibrium between the salt melt and the glass. Glass is considered as a solid equilibrium-phase with elastic properties ($T \lesssim T_g$). Its structure corresponds to that of a super-cooled glass melt. As a result of this ion-exchange equilibrium in the glass surface there will be generated an infinitely thin layer of cations from the salt melt (Ag^+ or Tl^+), which acts as a source for the ion-exchange in the bulk of the glass. In the bulk, the exchange of cations is controlled by the diffusion kinetics of the related ions in the given glass network. The interdiffusion process can be described by Eq. (1) (Second Fick law).

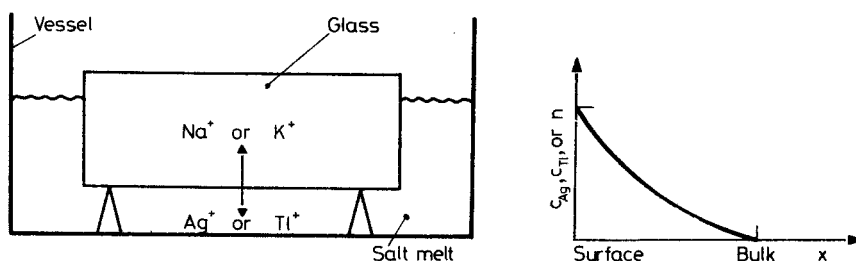
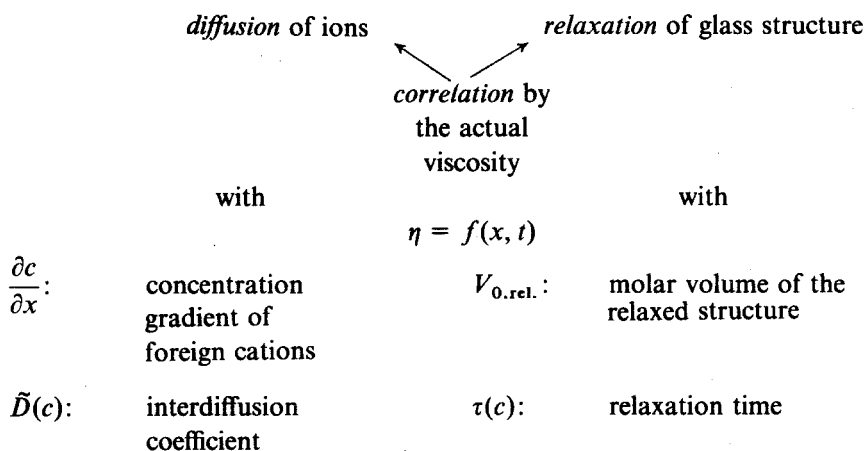


Fig. 1 Experimental arrangement for ion-exchange and qualitative profiles of concentration c and refractive index n

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(\tilde{D} \frac{\partial c}{\partial x} \right) \quad (1)$$

$$V = V_{0,\text{rel.}} \cdot e^{-t/\tau} \quad (2)$$



However, an other process takes also place, if the exchange temperature is comparable with the transition temperature of the glass ($T \approx T_g$). Under these conditions the glass structure relaxes in a more or less complete extent during the ion-exchange, corresponding to Eq. (2) for the molar volume V with $t \approx \tau$. At the characteristic temperature T_g glasses change their mechanical character from an elastic solid to a plastic super-cooled melt in compliance with a viscosity of $\eta = 10^{13}$ dPa·s. The ion-exchange at $T \gtrsim T_g$ is distinguished by a complicated interaction between diffusion and structure relaxation processes, effected by the actual viscosity $\eta = f(x, t)$ (remark: $\eta(c)$ and $c(x, t)$). It is seen from the Walden rule Eq. (3) and the equation of Maxwell-Kuhn Eq. (4), that there is a correlation

between \tilde{D} and τ

$$\tilde{D} \cdot \eta = \text{const.} \quad (3)$$

$$\eta = G \cdot \tau \quad (4)$$

with $G(c)$: torsion modulus.

In every case, a definite concentration profile $c(x)$ is generated after the ion-exchange with a duration t (see also Fig. 1). This profile $c(x)$ should be accompanied by a corresponding refractive index profile $n(x)$, expressed by the Eq. (5) of

Lorenz-Lorentz ($n = f\left(\frac{\alpha(x)}{V(x)}\right)$).

$$\frac{n^2 + 1}{n^2 - 2} = \frac{4}{3} \pi \cdot L \cdot \frac{\bar{\alpha}(x)}{V(x)} \quad (5)$$

$$\bar{\alpha}(x) = \sum N_i(x) \alpha_i \quad (5a)$$

$$V(x) = V_{0,\text{rel.}}(x) \cdot f\left(\frac{t}{\tau(x)}\right) \quad (5b)$$

with L : Loschmidt number

α : electronic polarizability of a particle i , average of all glass particles (ions)

V : volume of a mole of particles i (molar volume)

N_i : molar fraction

The Na/Tl exchange yields a remarkable change of polarizability $\bar{\alpha}$ (s. Eq. (5a)) and of refractive index, resp. ($\alpha_{\text{Na}} = 0.409 \cdot 10^6 \text{ pm}^3$ [2], $\alpha_{\text{Tl}} = 4.16$ [3] or 5.2 [4]). Because of the permanent tendency of the glass to reach the equilibrium state, the real molar volume V (see Eq. (5b)) at a depth x is a result from the "history" of the development of the chemical composition at this points. This should be represented by the single relation 5b. An exact analytical expression will not be so easy.

Experimental procedure

We investigated the Na/Tl exchange in two glasses:

disilicate glass

$\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ $T_g = 465^\circ$

(33.3 mole-% Na_2O)

and *commercial optical glass*

crown-flint "KF3" $T_g = 460^\circ$

(17.4 mole-% Na_2O)

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The used salt melts consisted of mixtures $(\text{NaNO}_3)_{1-z} (\text{TlNO}_3)_z$ with $z = 0.1$ and 0.6, resp.

For discussion of the form of the resulting profiles $c_{Tl}(x)$ or $n(x)$, we estimated in parallel investigation the change of viscosity with increasing Tl_2O content in the two glasses. Therefore we determined T_g values of glass samples with different Tl_2O contents to find the experimental dependence $T_g = f(c_{Tl_2O})$. Assuming at T_g a viscosity $\eta = 10^{13}$ dPa·s we can estimate the dependence of the viscosity η on the chemical composition ($\eta_T = f(c_{Tl_2O})$); considering the dependence on temperature: $\eta = \eta_0 \cdot \exp(E_A(T)/RT)$ with $E_A(T) > 0$, see also Vogel–Fulcher–Tammann equation [5, 6]).

For this purpose, homogeneous glass samples with different Tl_2O contents were prepared by the following way:

1. Na/Tl ion-exchange on powder of the two glasses with salt melts $(NaNO_3)_{1-z}(TlNO_3)_z$ with $0.1 \leq z \leq 1.0$ (310°, 20 h)
2. soft remelting and
3. reconsideration of the homogeneity by electron micro-probe.

The Tl_2O content was determined by atomic absorption spectroscopy (Perkin–Elmer 503) of resolved glass (Assumption: the change of chemical composition during the Na/Tl ion-exchange consists only in the substitution of Na^+ by Tl^+). A differential thermal analysis device (Rigaku Thermoflex, heating rate $5 \text{ deg} \cdot \text{min}^{-1}$) was available for estimation of the T_g values.

Results and discussion

Figure 2 shows the determined T_g temperatures in dependence on the Tl_2O content in the glasses $Na_2O \cdot 2SiO_2$ and “KF3”. In both cases, the glass transition temperature T_g (also viscosity η and relaxation time τ , resp. see Eq. (4)) drops drastically with increasing content of Tl_2O .

Obviously, the Na/Tl exchange is accompanied by a remarkable change of the chemical bond of mobile cations in a silicate glass. Figure 3 illustrates the

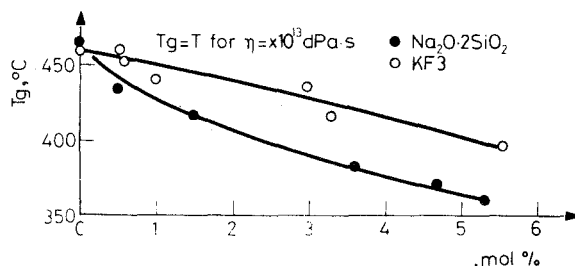


Fig. 2 Dependence of the glass transition temperature T_g on Tl_2O content in the glasses ($T_g = f(c_{Tl_2O})$)

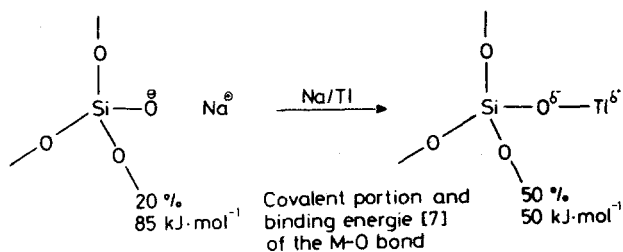


Fig. 3 Change in the chemical bond M—O

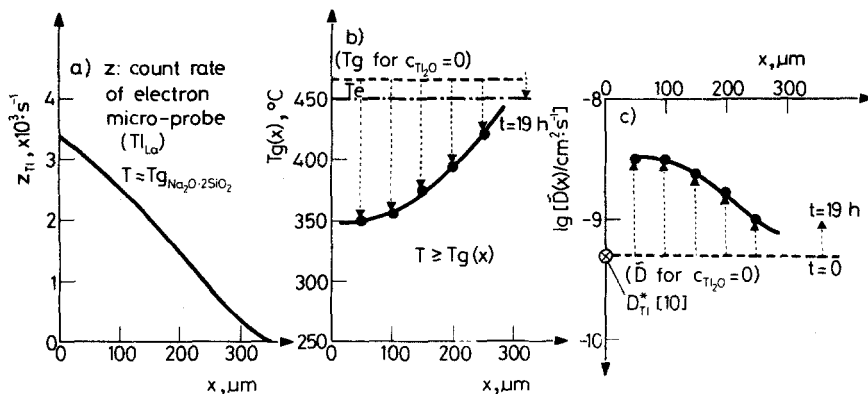


Fig. 4 Disilicate glass ($T_g = 465^\circ$) after ion exchange ($T_e = 450^\circ$, $t_e = 19$ h, melt $(\text{NaNO}_3)_{0.9}(\text{TlNO}_3)_{0.1}$)
 a) profile of Tl concentration measured by electron microprobe
 b) profile of (local) glass transformation temperature
 c) profile of interdiffusion coefficient

enlargement of covalent proportion in the M—O bond, which is joined with a decrease of the binding energy [7].

By help of the results of Fig. 3 we can discuss the experimental profiles $c_{\text{Tl}}(x)$ and $n(x)$ after a Na/Tl exchange in the glasses.

Figure 4 shows a Tl concentration profile $z_{\text{Tl}}(x)$, estimated by electron microprobe in the glass $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$. The small concave bending of the profile $z_{\text{Tl}}(x)$ is caused by a decrease of the interdiffusion coefficient $\bar{D}(x)$ (calculated by Boltzman–Matano method [8]) with diminishing Tl_2O content [9]. Corresponding to the Walden rule (Eq. (3)), this drop of $\bar{D}(x)$ is accompanied by an increase of $T_g(x)$ and viscosity $\eta(x)$, resp. (take into consideration: in every case $T(=450^\circ) \geq T_g(x)$ given at t by $T_g = f(c_{\text{Tl}_2\text{O}})$ with $c_{\text{Tl}_2\text{O}}(x)$). The dotted arrows represents in Fig. 4 the temporal change of corresponding values (T_g or \bar{D}) at a point x during the ion-exchange of the duration t . At every depth x the Na/Tl interdiffusion

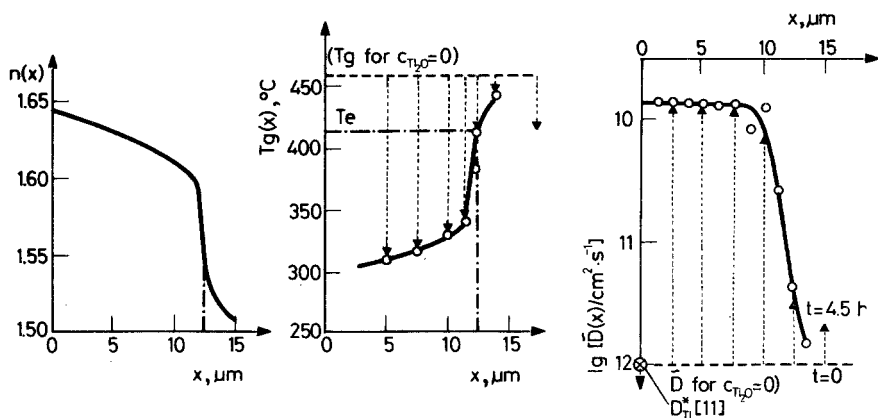


Fig. 5 Glass KF3 ($T_g = 460^\circ$) after ion exchange ($T_e = 415^\circ$, $t_e = 4.5$ h, melt $(\text{NaNO}_3)_{0.4}(\text{TlO}_3)_{0.6}$)
 a) profile of refractive index measured by laser mode spectroscopy
 b) ((cf. legend to Fig. 4))
 c)

starts with \tilde{D} for $c_{\text{Tl}_2\text{O}} = 0$, q.e. the Tl tracer diffusion coefficient D_{Tl}^* [10] (marked with little lines).

Figure 5 represents a) the refractive index profile $n(x)$, measured by laser mode spectroscopy after Na/Tl exchange at $T_e = 415^\circ$ in the optical glass "KF3". The pronounced bend (step-like) surprises as a result of a simple thermal ion-exchange at $T < T_{g\text{KF3}}$.

However, the local values $T_g(x)$ (or $T_g(c_{\text{Tl}_2\text{O}})$ with $c_{\text{Tl}_2\text{O}}(x)$) demonstrate, that at the depth $x = 12.5 \mu\text{m}$, where we find the strong drop of refractive index n , there is a transition from a glass with $T_e > T_g(x)$ to one with $T_e < T_g(x)$. Consequently, a relaxed structure exists near to the surface of the glass, whereas in the bulk the glass network ($V(x) < V_{0,\text{rel.}}(x)$) remains unrelaxed drastically retarding the Na/Tl exchange (notice the large difference of ionic radius: $r_{\text{Tl}} + (144 \text{ pm}) > r_{\text{Na}} + (95 \text{ pm})$). This additional diminution of the Na/Tl exchange rate (apart from the predictions of Walden rule) explains the step-like refractive index profile $n(x)$ in glass "KF3".

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Zusammenfassung — Der Na/Tl-Austausch wird in zwei Silicatgläsern ($\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ und Kron-Flintglas "KF3") anhand der Bestimmung von Konzentrations- oder Brechzahlprofilen ($c_{\text{Tl}}(x)$ oder $n(x)$) untersucht. Die Profilformen werden im Zusammenhang mit Änderungen der Glastransformations-Temperatur T_g bei steigendem Tl_2O -Gehalt diskutiert, die mittels DTA an homogenen Glasproben bestimmt wurden. Während des Na/Tl-Austausches verursacht die lokale und zeitliche Erhöhung des Tl_2O -Gehaltes ein drastisches Absinken der $T_g(x, t)$ -Werte bzw. der Viskosität $\eta(x, t)$, das zu einer bemerkenswerten Beschleunigung der Na/Tl-Interdiffusion führt.

Резюме — В двух силикатных стеклах ($\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ и флинтглас «КФ3») Na/Tl обмен изучен путем определения профилей концентраций и показателя преломления $c_{\text{Tl}}(x)$ и $n(x)$. Обсуждены формы этих профилей в связи с изменениям температуры стеклообразования T_g , обусловленного увеличением содержания оксида таллия, и определенных методом ДТА на гомогенных образцах стекла. В процессе Na/Tl обмена локальное и временное увеличение оксида таллия вызывает резкое уменьшение значений $T_g(x, t)$ и вязкости $\eta(x, t)$, что вызывает необыкновенное ускорение Na/Tl взаимной диффузии.