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Producing the Gradient Changes in Glass Refraction by the Ion Exchange Method — Selected Aspects

Roman Rogoziński

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Abstract

This chapter presents the chosen aspects of the ion exchange technological method. Results of research refer to the refractive index profiles of planar waveguides produced by the ion exchange method in various glasses. All refractive index profiles were determined by measuring the effective refractive indices of the waveguide modes. In the first part of this chapter the processes of electrodiffusion doping soda-lime glass with silver ions has been described. The second part contains a description of the two measurement methods allowing to estimate the equilibrium concentration basing on the example of the concentration of sodium in soda-lime glass. The third part describes the phenomenon of stress birefringence arising in borosilicate BK-7 glass doped with potassium ions K^+ . The fourth section presents the results of research on the real-time control of ion exchange diffusion processes. The results confirming the validity of this idea with examples of soda-lime glass (Menzel-Gläser company), BK-7 (Schott company) and Pyrex (Borosilicate 33 of Corning company) doped with Ag^+ silver ions and K^+ potassium ions are also presented here.

Keywords: ion exchange, planar waveguides, electrodiffusion

1. Introduction

The development of the ion exchange technological method as applied to the preparation of gradient changes of the refraction in the surface area of the glass was initiated in the 1970s. The produced changes in refraction can be used to conduct the electromagnetic wave along

the surface of the glass (then we talk about waveguide structures) or provide refractive areas for wave passing (perpendicular) through the glass. In each of these cases we have to deal with the gradient structures of planar topology (Fig.1). In the case of waveguide structures we can distinguish planar waveguides (Fig.1a) or waveguides of channel type (Fig.1b). In the first case the refractive index gradient has only one coordinate, while in the waveguides of channel type it has two. On the basis of such structures various elements of planar waveguide optics can be constructed, such as: splitters of Y type [1], splitters of 1xN type [2], multiplexers [3-7], directional couplers [8], ring resonators [9-10], planar polarizers [11], planar interferometers [12-13] or gradient MMI structures [14-16]. These elements can cooperate with the fiber waveguides. In addition to the passive components of planar optics, by the ion exchange method the structures of lasers and optical amplifiers can also be produced. For this purpose glasses doped with rare earth ions are used [17-23]. On the basis of gradient planar waveguide structures the optical sensors are also produced [24-28]. By the ion exchange method the refractive structures are produced as well [29-32]. In such structures (e.g., lenses or microlenses) the refraction gradient is generally three-dimensional (Fig.1c).

Figure 1. The classification of gradient structures in glass: (a) planar of slab type, (b) planar of channel type, (c) refractive.

The ion exchange technological method is relatively cheap both in terms of used materials, and the apparatus required for its implementation, which is undoubtedly its main advantage. It has been mainly applied to the composite oxide glasses. The physical basis of this method is the phenomenon of ionic conductivity of glasses. This phenomenon occurs in the glasses that contain modifier ions possessing low binding energy with glass network. In these glasses at elevated temperature the modifier ions obtain energy to enable them to migrate within the glass network [33]. This migration is manifested in the form of ionic current flowing through the glass in the presence of an electric field generated in the area. The migration of modifier ions at an elevated temperature enables also the realization of ion exchange in glass. This situation occurs when at a sufficiently high temperature the glass is in contact with the phase of the source of these ions. Most often it is a liquid phase in the form of molten salt [33]. The most commonly used liquid sources of admixture ions are molten nitrates, which have low melting points. Such sources can be considered as sources of constant productivity. At sufficiently high temperature ionized admixture obtains sufficient energy to overcome the

potential barrier at the surface of the glass. At the same time one modifier ion has to “come out” from the glass to the source of admixture, so that the electrical neutrality is maintained throughout the volume of the glass. In this way, the concentration gradient of admixture introduced into the glass is initiated in the surface area of glass. In this area the concentration gradient of the glass modifier ions is also formed. It has a direction opposite to the gradient of concentration of the admixture. Consequently, in the glass there are two opposing streams of ions: a stream of admixture ions directed into the glass and a stream of modifier ions directed to the surface of the glass. This phenomenon has a diffusive character. Its effect is to create in the glass area the gradient changes of its optical properties (refraction) and mechanical properties (stress). The local changes in the refractive index of the glass, which are the results of ion exchange, are the effect of the difference of their electric polarizabilities, as well as differences in their ionic radii.

This chapter is based on the physical basis of this phenomenon described in detail in work [33]. Here the chosen aspects of the ion exchange technological method are going to be presented. Results of research refer to the refractive index profiles of planar waveguides produced by the ion exchange method in various glasses. All refractive index profiles were determined by measuring the effective refractive indices of the waveguide modes. The goniometric method of synchronous angles measurements with the use of a prism coupler has been used. A detailed description of the measurement method and the method for determining the refractive index profiles was given in the work [33] (pp.166-172).

In the first part of this chapter, the process of electrodiffusion doping soda-lime glass with silver ions has been described. The second part contains a description of the two measurement methods allowing to estimate the equilibrium concentration basing on the example of the concentration of sodium in soda-lime glass. The third part describes the phenomenon of stress birefringence arising in borosilicate BK-7 glass doped with potassium ions K^+ . The fourth section presents the results of research on the real-time control of ion exchange diffusion processes. The idea of this method has been described in work [33]. Here are presented the results confirming the validity of this idea with examples of soda-lime glass (Menzel-Gläser company), BK-7 (Schott company) and Pyrex (Borosilicate 33 of Corning company) doped with Ag^+ silver ions and K^+ potassium ions.

2. Ion exchange in glasses in the presence of an electric field

In the two-component model of the ion exchange in the glass [33] there are two oppositely directed streams of ions: stream of admixture ions $\vec{\Phi}_A$ and stream of modifier ions $\vec{\Phi}_B$ (Fig.2). The stream of admixture ions diffusing in the glass in the ion exchange process is the sum of the two components [33] (p.174):

$$\vec{\Phi}_A = -D_A \nabla c_A + \mu_A c_A \vec{E}_0 \quad (m^{-2}s^{-1}) \quad (1)$$

The first one is related to the local concentration gradient of admixture in the glass. The second component expresses the electric drift of admixture ions in the local electric field. This electric field can be the effect of a difference in mobility of exchanged ions. In addition to the ion exchange processes based on a purely thermal diffusion of admixture ions, some processes are also carried out in the presence of an external electric field. In such processes an additional parameter occurs: the intensity of the external electric field $\vec{E}_e$ (Fig.2). These processes are briefly called electrodiffusion. They are characterized by a directed migration of ions introduced into the glass caused by the effects of an electric field.

Figure 2. Ion exchange process in glass.

The local field $\vec{E}_d$ is then a superposition of the diffuse field which is the result of differential mobility of exchanged ions and external field $\vec{E}_e$:

$$\vec{E}_0 = \vec{E}_d + \vec{E}_e \quad (2)$$

The form of the function describing the distribution of the admixture concentration $c_A(x)$, introduced into the glass in the electrodiffusion process is dependent from the interaction between the diffusion component $D_A c_A$ and the electric migration component $\mu_A c_A \vec{E}_0$ of the admixture stream (D_A and μ_A denote, respectively, the diffusion coefficient of the admixture and its electric mobility). In the case of electrodiffusion processes the local electric field takes the form [33] (p.176):

$$\vec{E}_0 = \frac{\vec{E}_e}{1 - \alpha u} + \frac{HkT}{e} \cdot \frac{\alpha}{1 - \alpha u} \nabla u, \quad (3)$$

where $u(x) = c_A(x)/c_0$, $\alpha = 1 - \mu_A(u)/\mu_B(1 - u)$.

In the above equations, c_0 - equilibrium concentration [33] (p.175), H - the correlation coefficient ($0 < H < 1$) [34], k - the Boltzmann constant, T - the absolute temperature, μ_A and μ_B - electrochemical mobilities of admixture ions and modifier ions respectively.

In the electrodiffusion processes the external electric field may have polarization established during the process. Then we talk about the electrodiffusion processes with fixed electric

polarization. The polarization of this field can also be changed during the implementation of the ion exchange process. Such processes are called processes with a change of electric polarization.

2.1. Electrodiffusion processes with fixed electric polarization

In the case of such electrodiffusion processes implemented with the use of a molten source of admixture, the molten salt (AgNO_3) contacts with one side of the glass plate. To the other side of the plate the solid electrode is applied. Between the molten salt and the solid electrode a potential difference is produced. The molten salt is at a positive potential in relation to the glass. With such polarization the silver ions Ag^+ in glass drift toward the electric field. At the same time the modifier ions (Na^+) in the volume of the glass drift toward the negative electrode. There their reduction to the atomic form occurs. As a result, between the glass surface and the negative electrode the metallic sodium is generated. This reduces the adhesion of the electrode to the glass surface.

Figure 3a presents the method of implementation of the electrodiffusion process with fixed polarization. The role of the solid electrode here is served by electrically conductive glue layer resistant to high temperatures. Figure 3b shows refractive index profiles of planar waveguides produced by the electrodiffusion processes for different values of electric field intensity. The durations of these processes are almost the same. Each process has been carried out at the temperature $T = 300^\circ\text{C}$. For comparison the refractive index profile of the waveguide produced in the same conditions (time and temperature) in the diffusion process ($\vec{E}_e = 0$) is presented. The presented refractive index profiles have been determined for the wavelength $\lambda = 677 \text{ nm}$.

Figure 3. (a) Implementation of electrodiffusion processes with fixed polarization. (b) Refractive index profiles of planar waveguides ($\lambda = 677 \text{ nm}$) produced in electrodiffusion processes for different values of electric field intensity.

Due to the kinetics of diffusion assisted by an electric field, the electrodiffusion processes can be used as a tool for producing deep waveguide structures in a relatively short time. This is not the only argument in favor of the use of this type of technological processes. Much more

important are there the opportunities to influence the shape of refractive index profiles of waveguides generated in the electrodiffusion processes through changes in polarization direction of the electric field.

2.2. Electrodiffusion processes with a change of the electric polarization

If a change in direction of the vector of external field $\vec{E}_e$ is made in the equation (3) describing the local electric field $\vec{E}_0$ in the electrodiffusion process, then this can obtain the value of the field $\vec{E}_0$ at which the change occurs in the direction of flow of admixture ions in the glass. This occurs only in situations where admixture ions are supplied on both sides of the glass substrate. It is then that the condition of continuity of ionic current flow through the glass can be satisfied. The electrodiffusion processes with the change in polarization of the external electric field are carried out under conditions of glass substrate being in contact with the liquid admixture sources on both sides [35-37].

Figure 4. The implementation of electrodiffusion processes with a change of the direction of the electric polarization.

The idea of using a cyclic change of polarization of the external electric field in the electrodiffusion processes has been described by Houde-Walter and Moore [35]. The authors have indicated there a theoretical ability to influence the final form of the refractive index profile of the waveguide in the electrodiffusion processes in which a multiple change of polarization of the electric field was applied. Such processes create major possibilities to influence the final form of the admixture distribution in the glass. The factors that determine here the shape of the resulting distribution of admixture in the glass are both the value and the polarization direction of the external electric field, as well as temporal relations between states with opposite polarizations. If a possibility of multiple repetitions of polarization changes of $\vec{E}_e$ field is also taken into consideration, the number of these factors will further increase.

In the electrodiffusion processes, where a change of the direction of polarization of the external electric field $\vec{E}_e$ is made, the admixture is introduced into the glass on both sides of the substrate.

Therefore the waveguide structures are formed on both sides of the glass plate. In order to distinguish between these two structures the following designations are used (Fig.4): waveguide “A” is formed on the side of the substrate, where the initial polarization of the electric field enhanced the process of migrating admixture into the glass, while the waveguide “B” is formed on the opposite side of the substrate, after the reversal of polarization. Figure 4 also indicates the conventionally adopted positive and negative polarization states.

Sample	Waveguide	Temperature of the process (°C)	Duration of the process (min)	Polarization and the electric field intensity (V/mm)	Electric charge (C)
1	A	272±1	30/30	+18.2/9.1	1.130
	B		30/30	18.2/+9.1	0.572
2	A	298 ±1	75/15	+18.2/9.1	5.680
	B		15/75	18.2/+9.1	0.572
3	A	298±1	60/30	+18.2/9.1	4.755
	B		30/60	18.2/+9.1	1.172
4	A	298±1	30/60	+18.2/9.1	3.280
	B		60/30	18.2/+9.1	2.951
5	A	298±1	45/45	+18.2/13.6	3.636
	B		45/45	18.2/+13.6	0.144
6	A	298±1	45/45	+18.2/9.1	3.719
	B		45/45	18.2/+9.1	1.774
7	A	298±1	45/45	+4.5/18.2	0.908
	B		45/45	4.5/+18.2	4.164
8	A	299±1	30/30	+18.2/9.1	2.554
	B		30/30	18.2/+9.1	1.252
9	A	299±1	45/45	+18.2/18.2	4.654
	B		45/45	18.2/+18.2	4.777
10	A	299±1	50/40	+18.2/9.1	3.688
	B		40/50	18.2/+9.1	1.803
11	A	300±1	45/45	+13.6/18.2	2.965
	B		45/45	13.6/+18.2	4.240
12	A	301±1	45/45	+9.1/18.2	1.628
	B		45/45	9.1/+18.2	3.791

Table 1. Electrodiffusion processes with a change of direction of the electric polarization.

Significant differences in the shapes of refractive index profiles that arise in the case of changes in the polarization direction of the electric field during the process can be explained by considering the situation where the polarization of the applied electric field is changed only once. During such a process, with a positive polarization (Fig.4a), the admixture ions enter the glass substrate from the waveguide "A". On the other side of the glass plate (despite its contact with the source of admixture) a waveguide is not formed, because the glass ions pass into the liquid phase due to the current i^+ flowing through the substrate.

After the change of polarization (Fig.4b), the situation is reversed. Through the glass substrate the current i now flows in the opposite direction. Waveguide "B" starts forming on the other side of the glass, while the opposite stream of admixture ions previously introduced into the glass with the glass modifiers ions changes the distribution of the introduced admixture in the positive polarization. Consequently, the shapes of the refractive index profile of waveguide "A" changes.

Figure 5. Comparison of refractive index profiles of waveguides produced in the electrodiffusion processes with a pre-determined value of electric field intensity for the positive value $E^+ = 18.2 \text{ V/mm}$ and $E^- = -9.1 \text{ V/mm}$ for the negative value, for various durations of "+" and "-" polarization. Waveguides produced on the first side of the substrate (a) and on the other side of the substrate (b).

The parameters of chosen technological processes with the use of a single change of the direction of the electric field polarization are summarized in Table 1. The soda-lime glass was used as the substrate. As liquid source of admixture on both sides of the substrate the molten silver nitrate (AgNO_3) was used. The electrodiffusion processes were realized with the use of the laboratory stand described in [33] (p.164). The temperatures of the processes were within the range: $272\div 301^\circ\text{C}$. The given duration of each process consists of two values relating respectively to the positive and negative polarization. In each glass plate two waveguides ("A" and "B") were produced on the opposite sides. The table shows the total electric charge of admixture ions that were introduced into the glass substrate from both sides. Figure 5a,b shows the refractive index profiles of waveguides produced in electrodiffusion processes, for which the field intensity for the "+" and "-" polarization have been established according to Fig.4.

Here the ratio of the duration of the polarization t^+ and t^- was a variable. In each case, the duration of the whole process was the same and was $t_{\text{tot}} = 90'$. The waveguides of "A" and "B" were formed on opposite sides of the glass plate. The equivalent centric symbols in both the charts (a) and (b) denote the same glass substrate in which the adequate waveguides were formed.

Figure 6. Comparison of refractive index profiles of waveguides produced by electrodiffusion processes with fixed polarization durations $t^+ = 45'$ and $t^- = 45'$, for different values of electric field intensity for polarization "+" and "-". Waveguides produced on the first side of the substrate (a) and the other side of the substrate (b).

Figure 6a,b shows a comparison of refractive index profiles of waveguides produced by processes in which a division of the duration of each polarization $t^+ = t^-$ has been set, with the total duration of the process $t_{\text{tot}} = 90'$. The values of the electric field intensity were altered for the two polarization states. As mentioned earlier, the waveguides of types "A" and "B" were formed here on the opposite sides of the glass plate. Here again, the same centric symbols in both figures (a and b) indicate the same glass substrates, in which adequate waveguides have been formed. In the case of this sequence of processes, a strong influence of polarization field "-" on the shape of waveguide of type "A" can be seen (Fig.6a). In the extreme case, for the values of electric field intensity: $E = +4.5$ V/mm and $E = -18.2$ V/mm, the obtained admixture distribution gives the concave shape of the refractive index profile.

As mentioned earlier, by selecting the duration of a specific state of polarization and electric field intensity, a specified form of the refractive index profile of the waveguide can be deliberately produced. Figure 7 presents the refractive index profiles of two waveguides of type "A" produced in the electrodiffusion processes in which the duration of polarization was $t^+ = t^- = 30'$ and the values of the electric field intensity were $E = +18.2$ V/mm and $E = -9.1$ V/mm respectively. The dependencies $n(x)$ are of almost linear nature. The temperatures of both processes were $T = 299^\circ\text{C}$ and 272°C respectively. The resulting refractive index profiles vary in depth, which is a result of electric mobility of ions depending on the temperature. In the case of a waveguide produced at a lower temperature, the effect of the diffusion component on the final form of the shape of the refractive index profile in comparison with the electric drift is much smaller.

Figure 7. Refractive index profiles of produced waveguides with shapes close to linear.

As an illustration of the applicability of the sequence of polarization direction changes of the electric field, Fig.8 shows the refractive index profiles of waveguides produced on both sides of the glass substrate in the electrodiffusion process, in which six different polarization states were applied. The total duration of the process was $t_{tot} = 60$ min. The durations of each of the processes were equal and were $t^+ = t^- = 10'$. In the case of waveguide of type "A" (Fig.4a), a 12-modal structure was obtained (TE polarization, $\lambda = 677$ nm). The shapes of the refractive index profile of this waveguide are similar to that obtained in the electrodiffusion processes with fixed polarization direction of the electric field (compare Fig.3b). For the resulting waveguide of type "B" (10-modal structure) a monotonic course of the refractive index profile with characteristic inflection point at a depth corresponding to the position of the turning point of the mode of 3rd order was obtained (Fig.8b). In both figures the total values of the electric charge that has passed through the substrate in either direction are given.

Figure 8. The refractive index profiles of the waveguides produced by electrodiffusion processes with a multiple change of the direction of polarization and of the values of the electric field intensity. The waveguide produced on the first side of the substrate (a) and on the other side of the substrate (b).

The presented measurement results of refractive index profiles of waveguides produced in the electrodiffusion processes (in which there is a change of polarization direction of the applied electric field) indicate a high possibility of the use of such processes to the intended shaping of refractive index profiles of produced waveguide structures.

3. Determination of the equilibrium concentration of modifier ions in the glass

In the theoretical calculations describing the ion exchange processes in glasses a two-component model of this phenomenon is adopted [33]. The nonlinear diffusion equation (electrodiffusion) is solved in the field of normalized concentration of exchanged ions (admixture ions introduced into the glass and mobile ions of its modifier). This normalization is made in relation to the equilibrium concentration, which is the total concentration in the glass of both types of exchanged ions. The value of this concentration remains constant during the whole process of ion exchange. This section presents two methods of estimating the value of this concentration. One of them is based on a calculation of the electric charge flowing through the glass in the electrodiffusion processes. The second one is based on a measurement of the mass of the glass substrate before and after the diffusion process. The experimental results are presented in relation to soda-lime glass, in which the $\text{Ag}^+ \leftrightarrow \text{Na}^+$ ion exchange processes were carried out.

3.1. The dependence of changes of the refractive index profile of the waveguide on the electric charge flowing in the electrodiffusion process

In the electrodiffusion process carried out at time τ , the amount of the charge Q_τ , which has passed through the glass can be determined on the basis of the current dependency $i(t)$:

$$Q_\tau = \int_0^\tau i(t) dt \quad (4)$$

Taking into account that $u(x) = c(x)/c_0$, where c_0 (m^{-3}) is the normalized concentration of mobile components of the glass, (which is a concentration of mobile modifier ions in the glass before the exchange process) the equation describing the relationship of the refractive index profile $n(x)$ with the normalized concentration of the admixture $u(x)$ takes the form:

$$n(x) = n_b + \Delta n_s \cdot \frac{c(x)}{c_0}, \quad (5)$$

where n_b - refractive index of the glass before the ion exchange process, Δn_s - increment of the refractive index of the glass (caused by the ion exchange process) at its surface, $c_A(x)$ - function

describing the distribution of the absolute concentration of admixture ions introduced into the glass (m^{-3}).

Figure 9. Determination of the cross section S of the exchange process.

By introducing the function, $\delta n(x) = n(x) - n_b$, from the equation (5) the following can be obtained.

$$c(x) = \delta n(x) \cdot \frac{c_0}{\Delta n_s} \quad (\text{m}^{-3}) \quad (6)$$

This equation describes the distribution of concentration of admixture introduced into the glass, expressed by the parameters of the refractive index profile $n(x)$ and of the equilibrium concentration c_0 . Integrating the expression (6) over the entire volume of the glass V , the total number of admixture ions N_τ introduced into the glass during the electrodiffusion process in the time τ is obtained as follows.

$$N_\tau = \int_V c(x) dV = \frac{c_0 \cdot S}{\Delta n} \int_0^\infty \delta n(x) dx \quad (7)$$

In this equation, S is the surface area of the glass substrate (cross section for the exchange - Fig.9) which comes in contact with a liquid admixture contained in the crucible. At the same time the total charge (4), which has flowed through the glass, allows to specify the number of admixture ions having a valence w , which have been introduced into the glass in the time τ :

$$N_\tau = \frac{1}{w \cdot e} \int_0^\tau i(t) d\tau = \frac{Q_\tau}{w \cdot e}, \quad (8)$$

where e - the elementary charge.

Comparing (7) and (8) the following equation is obtained.

$$\int_0^\infty \delta n(x) dx = \frac{\Delta n_s}{e \cdot w \cdot S \cdot c_0} \cdot Q_\tau \quad (\text{m}) \quad (9)$$

By calculating the above integral the product Sc_0 of the cross-section of the exchange and the equilibrium concentration can be determined.

Table 2 summarizes the results of calculation product Sc_0 based on equation (9) for several electrodiffusion processes carried out in the substrate of soda-lime glass, using a pure silver nitrate $AgNO_3$ as the source of admixture of Ag^+ ions. It also presents the maximum changes in refractive index profile Δn_s at the surface of the glass calculated on the basis of the determined refractive index profiles.

Q_τ (C)	$\int_0^\infty \delta n(x) dx$ (m)	Δn_s	E (V/mm)	T (°C)	τ (min)
0.572	$0.2967 \cdot 10^6$	0.0789	9.1	299 ± 1	15
1.172	$0.5064 \cdot 10^6$	0.0846	9.1	299 ± 1	30
1.774	$0.7264 \cdot 10^6$	0.0879	9.1	298 ± 1	45
2.951	$1.0289 \cdot 10^6$	0.0902	9.1	299 ± 1	60
3.791	$1.3337 \cdot 10^6$	0.0912	18.2	301 ± 1	45
4.164	$1.2699 \cdot 10^6$	0.0916	18.2	298 ± 1	45
4.240	$1.3527 \cdot 10^6$	0.0925	18.2	300 ± 1	45

Table 2. Electrodiffusion process parameters.

Figure 10 shows the method of calculating the product of Sc_0 according to the equation (10) on the basis of data from Table 2.

The cross-section S for the exchange process shown in Fig. 9 is defined by the geometry of the crucible. During the process it grows as a result of the gradual penetration of the molten salt into contact area of the glass and the crucible. The electric field is not uniform near the inner edge of the crucible. Based on the above facts, it is expected that the refractive index profile of the waveguide in these areas of the glass which are at the edge of the crucible is significantly different from the form that is obtained in the central portion of the glass plate. The integrals in Table 2 were calculated assuming a uniform shape of refractive index profile in the entire area of glass. With these reservations, on the basis of the data from Fig. 10, the equilibrium concentration c_0 of mobile ions in the glass substrate that was used in the process can be estimated. Assuming the cross-section of the crucible $S = (3.6 \pm 0.7) \cdot 10^{-4} \text{ m}^2$, identical for all processes listed in Table 2, the mean value $c_0 = (5.7 \pm 1.5) \cdot 10^{27} \text{ m}^{-3}$ was obtained.

3.2. The glass mass (weight) change due to the $Ag^+ \leftrightarrow Na^+$ ion exchange

Another phenomenon accompanying the process of ion exchange in the glass is a change in the weight of the glass. This phenomenon is the more perspicuous the larger the difference of the masses of exchanged ions. This is easy to observe in the case of heavy silver ions Ag^+ , which replace the mobile sodium ions Na^+ in the glass. For this type of exchange ($Ag^+ \leftrightarrow Na^+$) this

Figure 10. The calculation of the product Sc_0 according to (10).

effect will be greater if the sodium modifier is more in the glass. The difference of the masses of atoms (silver $\bar{m}_{Ag}$ and sodium $\bar{m}_{Na}$) can be expressed as:

$$\Delta M = \bar{m}_{Ag} - \bar{m}_{Na} = \frac{M_{Ag} - M_{Na}}{N_A}, \quad (10)$$

where M_{Ag} and M_{Na} - molar masses, N_A - Avogadro's number.

Figure 11. The cross section of a glass plate with a marked depth d of doped region.

The glass mass difference caused by the ion exchange can be calculated based on the amount of the ions N_e exchanged in the glass:

$$\Delta m = m_e - m_0 = N_e \cdot \Delta M, \quad (11)$$

where m_e , m_0 - glass masses before and after the ion exchange process respectively.

In the case of planar waveguides the amount of ions exchanged in the glass can be estimated by measuring their refractive index profile $n(x)$. The x coordinate is calculated here into the glass (on the surface $x = 0$) to the direction perpendicular to its surface. This profile can also be described theoretically using the normalized concentration $u(x)$ of admixture ions introduced into the glass - see equation (5).

Thus, appearing in equation (11), the quantity of ions exchanged in the glass N_e can be expressed as follows:

$$N_e = S \cdot \int_0^d c_A(x) dx = S c_0 \cdot \int_0^d u(x) dx, \quad (12)$$

where S - the total glass surface through which the ion exchange process was conducted, d - the depth of the area of doped glass (Fig.11).

On the basis of (10-12), the weight change of the glass due to the ion exchange of $\text{Ag}^+ \leftrightarrow \text{Na}^+$ is expressed in the equation:

$$\Delta m = \frac{M_{\text{Ag}} - M_{\text{Na}}}{N_A} c_0 S \cdot \int_0^d u(x) dx \quad (13)$$

The above relationship shows the possibility of estimating the equilibrium concentration c_0 on the basis of experimentally designated values: Δm , S and the refractive index profile $n(x)$ of produced waveguide.

κ	Δm (g)	S (mm ²)	$\int_0^d u(x) dx (\mu m)$	$S \cdot \int_0^d u(x) dx (mm^3)$	$T_{\text{ave}} (^{\circ}\text{C})$	t (h)
1	0.0147	2995.37	6.09	18.24	295 ± 1	2.12
1	0.0088	2515.12	4.71	11.84	290 ± 1	1.38
0.01	0.0183	2258.58	10.71	24.19	353 ± 1	3.24
0.001	0.0056	2184.85	3.09	6.75	354 ± 1	7.35
0.001	0.0057	2210.15	3.31	7.31	354 ± 1	7.52
0.0005	0.0058	2134.67	2.83	6.04	352 ± 1	23.33
0.00025	0.0029	2341.48	1.57	3.67	355 ± 1	26.02
0.00025	0.0036	2383.02	1.49	3.55	354 ± 1	26.00
0.00025	0.0030	2205.24	1.44	3.17	354 ± 1	26.00

Table 3. Mass change of glass substrates in the diffusion processes and the integrals of the normalized concentrations of the admixture.

Table 3 shows the results of an experiment involving the determination of weight increase of glass plates subjected to processes of diffusion doping with Ag^+ ions. The substrates were made of soda-lime glass (Menzel-Gläser Company). This glass contains a large amount of sodium oxide Na_2O . Thus in the case of $\text{Ag}^+ \leftrightarrow \text{Na}^+$, a considerable increase of the weight is obtained.

Chemical composition in % by weight of the glass [38]: 72.2% SiO₂, 14.3% Na₂O, 6.4% CaO, 4.3% MgO, 1.2% Al₂O₃, 1.2% K₂O, 0.3% SO₃, 0.03% Fe₂O₃. Diffusion processes were carried out with a liquid source of admixture. The silver nitrate AgNO₃ and its sodium nitrate NaNO₃ solutions have been used. These solutions are determined by the molar fraction κ [39] listed in Table 3.

Figure 12 shows the dependence of the mass increase of the glass substrates from the product of the total surface of the glass and the integral of the normalized concentration of the admixture (Ag⁺ ions).

Figure 12. The dependence of the mass increase of the sample on the product of its surface and the integral of the normalized concentration of the admixture.

This dependency is based on the results shown in Table 3. For : $M_{\text{Ag}} = 107.87$ (g/mol), $M_{\text{Na}} = 22.99$ (g/mol), $N_A = 6.02 \cdot 10^{23}$ (mol⁻¹), the following equation is obtained: $A/c_0 = 1.41 \cdot 10^{-22}$ (g).

Determined by this method the value of the equilibrium concentration in the glass is: $c_0 = A/1.41 \cdot 10^{-22} = (5.6 \pm 0.2) 10^{27}(\text{m}^{-3})$.

The results of the equilibrium concentration c_0 obtained by integrating the electric charge (Section 2.1) and by method of weighing presented here, comply within the limits of uncertainty calculation.

4. Optical birefringence phenomenon of the gradient area as the effect of ion exchange

Ion exchange in glass processes with the use of liquid source of admixture ions, among which the most widely used are nitrates, are carried out at temperatures much lower than transition temperature of glasses T_g . For example, for the borosilicate glass BK-7 (Schott), which is widely used in these processes, the temperature $T_g = 557^\circ\text{C}$ [40] is much higher than the temperature

$T_{\text{diff}} = 400^\circ\text{C}$ of the implementation of the $\text{K}^+ \leftrightarrow \text{Na}^+$ ion exchange processes with the use of liquid potassium nitrate KNO_3 as the source of K^+ ions. In such cases, changing the refractive index of the glass in its surface area where the ion exchange occurs is due not only to the difference of their electric polarizability, but also the result of the elastooptic phenomenon generated by mechanical stresses resulting in this area [41]. These stresses are the result of changes in the volume of glass in the doping area, which results from the difference of ionic radii of components exchanged as well as the difference in thermal expansion between the doped region and the rest of the glass.

Figure 13. Comparison of refractive index profiles of planar waveguides produced in soda-lime glass doped with ions: Ag^+ (a) or K^+ (b) with the refractive index profiles produced in BK-7 glass doped with ions: Ag^+ (c) or K^+ (d).

The ionic radii of the most commonly used admixtures K^+ and Ag^+ are $1.33 \text{ \AA}$ and $1.26 \text{ \AA}$ [41] respectively. Thus, in relation to the ionic radius of sodium ($0.95 \text{ \AA}$ [41]), which, due to one of the lowest binding energies with glass network, is its most easily replaceable component, the

change in volume in the case of $K^+ \leftrightarrow Na^+$ exchange is much larger than in the $Ag^+ \leftrightarrow Na^+$ exchange. After completion of the process, when the glass is cooled to a low room temperature, a resulted difference generates stress in the doping area of the glass. Also, the difference in thermal expansion of the doping area, in relation to the rest of the glass, makes a significant contribution to the resulting stress. According to the principle of additivity [41], the coefficient of thermal expansion of glass is:

$$\alpha = \sum_i \alpha_i \cdot c_i ,$$

(14)

where α_i and c_i represent, the coefficient of thermal expansion and the mole fraction of i-th component in glass respectively.

The coefficients of thermal expansion for sodium and potassium are $\alpha_{Na} = 39.5 \cdot 10^{-6} \text{ K}^{-1}$ and $\alpha_K = 46.5 \cdot 10^{-6} \text{ K}^{-1}$ [41] respectively. These values are related to the concentration of Na_2O and K_2O in the glass. These data indicate that ion exchange processes of $K^+ \leftrightarrow Na^+$ in the glasses will be accompanied by the generation of significant mechanical stresses. The presence of these stresses in the waveguide layer of the glass is apparent in the propagation of the electromagnetic wave. A difference in propagation constants of the modes of the same order occurs for a monochromatic wave depending on its state of polarization. This phenomenon is called stress birefringence. Its scale depends on the type of glass and the admixture into the glass. This is illustrated in Fig.13, in which the refractive index profiles of planar waveguides produced in two types of glass (soda-lime and BK-7) by doping them with silver ions Ag^+ and potassium ions K^+ are presented. These profiles were determined by measuring the propagation constants for the two polarization states: TE and TM. Measurement uncertainties of the effective refractive indices of the modes do not exceed $3 \cdot 10^{-4}$. In all the presented refractive index profiles, the modes with TM polarization have bigger values of effective refractive indices. As there is only a polarization mode dispersion it is therefore inversely than in the case of a waveguide without stresses.

Type of glass	Type of admixture ions			
	Ag^+		K^+	
soda-lime $n_b=1.5090$	$n_{s,TE}=1.6049$	$\Delta n_{s,TE}=0.0959$	$n_{s,TE}=1.5163$	$\Delta n_{s,TE}=0.0073$
	$n_{s,TM}=1.6062$	$\Delta n_{s,TM}=0.0972$	$n_{s,TM}=1.5176$	$\Delta n_{s,TM}=0.0086$
BK-7 $n_b=1.5137$	$n_{s,TE}=1.5929$	$\Delta n_{s,TE}=0.0792$	$n_{s,TE}=1.5219$	$\Delta n_{s,TE}=0.0082$
	$n_{s,TM}=1.5939$	$\Delta n_{s,TM}=0.0802$	$n_{s,TM}=1.5238$	$\Delta n_{s,TM}=0.0101$

Table 4. Changes in the refractive index (for $\lambda = 677\text{nm}$) at the glass surface depending on the type of admixture ions (data provided by refraction profiles of Fig.13).

For each case of the refractive index profile shown in Fig.13, the relative change in the refractive index at the glass surface for both polarization states, in relation to the TE polarization, has

been shown. These figures can provide a quantitative measure of the scale of the birefringence when comparing this phenomenon in various glass-admixture systems. A comparison of Fig. 13a,c shows that the size of the birefringence due to the doping of both types of glasses with the silver ions Ag^+ is practically the same, although the changes in refractive indices at the surface differ quite significantly (Table 4). In the case of doping both kinds of glass with potassium ions K^+ the measure of the birefringence defined above is significantly higher in the case of BK-7 glass.

4.1. Refractive birefringence and modal birefringence

In the description of the phenomenon of birefringence, which extends over the entire doping area of glass, we can use the concept of birefringence as a function whose domain is the depth of doping area of the glass, or the row of modes. The following definitions of stress birefringence refractive δn_σ and modal δN_σ are introduced.

Refractive birefringence is determined by the refractive index profiles for the TE and TM polarization of the waveguide structure and is a function of the depth x counted from the glass surface:

$$\delta n_\sigma(x) = n_{TM}(x) - n_{TE}(x) \quad (15)$$

The modal birefringence concerns the difference in the effective refractive indices of the modes of the same order for the TE and TM polarization. This value is a function of the mode order:

$$\delta N_\sigma(m) = N_{TM}(m) - N_{TE}(m) \quad (16)$$

The sense of the values incorporated herein is illustrated in Fig.14. Refractive birefringence describes the difference in the refractive indices of the refractive index profiles for the TE and TM polarization that occur at a depth x in the waveguide. It is related to the stresses arising in the glass, in relation to the concentration of admixture introduced into the volume of the glass during the ion exchange processes. Function $\delta n_\sigma(x)$ reaches a maximum at the glass surface ($x = 0$) and decreases monotonically to zero at the point of glass, which was not reached by the admixture. The modal birefringence can be determined only for those rows of modes for which simultaneously there exist modes of both TE and TM polarization.

4.2. The relationship between birefringence and stresses

Quantification of changes in the refractive index of glass, in which the mechanical stresses arise, requires knowledge of the nature of the stress and elastooptic constants of the glass. The resulting stresses in the doped glass are of compressive nature [41]. In the case of a planar waveguide structure, for which the doped region extends from the surface into the glass, there is a one-dimensional distribution of the admixture concentration. In a direction perpendicular to the surface of the glass the doped region is free to deform, as a result of which at this direction

Figure 14. Determination of refractive birefringence and modal birefringence in the planar waveguide.

the stresses do not occur $\sigma_{xx}(x) = 0$. In contrast, at the directions parallel to the glass surface, the stresses generated in the doped area will be the same: $\sigma_{xy}(x) = \sigma_{xz}(x)$. The geometries of the directions of the stresses are shown in Fig.15. These stresses are the functions of a depth x only, the same as one-dimensional concentration distribution of the admixture introduced into the glass.

Figure 15. The geometries of the directions of the stresses in a planar waveguide.

Changes in the refractive index of the glass, which result from the generated stress, are determined by the elastooptic constants [42]:

$$C_1 = \frac{dn_{//}}{d\sigma} \left(\frac{m^2}{N} \right) \quad C_2 = \frac{dn_{\perp}}{d\sigma} \left(\frac{m^2}{N} \right) \tag{17}$$

In the above equations, $dn_{//}$ and dn mean the differentials of change in refractive index for the wave with polarizations respectively parallel and perpendicular to the direction of stress σ .

The refractive index profiles $n_{TM}(x)$ and $n_{TE}(x)$ for the waveguides with TM and TE polarizations, propagating in the direction of the axis z (Fig.15), in a waveguide are (in the presence of stress) described by the Maxwell-Neumann equations [41,43]:

$$\begin{aligned} n_{TM}(x) &= n_0(x) + C_1 \sigma_{xx}(x) + C_2 [\sigma_{yx}(x) + \sigma_{zx}(x)] \\ n_{TE}(x) &= n_0(x) + C_1 \sigma_{yx}(x) + C_2 [\sigma_{xx}(x) + \sigma_{zx}(x)], \end{aligned} \quad (18)$$

where $n_0(x)$ is a refractive index profile of the waveguide in the absence of stress.

After taking into account the assumptions: $\sigma_{xx}(x) = 0$ and $\sigma_{yx}(x) = \sigma_{zx}(x) = \sigma(x)$, the equations (18) reduce to the following form:

$$\begin{aligned} n_{TM}(x) &= n_0(x) + 2C_2 \sigma(x) \\ n_{TE}(x) &= n_0(x) + (C_1 + C_2) \sigma(x) \end{aligned} \quad (19)$$

These relationships enable us to align the birefringence of refraction (15) with the distribution of stress $\sigma(x)$:

$$\delta n_\sigma(x) = n_{TM}(x) - n_{TE}(x) = (C_2 - C_1) \sigma(x) \quad (20)$$

The elastooptic constants for the BK-7 glass for the wavelength of $\lambda = 677$ nm are [40]:

$$C_1 = -0.5 \cdot 10^{-6} \text{ (mm}^2/\text{N)} \quad C_2 = -3.3 \cdot 10^{-6} \text{ (mm}^2/\text{N)} \quad (21)$$

They allow to specify the value of the stress generated in the doped area of the glass. As it stems from the equation (20):

$$\sigma(x) = \frac{n_{TM}(x) - n_{TE}(x)}{C_2 - C_1} \quad (22)$$

The maximum stresses which occur at the surface of the BK-7 glass ($x = 0$), by doping it with potassium ions K^+ and silver ions Ag^+ , can be determined based on the data presented in Table 4. They are $|\sigma(0)_{K^+}| = 678$ (N/mm²) and $|\sigma(0)_{Ag^+}| = 375$ (N/mm²) respectively.

Figure 16 illustrates the distributions of stresses occurring in the BK-7 glass after the diffusion processes of potassium ions K^+ , and silver ions Ag^+ , depending on their normalized concentrations u . This presentation allows to compare these functions, defined on the basis of different refractive index profiles.

4.3. The dependence of stress birefringence on the duration of the diffusion processes

During the doping of the glass, the emerging stresses are also accompanied by the relaxation processes. They are reflected in the reduction of the role of stresses in the changes of the

Figure 16. The dependence of stresses on normalized concentration of admixture in the BK-7 glass.

refractive index of the doped area of the glass. This phenomenon can be observed by comparing the refractive index profiles of waveguides produced in processes with different diffusion times.

The tests were carried out on BK-7 glass doped with potassium ions K^+ in the diffusion processes lasting from 24 to more than 500 h. The resulting waveguide structures were multimode. This guaranteed the fidelity of reconstruction of their refractive index profiles.

Figure 17. Refractive birefringence (at the glass surface) and modal birefringence, depending on the duration of the diffusion process.

The methodology of the experiment was as follows: 21 glass substrates made of BK-7 glass with the dimensions: $8 \times 30 \times 1.5$ mm were prepared. They were polished on one side and then placed in the holders of silica glass tubes, allowing their individual extraction from the crucible containing the molten potassium nitrate. Due to the long duration of the process, the volume

of salt (KNO_3) filling the crucible was large ($\sim 300 \text{ cm}^3$). During the entire process, the molten salt was continuously stirred. This ensured thermal and concentration uniformity for the entire bath. On alternate days an additional portion of salt was introduced into the crucible in order to supplement salt losses as a result of evaporation. From all the 21 substrates placed at the beginning of the process in the crucible, one was removed every 24 h. This substrate, after cooling and washing in distilled water, was subjected to further testing. The duration of the whole process was 504 h. The temperature of the salt in the crucible was measured with a thermocouple and recorded continuously. The averaged temperature was $(399 \pm 1)^\circ\text{C}$.

The measurements of synchronous angles of modes in produced waveguides were performed using a prism coupler [33] made of PSK-3 glass (of Schott company). They were carried out for a wavelength $\lambda = 677 \text{ nm}$ and the TE and TM polarization. The effective refractive indices of the modes N_m calculated on their basis have the uncertainty of measurement at the level of $\Delta N_m = 0.0002$.

Figure 17 shows the change in the refractive birefringence $\delta n_o(0)$ at the surface of the waveguides and in modal birefringence $\delta N_o(m)$ for the modes of 0-6 row, depending on the duration of the diffusion process. The course of the changes $\delta n_o(0)$ indicates a decrease in the birefringence on the surface of the waveguide with increasing duration of the diffusion. In contrast, the courses of modal birefringence tend to increase with the diffusion time. However, the nature of this growth is a function of the order of the mode. In the case of a zero-order mode, even a downward trend can be seen. The strongest increase in birefringence occurs for the modes of higher-order. The modal birefringence (16) is not related to the location in the waveguide, where there is a defined concentration of the admixture. It can be however assumed, that it reflects the nature of the stresses associated with the depth of diffusion of admixture into the glass.

4.4. The changes of stress birefringence in the heating processes

The relaxation phenomenon of a waveguide layer, in which the doping of the glass resulted in the appearance of stresses, is clearly visible after the heating processes. In order to observe this phenomenon, in the BK-7 glass the long-term heating processes were implemented in relation to the waveguide produced by the diffusion process of KNO_3 in 72 hours [44]. The durations of these heating processes, after which the measurements of effective refractive indices of modes for both polarization states made were 24, 48, 96, 192, and 384 h respectively. The temperature of the heating processes was $(399 \pm 1)^\circ\text{C}$.

Based on the determined effective refractive indices, the refractive index profiles of the waveguides were reconstructed and their modal birefringence as well as the refractive birefringence at the surface of the glass was estimated. The nature of the changes of these values depending on the duration of the heating process is shown in Fig.18a.

Birefringences for the time $t = 0$ shown in the graphs represent the values of these terms after the diffusion processes. In the case of the refractive birefringence at the glass surface, the character of its changes is always a decreasing function of the duration of the heating process. Whereas, for the modal birefringence, the course of the dependence of $\delta N_o(m)$ from the

duration of the heating is dependent on the order of m mode, which can be clearly seen in the cases of the modes of higher order. For the modes of 5th and 6th order (Fig.18a), the increase of the heating duration in the first 25 h is accompanied by the increase of the birefringence. This effect can be explained by the generation of stresses in the deeper areas of the glass, which are reached by the admixture due to the diffusion widening of the doping area during the heating of the waveguide structure.

On the basis of equation (22) and elastooptic constants (21) it can be calculated how the stresses at the glass surface change as a result of the heating processes. A graph of this relationship is shown in Fig.18 b. There can be seen that after a heating time of about 50 h, the value of stresses at the glass surface decreases to half its value after the diffusion process.

Figure 18. Refractive birefringence (at the glass surface) and modal birefringence depending on the time of the heating process $T_{\text{heat}} = (399 \pm 1)^\circ\text{C}$ (a). Changes in stresses at the glass surface in the heating processes (b).

5. Repeatability of the technological effects of diffusion manufacturing processes of gradient changes in the refractive index of glasses

The ion exchange in glass method can be considered as a technological method. With its use, the predictable and repeatable results are obtained. Those effects are the changes in glass refraction, which are of a gradient character. They are described by the refractive index profiles. Determination of the refractive index profiles is easy to implement in the case of planar waveguides. For this purpose a waveguide method with the use of selective excitation of modes using a prism coupler is used [33]. In this method, the measurements of synchronous angles are used, for which excitations of waveguide modes are obtained. Such measurements are made using a goniometer. Precision of the measurements of these angles is at the level of several tens of seconds. Based on the measured synchronous angles, the effective refractive

indices of the waveguide modes are calculated. The uncertainties of their determination are at the level of 10^{-4} . Based on the set of effective refractive indices of modes, a reconstruction of the refractive index profile of the waveguide is performed. For this purpose the procedure proposed in 1976 by White and Heidrich [45] is used. This procedure is based on the mode equation of the waveguide. Its specific application is shown in [33] (p.169).

The control of technological processes of diffusion doping of glasses in the ion exchange processes was proposed in the work [33] (p.181). The described method is used in producing one-dimensional planar waveguides. The basis of this method is to determine the temperature dependences of diffusion coefficients of ions exchanged in a glass-admixture system. Knowledge of these relationships allows to calculate the kinetics of diffusion process in the current process temperature. This is done by measuring the temperature of the process carried out by a thermocouple placed in the immediate vicinity of the glass plate. This measurement occurs at defined points in time t_p . Moments of the temperature measurement are a total multiples of Δt time step which is numerically integrated over one-dimensional diffusion equation [33] (p. 177):

$$\frac{\partial u}{\partial t} = \frac{D_{0A} e^{Au}}{1 - \alpha u} \cdot \frac{\partial^2 u}{\partial x^2} + \frac{D_{0A} e^{Au} [\alpha + (1-u)A] - u(1-\alpha)^2 D_{0B} e^{B(1-u)}}{(1 - \alpha u)^2} \left(\frac{\partial u}{\partial x} \right)^2, \quad (23)$$

where

$$\alpha = 1 - \frac{D_{0A}}{D_{0B}} \cdot \exp[u(A+B) - B] \quad (24)$$

In the above equations, $u(x)$ is a function describing the distribution of normalized concentration of admixture ions introduced into the glass. D_{0A} , D_{0B} , A , and B are coefficients that describe the functional dependence of diffusion coefficients of admixture ions $D_A(u)$ and the modifier $D_B(u)$ on normalized concentration of admixture introduced into the glass. These functions have the form [33]:

$$D_A(u) = D_{0A} e^{Au}, \quad D_B(u) = D_{0B} e^{B(1-u)} \quad (25)$$

The dependence of coefficients D_{0A} and D_{0B} on temperature is described by Arrhenius equations:

$$D_{0i}(T) = D_{0i}^* \cdot \exp\left(-\frac{\Delta Q_i}{RT}\right) \quad (i = A, B), \quad (26)$$

where ΔQ_i - activation energy of the i -th ion type, R - universal gas constant.

The function $u(x, t)$, which is a solution of the equation (23), transforms into one-dimensional refractive index profile $n(x, t)$ according to the relation (5):

$$n(x, t) = n_b + \Delta n_s \cdot u(x, t) \quad (27)$$

Thus, solving the diffusion equation is carried out in parallel with the realization of the diffusion process. The diffusion coefficients appearing in this equation are calculated at points in time t_p based on the knowledge of their temperature dependencies. In this way the course of the process temperature $T_p = T(t_p)$ by the diffusion coefficients $D_{0A}(T_p)$ and $D_{0B}(T_p)$ affects the form of solution $u(x, t_p)$ of the diffusion equation (23). On the basis of equation (27) the dependence of function describing the refraction distribution in the glass $n(x, t_p)$ is obtained. In turn, with the use of equation (28), the effective refractive indices of the modes $N_m(t_p)$ corresponding with the refractive index profile $n(x, t_p)$ are calculated (for the assumed wavelength and state of polarization). The modal equation in the case of planar optical waveguides with a monotonic refractive index profile has the form:

$$k_0 \int_0^{x_m} \sqrt{n^2(x, t_p) - N_m^2(t_p)} dx = \pi \left(m + \frac{1}{4} \right) + \arctg \left(r \sqrt{\frac{N_m^2(t_p) - n_c^2}{n_s^2 - N_m^2(t_p)}} \right), \quad (28)$$

where k_0 - wave number of an electromagnetic wave in a free space, x_m - position of the turning point of the m -th mode, $n(x, t_p)$ - refractive index profile of the waveguide, $N_m(t_p)$ - effective refractive index of the m -th mode, n_c - refractive index of the ambient (coverage) of the waveguide, n_s - refractive index of the waveguide at the glass surface, $r = 1$ (for TE polarization), $r = (n_s/n_c)^2$ (for TM polarization).

Visualization of the refractive index profile $n(x, t_p)$ and the resulting set of the effective refractive indices of modes $N_m(t_p)$ provide a direct control of the diffusion process. After the process, the duration of which was t_{diff} , a registered final refractive index profile of the glass $n(x, t_{diff})$ and a set of effective refractive indices $\{N_m(t_{diff}): m = 0, 1, \dots, M-1\}$ (M - number of modes) are obtained. Figure 19 schematically shows the principle of control of diffusion processes described earlier [46].

During the diffusion process control using the method mentioned earlier, the heat uniformity of the source of admixture has to be ensured. This is achieved by continuous mixing of the contents of the crucible. Thermocouple used to the measurements of the process temperature should be as close as possible to the glass substrate. The fulfillment of these conditions in the implemented technological processes was provided by a special handle made of silica glass (for details see [33] p.182).

In the continuation of this section the results being comparisons of effective refractive indices were presented. These comparisons relate to the effective refractive indices of modes calculated (N_{calc}) during the diffusion process control with the results obtained from the measurements (N_{meas}) of produced waveguides. The quantity of such comparisons are the absolute values of the differences of these values $|N_{calc} - N_{meas}|$ calculated for each row of mode m . They were made for three types of glass substrates and two kinds of admixture ions. The glass substrates were: soda-lime (of Menzel-Glasser company), BK-7 (of Schott company), and Pyrex (Borosilicate 33 of Corning company). The used admixture ions were silver ions Ag^+ (source: silver

Figure 19. The principle of the diffusion process control in real time based on temperature measurements.

nitrate AgNO_3) and potassium ions K^+ (source: potassium nitrate KNO_3). Table 5 summarizes the types of glass and the admixture ions, for which the temperature characteristics of diffusion coefficients were designated. The measurements of effective refractive indices of waveguide modes were performed for a wavelength $\lambda = 677 \text{ nm}$ (TE polarization).

Type of glass	Ion exchange type	Source of ions	Diffusion coefficients				$\lambda = 677 \text{ nm}$	
			$\Delta Q_A/R \text{ (K)}$	$\ln(D_{0A}^*)$	$\Delta Q_B/R \text{ (K)}$	$\ln(D_{0B}^*)$	n_b	Δn
Soda-lime	$\text{Ag}^+ \leftrightarrow \text{Na}^+$	AgNO_3	$1.1086 \cdot 10^4$	19.894	$9.2988 \cdot 10^3$	19.017	1.5105	0.0952
BK-7	$\text{K}^+ \leftrightarrow \text{Na}^+$	KNO_3	$1.5786 \cdot 10^4$	22.740	$1.3376 \cdot 10^4$	19.688	1.5137	0.0079
Pyrex	$\text{Ag}^+ \leftrightarrow \text{Na}^+$	AgNO_3	$1.0771 \cdot 10^4$	18.847	$1.1044 \cdot 10^4$	20.349	1.4678	0.0190

Table 5. The types of glass and admixture ions.

Table 6 summarizes a comparison of the waveguides produced in the soda-lime glass. In this glass the kinetics of $\text{Ag}^+ \leftrightarrow \text{Na}^+$ ion exchange is the highest among the other glass-admixture systems. A planar 3-modes waveguide is formed during a diffusion process with duration of 4 min. For the $\text{Ag}^+ \leftrightarrow \text{Na}^+$ ion exchange in this glass the largest absolute differences $|N_{\text{calc}} - N_{\text{meas}}|$ here are of the order of 10^{-3} .

m	$t_{\text{diff}} = 3\text{h}, T_{\text{ave}} = 288^\circ\text{C}$			$t_{\text{diff}} = 4\text{h}, T_{\text{ave}} = 280^\circ\text{C}$			$t_{\text{diff}} = 5\text{h}, T_{\text{ave}} = 260.4^\circ\text{C}$		
	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $
0	1.5924	1.5939	0.0015	1.5926	1.5938	0.0012	1.5906	1.5905	0.0001
1	1.5823	1.5833	0.0010	1.5826	1.5833	0.0007	1.5794	1.5786	0.0008
2	1.5744	1.5752	0.0008	1.5748	1.5752	0.0004	1.5702	1.5696	0.0006
3	1.5675	1.5682	0.0007	1.5679	1.5683	0.0004	1.5621	1.5614	0.0007
4	1.5611	1.5619	0.0008	1.5616	1.5620	0.0004	1.5544	1.5537	0.0007
5	1.5551	1.5558	0.0007	1.5555	1.5559	0.0004	1.5468	1.5463	0.0005
6	1.5492	1.5499	0.0007	1.5497	1.5501	0.0004	1.5392	1.5388	0.0004
7	1.5433	1.5440	0.0007	1.5438	1.5442	0.0004	1.5313	1.5313	0.0000
8	1.5373	1.5382	0.0009	1.5379	1.5384	0.0005	1.5235	1.5233	0.0002
9	1.5314	1.5323	0.0009	1.5319	1.5326	0.0007	1.5163	1.5162	0.0001
10	1.5254	1.5265	0.0011	1.5259	1.5268	0.0009			
11	1.5196	1.5206	0.0010	1.5201	1.5209	0.0008			
12	1.5143	1.5151	0.0008	1.5147	1.5153	0.0006			
Short time diffusion processes									
m	$t_{\text{diff}} = 15', T_{\text{ave}} = 300^\circ\text{C}$			$t_{\text{diff}} = 8', T_{\text{ave}} = 300^\circ\text{C}$			$t_{\text{diff}} = 4', T_{\text{ave}} = 302^\circ\text{C}$		
	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $
0	1.5805	1.5811	0.0006	1.5751	1.5760	0.0009	1.5712	1.5690	0.0022
1	1.5615	1.5621	0.0006	1.5513	1.5520	0.0007	1.5430	1.5389	0.0041
2	1.5454	1.5458	0.0004	1.5295	1.5310	0.0015	1.5154	1.5109	0.0045
3	1.5294	1.5297	0.0003						
4	1.5140	1.5143	0.0003						

Table 6. Diffusion processes in soda-lime glass. Ion exchange $\text{Ag}^+ \leftrightarrow \text{Na}^+$. Source of admixture ions: AgNO_3 . $\lambda = 677$ nm, polarization TE.

The diffusion processes of $\text{K}^+ \leftrightarrow \text{Na}^+$ ion exchange are the slowest in the BK-7 glass. Table 7 shows a comparison of the effective refractive indices of the modes for diffusion processes lasting from 48 h to 216 h. The temperatures of these processes were approximately 400°C . In these cases, the differences of effective refractive indices of modes are of the order of 10^{-4} . The

same differences occur in the control of the heating processes carried out in BK-7 glass. Table 8 presents the results referring to the heating processes for a waveguide produced in the preliminary diffusion process: $t_{\text{diff}} = 74.3\text{h}$, $T_{\text{ave}} = 401.2^\circ\text{C}$ then subjected to heating. The temperatures of heating processes were at 445°C . The durations of the heating processes were 1 h, 2 h, and 4 h respectively.

m	$t_{\text{diff}} = 48\text{h}, T_{\text{ave}} = 401^\circ\text{C}$			$t_{\text{diff}} = 74.3\text{h}, T_{\text{ave}} = 401.2^\circ\text{C}$			$t_{\text{diff}} = 216\text{h}, T_{\text{ave}} = 399^\circ\text{C}$		
	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $
0	1.5189	1.5193	0.0004	1.5193	1.5194	0.0001	1.5199	1.5203	0.0004
1	1.5171	1.5174	0.0003	1.5177	1.5177	0.0000	1.5187	1.5190	0.0003
2	1.5157	1.5161	0.0004	1.5164	1.5166	0.0002	1.5178	1.5180	0.0002
3	1.5146	1.5150	0.0004	1.5154	1.5156	0.0002	1.5170	1.5173	0.0003
4	1.5139	1.5142	0.0003	1.5146	1.5149	0.0003	1.5163	1.5166	0.0003
5				1.5140	1.5142	0.0002	1.5157	1.5160	0.0003
6							1.5151	1.5155	0.0004
7							1.5146	1.5150	0.0004
8							1.5142	1.5146	0.0004
9							1.5139	1.5203	0.0004

Table 7. Diffusion processes in BK-7 glass. Ion exchange $\text{K}^+ \leftrightarrow \text{Na}^+$. Source of admixture ions: KNO_3 . $\lambda = 677\text{ nm}$, polarization TE.

Table 9 shows the results referring to the Pyrex glass (Borosilicate 33). Also in this case the differences of calculated and measured effective refractive indices of modes are of the order of 10^{-4} . The kinetics of $\text{Ag}^+ \leftrightarrow \text{Na}^+$ exchange processes in this glass is moderate. The single-mode waveguides are formed during 1 h and at a temperature of about 290°C .

m	$t_{\text{diff}} = 74.3\text{h}, T_{\text{ave}} = 401.2^\circ\text{C} +$ $t_{\text{heat}} = 1\text{h}, T_{\text{ave}} = 445.8^\circ\text{C}$			$t_{\text{diff}} = 74.3\text{h}, T_{\text{ave}} = 401.2^\circ\text{C} +$ $t_{\text{heat}} = 2\text{h}, T_{\text{ave}} = 445.5^\circ\text{C}$			$t_{\text{diff}} = 74.3\text{h}, T_{\text{ave}} = 401.2^\circ\text{C} +$ $t_{\text{heat}} = 4\text{h}, T_{\text{ave}} = 446.3^\circ\text{C}$		
	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $
0	1.5191	1.5190	0.0001	1.5189	1.5186	0.0003	1.5186	1.5182	0.0004
1	1.5177	1.5176	0.0001	1.5176	1.5173	0.0003	1.5175	1.5171	0.0004
2	1.5165	1.5165	0.0000	1.5165	1.5163	0.0002	1.5165	1.5163	0.0002
3	1.5156	1.5156	0.0000	1.5156	1.5155	0.0001	1.5156	1.5155	0.0001
4	1.5148	1.5149	0.0001	1.5149	1.5147	0.0002	1.5149	1.5149	0.0000
5	1.5142	1.5142	0.0000	1.5142	1.5142	0.0000	1.5143	1.5143	0.0000
6							1.5138	1.5138	0.0000

Table 8. Heating processes in BK-7 glass. Ion exchange $\text{K}^+ \leftrightarrow \text{Na}^+$. $\lambda = 677\text{ nm}$, polarization TE.

The results of comparisons of calculated and measured effective refractive indices confirm the effectiveness of the method of control of the diffusion processes. It is based on the best possible determined temperature dependence of the diffusion coefficients of exchanged ions for the given glass-admixture system. The described method allows to guarantee the repeatability of effective refractive indices at the level of $\Delta N \sim 10^{-3}$.

This method can also be used to control the production of two- and three-dimensional structures in gradient glasses.

m	$t_{\text{diff}} = 21\text{h}, T_{\text{ave}} = 275.6^{\circ}\text{C}$			$t_{\text{diff}} = 23\text{h}, T_{\text{ave}} = 281.1^{\circ}\text{C}$			$t_{\text{diff}} = 22\text{h}, T_{\text{ave}} = 292.1^{\circ}\text{C}$		
	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $
0	1.4816	1.4812	0.0004	1.4820	1.4817	0.0003	1.4825	1.4833	0.0008
1	1.4775	1.4771	0.0004	1.4783	1.4779	0.0004	1.4792	1.4795	0.0003
2	1.4742	1.4738	0.0004	1.4753	1.4749	0.0004	1.4766	1.4766	0.0000
3	1.4714	1.4710	0.0004	1.4727	1.4723	0.0004	1.4742	1.4741	0.0001
4	1.4691	1.4689	0.0002	1.4705	1.4700	0.0005	1.4721	1.4719	0.0002
5				1.4687	1.4684	0.0003	1.4703	1.4700	0.0003
6							1.4688	1.4686	0.0002

Short time diffusion processes									
m	$t_{\text{diff}} = 3\text{h}, T_{\text{ave}} = 286^{\circ}\text{C}$			$t_{\text{diff}} = 2.9\text{h}, T_{\text{ave}} = 287^{\circ}\text{C}$			$t_{\text{diff}} = 1\text{h}, T_{\text{ave}} = 289^{\circ}\text{C}$		
	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $	N_{calc}	N_{meas}	$ N_{\text{calc}} - N_{\text{meas}} $
0	1.4780	1.4777	0.0003	1.4781	1.4791	0.0010	1.4750	1.4742	0.0008
1	1.4713	1.4714	0.0001	1.4713	1.4718	0.0005			

Table 9. Diffusion processes in Pyrex glass. Ion exchange $\text{Ag}^+ \leftrightarrow \text{Na}^+$. Source of admixture ions: AgNO_3 . $\lambda = 677\text{ nm}$, polarization TE.

6. Conclusions

The chapter presents selected aspects of the ion exchange in glass processes in terms of changes in the refractive index. The processes of electrodiffusion doping of soda-lime glass with Ag^+ ions have been described. Such processes, which are carried out with a change of polarization of the electric field, enable the production of refraction changes of the glass with refractive index profile of various characters. Using the electrodiffusion processes with a fixed polarization of electric field, the equilibrium concentration of mobile ions in the glass was estimated. These results were confirmed by a method based on glass substrates weighing before and after the diffusion process. The results of experimental studies of stress birefringence in BK-7 glass doped with potassium ions K^+ were also presented. Ion exchange processes $\text{K}^+ \leftrightarrow \text{Na}^+$ in the glass were carried out during more than 500 h. It also presents the results of changes of these

stresses in the long-term processes of glass heating. The final part of the chapter presents the results of a control of the diffusion and heating processes in a real-time implementation of these processes. The described method of controlling these processes allows to obtain a high repeatability of the effects of the ion exchange in glass.

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Author details

Roman Rogoziński*

Address all correspondence to: roman.rogozinski@polsl.pl

Optoelectronics Department, Silesian University of Technology, Gliwice, Poland

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