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Ion Exchange in Glass – The Changes of Glass Refraction

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1. Introduction

The phenomenon of ion exchange in glasses in the practical application has been known since the Middle Ages when it was used for coloring glass. However, the application of this phenomenon for the production of changes in the glass refraction associates with the waveguide technology. The development of this technology has started in the second half of the 20th century and was dictated by the huge potential of the optical transmission of information in comparison to its classical form that uses the transmission of electrical signals through wired links. The optical transmission, in turn, uses dielectric fibers, known as waveguides. The materials that since the beginning have been used for producing the fiber waveguides are oxide glasses. However, their attenuation in this study period were of about 1000 dB/km . In 1966 K.C. Kao and G.A. Hockman in their work [1] indicated the possibility of using for the near-infrared transmission a specially treated glass, devoid of impurities in the form of ions of iron, cobalt and copper, which are the main cause of the absorption of the energy in the propagating wave.

In 1972, Corning Glass company has developed a technology of the production of preforms for extracting the optical fibers, whose attenuation was approximately 4 dB/km , using the technology of production of synthetic silica in the high temperature hydrolysis of silicon chloride, occurring in the presence of oxygen with admixtures of chlorides of boron, phosphorus and germanium (CVD technology - *Chemical Vapor phase Deposition*). In addition to the development of material technologies designed for the production of low-loss fiber waveguides, the research has begun on the production of passive waveguide structures on flat substrates made of oxide glasses of small size (area of a few to several cm^2), which, by definition, were not designed for the long-distance transmission of optical signals. Therefore, the requirements for the purity of ingredients (from which the glasses used as substrates were produced) have become less important. The method, by which such

waveguide structures has started to be produced in glass, is called (from the physical phenomenon, which is its foundation) the *ion exchange method* [2,3]. This phenomenon is based on the mechanism of glass ionic conductivity [4], allowing in a sufficiently high temperature the substitution of natural components (called modifiers), by inserting, in the due process, the so-called admixture ions. In the result of their different properties, such as electric polarizability and ionic radius, the admixture ions introduced into the glass locally alter its optical properties (refractive index). Due to the diffusive nature of the ion exchange phenomenon and the fact that the admixture is introduced into glass by its surface, thus resulting waveguide structures are localized in the superficial area of glass substrate (planar structures), and the change in the glass refractive index has the gradient character.

The first waveguide structures were prepared by the ion exchange method in the early seventies of the last century [5-7]. The advantages of this method include first of all: the ease of implementation of the basic technological processes (a highly specialized technological apparatus is not required here), low production costs associated with the possibility of using commercially available glass as substrates and relatively cheap materials as a source of admixture, very good repeatability of obtained elements, a very good time stability, low attenuation ($<0.1 \text{ dB/cm}$), as well as good compatibility - in terms of producing changes in the refractive index - with the fiber waveguides used in telecommunications.

2. Ion exchange in glass phenomenon

The ion exchange in glass phenomenon is initiated in the phase boundary: glass - liquid admixture source. The system with a liquid source of admixture is the most common in the literature and its attractiveness is due to the main advantage: the simplicity of implementing such processes. In this case, subject to adequate conditions of the process realization, an unlimited source efficiency can be assumed in its theoretical description. For these reasons, the description of the ion exchange phenomena has been limited only to liquid phases of admixture sources.

The assumption of the binarity of the ion exchange process' character made in its description is rather a simplification. This postulate is commonly found in the literature [2,8-11] and as the only one is acceptable for the examination of the effects of this phenomenon by optical methods only. In the next part, for the description of the ion exchange phenomenon, the following designations has been adopted: (A) for the admixture ions and (B) for the modifier ions.

When discussing the ion exchange phenomenon in glass, which is realized through the contact of glass with liquid admixture at sufficiently high temperatures, the main aspects should be specified (Fig.1). These are:

- determination of the balance of ion exchange process in the phase boundary: glass-admixture source. The consequence of this balance is the relationship between the concentration of the admixture in the C_{As} source phase and the admixture concentration in the superficial area of glass C_{max} ,

- time dependence $c_{max}(t)$ in achieving the equilibrium value,
- phenomenon of transport of ions in the glass phase resulting from its structure, whose effect is the migration of admixture into the glass - a model description of this process,
- relationship between the concentration of admixture introduced into the glass $c_A(x)$ and the local change of the refractive index of glass $\delta n(x)$.

Figure 1. The main aspects of the ion exchange phenomenon in glass

The ion exchange phenomenon in the superficial area of glass, which is in contact with a source of admixture, can be described as a reaction in which the substrates are: in the source of ions A in the admixture source and ions B in the glass, and products are, respectively: ions A in the glass and ions B in the phase of the source. Thermodynamic equilibrium state of the exchange process at the phase boundary: glass - liquid source of admixture is then described by constant K [11,12]:

$$K = \frac{\bar{a}_A \cdot a_B}{a_A \cdot \bar{a}_B} \quad (1)$$

In the equation above $\bar{a}_A$ and a_A mean the thermodynamic activities of ions A , respectively: the glass phase and the source phase, likewise: $\bar{a}_B$ and a_B are the thermodynamic activities of ions B in the glass phase and the source phase.

Knowledge of the quantitative determination of the equilibrium in the ion exchange process at the phase boundary: liquid admixture source - glass, is essential for the theoretical description of the formation of spatial distribution of admixture introduced into the glass in the exchange process. The determination of constant equilibrium (at a given temperature of exchange process) for a particular glass-admixture system therefore requires the experimental determination of the relationship between the molar fraction of admixture ions in the liquid phase of source and its molar fraction providing at the glass surface.

In equation (1) the ratio of activities of exchanged ions in the glass phase can be expressed with the Rothmund - Kornfeld relationship [12,13]:

$$\frac{\bar{a}_A}{\bar{a}_B} = \left(\frac{\bar{N}_A}{\bar{N}_B} \right)^\eta, \quad (2)$$

where: $\bar{N}_i$ – means the molar fraction of ions in the glass phase ($i = A, B$) and η is expressed by the interaction energy of ions in the glass W_{A-B} :

$$\eta = 1 - \frac{W_{A-B}}{RT}, \quad (3)$$

where: R – universal gas constant, T – temperature.

In turn, the activities ratio of exchanged ions in the liquid phase of the source is given by their mole fractions N_i and activity coefficients γ_i :

$$\frac{a_B}{a_A} = \frac{N_B \gamma_B}{N_A \gamma_A} \quad (4)$$

After taking into account (2) and (4) in (1), we obtain:

$$\log \left(\frac{N_A}{N_B} \right) - \frac{Q_{A-B}}{RT} (1 - 2N_B) = \eta \cdot \log \left(\frac{\bar{N}_A}{\bar{N}_B} \right) - \log K \quad (5)$$

The equation above takes into account the relationship:

$$\log \left(\frac{\gamma_B}{\gamma_A} \right) = \frac{Q_{A-B}}{RT} (1 - 2N_B), \quad (6)$$

in which Q_{A-B} is the energy of interaction of ions in the source phase.

The knowledge of Q_{A-B} for the systems of liquid mixtures used as the admixture source allows on the basis of (5) to calculate the parameters η and K . The process of establishing the maximum concentration of admixture C_{Amax} introduced into the superficial area of glass will be characterized by a time constant $-\tau_d$. This should be considered in cases of carrying short-term exchange processes.

Glasses, which are used as the substrate of gradient waveguide structures, are, in the vast majority, the oxide glasses. The possibility of the realization of ion exchange phenomenon in glass is a consequence of its structure. There are many theories about the concept of this structure, among which one of the basic is Zachariasen theory [14] experimentally verified in studies of Warren [15]. It allows a pretty good description of the additive properties of glass, due to its composition. Based on this theory the mechanism of ion transport in glass can be explained, which is the basis of the ion exchange phenomenon [4]. This theory highlights the notion of a structural skeleton - called the glass network – which has features

of low-range ordering. The elementary unit of this structure (in the case of silicate glasses) are the coordination polyhedra in the shape of tetrahedra that are connected by corners. In the vertices of this tetrahedron there are the anions O^{2-} surrounding the cation Si^{4+} which is located in the middle.

The rules under which a merger of elementary cells occurs are determined by the conditions of Zachariasen vitrification [14]:

- each oxygen anion O^{2-} is directly related to only two cations,
- the cation coordination number should be 3 or 4 at most,
- the coordination polyhedra connect to the neighbors only with corners, not edges or walls,
- at least three corners of each coordination polyhedron may be included in the other polyhedra

Figure 2. Possible energy positions of ion Na^+ in glass structure as well as changes of the orientational polarization of the structure due to its hopping (by [4])

In the multicomponent oxide glasses in addition to the glass network there are also so-called modifiers, which are alkali metal ions, whose presence in the glass is required by giving it the appropriate physicochemical properties. When the sodium oxide (Na_2O), for example, is introduced into the structure of glass in its melting process, the network connections in the emerging structure are reduced due to excess oxygen. So then the non-bridging oxygen arise. The most likely places for sodium in the structure of the glass are around non-bridging oxygen, which have uncompensated negative charge (Figure 2). For alkali ions, it is possible to address more than one energetically equivalent position near the non-bridging oxygen. However, a suitable location for sodium ions is determined not only by the same oxygen bridges, but also throughout their environment - giving in the final effect a system with the lowest possible energy [4]. These fragments of glass network, surrounded by the trapping energy ions of modifiers that can fluctuate within a structural unit as a result of thermal induction, are polar elements of the glass network. In the thermally induced structure of glass, in addition to hopping to the local structural unit, hoppings of long range outside the polar unit are also more likely to appear. This is accompanied by dissociation of the polar unit, and the modifier ion migrates inside the glass network. Non-bridging oxygen ion remains fixed in the glass network, making a vacancy in it. The directions of migration of mobile modifier depends on the local environment of polar units. Each of them is able to intercept mobile cations after the dissociation. Since the structural units in glass forming its glass network don't create an arrangement of long range, so a random network of the most

probable directions of hopping arises. Those hoppings create (on a microscopic scale) the system of paths shown in Fig 3.

Figure 3. 2-D fragment of glass structure with marked preferential pathways of modifier ions (by [4])

The described ability of the modifier ions to move within the glass structure is the basis of the mechanism of glass ionic conductivity. In turn, this mechanism enables the ion exchange, which takes place in case of introducing other types of modifier ions (admixture) into the glass.

The appearance of admixture ions in the superficial area of glass creates the opposite directed concentration gradients of both: admixture ions and modifiers. Consequently, in the glass there are two divergent streams of ions: a stream of admixture ions directed into the glass and a stream of modifier ions directed to the glass surface.

Association of the diffusion coefficient D_σ with the electrical conductivity σ or mobility μ of exchanged ions in the crystal structures is described by the Nernst-Einstein equation:

$$D_\sigma = \frac{kT\sigma}{cq^2} = \frac{kT\mu}{q}, \quad (7)$$

where: c and q – are respectively: concentration and charge of diffusing ions, k is the Boltzmann constant, T - is the absolute temperature.

The relationship between the diffusion coefficient D_σ and the diffusion coefficient D^* , which is set by the tracer diffusion method, is determined by the correlation coefficient f , which, in the case of vacancy diffusion mechanism of ions in the three-dimensional glass network, is equal to the Haven ratio H [11.16]:

$$f = H = \frac{D^*}{D_\sigma} < 1 \quad (8)$$

So for the description of the two-component ion exchange process in glass the relationship between self-diffusion coefficients and electrical mobilities of both types of exchanged ions take the form:

$$D_i = \frac{H_i k T \mu_i}{q} \quad (i=A, B) \quad (9)$$

The final effect of the ion exchange process in glass, which has practical application in the manufacture of optical structures, is the change of the refractive index within its admixture area. Local changes in the refractive index of glass, which are the effect of the ion exchange, are the result of the differences in their electric polarizability and ionic radii.

According to the principle of additivity [9,17,18] refraction index of oxide glass consisting of a metal oxide M_mO_n can be represented as:

$$n_b = 1 + \frac{R_0}{V_0} = 1 + \frac{\sum_i a_i N_i}{C + \sum_i b_i N_i}, \quad (10)$$

where: R_0 , V_0 – are respectively: the refraction and the molar volume of oxide atoms constituting the glass, N_i – molar fraction of i -th component in the composition of the glass, a_i , b_i , C – empirical coefficients.

The ion exchange process starts with the glass surface, which contacts with the admixture source phase. Defining the fraction of exchanged ions in glass $u(x)$ as a function of depth measured from the surface of the glass, it can be written:

$$u(x) = \frac{N_A(x)}{N_0} = \frac{c_A(x)}{c_0}, \quad (11)$$

where: $N_A(x)$ – is the number of admixture ions (A), which replaced the glass ions at a depth x , N_0 – is the number of exchangeable ions in the whole glass volume, $c_A(x)$ and c_0 – are the concentrations corresponding to mentioned numbers of ions.

Therefore, the refractive index after the ion exchange, according to (10), reaches a value:

$$n(x) = 1 + \frac{R_0 + u(x)\Delta R}{V_0 + u(x)\Delta V}, \quad (12)$$

and its increase $\delta n(x)$, assuming $\Delta V \ll V_0$, can be expressed as:

$$\delta n(x) = n(x) - n_b = \frac{R_0 + u(x)\Delta R}{V_0 + u(x)\Delta V} - \frac{R_0}{V_0} = \dots = \frac{u(x)}{V_0} \left(\Delta R - R_0 \frac{\Delta V}{V_0} \right) \quad (13)$$

Assuming that in the contact of the glass surface with clean (undiluted) source phase all of the mobile ions at the glass surface ($x = 0$) are exchanged for admixture ions, then $u(0)=1$ and the relation occurs:

$$\delta n(0) = \Delta n_s = \frac{1}{V_0} \left(\Delta R - R_0 \frac{\Delta V}{V_0} \right) \quad (14)$$

The linearity of the change of refractive index of the normalized concentration of admixture introduced into the glass $u(x)$, expressed by equation (13), is taken as the fundamental relation describing the ion exchange processes [9,10].

In the cases of diluted admixture sources, according to (11), the normalized concentration of ions introduced at the glass surface takes values $u(0)<1$.

3. Technological processes of producing ion exchange in glass

As mentioned before, the ion exchange phenomenon in glass substrates occurs as a result of introduction of foreign admixture ions into the glass. The used admixtures are alkaline metal ions: lithium [19], potassium [20-29], rubidium [30], cesium [31], and ions of heavier elements: copper [32,33], silver [6,34-43] and thallium [7,44]. The most common sources of these admixtures are molten nitrates. They are characterized by relatively low temperatures of the extent of their liquid state (Table 2.1). This is important for the ion exchange processes in oxide glasses, for which the limitation is the transition temperature T_g [45]. Among the admixture ions listed in Table 2.1 the largest changes of the refractive index Δn_s are achieved when using thallium ions. However, due to the high toxicity of its compounds, it is not widely used. The second, in turn, in terms of the size of obtained changes in the refractive index, is silver ion (Ag^+). It is often used because of the possibility of controlling the refractive index change by using matched solutions of silver nitrate $AgNO_3$ in sodium nitrate $NaNO_3$ as its sources.

ion	source	T_{min} (°C)	T_{max} (°C)	Δn_s
Li^+	$LiNO_3$	261	600	0.012
Na^+	$NaNO_3$	307	380	-
K^+	KNO_3	334	410	0.01
Rb^+	$RbNO_3$	310	370	0.015-0.02
Cs^+	$CsNO_3$	414	510	0.04
Ag^+	$AgNO_3$	212	444	0.1
Tl^+	$TlNO_3$	206	430	0.1-0.2

Table 1. Sources of admixture in the form of nitrates used in the ion exchange

In [42] the applicability of such solutions with mole fractions of silver nitrate contained in the interval: $2,48 \cdot 10^{-4} \div 5 \cdot 10^{-2}$ was presented. For such obtained admixture sources the refractive index changes at the surface of the waveguide in the terms of: $0.01 \leq \Delta n_s \leq 0.09$. The temperatures of ion exchange processes, with the use of these solutions, ranged from 315 °C to 375 °C. Other mixtures of nitrates, enabling a lower temperature processes, are also used. The [46] presents results of research into the possibilities of low-temperature admixture sources based on the nitrates of potassium and silver. The mixtures of $KNO_3:AgNO_3$ (50:50% mol) in the temperature range of 160÷270 °C were used. For those nitrates the eutectic mixture (62% mol $AgNO_3$) has a melting point of 131 °C. Also in this work there are examples

of the use of mixtures of $KNO_3:NaNO_3$ (50:50% *mol*), with a melting point of 220 °C. For the latter mixtures the additives $0.001 \pm 0.05\%$ *mol* $AgNO_3$ were also used changing the operating temperature of the source of the 230 ± 375 °C. It also shows the possibility of using the eutectic mixture of $AgNO_3:TlNO_3$ (48% *mol* $TlNO_3$), whose melting point is 82.5 °C.

3.1. Processes of the preliminary thermal diffusion

The construction of the stand used for the thermal diffusion processes is shown in Fig.4a. It is an electric furnace. The molten salt is in the melting pot (crucible) with a glazed ceramic surface. The glass substrate is placed into a glass holder, at the same time fulfilling the role of the mixer (Fig.4b). This handle makes it easy to enter the plate into the crucible. Before each immersion of the substrate into the molten salt it is held over its surface for some time in order to equalize their temperatures. The connection of the tube holder with the pump generating pulsating pressure changes causes oscillating movements of molten salt in the holder, causing, as a result, mixing of the entire melted contents of the crucible. This way of implementation of the process ensures thermal and molar concentrations homogeneity of liquid admixture source. This is important during the long process of diffusion, because in no-mixed salt at the glass surface a layer with the poor admixture ions can be formed. A waveguide produced in such conditions would have a lowered refraction index at the glass surface. The element monitoring the temperature is a thermocouple placed in a silica glass tube, which is immersed directly into the crucible. During the implementation process the dependence of thermocouple voltage from time $U_T(t)$ is recorded. On its basis the average temperature throughout the duration of the process can be determined.

Figure 4. a) Cross section of the stands for the diffusion processes b) glass holder

3.2. Electrodiffusion processes

These are the most technologically advanced processes of glass doping in the case of the liquid sources of admixture usage. However, they give a lot of opportunities to influence the final form of the function describing the distribution of the refractive index profile in the produced waveguide structure. Scheme of the stand [47] is presented in Fig.5a. Molten salt, which is a source of admixture introduced into the glass, is located in the two vessels placed inside the furnace. Salt temperature is controlled with a thermocouple. An essential part of a stand is a system of two symmetric, aluminum crucibles (Fig.5b) between which a glass substrate is clenched. The proposed construction of two independent crucibles enables the electrodiffusion processes, where it is possible to change the polarization direction of the electric field. The seal between the glass and the two crucibles is achieved by using silicone paste resistant to temperatures up to 350 °C. Both crucibles are mounted on a special holder which allows them a precise introduction into the furnace. Crucibles are attached to the tubes of silica glass. They are used for suction of the molten salt into the crucibles, using negative pressure generated by a vacuum pump. Each crucible is also connected to the lead supplying voltage from the power supply. Also the temperature of the crucible is monitored by thermocouples. Installation of the substrates between the crucibles is made outside the furnace. Special shackles enable quick disconnection of crucibles and removal of the substrate after the process. After entering the crucibles into the furnace chamber the glass substrate does not come into a contact with the molten salt until they reach the same temperature (which has a molten salt). The molten salt is then sucked with the vacuum pump into both crucibles. In this way on both sides of the glass substrate there is molten salt, which is a liquid source of admixture.

Figure 5. a) Cross section of the stand for the electrodiffusion processes b) the crucibles

The inclusion of appropriate polarization of crucibles enables conducting of the electrodiffusion process, during which both the direction of polarization and the value of voltage applied to the crucibles can be freely changed. During the process a current value flowing through the glass substrate is being recorded. To prevent a situation in which the molten salt could be sucked by the pump outside the chamber of the furnace, on the glass tubes between the two crucibles with a vacuum pump the special contacts are placed, which are capable of inspecting the level of molten salt in both crucibles. After completion of the process the vacuum pump is switched off and the molten salt returns to the vessels inside the furnace, and both crucibles are immediately lifted and discharged outside of the furnace. They are then separated and the glass substrate is released. With the applied solutions the release time of the plate does not exceed 1 minute.

3.3. Heating processes

Spatial distributions of admixture introduced into the glass, in the preliminary diffusion or the electrodiffusion, may be a subject of further modification. The process which is relatively easiest to use is called here the heating process. This is achieved as a secondary process, in relation to pre-doped glass. During the heating the glass is located in the furnace without any contact with the source of admixture.

Figure 6. a) The stand cross section for heating processes b) the stage with a thermocouple

Then is a redistribution of the existing concentration of admixture in the glass occurs. The maximum value of the concentration at the glass surface is reduced while expanding its reach into the glass. During the heating of glass in which the waveguide is produced, it is

desirable to maintain the process temperature at a given level. Then the final result of the heating will depend only on its duration. However, during the implementation of the heating process, when placing a heated structure into the furnace, a disturbance of the temperature is inevitable. The scale of this phenomenon obviously depends on the thermal inertia of the furnace. During the heating the glass substrate eventually reaches the maximum temperature corresponding to the conditions of the process. At this time, the diffusion processes are already taking place. In contrast to the initial diffusion, there is no possibility of early matching the temperature of the heated sample to the temperature of the furnace. The Fig.6a shows the stand used for the heating process. Its main part is the capsule made of aluminum alloy, which is placed into the furnace. It has a cover that closes it over the top. Inside there is a massive block (aluminum alloy), aimed at increasing the thermal capacity of the entire system. The thermocouple controlling the temperature is attached into this block. Into the cavity of the block the sample subject to the heating is inserted. This sample is located on a special stage (Fig.6b) to allow a quick entry and removing from the furnace. In order to obtain as precise control of the actual temperature of the heated sample as possible, there is an additional thermocouple mounted to the table.

4. Measurements of ion exchange in glass' effects using optical methods

Determination of refractive index profile is a key issue in the metrology of waveguide structures. For the gradient waveguides produced in the glass substrates by ion exchange, many optical measuring methods using different phenomena directly related to the wave propagation in the waveguide structure have been developed. Among these methods, the most preferred one is the waveguide method, based on the measurements of effective refractive indexes of the modes [48-55]. This is a non-destructive method that provides at the same time the high-precision of determination of refractive index profiles. The basis of this method is the measurement of the synchronous angles φ_m of the modes. Goniometric measurements of these angles, using a prism coupler, can be performed with very small uncertainties in the order of tens of seconds of arc. In terms of the effective refractive indexes of the modes N_m it gives the uncertainty of their determination $\Delta N_m \sim 10^{-4}$ [53,54]. Refractive index profiles of the tested waveguides are then reconstructed by means of procedures [48,49,51], based on the modal equation.

4.1. Prism coupler

Using a prism as an element enabling the introduction of an electromagnetic wave to a thin-film structures is described in the work of Tien [56]. In later works of Ulrich [57] and Kernsten [58] there were presented the possibilities of using a prism coupler for the measurement of the properties of thin films. The analysis of the prism coupler work in the measurements of propagation characteristics of planar waveguide structures can be found in the papers [57-59]. In the measuring practice it is a prism having a refractive index greater than the refractive index at the surface of the tested waveguide. To allow it to fulfill the role of the measuring element, the calibration is required.

It involves the determination, with the greatest possible precision, of the breaking angle δ (Fig.7) and the determination of the refractive index n_p for the wavelength used in the measurements. In the case of spectral measurements it is also necessary to know the dispersion curve $n_p(\lambda)$ of the glass of the prism. When measuring with the use of the prism coupler the beam falling on the front wall at an angle φ_m is refracted reaching its base which is bordering the waveguide at an angle θ_m (Fig.7). This angle is bigger than the critical angle on the boundary: prism - the environment (air).

In the presence of a third medium (waveguide), a phenomenon of tunneling the energy of the wave reflected in the prism to the area of the waveguide may occur. A necessary condition for the occurrence of this phenomenon is to provide a so-called optical contact between the prism base and the surface of the waveguide. This contact is produced right on the edge of the prism base with the use of a mechanical clamp (Fig.8a). Optical contact area is visible as a dark spot while watching to the inside of the prism in the scattered light. The pressure size of the prism should not be too big in order not to introduce significant stress in both: the prism and in the waveguide. In practice, the minimum value of the pressure is used, at which the realization of the measurements is still possible [57,59,60].

The thickness of the interspace s produced in the optical contact (Fig.7) is of the order of a fraction of the wavelength used in the measurements. Thus, the part of the evanescent field of the wave reflected from the prism base spans the area of the waveguide. It is presented in Fig.8b. The waves stimulated in the waveguide along the axis z through the beam illuminating the prism base interfere with each other. For certain angles of incidence θ_m the interference is constructive in character, resulting in efficient energy transfer into the waveguide - stimulation

Figure 7. The geometry of the condition of the mode stimulation using the prism coupler

Figure 8. Coupling of a prism with a waveguide a), the penetration of the wave evanescent field in a prism to the waveguide area b), the resonant nature of the stimulation of the mode in the waveguide c)

of the mode (Fig.8c). This phenomenon is of a resonant character. The efficiency of energy tunneling into the waveguide modes, using a prism coupler, can reach a value of to tens of percent [57]. The coupler can also serve as an element, carrying a wave off of the waveguide.

The angles θ_m , for which there is a coupling, are called *the synchronous angles*. In Fig.9 a measuring system for recording these angles is shown. Still, the concept of synchronous angles θ_m will be identified with the values of the angles of incidence φ_m of the beam on the prism, because between these angles there is an unambiguous relationship expressed by the refraction index of the prism n_p and its breaking angle δ . Using the symbols of Fig.7 it can be easily shown that the equality holds:

$$n_p \cdot \sin \theta_m = \sin \delta \cdot \sqrt{n_p^2 - n_c^2 \cdot \sin^2 \varphi_m} + n_c \cdot \cos \delta \cdot \sin \varphi_m \quad (15)$$

In the case of tunneling of the wave energy from the prism to the waveguide, the fulfillment of boundary conditions for the wave field on the bottom surface of the prism and the waveguide requires the equality of the wave vector components in both of them. This means that the z component of the wave vector in the prism is equal to the corresponding component of the wave vector in the waveguide. On the basis of the equation (15) the expression for the dependence of the effective refractive index N_m of the m -th mode from the synchronous angle φ_m is achieved:

$$N_m(\varphi_m) = \sin \delta \cdot \sqrt{n_p^2 - n_c^2 \cdot \sin^2 \varphi_m} + n_c \cdot \cos \delta \cdot \sin \varphi_m, \quad (16)$$

where: δ – breaking angle of the prism, φ_m – synchronous angle calculated from the normal, n_p – the refraction index of the prism, n_c – the refraction index of the environment ($n_c=1$ the air).

Figure 9. Scheme of a registration stand for synchronous angles of the waveguide modes

4.2. Procedure of refractive profile reconstruction based on the modal equation

The measurement of the synchronous angles by goniometric method allows to determine a set of effective refractive indices of the own modes of the gradient waveguide or the step-index type. Due to the ease of the measurements made and their high accuracy, this method is used as a routine for determining the refractive index profiles of the examined structures. For the waveguides characterized by a monotonic character of the refractive index, a set of designated effective indices $\{N_i\}$ will be able to determine the refractive index profile of the waveguide if it will have assigned a set of turning points $\{x_i\}$ of the corresponding modes. These are the distances x_i calculated from the waveguide surface, for which the wave vector of the propagating wave (of i -th mode) has the only component in the direction of z ($k_x=0$) (Fig.10).

Figure 10. Determination of the turning point of the waveguide mode in the gradient waveguide of a monotonic profile

Procedure for calculating of these turning points for all modes of the waveguide, using the modal equation, was proposed in 1976 by White and Heidrich [48]. The reconstruction of the refractive index profile obtained in this way is its approximation, made in the number of points equal to the number of own modes. Thus, the precision of reconstruction of the refractive index profile, on the basis of the modal equation, depends on the number of modes that may propagate in the waveguide. For this reason, the reconstructing procedures of the refractive index profile of the waveguide based on the modal equation can not be used for the single-mode structures. Also, in the case of the multi-mode waveguides, their application requires a caution in inferring on the resulting refractive index. The refractive index profiles of the planar waveguides, characterized by a monotonic function of changes in the refractive index, are created in the processes of preliminary diffusion (electrodiffusion). The maximum value of refractive index, reflecting the distribution of admixture introduced into the glass, is right on its surface. Assuming the denominations of the refractive indices: n_b in the volume of the glass, n_s at the surface of the waveguide and n_c for the coating of the waveguide (Fig.11) and assuming the distribution of the refractive index in the glass given by a monotonic function $n(x)$, it is possible to write a modal equation for the gradient waveguide, indicating the condition of propagation of the mode of m -th order [48]:

$$k_0 \int_0^{x_m} \sqrt{n^2(x) - N_m^2} dx = \pi \left(m + \frac{1}{4} \right) + \arctg \left(r \sqrt{\frac{N_m^2 - n_c^2}{n_s^2 - N_m^2}} \right), \quad (17)$$

where: k_0 – wave number of the electromagnetic wave in free space, x_m –turning point of the mode of m -th order, $N_m = \beta_m/k_0$ – effective refractive index of the mode of m -th order, β_m – propagation constant of the mode of m -th order, $r=1$ (TE polarization), $r=(n_s/n_c)^2$ (TM polarization).

Figure 11. A gradient waveguide with a monotonic change of the refractive index

The White-Heidrich procedure is the simplest method that allows to specify monotonic profile of the planar waveguide $n(x)$. An approximation by a function linear in segments can be made. From the assumption itself: the greater the number of modes that can propagate in waveguide is, the more accurate such approximation will be. This limits the application of this procedure for the multimode waveguides only. Let the desired function $n(x)$ describing the distribution of the refractive index has the form (Fig.12):

$$n(x) = N_k + \frac{N_{k-1} - N_k}{x_k - x_{k-1}}(x_k - x) \quad (18)$$

for: $x_{k-1} < x < x_k$, where $k = 0, 1, 2 \dots M-1$; M – is the number of the modes.

Substituting expression (18) into the modal equation (17) one receives the phrase, in which the variable of integration occurs as a function of the square root. Then the left side of the equation (17) can be represented as:

$$\int_0^{x_m} \sqrt{n^2(x) - N_m^2} dx = \sum_{k=0}^m \int_{x_{k-1}}^{x_k} \sqrt{\left[N_k + \frac{N_{k-1} - N_k}{x_k - x_{k-1}}(x_k - x) \right]^2 - N_m^2} dx \quad (19)$$

After calculating the integrals, the m -th component can be distinguished now from the sum. Then a recursive expression is obtained allowing to calculate the turning points of individual modes:

$$\begin{aligned}
 x_m = x_{m-1} + & \frac{2(N_{m-1} - N_m)}{N_{m-1}\sqrt{N_{m-1}^2 - N_m^2} - N_m^2 \times \ln \left(\frac{N_m}{N_{m-1} - \sqrt{N_{m-1}^2 - N_m^2}} \right)} \times \\
 & \times \left\{ \frac{\lambda}{2\pi} \left[\pi(m + 0,25) + \text{arctg} \left(r \sqrt{\frac{N_m^2 - n_c^2}{n_s^2 - N_m^2}} \right) \right] - \sum_{k=0}^{m-1} \frac{x_k - x_{k-1}}{2(N_{k-1} - N_k)} \times \right. \\
 & \left. \left[N_{k-1}\sqrt{N_{k-1}^2 - N_m^2} - N_k\sqrt{N_k^2 - N_m^2} - N_m^2 \times \ln \left| \frac{\sqrt{N_k^2 - N_m^2} - N_k}{\sqrt{N_{k-1}^2 - N_m^2} - N_{k-1}} \right| \right] \right\} \\
 (m = 0, 1 \dots M-1)
 \end{aligned} \tag{20}$$

Figure 12. Rys.3.6. Approximation of a refractive index profile by a function linear in segments.

Figure 13. The criterion of smoothness of the reconstructed refractive index profile

for $m=0 \Rightarrow x_{-1}=0$ and $N_{-1}=n_s$:

$$x_0 = \frac{2(n_s - N_0)}{n_s \sqrt{n_s^2 - N_0^2} - N_0^2 \ln \left(\frac{N_0}{n_s - \sqrt{n_s^2 - N_0^2}} \right)} \times \frac{\lambda}{2\pi} \left[0,25\pi + \arctg \left(r \sqrt{\frac{N_0^2 - n_c^2}{n_s^2 - N_0^2}} \right) \right] \quad (21)$$

From equation (17) it follows that to determine the turning point x_0 of the zero-order mode it is needed to know the value of the refractive index at the surface of the waveguide ($N_{-1}=n_s$). In this method, it is not directly measured. This value is chosen here so that the designated points of the profile $\{x_k, N_k : k=-1..M-1\}$ meet certain criteria. As a physically reasonable criterion the smoothness of the resulting profile is assumed, as a quality of the diffusion processes. As shown in Fig.13, the minimization of the sum of the areas of all triangles S_t , spread on the three adjacent vertices of the reconstructed profile, was adopted as the criterion.

The Fig.14a illustrates a sample modes spectrum recorded in the measurement system of Fig.9. While the Fig.14b presents the refractive index profile of the waveguide calculated from the procedure mentioned above for the effective refractive indices resulting from the modes spectrum shown nearby.

Figure 14. a) The recorded modes spectrum of the waveguide, b) its reconstructed refractive index profile.

5. Mathematical model of binary ion exchange phenomenon

The ion exchange processes are initiated in the glass as a result of the appearance of the admixture ions in its superficial area. This situation occurs when a glass of a sufficiently high temperature is in contact with the liquid phase of the ion source (see Part 3). Then the alkali ions from the liquid phase move into the glass, and mobile modifier ions leave the glass going into the liquid. This keeps the condition of electrical neutrality of the glass. By

the appearance of admixture ions at the surface of the glass, with a simultaneous decrease in the concentration of the modifiers, two opposite directed streams of exchanged ions arise in the glass, due to their concentration gradients. Due to the diffusive nature of these phenomena they will continue to be called diffusion processes. The ionic nature of the thermal transport phenomena in the glass makes it possible to stimulate it by an external electric field. These are called the electrodiffusion processes. These two types of processes are used for the initial introduction of admixture ions into the glass area. Their effect is a change of the optical properties of glass (change of the refractive index). This change is proportional to the local concentration of introduced admixture ions (Part 2). The resulting distribution of the refractive index in the glass area may be subject to later modifications in the so-called secondary processes (diffusion, electrodiffusion, heating). This is undoubtedly the biggest advantage of the ion exchange technology, which, despite the restriction on the values of the changes of the refractive index received in the glass, gives wide possibilities of modifying its distribution.

Knowledge of the physical basis of the phenomenon of the ion exchange allows to create a theoretical model describing this process. It can be used to determine the kinetics of the exchange phenomenon for the concrete glass-admixture system.

A model description of the exchange phenomenon is easiest to refer to the preliminary diffusion process, in which the technological parameters are: the temperature and its duration. Temperature determines the kinetics of this process, while time is only an integrating factor. Thus, the kinetics parameters of the ion exchange, determined on the basis of diffusion processes for the selected glass-admixture system, will be dependent only on the temperature of the process.

The kinetics parameters of the ion exchange determined on the basis of diffusion processes should, by the assumed mathematical model, provide the opportunity to describe other cases of the ion exchange processes in the same glass-admixture system. The verification of the correctness of the model description of the ion exchange will be a confrontation of outcomes of specific processes calculated on its basis, with the measurement results of structures produced in the assumed conditions.

For the ion exchange processes, carried out in the multicomponent glasses, various types of modifier ions from the glass can make their share. In order, therefore, to determine their effect on the production of change in the refractive index (see equation (10) and (12)), it is needed to know the weight factors of their participation in the process. Still, a two-component model based on the ion exchange process has been adopted. For this model the following assumptions have been made:

- there are only two types of ions in this process. On the part of the source, these are the cations of the metal introduced into the glass (ions of *A* type). On the part of the glass substrate, these are the modifier cations (ions of *B* type), having the lowest activation energy,
- both types of ions have the same valence and diffuse by similar mechanisms,
- for each type of ions the relationship between an individual diffusion constant D_i and the electrochemical mobility μ_i is given by the Einstein equation:

$$\mu_i = \frac{e}{HkT} D_i \quad i = A, B \quad (m^2 V^{-1} s^{-1}), \quad (22)$$

where: e – elementary electrical charge, k – the Boltzmann constant, T – the absolute temperature, H – the correlation coefficient ($0 < H \leq 1$) [11]

- the coupling between the streams of exchanged ions occurs only by the electrostatic forces,
- self-diffusion coefficients of both types of exchanged ions can be a function of normalized concentration, given in the form [61]:

$$\begin{aligned} D_A &= D_A(u, T) = D_{0A}(T) \cdot f_A(u) \\ D_B &= D_B(w, T) = D_{0B}(T) \cdot f_B(w), \end{aligned} \quad (23)$$

where: u, w – normalized concentrations of ions, respectively A and B type, T – the temperature on an absolute scale.

The dependencies of the diffusion coefficients on the temperature are given by the Arrhenius equation:

$$D_{0i}(T) = D_{0i}^* \cdot \exp\left(-\frac{\Delta Q_i}{RT}\right) \quad (i=A, B), \quad (24)$$

where: ΔQ_i – activation energy of the ions i -type, R – universal gas constant.

In addition, as outlined in Part 2, there is an assumption of proportionality of the changes in the refractive index of the glass to the concentration of introduced admixture.

To describe the exchange processes in glass the arrangement geometry was assumed, as given in the Fig.15. In the glass, after the introduction of admixture (A), two streams of ions will occur due to their concentration gradients:

$$\begin{aligned} \vec{\Phi}_A &= -D_A \nabla c_A + \mu_A c_A \vec{E}_0 \quad (m^{-2} s^{-1}) \\ \vec{\Phi}_B &= -D_B \nabla c_B + \mu_B c_B \vec{E}_0 \quad (m^{-2} s^{-1}), \end{aligned} \quad (25)$$

where: D_A, D_B – self-diffusion coefficients of exchanged ions ($m^2 s^{-1}$), c_A, c_B – concentrations of ions A and B type (m^{-3}), μ_A, μ_B – electrical mobility of ions A and B type ($m^2 V^{-1} s^{-1}$).

Figure 15. The arrangement geometry

The vector $\vec{E}_0$ (Vm^{-1}) in the equations (25) means the local electric field intensity in the glass:

$$\vec{E}_0 = \vec{E}_e + \vec{E}_d, \quad (26)$$

where: $\vec{E}_e$ – external electric field (Vm^{-1}), $\vec{E}_d$ – diffusion electric field, resulting from the differences in the mobility of the exchanged ions (Vm^{-1}).

Figure 16. The concentration of the distributions of the admixture ions and modifier ions in the glass during the exchange process

If there is a difference in the diffusion coefficients D_A and D_B of both types of ions involved in the process, then in the glass the so-called diffusion potential occurs, resulting from the difference in their mobility. The associated electric field $\vec{E}_d$ is a coupling factor of the movement of the two streams (slower ions are accelerated and the faster ions are slowed down by this field). Taking into account an additional externally applied electric field $\vec{E}_e$, marked in the Fig.15, allows to generalize the considered ion exchange process to the diffusion with the electric field (electrodifusion).

In the area of the glass the equilibrium concentration c_0 is determined, defined as the concentration of all the mobile ions. The Fig.16 demonstratively presents the one-dimensional distributions of the concentration of exchanged ions, which in any place of the glass meet the condition:

$$c_A(x) + c_B(x) = c_0 \quad (27)$$

The situation here shows the state, in which the maximum concentration of the admixture introduced into the glass reaches on its surface the value $c_{Amax} < c_0$. This means that at the glass surface only part of the exchangeable ions of the glass has been replaced by the admixture ions. Such a situation may take place when using diluted sources of admixture ions. When normalizing the equation (27) to the value of c_0 , it is obtained:

$$\frac{c_A(x)}{c_0} + \frac{c_B(x)}{c_0} = 1 \quad (28)$$

The case $c_{Amax} = c_0$ corresponds to the total replacement of ions of its modifiers at the glass surface, by admixture ions. The normalized concentrations of both types of ions u and w are introduced as:

$$u(x) = \frac{c_A(x)}{c_0} \quad w(x) = \frac{c_B(x)}{c_0} \quad (29)$$

From the above definitions the obvious relations result:

$$\begin{aligned} u_{\max} = u(0) &= \frac{c_{A\max}}{c_0} & \lim_{x \rightarrow \infty} u(x) &= 0 \\ w_{\min} = w(0) &= 1 - u(0) & \lim_{x \rightarrow \infty} w(x) &= c_0 \\ w &= 1 - u & \Rightarrow \nabla w &= -\nabla u \end{aligned} \quad (30)$$

Using the relations (29), the equations (25) can be represented as:

$$\begin{aligned} \vec{\Phi}_u &= \frac{\vec{\Phi}_A}{c_0} = -D_A(u) \nabla u + \mu_A u \vec{E}_0 \quad (\text{ms}^{-1}) \\ \vec{\Phi}_w &= \frac{\vec{\Phi}_B}{c_0} = -D_B(w) \nabla w + \mu_B w \vec{E}_0 \quad (\text{ms}^{-1}) \end{aligned} \quad (31)$$

In the area of glass in which there is no admixture (ions A type) $c_A=0 \Rightarrow u=0$ there is no electric diffusion field, so the local electric field is equal to the external field ($\vec{E}_0 = \vec{E}_e$). Therefore the requirement of electrical neutrality of the glass puts the condition:

$$\vec{\Phi}_u + \vec{\Phi}_w = \mu_B \vec{E}_e \quad (32)$$

For the processes taking place without an external electric field, this condition reduces to the form:

$$\vec{\Phi}_u + \vec{\Phi}_w = 0 \quad (33)$$

Considering the equations (31), the condition (32) can be expressed as:

$$-D_A(u) \nabla u + \mu_A u \vec{E}_0 - D_B(w) \nabla w + \mu_B w \vec{E}_0 = \mu_B \vec{E}_e \quad (34)$$

By introducing the quantity:

$$\alpha = 1 - \frac{D_A(u)}{D_B(w)} = 1 - \frac{D_A(u)}{D_B(1-u)} \quad (35)$$

based on the equation (34), using the relations (30), an expression that describes a value of the local electric field in the glass is obtained:

$$\vec{E}_0 = \frac{\vec{E}_e}{1 - \alpha u} - \frac{HkT}{e} \cdot \frac{\alpha \nabla u}{1 - \alpha u} \quad (36)$$

The first component in (36) is associated with an external electric field, while the second expresses the diffusion field. Attention should be paid to the fact, that the sign of the

diffusive component in the above equation is determined by the quantity α , depending on the normalized concentration of admixture ions introduced into the glass.

For the vector of normalized flow of admixture ions $\vec{\Phi}_u$, the continuity equation is valid in the whole volume of the glass:

$$\frac{\partial u}{\partial t} + \nabla \cdot \vec{\Phi}_u = 0 \quad (37)$$

Taking into account (31) in equation (37) we obtain:

$$\frac{\partial u}{\partial t} = \nabla \cdot \left[D_A(u) \nabla u - \mu_A u \vec{E}_0 \right] \quad (38)$$

For the volume of the glass for the external electric field vector the equality must be fulfilled: $\nabla \cdot \vec{E}_e = 0$. Taking into account this fact in the calculation of the operator $\nabla \cdot \vec{E}_0$ in the equation (38), after the transformations the final form of the equation is obtained, describing the spatio-temporal changes in normalized concentration of admixture in the glass:

$$\begin{aligned} \frac{\partial u}{\partial t} = & \frac{D_A(u)}{1-\alpha u} \left[\Delta u + \frac{\alpha}{1-\alpha u} (\nabla u)^2 - \frac{e}{HkT} \frac{1}{1-\alpha u} \nabla u \cdot \vec{E}_e \right] + \\ & + \frac{1-u}{(1-\alpha u)^2} \left[\nabla u - \frac{e}{HkT} u \vec{E}_e \right] \cdot \nabla D_A + \frac{u(1-\alpha)^2}{(1-\alpha u)^2} \left[\nabla u - \frac{e}{HkT} u \vec{E}_e \right] \cdot \nabla D_B, \end{aligned} \quad (39)$$

where: $\alpha(u) = 1 - \frac{D_A(u)}{D_B(1-u)}$

Still, the dependence of the of diffusion coefficients from their normalized concentration was assumed in the form:

$$D_A(u) = D_{0A} e^{Au}, \quad D_B(u) = D_{0B} e^{B(1-u)} \quad (40)$$

In this case, for a one-dimensional diffusion with no external electric field, the equation (39) takes the form:

$$\frac{\partial u}{\partial t} = \frac{D_{0A} e^{Au}}{1-\alpha u} \cdot \frac{\partial^2 u}{\partial x^2} + \frac{D_{0A} e^{Au} [\alpha + (1-u)A] - u(1-\alpha)^2 D_{0B} e^{B(1-u)}}{(1-\alpha u)^2} \left(\frac{\partial u}{\partial x} \right)^2 \quad (41)$$

In the above equation:

$$\alpha = 1 - \frac{D_{0A}}{D_{0B}} \cdot \exp[u(A+B) - B] \quad (42)$$

Figure 17. Refractive index profile of the waveguide obtained by fitting the solution of the diffusion equation into measurement points, together with the designated parameters of the diffusion coefficients

From the assumption of proportionality of the changes of refractive index, to the concentration of introduced admixture, results the relationship (one-dimensional case):

$$n(x) = n_b + \Delta n_s \cdot u(x) \quad (43)$$

In the above equation $n(x)$ is the absolute value of the refractive index of glass, n_b is the refractive index of undoped glass, Δn_s is the maximum change in the doping of the glass (for the preliminary diffusion - at its surface), and $u(x)$ is the spatial distribution of normalized concentration of admixture introduced into the glass.

5.1. Determination of diffusion coefficients by solving the diffusion equation

This procedure is based on solving the equation (41) describing the process of thermal diffusion in the one-dimensional case. Determination of the parameters of the diffusion equation reduces to the problem of finding the minimum of the matching function $\Psi(\vec{p})$, defined on the four-dimensional vector of diffusion parameters: $\vec{p} = [D_{0A}, D_{0B}, A, B]$. The matching function $\Psi(\vec{p})$ is defined as the sum of squared differences between the solution of diffusion equation and the points, set of the measurements of the refractive index profile of the waveguide, then divided by the number of these points. Thus, the determined diffusion parameters are the coordinates of the vector $\vec{p}_{\min}$ minimizing the function $\Psi(\vec{p}_{\min})$. Fig.17 shows the example fitting of the theoretical profile to the measurement points and the values of the diffusion coefficients: D_{0A} , D_{0B} , A and B designated in this way. The shown example relates to the ion exchange of $Ag^+ \leftrightarrow Na^+$ realized in the soda-lime glass in the diffusion process of the Ag^+ ions from the source of $AgNO_3$. The temperature of the process $T=299^\circ C$, time of the diffusion $t=1h$.

5.2. Determination of the temperature dependences of exchanged ions' coefficients

The way of determining the diffusion coefficients (described in the previous part) is used to determine their dependencies on the temperature of these processes. This issue is very

important, because based on the diffusion coefficients the theoretical distributions of admixture concentration in the glass are calculated. The knowledge of the temperature dependencies $D_{0A}(T)$ and $D_{0B}(T)$ of the diffusion coefficients of glass-admixture system allows modeling the technological processes that can be implemented at different temperatures. A very important technological problem, which is the repeatability of produced optical structures' properties, needs also to determine the impact of temperature changes on the final result of the process.

Temperature dependence of the diffusion coefficients is exponential, given by the Arrhenius equation (24). To fully determine the relation of $D_{0A}(T)$ and $D_{0B}(T)$ two factors are needed to be known: D_{0i}^* and ΔQ_i ($i=A, B$).

To determine these factors, one should realize a minimum of two thermal diffusion processes, at different temperatures, and then determine the coefficients of linear regression for dependence $\ln D_{0i}(T^{-1})$. The duration of these processes must be chosen so as to produce the multimode waveguides in the glass, because for them the reconstruction procedure of the refractive index profiles ensures high reliability of restoring their shapes. An illustration of such proceedings, for soda-lime glass doped with silver ions, is set out below.

Figure 18. The refractive index profiles of waveguides produced in soda-lime glass in different temperatures diffusion of Ag^+ ions

Fig.18 shows the refractive index profiles of the waveguides produced in soda-lime glass in the processes of diffusion of silver ions realized at different temperatures. Times of diffusion processes have been chosen so that each refractive profile had to at least 10-modes for the wavelength of $\lambda=677 \text{ nm}$. Because, as a result of diffusion of silver ions into this type of glass, a significant stress birefringence in the emerging waveguide structures is not observed, therefore the measurements of the refractive index profiles are referenced only to one TE polarization state. For each refractive profile the parameters D_{0A} and D_{0B} of the diffusion equation were then determined. Results of the calculations of these parameters are summarized in Table 2.

temperature of the process T (°C) / (K)	ΔT (K)	D_{0A} ($\mu\text{m}^2/\text{h}$)	D_{0B} ($\mu\text{m}^2/\text{h}$)
253.3 / 526.5	± 0.5	0.296	3.77
260.4 / 533.6	± 0.5	0.407	4.86
271.4 / 544.6	± 0.5	0.658	7.28
280.0 / 553.2	± 0.5	0.910	9.22
288.0 / 561.2	± 0.5	1.21	11.9
301.6 / 574.8	± 0.5	1.71	15.9
314.7 / 587.9	± 0.5	2.79	25.1

Table 2. The determined D_{0A} and D_{0B} parameters of the diffusion equation for the ion exchange of $\text{Ag}^+ \leftrightarrow \text{Na}^+$ in soda-lime glass

The Fig.19 presents the measurement points of the temperature dependencies of the diffusion coefficients D_{0A} and D_{0B} , according to data compiled in Table 2. After taking the logarithm form of equation (24) and matching it to these points, the activation energies of exchanged ions ΔQ_A and ΔQ_B and the values of the logarithms of diffusion coefficients D_{0A}^* and D_{0B}^* are set.

Figure 19. The dependencies of the diffusion parameters: a) D_{0A} and b) D_{0B} from the temperature (according to the Table 2)

The determined values are as follows:

$$\Delta Q_A = (92.2 \pm 2.7) \text{ kJ/mol} \quad \ln D_{0A}^* = 19.9 \pm 0.6 \quad (44)$$

$$\Delta Q_B = (77.3 \pm 2.2) \text{ kJ/mol} \quad \ln D_{0B}^* = 19.1 \pm 0.5$$

The equations describing the temperature dependencies of the diffusion coefficients of exchanged ions have the form:

$$D_{0A}(T) = \exp\left(-\frac{11085.8}{T} + 19.9\right) \quad (\mu\text{m}^2/\text{h})$$

$$D_{0B}(T) = \exp\left(-\frac{9298.8}{T} + 19.1\right) \quad (\mu\text{m}^2/\text{h}) \quad (45)$$

6. The real-time control of diffusion processes in glass

Obtaining a repeatability of effects of diffusion processes (in terms of changes in refractive index of glass) requires a close monitoring of both time and temperature. Ensuring the stability of the diffusion process' temperature of the order of $^{\circ}\text{C}$ fraction at the typical for ion exchange $\text{Ag}^+ \leftrightarrow \text{Na}^+$ level of $\sim 300^{\circ}\text{C}$ is very difficult (practically impossible) to meet.

It is however possible to control the diffusion on an ongoing basis. The kinetics of this process is linked to its temperature by the Arrhenius equation (24). In turn, in equation (41) describing the diffusion of admixture ions into the glass, there are (in a transparent manner) the diffusion coefficients of exchanged ions $D_{0A}(T)$ and $D_{0B}(T)$, which are the functions of the temperature. Therefore, it is possible, by monitoring the temperature in the real time during the diffusion process, to determine the current values of these coefficients. Solving the equation (41) describing a one-dimensional diffusion is to integrate it in time. It takes a certain time step Δt . This step can be identified with the actual time, while not giving the upper cut-off time for the process of integrating the diffusion equation. By measuring the temperature in the crucible in certain moments of time t_p , which are the total multiples of the time step Δt , by the known temperature dependence $D_{0A}(T)$ and $D_{0B}(T)$, the current values of diffusion coefficients $D_{0A}(t_p)$ and $D_{0B}(t_p)$ can be calculated.

Figure 20. Illustration of the control of the diffusion process. a) Temperature dependence from the time b) Calculated refractive index profiles and the corresponding effective refractive indices of modes ($\lambda=677\text{nm}$, TE polarization) for the selected moments of time

In that case, if the duration of the integral equation (41) will run parallel to the actual time of the diffusion process, then the solution of this equation, at the current time t described by the function $u(x,t)$, will present the current distribution of normalized concentration of the admixture introduced into the glass. On the basis of the function $u(x,t)$ and equation (43), in which the disperse values $n_b(\lambda)$ and $\Delta n_s(\lambda)$ are known, the refractive waveguide profile $n(x,\lambda,t)$ is calculated for the current time t corresponding to the wavelength λ . Solving the mode equation (17) for the assumed polarization, which would be propagated in a waveguide with a refractive index $n(x,\lambda,t)$, one can calculate all the effective refractive indices of such modes of the waveguide.

This shows that such a way of monitoring the diffusion process creates the possibility of an ongoing control of the resulting waveguide, both in terms of its own modes and changes during their effective refractive indices. Figure 20 illustrates the example of the control of the diffusion process using this method. Glass substrate was immersed in the molten salt by means of the handle (Fig.21). It provides a direct contact of the thermocouple with the glass substrate. Pressure pulsations allow the continuous stirring of the contents of the crucible. The Figure 20 shows the temperature curve of a selected diffusion process. This method of process control also includes the process of cooling the substrate after removing it from the crucible. Time step of monitoring the process temperature was $t_p=2$ s. Fig.20b shows the refractive index profiles of the resulting waveguide, calculated at selected moments of time, with the resulting effective indices of modes. The calculated refractive index profiles correspond to the moments of time marked in Fig.20a. The Fig.20b also marks the effective indices obtained from measurements of the resulting waveguide for wavelength $\lambda=677\text{nm}$ with TE polarization. Their measurement uncertainties were $\Delta N_m=0.0004$. From the results shown in Fig.20b it can be seen that the calculated effective indices are slightly smaller than the measured values. This difference is the smallest for the TE_0 mode and is of 0.0006 . For higher order modes it increases, reaching the highest value of 0.004 for the TE_4 mode. These differences result from the numerical modeling of the process, and also from the

Figure 21. The glass holder

measurement method of the temperature of the substrate. The measurement thermocouple visible in the Fig.21 is placed in a protective glass tube. Therefore it has a rather large thermal inertia. As a result, the temperature recorded with its use does not reflect the actual temperature of a glass substrate, which it has at any given moment of time. The largest differences of the temperature indications occur at stages of heating and cooling of the glass substrate. Therefore the significance of these differences in made calculations will be large, especially for the short periods of diffusion.

Fig.22 presents the results of the seven diffusion processes of Ag^+ ions into the soda-lime glass. The aim of these processes was to obtain uniform waveguide structures in terms of both quantity and value of effective refractive indices of modes. All produced waveguides were 5-modes for the wavelength $\lambda=677$ nm, with TE polarization. Fig.22a shows the time dependences of each process' temperature. While the Fig.22b shows dispersion ($N_{m,max}-N_{m,min}$), of the measured effective refractive indices, shown as a function of the order of the modes. The measurement uncertainties of all effective refractive indices were: $\Delta N_m=0.0004$. The obtained results show good repeatability of the realized processes.

Figure 22. The repeatability of the diffusion processes (soda-lime glass, ion exchange: $\text{Ag}^+ \leftrightarrow \text{Na}^+$, admixture source: AgNO_3) a) time dependences of the temperatures of the processes b) dispersion of the measured effective refractive indices for the individual orders of modes

Fig.23 shows the enlarged fragments of the recorded temperatures of the processes from Fig.22a. This shows that the temperature differences are, in extreme cases, even of a few Celsius degrees. With such a dispersion of temperatures, obtaining the repeatability of effective refractive indices of produced waveguides would not be possible without the use of the proposed process control. The method used to monitor the diffusion process makes its final effect independent from the temperature. The same result is achieved in a shorter time of diffusion process, when the average temperature is higher and vice versa. This regularity is clearly visible in Fig.23.

Figure 23. The temperature differences of the diffusion processes

7. Ion exchange in glass application

The method of ion exchange as a technology tool to produce changes in refraction in the glass is still in use. Most of these applications takes place in optoelectronics. There are, of course, limits of its application. They arise from the possibility of physical effects generated by this method. The main limitation is the obtained maximum increment of refractive index of the glass Δn . The value of this increase depends on the type of glass and the type of admixture ions. The maximum reached value of Δn is of the order of 0.1. However, the big advantage of this method is its low price. Equipment requirements here are much smaller (cheaper) than in the case with other methods, such as vacuum technology. Also the materials used in this method: the glass substrates and ion admixture sources are relatively inexpensive.

A characteristic feature of the effect of changes in refractive index of glass obtained by this method is the gradient nature of those changes. This creates the possibility of implementing gradient micro-optic components. The greatest use of this method in optoelectronics are taking place in the production of waveguide structures. Attractive in particular are application of this method in the manufacture of optical amplifiers in glasses doped with rare earth ions, the production of the structures of planar lasers in glasses doped with rare earth elements Er^{3+} and Yb^{3+} (glass MM-2 of Kigre company [62], glass IOG-1 of Schott company [63]), and the production of the sensor structures. The combination of the ion exchange method and the zol-gel method is also interesting. The zol-gel method enables the production of thin (of the order of a fraction of micrometer) layers whose refractive index can take values in the range of 1.45÷2.2 [64]. These layers are the glasses received in the low-

temperature polymerization and gelation processes of the suitable solutions. Large (compared with the ion exchange) values of the refractive index of these layers make this method attractive for integrated optics. The waveguide structures produced in the glass substrates by ion exchange method are homogeneous structures, extending from the glass surface at a depth of several to tens (in some cases even more) μm . For example, for typical values of the refractive index of glass ~ 1.5 , with a maximum change of the refractive index of ~ 0.1 , the depths of the waveguide areas, providing the conditions for single mode propagation, are of the order of $1 \mu\text{m}$. On the other hand, using diluted admixture sources, which increments of the refractive index can be very small, to obtain single-mode structures requires a depth of doped glass in the range from a few to several μm . Greater depths of doped regions in the glass are formed by the multimode structures. Whereas the homogeneous waveguide layers, produced by the zol-gel method, because of their small thickness (tens to hundreds of nm) are single-mode structures with large values of the refractive index as compared to the waveguides produced by ion the exchange method. This combination of small changes in the refractive index with the large depths of glass doping areas at the same time, in the case of ion-exchange method with very small layer thicknesses (obtained by the zol-gel method) with a high refractive index, enables the production of hybrid waveguide structures. In this case, at the glass surface, in which the gradient structure is manufactured, a thin uniform layer of dielectric material is prepared by the zol-gel method. By appropriate selection of the refractive index and thickness of this layer in such a structure, the effect of conducting zero-order mode in the homogeneous layers, while propagating higher order modes in the gradient area of the glass, can be achieved. Such gradient-homogeneous waveguides may constitute a new category of leading light structures, with specific modes properties.

With the use of the zol-gel method the silica layers can also be applied to the glass surface. The use of photolithographic processes of shaping the topology of these layers makes that they can act as a dielectric masking coverings in technological processes of ion exchange. This method can also produce strip waveguide structures of *rib* type [65]. Therefore the combination of ion-exchange method and the zol-gel method creates new possibilities for creating the elements of integrated optics. The combination of both methods is also justified in the case of constructing the structures of amplitude optical sensors, using the evanescent field spectroscopy. In this case, the waveguide path is produced in the glass substrate by the ion exchange method, which refractive index profile can be shaped to a fairly large range, e.g. by the electrodiffusion processes. Then, by the zol-gel method, a sensor layer which covers the gradient waveguide [66, 67] is prepared. Another area of application of the ion exchange method is surface hardening of the glass. When using certain admixture ions (e.g. K^+) in the admixture area of the glass, a significant stress induces arising from the difference in radii of exchanged ions. These stresses are of a clamping character, and their magnitude is of the order of hundreds of N/mm^2 . When taking into account the depth of glass doping of tens of μm typical for ion exchange processes, the considerable stress gradients in the superficial area of glass are achieved. This gives the effect of its hardening.

Having regard to those facts, it can be stated that the ion exchange method remains as an attractive technological tool for both: technical and economical reasons. Therefore a further research related to its use for producing the gradient structures in the glass is very useful. Ensuring a high repeatability of processes, guaranteeing the established tolerance of the optical properties of produced structures, is a task that has made this method an effective technological tool.

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8. References

- [1] Kao K.C., Hockman G.A., *Dielectric fibre surface waveguides for optical frequencies*, Proc. IEEE, 1966, Vol.113, No.7, 1151-1158.
- [2] Doremus, R.H., *Exchange and Diffusion of Ions in Glass*, The Journal of Physical Chemistry, 1964, Vol.68, No.8, 2212-2218.
- [3] Doremus, R.H., *Ion Exchange in Glass*, in *Ion-Exchange*, Marinsky, J.A., Ed., New York: Marcel Dekker, 1969, Vol.2, 1-42.
- [4] Kahnt H., *Ionic transport in glasses*, Journal of Non-Crystalline Solids, 1996, Vol.203, 225-231.
- [5] French W.G., Pearson A.D., *Refractive index changes produced in glass by ion-exchange*, Ceramics Bulletin, 1970, Vol.49, No.11, p.474.
- [6] Giallorenzi T.G., West E.J., Kirk R., Ginter R., Andrews R.A., *Optical waveguides formed by thermal migration in glass*, Applied Optics, 1973, Vol.12, No.6, 1281-1285.
- [7] Izawa T., Nagakome H., *Optical Waveguide Formed by Electrically Induced Migration of Ions in Glass Plates*, Applied Physics Letters, 1972, Vol.21, 584-586.
- [8] Findakly T., *Glass Waveguides by Ion Exchange: A Review*, Optical Engineering, 1985, Vol.24, No.2, 244-250.
- [9] Najafi S.I., *Introduction to Glass Integrated Optics*, Ed., Boston: Artech House 1992.
- [10] Ramaswamy, R.V., Srivastava, R., *Ion-Exchange Glass Waveguides: A Review*, Journal of Lightwave Technology, 1988, Vol.6, No.6, 984-1002.
- [11] Terai R, Hayami R., *Ionic Diffusion in Glasses*, Journal of Non-Crystalline Solids, 1975, Vol.18, 217-264.
- [12] Garfinkel H. M., *Ion-exchange equilibria between glass and molten salts*, The Journal of Physical Chemistry, 1968, Vol.72, No.12, 4175-4181.

- [13] Araujo R.J., Likitvanichkul S., Thibault Y., Allan D.C., *Ion exchange equilibria between glass and molten salt*, Journal of Non-Crystalline Solids, 2003, Vol.318, 262-267.
- [14] Zachariasen W.H., *The atomic arrangement in glass*, Journal American Chemistry Society, 1932, Vol.54, 3841-3851.
- [15] Warren B.E., Loring A.D., *X-Ray diffraction study of the structure of soda-silica glasses*, Journal American Ceramic Society, 1935, Vol.18, 269-276.
- [16] Isard J.O., *The Haven ratio in glasses*, Journal of Non-Crystalline Solids, 1999, Vol.246, 16-26.
- [17] Fantone S.D., *Refractive Index and Spectral Models for Gradient-Index Materials*, Applied Optics, 1983, Vol.22, 432-440.
- [18] Huggins M. L., *The refractive index of silicate glasses as a function of composition*, Journal Optical Society of America, 1940, Vol.30, No.10, 495-504.
- [19] Chartier G.H., Jaussaud P., de Oliveira A.D., Parriaux O., *Fast Fabrication Method for Thick and Highly Multimode Optical Waveguides*, Electronics Letters, 1977, Vol.13, 763-764.
- [20] De Bernardi C., Malvicino C., Morasca S., Morra M., *Time and Temperature Influence on Surface Index Change K^+ - Na^+ Ion Exchanged Optical Waveguides*, Journal Applied Physics, 1988, Vol.63, No.1, 234-236.
- [21] Gortych J.E., Hall D.G., *Fabrication of Planar Optical Waveguides by K^+ -Ion Exchange in BK7 and Pyrex Glass*, IEEE Journal of Quantum Electronics, 1986, Vol.22, 892-895.
- [22] Honkanen S., Tervonen A., McCourt M., *Control of birefringence in ion-exchanged glass waveguides*, Applied Optics, 1987, Vol.26, No.22, 4710-4711.
- [23] Johansson J., Dianta G., Coutaz J.-L., *Optical Waveguides Fabricated by Ion Exchange in High-Index Commercial Glasses*, Applied Optics, 1992, Vol.31, No.15, 2796-2799.
- [24] Miliou A.N., Srivastava R., Ramaswamy R.V., *Modeling of the Index Change in K^+ - Na^+ Ion-Exchanged Glass*, Applied Optics, 1991, Vol.30, No.6, 674-681.
- [25] Najafi S.I., *Optical Behaviour of Potassium Ion-Exchanged Glass Waveguides*, Applied Optics, 1988, Vol.27, No.17, 3728-3731.
- [26] Noutsios P.C., Yip G.L., *Shallow buried waveguides made by purely thermal migration of K^+ ions in glass*, Optics Letters, 1990, Vol.15, No.4, 212-214.
- [27] Tervonen A., Honkanen S., *Feasibility of potassium-exchanged waveguides in BK7 glass for telecommunication devices*, Applied Optics, 1996, Vol.35, No.33, 6435-6437.
- [28] Urnes S., *Na^+ - K^+ exchange in silicate glasses*, Journal American Ceramics Society, 1973, Vol.56, No.10, 514-517.
- [29] Yip G.L., Albert J., *Characterization of Planar Optical Waveguides by K^+ -Ion Exchange in Glass*, Optics Letters, 1985, Vol.10, No.3, 151-153.
- [30] Neuman V., Parriaux O., Walpita L., *Double-Alkali Effect: Influence of Index Profile of Ion-Exchanged Waveguides*, Electronics Letters, 1979, Vol.15, 704-706.
- [31] Reichelt A., Clemens P.C., Mthlein H.F., *Single-Mode Waveguides and Components by Two-Step Cs^+ - K^+ Ion-Exchange in Glass*, Proc. SPIE-Int. Soc. Opt. Eng.: "Glasses for Optoelectronics" 1989, Vol.1126, 166-168.

- [32] Bogomolova L.D., Ganshin V.V., Jachkin V.A., Kubrinskaya M.E., Petrova V.Z., *EPR and Optical Study of Copper Diffusion Layers Produced by Ion Exchange in Oxide Glasses*, Journal of Non-Crystalline Solids, 1981, Vol.45, 249-255.
- [33] Gevorgyan S.S., *Single-step buried waveguides in glass by field-assisted copper ion-exchange*, Electronics Letters, 1990, Vol.26, No.1, 38-39.
- [34] Gallagher J.G., de La Rue R.M., *Single-Mode Stripe Optical Waveguides Formed by Silver Ion Exchange*, Electronics Letters, 1976, Vol.12, No.16, 397-398.
- [35] Gato L., Srivastava R., *Time Dependent Surface Index Change in Ion Exchanged Waveguides*, Optics Communications, 1996, Vol.123, No.4-6, 483-486.
- [36] Ghatak A.K., Khular E., Thyagarajan K., *Modes in Optical Waveguides Formed by Silver Sodium Ion Exchange*, IEEE Journal of Quantum Electron., 1978, Vol.14, No.6, 389-391.
- [37] Gonella F., *Stress-induced optical effect in $\text{Ag}^+\text{-Na}^+$ ion-exchanged glass waveguides*, Optics Letters, 1992, Vol.17, No.23, 1667-1669.
- [38] Martin M., Videau J.J., Canioni L., Adamietez F., Sarger L., Le Flem G., *Planar waveguides formed by $\text{Ag}^+\text{-Na}^+$ ion exchange in nonlinear optical glasses: diffusion and optical properties*, Applied Optics, 2000, Vol.39, No.3, 435-440.
- [39] Millar C.A., Hutchins R.H., *Manufacturing tolerances for silver-sodium ion-exchanged planar optical waveguides*, Journal Physics D; Applied Physics, 1978, Vol.11, 1567-1576.
- [40] Najafi S.I., Srivastava R., Ramaswamy R.V., *Wavelength-Dependent Propagation Characteristics of $\text{Ag}^+\text{-Na}^+$ Exchanged Planar Glass Waveguides*, Applied Optics, 1986, Vol.25, No.11, 1840-1843.
- [41] Ramaswamy R.V., Cheng H.C., Shirastava R., *Process optimization of buried $\text{Ag}^+\text{-Na}^+$ ion-exchanged waveguides: theory and experiment*, Applied Optics, 1988, Vol.27, No.9, 1814-1819.
- [42] Stewart G., Laybourn P.J.R., *Fabrication of Ion-Exchanged Optical Waveguides From Dilute Silver Nitrate Melts*, IEEE Journal of Quantum Electronics, 1978, Vol.14, No.12, 930-934.
- [43] Stewart G., Millar C.A., Laybourn P.J.R., Wilkinson C.D.W., De la Rue R.M., *Planar optical waveguides formed by silver-ion migration in glass*, IEEE Journal of Quantum Electronics, 1977, Vol.13, No.4, 192-200.
- [44] Camy P., Roman J.E., Willems F.W., Hempstead M., van der Plaats J.C., Pfel C., Beguin A., Koonen A.M.J., Wilkinson J.S., Lermينياux C., *Ion-Exchanged Planar Lossless Splitter at 1.5 μm* , Electronics Letters, 1996, Vol.32, 321-323.
- [45] Bach H., Neuroth N., *The Properties of Optical Glass*, Springer-Verlag Berlin Heidelberg 1995.
- [46] Jackel J.L., *Glass waveguides made using low melting point nitrate mixtures*, Applied Optics, 1988, Vol.27, No.3, 472-475.
- [47] Rogoziński R., *Refractive index profiles of planar waveguides produced in electrodiffusion processes*, Optica Applicata, 2004, Vol.34, No.4, 489-505.
- [48] White J.M., Heidrich P.F., *Optical waveguide refractive index profiles from measurement of mode indices: A simple analysis*, Applied Optics, 1976, Vol.15, No.1, 151-155.

- [49] Batchelor S., Oven R., Ashworth D.G., *Reconstruction of refractive index profiles from multiple wavelength mode indices*, Optics Communications, 1996, Vol.131, 31-36.
- [50] Albert J., Yip G.L., *Refractive-index Profiles of Planar Waveguides Made by Ion-Exchange in glass*, Applied Optics, 1985, Vol.24, No 10, 3692-3693.
- [51] Chiang K.S., *Construction of refractive-index profiles of planar dielectric waveguides from the distribution of effective indexes*, Journal of Lightwave Technology, 1985, Vol.3, No.2, 385-391.
- [52] Hertel P., Menzler H.P., *Improved Inverse WKB Procedure To Reconstruct Refractive Index Profiles of Dielectric Planar Waveguides*, Applied Physics, 1987, Vol.B 44, 75-80.
- [53] Liñares J., Lipovskii A.A., Tagantsev D.K., Turunen J., *Characterization of ion diffusion process in glasses with simple mode-index measurements*, Optical Materials, 2000, Vol.14, 115-120.
- [54] Rogoziński R., *Determination of refractive index profiles of planar buried waveguides on the basis of a set of modal propagation constants*, Optics Communications, 2003, Vol.219, 199-214.
- [55] Weiss M.N., Srivastava R., *Determination of ion-exchanged channel waveguide profile parameters by mode-index measurement*, Applied Optics, 1995, Vol.34, No.3, 455-458.
- [56] Tien P.K., Ulrich R., *Theory of prism-film coupler and thin film light guides*, Journal Optical Society of America, 1970, Vol.60, 1325-1337.
- [57] Ulrich R., Torge R., *Measurement of Thin Film Parameters with a Prism Coupler*, Applied Optics, 1973, Vol.12, No.2, 2901-2908.
- [58] Kersten R.T., *The prism-film coupler as a precision instrument*, Optica Acta, 1975, Vol.22, No.6, 503-521.
- [59] Seligson J., *Prism couplers in guided-wave optics: design considerations*, Applied Optics, 1987, Vol.26, No.13, 2609-2611.
- [60] Agan S., Ay F., Kocabas A., Aydinli A., *Stress effect in prism coupling measurements of thin polymer films*, Applied Physics A, 2003, Vol.80, 341-345.
- [61] Lupascu A., Kevorkian A., Boudet T., Saint-André F., Persegol D., Levy M., *Modeling ion exchange in glass with concentration-dependent diffusion coefficients and mobilities*, Optical Engineering, 1996, Vol.35, No.6, 1603-1610.
- [62] Kigre, Inc. 100 Marschland Road, Hilton Head, SC 29926, www.kigre.com
- [63] Schott AG, Hattenbergstrasse 10, 55122 Mainz, Germany, www.schott.com/advanced_optics
- [64] Orignac X., Vasconcelos H.C., Du X.M., Almeida R.M., *Influence of Solvent Concentration on the Microstructure of SiO₂-TiO₂ Sol-Gel Films*, Journal of Sol-Gel Science and Technology, 1997, Vol.8, 243-248.
- [65] Karasiński P., Rogoziński R., *Rib waveguides fabricated by means of chemical etching of sol-gel SiO₂:TiO₂ films*, Optics Communications, 2005, Vol.245, 237-242.
- [66] Karasiński P., Rogoziński R., *Influence of refractive profile shape on the distribution of modal attenuation in planar structures with absorption cover*, Optics Communications 2007, Vol.269, No.1, 76-88.

- [67] Karasiński P., *Sol-gel derived sensitive films for evanescent wave ammonia sensors*, *Optica Applicata*, 2003, Vol.33, No.2-3, 477-487.

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