Li^+ FOR Na^+ ION EXCHANGE IN Na_2O - RICH GLASS: AN EFFECTIVE METHOD FOR FABRICATING LOW-LOSS OPTICAL WAVEGUIDES

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The aim of this work is to develop and to test material and technological solution for the preparation of planar and channel optical waveguides in substrates made of special glasses using the $Li^+ \leftrightarrow Na^+$ ion exchange. This method should ensure wide parameter variability and low losses to these waveguides. We paid special attention to relations between the technological parameters of the preparation process and final waveguide properties.

INTRODUCTION

Optical waveguides based on the $Li^+ \leftrightarrow Na^+$ ion exchange were considered as potential candidates for different types of passive waveguide structures - most often for optical splitters and couplers, in the years 1975 - 1980. The results of performed experiments (see e.g. [1,2]) confirmed that planar optical waveguides could be produced on this principle, nevertheless they also showed that some of the waveguides' properties were unsatisfactory. It applied especially to relatively high optical losses, low numerical aperture (*NA*) and low reproducibility of waveguide preparation. For these reasons research of these types of the waveguides was soon abandoned. The attention was paid to working out methods of preparation of waveguides based on the $K^+ \leftrightarrow Na^+$, $Ag^+ \leftrightarrow Na^+$, and $Tl^+ \leftrightarrow Na^+$ ion exchanges (later also on $Cs^+ \leftrightarrow K^+$) [2,3], where the possibilities of practical use were expected to be better. As the research of new types of active waveguides in glass, $LiNbO_3$ and some other dielectric materials is on the way, we took an opportunity to get back to study the waveguides based on $Li^+ \leftrightarrow Na^+$ ion exchange once more. We tried to find, whether there is a possibility of eliminating their undesirable properties and keeping all of their positive properties at the same time.

TECHNOLOGICAL PROCESS AND MEASURING METHODS

Glass selection and ion sources

Pilot experiments performed with different optical and special silicate glasses revealed that glasses for these specific purposes have to fulfill two main criteria: a) they have to contain a relatively high number of sodium ions for the ion exchange, and b) to contain ingredients which ensure good resistance against surface re-crystallization at higher temperature and surface stress. Experiments with different Li^+ ion sources (melted nitrates, chlorides, sulfates) revealed, above all, that final waveguide quality is not as much related to a chemical structure of the melted ion sources, but depends in particular on optimal relation between the thickness of the ion exchanged (or waveguiding) area and on the used temperature of the process or that of the glass. Due to a high dispersion of ion radii in the exchange, there is usually high-pressure stress (up to 1000 N/mm^2) after cooling the glass down. This can lead to structural defects or, possibly, to the above mentioned surface re-crystallization. This effect is usually negligible when relatively shallow single-mode or multi-mode waveguides are prepared of suitable glasses and at proper conditions. In the case of relatively deep multimode channel waveguides it means that the ion exchange has to be performed in a temperature range within which the glass viscosity reaches maximum of 10^{11} to 10^{12} Pas. This condition is fulfilled for most glasses suitable for these purposes, approximately at a temperature of 500°C and higher. Substantially higher temperature of the ion exchange may cause deformation of the substrates and disintegration of most of the relevant melts. A suitable temperature range is approximately 540 to 590°C, depending on the specific glass type and on the required properties of the waveguide.

With respect to the above mentioned facts our first experiments were focused on preparation of all waveguide types using silicate glass substrates with a relatively high content of Na_2O, made of pure raw materials. The next step was selection of the most suitable Li^+ ion source, optimal ion exchange process temperature and provision of some other technological conditions.

Soda-lime silica glasses containing from 16 to 20 wt.% of Na_2O and a sufficiently high Al_2O_3 content made of very pure raw materials turned out to be the best choice. For glass composition of some of the types used see table 1.

Ion source for single-mode waveguide preparation

We obtained good results when we used multi-component mixtures containing $LiNO_3$ and Li_2SO_4 and some other compounds. The best source for preparation of multimode waveguides was a melted mixture of Li_2SO_4 and sulfates of some other metals (e.g., Na_2SO_4, K_2SO_4, $ZnSO_4$, $MnSO_4$). When using a mixture of two and more components, we can rather precisely set the required value of Δn (and consequently of the *NA*) and we can work at an optimal temperature, which is appropriate both for suitable glass viscosity and to avoid a possible surface re-crystallization.

Basic measurement methods

A basic tool for the measurement of the refractive index profile in the subsurface area of substrates, as well as of the surface change of the refractive index, was mode spectroscopy. In our case we used the prism-coupling setup and inversion WKB approximation for evaluation [2] of the measured data. Experimental data evaluation was performed using a computer program PLANPROF, which enables instant visualization of the profiles [4] . Optical loss measurement was usually performed using a classic method based on the measurement of the transmitted power as a function of the length of the guide - input and output coupling of light was realized by means of optical prism couplers made of suitable optical glass. Usually we used a two-prism setup, but in some cases also the three-prism setup was used. Basic measurements were performed at a wavelength of 0.63 µm; some samples were measured also at 1.3 or 1.5 µm, if needed.

Basic material - technological solution

For single-mode and several-mode waveguide preparation we used above-mentioned multi-component mixtures of $LiNO_3$, Li_2SO_4 and some other sulfates or nitrates, in accordance with particular requirements. We found that the mixture of Li_2SO_4 (80 mol%) and Na_2SO_4 (20 mol%) with the addition of $KHSO_4$ (2 wt.%) was the best choice for both orientation experiments and fabrication of the multimode waveguides samples. In some cases we also used melted mixtures of Li_2SO_4 (50 mol%) and $ZnSO_4$ (50 mol%), or Li_2SO_4 (66 mol%) and $MnSO_4$ (34 mol%) with the addition of $NaHSO_4$ (1.5 wt.%).

For sample preparation we used a reactor, whose basic part was a suitably sized and shaped corundum crucible placed in an oven with precise temperature control.

Table 1. Composition of selected glasses suitable for the $Li^+ \leftrightarrow Na^+$ ion exchange.

	SiO_2	CaO	MgO	Al_2O_3	Na_2O	K_2O	ZnO	note
				(wt.%)				
GIL4	73.28	6.0	4.1	1.1	14.57	0.45	-	fining As_2O_3
GIL4/1	73.28	6.0	3.0	1.1	14.57	0.45	1.1	
GIL49	73.28	6.0	4.1	1.1	14.57	0.45	-	fining As_2O_3
GIL5	71.28	6.0	4.1	1.1	16.57	0.45	-	fining As_2O_3
GIL6	71.28	3.0	4.1	2.55	18.57	-	-	
GIL7	69.28	3.0	4.1	2.55	20.57	-	-	
GIL8	69.33	3.0	4.1	2.0	21.07	-	-	
GIL29/1	69.28	3.0	3.0	2.55	20.57	-	1.1	fining As_2O_3
GIL30	72.53	1.5	3.0	0.8	20.57	-	1.1	
GIL31	72.93	1.5	2.0	0.5	20.57	-	2.0	

KINETICS OF THE $Li^+ \leftrightarrow Na^+$ ION EXCHANGE PROCESS

Part of the experiments was aimed at the acquisition of characteristic kinetic quantities and constants to clarify the $Li^+ \leftrightarrow Na^+$ ion exchange kinetics in different glasses at different physical and chemical conditions. This was necessary to ensure the final technical goals. The first step was the verification of linear dependence of depth increment d(x) on $\sqrt{t}$. With this assumption we can define [2]:

$$n\,(x) = n_s - \Delta n \;\frac{x}{2\sqrt{D(T)t}} \qquad (1)$$

where $D(T)$ is the effective diffusion coefficient at the temperature T. This way obtained diffusion coefficients can be advantageously used for further quantitative analysis of the fabrication processes. For practical specification of the required quantities we use the Arrhenius law

$$D_e = D_o \exp\left(-\frac{R}{kT}\right) \qquad (2)$$

where D_0 is the diffusion constant, Q is the activation energy, k is the Boltzmann constant and R is the gas constant. If we label $D(T)$ as D_e, temperature dependence of D_e can be expressed by a relation

$$D_e = C_1 \exp\left(-\frac{C_2}{T}\right) \qquad (3)$$

With help of graphic representation of the Arrhenius relation (i.e., ln $D_e(T)$ vs. $1/T$), we can specify the values of C_1 and C_2 (or D_0 and Q), using measured values of D_e for different temperatures T. This way determined values of D_0 and Q are for different glasses summarized in table 2.

Table 2. D_0 and Q values in different special glasses during the $Li^+ \leftrightarrow Na^+$ ion exchange

glass	D_0 ($m^2\ s^{-1}$)	Q (10^4J/mol)
FTD*	1.83×10-3	12.01
GIL5	4.80×10-2	8.42
GIL7	8.60×10-3	11.74
GIL27	3.27×10-4	9.73
GIL28	5.36×10-4	9.37
GIL29	2.29×10-4	10.27
GIL30	6.54×10-3	11.04
soda-lime**	5.39×10-3	14.2

* soda-lime glass with low contain of K_2O
** [1]

RESULTS OF THE MEASUREMENT OF OPTICAL LAYERS PROPERTIES

Value of the surface refractive index change

Experiments performed with soda-lime silica glasses containing Na_2O (14 to 23 wt.%) and melted mixtures described in the previous paragraph revealed the following facts: Glasses containing approximately 14 wt.% of Na_2O have maximum values of the refractive index surface change Δn_{max} around 0.008. The reached NA values are then approximately 0.1. These values roughly satisfy the conditions for single-mode planar waveguide preparation. The results, however, also confirmed that the reproducibility of waveguide preparation with a depth less than 10 μm was rather low at temperatures used (and thus at rather short ion exchange times). From the point of view of preparation of highly multimode waveguides (thus with high Δn_{max}) the best results were obtained using the glass containing 24 wt.% of Na_2O; nevertheless the waveguides somesometimes had damaged surface.

From the practical point of view, the most interesting results were obtained during multimode waveguide preparation with substrate glass containing 20 wt.% of Na_2O, when Δn_{max} on the substrate surface was approximately up to 0.016 and NA up to 0.19.

These experiments otherwise showed that the Li^+ ion sources based on lithium sulfate melting had at approximately 500 - 580 °C acceptable stability and did not damage surfaces of the substrates. At the same time we proved that the temperature over 540°C is acceptable from the viewpoint of sufficient decrease of induced mechanical stress in the surface layer; too big stress could potentially cause defects or surface re-crystallization. Somewhat negative finding was that at these temperatures the substrates were sometimes prone to deformation, which could have negative subsequences for some other technological processes (e.g., masking) and for some potential applications of the waveguides. Selection of optimal temperature is thus a very important factor.

Refractive index profiles

Figure 1 shows an example of the dependence $n(x) - n_s = f\,(t)$, which was obtained during the experimental preparation of relatively shallow several-mode waveguides (usually at temperatures below 500 °C), which was measured for TE polarization.

Figure 2 shows an example of the dependence $n(x) - n_s = f\,(t)$ at a typical operating temperature of 580 °C and for different $Li^+ \leftrightarrow Na^+$ ion exchange times measured for TE polarization. For simplicity, the refractive index depth profiles of multimode waveguides are presented as the full lines without points representing particular modes.

The number of modes in relatively shallow waveguides with *NA* around 0.1 and at the wavelength of 1.55 µm was from 1 to 10, in dependence on the particular depth.

The waveguides with *NA* around 0.1 and a depth of several tens of micrometers were usually able to support from 10 to 20 modes. Waveguides with this value of *NA* and the depth corresponding to the core diameter of a standard communication fiber (50 µm) were able to support up to several tens of modes. The number of modes guided by the rather deep (200 to 300 µm) waveguides with the maximum possible NA (over 0.2) was often over 200.

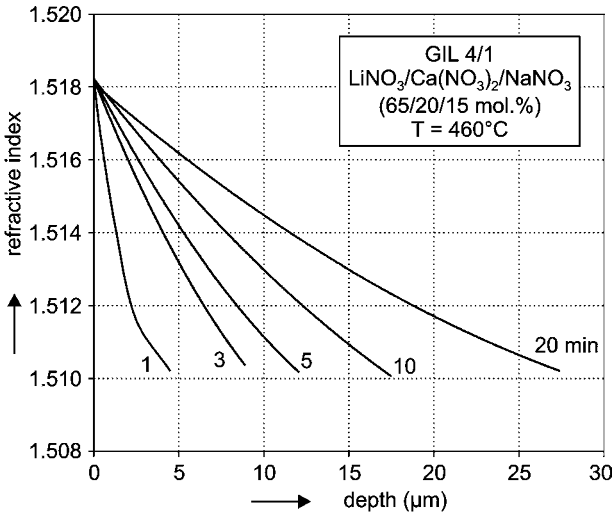

Figure 1. Refractive index profiles of several-mode planar waveguides prepared by the $Li^+ \leftrightarrow Na^+$ ion exchange in substrates made of GIL 4/1 glass.

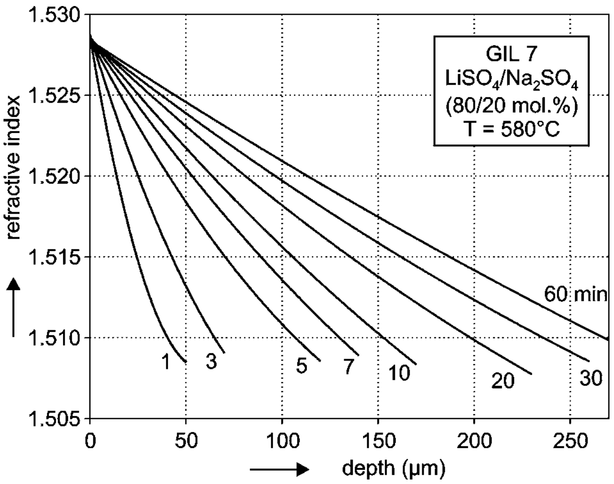

Figure 2. Refractive index profiles of multimode planar waveguides prepared on substrates of GIL 7 glass with different $Li^+ \leftrightarrow Na^+$ ion exchange times.

The comparison of a large number of the refractive index profiles of the waveguides prepared in various glass types using different technological conditions on side, and theoretical curves fitted to different profile types (erfc, gaussian, linear, second-order polynomial) using a least square method on the other side, shows that most profiles approach linear shape, whereas minority of them approach second-order polynomial profiles. The profiles approaching linear dependence are usually observed in multimode waveguides prepared at temperatures higher than T_g (transformation temperature of glass).

The most important finding during these experiment was that using

a) detailed knowledge of the $Li^+ \leftrightarrow Na^+$ ion exchange kinetics in the used glasses,
b) gained experience with preparation of waveguides based on the $K^+ \leftrightarrow Na^+$ the $Ag^+ \leftrightarrow Na^+$ exchange and
c) further careful optimization of the actual conditions during the whole process,

we were able to prepare single-mode, several-mode, or multimode waveguides according to particular requirements. In the case of the multimode waveguides in the glass containing 23 wt.% of Na_2O, we were able to increase the value of Δn_{max} approximately up to 0.19, i.e., to the level, which is necessary for the preparation of multimode waveguides for communication purposes (where *NA* is around 0.2).

Optical losses of the prepared waveguides

When the waveguides were prepared at technological conditions close to the optimal ones, measured optical losses were very low, i.e., approximately 0.1 dB/cm; in some case even lower. Unsuitable technological conditions caused the losses increased up to 1 - 5 dB/cm. In the case of severe surface damage of the samples, (e.g., by induced re-crystallization), the losses were substantially higher than 10 dB/cm. The optical losses of the deep (200 to 300 µm) waveguides that were prepared at optimal technological conditions were at 1.55 µm close to the losses in the used bulk glass, i.e., 0.1 dB/cm.

FACTORS AFFECTING THE REFRACTIVE INDEX PROFILES

Influence of the ion exchange kinetics

The $Li^+ \leftrightarrow Na^+$ ion exchange can considerably differ, depending on particular experimental conditions, mainly due to various compositions of the substrate glasses. This supports a hypothesis, that anomalous refractive index profiles (which we mentioned in the previous chapter) are primarily caused by different Na^+ and Li^+ ion mobility (μ_{Na} and μ_{Li}) during the exchange processes performed at different conditions. With respect to the facts stated for example in [2], the influence of different mobility of the participating ions can be quantitatively assessed using the parameter $\alpha = (1 - D_{Li}/D_{Na})$ in the one-dimensional diffusion equation

$$\frac{\partial N_{Li}}{\partial t} = \frac{\partial}{\partial x}\left(\frac{nD_{Li}}{1 - \alpha \bar{N}_{Li}}\right)\frac{\partial \bar{N}_{Li}}{\partial x} \tag{4}$$

where N_{Li} is molar concentration of Li^+ ions or in the equation for the inter-diffusion coefficient

$$D_{Li\text{-}Na} = \frac{nD_{Li}}{1 - \alpha \bar{N}_{Li}} = \frac{D_{Li} D_{Na} n}{D_{Li} \bar{N}_{Li} + D_{Na} \bar{N}_{Na}} \tag{5}$$

where $\bar{N}$ means the concentration of the considered exchanged ions in molar ratios and D_{Li} and D_{Na} are the respective (self)diffusion coefficients. Considerable influence of the coefficient α on the whole exchange character and thus on the resulting refractive index profile, shows a fact, that at real initial and boundary conditions considered at the solution of the diffusion equation, we can expect a steep, almost step-like, profile for $\alpha \to 1$, whereas for $\alpha \to 0$ the profile would be close to the complementary erfc function. This was verified by computation.

The approximate calculation shows that the values of α could be found in a broad interval ranging from 0.64 to 0.99. This strongly supports the hypothesis that the ratio of μ_{Na} and μ_{Li} at different diffusion conditions substantially affects the final shape of the refractive index profile.

Influence of mechanical stress

According to our knowledge some other factors could affect atypical or anomalous refractive index profiles, especially at lower temperature of the ion exchange ($T \leq 520$°C) or at some other conditions (use of special glasses containing more than 18 mol% of Na_2O or long exchange times). The most probable factor is the presence of in-homogeneities in the glass (gradient of the glass composition or the presence of a layer with different composition in the direction to the bottom of the vessel, where the molten glass had been poured into). Possible are also mechanical stress gradients, which occur during the waveguide preparation at lower temperature (thus at higher viscosity) caused by a significant difference of the $Li^+ \leftrightarrow Na^+$ ion radii ($r_{Li}/r_{Na} = 0.69$). The observed mechanical stress in the area of ion exchange raises a question, how this stress can contribute to the overall change of the refractive index. An estimative evaluation of the mechanical stress contribution in the waveguide area to the overall change of the refractive index during $Li^+ \leftrightarrow Na^+$ ion exchange showed that at real conditions this contribution could be between several thousandths up to ten-thousandths. However, for a number of reasons, the interpretation of these results, which could lead to a more general conclusion, is not simple.

INVERSE ION EXCHANGE

The depth refractive index profile and also the optical losses of the waveguides can be influenced by a complementary technological step. A short inverse $Na^+ \leftrightarrow Li^+$ ion exchange can complement the basic simple and purely thermal $Li^+ \leftrightarrow Na^+$ ion exchange. Examples of several multimode waveguide profiles created by means of this method are shown in figure 3. The figure clearly shows that at specific conditions we can obtain a completely symmetrical refractive index depth profile. This profile is very advantageous for coupling light to optical fibers. Using this method we can in practice completely eliminate the contribution of the surface scattering. The losses are then on the level corresponding to the losses of the used bulk glass (for the GIL3 to GIL6 glasses we obtained the losses below 0.1 dB/cm). Figure 3, however, shows, that reaching symmetric profiles using inverse the $Na^+ \leftrightarrow Li^+$ ion exchange causes considerable decrease of Δn_{max}, and thus the achieved range of the *NA* value is substantially limited. While for preparation of some multimode waveguide types this limitation can be critical, the inverse ion exchange can be a very useful technological step for the preparation of single-mode or few-mode waveguides.

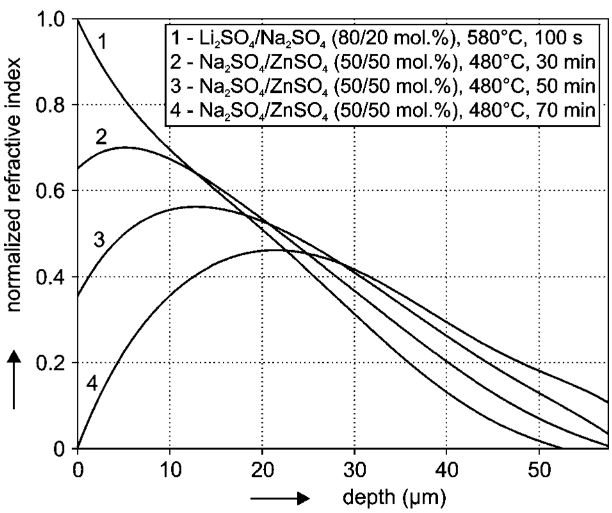

Figure 3. Refractive index profiles of the waveguides prepared using the $Li^+ \leftrightarrow Na^+$ ion exchange at different conditions of subsequent inverse $Na^+ \leftrightarrow Li^+$ ion exchange.

We expected that the purely thermal inverse $Na^+ \leftrightarrow Li^+$ ion exchange is in principle possible, because of the physical and chemical basis of the exchange processes in the glass. Nevertheless, somewhat surprising was its almost perfect reproducibility (i.e., maintenance of the N_{Na}/N_{Li} distribution and subsequently also of the refractive index profile) at the same thermodynamic conditions. Another surprise was that the multiple repetition of the bi-directional exchange did not significantly increased the number of structural defects in the surface glass layers.

PREPARATION OF CHANNEL WAVEGUIDES

The major problem of channel waveguide preparation was to acquire suitable material and to prepare a slot diffusion mask on the glass surface, which had to be sufficiently chemically and thermically resistant, as well as completely impenetrable for the Li^+ and Na^+ ions. We found that relatively high optical losses (usually 1 to 2 dB/cm at the wavelength of 0.63 μm, sometimes even higher) mentioned in the most of published papers were not in fact due to the losses of the waveguides themselves, but resulted from a thin highly-loss layer, which was formed during the preparation closely underneath the surface of the glass substrate (and thus in the surface part of the waveguides). That layer was formed owing to chemical interaction of a commonly used mask made of a thin layer of aluminum, and glass surface at high temperature necessary for the waveguide preparation (500 to 580°C). We eliminated this effect by the use of multilayer slot masks based on a combination of chromium and aluminum layers and then we were able to decrease the losses of the waveguides again to 0.1 dB/cm.

CONCLUSIONS

The results of the experiments have shown that using substrates made of special glasses and after optimization of the technological process, we can prepare single-mode, few-modes and multimode waveguides with properties suitable for a number of practical applications. These properties include not only the necessary value of the *NA* (0.1 to 0.2), low optical losses (achieving 0.1 dB/cm at $\lambda = 0.63$ μm), but also the possibility of various refractive index profiles. We also proved the possibility of overall improvement of the reproducibility of geometrical parameters of the channel waveguides and a decrease of their optical losses.

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IONTOVÁ VÝMĚNA $Li^+ \leftrightarrow Na^+$ VE SKLECH S VYSOKÝM OBSAHEM NA_2O: ÚČINNÁ METODA PRO PŘÍPRAVU NÍZKOZTRÁTOVÝCH OPTICKÝCH VLNOVODŮ

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V článku je popsáno studium přípravy a vlastností planárních optických vlnovodů iontovou výměnou $Li^+ \leftrightarrow Na^+$ ve speciálních optických sklech typu GIL. Iontové výměny byly prováděny při teplotách blízkých Tg ve směsích roztavených síranů obsahujících jako jednu ze složek síran lithný. Při tomto procesu vznikají velmi hluboké mnohovidové vlnovody (vedoucí až 200 vidů), ale jeho režim umožňuje i přípravu několikavidových a jednovidových vlnovodů s velmi nízkými optickými ztrátami (> 0.1 dB/cm) a relativně vysokou numerickou aperturou NA (0.2). Speciálně vyvinutá vícevrstvová maska umožnila i přípravu nízkoztrátových kanálkových vlnovodů vhodných k vazbě s optickými vlákny.