# PLANAR OPTICAL WAVEGUIDES IN NEWLY DEVELOPED Er:SILICATE GLASSES: A COMPARATIVE STUDY OF K$^+$ AND Ag$^+$ ION EXCHANGE

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*Materials containing laser-active ions (e.g. erbium and other rare earths) in combination with planar optical waveguides technology are being recently investigated in order to obtain optical amplifying or lasing structures for photonics applications. This contribution reports about fabrication of optical waveguides in newly designed silicate glass substrates by ion exchanges (IE) K$^+$ ↔ Na$^+$ and Ag$^+$ ↔ Na$^+$. The content of erbium and sodium in these glasses was kept constant while the ratio of glass intermediates, MgO, CaO and ZnO differed. The optical properties´ characterisation of the fabricated layers (i.e. number of modes and refractive index profile) was performed by dark mode spectroscopy at 671 nm. Another important information on depth of the optical layers was obtained by polarising optical microscope. Concentration depth profiles of the exchanged ions were analysed by scanning electron microscopy. Special attention was paid to possibility of Er ions migration during the fabrication process. The Ag$^+$ exchange proceeds with much higher velocity than the K$^+$ one and provides optical layers with more or less step-like refractive index profiles. On the other hand the K$^+$ waveguides have graded shape of these profiles with much smaller refractive index increment (approx. 0.009) compared with Ag$^+$ ones (approx. 0.09) and relatively high TE-TM birefringence. Neither difference in Er ions distribution nor micro-cluster formation was observed (being under the detection limit). The results are discussed from the point of view of the glass matrix permeability for the exchanged ions and potential applications of both types of the waveguides.*

## INTRODUCTION

The rapid development of erbium-doped silica fibre amplifiers and lasers has resulted in heightened interest in erbium doped planar waveguide devices ([1] and 210 references therein). Planar waveguides devices have the advantages that they can be defined photolitographically, and waveguides geometry may be varied along a device for efficient interfacing to external components and for optimisation of the individual components. Moreover, such devices are small, stable and easy to handle.

One of the most popular materials for planar waveguides is glass. Ion exchanged glass waveguides have the advantages that they are simple, inexpensive, well compatible with optical fibres and employ a very flexible fabrication process with straightforward control over the waveguide parameters. As a host matrix, silicate glass has been so far in a shade of phosphate glass, which was considered much better media for the Er$^{3+}$ performance (large emission cross section and a weak interaction among active ions, which may cause concentration quenching).

Silicate glasses, on the other hand, have much better chemical stability important for ion-exchange techniques to fabricate optical waveguides. Certain disadvantages of the up to now used silicate glasses have been a strong tendency to clustering of the rare earth ions, shorter lifetimes and lower optical gain obtained when using commercial substrates. However, feasibility to fabricate silicate glass in a wide range of possible compositions makes the question of usability of the silicate glass in active integrated optics structures still opened (e.g. [2, 3]).

We have already studied how the composition of the bulk glasses may affect properties of the $Er^{3+}$ ions from the point of view of their potential usability in active photonics devices [4]. Here we present the results of the study how the composition of the above mentioned erbium-containing glass influences the resultant properties of the ion-exchanged waveguides.

### EXPERIMENTAL

In our experiments we used a set of newly designed silicate glasses with constant $Er_2O_3$ and $Na_2O$ content and varying covalence of the matrix. Glass samples with different covalence were obtained by varying ratio of oxides of the divalent cations (MgO, CaO and ZnO), while their total molar content was kept constant (see table 1).

The samples were obtained from the bulk glass by cutting to rectangular parallelepipeds and both sides polishing to optical quality. The substrates were carefully pre-cleaned in a series of solvents (isopropyl alcohol, etc.) before the experiment and pre-heated to avoid cracking of the surface when immersing substrates in the reaction baths.

The optical waveguides were fabricated in these substrates by $Ag^+\leftrightarrow Na^+$ and $K^+\leftrightarrow Na^+$ ion exchanges. The ion exchange reactions occur after placing the samples in the melts (i.e. eutectic mixture of sodium and potassium nitrates with addition of 24 wt. % of silver nitrate; and pure potassium nitrate in the case of $Ag^+\leftrightarrow Na^+$ and $K^+\leftrightarrow Na^+$ exchange, respectively) at desired conditions. To fabricate few-modes planar waveguides, temperatures 375°C ($K^+$ ones) and 280°C ($Ag^+$ ones) were used, while duration of the reactions were 2–4 h and 5–20 min, respectively. The samples were cooled to room temperature after the ion exchange and washed with water and isopropyl alcohol to remove residuals of the melts.

Standard dark mode spectroscopy at 671 nm (employing the inverse WKB method) was used to characterize waveguiding properties of the fabricated layers, i.e. number of guided modes, refractive index vs. depth profile, total refractive index increment in the surface layer and effective depth of the optical (functional)

layer. Polarizing optical microscope was used to determine effective depth of the exchanged layer, i.e. depth of the anisotropic layer, which was formed by internal strain (introduced into the sample surface by exchange of ions with different ionic radii).

Changes in chemical composition of the surface layers of the substrates, i.e. concentration profiles of the exchanged ions ($Ag^+$, $K^+$, $Na^+$), was studied by Scanning Electron Microscopy (SEM) with Energy Dispersive Spectrometer (EDAX). Special attention was paid to possibility of (undesirable) changes in $Er^{3+}$ ion distribution during the fabrication process.

### RESULT

Permeability of the particular substrates

The main aim of this project was to find the experimental conditions for fabrication of few-modes planar optical waveguides in a set of newly developed glasses and characterize their properties.

In the first experiments we found out that particular glasses differ significantly in the effect of the ion exchange on the resultant properties of the fabricated layers. The glass samples can be divided into two groups (depending on their covalence) from the point of view of their permeability (i.e. invasion depths) for both types of ion exchange: i) MM40, MM42 (more covalent) and ii) MM38, MM39, MM41 (less covalent).

The substrates from the first group are much more permeable for the diffusing ions, i.e. fabricated layers are much deeper (more significant effect of IE). The waveguides fabricated in the substrates that belong to the second group (ii), both $K^+$ and $Ag^+$ ones, were supporting few modes even after longer times of ion exchange. To obtain few (2 or 3) modes waveguides in the first group of substrates (i) duration of the ion exchange had to be substantially shorten to decrease depths of the fabricated layers and consequently lower number of the guided modes. The waveguides with required properties were fabricated after decreasing duration of the IE reaction to one half ($K^+$ exchange) or even one quarter ($Ag^+$ one) of the value for (ii) glasses (table 2).

Table 1. Composition of the newly designed glass samples with increasing covalence of the structure.

| CaO | MgO | ZnO | Glass covalence | Na₂O | Er₂O₃ | Glass sample nr. |
|---|---|---|---|---|---|---|
| | (total content is constant) | | | | | |
| • | • | | | | | MM38 |
| • | | • | | | | MM39 |
| • | • | • | ⇓ | 12.0 | (2.0) | MM41 |
| | • | • | increase | wt.% | wt.% | MM40 |
| | | • | | | | MM42 |

### Chemical composition of the exchanged layers

Major difference between permeability of (i) and (ii) glass substrates can be also well seen from figure 1, in both cases functional ions diffused more readily into the more covalent glasses. The plot also shows different progression of the $Ag^+$ and $K^+$ ion exchange. Owing to the fact that $Ag^+$ ions are much smaller than $K^+$ ones, their velocity and consequently depth of their invasion is much higher. However, not only the depths of the fabricated layers are highly dependent on the type of ion exchange but also the shapes of the concentration profiles are completely different. The final distribution of potassium ions in the layers is much more graded (i.e. more homogeneous) and thus corresponds well with the slower ion exchange process.
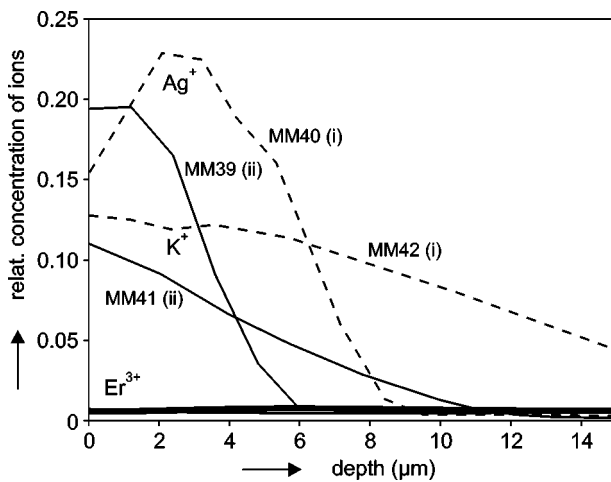


Figure 1. Depth profiles of relative (atomic % $XO/SiO_2$) concentration of the exchanged ions ($X = K^+$, $Ag^+$ and $Er^{3+}$) (fabrication conditions are: $K^+$ exchange: 375°C, 4 h and $Ag^+$: 280°C, 20 min).

SEM (Scanning Electron Microscopy) proved that the fabrication process did not affect the erbium ions distribution and luckily no microcluster formation was observed. The clusters in the waveguiding region would contribute to the optical losses and, first of all, deteriorate active function of the waveguides due to the quenching effect.

### Optical properties of the exchanged layers

The refractive index vs. depth profiles, obtained by dark mode spectroscopy, correspond well with the profiles of functional ions´ concentration. Typically, n(x) profiles of the $Ag^+$ waveguides are concave step-like curves with a relatively high total refractive index increment (approx. 0.1) on a short distance (depth of the few-mode waveguiding layers is approx. 3.5 µm). On the other hand, the $K^+$ waveguides exhibit a small total refractive index increment (about 10 % of the value of $Ag^+$ ones - table 3) while depths of the optical layers are almost 200 % of $Ag^+$ waveguides. This fact implies that the $Ag^+$ waveguides are "strongly guided", i.e. utilizable in integrated optics and as amplifiers, and the "weakly guided" $K^+$ waveguides are then potential candidates for optical sensors with high resolution.

Table 3. Total refractive index increment in the fabricated few-modes waveguiding layers. ($K^+$: 375°C, 2 or 4 h; $Ag^+$: 280°C, 5 or 20 min)

| Glass sample nr. | $\Delta n$ (mode spectroscopy) | |
|---|---|---|
| | $K^+$ | $Ag^+$ |
| MM38 | 0.00747 | 0.09605 |
| MM39 | 0.00813 | 0.09407 |
| MM40 | 0.00919 | 0.08552 |
| MM41 | 0.00889 | 0.08274 |
| MM42 | 0.00918 | 0.09296 |

Table 2. Conditions for fabrication of few-modes waveguides in novel glass substrates and their resultant optical properties [$T$($K^+$ exchange) = 375°C, $T$($Ag^+$ exchange) = 280°C]; * TE - polarisation of guided radiation.

| Glass sample nr. | IE times | | Number of modes* | | Depth* (µm) (mode spectroscopy) | | Depth (µm) (microscope) | |
|---|---|---|---|---|---|---|---|---|
| | $K^+$ | $Ag^+$ | $K^+$ | $Ag^+$ | $K^+$ | $Ag^+$ | $K^+$ | $Ag^+$ |
| MM38 (ii) | 4 hrs | 20 min | 2 | 3 | 5.7 | 3.2 | 11.3 | 4.5 |
| MM39 (ii) | 4 hrs | 20 min | 2 | 3 | 5.5 | 3.6 | 10.2 | 5.1 |
| MM40) (i) | 2 hrs | 5 min | 3 | 3 | 8.2 | 3.4 | 9.0 | 5.1 |
| MM41 (ii) | 4 hrs | 20 min | 3 | 3 | 6.8 | 3.4 | 9.0 | 6.1 |
| MM42 (i) | 2 hrs | 5 min | 3 | 3 | 8.2 | 3.6 | 7.3 | 6.0 |

Comparison of the depths of the fabricated layers determined by mode spectroscopy and by microscope (table 2) brought interesting information. There was also a great difference between the two types of ion exchanges observed - in both cases the depths obtained by microscope were bigger, but K⁺ exchanged layers were almost two times deeper. The reason for that is that in K⁺ waveguide fabrication the exchange occurs between ions of much more diverse ionic radii (K⁺ = 138 pm, Na⁺ = 102 pm *vs.* Ag⁺ = 115 pm), i.e. the internal strain (and depth of the anisotropic layer determined by polarising microscope) incorporated in the surface layers is in this case much higher. The relatively high strain in K⁺ waveguides approves itself as an optical birefringence, which can be found when comparing refractive index vs. depth profiles measured for TE (transversal electric) and TM (transversal magnetic) polarisation of the guided radiation. Optical birefringence in Ag⁺ waveguides is very small, i.e. n(x) profiles are almost identical, while K⁺ ones differ significantly, even in the number of guided modes.

## DISCUSSION

### Glass covalence and permeability

The observed differences in glass permeability can be explained by different chemical behaviour of each particular divalent cation present in the structure. The ionic character of the cations ($Ca^{2+}$ + $Mg^{2+}$) means quite strong electrostatic forces between the non-bridging oxygen and the neighbouring Na⁺ ion, which impedes the free movement of the sodium ion throughout the glass matrix slowing thus the exchange of the Na⁺ for another ions. Increasing covalence of the divalent

cations then results in weaker bonding interactions between non-bridging oxygen and glass modifiers (in this case Na⁺ ions). It means, that for the most covalent glass one can expect the deepest penetration of the diffusing particles and vice versa. The sequence Ca + Mg → Ca + Zn → Ca + Mg + Zn → Mg + Zn → Zn shows the increasing covalence (i.e. decreasing basicity) of the glass, which here corresponds very well with the properties of the ion-exchanged waveguides - the most ionic glass (containing CaO + MgO) produced the shallowest waveguides that supported the lowest number of guided modes and, on the other hand, the deepest multimode waveguides were created in the most covalent glass containing ZnO only.

### Difussion coefficients

To express different permeability of the particular glasses numerically, effective diffusion coefficients were calculated from the simple formula for depth of invasion of diffusing ions:

$$x = \sqrt{4.D.t} \quad \rightarrow \quad D_{eff} = \frac{x^2}{4.t}$$

where x is depth of the anisotropic layer obtained by polarising microscope, $D_{eff}$ is effective diffusion coefficient and t is duration of the ion exchange. The resultant values of diffusion coefficients are given in table 4. From this table it is clear that the MM42 glass is the most permeable one and the MM40 substrate is the second one for both types of ion exchange. The Ag⁺ exchange proceeds with much higher velocity than K⁺ one - even at lower temperature (280 vs. 375°C) and shorter duration (20 min vs. 4 hrs) - in these glasses at least two times faster.

## CONCLUSIONS

A series of newly designed glasses was examined from the point of view of few-mode waveguide fabrication. The experimental results showed that increasing covalence of the glass increases the rate of the ion exchange reactions. Waveguides fabricated in the most covalent glass (MM42, from divalent oxides containing only ZnO) were the deepest ones and supported the highest number of modes.

K⁺ and Ag⁺ few-mode optical waveguides were fabricated in all glass types and the effect of type of ion exchange was then studied. Weakly guided K⁺ waveguides were suggested to be utilizable in optical sensors while strongly guided Ag⁺ ones to be used in optical amplifiers.

Table 4. Total refractive index increment in the fabricated few-modes waveguiding layers. (K⁺: 375°C, 2 or 4 hrs; Ag⁺: 280°C, 5 or 20 min)

| Glass sample | Depth (μm) (microscope) | | Diffusion coefficient (10⁻³ μm²/s) | |
|---|---|---|---|---|
| | K⁺ | Ag⁺ | K⁺ | Ag⁺ |
| MM38 (ii) | 11.3 | 4.5 | 2.22 | 4.22 |
| MM39 (ii) | 10.2 | 5.1 | 1.81 | 5.42 |
| MM40 (i) | 13.4 | 7.7 | 3.12 | 12.35 |
| MM41 (ii) | 9.0 | 6.1 | 1.41 | 7.75 |
| MM42 (i) | 19.6 | 7.9 | 6.67 | 13.00 |

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## PLANÁRNÍ OPTICKÉ VLNOVODY V NOVĚ VYVINUTÝCH Er-DOPOVANÝCH KŘEMIČITÝCH SKLECH: SROVNÁVACÍ STUDIE IONTOVÉ VÝMĚNY K⁺ A Ag⁺

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Materiály obsahující laserově-aktivní ionty (např. erbium a další vzácné zeminy) v kombinaci s technologií planárních vlnovodů jsou v současnosti zkoumány jako optické zesilovače a laserující struktury pro fotonické aplikace. V této práci popisujeme přípravu optických vlnovodů v nově navrhovaných křemičitanových sklech iontovou výměnou (IE) K⁺ ↔ Na⁺ a Ag⁺ ↔ ↔ Na⁺. Obsah Er a Na v těchto sklech byla konstantní zatímco poměr dalších složek, tj. MgO, CaO a ZnO, se lišil. Charakterizace optických vlastností připravených vrstev, tj. počet vidů a profil indexu lomu, jsme prováděli vidovou spektroskopií při 671 nm. Další důležitá informace, hloubka optických vrstev, byla získána optickou polarizační mikroskopií. Hloubkové koncentrační profily vyměněných iontů byly analyzovány řádkovací elektronovou mikroskopií (SEM). Zvláštní pozornost jsme věnovali možnosti, že během přípravy migrují ionty Er. Výměna Ag⁺ probíhá s mnohem rychleji než výměna K⁺ a poskytuje optické vrstvy s víceméně skokovým profilem indexu lomu. Na druhé straně K⁺ vlnovody měly pozvolný tvar těchto profilů s mnohem menším přírůstkem indexu lomu (asi 0.009) než Ag⁺ (asi 0.09) a poměrně vysokým TE-TM dvojlomem. Nepozorovali jsme ani rozdíly v distribuci iontů Er ani tvorbu mikroklastrů (byly pod mezí detekce). Výsledky jsme diskutovali s ohledem k propustnosti skleněné matrice pro vyměňované ionty a možné použití obou typů vlnovodů.