Influence of transition metal ions on properties of planar glass optical waveguides

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We present a study of fabrication and properties of the planar optical waveguides fabricated by Ag^+, Cu^+, Cu^{2+} and Er^{3+} ion exchange (IE) in a variety of commercial as well as non-commercial optical glasses.

The properties of the waveguides are discussed from the point of view of the composition of the substrate glasses (esp. taking into account the ratios of the bridging and non-bridging oxygen atoms in the glass matrixes and fining agents), luminescence and waveguiding properties as refractive index profiles and birefringence. The samples containing exclusively Cu^+ exhibited very strong blue-green luminescence despite their low content in the exchanged layers. The Er^{3+} waveguides are presented for the first time.

Introduction

Optical techniques are in the forefront of a large variety of modern techniques due to their inherent high specificity. One of the possibilities to fabricate a large family of optical devices is ion exchange in glass. Ion-exchange technique occurs by immersing the glass substrate into the bath (typically a melt) containing a salt of the "functional" cation. This technique which has been used for more than a century to produce tinted glass, has received increased attention in recent years as it improves surface mechanical properties of glass and, maybe more important, may create a waveguiding region in glass[1-4]. Today, glass waveguides are considered to be prime candidates for optical signal processing applications in optical communications, sensors and other related areas. The importance of the glass waveguides components is borne out by their compatibility with optical fibers, potentially low cost, low propagation losses and the ease of their integration into the system. The refractive indices of the glass substrate cannot be changed by application of an external electric field, so the glass waveguides may be used only as passive optical components (in spite of e.g. lithium niobate waveguides, which may serve also as dynamical components with electro-optic properties). Nevertheless, the properties of glass can be tuned in a wide range of possibilities which, when laser active ions are incorporated into the substrate, allow also to utilize the glass waveguides as the active waveguides in optical amplifiers and/or waveguide lasers.

Experiments

The used substrates were several commercial glasses (as BK7, Corning 0211 or IOG10) and specially formulated silicate-based glasses with various content of alkali including lithium. Fabrication of the waveguides occurred by immersing the thoroughly pre-cleaned one or both sides polished glass wafers into the melted baths containing the Ag^+, Cu^+, Cu^{2+} and Er^{3+} salts and keeping there at the desired temperatures for the desired times. The actual conditions of the fabrication differed according to particular exchanged ions. Waveguiding properties of the samples were characterized at λ= 671 nm using the dark mode spectroscopy. Composition of the waveguiding layers was studied by using several methods. Concentration depth profiles of copper and erbium were determined by using the Rutherford Backscattering Spectrometry (RBS). Concentration depth profiles of the coppers and silver ions in thick layers were measured by using Scanning Electron Microscopy (SEM). Neutron Depth Profiling (NDP) measured lithium concentration depth profiles. The presence of Ag^0 and Cu^{2+} in the waveguides was detected by the Electron Paramagnetic Resonance (EPR) measurement. Photoluminescence spectra of the samples were taken in the range of 200 – 900 nm.

Transition metal ions-exchanged waveguides

Transition metal ions presented here as “functional” and/or the waveguide-forming cations are the ions of silver, copper and erbium. Each one of them has its advantages and drawbacks and poses special problems to be solved.

Silver

Waveguides made by Ag^+ ion exchange are perhaps the mostly and longest time used for fabrication of the ion-exchanged-based optical devices ([1-4] and references therein). The Ag^+ waveguides were widely studied during the eighties for utilization in multi-mode waveguides. Their popularity dropped down when the single-mode optical fibers were introduced into a routine use. It increased again in the end of the nineties, because they are useful especially for devices, which require strong directional coupling together with low-loss small-radius curves. Though a lot of papers on the Ag^+ waveguides are available there are still several issues, which have not yet been explicitly addressed in the literature. One of them is the serious drawback of the Ag^+ waveguides that the Ag^+ ions are susceptible to being reduced to metallic form and thereby may introduce higher optical losses into the resulting waveguides. Such metallization may be caused by several factors, some of them is presence of reducing fining agents in the glass matrix, and another one may be the ion-exchange process itself when carried out using reducing bath composition.

Investigation described in this paper was directed mainly to lowering the risks of the high optical losses caused by reduction of Ag^+ to Ag^0. The Ag^+ exchanged waveguides were fabricated by using melts of sodium nitrate (or eutectic mixtures of sodium-potassium nitrates) that contained various amounts of silver nitrates. The typical reaction temperatures ranged from 280 to 350 °C, duration of the exchange varied from minutes to several hours. In Fig. 1 are given the EPR spectra of some of the samples showing the typical feature of the Ag^0 in the As_2O_3-fined substrate glass in comparison with the waveguide that were fabricated in the special GIL49 glass where for fining was used different, non-reducing, approach. The presence of the reducing fining agents seems to have stronger effect on the metallization of the Ag^+ in the waveguiding region then the higher amount of the non-bridging oxygen atoms.

Copper

The copper-ion-exchanged waveguides were scarcely mentioned in literature ([5]and references therein) during last few years. Their perhaps the most interesting feature (and the drawback the same time) is the existence of two relatively stable oxidation states – Cu(I) and Cu(II), representing the cations Cu^+ and Cu^{2+}.

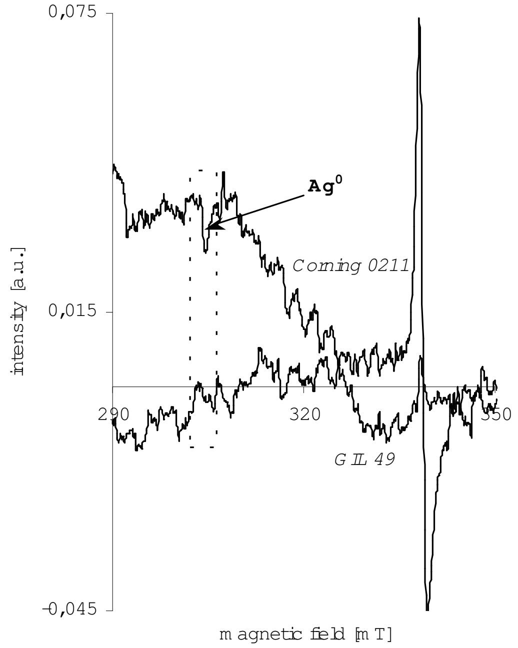

Fig. 1 EPR spectra of the Ag^+ exchanged waveguides in Corning 0211 and GIL 49 showing the signal of metallic silver in the Corning 0211.

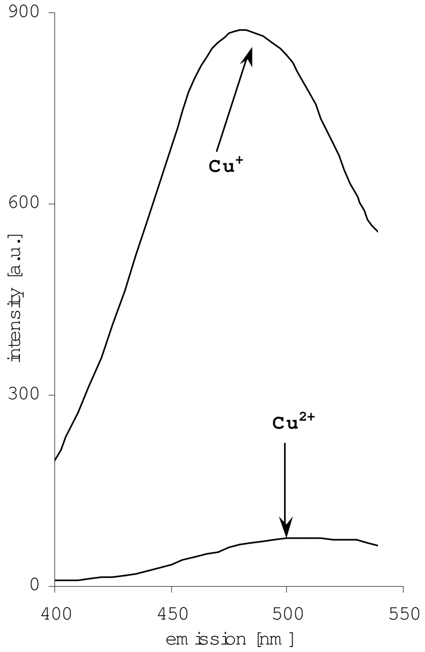

Fig. 2 Blue-green emission of the copper waveguides fabricated in GIL 49 ($[Cu^+]=9.98 \cdot 10^{15}$ at.cm^{-3}, $[Cu^{2+}]=1.99 \cdot 10^{17}$ at.cm^{-3})

Each of them has its characteristic performance. The ionic radius of the Cu^+ is very similar to that of Na^+, which makes the Cu^+ exchanged waveguides potentially suitable for the devices demanding zero or negligible birefringence.

We have carried out the ion exchange of the Cu^{2+} and Cu^+ ions with special focus on determination and/or stability of the each particular type of ion in the waveguiding layers. The waveguides were fabricated in a eutectic mixture of sodium and cupric sulphates (Cu^{2+}) or cuprous chloride in which the Cu^+ was stabilized with adding the zinc chloride into the reaction bath. The Cu^{2+} -ion exchange proceeded very quickly and resulted in formation of very deep waveguides with high refractive index increment (up to +0.0693) and surprisingly low birefringence. EPR measurement shows the presence of high amount of Cu^{2+} (Fig. 3), but no blue-green luminescence (Fig. 2), which is a unique property of the Cu^+.

In spite of that, the exclusively Cu^+ containing samples (the later fabrication approach) exhibited extremely strong blue-green luminescence[6,7], despite a very low concentration of the Cu^+ in the exchanged layers (10^{15} at.cm^{-3}). The explanation of the low birefringence of the Cu^{2+} exchanged waveguides may be that the terminal oxygen atoms (NBO) act as Lewis base and their non-binding electron pairs are partly donated to the Cu^{2+} ions (Lewis acid) in their vicinity making thus the Cu-O distance to that corresponding Cu_2O[5]. But this sharing of the electron pairs does not mean any real reduction of the Cu^{2+} to the Cu^+, as was proved by the absence of the blue-green luminescence of the Cu^{2+} exchanged samples.

Cu^{2+} exchanged waveguides may be considered a promising alternative to the Ag^+ exchanged waveguides as they would not suffer from the risk of the metallization causing high losses in the "silver" waveguides.

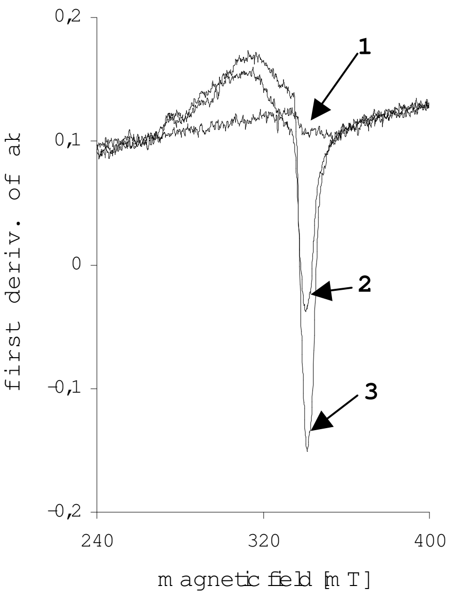

Fig. 3 EPR spectra of the copper waveguides in GIL 49
(Fabrication: 1 - Cu_2Cl_2 + $ZnCl_2$ melt, 2 - Cu_2Cl_2 melt, 3 - $CuSO_4$:Na_2SO_4 melt)

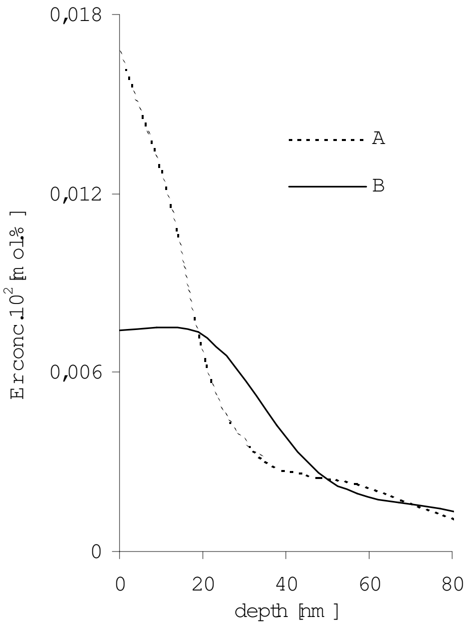

Fig. 4 Erbium depths profiles of ion-exchanged (A) and post-exchange annealed (B) waveguides in GIL49.

Erbium

Rare earth-doped waveguides are useful components to make active devices such as lasers, optical amplifiers and, recently also waveguide lasers. The most important property of the rare-earth doped waveguides is that they amplify optical signal. The mostly used rare-earth laser active ion is Er^{3+} due to its $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission at 1550 nm, i.e. in the third window used in telecommunications. Very recently also other transitions of the Er^{3+} are subject of intensive study. It was stated that high efficiency of the above mention emission can be gained only in phosphate glasses, nevertheless, recently appeared some hints on laser set-up based on erbium-doped silicate glass substrate. For the waveguide laser application a localized doping is more suitable so that the Er^{3+} ions are located only in the waveguiding layer. This was reported only for optical crystals (as lithium niobate) where the hightemperature diffusion of erbium occurs from a metal thin layer evaporated onto the surface of the single-crystalline wafer.

We have studied a possibility of using the ion-exchange approach to incorporate erbium ions into the silicate-based types of glass. The doping was done in bath of nitrates containing erbium nitrate and was successful when the electric-field assisted process was applied and also in several cases when the purely thermal diffusion occurred. The key factor for such a doping was the composition of the substrate glass, mainly the presence of mobile ions, which helped introducing the erbium ions into the glass matrices. The fabricated Er-in-diffused layers were rather shallow, but further annealing of the samples extended them deeper into the substrate (Fig. 4).

Conclusion

We have studied planar optical waveguides produced by ion exchange of transition metal ions with special focus on stability of the oxidation states of the exchanged ions (Ag^+, Cu^+ and Cu^{2+}) and on possibility of localized doping of Er^{3+} into the glass surfaces. Using the reducing fining agents increases the risk of high optical losses in the Ag^+ waveguides, due to reduction of Ag^+ to Ag^0. Adding zinc chloride into the cuprous chloride stabilized the Cu(I) in the waveguides which then exhibited very strong blue-green luminescence. Erbium-containing thin surface layers were fabricated by using electric-field-assisted diffusion with help of migration of mobile ions. All the studied waveguides are potentially suitable as active waveguides in the visible spectral region.

Acknowledgement

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