# Photosensitivity of ion-exchanged Er-doped phosphate glass using 248nm excimer laser radiation

**Stavros Pissadakis and Aris Ikiades**

*Institute of Electronic Structure and Laser, Foundation for Research and Technology – Hellas, PO Box 1527,*
*71 110 Heraklion, Greece*
pissas@iesl.forth.gr

**Ping Hua, Anna K. Sheridan and James S. Wilkinson**

*Optoelectronics Research Centre, University of Southampton, SO17 1BJ, Southampton UK*
jsw@orc.soton.ac.uk

**Abstract:** The photosensitivity to 248nm excimer laser radiation of Er-doped Schott IOG-1 phosphate glass is presented. The photosensitive mechanism is investigated by employing a grating recording process. Index changes of up to ~2.0x$10^{-3}$ were measured in silver ion-exchanged samples using diffraction efficiency measurements; whereas changes of only ~$10^{-5}$ were measured for non-ion-exchanged samples. Absorption measurements allowed the identification of specific color center bands, which were attributed to the glass matrix and to the silver ions. Investigation of the exposed ion-exchanged glass using scanning electron microscopy and energy dispersive x-ray microanalysis revealed that in addition to the color centers formed, silver ion migration and ionization contribute significantly to the UV-induced index changes.

**OCIS codes:** (160.5320) Photorefractive materials, (050.7330) Volume holographic gratings, (160.5690) Rare earth doped materials, (130.3130) Integrated optics materials

---

## References and links

1. B.C. Hwang, S. Jiang, T. Luo, J. Watson, S. Honkanen, Y. Hu, F. Smektala, J. Lucas, N. Peyghambarian, “Erbium-doped phosphate glass fibre amplifiers with gain per unit length of 2.1dB/cm,” Electron. Lett. **35**, 1007-1009 (1999).
2. D.L. Veasey, D.S. Funk, P.M. Peters, N.A. Sanford, G.E. Obarski, N. Fontaine, M. Young, A.P. Peskin, W.C. Liu, S.N. Houde-Walter, J.S. Hayden, “Yb/Er-codoped and Yb-doped waveguide lasers in phosphate glass,” J. Non-Cryst. Solids **263-264**, 369-381 (2000).
3. S. Blaize, L. Bastard, C. Cassagnetes, J.E. Broquin, “Multiwavelengths DFB waveguide laser array in Yb-Er codoped phosphate glass substrate,” IEEE Photon. Technol. Lett. **15**, 516-518 (2003).
4. P. Thamboon, D.M. Krol, “Second-order optical nonlinearities in thermally poled phosphate glass,” J. Appl. Phys. **93**, 32-7 (2003)
5. Y. Watanabe, G. Namikawa, T. Onuki, K. Nishio, T. Tsuchiya, “Photosensitivity in phosphate glass doped with $Ag^+$ upon exposure to near-ultraviolet femtosecond laser pulses,” Appl. Phys. Lett. **78**, 2125-2127 (2001)
6. Y. Watanabe, M. Inoue, T. Tsuchiya, “Intensity-dependent photobleaching through bulk oxide glass containing silver particles,” J. Appl. Phys. **84**, 6457-6459 (1998)
7. J.W. Chan, T.R. Huser, S.H. Risbud, J.S. Hayden, D.M. Krol, “Waveguide fabrication in phosphate glasses using femtosecond laser pulses,” Appl. Phys. Lett. **82**, 2371-2373 (2003)
8. S.Pissadakis, L.Reekie, M.N.Zervas, J.S.Wilkinson, “Sub-micron period relief gratings in $InO_x$ thin films and waveguides, patterned using 248nm excimer laser ablation,” J. Appl. Phys. **95**, 1634-41 (2004)
9. H.M. Smith (Editor), *Holographic recording materials 20*, Springer-Verlag (1977)

#4521 - $15.00 US
Received 2 June 2004; revised 30 June 2004; accepted 30 June 2004

10. J.-L. Archambault, “Photorefractive gratings in optical fibres,” PhD thesis, University of Southampton (1994)
11. A. Othonos and X. Lee, “Novel and improved methods of writing Bragg gratings with phase masks,” IEEE Photon. Technol. Lett. **7**, 1183-1185 (1995)
12. J.L. Archambault, L. Reekie, P.St. J.Russell, “100% reflectivity Bragg reflectors produced in optical fibres by single excimer laser pulses,” Electron. Lett. **29**, 453-5 (1993)
13. Schott Glass datasheets for IOG-1 glass
14. D. Ehrt, P. Ebeling, U. Nature, “UV transmission and radiation-induced defects in phosphate and fluoride-phosphate glasses,” J. Non-Cryst. Solids **263-264**, 240-50 (2000)
15. U. Kreibig, “Electronic properties of small silver particles: the optical constants and their temperature dependence,” J. Phys. F: Metal Phys. **4**, 999-1013 (1974)
16. G. Stewart, P.J.R. Laybourn, “Fabrication of ion-exchanged optical waveguides from dilute silver nitrate melts,” IEEE J. Quantum Electron. **QE-14**, 930-4 (1978)
17. D.Moncke, D.Ehrt, “Irradiation induced defects in glasses resulting in the photoionization of polyvalent dopants,” Opt. Mat. **25**, 425-37 (2004)

---

## 1. Introduction

Er-doped phosphate glasses are promising host materials for the fabrication of high-gain waveguide and fibre lasers and amplifiers operating in the 1.5μm band. Phosphate glasses combine beneficial material properties such as high solubility of Er ions and a large Yb/Er energy transfer coefficient in the 980nm pump band. These properties of Er-doped phosphate glasses render them attractive for the realization of short length, high gain, lasers and amplifiers operating with low pump power. Fibre [1] and waveguide [2,3] amplifiers and lasers have been realized in Er-doped phosphate glasses in recent years. In particular, in the waveguide geometry, high gain amplifiers and lasers have been presented in potassium [2] and silver [3] ion-exchanged waveguides in phosphate glass hosts. Moreover, second order nonlinearity has been recently induced in thermally poled phosphate glass [4], enhancing the potential for frequency converting waveguide laser sources.

The photosensitivity of phosphate glasses is of great importance, since significant changes in the refractive index of such glasses under intense irradiation at UV or visible wavelengths may lead to the development of highly efficient periodic structures or 3-D waveguide channels written in the bulk of the glass. High efficiency periodic structures can be applied in the realization of distributed feedback waveguide lasers or integrated gain-flattened optical amplifiers. Studies on the photosensitivity of phosphate glasses have been presented using ultra-fast near-UV [5] and visible radiation [6]. Furthermore, structural waveguide channels were formed in phosphate glasses using femtosecond laser radiation at 800nm [7].

The photosensitivity of silver ion-exchanged Er-doped glass using 248nm excimer laser radiation is studied here. The alteration of the refractive index of phosphate glass using a conventional laser source such as a nanosecond 248nm excimer laser is convenient since high quality complex periodic structures may be routinely recorded using the well known phase mask technique or by employing direct two beam interference [8].

## 2. Experimental

Planar waveguide samples were fabricated in Er-doped IOG-1 Schott glass substrates. Energy dispersive x-ray microanalysis (EDX) measurements performed in the glass samples provided the following oxide composition: 68% $P_2O_5$, 16% $Al_2O_3$, 5.5% $La_2O_3$, 6.5% $Na_2O$, 3.5% $Er_2O_3$, and 0.5% trace elements. A primary silver ion-exchange process was performed in agitated molten salt baths of $NaNO_3$ with 1.0%, 0.5% and 0.25% by weight $AgNO_3$ salt concentration, each at a temperature of 315°C. The ion-exchange time was 1h for all samples. A secondary ion-exchange process was performed for 30 minutes in pure $NaNO_3$ melt in order to slightly bury the silver ion-exchanged waveguides and also to anneal any silver clusters formed.

The index change was quantified by recording gratings using a phase mask configuration. The output of a Lambda Physik LPX 200 excimer laser, emitting at the wavelength of 248nm

Received 2 June 2004; revised 30 June 2004; accepted 30 June 2004

(35ns pulse duration) was interfered on the glass sample using a silica phase mask in contact mode. The phase mask used was optimised for operation at 248nm (suppressed 0th order) and had a periodicity of 1020nm. In order to adjust the energy density of the exposure a cylindrical lens was positioned before the phase mask with a rectangular aperture for selecting the optimum part of the beam. After recording, the grating samples were characterised using diffraction efficiency measurements by employing the output of a He-Cd laser at 442nm, probed in the grating region at the Bragg angle, and measuring the diffraction order corresponding to the inscribed period of 510nm. For the calculation of the refractive index change Δn the following equation was used:

$$\Delta n = \arcsin\left(e^{\alpha d/\cos\Theta}\sqrt{\eta}\right)\frac{\lambda\cos\Theta}{\pi d_{eff}} \qquad (1)$$

where $\alpha$ is the absorption coefficient ($\mu m^{-1}$) of the sample at the probe wavelength, $d_{eff}$ is the effective thickness of the grating, $\eta$ is the diffraction efficiency and $\Theta$ is the Bragg angle. Further samples were exposed to uniform radiation from the excimer laser at 248nm to enable determination of the absorption spectrum. The absorption coefficient $\alpha$ is evaluated by employing Beer's law for absorption in bulk media. Equation (1) is valid for thick, absorbing phase gratings [9].

Imperfections on the ion-exchanged glass surface, and the burial of the waveguides, did not allow the direct measurement of the refractive index profile of the ion-exchanged planar samples using prism coupling measurements and inverse WKB calculations. Instead, EDX measurements were used for the measurement of the depth profile of the silver ion concentration before and after exposure to UV radiation.

## 3. Results and discussion

We exposed both untreated and ion-exchanged glass samples in order to clarify the contributions of the host glass composition and the silver ion doping to the photosensitivity mechanism. We found that an index change occurs in both cases, accompanied by strong photodarkening, indicating significant defect formation.

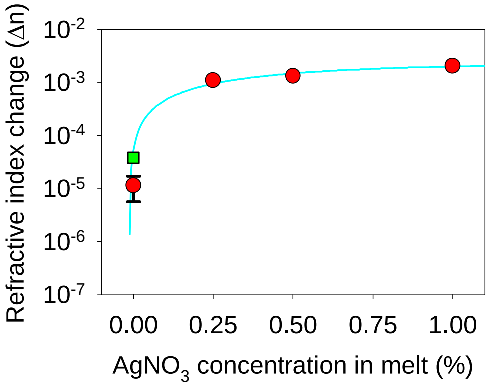

Fig. 1. Refractive index change vs. $AgNO_3$ concentration in ion-exchange melt for fixed exposures of $400mJ/cm^2$ energy density and 30000 pulses. Zero concentration refers to the non ion-exchanged glass sample. The green square represents the index change calculated using the Kramers-Kronig relations for the UV exposed non-ion-exchanged glass. The solid line indicates the index change obtained using diffraction efficiency measurements (red circles).

The dependence of the UV-induced index change upon the silver concentration in the ion-exchange melt is presented in Fig. 1 for grating exposures through the phase mask with 30000 pulses of energy density $400mJ/cm^2$. Exposures for greater energy densities resulted in clearly observable surface damage, indicating that the ablation threshold of the material had been

Received 2 June 2004; revised 30 June 2004; accepted 30 June 2004

exceeded. As it is shown in Fig.1, Δn does not significantly increase for samples prepared in sodium nitrate melt of silver nitrate concentration greater than ~0.2wt%.

The maximum index change obtained using Equation (1) is ~2.0x$10^{-3}$, which corresponds to the glass which has been ion-exchanged in the melt of concentration 1% $AgNO_3$, whereas the index change recorded in the un-treated glass sample is of the order of $10^{-5}$. For comparison, grating recording using 248nm excimer laser radiation in Er-doped aluminosilicate and phosphosilicate fibres resulted in index changes lower than $10^{-5}$ [10]. For the evaluation of the index change in the non ion-exchanged glass sample, it was assumed that the grating had been written to a depth of 100µm, which is the exposure depth within which high-contrast interference fringes are formed, due to the poor coherence length of the 248nm excimer laser source [11]. The error bar on Fig 1 indicates the refractive index change deduced assuming gratings of thickness 50µm and 150µm, respectively. For the evaluation of index changes in the ion-exchanged glass, the effective grating depth was taken to be the silver ion-exchange depth estimated using EDX measurements performed after the UV exposure. These depth-profiling measurements revealed that a significant change in the silver concentration profile occurred in the exposed waveguide areas (see Fig. 2), compared to the concentration profile of the unexposed waveguide.

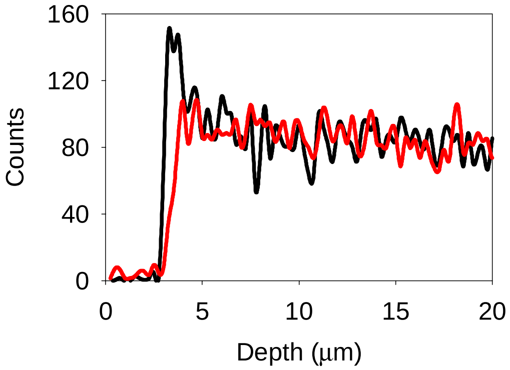

Fig. 2. Silver ion depth distribution obtained by EDX depth scans for ion-exchanged phosphate glass prepared in a $NaNO_3$ melt of 1.0% $AgNO_3$ concentration, before and after exposure to 248nm excimer laser radiation. Red line: ion-distribution before UV exposure. Black line: ion-distribution after exposure to 30000 pulses of 400mJ/$cm^2$ energy density.

The ion-yield data presented in Fig. 2 illustrate that the exposure to 248nm excimer laser radiation shifts the silver ion distribution towards the upper surface of the exposed area. This ion shift creates a region of high silver concentration of approximately 3µm thickness, compared to that before UV exposure. The effective grating thickness used in the diffraction efficiency calculation presented in Fig. 1 was therefore chosen to be 3µm.

Surface changes were also observed using scanning electron microscopy of the surfaces of the exposed gratings in the ion-exchanged glass. The SEM scan presented in Fig. 3 shows that where the UV irradiation formed bright interference fringes, shallow relief structures have been formed. The widths of the raised regions in the corrugated structures show an average value of 150nm, corresponding to a duty cycle of ≈30%. By applying an index matching fluid to the top of the corrugations, contained by a 100µm thick glass cover-slide, the contribution of these relief structures to the diffraction efficiency was measured to be approximately 10% of the total diffracted signal for the grating presented in Fig. 3.

We believe that the relief structures created are not high volume damage gratings like those observed during high-fluence grating inscription in other optical materials [8, 12] (i.e., Type II structural modifications). Here the relief structures may be attributed to extensive silver ion migration, which is assisted by volume thermal dissipation. This explanation is supported by the observation that the thermal diffusivity factor σ for IOG-1 glass is 3.15x$10^{-}$

Received 2 June 2004; revised 30 June 2004; accepted 30 June 2004

$^{7}$m$^2$/sec; so that significant thermal dissipation will occur over a heat affected zone of ~150nm for exposures using 35ns pulse duration [13]. The minor extent of material damage was also verified by optical microscopy observations in transmission mode, performed in the ion-exchanged samples. The optical microscopy inspection showed observable periodic index variation, without significant damage in the form of melting or amorphisation.

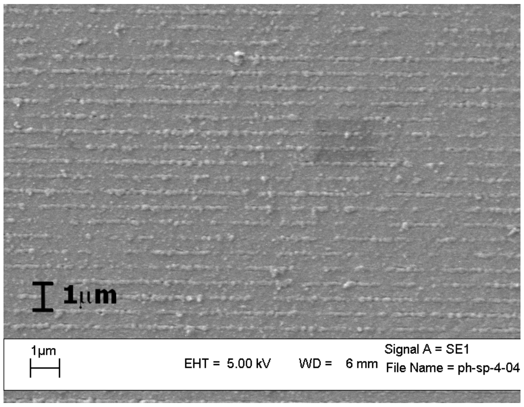

Fig. 3. SEM microscan of grating inscribed in ion-exchanged glass, prepared in 1% wt concentration of $AgNO_3$. Exposure conditions: 30000 pulses of 400mJ/cm$^2$ energy density.

Large-area non-grating exposures were performed on the glasses using the same exposure conditions as for grating inscription. The changes in the absorption $\Delta\alpha$ due to UV irradiation of untreated and ion-exchanged glass are presented in Fig. 4.

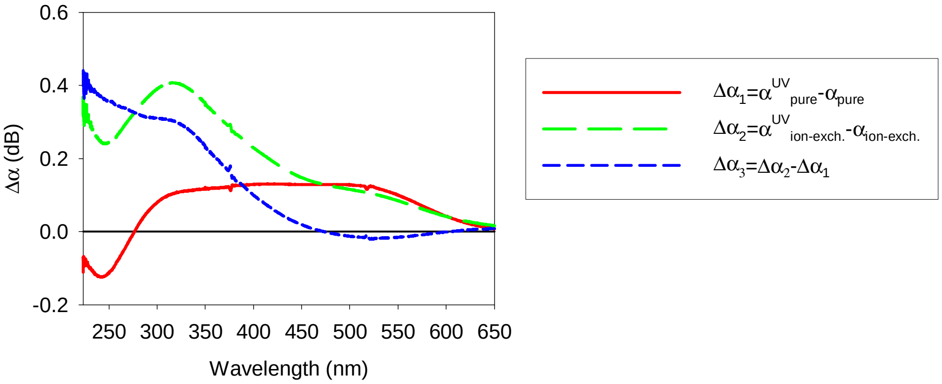

Fig. 4. Absorption spectra changes $\Delta\alpha$ of pure and ion-exchanged Er-doped IOG-1 glass prepared in a $NaNO_3$ melt of 1.0% $AgNO_3$ concentration, due to UV irradiation. Exposure conditions for all glasses: 30000 pulses of 400mJ/cm$^2$ energy density. Data have not been normalized to sample thickness. Absorption change data for wavelengths longer than 650nm are not presented here, since they do not exhibit any significant change.

In the case of the untreated IOG-1 Er-doped glass (solid red line) two definite spectral features are observed after UV irradiation: the first feature is an extended absorption band formed between 275nm and 650nm, and the second is a bleaching band created around the center of the exposure wavelength (248nm). The long wavelength absorption band may be attributed to PO-bond hole center defects, as has been observed in other ultraphosphate glasses following UV exposure [14].

The microscopic origin of the bleaching band observed at 248nm is presently under consideration. Other reports [e.g., 4] claim the presence of Ce in IOG-1 glass, which may provide such a bleaching band; however, we could not detect any trace of Ce with our EDX

Received 2 June 2004; revised 30 June 2004; accepted 30 June 2004

apparatus. The $PO_4$ electron center located at 242nm, observed in other phosphate glasses after 248nm excimer laser irradiation, constitutes an absorption band rather than a bleaching band [14]. Other impurities such as Fe may be responsible for such a spectral feature, however this could not be verified by our analysis. Thus, the origin of this bleaching band is not yet clear. By normalizing the absorption results to the sample thickness (3mm), and applying a Kramers-Kronig (KK) transformation for the 442nm probe wavelength, in the band between 220nm and 900nm, we obtain an index change of $3.8\text{x}10^{-5}$ (Green square in Fig. 1). This index change is in good agreement with the maximum value evaluated using diffraction efficiency measurements ($\Delta n=1.7\text{x}10^{-5}$), where a grating depth of 100μm was assumed.

Two curves are presented in Fig. 4 quantifying the absorption changes in the ion-exchanged sample. The long-dashed green curve ($\Delta\alpha_2$) represents the absorption change of the UV exposed sample, normalized to the absorption of the un-irradiated ion-exchanged sample; and the short-dashed blue curve ($\Delta\alpha_3$) is $\Delta\alpha_2$ with the absorption due to the glass matrix ($\Delta\alpha_1$) subtracted. A prominent feature observed in curve $\Delta\alpha_2$ is the strong absorption band formed around a wavelength of 320nm. Such a localized absorption band is a common feature of UV or X-ray exposed silver ion-exchanged glasses, due to plasmon resonance effects that occur in dispersed silver nanoparticles [15]. However, by subtracting the absorption due to the phosphate glass, this feature becomes less distinct, with its peak shifting to shorter wavelengths (≈305nm). By normalizing the deduced absorption change $\Delta\alpha_3$ to a thickness of the ion-exchange depth of 40μm, estimated from the EDX data presented in Fig. 2, and applying a KK transformation, an index change of $\approx 5.6\text{x}10^{-2}$ is obtained. Subsequently, by subtracting the index change contribution due to silver ion-exchange process for 1.0% $AgNO_3$ melt concentration, which has been estimated to be $1.1\text{x}10^{-2}$ [16], the index change that corresponds to UV irradiation becomes $4.5\text{x}10^{-2}$. This value is ~23 times greater than that obtained using diffraction efficiency measurements for the same exposure conditions. The discrepancy between the index change evaluated from the Kramers-Kronig relations and that measured directly by diffraction may be due to the grating writing process generating a large component of uniform index change over the grating area, which does not contribute to the diffraction efficiency, in addition to the smaller periodic component which does. The UV-induced index changes may be attributed to combination of silver ion-migration and defects attributed to photoionisation of $Ag^0$ and $Ag^+$ species [5, 17], and thermal effects are likely to result in a strong component of uniform index elevation. However, the strength of the index modulation at the writing period of 510nm is the most important optical parameter considered for grating fabrication.

## 4. Conclusions

Summarizing, strong index changes have been observed in silver ion-exchanged, Er-doped IOG-1 phosphate glass. Index changes of $\sim 2.0\text{x}10^{-3}$ have been measured for ion-exchanged glass exposed to 3000 pulses of energy density $400\text{mJ/cm}^2$ at a wavelength of 248nm. SEM and EDX measurements revealed that exposure to UV radiation creates significant silver ion migration due to thermal effects. However, by employing absorption measurements and Kramers-Kronig transformation, greater overall index changes of the order of $5\text{x}10^{-2}$ are estimated. Grating recording in silver ion-exchanged channel waveguides formed in Er-doped IOG-1 glass for the development of distributed feedback waveguide lasers is currently being carried out.

## Acknowledgments

SP and JSW would like to acknowledge support from the Ultraviolet Laser Facility operating at FO.R.T.H. under the Improving Human Potential (IHP) -Access to Research Infrastructures Programme of the EC (contract Nos HPRI-CT-1999-00074 and HPRI-CT-2001-00139). SP gratefully acknowledges Dr. Michail Velegrakis (IESL-FORTH) for constructive discussions.

Received 2 June 2004; revised 30 June 2004; accepted 30 June 2004