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Effects of rare-earth doping on femtosecond laser waveguide writing in zinc polyphosphate glass

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We have investigated waveguide writing in Er-Yb doped zinc polyphosphate glass using a femtosecond laser with a repetition rate of 1 KHz. We find that fabrication of good waveguides requires a glass composition with an O/P ratio of 3.25. The dependence on laser writing parameters including laser fluence, focusing conditions, and scan speed is reported. Waveguide properties together with absorption and emission data indicate that these glasses can be used for the fabrication of compact, high gain amplifying devices. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4739288]

I. INTRODUCTION

Femtosecond laser micromachining of rare-earth doped glass substrates is a promising technique to fabricate compact and robust high gain waveguide lasers and amplifiers.[1–6] Phosphate glasses are ideal host materials for the fabrication of active devices because they can incorporate high concentrations of rare-earth ions. Fs-laser written waveguide characteristics, such as refractive index profile and loss, not only depend on the laser processing conditions, but the composition of the glass substrate also plays a major role. Zinc phosphate glasses within the metaphosphate and polyphosphate regime, $3.0 \leq [O]/[P] \leq 3.5$, have proven to be excellent glass systems for achieving high rare-earth oxide concentrations with low luminescence quenching effects.[7–10]

We have recently found[11] that zinc polyphosphate glasses with an [O]/[P] ratio near 3.25 (molar composition $60ZnO-40P_2O_5$) exhibit a localized positive change in refractive index inside the irradiated area, which make them excellent substrate materials for fs-laser fabrication of single-mode waveguides. In those studies, it was also observed that waveguide quality depends very strongly on relatively small changes in glass composition and structure. In this paper, we have investigated the effect of Er-Yb doping on fs-laser written waveguides in $60ZnO-40P_2O_5$ glass. Changing the glass composition by adding rare-earth oxides to the host material will alter the glass structure.[8,9] Erbium oxide and ytterbium oxide behave as network modifiers by contributing oxygens through Er,Yb-O-P bonds that produce smaller phosphate anions as the overall O/P ratio increases. To maintain a constant phosphate anion structure in a zinc phosphate base glass, Er/Yb-doping can be accompanied by a reduction in the ZnO content to retain a constant O/P ratio. One goal of the present work is to describe the effects of these different approaches to doping, and so the role of subtle changes in glass structure, on the response to the fs-laser.

To make a functional amplifying device, it is also important to minimize waveguide losses that occur from the fs-laser writing process. Minimizing losses in the system will help maximize the signal gain and the pumping efficiency that is needed for the construction of a compact waveguide amplifier.[12] In this study, we have systematically investigated how writing parameters such as the laser pulse energy, the scan speed, the beam focusing, and the writing geometry influence refractive index changes and waveguide losses in Er-Yb doped zinc polyphosphate glass.

II. EXPERIMENTAL

A $60.0ZnO-40.0P_2O_5$ (molar composition) base glass (ZP) and two Er-Yb doped versions, with nominal molar compositions of $0.7Er_2O_3-1.3Yb_2O_3-58.8ZnO-39.2P_2O_5$ (ZP-m1) and $0.7Er_2O_3-1.3Yb_2O_3-56.0ZnO-42.0P_2O_5$ (ZP-m2), were investigated. For ZP-m1, the rare earth oxides were added to the ZP base glass, increasing the nominal [O]/[P] ratio while keeping a constant [P]/[Zn] ratio (Table I). For ZP-m2, the rare earth oxides were added to substitute for ZnO to maintain a constant [O]/[P] ratio while increasing [P]/[Zn] (Table I).

Direct fs-laser writing experiments were performed using a regenerative amplified Ti:Sapphire 1 kHz, 180 fs-laser system. Experimental details and sample preparation methods can be found in Ref. 13. Fs-laser writing parameters, such as the laser pulse energy, the scan speed, the beam focusing, and the writing geometry were studied. Near field and far field waveguide profiles, as well as white light images and insertion losses were measured after waveguides were written. A diagram of this setup is shown in Figure 1.

White light images of the modified areas were collected both perpendicular to, and normal to, the fs-laser beam propagation direction, using a $20\times$ (0.40 NA) objective and a CCD camera. A $10\times$ (0.21 NA) objective was used to focus 660 nm laser light into the input waveguide facet, and a $10\times$ (0.20 NA) objective was focused at the output facet in order to characterize the guiding properties. Mode profiles of the transmitted 660 nm laser light were obtained by imaging the near-field intensity at the output facet of the waveguide using a CCD camera. Positive refractive index changes were calculated by analyzing the cone of the 633-nm coupled output light in the far field.[14]

TABLE I. Phosphate glass compositions (mol. %).

Designation	Composition	[O]/[P]	[P]/[Zn]
ZP	$60ZnO-40P_2O_5$	*3.25*	*1.33*
ZP-m1	$0.7Er_2O_3-1.3Yb_2O_3-58.8ZnO-39.2P_2O_5$	3.32	*1.33*
ZP-m2	$0.7Er_2O_3-1.3Yb_2O_3-56.0ZnO-42.0P_2O_5$	*3.25*	1.50

Optical absorption spectra were measured using a single beam spectrophotometer, where the relative light intensity of a collimated tungsten halogen white light source (Ocean Optics DH-2000) was measured as a function of wavelength with and without the bulk Er-Yb zinc polyphosphate glass sample in the transmitted beam path. The transmitted light was collected with two different mini-spectrometers (Ocean Optics (SD2000) and Hamamatsu (C9406GC)), in the UV-visible (VIS) and near-infrared (NIR) wavelength region, respectively. Fluorescence spectra were measured by exciting the fs-laser modified glass sample with 473 nm laser light and collecting the backscatter signals emitted in the visible wavelength range. Details of the set-up are described elsewhere.[13]

III. RESULTS AND DISCUSSION

A. Fs-laser modified Er-Yb zinc polyphosphate glass

The first part of our investigation examines the relationship between the initial glass structure and the fs-laser induced change in refractive index. Previous studies[11] have shown that fs-pulse fluences close to 8 J/cm^2 produce changes to the structure of $60ZnO-40P_2O_5$ glass that result in the formation of good waveguides. By maintaining this constant fluence and studying the resulting modification properties as a function of changing composition, it is possible to study how important a very small change to the glass composition is with respect to fs-laser irradiation.

Figure 2 shows the changes in glass morphology after fs-laser irradiation at fluences of 8 J/cm^2 for the ZP base glass and the two Er-Yb glasses, along with the near field output profile of 660 nm laser light. Guiding behavior is indicated for the ZP base glass, due to the local increase in refractive index in the regions irradiated by the fs-laser.[11] Similar behavior is indicated for the fs-laser written lines in the ZP-m2 glass (constant [O]/[P]), whereas no guiding is observed for the ZP-m1 glass (constant [P]/[Zn]); the later behavior indicates a negative refractive index change. These results demonstrate that very small changes in bulk glass composition can be of importance in the development of high quality waveguides and functional waveguide amplifiers.

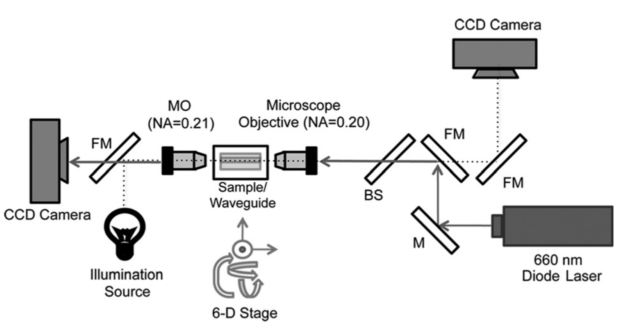

FIG. 1. Diagram of the waveguide/modification characterization setup: 660 nm coupling laser, 50/50 dichroic beam splitter, 10 × (0.20 NA) microscope objective, xyz translation stage, phosphate glass sample, white-light lamp, CCD camera (white-light microscopy and alignment), flip mirrors, mirrors, and 10 × (0.21 NA) microscope objective.

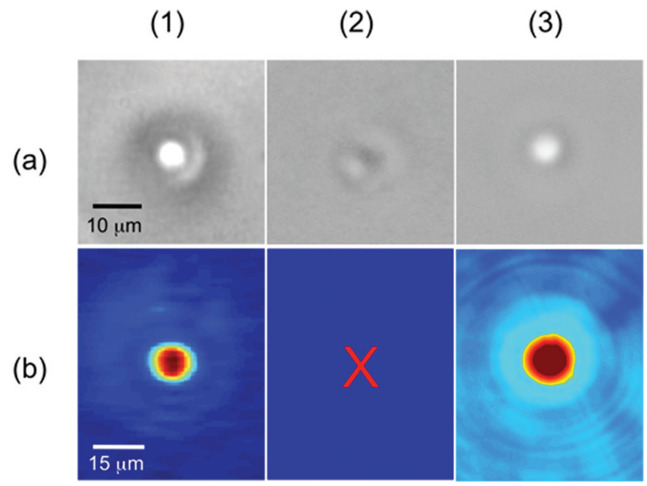

FIG. 2. Modification cross-section images. (a) White light microscope images and (b) 660 nm laser near field guiding intensity profiles for (1) ZP base glass, (2) ZP-m1 glass, and (3) ZP-m2 glass modified using a constant fs-laser pulse fluence of 8 J/cm^2 and a sample translation speed of 50 μm/s.

In order to understand the subtle differences between these two glass compositions and the molecular level structure of the glass network, we have used confocal Raman spectroscopy to characterize differences in the vibrational modes associated with the P-O bonds that constitute the glass structures. We have shown elsewhere[13] that there are strong similarities between the Raman spectrum of the ZP base glass and the spectrum of the ZP-m2 glass, consistent with their similar [O]/[P] ratios. On the other hand, ZP-m1 has a Raman spectrum more similar to a $65ZnO-35P_2O_5$ base glass. This latter base glass does not produce good waveguides with the fs-laser writing technique.[13] The results in the doped glasses further support our earlier conclusion that the phosphate glass network structure, which can be correlated with the O/P ratio, determines the way the glass responds to the fs-laser. For all three glasses used in the present study, Raman spectra of the modified regions do not show any significant changes with respect to the unmodified glass. These results are again consistent with our observations for a series of undoped zinc phosphate glasses.[11,13] In those glasses, changes in the Raman spectra and defect fluorescence from non-bridging oxygen hole centers (NBOHC) centers were both observed for glasses with O/P ratios of 3.11 and below, but not for O/P = 3.25. We are currently carrying out further studies towards understanding the structural changes associated with fs-laser modification in undoped zinc phosphate glasses using a wider range of compositions and structural characterization tools.

B. Waveguide fabrication and characterization

To study the waveguide characteristics of Er-Yb doped polyphosphate glass, in the context of device fabrication, the

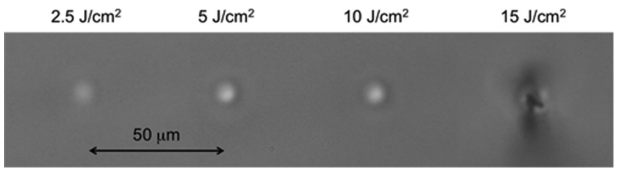

FIG. 3. White light microscope waveguide cross-section images of ZP-m2 glass modified as a function of changing fs-laser pulse fluence for a constant sample translation speed of 50 μm/s.

remainder of this paper will primarily focus on the ZP-m2 Er-Yb polyphosphate glass system that exhibits a positive change in refractive index after fs-laser modification. Waveguides of approximately 8 μm in diameter were created under a longitudinal writing geometry (using a 0.21 NA focusing objective) at a constant scan speed of 50 μm/s, with laser pulse fluences above the measured modification threshold of 2 J/cm^2. The ZP-m2 glass shows a relatively larger range of fs-laser writing conditions that produce usable waveguides (Fig. 3) than what is reported for the ZP base glass.[11] Fluences beyond 15 J/cm^2 give rise to physical damage to the glass structure (Figure 3, right) that results in poor waveguiding characteristics. The greatest positive change in the refractive index was found for a fluence of approximately 10 J/cm^2; for greater fluences, the index change seemed to saturate. Due to small power fluctuations in the output beam of the femtosecond laser system, it is not practical to fabricate usable waveguides near the damage threshold condition. Therefore, the ideal processing fluence would be at the Δn saturation point of 10 J/cm^2. Analysis of the near field and far field waveguide output profiles showed single-mode guiding characteristics using 660 nm laser light, with a maximum measured Δn of 1×10^{-3} and a total overall insertion loss of 4.3 ± 0.4 dB (with an estimated total coupling loss of 2.3 ± 0.2 dB, Fresnel losses of 0.360 ± 0.005 dB, and a Er^{3+} absorption of 1.27 ± 0.1 dB at 660 nm (cf. Fig. 7)) over a waveguide length of 5 mm. Note that there is an overall improvement in the losses measured in the ZP-m2 glass sample, compared to the 60ZnO-40P_2O_5 base glass for which an insertion loss of 6.69 dB was reported.[11] This improvement may be related to improved quality of the ZP-m2 glass. The addition of erbium and ytterbium oxide can improve the overall chemical durability of phosphate glass,[15,16] leading to improved surface polishing capabilities and fs-beam focusing conditions.

C. Slit writing technique

Slit writing is a simple technique for fabricating waveguides of arbitrary length throughout the entire glass sample.[17] Figures 4–6 all illustrate how waveguide characteristics in the ZP-m2 glass depend on slit parameters and processing conditions involved in writing low loss single scan waveguides.

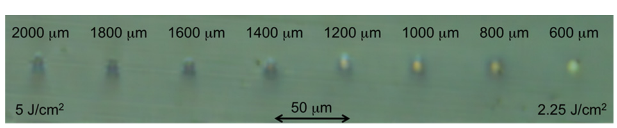

FIG. 4. White light microscope images of modification cross-sections inside ZP-m2 glass as a function of changing slit size for a constant sample translation speed of 50 μm/s and fs-laser pulse energy of 250 nJ, 200 μm below the surface.

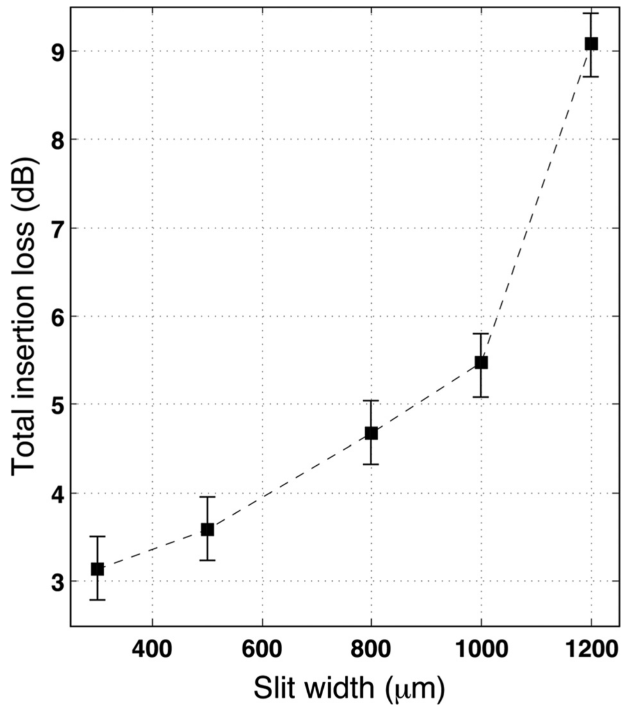

FIG. 5. Total insertion loss of 632.8 nm He-Ne laser light over 1.5 cm length waveguides in ZP-m2 glass written with a constant sample translation speed of 50 μm/s and fs-laser pulse fluence of 10 J/cm^2 as a function of changing slit size.

Figure 4 shows cross-sections of waveguides written with a constant fs-pulse energy of 250 nJ (using a 0.55 NA focusing objective) as a function of changing slit size. It is important to note that as the slit size is decreased, the waveguide cross-section becomes more circular. The shape of a waveguide written with a slit size of 2 mm has an elliptically shaped core with an aspect ratio of approximately 4:1. This is consistent with previous observations by other groups reporting on transverse writing.[17,18] By introducing a 600 μm wide slit before the focusing objective, a waveguide can be written with a near-circular profile, 200 μm below the sample surface. However, at a slit width less than 600 μm is used, as is required to achieve a 1:1 aspect ratio; the fs-laser fluence is too small to modify the glass as the focal area becomes significantly larger. Therefore, it is important to balance the fs-laser pulse energy delivered to the sample with the proper slit size in order to achieve the necessary writing fluence.

To study the evolution of the modification cross-section as a function of changing slit size and pulse energy, along with its effect on the insertion losses of the waveguide, an array of waveguides was written into a ZP-m2 substrate by changing both the slit width (1200 μm–300 μm) and the fs-laser pulse energy (250 nJ–4 μJ). As has been shown, the fs-laser fluence is an important variable to maintain and optimize for waveguide fabrication. In order to study the loss contributions from the geometry of the cross-section and not from changes in the pulse fluence, it is necessary to examine waveguides that are fabricated with a constant fs-pulse fluence of approximately 10 J/cm^2.

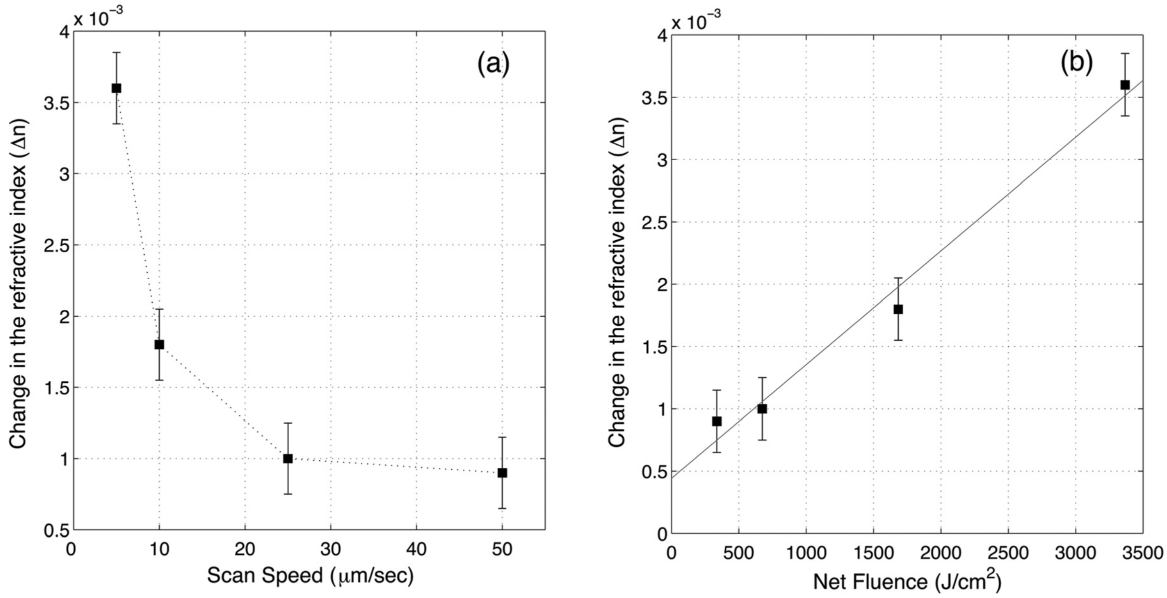

FIG. 6. Change in refractive index of ZP-m2 glass as a function of (a) sample scan speed and (b) net fluence for a constant fs-laser pulse fluence of 10 J/cm^2 (longitudinal writing with a 0.55 NA focusing objective).

We consider a writing geometry in which the beam is propagating along the z-direction. The waveguides are written by moving the sample along the x-direction and the slit is affecting the dimensions of the beam in the y-direction. Following the approach in Ref. 17, the beam dimensions before the objective are denoted by W_y and W_x. With the above geometry, W_y is determined by the slit size, and we take W_x to be determined by the aperture of the focusing objective. The following equations can then be used to describe relationship between pulse energy (E), fluence (F), and slit size (W_y):

$$F = \frac{E}{A}\gamma = \frac{E}{\pi(w_x w_y)}\gamma, \text{ where } w_x \approx \frac{1.22\lambda}{2NA_x}, \text{ and } w_y = \left(\frac{W_x}{W_y}\right) w_x, \tag{1}$$

$$E(W_y) = \frac{F\pi}{\gamma}\left(\frac{1.22\lambda}{2NA_x}\right)^2 \left(\frac{W_x}{W_y}\right). \tag{2}$$

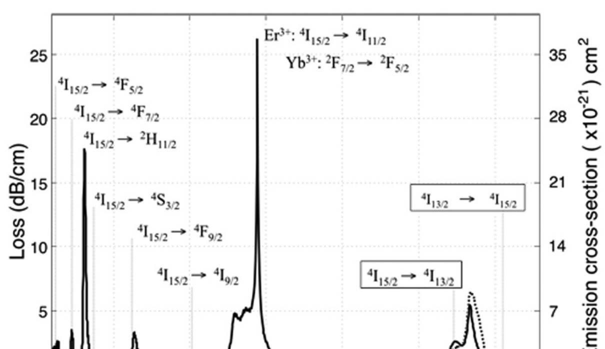

FIG. 7. Absorption (blue curve) and emission spectrum (red curve) of ZP-m2 glass; for the emission spectrum, an excitation source at 976 nm was used.

Here, w_x and w_y are the focal spot waists in the x and y directions, respectively; $\gamma = $ the $50\times$ microscope objective transmission ($\gamma = 0.55$), λ is the focusing wavelength ($\lambda = 800$ nm), NA is the numerical aperture ($NA_x = 0.55$), and W_x is equal to the objective aperture diameter = 2 mm. The relationship shown in Eq. (2) can be used to find the pulse energy required for a constant fluence of 10 J/cm^2 as a function of slit size. Based on this calculation, waveguides were fabricated using the following combinations of slit sizes and pulse energies: 1.2 mm-800 nJ, 1.0 mm-900 nJ, 800 μm-1.10 μJ, 500 μm-1.80 μJ, and 300 μm-3 μJ.

Figure 5 shows the total insertion loss of the waveguides as a function of changing slit size at a fs-laser fluence of 10 J/cm^2. At large slit sizes, the waveguide cross-section is too elliptical resulting in higher insertion loss. To achieve a waveguide with a circular cross-section, a 300 μm slit size is required. Such an observed slit size is consistent with the calculated value that can be obtained using Eq. (6) from Ref. 17. According to the equation, the expected slit size, W_y, to achieve circular waveguides under our experimental conditions ($NA = 0.55$, $W_x = 2$ mm (objective aperture diameter), $n = 1.577$) should be 320 μm.

The effect of maximizing the pulse fluence and the slit width results in the ability to fabricate single-mode, circular waveguides of 1.5 cm length with a total overall insertion loss of 3.0 ± 0.4 dB (Fig. 5), and a propagation loss of approximately 0.54 ± 0.14 dB/cm at 632.8 nm (with Fresnel losses of 0.360 ± 0.005 dB and an estimated total coupling loss of 1.9 ± 0.2 dB). He-Ne laser light (632.8 nm) was used to perform loss experiments in this case because at 660 nm light there are additional losses due to Er^{3+} absorption (Fig. 7).

Once the optimum fluence and slit size are determined, it is possible to systematically study how the sample scanning speed affects the waveguide properties (Fig. 6(a)). A slow scanning speed can result in a cumulative change to the refractive index.[19,20] In the case of ZP-m2 glass, as the sample translation speed decreases, the change in refractive index increases, where a scan speed of 5 μm/s results in a change in refractive index of 3.5×10^{-3}, effectively tripling the change in the refractive index measured after waveguide fabrication with a scanning speed that is 10 times as fast. For comparison with experiments at other repetition rates, it is useful to quantify the effect of scan speed in terms of a net fluence, NF, which, for the longitudinal writing geometry used in this experiment, is given by

$$NF = \frac{Frb}{v}. \tag{3}$$

Here, F is the pulse fluence, r the laser repetition rate, b the depth of focus, and v the scan speed.

The results in Fig. 6(b) show a linear relationship between induced index change and net fluence.

D. Absorption and fluorescence spectroscopy

In order to fabricate active optical devices using femtosecond laser writing techniques, it is important to understand the absorption and emission properties of the erbium transitions, especially for the 1.53 μm emission transition. Among the Er^{3+} emission bands, the band at 1535 nm (Fig. 7—red curve) arising from the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition is the most important one as it is useful for optical communication and IR laser applications.[7,10] This emission band was recorded with the same fiber spectrophotometer setup by exciting the glass sample with a 976 nm, 30 mW laser diode. The photoluminescence has a FWHM of 50 nm with a peak emission wavelength of $\lambda_p = 1535$ nm.

Figure 7 (blue curve) shows the absorption bands from the Er^{3+} ground state ($^4I_{15/2}$) and the Yb^{3+} ground state ($^2F_{7/2}$). A total of 9 absorption bands, corresponding to erbium and ytterbium transitions to various excited states, are identified and assigned.[21] The ytterbium absorption spectrum is characterized by a single large peak at 976 nm mainly due to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of the Yb^{3+} ion that is used to optically pump an active waveguide device.

Using the glass composition and glass density of 3.31 g/cm^3, the erbium and ytterbium ion concentrations can be calculated to be $N_{Er3+} = 2.0 \times 10^{20}$ ions/cm^3 and N_{Yb3+} 4.0×10^{20} ions/cm^2. The absorption cross-sections of the 1534 nm transition, $\sigma_a(1534) = 1.06 \times 10^{-20}$ cm^2, and the 976 nm transition, $\sigma_a(976) = 1.71 \times 10^{-20}$ cm^2 were calculated using the maximum measured loss of 5.62 dB/cm and 26.21 dB/cm, respectively (see Figure 7) together with the respective active ion densities. Accordingly, the emission cross-section of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition is approximately $\sigma_e(1534) = 8.3 \times 10^{-21}$ cm^2 using the measured absorption cross-section and the McCumber relationship.[22,23] These absorption and emission properties are well-suited for fabricating compact waveguide devices that operate with a relatively high gain bandwidth over most of the telecommunications window (1530 nm–1565 nm). We have carried out gain experiments, described in more detail elsewhere,[24] in waveguides that were fabricated with the following optimized writing parameters: sample translation speed of 5 μm/s, a pulse fluence of 10 J/cm^2, writing with a 300 μm wide slit placed before a 0.55 NA focusing objective. By optically pumping the waveguides with a maximum 500 mW of 976 nm pump power, a total 1534 nm signal enhancement of approximately 10 dB was measured over a 1.5 cm length, resulting in an internal gain of close to 1 dB/cm.

IV. CONCLUSIONS

The results from this study have shown that it is possible to fabricate low loss, single-mode waveguides inside Er-Yb doped zinc polyphosphate glasses with an [O]/[P] ratio of 3.25. Laser pulse fluences above the measured modification threshold of 2 J/cm^2 and below the observed glass damage threshold of 15 J/cm^2 create a positive change to the refractive index for guiding. By adjusting the sample translation speed, fs-pulse fluences, and by varying the input writing beam (slit width), it is possible to directly create optical waveguides 200 μm below the sample surface that can be used for single-mode active device fabrication. Optimized parameters include a scan speed of 5 μm/s, a pulse fluence of 10 J/cm^2, and a slit with a width of approximately 250–350 μm placed before the focusing objective (0.40 NA–0.60 NA).

Currently, fs-laser micromachining can be limited because there is insufficient control over the resulting change to the glass structure after modification. Our study has demonstrated that controllable changes to the glass structure inside a phosphate glasses can be induced with femtosecond laser pulses, simply by altering the initial glass composition rather than adjusting the processing conditions. Such a material engineering approach should be considered together with waveguide fabrication methods to fully exploit the potential of fs-laser fabrication of glass-based photonic devices.

ACKNOWLEDGMENTS

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