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Direct femtosecond laser waveguide writing inside zinc phosphate glass

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Abstract: We report the relationship between the initial glass composition and the resulting microstructural changes after direct femtosecond laser waveguide writing with a 1 kHz repetition rate Ti:sapphire laser system. A zinc polyphosphate glass composition with an oxygen to phosphorus ratio of 3.25 has demonstrated positive refractive index changes induced inside the focal volume of a focusing microscope objective for laser pulse energies that can achieve intensities above the modification threshold. The permanent photo-induced changes can be used for direct fabrication of optical waveguides using single scan writing techniques. Changes to the localized glass network structure that produce positive changes in the refractive index of zinc phosphate glasses upon femtosecond laser irradiation have been studied using scanning confocal micro-Raman and fluorescence spectroscopy.

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1. Introduction

Femtosecond lasers pulses in the near IR, when focused inside transparent glass substrates, can achieve high enough intensities to give rise to permanent modification of the glass structure. Such photo-induced modifications often result in a change in the refractive index of the glass that is highly confined to the focal volume of a high NA lens or microscope objective [1,2]. By translating the glass with respect to the focal volume it is possible to fabricate 3-D subsurface optical waveguides with high spatial precision in a variety of optical materials [3–7].

Phosphate glasses can incorporate large concentrations of rare earth ions [8], making them an ideal host materials for fabricating compact high-gain waveguide lasers and amplifiers that operate in the C-band [9,10]. However, many phosphate glasses will typically exhibit or favor negative changes to the index of refraction inside the fs-laser irradiated region [11,12]. As a consequence, high quality single-mode waveguides cannot be easily fabricated by direct waveguide writing techniques. Femtosecond laser writing in commercially available phosphate glasses, such as Schott IOG-1 or Kigre Er-Yb QX and MM2a glass, has demonstrated that both the magnitude and the sign of the induced net refractive index change inside the focal volume is highly sensitive to the fs-laser writing conditions [13–19]. The resulting micro-structure changes, induced by femtosecond laser inscription, result in complex refractive index profiles that can be used for waveguiding only when very specific combinations of laser processing parameters are used, thus limiting the effectiveness of these glasses as substrates for direct fs-laser waveguide writing. Progress in fs-laser

micromachining can be greatly enhanced by utilizing phosphate glass compositions that can yield good waveguides when fabricated under a wider range of laser processing conditions.

While much attention has focused on the writing techniques used to achieve positive changes to the refractive index, the dependence on the initial glass composition has often been overlooked. It is important to understand the relationships between the initial composition of simple phosphate glasses and the structural changes that result from fs-laser modification. To date, no study has been performed which has systematically examined how changes to the initial glass structure effect the resulting changes after fs-laser modification. Zinc phosphate glasses are excellent candidates to examine both the fundamental relationships of this interaction as well as provide a suitable glass structure to investigate the desired positive changes to the refractive index. Zinc phosphate glasses are excellent optical materials to study this phenomenon due to three important characteristics:

- (i) Zinc phosphate glasses have structures based on linkages between corner-shared Zn- and P-tetrahedra. Fused silica glass also has a tetrahedral network and the resulting open structures are believed to be associated with anomalous temperature-dependence of a variety of properties, including thermal expansion, acoustic absorption, and sound velocity [20–24], for both fused silica and the zinc phosphate glasses.
- (ii) Zinc phosphate glasses can be prepared in a wide range of compositions to support studies of the relationships between glass structures and properties [21].
- (iii) Due to its large glass forming range beyond the metaphosphate composition, the zinc phosphate glass system is one of only a few binary phosphate glass systems that provides an open phosphate chain-like structure that is capable of incorporating high concentrations of rare earth ions without concentration quenching effects as a result of ion clustering [8,21].

In this paper we will show that variations in glass composition within the metaphosphate and polyphosphate regime, $3.5 \geq [\text{O}]/[\text{P}] \geq 3.0$, have a direct effect on the glass network structure and initial glass properties resulting in different responses to femtosecond laser waveguide writing. The observed micro-structure, refractive index, and guiding properties of the waveguides indicate that the initial glass network affects the resulting morphological changes to the glass after modification by femtosecond pulses. Waveguides fabricated in glasses with $[\text{O}]/[\text{P}]$ ratio of 3.25, at fs-laser pulse fluences below 10 J/cm^2 , demonstrate a single mode guiding region in the center of the induced modification under longitudinal focusing conditions. Local changes to the both the glass structure and the guiding properties inside the laser-irradiated area are investigated through the use of scanning Raman and fluorescence microscopy.

2. Experiment

In this study we have induced modifications in several different metaphosphate ($[\text{O}]/[\text{P}] = 3.0$) and polyphosphate ($3.0 < [\text{O}]/[\text{P}] \leq 3.5$) glasses. Binary zinc phosphate glasses with nominal ZnO contents between 50 and 65 mol% were prepared using reagent grade ZnO (zinc oxide), and $\text{NH}_4\text{H}_2\text{PO}_4$ (ammonium phosphate). A zinc aluminophosphate glass with a nominal metaphosphate composition ($30\text{ZnO}-10\text{Al}_2\text{O}_3-60\text{P}_2\text{O}_5$) was prepared from a mixture of ZnO, crystalline $\text{Al}(\text{PO}_3)_3$ and $\text{NH}_4\text{H}_2\text{PO}_4$. In each batch, raw materials were thoroughly mixed and calcined at 500°C for 12 hours. The glasses were first melted in alumina crucibles at 1000°C for two hours and then rapidly quenched to form glass frit. The fritted glass was ground in a mortar and pestle and the powders were remelted in a Pt crucible for one hour at 1050°C to form a homogeneous melt. The melts were poured into steel molds, cooled and then annealed for 2 hours near T_g . Annealed samples were polished using SiC paper and diamond pastes to a finish of 0.25 microns.

In each polished glass sample, a series of waveguides was fabricated using a regeneratively amplified Ti:sapphire 1 kHz, 180 fs laser system (Merlin-Spitfire Spectra Physics) with pulse energies ranging from 0.2 μJ – 4 μJ . The femtosecond laser beam was directed through a 20x (0.40 NA) microscope and the glass sample was translated parallel to the femtosecond laser beam at a constant scan speed of 50 $\mu\text{m/s}$. Near field and far field waveguide profiles, as well as white light images and insertion losses were measured after waveguides were written. White light images of the modified areas were collected both perpendicular to, and normal to, the fs-laser beam propagation direction using a 20x (0.40 NA) objective and a CCD camera. A 10x (0.21 NA) objective was used to focus 660 nm laser light into the input waveguide facet, and a 10x (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 measuring the numerical aperture of the waveguide.

Confocal Raman and fluorescence spectroscopy was performed on the fs-laser induced modifications using a 473 nm cw laser (Laserglow.com Limited LRS-473). The 473 nm excitation beam was directed through a 50x (0.55 NA) objective using a 50/50 broadband dielectric beam splitter and focused into the glass sample, which was placed on a Newport 3-axis xyz motorized stage. Backscatter signals produced by the 473 nm laser excitation were collected by the same 50x objective and directed through the 50/50 beam splitter. A 50 μm diameter pinhole was used to ensure Raman signals were only collected from the focal volume of the objective. An Oriel 500 spectrometer in conjunction with a CCD camera (LN-CCD Princeton Instruments) was used to collect spectral signals that passed through the pinhole setup. The spectrometer was used with a 1200 grooves/mm grating to collect Raman signals, and a 600 grooves/mm grating to collect fluorescence signals.

3. Results and discussion

3.1. Physical changes to fs-laser modified zinc phosphate glass

Figure 1(a) and 1(b) show white light microscope images of waveguides created by the femtosecond laser direct-write technique applied to the five different zinc phosphate glasses. Figure 1(c) shows the near field images from waveguiding experiments in the respective glasses. These microscopic images and waveguiding experiments showed significant differences in the responses of the five phosphate glasses to the femtosecond laser. For example, the waveguiding experiments on the laser-modified zinc phosphate glasses usually demonstrated negative changes in the index of refraction inside the fs-laser irradiated region, resulting in poor guiding characteristics (Fig. 1(c)). The exception was the 60ZnO-40P₂O₅ polyphosphate sample (Fig. 1(4c)) where a positive change in the refractive index within the focal volume was found. Transverse microscope images of the modified regions showed visible damage to many of the glasses after irradiation, (Fig. 1(1a)–1(3a)), even for comparatively low fs-laser pulse fluences (below 10 J/cm²). However, the 60ZnO-40P₂O₅ and 65ZnO-35P₂O₅ polyphosphate glasses did not exhibit this same behavior. The 65ZnO-35P₂O₅ polyphosphate glass sample demonstrated relatively smooth modification to the glass for low fs-laser fluences in comparison to many of the other glass samples (Fig. 1(5a)). The observed refractive index changes, however, were not optimal for waveguiding (Fig. 1(5b)). In contrast, the 60ZnO-40P₂O₅ polyphosphate glass yielded good waveguiding characteristics and smooth modification for the same low energy fs-laser writing parameters (Fig. 1(4a) and 1(4c)). The obvious differences in response to fs-laser exposure of the 60ZnO-40P₂O₅ glass compared to that of the other zinc phosphate glass compositions, indicate an important role for the initial phosphate glass composition (or structure) in the development of high quality waveguides.

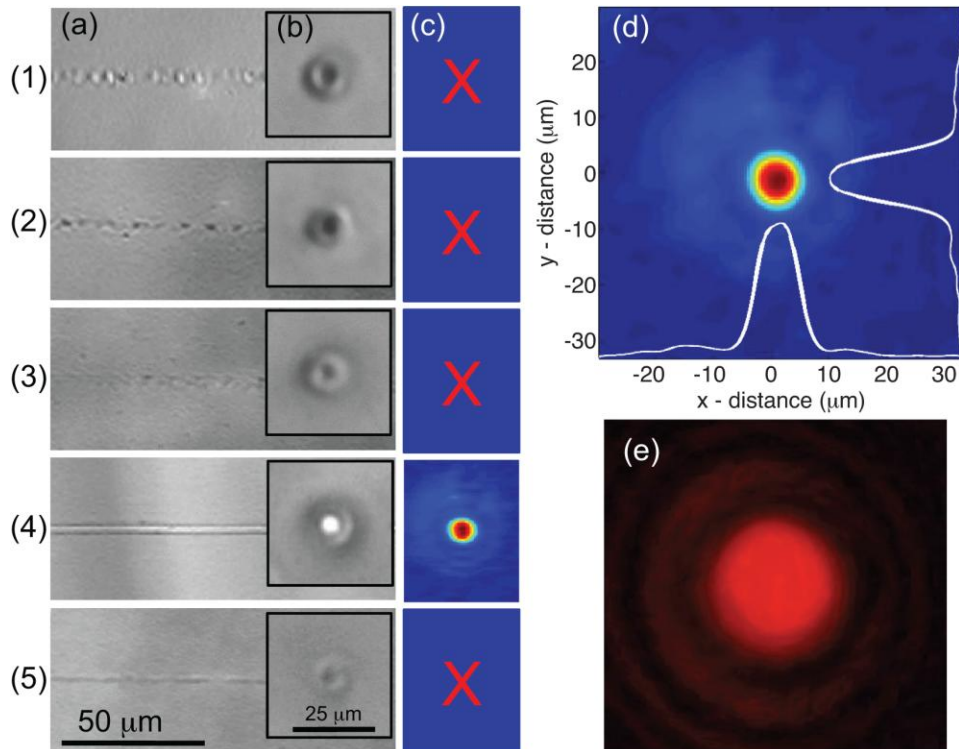


Fig. 1. Microscope images of fs-modified zinc phosphate glass written with fs-laser fluences of 8 J/cm^2 (1) $30\text{ZnO-}10\text{Al}_2\text{O}_3\text{-}60\text{P}_2\text{O}_5$ glass (2) $50\text{ZnO-}50\text{P}_2\text{O}_5$ glass (3) $55\text{ZnO-}45\text{P}_2\text{O}_5$ glass (4) $60\text{ZnO-}40\text{P}_2\text{O}_5$ glass (5) $65\text{ZnO-}35\text{P}_2\text{O}_5$; (a) white light images of the modification along the waveguide direction (b) Transmission white light images of the modification cross section (c) 660 nm transmission near field images (d) Waveguide near field output guiding profile for $60\text{ZnO-}40\text{P}_2\text{O}_5$ glass (e) Waveguide far field output profile for $60\text{ZnO-}40\text{P}_2\text{O}_5$ glass.

Detailed analysis of the near field and far field waveguide output profiles, for the modified $60\text{ZnO-}40\text{P}_2\text{O}_5$ glass, showed single mode guiding characteristics using 660 nm laser light (Fig. 1(d), Fig. 1(e)), with a maximum measured Δn of 5×10^{-4} and a total overall insertion loss of 6.69 dB (with an estimated coupling loss of 2 dB), over a waveguide length of 3 mm . The high losses measured in this experiment are most likely caused by observed inhomogeneities in the bulk glass sample that were present before fs-laser waveguide writing. Such inhomogeneities can have a detrimental effect on the light propagation inside the waveguide as well as on the overall manufacturing precision of the waveguides due to deviations in the fs-laser focusing conditions. Positive refractive index changes inside the focal volume were observed for fs-laser fluences between 2 J/cm^2 (threshold for modification) and 10 J/cm^2 . For fs-laser fluences above 10 J/cm^2 , the irradiated region exhibited visible material damage and inhomogeneous changes for all the glasses used in this study, including the $60\text{ZnO-}40\text{P}_2\text{O}_5$ glass.

3.2. Confocal Raman and fluorescence microscopy

Raman spectroscopy provides information about the molecular-level structure of phosphate glasses. Figure 2 shows the Raman spectra collected from the five zinc phosphate glasses prior to fs-laser irradiation. The spectra are similar to those reported in the literature [21] and reveal systematic changes in the phosphate structural network with changes in composition. The peak centered near 1200 cm^{-1} is assigned to the symmetric stretching modes, $(\text{PO}_2)_{\text{sym}}$, of

the non-bridging P-O bonds on tetrahedra that link two neighboring tetrahedra (Q^2 tetrahedra) and the peak centered near 1000 cm^{-1} is assigned to the symmetric stretching modes, $(\text{PO}_3)_{\text{sym}}$,

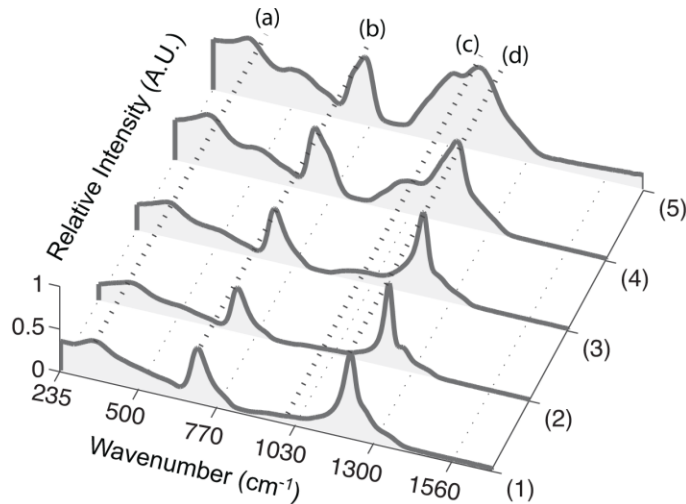


Fig. 2. Raman spectra of unmodified bulk phosphate glasses (1) $30\text{ZnO}-10\text{Al}_2\text{O}_3-60\text{P}_2\text{O}_5$ glass (2) $50\text{ZnO}-50\text{P}_2\text{O}_5$ glass (3) $55\text{ZnO}-45\text{P}_2\text{O}_5$ glass (4) $60\text{ZnO}-40\text{P}_2\text{O}_5$ glass (5) $65\text{ZnO}-35\text{P}_2\text{O}_5$; (a) in chain PO_2 and OPO bending (b) (POP) symmetric stretch (bridging oxygen), Q^2 species (c) P-O stretch, Q^1 chain terminator (d) (PO_2) symmetric stretch (non-bridging oxygen), Q^2 species.

of P-O bonds on tetrahedra that link one other tetrahedron (Q^1). With an increase in the $[\text{O}]/[\text{P}]$ ratio, the spectra reveal that Q^2 tetrahedra that form long chains in metaphosphate glasses ($[\text{O}]/[\text{P}] = 3.0$) are replaced by Q^1 tetrahedra that terminate progressively shorter chains in the polyphosphate compositions.

In order to understand the atomic scale changes to the initial glass structure, confocal Raman and fluorescence experiments were performed on all fs-laser modified zinc phosphate glass samples. The results demonstrated systematic changes in the Raman spectra of the modified glass. In the modified regions of glasses where no favorable waveguiding structures could be produced, the 1209 cm^{-1} Raman peak associated with P-O bonds on Q^2 tetrahedra showed a consistent shift to lower wavenumbers (Fig. 3(a)). We measured the shift by carefully scanning over the modified cross section in $1.5\text{ }\mu\text{m}$ step sizes and recording the maximum shift, relative to the bulk material, that typically occurred at the very center of the modified area (Fig. 3(b)). The magnitude of the maximum shift of the modified zinc phosphate glass not only varied from sample to sample (Fig. 4(b) below), but it also depended on the amount of fs-laser energy deposited into the glass (Fig. 3(a)).

Popovic *et al.* have shown that the positions of Raman peaks from crystalline inorganic phosphates correlates with the P-O bond length, where generally longer bonds are associated with lower wavenumbers [25]. If a similar correlation exists for the modified zinc phosphate glasses, then the decrease in the $(\text{PO}_2)_{\text{sym}}$ peak position of the modified glasses shown in Fig. 3 can be attributed to an expansion of the glass network in the fs-laser irradiated region, resulting in longer P-O bonds and correspondingly lower refractive index and density. This behavior is similar to what has been observed for commercial phosphate glasses examined in previous experiments [15]. For commercial phosphate glasses we have correlated the negative Raman shifts with negative index changes.

For the $60\text{ZnO}-40\text{P}_2\text{O}_5$ glass, however, no measurable shift of the $(\text{PO}_2)_{\text{sym}}$ Raman peak was observed within the modified area for any fs-laser fluences used. This indicates that the structure of this glass has not been altered in the same way as those with lower ZnO contents, consistent with the increase in refractive index and positive waveguiding performance. The

peak at 1209cm^{-1} could not be distinguished in the Raman spectrum of the $65\text{ZnO}-35\text{P}_2\text{O}_5$ glass which has relatively few Q^2 tetrahedra (about 15%) [21], thus making it more difficult to characterize in the same manner as the other glass samples used in this experiment.

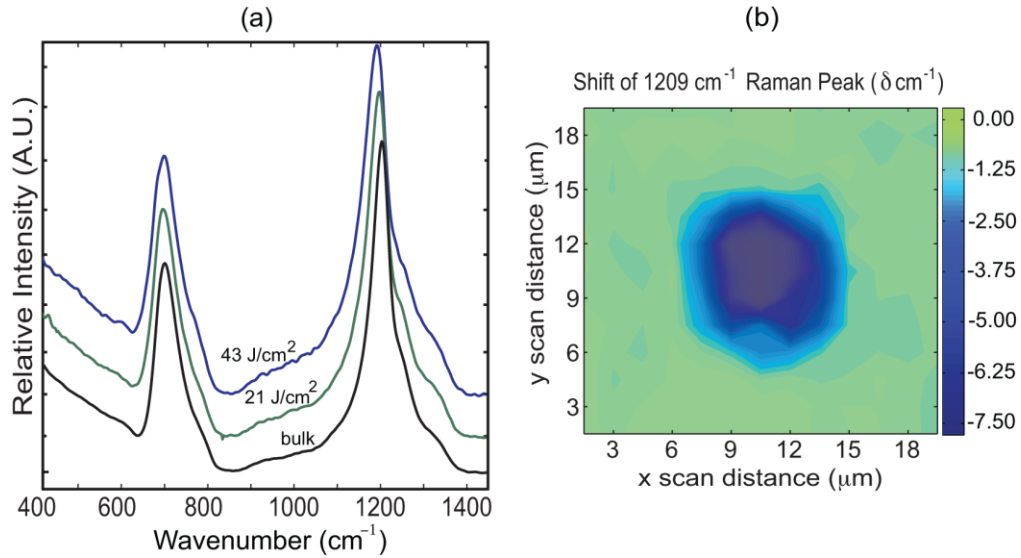


Fig. 3. (Color online) (a) Spectral profile of the 1209cm^{-1} Raman mode of modified and unmodified $30\text{ZnO}-10\text{Al}_2\text{O}_3-60\text{P}_2\text{O}_5$ glass for various fs-laser fluences (b) Color map of shifts in the relative spectral position of the 1209cm^{-1} Raman peak as a function of the spatial position for $30\text{ZnO}-10\text{Al}_2\text{O}_3-60\text{P}_2\text{O}_5$ glass modified with a fs-laser fluence of $43\text{J}/\text{cm}^2$.

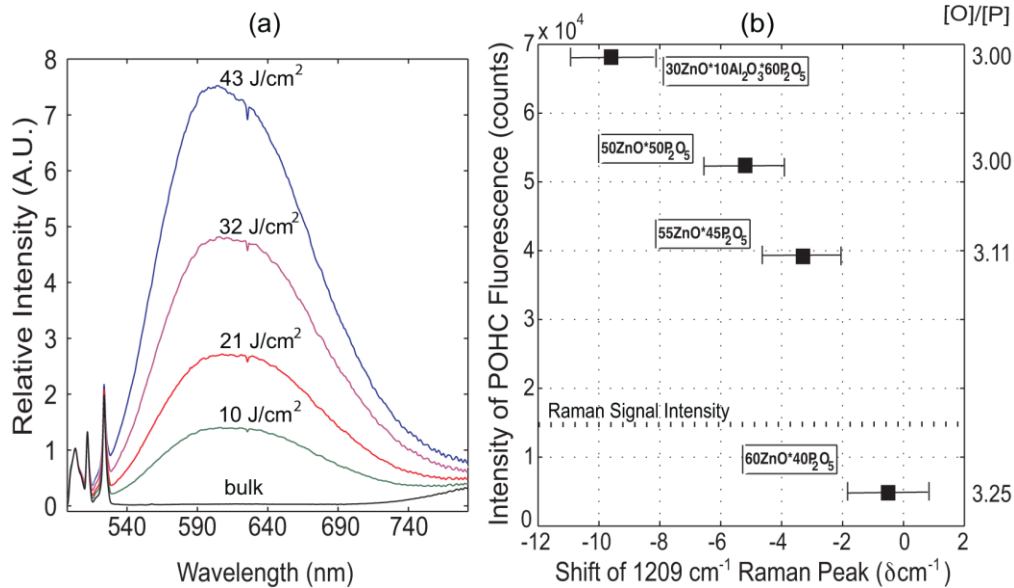


Fig. 4. (Color online) (a) Fluorescence spectra of modified and unmodified $30\text{ZnO}-10\text{Al}_2\text{O}_3-60\text{P}_2\text{O}_5$ glass for various fs-laser fluences (b) Maximum change in intensity of POHC fluorescence as a function of the maximum 1209cm^{-1} Raman mode shift for various glass compositions modified with a fs-laser fluence of $43\text{J}/\text{cm}^2$.

In addition to Raman spectroscopy we have also measured the fluorescence spectra of fs-laser modified zinc phosphate glass. At wavelengths beyond 535 nm, a very broad and noticeable photoluminescence peak centered at 630 nm was observed (Fig. 4(a)) within the

modified volume of phosphate glasses with $[O]/[P] < 3.25$. This fluorescence peak has been attributed to the presence of fs-laser induced POHC (phosphorus-oxygen-hole-center) defects. This fluorescence is typically indicative of a damage of the phosphate network as a result of laser irradiation [26].

The overall fluorescence intensity, and thus concentration of the induced POHC defects, also depends on the initial glass composition. Figure 4(b) shows that glasses with greater fluorescence intensities from laser modified regions possess greater shifts in the $(PO_2)_{sym}$ Raman peak frequency. This relationship indicates that the mechanism of glass network expansion caused by the absorption of fs-laser pulses results in broken P-O bonds and a lower glass density. It also shows the distinctly different response of the 60ZnO-40P₂O₅ glass to the fs-laser, compared to glasses with lower $[O]/[P]$ ratios. No significant POHC fluorescence or significant Raman shift was measured from the 60ZnO-40P₂O₅ polyphosphate glass composition, even under high energy writing conditions where 43 J/cm² fs-laser fluence was used. The measured relationship at the molecular level is consistent with the observed behavior at the microscopic scale where lower refractive index changes to the glass persisted for all but the 60ZnO-40P₂O₅ glass composition (Fig. 1(c)). However, it is worth noting that the results for the 65ZnO-35P₂O₅ are not conclusive; in fact, no significant Raman changes or POHC fluorescence signals have been observed within the modified region of this phosphate glass composition. While the modified glass morphology suggests that the changes in the refractive index are negative, such an observation is only qualitative. Thus, it is possible that the induced index change is positive, albeit a low positive change that demonstrates poor waveguiding characteristics.

Micro-Raman measurements specifically performed on the waveguides in the 60ZnO-40P₂O₅ glass sample did not exhibit any measurable positive shifts in the 1209 cm⁻¹ Raman peak that would indicate a contraction of the phosphate network. Other refractive index mechanisms, such as changes in the network polarizability by an increased proportion of Q¹ tetrahedra, previously reported in Yb doped phosphate glass by *Little et al.* [27], were not observed in our analysis. It is possible that changes may result from photo-induced stresses that may not affect the Raman peak positions [15]. While the mechanism responsible for an increase in refractive index remains the subject of further study, it is clear that for most phosphate glass compositions studied in this experiment, a decrease in refractive index caused by an expansion of the network is the dominant response mechanism.

4. Conclusions

In this work, we have demonstrated that direct femtosecond laser irradiation of zinc polyphosphate glass with an oxygen to phosphorus ratio of 3.25 (60ZnO-40P₂O₅ glass) produces a positive refractive index change, as much as 5×10^{-4} , that can be used to fabricate optical waveguides. Such waveguides have been created under longitudinal focusing geometries using a 1 kHz, 180 fs laser system with laser pulse fluences above the measured modification threshold of 2 J/cm² and below the observed glass damage threshold of 10 J/cm². The positive refractive index changes reported are symmetric and confined to within the focal volume of the 20x (0.40 NA) fs-laser writing objective.

We have observed that femtosecond laser waveguide writing in phosphate glass highly depends on the initial glass composition. It is a very important variable that cannot be overlooked when fabricating high quality optical waveguides inside phosphate glasses. The changes to the network structure can be measured using confocal fluorescence and Raman microscopy. Most phosphate glass compositions have molecular-level structures that expand under the femtosecond laser and produce POHC defects, making them less practical for laser-written waveguides. However, the 60ZnO-40P₂O₅ glass has a structure that appears to modify in a way that produces a positive refractive index change, and that does not generate POHC defects under the femtosecond laser irradiation, making this glass an attractive material for waveguiding applications.