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 $60ZnO\text{-}40P_2O_5$ 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 $60ZnO\text{-}40P_2O_5$ polyphosphate glass composition, even under high energy writing conditions where 43 J/cm^2 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 $60ZnO\text{-}40P_2O_5$ glass composition (Fig. 1(c)). However, it is worth noting that the results for the $65ZnO\text{-}35P_2O_5$ 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 $60ZnO\text{-}40P_2O_5$ 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 Q^1 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 ($60ZnO\text{-}40P_2O_5$ glass) produces a positive refractive index change, as much as $5x10^{-4}$, 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/cm^2 and below the observed glass damage threshold of 10 J/cm^2. 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 $60ZnO\text{-}40P_2O_5$ 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.

#141431 - $15.00 USD Received 24 Jan 2011; revised 21 Feb 2011; accepted 22 Feb 2011; published 11 Apr 2011