Structural modification in Er-Yb doped zinc phosphate glasses with megahertz repetition rate femtosecond pulses

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ABSTRACT

Focused femtosecond laser pulses from a 1 MHz fiber laser were used to create modifications in Er-Yb doped zinc phosphate glass. Two glasses with similar phosphate glass networks but different network modifiers were investigated. To understand the resulting changes caused by the femtosecond laser pulses various characterization techniques were employed: glass structural changes were investigated with confocal Raman spectroscopy, defect generation as well as local Er and Yb environment were investigated with confocal fluorescence spectroscopy, and elemental segregation resulting from heat accumulation effects was ascertained by scanning electron microscopy.

Keywords: femtosecond laser writing, waveguide fabrication, zinc phosphate glass, elemental segregation, heat accumulation, Raman spectroscopy, fluorescence, erbium ytterbium

1. INTRODUCTION

Femtosecond laser waveguide writing inside rare-earth doped glasses is a promising technique for the fabrication of compact waveguide amplifiers and lasers [see e.g. 1, 2]. We have recently found that zinc polyphosphate glasses with an oxygen to phosphorus ratio (O/P) of 3.25 are well suited as host materials for fs-laser writing of waveguides [3, 4]. These glasses exhibit positive index changes in the laser-exposed regions under a wide range of laser processing conditions when using a fs laser with a repetition rate of 1 KHz. Fs laser writing with repetition rates of 1 MHz allows for much faster processing speeds but when the repetition rate of the pulses is faster than the energy dissipation of the affected volumes heat accumulation effects can take place [5], which result in very different characteristics of the laser-modified material. This prolonged heating of the affected volume can lead to elemental segregation and the subsequent cooling of the glass leads to a locked-in glass structure lacking a homogenous distribution of ions [6]. In order to understand the ramifications of these high repetition-rate lasers for waveguide fabrication we have studied two zinc phosphate glasses that have similar initial glass networks but differ in the network modifying ions. Through the use of confocal Raman and fluorescence spectroscopy the local glass network structure has been determined. Combining these techniques in an imaging mode with elemental mapping from a scanning electron microscope (SEM) allows us to get further insight into the changes induced in this heat accumulation regime.

2. EXPERIMENTAL METHODS

Glass samples with molar compositions 56.0 ZnO 42.0 P_2O_5 0.7 Er_2O_3 1.3 Yb_2O_3 and 28.0 ZnO 28.0 MgO 42.0 P_2O_5 0.7 Er_2O_3 1.3 Yb_2O_3 were prepared using reagent grade ZnO, MgO, Er_2O_3, Yb_2O_3 and $NH_4H_2PO_4$. Raw materials were mixed and calcined at 500°C for 12 hours, after which they were melted in alumina crucibles at 1000°C for 2 hours and then quenched rapidly to form a glass frit. The fritted glass was ground with a mortar and pestle and remelted in a Pt

crucible for 1 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 ground to rough dimensions with the use of 25, 12, and then 9 um aluminum oxide polishing compound. Final polishing was accomplished by using a pitch plate with 5 um aluminum oxide compound after which surface flatness was tested with a Zygo interferometer to be less than $\lambda/5$ over the writing surfaces. The resulting samples showed excellent optical quality in terms of a lack of bubbles as well as their polished surfaces, making them well suited for waveguide fabrication. The composition of the final glass samples were determined by SEM-WDS analysis and the results can be found in Table 1 together with their nominal compositions. Slight differences in the final composition can be noted, such as the presence of Al from the crucible but the compositions are well within expected tolerances.

Table 1. Composition of zinc phosphate glasses

Sample name	Nominal composition (mole %)	composition in at %*							
		P	Zn	Mg	Al	Er	Yb	O	O/P
ZnP	56.0 ZnO 42.0P_2O_5 0.7Er_2O_3 1.3Yb_2O_3	20.4	12.4	<.01	0.6	0.3	0.6	65.7	3.22
ZnMgP	28.0ZnO 28.0MgO 42.0P_2O_5 0.7Er_2O_3 1.3Yb_2O_3	20.4	6.2	6.1	0.6	0.3	0.6	65.8	3.23

*determined by SEM

The femtosecond laser used in the writing experiments was an all-fiber ytterbium laser operating at 1030 nm (Polaronyx Uranus). The pulse repetition rate was set at a fixed 1 MHz with a pulse width of 750 fs. The pulse energy is modulated with a waveplate and polarizer setup to a maximum deliverable energy of 1 uJ per pulse. For all modifications the laser was focused by an aspheric lens with an effective numerical aperture (NA) of 0.3, at a depth of 250 um beneath the polished surface of the glass sample. The samples were then translated transversely to the laser propagation direction at a rate of 1 mm/s (Aerotech ABL1000) with the electric field polarized parallel to the translation direction.

After modification the samples were investigated using confocal fluorescence (FL) and Raman spectroscopy. A 473 nm diode laser was used for all Raman spectroscopy as well as for FL excitation of phosphorus oxygen hole centers (POHCs) [3, 4] and the $^4F_{7/2}$ level of Er^{3+} ions.

Information about the local composition is obtained by an SEM (Cameca SX-100) equipped with wavelength dispersive spectrometers (WDS). Due to the low atomic percentage of the rare-earth ions in the samples the SEM is insensitive to them when used in an elemental mapping mode.

3. RESULTS AND DISCUSSION

Femtosecond modified lines were made inside the two samples as described above with pulse energies ranging from 315 nJ to 630 nJ. White light transmission images of the lines, shown in figure 1, show a rather "rough" modification transversely and a teardrop shape in their cross-section. Under high pulse energies (>400 nJ) a heat accumulation ring, or bloom, can be seen in the ZnP sample. It was not possible to create this behavior in the MgZnP sample with the energies available. Although the glasses have a similar network structure the replacement of half of the Zn with Mg appears to distinctly change the visible characteristics of the modification. We have also noticed that the MgZnP sample has a higher modification threshold compared to the ZnP sample, which might be caused by the tighter bonding of the Mg^{2+} ions compared to the Zn^{2+} ions in the glass network.

Using the elemental mapping capabilities of the SEM we were able to observe elemental segregation within the modified volume, figures 2a and 2b (ZnP) and figures 5a, 5b, and 5c (MgZnP). The ZnP and the MgZnP samples both exhibit similar behavior in that enhanced concentrations of network modifiers (Zn and Mg) are found towards the center of the modified volume whereas the concentration of network former (P) is enhanced in the "tail" of the modified volume. Although a relatively small change in concentration was noticed (~5%) this is still large enough to suggest that the phosphate glass network in these regions differs significantly from the bulk.
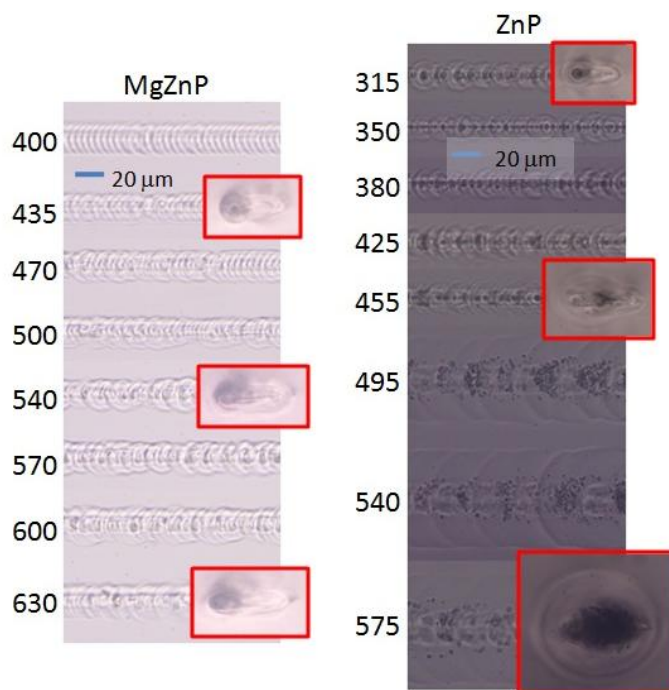
Figure 1. White light transmission images of the modified lines, seen transversely and in cross-section (red bordered images), inside the MgZnP sample (left) and the ZnP sample (right). The energy per pulse (nJ,) is given for each modification. For cross sectional images the laser input direction is from the left.

Raman spectroscopy on the bulk of the two samples (figure 3) shows similar features that suggest that the initial phosphate glass network in both of the glasses is very much the same. This is expected since the O/P ratio for the two glasses is very nearly the same at ~3.22 - 3.23. The Raman spectra for these zinc phosphate glasses consist of many different overlapping vibrational modes of the phosphate network; however, zinc polyphosphate glasses have been heavily researched and many of the modes that arise from the different Q^i species have been identified [7], where the Q^i notation refers to the number of bridging oxygens ("i") that each phosphorus in a phosphate glass network has. It turns out that in the wavenumber range between $900 – 1400$ cm^{-1} vibrational modes of both Q^2 and Q^1 species exist but they occupy different areas of the energy spectrum. The Q^2 vibrational modes occur predominantly at higher energies (1200-1250 cm^{-1}) whereas the Q^1 vibrational modes are located at lower energies ($1000 – 1150$ cm^{-1}).
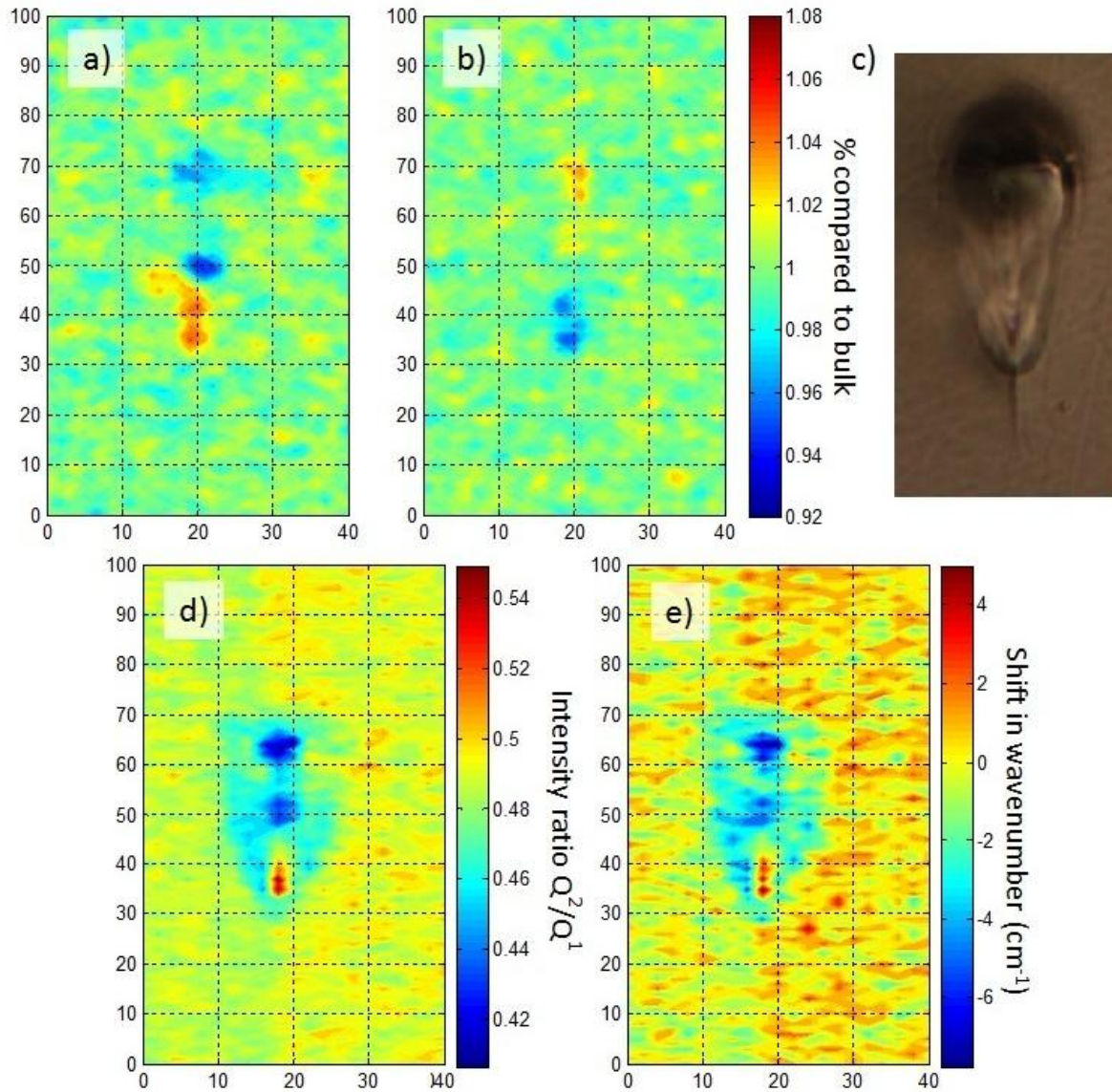
Figure 2. Different mapping techniques for a 40 μm x100 μm modification made in the ZnP sample with 350 nJ pulse energy; the input is from the top of the maps. Elemental mapping has been done on the modification for P (a) and Zn (b); the color scale shows the difference in concentration percentage from the bulk. White light transmission image of the modification (c). Qualitative mapping of the change in Q^i species, as determined by Raman spectroscopy, throughout the modification (d); color scale depicts the severity of change in the Q^i species towards Q^2 (red) or Q^1 (blue). Shift in the peak location of the ~1200 cm^{-1} Raman peak (e), color scale maps to wavenumber change from the bulk. All distance scales are in microns.
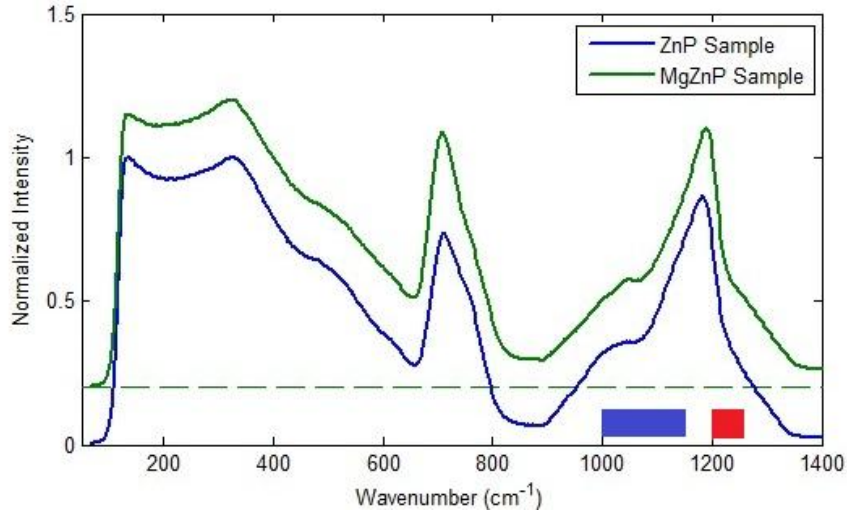
Figure 3. Raman spectra of the bulk of the ZnP and ZnMgP samples. Plots shifted vertically for clarity where the dashed line indicates the zero for the shifted plot. The blue and red box denotes the energies associated with Q^1 and Q^2 vibrational modes, respectively.

In figure 4 we show the changes to the Raman spectra acquired at different locations within a single modification area. By comparing the integrated intensity values in the Q^2 (1200-1250 cm^{-1}) vs. the Q^1 (1000-1150 cm^{-1}) regions we can qualitatively say that there is a change in the modified glass structure from the initial Q^i species mix towards one species or the other and to better visualize the changes we can map the ratio of the integrated Q^2 and Q^1 intensities throughout the modification, as shown in figures 2d and 5d.
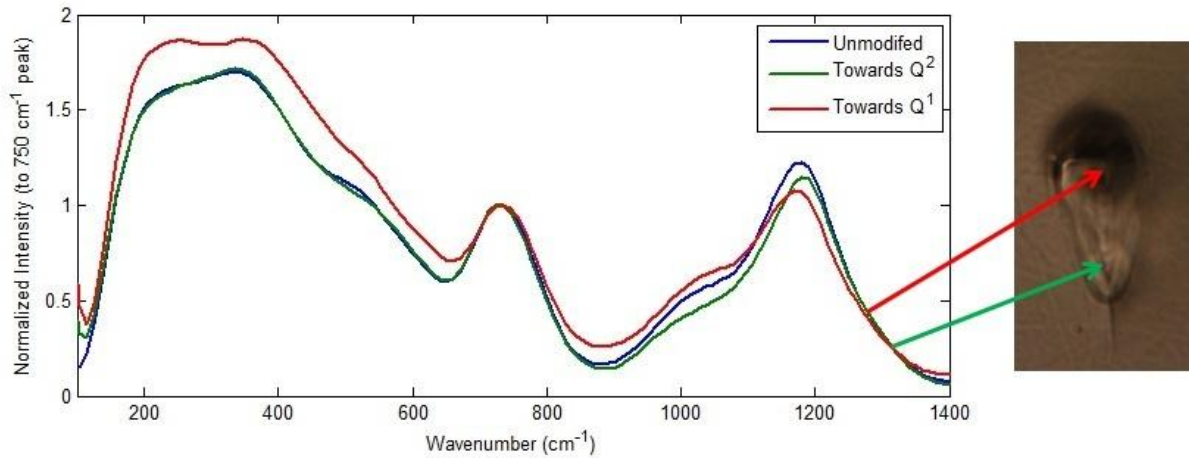

Figure 4. Raman spectra from three regions in the ZnP sample: unmodified glass (blue), region depicting a shift towards a Q^2 phopshate network (green), and a region depicting a shift to Q^1 phosphate network (red). Arrows depict the locations of the respective Raman spectra.
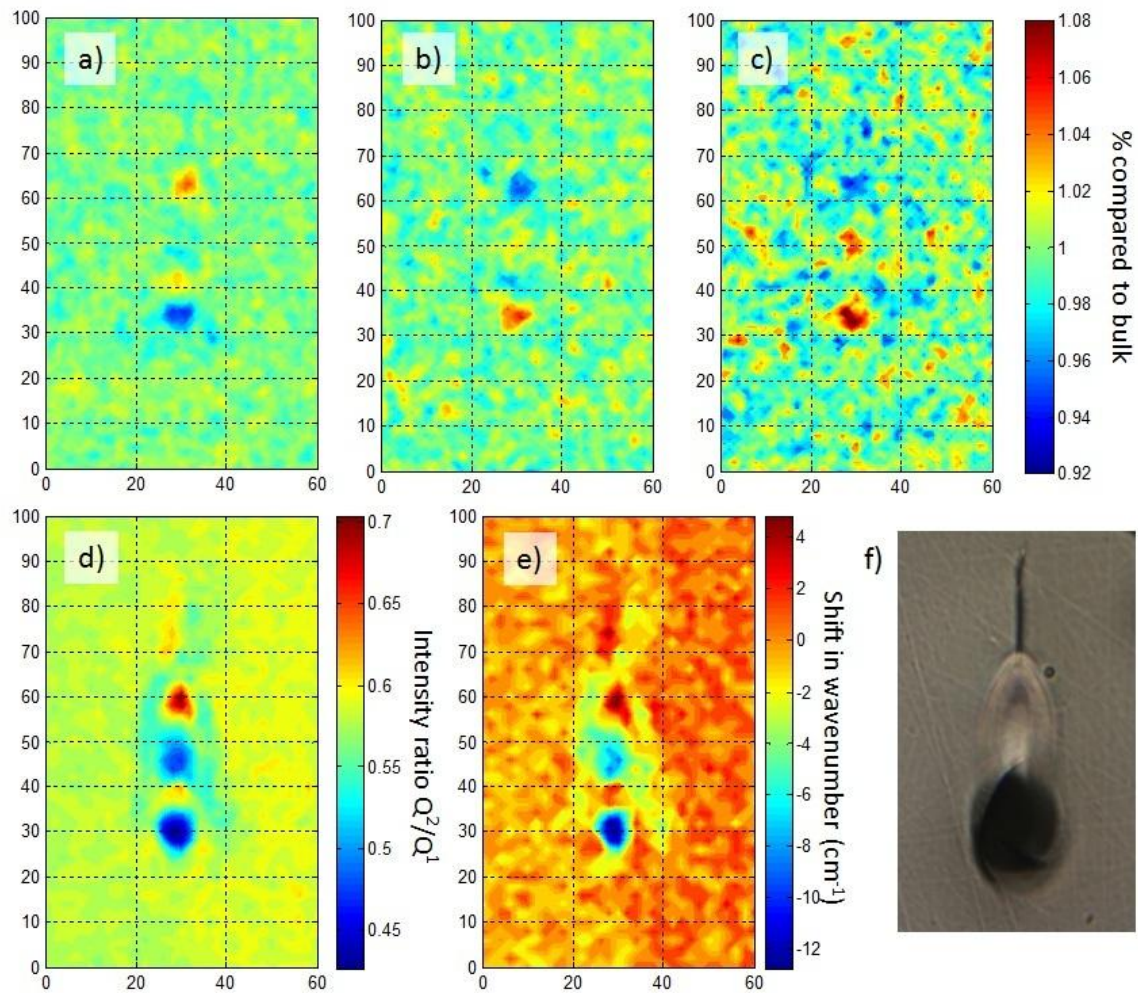
Figure 5. Different mapping techniques for a 60 μm x100 μm modification made in the MgZnP sample with 430 nJ pulse energy; the input is from the bottom of the maps. Elemental mapping has been done on the modification for P (a), Zn (b), and Mg (c); the color scale shows the difference in concentration percentage from the bulk. Qualitative mapping of the change in Q^i species, as determined by Raman spectroscopy, throughout the modification (d); color scale depicts the severity of change in the Q^i species towards Q^2 (red) or Q^1 (blue). Shift in the peak location of the ~1200 cm^{-1} Raman peak (e), color scale maps to wavenumber change from the bulk. White light transmission image of the modification (f). All distance scales are in microns.

By comparing the elemental maps (Figs. 2 and 5, a) through c)) with the Raman maps (Figs 2d and 5d) we see that the modifier-rich (zinc and magnesium) regions exhibit a change towards a Q^1 species as opposed to the phosphorus-rich regions, which exhibit a change towards Q^2 species. This behavior is consistent with the fact that an increase in modifier concentrations is accompanied by a change towards shorter phosphate chains and, therefore, an increase in Q^1 species. It should be noted that in previous studies of similar glasses modified with a 1kHz repetition rate fs laser we observed a shift in the peak location of the ~1200 cm-1 peak [3]. This peak shift was interpreted as a compaction (higher wavenumber) or expansion (lower wavenumber) of the network. Under those low repetition rate laser processing conditions the induced modification does not involve any elemental segregation and redistribution of Q^2 and Q^1 species probably does not occur. We have also mapped our current Raman data in terms of peak shifts and those results are shown in figures 2e and 5e. The reason that these two different mapping techniques in this MHz regime give similar results may be related to the fact that changes in phosphate network structure involve changes in peak position as well as

relative intensity. This is a subject of further study. Finally, we also tested these glasses for the presence of any POHC fluorescence in the irradiated areas but none was found.

Recently Ferrer et al. showed that, for fs-laser modification in the kHz regime, the fluorescence properties of Er^{3+} ion in a phosphate-based glass could be used to gain information about the compaction or expansion of the network surrounding the Er^{3+} ion [8]. They found an increase in the 553 nm Er^{3+} fluorescence in the fs-laser modified volume, which was attributed to reduced energy transfer from Er^{3+} to Yb^3 due to expansion of the network. . We also investigated possible changes in Er^{3+} fluorescence resulting from fs-laser modification in our samples. The results are shown in Figure 6 for the ZnP sample. The ZnP sample has a fluorescence intensity variation of up to 80% compared to the bulk with a rather complex mapping. These fluctuations in the signal are much larger than what has been observed in the kHz regime, where the intensity fluctuations of the 553 nm ($^4S_{3/2} - {}^4I_{15/2}$) fluorescence was only on the order of 5%. It should be noted that the spatial map of the FL data (Fig 6b) does not overlap well with the SEM and Raman maps. Further studies are needed to fully understand these FL results.
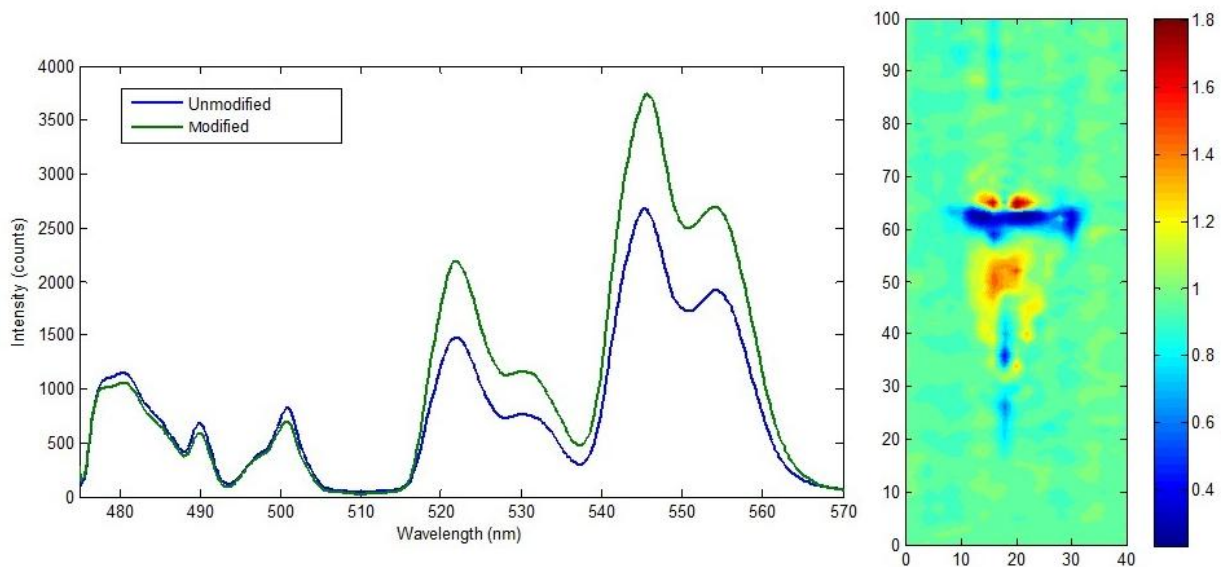

Figure 6. Fluorescence spectra (left) of ZnP sample taken from the bulk (Unmodified) as well as from the laser-modified glass. Map of the total 540 – 565 nm fluorescence signal (right). The spectral signal below 510 nm is due to Raman scattering. Color bar on map indicates the normalized total intensity and the scale around the image is distance in microns.

4. REFERENCES

[1] Taccheo, S.,Della Valle, D., Osellame, R., Cerullo, G., Chiodo, N.,Laporta, P., Svelto, O., Killi, A., Morgner, U., Lederer, M., and Kopf, D., "Er:Yb-doped waveguide laser fabricated by femtosecond laser pulses," Opt. Lett. **29**, 2626-2628 (2004).
[2] Ams, M., Dekker, P., Marshall, G. D., and Withford, M. J., "Monolithic 100 mW Yb waveguide laser fabricated using the femtosecond-laser direct-write technique," Opt. Lett. **34**, 247-249 (2009).
[3] Fletcher, L. B., Witcher, J. J., Troy, N., Reis, S. T., Brow, R. K., and Krol, D. M., "Direct femtosecond laser waveguide writing inside zinc phosphate glass," Opt. Express **19**, 7929-7936 (2011).
[4] Fletcher, L. B., Witcher, J. J., Troy, N., Reis, S. T., Brow, R. K., Vazquez, R. M., Osellame, R., and Krol, D. M., "Femtosecond laser writing of waveguides in zinc phosphate glasses," Opt. Mat. Express 1, 845 (2011).
[5] Eaton, S., Zhang, H., Herman, P., Yoshino, F., Shah, L., Bovatsek, J., and Arai, A., "Heat accumulation effects in femtosecond laser-written waveguides with variable repetition rate," Opt. Express **13**, 4708-4716 (2005).

[6] Yonesaki, Y., Miura, K., Araki, R., Fujita, K., Hirao, K., "Space-selective precipitation of non-linear optical crystals inside silicate glasses using near-infrared femtosecond laser," Journal of Non-Crystalline Solids, **351**,885-892, (2005).

[7] Brow, R. K., Tallant, D. R., Myers, S. T., Phifer, C. C., "The short-range structure of zinc polyphosphate glass," Journal of Non-Crystalline Solids, 191, 45-55 (1995).

[8] Ferrer, A., Jaque, D., Siegel, J., Ruiz de la Cruz, A., Solid, J., "Study of the refractive index modification mechanisms of femtosecond laser processed waveguides in doped phosphate glass through its micro photoluminescence properties," *Lasers and Electro-Optics Europe (CLEO Europe/EQEC), 2011 Conference on and 12th European Quantum Electronics Conference*, **1**, 22-26 (2011).