



An IMI Video Reproduction of Invited Lectures  
from the 17th University Glass Conference

# Using Ultrafast Lasers to Add New Functionality to Glass

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**17th University Conference on Glass  
New Functionality in Glasses  
Penn State, June 2005**



## Adding new functionalities to glass

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Usually the functionality of glass is determined by

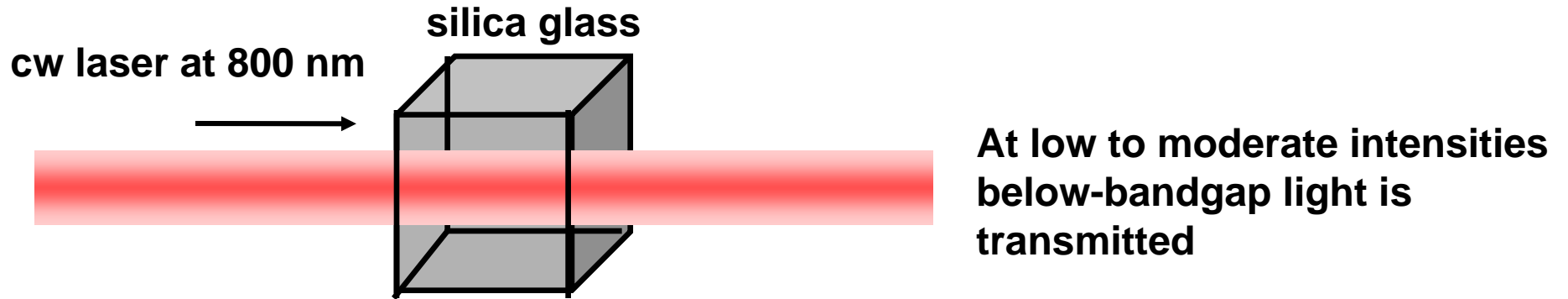
- **composition**                      oxides, chalcogenides, fluorides  
   continuous variation
- **doping**                                 $\text{SiO}_2$  (passive optical components)  
   vs  $\text{SiO}_2:\text{Er}^{3+}$  (active components)
- **processing**                            bulk glass  
   vs optical fiber, microspheres

But functionality can also be modified by

- **light**                                    UV inscription of Bragg gratings  
   in  $\text{SiO}_2:\text{Ge}$  optical fibers
- **electric field**                        thermal poling to induce  $\chi^{(2)}$

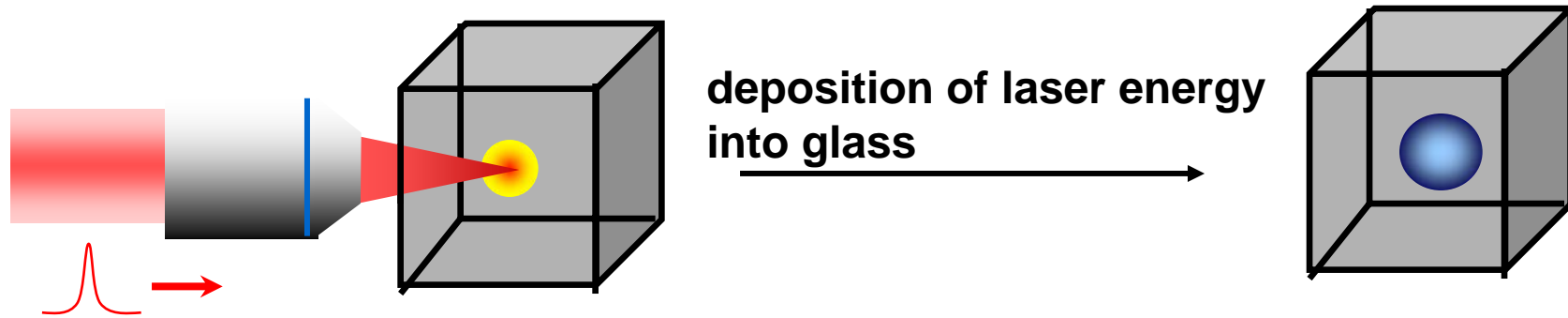


# Femtosecond laser modification in glass



ultrashort (100fs) pulses  
and tight focusing ( $\mu\text{m}$ -size spot)

Light-matter Interaction is localized  
in time and space ->  
3-D control of modification





# Femtosecond laser pulses can modify various glass properties

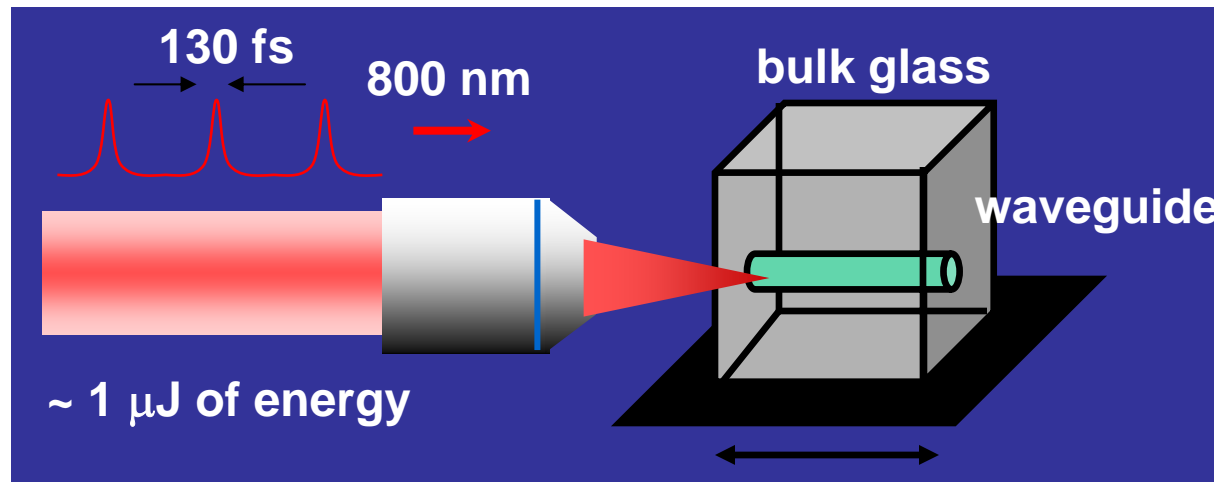
Properties that can be modified:

- **Refractive index**
- **Absorption**
- **Composition**
- **Valence state**
- **Crystal nucleation**

phase separation

$\text{Sm}^{3+} \rightarrow \text{Sm}^{2+}$

Ag and Au colloids in glass



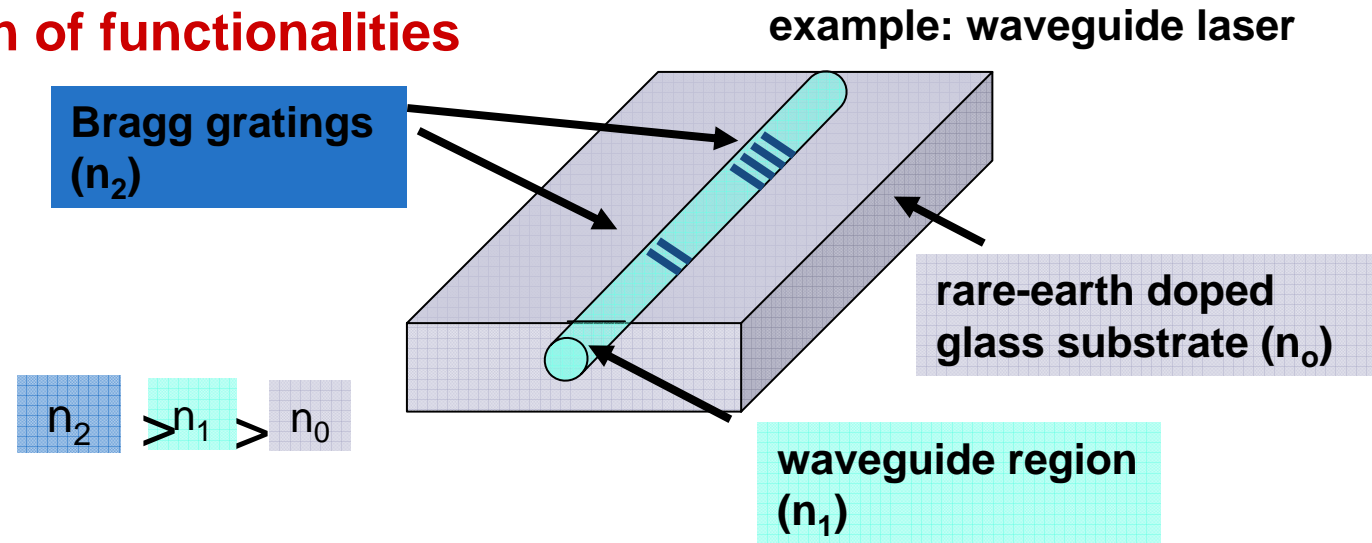
Davis *et. al*, *Opt. Lett.*, 21, 1729 (1996)

Homoelle *et. al*, *Opt. Lett.*, 24, 1311 (1999)

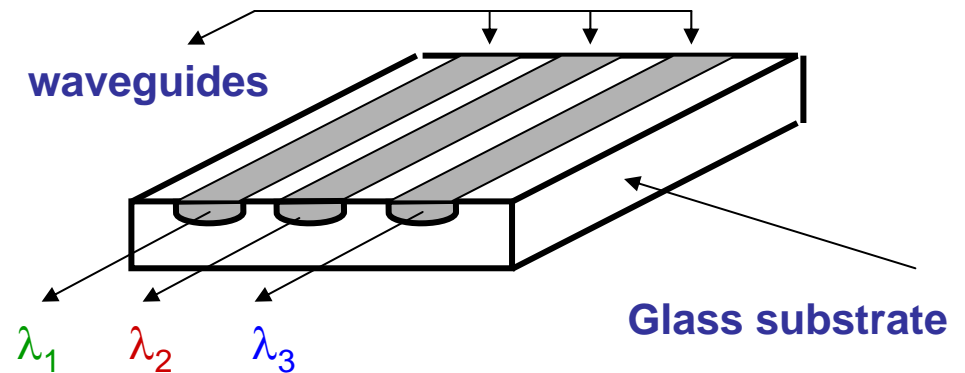


# Femtosecond laser fabrication of components for integrated optics

## – Integration of functionalities



## – Component arrays

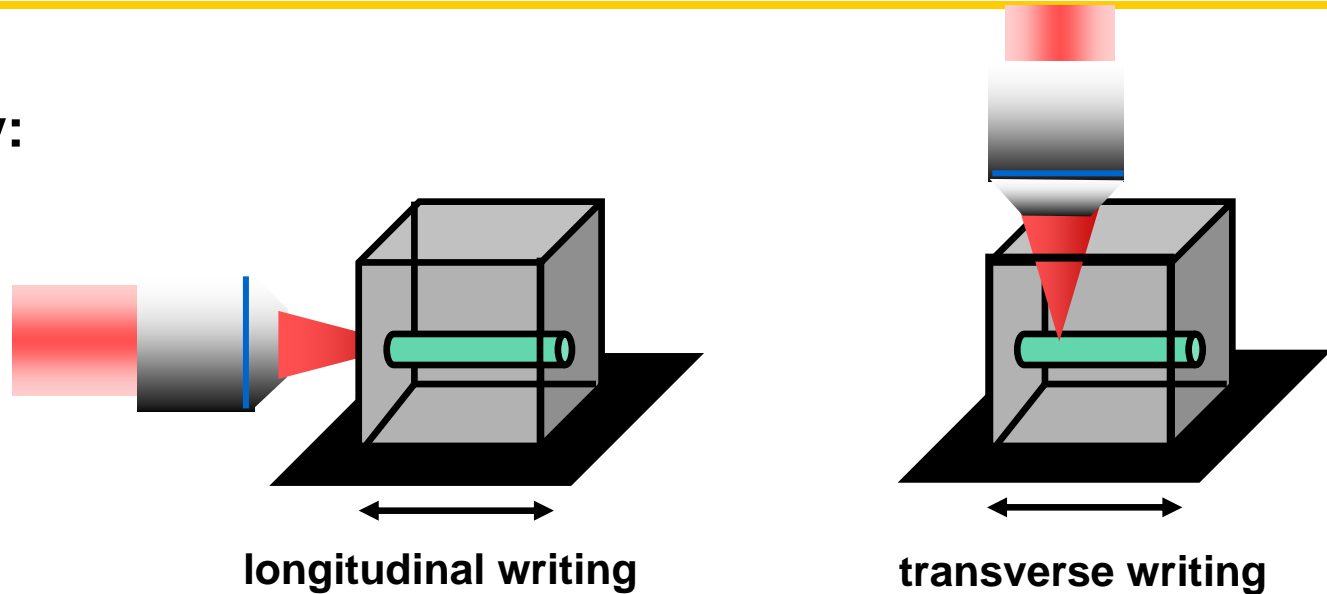


## – Ability to fabricate 3D structures



# Experimental parameters in fs-laser writing

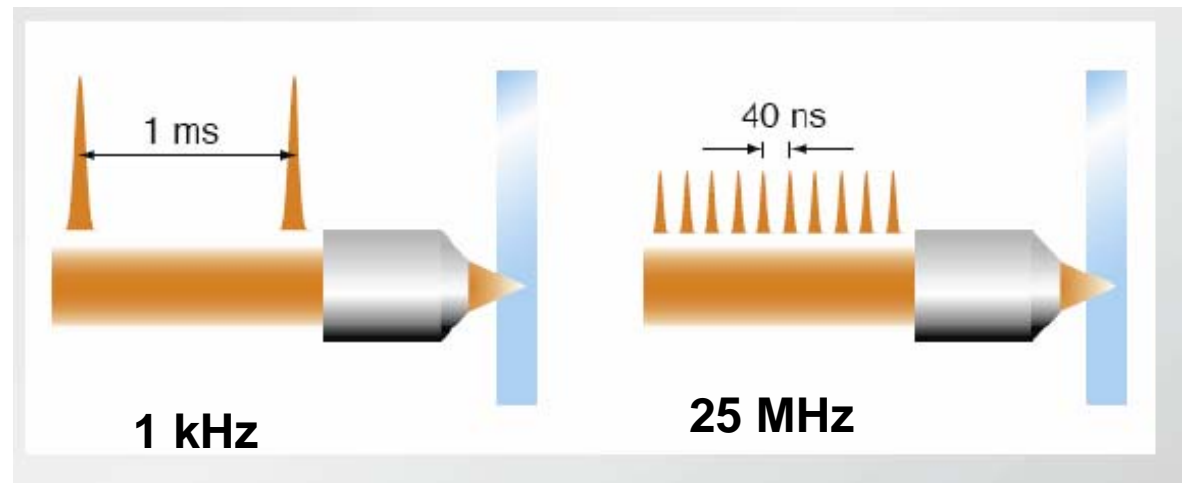
## ➤ writing geometry:



## ➤ pulse energy: 0.1-10 $\mu\text{J}$ :

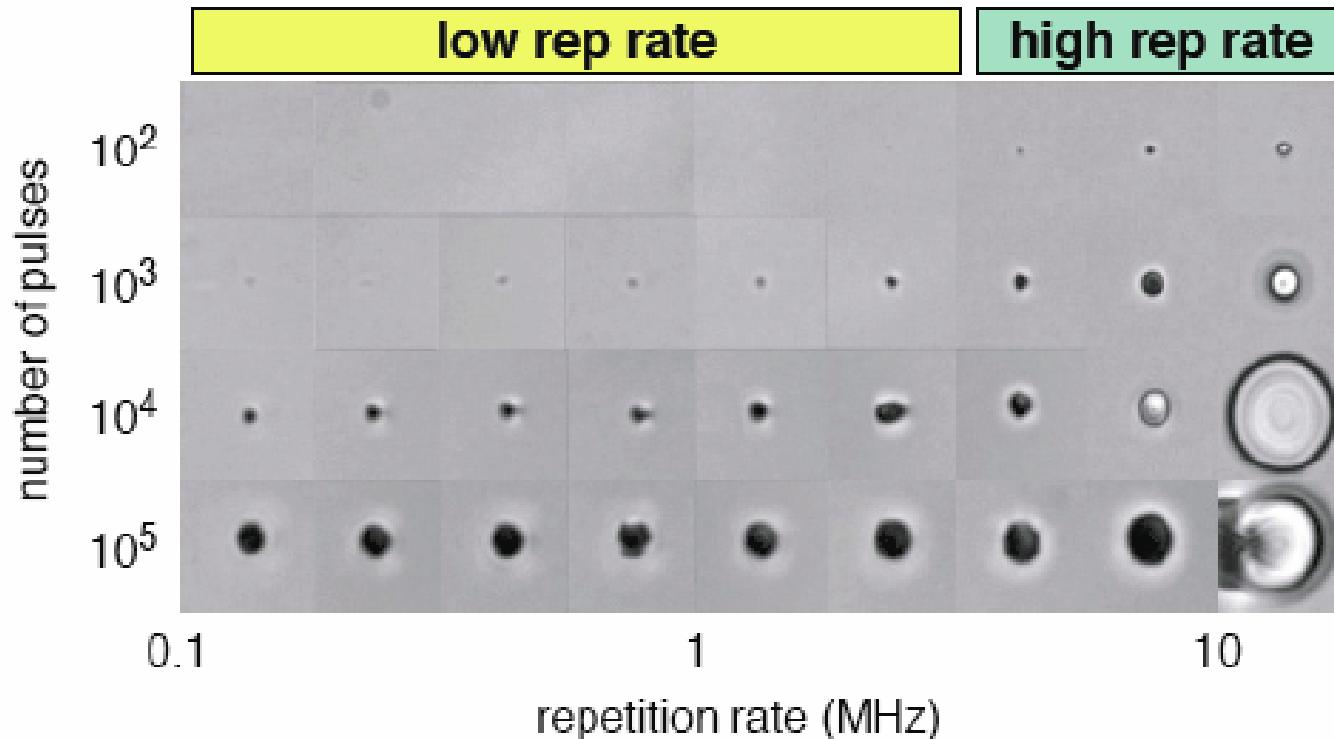
## ➤ laser wavelength: 800 nm

## ➤ pulse repetition rate





# Difference between high and low pulse repetition rate

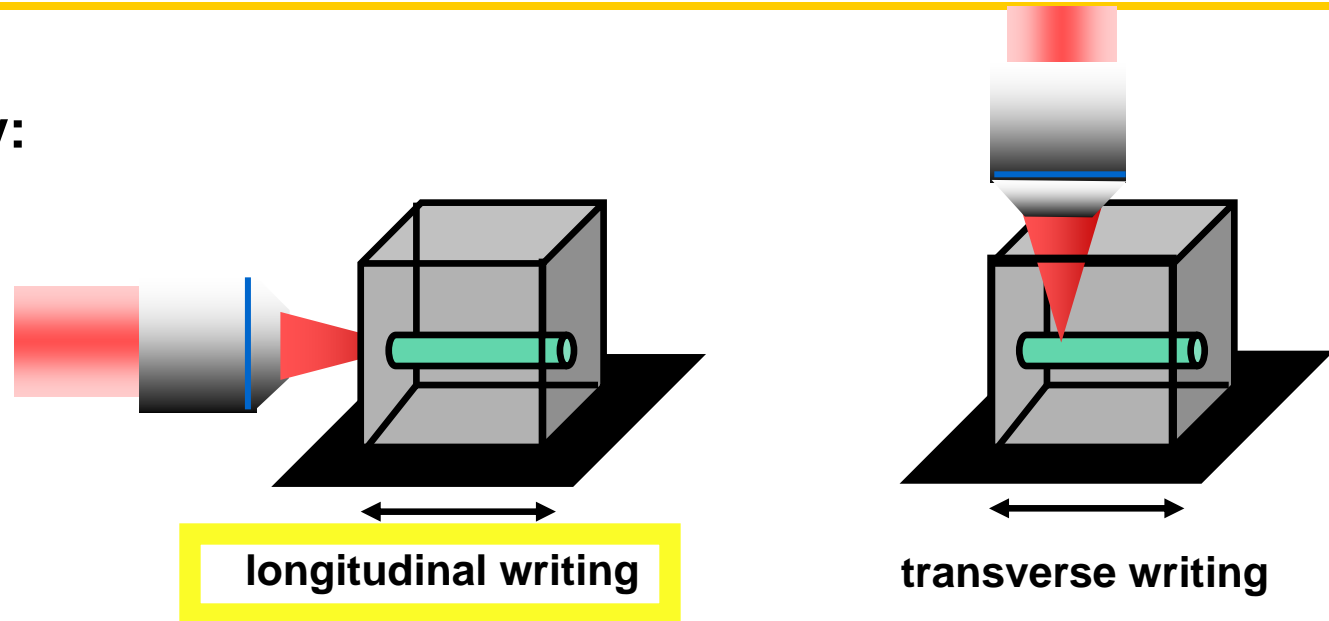


**Is the structure of the modified material different for the low and high rep rate regimes ?**



# Experimental parameters used in our experiments

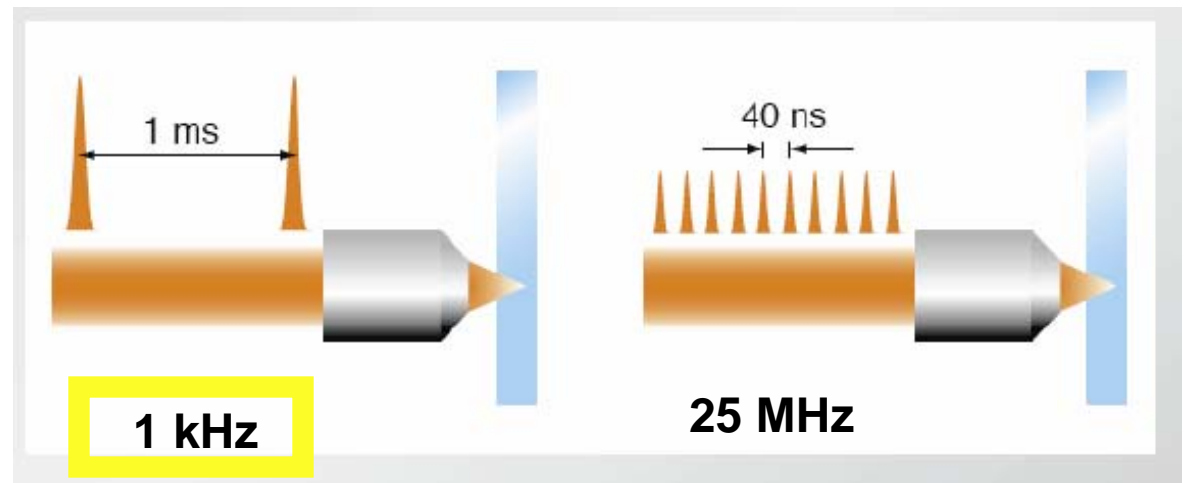
## ➤ writing geometry:



## ➤ pulse energy: 0.1-10 $\mu\text{J}$ :

## ➤ laser wavelength: 800 nm

## ➤ pulse repetition rate







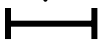
# White light micrographs of lines written with different fs pulse energies in fused silica

laser parameters: 800 nm, 130 fs, 1 kHz

scan speed:

40  $\mu\text{m/s}$

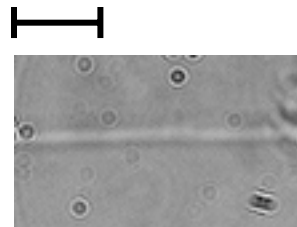
MO: 50x, 0.55 NA

5  $\mu\text{m}$   


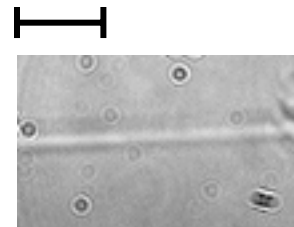


0.00

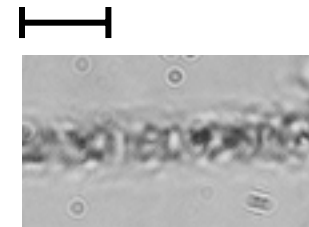
fs energy ( $\mu\text{J}$ )



0.15



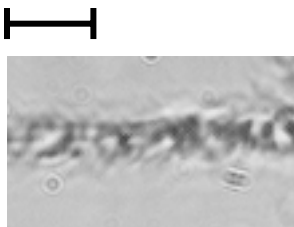
0.25



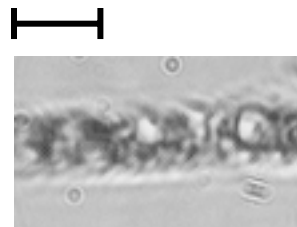
0.7

Slight modification

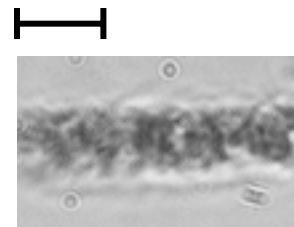
Damage



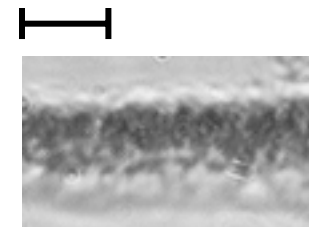
1.3



2.0



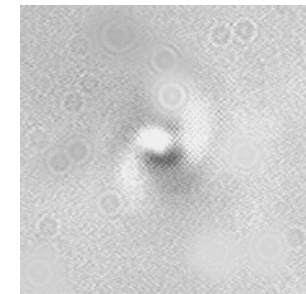
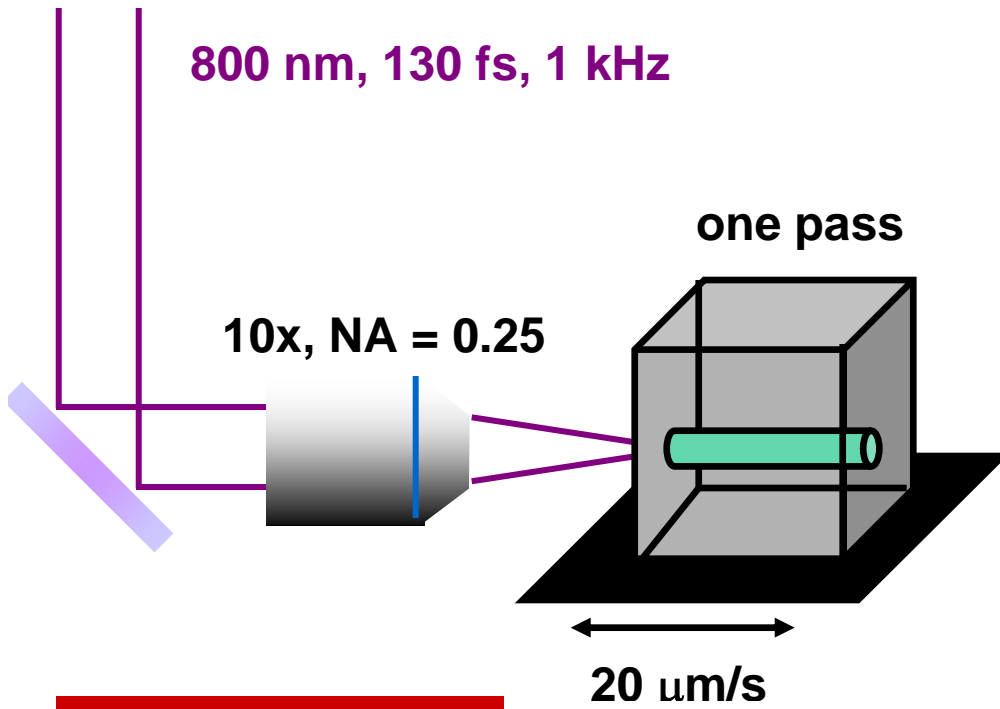
2.7



5.9

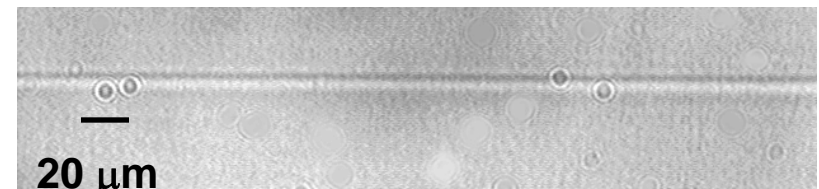


# Waveguides are written with 1 μJ of pulse energy

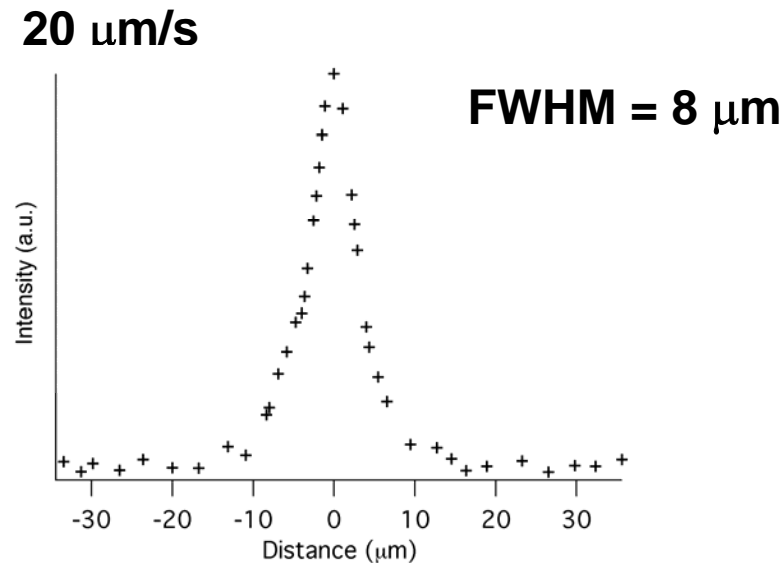
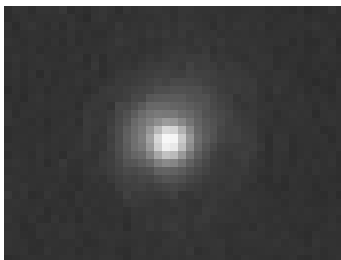


white light images

9 μm



Near field profile at 633 nm



Far field profile

$$NA \sim \tan \theta$$

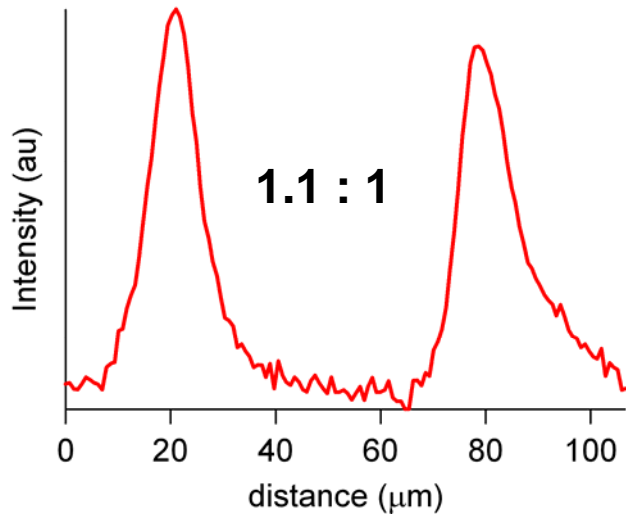
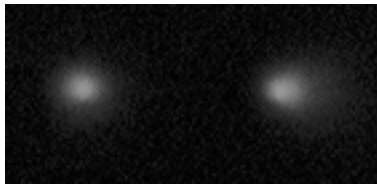
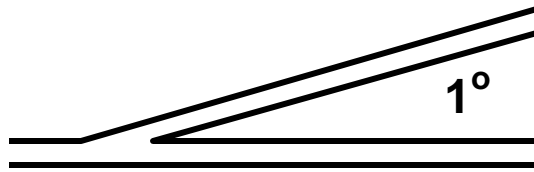
$$NA = \sqrt{2n_o \Delta n}$$

$$\Delta n \approx 10^{-4}$$

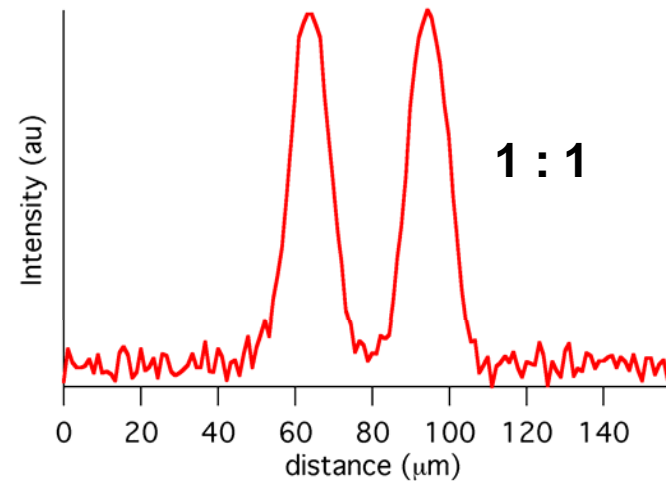
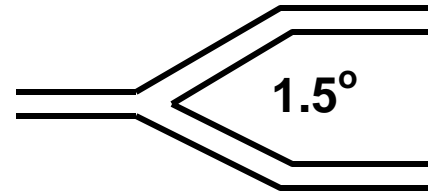


# Splitters are made by scanning along multiple axes

Asymmetric splitter

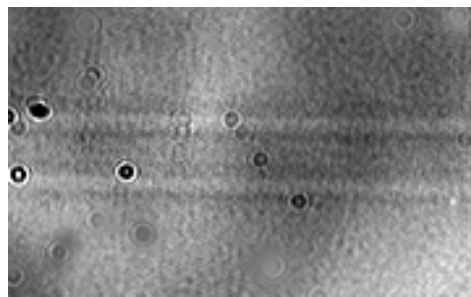


Y-branch splitter

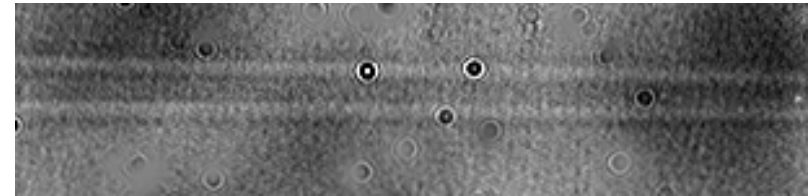




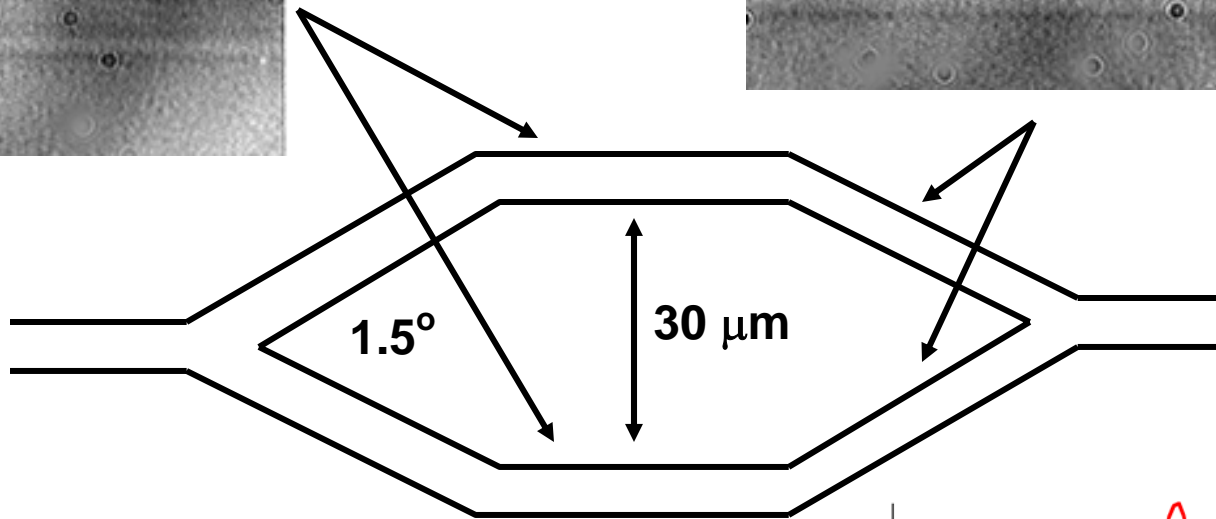
# Mach-Zehnder interferometer inside fused silica



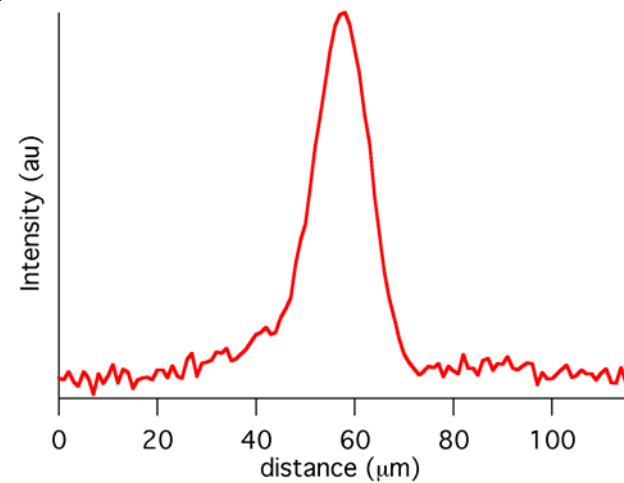
20 μm



20 μm



Near field profile at 633 nm





## Fs pulses have been used to write fiber Bragg gratings

Mihailov et al., Opt. Lett. 28, 995 (2003)

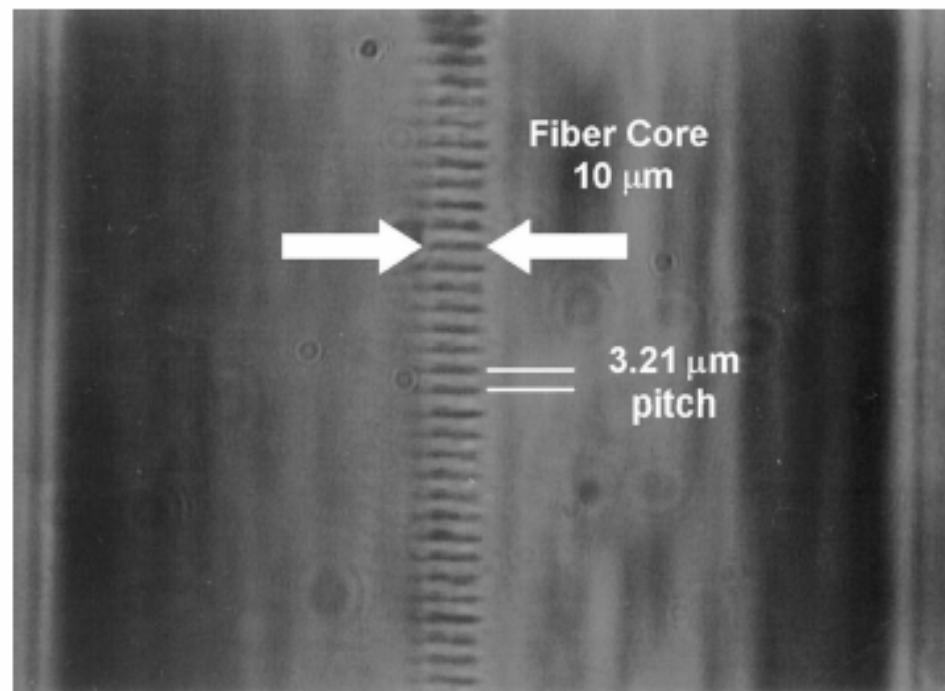


Fig. 4. Photographic image of photoinduced index modulation as seen through an optical microscope. The spacing between lines in the image corresponds to the  $3.213\text{-}\mu\text{m}$  period of the phase mask.



# Fs pulses have been used to write Er:Yb doped waveguide laser

Taccheo et al., Opt. Lett. 29, 2626 (2004)

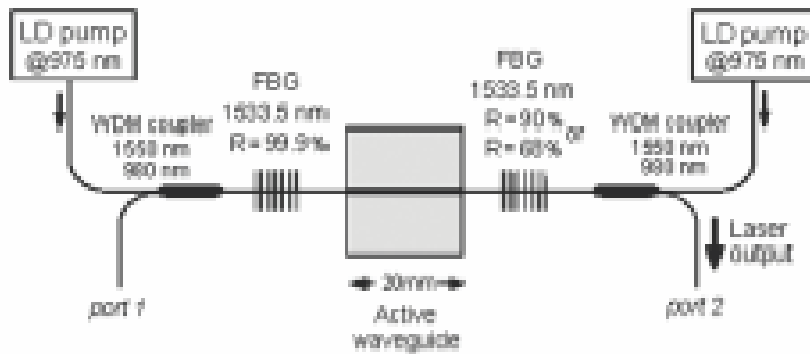


Fig. 3. Waveguide laser cavity configuration. Waveguide characterization was performed by removing the FBGs and coupling a tunable laser source throughout port 1. LD, laser diode; R, reflectivity.

**Er:Yb-doped phosphate glass**  
**Lasing wavelength: 1533.5 nm**  
**Output power: 1.7 mW**

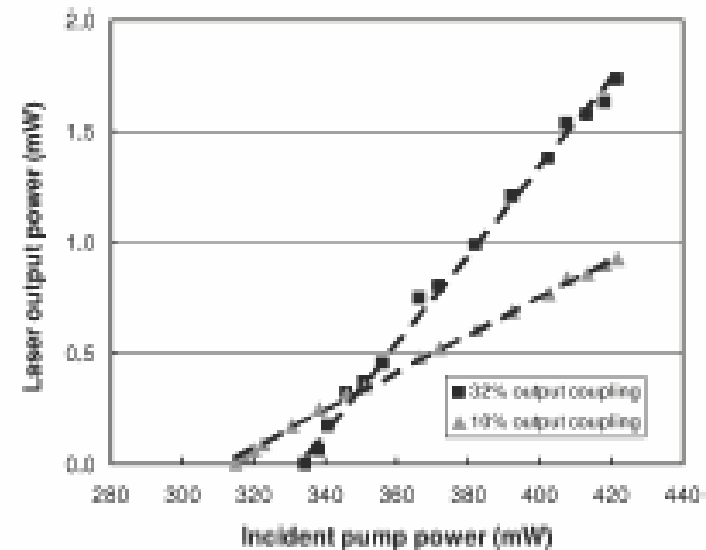


Fig. 4. Laser output power versus incident pump power for two different output couplers. The inset shows the RIN laser spectrum corresponding to 32% output coupling.



## Objectives

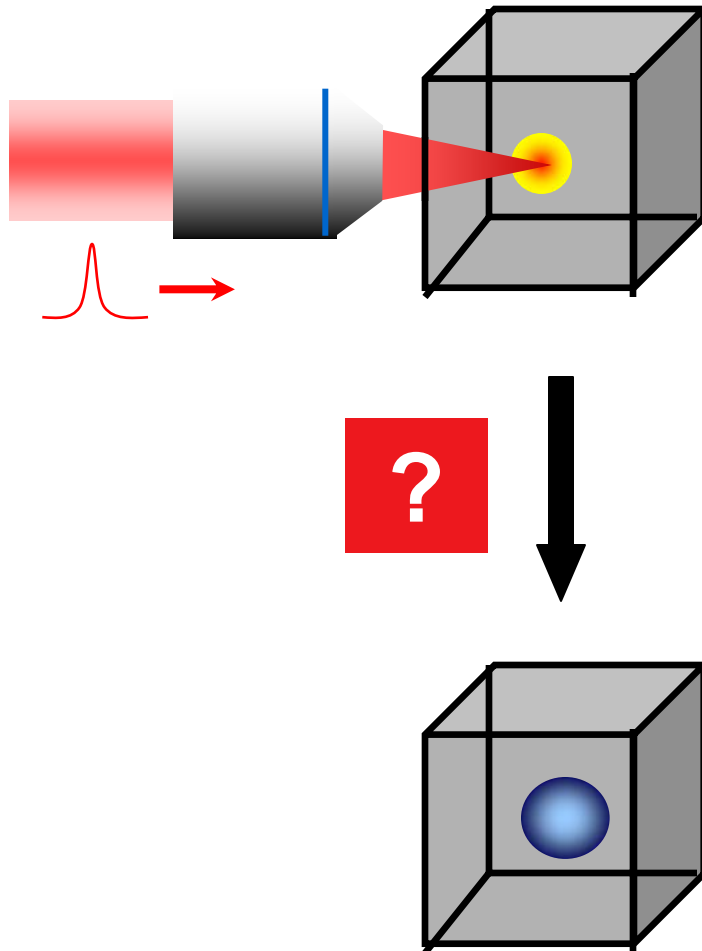
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- ➔ **Investigate the use of fs laser pulses to fabricate optical devices in glass**
  - ↗ write waveguides: pulse energies, scan speed
  - ↗ characterize waveguides: mode profile, loss

**what is the effect of glass composition?**



# Femtosecond laser modification in glass



1) Multiphoton absorption

2) Avalanche photoionization

3) Plasma formation

Stuart *et. al*, Phys. Rev. Lett., 74, 2248 (1995)

Lenzner *et. al*, Phys. Rev. Lett., 80, 4076 (1998)

4) Proposed mechanism:

Shockwave propagation - microexplosion

Glezer *et. al*, Appl. Phys. Lett., 71, 882 (1997)

5) Modified spot

Localized  $\Delta n$

How does the material change on an atomic scale? - relation to  $\Delta n$ ?





## Objectives

- Investigate the use of fs laser pulses to fabricate optical devices in glass
  - ↗ write waveguides: pulse energies, scan speed
  - ↗ characterize waveguides: mode profile, loss
- Study atomic scale structural changes in the glass network due to exposure to fs laser pulses

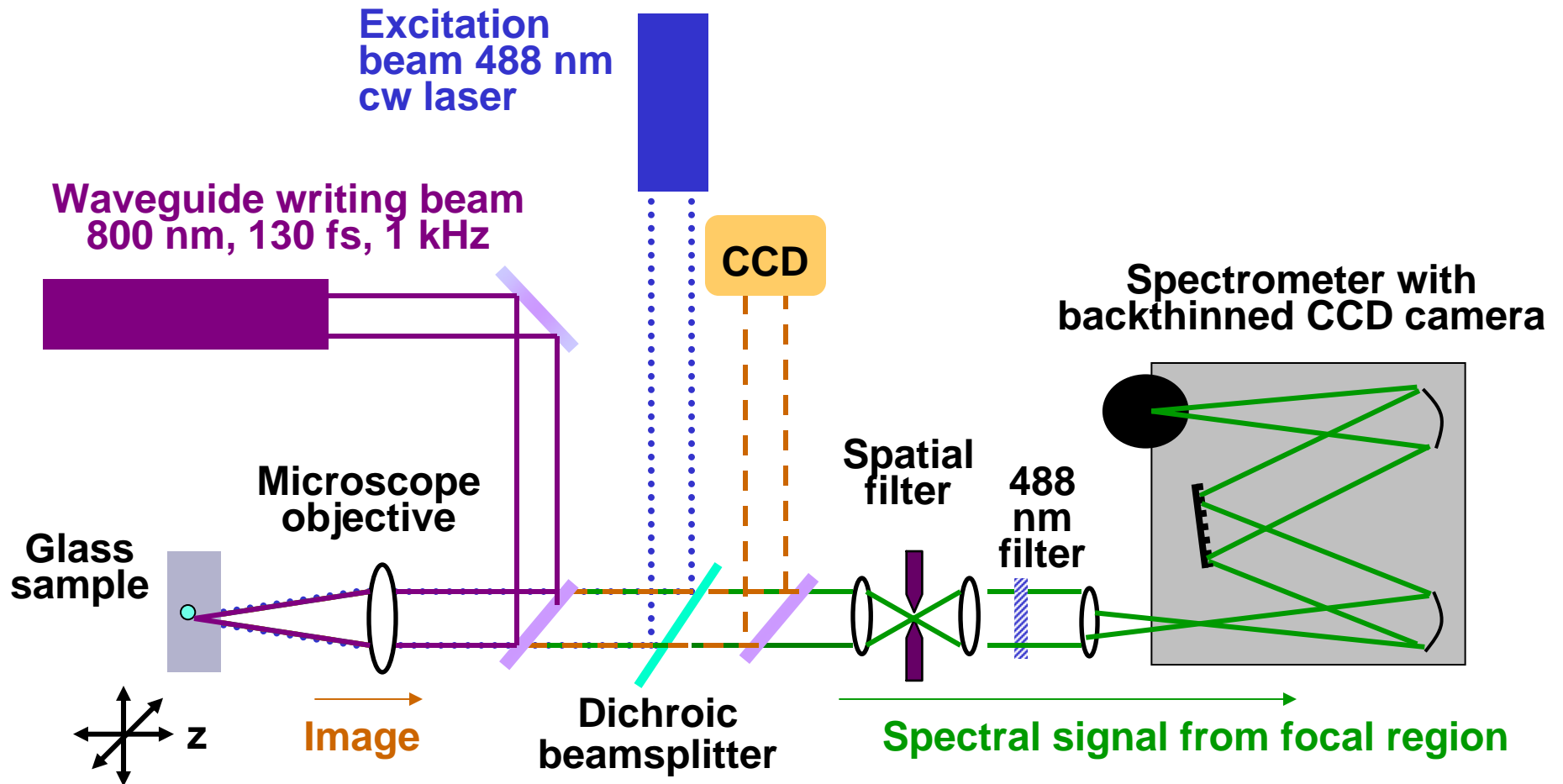
**We want to selectively probe the fs-modified glass using confocal fluorescence microscopy**

- ↗ Raman spectroscopy - information on glass network
- ↗ Fluorescence spectroscopy - information on defects

**what is the effect of glass composition?**



# Scanning confocal spectroscopy setup





Comparison between

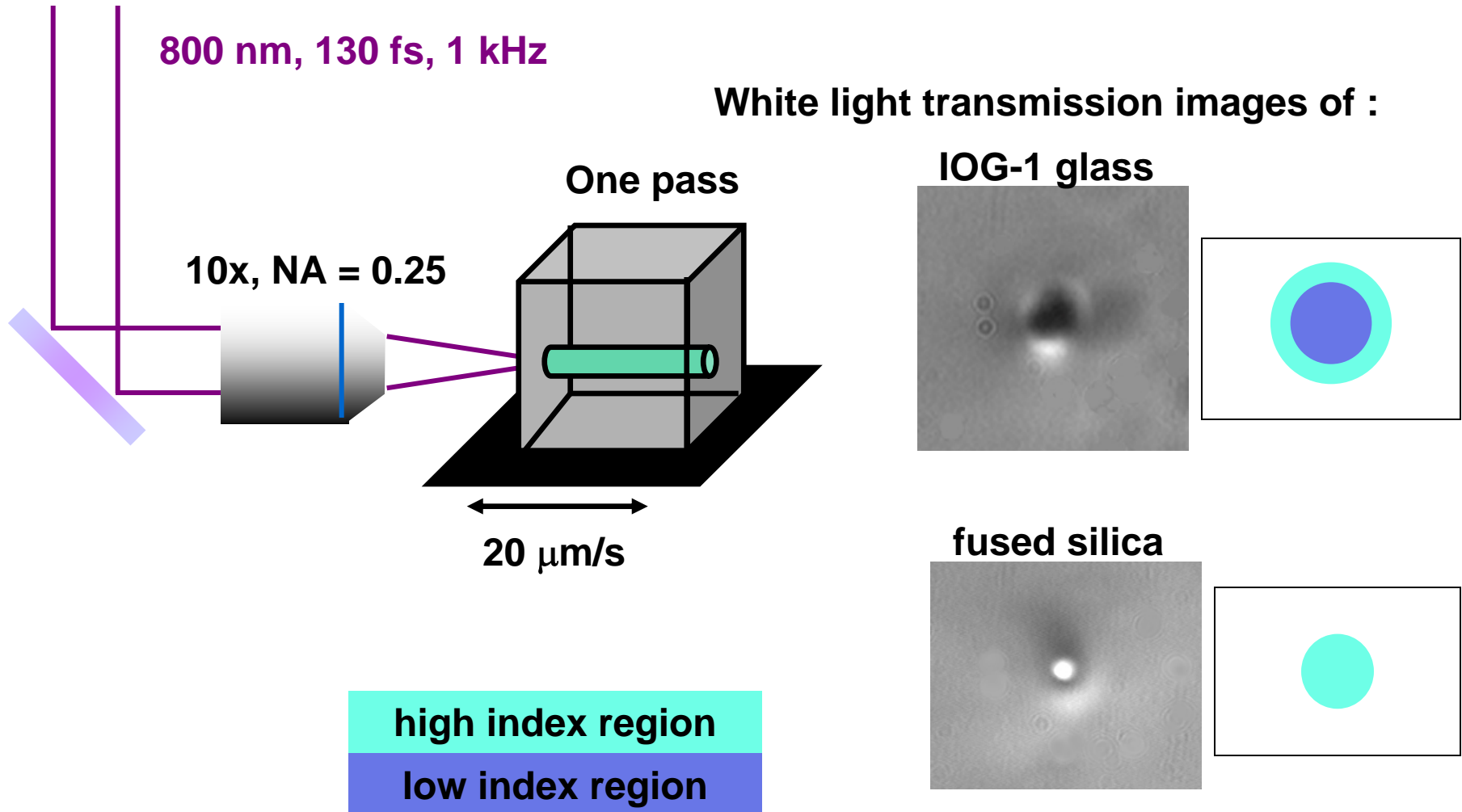
**Fused silica (Corning 7940)**

and

**Phosphate glass (Schott Glass IOG-1)**

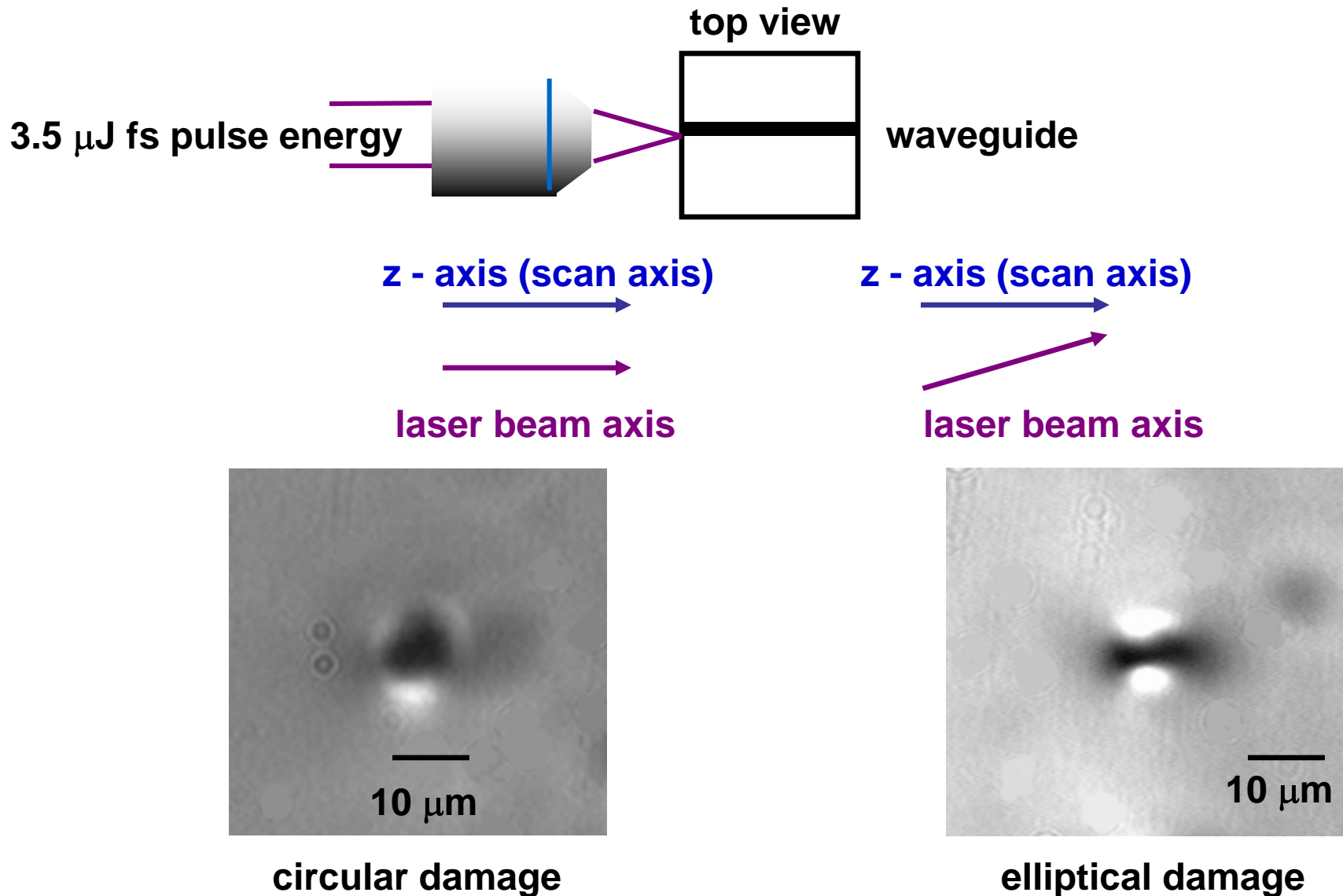


# Modification in IOG-1 is different from fused silica



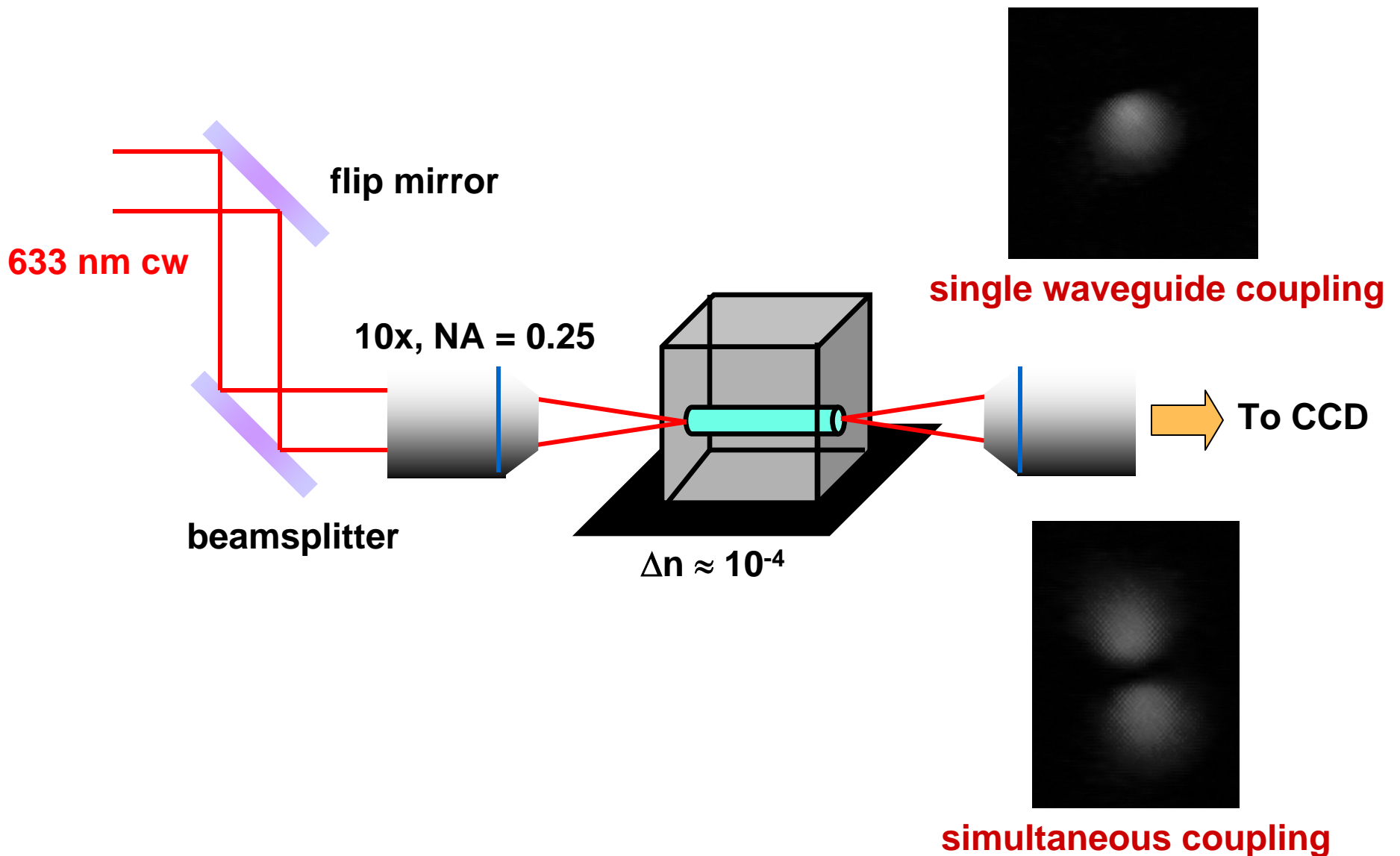


# The induced modification is sensitive to laser propagation direction





# Near field profiles confirm that two waveguides are created in case of elliptical damage





## Objectives

- Investigate the use of fs laser pulses to fabricate optical devices in glass
  - ↗ write waveguides: pulse energies, scan speed
  - ↗ characterize waveguides: mode profile, loss
  - ↗ what is the effect of glass composition?

waveguides in fused silica (Corning 7940) & phosphate glass (Schott Glass IOG-1) are different

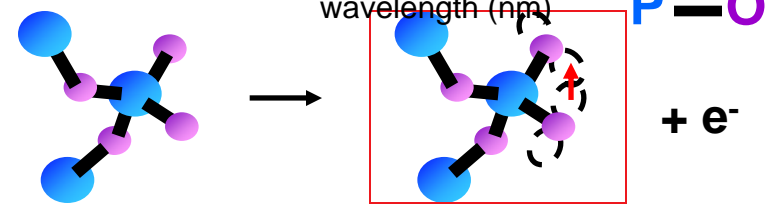
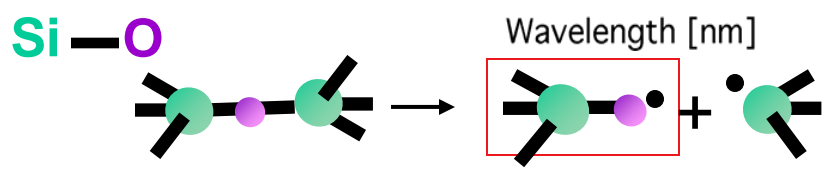
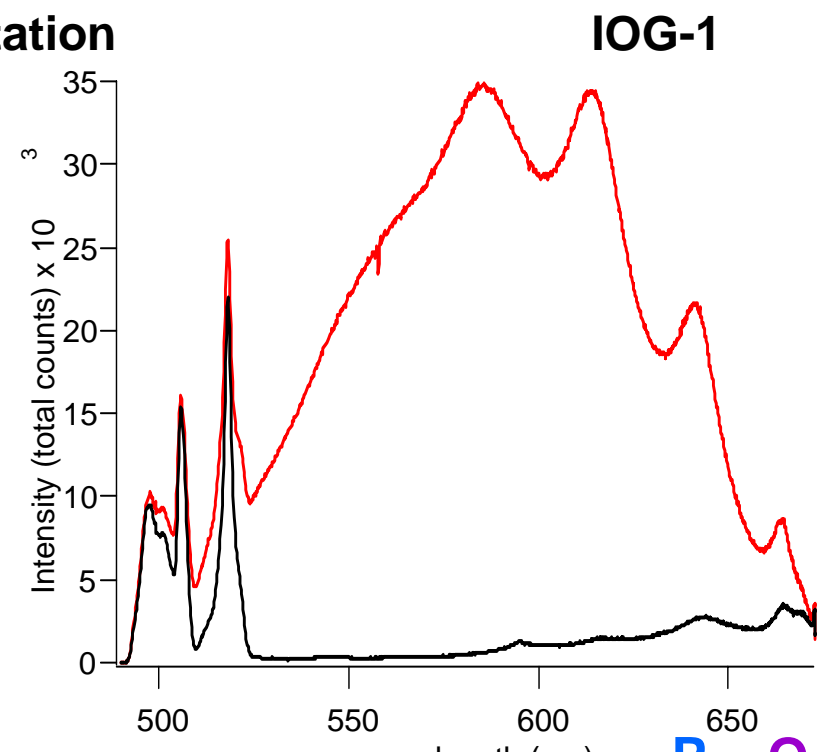
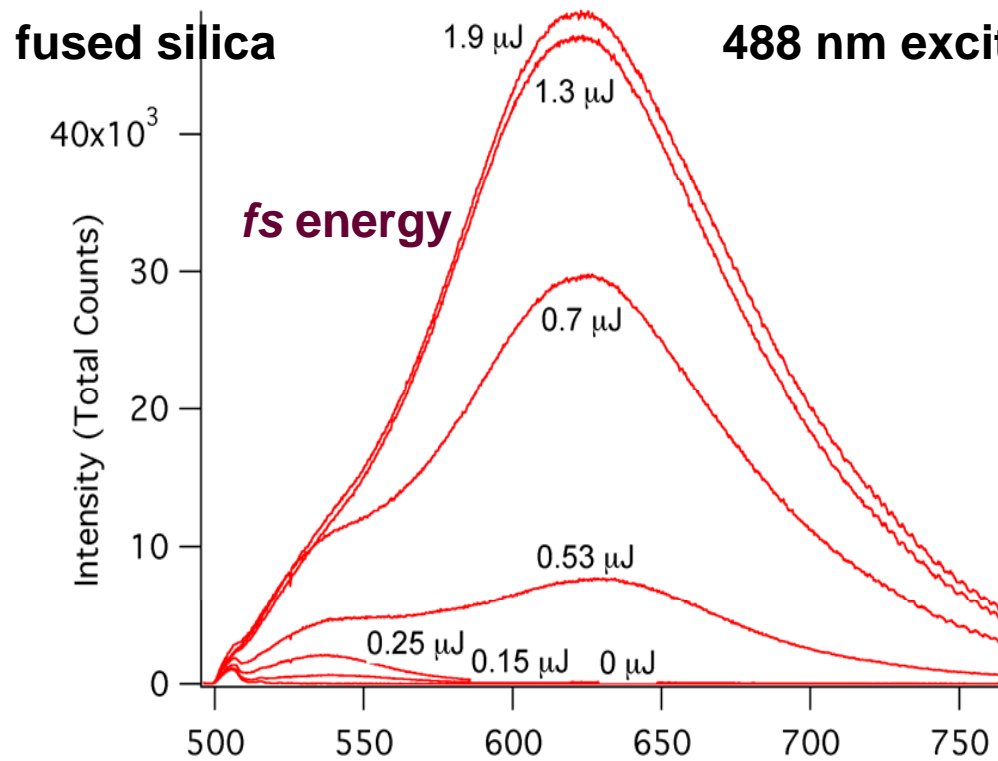
- Study atomic scale structural changes in the glass network due to exposure to fs laser pulses

We want to selectively probe the fs-modified glass using confocal fluorescence microscopy

- ↗ Raman spectroscopy - information on glass network
- ↗ Fluorescence spectroscopy - information on defects



# Fluorescence spectra of fs-modified glass



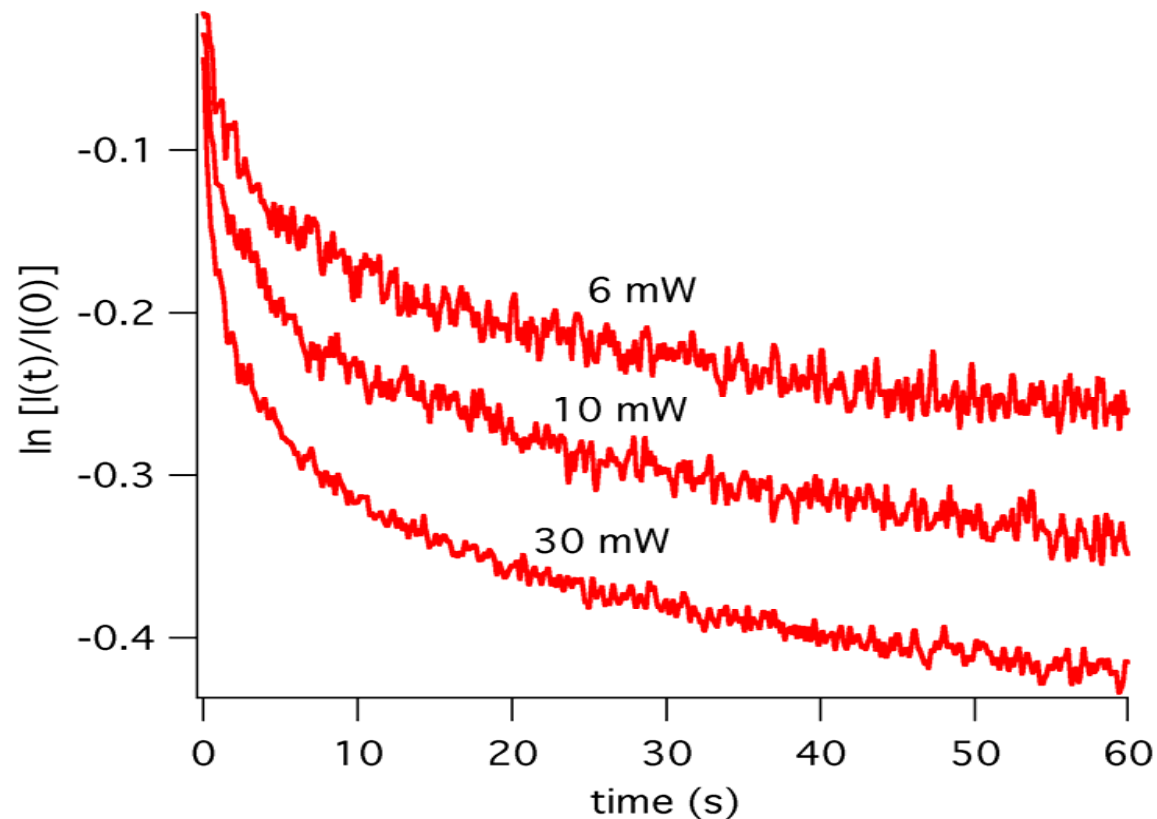
**fs-laser modification produces non-bridging oxygen hole centers (NBOHC)**

Chan et. al, Appl. Phys. A, 76, 367 (2003), Sun et. al, J. Phys. Chem. B, 104, 3450 (2000), Chan et. al, J. Am. Ceram. Soc. 85, 1037 (2002).





## NBOHC fluorescence bleaches with cw 488 nm exposure



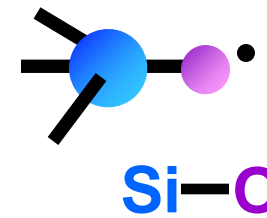
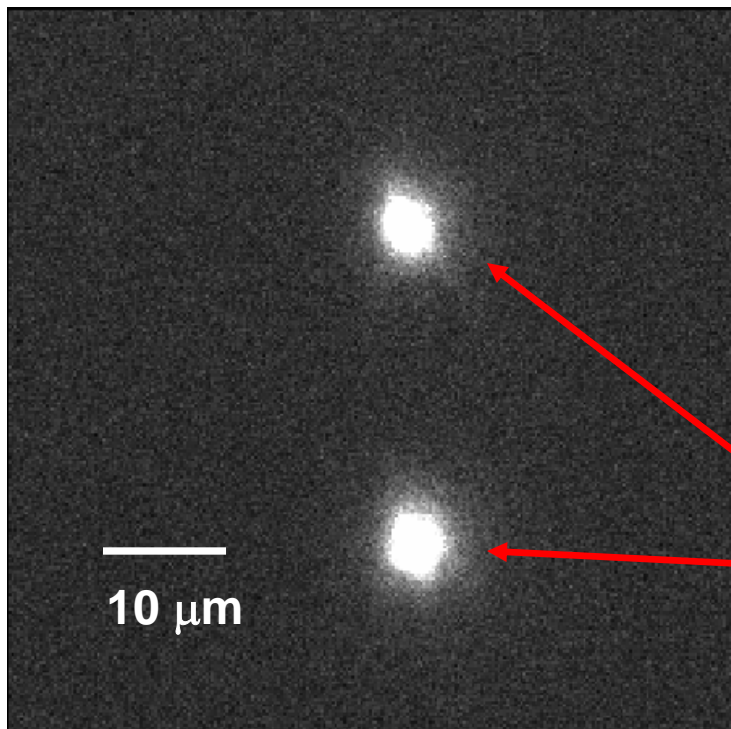
Decay of 630 nm fluorescence from modified fused silica continuously exposed to 488 nm light.

**broken bonds are healed by 488 nm light**



# Fluorescence images of waveguides show spatial profile of color centers

scan sample with focused 488 nm beam (100x objective)  
yields x-y spatial profile of color centers

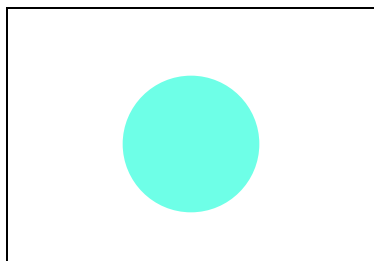
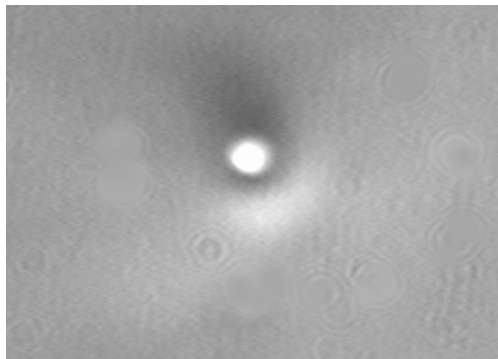


non-bridging oxygen hole centers (NBOHC) located within waveguide regions

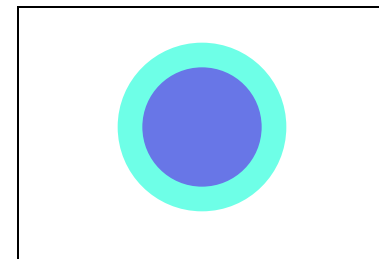
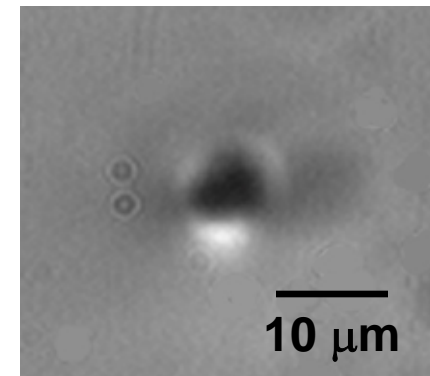
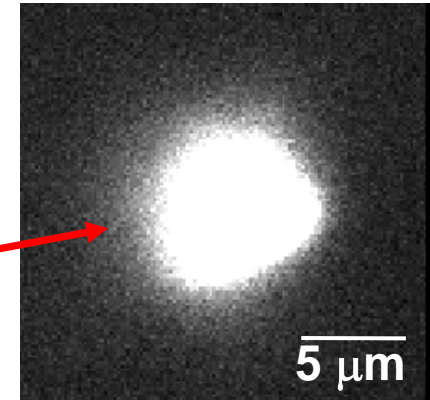


# Color centers are located in the central damaged region of the modified glass

fused silica



phosphate glass



fluorescence images

**NO color centers in w.g. regions**

w.g. regions not directly exposed to fs pulses

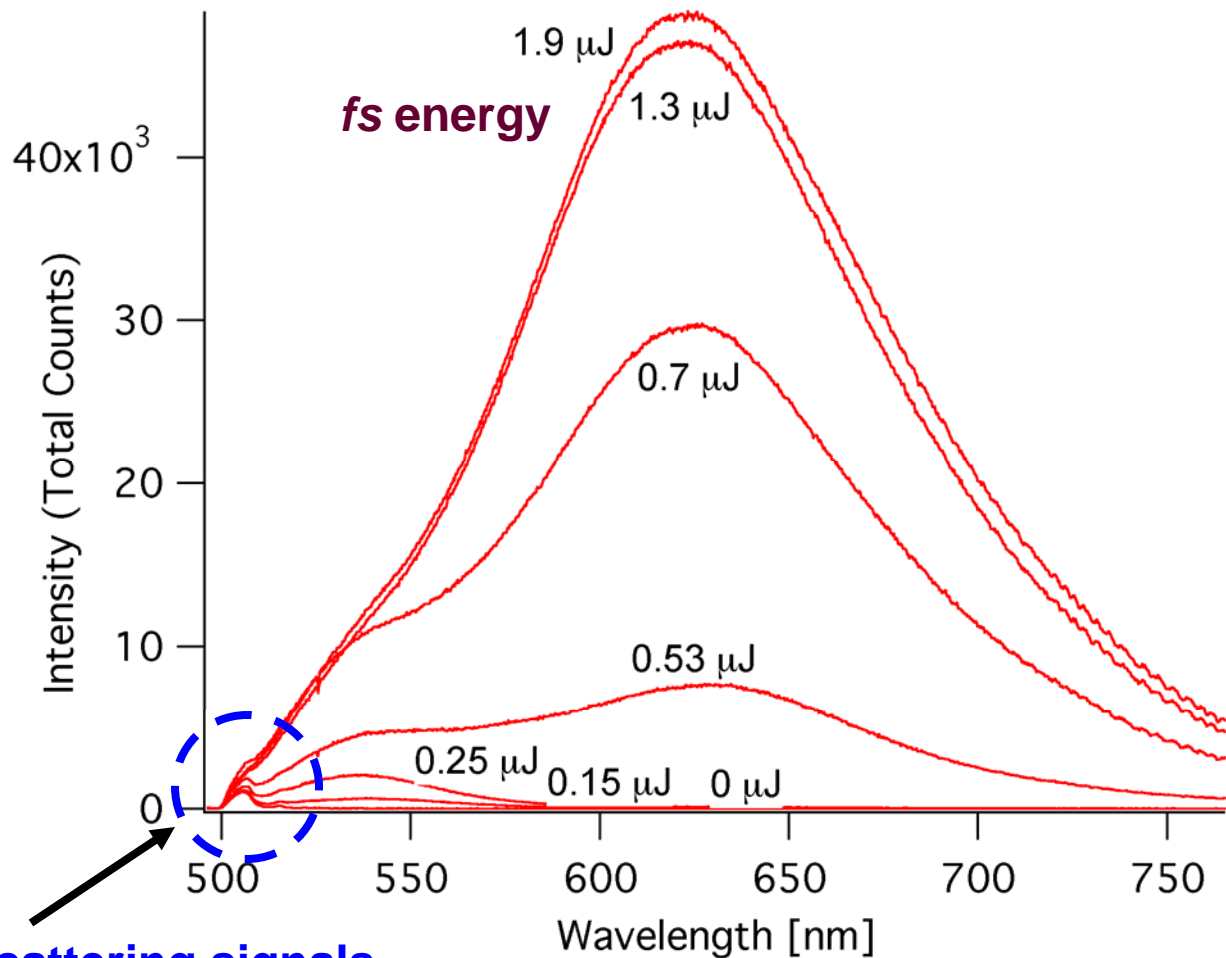
white light images

high index region  
low index region



# Raman scattering signals lie on the edge of broad fluorescence

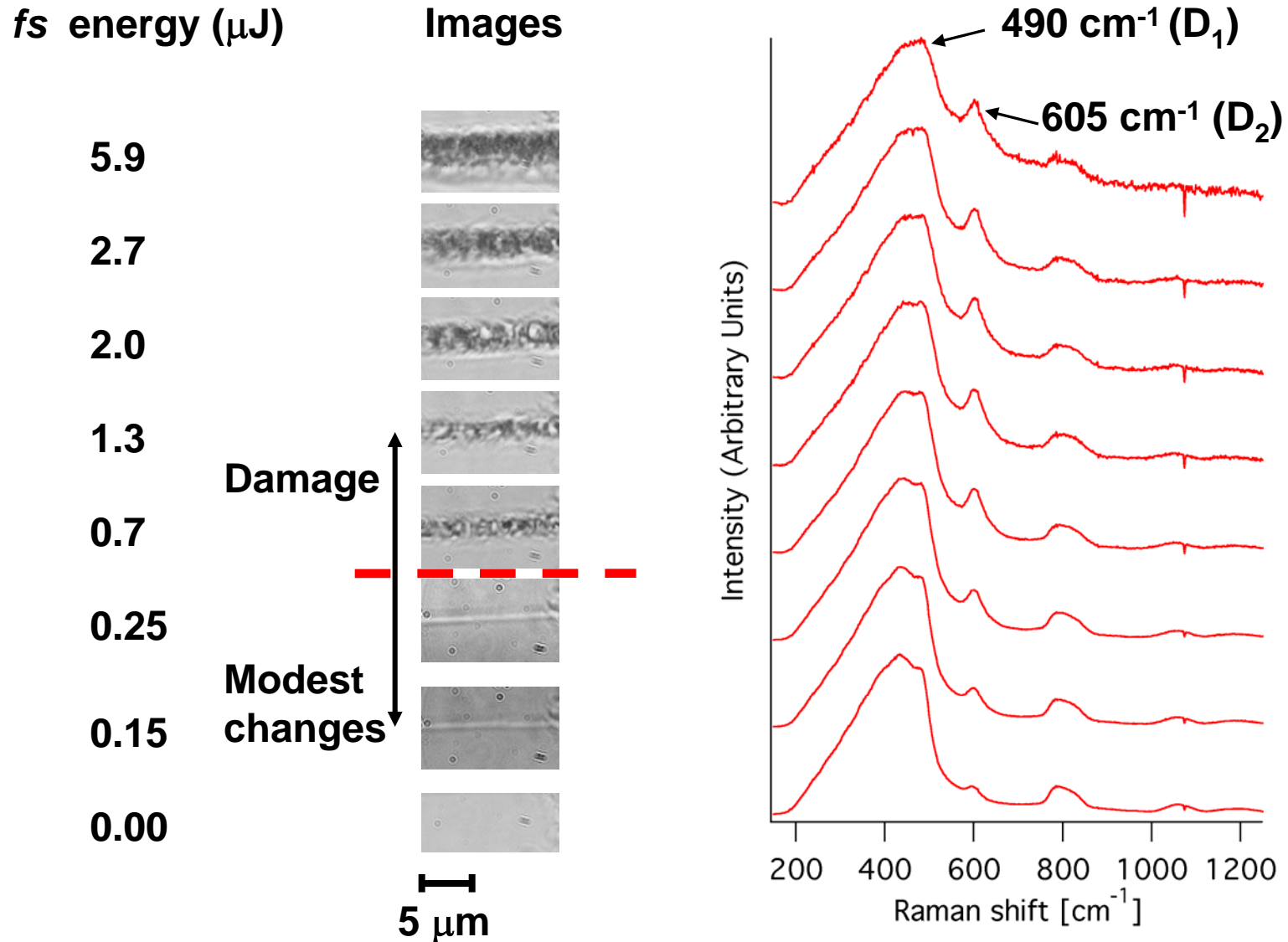
15 mW 488 nm light



Raman scattering signals

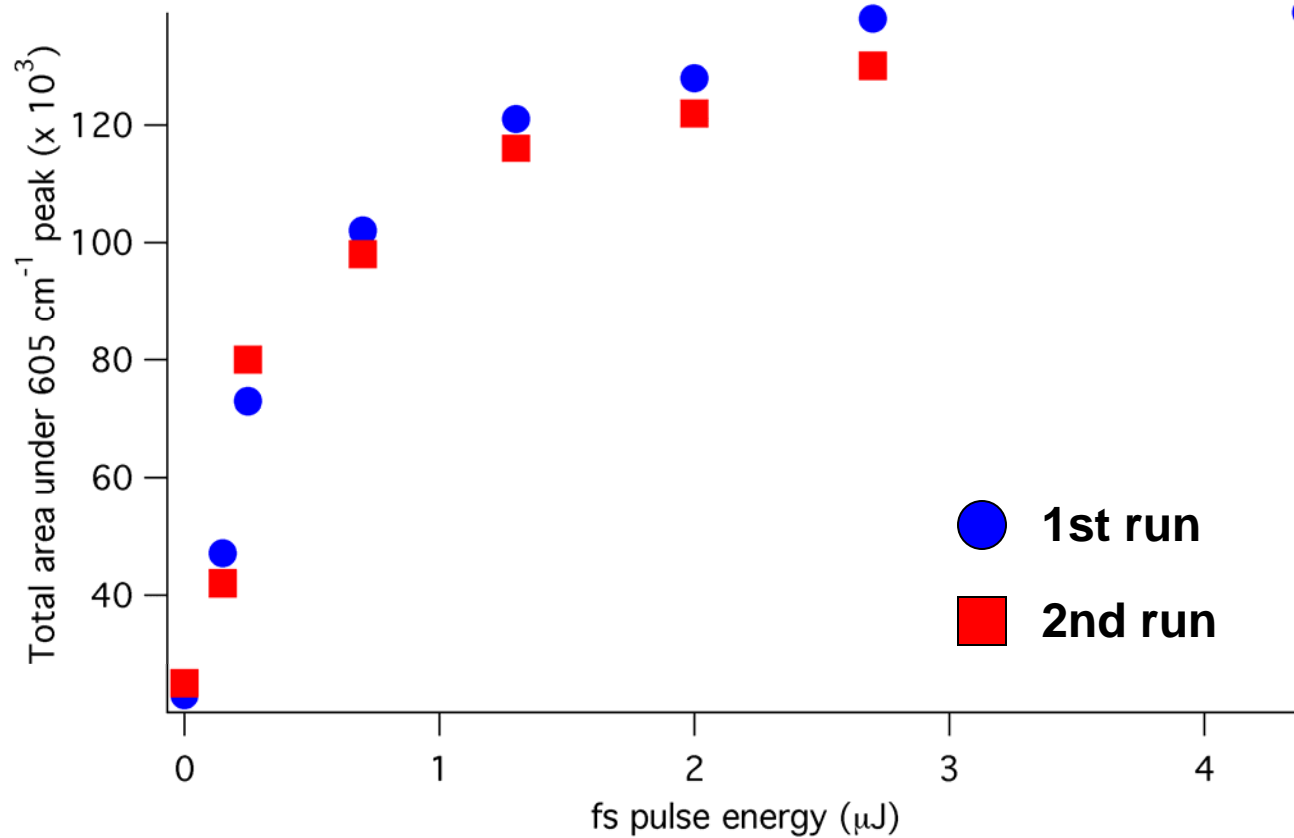


# The 490 $\text{cm}^{-1}$ and 605 $\text{cm}^{-1}$ peaks in the Raman spectra increase with fs pulse energy





## Increase of the D<sub>2</sub> peak area with fs pulse energy



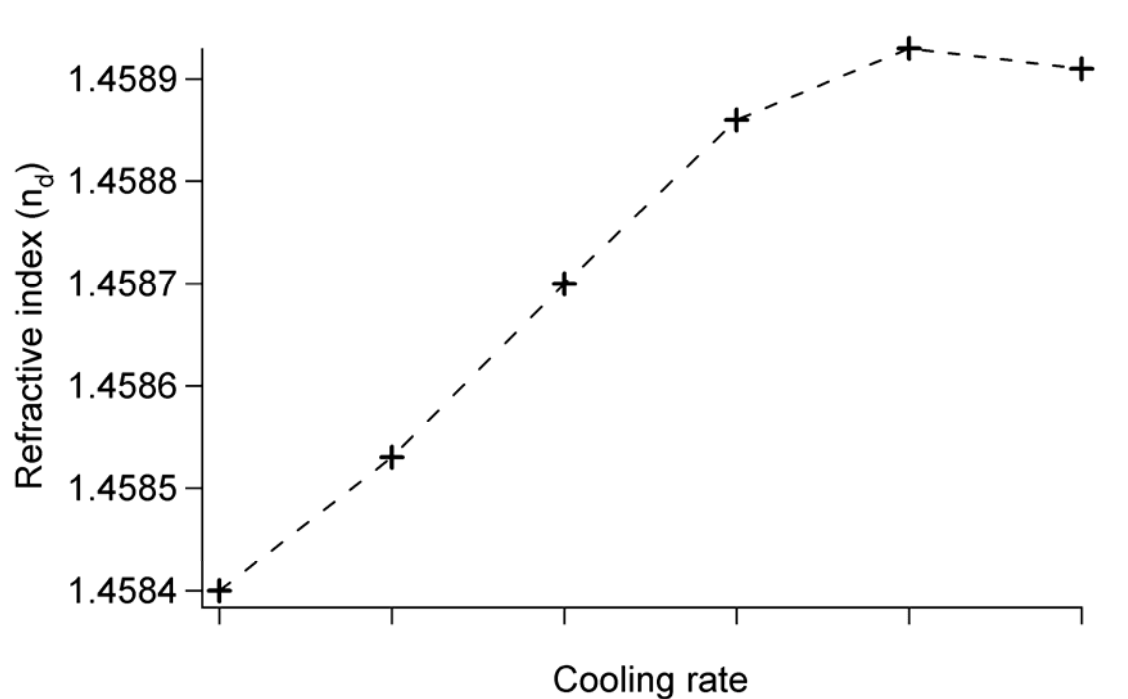
***fs* pulses induce an increase in the number of 3- and 4- membered rings**



**increase in density and index**



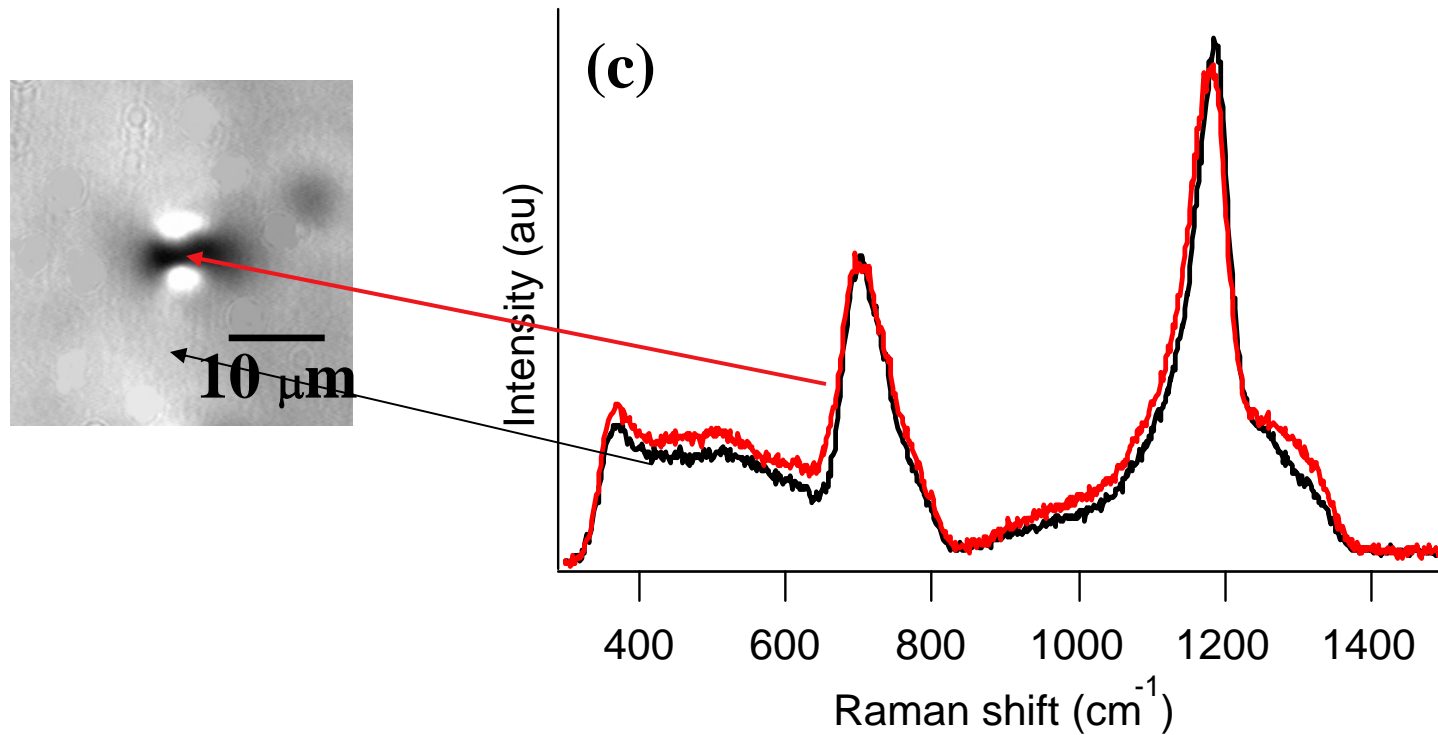
## Refractive index of fused silica vs quenching rate



**Data from R. Bruckner, J. Non-Cryst. Solids 5, 123 (1970)**



# Raman spectrum of modified IOG-1

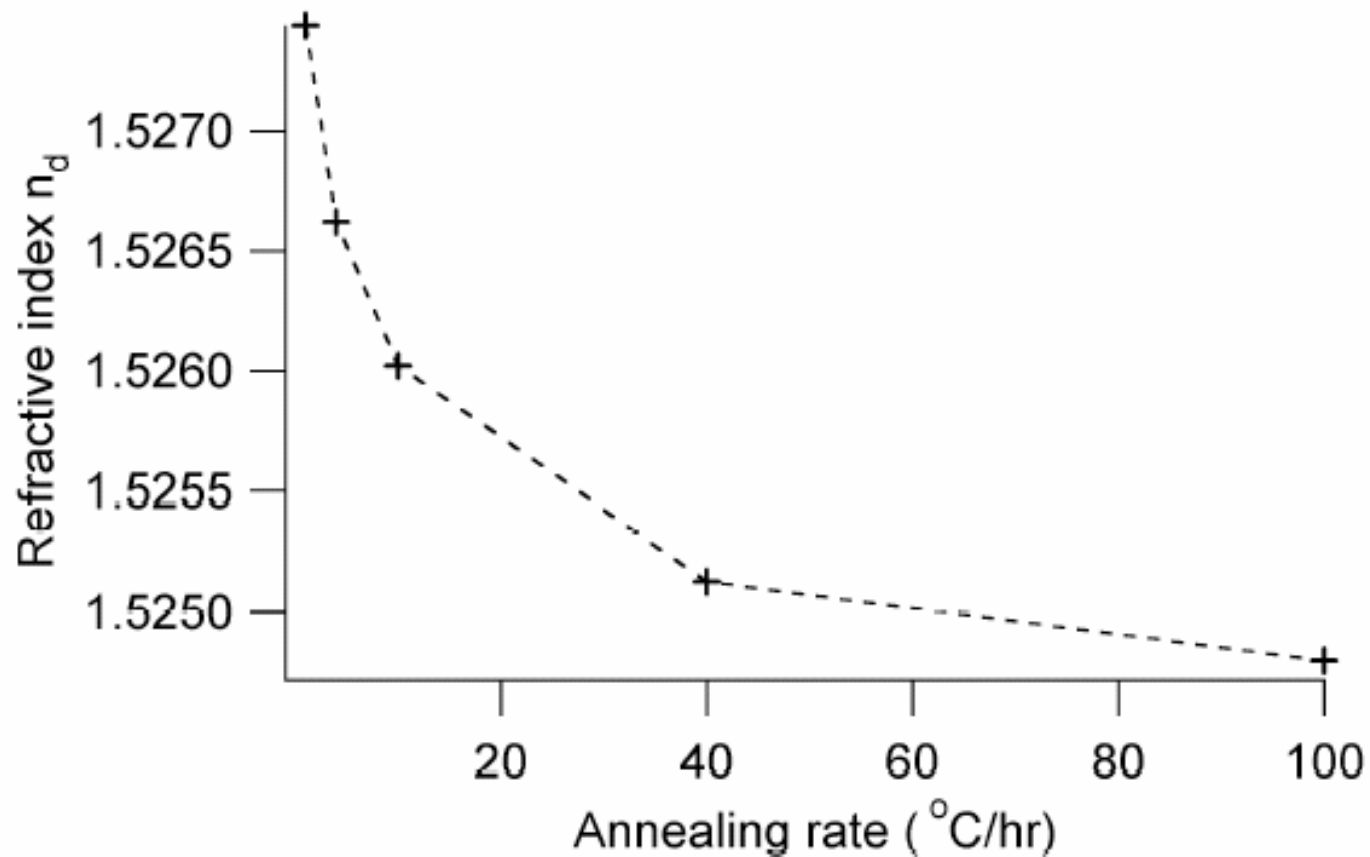


**Raman changes consistent with break-up of phosphate network**





## Refractive index of IOG-1 vs quenching rate



**Fig. 3. Dependence of refractive index of IOG-1 glass on the quenching rate from above the glass transition temperature. (Data from Schott Glass Tech., Inc.)**



## Comparison between fused silica and IOG-1

Fused silica

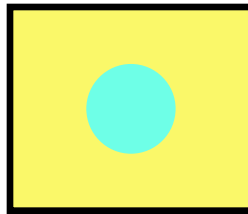
Phosphate glass

Deposition of femtosecond laser energy results in “fast heating and cooling” of material so that the exposed glass is similar to glass which is rapidly quenched from a high melting temperature (higher  $T_f$ )

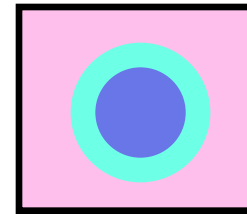


Refractive index of glass depends on quenching rate ( $T_f$ )

n increases with  
quenching rate



n decreases with  
quenching rate



high index (guiding) regions

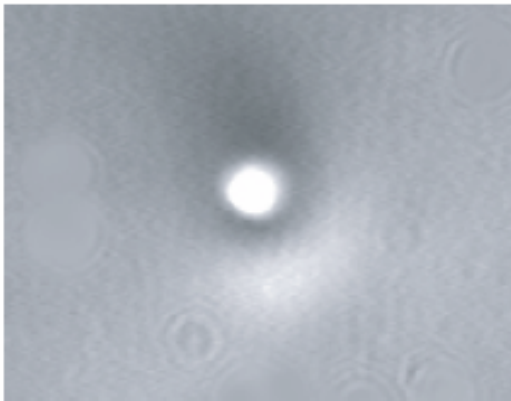
low index regions



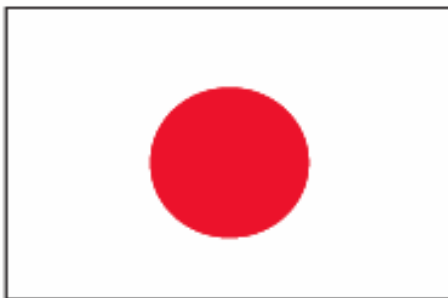
# What about other glass compositions??

Type 1

Fused Silica



n increases with quenching rate



Type 2

Soda Lime Silicate Glasses

	SCG 4-2	SCG 6
SiO <sub>2</sub>	60	70
CaO	20	15
Na <sub>2</sub> O	20	15

n decreases with quenching rate

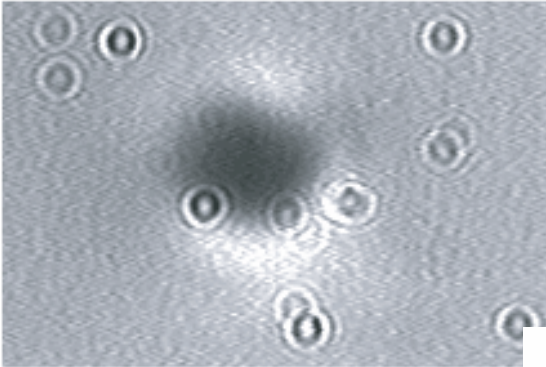


high index region  
low index region

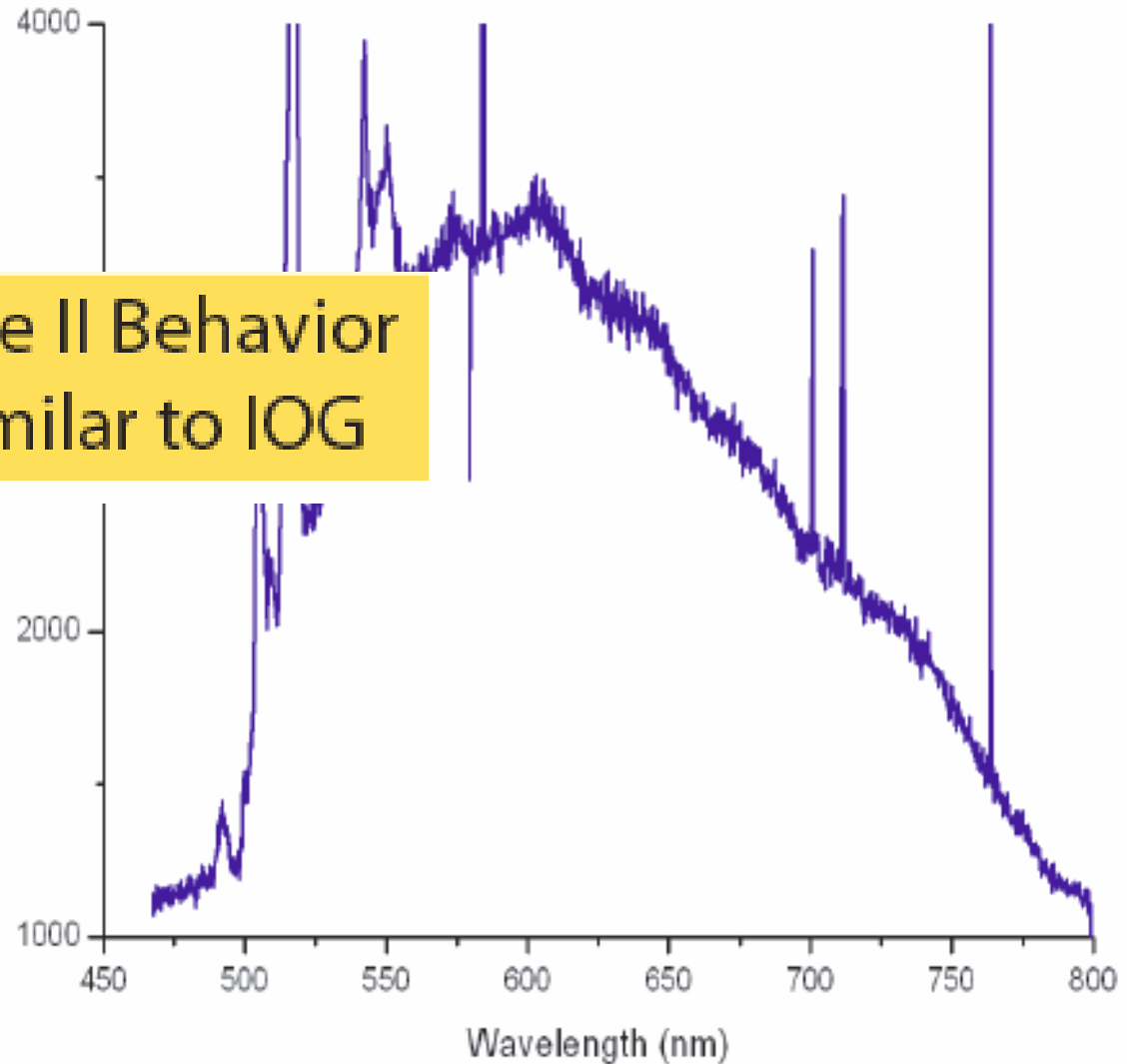


# Results for 15 Na<sub>2</sub>O 10 CaO 70SiO<sub>2</sub>

White Light Transmission

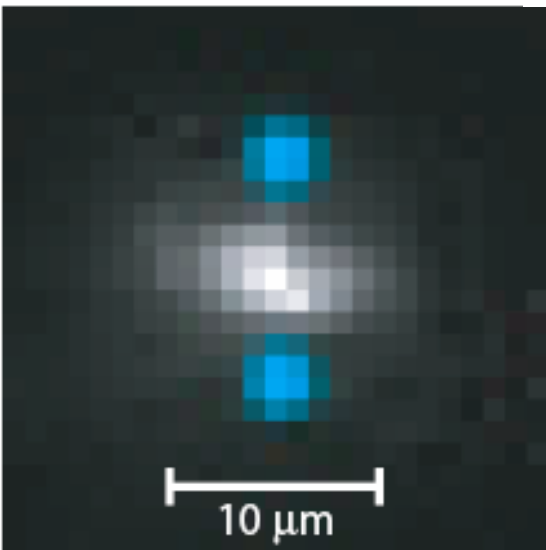


Fluorescence Spectra indicate the presence of Non-Bridging Oxygen Hole Center (NBOHC) Defects



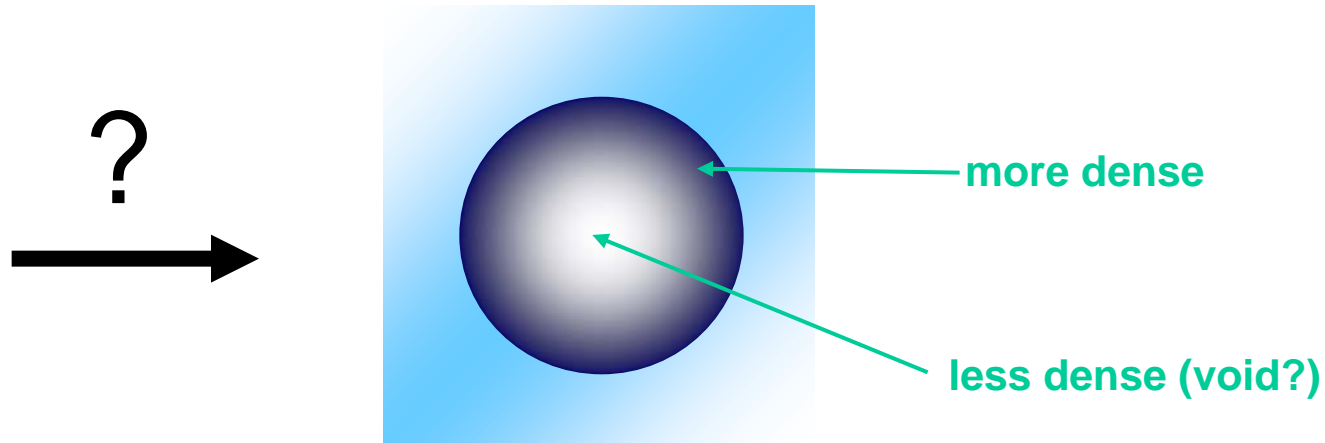
Type II Behavior  
Similar to IOG

Fluorescence Intensity, with Waveguides Superimposed





## Mechanism revisited

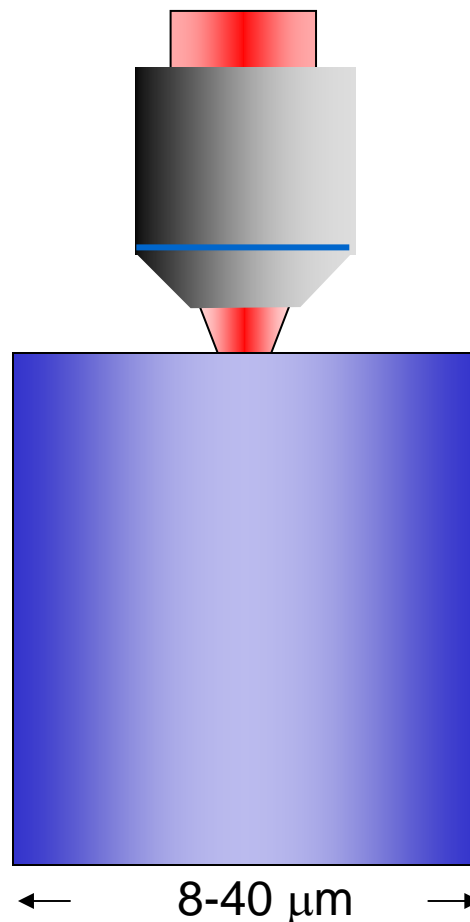


- Results show that densification occurs in some region of modified spot -> conservation of matter means that other regions must be less dense
- Modified spot with central void?
- **The spatial profile of the resulting spot's atomic structure as measured by Raman and fluorescence spectroscopy may indicate if this idea is correct.**



## Objective

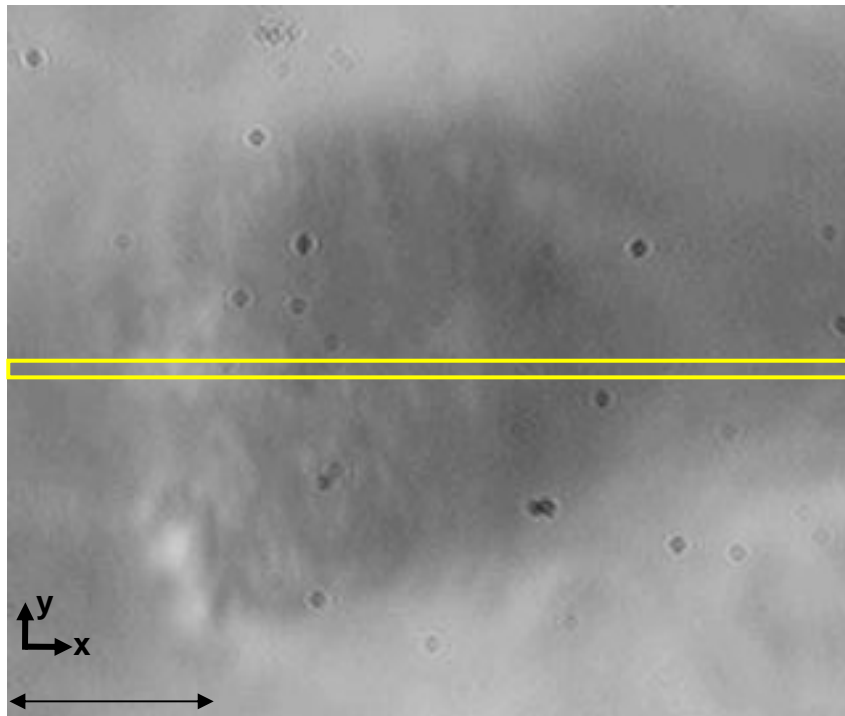
To determine the spatial profile of the modified lines using fluorescence and Raman spectroscopy.





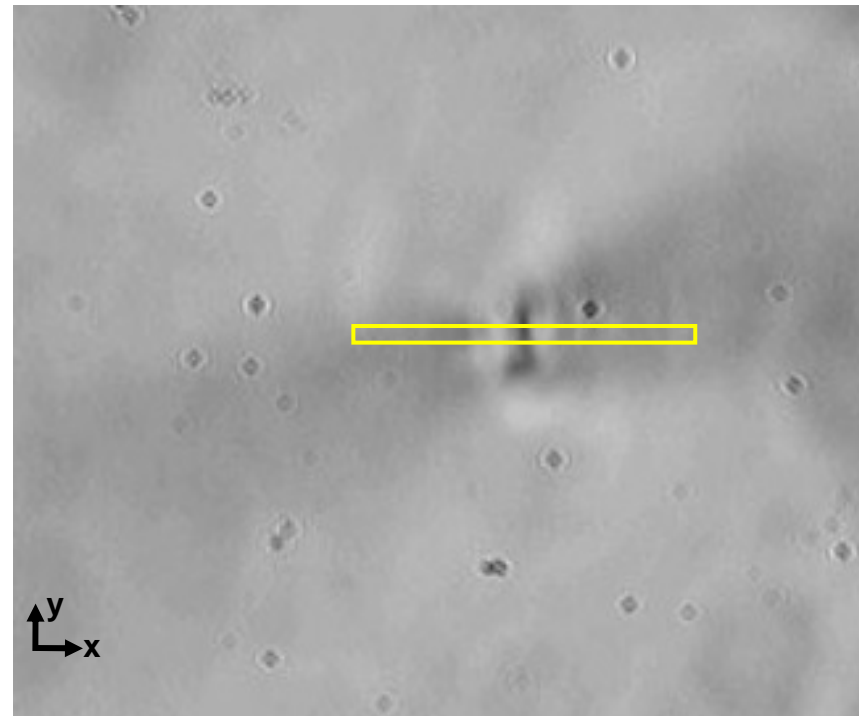
# White Light Images

25  $\mu\text{J}$  Line



20  $\mu\text{m}$

9  $\mu\text{J}$  Line



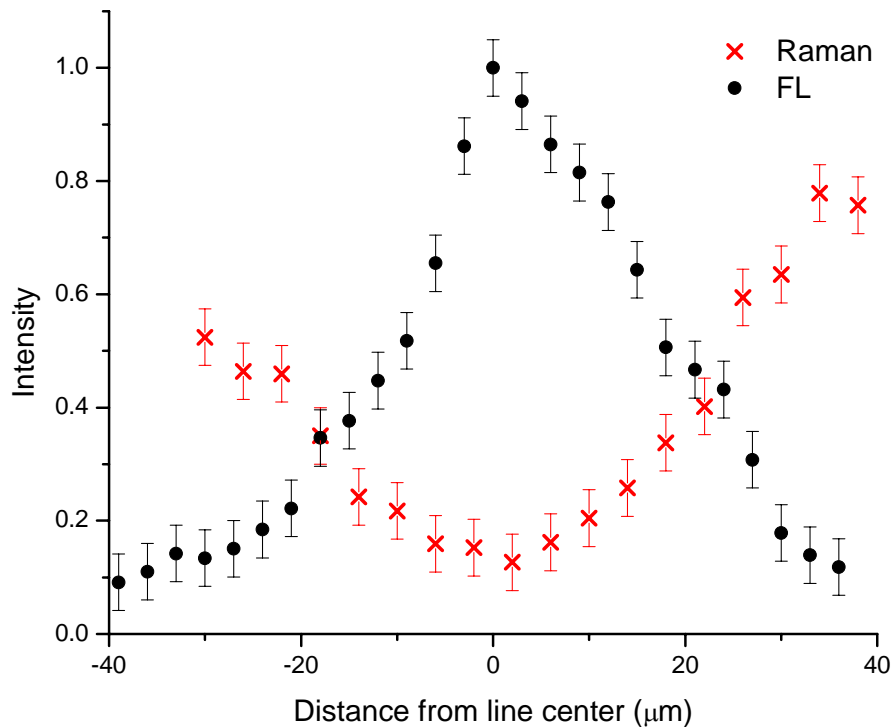
For spectroscopic characterization, the 25  $\mu\text{J}$  line was scanned with a 3  $\mu\text{m}$  spot spacing, and the 9  $\mu\text{J}$  line was scanned with a 2  $\mu\text{m}$  spot spacing along the paths shown.



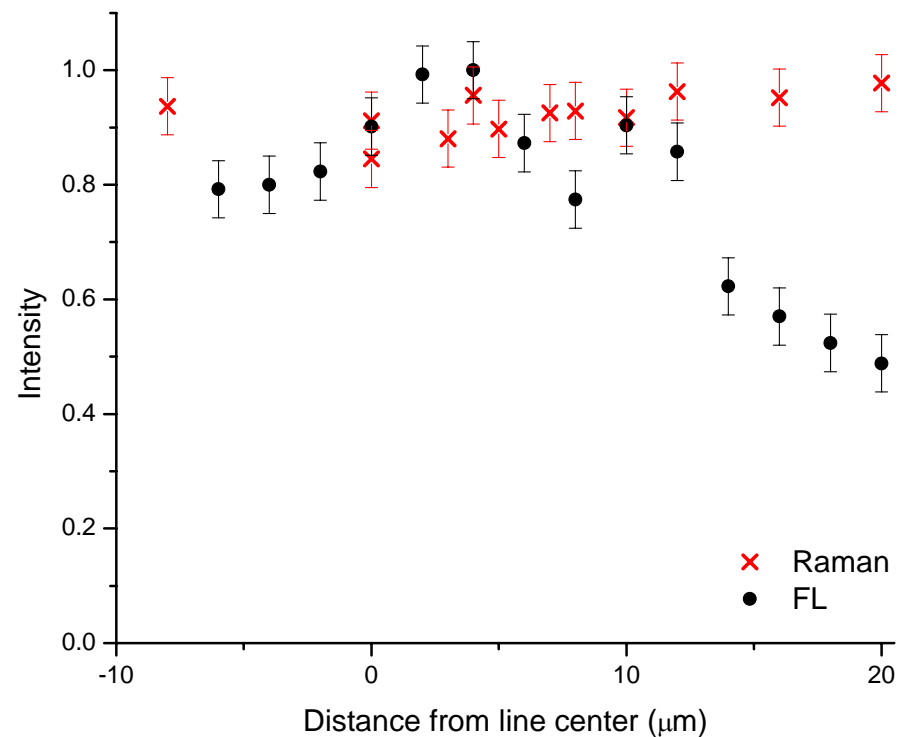
## Fluorescence and Raman cross-sections

The Raman intensity reaches a minimum and the fluorescence intensity reaches a maximum at the center of each line.

25  $\mu\text{J}$  Line



9  $\mu\text{J}$  Line







## Fluorescence and Raman results for large spots

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### Fluorescence Results

- The concentration of laser-induced defects **increases** towards the center of the modified spot.

### Raman Results

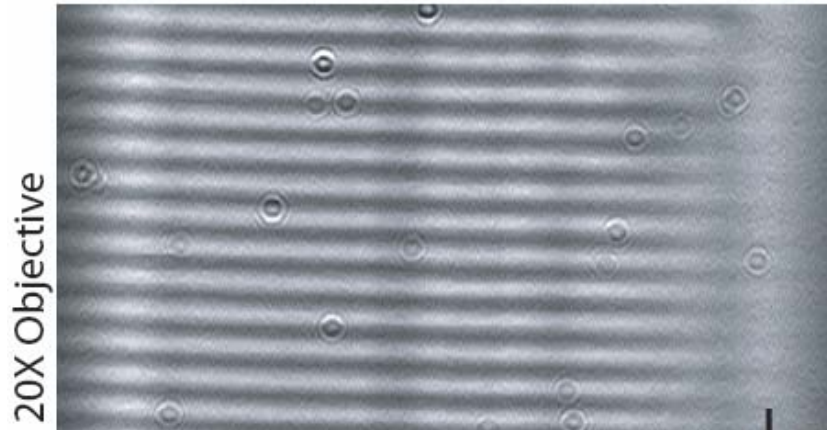
- There is **no apparent variation** in the concentration of three- and four-membered rings across the modified spot.
- The total Raman intensity **decreases** towards the center of the modified spot.

### Possible explanations:

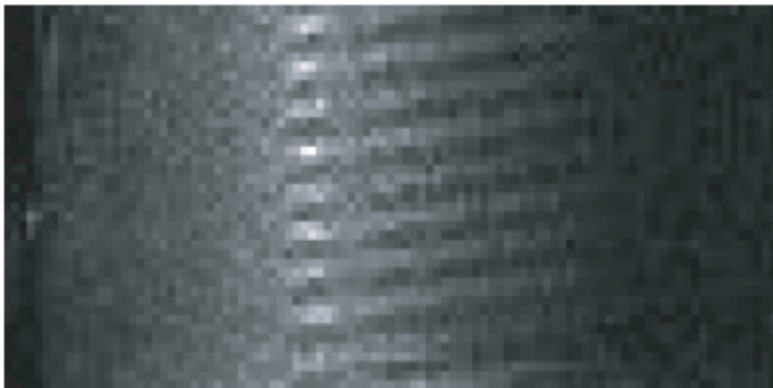
- Rarefaction of the silica – not a void.
- Scattering / absorption.



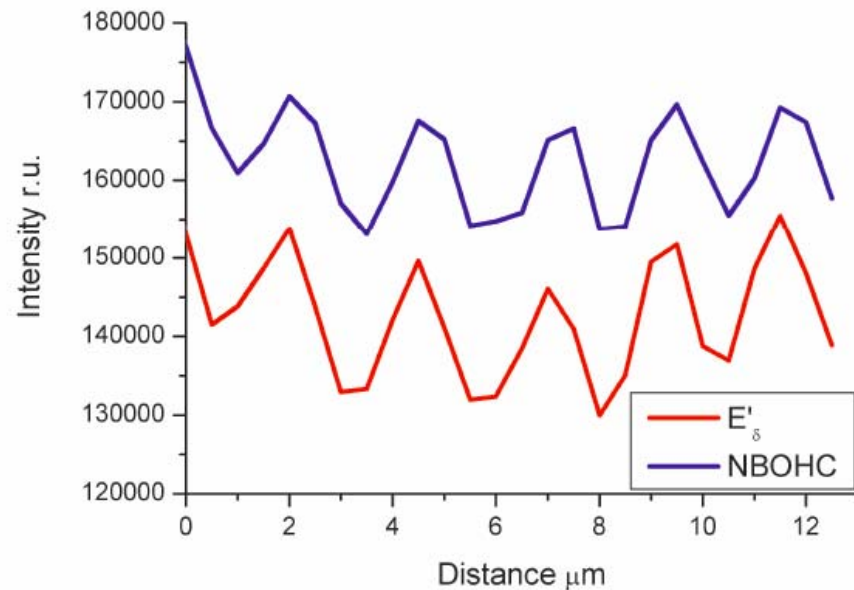
# Bragg gratings fabricated with ultrafast lasers



White light microscope image



fluorescence image





## Summary

- Ultrafast lasers can be used to directly write photonic structures in glass
- A confocal microscope setup was used to probe the fs-modified regions of the glass for Raman changes and fluorescence signals
- Results indicate that the material response to fs pulses is not the same for all glass systems

Dependence of refractive index on cooling rate explains observed behavior for glasses investigated so far

Still many aspects not well understood:

- Dynamics
- Laser rep rate
- ....



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