Localized generation of nanoparticles in tungsten lead-pyrophosphate glasses using femtosecond laser

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Third-order nonlinearities of the bismuth germanium glassy matrix

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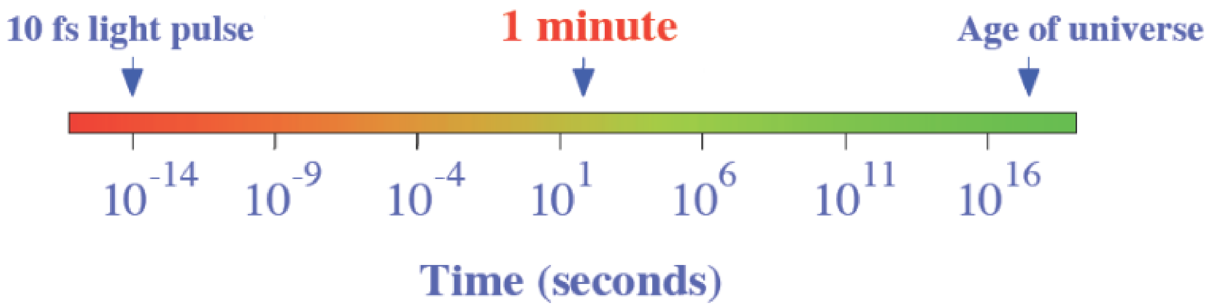
Outline

- Overview:
  - Femtosecond laser pulses
  - Nonlinear optics
- (FL9.3) Localized generation of nanoparticles in tungsten lead-pyrophosphate glasses using femtosecond laser micromachining
- (FL9.4) Third-order nonlinearities of the bismuth germanium glassy matrix

Femtosecond laser pulses

- How short is a femtosecond (fs) pulse?

1fs = 10^{-15}s



- Why ultra-short laser pulses are important?

Intensity = Power/Area

Peak Power = $\frac{\text{Pulse Energy}}{\text{Pulse Duration}}$

→ Peak Intensity ↑ = $\frac{\text{Pulse Energy}}{\downarrow \text{Pulse Duration x Area}}$

Ultra-short laser pulses → Ultra-intensity laser pulses

Nonlinear Optics

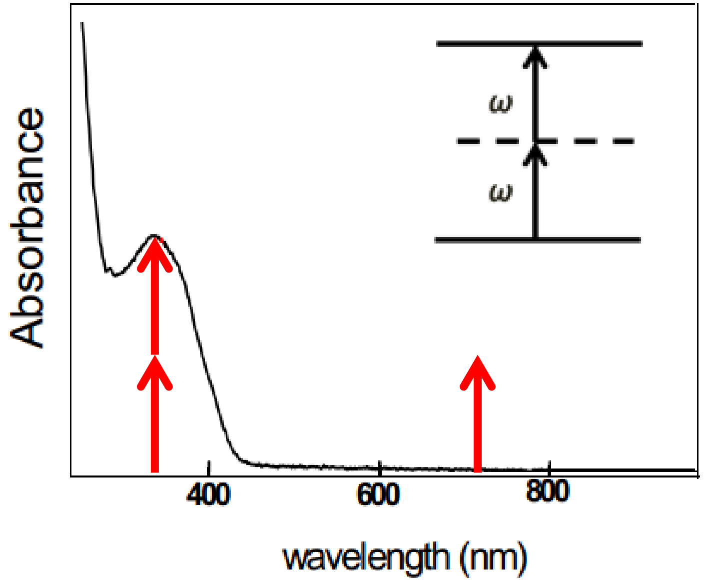
The branch of optics that describes optical phenomena that occur when very intense light is used.

Nonlinear Optical Phenomena

- Nonlinear Absorption
- Optical Kerr Effect
- Multiphoton Ionization

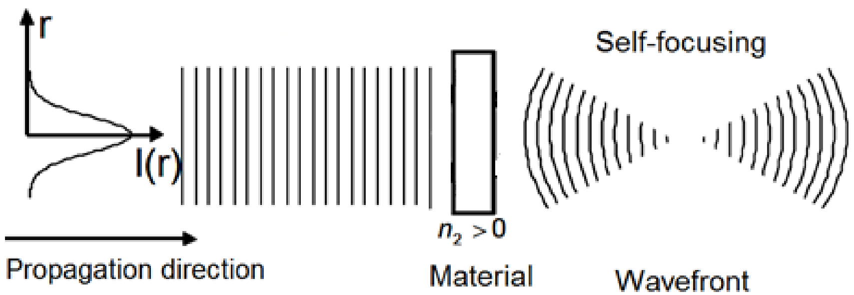
Nonlinear absorption

Optical Kerr Effect



Two photons absorption

$$\alpha = \alpha_0 + \beta I$$



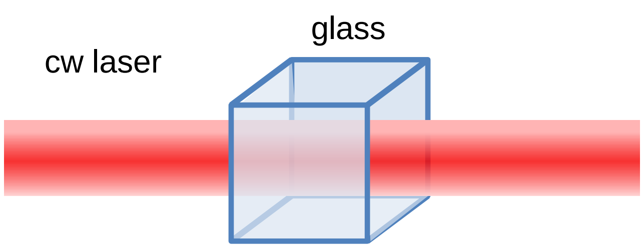
Self-focusing effect

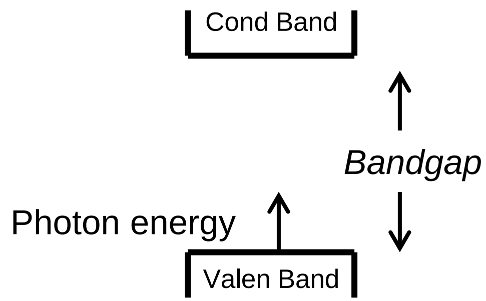
$$n = n_0 + \gamma I$$

Third order nonlinear process

Multiphoton Ionization

At low intensities sub- band gap
light is transmited

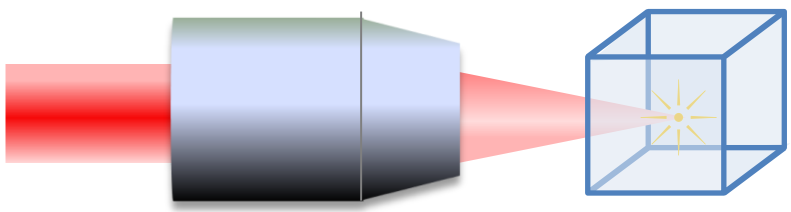


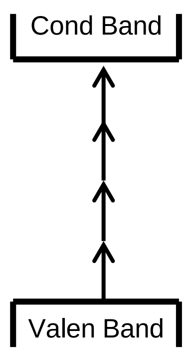


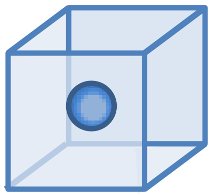
At high intensities multiphoton
ionization occurs

Deposition of energy into glass
leads to permanent modification

Ultrashort pulses (100 fs)
and a tight focusing







Localized generation of nanoparticles in tungsten lead-pyrophosphate glasses using femtosecond laser

Why obtain nanoparticles in glass?

- They are promising materials for photonic applications once they can exhibit ultrafast response times and high third order nonlinearities

- Local field enhancement effect

Why using fs-laser micromachining?

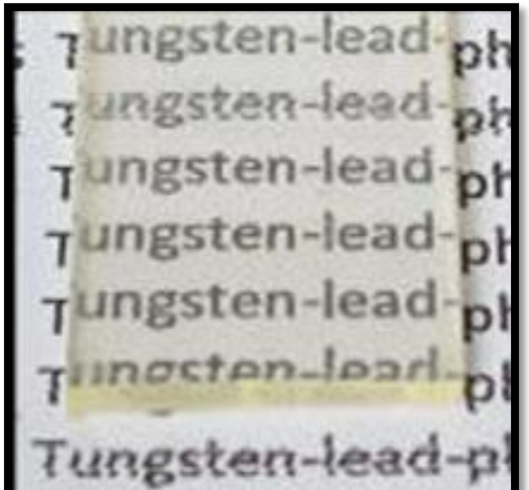
- It is possible to fabricate 3D microscopic structures inside the materials with high spatial resolution without causing damage on the surface.

Purpose

The purpose of this study was to produce and control silver nanoparticles at small regions inside a glass

J. M. P. Almeida, L. De Boni, W. Avansi, C. Ribeiro, E. Longo, A. C. Hernandes, and C. R. Mendonca, "**Generation of copper nanoparticles induced by fs-laser irradiation in borosilicate glass**," Optics Express 20, 15106-15113 (2012).

Material



$70Pb_2P_2O_7$–$30WO_3$: $1AgCl$ (mol%)

λ_c absorption edge = 380 nm; E_{gap} =3.26eV
n - Index of refraction = 1.9
Tg - glass transition temperature = 432 °C
Tx - onset of crystallization peak = 520 °C
ΔT - thermal stability = 88°C

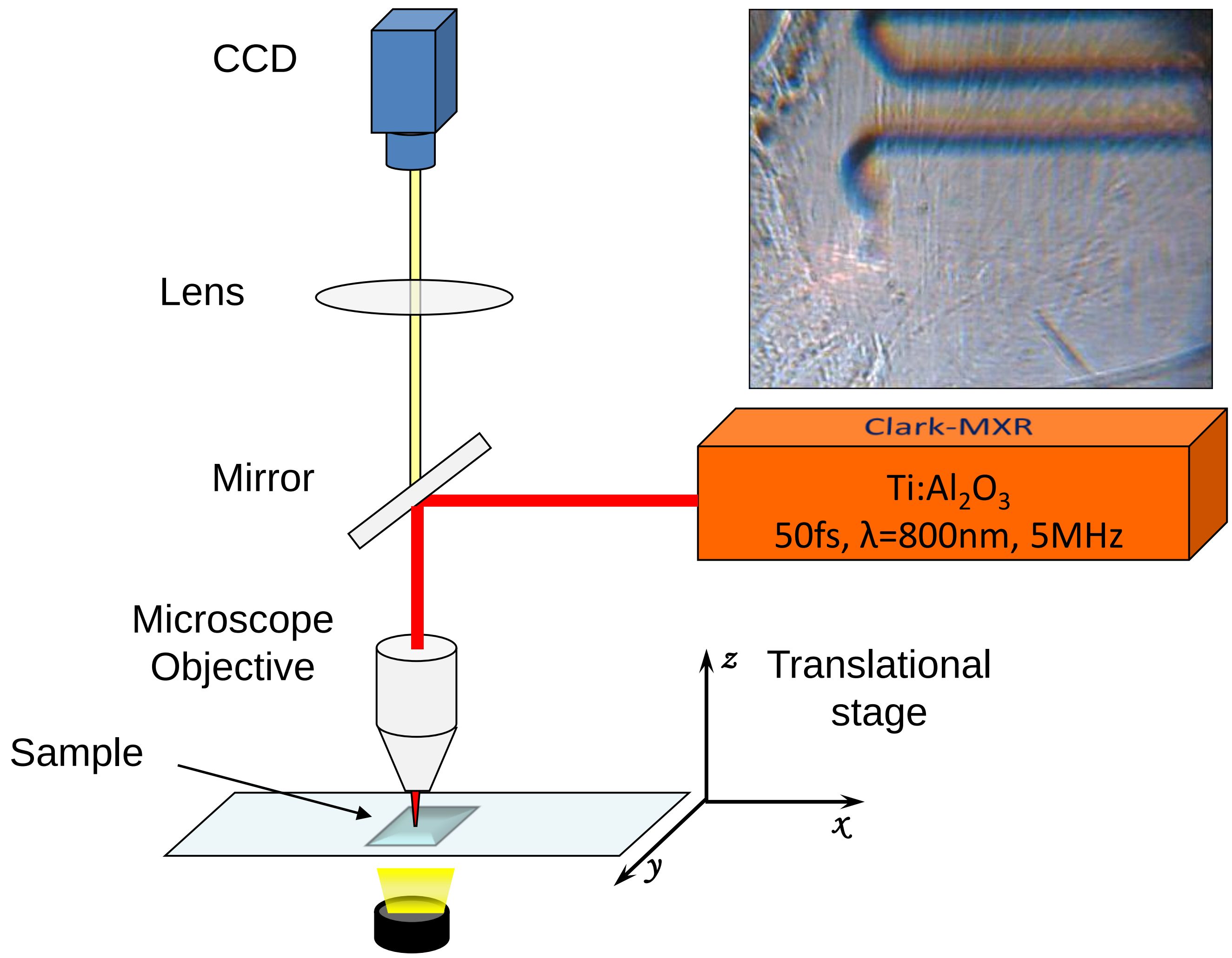
D. Manzani, R. G. Fernandes, Y. Messaddeq, S. J. L. Ribeiro, F. C. Cassanjes, and G. Poirier, "**Thermal, structural and optical properties of new tungsten lead-pyrophosphate glasses**," Optical Materials 33, 1862-1866 (2011).

unesp

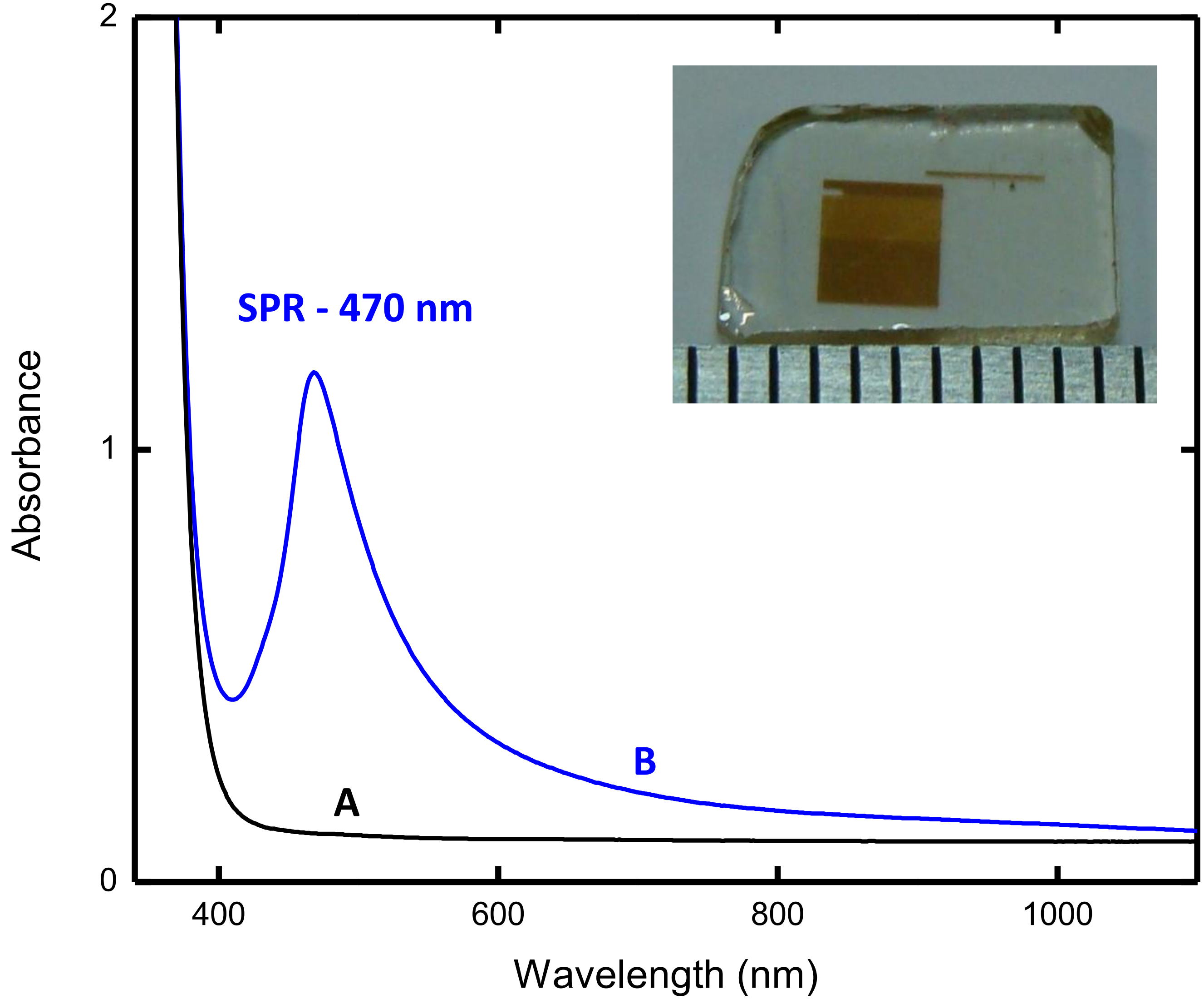
Methodology

Fs-laser irradiation

Micromachining set up

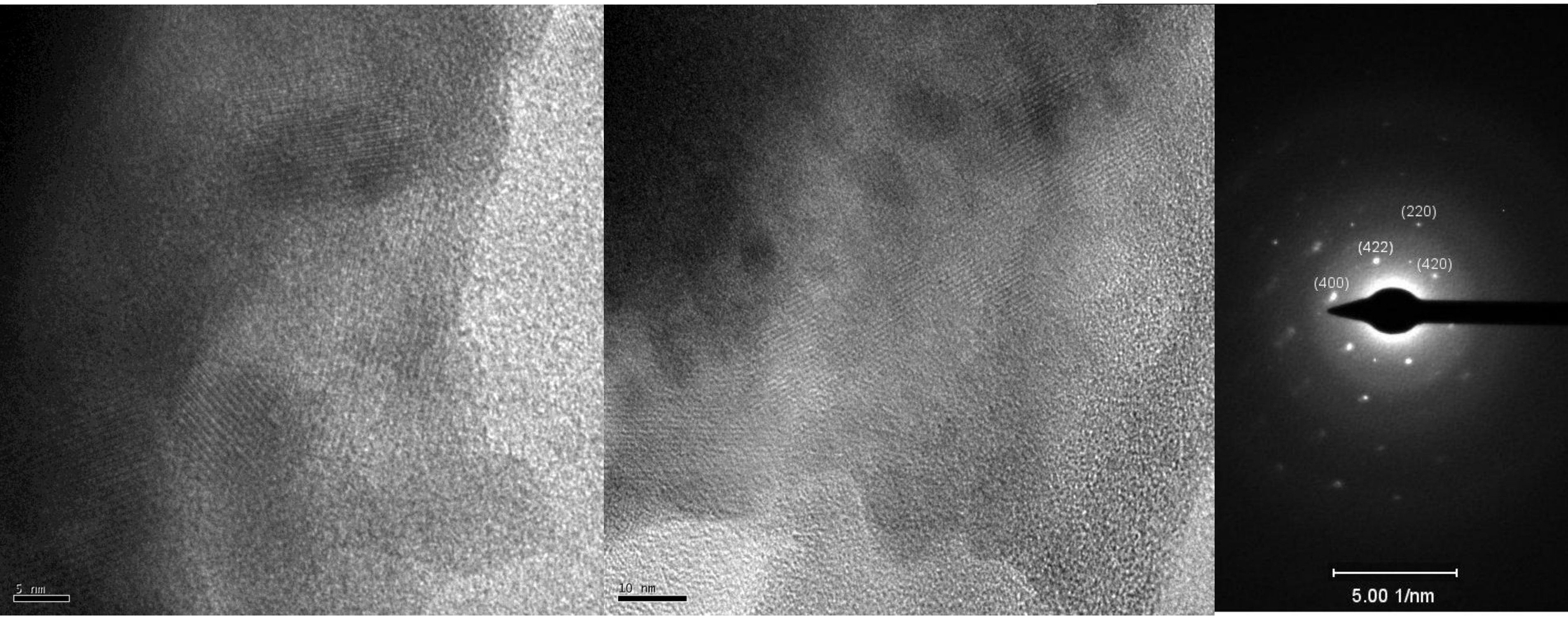


Results

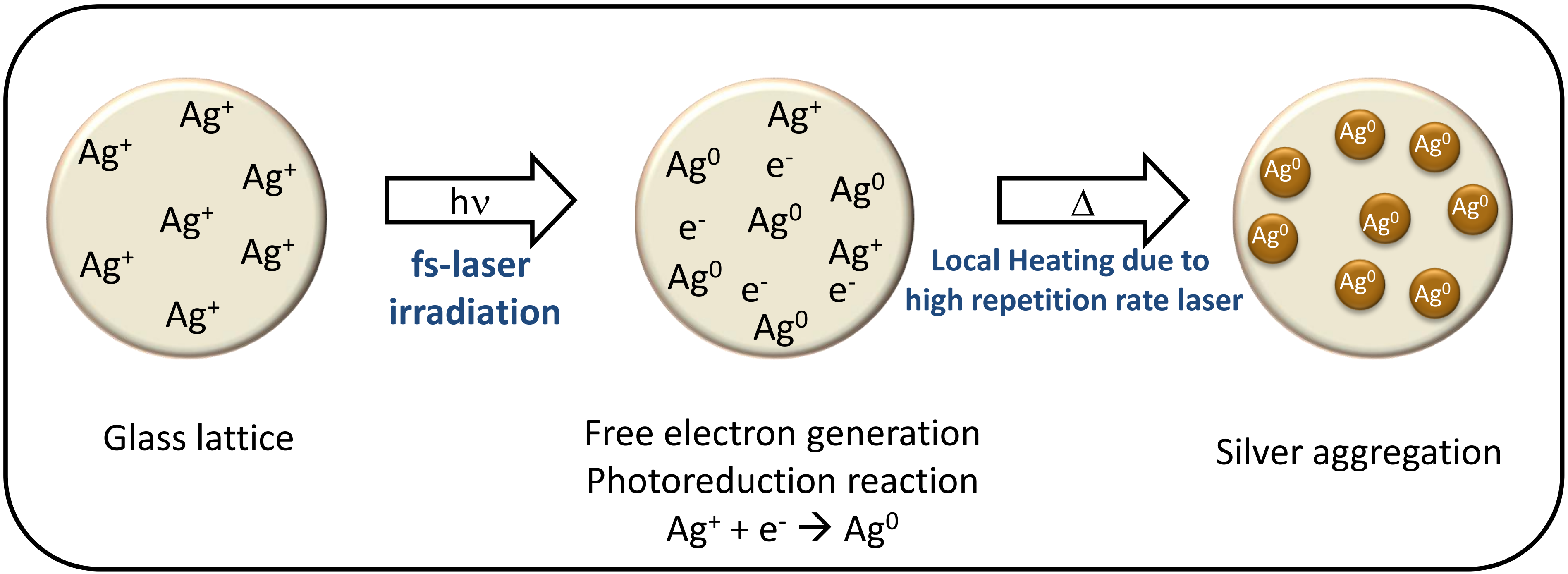


Absorption spectrum of the P7W3:Ag glass as prepared (curve A), and after the fs-laser irradiation in the bulk using NA = 0.65, v = 100 µm/s, E = 30 nJ (curve B).

Transmission electron microscopy and electron diffraction

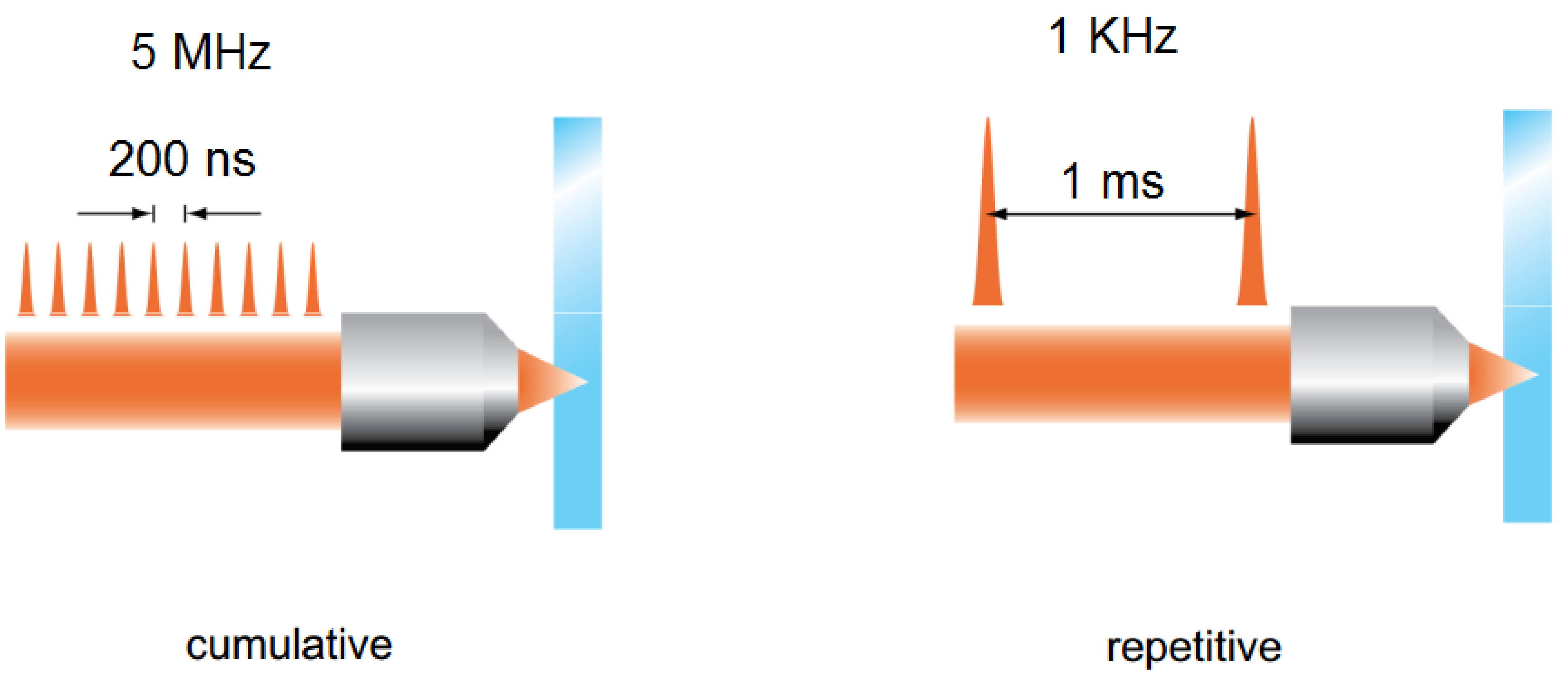


Formation of Metallic nanoparticles

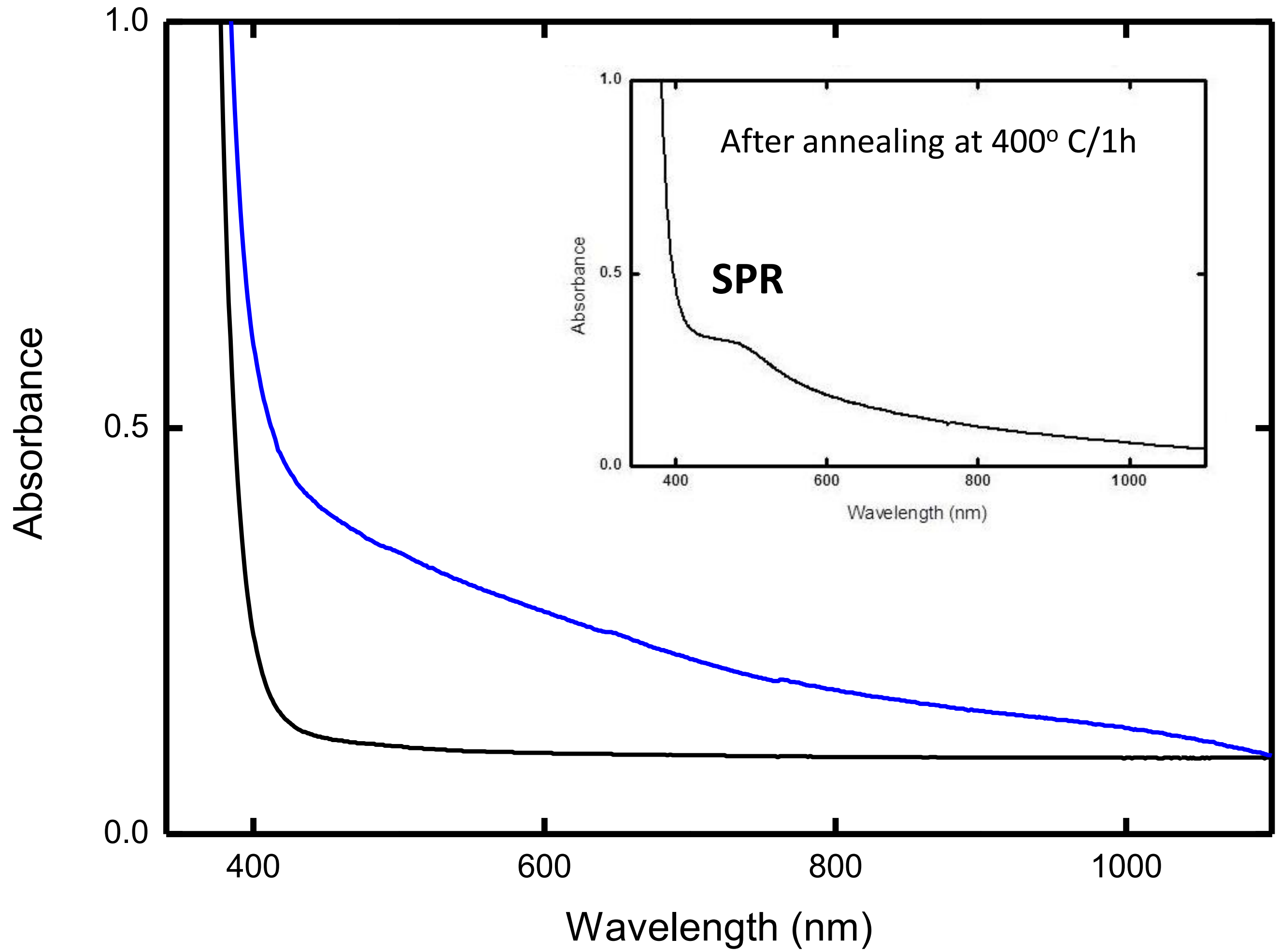


- But, femtosecond laser are known for minimizing thermal effects outside the focal volume!!!

- Then, why we are having a local heating to form NPs?



Low repetition rate (1 KHz)



Absorption spectrum of the P7W3:Ag glass as prepared (curve A), and after the fs-laser irradiation in the bulk using NA = 0.65, v = 100 μm/s, E = 380 μJ (curve B).

In summary

We have shown the formation of silver nanoparticles only in the irradiated area due to the fs-laser induced photoreduction

Third-order nonlinearities of the bismuth germanium glassy matrix

Motivation

Find new materials for telecommunications, as all-optical switches and waveguides.

↓

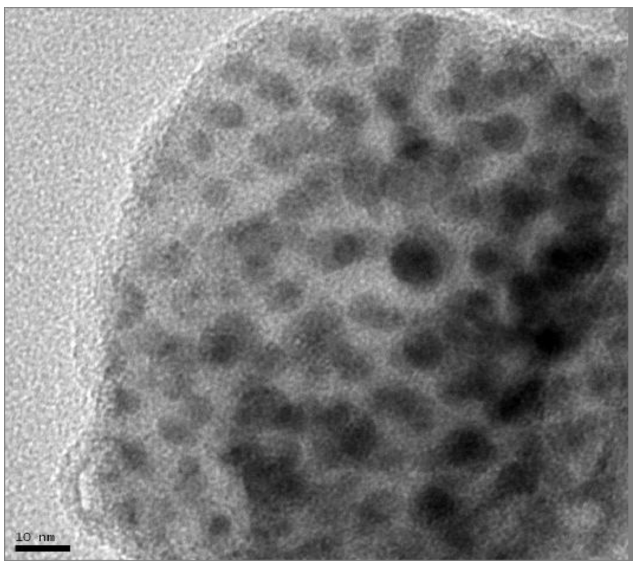
To measure the nonlinear optical properties

Material

Bismuth germanium

1) 58.4 GeO_2–41.6 Bi_2O_3(wt%)

2) [58.4 GeO_2–41.6 Bi_2O_3]: 0.5 Eu_2O_3 - 3.0 Au_2O_3 (wt%) → 420 ^oC/3h → Gold nanoparticles



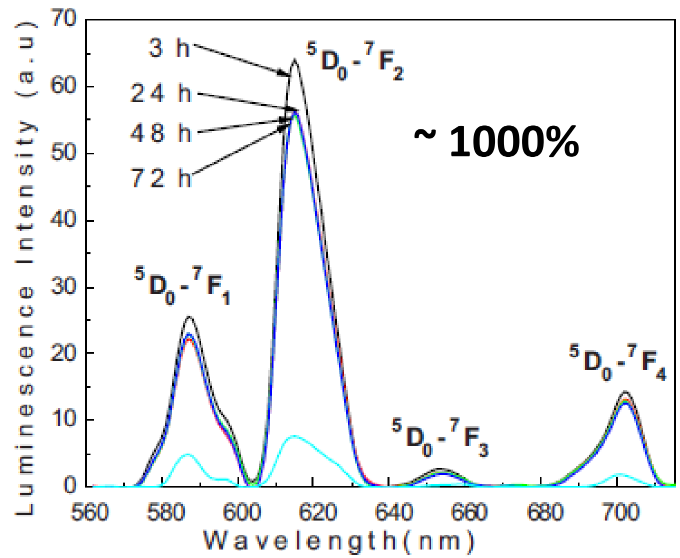


FIG. 3. (Color online) PL spectra of the samples heat-treated for different times (excitation at 405 nm). The spectrum for the sample doped with 0.5 wt % of Eu_2O_3 and no metal NPs is also shown to illustrate the luminescence enhancement.

L. R. P. Kassab, D. S. da Silva, R. de Almeida, and C. B. de Araujo, "**Photoluminescence enhancement by gold nanoparticles in Eu3+ doped GeO2-Bi2O3 glasses**," Applied Physics Letters 94 (2009).

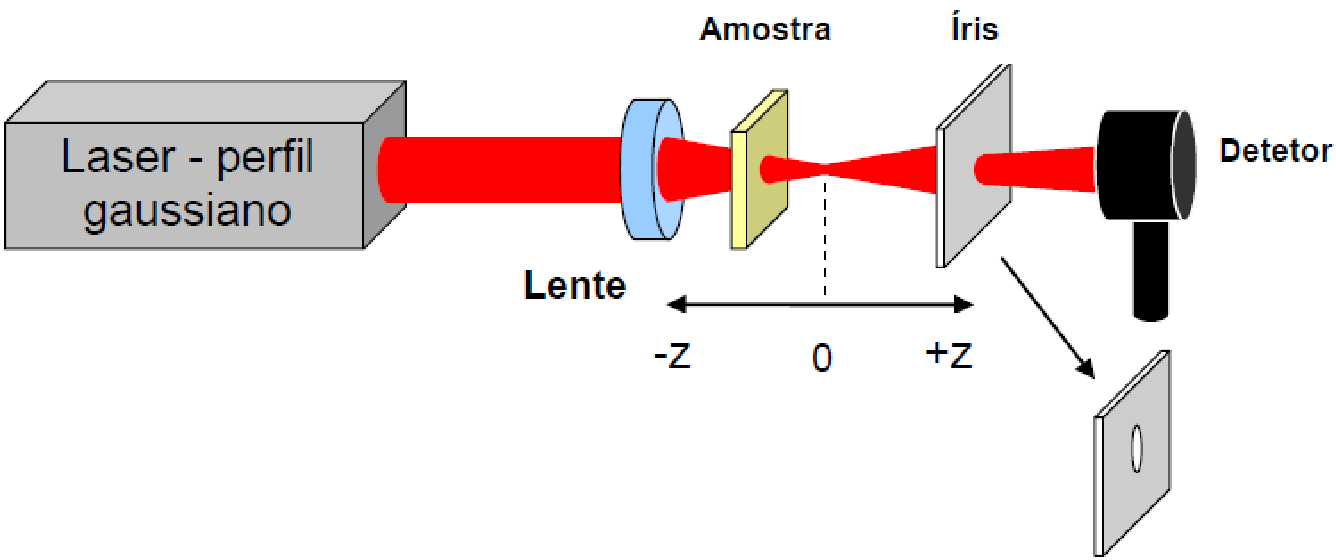
Purpose

To obtain the nonlinear refraction spectrum of a heavy metal oxide glass and verifying if the nonlinear index of refraction is increased by the presence of gold nanoparticles

J. M. P. Almeida, L. De Boni, A. C. Hernandes, and C. R. Mendonca, "**Third-order nonlinear spectra and optical limiting of lead oxifluoroborate glasses**," Optics Express 19, 17220-17225 (2011).

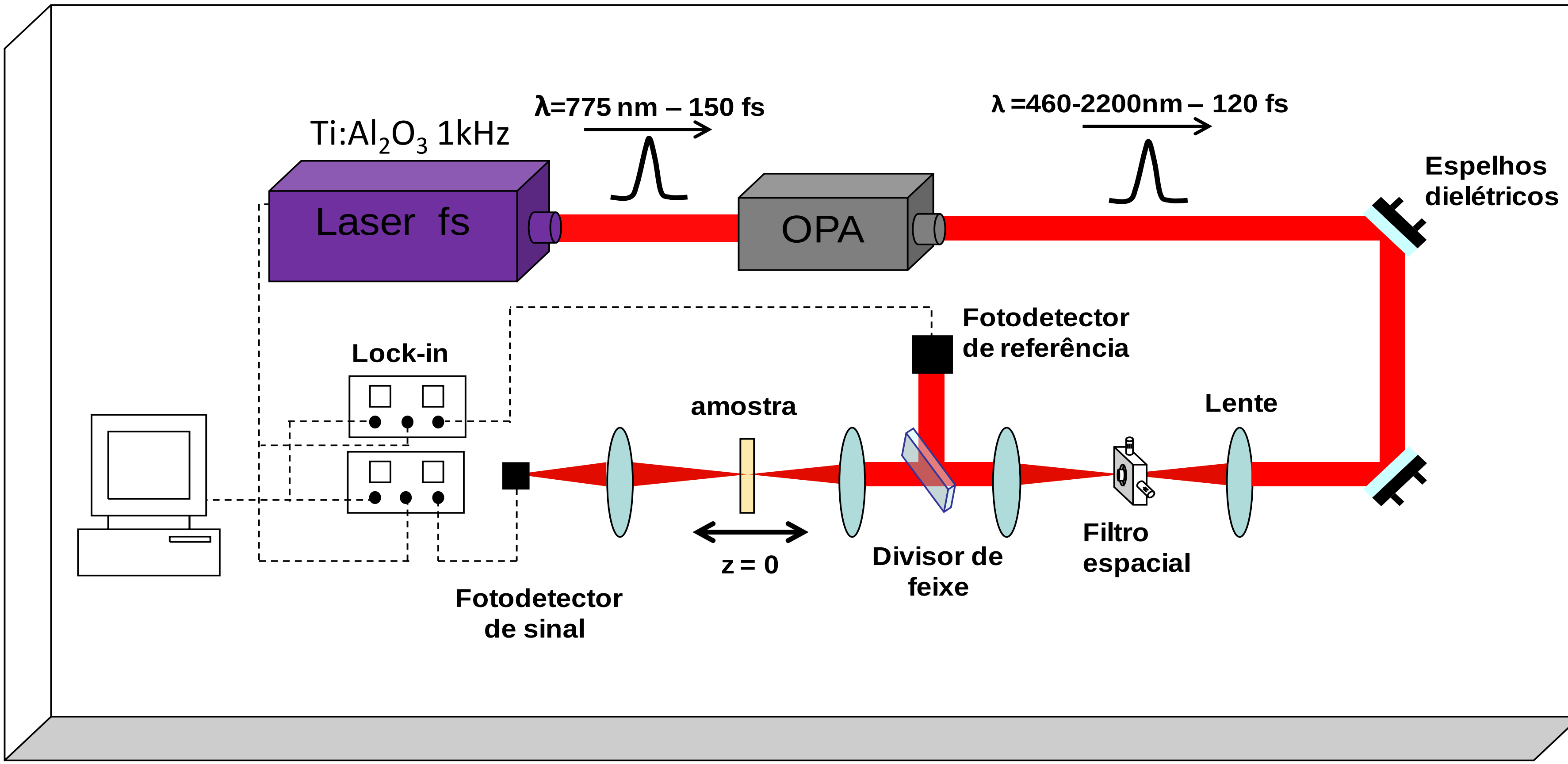
Methodology: Z-Scan technique

"The transmittance of a sample is measured through a finite aperture in the far field while the sample is moved along the propagation path (z) of a gaussian beam"

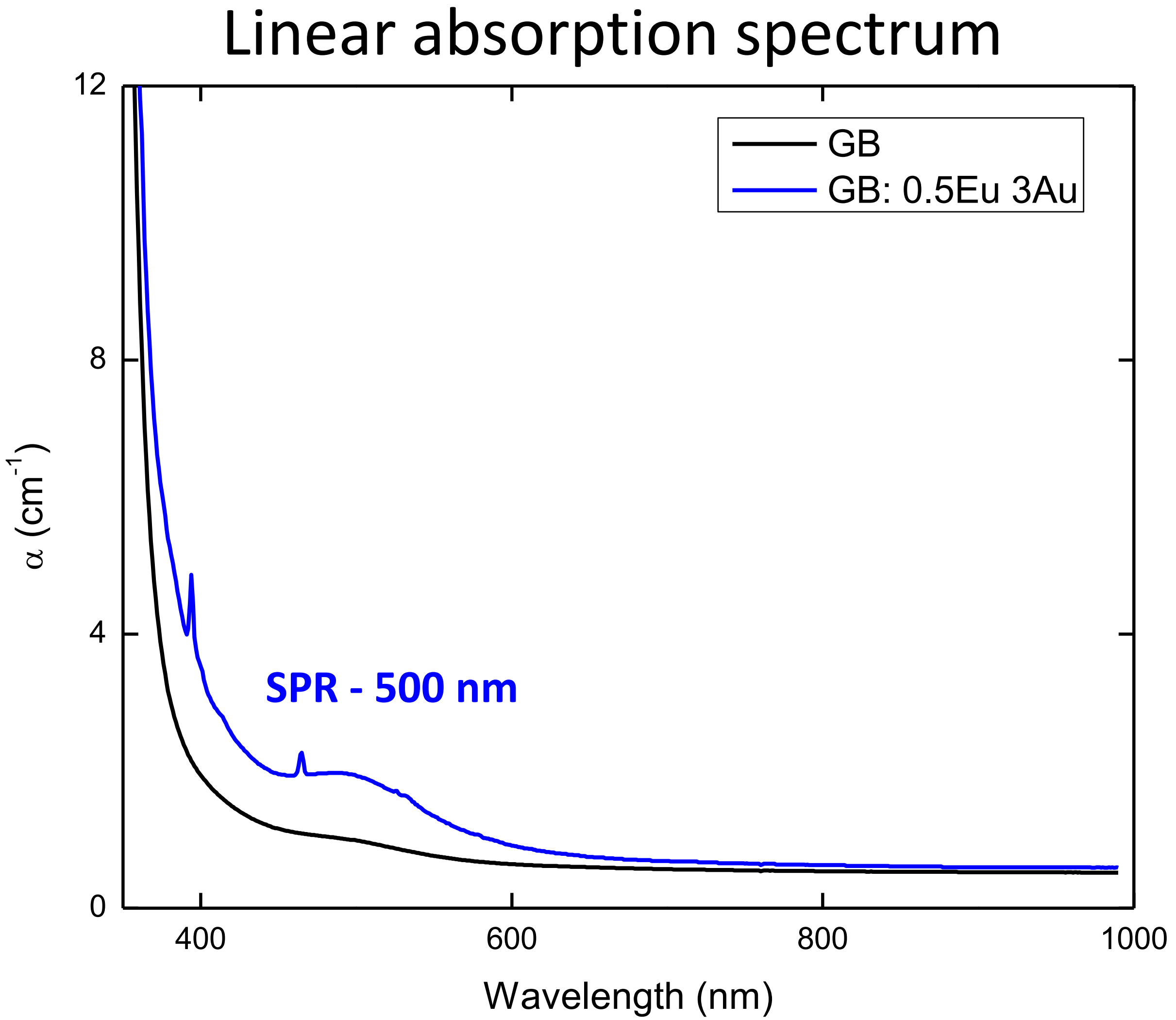


M. Sheik-bahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. Vanstryland, "Sensitive Measurement of Optical Nonlinearities Using a Single Beam," Ieee Journal of Quantum Electronics **26**, 760-769 (1990)

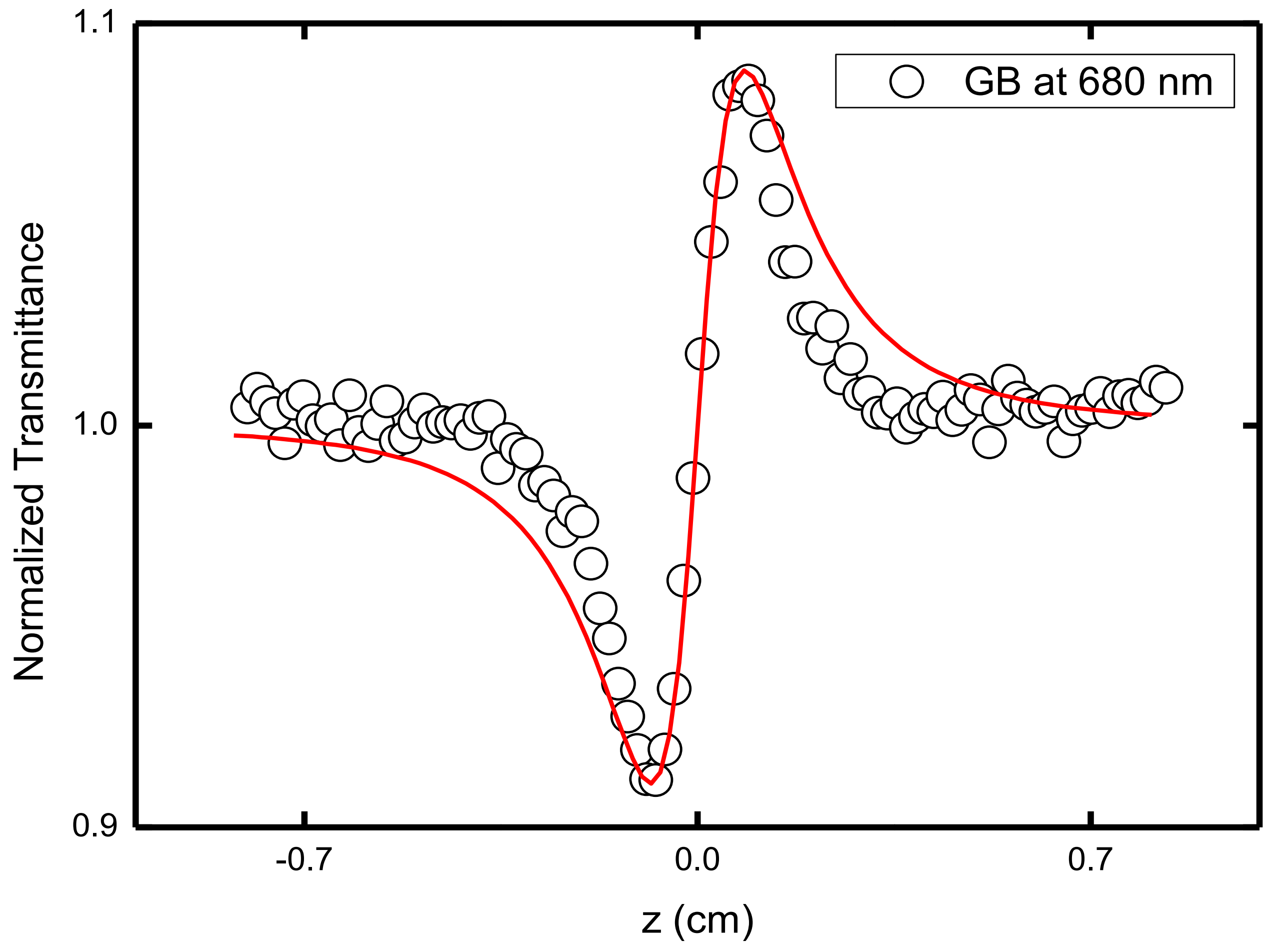
Experimental Setup



Results


Linear absorption spectrum
12
8
4
0
400
600
800
1000
Wavelength (nm)
α (cm-1)
GB
GB: 0.5Eu 3Au
SPR - 500 nm

Refractive Z-scan signature

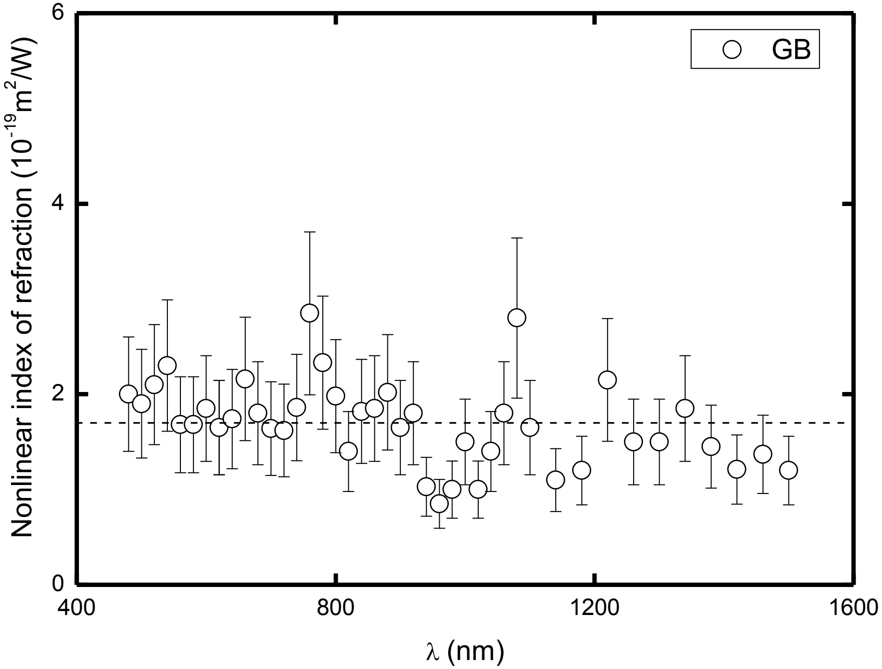


$$\Delta T_{P-V} = 0{,}406.\Delta\phi_0$$

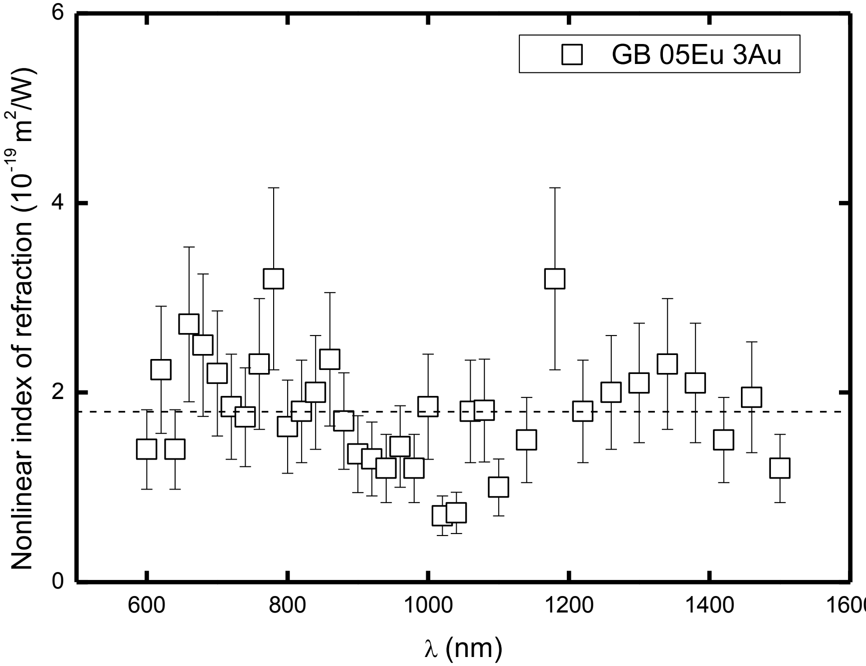
$$\Delta\phi_0 = \frac{k.\gamma.I_0.L}{\sqrt{2}}$$

Nonlinear refraction spectrum

GB matrix
$\Upsilon_{average} = 1.7 \times 10^{-19}\ m^2/W$



GB containing gold NPs
$\Upsilon_{average} = 1.9 \times 10^{-19}\ m^2/W$



In Summary

- No significant enhancement effect was found for the sample containing gold NPs.

- Nevertheless, these bismuth germanate glasses present nonlinear index of refraction 1.6 times larger than the lead-germanium glasses containing silver NPs.

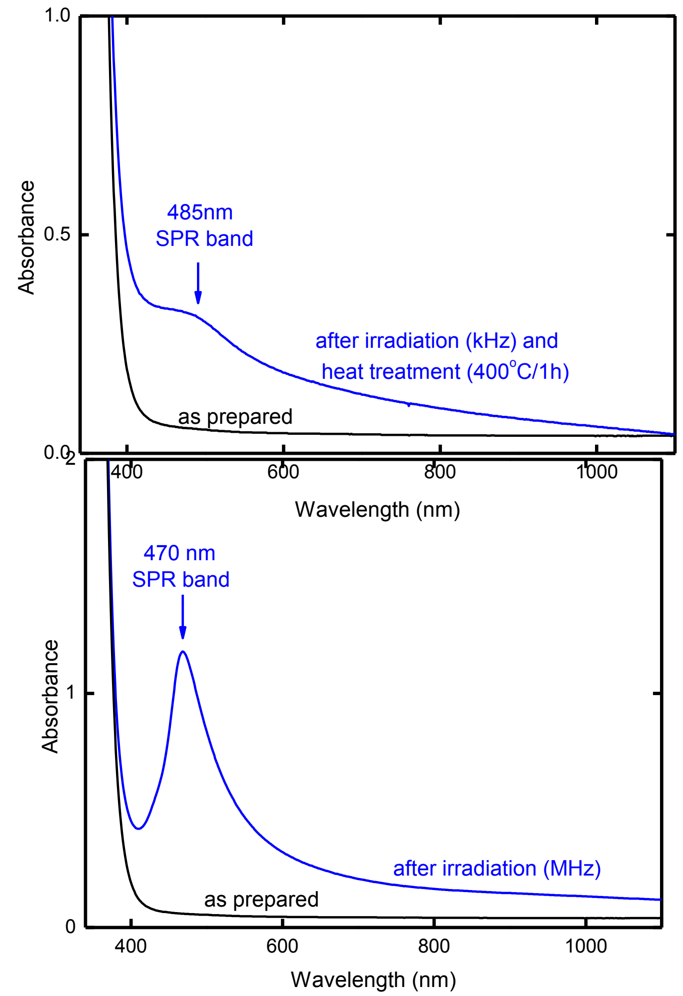
Acknowledgements

FAPESP

CAPES

CNPq

IFSC-USP
Fotônica


1.0
0.5
0.0
Absorbance
485nm
SPR band
after irradiation (kHz) and
heat treatment (400°C/1h)
as prepared
400
600
800
1000
Wavelength (nm)
2
1
0
Absorbance
470 nm
SPR band
after irradiation (MHz)
as prepared
400
600
800
1000
Wavelength (nm)