Glass and glass ceramic for nonlinear optics: fundamentals to applications

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NonLinear Optical Materials

Nonlinear Parameters

Third order Nonlinearities

Second order Nonlinearities

Nonlinear Absorption

Nonlinear optics

❑ Nonlinear optical effects

$$P = \varepsilon_0 \left(\chi^{(1)}E(\omega) + \chi^{(2)}E(\omega)E(\omega) + \chi^{(3)}E(\omega)E(\omega)E(\omega) + \ldots \right)$$

n_0

SHG (2ω)

$n \approx f(E)$

$n = n_0 + \zeta E$

THG (3ω)

$n \approx f(E^2)$

$n = n_0 + n_2 I$

P	:	Polarisation	n	:	Refractive Index
E	:	Electric Field	SHG	:	Second Harmonic Generation
$\chi^{(n)}$	:	Linear and Nonlinear susceptibilities	THG	:	Third Harmonic Generation

Third order nonlinearity

- **Four wave mixing** $\chi^{(3)}(-\omega_4,\omega_1,-\omega_2,\omega_3)$

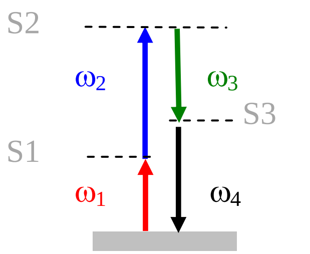
- **Kerr effect** $\chi^{(3)}(-\omega,\omega,-\omega,\omega)$

  Self focusing
  Self phase modulation
  Soliton Propagation
  Optical switching

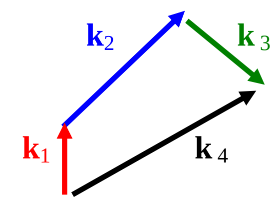
- **Third Harmonic generation** $\chi^{(3)}(-3\omega,-\omega,\omega,\omega)$

- **Stimulated Raman** $\chi^{(3)}(-\omega_s,\omega_p,-\omega_s,\omega_p)$

- **Two photon absorption** $\chi^{(3)}(-\omega,-\omega,\omega,\omega)$



$\omega_4 = \omega_1+\omega_2- \omega_3$



$k_4 = k_1 + k_2 + k_3$

The formalism of nonlinear optics

- ***Polarization of the material*** described by a perturbative development:

$$\vec{P}_i(\vec{r};t) = \underbrace{\cancel{\vec{P}_i^{(0)}(\vec{r};t)} + \vec{P}_i^{(1)}(\vec{r};t)}_{\text{linear polarization}} + \underbrace{\cancel{\vec{P}_i^{(2)}(\vec{r};t)} + \vec{P}_i^{(3)}(\vec{r};t) + \ldots}_{\text{nonlinear polarization}}$$

- ***3^rd^-order polarization***:

$$\vec{P}_i^{(3)}(\vec{r};t) = \varepsilon_0 \int_{-\infty}^{t}\int_{-\infty}^{t}\int_{-\infty}^{t} R_{ijkl}^{(3)}(\vec{r};t-t_1,t-t_2,t-t_3)\vec{E}_j(\vec{r};t_1)\vec{E}_k(\vec{r};t_2)\vec{E}_l(\vec{r};t_3)dt_1dt_2dt_3$$

- ***3^rd^-order susceptibility*** = Fourier transform of the 3^rd^-order response function. → describes the nonlinearities of the glass.

$$\chi_{ijkl}^{(3)}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \int_{-\infty}^{+\infty} R_{ijkl}^{(3)}(t_1,t_2,t_3)\exp\left[i(\omega_1 t_1 + \omega_2 t_2 + \omega_3 t_3)\right]dt_1dt_2dt_3$$

The different contributions to the nonlinear response

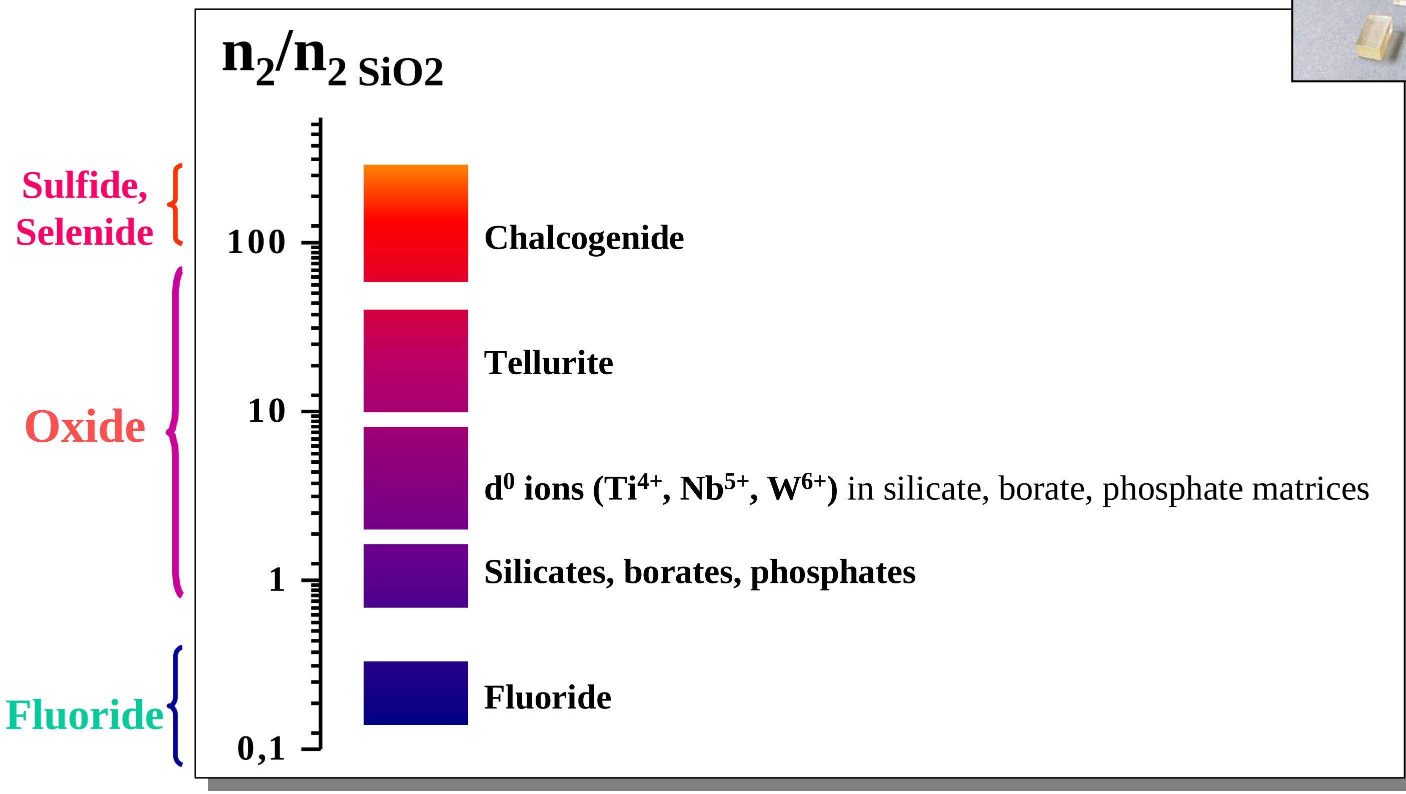
- ***Electronic polarization***: instantaneous nonlinear distortion of the electronic cloud around the nucleus (response time ~ 1 fs).
- ***Nuclear response***: rearrangement of the nucleus position in the new potential created by the electrons electric field (response time ~ 100 fs-1 ps).
- ***Electrostrictive response***: increase of the density, inducing an increase of the nonlinear response (response time ~ 1 ns).
- ***Thermal response***: absorption of the electric field followed by dissipation of the energy under the form of heat, inducing a variation of the nonlinear response (response time ~ 10 µs).

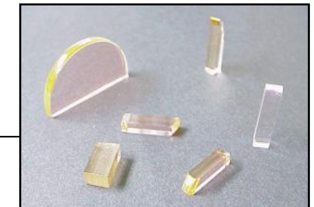
$$\chi^{(3)} = \chi^{(3)}_{elec} + \chi^{(3)}_{nuc} + \cancel{\chi^{(3)}_{str}} + \cancel{\chi^{(3)}_{th}}$$

With fs pulses, electrostrictive and thermal contributions are neglected because their building-up time is too long compared to the pulse duration.

Third order nonlinearity

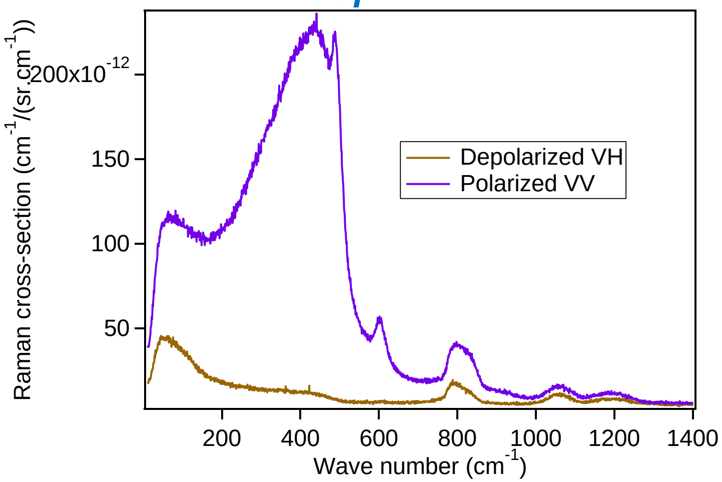
Measured at 1.5 µm

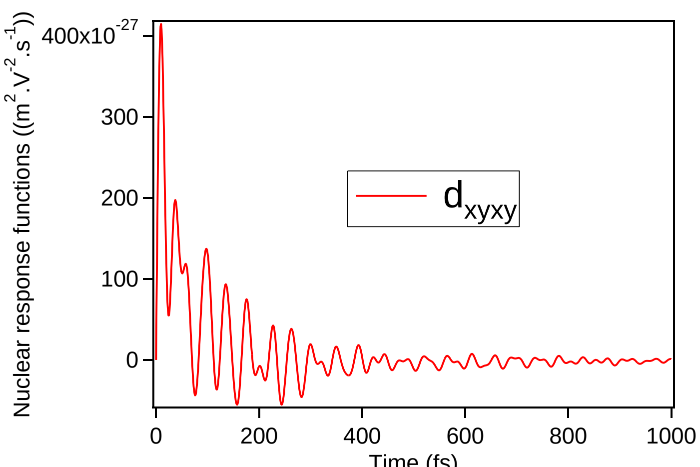




Fused silica

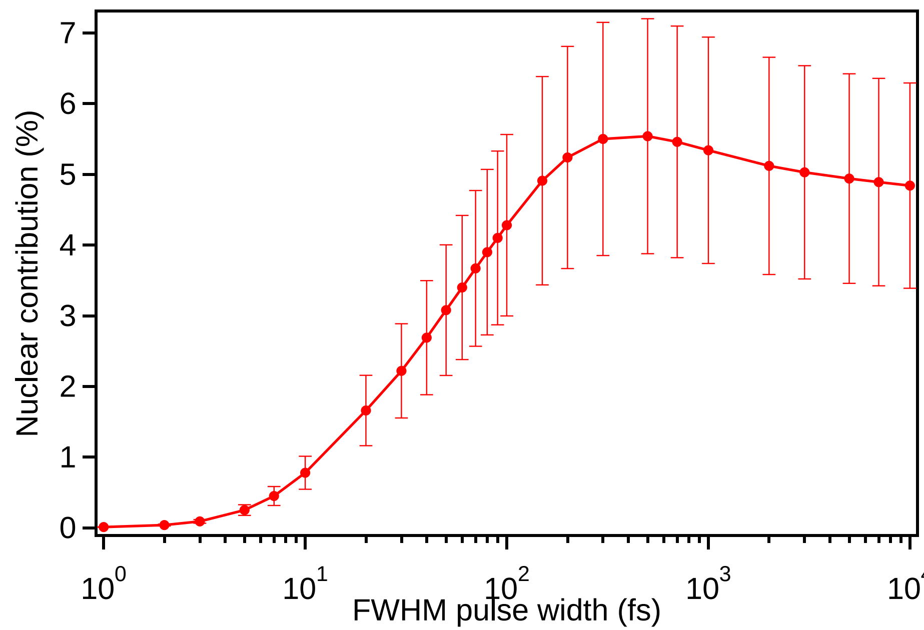
Raman Spectrum





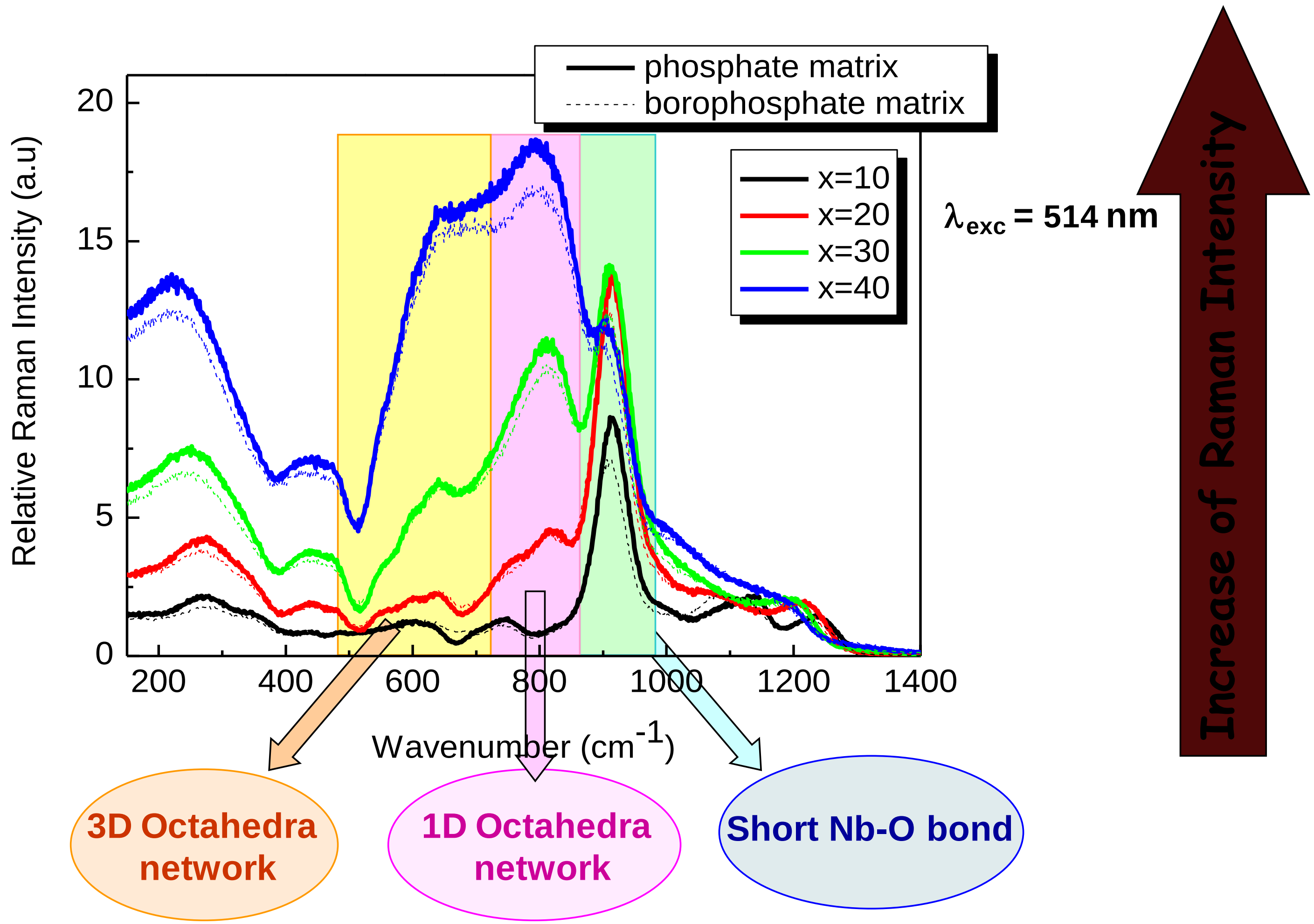
Vibrational Contribution

$$\sigma^{(3)}_{xxxx} = 2.65\times10^{-22}\,\mathrm{m}^2.\mathrm{V}^{-2}$$



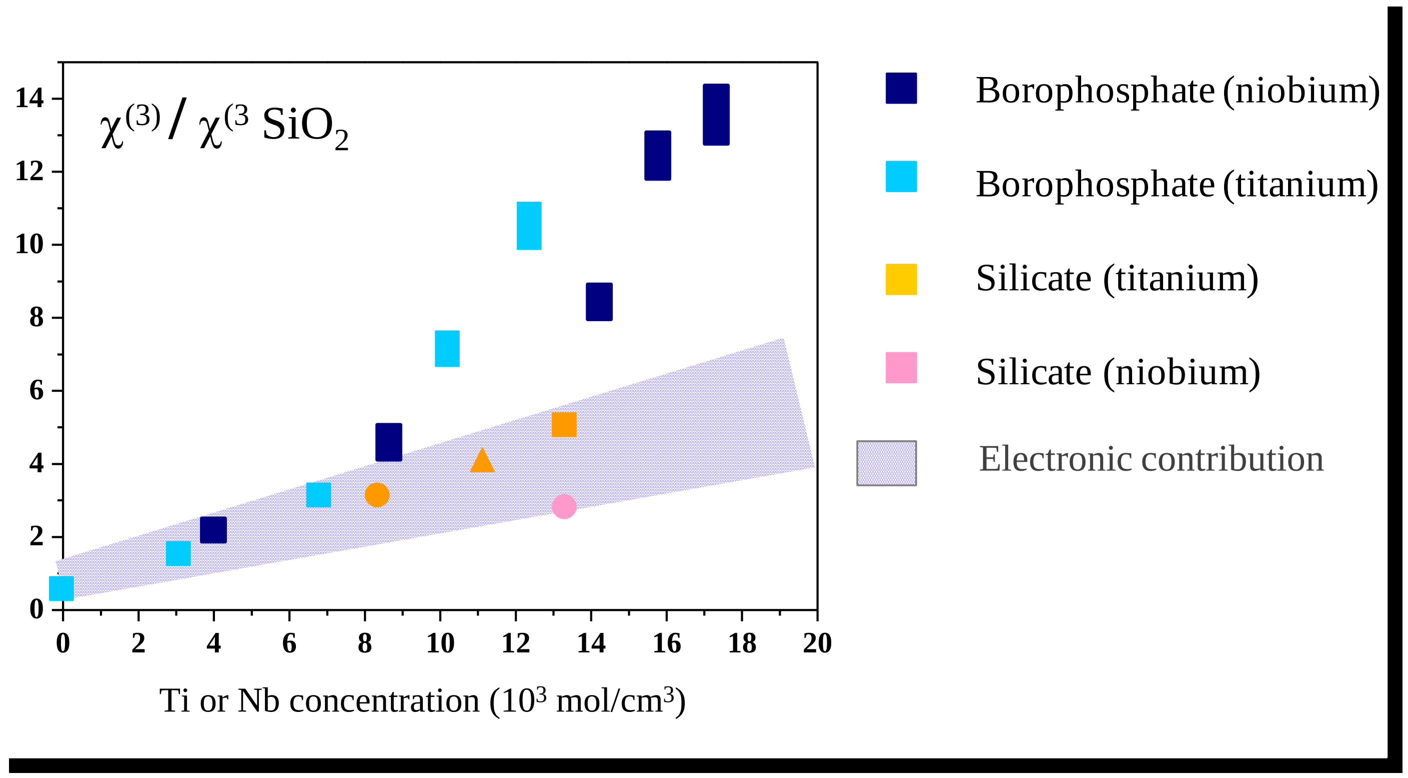
Nuclear contribution up to 6% to the n_2

Niobium oxide containing Glasses

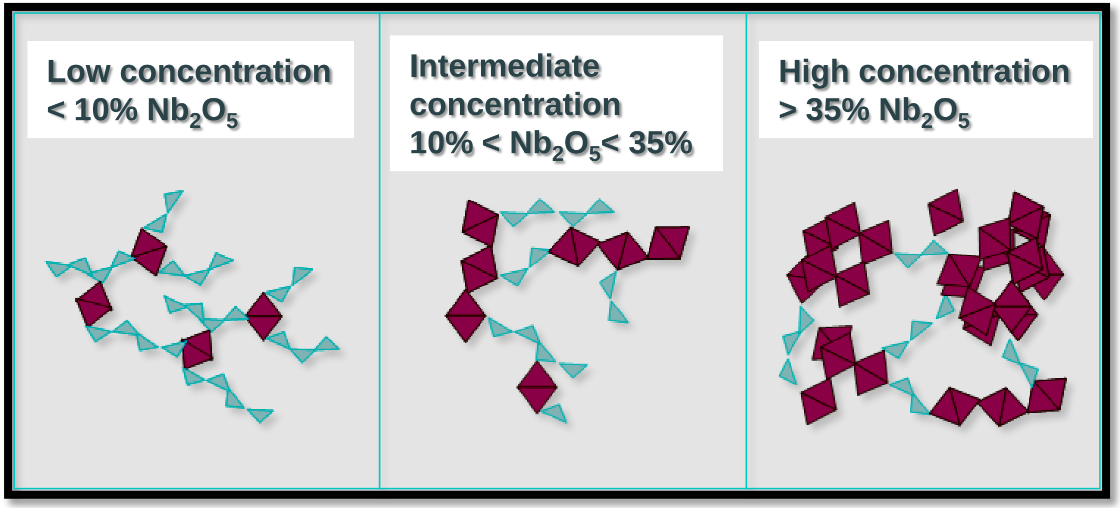


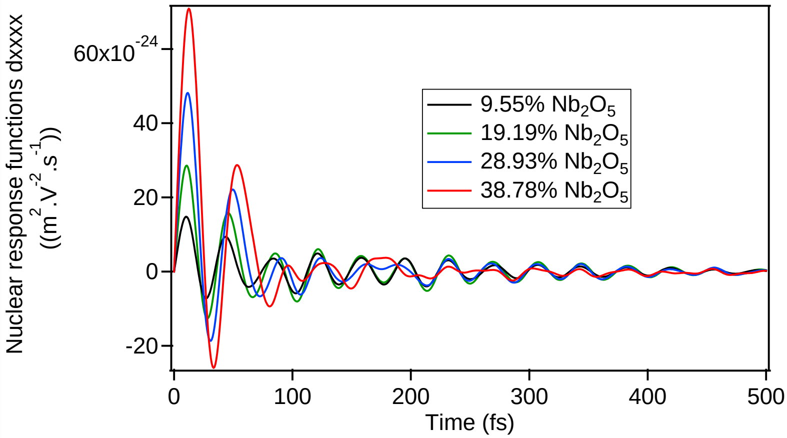
Evolution of the Kerr effect

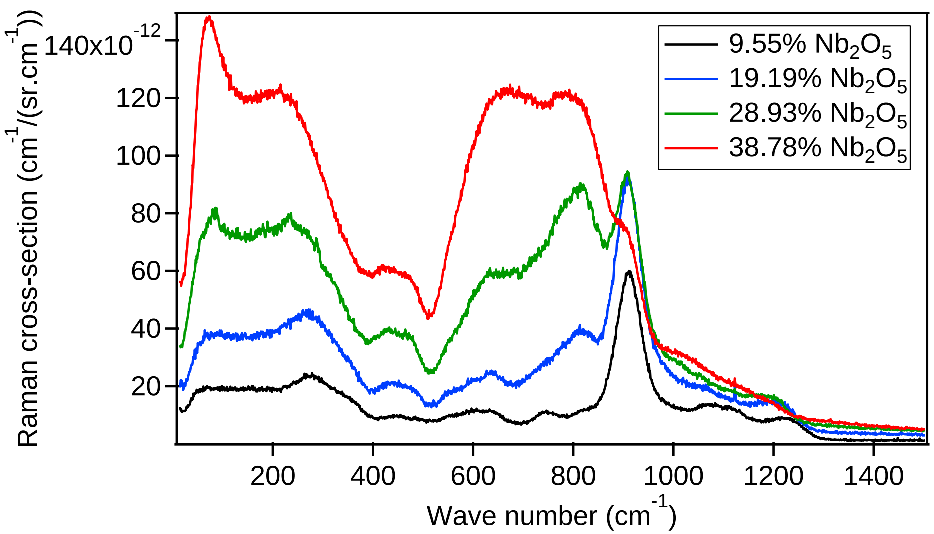
Measured at 800 nm



Glass local structure







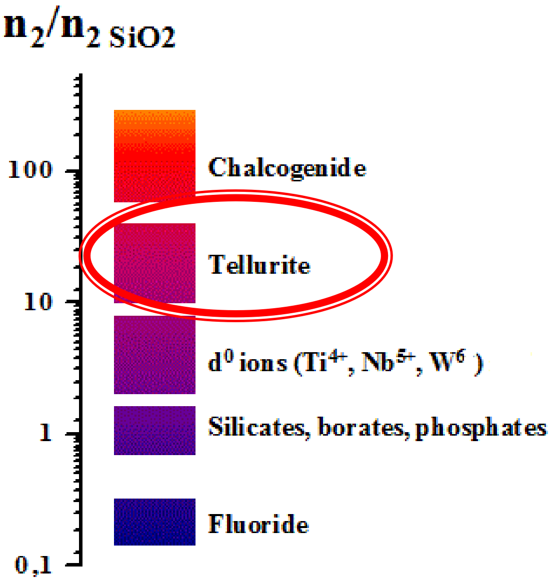
From less than **10%**

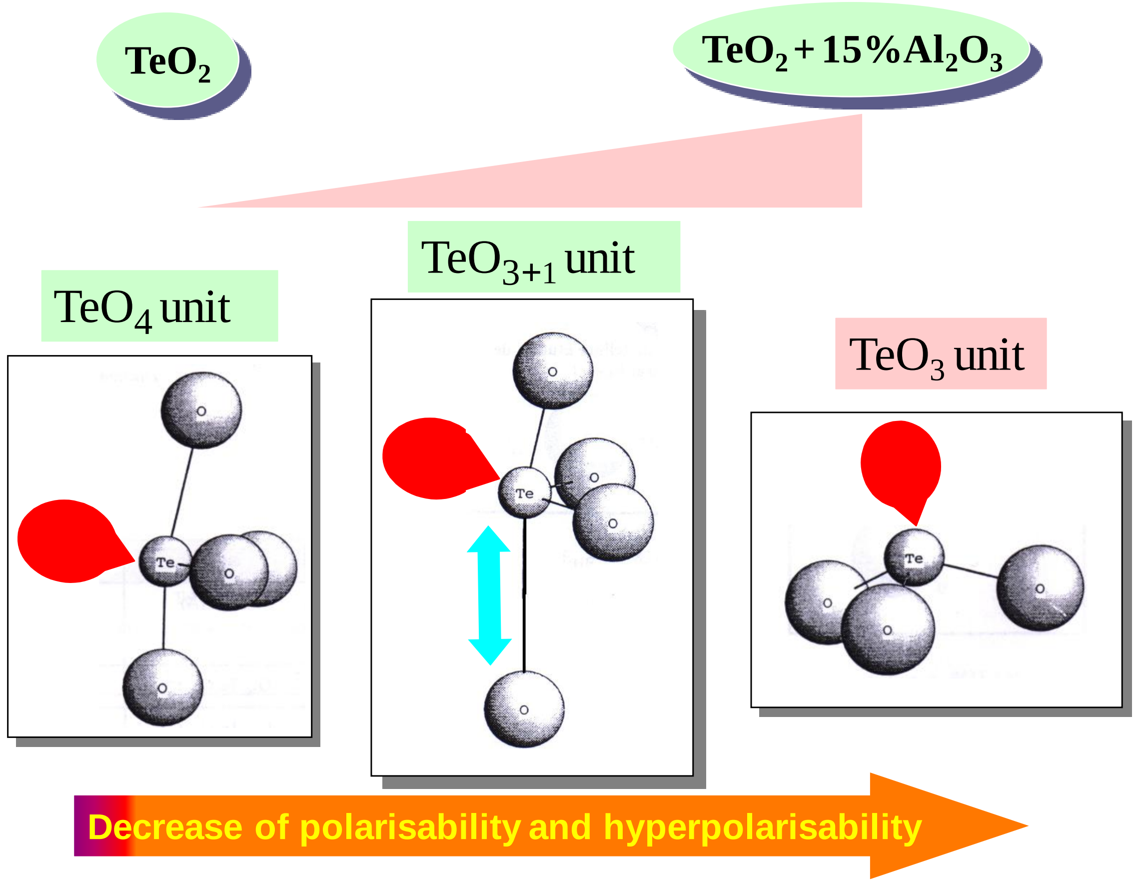
of **nuclear contribution**

to **60%**

to the $\mathbf{n_2}$

Structural units of Tellurite network

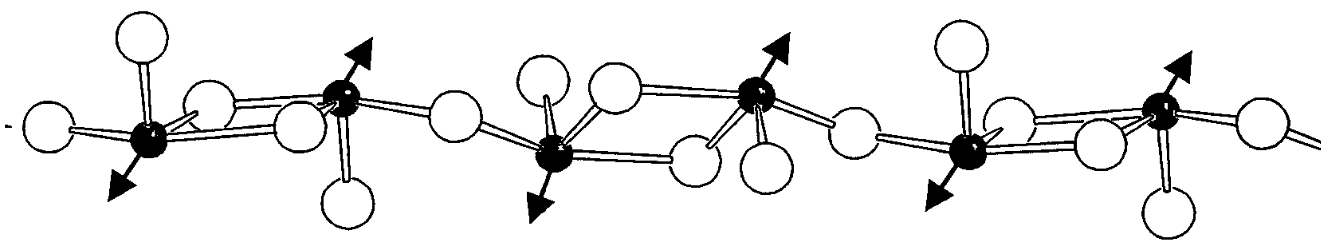




Medium range order

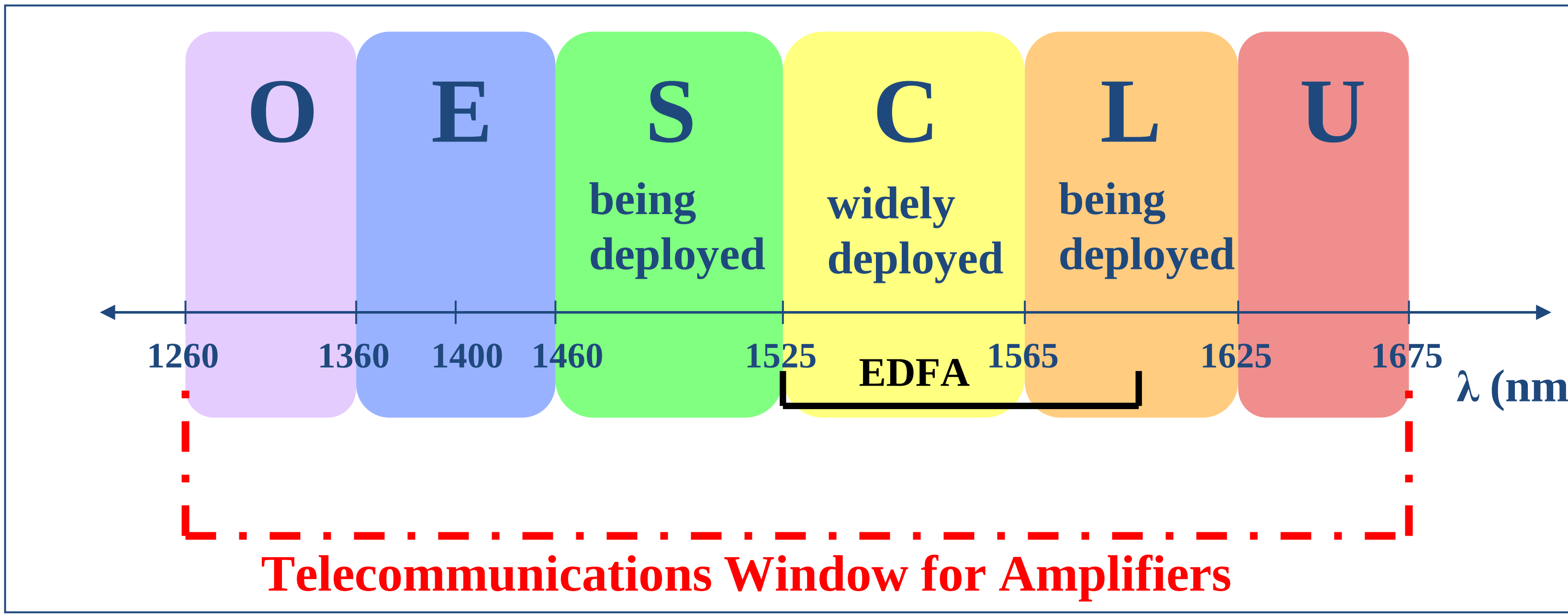
OKE : optical Kerr effect

Tellurium-Thallium glass	$50TeO_2$-$50Tl_2O$	$70TeO_2$-$30Tl_2O$ Electronic	$75TeO_2$-$25Tl_2O$
THG susceptibility ($\times 10^{-22}$ $m^2.V^{-2}$) ($\pm$ 30%)	1042.1	973.4	668.9
OKE susceptibility ($\times 10^{-22}$ $m^2.V^{-2}$) ($\pm$ 10%)	29.4	47.6	48.2



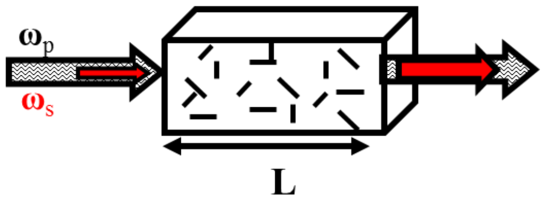
Strong relation between the **glass network** and the **third order nonlinearity**

Fiber Transmission

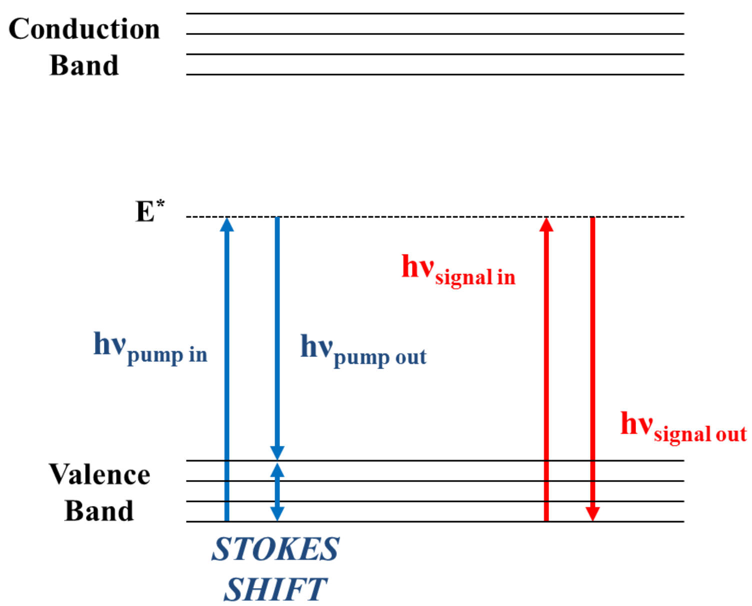


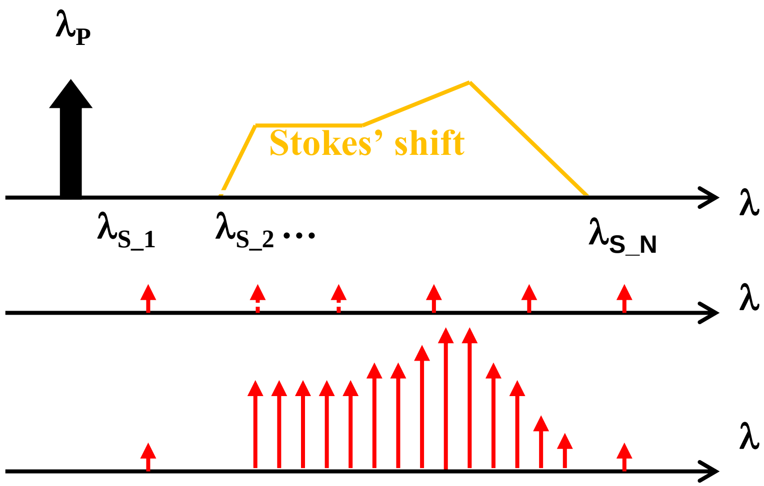
Raman gain

$$P_i = \varepsilon_0\left(\chi_{ij}^{(1)}E_j + \chi_{ijk}^{(2)}E_jE_k + \boxed{\chi_{ijkl}^{(3)}E_jE_kE_l} + \dots\right)$$

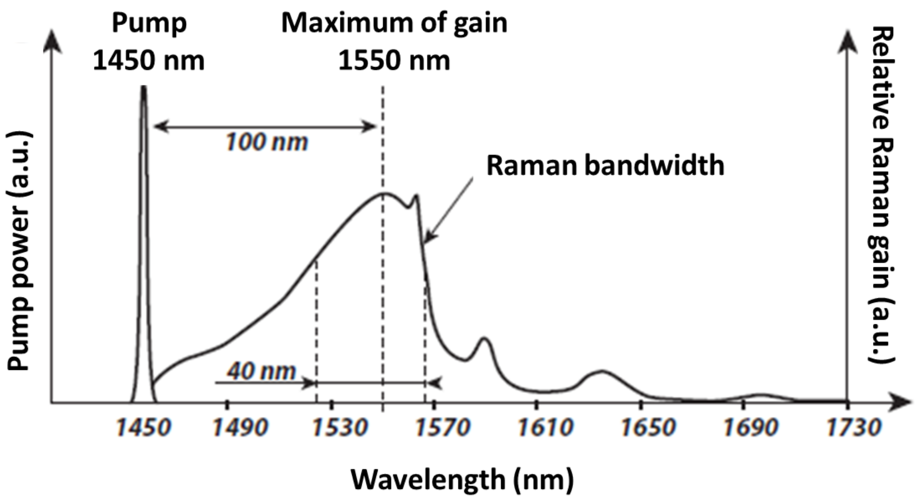


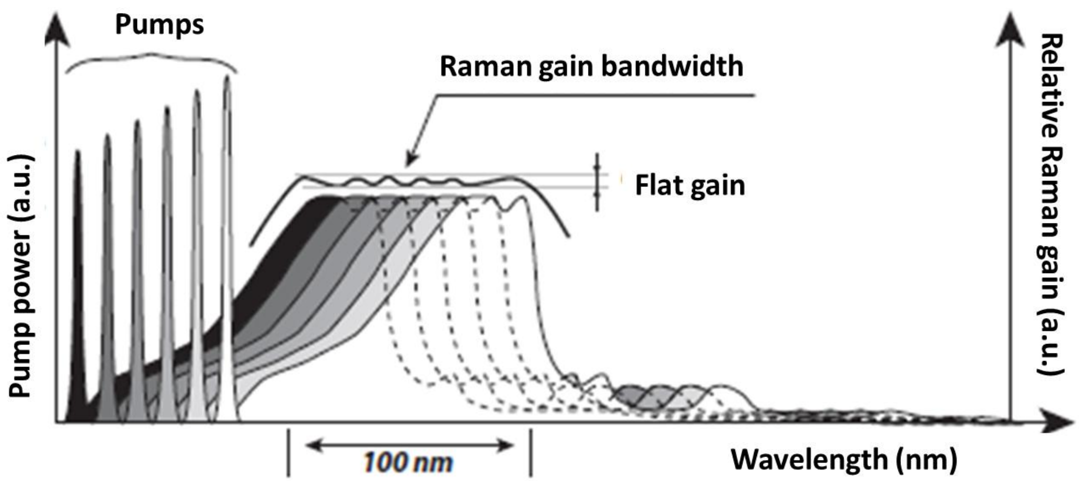
Raman gain results from 4 waves mixing phenomena (3rd order nonlinearity) combining excitation, signal and vibration mode.





Raman gain in fused silica

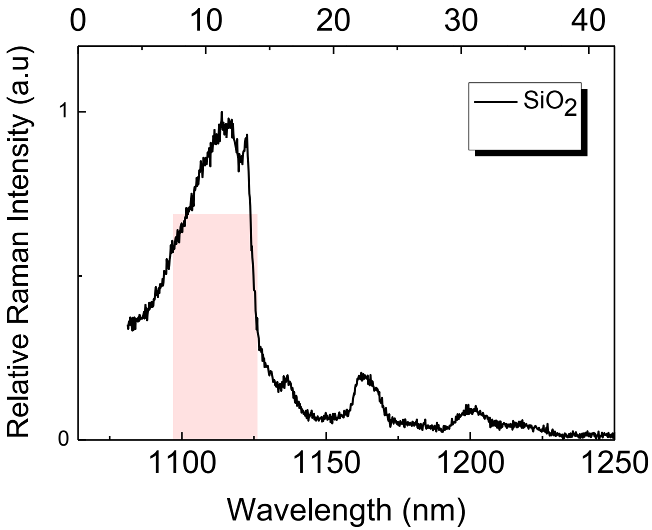


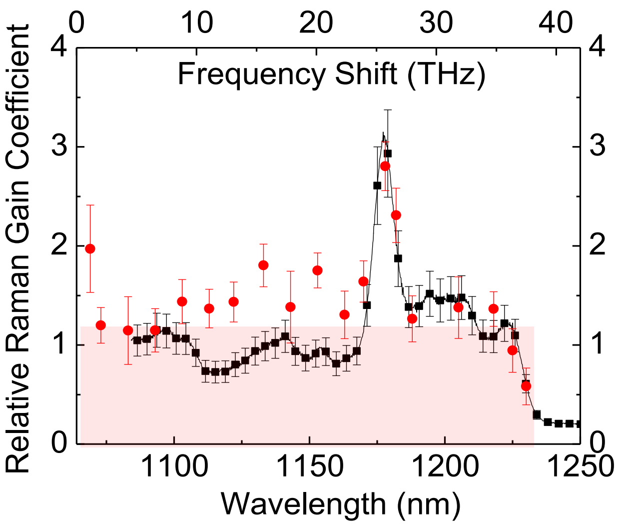


Raman gain bandwidths are fixed by the **bandwidth of the Raman active medium**.

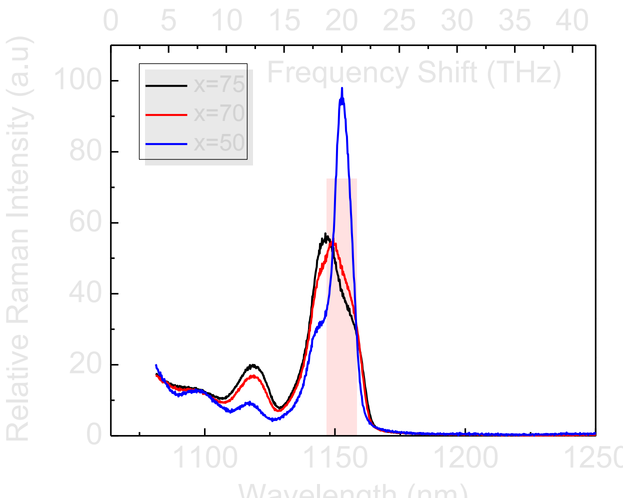
Raman Gain Spectrum

SiO_2





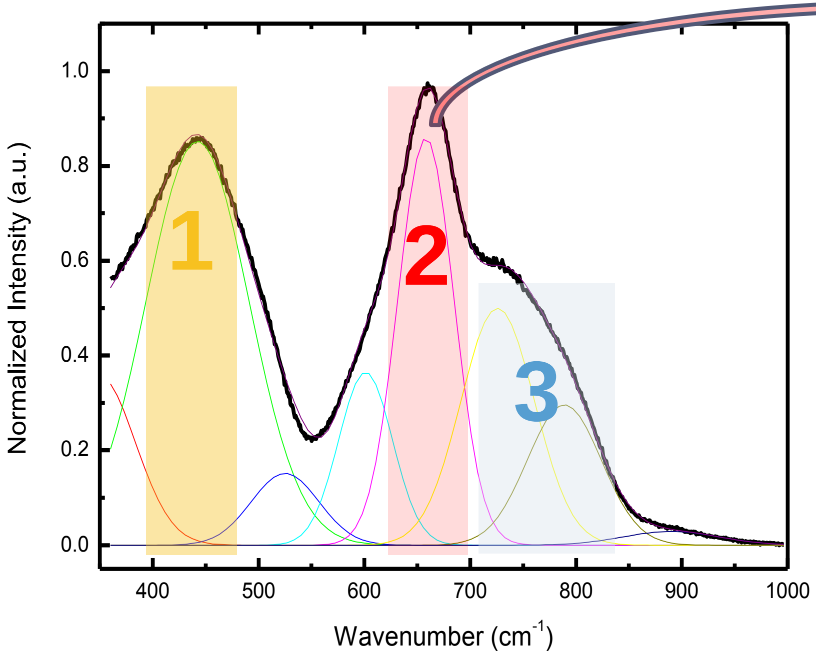
Borophosphate

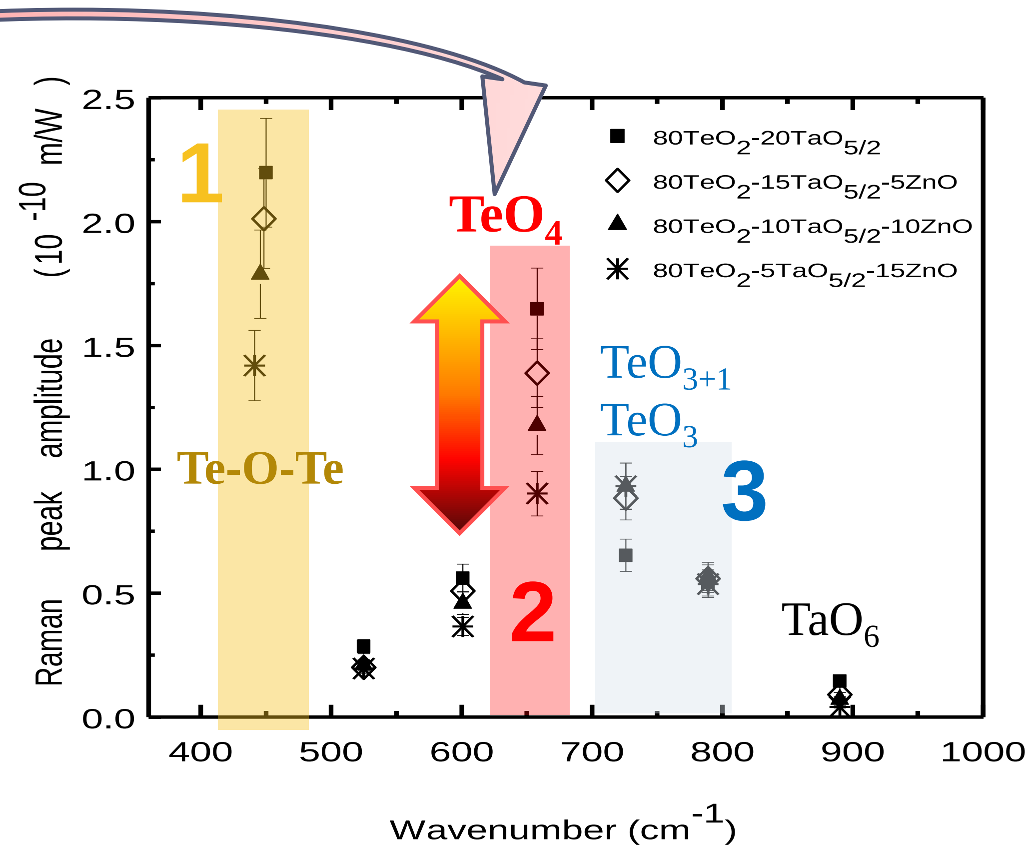


x TeO_2 - (100-x) $TlO_{0.5}$

Vibrational response

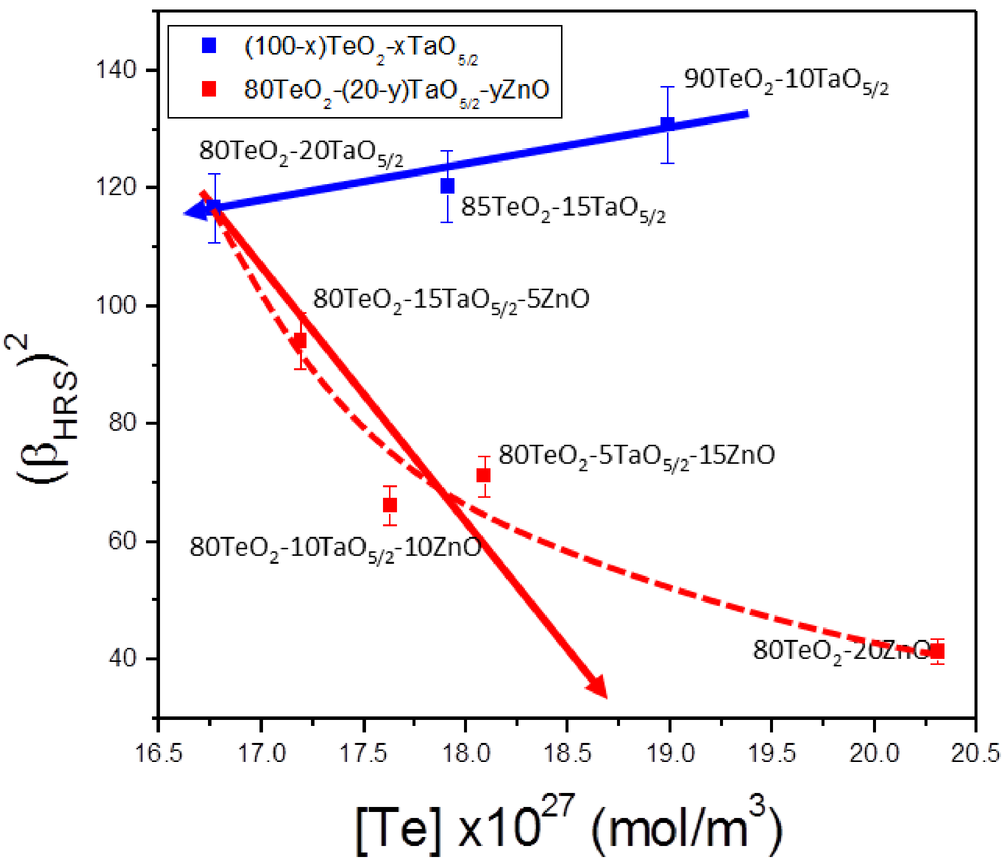
80TeO$_2$-(20-y)TaO$_{5/2}$-yZnO

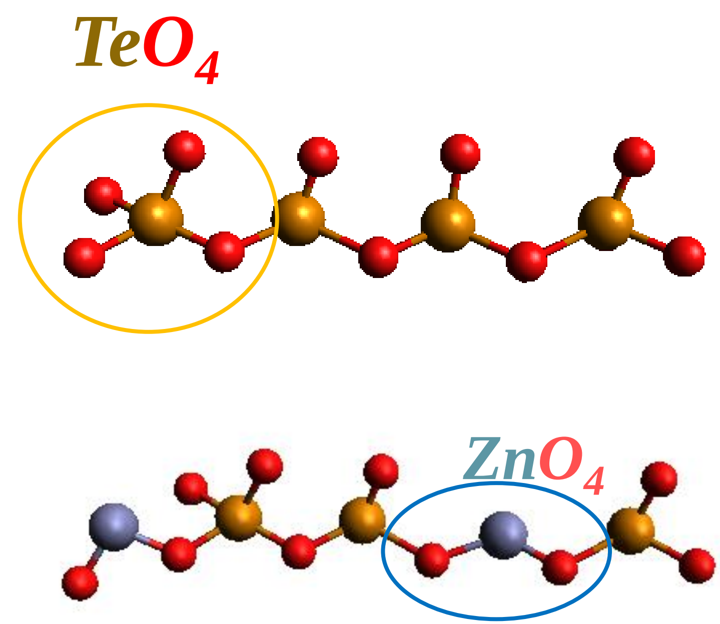




Hyperpolarisability and glass structure

Hyper Rayleigh

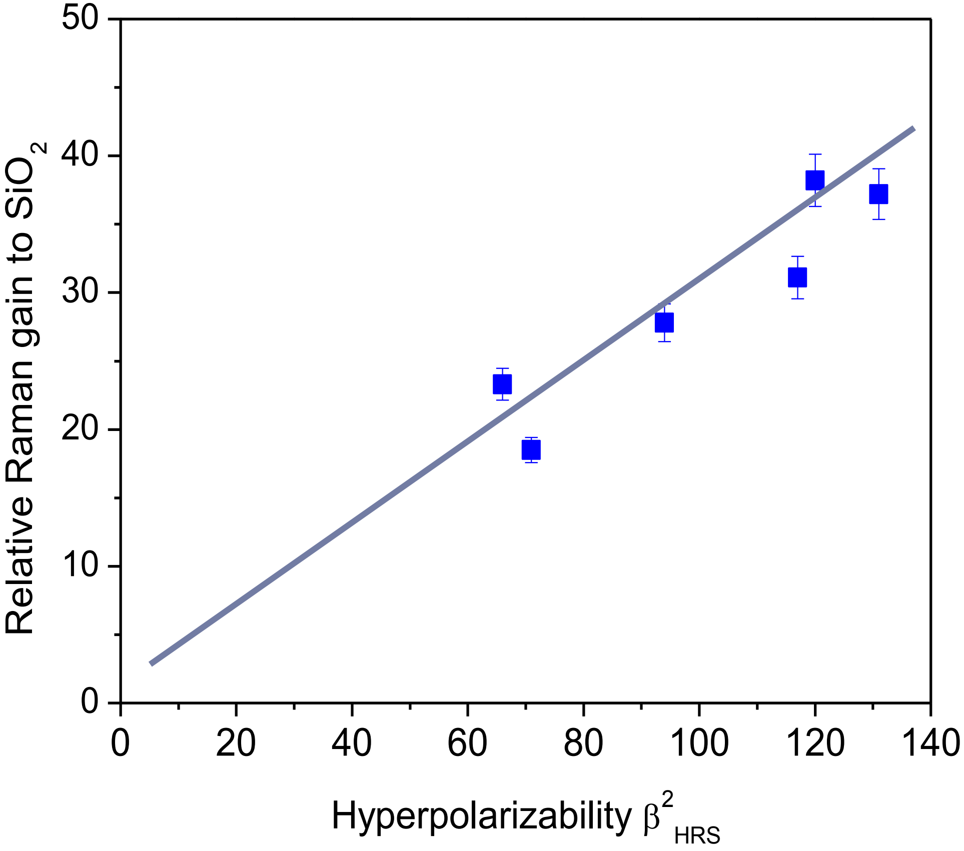




→Reduction of the **tellurite network polarization**.

Drastic decrease of the hyperpolarizability during the ZnO introduction.

Hyperpolarizability and Raman Gain



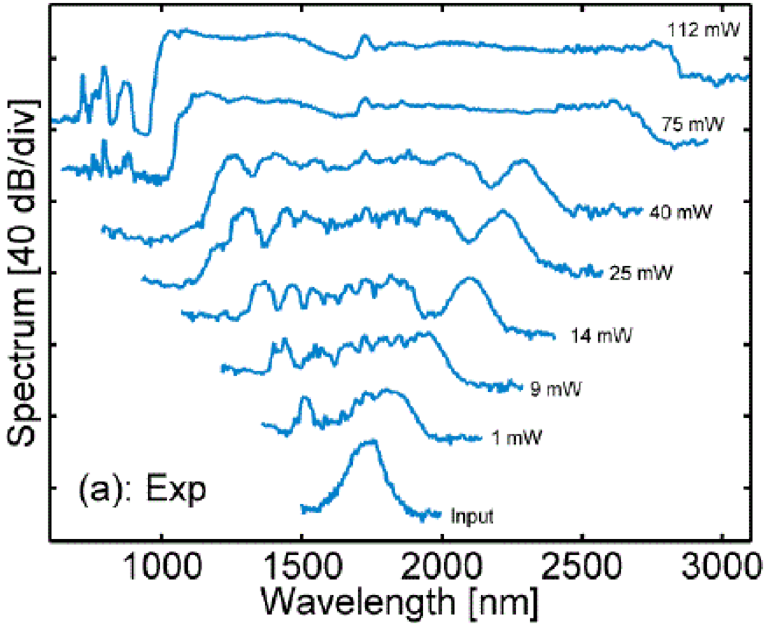
- **Raman gain** linearly proportional to **hyperpolarizability** ($\chi^{(2)}$ α $\chi^{(3)}$)

→Relationship between a **local measurement** *(hyperpolarizability)*

and a **macroscopic property** *(Raman gain)*

Supercontinuum generation

$80TeO_2$-$10ZnO$-$10Na_2O$



I. Savelii et al., Optics Express, Vol. 20 Issue 24, pp.27083-27093 (2012)

Self phase modulation

Raman Gain

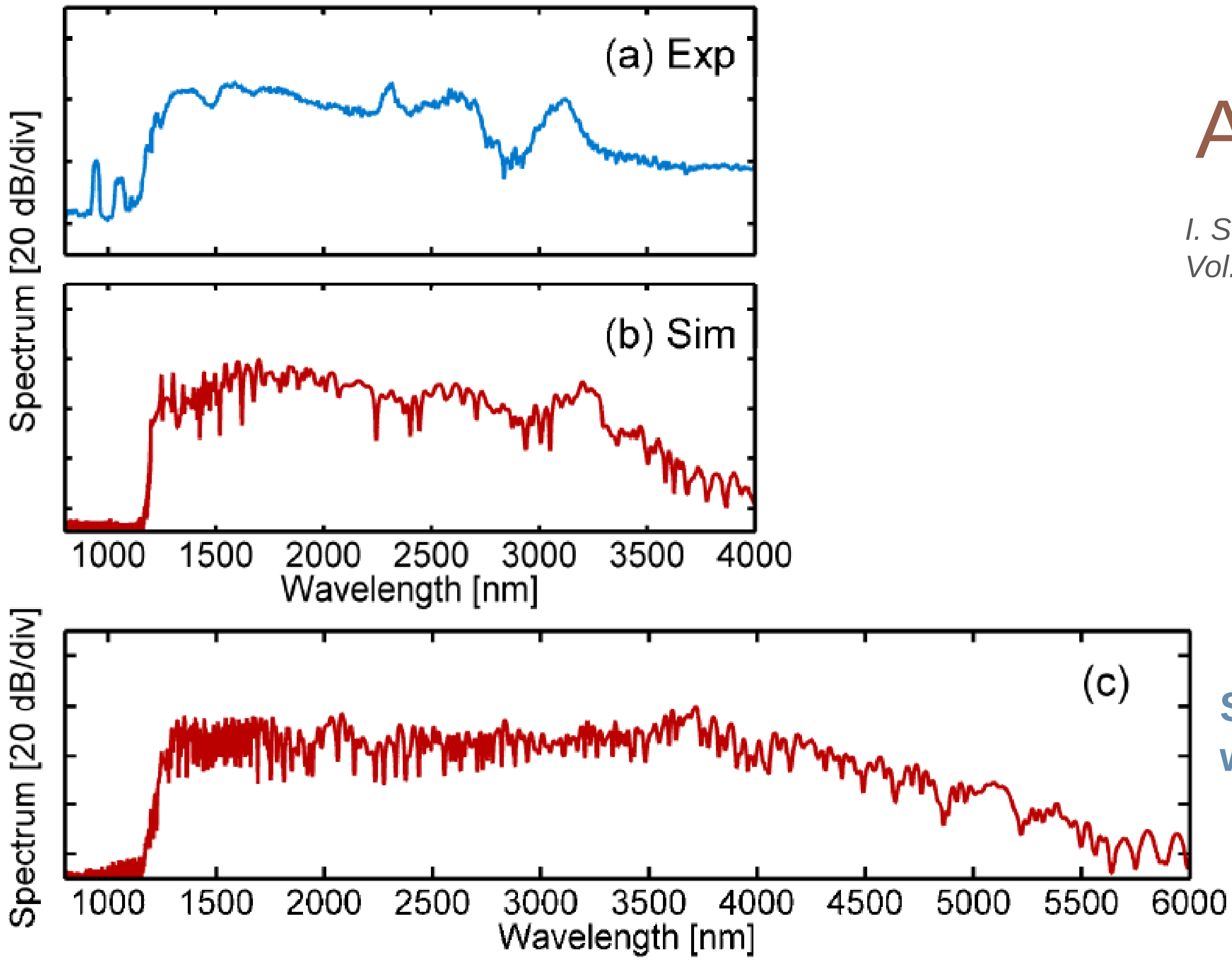
Four Wave Mixing

THG

Theoretically up to 3000 nm if no Hydroxyls

M. Liao, Optics Express, 20, 26 (2012), p574

Supercontinuum generation

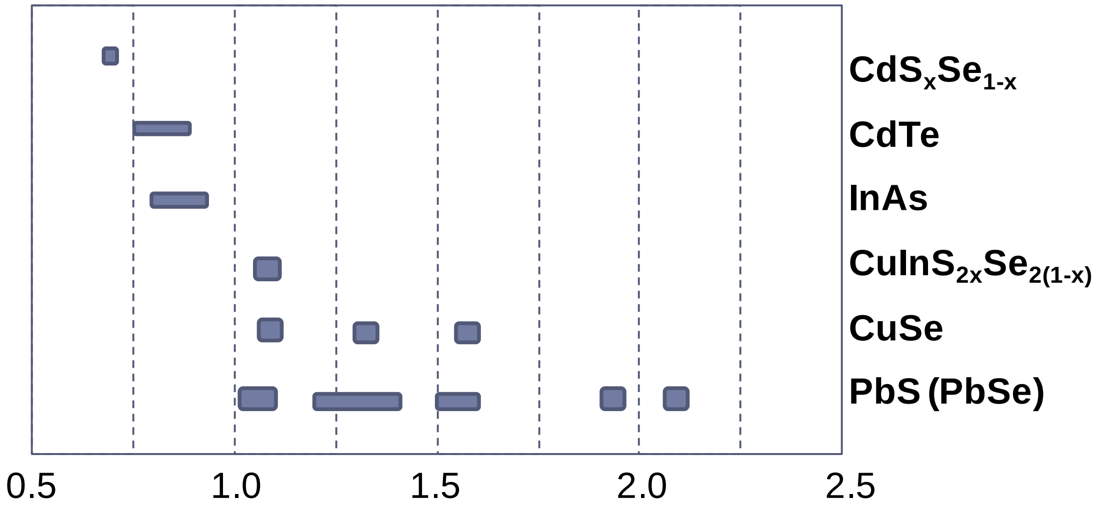


As_2S_3

I. Savelii et al., Optics Express, Vol. 20 Issue 24, pp.27083-27093 (2012)

Simulation without SH and OH groups

Quantum dots for NLO



$CdS_{(1-x)}Se_x$

$$W = \Delta n_{sat}/\alpha_0\tau$$

Finlayson et al.,
Vol. 6, No. 4/April 1989/J. Opt. Soc. Am. B

Glasses doped semiconductor quantum dots
PbS , PbSe , PbTe

- **narrow band-gap,**
- **large optical nonlinearity**
- **fast response time**

S. Ju,
Optics Express, 19, 3, (2011), p2599

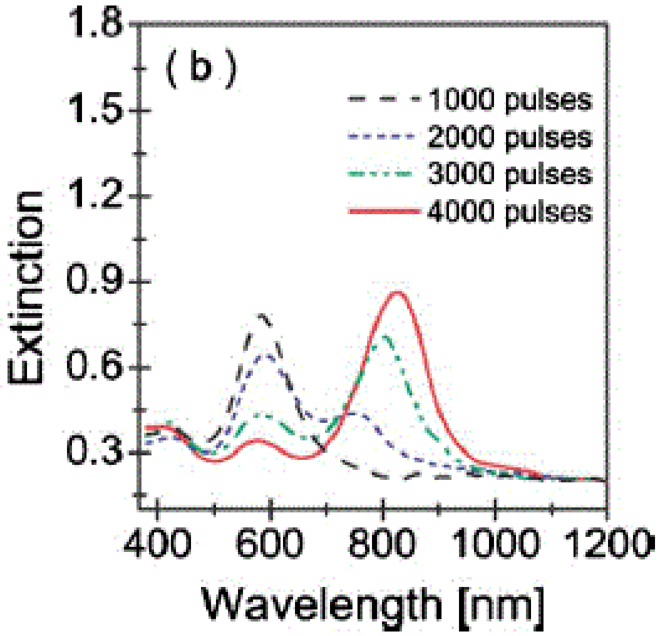
metallic nanoparticles for NLO

non-spherical
silver nanoparticles

Enhancement of nonlinearity
2 order of magnitude

A. Stalmashonak ,
Optics Letters 35, 10, (2010), p1673
S. Mohan
Optics Express, 20, 27, (2012, p28655

Large aspect ratio
metal nanoparticles



Second order nonlinearity

❑ Nonlinear optical effects

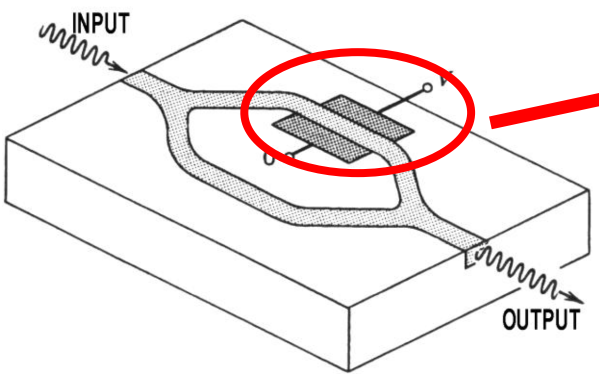
$$P = \varepsilon_0 \left(\chi^{(1)}E(\omega) + \boxed{\chi^{(2)}E(\omega)E(\omega)} + \chi^{(3)}E(\omega)E(\omega)E(\omega) + \ldots \right)$$

SHG (2ω)

$n \approx f(E)$

$n = n_0 + \zeta E$

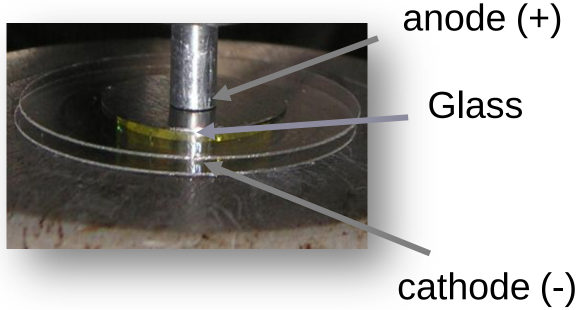
Applications

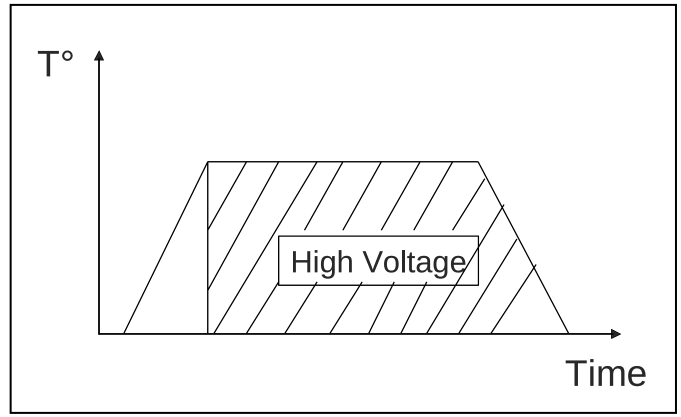


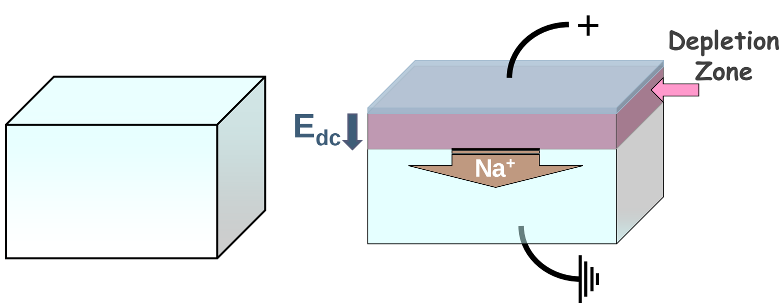
Variation of the refractive index

Modulation or switching of the light

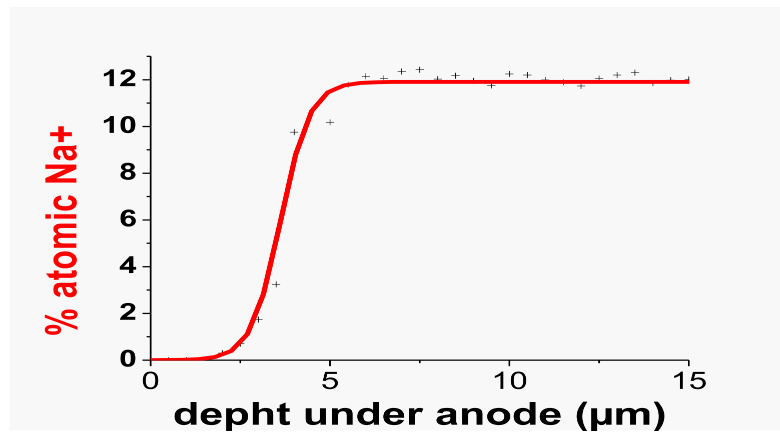
Sample placed between two electrodes







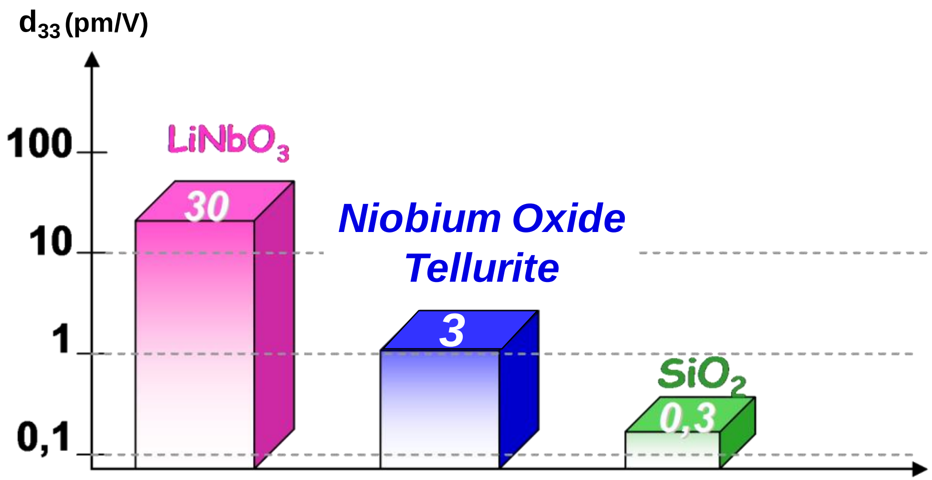
$C_{\infty v}$



$$P^{NL}(2\omega) = \boxed{\chi^{(3)} E_{dc}}\, E(\omega)E(\omega)$$

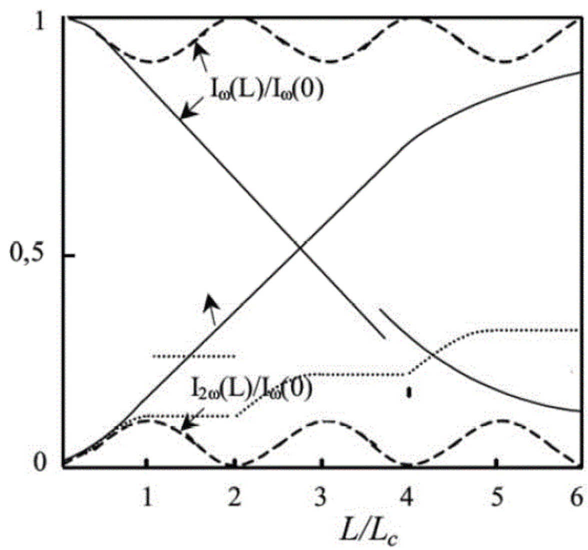
$$\approx \chi^{(2)}$$

Material performance



$$P^{NL}(2\omega) = \boxed{\chi^{(3)} E_{dc}} E(\omega)E(\omega)$$

$$\approx \chi^{(2)}$$



Need for quasi phase matching

P. N. Butcher and D. Cotter, *The elements of non linear optics. Cambridge University* press, 1990.

Structuration of SHG

Ag thin film (200 nm) :

Anode

↓

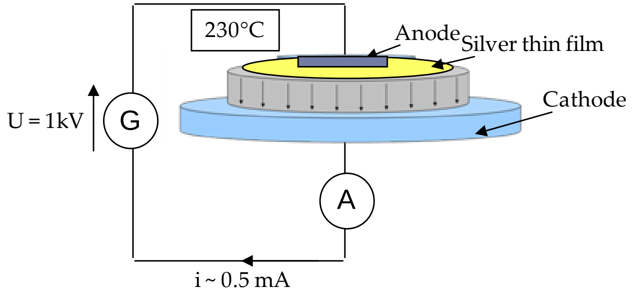
Laser Ablation of Ag Lines

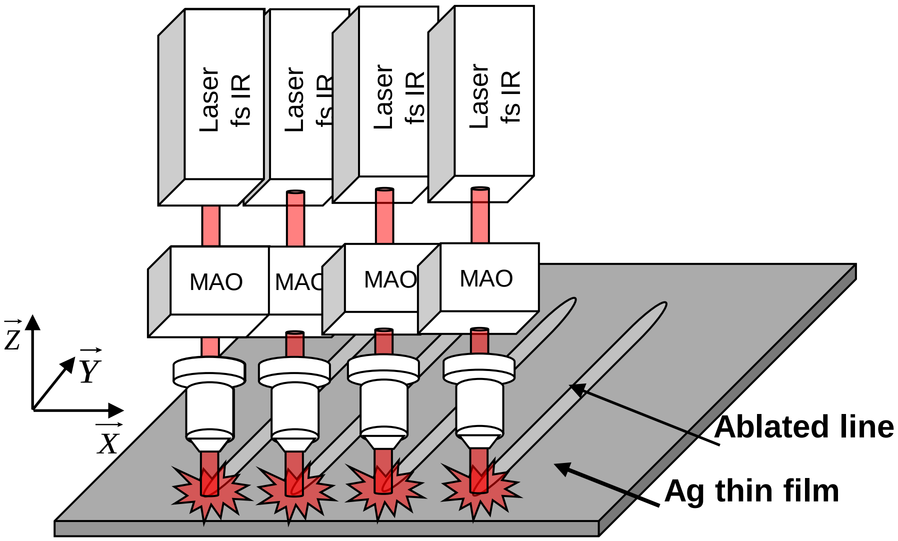
Structured Anode

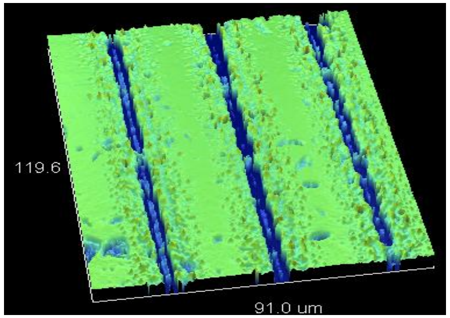
↓

Thermal poling

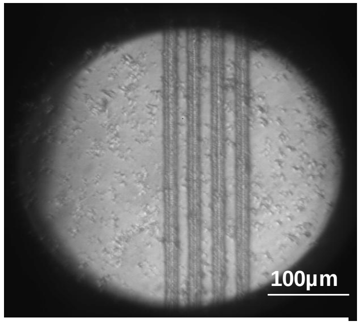
230 °C, t = 1 h, U = 1 kV, i_0 ~ 0.5 mA





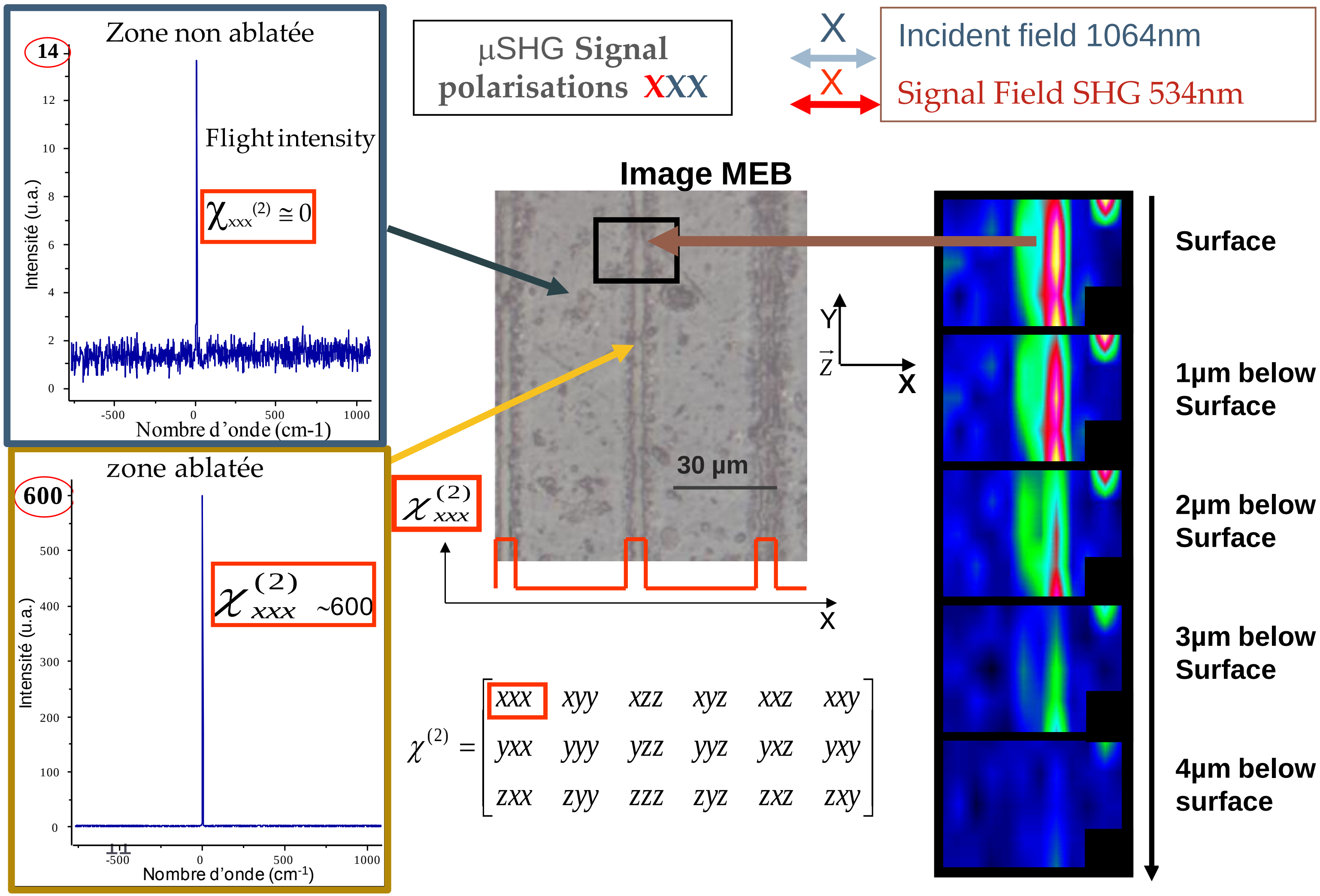


Surface profile after laser ablation

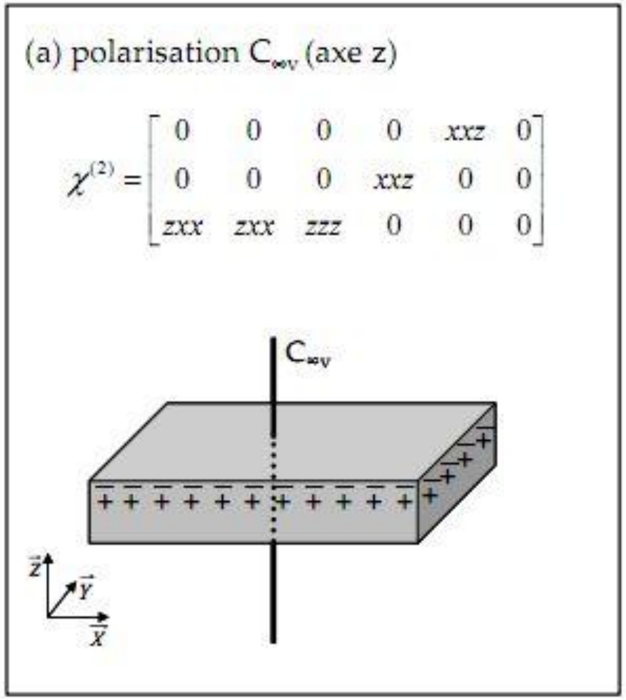


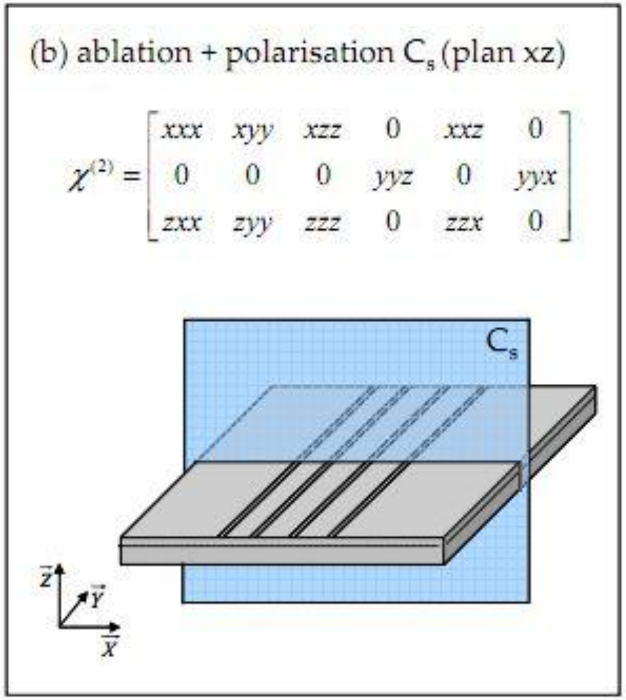
SEM

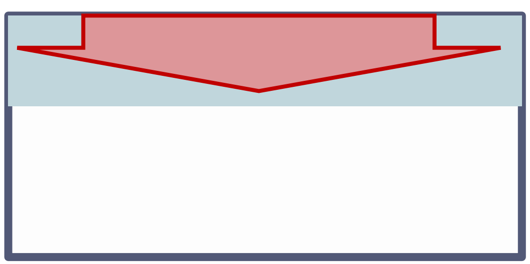
Analysis of µSHG signal

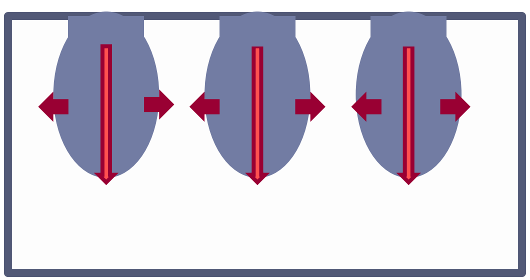


Symetry control

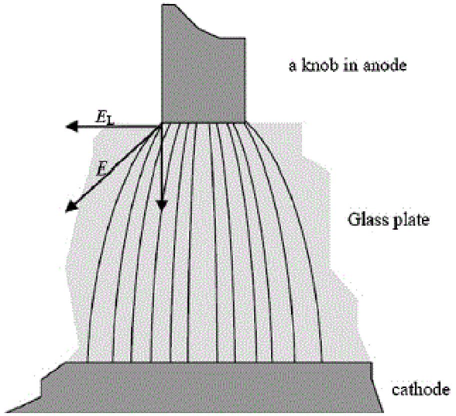




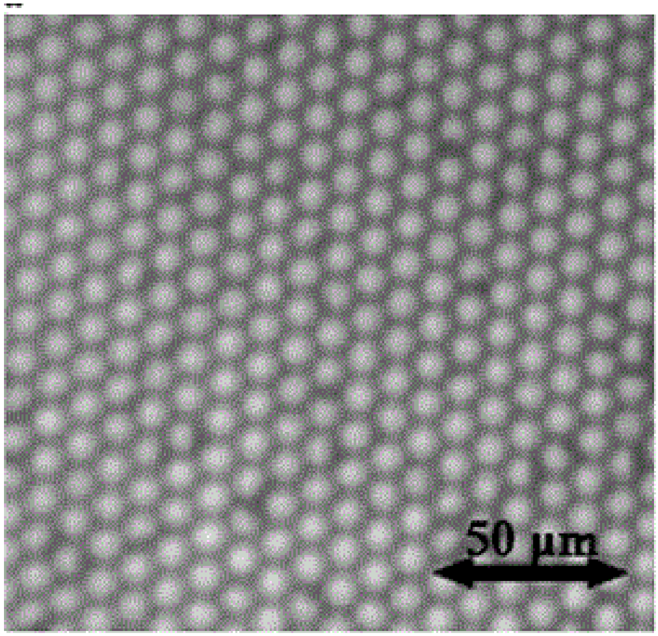


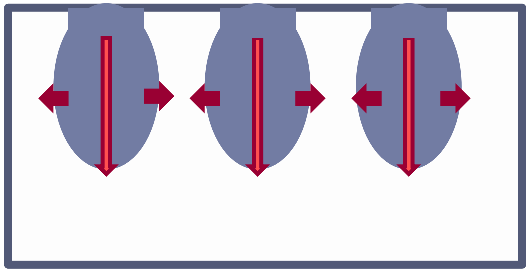


Pattern implementation

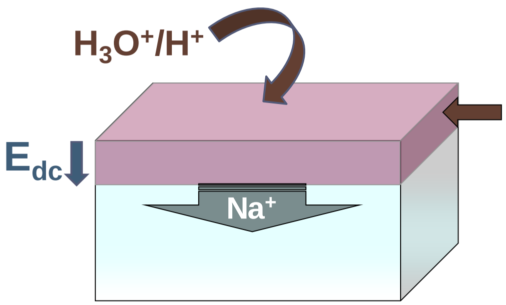


A. Lipovskii et al.,
B. Solid State Ionics 181 (2010) 849–855





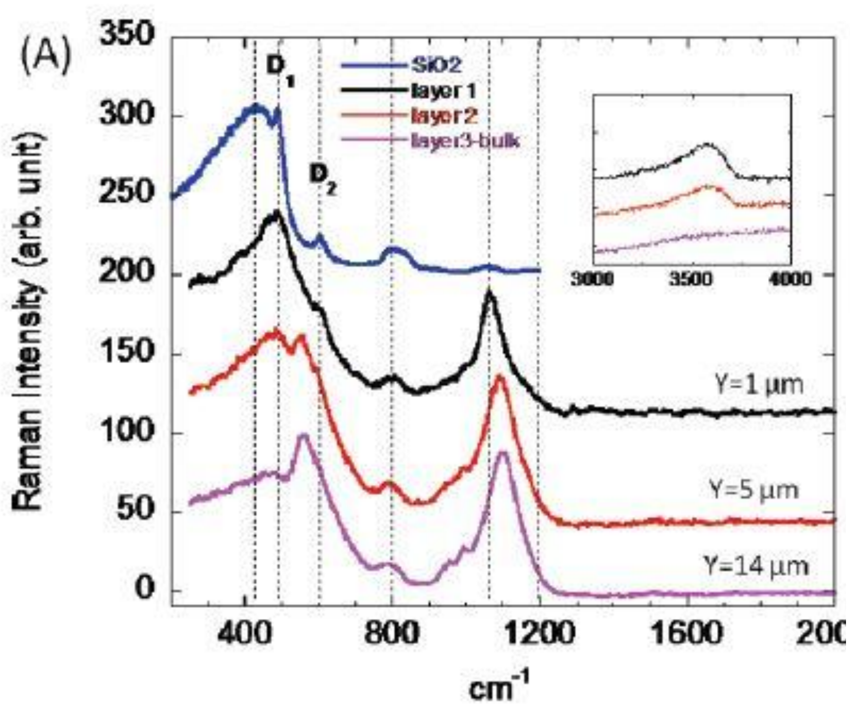
Materials structure modification

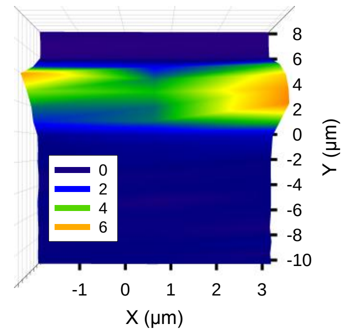


Depletion Zone

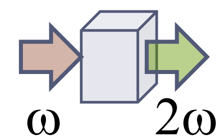
Material Structure modification

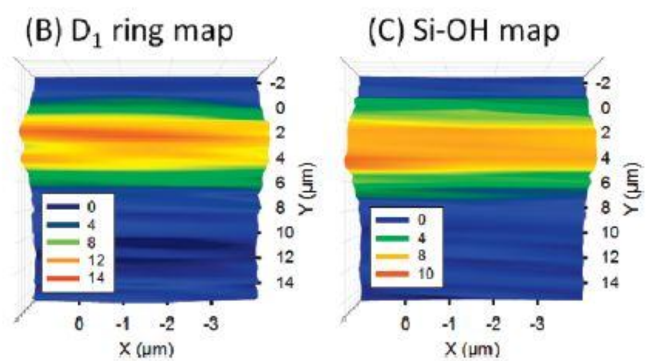
Silicate





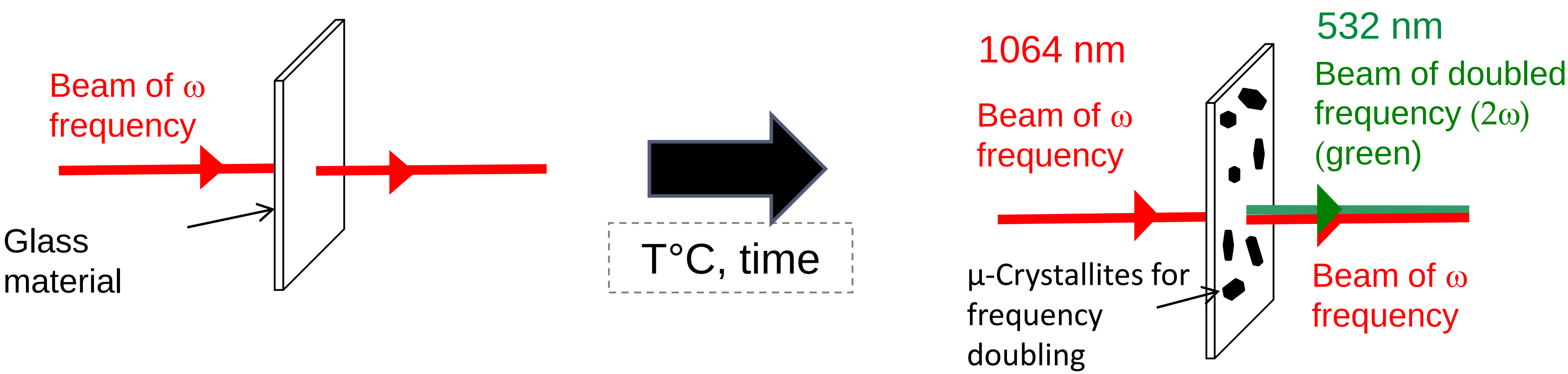
µSHG





M. Dussauze et al., The journal of physical chemistry. C Vol. :114 iss :29 ,2010, 12754 -12759.

A glass-ceramic for frequency doubling



Before heat treatment

Centrosymetric glass

After heat treatment

Non-Centrosymetric crystallites

➢ ***Characteristics :***

Size and space control of μ-crystallites precipitation :

- Sub – micro or nano crystals for transparency or

  low refractive index difference between the matrix and the crystallites

- Homogenous bulk crystallization

H. Jain, *Ferroelectrics*, 306, 111-127 (2004)

Framework

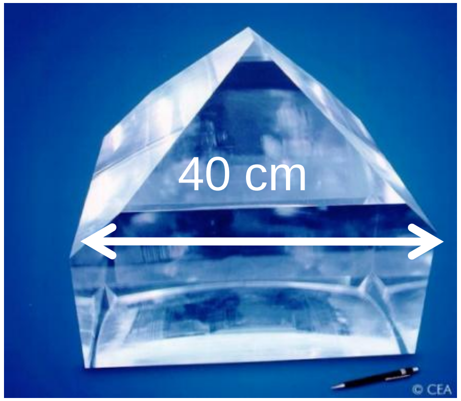
High Power Laser

Nuclear simulation test
NIF

Medical research
Hyper

Electricity production ?
LMJ

Current material :



Potassium Dihydrogen Phosphate

- Large-sized Monocristals
- Cut out with a specific way

↗Cost

Vitroceramic for NLO

$KNbO_3$
$KTiOPO_4$ (KTP)
$Ba_2TiSi_2O_8$
$LiNbO_3$

SHG Increases
with crystallization ratio

Trade off to be reached:

Transparency/SHG activity

Control of low refractive index difference between the crystalline phase and the glass

$25La_2O_3$-25 B_2O_3-$50GeO_2$
Crystalline phase $LaBGeO_5$
(200 nm à 200 µm)

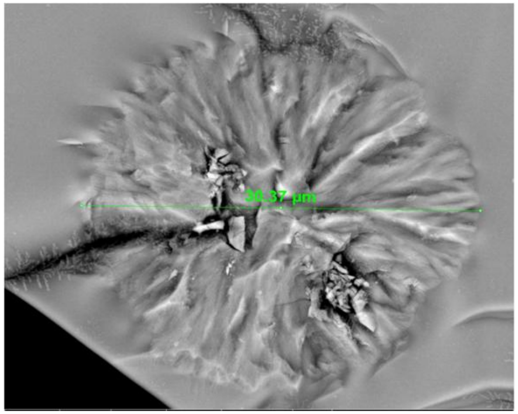
$15K_2O$- $15Nb_2O_5$-$68TeO_2$-$2MoO_3$
Crystalline phase $KNbO_3$

Effect of Poling

$15K_2O$- $15Nb_2O_5$-$68TeO_2$-$2MoO_3$, Crystallites $KNbO_3$
Second order NLO increase by a factor 6 to 20 [58].

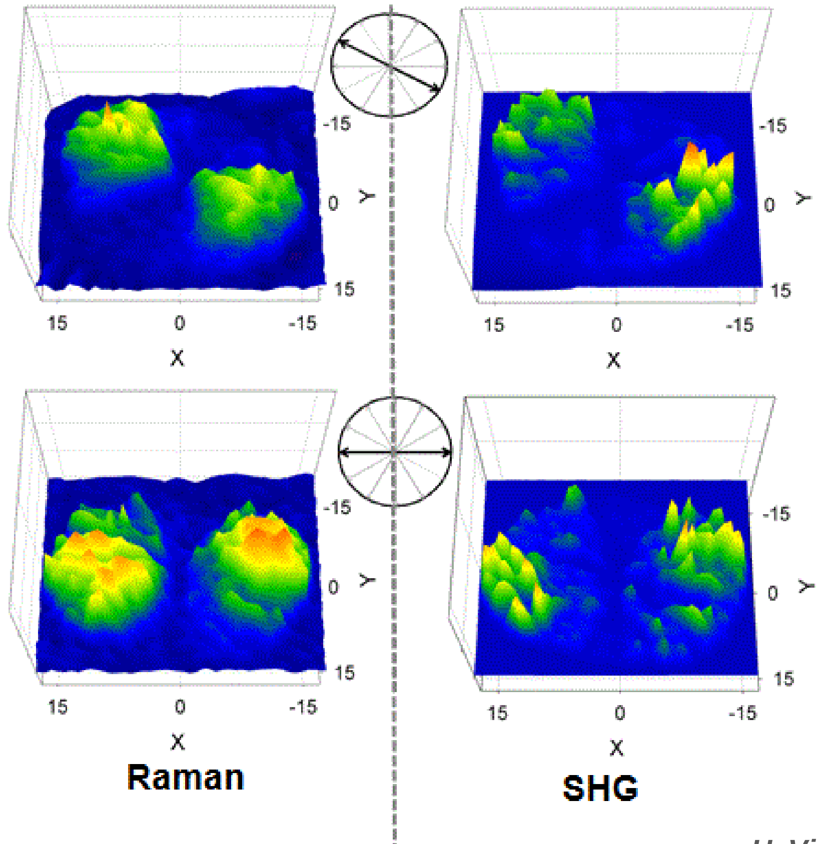
In $0.7Na_2B_4O_7$-$0.3Nb_2O_5$, Crystallites $NaNbO_3$ (30 nm)
SHG signal measured after poling

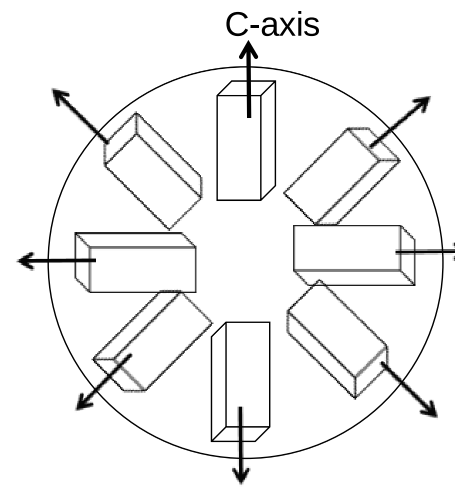
Spherulite



Li_2O-SiO_2-Nb_2O_5

X, Y axis : 30 X 30 µm





Radial distribution

Spherulites distributed in the matrix with distances greater than the coherence length,

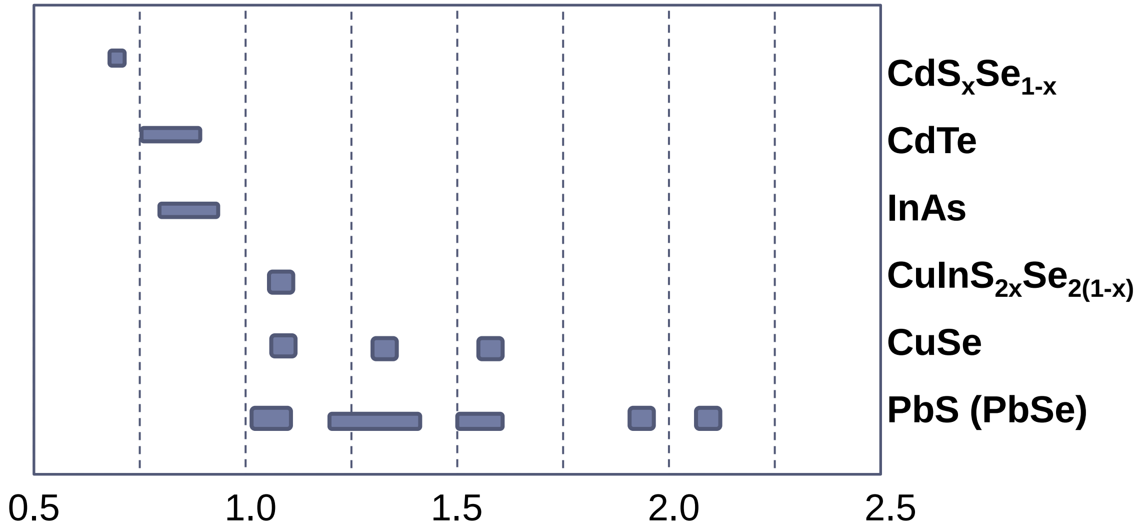
Total second harmonic intensity Sum of the individual contributions (incoherent case).

Similar phenomenon in
$25La_2O_3$-25 B_2O_3-$50GeO_2$
Cristalline phase $LaBGeO_5$

H. Vigouroux
Adv. Funct. Mater. 2012, 22, 3985–3993

Nonlinear absorption

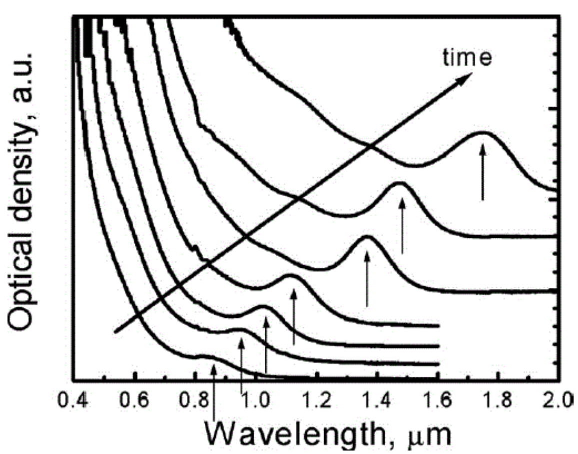
A.M. Malyarevich, et al.,
J. Appl. Phys. 103, 081301 2008



Q switching and mode locking of near-infrared solid-state lasers

to obtain light pulses of high power and short/ultrashort duration

PbSe

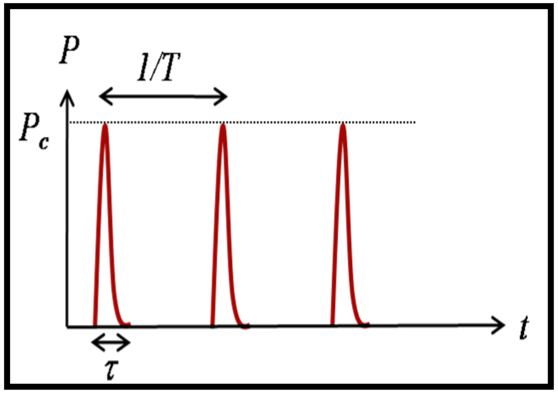


Key parameters :
Ground-state absorption cross section,
Residual non saturable absorption,
Bleaching relaxation absorption recovery time (ps)
Saturation intensity

Size distribution : 5%–10% around their main diameter

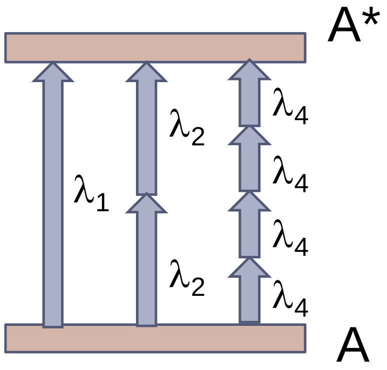
Nonlinear absorption

Short pulsed Lasers



$P_c \approx$ GW - TW

Dye Fluorescence in solution

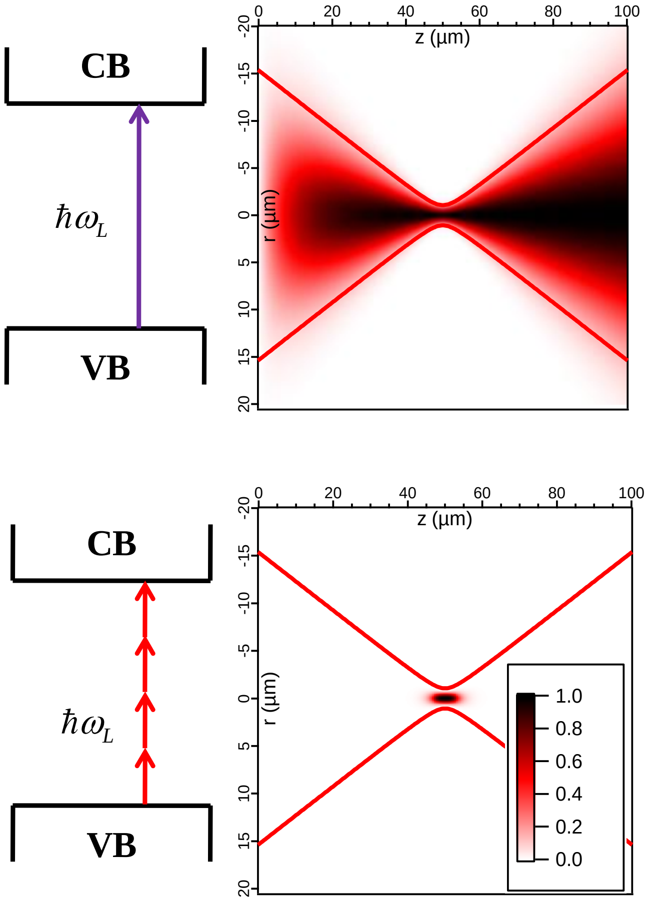


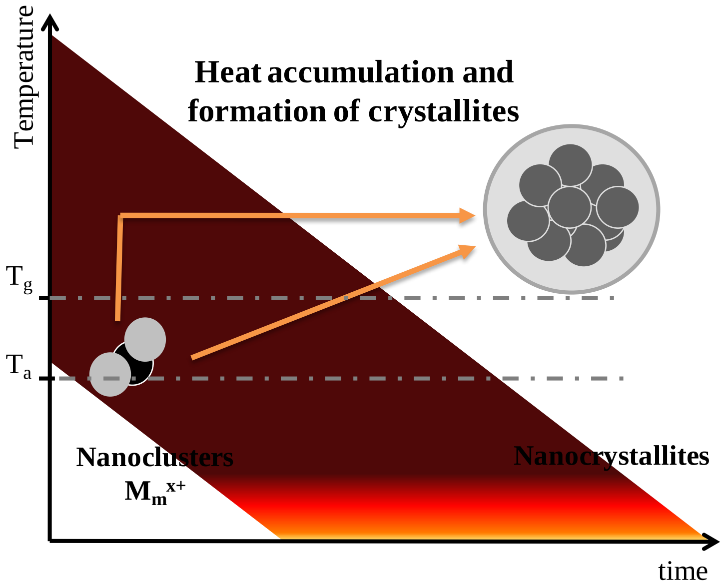
Nonlinear effect
= **multiphoton**

Localized absorption

Linear effect:
Absorption along the light propagation

Nonlinear Absorption





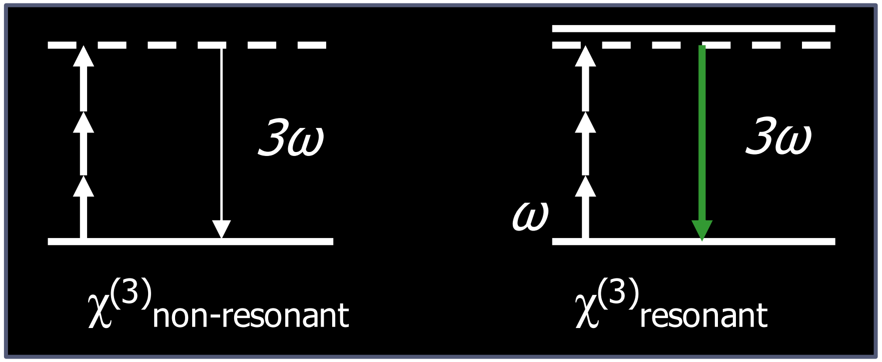
Possible to implement local $\chi^{(2)}$ and $\chi^{(3)}$

Local THG in silver containing glass

THG microscopy

3ω resonant species induced by femtosecond laser irradiation

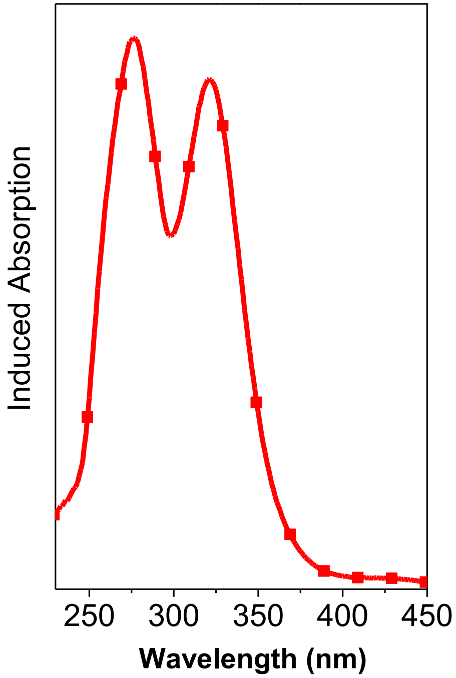
λ = 1030 nm



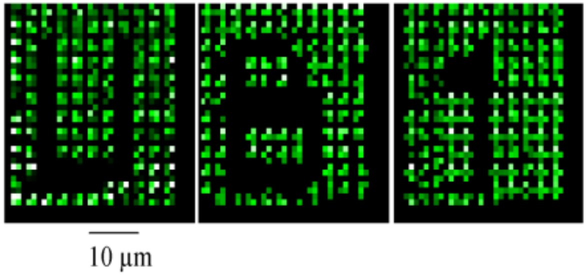
Local Formation of Clusters

Ag_m^{x+}

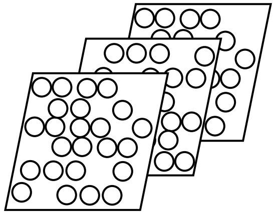
(formed of Ag^0 atoms and Ag^+ ions)



THG for data storage



THG imaging of the 3 layers



L. Canioni, Optics Letters, Vol. 33 Issue 4, pp.360-362 (2008)

Exaltation of the THG signal due to the resonance

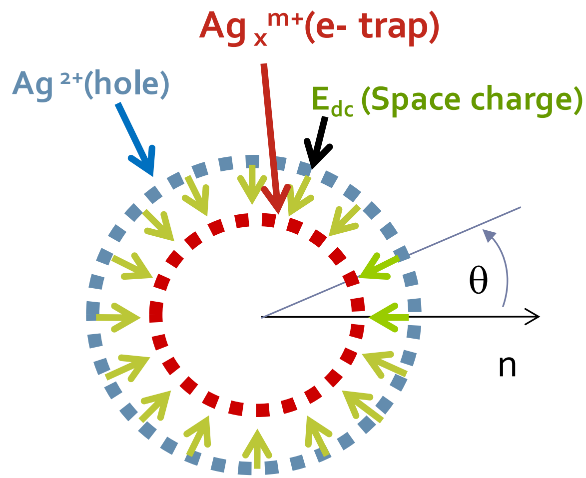
3D data recording and reading

Nonlinear optical process ⟺ Confocal per nature

Local SHG in silver containing glass

Laser:
Wavelength: 1.04 µm
Duration : 400 fs
Repetition rate: 10 Mhz

Silver containing phosphate glass

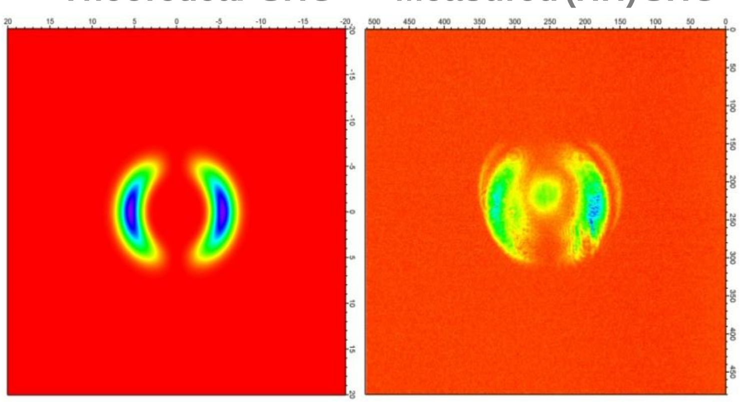


$$P^{NL}(2\omega) = \boxed{\chi^{(3)} E_{dc}} E(\omega)E(\omega)$$

$$\approx \chi^{(2)}$$

EFISH process

Theoretical SHG   Measured (HH) SHG



Charge separation process

And thanks to the glass composition

Stabilization of the **charge separation**

Summary

- Understanding of the relation **glass structure** / **NLO properties**
  - ✓ resonant (**Raman gain**, **Nonlinear absorption**)
  - ✓ non-resonant (**Kerr effect**, **THG**)
  - ✓ **Nonlinear absorption**
- Impact of **glassceramics** (Loss issues)
  - ✓ **Second order nonlinearity**
  - ✓ **Metal** or **semiconductor**
- Control of **local phase separation** or **local crystallization**
  - ✓ **Third order** and **Second order nonlinearity**

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CREOL, University of Central Florida, USA
*(*co-tutelle de thèse-Univ. Bordeaux1)*

IMI NFG

Agence Nationale de la Recherche ANR

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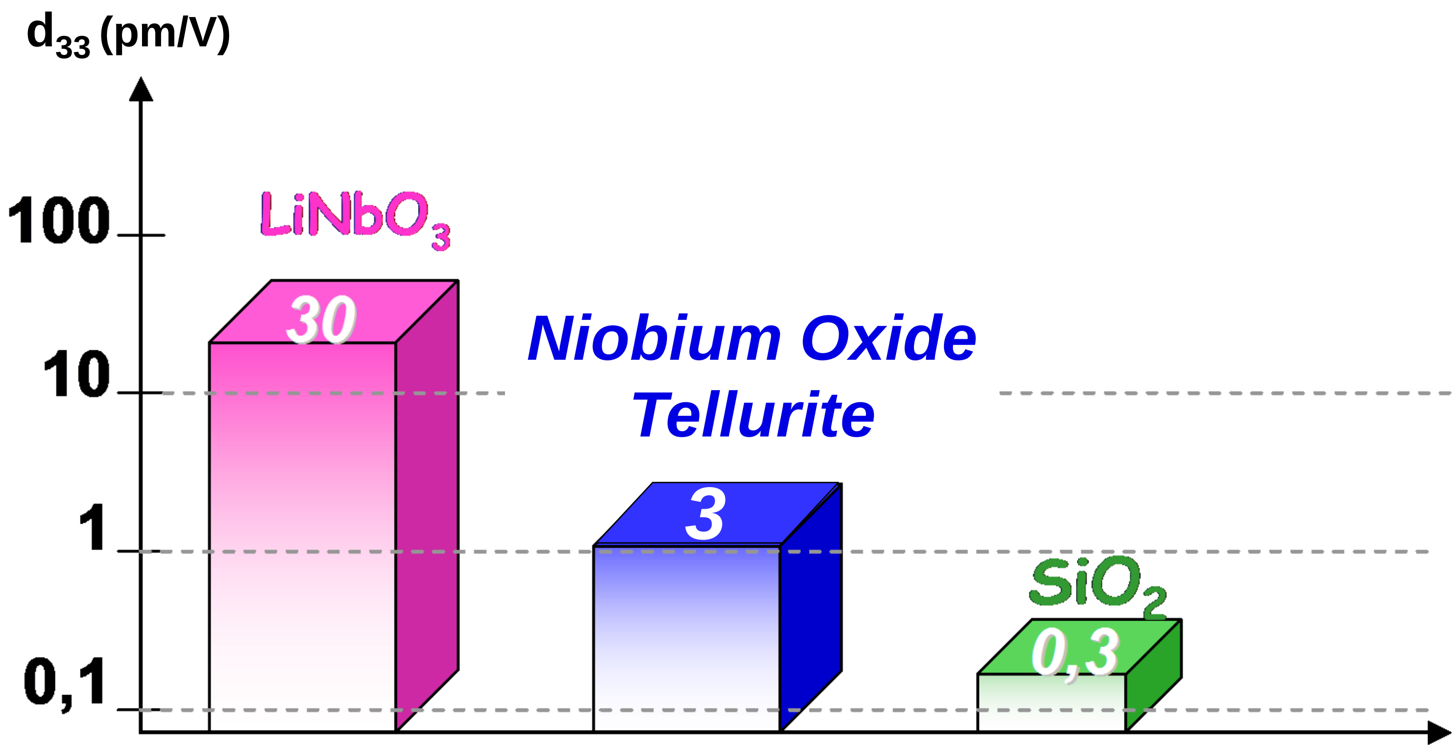
Aquitaine Lasers, Photonique & Applications

Table 1. Various highly nonlinear fibers and their SC generations in picosecond regime. 10 dB bandwidths were obtained from the SC spectra in the publications. When determining the 10 dB bandwidth, the strong pump peak was excluded.

Fiber	Pump wavelength (nm)	Nonlinear coefficient ($km^{-1}W^{-1}$)	Fiber length (m)	Pulse width (ps)	Peak power of pulse (W)	SC total bandwidth (nm)	10 dB bandwidth (nm)
Our tapered fiber	1064	800-5500	0.75	15	375	350-2000	780-1890
Silica tapered fiber [20]	1064	8-40	2	3-4	19608-32680	350-1750	380-1750
Silica microstructured fiber [21]	1064	-	2	21	24000	400-2250	420-1620
Silica microstructured fiber [22]	1064.5	8.5	100	600	4200	600-1750	650-1750
Silica microstructured fiber [5]	647.1	150	3	60	400	440-1130	480-940
Silica microstructured fiber [23]	1050	11	5	350	8893	400-1700	600-1700

M. Liao, Optics Express, 20, 26 (2012), p574

Material performance



SHG nanocrystallites

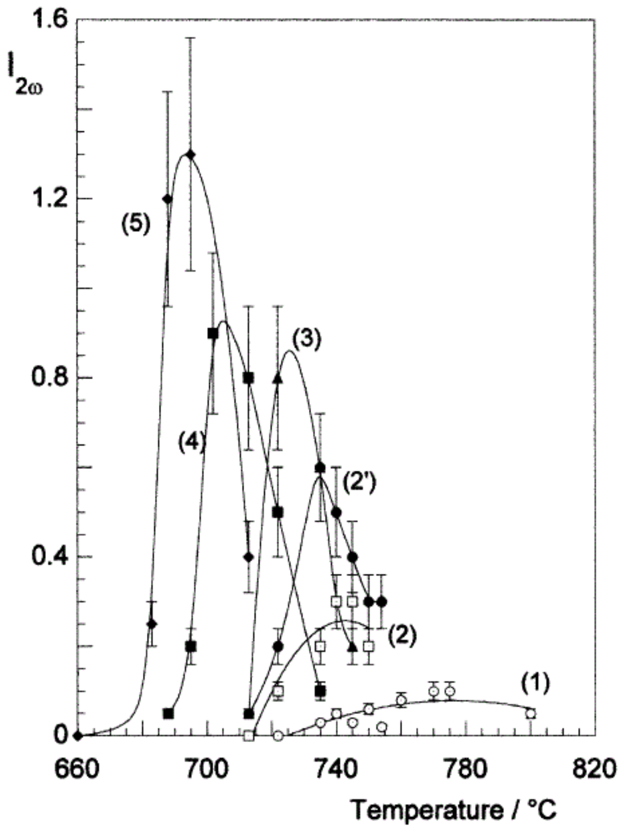
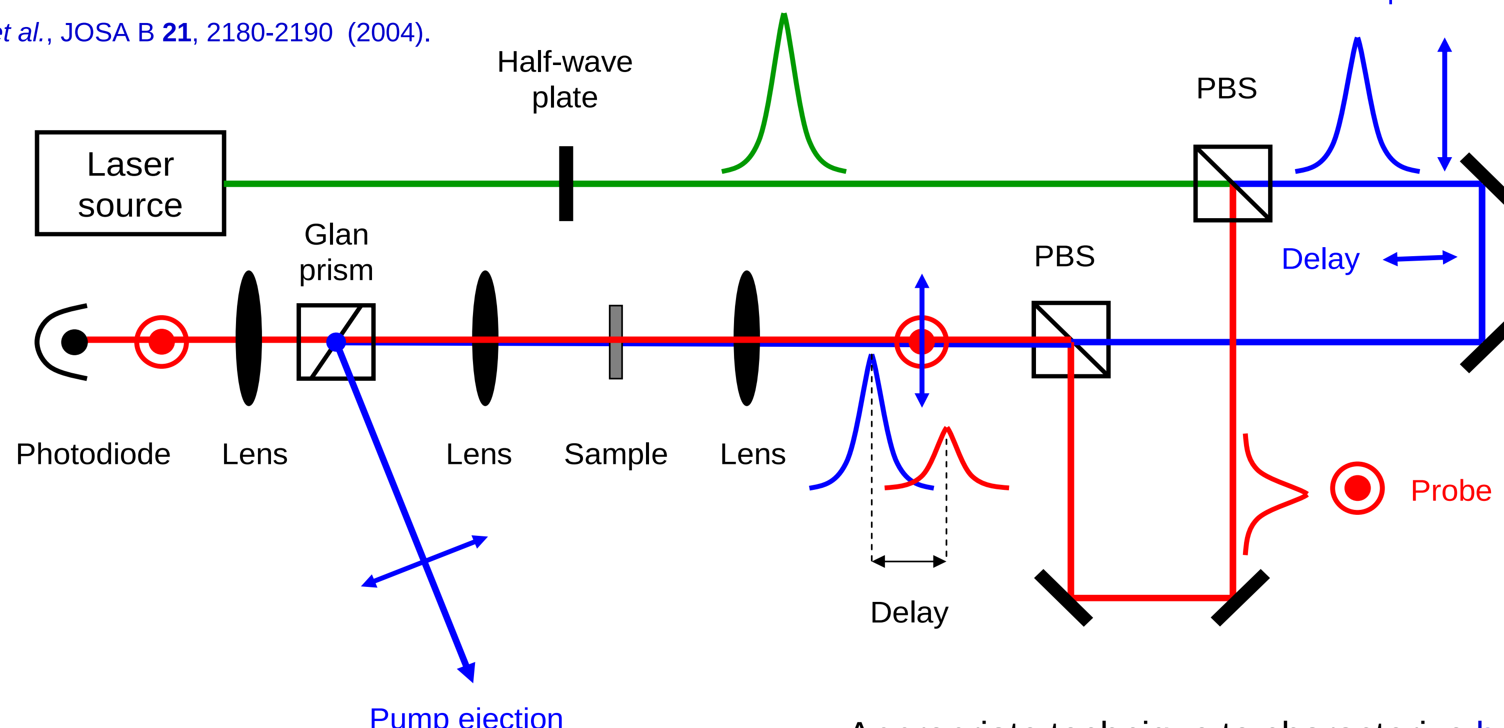


Fig. 4. SHG efficiency of KNS glasses vs heating temperature for 24 h and 48 h (no. 2′) treatments.

SHG efficiency can be connected to combination of third-order non-linearity with spatial modulation of linear polarizability

Pump-probe experimental setup

Santran *et al.*, JOSA B **21**, 2180-2190 (2004).



- Absolute measurements.
- Measurement uncertainty ~10%.

- Appropriate technique to characterize bulk materials.
- Difficult to implement on structured materials (maintain of the polarization under microscope, small nonlinear interaction length, etc…).