

Transformations et structurations induites par laser femtoseconde dans les verres.

B. Poumellec, M. Lancry

Groupe Matériaux Avancés pour la Photonique.
Equipe Structure Propriétés et Modélisation des
Matériaux

Institut de Chimie Moléculaire et des Matériaux d'Orsay
(ICMMO)

UMR 8182 CNRS et Université de Paris Sud, Orsay.
Dans l'Université Paris-Saclay.

Intro 1: Spécificités du laser femtoseconde

$f_s = 10^{-15}$ s, durée typique de l'impulsion: 100-300 fs

45 fs = 10 μm in silica glass

1 ps pour relaxer les excitations électroniques dans le réseau
i.e. l'impulsion se termine avant que le réseau soit chaud.

Longueur d'onde: 1000-400 nm

Focalisation du faisceau (typ. NA 0.5-0.8)

i.e. waist \cong 1.5 μm

Energie de l'impulsion: 0.01-1 μJ (10^{12-14} W/cm²)

L'énergie déposée dans le volume focal par
1 impulsion \cong énergie de formation du verre

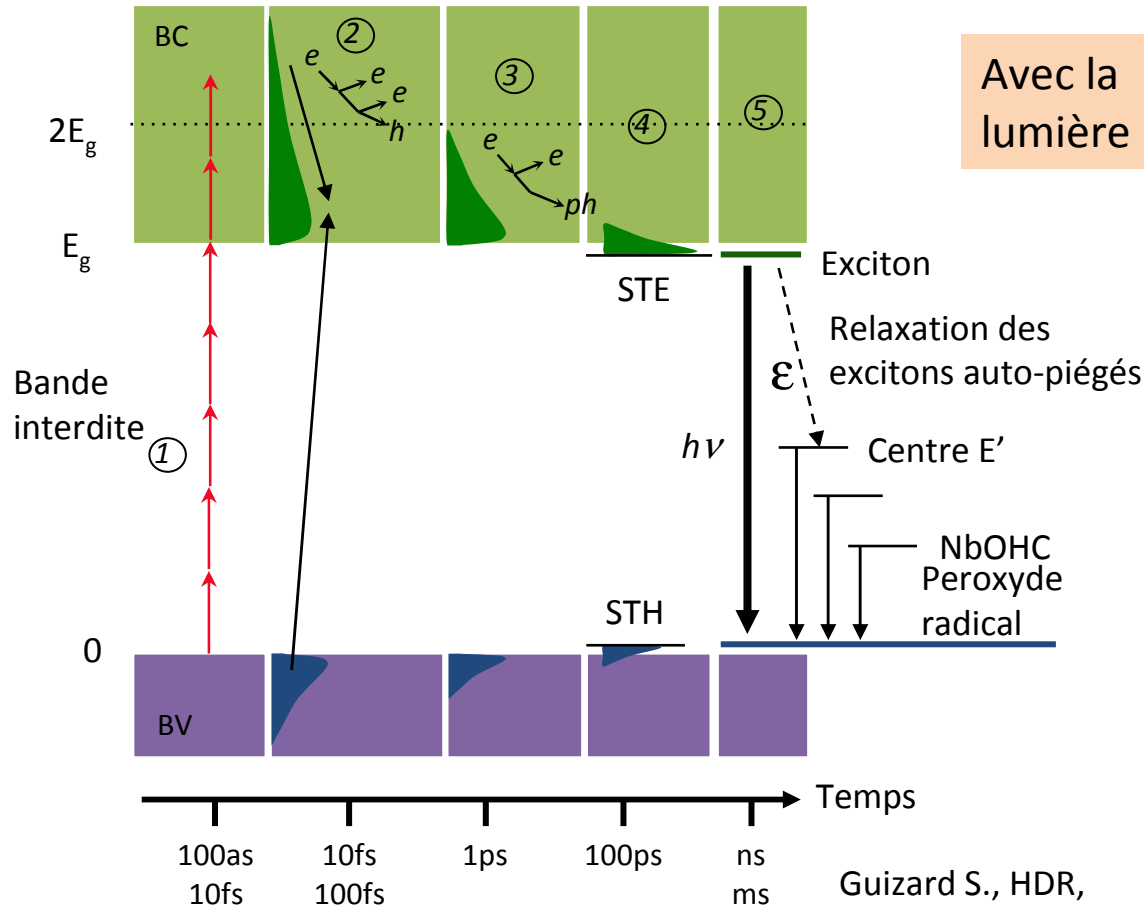
Fréquence de répétition des impulsions.: 1 kHz-1 MHz

Temps de diffusion de la chaleur = 1 μs
Pour <100 kHz, la chaleur est dissipée
avant l'arrivée de l'impulsion suivante.

Pour >100 kHz,
accumulation thermique.

I. Quelques éléments sur le mécanisme d'interaction de la lumière laser femtoseconde avec les verres

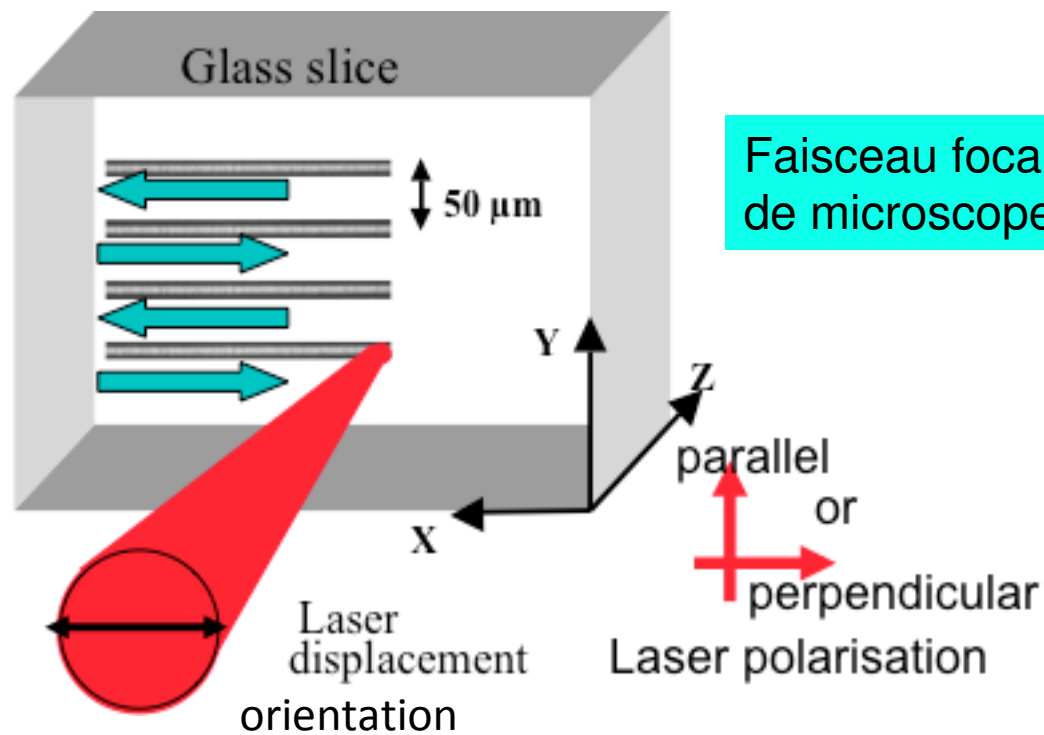
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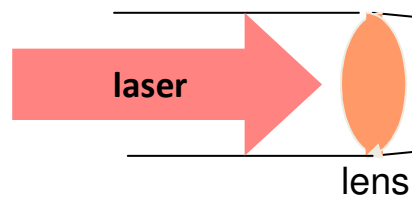
Guizard S., HDR,
CEA Saclay

- 1) Production d'un plasma d'électrons quasi-libres à travers l'ionisation multiphotonique.
- 2) Processus de collisions inélastiques $e-e$ ou ionisation par impact peuvent se produire (avalanche).
- 3) Relaxation électronique : thermalisation via collisions avec le réseau (chauffage du réseau)
- 4) Piégeage et localisation des charges : Production de STE (Self-Trapped Excitons)
- 5) Recombinaison des excitons : émission de photons ou transfert de l'énergie au réseau et production de défauts, modifications structurales.

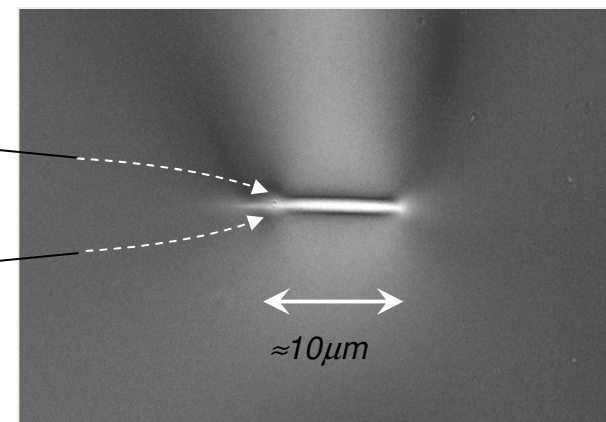
I. Configuration d'irradiation



Faisceau focalisé sous la surface avec un objectif de microscope longue focale (NA 0.5 - 0.8).

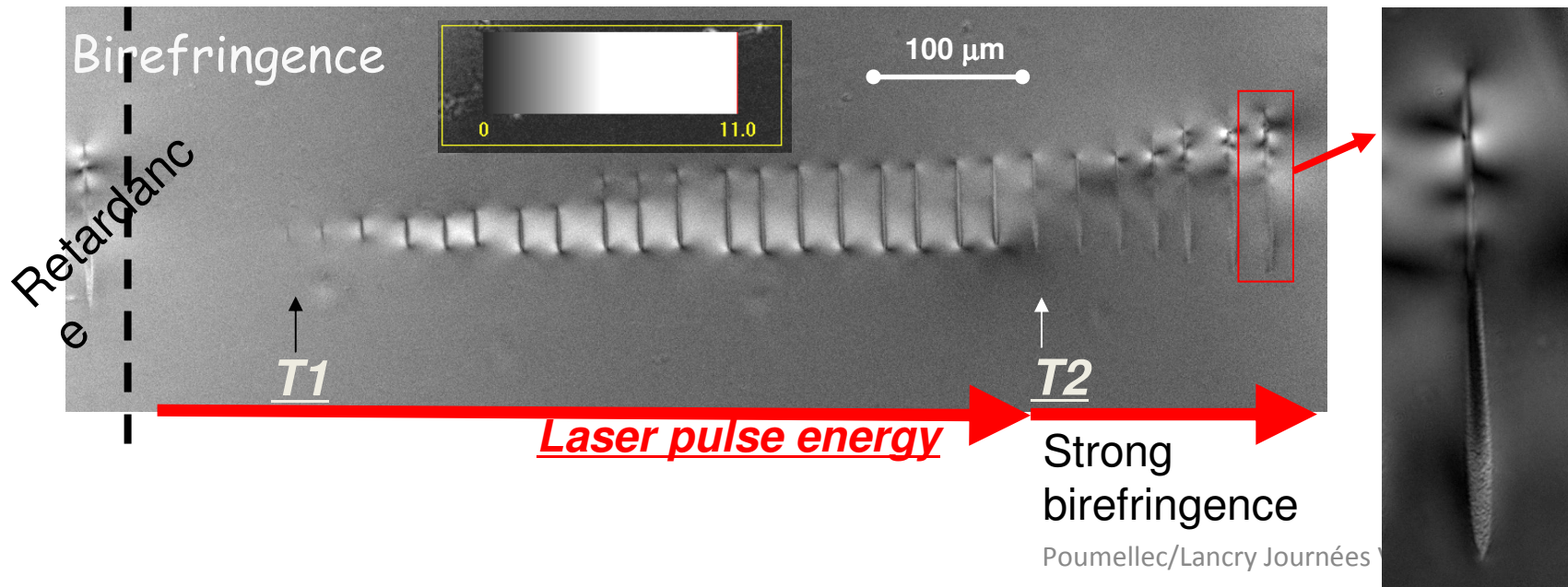
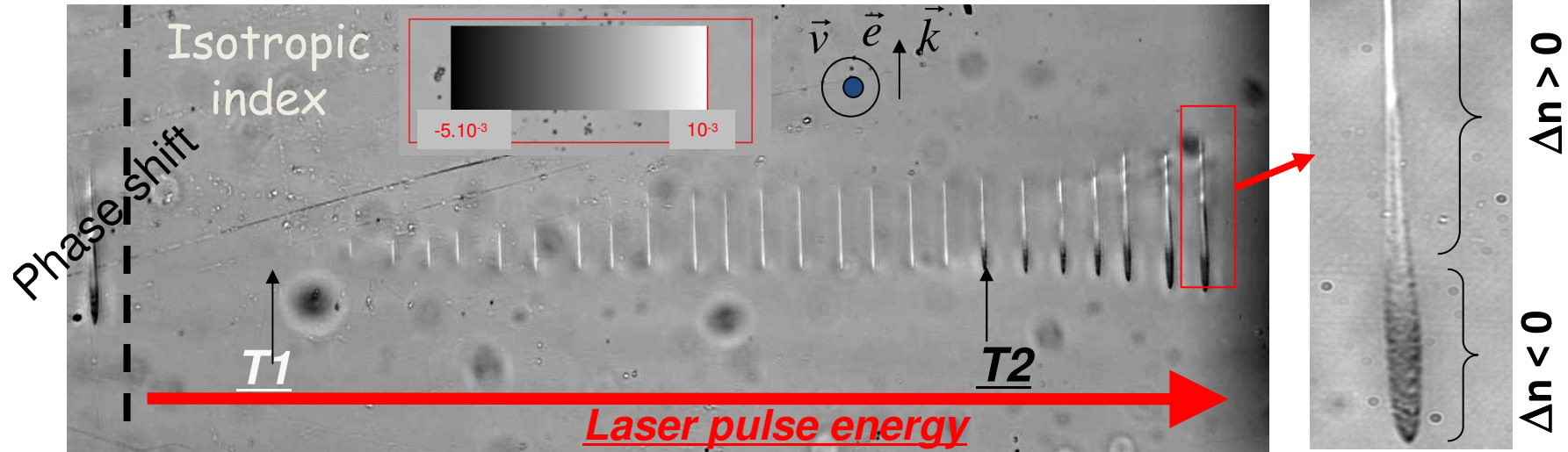


800 nm, 160 fs, 0.1 $\mu\text{J}/\text{pulse}$ and 250 kHz. NA 0.50.



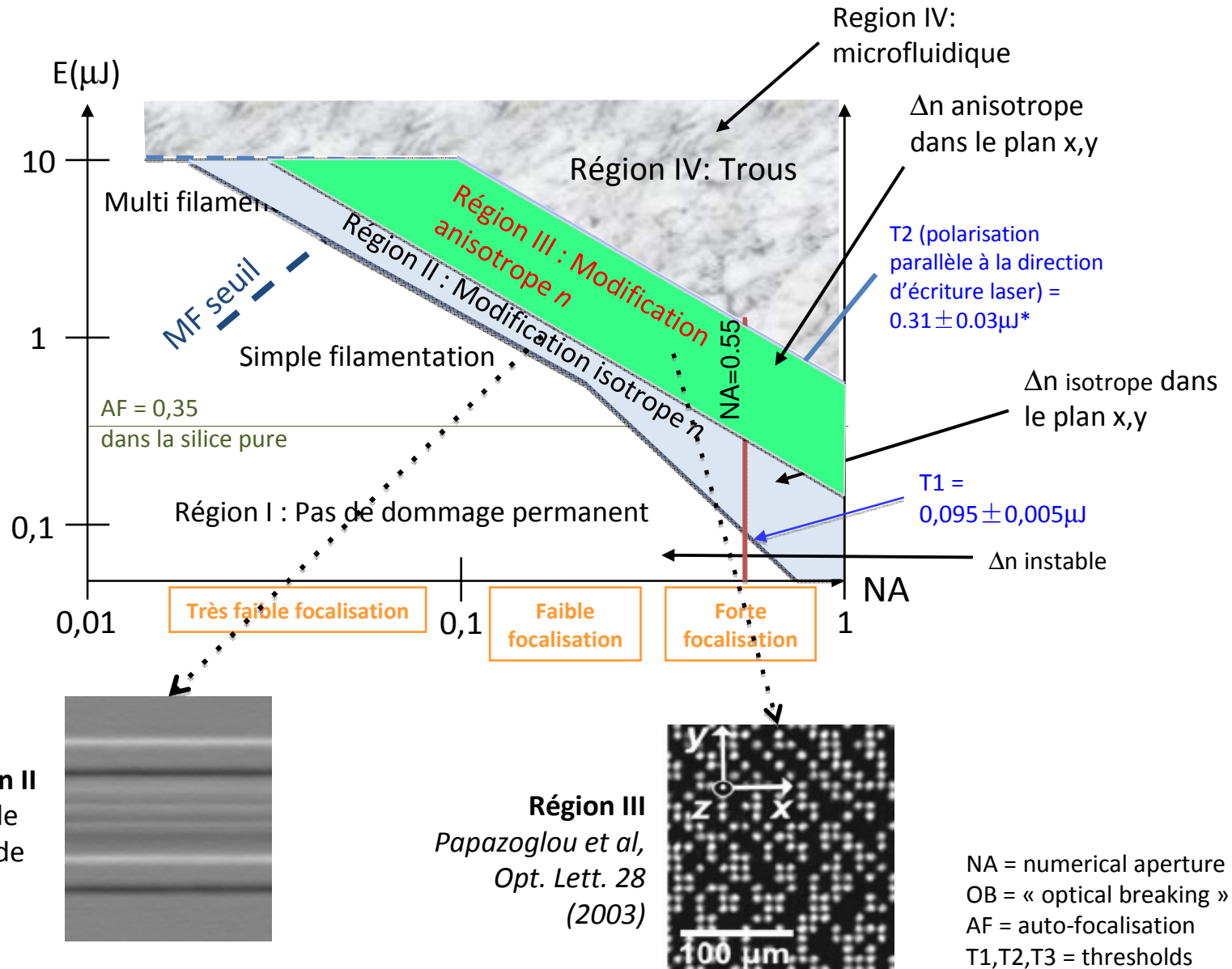
I. Variation de la trace avec l'énergie de l'impulsion à forte focalisation.

SiO₂



I. Domaines de modifications permanentes de la silice.

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B. Poumellec et al. Optical Material Express 2011, Vol. 1, Issue 4, pp. 766-782

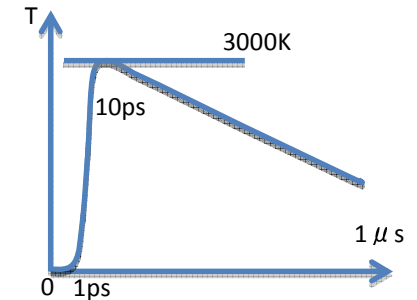
SiO_2 , 800nm ; 160fs ; 100kHz ; 100 $\mu\text{m/s}$; polarisation parallèle

II. Mécanisme du premier seuil de transformation dans les verres

L'impulsion arrive, $t=0$, elle dure quelques 100fs

L'énergie de l'impulsion est absorbée (partiellement), car limitée par un effet miroir dû à la formation du plasma d'électrons: quelques fs.

Le transfert de chaleur vers le réseau débute après 1 ps. La température monte à plusieurs 1000K après quelques 10ps et retrouve la température ambiante après diffusion thermique en une fraction de microseconde.



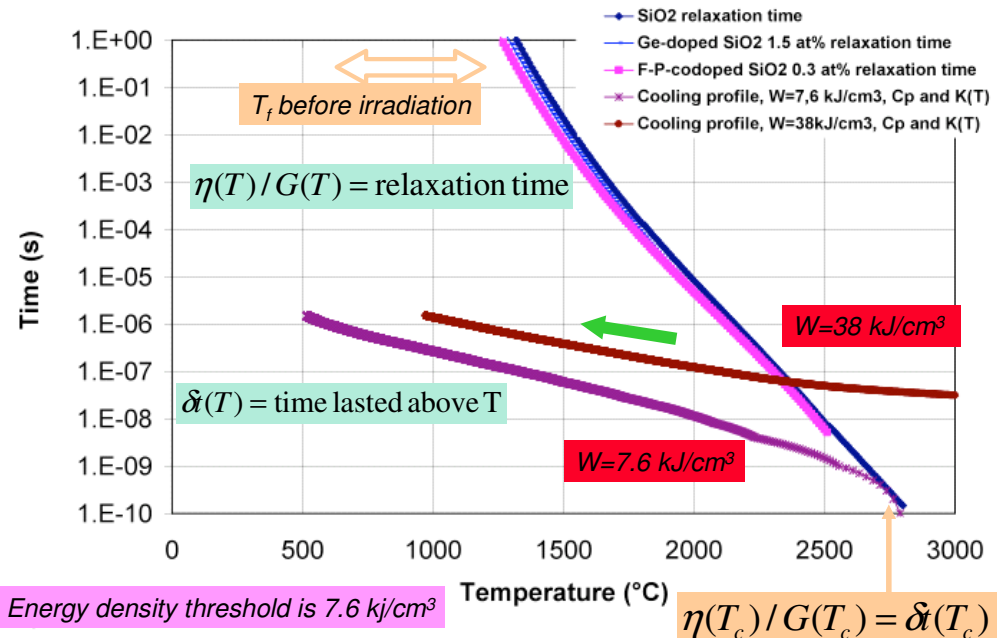
Mais il faut du temps pour effectuer une transformation dans le verre, combien?

Celui-ci est donné par le temps de relaxation η / G qui dépend de la température.

La température fictive du verre croît, par exemple pour la silice, on atteint 2800°C

Pour la silice, la densité croît \rightarrow L'indice de réfraction croît

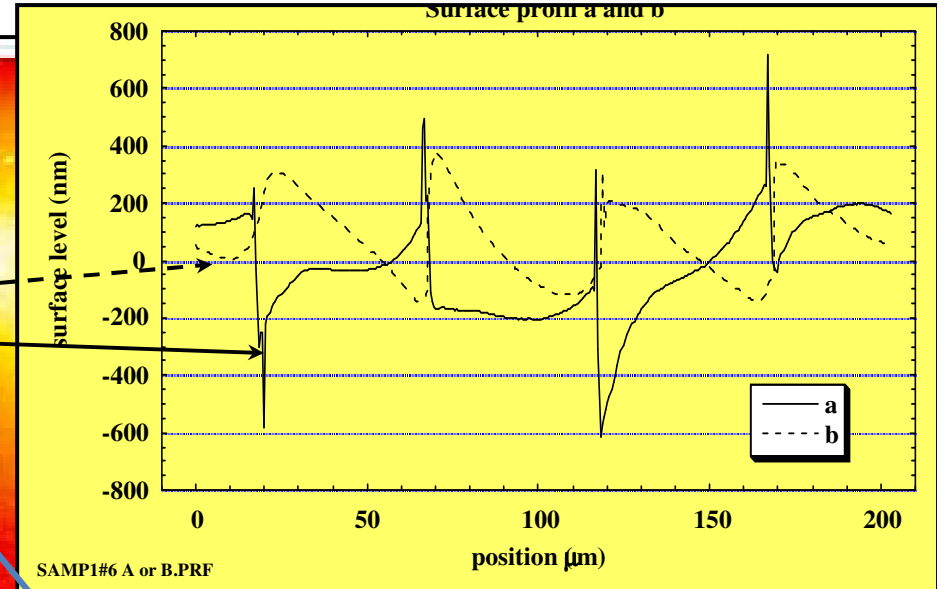
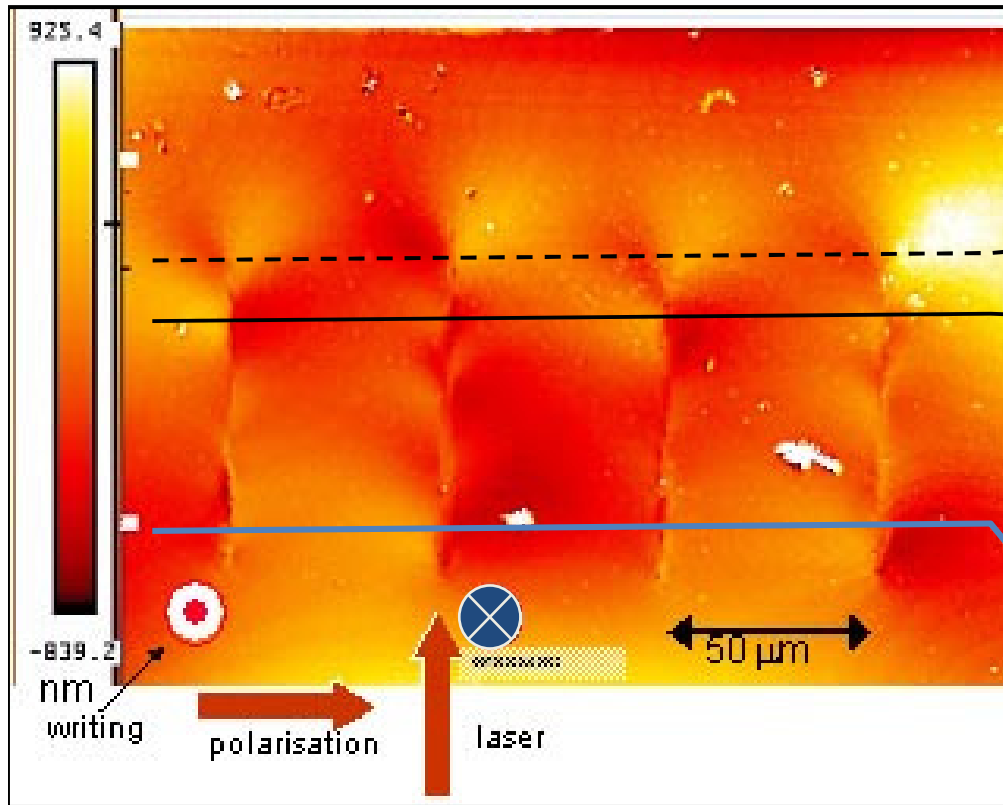
Dans la plupart des verres c'est l'inverse.



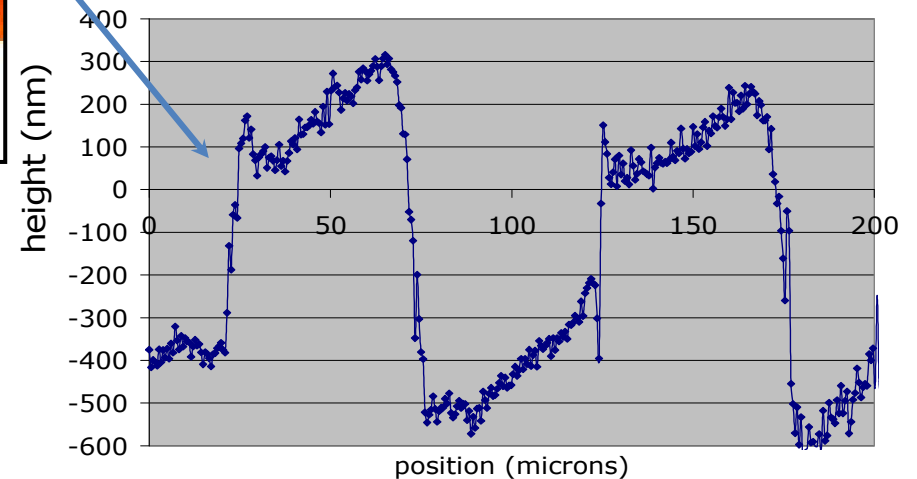
III: E>T2 (forte birefringence)

Ecriture orientationnelle asymétrique

Pure silica



Topography profile across laser tracks



Poumellec et al.
Optics Express
(1070) 2003

Trace dépend de
l'orientation de
l'écriture.

Overlap = 0.998

800nm, 160fs, 1.1 μJ/pulse,
200 kHz, NA=0.5, 20 μm/s

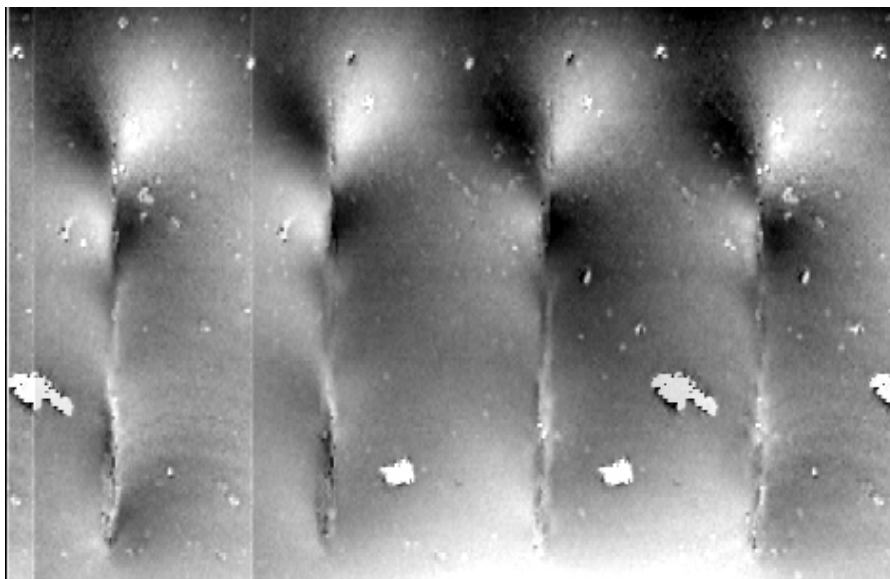
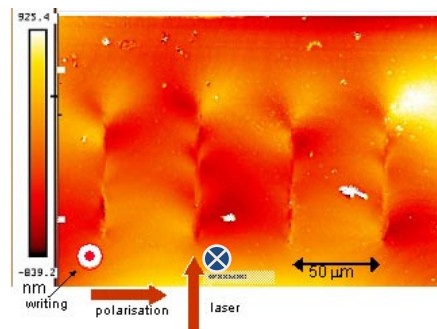
III: E>T2 (écriture orientationnelle asymétrique)

Décomposition des effets

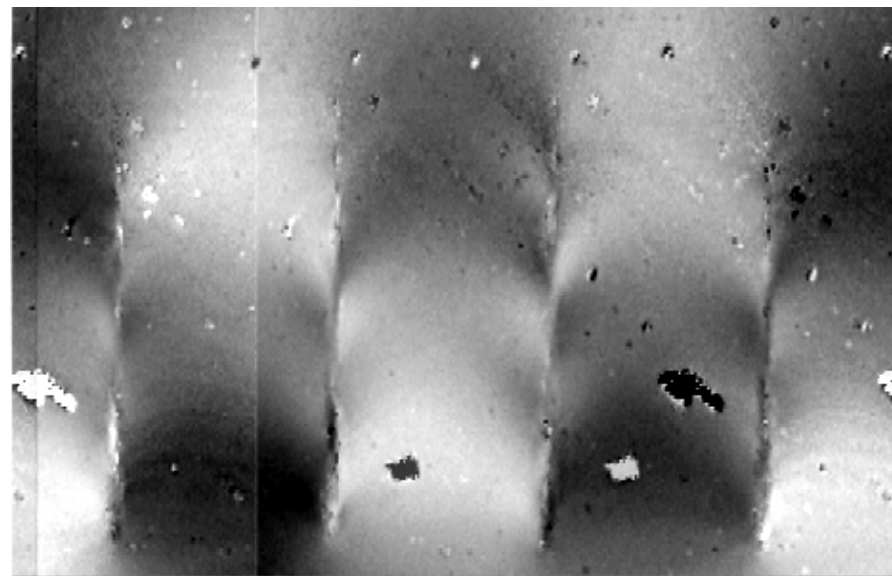
$$\text{Im}_{up} = S + AS ; \quad \text{Im}_{down} = S - AS$$

$$S = \frac{\text{Im}_{up} + \text{Im}_{down}}{2} ; \quad AS = \frac{\text{Im}_{up} - \text{Im}_{down}}{2}$$

800nm, 160fs, 1.1
 $\mu\text{J}/\text{pulse}$, 200 kHz,
NA=0.5, 20 $\mu\text{m}/\text{s}$



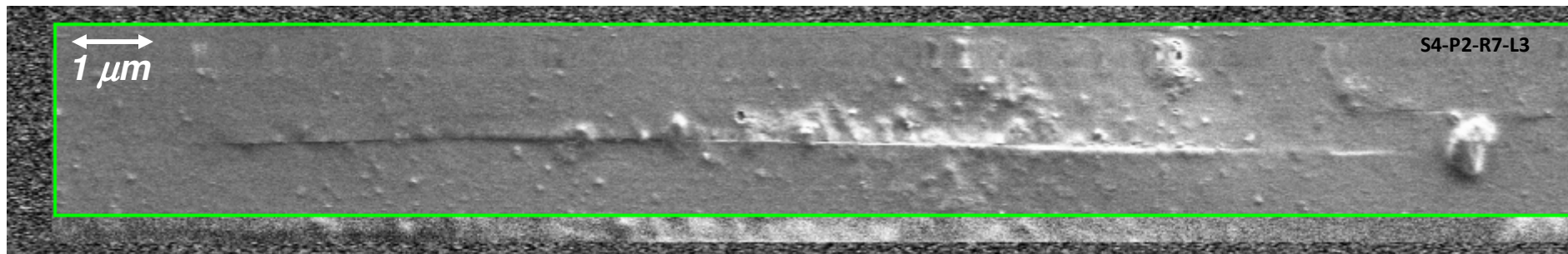
Independent de l'orientation d'écriture
Chirale d'un type



Dépendent de l'orientation d'écriture
Réversible

III. La structure interne de la trace laser est complètement différente quand on passe le deuxième seuil d'énergie où la biréfringence apparaît.

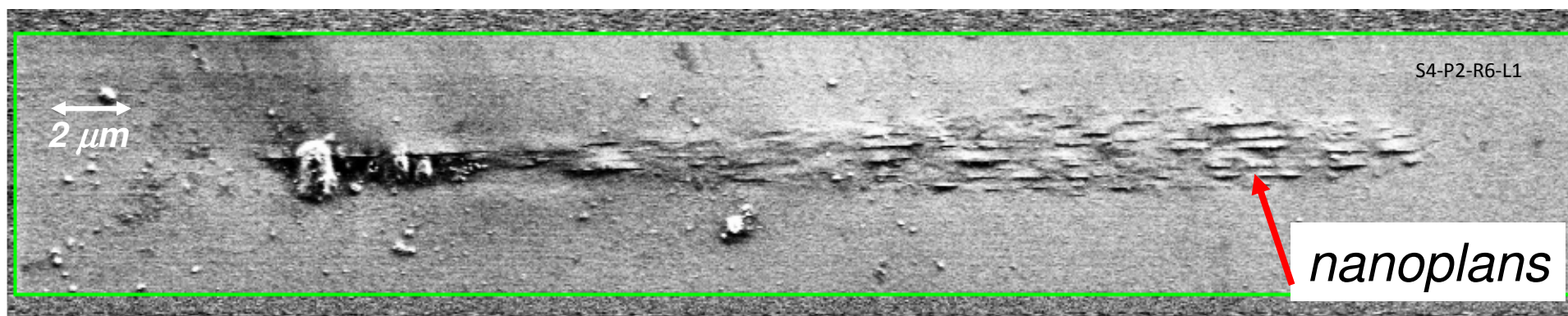
SEM observation for $E(0.23\mu\text{J/p})$ below T2



↑ Laser
polarisation

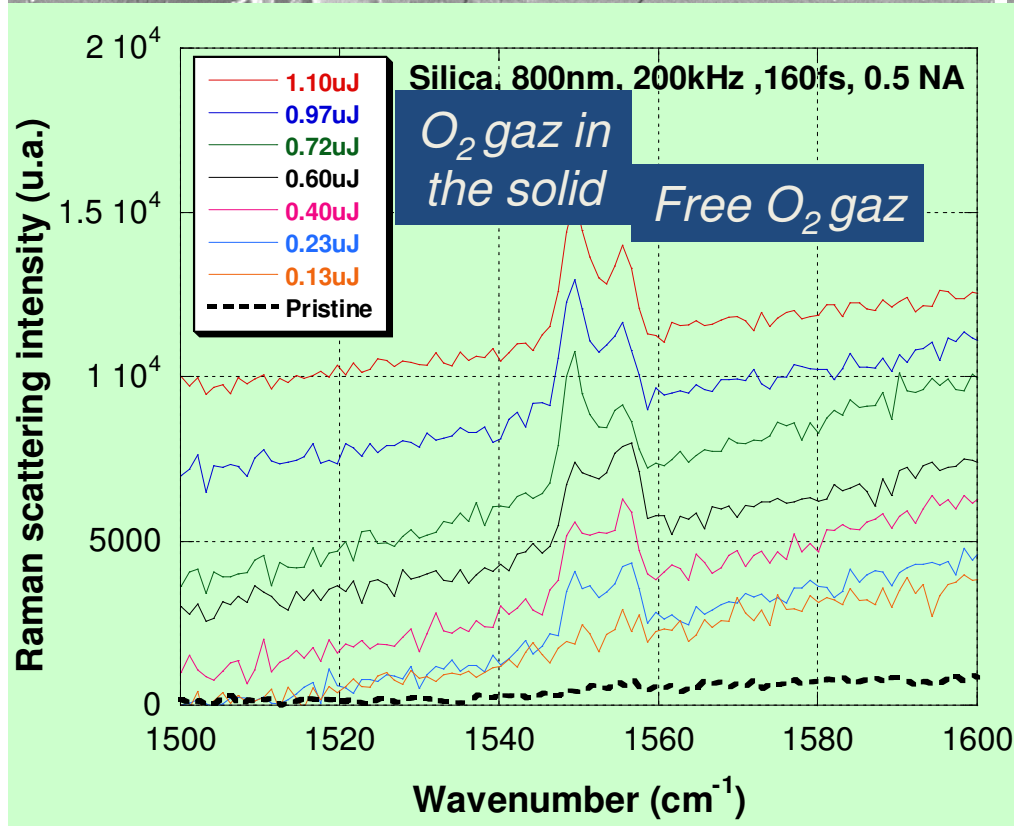
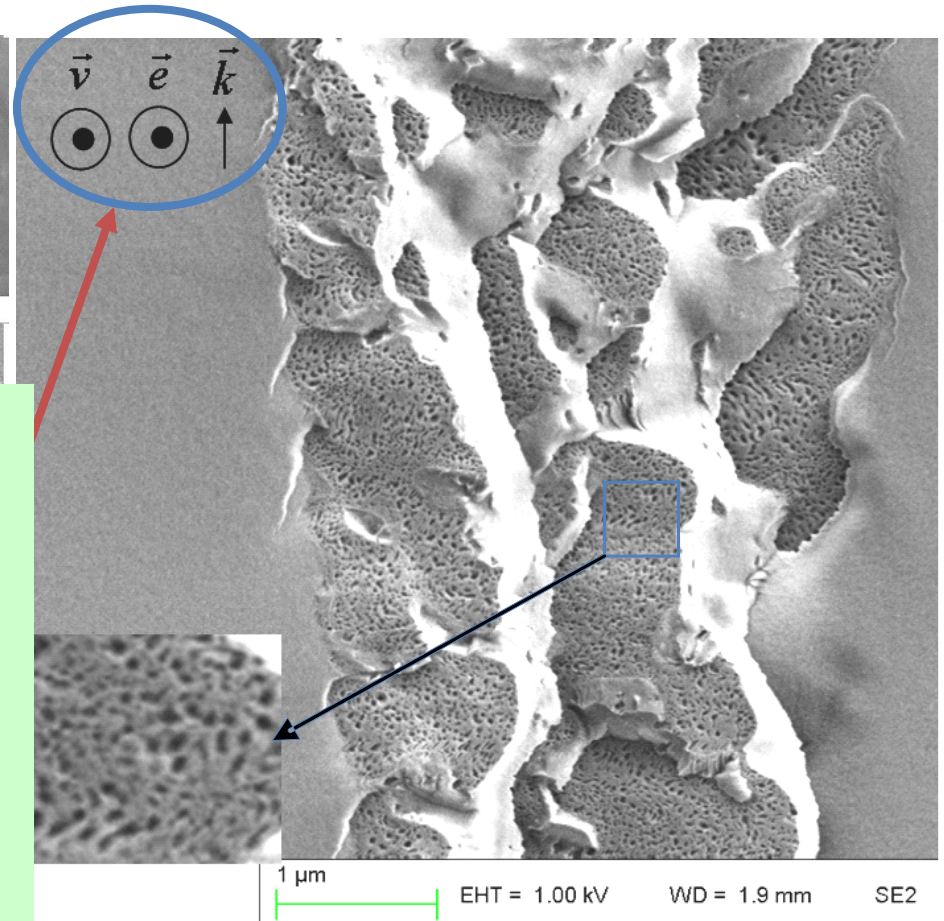
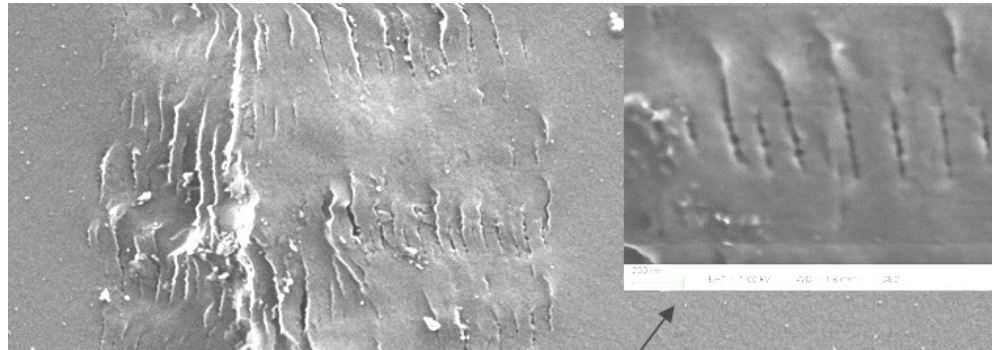
← Laser propagation

SEM observation for $E(0.40\mu\text{J/p})$ above T2



Nanostructures orientables

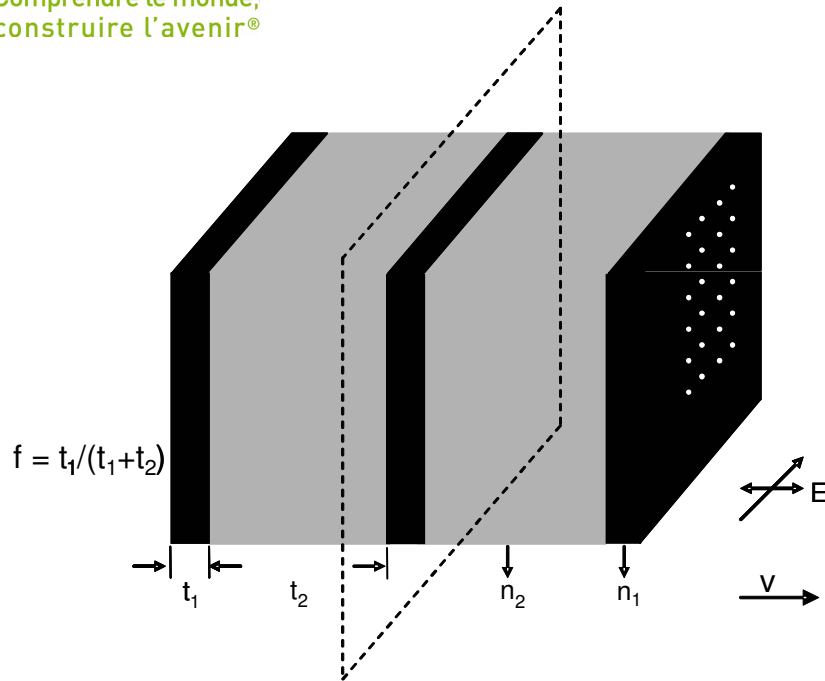
III. Que sont ces nanoplans? SEM au cœur de la trace laser.



SiO₂ décomposition en moins de 1 μs, mais il faut 100 impulsions pour les voir

III: Les nanoplans produisent une biréfringence de forme

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material between the nanoplanes unchanged i.e. pure silica $n_2=1.46$

Bricchi, E., B. G. Klappauf, et al. (2004). "Form birefringence and negative index change created by femtosecond direct writing in transparent materials." *Optics Letters* **29(1): 119-121.**

Desmarchelier, R., Poumellec B. et al.. (2015). « In the heart of femtosecond laser induced nanogratings from porous nanoplanes to form birefringence." *WJNSE on line* DOI 10.4236.

Nanogratings filling factor (deduced from SEM observations): $f = t_1/(t_1+t_2)$

$$\Delta n_e = \left[\sqrt{\frac{n_1^2 n_2^2}{f n_2^2 + (1-f)n_1^2}} - n_{bg} \right], \quad // \text{ writing polarization}$$

$$\Delta n_o = \left[\sqrt{f n_1^2 + (1-f)n_2^2} - n_{bg} \right]$$

material in the nanoplanes decreases $n_1=1.25$

The index between bubbles has decreased also (1.40)
⇒ Frenkel defects

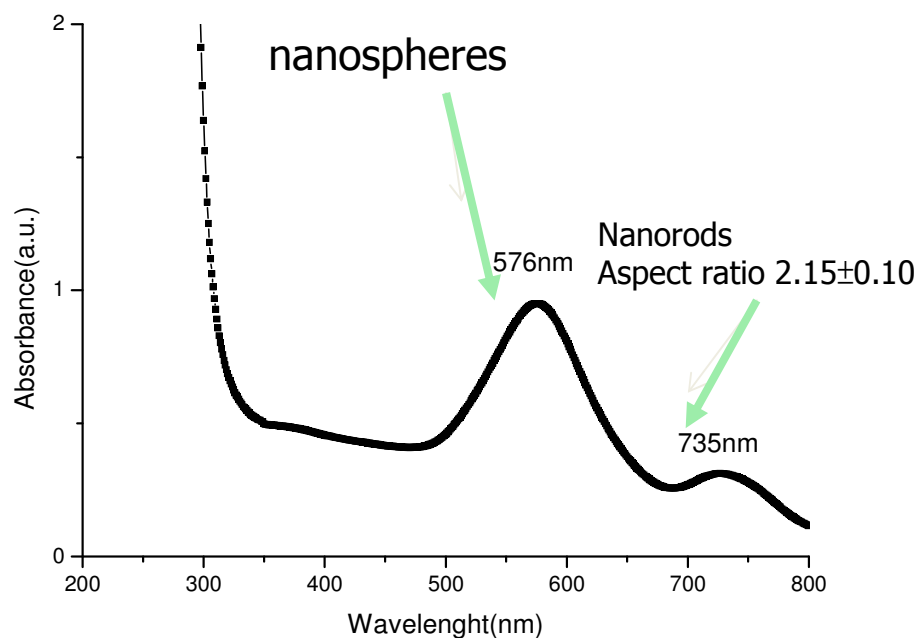
Large interest: birefringence is large 10^{-2} , orientable, local and extremely stable

Many possibilities for elaborating lenses with unpreceding thermal resistance, but only in pure silica at this date.

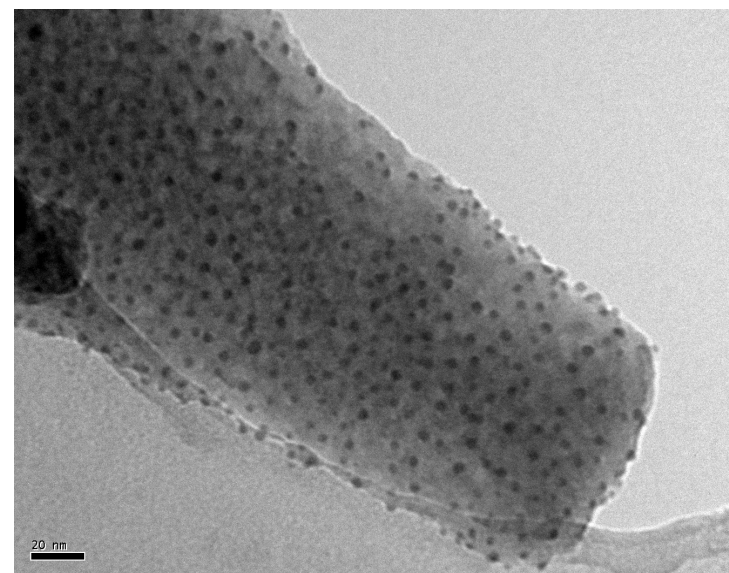
IV. Propriété oxydo-réductrice de l'irradiation

Nanoparticles thermal precipitation in $\text{Na}_2\text{O-CaO-PbO-SiO}_2$:0.01 mol% Au glass

melting at 1550°C during 4 hrs, heat treatment at 560°C for 4 hours



The absorption spectrum of the glass



spherical nanoparticles in TEM
observation

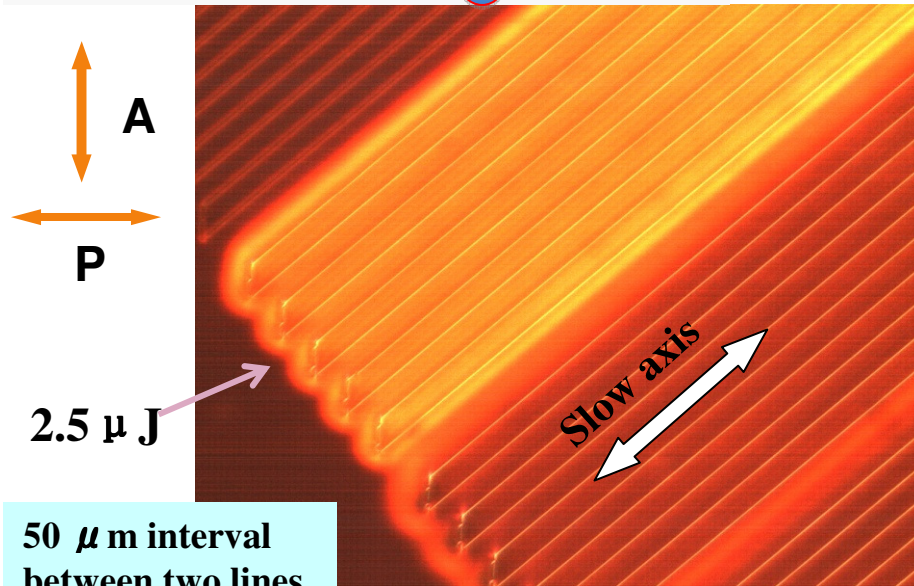
Changement de forme des particules par irradiation

C. Fan B. Poumellec, et al. . J Physical Chemistry C. (2012), 116, 2647-2655

IV. Birefringence dependence on pulse energy

0.3, 2.5, 5.87, 8.83, 10 μ J

620 nm, 120 fs, 50 μ m/s, 1 kHz, NA=0.6
focal depth = 300 μ m. \otimes k



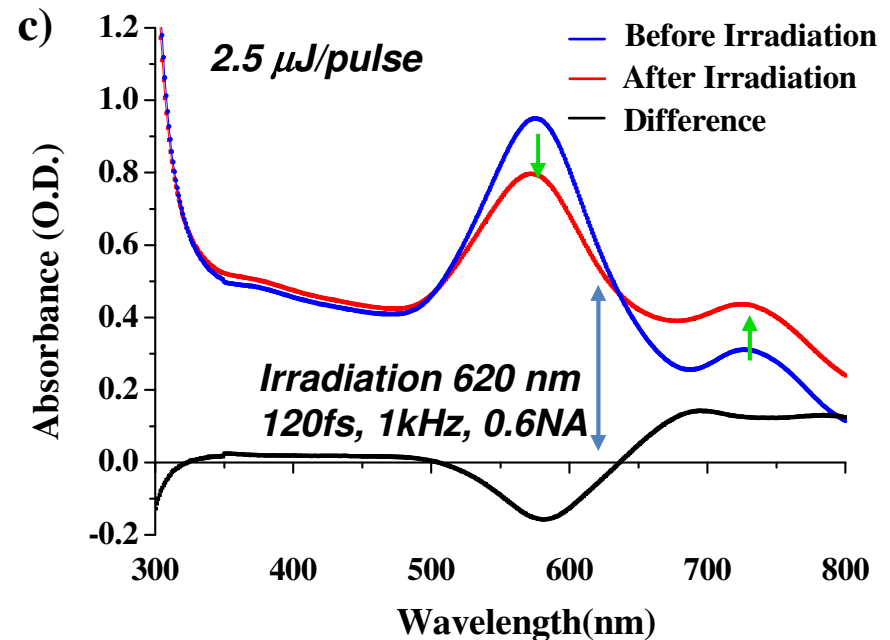
- 1) The average red color is arising from Surface Plasma Resonance absorption at 576 nm.
- 2) For energy different from 2.5 μ J/pulse, the line appearance results from birefringence only (almost)
- 3) For 2.5 μ J/pulse, the yellow color is from dichroism.

Moreover, the red halo bordering some lines indicates a birefringence induced out of the irradiated volume.

N.B.: Transmitted light between crossed polarizers resulting from sample birefringence and dichroism.

a) Birefringence is weakly dependent on $\lambda \Rightarrow$ white light

b) but not absorption \Rightarrow colored light

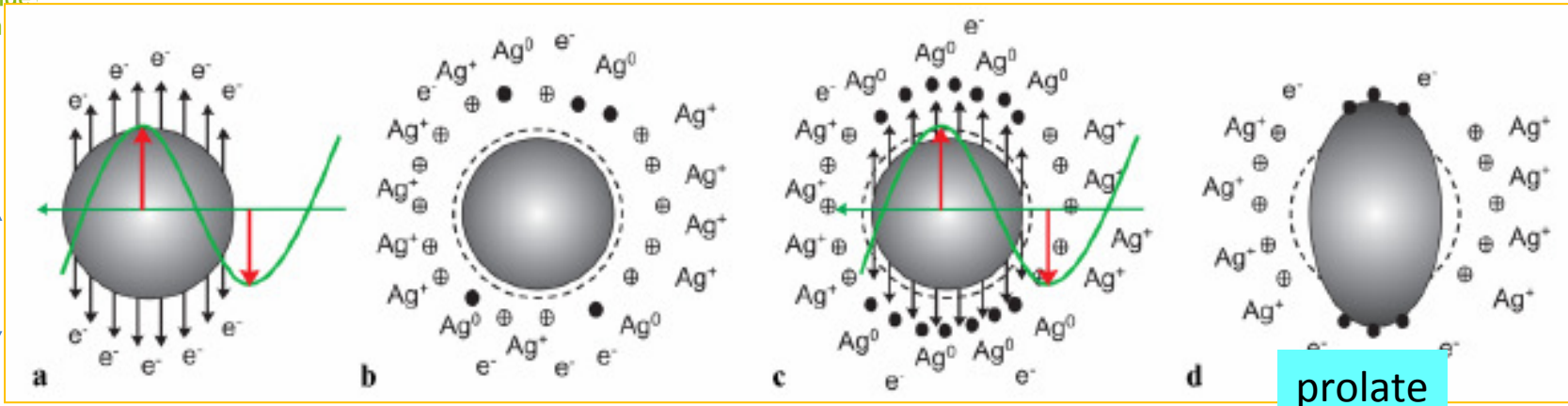


Spherical particles are transformed into prolate ones (elongated) in the direction of the laser polarization (electric field).

IV. Precipitation, dissolving and shaping of metal nanoparticles in glasses

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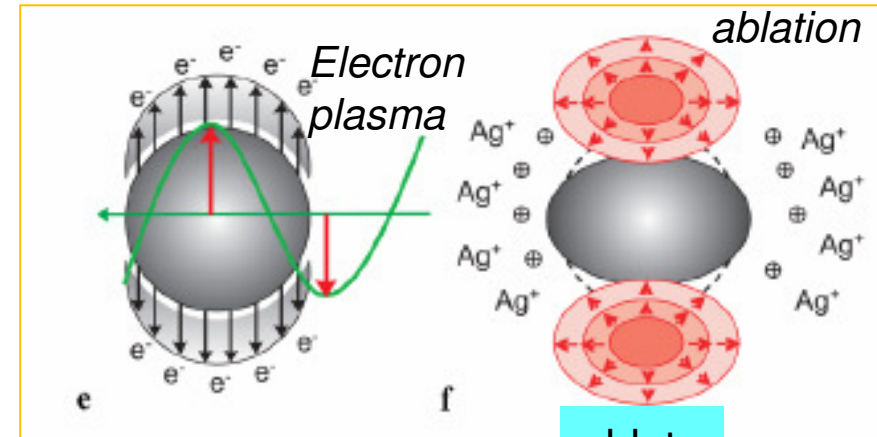
Laser
polarization
direction



prolate

Modification in low intensity mode

- A: electron emission from the nanoparticle into the dielectric matrix parallelly to the laser polarization
- B: Ag^+ ions in the dielectric matrix trap the electrons forming Ag^0
- C: the Ag^0 concentration is amplified by the next pulse
- D: the spherical nanoparticle grows in the direction of the polarization becoming elongated (prolate)
- E: the high intensity gives rise to high plasma density at the nanoparticle-matrix interface
- F: ablation of the particle becoming oblate



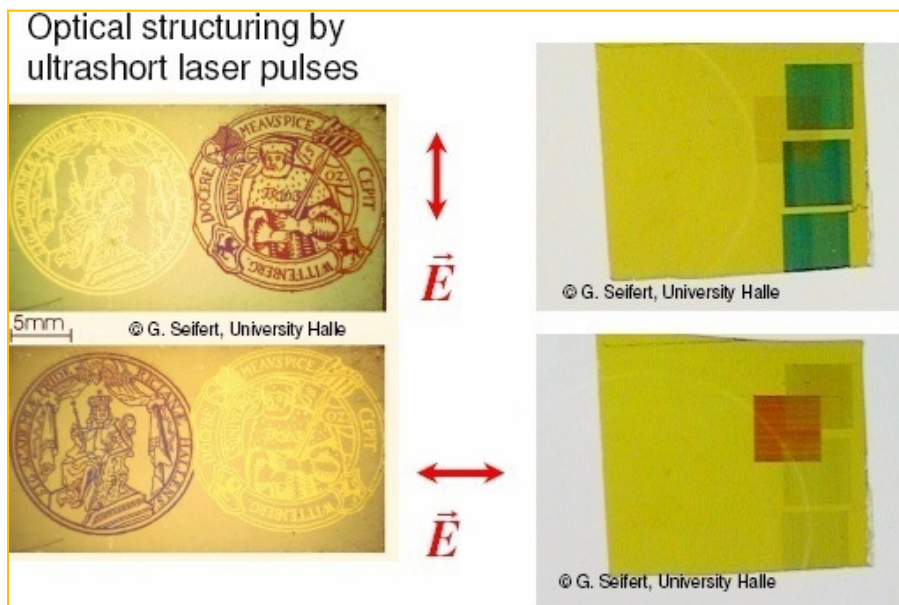
oblate

Modification in high intensity mode

Changement de couleur Podlipensky et al.

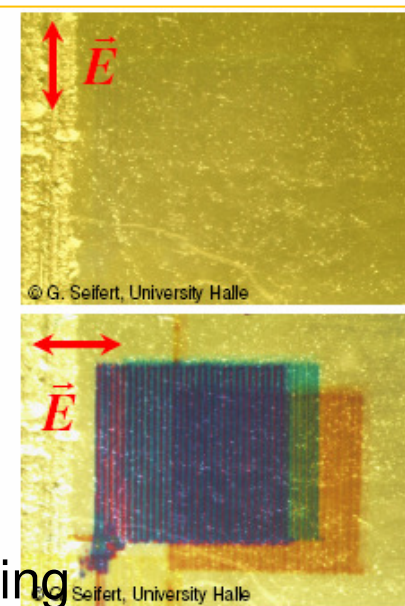
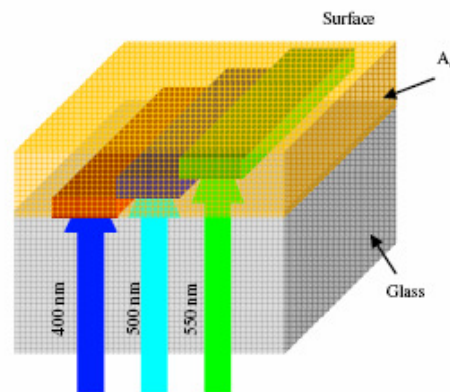
IV: Applications of dichroism induced by the metallic nanoparticle reshaping.

Seifert et al. 2008
Univ. Halle, G



Polarisation dependent reading

3D structuring by fs laser pulses



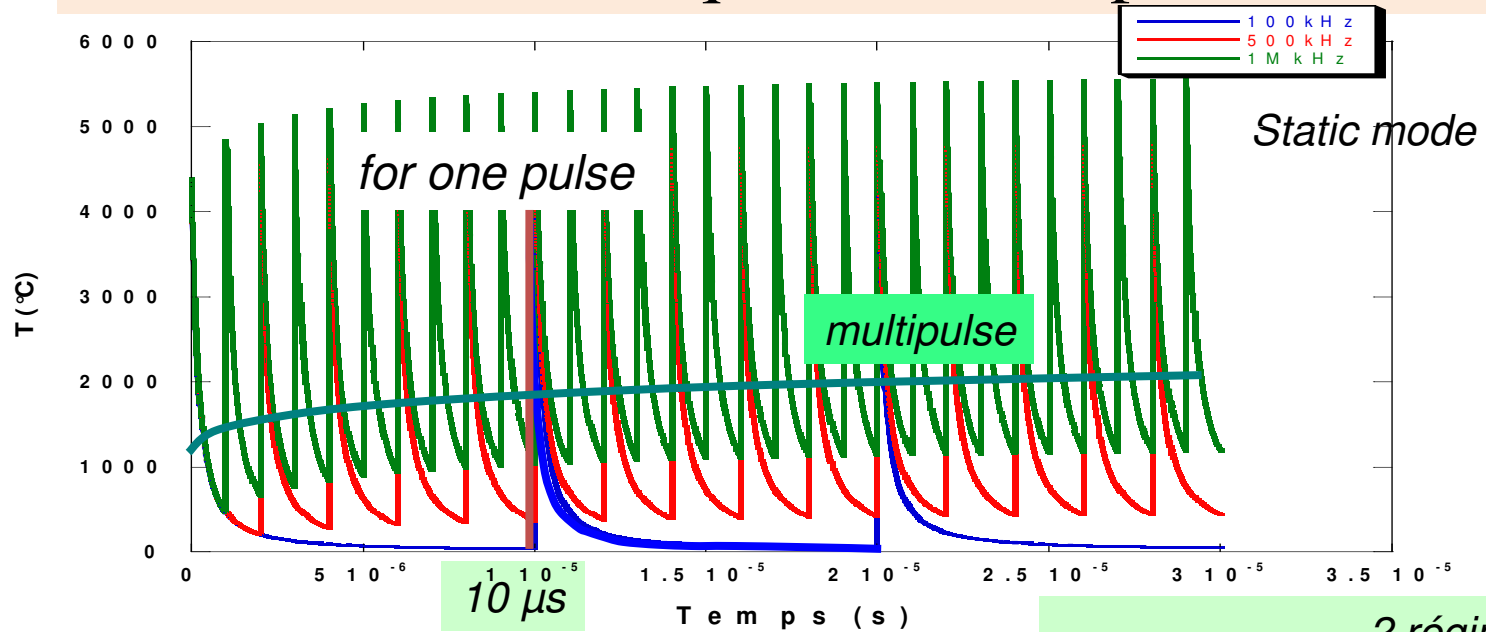
Wavelength dependent reading

The particle size changing

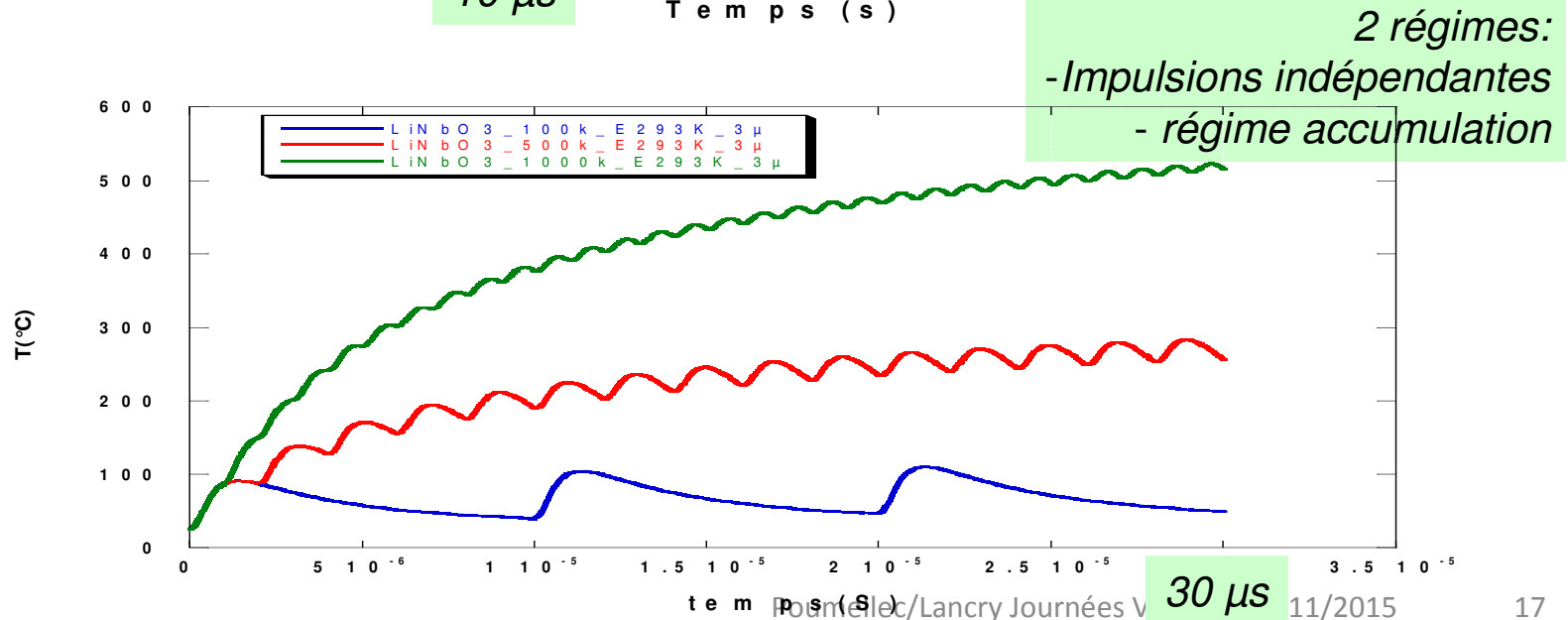
5D coding

V. Les variations de température du verre en fonction de la fréquence des impulsions

Variation temporelle de la température au centre de la trace



Variation temporelle de la température à 3 μm du centre de la trace



0.25 μJ/pulse

V. Crystallization under heating accumulation regime

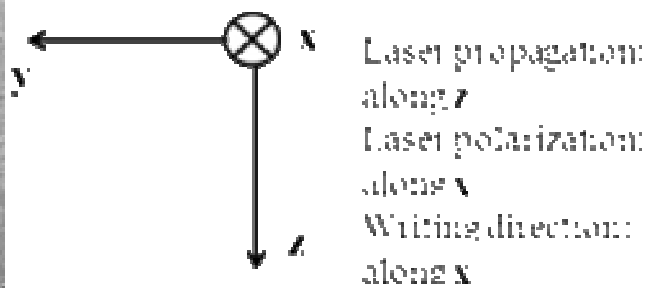
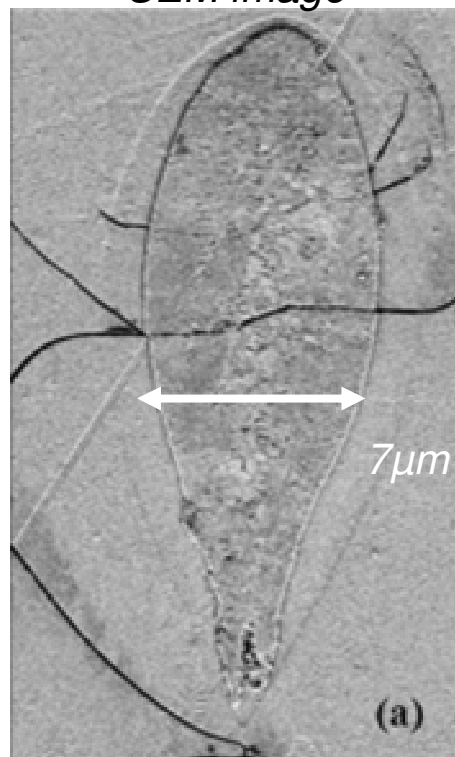
Pulse period < thermal diffusion time $\cong 1\mu\text{s}$

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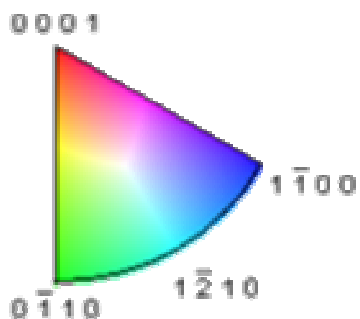
Glass : $33\text{Li}_2\text{O}-33\text{Nb}_2\text{O}_5-34\text{SiO}_2$
 LiNbO_3 strong non-linear crystal

Cross section of laser trace

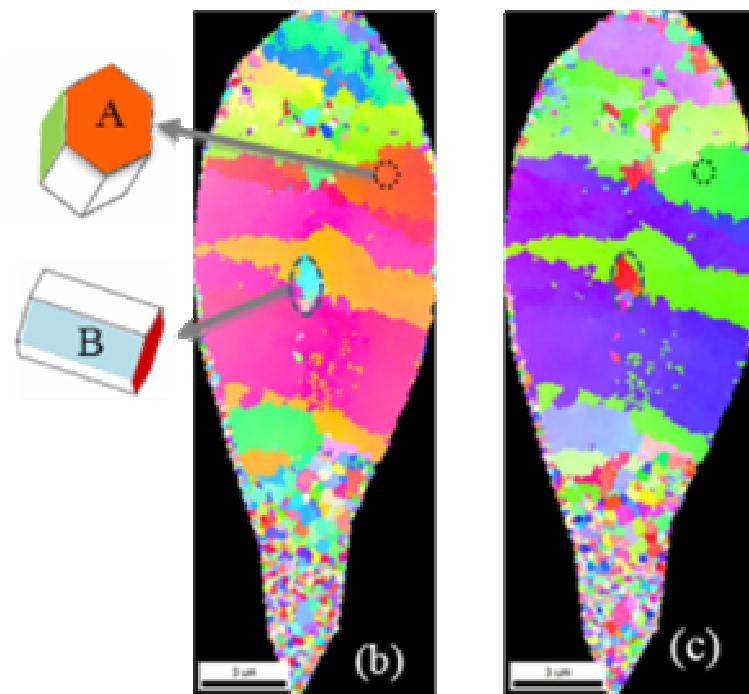
SEM image



LiNbO_3



EBSD image ($R3c$, $n^\circ 161$)



Cristal axis in
the direction
along x

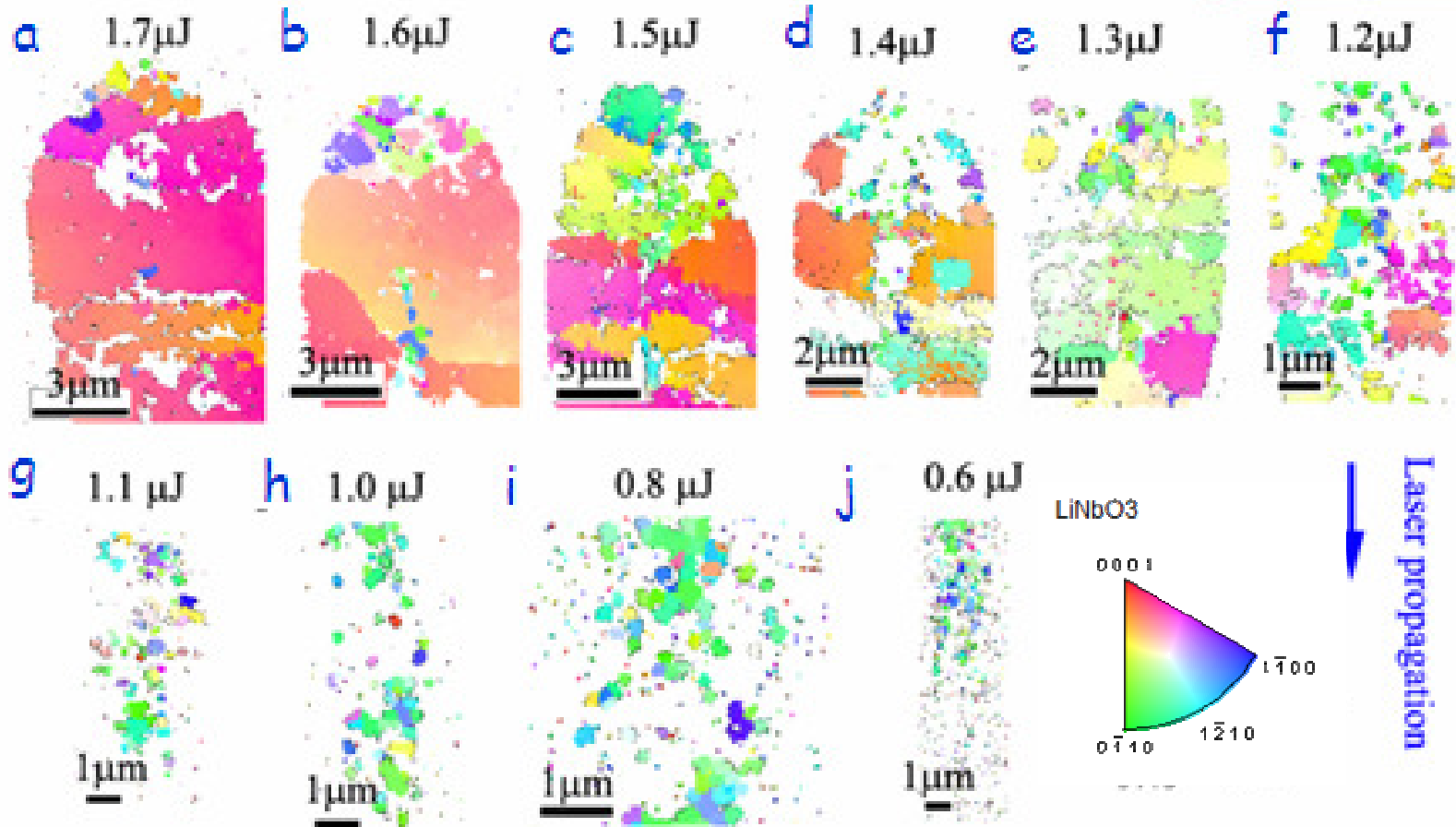
Cristal axis in
the direction
along y

300 kHz, $5 \mu\text{m/s}$, 300 fs, 1030 nm, $\text{NA} = 0.6$, laser
polarization **parallel** to the writing direction

V. Crystallization orientation dependence on the pulse energy

SUD
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EBSD picture
of the cross
sections
coded in the
direction of
writing
(perpendicu-
lar to the
cross section)



For large pulse energies, the growth induces the c axis in the direction of writing

For low pulse energies, only the nucleation appears with the c axis avoiding to be in the direction of laser polarization.

33Li₂O-33Nb₂O₅-34SiO₂
300 kHz, 5 μm/s, 300 fs, 1030 nm, NA = 0.6, laser polarization **parallel** to the writing direction

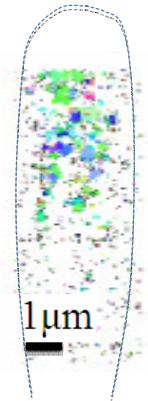
V. Unusual effect: Dependence of crystallization on laser polarization

$$\vec{e} \parallel \vec{v}$$

At low energy, the polar axis of crystals **avoid** to be oriented in the laser polarization direction.

At high energy, the polar axis of crystals have a **preferential orientation in the writing direction**.

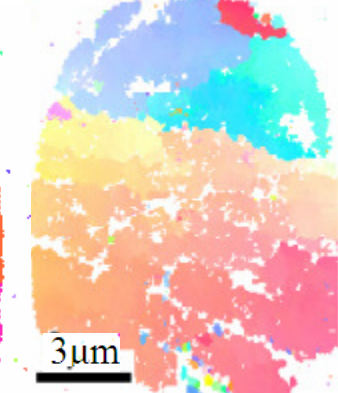
0.6 μ J



1.5 μ J

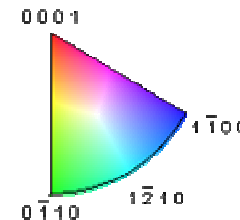


2.0 μ J



$$\vec{e} \perp \vec{v}$$

*The interaction volume is smaller,
The crystal size is smaller,
The crystallization is disordered,
Another force, other than thermal,
i.e. optical one is playing a role.*



2.0 μ J



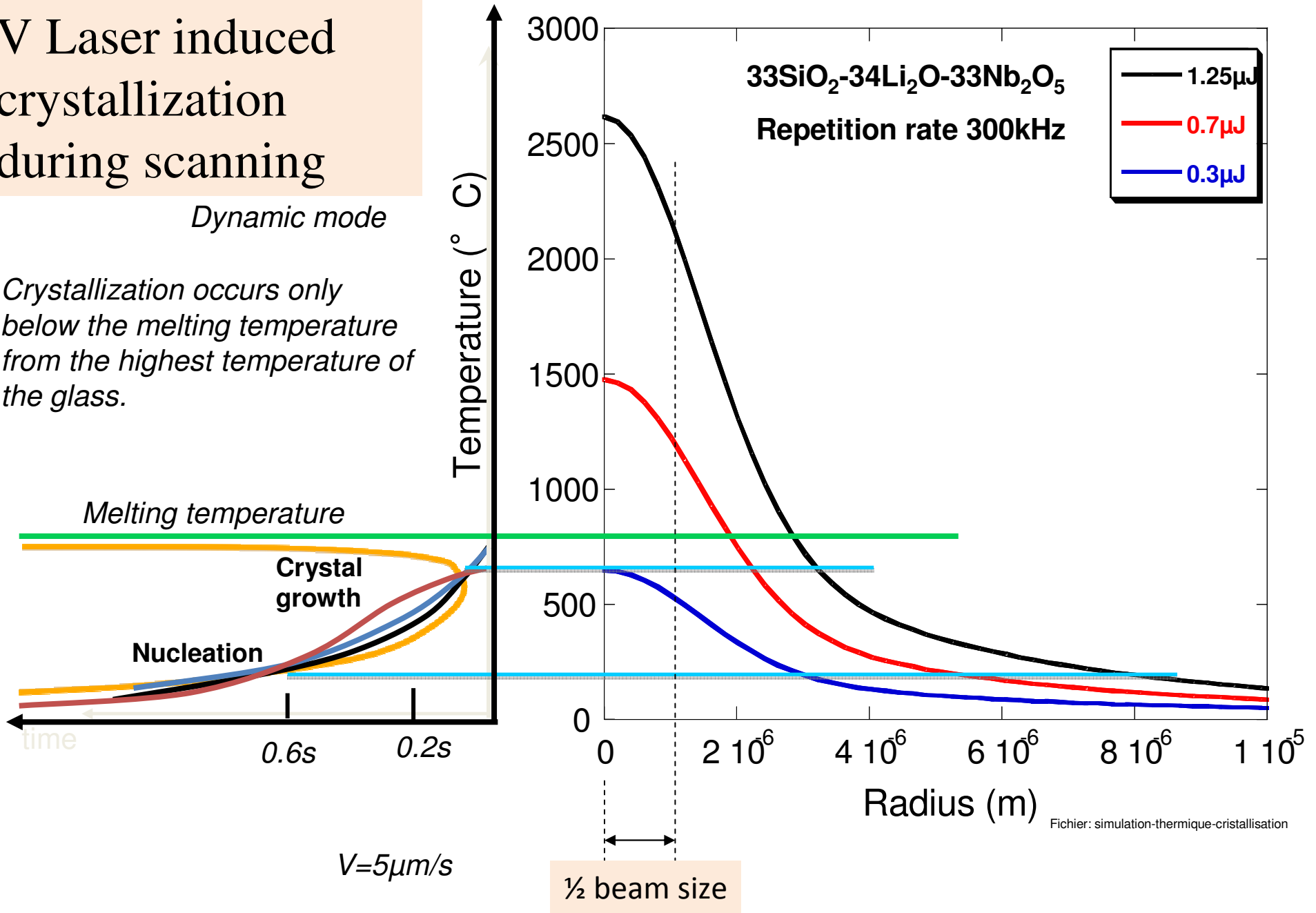
33Li2O-33Nb2O5-34SiO2

Laser parameters: 300 kHz, 5 μ m/s, 300 fs, 1030 nm, NA = 0.6, laser polarization **parallel** to the writing direction

V Laser induced crystallization during scanning

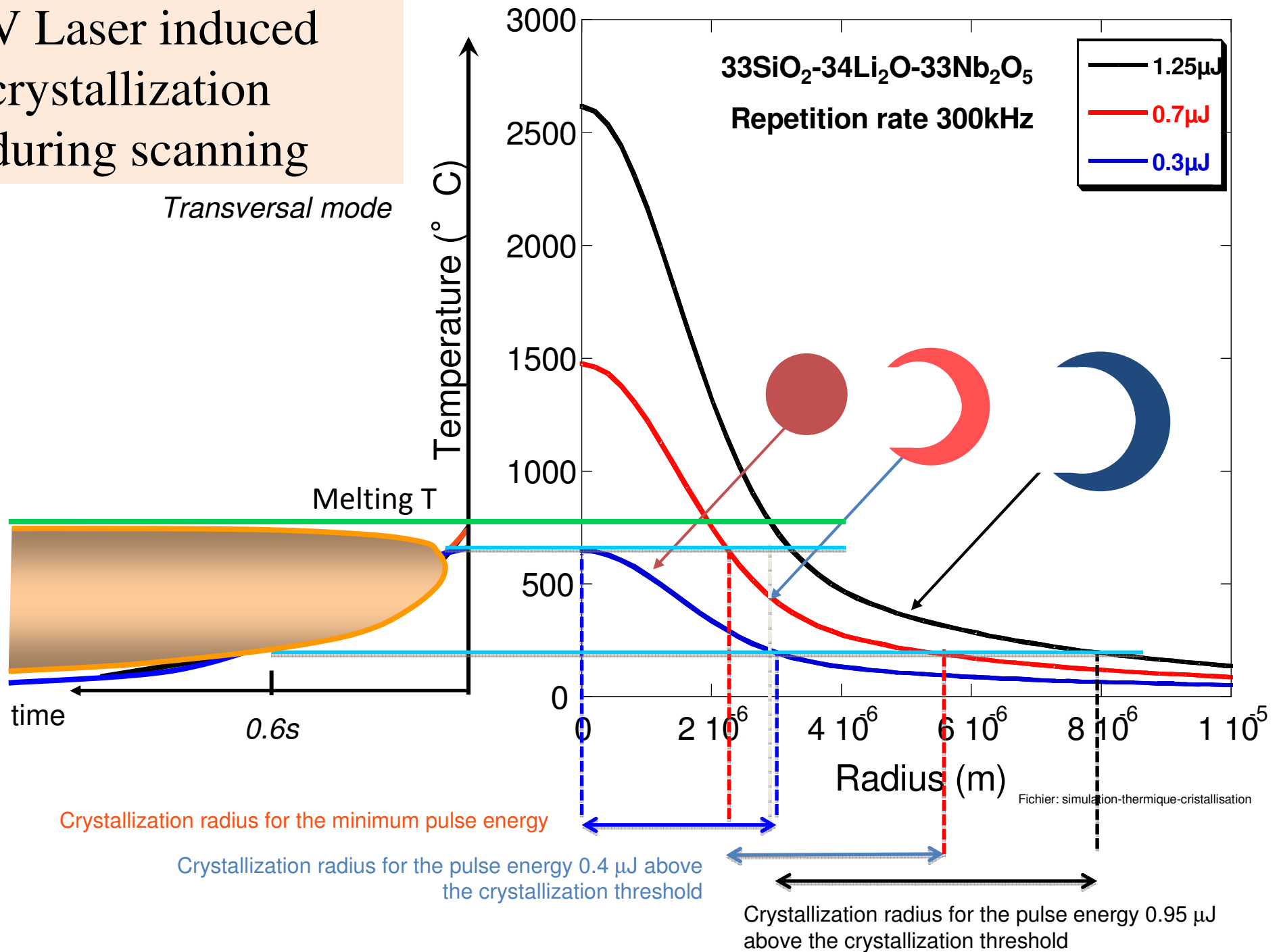
Dynamic mode

Crystallization occurs only below the melting temperature from the highest temperature of the glass.



V Laser induced crystallization during scanning

Transversal mode

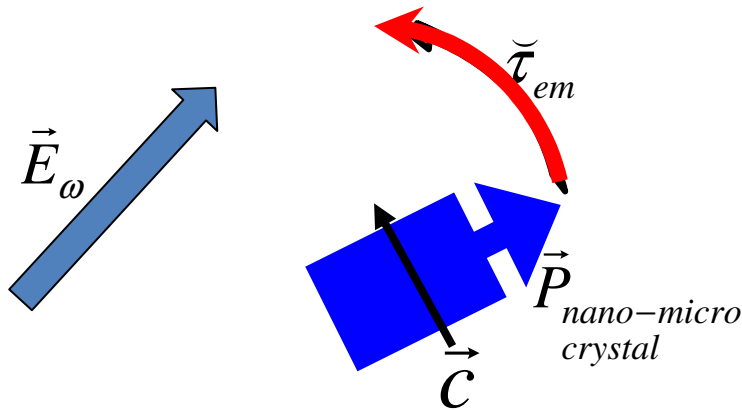


V. Un essai d'interprétation de l'influence de la polarisation

$$\vec{\tau}_{em} = \vec{P}_{nano\ crystal} \wedge \vec{E}_\omega$$

$$\vec{P}_L = \overline{\overline{\chi}} \vec{E}$$

Le cristal est anisotrope, il a donc une polarisation induite qui n'est pas parallèle au champ E excitateur



$$\overline{\overline{\chi}}$$

Possède sa plus grande composante, perpendiculaire à c (axe polaire)



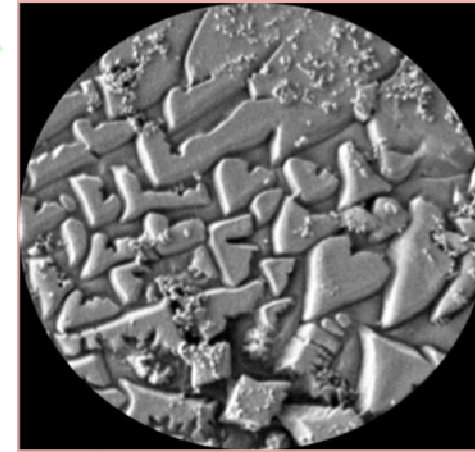
$$\vec{c} \perp \vec{E}$$

Comme dans les observations basse énergie

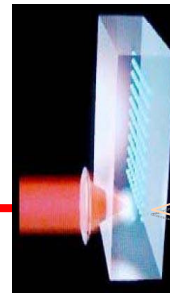
LiNbO₃ strong non-linear crystal
R3c, n° 161

Even more unusual!

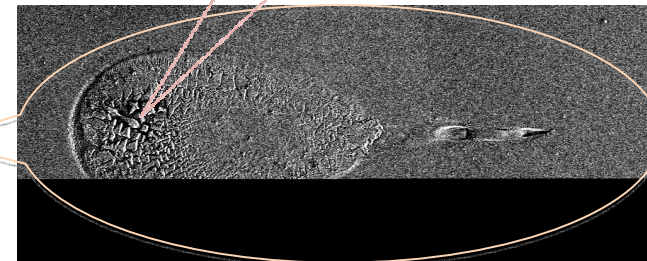
But what is he targeting?



Cupid*
delivering laser
arrows...



$\text{SrO-TiO}_2\text{-SiO}_2$



...in the heart of the glass

**Cupid is the god of love who
triggers love at people by
delivering an arrow in their heart.*

$40\text{SrO-}20\text{TiO}_2\text{-}40\text{SiO}_2$

1.5 $\mu\text{J/pulse}$, 1030nm; 350kHz; 10 $\mu\text{m/s}$, 0.6NA; 300fs; focal depth =
150 μm . Laser polarization parallel to the writing direction

Acknowledgments to FLAG consortium

Femtosecond Laser for Applications in Glasses

UPS/ICMMO, UPS/ISMO, CEA/LSI, UVSQ/LISV, UB1/CPMOH, THALES RT

Supported by

Agence Nationale pour la
Recherche

RTRA Triangle de la Physique

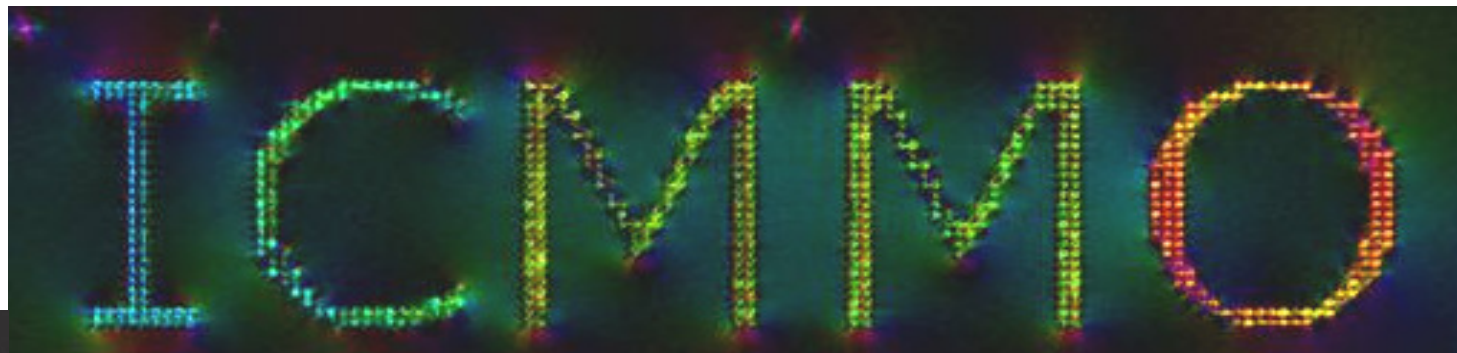
PRES UniverSud Paris

Département de l'Essonne

MAE and Europe Commission



Written
with
femtosecond
laser in
silica



The different colors of each letter correspond to different orientations of the slow axis of the birefringence (due to different nanograting orientation).