Fonctionnaliser des verres par laser pour des applications optiques à haute température : tendances, limites et opportunités

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Journées USTV – Dijon, Nov 2024

1. Context and objectives

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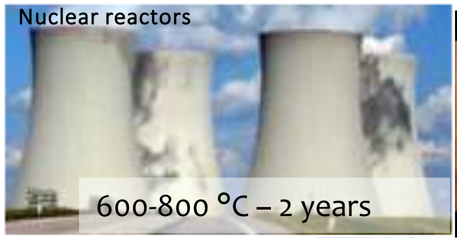
Functionalizing glasses at high temperatures

Why using glass at high temperature ?

- Complex manufacturing shaping (including ***optical fibers***).
- ***Optical sensors (T, P, σ)*** with: Multiplexing, chemical/ radiative/ electromagnetic resistance, compactness, lightness, flexibility, long distance...
- Refractory ceramics are a solution but no bending / costly / multimoded / lossy

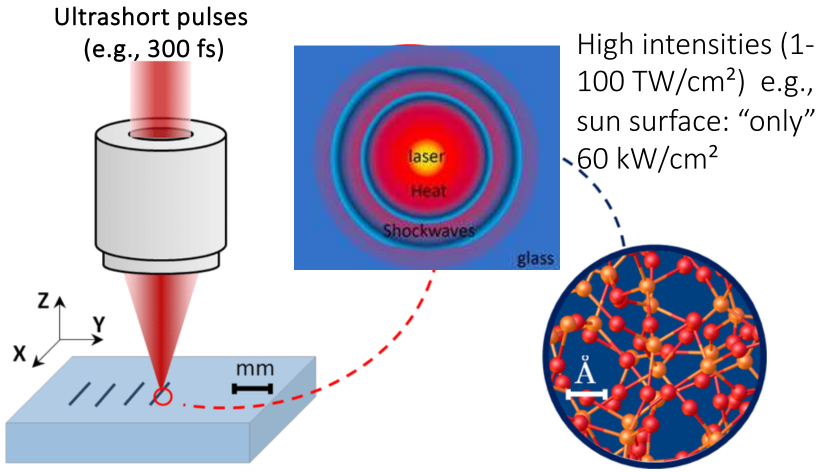
Ok but… what for?



Laffont et al. Sensors, 2018
Bao et al., Sensors, 2019
Mihailov. et al, Sensors, 2017

Optical sensors (FBGs) for Oxy-Fuel fluidized bed combustors gaz turbine combustors, engines, next-generation nuclear reactors, process monitoring

How? 3D Ultrafast laser direct writing !



<u>A 3D confined HP-HT micro-reactor :</u>

- High Temperatures (1000's K)
- High Pressures (>100's GPa)
- Each pulse contain E > glass formation enthalpy
- Strong gradients (T, P, I, E_{dc})

1. Context and objectives

Femtosecond laser direct writing (FLDW)

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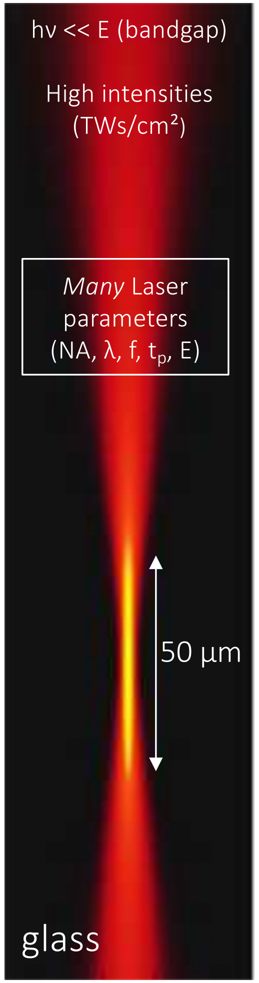
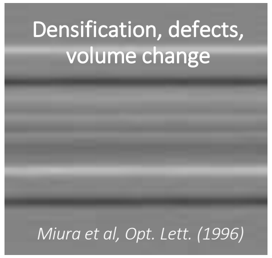
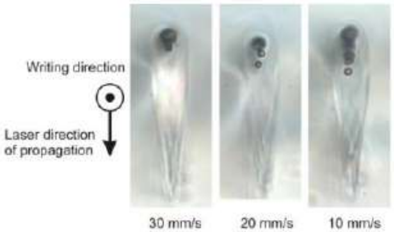


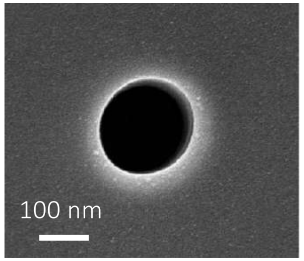


Isotropic refractive index change (Type I)

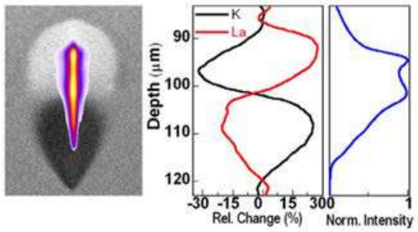
Bellouard et al., Optics Express, 2011



bubbles

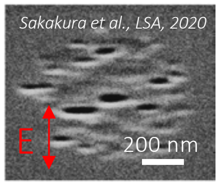


Nanovoids / cavities (Type III)



Fernandez et al., J. Phys. D, 2015

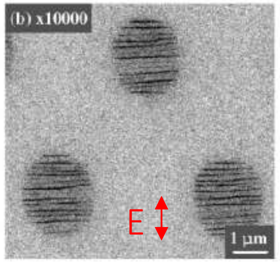
Chemical migration, Electron plasma distribution



Elongated nanopores polarization oriented (Type X)

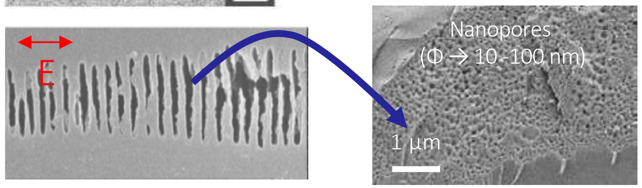
Nanogratings (Type II)

1) Porous nanolayers (silica, silica-rich glasses)

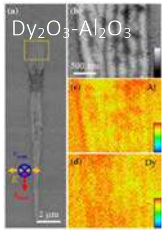


- light forced organized pattern
- $SiO_2 \rightarrow SiO_{2(1-x)} + xO_2$

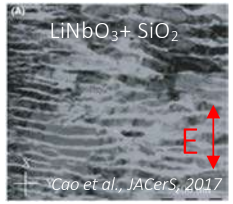
Shimotsuma et al., APL, 2003
Lancry et al., LPR, 2013
Bricchi et al., Optics Letters, 2004
Richter et al., JLA, 2012



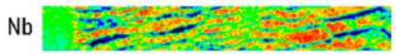
2) Crystal / glass phase separation



Shimotsuma et al., Applied Physics A, 2018



- Perovskite / garnet / nonlinear crystal precipitiation
- Chemical migration



Cavillon et al., Crystals, 2022

1. Context and objectives
HT sensor using fs-Fiber Bragg Gratings (FBG)

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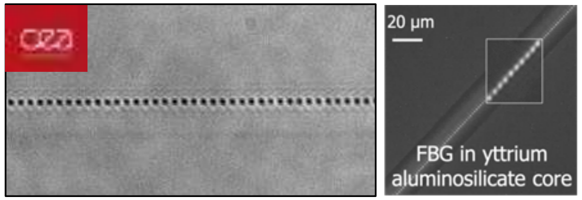
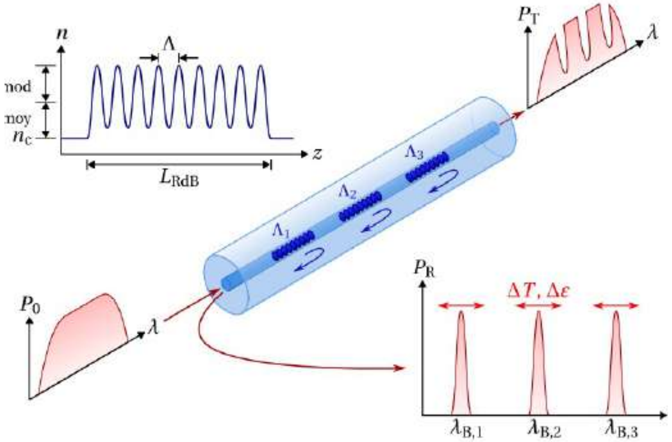
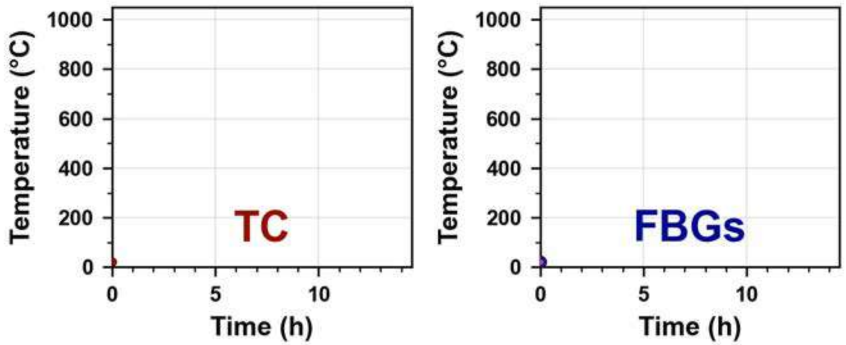
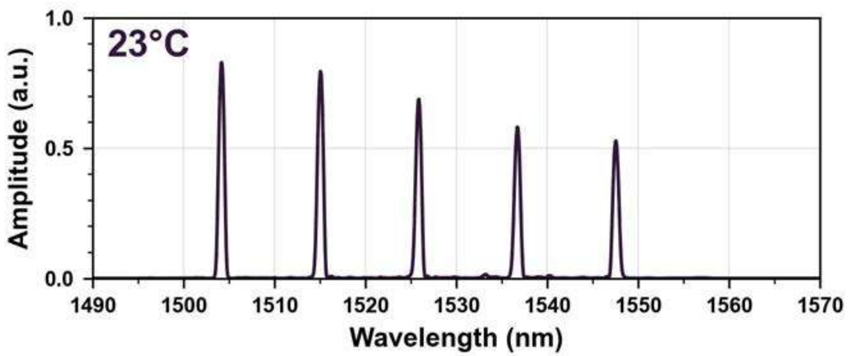
How works such optical fiber sensors ?



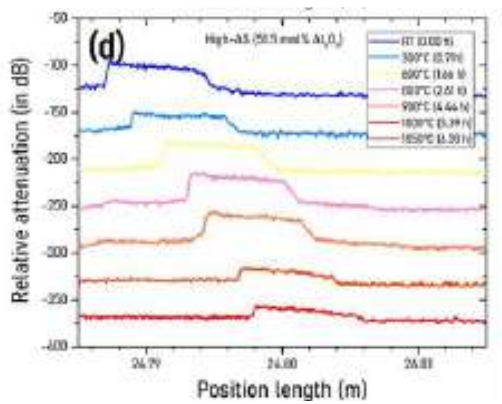






But also other types of optical sensors like Fabry-Pérot,

or Rayleigh enhanced scattering

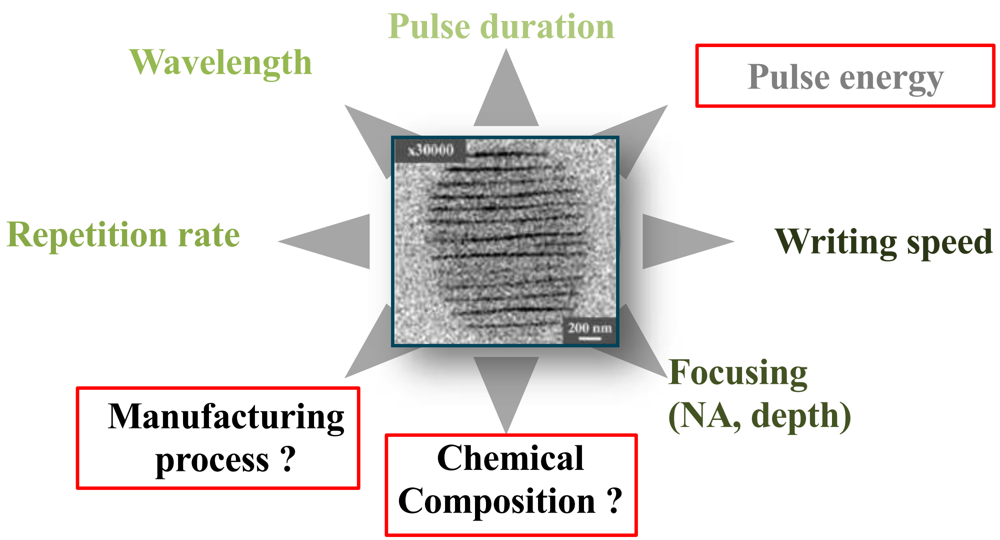


$\boldsymbol{\lambda_B}$ sensitive to temperature (or σ, ε)

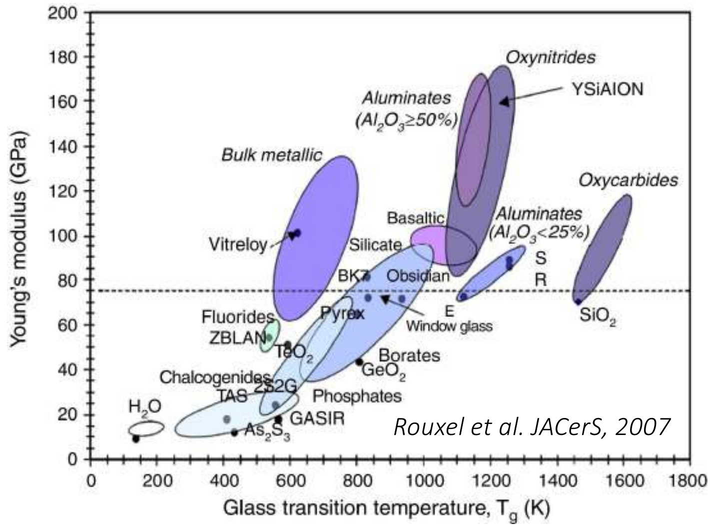
Sensibility : $\frac{d\lambda B}{dT} \approx 11{,}2pm/°C$ at $\lambda \approx 1550\ nm$

Can we go beyond silica ?

Improve/predict the thermal stability



Additional properties ?



Classical investigations

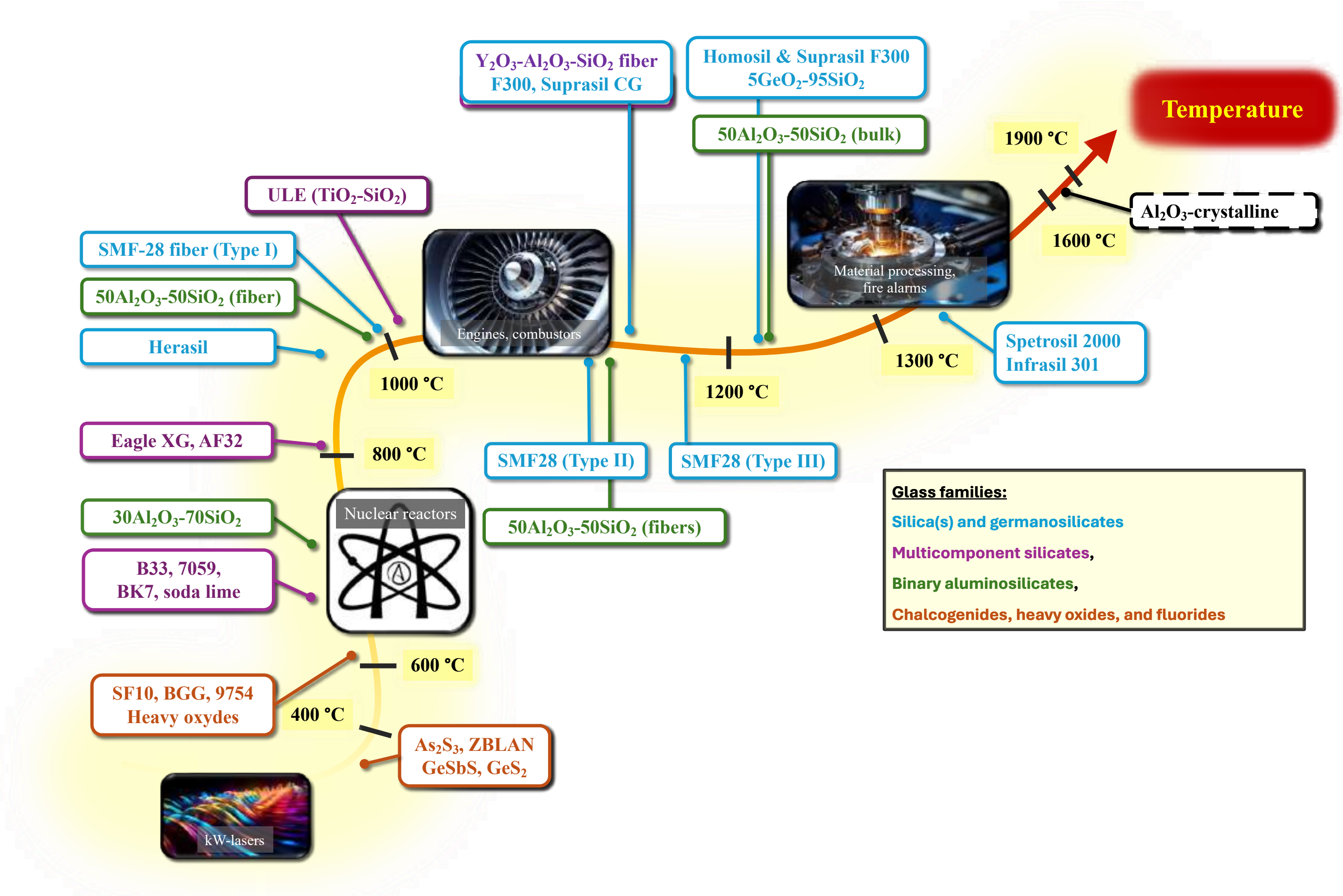
- Silica glass
- Impurities (Cl, OH)
- GeO_2 dopant
- Laser parameters (energy, speed…)

"Inspired" research

- Oriented eutectic (Al_2O_3/ZrO_2)
- Phase separation
- Nanocrystal
- Non-conventional fabrication method

Litterature overview

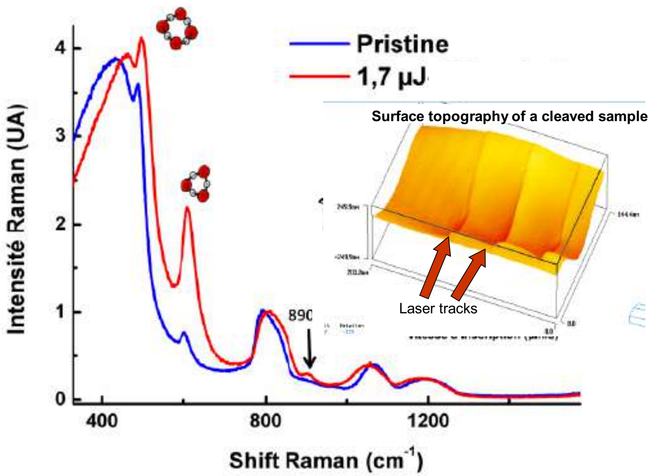
Trends and limits



Type I – Defects but mostly densification

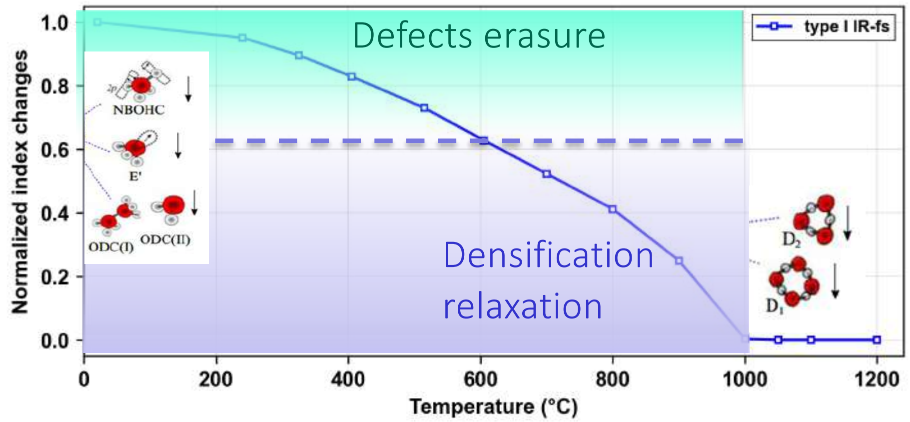
Optical structure - mechanism

Raman spectra of fs-irradiated SiO_2



Spectral signature of a permanent densification in SiO_2

Optical property thermal stability

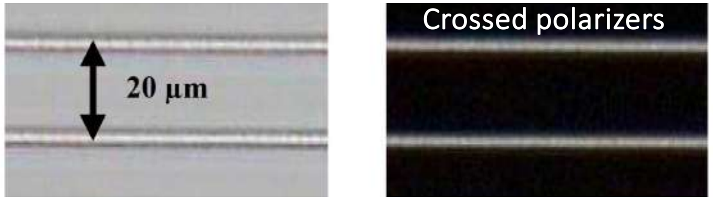


A thermal stability limited by glass structural relaxation η(T)/G(T)

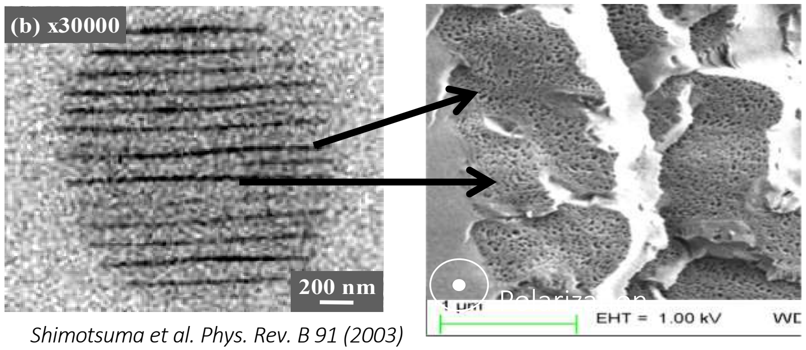
M. Lancry et al. Optical Material Express, Vol. 1, Issue 4 (2011)

Type II – Self-assembly of porous nanolayers

Optical structure - mechanism



« The smallest self-organized nanostructures created by light in glass volume »

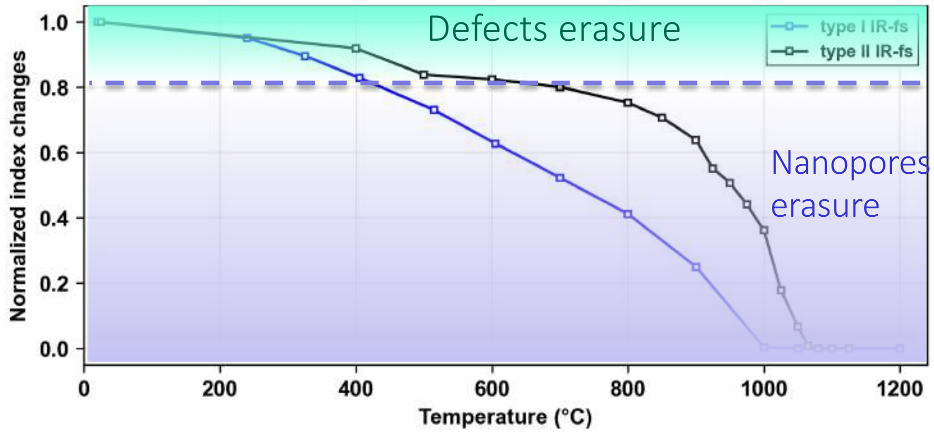


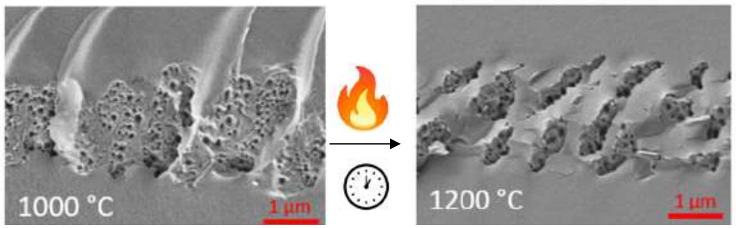
Shimotsuma et al. Phys. Rev. B 91 (2003)

Ultrafast decomposition of SiO_2 into $x.O_2$ + $SiO_{2(1-x)}$ in less than 1 µs !

M. Lancry et al. Laser Photonics Rev. 7 (2013)

Optical property thermal stability

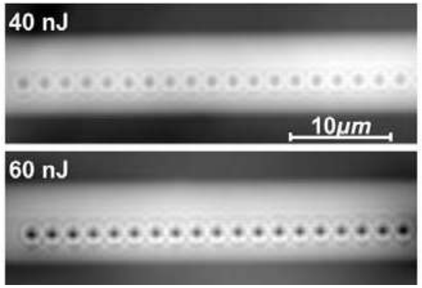


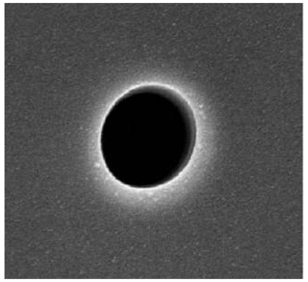


Part related to defects & stress relaxation
But ultimate erasure of nanopores is viscosity driven (mostly)

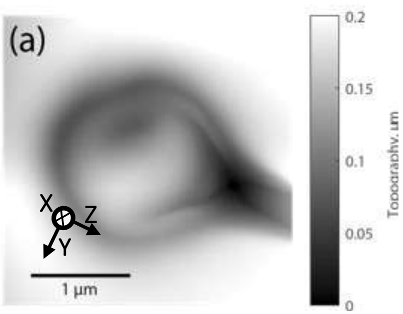
Type III – Voids with HPHT densified shell

Optical structure - mechanism



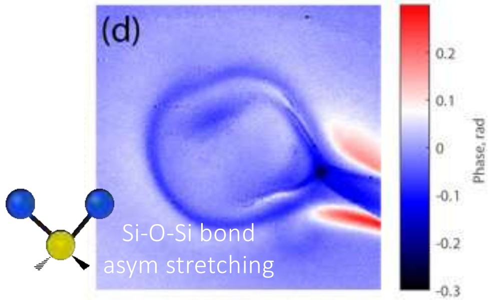


Topology of the surface measured by AFM



Mechanical signature of densification

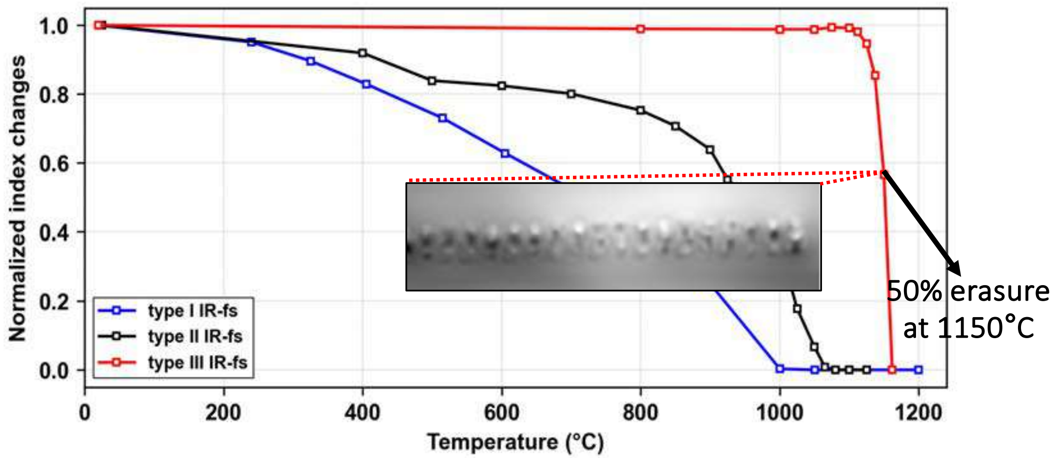
Near-field phase map at 1130 cm^{-1} (s-SNOM)

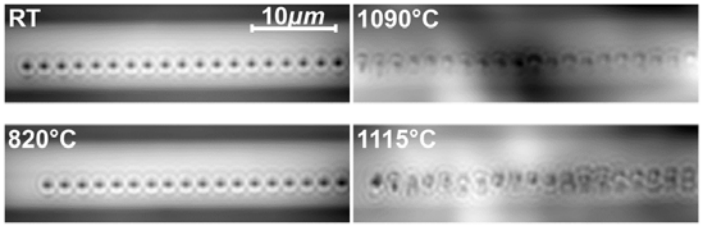


IR optical signature of densification

s-SNOM scattering-type scanning near field optical microscopy made at SOLEIL Synchrotron (SMIS)

Optical property thermal stability

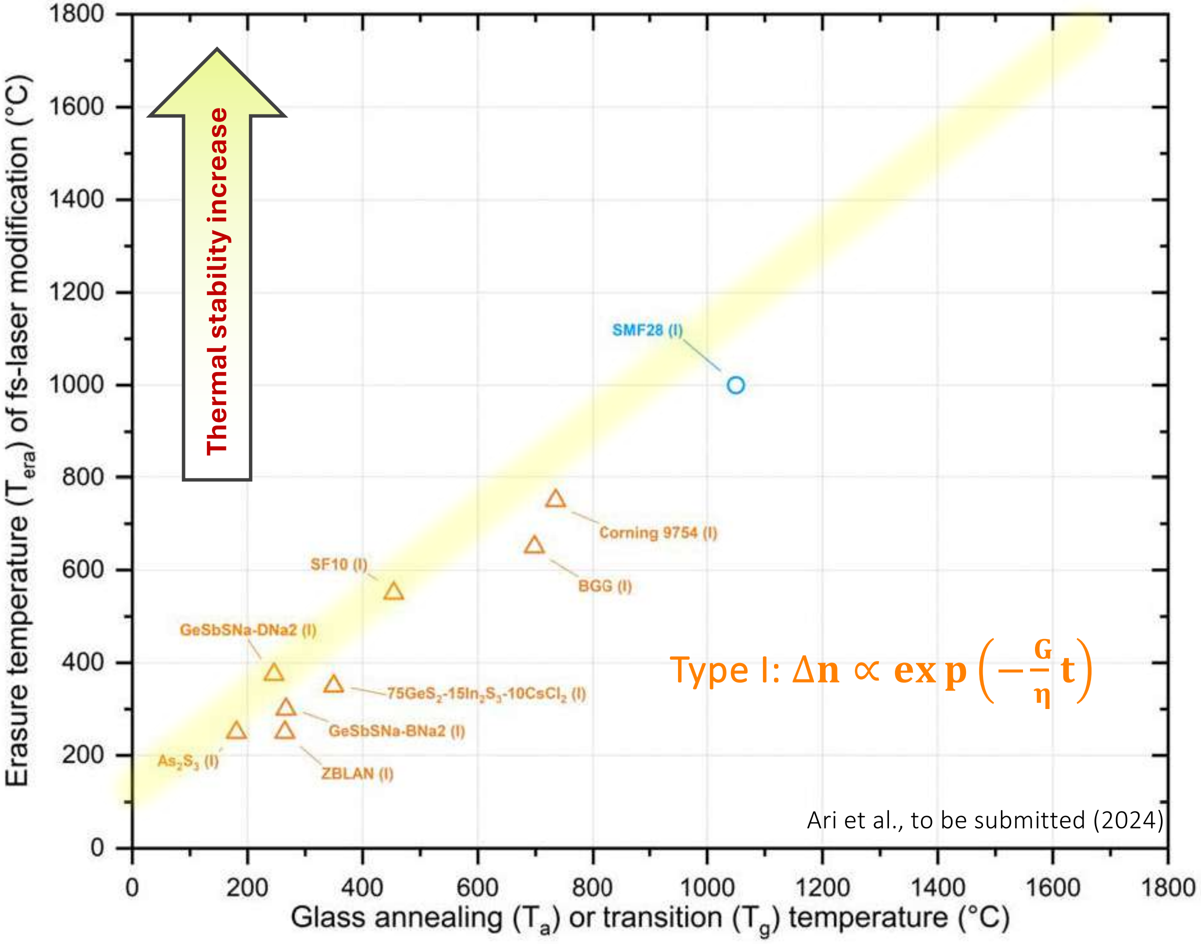




Thermal stability mostly dictate by nanovoids growth & deformation and densified shell relaxation at high T

2. Trends and limits

Generalization vs chemical composition - **Type I**



Compilation of results – isochronal annealing experiments (Δt = 30 min)

Symbol code:
△ ○ Types I, Stress (in bulk)
● Types II (in bulk)
★ Type II (in fibers or fiber preforms)

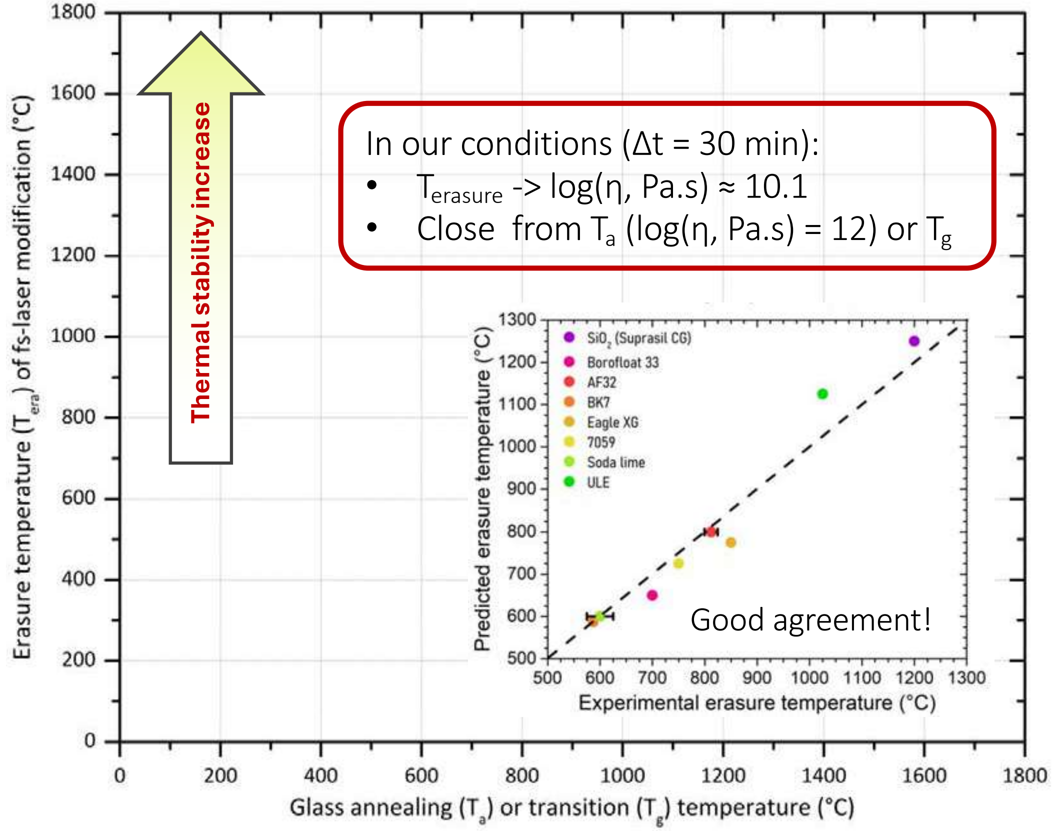
Glass color code:
- Silica(s) and Ge-doped silica
- Multicomponent silicates
- Chalcogenides, heavy oxides, fluorides

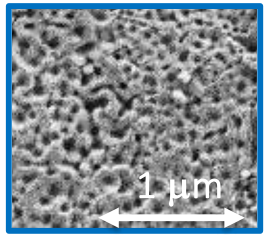
Type I modifications

- Thermal stability mostly related to defects and glass densification/expansion
- Thermal erasure is somehow limited by glass structural relaxation i.e. $\frac{\eta}{G}$

2. Trends and limits

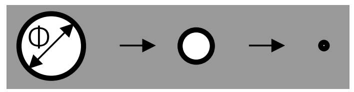
Generalization vs chemical composition - **Type II**





Rayleigh-Plesset equation [1-2]:

Evolution of a pore diam Φ in a viscous medium



$$\frac{d\Phi}{dt} = \frac{\Phi \Delta P}{2\eta} - \frac{\sigma}{\eta}$$

Pressure difference (small)

Viscosity

Surface tension

Going from Φ(t,T) to optical property (t,T):

Φ(t,T) → **Δn** → B

Maxwell-Garnett

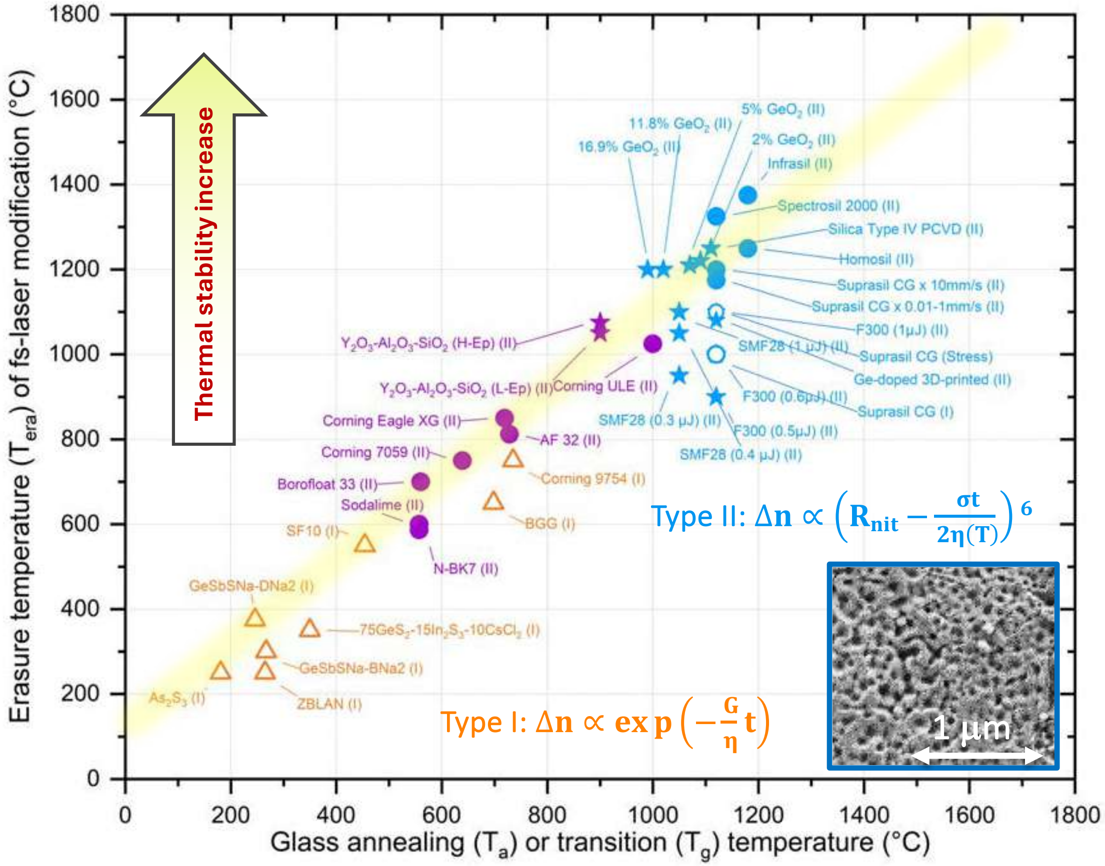
Form birefringence

- Thermal erasure is viscosity driven (mostly) but also related to σ and Φ_{init}

[1]: Cavillon et al., Appl. Phys. A, 2020
[2]: Q. Xie et al., Applied Optics, 2023

2. Trends and limits

Generalization vs chemical composition - **Type II**



Xie et al., Applied Optics (vol. 62, 2023)
Shuen et al., Sensors (vol. 20, 2020)

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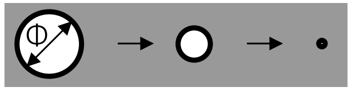

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Viscosity

Surface tension

Going from Φ(t,T) to optical property (t,T):

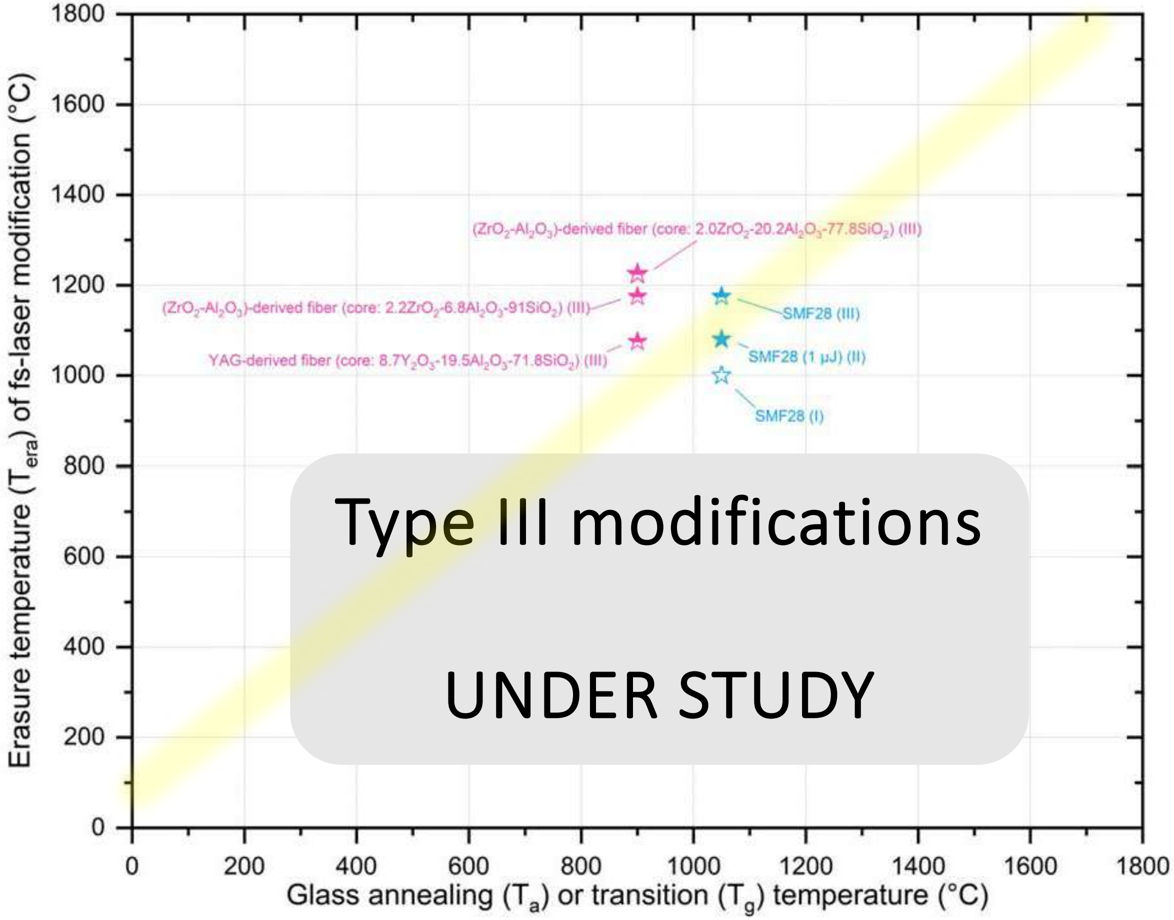
$\Phi(t,T) \rightarrow \Delta n \rightarrow B$

Maxwell-Garnett · Form birefringence

- Good agreement experiment / model
- So SiO_2 would be the best performer?

2. Trends and limits

Generalization vs chemical composition - **Type III**



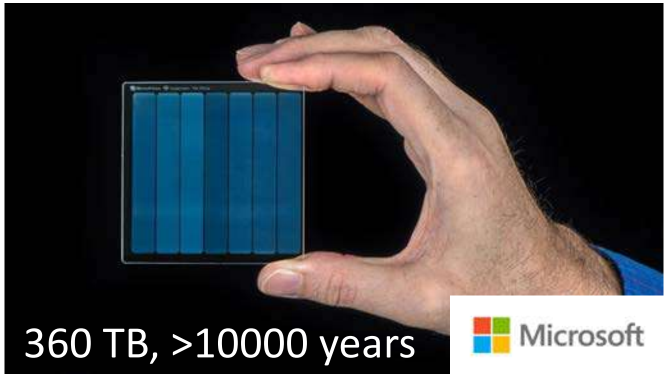
Type III modifications

UNDER STUDY

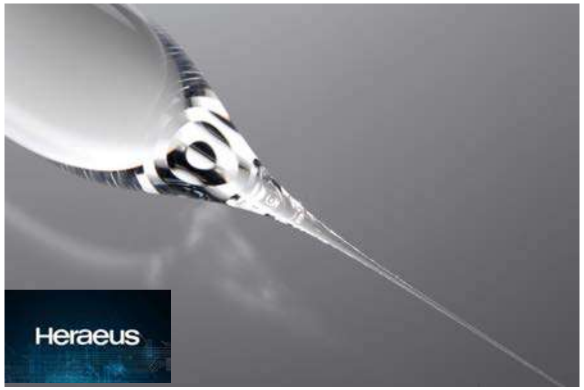
Any opportunities

Going « beyond silica » golden material ?

Silica “superman” 5D memory



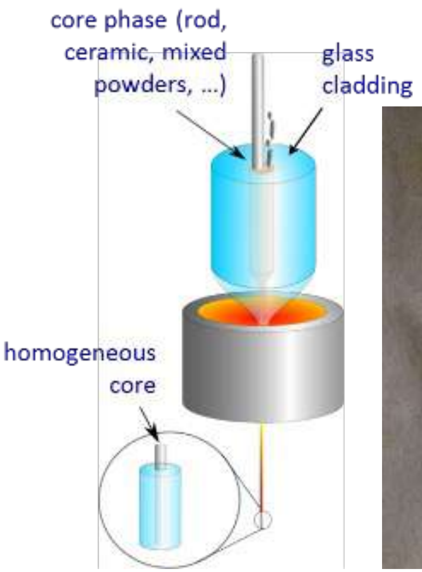
Ultra-transparent silica fibers



Non-conventional manufacturing

➢ Bulk glass and optical fiber fabrication

Molten core method



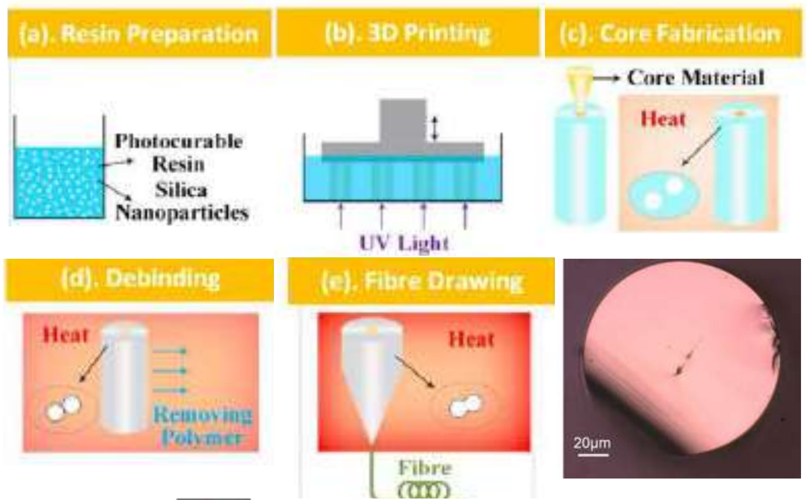
CLEMSON UNIVERSITY COMSET CENTER for OPTICAL MATERIALS SCIENCE & ENGINEERING TECHNOLOGIES

- Very large choice of compositions to be "fiberized" & simple technique;
- High quenching rates;
- Enhanced tunability (e.g. optical/ acoustic) properties;
- **Sapphire, YAG or ZrO_2 derived fibers.**

D. A. Coucheron et al., Nature Communications 7, 2016.

Leibniz ipht LEIBNIZ INSTITUTE of PHOTONIC TECHNOLOGY

3D printed preform method

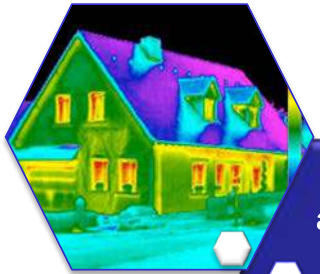


UTS UNIVERSITY OF TECHNOLOGY, SYDNEY UNSW SYDNEY *Chu et al., Opt.Lett, 2019.*

Coupling fs-laser with Molten core , 3D printed method:
→ Induce "laser modifications" into "non-conventional" glassy fibers or bulk glasses
→ Our objective: Go beyond thermal stability limitations of conventional fibers (e.g. SMF28)

3. Beyond silica and silicates

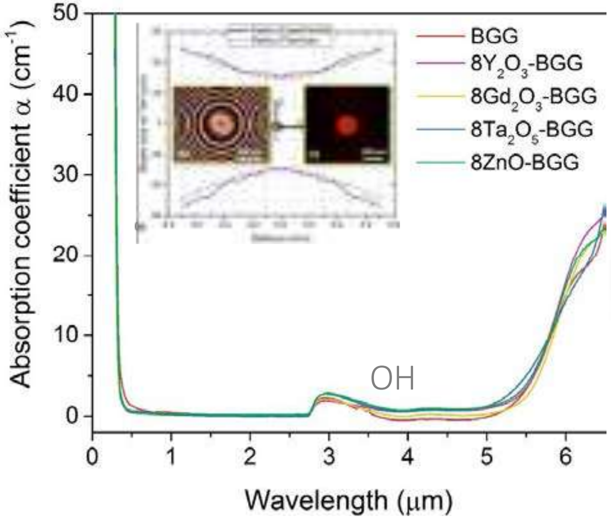
2020-2023 Chalco & Gallo-germanate glasses ($BaO - Ga_2O_3 - GeO_2$)



Mid-IR applications (imaging, optics)

Thorlabs, Horiba, Thales, ONERA,..

Mid-IR transparent oxide



L'homme aux oxydes lourds !

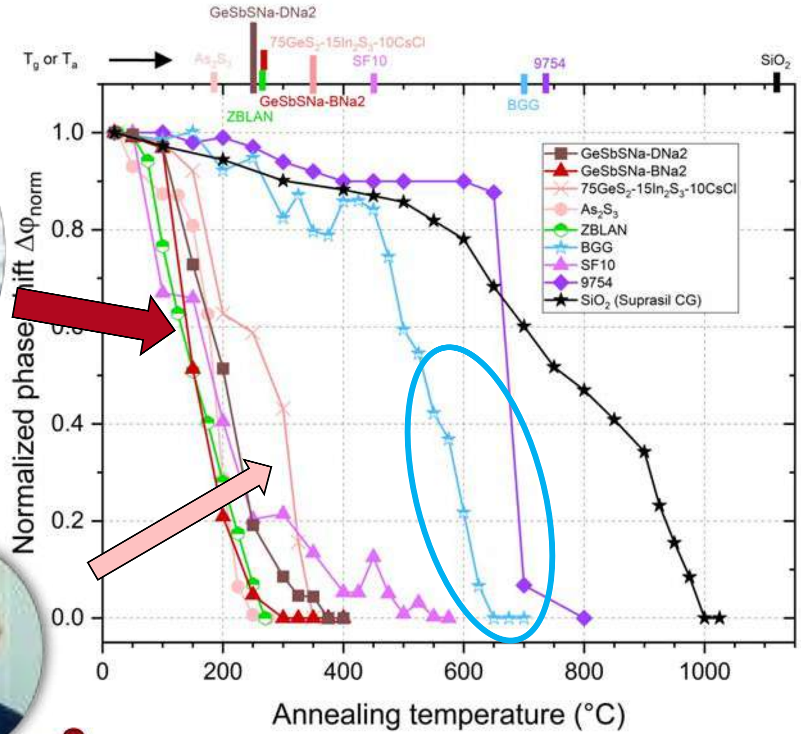
icmcb

Nos deux "mines" de verres chalco ?

ISM

Institut des Sciences Chimiques de Rennes
UMR CNRS 6226

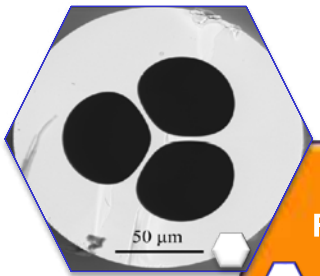
Mid-IR transparent glass/fibers for "high T" applications



3. Beyond silica dedicated to optical telecommunication

2020

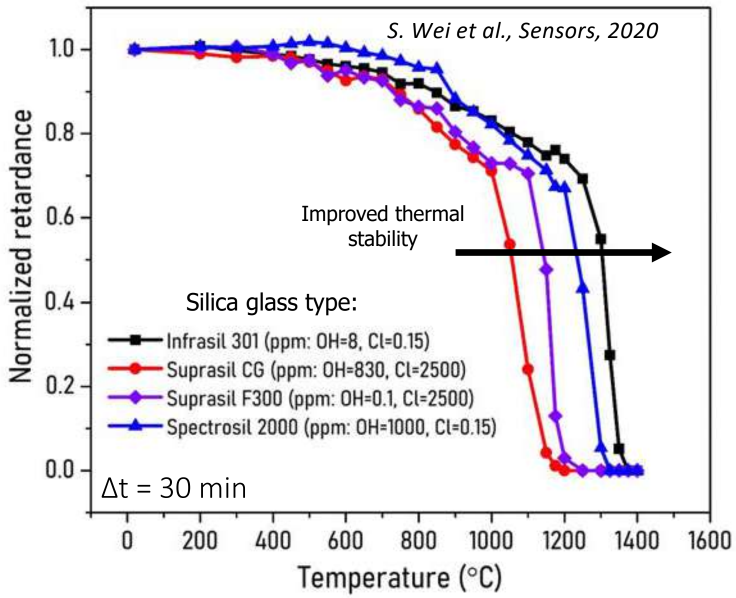
Silica or silica - Which type ?



From optical Telecom to sensors (OFS, FBGs, …)

Next step : fiber drawing !

Towards new silica fibers dedicated to HT sensors ?

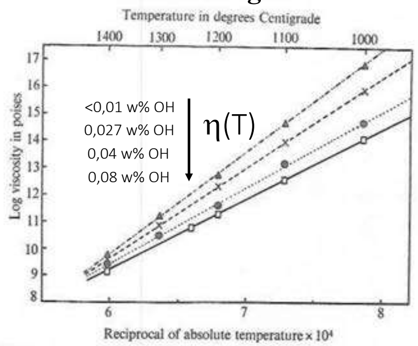


Clearly a viscosity driven effect

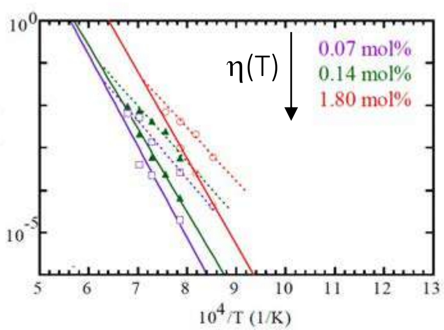
Some silica own higher thermal stability than "optical fiber golden silica"

Impurities impact on viscosity

OH silica glass



Cl-doped silica glass



3. Beyond silica dedicated to optical telecommunication

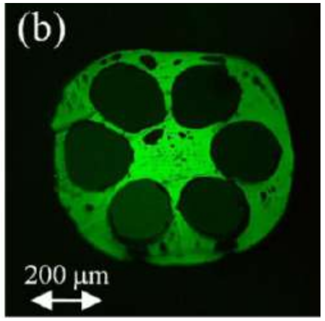
2020

3D printed Silica glass

université PARIS-SACLAY

3D printed « telecommunication like » fibers

UNSW SYDNEY



1st cheesy optical fiber

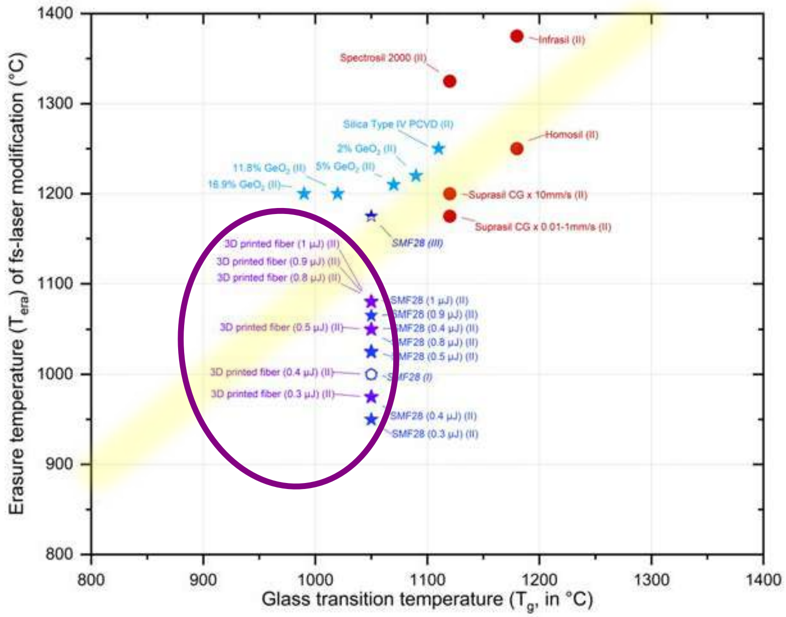
3D Printed Silica Optical Fibre - a "Game Changer" Technology in Optical Fibre Manufacture

PhLAM Physique des Lasers Atomes et Molécules

See 3D printed talk on Friday

Next step : refractory oxide glasses by 3D printing … a long way

3D printed fibers for sensors ?



- Emerging 3D printed demonstrates similar thermal performances as "golden standard" SMF28 !

3. Beyond silica

2020-2023

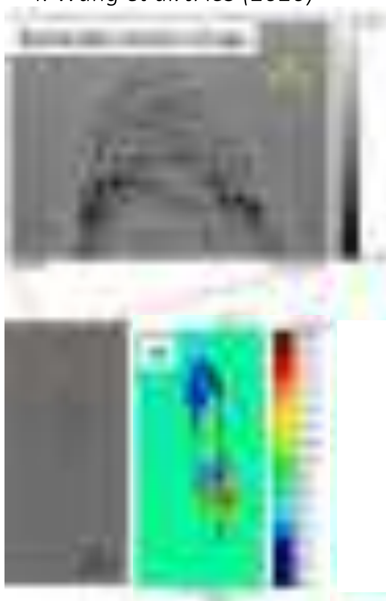
Alumino-silicate glasses (SiO_2 - Al_2O_3)

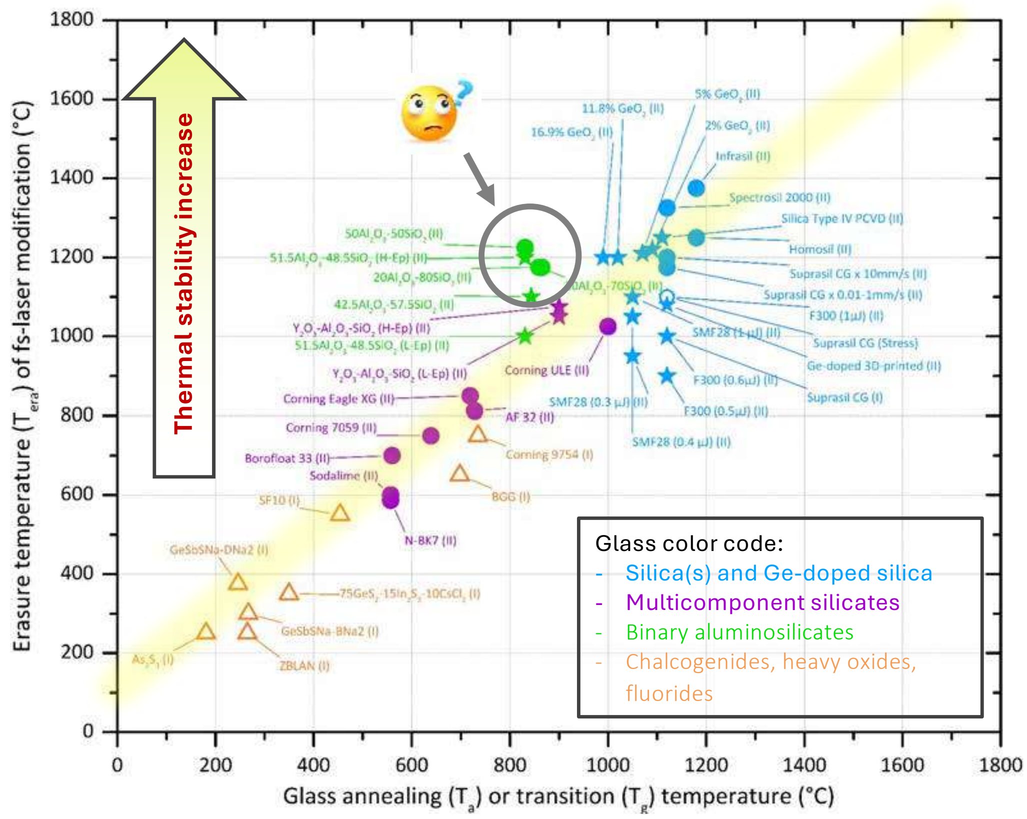
Sensors in Harsh environment:
CEA, SAFRAN…

$50Al_2O_3/50SiO_2$ (bulk)

Y. Wang et al. JACS (2020)

Phase separation : nanogratings + Likely Mullite formation





Wang et al., JACerS, 2020

Wang et al., Advanced Optical Materials, 2022

Al[5]

Daniel "Otto" Neuville

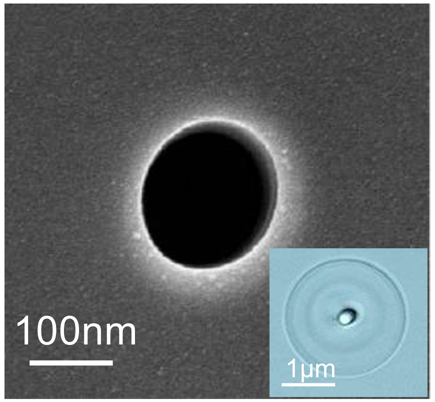
IPGP

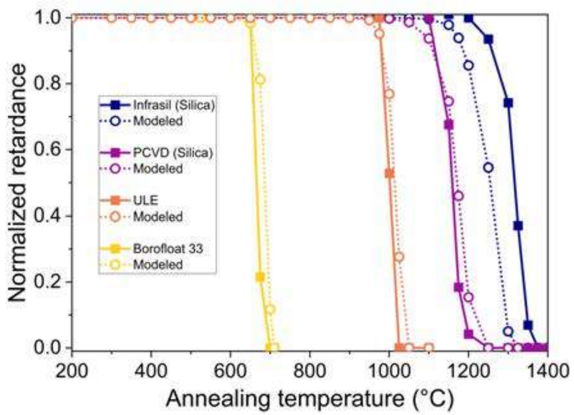
Conclusion and perspectives

Conclusions

- **Overview** of fs-induced index changes thermal stability
- **Materials**: We can beat "telecom silica" !!!
- **Functionalizing approach:** Fs laser induced High temperature nanocrystals
- **Modeling:** Rayleigh-Plesset model -> predict nanopore/voids evolution(t,T) and associated optical property

  but high Al_2O_3 glass systems deviate from this trend





Projects: FLAG-IR (2019-2022),
REFRACTEMP (2023 – 2026)

Perspectives

- Need to develop sensing dedicated fibers (and not simply exploiting existing ones)
- **Materials**: Molten core, 3D printed fibers: towards new compositions.
- **Model**: Build a new predictive model including crystal growth / elemental migration, …
- **Applications**: Can be also exploited for other sensors, 5D data storage, IR birefringent devices…

Thank you !

3D Printed Silica Optical Fibre - a "Game Changer" Technology in Optical Fibre Manufacture

This new 3D printing method could make fiber optics cheaper

Cloud Storage Solutions for the Zettabyte Era !

The different colors of each letter correspond to different orientations of the slow axis of the birefringence

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