Observing mechanical and elastic properties of glasses by spectroscopic methods: towards weight-lightening of glass

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1. May 2024, Lloret del Mar, Spain

ICG- Glass for a sustainable future

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The 3 R's

Thin glass

Fibers

Need to be reinforced

Strength?

Problem if chemistry change

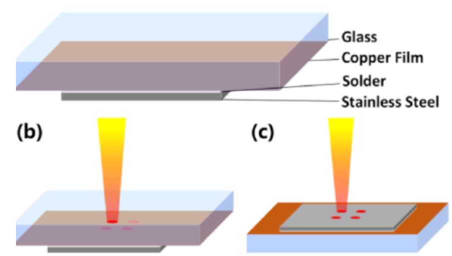
Reinforcement strategy

Internal strength

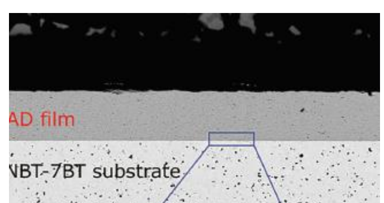
- Thermal tempering
- Chemical tempering

Exoskeleton

- Composite
- Cutting and soldering
- Glass as coating



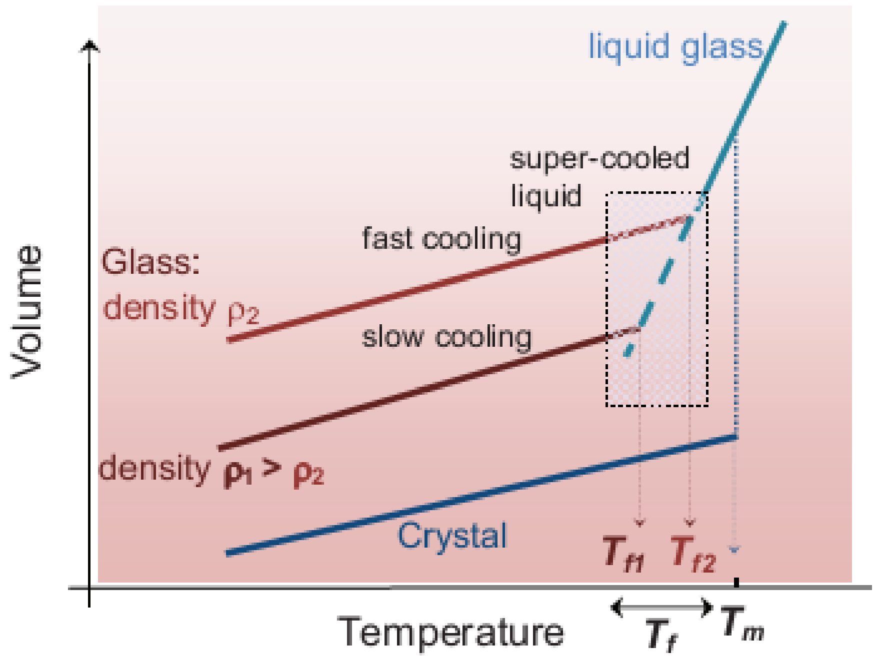
H. Ren et al. Optics and Laser Technology 176 (2024)



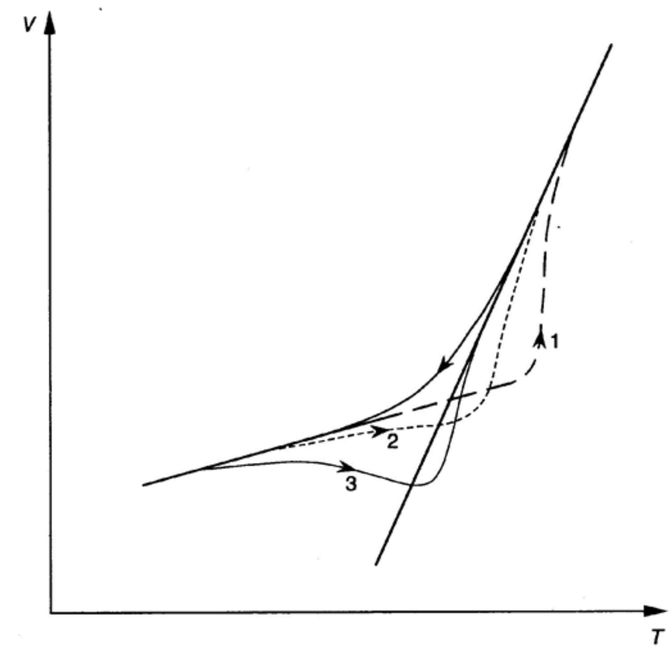
Outlines

- Weight-lightening of glass some specific needs
- How glass register its formation and internal stress conditions
- How can we read it
- Applications Internal strength
  - Cooling rate of glass fibers
  - Tempered glass
  - Cation exchanged glasses
- Applications Exoskeleton
  - Cutting glass with short pulse lasers
  - Cooling rate around short pulse laser modified area
  - Aerosol deposition

Effect of temperature



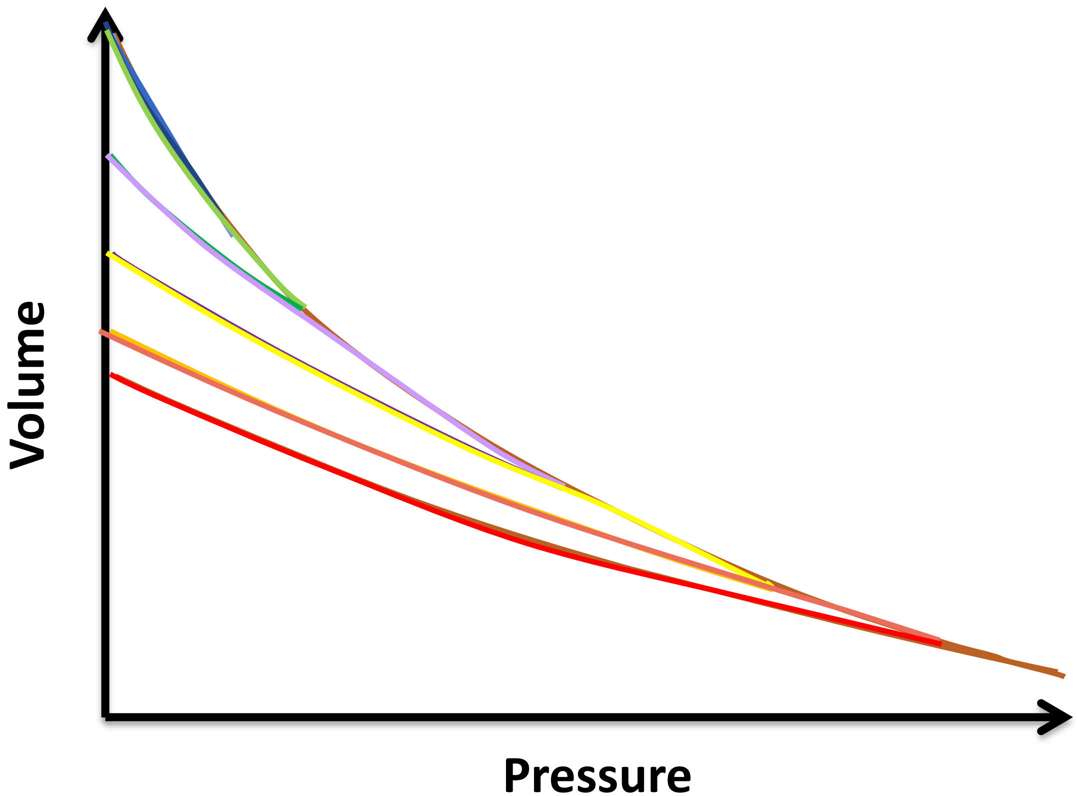
Colling at different speed

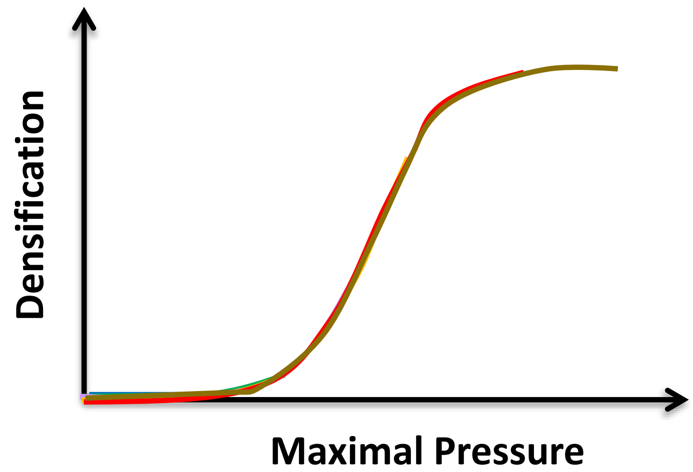


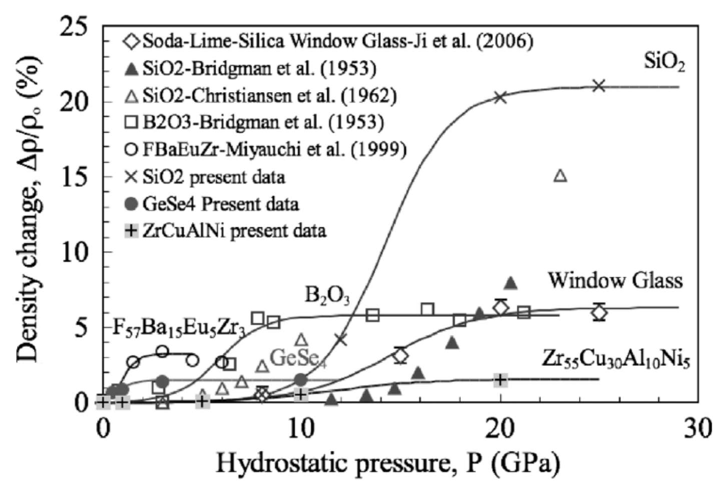
Heating at different speed

The cooling rate in the glass transition zone is recorded.
The fictitious temperature represents the glass transition temperature for a given cooling rate.

Effect of pressure

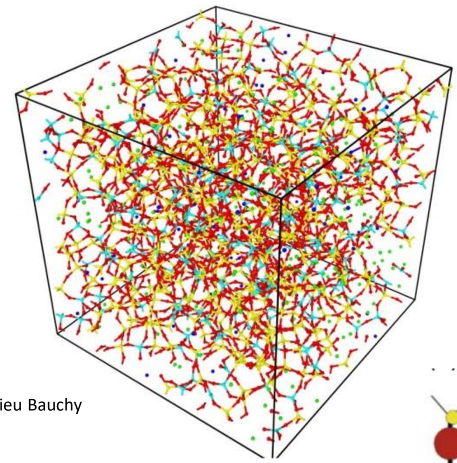




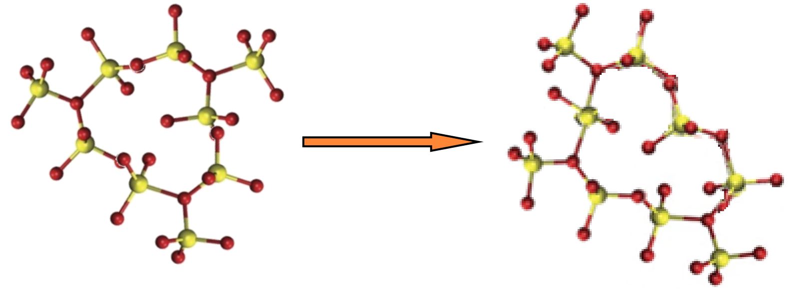


The maximal pressure is recorded

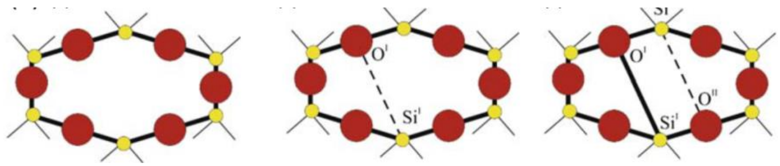
Atomic changes related to volume changes



Mathieu Bauchy

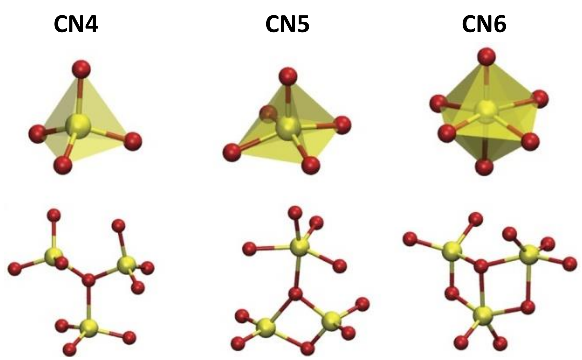


Change of angle between tetrahedrons



Zeidler et al. 2014 PRL 113, 135501

Change of ring sizes



Misawa et al. Science Advances 2017

Modification of the oxygen coordination of the network former elements Si, B, Al

also causes a modification of the angle and of the angle and the size of the rings.

	T_f	P_{max}
Si-O-Si	+	-
small/big	+/+	+/-
CN	-	+

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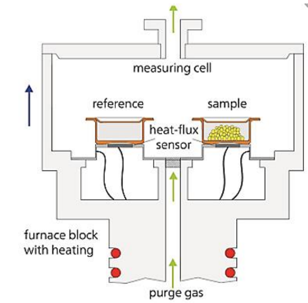
Reading the memory of the glass

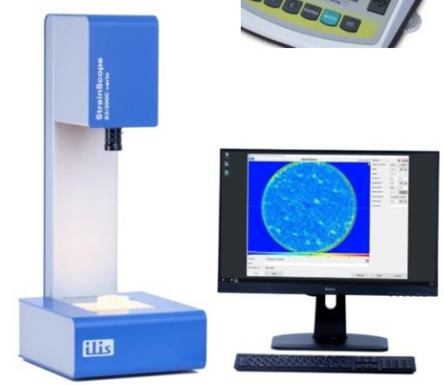
Different instruments

Methode	Size observed	Sample preparation	Calibration
DSC Calorimetry	mm	Poudre	no
Volume	mm	Regular shape	no
Refractive index	100 µm	Regular shape	Photoelastic coef.
Density	cm	no	no
Raman	1 µm	no	Specific to chemistry
Brillouin	1 µm	no	Specific to chemistry
Luminescence	1 µm	no	Specific to chemistry

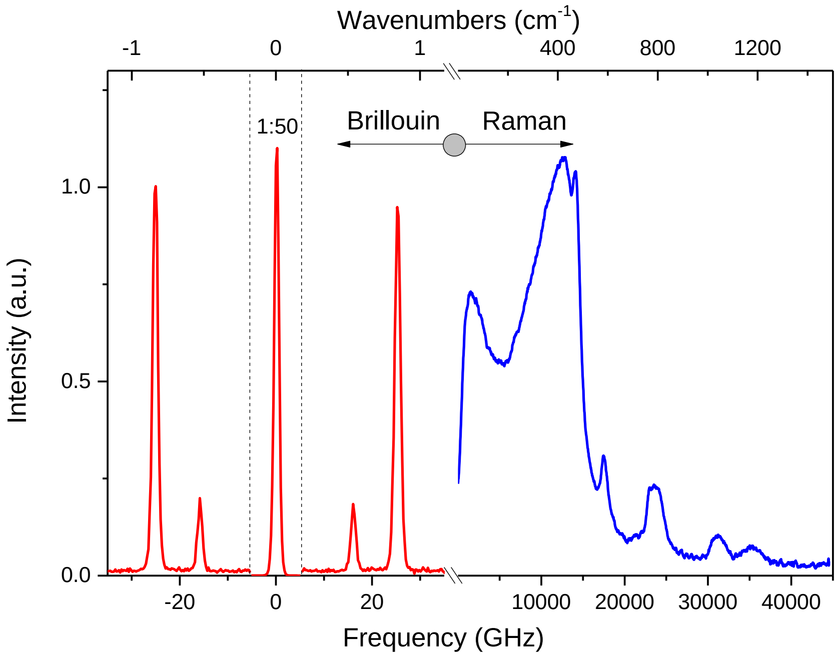
Very quick

Calibrations needed

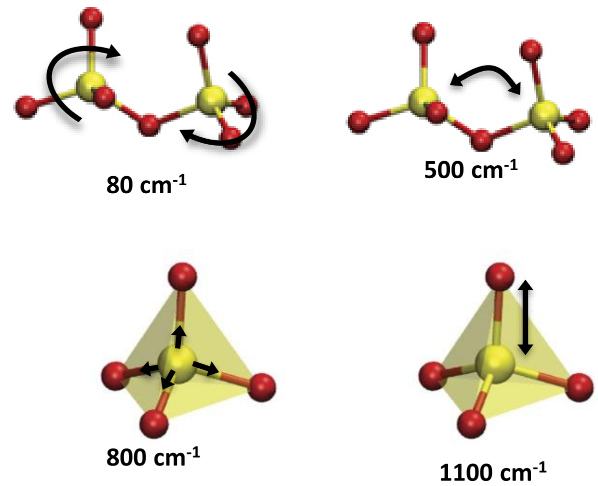




Vibrational Spectroscopies



Raman analysis



Brillouin interpretation

Sound velocity

$$c = \frac{\lambda}{\sqrt{2}n} f^{90}$$

λ – laser wavelength
n – refractive index
f^{90} – frequency

$$K = \rho c_l^2 - \frac{4}{3}\mu$$

Bulk modulus

Shear modulus

$$G = \rho c_t^2$$

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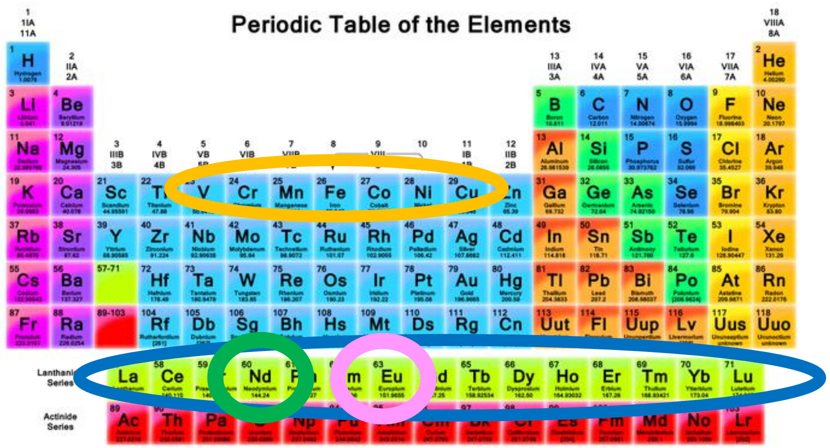
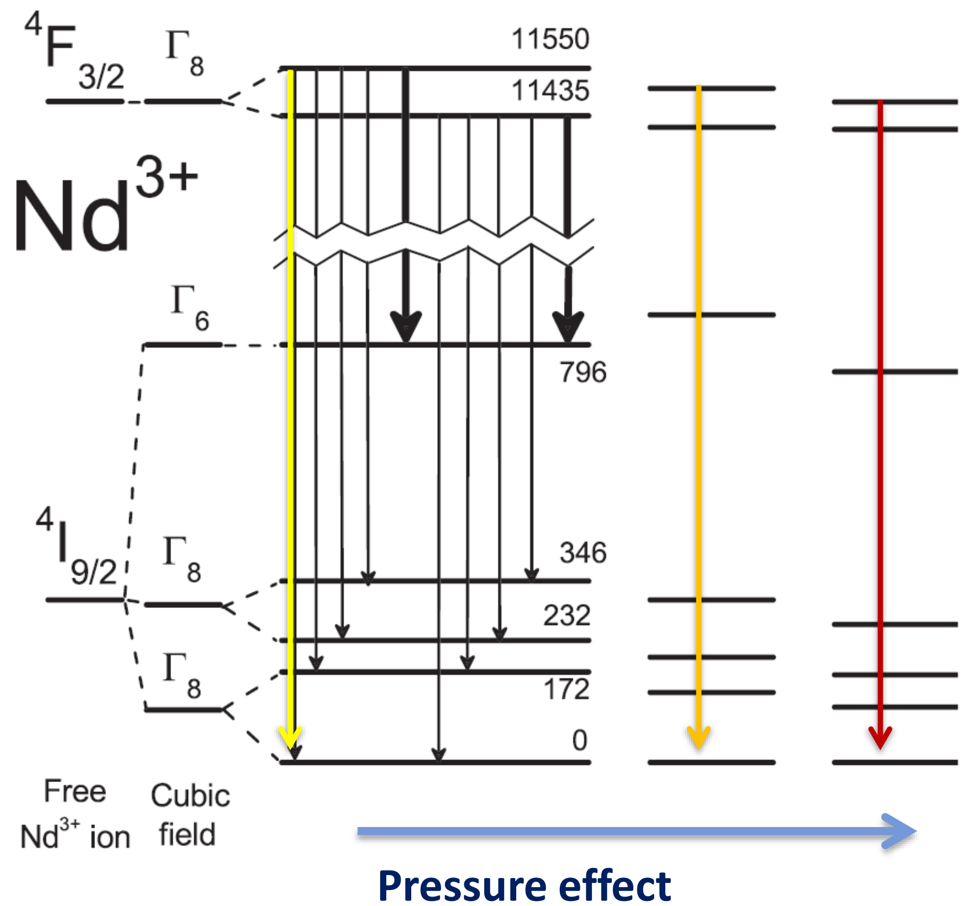
Luminescence of Rare Earth Elements



Emission frequency is a function of the crystalline field around the element.

Local gauge



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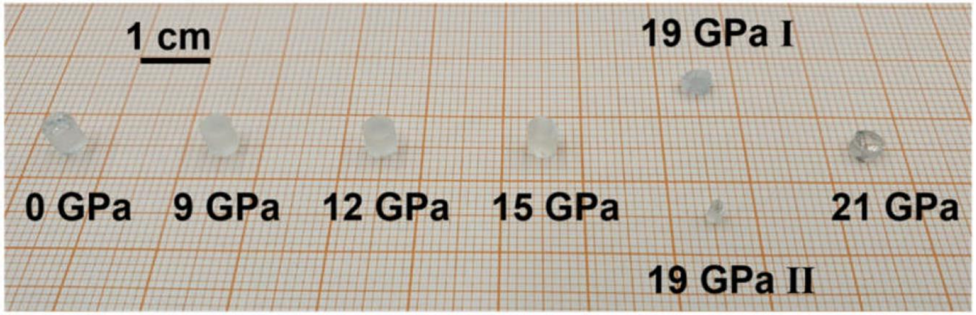
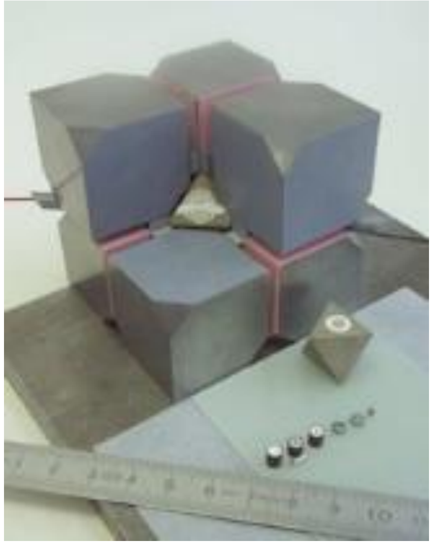
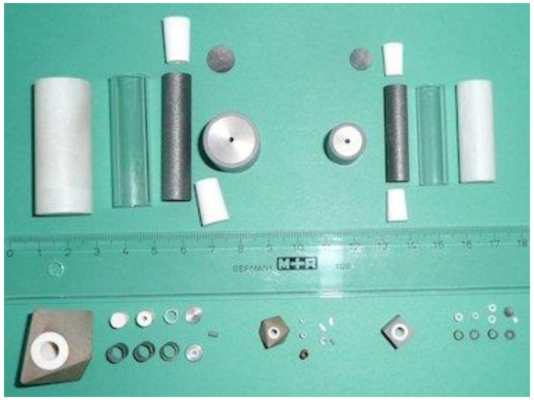
Densification of window glass



F. Werr et al.
Materials **2021**, *14*, 1831





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BGI Bayerisches Geoinstitut

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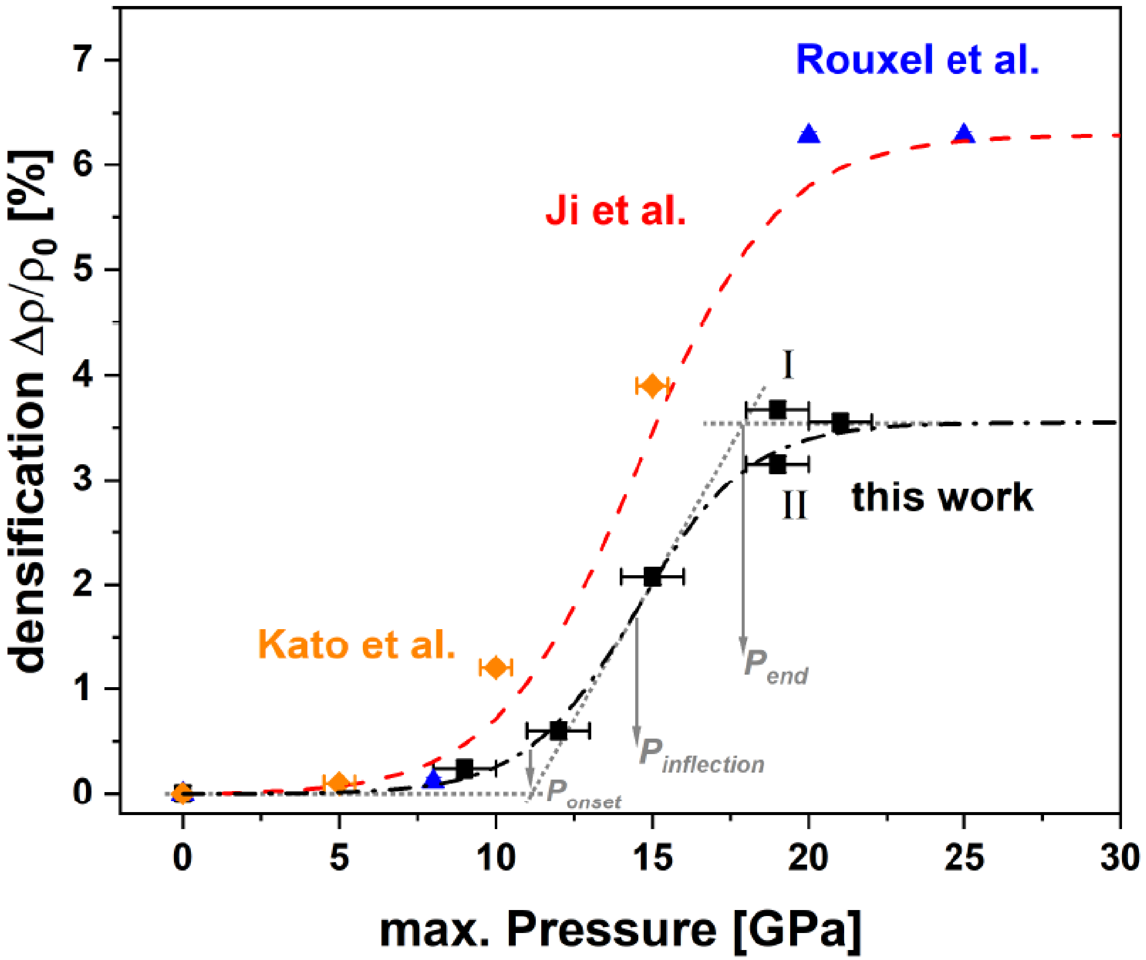
Evolution of the density



Our study differ significantly from previous one. Lower densification and shift to higher pressure:

- More precise measurement of the density by the floatation method
- Better hydrostatic conditions

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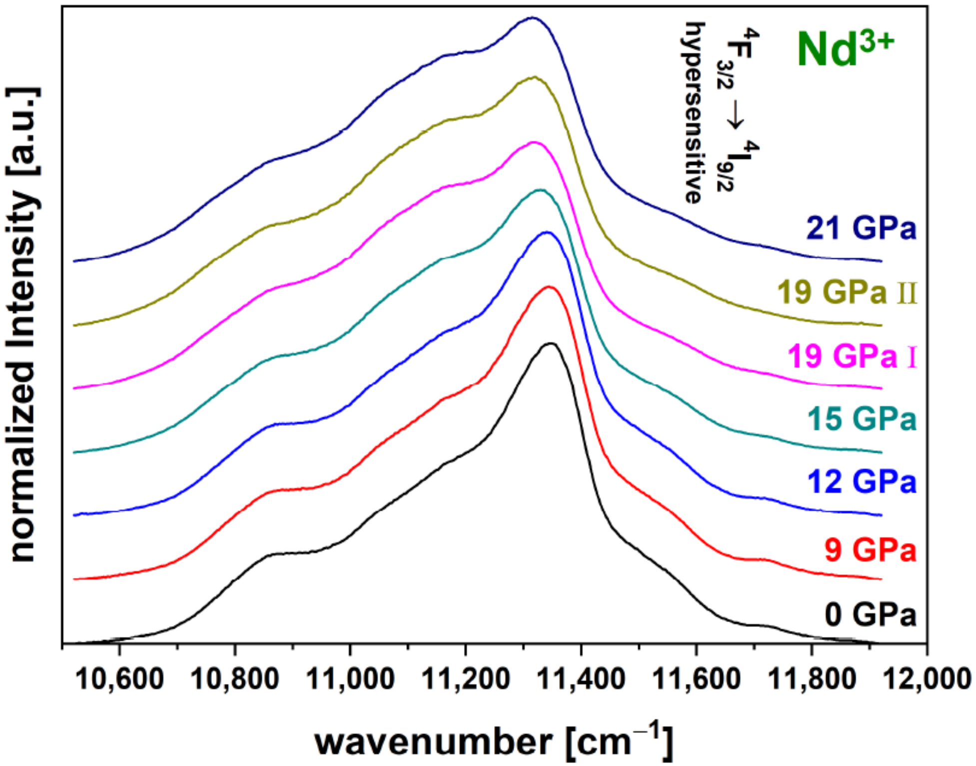
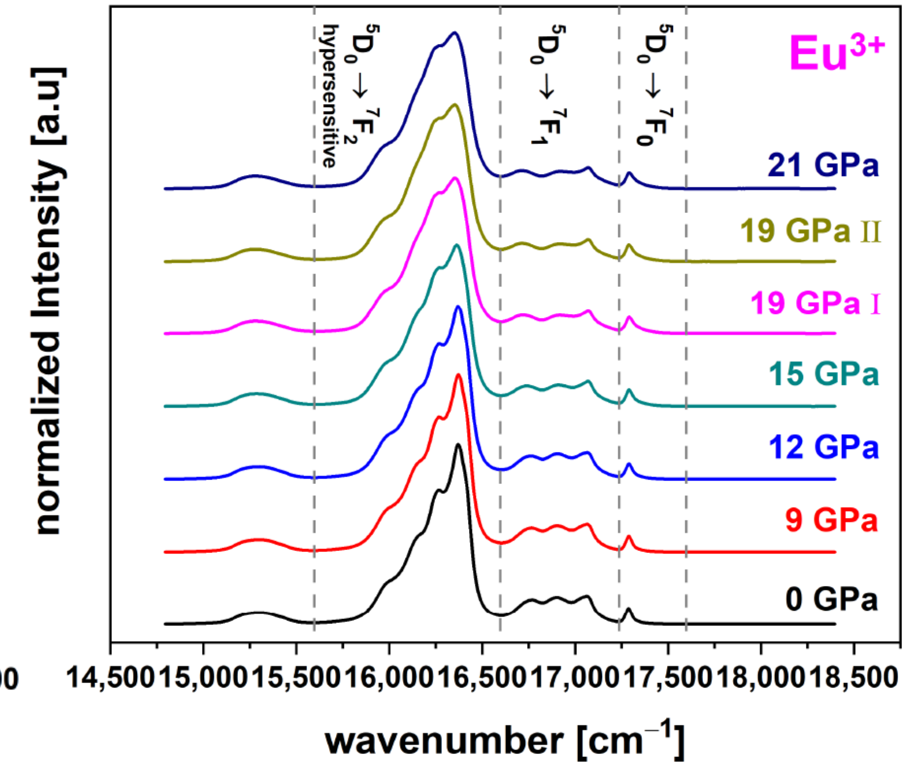
Luminescence and densification





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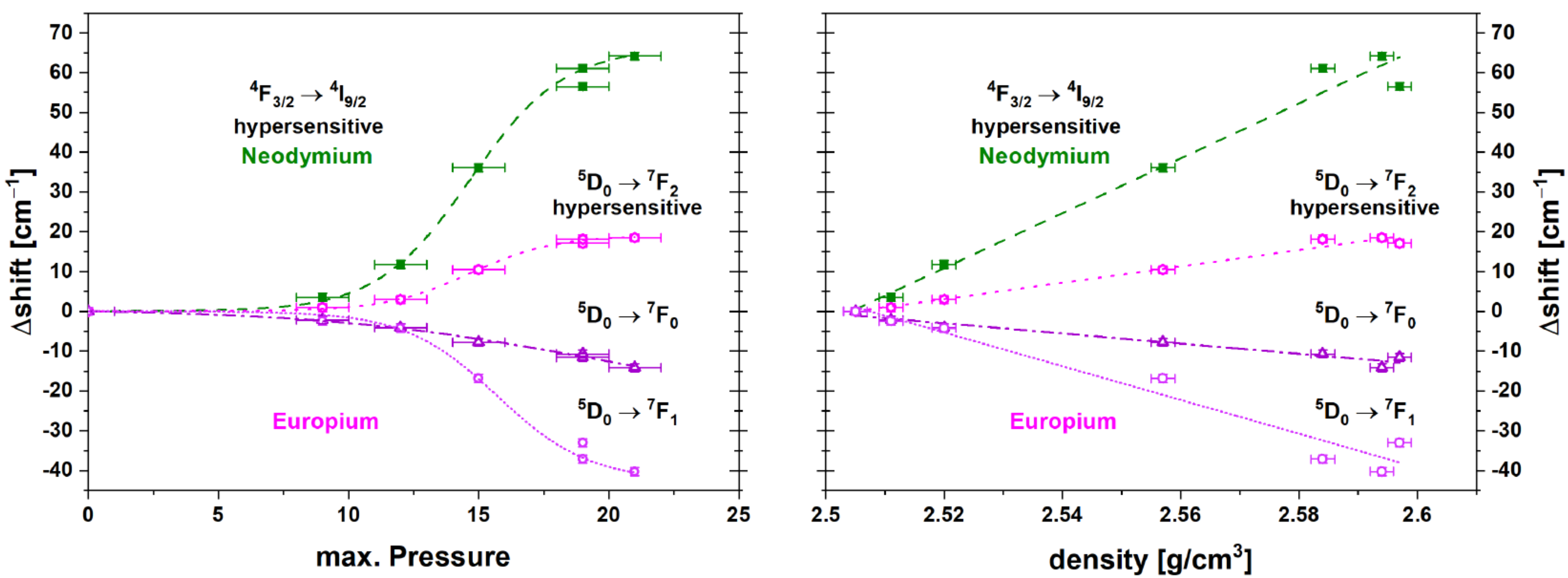
Full reorganization of all the sub levels, complicated shift variations

Fit complicated and not robust

Centroid integration method more stable

$$\frac{1}{2} = \frac{\int_{\omega 1}^{\sigma} I_{spectra}(\omega)\, d\omega}{\int_{\omega 1}^{\omega 2} I_{spectra}(\omega)\, d\omega}$$

Luminescence and densification



Same sigmoidal function than density with the position for the inflection point

Linear behavior in function of the density

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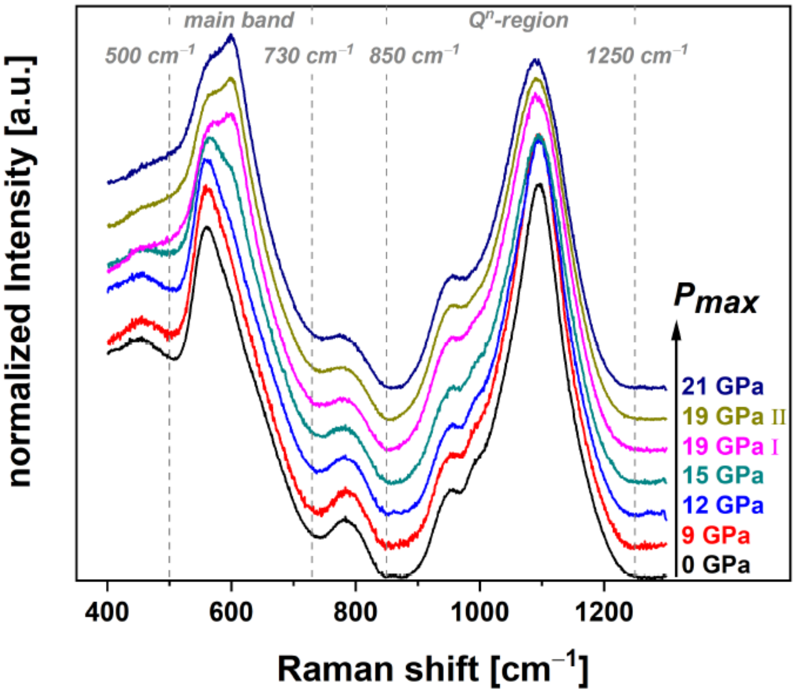
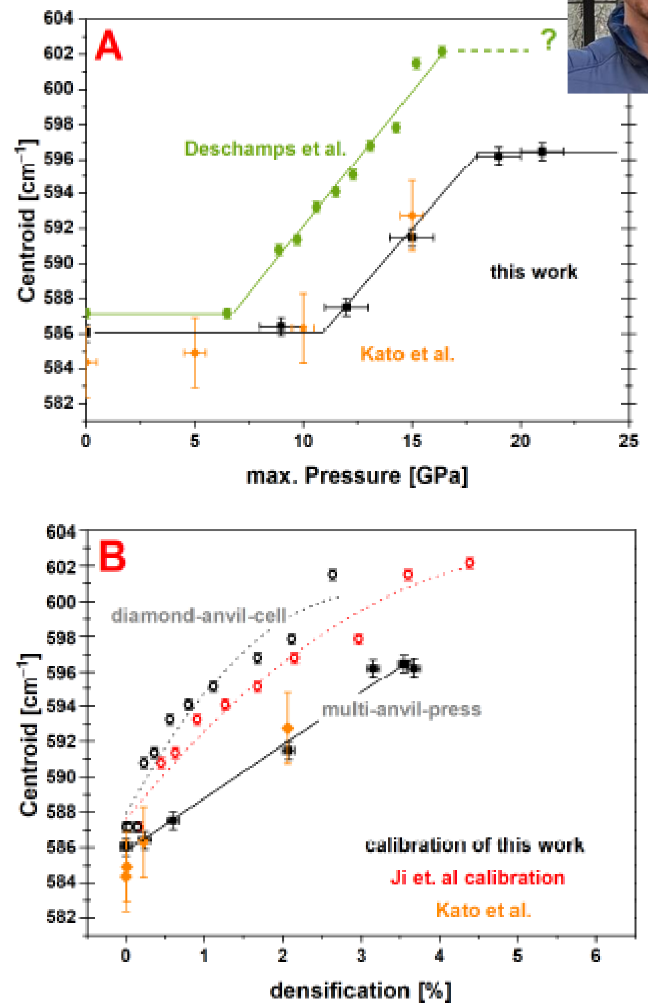
Raman and densification





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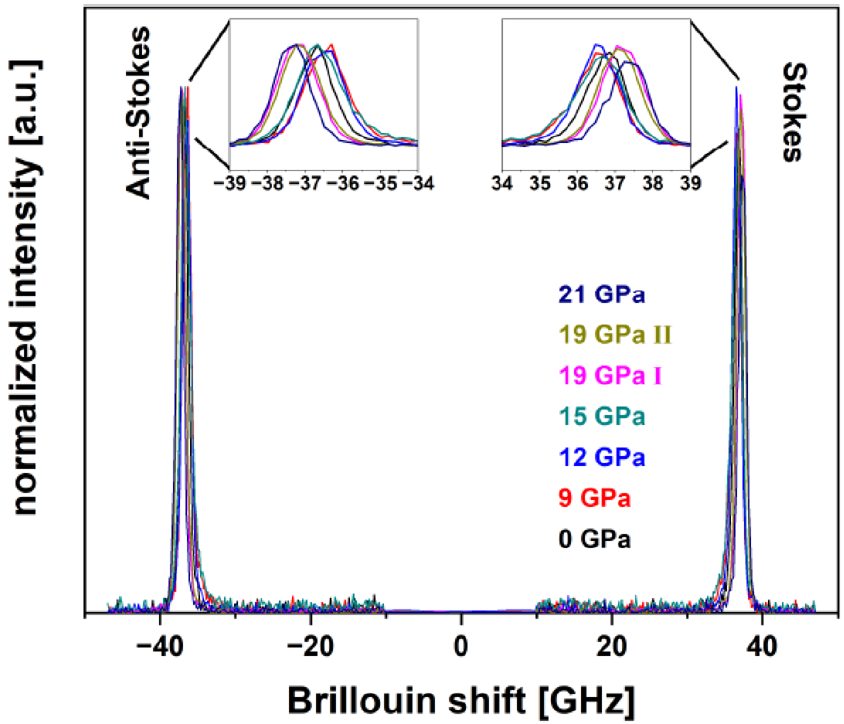
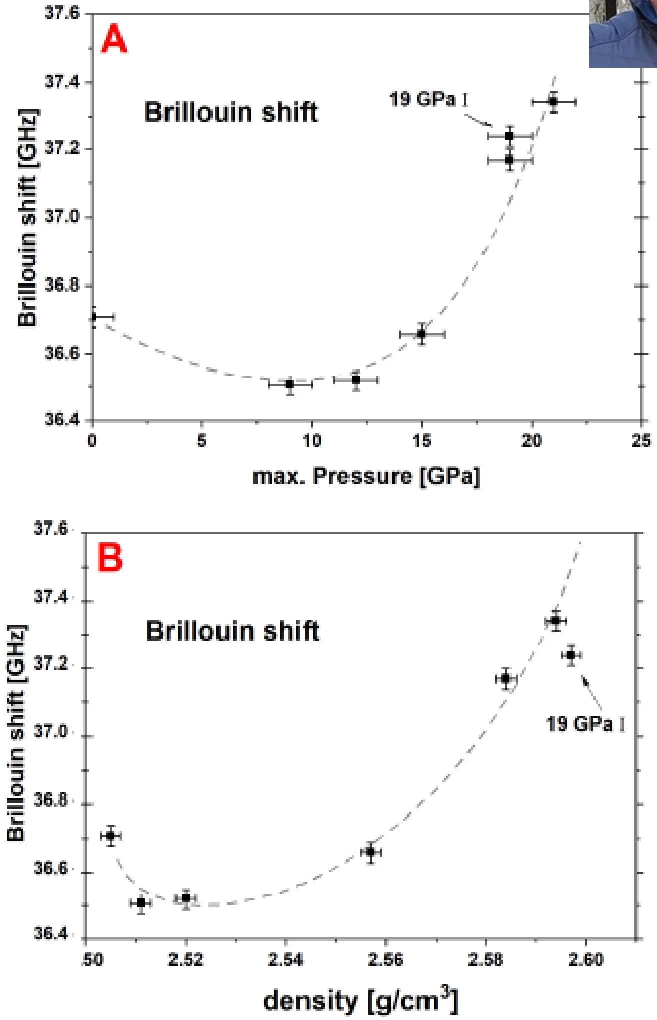
Brillouin and densification





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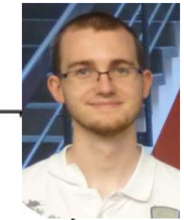
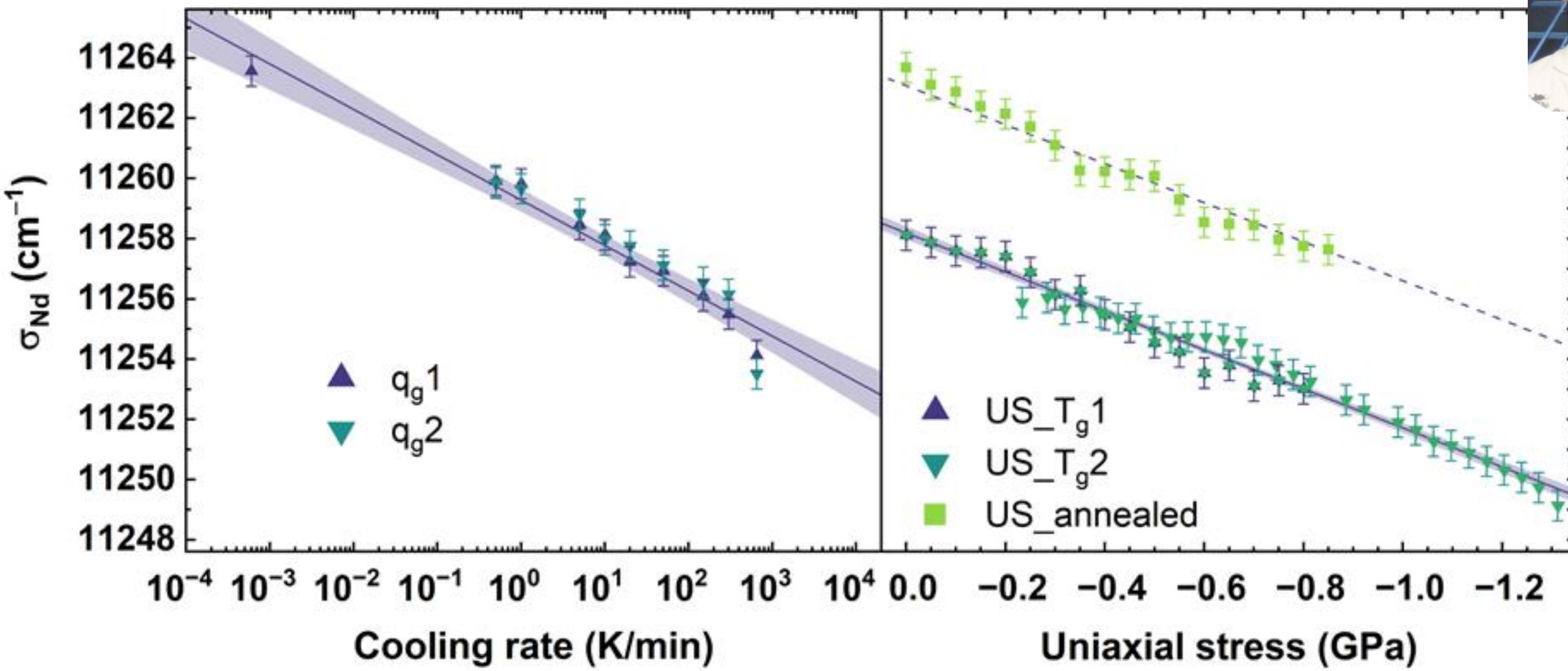
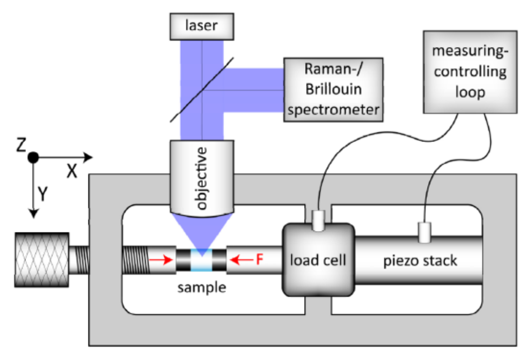
Changing the density differently







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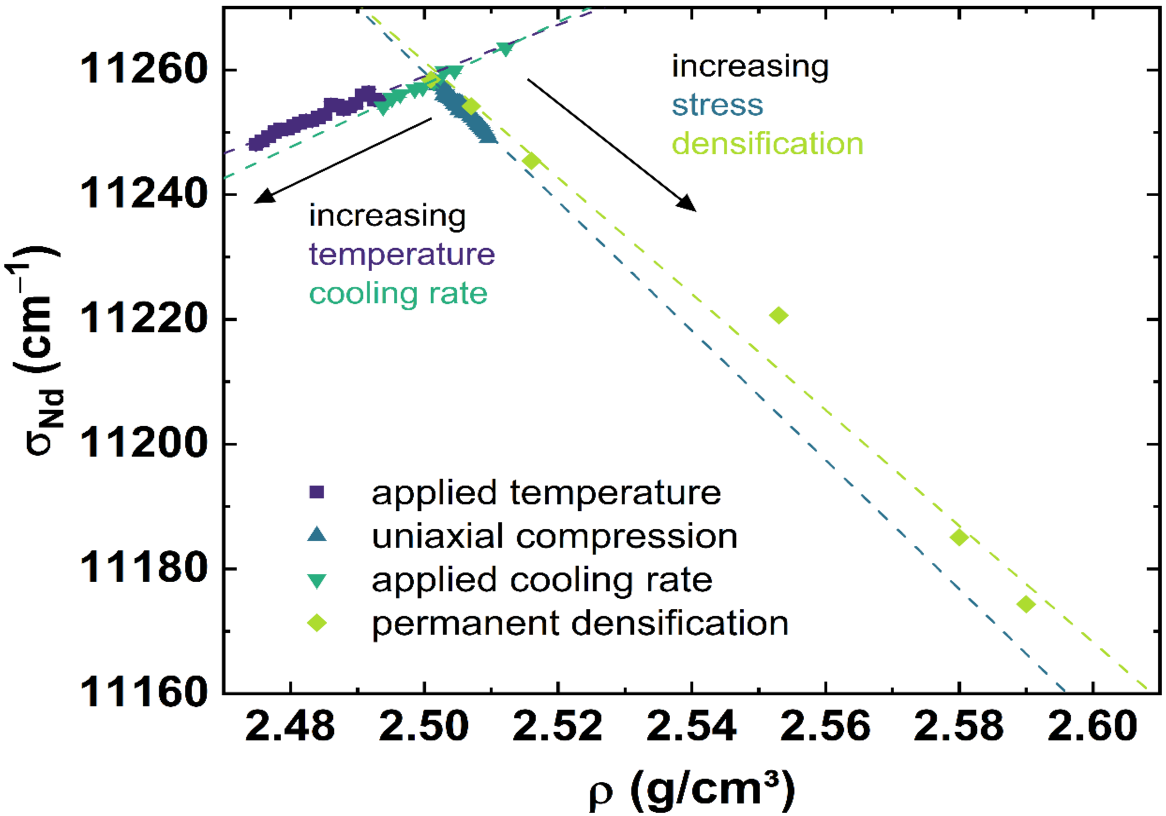
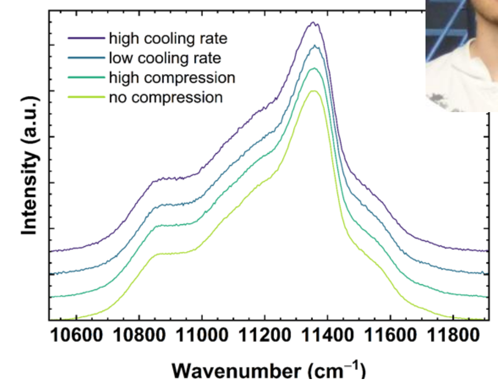
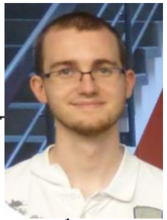
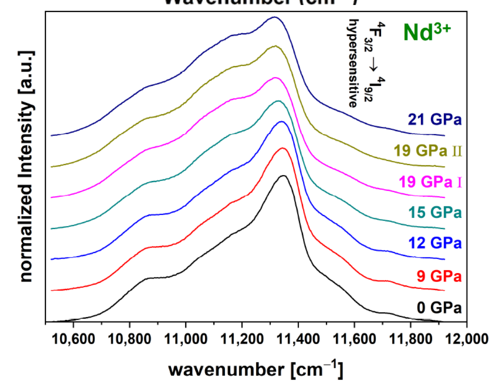
Nd^{3+} emission versus density









Two lines :

- thermaly activated changes: cooling rate and increasing T
- Pressure induced: uniaxial compression and plastic densification

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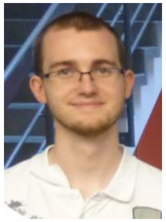
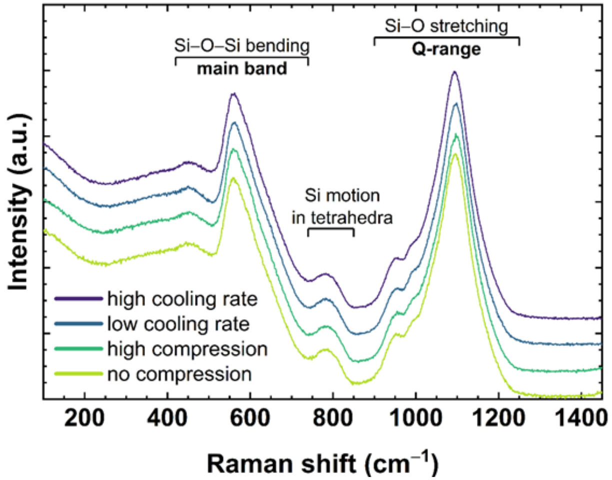
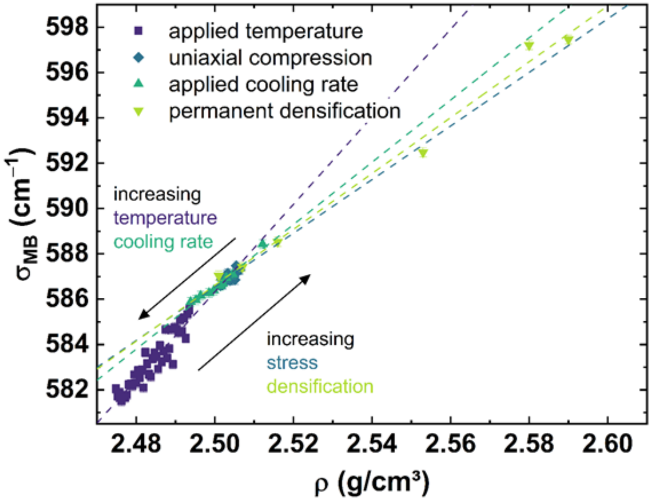
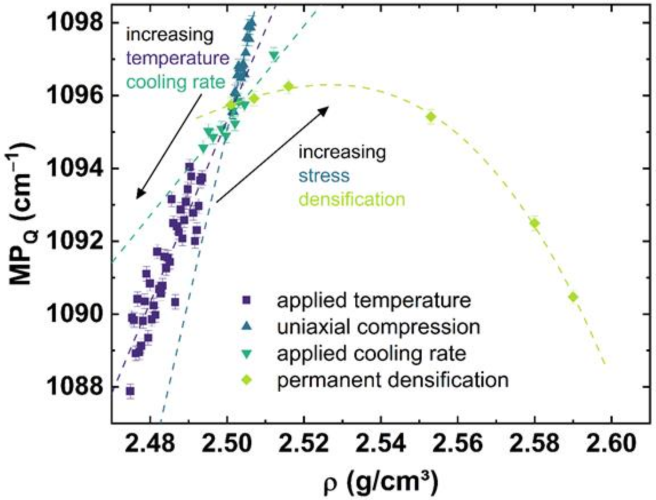
Raman versus density









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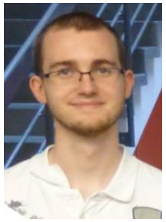
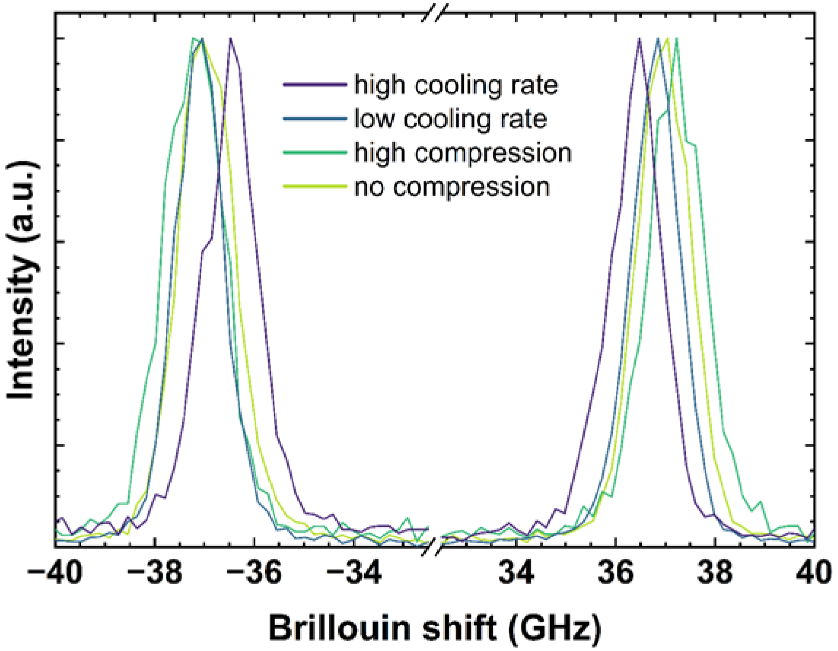
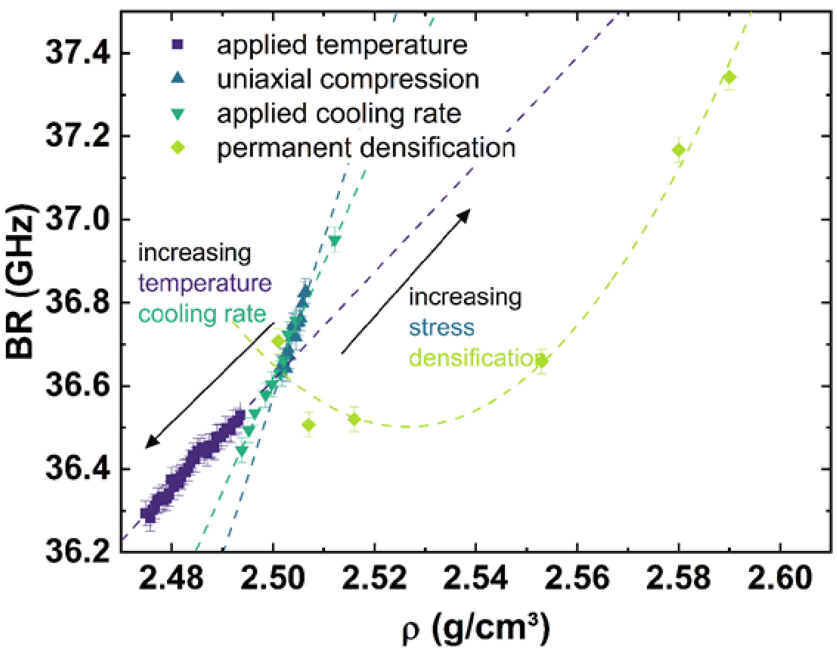
Brillouin versus density







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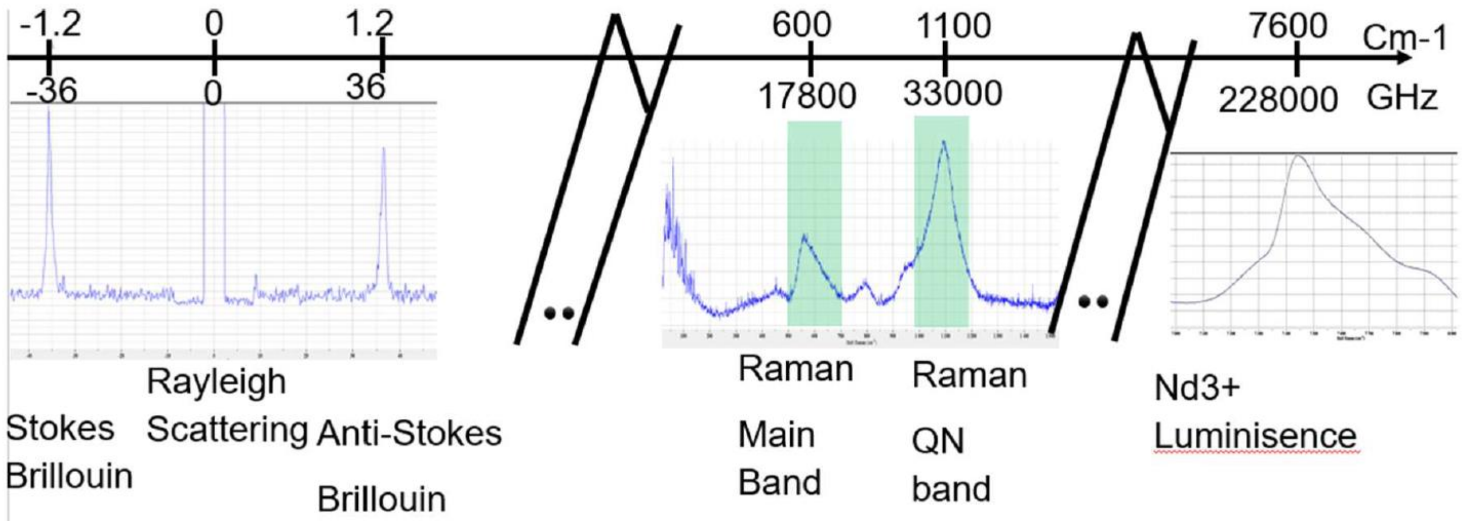
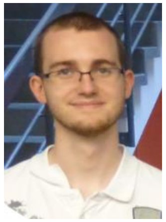
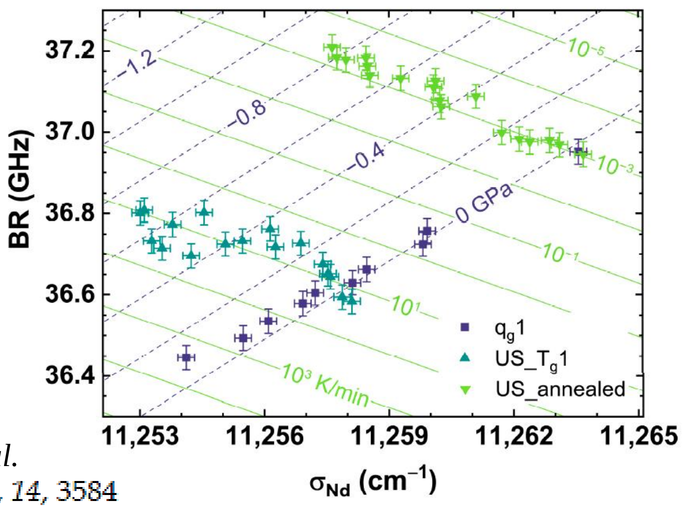
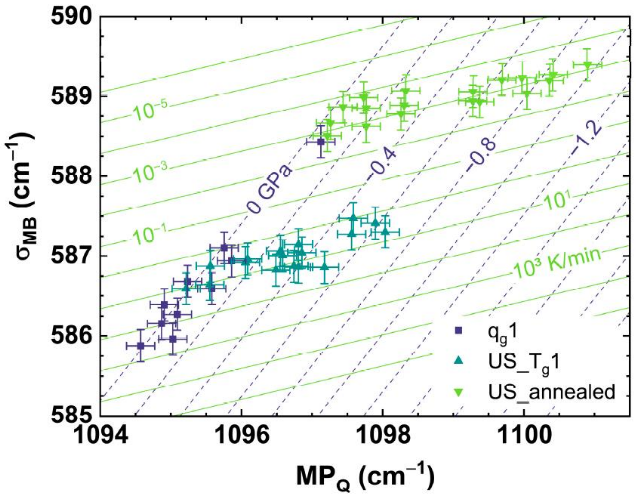
Cross the informations









M. Bergler et al.
Materials **2021**, *14*, 3584

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Fibers formation conditions

ISG International Standard Glass
60.2 SiO_2 -16.0 B_2O_3 -12.6 Na_2O -3.8 Al_2O_3 - 5.7 CaO -1.7 ZrO_2

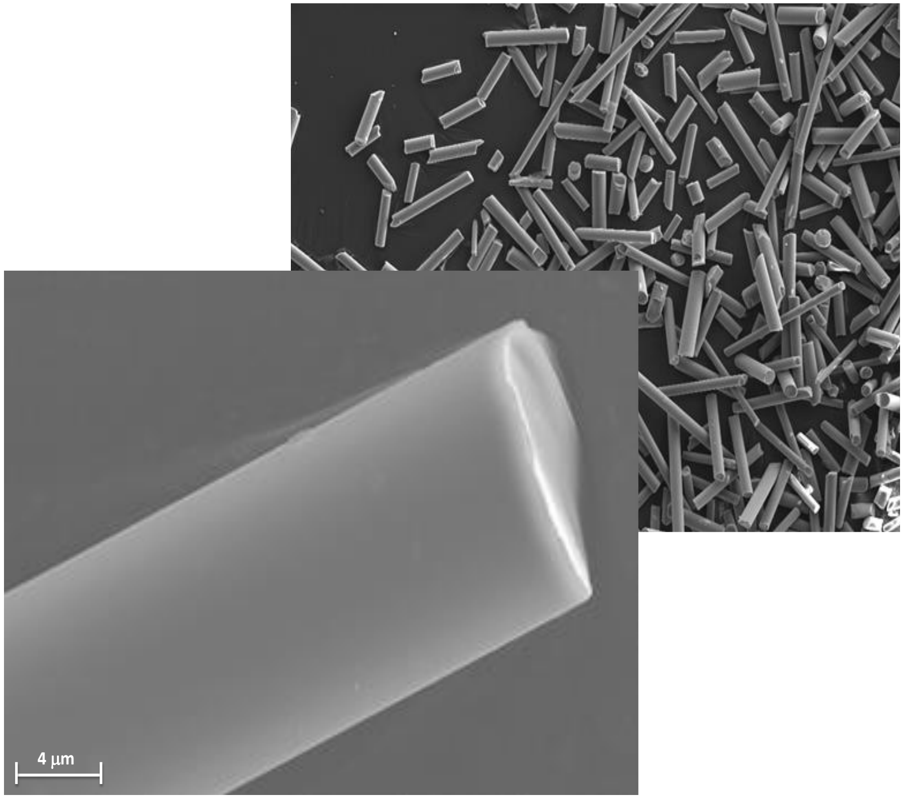
Analogy between self irradiation and high fictive temperature

Difficult to produce large irradiated samples

Fibers a good way to get hyper quenched samples

What is the cooling rate or fictive temperature of the fiber ?

Here difficult to do direct DSC measurement



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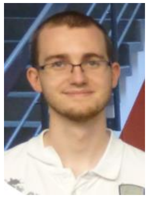
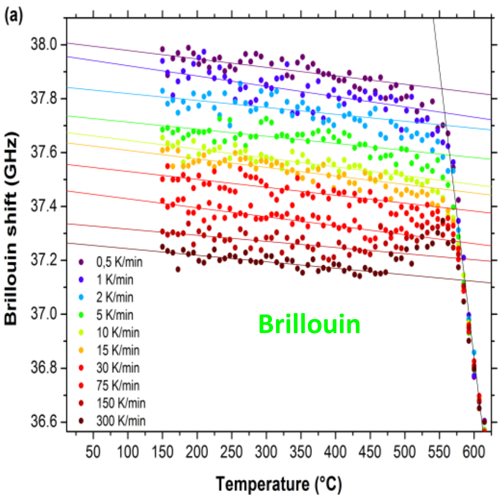
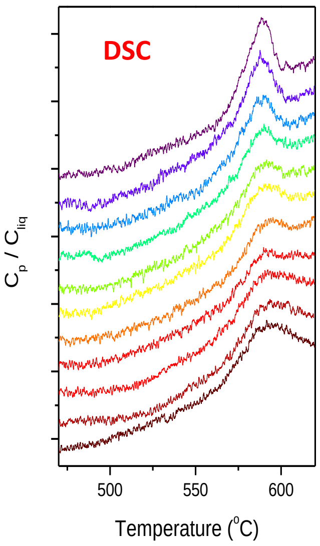
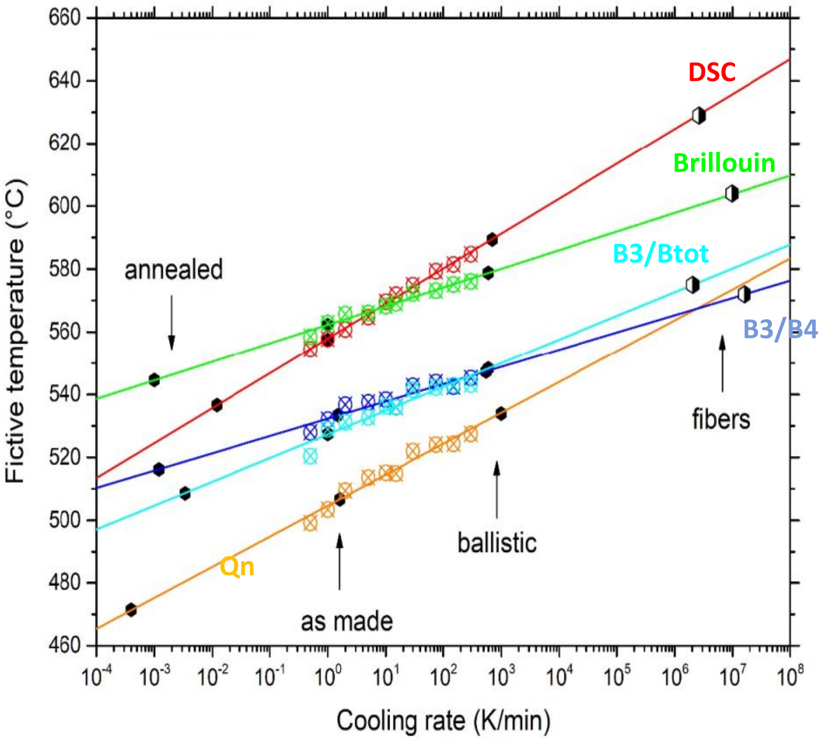
Calibration and determination of the cooling rate

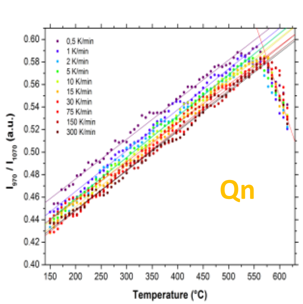


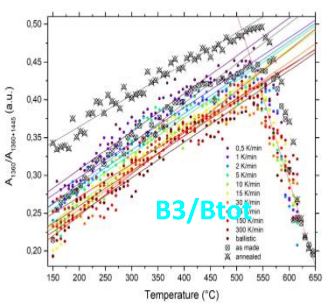


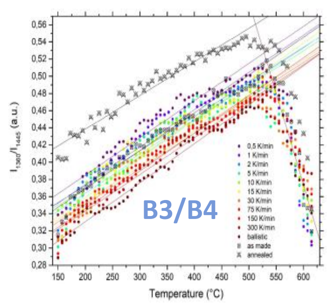




Raman

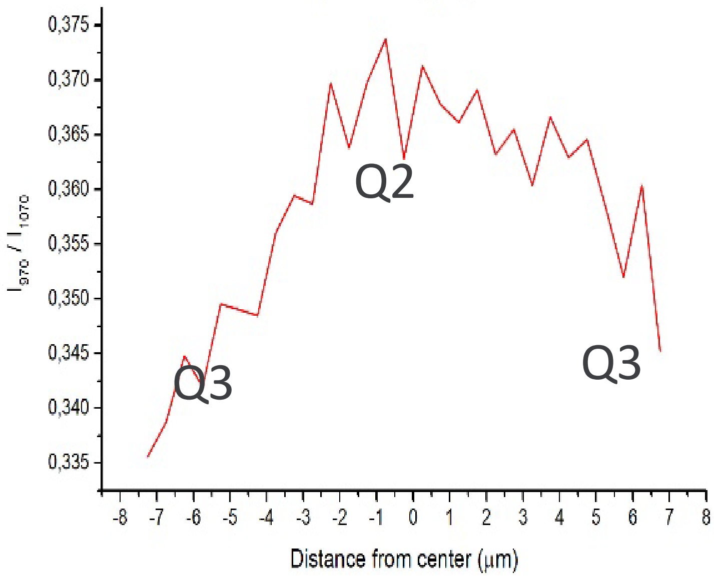


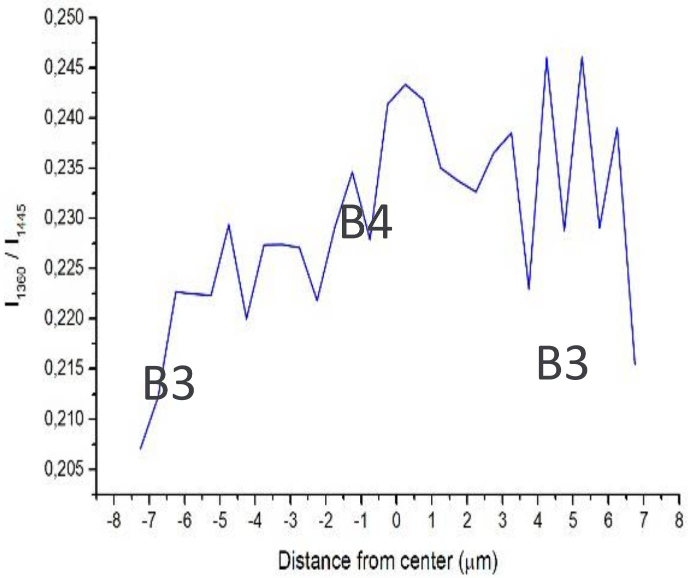


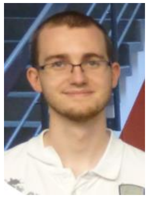


Change of the Qn then B and at the same time long distance interaction volume and bond breaking

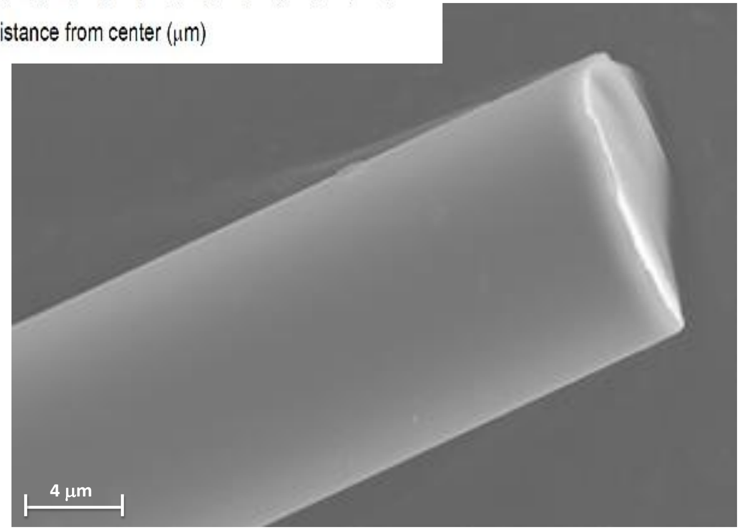
Local evolution of the cooing conditions







Strong signature of the evolution of the cooling rate in the diameter of the fiber



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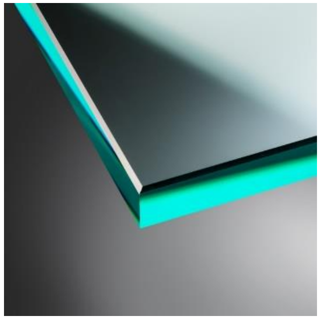
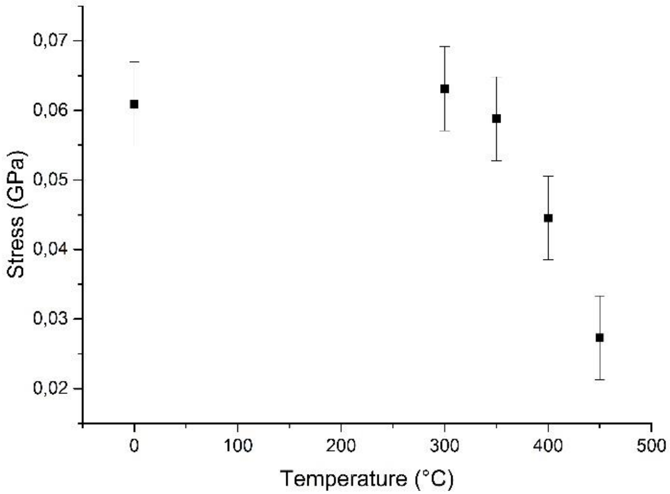
Relaxation of a tempered glass

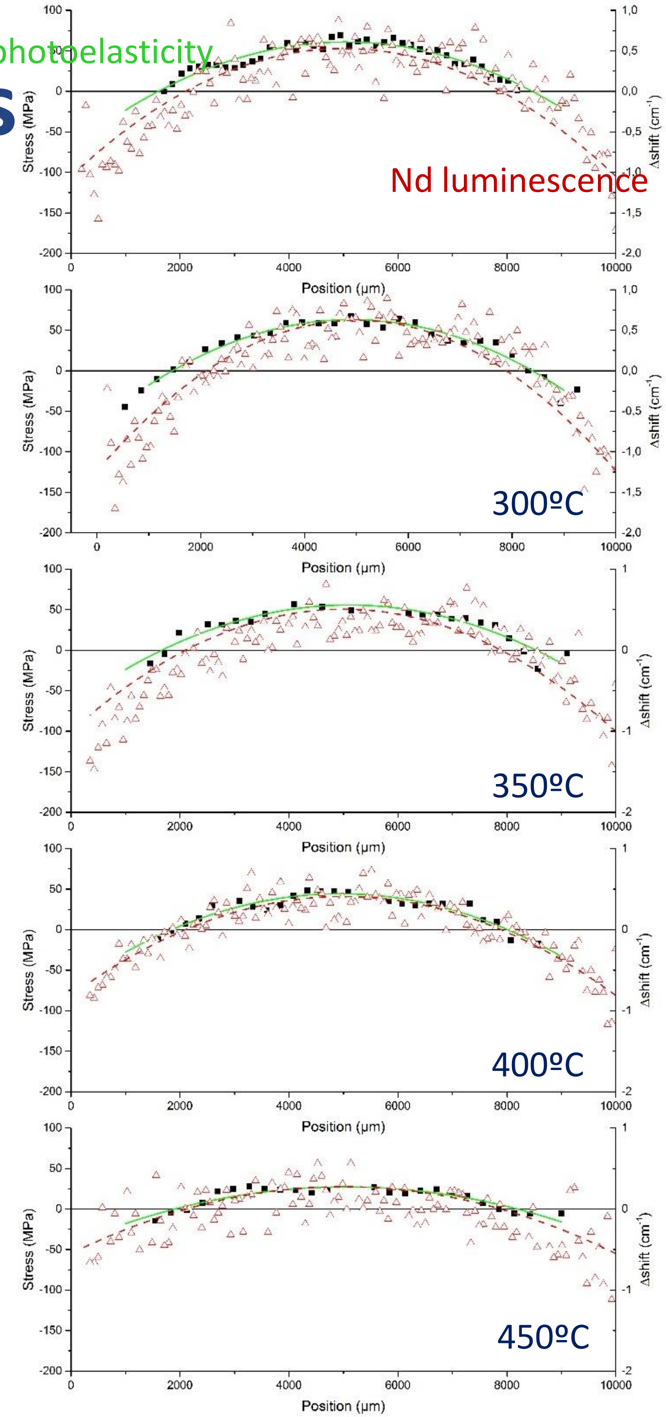
Very good agreement between photoelasticity and luminescence results of Nd

Relaxation of glass at 10^{14} poise around 500ºC

Relaxation of tempered glass starts at 350ºC
Effect of residual stresses







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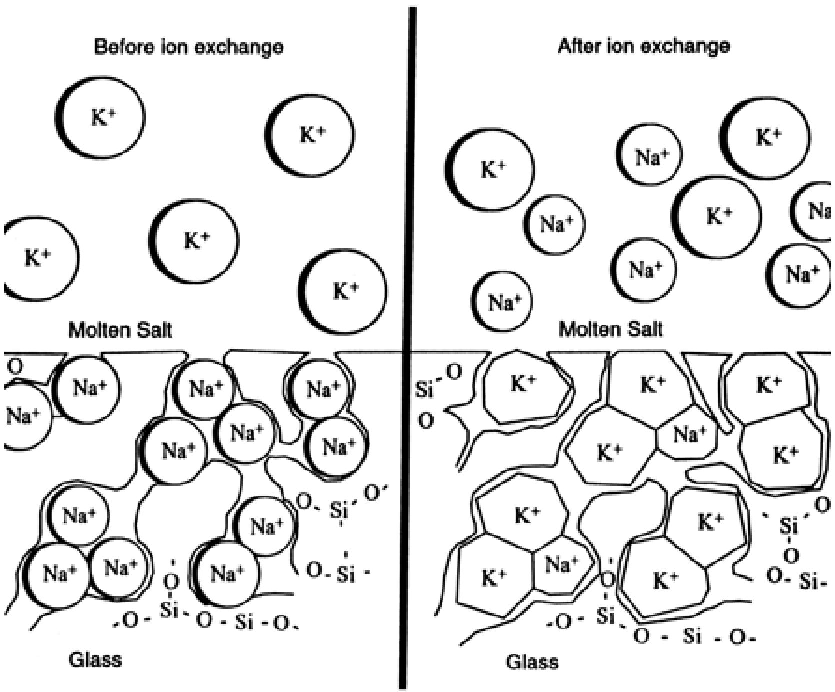
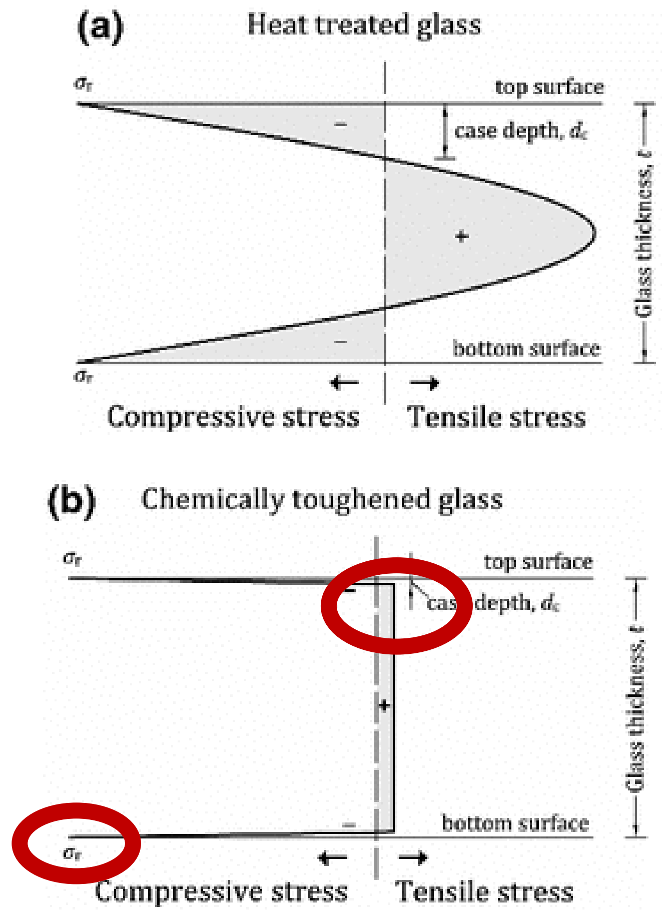
Chemical Tempering principle



Vashneya et al – 2010



Datsiou, Kyriaki Corinna & Overend, Mauro, 2017

Case depth (CD) or Depth of layer (DOL), and compressive stress (CS) at the surface

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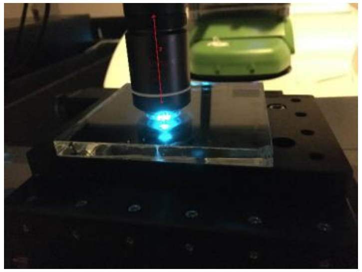
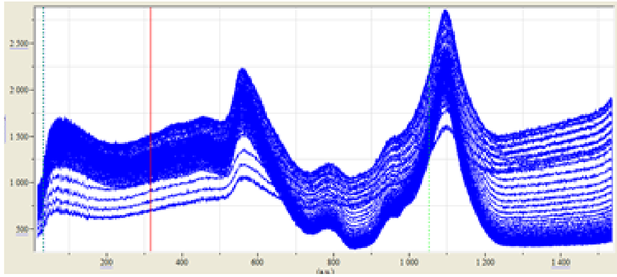
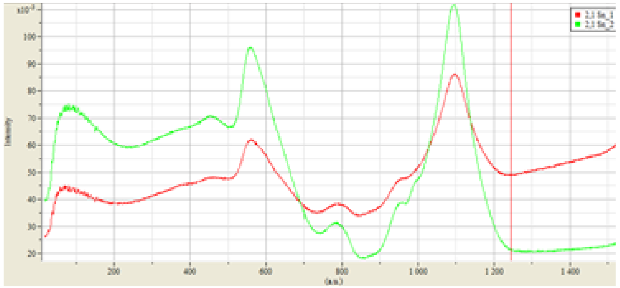
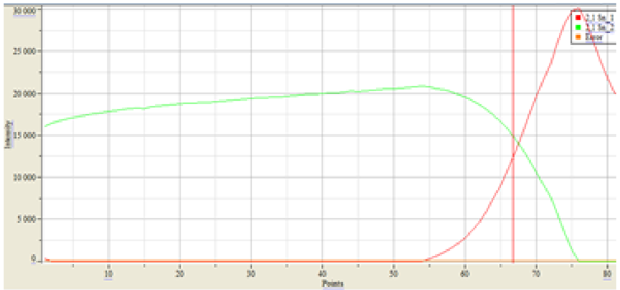
Cation exchanged glasses

Calibration of K-rich end member





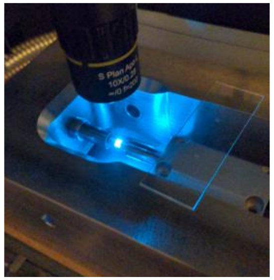


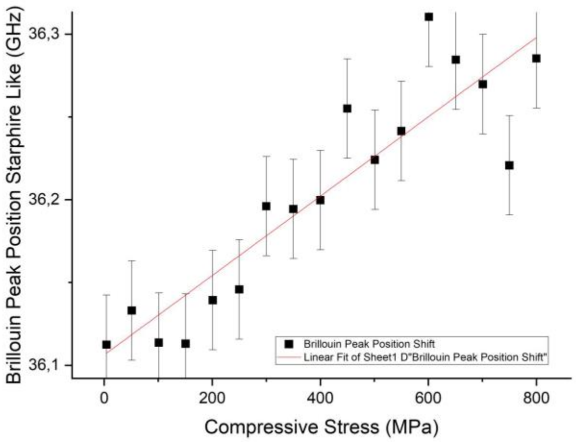


Depth profile

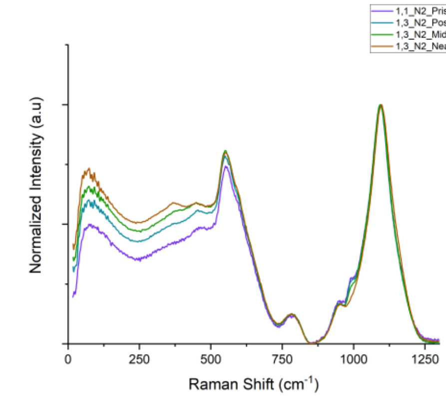
PCA
2 components

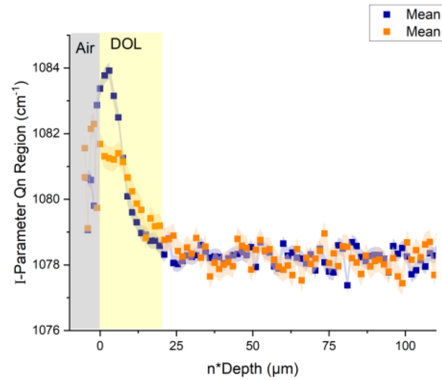
%
 Chemical
variation

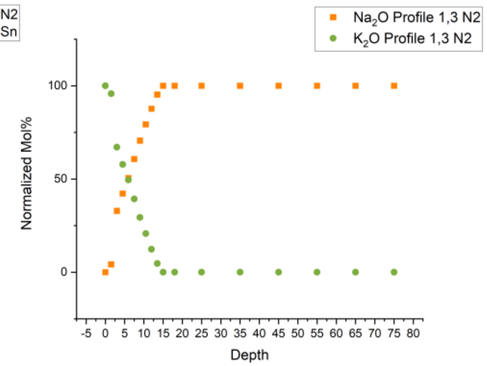


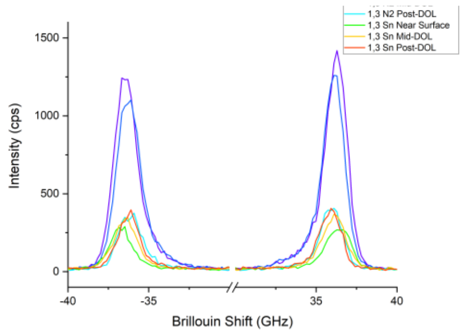


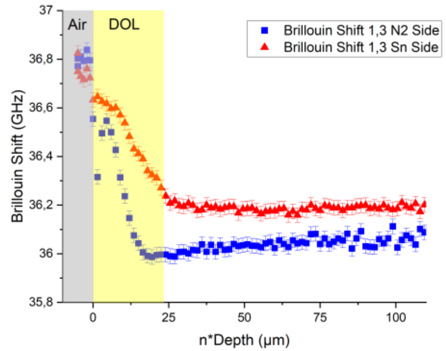
Cation exchange glasses

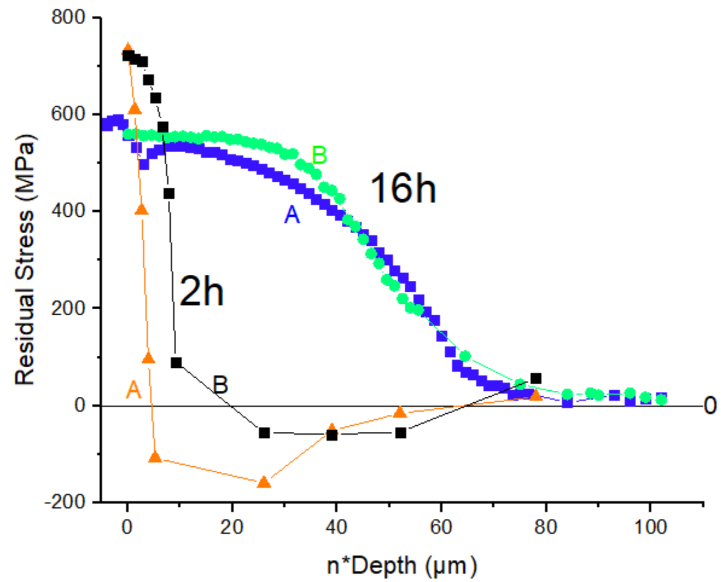












$$\sigma = \frac{BS_{measured} - xB_{K^+} - (1-x)B_{Na^+} + \delta}{(1-x)A_{Na^+} + xA_{K^+}}$$

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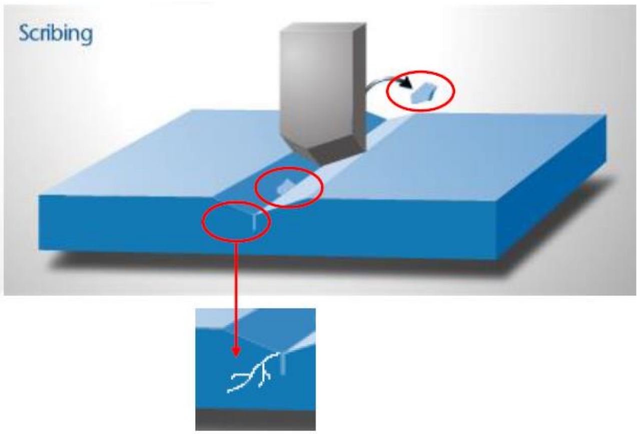
Outlines

- Weight-lightening of glass some specific needs
- How glass register its formation and internal stress conditions
- How can we read it
- Applications Internal strength
  - Cooling rate of glass fibers
  - Tempered glass
  - Cation exchanged glasses
- Applications Exoskeleton
  - Cutting glass with short pulse lasers
  - Cooling rate around short pulse laser modified area
  - Aerosol deposition

Methods of cutting glass

The glass is scribed with a diamond or hard metal wheel and afterwards separated at the flaw line

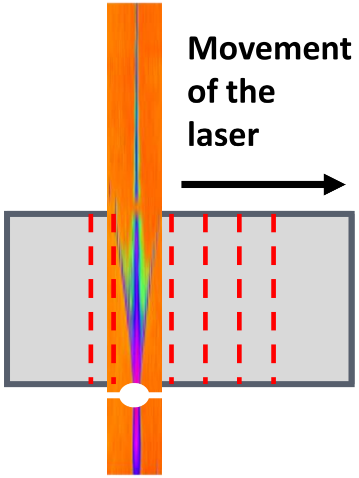
- cut not necessarily perpendicular to the surface
- chippings and micro cracks
→ grinding of the edge necessary
- limited to the cuttable geometries

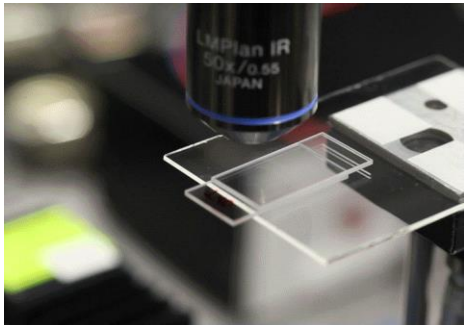


Hermanns C., 2
Available at: www.lehigh.edu/imi [Acessed 21 March 2018]

Ultra-Short-Laser-Pulses (Nd:YAG-laser)

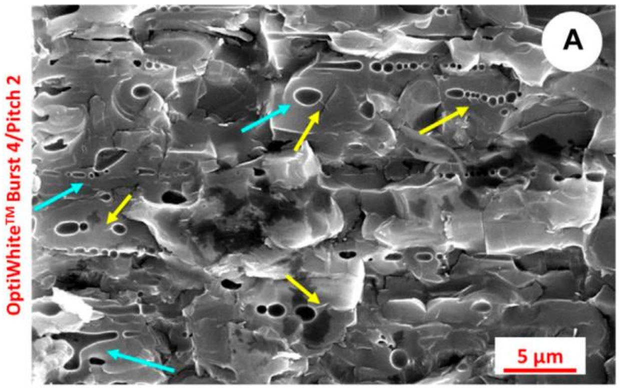
+ surface toughened glass is cuttable
+ free form cutting
+ small heat affected zone
+ ground like edges



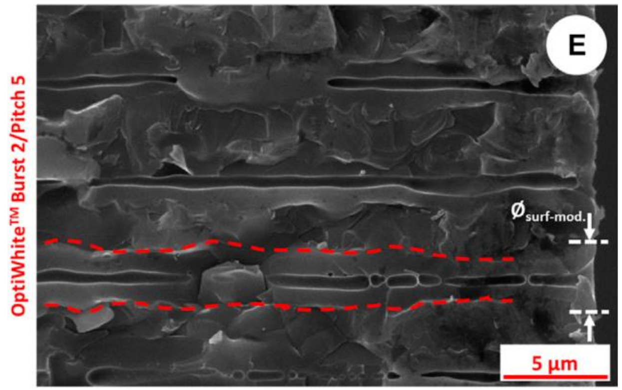


SEM of modified regions

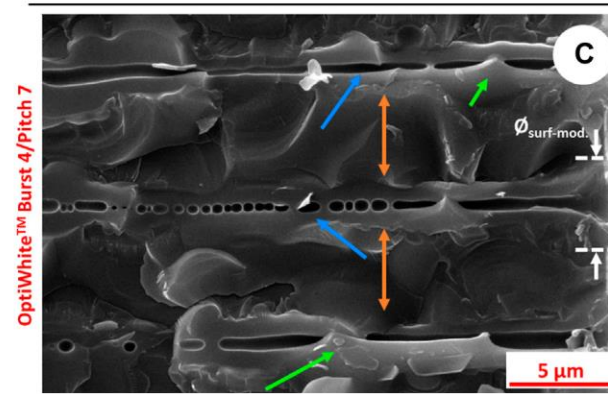
Burst 4 / Pitch 2

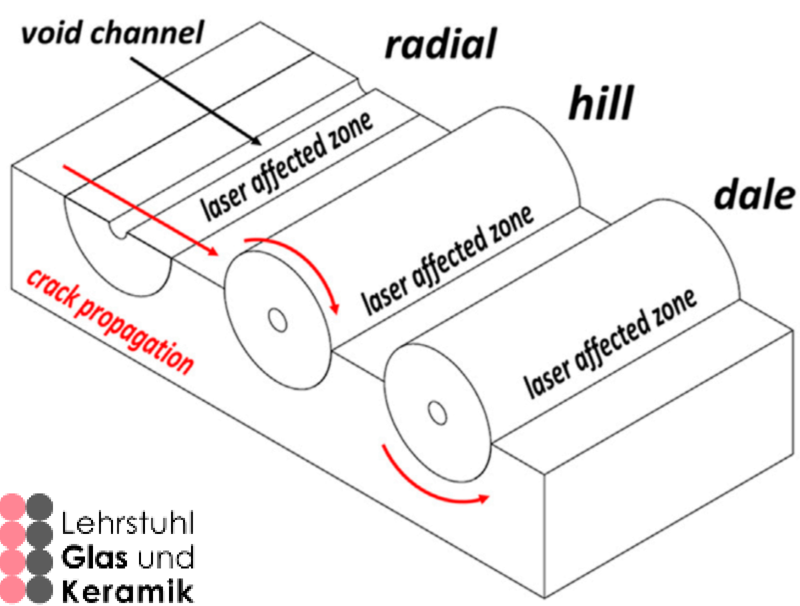


Burst 2 / Pitch 5



Burst 4 /

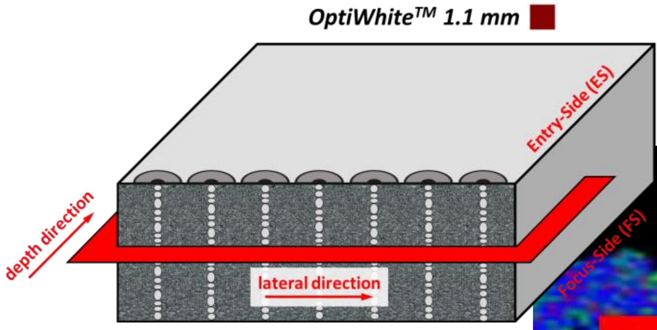


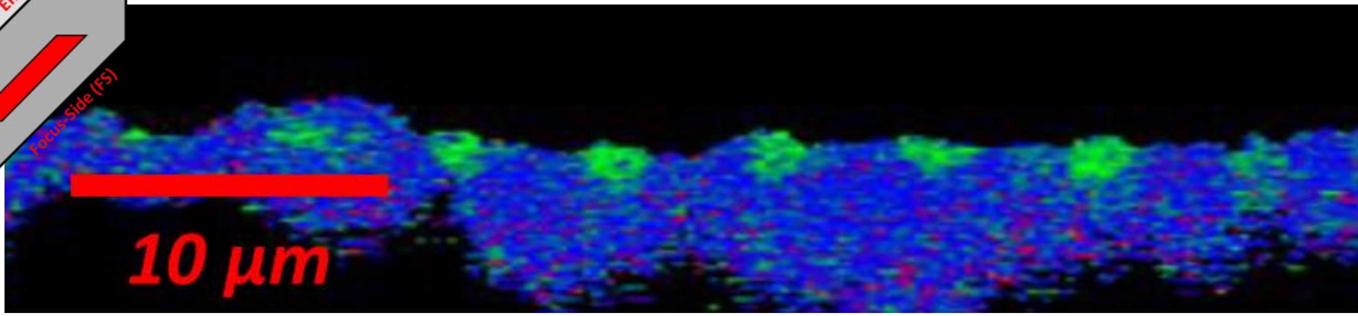


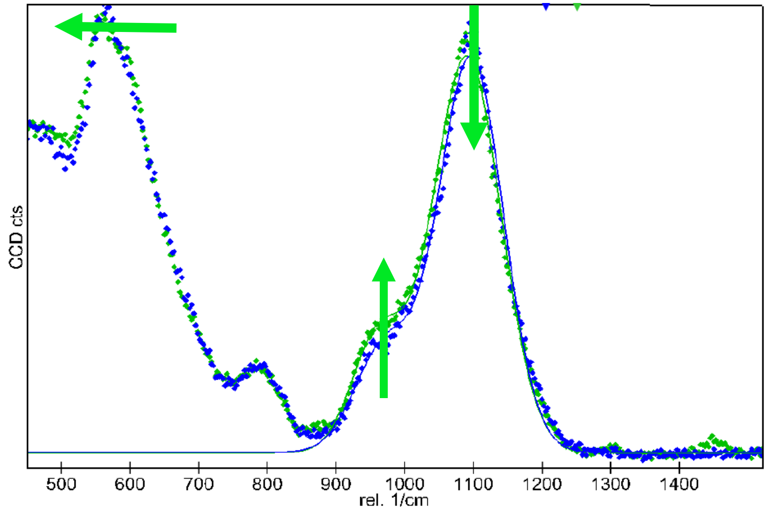
Two dinstict cracks population

- Throw the affected zone
- Around the affected zone

Raman mapping of the laser modified zone



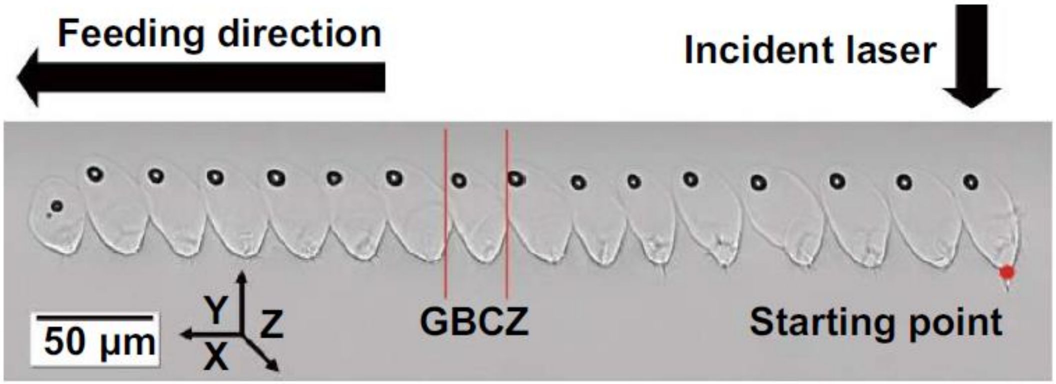


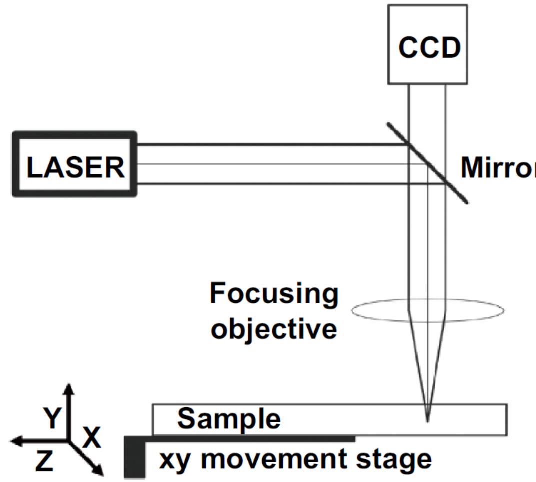


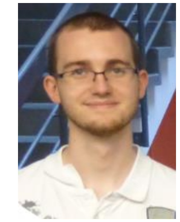
Prominent effect due to an increase of the cooling rate

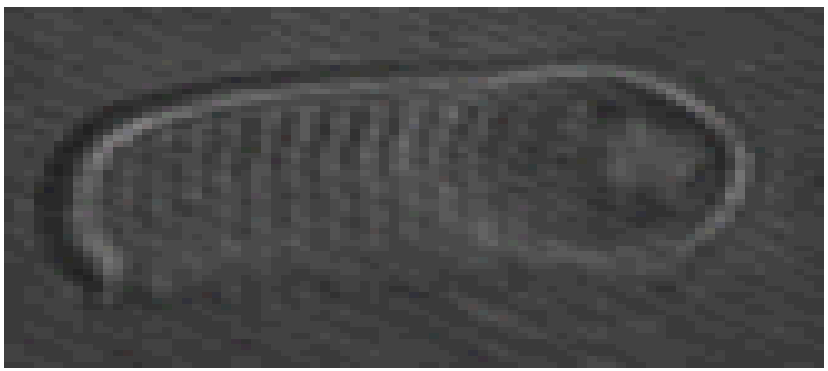
Residual stress cannot be excluded

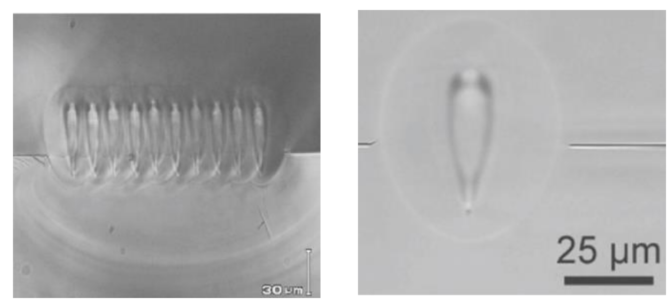
Modification of SiO_2 glass with picosecond laser











J. Bovatsek, A. Araia, C.B. Schaffer, in *Proceeding of the CLEO/Europe—EQEC2005*, vol. 1, 2005

Continuous or spot welding

Nd:YVO4-laser, 10 ps, 1064 nm, 2MHz, 3W

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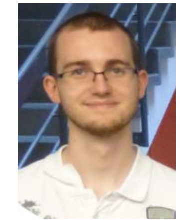
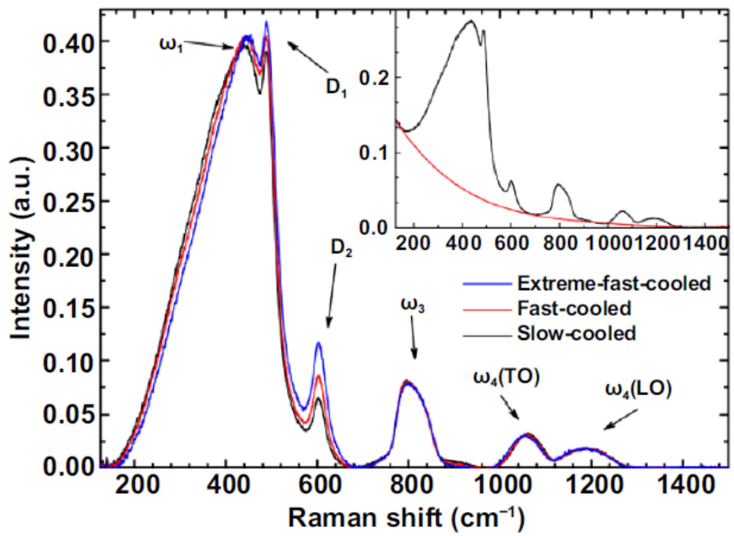
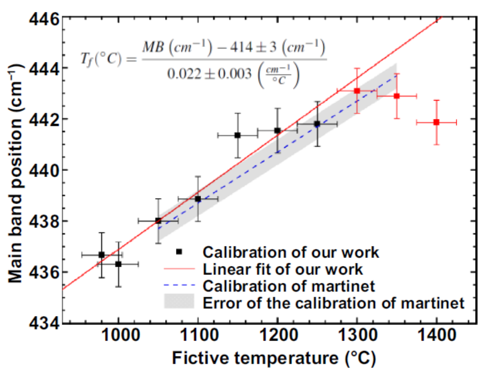
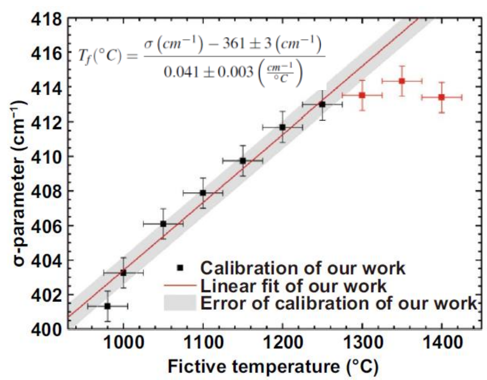
Accurate calibration with cooling rate

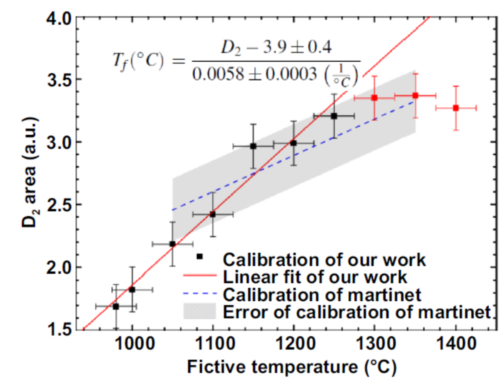




$$
\begin{aligned}
\log\left(q_g\left(T_f\right)\right) &= 13 - \log\left(\eta\left(T_f\right)\right) \\
&= 13 - A + \frac{B}{\left(T_f - T_0\right)} \\
&= -5.66 + \frac{19433}{\left(T_f - 364.15\right)}
\end{aligned}
$$

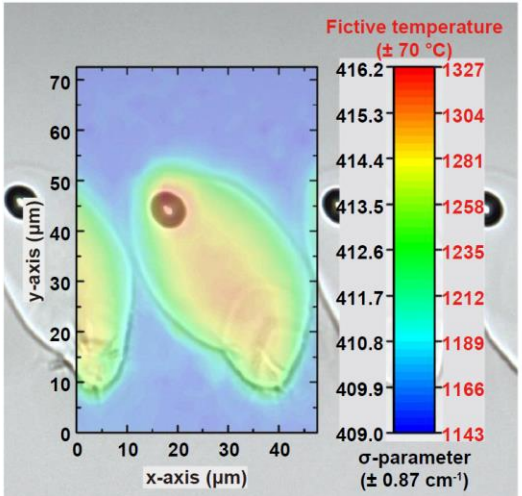




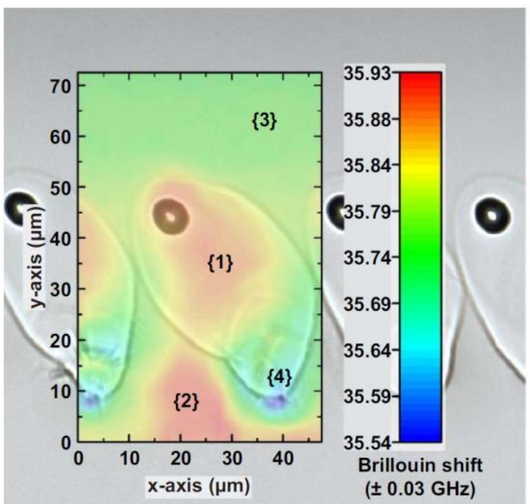


Coupling the spectroscopies

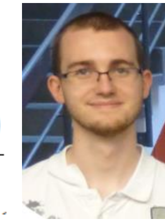
Raman

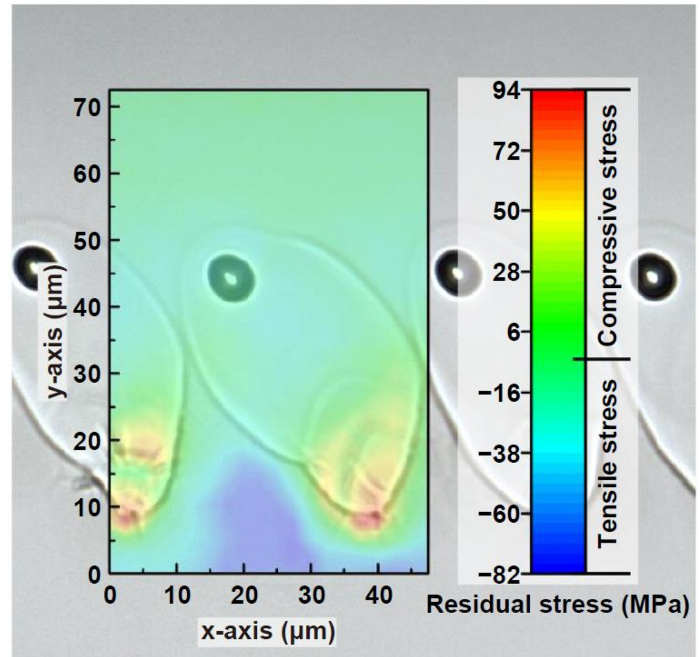


Brillouin



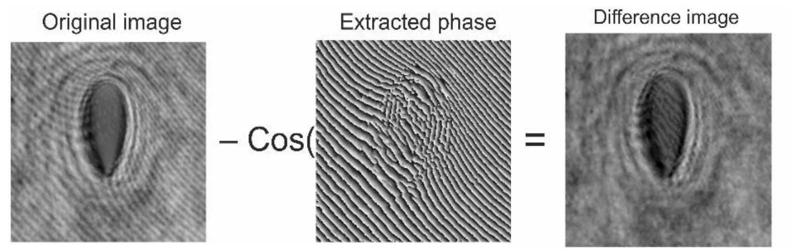
$$RS\ (GPa) = \frac{BR\ (GHz) - 0.0173\ \left(\frac{GHz}{cm^{-1}}\right) \cdot \sigma\ (cm^{-1}) - 28.6\ (GHz)}{-2.5\ \left(\frac{GHz}{GPa}\right)}$$

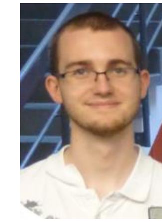


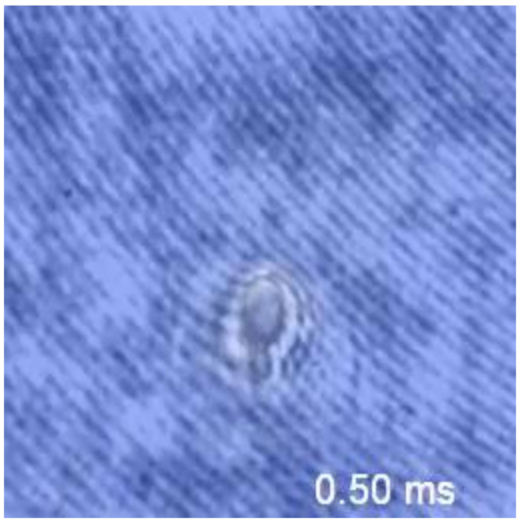


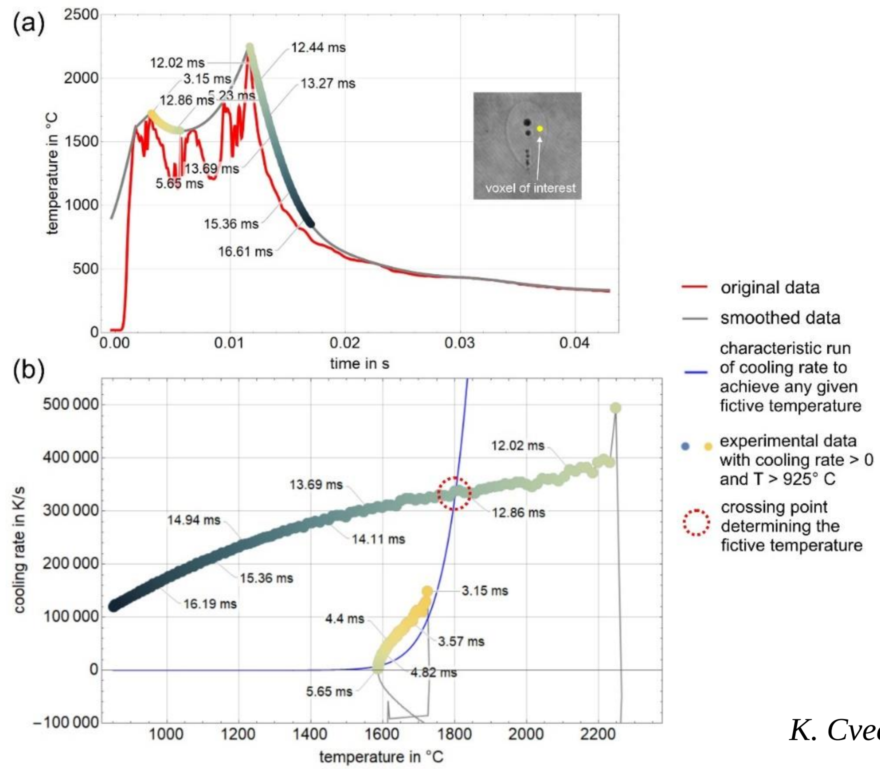
Possibility to determine residual stress in the modified region

Modification laser stationnaire









Using the local change of the refractive index to trace the cooling rate

K. Cvecek et al. 2020

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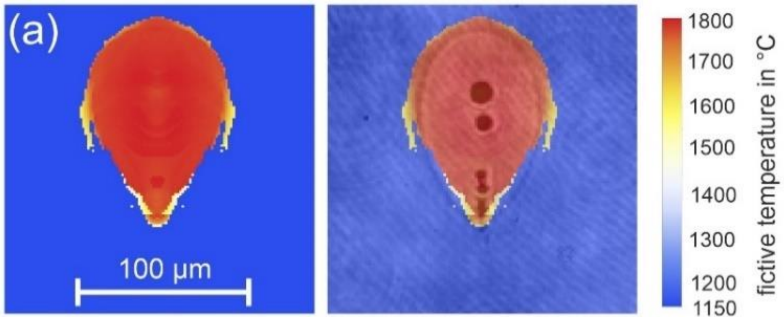
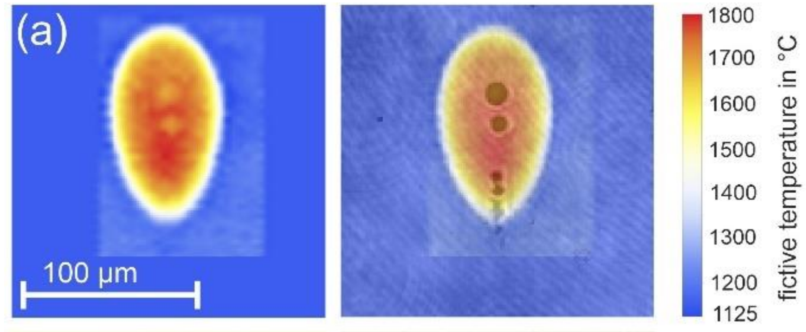
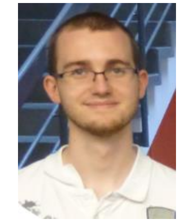
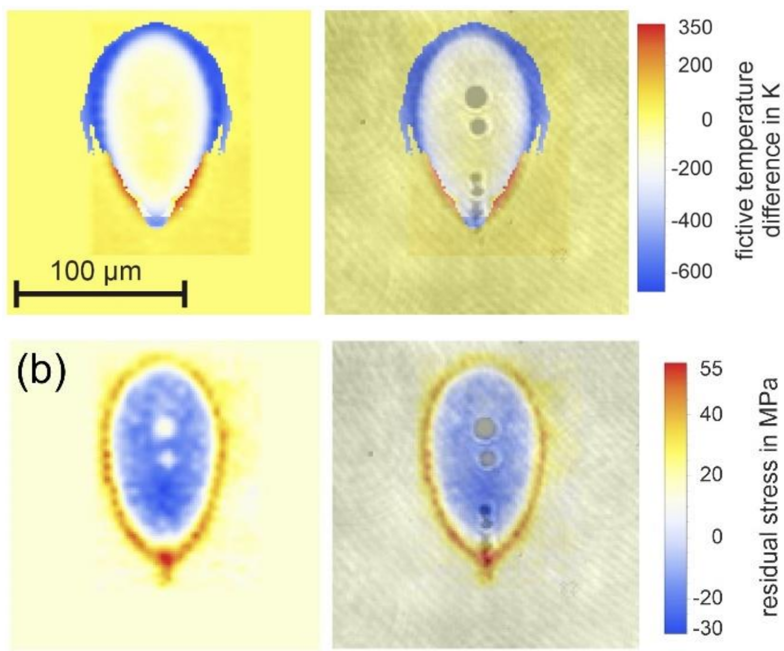
in situ versus ex situ







Pump probe - Raman



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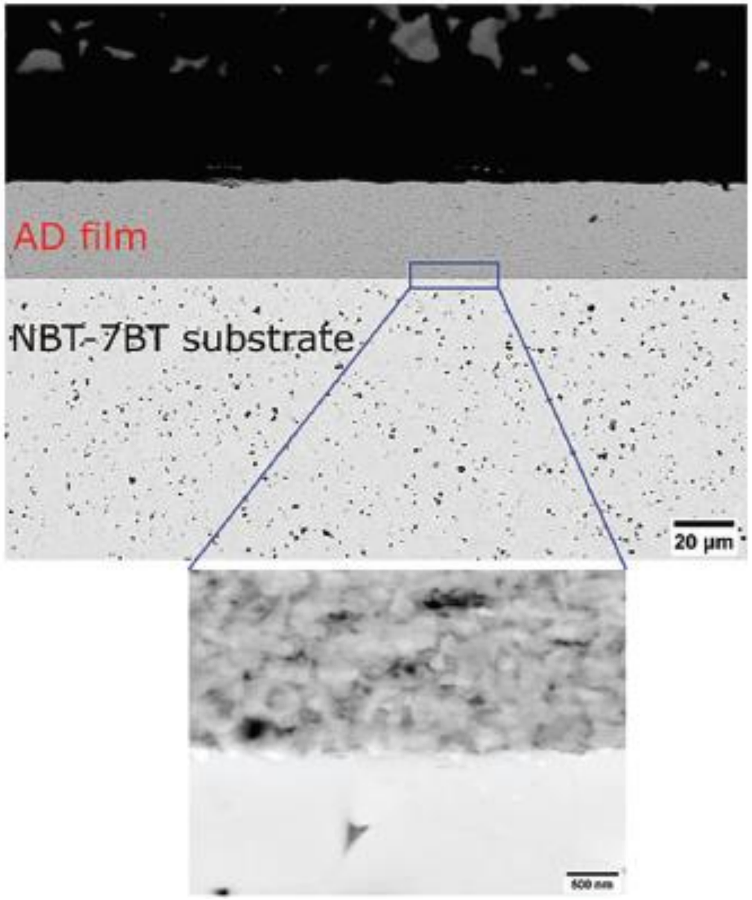
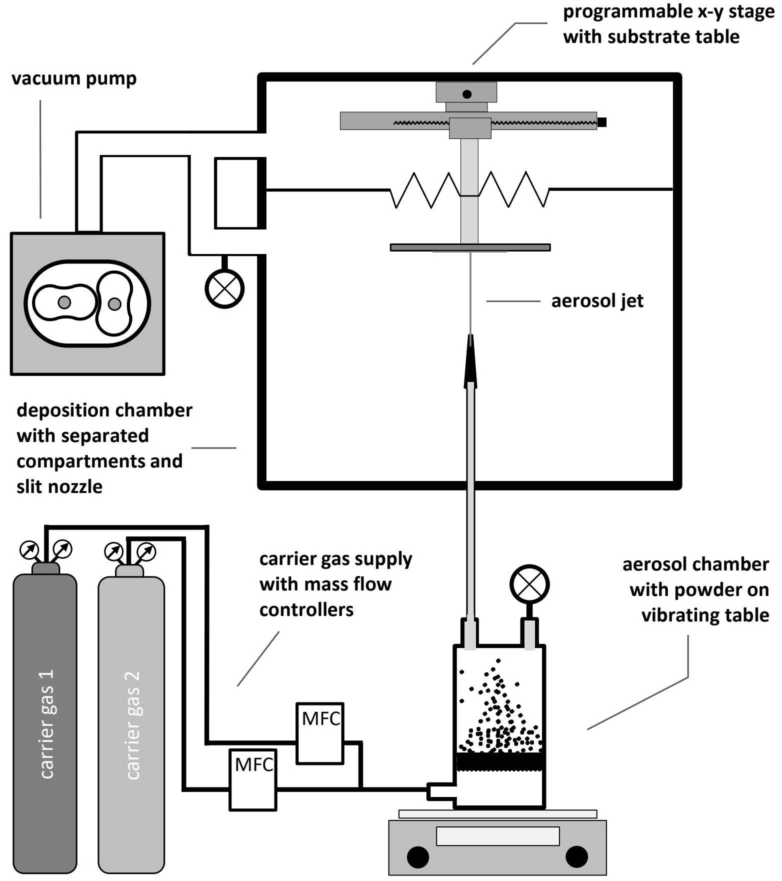
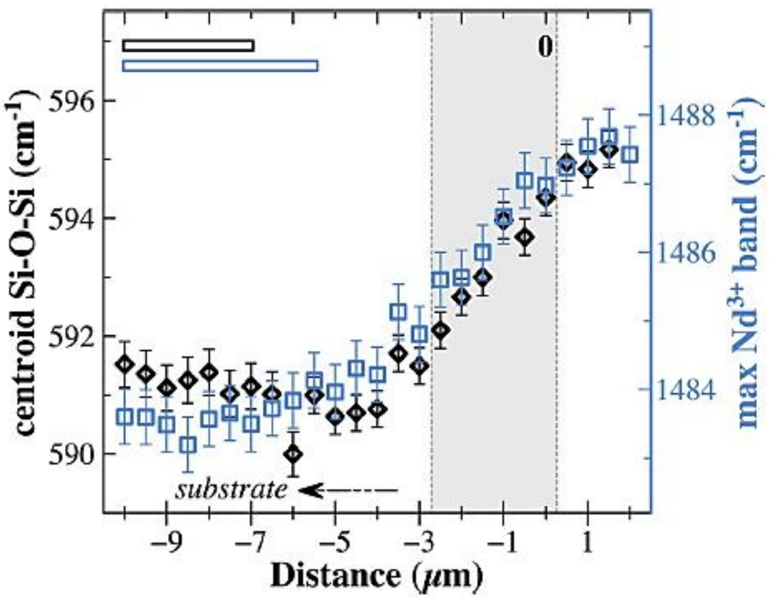
Aerosol deposition

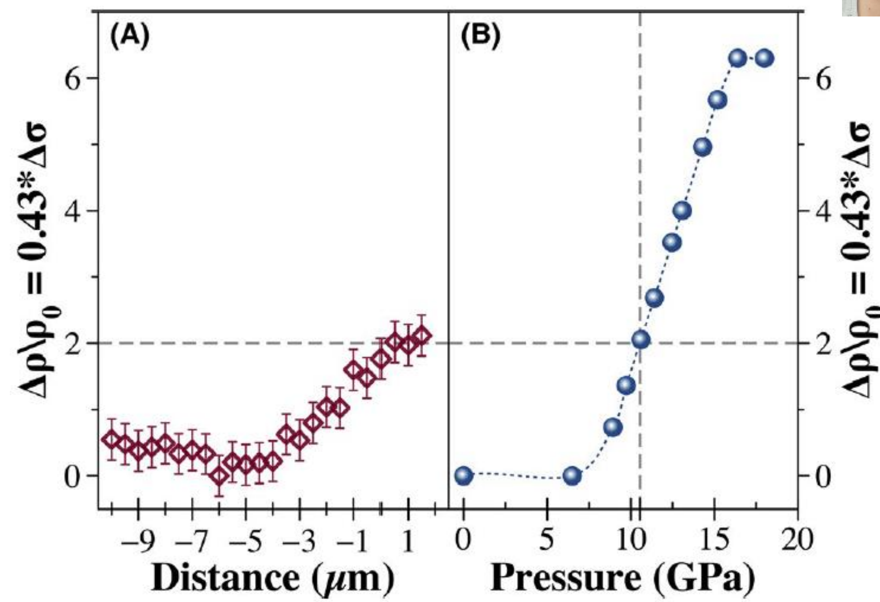




Cicconi et al. JACS 2019

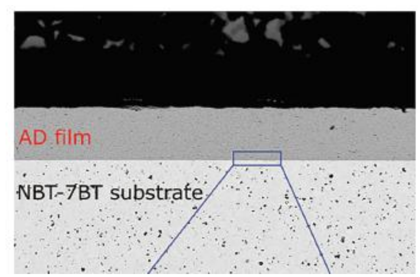
Aerosol deposition





Cicconi et al. JACS 2019

During the deposition the pressure increases up to 10GPa



1st of May


Environment
Bearable
Viable
Sustainable
Social
Equitable
Economic


6
1
5
2
4
3
"The others first !"
"It's just a matter of..."
Source : Pierre Peyretou

Conclusion

- Glass has a memory
- This memory can be read using vibration and luminescence spectroscopy
- But calibrations are needed
- Help to understand residual stress in thin glass
- Help to understand processes