Structural characterization of amorphous oxide films by Raman and Brillouin spectroscopies

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context

mirror Bragg reflectors : superposition of oxide films TiO2 doped Ta2O5 and silica SiO_2

The aim → To reduce mechanical losses of these mirrors

Gianpietro Cagnoli

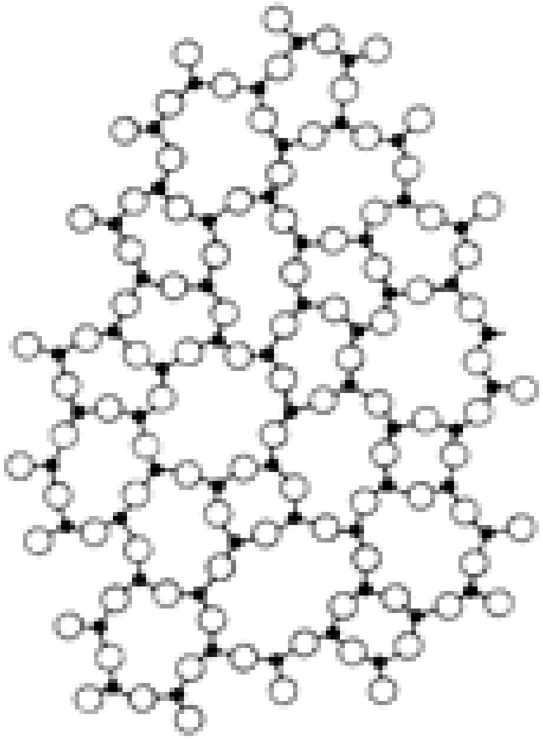
"Why does fused silica have a very deep minimum of losses at room temperature? And why the other oxides don't?"

ILM

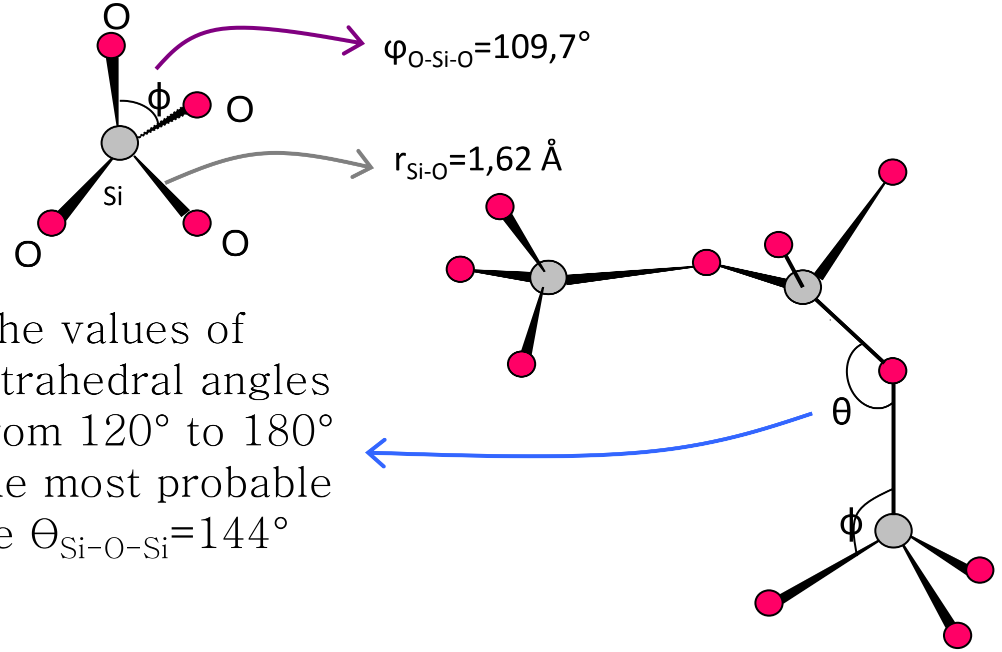
Optical and mechanical properties studies of silica glass

SiO_2 : anomalous material

Silica glass structure



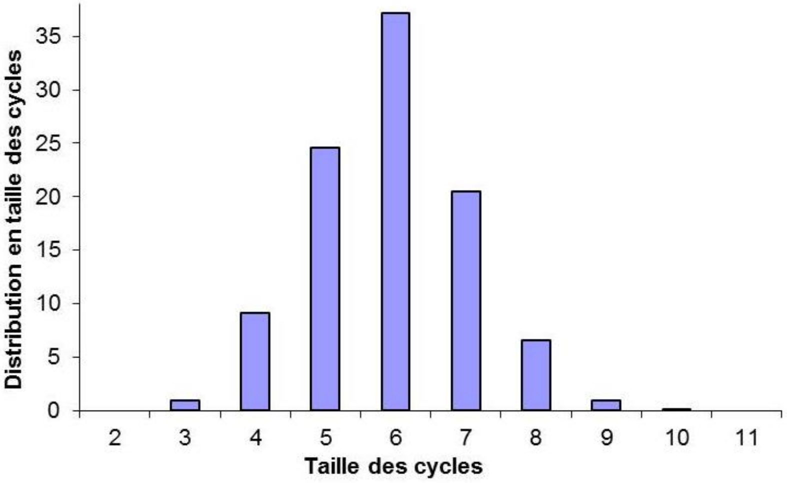
Zachariasen JACS **54** (1932)



$\varphi_{O\text{-}Si\text{-}O}$=109,7°

$r_{Si\text{-}O}$=1,62 Å

The values of intertetrahedral angles vary from 120° to 180° with the most probable value $\Theta_{Si\text{-}O\text{-}Si}$=144°



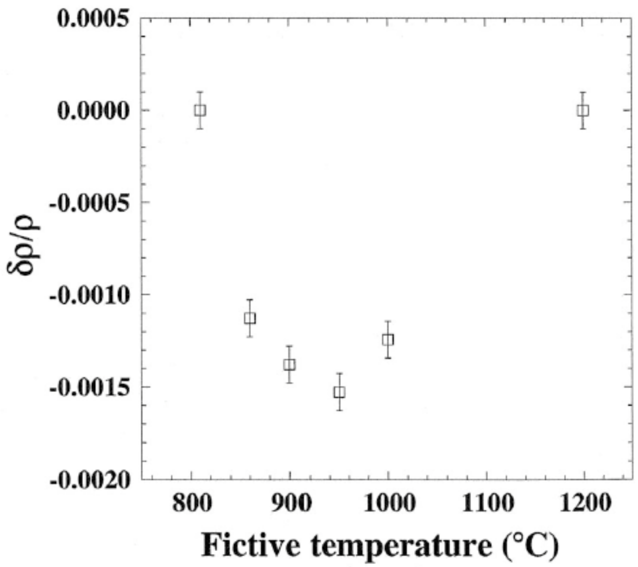
Jin PRB **50** (1994)

Silica glass : an anomalous material

Evolution with Temperature

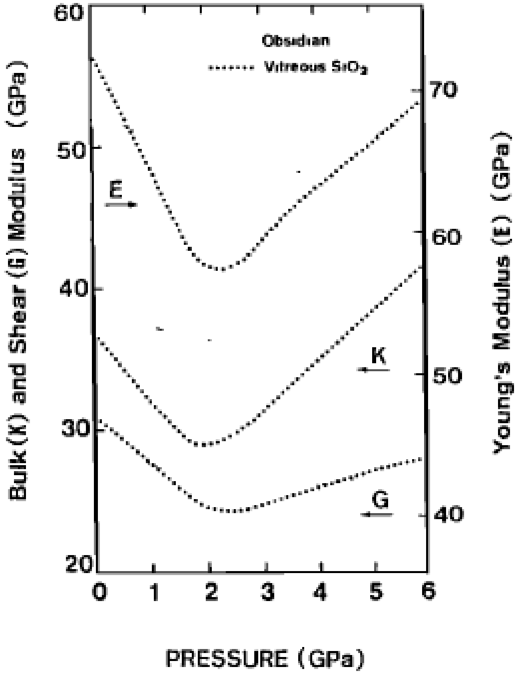
Observation of an Anomalous Density Minimum in Vitreous Silica

Sabyasachi Sen, Ron L. Andrus, David E. Baker, and Michael T. Murtagh
Glass Research Division, Corning Incorporated, Corning, New York 14831, USA



Density anomaly

Evolution with Pressure



K.Suito: High Pressure research, 1992

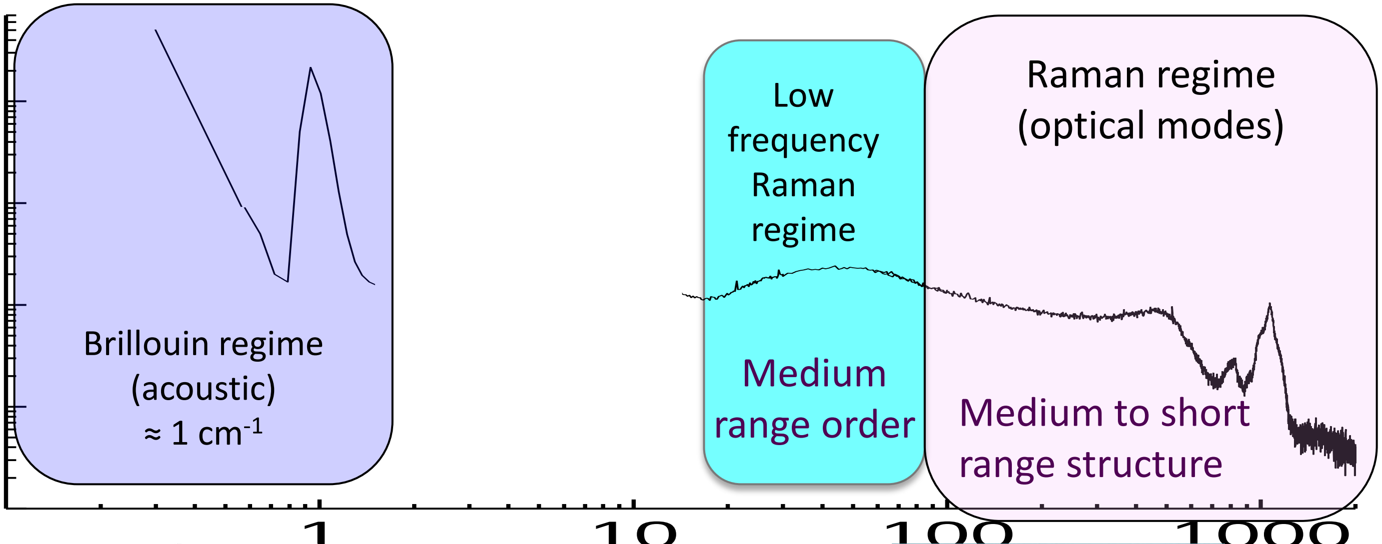
Bulk modulus ↘
Silica glass is more compressible,
its structure softens
It's the ELASTIC ANOMALY

1 Vibrational spectroscopies and results obtained on bulk silica glass

2 First results on thin films

Inelastic light scattering

Raman/Brillouin scattering arise from fluctuations of polarizability/dielectric susceptibility induced by vibrations



Brillouin regime
(acoustic)
≈ 1 cm^{-1}

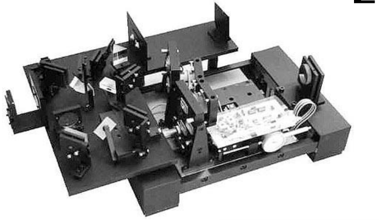
Low
frequency
Raman
regime

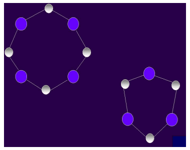
Medium
range order

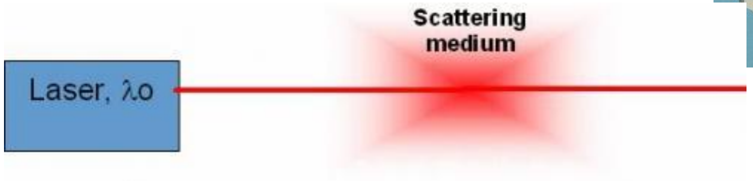
Raman regime
(optical modes)

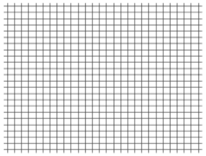
Medium to short
range structure

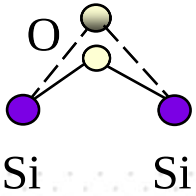
1 cm^{-1} = 30 GHz











Continuous media

different technologies

Inelastic light scattering

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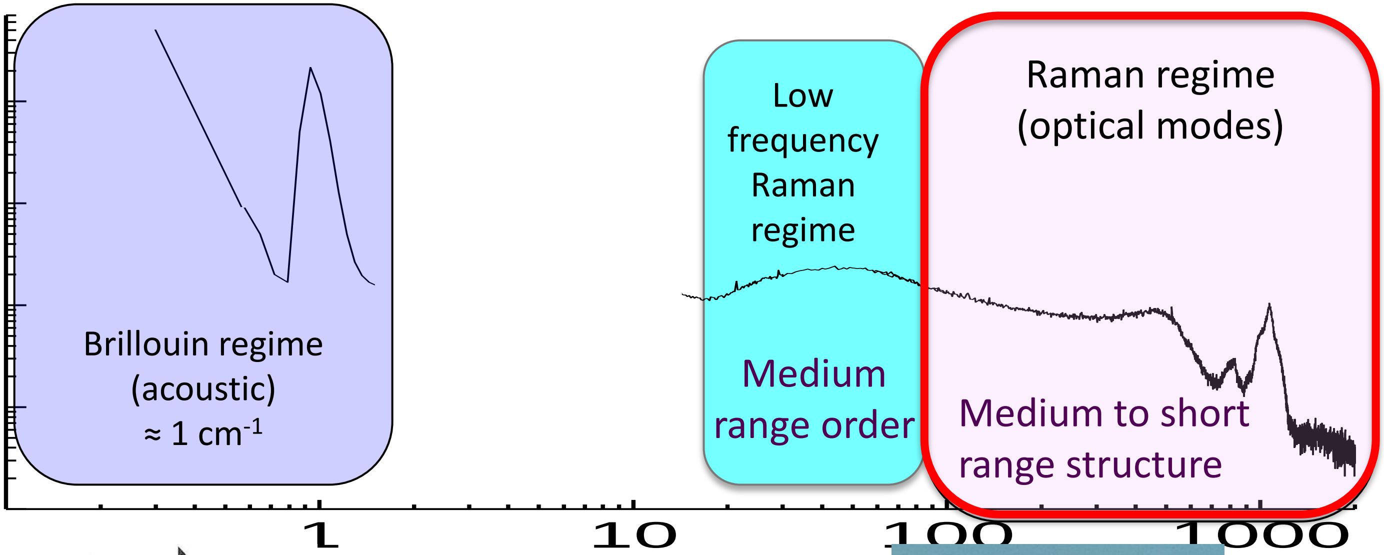

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Low frequency Raman regime

Medium range order

Raman regime
(optical modes)

Medium to short range structure

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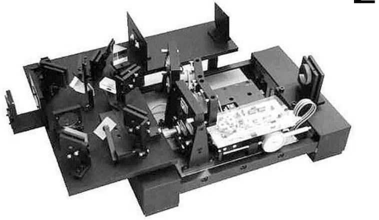
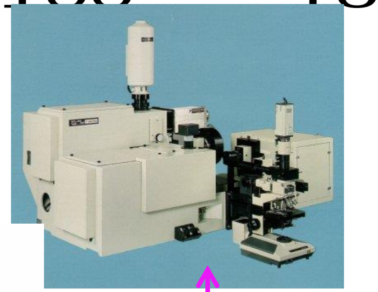
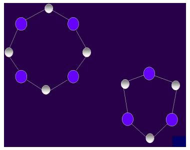
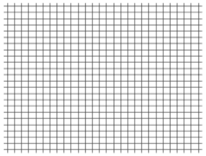
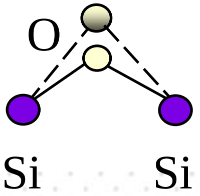








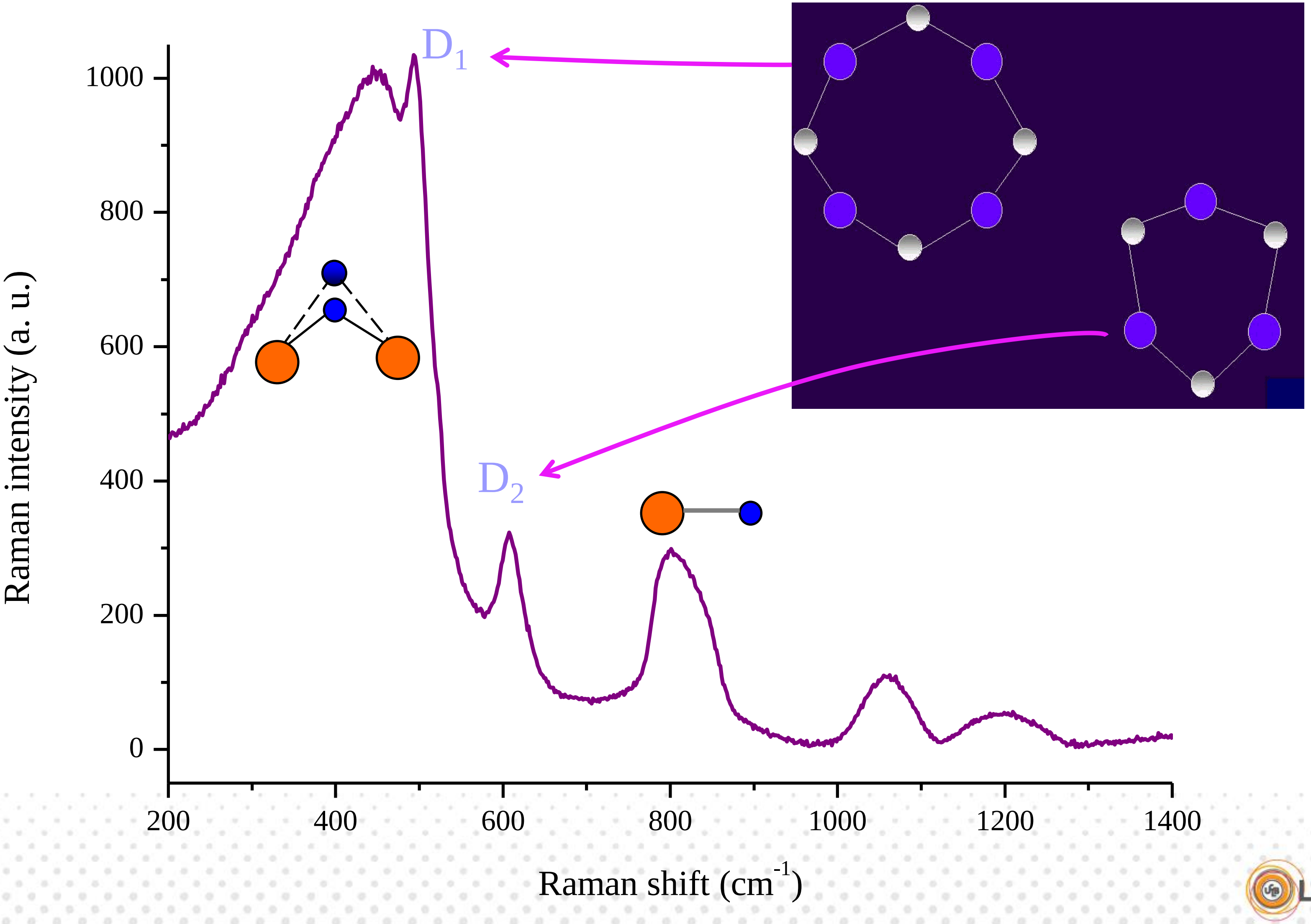


Continuous media

different technologies

Raman scattering

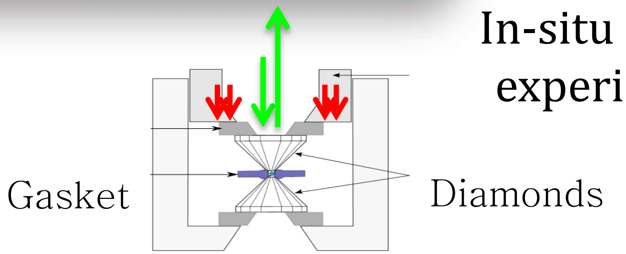
Raman ($\upsilon > 100\ \text{cm}^{-1}$) → Structural information at short scale :
intertetrahedral angle, interatomic bonds…



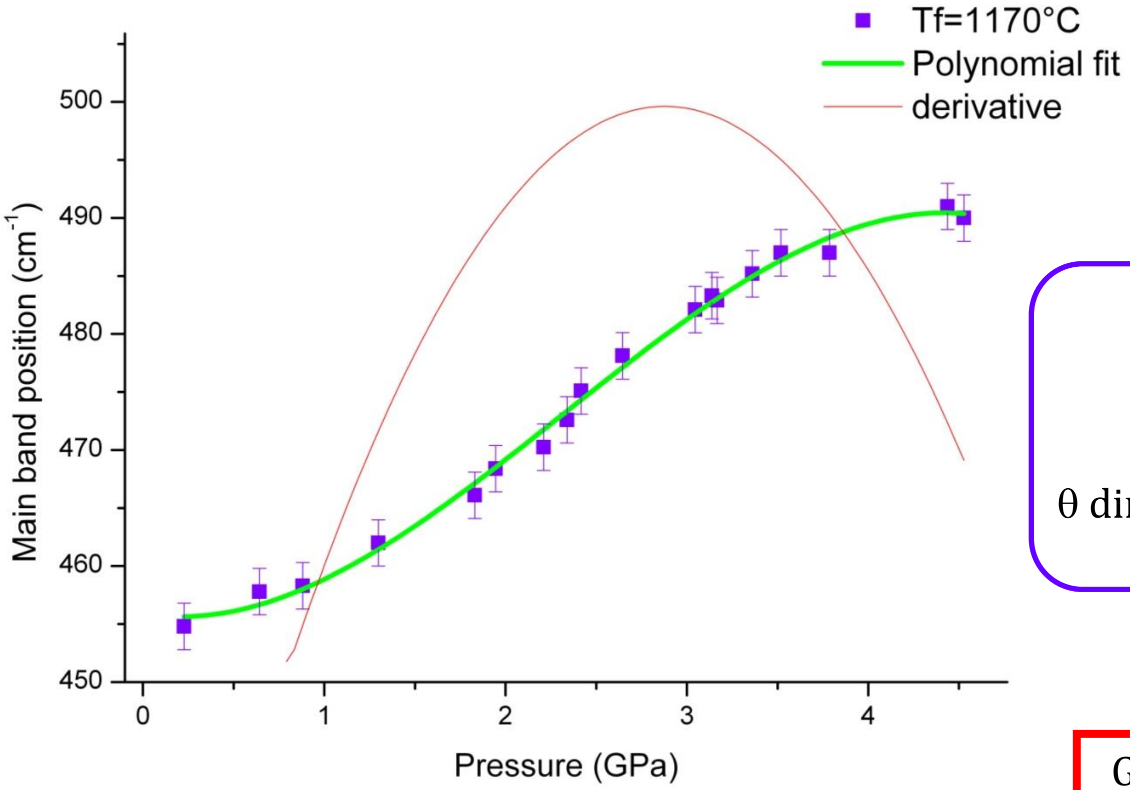
From the evolution of spectroscopic signatures, it’s possible to get structural informations

Evolution of the main band as function of pressure → Structural interpretation of elastic anomaly

Elastic domain :Impact of Tf on anomaly



In-situ high pressure experiments (DAC)



Inflexion point at around 2,5 GPa

No linear shift of the main band

↓

A maximum variation has been observed at 2.5 GPa

Between 1,5 and 3 Gpa

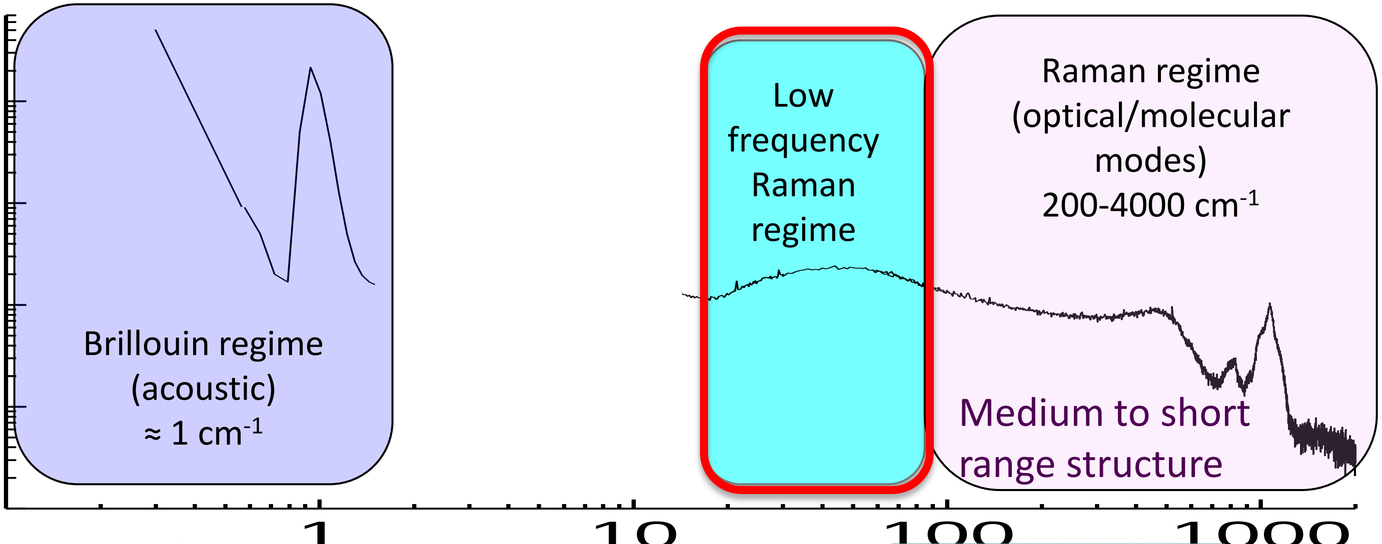
↓

Structural rearrangements fast,
θ diminishes faster around 2.5 GPa → the rigidity is minimum at these P°

Good correlation with a minimum in the bulk modulus = ANOMALY

Inelastic light scattering

Brillouin and Raman : parent spectroscopies but different technologies



Brillouin regime (acoustic) ≈ 1 cm^{-1}

Low frequency Raman regime

Raman regime (optical/molecular modes) 200-4000 cm^{-1}

Medium to short range structure

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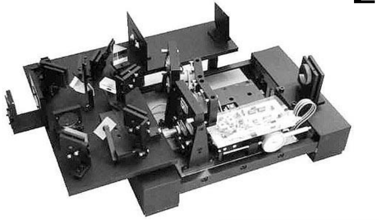
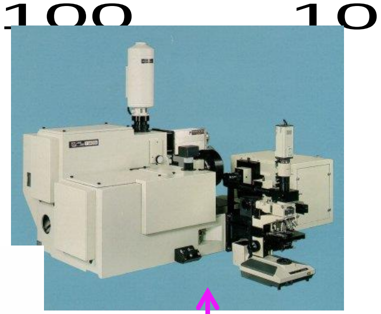
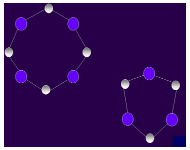
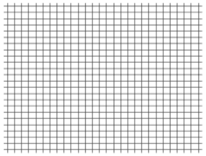
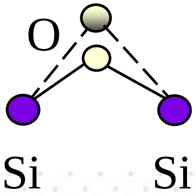








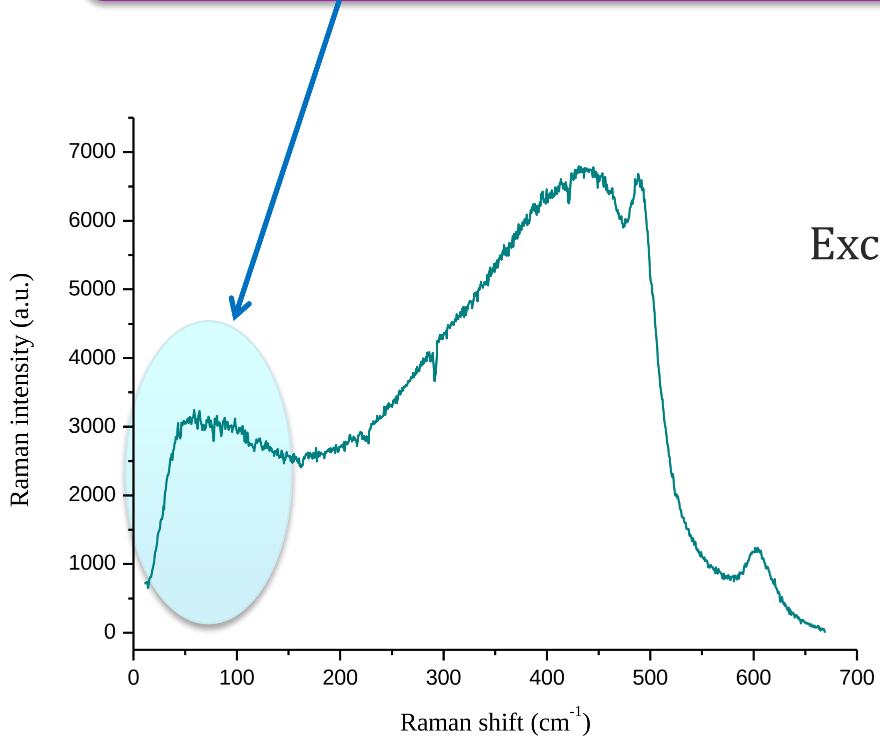
Continuous media



different technologies

Low frequency Raman scattering

Boson peak $\approx$ 5-100 cm^{-1} → Medium range order
Typical length : few nm



Excess of VDOS compared to the Debye Theory

Universal vibrational feature characteristic of amorphous materials : its origin is still debated

$$\langle D \rangle \approx \frac{V_{sound}}{\nu_{BP}}$$

ex: SiO2
V_{sound}~3770 m/s
ν_{BP}~6.2 meV (1.5 THz)

$$\langle D \rangle \approx 2.5 nm$$

BP Duval et al. JOP **2** (1990)

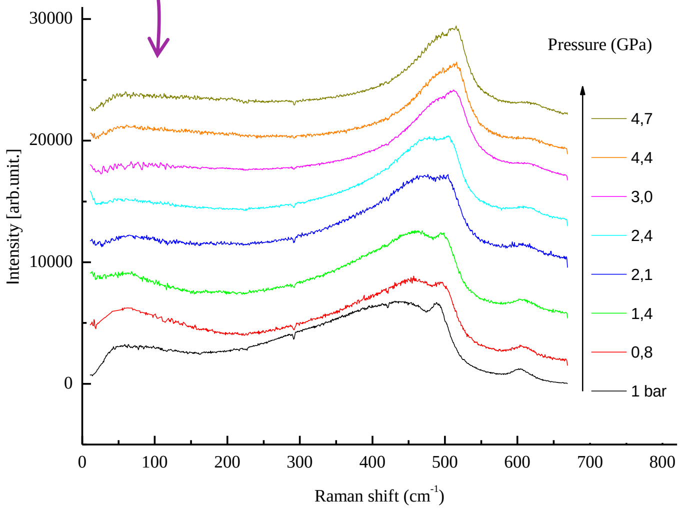
Frequency of the Boson peak → Typical length : few nm

Low frequency Raman scattering : SiO$_2$

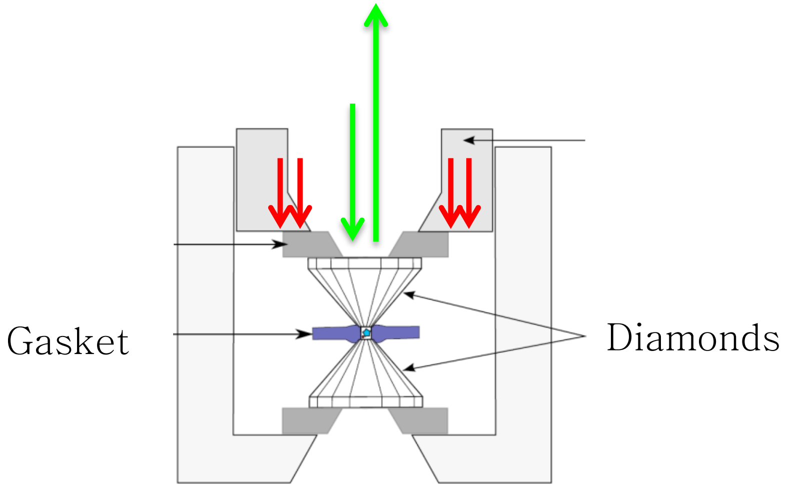
Boson peak

Silica under hydrostatic pressure: A non continuous medium behavior

T. Deschamps[a], C. Martinet[a], D.R. Neuville[b], D. de Ligny[a], C. Coussa-Simon[a], B. Champagnon[a,*]



Silica glass under pressure (DAC)



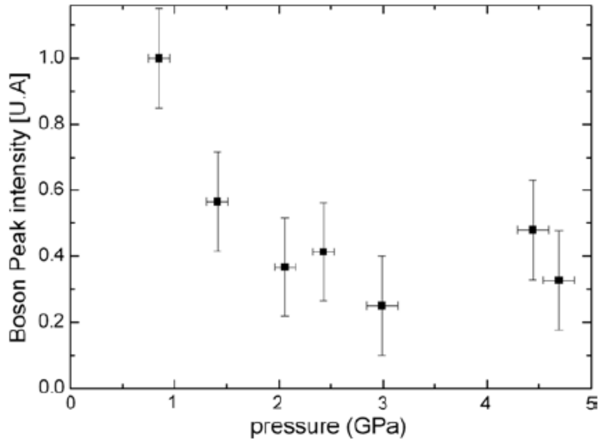
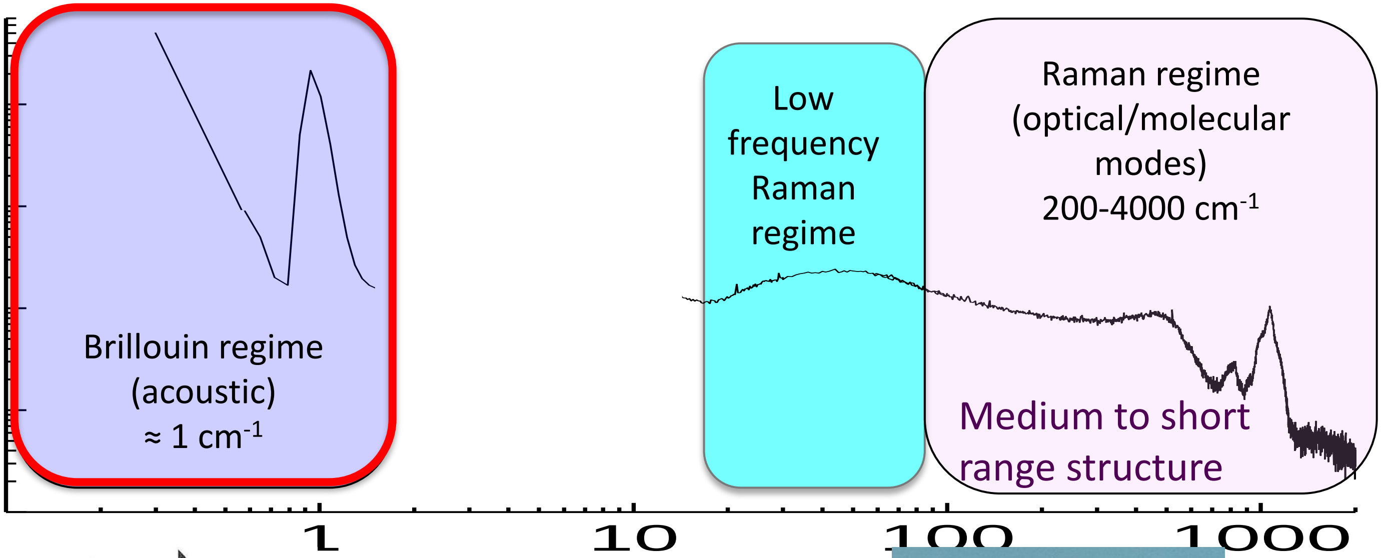


Fig. 2a. Normalized Boson peak intensity $I_R = I(\omega)/[n(\omega)+1]\,\omega$ of silica integrated between 25 cm^{-1} and 160 cm^{-1} as function of pressure.

$P\nearrow$ $\xrightarrow{I_{BP}\searrow}$ homogenisation

Inelastic light scattering

Brillouin and Raman : parent spectroscopies but different technologies



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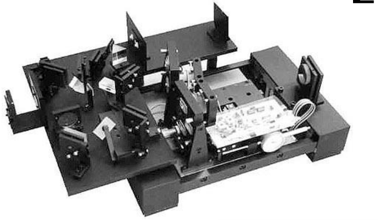
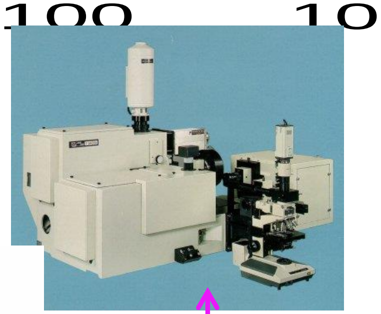
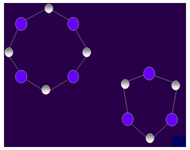
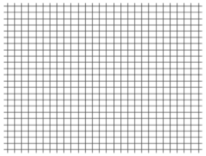
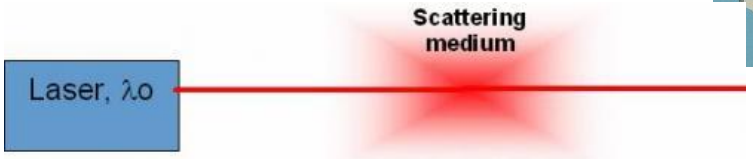
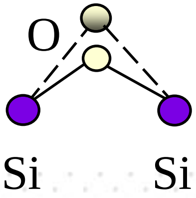










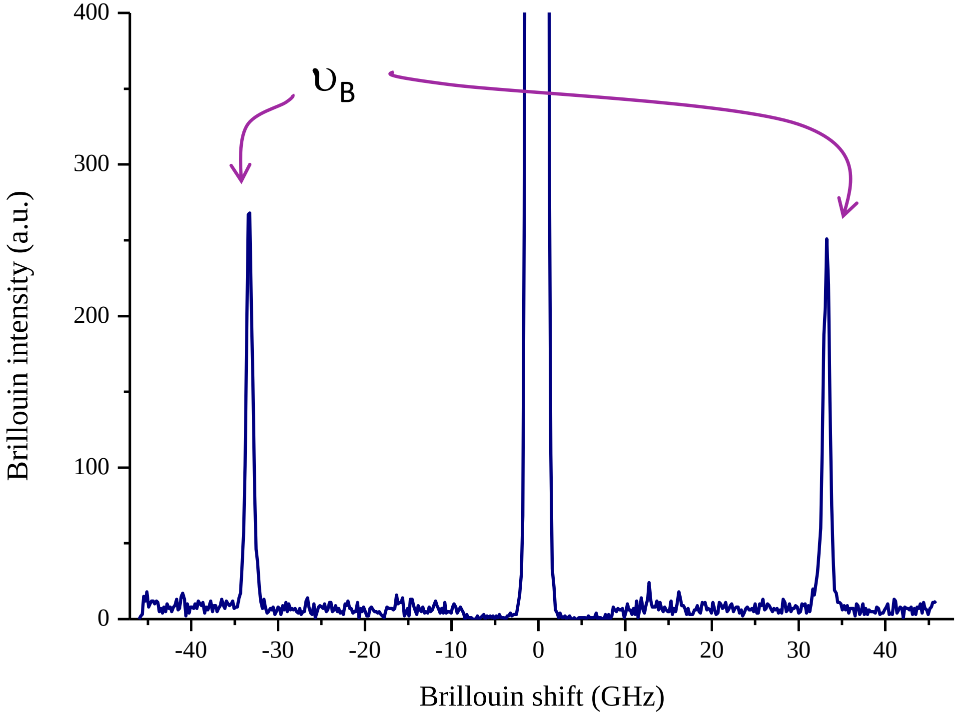


Continuous media

different technologies

Brillouin scattering

Principle : scattering of the laser light from acoustic modes



$$V_L = \frac{\lambda_0 \upsilon_{180^\circ}}{2n}$$

Brillouin scattering → Macroscopic properties

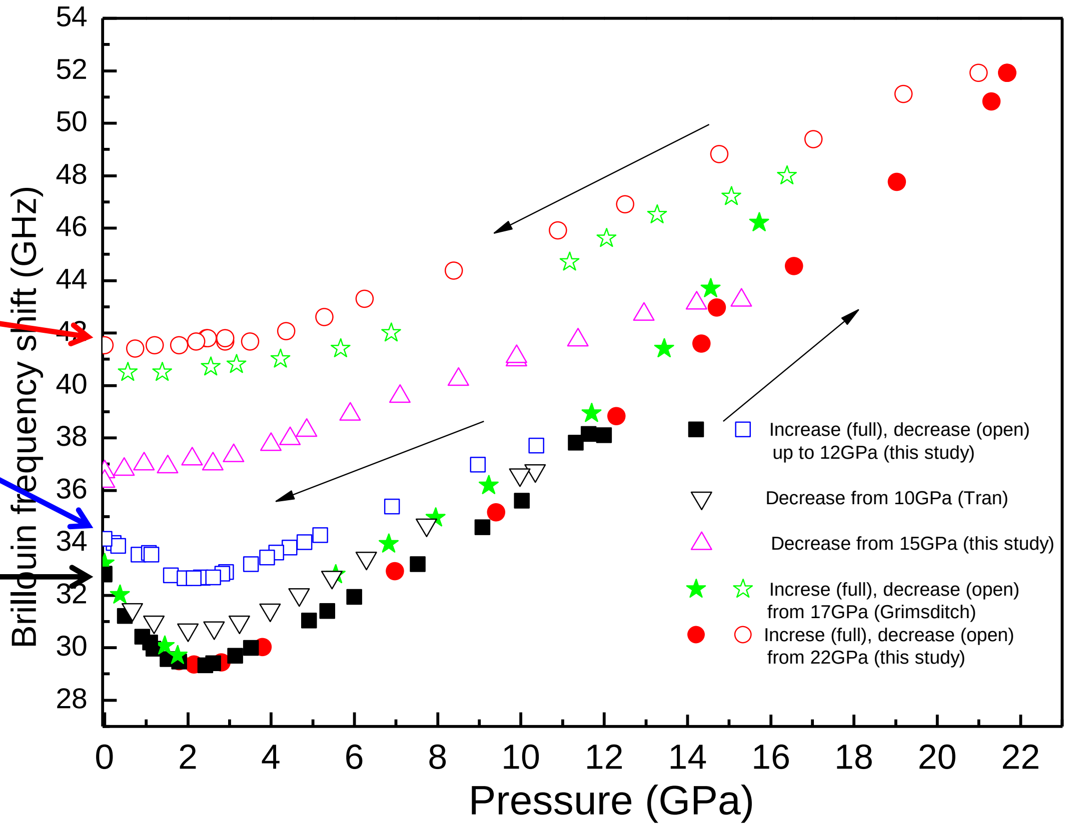
- Sound velocity
- Elastic moduli
- Density
- Optical index

BrillElastic anomaly of SiO_2

22 Gpa Δd/d=20%

12 GPa Δd/d=4%

10 GPa(Tran) Δd/d=0%



Sonneville et al.,THE JOURNAL OF CHEMICAL PHYSICS 137, 124505 (2012)

Progressive vanishing of the elastic anomaly when density increases

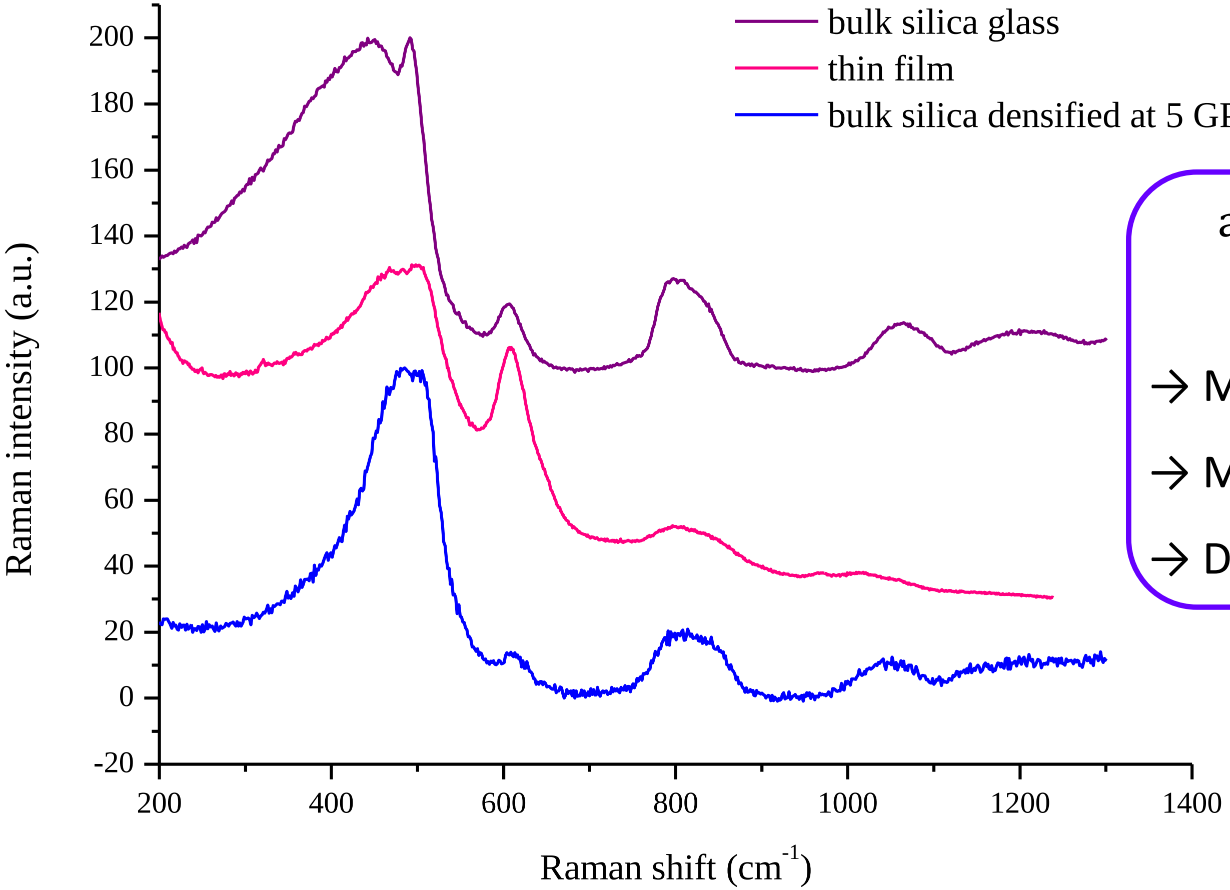
Characteristic of structural modification at long scale

STRUCTURAL INFORMATIONS ON OXIDE FILMS OBTAINED BY VIBRATIONNAL SPECTROSCOPIES (First results)

OXIDE FILMS = Ta_2O_5 and SiO_2 provided by LMA

Raman and Brillouin spectroscopies performed at ILM

SiO_2 films : comparison with bulk silica



as received silica glass film

↓

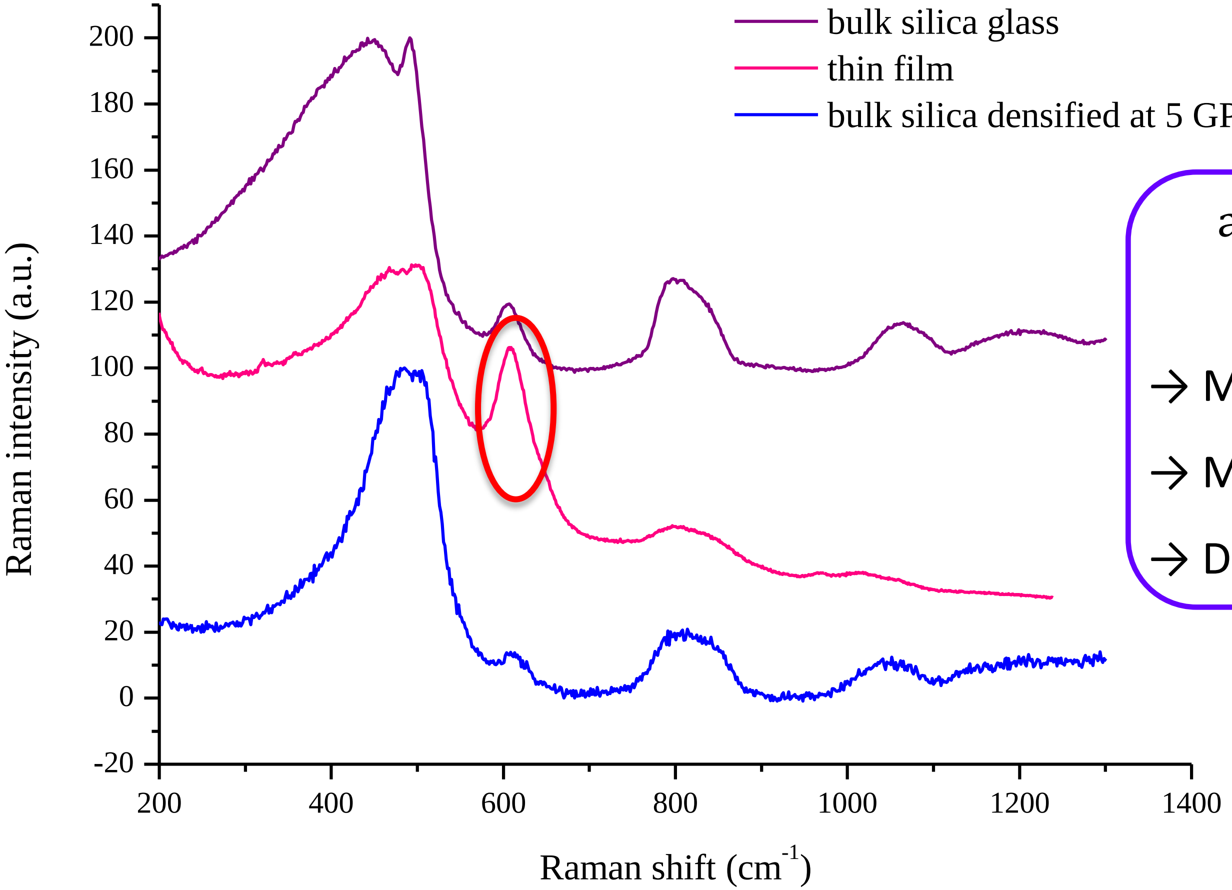
→ Main band is shifted towards HF

→ Main band and D1

→ D_2 : very intense

The silica film is denser than bulk silica : due to deposition conditions?

SiO_2 films : comparison with bulk silica



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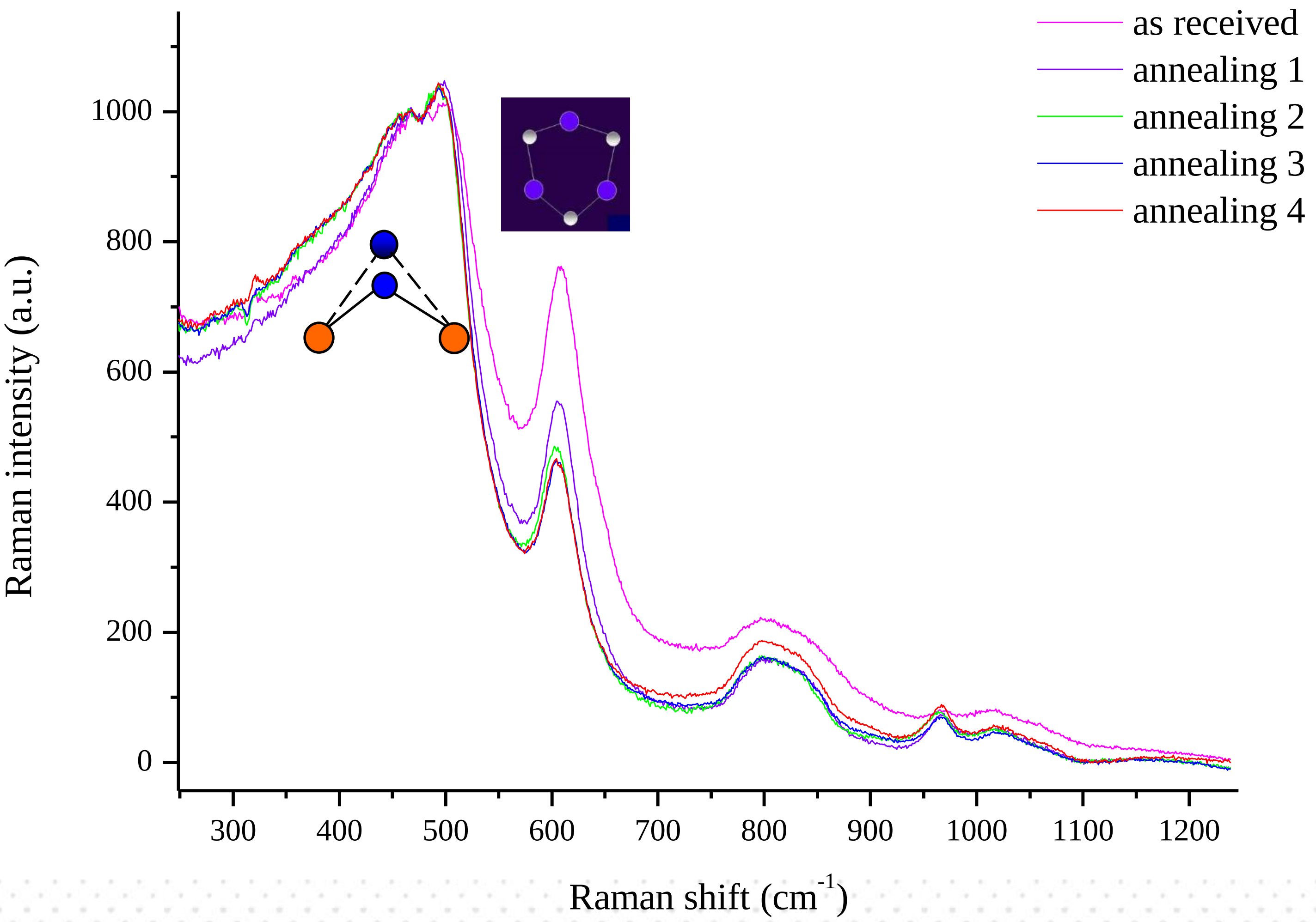
SiO_2 films : annealing effect

Annealing effect on spectroscopic signatures (Raman scattering)



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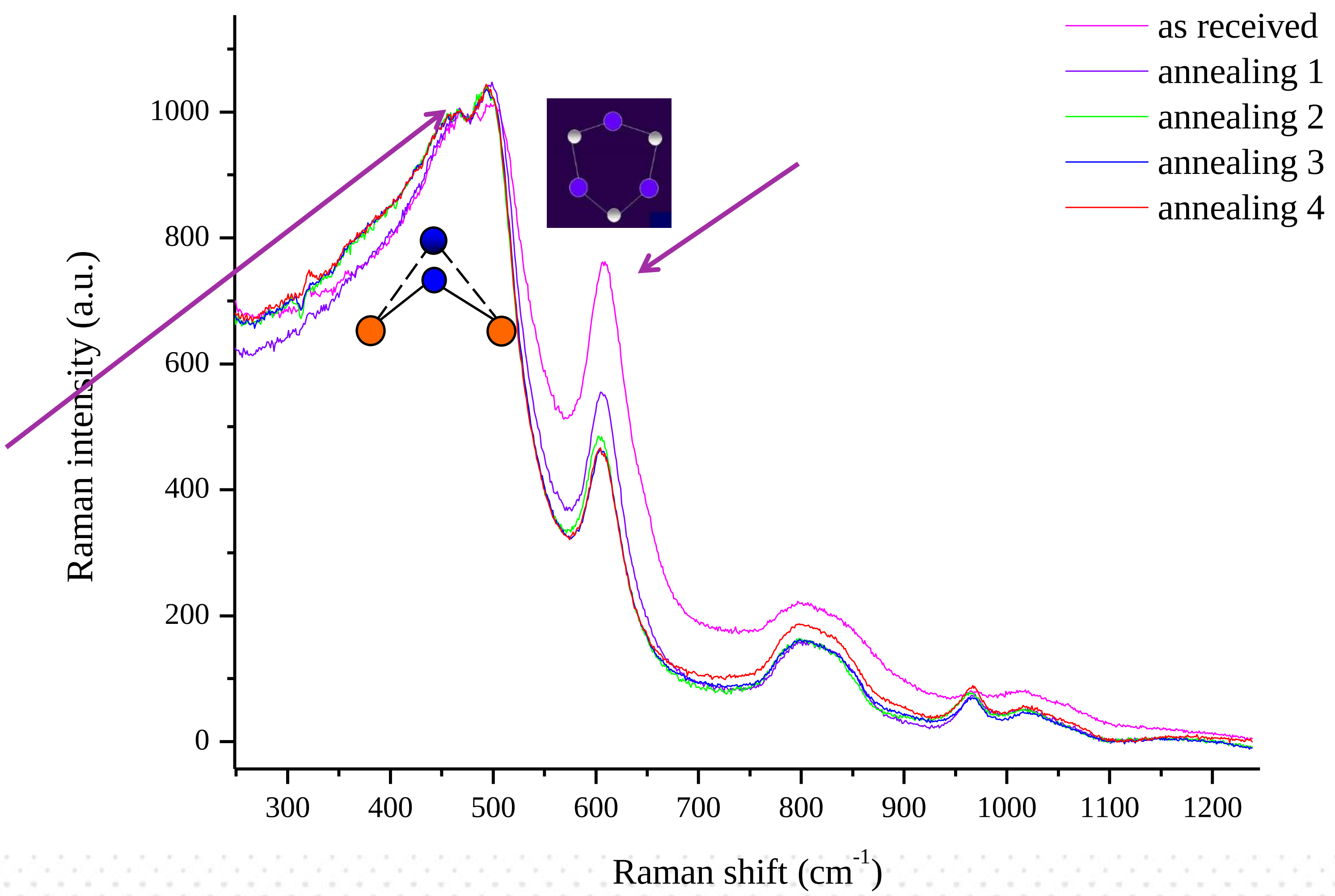
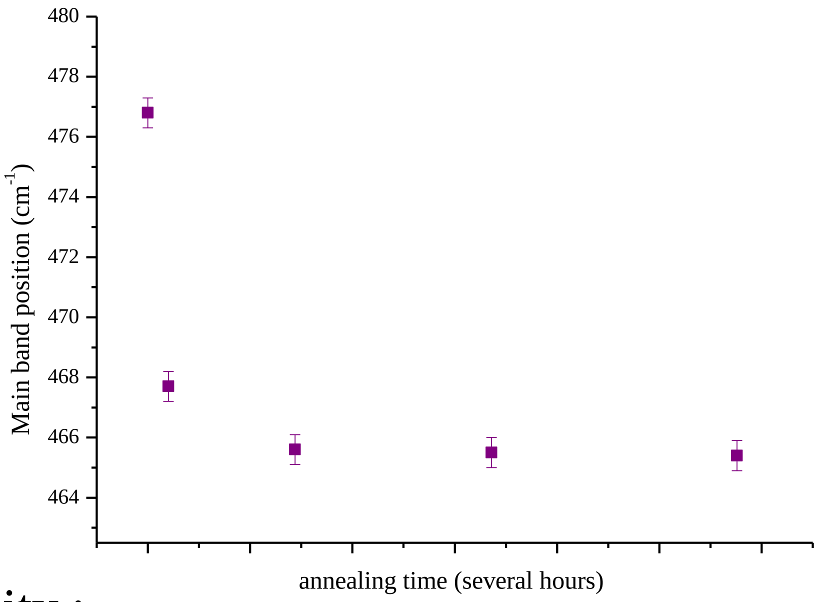
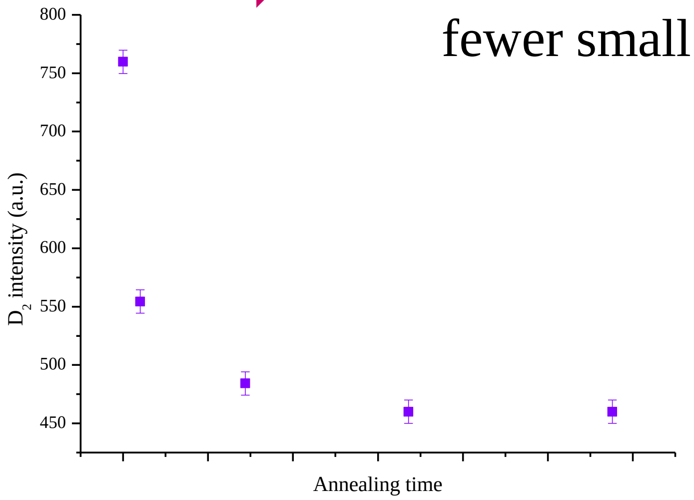


SiO_2 films : annealing effect

Shift of the main band towards lower frequencies
→ θ increases

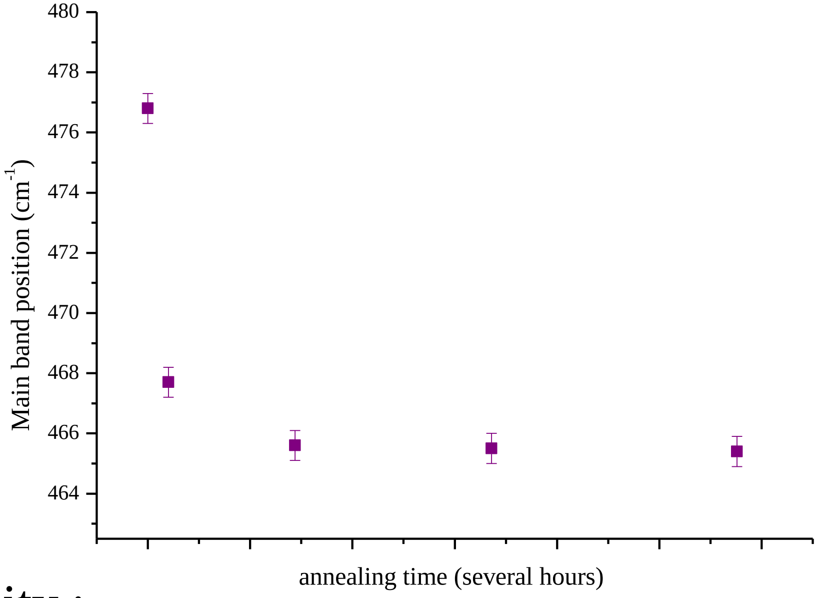


Decrease of the D_2 intensity : fewer small cycles



An annealing of few hours leads to a structure less dense : structural relaxation even at temperature significantly under Tg

SiO_2 films : annealing effect



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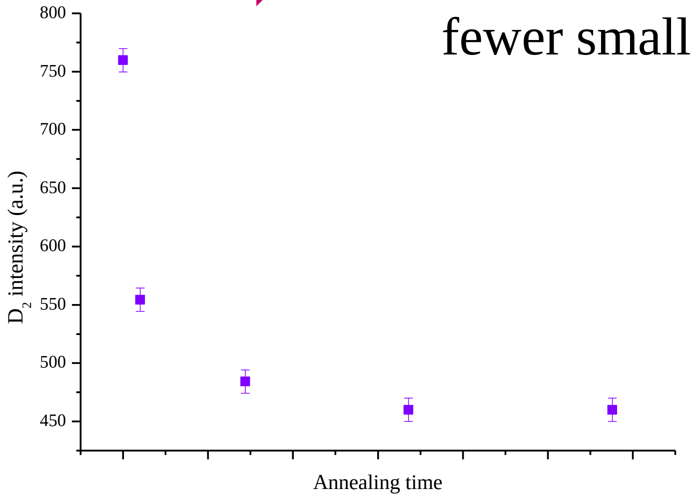
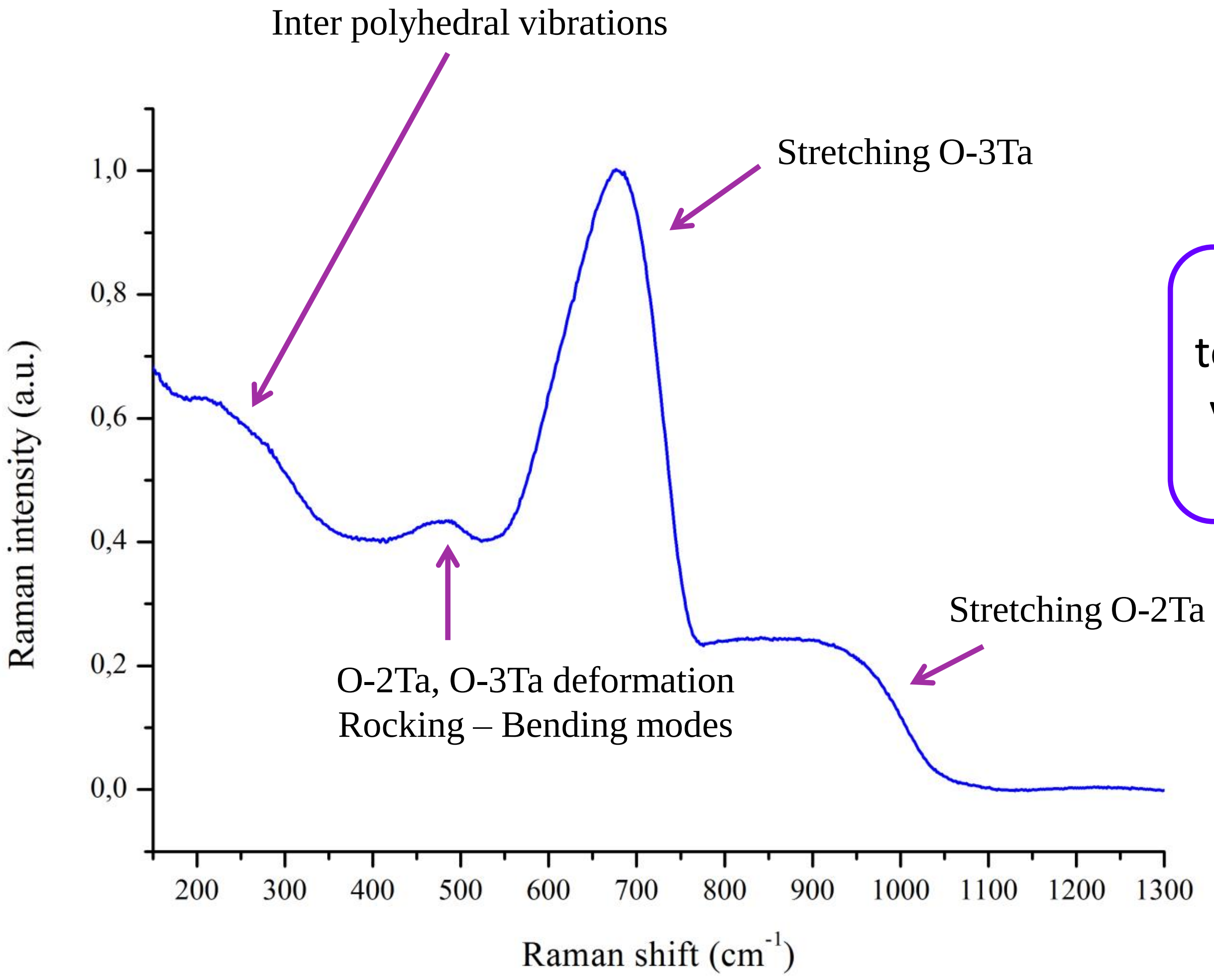


An annealing of few hours leads to a structure less dense : structural relaxation even at temperature significantly under Tg

Link with mechanical losses : Massimo Granata

Ta_2O_5 films : structural informations



Inter polyhedral vibrations

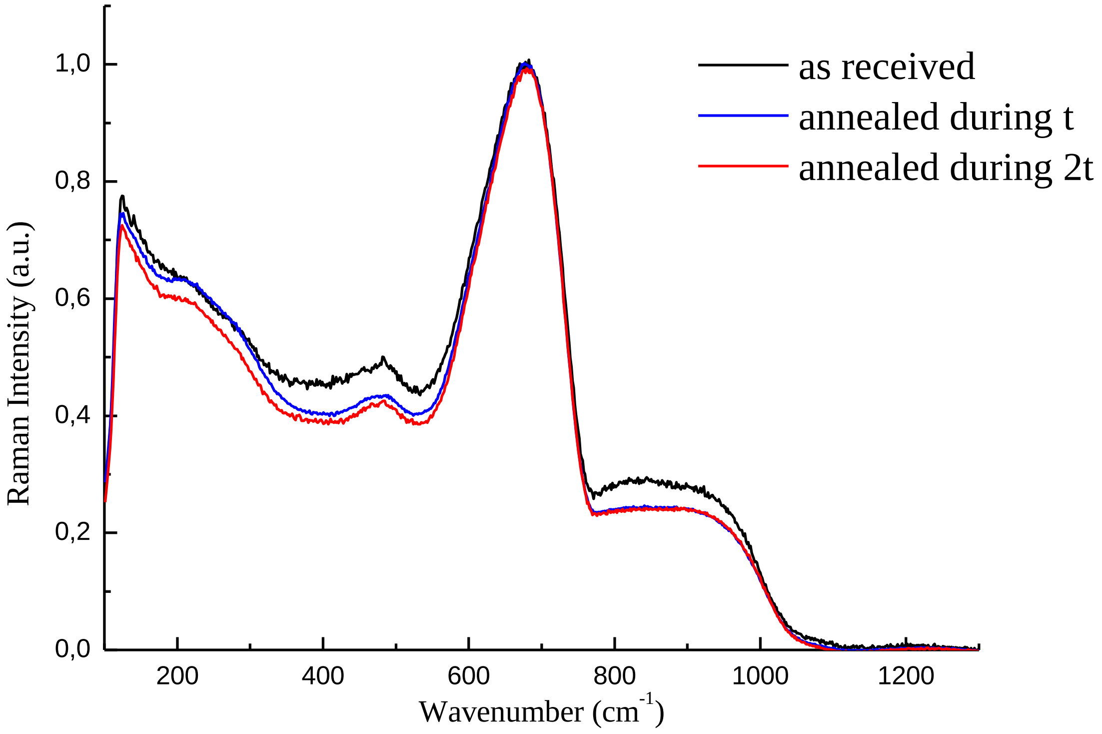
Stretching O-3Ta

O-2Ta, O-3Ta deformation
Rocking – Bending modes

Stretching O-2Ta

Band attribution according to Joseph et al.(2011, JRS) but the vitreous structure is still on debate

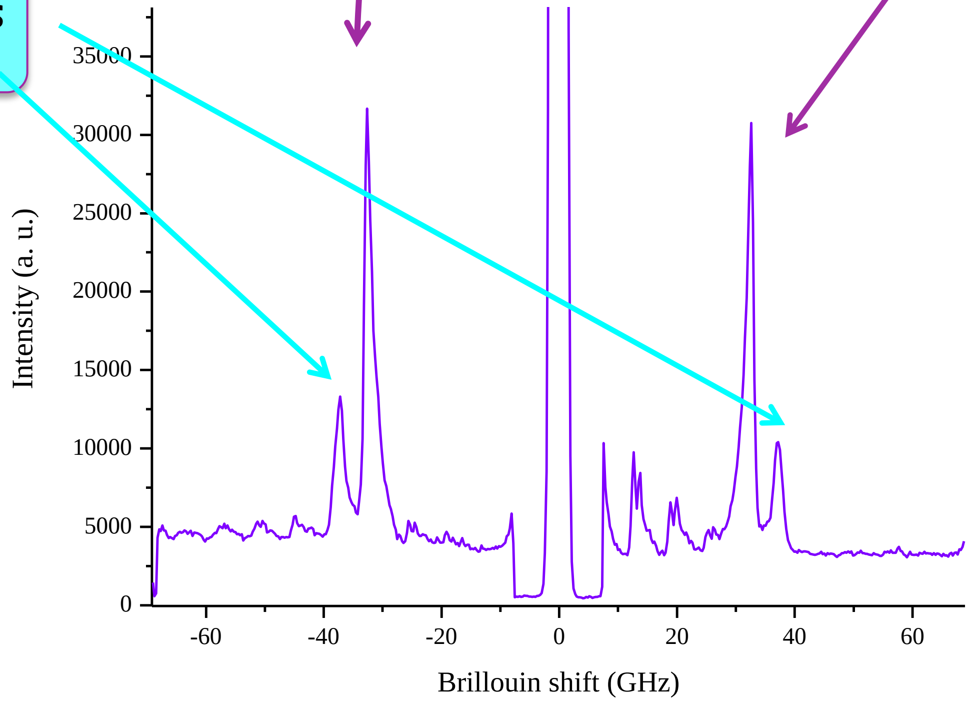
Ta_2O_5 films : annealing effect



Band at 680 cm^{-1} becomes narrower but no shift

The annealing time isn't sufficient to change significantly the structure → annealing in progress

Ta_2O_5 films : Brillouin spectrum



Silica substrate peaks υ =32,5 GHz

Ta_2O_5 peaks υ = 37,2 GHz

This film was annealed during few hours

Ta_2O_5 film is denser than bulk silica

No shift of the Brillouin peak for the film annealed few more hours

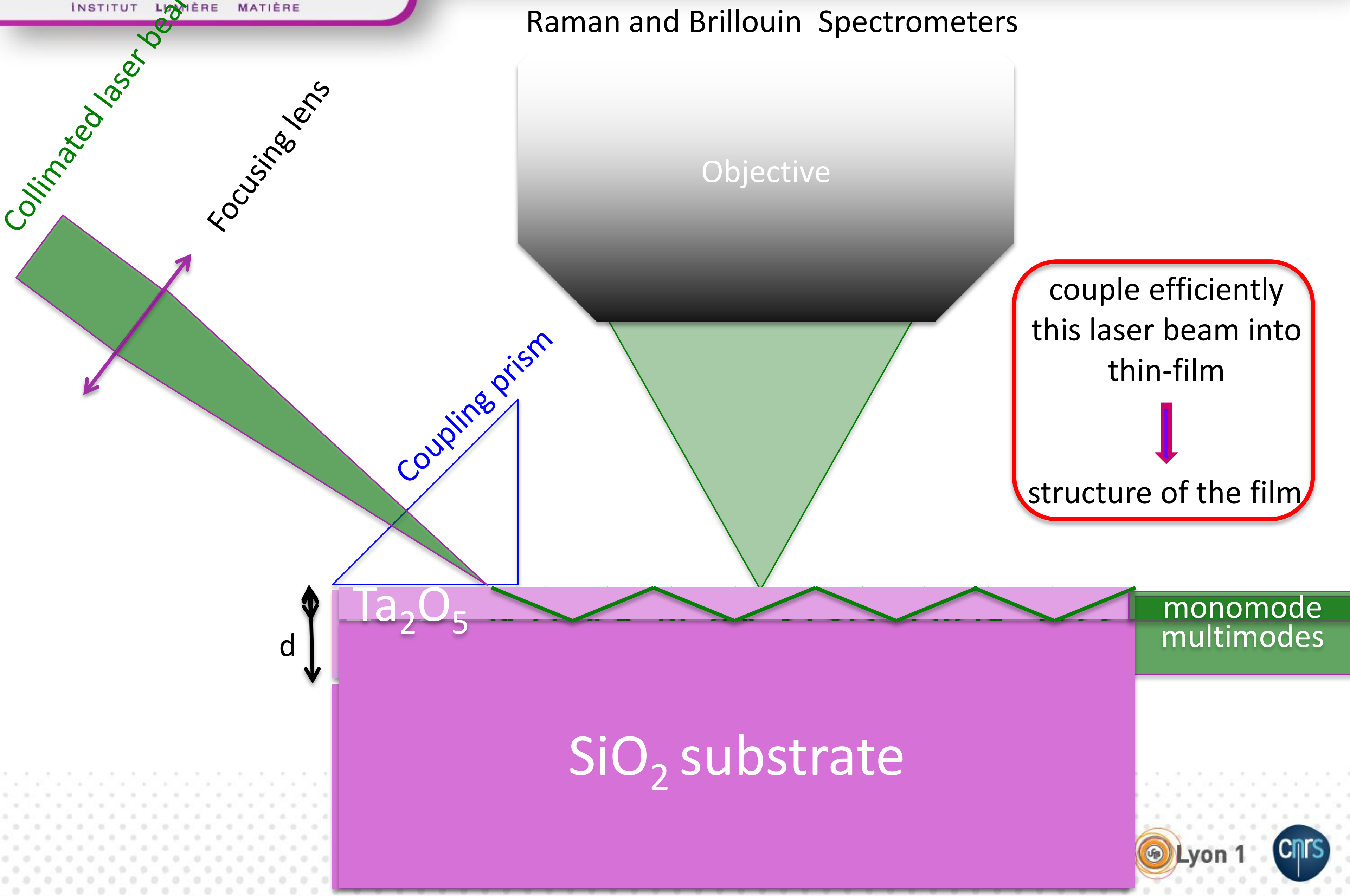
Conclusions and perspectives

It’s possible to get structural informations (**from short to long scale**)on thin films thanks to vibrationnal spectroscopies

Simulations of the structure of Ta_2O_5 (D. Rodney and T. Damart)

Doping with TiO_2 : known to reduce thermal noise – what is the impact on the Ta_2O_5 structure?

Wave guide raman spectroscopy in order to optimize the signal



Raman and Brillouin Spectrometers

Objective

Collimated laser beam

Focusing lens

Coupling prism

couple efficiently this laser beam into thin-film

↓

structure of the film

Ta_2O_5

d

monomode

multimodes

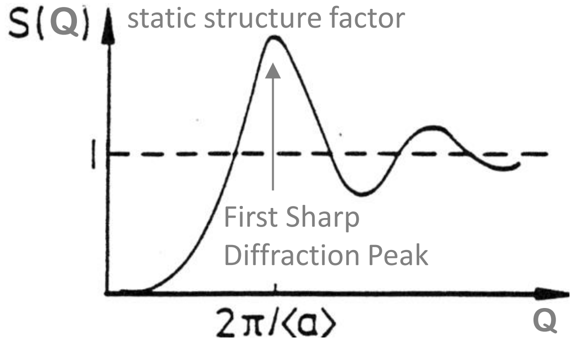
SiO_2 substrate

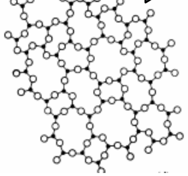
Thank you for your attention !!!

Low frequency Raman scattering

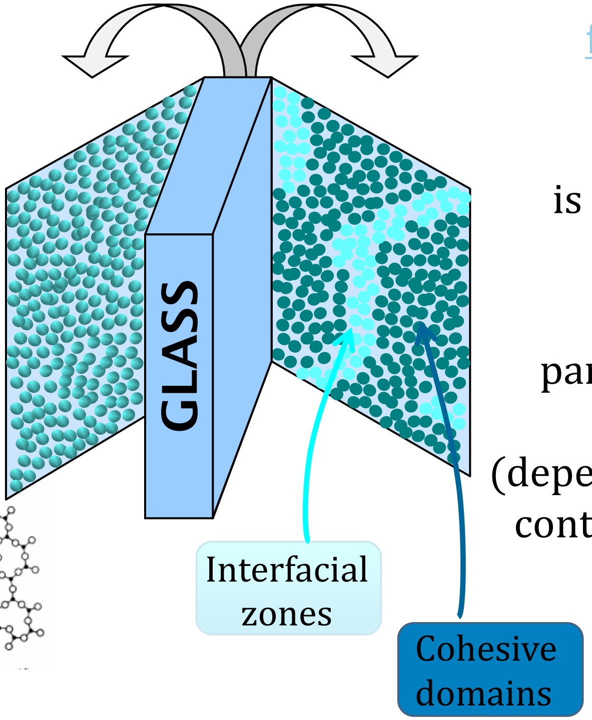
≈ 5-50 cm^{-1} → Medium range order
Typical length : few nm

from static properties





Glasses ≡ homogeneous network



from vibrational properties

the elastic network of glasses
is disrupted at the nanometric scale

partial localization of acoustic modes
around nanodomains,
(depending on the magnitude of the elastic
contrast between soft and hard regions)

Spectroscopic signature of these cohesive domains vibrations → Boson peak

Low frequency Raman scattering

One interpretation of BP Duval et al. JOP **2** (1990)

Inhomogeneous nano-structure of glasses

Cohesive domains

Interfacial zones (softer)

Elastic inhomogeneities at nanometer scale

$$\langle D \rangle \approx \frac{V_{sound}}{\nu_{BP}}$$

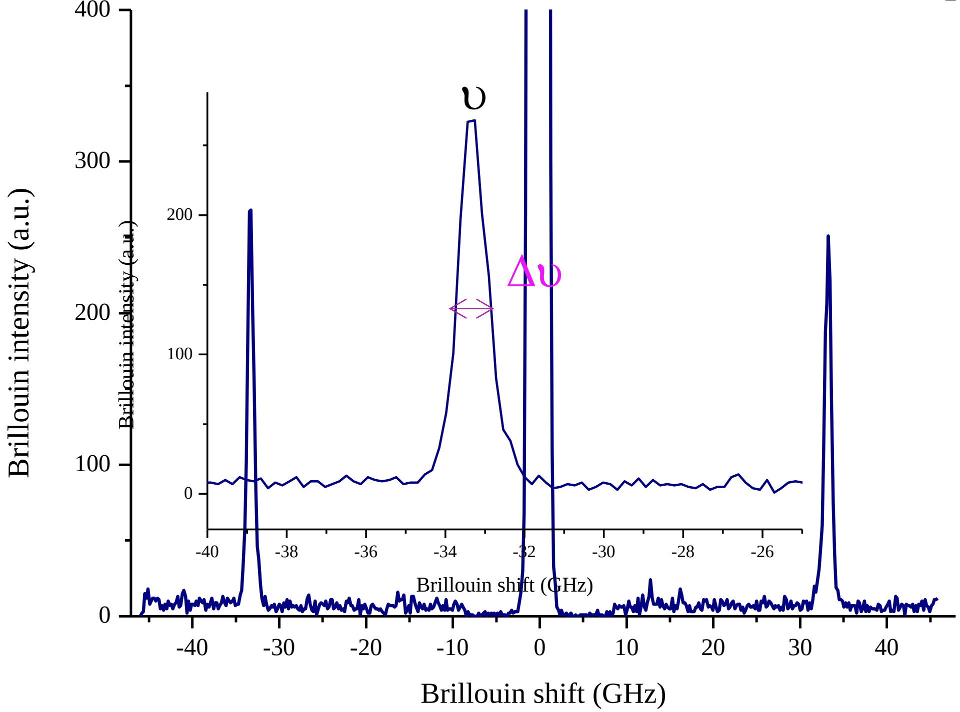
ex: SiO2

V_{sound}~3770 m/s

ν_{BP}~6.2 meV (1.5 THz)

$$\langle D \rangle \approx 2.5 nm$$

Brillouin scattering



From Δυ ⟶ Internal friction = $Q^{-1} = \frac{\Delta \upsilon}{\upsilon}$

Sound attenuation

Low internal friction = acoustic waves are less attenuated

↓

The structure is more homogeneous

Q-1 : plusieurs facteurs cf tran

Brillouin scattering

$C_{11} = \rho V_L$ and $C_{44} = \rho V_T$

Shear modulus : $C_{44} = G$

Compressibility modulus : $\frac{1}{K} = C_{11} - \frac{3}{4} C_{44}$

Bulk modulus : K

Coefficient de poisson: $\sigma = (C_{11} - 2C_{44})/2(C_{11} - C_{44})$

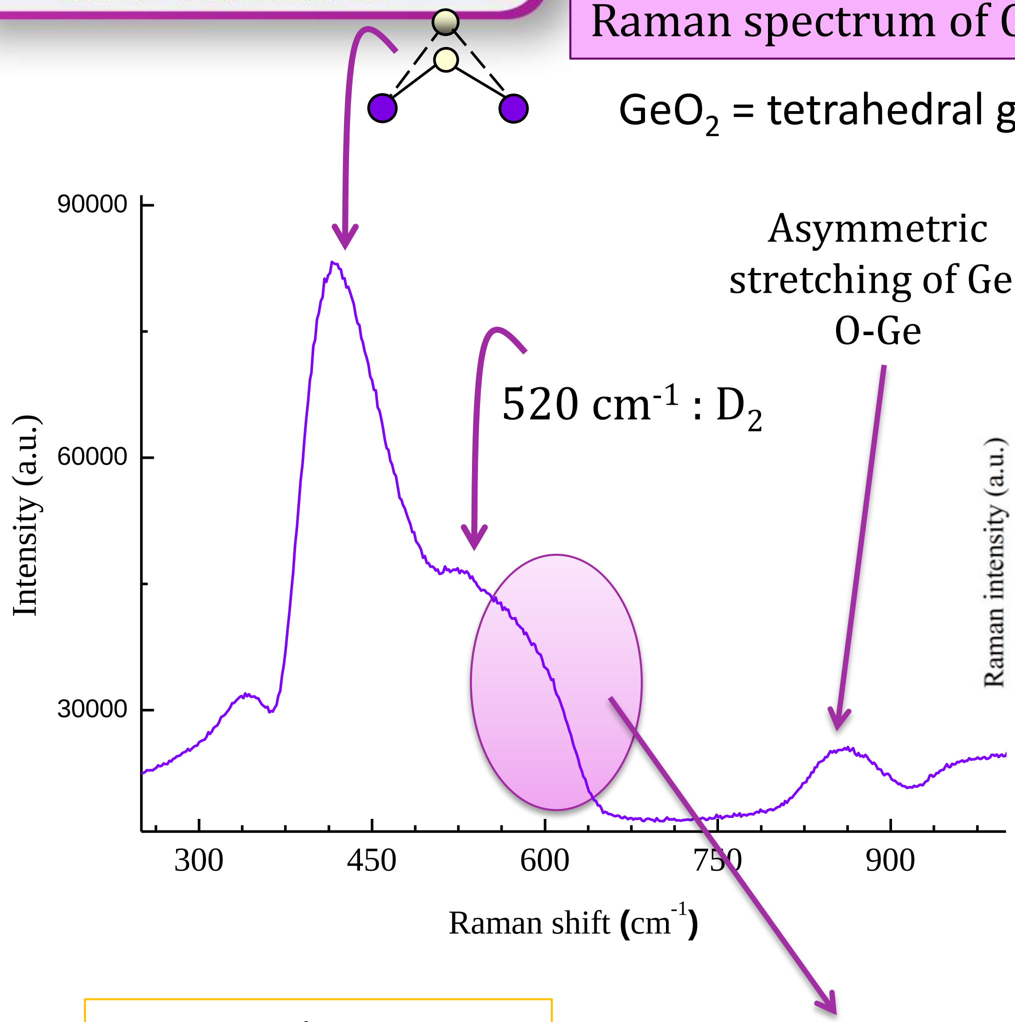
Module de Young: $E = \frac{C_{44}(3C_{11} - 4C_{44})}{C_{11} - C_{44}}$

$$V_L = \left(\frac{K + \frac{4}{3}G}{\rho}\right)^{1/2}$$

Ta_2O_5 and GeO_2 : spectroscopic similarities

Raman spectrum of GeO_2 glass

GeO_2 = tetrahedral glass

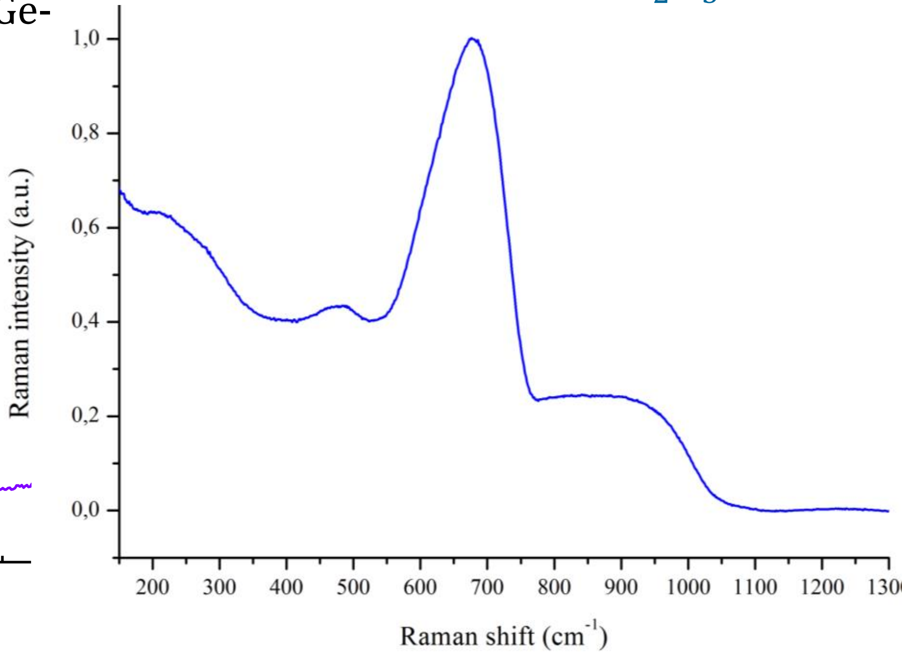


Asymmetric stretching of Ge-O-Ge

520 cm^{-1} : D_2

Stretching of Ge-O bonds (LO/TO)

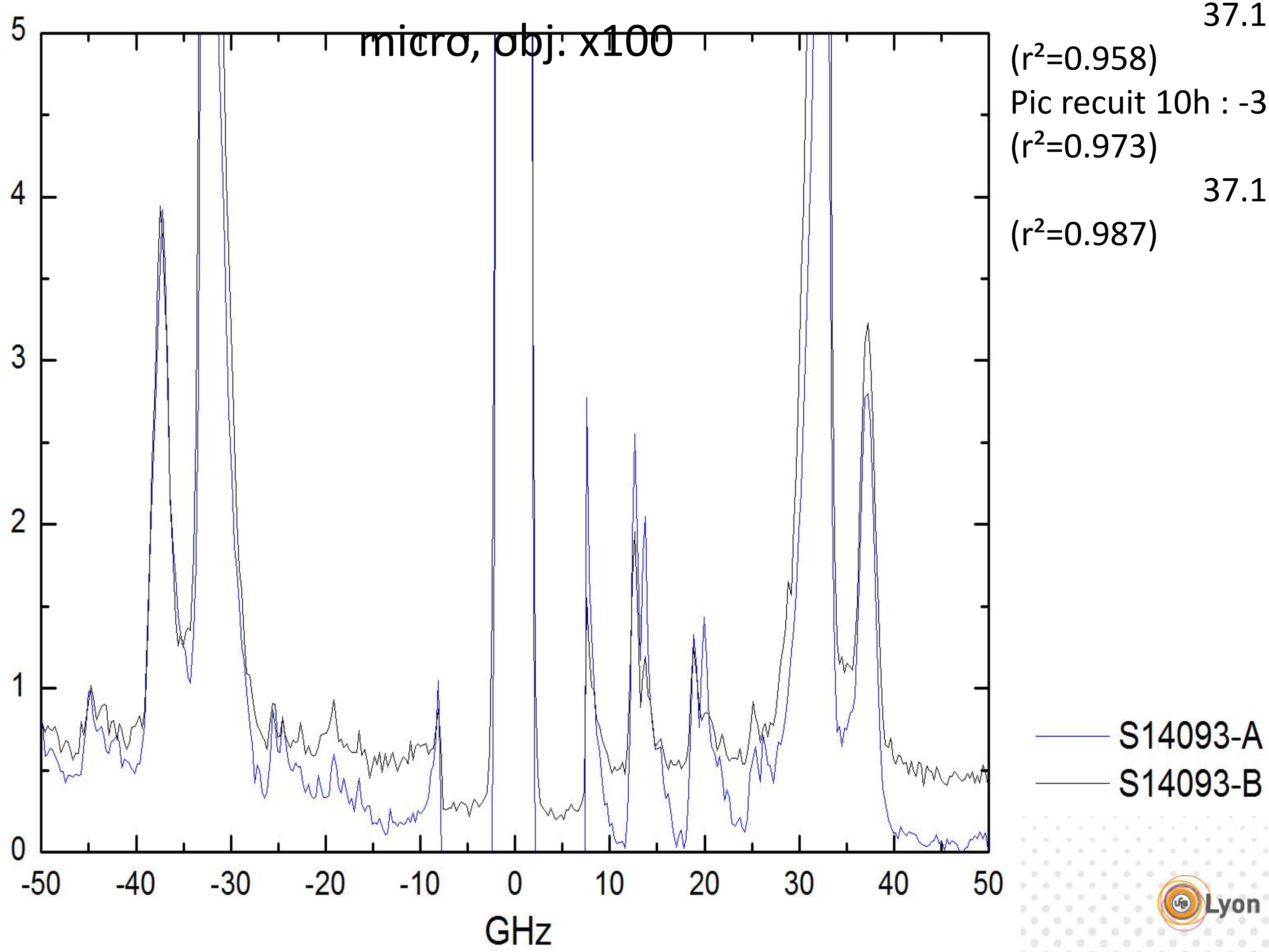
Raman spectrum of Ta_2O_5 films



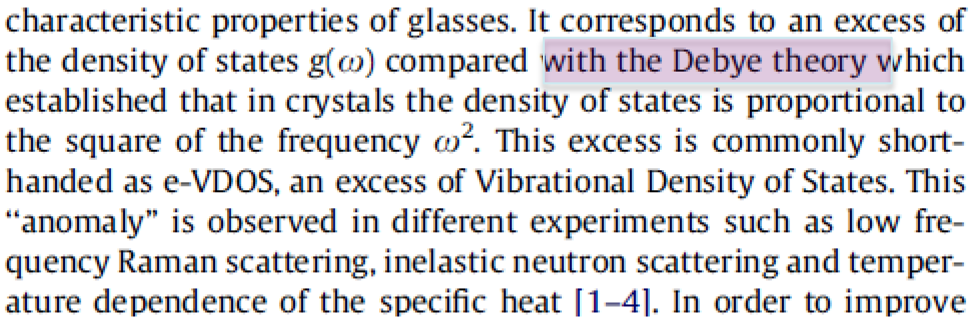
Just an observation but no explanation at this time !!

Couche de Ta_2O_5 sans pastille de tantale sur substrat silice – Brillouin micro, obj: x100

Pic recuit 20h : -37.2 (r^2=0.953)
37.1 (r^2=0.958)
Pic recuit 10h : -37.3 (r^2=0.973)
37.1 (r^2=0.987)



Excess of VDOS compared to the Debye Theory



characteristic properties of glasses. It corresponds to an excess of the density of states $g(\omega)$ compared with the Debye theory which established that in crystals the density of states is proportional to the square of the frequency ω^2. This excess is commonly shorthanded as e-VDOS, an excess of Vibrational Density of States. This "anomaly" is observed in different experiments such as low frequency Raman scattering, inelastic neutron scattering and temperature dependence of the specific heat [1–4]. In order to improve

An interpretation of this elastic anomaly consists of making an analogy with the β to α transition in cristobalite. Huang and K performed MD simulations which are in agreement with this analogy. Between ambient pressure to around 2.5 GPa, the β cycles that are more symmetric and therefore more rigid become α cycles that are less symmetric and therefore more compressible. This cycle transformation explains the fact that the structure becomes more compressible (therefore a lower bulk modulus) when the pressure increases until 2.5 GPa. Their simulations explain correctly also the fast increases in density and the bulk modulus decreases when the pressure increases.