A transparent tellurite ceramic for near infrared applications

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SPCTS Science des Procédés Céramiques et de Traitements de Surface

Université de Limoges

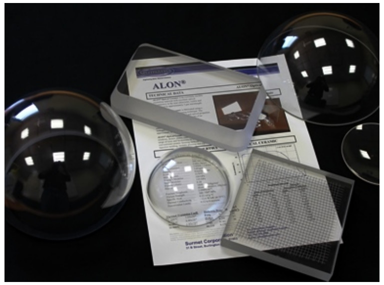
CNRS dépasser les frontières

ENSCI École Nationale Supérieure de Céramique Industrielle

Transparent ceramics

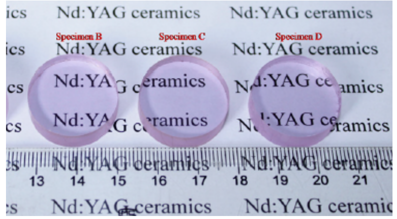
PROPERTIES

- Mechanical
- Dielectric
- Thermal
- **OPTICAL**



ALON Infrared windows optical lenses [1]

$MgAl_2O_4$ Transparent armor [2]



Nd:YAG
Laser ceramic [3]

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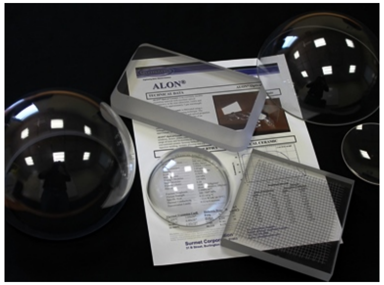

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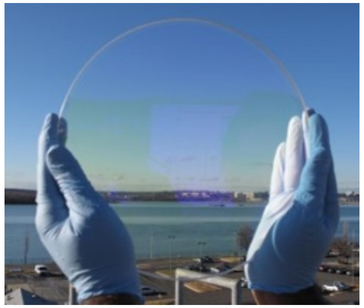

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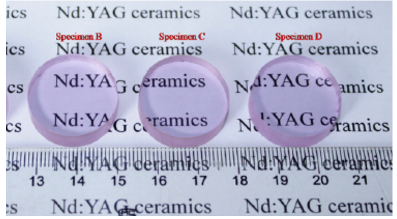
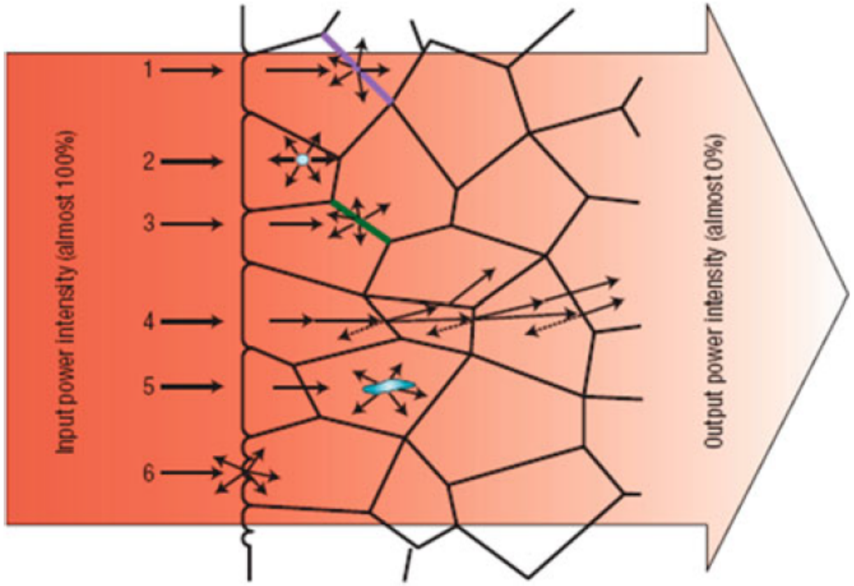


Nd:YAG
Laser ceramic [3]

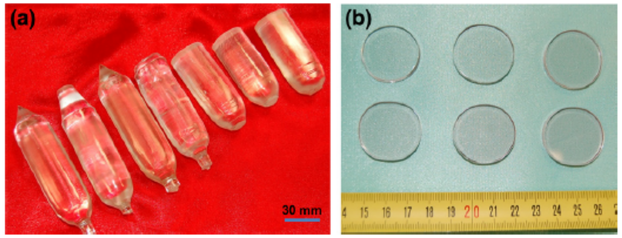
Light scattering sources [4]:

- 1: Grain boundary
- 2: residual pores
- 3: secondary phase(s)
- 4: double refraction
- 5: inclusions
- 6: surface roughness



[1] http://www.surmet.com/technology/alon-optical-ceramics/
[2] A. Goldstein, et al., *Journal of the European Ceramic Society* **2012**, *32*, 2869-2886 .
[3] W. Liu, et al., *Ceramics International* **2012**, *38*, 259-264
[4] L. B. Kong, et al., *Transparent Ceramics*. Editor, Springer International Publishing, **2015**.

Transparent crystalline material elaboration



Sapphire crystals
Conventional single-crystal growth by **Czochralski** [5]

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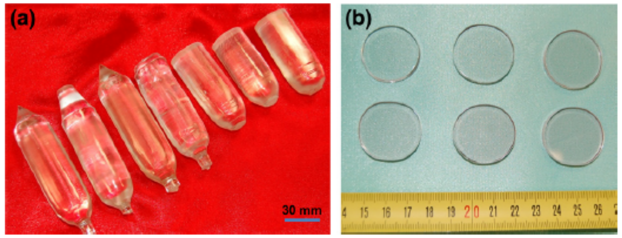

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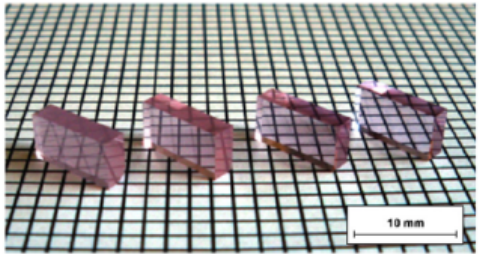

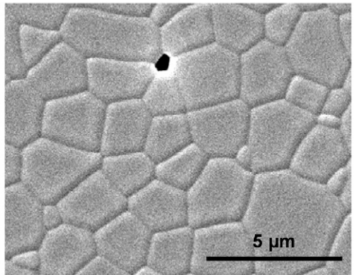

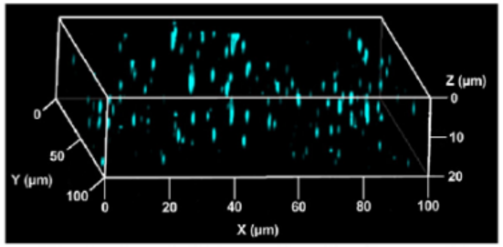

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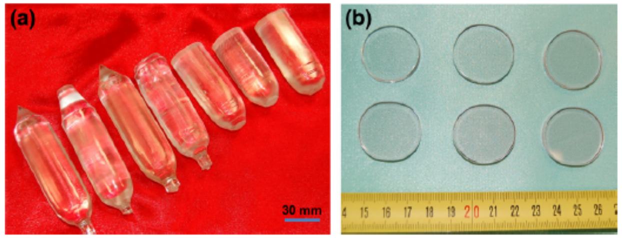

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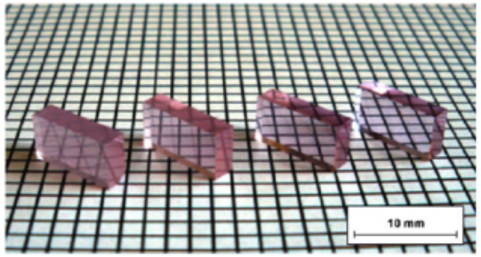

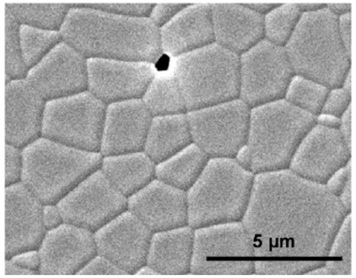

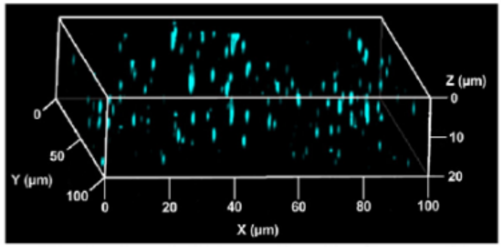

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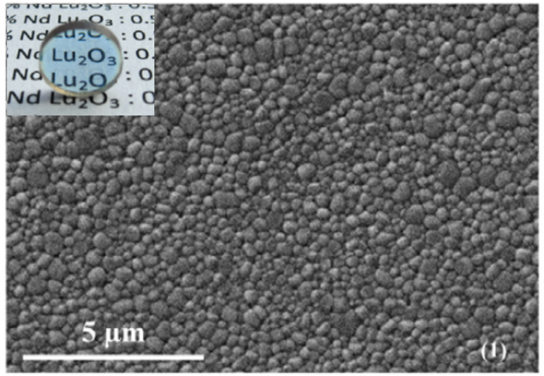
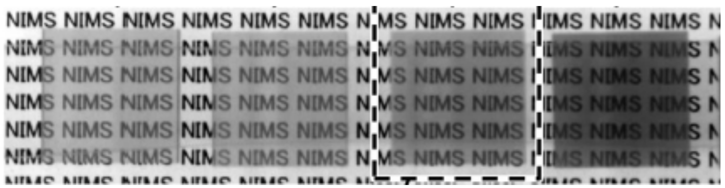


Nd:Lu_2O_3 Slip-casting coupled with **Spark Plasma Sintering** (SPS) [8]



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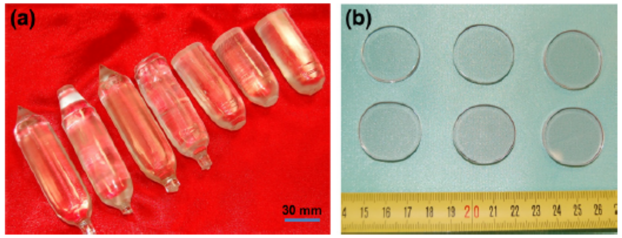

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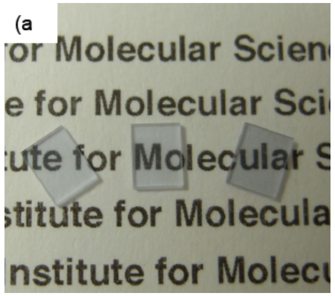
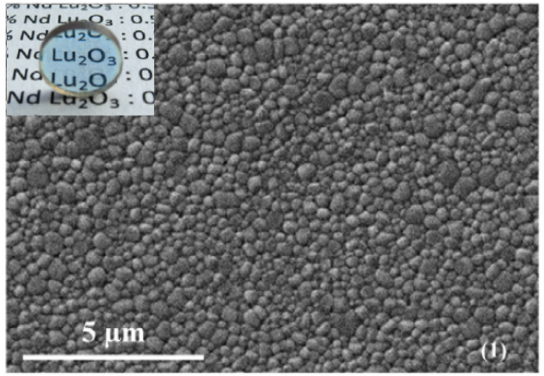


Anisotropic Nd:FAP (Fluorapatite) ceramic [9]



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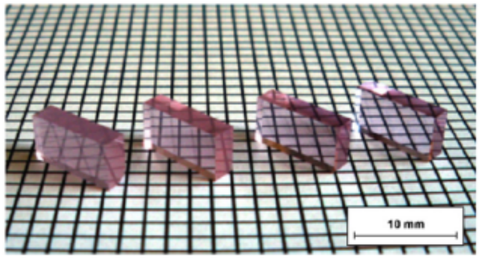

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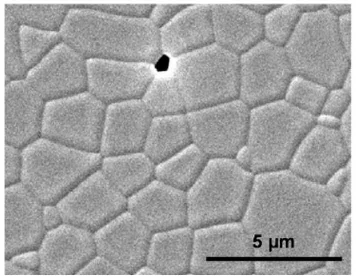

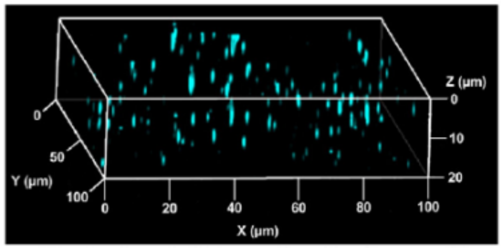

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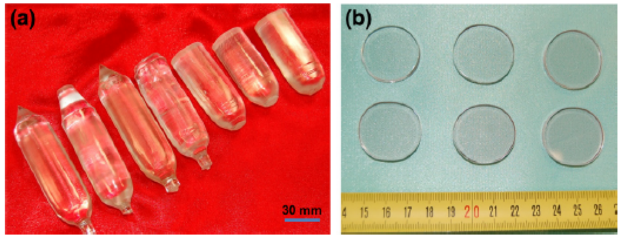

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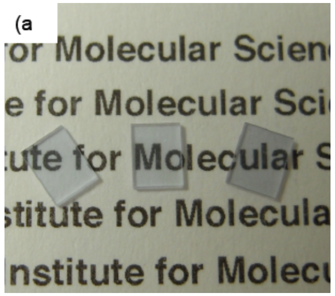

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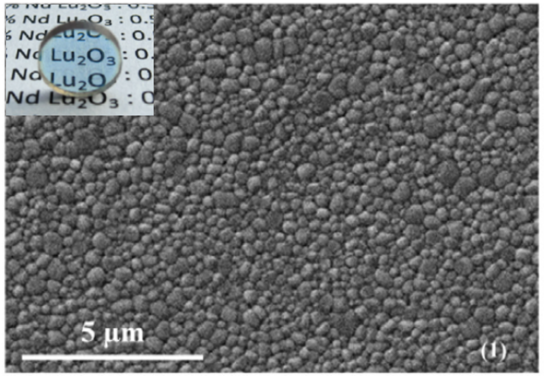

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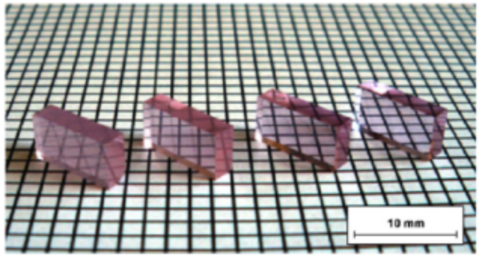

Time consuming

Post-treatment

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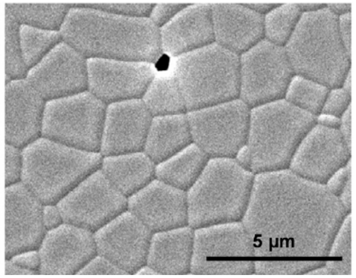
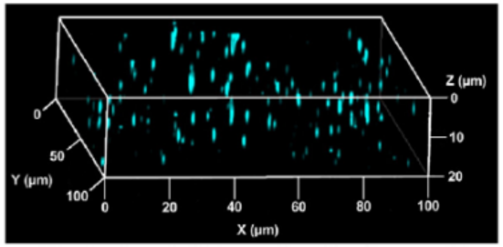
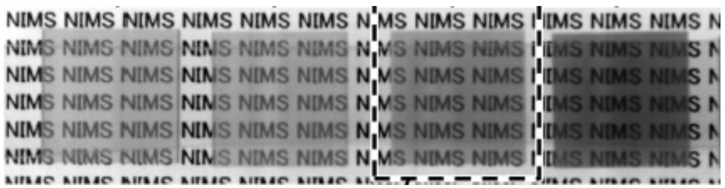
Presence of porosity

Carbon contamination







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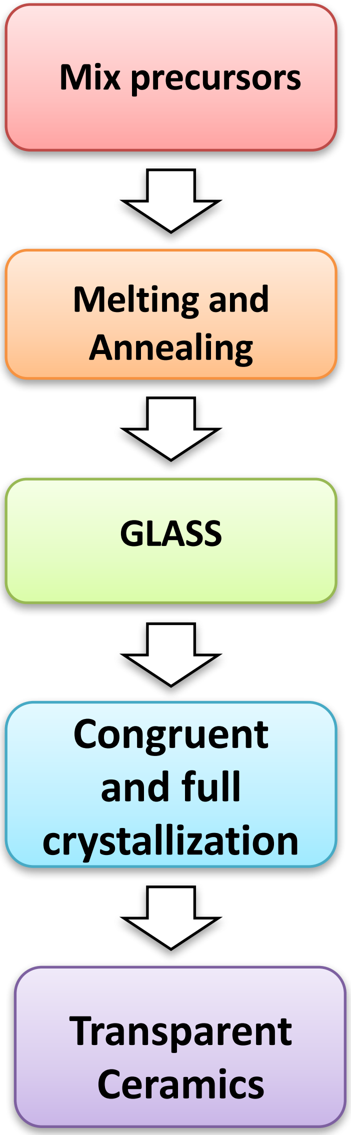
Full crystallization from glass technique



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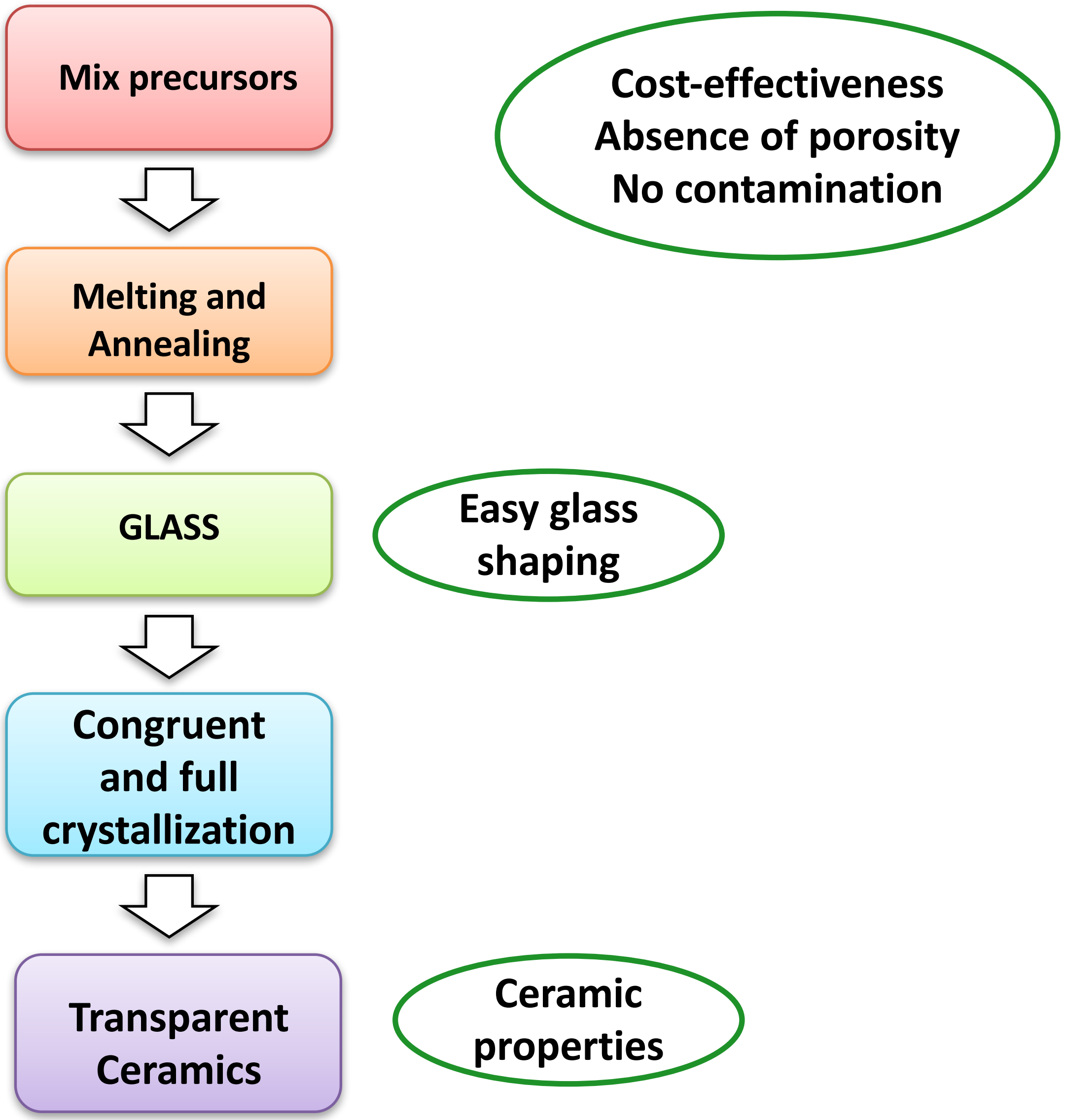


Full crystallization from glass technique

Mix precursors

⇩

Melting and Annealing

⇩

GLASS

⇩

Congruent and full crystallization

⇩

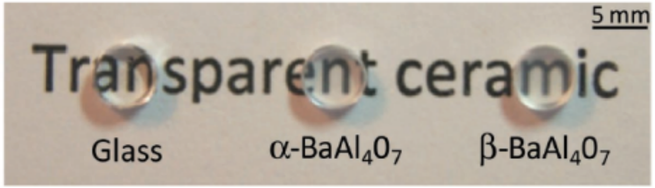
Transparent Ceramics

Cost-effectiveness
Absence of porosity
No contamination

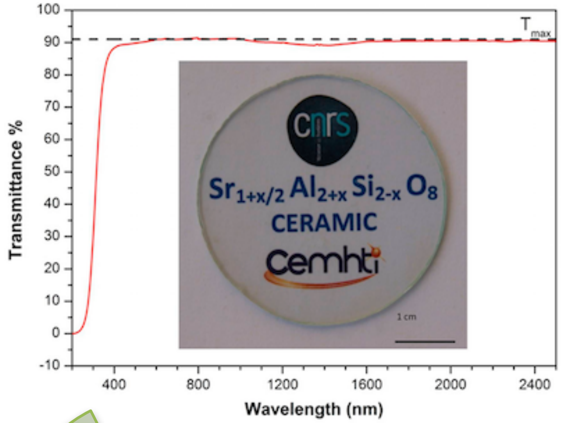
Easy glass shaping

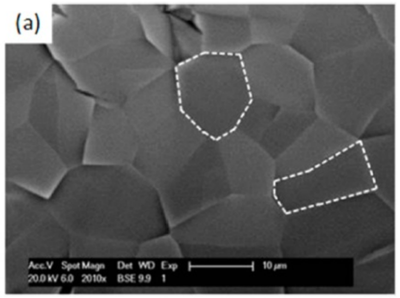
Ceramic properties

Aluminate [10]

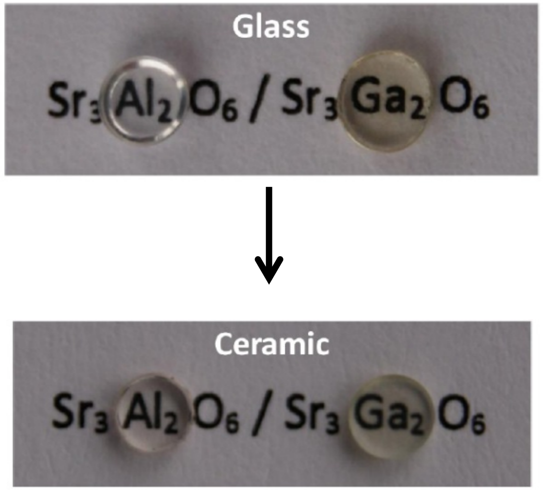


Silico-aluminate [12]





Aluminate et gallate [11]



[10] M. Allix, et al., *Advanced Materials* **2012**, *24*, 5570-5575
[11] S. Alahraché, et al., *Chemistry of Materials* **2013**, *25*, 4017-4024
[12] K. Al Saghir, et al., *Chemistry of Materials* **2015**, *27*, 508-514

1^{st} Transparent tellurite ceramic

75 TeO_2 - 12.5 Nb_2O_5 - 12.5 Bi_2O_3

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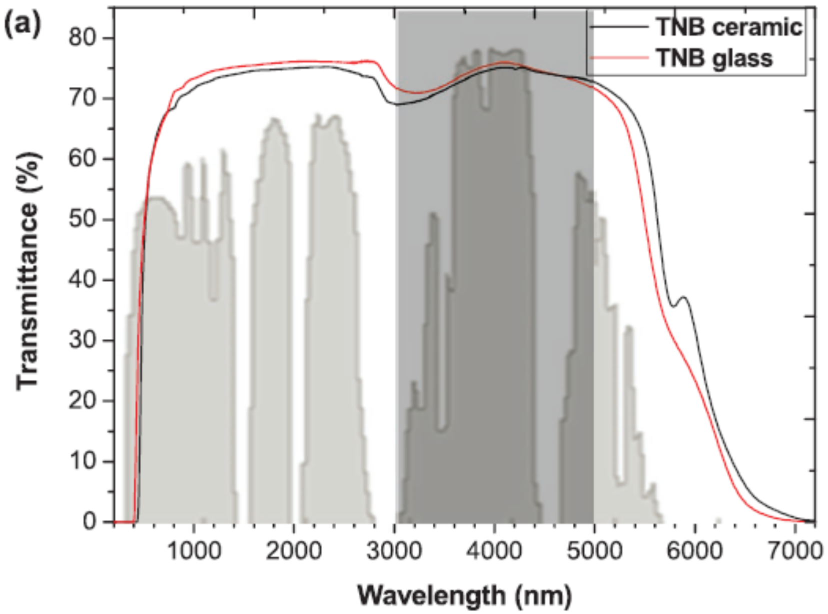

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Outline

- **Characteristic of the TNB glass**
  - **Glass composition**
  - **DSC curves**

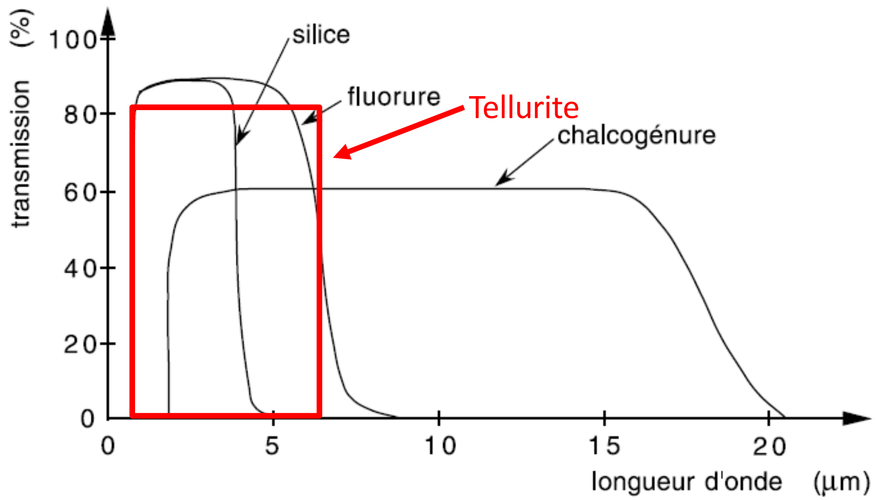
- **Study of the crystallization by X-ray diffraction**

- **Characteristic of the TNB ceramic**
  - **Optical properties**
  - **Microstructure and thermo-mechanical properties**

Glass composition

Tellurite glasses vs silica glasses [14]

- Higher transparency
- Lower melting point (800 -900°C)
- High refractive index
- Good non linear optical properties



[14] R. A. El-Mallawany, in *Book Tellurite Glasses Handbook: Physical Properties and Data*, ed. by Editor, CRC press, City, **2011**, Chapter.

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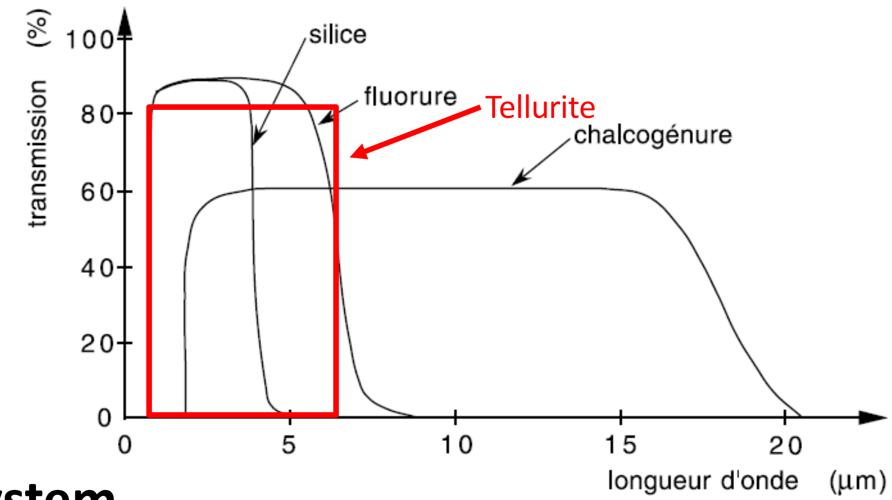


Glass system

75 TeO_2 - 12.5 Nb_2O_5 - 12.5 Bi_2O_3

TeO_2 → Non-linear optical properties

Nb_2O_5 → Thermomechanical properties ($E_{liaison}$ Nb-O-Te > $E_{liaison}$ Te-O-Te)

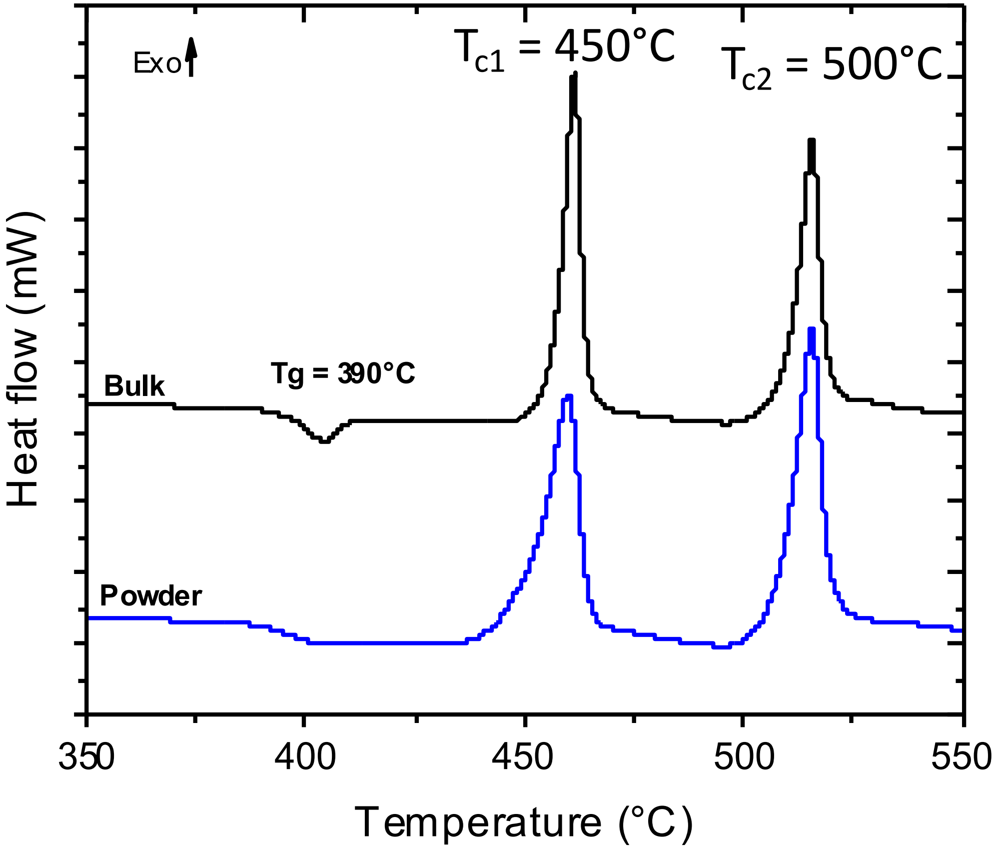
Bi_2O_3 → Homogeneous nucleation lead to crystallization in volume

Congruent crystallization with a **cubic** symmetry

[14] R. A. El-Mallawany, in *Book Tellurite Glasses Handbook: Physical Properties and Data*, ed. by Editor, CRC press, City, **2011**, Chapter

Characteristic of the TNB glass

Mix precursors (TeO_2, Nb_2O_5, Bi_2O_3) → Melting at relatively low temperature: 850°C → PARENT GLASS



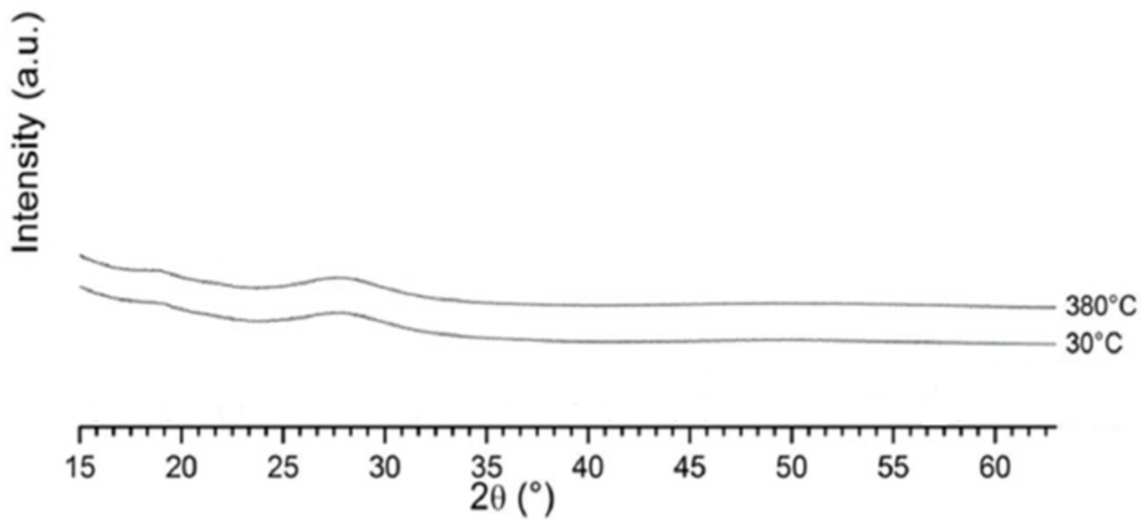
- Similar DSC curves between powder and bulk glass
- Stability of the glass ≈ 60°C

↓

Homogeneous crystallization

Study of the crystallization

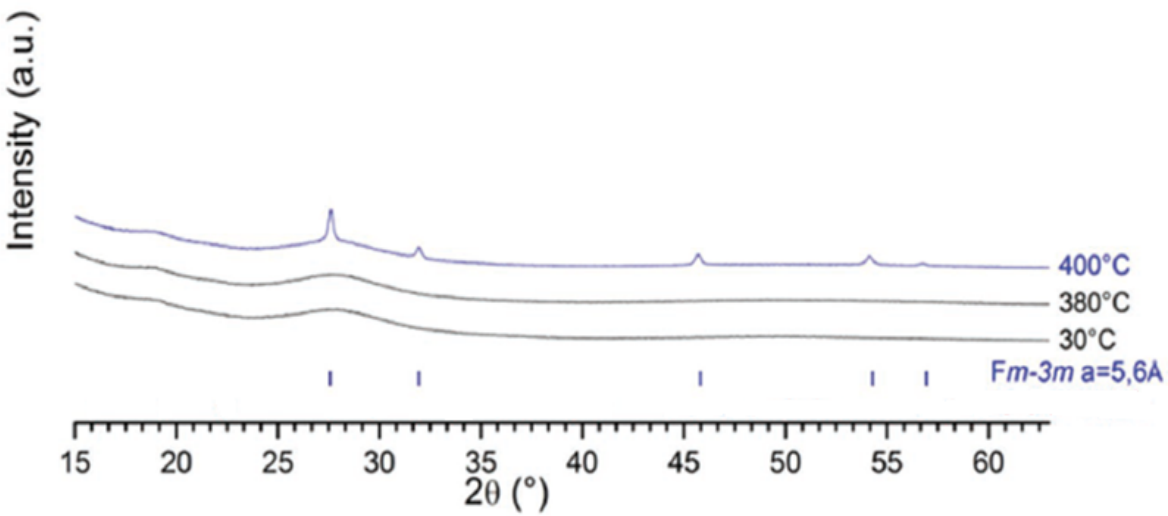
In-situ X-ray diffraction



T < 400°C: Glass

Study of the crystallization

In-situ X-ray diffraction



400°C: Cubic phase $Bi_{0,8}Nb_{0,8}Te_{2,4}O_8$ (anti-glass β-$Bi_2Te_4O_{11}$)

T < 400°C: Glass

Study of the crystallization

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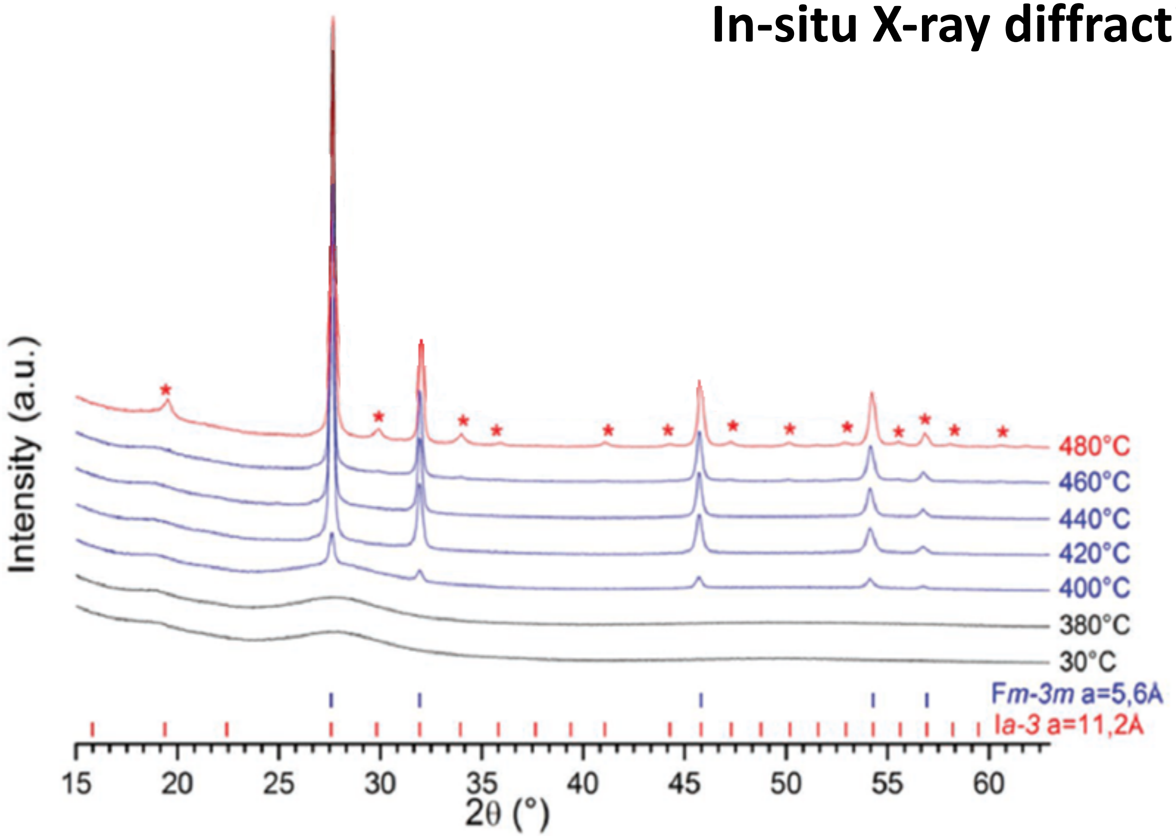

480°C: Transformation into another polymorph of $Bi_{0,8}Nb_{0,8}Te_{2,4}O_8$ (isostructural to $SnTe_3O_8$)

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T < 400°C: Glass

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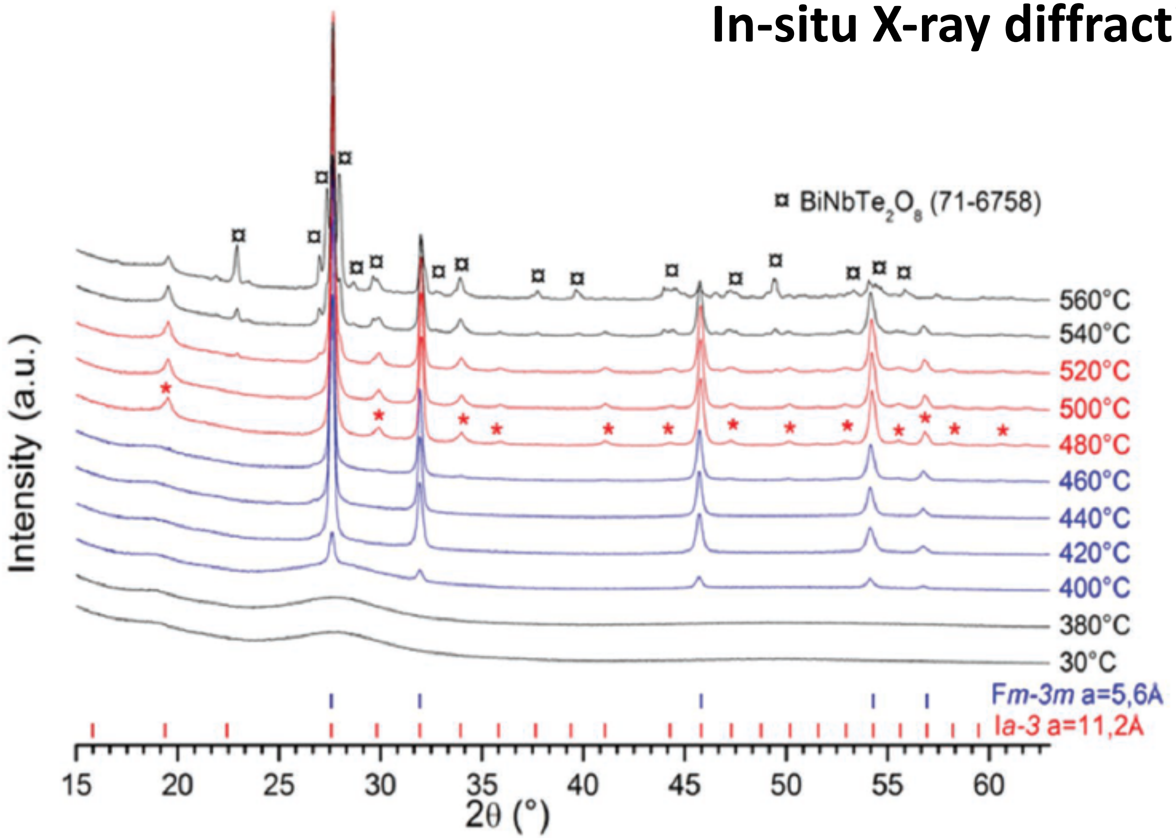

T > 520°C: Secondary phases ($BiNbTe_2O_8$)

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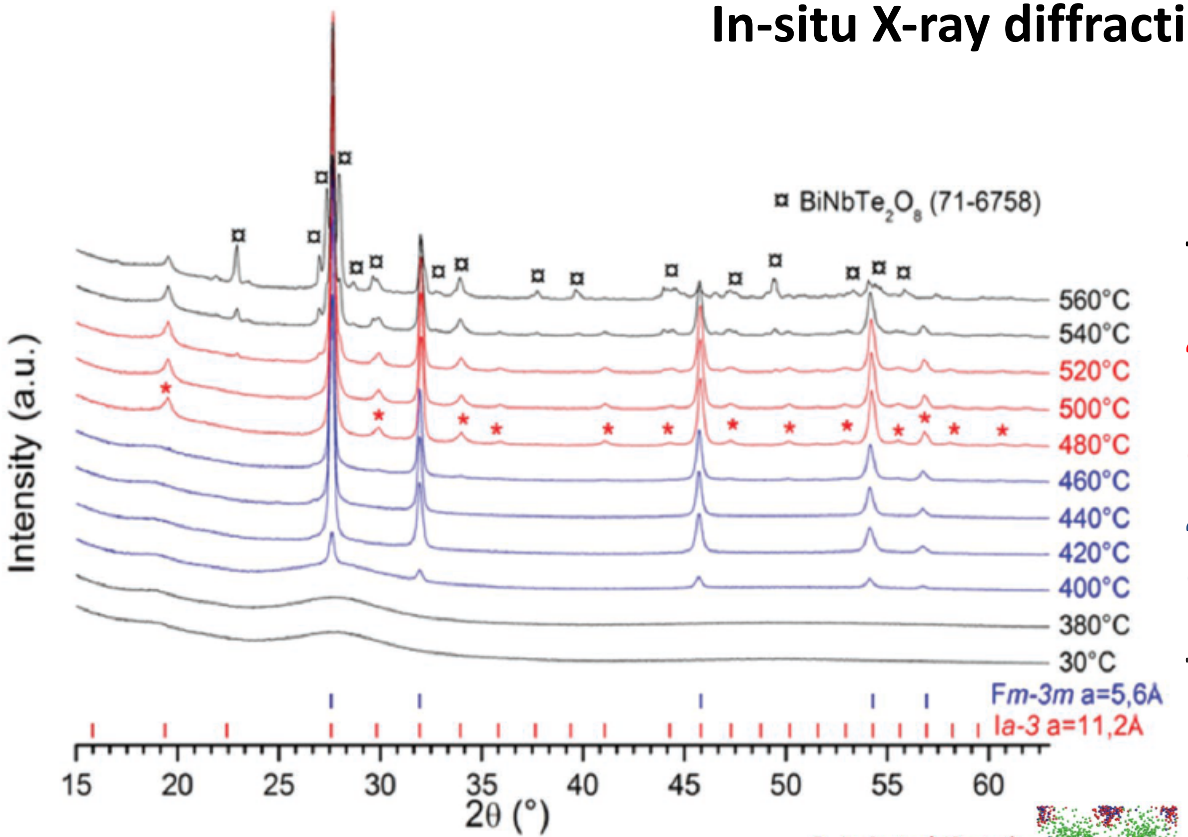
T < 400°C: Glass

Temperature range
400°C < T < 520°C

Study of the crystallization

In-situ X-ray diffraction



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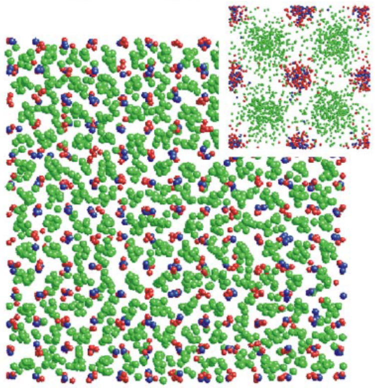
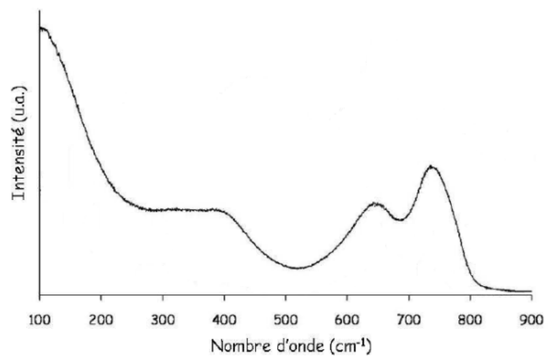
T < 400°C: Glass

Anti-glass:
concept introduce by Trömel [15] in 1983 in tellurite-based glasses. Structure: a cationic periodic order at long range order and a disorder of the anions [16]

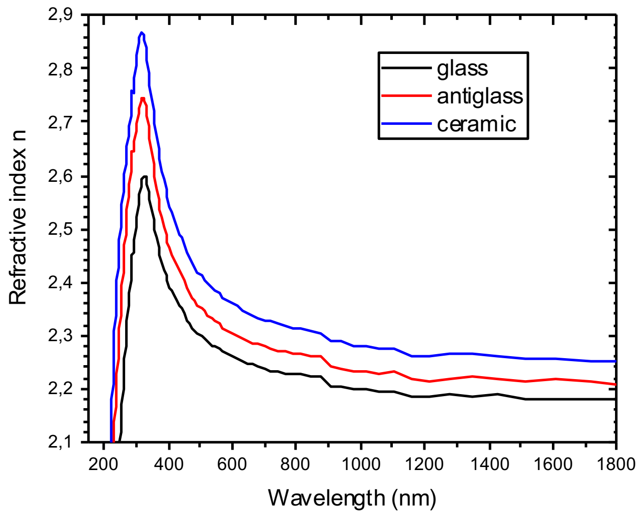


Raman spectra of β-$Bi_2Te_4O_{11}$ [17]



[15] M. Trömel, et al., *Journal of The Less-Common Metals* **1985**, *110*, 421-424
[16] O. Masson, et al., *Journal of Solid State Chemistry* **2004**, *177*, 2168-2176.
[17] O. Durand, "Propriétés structurales et vibrationnelles des phases désordonnées dans le système TeO_2-Bi_2O_3", Université de Limoges, **2006**.

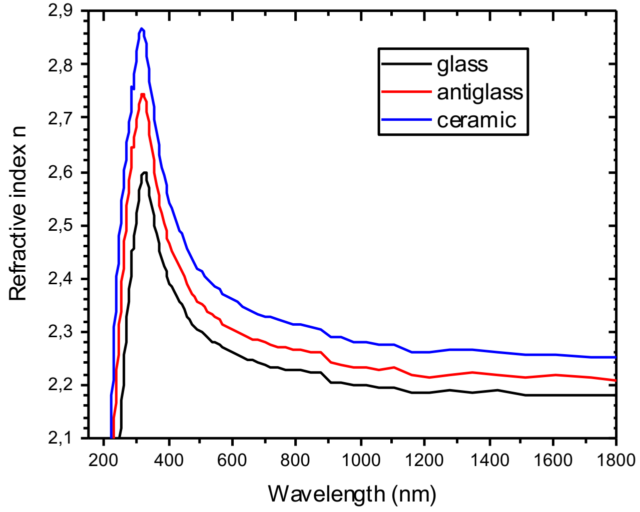
Optical characterization



Refractive index

Slight difference between glass, antiglass and ceramic

Optical characterization



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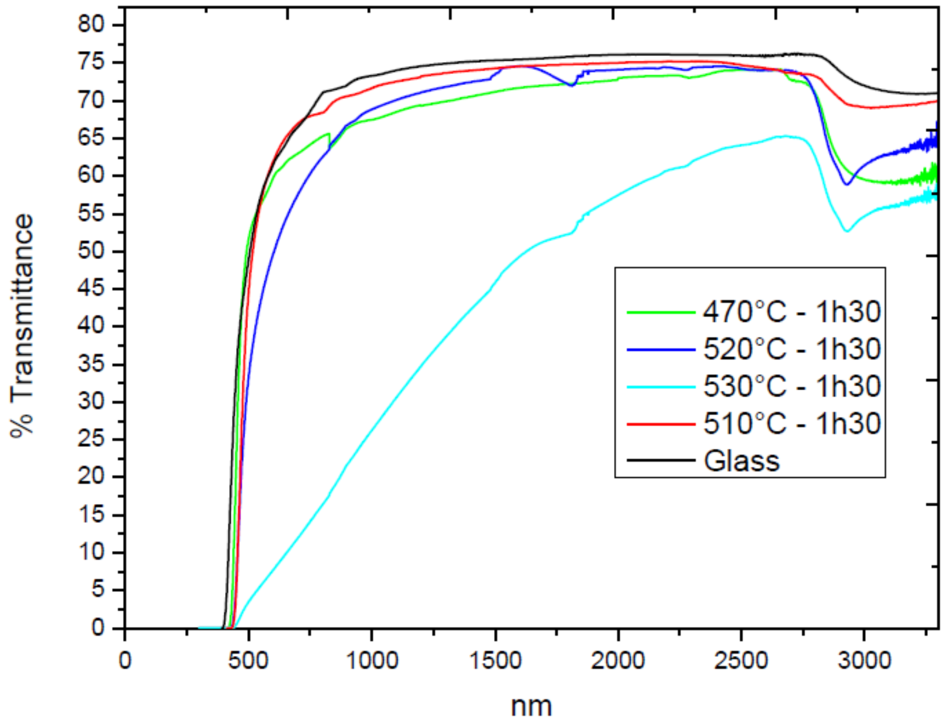


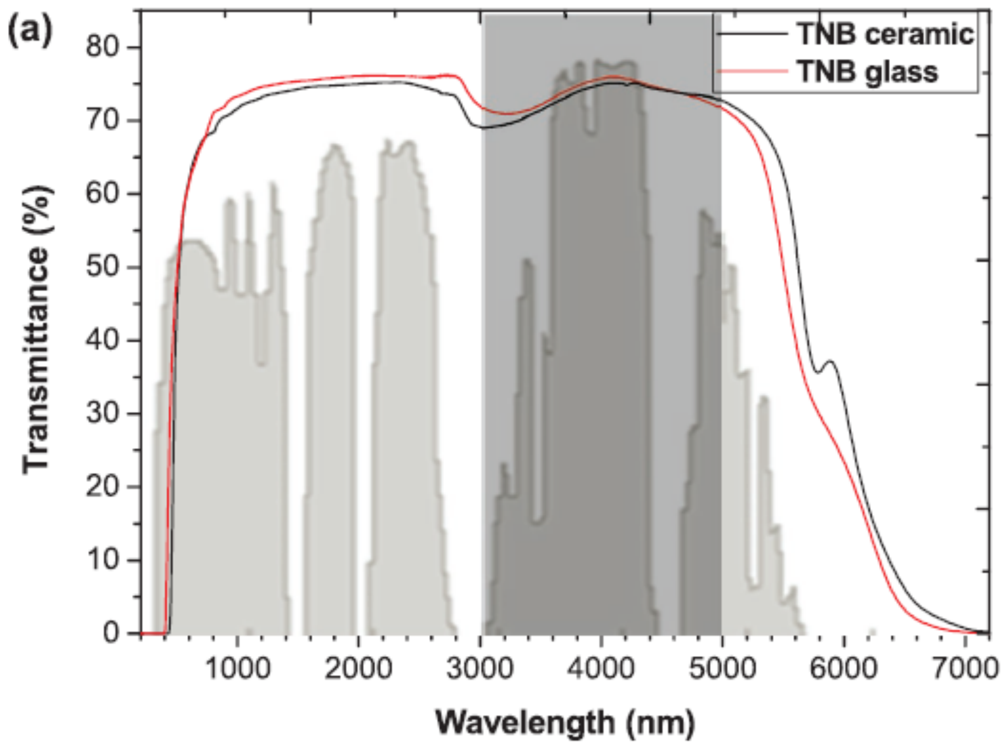
T < 510°C: light scattering (residual glass and/or antiglass with a different n)

T > 510°C: translucent and opaque ceramics (cubic phase decomposition and cracks at grain boundaries)

510°C – 1h30

Transparent ceramic

Parent glass → **Crystallization (510°C – 1h30)** → **TRANSPARENT CERAMIC**



- High transparency up to **74%** (15 cm between ceramic and text)
- Transparent in the MIR (**3 - 5 µm**)

Properties of the ceramic

EDS analysis

Congruent crystallization

Sample	Nb	Te	Bi
Glass	21.0(3)	58.6(3)	20.4(3)
Ceramic (510 °C, 1 h 30 min)	20.9(3)	58.7(2)	20.4(2)

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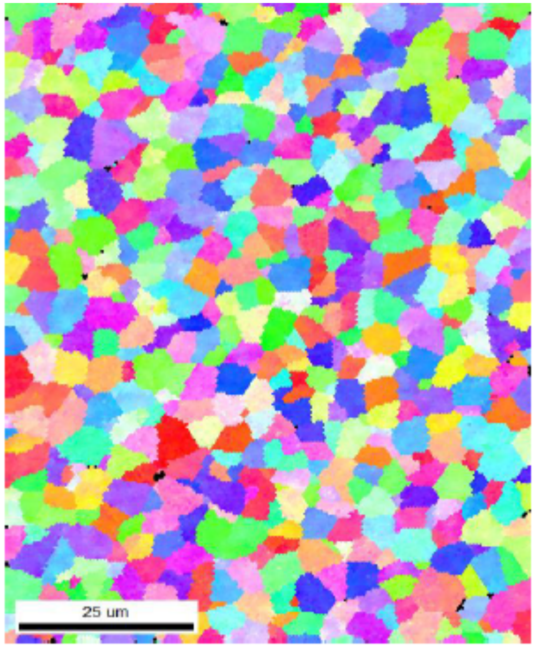
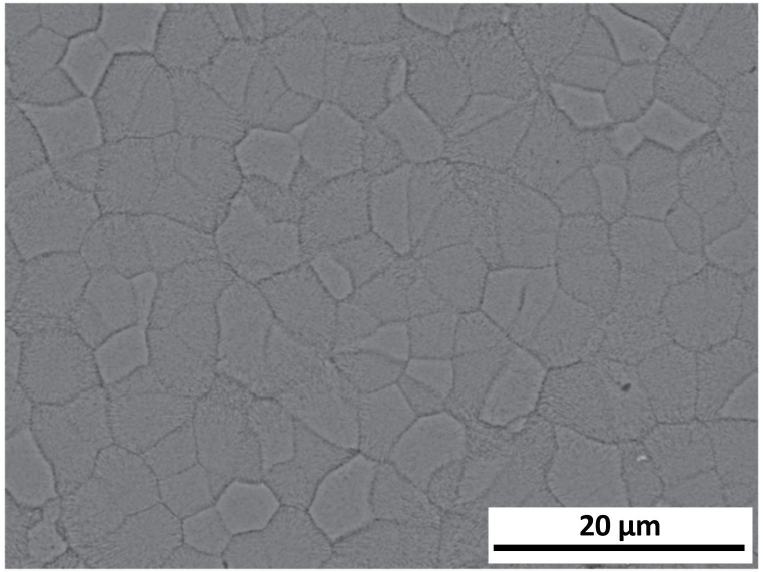


EBSD-SEM map
(F. Brisset, ICMMO)



SEM image
(Y. Launay, SPCTS)

Absence of porosity
No residual anti-glass phase
Thin grain boundaries

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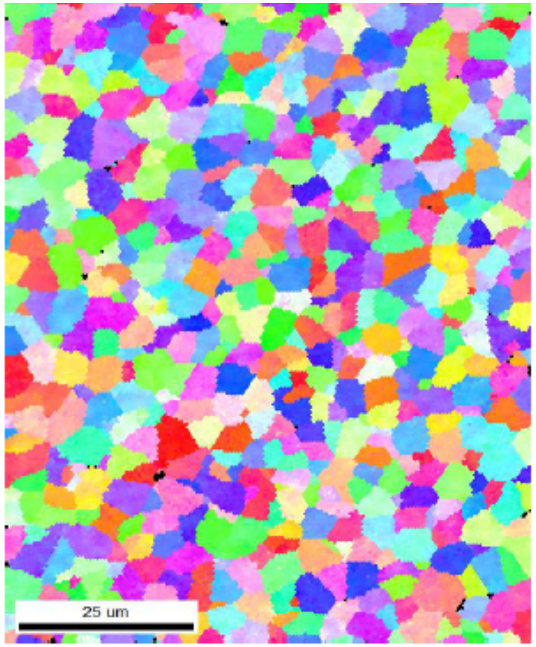

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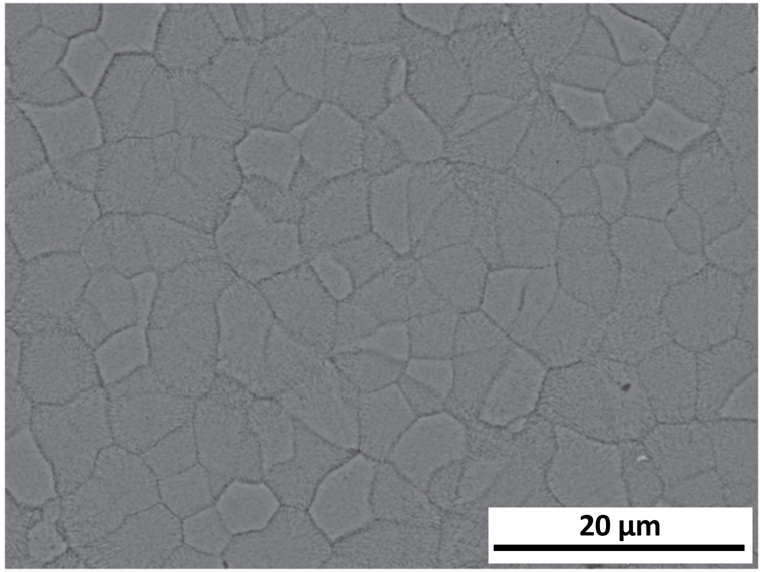

SEM image
(Y. Launay, SPCTS)

Absence of porosity
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Thin grain boundaries

	TNB glass	TNB ceramic
Young's modulus, E [GPa]	59.4	**79.5**
Thermal conductivity [W m^{-1} K^{-1}]	0.75	**1.1**

Conclusion

Cost-effective process

Intricate shape (bulk, fibers, …)

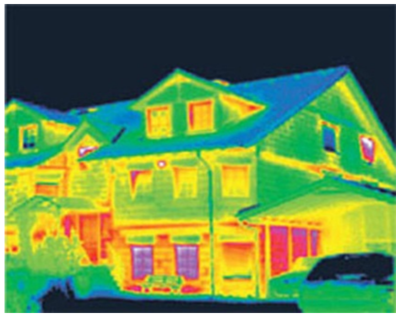
High transparency (up to 5.5 µm)

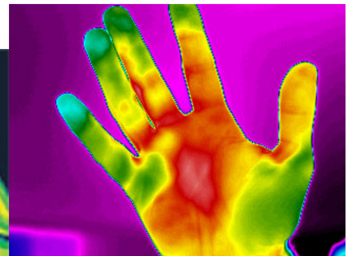
Parent glass → **Full and congruent crystallization** → **Ceramic**

High refractive index good thermo-mechanical properties

No residual porosity no contamination

Application: infrared lenses for thermal imaging cameras





Thank you

for

your attention

SPCTS Science des Procédés Céramiques et de Traitements de Surface

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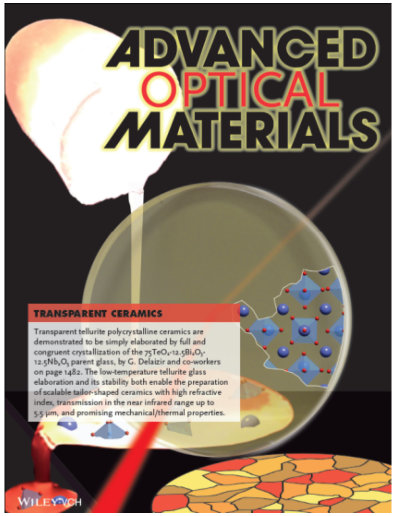
Cemhti

cnrs dépasser les frontières

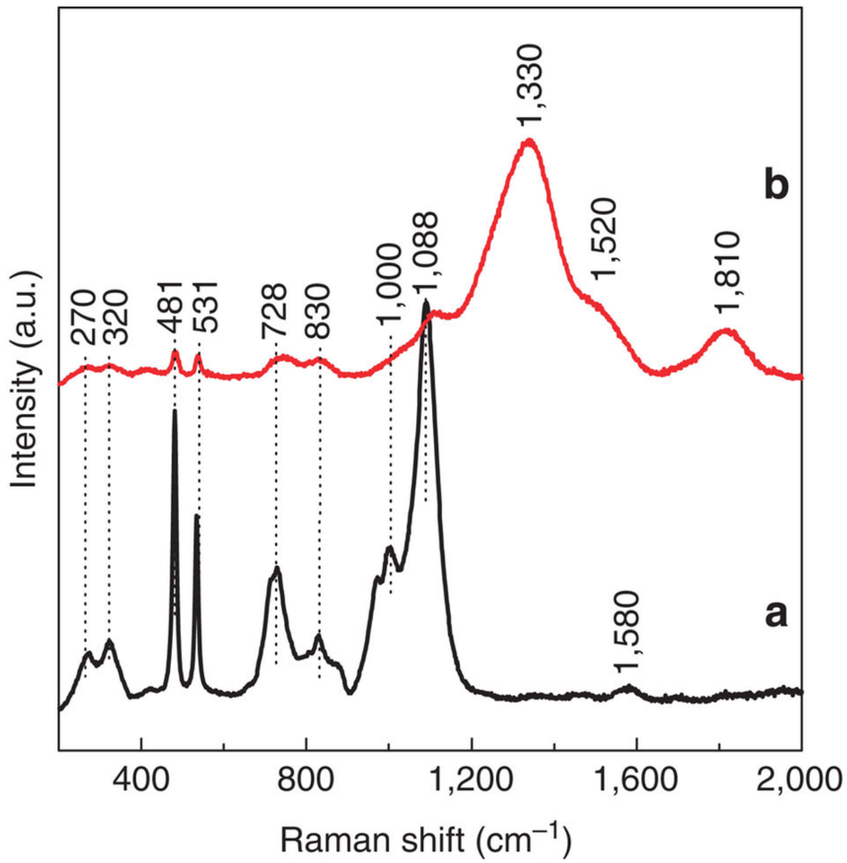


A. Bertrand, et al., *Advanced Optical Materials* **2016**, *4*, 1482-1486

E-mail: morgane.dolhen@unilim.fr

Xlim Institut de recherche

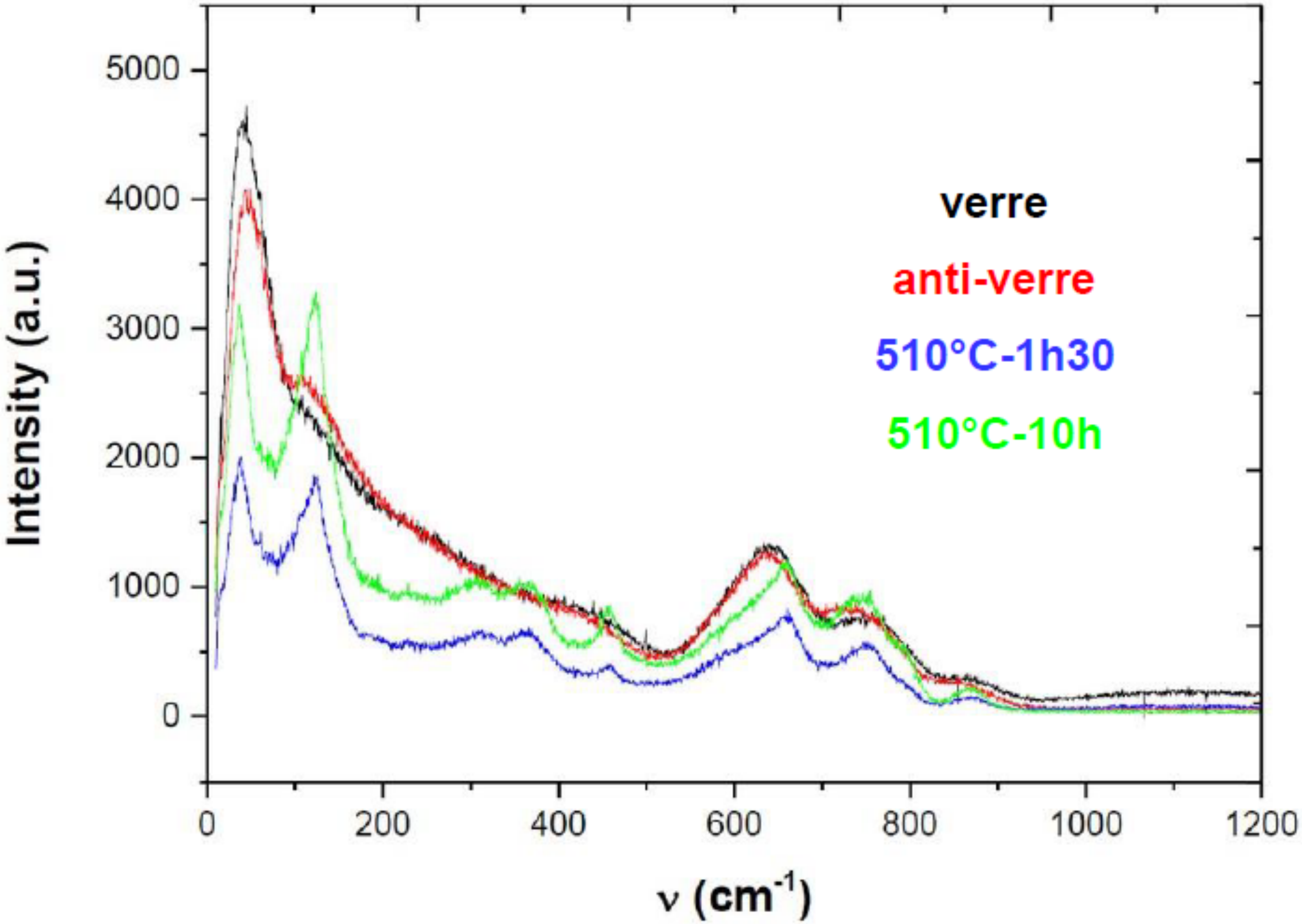
Raman spectra of amorphous and crystallized phase



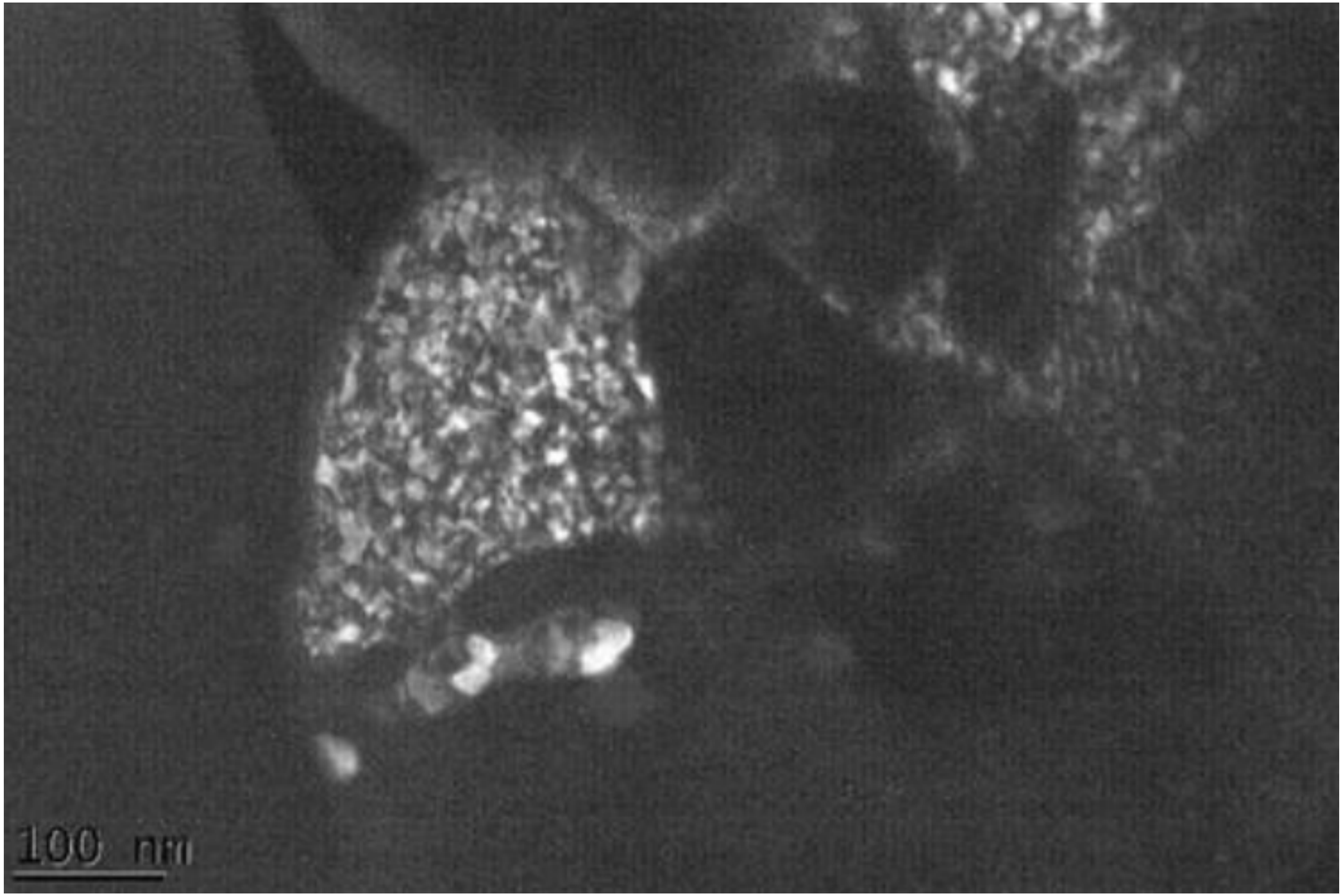
amorphous

crystallized

Raman spectra of glass, anti-glass and ceramic



Transmission Electron Microscopy



TEM image of a ceramic (thermally treated at 510°C – 1h30)

Laser Emission ?

J. Carreaud, A. Labruyère, H. Dardar, F. Moisy, J. R. Duclère, V. Couderc, A. Bertrand, M. Dutreilh-Colas, G. Delaizir, T. Hayakawa, A. Crunteanu, P. Thomas, *Optical Materials* **2015**, *47*, 99-107