Summer school:
"Structural role of elements in glasses, from classical concepts to a reflexion over broad composition range"

Tellurite (TeO_2-based) glasses

27th to 31st March, 2017 - Cargèse

dépasser les frontières

Université de Limoges

Science of Ceramic Processes and of Surface Treatments

UMR CNRS 7315
University of Limoges – ENSCI - CNRS
www.unilim.fr/spcts

European Ceramic Center
Director : Thierry Chartier

204 staff - 106 permanents

66 Professors and Associate Professors
13 CNRS researchers
26 Engineers and Technicians
98 PhD Students and Post-docs

Labex Sigma-Lim,
Limoges, France

Outline

- Introduction / Interest of TeO_2-based glasses

- Structural features and peculiarities
  - The role of cation's valence / structure

  (Notion of « weak, intermediate and strong » modifier)

  - Is TeO_2 really a glass former?

- What's the origin of high 3rd-order NLO property ? Structure / nonlinear optical properties relationships

- Some examples of tellurite materials elaborated in SPCTS : transparent glass-ceramics and ceramics …

Introduction / Interest of TeO_2-based glasses

- Relatively low melting temperature (700-900° C)
- Good chemical and thermal stability
- High linear and non-linear refractive indices $\chi^{(3)}$) . n≈ 2- 2.2
- Good optical transmission in the near infrared (up to 6 mm)
- High Raman gain coefficients (60 times as large as silicate glass)
- High solubility of the rare earth ions
- Lower phonon energies (other oxide glasses) → Favour radiative transitions
- High emission and absorption cross sections *(highest emission cross section among the Nd^{3+} doped glasses)*

n_2, $\chi^{(3)}$ > × 50 that of silica

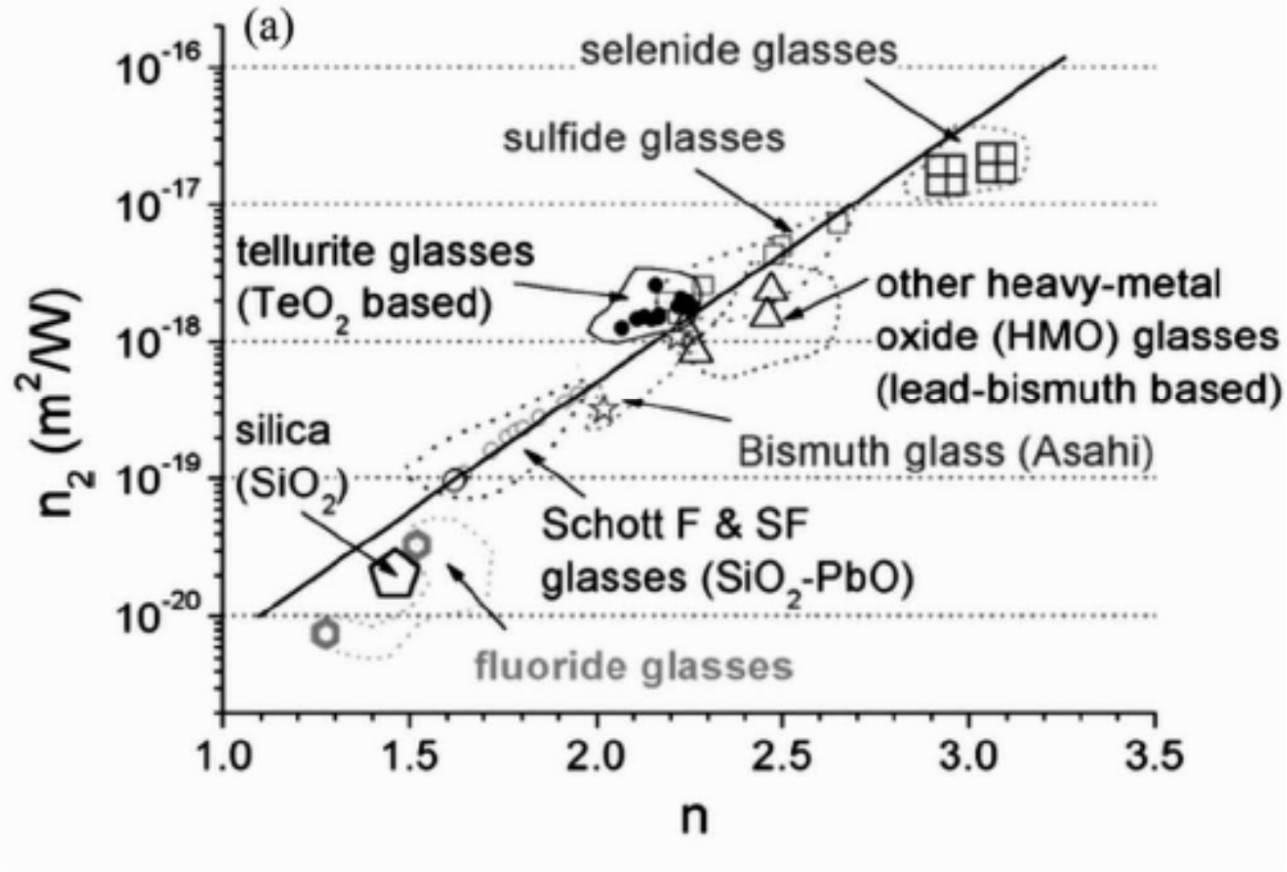
Glass Matrix	hω (cm^{-1})
Borate	1400
Phosphate	1200
Silicate	1100
Germanate	880
Tellurite	700-800

LASER APPLICATIONS

$$P = \varepsilon_0(\chi^{(1)} \cdot E + \chi^{(2)} \cdot E \cdot E + \chi^{(3)} \cdot E \cdot E \cdot E + \cdots)$$

Introduction / Interest of TeO_2-based glasses

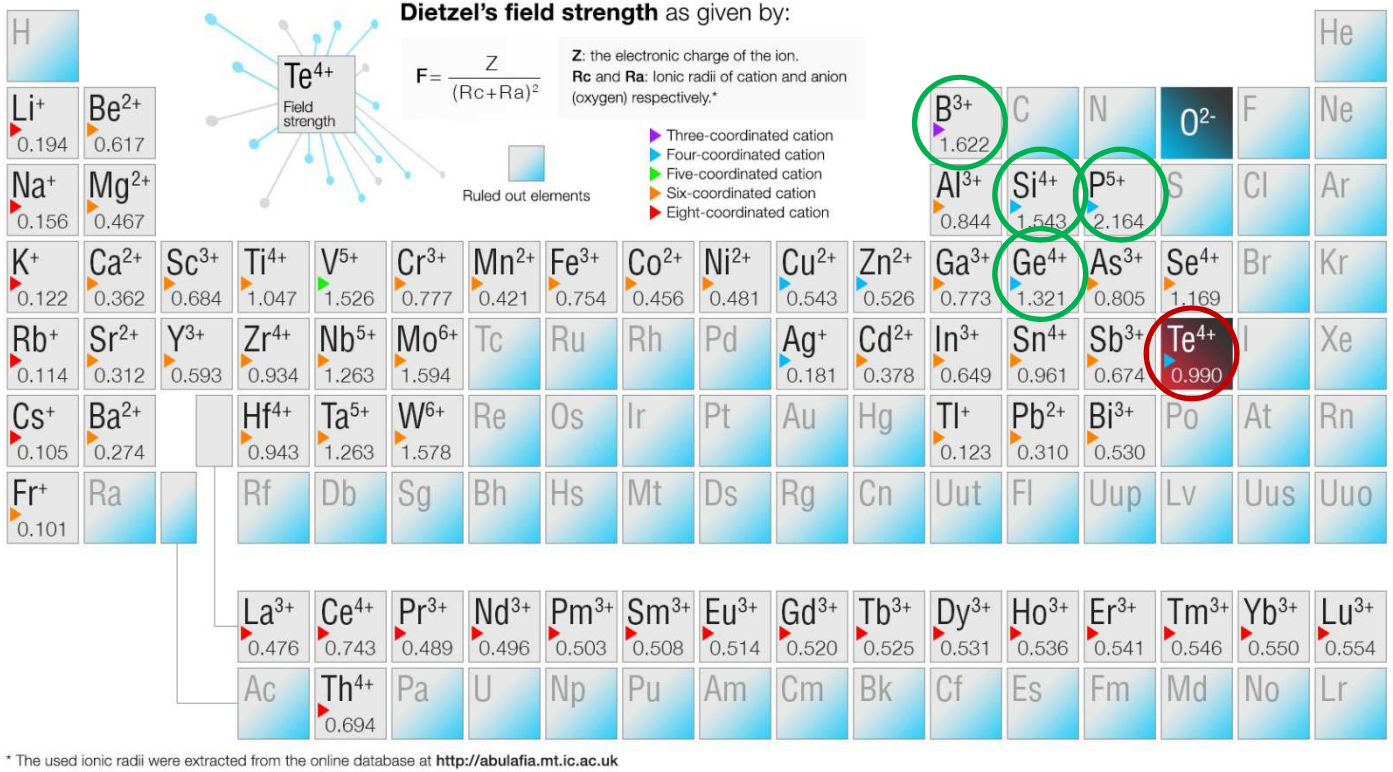
Nonlinear optical properties



Introduction / Interest of TeO_2-based glasses

Glass former ?

Oxide glasses



Dietzel (1942) Field Strength : high F.S. cations – high cation-oxygen bond energy

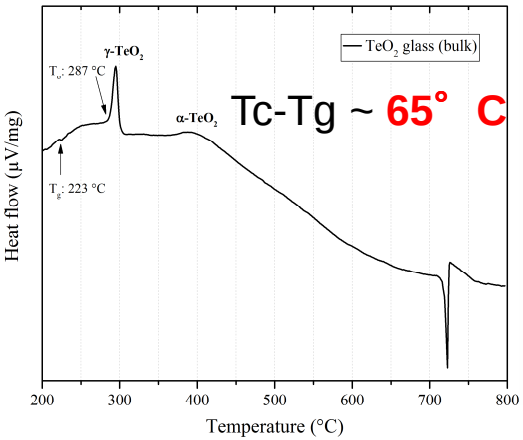
Glass formers	> 1.3
Glass modifiers	< 0.4
Intermediates	0.4 ≤ F.S. ≤ 1.3

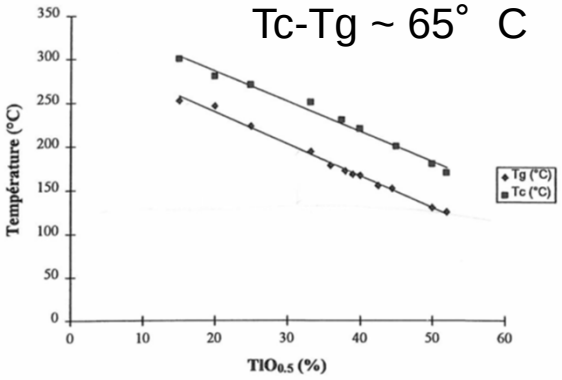
Introduction / Interest of TeO_2-based glasses

Ab-initio modelling : best $\chi(3)$ for pure TeO_2 glass

Pure TeO_2 glass impossible to prepare in bulk pieces !!

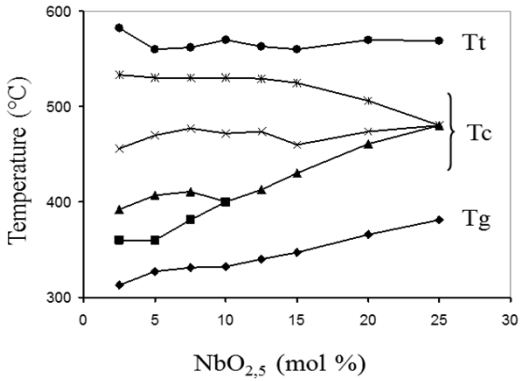
Addition of modifier oxides is necessary to improve the thermal stability (Tc-Tg): large glassy domains





TeO_2-Tl_2O

Tc-Tg > 100° C



TeO_2-Nb_2O_5

Objective: compromise between the thermal stability and the nonlinear optical properties

Modifier oxides

- hyperpolarisable cations: electronic lone pair holders (Tl^+, Pb^{2+}, Bi^{3+}…)
- d^0 ions (Ti^{4+}, Nb^{5+}, W^{6+} …)

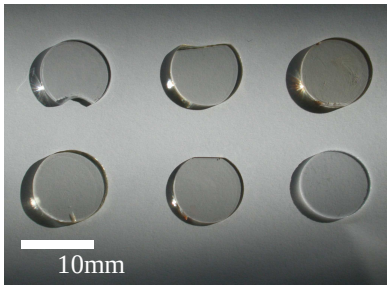
Introduction / Interest of TeO_2-based glasses

Glass forming domains

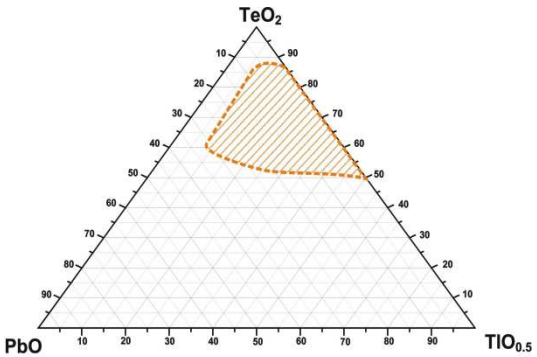
Synthesis / Processing

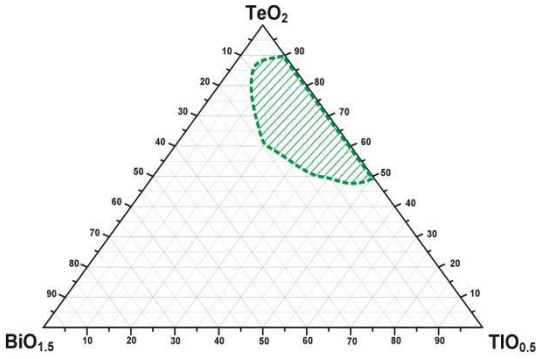
Melting in platinum crucibles

Shaping: air-quenching of the melt by flattening between two brass blocks separated by a brass ring

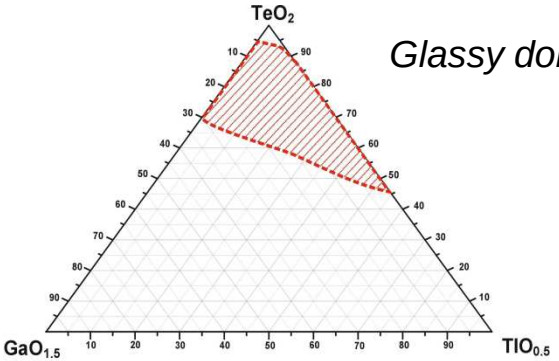


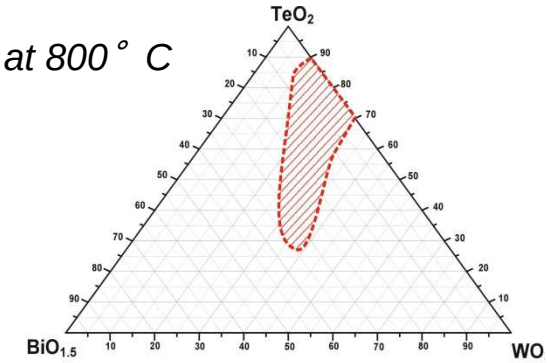
Annealing / Polishing

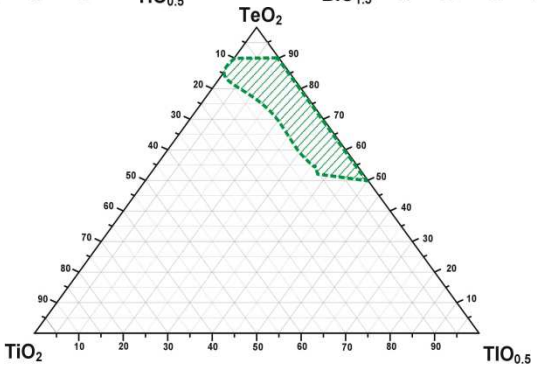




Glassy domains at 800 ° C

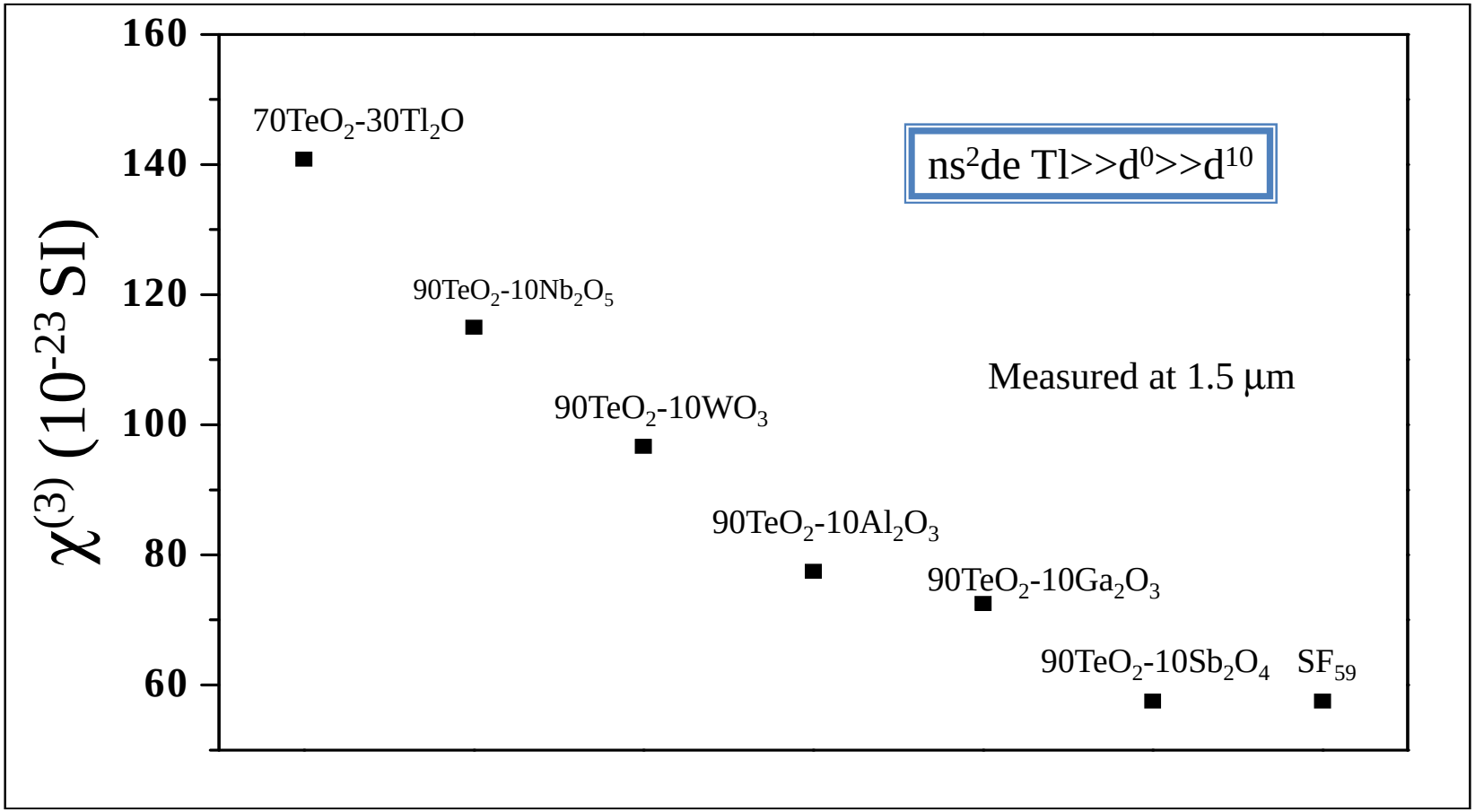






Introduction / Interest of TeO_2-based glasses

Nonlinear optical properties



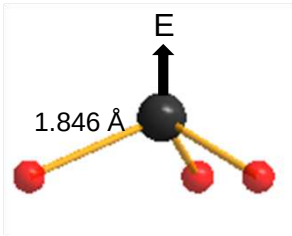
- The non-linear properties of such glasses are higher than that of a lead-silica glass and clearly dependent of the nature of the modifier oxide.

- The third order nonlinearity increases with the linear polarizability of the adding cation

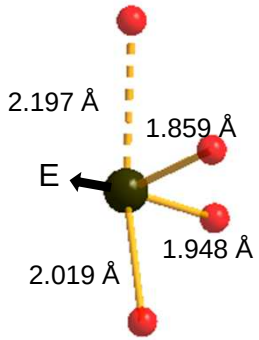
Structural features and peculiarities

4^+ !!!

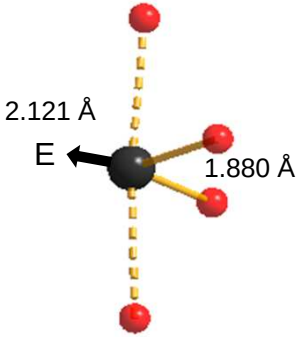
- Different **local** environment of Te(IV) atoms (Asymmetry of the local environment of Te^{IV} due to the steric effect of its **lone pair**: large variability of TeO_x structural units:



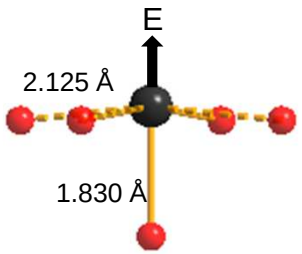
TeO_3



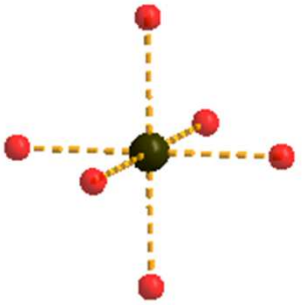
TeO_{3+1}



TeO_4

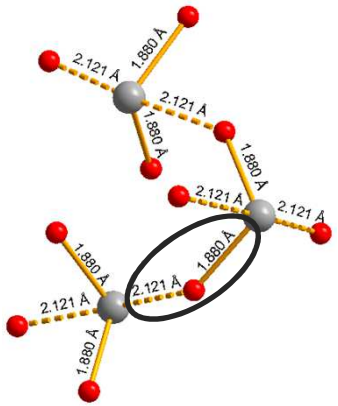


TeO_5

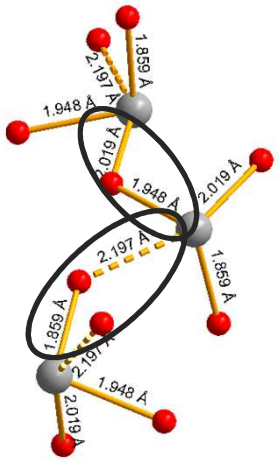


TeO_6

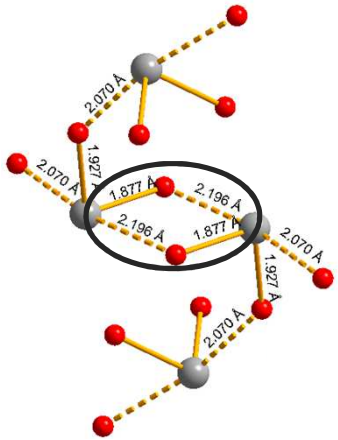
- **Medium-range** order (large variability of TeO_x structural units connection):



Chains with highly asymmetrical bridges



Chains with nearly symmetrical and highly asymmetrical bridges



Chains with double bridges

Structural features and peculiarities

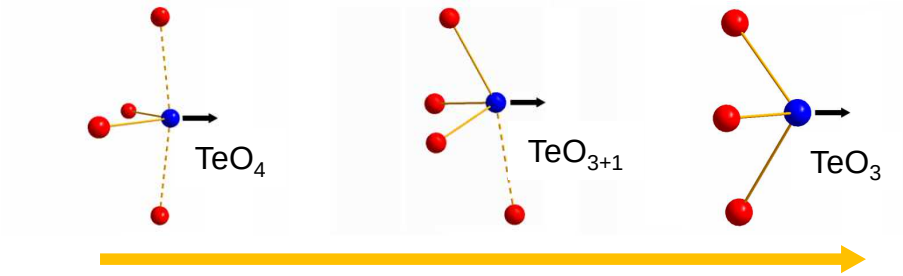
- Origin of the nonlinear optical properties: ???
  - Te(IV) electronic lone pair (Te^{4+}: [Kr] $4d^{10}$ $5s^2$)
  - Influence of the structure (short and medium range order)

- TeO_2 : “conditional” glass former (low thermal stability, addition of modifiers)
- **Need of a better understanding of the actual glass structure**

  Either for pure TeO_2 and TeO_2-based glasses

  1) With respect to the nature of the modifier: cation’s valence

  (Raman spectroscopy, Lattice Dynamics)



- Raman and IR spectroscopies
- Modelling: Lattice Dynamics (Lady)

- EXAFS, XANES, RMN, Mossbauer…

- X-ray and neutron diffraction
- X-ray and neutron Total Scattering

- Atomic scale Modelling
Reverse Monte Carlo (RMC)
Molecular dynamics (MD)

*The **structural units vary with the addition of a modifier oxide***
(contrary to silicates …) associated with a depolymerisation of the tellurite framewok

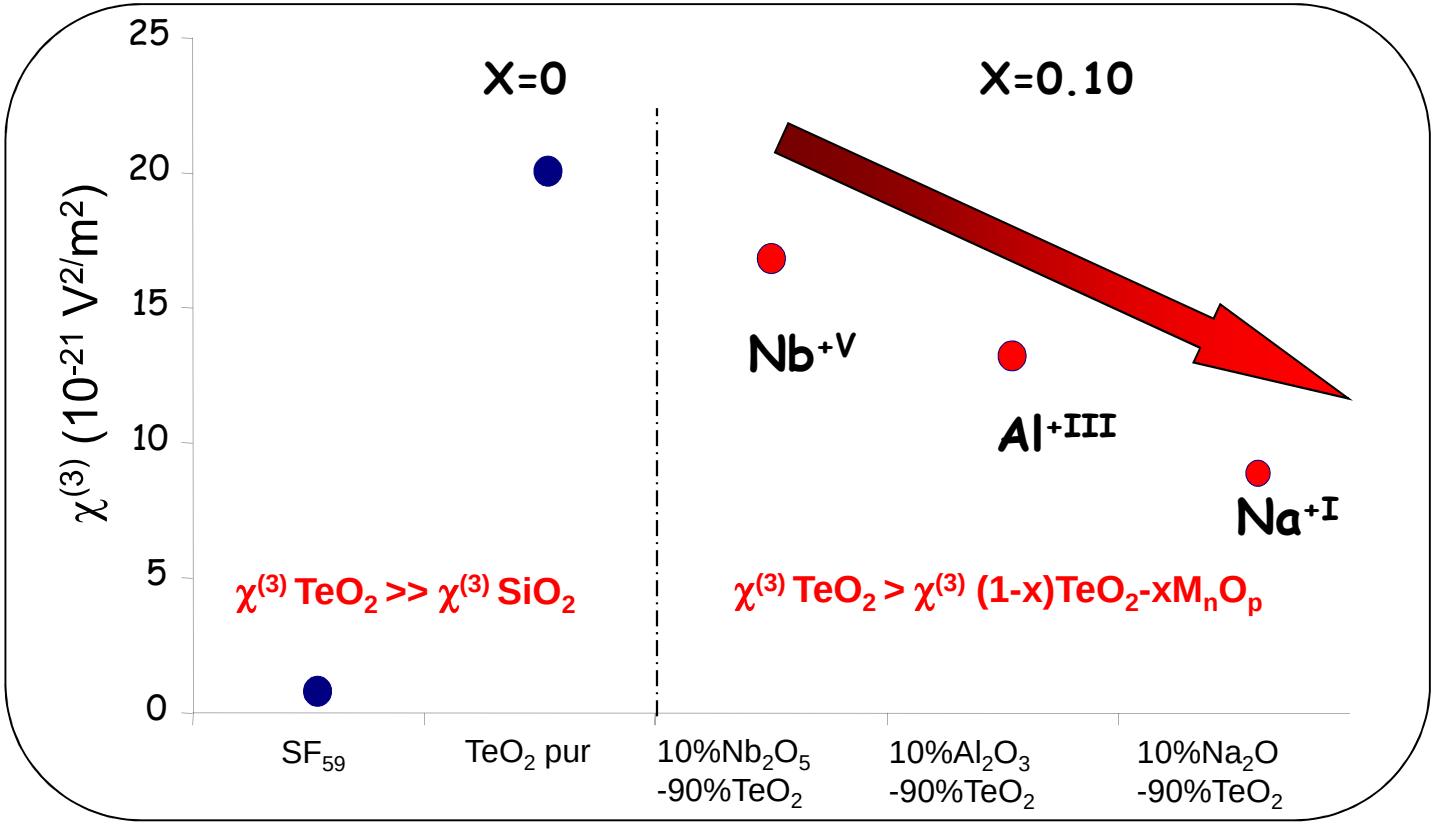
Drawback: decrease of the optical properties

2) Pure TeO_2

Combined experimental *(Raman, X ray and neutron Total Scattering / PDF)* and atomic scale modelling *(RMC, MD) methods*

Structural features and peculiarities

The role of cation's valence / structure



Hypothesis: the « strength » of the modifier's cation (its oxidation's state) induces the polymerization degree of the TeO_2-M_nO_p glasses

Investigation of the structure of the glass with respect to the nature of the modifier

Structural features and peculiarities

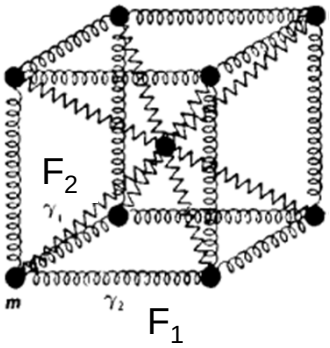
The role of cation's valence / structure

To understand the rules which are driving the structural modifications of $Te^{4+}O_2$-based glasses transformation by studying three types of modifiers :

- "weak" cation Tl^{+} : TeO_2 - Tl_2O
- "intermediate" cation Ti^{4+} : TeO_2 - TiO_2
- "strong" cation Nb^{5+} : TeO_2 - Nb_2O_5

Method:

- Modelling (lattice dynamics) of the Raman spectra of crystalline compounds
- Structural investigation and evolution of the Raman spectra of glasses with respect to the addition of modifier



$$\omega_n \sim \sqrt{\frac{F_n}{m}}$$

LADY (LAttices Dynamics) program

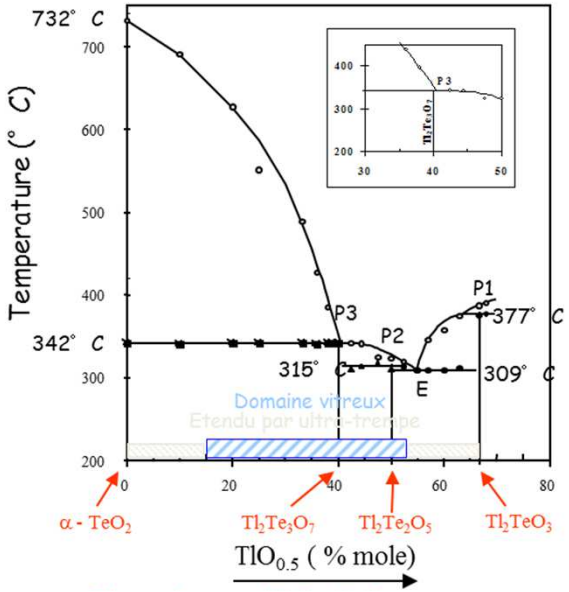
VFF (Valence Force Field) Potentiel

Force constants F – stiffness of interatomic springs

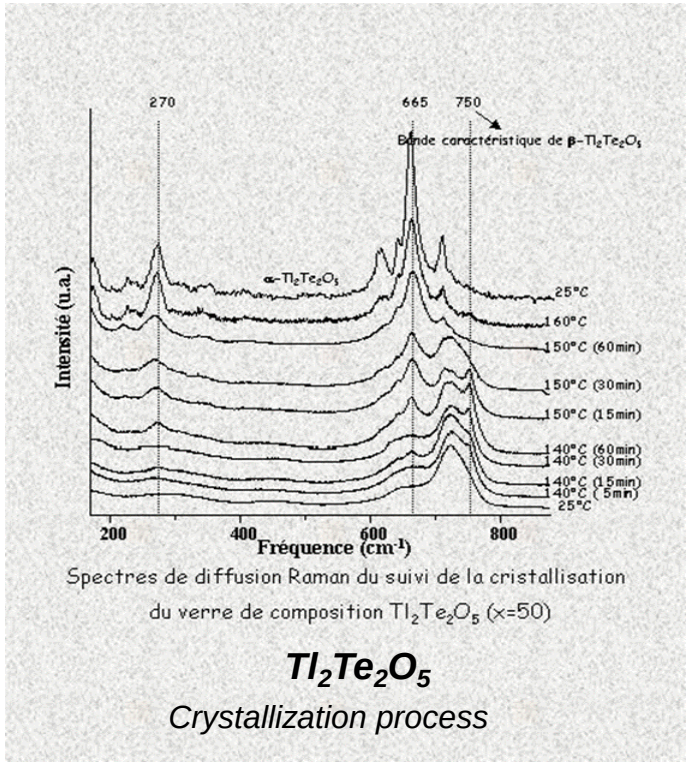
The phonon dispersion w(k) provides us information on stiffness of interatomic bonds
This information can be derived by using the lattice dynamics modelling

Structural features and peculiarities

The role of cation's valence / structure



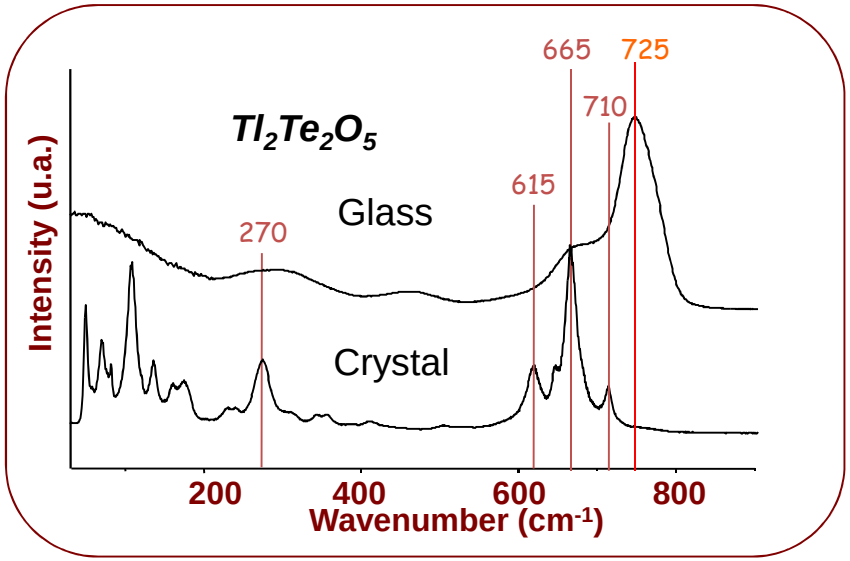
TeO_2-Tl_2O phase diagram



Spectres de diffusion Raman du suivi de la cristallisation du verre de composition $Tl_2Te_2O_5$ (x=50)

$Tl_2Te_2O_5$

Crystallization process



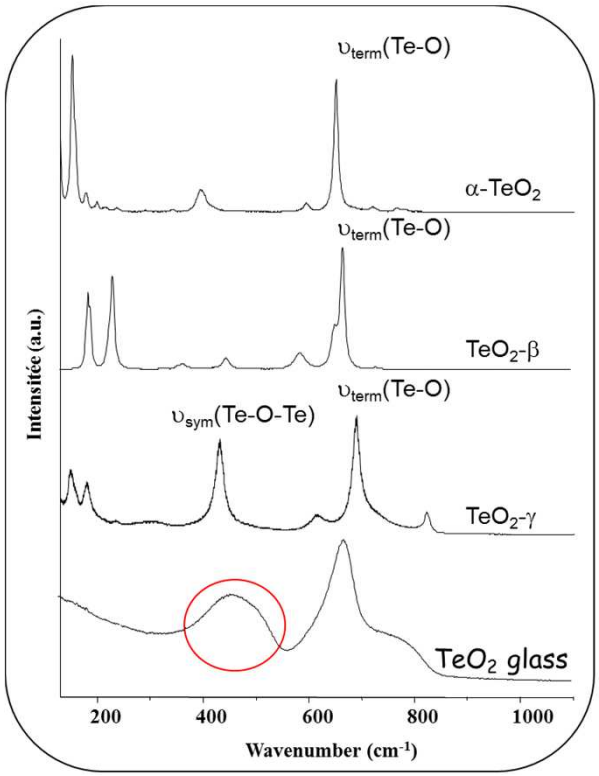
Tellurite glasses: no systematic matching between Raman spectra of glass ("envelope") and crystal of same composition

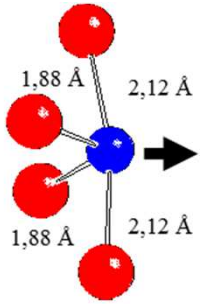
Contrary to general rule in « classical » glasses (silicates, germanates, …)

Structural features and peculiarities

TeO_2 phases and glass

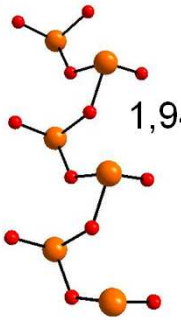
The role of cation's valence / structure



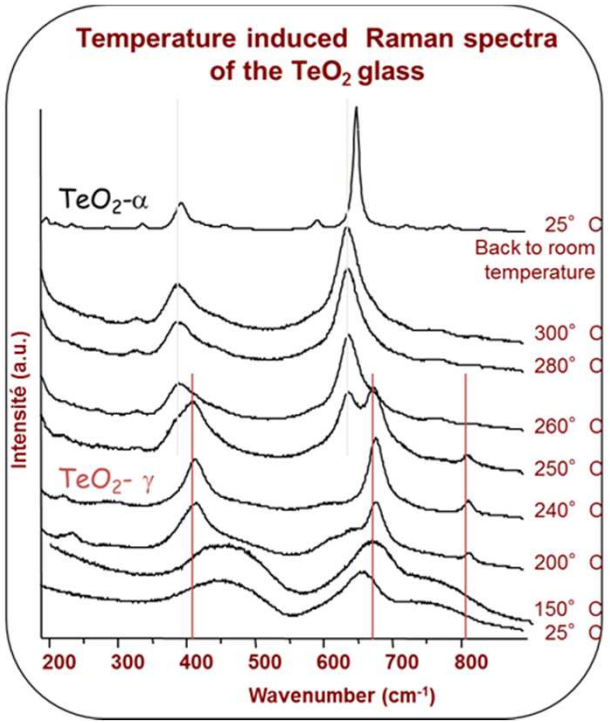


"isolated-like"

TeO_2 molecules



1,94-2,02 Å



γ-TeO_2 first compound to crystallize from the glass

→ Main characteristic of γ-TeO_2

Chain-like polymerized TeO_2 molecules

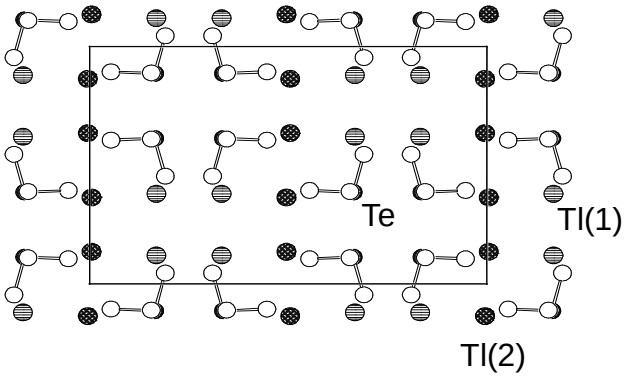
→ **γ-TeO_2 « parent » structure of the glass**

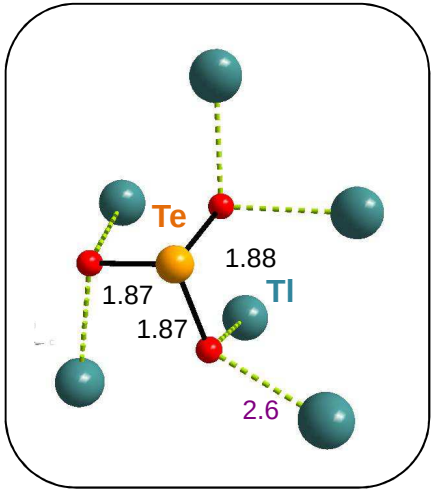
Structural features and peculiarities

"Weak" cation Tl^+ : TeO_2 - Tl_2O — *The role of cation's valence / structure*

Tl_2TeO_3 Example of a complete depolymerized tellurite structure

P b a n (D_{2h}^4) orthorhombic



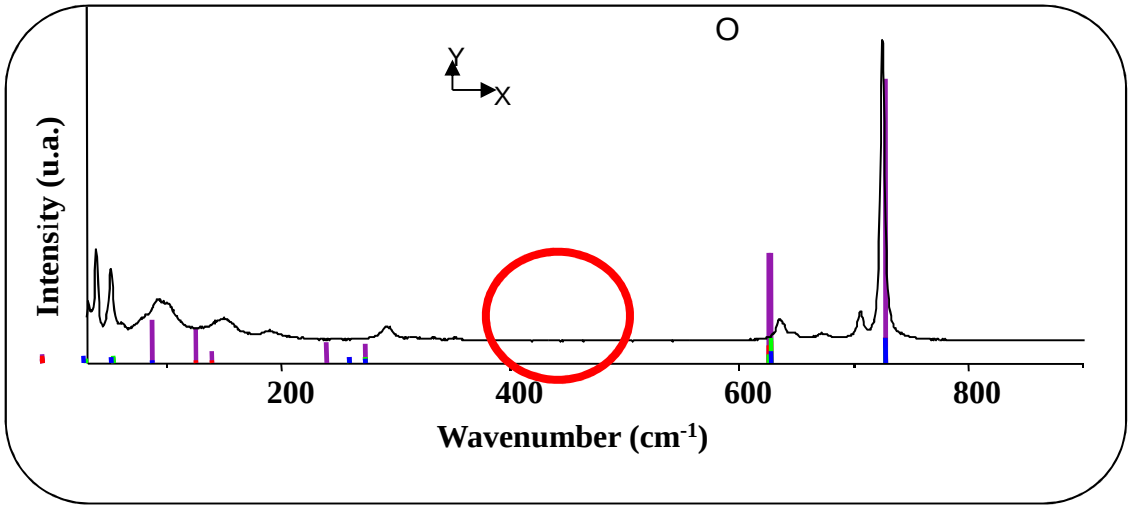


Tellurite framework: isolated $[TeO_3]^{2-}$ pyramids

Te-O-Tl bridges

dTe-O ≃ 1.87 Å

dTl-O ≃ 2.6 Å

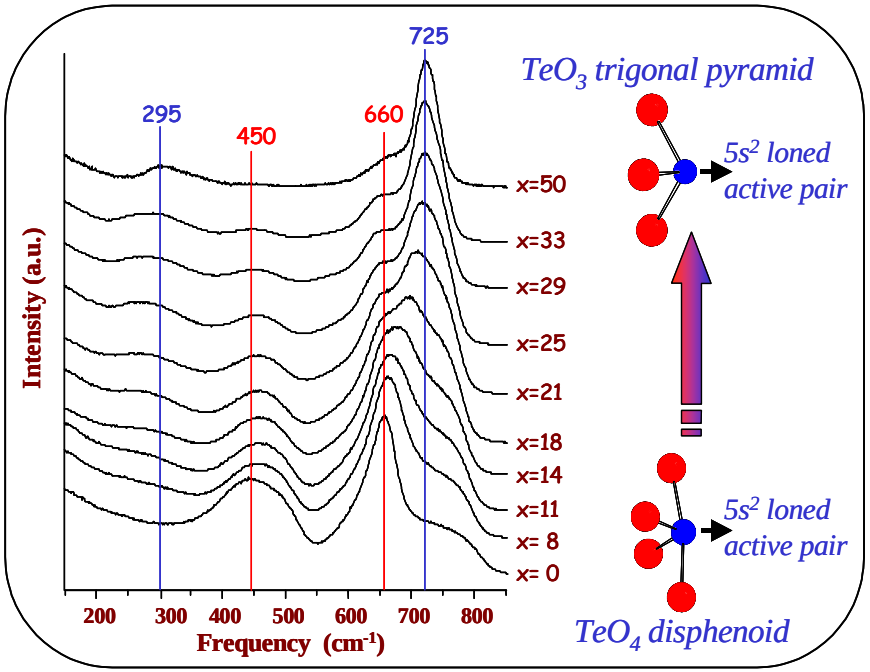


No Te-O-Te bridge: no vibrational band in the range 400-500 cm^{-1}

Isolated $[TeO_3]^{2-}$ pyramids

Structural features and peculiarities

"Weak" cation Tl^+ : TeO_2 - Tl_2O — *The role of cation's valence / structure*



Raman spectra of glasses in the system x Tl_2O - (100-x) TeO_2

Addition of modifier :

Increase of the intensity of the band at 725 cm^{-1}

Decrease of the intensity of the band at 660 cm^{-1} and of the band near 450 cm^{-1}

Breaking of the Te-O-Te et bridges and appearance of isolated TeO_3^{2-} ortho-anions

Depolymerization

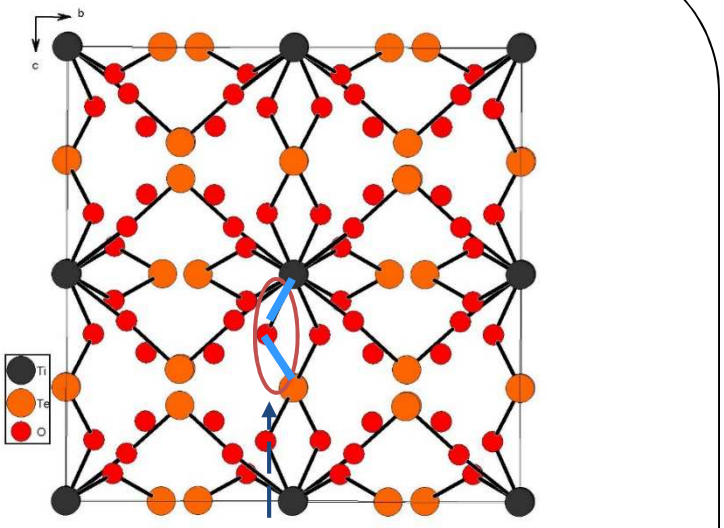
<u>Interpretation:</u> a weak cation Tl^+ **« gives »** all its oxygen atoms to TeO_2 units *(in fact TeO_{2+2})* which transform into TeO_3^{2-} ions (more and more TeO_3^{2-} with increasing Tl^+ content). This transformation is associated logically to a depolymerization of the tellurite framework of the glass

Structural features and peculiarities

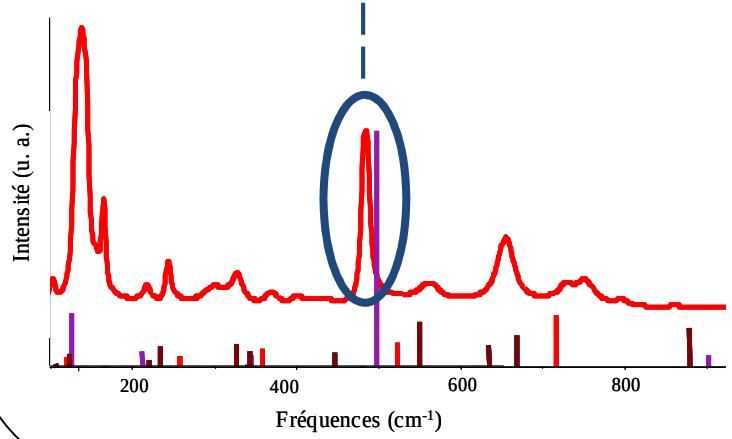
"Intermediate" cation Ti^{4+} : TeO_2 - TiO_2

The role of cation's valence / structure

$TiTe_3O_8$



Projection of the cubic cell of the $TiTe_3O_8$ crystal lattice on the (010) plan



Te-O and Ti-O bond lenghts are close

dTe-O ≃ 1.86 Å
dTi-O ≃ 1.96 Å

Force constants of Te-O and Ti-O « close »

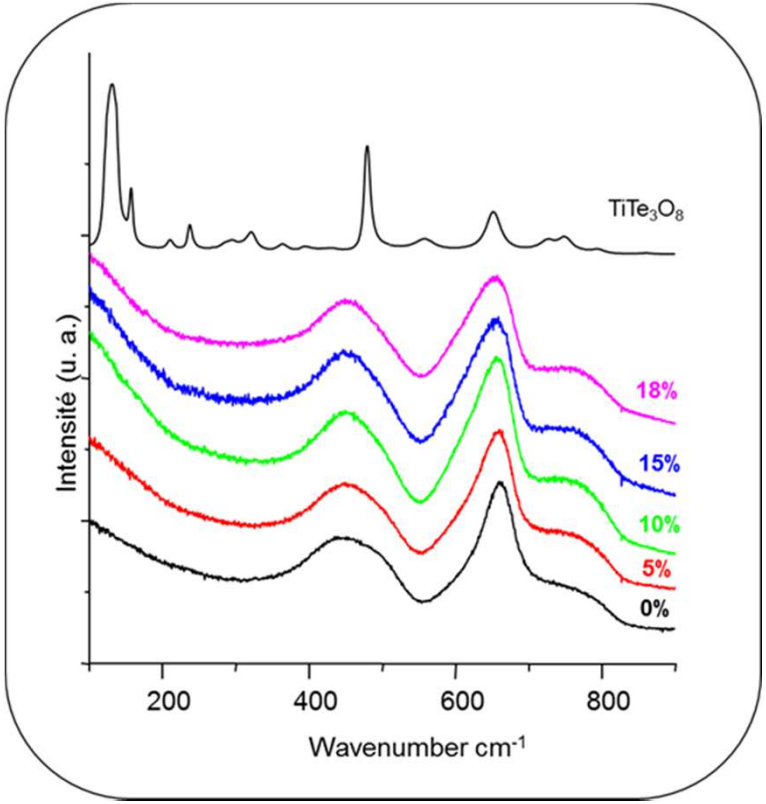
Presence of symmetric Te-O-Ti vibrational bridges

Intense band near 490 cm^{-1}

Structural features and peculiarities

"Intermediate" cation Ti^{4+} : TeO_2 - TiO_2

The role of cation's valence / structure



Raman spectra of the $xTiO_2$-$(100-x)TeO_2$ glasses and of the $TiTe_3O_8$ phase

Addition of modifier :

No evident evolution of the intensity of the bands at about 450 cm^{-1} and near 650 cm^{-1}

No depolymerization : progressive substitution of Te-O-Te bridges by Te-O-Ti ones

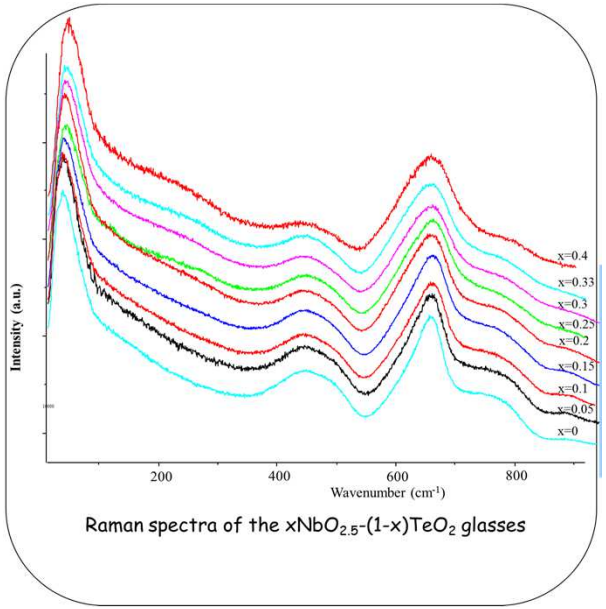
Ti^{4+} doesn't «give» its oxygen to the TeO_2 pseudo-molecules units.
No TeO_3^{2-} orthoanions exists.

<u>Interpretation</u>: glass structure is close to that of the $TiTe_3O_8$ crystalline compound:
Ti^{4+} and Te^{4+} atoms are **sharing** their oxygen atoms
(shown by the weak intensity of the 800 cm^{-1} band attributed to the antisymetric vibration of the Ti-O-Te bridge)
so the glass could be described as a "solid solution" of TiO_2 in TeO_2.

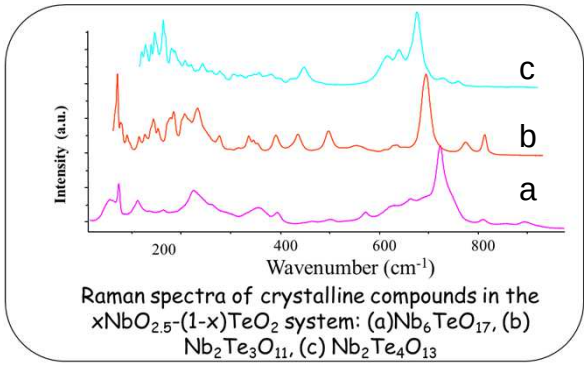
Structural features and peculiarities

"Strong" cation Nb^{5+} : TeO_2 - Nb_2O_5

The role of cation's valence / structure



Raman spectra of the $xNbO_{2.5}$-(1-x)TeO_2 glasses



Raman spectra of crystalline compounds in the $xNbO_{2.5}$-(1-x)TeO_2 system: (a)Nb_6TeO_{17}, (b) $Nb_2Te_3O_{11}$, (c) $Nb_2Te_4O_{13}$

$Nb_2Te_4O_{13}$

Bridges:
Te-O-Nb (1,90-2,00 Å)
Nb-O-Nb (1,80-2,10 Å)
Te-O-Te (1,92-2,00 Å)

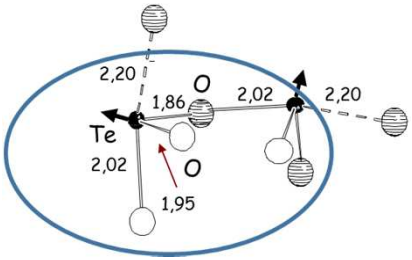
Addition of modifier :

- No noticeable variation of the Raman spectra

Progressive substitution of Te-O-Te bridges by Te-O-Nb ones («chemically close »)

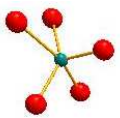
Temperature induced Raman spectroscopy can evidence the local structure of glasses (first compound to crystallize)

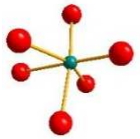
Evidence of Te_2O_5 or TeO_3 units (for rich-modifier compositions) in the glasses



<u>Interpretation:</u> Niobium atoms are « strong » cations but **they cannot keep** all their oxygen atoms and so favor the formation of some tellurite structural fragments (like Te_2O_5 or TeO_3).

This is certainly due to the anisotropic environment of niobium atom. In fact around niobium atoms, there are some close oxygen atoms and other are less connected and are "given" to TeO_2 units.





Structural features and peculiarities

Summary ***The role of cation's valence / structure***

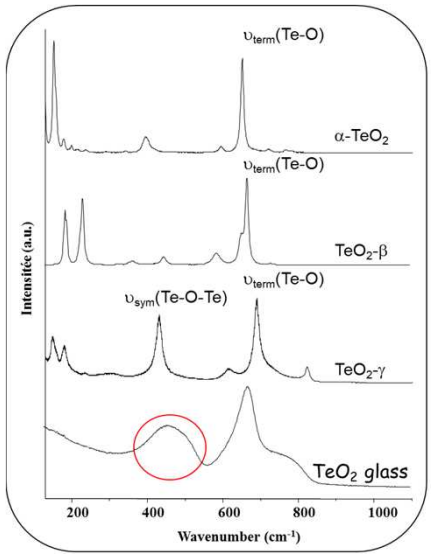
Modifier's cation valence plays a role in structural properties of TeO_2-based glasses

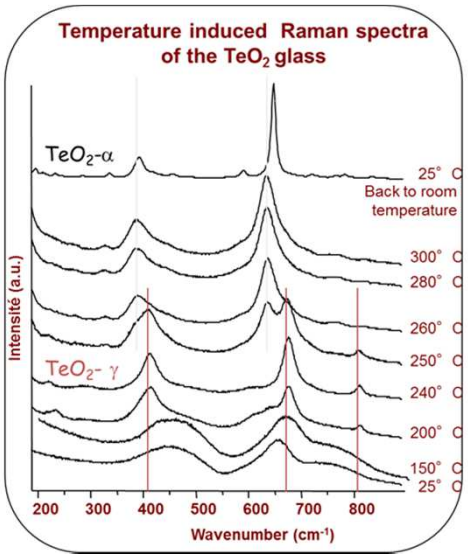
Weak modifier's cation (as Tl^{+}) : island-type structure , isolated TeO_3^{2-} anions : **glass depolymerization**

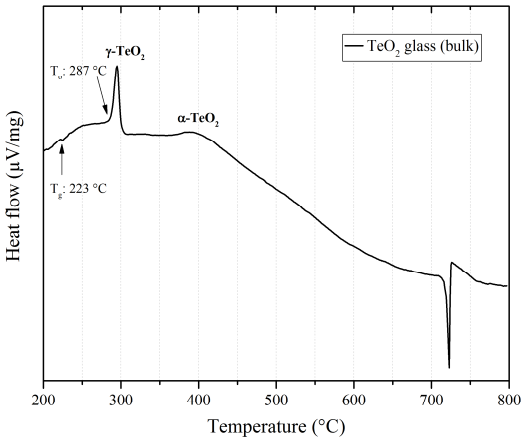
Intermediate or strong modifier's cations M (as Ti^{4+}, Nb^{5+}) in the $(1-x)TeO_2$-xM_nO_m glasses: substitution of Te-O-Te bridges by Te-O-M ones
Because of chemical resemblance of cations Te and M (similar or close valences and radii) the framework-type structure can be kept : **no glass depolymerization**

Structural features and peculiarities

Is TeO_2 really a glass former ?







Structure of pure TeO_2 glass

Is TeO_2 really a glass former?

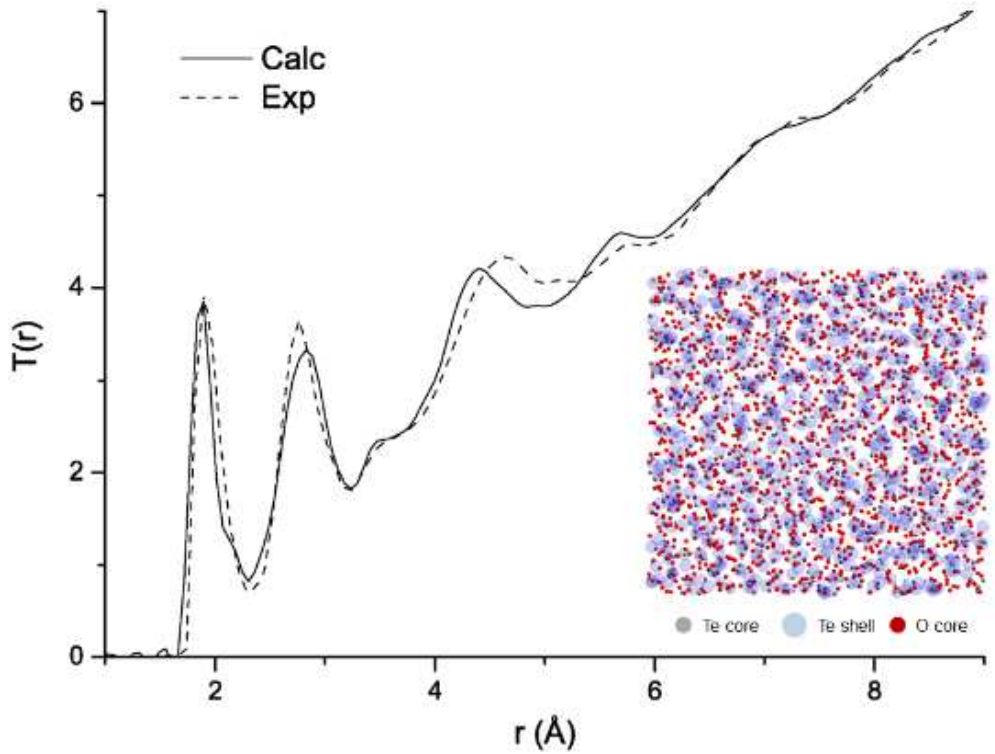
A combined approach using the Pair Distribution Function (PDF) method and Reverse Monte Carlo (RMC) method or Molecular Dynamics (MD) simulation

Structural features and peculiarities

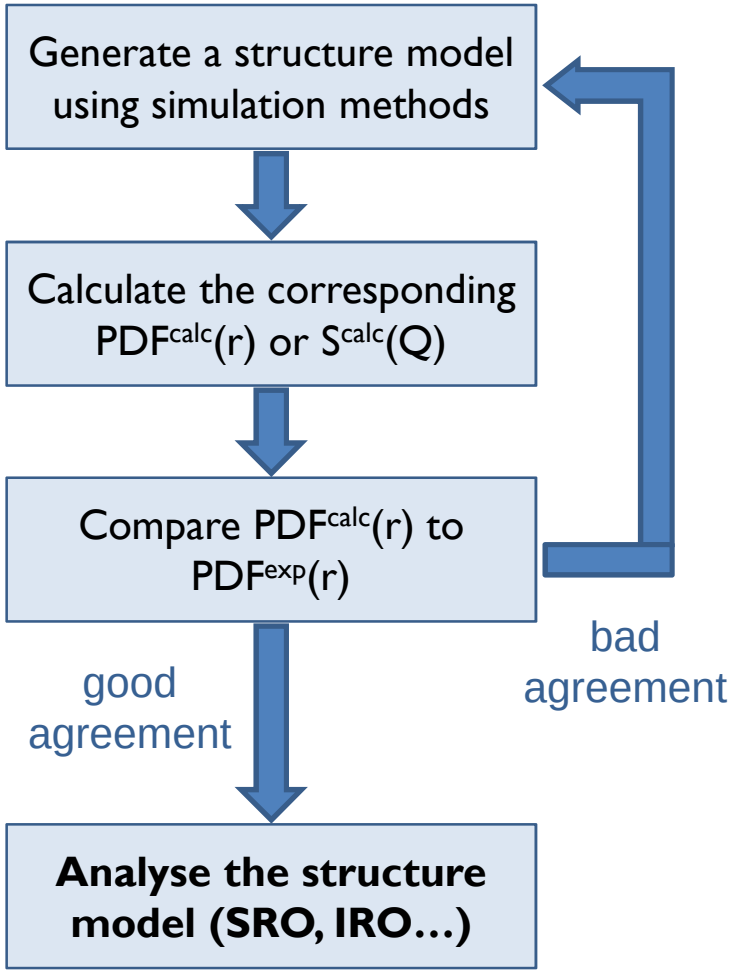
Computer simulation methods at the atomic scale — *Is TeO_2 really a glass former ?*

- Reverse Monte-Carlo (RMC)
- Molecular dynamics (MD)

⇒ In both cases: structure models made of several thousands of atoms are generated and tested against experimental data



Total PDF calculated from TeO_2 glass model obtained from MD simulations (solid line) compared with exp. ND-PDF (dotted line).

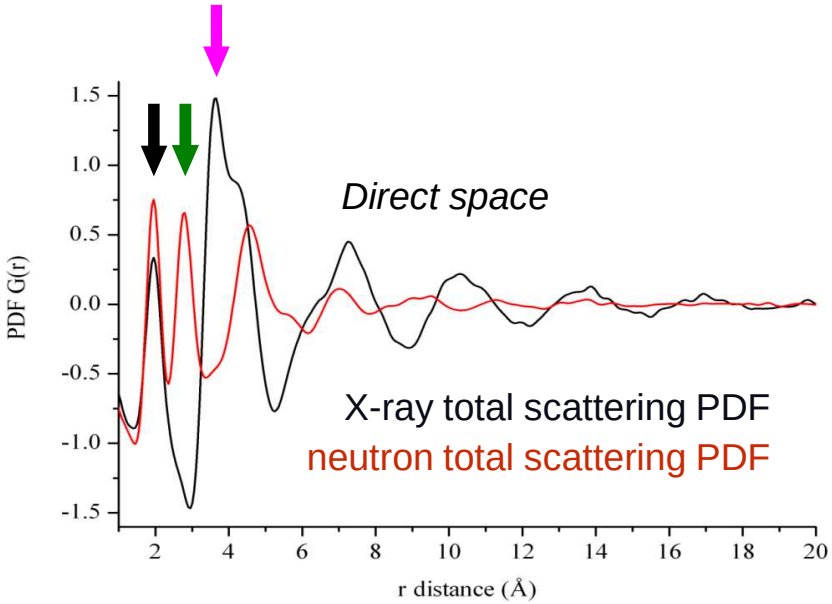


Structural features and peculiarities

Total scattering - PDF

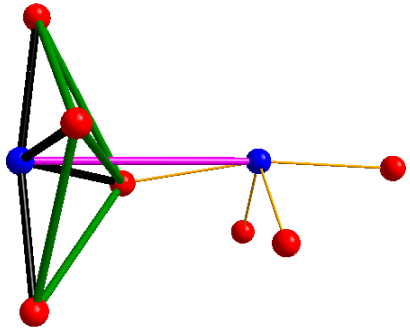
Is TeO_2 really a glass former ?

X-ray and neutron Total Scattering : pair distribution function analysis

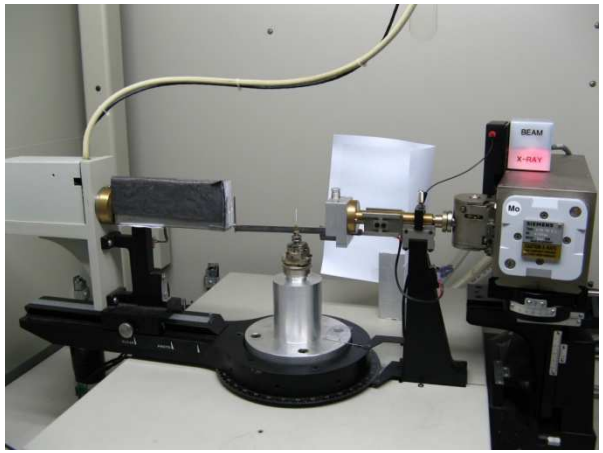


G(r) (Pair distribution function) :

- Peak position -> interatomic distance
- Peak area -> coordination number
- Peak width -> disorder



Total scattering diffractometer at SPCTS

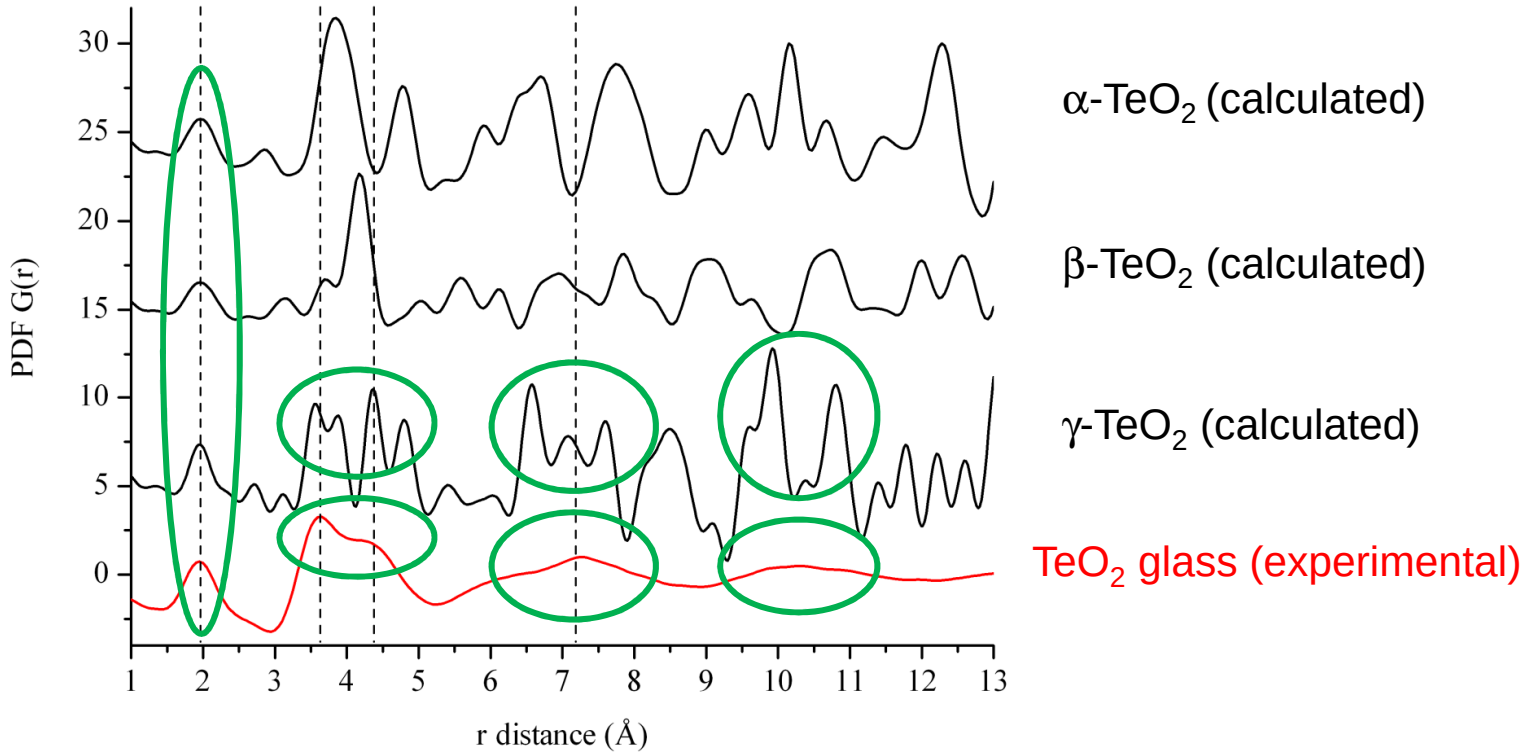


- Optics optimized for high photon flux
- Mo X-ray tube (λ = 0.71 Å)

Structural features and peculiarities

Structural characterization / RMC method — *Is TeO_2 really a glass former ?*

The starting structural configuration:
comparative study of the TeO_2 glass with TeO_2 polymorphs



- 1.9 Å: common peak for the 4 compounds (structural units)
- at medium range order: similitude between the TeO_2 glass and the γ-TeO_2 polymorph

The TeO_2 glass structure is close to the γ-TeO_2 structure (as seen by using Raman spectroscopy)

RMC: Our short range structural model

$$\chi^2 = \sum_i w_i (y_{io} - y_{ic})^2 + \alpha C_1 + \beta C_2$$

$$C_1 = \sum_j \sum_k \left| V_{kj} - V_j \right|^{c_j}$$

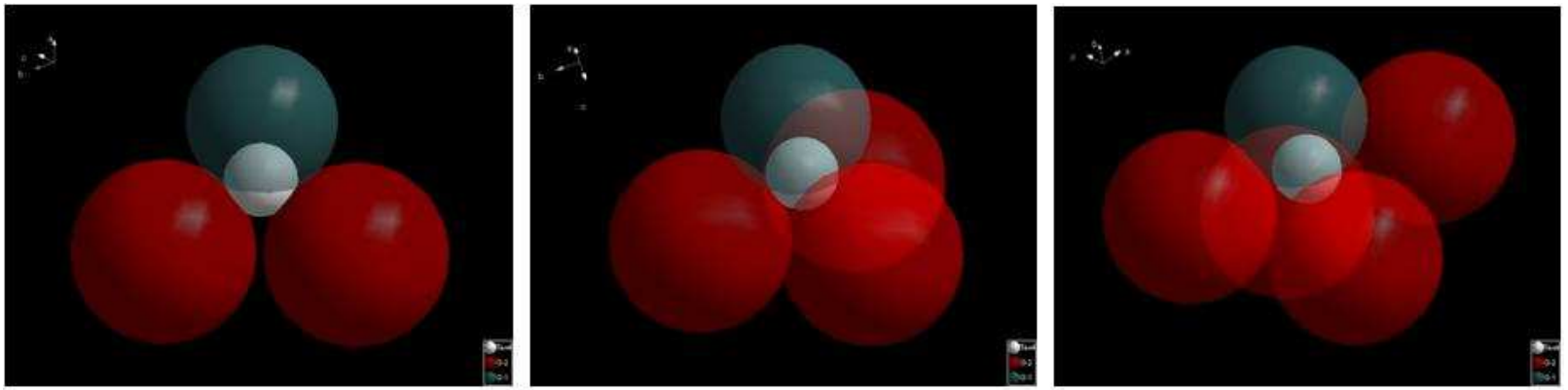
$$C_2 = \frac{1}{2} \sum_j \sum_k \sum_{j'} \sum_{k'} A_{jj'} \exp\left(- R_{kk'} / \rho_{jj'}\right)$$

Optimized parameters

	$A_{jj'}$	$r_{jj'}$	c_j
O-O	711.0	0.324	1.0
O-LP	637.1	0.307	1.0
Te-O	3929.0	0.236	1.0

- Bond valence constraints
- + Lone-pair steric effect constraints

The obtained parameters were tested by reproducing known structural units



TeO_2 TeO_3 TeO_4

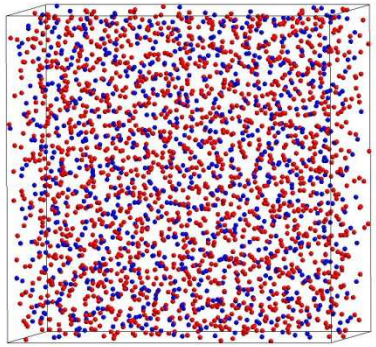
=> Application to RMC study of TeO_2 glass

Structural features and peculiarities

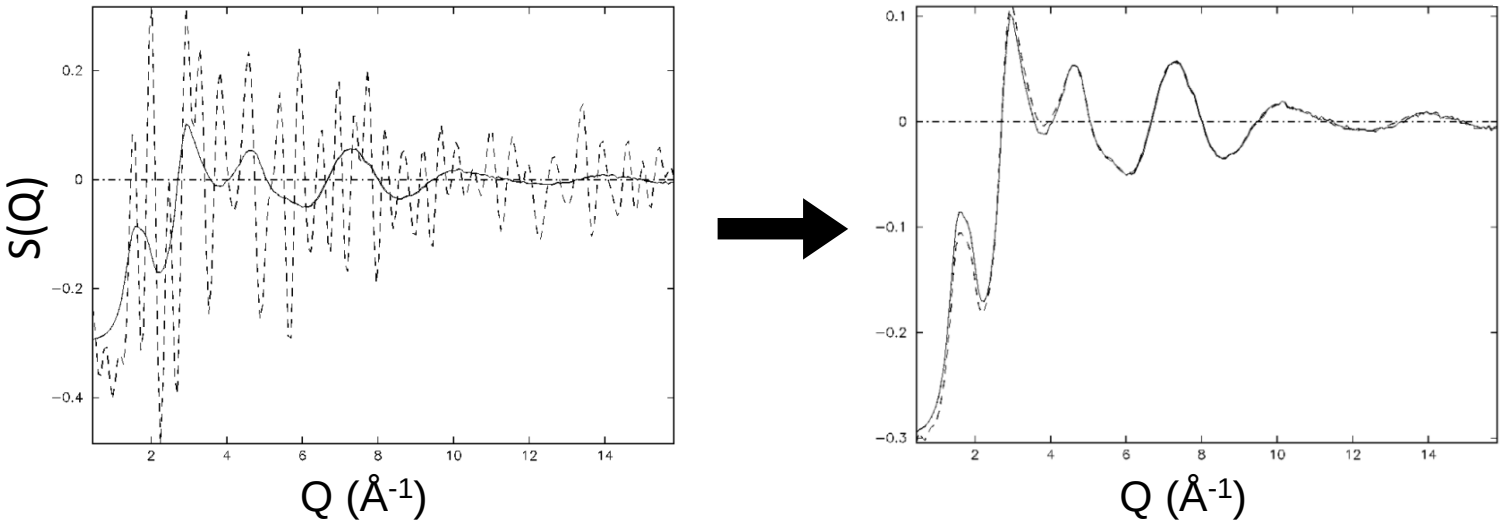
Structural characterization / RMC method — *Is TeO_2 really a glass former ?*

RMC modelling of TeO_2 glass

- starting structural configuration: γ-TeO_2 structure
- constraints of our structural model
- fit performed against the experimental data



RMC simulation box



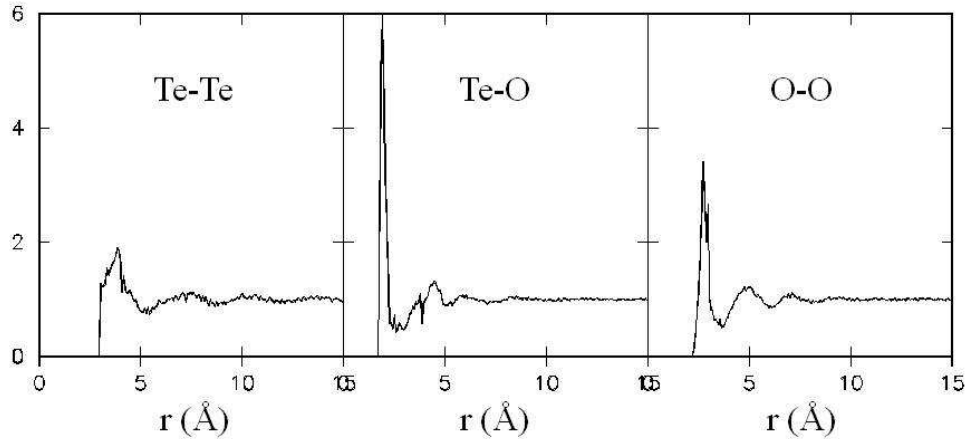
The experimental and calculated data match

atom type	number of atoms	mean valence (γ-TeO_2)	mean valence (TeO_2 glass)	satisfaction of the constraint
Te	876	3.9	3.8	92 %
O	1792	-1.9	-1.9	90 %

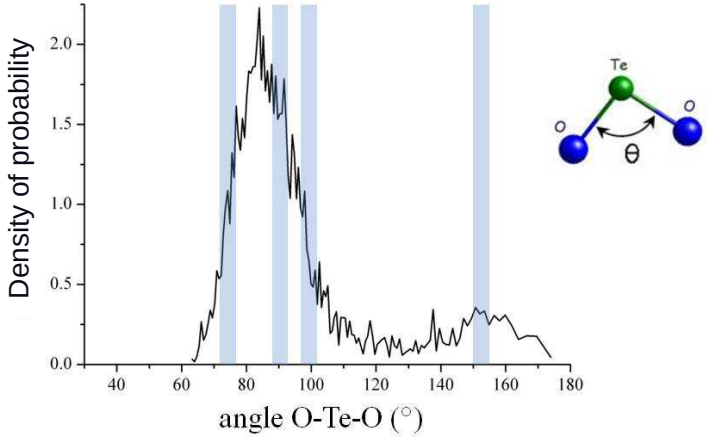
Structural features and peculiarities

Structural characterization / RMC method — *Is TeO_2 really a glass former ?*

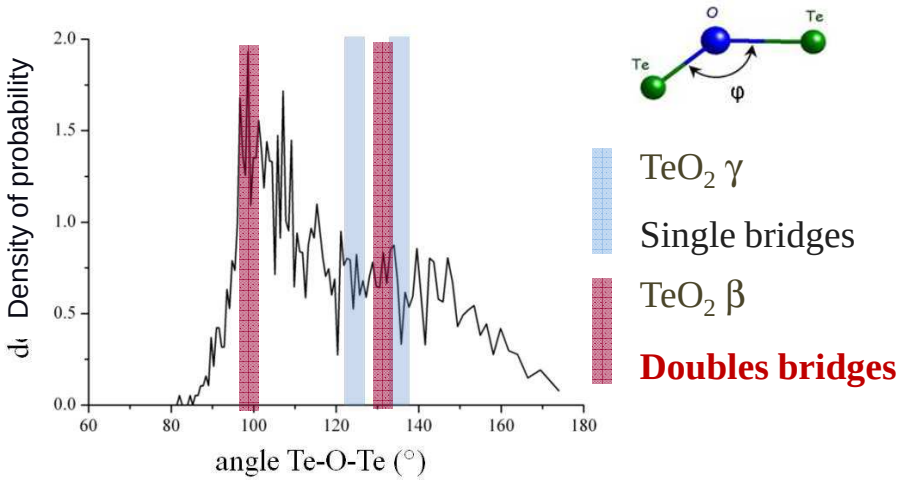
Partial Pair Distribution Functions



Angular distributions



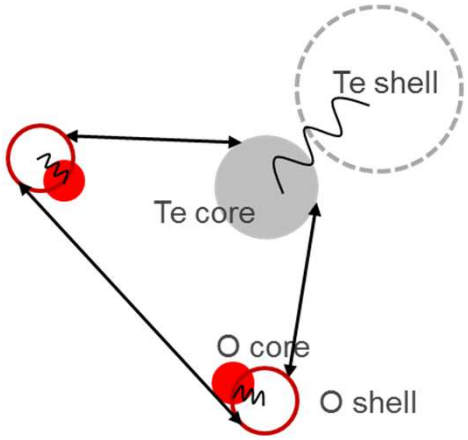
- characteristic of the structural units:
presence of TeO_3, TeO_{3+1} and TeO_4 units



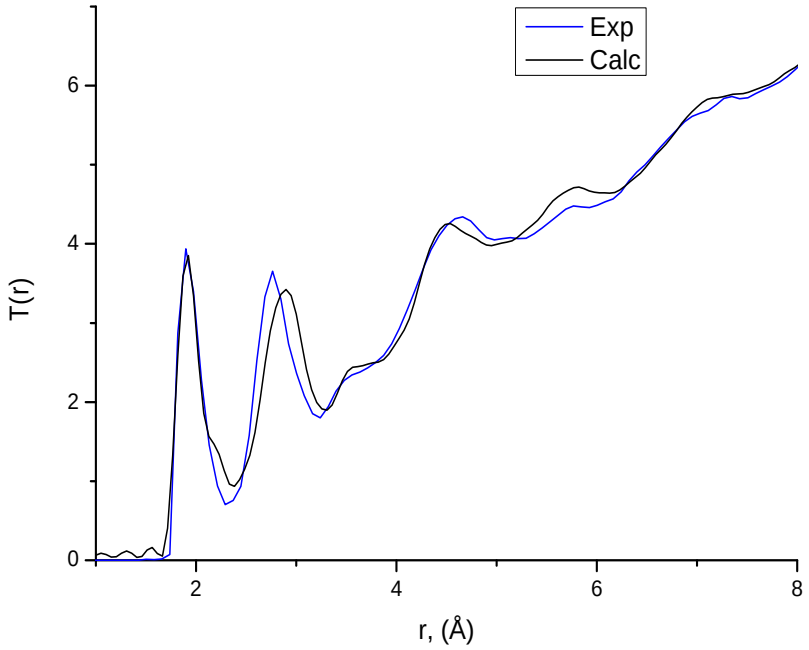
- characteristic of the structural units linkage:
chains not directed along one axis
and presence of double bridges

Molecular dynamics simulation of TeO_2 glass

Interatomic potentials developed for TeO_2 system with GULP [1] software
MD simulations for pure amorphous TeO_2 performed with DL_POLY software [2].



Core-shell model for both Te and O atoms



Calculated and experimental total distribution functions

Check on all known tellurite structures

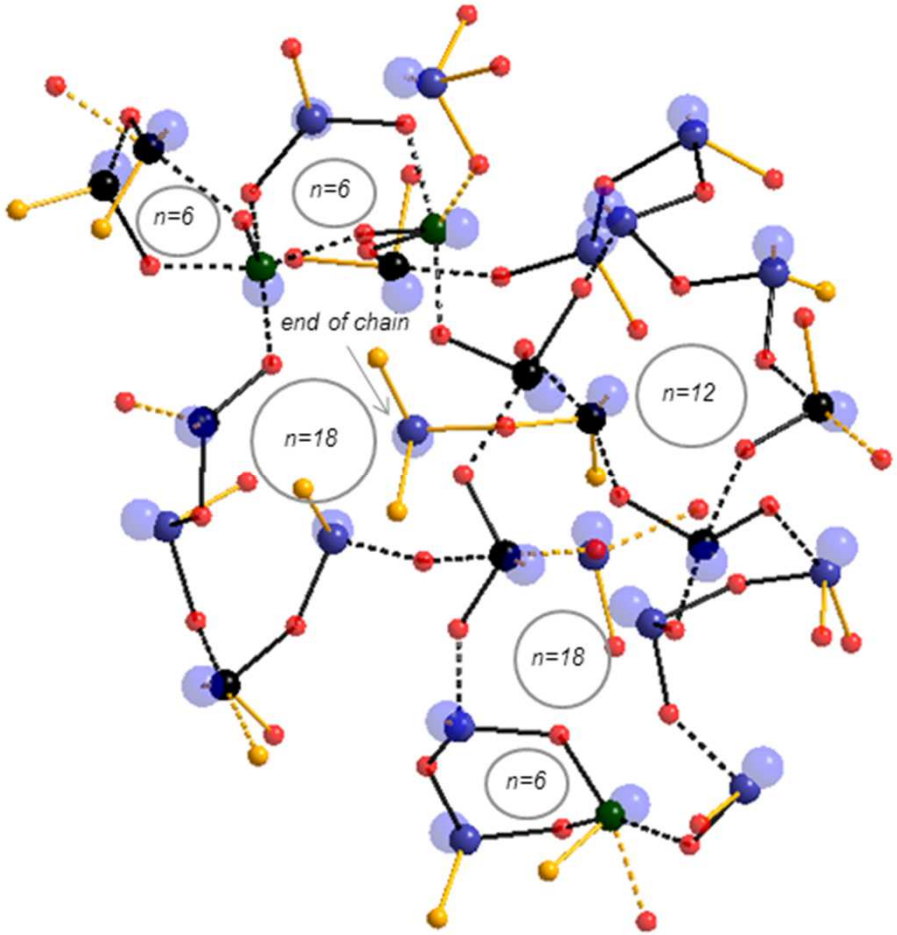
1. GULP - a computer program for the symmetry adapted simulation of solids, J.D. Gale, *JCS Faraday Trans.*, **93**, 629 (1997)
2. http://www.ccp5.ac.uk/DL_POLY_CLASSIC/ "The DL_POLY Classic User Manual", by W. Smith, T.R. Forester and I.T.Todorov, published by Daresbury Laboratory, United Kingdom.

Structural features and peculiarities

Structural characterization / MD simulation — *Is TeO_2 really a glass former ?*

Modelled glass network topology

TeO_2 a GLASS FORMER???



Fragment of pure TeO_2 glass structure obtained by MD simulations

- TeO_2 glass consists of wide variety structural units with broad bond lengths distribution
- TeO_x units tend to form large rings ($n \geq 10$)
- Large concentration of NBO (21%)
- Strong influence on the network of the LP steric effect

→ Open network with chain breaks and voids

→ Thermal instability

→ Good ability to accommodate the modifiers

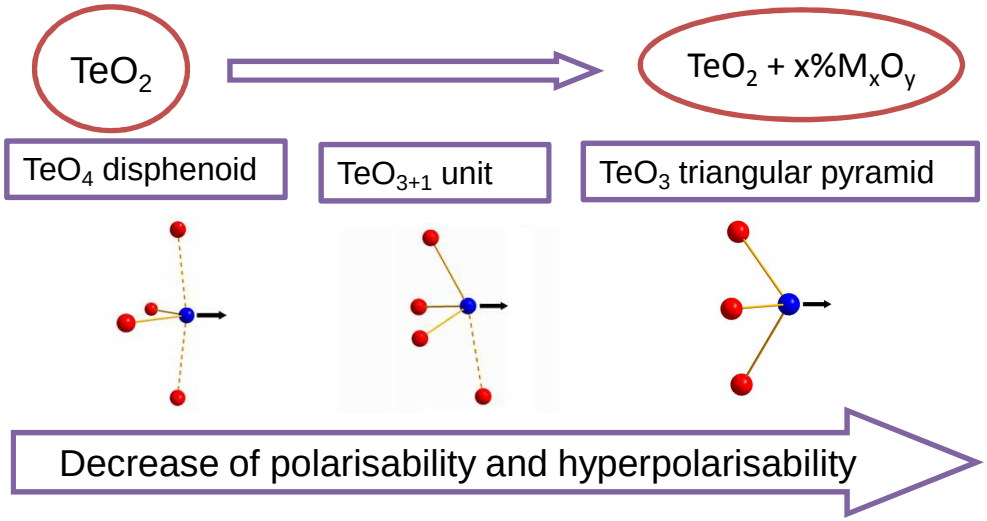
- 3-coordinated Te atoms
- 4-coordinated Te atoms
- 5-coordinated Te atoms
- BO atoms
- NBO atoms

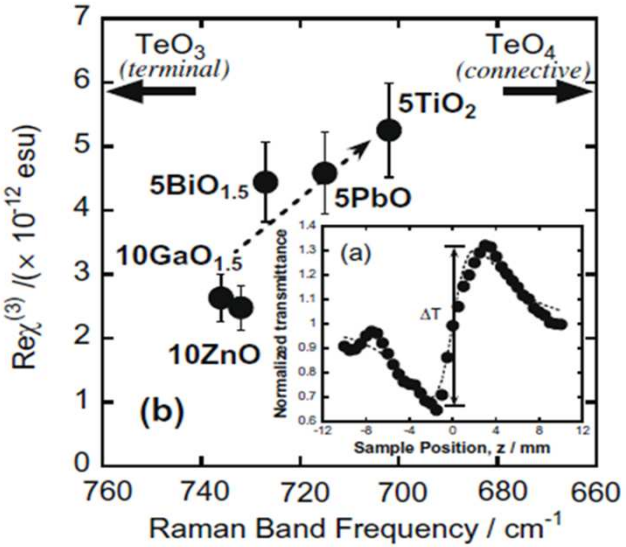
Short Te-O bonds (< 2.02 Å)

Intermediate Te-O bonds (2.02 Å < *x* < 2.36 Å)

What's the origin of high 3rd-order NLO property ?

Structure / nonlinear optical properties relationships

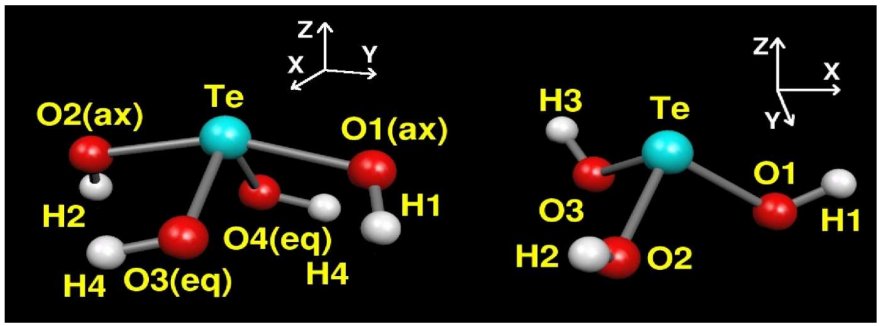


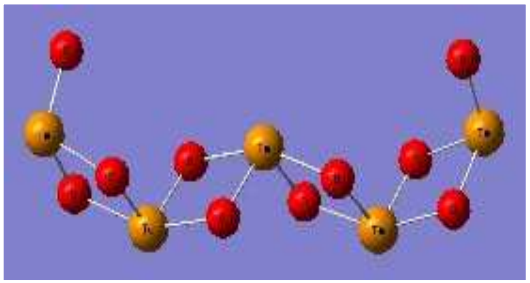


Influence de la concentration et du rapport TeO_4 / TeO_3

Ab initio (DFT) Molecular Orbital calculations

$\gamma(TeO_4H_4)$= 2018 $\gamma(TeO_3H_3^+)$= 1134



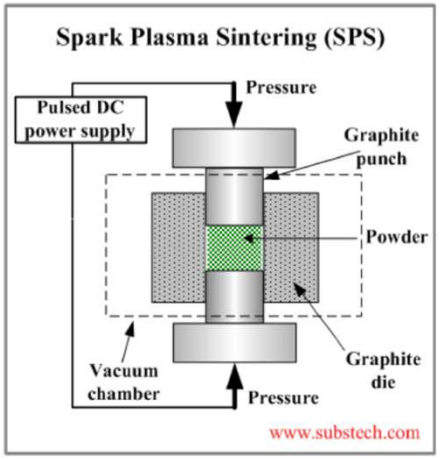


. $\chi(3)$ linear chain-like structure ~ $\chi(3)$ (exp.)
. **The polymerization** contributes strongly to the hyperpolarisability (Te lone pairs 5%!!): electronic delocalization within the chains.

Some examples of tellurite materials elaborated in SPCTS : transparent glass-ceramics and ceramics …

Transparent glass-ceramics and ceramics:

- Improvement of the non-linear optical properties
- Strengthen the mechanical properties of the glass
- Keep the optical transparency



. Conventional annealing in a classical furnace

. **Spark Plasma Sintering (SPS)**

- *Partial devitrification and shaping of the "powder"* ***in 1 step***
- *Higher crystallization kinetics rate in comparison with a heat treatment in a conventional furnace (×100)*
- *But problem of carbon contamination !!!* ***Solution : pre-sintering***

$85TeO_2$-$15WO_3$

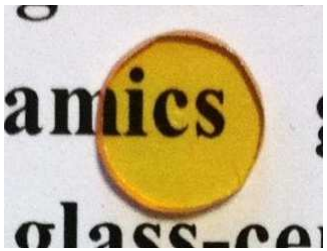
Pre-sintering step (of the glass powder)
+ SPS

T_g+15°C

Density > 95 %

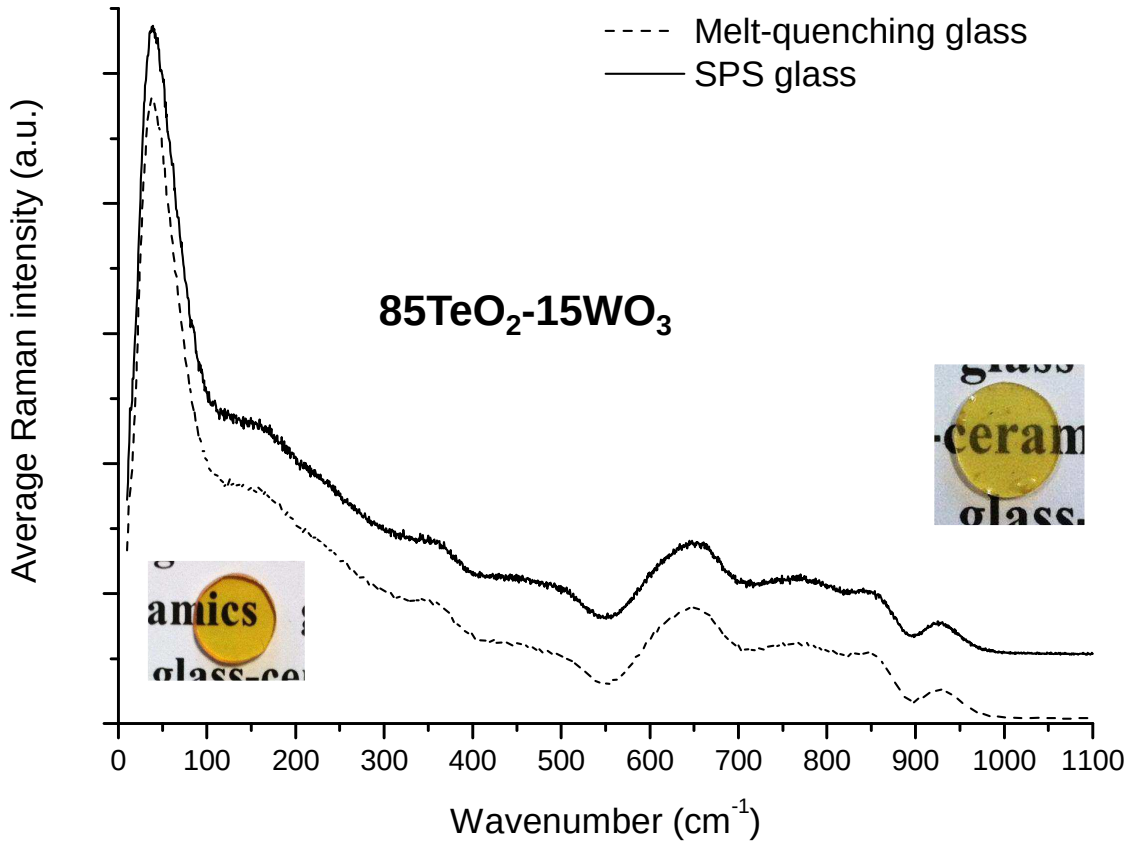
Density > 99%

Melt - Quenched reference glass



Some examples of tellurite materials elaborated in SPCTS : transparent glass-ceramics and ceramics …

Comparing the structure of SPS and MQ glasses

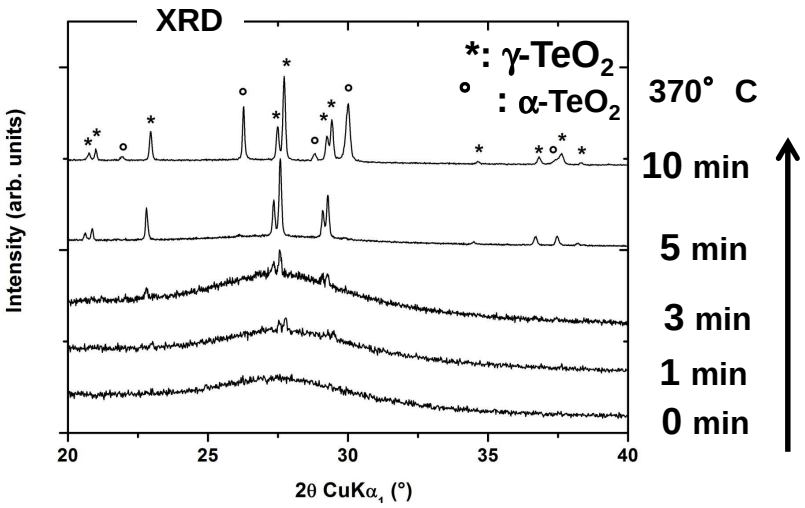


The SPS step does not modify the structure of MQ glasses !

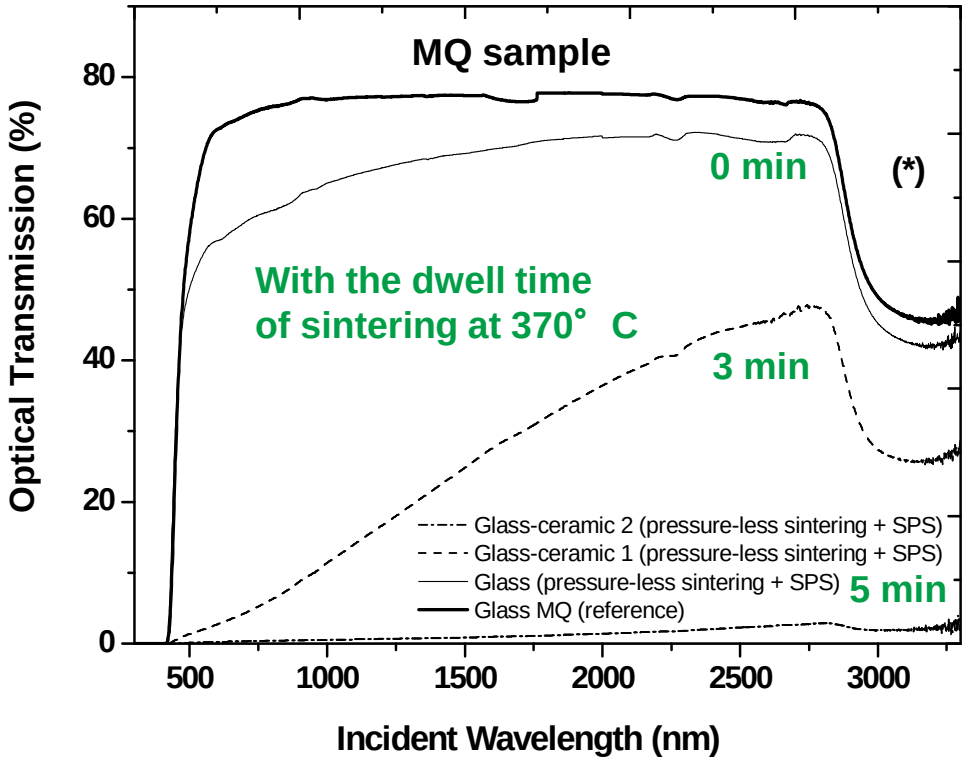
Some examples of tellurite materials elaborated in SPCTS : transparent glass-ceramics and ceramics …

From glass to glass-ceramics

0 min 3 min 5 min



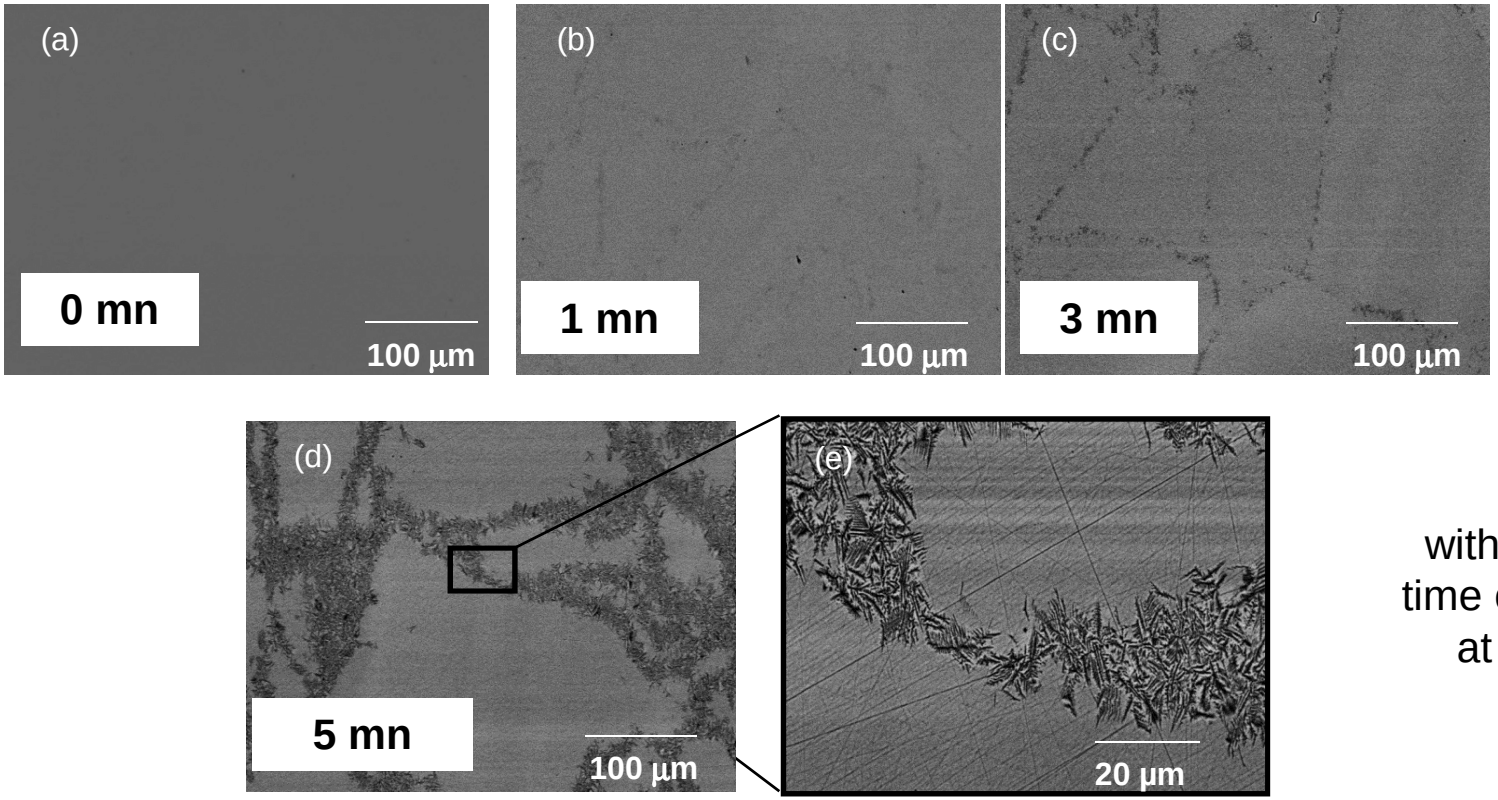
γ-TeO_2 phase crystallizes first !
Non-centrosymmetric phase : perfect for SHG !



The optical transmission strongly drops for glass-ceramics

Some examples of tellurite materials elaborated in SPCTS : transparent glass-ceramics and ceramics …

From glass to glass-ceramics / Microstructure



with the dwell time of sintering at 370° C

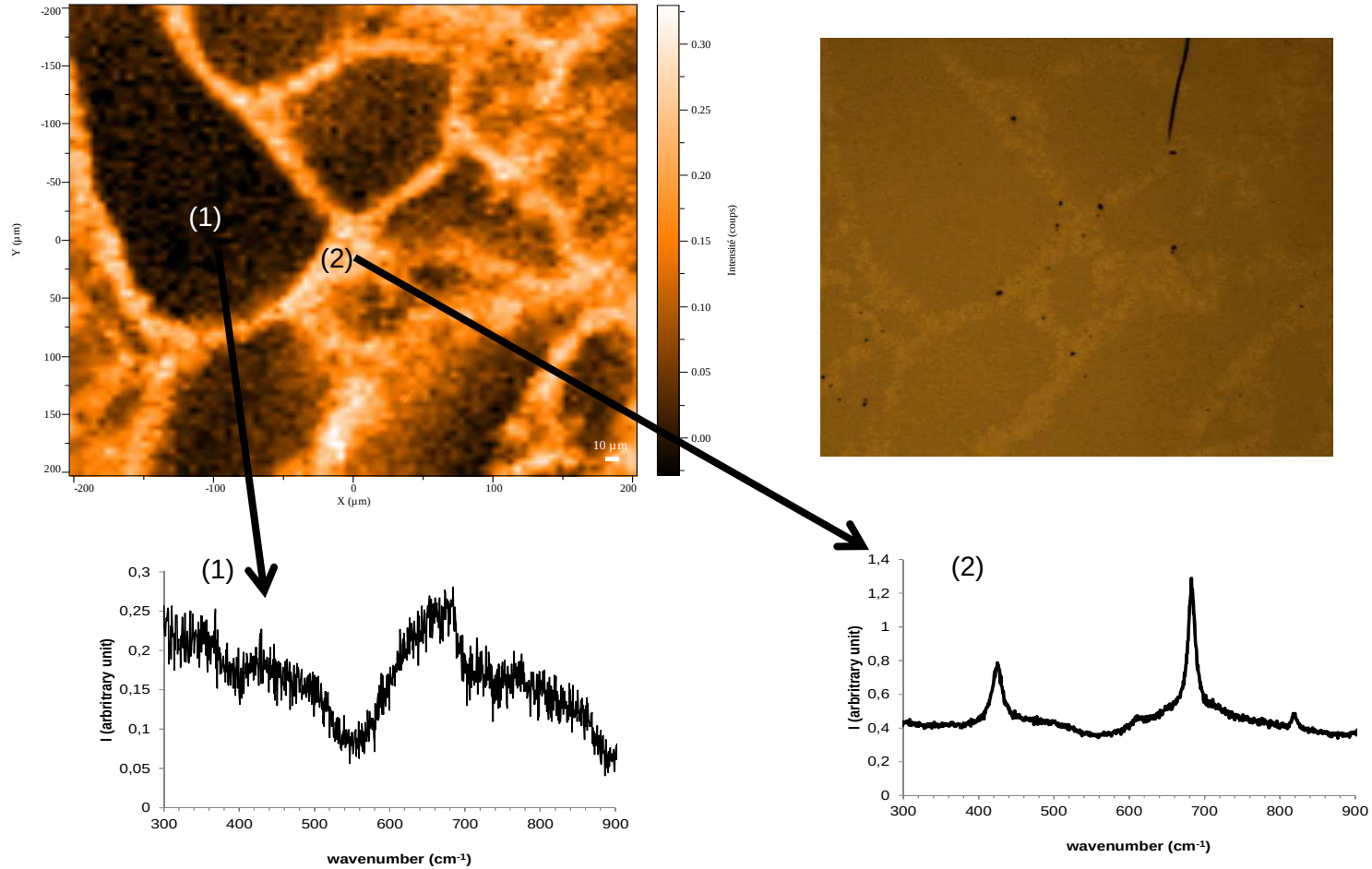
Observation of freshly polished surfaces by SEM

Crystals are still located at the surface of the glass grains !

⇒ Crystals are disseminated within the whole volume of the samples !

Some examples of tellurite materials elaborated in SPCTS : transparent glass-ceramics and ceramics …

From glass to glass-ceramics / Nature of crystals: γ-TeO_2

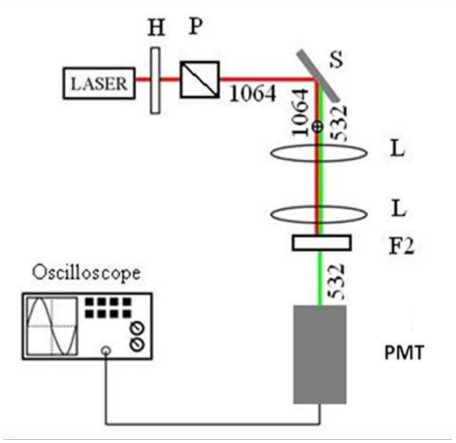


The core of the grains remains amorphous
γ-TeO_2 crystallizes at the surface of the grains !

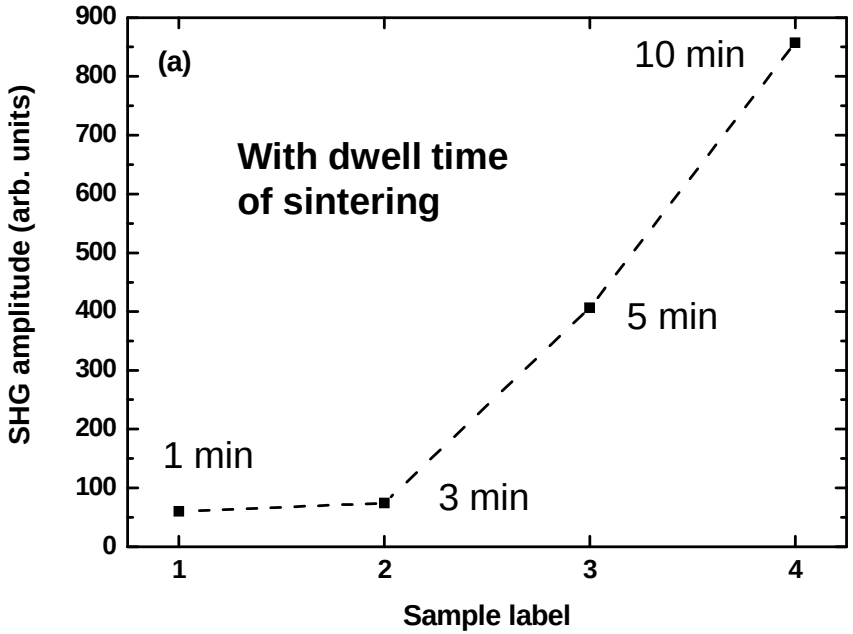
Some examples of tellurite materials elaborated in SPCTS : transparent glass-ceramics and ceramics …

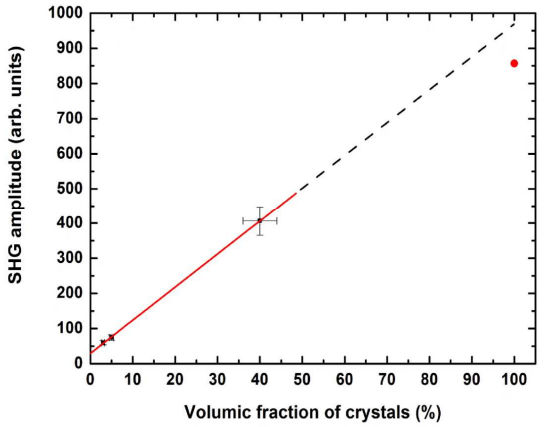
From glass to glass-ceramics / Evidence of SHG

Measurements carried out in reflection mode



SHG properties





Detection of SHG signal ⇔ Glass-ceramics containing non-centrosymetric crystals

In agreement with the XRD and Raman data (evidence of a majority of γ-TeO_2 phase)

SHG intensity proportional to the quantity of crystals

Some examples of tellurite materials elaborated in SPCTS : transparent glass-ceramics and ceramics …

Elaboration of transparent tellurite ceramic by full and congruent crystallization from glass

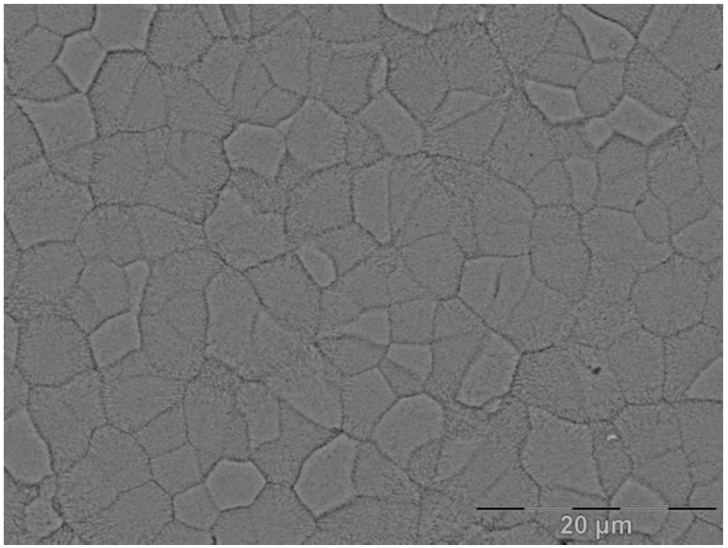
Glass composition : TNB : $75TeO_2$-$12.5Nb_2O_5$-$12.5Bi_2O_3$

Ceramic

1.5h 520° C

Complete crystallization (EBSD)

Grain boundaries (SEM)



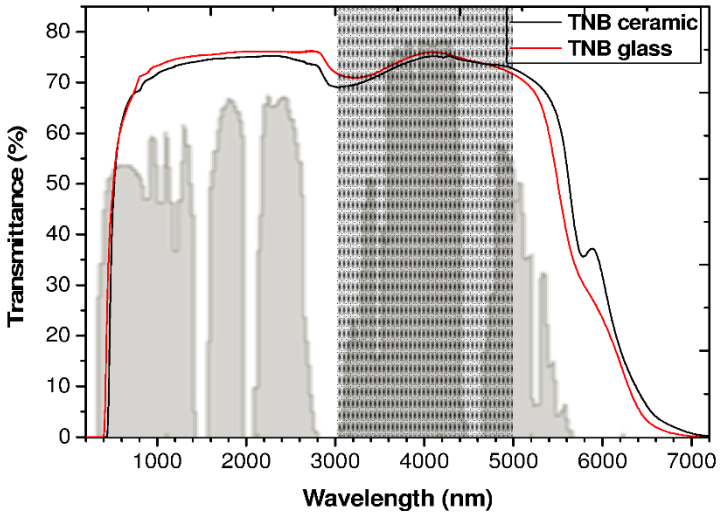
No porosity; grain size average: 5 µm

Some examples of tellurite materials elaborated in SPCTS : transparent glass-ceramics and ceramics …

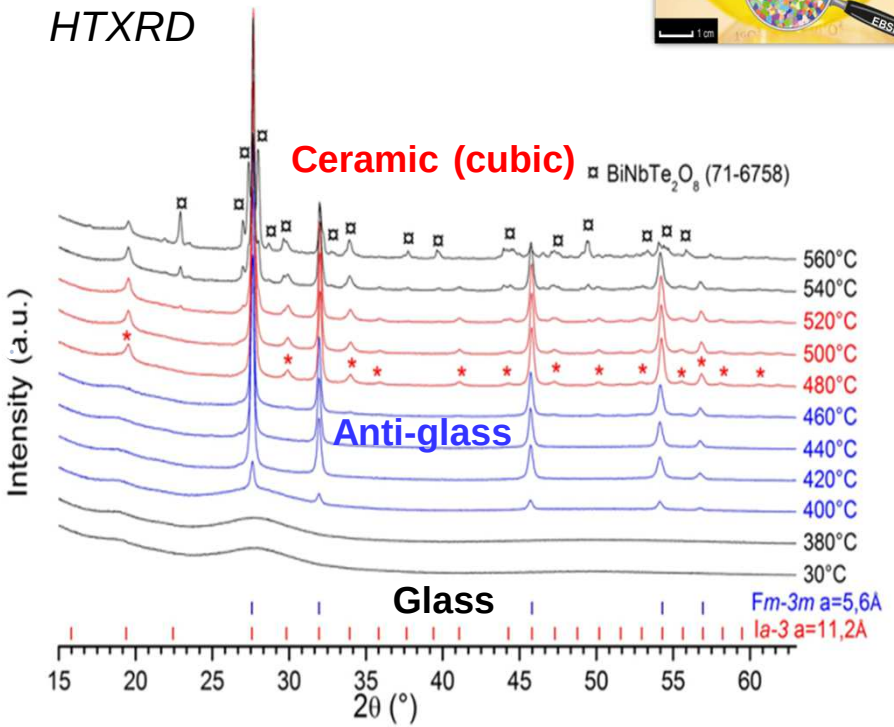
Elaboration of transparent tellurite ceramic by full and congruent crystallization from glass

Glass composition: TNB : $75TeO_2$-$12.5Nb_2O_5$-$12.5Bi_2O_3$

Optical transmittance



HTXRD



Glass / Ceramic: same transparency

Excellent transmission in the near-IR (3-5 µm)

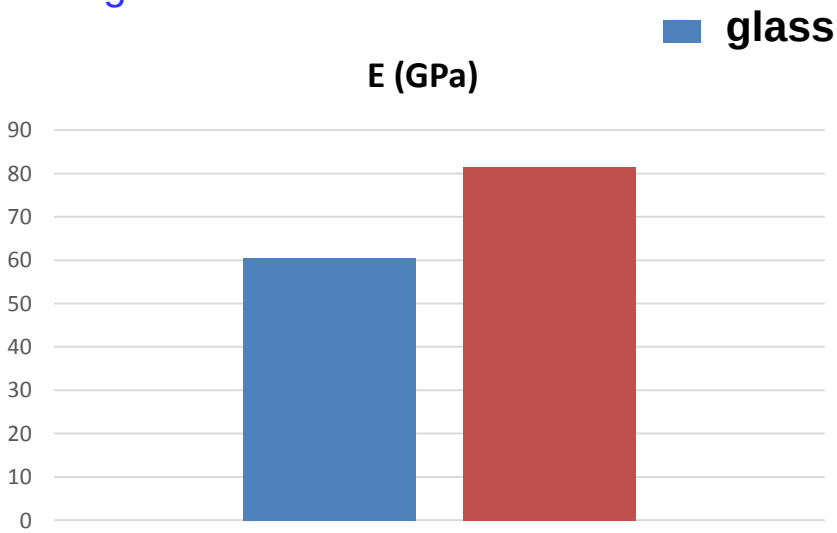
Some examples of tellurite materials elaborated in SPCTS : transparent glass-ceramics and ceramics …

Elaboration of transparent tellurite ceramic by full and congruent crystallization from glass

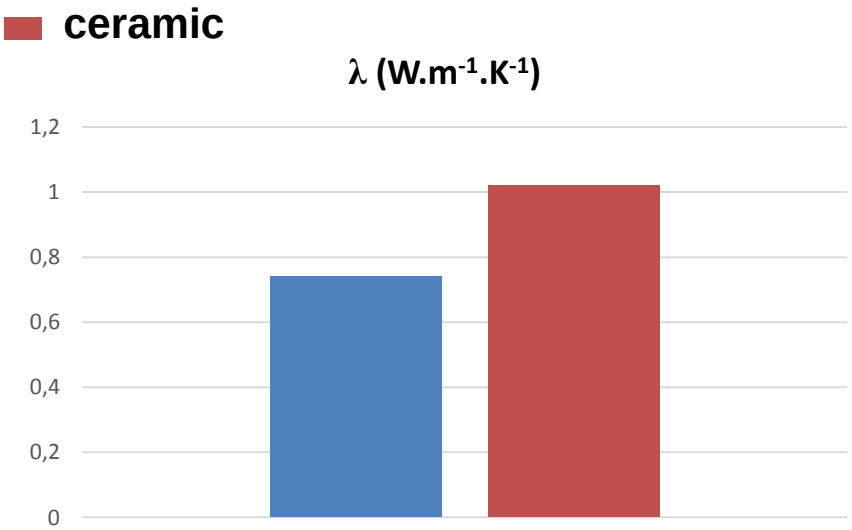
Glass composition: TNB : $75TeO_2$-$12.5Nb_2O_5$-$12.5Bi_2O_3$

Thermo-mechanical properties

Young Modulus



Thermal conductivity



- Glass to ceramic:
  - Improvment of mechanical properties
  - Increase of thermal conductivity

➔ promising for laser applications

European Ceramic Center, Limoges, FRANCE

Thank you for your attention

Thank you to organizers

Questions / Discussions ?

A. Gulenko, M. Dolhen, R. Zaki, L. Torzuoli, J. De Clermont-Gallerande, M. Colas, J. Cornette, J.-R. Duclèr
V. Couderc, G. Delaizir, S. Chenu, O. Noguera, D. Hamani, J. Jouin, O. Masson

and national and international collaborators

37ÈMES JOURNÉES NATIONALES D'OPTIQUE GUIDÉE

04-06 JUILLET

LIMOGES

JNOG 2017

DATE LIMITE DE SOUMISSION : 02 AVRIL 2017

www.jnog-omw2017.fr

Evènements jumelés :
Le journée du Club Optique et Microondes - 03/07
Les rencontres pédagogiques enseignement de l'optique et didactique - 05/07
Une exposition industrielle au plus près des participants - 03 au 06/07

Campus Centre-Ville, 5 Rue Félix Eboué, Limoges

A unique opportunity for students, researchers and engineers from all over the world to discover or extend their knowledge in materials for optics.

Held at the "Le Green Saint-Lazare"
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Summer School includes high-level invited talks, SPCTS & XLIM labs tour, company visits, social events...

Registration fees: *(the registration fees include access to all technical sessions, admission to get-together party, banquet, accommodation, lunch breaks)*

□ student (400€)

□ non-student (500€)

GUEST SPEAKERS

Dr. Rémy BOULESTEIX
University of Limoges, France

Prof. Lionel CANIONI,
University of Bordeaux, France

Dr. Vincent COUDERC
XLIM Institute, CNRS, France

Dr. Jean-René DUCLERE
University of Limoges, France

Prof. Tomokatsu HAYAKAWA,
Nagoya Institute of Technology, Japan

Prof. Euan HENDRY,
University of Exeter, UK

Dr. Hervé MAILLOTTE
FEMTO-ST Institute, CNRS

Prof. Armando RASTELLI
Johannes Kepler University Linz, Austria

Prof. Maroo ROMAGNOLI,
Sant'Anna School of Advanced Studies, Italy

Dr. Frédéric SANDOZ,
Ex. Plant Manager of SILITEC Fibers SA, Switzerland

Prof. Angela SEDDON,
University of Nottingham, UK

Dr. Takunori TAIRA,
Institute for Molecular Science, Japan

Dr. Xiang-Hua ZHANG,
University of Rennes, France

Partners

Contact and inscriptions:
celine.parvy@unilim.fr
there are a limited number of places available so please book early

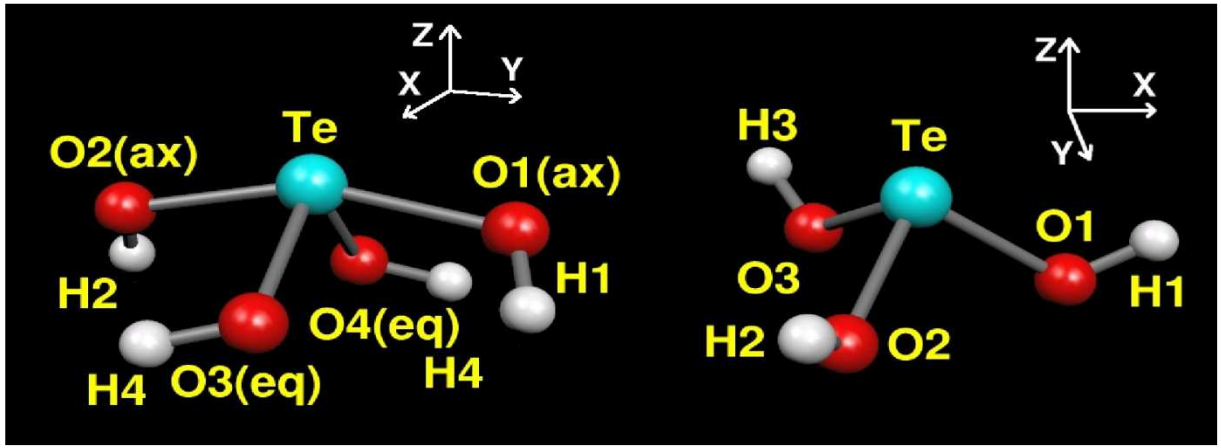
http://www.unilim.fr/sigmatech-days/agenda-2/

Modelling of the non-linear optical properties

What's the origin of high 3rd-order NLO property ?

Ab initio (DFT) Molecular Orbital calculations on TeO_4 and TeO_3 structural units.

TeO_4H_4 $TeO_3H_3^+$



	TeO4H4	$TeO3H3^+$	Remark
$<\gamma^{Te lp}>$	470	203	>>
$<\gamma^{Te\text{-}O bp}>$	206	175	~
$<\gamma^{O lp}>$	71	60	~
$<\gamma^{O\text{-}H bp}>$	39	17	Small values
$<\gamma^{cluster}>$	2018	1134	$\sum<\gamma^{bond}>$

Te *lp* in the TeO_4 geometry is a *key* of high γ in TeO_2-based glasses

S. SUEHARA, P. THOMAS, A.P. MIRGORODSKY and al., *Phys. Rev. B, (70), (2004), 205121-1 – 205121-7.*

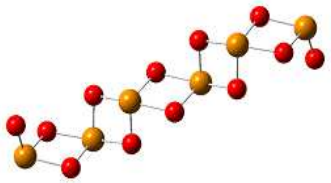
Modelling of the non-linear optical properties

What's the origin of high 3rd-order NLO property ?

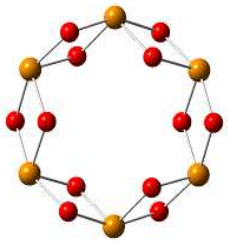
Ab initio (DFT) **Molecular approach**

Geometry determination of a series of $(TeO_2)_p$ clusters

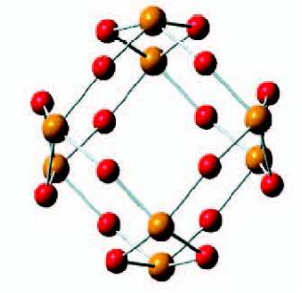
Many more-or-less realistic stable clusters



1D « chain-like »; p=6



2D « circle »; p=6

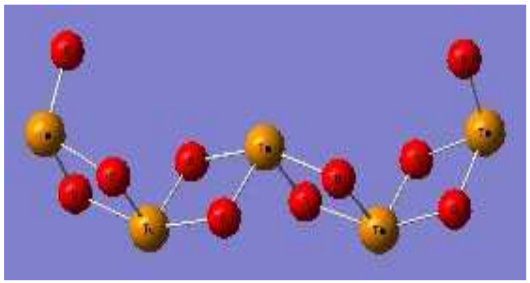


3D « cage »; p=8

Nonlinear susceptibility χ^3

. $\chi(3)$ linear chain-like structure ~ $\chi(3)$ (exp.)

. **The polymerization** contributes strongly to the hyperpolarisability (Te lone pairs 5%!!): electronic delocalization within the chains.

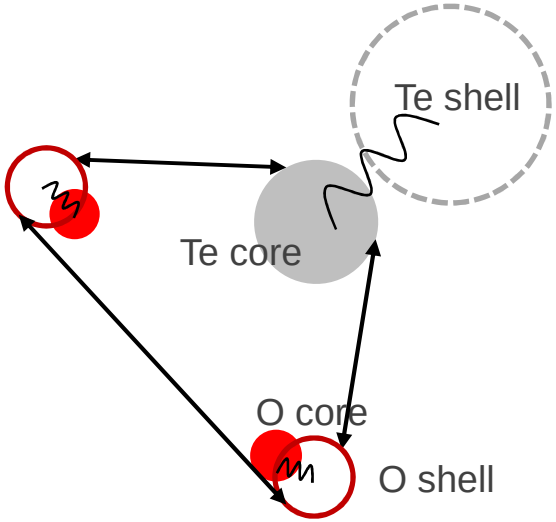


A.P.Mirgorodsky, M.Smirnov, M.Soulis, P.Thomas, T.Merle-Méjean, Phys. Rev. B 73, 134206, 2006

Interatomic potentials model

- Coulombic interaction for **fully ionic** model of Born: $U_{ij}^{coul} = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$
- Short - range interaction: Buckingham potential form: $U_{ij} = Ae^{-r_{ij}/\rho} - Cr_{ij}^{-6}$
- Core-shell model for both Te and O atoms: $U_{spr} = \frac{1}{2}k_2x^2 + \frac{1}{24}k_4x^4$

Interaction	Parameters
$Te^{4+} – O^{2-}$	A_1, ρ_1, C_1
$O^{2-} – O^{2-}$	A_2, ρ_2, C_2
Te (core) – Te (shell)	k^1_2, k^1_4, q^1_{sh}
O (core) – O (shell)	k^2_2, q^2_{sh}



r_{ij} – distance between atoms; A, C, ρ – constants; q_i, q_j – ion charges

=> Parametrization of IAP using 11 parameters