JOURNÉES VERRE 2024

DIJON

13 – 15 Novembre 2024

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irCer institut de recherche sur les céramiques

Région Nouvelle-Aquitaine

LABEX Σ LIM

anr

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Université de Limoges

Outline

I) Brief context of the study

II) Fabrication and characterizations of bismuth borotellurite glasses and glass-ceramics

III) Conclusions / Prospects

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Brief context of the study

Tellurite glasses

Advantages 📖:

- **Relatively low melting point**
- Good thermal stability
- **Large transparency window (up to 5-6 µm)**
- High linear refractive indices
- **Excellent 3rd-order nonlinear optical properties**

Borotellurite glasses

Main application: Radiation shielding properties 📖

Specificity:

Occurrence of liquid-liquid phase separation that will lead to chemical demixtion 📖

Idea: use that chemical demixtion to then "tailor" glass-ceramics

📖 R. A. H. El-Mallawany, *Tellurite Glasses Handbook: Physical Properties and Data*, CRC Press, 2012, Second Edition.

📖 V. A. G.Rivera, D. Manzani "Technological Advances in Tellurite Glasses: Properties, Processing and Applications Springer Series in Materials Science, 2017, 254.

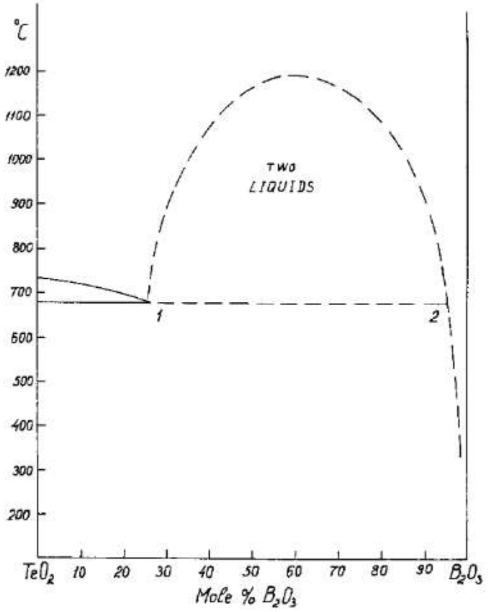
📖 P. Patra, K. Annapurna, *Transparent Tellurite Glass-Ceramics for photonics applications: A Comprehensive Review on crystalline phases and crystallization mechanisms*, Progress in Mater. Sci., 125 (2022) 100890.

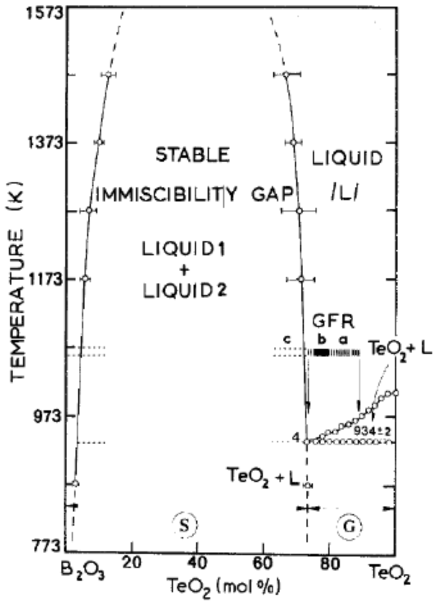
📖 Y. Dimitriev, E. Kashchieva, *Immiscibility in the TeO_2-B_2O_3 system*, J. Mater. Sci., 10 (1975) 1419-1424.

📖 E. Kashchieva, M. Pankova, Y. Dimitriev, *Liquid Phase Separation in the Systems TeO_2-B_2O_3-M_2O_3 (M_2O_3 = Al_2O_3, Ga_2O_3, Sc_2O_3, La_2O_3, Bi_2O_3)*, Ceramics – Silikáty, 45 (2001) 111-114.

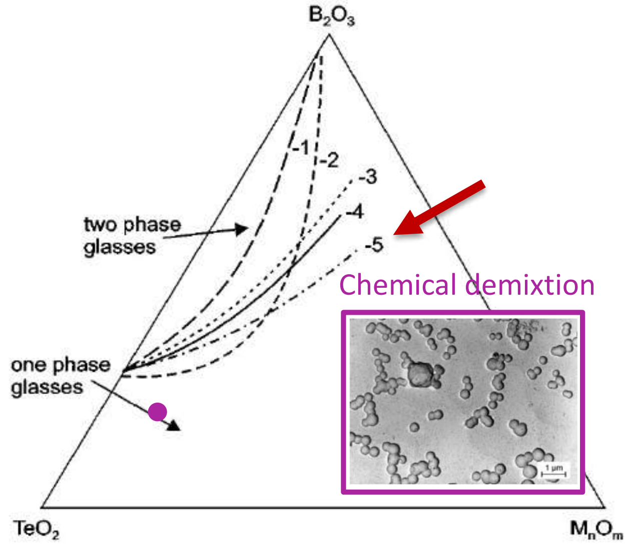
Brief context of the study

TeO_2-B_2O_3 system





TeO_2-B_2O_3-Bi_2O_3 system



" Immiscibility droplets and micro-aggregates in one-phase glass with composition $70TeO_2$-$20B_2O_3$-$10Bi_2O_3$ (%mol) "

- Y. Dimitriev, E. Kashchieva, *Immiscibility in the TeO_2-B_2O_3 system*, J. Mater. Sci., 10 (1975) 1419-1424.
- H. Borger, W. Vogel, V. Kozhukharov, M. Marinov, *Phase equilibrium, glass-forming, properties and structure of glasses in the TeO_2-B_2O_3 system,* J. Mater. Sci., 19 (1984) 403-412.
- E. Kashchieva, M. Pankova, Y. Dimitriev, *Liquid Phase Separation in the Systems TeO_2-B_2O_3-M_2O_3 (M_2O_3 = Al_2O_3, Ga_2O_3, Sc_2O_3, La_2O_3, Bi_2O_3)*, Ceramics – Silikáty, 45 (2001) 111-114.

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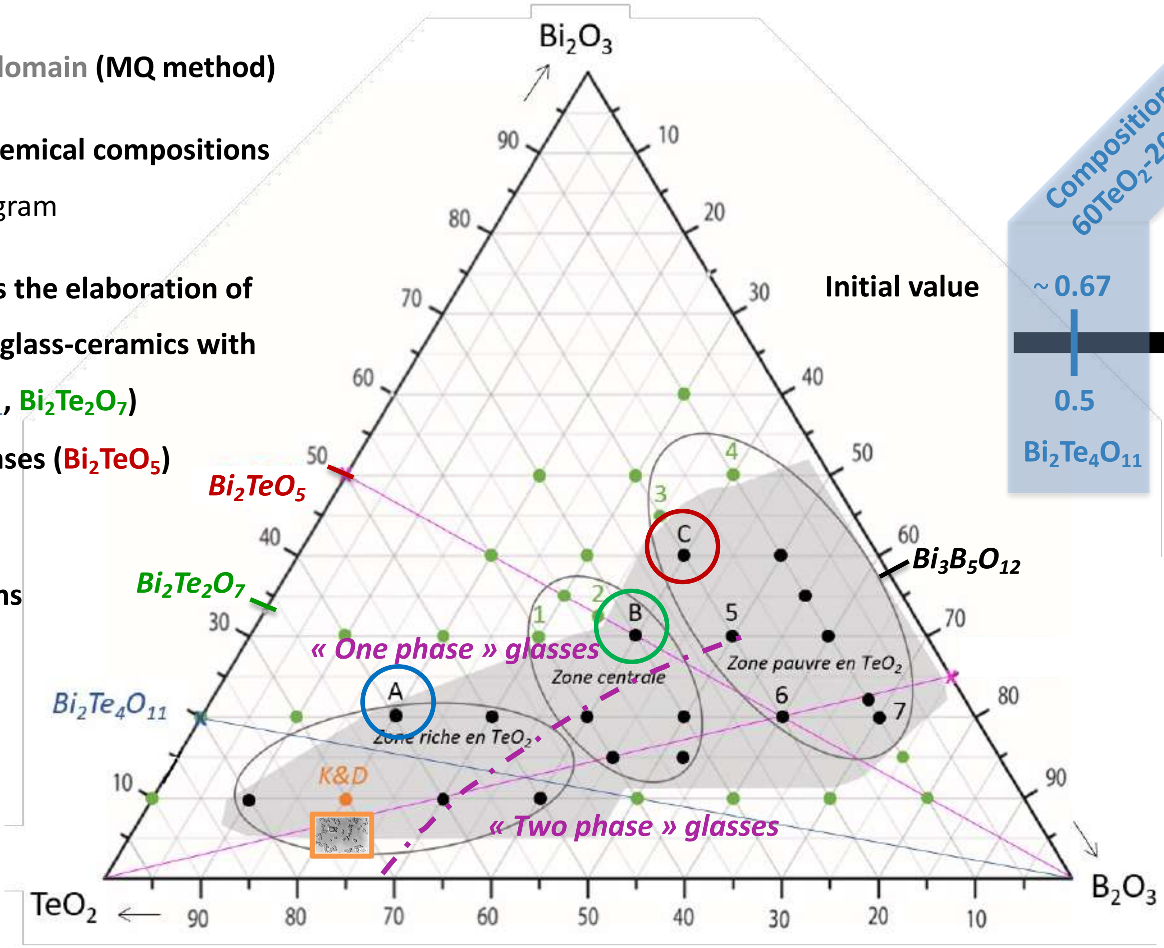
Overview of the conducted work

1) Determination of the glassy domain **(MQ method)**

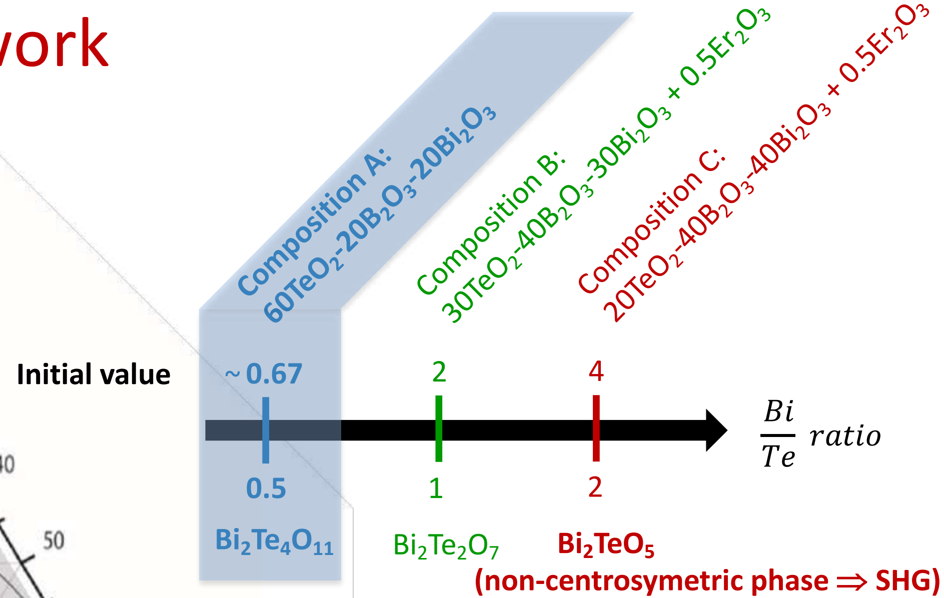
2) Selection of some **relevant chemical compositions** within different areas of the diagram

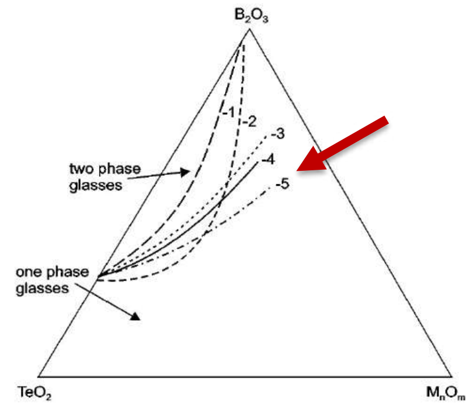
3) Partial crystallization towards the elaboration of new transparent or translucent glass-ceramics with either centrosymetric ($Bi_2Te_4O_{11}$, $Bi_2Te_2O_7$) or even non-centrosymetric phases (Bi_2TeO_5)

4) Comprehension of the crystallization mechanisms



- Devitrified material
- Glass






Journal of Non-Crystalline Solids 598 (2022) 121953

Contents lists available at ScienceDirect

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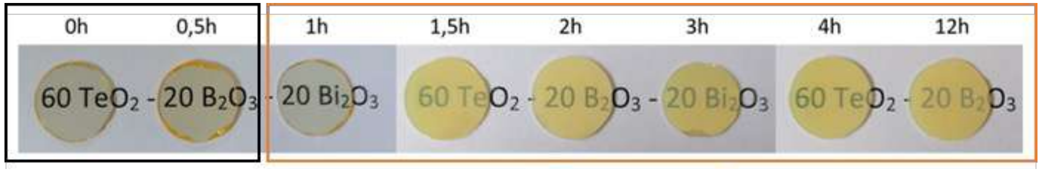
journal homepage: www.elsevier.com/locate/jnoncrysol

Highly transparent bismuth borotellurite glass-ceramics: Comprehension of crystallization mechanisms

Marine Cholin[a,b], Cécile Genevois[c], Pierre Carles[a], Julie Cornette[a], Sébastien Chenu[a,d], Mathieu Allix[c], Gaëlle Delaizir[a], Philippe Thomas[a], Vincent Couderc[b], Jean-René Duclère[a,*]

Composition A: $60TeO_2$-$20B_2O_3$-$20Bi_2O_3$

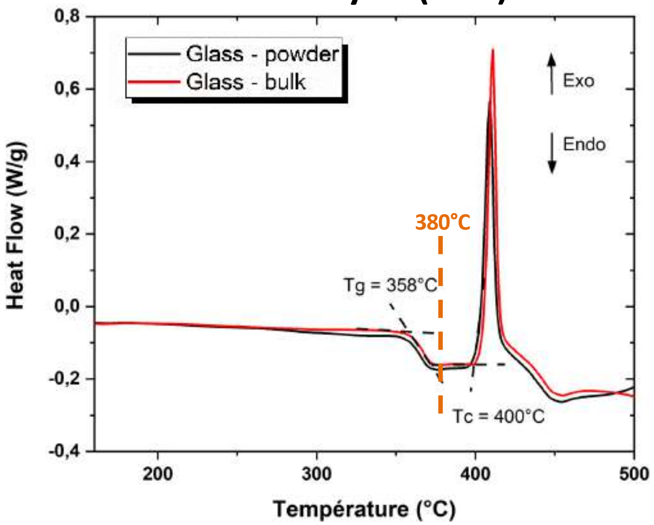
Combined nucleation/growth heat treatment at **T = 380°C**:



Glasses

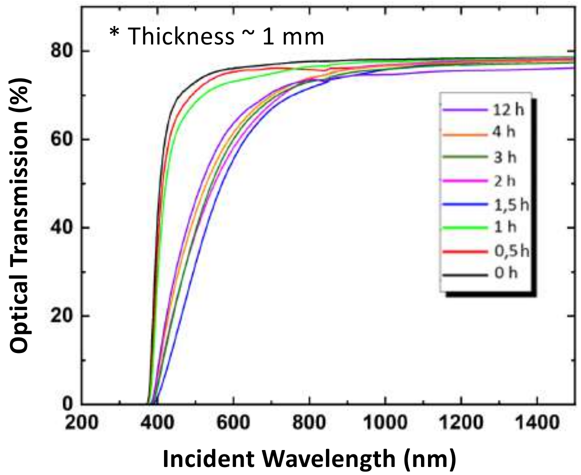
Highly transparent Glass-Ceramics (GCs) with the unique $Bi_2Te_4O_{11}$ crystal phase

Thermal analysis (DSC) data

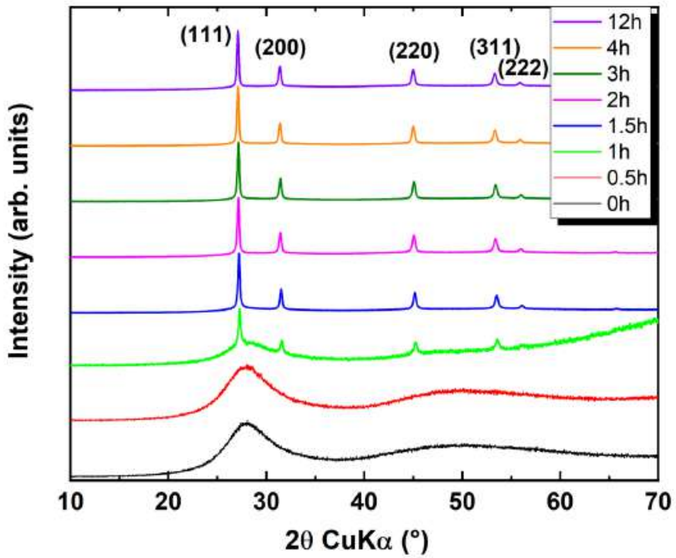


➡ **Volume crystallization**

Optical transmission

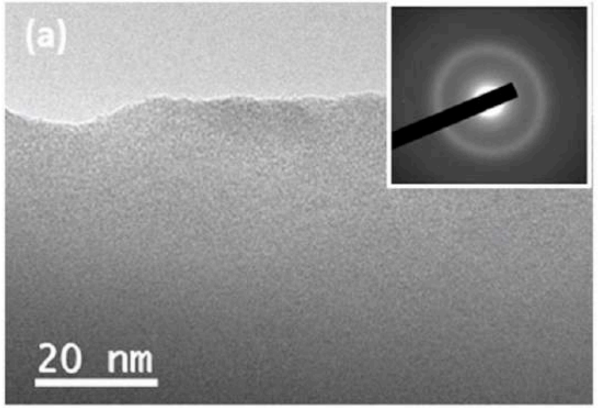


X-ray diffraction (XRD) data



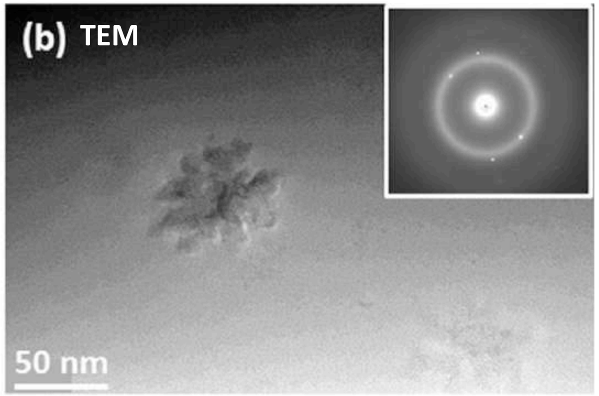
Composition A: $60TeO_2$-$20B_2O_3$-$20Bi_2O_3$

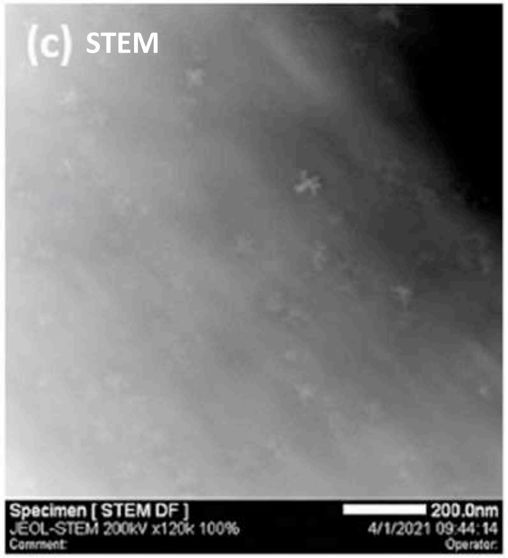
TEM/STEM observations



Quenched sample

⇒ Homogeneous glass





GC sample: 1h at T = 380°C

⇒ Polycrystalline $Bi_2Te_4O_{11}$ entities dispersed in a homogeneous glass matrix

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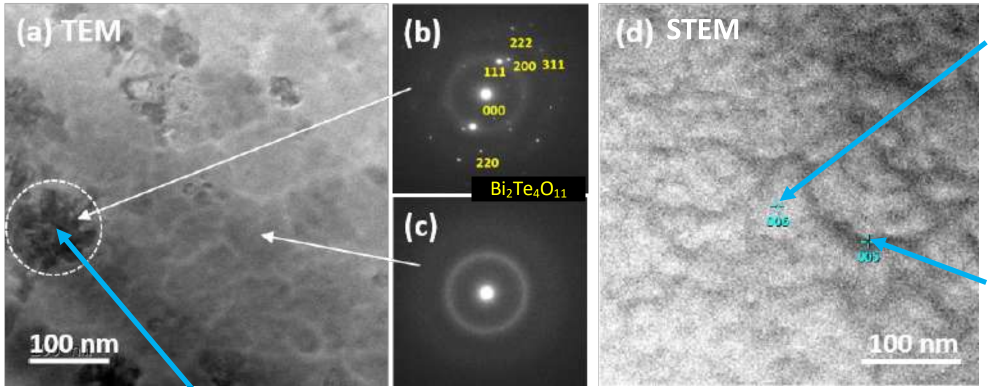
Composition A: $60TeO_2$-$20B_2O_3$-$20Bi_2O_3$

Cécile Genevois

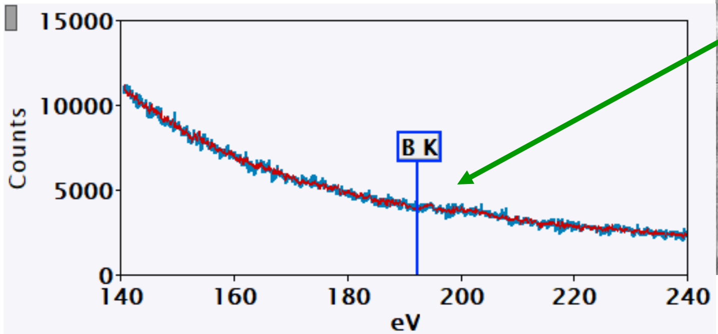
Cemhti

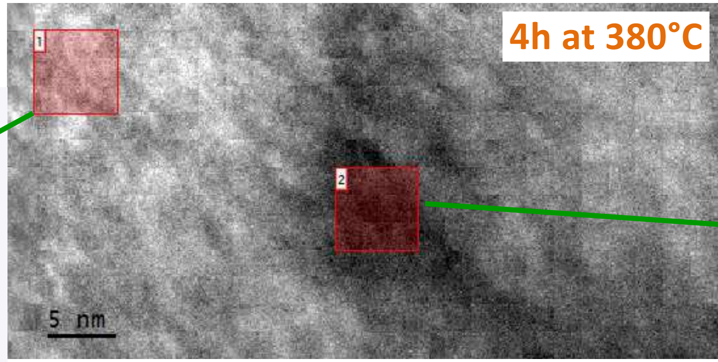
TEM/STEM observations of GC samples (2h-12h at 380°C)



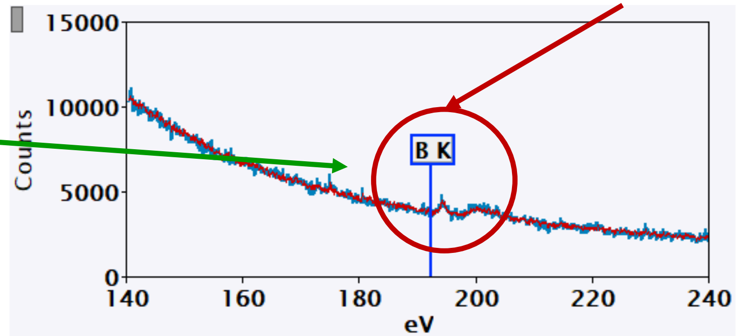
Polycrystalline $Bi_2Te_4O_{11}$ entities (~ 100 nm) dispersed in a heterogeneous residual matrix, composed of two amorphous phases

⇒ Recent (April 2024) results:
First evidence of a chemical demixtion in this system





EELS analyses (Boron) at high energy



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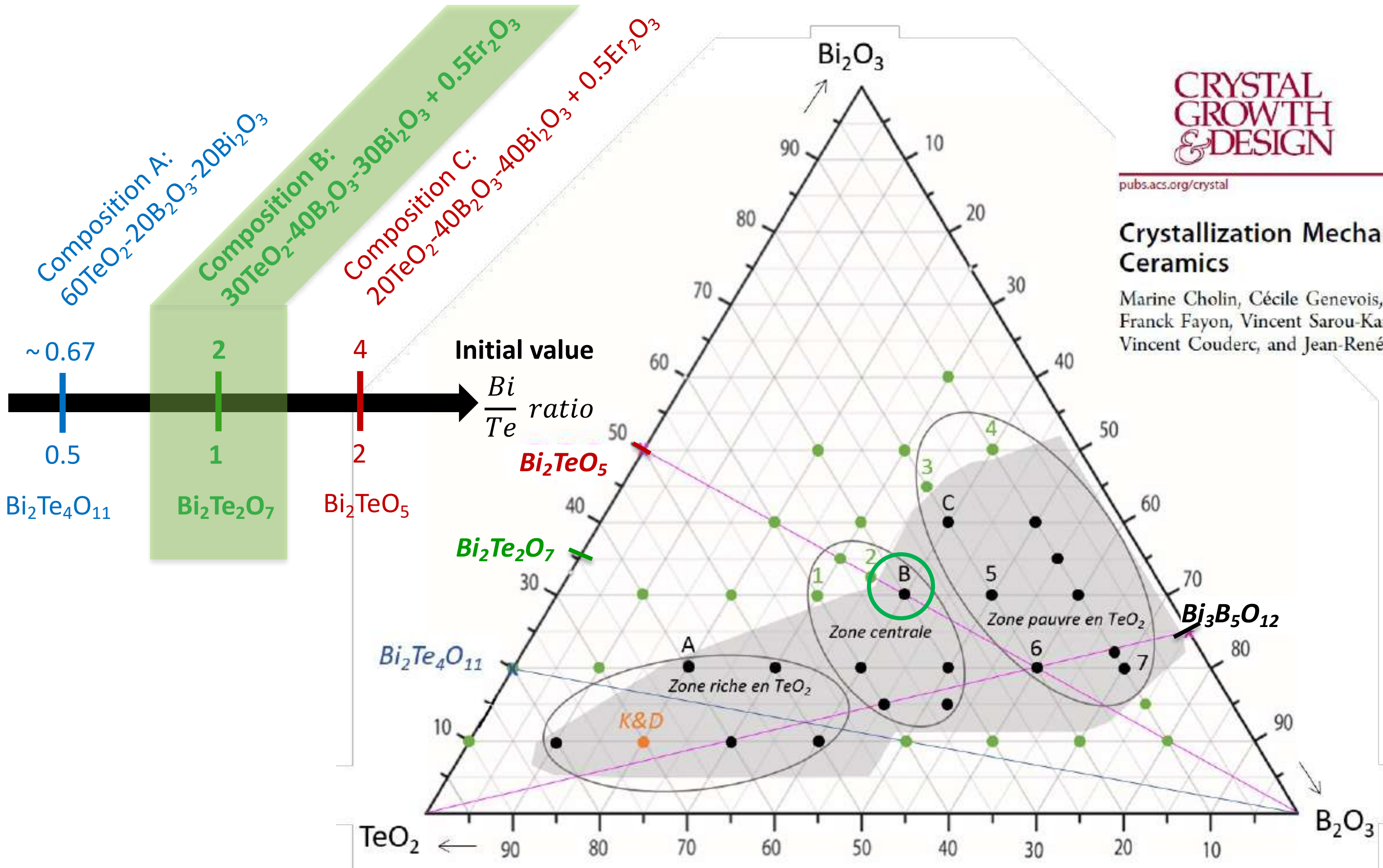
Overview of the conducted work

Towards a composition poorer in TeO_2 and richer in Bi_2O_3 and B_2O_3 (larger Bi/Te ratio)



CRYSTAL GROWTH & DESIGN

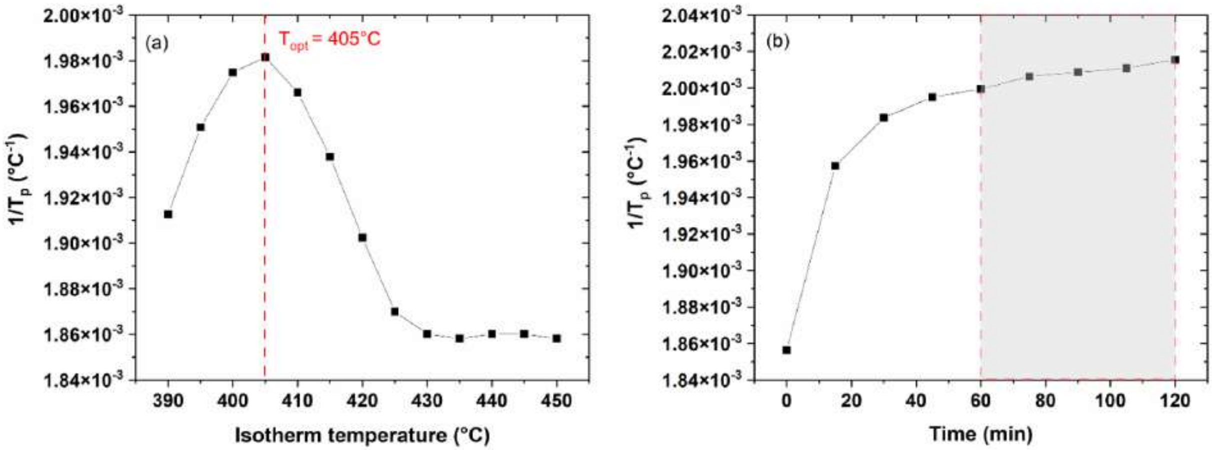
pubs.acs.org/crystal Article

Crystallization Mechanisms in New Bismuth Borotellurite Glass-Ceramics

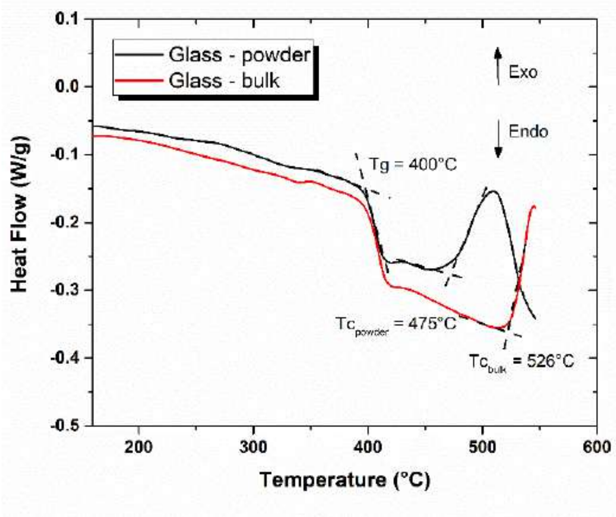
Marine Cholin, Cécile Genevois, Pierre Carles, Mathieu Allix, Julie Cornette, Maggy Colas, Franck Fayon, Vincent Sarou-Kanian, Gaëlle Delaizir, Philippe Thomas, Sébastien Chenu, Vincent Couderc, and Jean-René Duclère*

Composition B: $30TeO_2$-$40B_2O_3$-$30Bi_2O_3$ + $0.5Er_2O_3$

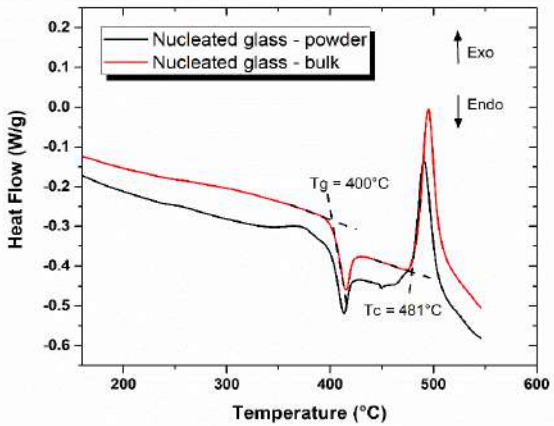
Nucleation study



Initial DSC data



Surface crystallization



Volume crystallization now competes with surface crystallization

$\Delta T = T_c - T_g = 80°C$

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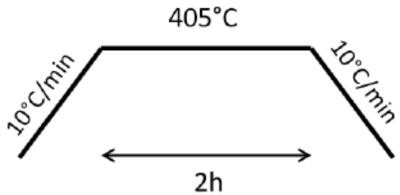
Composition B: $30TeO_2$-$40B_2O_3$-$30Bi_2O_3$ + $0.5Er_2O_3$

Two step heat-treatment

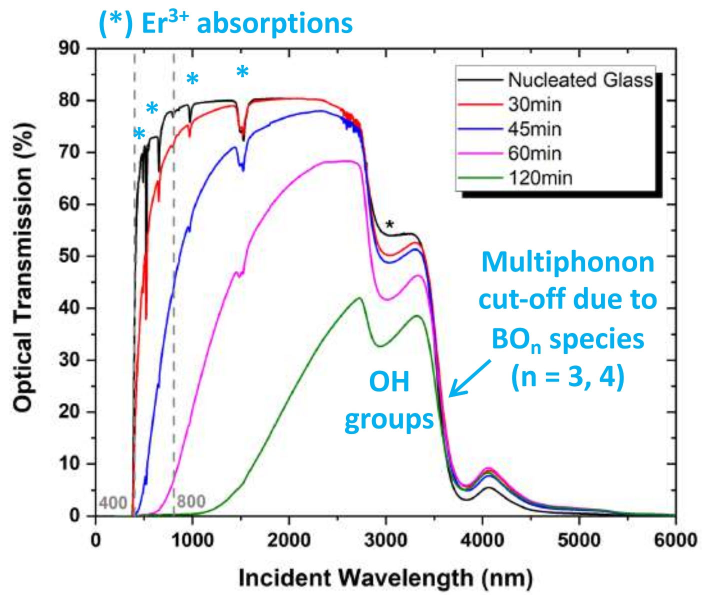
1) **Nucleation**



2) **Growth**

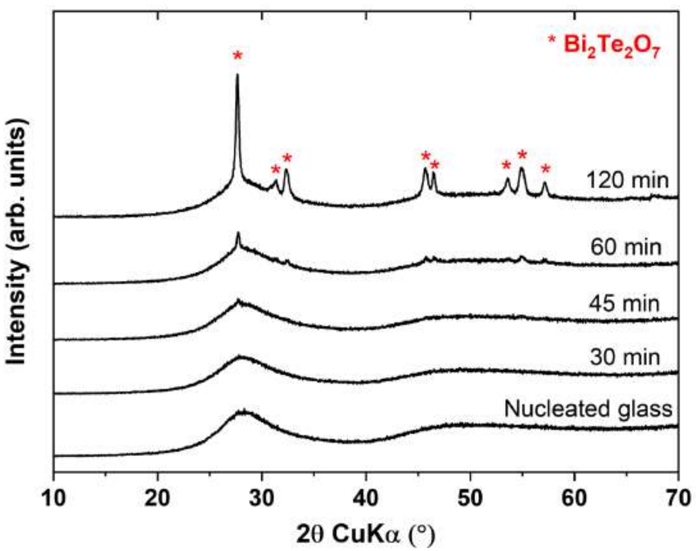
$T_{HT} = T_c - 30°C = 450°C$

Optical transmission (UV-Vis-FTIR)



Composition B: $30TeO_2$-$40B_2O_3$-$30Bi_2O_3$ + $0.5Er_2O_3$

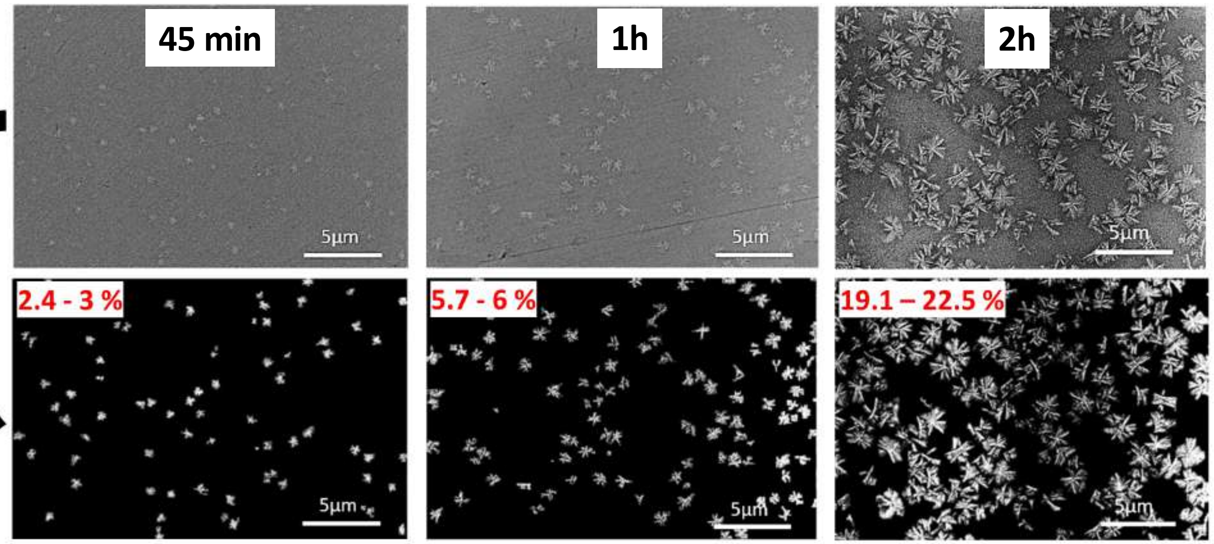
XRD data



First signs of the crystallization of the orthorhombic phase **$Bi_2Te_2O_7$** after 45min of heat treatment.

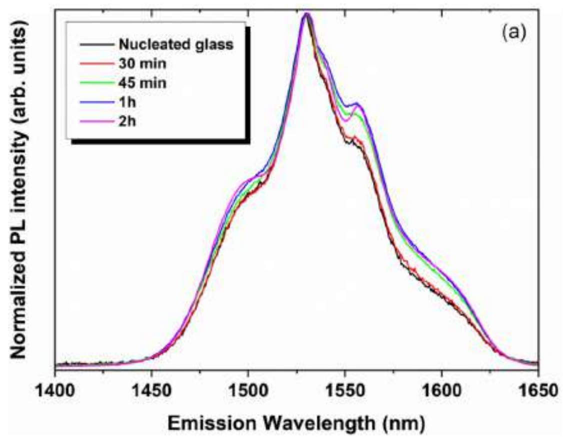
SEM observations

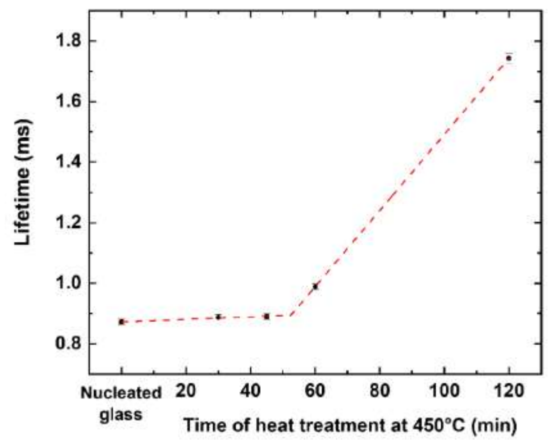
Image analysis (ImageJ) employed to extract the crystalline fraction at the surface



Photoluminescence properties

$^4I_{13/2}$–$^4I_{15/2}$ electronic transition





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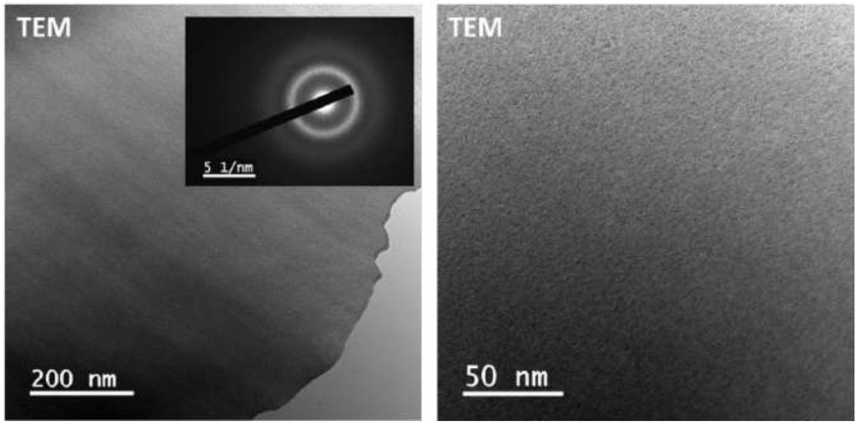
Composition B: $30TeO_2$-$40B_2O_3$-$30Bi_2O_3$ + $0.5Er_2O_3$

The chemical composition is $30TeO_2$-$40B_2O_3$-$30Bi_2O_3$ + 1% mol. Er
⇒ Theoretical Bi/Te ratio = 2

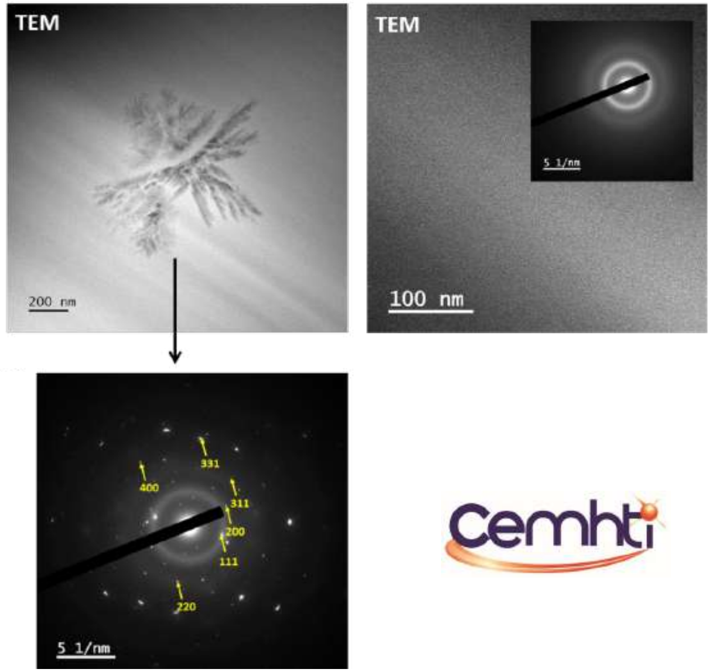
So, why the crystallization of the $Bi_2Te_2O_7$ phase, where Bi/Te ratio = 1 ?

TEM microscopy data

Nucleated glass = one phase homogeneous glass



Glass-ceramic (nucleation + 1h - 450°C)
Polycrystalline entities dispersed in a homogeneous amorphous matrix



*** Can be indexed by $Bi_2Te_2O_7$**

cemhti

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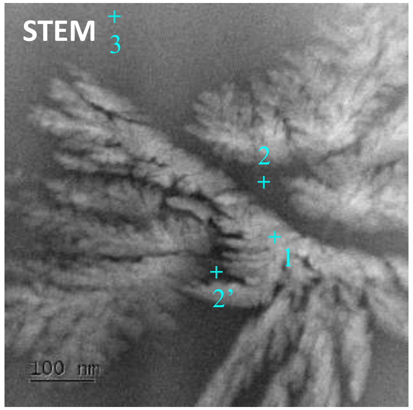
Composition B: $30TeO_2$-$40B_2O_3$-$30Bi_2O_3$ + $0.5Er_2O_3$

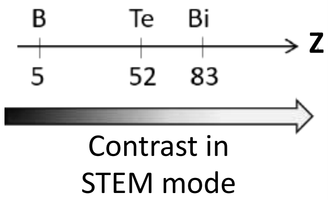
Chemical analysis: STEM imaging/EDS

$30TeO_2$-$40B_2O_3$-$30Bi_2O_3$ + 1 mol.% in Er

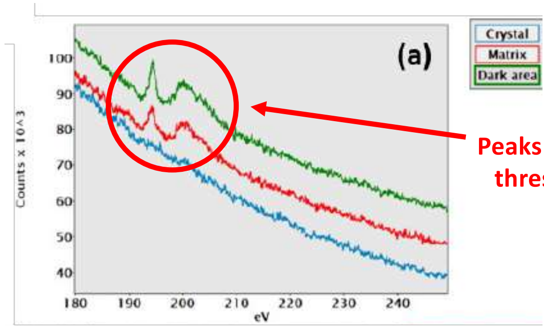


Global composition

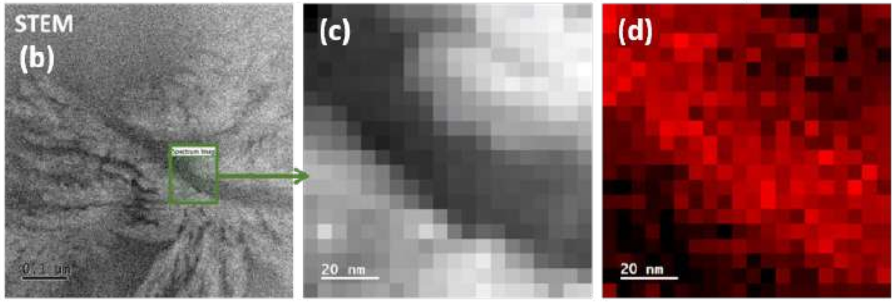
Bi / Te ratio = 2



EDS Local point	Bi / Te ratio
1 Polycrystal	~ 1.2
3 Amorphous matrix	~ 1.7
2-2' Dark area	~ 2.5



EELS data



Crystallization of the « $Bi_2Te_2O_7$ » phase

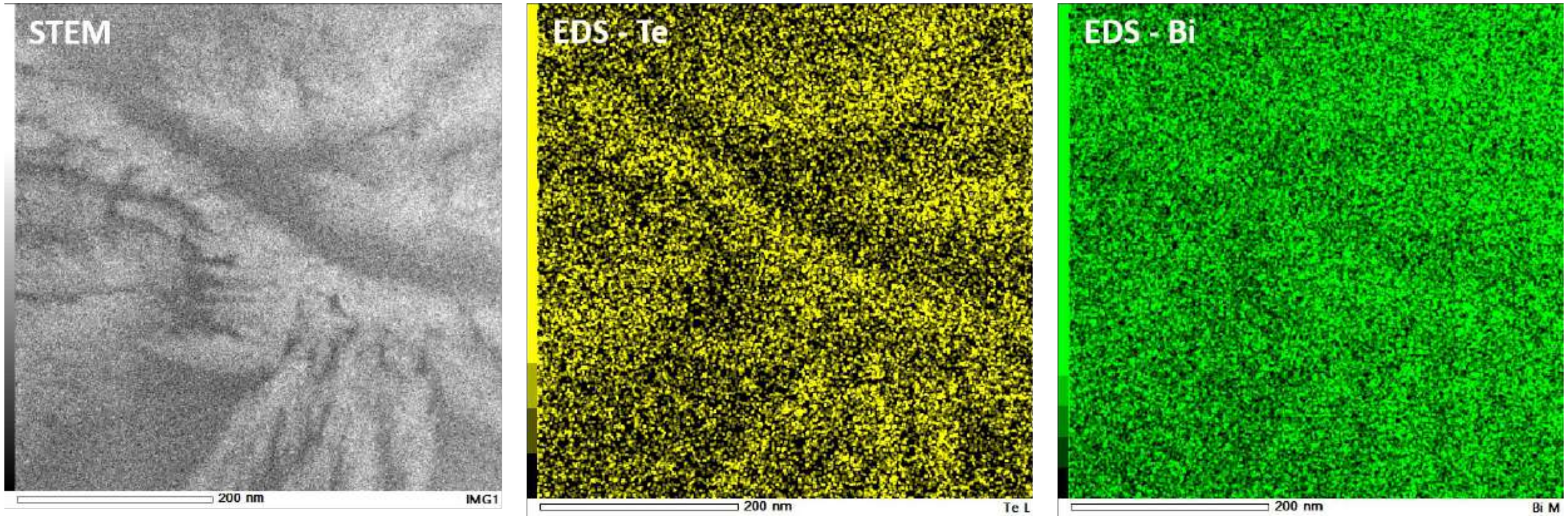
⇒ **Boron oxide is expelled from polycrystals**

⇒ **Clear evidence of a chemical demixtion**

* Boron oxide, very concentrated, induces a dark contrast in STEM mode (**average contrast B-Bi**)

Composition B: $30TeO_2$-$40B_2O_3$-$30Bi_2O_3$ + $0.5Er_2O_3$

STEM imaging



In respect with the initial Bi / Te ratio of 2

EDS Local point	Bi/Te ratio
1 Polycrystal	~ 1.2
3 Amorphous matrix	~ 1.7
2-2' Dark area	~ 2.5

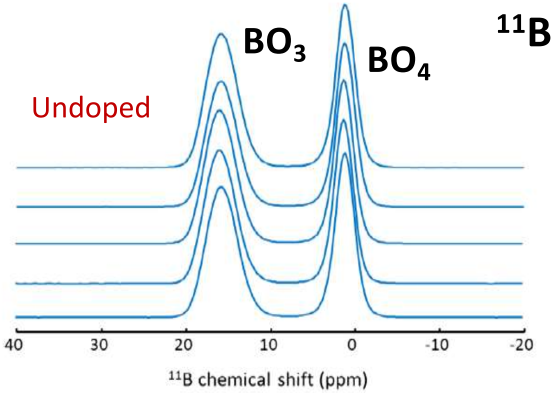
↗↗ Te ↗ Bi

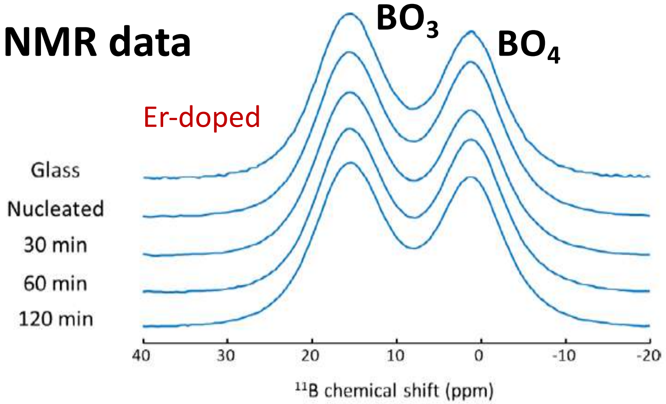
↘↘ Te ↘ Bi

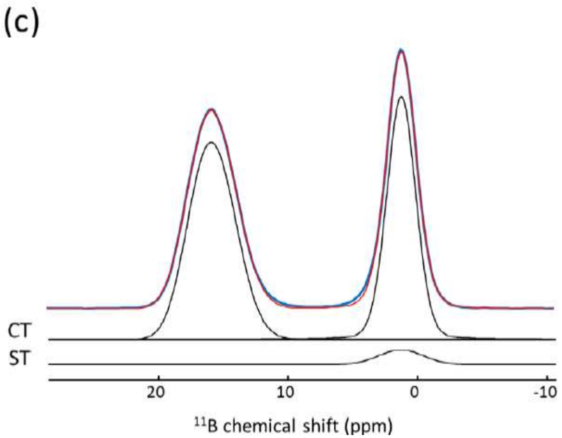
Franck Fayon Vincent Sarou-Kanian

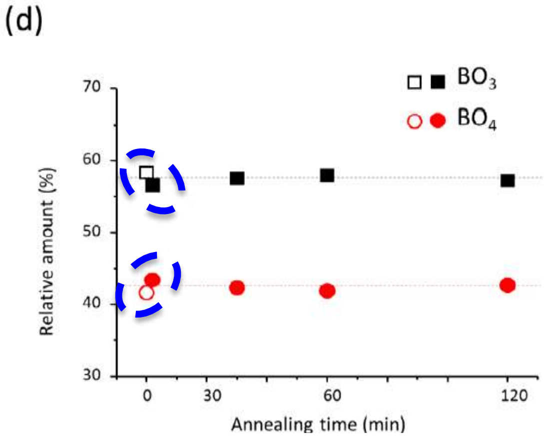
Composition B: $30TeO_2$-$40B_2O_3$-$30Bi_2O_3$ + $0.5Er_2O_3$

^{11}B NMR data









No modification of the relative amount of BO_4 / BO_3 units:

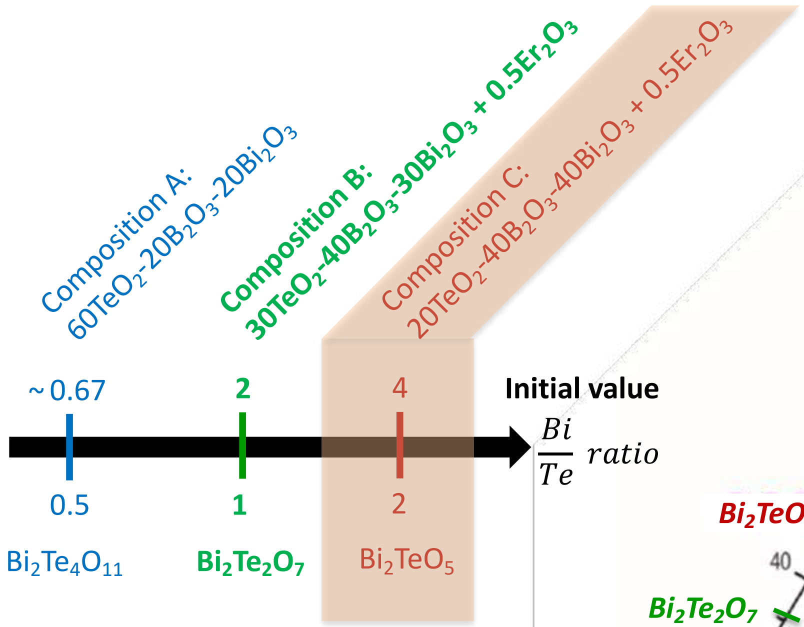
- **with the nucleation step**
- **during the partial crystallization**

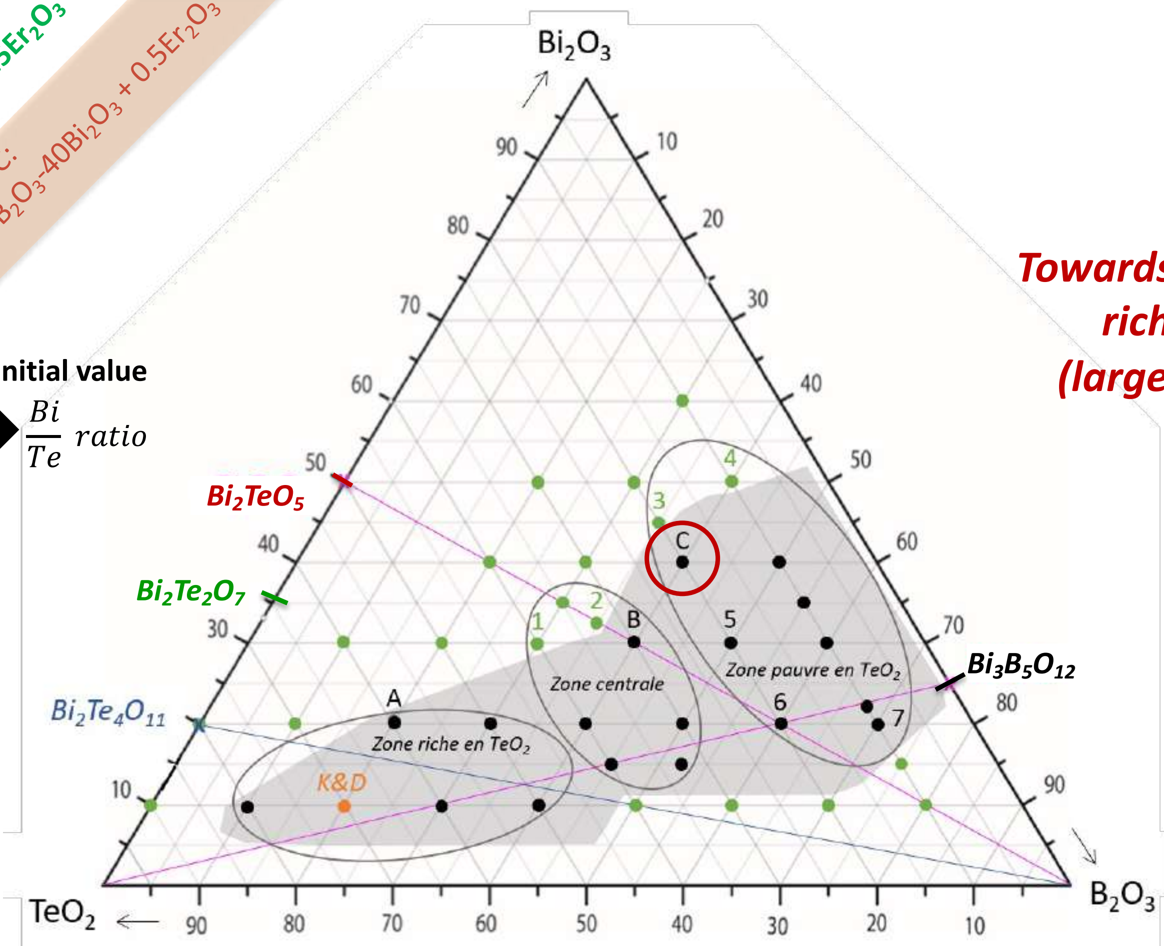
⇒ Apparently, only little modifications of the borate-rich glassy network

⇓

Some aspects are still under investigation

Overview of the conducted work





Towards a composition richer in Bi_2O_3 (larger Bi/Te ratio)

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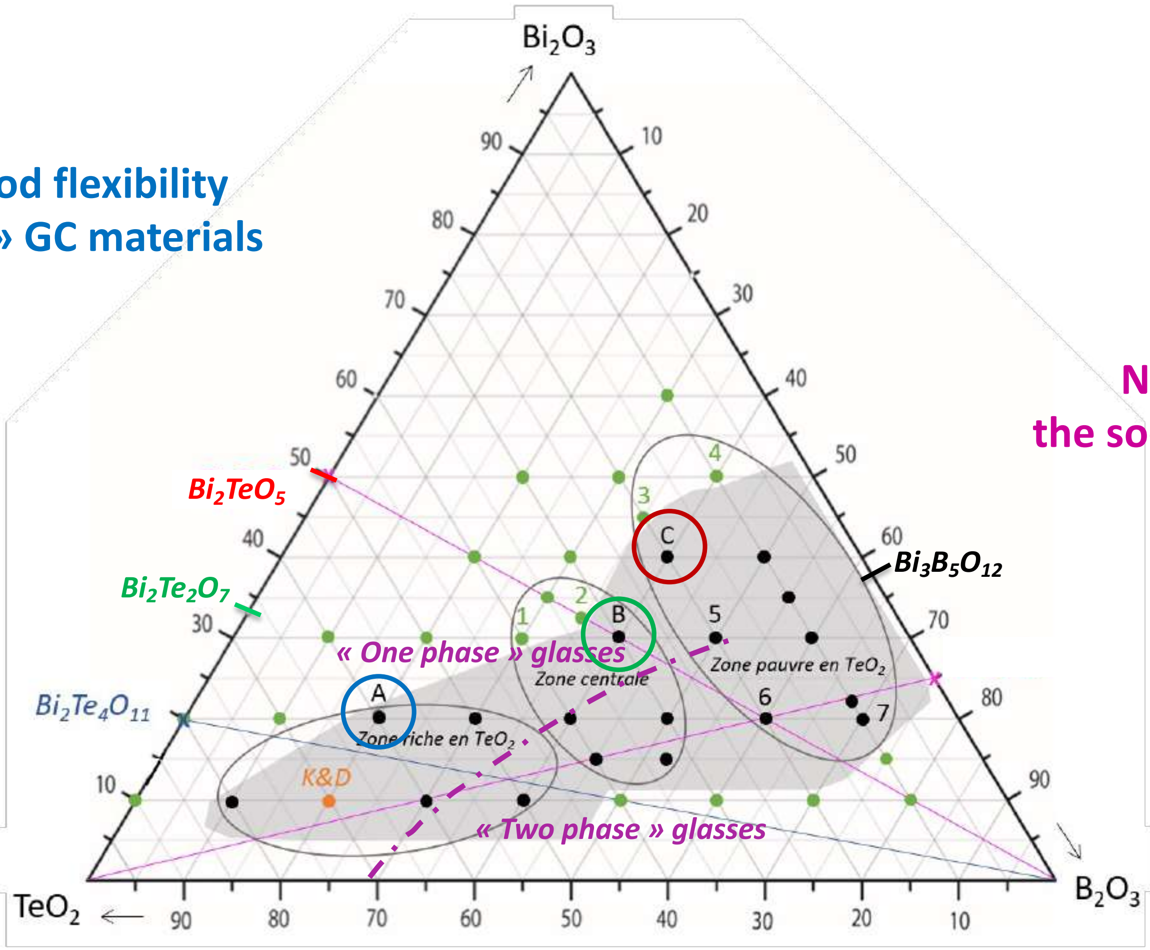
Conclusions / Prospects within the TeO_2-B_2O_3-Bi_2O_3 system

There is a good flexibility for « tailoring » GC materials



Need to deeply explore the so-called « Two phase » area

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THANK YOU
FOR YOUR KIND ATTENTION