Contrôle de la démixtion et de la cristallisation dans les verres : Exemples d'applications

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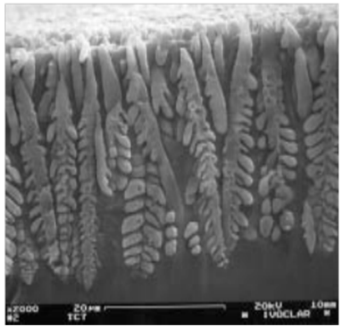
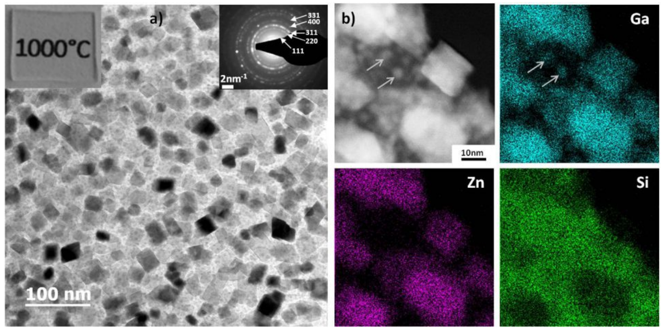
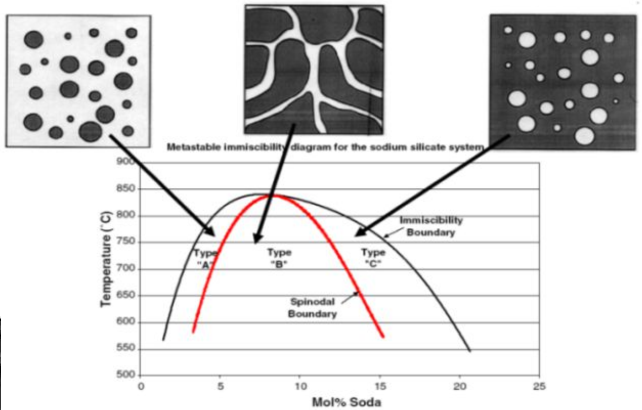


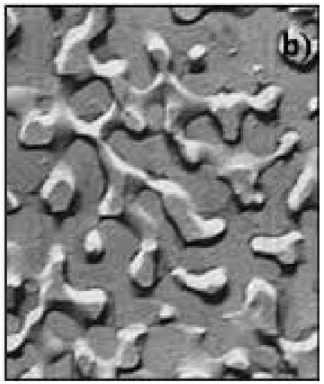


11 octobre 2016 – Atelier Thermodynamique des verres – Marseille

Phase separation / crystallization processes are usually not desired in the glass industry

But they can be controlled!





Opals:

Pyrex®

Vycor®

A glass-ceramic material is elaborated by partial and controlled crystallization from glass

René-Antoine Ferchault de Réaumur (1683-1757)

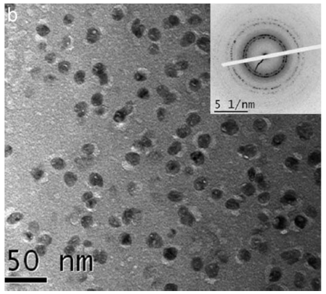
Stanley D. Stookey (1915-2014)

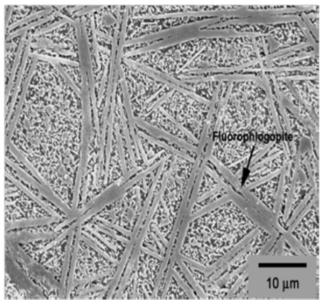
Fortuitous discovery of

glass-ceramics (1953)

"lucky accident"

Control of nucleation/growth processes ⇒ Wide range of accessible properties

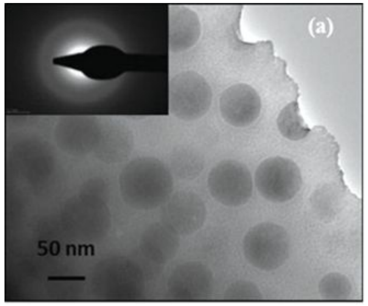


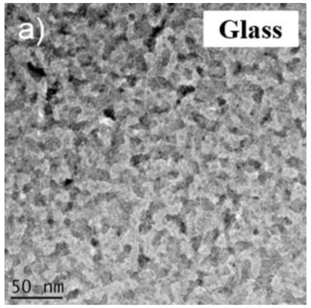


Outline

I. Phase separation in glass: applications

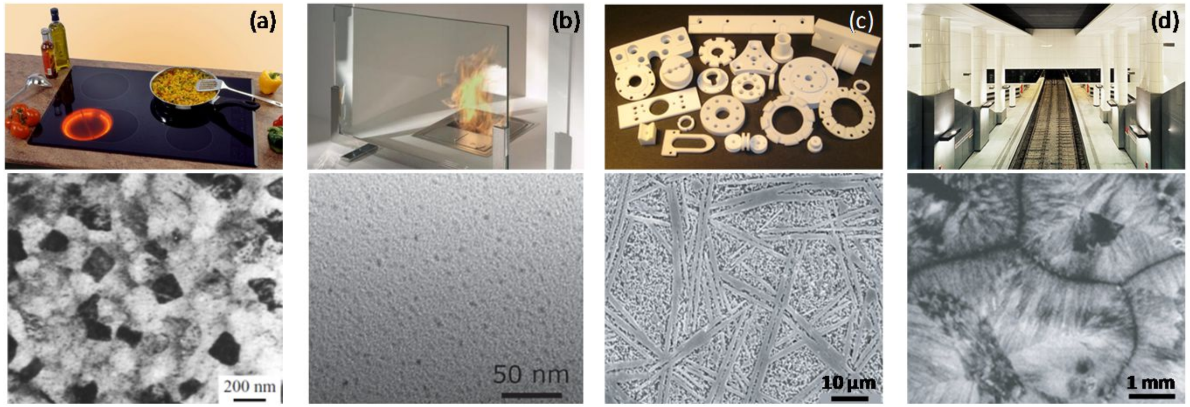
- SiO_2-B_2O_3-Na_2O system (Pyrex® / Vycor®)
- SiO_2-Al_2O_3-CaO system
- GeO_2-ZnO-Ga_2O_3 system





II. Glass-ceramics: crystallization processes

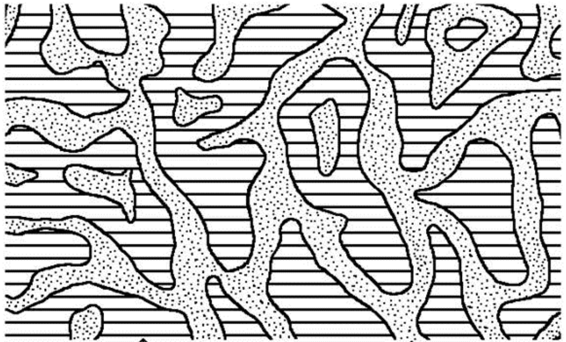
- Homogenous nucleation
- Heterogeneous nucleation
  - *Surface crystallization*
  - *From nucleation agents*
  - *From phase separated glasses*

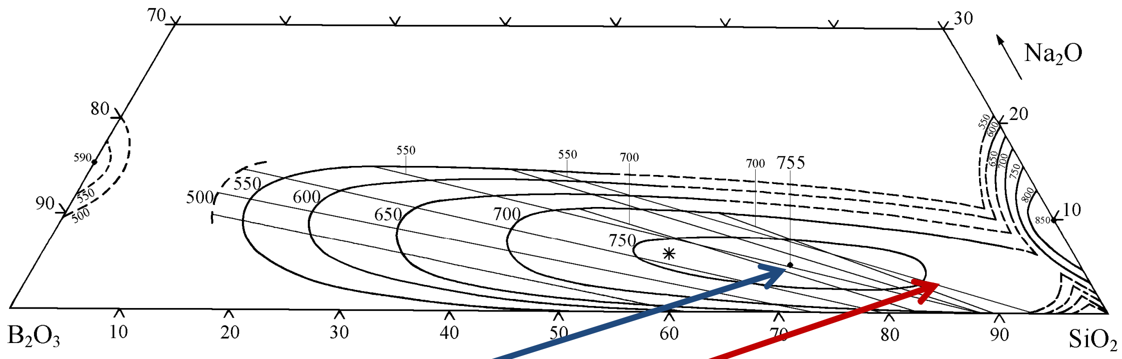


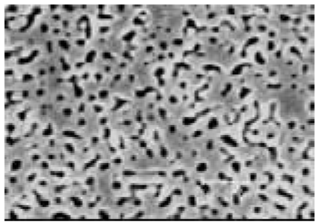
Conclusion/discussion: which thermodynamic model should be used?

Phase separation in glass: SiO_2-B_2O_3-Na_2O system

Phase separation below $T_{liquidus}$ has significant influence on the properties - Importance of thermal history







Glass	Oxide content, in wt% SiO_2	B_2O_3	Al_2O_3	Na_2O
Vycor® Corning code 7930	96	3	< 1	0·4
Pyrex® *Corning Code 7740*	80·6	13·0	2·3	4·0

⇒ Low thermal expansion, high thermal shock resistance

Center of immiscibility dome → Spinodal microstructure.

1) Melting @1500°C, 2) Processing at T>Tc, 3) Heating at ~600°C

⇒ ① ~96% SiO_2 + ② Na-borosilicate glass (acid soluble)

→ High-SiO_2 skeleton as porous substrate (filters, catalyst supports…) or sintered to dense glass at 1200°C (substitute for pure silica).

Close to edge of immiscibility dome

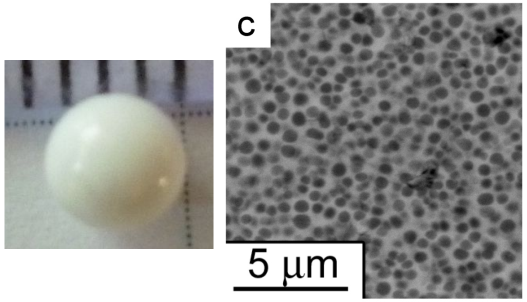
→ 'Nucleation and growth' morphology

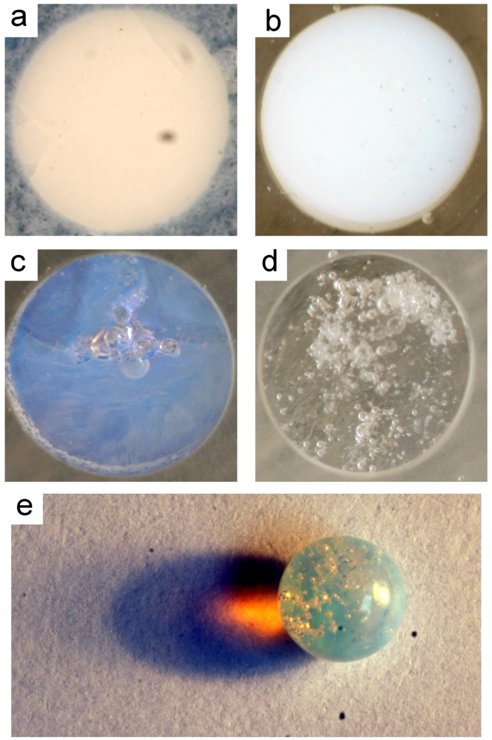
Rapid cooling → nm scale Na-B droplets in SiO_2 matrix.

⇒ Low T process, low CTE and droplet microstructure which ensures chemical durability.

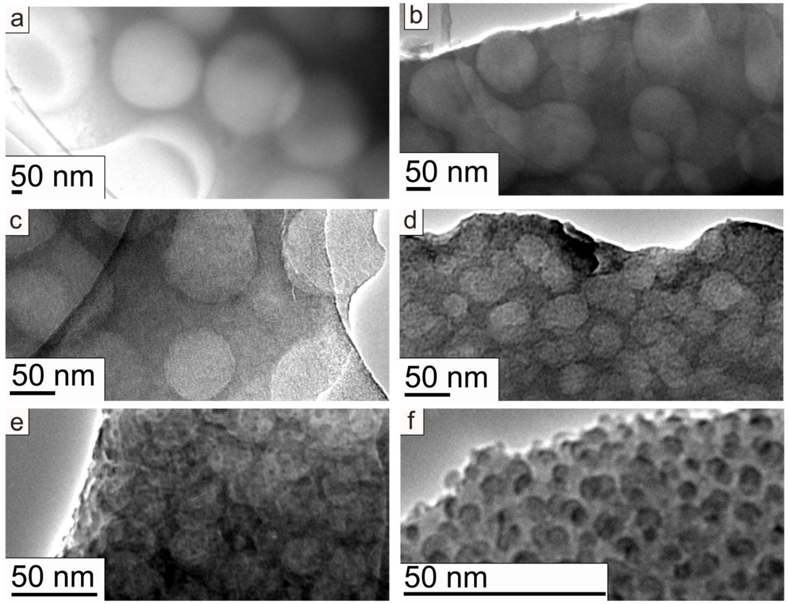
Phase separation in glass: SiO_2-Al_2O_3-CaO system

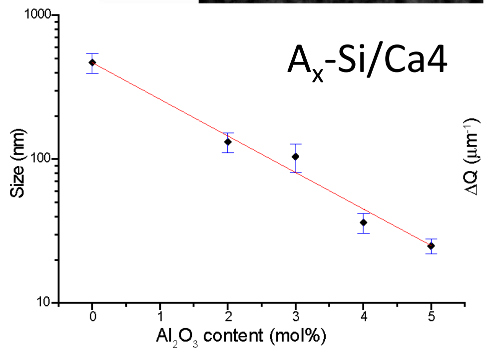
Nanostructured glasses with controlled nanodomain sizes by Al_2O_3 addition in phase-separated Ca silicates

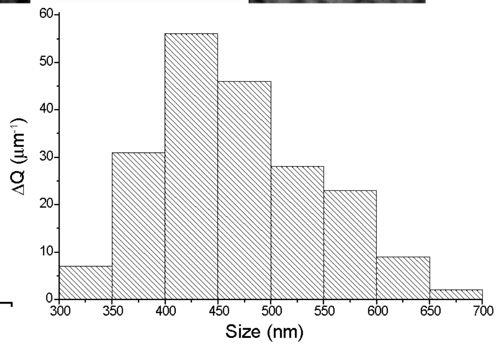




Martel, ***J. Phys. Chem. C***, 2011







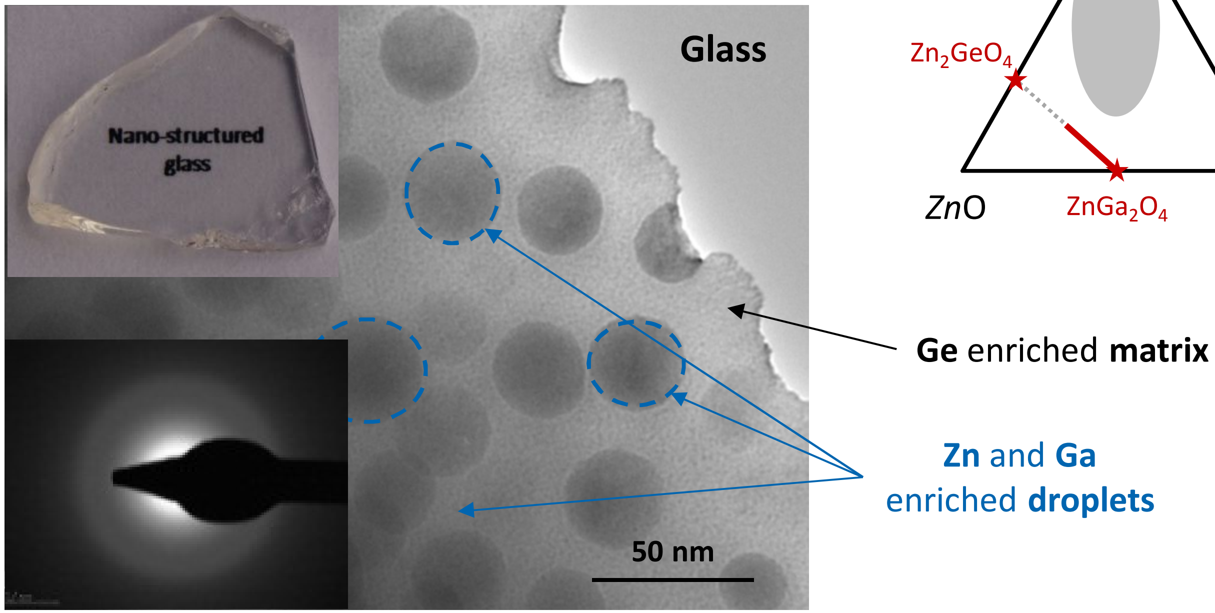
Extension of the range of immiscibility as compared to previous studies

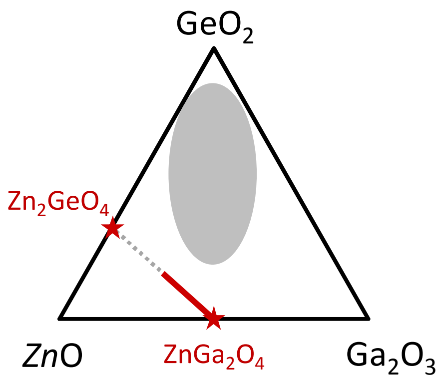
⇒ The definition of the limits of the immiscibility domain strongly depends on the probe used to study phase separation!

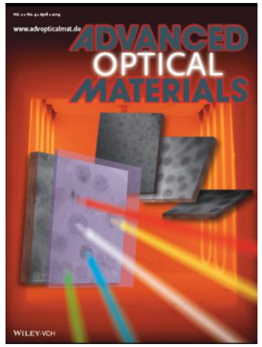
Phase separation in glass: GeO_2-ZnO-Ga_2O_3 system

Glass synthesis: Conventional melt-quenching process (melting @ 1300-1400°C - Pt crucible)

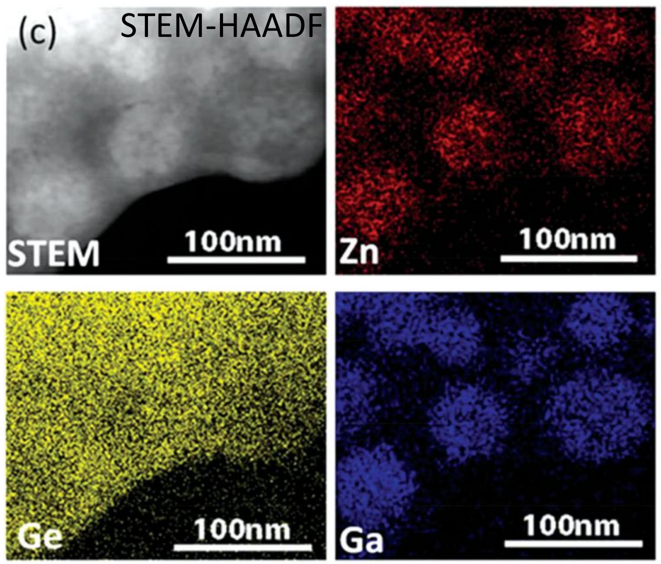
$80GeO_2$ –$10ZnO$–$10Ga_2O_3$ (+$2.5Na_2O$)







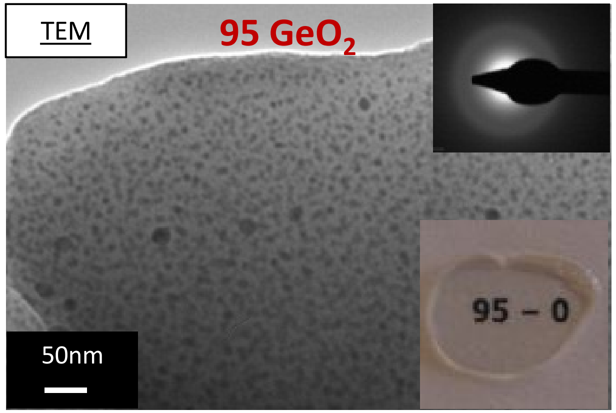
Chenu, ***Advanced Optical Materials***, 2013

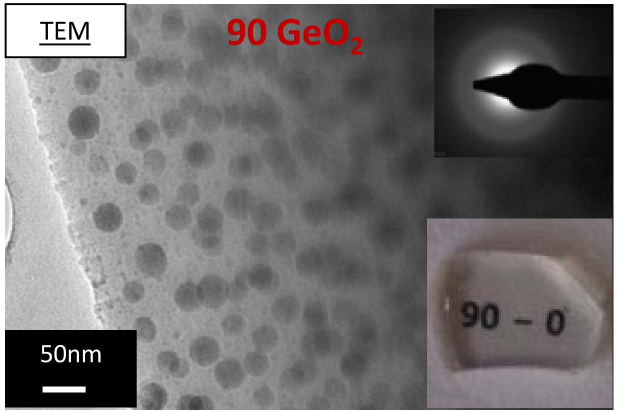


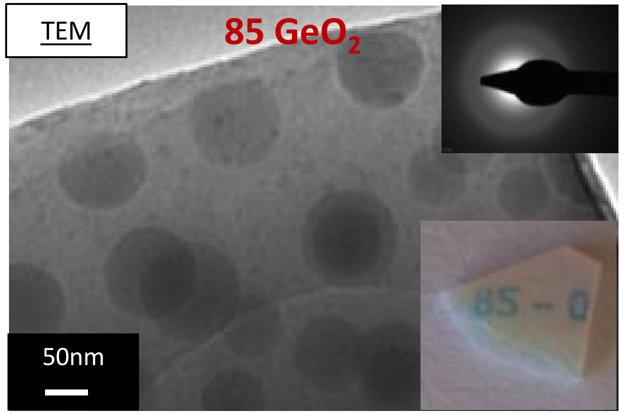
- Nanoscale "Nucleation and growth" phase separation
- Homogenous distribution
- High transparency

Phase separation in glass: GeO_2-ZnO-Ga_2O_3 system

❖ **(100-x-y) GeO_2 – x ZnO – y Ga_2O_3 glass compositions**

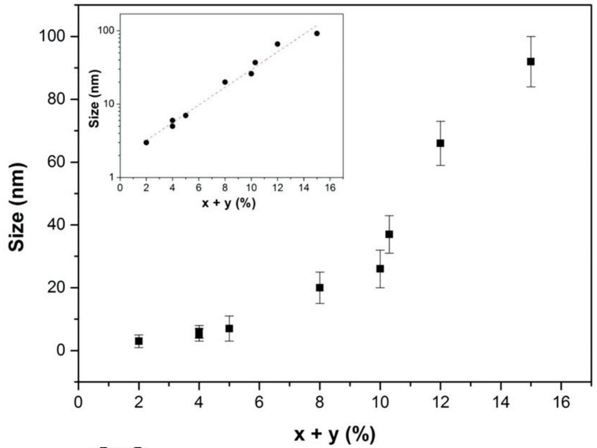


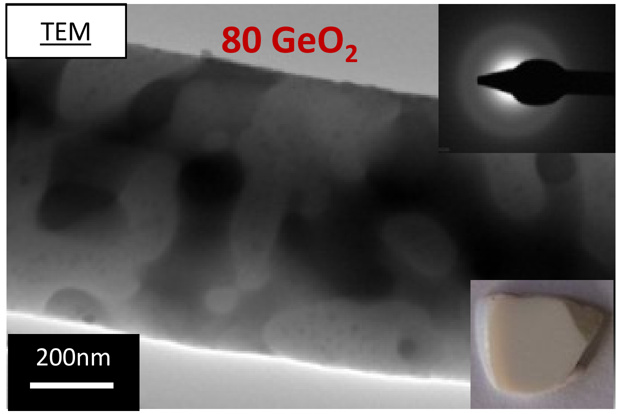


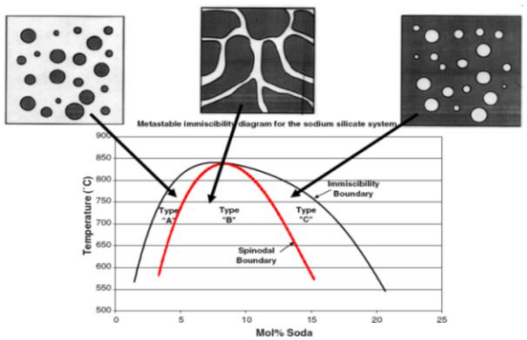


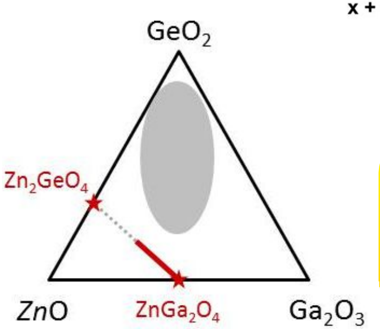
Composition effect:

- ✓ Dark spherical droplets
- ✓ Transparency evolution
- ✓ Droplet size increases with ZnO and Ga_2O_3 content







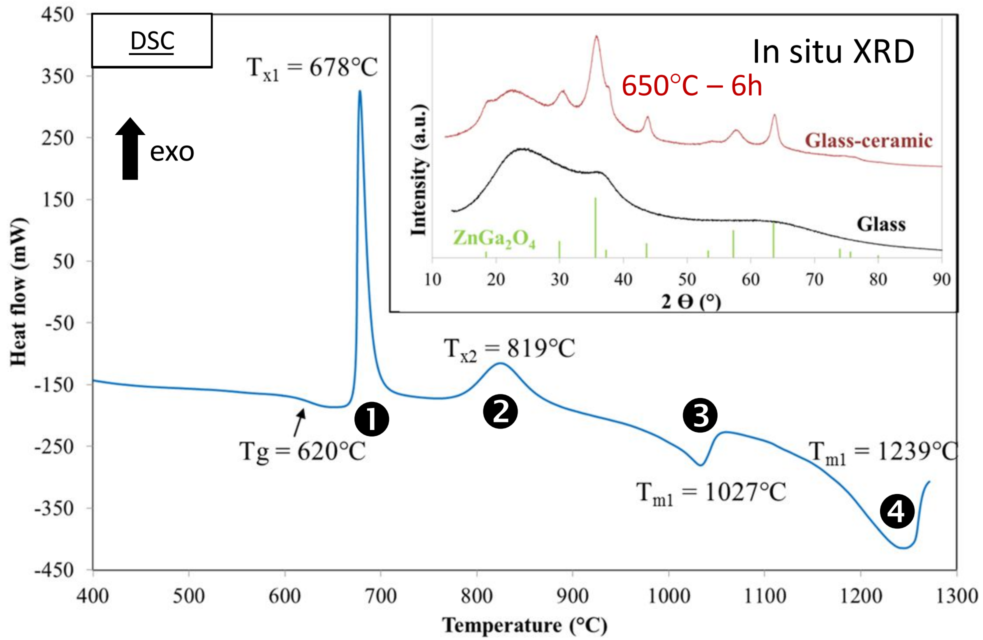


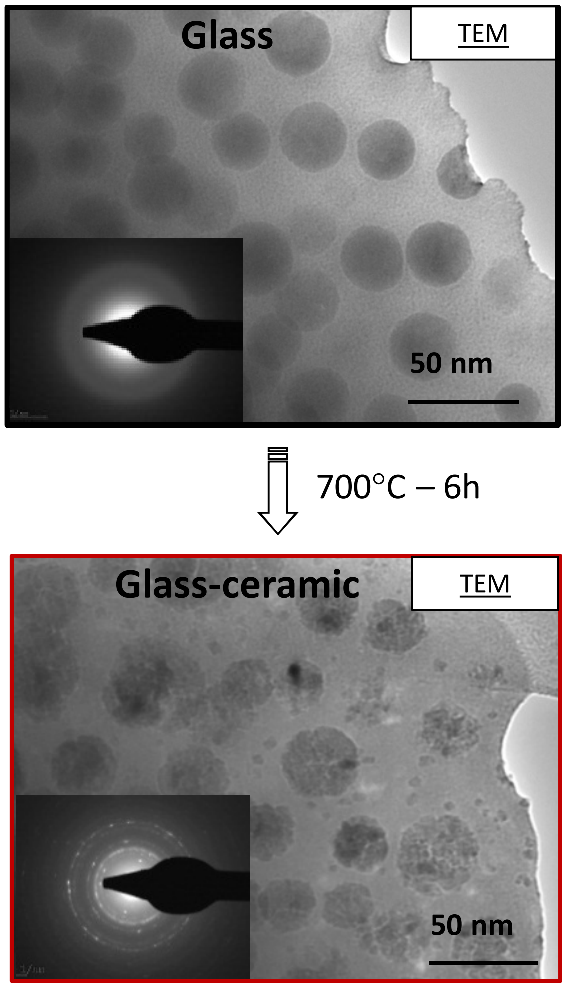
Size dependence versus glass composition

→ **Control of the phase separation**

Phase separation in glass: GeO_2-ZnO-Ga_2O_3 system

10ZnO - 10Ga_2O_3 - 80GeO_2 + 2.5Na_2O glass composition





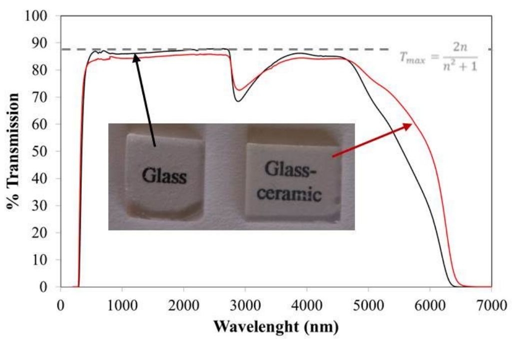
❶ $ZnGa_2O_4$ crystallization

❷ Crystallization of the glass matrix

❸ Melting of the matrix (GeO_2)

❹ Melting of the whole material

✓ **Single heat treatment** to crystallize $ZnGa_2O_4$ exclusively



Chenu, ***Advanced Optical Materials***, 2013

Nanostructure retained during crystallization

Nanocrystal growth is limited by the size of the phase separation

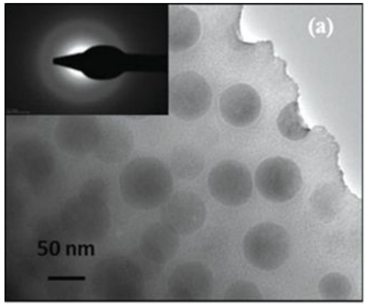
Outline

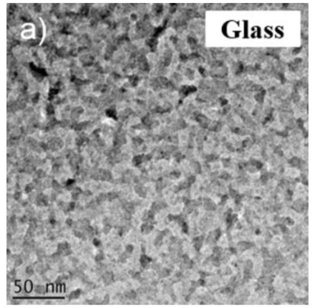
I. Phase separation in glass: applications

- SiO_2-B_2O_3-Na_2O system (Pyrex® / Vycor®)

- SiO_2-Al_2O_3-CaO system

- GeO_2-ZnO-Ga_2O_3 system





II. Glass-ceramics: crystallization processes

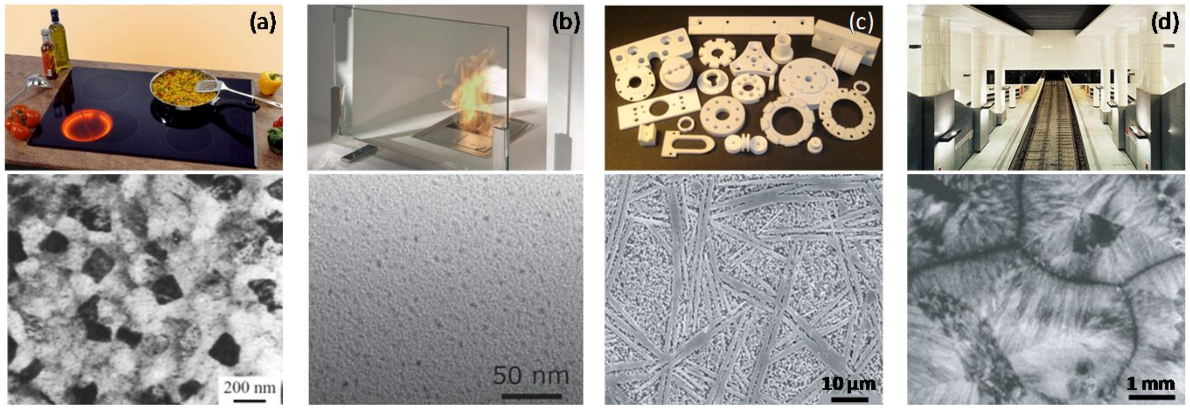
- Homogenous nucleation

- Heterogeneous nucleation

  - *Surface crystallization*

  - *From nucleation agents*

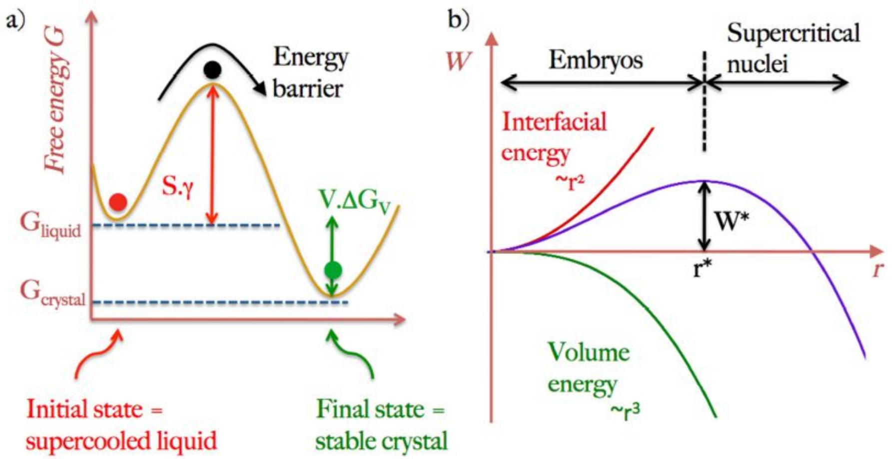
  - *From phase separated glasses*



Conclusion/discussion: which thermodynamic model should be used?

homogenous nucleation

- **Initiated from local fluctuations**
- T_{gr} (T_g / $T_{liquidus}$) < 0.58-0.6
- Low Δdensity btw G and C
- **Structural similarities** at local and medium ranges



$$W = 4\pi r^2 \gamma + \frac{4\pi}{3} r^3 \Delta G_V + \Delta G_E$$

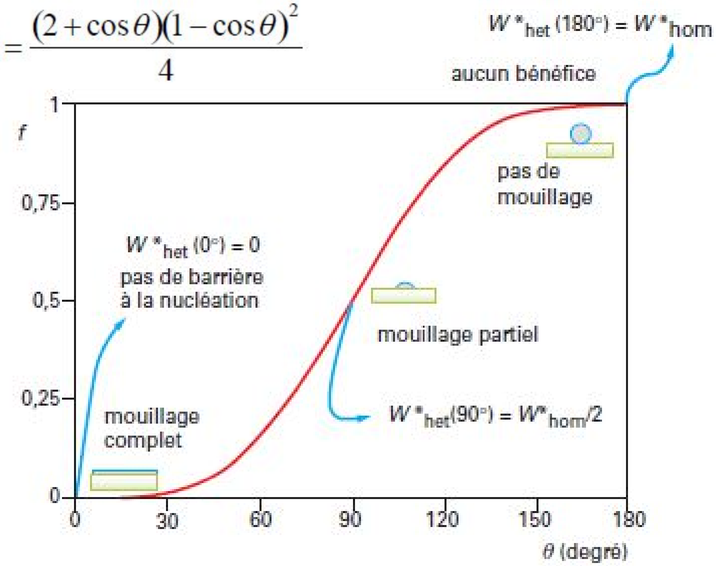
- **Only a few examples**: Li/Na_2SiO_3, $Li_2Si_2O_5$, $CaSiO_3$, $BaSi_2O_5$, $Li_2B_4O_7$, $Na_2Ca_2Si_3O_9$, $Ba_2TiSi_2O_8$,…

heterogeneous nucleation

- **Initiated from surfaces / impurities / bubbles…**
- T_{gr} (T_g / $T_{liquidus}$) > 0.58-0.6
- High Δdensity btw G and C

$$W_{het} = W_{hom} \times f(\theta)$$

with $$f(\theta) = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4}$$



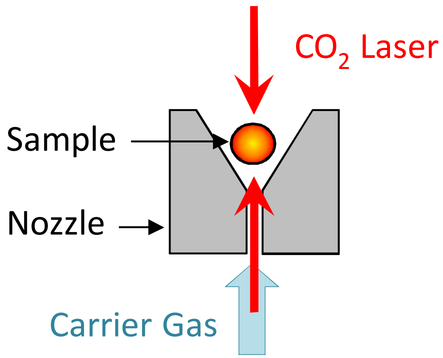
$\Rightarrow$ Crystallization from:
- **Surface**
- **Nucleation agents**
- **Phase separation**

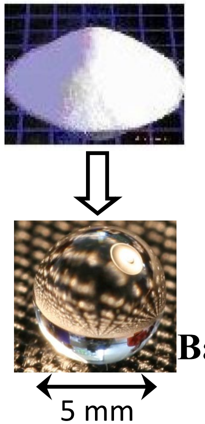
Cormier, chap. 1, **"Du verre au cristal"**, 2012

Homogenous nucleation: full crystallization from glass

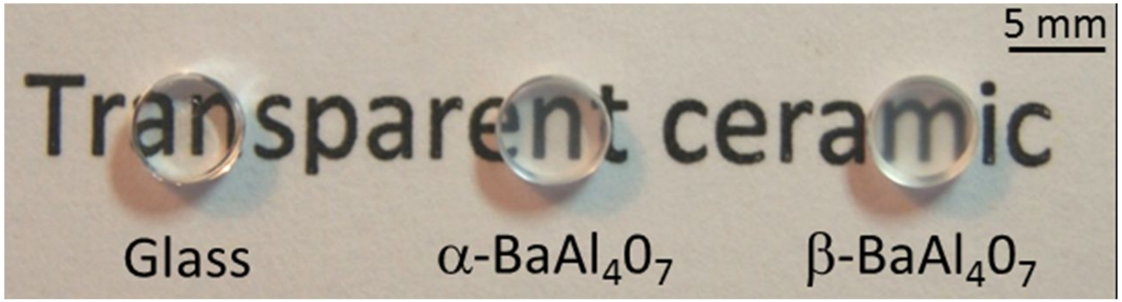
Glass synthesis:
Aerodynamic levitation / Laser heating system

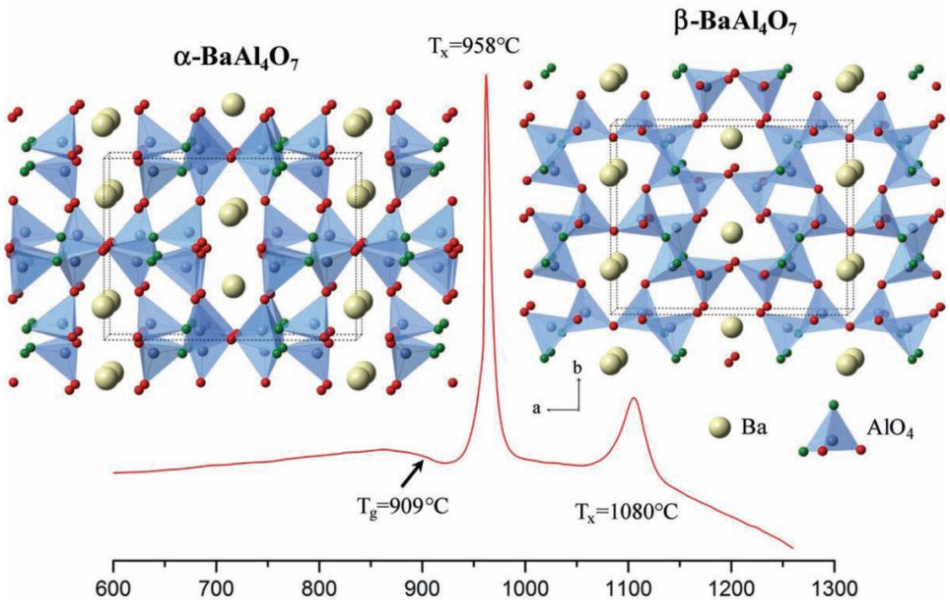
Allix, ***Advanced Materials***, 2012



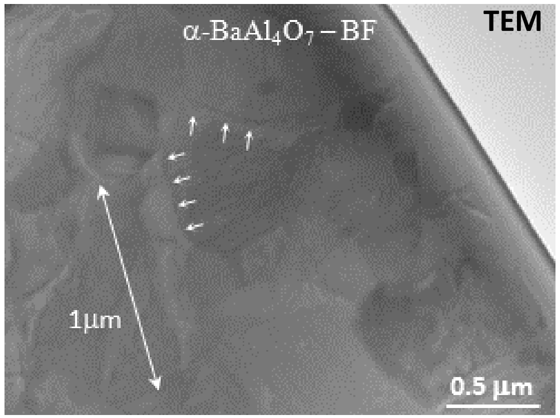


$BaAl_4O_7$ glass





Microstructure:



- **100% crystalline ⇒ Full crystallization from glass**
- **G/C density match ⇒ No porosity**
- Very thin grain boundaries

- **Presence of tri-coordinated oxygen in both G (NMR) and C !**

Heterogeneous nucleation: surface crystallization

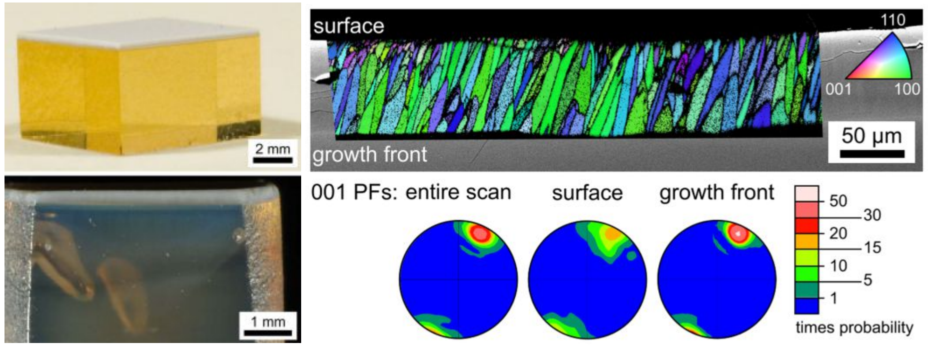
Neoparies® (NEG)
wollastonite ($CaSiO_3$)

Random nucleation +

anisotropic growth governed by

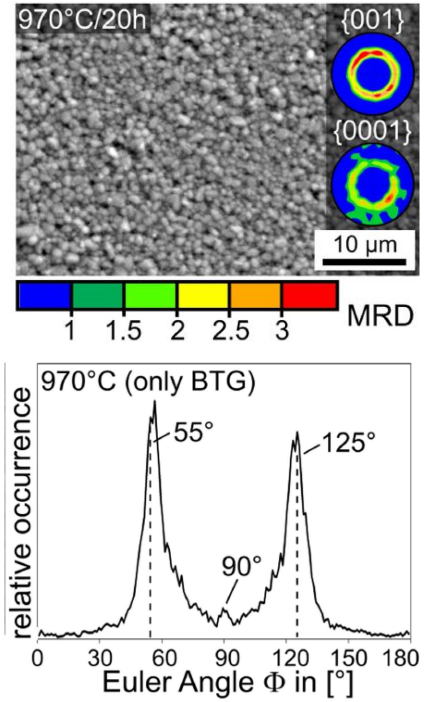
interface reactions,

heat and mass transfers?



Experiments show that surface crystallization processes are complex…

There are textures preferred during nucleation and growth



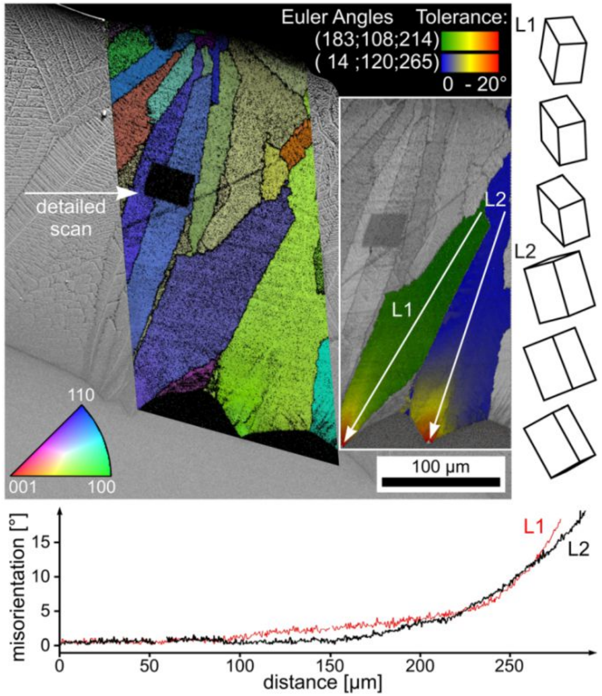
$Sr_2TiSi_2O_8$ Fresnoite

"statistically oriented nucleation in theoretical models is questionable"

Wisniewski, ***Scientific Report***, 2016

Reorientation → "dendritic growth and viscous fingering"

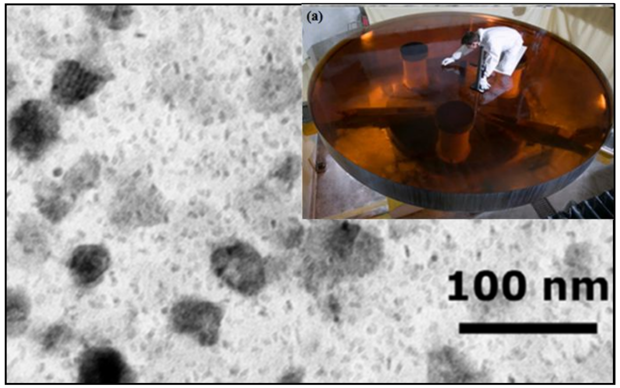
Wisniewski, ***Scientific Report***, 2013



Heterogeneous nucleation: nucleation agents

- metals (Au, Ag, Pt, Pd, etc.)
- non metals (**TiO_2, ZrO_2**, Ta_2O_5 , WO_3 , MoO_3, etc.)

LAS system (Li_2O-Al_2O_3-SiO_2) + Nucleation agents → β-quartz



Höland, **"Glass-ceramic technology"**, 2012

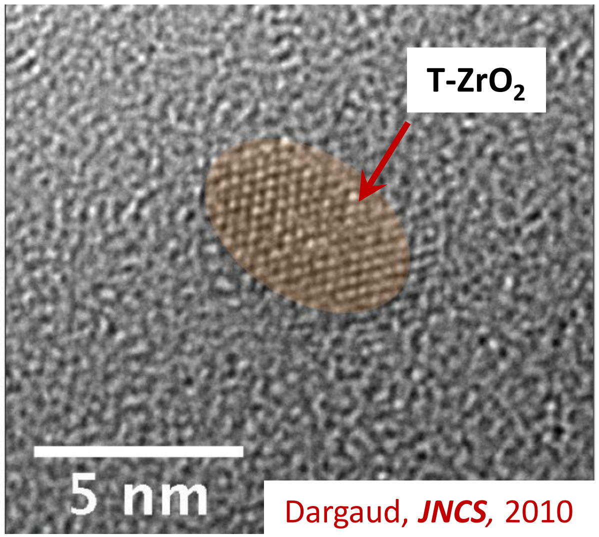
Strong volume nucleation which can be controlled

⇒ Variable crystallization rate (few % - > 90 %)

⇒ Control of the crystal size (< 100nm)

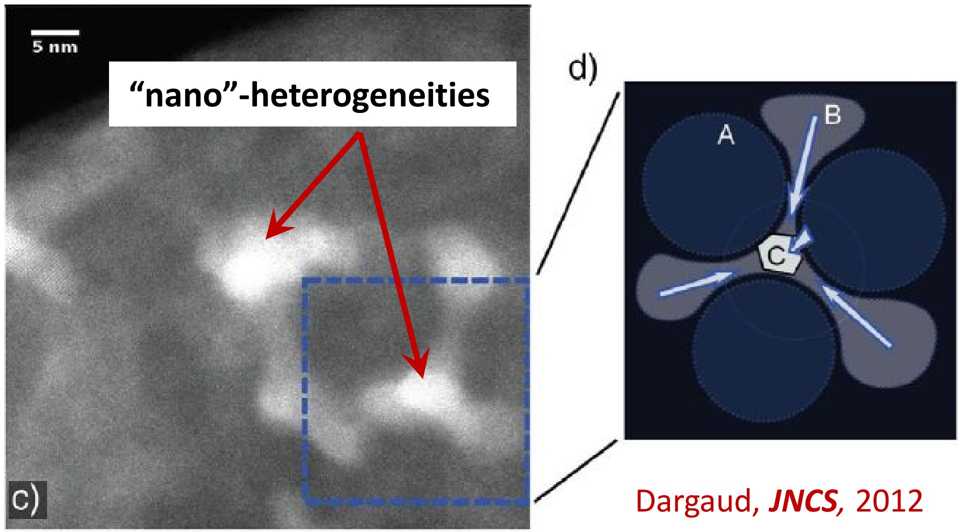
⇒
- **Low CTE GC** (CTE of the crystalline phase <0)
- **Transparency** (crystals < 70 nm)
- **Enhanced mechanical properties**

First crystallization steps:



Dargaud, ***JNCS***, 2010

Non spherical first nucleus



Dargaud, ***JNCS***, 2012

Non homogeneity of the annealed glass

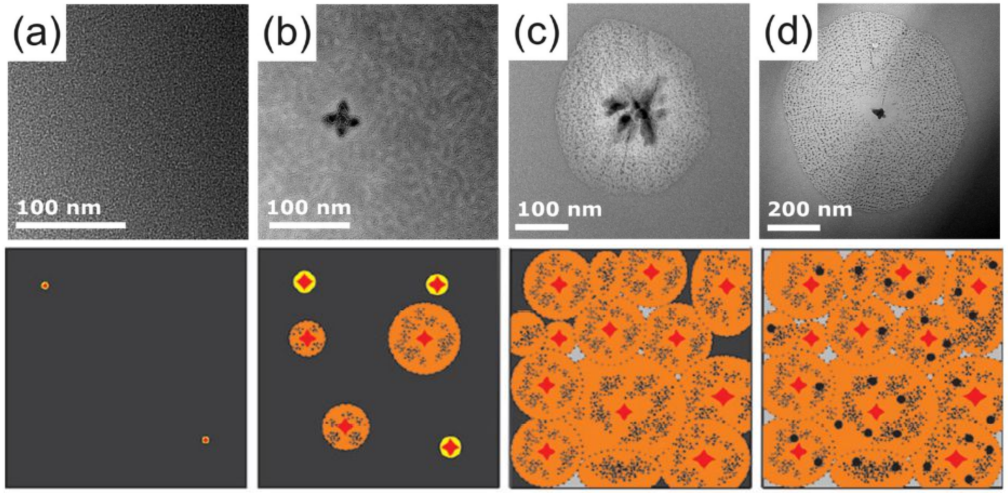
Heterogeneous nucleation: nucleation agents

Temporal evolution of crystallization

MAS system + ZrO_2 glass

$\blacklozenge$ ZrO_2 • $MgAl_2O_4$/ $Mg_2Al_4Si_5O_{18}$
ZrO_2

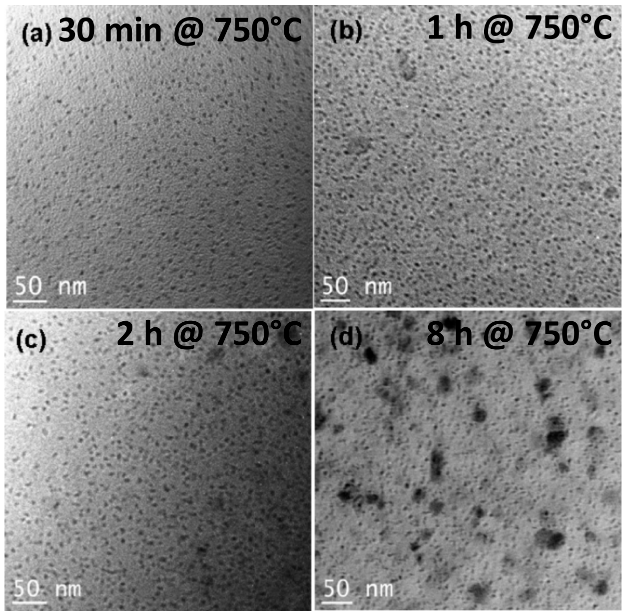
base glass
remnant glass (Zr free)
quartz solid solution
Zr- depleted glass

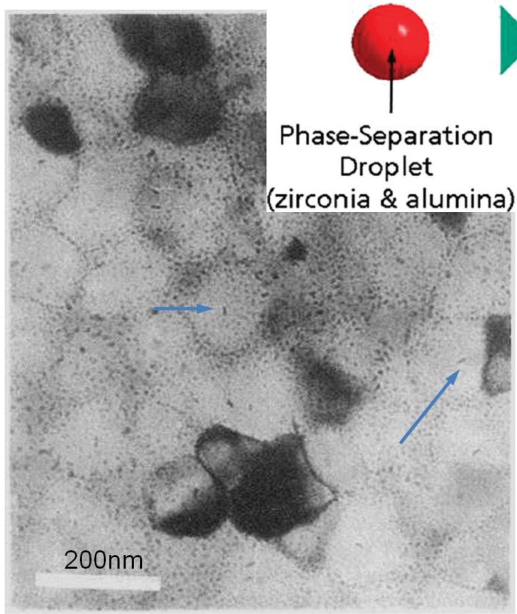


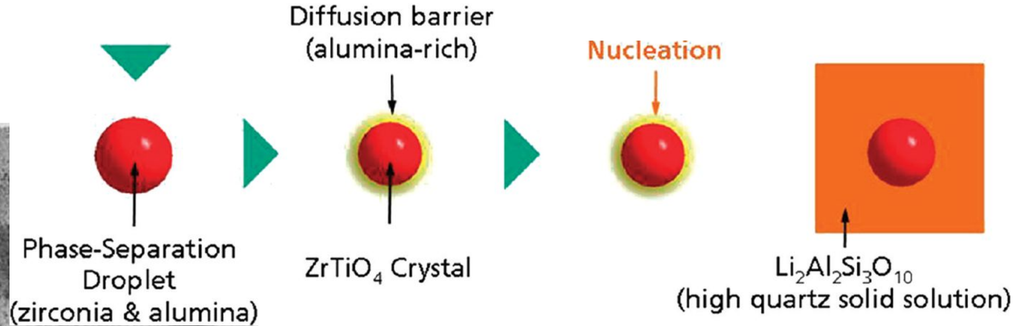
Bhattacharyya, ***Cryst. Growth Des.**, 2010 ;* Maier, ***JACerS**, 1987*

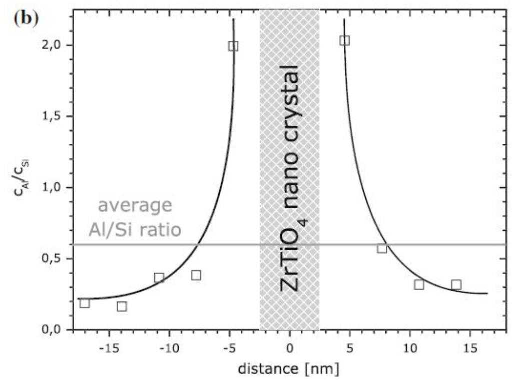
Höche, ***Cryst. Growth Des.***, 2012 ; Patzig, ***Cryst. Growth Des.**, 2012*

LAS system (Li_2O-Al_2O_3-SiO_2) + TiO_2, ZrO_2



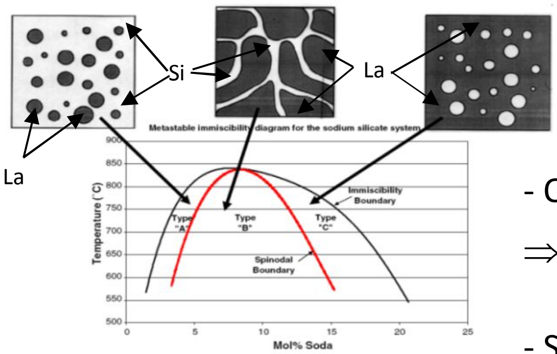






Heterogeneous nucleation: phase separated glasses

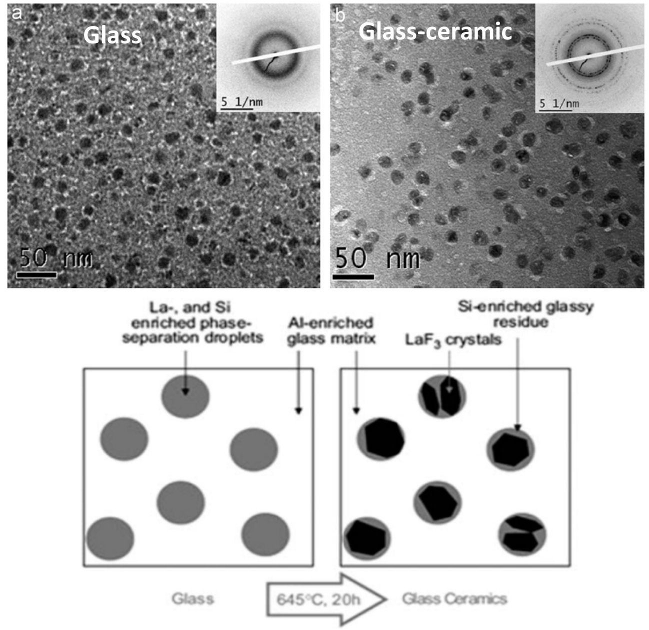
❖ **Control of phase separation ; Na_2O-Al_2O_3-SiO_2-LaF_3 system**



- Oxide / fluoride phase separation

⇒ Fluoride nanocrystals in oxide matrix

- Segregation of dopants (RE) in nanocrystals

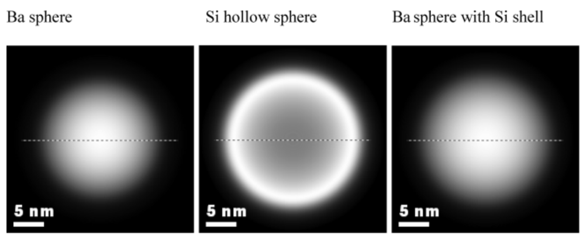


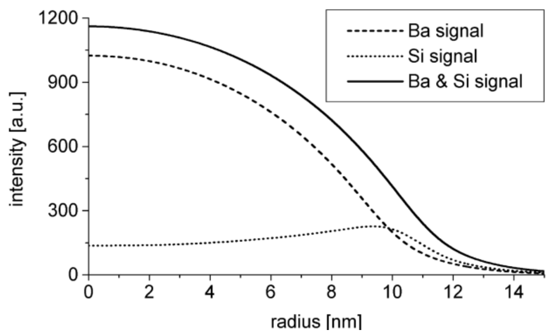
*Dejneka, **JNCS**, 1998 ; De Pablos, **Internat. Mat. Rev.**, 2012 ;*
*Wheaton, **JNCS**, 2007 ; Bhattacharyya, **J Cryst Growth**, 2009*

❖ **Self-Limited Growth of Nanocrystals in Glass**

$SiO_2/Al_2O_3/Na_2O/K_2O/BaF_2$ system

Bhattacharyya, **Nano Letters**, 2009

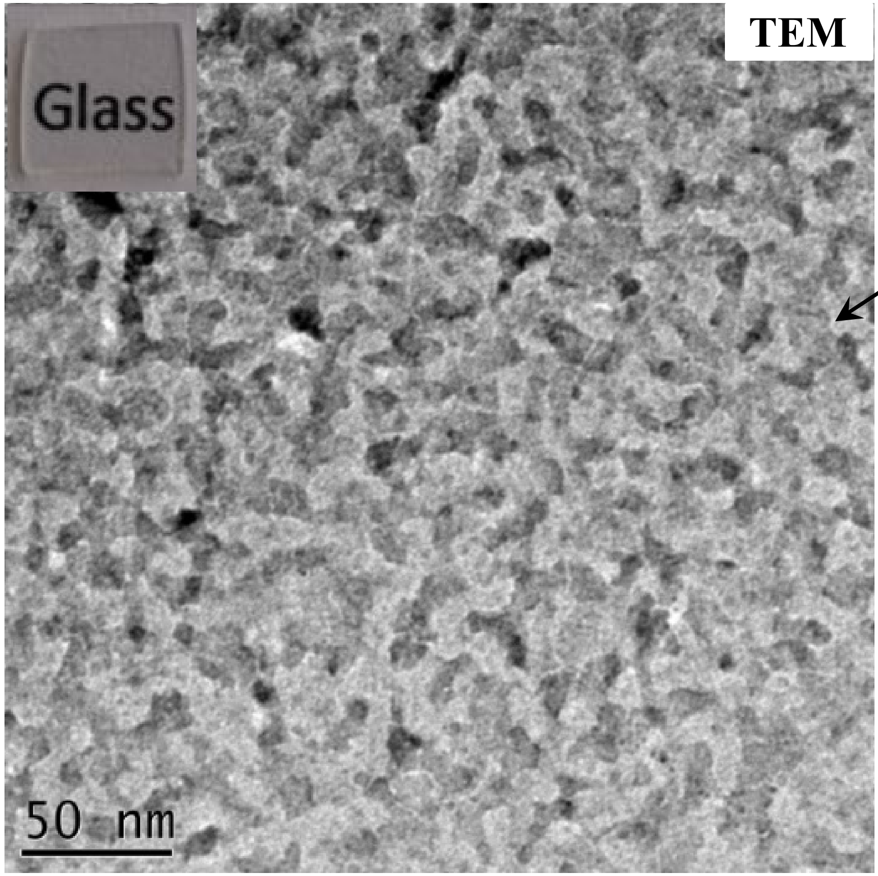


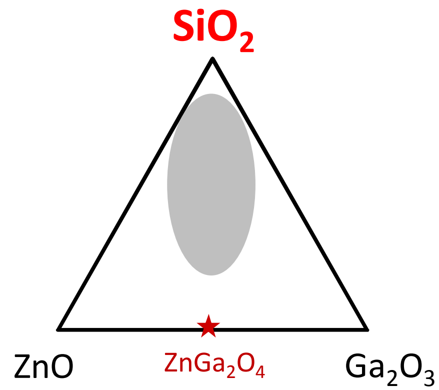


⇒ Diffusion barrier enriched in silica

⇒ No coarsening of nanocrystals

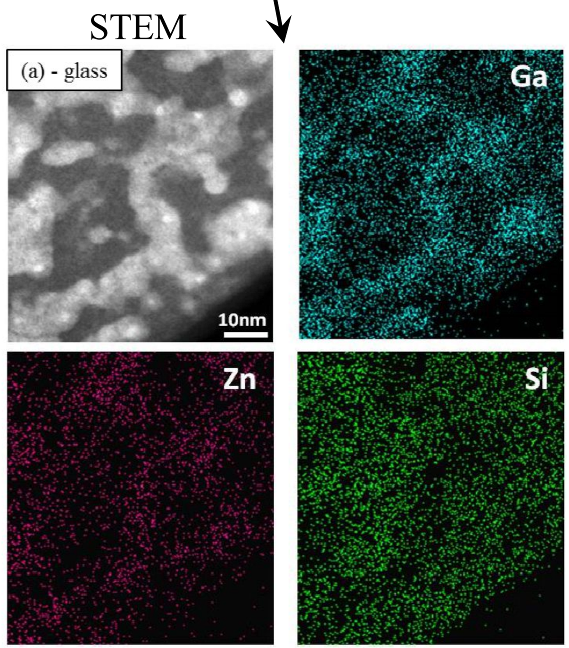
Heterogeneous nucleation: phase separated glasses





Glass composition:

$55SiO_2 – 5Na_2O – 17ZnO – 23\ Ga_2O_3$

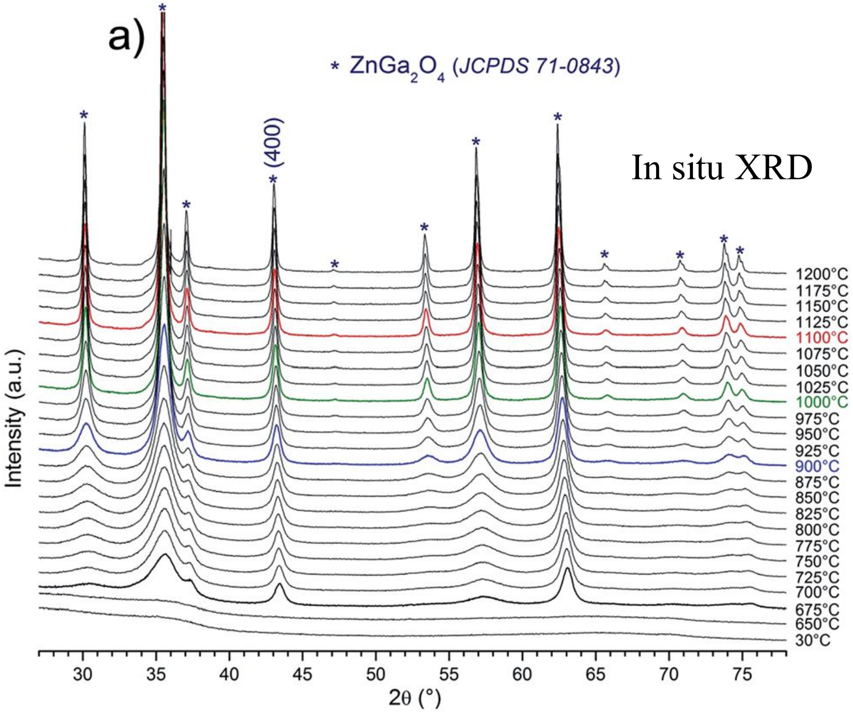


- ✓ **Transparent glass**
- ✓ **Nanometer scale spinodal separation phase**

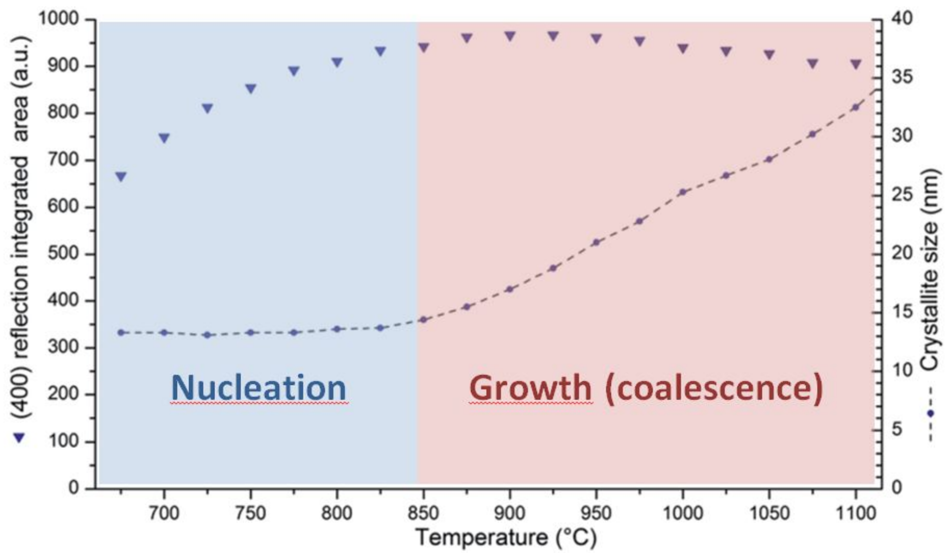
Chenu, ***J. Mater. Chem. C***, 2014

Heterogeneous nucleation: phase separated glasses

$55SiO_2 – 5Na_2O – 17ZnO – 23\ Ga_2O_3$



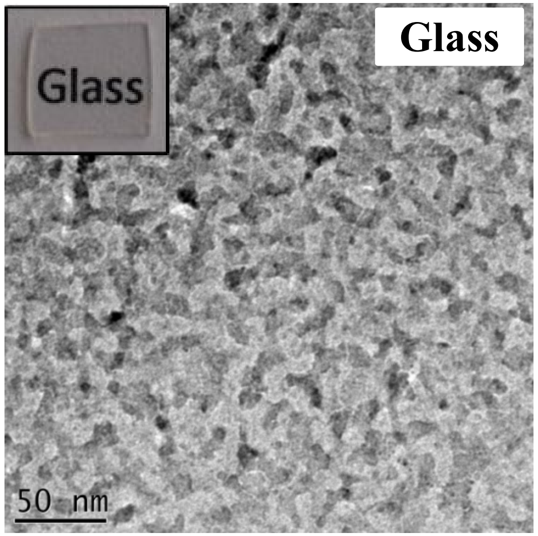
⇒

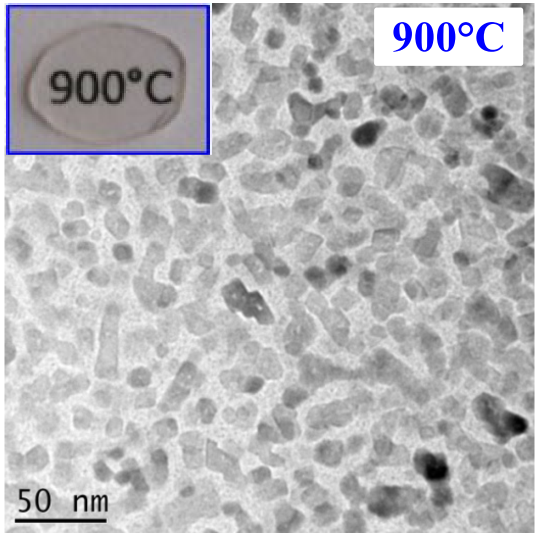


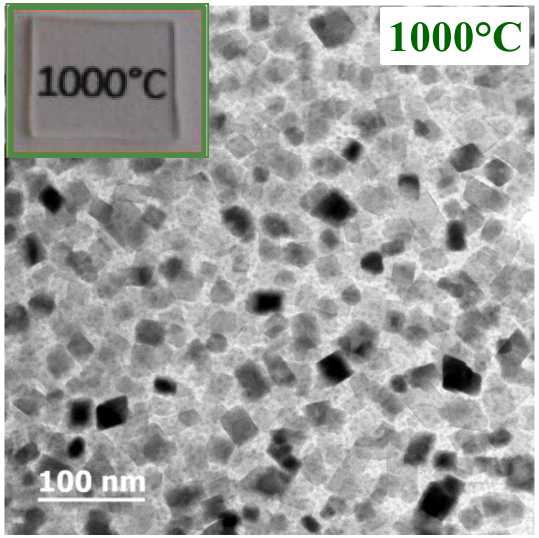
- ✓ **1st steps: ″pseudo-spinel″ crystallization (not cubic!)**
- ✓ Exclusive $ZnGa_2O_4$ crystallization
- ✓ No matrix crystallization
- ✓ **Up to 850°C: crystalline fraction increase (nucleation)**
- ✓ **Above 850°C: crystal growth by coalescence effect**

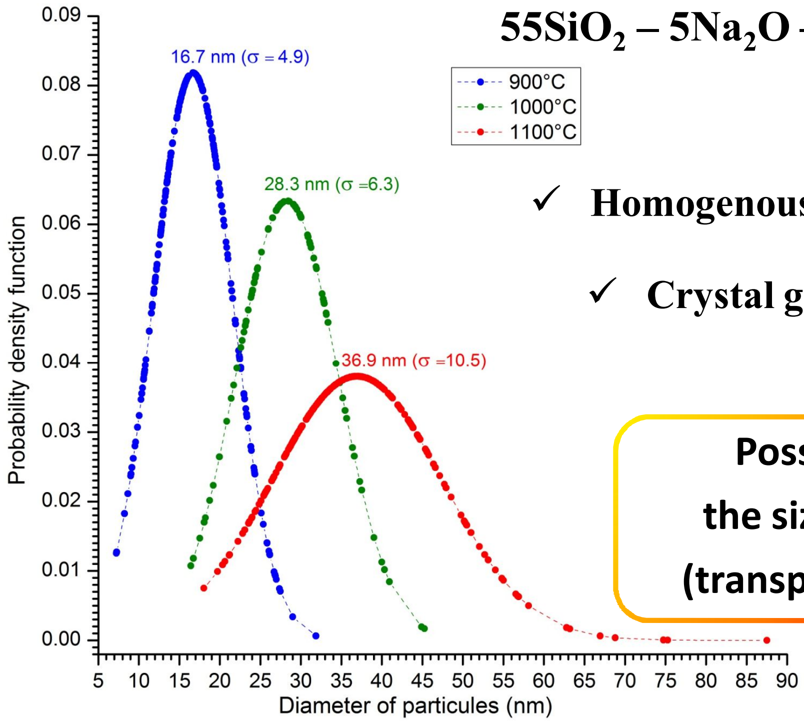
Chenu, ***J. Mater. Chem. C***, 2014

Heterogeneous nucleation: phase separated glasses





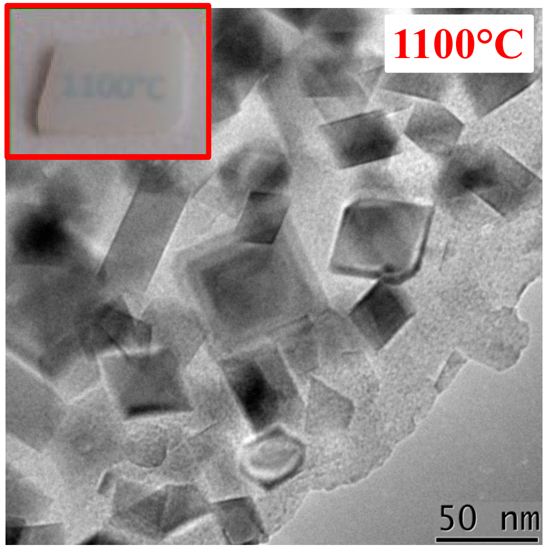




$55SiO_2 – 5Na_2O – 17ZnO – 23\ Ga_2O_3$

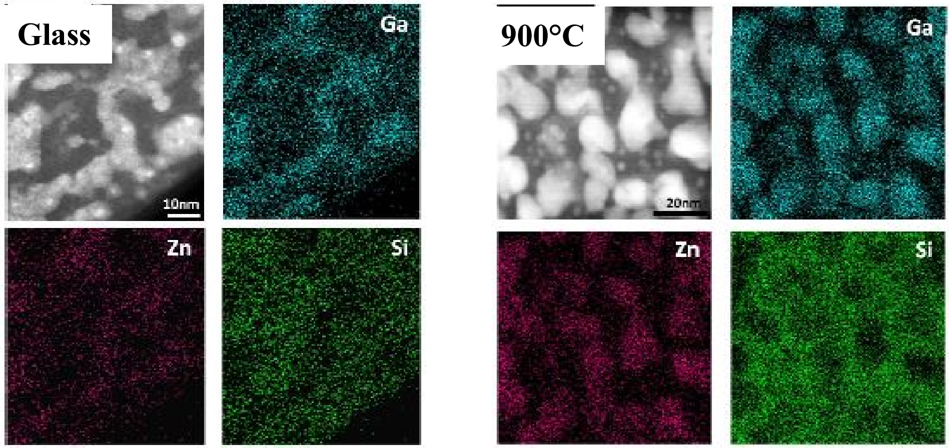
- ✓ **Homogenous size and shape of crystals**
- ✓ **Crystal growth and coalescence**

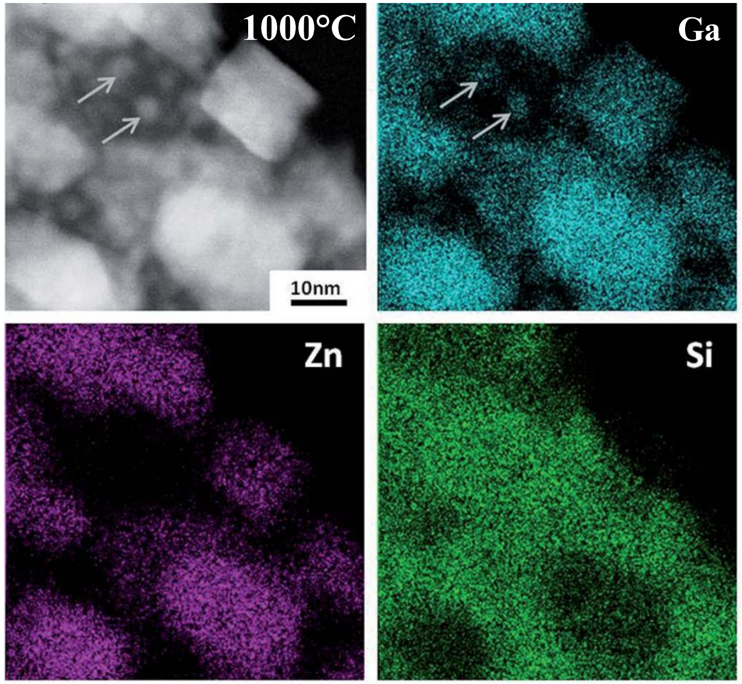
Possible to control the size of the crystals (transparency of the GC)

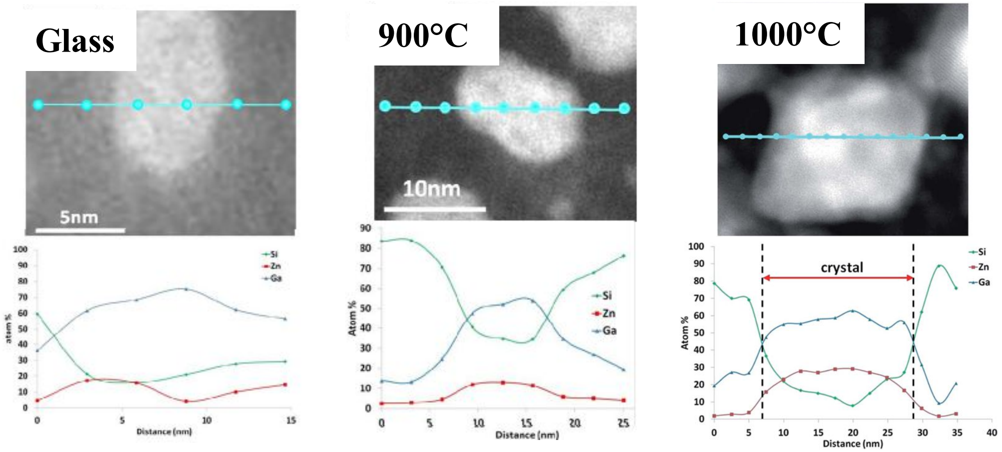


Chenu, ***J. Mater. Chem. C***, 2014

Heterogeneous nucleation: phase separated glasses



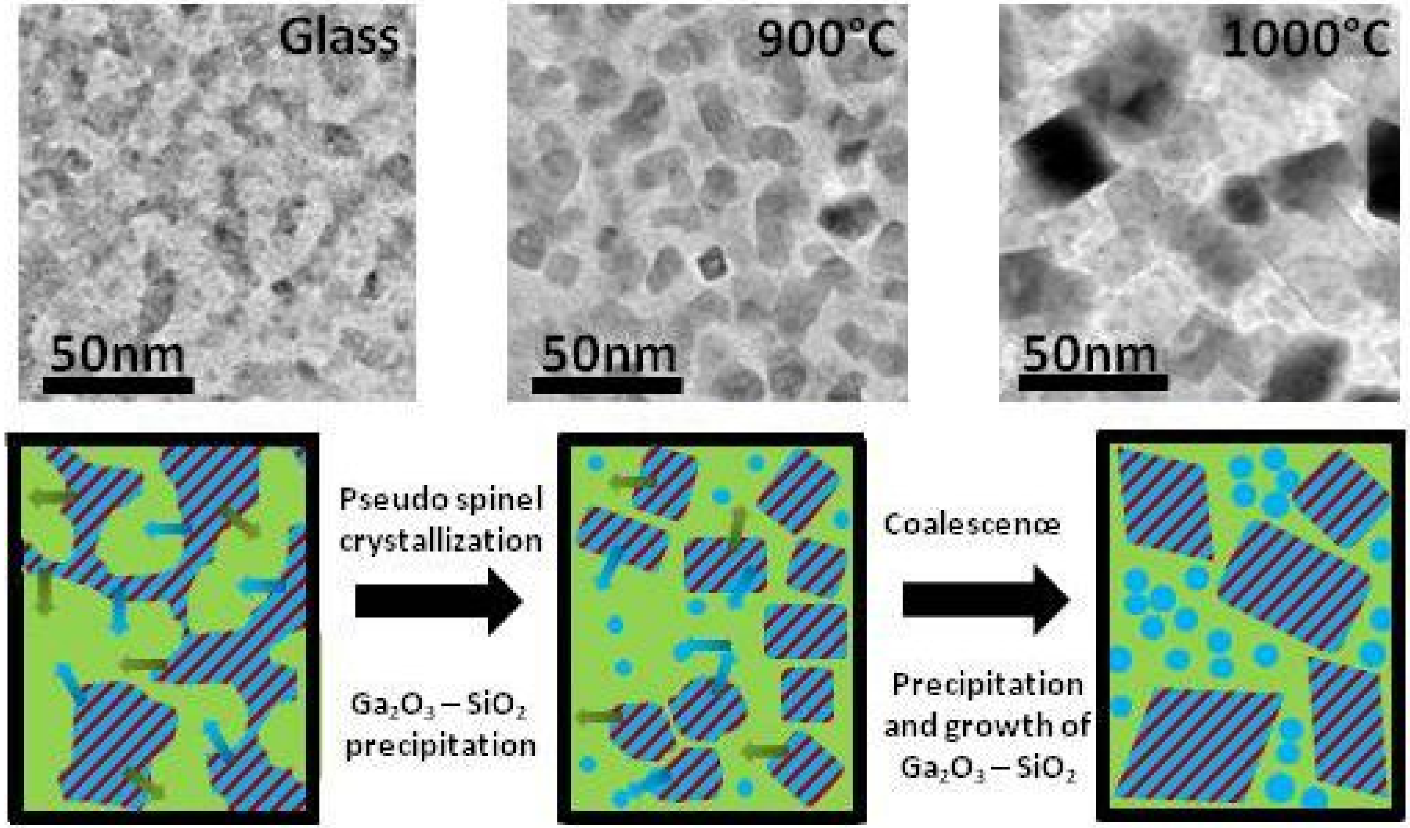




- ✓ **Ga/Zn ratio decreasing from 4 to 2**
  → Spinel formation
- ✓ **Si/Zn ratio decreases**
- ✓ **Formation of Ga rich droplets (GaO-SiO_2)**
  ((ZnO)<(Ga_2O_3))

⇒ Diffusion of Ga and Si oxides to the matrix

Heterogeneous nucleation: phase separated glasses



---------------------------- Continuous Ga and Si oxides diffusion to the matrix ------------------->

- ✓ **Nucleation**
- ✓ **Crystal growth**
- ✓ **Coalescence**

- ✓ **Zn/Ga≈4**
- ✓ **Zn/Ga≈3** (pseudo-spinel)
- ✓ **Zn/Ga≈2** ($ZnGa_2O_4$)

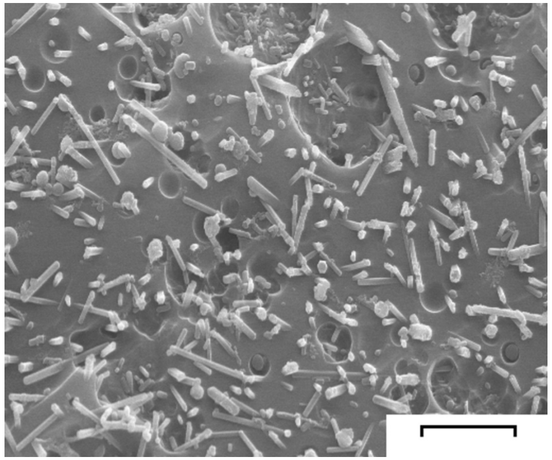
Chenu, ***J. Mater. Chem. C***, 2014

Heterogeneous nucleation: complex crystallization processes…

Double nucleation mechanism ⇒ coexistence of 2 distinct nucleation mechanisms ⇒ 2 crystalline phases

Application : glass-ceramics for dental restoration. Improvement of aesthetic and mechanical properties.

Ex: SiO_2–Al_2O_3–CaO–Na_2O–K_2O–P_2O_5–F system ⇒ **leucite-fluoroapatite glass-ceramic**



Höland, **Phil. Trans. R. Soc. A**, 2003

Surface nucleation ⇒ Leucite

Volume nucleation (phase separation) ⇒ fluoroapatite (needles)

⇒

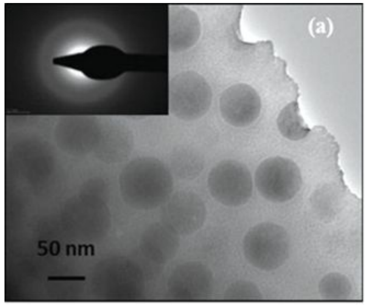
- Strong crystallization (30-40%)
- Translucency
- Opalescence
- Machinability (CAD/CAM)

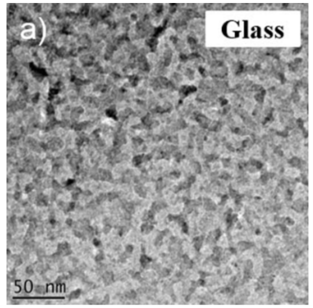
⇒ **Biomimetics** (microstructure similar to a natural tooth)

Outline

I. Phase separation in glass: applications

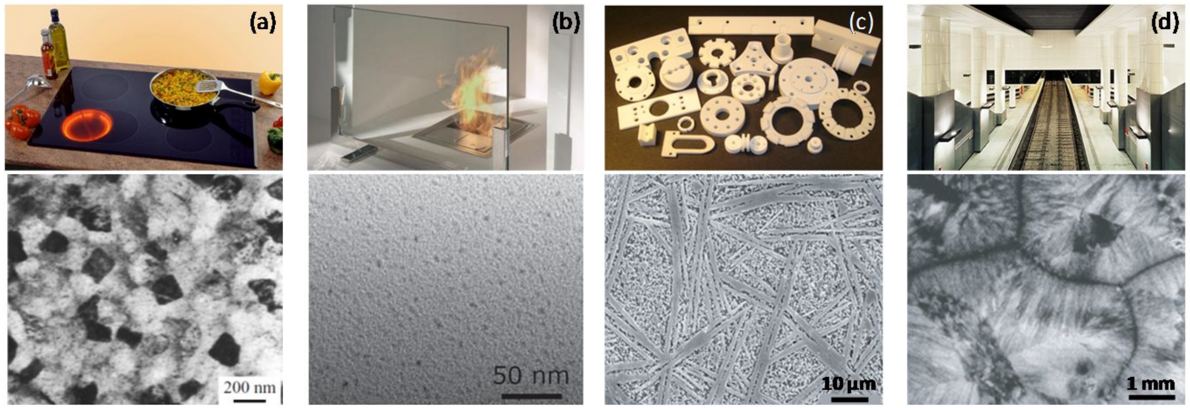
- SiO_2-B_2O_3-Na_2O system (Pyrex® / Vycor®)
- SiO_2-Al_2O_3-CaO system
- GeO_2-ZnO-Ga_2O_3 system





II. Glass-ceramics: crystallization processes

- Homogenous nucleation
- Heterogeneous nucleation
  - *Surface crystallization*
  - *From nucleation agents*
  - *From phase separated glasses*



Conclusion/discussion: which thermodynamic model should be used?

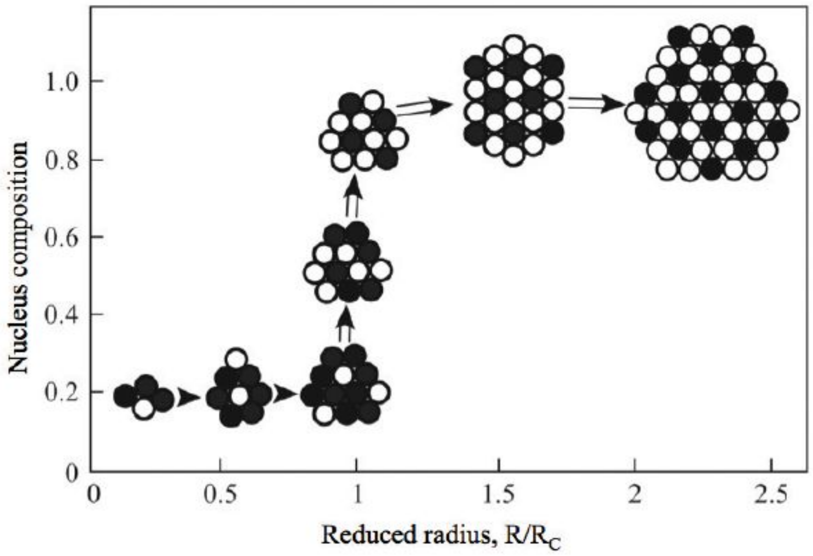
Which thermodynamic model should be used?

Phase separation and crystallization mechanisms are complex…

CNT: qualitative description only $\Rightarrow$ New theories are emerging

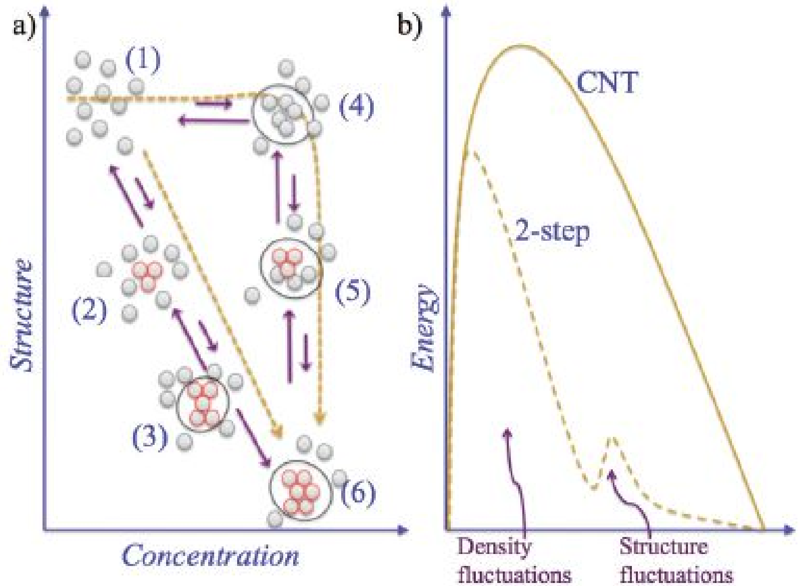
❖ General Gibbs approach

The composition evolution of the germ is taken into account



❖ Two step-model

Density and structural fluctuations are separated in time



Cormier, chap. 2, **“Du verre au cristal”**, 2012

These models remain non perfect and hardly compatible with complex systems

A general theory of nucleation still needs to be established…