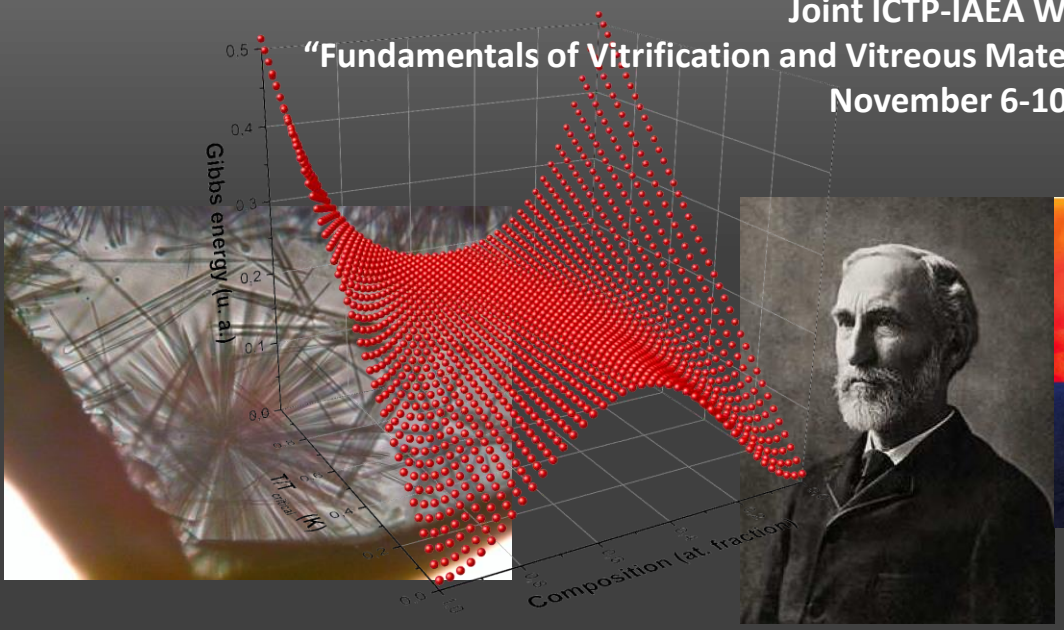
Glass, crystallization and phase separation

Sophie SCHULLER, Elise RÉGNIER, Judith FOURNIER-RENAUD, Hélène PABLO,
*Stéphane GOSSÉ, *Alain CARTALADE

DE2D/SEVT/- CEA Marcoule - *CEA Saclay

Joint ICTP-IAEA Workshop
"Fundamentals of Vitrification and Vitreous Materials for Nuclear Waste Immobilization"
November 6-10 2017



Nuclear glasses

Glass precursors

- Borosilicate
  Phosphate
- Aluminate

Nuclear wastes

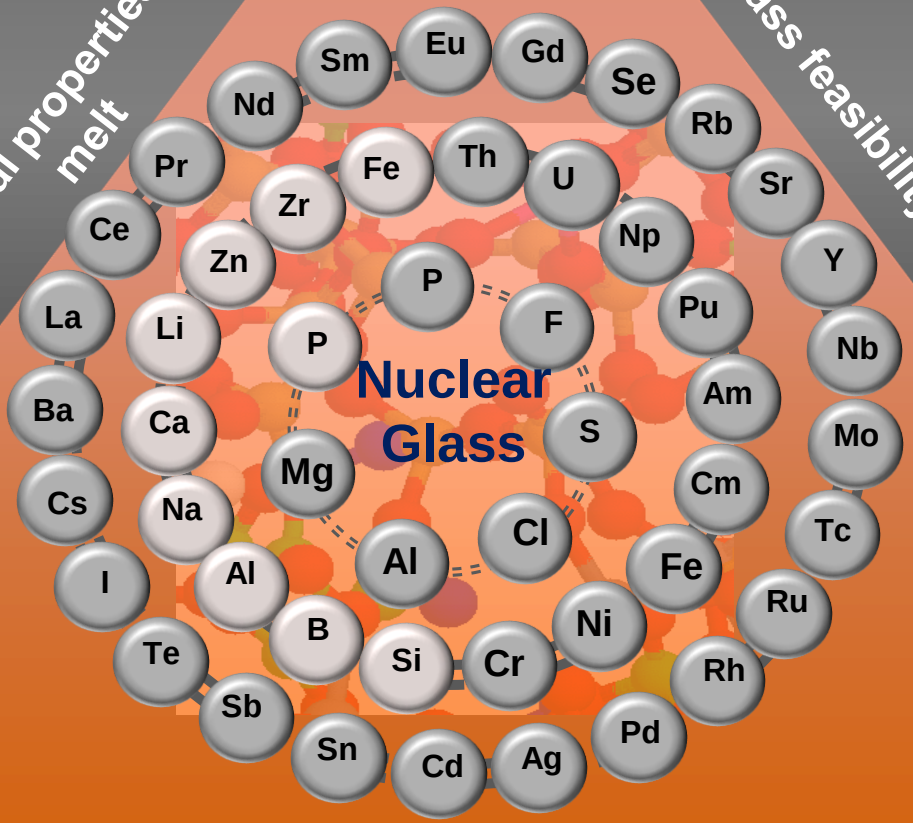
- Fission products
- Actinides
- Corrosion products

HLW (UOx, MOx, UMo), MLW (actinides, plant rinsing before decommissioning)

Physico-chemical properties of glass and melt

Loading rate

Glass feasibility



Containment properties

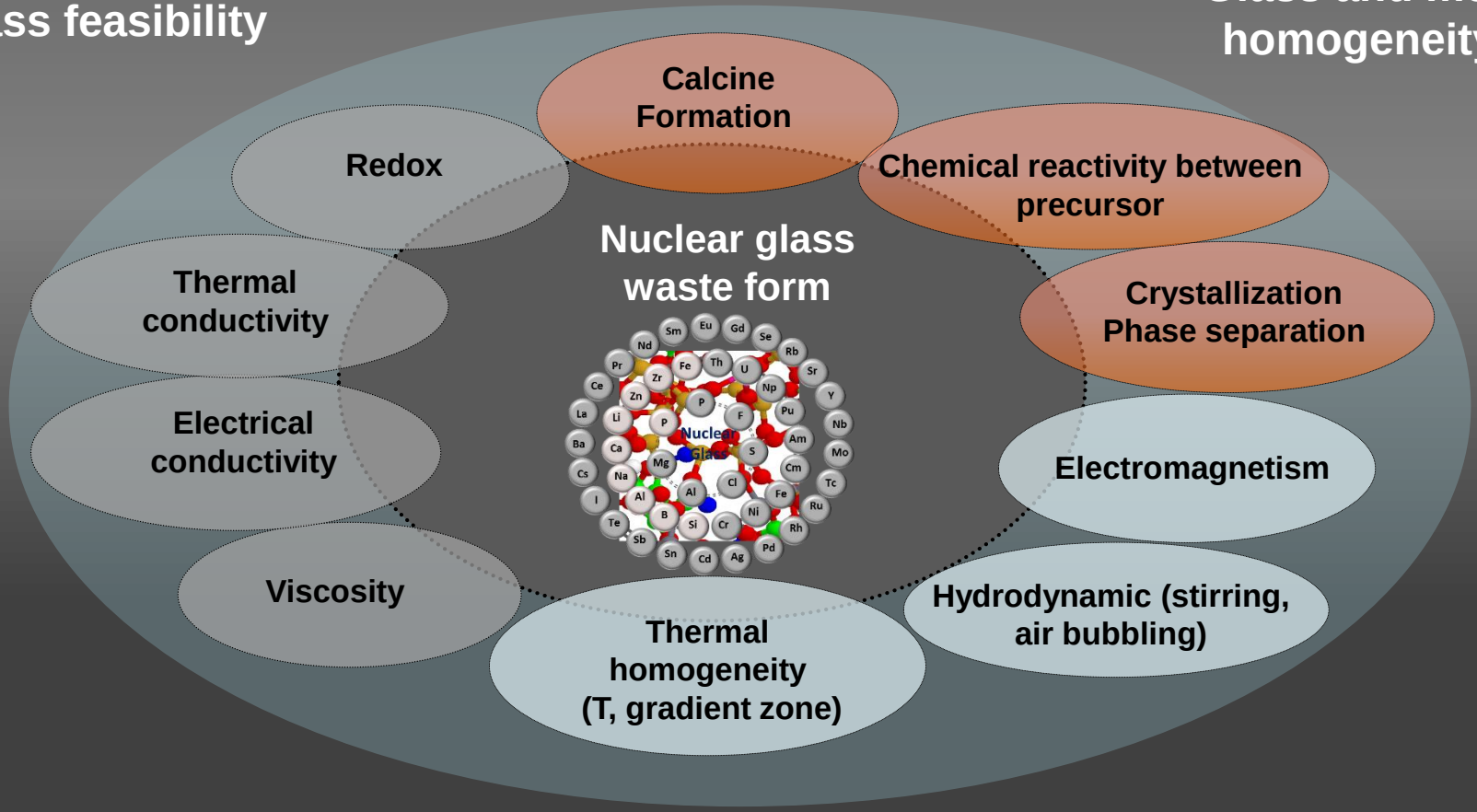
S. Gin, P. Jollivet, M. Tribet, S. Peuget, S. Schuller Radiochimica Acta
"Radionuclides containment in nuclear glasses: an overview" 2017

Finding the best matrices

Find the best compromise

Glass feasibility

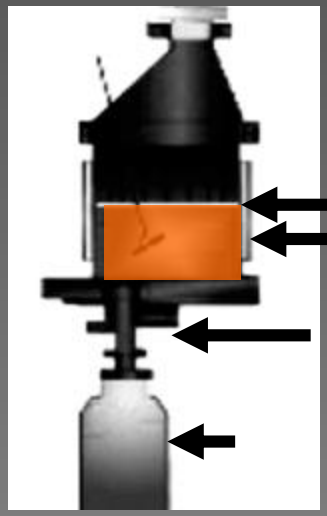
Glass and melt homogeneity



Long term behavior

Vitrification process

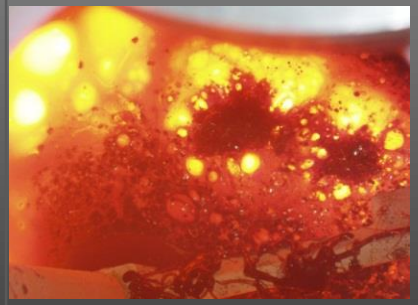
Academic research



Crystallization
Phase separation

How to control vitrification, crystallization and phase separation processes ?

During glass synthesis

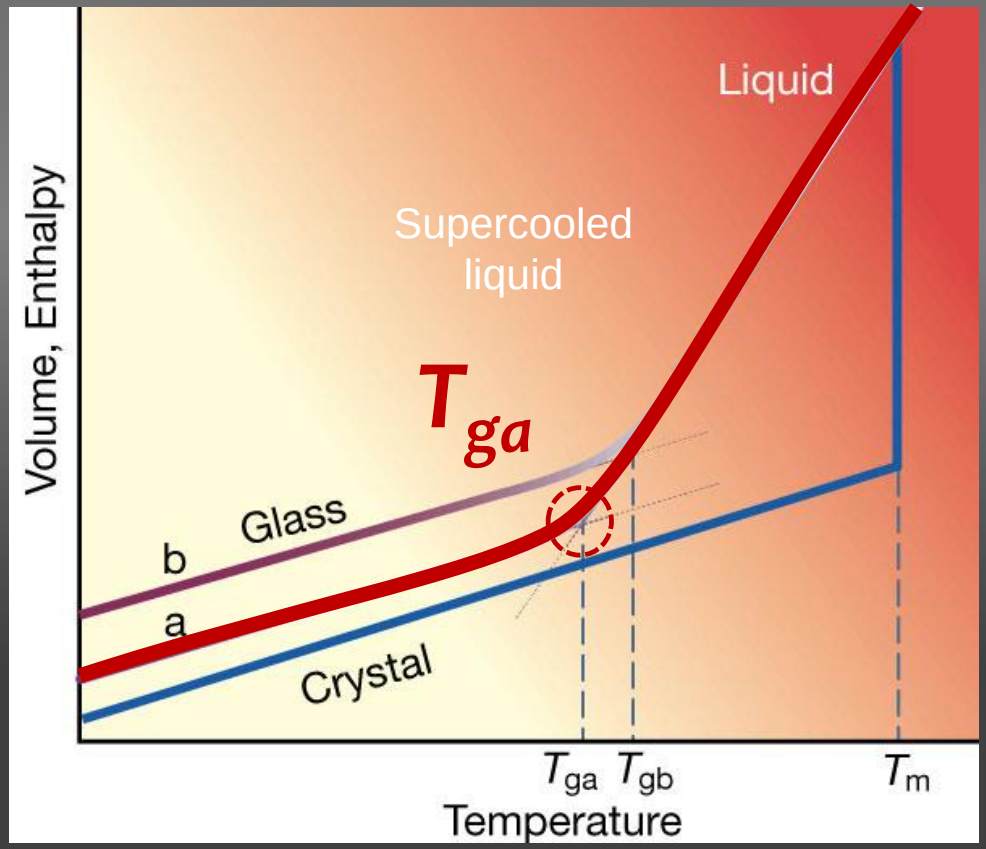
Zone 1	Zone 2	Zone 3	Zone 4
			
Glass surface	Homogenous Liquid	Surpercooled liquid	Glass
Chemical reactions	1100°C - 1200°C	Cooling	Glass stability

T

g

Time

Crystallization
Phase separation



P. G. Debenedetti , 2001

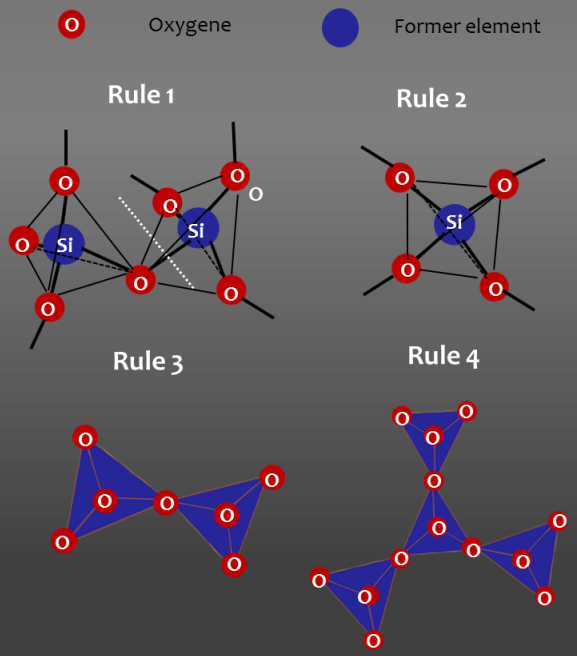
...But depending on the:

- Composition
- Structure
- Temperature
- Time

… Crystallization and phase separation are difficult to be predict

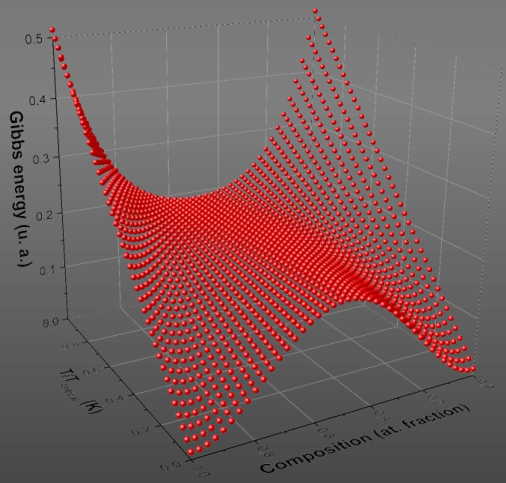
Three main approaches

Structural aspect



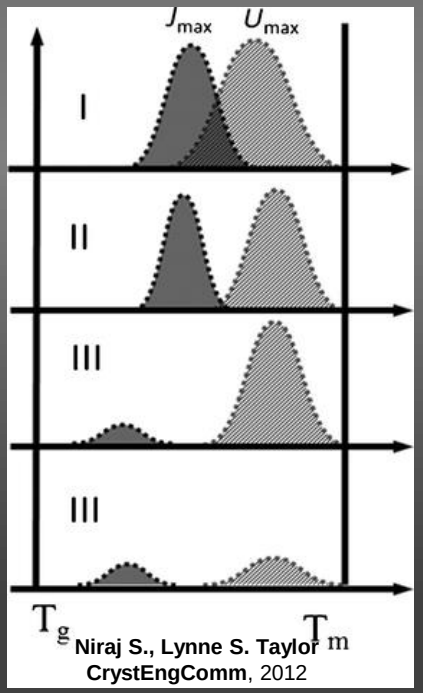
Models (Zachariasen, Dietzel, Sun Warren& Pincus, Block and Levin, McGahay, Tomozawa,…)

Thermodynamic



Thermodynamic stability (free enthalpies, entropies, temperature)

Kinetic

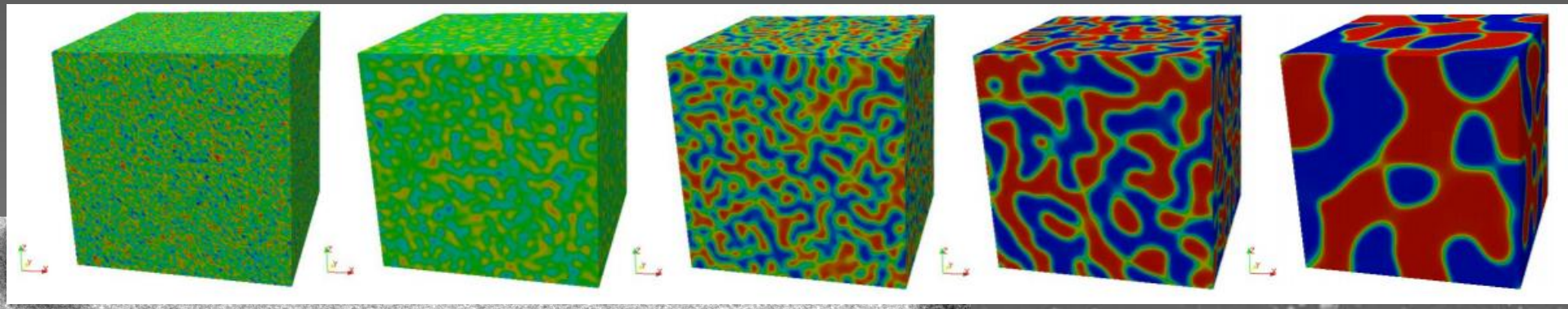


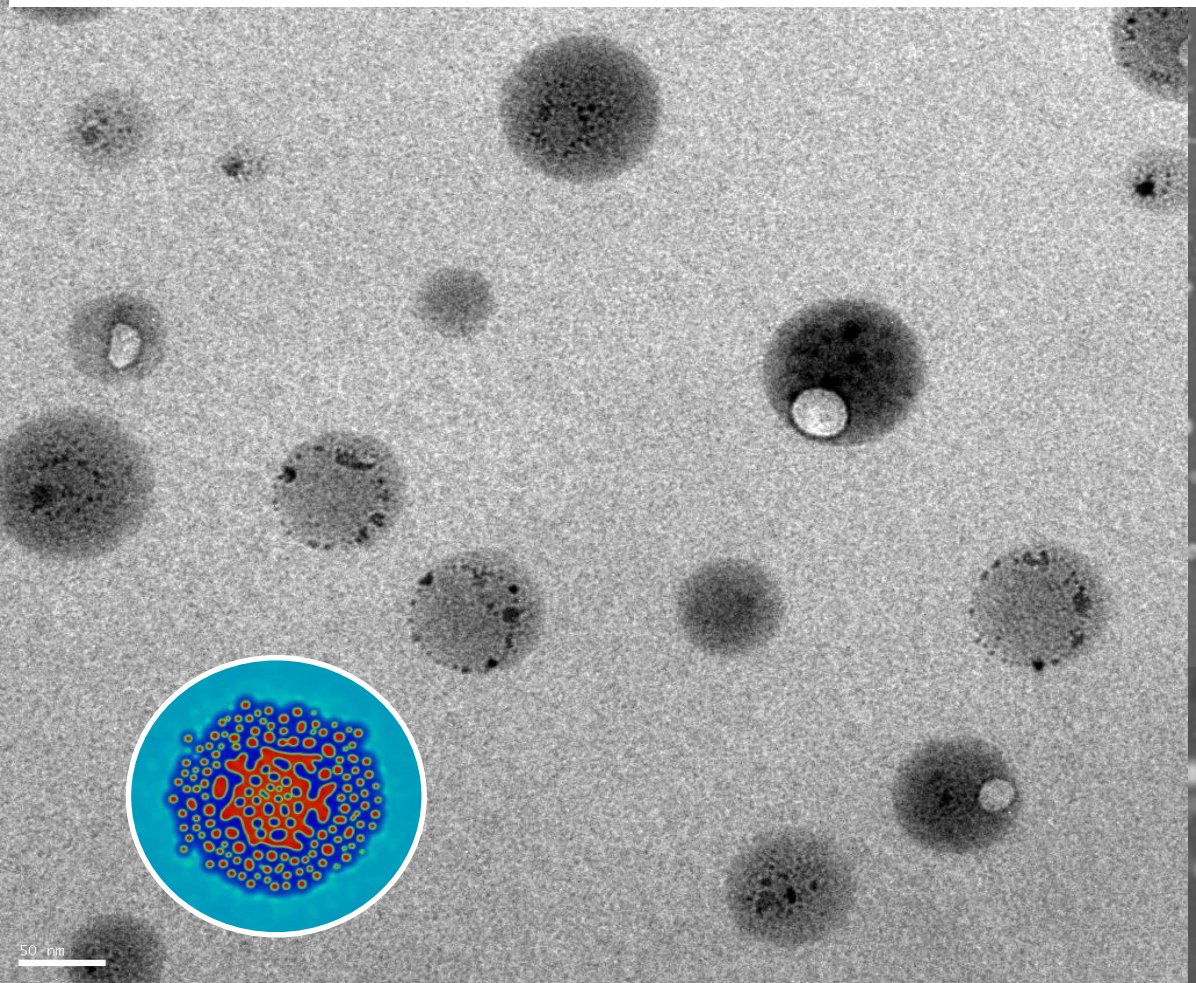
Niraj S., Lynne S. Taylor **CrystEngComm**, 2012

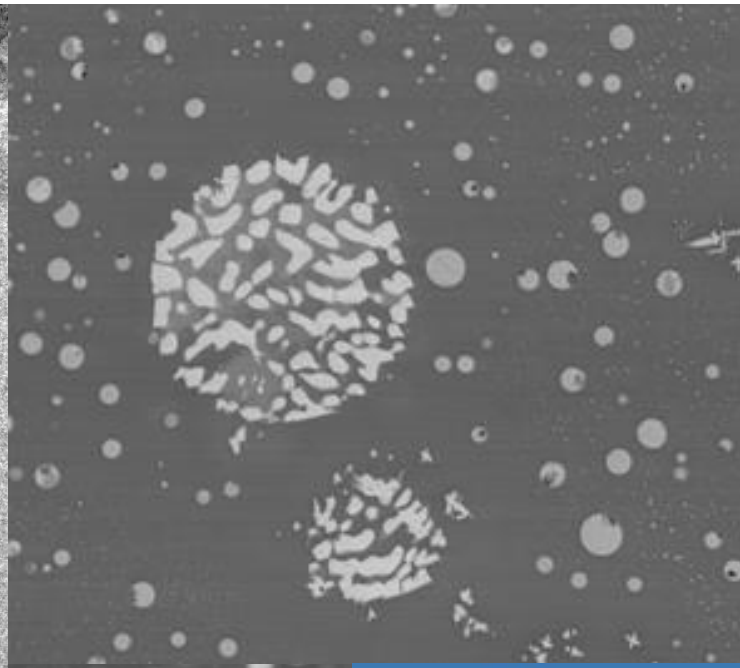
Crystallization rate, morphology and diffusion

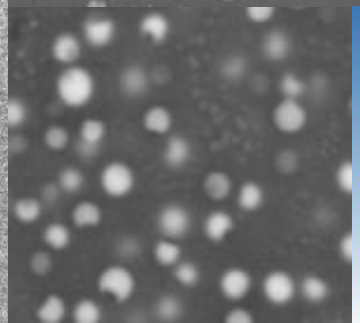
Theories and the experimental work

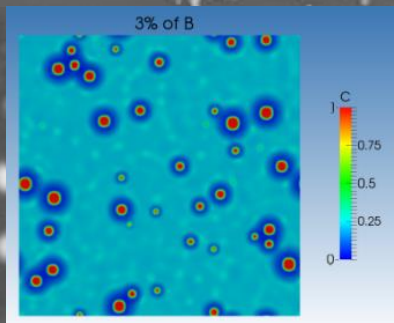
Phase separation







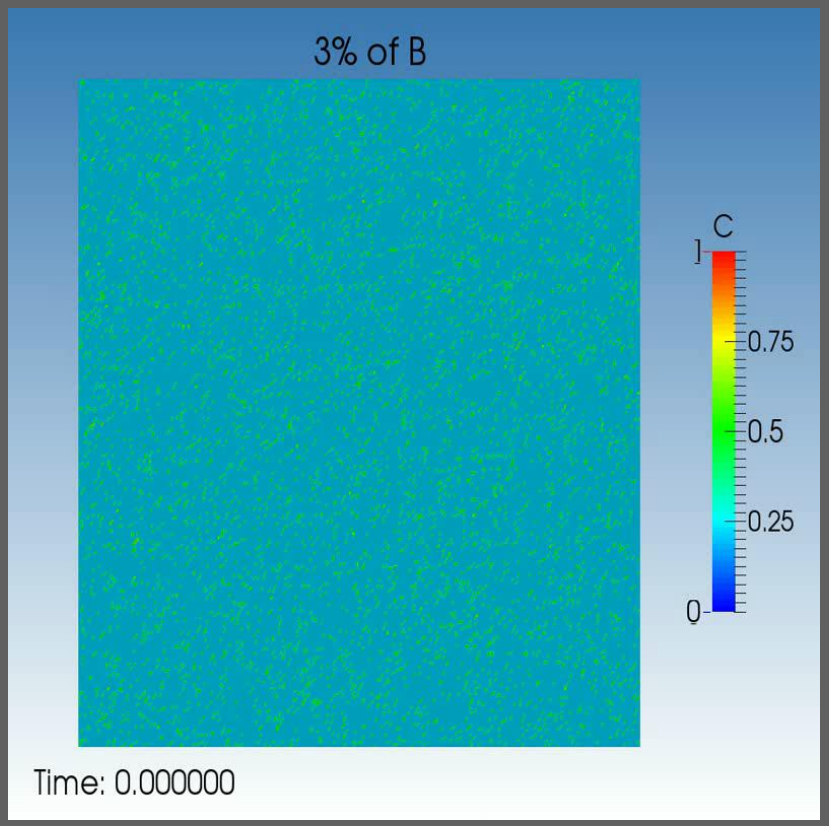


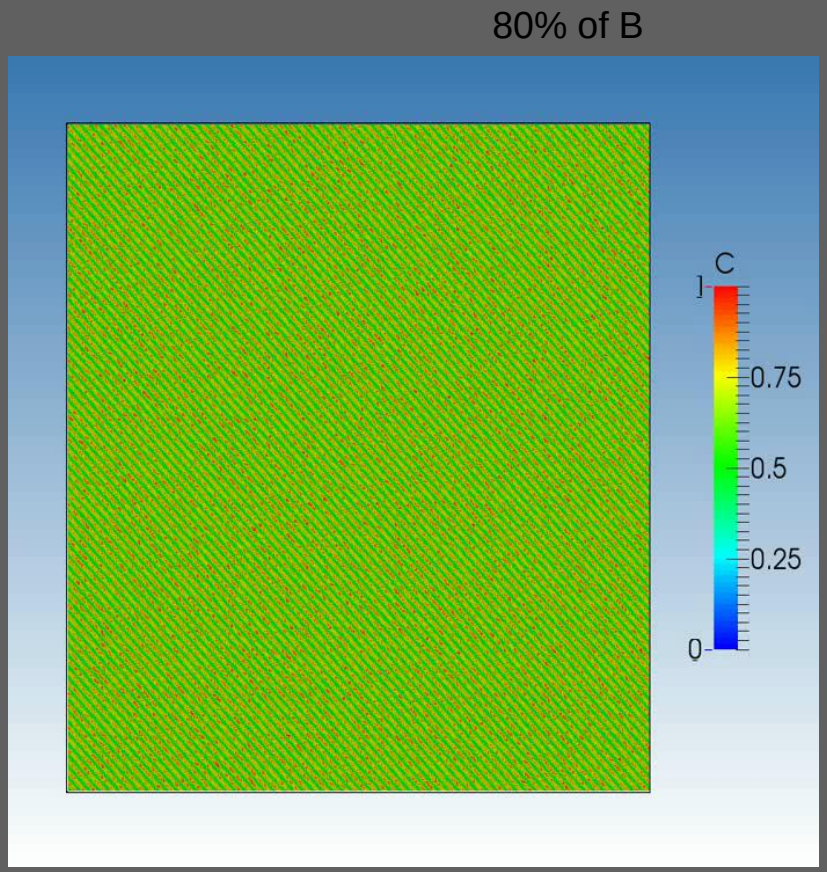


Phase separation mechanism

Nucleation and growth

Separated phases are spherical with low connectivity



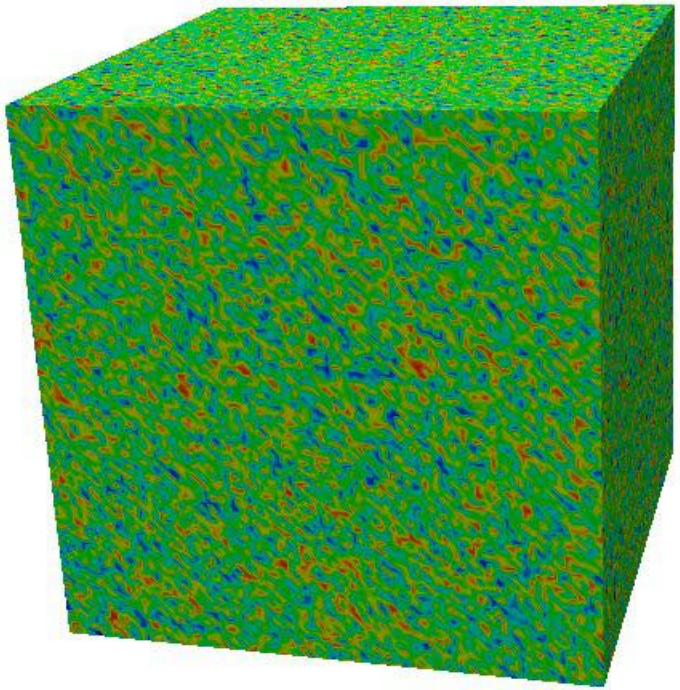


Simulation coupled Cahn-Hilliard and Navier-Stokes equations – Alain Cartalade CEA Saclay

Phase separation mechanism

Spinodal decomposition

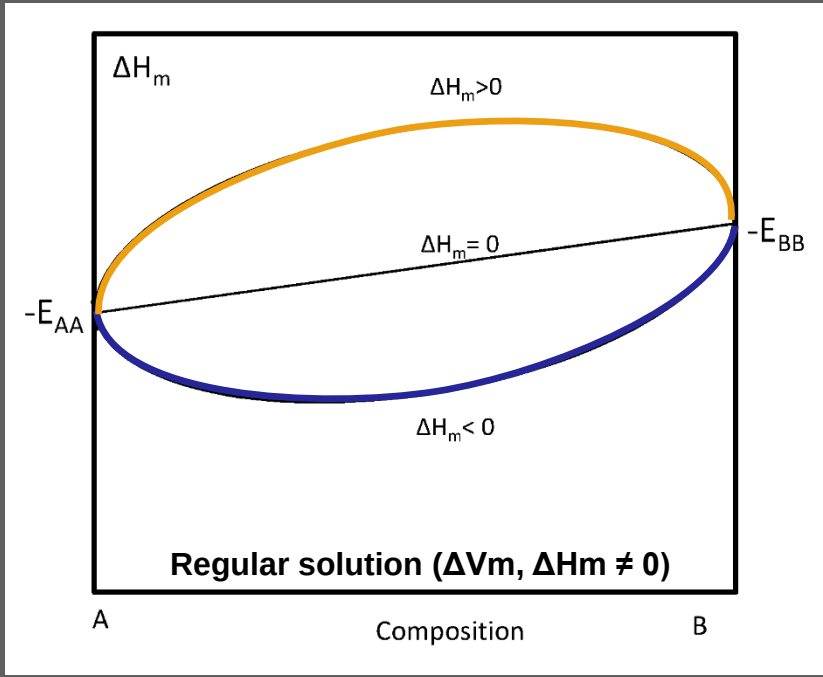
Separated phases are not spherical and connected



Cahn-Hilliard coupled to Navier-Stokes equations – Simulation result Alain Cartalade CEA Saclay

Like in solutions, phase separation depends on the mixing enthalpy and the energy bonds between A and B

ΔH_m : Mixing enthalpy



$\Delta H_m < 0$

→ Any combination of components leads to a reduction of ΔG_m

↓

$\Delta G_m < 0$

$\Delta H_m > 0$

Bond AB weaker than AA and BB

→**Immiscibility**

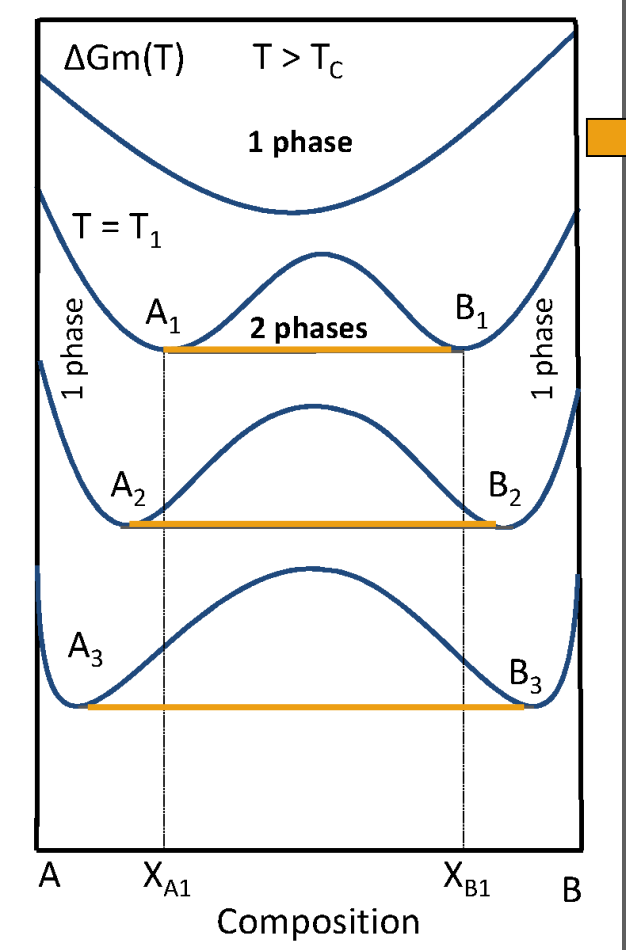
↓

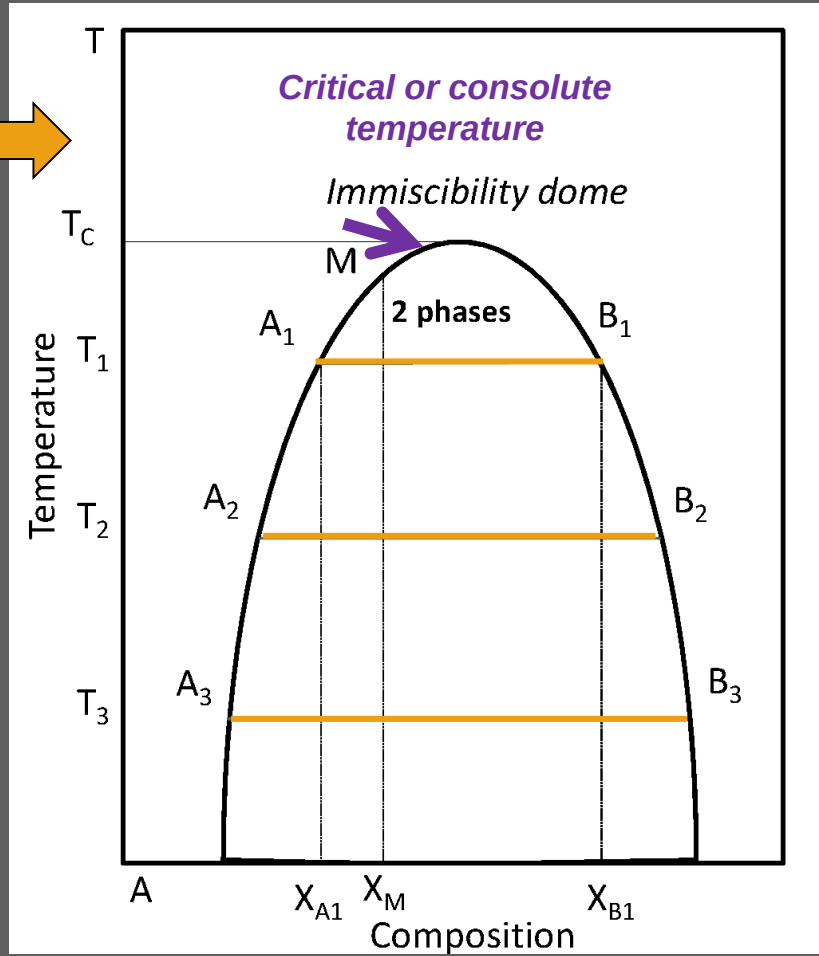
ΔG_m depends on entropy

Immiscibility field

$\Delta H_m > 0$: Competition between entropy and temperature $\Delta G_m = \Delta H_m - T\,\Delta S_m$

- ✓ High temperature : $\Delta S \uparrow$, free enthalpy is minimum → Miscibility region
- ✓ Temperature decrease : $\Delta S \downarrow$, the system is divided into 2 phases to minimize ΔG_m





The immiscibility field is limited by a binodal curve

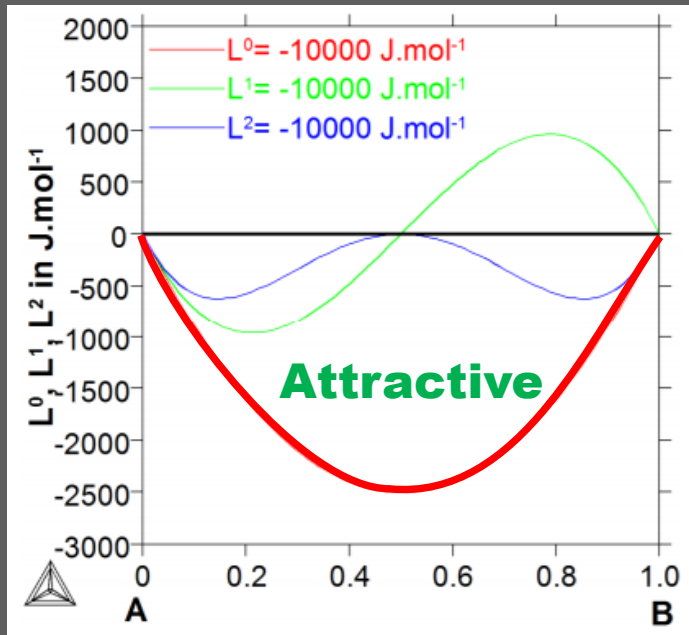
Free enthalpy of excess

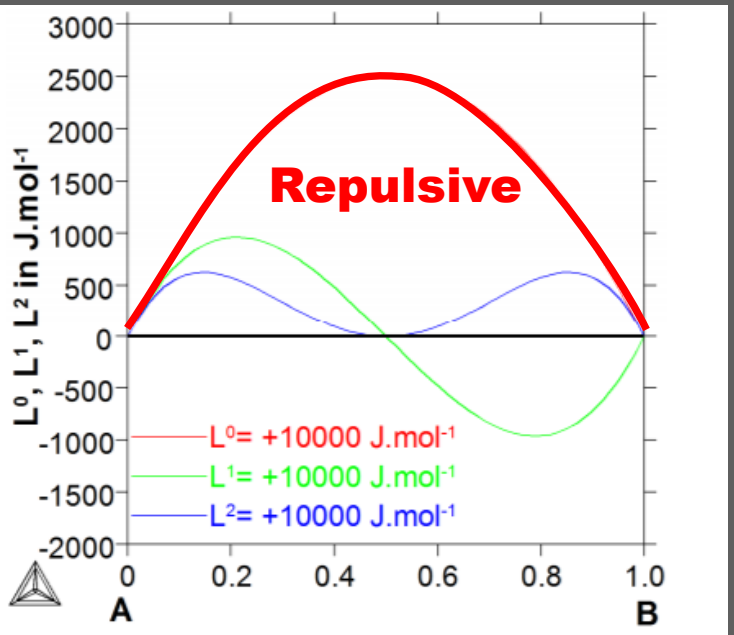
$$\Delta G_m = Gliq_{ref} + Gliq_{ideal} + Gliq_{excess}$$

$$\Delta G_m = x_A {}^0G_A + x_B {}^0G_B + RT(x_A \ln x_A + x_B \ln x_B x_B) + x_A x_B L_{AB}$$

x = molar fraction, L_{AB} = Interaction parameter attractive or repulsive between A and B

L_{AB} = Interaction parameter : determines the positive or negative sign of the free enthalpy of excess





CALPHAD calculation - Stéphane Gossé CEA Saclay

$$L_{AB} = -ZN_A[E_{AB} - 1/2(E_{AA} + E_{BB})]$$

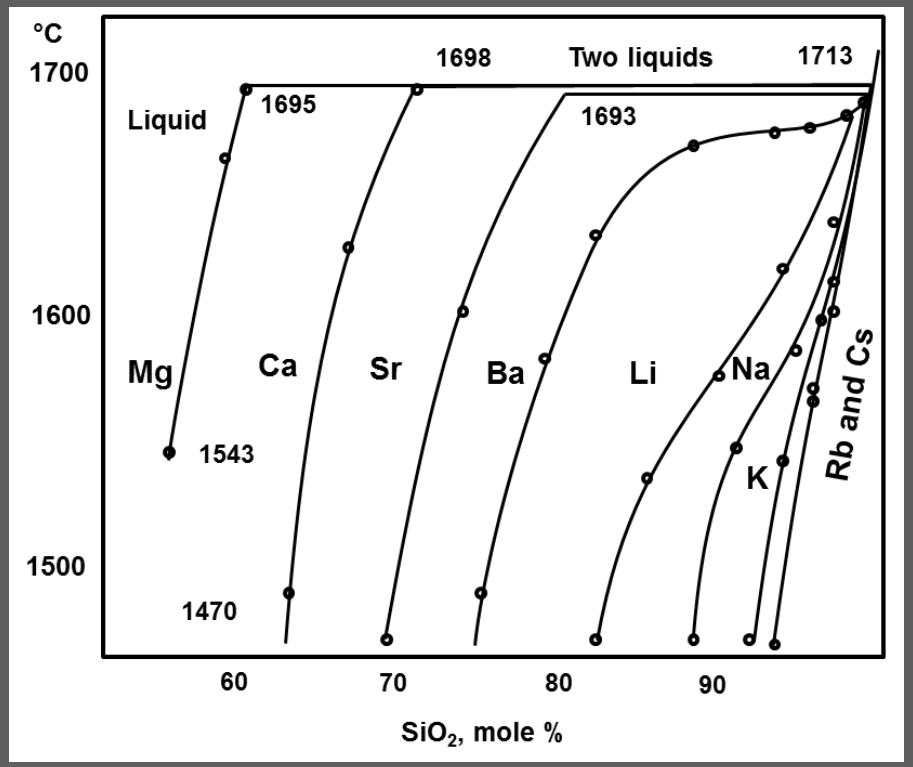
Link to the structure of glass

In the alkali and alkali earth silica glasses, cation field strength has an impact on the liquidus curves

Type of liquidus curves is correlated to z/r

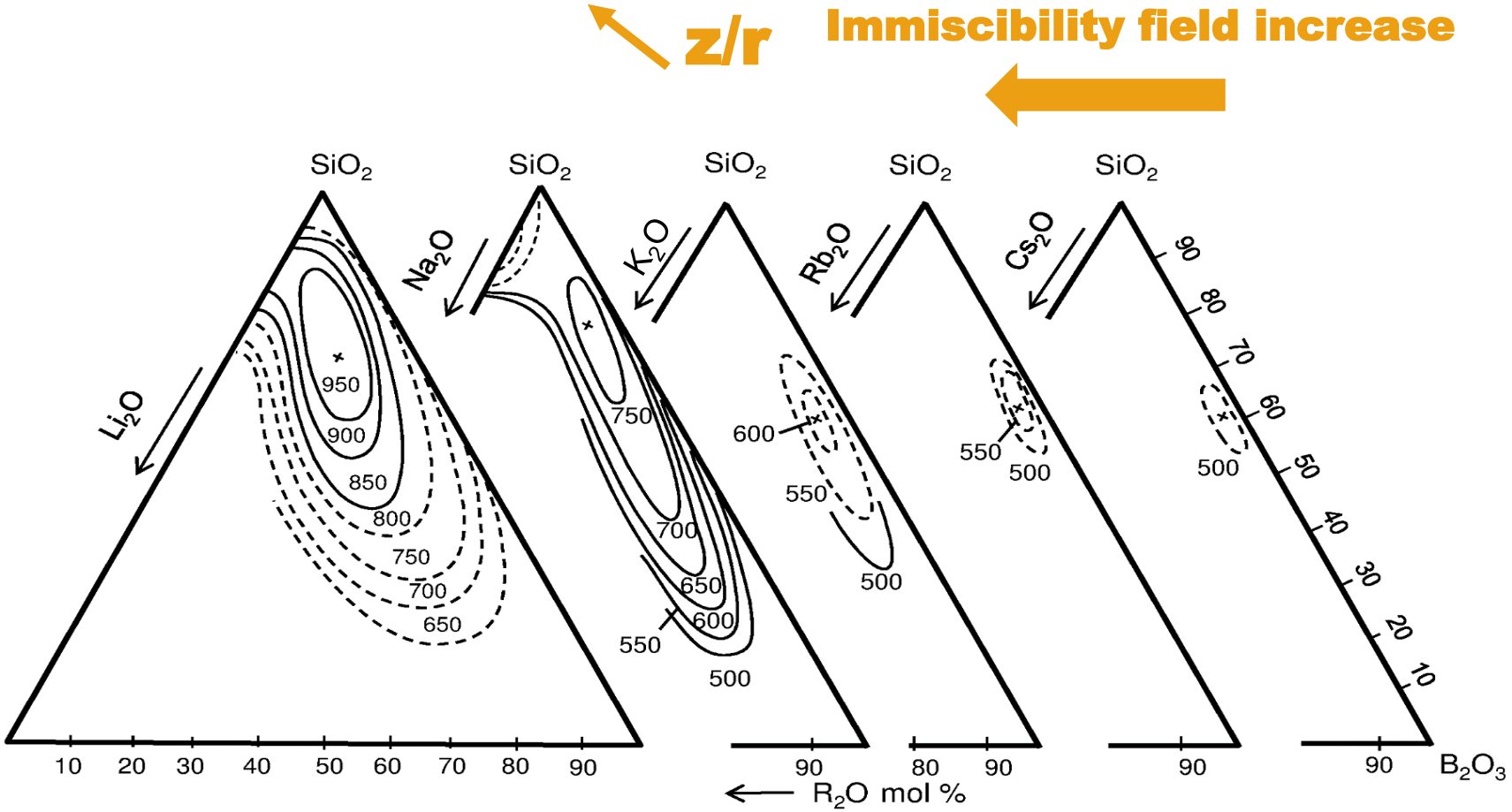
Cation	Ionic radius, r (Å)	Cation field strength z/r	Type of curve
Cs	1,64	0,61	Straight line
Rb	1,49	0,67	
K	1,33	0,75	
Na	0,98	1,02	S-shaped
Li	0,78	1,28	
Ba	1,43	1,40	
Sr	1,27	1,57	Plateau near the monotectic
Ca	**1,06**	1,89	
Mg	0,78	2,56	

Type of liquidus curve depending on cation field strength



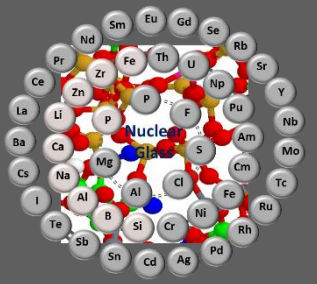
Kracek, F.C., Journal of American Chemical Society 1930. ***52****(4)*

Increasing of immiscibility field in alkali borosilicate glasses with cation field strength



Porai-Koshits, E.A., *Phase separation in glass*, ed. E.A.P.-K. O.V Mazurin. 1984, Amsterdam, New York ; North-Holland

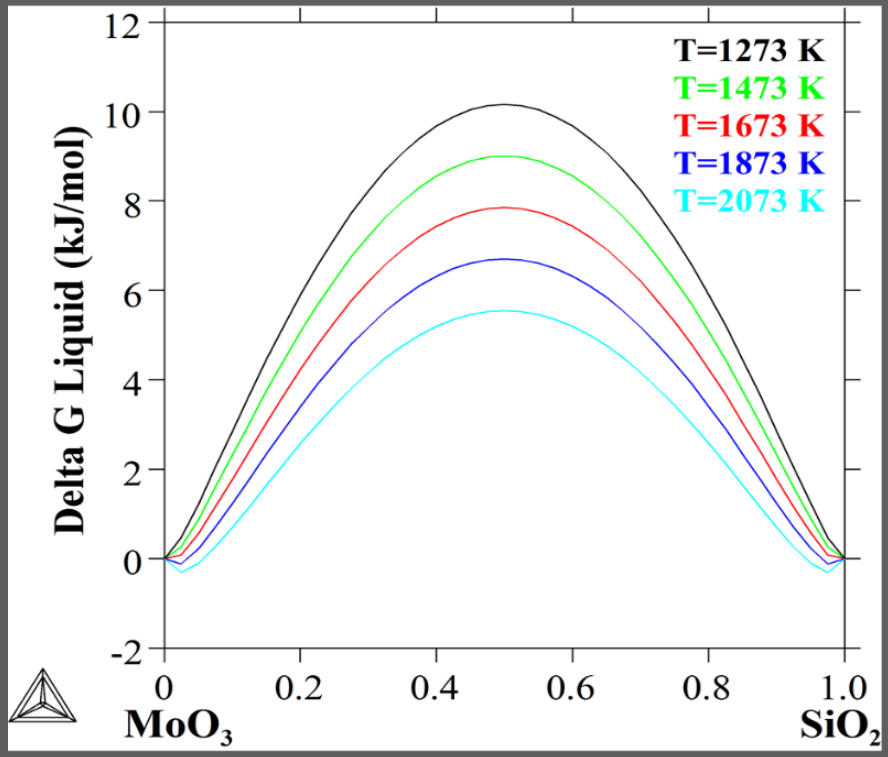
Molybdenum silica glass : SiO_2-MoO_3

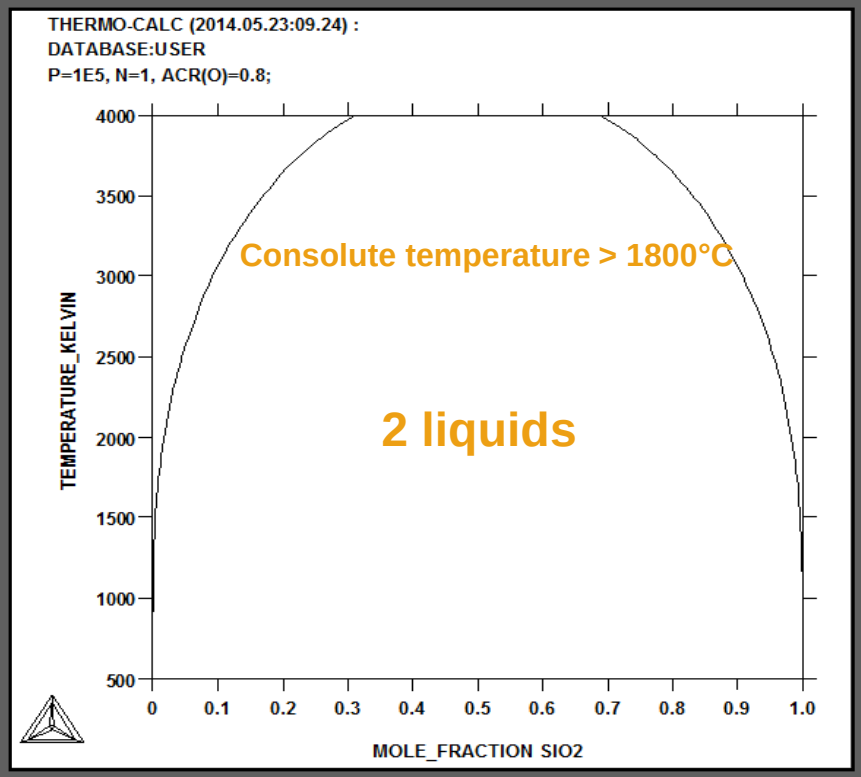


Cation field strength Mo-O (z/r) = 10,2

Interaction between SiO_2 and MoO_3 is repulsive

$L_{MoO3-SiO2}$ = + 70 KJ/mol

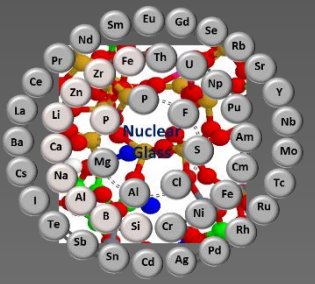




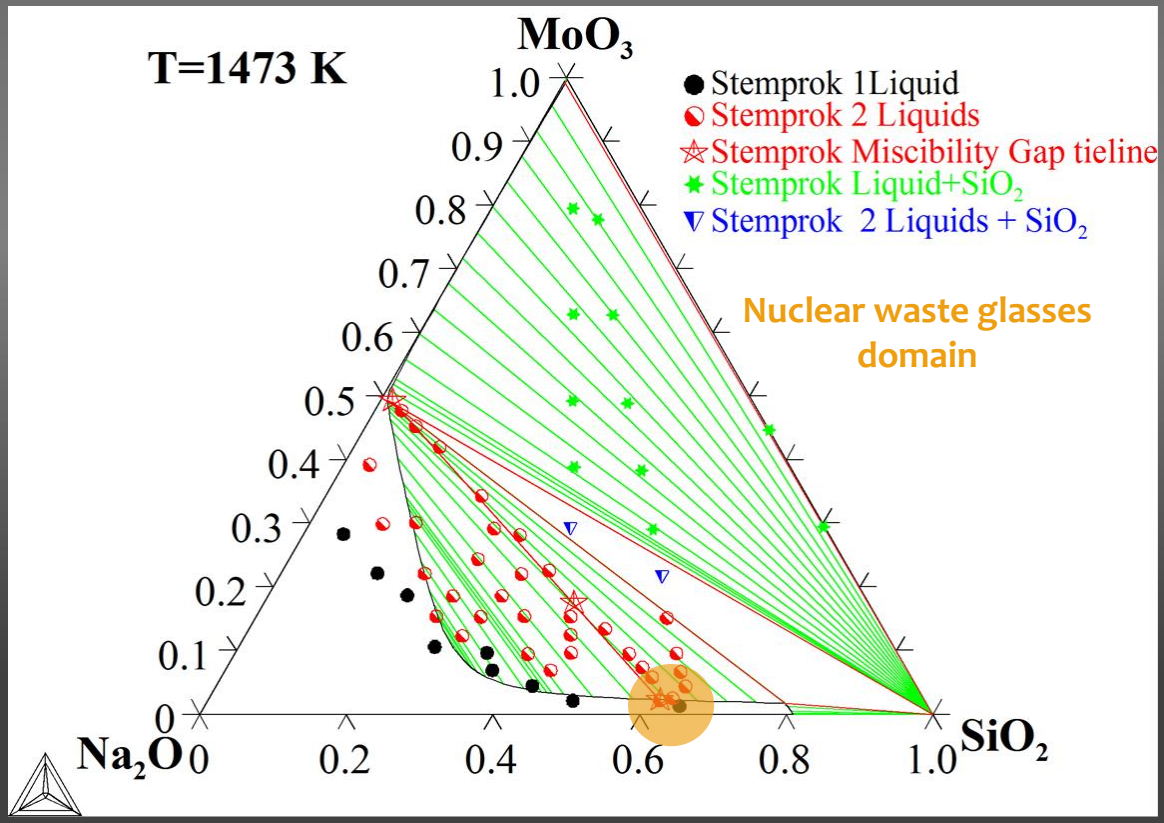
CALPHAD calculation - Stéphane Gossé CEA Saclay

Large immiscibility field in the liquid.

Tendency towards phase separation is limited by the addition of sodium oxide



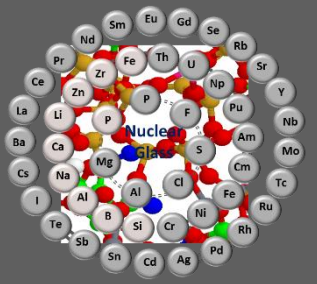
Immiscibility field in SiO_2-Na_2O-MoO_3

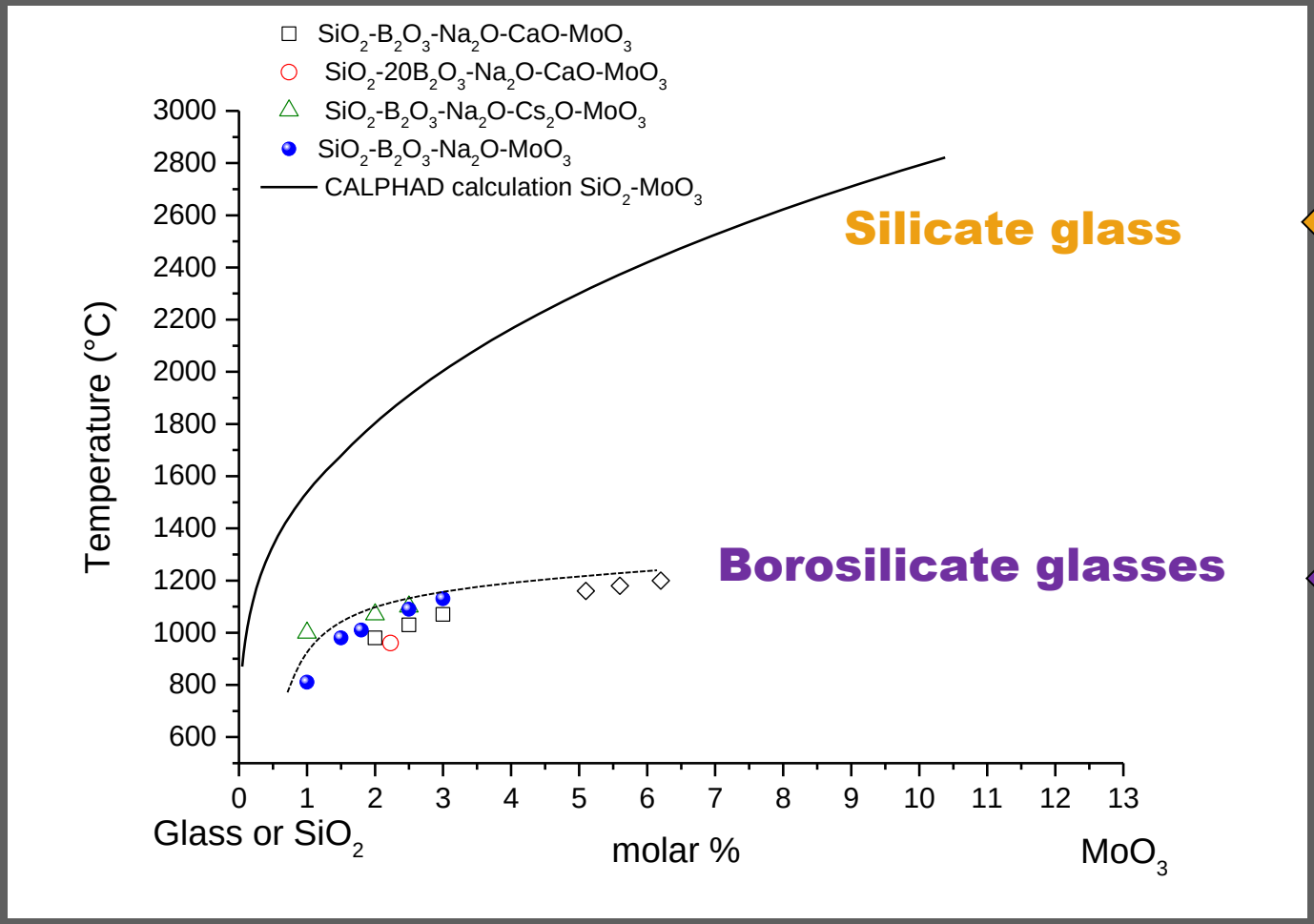


M. Stemprok (1974) "Geological significance of immiscibility in fused silicate systems containing tungsten and molybdenum" Internat. Geology Rev.,17 (11), 1306-1310.

S. Gossé, C. Guéneau, S. Bordier, S. Schuller, A. Laplace, J.Rogez (2014) "A Thermodynamic Approach to predict the Metallic and OxidePhases Precipitations in Nuclear Waste Glass Melts" Summer School Sumglass, Procedia Materials Science.

Immiscibility temperature decrease in alkali and alkali earth borosilicate SiO_2-B_2O_3-Na_2O-MO-MoO_3





CALPHAD calculation

Experimental data obtained by viscosity measurements

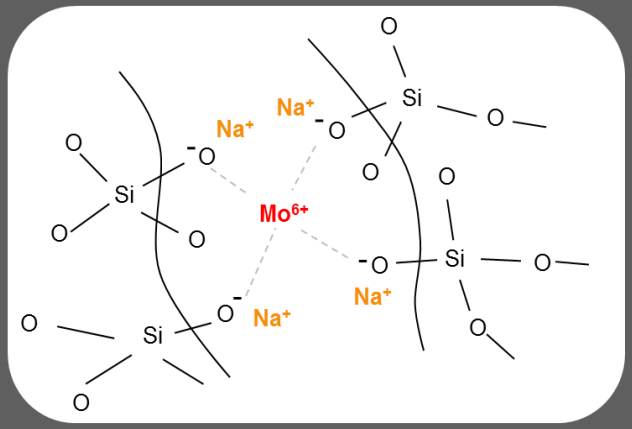
S. Schuller, O. Pinet, B. Penelon (2011) "Liquid-liquid phase separation process in borosilicate liquids enriched in molybdenum and phosphorus oxides." J. Am. Ceram. Soc., 94, 447-454.

Liquidus curves are lower in borosilicate glasses than in silicate glasses

Structural explanation

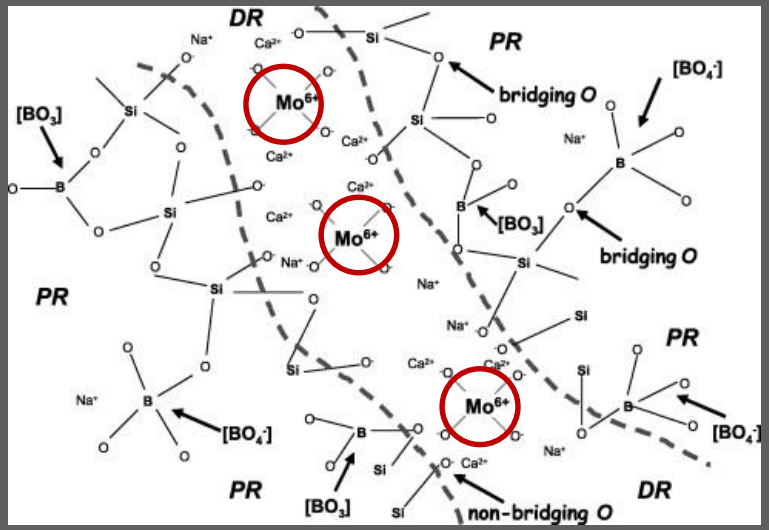
Stabilization of molybdate units by sodium that compensated molybdate and modified the silica network

Schematic silicate glass network



Structural stabilization of MoO_4^{2-} unit in sodium silicate glass

borosilicate glass network

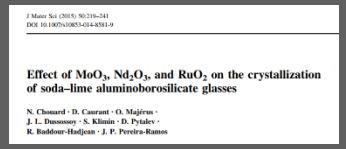


D. Caurant, O. Majerus, E. Fadel, A. Quintas, C. Gervais, T. Charpentier, D. Neuville (2010) "Structural investigation of boroslicate glasses containing MoO_3 by NMR and Raman spectroscopies." Journal of Nuclear Materials, 396, 94-101.

Favorable effect of rare earths (Nd, Gd) to stabilized Mo^{6+} in borosilicate glass


Journal of Alloys and Compounds

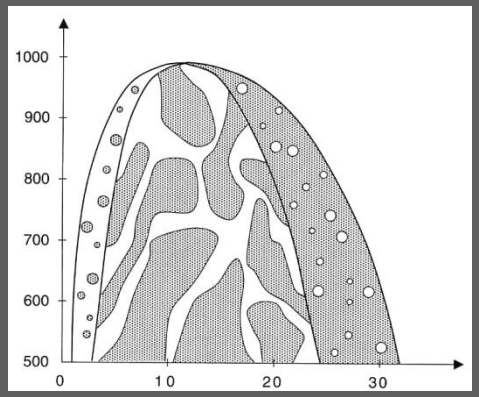
Thermal stability of SiO_2–B_2O_3–Al_2O_3–Na_2O–CaO glasses with high Nd_2O_3 and MoO_3 concentrations


Effect of MoO_3, Nd_2O_3, and RuO_2 on the crystallization of soda–lime aluminoborosilicate glasses


Compositional dependence of solubility/retention of molybdenum oxides in aluminoborosilicate based model nuclear waste glasses

Rare earths increase the charge close to the molybdates, and modified the silica network

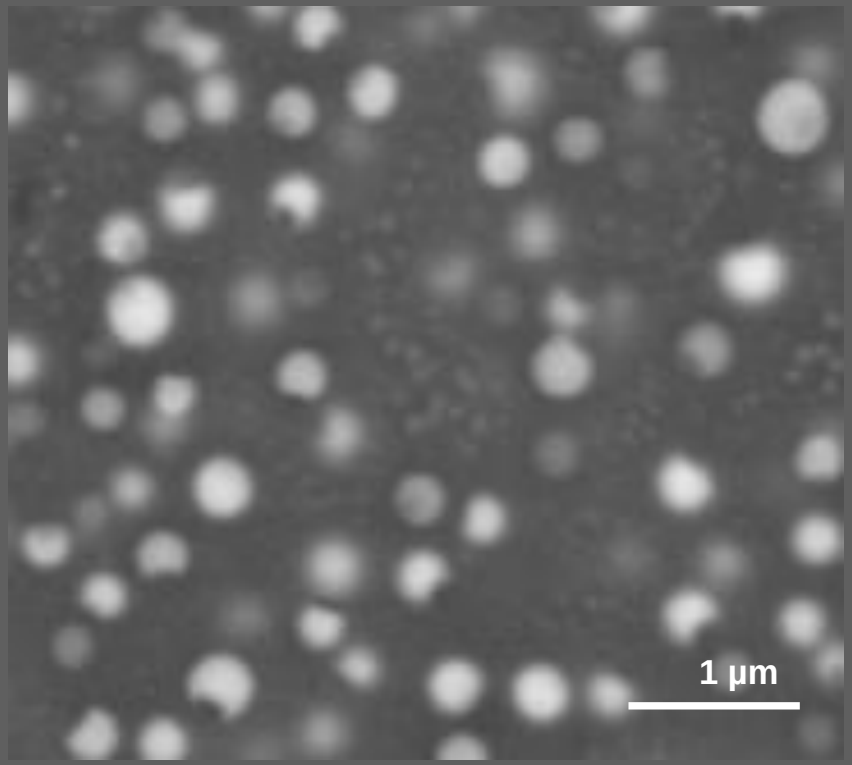
Mechanism of phase separation and the kinetic



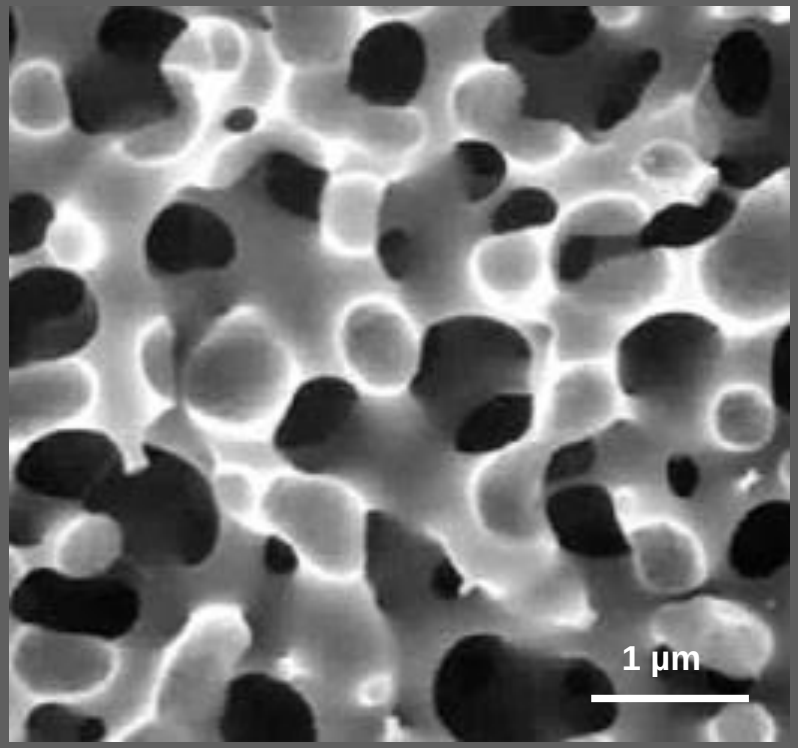
Haller et al : data thermodynamic interpretation
J. Am. Ceram. Soc. 57 (3), 120-126 (1974)

- ✓ **Nucleation-type mechanism : separated phases are spherical with low connectivity**
- ✓ **Spinodal-type mechanism : separated phases are not spherical and have high connectivity**

Nucleation and growth



Spinodal decomposition



Kukizaki, M., Journal of Membrane Science 2010. **360**(1-2)

It depends on the composition and temperature

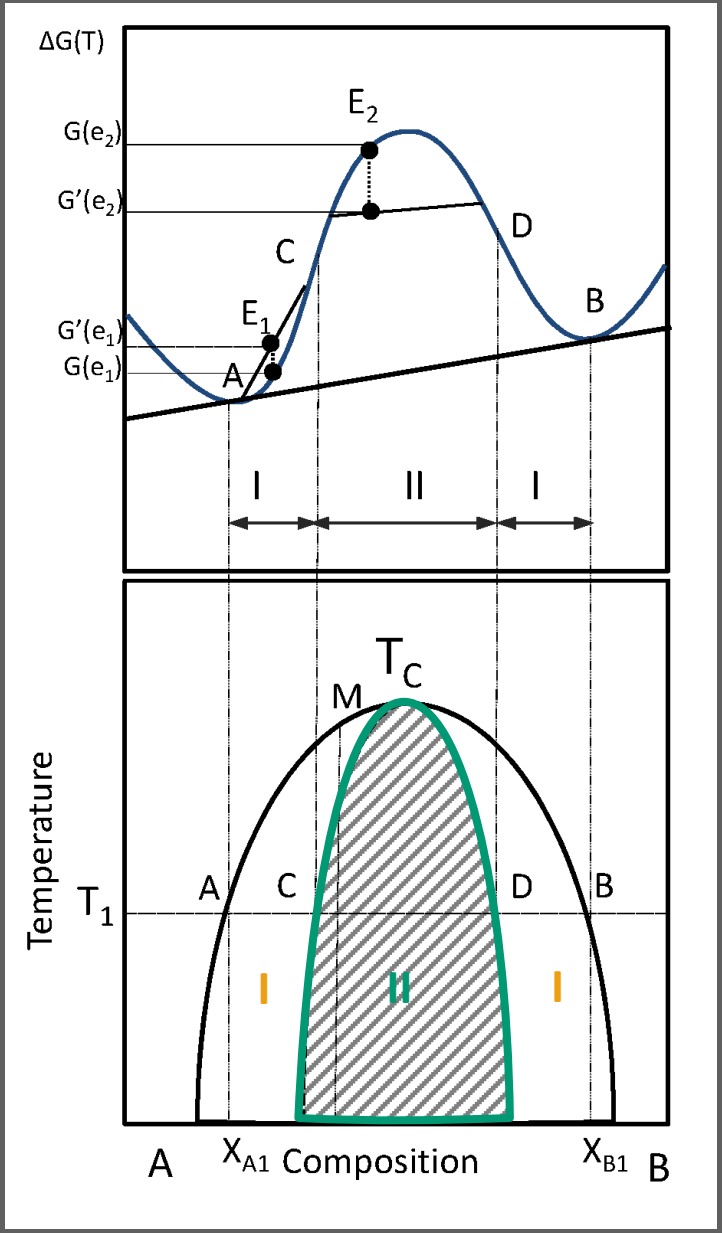
Field I

$G'(E_1) > G(E_1)$

G'' > 0 : in the convex portion of the ΔG curve

Nucleation and growth

→ *the system is stable for a small variation of composition*



Field II

$G'(E_2) < G(E_2)$

G'' < 0 : in the concave portion of the ΔG curve

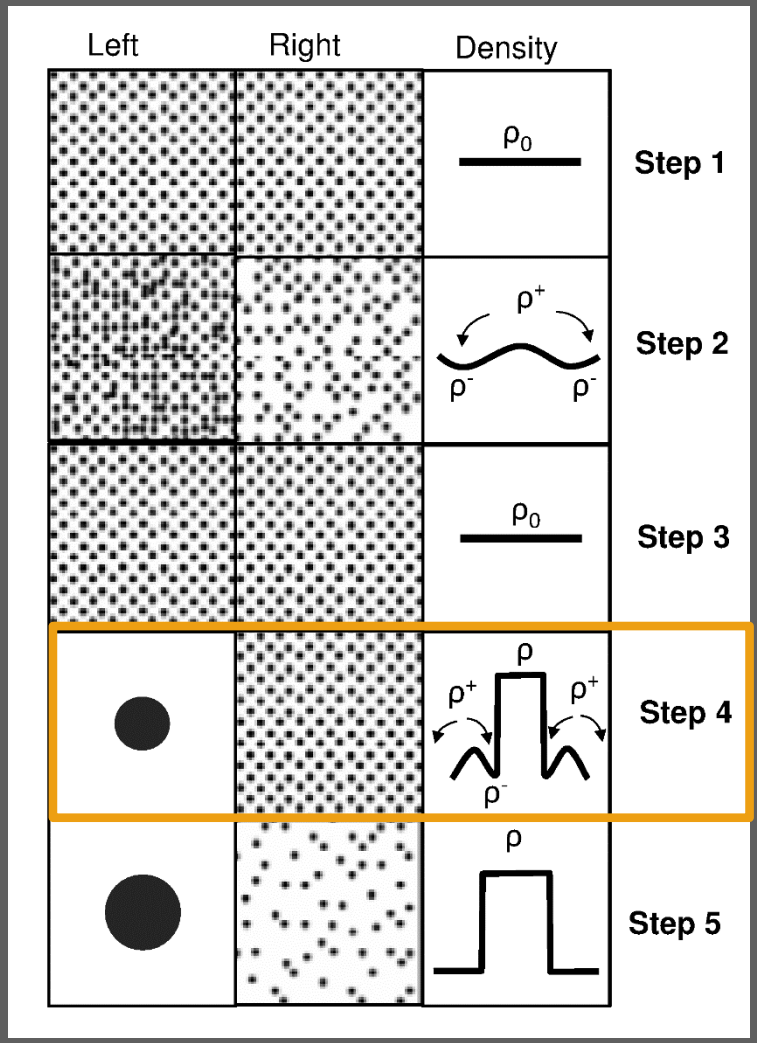
Spinodal decomposition

→ *A small variation of composition causes an instability*

Nucleation and growth

Down-Hill diffusion

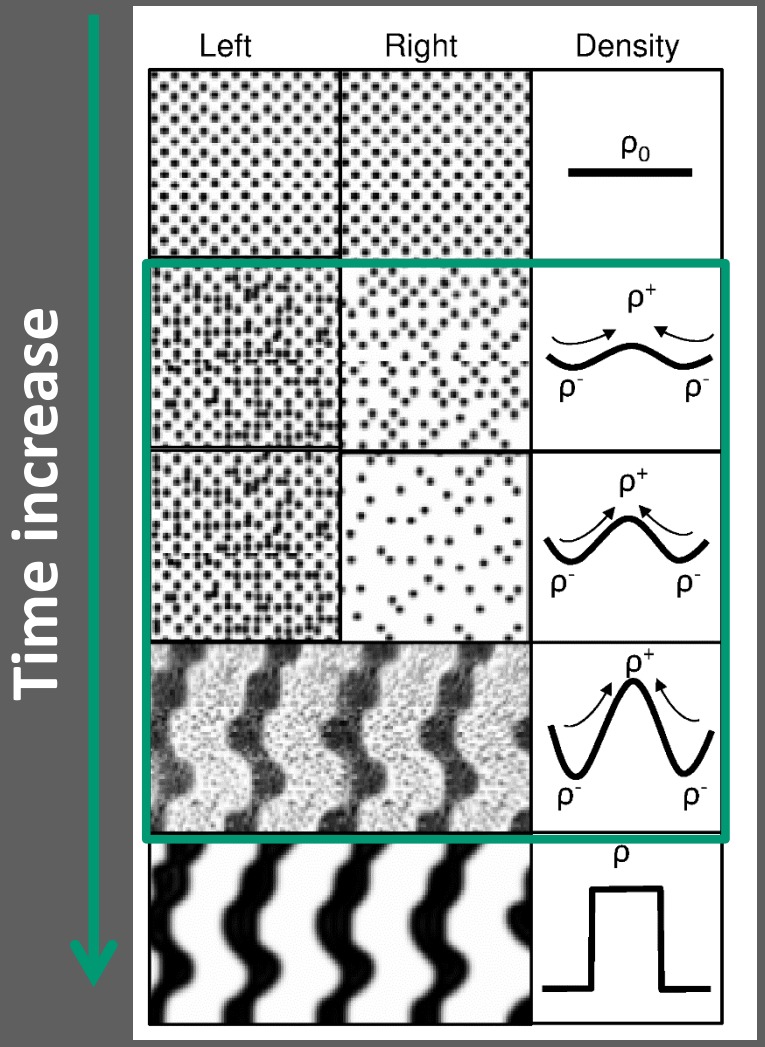
Fixed compositions with sharp interfaces



Spinodal decomposition

Up Hill diffusion

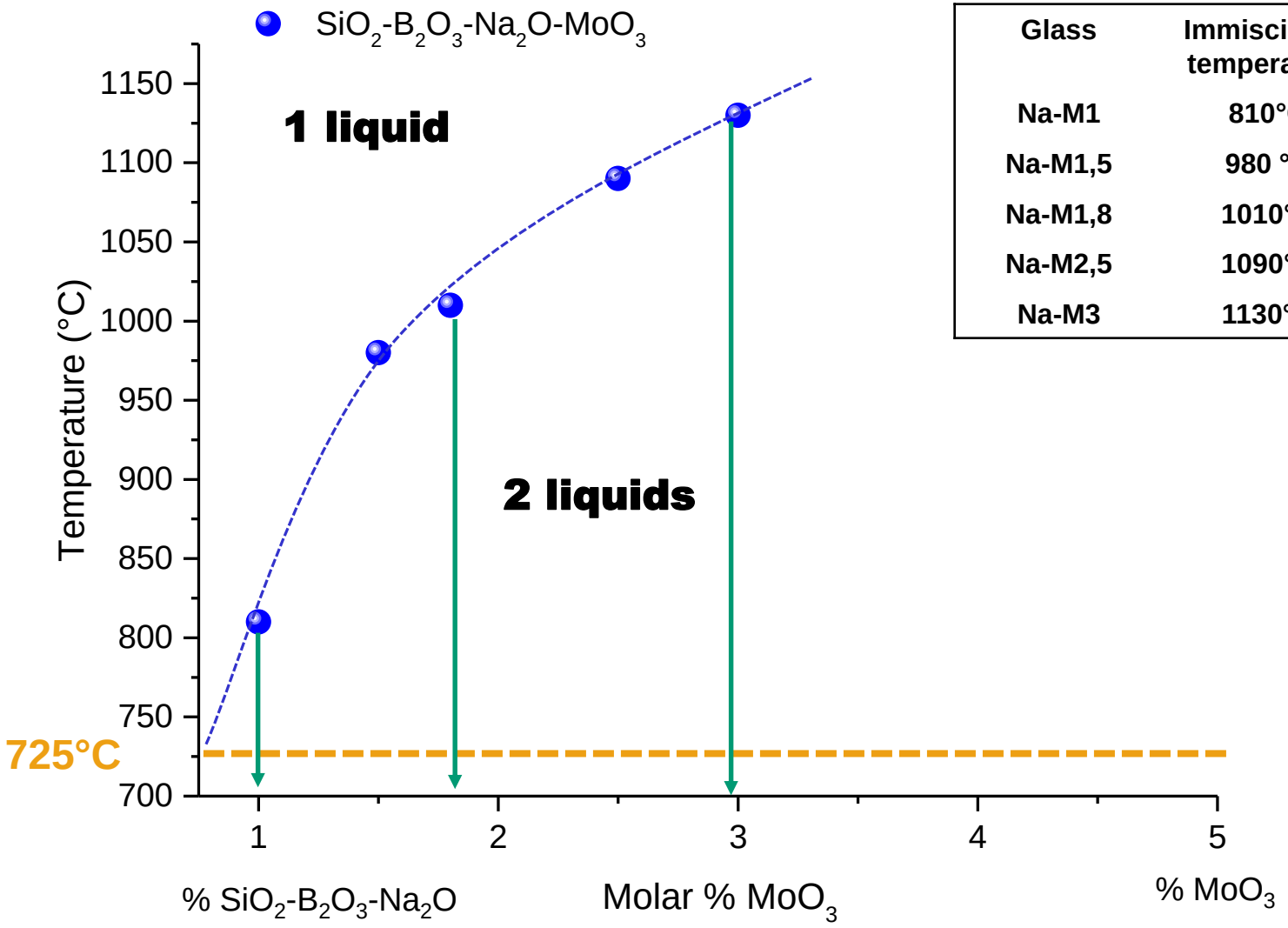
Small fluctuation of composition gradually grows over a period of time via Up-Hill diffusion



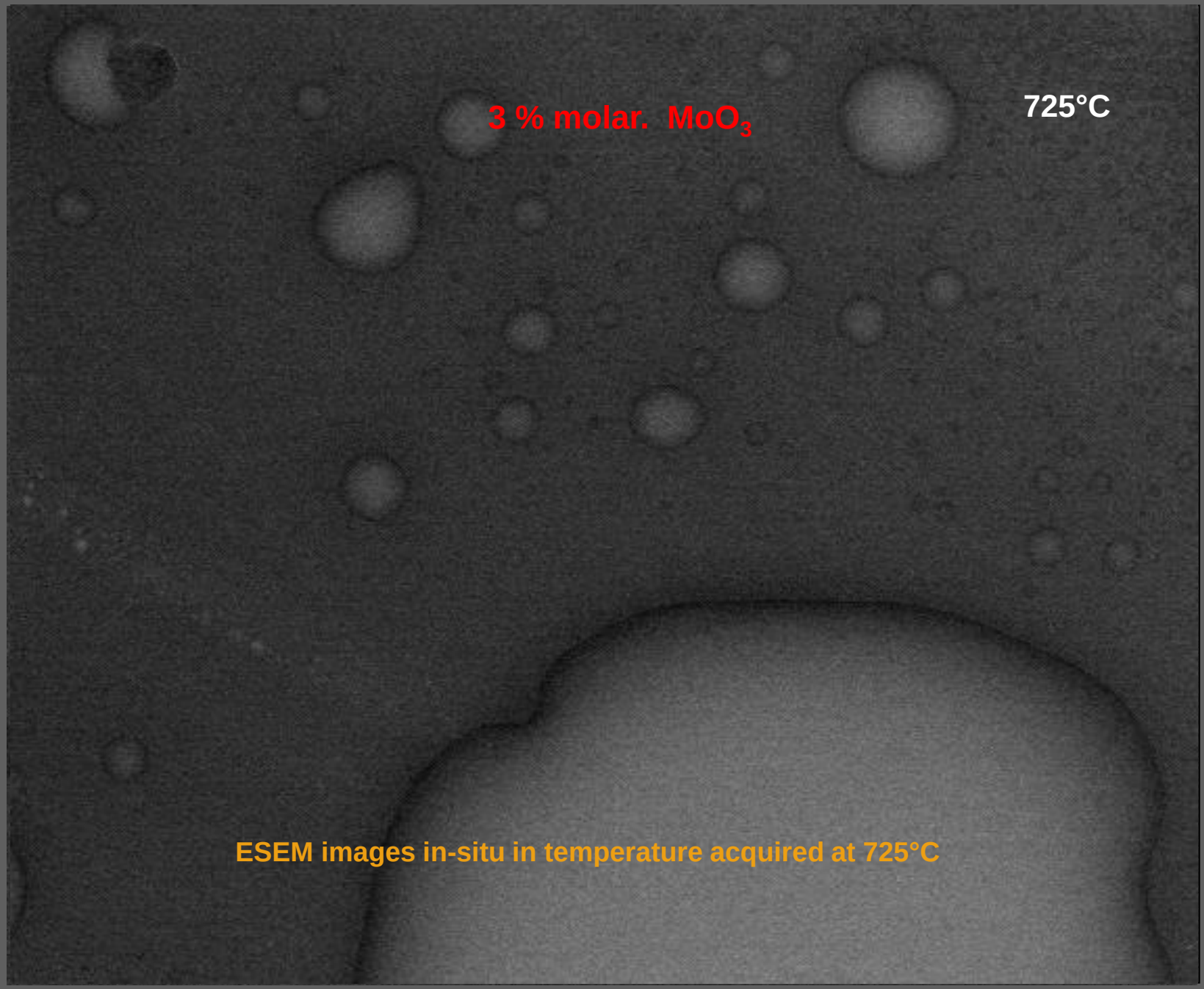
E.P. Favras, A.C.M., *What is spinodal decomposition*, in *lecture note*, E.s.a.T. review, Editor. 2008. p. 25-27.

Example of sodium borosilicate glass enriched in MoO3

Morphology ?

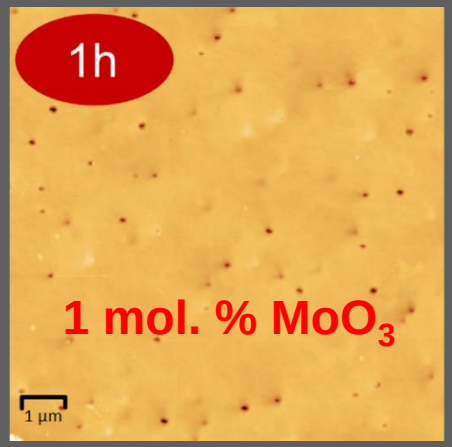


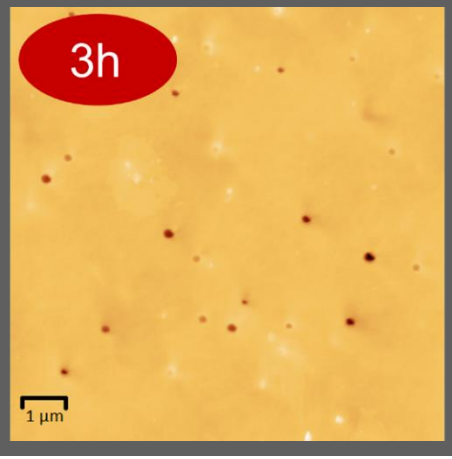
Glass	Immiscibility temperature
Na-M1	810°C
Na-M1,5	980 °C
Na-M1,8	1010°C
Na-M2,5	1090°C
Na-M3	1130°C

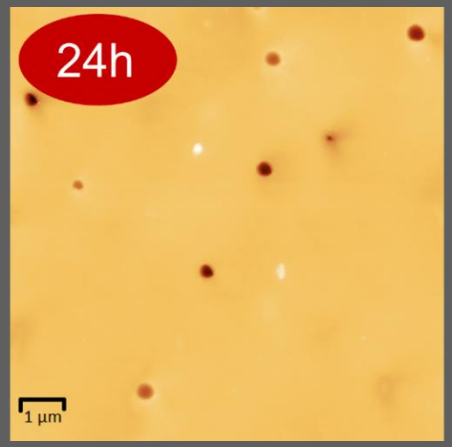

3 % molar. MoO_3
725°C
ESEM images in-situ in temperature acquired at 725°C

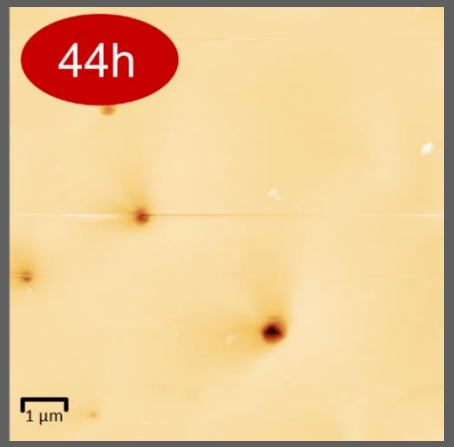
What is the evolution of separated phases with time ?
Example of SiO_2-B_2O_3-Na_2O-MoO_3

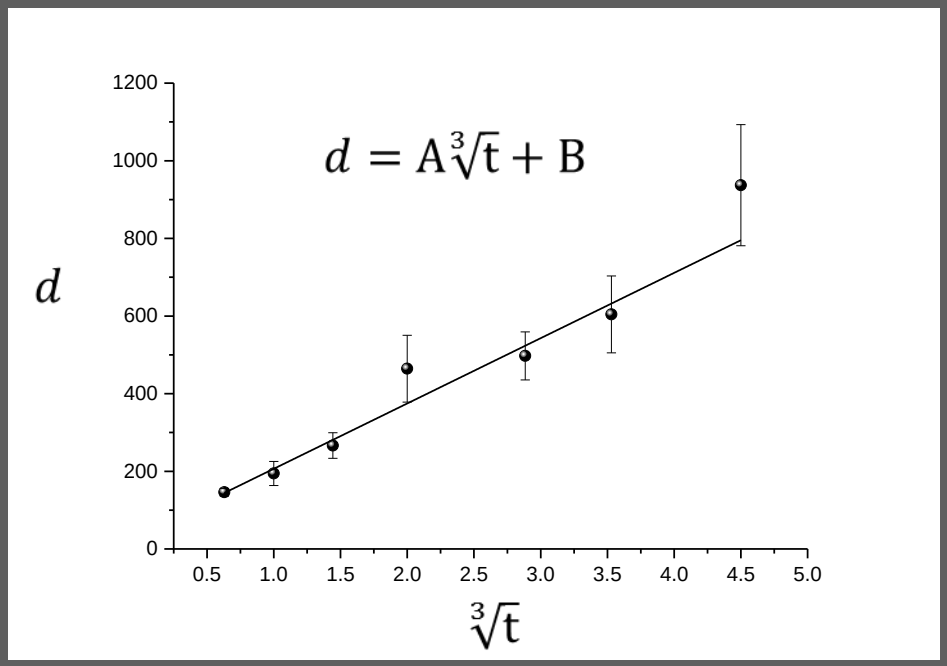
AFM images obtained after heat treatment at 800°C – 1h to 44h











$d = 168\sqrt[3]{t} + 38$

The growth is produced by an Ostwald ripening mechanism due to a diffusion process

Cooperation with Andrea Piarristeguy and Annie Pradel - *Charles Gerhardt Institute (ICG),* University of Montpellier

Phase separation - Summary

How to control the phase separation in glass ?

Theory

Thermodynamic data at equilibrium

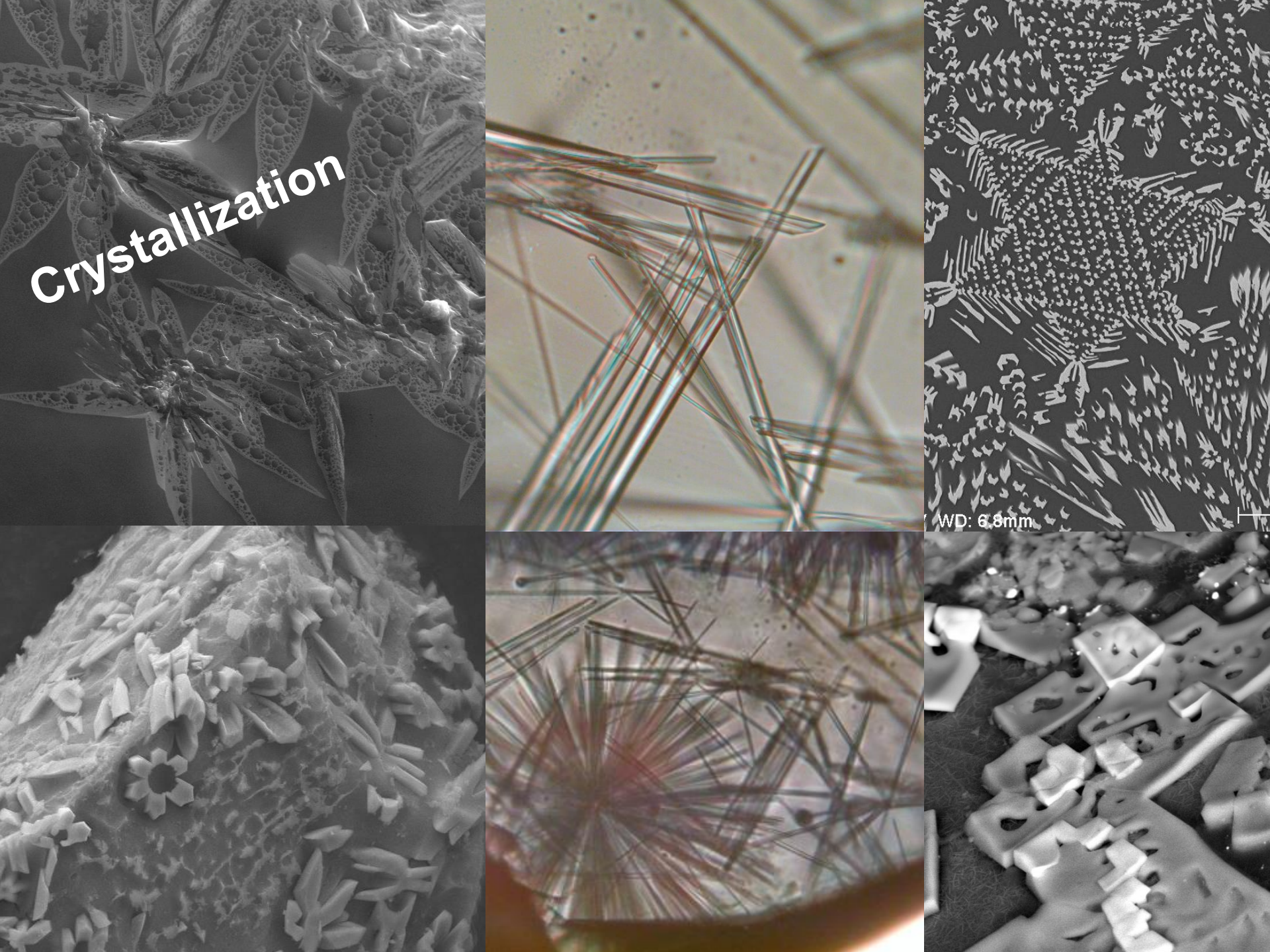
Experimental approaches

- Mechanism of phase separation (stable, metastable, nucleation and growth, spinodal decomposition)
- Morphology of separated phases
- Binodal curve, immiscibility temperature
- Composition of separated phases formed
- The structural role of elements that promote phase separation
- Kinetic of phase separation

It is difficult to accurately predict metastable phase separation and the vitrification domain

Is one of the challenges of French research national groups GDR TherMatHT, GDR verre and USTV, associated with the CEA

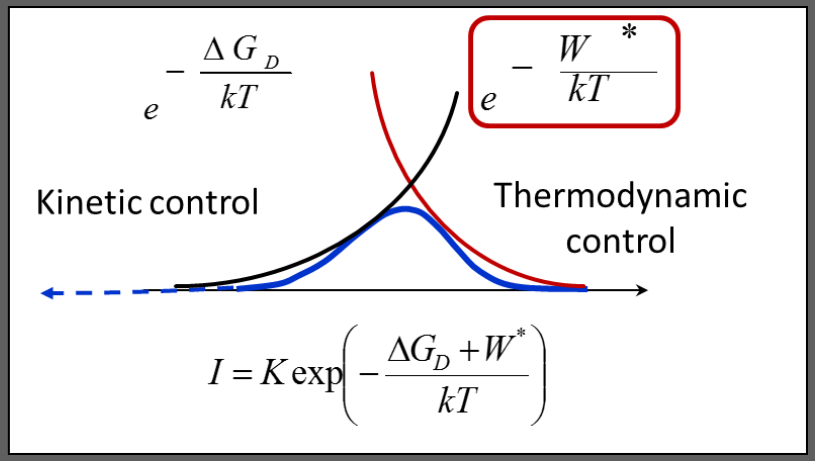
See Lecture Pierre Benigni on Thursday 9th


Crystallization
WD: 6.8mm

How to control mechanism of crystallization and kinetic ?

CNT : Classical Nucleation Theory

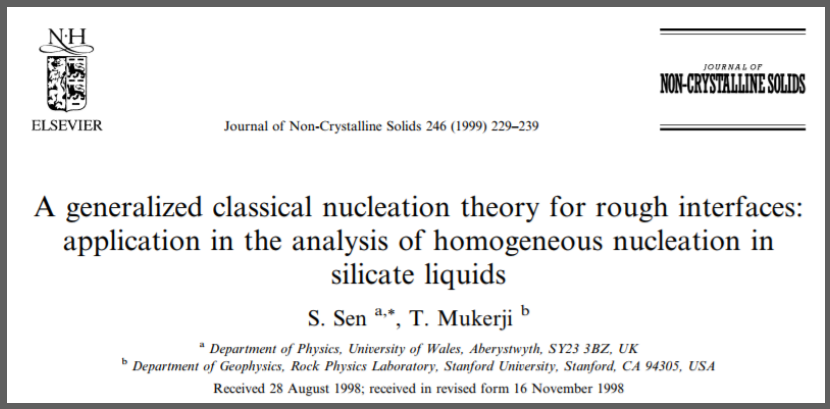
Volmer – Becker – Döring (de 1926 à 1935)



Simple law considers too many hypotheses (spherical nucleus, non variation of composition, D is related to Stokes-Einstein equation…) and causes too much controversy !!

Other more complex laws

Empirical models


ELSEVIER

Journal of Non-Crystalline Solids 246 (1999) 229–239

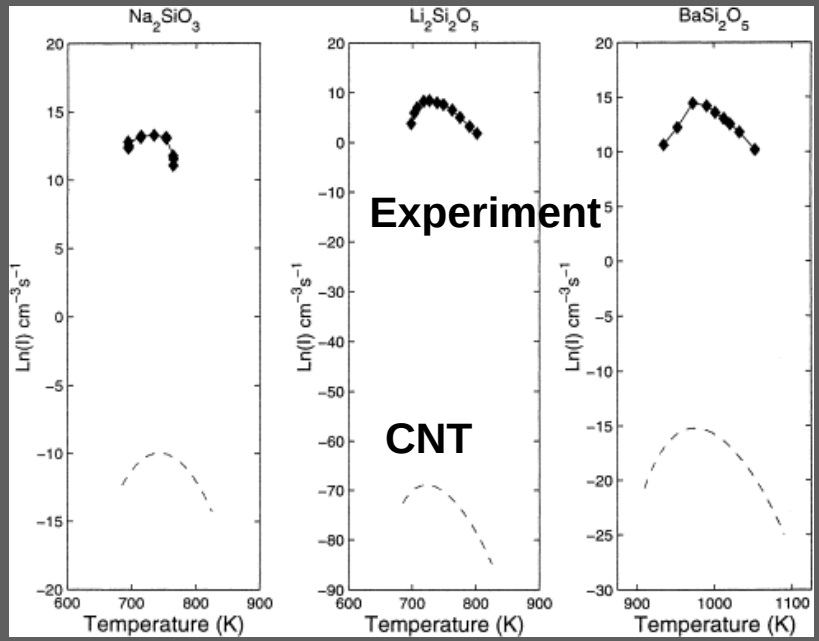
JOURNAL OF NON-CRYSTALLINE SOLIDS

A generalized classical nucleation theory for rough interfaces: application in the analysis of homogeneous nucleation in silicate liquids

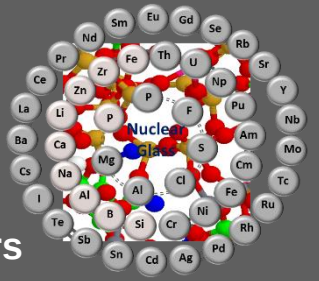
S. Sen [a,*], T. Mukerji [b]

[a] Department of Physics, University of Wales, Aberystwyth, SY23 3BZ, UK
[b] Department of Geophysics, Rock Physics Laboratory, Stanford University, Stanford, CA 94305, USA

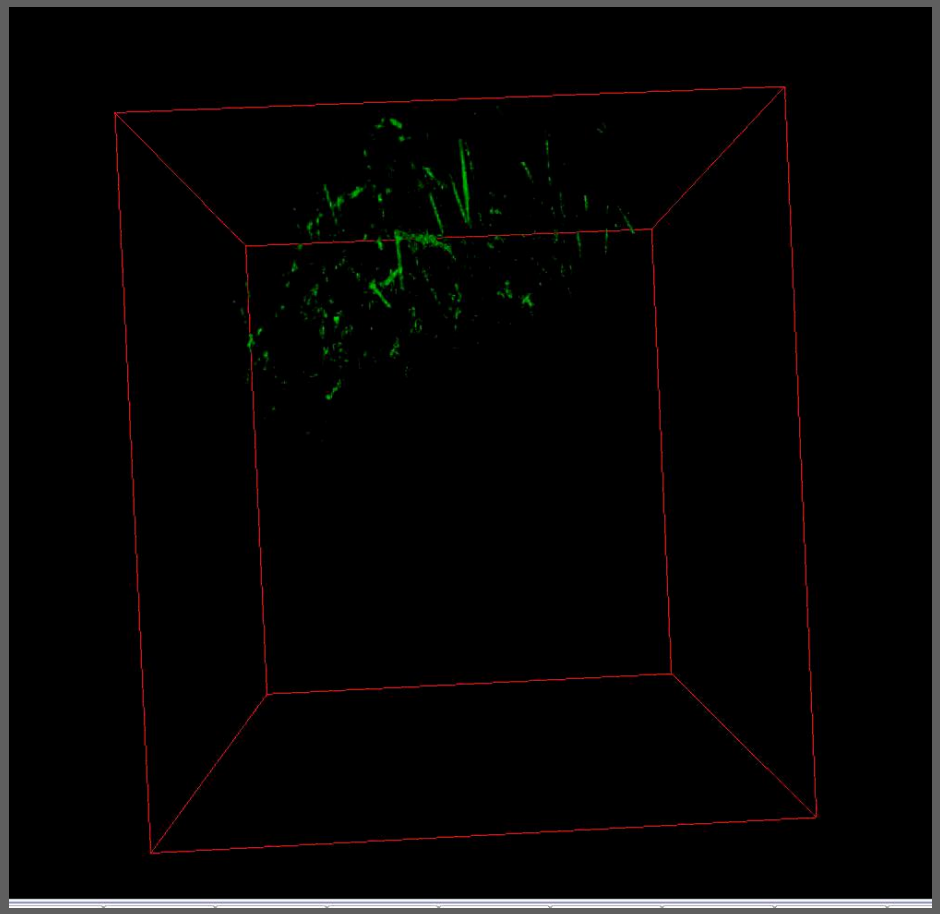
Received 28 August 1998; received in revised form 16 November 1998



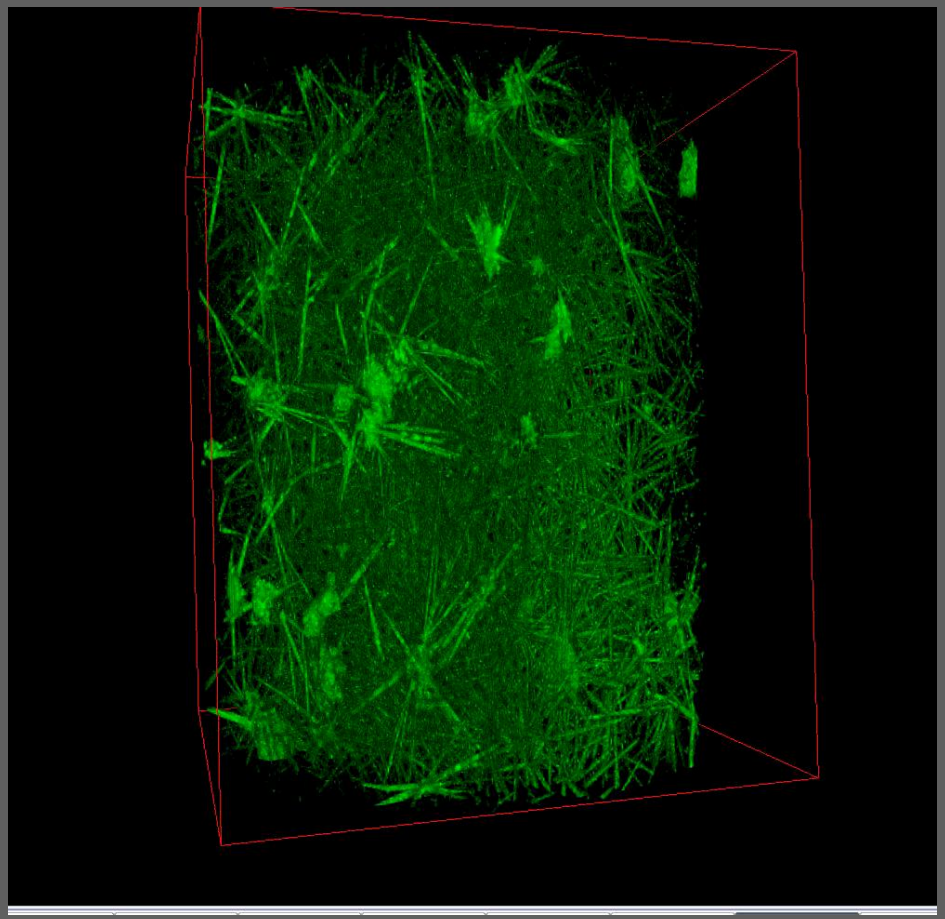
Example of crystallization in simplified nuclear glass



Apatite needles grow parallel to each other, perpendicular to the interface.



HLW glass exposed to 700°C, 89hrs



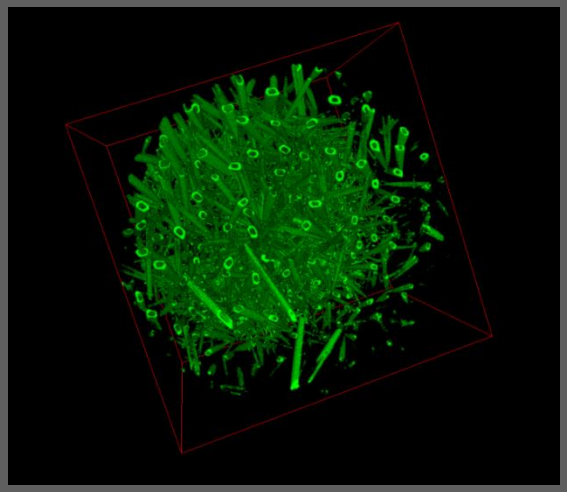
E. Régnier (CEA Marcoule), O. Delattre, in cooperation with E. Gouillard (St Gobain Recherche)

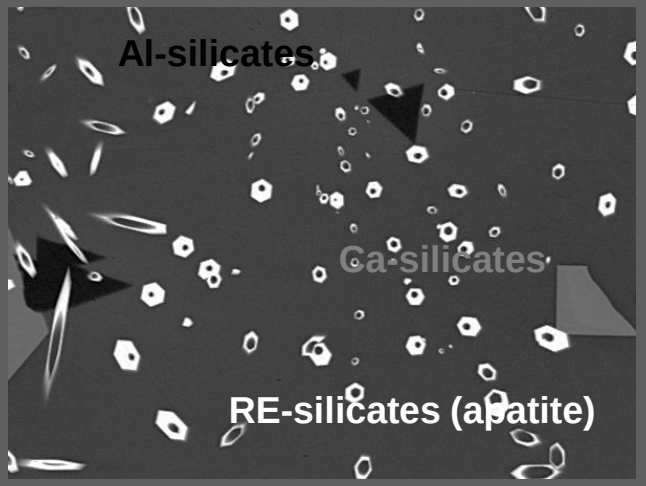
Micro-tomography experiments (ESRF- ID19)

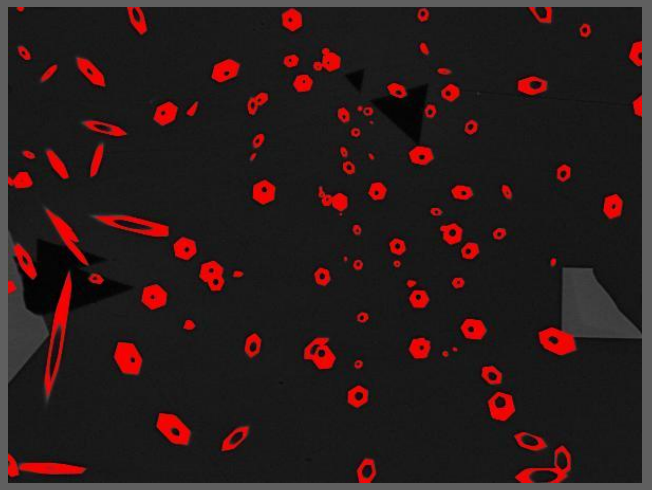
Preferential crystallization of phases around ruthenium oxide seeds

Kinetic of apatite crystallization

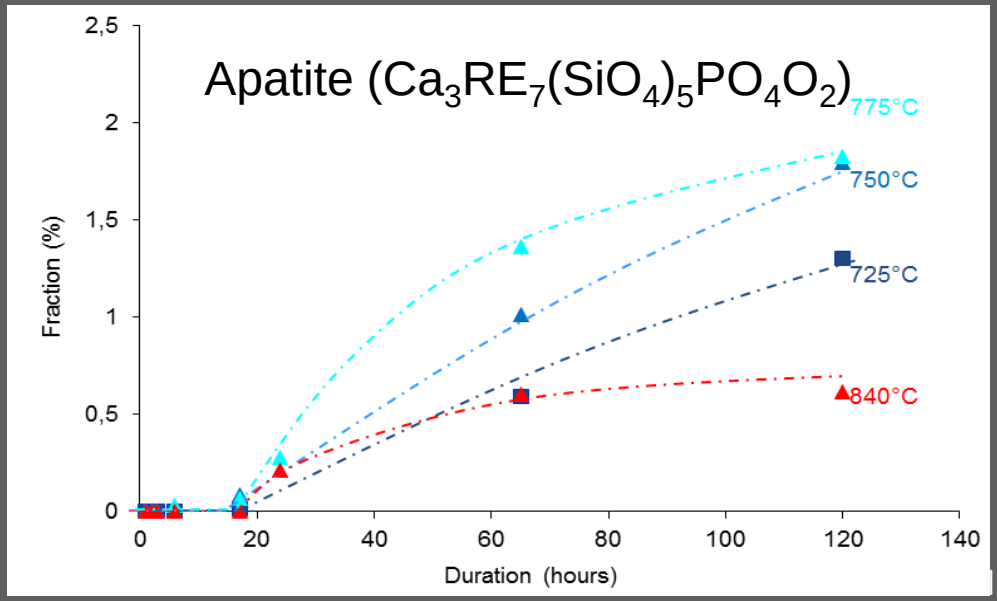
⇒ Quantification by 2D SEM Imaging analyses







Validation by
3D imaging Microtomography

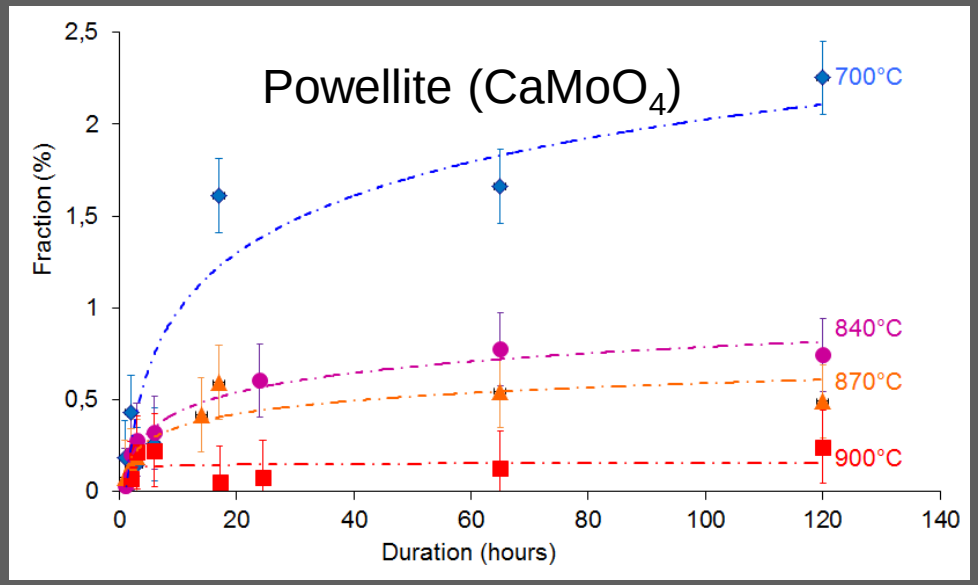


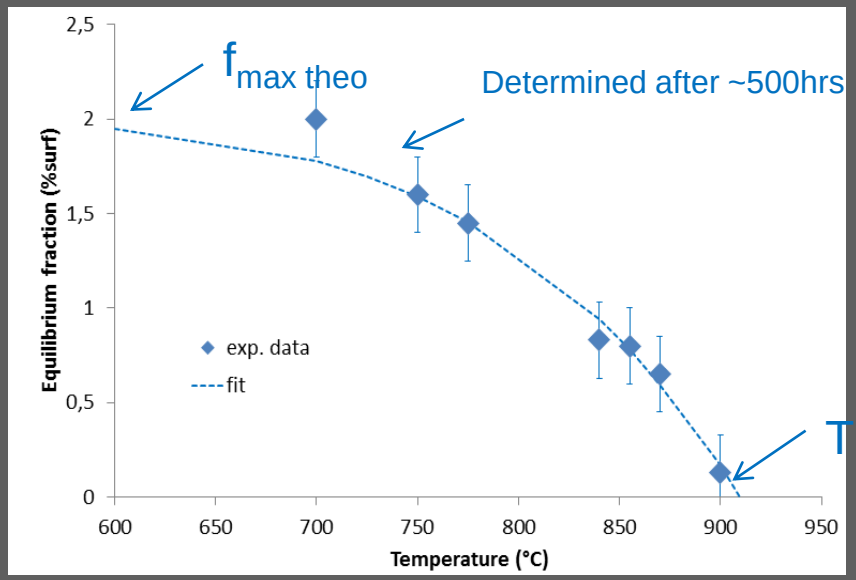
Evolution of crystalline fraction of apatite with time from 775°C to 840°C in complex UOX glass

Thesis Olivier Delattre (CEA Marcoule 2014)

Kinetic of crystallization can be fitted as a JMAK equation

JMAK : Johnson, Mehl, Avrami and Kolmogorov





$$f(t) = f_{max}\{1 - exp[-k(t^n)]\}$$

$f(t)$: *Crystalline fraction*

$n = 1{,}5$: *Avrami exponent*

$k = 3\ 10^{-7}$: *Crystallisation constant*

$$f(T) = f_{max}\left\{1 - exp\left[-B_L\left(\frac{1}{T} - \frac{1}{T_{liq}}\right)\right]\right\}$$

$f_{max\ théo} = 2\%_{surf}$

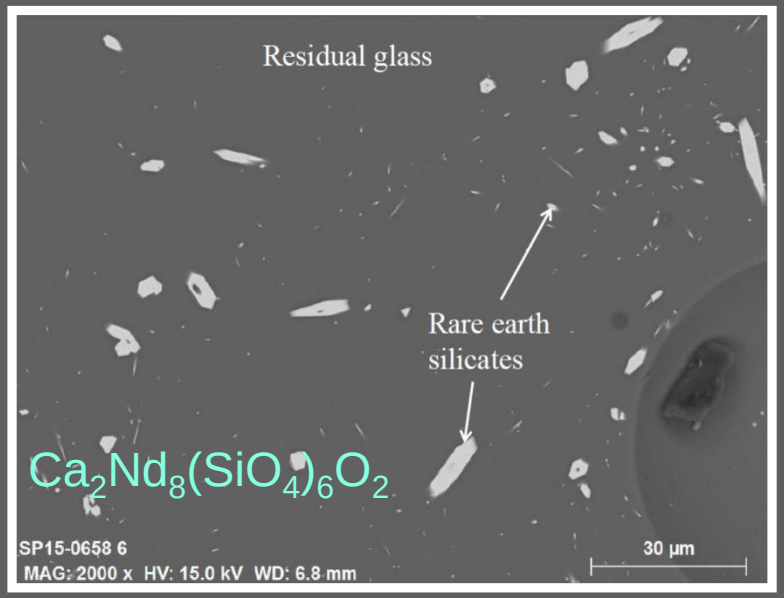
$T_{liq} = 1183\ K$

$B_l = 2000K$

Ea cristallisation ~ Ea viscosity ~ 200-250 KJ/mol

Crystallization is probably not limited by diffusion, but controlled by viscosity

Dissolution kinetics of apatite in neodymium borosilicate glass



Thesis Judith Fournier - Renaud (CEA Marcoule 2017)

"Modeling of dissolution kinetics of rare earth crystals in a borosilicate glass melt"J. Fournier, E. Régnier, F. Faure, X. Le Goffc, H-P. Brau, E. Brackx, O. Pinet, in publish, JACers 2017

The undissolved volume fraction with time can be fitted with the JMAK equation (above T_l)

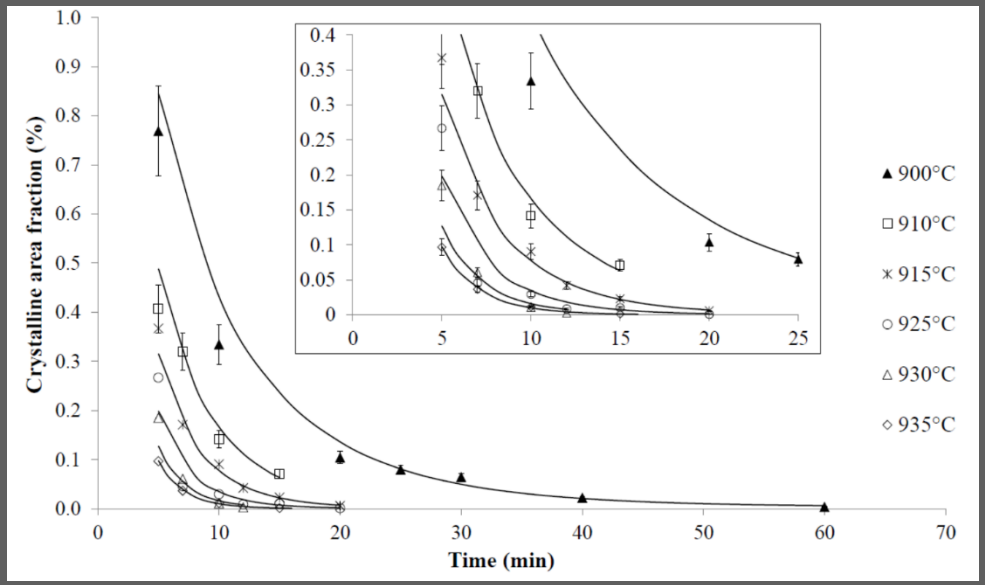
$$f_v(t) = f_{v0}\{exp[-k(t^n)]\}$$

$fv(t)$: *Undissolved volume cristalline fraction*

f_{v0} : *Initial crystalline fraction*

$n = 0{,}84$: *Avrami exponent*

k = *Dissolution constant*

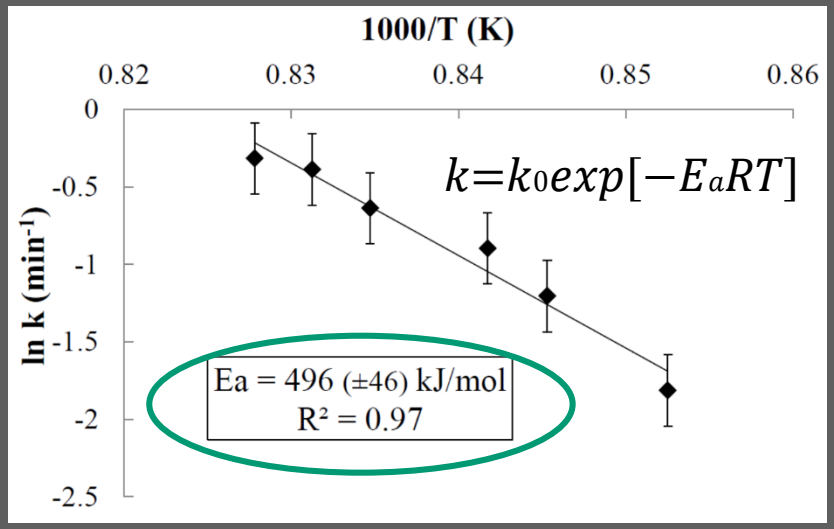


According to Christian (1975), the dissolution is controlled by diffusion

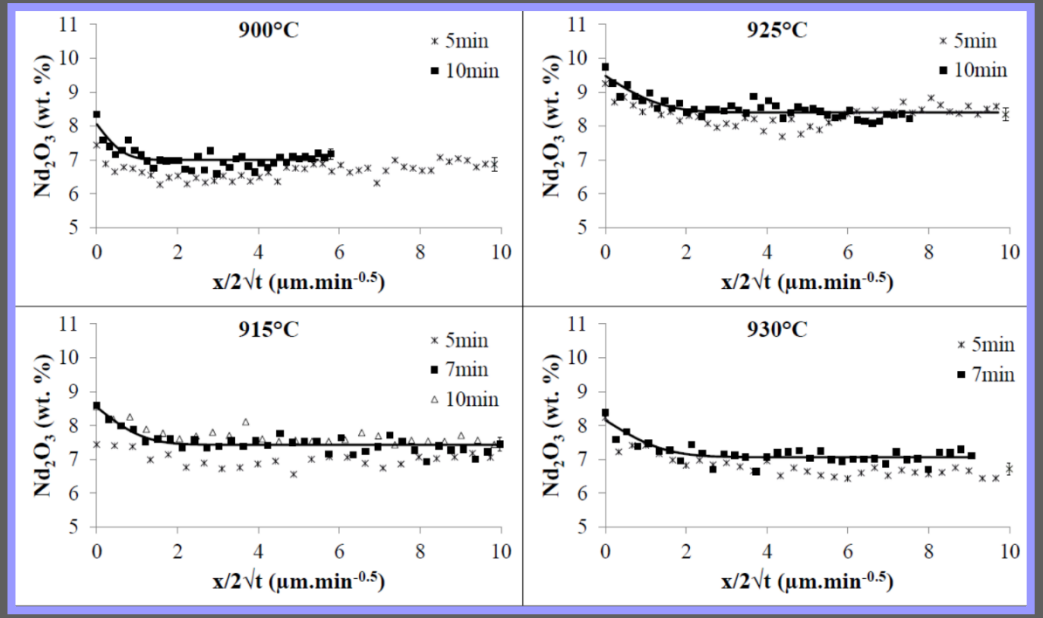
Christian « The theory of transformations in metals and alloys » part 1, 1975 , Pergamon

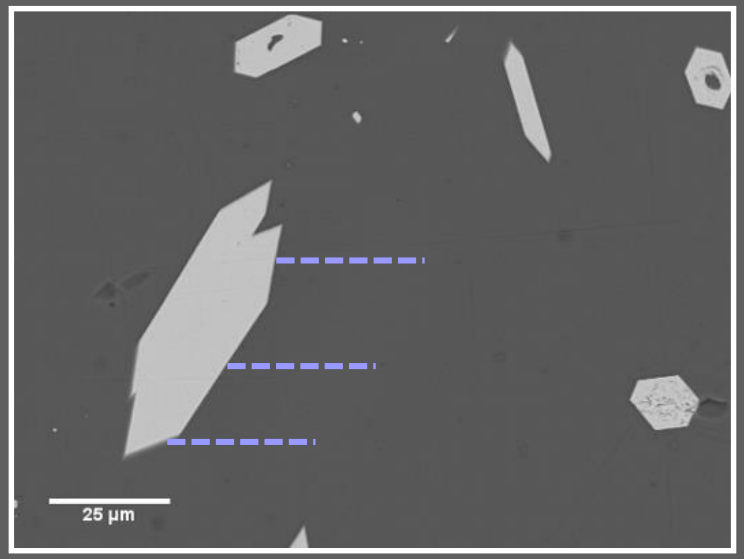
Dissolution kinetics controlled by diffusion in rare earth borosilicate glass

Activation energy of dissolution : E_a



Chemical profiles of Nd_2O_3 at the crystal/melt interfaces for 900°C, 915°C, 925°C and 930°C obtained by microprobe

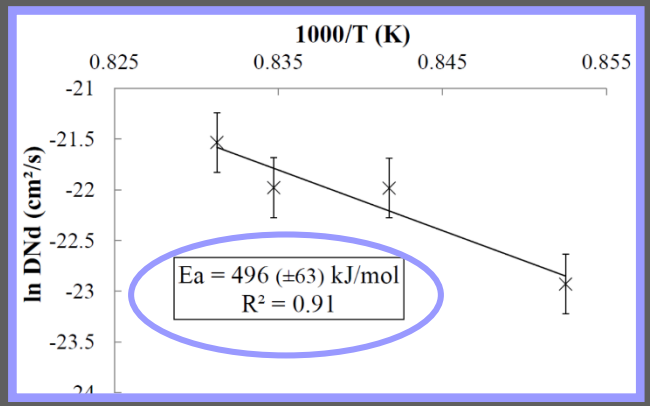




Effective Binary Diffusion Coefficient (EBDC) of Nd

$$C=C\infty+C0-C\infty erfc(-\alpha)erfc(x2\sqrt{DNd}t-\alpha)$$

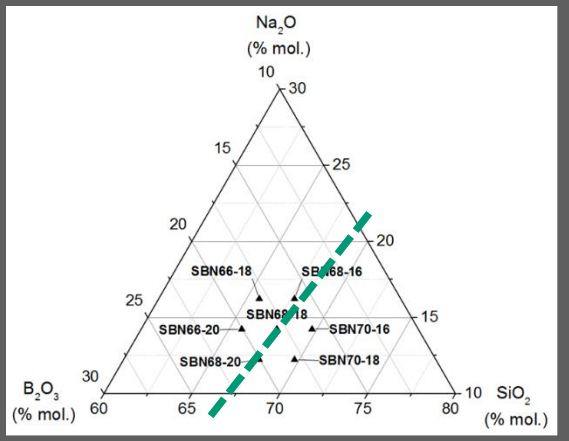
where α satisfies: $\sqrt{\pi}\alpha e\alpha 2erfc(\alpha)=C0-C\infty Cc-C0$

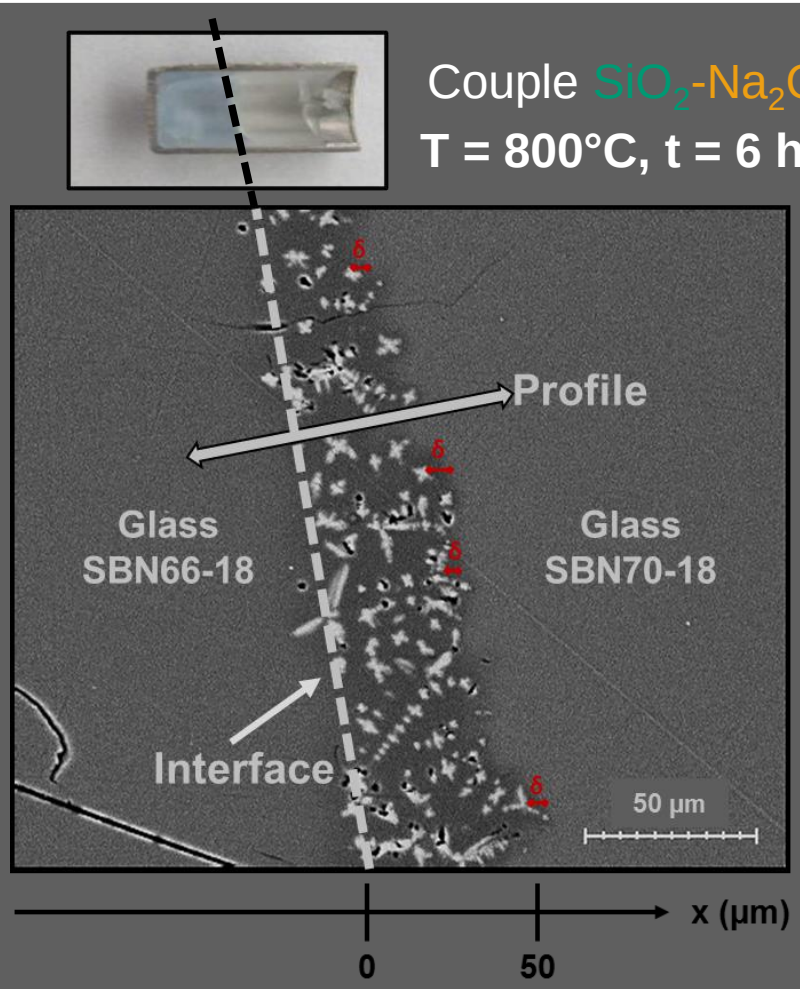


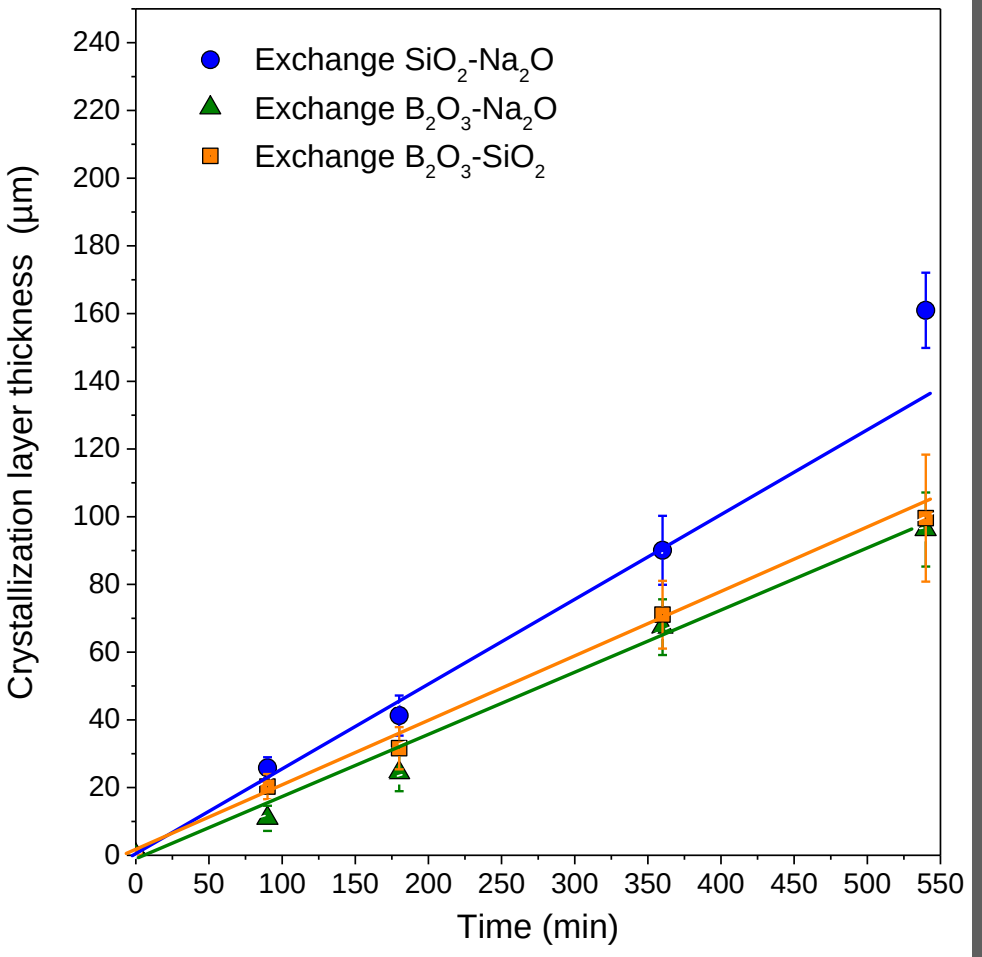
Example of kinetic controlled by multicomponent diffusion in borosilicate glass

Thesis Hélène Pablo (CEA Marcoule 2017)

H. Pablo, S. Schuller, M.J. Toplis, E. Gouillart, S. Mostefaoui, T. Charpentier, M. Roskosz "Multicomponent diffusion in sodium borosilicate glasses" In Journal of Non-Crystalline Solids, 2017







Cristobalite crystallization controlled by multicomponent diffusion in borosilicate glass

Chemical interdiffusion coefficient corresponding to Eigen values of the multicomponent matrix for the primary diffusive exchange reaction

$$D_{SiO2-Na2O} = 8{,}57 \times 10^{-10}\ cm^2/s$$

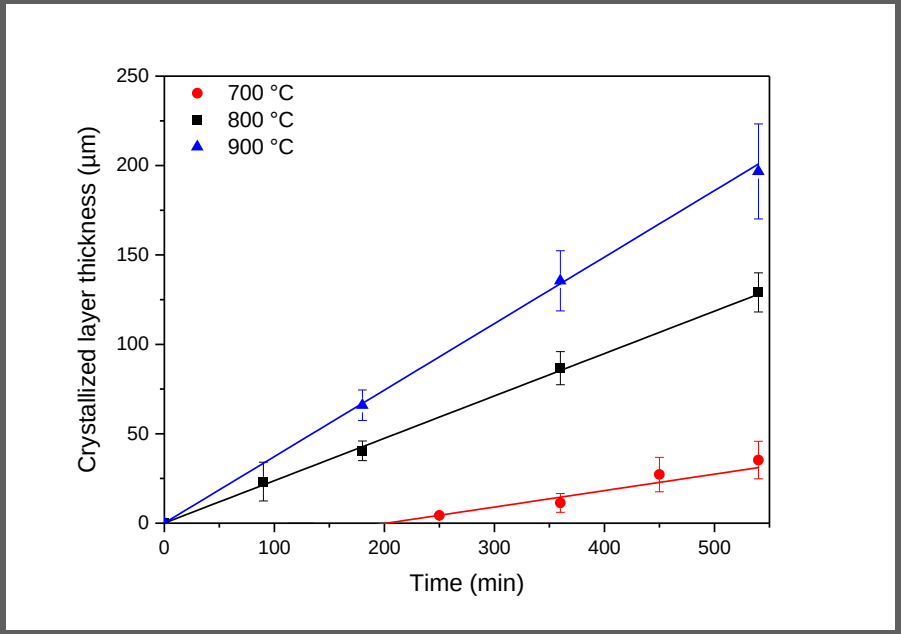
$$0{,}10\ B_2O_3 + 0{,}90\ SiO_2 \leftrightarrow 1\ Na_2O$$

Validation of the dendritic growth model of Christensen, Cooper and Rawal

$$U = \frac{[D_{SiO_2-Na_2O}](C_0 - C_s)}{[\delta(1 - C_s)]}$$

- U: Rate of growth
- δ: Effective bondary-layer thickness
- D: Chemical interdiffusion coefficient of SiO_2-Na_2O system (m^2/s)

$$U = 4{,}28.10^{-7}\ cm/s$$



$Ea_{crystallization}$ = 60 kJ/mol

$Ea_{viscosity}$ = 200 kJ/mol

$Ea_{Conductivity}$ = 87 KJ/mol

The limitation of the crystallization is not due to viscosity but is probably due to the migration of sodium away from crystals and due to the local multicomponent diffusion

Crystallization- Summary

- ✓ Viscosity
- ✓ Autodiffusion
- ✓ Multicomponent diffusion

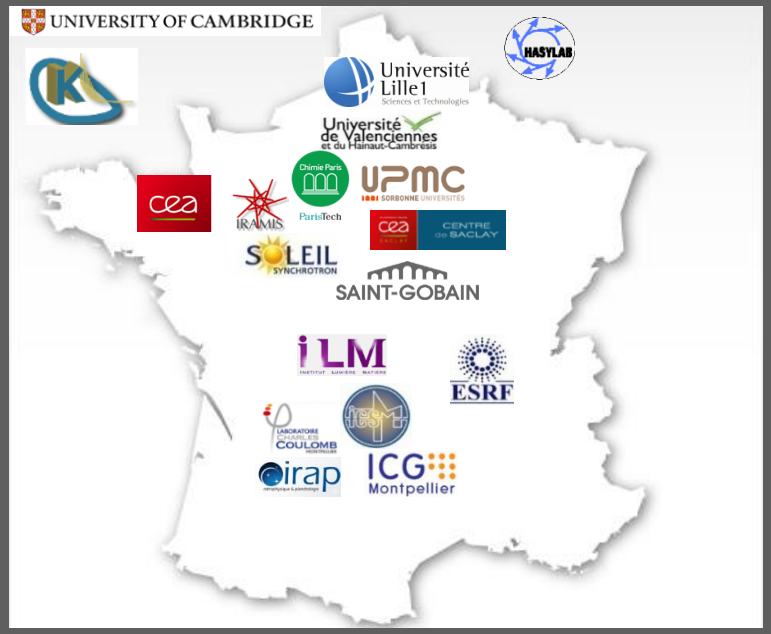
have a high impact on crystallization kinetic

Take into account the multicomponent diffusion will probably improves theoretical models

Empirical models lead to accurately describe mechanism of crystallization

LCV
Joint Vitrification Lab
CEA AREVA

In cooperation with University



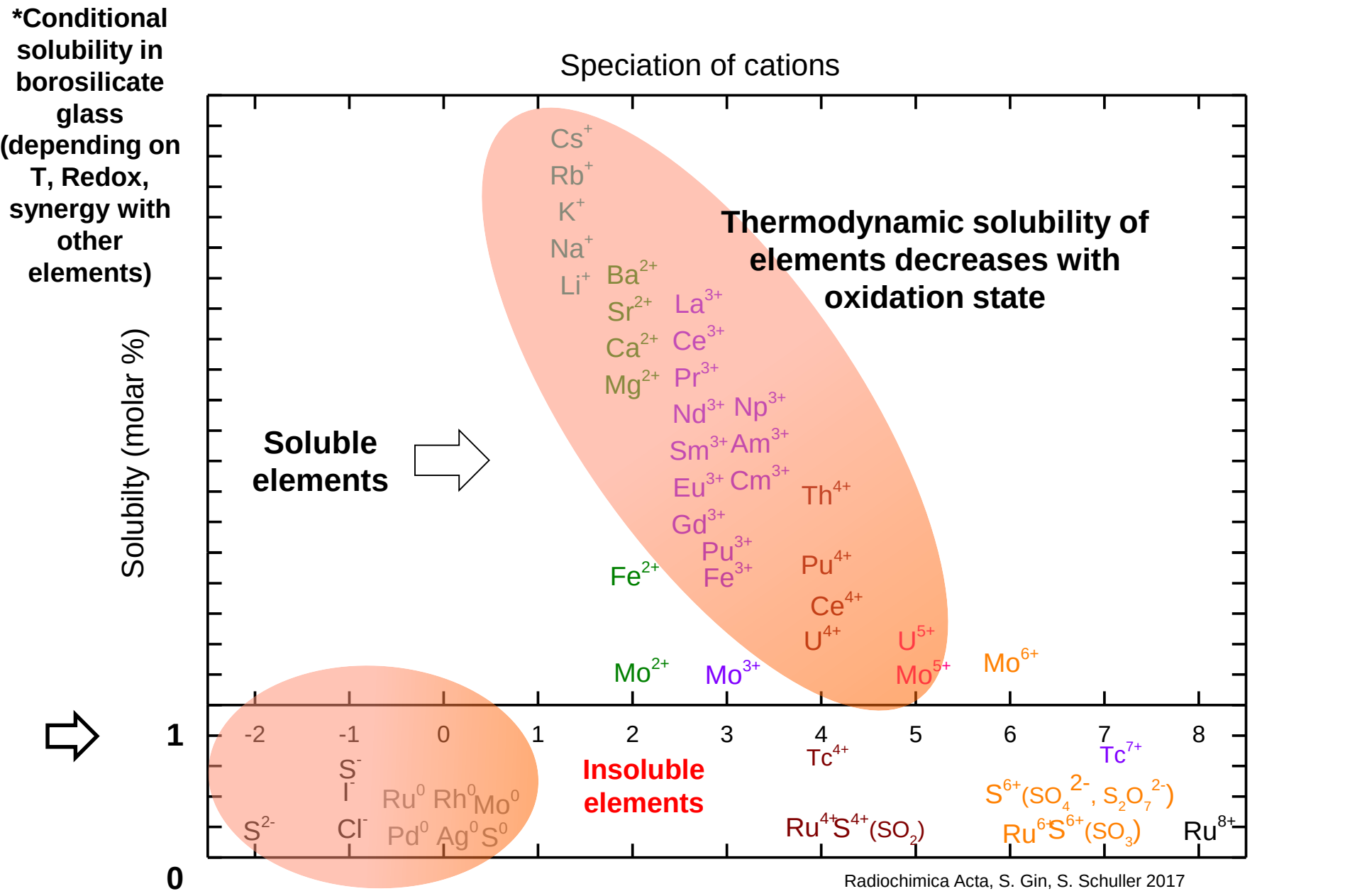
CEA Marcoule
CEA Saclay
FRANCE

Thermodynamique des matériaux
Hautes températures
Calculs
Applications
Mesures expérimentales
TherMatHT
GDR CNRS

cnrs GDR Verres
GDR 3338

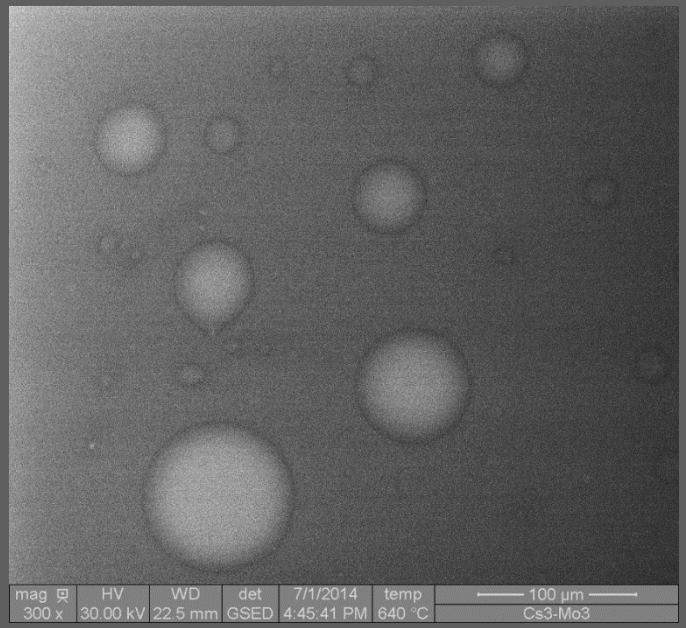
UNION POUR LA SCIENCE ET LA TECHNOLOGIE VERRIÈRES

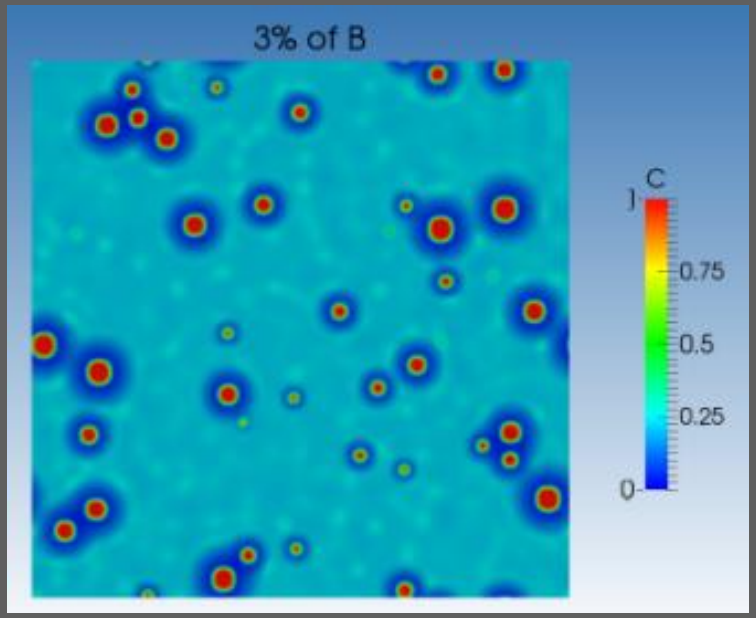
Thank you for your attention



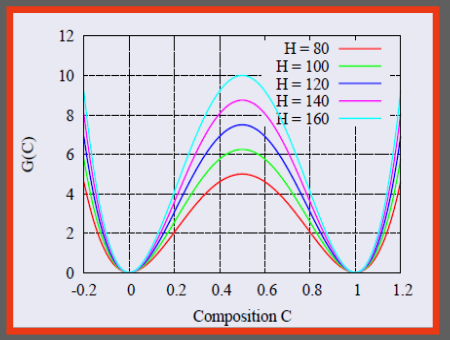
Radiochimica Acta, S. Gin, S. Schuller 2017

Cahn-Hillard : A theorical model can helps to predict the kinetic of coalescence





$$G(C) = H(T) \times C^2(1-C)^2$$



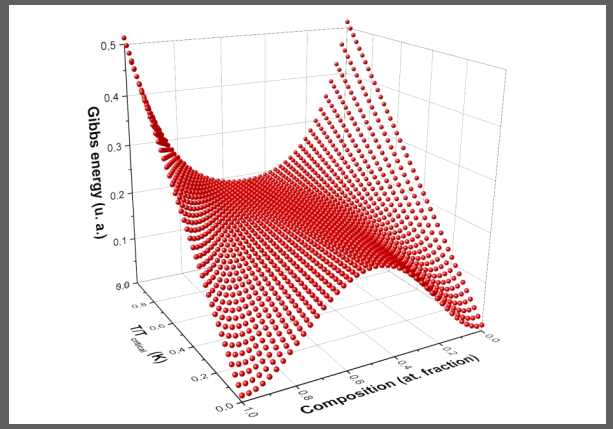
Cahn-Hillard model 1958

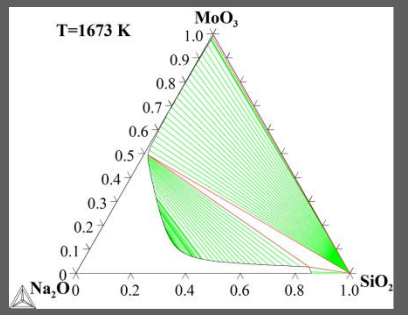
Energie de Gibbs *Energie d'interface*

$$F = \int_V G(C) + \frac{1}{2}\kappa|\nabla C|^2 dV$$

$\kappa|\nabla C|^2$: Coefficient de gradient d'énergie × Gradient de *concentration*

CALPHAD calculation of SiO_2-B_2O_3-Na_2O-MoO_3



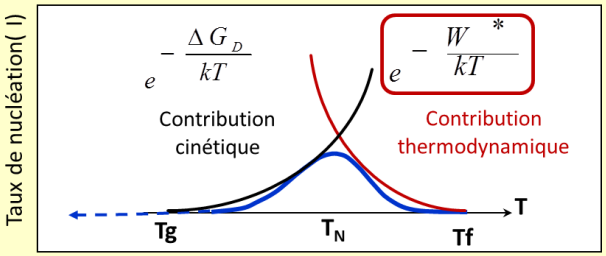


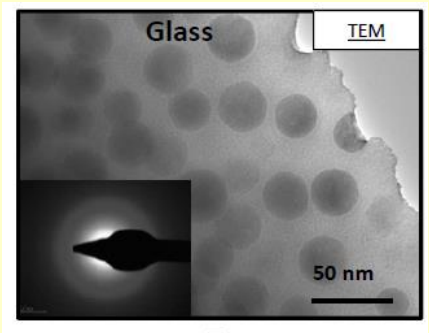
3. Quelles cinétiques de transformations de phases prendre en compte (nucléation, croissance) ?

Exposés J. Rogez / S. Schuller / M. Allix : Prise en compte des cinétiques de nucléation-croissance

Théorie CNT

$$I = K \exp\left(-\frac{\Delta G_D + W^*}{kT}\right)$$



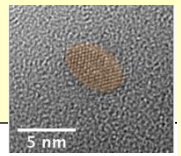


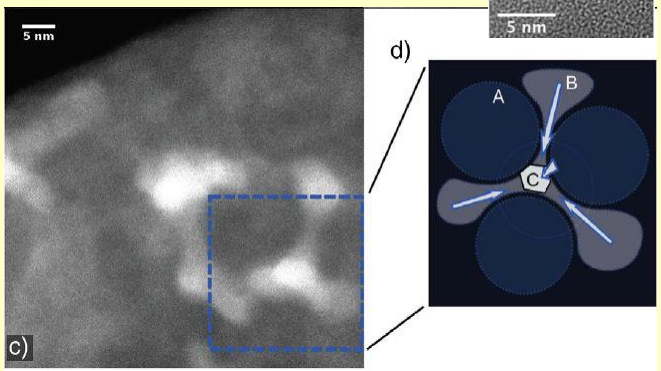
Les hypothèses simplificatrices limitent son utilisation

- Morphologie des germes
- Composition
- Diffusion

Les théories plus récentes

- Dynamique d'amas
- Fonctionnelle de la densité
- Modèles de germe non classique
- Système désordonné non-homogène
- Approche généralisée de Gibbs (GNT)
- Modèle à deux-étapes



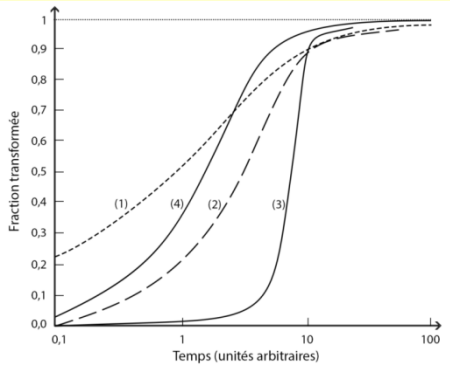


Modèle plus complexe à considérer

Approche empirique

Loi cinétique de Kolgomorov-Johnson-Mehl-Avrami (KJMA)

$$\frac{V_\beta}{V} = 1 - \exp\left(-kt^n\right)$$



Modèle simple – pourrait être utilisé pour un 1er calcul

Nucleation and growth

Schematic diagram illustrating possible effects of liquid-liquid phase separation on crystallization phenomena

(A) Crystallize droplets served as seeds for the subsequent crystallization of the matrix phase