Glass crystallization – recent advances

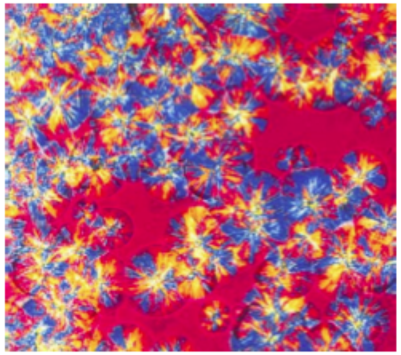
Laurent Cormier

Institute of Mineralogy, Material Physics and Cosmochemistry,

University Pierre et Marie Curie –

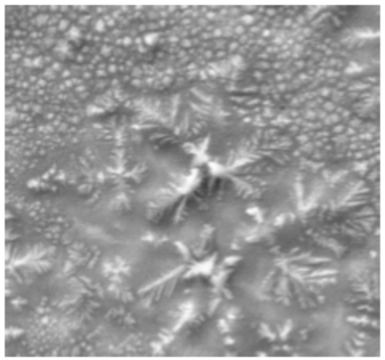
CNRS, Paris, France

POLYMER



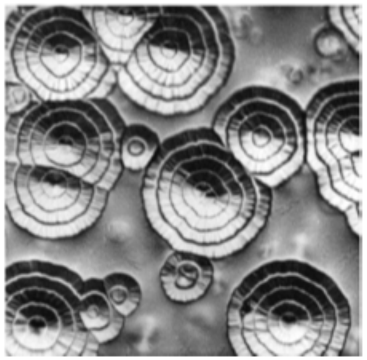
Polypropilene

METALLIC



$Zr_{55}Cu_{30}Ni_5Al_{10}$

& INORGANIC GLASSES



$Na_2O{\cdot}2CaO{\cdot}3SiO_2$

Collaborators

IMPMC, Paris
Olivier Dargaud
Gerald Lelong
Nicolas Menguy
Georges Calas

Saint-Gobain Recherche
Cécile Jousseaume
Gilles Quérel
Sophie Papin

LPN, Marcoussis
Gilles Patriarche

Elettra, Italie
Luca Olivi

SOLEIL, France
Nicolas Trcera
Stéphanie Belin

APS, USA
Mat Newville

✓ ANR

AGENCE NATIONALE DE LA RECHERCHE ANR

Structure and nucleation

Structural similarity between the glass and crystal

First to understand the homogeneous / heterogeneous behavior

Idea : work of formation for the nucleus (thermodynamic barrier to form a critical nucleus) is small if short range order (SRO) and medium range order (MRO) of glass and crystal are similar

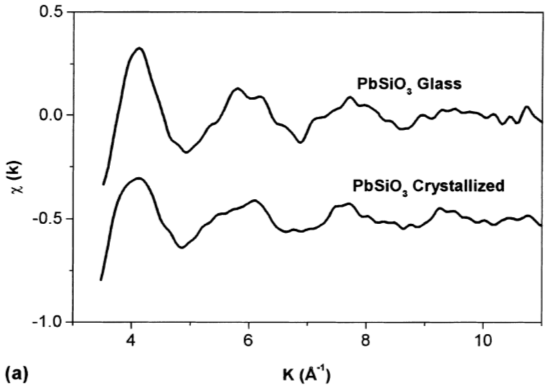
Focus on cation environment and anion structure

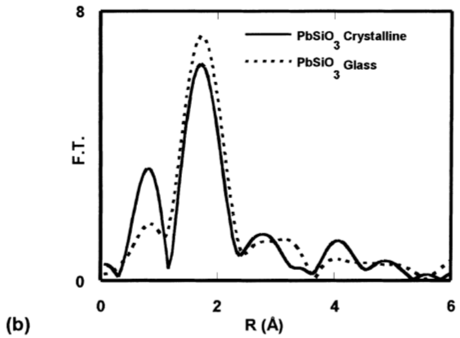
$\Rightarrow$ for glasses displaying measurable homogeneous nucleation rates, both the cationic and anionic arrangements in glass and isochemical crystal are similar but several exceptions to this trend are found

Müller et al. Z. Kristallogr., 200 (1992) 287
Müller et al. J. Non-Cryst. Solids, 155 (1993) 56

Early EXAFS investigation

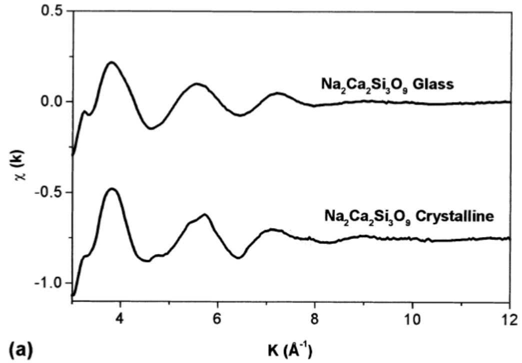
Pb L3-edge EXAFS

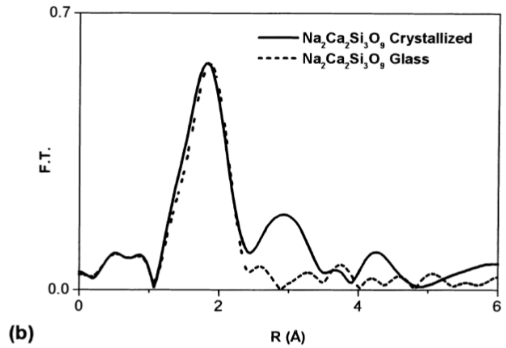




$PbSiO_3$

Ca K-edge EXAFS





$Na_2Ca_2Si_3O_9$ combeite

Mastelaro et al. JNCS 262 (2000) 191

Medium range order (MRO)

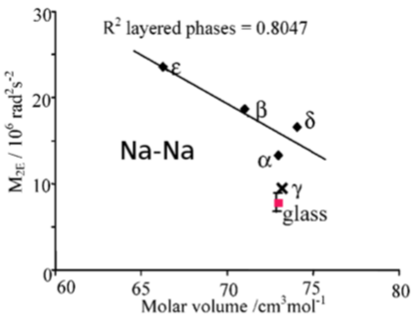
- Importance of organisation at medium range order

NMR

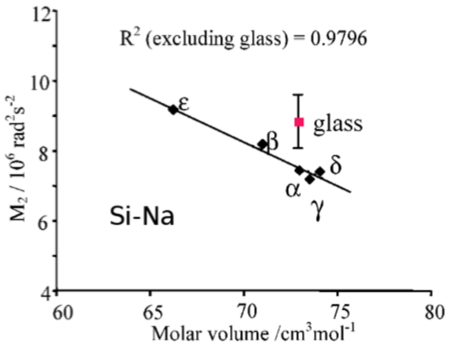
$$M_2 \propto \int \frac{g(r)}{r^6} 4\pi r^2 dr$$

• Li-Li distances close for the glass and the crystal, but Na-Na distances longer in the glass compared to the cristal *(M2 smaller)*

• Si-Li distances close for the glass and the cristal, but Si-Na distances shorter in the glass compared to the cristal *(M2 longer)*

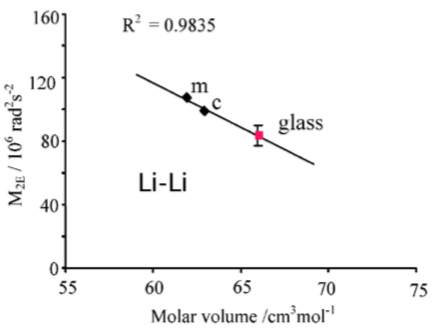


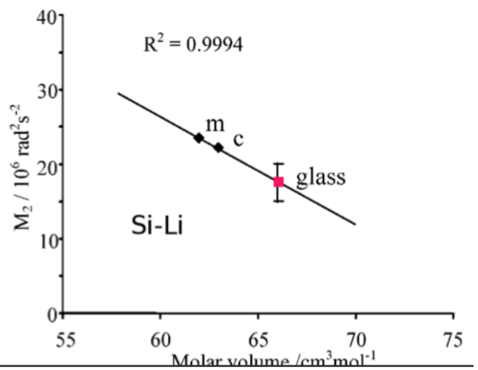
(a) $Na_2O{\bullet}2SiO_2$



(a) $Na_2O{\bullet}2SiO_2$

NS2
heterogeneous





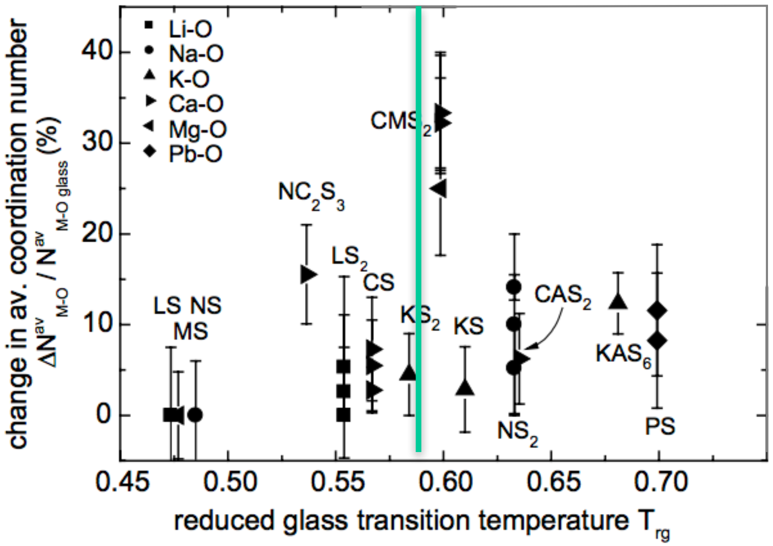
LS2
homogeneous

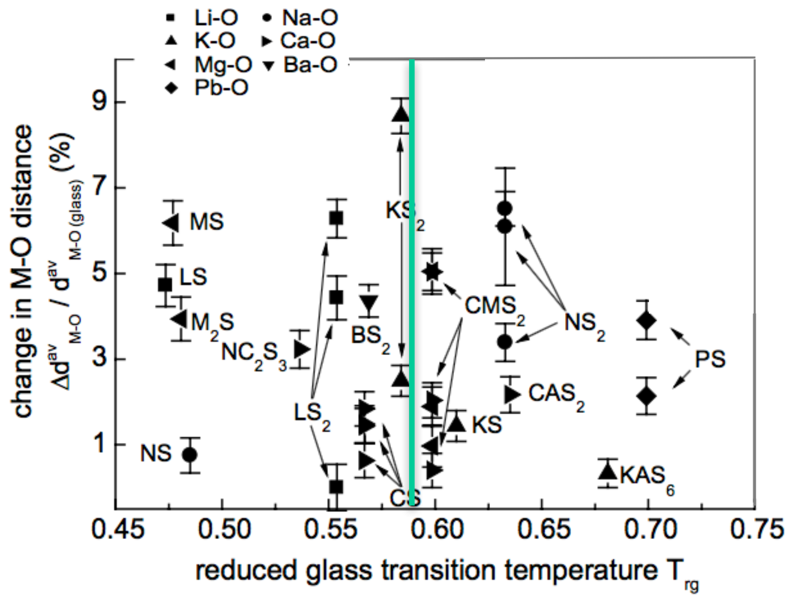
Longstaffe et al. J. Phys. Chem. C 112(2008)6151
Chen et al. J. Phys. Chem. C 113(2009)20725

A more systematic study: short range order

Trg = Tg / Tliq < 0.58 volume nucleation

Fokin et al. J. Non-Cryst. Solids, 321 (2003) 52



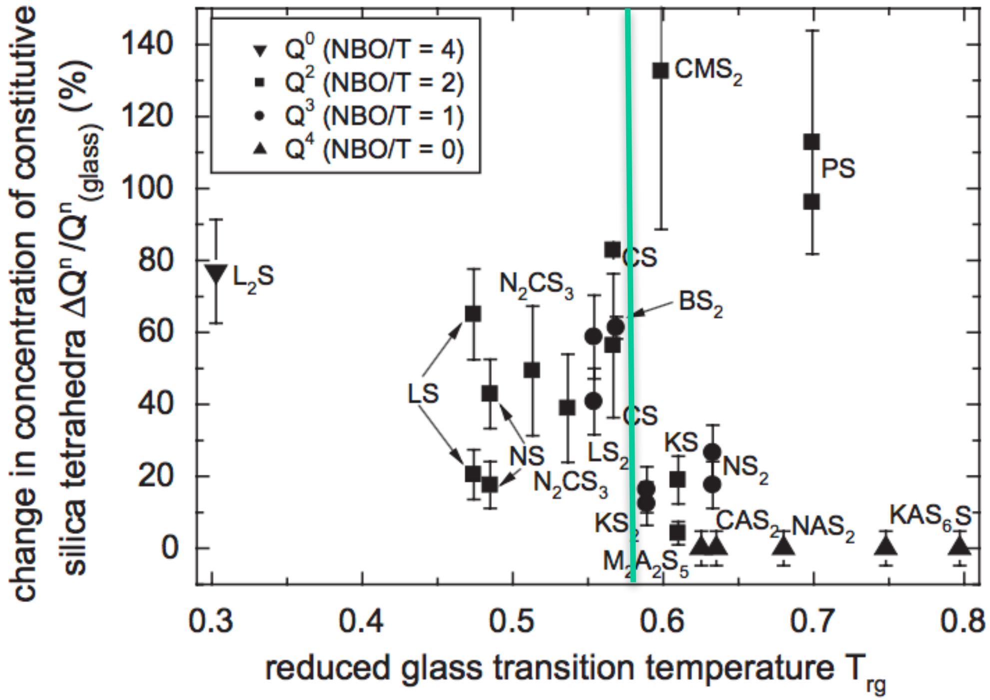


no direct proof that the short-range structure affects nucleation in glasses

Deubener, JNCS 351 (2005) 1500

A more systematic study: medium range order

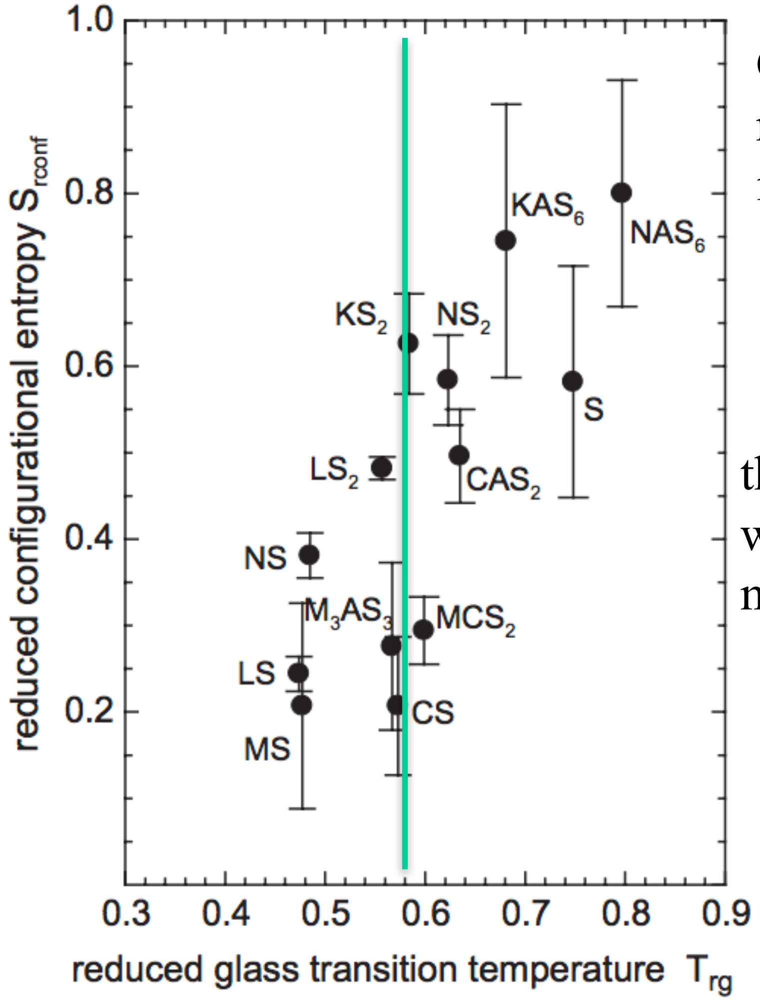
Trg = Tg / Tliq < 0.58 volume nucleation



Change in concentration of constitutive silica tetrahedra $\Delta Q^n/Q^n_{glass}$ vs. reduced glass transition temperature Trg

Deubener, JNCS 351 (2005) 1500

A more systematic study: medium range order



Configurational entropy is a thermodynamic measure of the structural disorder in the short and intermediate ranges of a liquid

the number of configurational states is reduced when the melt is cooling down in the metastable state

Trg = Tg / Tliq < 0.58 volume nucleation

Deubener, JNCS 351 (2005) 1500

Is the local site important ?

- Interest in transition elements, Ti, Zr, Ni
- Nucleating agents
- Sometimes additional optical properties

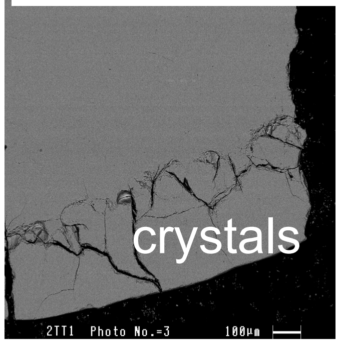
•Questions

are there specific sites for nucleation such as specific coordination number or symmetry ?

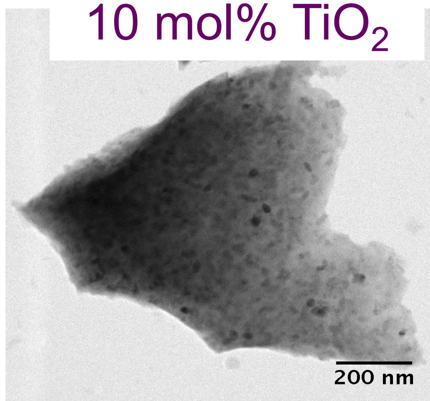
Effect of TiO_2 content

JEOL 2100F IMPMC

Without TiO_2



10 mol% TiO_2



Champ clair

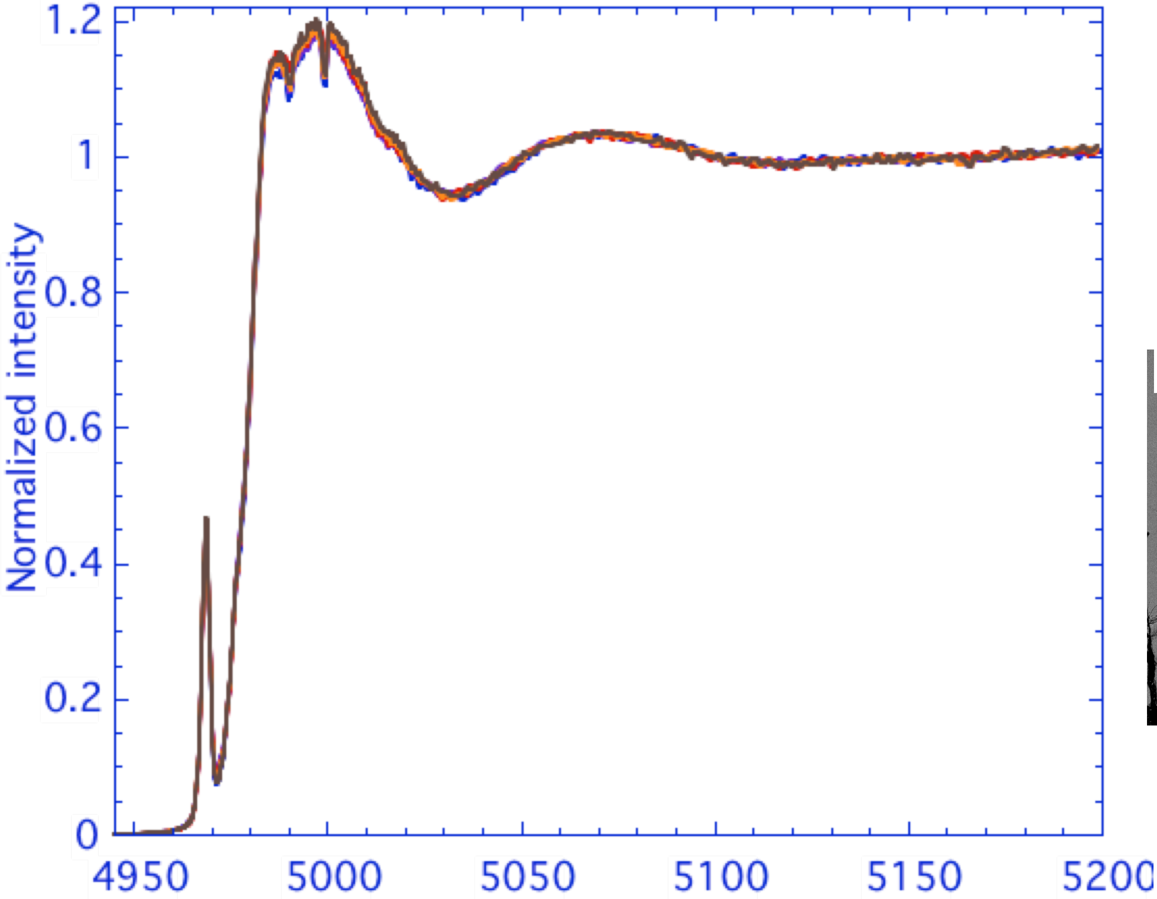
Threshold between 7-8 mol % TiO_2

Fokin and Zanotto, J. Non-Cryst. Solids 246(1999)115

- Cristallization in volume
  for x > 7 % mol TiO_2

- Phases $(MgTi_2O_5)_{0.4}(Al_2TiO_5)_{0.6}$

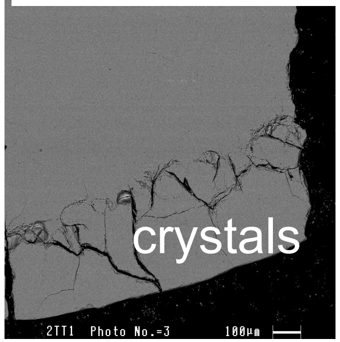
Effect of TiO_2 content



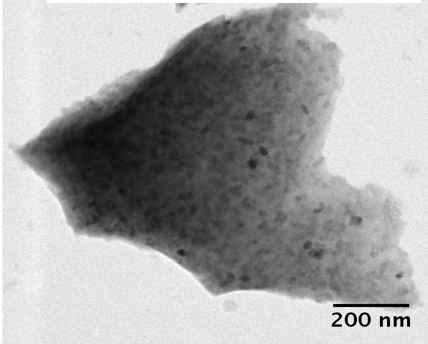
Ti K-edge XANES LUCIA

JEOL 2100F IMPMC

Without TiO_2



10 mol% TiO_2



Champ clair

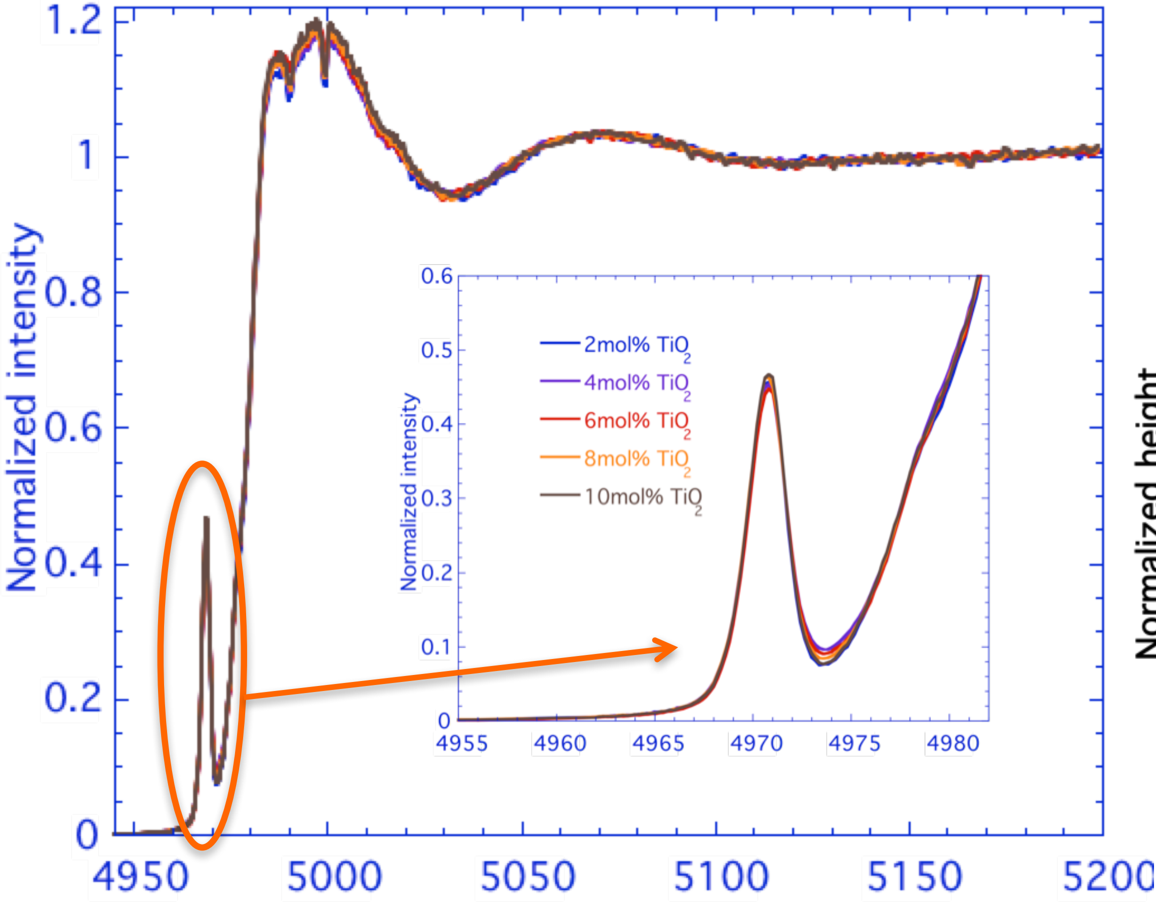
Threshold between 7-8 mol % TiO_2

- Cristallization in volume
  for x > 7 % mol TiO_2

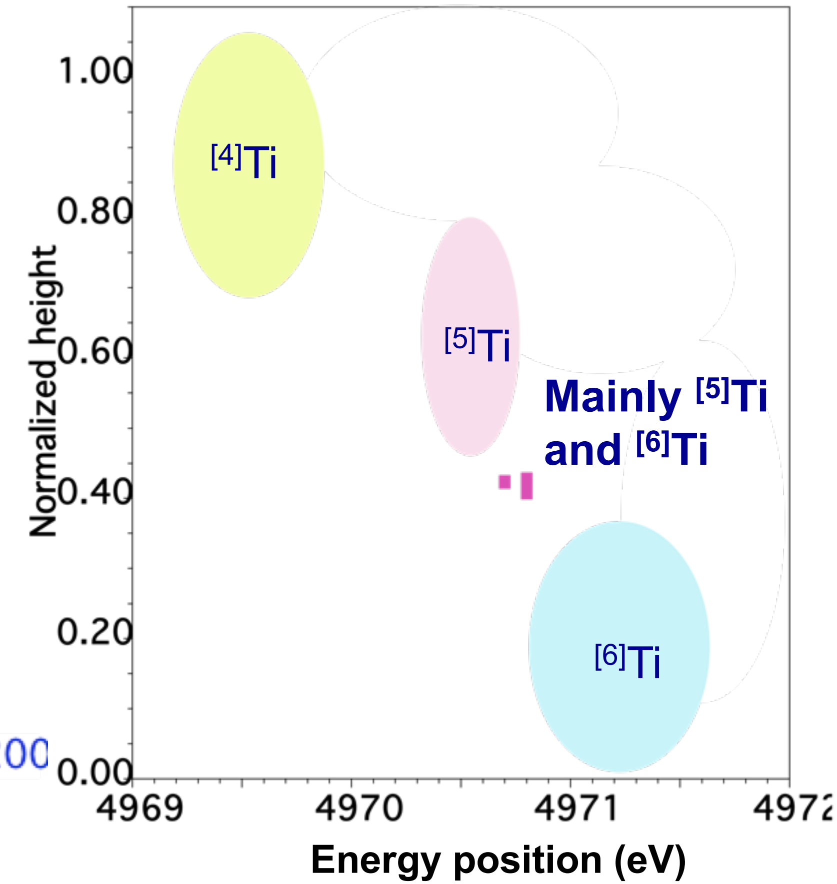
⇒ specific site for nucleation ?

⇒ evolution of the Ti environment with TiO_2 content ?

Effect of TiO_2 content



Ti K-edge XANES LUCIA

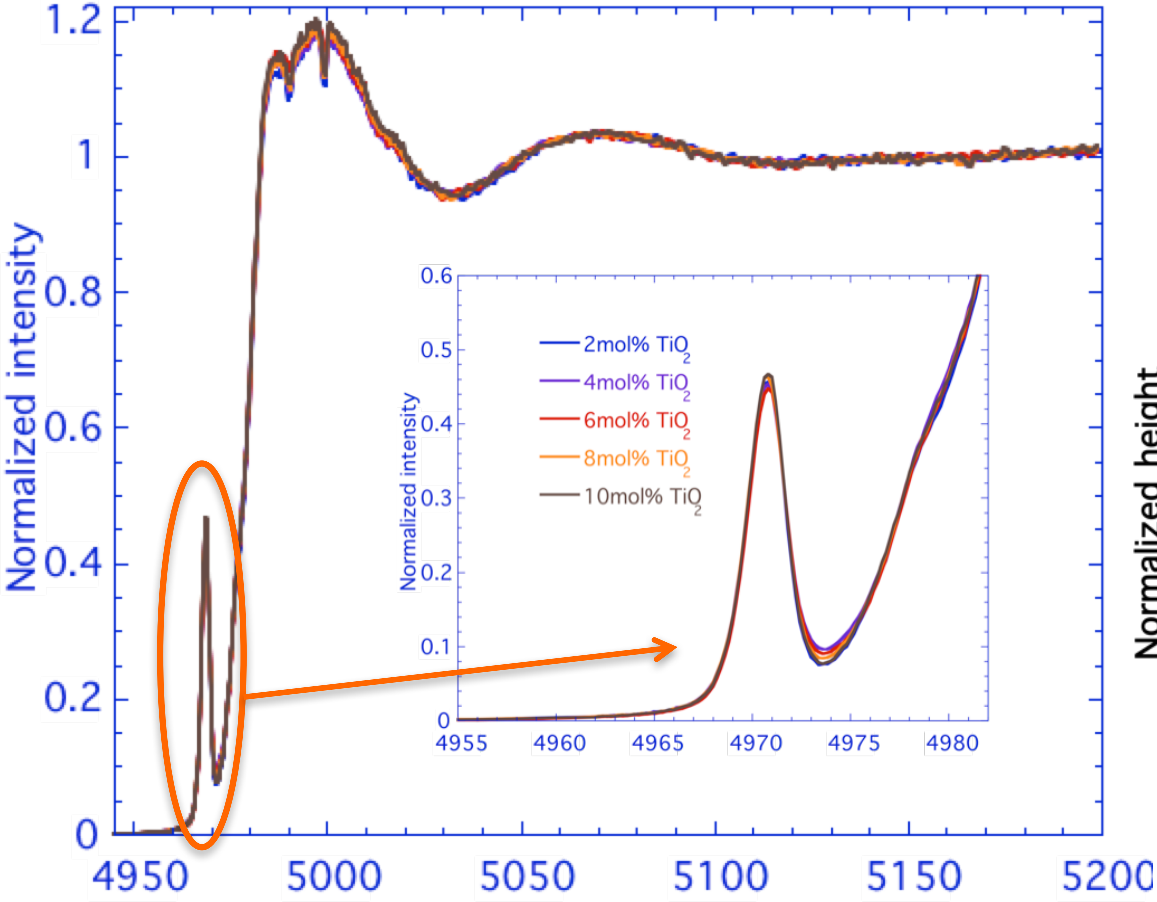


Threshold between 7-8 mol % TiO2

Fokin and Zanotto, J. Non-Cryst. Solids 246(1999)115

Cormier et al. Crystal Growth & Design 11(2011)311

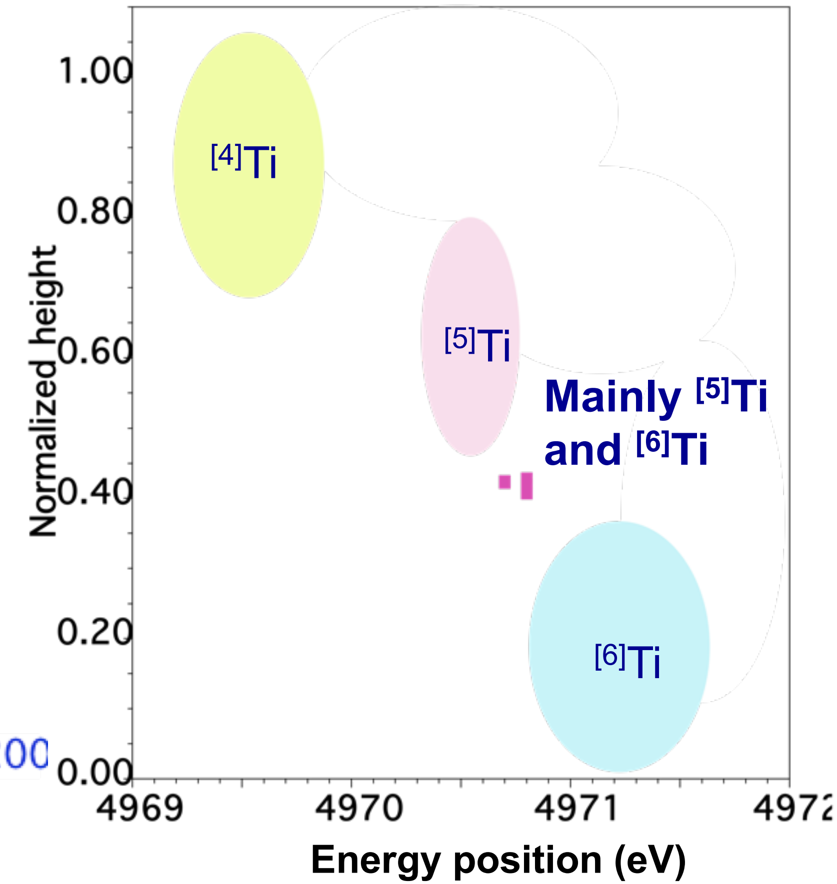
Effect of TiO_2 content



Threshold between 7-8 mol % TiO2

⇒ **not related to Ti local environment**

Ti K-edge XANES LUCIA



Cormier et al. Crystal Growth & Design 11(2011)311

Various aluminosilicate glasses with and without ZrO_2

Substitution of the alkali – alkaline earth – metal cation

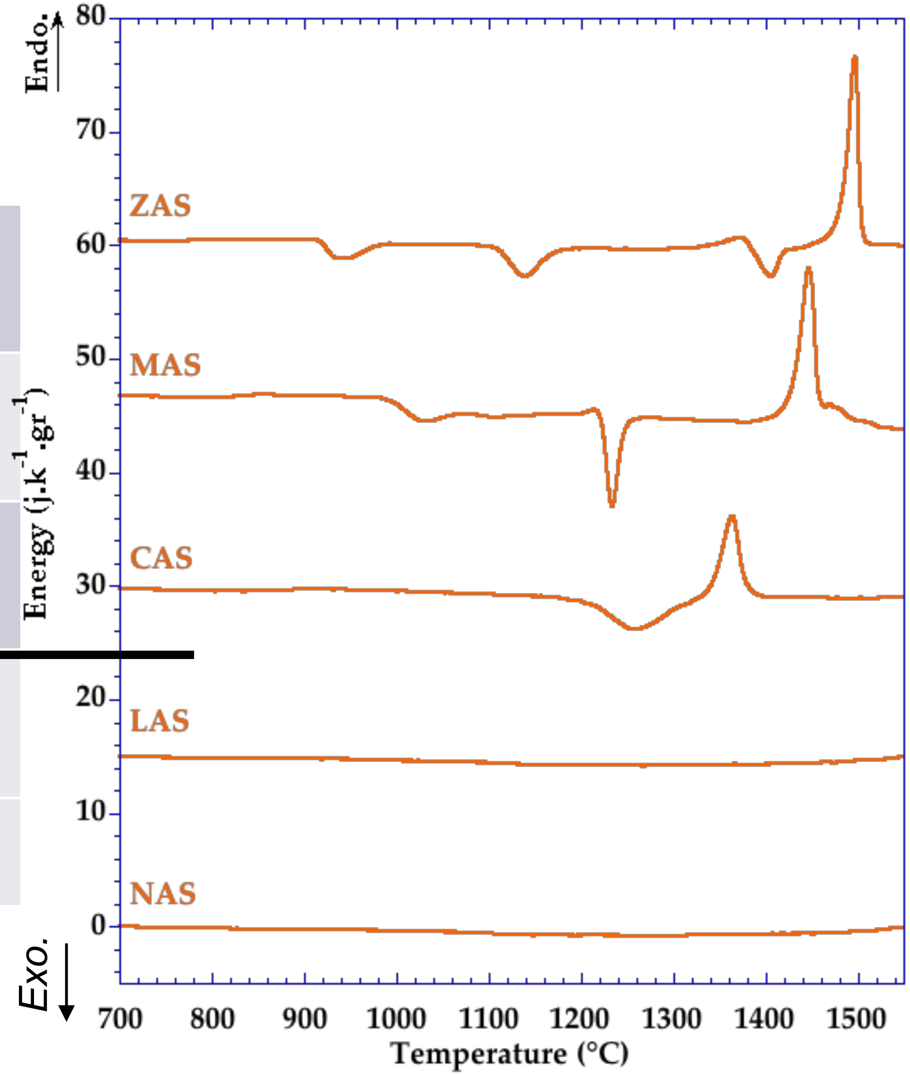
ZnAS-Zr	$1ZnO-1,21Al_2O_3-6,8\ SiO_2$	
MgAS-Zr	$1MgO-1,21Al_2O_3-6,8\ SiO_2$	
CaAS-Zr	$1CaO-1,21Al_2O_3-6,8\ SiO_2$	
ZnMgAS-Zr	$1(MgO/ZnO)-1,21Al_2O_3-6,8\ SiO_2$	
LiAS-Zr	$1Li_2O-1,21Al_2O_3-6,8\ SiO_2$	
NaAS-Zr	$1Na_2O-1,21Al_2O_3-6,8\ SiO_2$	

DSC measurements

Setaram Multi-HTC 96, under N2 flux

ZnAS-Zr	1ZnO-1,21Al_2O_3-6,8 SiO_2	
MgAS-Zr	1MgO-1,21Al_2O_3-6,8 SiO_2	
CaAS-Zr	1CaO-1,21Al_2O_3-6,8 SiO_2	
LiAS-Zr	1Li_2O-1,21Al_2O_3-6,8 SiO_2	
NaAS-Zr	1Na_2O-1,21Al_2O_3-6,8 SiO_2	

DSC 5 K.min^{-1}

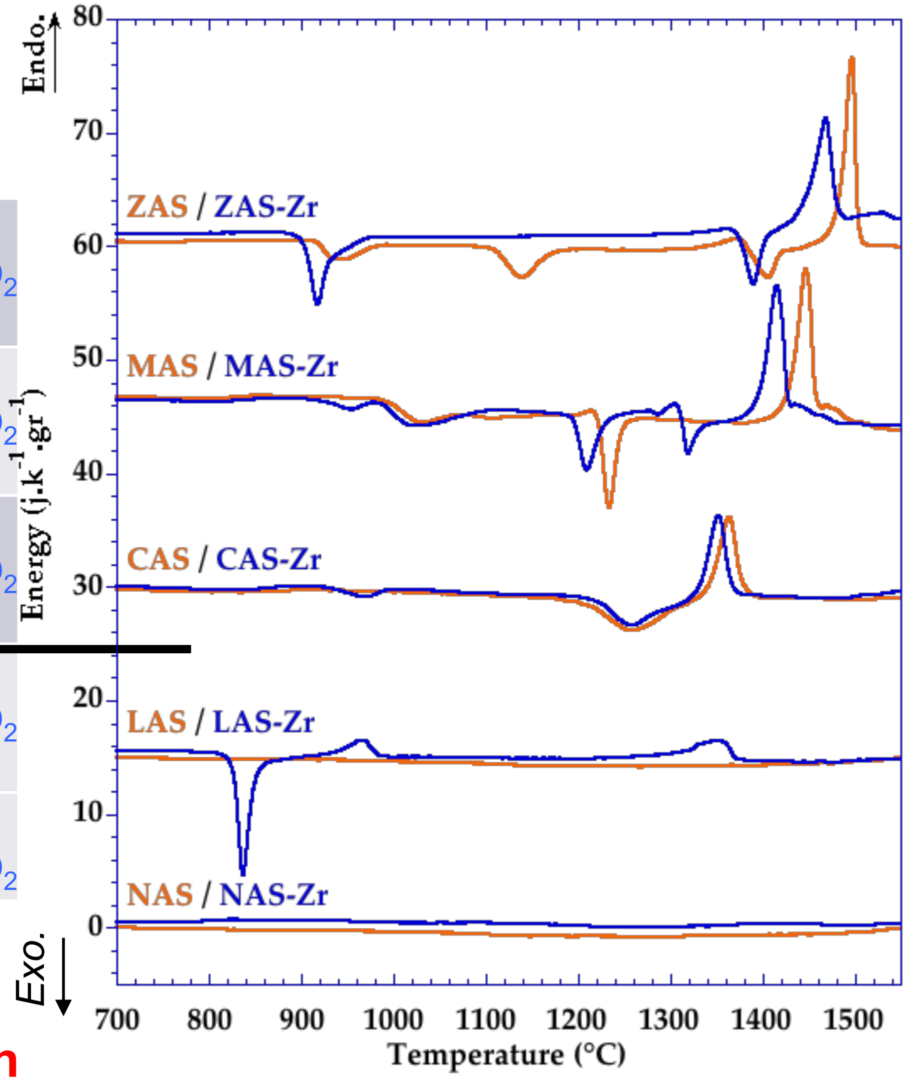


DSC measurements

Setaram Multi-HTC 96, under N2 flux

ZnAS-Zr	1ZnO-1,21Al_2O_3-6,8 SiO_2	4$\%_{wt}$ ZrO_2
MgAS-Zr	1MgO-1,21Al_2O_3-6,8 SiO_2	4$\%_{wt}$ ZrO_2
CaAS-Zr	1CaO-1,21Al_2O_3-6,8 SiO_2	4$\%_{wt}$ ZrO_2
LiAS-Zr	1Li_2O-1,21Al_2O_3-6,8 SiO_2	4$\%_{wt}$ ZrO_2
NaAS-Zr	1Na_2O-1,21Al_2O_3-6,8 SiO_2	4$\%_{wt}$ ZrO_2

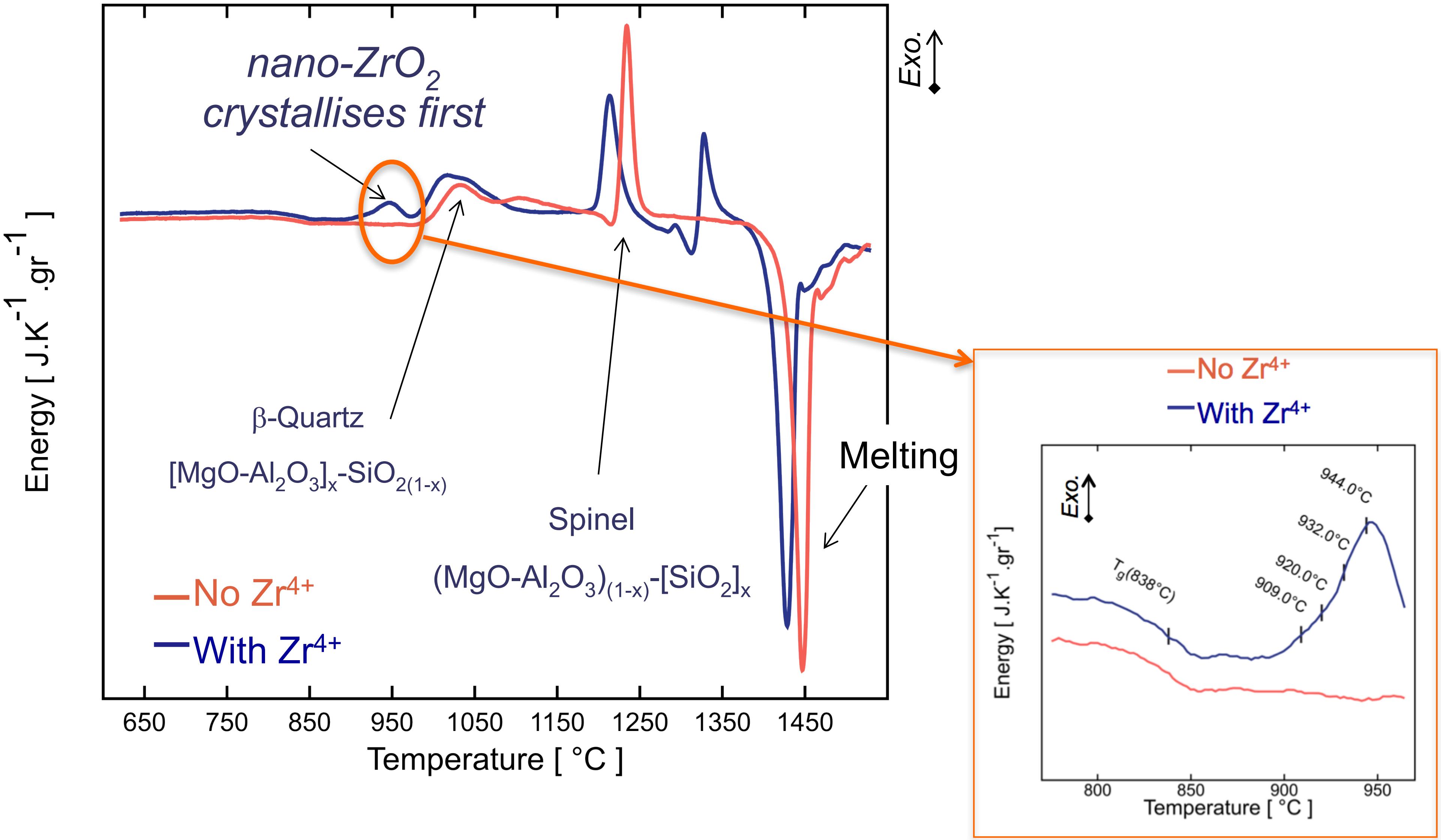
DSC 5 $K.min^{-1}$



Role of Zr^{4+} in those matrices: Comparison of Zr^{4+} bearing and Zr^{4+} free parent-glasses

Thermal behaviour of MAS-Zr

Setaram Multi-HTC 96, under N_2 flux

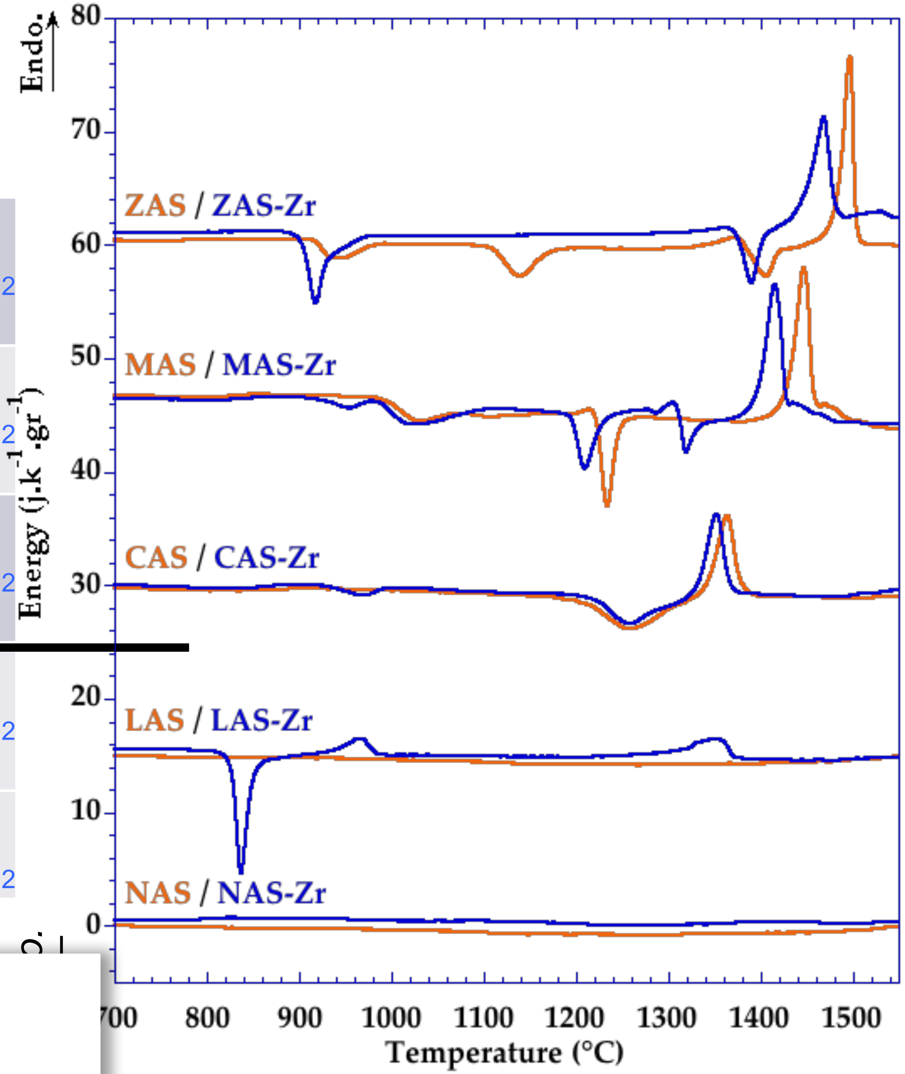


DSC measurements

Setaram Multi-HTC 96, under N2 flux

ZnAS-Zr	1ZnO-1,21Al_2O_3-6,8 SiO_2	4$\%_{wt}$ ZrO_2
MgAS-Zr	1MgO-1,21Al_2O_3-6,8 SiO_2	4$\%_{wt}$ ZrO_2
CaAS-Zr	1CaO-1,21Al_2O_3-6,8 SiO_2	4$\%_{wt}$ ZrO_2
LiAS-Zr	1Li_2O-1,21Al_2O_3-6,8 SiO_2	4$\%_{wt}$ ZrO_2
NaAS-Zr	1Na_2O-1,21Al_2O_3-6,8 SiO_2	4$\%_{wt}$ ZrO_2

DSC 5 $K.min^{-1}$



Is it linked to the Zr^{4+} local environment ?

Various aluminosilicate glasses with and without ZrO_2

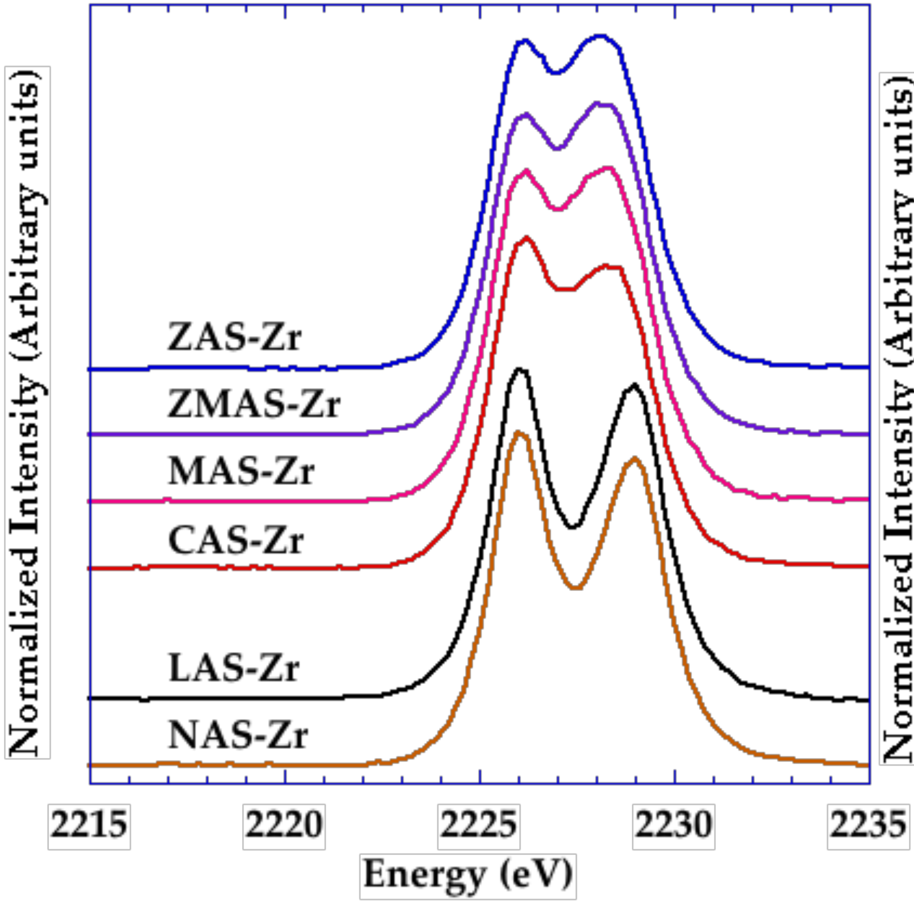
Substitution of the alkali – alkaline earth – metal cation

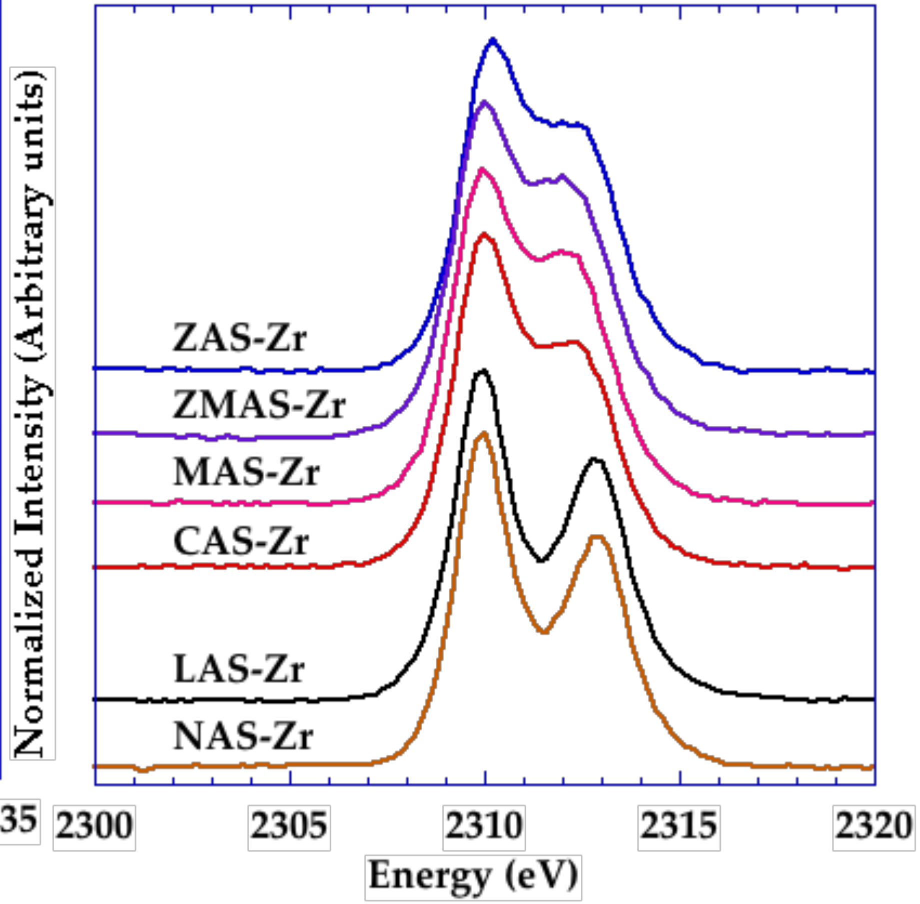
ZnAS-Zr	1ZnO-1,21Al_2O_3-6,8 SiO_2	4%$_{wt}$ ZrO_2	Strong nucleation effect	Glass ceramics
MgAS-Zr	1MgO-1,21Al_2O_3-6,8 SiO_2	4%$_{wt}$ ZrO_2	Nucleation effect	Glass ceramics
CaAS-Zr	1CaO-1,21Al_2O_3-6,8 SiO_2	4%$_{wt}$ ZrO_2	Weak nucleation effect	Glass ceramics
ZnMgAS-Zr	1(MgO/ZnO)-1,21Al_2O_3-6,8 SiO_2	4%$_{wt}$ ZrO_2	Nucleation effect	Glass ceramics
LiAS-Zr	1Li_2O-1,21Al_2O_3-6,8 SiO_2	4%$_{wt}$ ZrO_2	Strong nucleation effect	Glass ceramics
NaAS-Zr	1Na_2O-1,21Al_2O_3-6,8 SiO_2	4%$_{wt}$ ZrO_2	No nucleation effect	Glass

Zr local environment

LUCIA beamline – SOLEIL (France)

Zr L2,3-edges

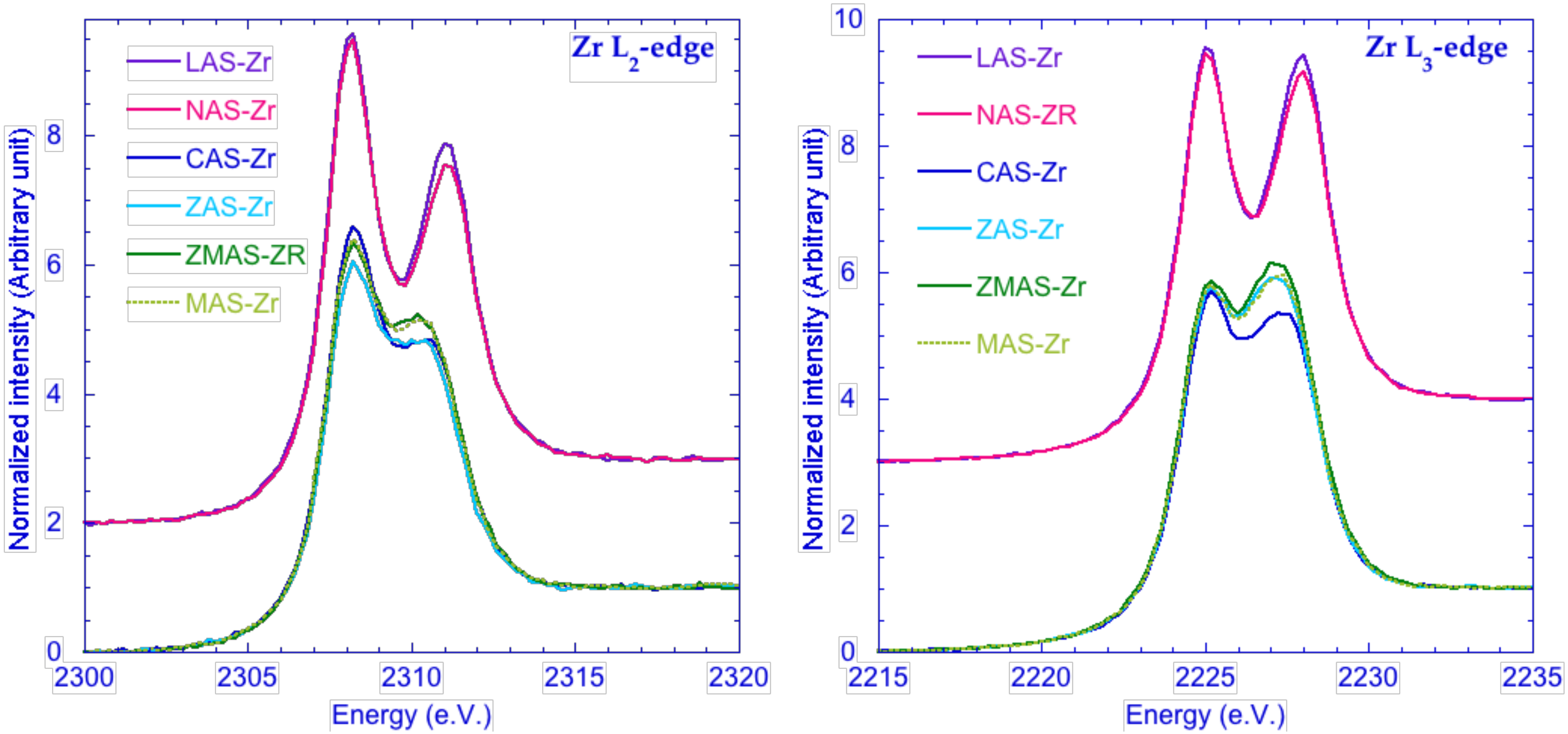




Zr local environment

LUCIA beamline – SOLEIL (France)

Zr L2,3-edges

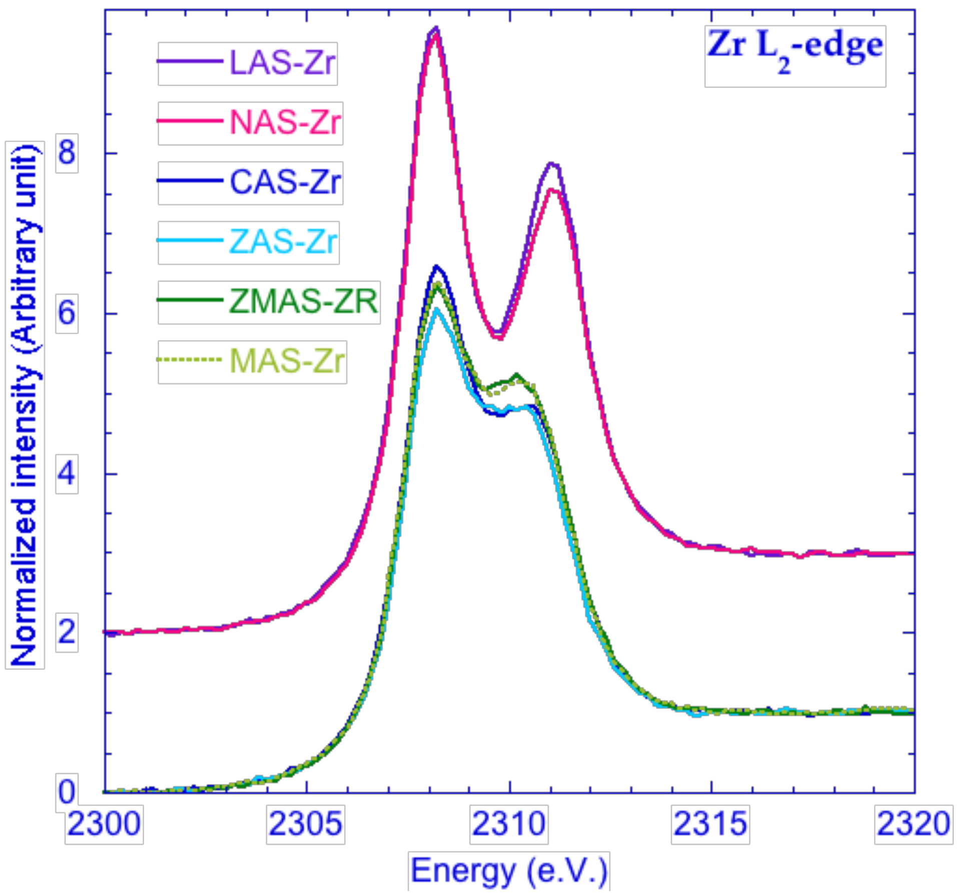


Comparison with crystalline references

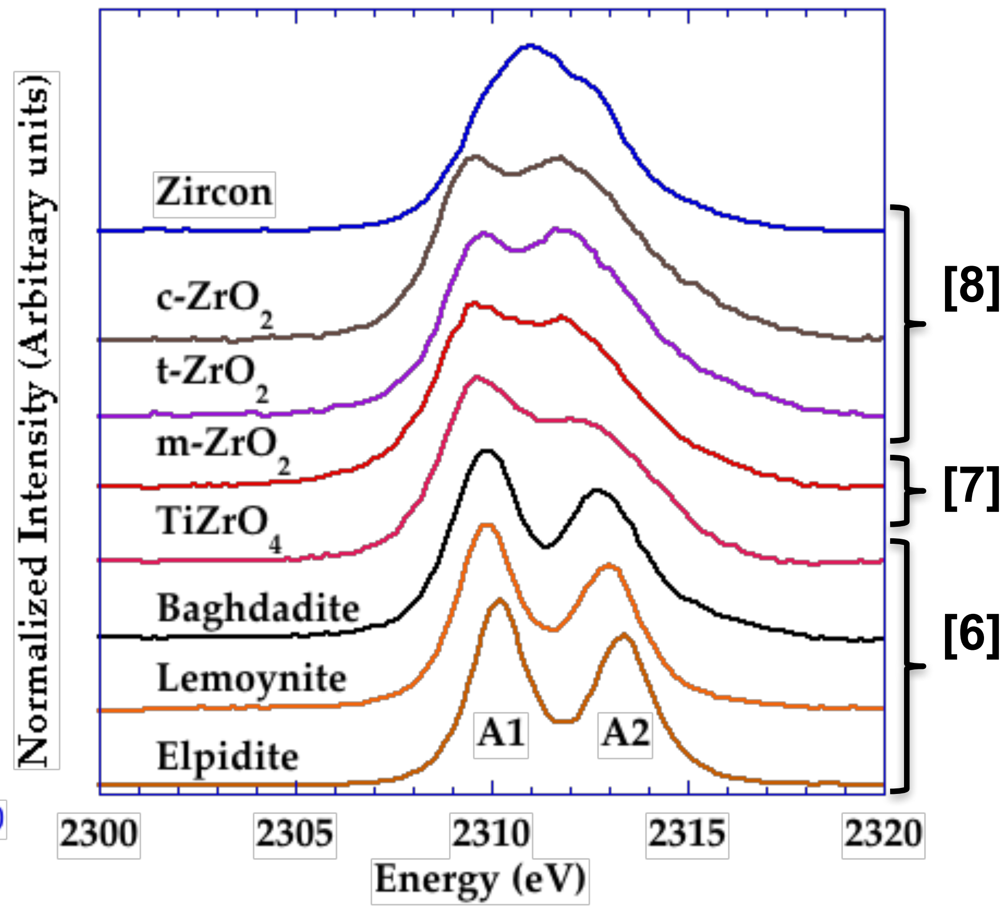
LUCIA beamline – SOLEIL (France)

Zr L2,3-edges

Glasses



Crystals



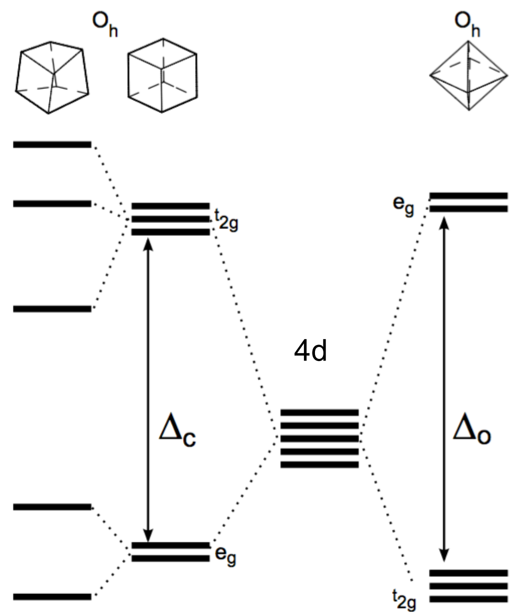
L2,3-edges highly sensitive to local geometry

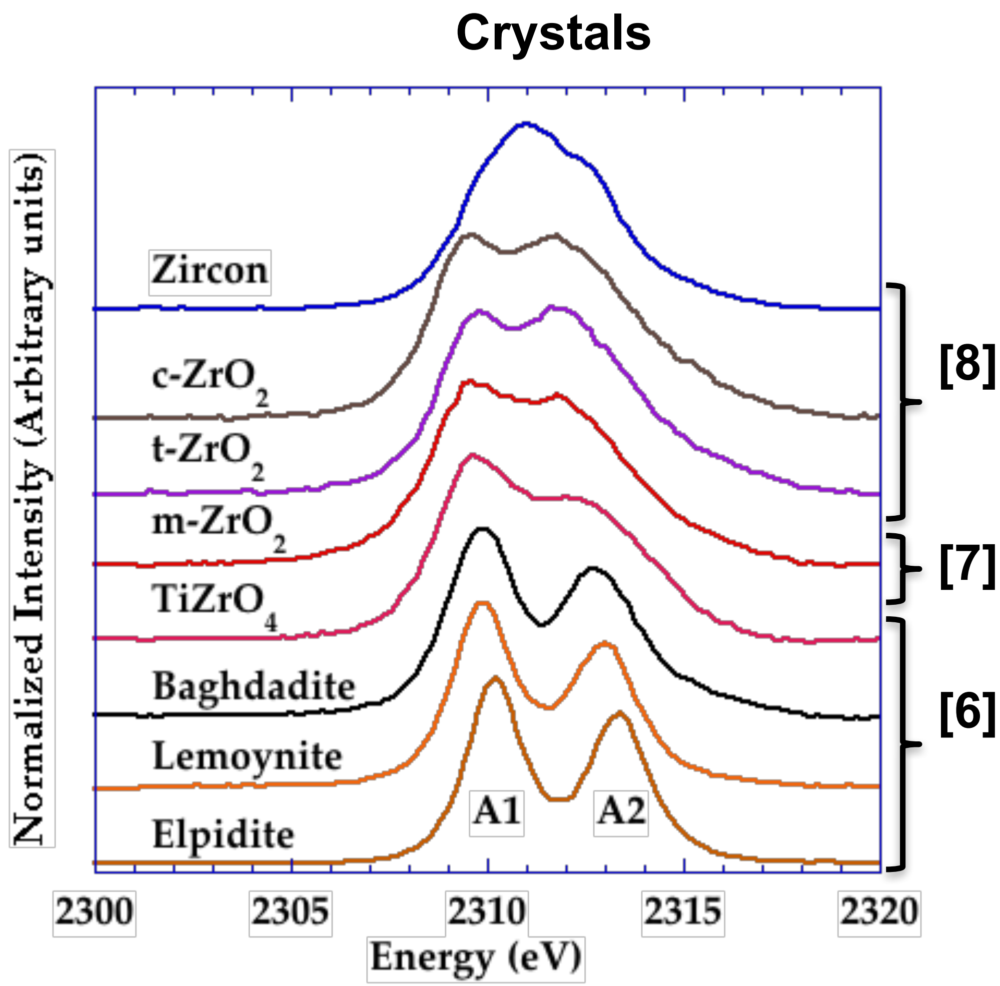
Zr L-edges

$L_{2,3}$-edges

transition from 2p to 4d states

two peaks in the Zr $L_{2,3}$-edges spectra associated with the crystal field splitting of the 4d states into t2g and eg empty states



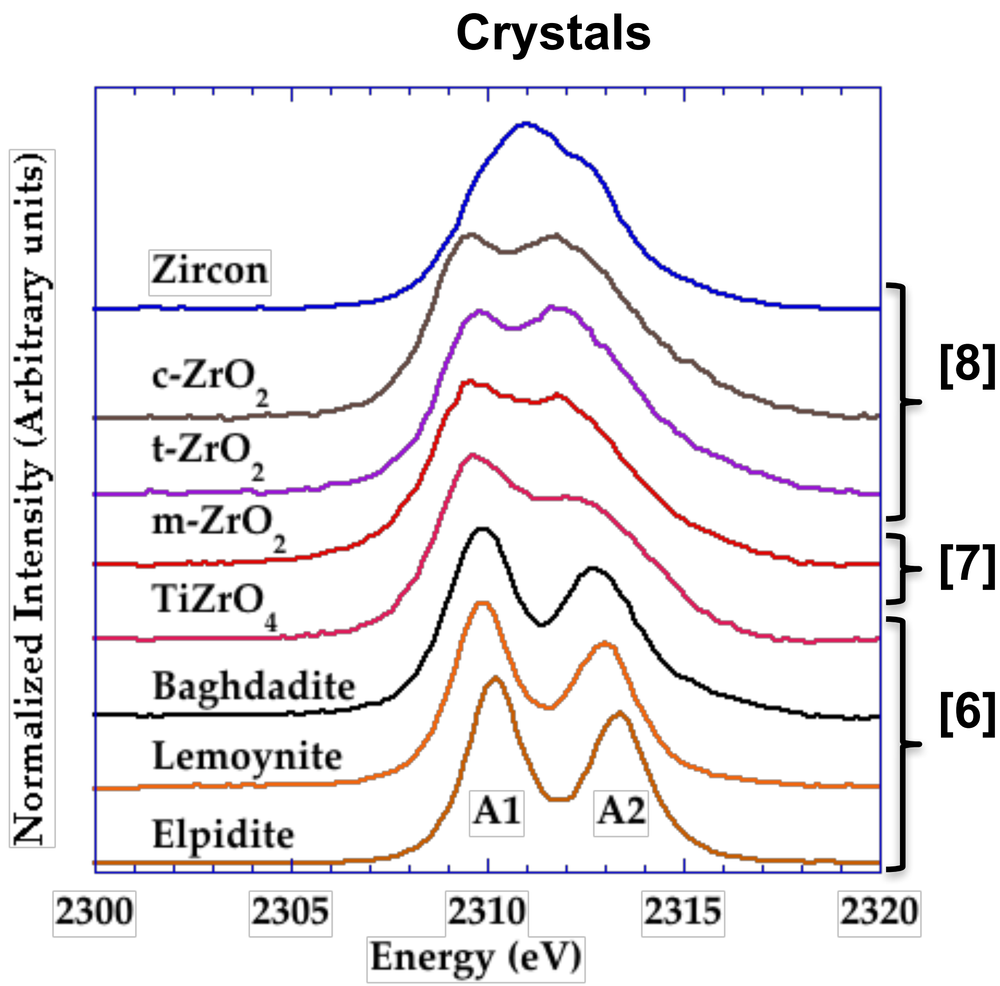


Comparison with crystalline references

$\Delta_{apparent}$ = 3.0 ± 0.5 eV for [6]Zr
$\Delta_{apparent}$ = 2.1 ± 0.5 eV for [7]Zr and 8]Zr

consistent with multiplet calculations

Galoisy et al., J. Am. Ceram. Soc., 82 (1999) 2219

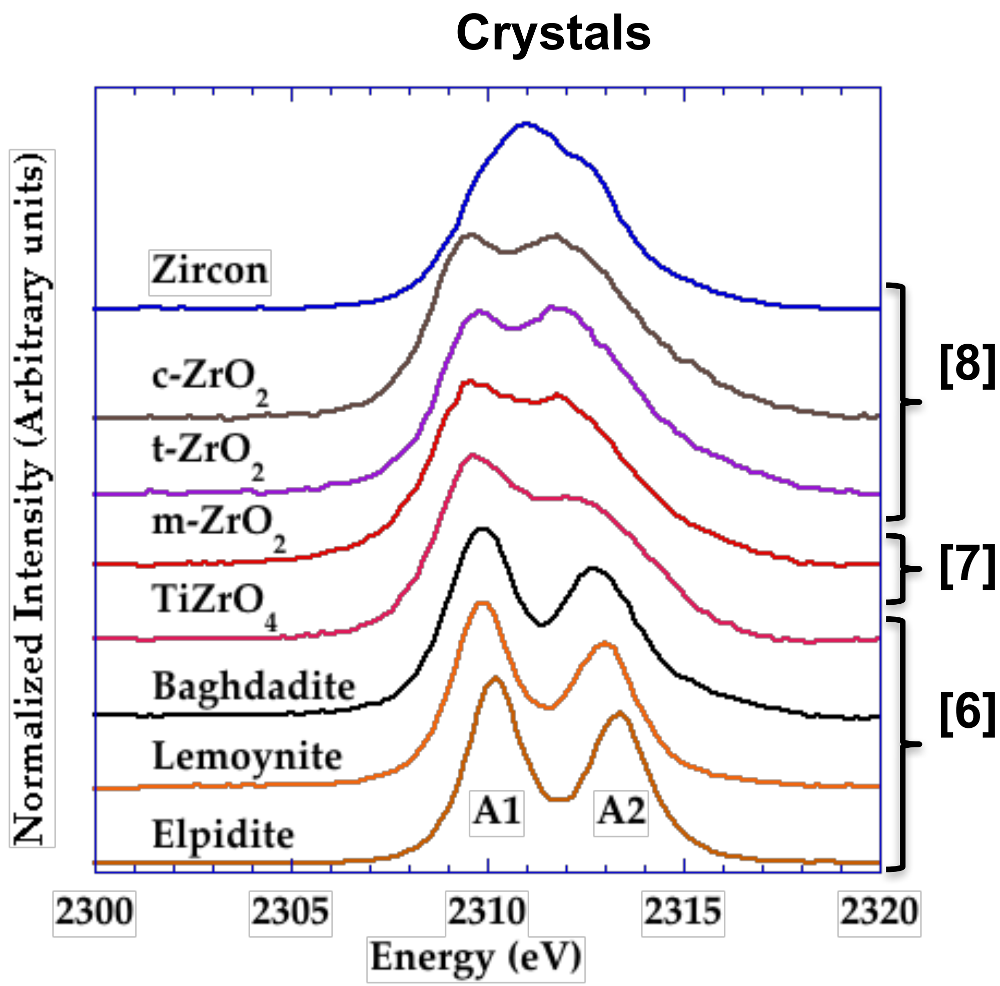


Comparison with crystalline references

$\Delta_{apparent}$ = 3.0 ± 0.5 eV for [6]Zr
$\Delta_{apparent}$ = 2.1 ± 0.5 eV for [7]Zr and 8]Zr

consistent with multiplet calculations

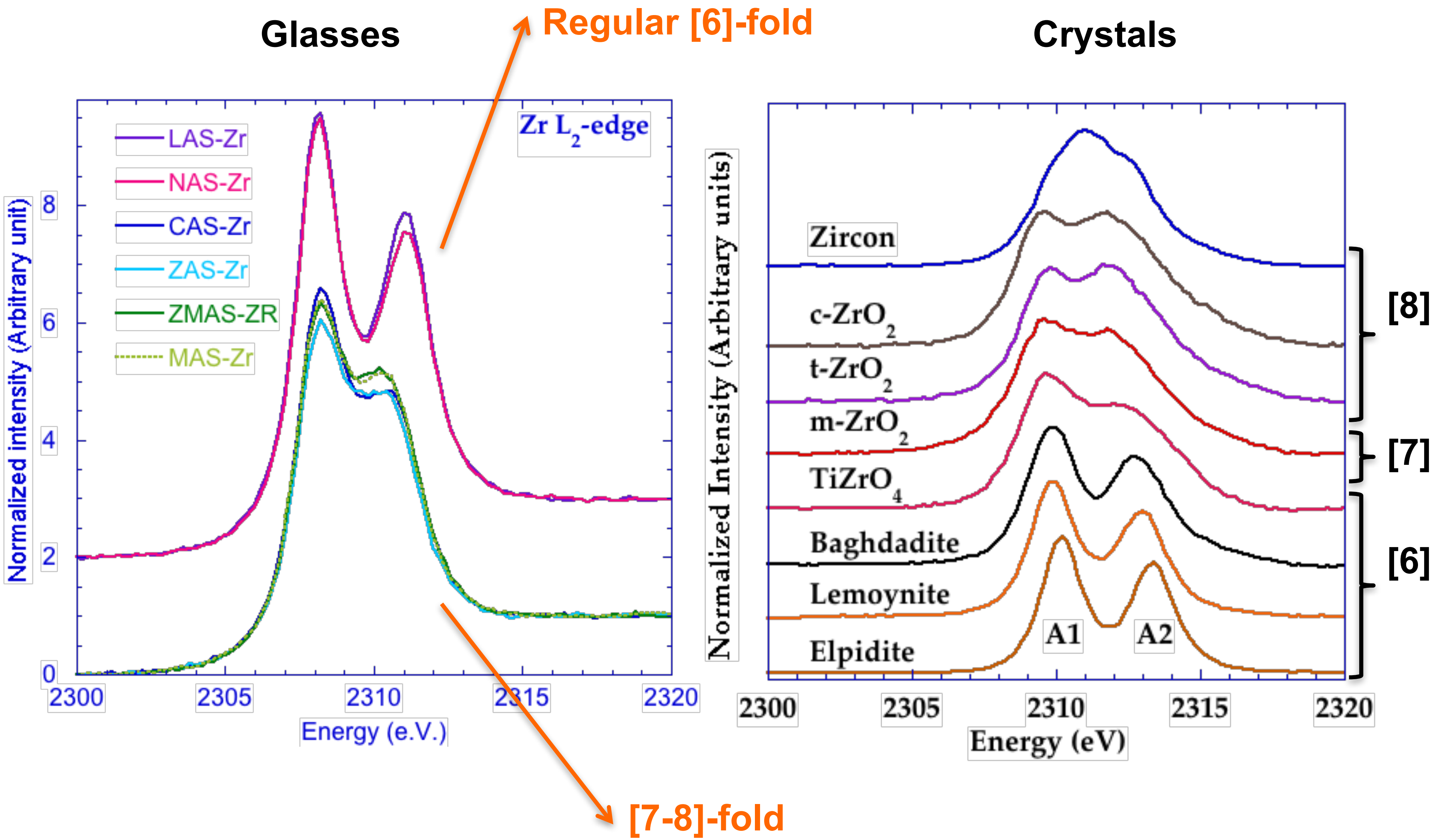
Galoisy et al., J. Am. Ceram. Soc., 82 (1999) 2219



$\Delta_{apparent}$ = 3.0 ± 0.5 eV for NAS and LAS

$\Delta_{apparent}$ = 2.1 ± 0.5 eV for (Ca,Mg,Zn)AS

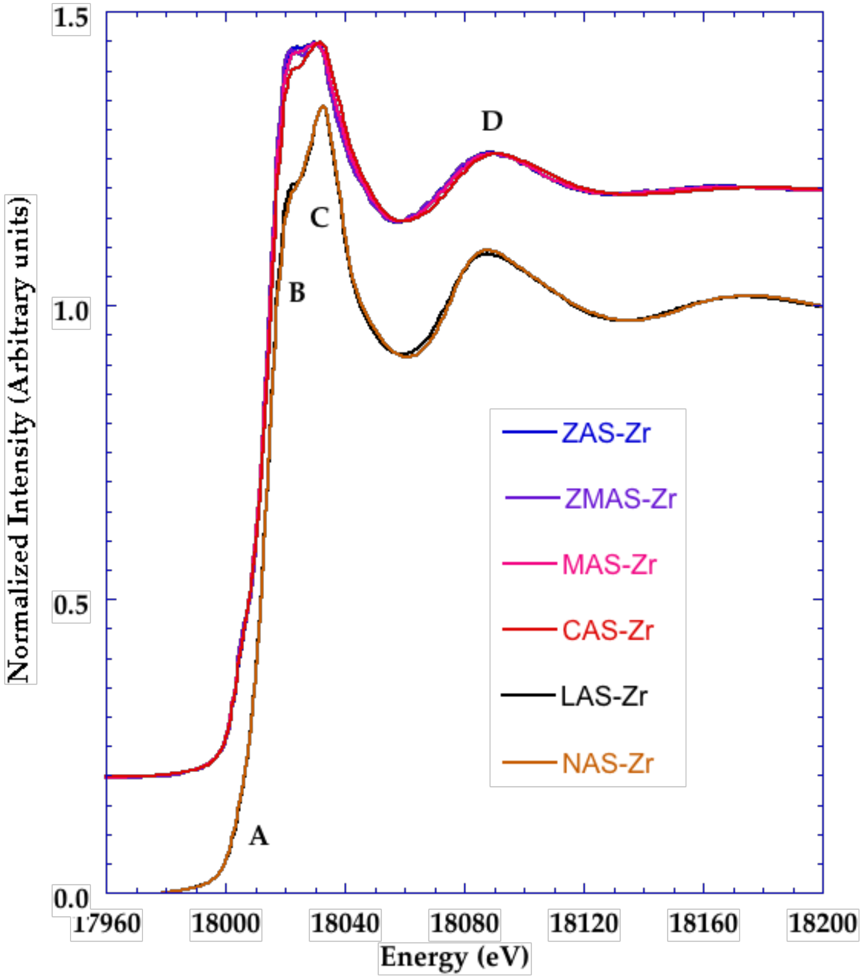
Comparison with crystalline references



Cormier et al., Mater. Chem. Phys. 152 (2015) 41

Zr local environment

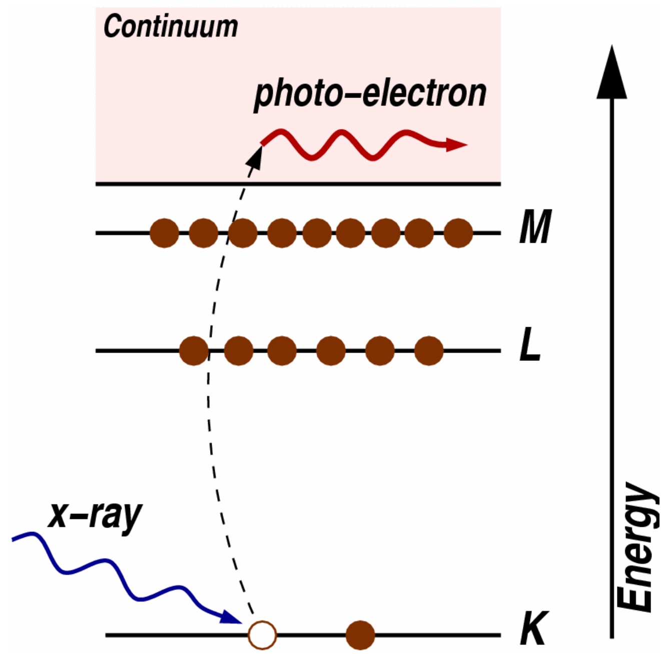
XAS beamline – Elettra (Italy)
Glasses



Zr K-edge

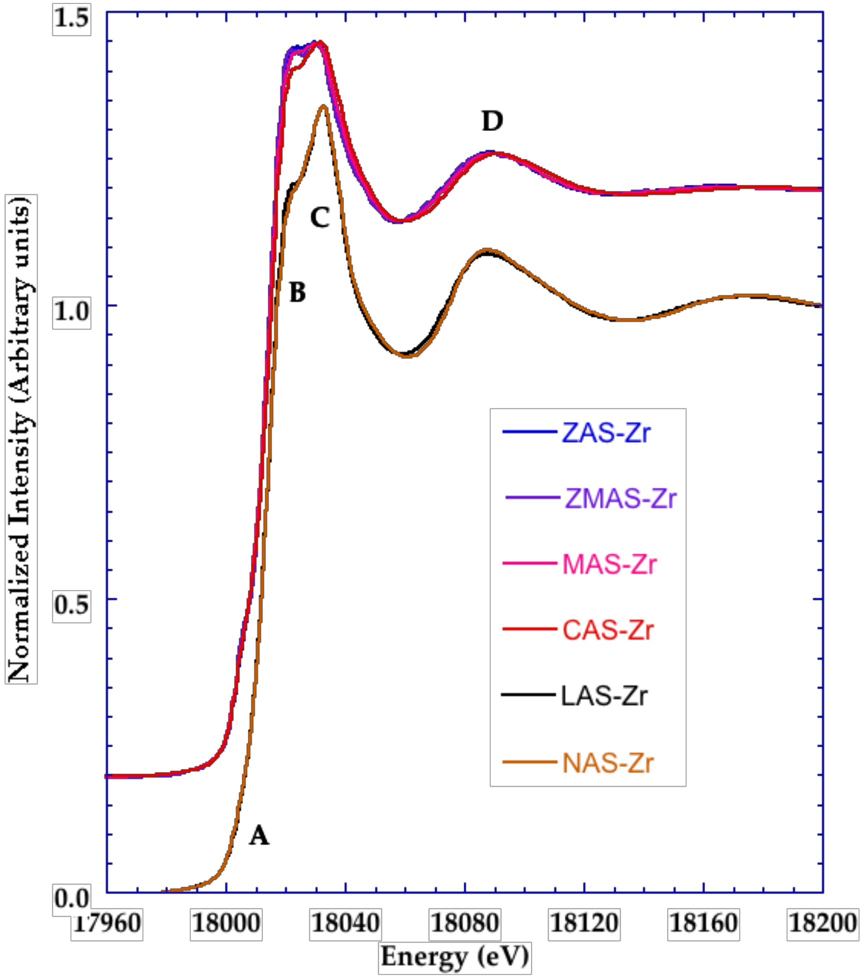
K-edge

transition from 1s to continuum

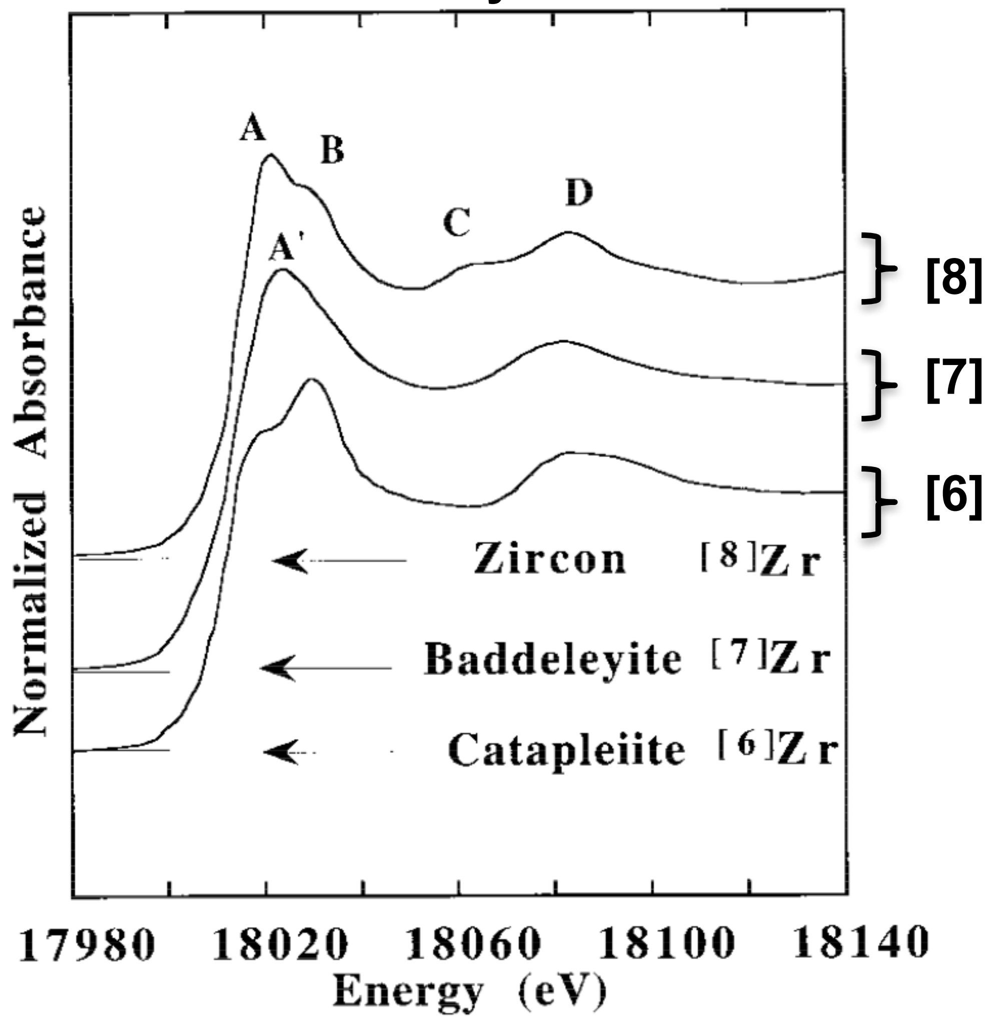


Zr local environment

XAS beamline – Elettra (Italy)
Glasses



Zr K-edge
Crystals

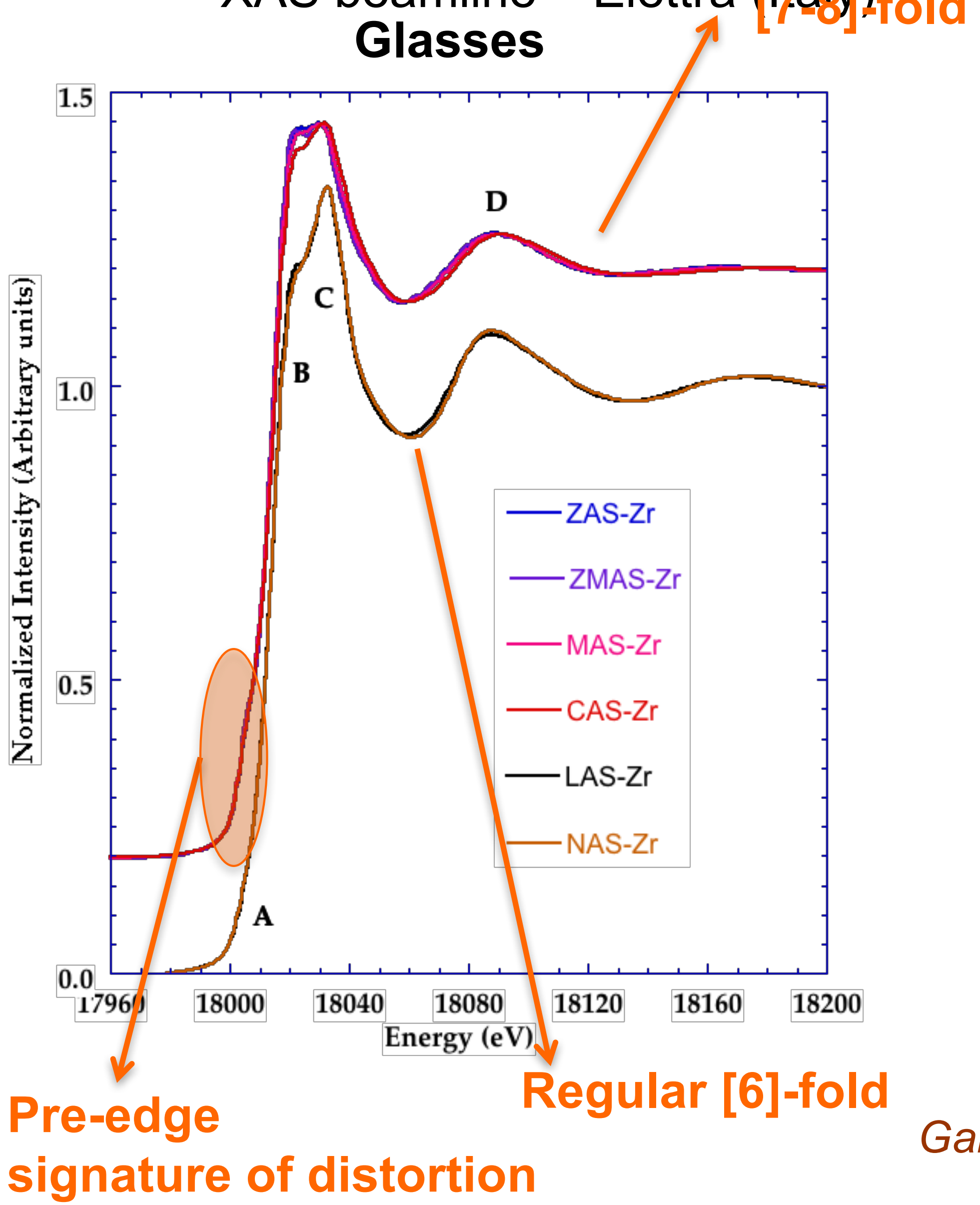


Galoisy et al., J. Am. Ceram. Soc., 82 (1999) 2219

Zr local environment

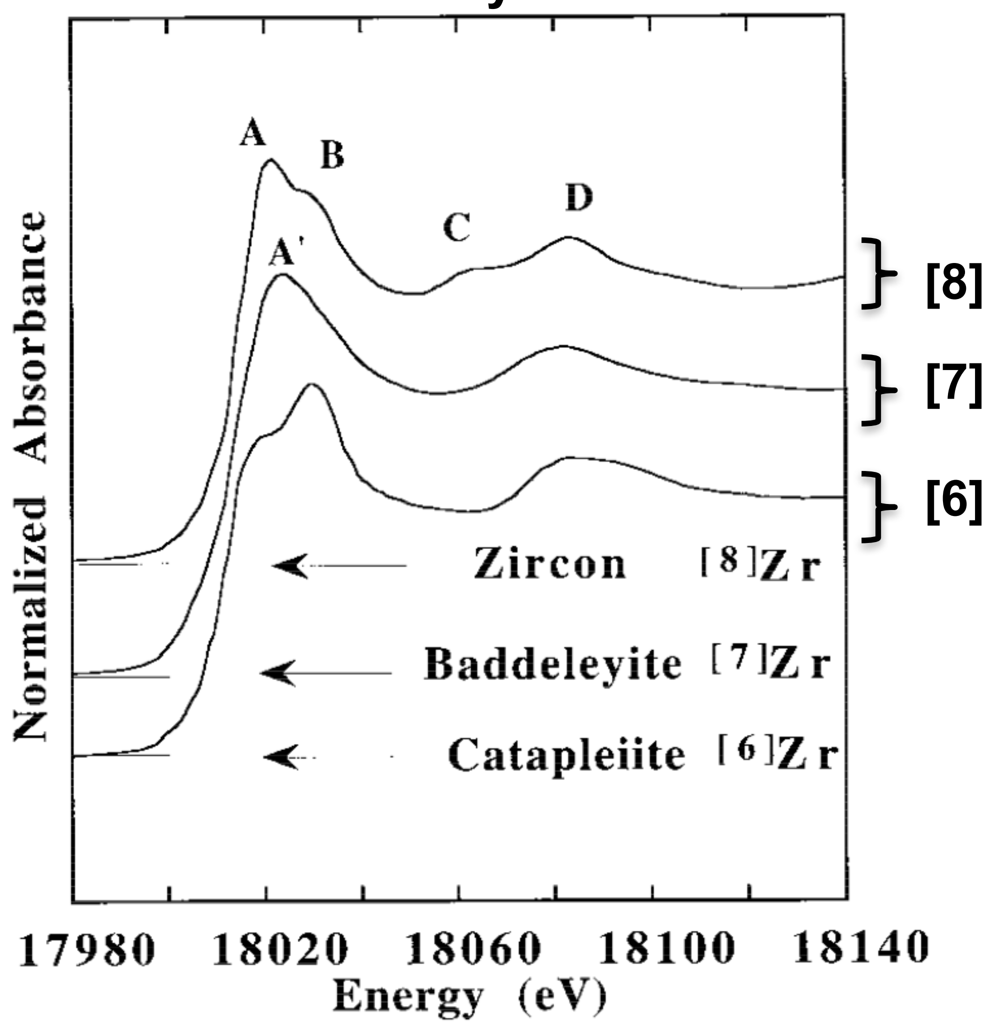
XAS beamline – Elettra (Italy)

Glasses



Zr K-edge

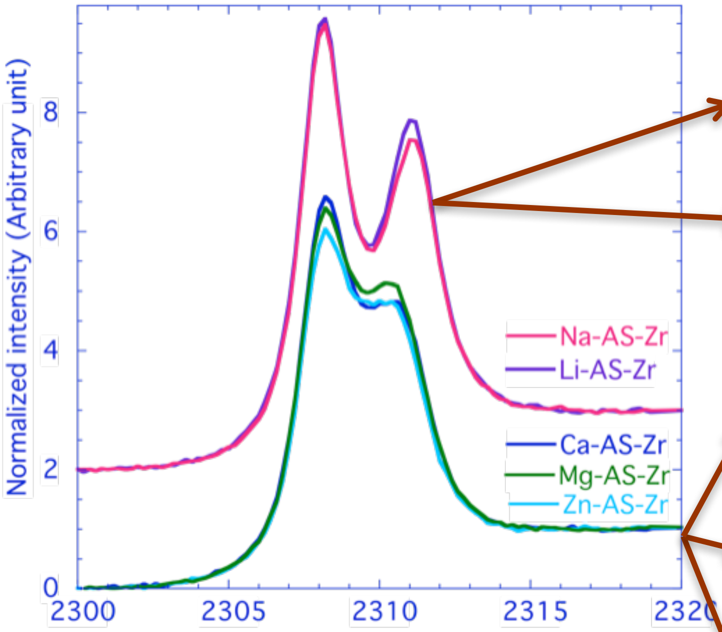
Crystals



Galoisy et al., J. Am. Ceram. Soc., 82 (1999) 2219

Zr environment: is the local site important ?

Zr $L_{2,3}$-edge XANES (SOLEIL)



Na-AS-Zr
No nucleation effect

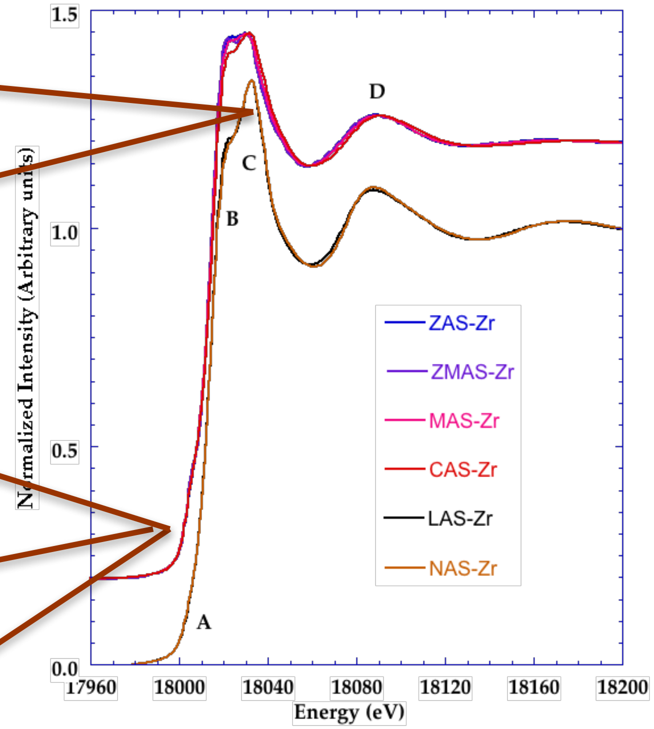
Li-AS-Zr
Strong nucleation effect

Ca-AS-Zr
Weak nucleation effect

Mg-AS-Zr
Nucleation effect

Zn-AS-Zr
Strong nucleation effect

LUCIA



➔ No link between coordination and nucleation effect

Cormier et al., Mater. Chem. Phys. 152 (2015) 41

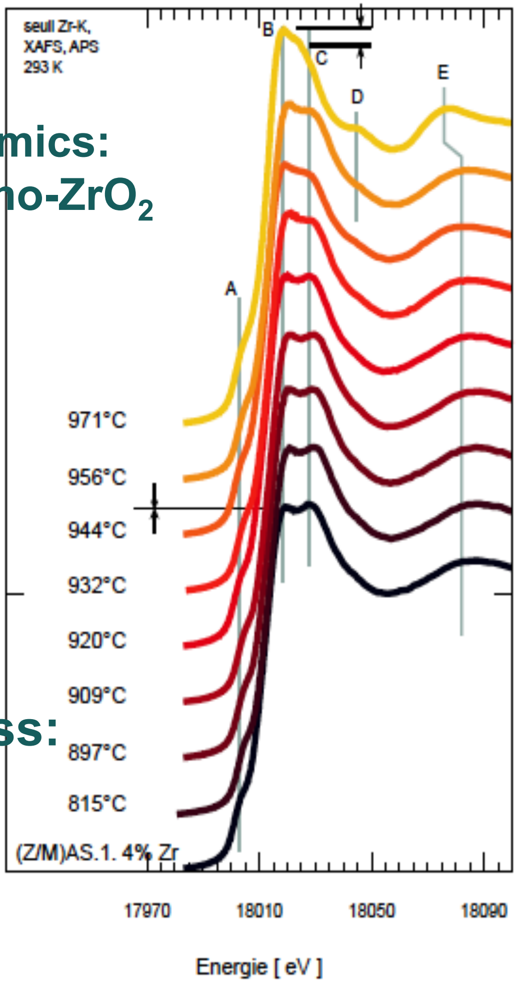
Zr environment in initial and final glass-ceramics

Zr K-edge XANES GESCARS – APS (USA)

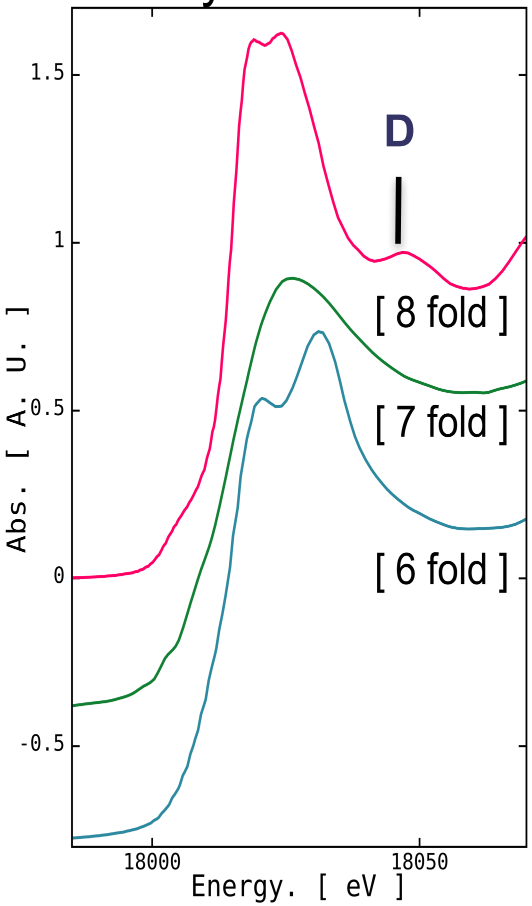
Glass and glass-ceramics

Glass-ceramics: peculiar nano-ZrO_2

Initial glass: $^{[7]}Zr$



Crystalline references



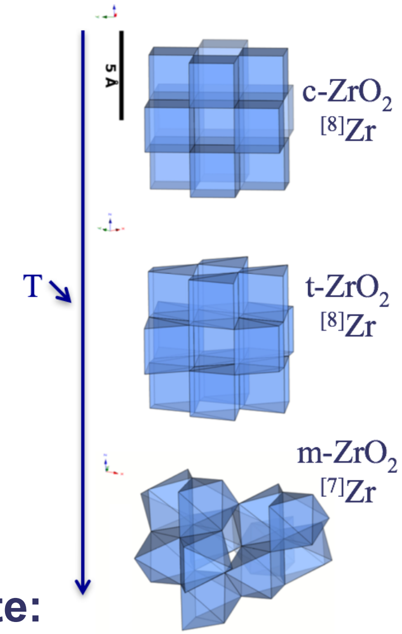
Energie [eV]

t-ZrO2

c-ZrO2

m-ZrO2

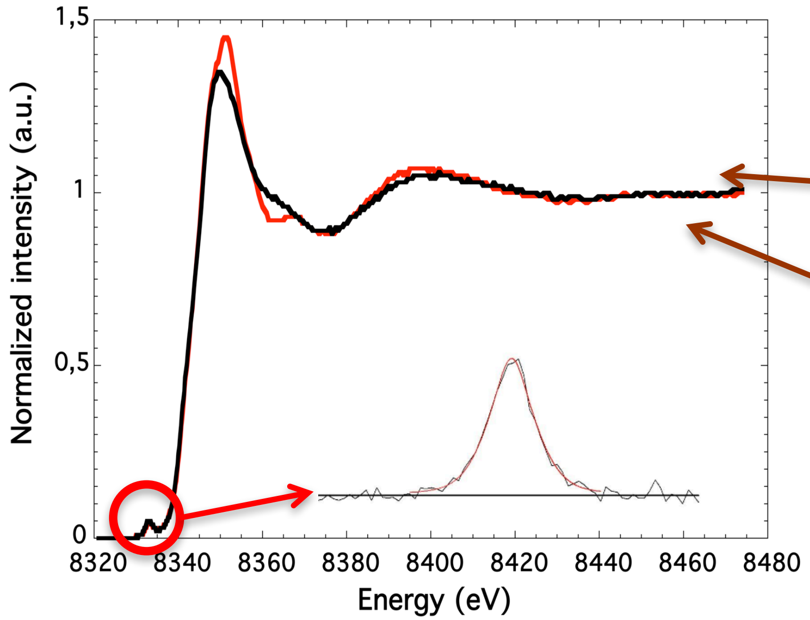
Baghdadite: Ca3ZrSiO9



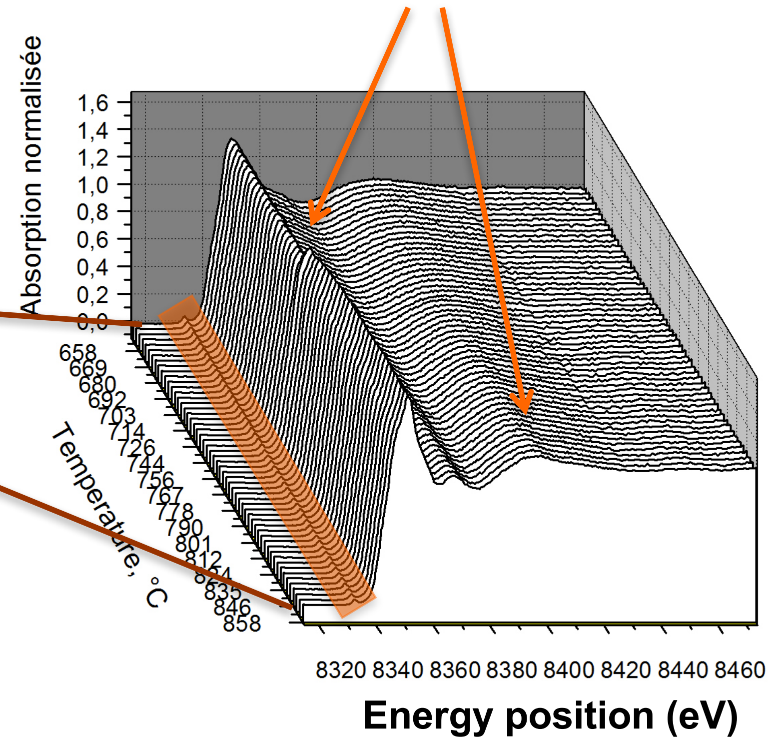
Difference between nanocrystals and macroscopic crystals: importance of nano-size, constraints on nanophases?

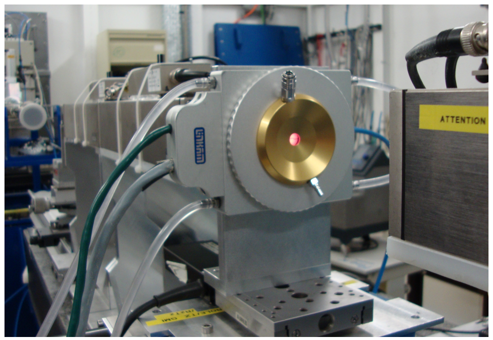
In situ nucleation: Ni K-edge XANES study

SAMBA (SOLEIL)
Ni K-edge XANES
Linkam heating stage + Quick-EXAFS



Change in Ni coordination





In-situ XAS: determination of the Ni environment and its evolution during the heat treatment

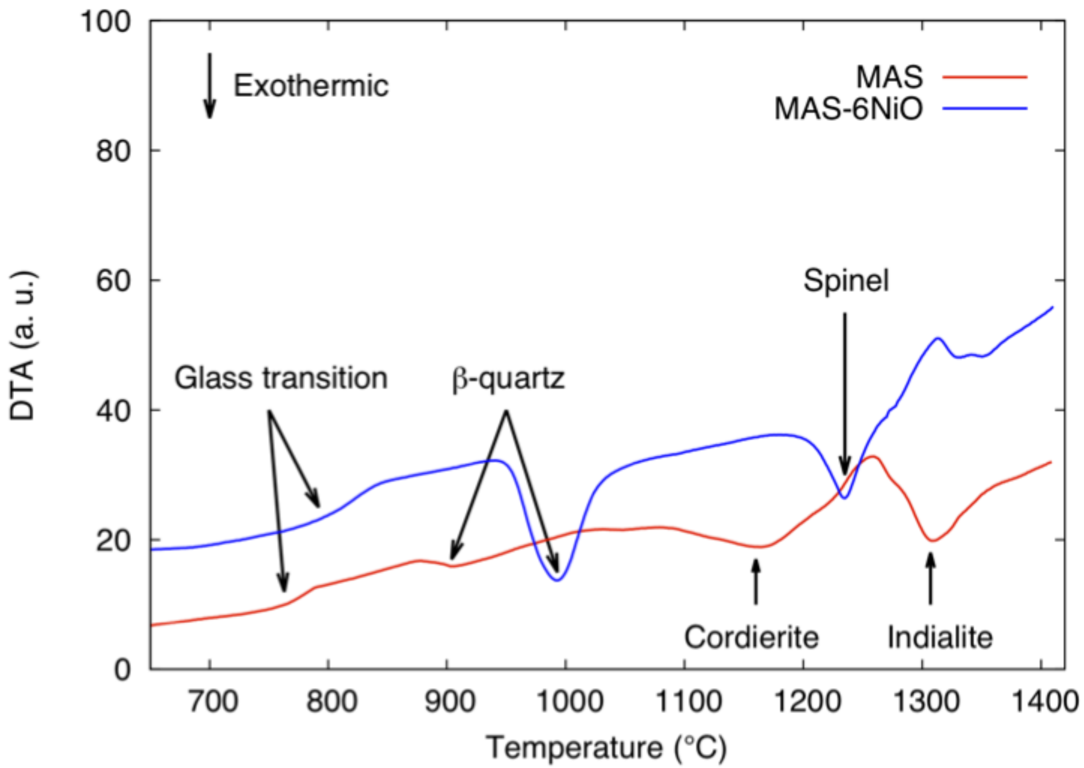
Quick-XAS mode: kinetics of these transformations with acquisition of a XAS spectra every second

Ni in $MgO-Al_2O_3-SiO_2$ glass

Differential thermal analysis of MAS and MAS-6NiO glass

✓ Heating slope: 10K/min, grain size: 80-125mm, Pt crucible

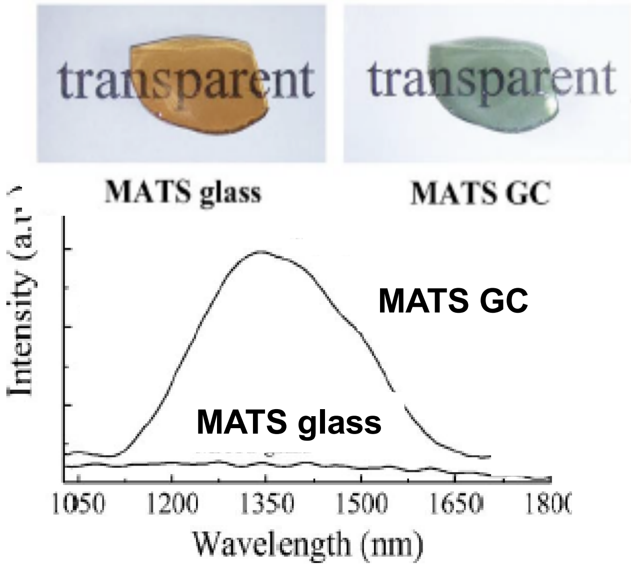
✓ Glass transition temperatures: MAS =763 ± 2 ° C and MAS-6NiO = 792 ± 2 ° C



Ni in transparent glass-ceramics

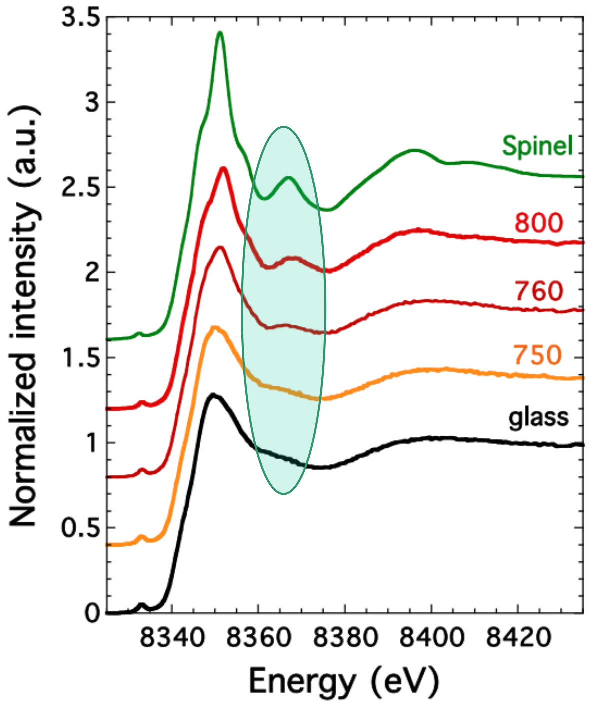
Increase strength (bending strength: 90Mpa to 590MPa, Vogel, 1994)

Transparent glass-ceramics
Broad emission band in the infra-red region
Wu et al., J., Opt. Mater. 30(2008)1900;
Suzuki et al., J. Non-Cryst. Solids 351(2005)2304



Ni^{2+} luminescence in glass and glass-ceramics
Zhou et al., J. Appl. Phys. 102(2007)063106

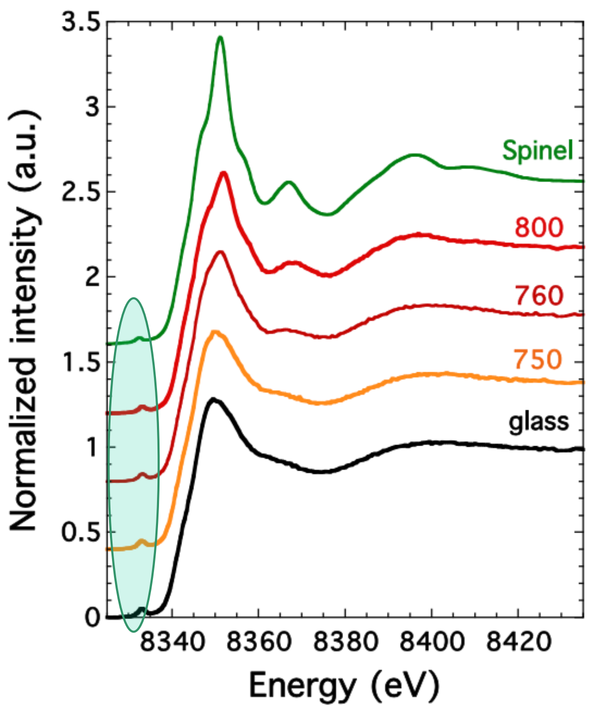
Ni environment: is the local site important ?



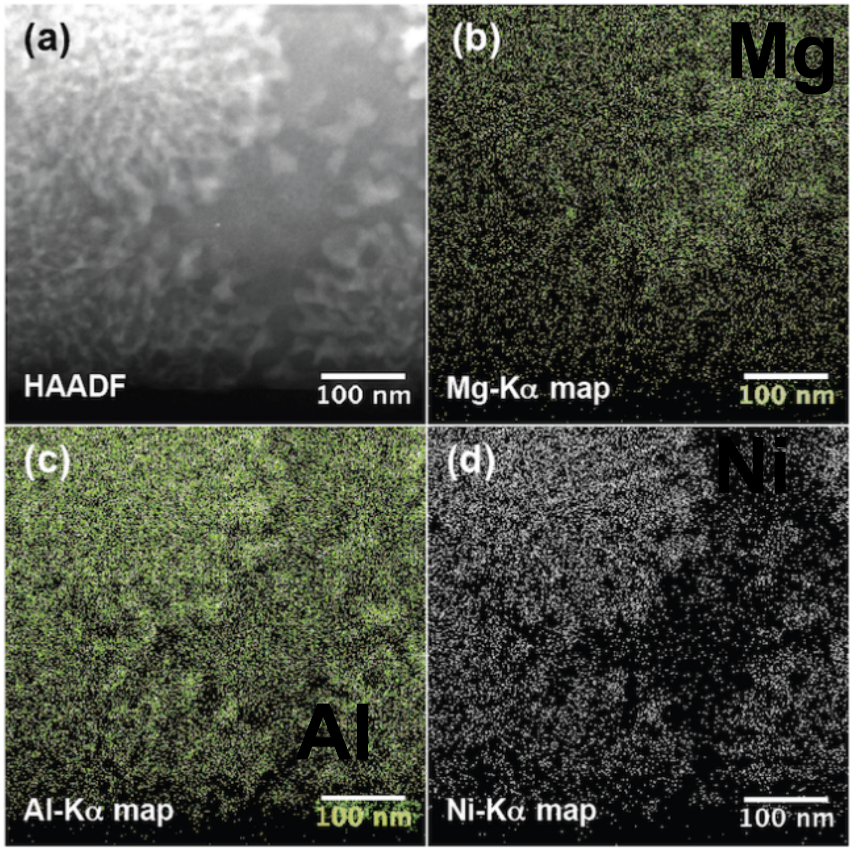
-Formation of spinel

Cochain et al., JNCS 408 (2015) 7

Ni environment: is the local site important ?



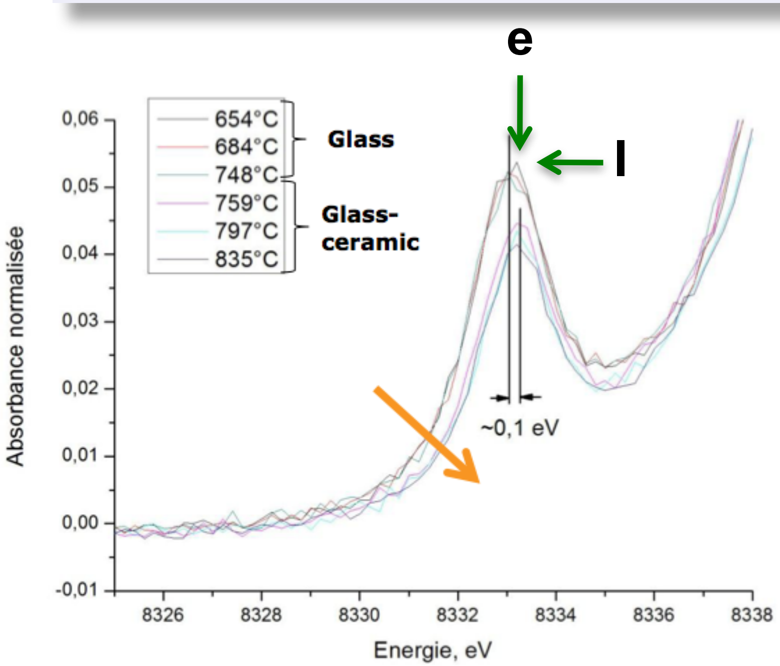
-Formation of spinel

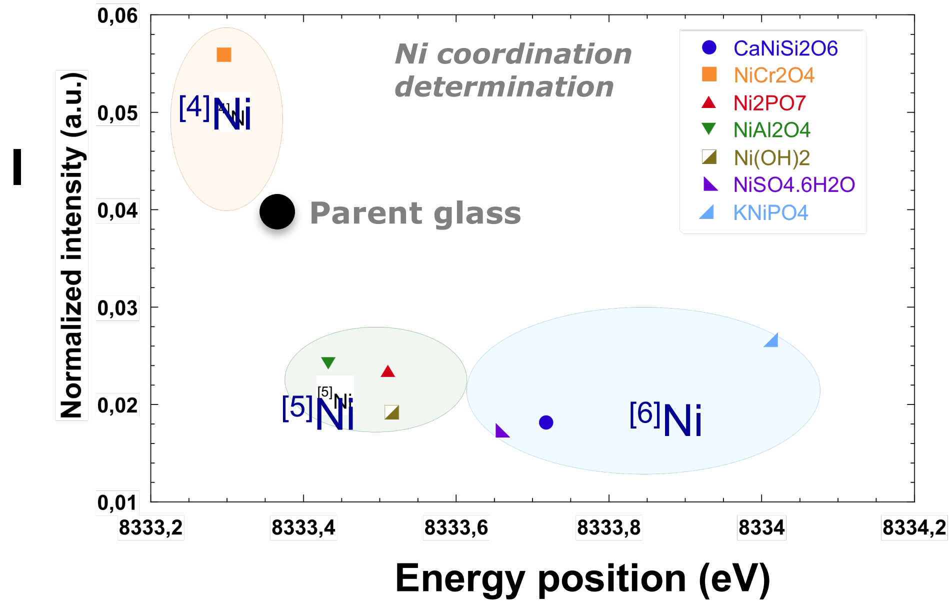


Cochain et al., JNCS 408 (2015) 7

$Ni_xMg_{(1-x)}Al_2O_4$

In situ nucleation: Ni K-edge XANES study

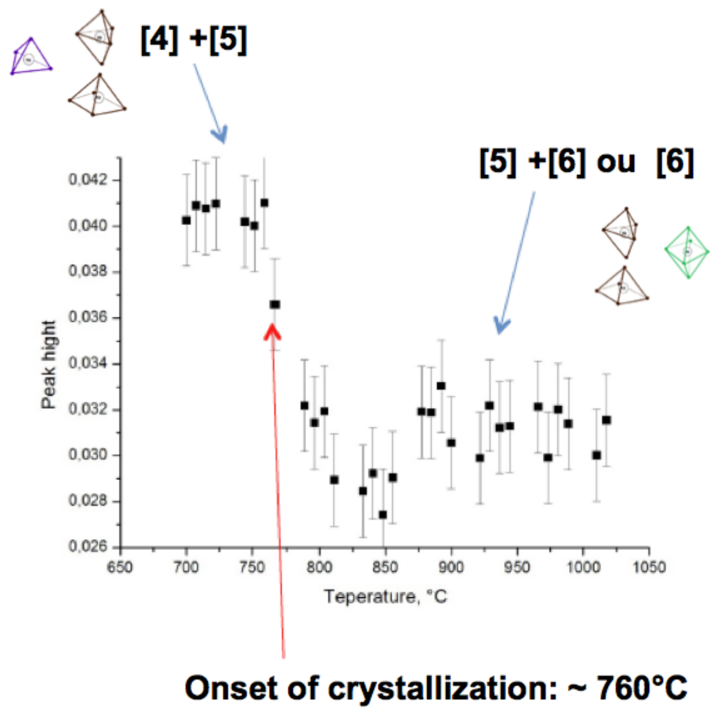




-Ni coordination changes (pre-edge study)

-At 759° C => decrease of pre-edge intensity (onset of crystallization)

-Increase of 6-fold coordinated Ni

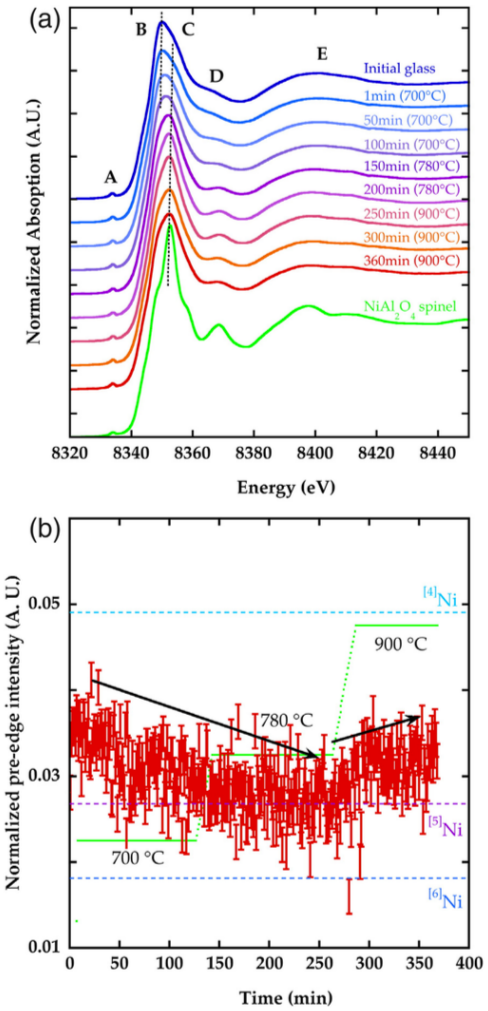


In situ nucleation: Ni K-edge XANES study

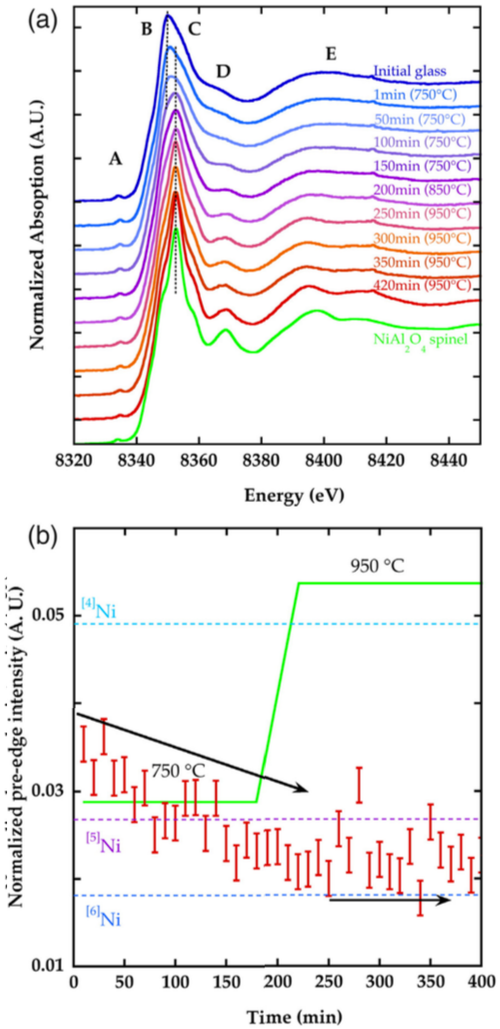
-[5]Ni in glass

-[6]Ni in spinel

- then [4]Ni increases



-**LAS-Ti-Ni**



-**ZAS-Ti-Ni**

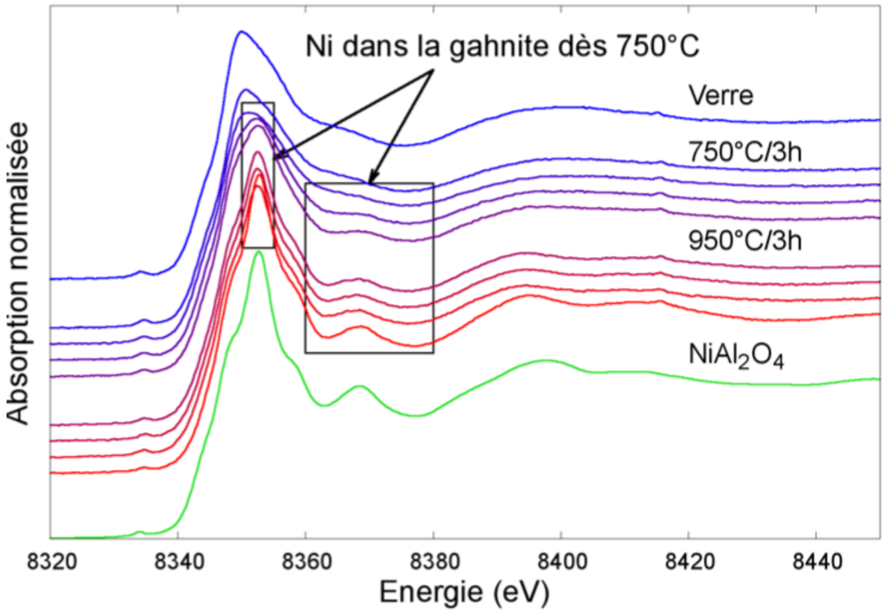
-[5]Ni in glass

-[6]Ni in stabilized in gahnite (spinel)

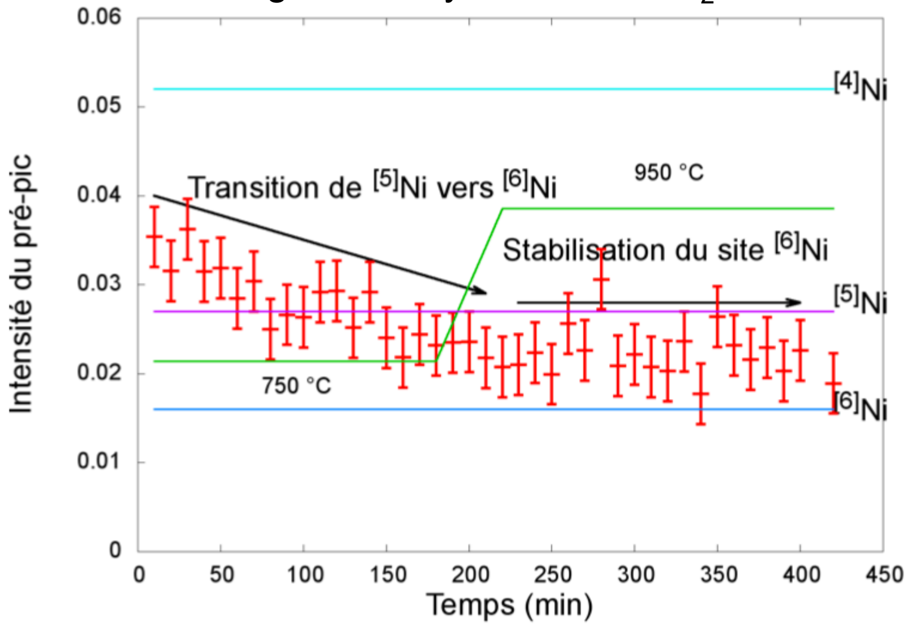
Dugue et al. JNCS 413 (2015) 24

Ni in transparent glass-ceramics : LAS, ZAS system

XANES for ZAS-9TiO_2-2NiO



Pre-edge intensity for ZAS-9TiO_2-2NiO

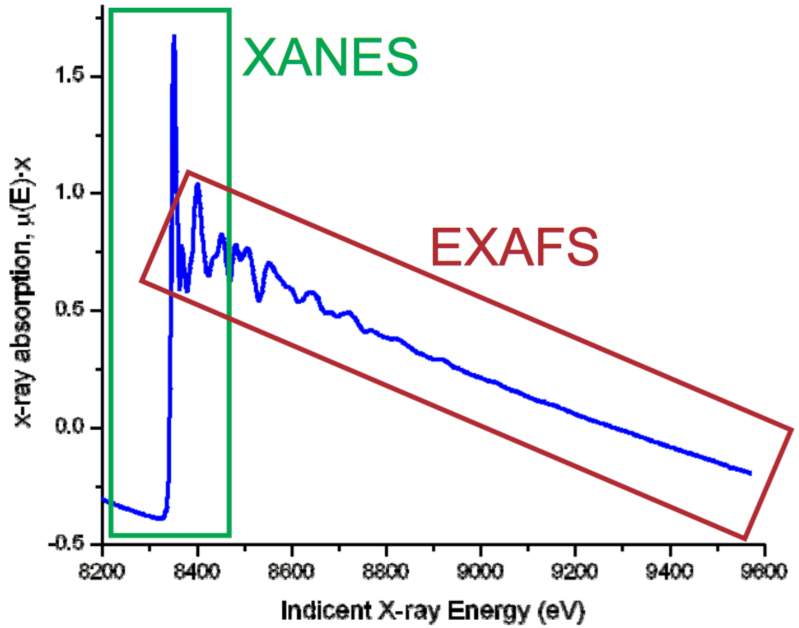


Crystallization temperature lower for Ni-ZAS than for Ni-MAS or Ni-LAS

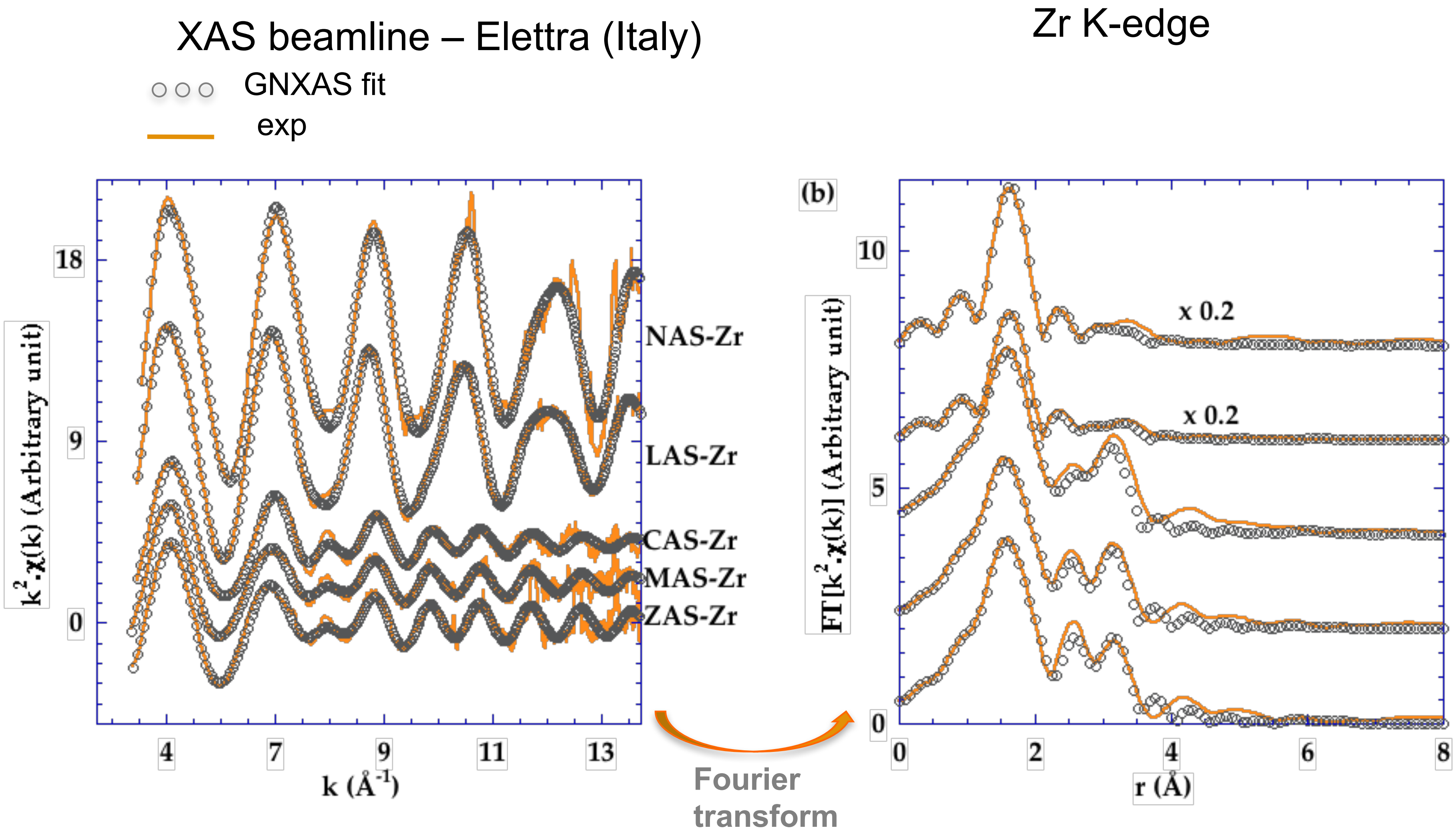
Effect of Zn on the crystallization of gahnite

Strong preference for Zn in tetrahedral site in gahnite: stabilization of $^{[6]}$Ni

Is the medium range order important ?



Zr local environment

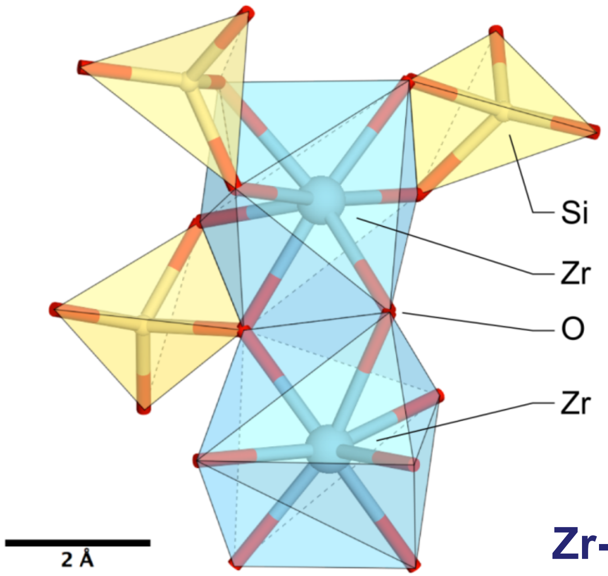


EXAFS information :

- accurate determination of the first shell
- beyond the first shell

Environment around Zr using EXAFS

Glass $MgO-Al_2O_3-SiO_2-ZrO_2$
Zr K-edge EXAFS



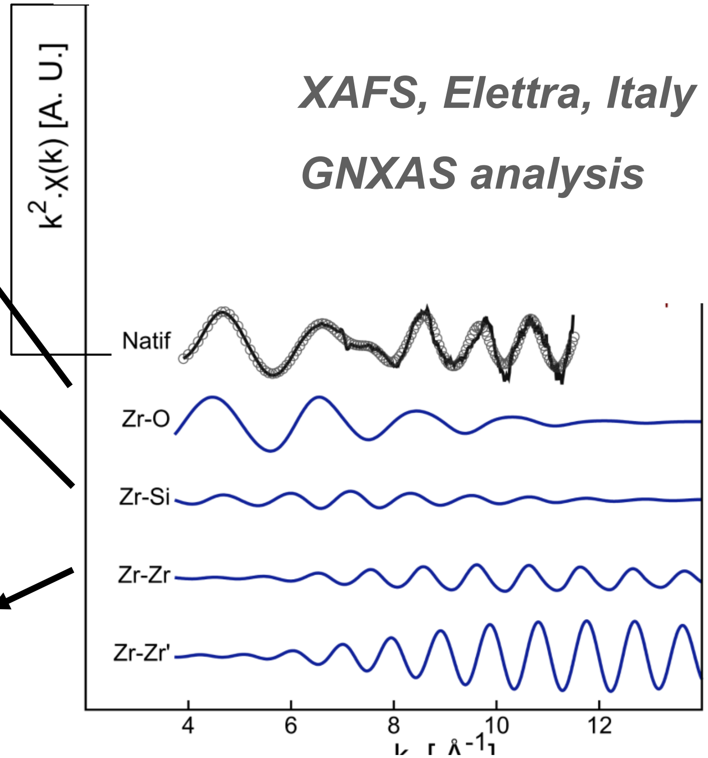
Zr-O distance at 2.11Å
~ 7 fold

at 3.10Å
Zr-Si(Mg,Al)

Zr-Zr at 3.25Å
Edge-sharing as in mono. ZrO_2

XAFS, Elettra, Italy

GNXAS analysis



different contributions in the GNXAS model

Dargaud et al. J. Am. Ceram. Soc 93 (2010) 342
Dargaud et al. JNCS 356 (2010) 2928

Zr local environment

XAS beamline – Elettra (Italy)

Zr K-edge

Zr-O shell	N	R (Å)	σ (Å^2)
MAS-Zr	7.2 ± 0.3	2.11 ± 0.01	0.019 ± 0.002
ZAS-Zr	7.2 ± 0.8	2.12 ± 0.01	0.018 ± 0.002
CAS-Zr	7.1 ± 0.4	2.10 ± 0.01	0.018 ± 0.002
LAS-Zr	6.0 ± 0.1	2.09 ± 0.01	0.004 ± 0.002
NAS-Zr	6.1 ± 0.1	2.08 ± 0.01	0.002 ± 0.002
Zr-(Si,Al) shell	**N**	**R (Å)**	**σ (Å^2)**
MAS-Zr	3.1 ± 0.5	3.12 ± 0.02	0.024 ± 0.003
ZAS-Zr	2.8 ± 1.7	3.11 ± 0.02	0.021 ± 0.003
CAS-Zr	3.1 ± 1.4	3.11 ± 0.02	0.032 ± 0.003
LAS-Zr	1.1 ± 0.7	3.07 ± 0.03	0.014 ± 0.008
NAS-Zr	1.0 ± 0.5	3.42 ± 0.02	0.001 ± 0.003
Zr-Zr shell	**N**	**R (Å)**	**σ (Å^2)**
MAS-Zr	0.8 ± 0.3	3.38 ± 0.03	0.005 ± 0.004
ZAS-Zr	0.7 ± 0.3	3.38 ± 0.03	0.004 ± 0.004
CAS-Zr	1.2 ± 0.3	3.38 ± 0.03	0.008 ± 0.004
LAS-Zr	0.9 ± 0.3	3.42 ± 0.03	0.006 ± 0.004

Confirm coordination number

Zr local environment

XAS beamline – Elettra (Italy)

Zr K-edge

Zr-O shell	N	R (Å)	σ (Å^2)
MAS-Zr	7.2 ± 0.3	2.11 ± 0.01	0.019 ± 0.002
ZAS-Zr	7.2 ± 0.8	2.12 ± 0.01	0.018 ± 0.002
CAS-Zr	7.1 ± 0.4	2.10 ± 0.01	0.018 ± 0.002
LAS-Zr	6.0 ± 0.1	2.09 ± 0.01	0.004 ± 0.002
NAS-Zr	6.1 ± 0.1	2.08 ± 0.01	0.002 ± 0.002
Zr-(Si,Al) shell	**N**	**R (Å)**	**σ (Å^2)**
MAS-Zr	3.1 ± 0.5	3.12 ± 0.02	0.024 ± 0.003
ZAS-Zr	2.8 ± 1.7	3.11 ± 0.02	0.021 ± 0.003
CAS-Zr	3.1 ± 1.4	3.11 ± 0.02	0.032 ± 0.003
LAS-Zr	1.1 ± 0.7	3.07 ± 0.03	0.014 ± 0.008
NAS-Zr	1.0 ± 0.5	3.42 ± 0.02	0.001 ± 0.003
Zr-Zr shell	**N**	**R (Å)**	**σ (Å^2)**
MAS-Zr	0.8 ± 0.3	3.38 ± 0.03	0.005 ± 0.004
ZAS-Zr	0.7 ± 0.3	3.38 ± 0.03	0.004 ± 0.004
CAS-Zr	1.2 ± 0.3	3.38 ± 0.03	0.008 ± 0.004
LAS-Zr	0.9 ± 0.3	3.42 ± 0.03	0.006 ± 0.004

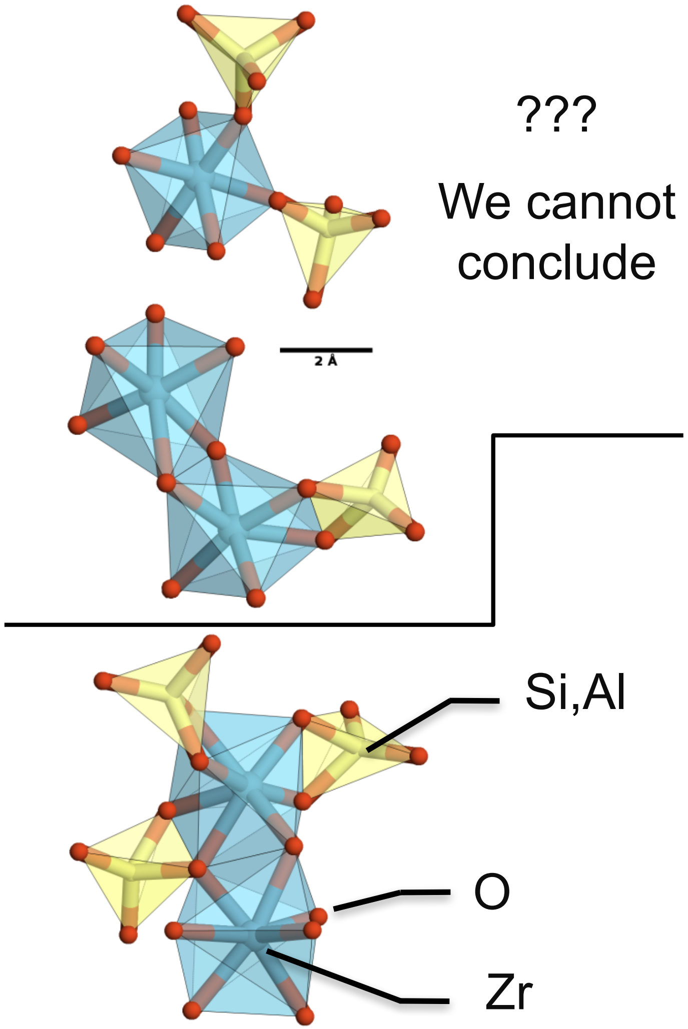
Confirm coordination number

Edge-sharing

Corner-sharing

Understand the connection with the network (Si,Al) or other Zr polyhedra

Models for Zr local environment

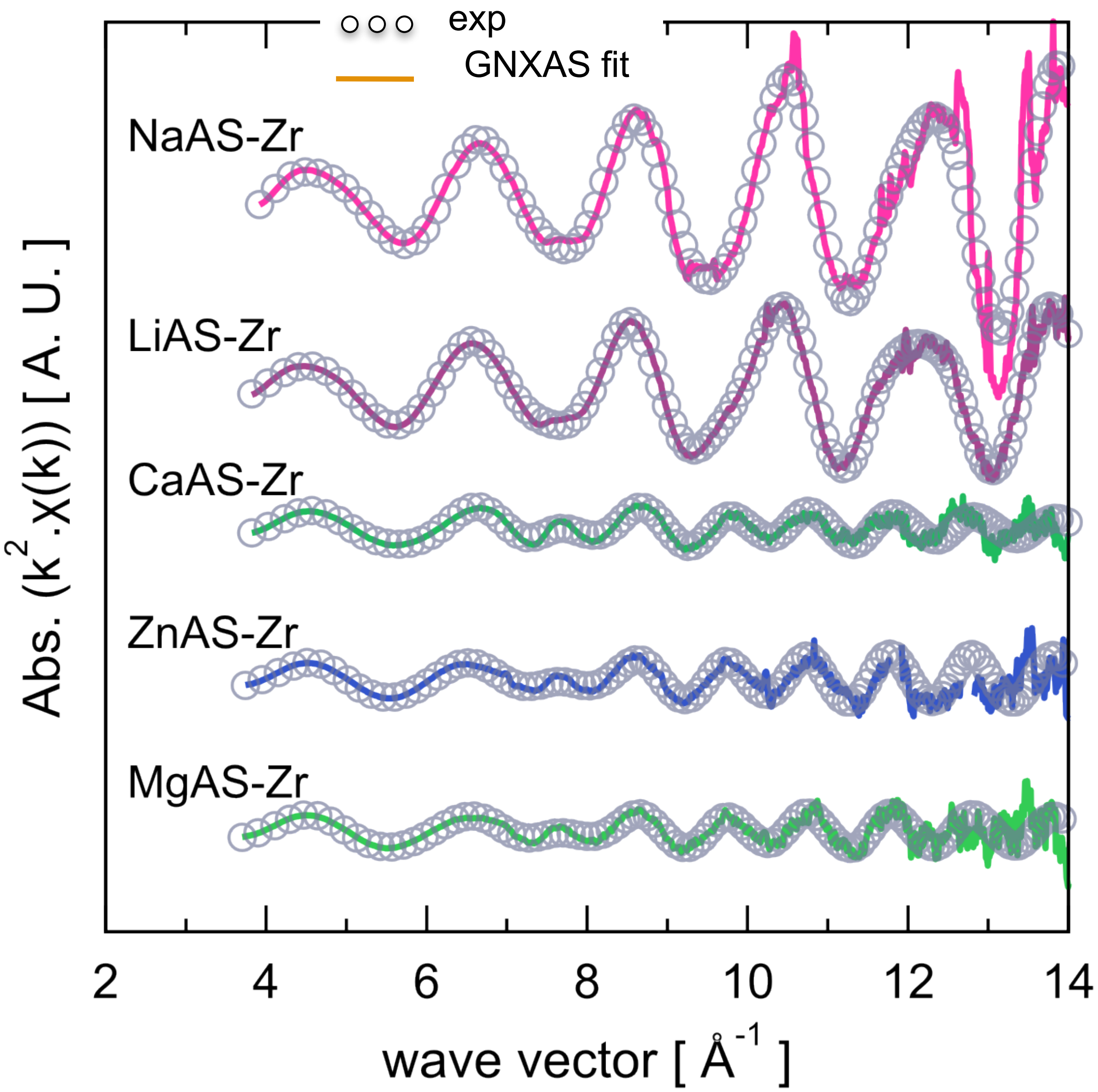


???

We cannot conclude

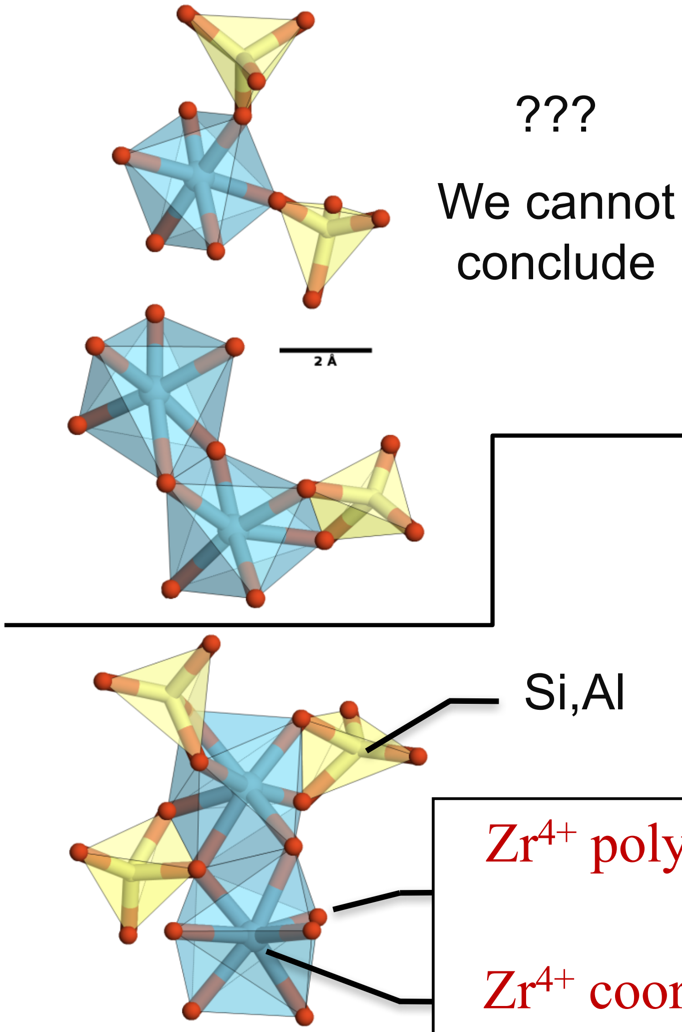
Zr K-edge EXAFS (GNXAS)

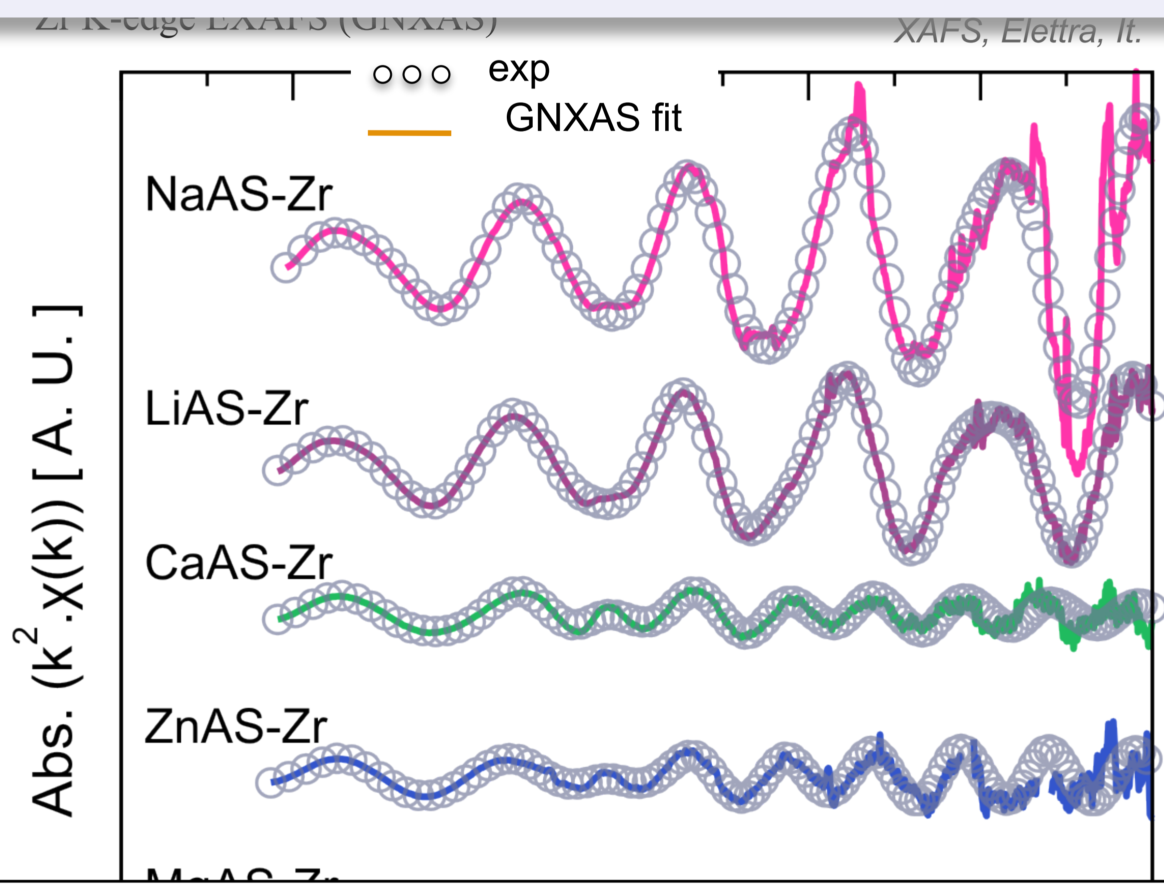
XAFS, Elettra, It.



Cormier et al., Mater. Chem. Phys. 152 (2015) 41

Models for Zr local environment





Zr^{4+} polyhedron linking with other Zr^{4+} seems to predominate for divalent cations, Ca^{2+}, Zn^{2+} and Mg^{2+}

Zr^{4+} coordination does not seem to impose the Zr^{4+} nucleating role...

Mesoscopic order in glasses

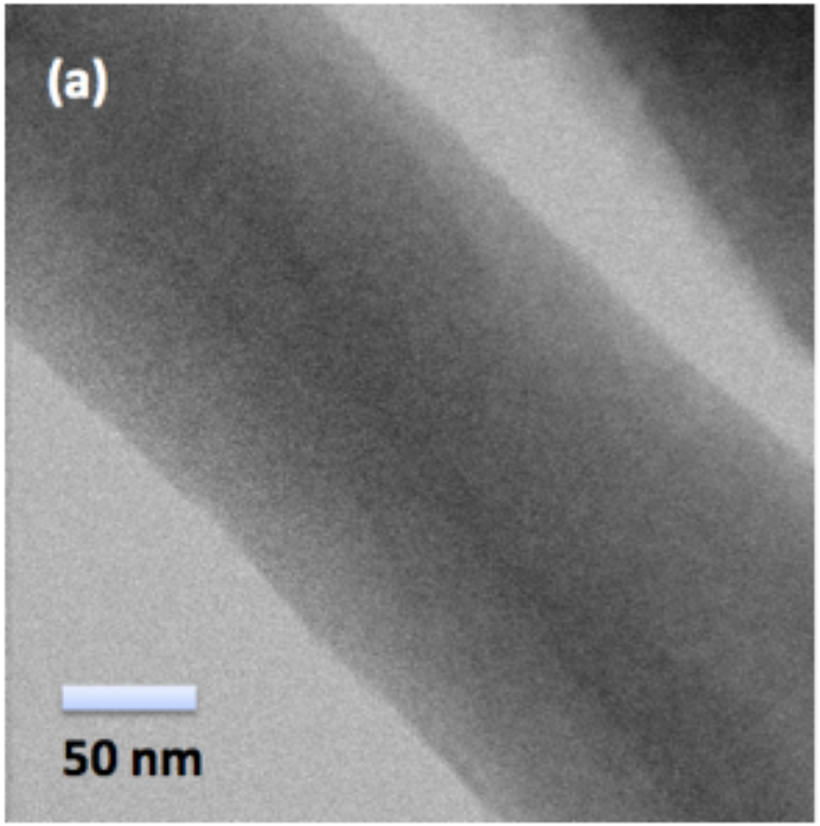
Glass $MgO-Al_2O_3-SiO_2-ZrO_2$

Mesoscopic order in glasses

Glass $MgO-Al_2O_3-SiO_2-ZrO_2$

No amorphous-amorphous separation

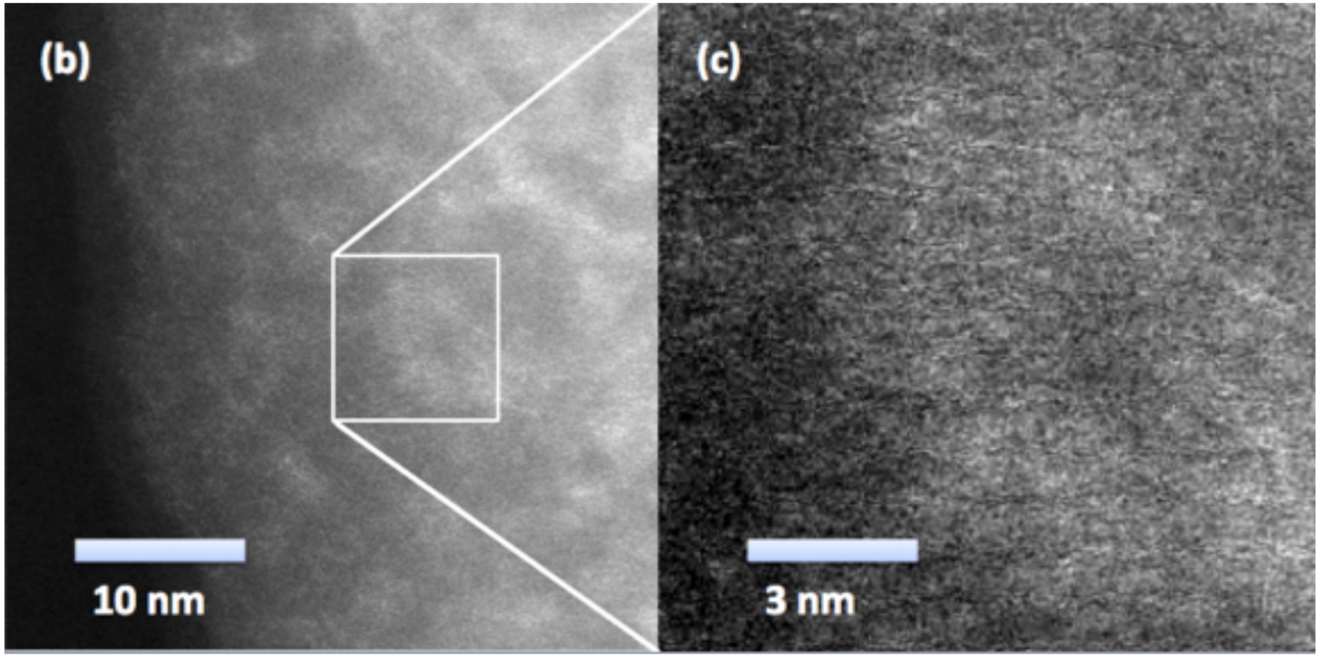
Transmission Electron Microsocopy ➪
glass is homogeneous



Mesoscopic order in glasses

Glass $MgO-Al_2O_3-SiO_2-ZrO_2$

Electron microscopy in HAADF mode ➪ chemical information (Z contrast)



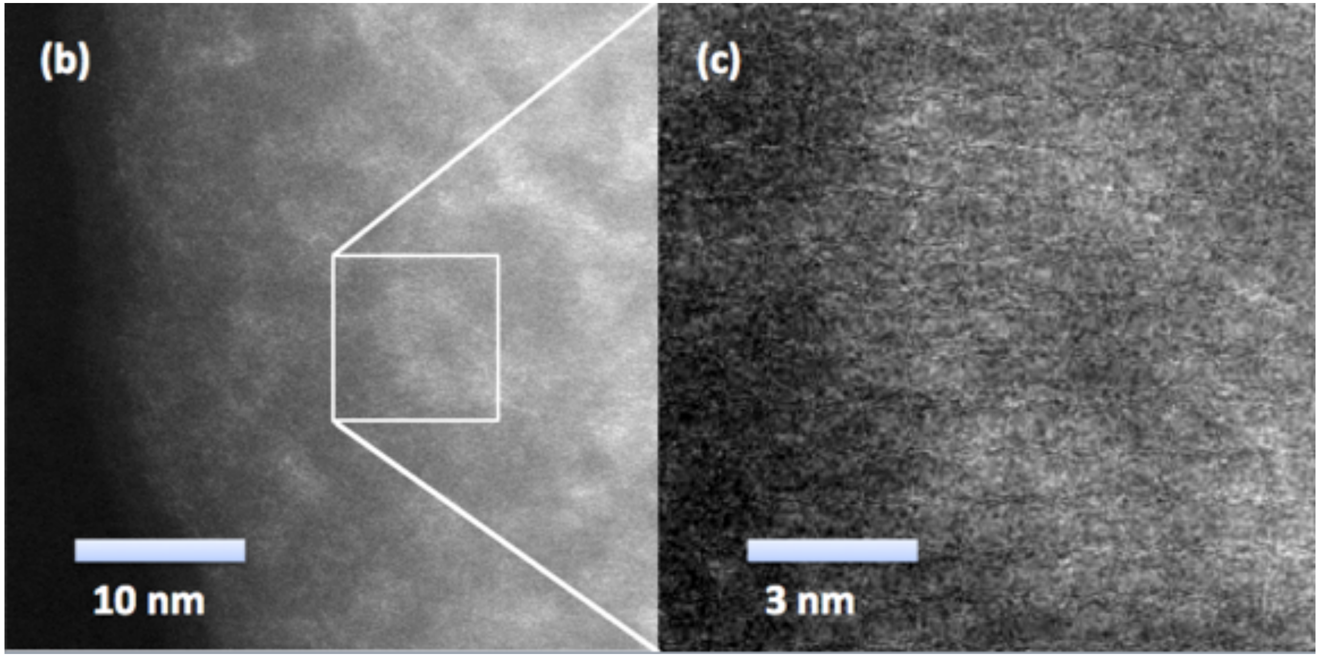
White regions = regions enriched with Zr

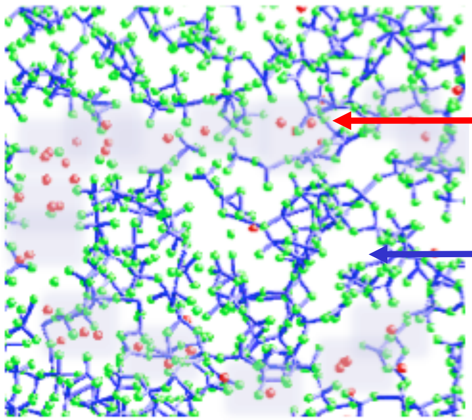
Dargaud et al. J. Appl. Phys. 99 (2011) 021904

Mesoscopic order in glasses

Glass $MgO-Al_2O_3-SiO_2-ZrO_2$

Electron microscopy in HAADF mode ➪ chemical information





Zones enriched in non-network formers

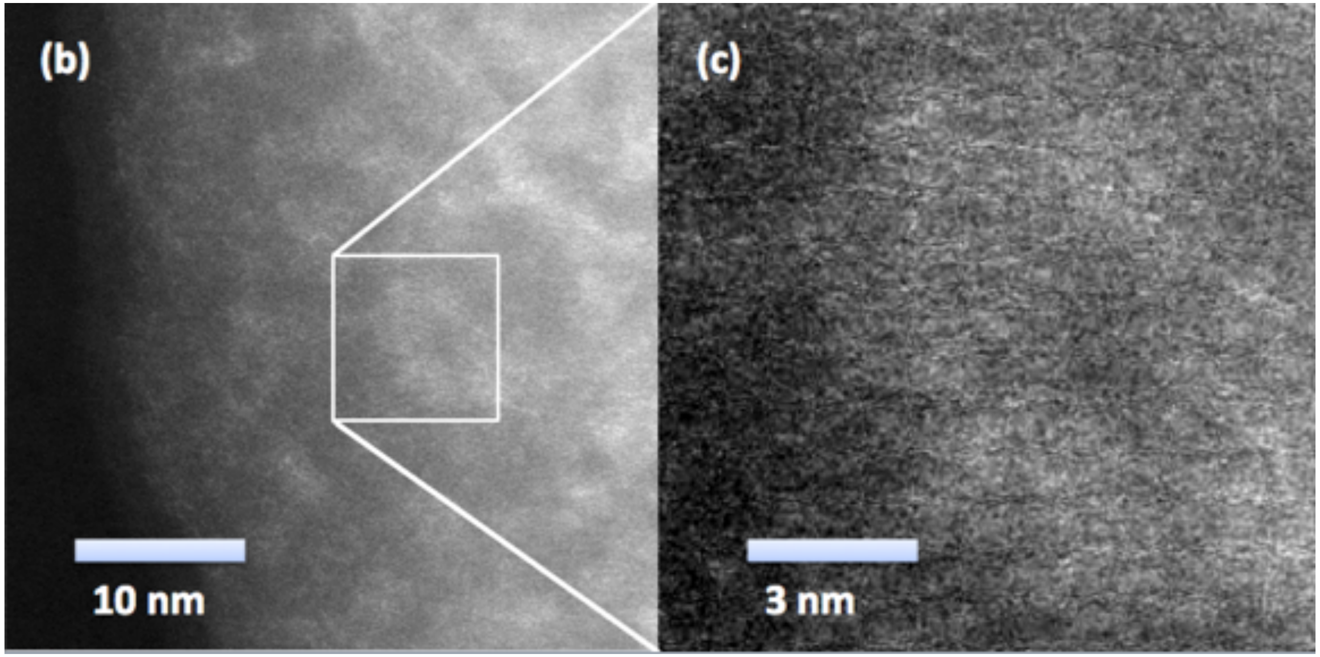
Zones enriched in network formers

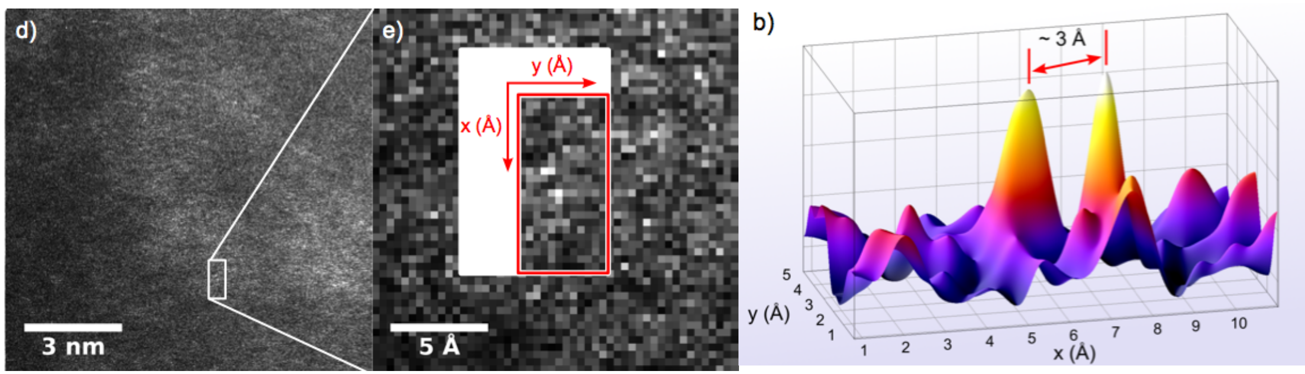
Greaves's model

Mesoscopic order in glasses

Glass $MgO-Al_2O_3-SiO_2-ZrO_2$

Electron microscopy in HAADF mode ➪ chemical information

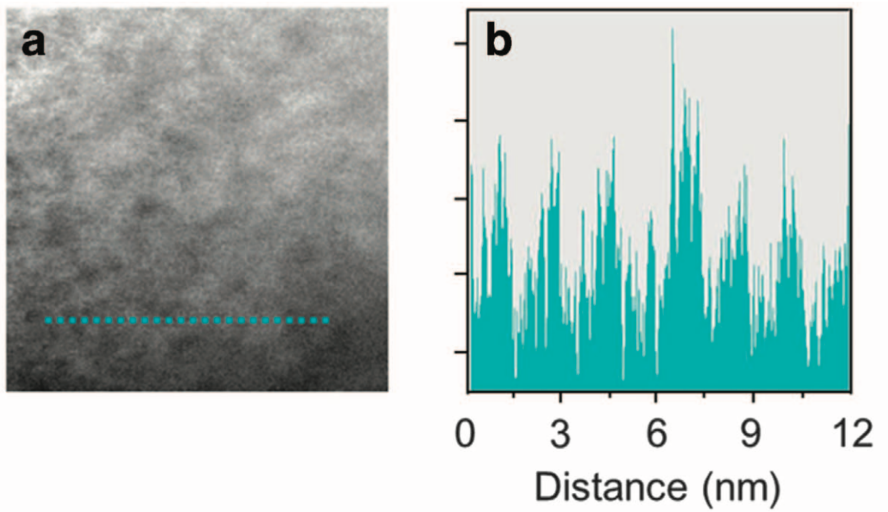




➪ compatible with short Zr-Zr distances found by EXAFS

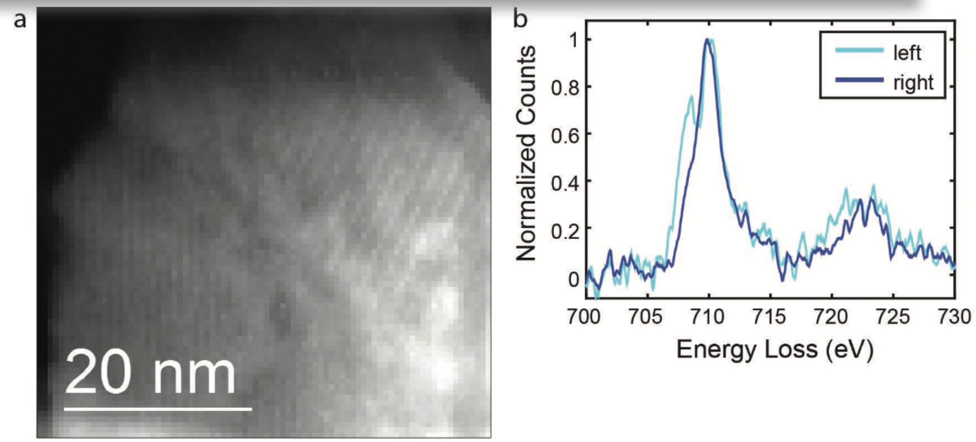
Mesoscopic order in glasses

Electron microscopy in HAADF mode



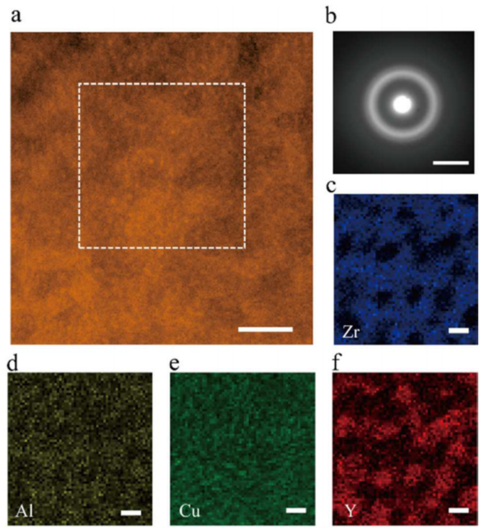
Mesoscale structure in the host
Li_2O-Ta_2O_5-Al_2O_3-SiO_2 glass

Yu et al. Asia Materials 8(2016)e318



Submicrometer-scale spatial heterogeneity in silicate glasses

Burgess et al., American Mineralogist 101(2016)2677

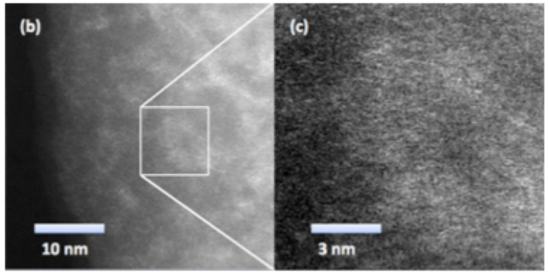


ZrCuAlY alloy
chemically inhomogeneous

spinodal decomposition

Jiao et al., Chemistry of materials 29(2017)4478

Importance of medium range order

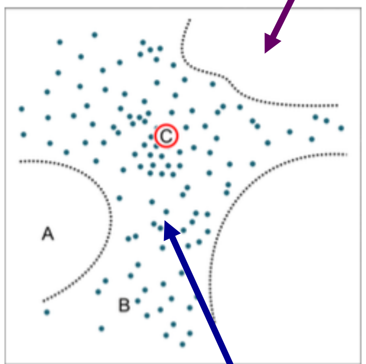


Initial glass

STEM-HAADF

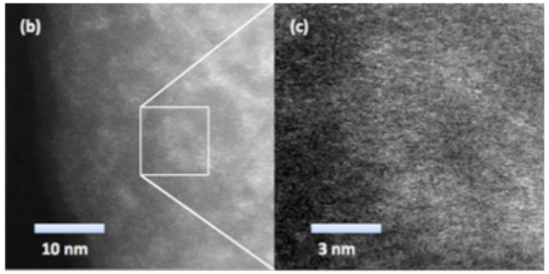
- ➪ Zr: non-homogeneous distribution

Zr-poor regions



Zr-rich regions

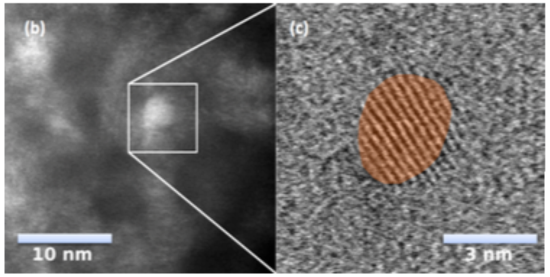
Importance of medium range order



Initial glass

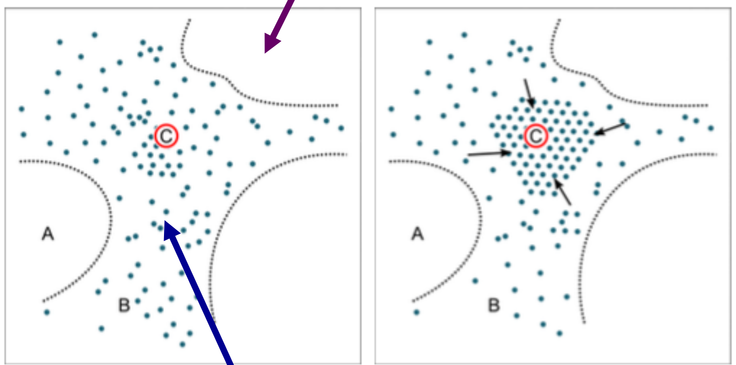
STEM-HAADF

- ➪ Zr: non-homogeneous distribution
- ➪ Zr-rich regions: loci for nucleation



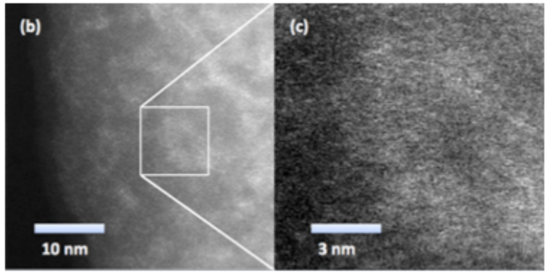
Heat-treatment at 920° C

Zr-poor regions



Zr-rich regions

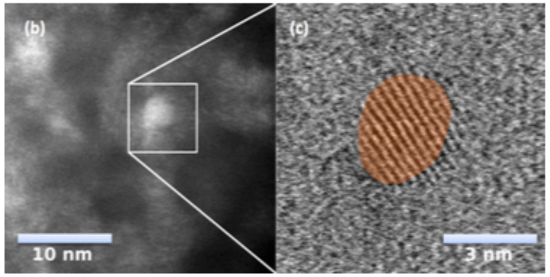
Importance of medium range order



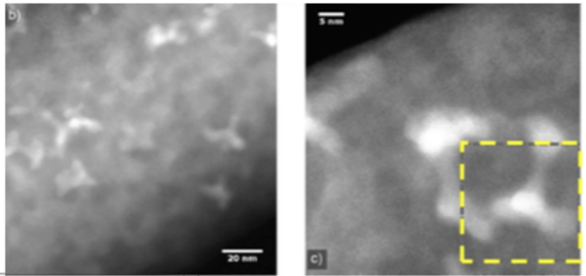
Initial glass

STEM-HAADF

- ➪ Zr: non-homogeneous distribution
- ➪ Zr-rich regions: loci for nucleation
- ➪ then multipodal geometry

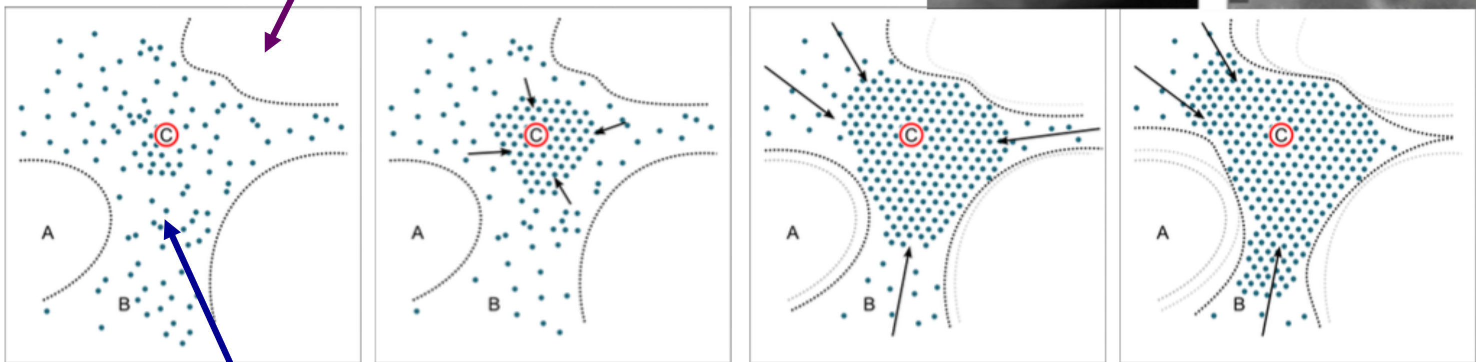


Heat-treatment at 920° C



Heat-treatment at 975° C

Zr-poor regions



Zr-rich regions

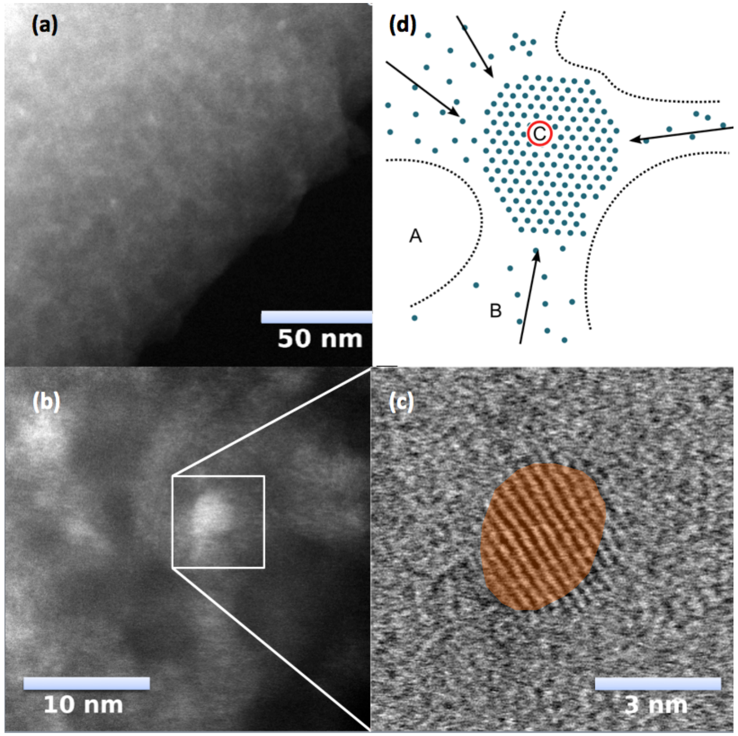
Dargaud et al., Appl. Phys. Lett. 99 (2011) 21904
Dargaud et al., JNCS 356 (2010) 2928

Implications for nucleation

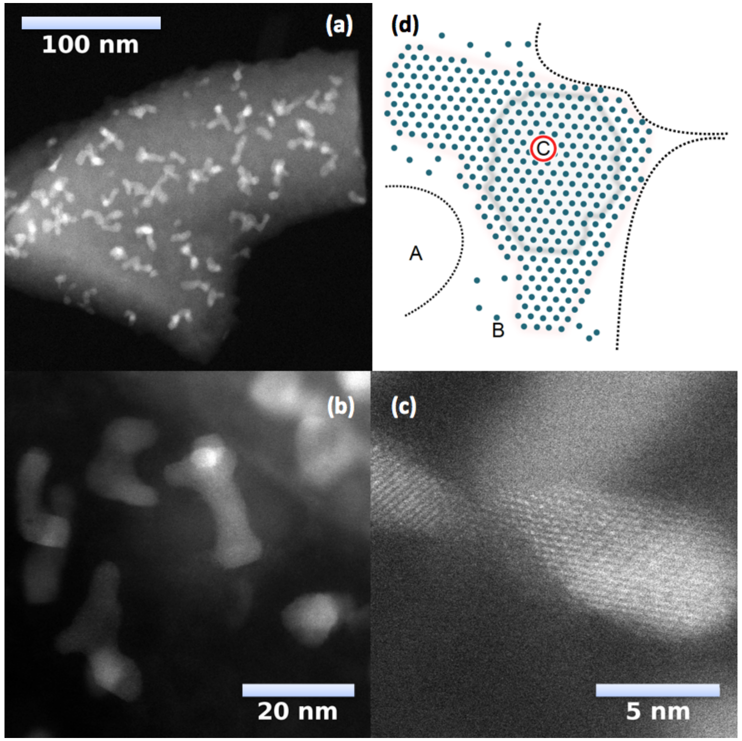
Glass MgO-Al2O3-SiO2-ZrO2

STEM-HAADF

Heat-treatment at 920° C



Heat-treatment at 975° C



- ➪ Zr-rich regions: loci for nucleation
- ➪ first nuclei slightly ellipitic
- ➪ then multipodal geometry

Zr: non-homogeneous distribution

➪ **pre-organization favors nucleation**

Dargaud et al. J. Appl. Phys. 99 (2011) 021904

Nanometer scale inhomogeneities in glasses

Small angle scattering (SAXS, SANS)
Porai-Koshits, JNCS 49(1982)143

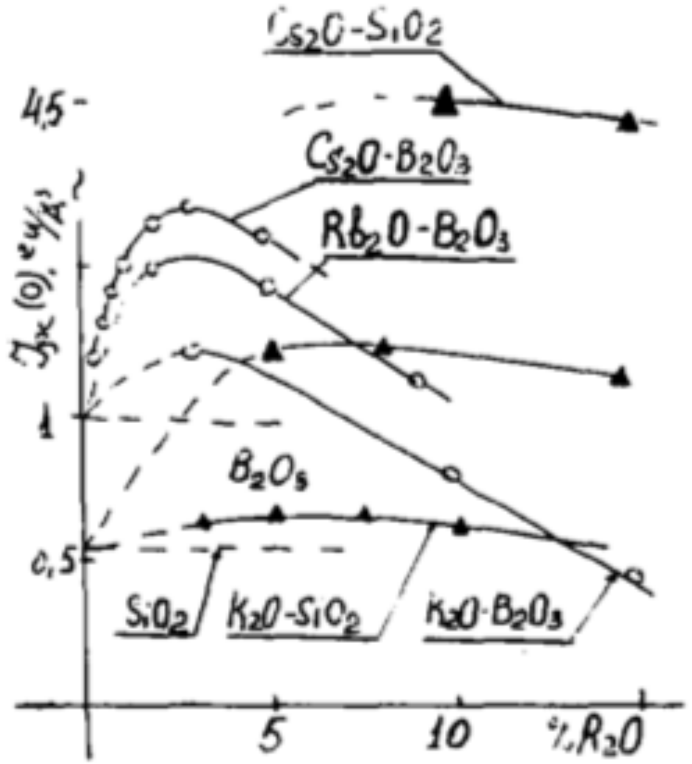
⇒ Thermal density fluctuations
1 component system or no modifiers

⇒ Thermal composition fluctuations
Multicomponent glasses

Ex:
Size of the inhomogeneities
Alkali borate **1.0-1.5 nm**
Borosilicate and borogermanate **1-1.2 nm**
Alkali silicate **2-3 nm**

⇒ Supercritical fluctuations

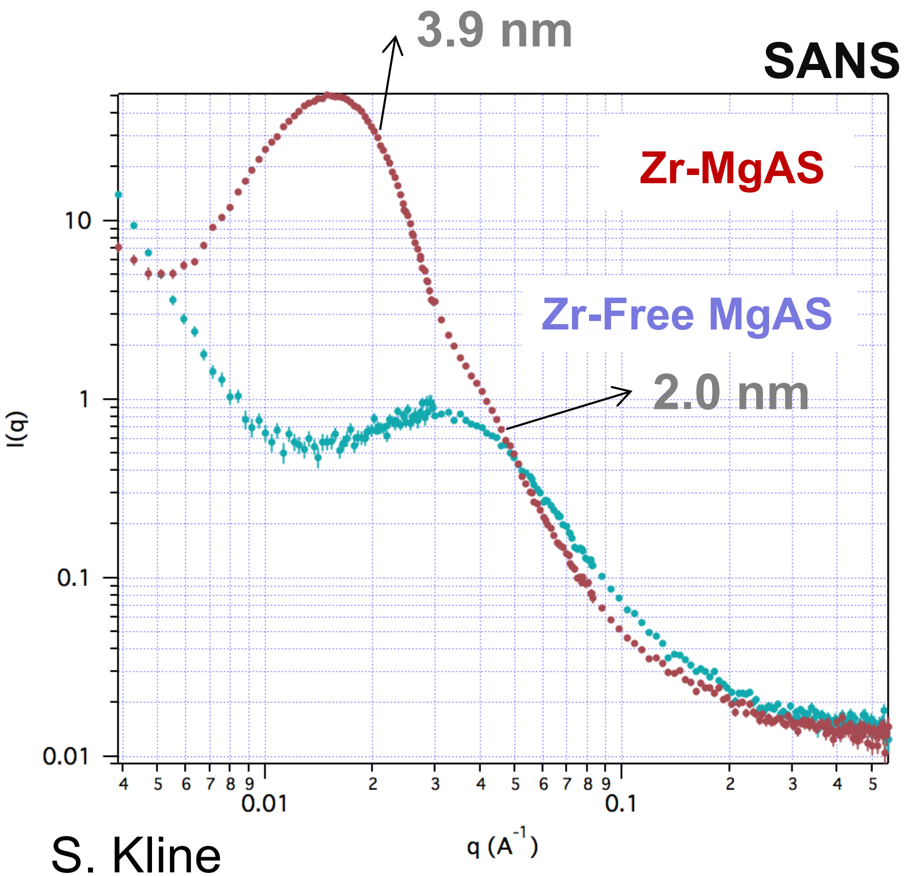
Ex:
Size of the inhomogeneities
Na borosilicates **30-40 nm**
Pb Aluminoborate **3-10 nm**



Nature of those inhomogeneities ?

Small angle scatterings

SANS and SAXS signal of Zr and Zr-free MgAS

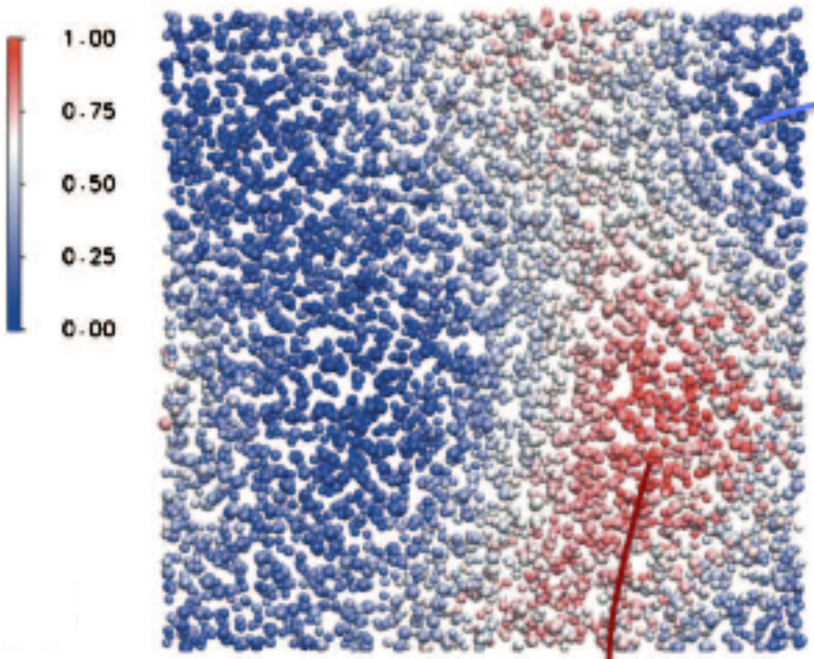


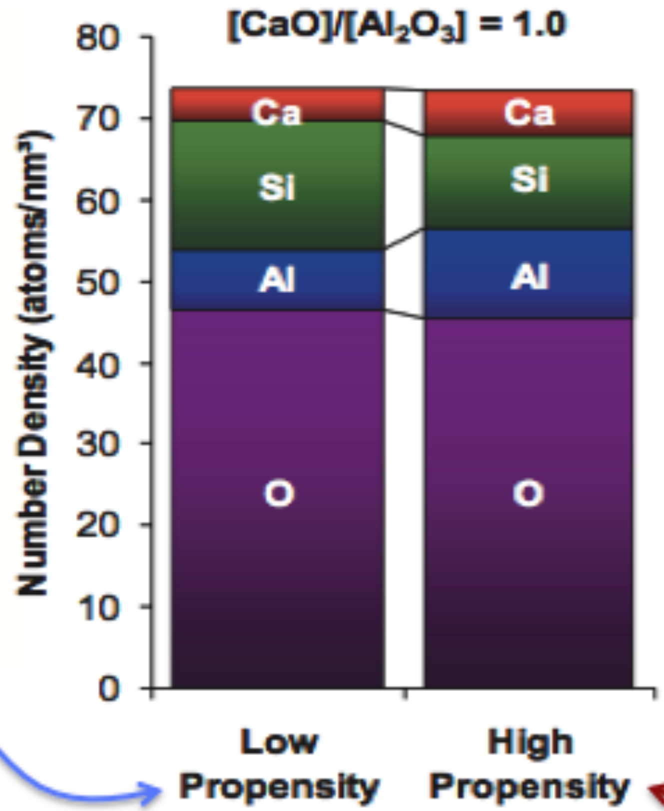
S. Kline

NIST – Center for Neutron research, USA

Structural/compositional heterogeneities and dynamical heterogeneities

Dynamical heterogeneties associated with concentration fluctuations





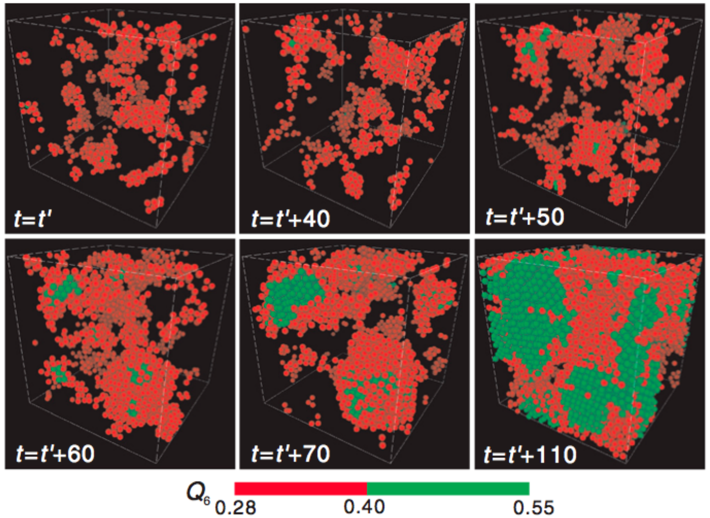
➪ Regions of high dynamics propensity have higher concentration of Al et Ca (and more dense regions)

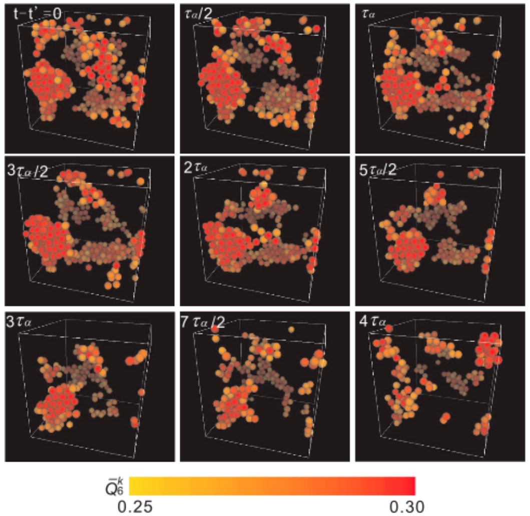
Vargheese et al. J. Chem. Phys. 132(2010)194501

Order in the supercooled melt

Simulations of colloidal supercooled melts

Hiden static order in the supercooled melt ➪ supercooled liquid is not homogeneous
medium-range crystalline order" (MRCO)





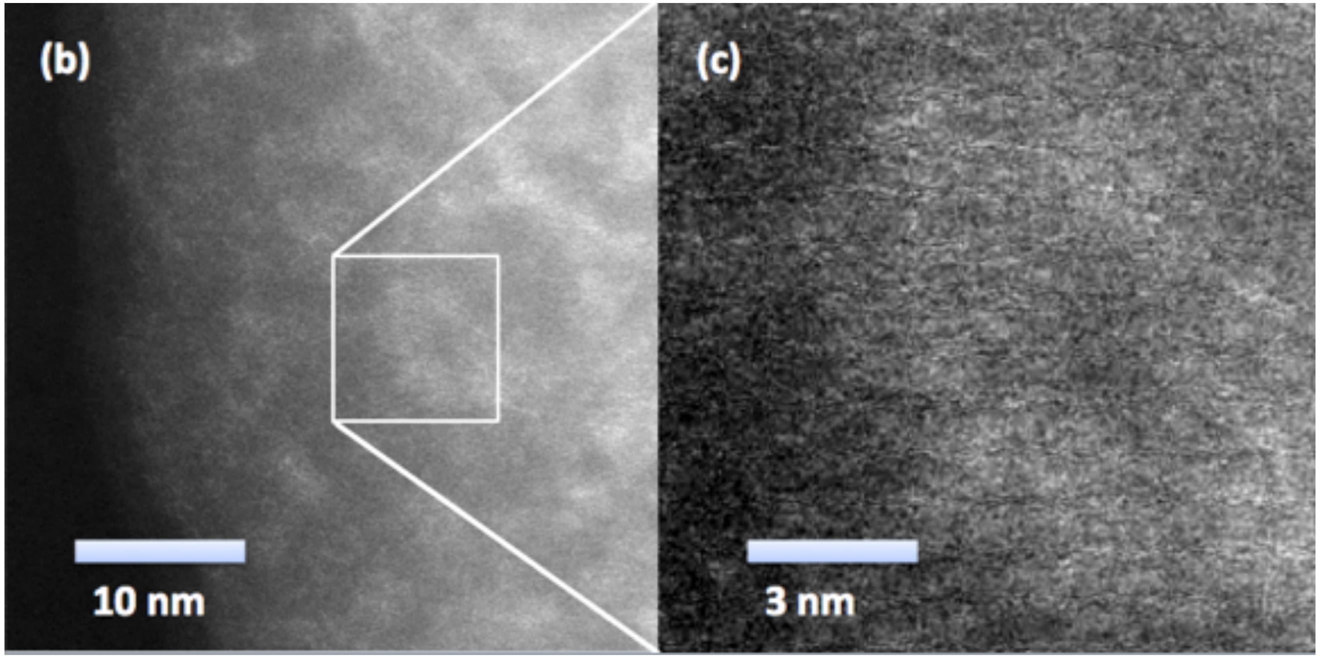
MRCO have a finite lifetime ≠ crystalline nuclei

➪ First crystals do not have the symmetry of the most stable crystal

➪ Organization corresponds to transcient spontaneous fluctuations, intrinsic to the supercooled liquid

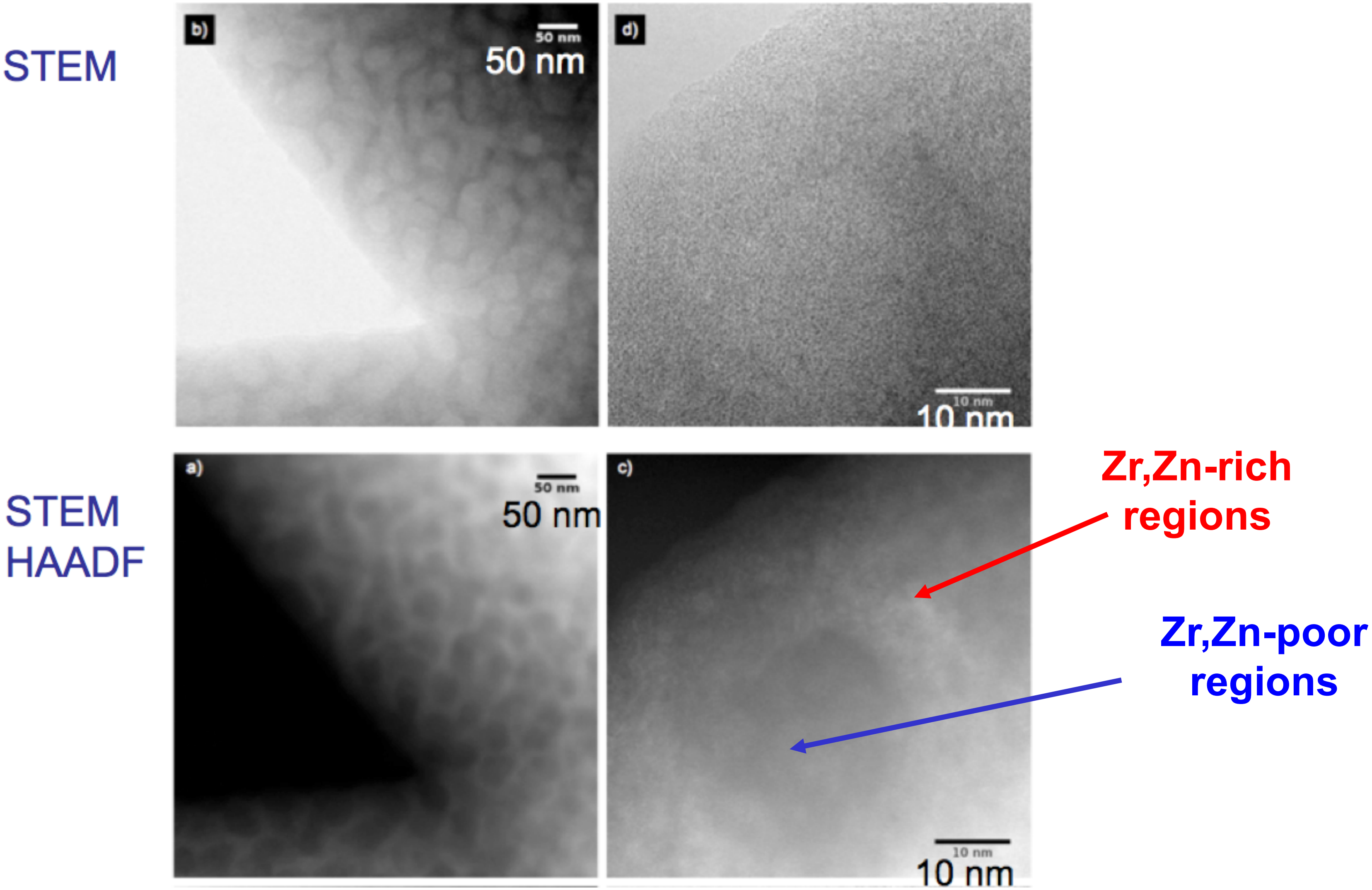
Kawasaki &Tanaka, PNAS 107 (2010) 14036

Is it phase separation ?



Heterogeneities and amorphous-amorphous separation (A-A)

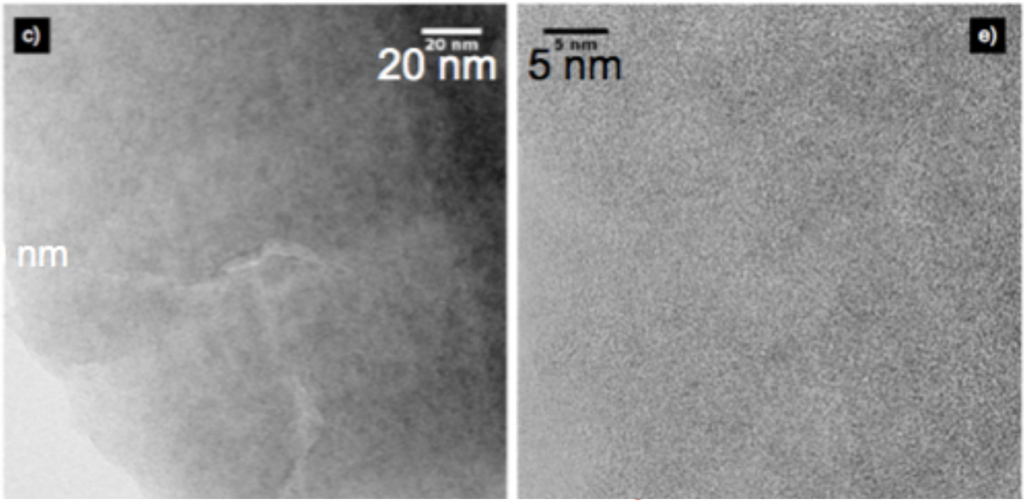
Glass MAS+Zr+Zn normal quench ➪ **Macroscopic A-A separation (opalescence)**



Heterogeneities and amorphous-amorphous separation (A-A)

Same glass MAS+Zr+Zn with rapid quench

➪ **no opalescence**

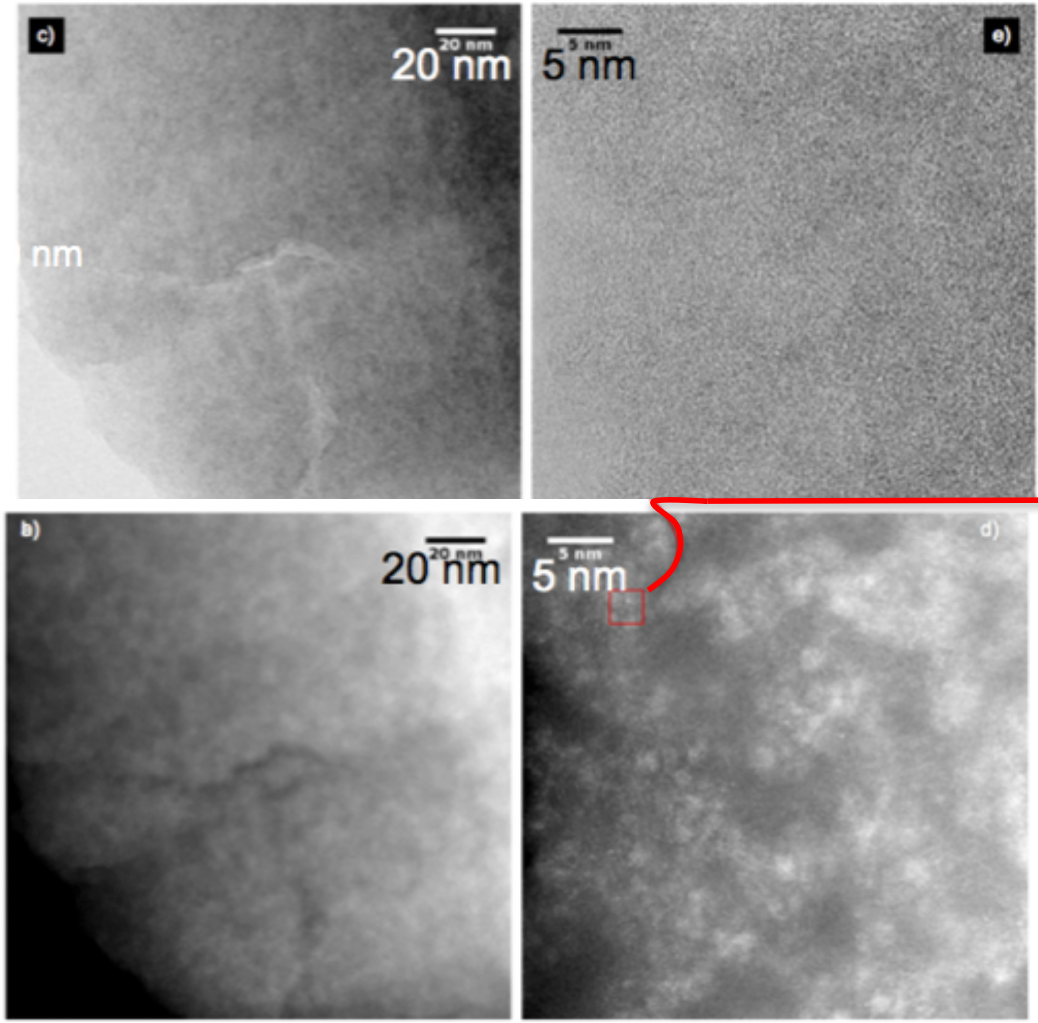


STEM

Heterogeneities and amorphous-amorphous separation (A-A)

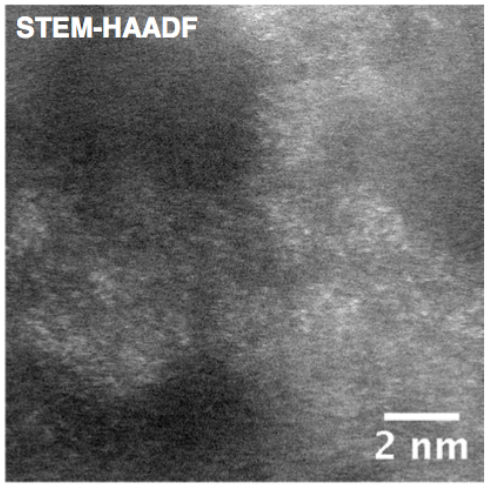
Same glass MAS+Zr+Zn with rapid quench

➪ **no opalescence**
but still non-homogeneous distribution



STEM

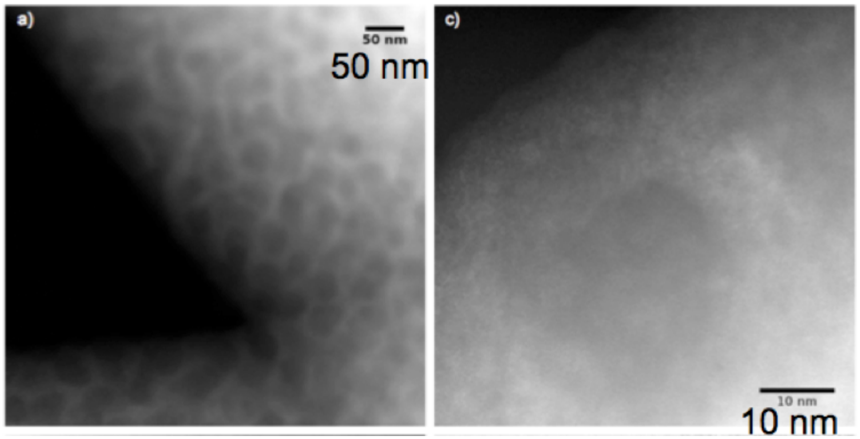
STEM HAADF



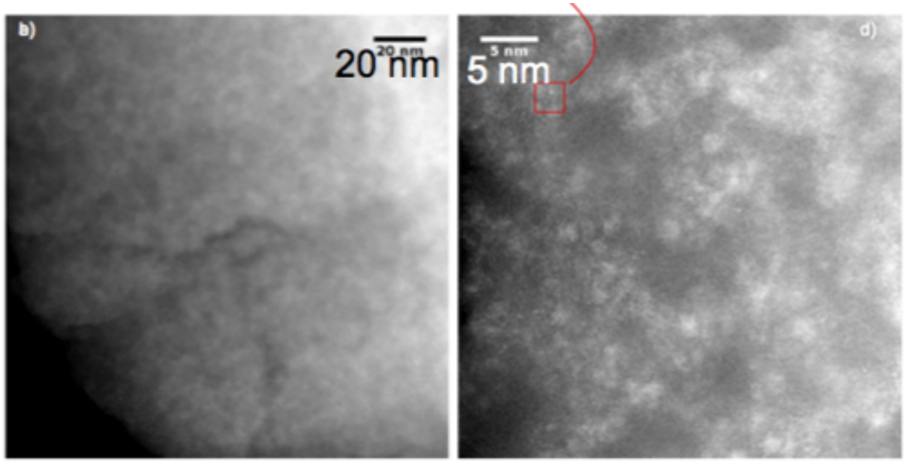
Heterogeneities and amorphous-amorphous separation (A-A)

Glass MAS+Zr+Zn

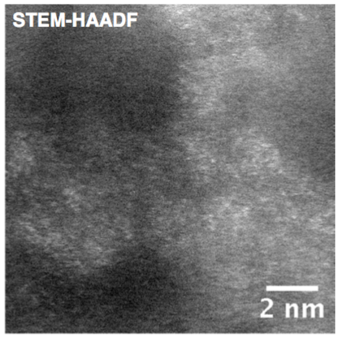
➪ Macroscopic A-A separation



➪ No macroscopic A-A separation



➪ Heterogeneities visible even without macroscopic A-A separation
➪ At which scale is there an A-A separation?



Dargaud et al. JNCS 358 (2012) 1257

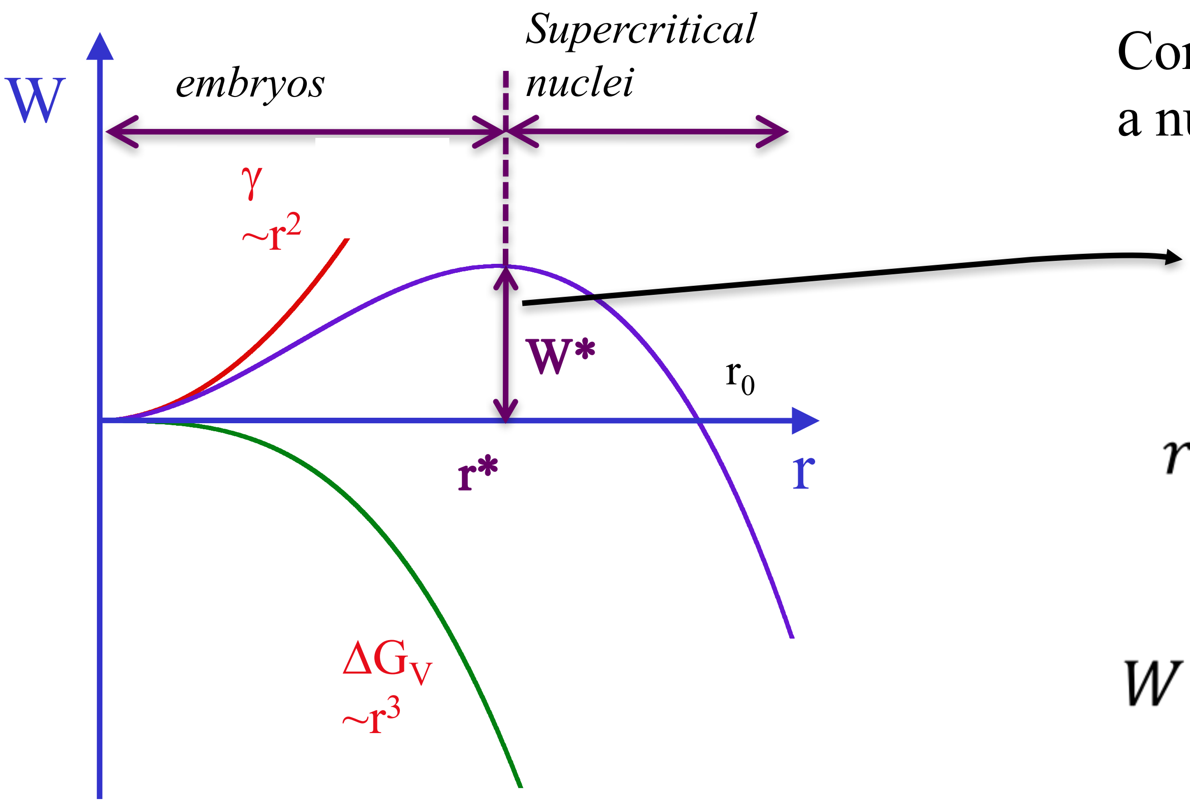
Relationship with nucleation theory

Classical nucleation theory

Thermodynamic contributions

balance between surface energy and volume energy

$$W = 4\pi r^2 \gamma - \frac{4\pi}{3} r^3 \Delta G_V$$ Work of formation



Condition for the formation of a nucleus of critical size:

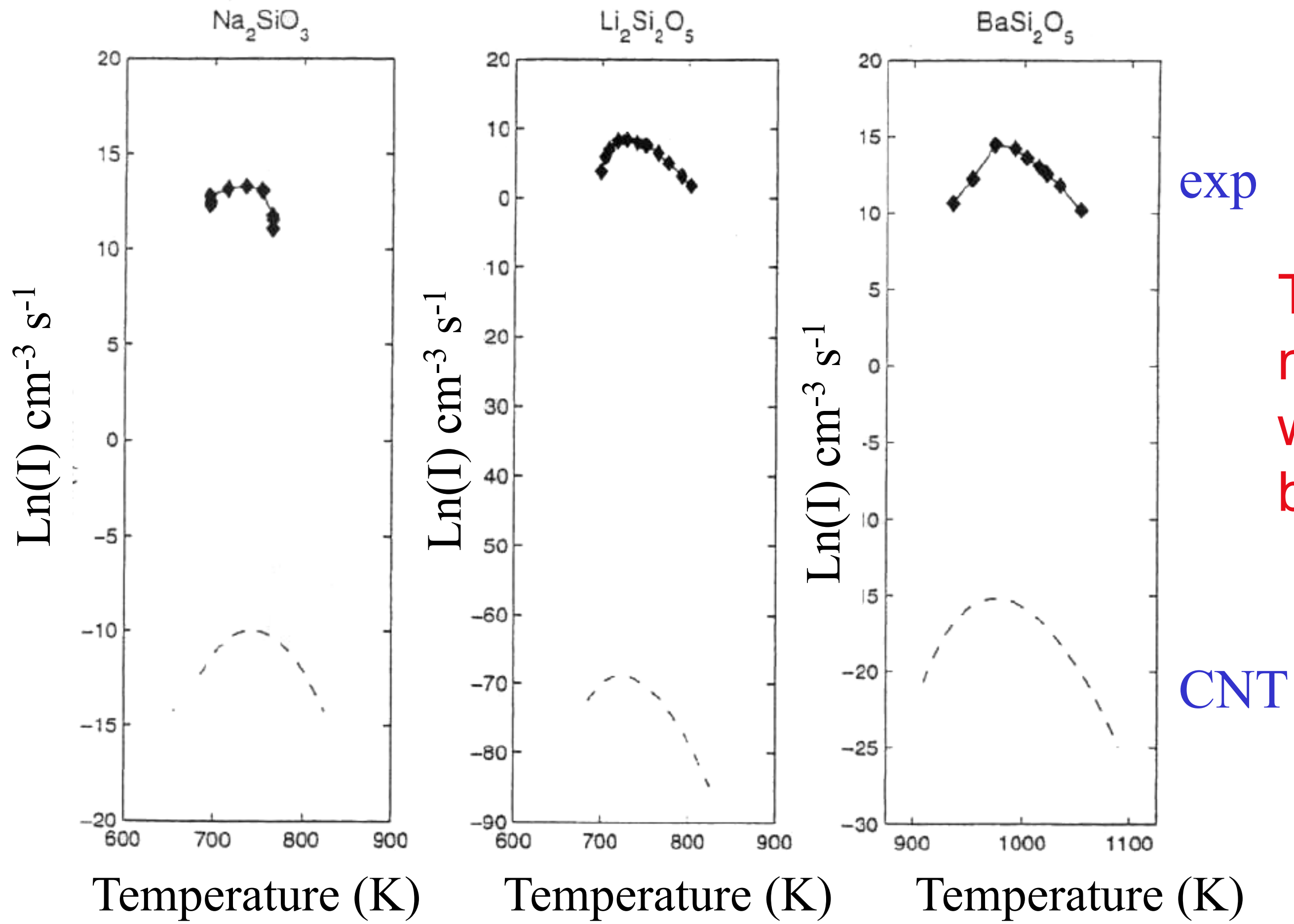
$$\frac{\partial W}{\partial r} = 0$$

$$r^* = \frac{2\gamma}{\Delta G_V}$$

$$W^* = \frac{16\pi}{3} \frac{\gamma^3}{\Delta G_V^2}$$

Theory and experiments

Discrepancies between nucleation rates experimentally observed and numerically predicted



Theory of the nucleation describes well the experiment but is not quantitative !

Sen & Mukerji, JNCS 246(1999)229

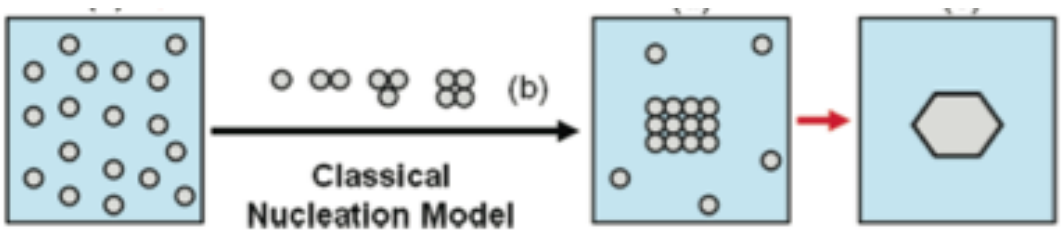
Limits of the Classical Nucleation theory (CNT)

• CNT allows to estimate the size of the critical nuclei and the nucleation rate

• CNT : the critical nucleus is essential

… but no information of the pathways leading to their formation

• CNT a single order parameter: atoms are clustering and simultaneously adopt a crystalline environment



• The pathways driving to the formation of nuclei are in the heart of the recent theories

Generalized Gibbs Approach (GGA)

✓ Nucleation of a phase with different properties compared to the final stable phase

✓ Change in composition and/or structure

✓ Determination of the pathways transforming the nuclei to the stable phase

Schmelzer et al.,

J. Colloid. Interface Sc. 272(2004)109

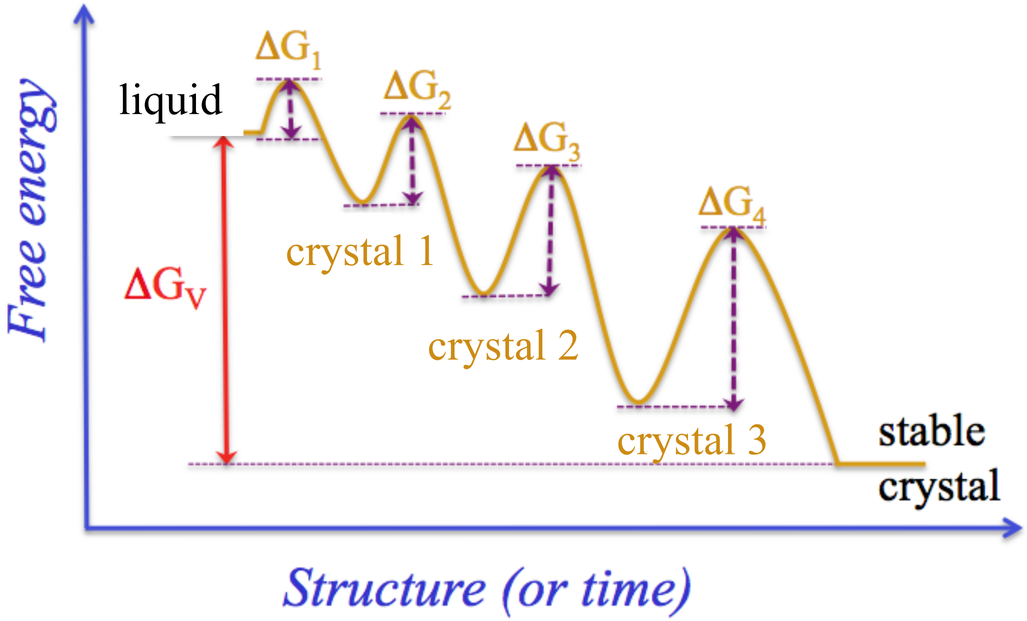
Int. J. Appl. Glass Sci. 1(2010)16

Ostwald rule of stage

✓nucleation of a phase with different properties compared to the final stable phase
✓change in composition and/or structure
✓Determination of the pathways transforming the nuclei to the stable phase

Ostwald rule

Ostwald in 1897



"...in the course of transformation of an unstable (or metastable) state into a stable one the system **does not go directly to the most stable conformation** (corresponding to the modification with the lowest free energy) but **prefers to reach intermediate stages** (corresponding to other metastable modifications) having the closest free energy to the initial state"

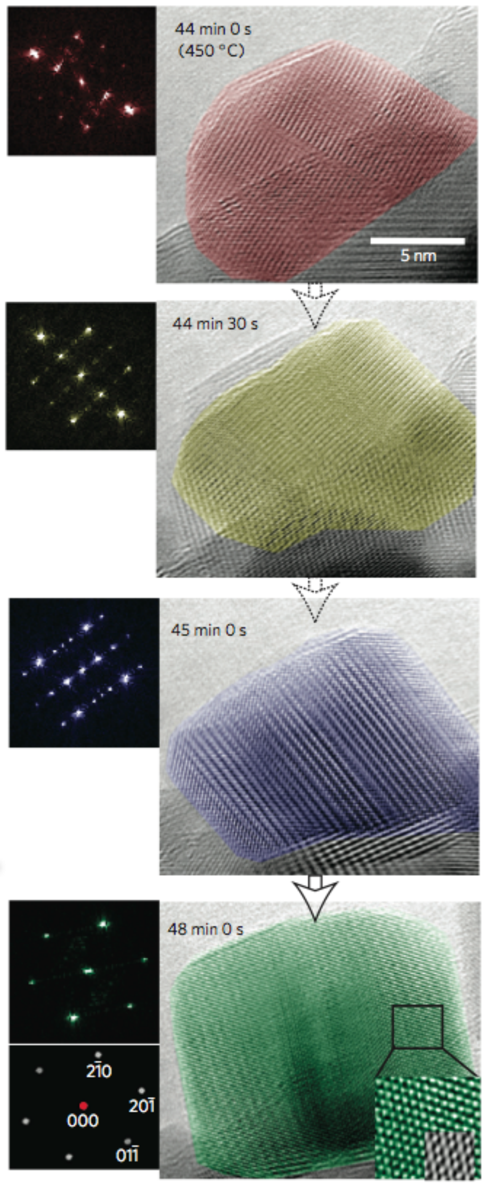
In situ growth

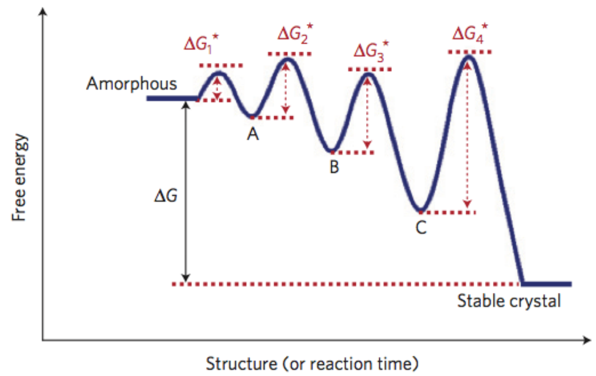
High temperature high resolution electron microscopy

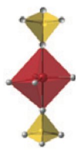
$LiFePO_4$ at
450° C

Transcient
metastable
crystalline states

Olivine structure:
stable crystalline
form







➪ Confirm that first crystalline phases are not the most stable phase

➪ Crystal with the lowest energy barrier will appear first, then will transform with the structure having the smallest difference in energy

Chung et al., Nature Physics 5(2009)68

Generalized Gibbs Approach (GGA)

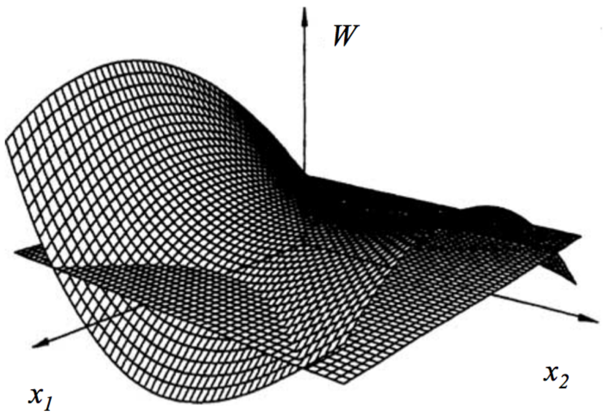
Critical parameters are now depending of the composition of the nucleus α

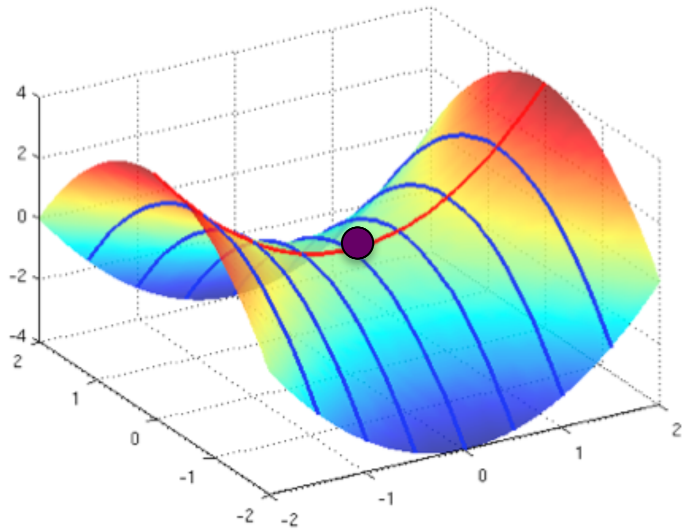
$$r^* = \frac{2\gamma}{c_\alpha \Delta\mu} \qquad W^* = \frac{16\pi}{3}\frac{\gamma^3}{(c_\alpha \Delta\mu)^2} \qquad \Delta\mu = \sum x_{j\alpha}\left[\mu_{j\alpha} - \mu_{j\beta}\right]$$

✓Therefore the critical nucleus corresponds to the minimum of W^* with regard to any composition allowed for the nucleus:
the nucleus can change is size AND composition

$$\left.\frac{\partial W^*}{\partial x_{j\alpha}}\right|_{x_{i\alpha=const,\, i\neq j;\, \{x_\beta\}=const}} = 0$$

✓Maxima for *W* as a function of the cluster size and minima of *W* as a function of the composition variations

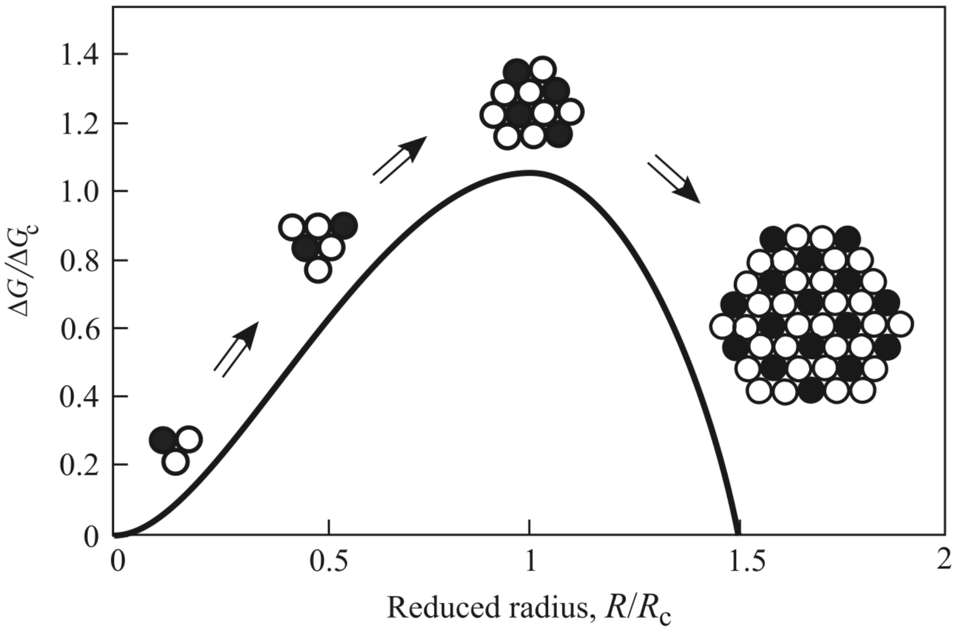




Generalized Gibbs Approach (GGA)

What do we learn from this theory ?

CNT

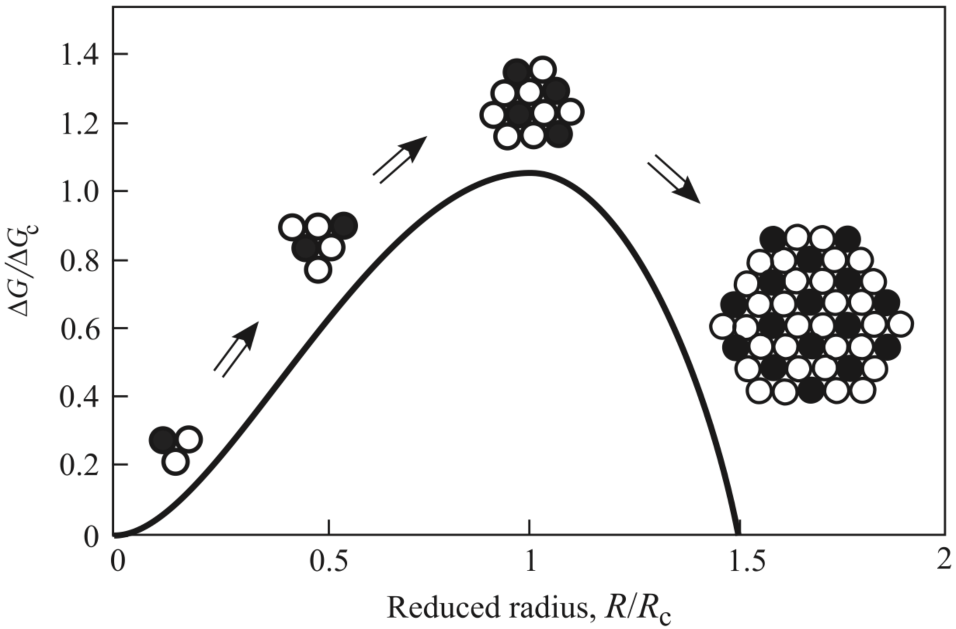


Continuous evolution of the size of the nucleus with a constant composition and structure corresponding to the final macroscopic phase

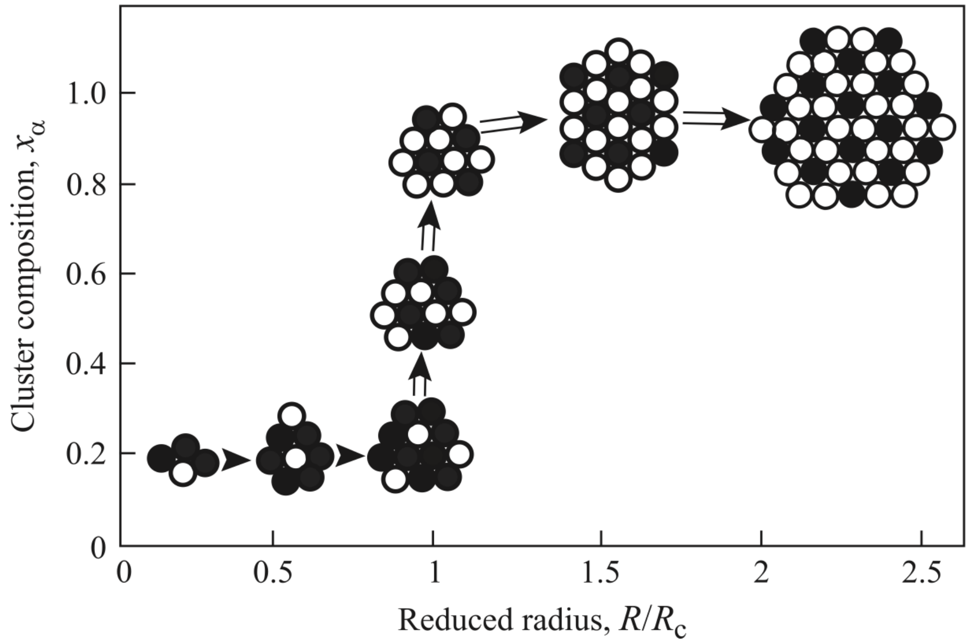
Generalized Gibbs Approach (GGA)

What do we learn from this theory ?

CNT



GGA



Continuous evolution of the size of the nucleus with a constant composition and structure corresponding to the final macroscopic phase

composition change, r cst

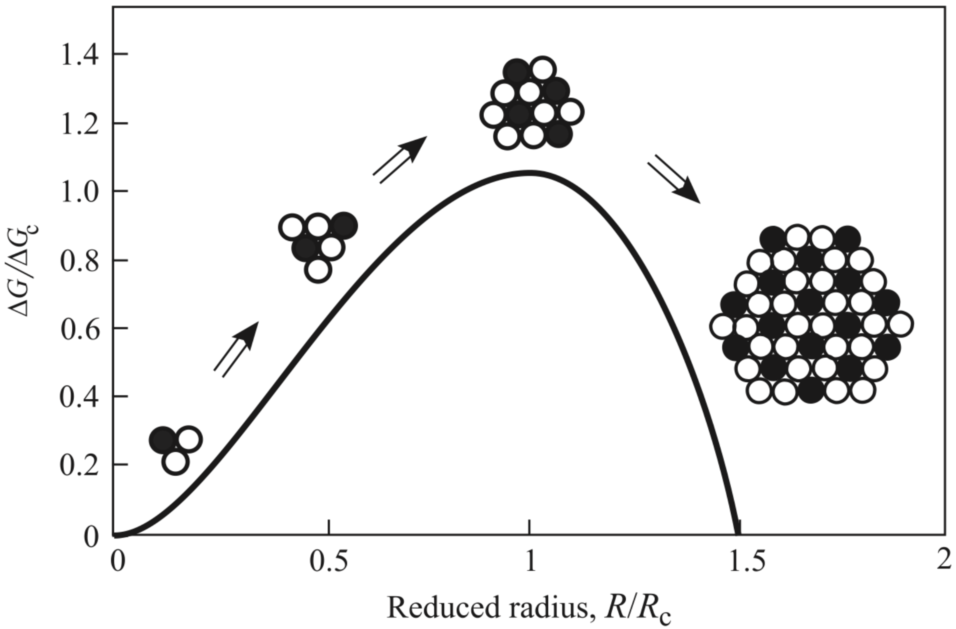
Nucleus grows, cst composition

r is changes up to the critical size, but no change in composition

Generalized Gibbs Approach (GGA)

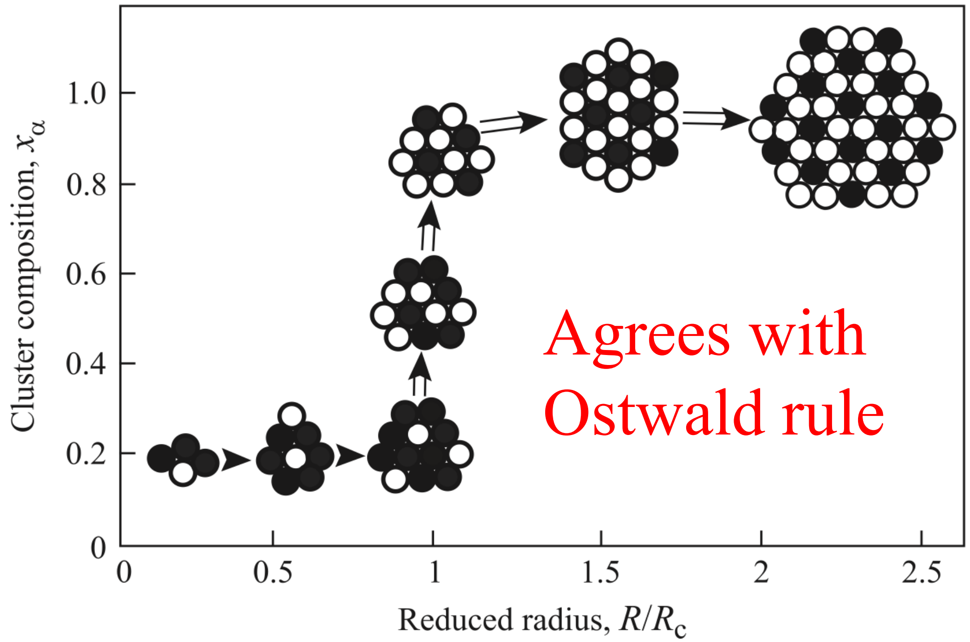
What do we learn from this theory ?

CNT



Continuous evolution of the size of the nucleus with a constant composition and structure corresponding to the final macroscopic phase

GGA



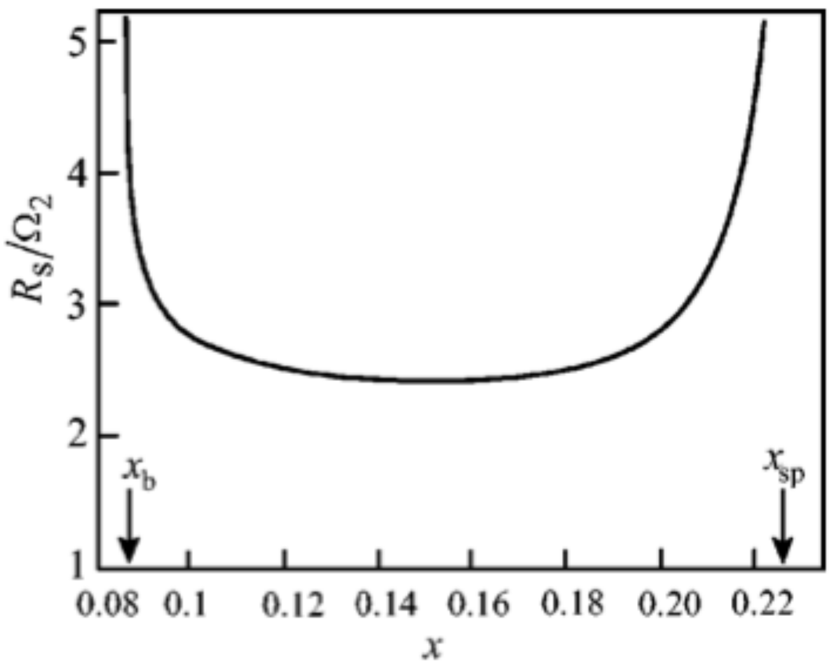
composition change, r cst

Nucleus grows, cst composition

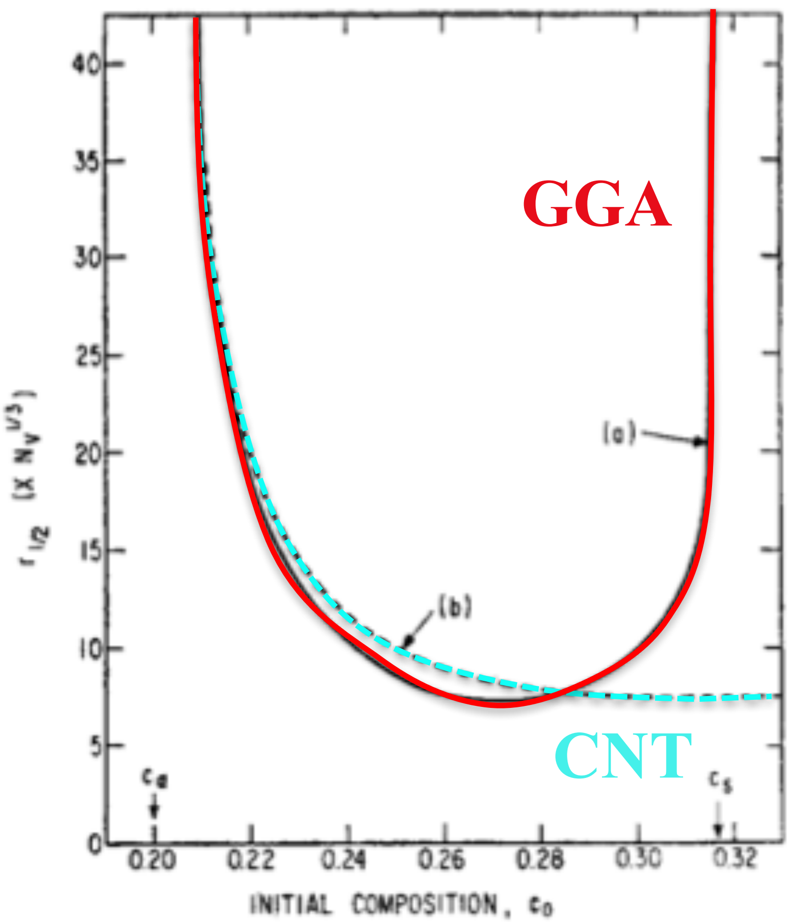
r is changes up to the critical size, but no change in composition

Generalized Gibbs Approach (GGA)

What do we learn from this theory ?



Same evolution of the critical size than with Cahn-Hillard
= takes into account the spinodal



Generalized Gibbs Approach (GGA)

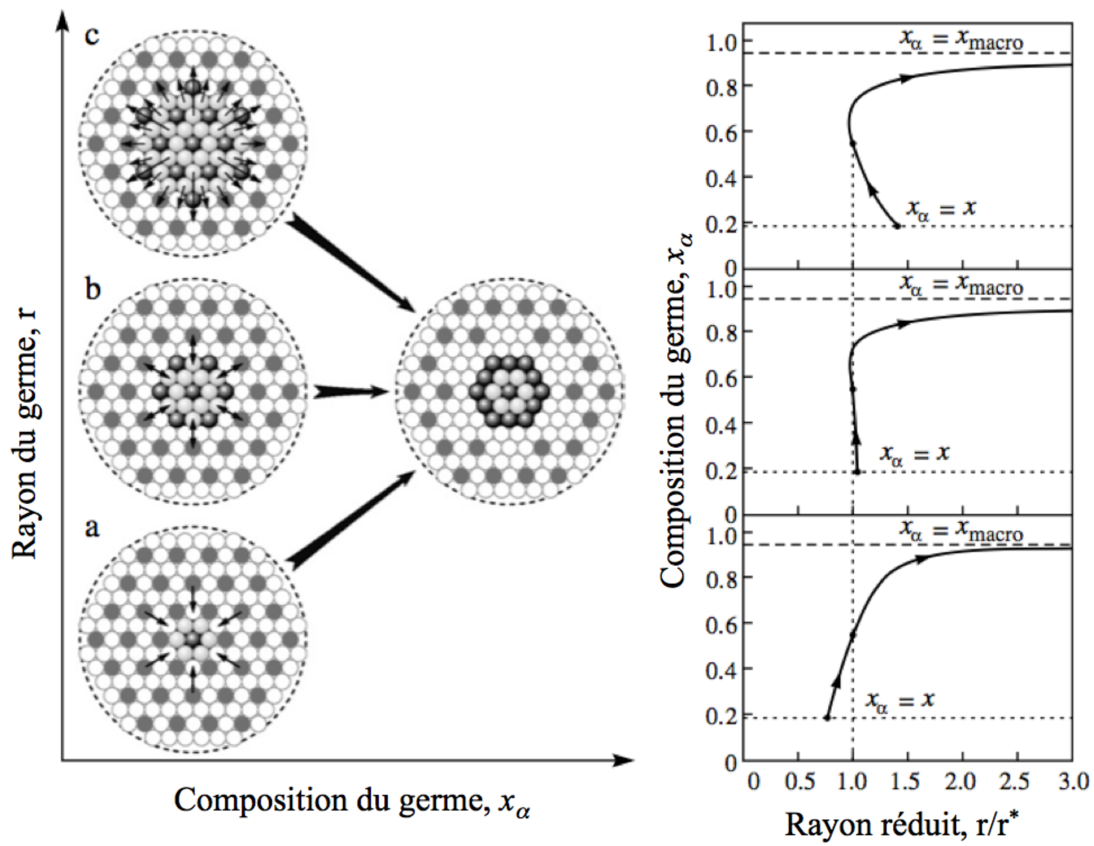
What do we learn from this theory ?

GGA

Preferential pathways of the nucleus towards the new macroscopic phase depend of the diffusion coefficients of each element

Need to know each atomic diffusion coefficient

⇒ this resolves a limit of the CNT: kinetic hypothesis



$D_2 << D_1$, $D_2 \cong D_1$, $D_2 >> D_1$

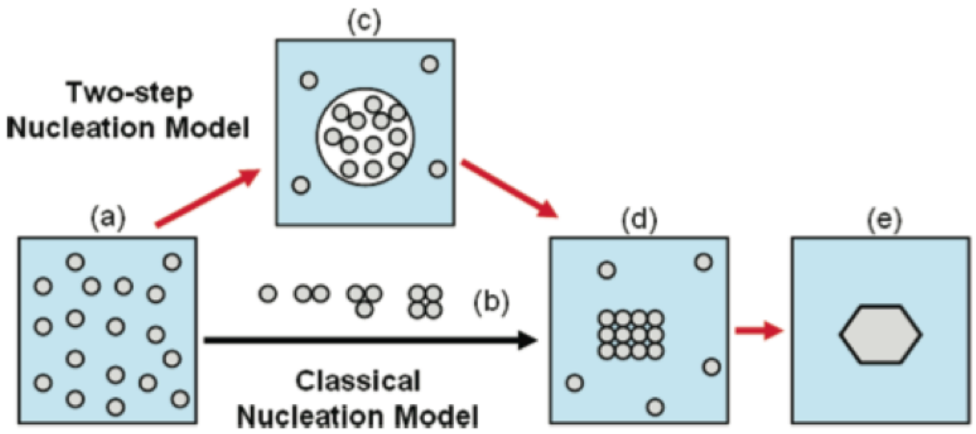
Two-step model

• CNT a single order parameter: atoms are clustering and simultaneously adopt a crystalline environement

• … but in a liquid-solid transition, we have to consider both **fluctuations in density and in structure**

➪ 2 order parameters !

Erdemir Accounts Chem. Res. 42(2009)621



Two-step model

• CNT a single order parameter: atoms are clustering and simultaneously adopt a crystalline environement

• … but in a liquid-solid transition, we have to consider both **fluctuations in density and in structure**

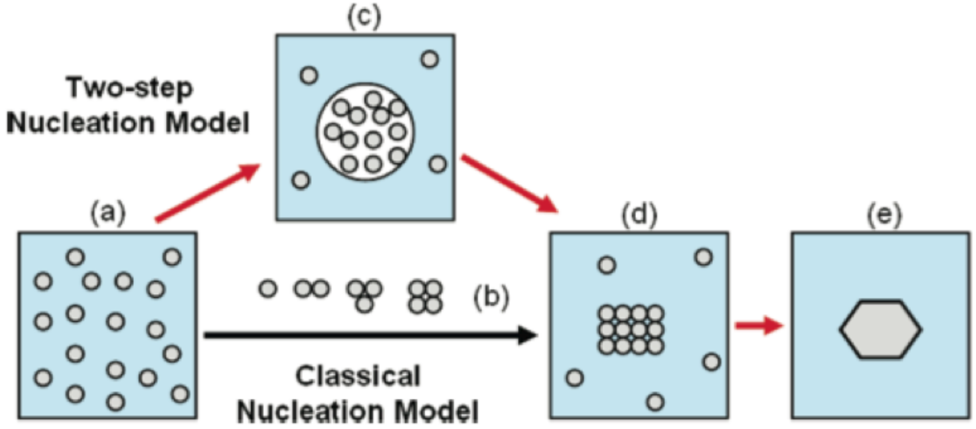
➪ 2 order parameters !

If several order parameters has to be taken into account, CNT cannot identify the different pathways leading to crystallization when the different order parameters are not evolving together

➪ two-step mechanism

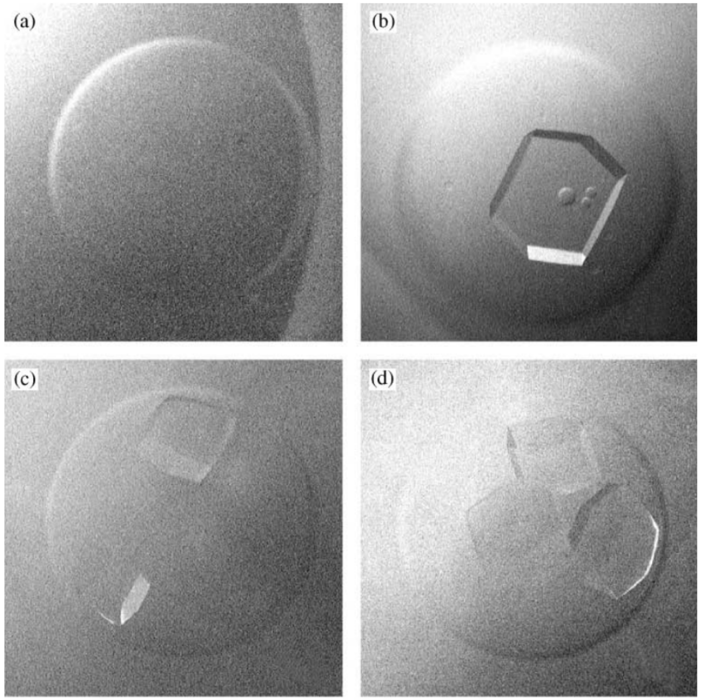
Experimental observations

for nucleation of colloids or proteins



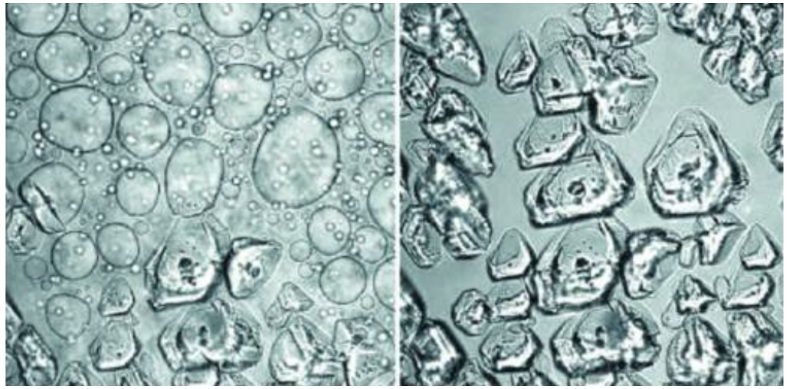
•*ten Wolde & Frenkel, Science 277(1997)1975*
•*Talanquer & Oxtoby, J. Chem. Phys. 109(1998)223*
•*Galkin & Vekilov, PNAS 97(2000)6277*
•*Vekilov, Crystal Growth & Design 4(2004)671*

Two-step model



model protein lysozyme

Galkin & Vekilov, PNAS 97(2000)6277



nucleation of crystals of glucose isomerase

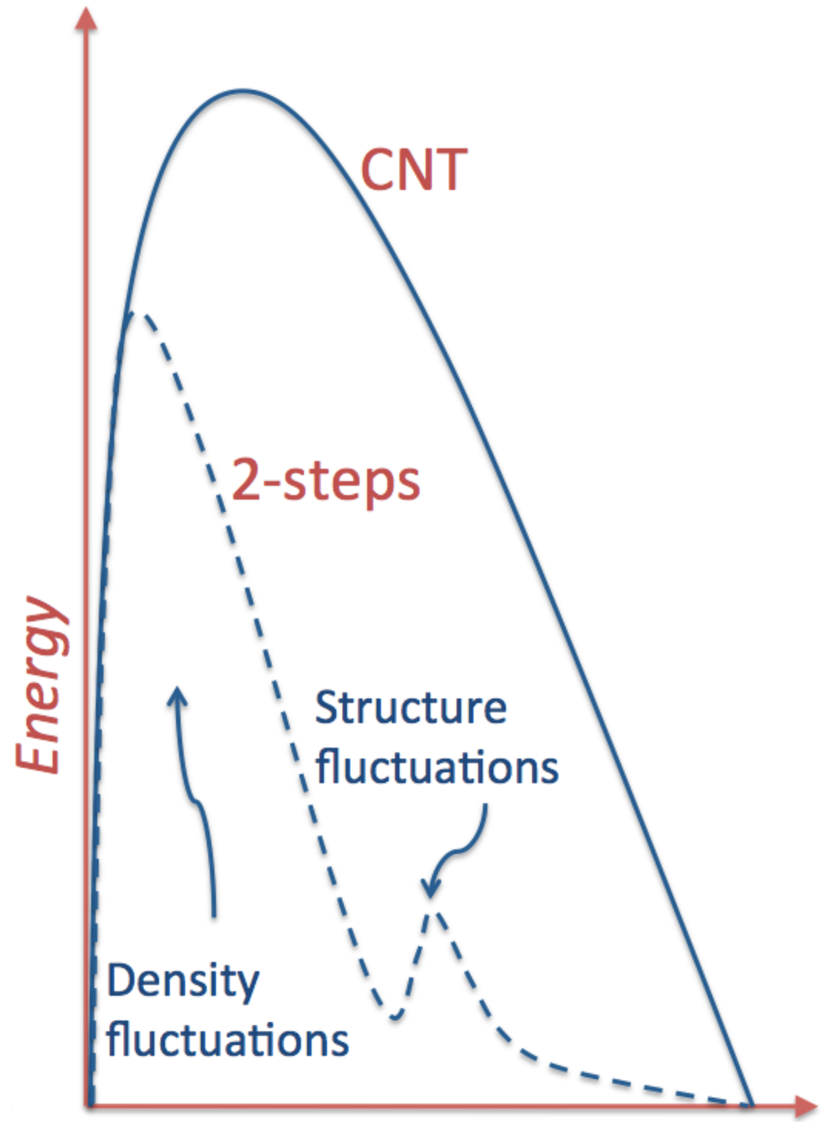
Vekilov, Crystal Growth & Design 10(2010)5007

Two-step model

Consequence: nucleation is a process with at least two thermodynamic barriers

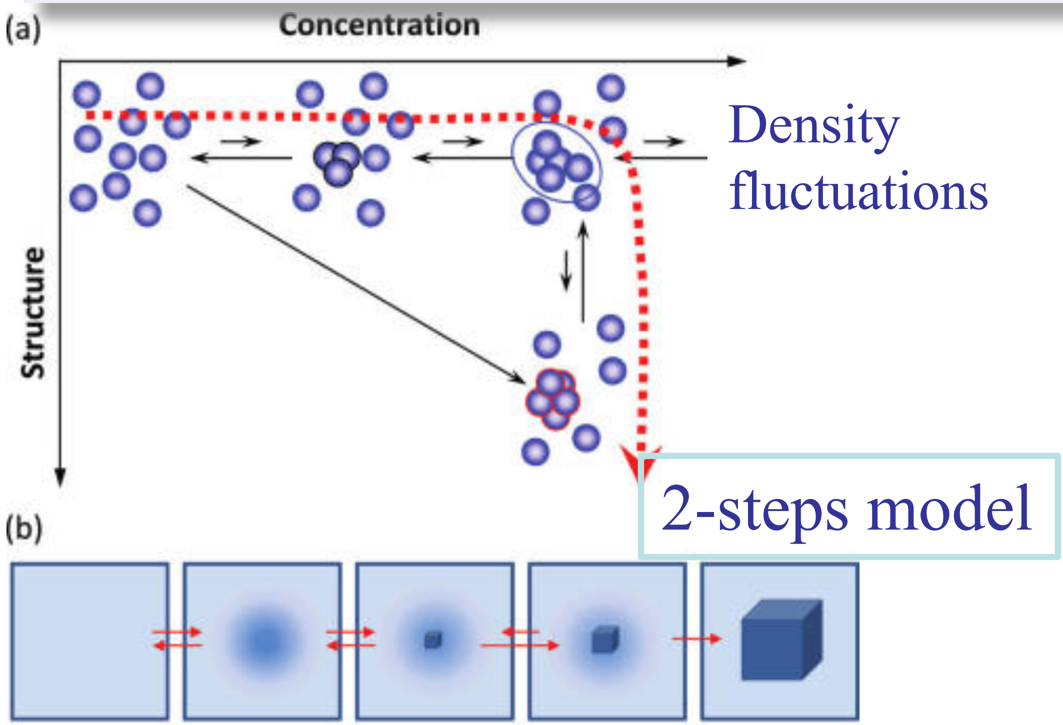
➪ First barrier for the formation of a nucleus and second barrier for the transformation of this cluster into a crystalline germ

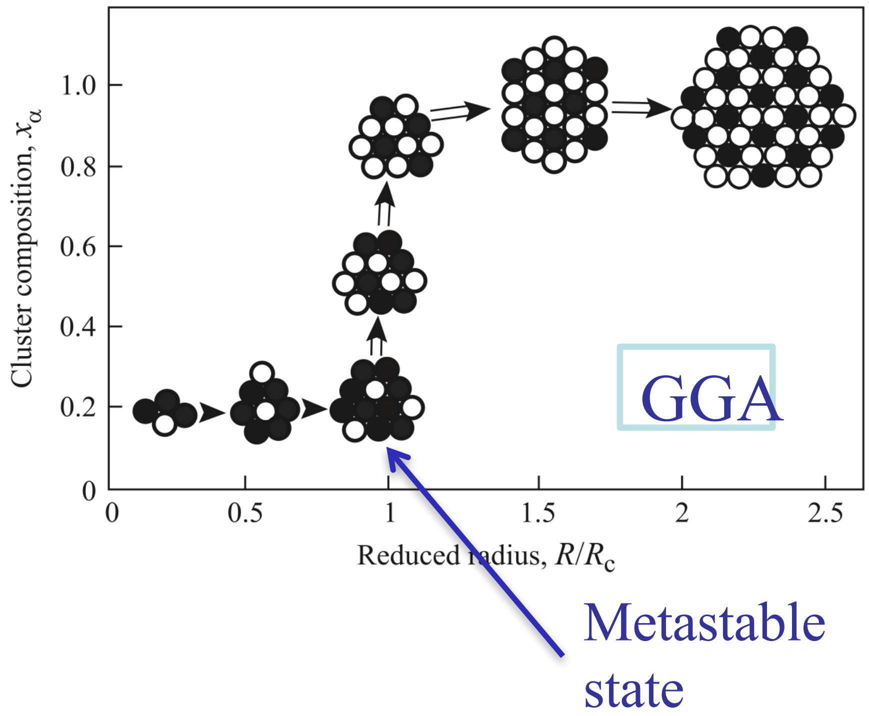
➪ Low activation energy for each step



Lutsko & Nicolis, Phys. Rev. Lett., 96(2006)046102

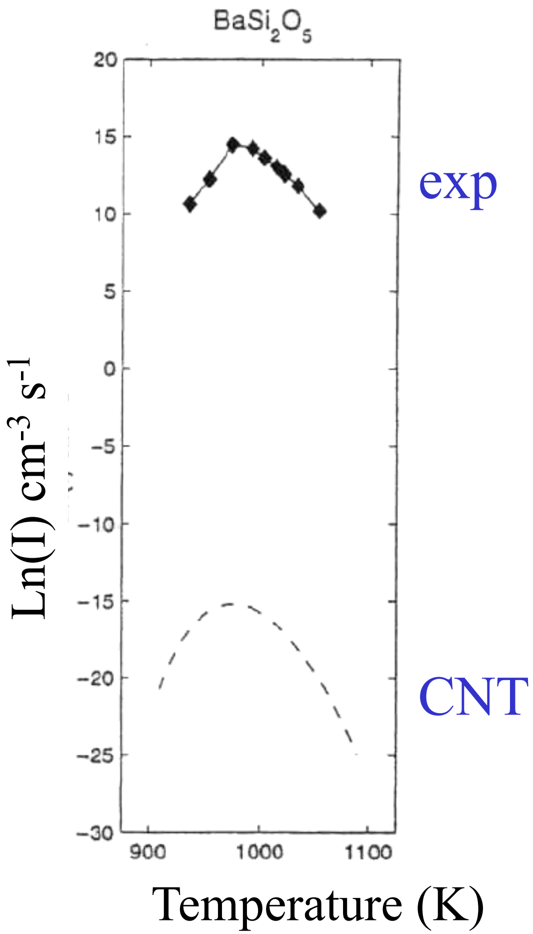
GGA and two-step model





➪ Similarities with the 2-steps model and GGA

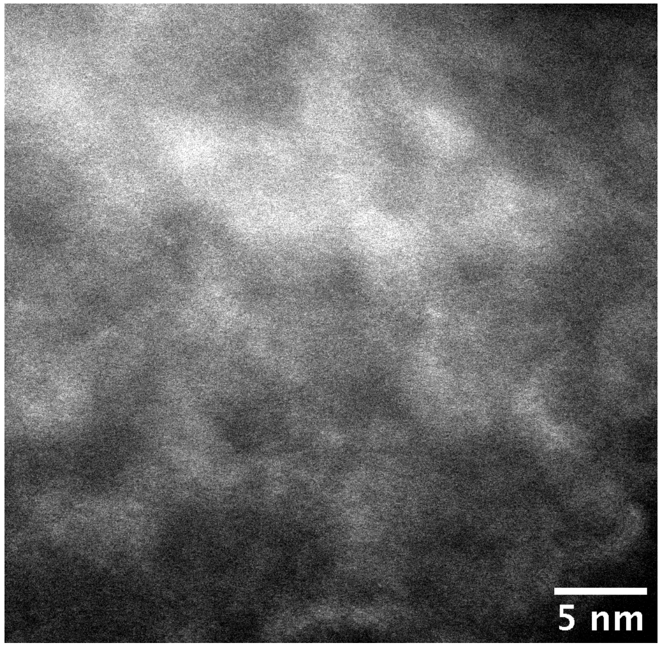
Heterogeneities



Sen & Mukerji, JNCS 246(1999)229

STEM-HAADF

LPS, Marcoussis
Gilles Patriarche



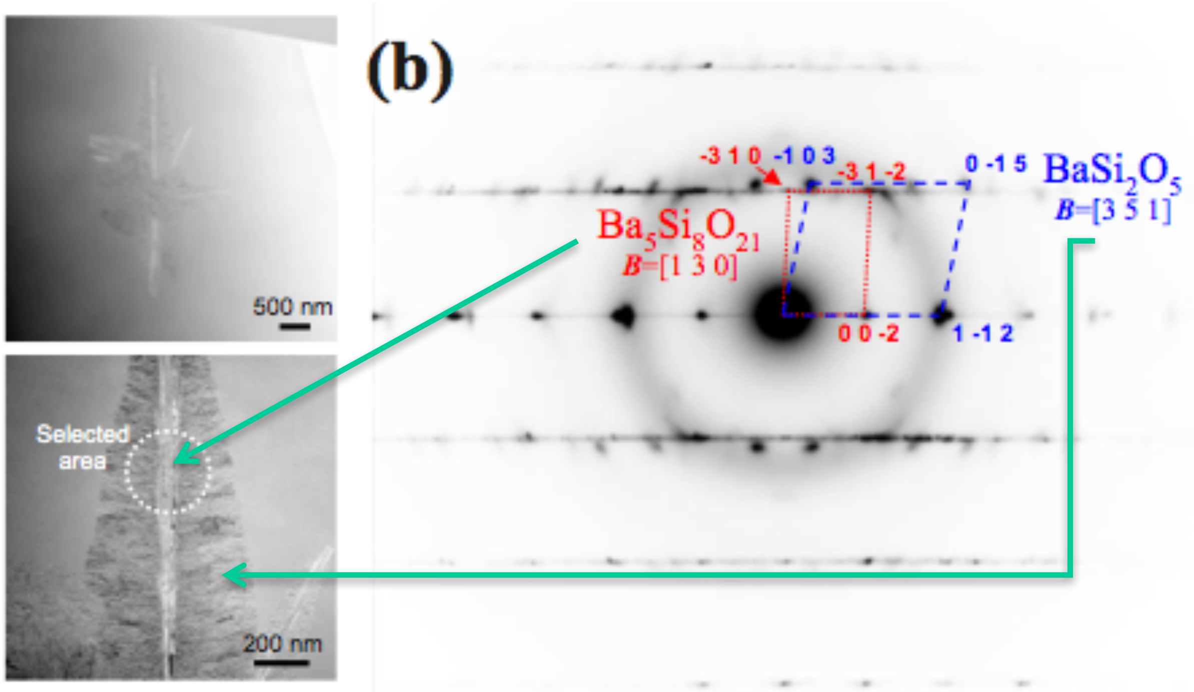
BaO-3SiO_2

Effect of static disorder : model proposed by Karpov & Oxtoby

Karpov & Oxtoby Phys. Rev. B 54 (1996) 9734

Crystallization in BaO-SiO_2 glasses

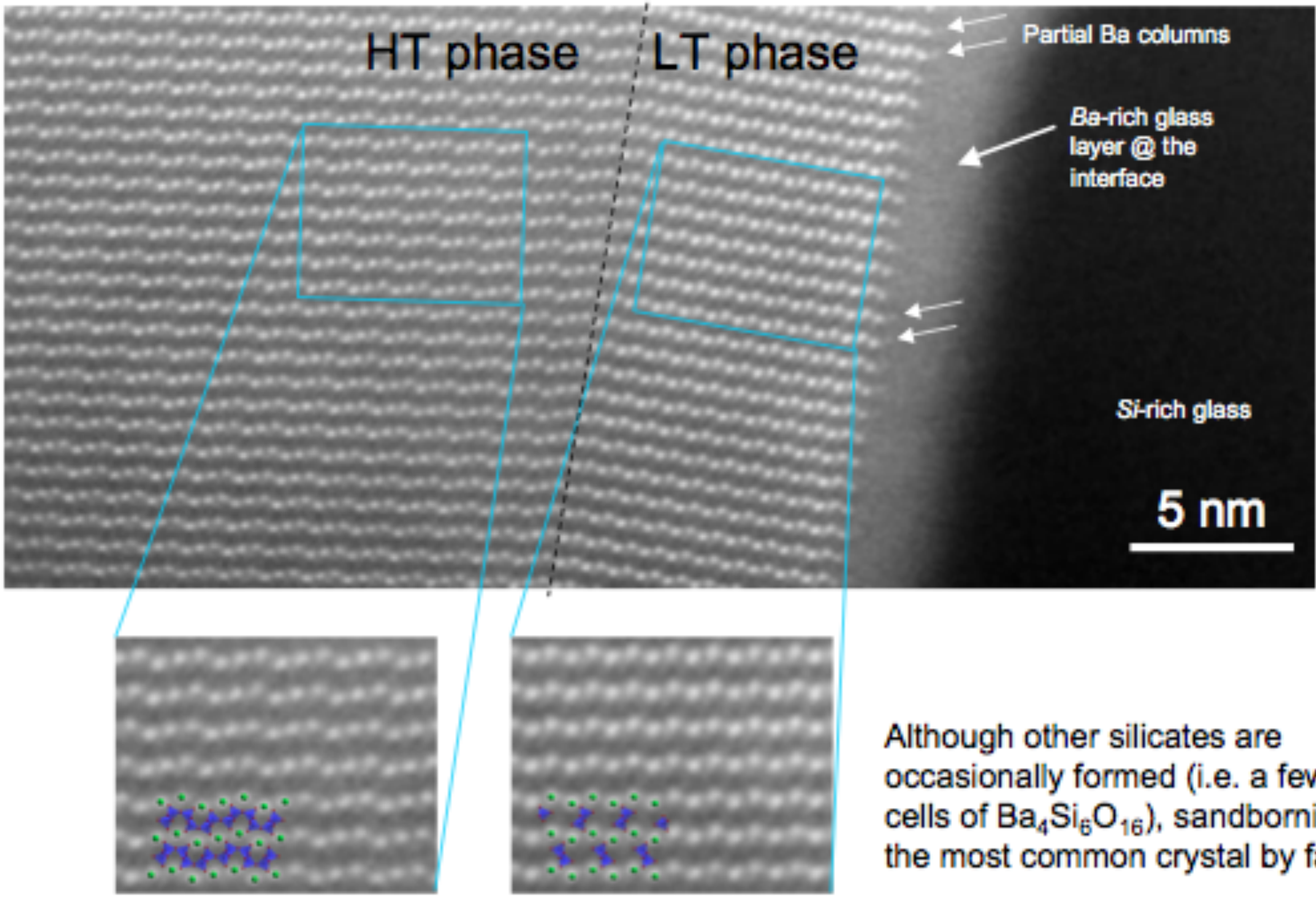
- In BaO-$2SiO_2$, initial formation of the crystalline $Ba_5Si_8O_{21}$ (Ba-rich phase)



Takahashi et al., Appl. Phys. Lett. 95(2009)071904

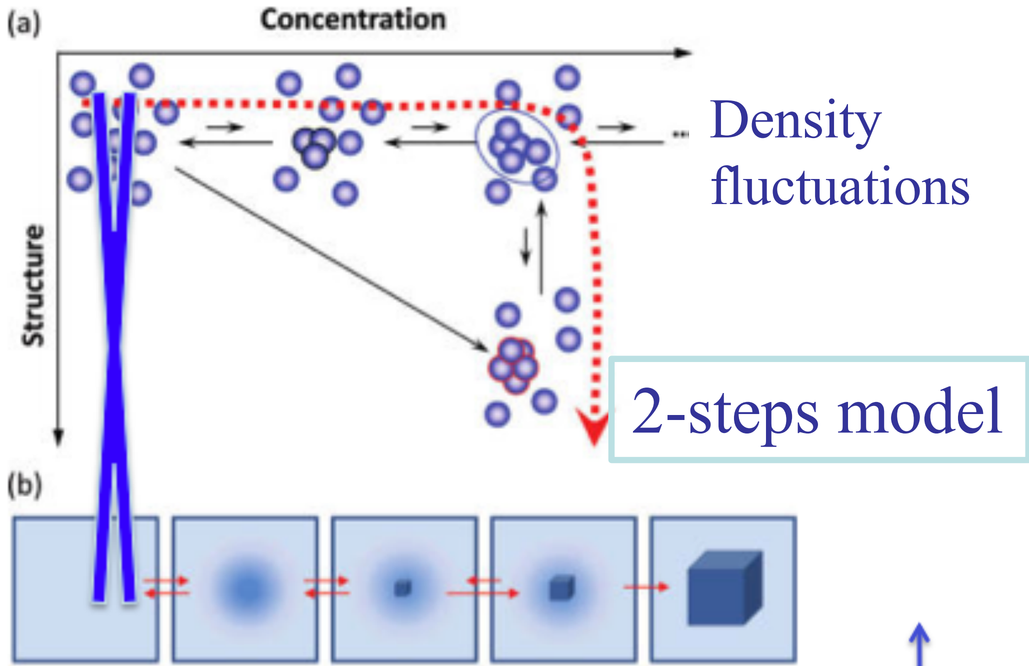
Crystallization in BaO-SiO$_2$ glasses

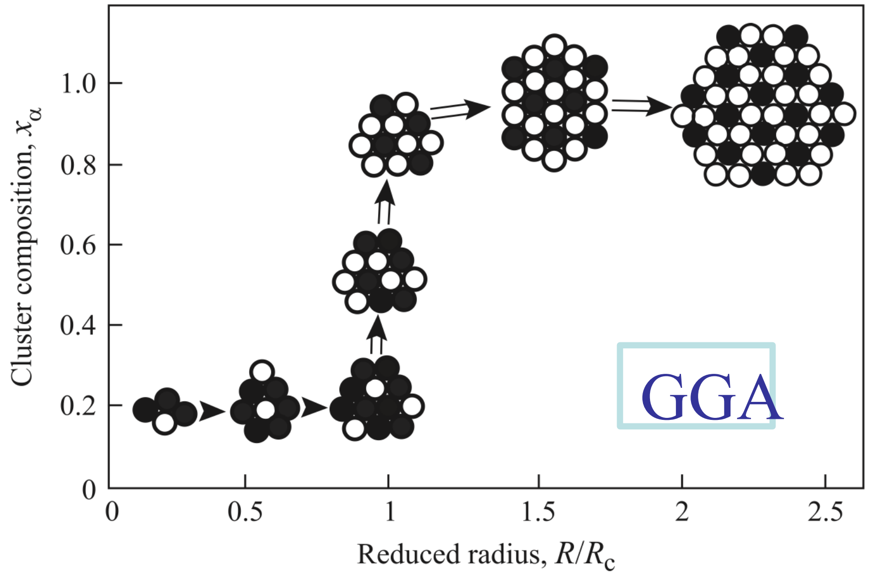
Interface of $Ba_2Si_4O_{10}$ with the matrix along [001]

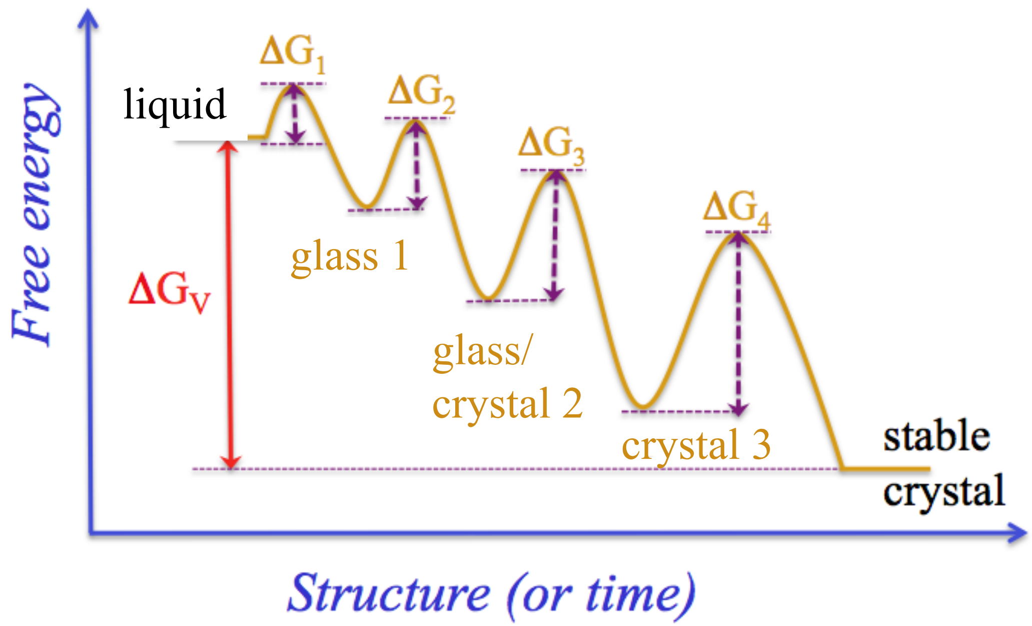


Although other silicates are occasionally formed (i.e. a few unit cells of $Ba_4Si_6O_{16}$), sandbornite is the most common crystal by far.

GGA and two-step model







➪ Similarities with the 2-steps model and GGA
➪ Heterogeneities pre-exist in the glass
➪ Heterogeneities or phase separation?

Summary

✓ Local structural information is required to investigate nucleation / crystallization mechanisms

⇒ Ni in spinel phase

⇒ Nanocrystals embedded in glass matrix

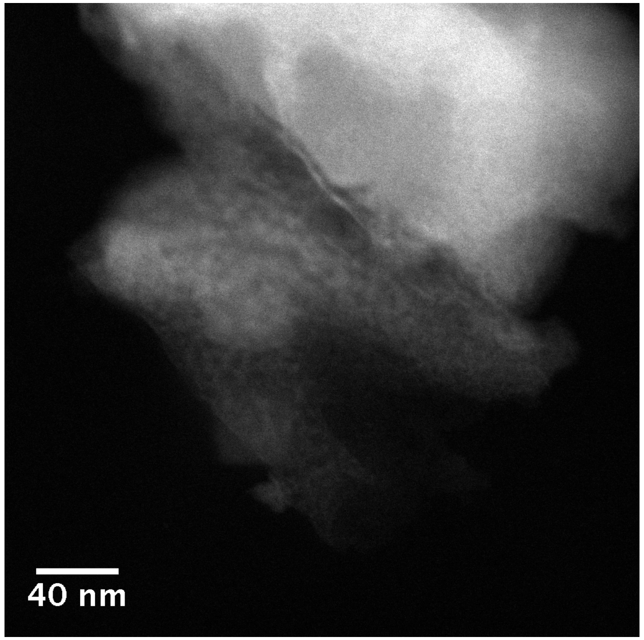
✓ Local environment not necessarily meaningful to understand nucleation

⇒ Importance of medium range structure to rationalize nucleation properties

⇒ Compositional/structural fluctuations in the initial glass

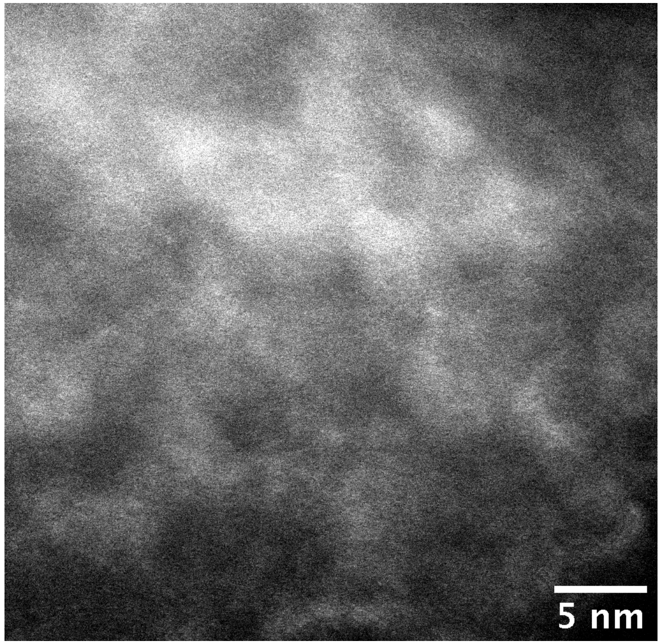
Glass BaO-$3SiO_2$

Before

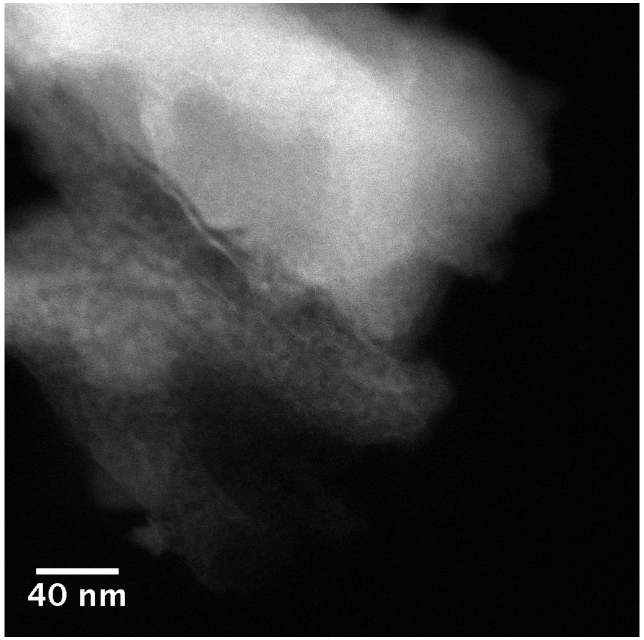


STEM-HAADF

White regions = enriched in Ba

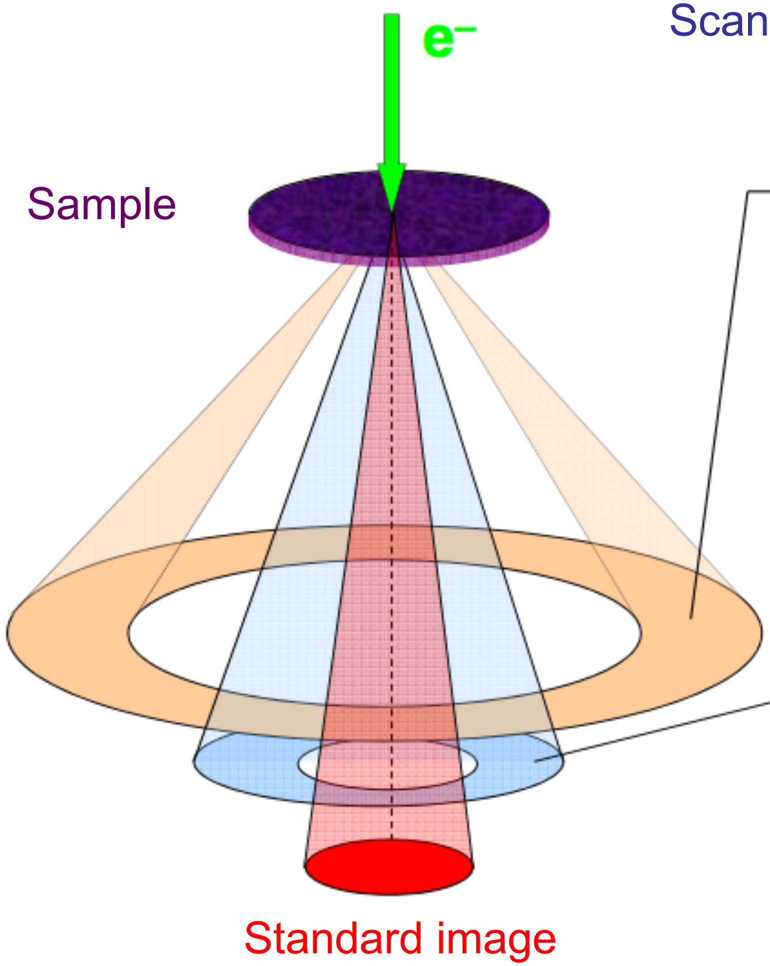


After



STEM-HAADF (High Angle Annular Dark Field)

Scanning Transmission Electron Microscopy (STEM)



High Angle Annular Dark Field (HAADF)
Diffusion at high angle

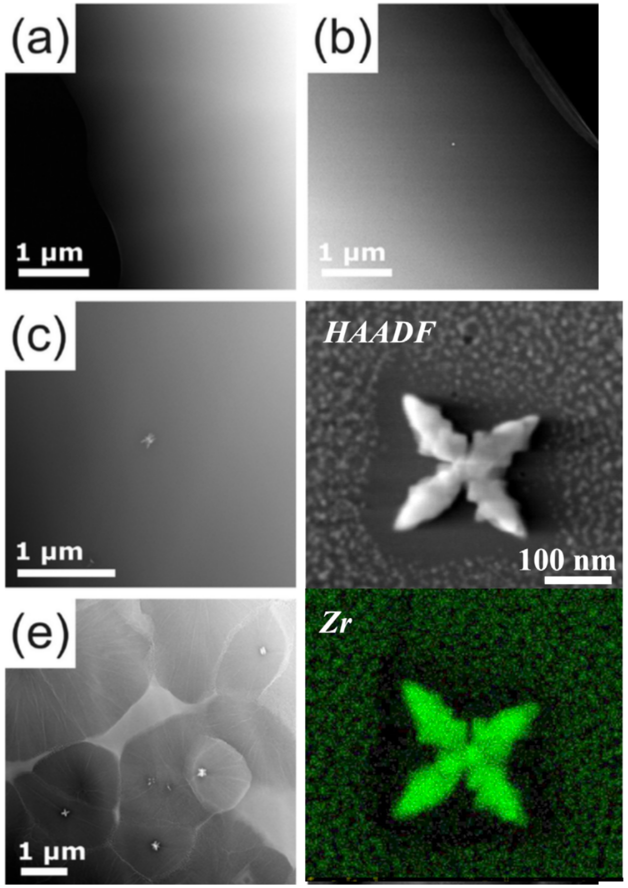
-Intensity $\sim \rho \cdot t \cdot Z^{3/2}$

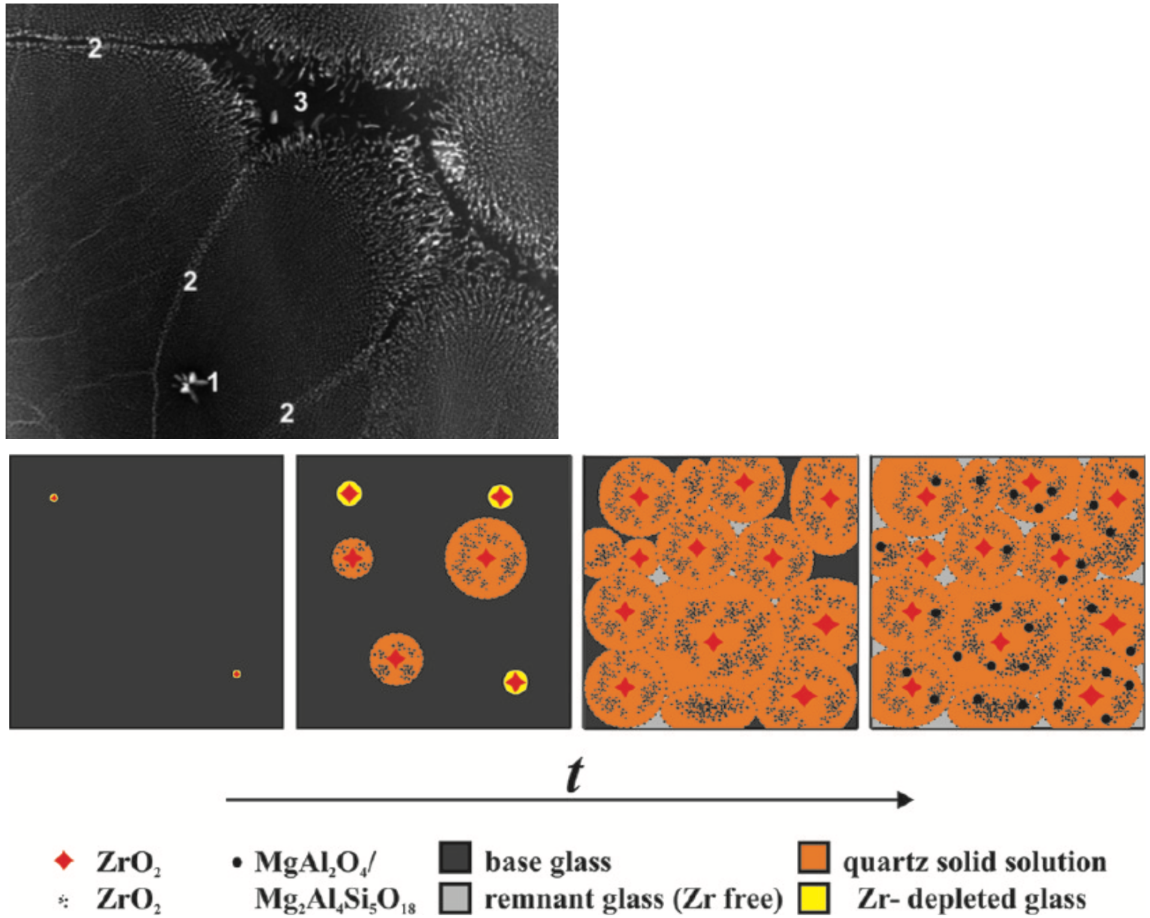
ρ : density of the material
t : thickness of the sample
Z : atomic number

Annular Dark Field (ADF)

STEM-HAADF ⇨Z contrast technique

After ZrO_2 nucleation





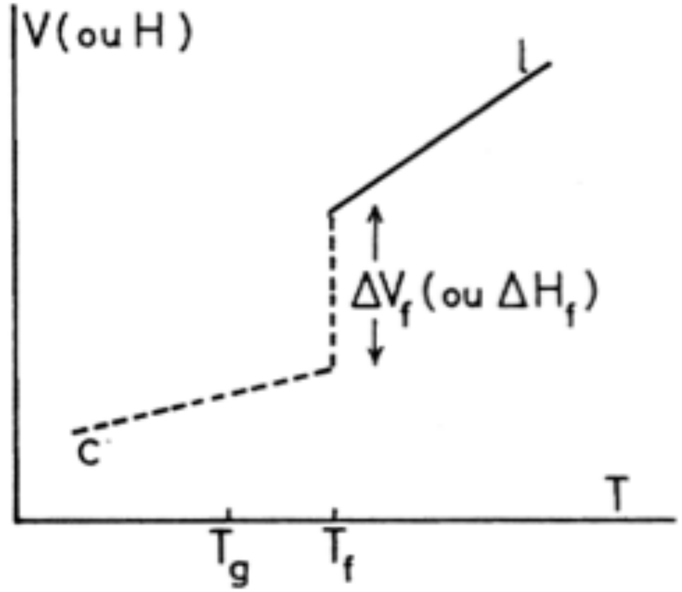
HAADF images

Patzig et al., Crystal Growth & Des. 12 (2012) 2059
JNCS 384 (2014) 47

Crystallization

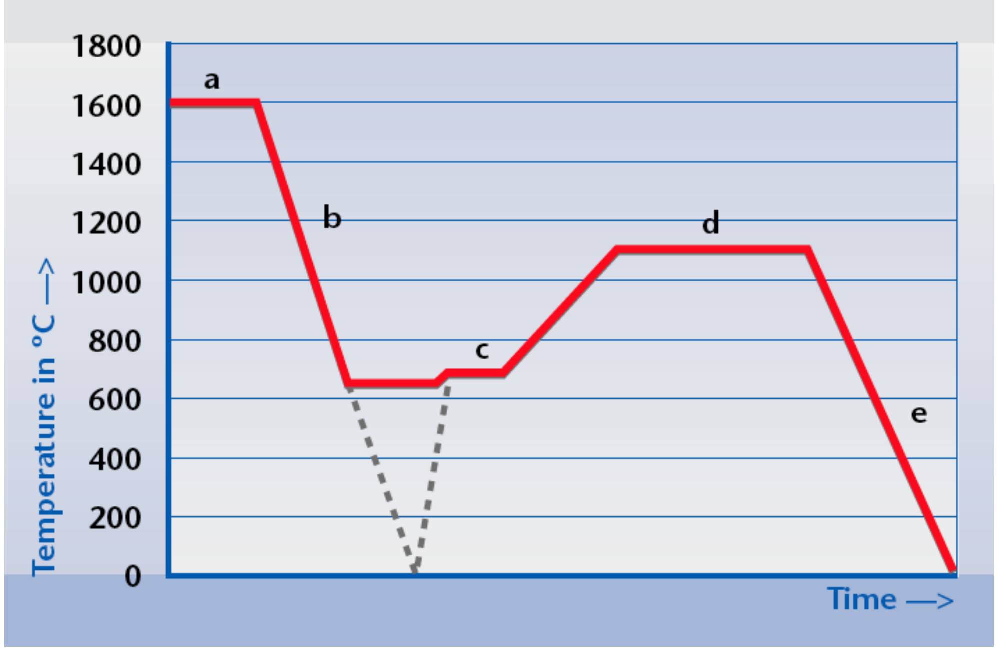
• crystallization can occur when cooling a liquid

⇒ very important for geological processes



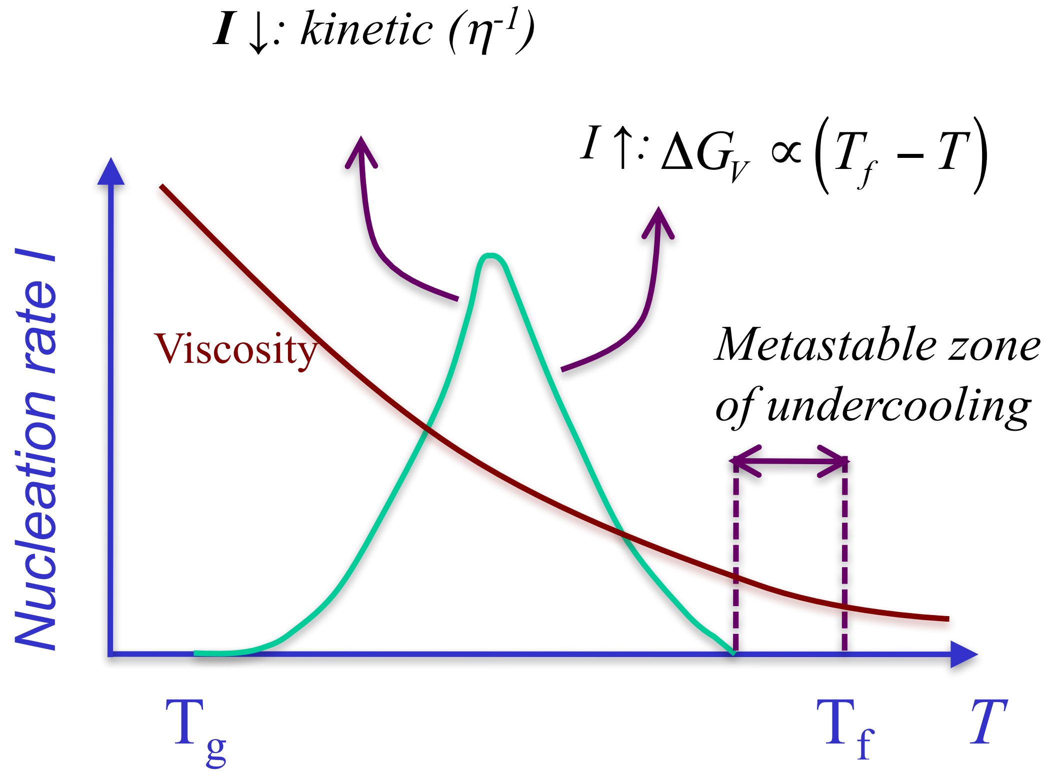
• if we obtain a glass, we can devitrify it with a thermal treatment above T_g

⇒ case of glass-ceramics



Nucleation rate

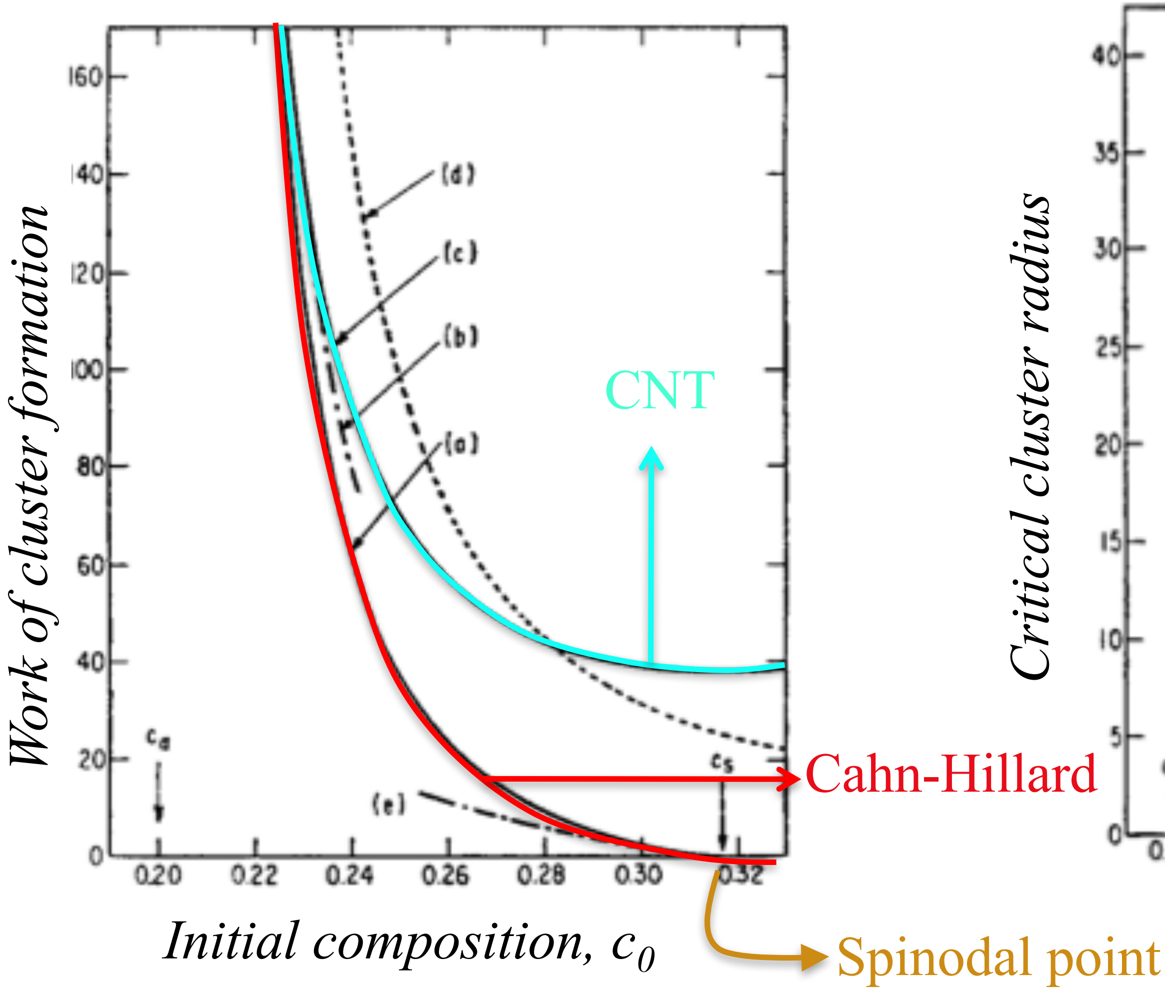
$$I_{st}(T) = \frac{I_0 h}{3\pi\lambda^3\eta}\exp\left[-\frac{W_*}{kT}\right]$$

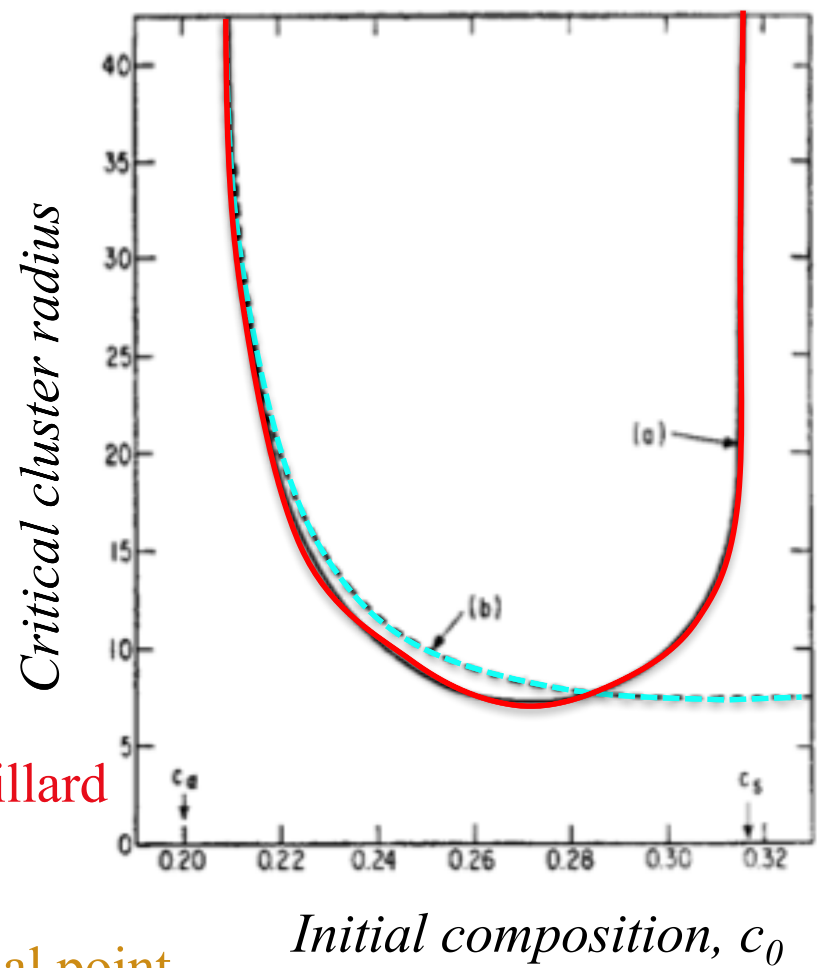


viscosity increases
➪ I decreases which counterbalances ΔG_V

Metastable zone of undercooling: no stable nuclei because surface energy is too important

Density functional theory (DFT)





⇒ CNT : nucleation barrier has a value at the spinodal point

⇒ DFT : close to the spinodal, work of formation W tends to zero: metastable state ⇒ instable state

Small fluctuations in density but with a large spatial extension