CORNING

Science & Technology

Glass-ceramics: developement of commercial materials

Monique Comte

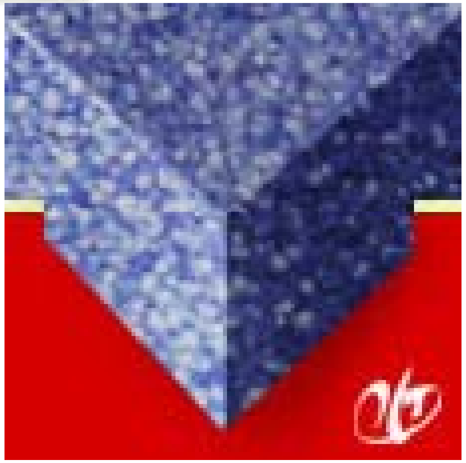
USTV, Orléans (France) Nov. 5, 2009

Different products

Eurokera website

NEG website

Neoparies –
Hexingtai Stone
Materials website



Ivoclar - Vivadent
website

Introduction: what is a glass-ceramic ?

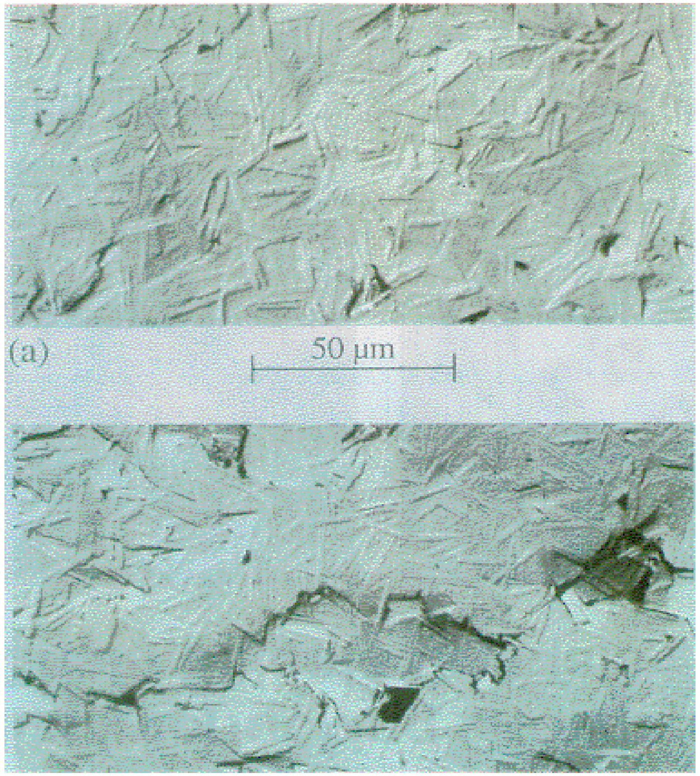
- A matérial
  - Melted and formed as glass article
  - Partially crystallized by a further thermal treatment

  (nucleation and growth)

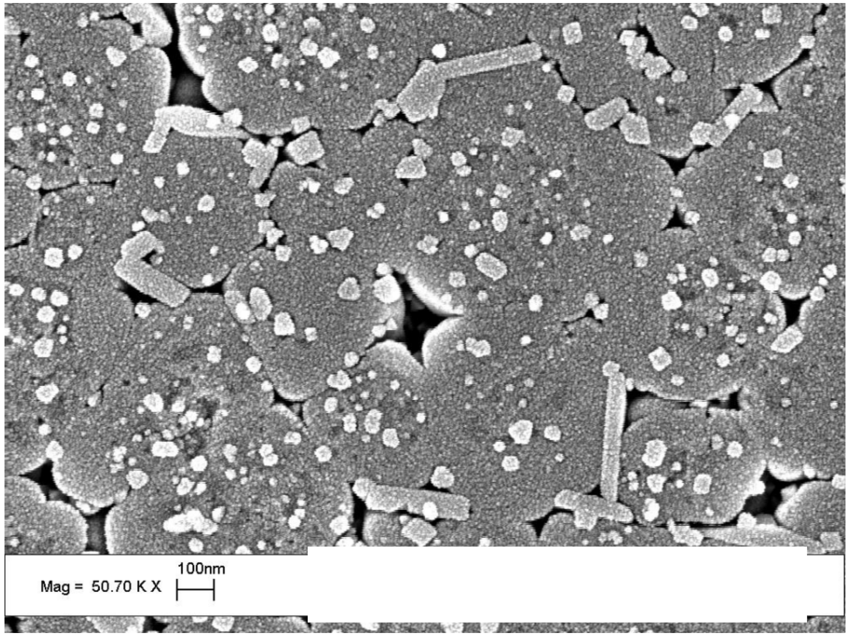
- According to the nature of the crystals and to microstructure, obtention of materials with unique properties

- Crystallization increases the viscosity of the material and its resistance to temperature.

Controlled crystallization



Macor®
(Micas g.c)



Kerawhite®
(β–spodumene g.c)

Introduction: what is a glass-ceramic ?

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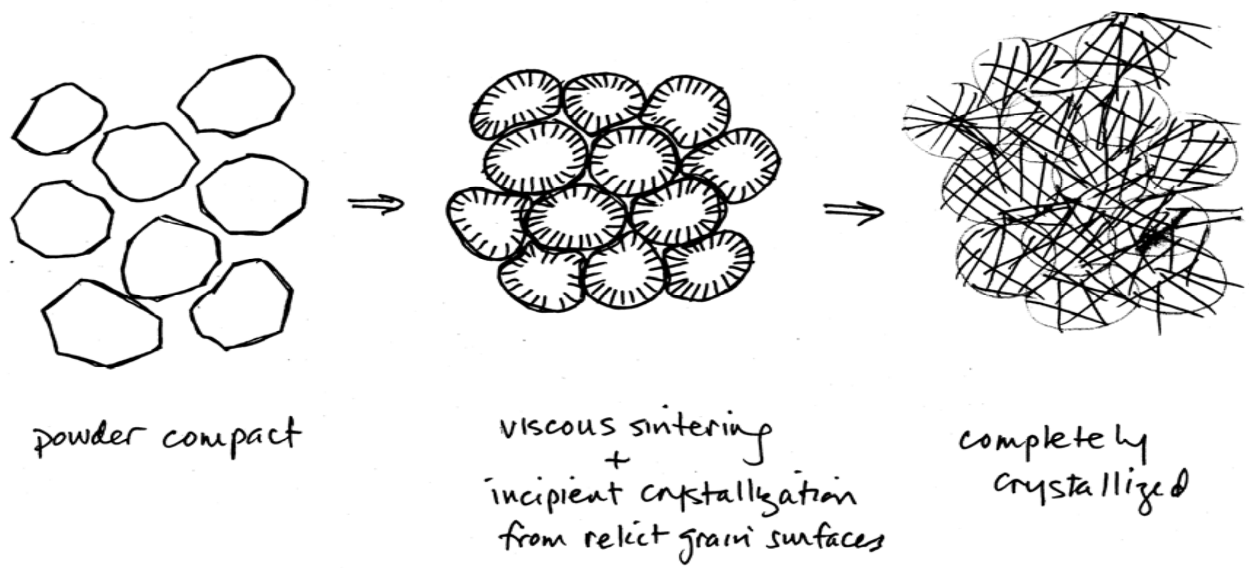
Nucleation

- For most glasses
  - Homogeneous nucleation is difficult
  - Crystallization develops from surface or defects

- Two kinds of glass-ceramics
  - From glass frit: sintering and crystallization(surface nucleation)
  - From bulk: heterogeneous nucleation (nucleating agents)

Glass-ceramic formation by surface nucleation

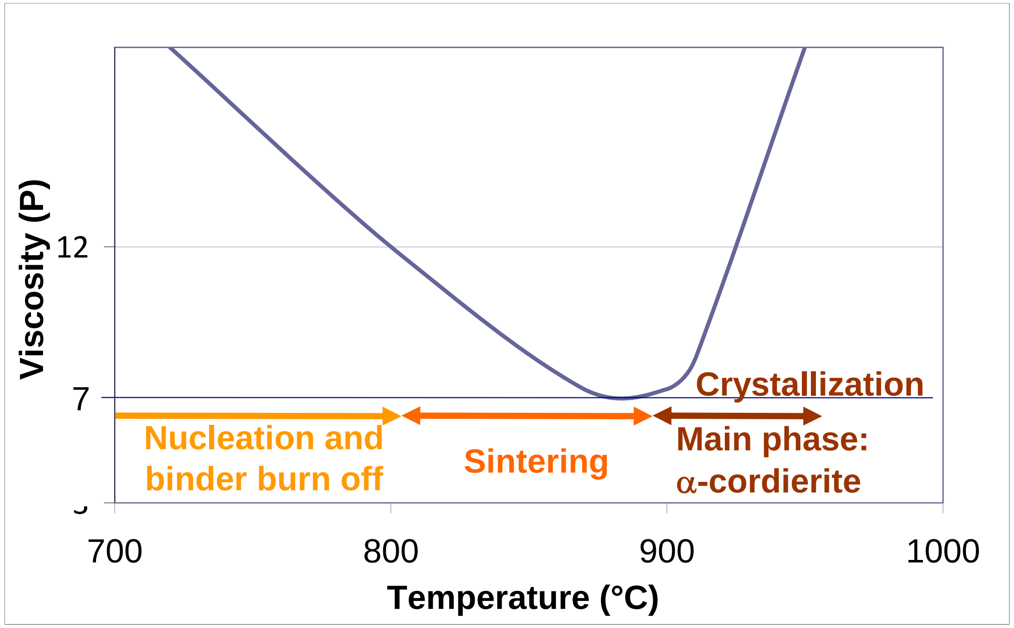


L.R. Pinckney – Corning

Example:
Cordierite glass-ceramics for electronic packaging

Interests (vs Alumina): - lower dielectric constant
- Possible cofiring with Cu below 1000° C

Compos (wt%)	
SiO_2	50 – 55
Al_2O_3	18 - 23
MgO	18 - 25
$B_2O_3+P_2O_5$	0 - 6
CTE (25-200° C)	3 x10^{-6} K^{-1}
Dielectric cst	5



R. Tummala J. Am. Ceram. Soc 74 (1991) 895

Glass-ceramic formation by internal nucleation

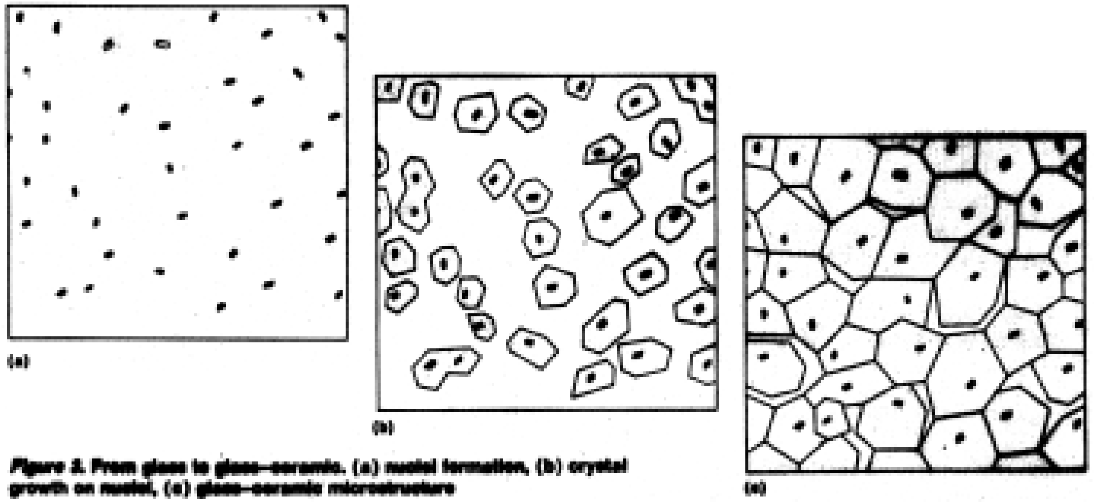


Figure 2. From glass to glass–ceramic. (a) nuclei formation, (b) crystal growth on nuclei, (c) glass–ceramic microstructure

L.R. Pinckney – Corning

Heterogeneous nucleation

Examples of nucleating agents	Effect
TiO_2, ZrO_2	• Efficient in a lot of aluminosilicate glasses
Fluorine	• Crystallization of fluorine bearing phases (apatite, micas, amphiboles..)
Metal colloids (Ag, Pt, Au..)	• Nucleate lithium silicate (via UV irradiation)

Favors

- Phase separation
- Precipitation of a first crystalline phase which acts as a nucleant

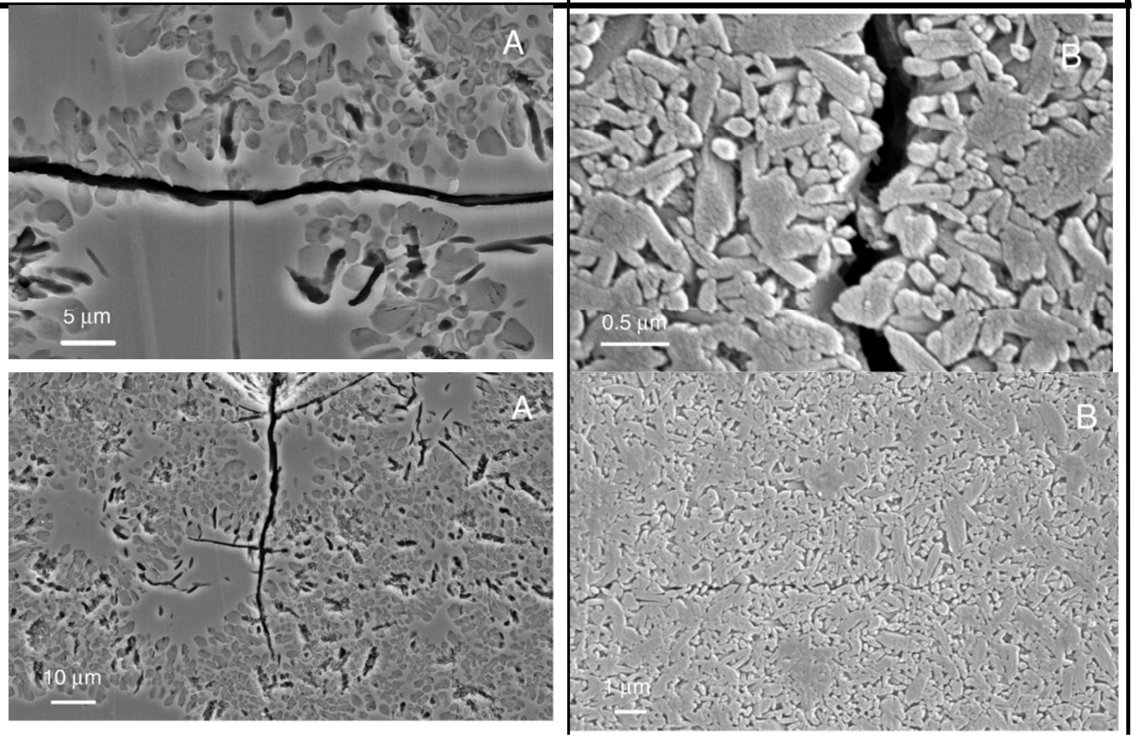
A few specific properties of bulk glass-ceramics

- Formation of metastable phases
  - Crystallization at high degree of supercooling favors formation of metastable phase
  - At higher temperature they transform to a stable assemblage
  - These phases could have unique properties
- Possibility to obtain transparent materials
- Wide range of CTE:
  - -40 to 120 $x10^{-7}K^{-1}$
- Wide range of mechanical strength
- Refractory materials

Crack propagation in glass-ceramics
Examples

Cristalline phase	Leucite (K_2O-Al_2O_3-$4SiO_2$)	Disilicate de Li
% of crystals	30%	60%
K_{IC} ($MPam^{1/2}$)	1,1	2,7

E. Apel et al.
J of mechanical behaviour of biomedical mat.
I (2008) 313-325



Examples

Nucleating agents	Crystalline phases	Main properties
TiO_2, ZrO_2	B-quartz B-spodumene	Transparent Zero-expansion
	Spinel	Transparent High strain point
	Cordierite +… Feldspar +…	Refractory
Ag^0	Li silicate Li disilicate	Photosensitive
F	Micas	Machinable

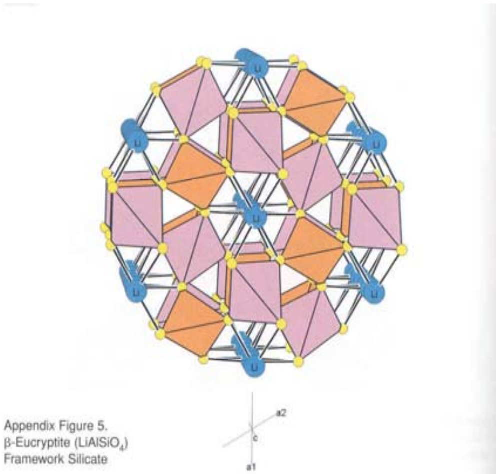
B-quartz, Li silicate: metastable phases

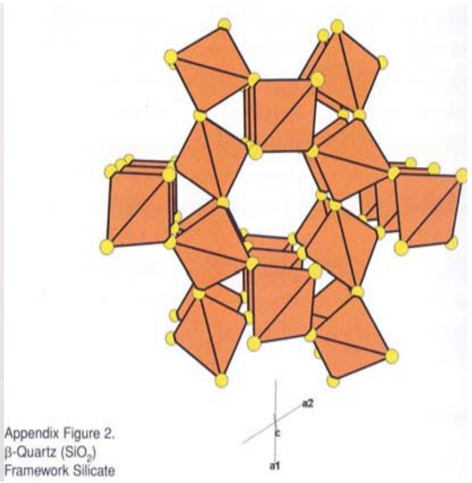
Design of commercial glass-ceramics:

	Requirements
Set of product properties	Phase assemblage and microstructure
Glass melting	Compatiblity with furnaces operations
Glass forming	Low enough liquidus (low temperature / high viscosity)
Glass-ceramic formation	• « Short » thermal treatment length (hours) • Control of the shape of the glass article

LAS glass-ceramic:
Transparent and zero-expansion material

Solid solution:
$Li_{2-2(x+y)}Mg_xZn_yO.Al_2O_3.nSiO_2$
n: 2 to 10
(6 to 8 in commercial products)





According to the composition expansion strongly varies (-50 to +50 $x10^{-7}K^{-1}$)

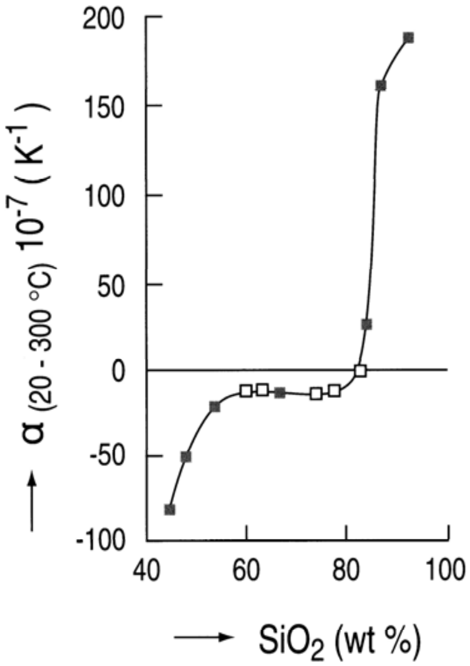


Figure 1-8 Coefficient of thermal expansion of solid solutions of β-quartz crystallized from glasses in the SiO_2–$LiAlO_2$ system (after Petzoldt 1967).

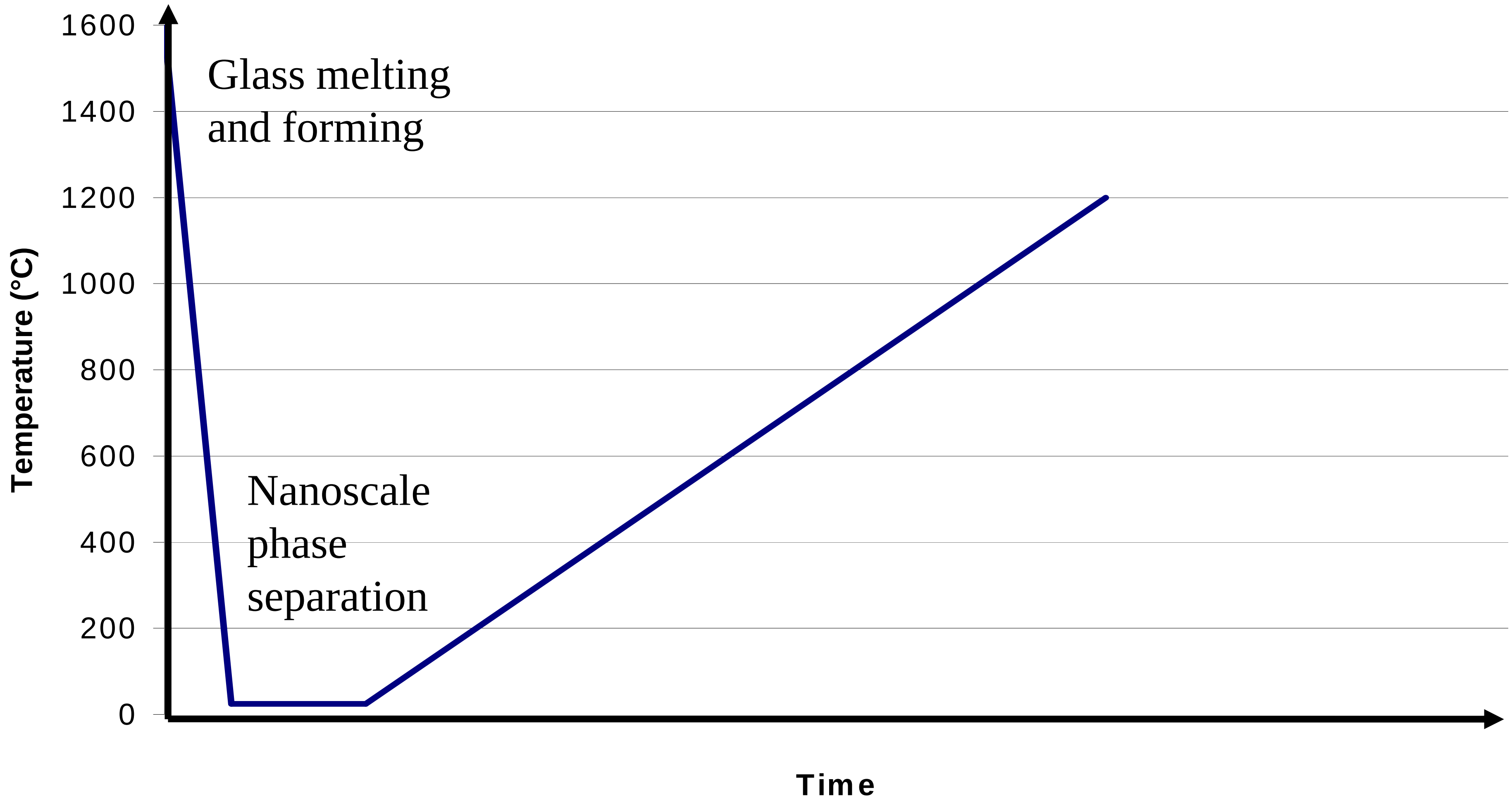
Glass-ceramic technology :
W. Höland and G. Beall
Am. ceram. Soc (2002)

LAS glass-ceramic
Typical composition range for parent glass

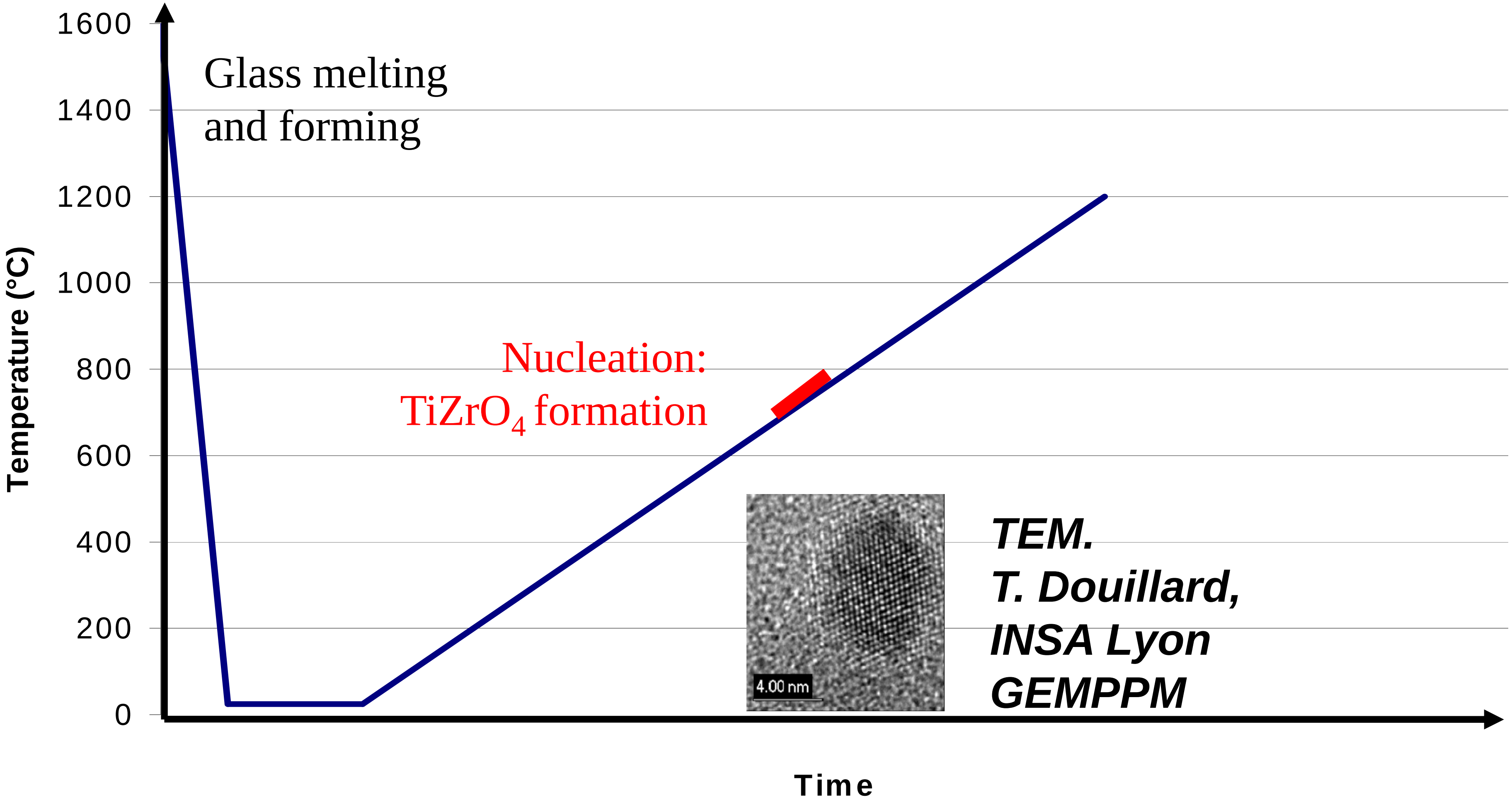
- SiO_2 : 55 - 70 (wt%)
- Al_2O_3 : 15 - 27
- Li_2O : 1 - 5
- MgO : 0 - 4
- ZnO: 0 - 4
- $TiO_2 + ZrO_2$: 2 – 5 (nucleating agents)
- Other: 0 - 5 (fining agents, coloring oxides…)

- Possible to taylor properties (expansion, transparency) playing on compositions and microstructure.

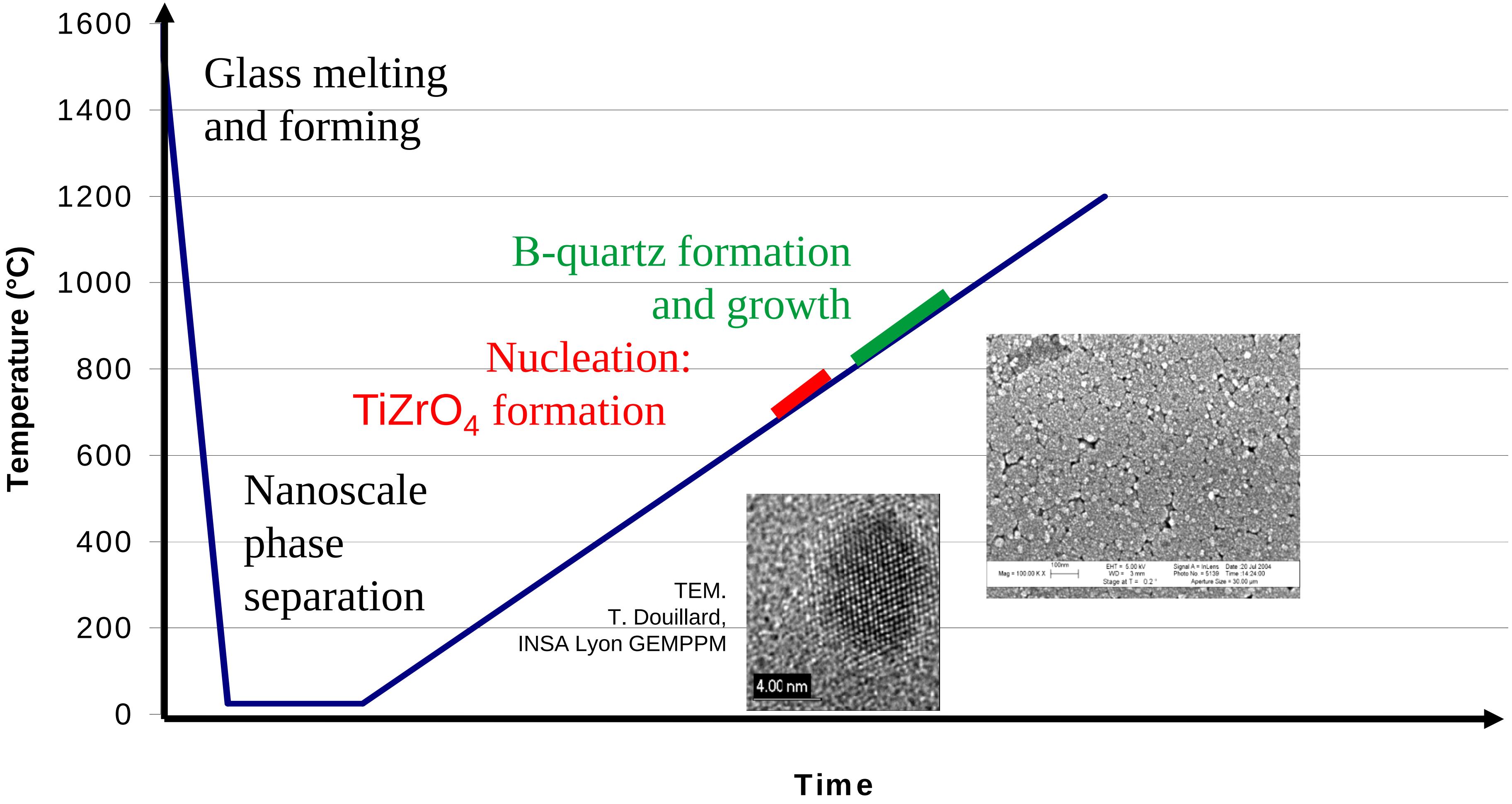
Crystallization sequence



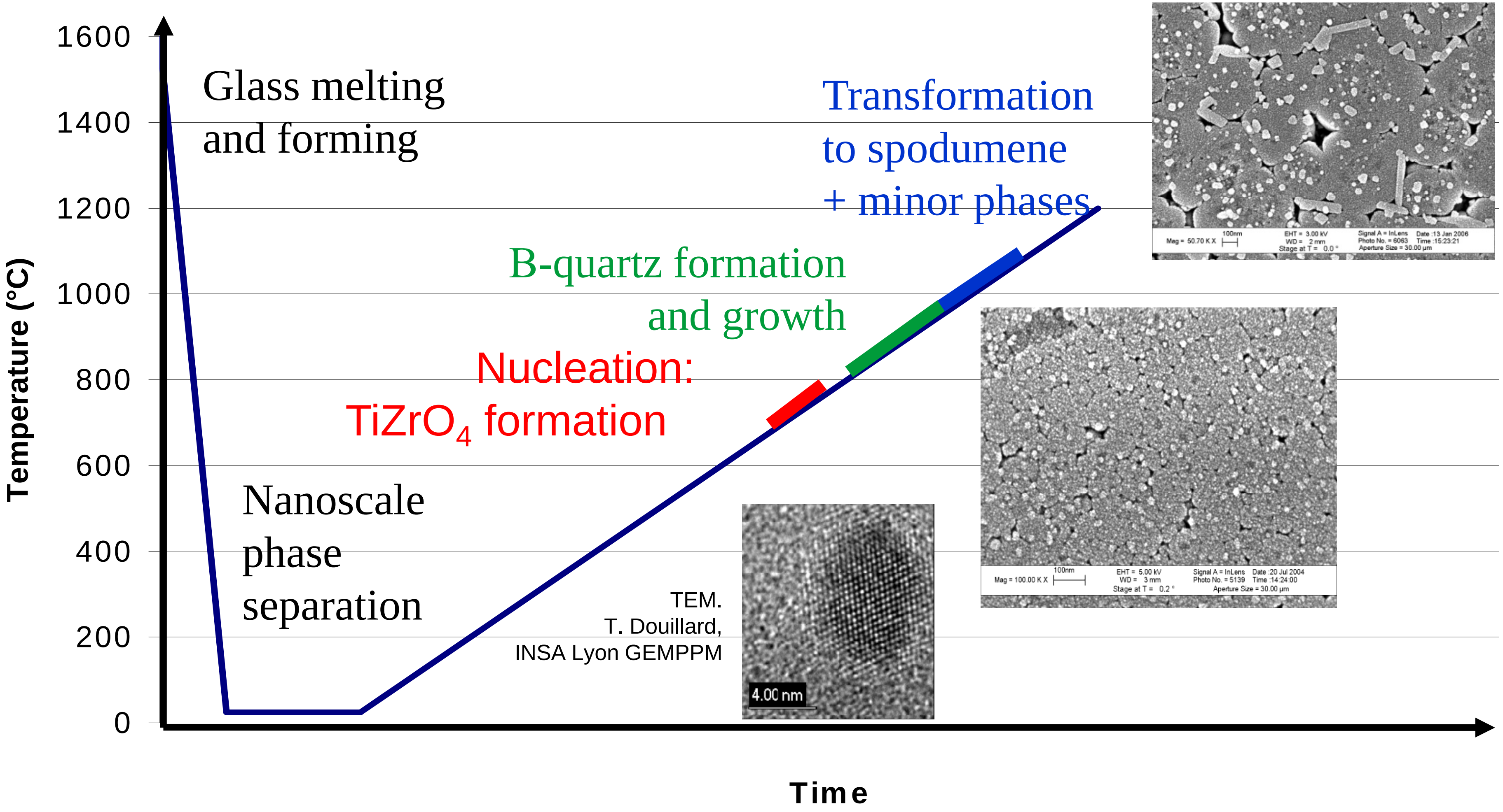
Crystallization sequence



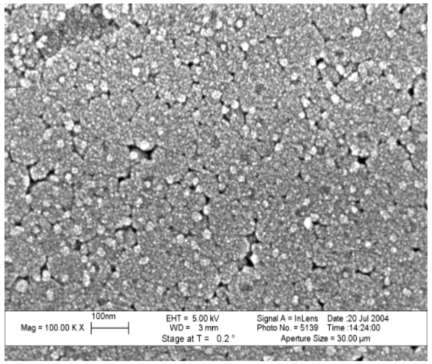
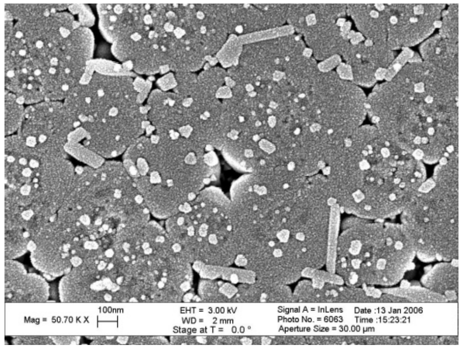
Crystallization sequence



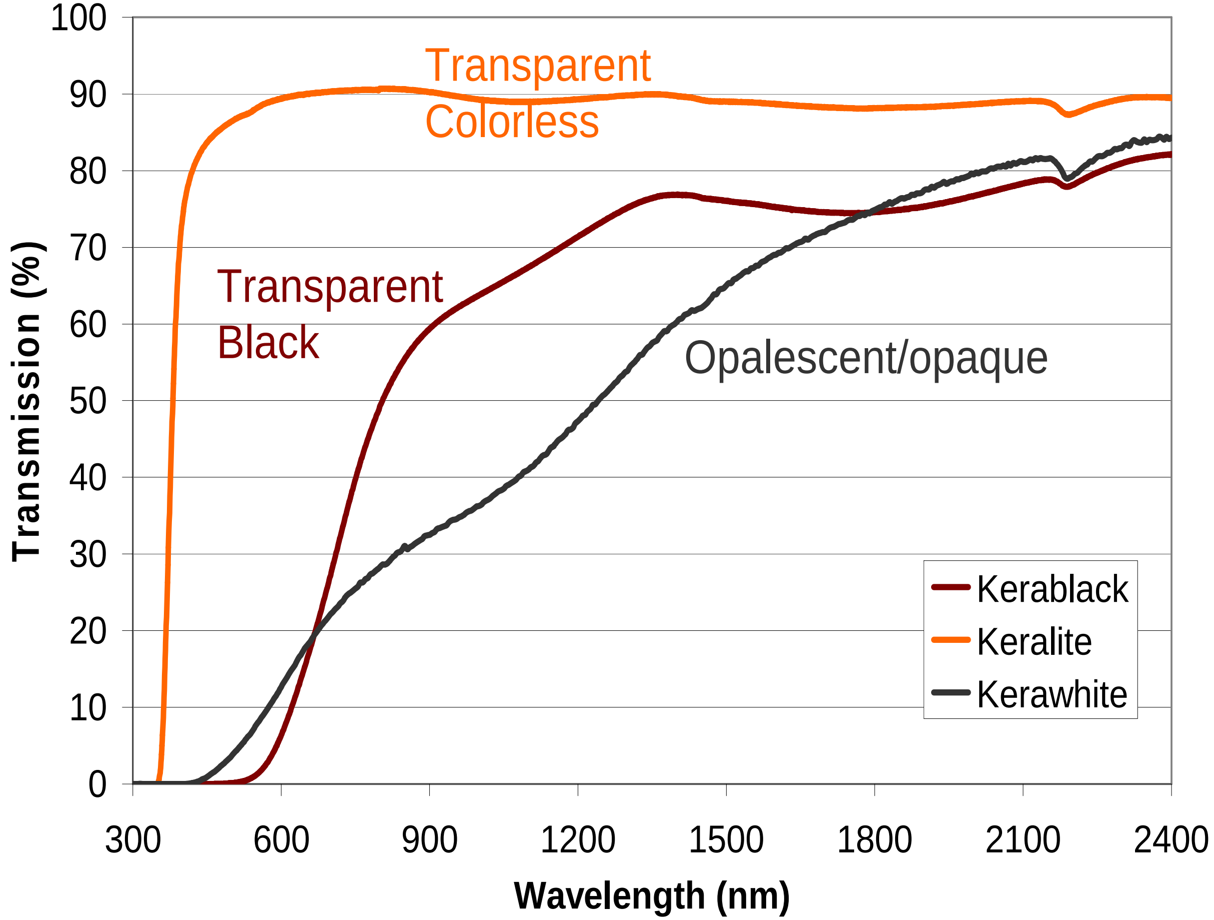
Crystallization sequence



LAS glass-ceramics (manufactured by Eurokera) Microstructure

	Kerablack ®	Kerawhite ®
Main crystalline phase Mean crystallite size (XRD)	B–quartz 70 nm	B–spodumene 160 nm
Other crystalline phases (< 5wt%) (mean crystal size) Residual glass: wt%	$TiZrO_4$ (2,5 nm) Around 15%	$TiZrO_4$ (2,5 nm) B–quartz, Spinel
Microstructure (SEM)		

LAS glass-ceramic (manufactured by Eurokera) Properties



CTE 0-700° C $(10^{-7}K^{-1})$	
Kerablack®	-1
Keralite®	1
Kerawhite®	10

Crystallization of a LAS glass-ceramic Studied by in situ HT XRD

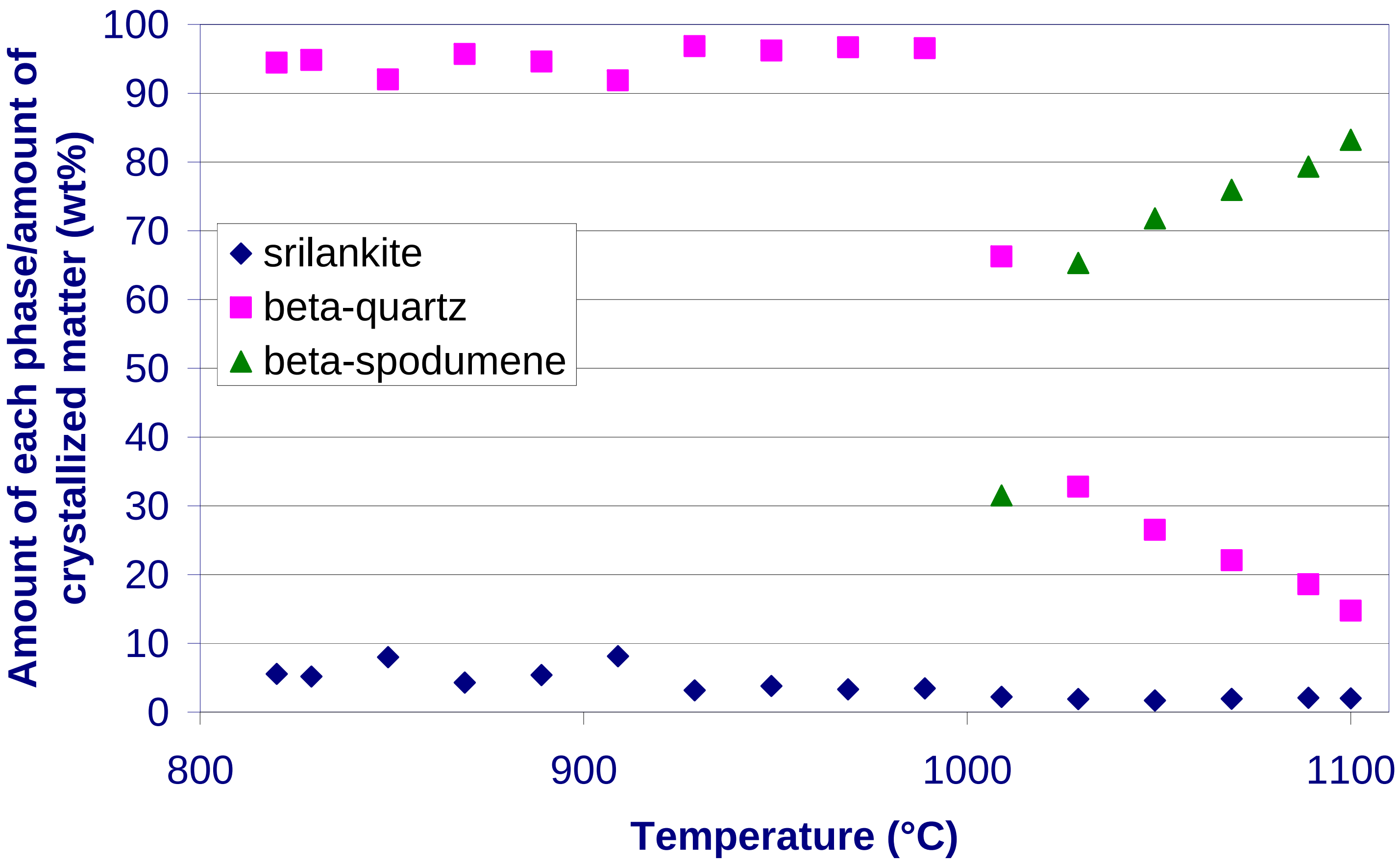
- Experimental:
  - Anton Paar HTK 1200 furnace (max. temp.: 1200° C)
  - TT: 30° C/min up to 660° C

  3.5° C/min from 660 to 1100° C
  - Diffractometer: Panalytical X'Pert Pro with a q/2q Bragg Brentano geometry
  - Cu monochromatic configuration
  - PIXel solid-state detector in scanning mode was used. Acquisition times: 3min
  - Used of Fullprof program to performe Rietveld Refinement Analysis

(J. Rodrigez-Carvajal, Commission on powder diff. Newsl (2001)26,12)

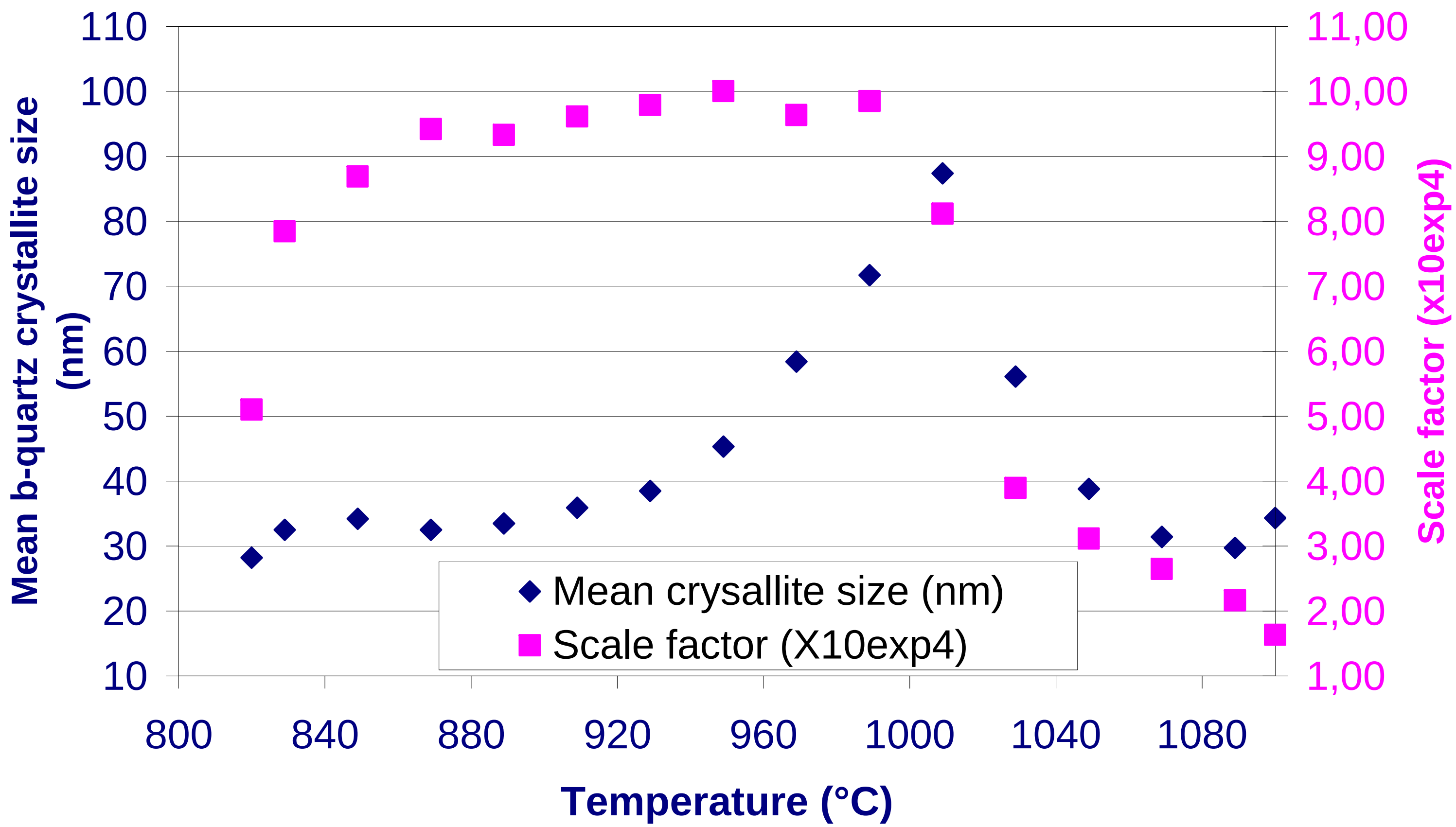
Crystallization of a LAS glass-ceramic:

Amount of crystalline phases vs temperature



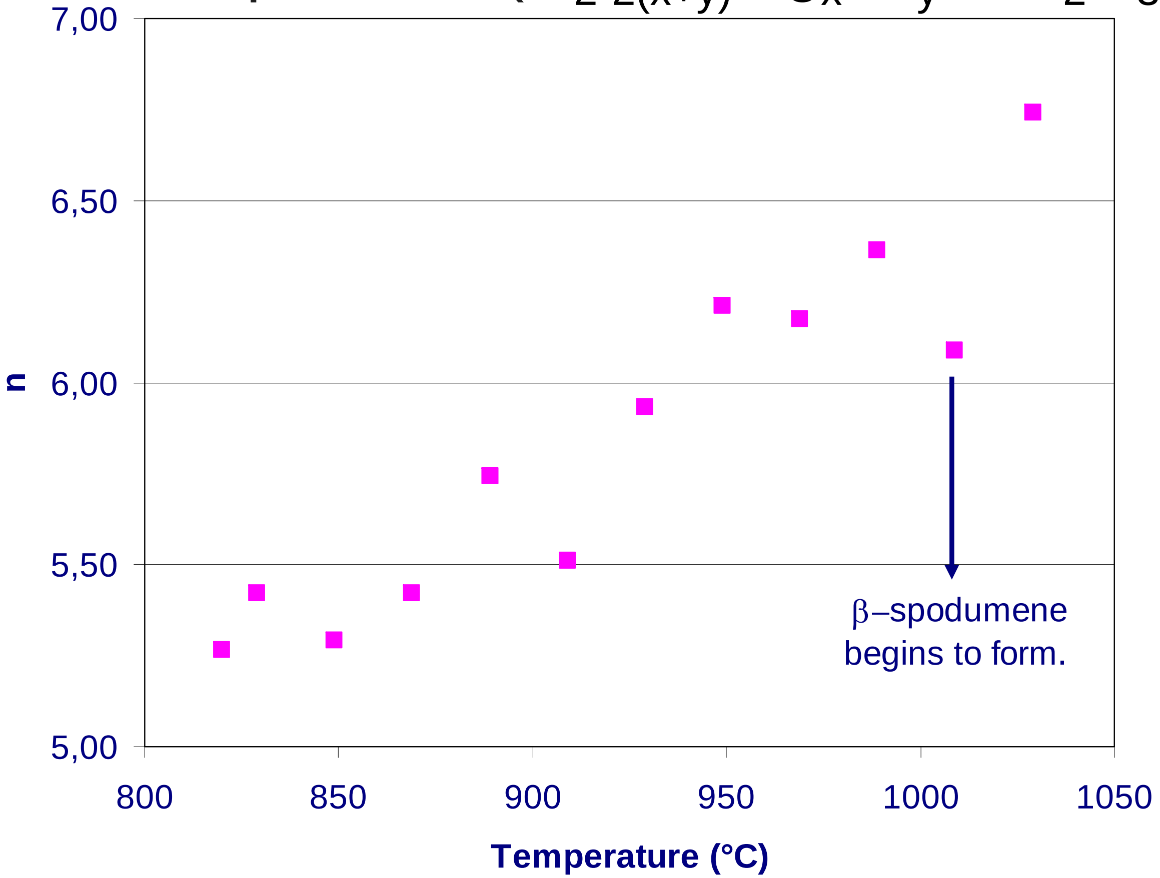
Crystallization of a LAS glass-ceramic

β-quartz amount and mean crystallite size vs temperature



Crystallization of a LAS glass-ceramic

Variation of composition of b-quartz solid solution with temperature ($Li_{2-2(x+y)}Mg_xZn_yO.Al_2O_3.nSiO_2$)



(Z, M)AS glass-ceramic

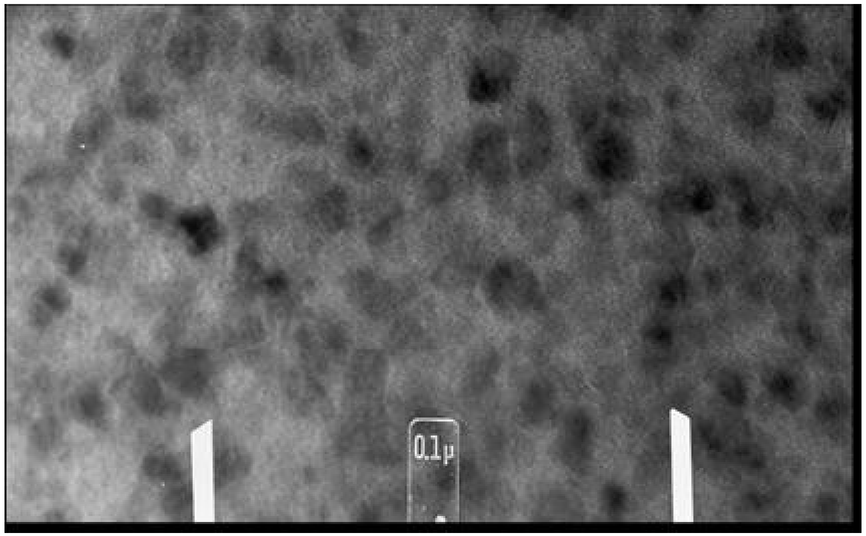
- Composition: SiO_2-Al_2O_3-ZnO-MgO-TiO_2-ZrO_2
- Phase assemblage: Crystals of spinel $(Zn,Mg)Al_2O_4$ in a continuous matrix of silica –rich glass
- Microstructure:

  uniformly dispersed,

  10-20 nm crystals

  ↓

  Transparent material



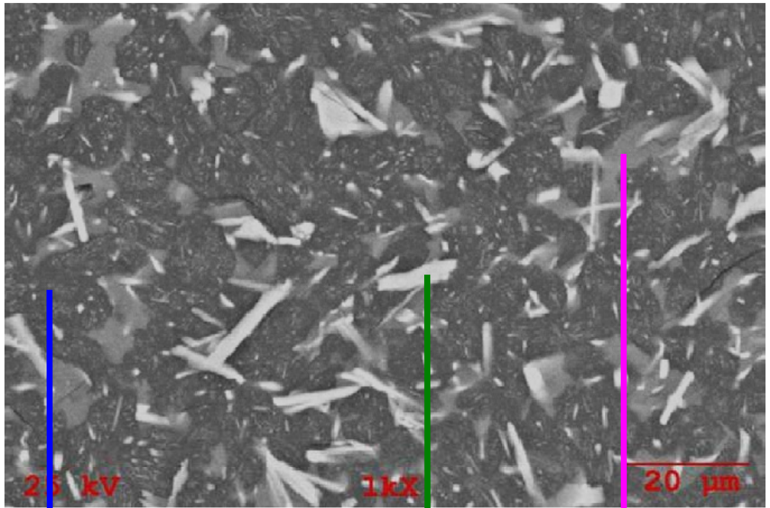
L.R. Pinckney
J.of non-Cryst. Sol.
255(1999)171

(Z, M)AS glass-ceramic Properties

	Spinel glass-ceramic	Vitreous silica	Code 1737
CTE (25-300° C) ($x10^{-7}K^{-1}$)	37	6	38
Strain point	945° C	990-1090° C	666° C
Young modulus (GPa)	98	72	73
Knoop hardness (KHN_{100})	650	500	460
MOR (MPa)	73	60	56

Refractory glass-ceramics
1- MgO-Al_2O_3-SiO_2-TiO_2 system

SiO_2 (wt%)	43,8
Al_2O_3	24,7
MgO	18,7
CaO	1,4
TiO_2	11,4
Heat treatment	825° C/ 2h 1200° C/ 10h
CTE (25-1000° C°)	41 $x10^{-7}K^{-1}$
E modulus	130 GPa
Abraded MOR	165 +/- 6 MPa
K_{1C}	4.3 +/- 0.4 MPa $m^{0.5}$
KHn	984 +/- 16
Thermal stability	1250° C



Indialite
$Mg_2Al_4Si_5O_{18}$
Low CTE

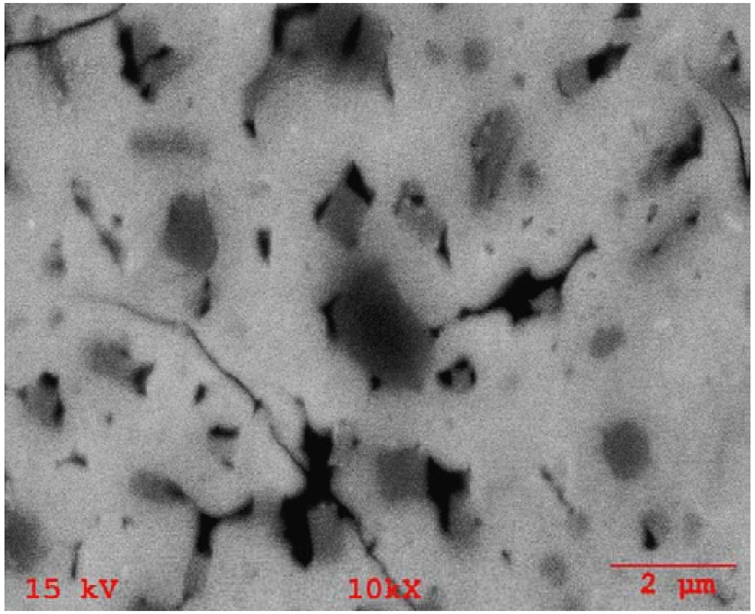
Karroite
MgTi2O5
High E

Enstatite
$MgSiO_3$
Lamellar twinning

G.H. Beall, J. Europ. Ceram. Soc. 29(2009)1211

Refractory glass-ceramics
2- SrO-Al_2O_3-SiO_2-TiO_2 system

SiO_2 (wt%) Al_2O_3 SrO TiO_2	34.1 32.9 23.9 9.1
Heat treatment	850° C/ 2h 1425° C/ 6h
CTE (25-1000° C°) Abraded MOR (MPa) K_{1C} (MPa $m^{0.5}$) Thermal stability	$43 \times 10^{-7} K^{-1}$ 132 +/- 17 MPa 2.67 +/- 0.2 1450° C



Sr-feldspar $SrAl_2Si_2O_8$
+ Tielite (Al_2TiO_5)

G.H. Beall, J. Europ. Ceram. Soc. 29(2009)1211

Refractory glass-ceramics

- Alkaline-earth aluminosilicates
- Internally nucleated with TiO_2
- Maximum use temperature: 1200-1500° C range
- Potential applications:
  - Improved radomes
  - Engine components
  - Substrates for semi-conductors
  - Precision metallurgical molds

Metal colloids used as nucleating agents: Photosensitive glass-ceramics

- FOTOFORM® /FOTOCERAM® or FOTURAN®

- Use: Etched patterned materials

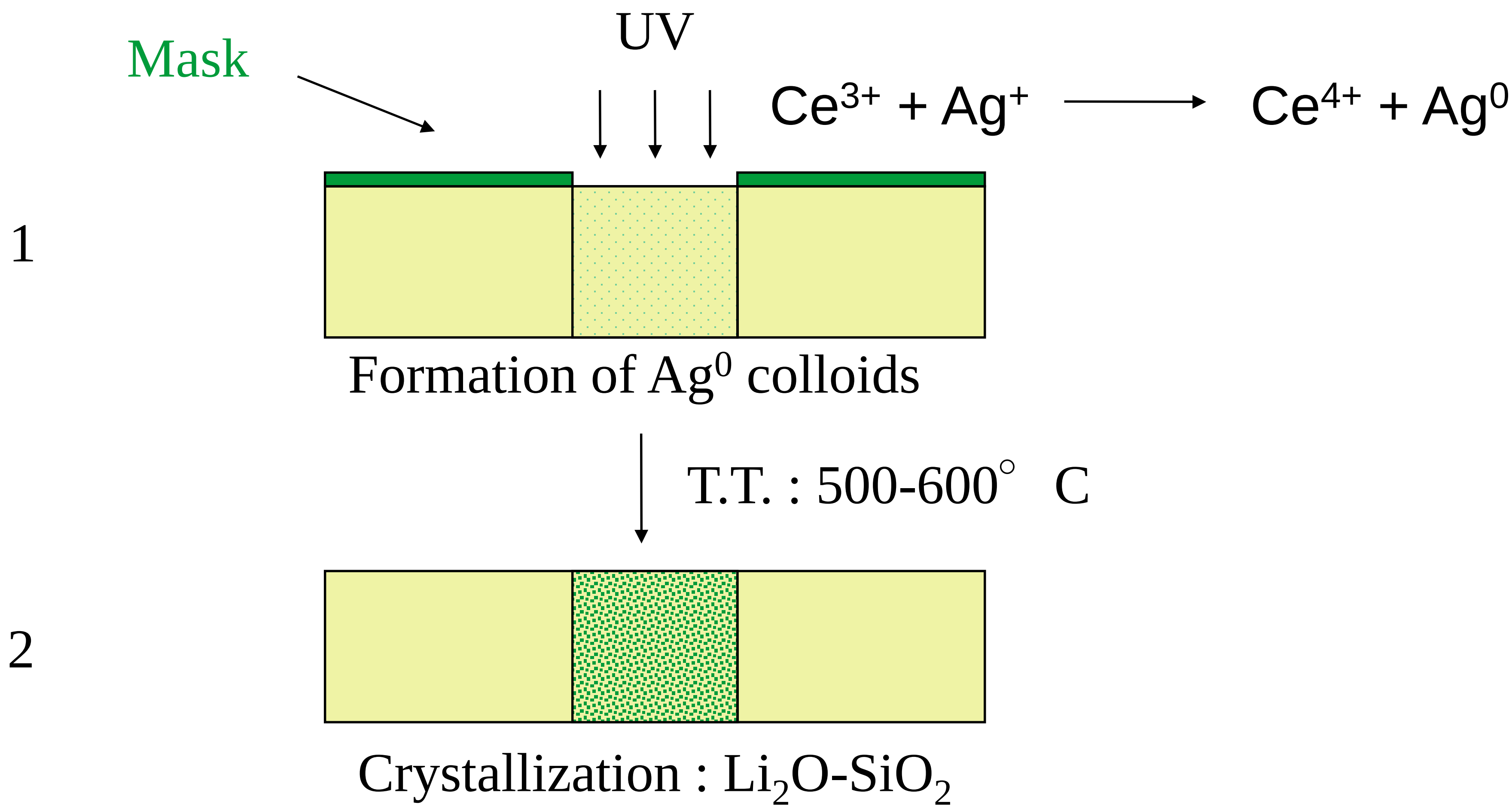
- Composition:
  - SiO_2 : 80 % wt

  Al_2O_3 : 4

  Li_2O : 10

  others: 6
  - Nucleating agent: Ag^0 (with Ce^{3+})

Process (FOTOFORM® /FOTOCERAM® or FOTURAN®) (1)



Process (FOTOFORM® /FOTOCERAM® or FOTURAN®) (2)

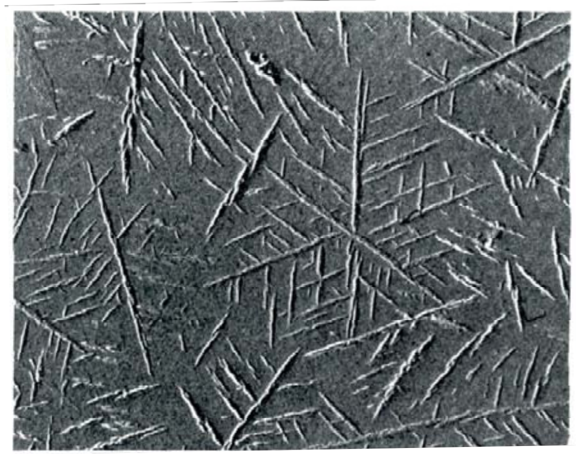
3

Chemical etching (HF 10%)

↓ UV + T.T. : 600-700° C

4

Crystallization : Li_2O-$2SiO_2$

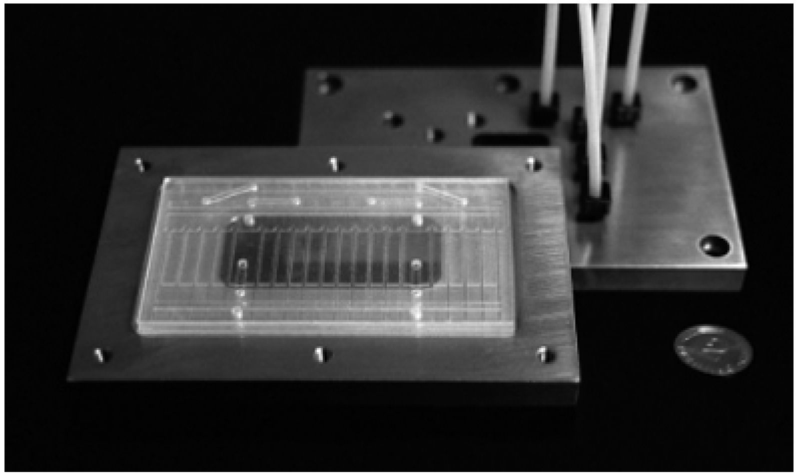


Dendritic crystallization of Li_2O-SiO_2

FOTOFORM® /FOTOCERAM® or FOTURAN®

- Use: fabrication of high-precison components

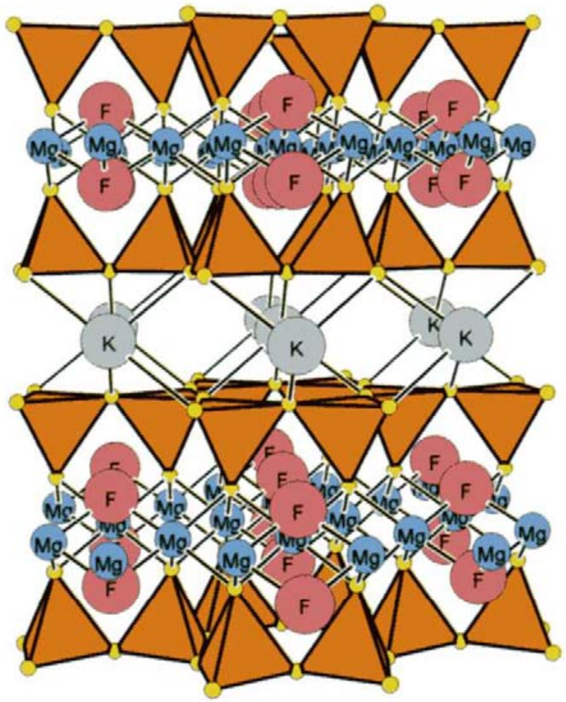
  Smallest structures: 25 µm are possible with a roughness of 1 µm.
- Use: micro-mechanics, micro-optics, fluid devices…

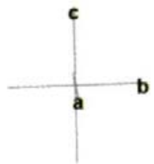


Microreactor
Mikroglas website

Machinable glass-ceramics
Composition and microstructure

Example	Macor
SiO_2	47,2
Al_2O_3	16,7
B_2O_3	8,5
MgO	14,5
K_2O	9,5
F	6,3





Appendix Figure 13.
Fluorophlogopite ($KMg_3AlSi_3O_{10}F_2$)
Layer Silicate

From Glass-ceramic technology :
W. Höland and G. Beall (Am. ceram. Soc (2002))

Machinable glass-ceramics: Properties and applications

Table 4-7

Properties of MACOR® Glass-Ceramic (MACOR® 1992)

Properties	MACOR™ Machinable Glass-Ceramic
Mechanical	
Density	2.52 g/cm^3
Porosity	0%
Hardness (Knoop)	250 NA
Compressive strength	50,000 psi 350 MPa
Flexural strength	15,000 psi 104 MPa
Thermal	
Coefficient of thermal expansion	5.2×10^{-6} K^{-1} (T in °F) 9.4×10^{-6} K^{-1} (T in °C)
Maximum use temperature (no load)	1832°F / 1000°C
Electrical	
Dielectric strength (a.c.)	1,000 volts / (10^{-3} inch)
Volume resistivity	> 10^{14} Ω·cm

Conclusion

- Glass-ceramics are very versatile materials

  (even if the developement of commercial materials can be tough)

- Development of new materials would benefit from a better understanding of crystallization (especially nucleation) mechanisms.
- The recent advances in glass structural studies (via solid state NMR, SAXS, X-Ray diffraction and absorption…) would allow significant progresses in this area.