Glass Processing

Lecture #16 Glass-ceramics: Nature, properties and processing

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Lectures available at:
www.lehigh.edu/imi

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Glass-ceramics: nature, applications and processing (2.5 h)

1- High temperature reactions, melting, homogeneization and fining
2- Glass forming: previous lectures

3- Glass-ceramics: definition & applications (March 19)

Today, March 24:
4- Composition and properties - examples
5- Thermal treatments – Sintering (of glass powder compactd) or
-Controlled nucleation and growth in the glass bulk
6- Micro and nano structure development

April 16
7- Sophisticated processing techniques
8- GC types and applications
9- Concluding remmarks



Review of Lecture 15

Glass-ceramics

-Definition

-History

-Nature, main characteristics

-Statistics on papers / patents

- Properties, thermal treatments micro/ nanostructure design

Reading assignments

E. D. Zanotto – *Am. Ceram. Soc. Bull.*, October 2010

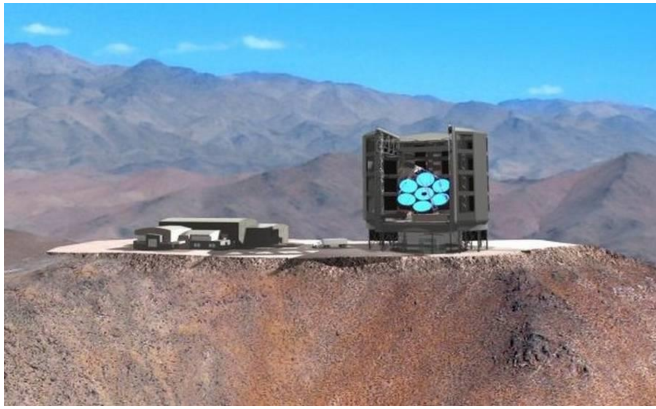
The discovery of GC

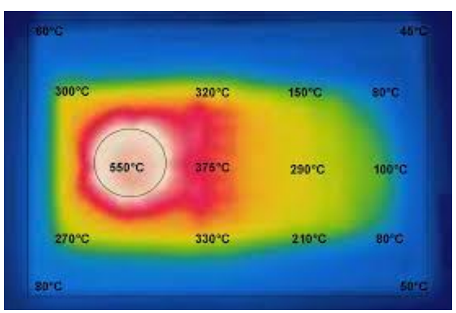
Natural glass-ceramics, such as some types of obsidian "always" existed.

René F. Réaumur – 1739 "porcelain" experiments…

In 1953, Stanley D. Stookey, then a young researcher at Corning Glass Works, USA, made a serendipitous discovery ......

GLASS Ceramics





<rms> 1nm

Zanotto

Transparent GC for domestic uses

Company	Products	Crystal type	Applications
SCHOTT, Germany	Foturan®	Lithium-silicate	Photosensitive and etched patterned materials
	Zerodur®	β-quartz ss	Telescope mirrors
	Ceran® / Robax®	β-quartz ss	Cookware, stovetops, cooktop and oven doors
	Nextrema®	Lithium Aluminosilicate	Fireproof windows and doors
Corning, USA	Pyroceram®	β-Spodumene ss	Cookware
	Fotoform® / Fotoceram®	Lithium silicate	Photosensitive and etched patterned materials
	Cercor®	β-Spodumene ss	Gas turbines and heat exchangers
	Centura®	Barium silicate	Microwave tableware
	Vision®	β-quartz ss	Cookware and cooktop
	9606®	Cordierite	Radomes
	MACOR®	Mica	Machinable glass-ceramic
	9664®	Spinel-enstatite	Magnetic memory disk substrate
	DICOR®	Mica	Dental restoration
Nippon Electric Glass, Japan	ML-05™	Lithium disilicate	Magnetic memory disk substrate
	Neoparies®	β-wollastonite	Architectural glass-ceramic
	Firelite™	β-quartz ss	Architectural fire-resistant windows
	Neoceram™ N-11	β-Spodumene ss	Cooktop and kitchenware
	Narumi®	β-quartz ss	Low thermal expansion GC
	Neoceram™ N-0	β-quartz ss	Color filter substrates for LCD panels

GC processing

- Composition + nucleating agents
- Melting, homogeneization, fining, cooling, shaping (annealing the glass?)
- Thermal treatment
- Nano / microstructure
- Properties
- Application

GC with β-Quartz$_{ss}$ – $(Li,R)O.Al_2O_3.nSiO_2$, R = Mg^{2+}, Zn^{2+}, n=2-10

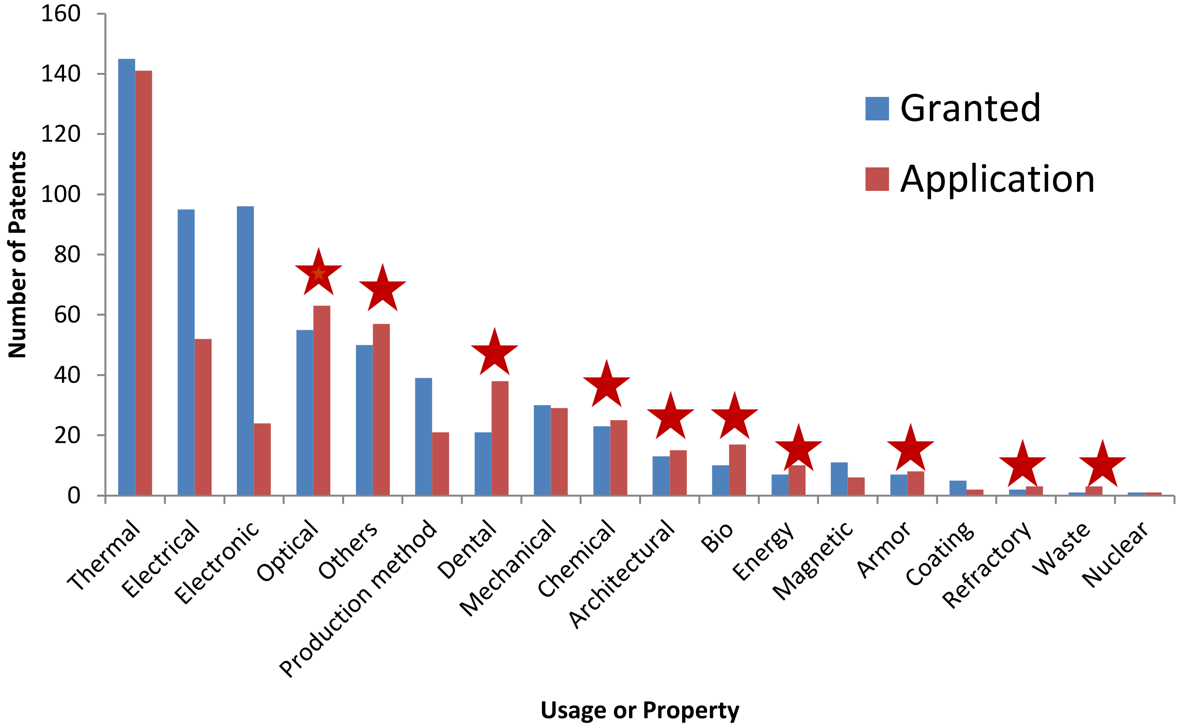
Components	Vision ® Corning	Zerodur ® Schott	Narumi ® NEG	NeoceramN-0™ NEG	Ceram ® Schott
SiO_2	68,8	55,4	65,1	65,7	64,0
Al_2O_3	19,2	25,4	22,6	22,0	21,3
Li_2O	2,7	3,7	4,2	4,5	3,5
MgO	1,8	1,0	0,5	0,5	0,1
ZnO	1,0	1,6	-		1,5
P_2O_5	-	7,2	1,2	1,0	
F	-	-	0,1		
Na_2O	0,2	0,2	0,6	0,5	0,6
K_2O	0,1	0,6	0,3	0,3	0,5
BaO	0,8				2,5
CaO					0,2
TiO_2	2,7	2,3	2,0	2,0	2,3
ZrO_2	1,8	1,8	2,9	2,5	1,6
As_2O_3	0,8	0,5	1,1	1,0	
Sb_2O_3					0,85
Fe_2O_3	0,1	0,03	0,03		0,23
CoO	50 ppm				0,37
Cr_2O_3	50 ppm				
MnO_2	-				0,65
NiO				0,06	

GC with β-Quartz$_{ss}$ = $(Li,R)O.Al_2O_3.nSiO_2$

Properties	"NCS Glass"	Neoceram™N-0	Ceram ®	Robax ®
Bending strength (MPa) -	40	140	110	~ 75
Knoop Hardness	<500	500	600	-----
E (GPa)	70	90	≤ 95	~ 92
TEC 20-700°C ($10^{-7}.K^{-1}$)	100	- 3	0 ± 1.5	0 ± 3
Tmax - long time (°C)	500	700	700	680
Critical thermal shock (°C)	70	800	700	~ 700

Number of granted patents and patent applications extracted manually from the FPO website using the keywords “glass ceramic” or “glass-ceramic” in the patent title. Jan 2001 - July 2014

Per intended use

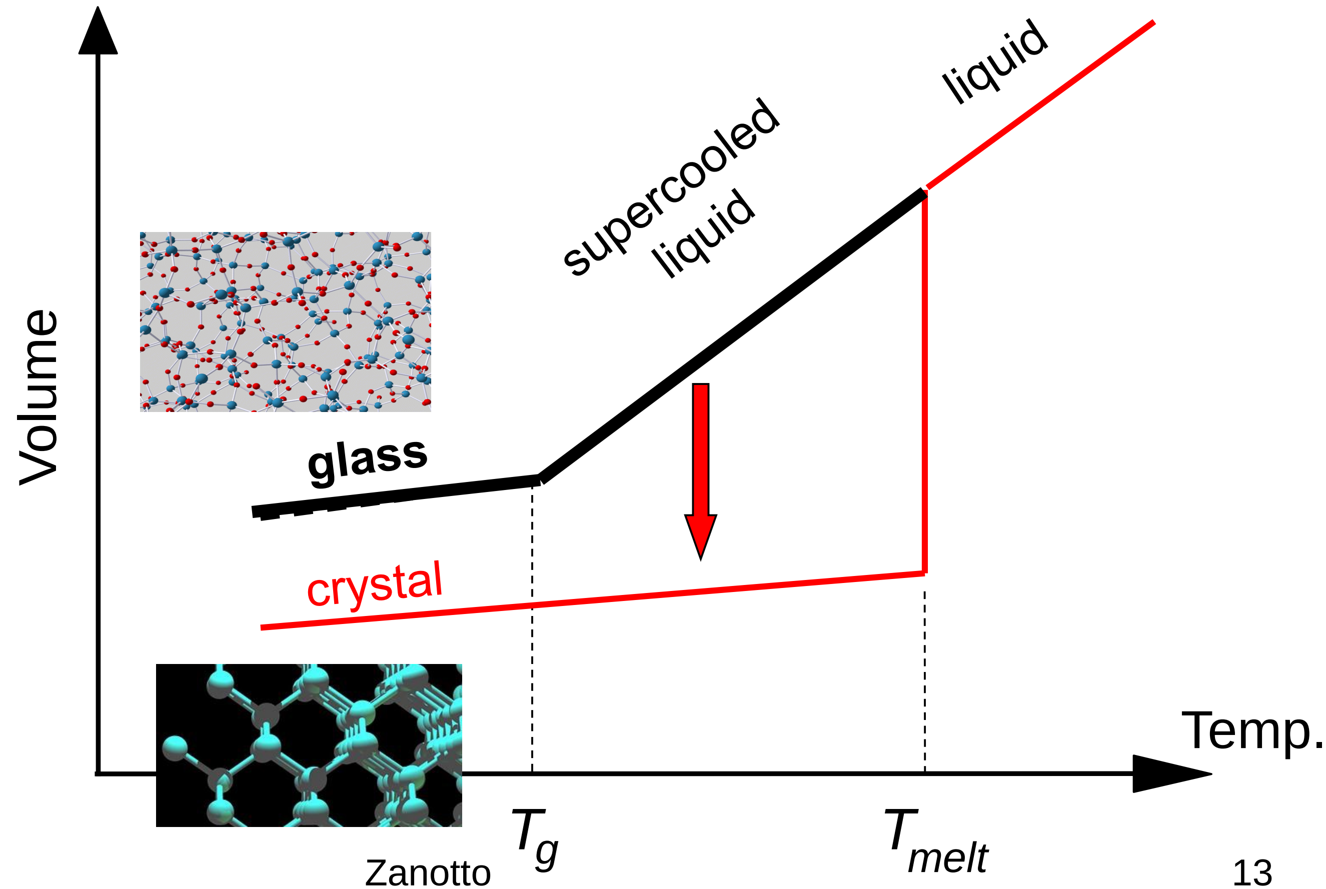


Am. Cer. Soc. Bull., May 2015

Statistical Overview of Glass-Ceramic Science and Technology

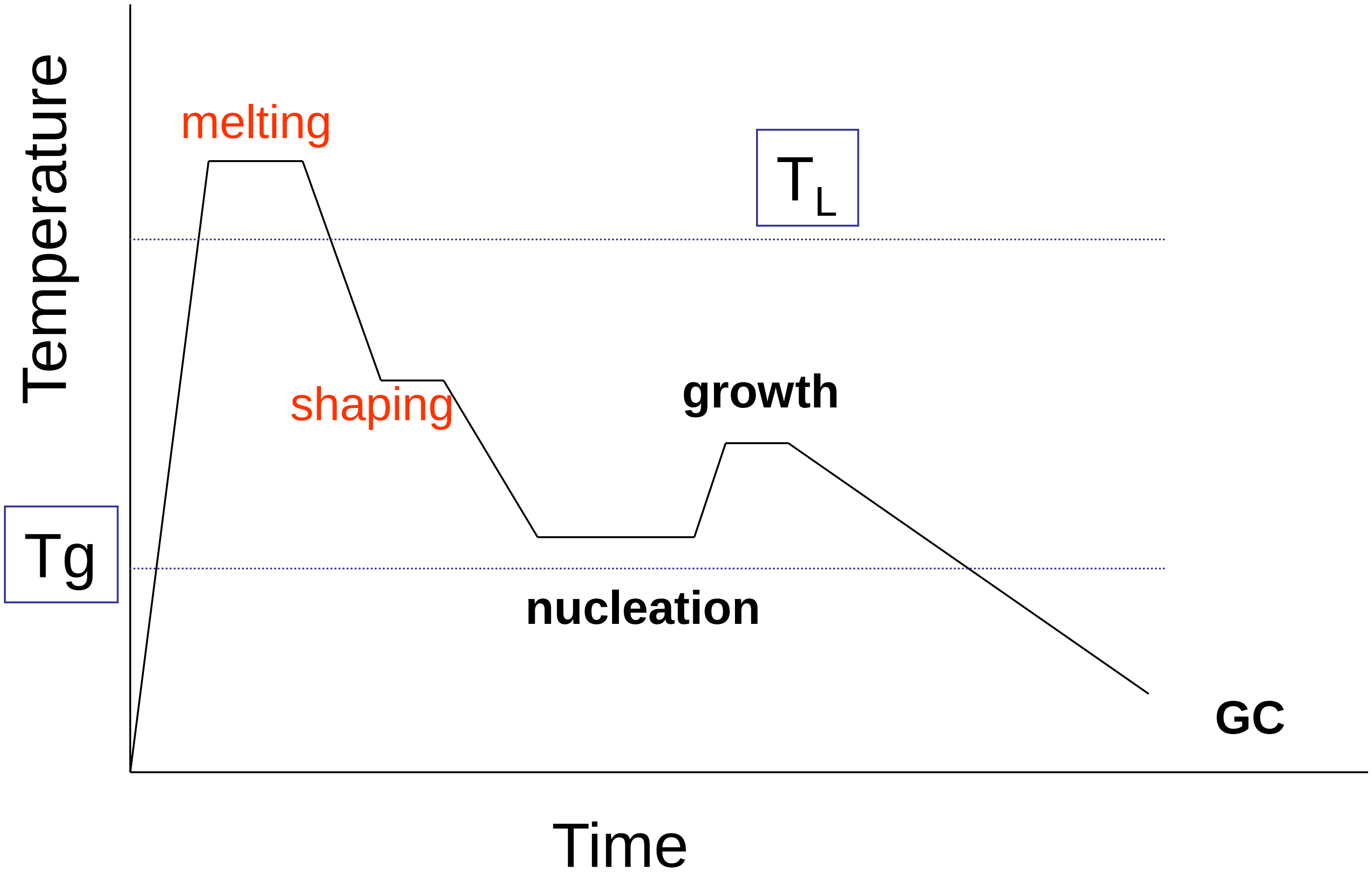
Maziar Montazerian, Shiv P. Singh, Edgar D. Zanotto

Glasses and glass-ceramics



Zanotto

Traditional processing steps

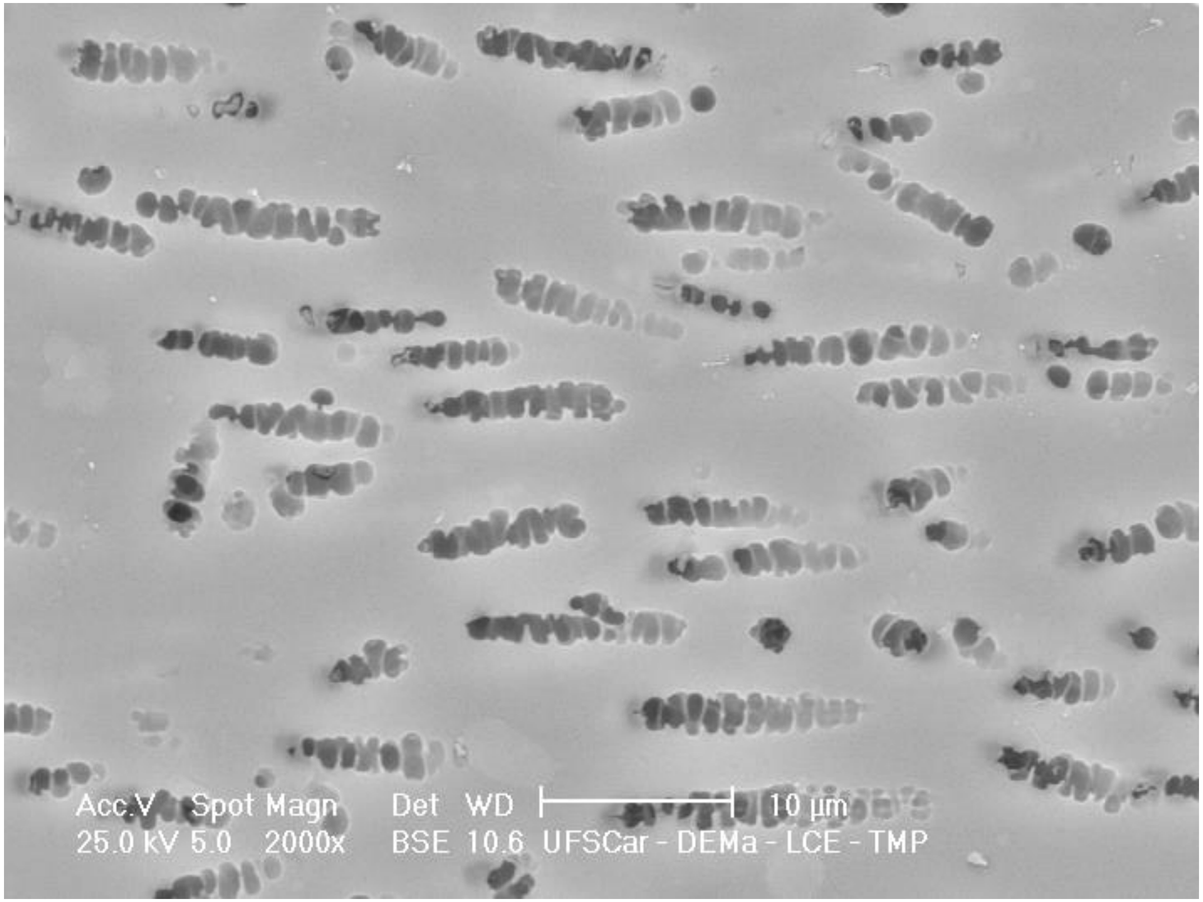


Design of nano and microstructures

Controlled crystallization of glass

A meeting of <u>art</u> and <u>science!</u>

LaMaV's gallery

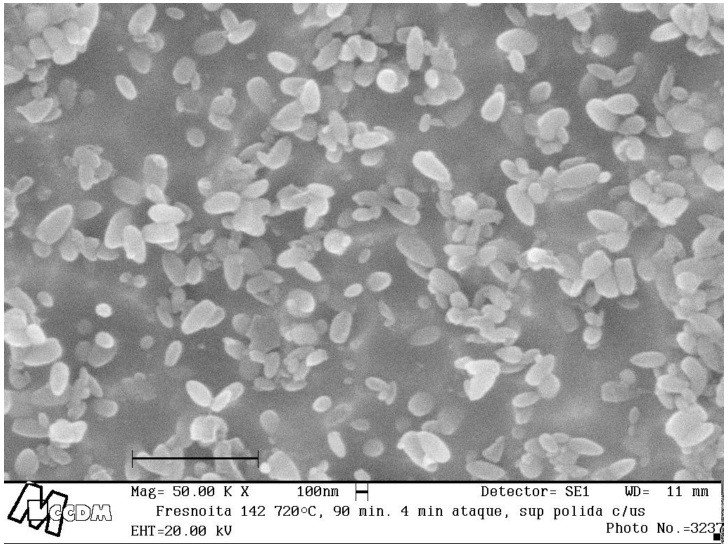


Worm-like textured crystals in a bioactive glass

Photo by Ma Trevelin and Mu Crovacce (2011)

LaMaV's gallery

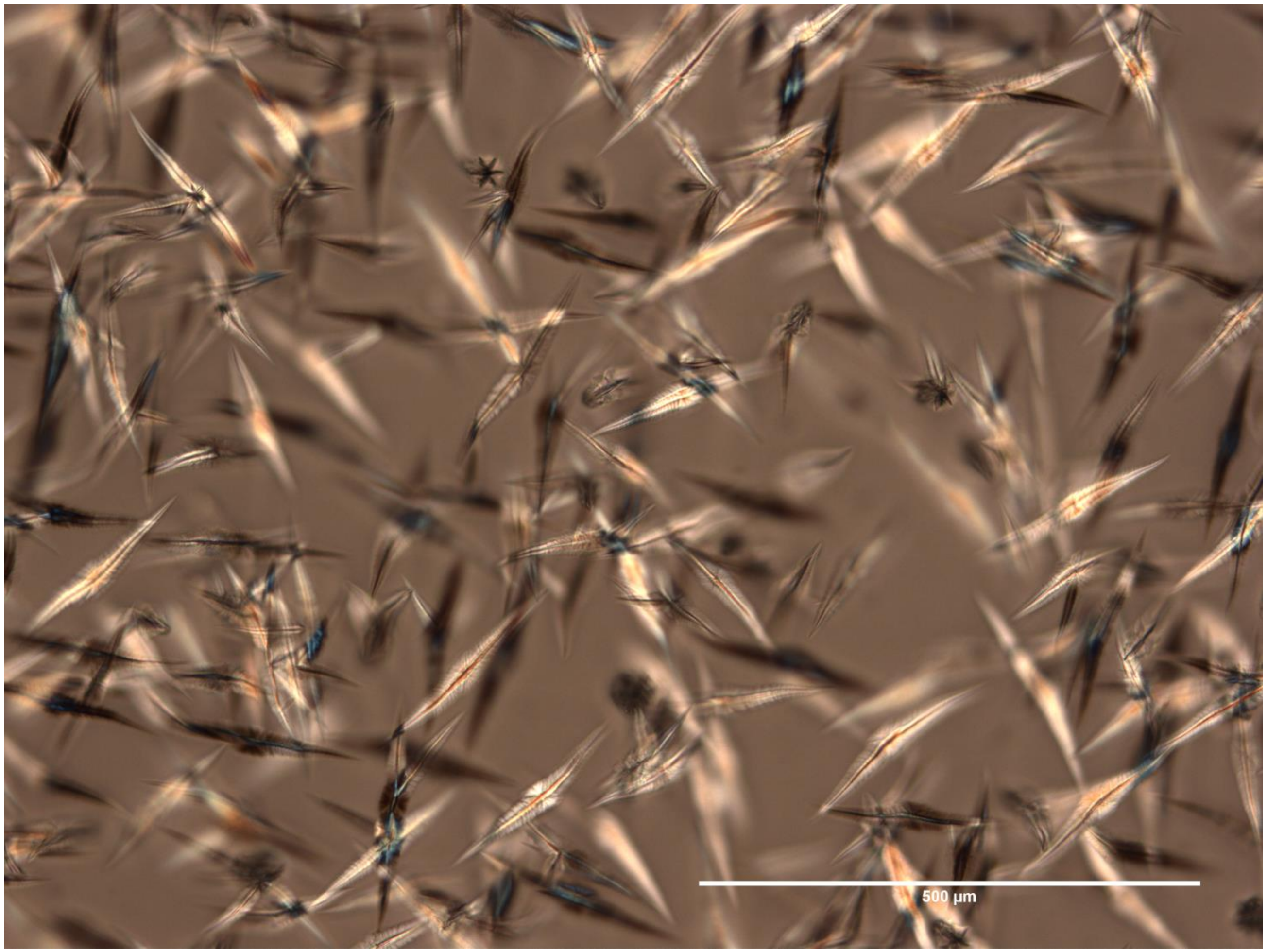
Papaya by Daniele Ballerini



Papaya seed crystals in fresnoite glass

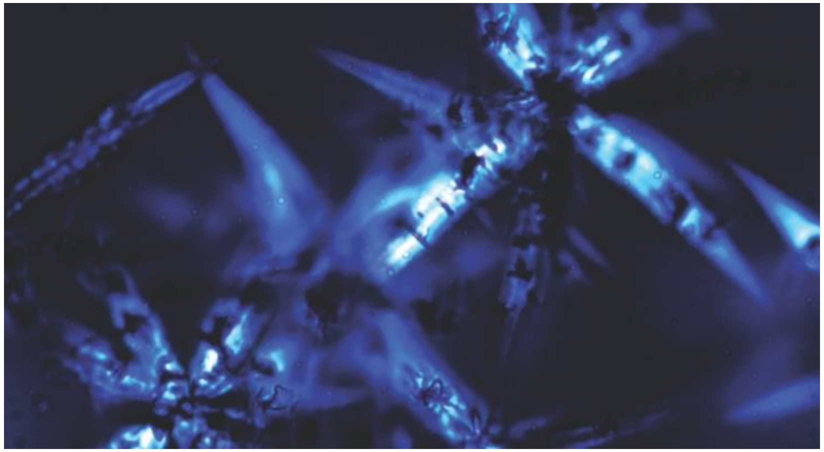
Photo by Alu Cabral, LaMaV (2000)

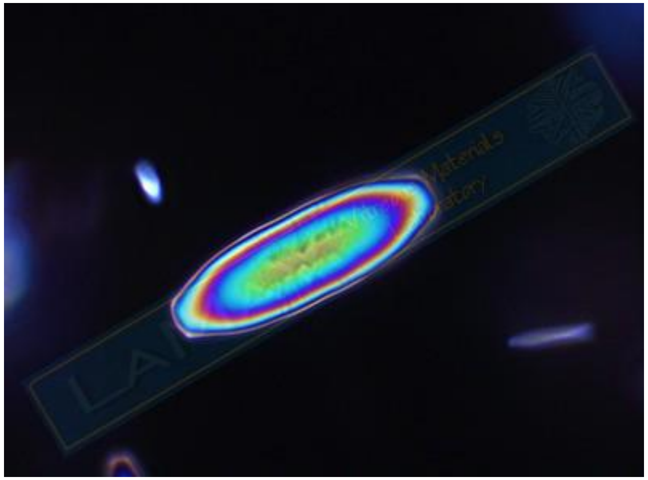
LaMaV's gallery



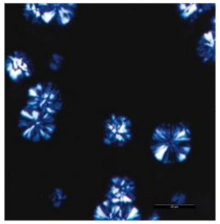
Hammingbirds In a Li_2O-CaO-SiO_2 glass

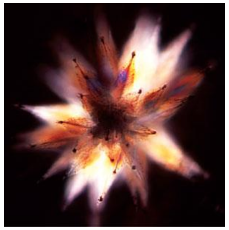
Photo by Vlad Fokin 2011 LaMaV



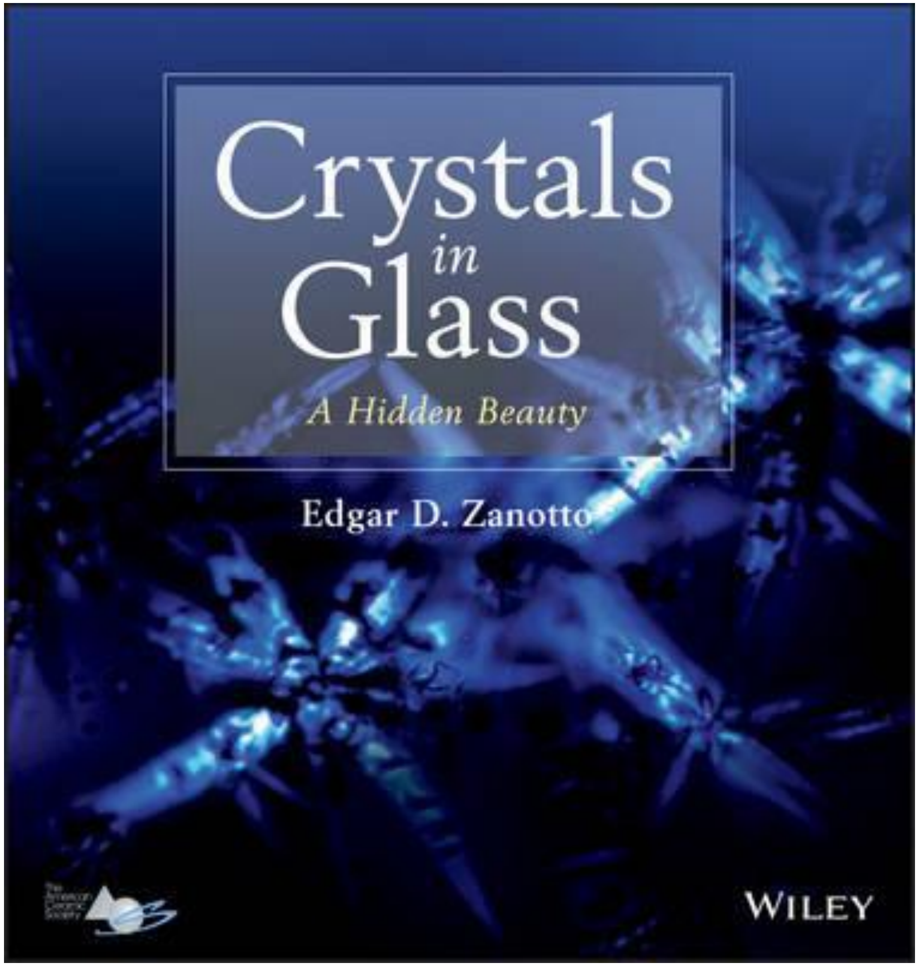


Designed micro and nanostrucures lead to GC





Crystals in Glass: A Hidden Beauty
E. D. Zanotto
ISBN: 978-1-118-52143-4
136 pages, October 2013



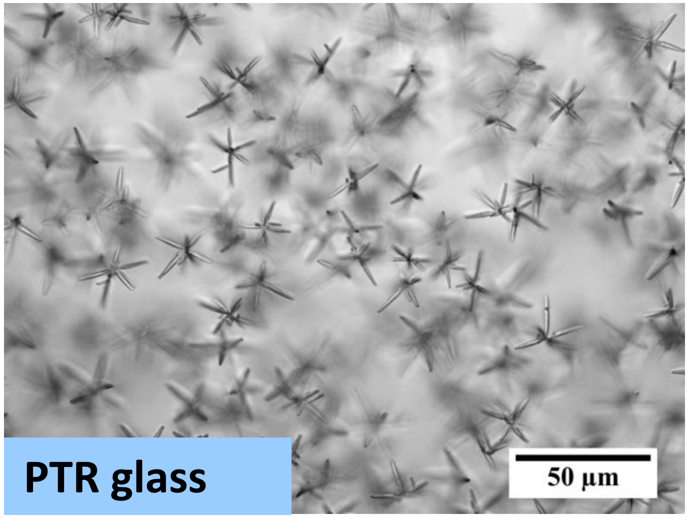
Traditional processing of GC

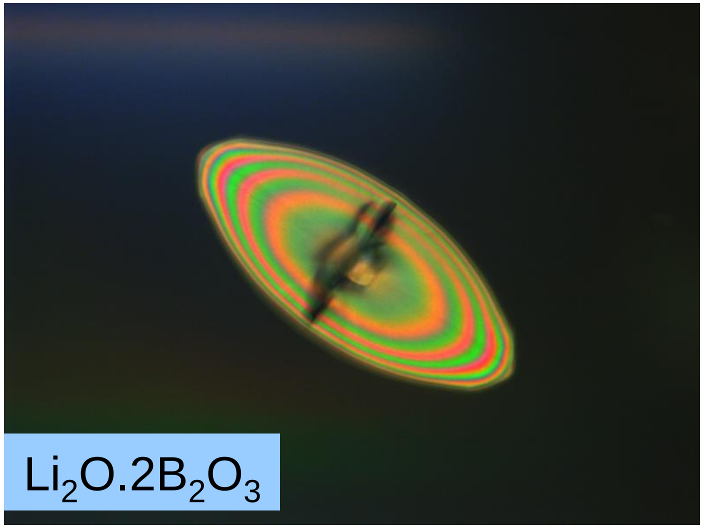
GC are normally produced in two steps:

- i) a glass is made by a standard glass manufacturing process,
- ii) the glass article is shaped, cooled down and then reheated somewhat above its glass transition temperature in a second and even a third step.

In most cases, nucleating agents such as noble metals, fluorides, ZrO_2, TiO_2, P_2O_5, Cr_2O_3 or Fe_2O_3 are added.

Glass crystallization processes



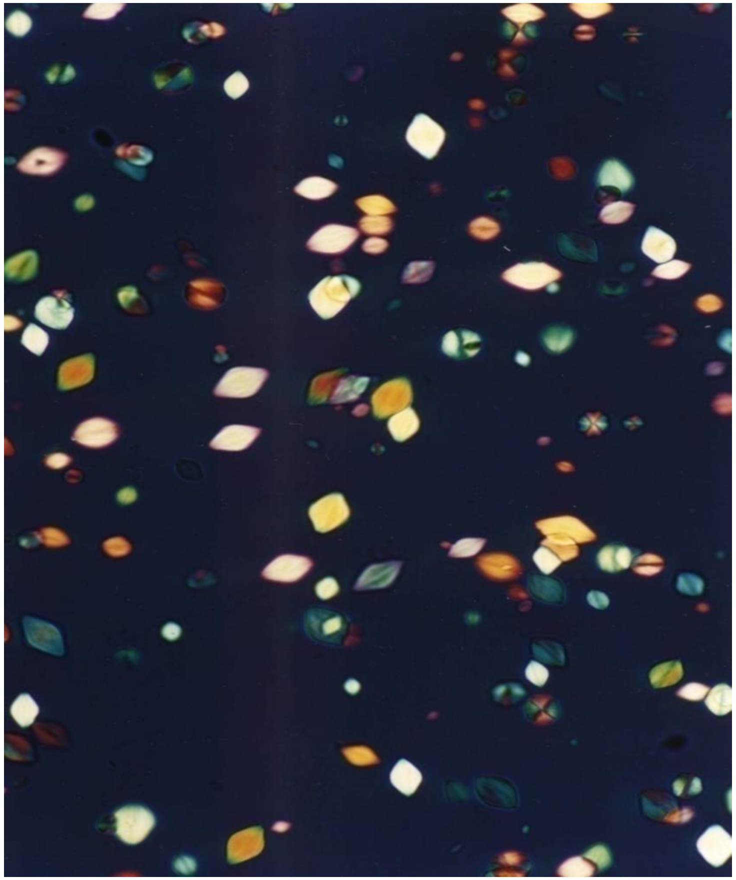


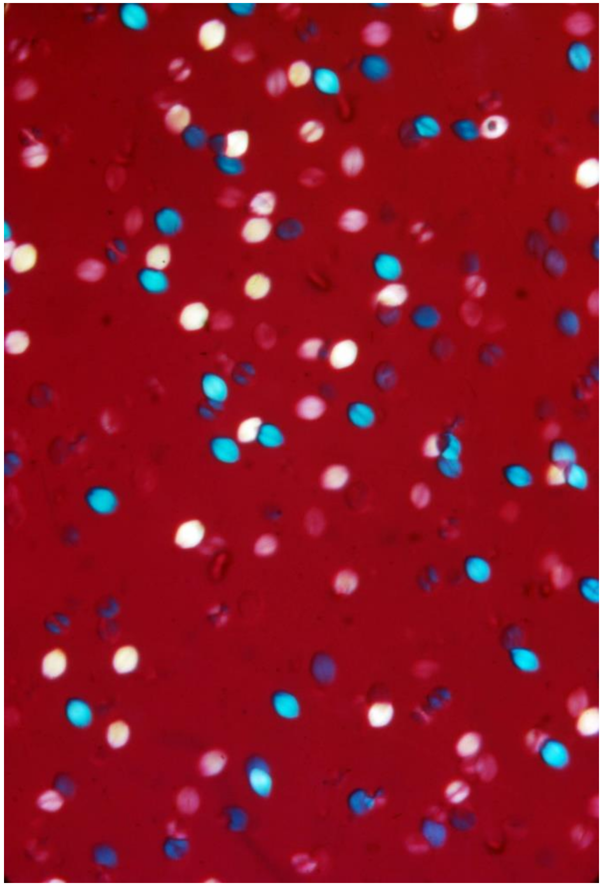
Nucleation: internal *vs.* surface, steady *vs.* non-steady, homogeneous *vs.* hetero, polymorphic *vs*. non-stoichiometric

Growth: uni, two, tri-dimensional, single-crystals, spherulitic, dendritic, random, textured, diffusion controlled, polymorphic, single phase, multiphase…

Overall Crystallization: a combination of the above listed cases

Internal nucleation



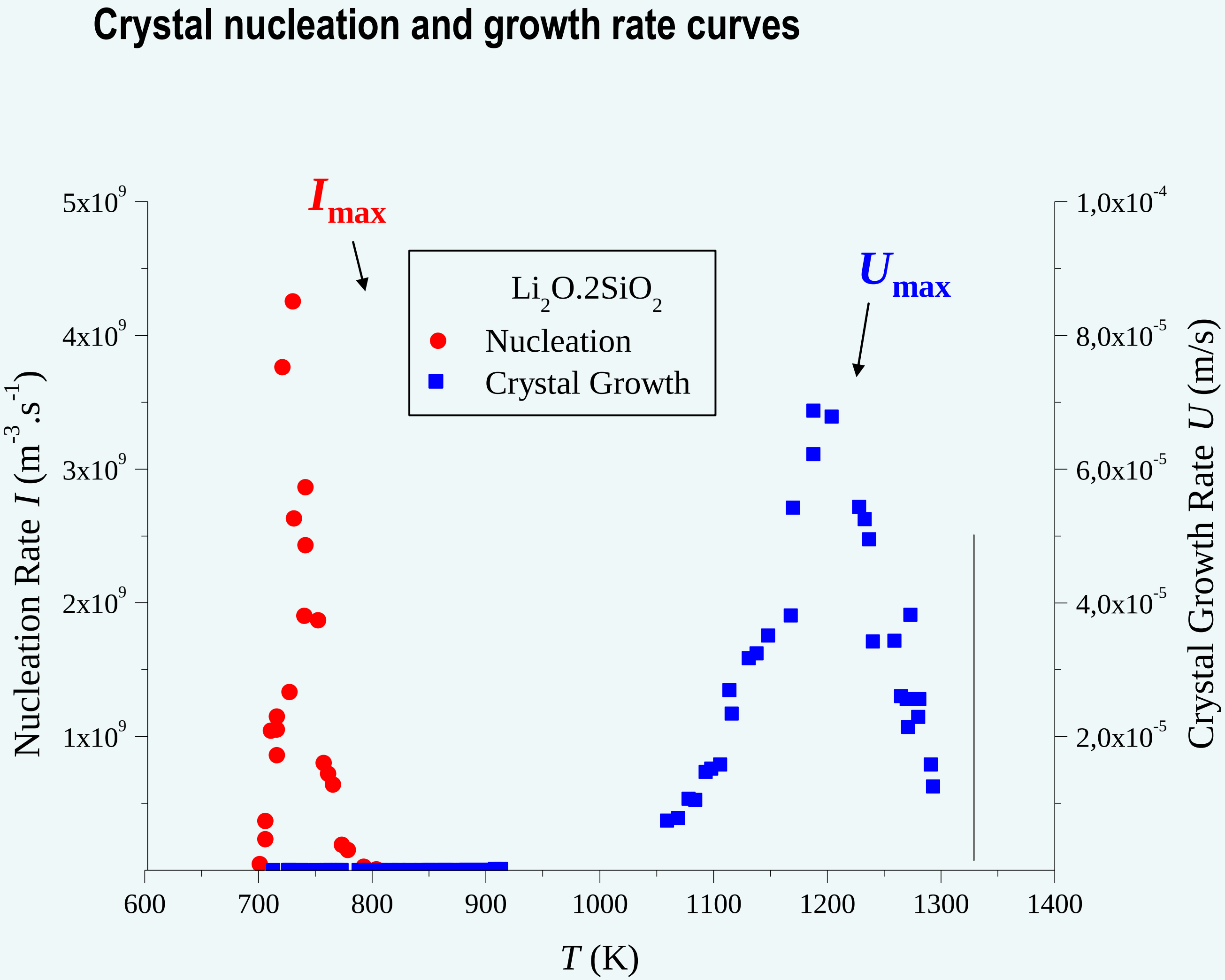


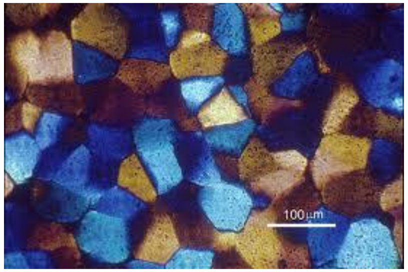
Lithium disilicate:
the “*Drosophila*”
of glass
crystallization
studies

Photos by Vlad Fokin
and Ed Zanotto

Solid knowledge about crystallization is key!

Homogeneous nucleation

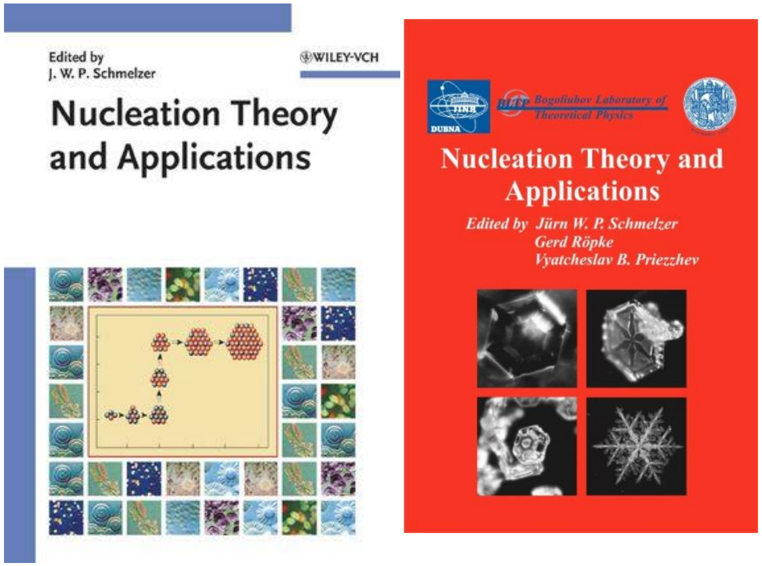




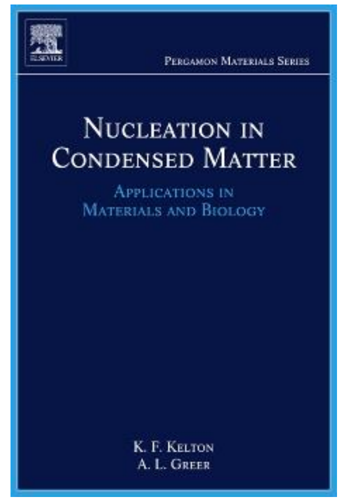
CeRTEV

ufscar

Zanotto



1999, 2002, 2005, 2009, 2011



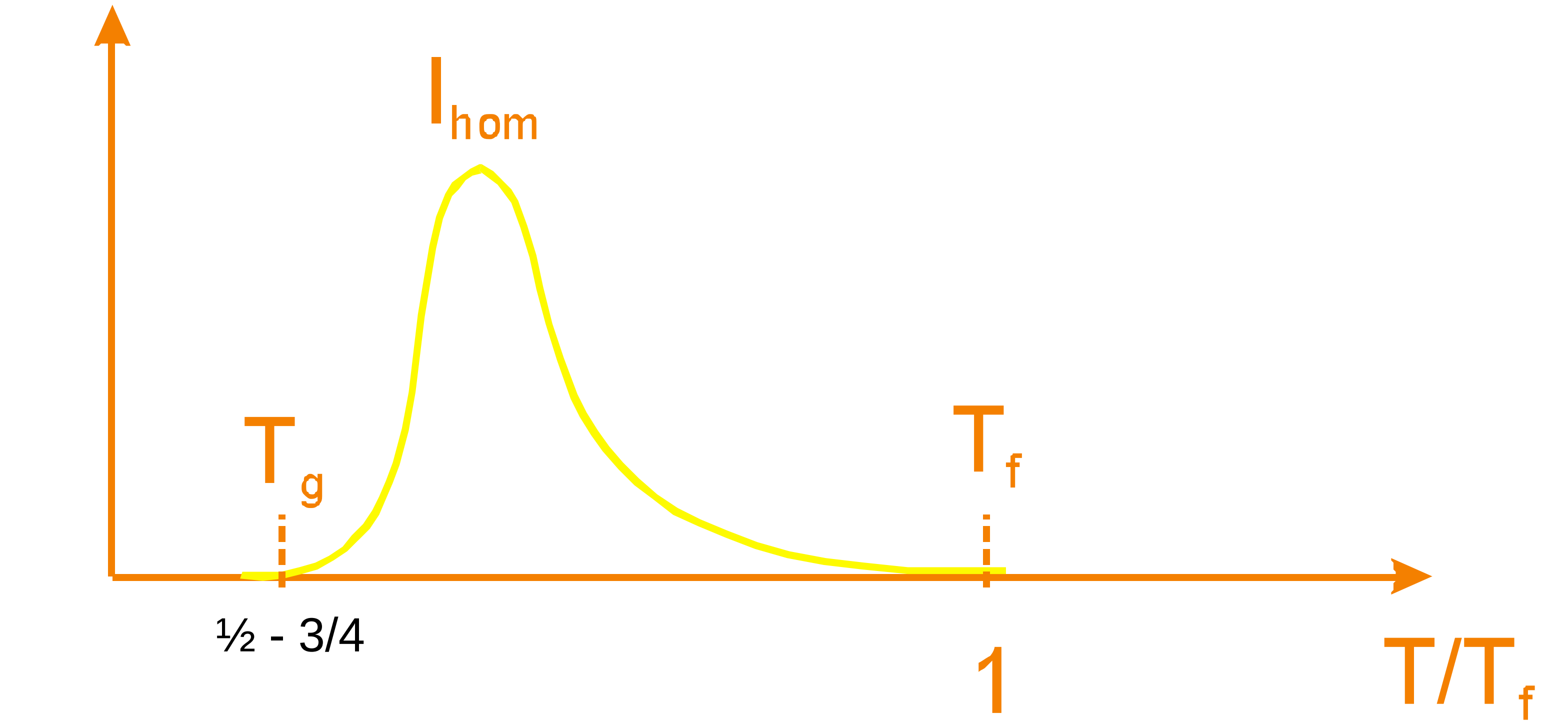
2010

2012

Thermodynamic

$$I_{hom} = A\exp\left(-\frac{W^*}{kT}\right)\exp\left(-\frac{Q}{kT}\right)$$

Transport



from E.B.Ferreira

Tests of CNT for oxide glasses

Profª Drª Sati Manrich, UFSCar-DEMa.

$CaO.SiO_2$ | $BaO.2SiO_2$ | $Na_2O.2CaO.3SiO_2$ | $2Na_2O.CaO.3SiO_2$

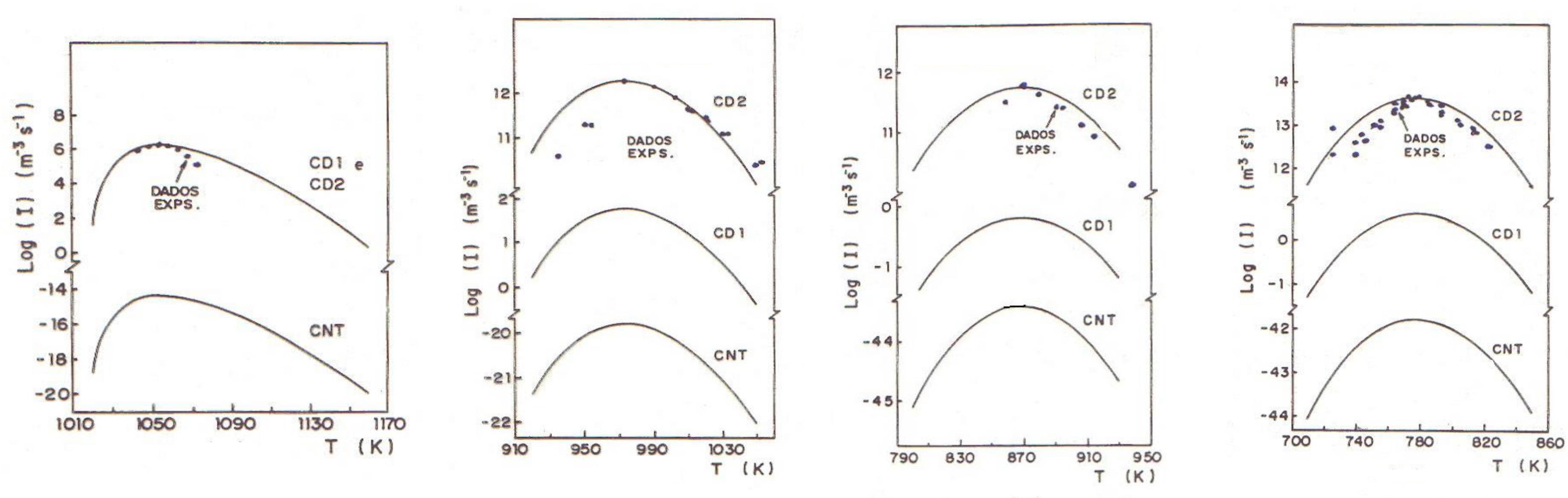


Figure 9b: Calculated nucleation rates by CNT, and modifications with one (CD1) and two (CD2) adjustable parameters.

Manrich & Zanotto, *Cerâmica* (1995)

Crystal growth in GF liquids

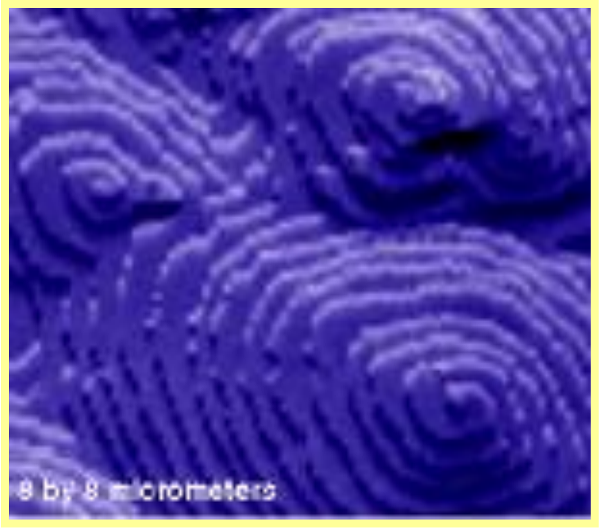
Screw dislocation mediated growth, the most common growth mechanism in undercooled oxide GF liquids

$$\mathbf{u = f \frac{D_{ef}}{\lambda}\left[1 - exp\left(-\frac{|\Delta G_v|}{RT}\right)\right]}$$

$$f = \frac{\lambda \Delta G}{4\pi\sigma V_M}$$

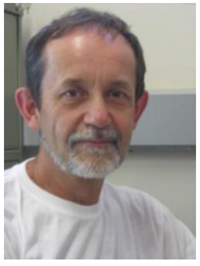
Def = diffusion coefficient

ΔG = driving force



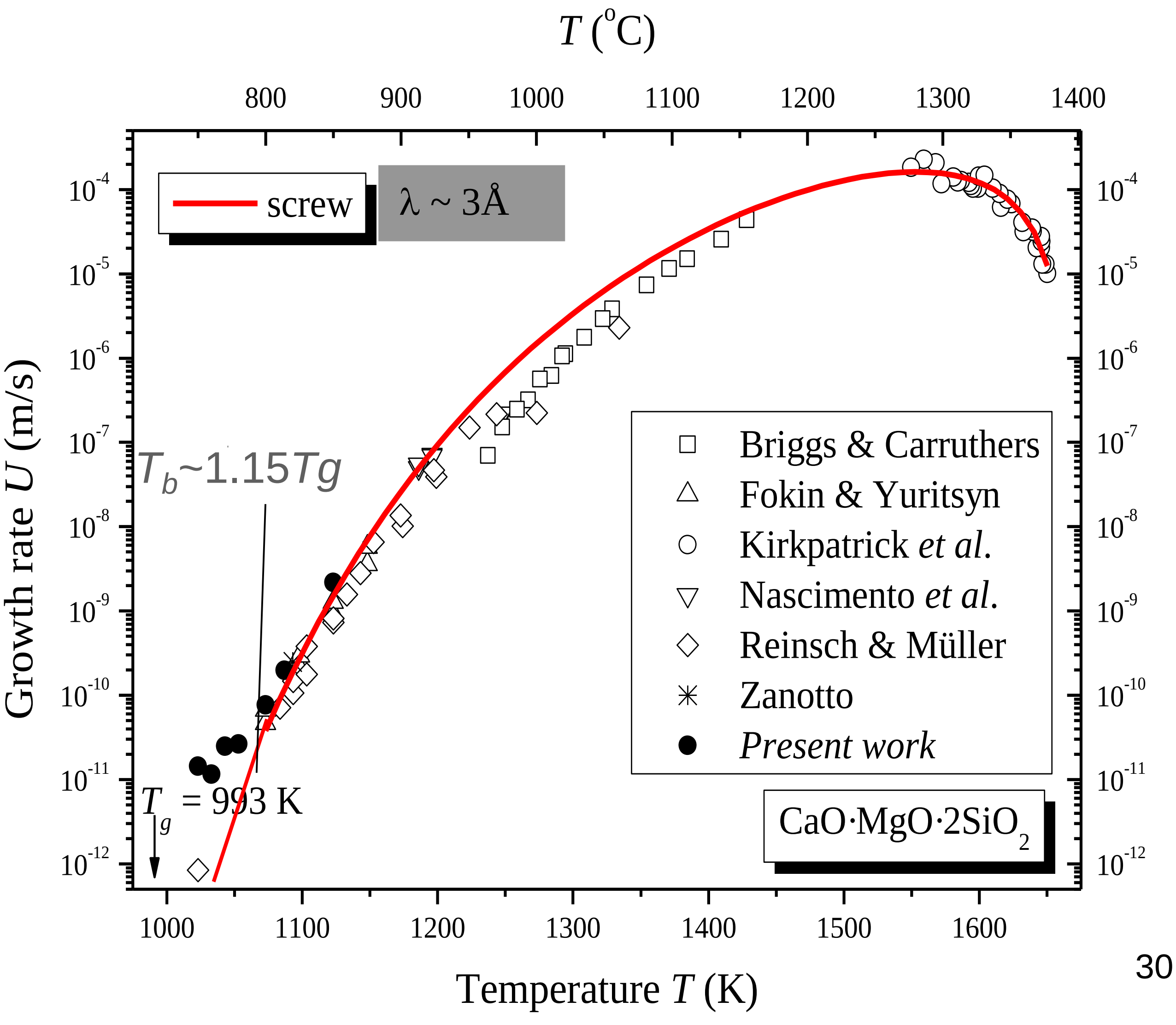
Crystal growth rates

Daniel Cassar



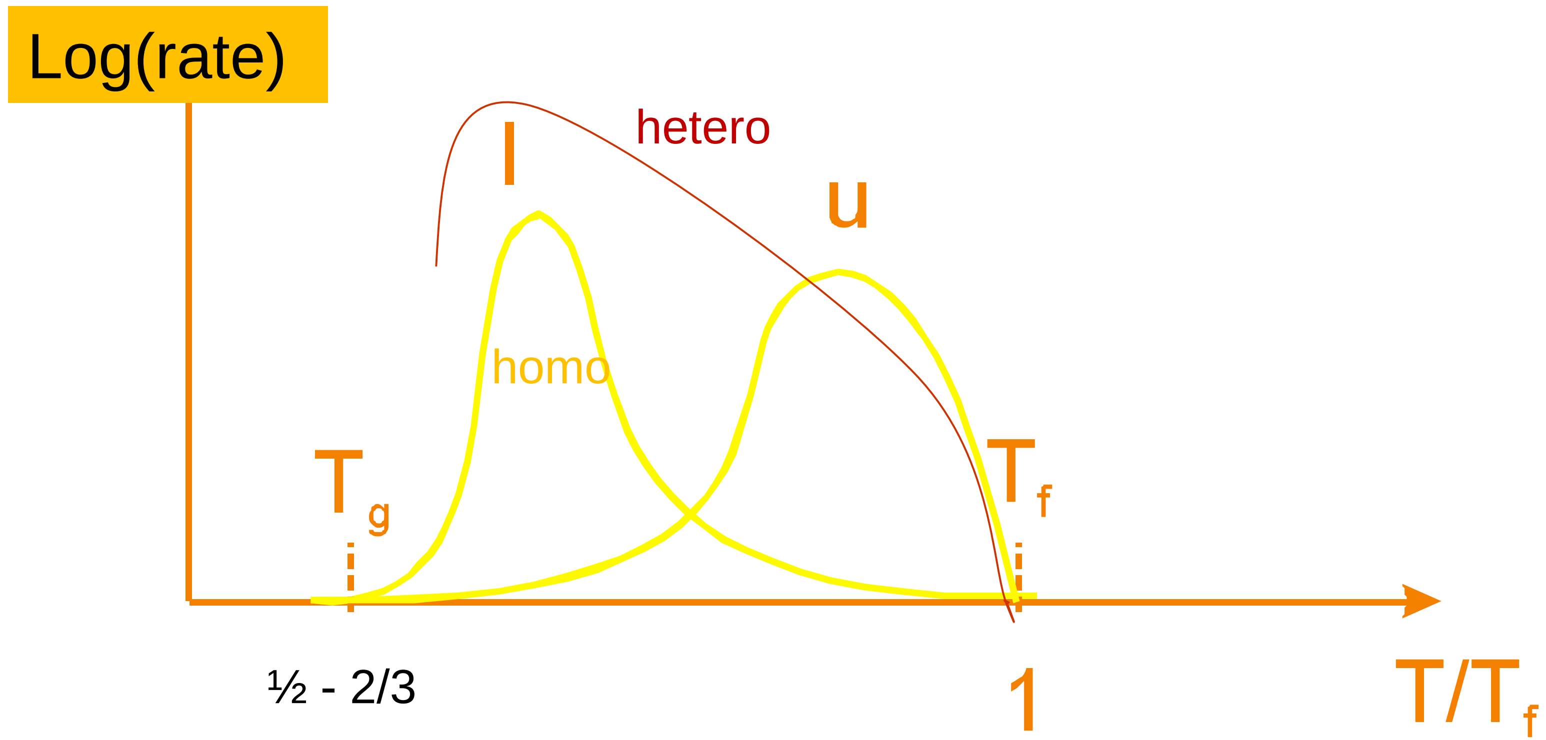
Vlad Fokin

Ralf Mueller



Overall crystallization, JMAK

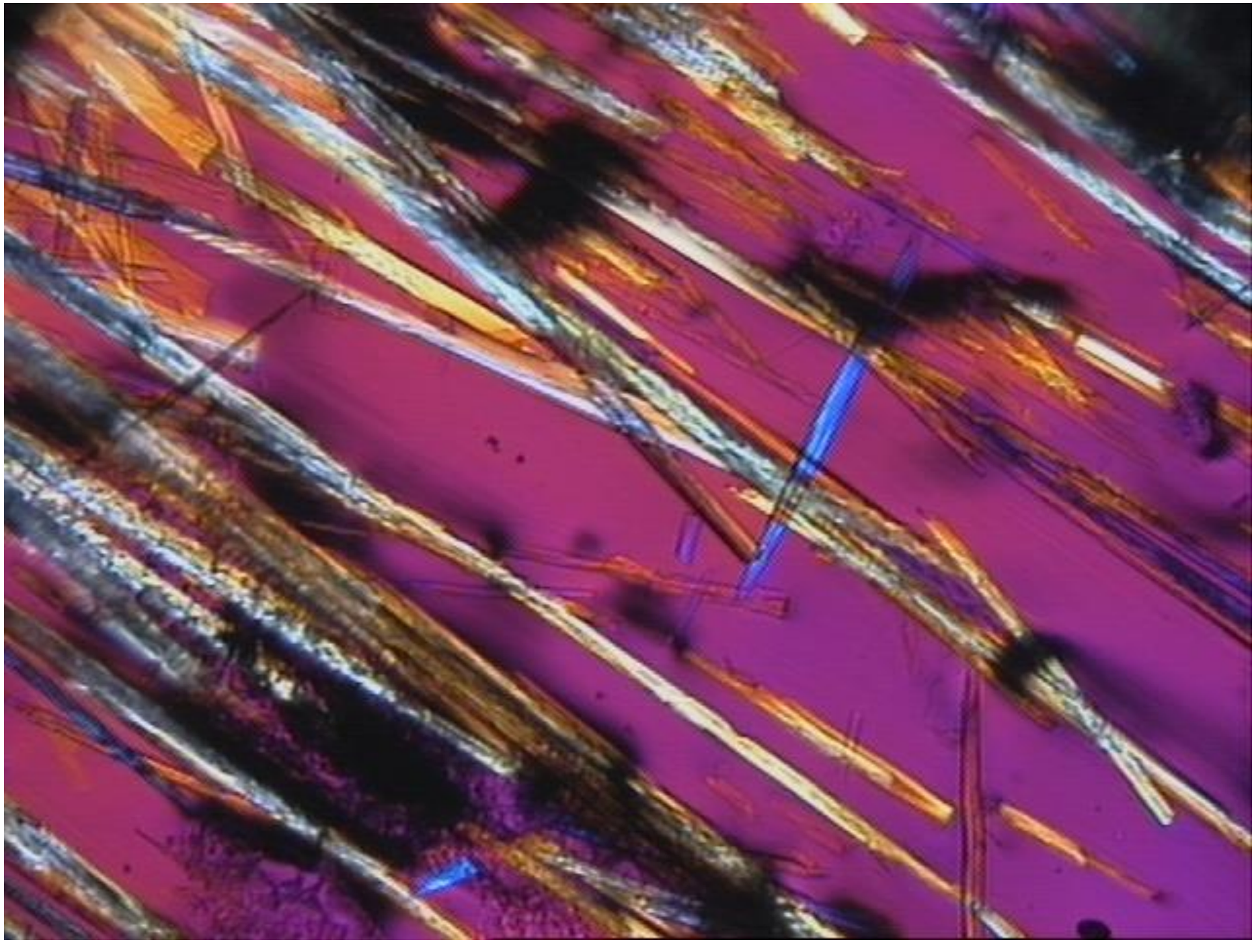
$$X_V = 1 - \exp(\frac{4}{3}\pi I u^3 t^4)$$



From E.B. Ferreira

Surface nucleation and sintering

Surface nucleation

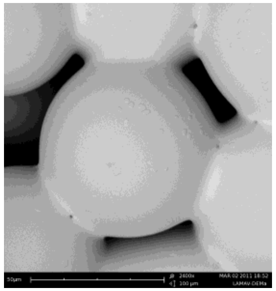


<u>Unwanted</u>

Spontaneous devitrification of Wollastonite needles in a window glass

Photo by Du Ferreira (2003) LaMaV

Production by sintering



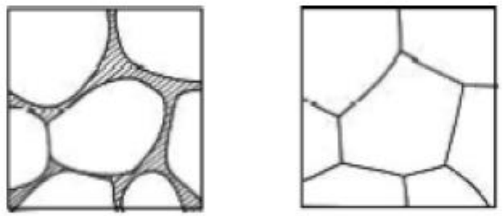
- Glass-ceramics may also be produced by concurrent sinter-crystallization of glass particle compacts.

- Crystallization starts at glass particles interfaces and thus nucleating agents are <u>not</u> necessary,
- but 0.5-3.0% residual porosity often remains.

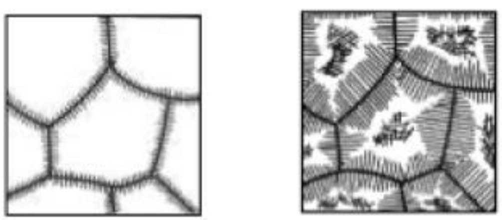
- The sintering route is attractive to produce CGs from reluctant glass-forming compositions, which could be made as a “frit”, molded and sinter-crystallized.

- Commercial applications :
  - marble-like floor and wall tiles (Neopariés and similar)
  - devitrifying frit solder glasses for sealing TV tubes,
  - co-fired multilayer substrates for electronic packaging,
  - bio active glass-ceramic scaffolds

Sintering with concurrent crystallization



(1) Granules of CaO $-Al_2O_3-SiO_2$ glass. (2) Sintering (850°C).



(3) Nucleation at granule interface. (4) Crystallization of β-wollastonite (1150°C).

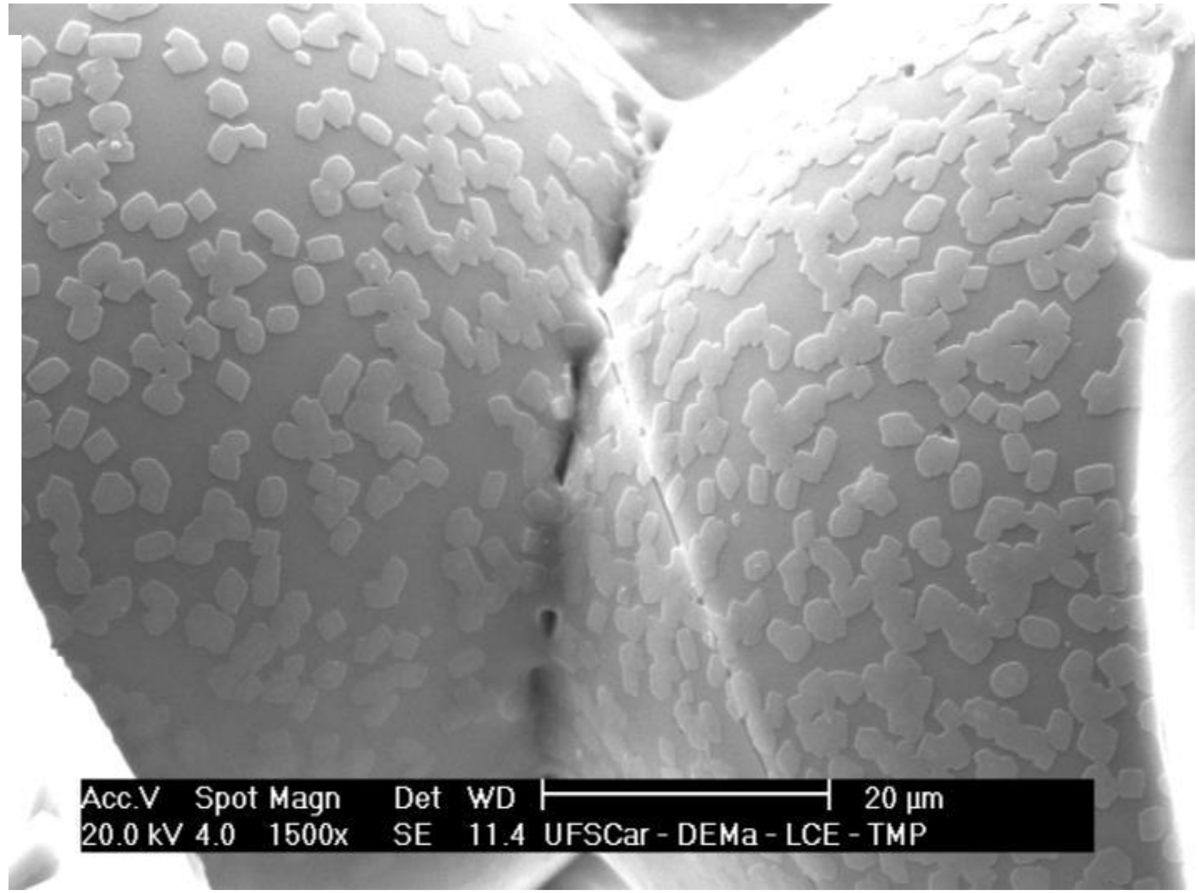


Photo by Vivi Oliveira and Rapha Reis (2009) LaMaV

Refs. on glass sintering with concurrent crystallization

- Model for sintering polydispersed glass particles MO Prado, ED Zanotto, R Müller - Journal of Non-Crystalline Solids 279 (2), 169-178 (2001)
- Isothermal sintering with concurrent crystallisation of monodispersed and polydispersed glass particles. Part 1 ED Zanotto, MO Prado

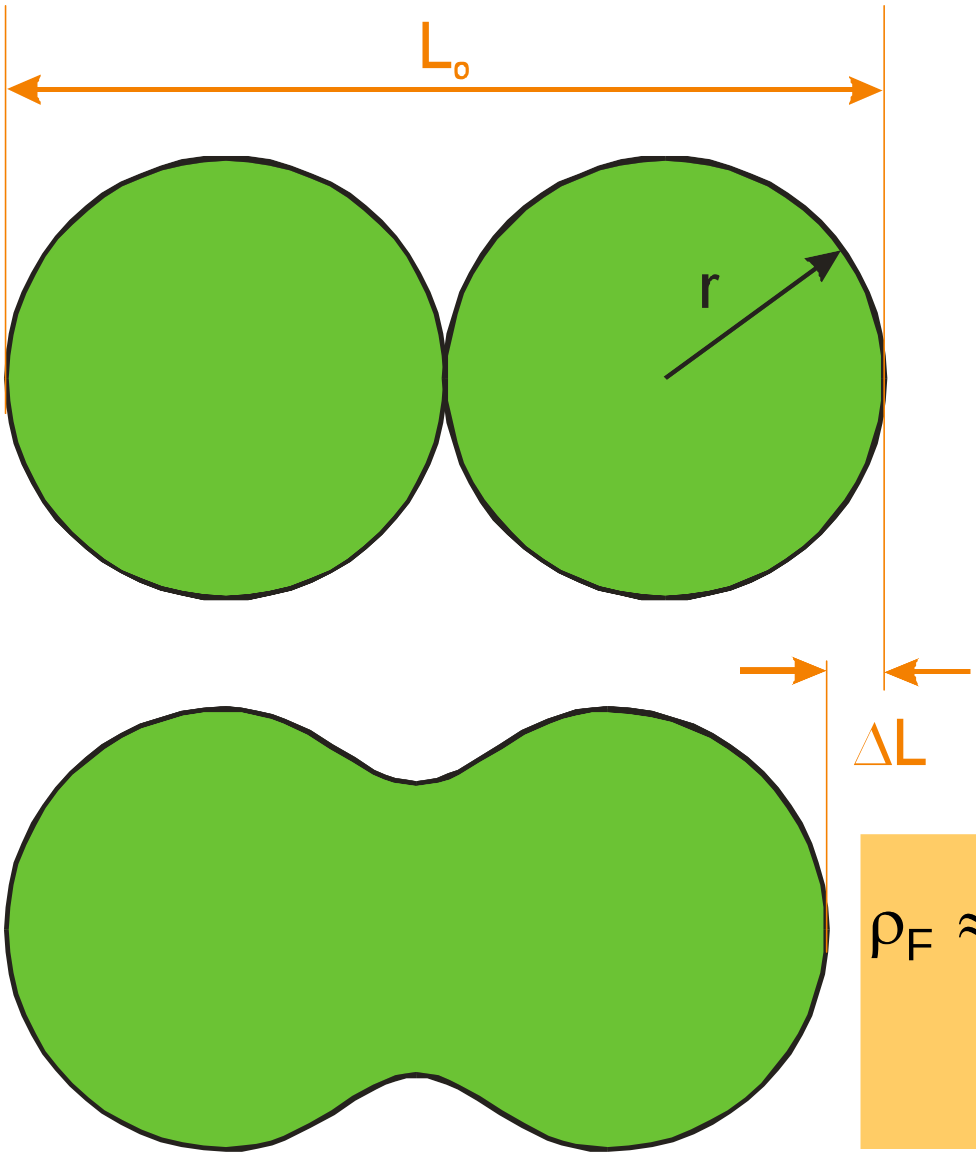
  Physics and Chemistry of Glasses-European Journal of Glass Science and ....(2001)
- Glass sintering with concurrent crystallization MO Prado, ED Zanotto

  Comptes Rendus Chimie 5 (11) 773-786 (2002)
- Non-isothermal sintering with concurrent crystallization of polydispersed soda–lime–silica glass beads MO Prado, C Fredericci, ED Zanotto

  Journal of non-crystalline solids 331 (1) 157-167 (2003)
- On the sinterability of crystallizing glass powders MO Prado, MLF Nascimento, ED Zanotto - Journal of Non-Crystalline Solids 354 (40) 4589-4597 (2008)

Sintering models

Early stages: Frenkel

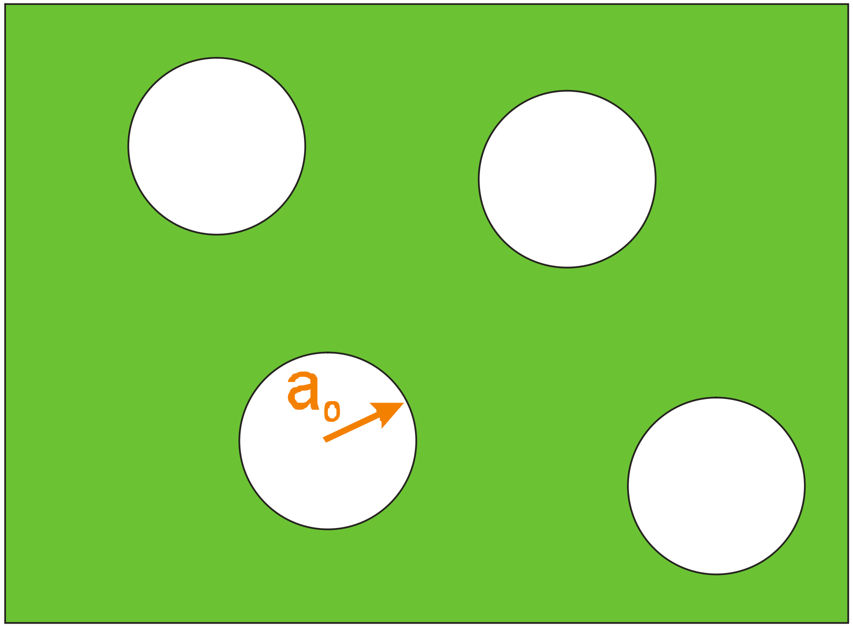


spherical particles
= sized
size does not change

$$\frac{\Delta L}{L_o} = \frac{3}{8}\frac{\gamma}{\eta(T).r}t$$

$$\rho_F \approx \frac{\rho_o}{\left(1-\frac{\Delta L}{L_o}\right)^3} = \frac{\rho_o}{\left(1-\frac{3\cdot\gamma\cdot t}{8\cdot\eta(T)\cdot r}\right)^3}$$

Final stage: Mackenzie-Shuttleworth



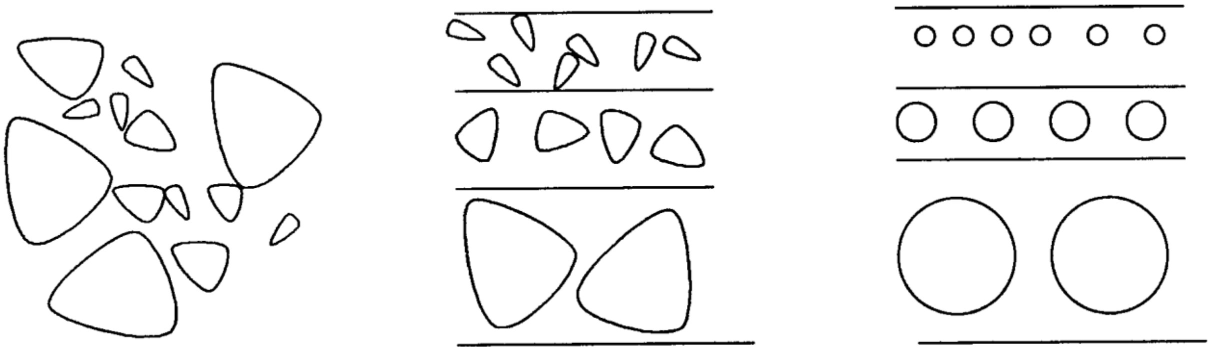
Isolated spherical pores
=size
size does not change

$$\frac{d\rho_{MS}}{dt} = \frac{3 \cdot \gamma}{2 \cdot a_o \cdot \eta(T)} \cdot (1 - \rho_{MS})$$

$$\rho_{MS} = 1 - (1 - \rho_o)\exp\left(-\frac{3\gamma t}{2 a_o \eta(T)}\right)$$

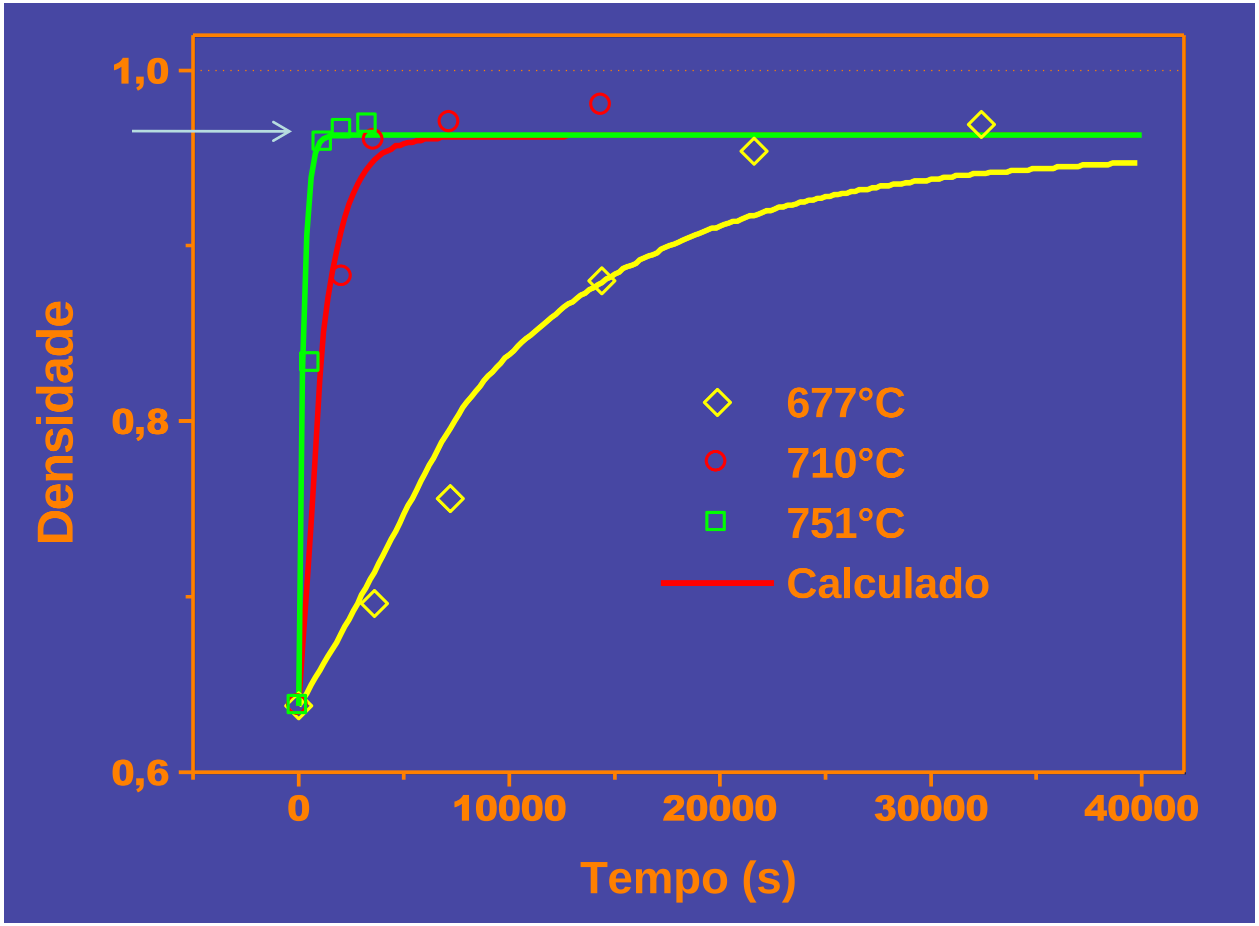
“Clusters” model - LaMaV

$$\rho(t,T) = \sum_r \left(\rho_F \cdot \theta(t_b - t) + \rho_{MS} \cdot \theta(t - t_b)\right).v_r$$



“*Clusters*” model - results

Soda-cal-silica glass spheres, <r> ~ 0.1 mm
Isothermal sintering



(Sintered) construction materials

- **A high-end use construction and architecture CG is Neopariés® (and similar materials) pioneered by Nippon Electric glass > 20 years ago. This CG is one of the few commercial products made by sintering, and its main crystal phase is wollastonite (calcium metasilicate).**

- **Neopariés® is a low porosity, partially crystallized material with a soft rich appearance similar to marble and granite, but with none of the maintenance problems of natural stone. It is an attractive material for both exterior and interior building walls, and table tops.**

- **Neopariés® comes in a variety of colors.**

- **It can be formed from flat into convex and concave surfaces increasing the design flexibility**

- **With growing concern in sustainability and exhausting reserves of natural stones, this is one field which deserves much attention.**

GC for architecture

GC for architecture

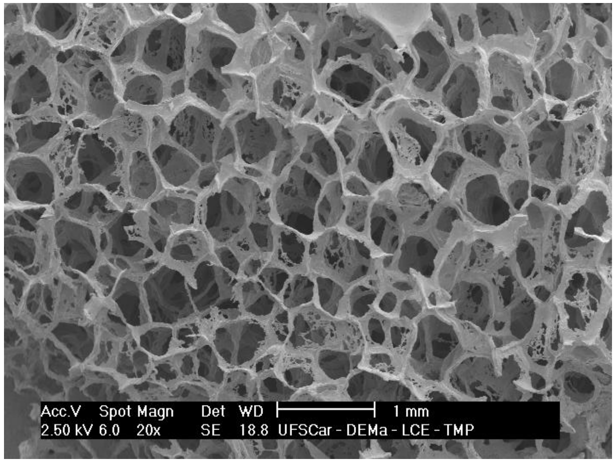
HEAD OFFICE BUILDING
DEMIRBANK ISTANBUL

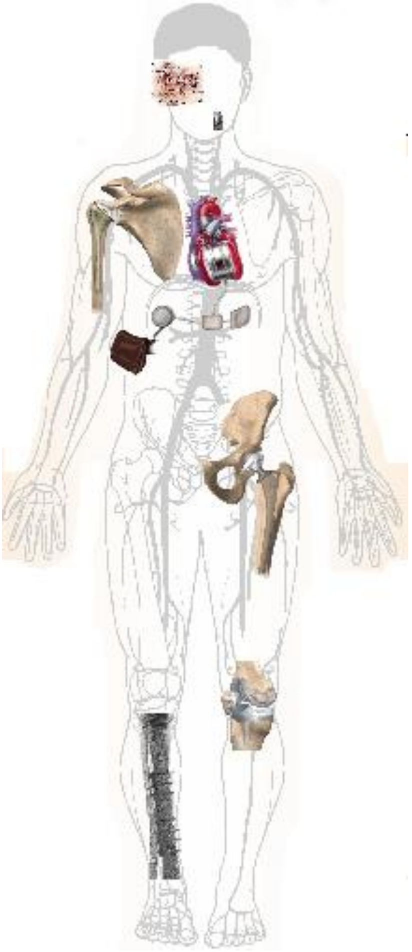
HYATT REGENCY OSAKA
Osaka

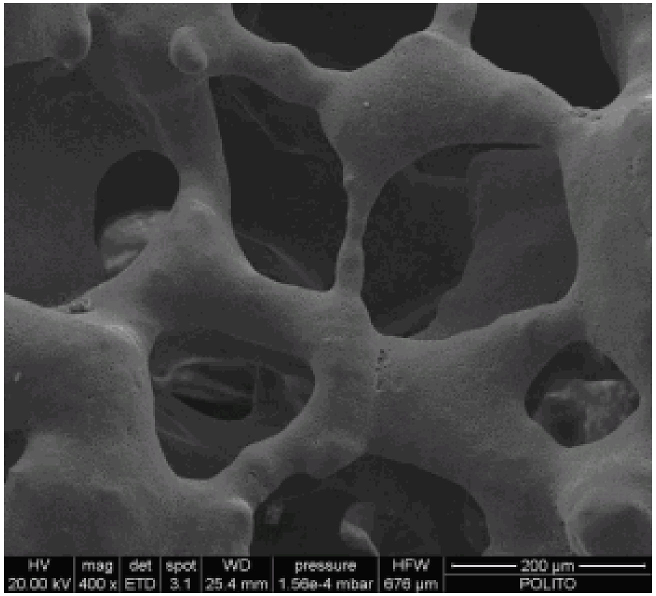
GC for architecture

JK Shopping Center, São Paulo, Brazil

Bioactive GC Scaffolds



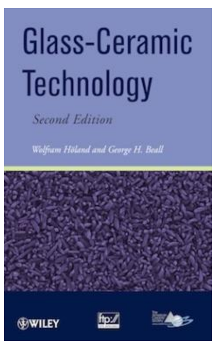


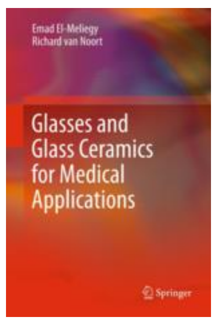


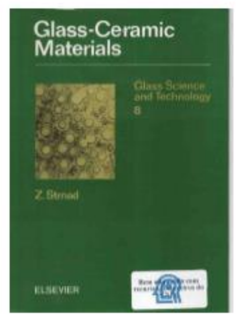
References

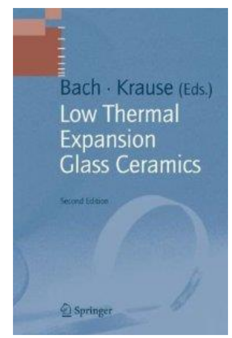
From glass to crystal: nucleation, growth and phase separation, from research to applications - D. Neuville et al. (2015)

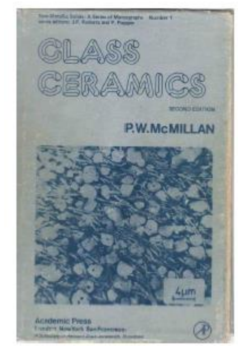
Nano-Glass Ceramics: Processing, Properties and Applications. Marghussian, V., 1st Edition, Elsevier, 2015.











+ review articles by:

Beall & Pinckney, Hoeland, Pannhorst, James, Davis, Zanotto, Dymshits…

Thanks, guys!