Glass Processing

Lecture # 21 Glass-ceramics: Nature, properties and processing

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Lectures available at:

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Federal University
of São Carlos

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

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

March 19, 2015
3- Glass-ceramics: definition, characteristics, history & applications

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 9
7- Review of item 5
7ª - selcted examples of traditional and sintered GC
8- "New" processing techniques
Exotic GC types and applications
9- Open issues on GC
10- Concluding remmarks

Reading assignments

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

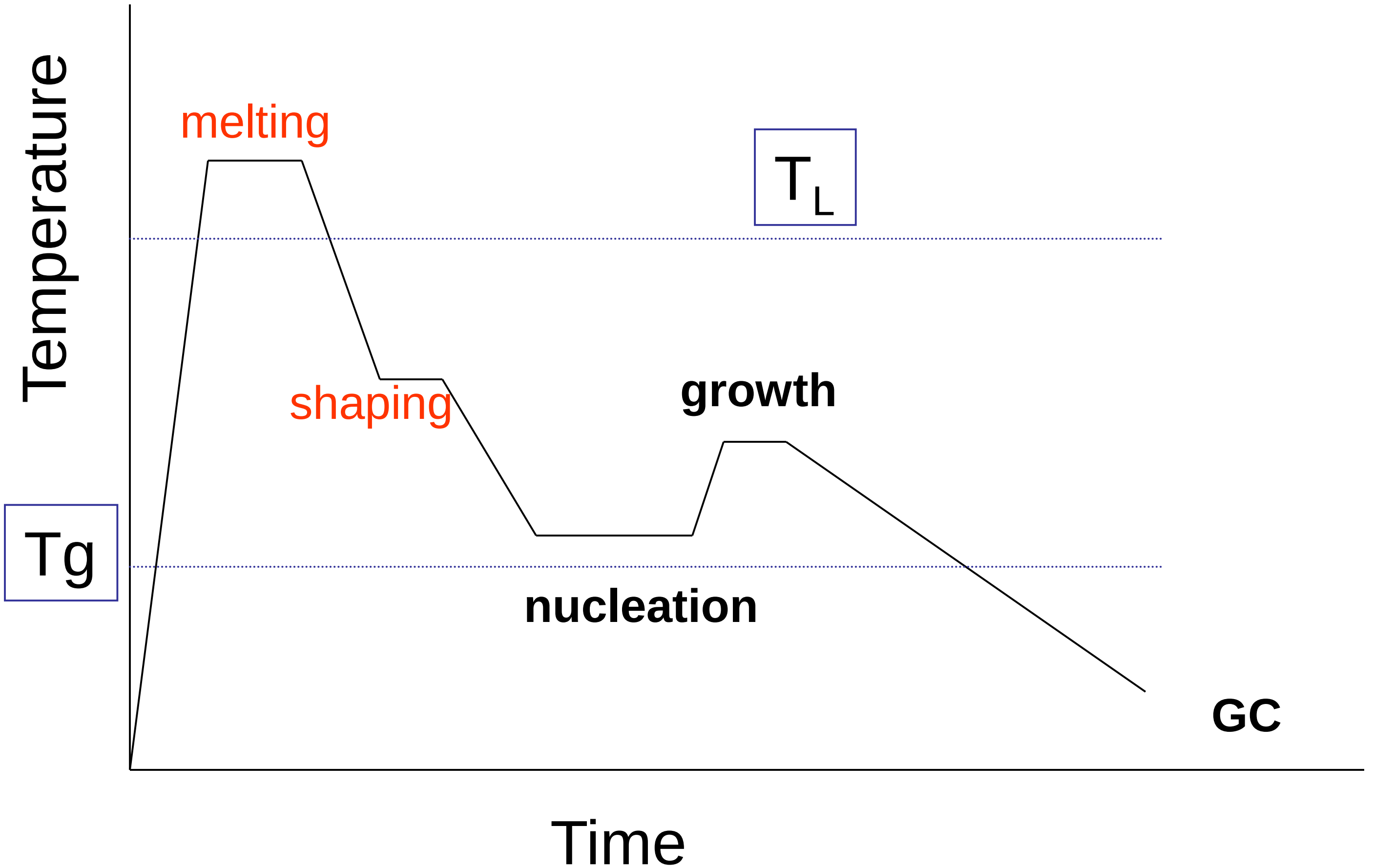
Traditional processing of GC

GC are normally produced in two steps:

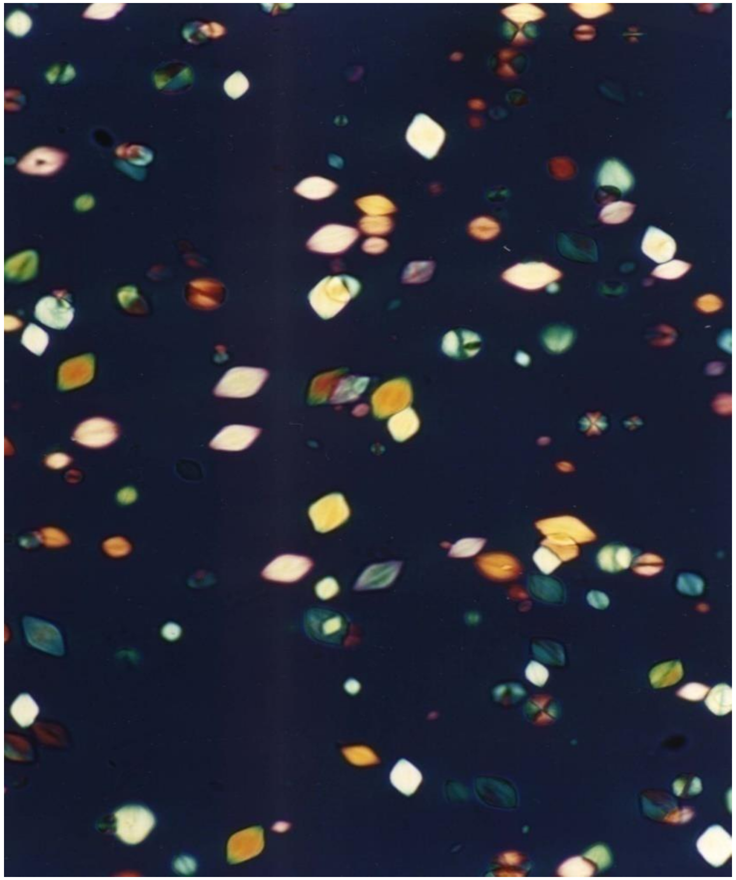
- i) a glass is made by a standard glass manufacturing process,
- ii) the glass article is shaped, cooled down and then reheated somewhat above its glass transition temperature in a second and even a third step.

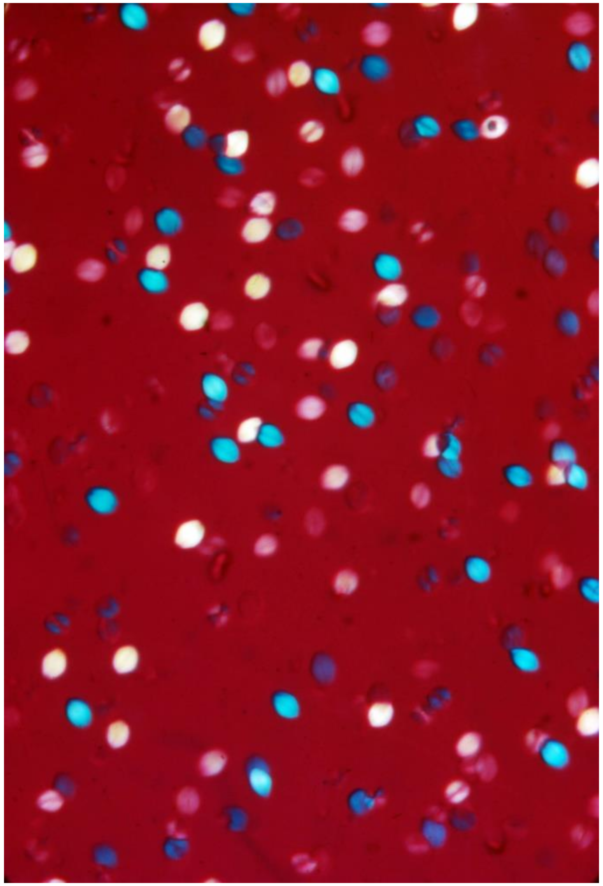
In most cases, nucleating agents such as noble metals, fluorides, ZrO_2, TiO_2, P_2O_5, Cr_2O_3 or Fe_2O_3 are added.

Traditional processing steps



Internal nucleation



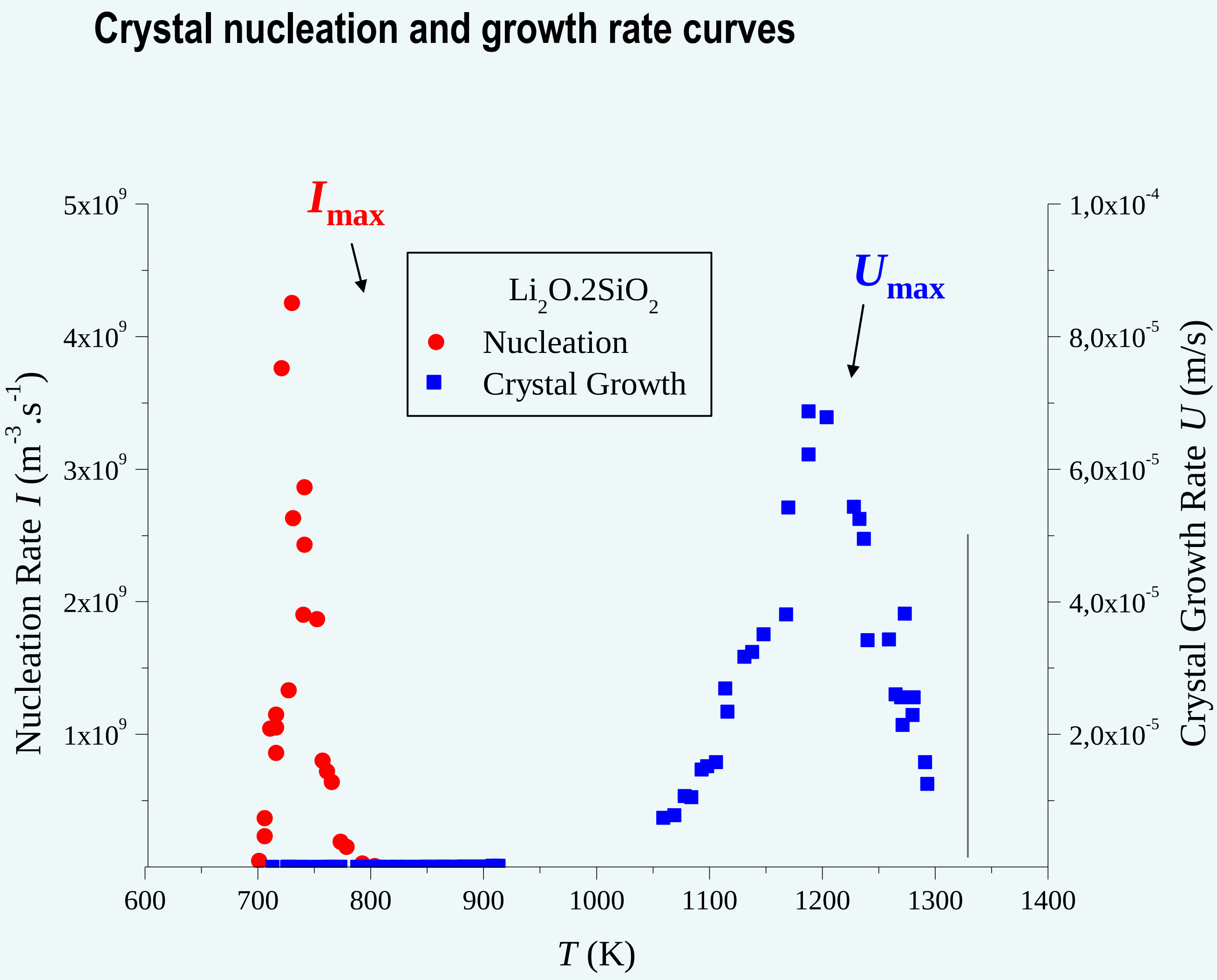


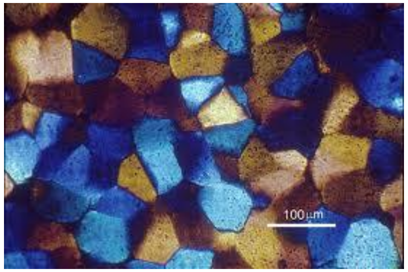
Lithium disilicate:
the "*Drosophila*"
of glass
crystallization
studies

Photos by Vlad Fokin
and Ed Zanotto

Solid knowledge about crystallization is key!

Homogeneous nucleation



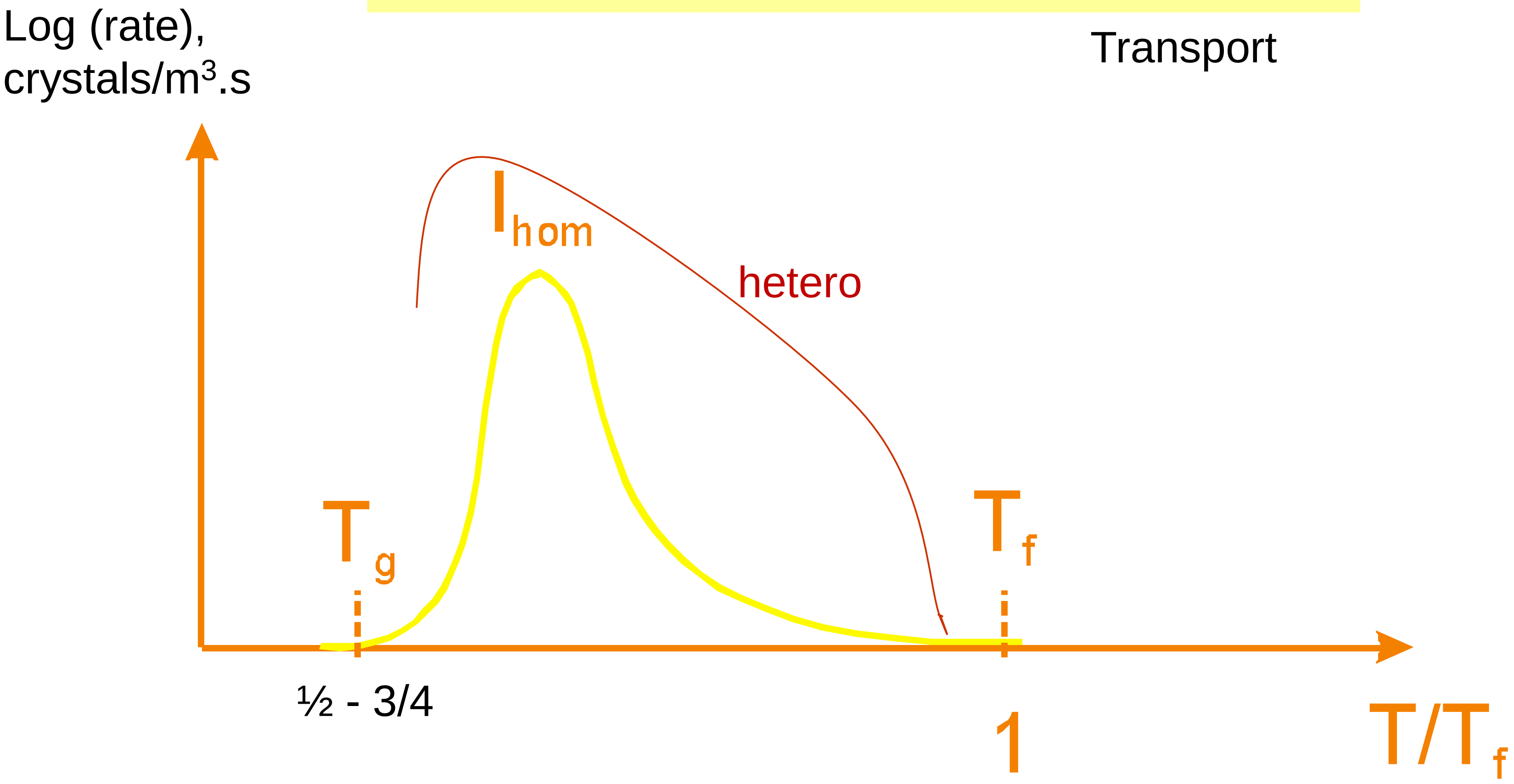


Zanotto

Thermodynamic

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

Transport



Tests of CNT for oxide glasses

Profª Drª Sati Manrich, UFSCar-DEMa.

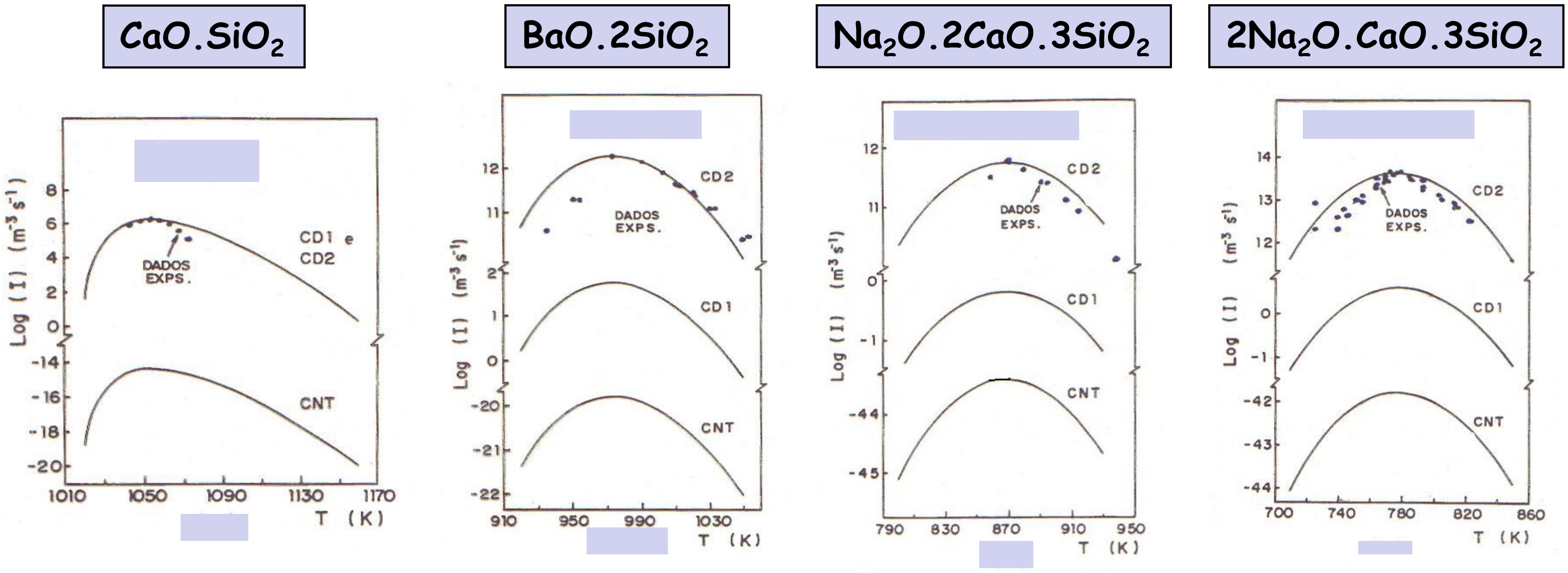


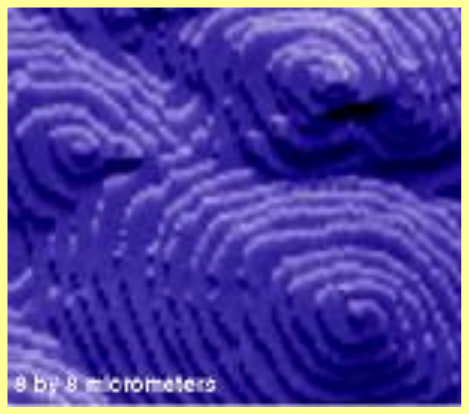
Figure 9b: Calculated nucleation rates by CNT, and modifications with one (CD1) and two (CD2) adjustable parameters.

Manrich & Zanotto, *Cerâmica* (1995)

Crystal Growth in GF liquids

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

Screw dislocation mediated growth



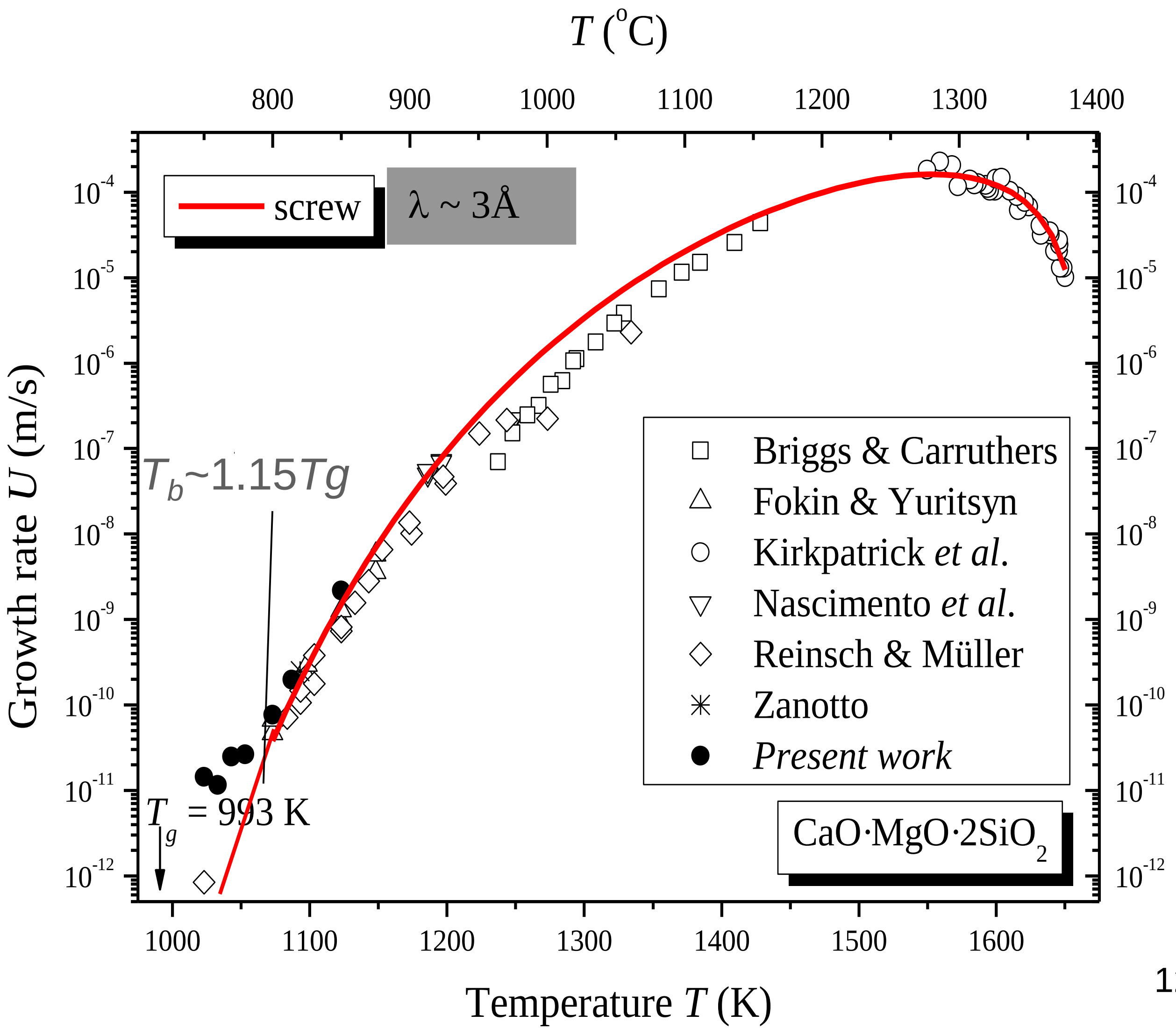
$$f = \frac{\lambda \Delta G}{4\pi\sigma V_M}$$

Crystal Growth Rates

Daniel Cassar

Vlad Fokin

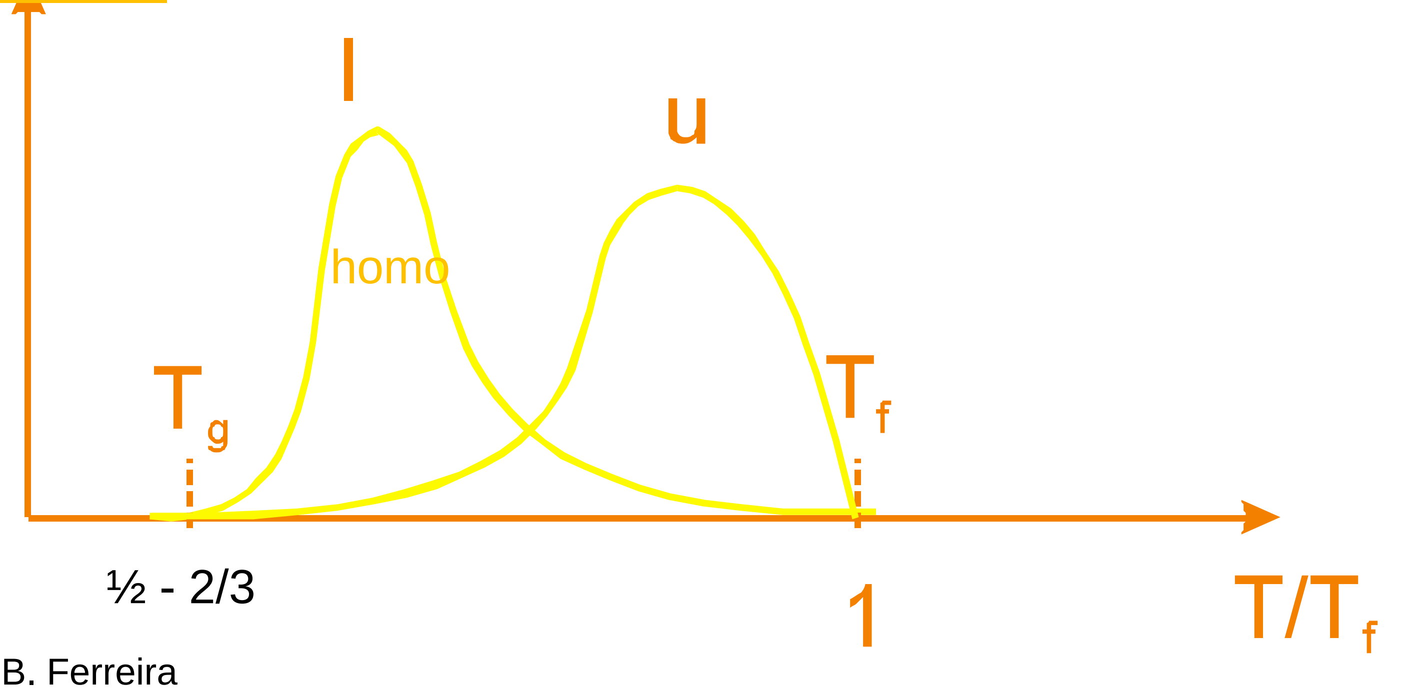
Ralf Mueller



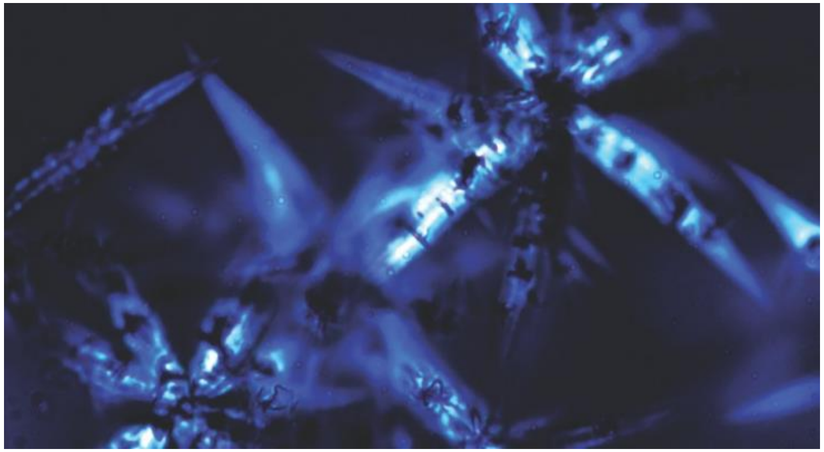
Overall crystallization, JMAK

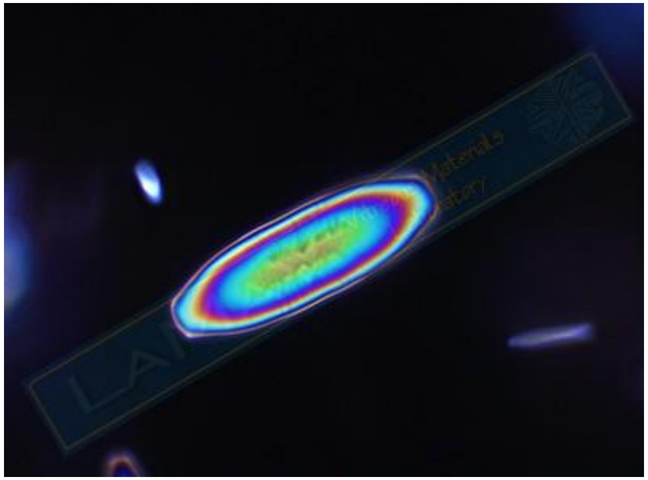
$$X_v = 1 - \exp\left(\frac{4}{3}\pi I u^3 t^4\right)$$

Log(rate)

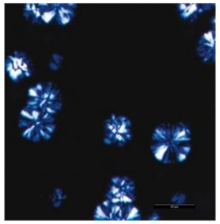


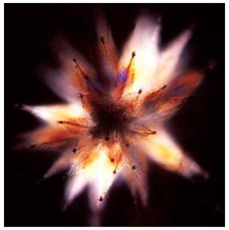
From E.B. Ferreira

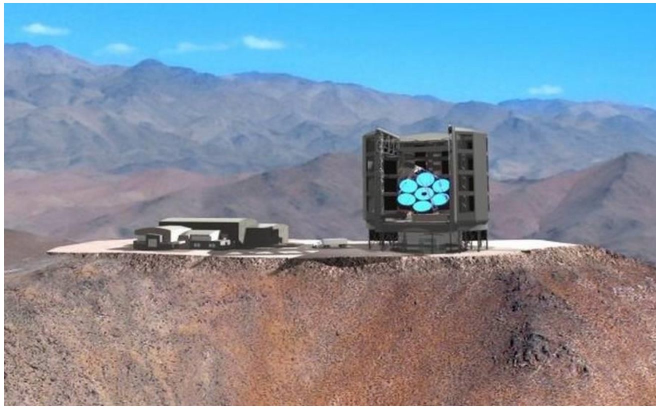




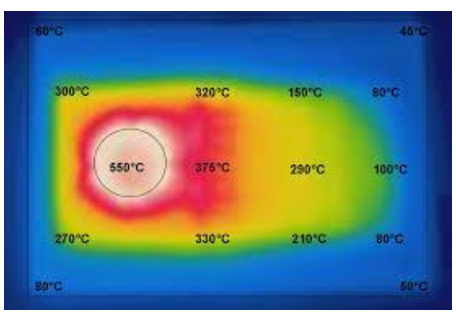
Designed micro and nanostrucures lead to GC







Glass Ceramics



<rms> 1nm

Zanotto

One selected example
Bioactive GC

Bioactive glass-ceramics

- **Starting in the 80s with the pioneer work of Larry Hench, Werner Vogel and Tadashi Kokubo. Several compositions developed for bone repair are osteoinductive and/ or osteoconductive, having the ability to induce bone cell growth and healing following implantation**

- **Bioactive CGs form *in-situ* a biologically active layer of hydroxicarbonate apatite that bonds to bone and teeth, and sometimes even to soft tissue.**

- **In addition, load-bearing applications require excellent mechanical properties. Some products reached commercial success, for instance Cerabone® A-W (apatite–wollastonite), Ceravital® (apatite-devitrite), Bioverit I® (mica-apatite) and II (mica) and Ilmaplant® L1 and AP40 have been used as granular fillers, artificial vertebrae, scaffolds, iliac spacers, spinous spacers, inter vertebral spacers, middle-ear implants and in other types of small bone replacements.**

Bioactive GC

- Cerabone® - developed by Tadashi Kokubo and produced by Nippon Electric glass Co. Ltd. - is probably the most widely used bio-CG for bone replacement. Numerous clinical trials have shown intergrowth between this GG and human bone. Tadashi mentioned to us in 2009 that about 60,000 successful implants had already been made with Cerabone®.

- Bioverit® are machineable GCs, which is very useful because they can easily be modified during the clinical procedures.

Bioactive glass-ceramics

- A different type of highly bioactive GC was developed by Peitl and colleagues in 1995. This is a low density CG in the Na-Ca-Si-P-O system with lower Young's modulus (closer to that of cortical bone) and much higher bioactivity than the previous bio-CGs.

- This particular combination of properties is desired for a number of applications. This CG is about 30-50% crystalline and its main phase is $Na_2O.2CaO.3SiO_2$.

Peitl, O., Zanotto E.D.; Hench L. L. – *"Highly bioactive P2O5-Na2O-CaO-SiO2 glass-ceramics"* – JNCS 292 (2001) 115-126

Relevant properties of some bioactive glass-ceramics

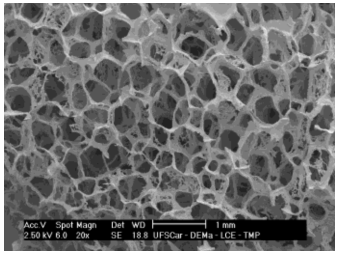
	Cerabone®	Bioverit I®	BioS
Bioactivity class	B1	B1	A2
Machinability	low	good	fair
Density (g/cc)	3.1	2.8	2.6
3pS$_f$ (MPa)	215	140-180	210
E (GPa)	120	70-90	70
Hard Vickers	680	500	600
K_{Ic} (MPa.m$^{1/2}$)	2.0	1.2-2.1	0.95
Slow crack growth	33	------	------

Highly bioactive GC - BioS

- About 10years ago a new glass-ceramic based on the same Na-Ca-Si-P-O system (Biosilicate®), but with some compositional modifications and >99% crystallinity was developed by Peitl, Zanotto and colleagues.

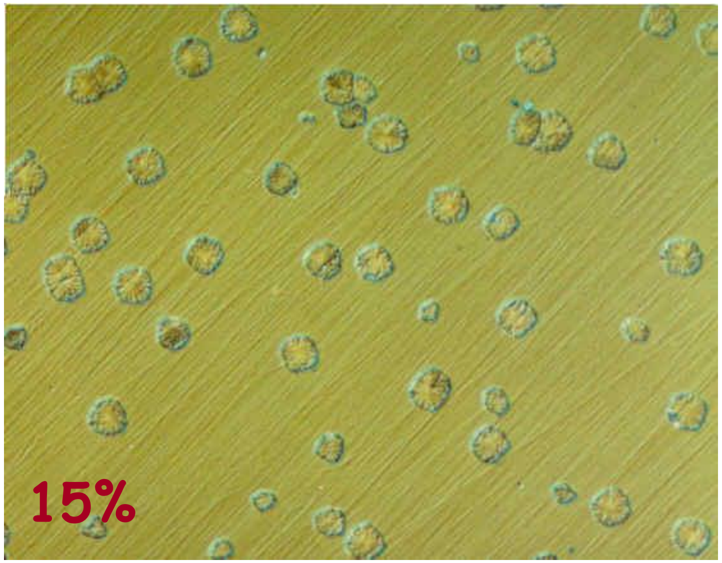
- This GC is as bioactive as the “golden standard” bioglass 45S5 invented by Larry Hench. Clinical tests of treatment with Biosilicate powder for dentin hypersensitivity in 16O sensitive teeth carried out by dentist Jessica Cavalle are shown in the next figure.

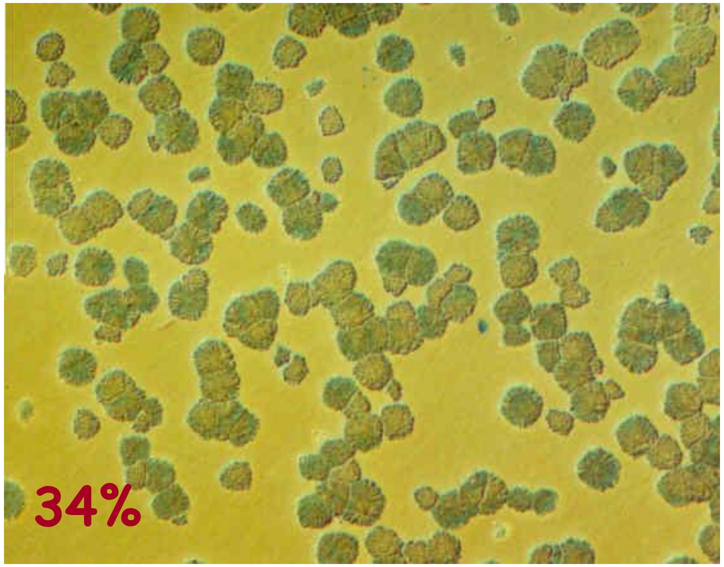
- This powdered glass-ceramic is also useful for making small sintered bones and bio active scaffolds,

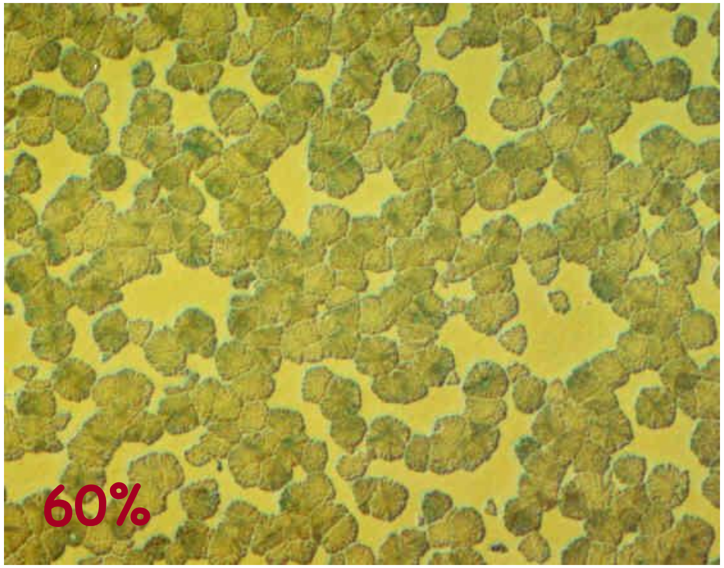


Controlled microstructure BioS/ 1.5N-5C-3S-1.7P

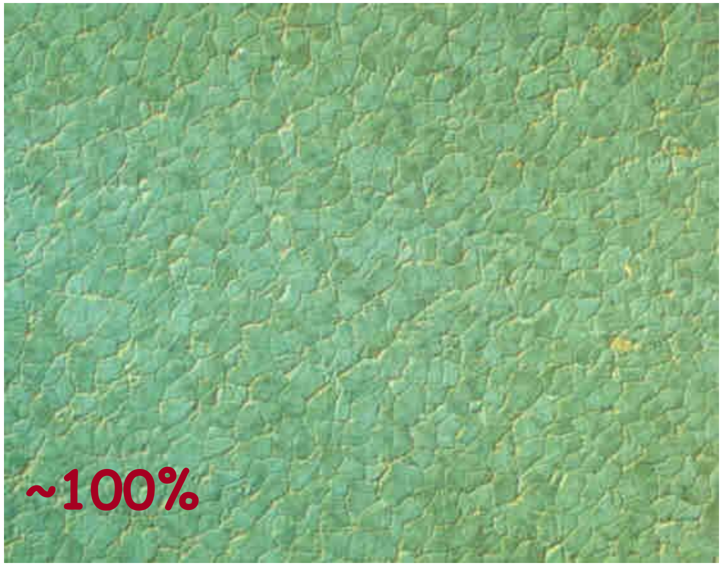
15%, 34%, 60% and ~99,5% crystallized



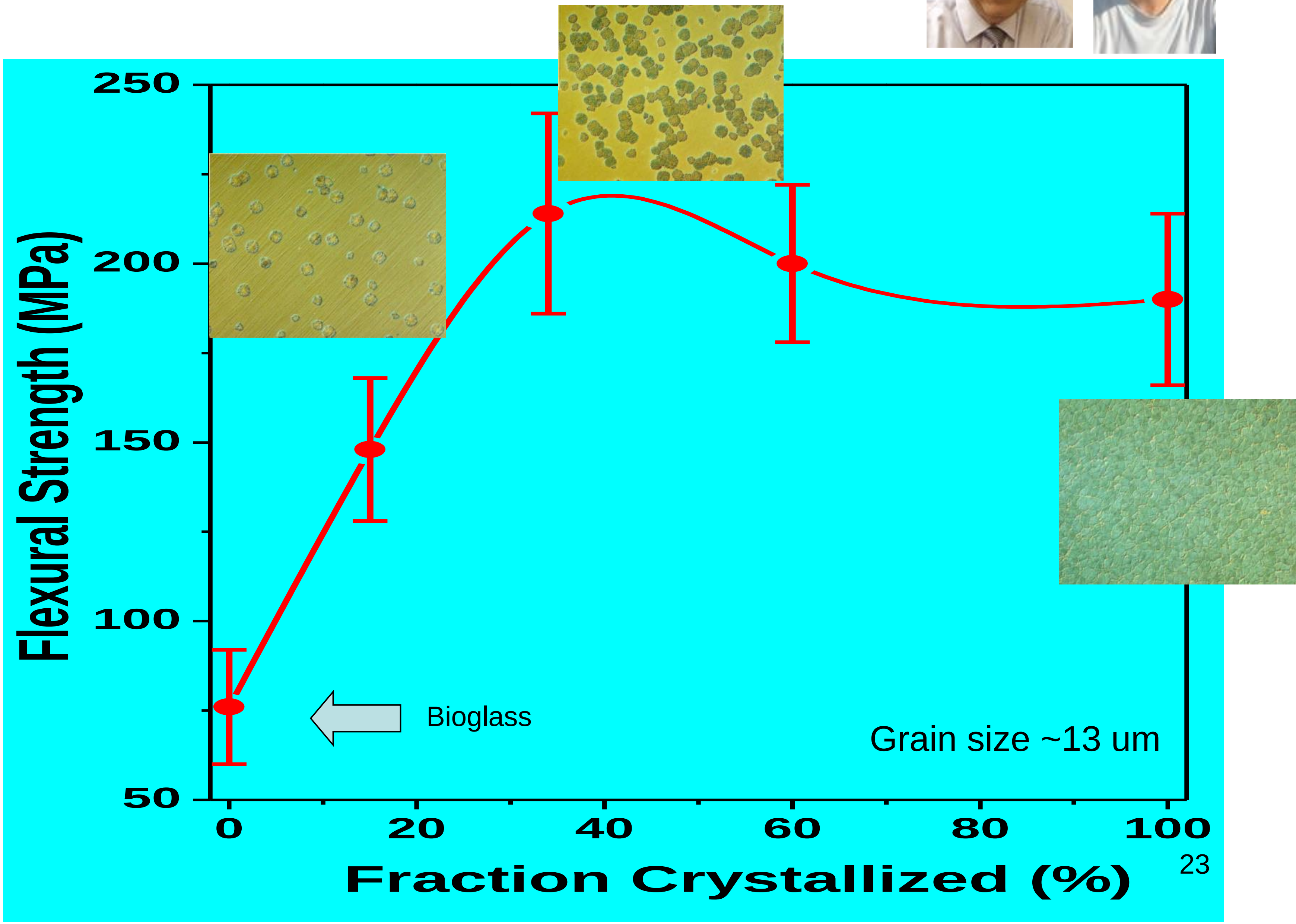




13um



4-point bending, average of 6 specimens.
Polished with CeO_2 - 1um



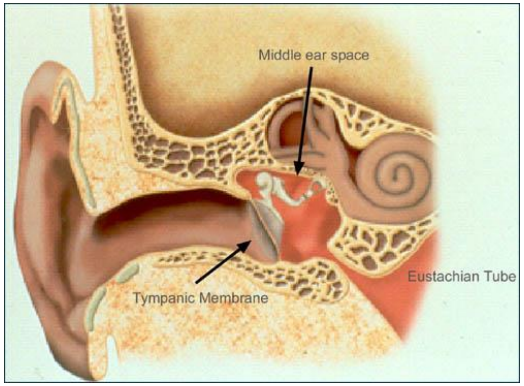
Clinical trials

Middle ear ossicular chain - Humans

The first clinical trials for middle ear bone replacements in 30 patients yielded very positive results:

- No extrusion
- Clinical test at USP-RP – Hydroxyapatite showed 70% extrusion

. Recovered 50 - 100% of the hearing ability



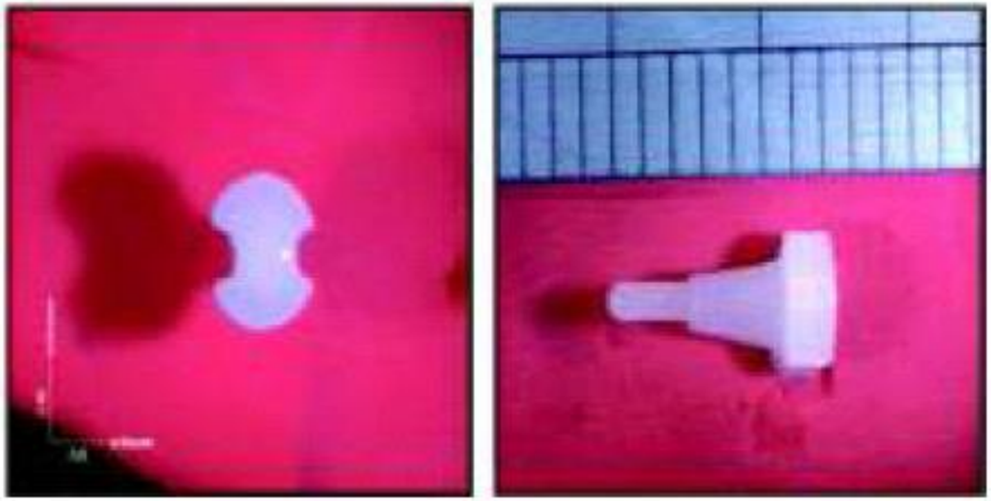
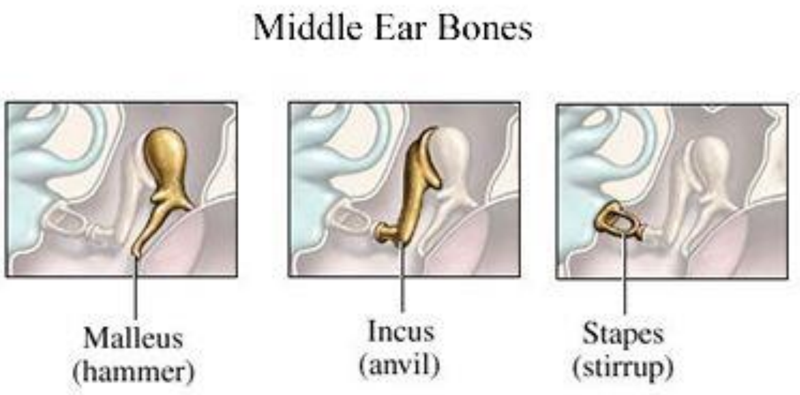
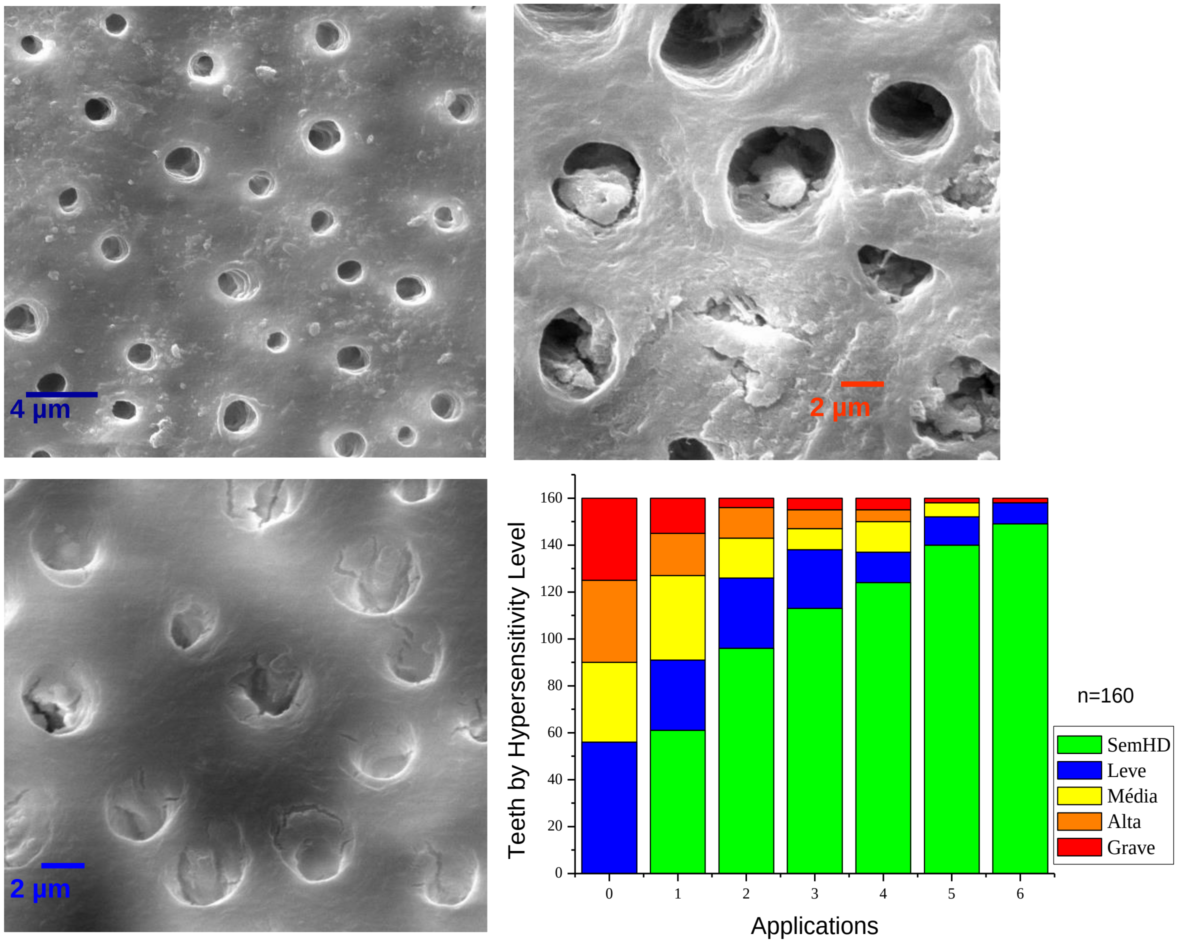


Figura 7. Prótese de Otossilicato desenvolvida e empregada na reconstituição da cadeia ossicular da orelha média de seres humanos. Adaptada da ref. 73



Biosilicate - Clinical trial results for dentin hypersensitivity



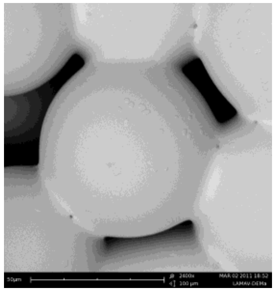
Dentine tubules before and after treatment.

No sensitivity- green
Light - blue
Medium- yellow
High - orange
Extreme – red

Courtesy of Jessica Cavalle

Surface nucleation and sintering

Production by sintering



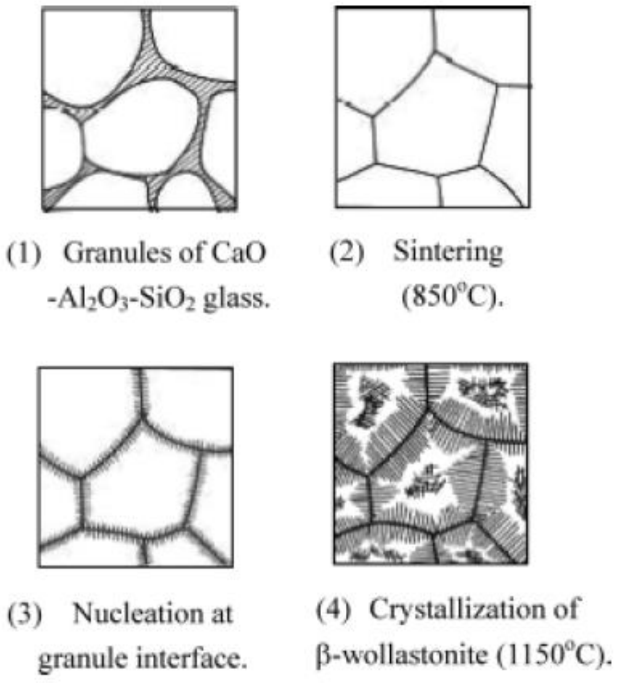
- Glass-ceramics may also be produced by concurrent sinter-crystallization of glass particle compacts.

- Crystallization starts at glass particles interfaces and thus nucleating agents are not 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



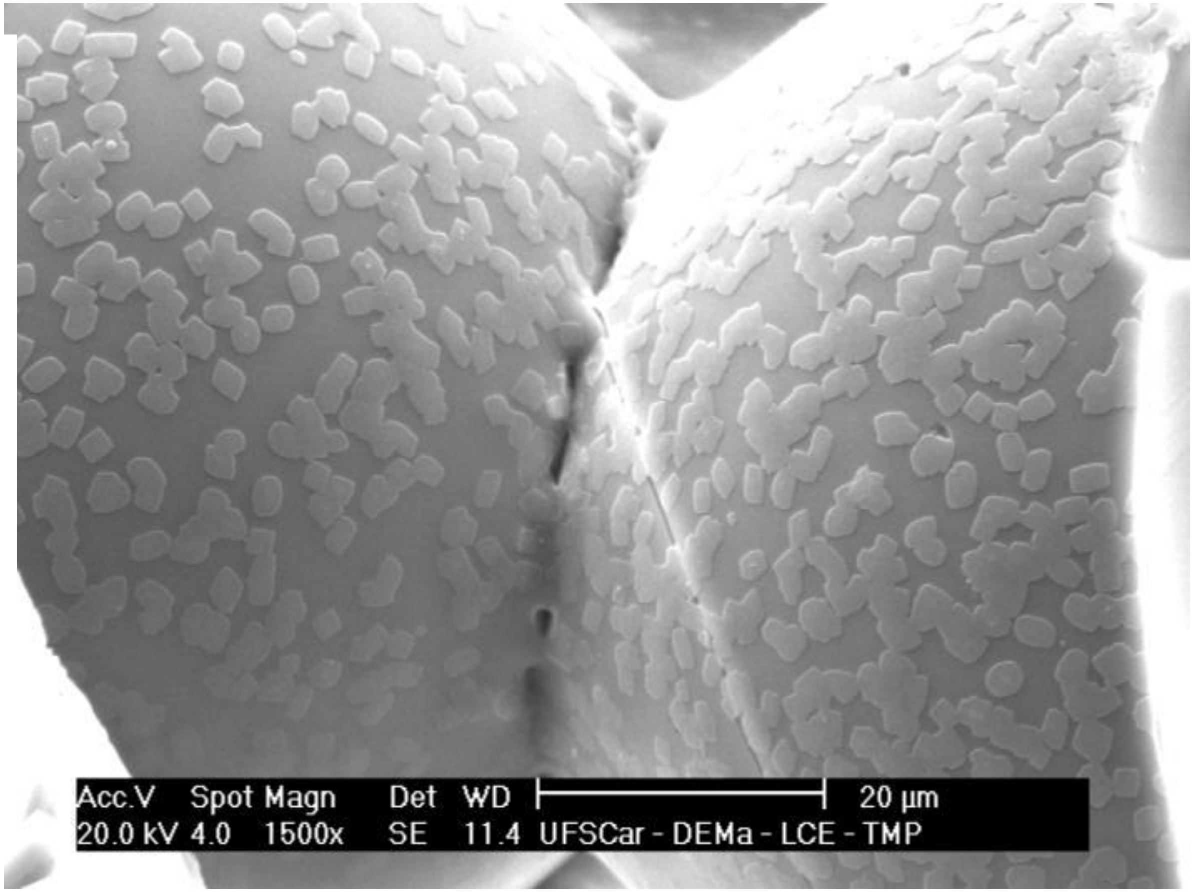


Photo by Vivi Oliveira and Rapha Reis (2009) LaMaV

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 Technology (2001)

- Glass sintering with concurrent crystallization MO Prado, ED Zanotto

  Comptes Rendus Chimie 5 (11) 773-786 (2002)

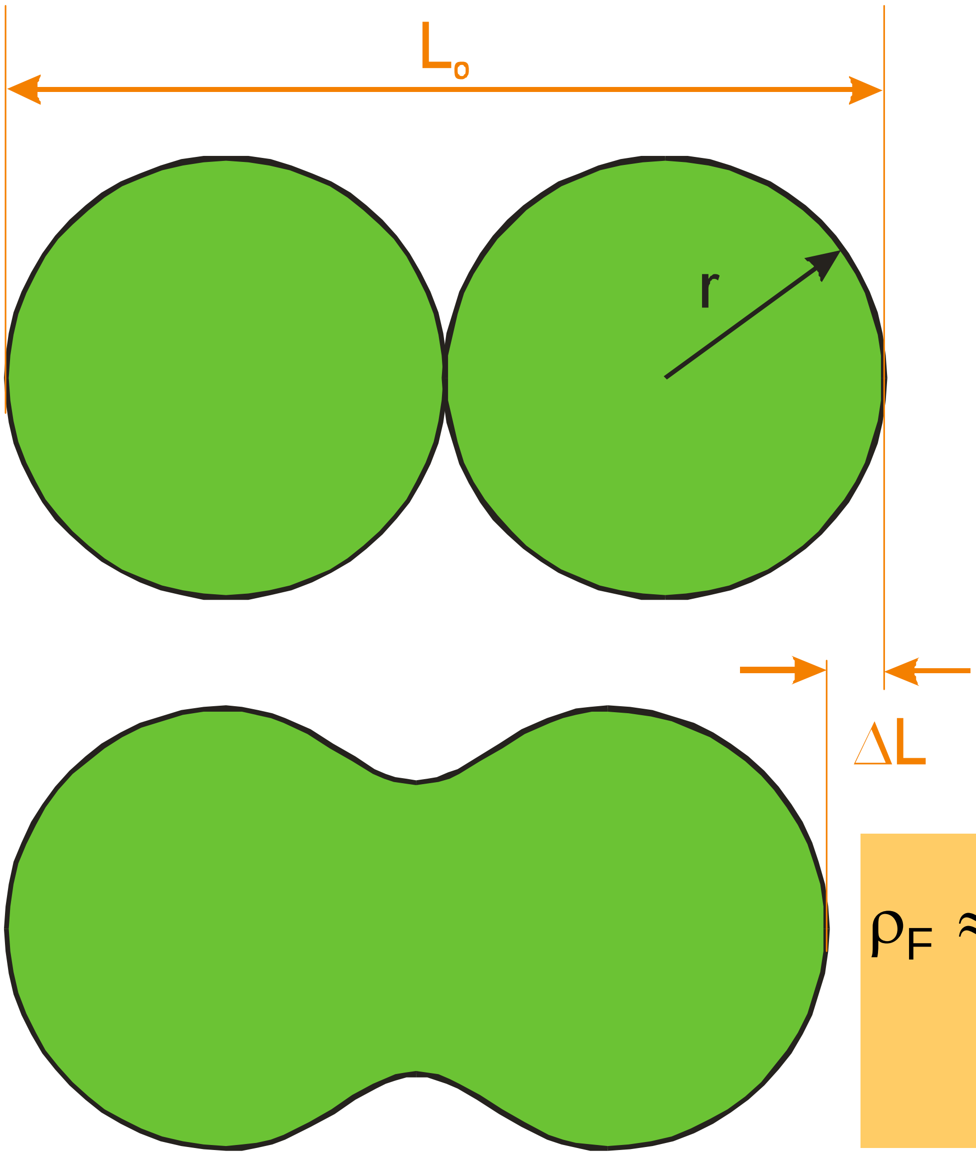
- Non-isothermal sintering with concurrent crystallization of polydispersed soda–lime–silica glass beads MO Prado, C Fredericci, ED Zanotto

  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

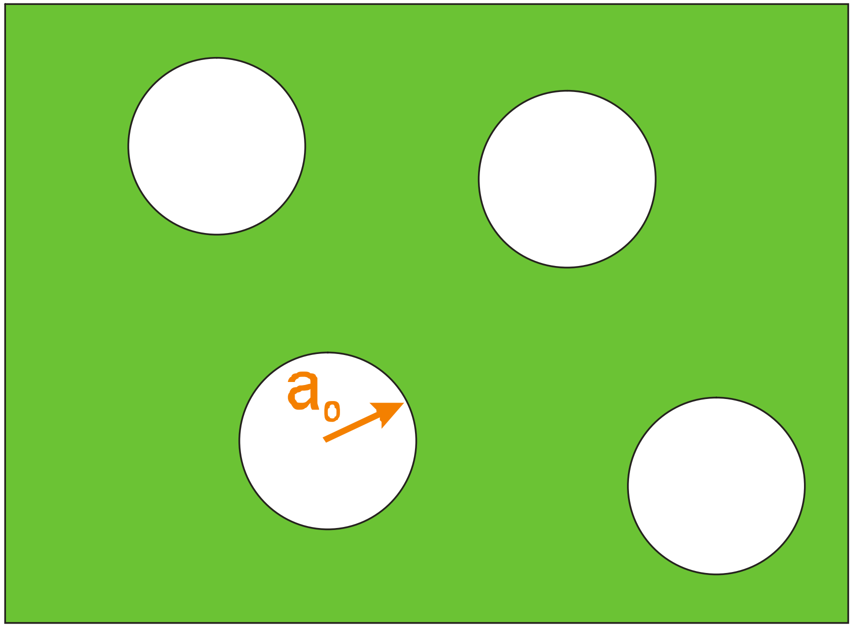


spherical particles
= sized
size does not change

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

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

Final stage: Mackenzie-Shuttleworth



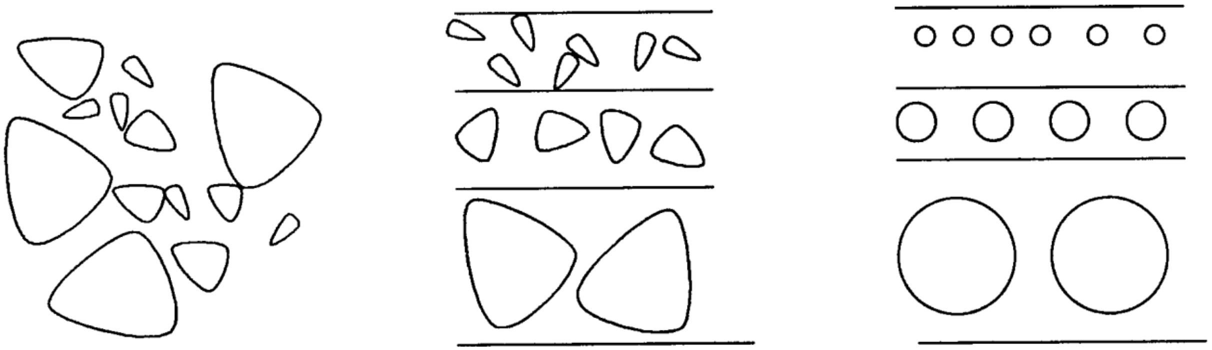
Isolated spherical pores
=size
size does not change

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

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

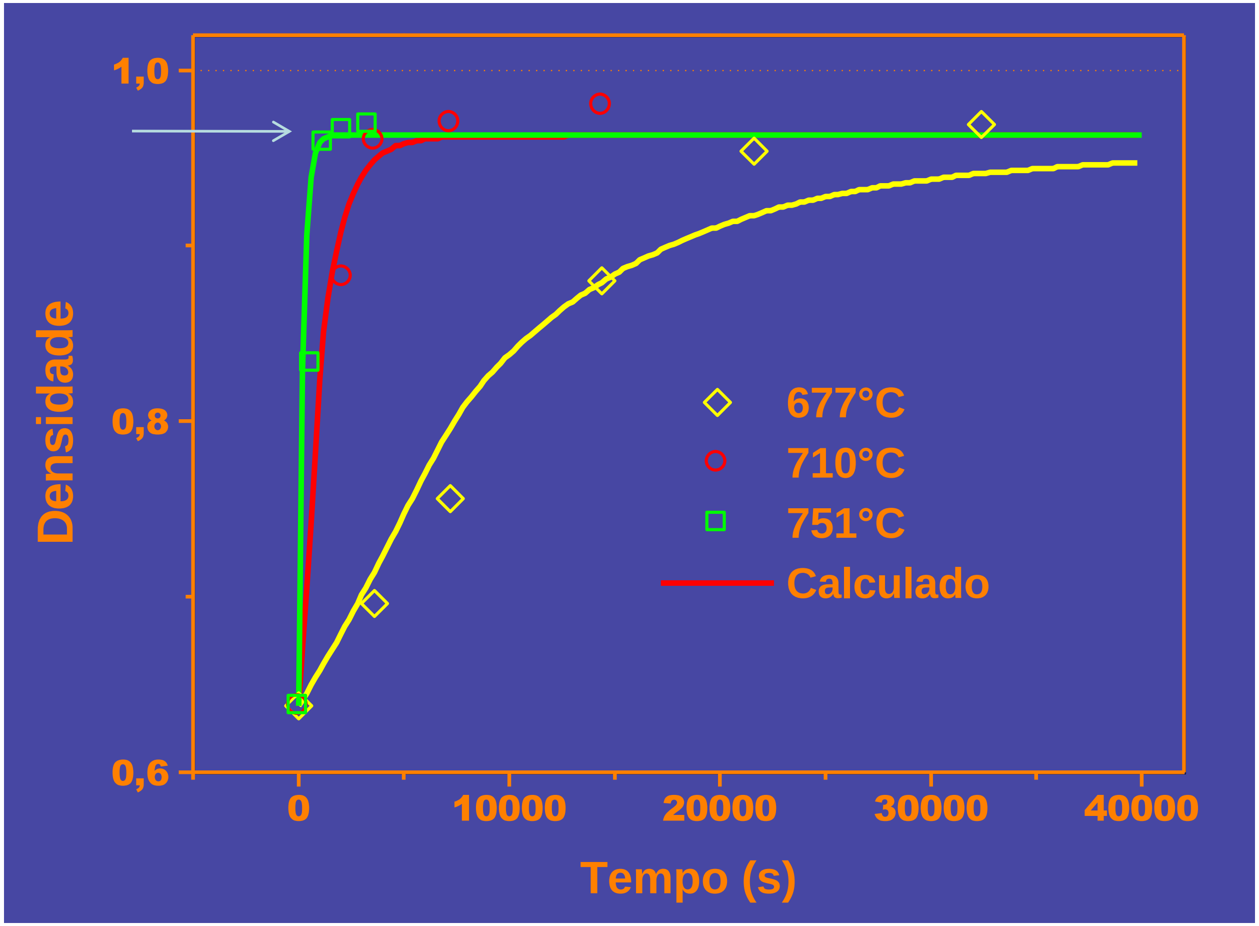
“Clusters” model - LaMaV

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



“*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

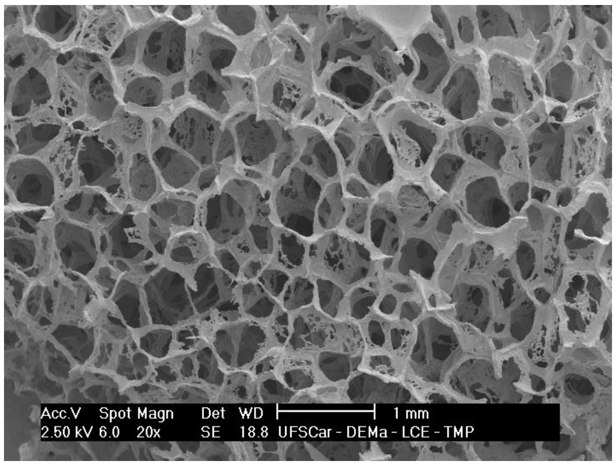
HEAD OFFICE BUILDING DEMIRBANK ISTANBUL

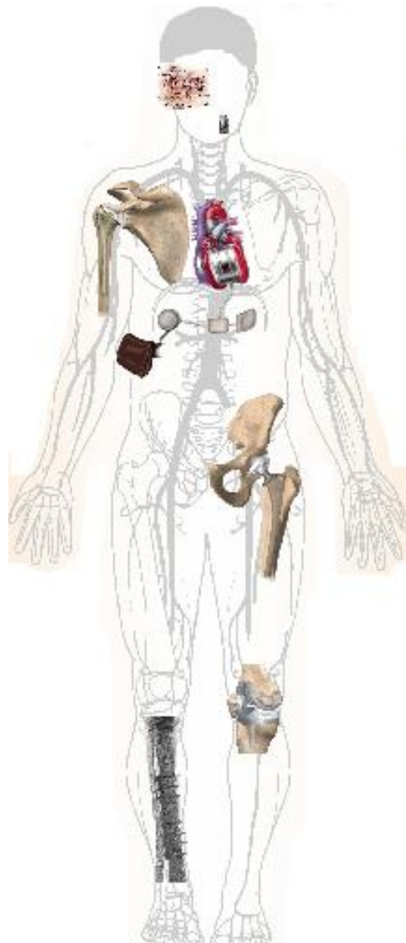
HYATT REGENCY OSAKA Osaka

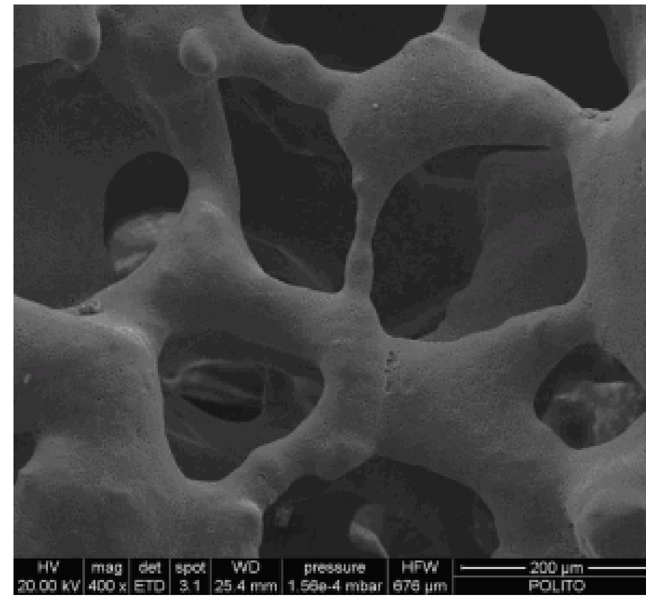
GC for architecture

JK Shopping Center, São Paulo, Brazil

Bioactive GC Scaffolds





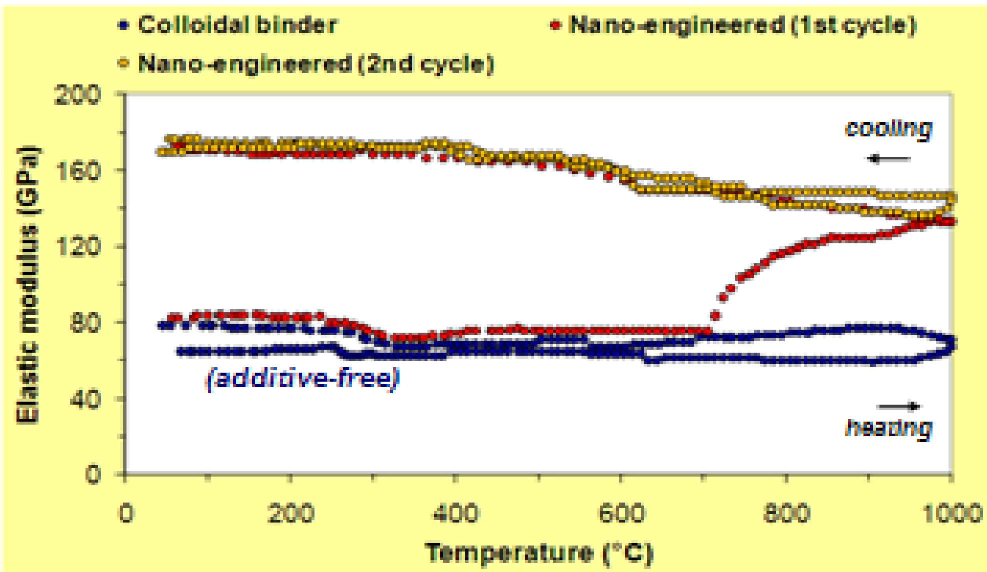


Cristallization of the residual glass phase in a refractory

High temperature elastic modulus

Summary of nano-structured castable's results at 1000°C		
HMOR (MPa)	Eroded volume (cm^3)	Initial MOE (GPa)
27.7	1.0	161.6

⇨ Efficient densification



No decrease after the second MOE x T cycle

⇩

Transient liquid formation

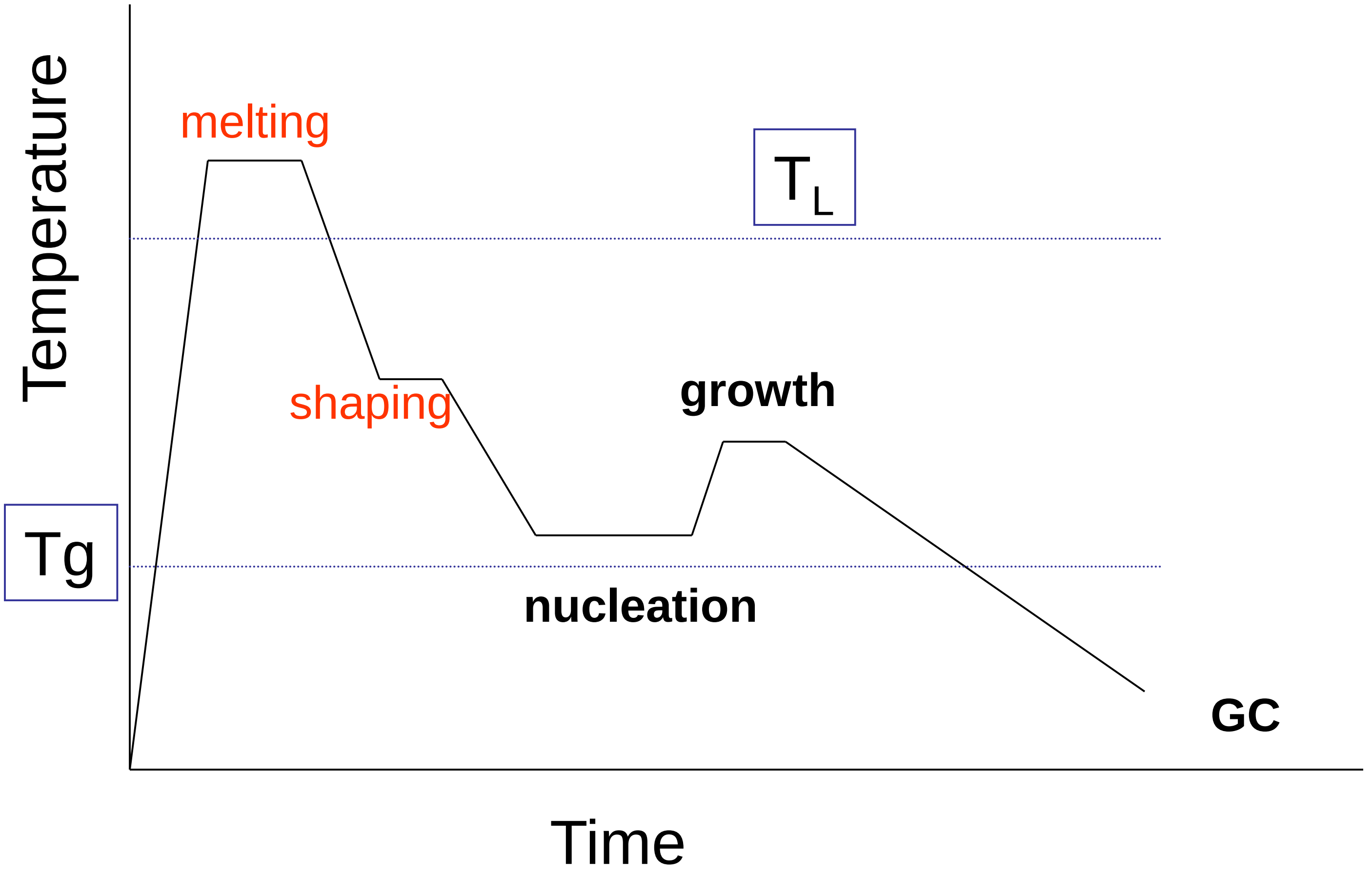
Research, Development and Innovation - Alcoa
Materials Microstructure Engineering Group - GEMM

GEMM

From V.C. Pandolfelli, UFSCar

Sophisticated processing techniques

Traditional processing steps



Laser crystallization

Nagaoka

Rare-earth (Samarium) atom heat processing

1. CW Nd:YAG laser irradiation to Sm_2O_3 or Dy_2O_3 containing glasses

2. Absorption and non-radiative relaxation

Irradiated region is heated → Crystallization

Writing of nonlinear optical/ferroelectric crystal dots and lines

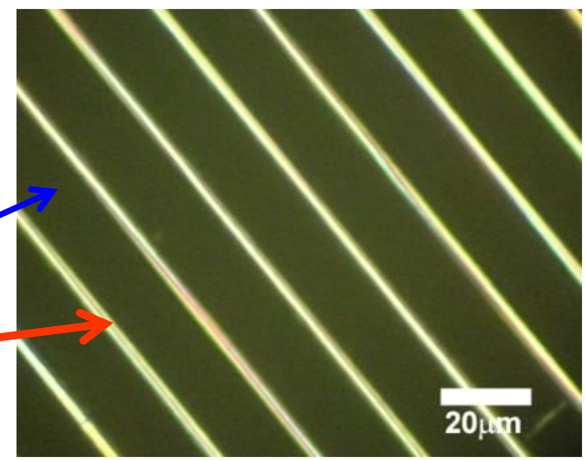
20,000 J/cm^2

Sm_2O_3-Bi_2O_3-B_2O_3 glass

$Sm_xBi_{1-x}BO_3$ crystal

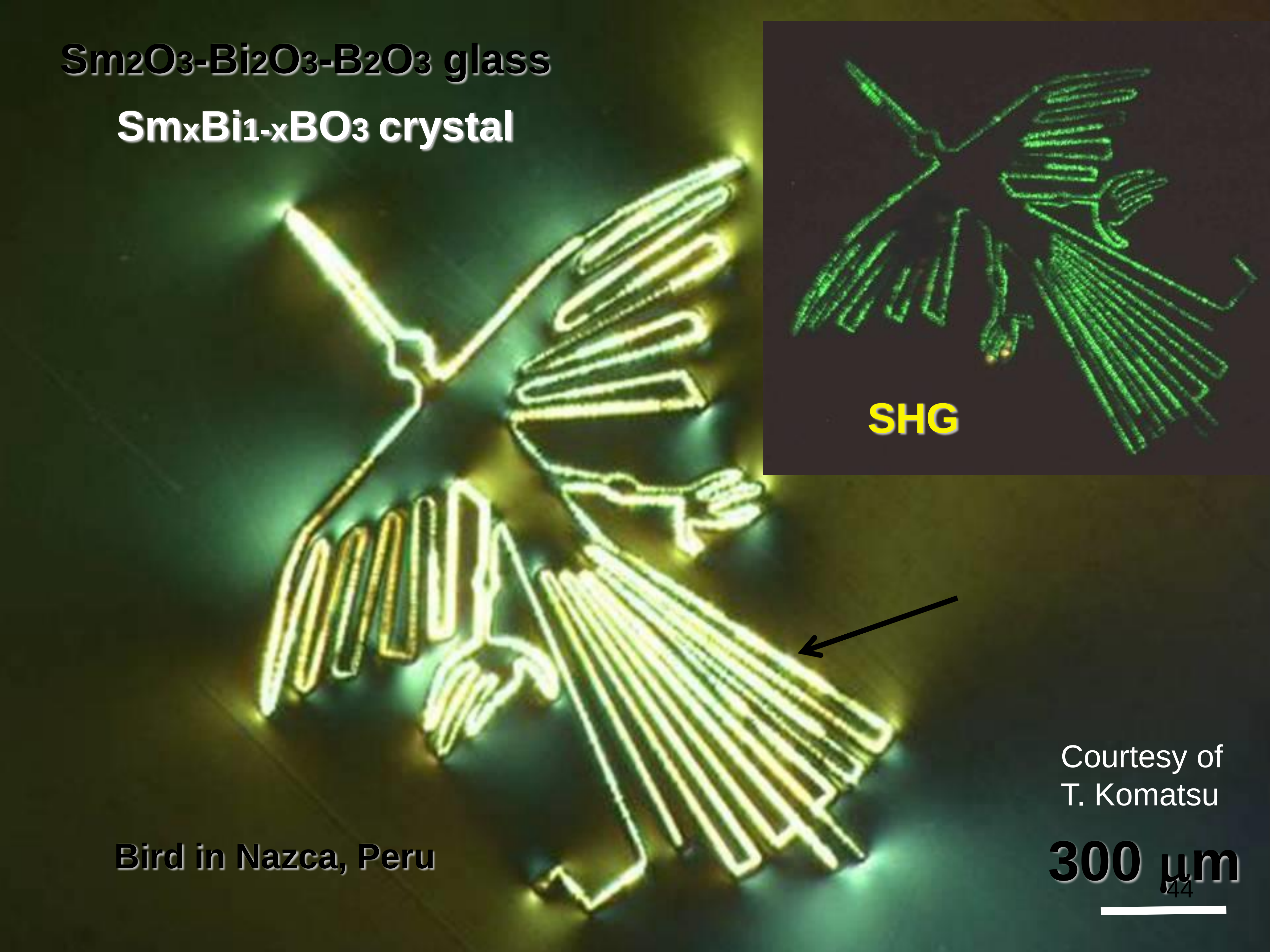
Power: 0.66W

Scanning speed: 10μm/s



Komatsu

Polarization optical microscope


Sm_2O_3-Bi_2O_3-B_2O_3 glass
$Sm_xBi_{1-x}BO_3$ crystal
SHG
Bird in Nazca, Peru
Courtesy of
T. Komatsu
300 µm

CO_2 Laser induced crystallization

Carlos A. C. Feitosa, Lauro J. Q. Maia, André L. Martinez, Valmor R. Mastelaro, A. C. Hernandes

IFSC – USP, São Carlos

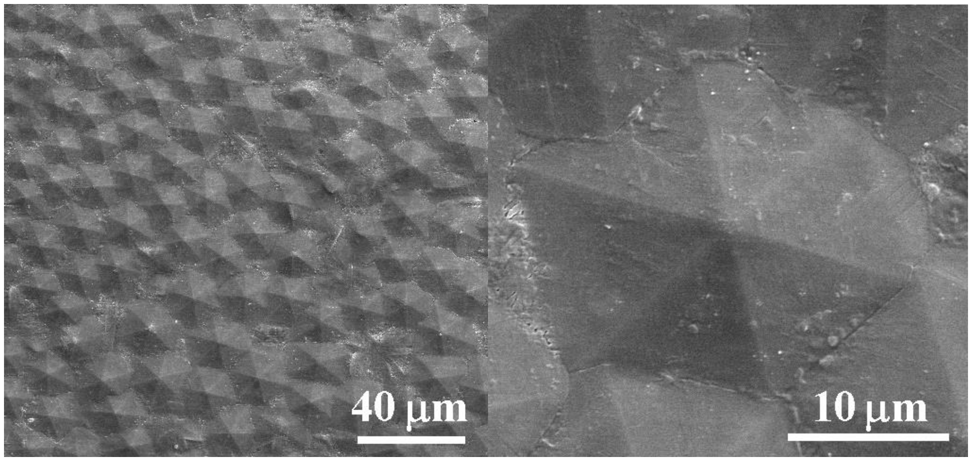
Objectives

- Surface crystallization of certain glass by CO_2 Laser.

- Characterize optical properties

Surface crystallization of a

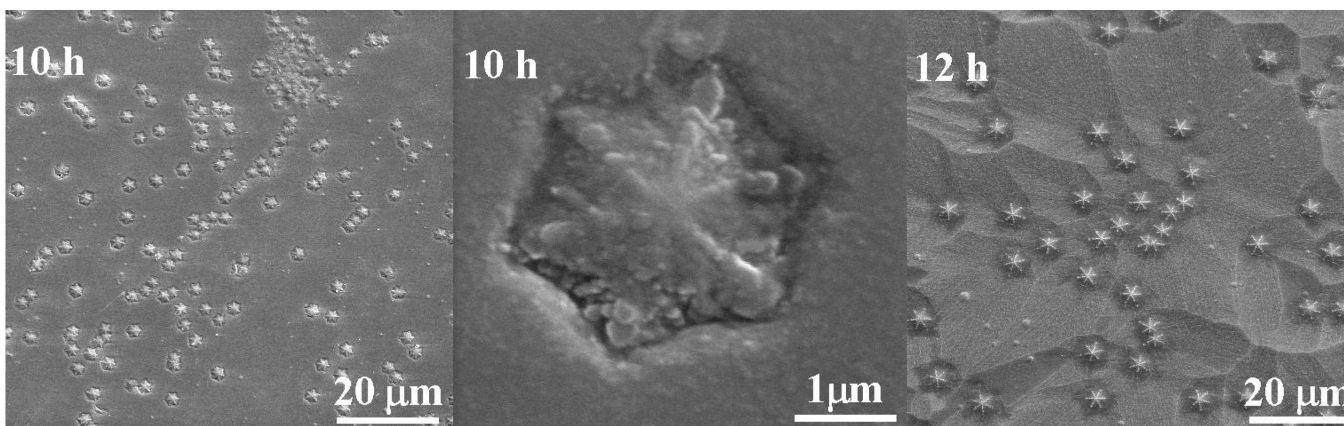
40BaO - 45B_2O_3 - 15 TiO_2 (BBT) glass



BBT after CO_2 Laser irradiation (λ = 10.6 μm)

4 minutes with 40 W/cm^2.
Glass kept at 300°C (T_g = 580°C)

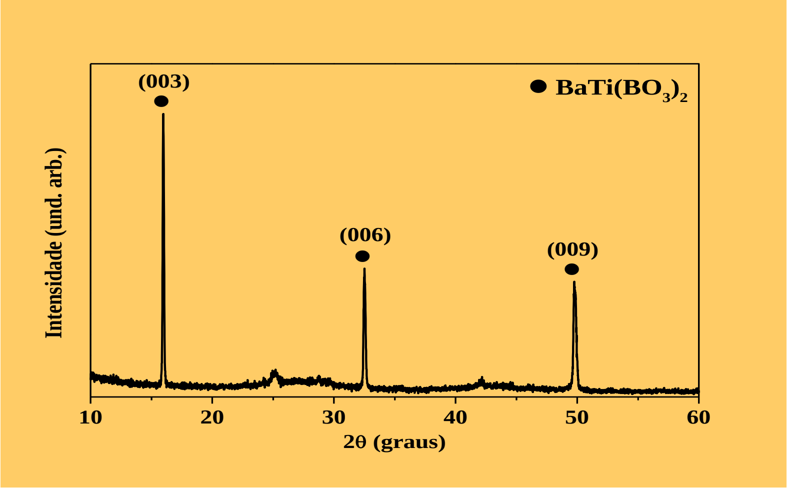
BBT crystallized in a regular furnace at 620°C (T_g = 580°C)

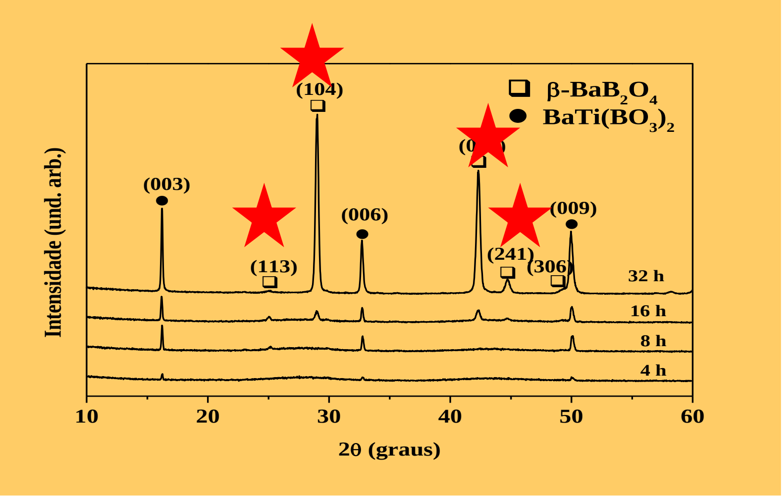


Results for BBT glass

CO_2 Laser

Electric furnace



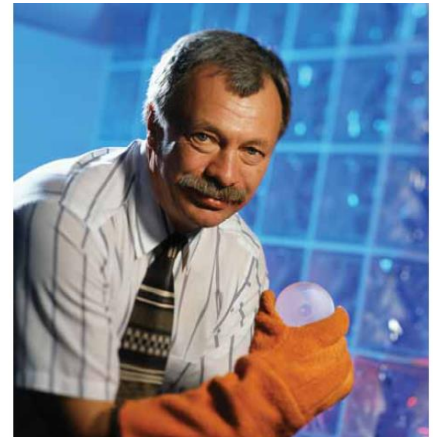


More pronounced texture in

The Laser processed material.

Femtosecond Laser
10^{-15} s

PTR glasses



cializing the technology for the past six years, it is also a prime example of the many stages involved in transferring university technology to the marketplace.

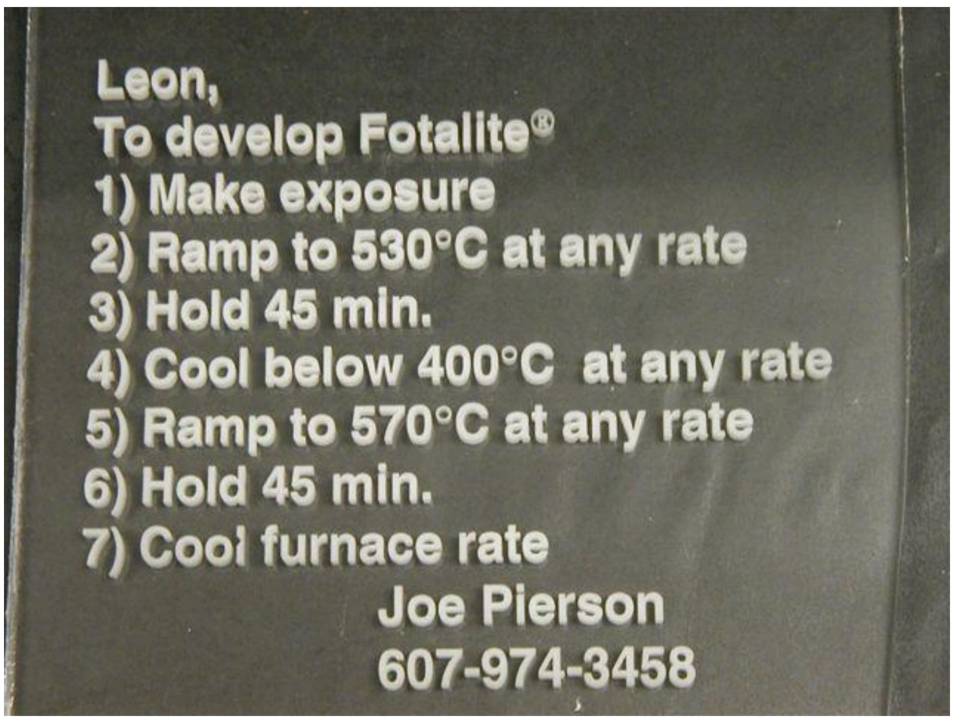
Leon Glebov, who had served as director of the Vavilov Institute during the tumultuous period prior to the dissolution of the USSR, was recruited to UCF in 1995 by M.J. Soileau, current vice president for research who at that time was director of CREOL. At the time Glebov was participating in the U.S. government-funded program on transitioning from a state economy to a market economy and he decided he liked the market economy model enough to stay in the U.S. His wife Larissa joined him later that year.

Glebov began working with Hogan shortly after his arrival at UCF and attended Success Solutions seminars sponsored by CFIC for emerging companies.

In 1996, several CREOL researchers including Glebov received a grant from the Ballistic Missiles Defense Agency (BMDA) for development of holographic optical elements based on a photosensitive glass. In 1999, in partnership with the Raytheon Corporation, he was

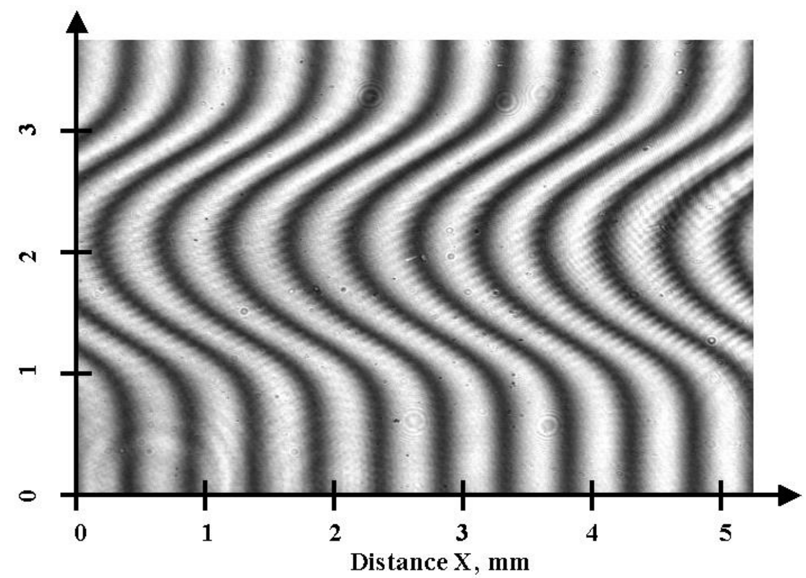
S.D. Stookey et. al.

Corning's Fotalite



Creol's PTRG

Hologram **Leon Glebov et. al.**



PTRG process

Fluor silicate glass containing Ag^{+1} and Ce^{+3}

Exposure of certain parts to UV Laser 325nm

$h\nu$

$Ag^{+1} + Ce^{+3 =} = Ag^{o} + Ce^{+4}$

Heat at 470 ^{o}C for 1 hour

Ag^{o} (atoms) = nAg^{o} (nanosized clusters)

Heat at 520 ^{o}C

NaF nanocrystals crystallize heterogeneously on the surface of nAg^{o}

Summary

- Forming: articles of any shape can in principle be made by any glass processing method that already exists or may be invented

- Thermal treatment: none (i.e. crystallization induced on the cooling path), one step or multiple step

- Microstructure: can be engineered for nano, micro or macro grains; low or high crystallinity; zero, low or high porosity; one or multiple crystal phases; random or aligned crystals; surface induced or internal crystallization

- Thermal: controlled thermal expansion: negative, zero or highly positive; stability from about 400 to 1450 ^{o}C, low thermal conductivity

Summary

Mechanical: Much higher strength and toughness than glasses. The limits are far from being reached, possibility to be further strengthened by fiber addition, chemical and thermal methods, hard, some are machinable

Chemical: resorbable or highly durable

Biological: biocompatible (inerte) or bioactive

Electrical and magnetic: low or high dielectric constant and loss, high breakdown voltage, ionic conducting or insulator; superconductor, piezoelectric and ferromagnetic

Optical: Translucent or opaque; opalescent, fluorescent; photo-induction nucleation is possible, colored

- Plenty is already known about glass-ceramic technology, but many challenges and opportunities in CG research and development are ahead. They include:

- the search for new compositions (and there are many alternatives to explore),
- other and more potent nucleating agents,
- new or improved crystallization processes, for instance: microwave heating, bio mimetic microstructures, textured crystallization, laser crystallization, etc.,
- A deeper understanding and control of photo thermal-induced nucleation associated or not with chemical etching,
- the development of harder, stiffer, stronger and tougher glass-ceramics,
- CGs with increased transparency or
- more conducting…

Unexpected applications will probably surface that require a new combination of material properties.

Conclusions

- There are many R & D opportunities to explore on GCs!
- Due to their glorious past (starting with Stookey´s discovery); to very successful commercial products; impressive range of properties and the exciting potential applications, glass-ceramics have indeed a *bright future!*

Letter received in 2010 from?

Oct. 14

Dear Professor Zanotto:

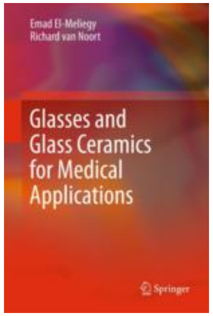
It is a pleasure to congratulate you on the history-making paper you wrote for the new ACERS BULLETIN. I truly believe that, by applying the worldwide knowledge assembled in the article, a new "stone age" can be started, in which, for example, beautiful indestructible buildings can be made from inexpensive materials. Structures can be made that are resistant to fire, corrosion, age, etc.

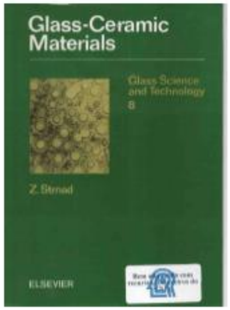
I hope that the new generation of scientists and engineers will make use of this knowledge and expand on it.

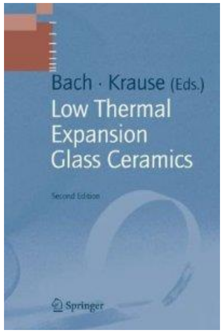
References

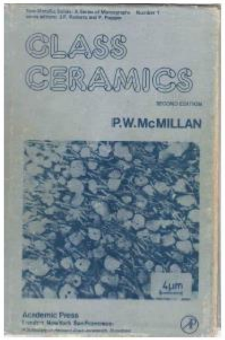
From glass to crystal: nucleation, growth and phase separation, from research to applications - D. Neuville et al. (2015)

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!