

Glass Processing

Lecture #15 Glass-ceramics: Nature, properties and processing



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Lectures available at:

www.lehigh.edu/imi

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Center for Research Technology and Education in Vitreous Materials





The Vitreous State



August – Nov. 2015 (15 weeks = 30+30h)
LaMaV - Federal University of São Carlos

Instructor: EDZ

Glass – nature and properties

Glass structure

Relaxation - glass transition

Liquid-liquid phase separation

Crystal nucleation kinetics

Crystal growth kinetics

Overall crystallization

Sintering with concurrent crystallization

Glass forming ability - CCR

Glass stability against devitrification

Glass-ceramics

Nucleation, Growth and Crystallization in Glasses — Fundamentals and Applications

May 16-17, 2015 | 1:00 p.m. – 5:00 p.m.; 8:00 a.m.

– Noon | 8h

Hilton Miami Downtown

Instructor: EDZ



Fundamentals:

- Crystal nucleation
- Crystal growth
- Overall crystallization

Applications:

- Sintering with concurrent crystallization
- Glass forming ability - CCR
- Glass stability against devitrification
- Glass-ceramics**

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

High T reactions, melting, homogeneization and fining = previous lectures!

Glass forming: previous lectures!

Glass-ceramics: definition, properties & applications

Thermal treatments – Sintering (of a glass powder compact) or
Controlled nucleation and growth in the glass interior

Micro and nano structure development



Concluding remarks

IMI

Zanotto



Reading assignments



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



Properties of inorganic glasses

Isotropic

Transparent, opaque, colorless **colored**

Refractive index: 1.2 – 2.2

Electrical conductivity (T_{amb}): $10^{-6} - 10^{-18} \text{ (ohm.cm)}^{-1}$

T_g : 150°C - 1200°C.

Low thermal conductivity: $k \leq 1 \text{ W/m.K}$

Hardness: 3 -15GPa

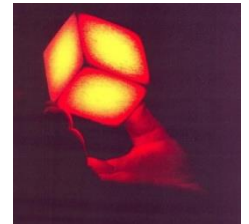
Resistant to acids to soluble in H_2O

Fragile: $K_{IC} < 1 \text{ MPa.m}^{1/2}$

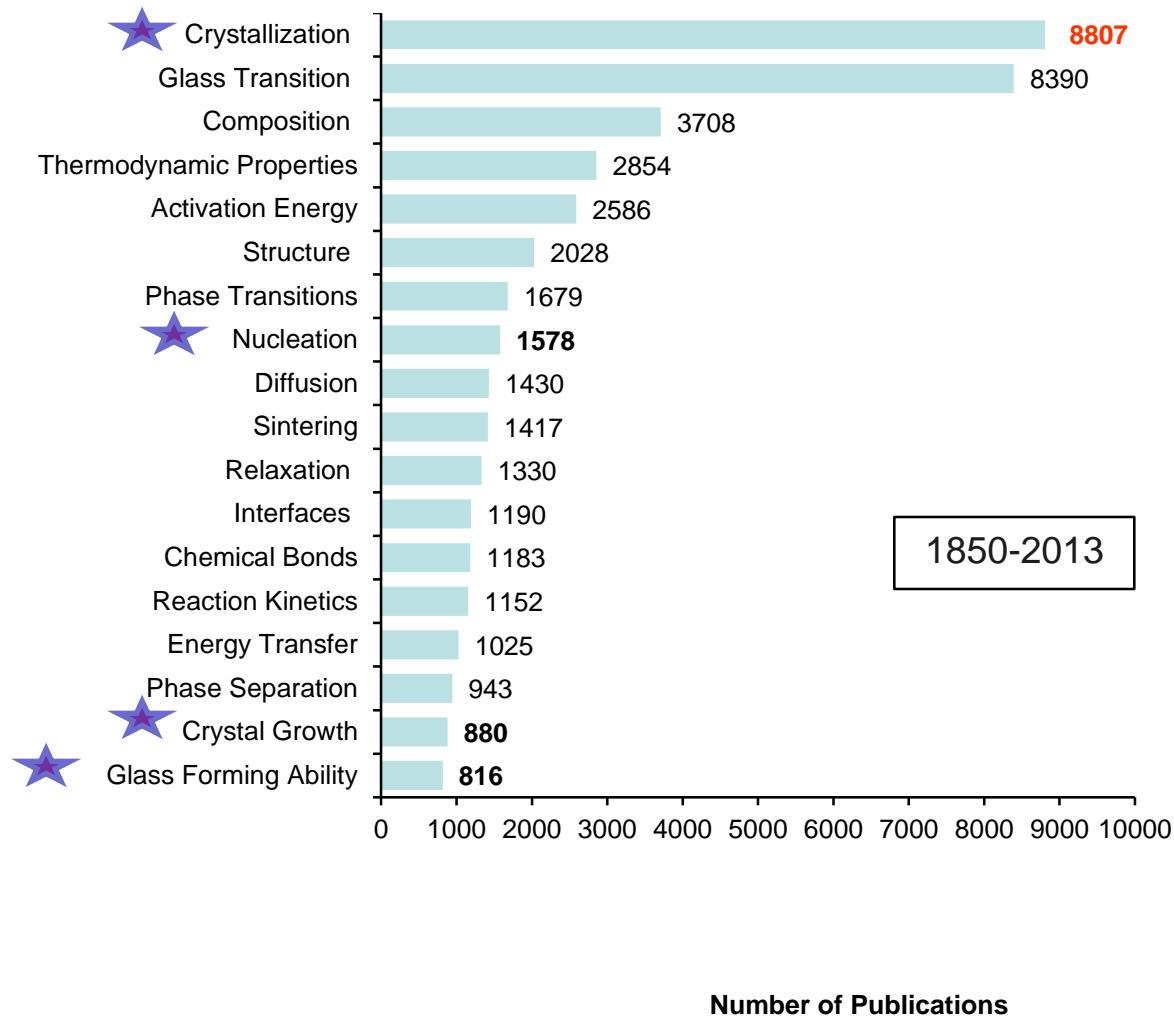
Conchoidal fracture ...

Metastable!

Tend to devitrify on slow cooling or heating



Most frequent keywords in the history of glass research



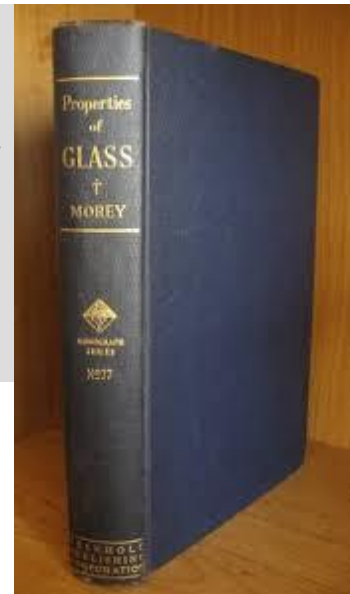
J.C. Mauro & E. D. Zanotto - "200 years of glass research..."
IJAGS, 2014



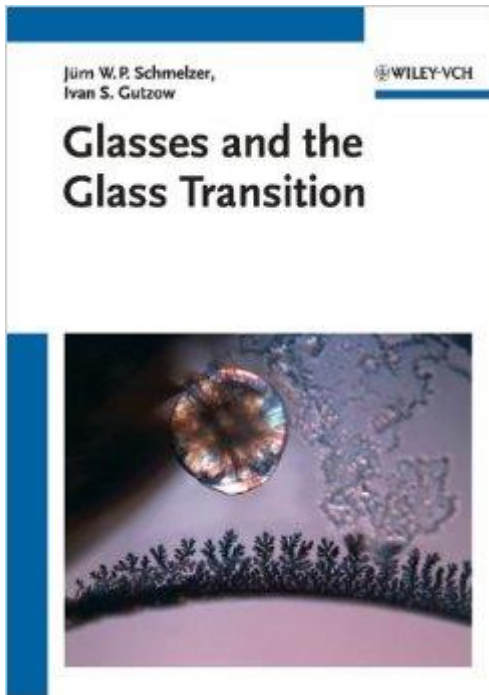
*"Devitrification is the chief factor which **limits** the composition range of practical glasses, it is an ever-present **danger** in all glass manufacture and working, and takes place promptly with any error in composition or technique"*



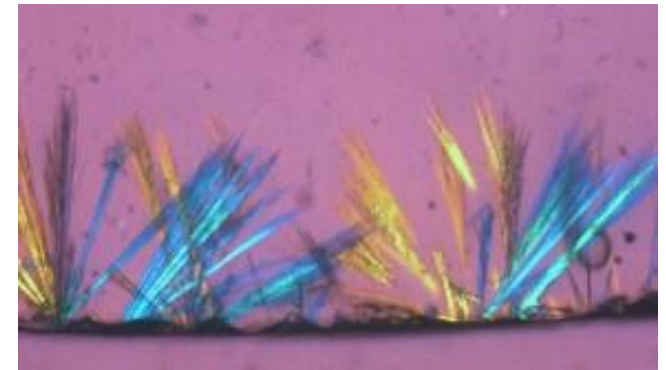
G. W. Morey
The Properties of Glass
Reinhold Pub, NY
1938 & 1954



Heterogeneous (surface) nucleation on silicate glasses



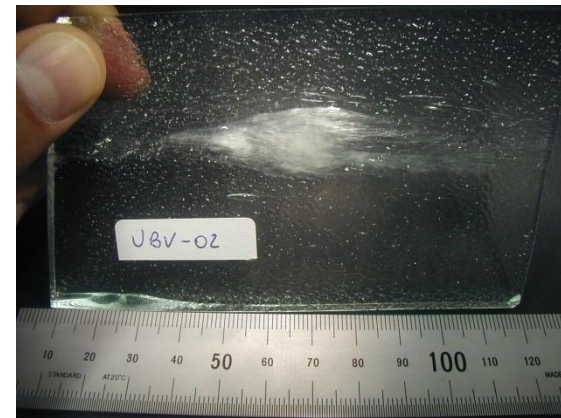
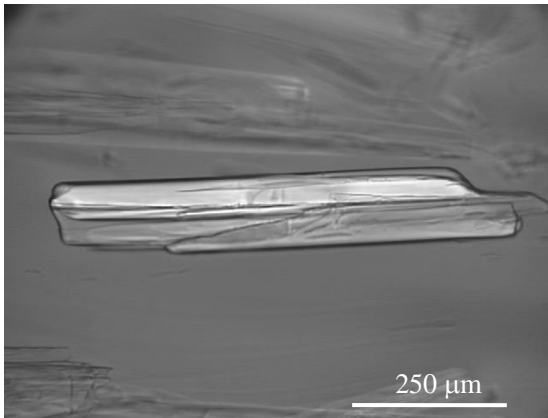
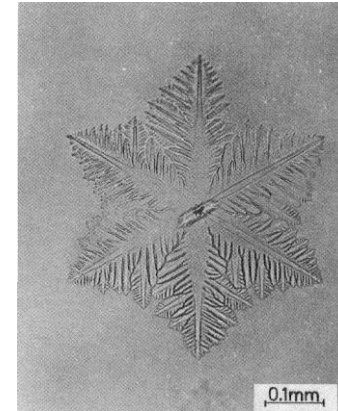
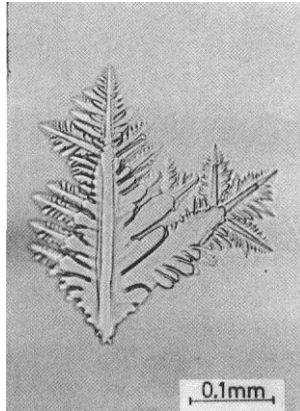
LS + CS



Devitrite

R.Muller, V. Fokin, E.D. Zanotto- *J. Non-Crystalline Solids* (2001)

Defect: devitrification



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* when a furnace containing a piece of a lithium silicate glass with precipitated silver particles (meant to form a permanent photographic image) accidentally overheated to about 900°C, instead of 600°C...



Volfram Hoeland and George Beall mention in their book that: “*knowledge of the literature, good observation skills, and deductive reasoning were clearly evident in allowing the chance events to bear fruit*”.

Crystallization symposium, Stone Mountain (2006)

TC 7 members and guests



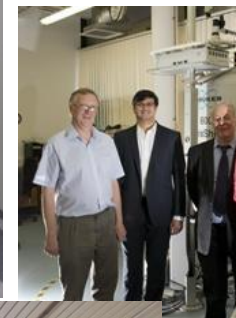
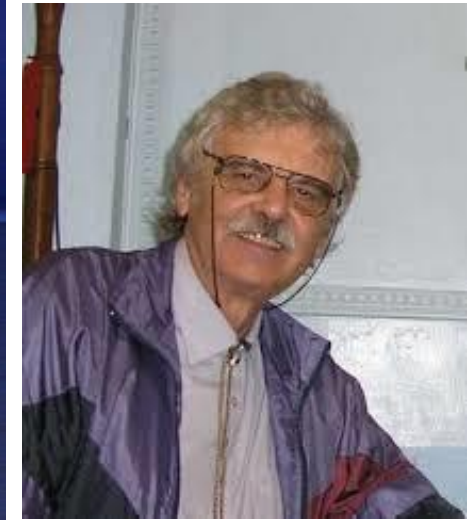
S.D. Stookey



Zanotto

Photo by Mark Davis¹⁴

ICG TC-7



TC 7

The next symp in the series

Crystallization 2015



11th International Symposium on
Crystallization in Glasses and Liquids

October 11-14, Nagaoka, Japan

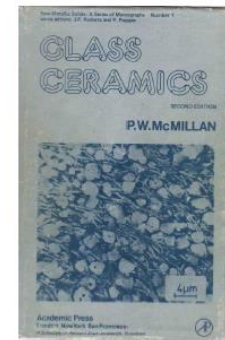
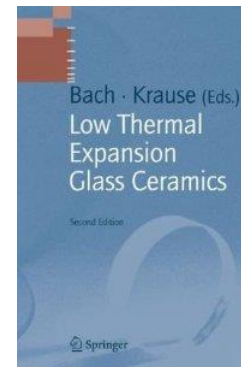
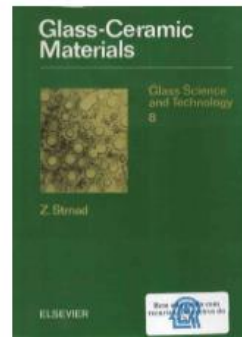
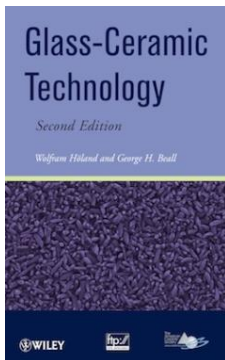
<http://crystallization-2015.jp/>

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, Zanutto, Dymshits...

Zanutto

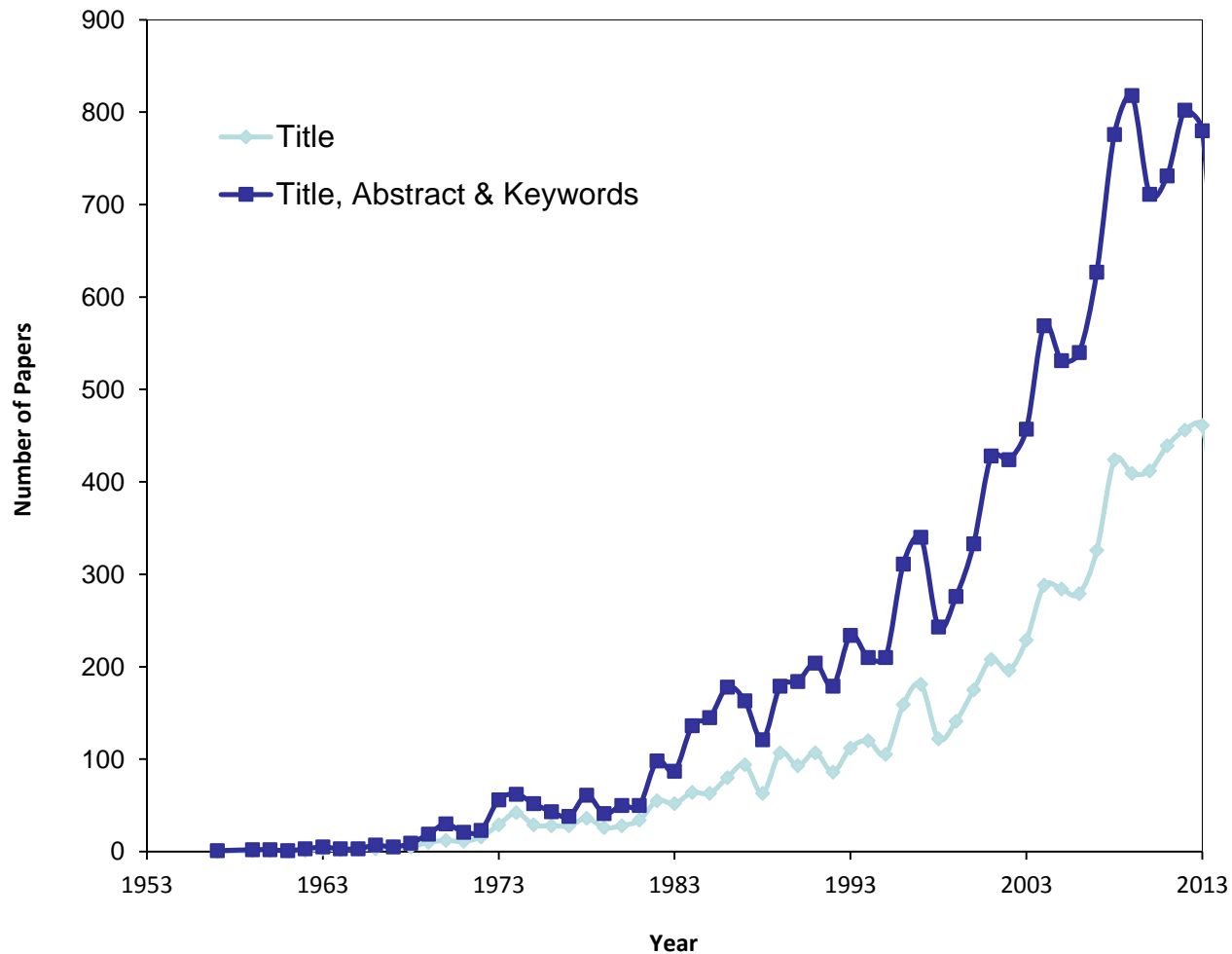
Statistics /scientific papers

July 2014 search

- Scopus database with the keywords (glass-ceramic*) OR (“glass ceramic*”) in the title or abstract or keywords in all types of docs: ~13,000 articles
or ~7,000 using only article titles



GC: papers / year



Am. Cer. Soc. Bull. May 2015

A Statistical Overview of Glass-Ceramic Science and Technology

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

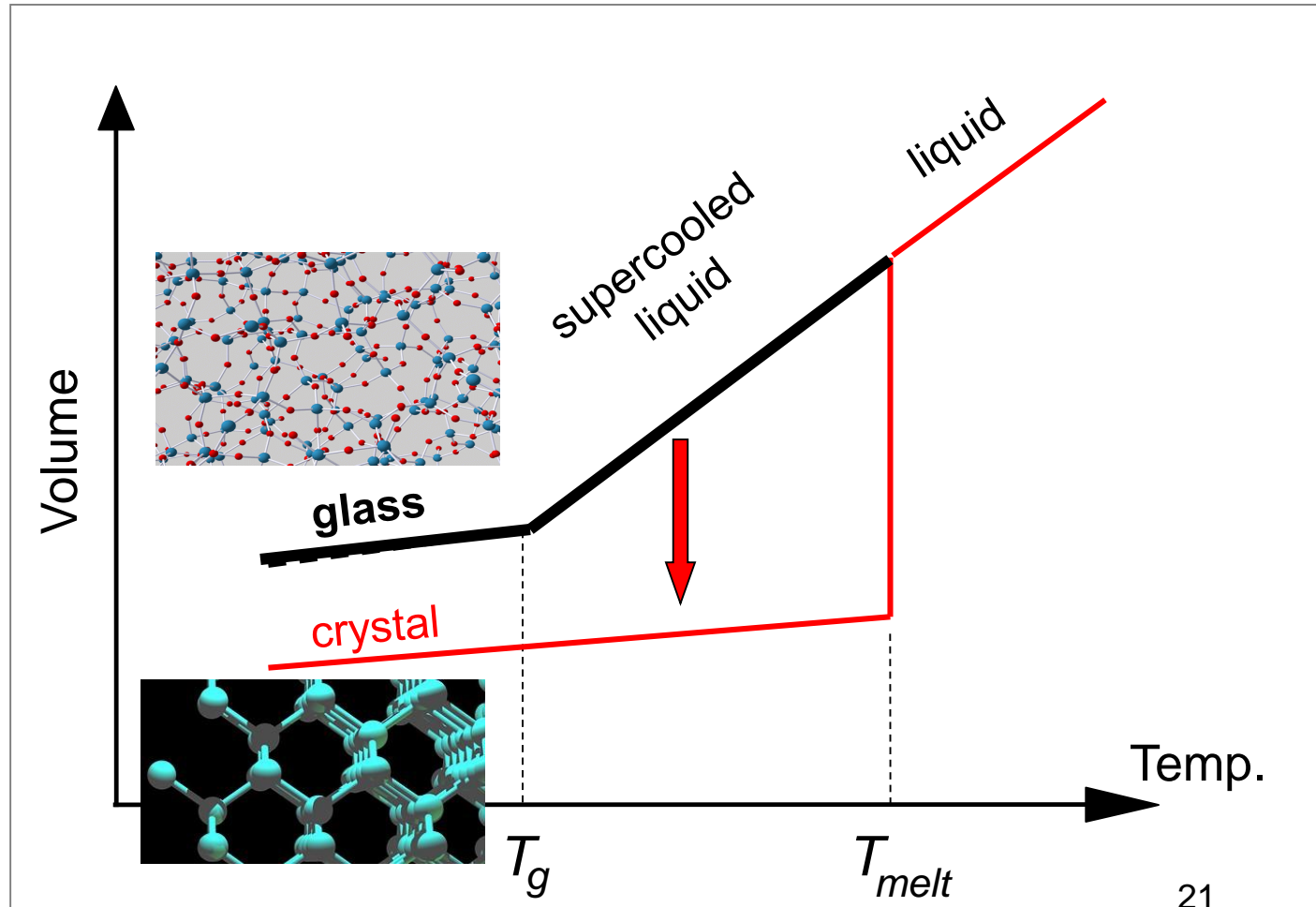
Objectives

Critically comment on a number of exciting **new types** of GC that are being currently developed;

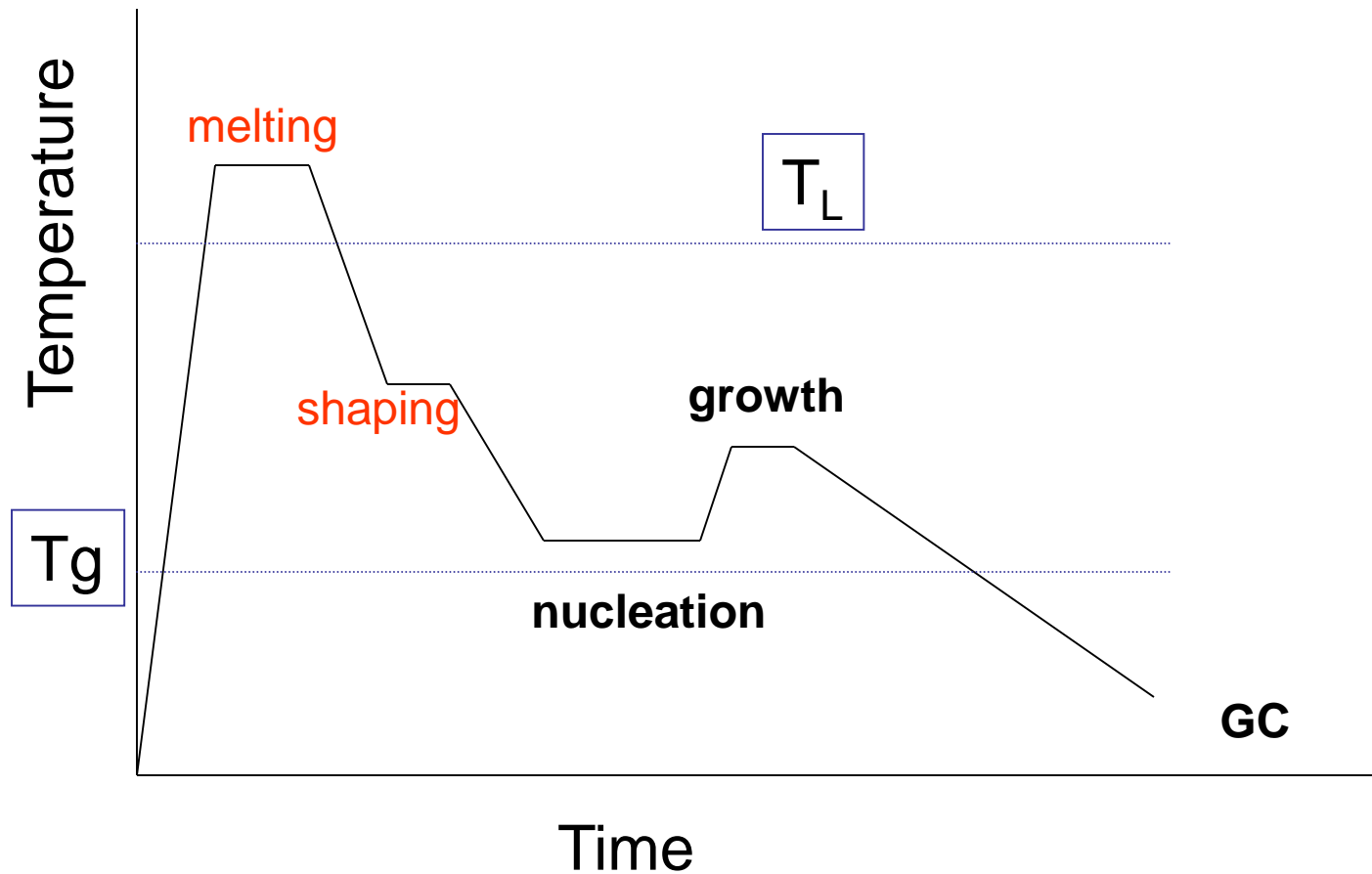
Discuss some critical issues regarding GC **processing**



Glasses and Glass-ceramics



Production steps



Glass-ceramics (GC) =
glass ceramics, vitrocerams, pyrocerams, vitrocerâmicos,
vitroceramiques or sittals

GC always contain a residual glassy phase and one or more embedded crystalline phases – with widely varying crystallinity between 0.5% and 99.5%, most frequently 30-70%.

Advantages of CGs:

- can be mass produced by any glass forming technique
- it is possible to design the material's nano or microstructure
- most have zero or very low porosity,
- It is possible to combine desired properties

Microstructural Design

grain size distribution & shape, texture, porosity, %crystallinity, type and # crystal phases...

GLASS-CERAMICS

high thermal and chemical stability

harder and tougher than glasses

controllable electrical properties

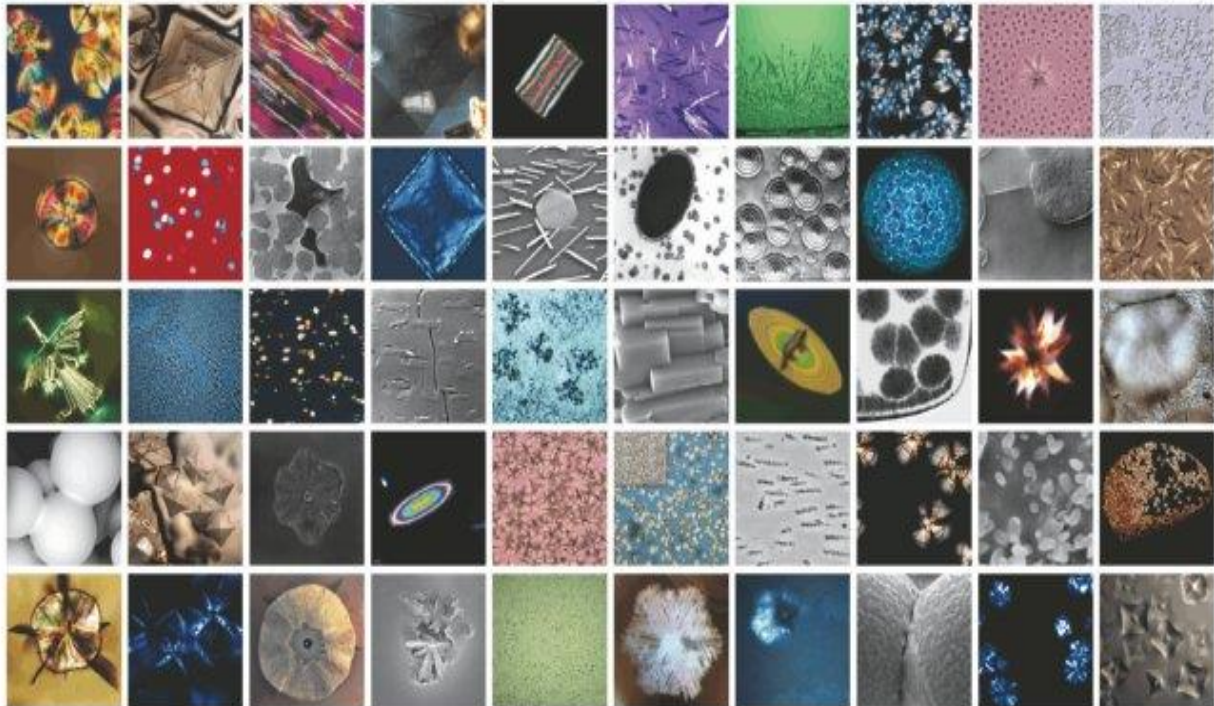


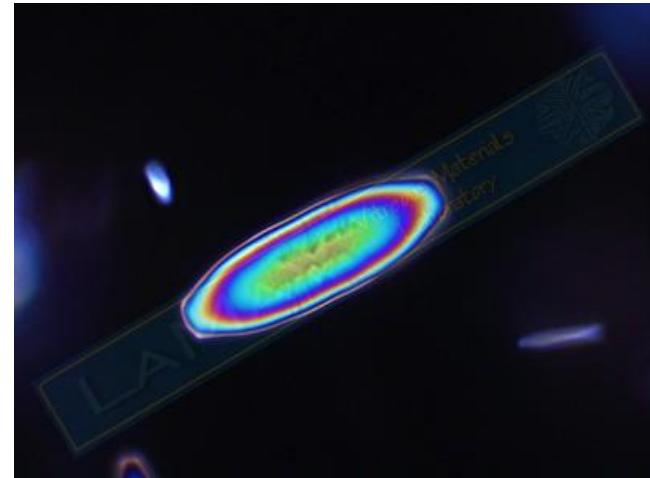
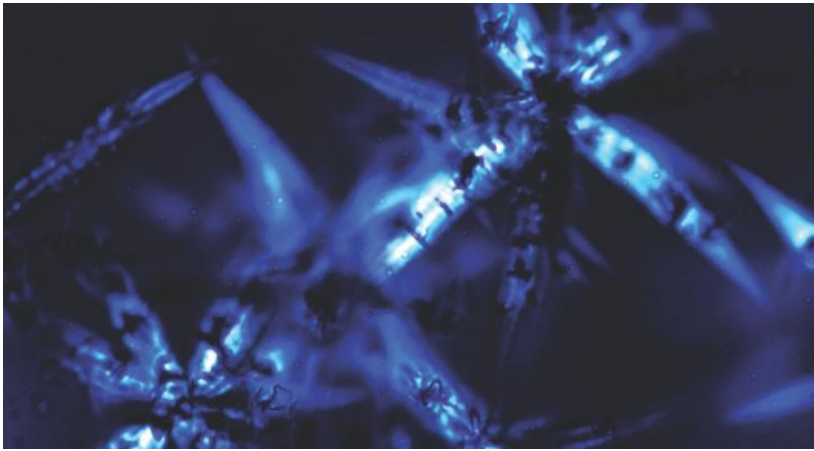
Combination of properties

optical transparency

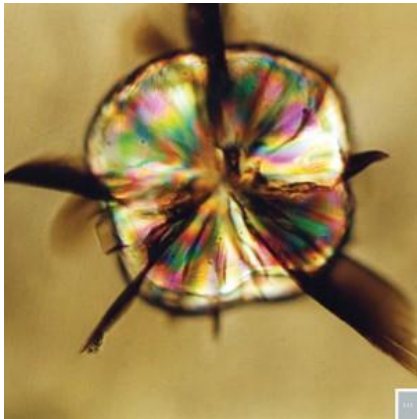
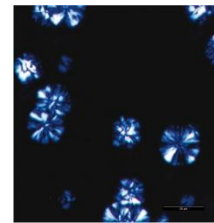
bioactivity

controllable TEC





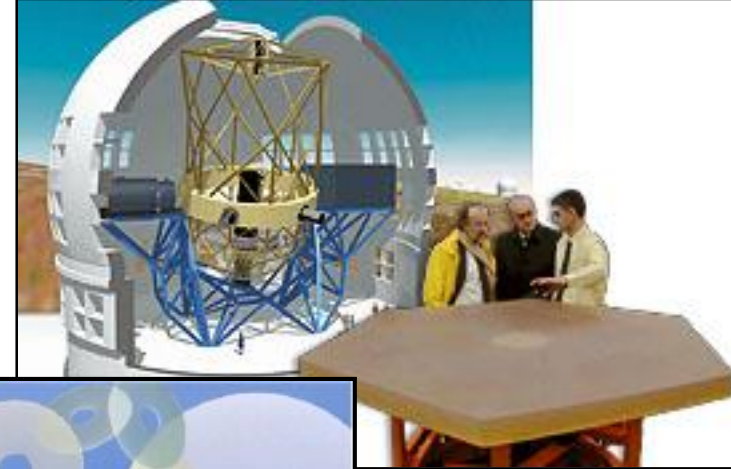
Designed micro
and
nanostructures
lead to...



glass-ceramic products



Donald Stookey
(2000)



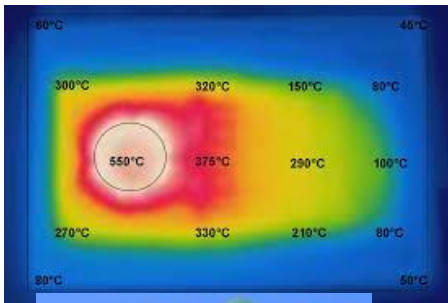
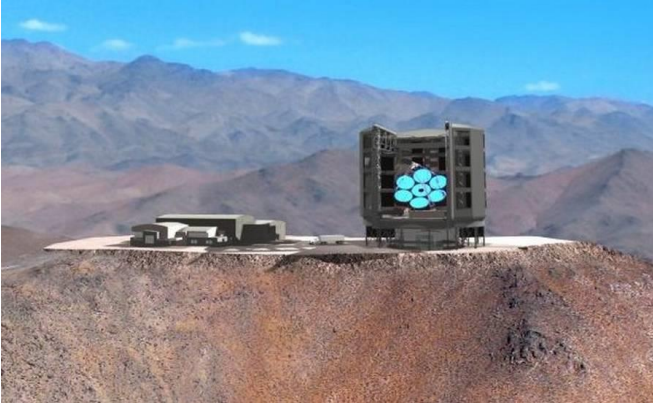
HD Substrate



Otawa Dental Lab.

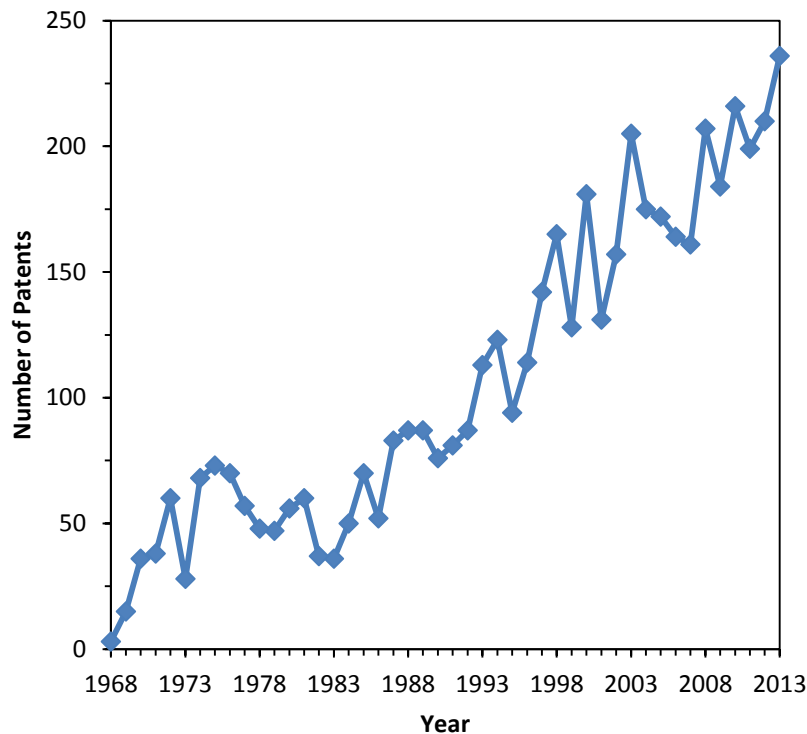


Cooktop



$\langle \text{rms} \rangle$ 1nm

Patents granted per year extracted from the DWPI by searching for “glass-ceramic*” OR “glass ceramic*” keywords in the patent title.



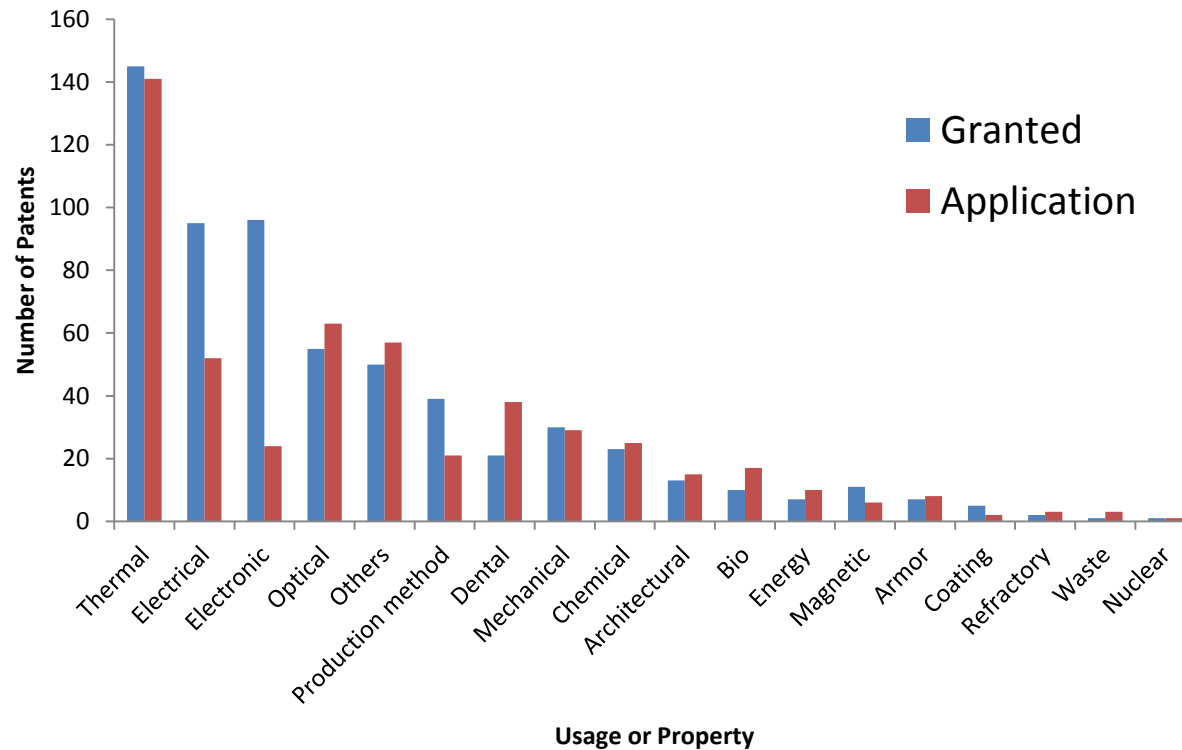
Derwent Innovation Index search
~5,000 granted patents on GCs

Am. Cer. Soc. Bull., May 2015

Statistical Overview of Glass-Ceramic Science and Technology

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

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 application

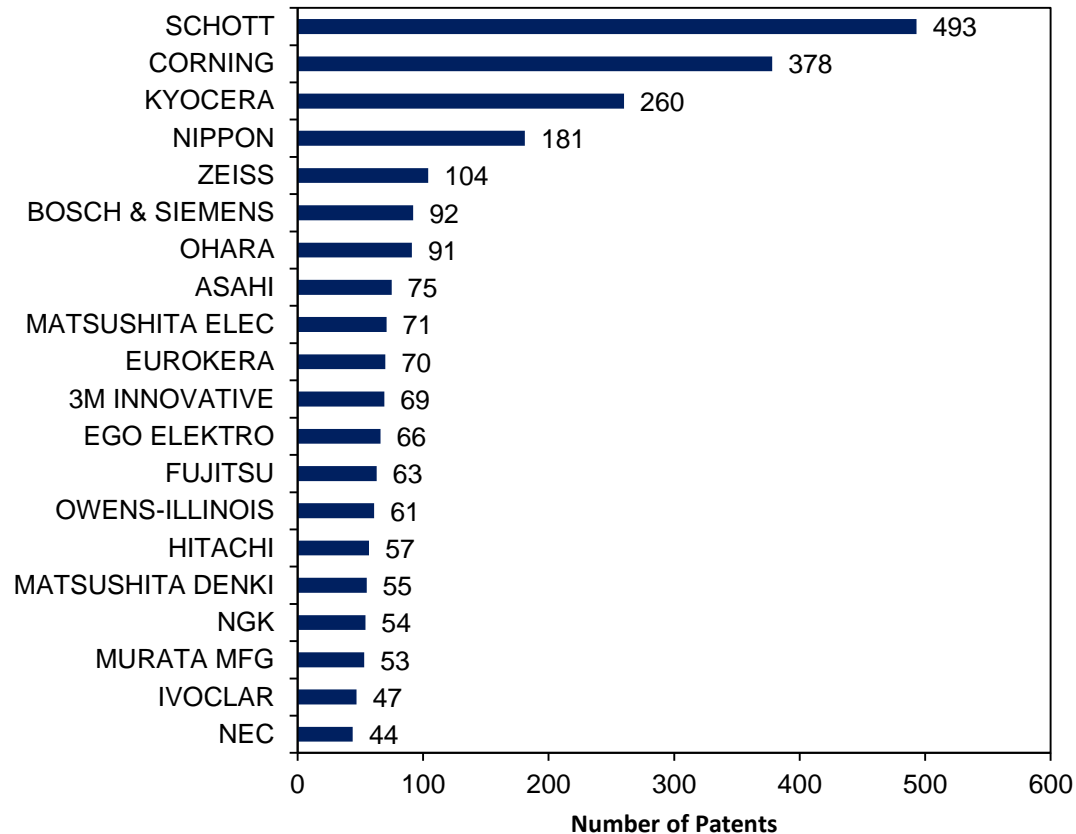


Am. Cer. Soc. Bull., May 2015

Statistical Overview of Glass-Ceramic Science and Technology

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Twenty most prolific companies with largest number of glass-ceramic patents granted from 1968 to 2014. “Glass-ceramic*” or “glass ceramic*” keywords were searched in the patent title. Source: DWPI



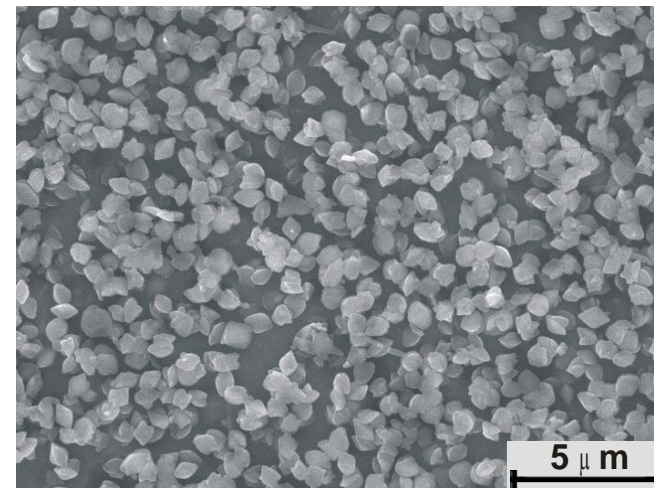
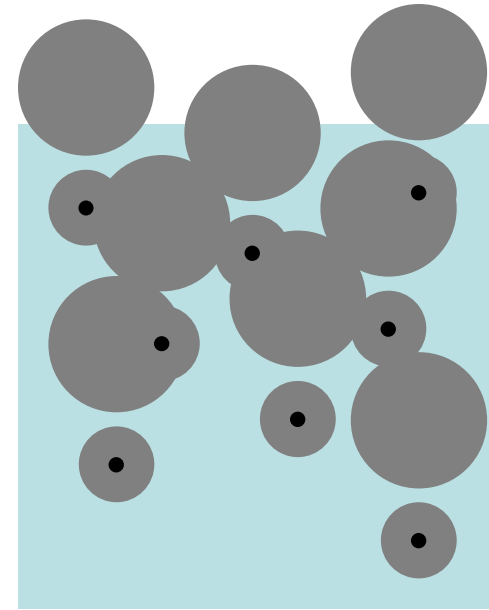
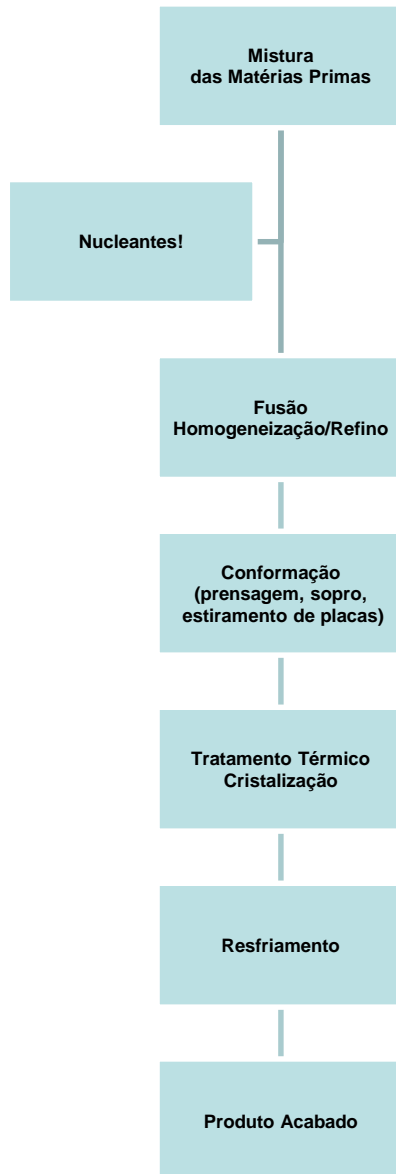
Am. Cer. Soc. Bull., May 2015

Statistical Overview of Glass-Ceramic Science and Technology

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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 exchanger
	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 Zanotto	Color filter substrates for LCD panels

Fabricação – via cristalização volumétrica



Fabricação – via sinterização

From E.B. Ferreira - 34

