Summer School "Ceramic and Glass Science and Technology, application to bioceramics and bioglasses"
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Glasses and Glass-ceramics: a general overview

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Outline of the presentation

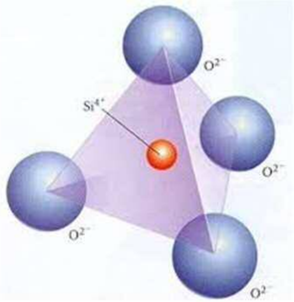
1. The Nature of glass
    - 1.1. What is glass? Classification
    - 1.2. Making glass
    - 1.3. Phase separation and devitrification
    - 1.4. Controlled devitrification. Glass-ceramics

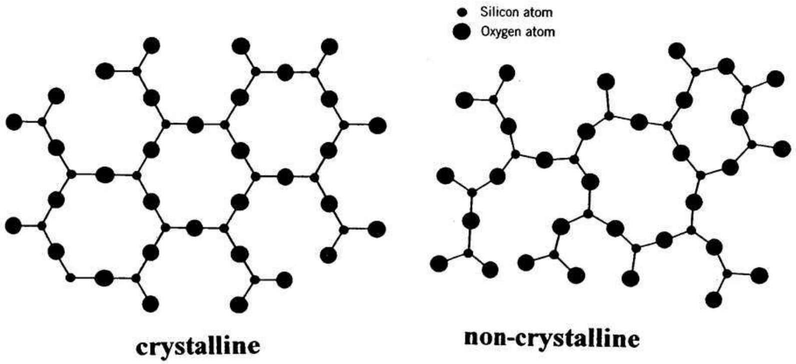
2. Melt-derived bioactive glass. Bioglass
3. Bioactive sol-gel glass
4. Phosphate glasses
5. Bioactive borate glasses
6. Bio-Glass-ceramics
7. Bioactive glass coatings and composites
8. Glasses for radiotherapy

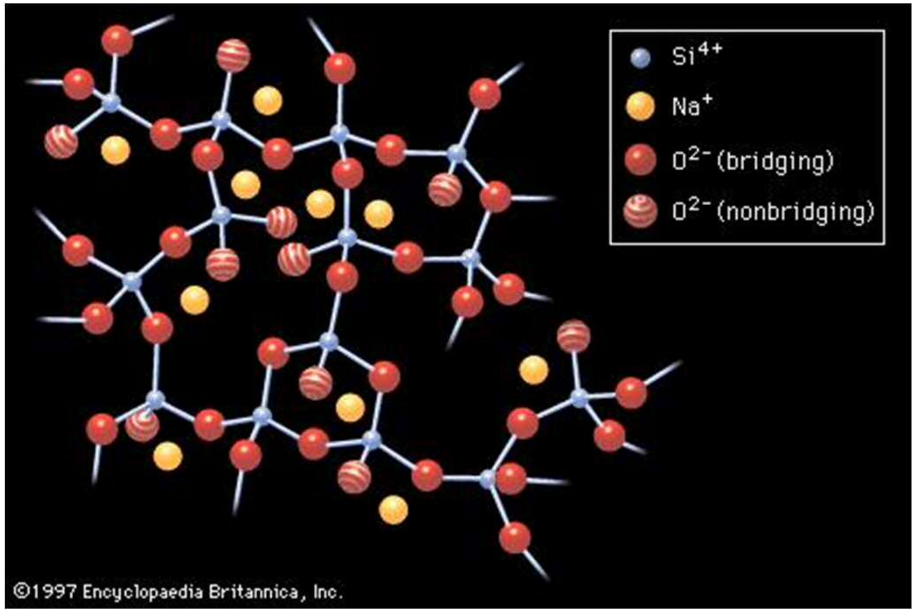
What is glass?

What is glass?

- Glass is not a single composition but rather is a state of matter, a subset of the solid state
- A glass is a network of atoms (most commonly silicon) bonded to each other through covalent bonds with oxygen atoms
- A silica-based glass is formed of silica tetrahedra bonded together in a random arrangement
- Window glass is usually based on the soda-lime-silica (Na_2O-CaO-SiO_2) system. Bioactive glasses also contains these components, but in different proportions to inert glasses







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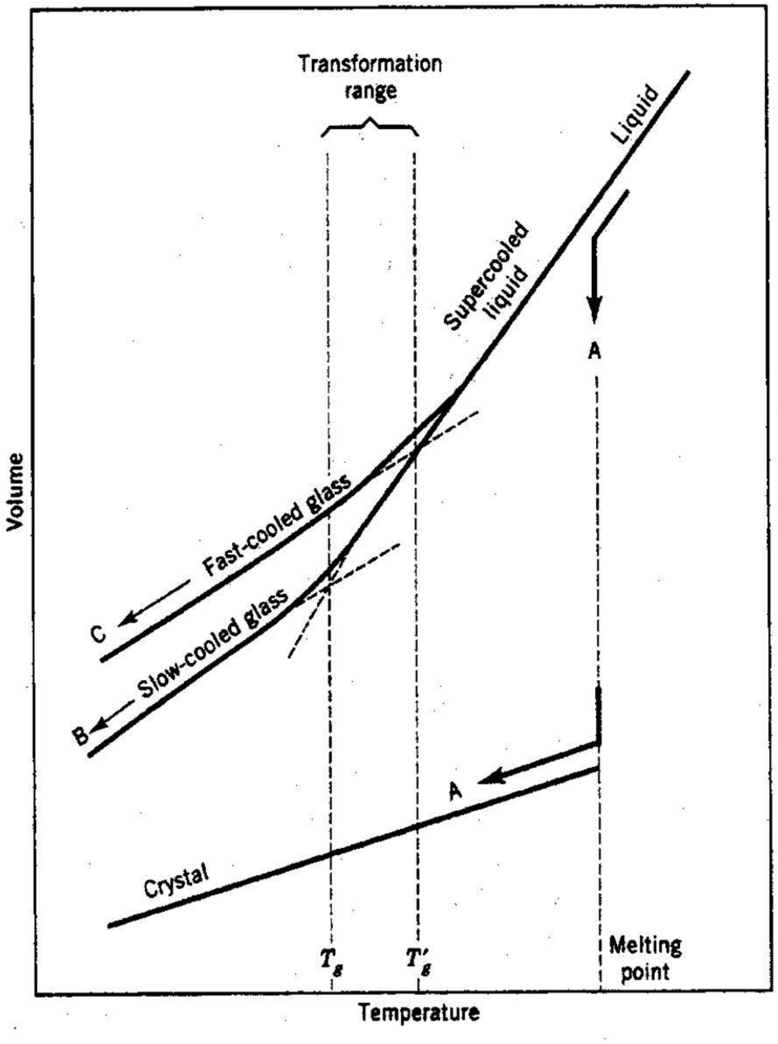
What is glass?



Operational definition (ASTM)

- A glass is an inorganic product of melting which has cooled and become rigid without crystallising

Structural definition

- A glass is a non-crystalline solid

Structural definition + internal stability

A glass is a non-crystalline solid that presents the glass-transition phenomenon. The physical state is called the vitreous state

T_G : transition temperature, $\eta(T_G) \sim 10^{13}$ dPa.s

What is glass?

Classification

- **Natural glasses**

✓ Eruptive rocks: obsidian

✓Shock-wave melting (meteorites): tektite

- **Artificial glasses**

✓ Oxide glasses

✓ Halogenide glasses

✓ Calcogenide glasses

✓ Metallic glasses

What is glass?

Classification

- ✓ Oxide glasses
  - One network former
  - Various network formers
  - Network former - network modifier

- ✓ Halogenide glasses
  - BeF_2 glasses
  - Heavy fluorides glasses (ZrF_4, BaF_2-RFn)

- ✓ Calcogenide glasses
  - Elements of the group VI + V y IV
    (S, Se, Te) + (P, As), (Si, Ge)

- ✓ Metallic glasses
  - alloys metal-metaloide
    $(Au, Pd, Pt, Fe, Ni)_{80} + (Si, Ge, P, C, B)_{20}$
  - alloys metal-metal
    ($Mg_{65}Cu_{35}$, $Ni_{60}Nb_{40}$, $Zr_{72}Co_{28}$)

What is glass?

Classification

Oxide glasses

- One network former

SiO_2, B_2O_3, P_2O_5, GeO_2

- Several formers

SiO_2 - B_2O_3, SiO_2 - GeO_2

- Former-modifier

Silicates (SiO_2-CaO-Na_2O)
Borates (B_2O_3-R_2O, B_2O_3-RO)
Borosilicates (B_2O_3-SiO_2-Na_2O)
Boroaluminates (B_2O_3-CaO-Al_2O_3)
Phosphates (P_2O_5-RO-R_2O)
Germanates
Vanadates
Telurites, aluminates

What is glass?

The properties of inorganic glasses

- Isotropy
- Transparent, opaque, colourless, coloured. Optical properties
- Refractive index: 1.2-2.2
- Homogeneous
- Solvent properties
- Continuous fitting of properties
- T_g: 150 - 1200ºC
- Workability. Versatility
- Durability. Chemical resistance (can vary from resistance to acids to soluble in H_2O)
- Tightness
- Electrical behaviour from insulator to semiconductor, σ (T_{amb}: 10^{-6}-10^{-18} $(ohm.cm)^{-1}$)
- Fragile (K_{IC}<1 $MPa.m^{1/2}$) conchoidal fracture, but hard (3-15 GPa) and resistant
- Heat resistant
- Low thermal conductivity k≤ 1W/m.K
- Recyclable

Metastable! Tend to devitrify on slow cooling or heating
Glass can be microstructurally engineered through
liquid-liquid phase separation or devitrification (crystallization)

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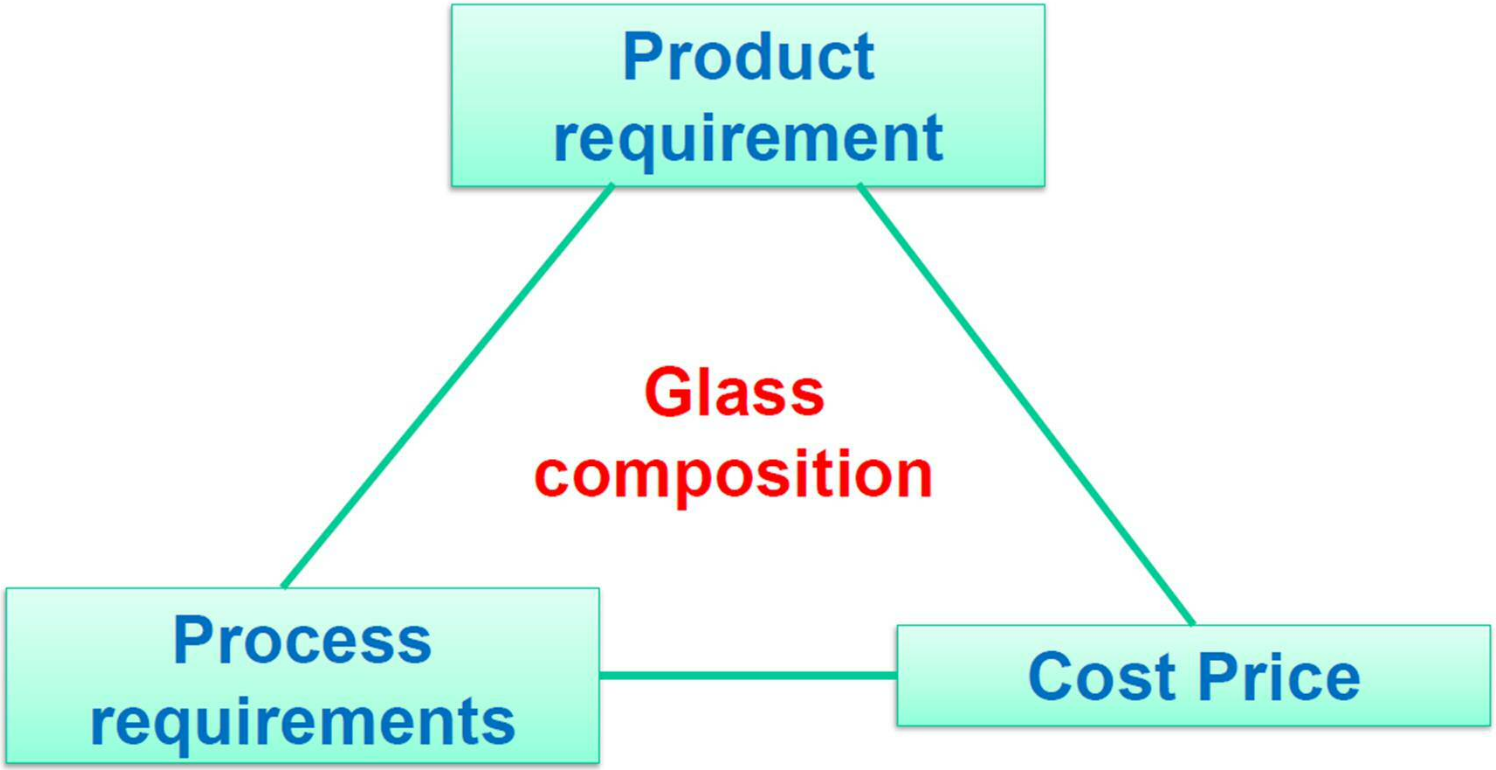
Making glass

How do I choose my glass composition?



Product requirement

Glass composition

Process requirements

Cost Price

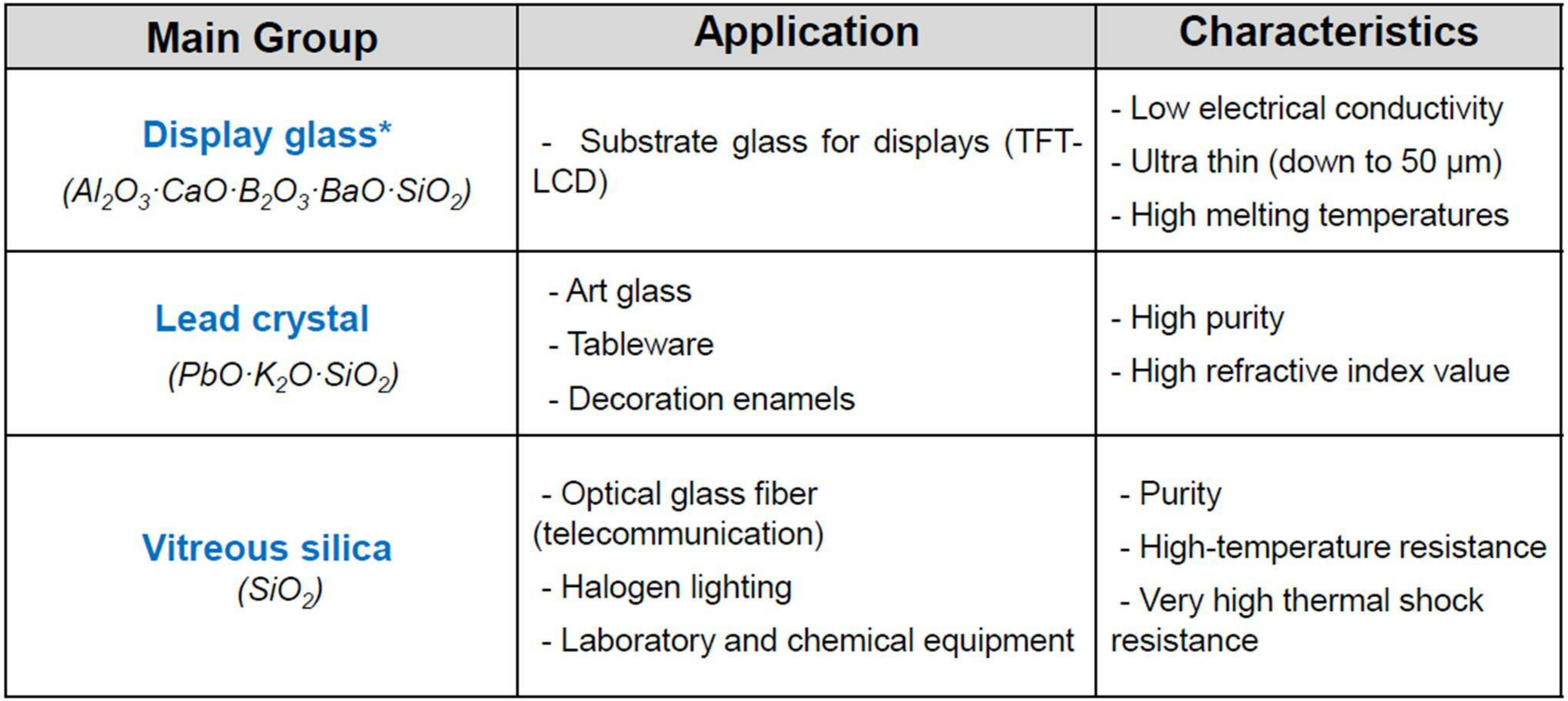
Making glass

Main types of commercial glasses (1/2)

Main Group	Application	Characteristics
Soda-Lime-Silica glass ($Na_2O \cdot CaO \cdot SiO_2$)	- Flat glass - Container glass - Tableware - Lamp glass (lighting) - Lenses	- Mass production - Low cost
Sodium-borosilicate ($Na_2O \cdot B_2O_3 \cdot SiO_2$)	- Laboratory glass (ex: Pyrex® or Duran®) - Cooking utensils - Headlights	- Thermal shock resistant
E-glass ($CaO \cdot Al_2O_3 \cdot B_2O_3 \cdot SiO_2$) *Sometimes without B_2O_3 other components: MgO, TiO_2	- Textile glass fiber - Reinforcement fibers for plastics - Fibers for printed circuit boards	- Mechanical strength - Low electrical conductivity - Fiberizability
A-glass ($Na_2O \cdot CaO \cdot B_2O_3 \cdot SiO_2$)	- Glass wool (insulation) - Glass fiber (reinforcement)	- Fiberizability - Low cost

Making glass

Main types of commercial glasses (2/2)

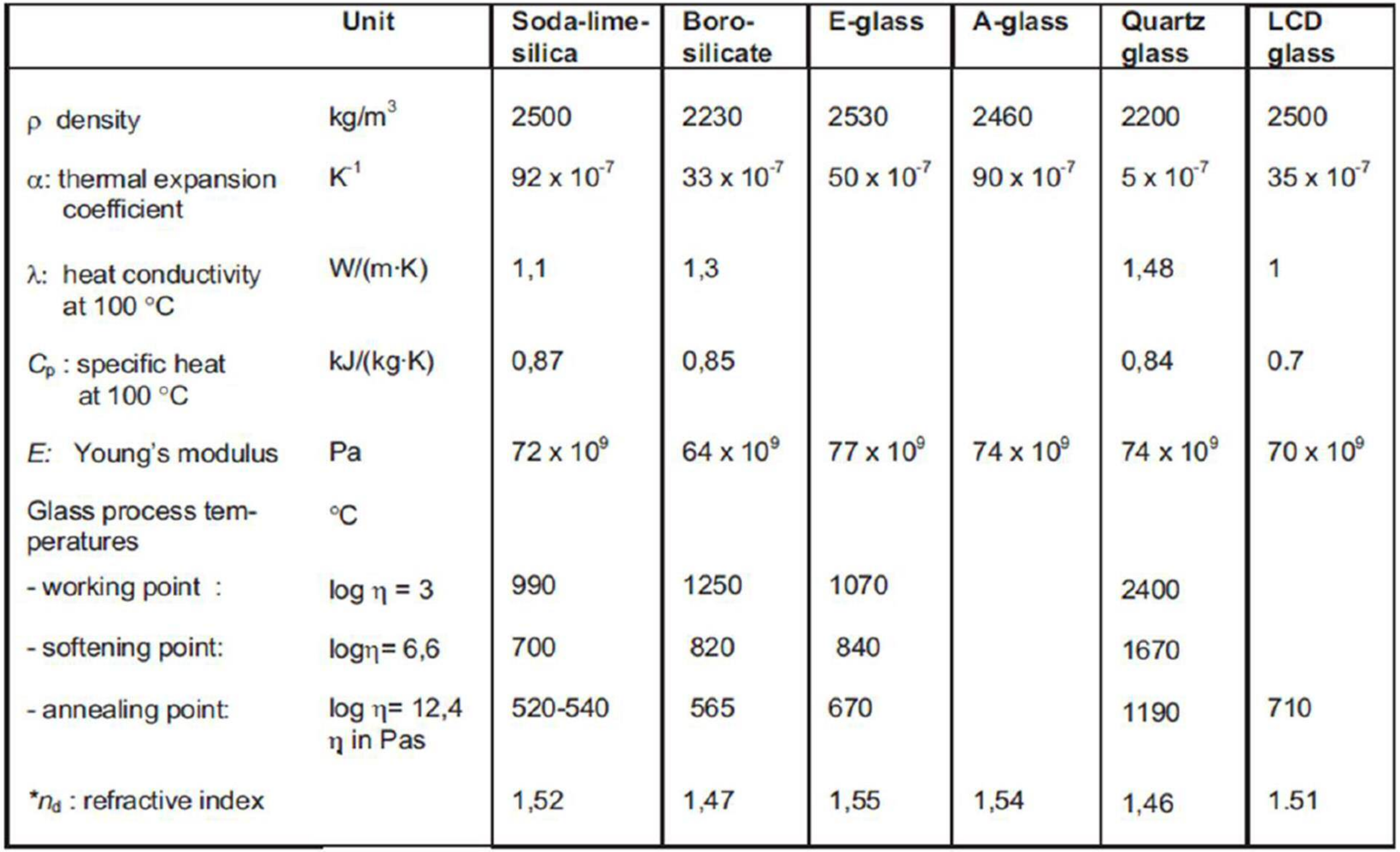


Main Group	Application	Characteristics
Display glass* ($Al_2O_3 \cdot CaO \cdot B_2O_3 \cdot BaO \cdot SiO_2$)	- Substrate glass for displays (TFT-LCD)	- Low electrical conductivity - Ultra thin (down to 50 µm) - High melting temperatures
Lead crystal ($PbO \cdot K_2O \cdot SiO_2$)	- Art glass - Tableware - Decoration enamels	- High purity - High refractive index value
Vitreous silica (SiO_2)	- Optical glass fiber (telecommunication) - Halogen lighting - Laboratory and chemical equipment	- Purity - High-temperature resistance - Very high thermal shock resistance

* Several types of display glasses exist, depending on their use (e.g. in contact with electronics or cover glass). Cover glasses also contain alkalis (mainly sodium) to enable strengthening by ion exchange treatment

Making glass

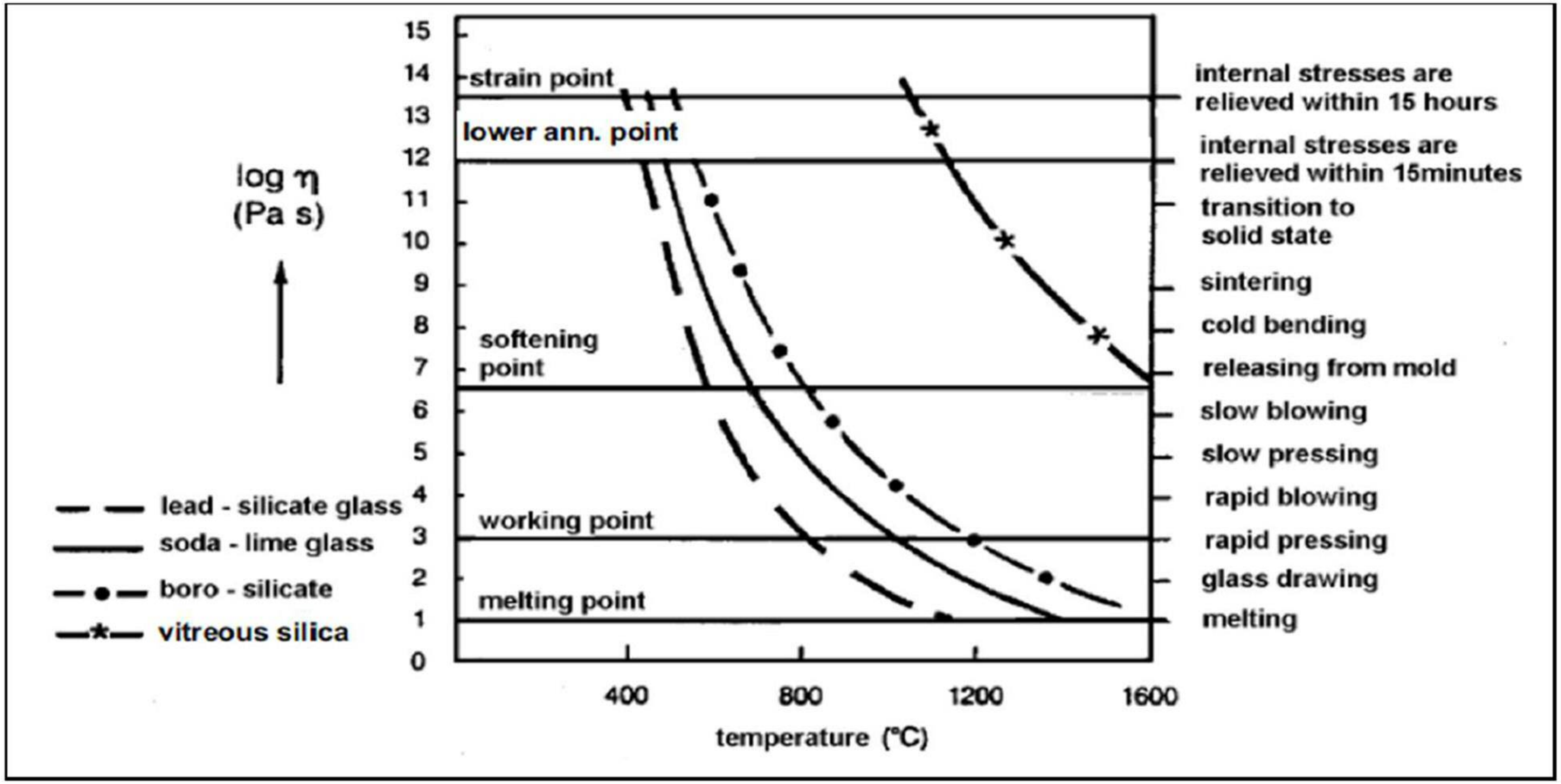
Example of some of glass properties



	Unit	Soda-lime-silica	Boro-silicate	E-glass	A-glass	Quartz glass	LCD glass
ρ density	kg/m^3	2500	2230	2530	2460	2200	2500
α: thermal expansion coefficient	K^{-1}	92 x 10^{-7}	33 x 10^{-7}	50 x 10^{-7}	90 x 10^{-7}	5 x 10^{-7}	35 x 10^{-7}
λ: heat conductivity at 100 °C	W/(m·K)	1,1	1,3			1,48	1
C_p : specific heat at 100 °C	kJ/(kg·K)	0,87	0,85			0,84	0.7
E: Young's modulus	Pa	72 x 10^9	64 x 10^9	77 x 10^9	74 x 10^9	74 x 10^9	70 x 10^9
Glass process temperatures	°C						
- working point :	log η = 3	990	1250	1070		2400	
- softening point:	logη= 6,6	700	820	840		1670	
- annealing point:	log η= 12,4 η in Pas	520-540	565	670		1190	710
*n_d : refractive index		1,52	1,47	1,55	1,54	1,46	1.51

Making glass

Viscosity of commercial glasses



<u>Important note</u>: melting at higher temperatures induce higher costs for melting (energy required) and can also require use of materials with higher thermal resistance for the melting (e.g. refractories), i.e. more expensive

Making glass

Commercial glass compositions

- As seen from the first tables, **different types of applications require different types of glass**

- The composition of the glass is governed by the targeted properties/application, as well as technical and economical considerations

- **Each element brings specific benefits** (but also constraints), and the final commercial composition corresponds to the **best compromise** between these different aspects

- Only the main elements have been presented (SiO_2, Na_2O, CaO, MgO, B_2O_3, Al_2O_3…), but commercial glass batches (often) include numerous other elements in lower quantities to bring specific features (to modify the batch and/or the final glass properties)

Making glass

Commercial glass compositions

- These elements added in smaller quantities can include:
  - ✓ Coloring agents
  - ✓ Fining agents (to promote homogenization during industrial melting and removal of bubbles)
  - ✓ Melting flux (to promote melting at lower temperatures)
  - ✓ Redox active species (to oxidize or reduce the glass melt)
  - ✓ *Nucleating agents (for production of glass-ceramics)*
  - ✓ Other elements to improve specific properties (e.g. modify the refractive index)

- The final combination of all these elements will govern the behavior of the batch during melting and the final properties of the glass produced

Making glass

From the glass composition to the raw materials

- Each element (besides impurity) is added to the glass batch to provide some specific property regarding the glass itself and/or for influencing the melting/processing of the glass

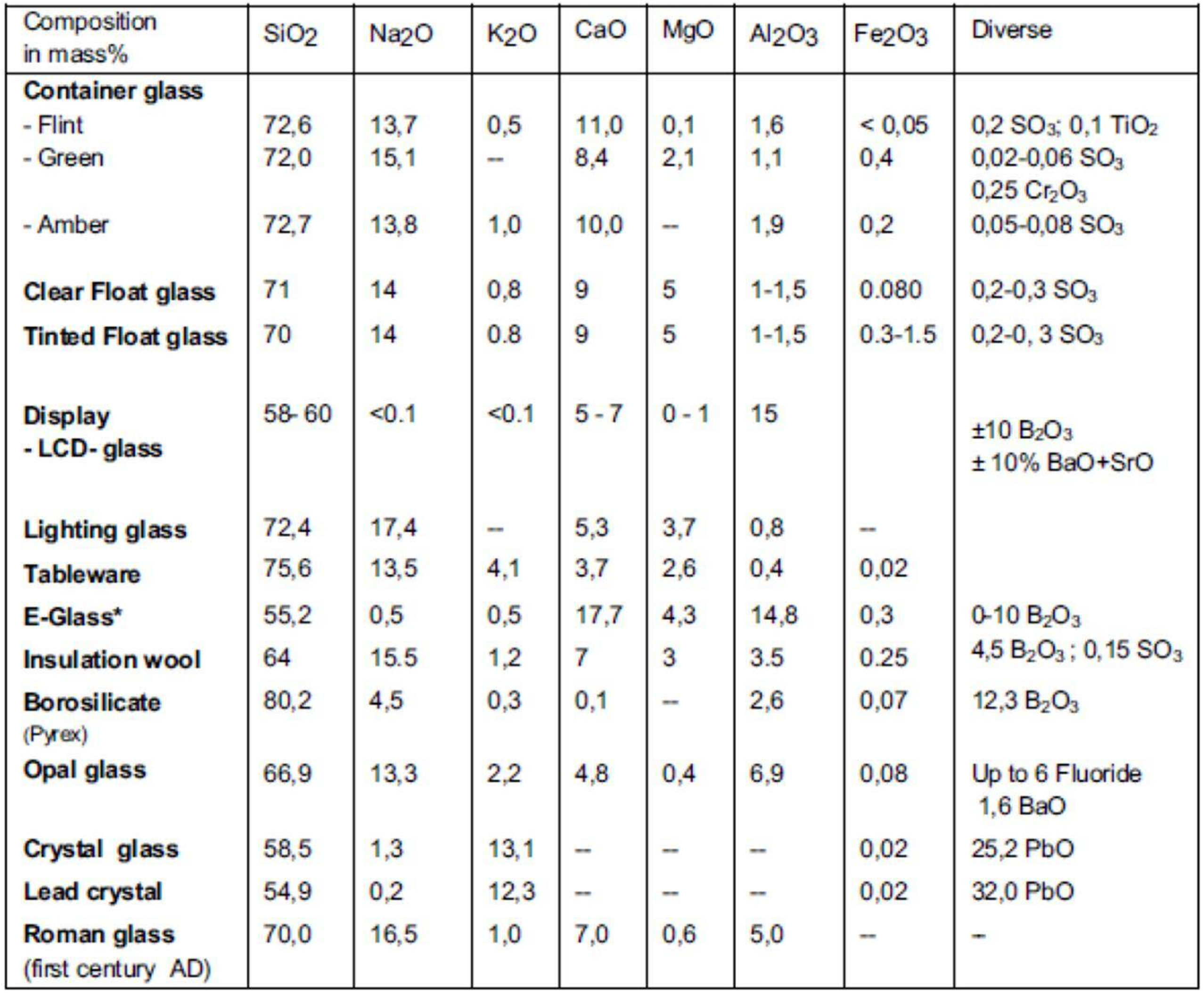
- So far, the glass compositions have been expressed in “% oxide”, but the raw materials are not necessarily introduced in this form

- Each element can be **classified as function of its role** in the final glass and/or in the melting process (network forming, network modifying, intermediate oxides, fining and fluxing agents, coloring ions, cullet…)

- The choice of the raw material will be based on several criteria, described in the following slides

Making glass

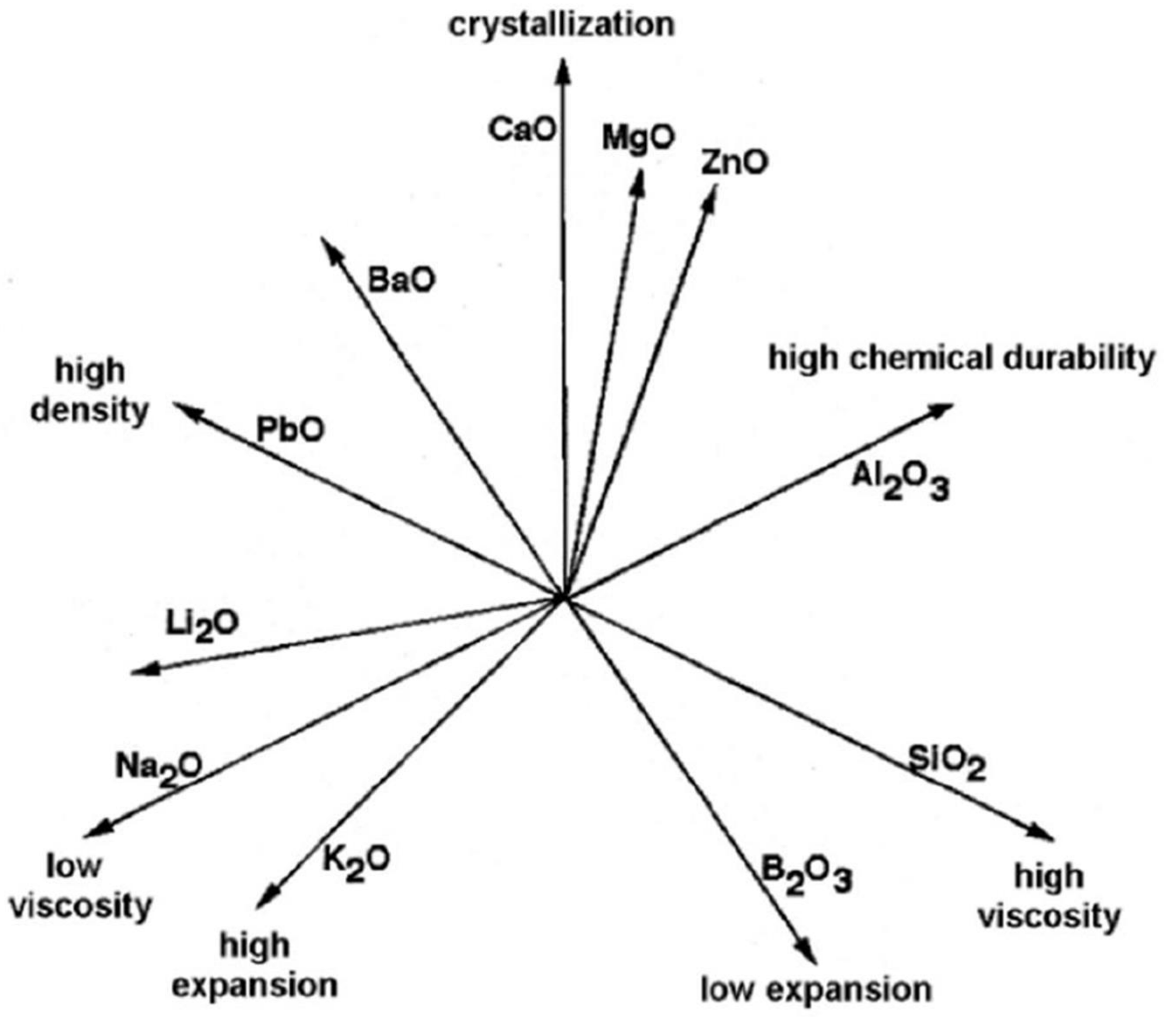
From the glass composition to the raw materials



Composition in mass%	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3	Diverse
Container glass								
- Flint	72,6	13,7	0,5	11,0	0,1	1,6	< 0,05	0,2 SO_3; 0,1 TiO_2
- Green	72,0	15,1	--	8,4	2,1	1,1	0,4	0,02-0,06 SO_3 0,25 Cr_2O_3
- Amber	72,7	13,8	1,0	10,0	--	1,9	0,2	0,05-0,08 SO_3
Clear Float glass	71	14	0,8	9	5	1-1,5	0.080	0,2-0,3 SO_3
Tinted Float glass	70	14	0.8	9	5	1-1,5	0.3-1.5	0,2-0, 3 SO_3
Display - LCD- glass	58- 60	<0.1	<0.1	5 - 7	0 - 1	15		±10 B_2O_3 ± 10% BaO+SrO
Lighting glass	72,4	17,4	--	5,3	3,7	0,8	--	
Tableware	75,6	13,5	4,1	3,7	2,6	0,4	0,02	
E-Glass*	55,2	0,5	0,5	17,7	4,3	14,8	0,3	0-10 B_2O_3
Insulation wool	64	15.5	1,2	7	3	3.5	0.25	4,5 B_2O_3 ; 0,15 SO_3
Borosilicate (Pyrex)	80,2	4,5	0,3	0,1	--	2,6	0,07	12,3 B_2O_3
Opal glass	66,9	13,3	2,2	4,8	0,4	6,9	0,08	Up to 6 Fluoride 1,6 BaO
Crystal glass	58,5	1,3	13,1	--	--	--	0,02	25,2 PbO
Lead crystal	54,9	0,2	12,3	--	--	--	0,02	32,0 PbO
Roman glass (first century AD)	70,0	16,5	1,0	7,0	0,6	5,0	--	--

Making glass

Schematic – elements versus effect on properties



Making glass

Main elements and raw materials employed

- **Network forming oxides**
  - SiO_2, B_2O_3, P_2O_5, GeO_2
  - *Non-oxide components: fluorides, halides, chalcogenides (As_2S_3, GeS_2)*
- **Network modifying oxides**
  - Na_2O, K_2O, Li_2O
  - CaO, BaO, MgO, SrO
- **Intermediate oxides**
  - Al_2O_3, PbO, ZnO, ZrO_2
- **Fining agents/redox active components**
  - Sulphates: Na_2SO_4, $CaSO_4$
  - Oxides: As_2O_3, Sb_2O_3, CeO_2
  - Chlorides: NaCl - Nitrates: KNO_3, $NaNO_3$ - Carbon
- **Fluxing agents**
  - CaF_2, Spodumene (lithium raw material), blast furnace slags/calumite
- **Colouring agents**
  - Fe_2O_3, Cr_2O_3, CoO, Mn_2O_3, Se, Fe^{3+}/S^{2-}, rare earth oxides, sulfides, selenides
- **Cullet (recycled glass, own or external cullet)**

Making glass

Colouring elements- Transition metals

Ion	Content expressed as	Color effect
Fe^{2+}	Fe_2O_3	green
Fe^{3+}	Fe_2O_3	soft yellow
Co^{2+}	Co_3O_4	blue
Ni^{2+}	NiO	brown
Cr^{3+}	Cr_2O_3	green
Cr^{6+}	Cr_2O_3	soft yellow
Mn^{3+}	MnO_2	purple
Cu^{2+}	CuO	blue green

Reminder: Fe is always present as an impurity from the raw materials. The iron content must be carefully controlled as it has a strong impact n the final coloration of the glass

Making glass

Colouring elements- Other elements

- Residual **ferric iron (Fe^{3+}),** in combination with **sulfides** (reduced molten glass) and alkali components, will cause formation of amber chromophore, coloring the glass **amber**.
- **Cadmium sulfides** (CdS) for yellow glass
- **Cadmium selenides** (CdSe) or **Gold chloride** $AuCl_3$ with reduction agent (forms very small gold particles in the glass) for **red** colorizing
- **Selenium** is the colorizing agent for **bronze** glass
- **Cerium oxides**, to oxidize the melt and for absorption of X-Rays. At high concentrations cerium oxide may colour the glass light yellow
- A mixture of **Nd_2O_3 & Pr_2O_3** colorize the glass **blue**
- NB: A combination of selenium + cobalt can be used as "decolorizing" agent in flint glass production to mask the coloration due to the presence of iron as impurity

Making glass

Example – Oxide content in raw materials

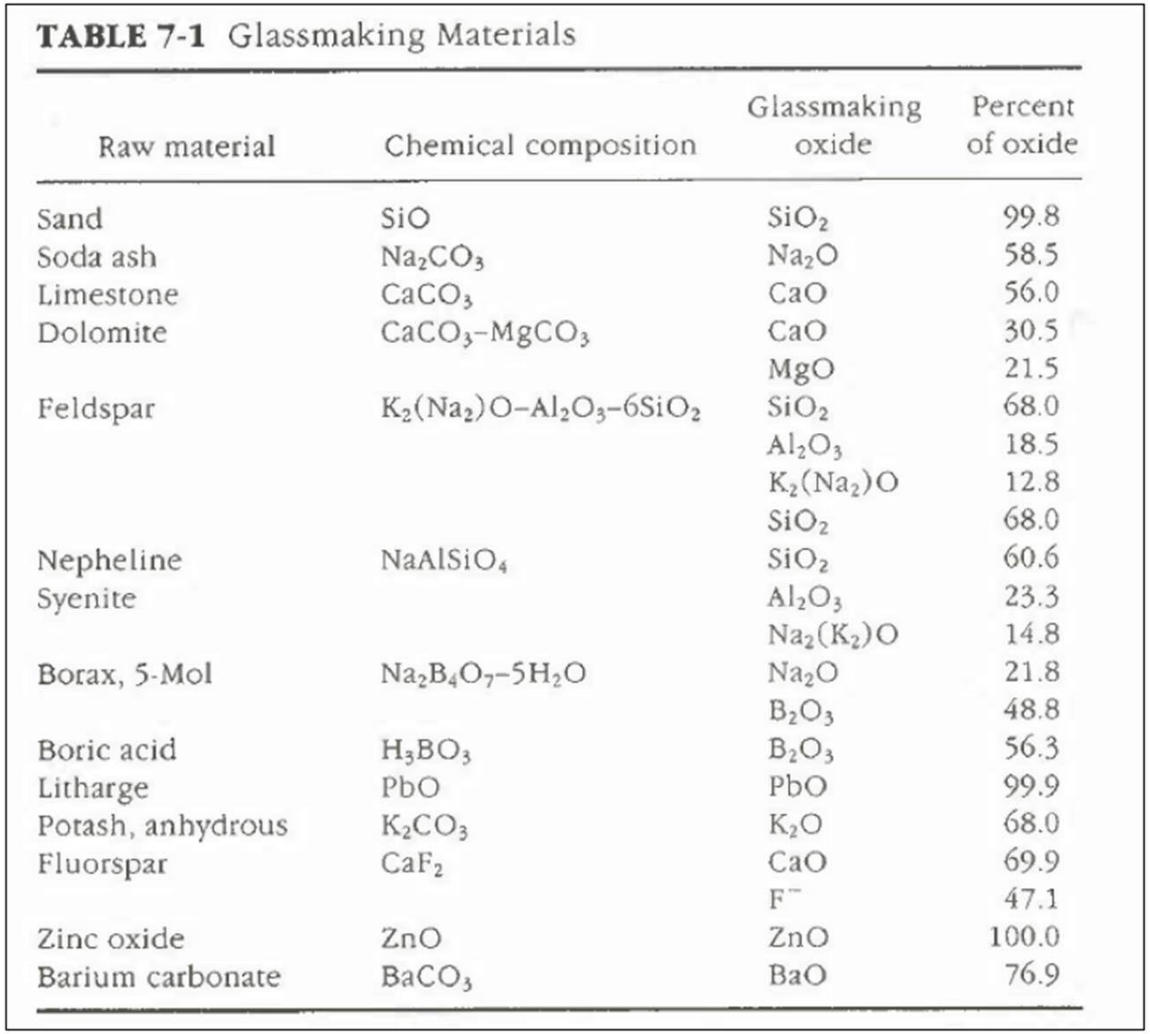


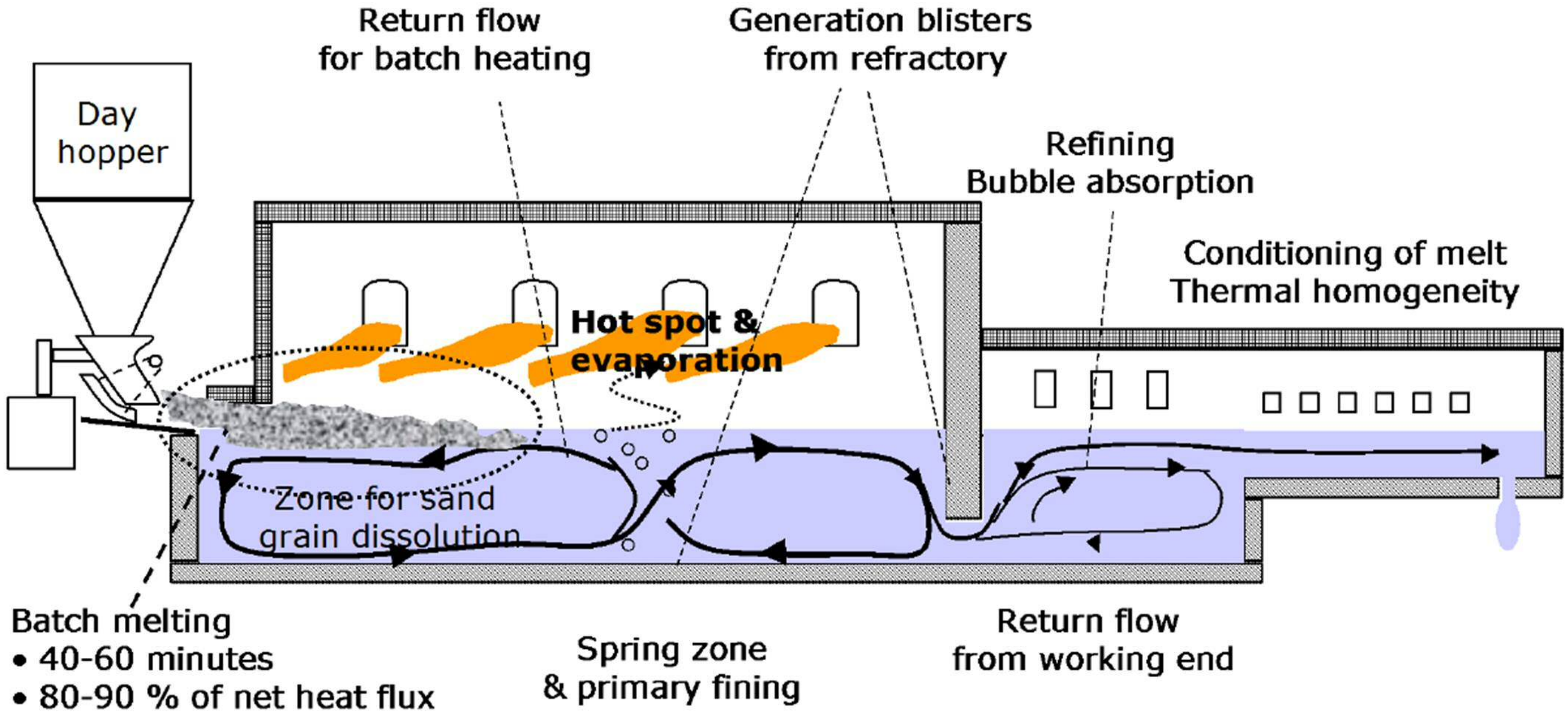
TABLE 7-1 Glassmaking Materials

Raw material	Chemical composition	Glassmaking oxide	Percent of oxide
Sand	SiO	SiO_2	99.8
Soda ash	Na_2CO_3	Na_2O	58.5
Limestone	$CaCO_3$	CaO	56.0
Dolomite	$CaCO_3$–$MgCO_3$	CaO	30.5
		MgO	21.5
Feldspar	$K_2(Na_2)O$–Al_2O_3–$6SiO_2$	SiO_2	68.0
		Al_2O_3	18.5
		$K_2(Na_2)O$	12.8
		SiO_2	68.0
Nepheline	$NaAlSiO_4$	SiO_2	60.6
Syenite		Al_2O_3	23.3
		$Na_2(K_2)O$	14.8
Borax, 5-Mol	$Na_2B_4O_7$–$5H_2O$	Na_2O	21.8
		B_2O_3	48.8
Boric acid	H_3BO_3	B_2O_3	56.3
Litharge	PbO	PbO	99.9
Potash, anhydrous	K_2CO_3	K_2O	68.0
Fluorspar	CaF_2	CaO	69.9
		F^-	47.1
Zinc oxide	ZnO	ZnO	100.0
Barium carbonate	$BaCO_3$	BaO	76.9

G. McLellan and E. Shand, Glass Engineering Handbook, 3rd edition, 1984, Ed: McGraw-Hill Book Company

Making glass

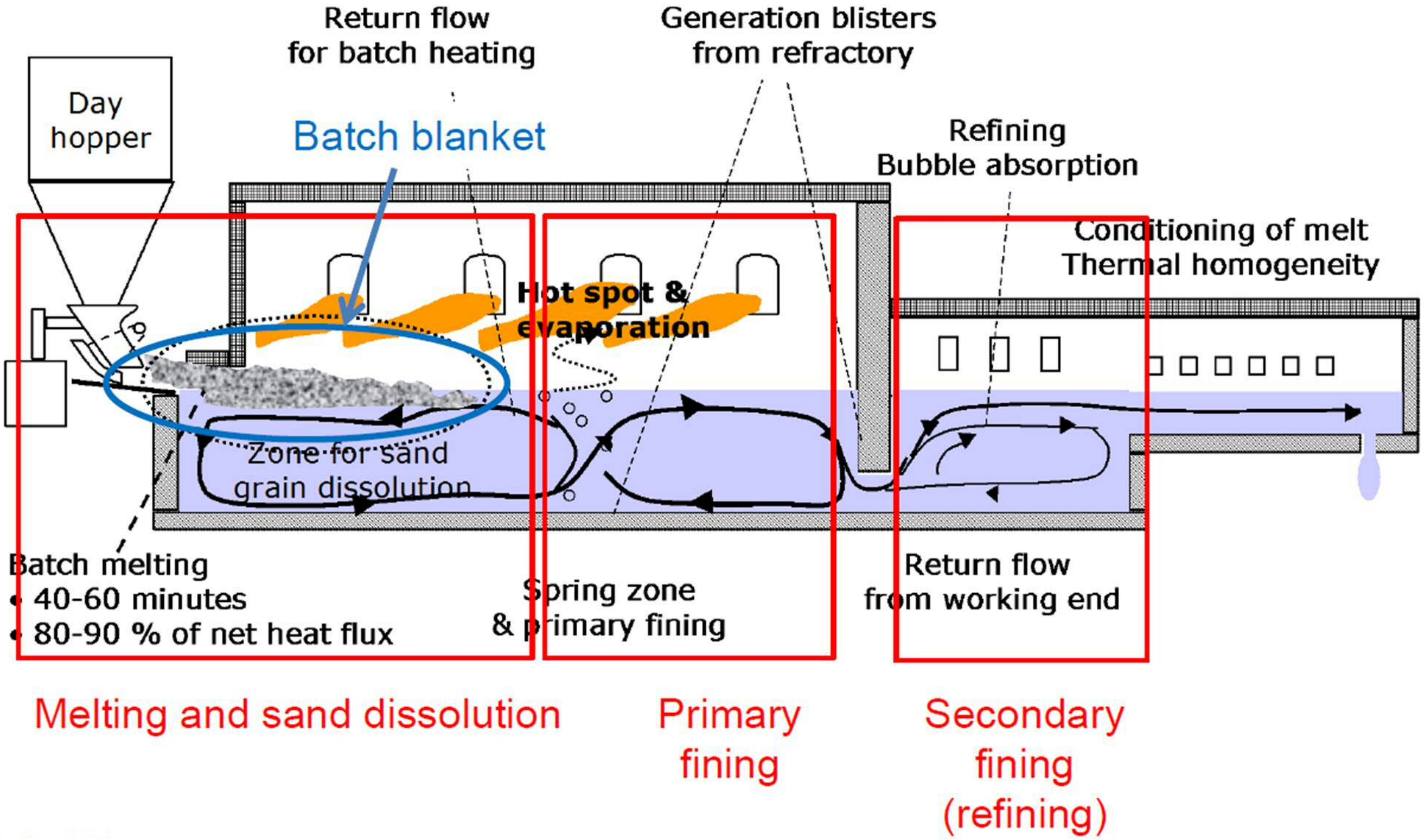
Schematic of an industrial glass melting tank



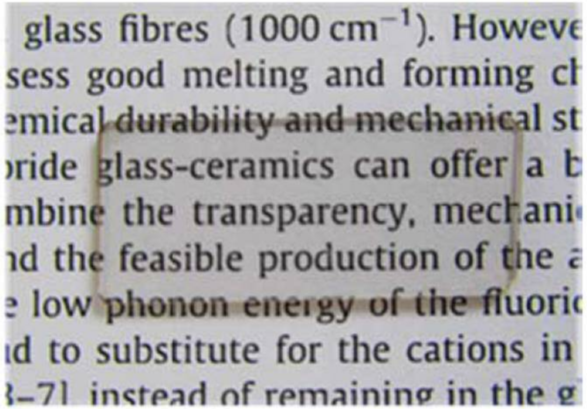
* *This is a schematic representation, but many different furnace designs exist*

Making glass

Melting and fining in the furnace



Forming



glass fibres (1000 cm^{-1}). Howev
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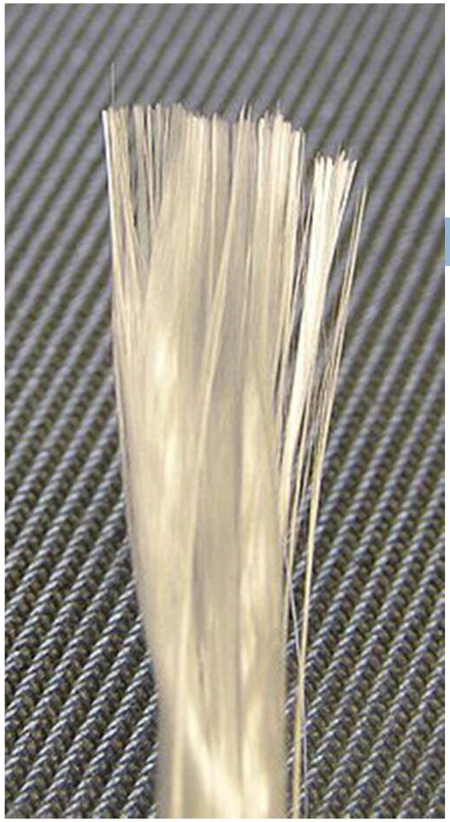

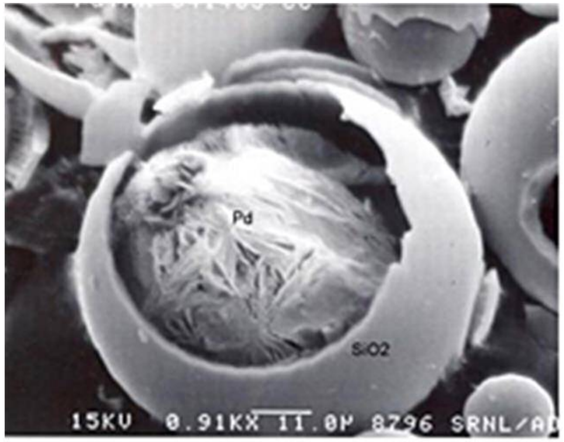

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Homogeneity and phase separation

We tend to think of glass as a very homogeneous material, but it can be inhomogeneous to a greater or lesser extent. Even silica, the most homogeneous of glasses, is inhomogeneous on a scale smaller than the wavelength of light. The fundamental random nature of glass means that there are small fluctuations in density. Even in commercial soda-lime-silica glass, there is some regions of the structure consisting of compositional variations.

On the other hand, a great variety of binary and multicomponent systems show liquid-liquid immiscibility and tend to separate into two or more liquid phases in a well defined interval of compositions and temperatures. It is a phenomenon known in oxide glass forming systems, particularly, SiO_2 and B_2O_3.

Controlled phase separation provides glasses with special properties
Phase separation is often the precursor of controlled crystallization in glass-ceramics

Homegeneity and phase separation

-The most common systems present phase separation (with a suitable thermal history)

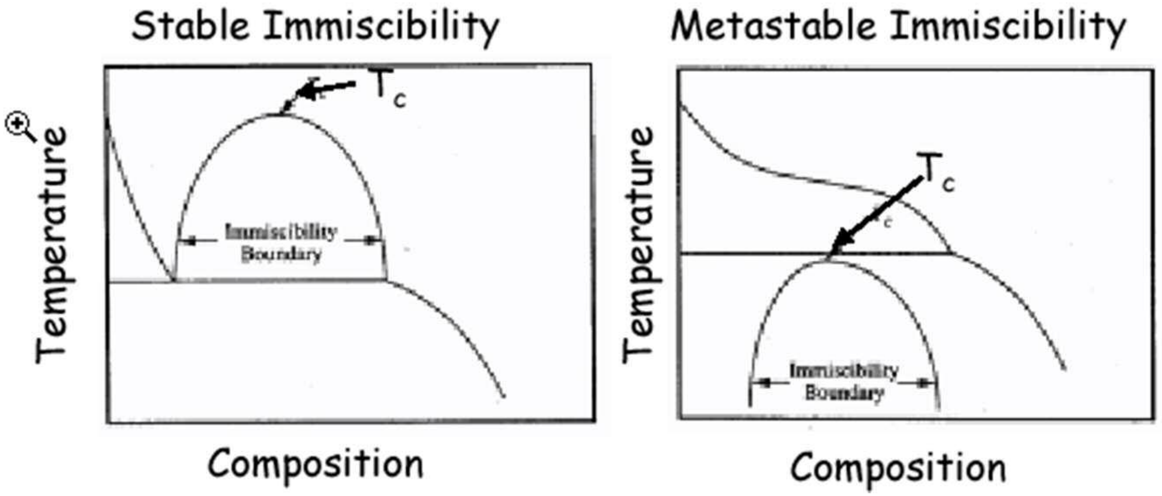
-The size of the phase separation regions depends on the cooling rate- analogous to the critical cooling rate for nucleation/crystallization

-Fast cooling up to temperatures below T_g to avoid phase separation. There is no separation when $T>T_C$ or $T<T_g$

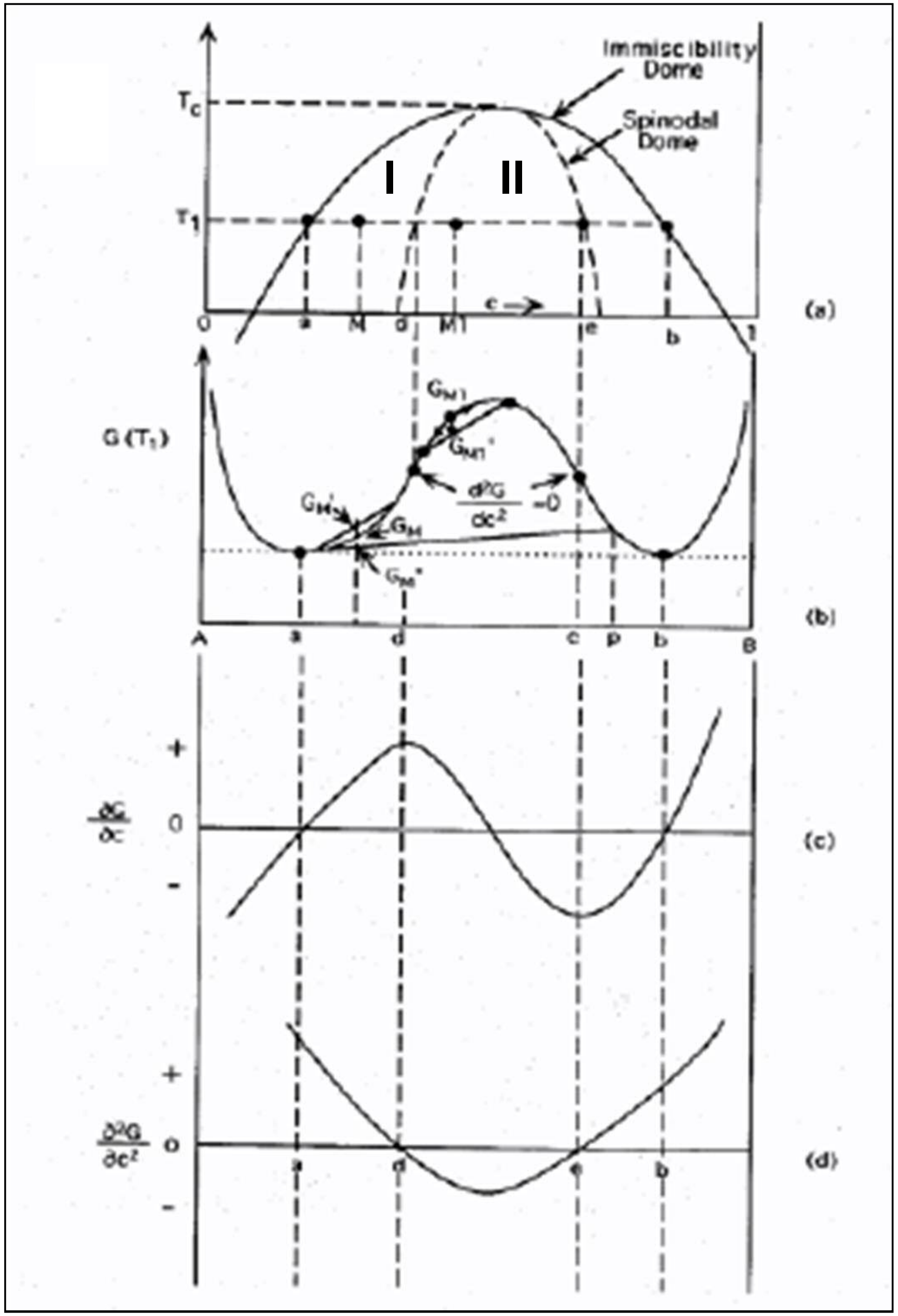
-The more viscous melts are less prone to phase separation than the more fluid ones ($D \sim \eta^{-1}$)

***Stable immiscibility*: $T_C>T_{líquidus}$** ($T_{liq.}$ is the maximum temperature at which the crystals are stable in the melt).
-very common in binary systems RO-SiO_2, -GeO_2, -B_2O_3.
-fast kinetics (low viscosity)

Metastable immiscibility: $T_C<T_{líquidus}$: "Liquidus curve takes S form"
- The crystals are stable, but in general, the kinetics of phase separation are faster than for crystallization (the necessary atomic rearrangements for crystallization slow down this process)
-Slower kinetics (high viscosity)
-Binary system Li_2O-SiO_2, Na_2O-SiO_2, Na-borosilicates



Phase-separation mechanisms



Zone I: $\frac{\partial G}{\partial x}$ increases $\frac{\partial^2 G}{\partial x^2} > 0$

Metastability

Nucleation and growing, ΔG*

Zone II: $\frac{\partial G}{\partial x}$ decreases $\frac{\partial^2 G}{\partial x^2} < 0$

Instability

Spinodal decomposition

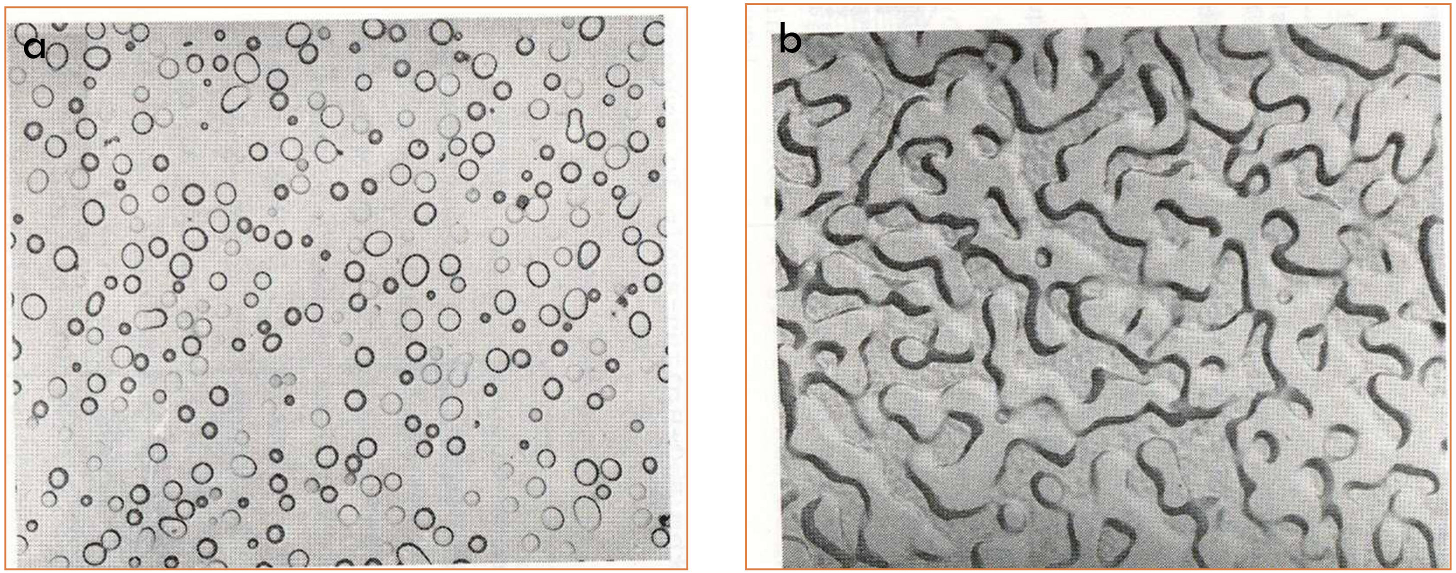
Without considering the involved mechanism, the final result of the separation will be the equilibrium of phases A and B, whose relative proportions are determined from the Lever Rule.

T_C o T_M: critical temperature or miscibility temperature

http://web.mst.edu/~brow/PDF_phase_sep.pdf

Homegeneity and phase separation

Different mechanisms lead to different microstructures of the phase-separated systems:
-Nucleation: discrete, one of the phases (in the case of a binary system) is discontinuous, well-defined interphases, different composition.
-Spinodal: interconnected phases with a gradual variation of the composition from one to the other. Diffuse interphases, the compositions vary with time



Nucleación **Espinodal**

Separation textures:
a) Sodalime glass treated at 740ºC, 7 1/2 h (x14000),
b) Vycor glass (borosilicate glass) treated at 700ºC, 5 1/2 h (x24000)

Homegeneity and phase separation

The SiO_2-B_2O_3-Na_2O system

Vycor (96% SiO_2)

-Choose a composition close to the center of the immiscibility gap in order to create a spinodal-type microstructure.

- Melting at 1500°C, processing (pressed, blown, etc.) at $T>T_C$.

-Thermal treatment at ~ 600ºC to develop a microstructure of interpenetrated phases with limited compositions.

One phase is 96% SiO_2

The other phases is Na-borosilicate soluble in acid

-The soluble phase is lixiviated in H_2SO_4 at 90ºC to leave a porous skeleton rich in silica.

-Porous substrate (filters, catalytic supports, etc.)

-The key is the development of a spinodal microstructure

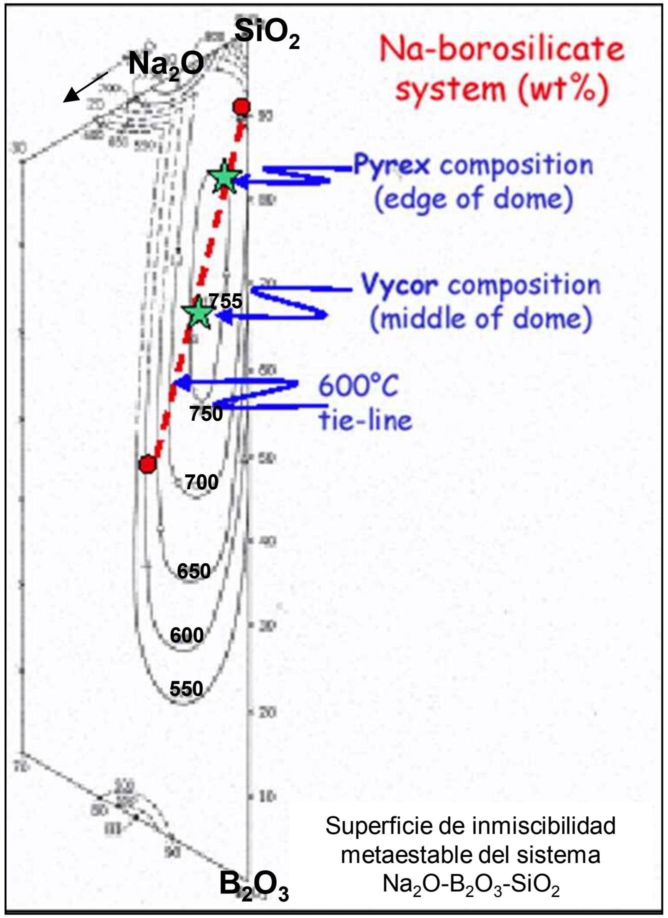
Pyrex:

Another phase-separated sodium borosilicate glass composition.

-Lower content in B_2O_3 and Na_2O than Vycor; close to the border of the immiscibility gap. Morphology of nucleated droplets in the matrix

-Fast cooling through T_g to produce sodium-borate droplets 20-50 Å in a matrix rich in chemically inter silica.

-The sodium borate reduces the melting temperature but the microstructure of the droplets ensure good chemical durability (and a low thermal expansion coefficient)



Superficie de inmiscibilidad metaestable del sistema Na_2O-B_2O_3-SiO_2

Devitrification or glass crystallization

-The process in which a stable solid phase with regular geometric order is formed from a structurally disordered precursor.

-The driving force is the decrease in the energy of the system when the melt is cooled down below the “liquidus” temperature.

-The vitreous substances are frozen in an undercooled state with a energetic content higher than that of the thermodynamic equilibrium and they can evolve (under favorable conditions) towards the formation of stable crystalline phases. In such cases, the crystallization is defined as devitrification, since it is a phenomenon that goes against the proper glass nature.

-Main mechanisms (Tamman): **Nucleation and crystallization**

Devitrification or glass crystallization

Nucleation

Homogeneous nucleation

The nuclei are formed from the melt components and they are of the same chemical composition as the crystalline phase that develops from them. Classical theory for the stationary-state thermal nucleation (equilibrium). Embryo---critical size---nucleus

Heterogeneous nucleation

Nucleation from already existing particles of chemical composition not related with the melt composition due to impurities, bubbles, container walls, glass surface. There is a decrease of the interfacial energy and hence a variation of the free energy with respect to the homogeneous nucleation.

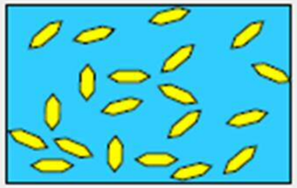
$$\cos\vartheta = \frac{\sigma_{HF} - \sigma_{HC}}{\sigma_{CF}} \qquad \left(\Delta G_{\text{máx}}\right)_{het} = \Delta G_{\text{máx}} \bullet f_{\vartheta}$$

Influence of phase separation on nucleation

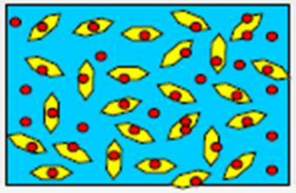
- ✓ Formation of new phases with a new chemical composition
- ✓ Formation of a new interphase liquid-liquid

Devitrification or glass crystallization

Nucleation

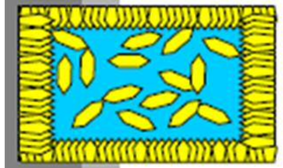


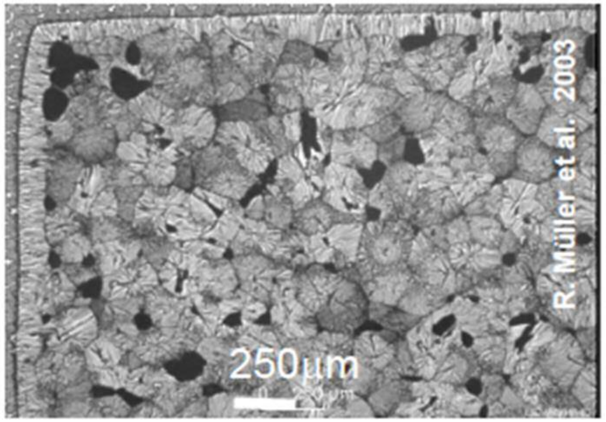
„homogeneous“
volume nucleation
quasi *iso-chemical*
quasi *polymorphic*
transformation



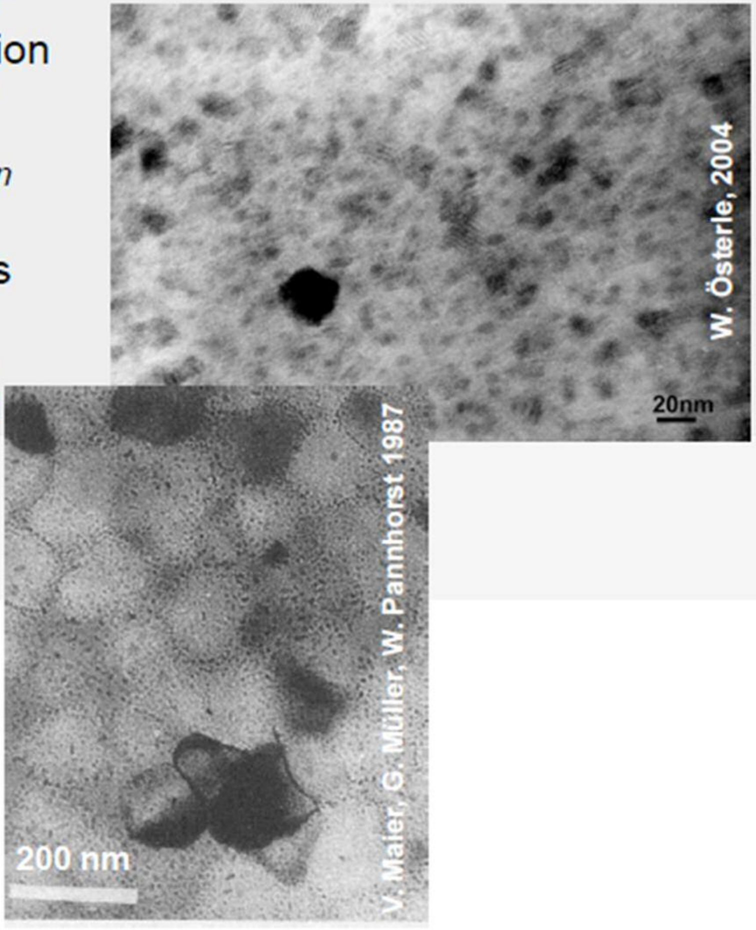
catalyzed hetrogeneous
volume nucleation
liquid-liquid phase separation
redox-change, photo induced,
change of coordination,

surface vs. volume nucleation
coast –island structures





R. Müller et al. 2003

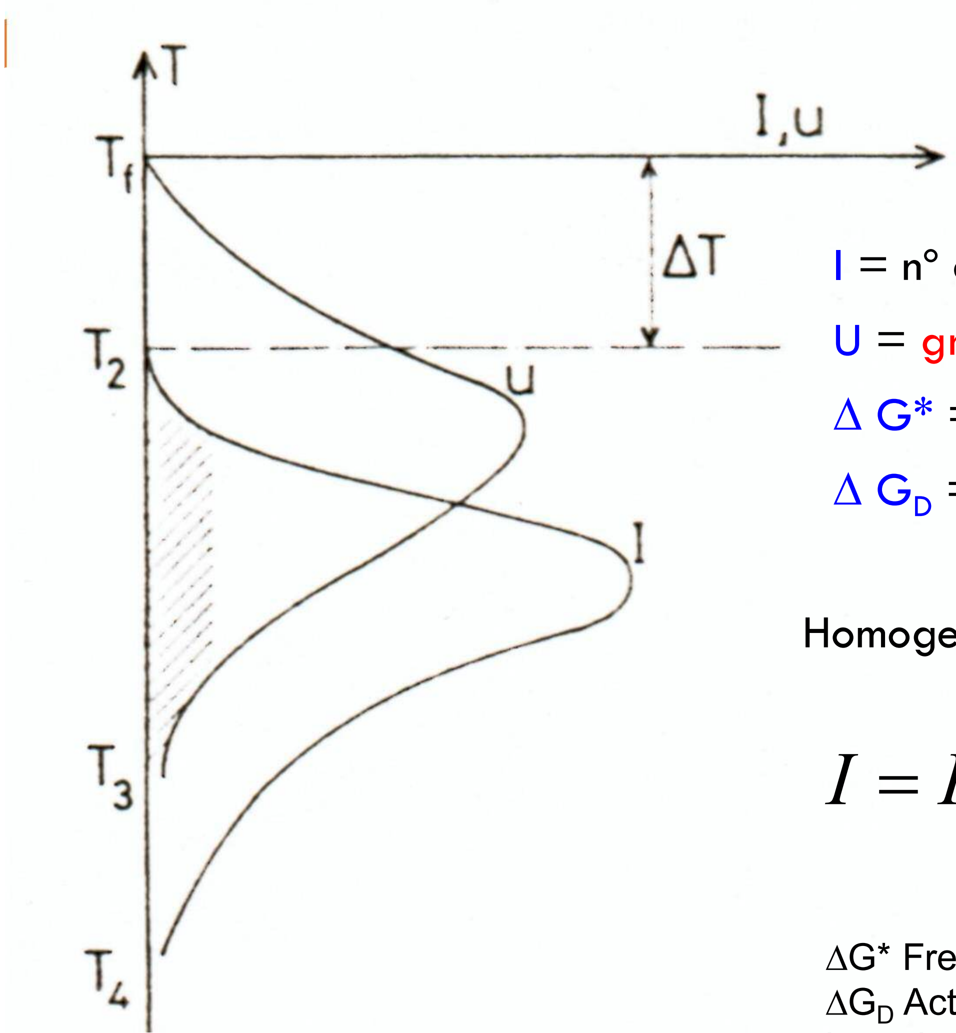


W. Österle, 2004

V. Maier, G. Müller, W. Pannhorst 1987

Devitrification or glass crystallization

Nucleation



I = n° de nuclei/time = nucleation rate

U = growing rate

ΔG^* = potential-energy barrier

ΔG_D = diffusional barrier

Homogeneous nucleation

$$I = K_v \exp(\Delta G_D + \Delta G^*)/KT$$

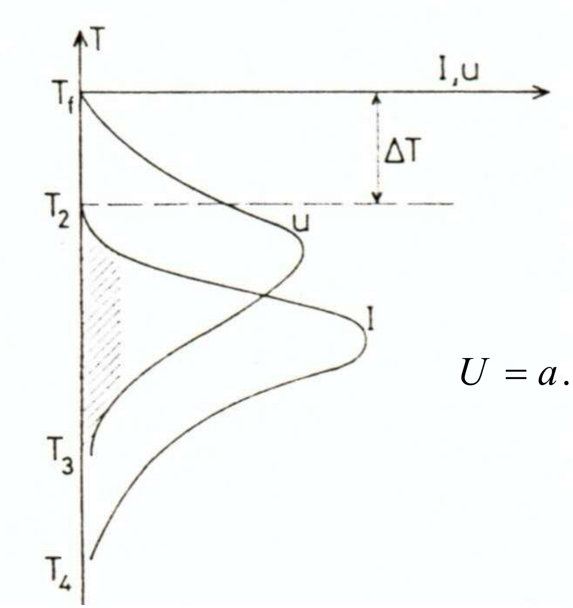
ΔG^* Free energy to form a critical nucleus
ΔG_D Activation energy for the transport through the interphase (diffusion barrier of the ions)
K_v is essentially constant

Devitrification or glass crystallization

Crystal growth

-Successive deposition of material on nuclei with critical size to form crystals.
- Depends (to a greater extent than for nucleation) on the transport possibilities of the chemical components to the developing crystal.
- U presents, as well nucleation rate I, a maximum as a function of T.

At elevated T, growth is limited: difficulty to dissipate the liberated crystallization heat, and at low T, growth is stopped by the continuous and fast increase in the glass viscosity which hinders the diffusion of the elements constituting the crystal.



$$U = a.A.\left[\exp\frac{-E_D}{RT}\right]\left[1-\exp\frac{-\Delta G}{RT}\right]$$

$$\Delta G = \frac{T_L - T}{T_L} \times L$$

a, linear crystal growth; A, frequency factor; $E_{D,}$ activation energy for the diffusion; L latent molar melting heat

*The maxima of the rate curves I and U are not normally coincident. If the cooling from the melt is slow in the interval of U maximum and fast in the maximum of I, a small number of crystals is obtained. The opposite leads to the uniform formation of numerous crystals more or less developed depending on the cooling rate.
In industrial production, it is important to determine the suitable cooling curve of the glass, in some cases for avoiding undesirable devitrification and in other cases to control it, as is the case of glass-ceramics.

Devitrification or glass crystallization

Kinetic considerations for glass forming

The qualitative description of the ability of glass formation must consider not only the simultaneous nucleation and growing processes but also the cooling rate.

Uhlman $X = \frac{V_C}{V} < 10^{-6}$

If $V_C << V$

$$\frac{V_C}{V} \approx g I_0 U^3 \tau^4$$ at T=cte

Critical cooling rate

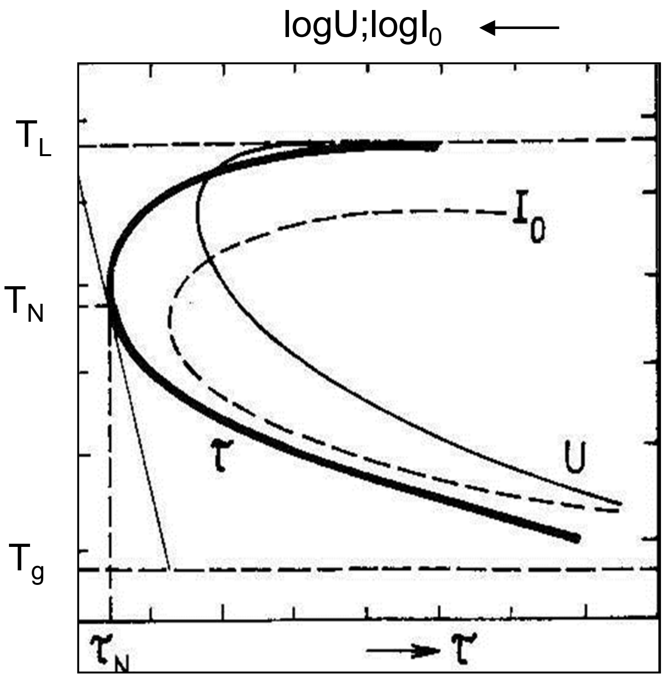
$$\boxed{\left(\frac{dT}{d\tau}\right)_k = \frac{\Delta T_N}{\tau_N} \qquad (Ks^{-1})}$$

$\Delta T_N = T_L - T_N$

Isothermal TTT diagram

(TTT-time, temperature, transformation)

Dependence of time with temperature at X constant



$X = V/V_C = 10^{-6}$, from the equation

Devitrification or glass crystallization

Kinetic of volume crystallization

Kolmogorov, Johnson, Mehl, Abrami (KJMA) Equation

Crystallization $\alpha \longrightarrow \beta$ $$X_\tau = \frac{V_\tau^\beta}{V^\alpha}$$

Conversion degree as a function of t at a given T

Polycrystalline material

$$X_\tau = 1 - \exp\left(-k\tau^m\right)$$

$$\log \ln \frac{1}{1 - X_\tau} = m \log \tau + \log k$$

m, Avrami constant

Indicates the order of the temporal dependence
of the nucleation and the number of growing directions

m decreases one unit if the nucleation
is independent of time

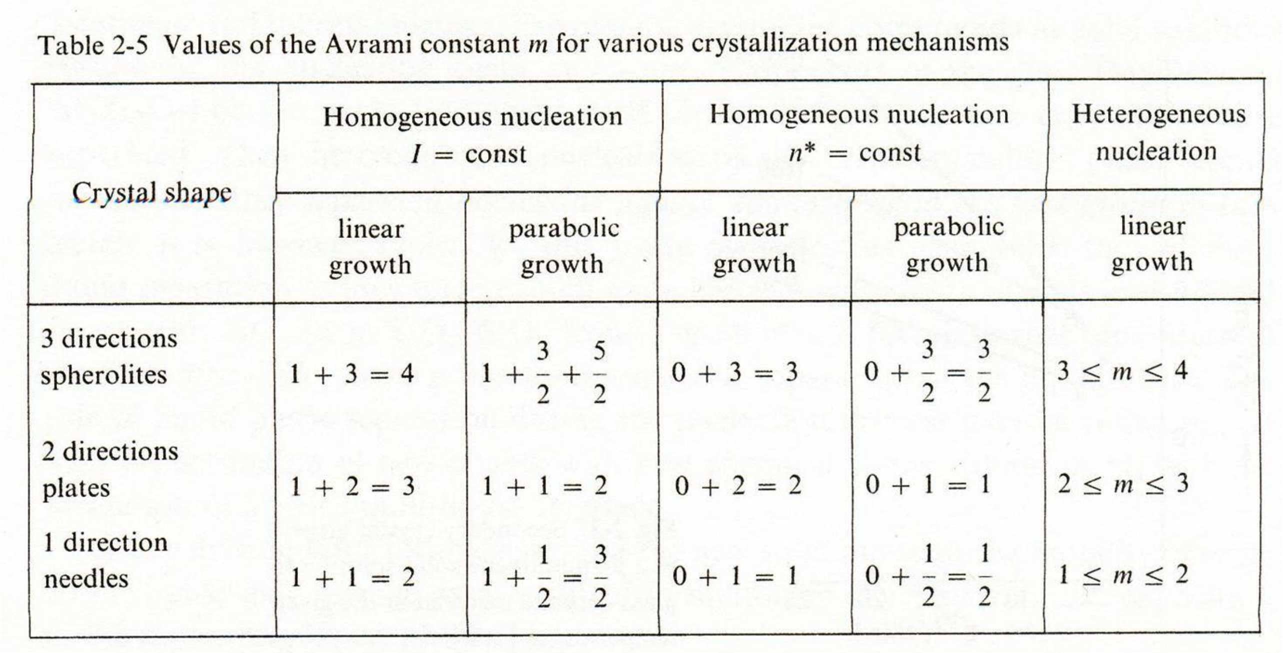


Table 2-5 Values of the Avrami constant m for various crystallization mechanisms

Crystal shape	Homogeneous nucleation I = const		Homogeneous nucleation n^* = const		Heterogeneous nucleation
	linear growth	parabolic growth	linear growth	parabolic growth	linear growth
3 directions spherolites	$1 + 3 = 4$	$1 + \frac{3}{2} + \frac{5}{2}$	$0 + 3 = 3$	$0 + \frac{3}{2} = \frac{3}{2}$	$3 \leq m \leq 4$
2 directions plates	$1 + 2 = 3$	$1 + 1 = 2$	$0 + 2 = 2$	$0 + 1 = 1$	$2 \leq m \leq 3$
1 direction needles	$1 + 1 = 2$	$1 + \frac{1}{2} = \frac{3}{2}$	$0 + 1 = 1$	$0 + \frac{1}{2} = \frac{1}{2}$	$1 \leq m \leq 2$

Devitrification or glass crystallization

Examples of systems with volume crystallization

1. SiO_2-R_2O: R=Li ($Li_2O.2SiO_2$ o $Li_2O.SiO_2$)
2. SiO_2-Al_2O_3 (mullite)
3. SiO_2-$Al_2O_3.Li_2O$
4. SiO_2-Al_2O_3-MgO
5. SiO_2-Al_2O_3-ZnO
6. SiO_2-Al_2O_3-CaO
7. SiO_2-Al_2O_3-MgO-K_2O (fluoromicas)
8. CaO-P_2O_5-Na_2O-K_2O-MgO
9. SiO_2-Al_2O_3-Si_3N_4-(Li_2O, Na_2O, MgO, BaO, BeO, Y_2O_3)
10. SiO_2-Al_2O_3-B_2O_3-(MgO,CaO,BaO, ZnO, PbO)

Outline of the presentation

1. The Nature of glass
    - 1.1. What is glass? Classification
    - 1.2. Making glass
    - 1.3. Phase separation and devitrification
    - 1.4. Controlled devitrification. Glass-ceramics

2. Melt-derived bioactive glass. Bioglass
3. Bioactive sol-gel glass
4. Phosphate glasses
5. Bioactive borate glasses
6. Bio-Glass-ceramics
7. Bioactive glass coatings and composites
8. Glasses for radiotherapy

Controlled devitrification. Glass-ceramics

- Glass-ceramic materials are polycrystalline solids which contain a residual glassy phase obtained from the controlled crystallization of glasses.
- Widely varying crystallinity between 0.5% and 99.5%, most frequently 30-70%
- Can be mass produced by any glass-forming technique
- It is possible to design the nano or microstructure of the material
- Most have zero or very low porosity
- It is possible to combine desired properties
- Stockey 1959

Controlled devitrification. Glass-ceramics

Microstructural Design

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

GLASS-CERAMICS

Combination of properties

high thermal and chemical stability

harder and tougher than glasses

controllable electrical properties

optical transparency

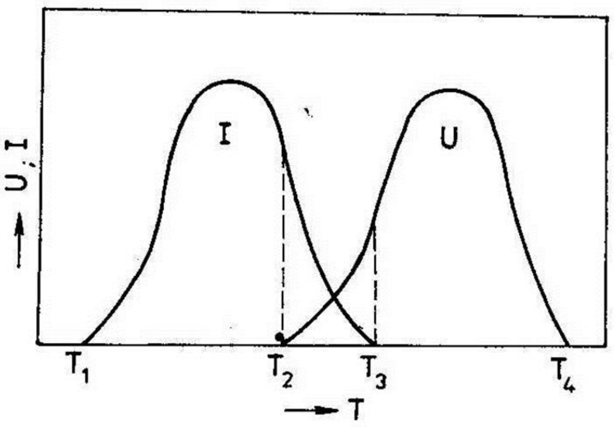
bioactivity

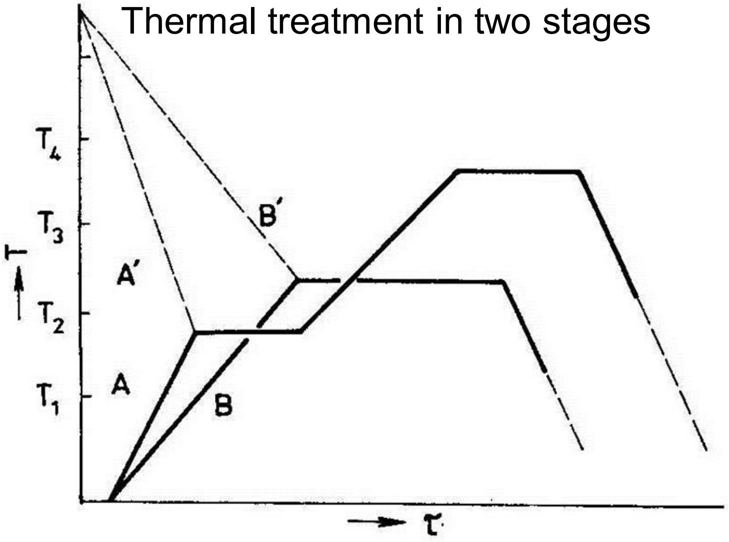
controllable TEC

Controlled devitrification. Glass-ceramics

- Melting and forming using the conventional procedures employed in the glass industry.
- Piece forming: pouring, pressing, blowing, rollers…
- Suitable thermal treatment:

  Nuclei formation and microcrystal growth




Thermal treatment in two stages

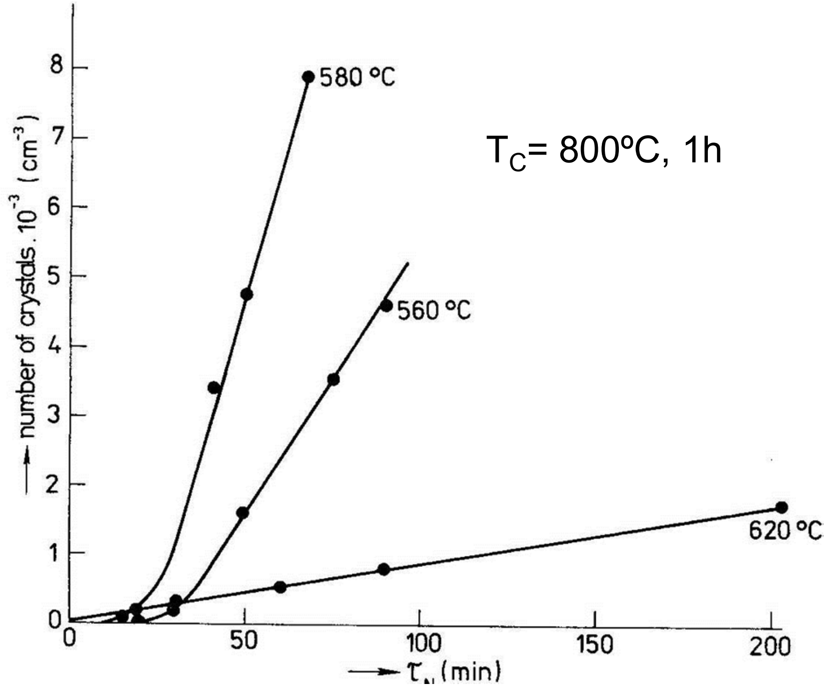
- Nucleating agents: TiO_2, ZrO_2, P_2O_5, V_2O_5, Cr_2O_3, phosphates, fluorides....sulphides, metals Cu, Ag, Au, Pt, other noble metals. Photo-nucleation

The nucleating substances must dissolve into the glass at high T, but their solubility must decrease during cooling to favor segregation. The nucleation rate must be elevated. The deposition of the precipitated phase is favored by the low interfacial tension, and the epitaxial growth of new crystals is guaranteed by a close similarity between the reticular parameters of both phases.

Controlled devitrification. Glass-ceramics

Methods of study

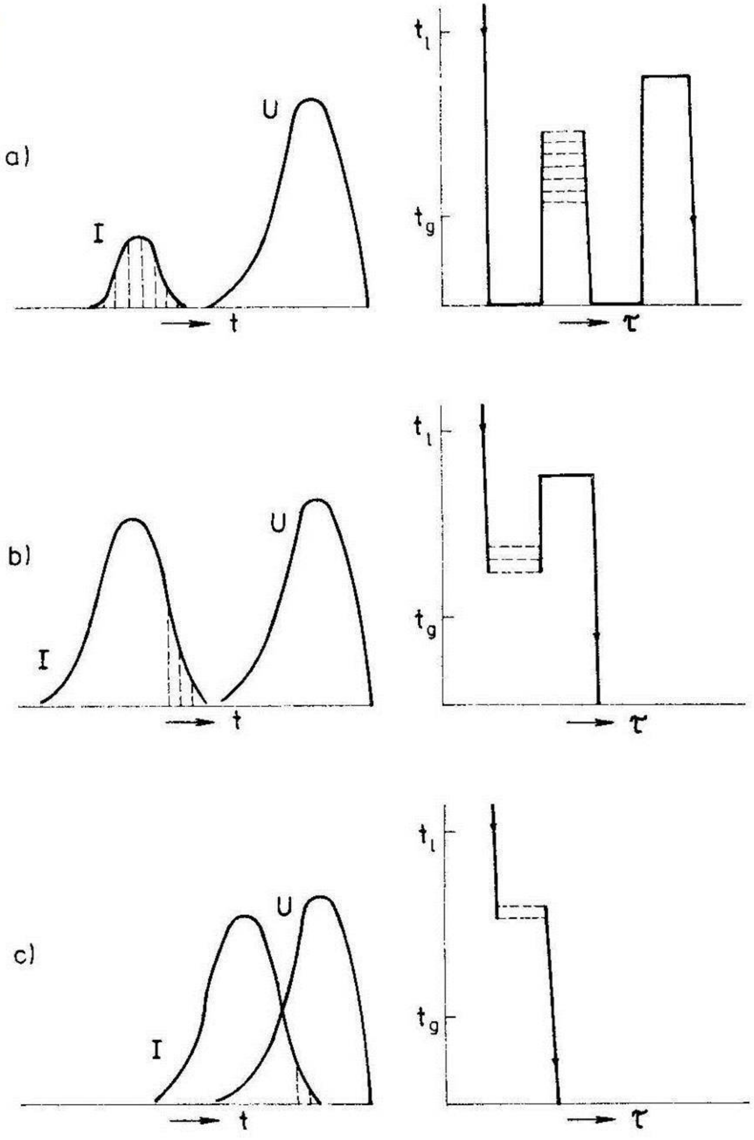
1) Methods of thermal treatment



T_C= 800ºC, 1h

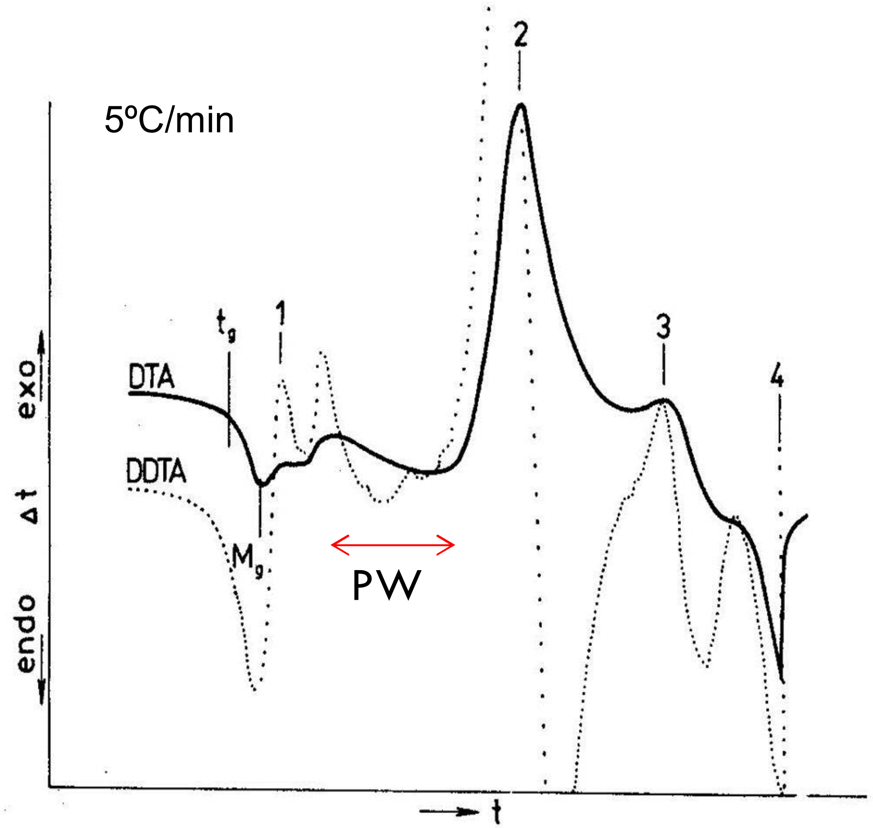
Sodalime glass

Crystals $Na_2O.CaO.3SiO_2$

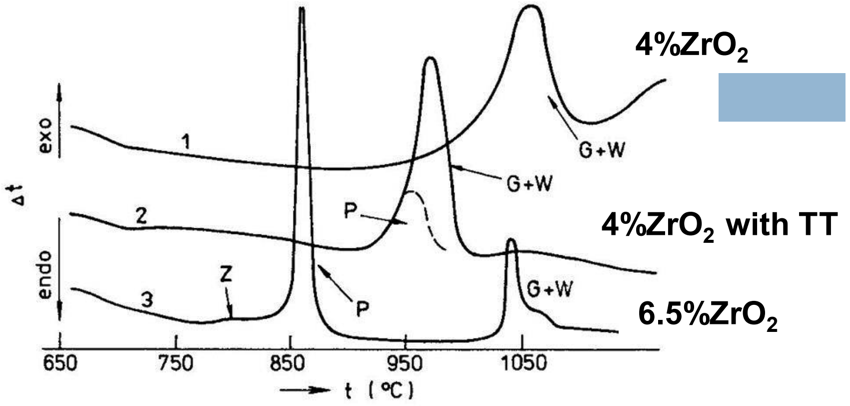


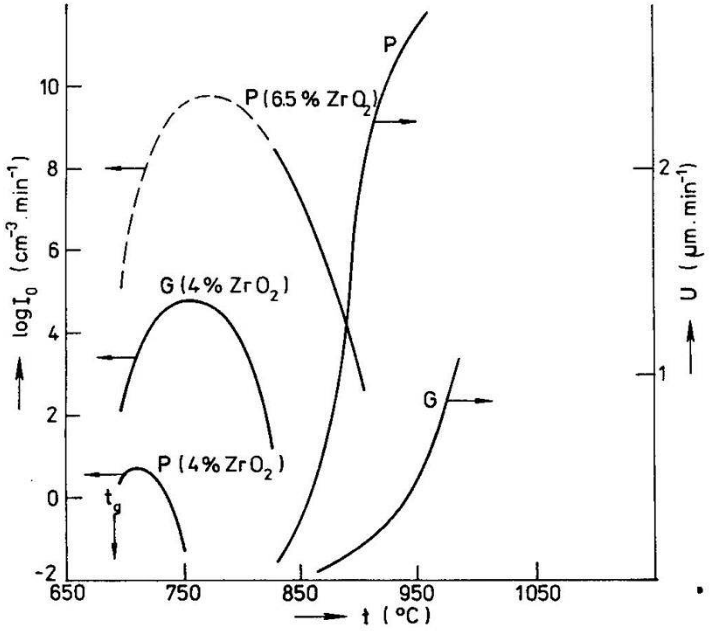
Methods of study

2) Differential thermal analysis



DTA curves of glasses with molar composition $70SiO_2.10Al_2O_3.20ZnO$ (wt%)

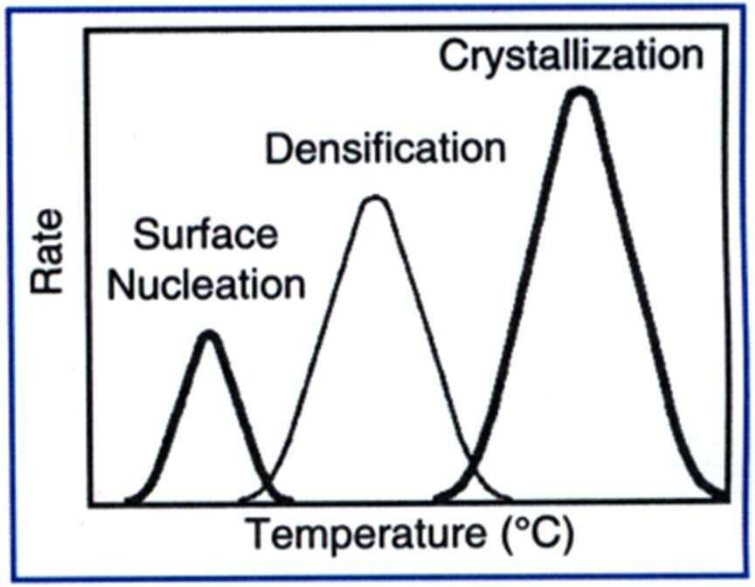




1. Two phase-separated phases
2,3. Exothermal maximum of crystallization
4. Endothermal minimum of melting of the crystalline phase
PW. Processing window (sometimes called sintering window)

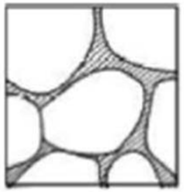
G: gahnite ($ZnO.Al_2O_3$) W: willemite ($SiO_2.2ZnO$)
P: Zn-petalite (similar to $Li_2O.Al_2O_3.8SiO_2$)

Sintering of glasses and glass-ceramics

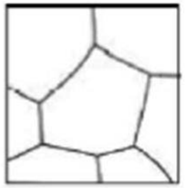


Sintering with concurrent crystallization

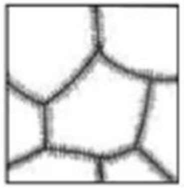
Viscous flow mechanism



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).

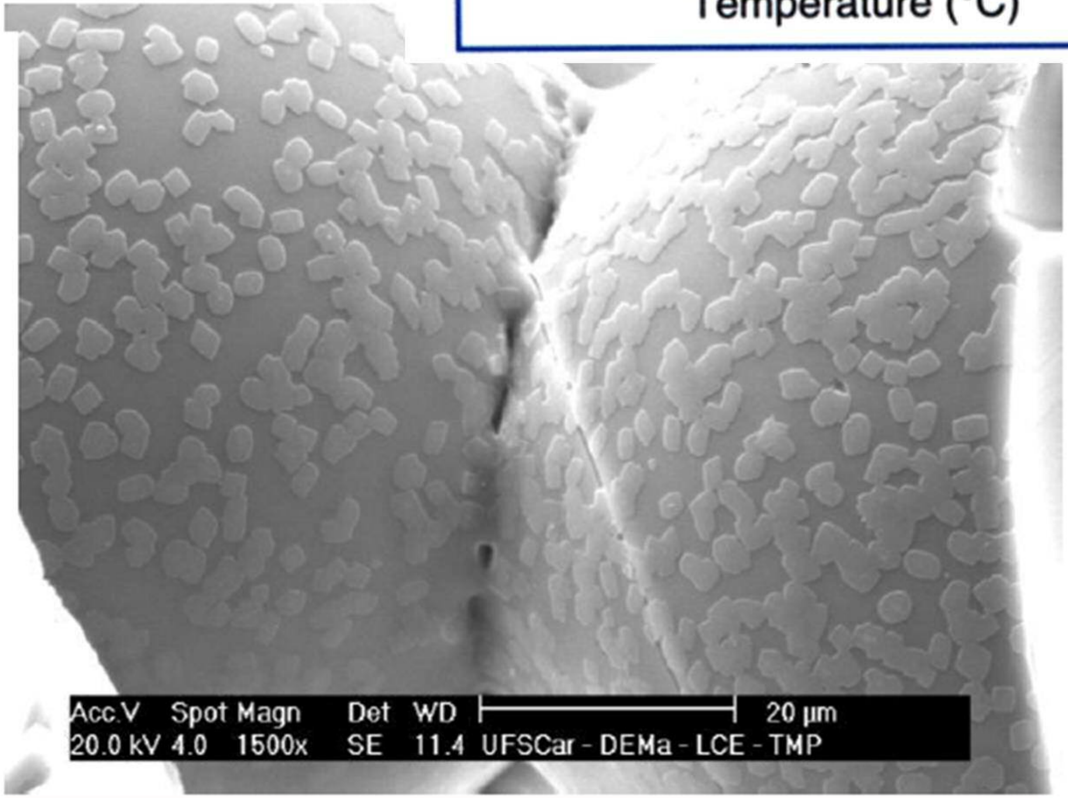
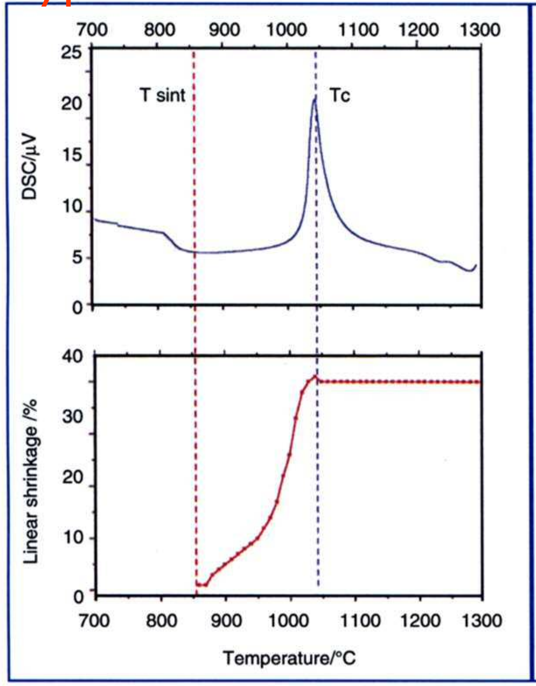


Photo by Vivi Oliveira and Rapha Reis (2009) LaMaV

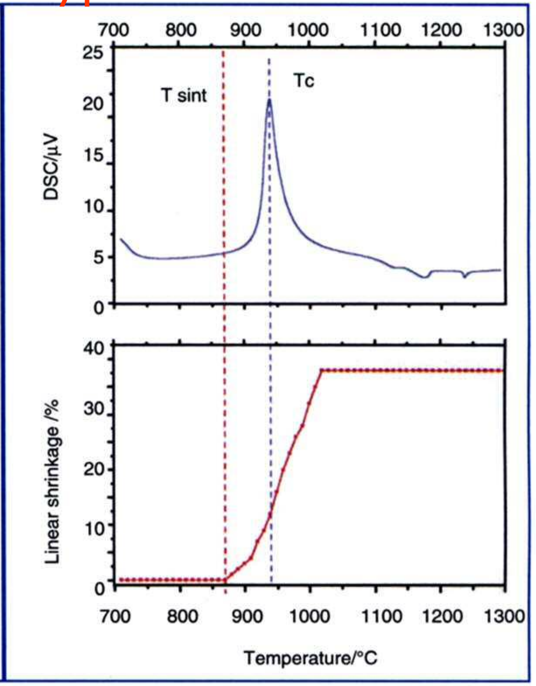
Sintering of glasses and glass-ceramics

Hot-stage microscopy + thermal analysis

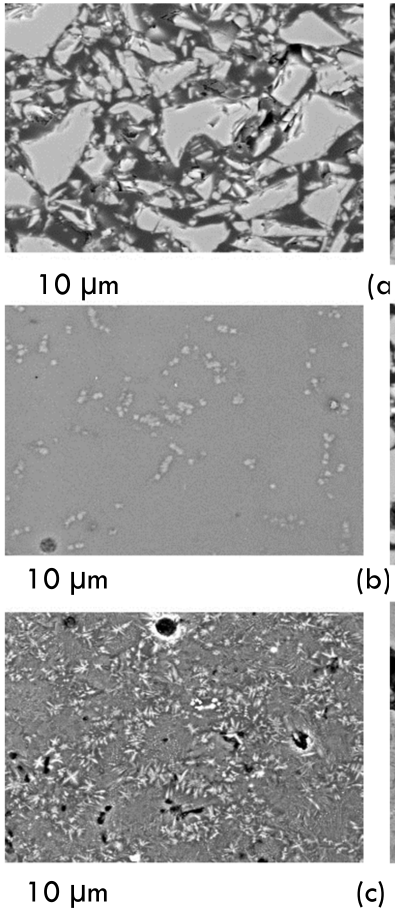
Type A



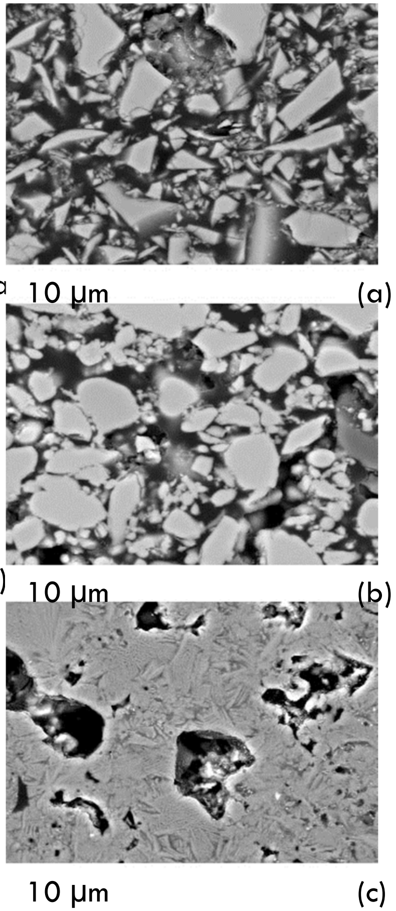
Type B



Type A



Type B



Sinterability parameter:

T_X-T_{MS} (S_C): parameter for sinterability

T_{MS}: maximum shrinkage T (HSM).

T_X: onset crystallization T (HSM).

T_C: crystallization T (HSM).

S_C greater than 25°C and typically between 40 and 60°C: good densification

C.Lara et al. Journal of Non-Crystalline Solids 348 (2004) 149–155

Controlled devitrification. Glass-ceramics

Mechanical properties

As well as the ceramics or the initial glasses, the glass-ceramics are fragile at room T and do not exhibit ductility or plasticity but behave as elastic substances up to a fracture tension.

(1) Partial size and crystalline volume fraction.
(2) Interfacial bond strength.
(3) Differences in elastic moduli.
4) Differences in thermal expansion coefficient.

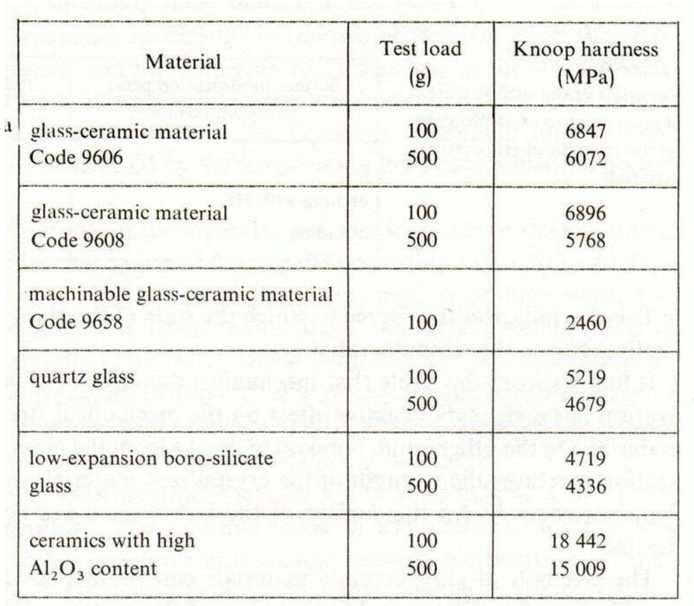
Mechanical resistance, elasticity, hardness

-Higher mechanical resistance than the base glass.

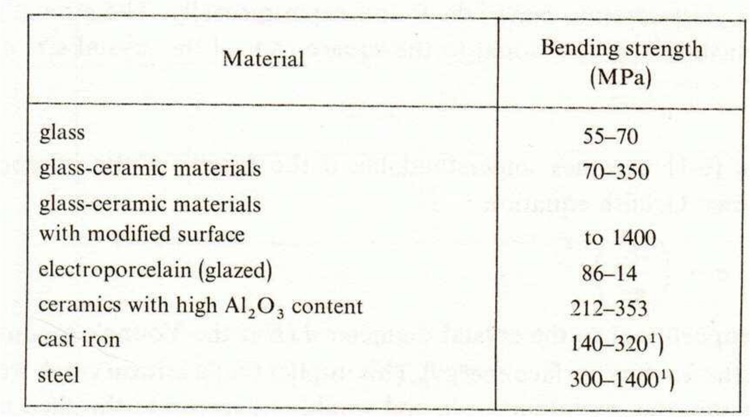
Factors: Fine grains (uniform microstructure).
Micro-stresses in the limit between vitreous and crystalline phases due to different TEC.

-Higher bending strength and elastic modulus than the base glass.

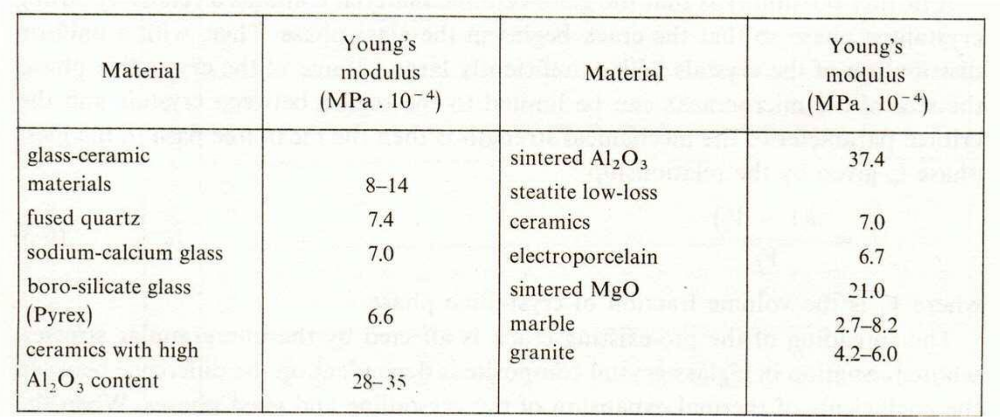
-Good hardness properties.



Material	Test load (g)	Knoop hardness (MPa)
glass-ceramic material Code 9606	100 500	6847 6072
glass-ceramic material Code 9608	100 500	6896 5768
machinable glass-ceramic material Code 9658	100	2460
quartz glass	100 500	5219 4679
low-expansion boro-silicate glass	100 500	4719 4336
ceramics with high Al_2O_3 content	100 500	18 442 15 009



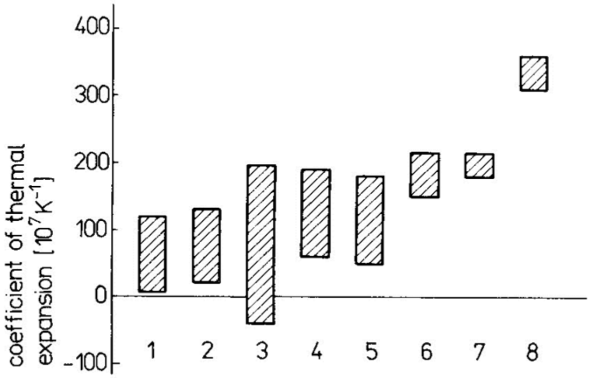
Material	Bending strength (MPa)
glass	55–70
glass-ceramic materials	70–350
glass-ceramic materials with modified surface	to 1400
electroporcelain (glazed)	86–14
ceramics with high Al_2O_3 content	212–353
cast iron	140–320 1)
steel	300–1400 1)



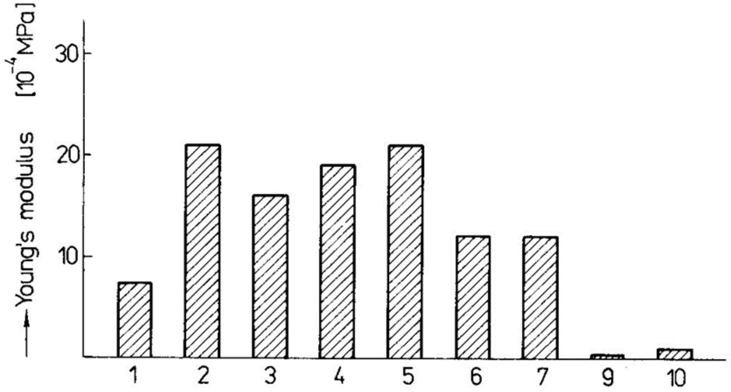
Material	Young's modulus (MPa . 10^{-4})	Material	Young's modulus (MPa . 10^{-4})
glass-ceramic materials	8–14	sintered Al_2O_3	37.4
fused quartz	7.4	steatite low-loss ceramics	7.0
sodium-calcium glass	7.0	electroporcelain	6.7
boro-silicate glass (Pyrex)	6.6	sintered MgO	21.0
ceramics with high Al_2O_3 content	28–35	marble	2.7–8.2
		granite	4.2–6.0

Uses and applications of glass-ceramic materials
Commercial glass-ceramics

Due to their mechanical, thermal and electrical properties, glass-ceramics not only compete with the traditional materials but are often superior. Additionally, they may have good optical properties and high chemical resistance.
Industrial use, laboratories, technology, medicine, cookware



Coefficient of thermal expansion
1- glasses, 2 - ceramics
3- glass-ceramics
4- casted iron, 5-steel, 6-bronze
7- brass, 8- Teflon



Young modulus
1- glasses, 2 - ceramics
3- glass-ceramics
4- casted iron, 5-steel, 6-bronze
7- brass, 8- Teflon, 9-acrilates, epoxides,
10- nylon

Outline of the presentation

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5. Bioactive borate glasses
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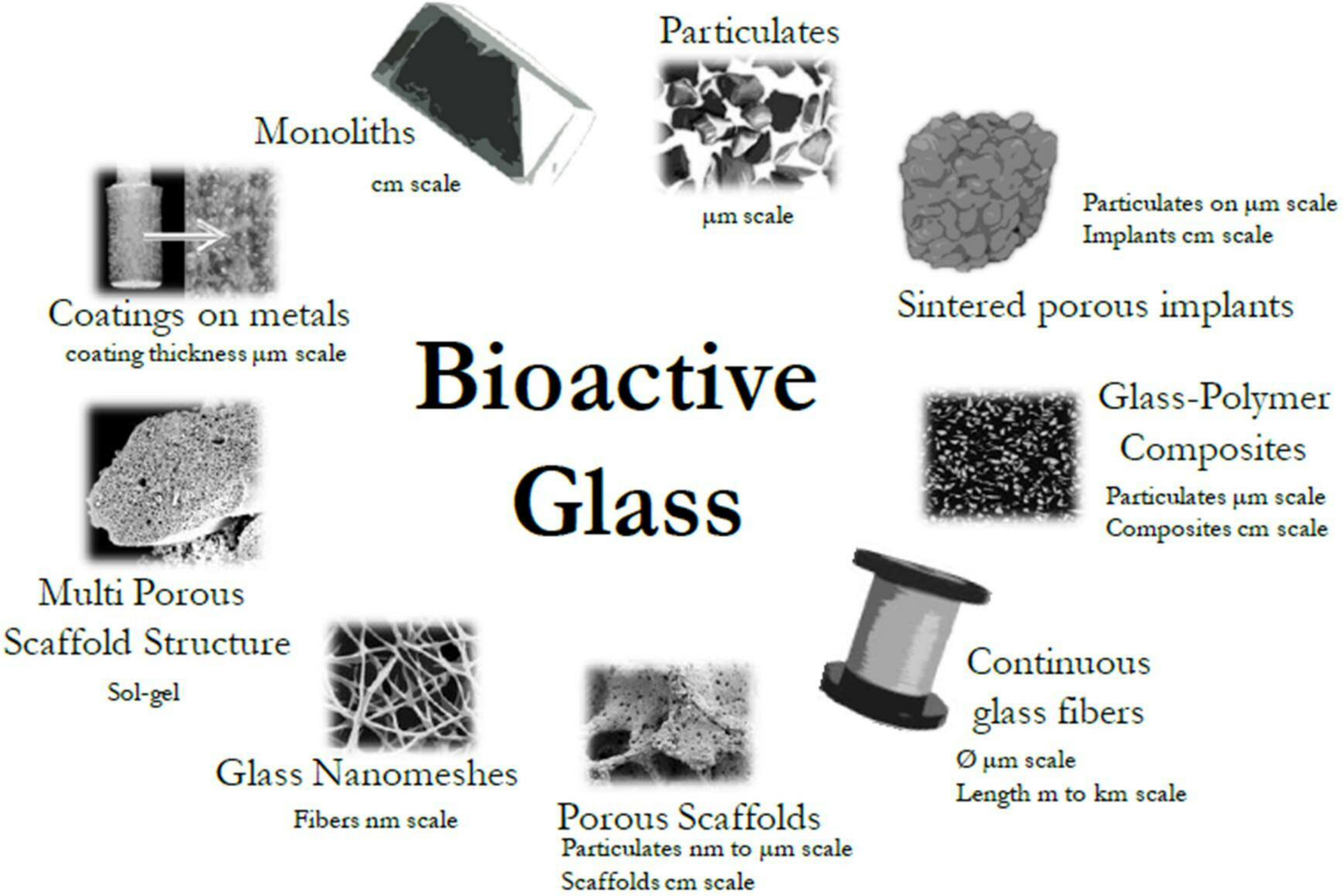
7. Bioactive glass coatings and composites
8. Glasses for radiotherapy

Versatile product forms manufactured from bioactive glasses with various methods



Bioactive glasses and glass-ceramics can bond effectively to bone and also stimulate osteoblast differentiation and proliferation (an osteoconductive material)

Melt-derived bioactive glasses

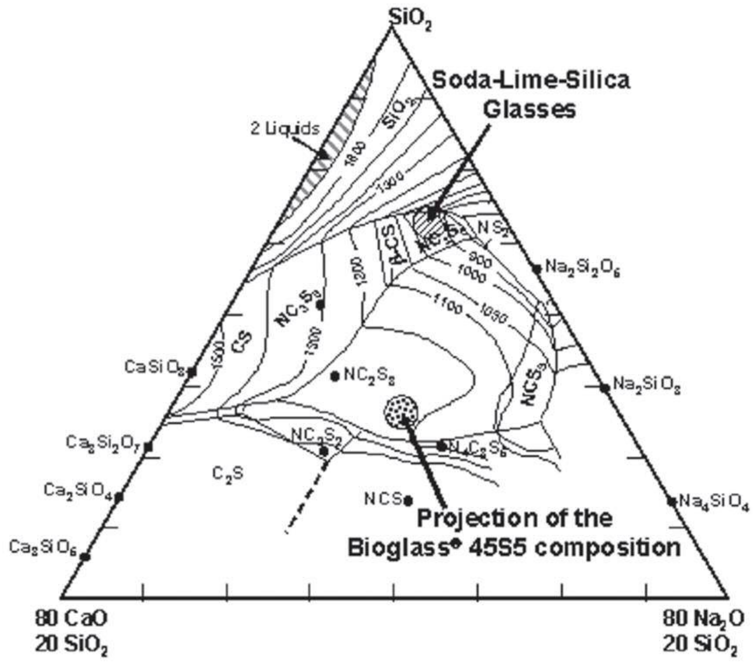
Bioglass® (45S5 bioactive glass), the first material that was found to form a bond with bone
Late 1960s by Larry Hech

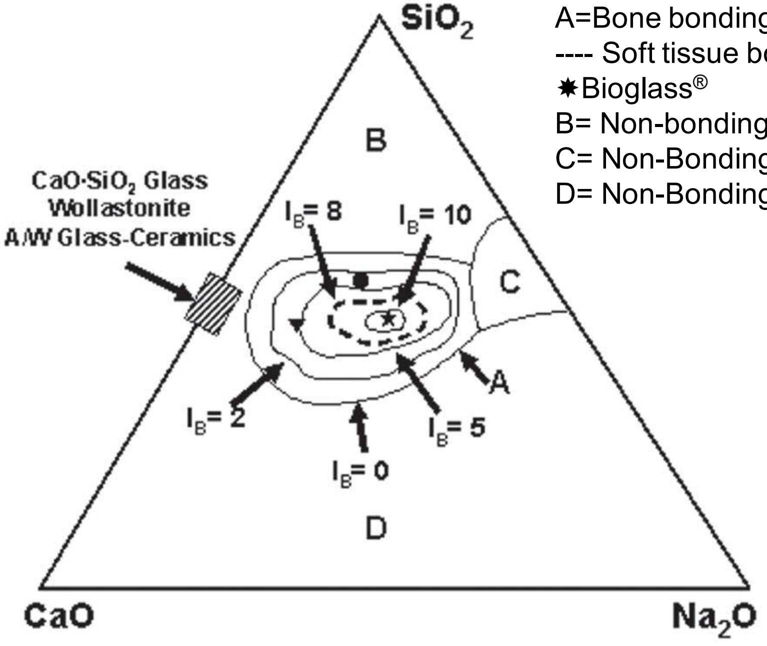
Composition	SiO_2	Na_2O	CaO	P_2O_5
Mol%	46.13	24.35	26.91	2.60
Wt%	45.00	24.50	24.50	6.00

Bioactivity index

$$I_B = [100/t_{0.5}](\text{days}^{-1})$$

time needed for 50% of an implant surface to attach to bone, $t_{0.5}$



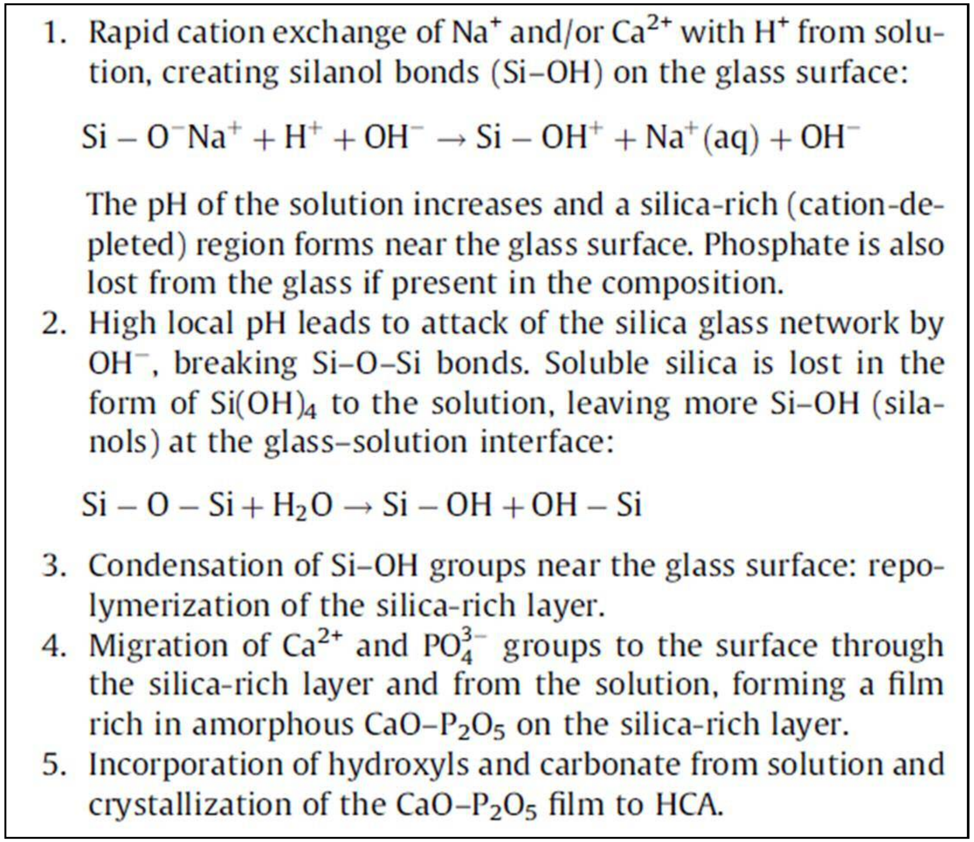


A=Bone bonding
---- Soft tissue bonding
✸Bioglass®
B= Non-bonding (reactivity too low)
C= Non-Bonding (reactivity too high)
D= Non-Bonding (non glass forming)

All at 6 wt% of P_2O_5

Melt-derived bioactive glasses

Mechanism for dissolution and bone bonding of a bioactive glass



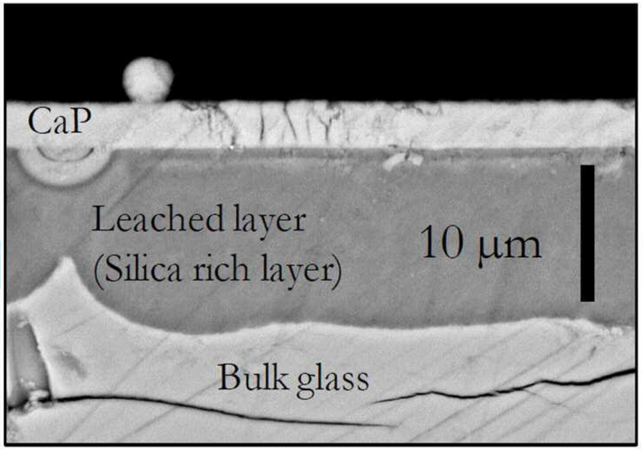
1. Rapid cation exchange of Na^+ and/or Ca^{2+} with H^+ from solution, creating silanol bonds (Si–OH) on the glass surface:

   $$Si - O^-Na^+ + H^+ + OH^- \rightarrow Si - OH^+ + Na^+(aq) + OH^-$$

   The pH of the solution increases and a silica-rich (cation-depleted) region forms near the glass surface. Phosphate is also lost from the glass if present in the composition.
2. High local pH leads to attack of the silica glass network by OH^-, breaking Si–O–Si bonds. Soluble silica is lost in the form of $Si(OH)_4$ to the solution, leaving more Si–OH (silanols) at the glass–solution interface:

   $$Si - O - Si + H_2O \rightarrow Si - OH + OH - Si$$

3. Condensation of Si–OH groups near the glass surface: repolymerization of the silica-rich layer.
4. Migration of Ca^{2+} and PO_4^{3-} groups to the surface through the silica-rich layer and from the solution, forming a film rich in amorphous $CaO–P_2O_5$ on the silica-rich layer.
5. Incorporation of hydroxyls and carbonate from solution and crystallization of the $CaO–P_2O_5$ film to HCA.



Network connectivity (NC) and Bioactivity

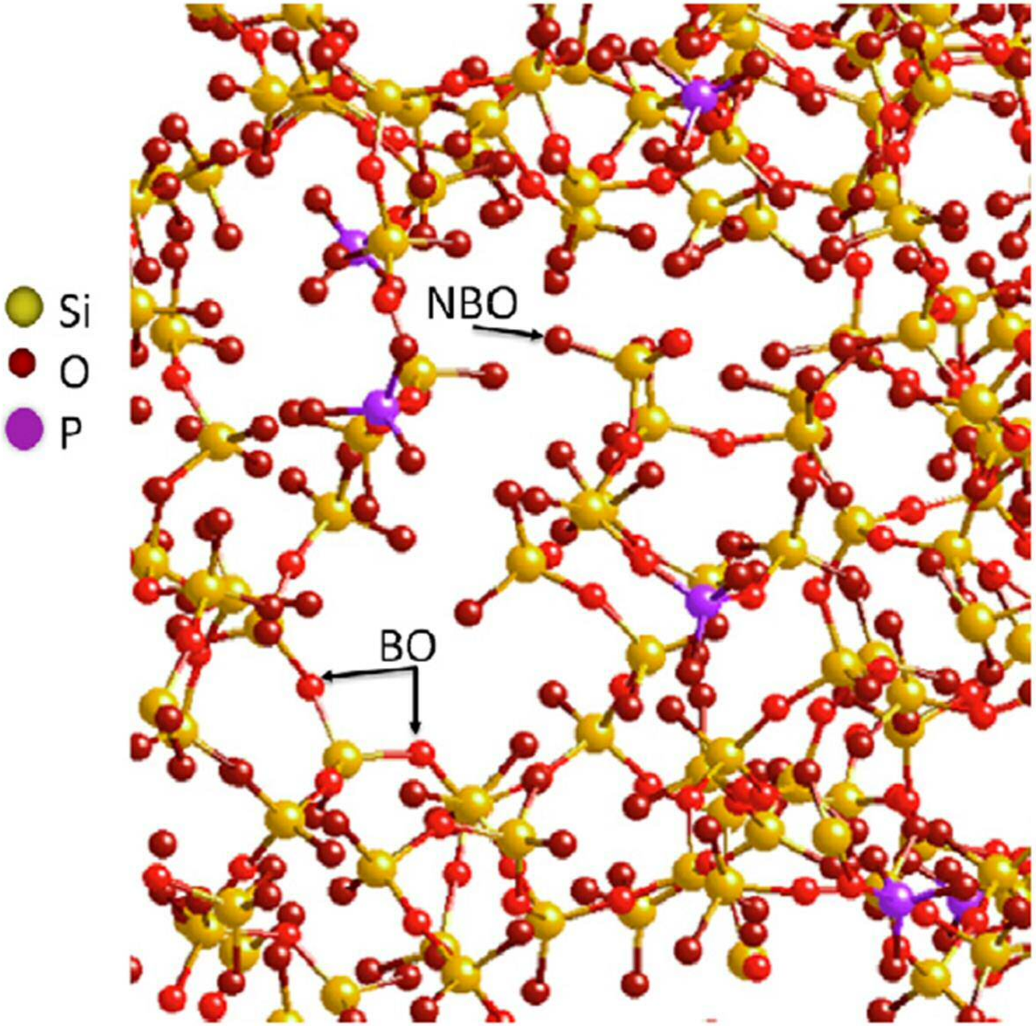
-Number of bridging oxygen bonds per silicon atom
-Glasses with more than 60% silica are not bioactive
45S5 Bioglass NC= 2
Above NC=2, the rate of HCA layer deposition decreases rapidly

$$NC = 2 + \frac{BO - NBO}{G}$$

BO: Total number of bridging oxygens per network-forming ion
NBO: Total number of non-brinding oxygens per network modifier ion
G: total number of glass-forming units

Melt-derived bioactive glasses

Bioglass® (45S5 bioactive glass)



Snapshot of a molecular dynamics model of Bioglass® 45S5 structure, with the Na and Ca ions removed for clarity.

NBO= non-bridging oxygen,

BO= bridging oxygen.

The silica tetrahedron and its associated bonds can be described by Q^n notation, where n is the number of bridging oxygen bonds. A ^{29}Si solid-state NMR study showed that Bioglass primarily consists of 69% chains and rings of Q^2, with 31% of Q^3 units providing some cross-linking. According to NMR, the phosphorus is present in an orthophosphate environment (Q^0), charge balanced by sodium and/or calcium (^{31}P and ^{17}O NMR) without any P-O-Si bonds. The phosphorus is therefore isolated from the silica network and removes sodium and calcium cations for their network-modifying role. This explains why phosphate is rapidly lost from the glass on exposure to an aqueous environment.

Melt-derived bioactive glasses

Bioglass® (45S5 bioactive glass)

Property	Value
Density	2.7g/cm3
Glass-transition temperature	538ºC
Crystallisation onset temperature	677ºC
Melting temperature	1224 and 1264ºC
Thermal expansion coefficient	15.1×10^{-6}ºC^{-1}
Refractive index	1.59
Tensile strength	42 MPa
Young´s modulus (stiffness)	35 MPa
Shear modulus	30.7 GPa
Fracture toughness	0.6 MPam$^{1/2}$
Vickers hardness	5.75 GPa

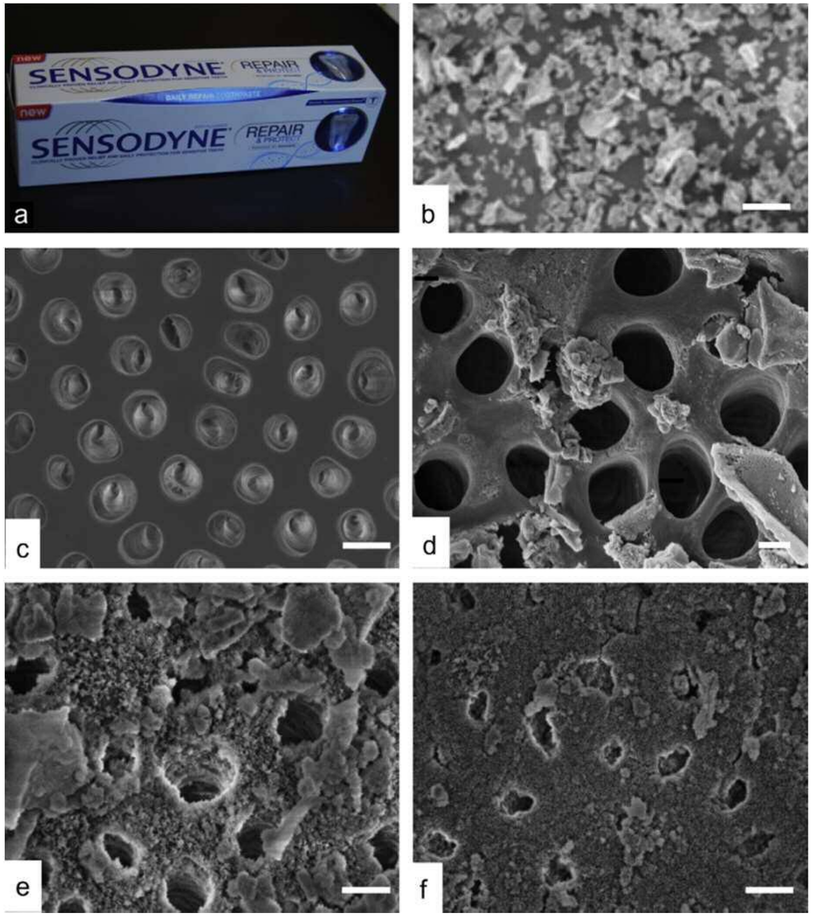
Poor mechanical properties
Crystallises rapidly when heated above Tg
Poor sinterability properties (large pieces of glass, porous constructs or scaffolds or coatings)

Alternative bioactive glass compositions

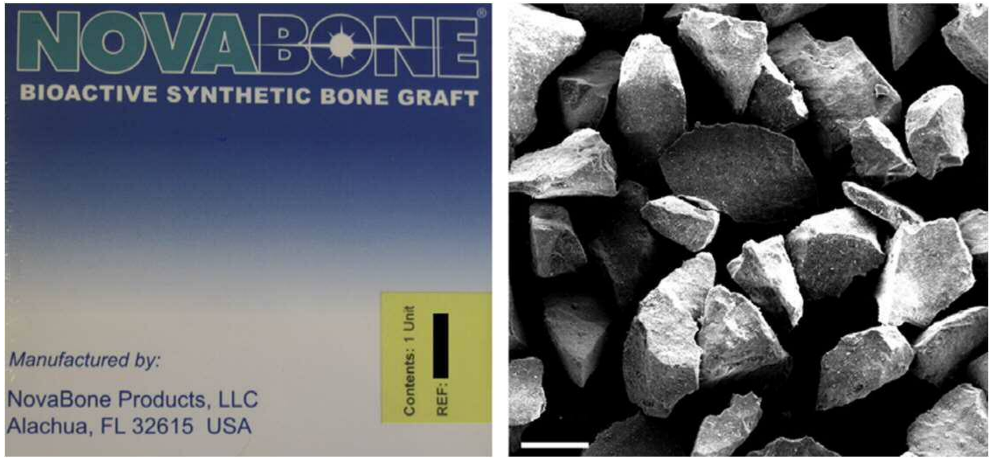
-Zn, Mg, B: stabilise the working range to enable viscous flow sintering and alter TEC to match those of metal alloys
-K, F for slow release of fluoride
-Ag bacterial actions
-Sr (StronBone^{TM}). Bone growth.
The release of these ions can be controlled altering the NC and particle size of glasses.
-Mg particular case
-Glass-ceramic compositions

Application: Synthetic bone graft for orthopaedic and periodontal use

Melt-derived bioactive glasses



Sensodyne Repair and Protect tooth paste, which contains Novamin, a fine particulate of Bioglass 45S5. Scale Bar 1 µm



NovaBone packaging, with an SEM image of the particles. Scale bar is 200 µm.

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Bioactive sol-gel glass

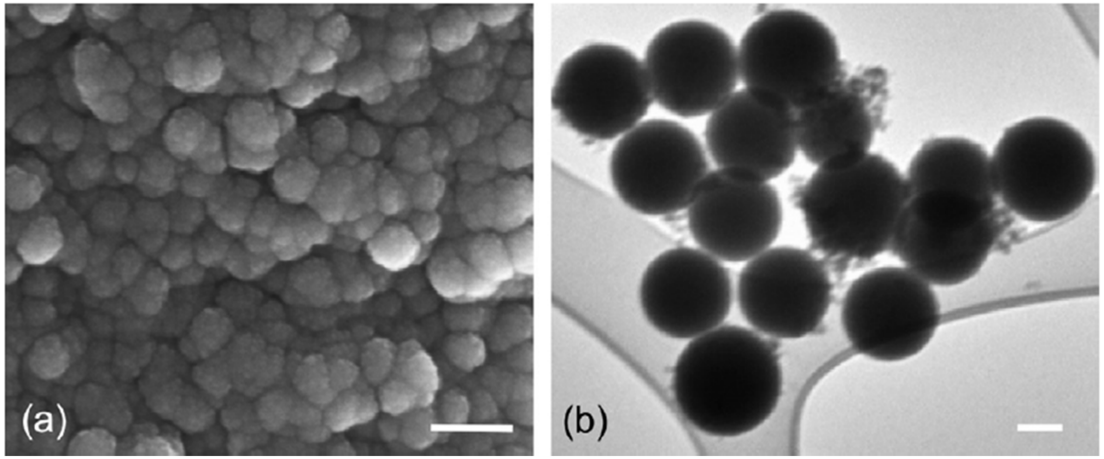
Glass can be made using two processing methods:
the traditional melt-quenching route and
the sol-gel route.

- The sol-gel route essentially forms and assembles nanoparticles of silica at room T. It is a chemistry-based synthesis route where a solution containing the compositional precursors undergoes polymer-type reactions at room T to form a gel. The gel is a wet inorganic network of covalently bonded silica, which can then be dried and heated, e.g. to 600ºC, to become a glass.

- Typical bioactive compositions are in the ternary system, e.g. 58S ($60SiO_2.36CaO.4P_2O_5$, mol%.) and 77S ($80SiO_2.16CaO.4P_2O_5$), or binary system 70S30C ($70SiO_2.30CaO$, mol%.). Sol-gel glasses tend to have an inherent nanoporosity whereas melt-quenched glasses are dense. The nanoporosity can result in improved cellular response due to nanotopography and a specific surface two orders of magnitude higher than for similar compositions of melt derived glasses.

- The high surface area of sol-gel glasses results in high dissolution rates and, as there is no melting involved, sodium is not required in the composition. Nonetheless, sol-gel glasses close to the 45S5 composition have been produced.

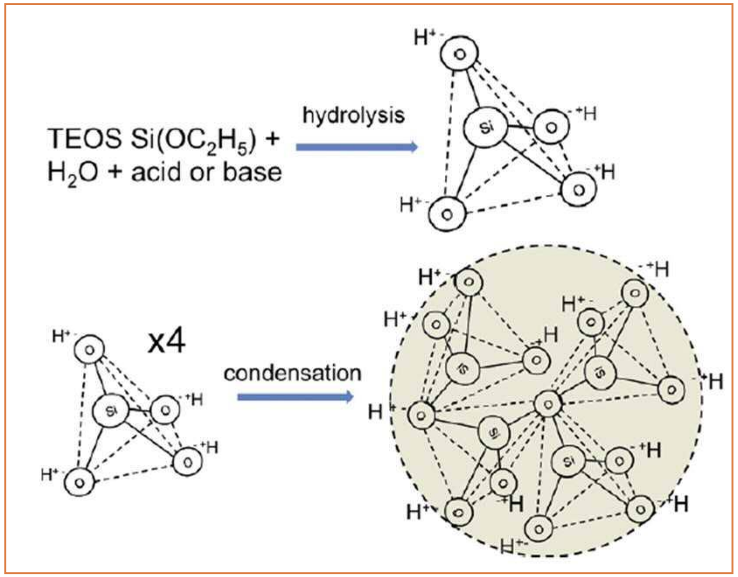
- The sol-gel process has great versatility: bioactive glasses can be made as nanoporous powders or monoliths or as nanoparticles simply by changing the pH of the process.



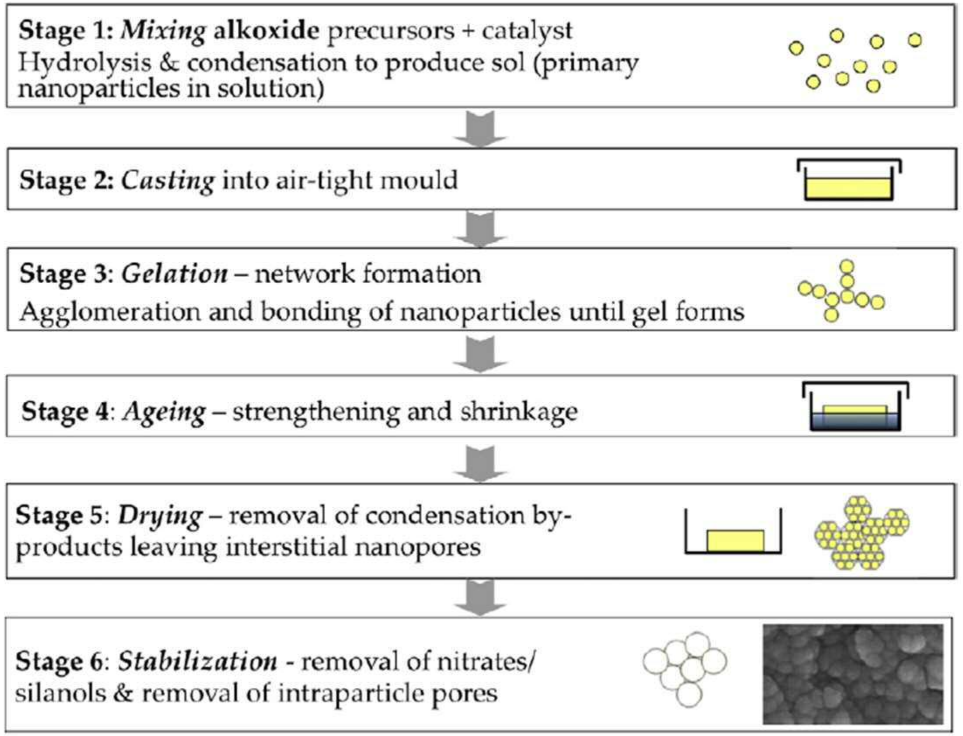
a) Bioactive sol-gel glass monolith made under acid catalysis. b) Bioactive glass nanoparticles. Bars are 100 nm

Bioactive sol-gel glass

A typical silicate precursor is tetraethyl orthosilicate (TEOS), $Si(OC_2H_5)$, which reacts with water (hydrolysis) under acidic or basic conditions to form a solution (sol) containing nanoparticles. If synthesis is carried out under basic conditions (Stöber process), spherical bioactive nanoparticles and sub-micrometre particles can be formed. Micro-particles, monoliths or foams are produced using acidic catalysis. Under acidic catalysis the primary nanoparticles (~2 nm) that form in the sol coalesce and condensation (polymerization) occurs, forming Si-O-Si bonds. The nanoparticles coarsen, coalesce and bond together, forming a gel network of assembled nanoparticles. The gel is wet due to excess water in the reagents and the water and ethanol produced during the condensation reactions. Thermal processing is used to age (continued condensation in sealed conditions), dry and stabilize the gel to produce a nano-porous glass. As the water and alcohol evaporate during drying, they leave behind an interconnected pore network. The pores are the interstices between the coalesced nanoparticles and their size depends on the precursor used, the glass composition and the pH of the reaction. Pore diameters are typically in the range 1-30 nm.



Schematic of reactions in the sol-gel process: formation of silica tetrahedra and nanoparticles at room T


Stage 1: ***Mixing*** **alkoxide** precursors + catalyst
Hydrolysis & condensation to produce sol (primary nanoparticles in solution)

Stage 2: ***Casting*** into air-tight mould

Stage 3: ***Gelation*** – network formation
Agglomeration and bonding of nanoparticles until gel forms

Stage 4: ***Ageing*** – strengthening and shrinkage

Stage 5: ***Drying*** – removal of condensation by-products leaving interstitial nanopores

Stage 6: ***Stabilization*** - removal of nitrates/ silanols & removal of intraparticle pores

A flow chart of the acid-catalysed sol-gel process of synthesis of a bioactive glass with schematics of the evolution of the gel and its nanoporosity.

Bioactive sol-gel glass

The usual method is to heat the dried gel to temperatures above 700ºC to produce a nanoporous bioactive glass. Typical 58S and 70S30C glasses have nanopore size of 6-17 nm, and particles with a size range of 1-32 μm have specific surface areas of 70-130 m^2-g^{-1}, compared to 2.7 m^2g^{-1} for Bioglass 45S5 particles of similar size. Common precursors for introducing calcium and phosphate into the sol-gel are calcium nitrate tetrahydrate and triethylphosphate, respectively. The thermal process also removes by-products of the non-alkoxide precursors, such as nitrates from calcium nitrate. The low-temperature process provides opportunities to make porous scaffolds and allows incorporation of polymers and organic molecules to make less brittle hybrid materials.

Ordered mesopores can also be created by introducing surfactants that act as templates. Ordered mesoporous silicates are of great interest in drug-delivery applications, as the drug can be stored within the mesoporous network.

Disadvantages of the sol-gel method:

-Difficult to obtain crack-free bioactive glass monoliths with diameters in excess of 1 cm, because larger monoliths crack during drying and evaporation of the liquid by-products of the condensation reaction. For small cross-sections, such as in powders, coatings or fibers, drying stresses are small, as the path of evaporation is short and the stresses can be accommodated by the material.

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Phosphate glasses

Phosphate (rather than silicate or borosilicate) as the glass former

Phosphate glasses can dissolve completely in aqueous solution giving ionic species commonly found in the human body, which offers various possibilities for their application as degradable implant materials.

Therapeutic ions such as Sr, Zn or F can incorporate into the glass to be released upon degradation for stimulation of bone growth and wound healing and for prevention of infections.
Versatile biomaterial for tissue regeneration.

- Raw materials: powders of phosphates, oxides and carbonates; sometimes phosphoric acid.

- Pt crucibles; Al crucibles should be avoided Al is a neurotoxin and affects bone mineralization.

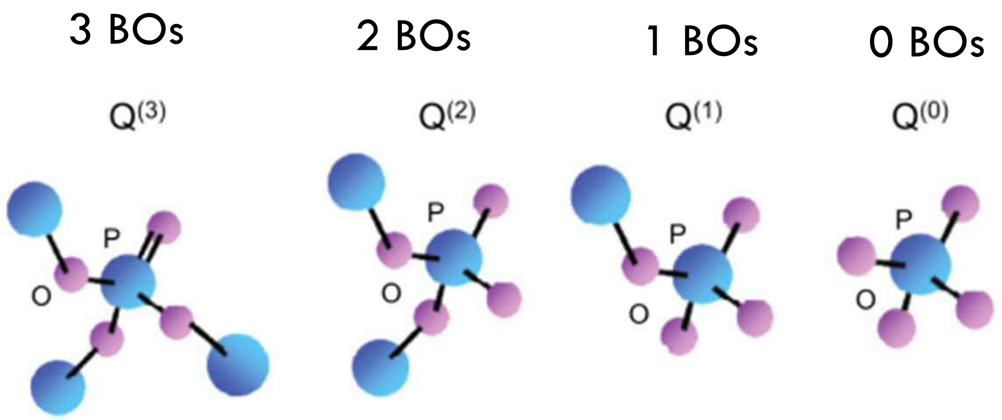
- Melting temperature: 800-1300ºC

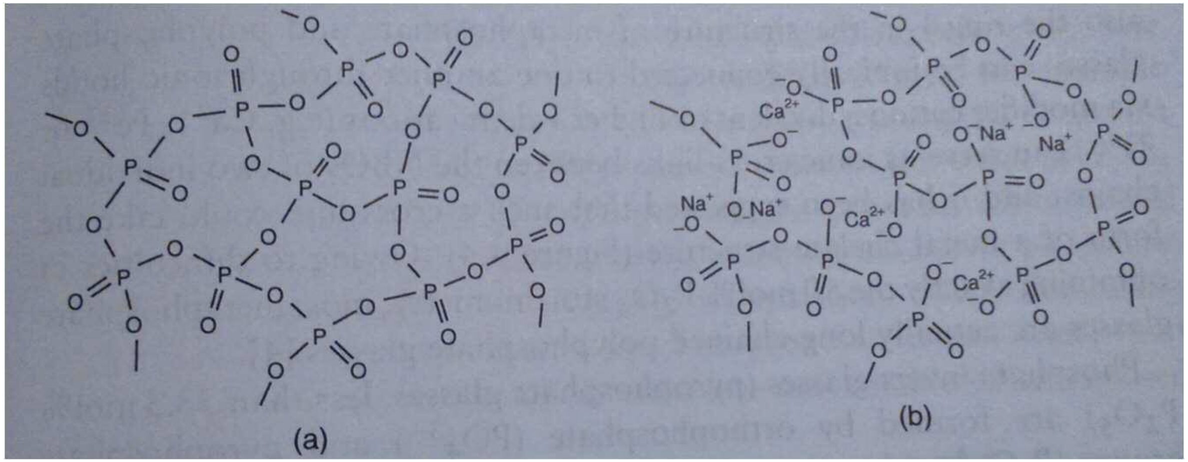
- Alternative sol-gel route: more fragile than bioactive silicate sol-gel glasses and very soluble for most biomedical applications

Phosphate glasses

The glass-forming component is P_2O_5, and the basic unit in the phosphate structure is the orthophosphate (PO_4^{3-}) tetrahedron, which is a phosphorus atom surrounded by four oxygen atoms.

Orthophosphate tetrahedra can be arranged to form chains, rings or branching networks





BOs

NBOs

The structure of simple phosphate glasses: a review. R.K.Brow. Journal of Non-Crystalline solids, 263, 1-28 (2000)

Phosphate glasses

Corresponding to their structure, phosphate glasses can be divided into different groups:

- Ultraphosphate glasses:

More than 50 mol% P_2O_5, consisting of two- to three-dimensional phosphate networks

- Polyphosphate glasses:

Less than 50 mol% P_2O_5, they are built of phosphate chains and rings, with the chain length decreasing with decreasing phosphate content

- Metaphosphate glasses

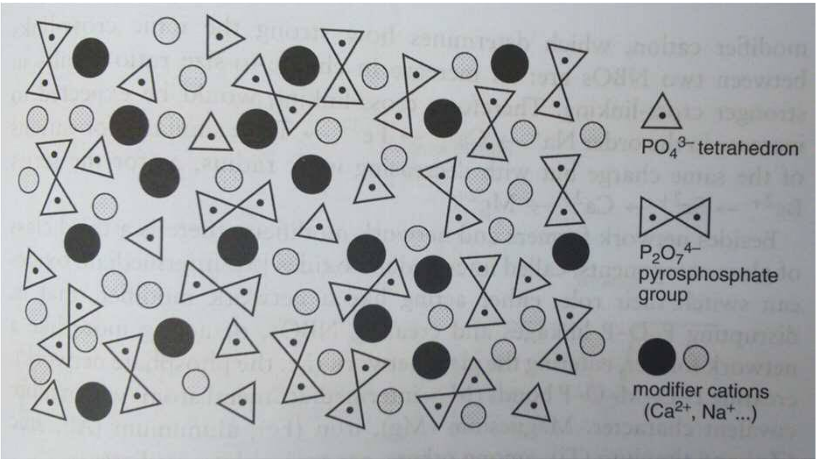
50 mol% P_2O_5, chains of infinite length or rings, and better described as consisting of entangled “molecular” or “polymeric” chains, rather than a “network”

The linear phosphate chains (but also the rings) in the structure of metaphosphate and polyphosphate glasses can be ionically connected to one another through ionic bonds via modifier cations; divalent or higher valence cations (ej. Ca^{2+}, Fe^{3+}, Ti^{4+}) can serve as ionic cross-links between the NBOs of two individual chains, and it has been suggested that such cross-linking could take the form of a metal chelate structure. Owing to difficulties in obtaining exactly 50 mol% stoichiometry, most metaphosphate glasses are actually long-chained polyphosphate glasses.

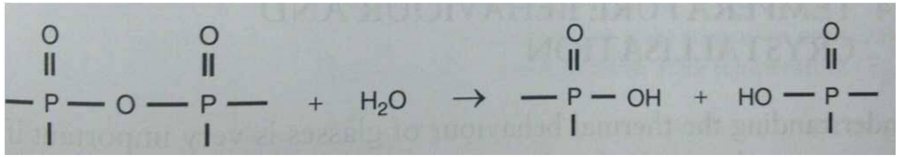
Phosphate glasses

- Pyrophosphate glasses (phosphate invert glasses):

Less than 33.3 mol% P_2O_5, formed by orthophosphate (PO_4^{3-}) and pyrophosphate groups ($P_2O_7^{4-}$; phosphate dimers). The glassy state is caused neither by a relatively stiff network nor by entangled chains but by the interaction of cations and phosphate groups, which is why they are often referred to as invert glasses.



Effect of water



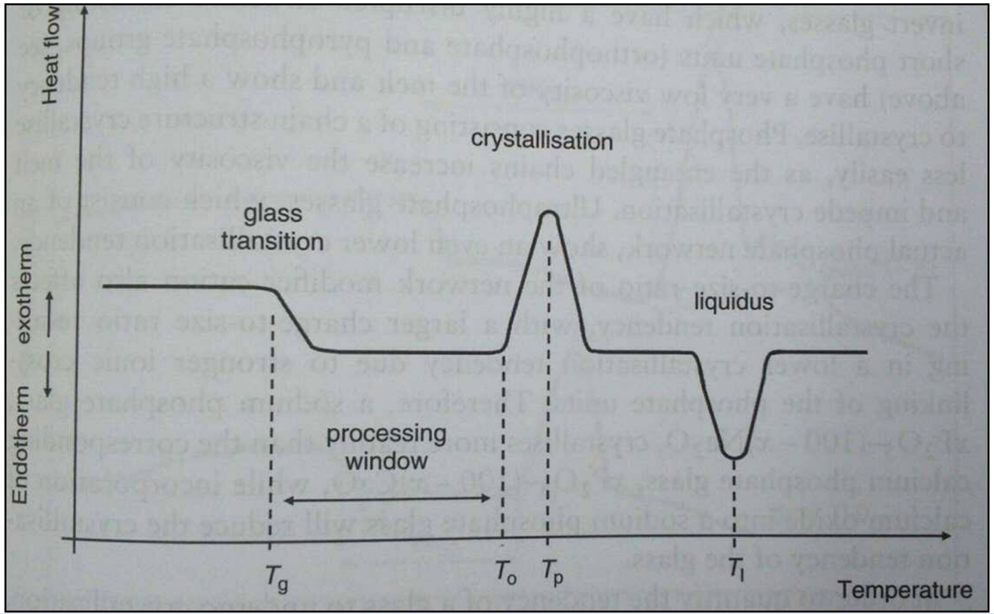
$$-\overset{\overset{\displaystyle O}{\|}}{\underset{|}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{|}{P}}- \;+\; H_2O \;\rightarrow\; -\overset{\overset{\displaystyle O}{\|}}{\underset{|}{P}}-OH \;+\; HO-\overset{\overset{\displaystyle O}{\|}}{\underset{|}{P}}-$$

Glass properties
Crystallization tendency
Mechanical properties
Hydrolytic resistance

- Phosphate content (phosphate glass structure)
- Charge-to-size ratio of the network-modifier cation, determines how strong the ionic cross-links between two NBOs are.
  $Na^{+} < Ca^{2+} < Fe^{3+} < Ti^{4+}$
  $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+}$
- Mg, Fe, Al, Zn and Ti are typical intermediates (P-O-M-O-P)

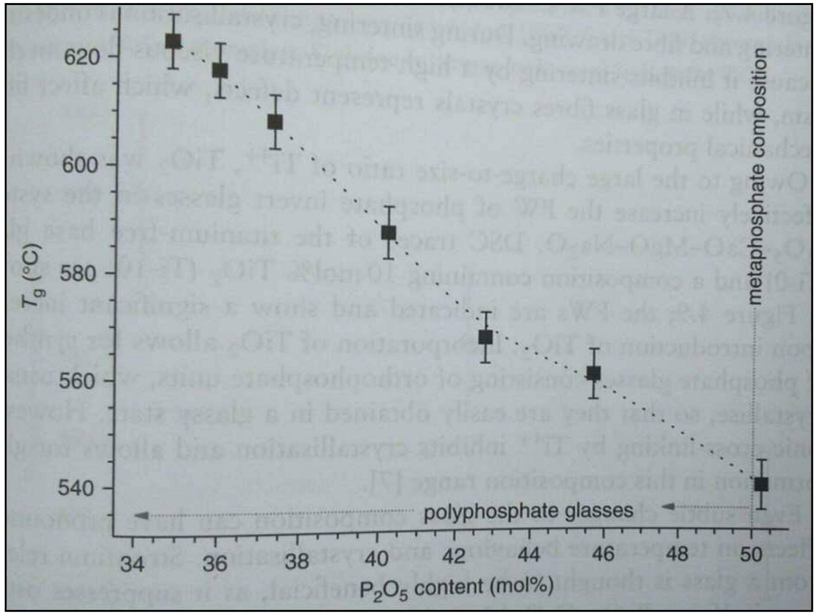
Phosphate glasses

Temperature behaviour and crystallization



Schematic of DSC trace of a glass showing glass transition temperature T_g, crystallization onset temperature T_o, crystallization peak temperature T_p as well as liquidus temperature T_l.

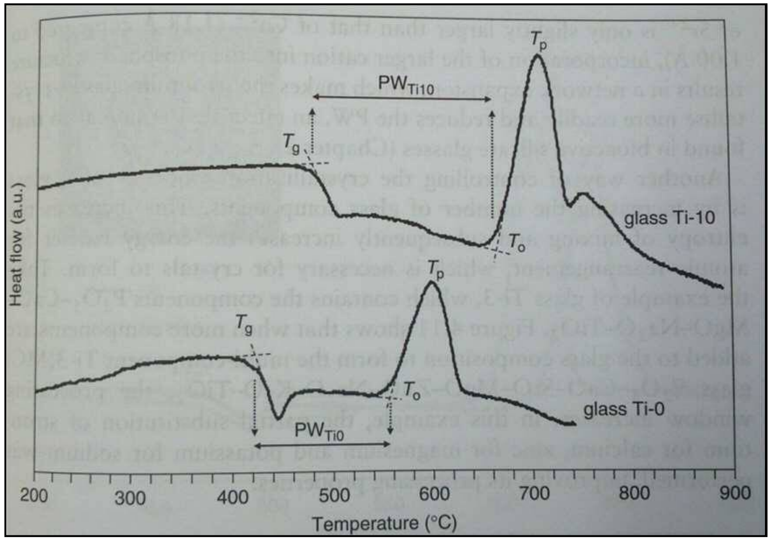
- Decreasing ionic cross-linking results in lower Tg
- The more disrupted the phosphate structure (the smaller the phosphate units), the more easily the glass crystallizes
- Lower viscosity enhances crystallization. High tendency to crystallize of inverted phosphate glasses
- A larger charge-to-size ratio of the network modifier cation results in lower tendency for crystallization

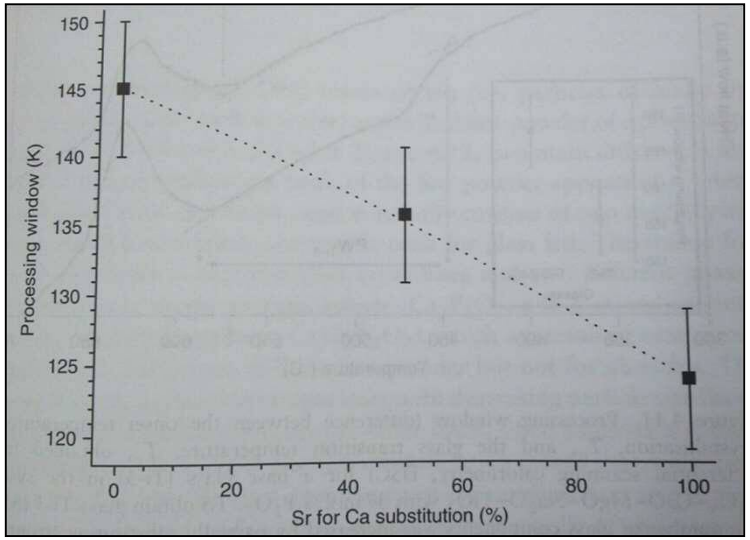


Glass transition temperature T_g of binary P_2O_5-MgO glasses versus nominal P_2O_5

Phosphate glasses

Temperature behaviour and crystallization





- Owing to the large charge-to-size ration of Ti^{4+}, TiO_2 was shown to effectively increase the PW of phosphate invert glasses in the system P_2O_5-CaO-MgO-Na_2O
- Sr glasses crystallise more readily
- Increasing the number of glass components increases the entropy of mixing and subsequently increases the energy barrier for atomic rearrangement, which is necessary for crystals to form

Phosphate glasses

- Phosphate glasses are soluble in aqueous solution, and can have a composition similar to mineralised tissue, which makes them of interest for use as degradable materials for bone regeneration, but also for use as materials for controlled release of ions in therapeutic concentration. Glass solubility is closely related to its composition and structure, and controlling degradation and ion release are critical for successful applications of these materials.

- Solubility:

  Metaphosphate > Polyphosphate > Invert glasses

- By making glass fibres or sintered porous scaffolds, substrates for a variety of applications can be produced. Composite materials based on degradable polymers such as PLA (poly(lactic acid)) and phosphate glasses are a promising way of modulating the mechanical properties to match them to the surrounding tissue in the body.

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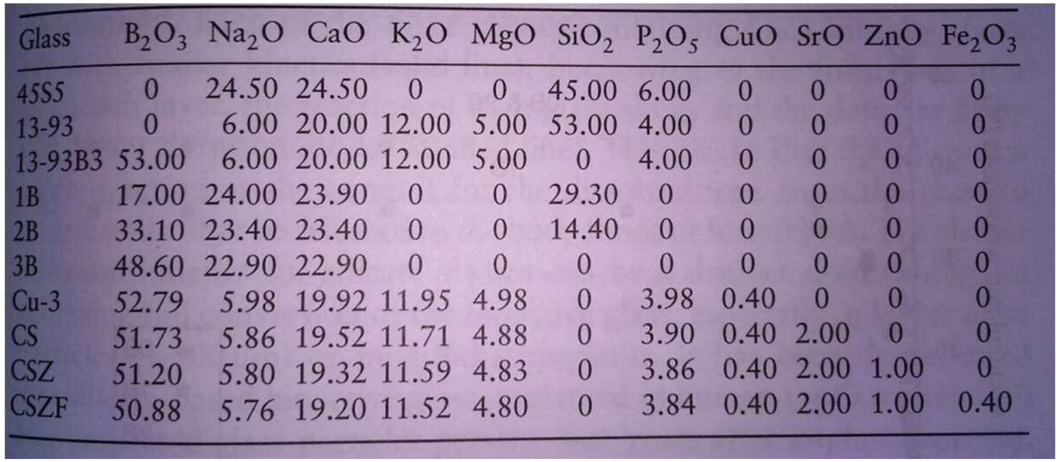
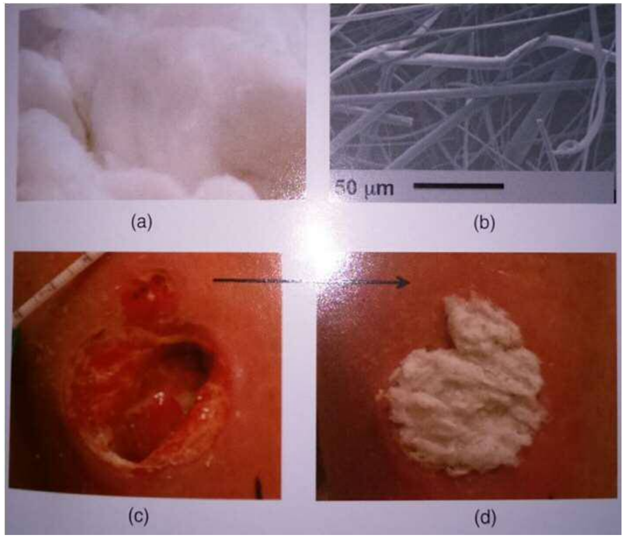
Bioactive borate glasses

The major glass former is B_2O_3, and the compositions can contain an array of alkali metal (Li, Na, K, etc.), alkaline-earth (Mg, Ca, Sr, Ba, etc.) and transition-metal (Fe, Cu, Zn, Ag, Au) elements.

Compositions of some common bioactive glass (wt%)



Glass	B_2O_3	Na_2O	CaO	K_2O	MgO	SiO_2	P_2O_5	CuO	SrO	ZnO	Fe_2O_3
45S5	0	24.50	24.50	0	0	45.00	6.00	0	0	0	0
13-93	0	6.00	20.00	12.00	5.00	53.00	4.00	0	0	0	0
13-93B3	53.00	6.00	20.00	12.00	5.00	0	4.00	0	0	0	0
1B	17.00	24.00	23.90	0	0	29.30	0	0	0	0	0
2B	33.10	23.40	23.40	0	0	14.40	0	0	0	0	0
3B	48.60	22.90	22.90	0	0	0	0	0	0	0	0
Cu-3	52.79	5.98	19.92	11.95	4.98	0	3.98	0.40	0	0	0
CS	51.73	5.86	19.52	11.71	4.88	0	3.90	0.40	2.00	0	0
CSZ	51.20	5.80	19.32	11.59	4.83	0	3.86	0.40	2.00	1.00	0
CSZF	50.88	5.76	19.20	11.52	4.80	0	3.84	0.40	2.00	1.00	0.40



Borate glass nanofibres

- Bioactive borate glasses, unlike silicate glasses, form HCA directly on the surface of the underlying unreacted glass, without forming a borate-rich layer. This is because the borate is readily soluble in body fluids, similar to the phosphate glasses. The degradation products of the glass can be passed through the body naturally, predominantly through urine. The lack of a diffusion layer allows borate glasses to react to completion without a significant reduction in the dissolution kinetics.
- With many exciting results, such as bone growth and the successful healing of diabetic wounds, the future of bioactive borate glasses looks bright.

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Bioactive glass-ceramics

Despite its excellent bioactive properties, the major disadvantages of bioactive glasses are their low mechanical strength and low fracture toughness. These characteristics restrict their use to a few applications. To improve the mechanical performance, bioactive glass-ceramics have been developed.

Bioactivity index and mechanical properties of bioactive materials used in clinical procedures

Bioceramics	**Bioglass® 45S5**	**Bioglass® 52S4.6**	**Cerabone® A/W**	**Ceravital®**	**Bioverit® I**	**HAs**	**Biolox® Forte**	**Biosilicate® (monolithic)**	**Cortical bone (longitudinal)**	**Cancellous bone**
Bioactivity index (BI)	12.5	10.5	6	5,6	IB<8	3,1	0	IB>8	-	-
Flexural strength (MPa)	40	40	215	100-150	140-180	50-200	466	120-210	-	-
Compressive Strength (MPa)	?	?	1080	500	500	500-100	4400	?	100-133	1.5-7.5
Young´s modulus (GPA)	60	60	120	100-160	70-90	80-110	380	70-80	12-17.7	0.2-0.6
Structure	Glass	Glass	(1) β-CaSiO3+ apatite+ glass	(1) devitrite+ apatite+ glass	(1) mica+ apatite+ glass	(2) apatite	α-Al2O3	1N2C3S	Apatite+ organic material	Apatite+ organic material
Machinability	Poor	Poor	Poor	Poor	Good	Poor	Poor	Moderate	-	-

?: not found data. Cerabone® A/W: glass-ceramic/β-$CaSiO_3$: beta-wollastonite/(1): undefined composition. Ceravital®:glass-ceramic/(1): undefined composition. Bioverit® I:glass-ceramic/(1):undefined composition. HAs: synthetic hydroxyapatite/(2): $(Ca)_{10}(PO_4)_6(OH)_2$. Biosilicate®: glass-ceramic 100% crystallized. 1N2C3S: Sodium Calcium Silicate (1N=sodium; 2C= calcium; 3S = silicon).

M.C. Crovace, et al., Biosilicate®-A multipurpose, highly bioactive glass-ceramic. In vitro, in vivo and clinical trials, J. Non-Cryst. Solids (2015),http://dx.doi.org/10.1016/j.jnoncrysol.2015.03.022

Bioactive glass-ceramics

Compound (wt%)	Bioglass® 45S5	Ceravital®	Cerabone® A/W	Ilmaplant®	Bioverit®	Biosilicate®
Na_2O	24.5	5-10	0	4.6	3-8	23.75
K_2O	0	0.5-3.0	0	0.2	0	-
MgO	0	2.5-5	4.6	2.8	2-21	-
CaO	24.5	30-35	44.7	31.9	10-34	23.75
Al_2O_3	0	0	0	0	8-15	-
SiO_2	45.0	40-50	34.0	44.3	19-54	48.5
P_2O_5	6.0	10-50	6.2	11.2	2-10	4
CaF_2	0	0	0.5	5.0	3-23	-
Phases	Glass	Devitrite+ Apatite+ Glass	Apatite+ β-$CaSiO_3$+ Glass	Apatite+ β-$CaSiO_3$+ Glass	Flogopite+ Apatite+ Glass	$Na_2CaSi_2O_6$ or $Na_2CaSi_2O_6$ + $NaCaPO_4$

Bioactive glass-ceramics

- The most well-known bioactive glass-ceramics are Ceravital®, Bioverit® and A/W Cerabone® (developed by Kokubo in the late 1980s).

- Ceravital® is composed of a glassy phase, devitrite and apatite crystals. The main application of this glass-ceramic is as substitute of the ossicular chain in the middle ear.

- In addition to the glassy phase, Bioverit® is composed of apatite and mica crystals, which are responsible for its excellent machinability. Bioverit ® pieces have been implanted in more than 850 orthopedic surgeries up to 1992, such as in spinal spacers and in head and neck surgery.

- The A/W Cerabone® glass-ceramic is composed of an apatite matrix reinforced by needle-like wollastonite crystals, which yields a K_{IC} of 2 $MPa.m^{1/2}$, the highest value among all of the bioactive glass-ceramics. Among other applications, A/W Cerabone ® has been used in the substitution of the iliac bone crest. This glass-ceramic was produced from 1991 to 2000 and applied with success in more than 60000 patients.

- All of the three glass-ceramics cited are composed of an apatite-like crystalline phase, which is much less soluble than Bioglass ® 45S5. Although these glass-ceramics exhibit better mechanical performance than any glass, their bioactivity level is relatively low and is comparable to that of traditional calcium phosphate ceramics.

- Biosilicate® shows in-vitro and in-vivo bioactivities comparable to that of Bioglass ® 45S5. It can be applied in powder, monolithic or 3D forms that could be easily machined before or during surgical process. Nevertheless, clinical studies have to be conducted.

Bioactive glass-ceramics

Biosilicate®

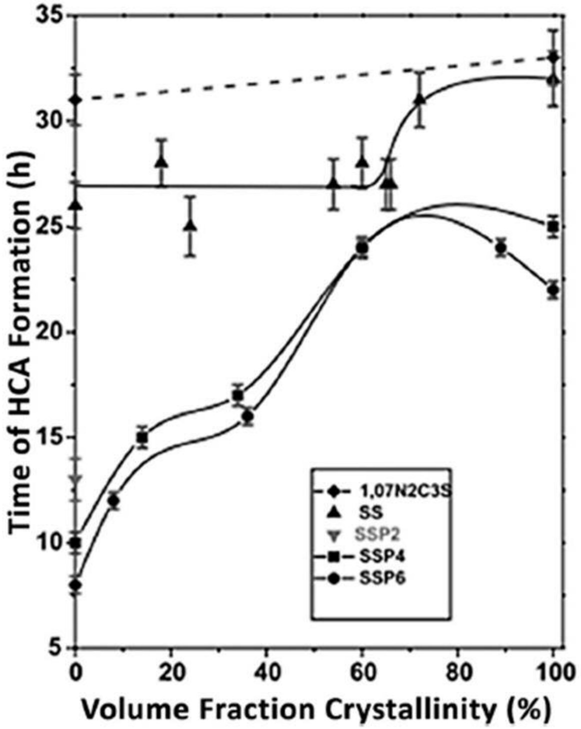


Fig. 1. Onset time for HCA formation as a function of the crystallized volume fraction (1.07N2C3S = $18.5Na_2O-31.3CaO-50.3SiO_2$; SS = $24.8Na_2O-24.8CaO-50.5SiO_2$; SSP2 = $24.2Na_2O-24.2CaO-49.5SiO_2-2P_2O_5$; SSP4 = $23.8Na_2O-23.8CaO-48.5SiO_2-4P_2O_5$; SSP6 = $23.2Na_2O-23.2CaO-47.5SiO_2-6P_2O_5$ – wt.%) [28].

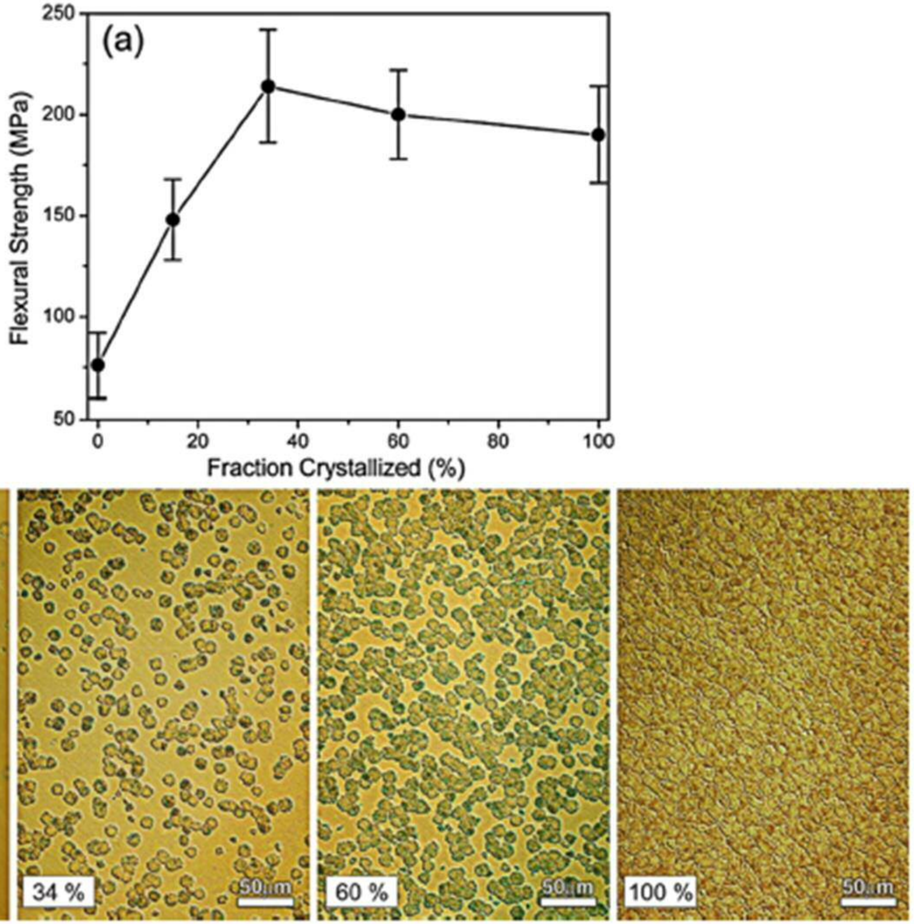


Fig. 2. (a) 3-point or 4-point bending strength versus crystalline volume fraction for a $23.8Na_2O-23.8CaO-48.5SiO_2-4P_2O_5$ (wt.%) glass-ceramic with a constant crystal size of 13 μm; (b) optical micrographs of the corresponding microstructures for 15%, 34%, 60% and fully crystallized samples (b) [29].

High-strength, moldable biocompatible glass-ceramics for dental restoration

Lithium disilicate glass-ceramics ($Li_2Si_2O_5$)
Leucite glass-ceramics ($KAlSi_2O_6$)

- Both high strength and moldability are important features of the biocompatible materials used to repair teeth. Very strong lithium disilicate glass-ceramics, are popular for making dental crowns and bridges that do not need to be strengthened with metal. A very strong glass-ceramic is used to make a base. Another glass-ceramic material containing apatite crystals is applied on this base and shaped to resemble the original tooth.

The figure shows a bridge that has been made to replace one missing tooth. The amazing thing about these materials is not just their mechanical properties. Their optical properties are such that it is difficult to tell the difference between the glass-ceramics and the natural teeth- they even have the right colour.

Products IPS e.max® Press, IPS e.max® Ceram, IPS e.max® CAD

W. Hölland, Ivoclar

Outline of the presentation

1. The Nature of glass
    - 1.1. What is glass?. Classification
    - 1.2. Making glass
    - 1.3. Phase separation and devitrification
    - 1.4. Controlled devitrification. Glass-ceramics

2. Melt-derived bioactive glass. Bioglass
3. Bioactive sol-gel glass
4. Phosphate glasses
5. Bioactive borate glasses
6. Bio-Glass-ceramics
7. Bioactive glass coatings and composites
8. Glasses for radiotherapy

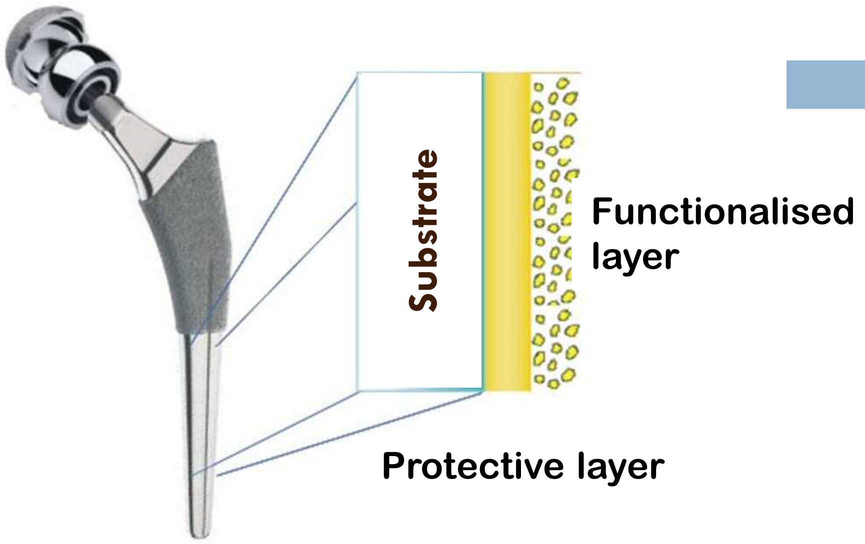
Bioactive Glass coatings and Composites

- The greatest constraint on a wider use of bioactive glasses and glass-ceramics is derived from their relatively poor mechanical properties, especially in zones under mechanical loads. This shortcoming has been circumvented by using various methods to increase the strength of these glass materials and facilitate their use as implants.

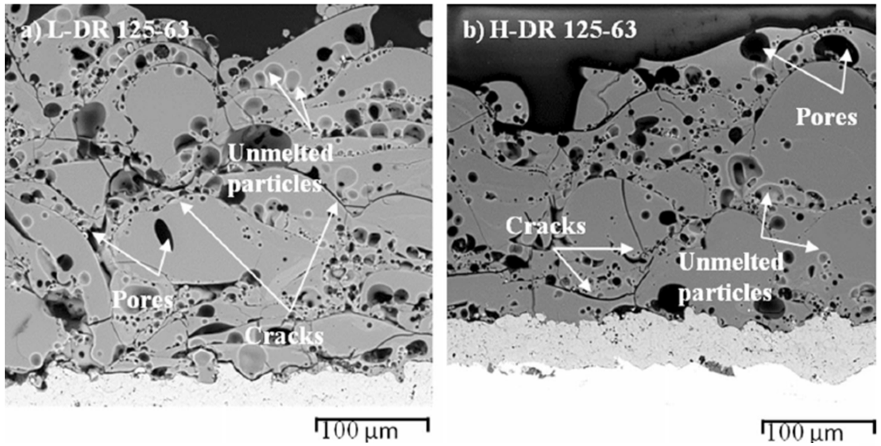
- One solution to the problem is using bioactive glasses as a coating for materials with a high mechanical strength. This method has been used with a number of substrates, including dense alumina, various types of stainless steel, cobalt-chromium alloys and titanium alloys. This last alloy is especially attractive on account of its high strength, low elastic modulus and good biocompatibility.

- The methods used to prepare coatings range from immersion in the molten glass or in a solution, suspension or gel (dip-coating), electrophoresis from a solution or suspension (the metal to be coated acting as an electrode), biomimetic coating growth or flame or plasma spraying. The last choice is the most widely used at present to deposit bioactive glass onto a metal substrate.

P.N.de Aza et al., Bol.Soc.Esp.Ceram.Vidr., 45 (2006)
Bio-glasses: An introduction, J.R.Jones (2012)



Sol-gel coatings



Coatings of 45S5 on AISI 304 by atmospheric plasma spraying
V.López Calvo et al., J.Mater. Sci., 49 (2014) 7933-7942

Bioactive Glass coatings and Composites

- Another application of bioactive glasses is in the production of composites, in which the bioactive glass is reinforced with a second phase. Materials thus obtained include “biofibre glass” and alumina, organic polymers or metal fibres. The former has fallen short of the original expectations as it seemingly releases large amounts of alumina powder that are detrimental for tissues. The materials reinforced with metal fibres are those with the strongest potential. In fact metal fibres strengthen bioactive glasses and improve their deformability. The most widely used procedure for producing these materials is hot pressing.

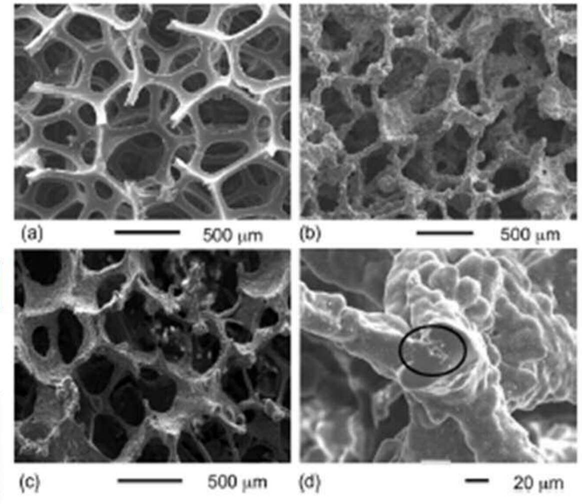
- Decheyne and Hench reported a composite material consisting of Bioglass 45S5 and metal fibres of AISI 316L stainless steel. The material, which was prepared by immersing the metal fibres in molten glass, exhibited improved mechanical strength and ductility, in addition to a Young modulus comparable to that of the human cortical bond.

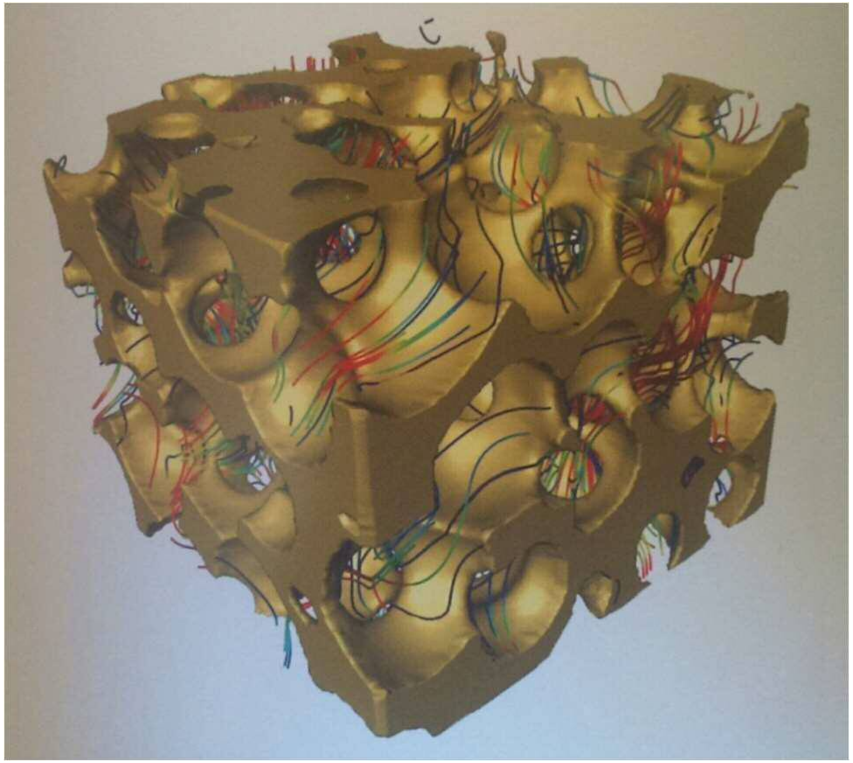
- Other glass-based composite materials include Ceravital® reinforced with titanium particles and A/W glass-ceramic reinforced with partially stabilized zirconia or polyethylene.

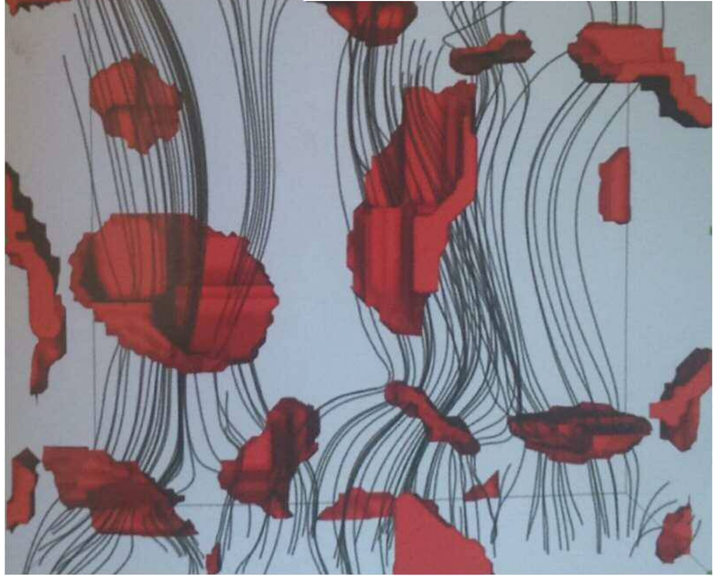
- The essential requirements for these composite materials to be useful as dental implants or in orthopedic applications are a low elastic modulus, good deformability, good tensile strength, good impact resistance and ready machinability.

- Finally, bioactive composites containing bioactive glass within a biodegradable matrix have also been produced in highly porous 3D structures, which are often known as tissue scaffolds because they can act as temporary templates to guide tissue growth and repair.

Bioactive glass scaffolds







3D (microtomography) image of a bioactive-glass scaffold. The lines are predicted flow paths of body fluid through the scaffold. Using image-analysis techniques, the pores and interconnects between them can be quantified. The interconnects of a scaffold (the scaffold itself made transparent) and predicted flow paths through them.

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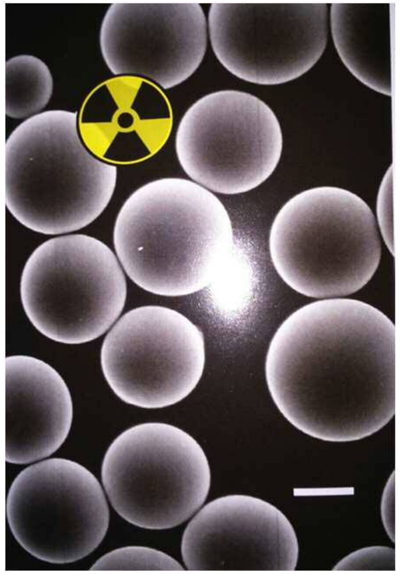
Glasses for Radiotherapy

- An expanding number of investigations have shown that glass microspheres are effective as in situ radiation delivery vehicles for treating diseases such as cancer and rheumatoid arthritis. The versatility of glass is an important advantage to its use in medicine since its properties can be varied over a wide range and tailored to a particular application by simple changes in its compositions.

- Glass microspheres can range from bio-inert to bioactive, from almost completely insoluble to biodegradable in the body. Similarly, the radiation emitted by glass microspheres can be tailored for a particular organ by using a glass that contains one or more neutron activable elements (e.g. REs) that emit the optimum radiation for the organ being treated.

- ^{90}YAS glass microspheres offer a safe and reliable way of delivering unusually large doses of beta radiation to malignant tumors in the liver with minimum side effects.



YAS: yttrium aluminosilicate glass

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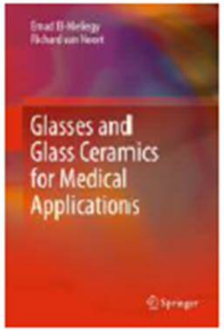

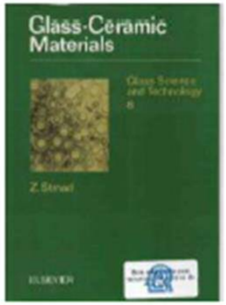

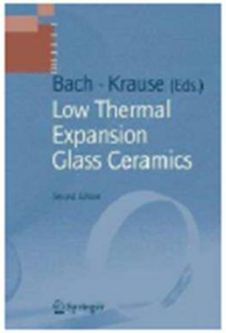

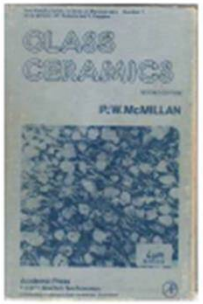

+ review articles by:

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

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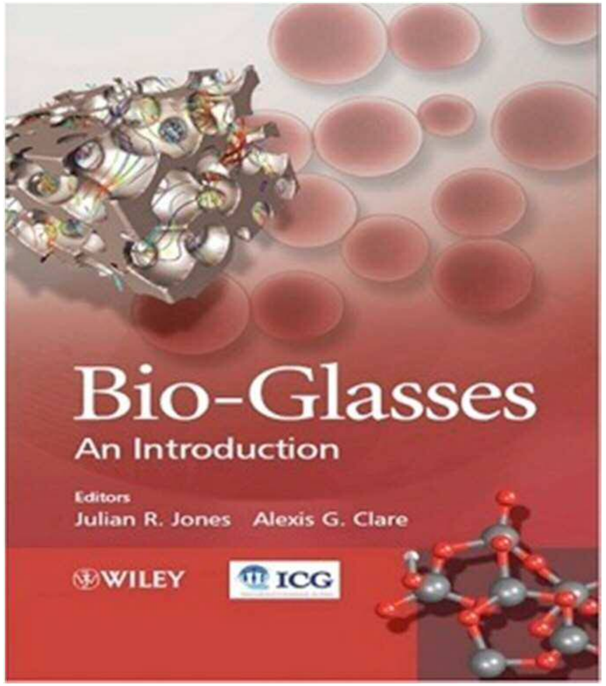
Bioceramics and their clinical applications



Bio-Glasses

An Introduction

Editors

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WILEY ICG

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