Crystallization of Glass

Materials Tetrahedron

Processing

Performance

Microstructure

Properties
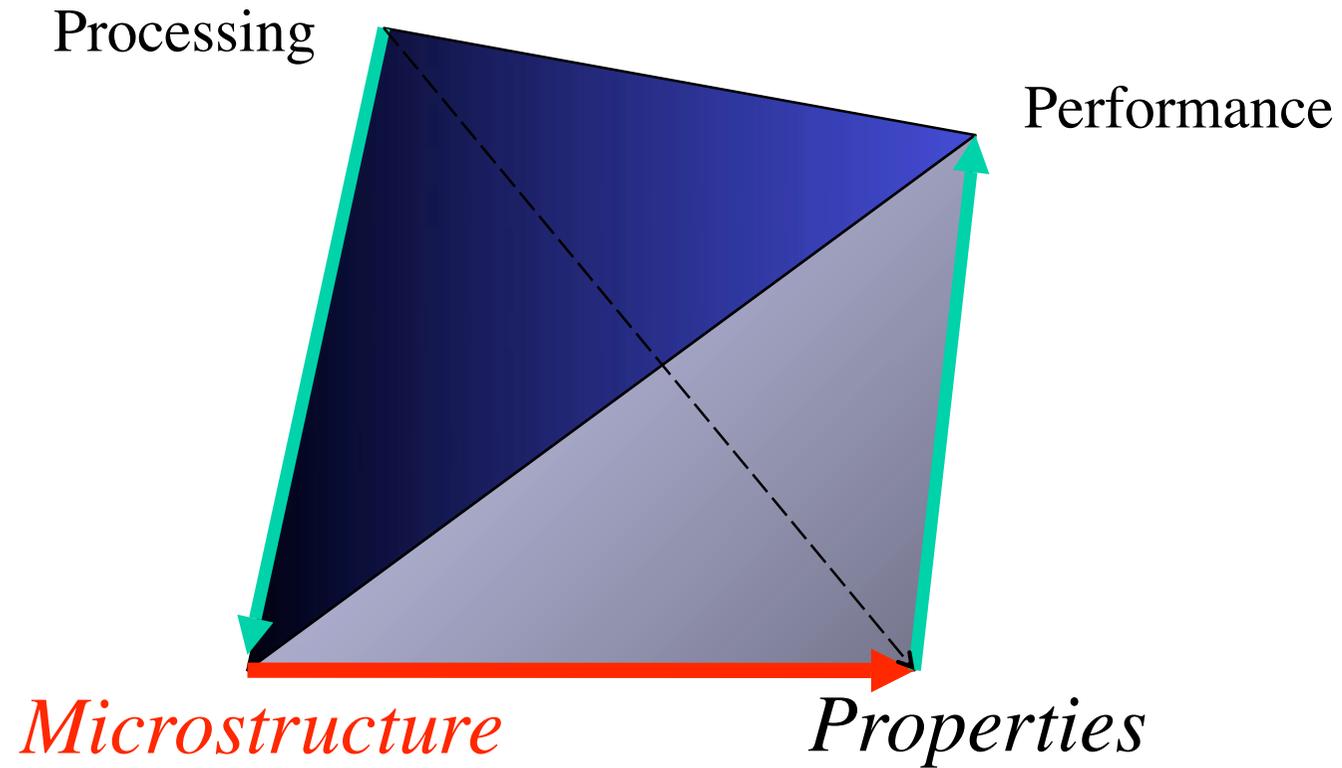
Objective

- The objective of this lecture is to provide some background for the experiment involving crystallization of glass-ceramic.

- The material discussed in this lecture should be familiar to students from the lectures on nucleation and growth.

Bibliography

- <u>Glass-Ceramics</u> (1979), P.W. McMillan, Academic Press, New York.

- <u>Glass-Ceramic Technology</u> (2002), W. Höland & G. Beall, The American Ceramic Society, Westerville, OH.

- <u>Introduction to Ceramics</u> (1976), Kingery, Bowen, Ullman, Wiley.

Glasses crystallization

- Crystallization in glasses is generally a phenomenon to be avoided if at all possible. Crystallization makes glass opaque, for example, and does improve its other properties.

- The exception is the case of glass-ceramics.

- Most glass-ceramics are valued for a combination of chemical inertness and thermal shock resistance.

- Thermal shock resistance depends on *low* CTE. Low CTE means that strains developed on cooling from high temperatures generate small stresses and the breaking strength is less likely to be exceeded.

Glass Ceramics

- Other glass ceramic materials are optimized for:
    - High mechanical strength
    - High temperature capability
    - Photosensitivity
    - Low dielectric constant (electronic packaging)
    - Dielectric-breakdown resistance
    - Biological compatibility
    - Machinability (through the inclusion of micaceous phases)

Applications of Glass Ceramics

- Radomes - Corning 9606, cordierite glass-ceramic. Required properties: transparency to radar, low dielectric constant, low CTE, high strength, high abrasion resistance, high thermal shock resistance.

- Photosensitive glass-ceramics based on lithium disilicate, $Li_2Si_2O_5$, as the crystalline phase that can be selectively etched (UV light) to develop very fine features (holes, channels etc.). The parent glass has lithium metasilicate. Example: Foturan, Fotoceram.

- Machinable glass-ceramics, e.g. MACOR, based on fluorine-phlogopite, $KMg_3AlSi_3O_{10}F_2$), with additions of B_2O_3 and SiO_2 to form a glass. The fluorine compound is micaceous which allows easy cleavage over short distances. The material is very useful as a machinable insulator, used in welding equipment, medical equipment.

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Applications, contd.

- Substrates for magnetic recording disks. Spinel-enstatite glass-ceramics allow high modulus, high softening point (~1000°C), high toughness, insulating substrates.

- Cookware based on glass-ceramics with beta-spodumene, $LiAlSi_2O_6$-SiO_2, e.g. Corning Ware 9608. The latter compound has low CTE, is white in color, and can be easily fabricated.

- Low expansion glasses such as Zerodur containing mainly beta-quartz. These are useful for telescope mirrors and ring lasers (low He permeability also essential here).

VLT telescope in Chile (8.2 m mirrors with adaptive optics)

On the road to Cerro
Paranal, Chile

Mirror fabrication
in Mainz, Germany

(www.eso.org)

# Ring Laser Gyroscope (RLG)
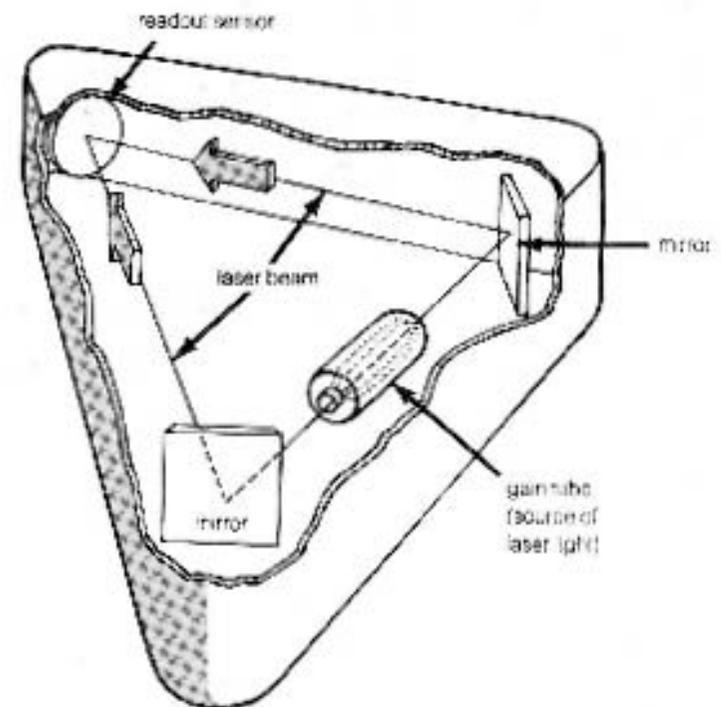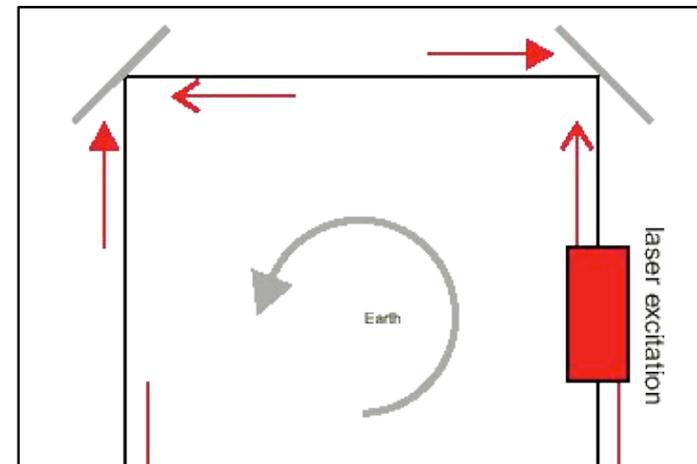
Figure 1. Ring laser gyroscope
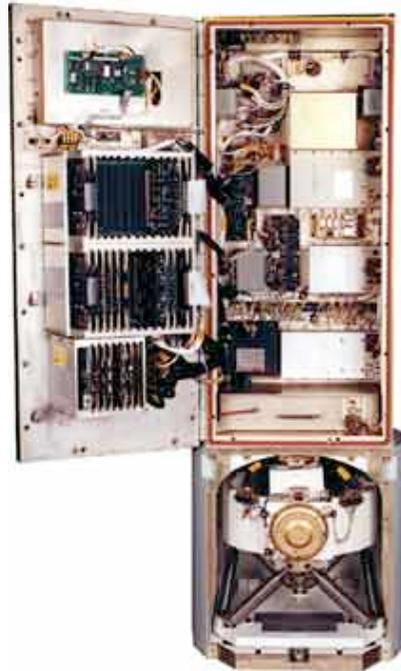
RLG examples

Complete navigation system

What is Zerodur ?
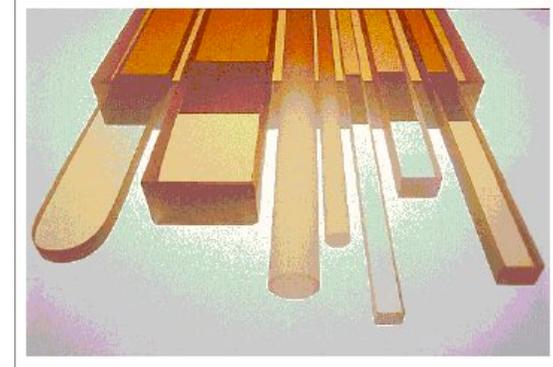
oxide	wt %	mol %	function
SiO2	55.4	63.8	form beta-quartz ss
Al2O3	25.4	17.2	form beta-quartz ss
P2O5	7.2	3.5	form beta-quartz ss
Li2O	3.7	8.6	form beta-quartz ss
MgO	1.0	1.7	form beta-quartz ss
ZnO	1.6	1.4	form beta-quartz ss
Na2O	0.2	0.2	improve glass melting
K2O	0.6	0.4	improve glass melting
TiO2	2.3	2.0	nucleating agent
ZrO2	1.8	1.0	nucleating agent
As2O3	0.6	0.2	fining agent

Zerodur Production
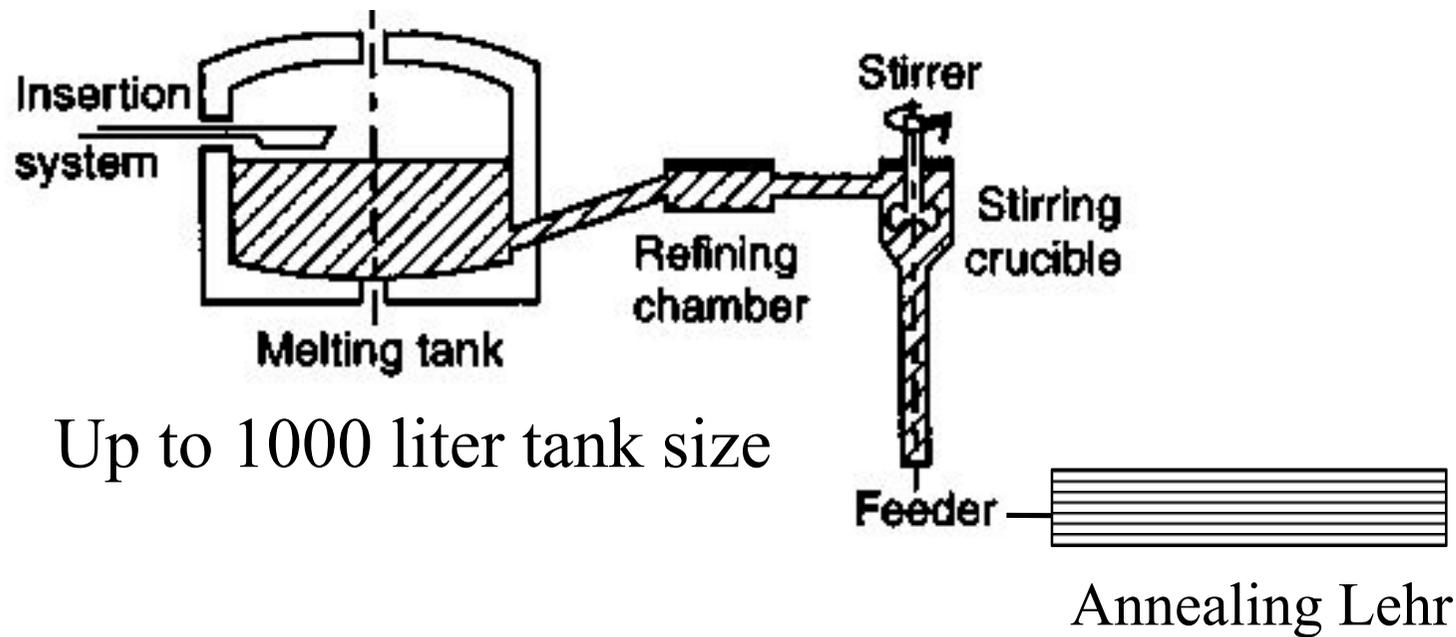


Up to 1000 liter tank size

Annealing Lehr

Up to 1000 gm/min
flow rate

Thermal History Used in Production
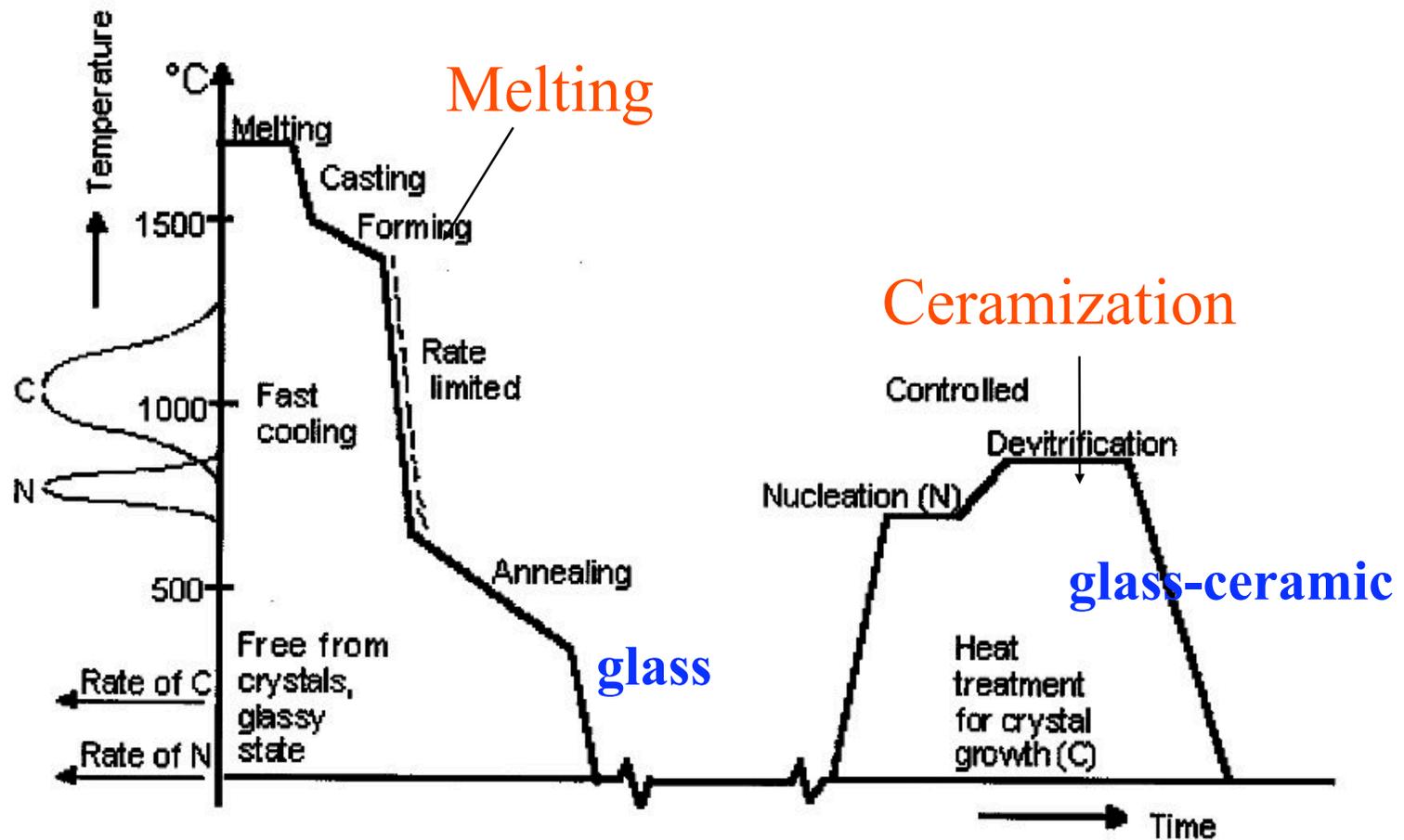
Thermal expansion of LAS

$Li_{2-2(v+w)}Mg_vZn_wO \cdot Al_2O_3 \cdot xAlPO_4 \cdot (y-2x)SiO_2$
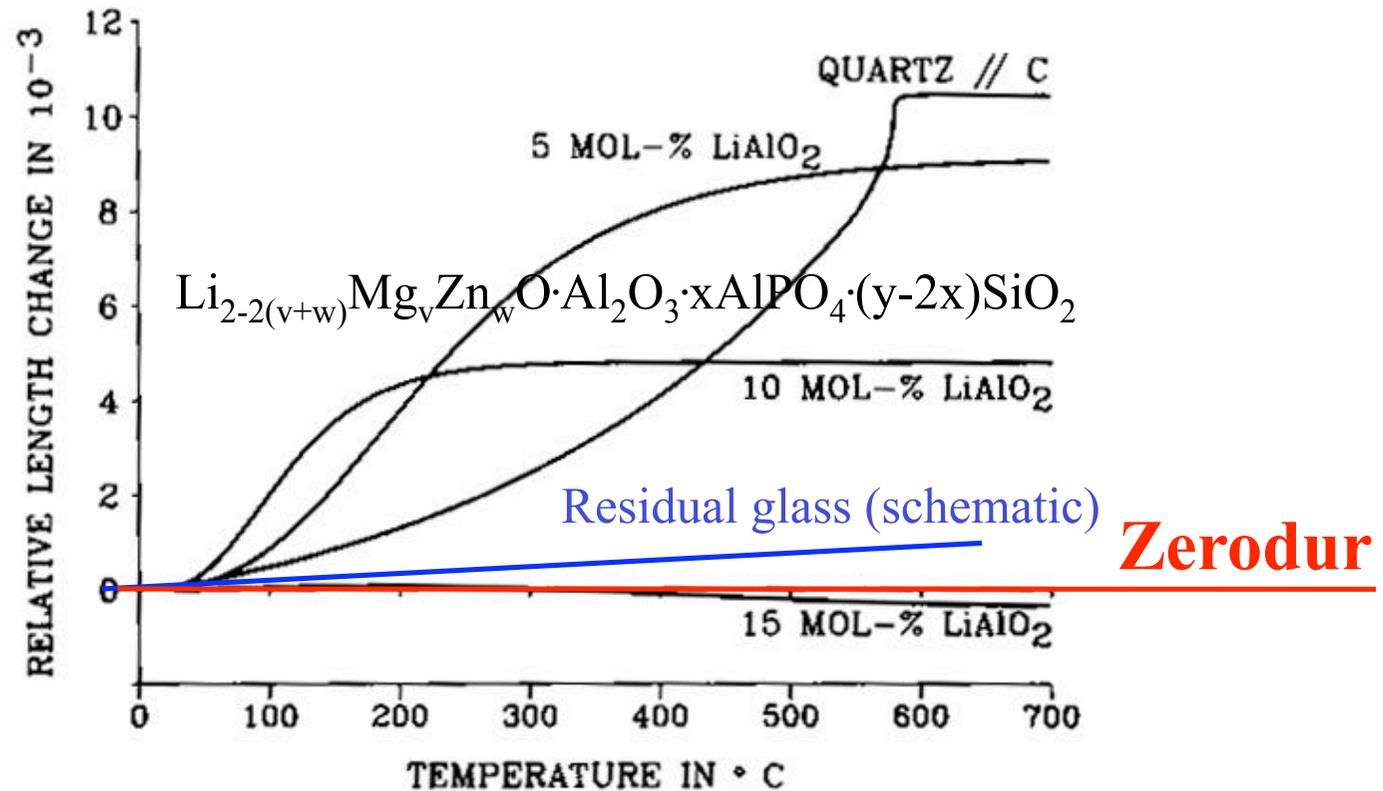
Petzoldt and Pannhorst, 1991

Control of expansion through ceramization times
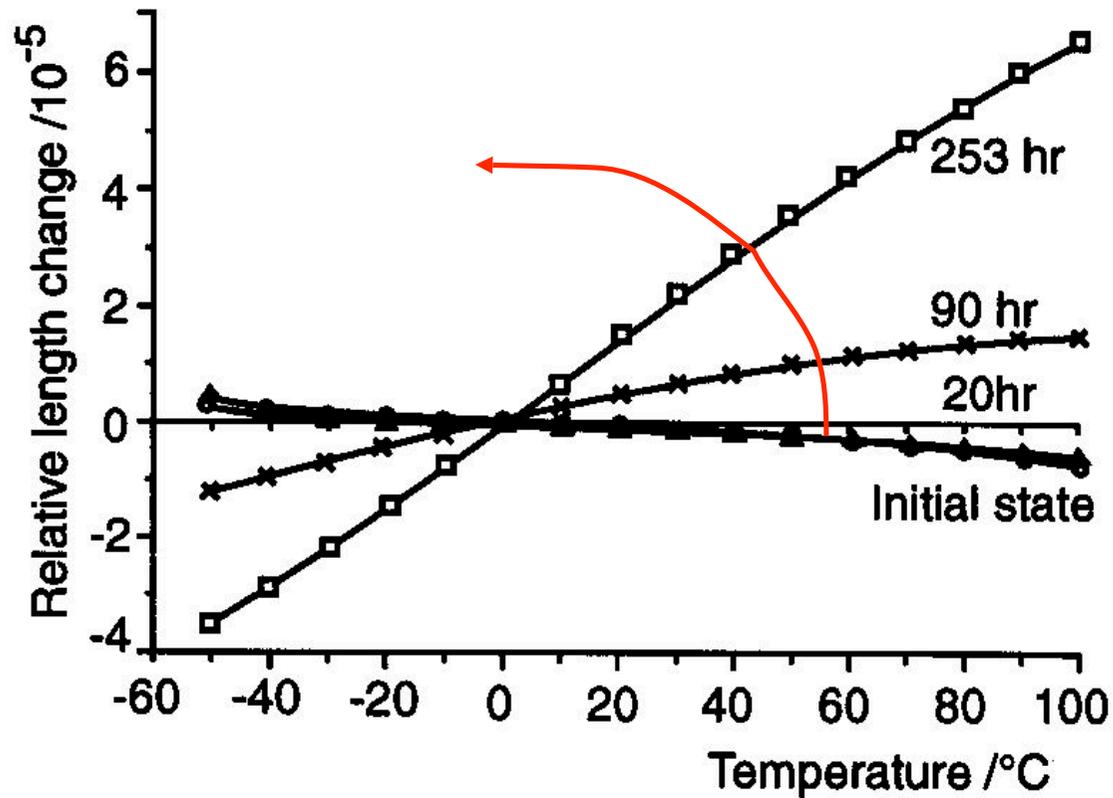
Exchange 0.1 wt% Li₂O for ZnO:
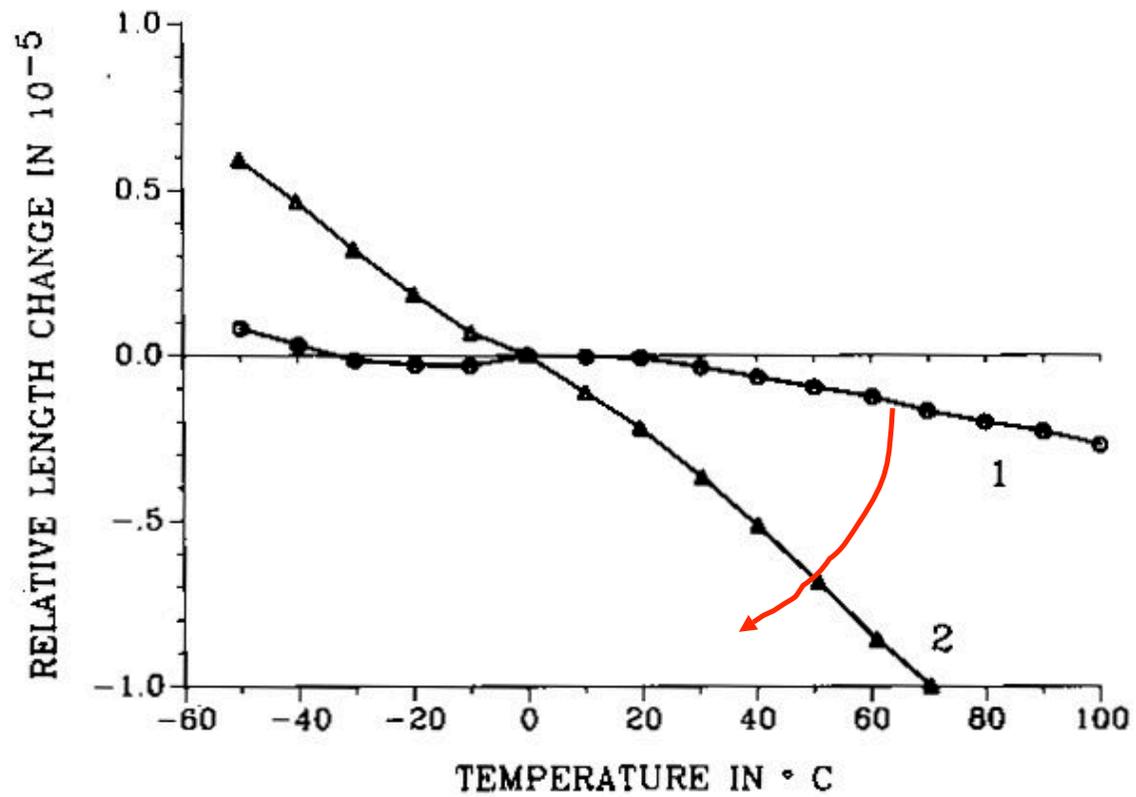
Petzoldt and Pannhorst, 1991

Microstructure development

- The history of glass-ceramics starts with a mistake by a researcher (Stookey) who left an oven on at too high a temperature with a sample of lithium silicate glass containing silver. He expected to find a puddle of glass once he realized his mistake, but instead found a piece of white ceramic because his glass had crystallized *with a fine grain size*.

- This lead to the use of titania as a *nucleating agent* in alumino-silicate glasses.

- Control of crystallization (=devitrification) depends on inclusion of a (well dispersed) nucleating agent. This is akin to grain refinement in solidification (addition of TiB_2 to aluminum melts).

Nucleation + Growth

- In contrast to metals, where isothermal treatments are common, two-steps anneals in glass-ceramics are the norm.

- The typical sequence involves a *nucleation step* of a small volume fraction of, e.g. TiO_2, followed by bulk growth of other phases.

- The *nucleation step* is carried out at lower temperatures, presumably to obtain higher driving forces.

- The *growth step* is carried out at higher temperatures, again presumably to obtain higher growth rates (more rapid diffusion).

Heat Treatment of Glass-Ceramics

- Typical heat treatments require cooling past the "nose" of the crystallization curve, followed by a low temperature treatment to maximize nucleus density and finally a higher temperature treatment to grow the grains.

[Chiang]
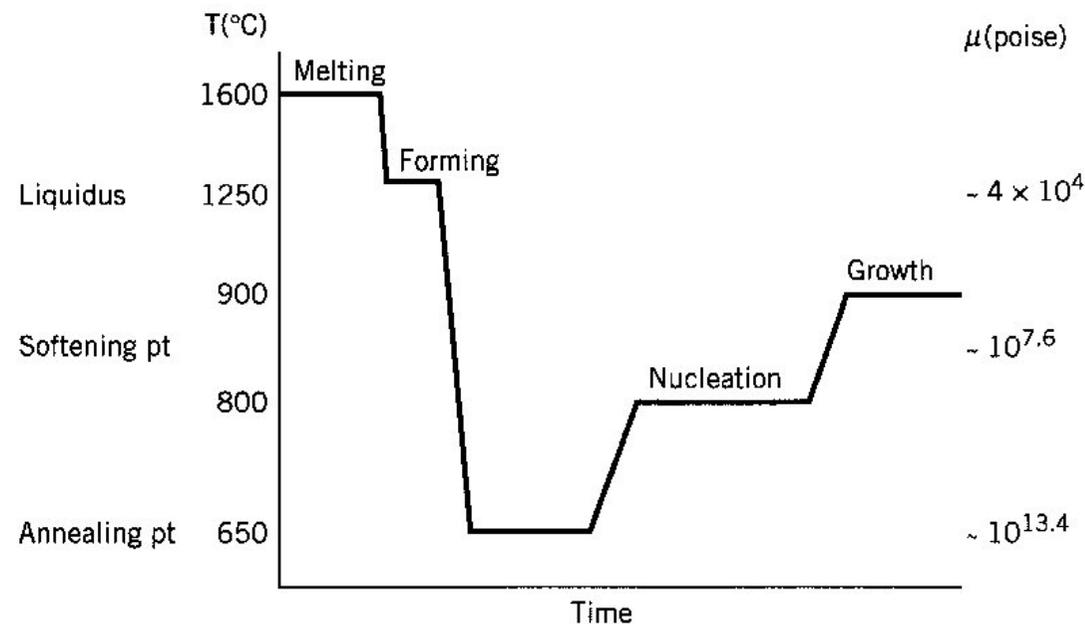
Fig. 5.75 Typical processing cycle for Li_2O-Al_2O_3-SiO_2 glass ceramics.

Nucleation, grain size,

[McMillan]
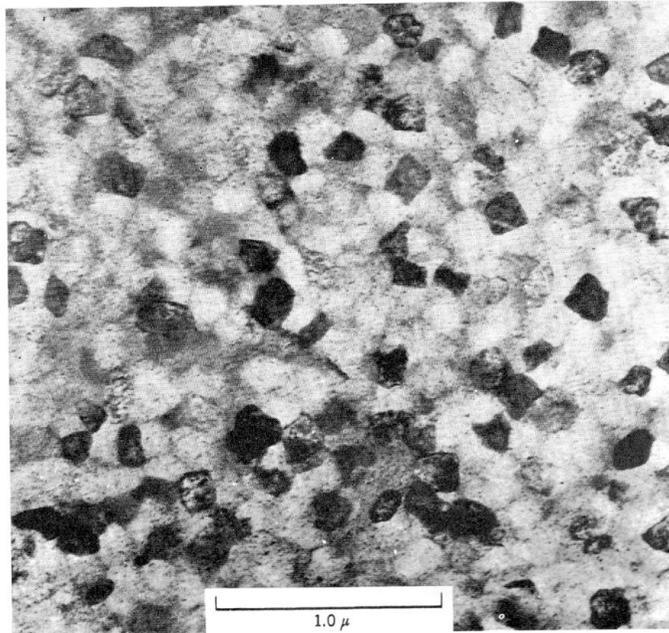
Fig. **5.76** (a) Microstructure in Li$_2$O-Al$_2$O$_3$-SiO$_2$ glass ceramic held at 775°C for 2 h. before heating to 975°C for 2 min.

Fig. **5.76** (b) Identical composition heated rapidly to 875°C and held for 25 min. (From P.E. Doherty in R.M. Fulrath and J.A. Pask, Eds., *Ceramic Microstructures*, John Wiley and Sons, New York, 1968, pp. 161-185.)

Low temperature nucleation step included -> fine grain size

Rapid heating to high temperature (875°C)

Nucleation Rate - Viscosity

- There is a useful relationship between viscosity and nucleation rate for crystallization in glasses.

- The nucleation rate, *N (or I_V), is determined by the critical free energy for nucleation and a Boltzmann factor as seen previously:

$$G^* = 16 \ \gamma^3/3 \ G_V^2$$

$$N = \omega \ C_0 \ exp\text{-}\{ \ G^*/kT\}$$

where ω is an attempt frequency or vibration frequency of order 10^{11} per second, C_0 (or N_V) is the density of molecules per unit volume of order 10^{29} per m^3.

- In glasses one must adjust the attachment frequency based on the viscosity since this can vary so markedly with temperature. Using the Stokes-Einstein relation for atomic diffusivity in a melt:

$$D = kT/3 \ a_0\eta = \omega a_0^2$$

- This suggests that we can take ω to be inversely proportional to the viscosity, η.

Viscosity dependent nucleation rate

- Adjusting the attachment frequency to match experimental data (larger than theory suggests),

$$N = 40\ C_0\, kT\, /\, 3\ a_0^2 \eta\ .\ exp\text{-}\{\ G^*/kT\}$$

- Given that the viscosity dominates the temperature dependence of all the terms in this expression, we can simplify to this:

$$N = K\, /\, \eta\ .\ exp\text{-}\{\ G^*/kT\}$$

where K is a constant of order 10^{36} $m^{-3}sec^{-1}$poise for oxide glass formers.

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Viscosity dependent nucleation rate

- In the previous development of driving forces, we approximated the driving force as $\Delta T\, L_f/T_m$, where L_f is the latent heat of transformation (melting, e.g.). Hoffmann developed the following improved approximation for the case that the difference in specific heat between solid and liquid is significant but constant (with changing temperature):

$$\Delta G_m = \Delta H_m\, \Delta T.T/T_m{}^2$$

- This can be inserted into the standard expression for nucleation rate:

$$N = \frac{K}{\eta}\exp\left\{\frac{16\pi}{3kT}\frac{V_m^2\gamma_{SL}^3}{\Delta H_m^2\left(\dfrac{\Delta T\cdot T}{T_m^2}\right)^2}\right\}$$

Comparisons

- Calculated and experimental TTT curves agree well for sodium disilicate and anorthite.

- Crystallization detected by X-ray diffraction.
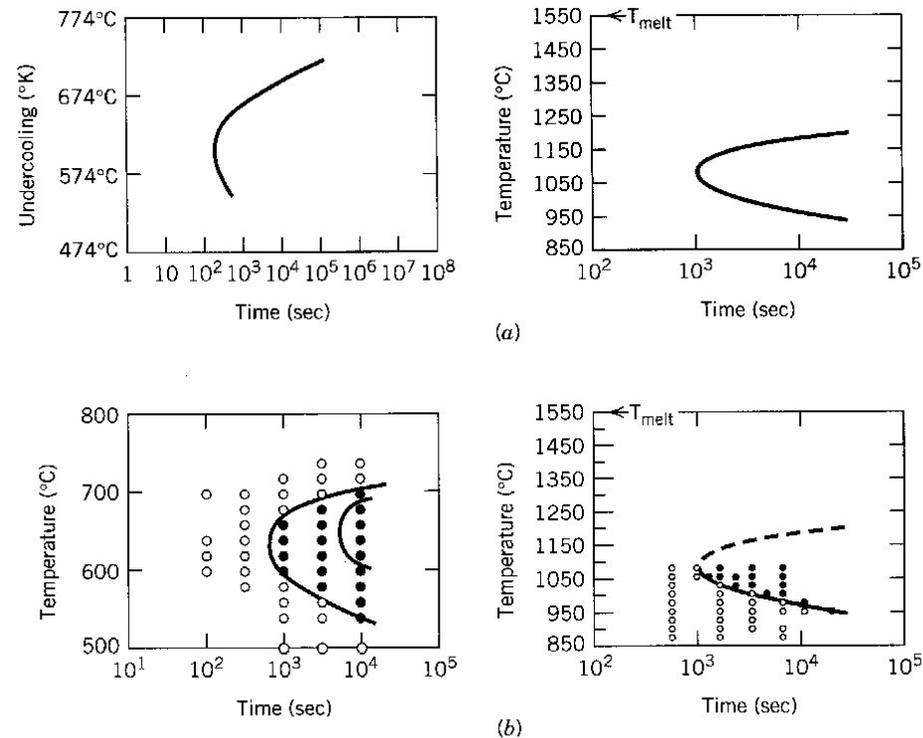
Fig. 5.71 (*a*) Calculated TTT curves for $Na_2O \cdot 2SiO_2$ at $V_c/V = 10^{-6}$ and $CaO \cdot Al_2O_3 \cdot 2SiO_2$ (anorthite) at $V_c/V = 10^{-3}$. (*b*) Experimental observations of crystallized (closed symbols) and glassy (open symbols) samples. (From G.S. Meiling and D.R. Uhlmann, *Phys. Chem. Glasses*, **8**, 62 (1967), D. Cranmer, R. Salomaa, H. Yinnon, and D.R. Uhlmann, *J. Non-Cryst. Solids*, **45**, 127, 1981, and H. Yinnon and D.R. Uhlmann, in *Glass: Science and Technology*, Vol. 1, D.R. Uhlmann and N.J. Kreidl, Editors, Academic Press, 1983.)

CCT versus TTT

- Crucial difference between idealized TTT diagrams that assume *isothermal anneals* and realistic quenching is the effect of continuously decreasing temperature. Re-drawing the diagrams as CCT diagrams allows the increase in time for a given fraction transformed to be depicted.
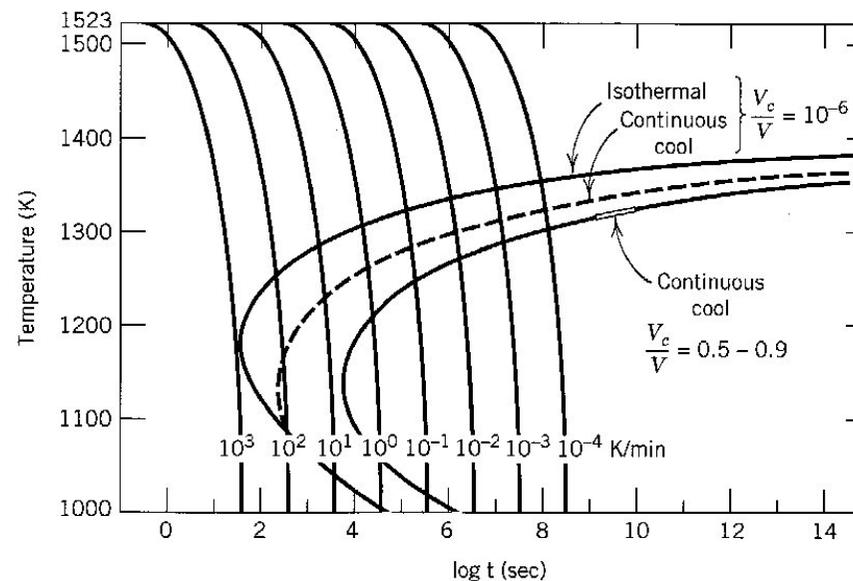

Fig. 5.72 Isothermal and constant-rate cooling TTT curves corresponding to $V_c/V = 10^{-6}$ for lunar glass. (From H. Yinnon and D.R. Uhlmann, in *Glass: Science and Technology*, Vol. 1, D.R. Uhlmann and N.J. Kreidl, Editors, Academic Press, 1983.)

Heterogeneous nucleation

- Heterogeneous nucleation is as important in glasses as it is in metals.

- In glass, one must be careful to avoid including phases that can act as nucleation sites for crystallization.

- In glass-ceramics, the situation is reversed and one typically adds nucleating agents deliberately.

- Examples are TiO_2 and ZrO_2.

Approximate TTT

- Uhlmann and Onorato provide an approximate model for TTT diagrams in glasses (in the sense of how to avoid crystallization).

- For many cases, the "nose" of the crystallization curve occurs at 0.77 T_m. This allows the critical cooling rate to be calculated based on just one temperature.

- Also, the nucleation barrier can be approximated by the following, where $T^* \approx 0.8T_m$:

$$\Delta G^* \approx 12.6 \ \Delta S_m/R \ kT^* = BkT^*$$

and the constant, *B*, is of order 50. This allows an formula for the critical cooling rate to be obtained:

$$dT/dt_{crit} = AT_m{}^2/\eta \ exp\text{-}(0.212B)\{1\text{-}exp(0.3 \ H_m/RT_m)\}^{0.75}$$

where the constant *A* is of order 40,000 J.m^{-3}K^{-1} and the viscosity, η, is that at the nose of the curve, 0.77T_m.

Typical glass ceramic compositions

- Low expansion glass ceramics result from the particular compositions used.

- Al and Li substitute into beta-quartz (silica): Al^{3+} substitutes for Si^{4+} with Li^+ providing charge neutrality as an interstitial ion.

- Lithia-alumina-silica compositions for Pyroceram contain beta-spodumene, $LiAl[Si_2O_6]$, which has a weak positive CTE, $\sim 10^{-6}.°C^{-1}$.

- At higher levels of Al and Li substitution, the CTE can become negative.

- Substitution limit is beta-eucryptite, $LiAl[SiO_4]$.

References

- Phase transformations in metals and alloys, D.A. Porter, & K.E. Easterling, Chapman & Hall.

- Physical Ceramics (1997), Y.-T. Chiang, D.P. Birnie III, W.D. Kingery, Wiley, New York, *pp430-450*.

- Materials Principles & Practice, Butterworth Heinemann, Edited by C. Newey & G. Weaver.

- Glass-Ceramics (1979), P.W. McMillan, Academic Press, New York.

- Glass-Ceramic Technology (2002), W. Höland & G. Beall, The American Ceramic Society, Westerville, OH.

- Applications, Production, and Crystallization Behavior of an Ultra-Low Expansion Glass-Ceramic: Zerodur, presentation by Dr. Mark J. Davis, Schott Glass Technologies, Oct. 17th at CMU.