Practical aspects and implications of interfaces in glass-ceramics

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Outline

- Key questions to address
- Interfacial effects in glass-ceramics---a laundry list
- Glass-ceramics in general: SCHOTT commercial examples
- Commercial or near-commercial gc / interface examples
- Key questions: review

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Key Questions (from H. Jain)

- *What has been the role of interfaces in the development of emerging applications?*
- *With regard to applications, what aspects of interfaces are most important and why?*
- *What are the scientific issues that require basic understanding of interfaces in glass-ceramics? What is the relative importance of each?*
- *What properties of glass-ceramics hold promise for the future?*

Practical Effects (Internal)

- Microstructural development
  - surface energies and their impact on nucleation
  - general glass stability; controlled vs. un-controlled crystallization (i.e., critical cooling rate in a commercial setting vs. academic…)
- Structural
  - detailed nature of interface (e.g., "pristine", microcracked…)
  - crack blunting processes
  - residual stresses, crystal clamping
  - permeability
- Electrical
  - Effective connectivity
  - Resistive / capacitive behavior
- Optical
  - scattering effects

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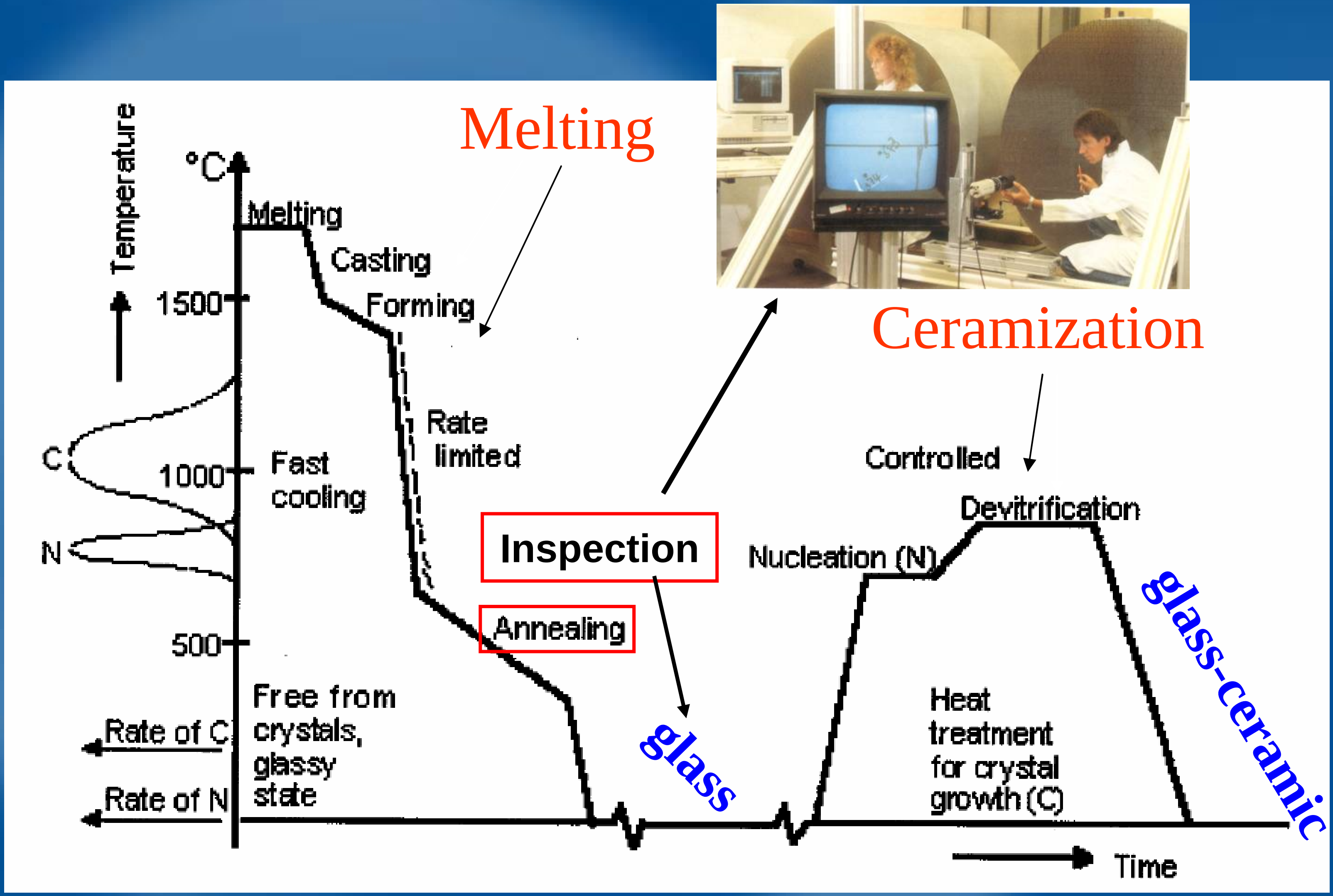
Practical Effects (External)

- Joining (*low-temperature*)
  - Hydrophilic vs. hydrophobic surfaces
  - Competitive bonding technologies
- Glass-to-metal sealing (*high-temperature*)
  - Flow vs. crystallization “stiffening”
  - Interfacial reactions
  - Hermeticity (CTE matching)
- Polishing
  - Crystal vs. glass effects (mostly proprietary know-how)

Why glass-ceramics?

- Single Crystals often exhibit the highest property performance, but are generally more difficult and expensive to manufacture
- Ceramics are easier to manufacture, but are typically porous to some degree and may exhibit inhomogeneities, aging, decreased strength, etc.
- Glasses take advantage of processing ease, homogenization efficiency, and tailorable compositions, but lack certain functions (e.g., novel CTE combinations, lack of center-of-symmetry)
- Glass-ceramics can be seen as "*glass packaged crystals*" and combine the ease of glass processing and potential for new property combinations (e.g., ultra-low thermal expansion, 2nd-harmonic generation, piezoelectricity)

How is a commercial glass-ceramic produced?



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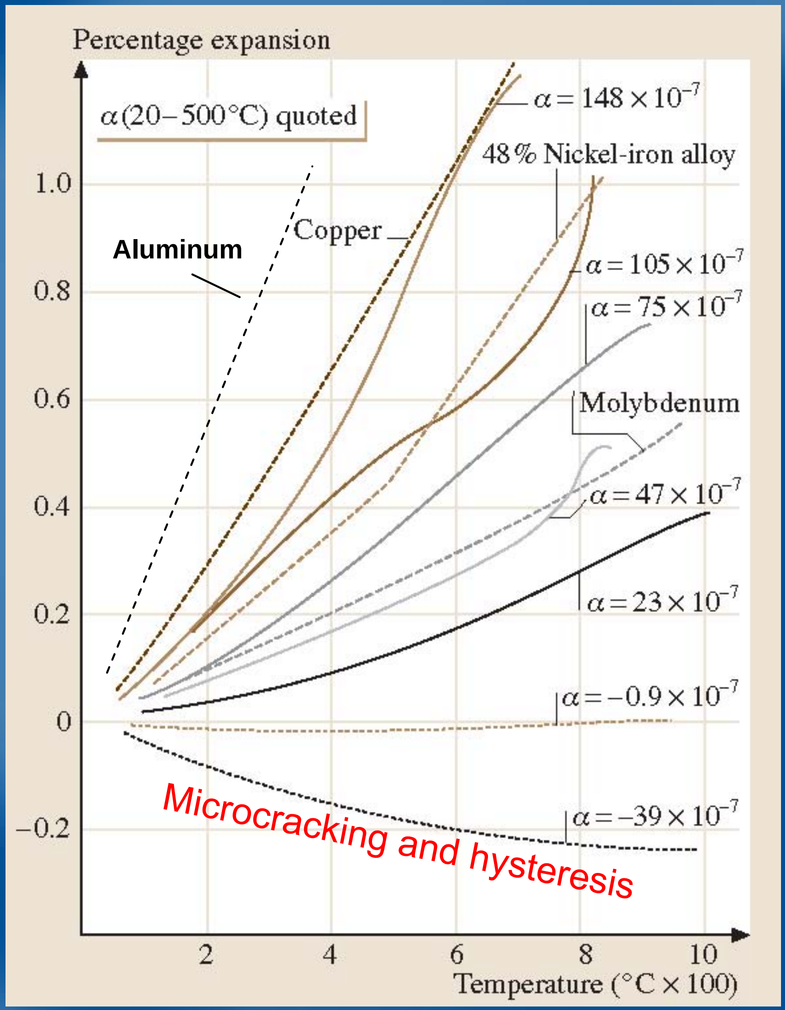
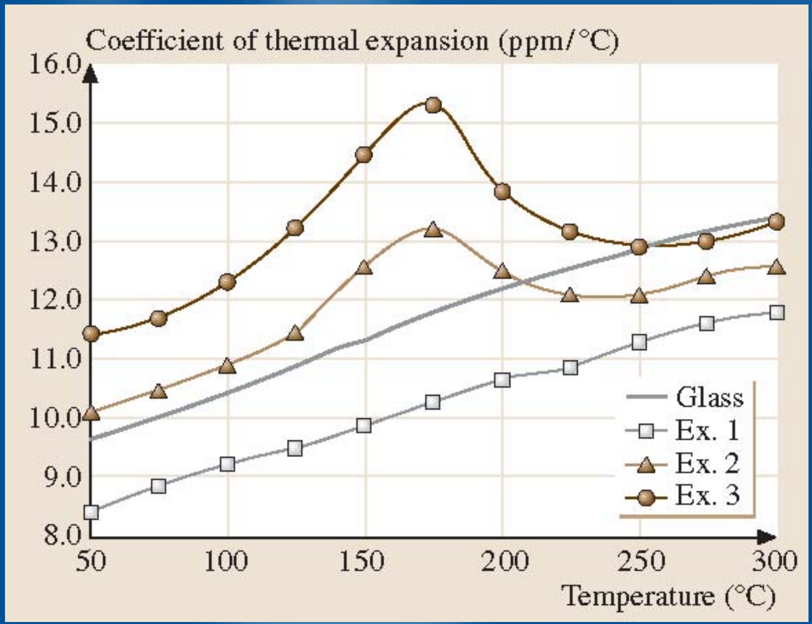
Thermal expansion tailoring



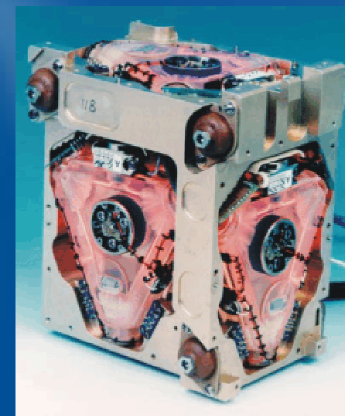


Same composition for all curves

From Sect. 6.5, Glass-Ceramics for Optical Applications, M. Davis
in Optical Materials and Their Applications, Springer-Verlag

Examples of SCHOTT glass-ceramics

8.2 m telescope mirror blanks



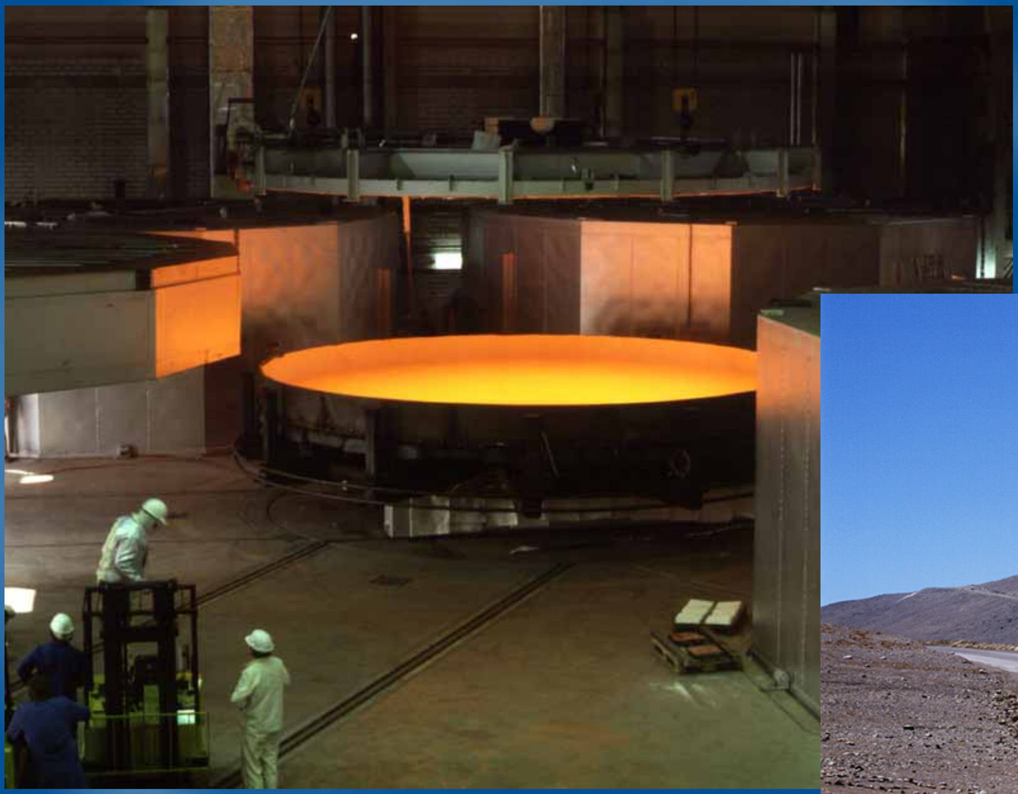
Ring-laser gyroscopes

Glass-ceramic cooktops

Pressed glass-ceramic reflectors

Large mirror blank production (Zerodur)

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



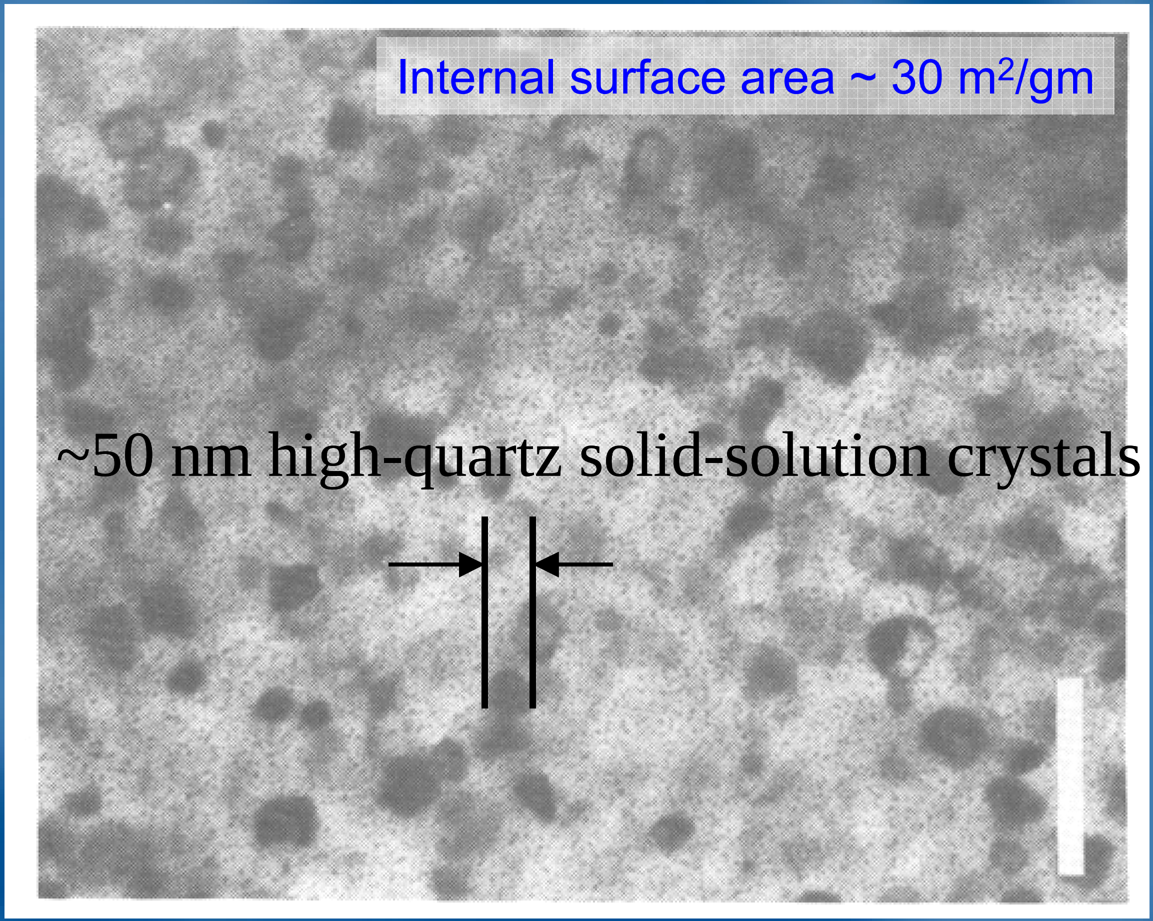
On the road to Cerro Paranal, Chile

Zerodur mirror fabrication

(www.eso.org)

Typical LAS (Zerodur) glass-ceramic microstructure

Non-isothermal ~2 °C/hr



~10^{22} m^{-3} HQSS crystals

~10^{25} m^{-3} $ZrTiO_4$ crystals

bar = 200 nm

Maier and Muller, 1987

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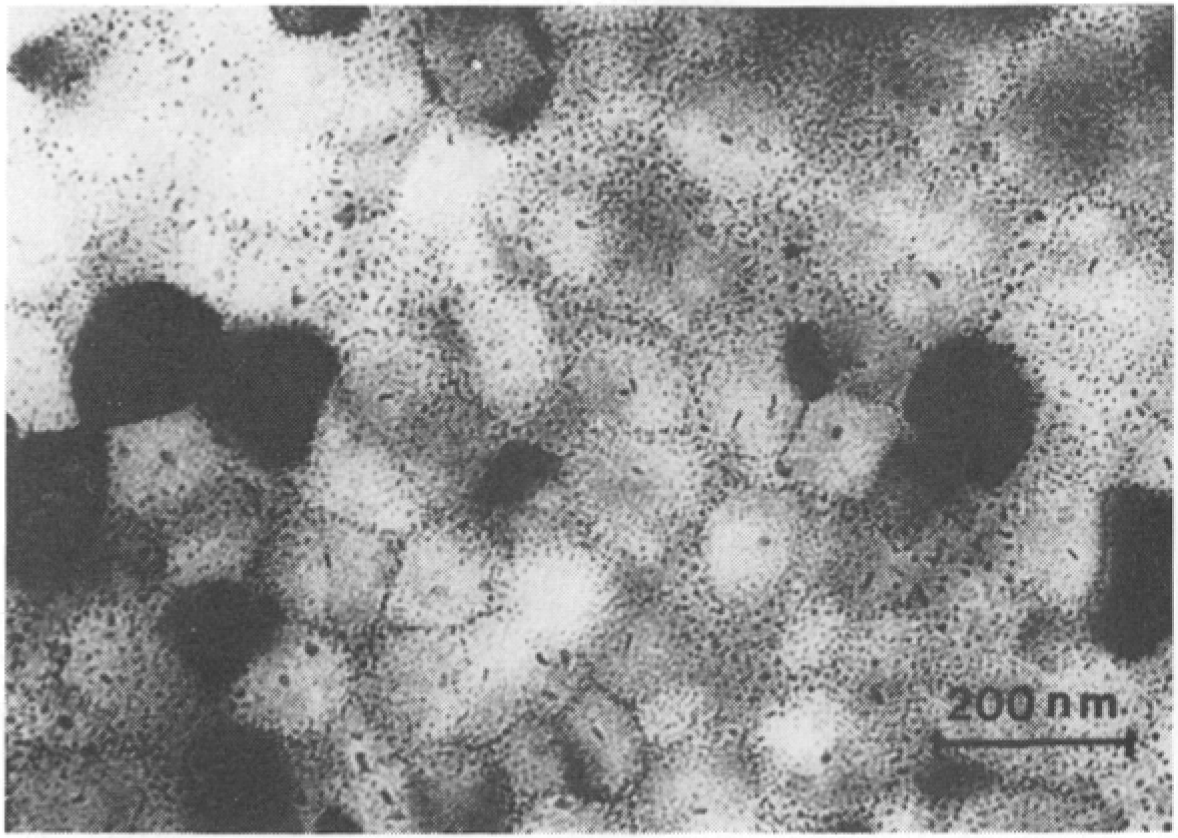
Isothermal heat treatment



Petzoldt and Pannhorst, 1991

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Permeability of Zerodur

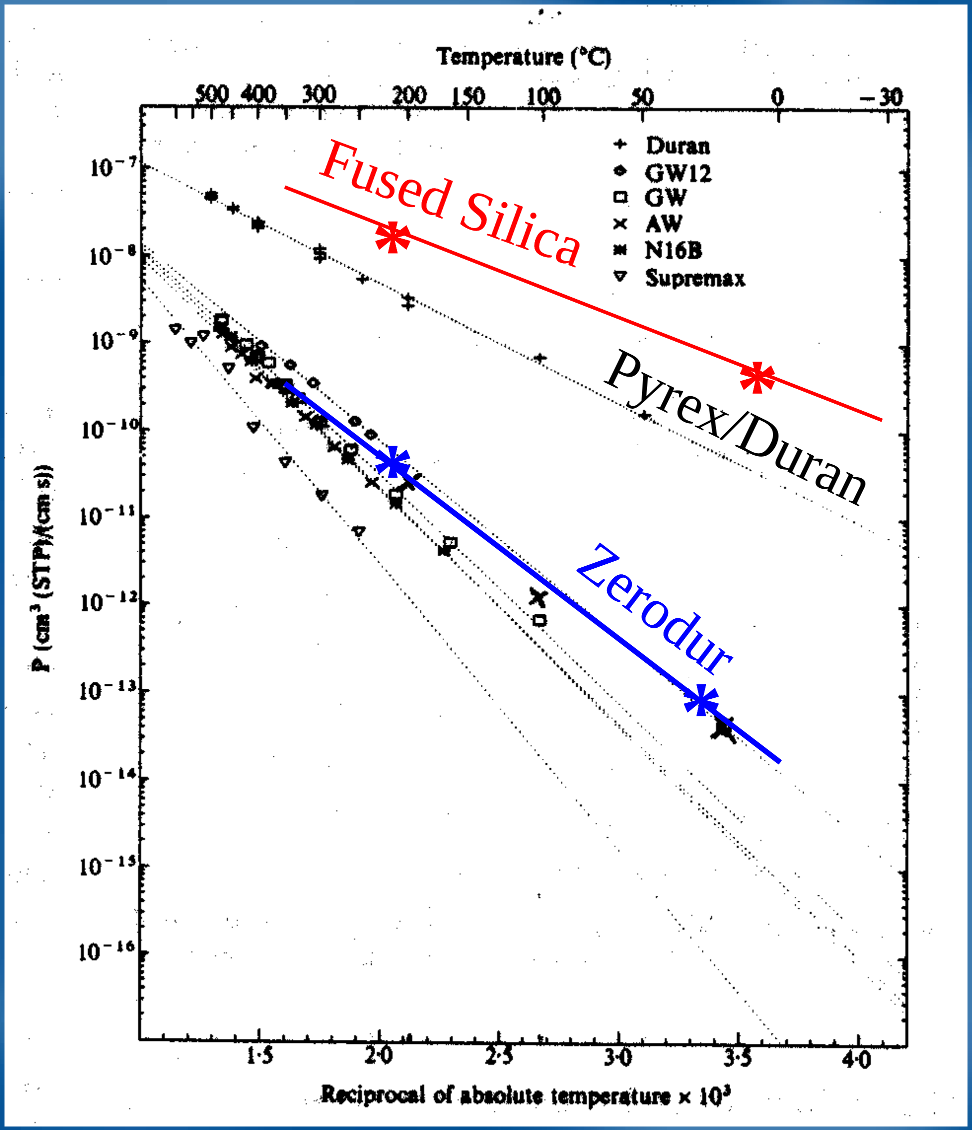

Figure from Suckow et al. (1990)

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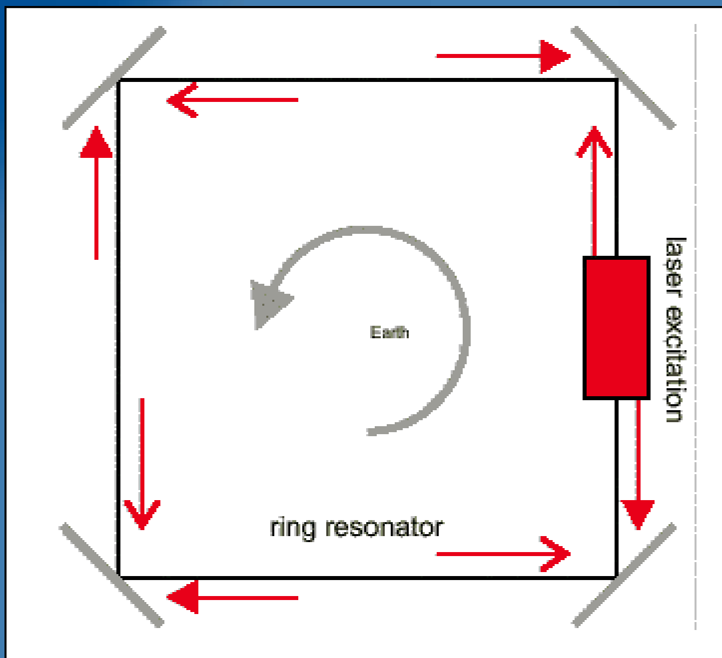
Zerodur permeability enables high-precision RLG production



Sagnac Effect

Ring Laser Gyroscope (RLG)

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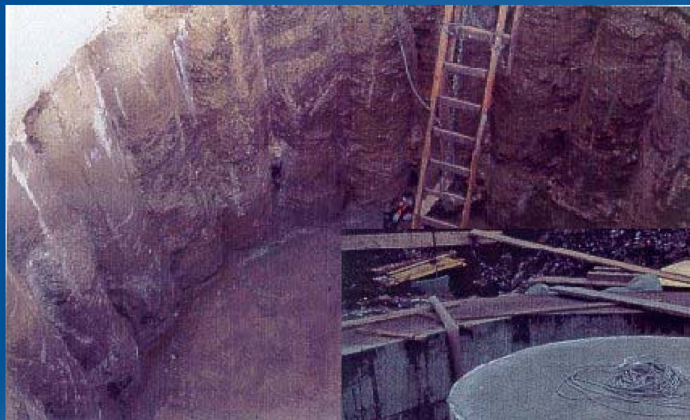
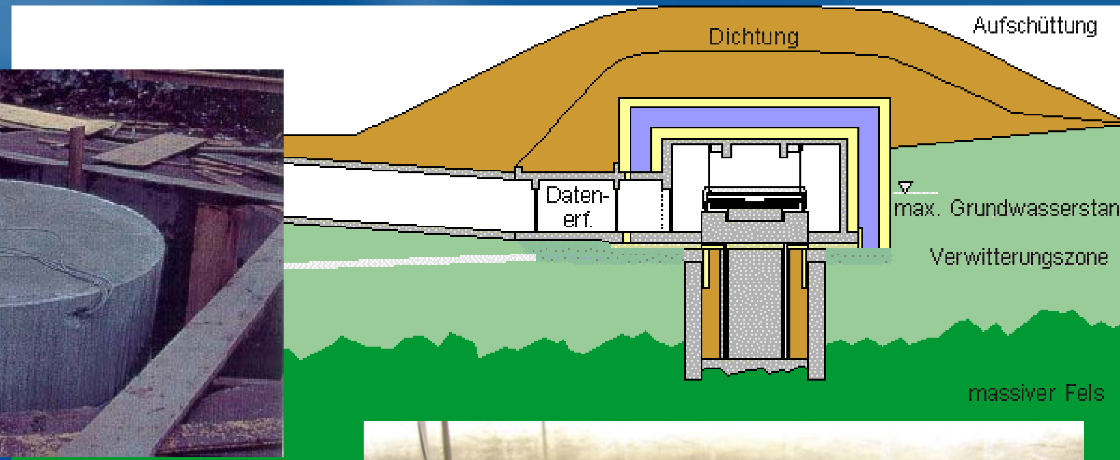
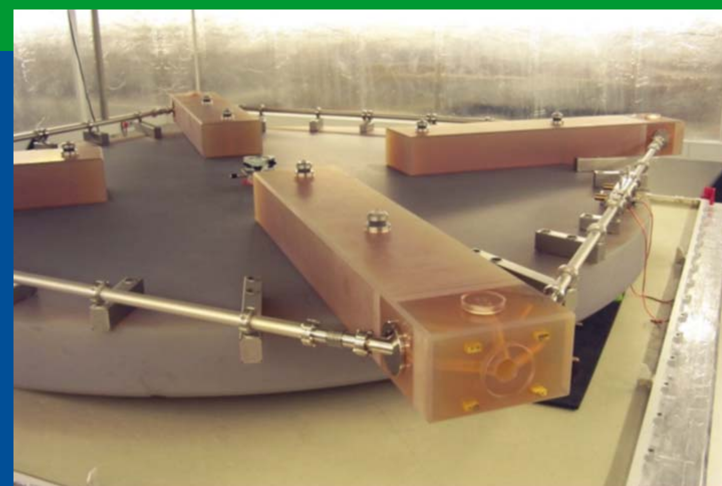
World’s biggest RLG (Bavarian Forest) to measure subtle Earth motions







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Scattering example in glass-ceramics (DWDM substrate)

small particle limit:

$$\tau = \frac{4a^3}{3}(n \cdot \Delta n)^2 \frac{1}{\lambda^4} \rho$$

Rayleigh (1881)

Visible light only (IR blocking filter KG3)
$\lambda < 850$ nm

Sample thickness ~ 35 mm

Crystal size ~35 nm

IR only (visible blocking filter RG 1000)
$\lambda > 850$ nm

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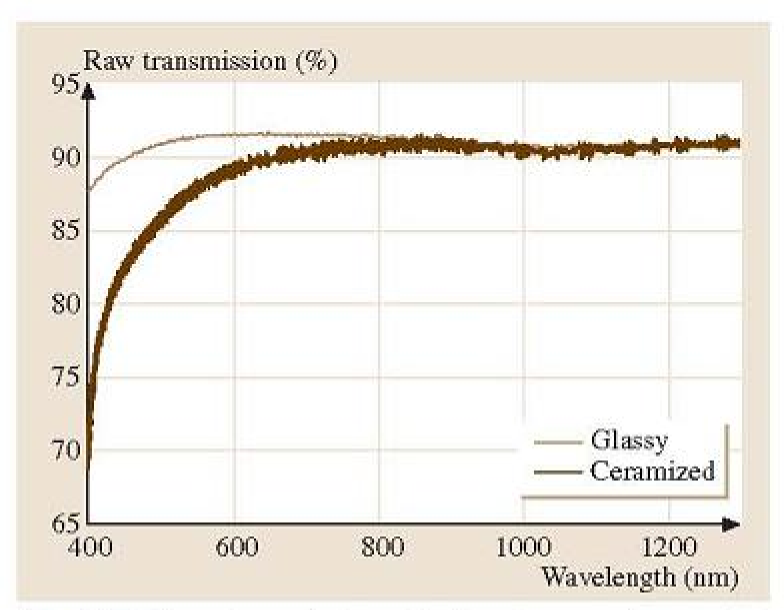
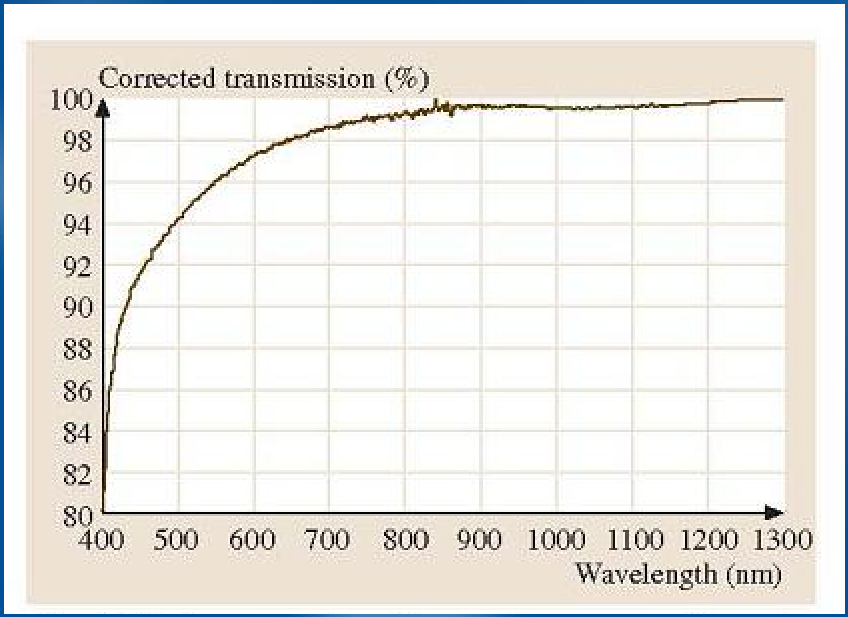
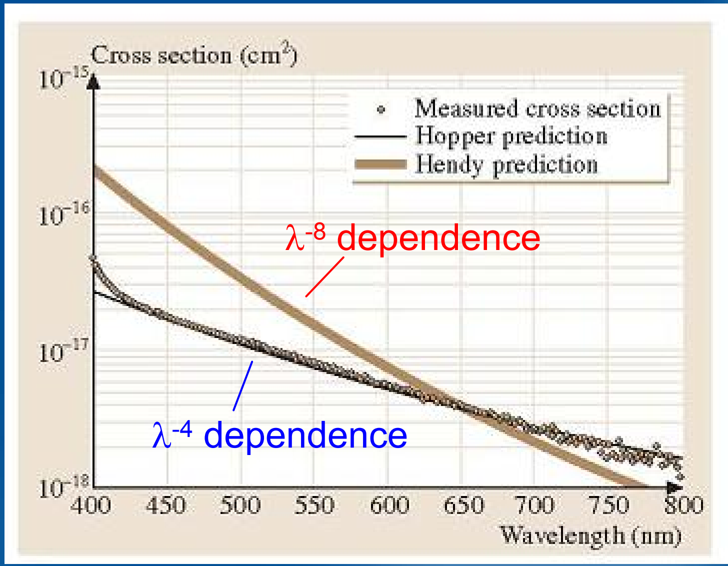
Quantitative scattering example in glass-ceramics (Zerodur)







From Sect. 6.5, Glass-Ceramics for Optical Applications, M. Davis
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Crystal clamping of a FE phase (Lynch and Shelby 1984)

Also Grossman and Isard (1969)

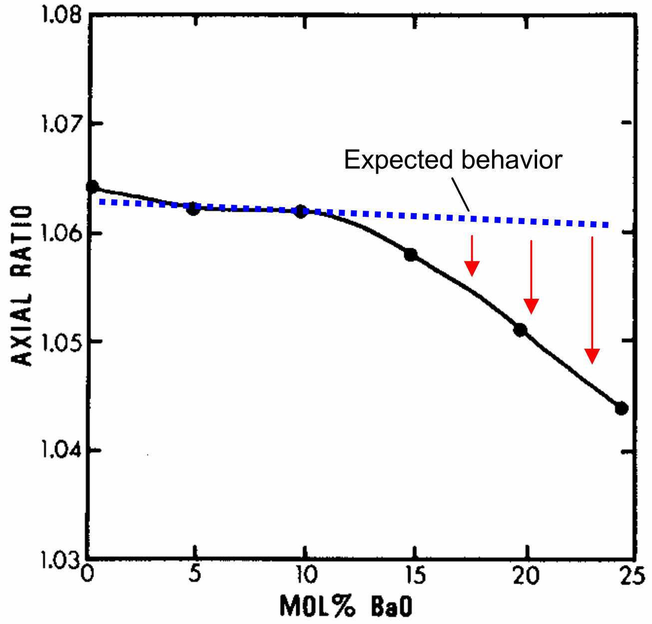


Fig. 4. Axial ratio (c/a) of clamped lead titanate crystals vs composition of initial glass.

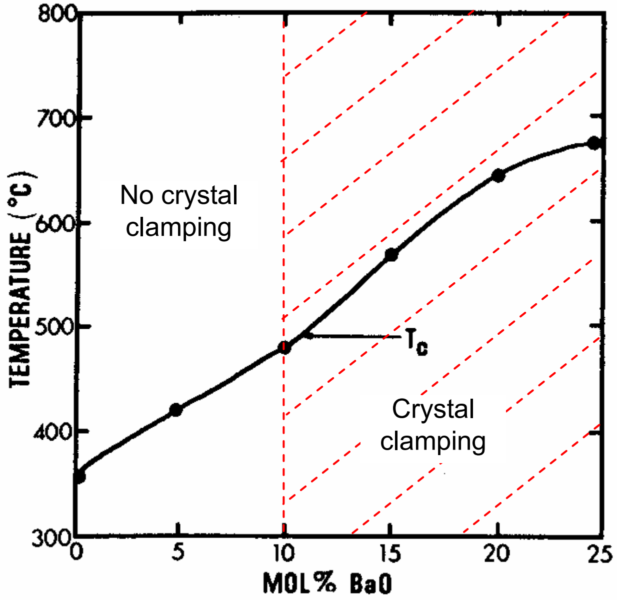
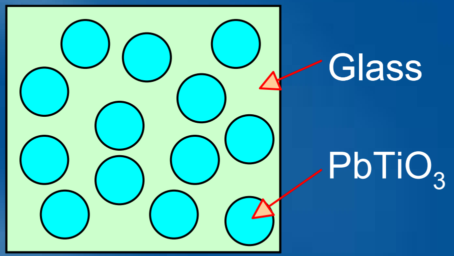


Fig. 5. Transition temperature of residual glass of fully crystallized samples vs composition of initial glass.



Assuming ~1% strains and E ~ 260 GPa, calculated residual stresses ~ 3 GPa (!)

Residual stress studies (crystal/glass interface)

System	Max $|\sigma|$ (MPa)	Source
Li_2O-$2SiO_2$	~150	Mastelaro and Zanotto (1999)
Soda-lime silicate	~200	Mastelaro and Zanotto (1996)
LAS	~400	Zevin et al. (1978)
$PbTiO_3$ – BaO – B_2O_3	~3000 (?)	Estimated from data of Grossman and Isard (1969)

⇒ In all cases, calculated stresses >> nominal 20 MPa tensile strength of typical (imperfect) external glass surfaces

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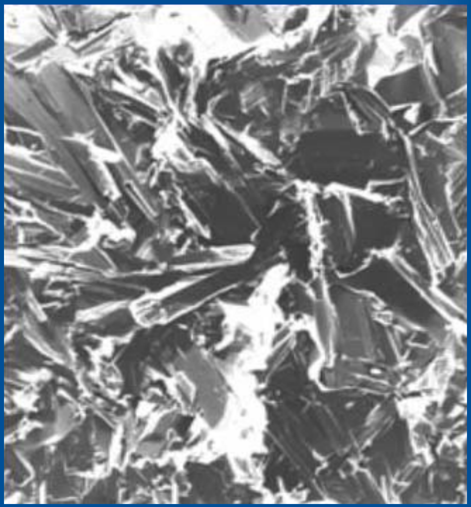
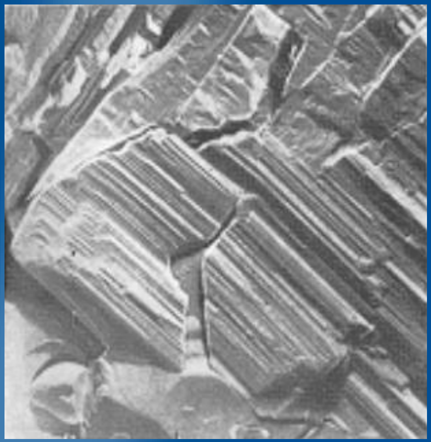
Engineered microstructure examples (G. Beall)

Fluorrichterite



Canasite



Enstatite

- High Crystallinity
- Interlocking Crystals
- Grain-size from 1-10 µm
- Acicular Crystals (Rods)
- Bladed Crystals (Laths)
- Polysynthetic Twinning

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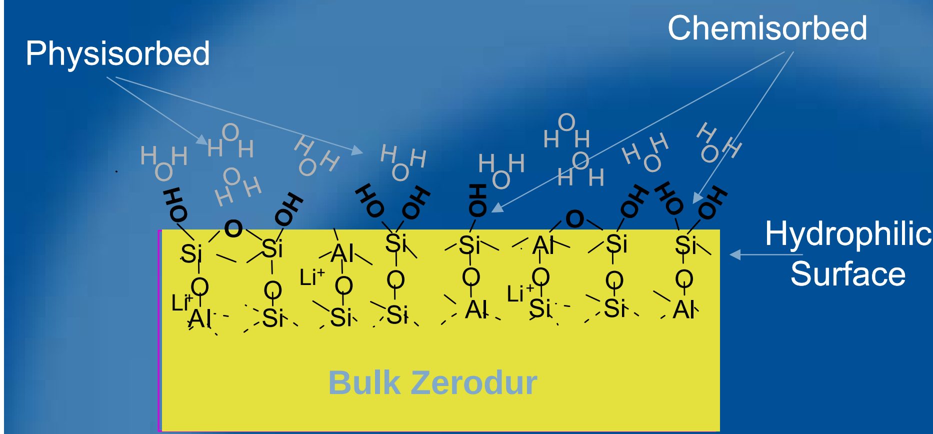
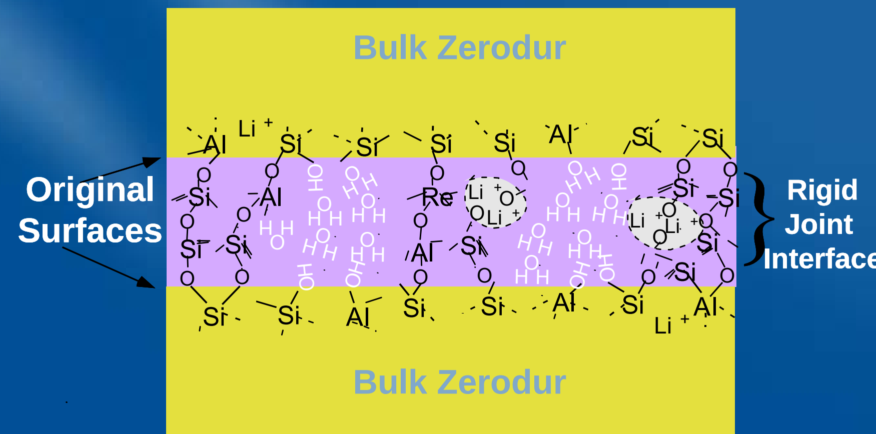
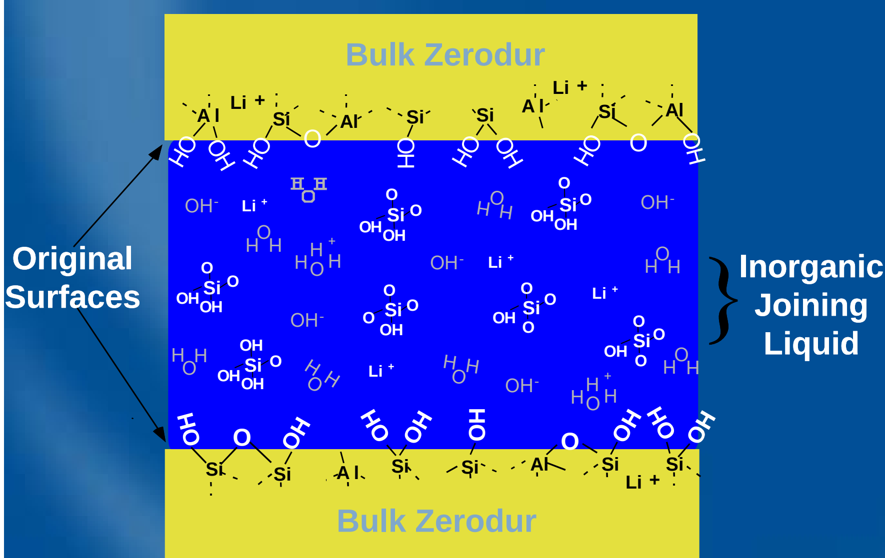
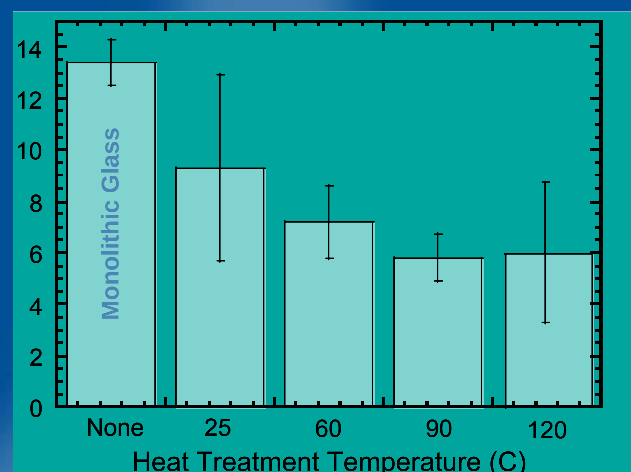
Aqueous based low-temperature bonding









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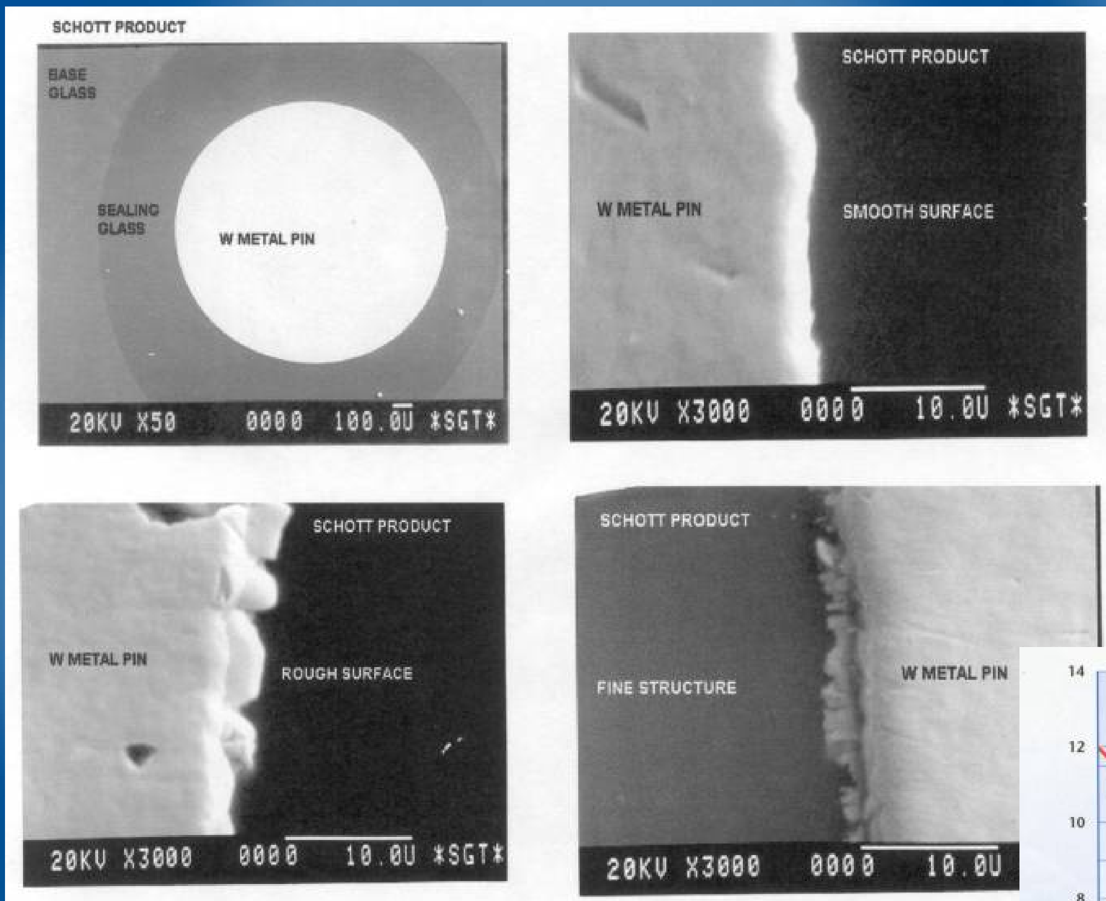
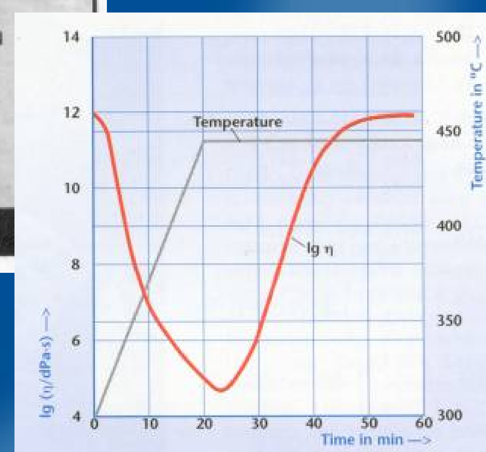
Glass and glass-ceramic sealing materials



Metal / glass-ceramic chemical reaction

High overpressure tolerance

Good high-CTE match



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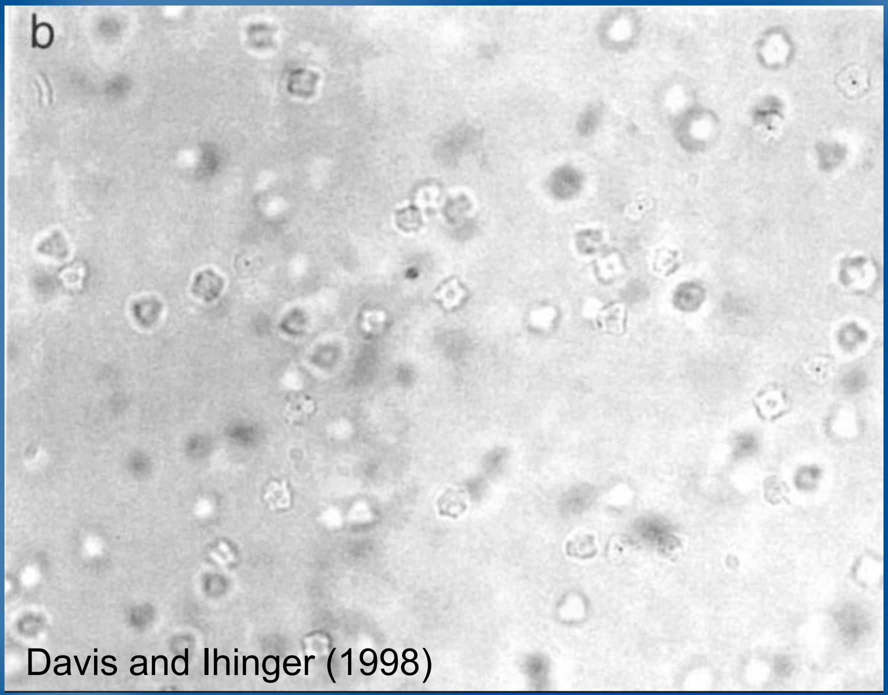
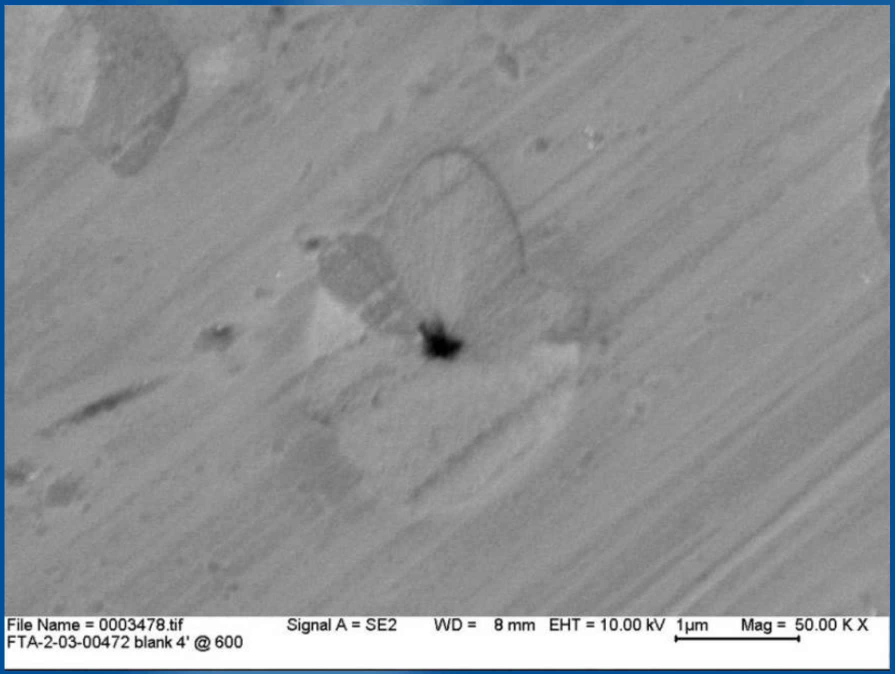
Bubble interfaces as nucleation sites
- curiosity or more widespread?

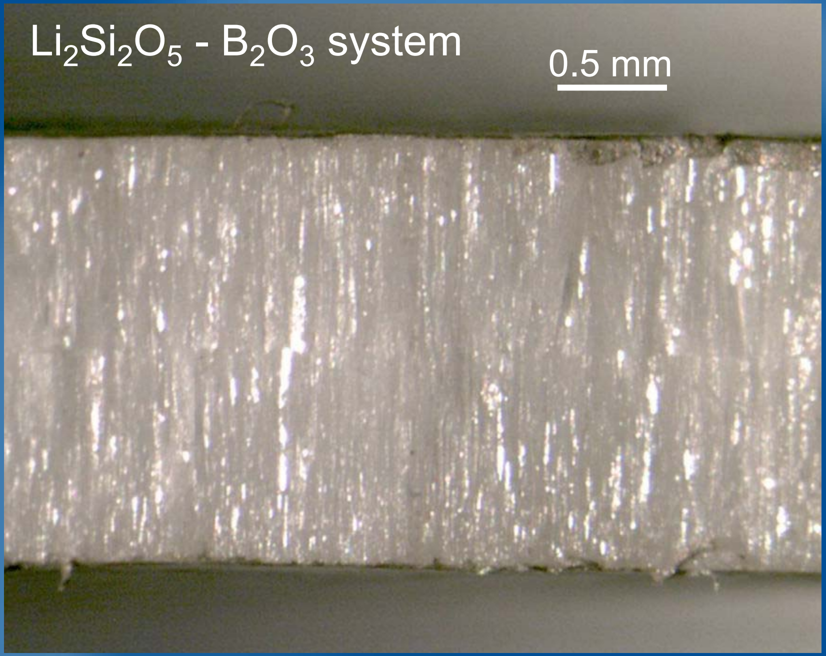


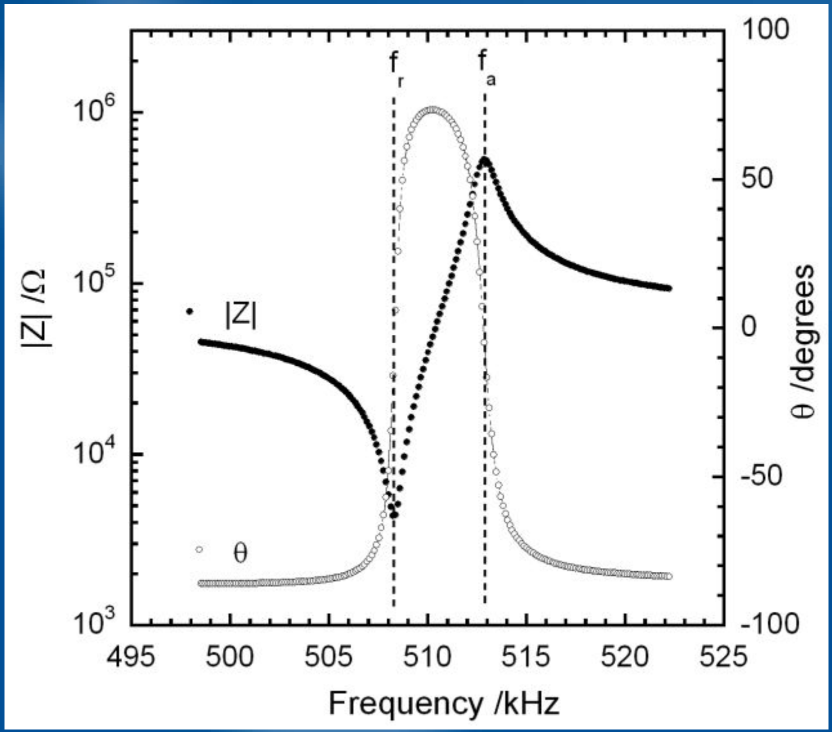
Davis and Ihinger (1998)

Lithium disilicate composition

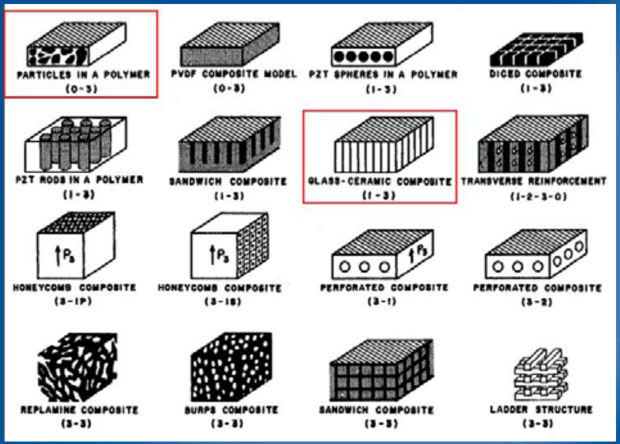


Piezoelectric glass-ceramics (SCHOTT)





- Strong crystalline alignment
- Non-ferroelectric (polar)



R.E. Newnham, PSU

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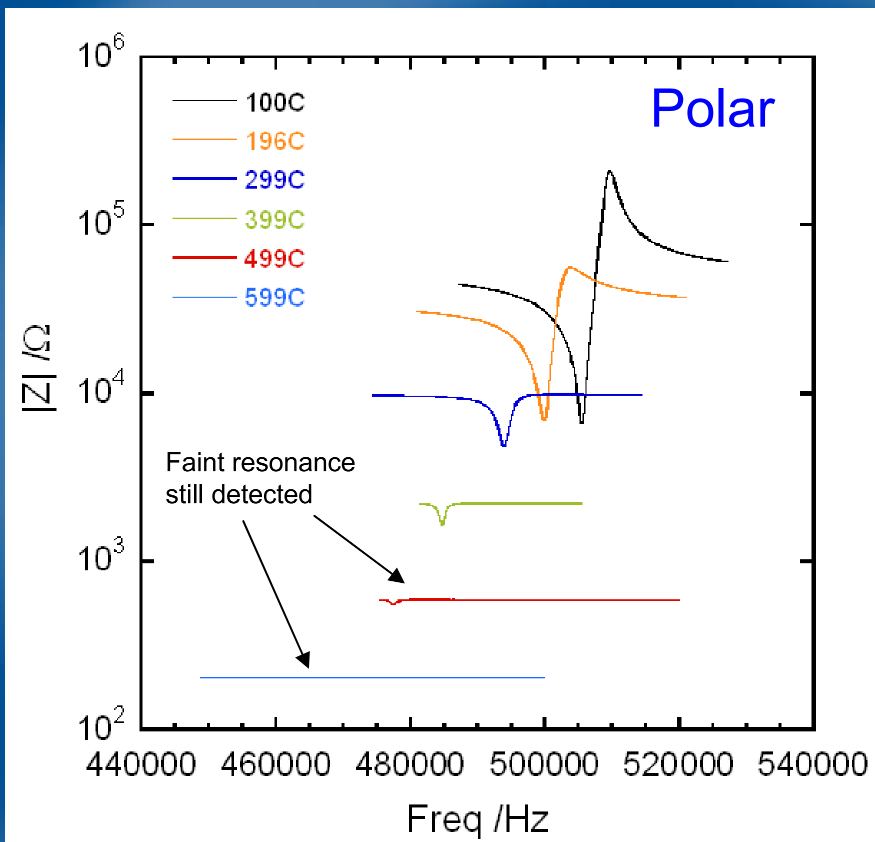
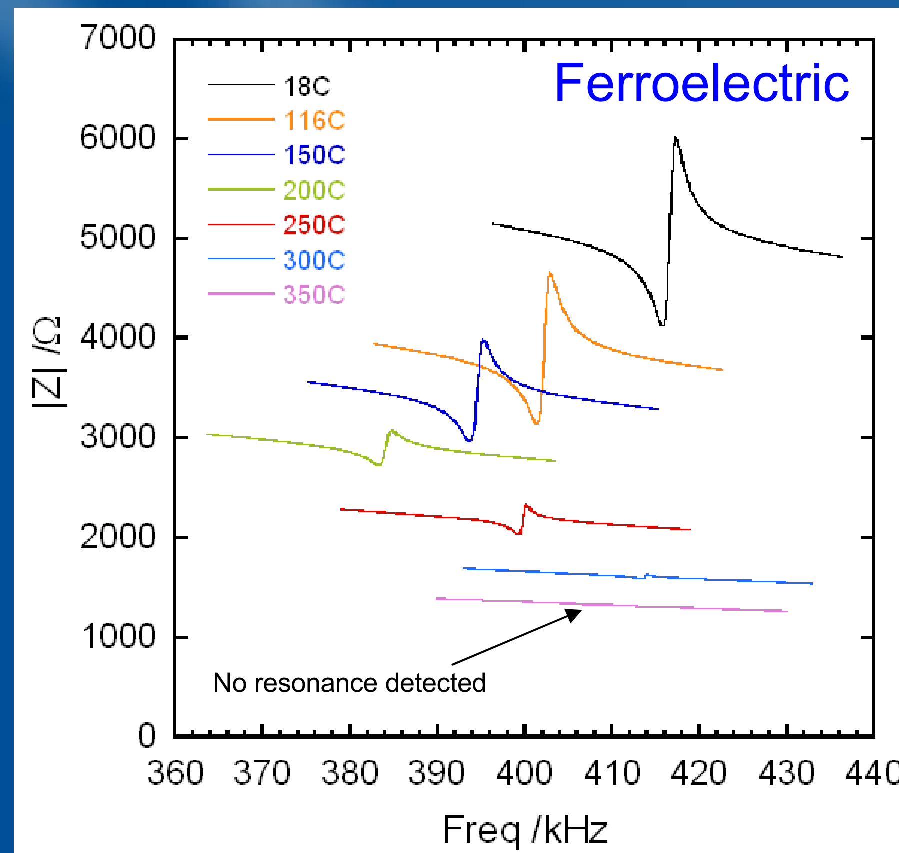
Piezo resonance results

35 mm disks



$Li_2Si_2O_5$ - B_2O_3 system



$NaNbO_3$ – SiO_2 system

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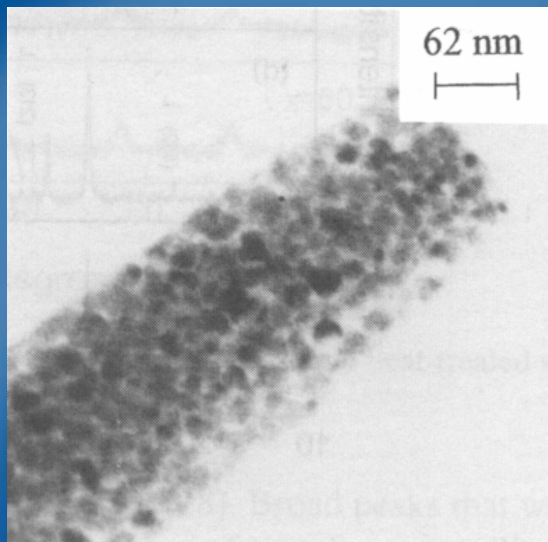
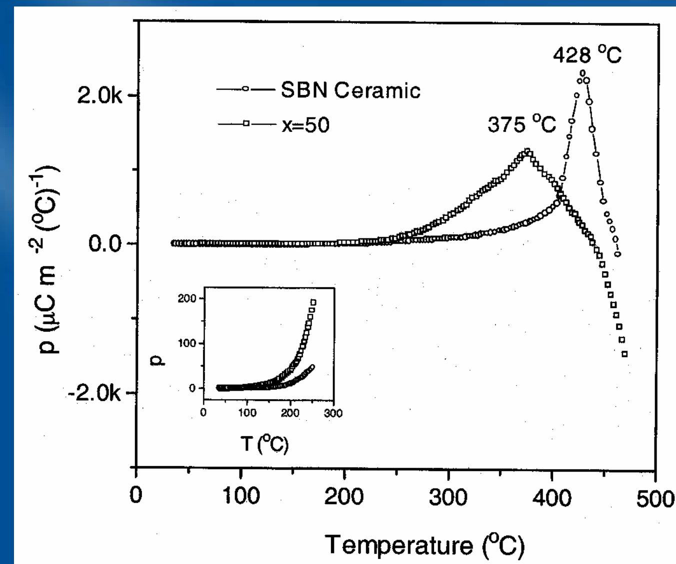
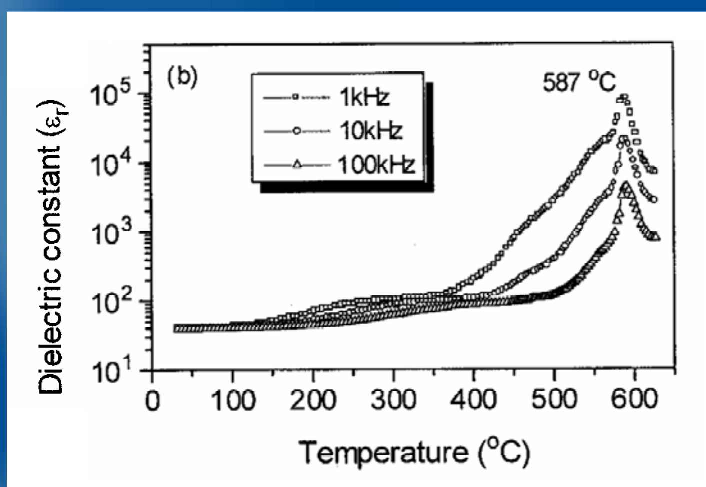
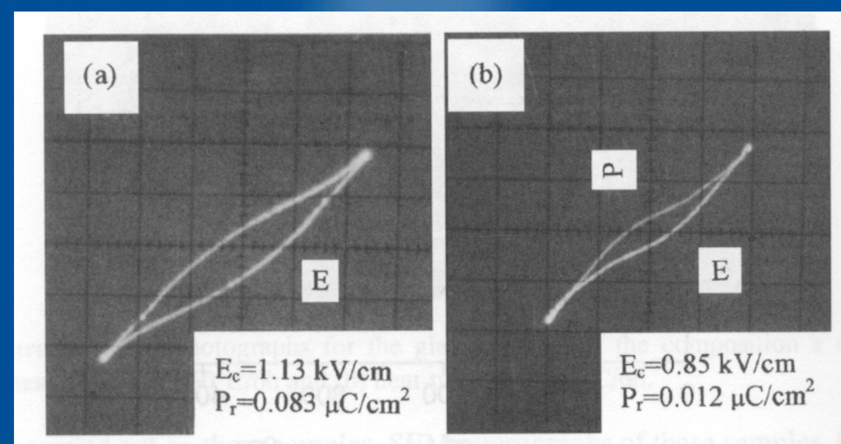
Ferroelectric glass-ceramic: SBN + $Li_2B_4O_7$





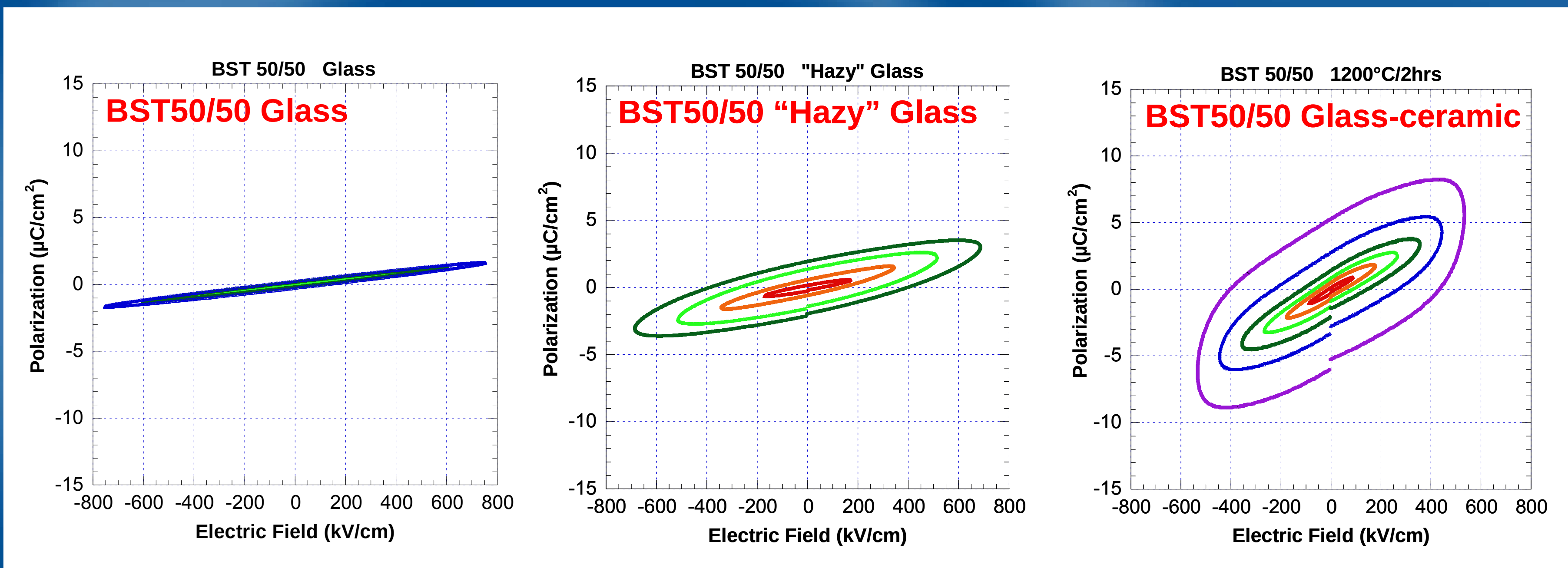


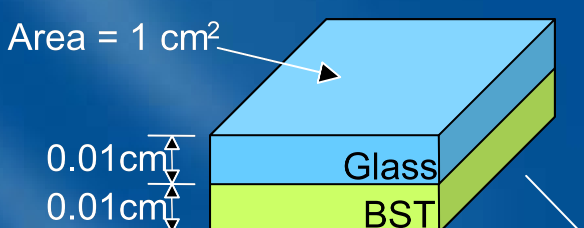


Prasad et al. (2002)

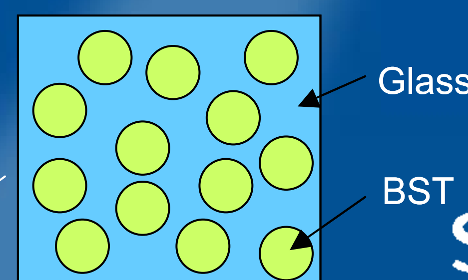
Hysteresis due to interfacial polarization (alk.-niobate gc's)

Ming-Jen Pan, NRL





How best to model?



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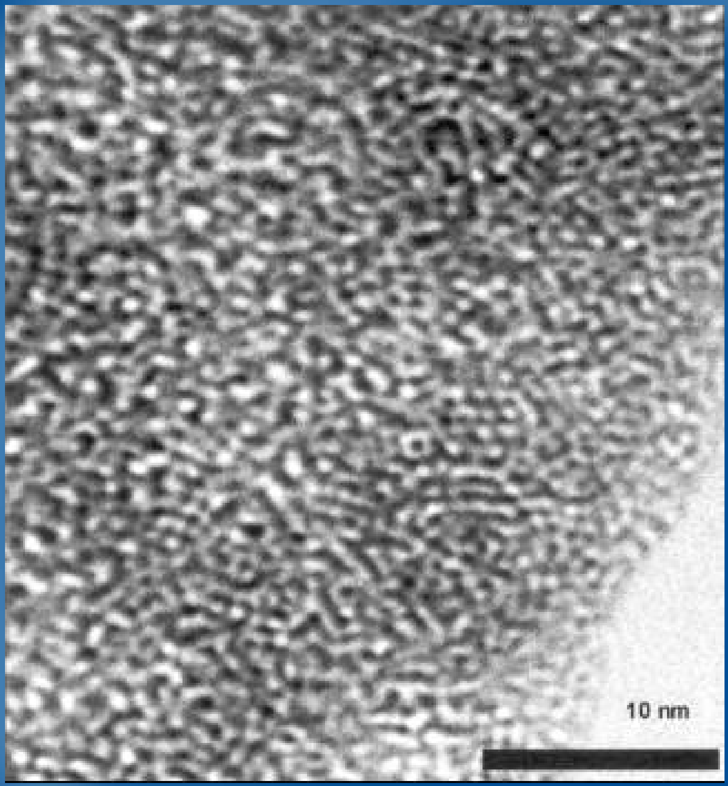
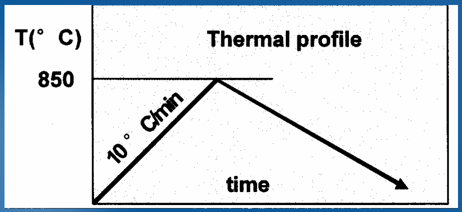
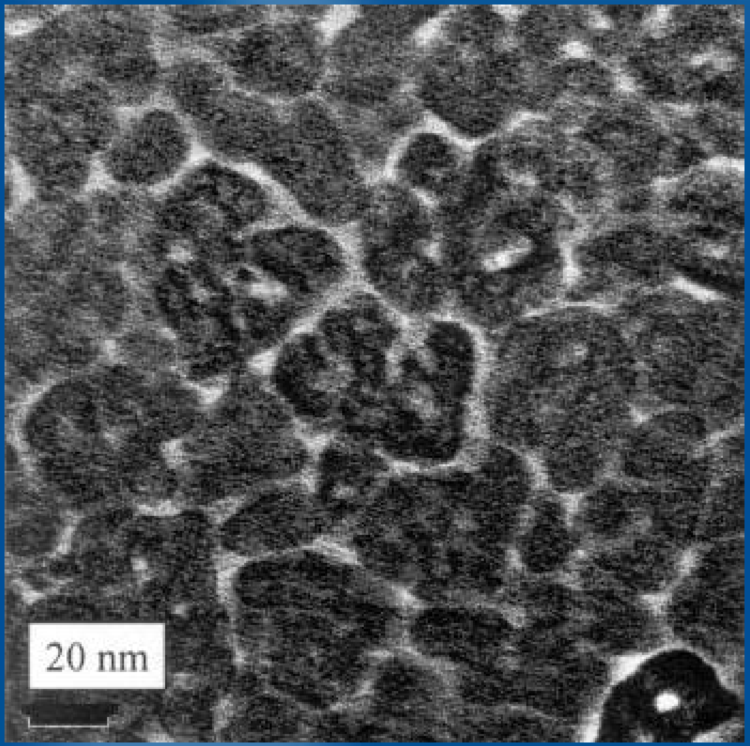
Alkali-niobate-silicate glass-ceramics (1)

As-quenched glass







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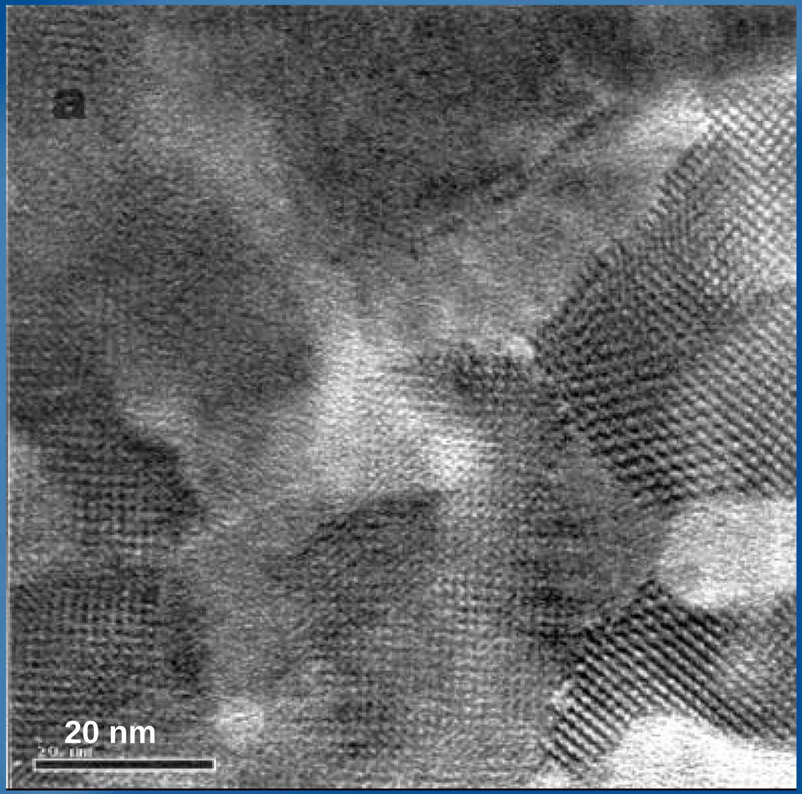
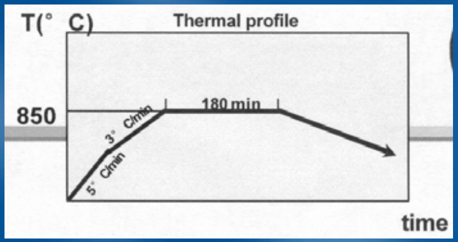
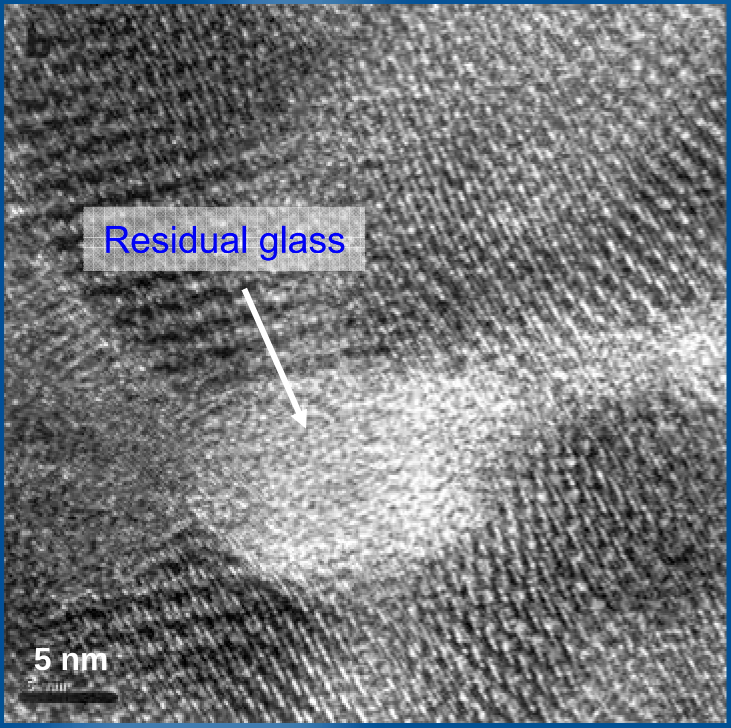
TEM micrographs courtesy of M. Lanagan and G. Yang (PSU) and Ming-Jen Pan (NRL)

Alkali-niobate-silicate glass-ceramics (2)







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TEM micrographs courtesy of M. Lanagan and G. Yang (PSU) and Ming-Jen Pan (NRL)

Key Questions Review (1)

- What has been the role of interfaces in the development of emerging applications (for *glass-ceramics*)?

Somewhat taken for granted to date with the exception of special "tough" glass-ceramics (e.g., amphibole-bearing…)

Key Questions Review (2)

- With regard to applications, what aspects of interfaces are most important and why?

  - *Structural integrity*
  - *Impact on optical scattering*
  - *Effect on electrical properties*

Key Questions Review (3)

- What are the scientific issues that require basic understanding of interfaces in glass-ceramics? (What is the relative importance of each?)
  - *Stress environment in high-crystal fraction glass-ceramics and means by which to control/predict*
  - *Quantitative optical scattering models for "non-dilute" glass-ceramics*
  - *Advanced techniques (e.g., impedance spectroscopy) to investigate electrical properties of complex glass-ceramics <u>in light of structure-property relations to design superior materials</u>*

Key Questions Review (4)

- What properties of glass-ceramics hold promise for the future?

Good Question!

- *Mechanical (e.g., ballistic performance)*
- *Optical (e.g., a more measured look at gc lasers, etc)*
- *Electrical (true competitors to well-known, low-cost ceramics?)*

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