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15:15 -15:45 C11-19 Processing-Microstructure-Property Relations in Ceramics

Glass-Ceramic Processing-Microstructure-Property Relations

K.G. Ewsuk

Materials & Process Sciences Center, Sandia National Laboratories

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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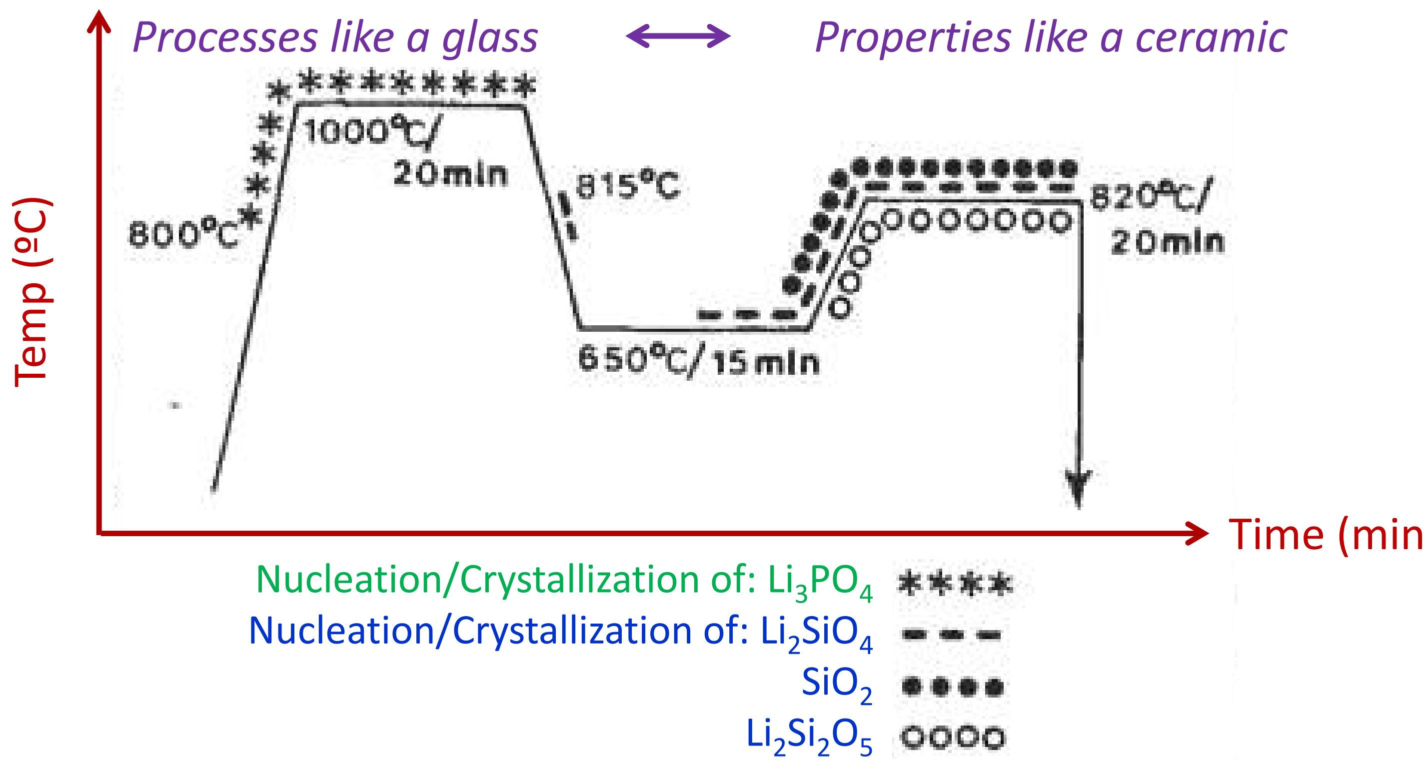
A Glass-Ceramic (GC) Is A Composite of Ceramic Crystals In A Glass Matrix

- **Applications**
  - Thermal shock resistant, low thermal expansion cooktops
  - Machinable ceramics
  - Low dielectric loss low-temperature cofired ceramic (LTCC) electronic packaging
  - Solid oxide fuel cells (SOFCs) joining
- **Advantages**
  - Improved processability vs. ceramic
    - The processability of a glass with the properties of a ceramic
  - Improved properties vs. glass
    - Higher crack tolerance vs. a glass
  - Tunable properties (e.g., CTE from 10-20 E-6 in/in/^{o}C
- **Disadvantages**
  - Process sensitivity

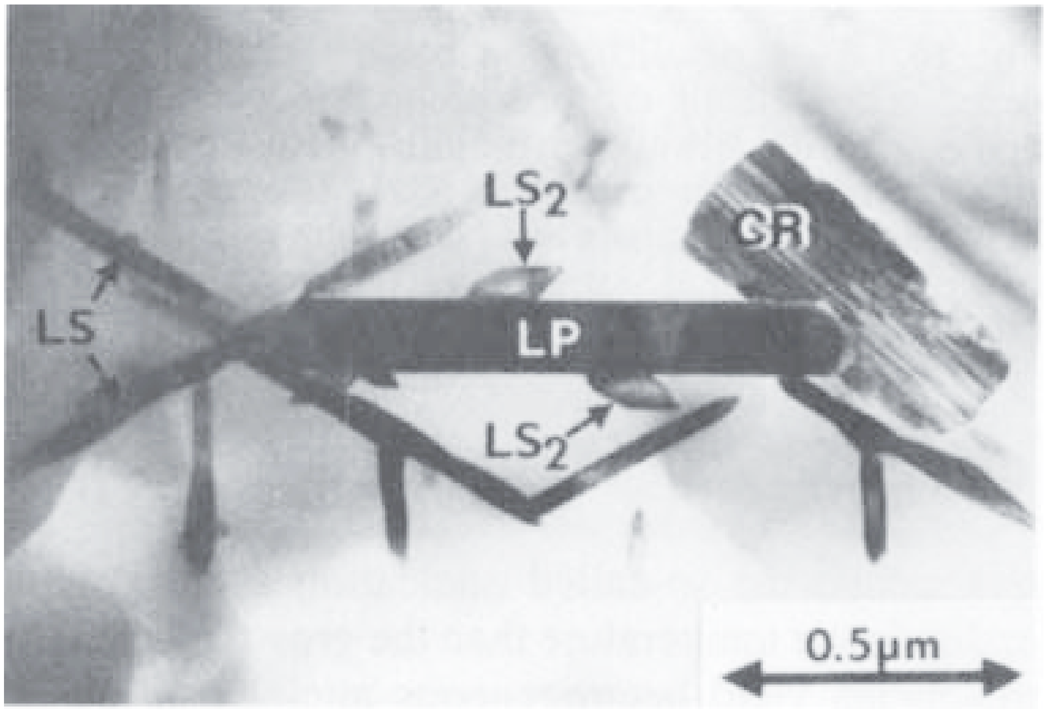
Thermal Processing Determines The Glass-Ceramic Microstructure And Properties

Thermal Processing Determines The
Microstructure & Properties Of The Glass-Ceramic



Headley & Loehman, "Crystallization of a Glass-Ceramic by Epitaxial Growth", J Am Ceram Soc, 67 [9] 620-25 (1984).

All Three Silicate Phases Grow Epitaxially On The Lithium Orthophosphate



Nucleation & Growth In Li-Modified SiO_2 Glass

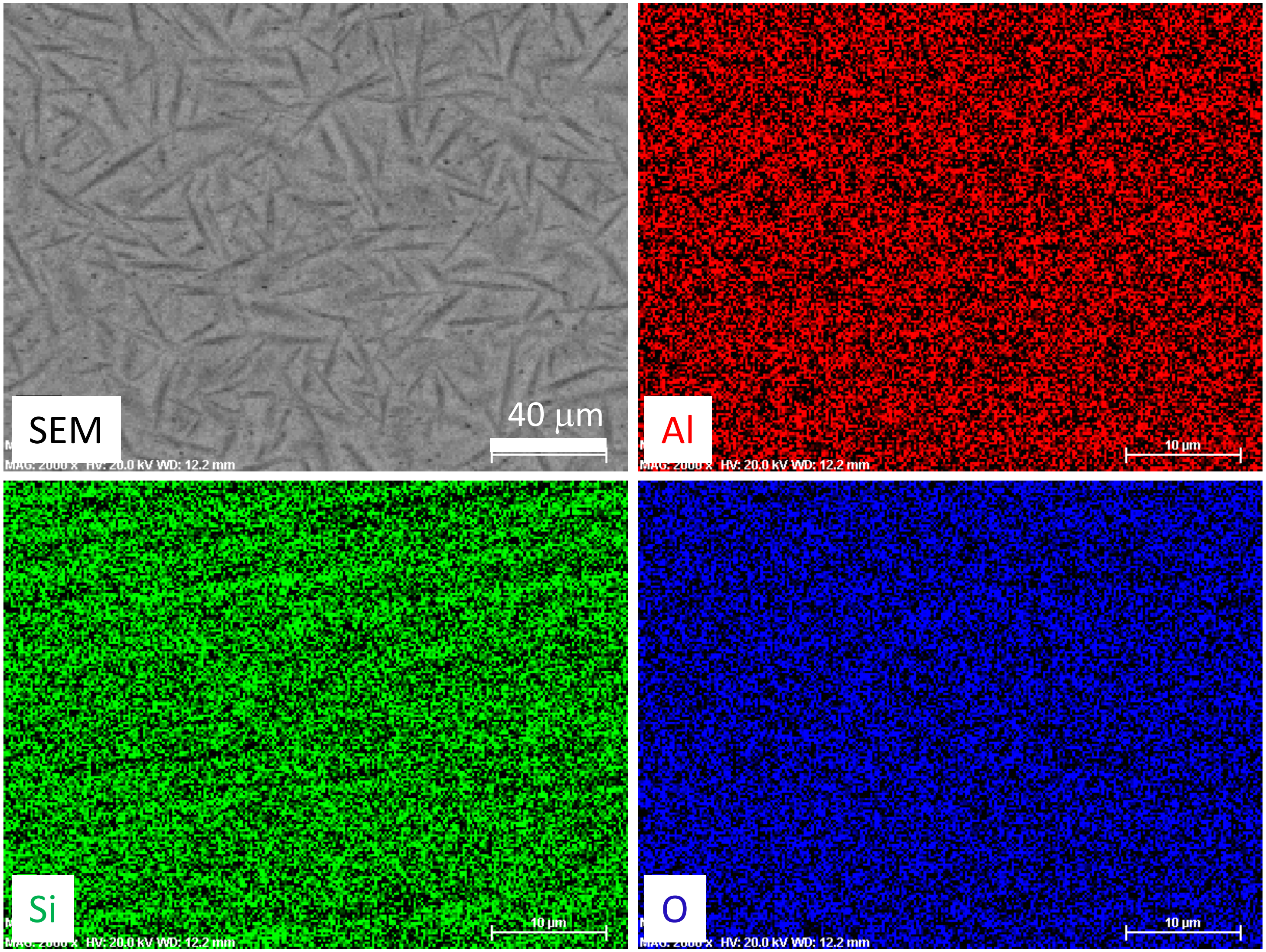
- Li_2O Reacts w/P_2O_5
- Silicate Phases Nucleate & Grow On Li_3PO_4
- t-T Profile Determines Microstructure & Properties

LP - Lithium Orthophosphate (Li_3PO_4)
CR - Cristobalite (SiO_2)
LS - Lithium Metasilicate (Li_2SiO_3)
LS_2 - Lithium Disilicate ($Li_2Si_2O_3$)

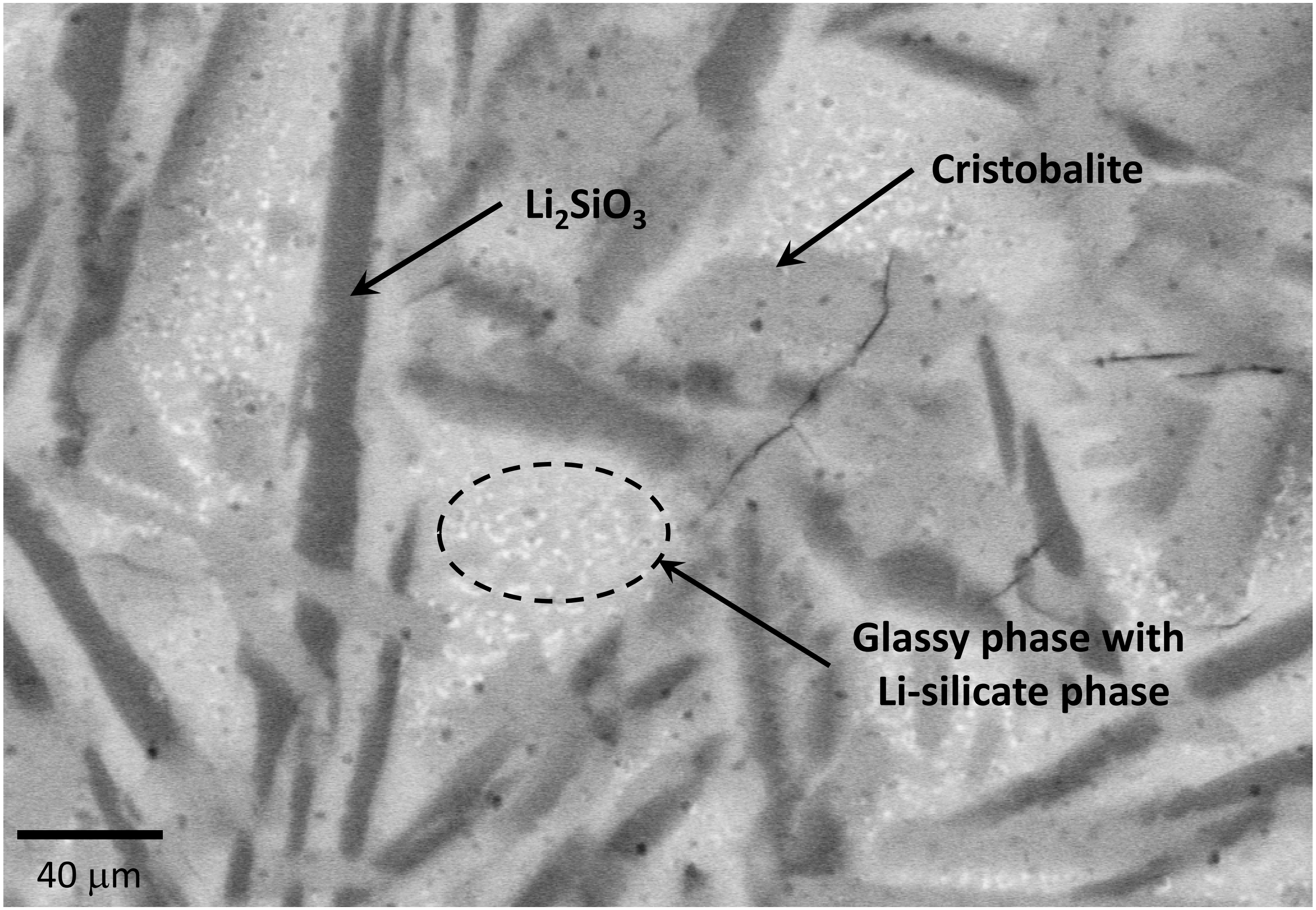
Nucleation & growth affected by: time & temperature, pressure, chemistry

Headley & Loehman, "Crystallization of a Glass-Ceramic by Epitaxial Growth", J Am Ceram Soc, 67 [9] 620-25 (1984).

Controlled Devitrification Produces A Uniform Microstructure & Chemistry GC



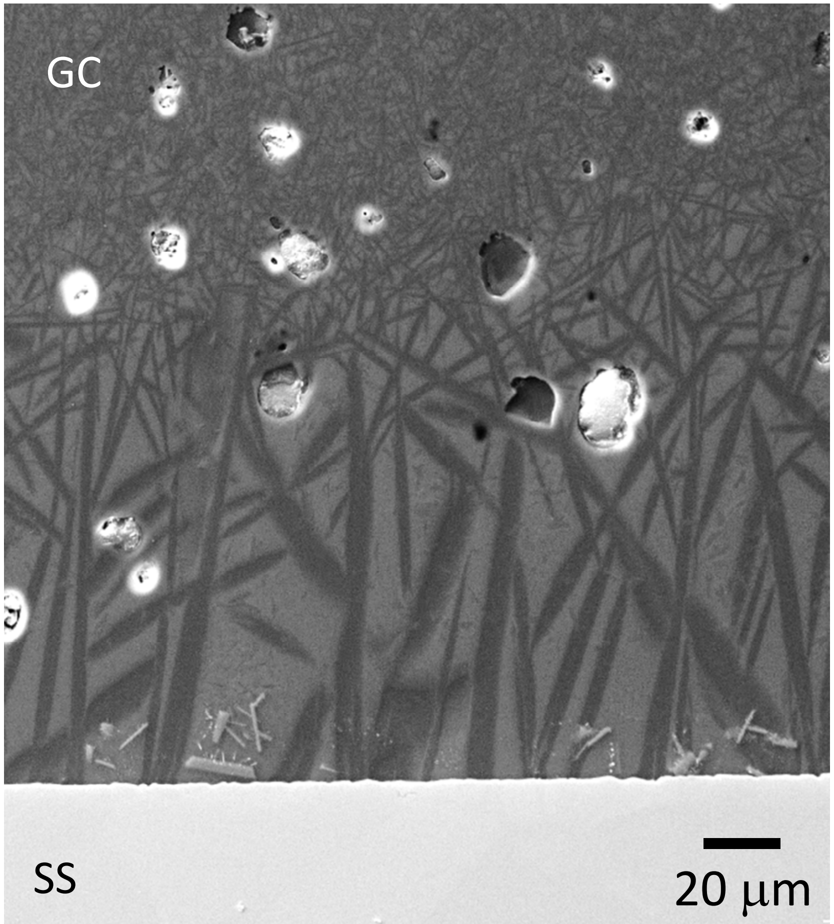
The Glass-Ceramic (GC) Microstructure Is Complex

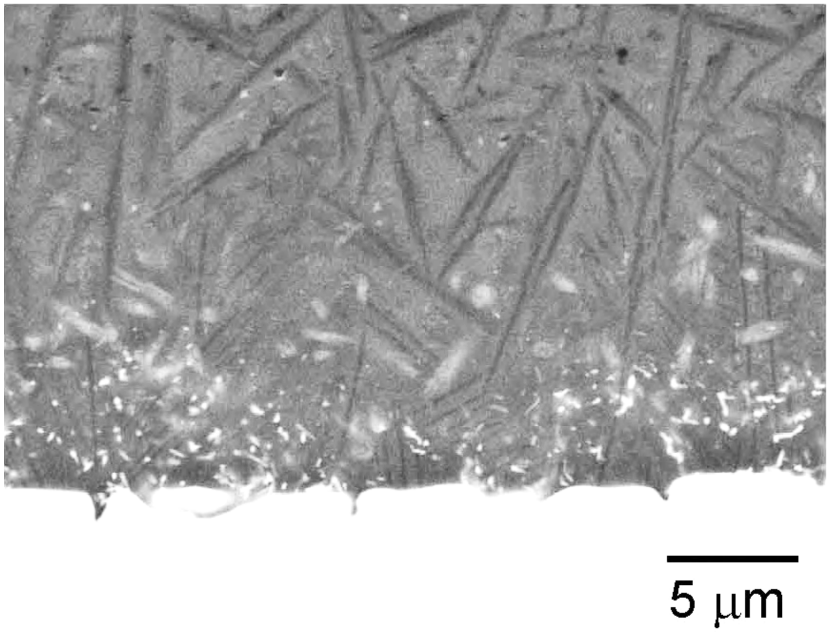


Objective: Characterize Li-Silicate GC Processing-Microstructure-Property Relations

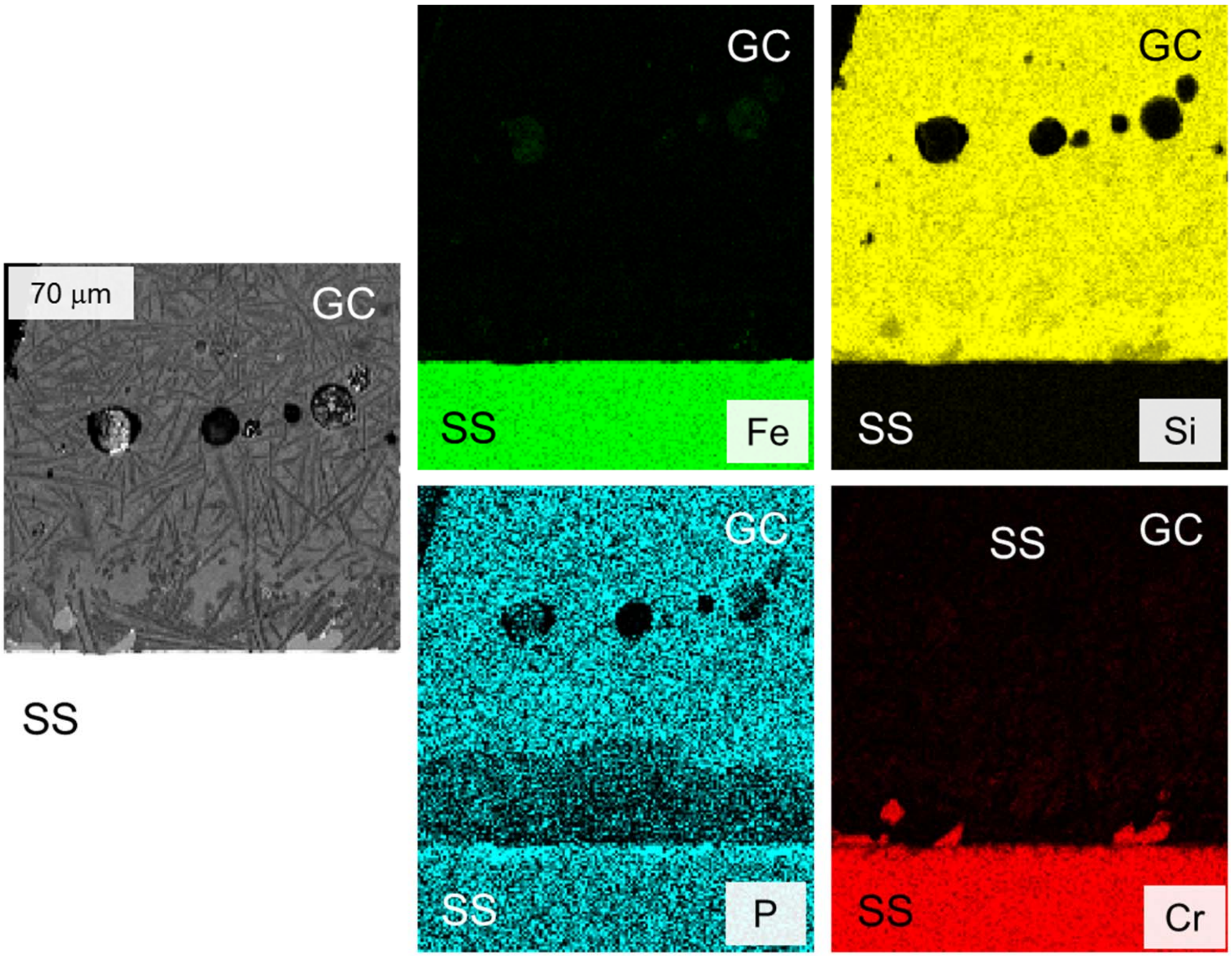
- **Glass Microstructure, Chemistry, & Devitrification**
  - Microstructure
    - Scanning Electron Microscopy (SEM)
  - Chemistry
    - Energy Dispersive Spectroscopy (EDS)
    - Electron Probe Microanalysis (EPMA)
  - Crystallization
    - Differential Scanning Calorimetry (DSC)
    - High-Temperature X-Ray Diffraction (XRD)
- **Glass Processing**
  - Wetting
- **Glass-Ceramic Properties**
  - Strength
    - 4-Point Bend Tests
  - Fractography
    - Scanning Electron Microscopy (SEM)
  - Toughness
    - Single Edged V-Notched Beam (SEVNB)
    - Indentation Crack Length

Interface Microstructure Can Vary Significantly From The Bulk Glass-Ceramic





Elemental Maps Show Cr Migration Into And P Depletion From The Glass-Ceramic Interface



Cr Redox Chemistry Significantly Affects The Microstructure At The GC Interface

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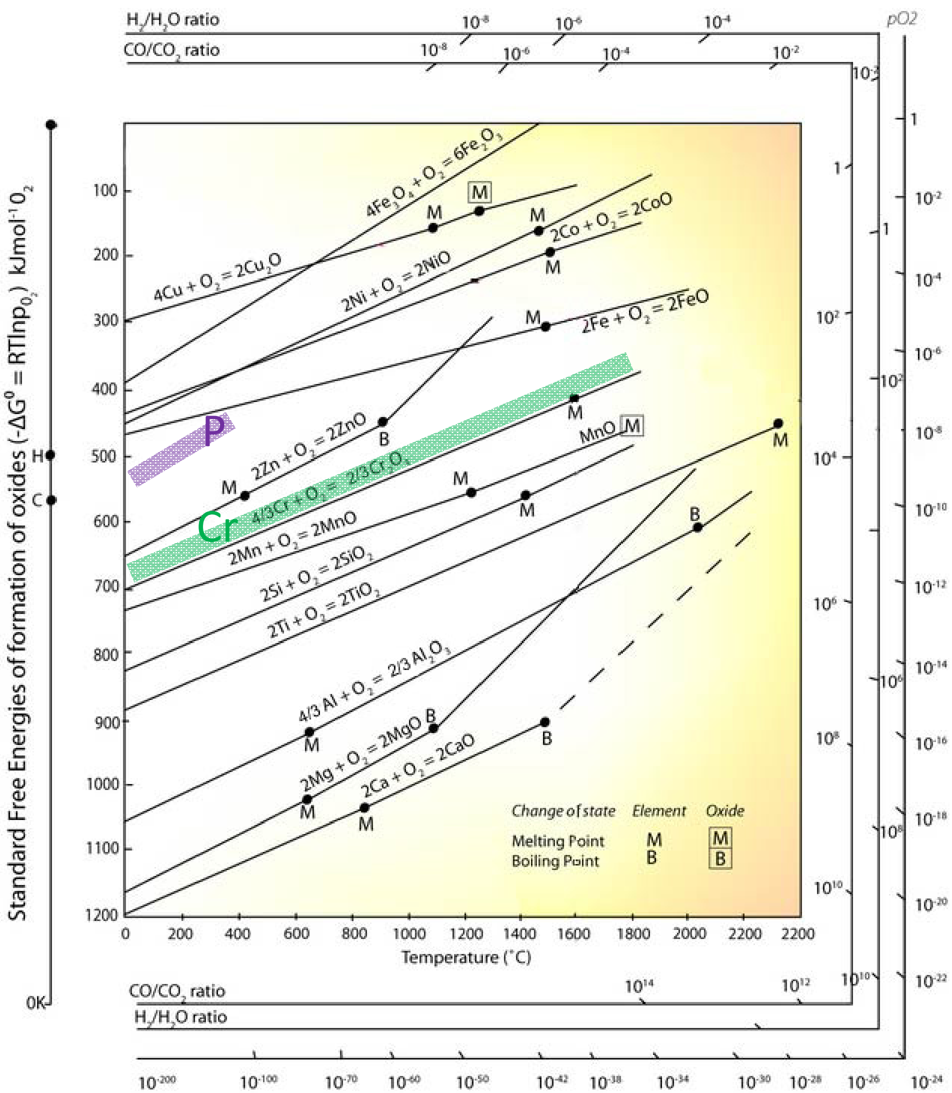
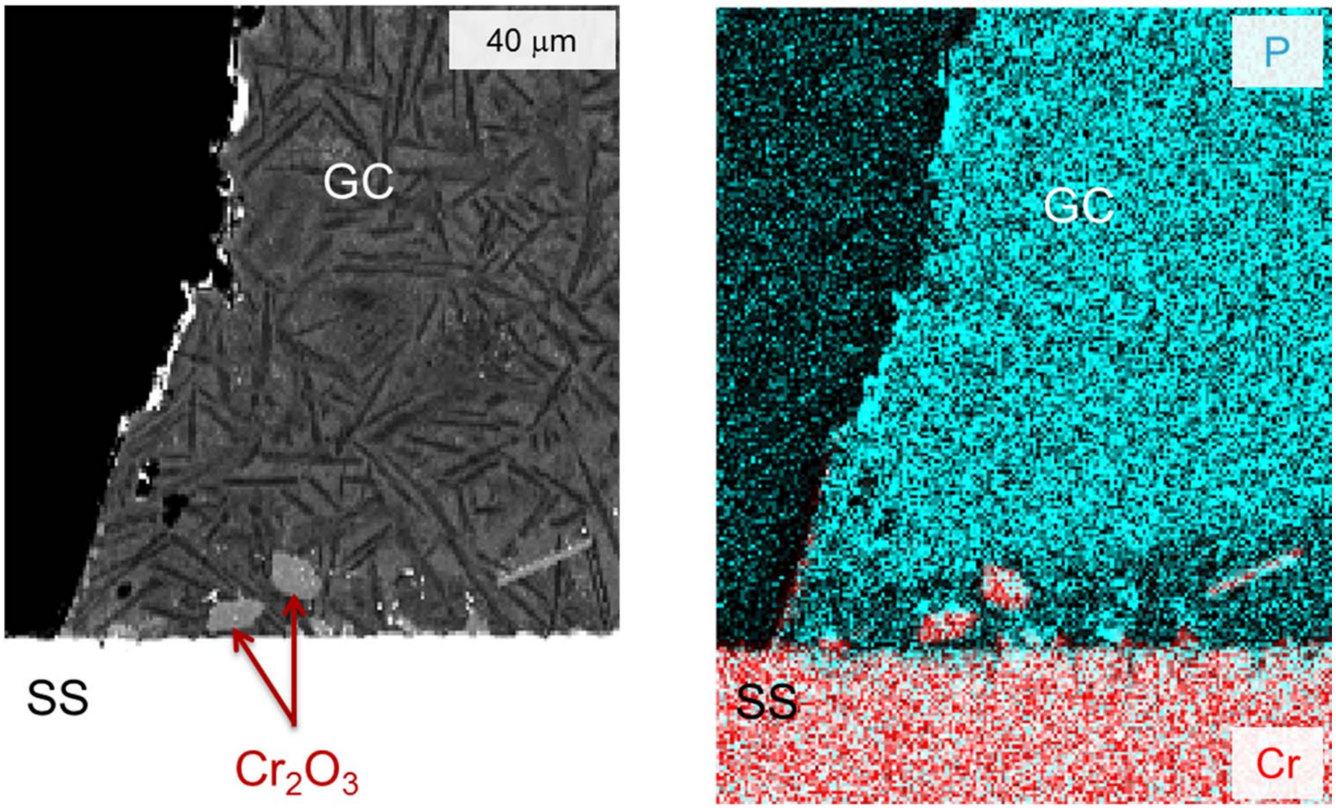


- Cr Reduces P_2O_5.
- Cr Significantly Changes The Viscosity Of The Glass.
- Cr solubility depends on PO_2.

- *Darken & Gurry, Physical Chemistry of Metals, McGraw-Hill, New York, 1953.*
- *Brow, "Oxidation States of Chromium Dissolved in Glass Determined by X-ray Photoelectron Spectroscopy", J Am Ceram Soc, 70 [6] C129-131 (1987).*
- *Khedim et al. "Redox-Control Solubility of Chromium Oxide in Soda-Silicate Melts", J. Am. Ceram. Soc., 91 [11] 3571–3579 (2008).*
- *Kido et al. "The effect of viscosity on the kinetics of redox reactions in highly viscous silicate liquids," J Chem Phys. 136 [22] (2012).*

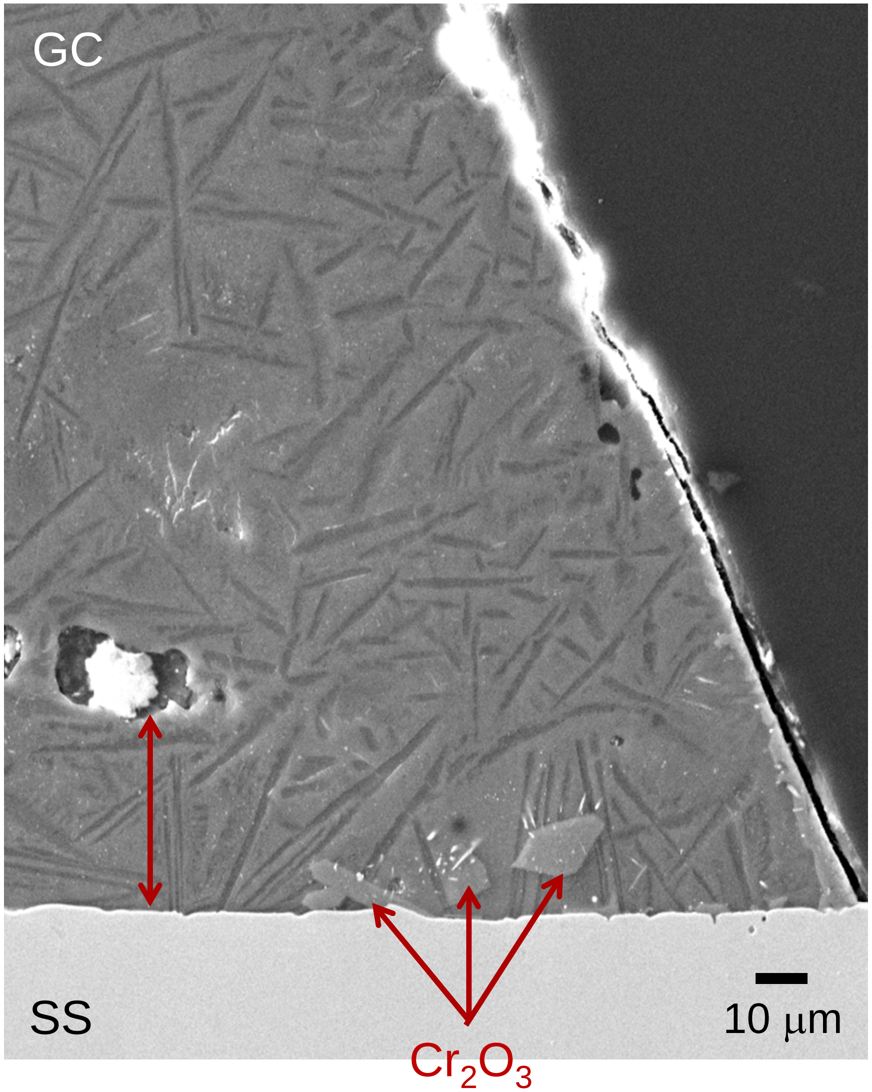
Elemental Mapping Shows Cr Migration Into And P Depletion From The Glass-Ceramic



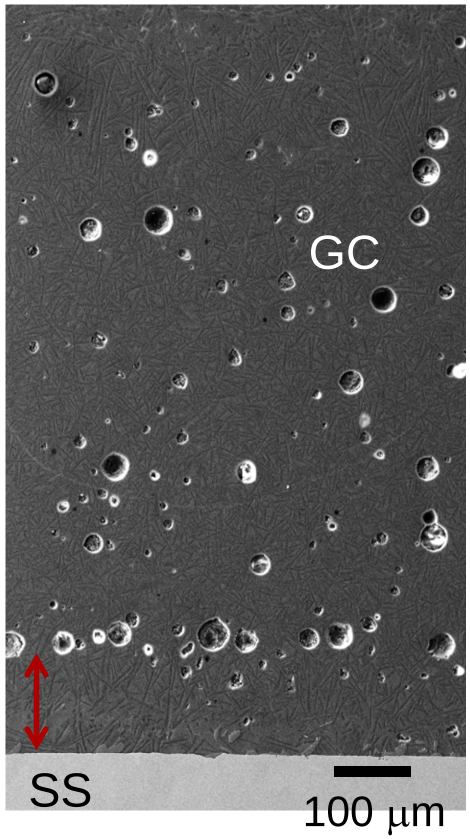
SEM

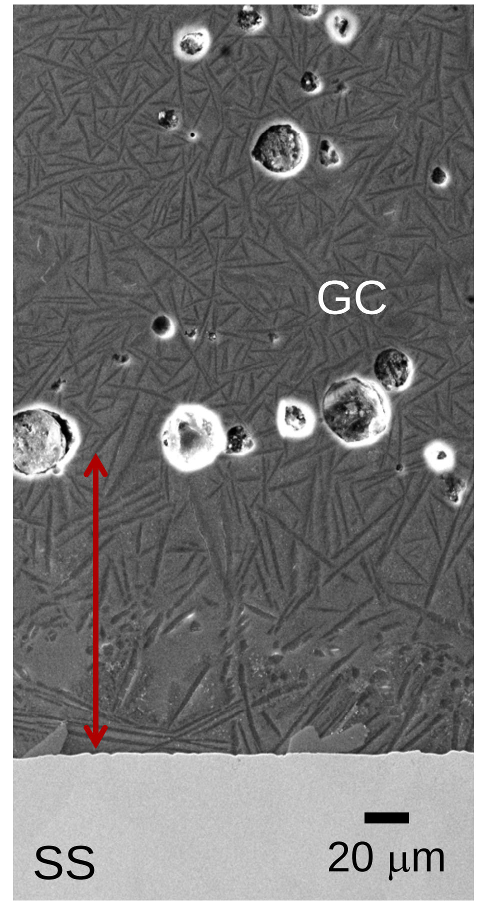
EDS Elemental Map

Cr_2O_3 Particles Surrounded By Fine Cr-Fe Crystals Form In The Dense GC Region

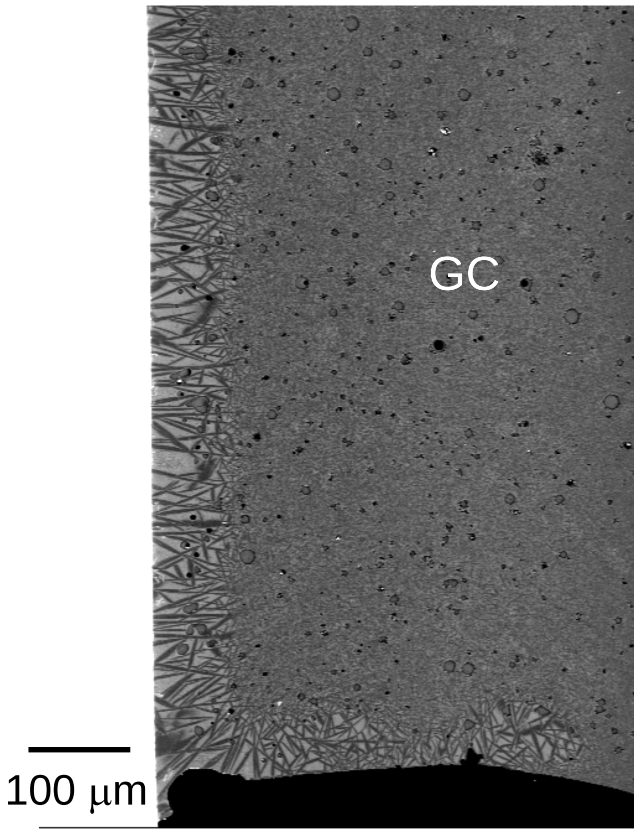


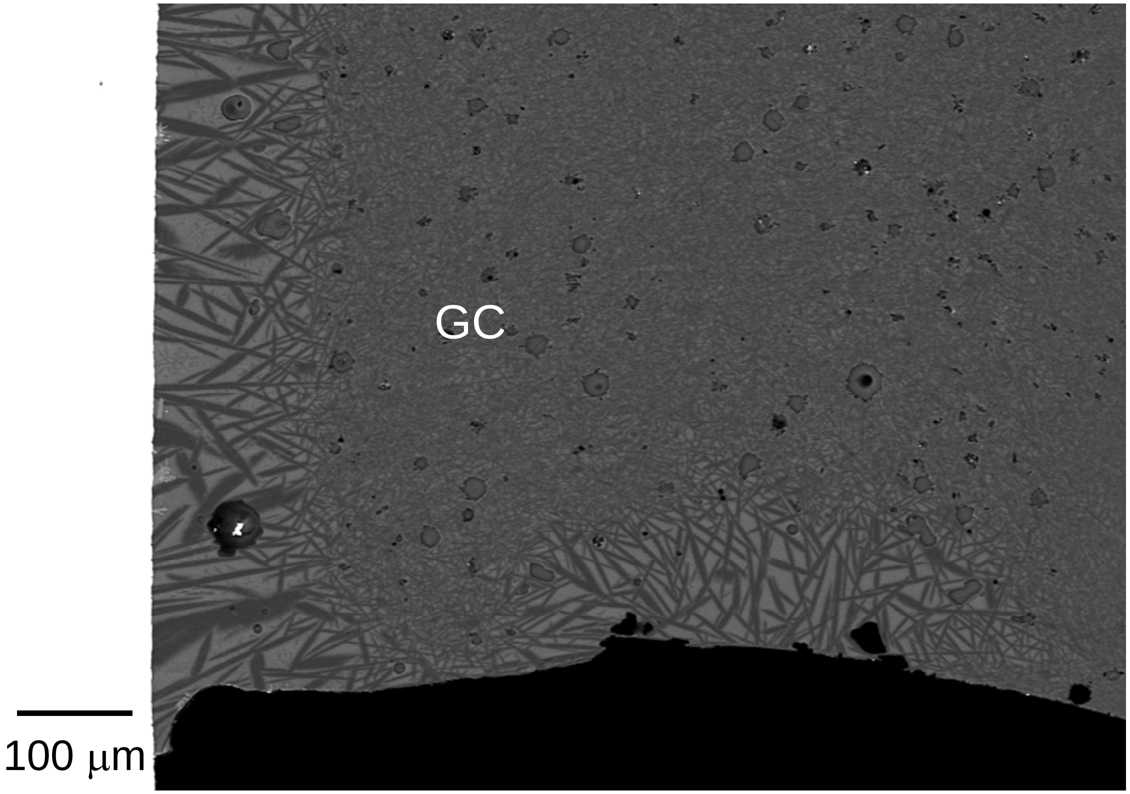
A Dense Glass-Ceramic Region Forms At The Stainless Steel Interface





Nucleation & Silicate Crystal Growth Occurs On The Glass (Preform) Surface





- $Li_2Si_2O_5$ Crystals Form/Grow On Glass Surfaces

Glass Preform Characteristics Affect Viscosity And Wetting

T=980.2°C

T=983.1°C

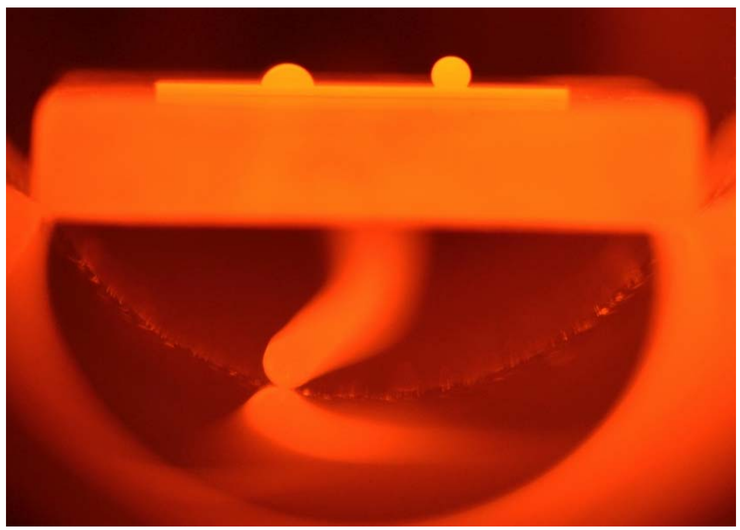
T=986.0°C

T=986.9°C

T=987.4°C

T=987.9°C

T=1002.6°C



Glass Chemistry And Properties Change With Crystallization Of The Silicate Phases

Crystal Product	Glass SiO_2 Content	Glass Viscosity
Cristobalite	↓	↓
Li_2SiO_3	↑	↑

$Li_2O-Al_2O_3-SiO_2$

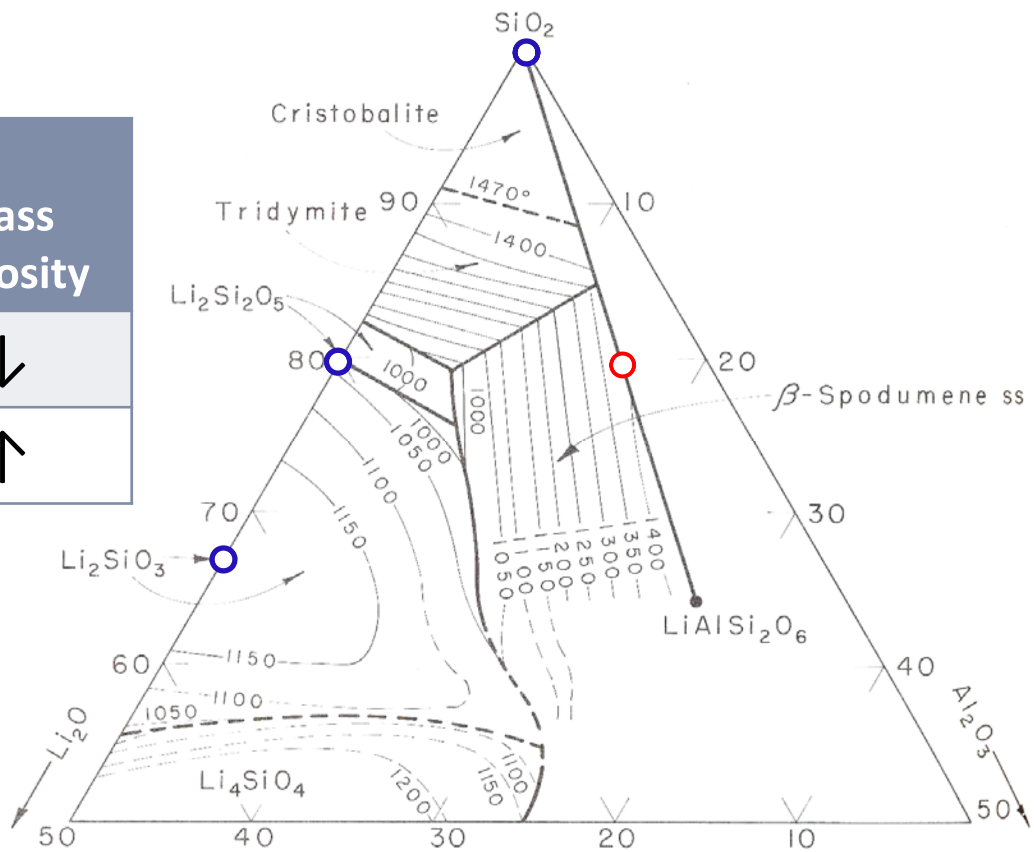
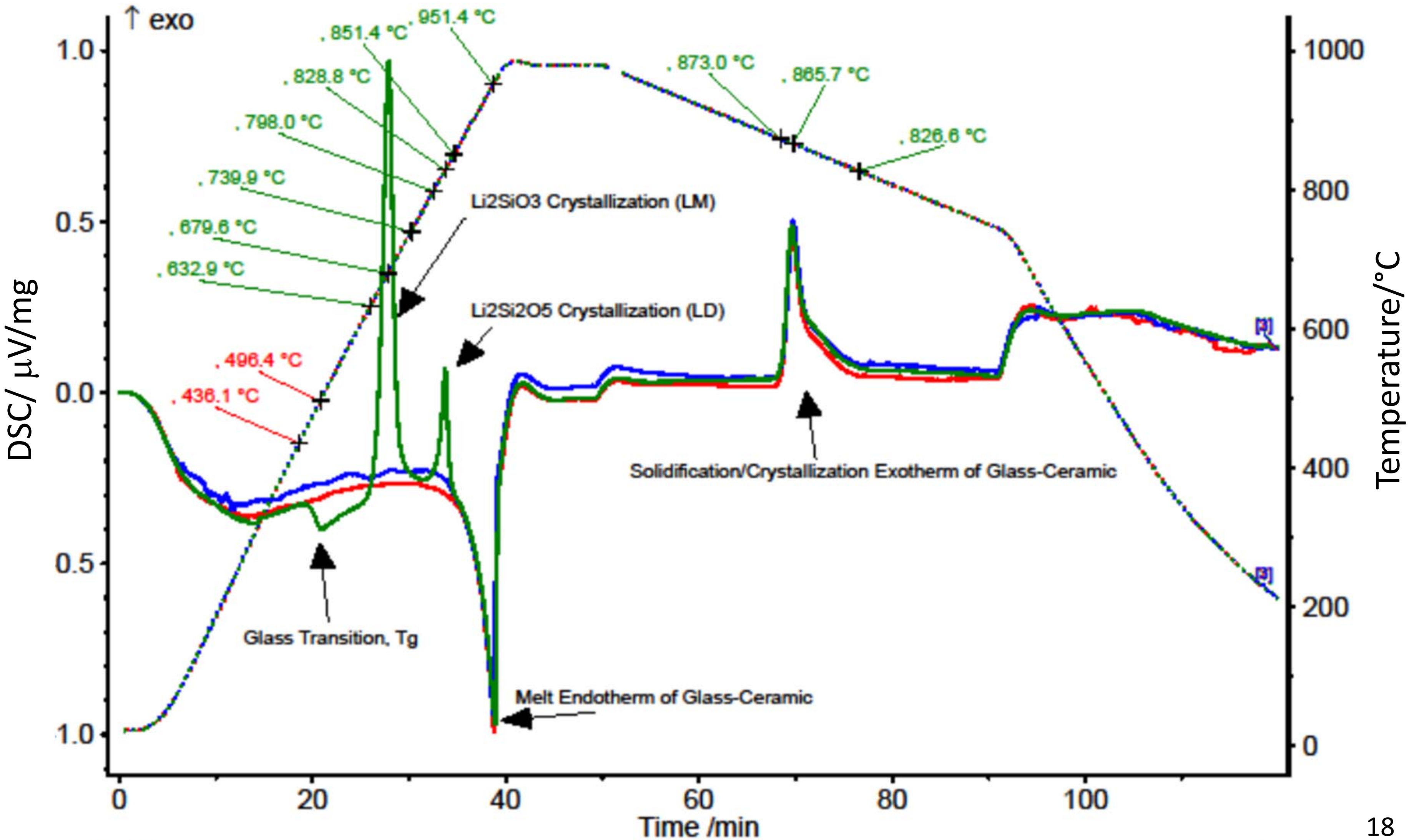


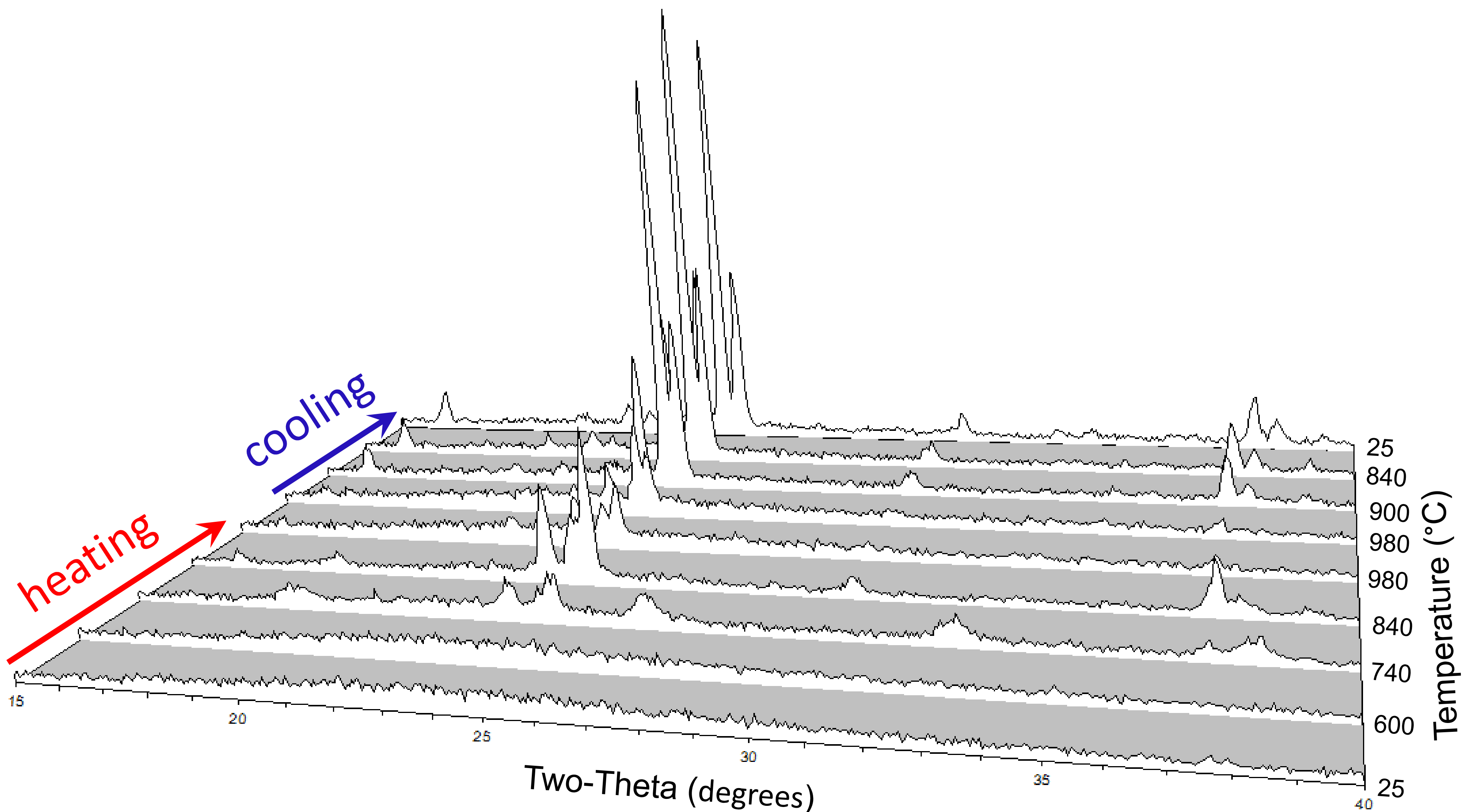
FIG. 2426.—System $Li_2O-Al_2O_3-SiO_2$ showing proposed liquidus.

R. A. Eppler, *J. Am. Ceram. Soc.*, 46 [2] 100 (1963).

Differential Scanning Calorimetry (DSC) Shows Preform Processing Affects Devitrification



High Temperature X-Ray Diffraction (XRD) Was Used To Study Glass Devitrification

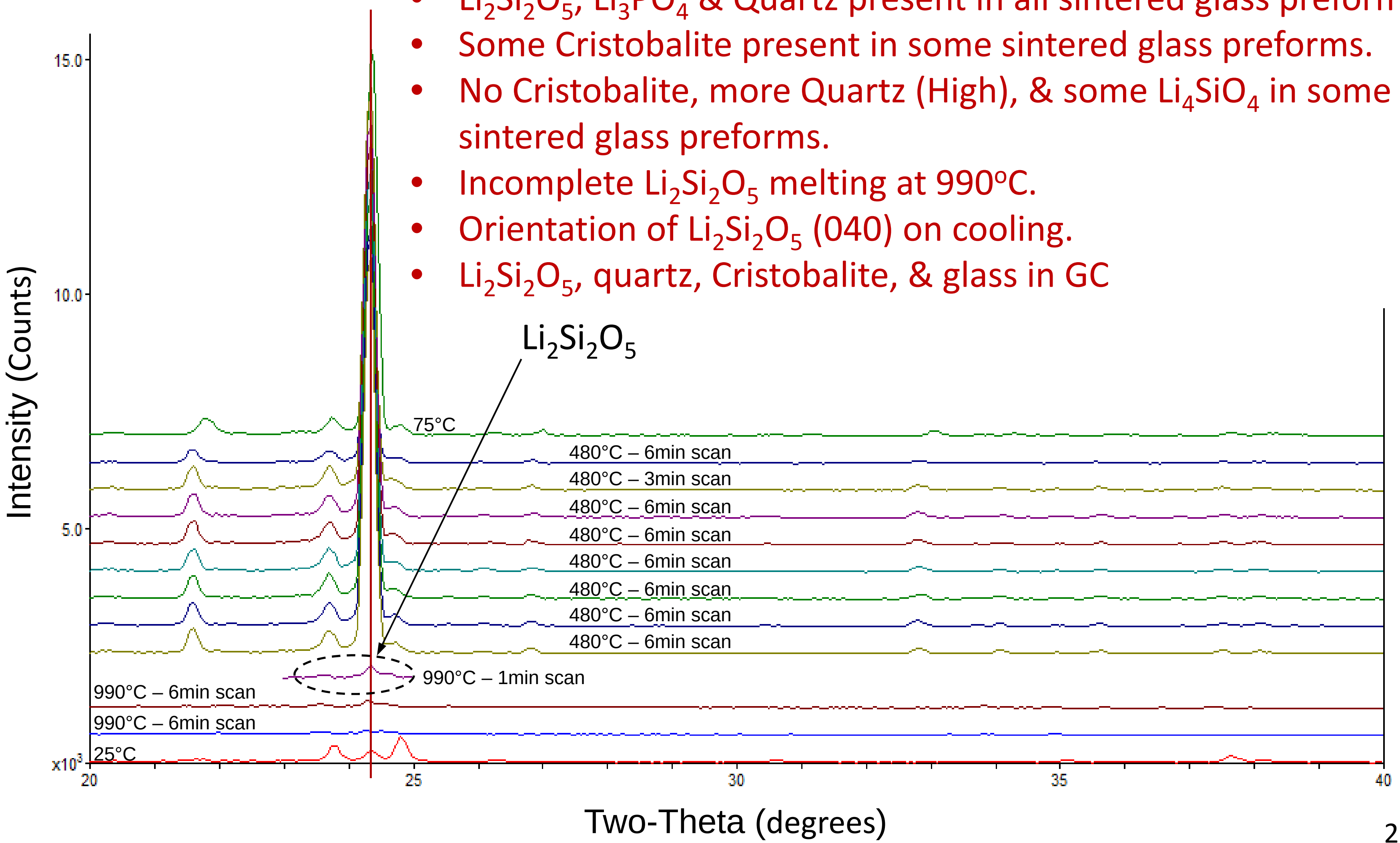


The Transformation From An Amorphous Glass To A Glass-Ceramic Is Complex

- Amorphous up to 600°C.
- Li_2SiO_3 crystallization between 600 and 740°C.
- $Li_2Si_2O_5$ crystallization at 740°C.
- $Li_2Si_2O_5$ becomes dominant crystalline phase at 840°C.
- At 980°C, Li_2SiO_3 disappears and $Li_2Si_2O_5$ decreases.
- Reorientation of $Li_2Si_2O_5$ to a preferred (040) at 980°C.
- On cooling to 840°C, $Li_2Si_2O_5$ re-crystallization and Cristobalite.
- Cristobalite peak increases on cooling to room temperature.

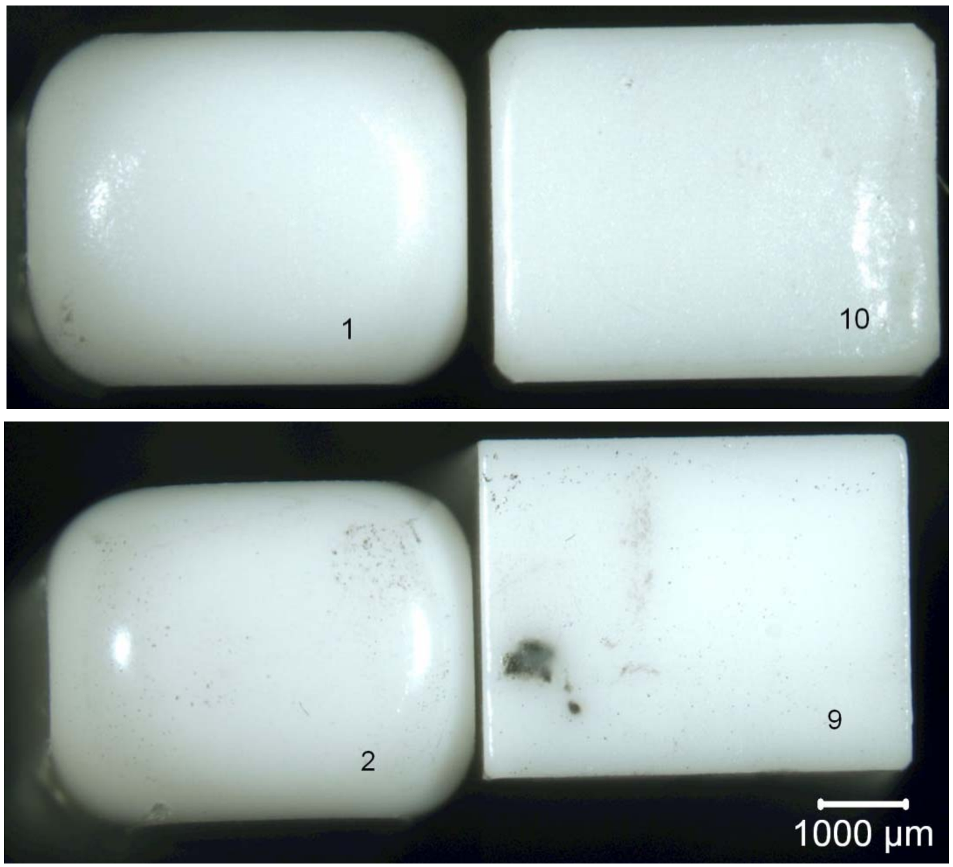
$Li_2Si_2O_5$ In The Glass Preform Does Not Completely Melt Before Cooling

- $Li_2Si_2O_5$, Li_3PO_4 & Quartz present in all sintered glass preforms.
- Some Cristobalite present in some sintered glass preforms.
- No Cristobalite, more Quartz (High), & some Li_4SiO_4 in some sintered glass preforms.
- Incomplete $Li_2Si_2O_5$ melting at 990°C.
- Orientation of $Li_2Si_2O_5$ (040) on cooling.
- $Li_2Si_2O_5$, quartz, Cristobalite, & glass in GC

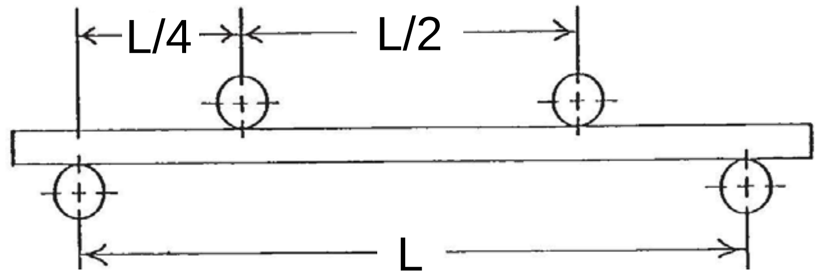


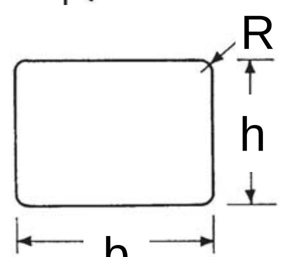
4-Point Bend Strength Was Corrected To Account For The Non-Ideal GC Bar Geometry

Glass Bars Were Reflowed In Graphite Molds To Produce GC Bend Bars



4-Point Bend Strength Was Measured On The "As-Formed" GC Bars



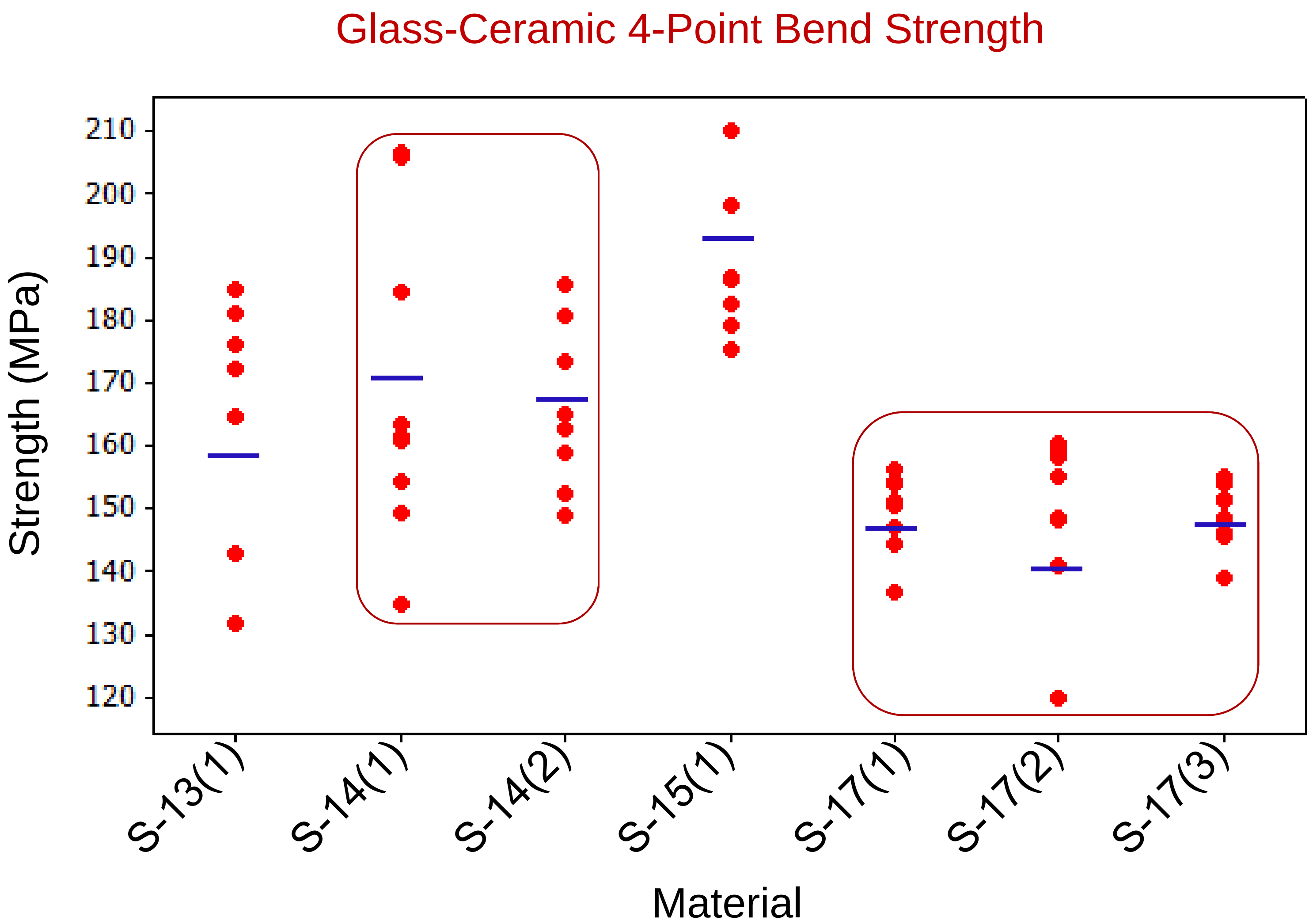


$$\sigma = F\frac{3PL}{4bh^2}$$

σ = Bend Strength
P = Load
F = Corner R Correction Factor

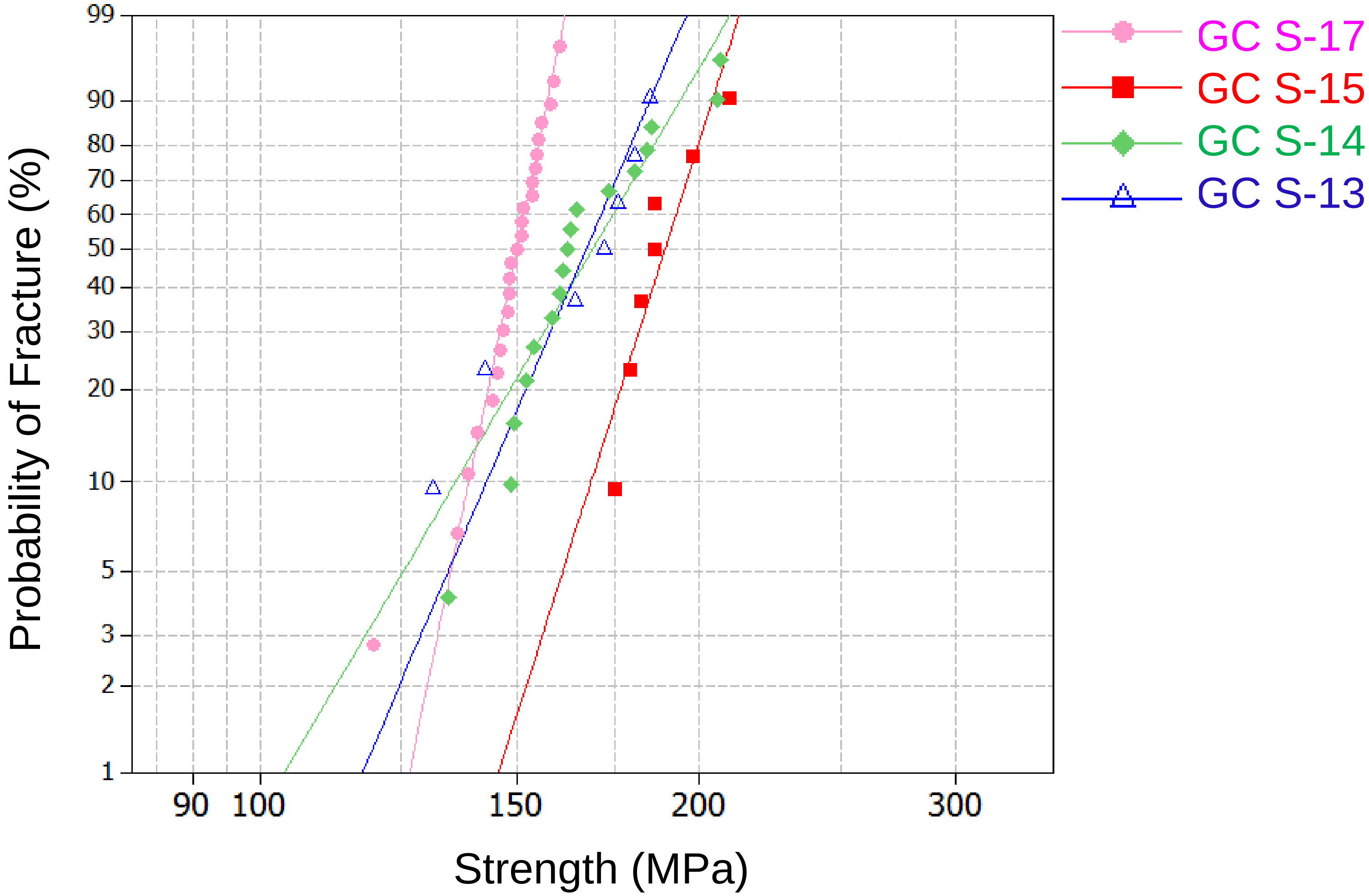
Flexural Strength of Advanced Ceramics at Ambient Temperature - ASTM C1161 (2008)

As-Formed Glass-Ceramic Strength Varies With Thermal Processing/CTE



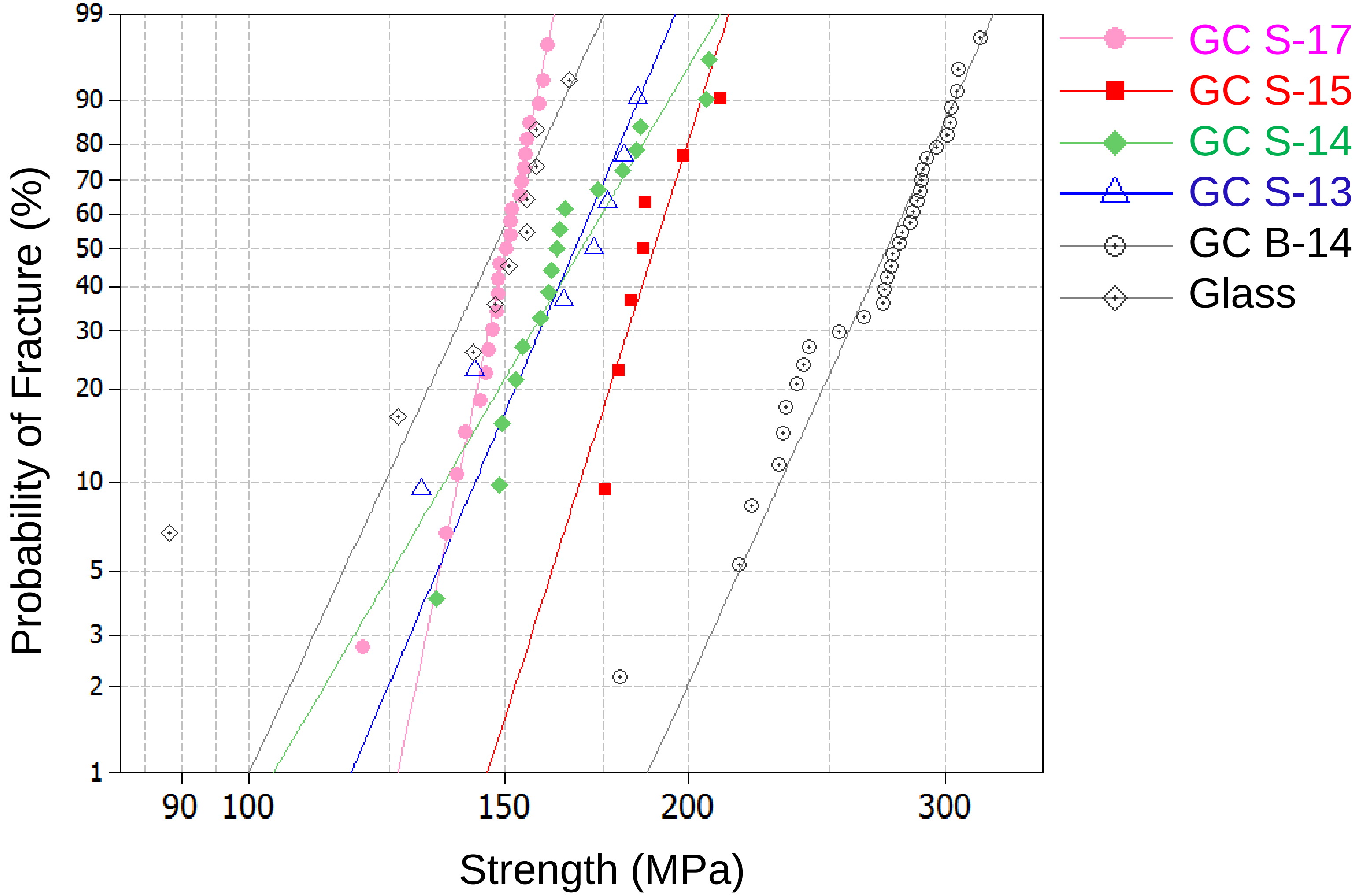
S Glass-Ceramic With A CTE Of 15 Has The Highest Strength

Weibull Plot Of Glass-Ceramic Strength



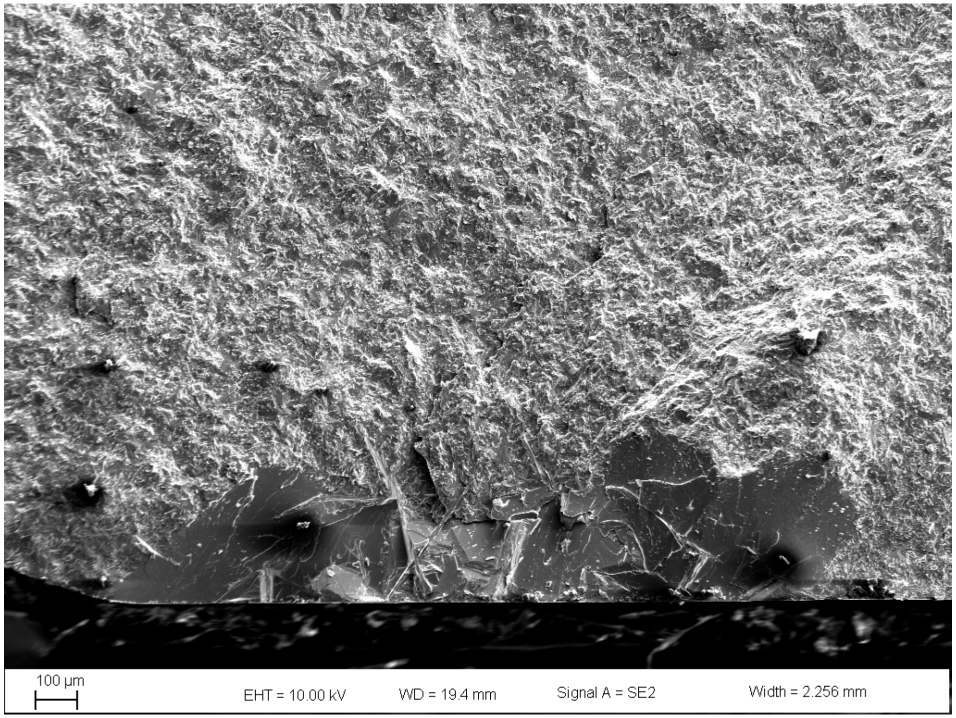
S Glass-Ceramic And Glass Strength Are Comparable

Weibull Plot Of Glass-Ceramic Strength Compared To Glass

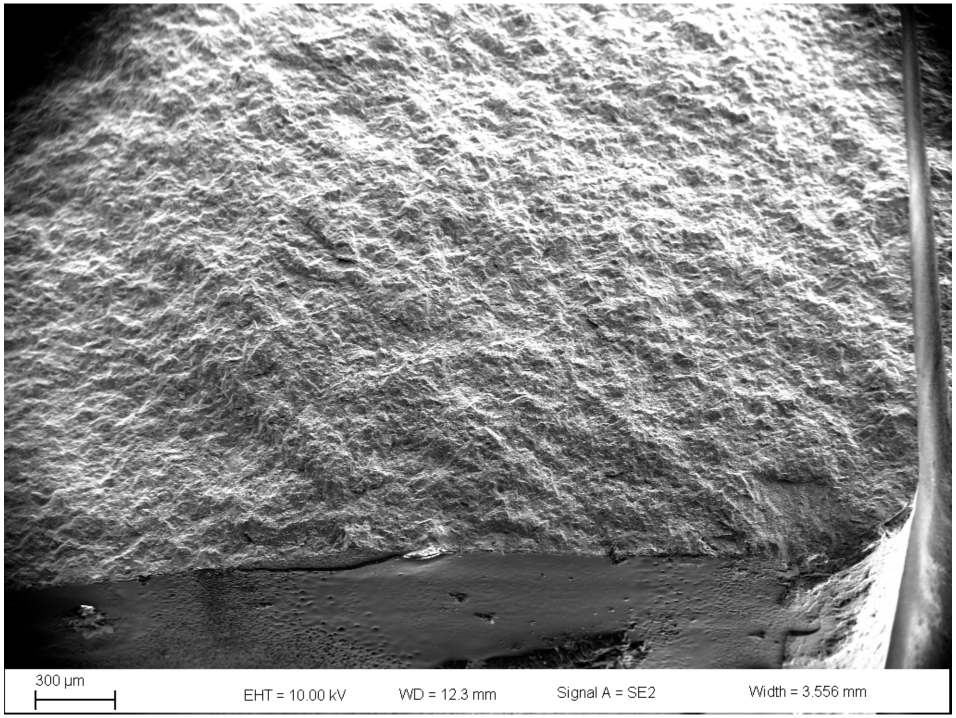


Glass-Ceramic Bend Strength Decreases With Increasing Flaw Size

Fractography of GC S-17 Fracture Surfaces



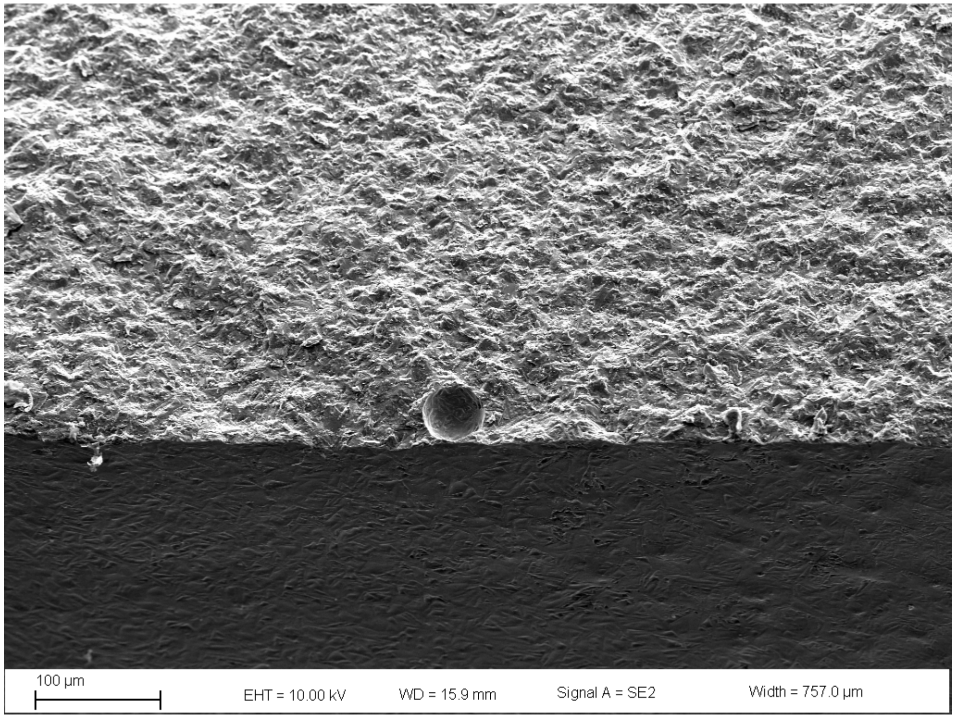
Low Strength



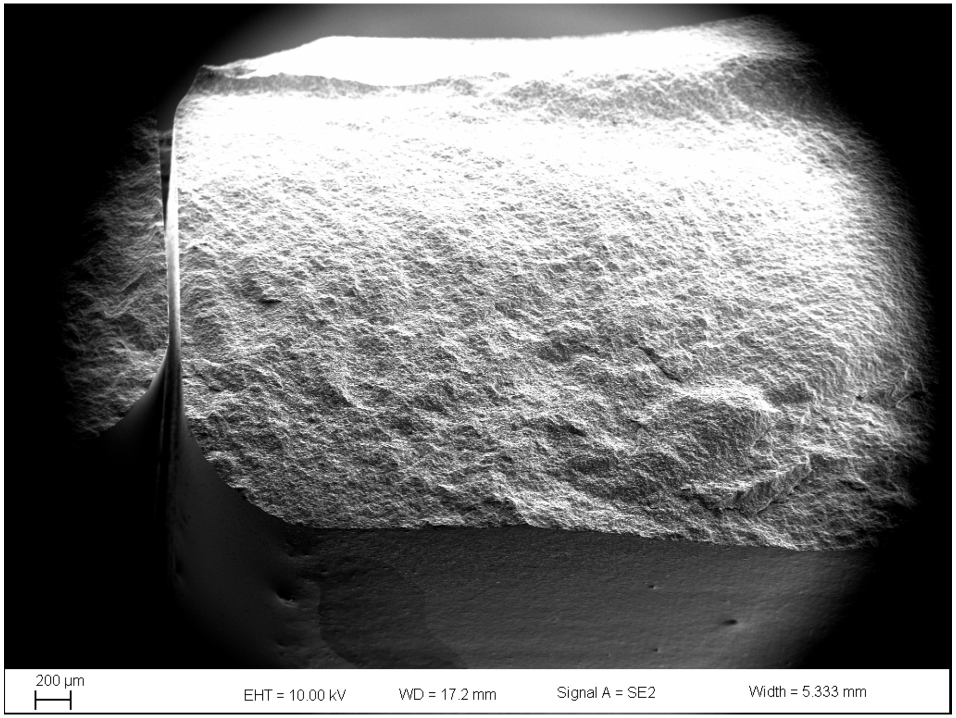
High Strength

Glass-Ceramic Bend Strength Decreases With Increasing Flaw Size

Fractography of GC S-15 Fracture Surfaces



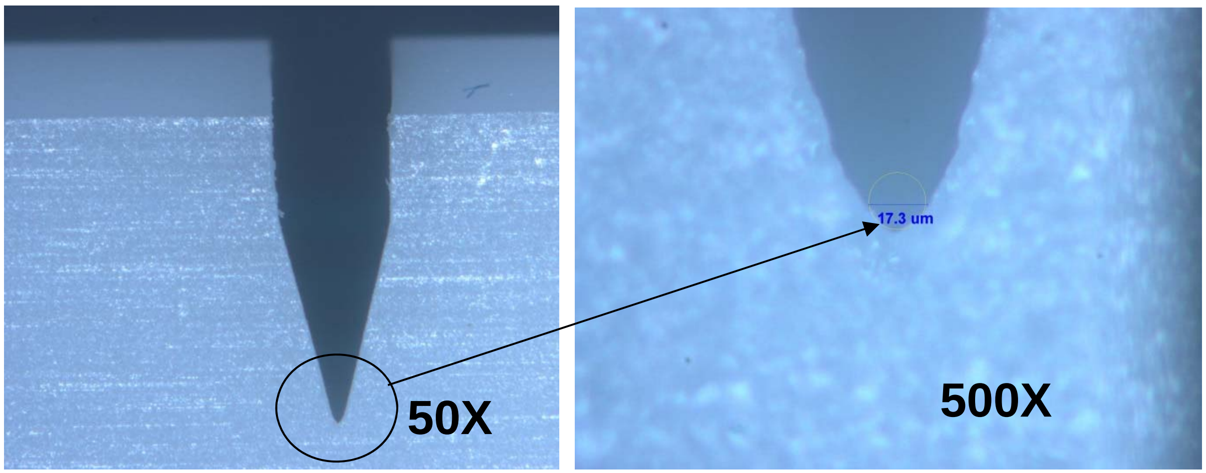
Low Strength



High Strength

GC Fracture Toughness Was Measured Using A Single Edged V-Notched Beam (SEVNB)

A Sharp Tip Notch (r < 20μm) Was Machined Into A Bend Bar

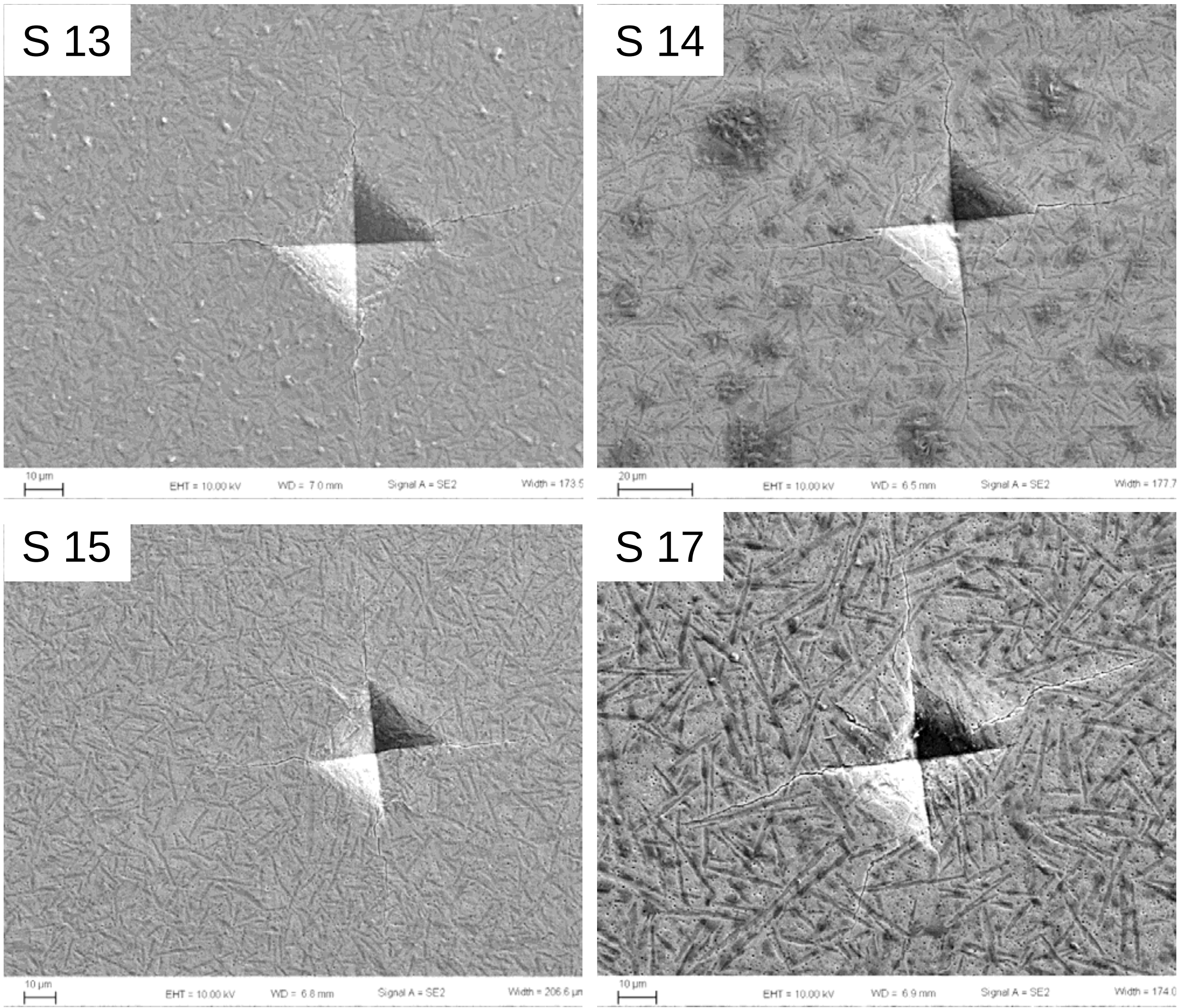


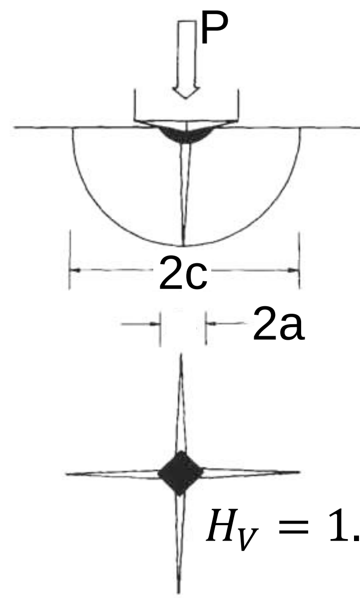
$$K_I = \left[Y' h \frac{\alpha^{1/2}}{(1-\alpha)^{3/2}} \right] \left[\frac{3}{2} P \frac{L/2}{bh^2} \right]$$

$$Y' = 1.9887 - 1.326\alpha - (3.49 - 0.68\alpha + 1.35\alpha^2)\alpha(1-\alpha)(1+\alpha)^{-2}$$

$$\alpha = \frac{length\ of\ notch}{h}$$

GC Toughness (K_{IC}) & Hardness (H_V) Were Determined From Vickers Indentation





$$H_V = 1.8544\frac{P}{(2a)^2}$$

$$K_{IC} = 0.016\frac{P}{C^{3/2}}\left(\frac{E}{H_V}\right)^{1/2}$$

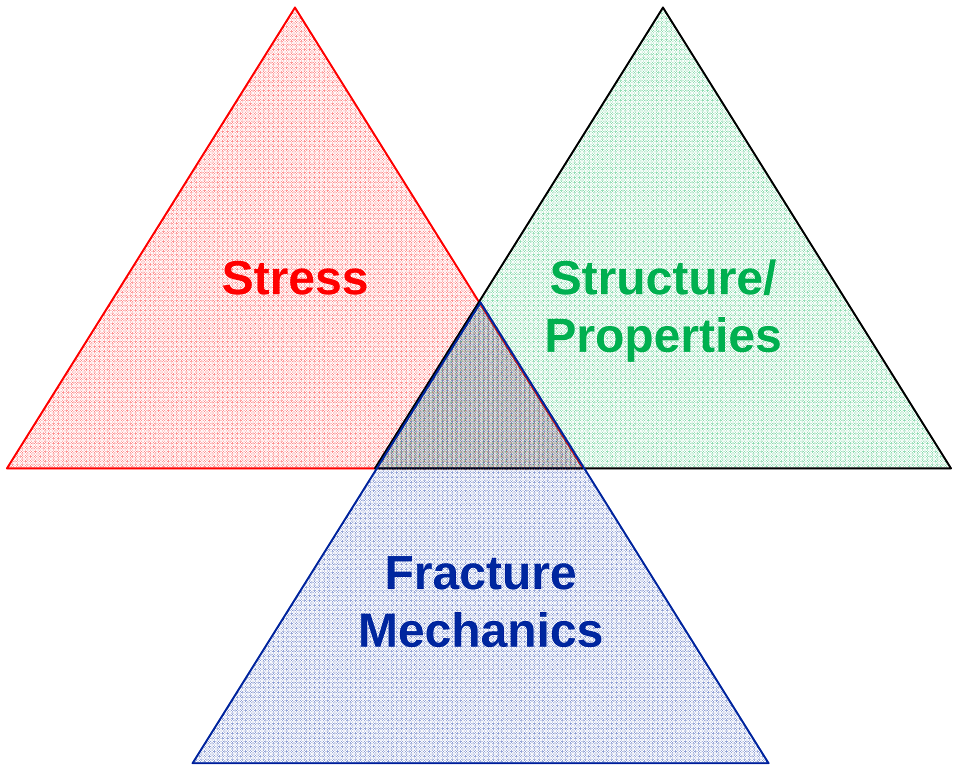
Anstis et al., 'A Critical Evaluation of Indentation Techniques for Measuring Fracture Toughness: I, Direct Crack Measurements," J Am Ceram Soc 64 [9] 633-8 (1981)

Glass-Ceramics Are Tougher Than Glass

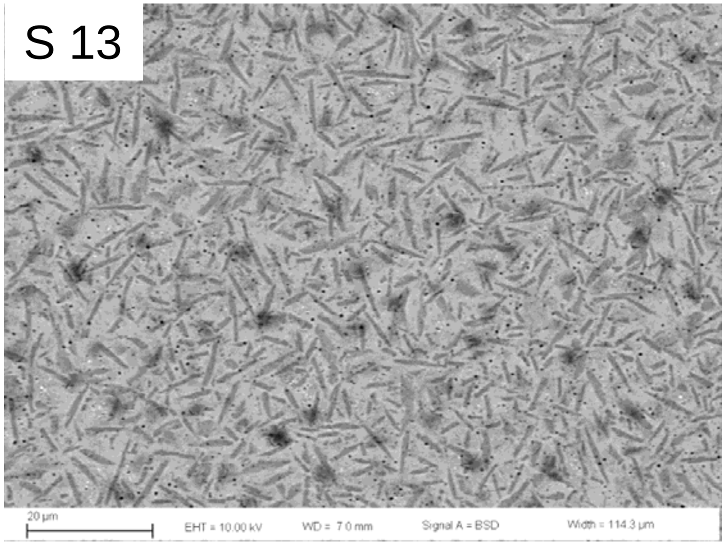
Sample	K_{IC} (MPa·m$^{1/2}$)	Vickers Hardness GPa	Relative Humidity (%)	Measurement Method
Glass (typical)	0.7-0.8	---	---	
GC B-11	1.97 ± 0.05	---	21	SEVNB
GC B-14	2.76 ± 0.16	---	21	SEVNB
GC S-13	1.52 ± 0.26	4.61 ± 0.26	---	Indentation
GC S-14	1.79 ± 0.32	4.60 ± 0.17	---	Indentation
GC S-15	1.92 ± 0.22	4.18 ± 0.24	---	Indentation
GC S-17	1.40 ± 0.26	4.41 ± 0.59	---	Indentation

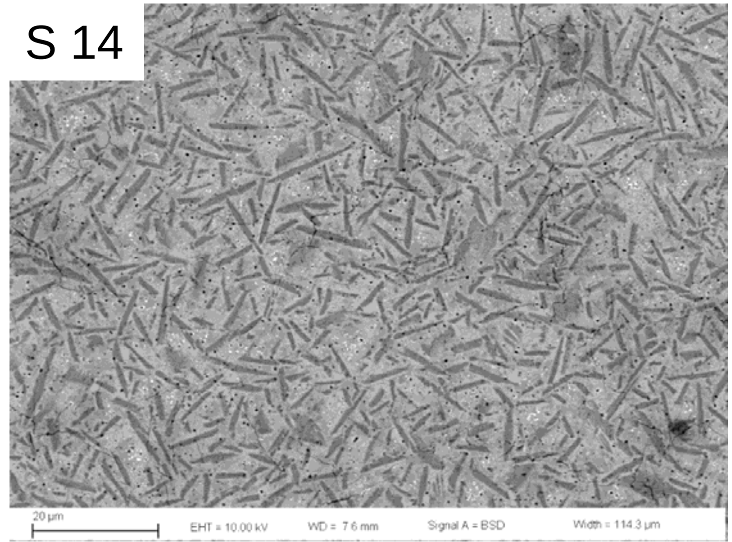
A Higher Toughness Glass-Ceramic Requires A Higher Stress To Crack

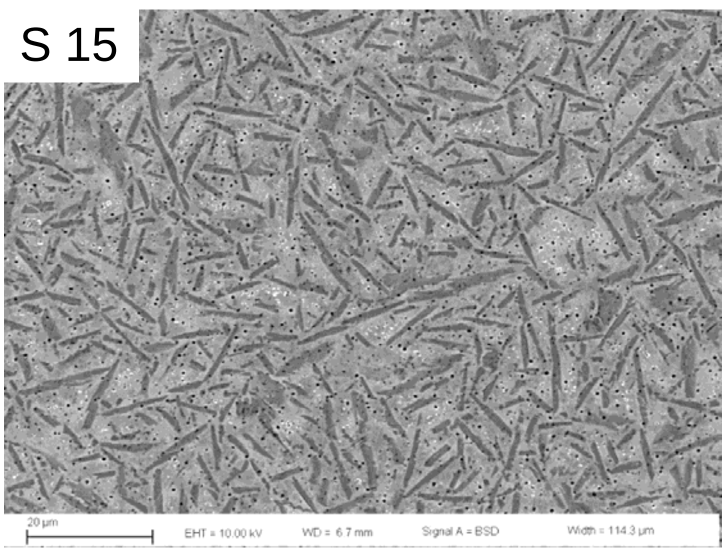
$$K \approx \sigma \sqrt{a} \approx K_{IC}$$

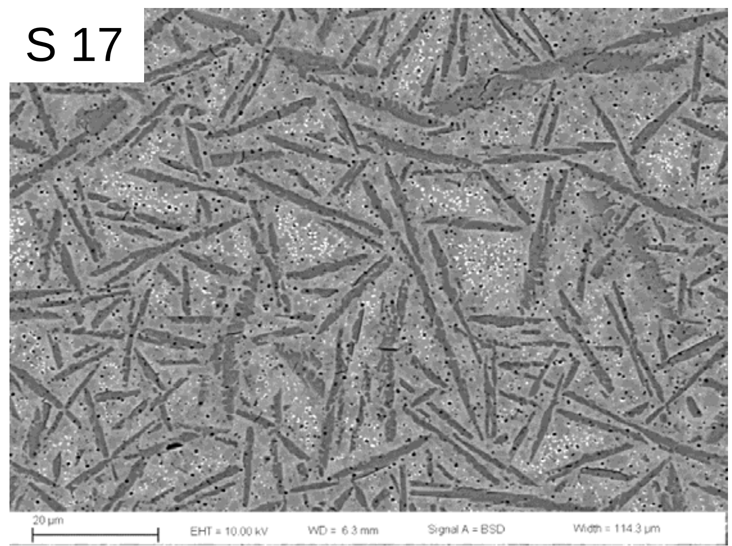


The Glass-Ceramic Crystal Structure Gets Coarser With Increasing CTE

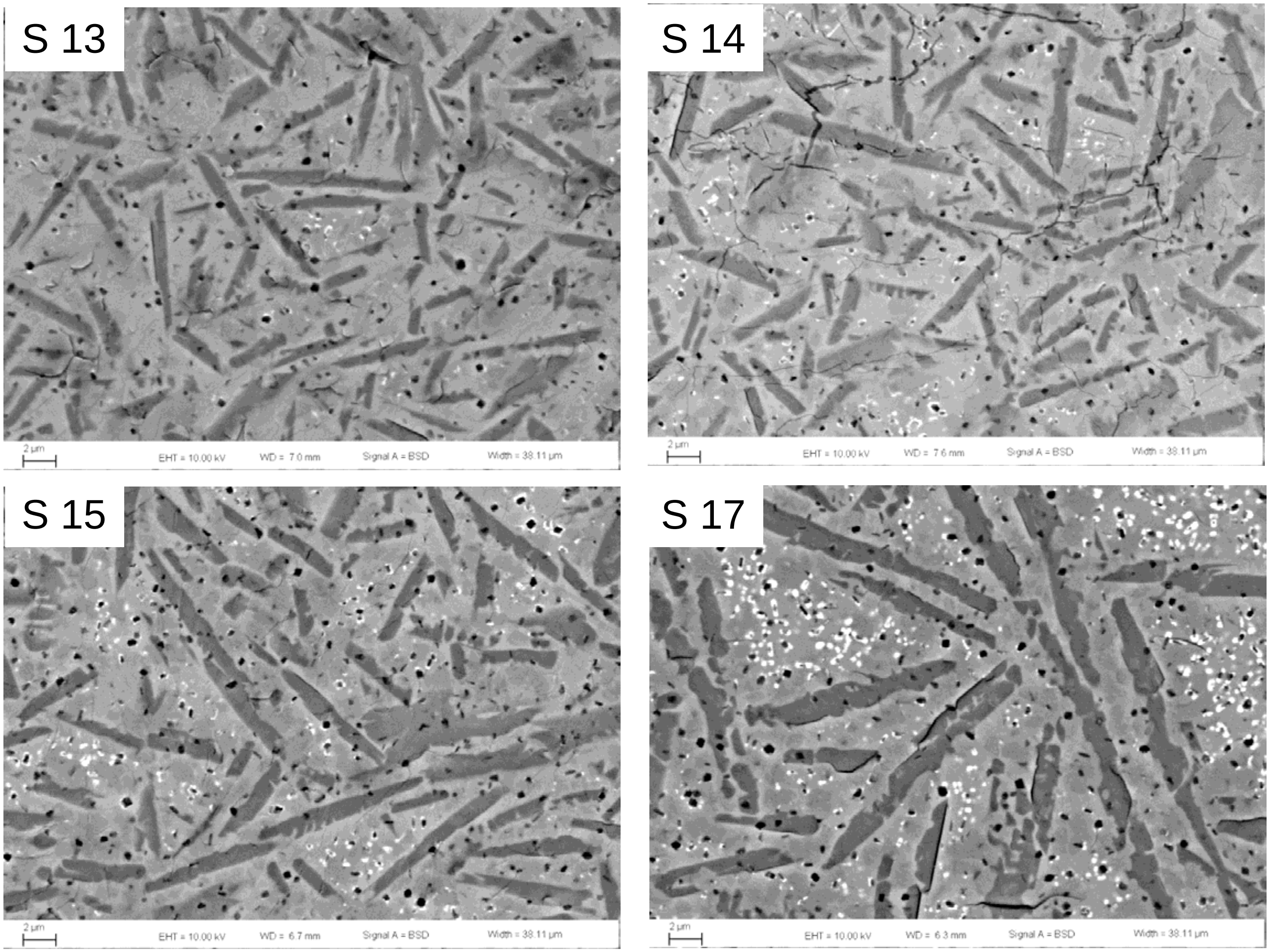








Cracks Are Observed Throughout The Glass-Ceramic Microstructure



Glass-Ceramics Are More Crack Tolerant Than Glass Because Of Their Higher Toughness

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Summary

- **Strength**
  - GC S Is Comparable to Glass
    - Long cracks in microstructure
  - GC SB Is Higher Than Glass
- **Hardness**
  - GC S Is Lower Than Glass
- **Toughness**
  - GC Is 2-3X Glass

Surface Crystallization May Be Critical For GC Processing-Microstructure-Properties

Summary

- **GC Chemistry**
  - P Depletion At GC Interface
    - Depletion of Li_3PO_4 heterogeneous nucleation sites at GC interface
  - Slight Cr Enrichment At GC Interface
    - Decreases glass viscosity
- **GC Microstructure In Bulk**
  - time-Temp Controlled Nucleation/Growth per Headley & Loehman
- **GC Microstructure At Interface**
  - Cr Redox Chemistry Related
    - Dense glass region
    - Cr_2O_3 particles
    - Porosity (from gas and/or volume change on crystallization)
  - Glass Preform (Processing) Related
    - $Li_2Si_2O_5$ surface crystals affect viscosity and microstructure.