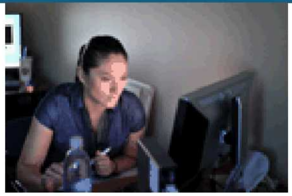
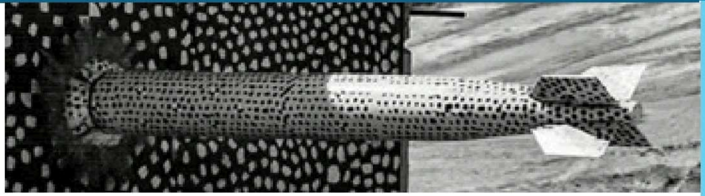
SAND2019-6426C

Microstructure of Sealing Glass-ceramics





PRESENTED BY

Steve Dai, Bonnie McKenzie, Paul Kotula, Mark Rodriguez, and Ana Baca

Sandia National laboratories, New Mexico, USA

International Congress of Glasses 2019, Boston, USA

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Outline

Overview of glass-to-metal (GtM) and glass-ceramic-to-metal (GCtM) seals

Thermal strain of existing step-like (SL16) glass-ceramics

- Dominant crystallization: **Cristobalite**
- Inversion in Cristobalite → step-like thermal strain

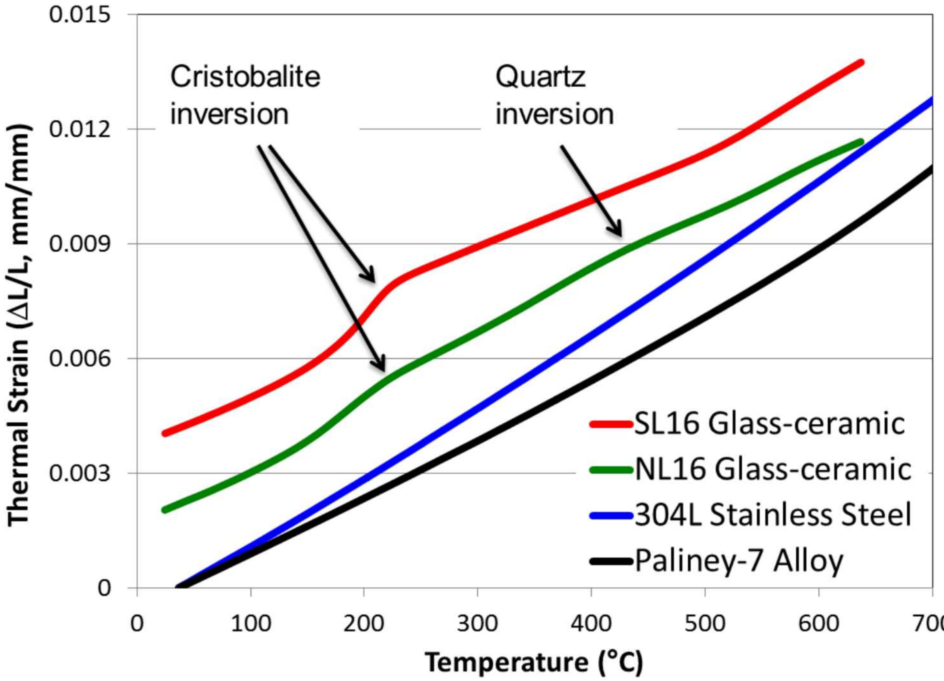
Thermal strain of next gen near-linear (NL16) glass-ceramic

- Multi-crystallizations: **Quartz** and **Cristobalite**
- Multiple inversions → near-linear thermal strain

Microstructure of sealing glass-ceramics

- XRD phase identification
- Etching study: SEM, AFM and TEM results

Summary



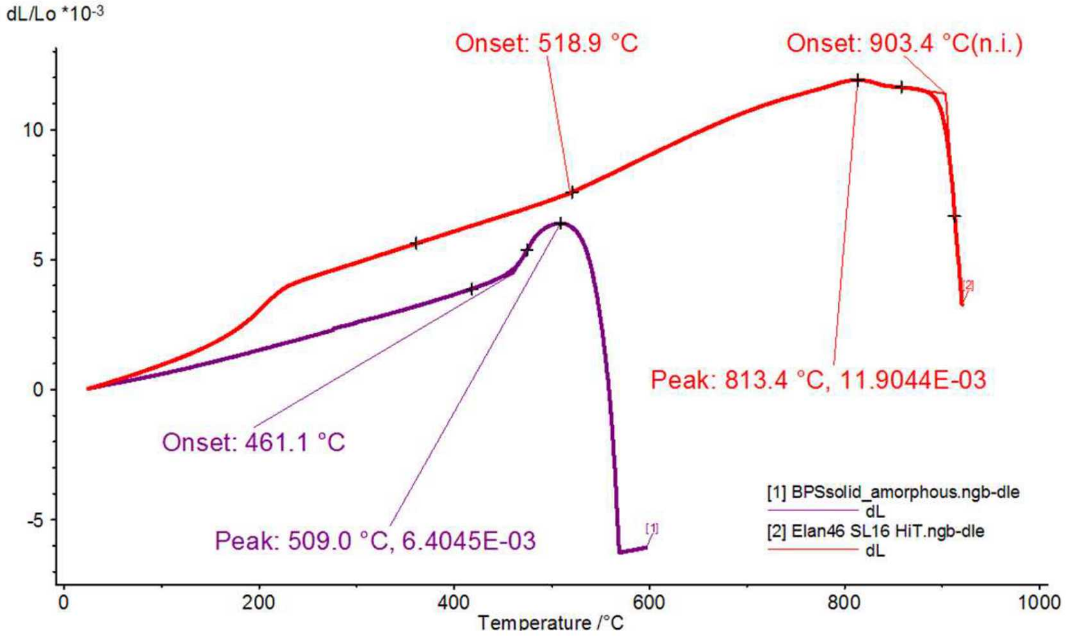
GCtM seals

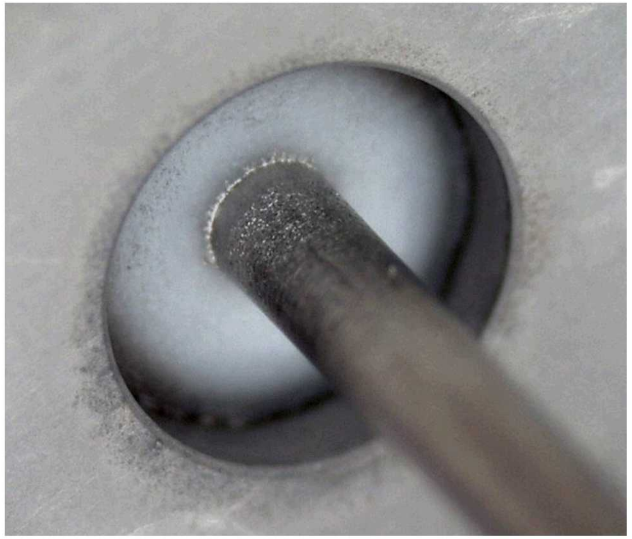
Process/reflow like glasses

High temp stability after crystallization

High coefficient of thermal expansion (CTE)
- CTE of most sealing glasses < 12 ppm/°C

Crystallization → tunable CTE
- Matched seals I CTE_GC ≤ CTE_housing

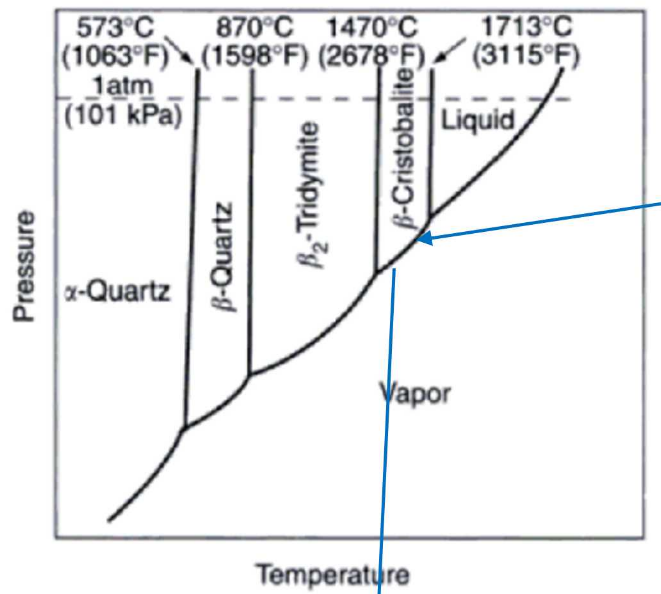


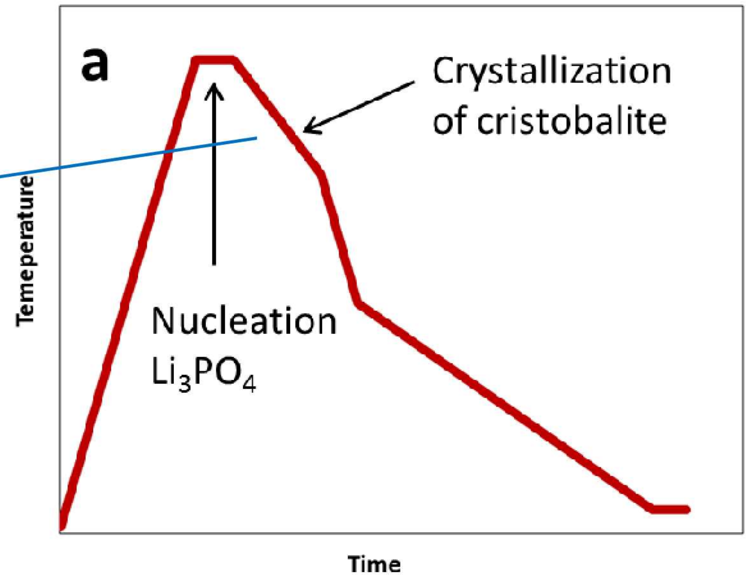


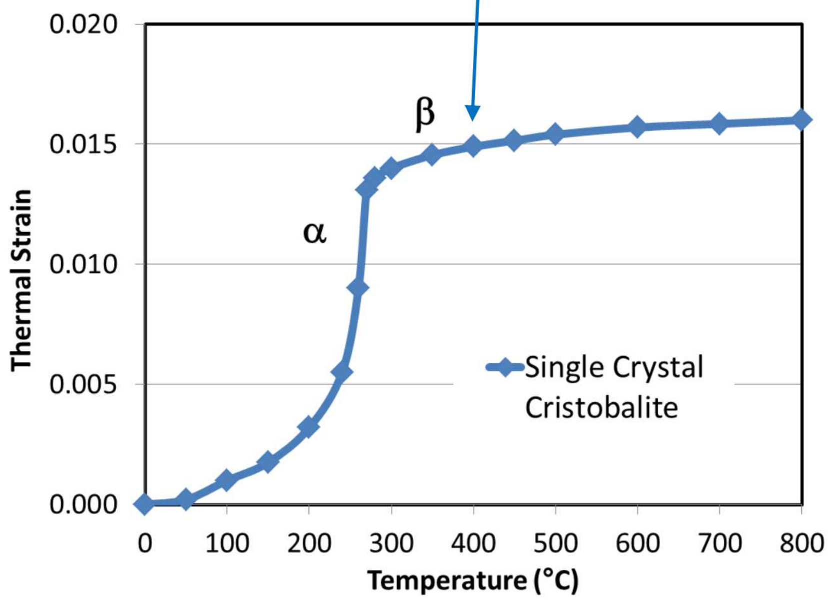
Material	CTE (ppm/°C) (40 -600°C)
304L SS shell	18.89
BPS GC*	16-17
Paliney7 pin	15.76

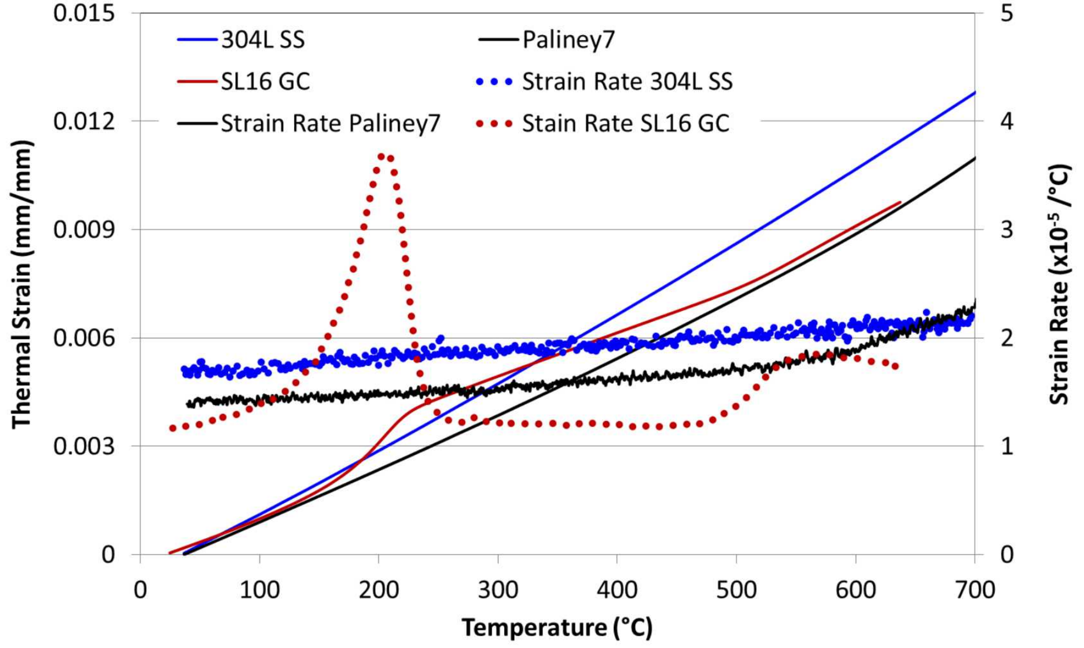
*Belt-processable glass

Matched Thermal Strain – existing SL16 GC

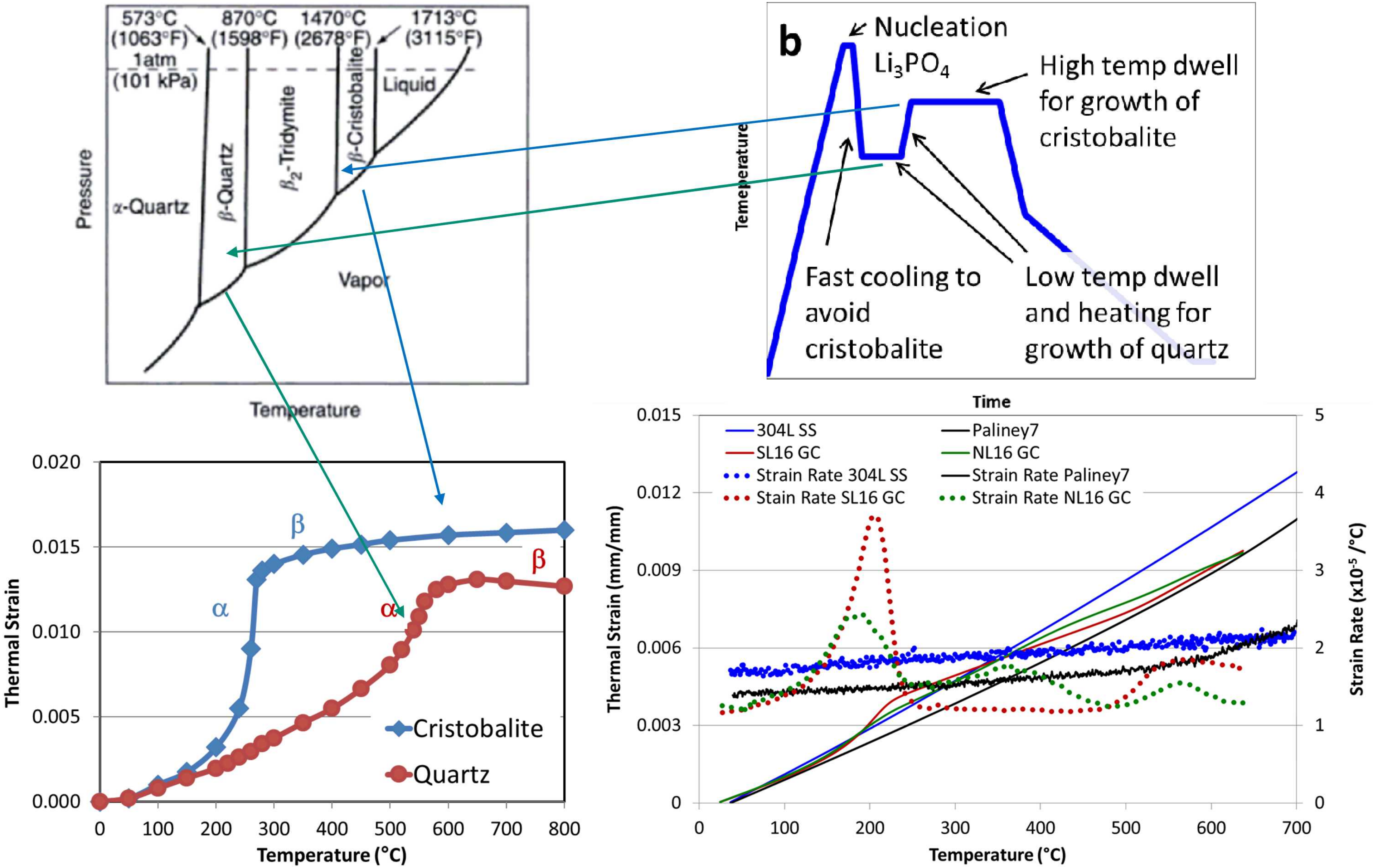








Matched Thermal Strain and Strain Rate – New NL16 GC

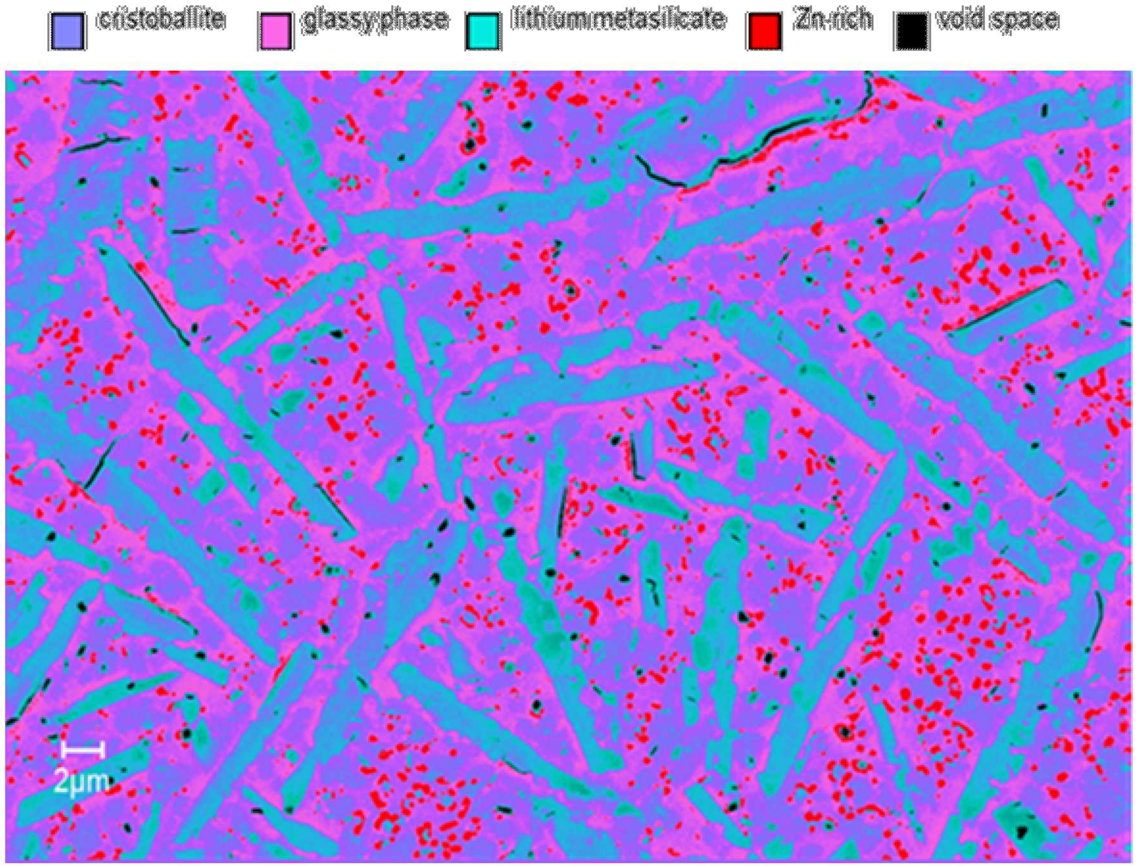


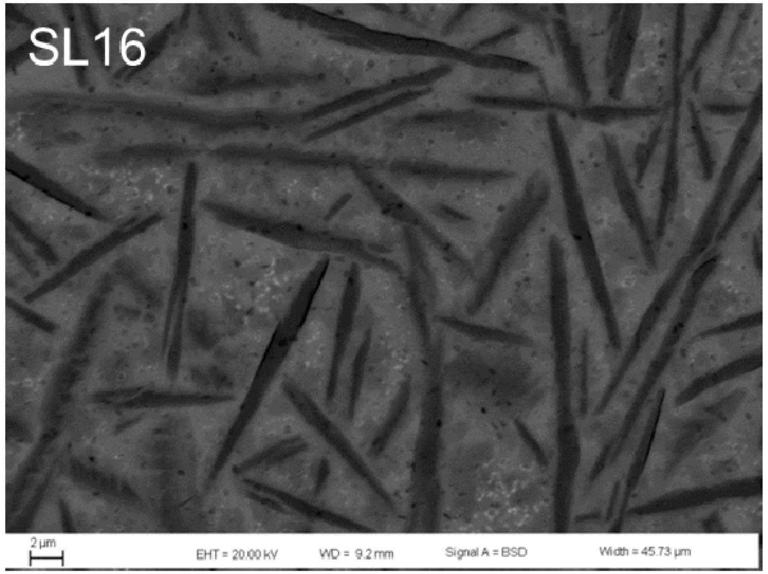
Morphology: cristobalite and quartz?

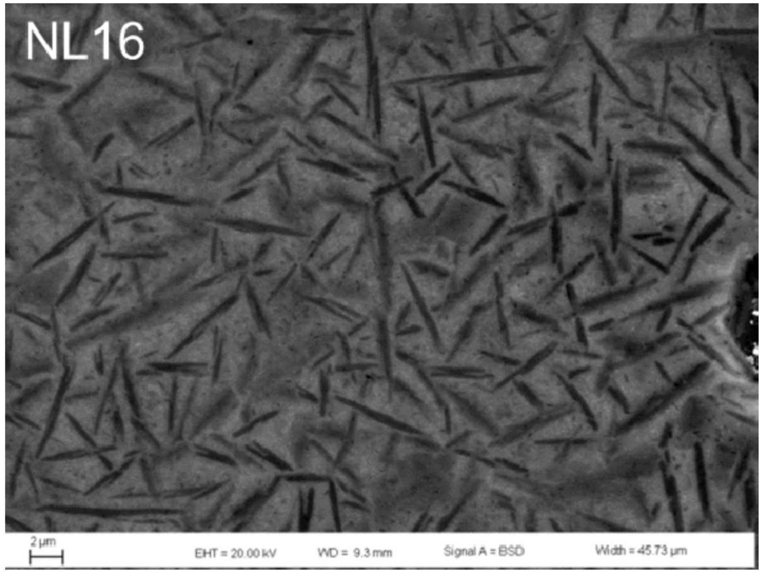
Li_2SiO_3 crystals obvious

Cristobalite and quartz visible but fuzzy images

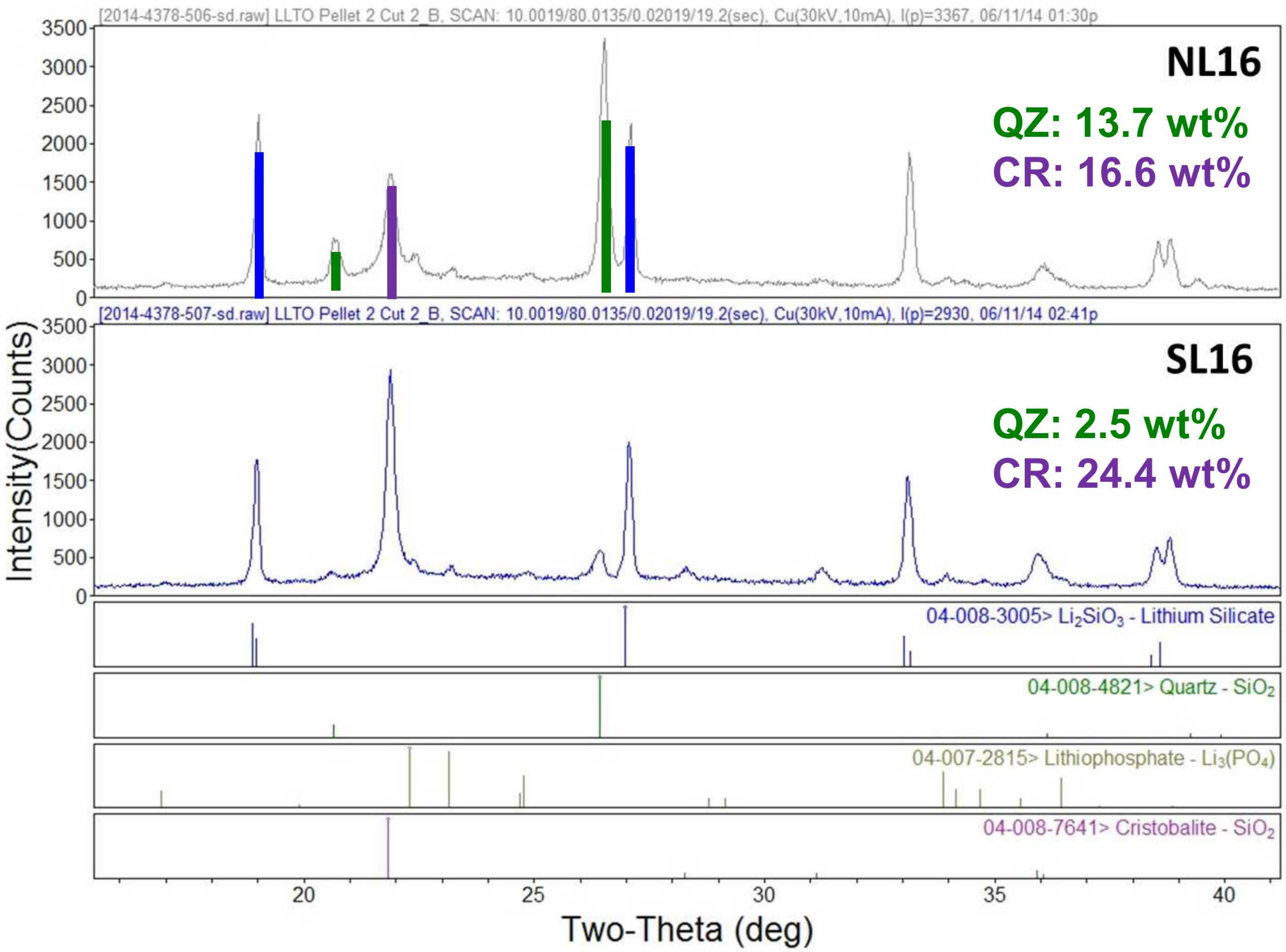
"Grey-scale" phase ide dentification





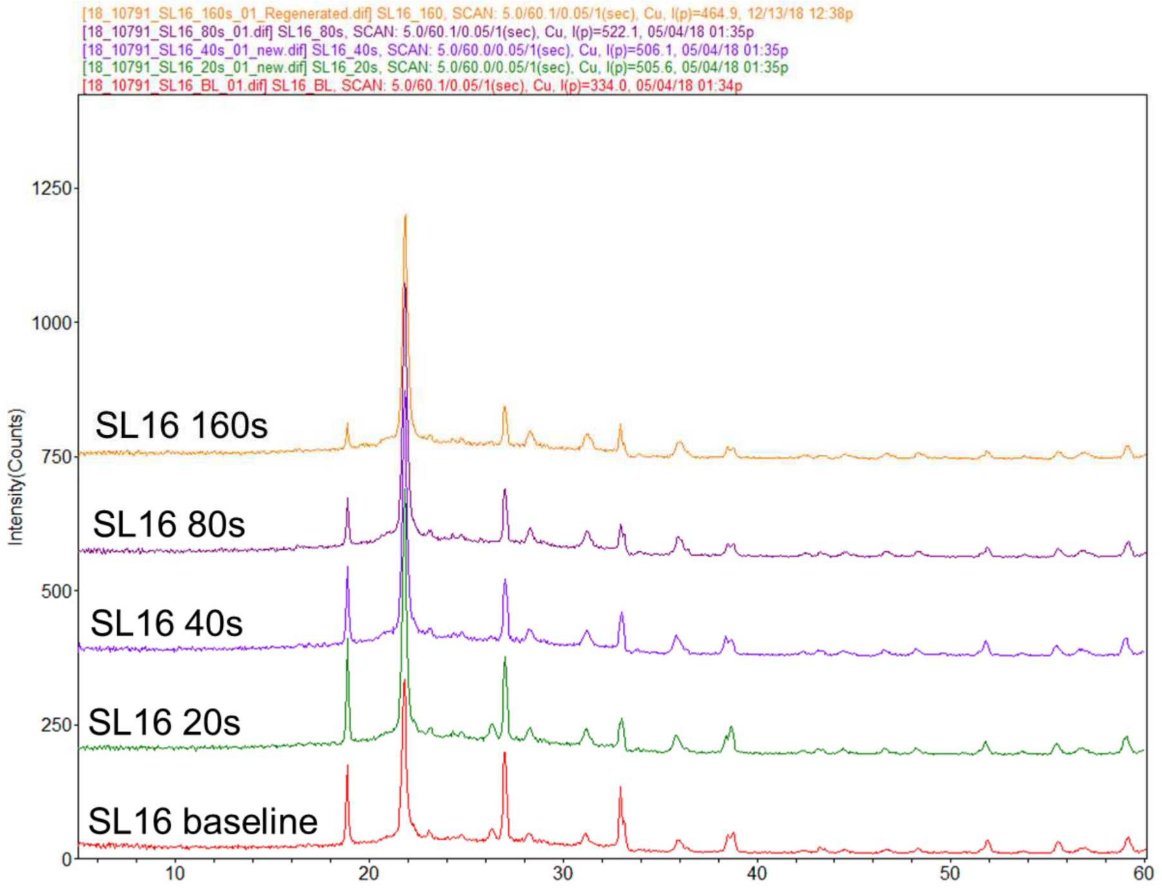


XRD quantitative analysis of crystalline phases



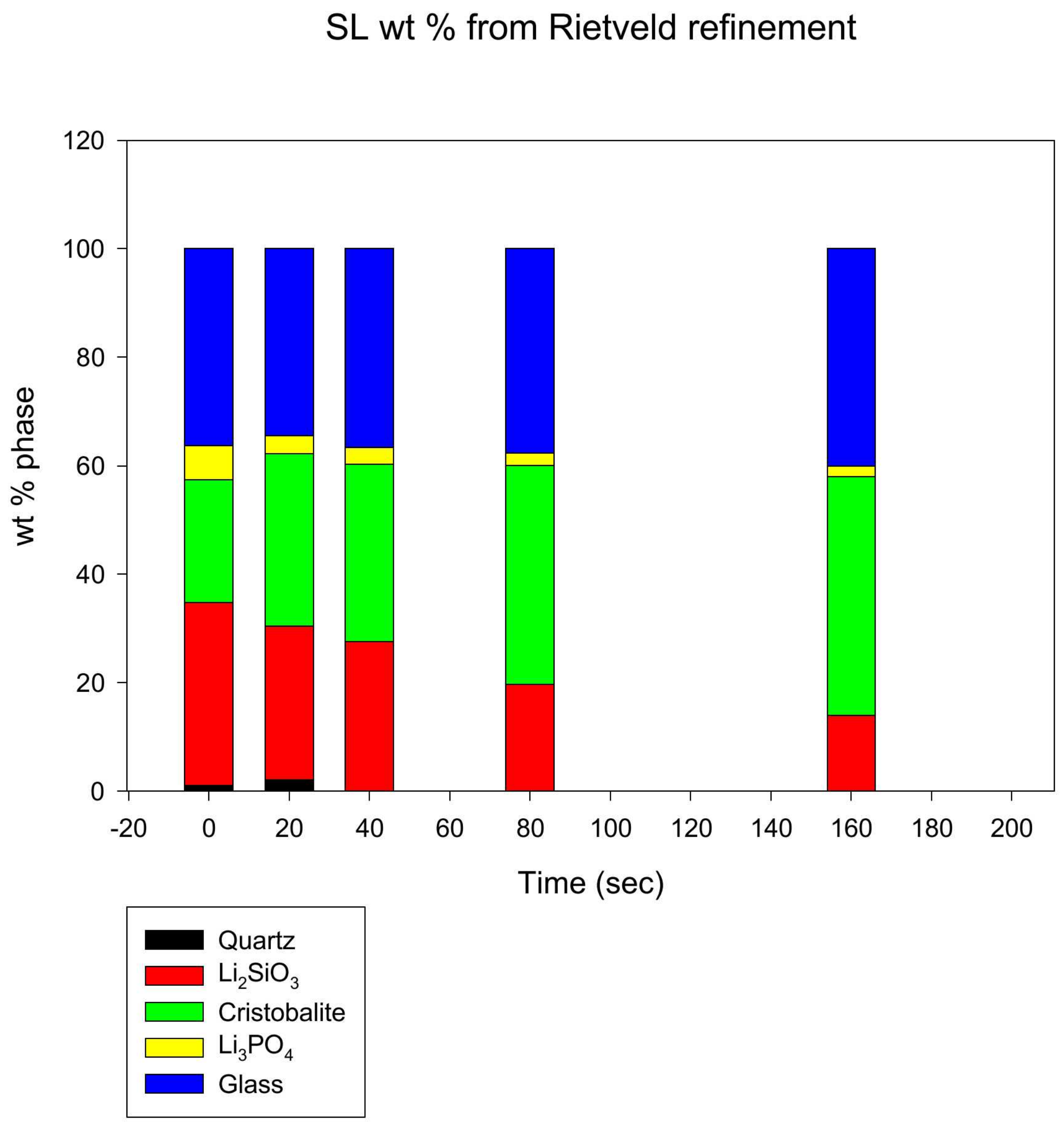
Phase	SL16	NL16
	wt%	wt%
Quartz Low SiO_2	2.51	13.71
Cristobalite SiO_2	24.37	16.55
Li_2SiO_3	36.82	37.95
Li_3PO_4	7.94	7.36
Amorphous	28.36	24.42

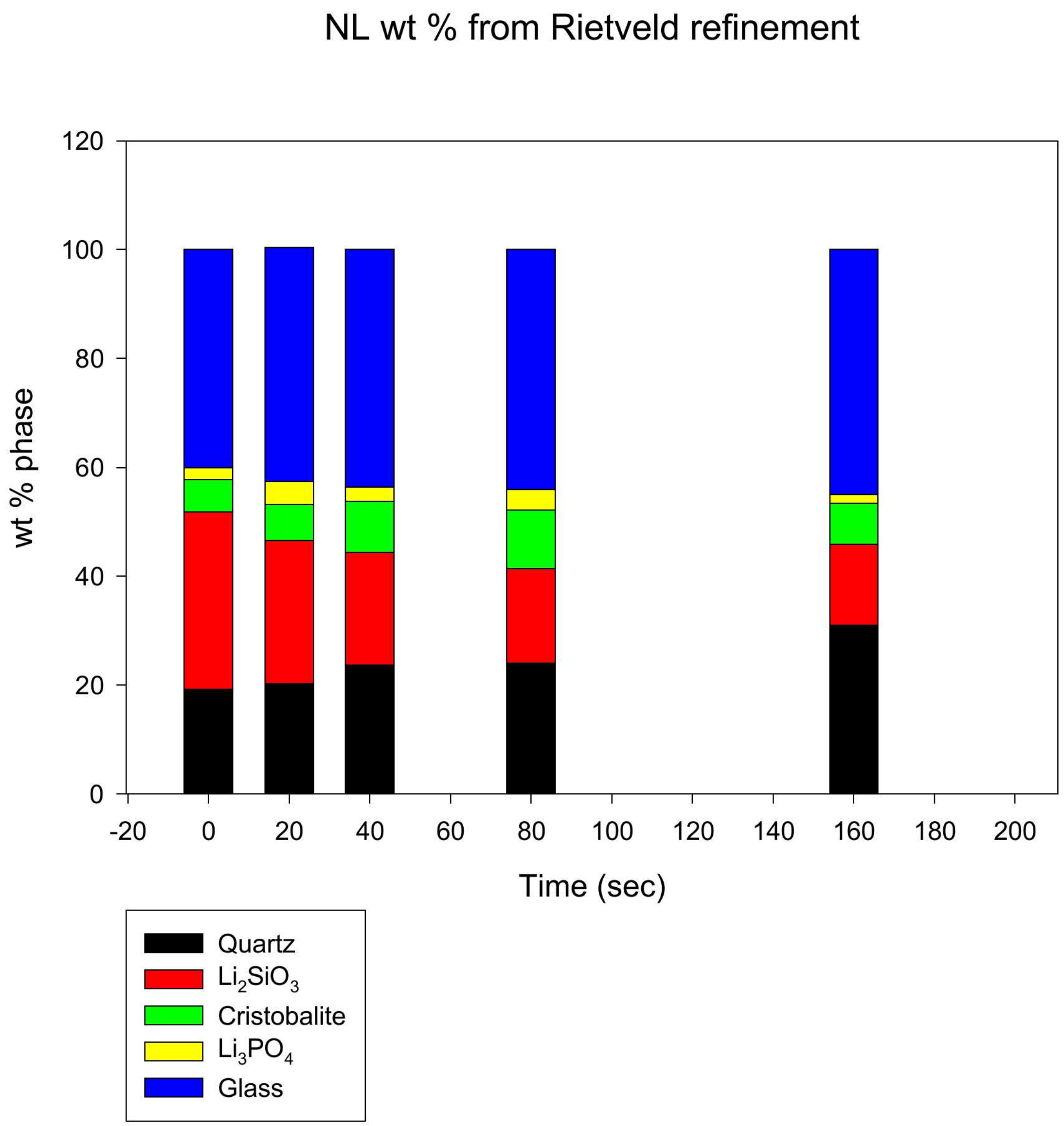
XRD scans and wt% via Rietveld Refinement (TOPAS V5), SL16



Wt% with ± errors						
Sample ID	SiO_2 (Qtz)	Li_2SiO_3	SiO_2 (Crs)	Li_3PO_4	Amorphous (11 Å peak)	Refinement Rp Value
SL16 BL	**1.0**	**33.7**	**22.7**	**6.2**	**36.4 (w/ Bkg 2)**	9.48
±	0.2	1.0	0.7	0.5	1.6	
SL16 20s As-Is	**2.1** / 1.1	**28.4** / **-5.3**	**31.7** / **9**	**3.3** / **-2.9**	**34.5 (w/ Bkg 2) / -1.9**	8.49
±	0.2	0.9	0.9	0.3	1.7	
SL16 40s As-Is	-	**27.6** / **-6.1**	**32.7** / **10**	**3.0** / **-3.2**	**36.7 (w/ Bkg 2) / 0.3**	8.98
±	-	0.9	0.9	0.3	1.6	
SL16 80s As-Is	-	**19.7** / **-14.7**	**40.4** / **17.7**	**2.3** / **-3.9**	**37.6 (w/ Bkg 2) / 1.2**	8.6
±	-	2	3	0.3	3	
SL16 160s As-Is Redo 2	-	**14.1** / **-19.6**	**44.0** / **21.3**	**1.8** / **-4.4**	**40.1 (w/ Bkg 2) / 3.7**	9.54
±	-	0.7	1.3	0.2	1.7	

Obvious etching of Li_2SiO_3, but residual glass wt% stable





X-Ray penetration ~ 10x microns so the actual wt change on surface is much higher

5 vol% HF etching, SL16

Appears Li_2SiO_3 etched away initially

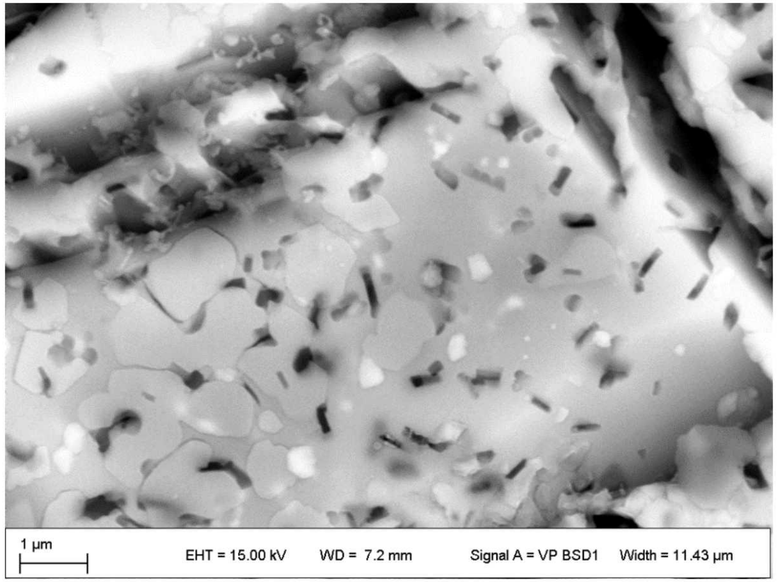
- Consistent with early Coring publication*

Residual glass next

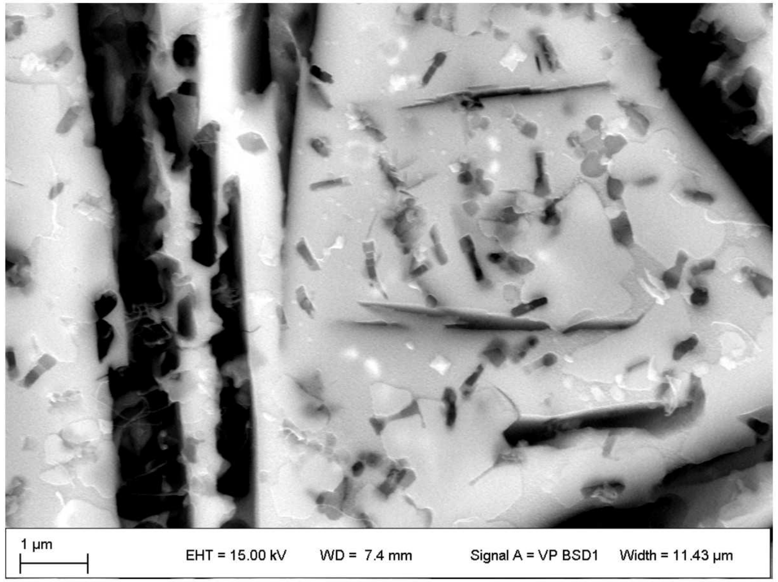
160 Sec etching reveals most subsurface

- Crystalline phase = cristobalite?

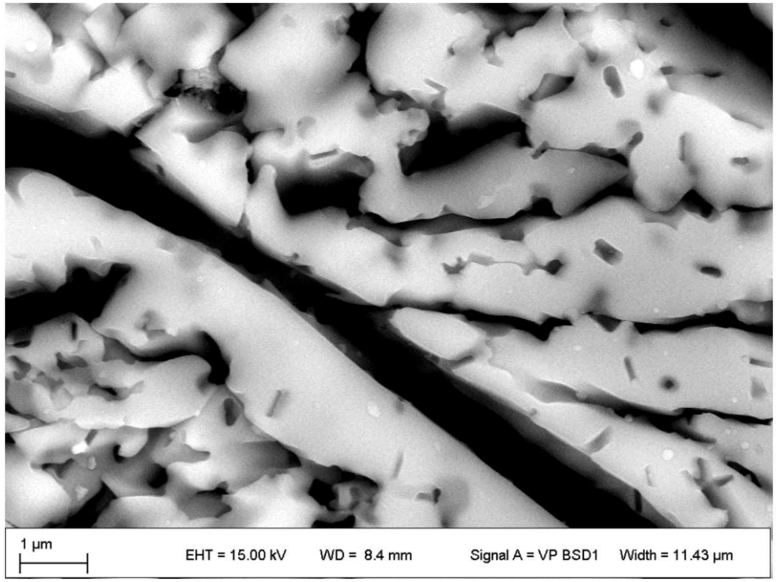
20s



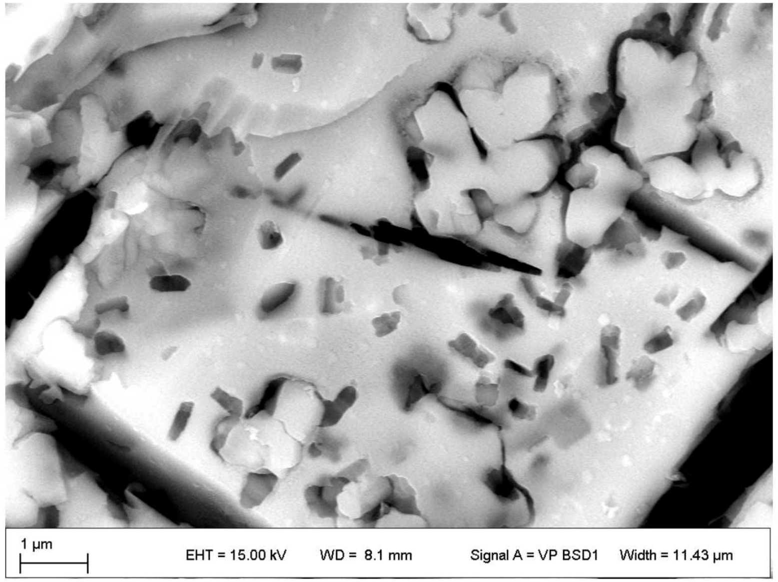
40s



80s



160s



*S. D. STOOKEY, "chemical machining o photosensitive glass", Industrial and Engineering Chemistry, pp 115 - 118, Jan 1953

5 vol% HF etching, NL16

Appears Li_2SiO_3 etched away initially

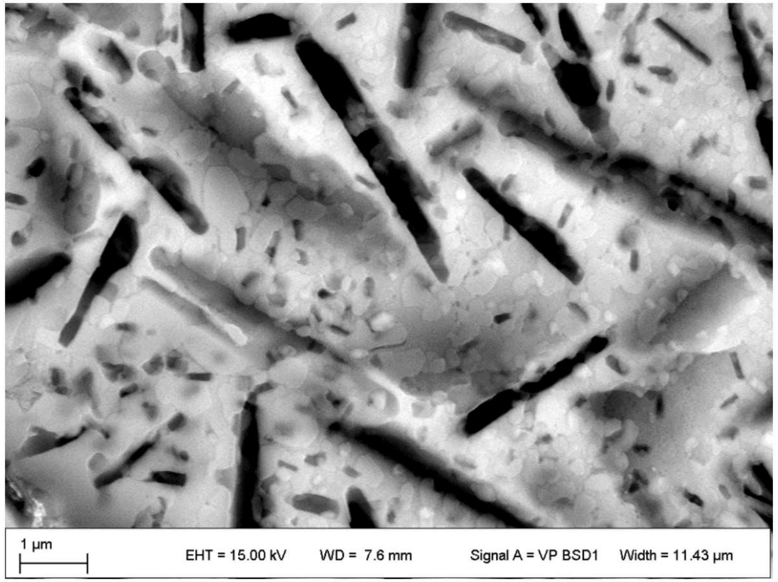
Residual glass next

Crystalline phases becomes obvious after 40s etching

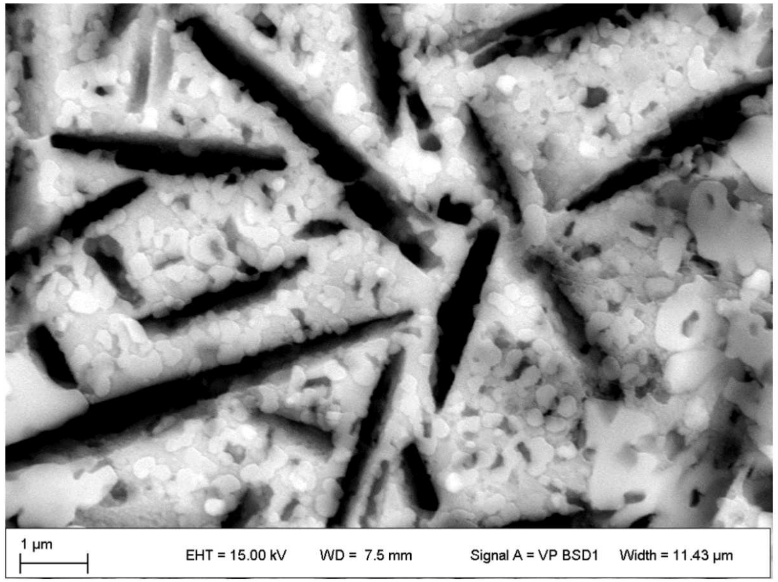
160 Sec etching reveals most subsurface

Two distinct morphologies of crystalline phases

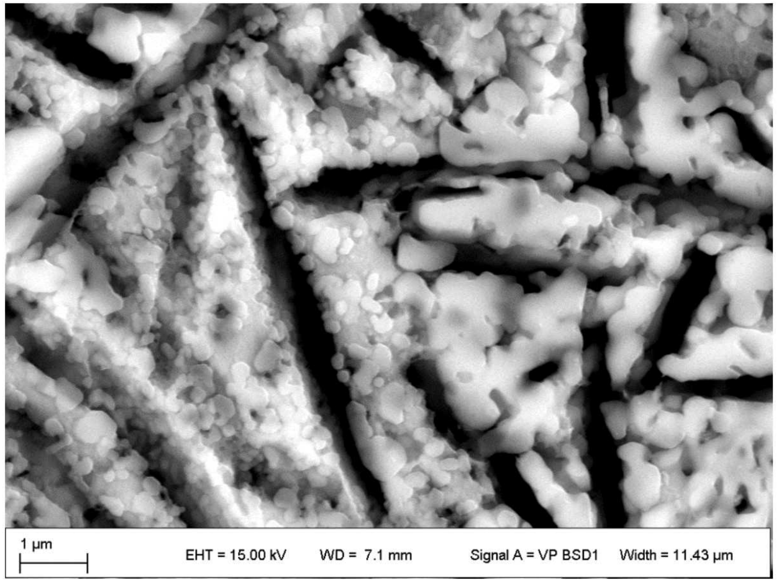
20s



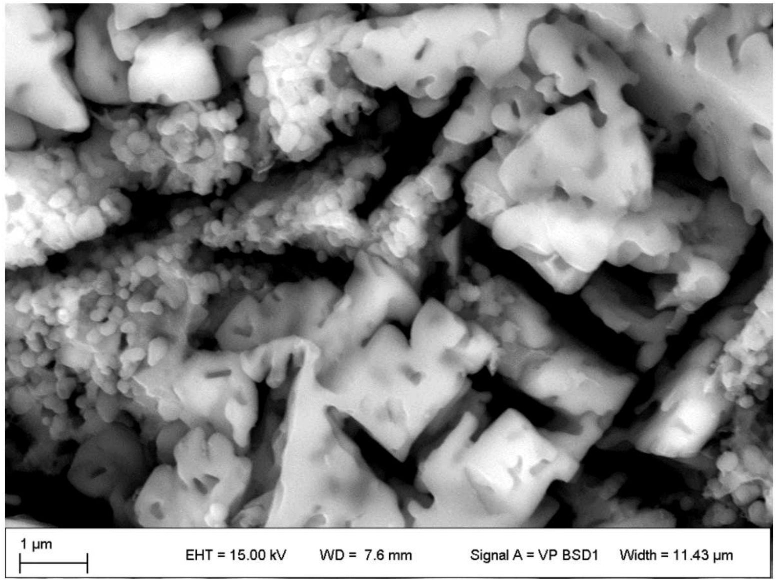
40s



80s



160s



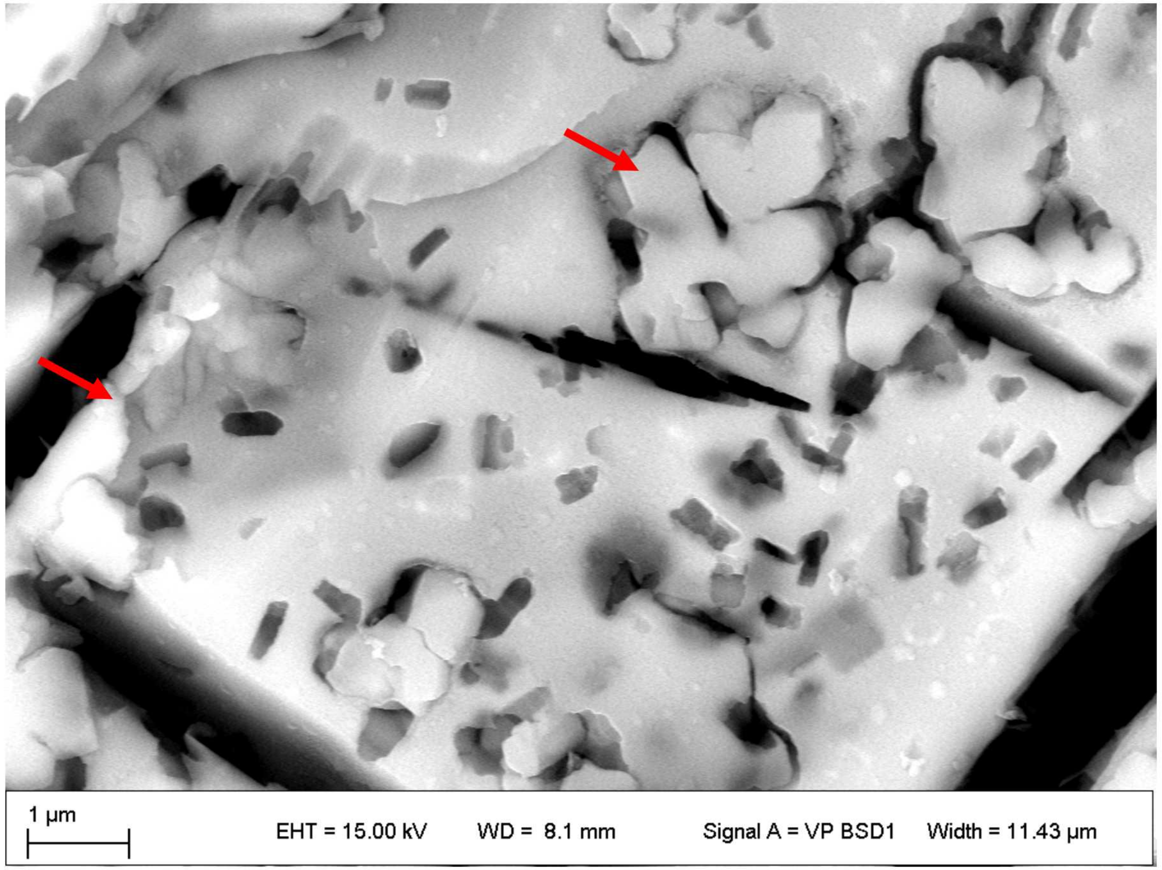
SL16 vs NL16, 5 vol% HF etching 160s

Residual glass etched away

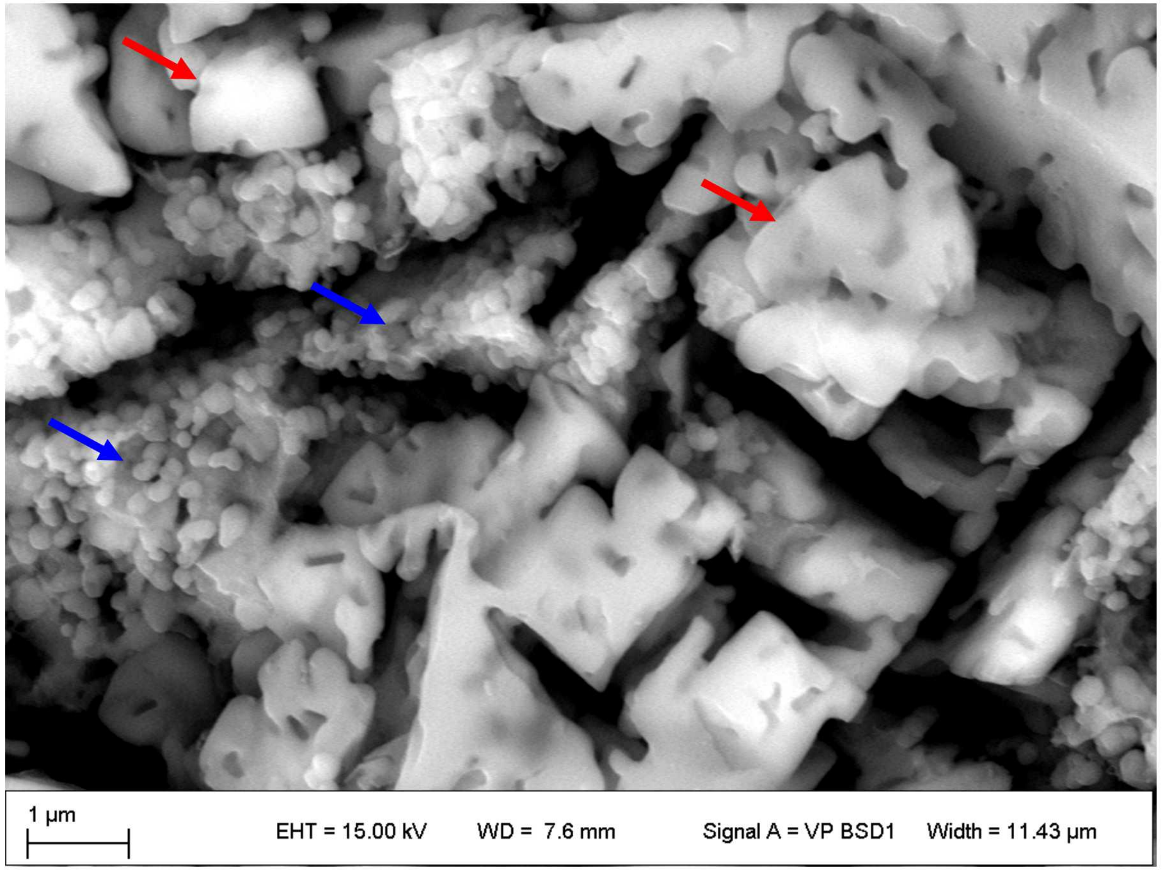
Cristobalite = large crystals at 1 -10 μm, quartz = clustered fine crystals << 1 μm.

Different nucleation and growth mechanism?

SL16, QZ: 2.5 wt%, CR: 24.4 wt%

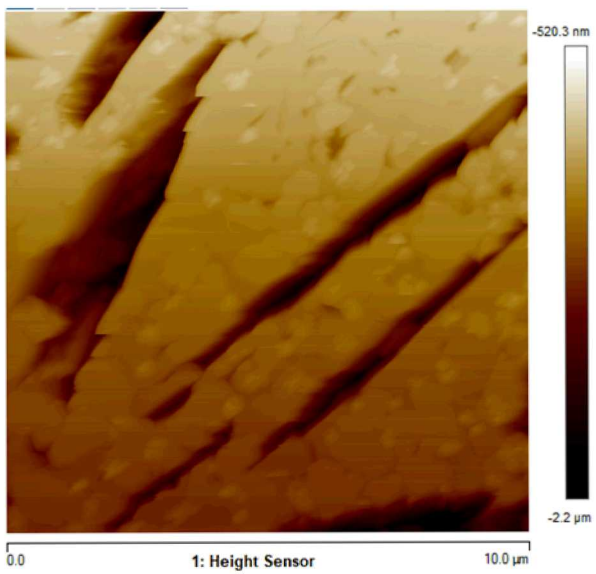


NL16, QZ: 13.7 wt%, CR: 16.6 wt%

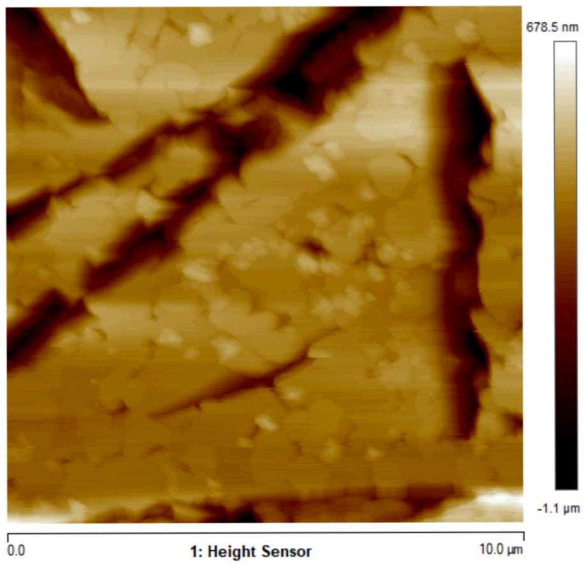


5 vol% HF etching, SL16, AFM 10x10 μm

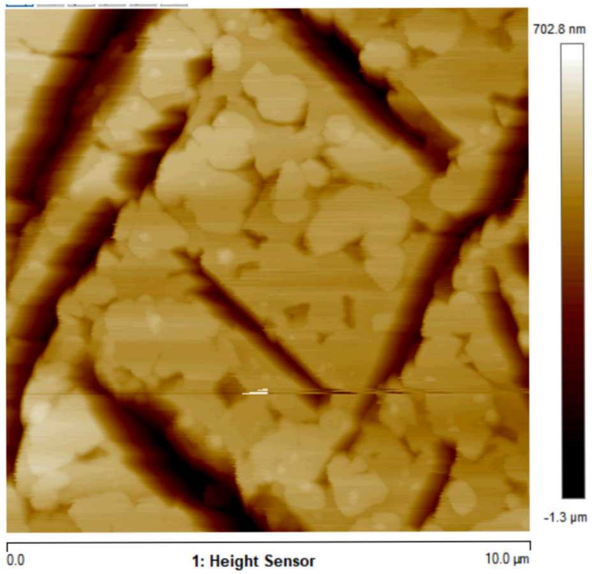
20s
Roughness Sa = 133nm



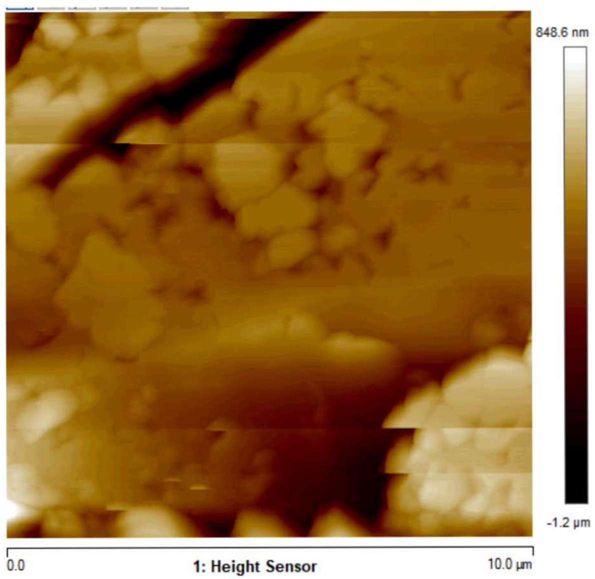
40s
Roughness Sa = 170nm



80s
Roughness Sa = 217nm



160s
Roughness Sa = 228nm



20s etched: primarily Li_2SiO_3

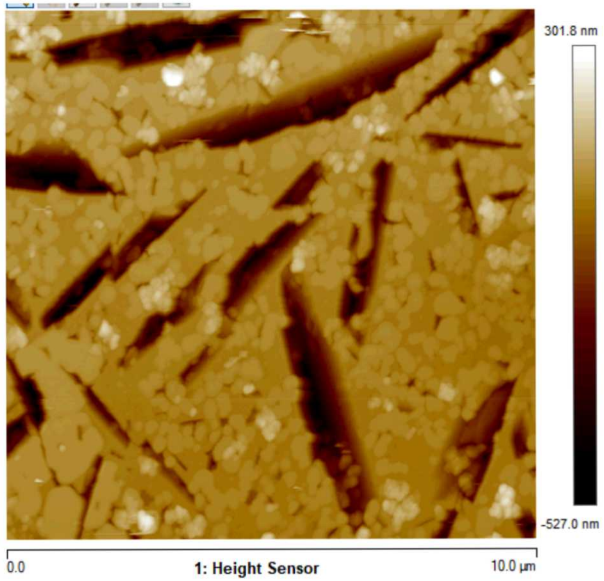
40s etched: start to reveal cristobalite crystals

80s etched: appears the glass between cristobalite start to disappear

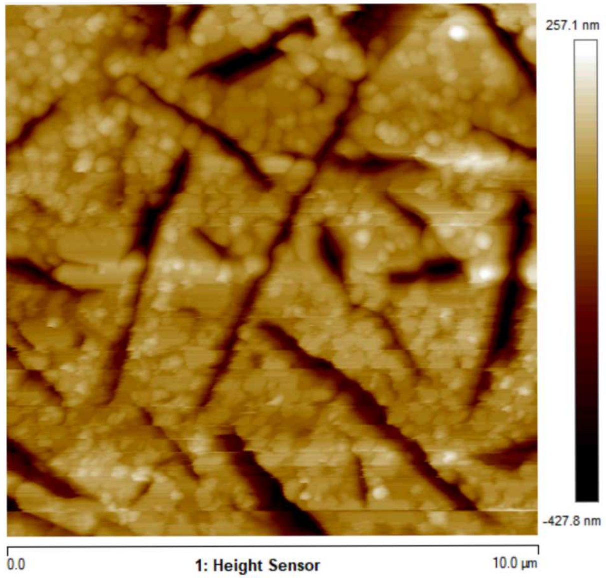
160s etched: “stand along” crystals appears

5 vol% HF etching, NL16, AFM 10x10 μm

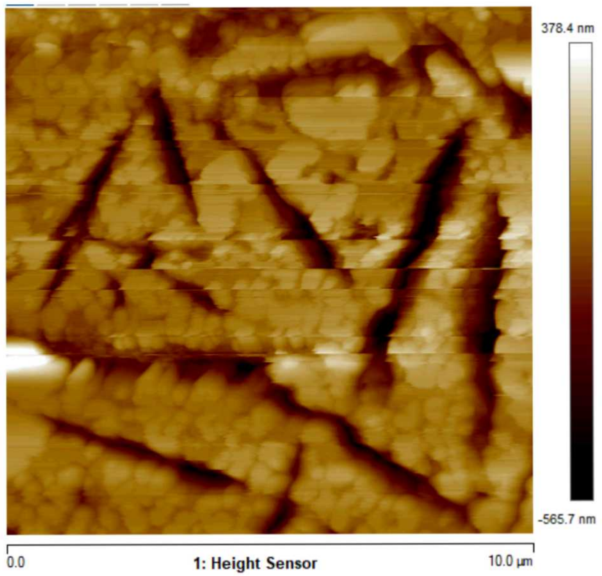
20s
Roughness Sa = 81nm



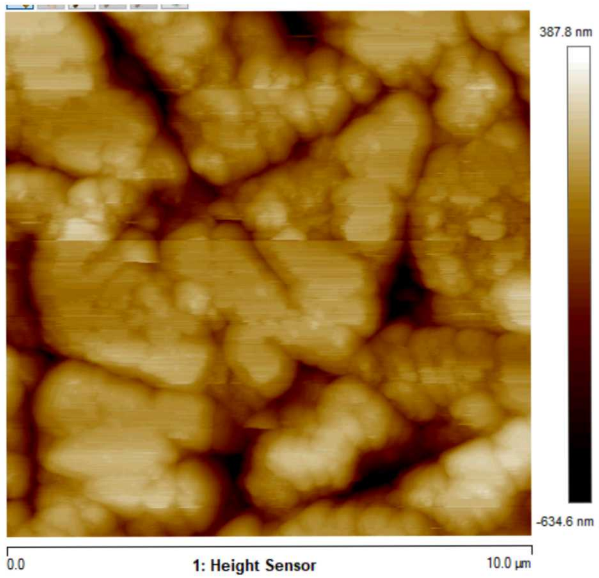
40s
Roughness Sa = 65nm



80s
Roughness Sa = 90nm



160s
Roughness Sa = 102nm



20s etched: primarily Li_2SiO_3 was etched away. Presence of Cristobalite appears.

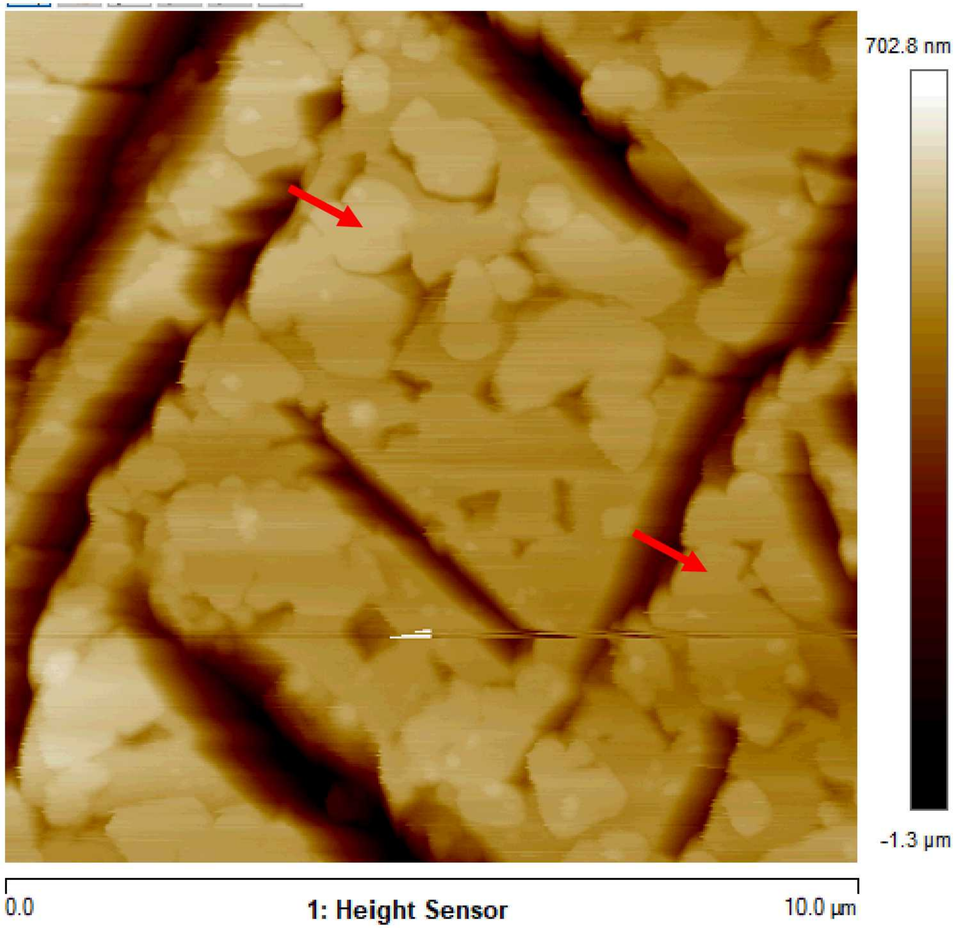
40s etched: start to reveal finer Quartz crystals

80s etched: the glass between cristobalite start to disappear. Two types of crsytals

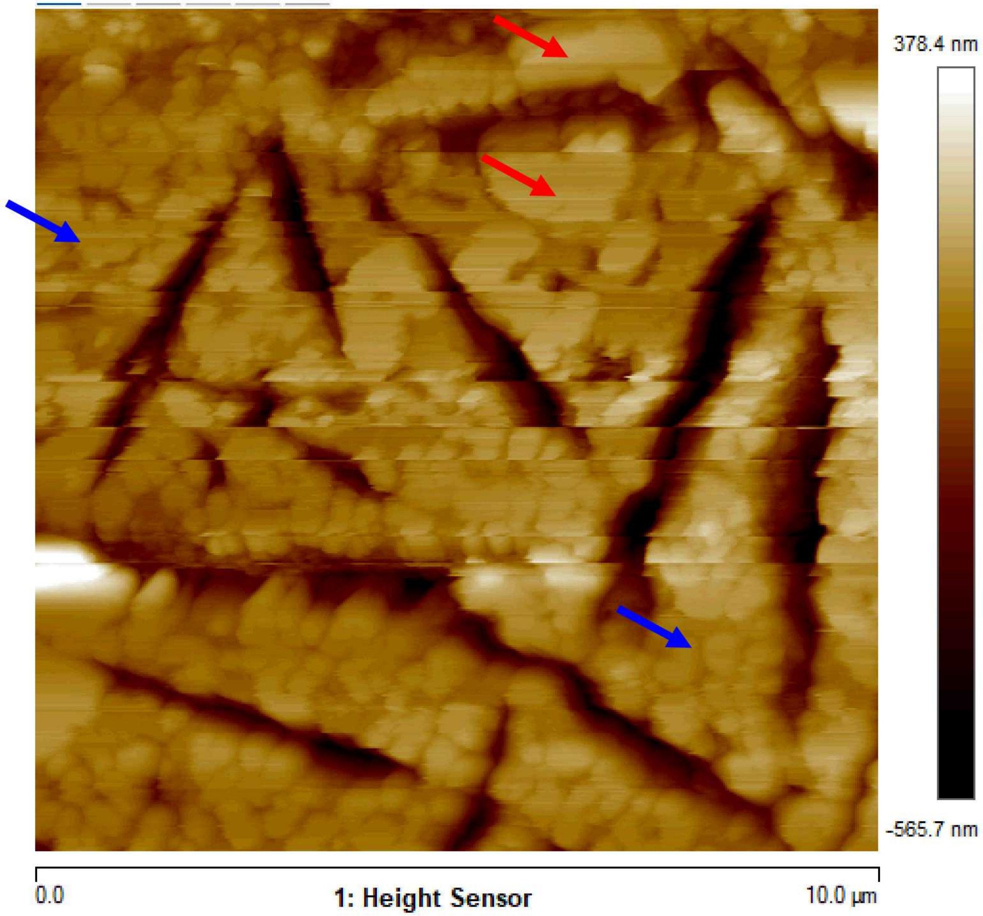
160s etched: “stand along” crystals appear

SL16 vs NL16, 5 vol% HF etching 80s, AFM images

SL16, QZ: 2.5 wt%, CR: 24.4 wt%

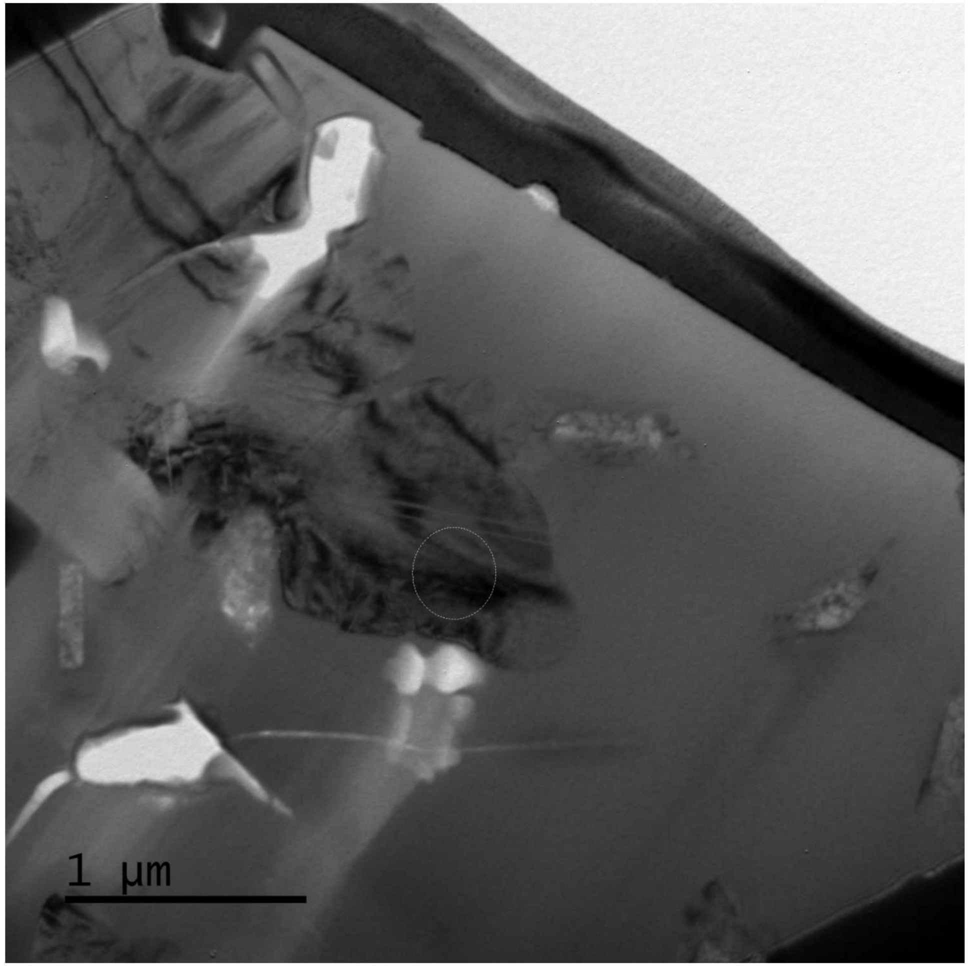


NL16, QZ: 13.7 wt%, CR: 16.6 wt%

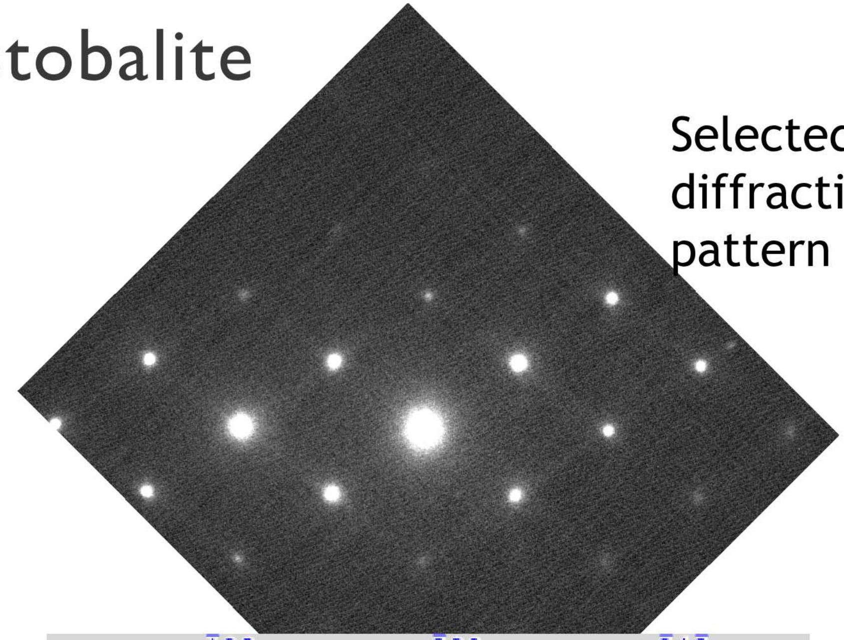


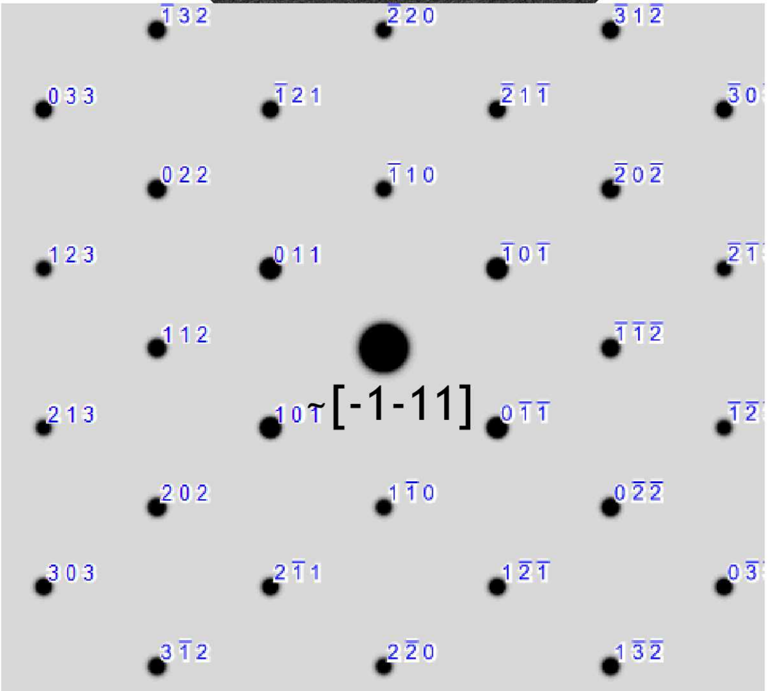
5 vol% HF etching, SL16, 40 sec, cristobalite

Bright-field TEM, size ~ μm



Selected-area diffraction pattern





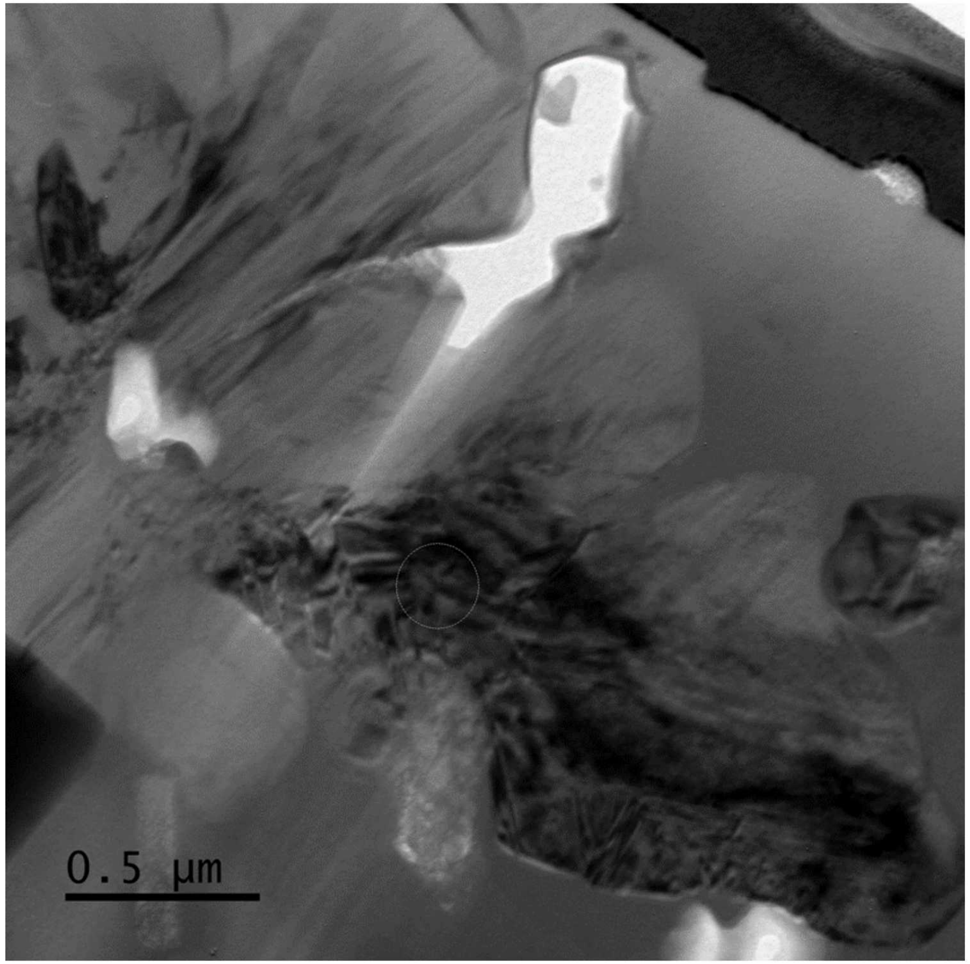
Diffraction simulation from SingleCrystal™

Consistent with the [-1-11] direction of Cristobalite

PDF 00-039-1425 (Tetragonal, a=4.97 Å; c=6.92 Å)

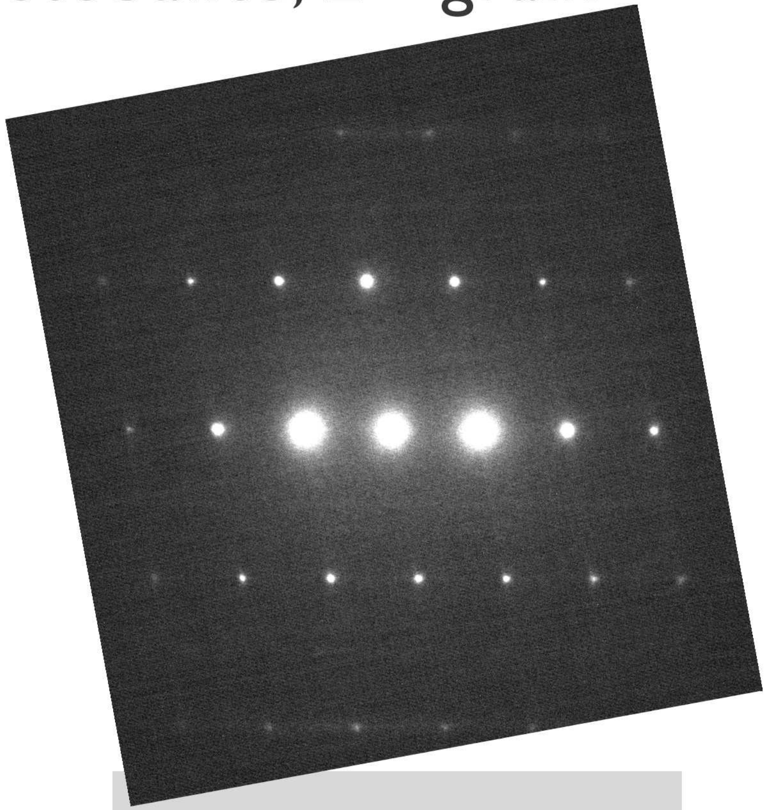
5 vol% HF etching, SL16, 40 sec, cristobalite, 2^{nd} grain

Bright-field TEM, size ~ μm

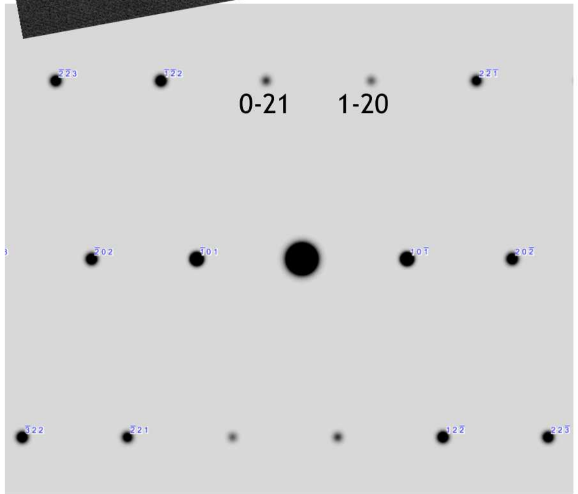


Consistent with ~[212] direction of Cristobalite

PDF 00-039-1425 (Tetragonal, a=4.97 Å; c=6.92 Å)



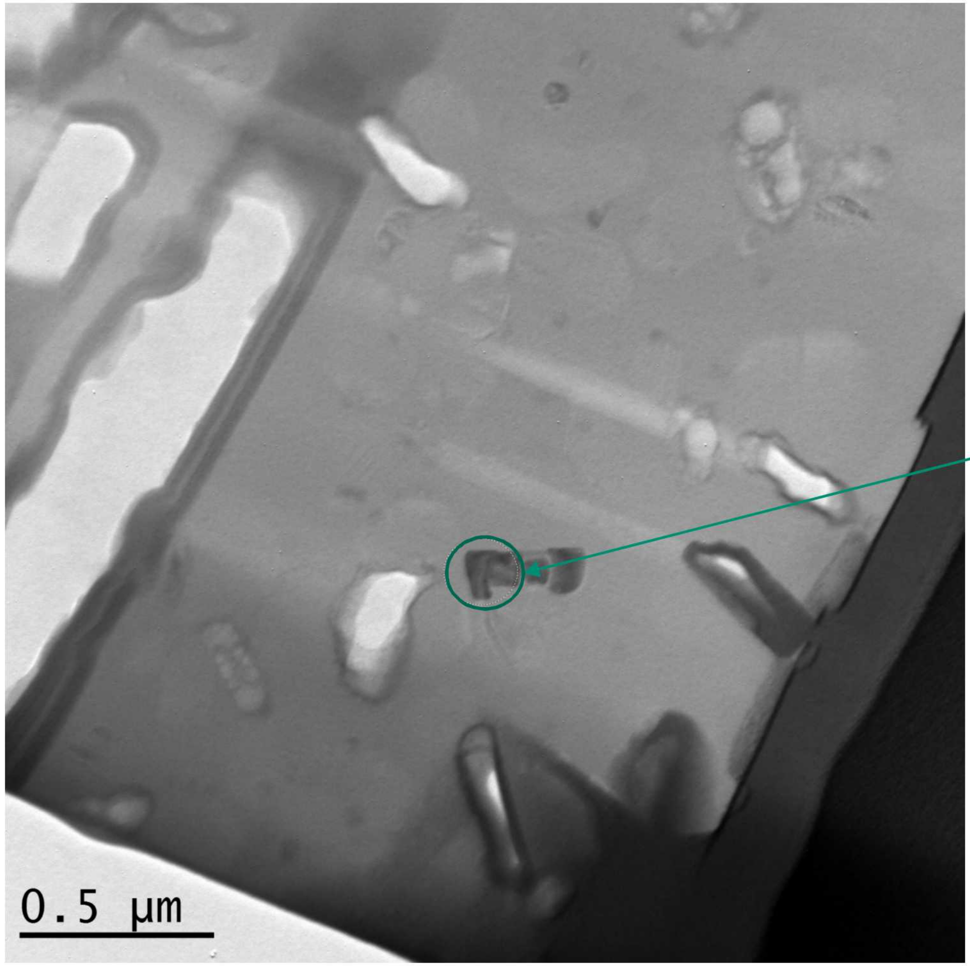
Selected-area diffraction pattern



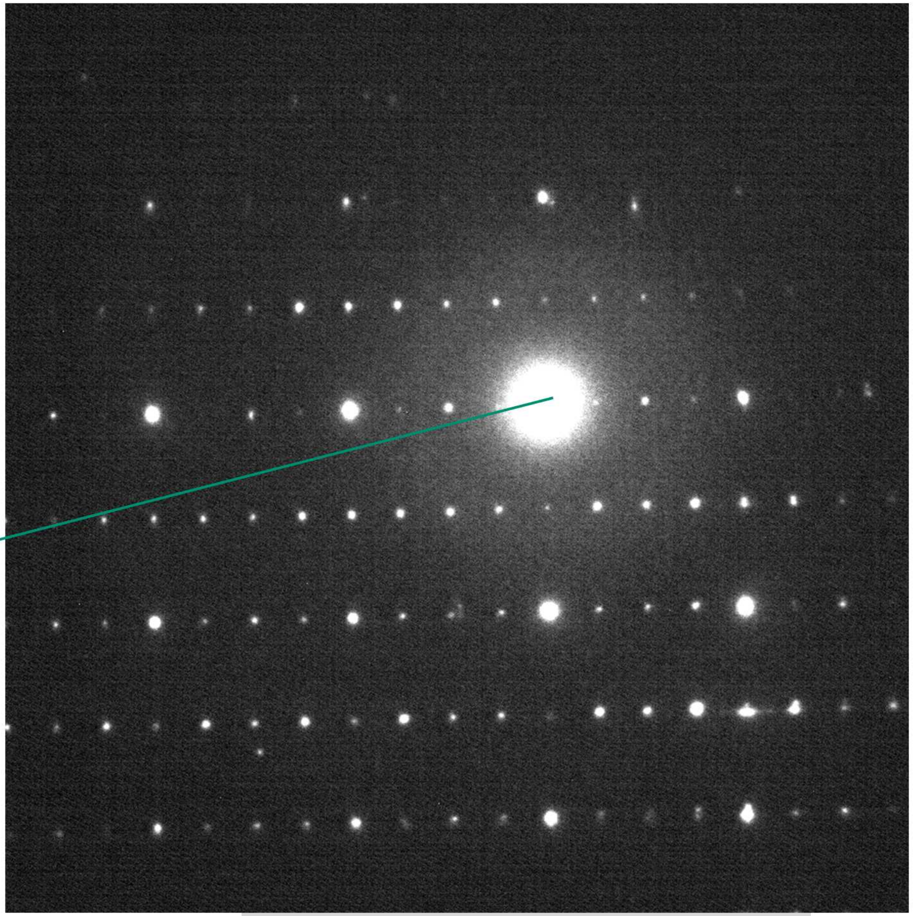
Diffraction simulation from SingleCrystal™

5 vol% HF etching, NL16, 40 sec, small crystal, quartz?

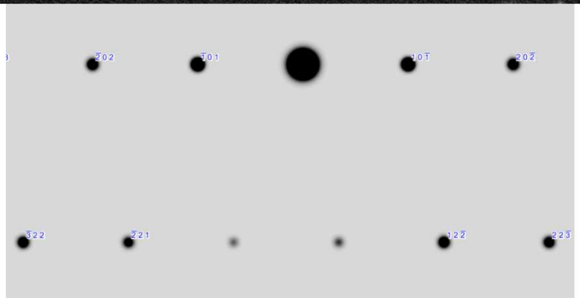
Bright-field TEM, size ~ sub μm



Larger d-spacings are inconsistent with most candidate SiO_2 polymorphs. The data are most consistent with Tridymite, monoclinic



Selected-area diffraction pattern



Diffraction simulation from SingleCrystal™

Summary

Etched glass-ceramics analyzed by multiple characterization methods

- Li_2SiO_3 was the 1st to be etched away by HF, in 10s sec
- Cristobalite crystals are at 1 – 10 μm
- Quartz present as clustered fine (<< 1 μm) spherical crystals
- Nucleation and growth mechanism to be investigated

Backup

Sandia Patented BPS Glass Chemistry

Oxide	wt%			mol%
	Min	Max	Target	
SiO_2	65	80	74.35	69.44
B_2O_3	0.5	7	1.20	0.97
Li_2O	8	16	12.70	23.85
Al_2O_3	2	8	3.80	2.09
K_2O	1	8	2.95	1.76
P_2O_5	1	5	3.15	0.62
ZnO	0	5	1.85	1.28

SiO_2, B_2O_3: Glass network former

Li_2O, Al_2O_3, K_2O: Glass network modifier

P_2O_5 → Li_3PO_4 nuclei for crystallization

ZnO → Corrosion resistance

Reaction	ΔG° (Kcal, 25 °C)	CTE (ppm/°C, 40 – 600 °C)
$Si + O_2 = SiO_2$, glass	-203.3	0.5
$Si + O_2 = SiO_2$, Quartz	-204.7	23.3
$Si + O_2 = SiO_2$, Cristobalite	-204.2	27.1
Li_2O (s) + SiO_2 (s) = Li_2SiO_3 (s)	-33.2	13 .0 (20-300 °C)
Li_2O (s) + $2SiO_2$ (s) = $Li_2Si_2O_5$ (s)	-33.6	11.0

Major high expansion phase in existing profile

Li_2SiO_3 ✓

Up to 46 mol% SiO_2 for crystallization

$Li_2Si_2O_5$ ✗

Up to 22 mol% SiO_2 for crystallization

CtM seals

Compression seal

Material	CTE (ppm/°C) (600°C → 30°C)
304L Stainless Steel	18.9
Schott S8061 Glass	10.2*
Alloy 52	10.2

* : reported value from 400°C to 30°C

Advantages
- Hermetic seals
- Easy fabrication processes
- Low cost Alloy 52 pin materials

Challenges
- Not for abnormal environment (500°C/500Psi)
  - Tg = 467 °C
  - Annealing point= = 480 °C
  - Softening point = = 677 °C
- Cracking/chipping due to high stresses
- Stress complication in multi-pin seals

Section Break Slide