3D Nano-CT

Zirconia Crystallization:
A View from Different Tools
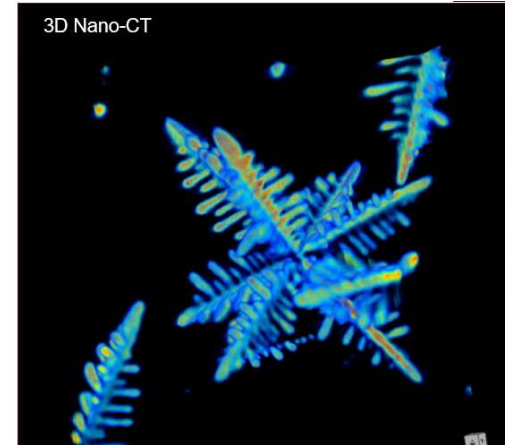
I. Peterson[1], Y. Shi[1], Y. Chen[2], K. An[2], J. Wright[1],
S. Halstead[1], B. Wheaton[1], G. Moore[1], J. Bussey[3], J. McCloy[3], M. Zhang[4]

[1] Corning Research and Development Corporation, Corning, New York, USA
[2] Neutron Scattering Division, Spallation Neutron Source, Oak Ridge National Laborator
   Oak Ridge, Tennessee, USA
[3] Washington State University, Pullman, Washington, USA
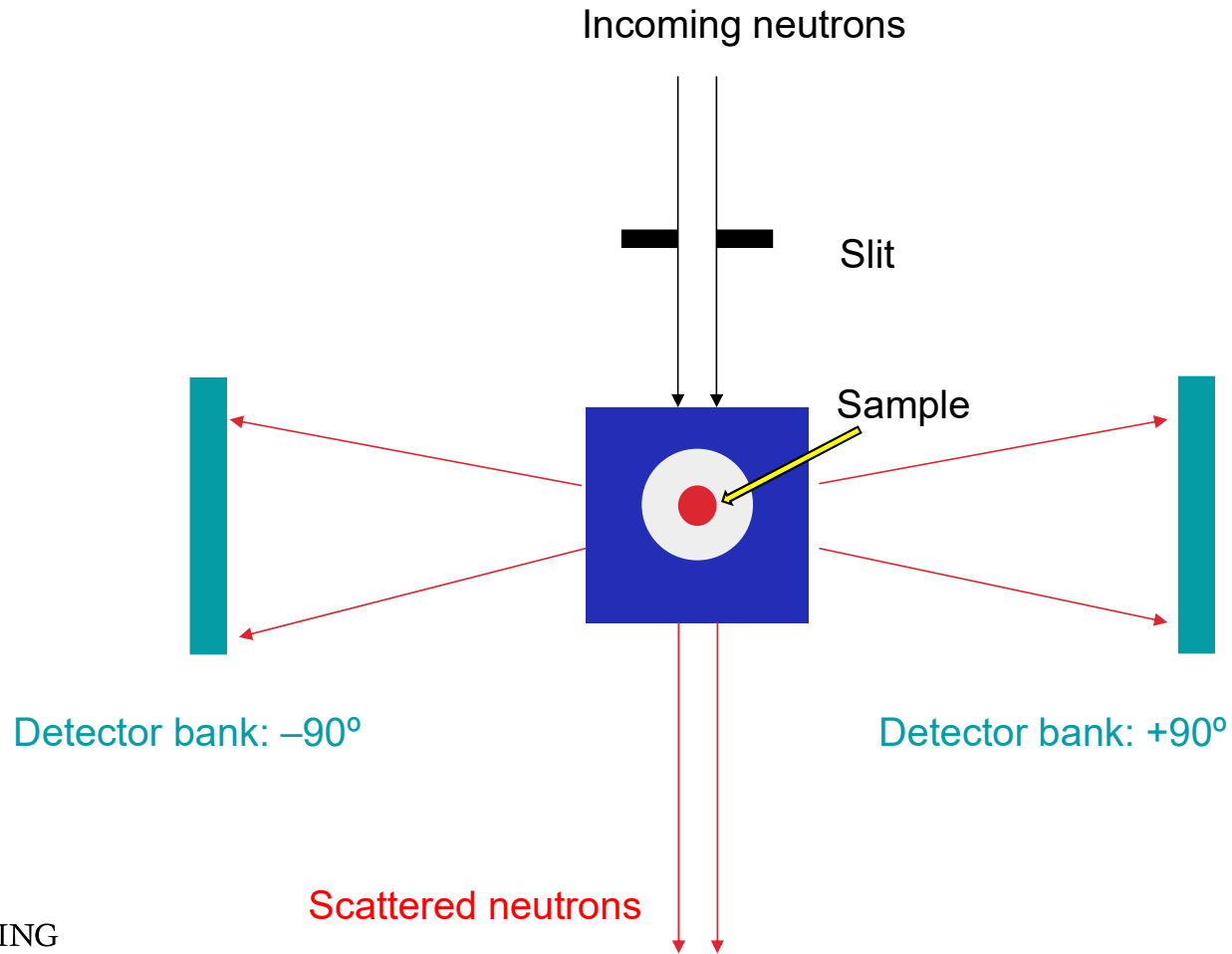[4] GlobalFoundries, Albany, New York, USA

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Crystallization can occur along a complex thermal path

Melting

Stirring

Forming

Temperature
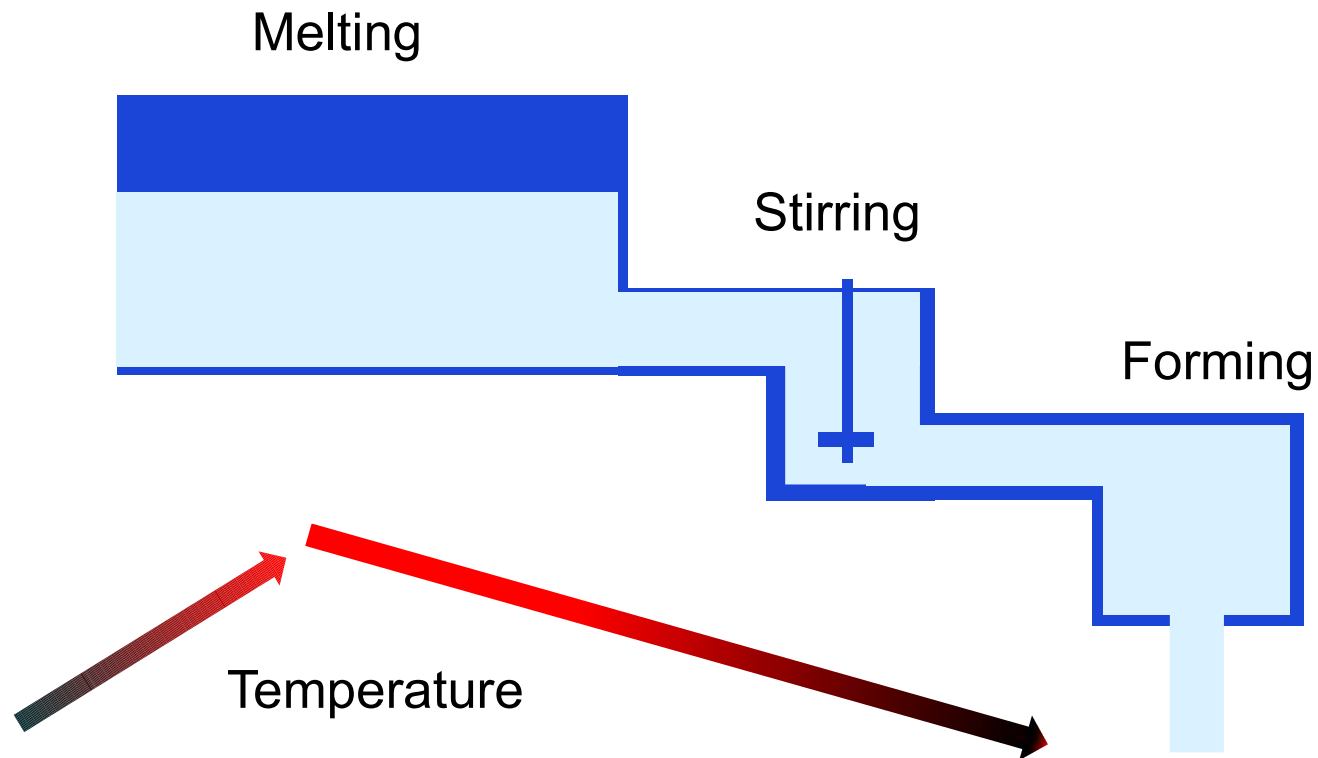
How can non-isothermal crystallization be measured and described?

Neutron diffraction used for in-situ crystallization experiments

Incoming neutrons

Slit

Sample

Detector bank: −90º

Detector bank: +90º

Scattered neutrons

TC

B2

B1

Incident neutrons

Crucible

Oak Ridge National Laboratory Spallation Neutron Source

VULCAN Beamline (BL-7)

– 30 Hz Chopper Speed

– 2.88 Å Bandwidth, 2.40 Å Center Wavelength

– 4mm Horizontal Beam Aperture, 10mm Vertical Beam Aperture

– 5mm Collimators – only neutrons from the sample are detected

– Controlled atmosphere furnace (1500°C max)

Experiments performed under General User Proposal

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# Advantages of in-situ neutron diffraction on Vulcan beamline

- Larger penetration depth of neutrons compared to x-rays
- Sample surface : volume ratio reduces surface effects
- Beam focused inside the sample to measure bulk crystallization
- Much faster signal detection – better time resolution
- Larger beam size, moveable detection location
- Higher temperature capability

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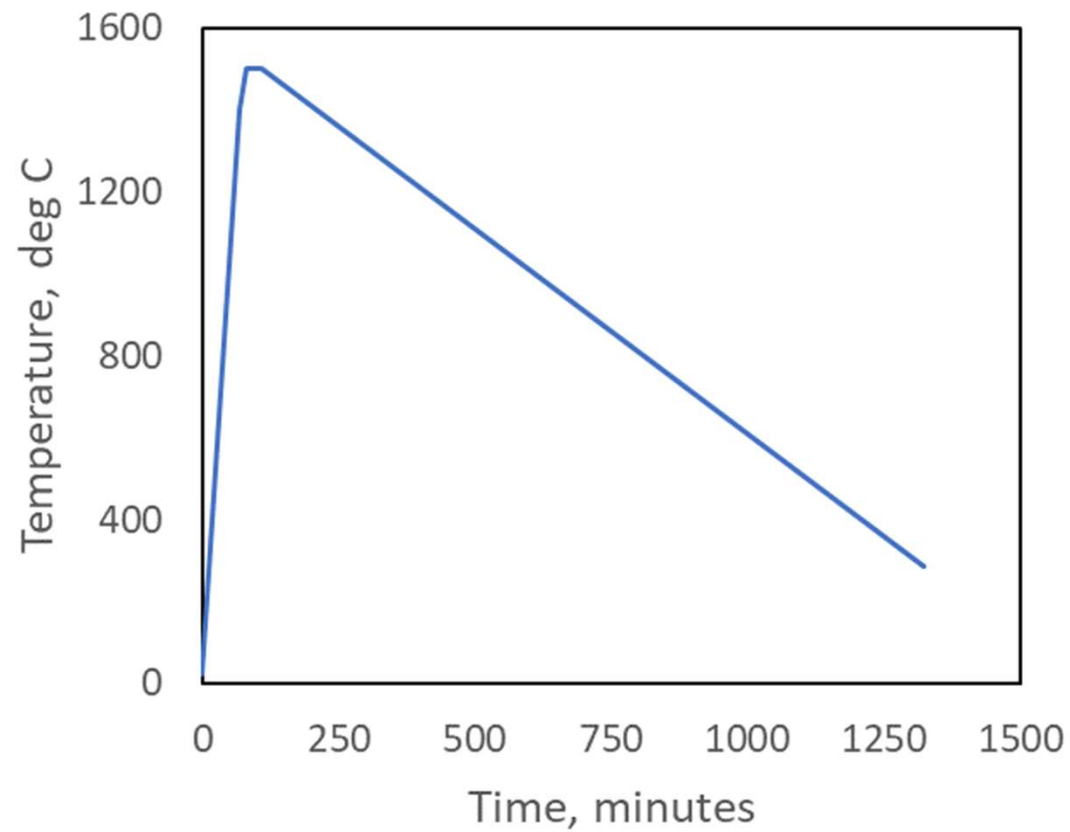# Zirconia-rich model glass designed for measurements

Composition

Oxide	Wt %
SiO_2	55.7
Al_2O_3	15.5
Na_2O	13.5
MgO	4.6
SnO_2	0.4
ZrO_2	10.0

Amorphous after melting at 1600°C
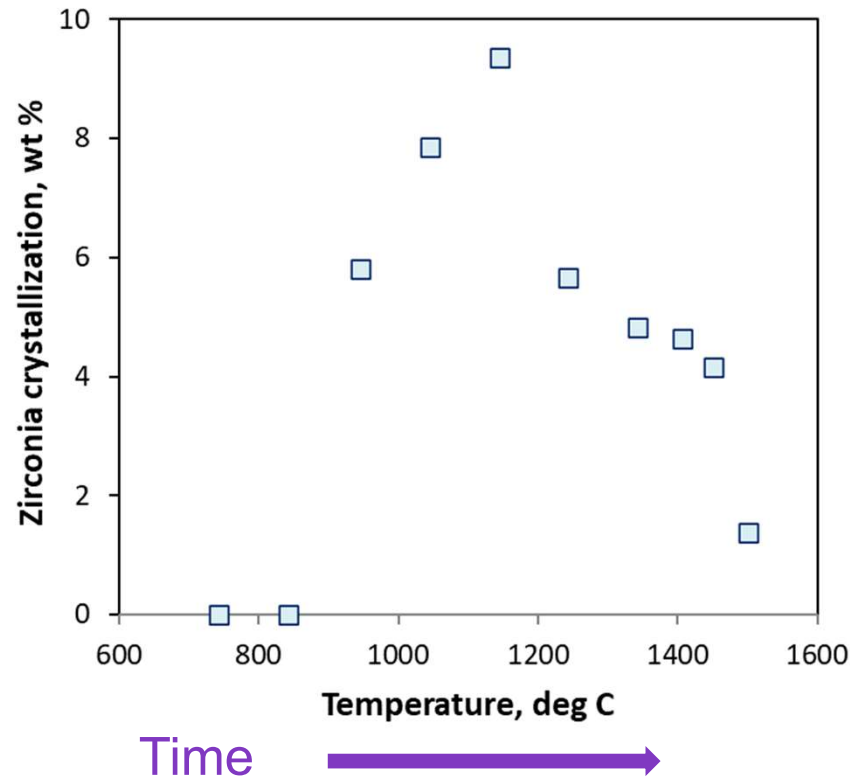

Two theta angle, degrees

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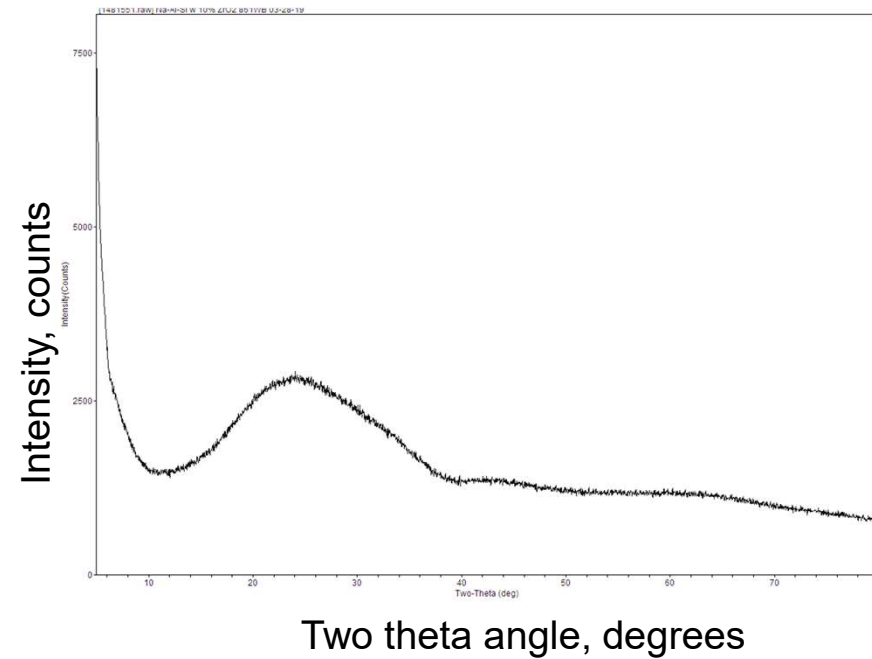
Neutron diffraction experiment

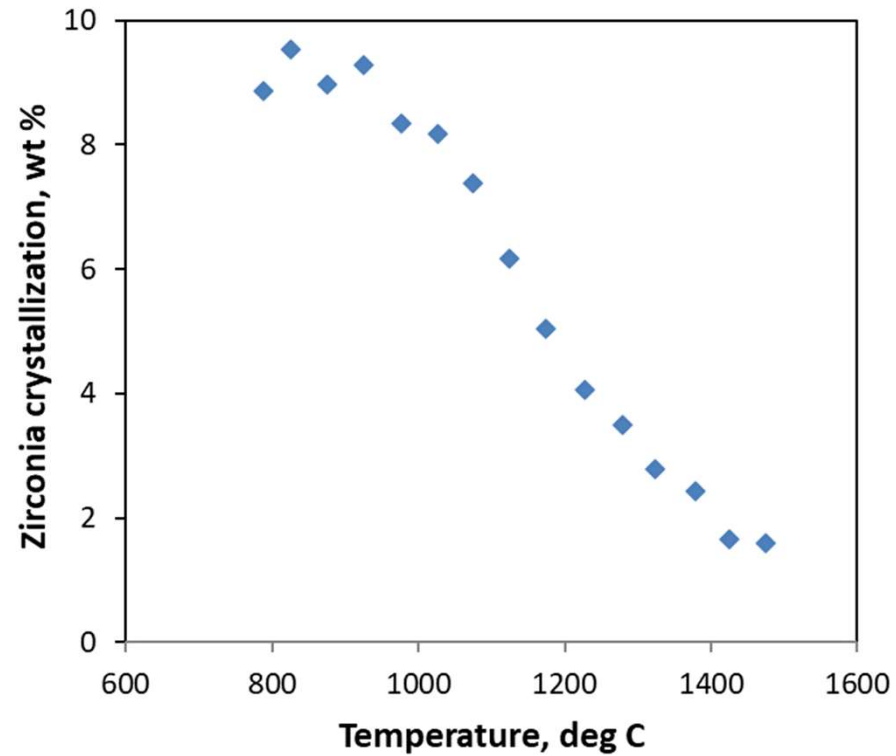- One 5-gram bar of glass was placed into a MgO crucible at room temperature

Zirconia crystallized fast and then dissolved during heating

Time ⟶

Crystallization kinetics were faster than the 20ºC/min heating rate
Dissolution removed 80% of the crystals before the cooling started

Zirconia crystallized during cooling at 1ºC/min

Can Johnson-Mehl-Avrami-Kolmogorov equation be used under non-isothermal conditions?

$$\frac{dx}{dt} = A(1-x)^n exp\left(\frac{-B}{T}\right)$$

$$x_i = \frac{Amount\ of\ species\ i\ at\ time\ t}{Maximum\ amount\ of\ species\ i}$$

t = time

A = reaction constant

n = reaction order

B or Q/R = activation energy, in units of K

T = temperature, K

D.A. Pierce et al, Thermal Analysis of Waste Glass Batches: Effect of Batch Makeup on Gas-Evolving Reactions in Thermal Analysis of Micro-,Nano- and Non-Crystalline Materials, Hot Topics in Thermal Analysis and Calorimetry 9 Springer Science and Business Media Dordreacht 2013 pp 429-439
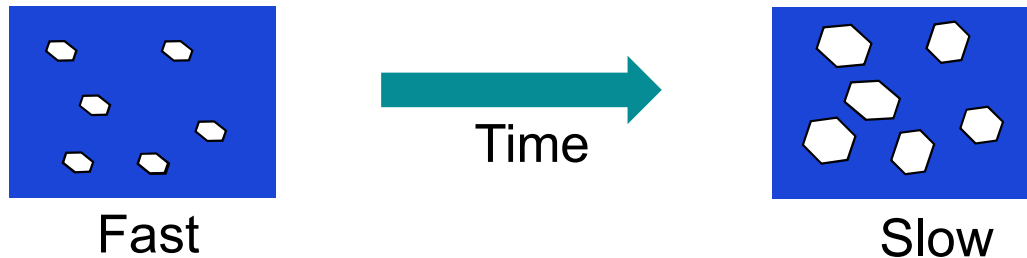
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Situations when JMAK equation can be used under non-isothermal conditions

1. Nucleation rate is proportional to growth rate - unlikely

OR

2. Nucleation occurs very early in the crystallization sequence and then its rate drops to near zero

   Site saturation

Fast → Time → Slow

M. Weinberg and E. Zanotto, Calculation of the Volume Fraction Crystallised in Non-isothermal Transformations, Physics and Chemistry of Glasses 30 [3] (1989)
D. Henderson , Thermal Analysis of Non-Isothermal Crystallization Kinetics in Glass-Forming Liquids, J. Non-Cryst. Solids 30 (1979) 310-315
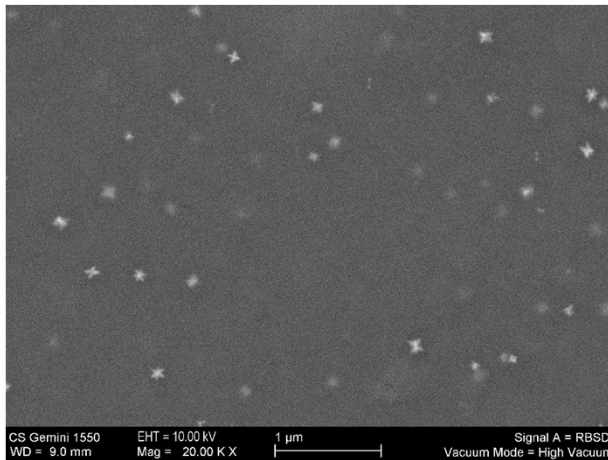J.Cahn, Transformation Kinetics During Continuous Cooling, Acta Met. 4(1956) 572-575

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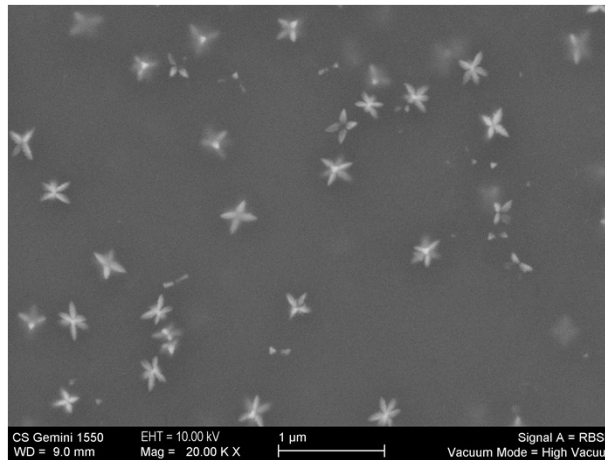# Does site saturation occur in this system?
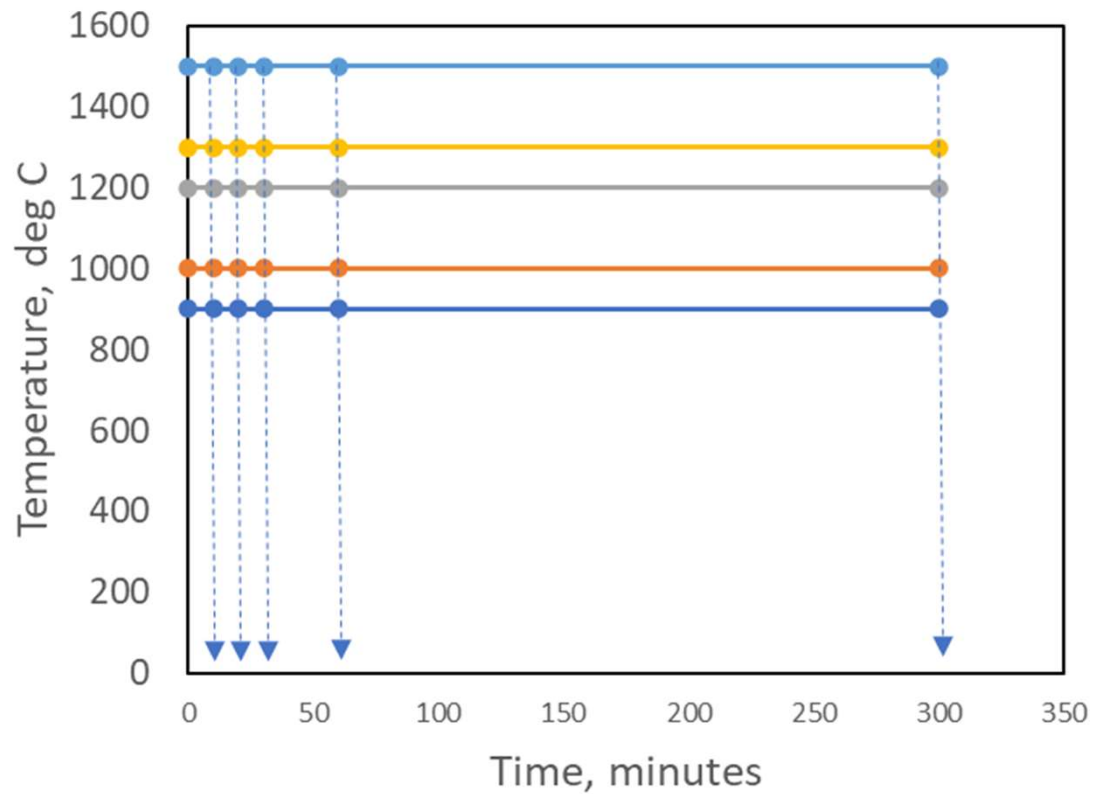
Isothermal heat treatments followed by microstructure examination
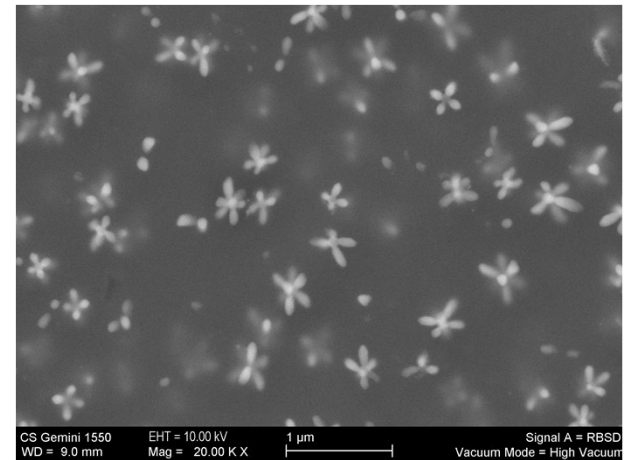
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Microstructure evolution during isothermal experiments

Heat treatment at 900ºC
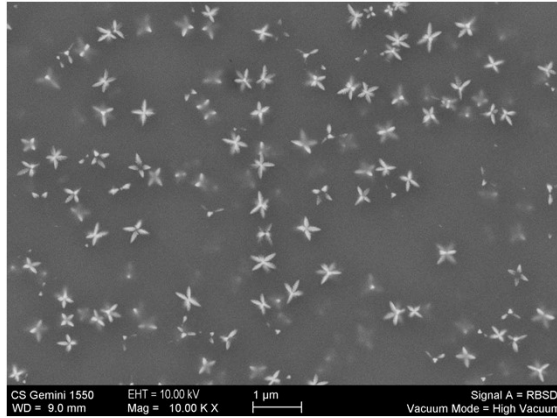

30 min
(first appearance)

60 min

300 min

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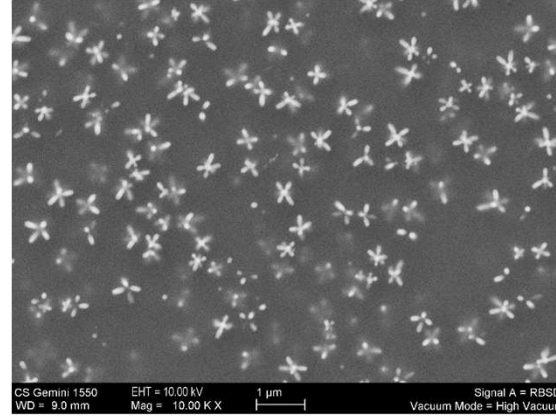
Burst of fast nucleation – followed by growth later
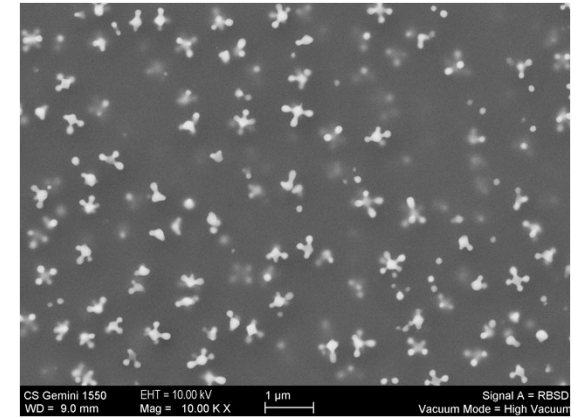
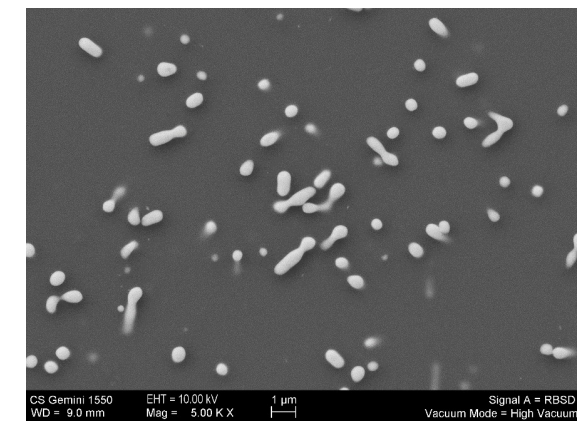# Fast nucleation followed by slower growth and coarsening
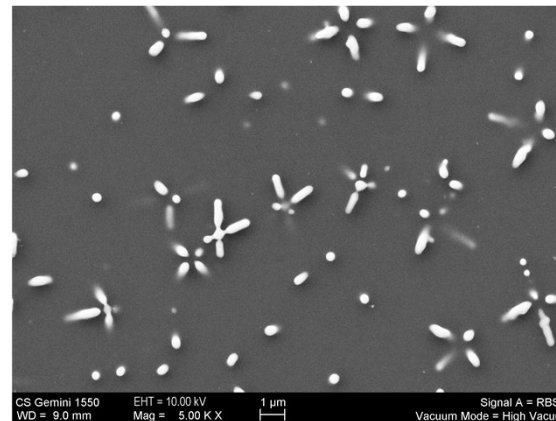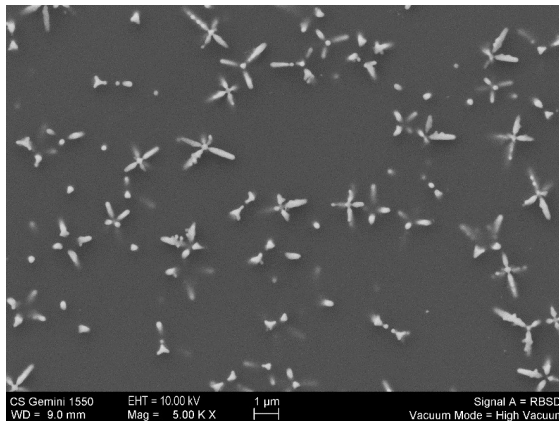

1000ºC

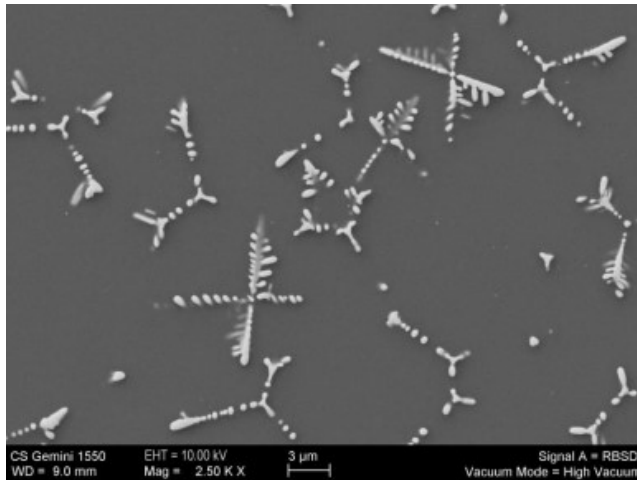10 min   60 min   300 min

1200ºC

A closer look at structure using nano-X-ray CT
Data and analysis from John Bussey and John McCloy at WSU IMR
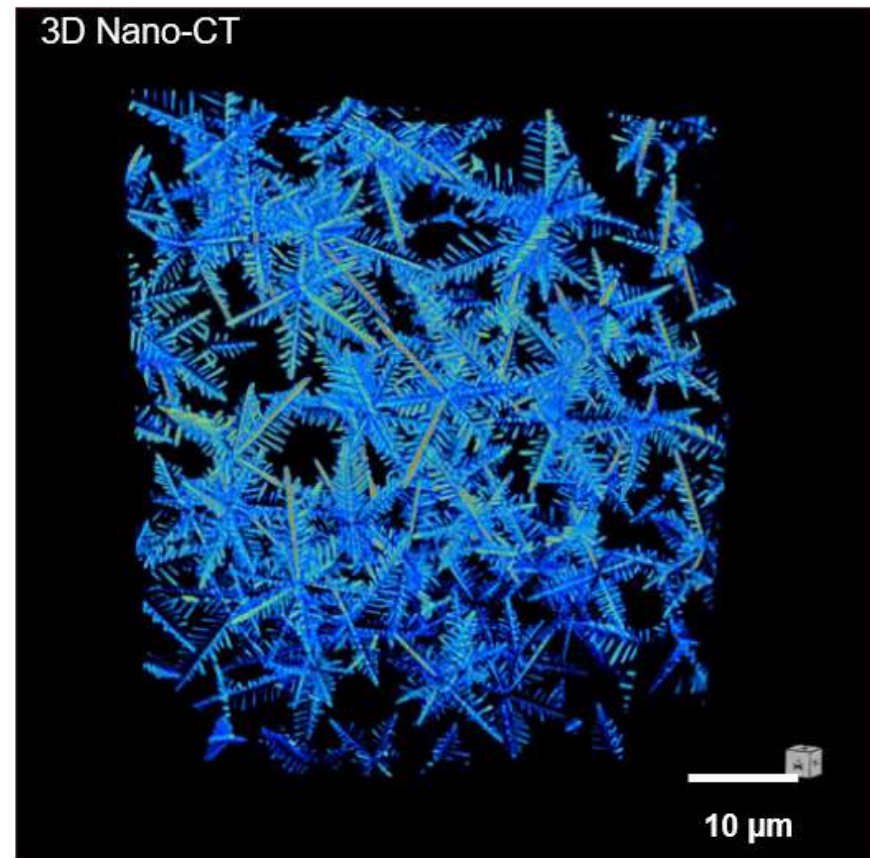
Zeiss Xradia 810 Ultra

- LFOV Mode

  150 nm resolution (64 nm voxels)

- 721 projections, 75s per projection

SEM image
Heat treatment at 1300ºC for 10 minutes

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Analysis of complex dendritic growth
Data and analysis from John Bussey, John McCloy at WSU IMR

- ~3 vol% phase fraction (significant segmentation error possible)

- N_v: ~ .0002 phases/μm^3

- 8 primary arms

  - Secondary dendrites – significant undercooling

  - 3 secondary dendrites arrayed around primary arms (120° between secondary dendrites)

  - Non 90° angles between primary stems

- Possible to export segmented 3D model of crystal for inputs into models

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3D Nano-CT
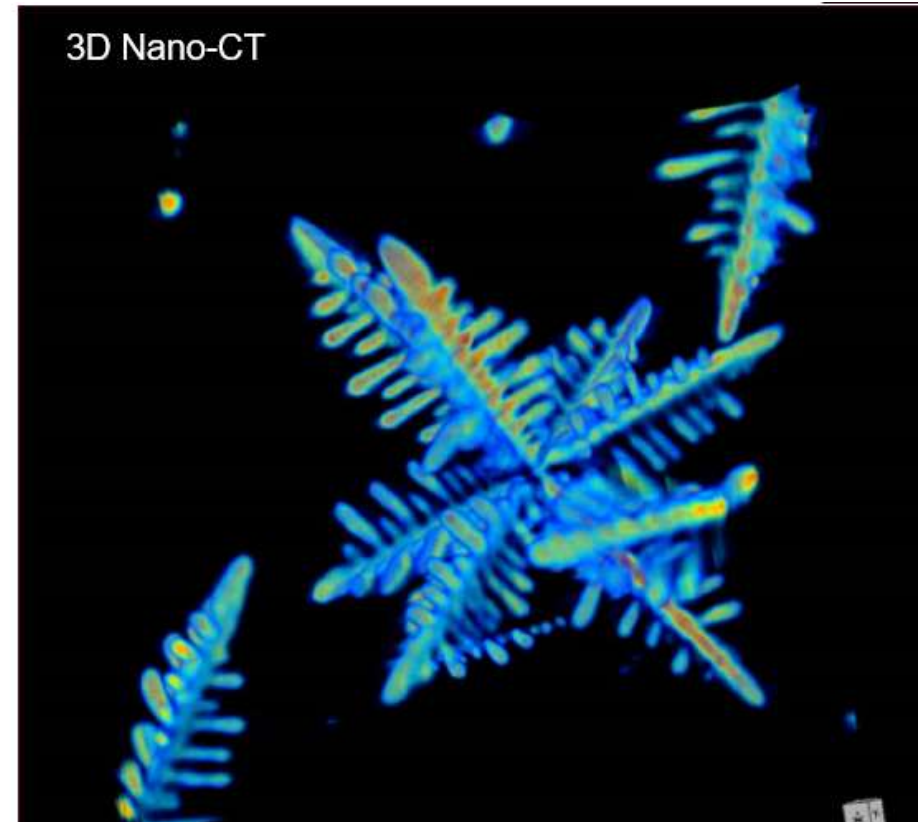
Heat treatment at 1300°C for 10 min

Literature modeling of crystal morphology with phase-field models

Calculation for a pure substance as a function of undercooling, μ_0:

$$\mu_0 = C_p(T_0 - T_m)/L < 0$$
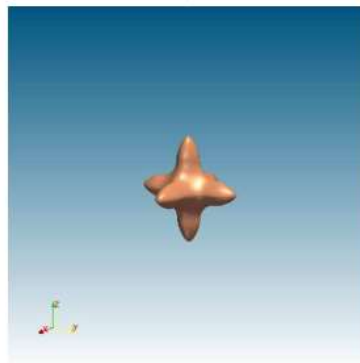
$\mu_0 = -0.2$ $\qquad\qquad$ $\mu_0 = -0.25$ $\qquad\qquad$ $\mu_0 = -0.3$

Growth morphology in literature looks similar to experimental results in this study

Cartalade A, Younsi A, Régnier É, Schuller S. Simulations of phase-field models for crystal growth and phase separation. Procedia Materials Science. (2014) Jan 1;7:72-8.

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How much does the activation energy change over the crystallization range?

Crystallization exotherm peak measured using differential scanning calorimetry (DSC) at five different heating rates

- 1, 5, 10, 20 and 50ºC/min
- Lowest heating rate did not give a distinct crystallization peak
- Used Kissinger's equation to see if slope changed

Worked with crystallization on heating to accommodate lab instruments

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Use of Kissinger Equation to fit an activation energy

How much does the activation energy for crystallization change with temperature in our system?

$$\frac{d\ln\left(\phi/T_p^2\right)}{d(1/T_p)} = -\frac{E_a}{R}$$
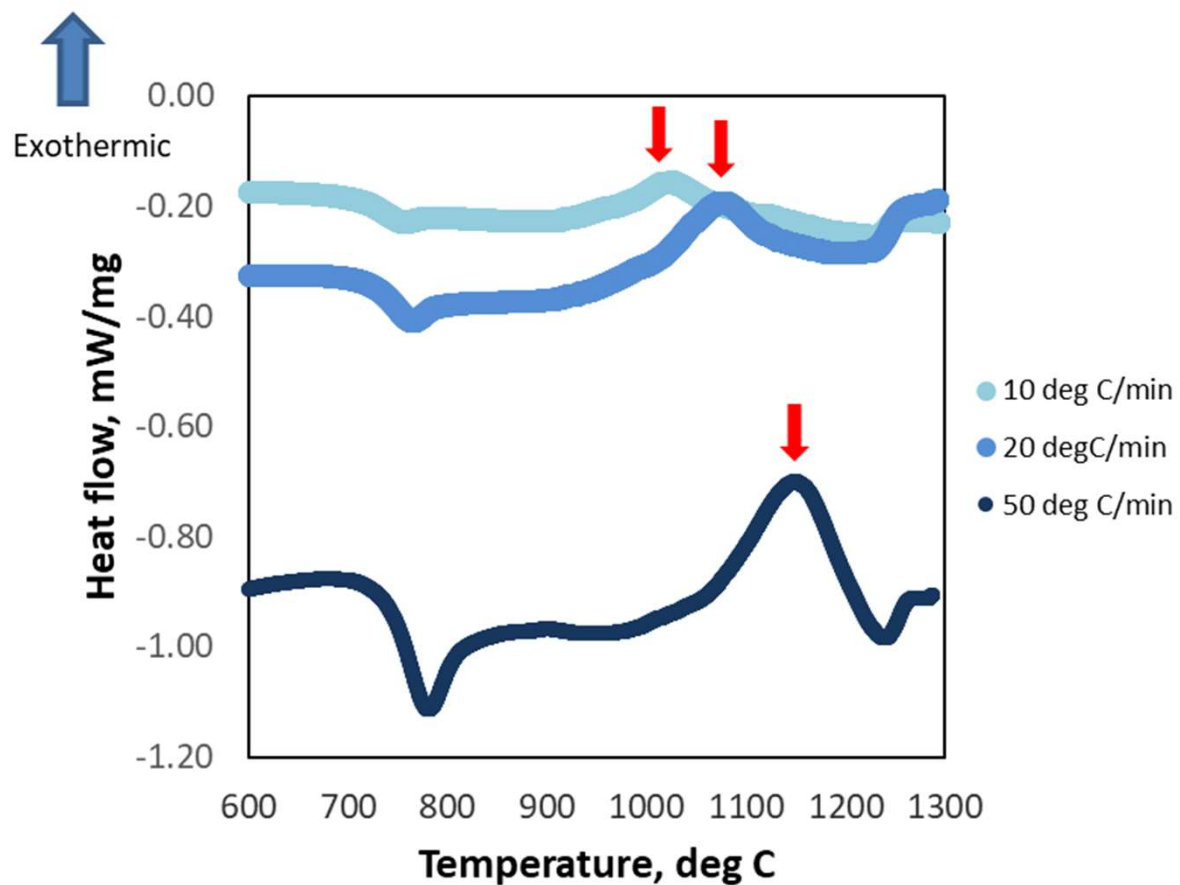
ϕ is the heating rate
T_p is the temperature of the exothermic crystallization peak
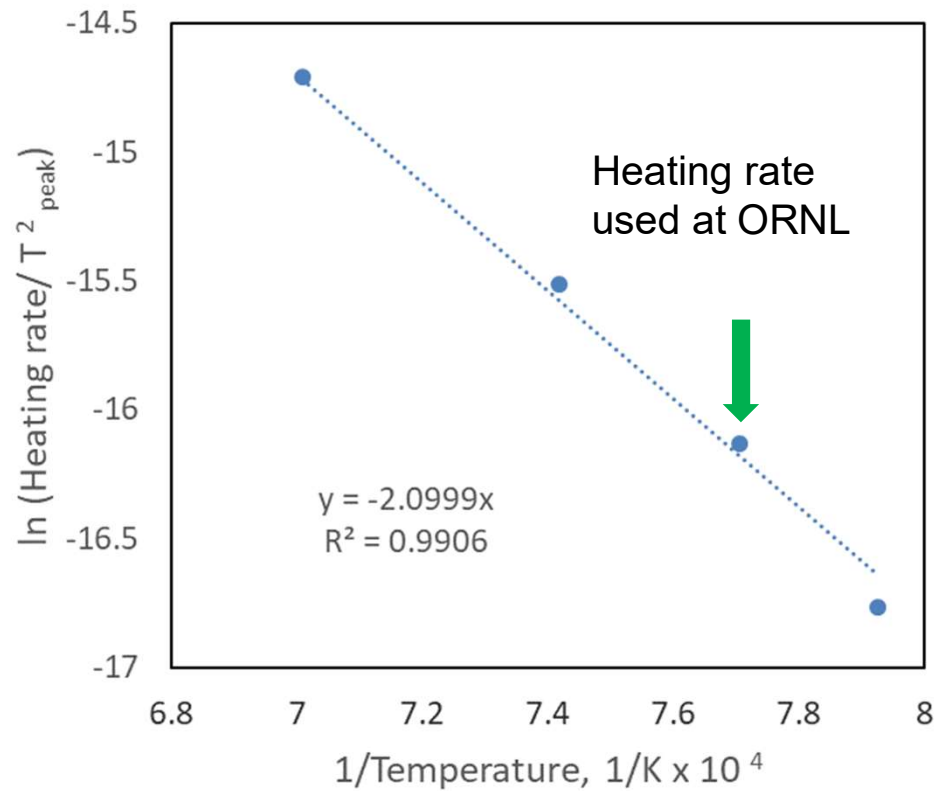E_a is the activation energy
R is a constant 8.314 J/(mol * deg K)

R. Wellen and E. Canedo , On the Kissinger Equation and the Estimate of Activation Energies for Non-isothermal Cold Crystallization of PET, Polymer Testing 40 (2014) 33-38

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Exotherm peak temperature increases with heating rate (DSC)

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Activation energy looks constant over the temperature range

Heating rate used at ORNL

$y = -2.0999x$
$R^2 = 0.9906$

x-axis: 1/Temperature, 1/K x 10^4

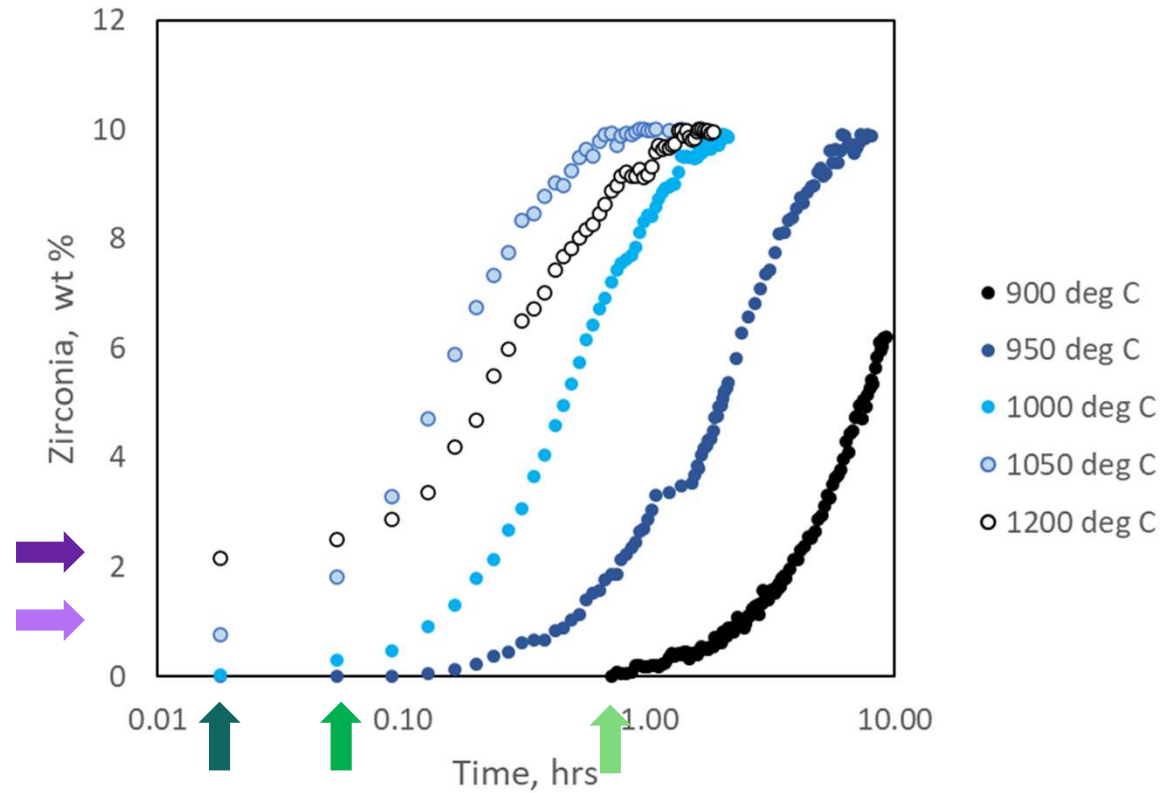y-axis: ln (Heating rate/ T^2 $_{peak}$)

Data has one activation energy in temperature range of interest

High temperature X-ray diffraction
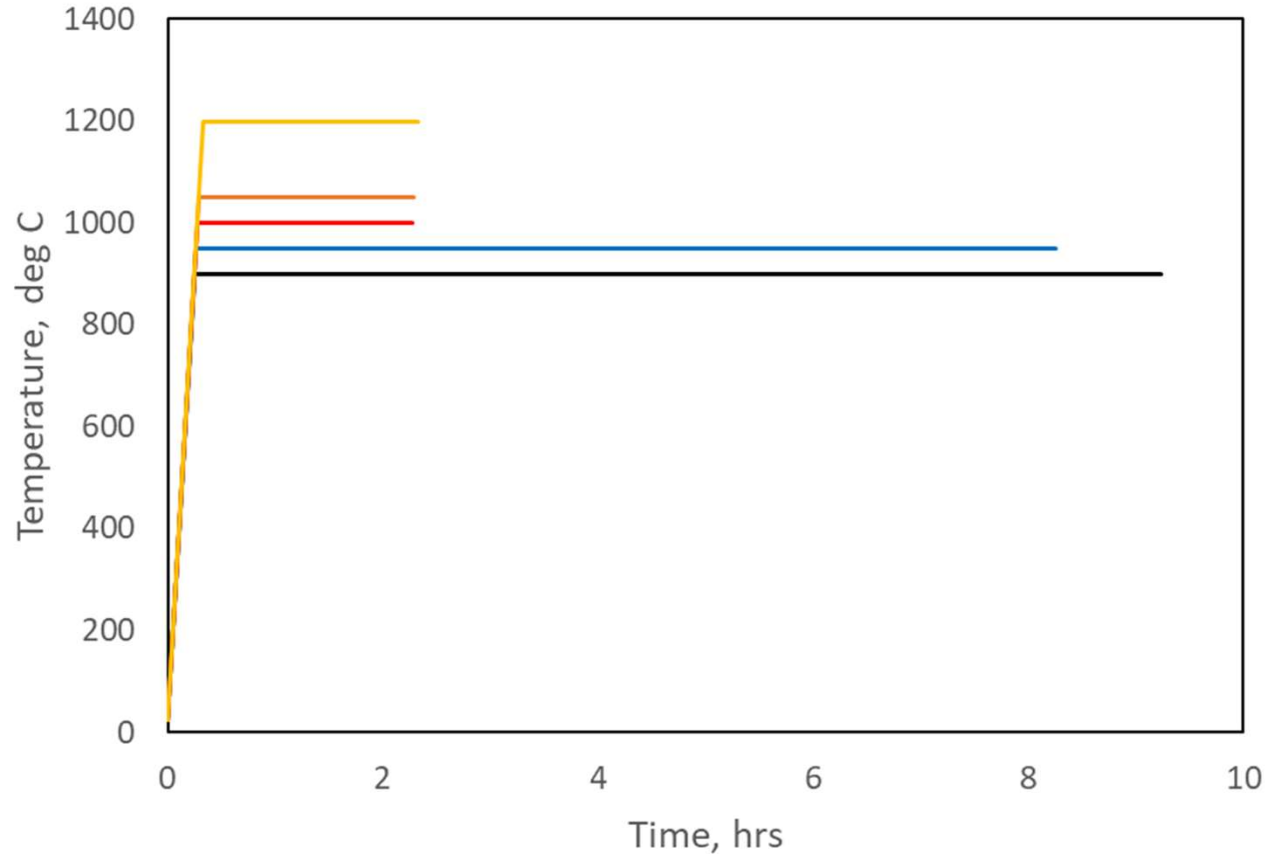
60°C/min heating rate to target temperature, followed by isothermal hold
Disks of glass were placed into the HTXRD crucible to minimize surface crystallization

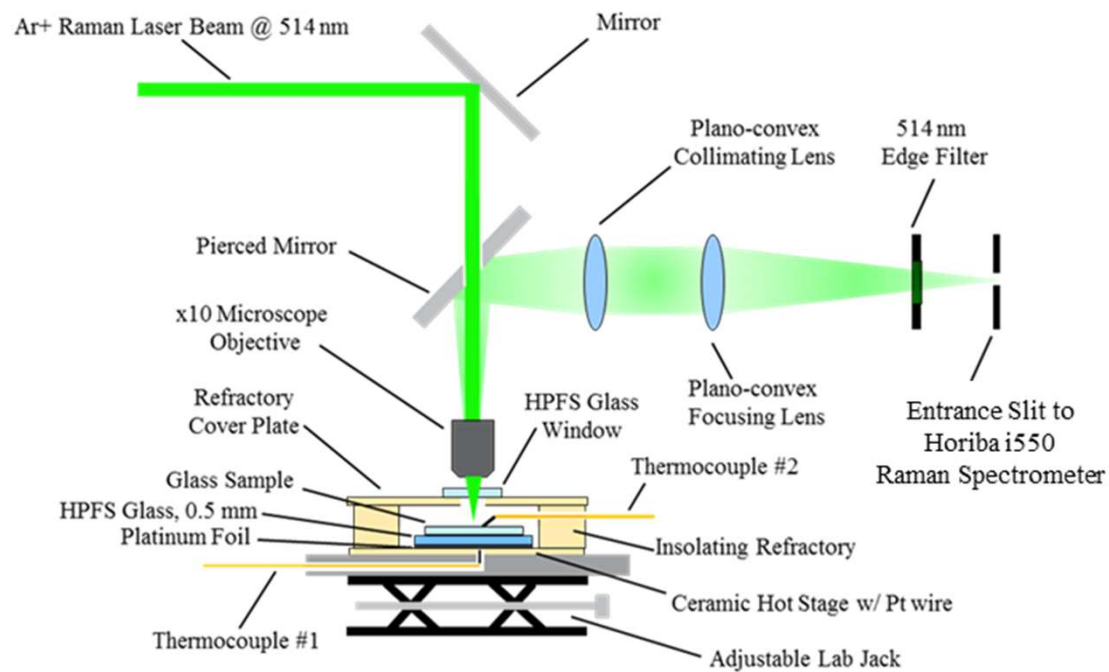# High temperature X-ray diffraction

Latency period at temperatures $\leq 1000ºC$
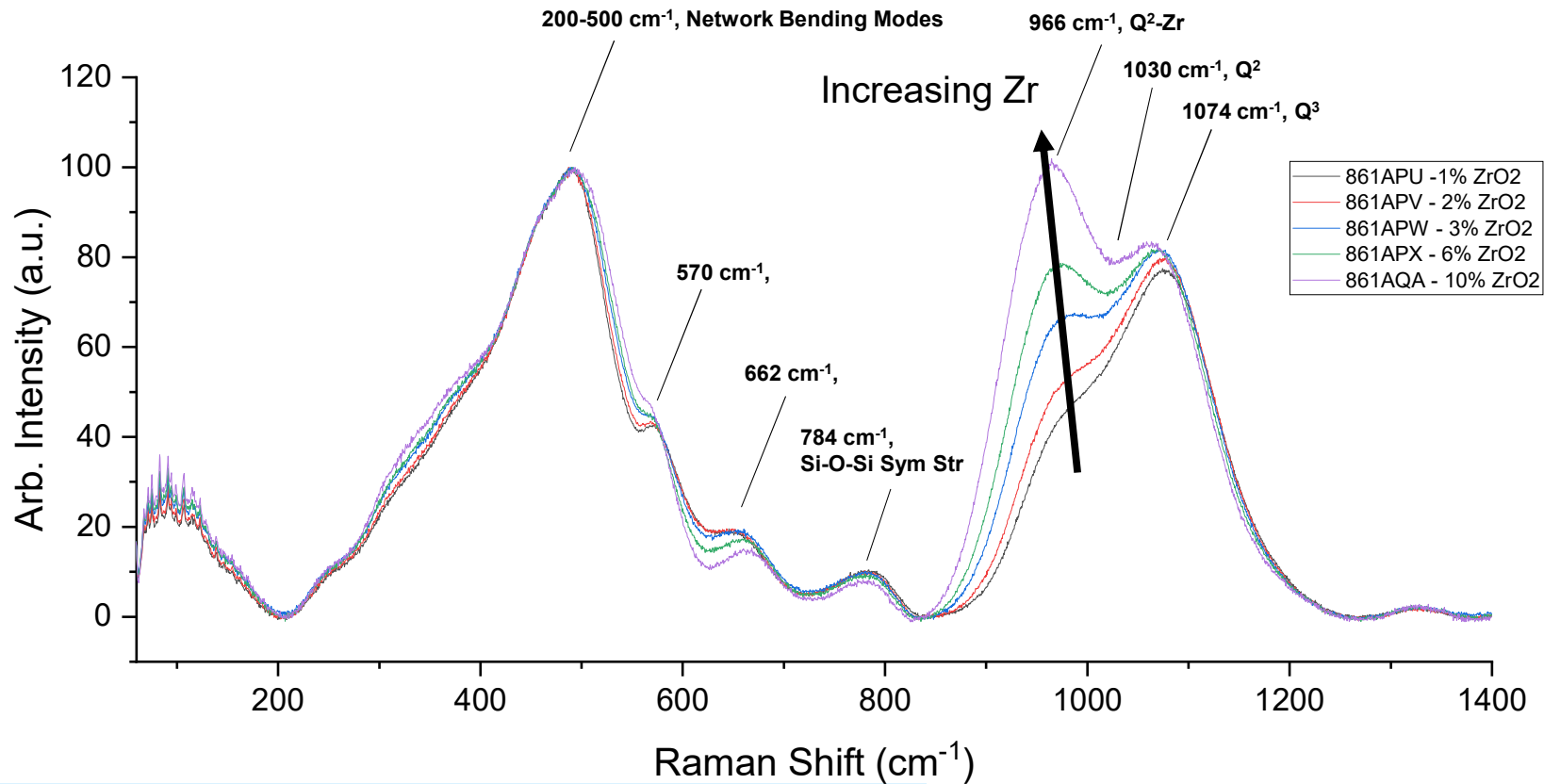Crystallization during heating ramp to temperatures $\geq 1050ºC$

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What happens in the glass before crystals form?

Raman spectrometer with heating capability

Raman spectra of glasses with increasing ZrO₂ concentration

Raman results from literature

Similar spectral shifts observed with increasing Zr content by Fischeux *et al* in high zirconia aluminosilicate glasses

400-600 cm^{-1}: bending of Si-O-Si bonds.

       500 cm^{-1} shift to higher wavenumbers

       Zr atoms deforming silicate network or to crystallization of ZrO_2-containing phases
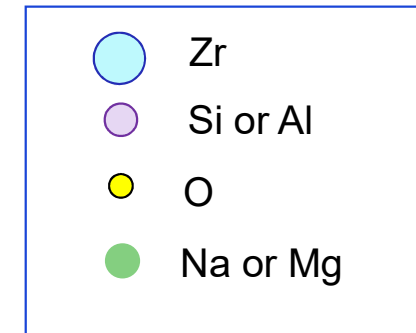
850-1200 cm^{-1}: stretching modes of Si-O bonds SiO_4 tetrahedra

       1080 cm^{-1} intensity decreases while 980 cm^{-1} increased

       1080 cm^{-1} characteristic vibration of Q^3 species

       980 cm^{-1} attributed to Si-O-Zr Q^3 SiO_4 units associated with one ZrO_6 octahedron $Q^3(Zr)$

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Local environment of Zr

Legend:
- Zr
- Si or Al
- O
- Na or Mg
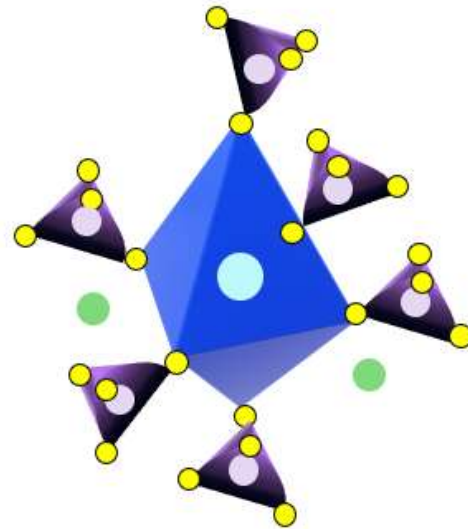
[ZrO$_6$] octahedra share corners with [(Si,Al)O$_4$] tetrahedra

Based on description in X. Lu et al, Effect of ZrO$_2$ on the structure and properties of soda-lime silicate glasses from molecular dynamics simulations, J Non-Cryst. Solids, 491 (2018)141-150

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High temperature Raman experiments on sample with 10 wt% ZrO$_2$
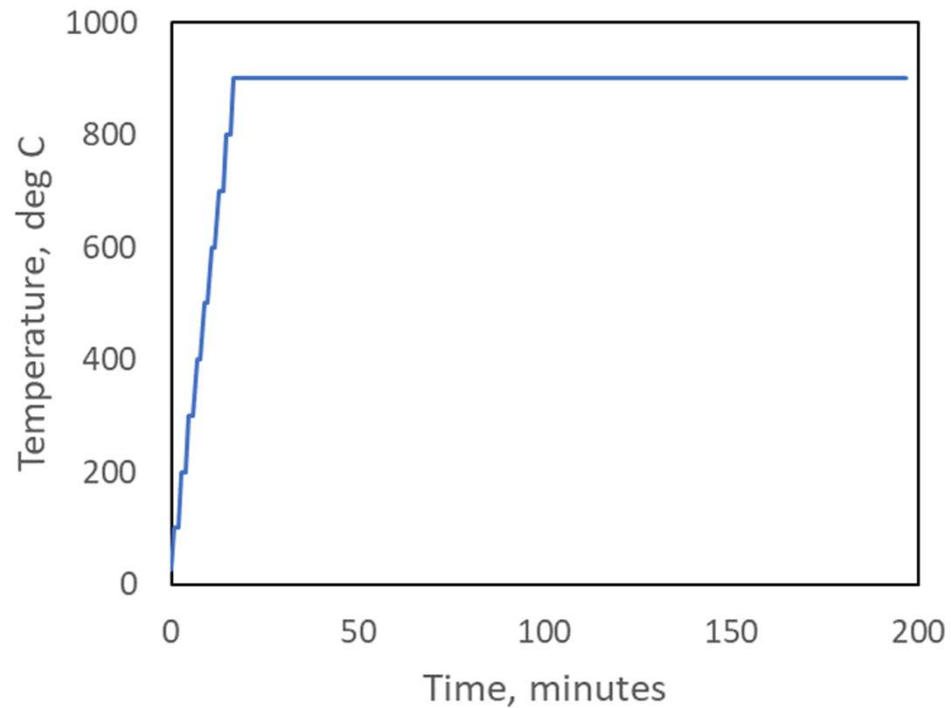
Heating rate 100°C/min - Spectrum taken every 100°C
Hold at 900°C for 3 hrs - Spectra taken continuously every minute

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High temperature Raman spectra during heating and isothermal hold

930cm^{-1}, NBO Q^2

Arb. Intensity (a.u.)

Spectrum #

Raman Shift (cm^{-1})
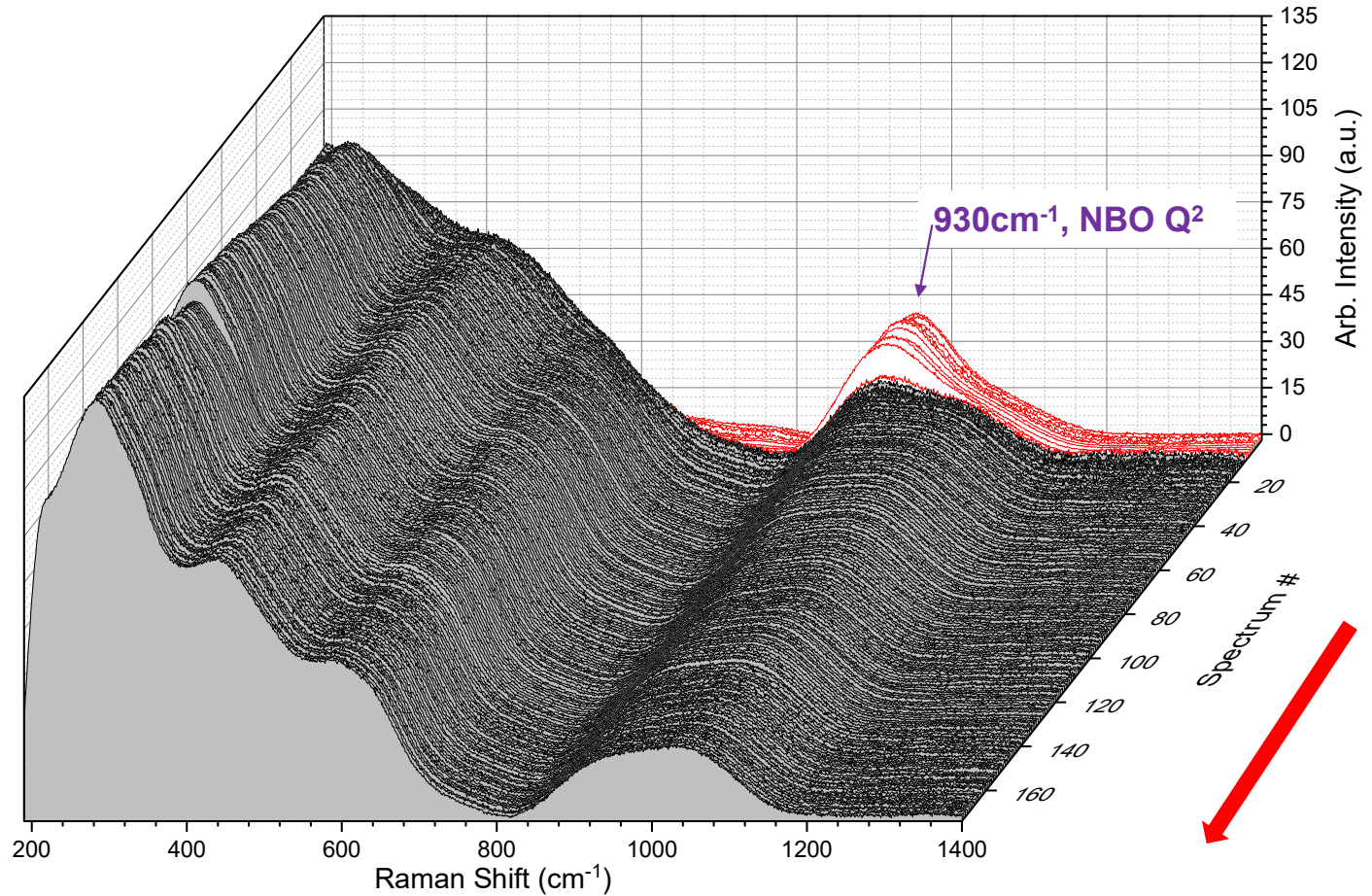
CORNING   Signal from Q^{2}Zr in glass structure drops dramatically and immediately at 900°C

Raman spectra show clustering and nucleation of ZrO$_2$
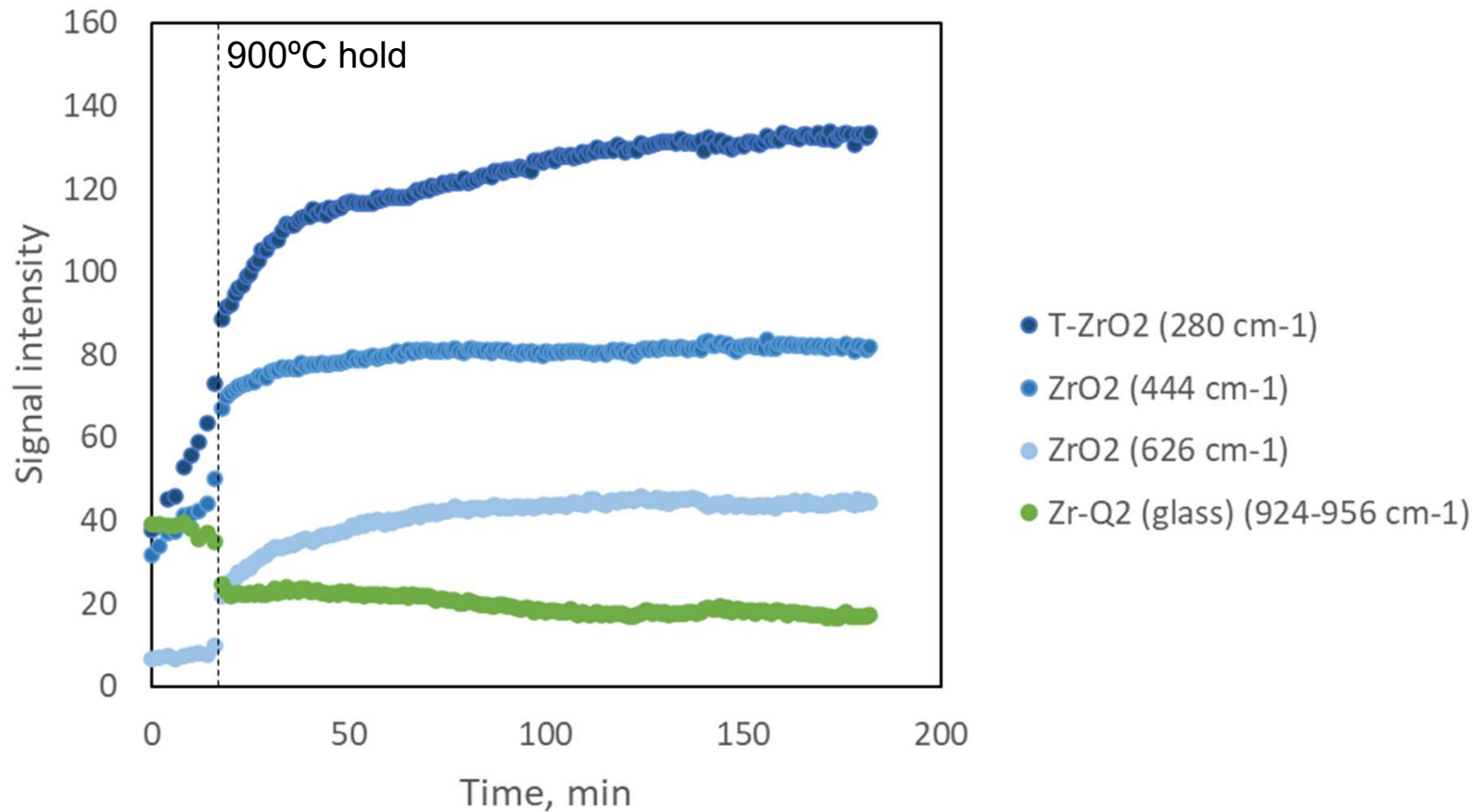
Raman shows nucleation of initial crystals long before they were detectable by diffraction

Raman Conclusions

- HT Raman spectroscopy (isothermal hold @ 900°C) was performed on Na_2O-MgO-Al_2O_3-SiO_2 glass with 10% ZrO_2

- A decrease in the 960 cm^{-1} band associated with an NBO Q^2-Zr (NBO associated with Zr) in glass (demonstrates the consumption of Zr to form ZrO_2 crystals)

- An increase in crystalline ZrO_2 bands @ 280, 318, 458, and 640 cm^{-1} (both tetragonal and cubic phases were detected)

- The cubic phase appears before the tetragonal as shown by the increase in the 318 cm^{-1} band before the increase in the 280 cm^{-1} band

- There is a shift in the high wavenumber region to lower wavenumbers with increasing temperature until 900°C where the ZrO_2 band intensity drops

    -This could be associated with either an expansion change (CTE) (change in bond angle and lengths) or it could be the first sign of nucleation (possibly effected by diffusion)

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Conclusions

- In-situ high temperature neutron diffraction gave detailed information on crystallization of zirconia during heating and cooling

- SEM and x-ray micro-CT showed rapid nucleation followed by slower growth in a complex dendritic morphology

- This morphology looked similar to the one predicted by literature phase field modeling

- Raman spectroscopy during the latency period at 900ºC revealed an immediate decrease in the Q^2 units associated with Zr and appearance of bond vibrations associated with crystalline zirconia structures – first cubic, then tetragonal

- DSC at a series of different heating rates showed a similar activation energy across the temperature range – probably reflecting the kinetics for growth

- This system meets the criteria for use of the JMAK kinetics equation because of site saturation

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