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Process Understanding And Control Using The Master Sintering Curve

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I. Linking the MSC to Other Sintering Models

The Foundation For The MSC Is The Combined-Stage Sintering Model

Johnson's Combined Stage Sintering Model:

$$-\frac{dL}{Ldt} = \frac{d\rho}{3\rho dt} = \frac{\gamma\Omega}{kT}\left(\frac{\delta D_b \Gamma_b}{G^4} + \frac{D_v \Gamma_v}{G^3}\right)$$

L = length, ρ = relative density (assume isotropic sintering)

D = diffusion coefficients

v and *b* = volume or boundary diffusion

δ = width of grain boundary

G = mean grain diameter

Γ = microstructural scaling parameter

γ = surface energy, Ω = atomic volume

k = Boltzmann constant

T = absolute temperature, - t = time

Assume one dominant diffusion mechanism:

$$\frac{d\rho}{3\rho dt} = \frac{\gamma\Omega(\Gamma(\rho))D_o}{kT(G(\rho))^n}\exp\left(-\frac{Q}{RT}\right)$$

Q = activation energy

J. Am. Ceram. Soc., 75 [5] 1129-35 (1992)

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The MSC Derives From The Combined-Stage Sintering Model

Rearrange and Integrate:

$$\int_0^t \frac{1}{T}\exp\left(-\frac{Q}{RT}\right)dt = \frac{k}{\gamma\Omega D_o}\int_{\rho_o}^{\rho}\frac{(G(\rho))^n}{3\rho\Gamma(\rho)}d\rho$$

$\theta(t,T(t))$

Depends on Q and the t-T sintering profile.

$\phi(\rho)$

Includes microstructural and materials properties.

$$\theta(t,T(t)) \equiv \phi(\rho) \equiv \rho(t,T)$$

The Master Sintering Curve (MSC) is a plot of $\rho(t,T)$ vs. $\theta(t,T(t))$

Assumptions:

- Isotropic sintering
- A single (or dominant) diffusion mechanism
- $G(\rho)$ and $\Gamma(\rho)$ are functions of density only, not the t-T profile
- MSC is unique for a given powder, and green microstructure & density

J. Am. Ceram. Soc., 79 [12] 3211-17 (1996)

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Activation Energy , Q, Is Determined From The Sintering Data

- From CSS Model assuming a single dominant diffusion mechanism:

$$-\frac{dL}{Ldt} = \frac{\gamma\Omega}{kT}\left(\frac{\Gamma D_o \exp[-Q/(RT)]}{G^n}\right)$$

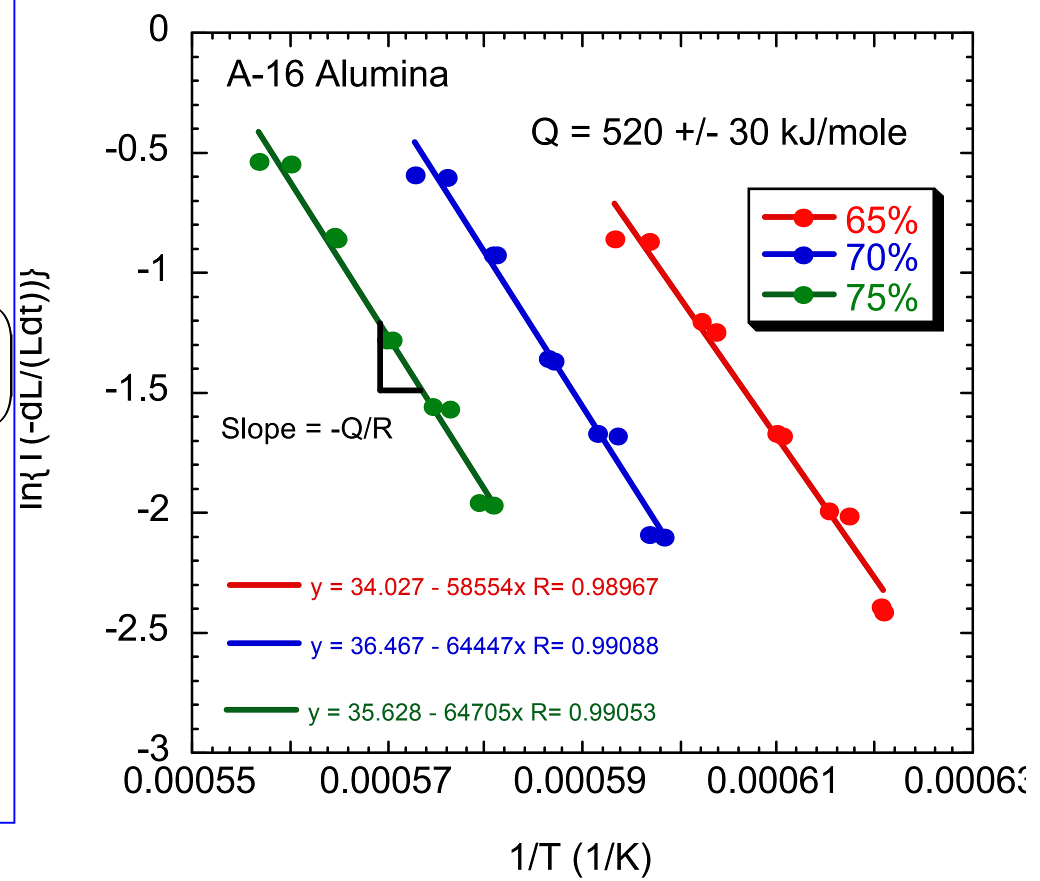
- Rearrange and take logarithms:

$$\ln\left(-T\frac{dL}{Ldt}\right) = -\frac{Q}{RT} + \ln\left(\frac{\gamma\Omega D_o}{k}\right) + \ln\left(\frac{\Gamma(\rho)}{G(\rho)^n}\right)$$

- At same relative density for different heating rates:

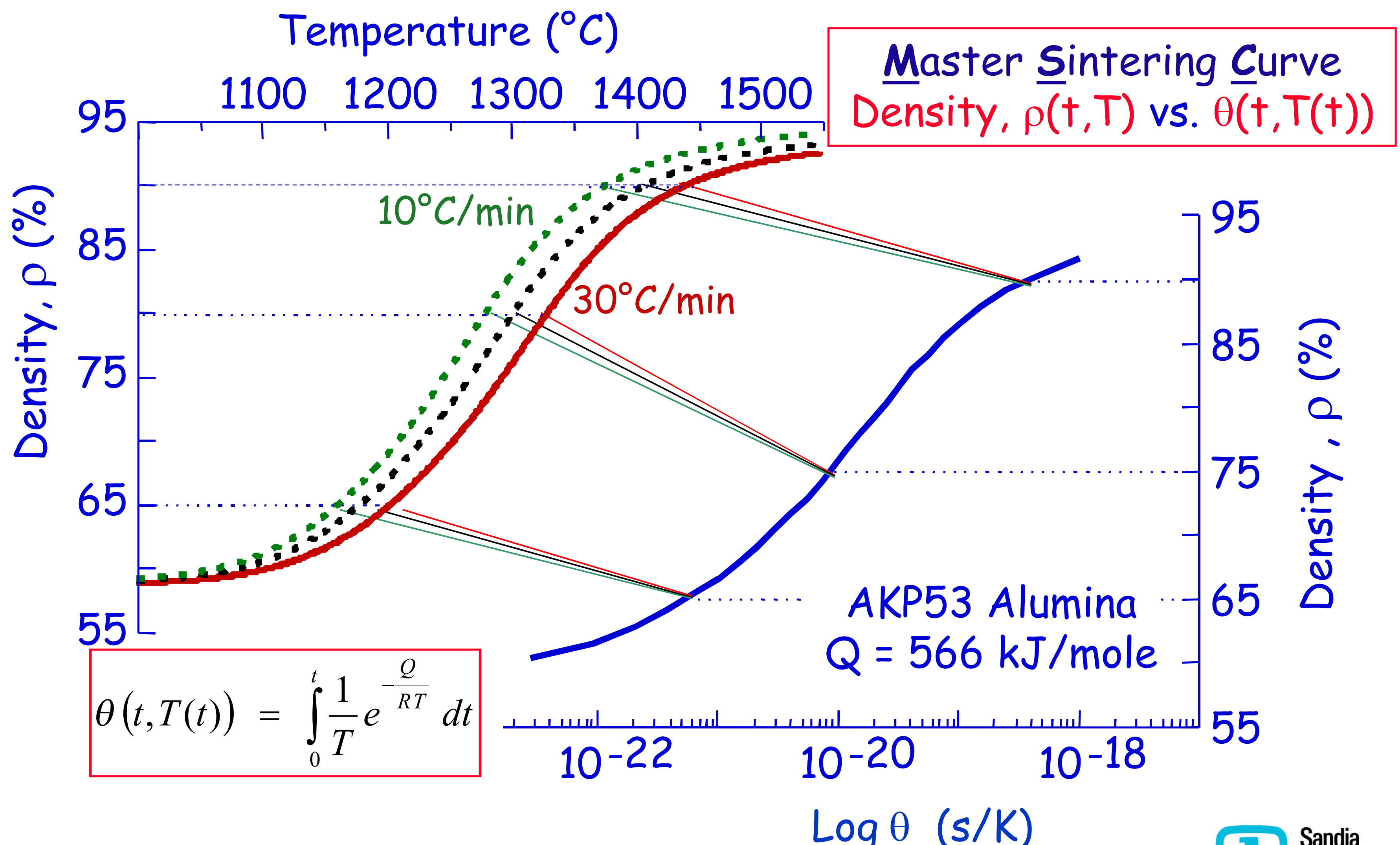
Plot: $\ln\left(-T\frac{dL}{Ldt}\right)$ vs. 1/T

Slope = -Q/R



J. Am. Ceram. Soc. 79 [12] 3199-210 (1996)

ρ(t,T) Sintering Data Collapse Onto A Single "Master" Sintering Curve (MSC)



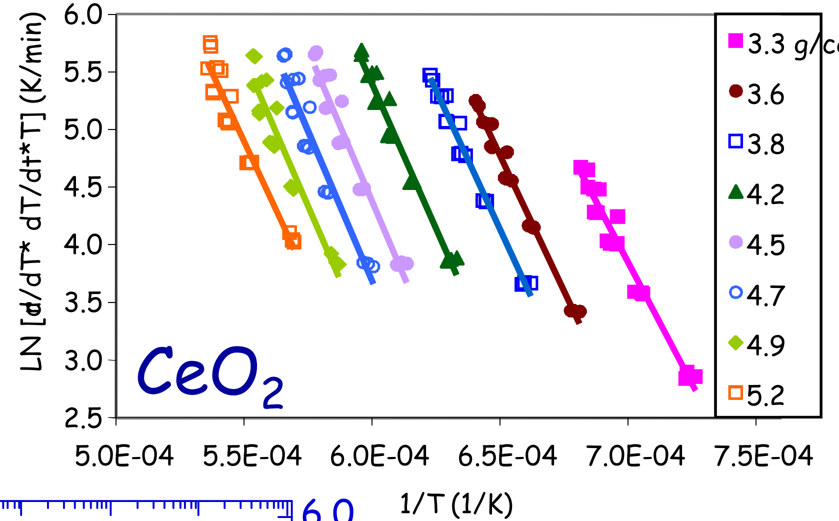
$$\theta\left(t,T(t)\right) = \int_0^t \frac{1}{T} e^{-\frac{Q}{RT}}\, dt$$

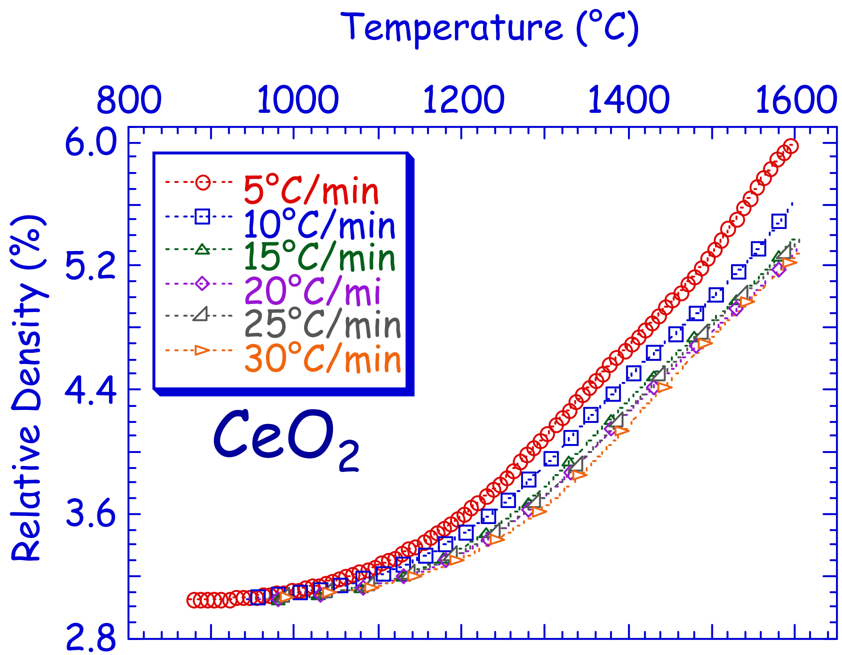
MSCs Have Been Constructed For Numerous Solid State Sintering Systems

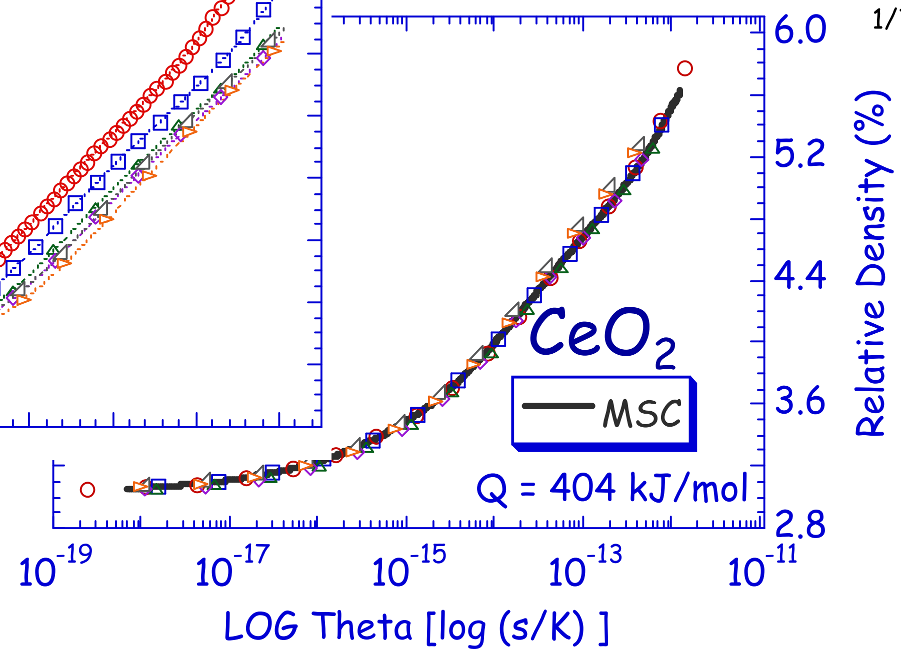
Systems Studied

A15, A16, AKP53, & OMS Al_2O_3

CeO_2, SrTiO3, ZnO, ZrO_2 CeO_2

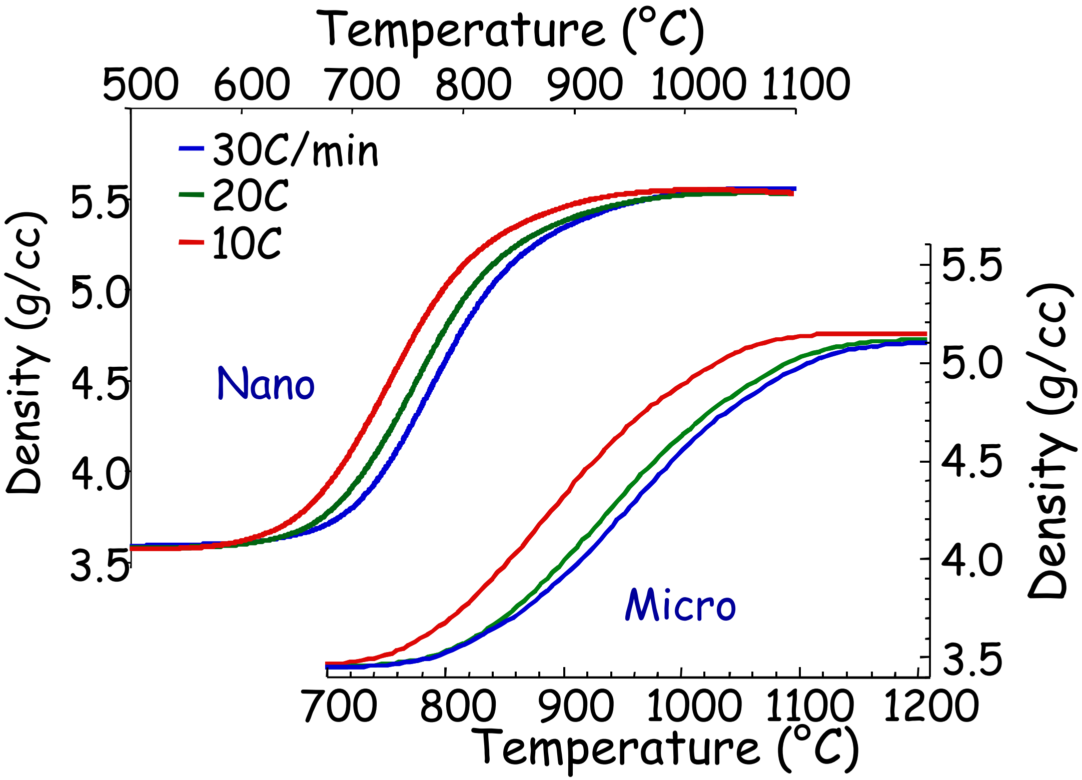


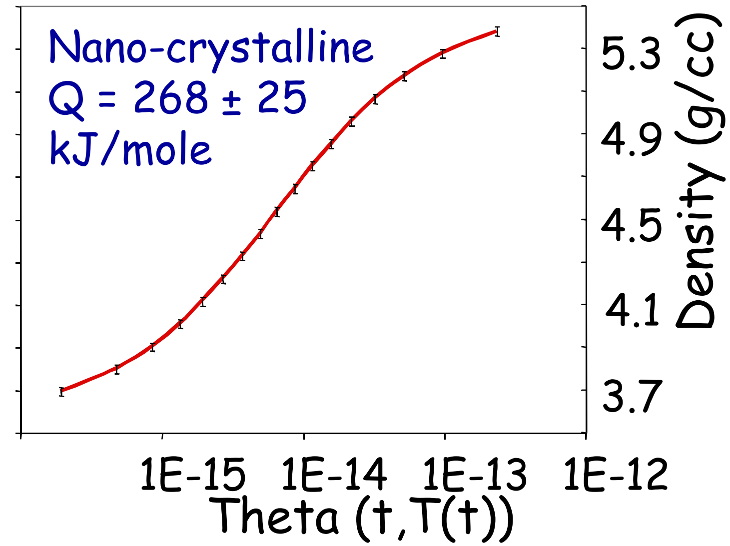


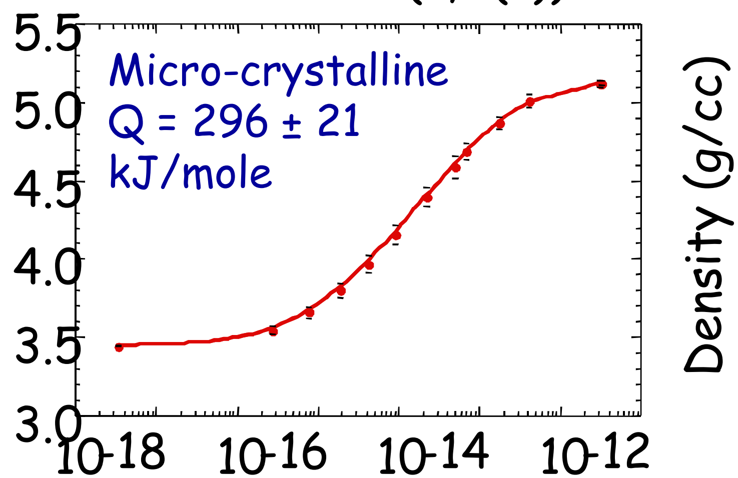


The MSC Concept Was Successfully Applied To Nano-Crystalline Ceramics

ZnO Sintering







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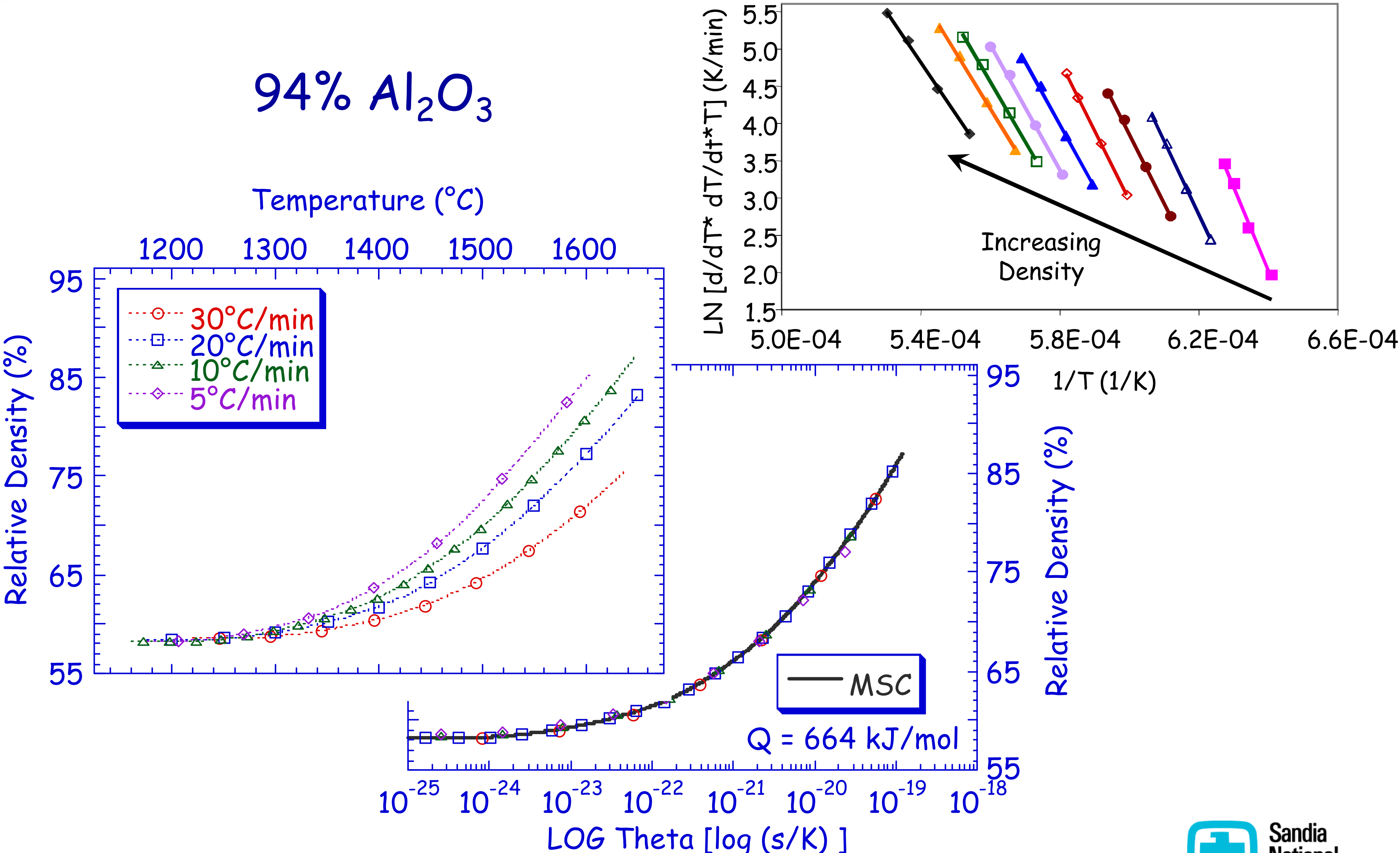
The MSC Concept Was Extended To Reactive Glass/Ceramic Sintering



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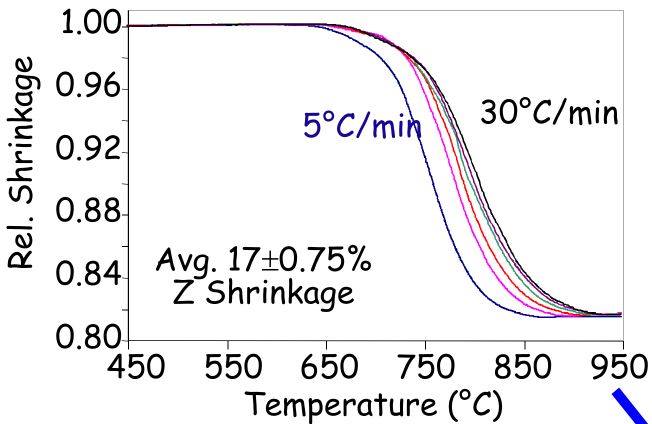
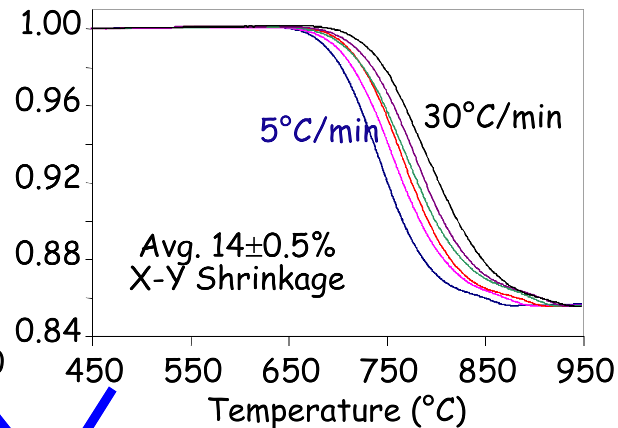
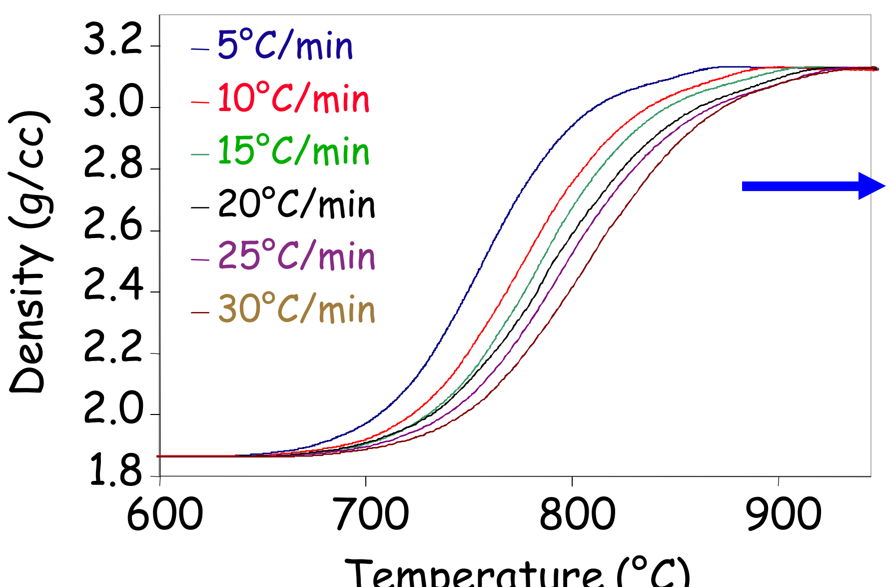
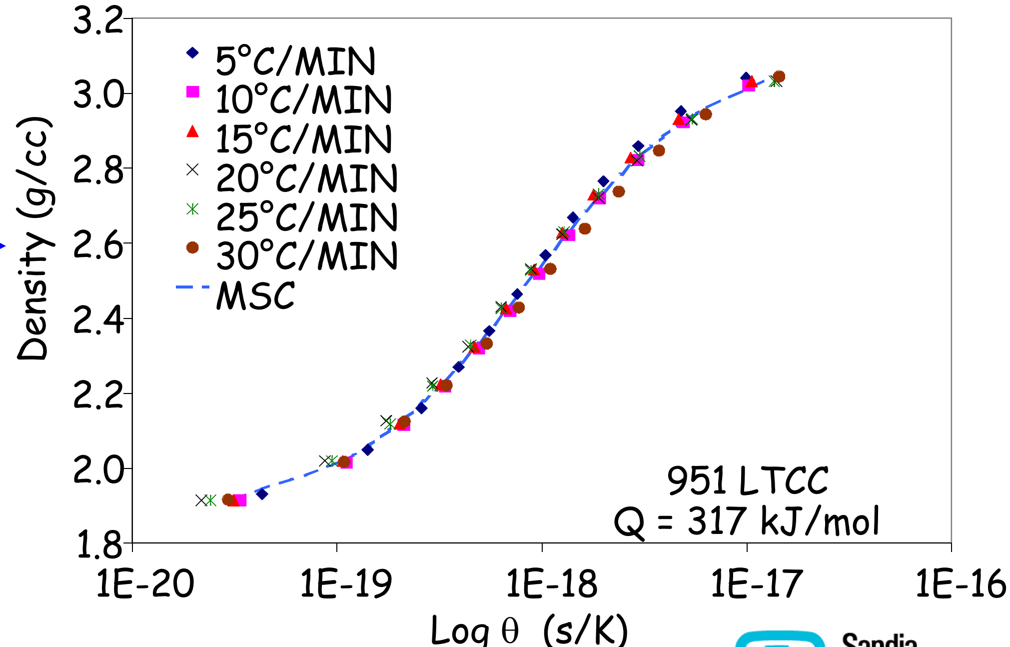
The MSC Concept Was Extended To Viscous & Anisotropic Sintering





DuPont 951 LTCC Ceramic-Filled Glass Composite





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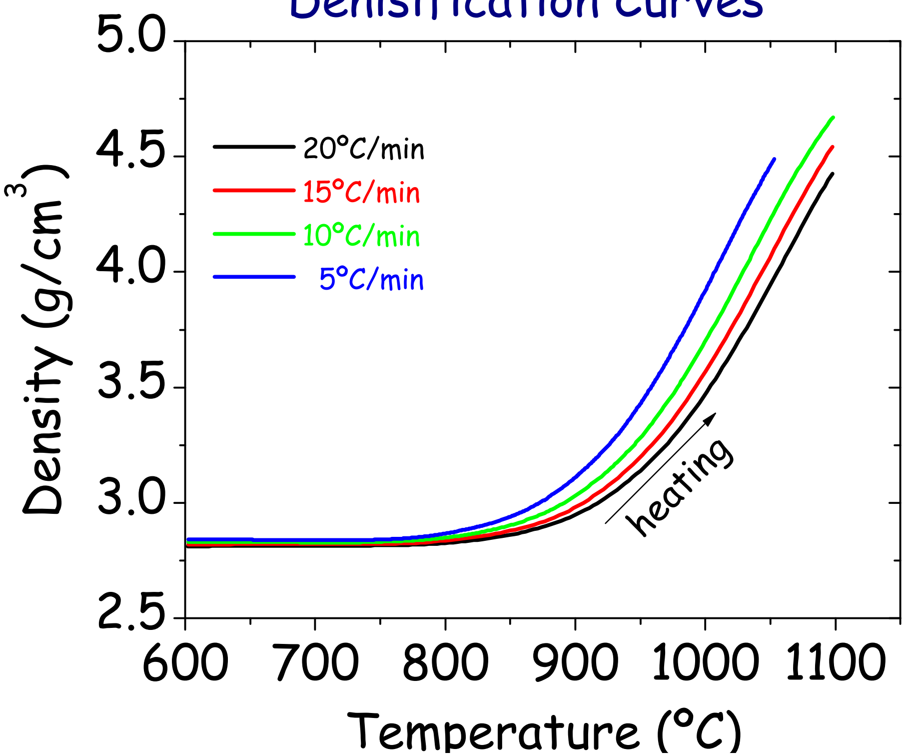
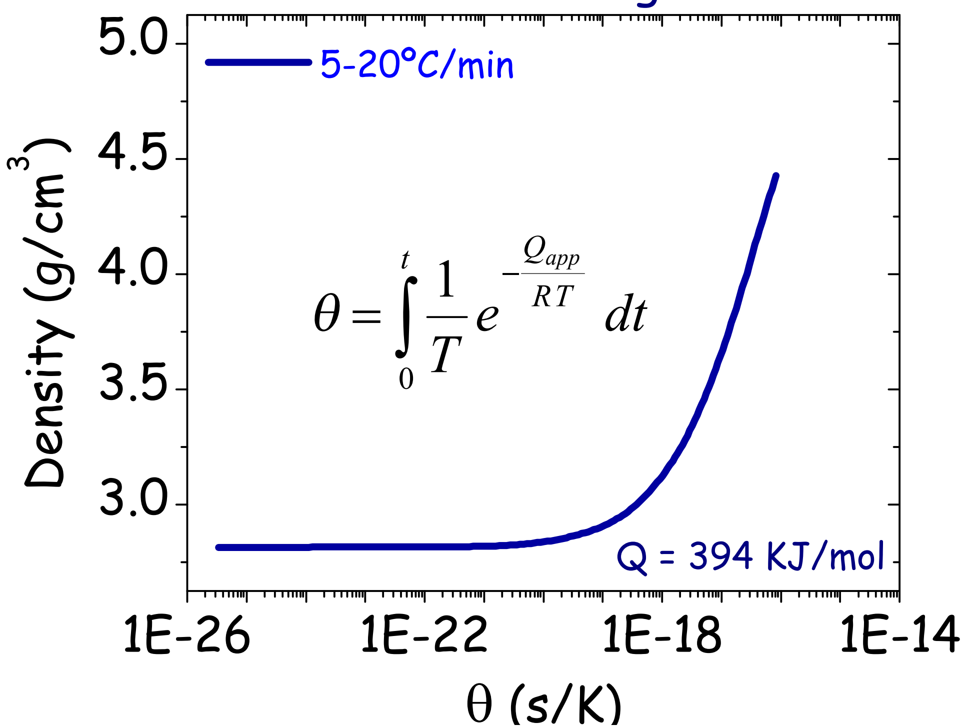
The MSC Concept Was Extended To Reactive Liquid Phase Sintering

Mixed-Oxide ZnO Varistor

Denisification Curves



Master Sintering Curve



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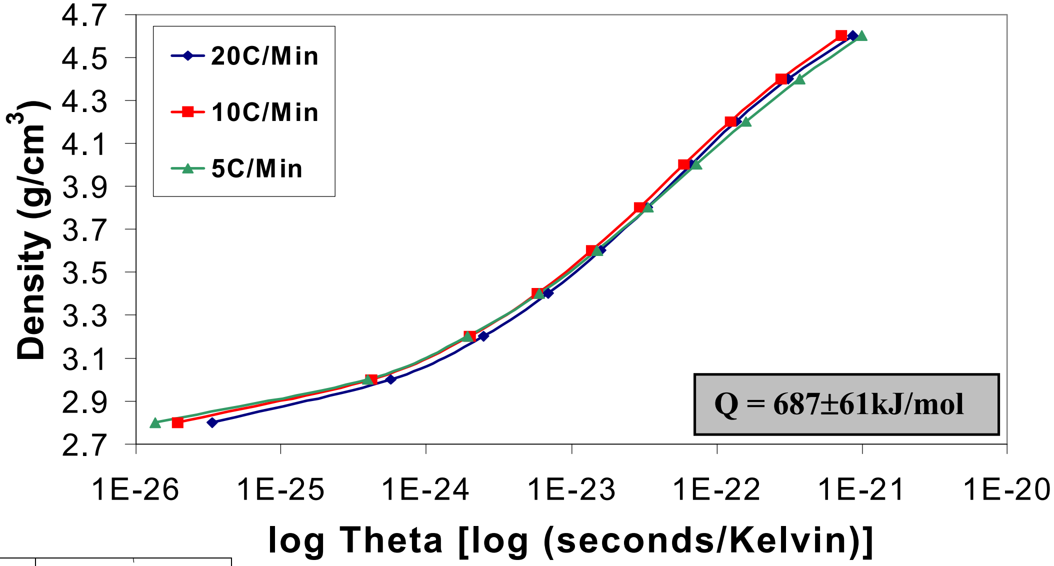
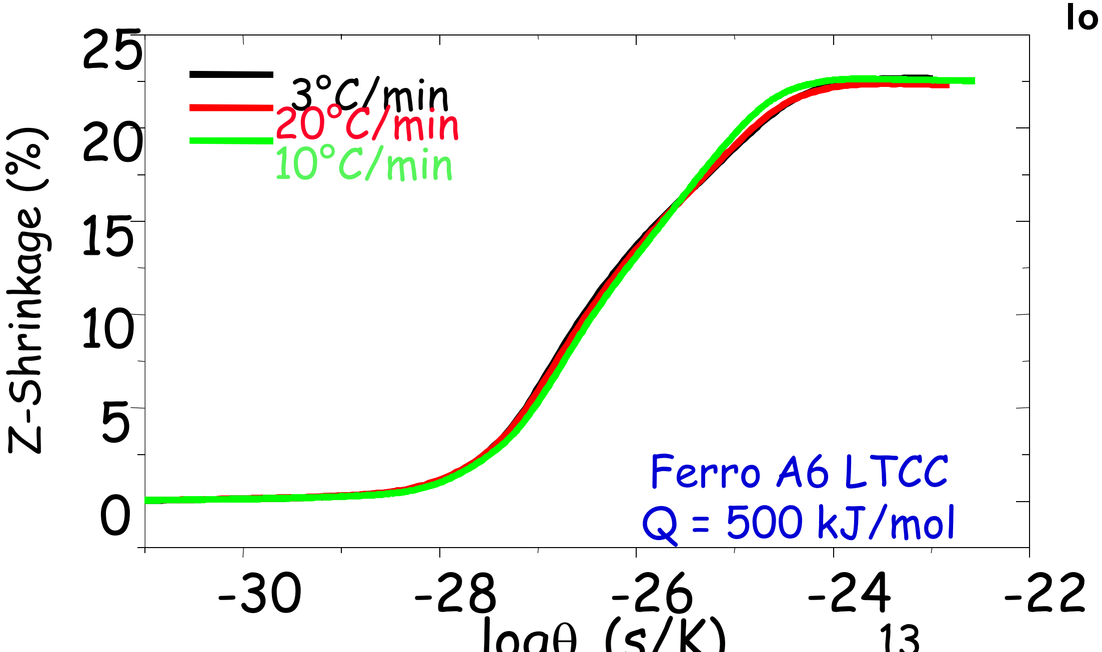
The MSC Was Applied To Solid-State And Liquid-Phase Sintering Composites

50:50 Composite

AKP53 Al_2O_3 : TZ-3YB-E ZrO_2

(566±10kJ/mol) (518±10kJ/mol)





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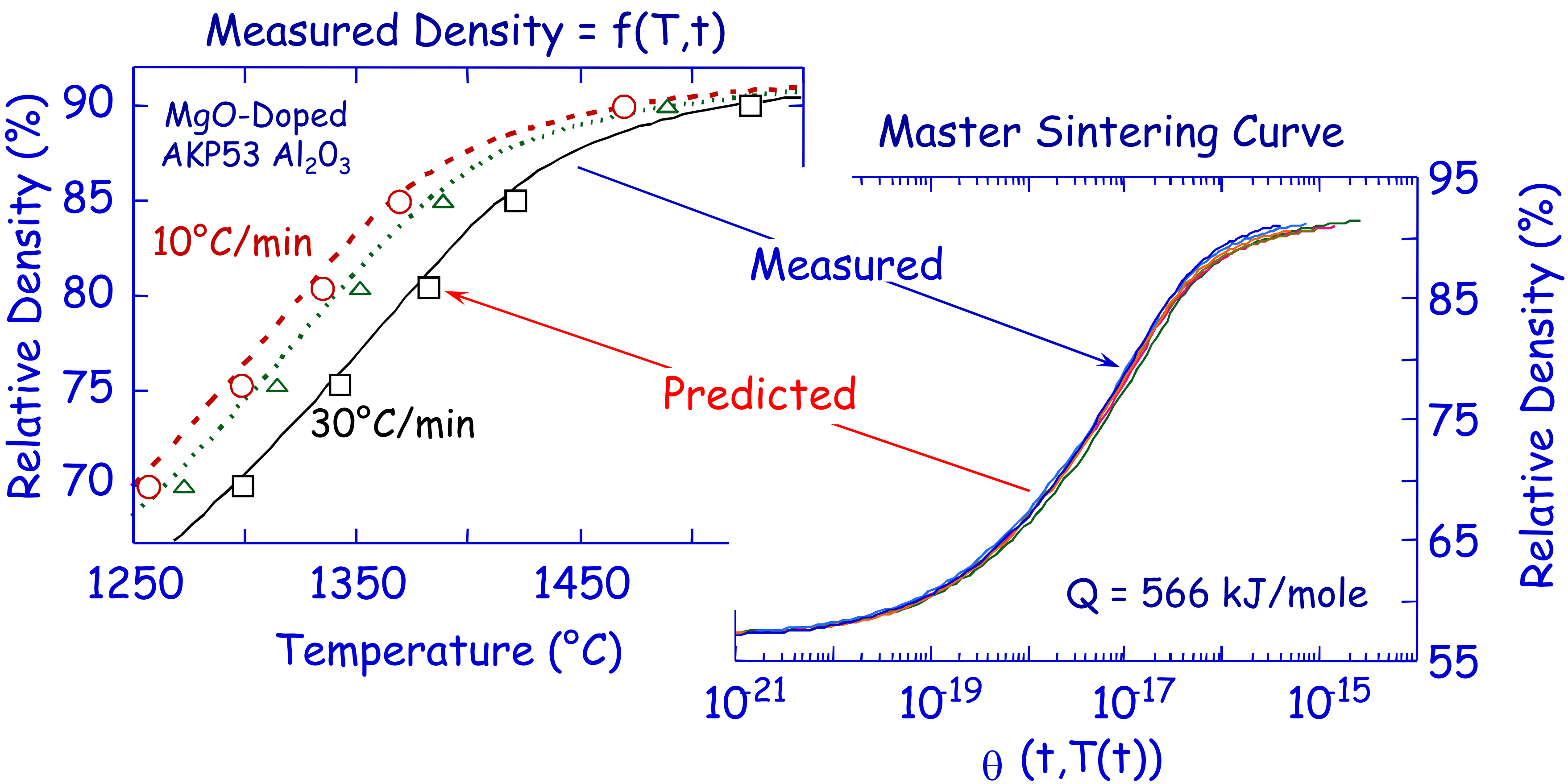
The MSC Can Be Used To Predict & Control Densification During Sintering



$$\int_o^t \frac{1}{T}\exp\left(-\frac{Q}{RT}\right)dt = \theta(t,T(t))$$

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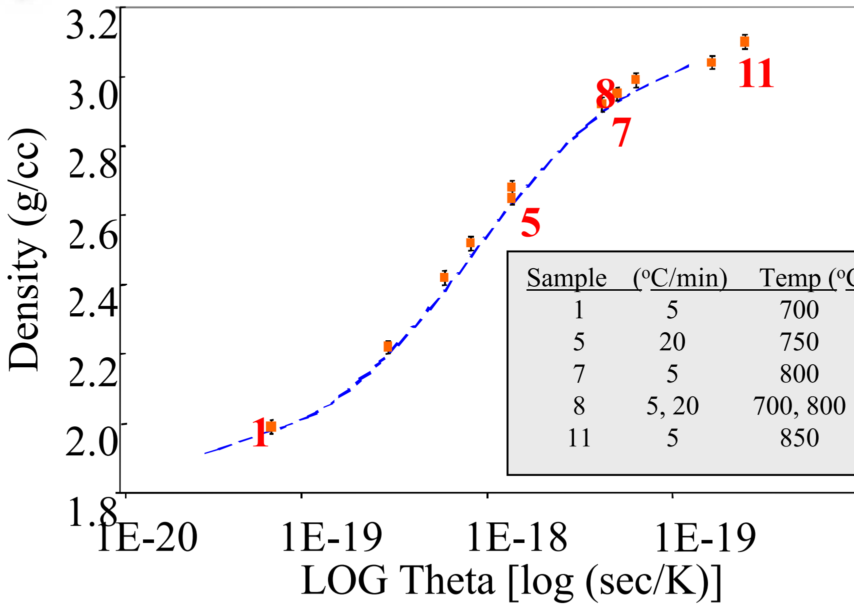
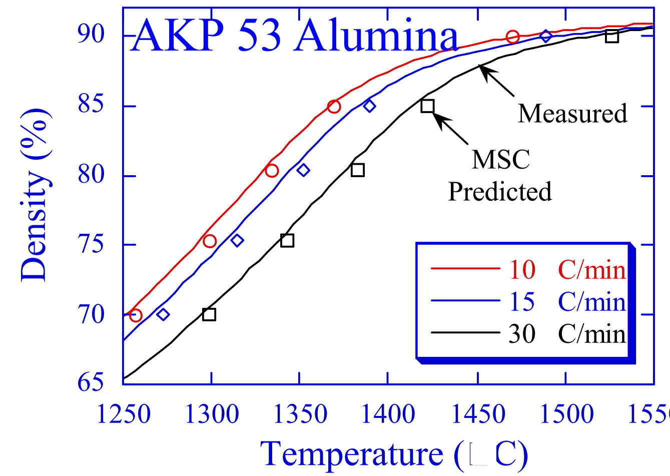
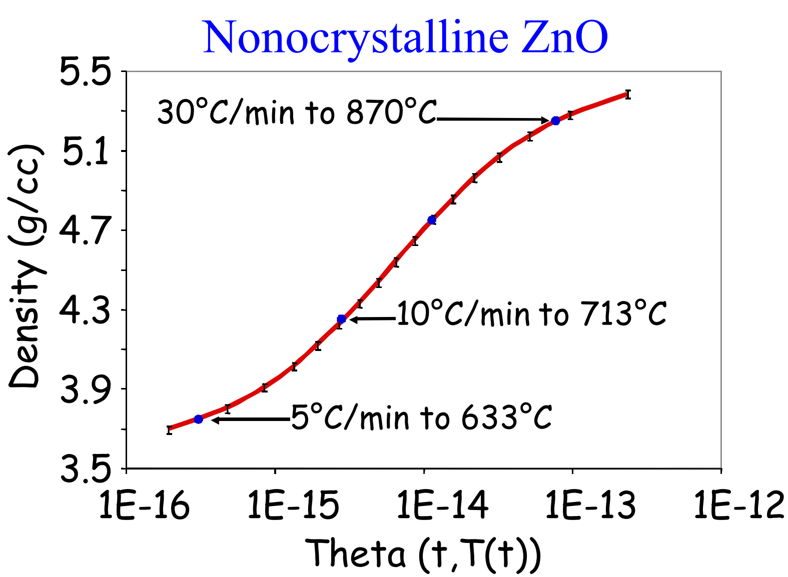
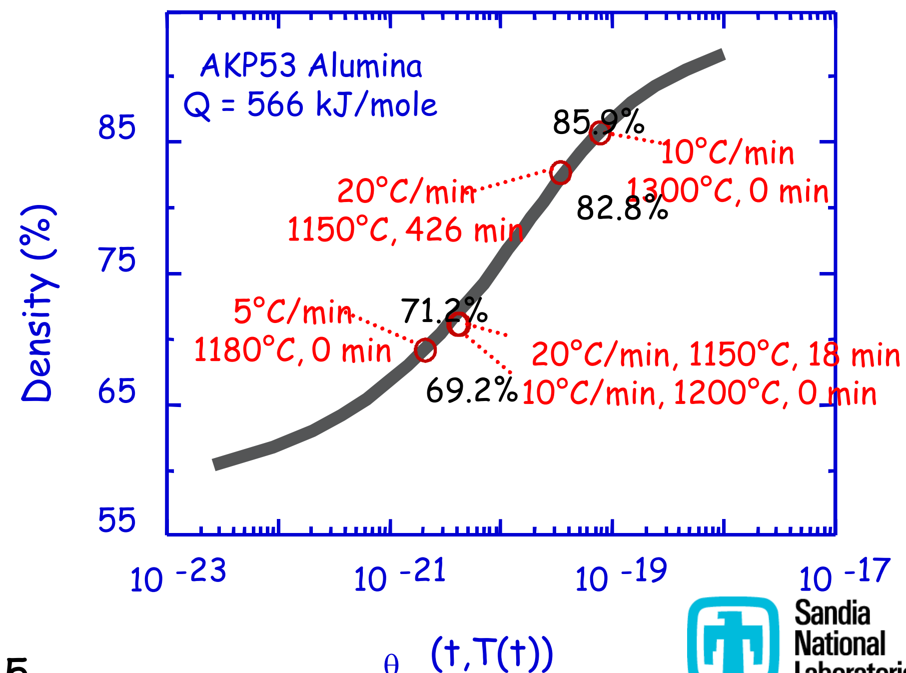
The MSC Predicts Sintered Density For A Given t-T Firing Profile



Sample	(°C/min)	Temp (°C)	Soak (min)
1	5	700	Quench
5	20	750	10
7	5	800	Quench
8	5, 20	700, 800	5, 5
11	5	850	Quench







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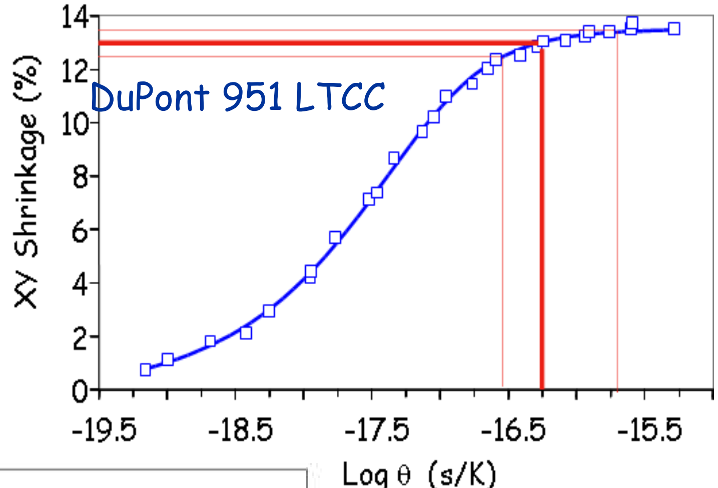
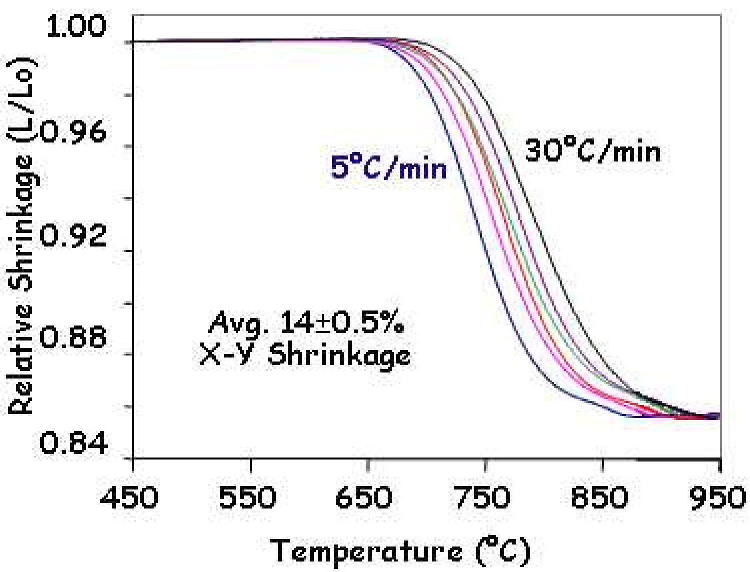
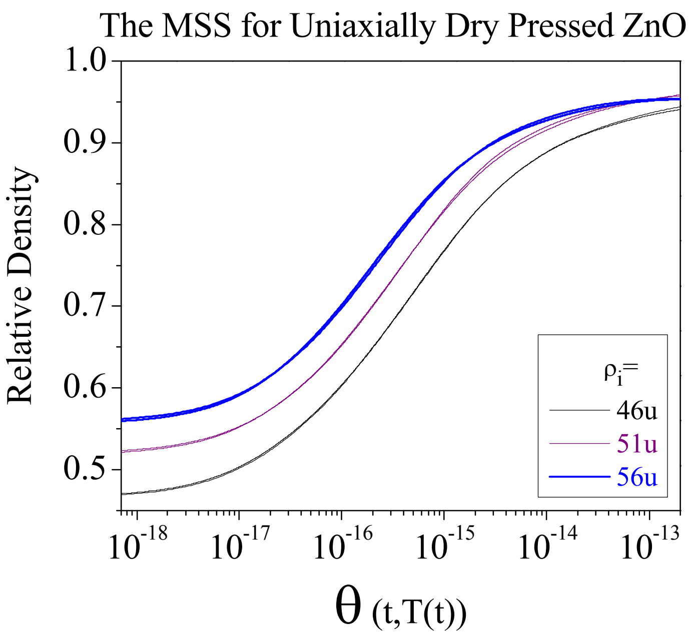
The Master Sintering Curve Concept Can Be Applied To Improve Process Control

Master Sintering Shrinkage Curve Was Developed To Predict X-Y Shrinkage





A Master Sintering Surface Can Be constructed From A Series of MSCs



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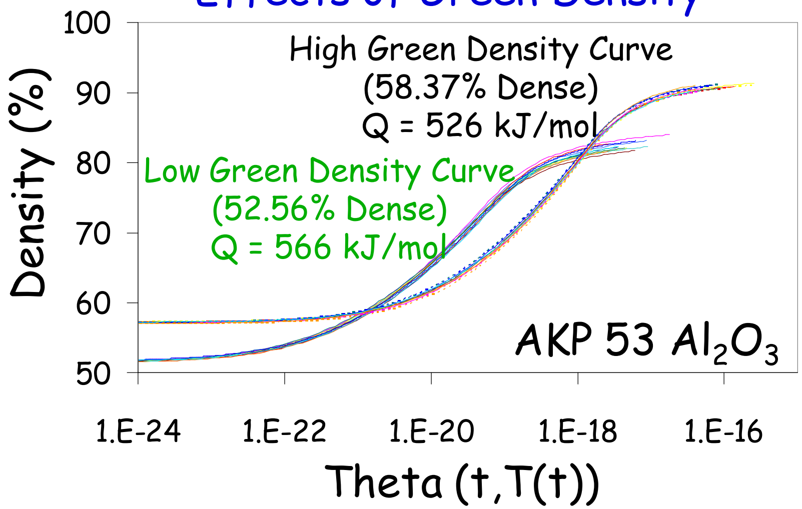
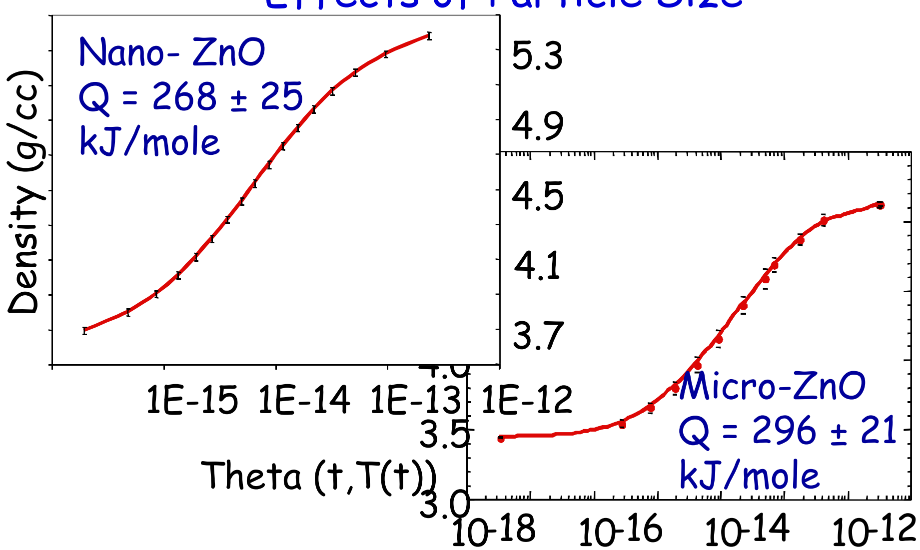
Green Microstructure/Density Affect Q And The MSC

Effects of Green Density

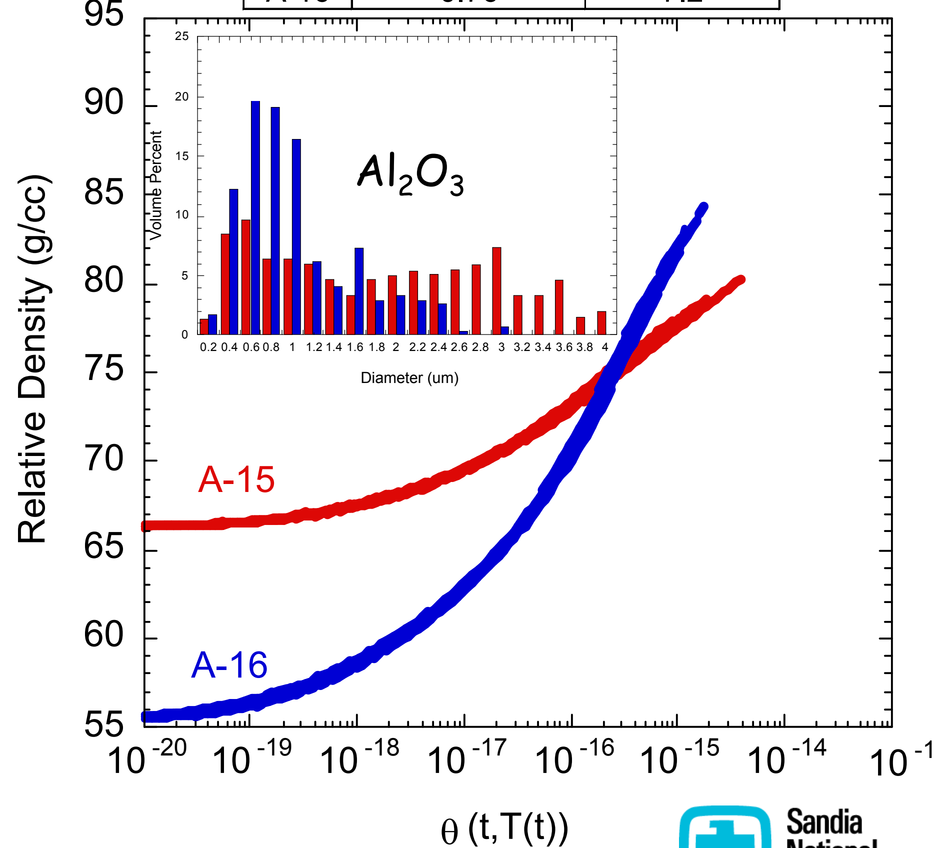


Effects of Particle Size



Effects of Particle Size and Green Density

	Median Particle Size (um)	Surface Area (m^2/g)
A-15	1.7	5.5
A-16	0.76	7.2



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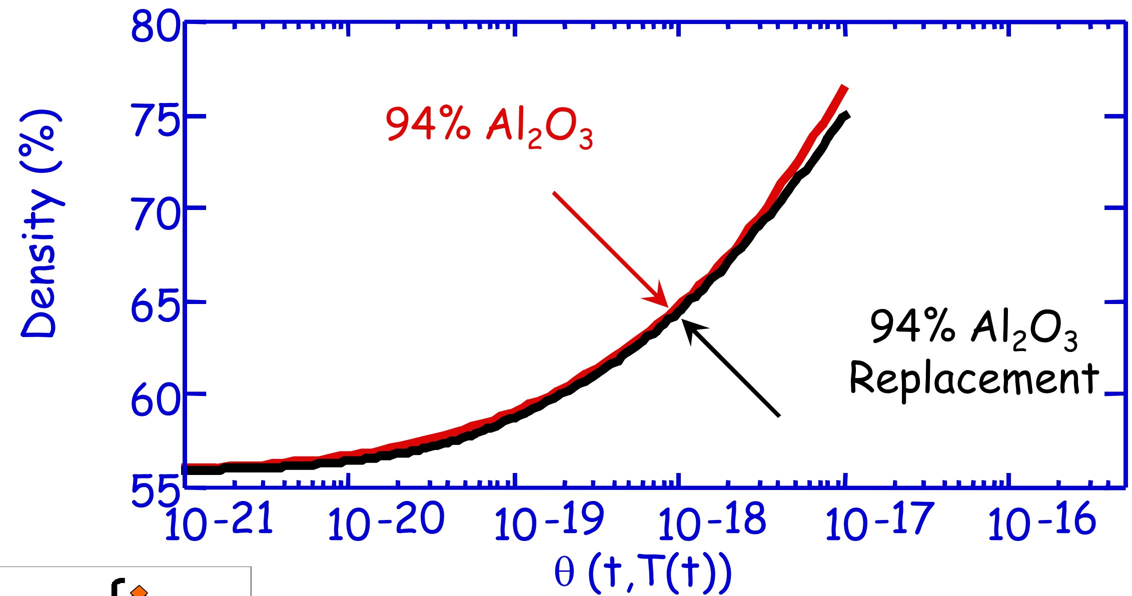
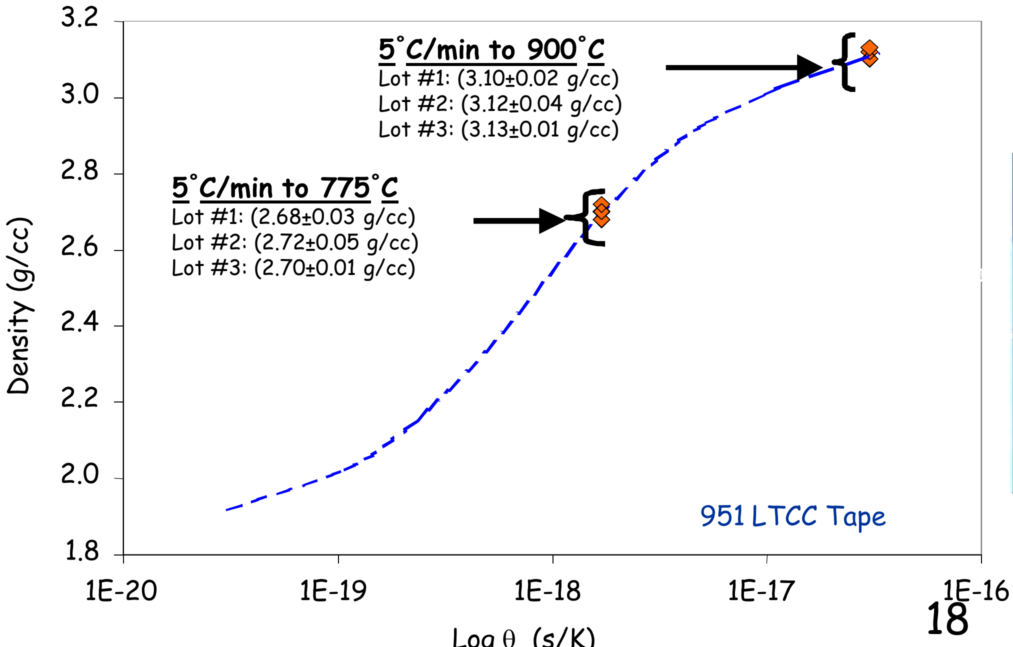
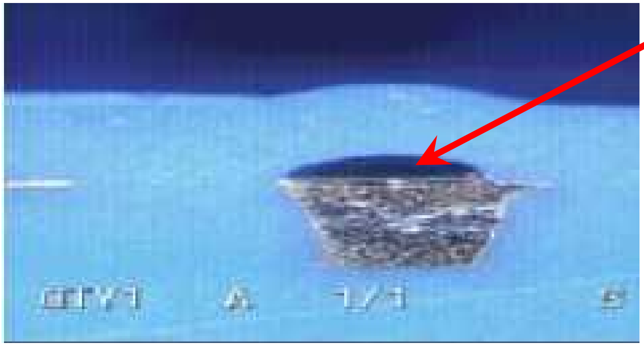
The MSC Can Be Used To Assess Materials & Process Quality Control

The same material processed the same way will have the same MSC







"Blister" in LTCC multilayer

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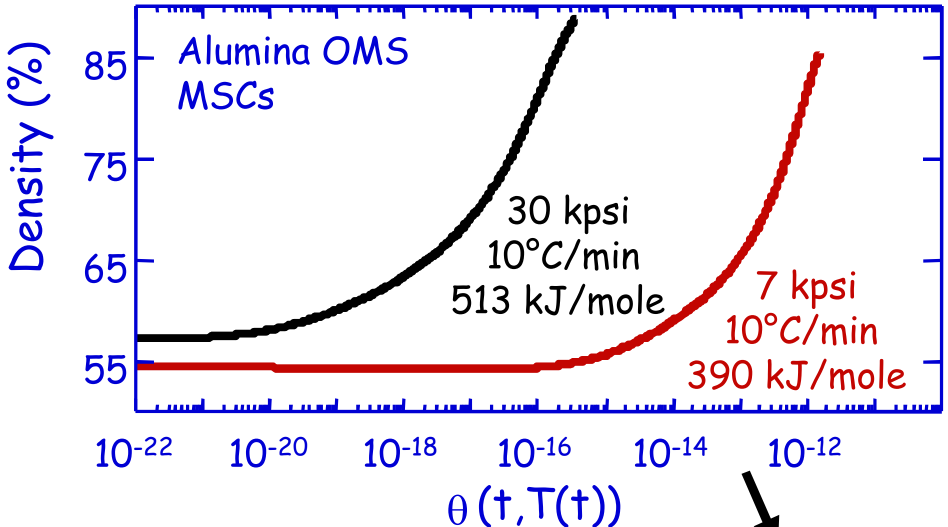
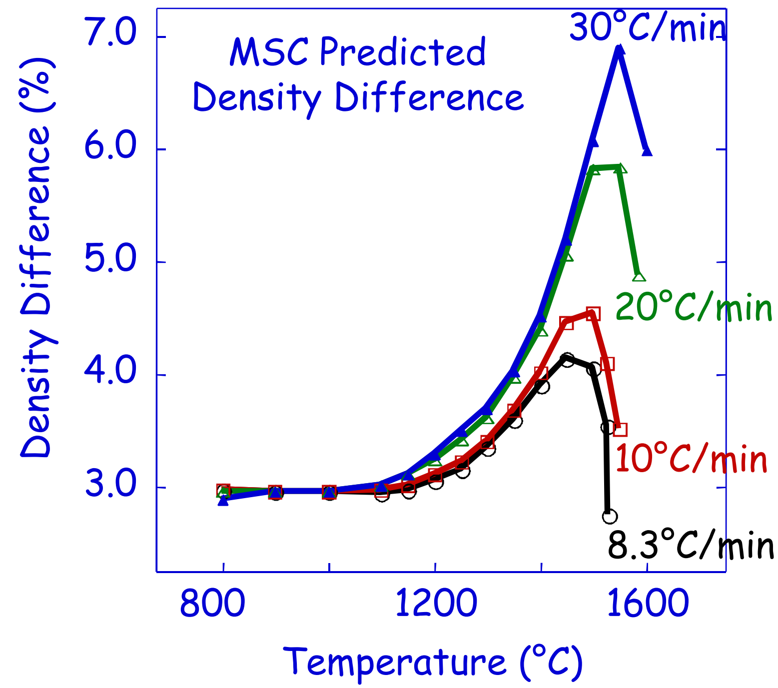
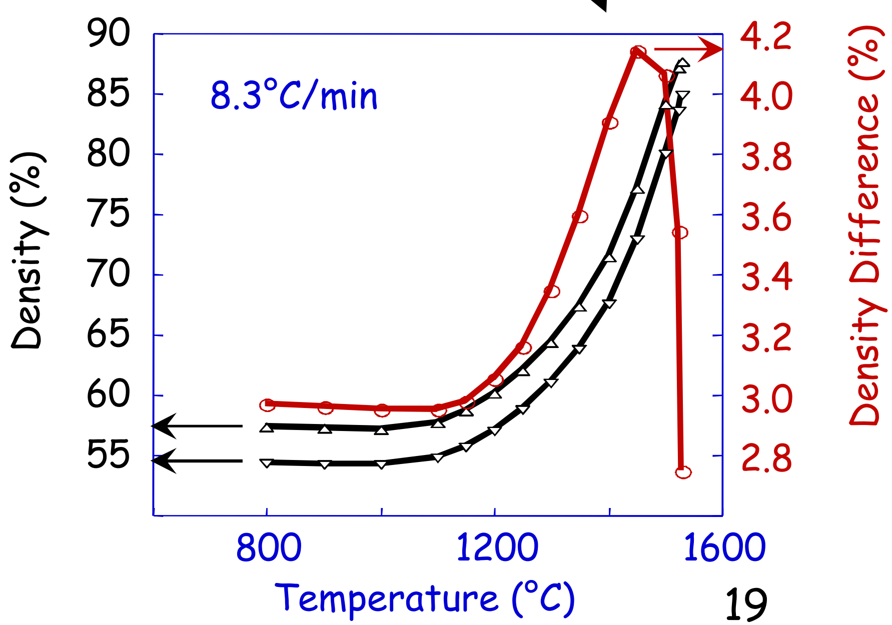
Effects Of Density Gradients On Sintering Can Be Assessed

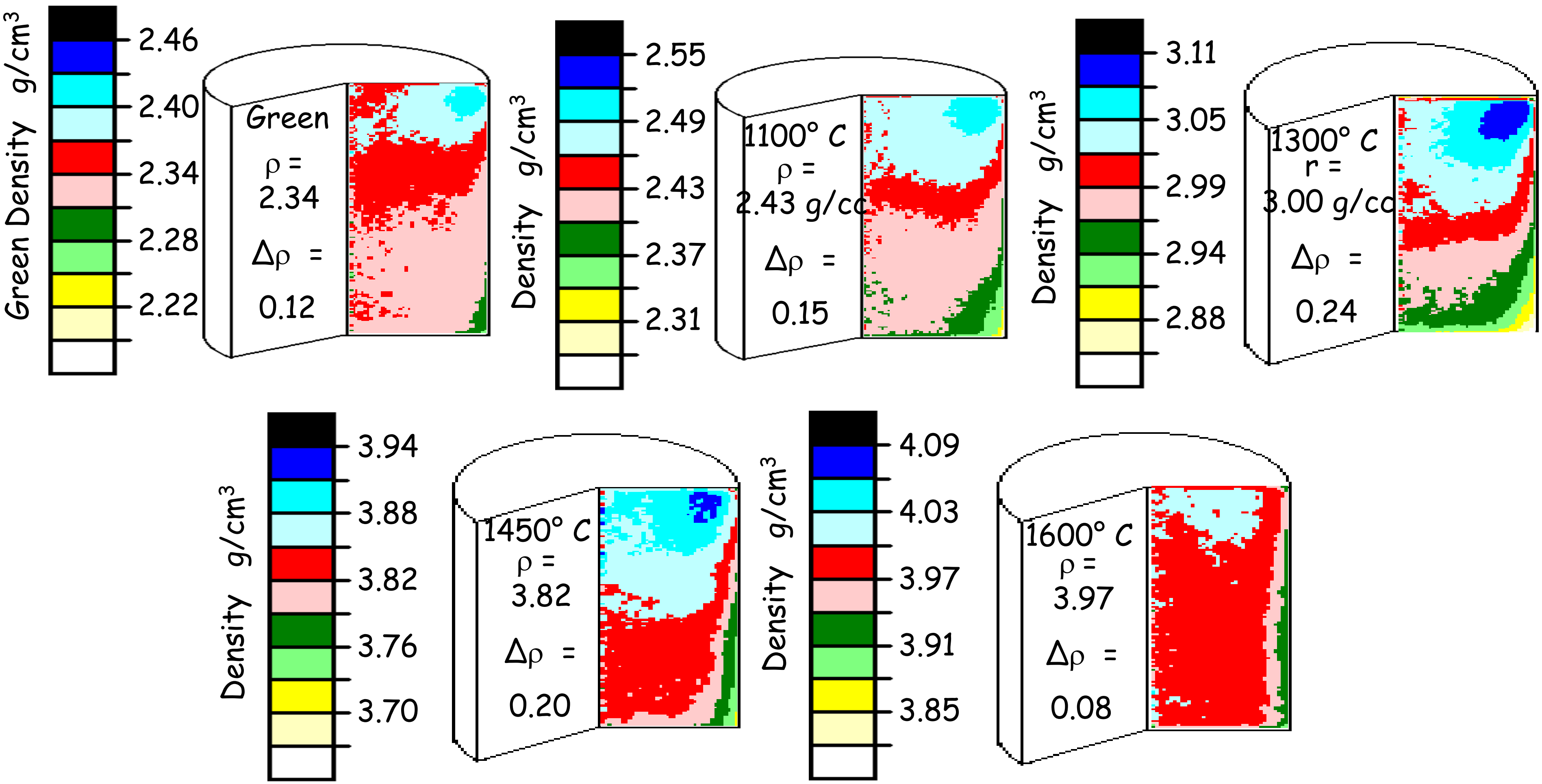






MSC Predictions Are Consistent With XRCT Measured Density Gradients

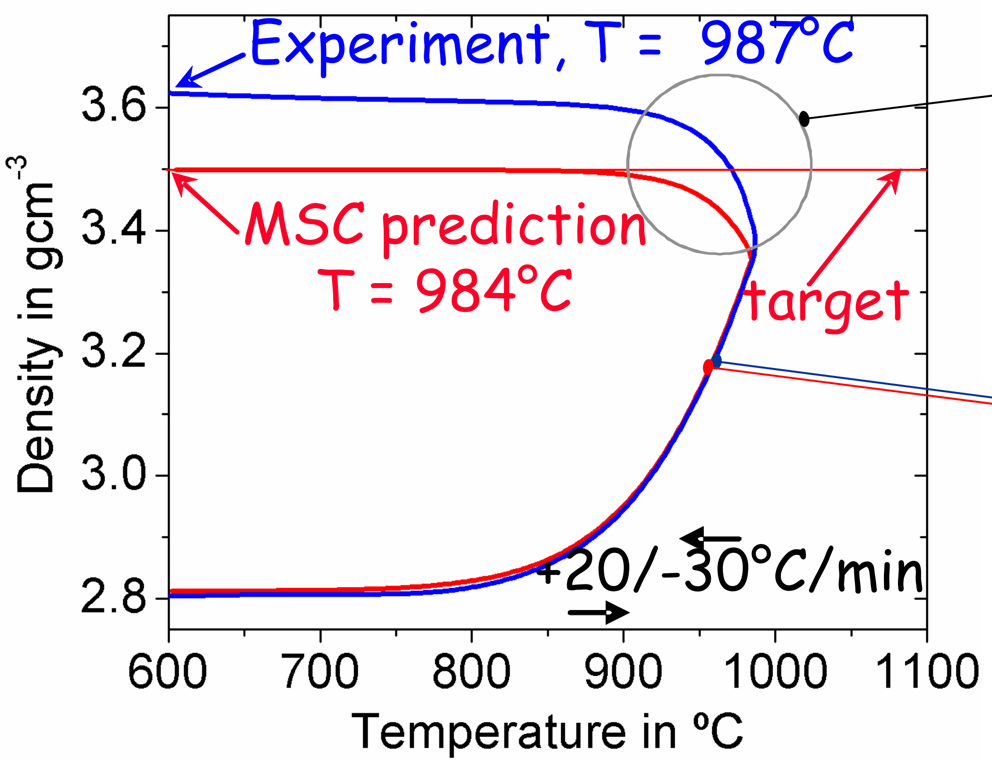
Alumina OMS



T. Rabe, BAM

MSC Predictions Can Reveal Firing Process Sensitivity

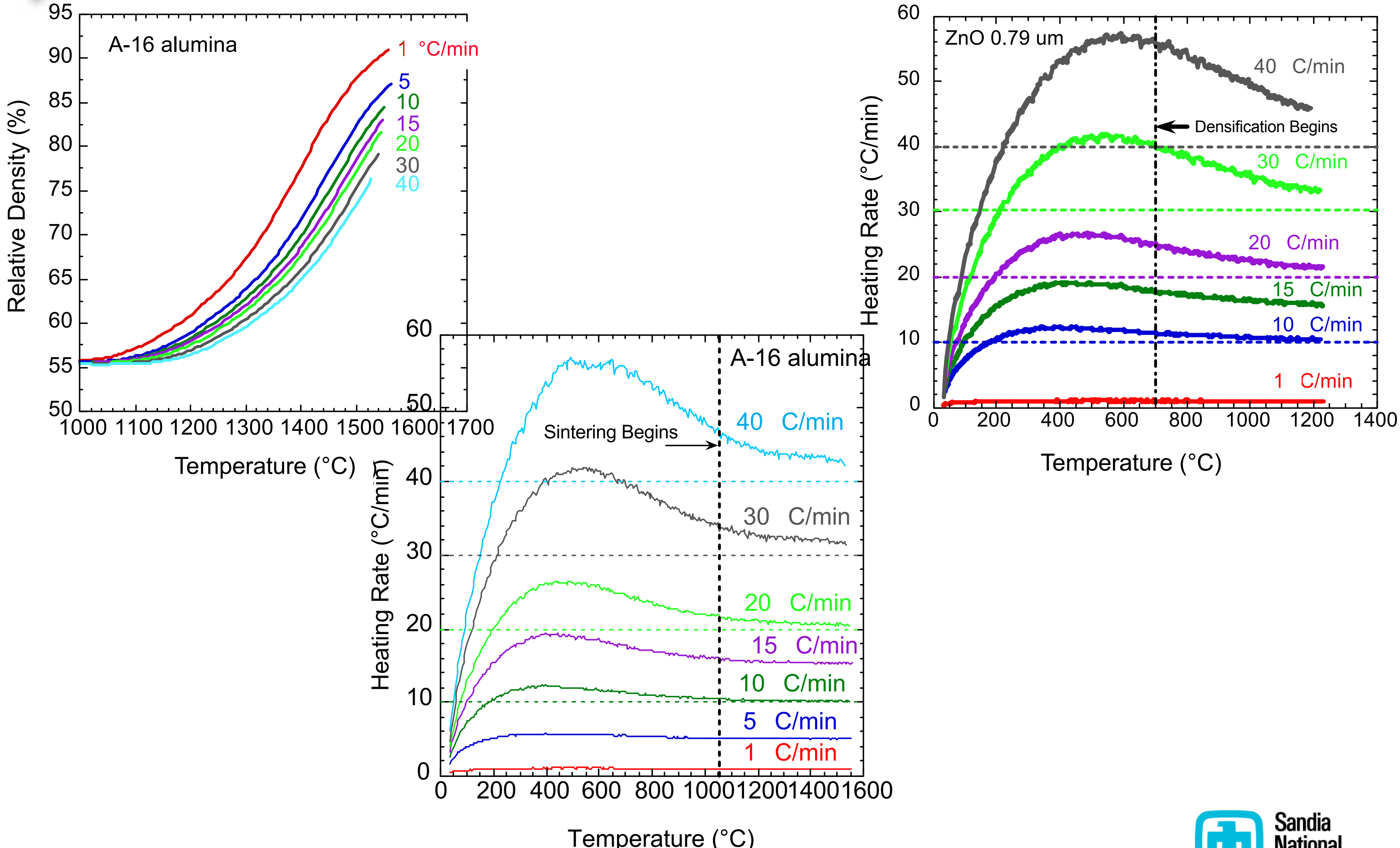
ZnO Mixed-Oxide Varistor



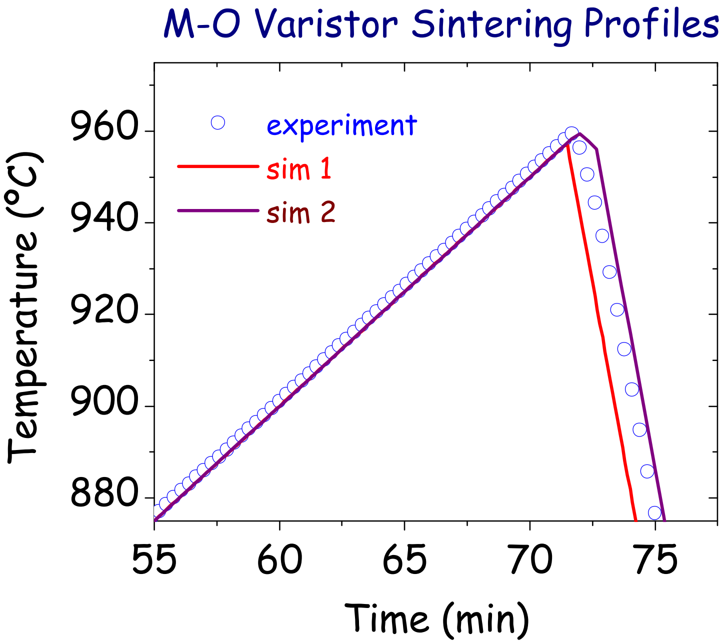
- Modeling varistor firing reveals process sensitivity
- Predictive modeling was used to design & control varistor firing

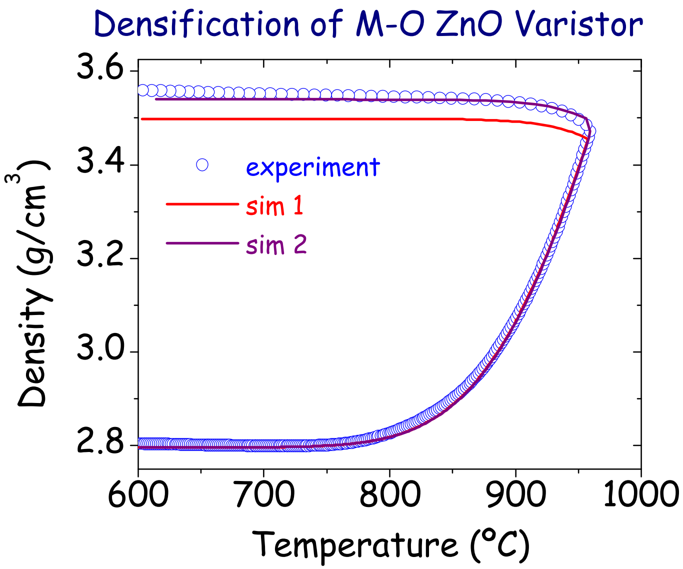
The sensitivity of varistor density (and microstructure) to minor deviations in sintering time & Temperature can contribute to variability in varistor performance.

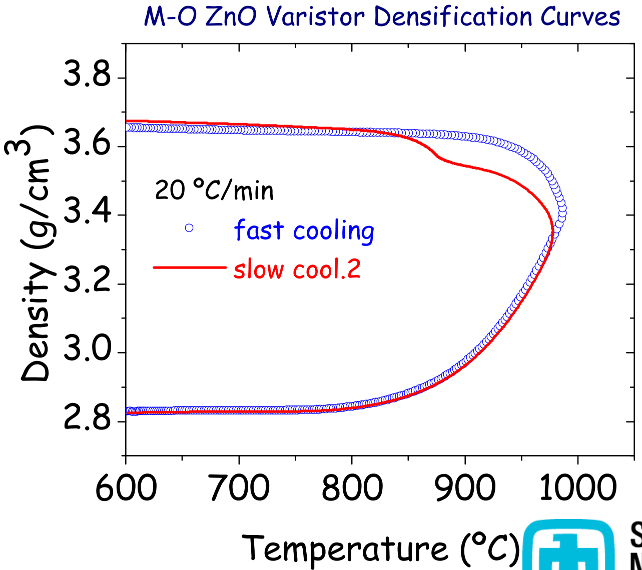
The Thermal “Lag” In Experiments Must Be considered In The Modeling



MSC-Based t-T Profiles Predict The Experimentally Observed Densification







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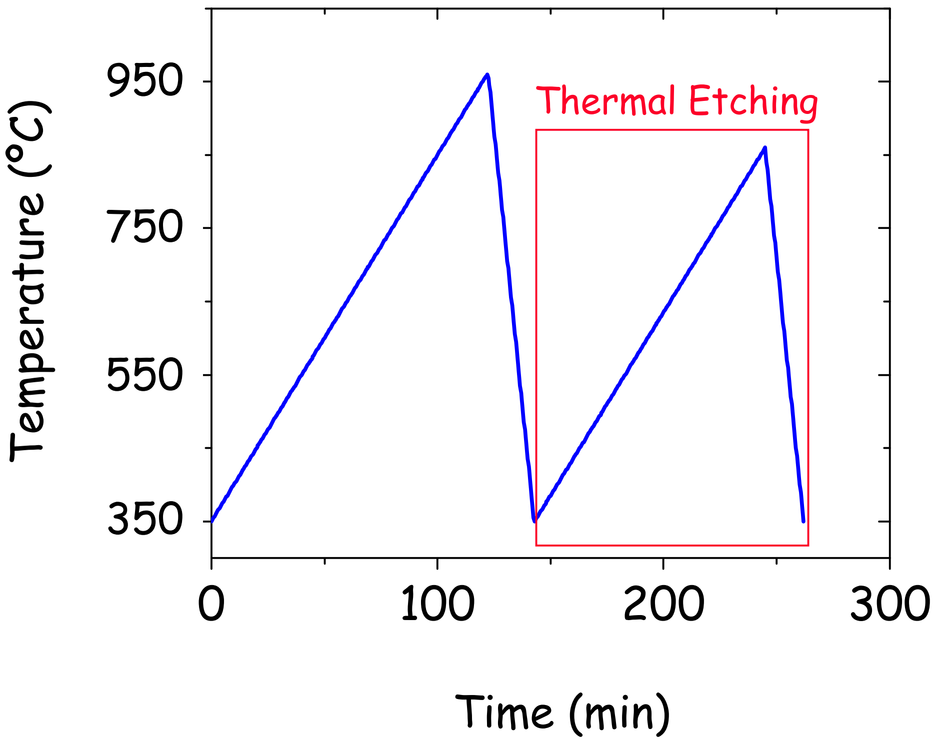
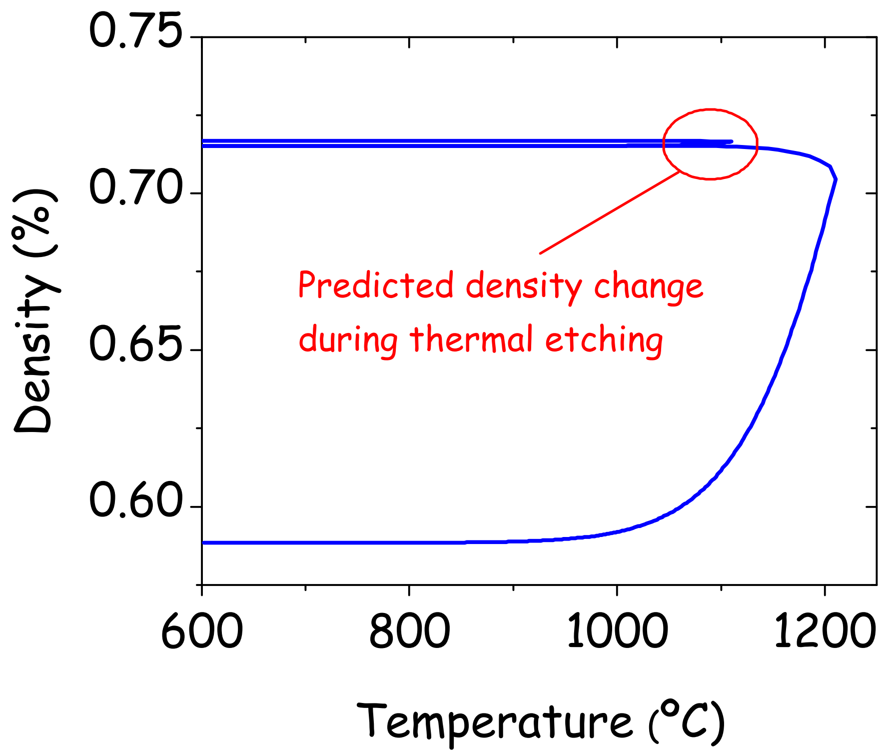
MSC t-T Proflies Enable Thermal Etching Without Changing Density

Mixed-Oxide ZnO Varistor





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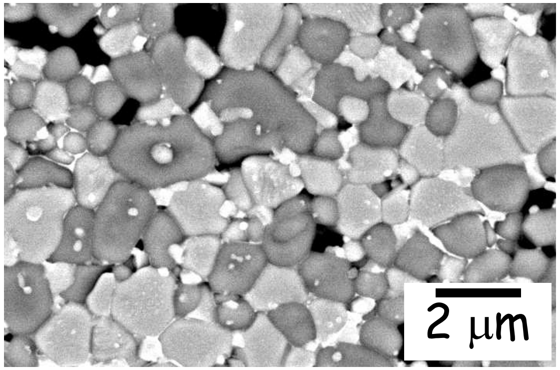
The Master Sintering Curve (MSC) Links Processing & Microstructure

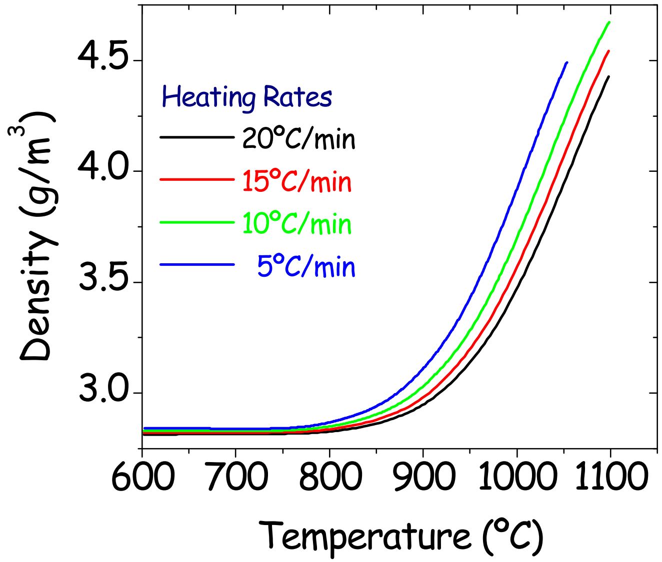
Instantaneous linear shrinkage

$$-\frac{dL}{L\,dt} = \frac{d\rho}{3\rho\,dt} = \frac{\gamma_s \Omega}{kT}\left(\frac{\Gamma_v D_v}{G^3} + \frac{\Gamma_b D_b}{G^4}\right)$$

Simplify and rearrange:

$$\int_{\rho_0}^{\rho} \frac{(G(\rho))^n}{3\rho\,\Gamma(\rho)}\,d\rho = \int_0^t \frac{\gamma_s \Omega D_0}{kT}\, e^{-\frac{Q_{app}}{RT}}\, dt$$





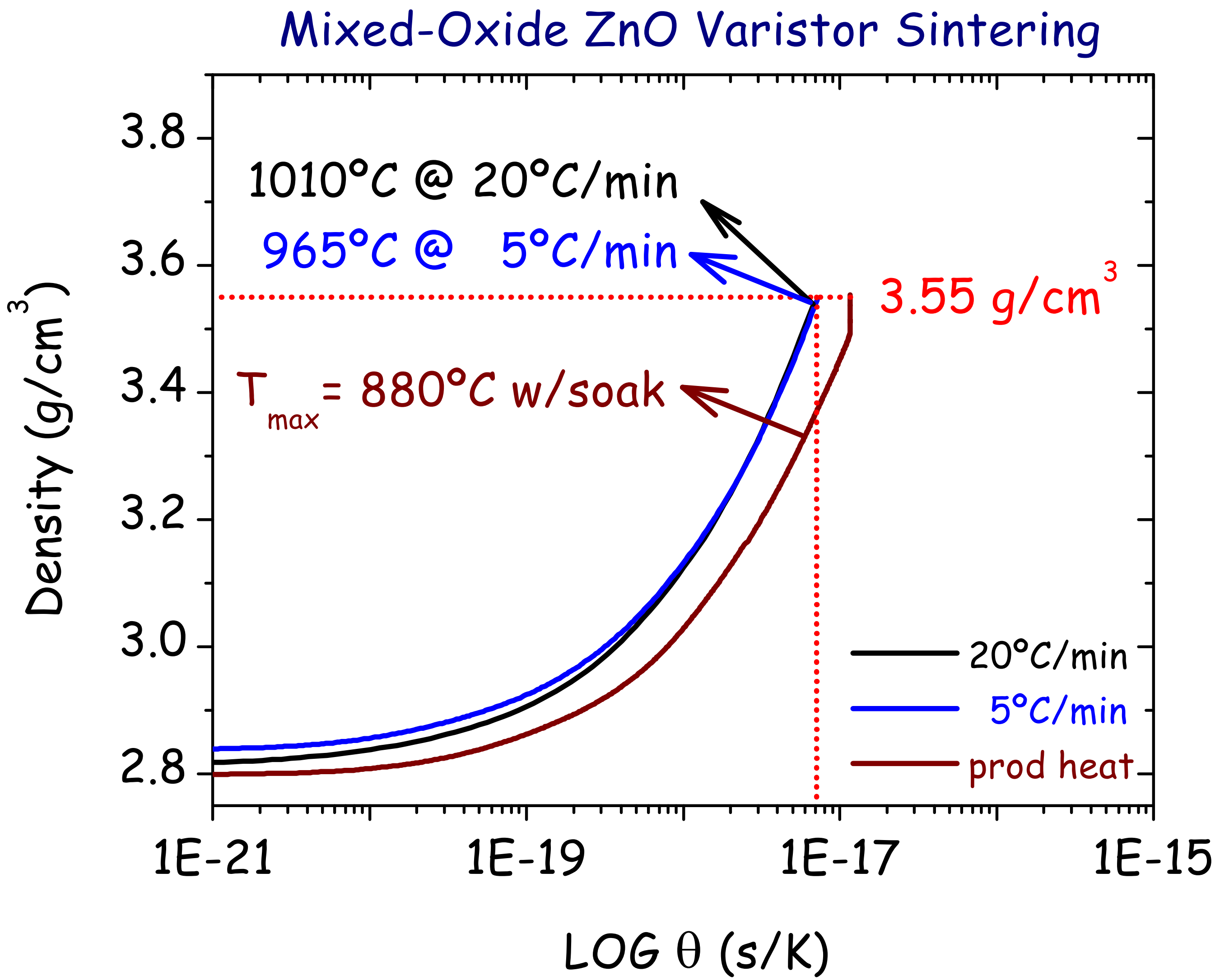
Microstructure & Properties:

Temperature-time profile:

$$\Phi(\rho) = \frac{k}{\gamma_s \Omega D_0}\int_{\rho_0}^{\rho} \frac{G((\rho))^n}{3\,\rho\,\Gamma(\rho)}\,d\rho \equiv \theta\left(t, T(t)\right) = \int_0^t \frac{1}{T} e^{-\frac{Q_{app}}{RT}}\, dt$$

H. Su, D.L Johnson, "Master Sintering Curve: A Practical Approach to Sintering"
J. Am. Ceram. Soc. **79** 3211-17 (1996)

MSC t-T Firing Profiles Can Be Designed To Achieve A Target Density



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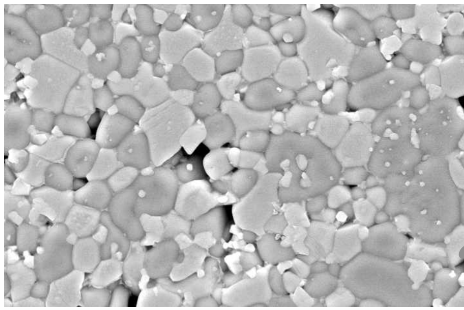
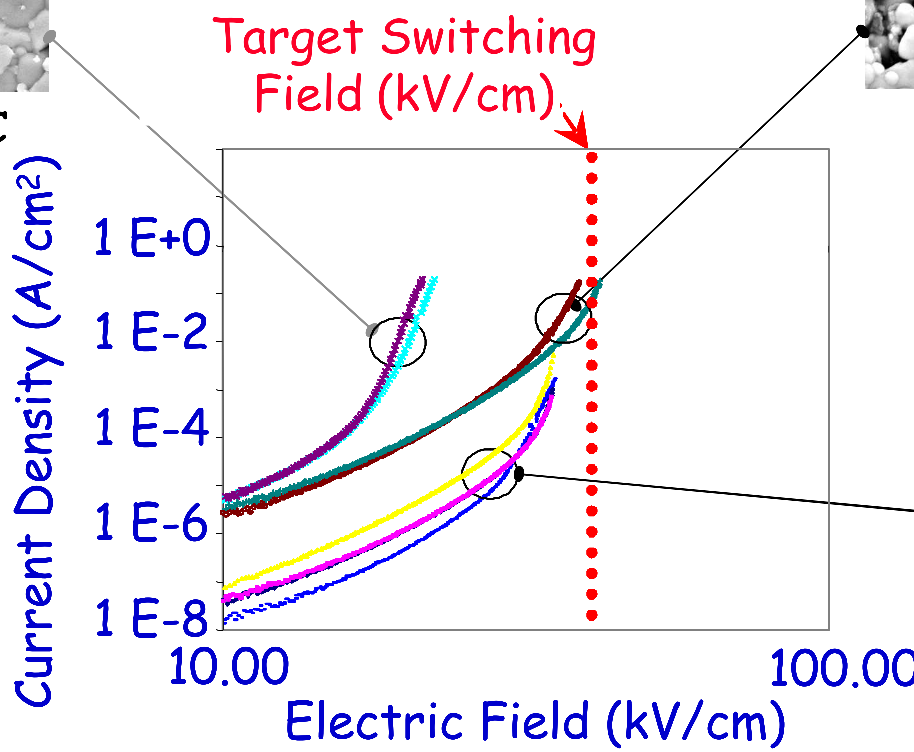
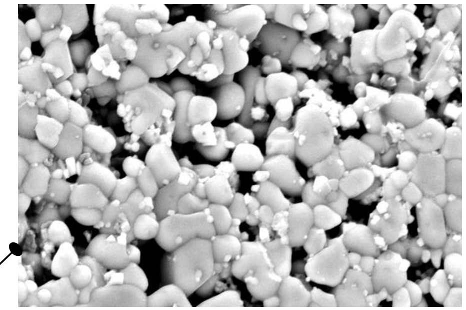
Controlled Microstructure And Property Varistors Were Produced

Model-derived sintering profiles were used to control processing to systematically control the density, microstructure, & electrical properties of ZnO varistors.

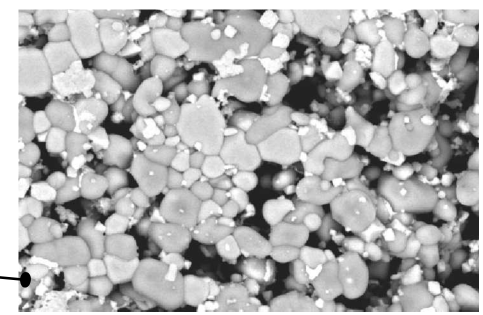


10°C/min to 1100°C
(4.59 g/cm³)



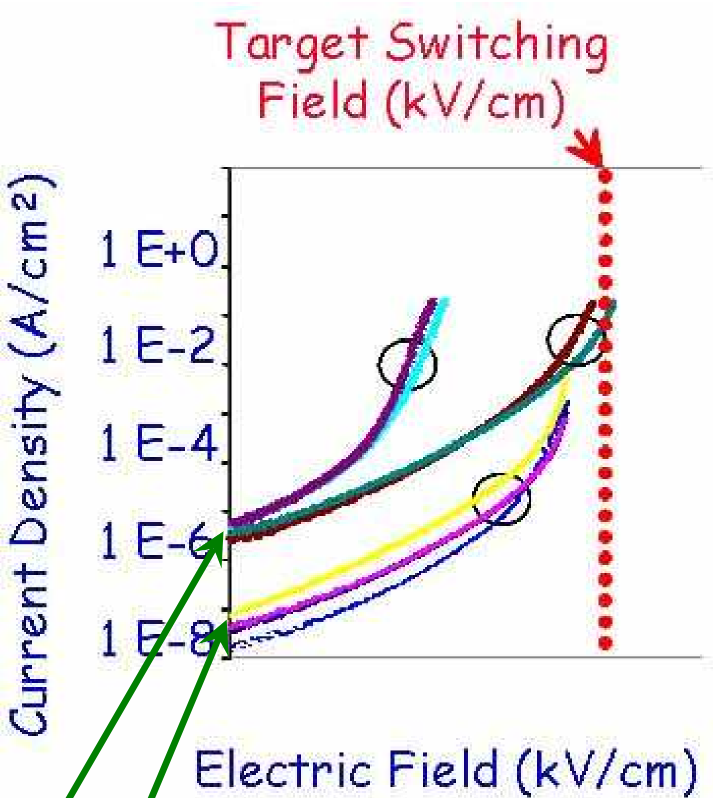


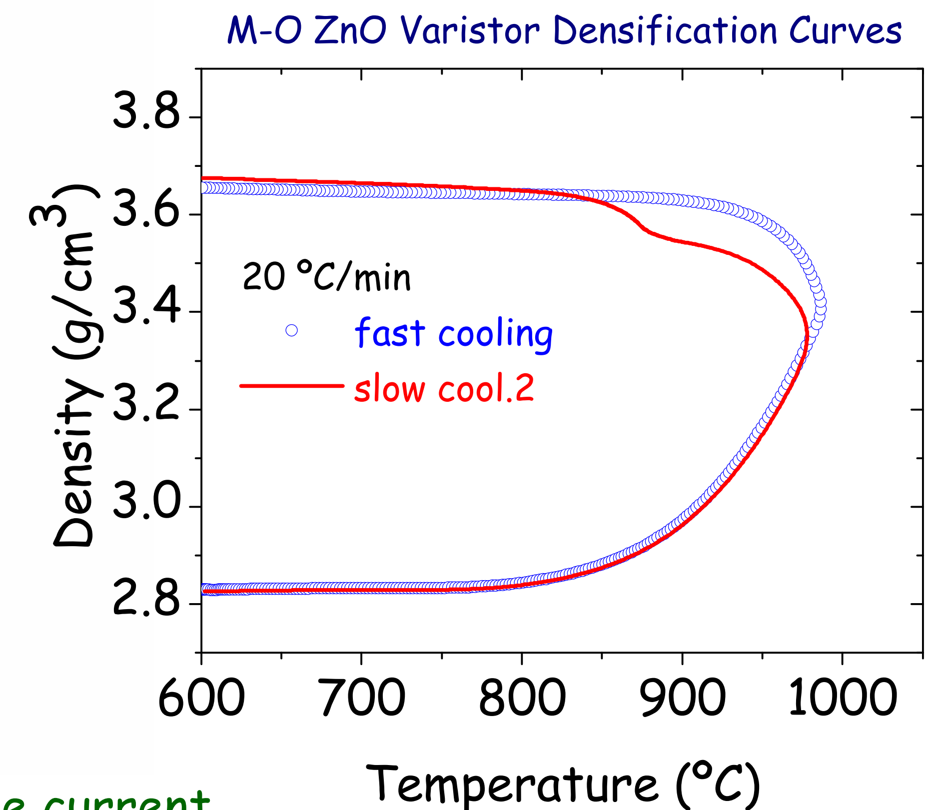
5°C/min to 960°C
(3.50 g/cm³)



0.5°C/min to 880°C
(3.55 g/cm³)
"Production"

Leakage Current Is Reduced By Slow Cooling After Fast Firing





- Slow cooling decreases leakage current
- Fast firing increased the leakage current

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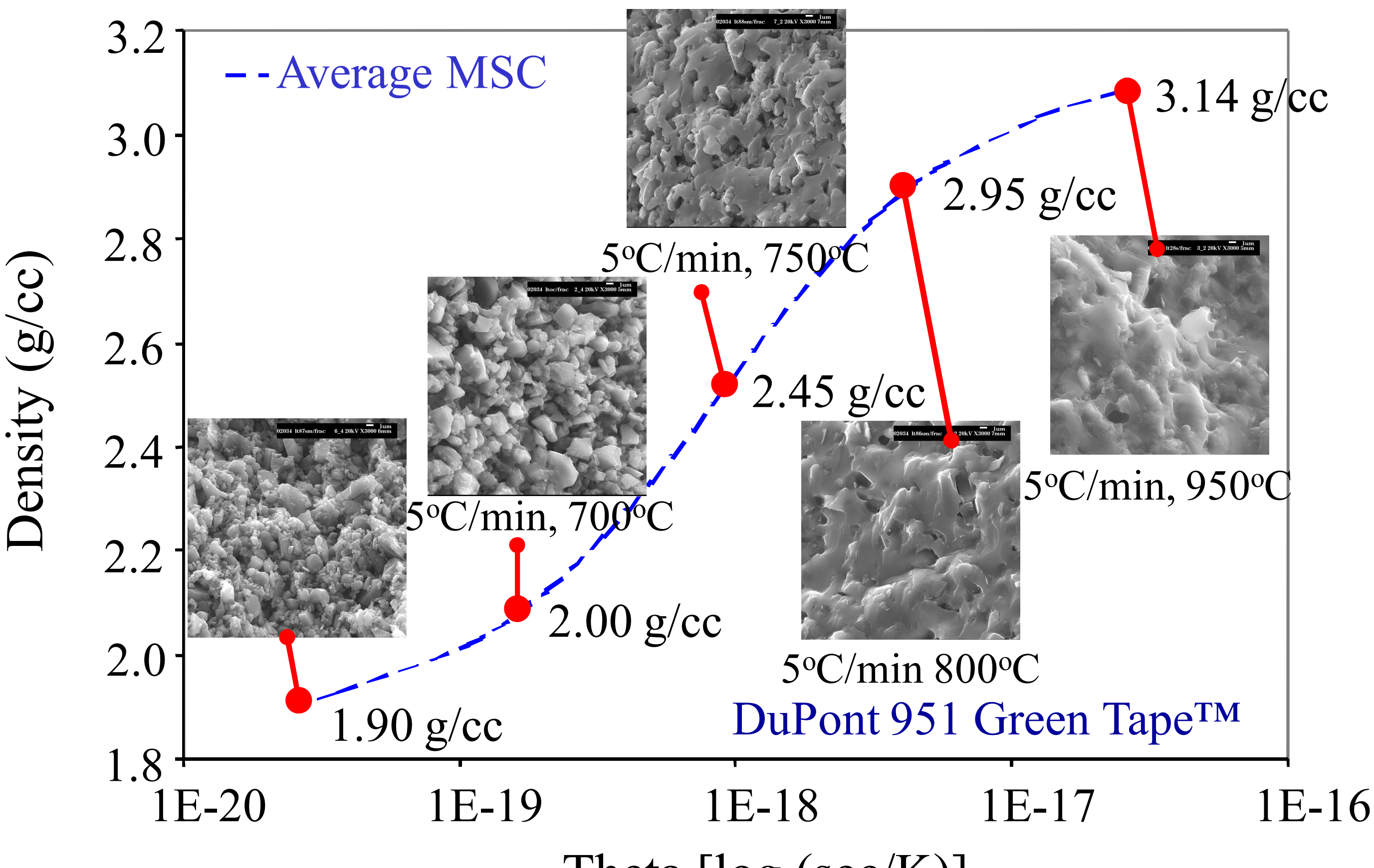
Scientific Understanding Can Be Gleaned From The Master Sintering Curve

Sintering Time And Temperature

$$\rho \equiv \Phi(\rho) \equiv \frac{k}{\gamma \Omega D_o} \int_{\rho_o}^{\rho} \frac{(G(\rho))^n}{3\rho\Gamma(\rho)} d\rho$$

Microstructure & Properties



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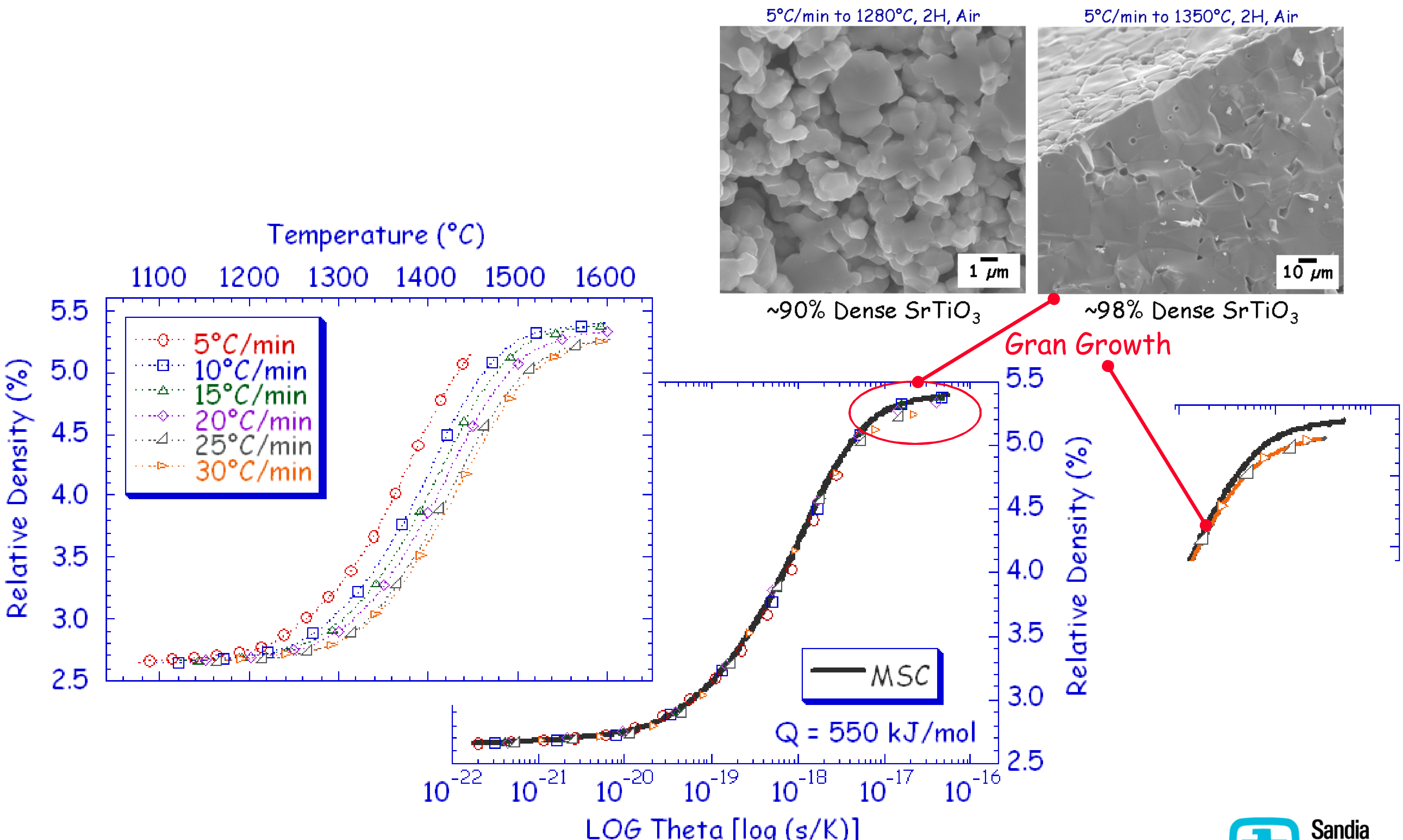
Master Microstructure-Density Trajectory Deviations Alter The MSC



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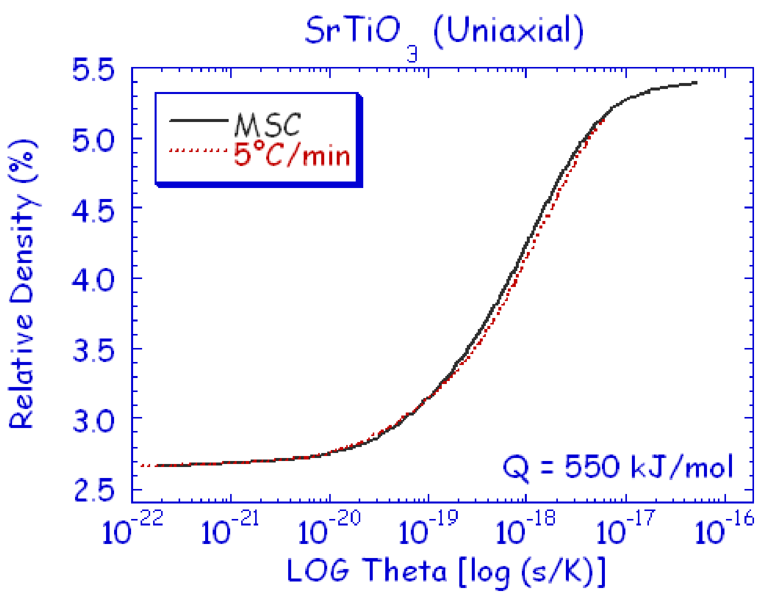
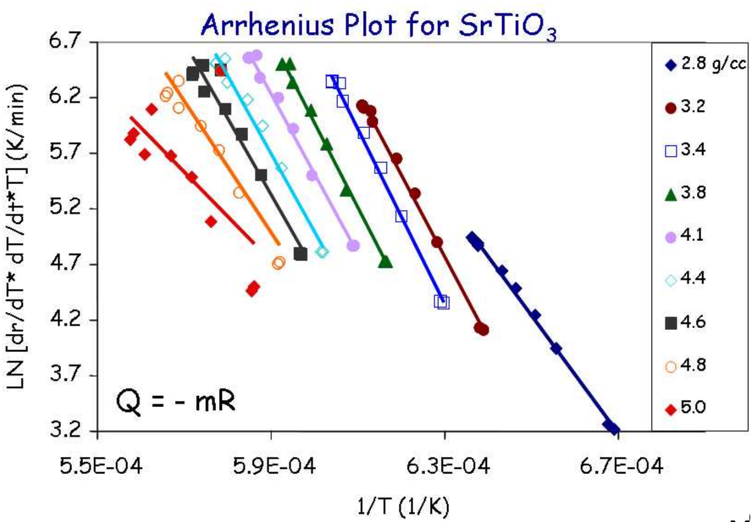
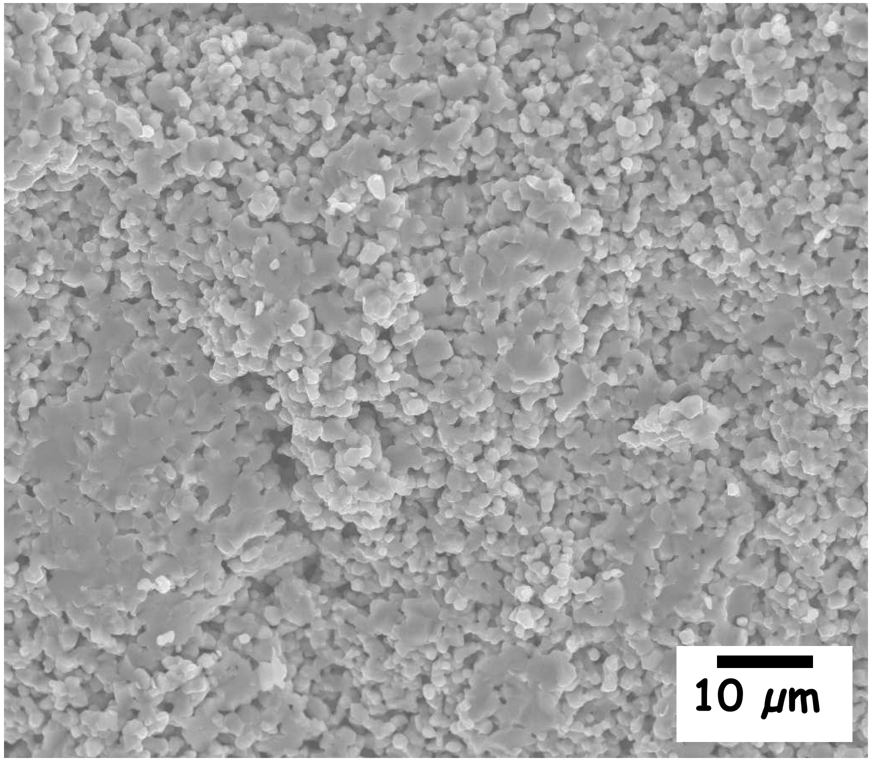
MSC Deviations May Be Due To Heterogeneous Microstructure Evolution





Sintered $SrTiO_3$ Has A Heterogeneous Microstructure

~90% Dense $SrTiO_3$



1°C/min to 600°C, 2H, Air
5°C/min to 1280°C, 2H, Air

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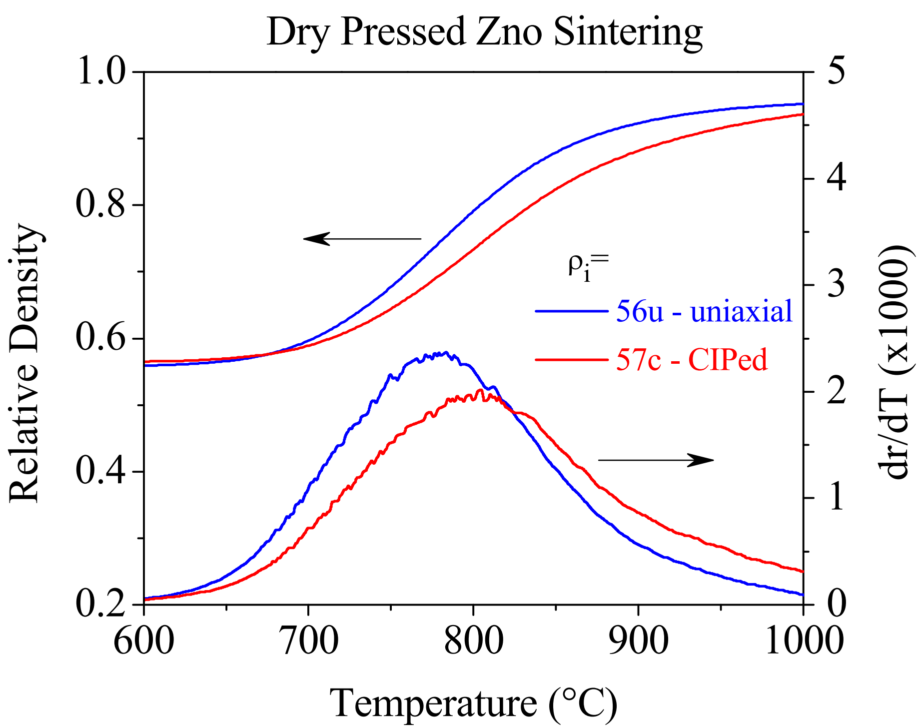
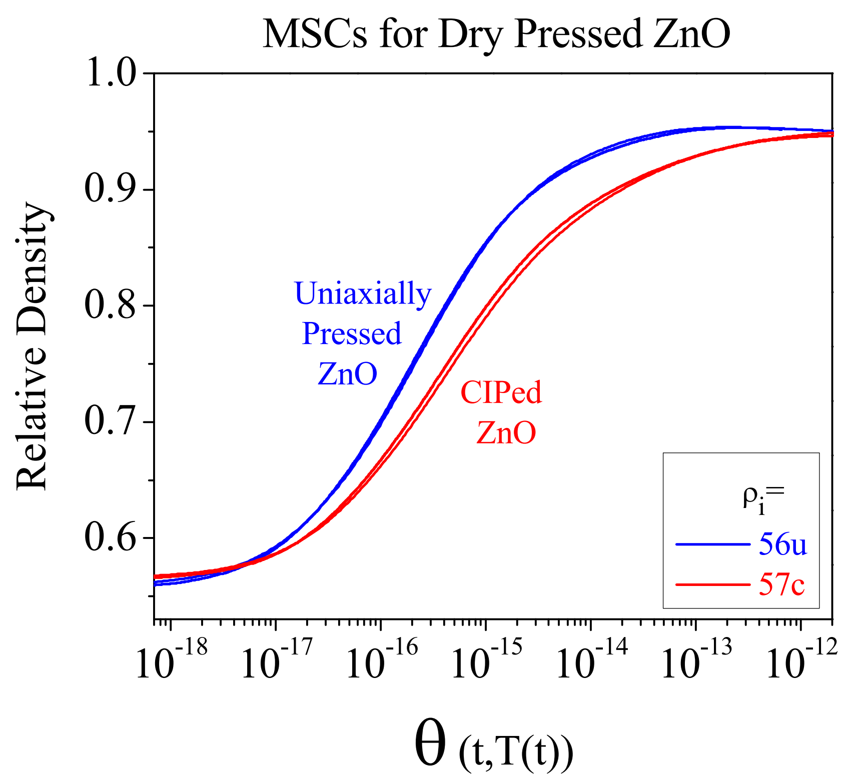
The MSC Provides Insight Into Process Improvements For Manufacturing





CIPed ZnO shows evidence of constrained sintering

Processing-induced constrained sintering may provide a path to more reproducibly manufacture controlled microstructure & property ceramics

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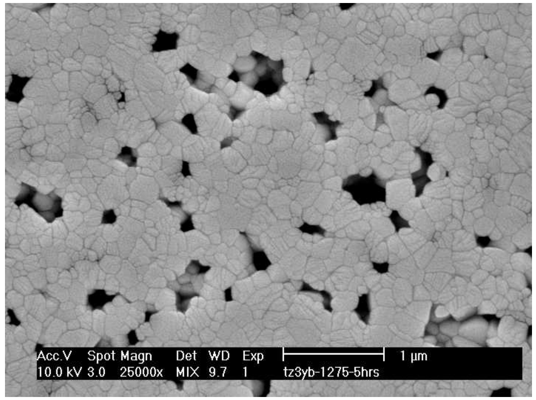
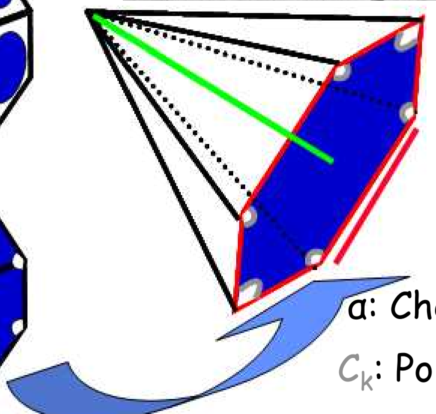
The C-SS Model Unit Cell Can Handle Microstructural Hierarchy





$$\Gamma_b = \frac{\alpha C_k C_b}{C_\lambda C_a C_h}$$

α: Chemical potential

C_k: Pore curvature

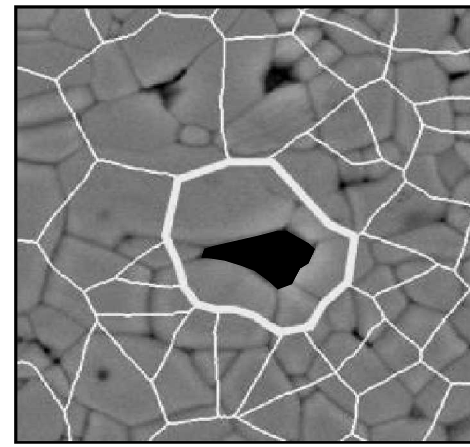
C_b: Grain boundary diffusion area

C_λ: Diffusion distance

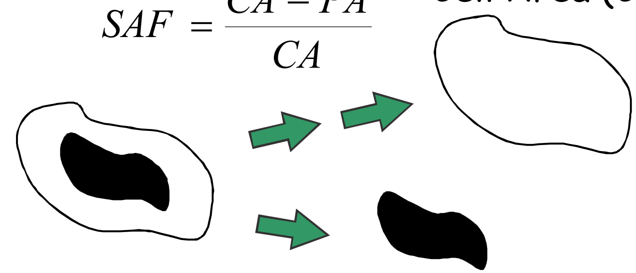
C_a: Cell area

C_h: Cell height

Heterogeneous Microstructure Can Be Characterized Using Pore Boundary Tessellation



$$SAF = \frac{CA - PA}{CA}$$



Hansen, Rusin, Teng, & Johnson, "Combined-Stage Sintering Model" J. Am. Ceram. Soc. **75** 1129-35 (1992)

- Mon Nov 17 10:00 - 10:20 AM - New Effective Diffusion Distance for Sintering Ceramic Microstructures, Chen, Nettleship, Hinklin, Ewsuk

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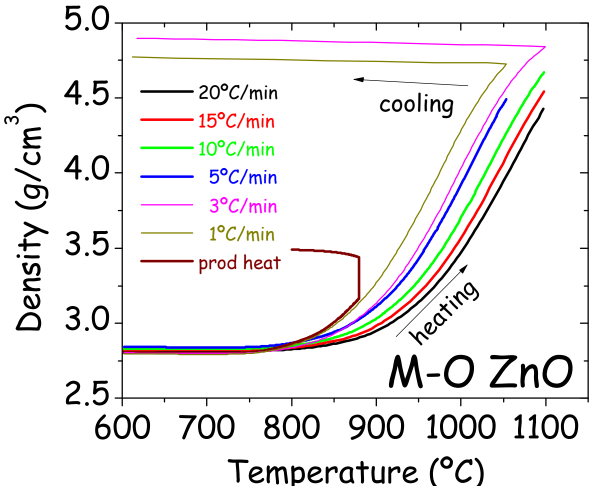
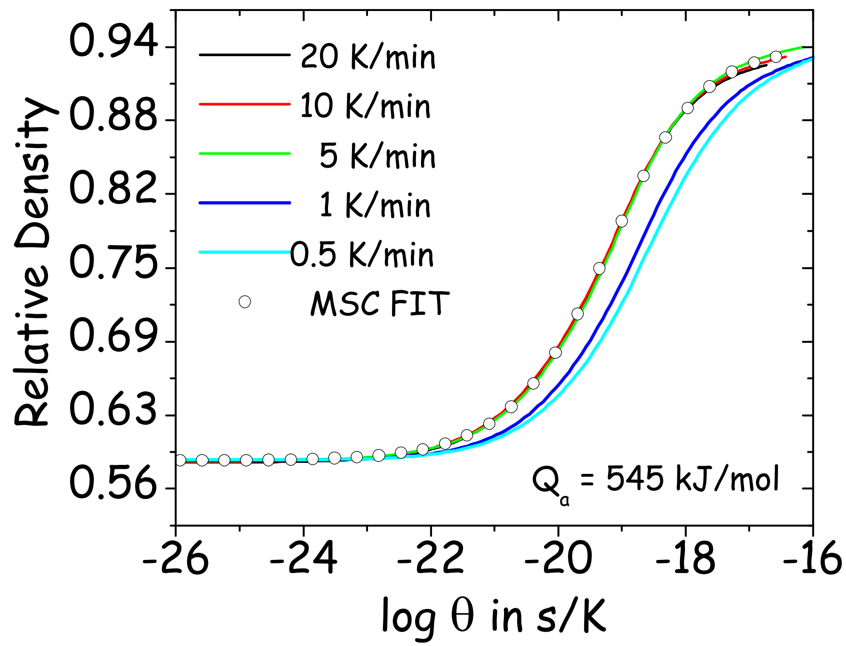
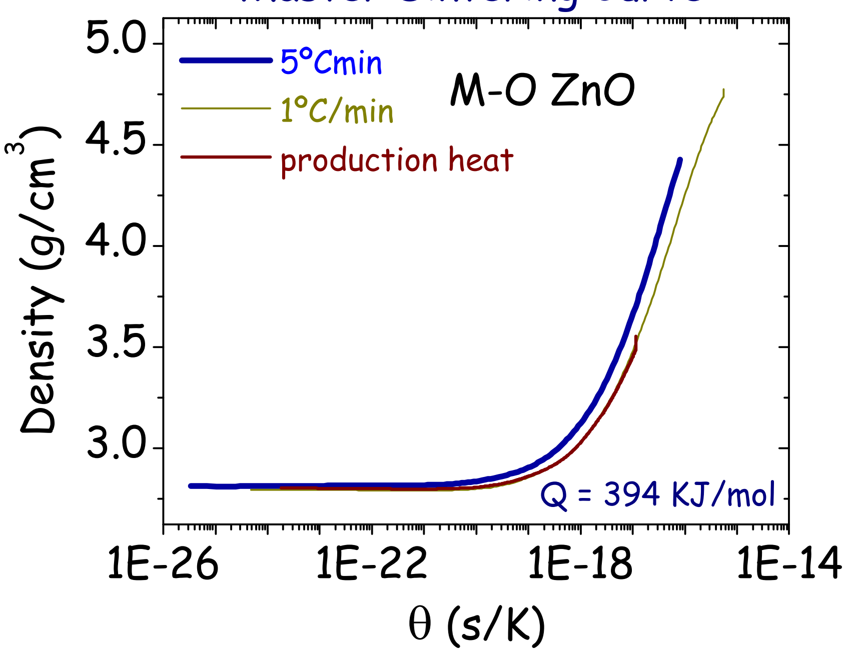
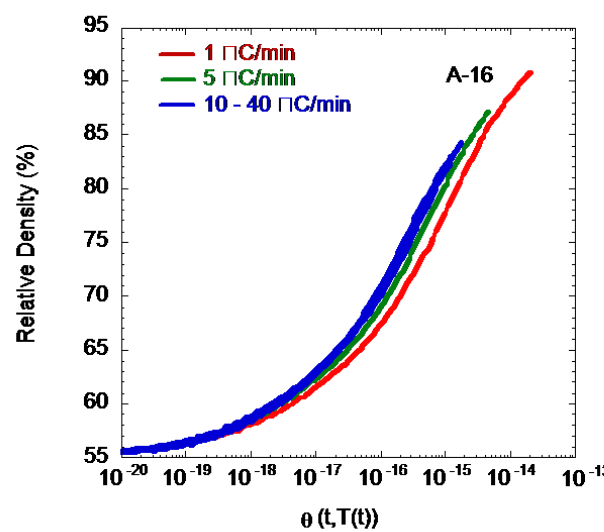
Low Heating Rate Sintering Data “Typically“ Deviate From The MSC



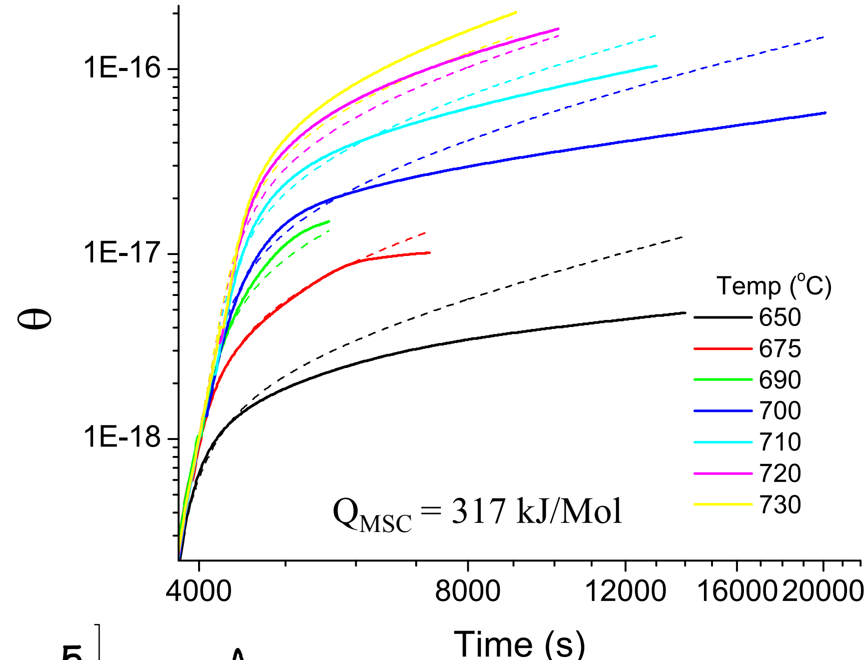


Master Sintering Curve



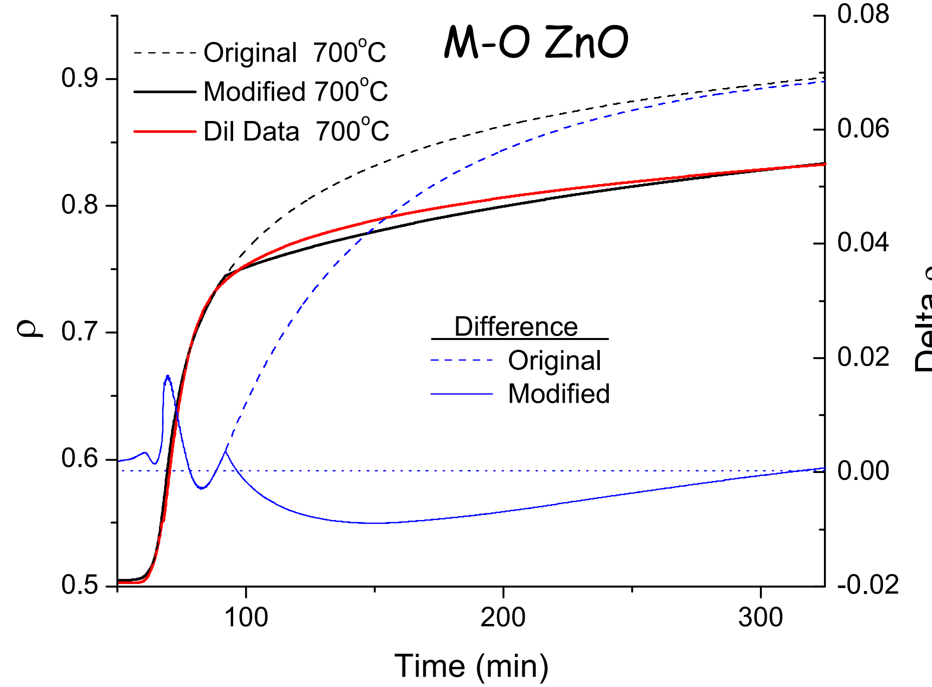


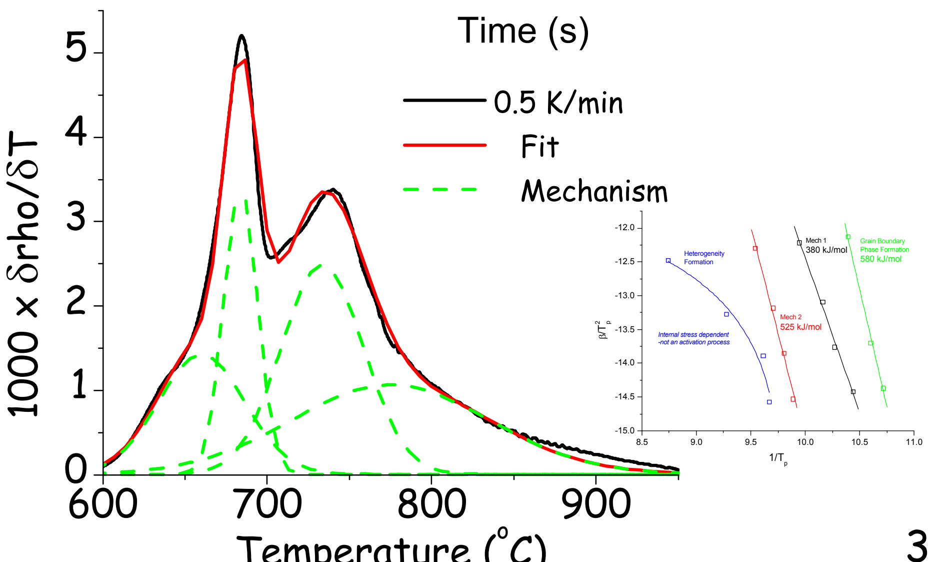
Multiple "Sintering" Mechanisms Have Been Addressed With A θ_{Drag} Term



$$\rho = \rho_o + \frac{\rho_f - \rho_o}{\left[1 + \exp\left(-\frac{\log(\theta) - \log(\theta_o)}{a}\right)\right]^b}$$

$$\rho_o = .506;\ \rho_f = 99.5;\ \theta_o\ \text{-}17.15;\ \mathrm{a} = 0.675;\ b = 1.72$$





The MSC Links To Other Sintering Models Through The Activation Energy

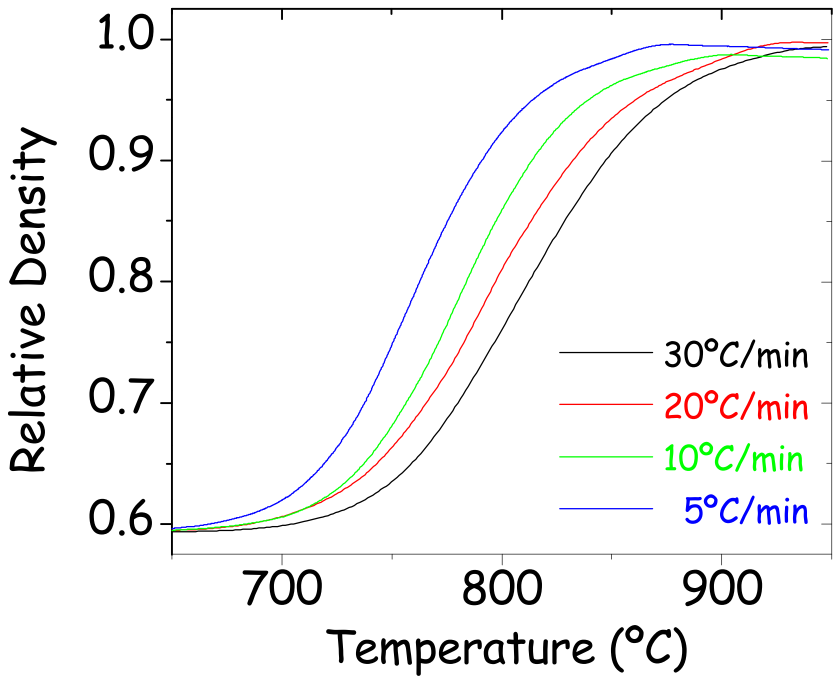
Master Sintering Curve (MSC)

$$\theta(t, T(t)) \equiv \int_0^t \frac{1}{T} e^{-\frac{Q_{MSC}}{RT}} dt$$

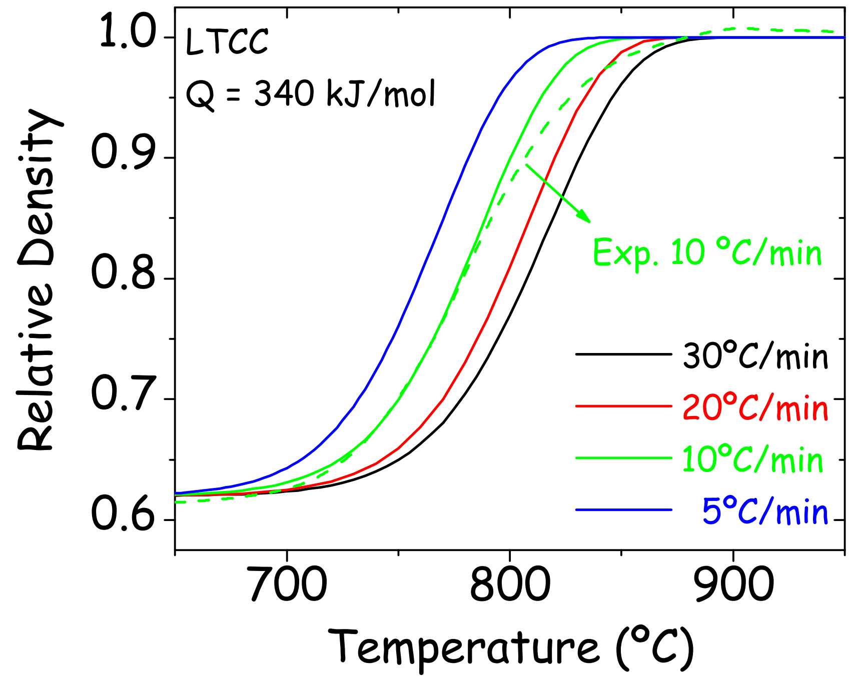
$\eta_o(T)$ function for SOVS Model

$$\eta_0(T) = A\,T\,e^{\frac{Q_{SOVS}}{RT}}$$

Measured LTCC Densification



Simulated LTCC Densification



- Mon Nov 17 3:00 – 3:20 PM "Analysis of Four Different Approaches to Predict and Control Sintering" Reiterer & G Ewsuk; - Tue Nov 18 10:00 – 10:20 AM "Verification, Performance, and Validation of a Modified SOVS Continuum Constitutive Model in a Nonlinear Large-Deformation Finite Element Code" Arguello, Ewsuk, & Reiterer

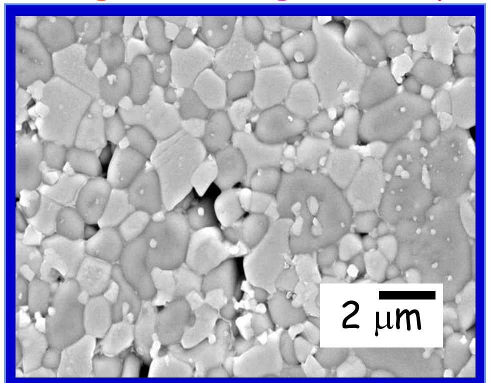
Summary

I. The MSC Can Be Applied to Many/Most Sintering
   A. Systems Solid-State Sintering
      1. Micro & Nanocrystalline
   B. Liquid-Phase Sintering
      1. Reactive glass, viscous/anisotropic, & reactive LPS
   C. Composite Sintering
- The MSC has Broad Application for Process Understanding/Control
   A. Predicting Density for t-T Profiles and reverse
   B. Process (Sensitivity) Understanding & Control
      1. Green Microstructure/Density, Heating Rate
   C. Materials & Process Quality Control
- The Master Microstructure-Density Curve Enables Fundamental Insight
   A. Controlled Processing-Microstructure- Properties
   B. Deviations from the MSC / Microstructure-Density Curve
      1. Grain Growth
      2. Heterogeneous Microstructure Evolution
         a. Effective Diffusion Distance
         b. Self-Constrained Sintering
      3. Multiple Mechanisms
         a. Theta Drag Correction

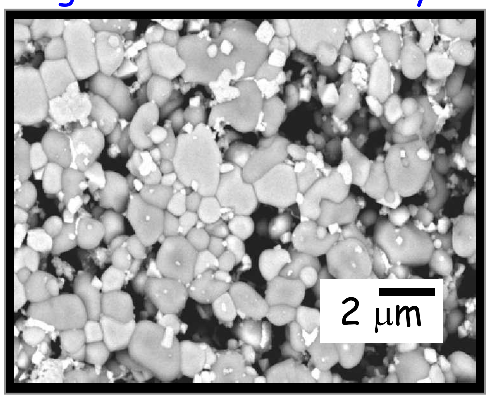
I. The MSC can be Linked to Other Sintering Models

The Master Sintering Curve Links Processing, Microstructure, & Properties

10°C/min to 1050°C
(4.65 g/cm³) "High density"

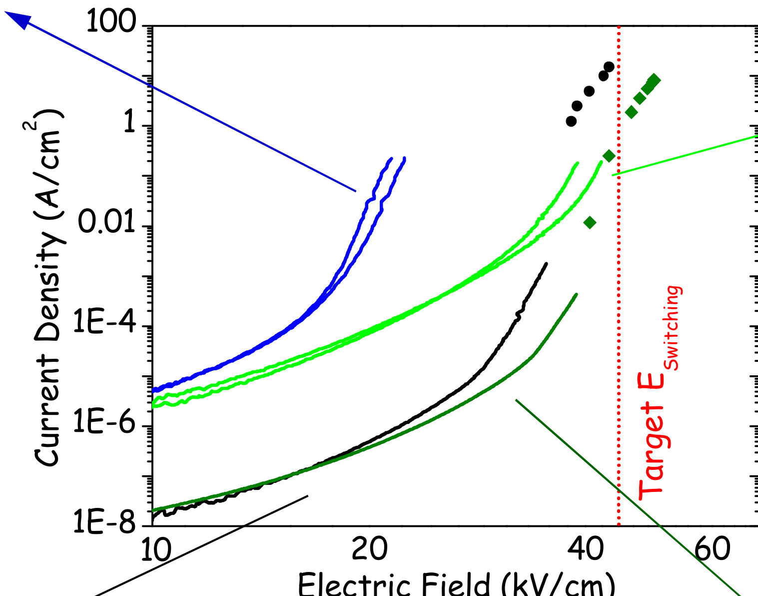


$E_{switching}$ decreases with grain size and density



~0.5°C/min to 880°C
(3.55 g/cm³)
"Production Heat"

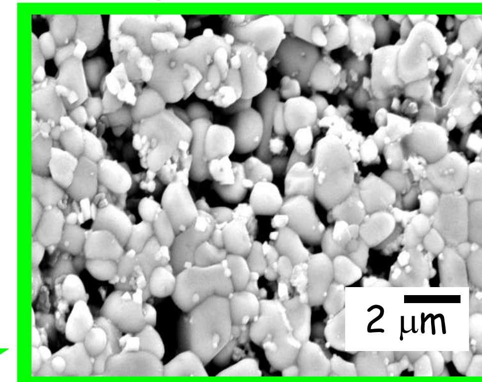
MSC-derived sintering profiles were used to control ZnO varistor processing to systematically control density, microstructure & electrical properties



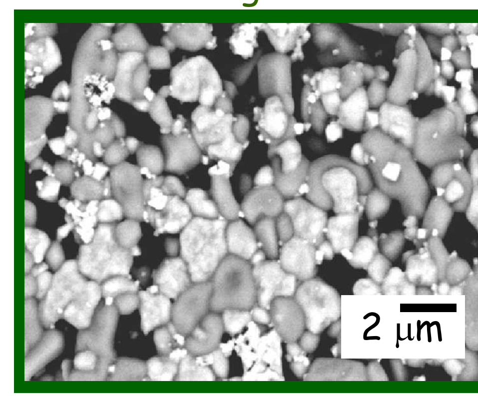
Like Microstructure

Varistors Have
Similar Like Properties

5°C/min to 960°C
(3.52 g/cm³)"Fast Cool"



Slow cooling reduces the leakage current



20°C/min to 980°C
(3.51 g/cm³) "Slow Cool"

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