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Controlled Processing, Microstructure, & Properties of ZnO-Based Varistors

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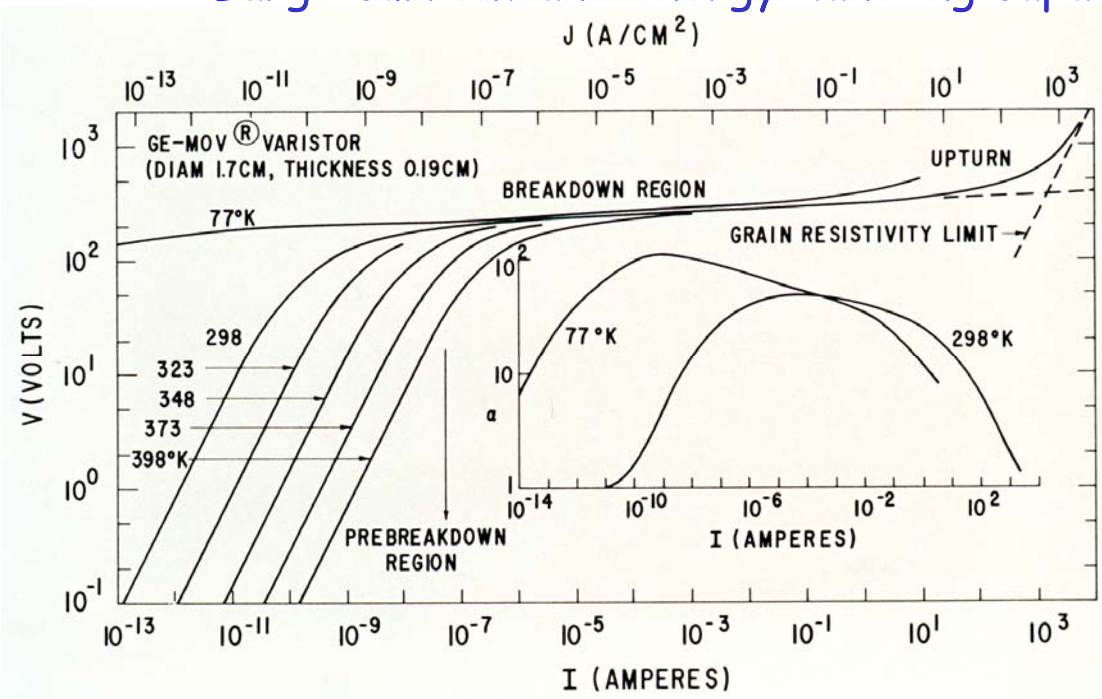
Varistors Have Highly Nonlinear Current-Voltage (I-V) Characteristics

- ZnO Varistor
  - Ceramic semiconductor based on zinc oxide and dopant elements
  - Highly nonlinear current-voltage (I-V) characteristics
    - » Large current and energy handling capabilities



Nonlinearity Coefficient,

$$\alpha = \Delta\ln(J) / \Delta\ln(E)$$

Levinson, L. M. "Zinc Oxide Varistors – A Review"
Amer. Ceram. Soc. Bull., **65** No. 4 (1986)

Dopants Are Used To Control The ZnO Varistor Properties

Varistor Composition

- **ZnO 81.45 mol%**
- Bi_2O_3 2.43 mol%
- CoO 0.87 mol%
- MnO_2 0.45 mol%,
- Sb_2O_3 3.04 mol %
- Cr_2O_3 0.79 mol%
- SiO_2 9.84 mol%
- NiO 0.78 mol%
- H_3BO_3 0.13 mol%
- $BaCO_3$ 0.21 mole
- Al 0.01 mol%

Typical Role of Dopant

- Non-linearity enhancer – Co, Mn
- Non-linearity inducer – Bi
- Grain growth retardant – Si, Sb
- Grain growth enhancer – Al
- Stability Enhancer - Na
- ZnO conductivity enhancer – Al

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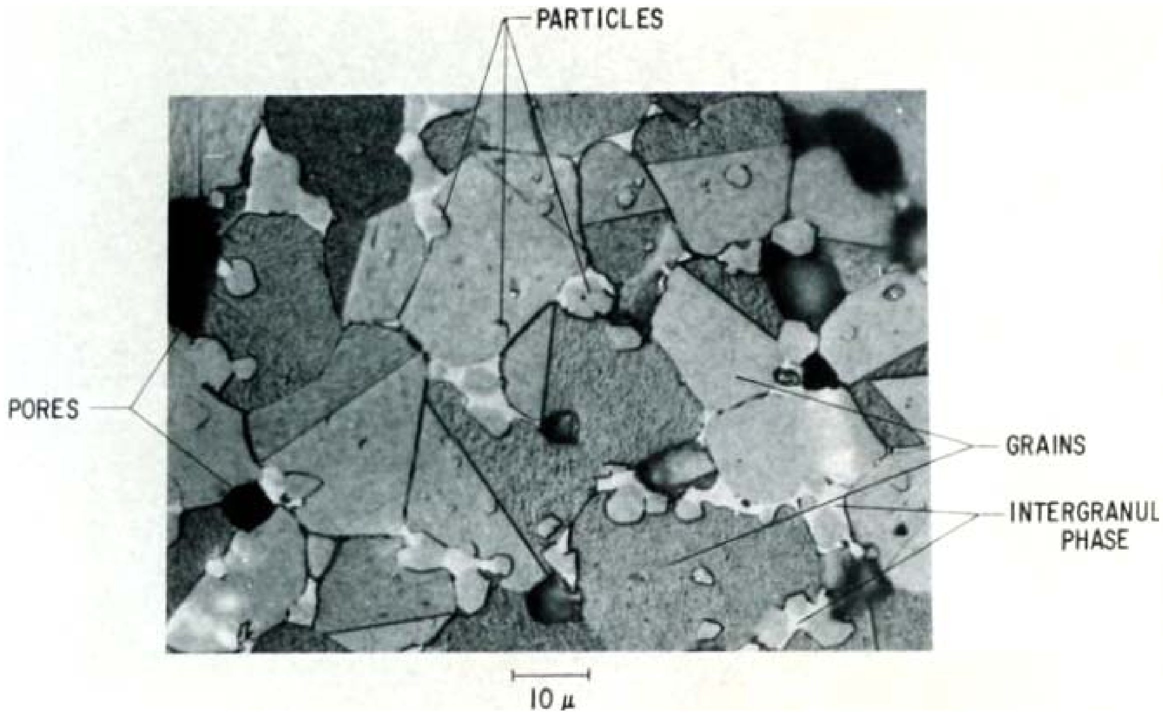
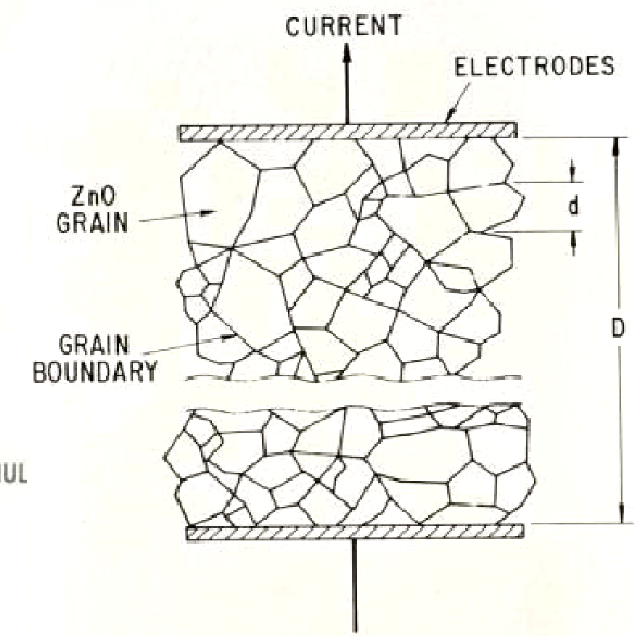
The Varistor Microstructure Produces The I-V Characteristics

- ZnO Varistor
  - Conductive ZnO grains are surrounded by an insulating grain boundary





  - Microstructure (e.g., GS, ρ, GB chemistry) and dimensions control properties

Levinson, L. M. "Zinc Oxide Varistors – A Review"
Amer. Ceram. Soc. Bull., **65** No. 4 (1986)

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Science-Based Processing Can Be Used To Control Microstructure & Properties

- Varistors regulate voltage to protect electrical circuits
  - Limit voltage applied to devices or components
- Microstructure determines varistor properties
  - Grain size, the grain boundary, & density affect I-V characteristics
  - Small flaws and/or inhomogeneities can result in high-voltage breakdown
- Processing controls microstructure & properties
  - The Master Sintering Curve (MSC) approach can be applied

Clarke, D.R., "Varistor Ceramics"
J. Am. Ceram. Soc., **82** [3] 485-502 (1999)

The Master Sintering Curve (MSC) Links Processing & Microstructure

Key Equations

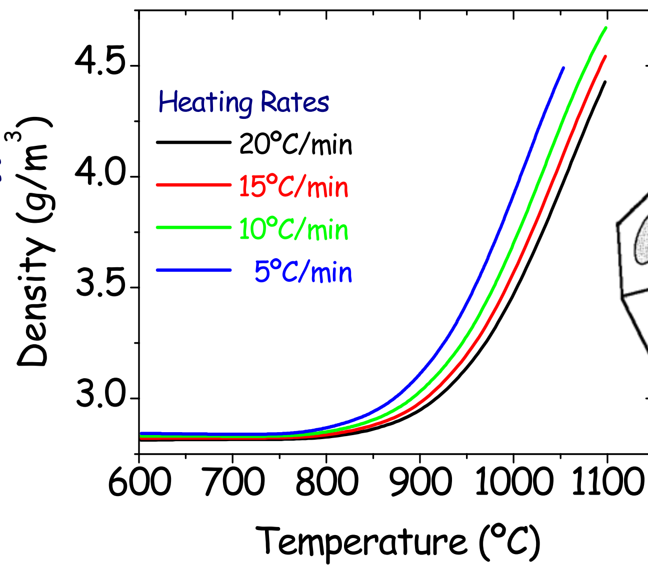
Instantaneous linear shrinkage:

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

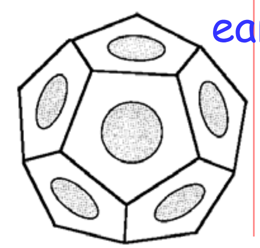
For one dominant mechanism:

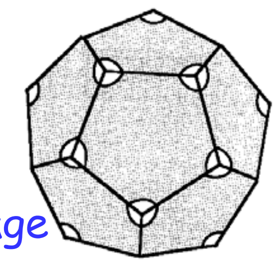
$$\int_{\rho_0}^{\rho}\frac{(G(\rho))^n}{3\rho\Gamma(\rho)}d\rho=\int_0^t\frac{\gamma_s\Omega D_0}{kT}e^{-\frac{Q_{app}}{RT}}dt$$

Varistor Densification Curves



early stage





late stage

Microstructure & Properties: time-Temperature profile:

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

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

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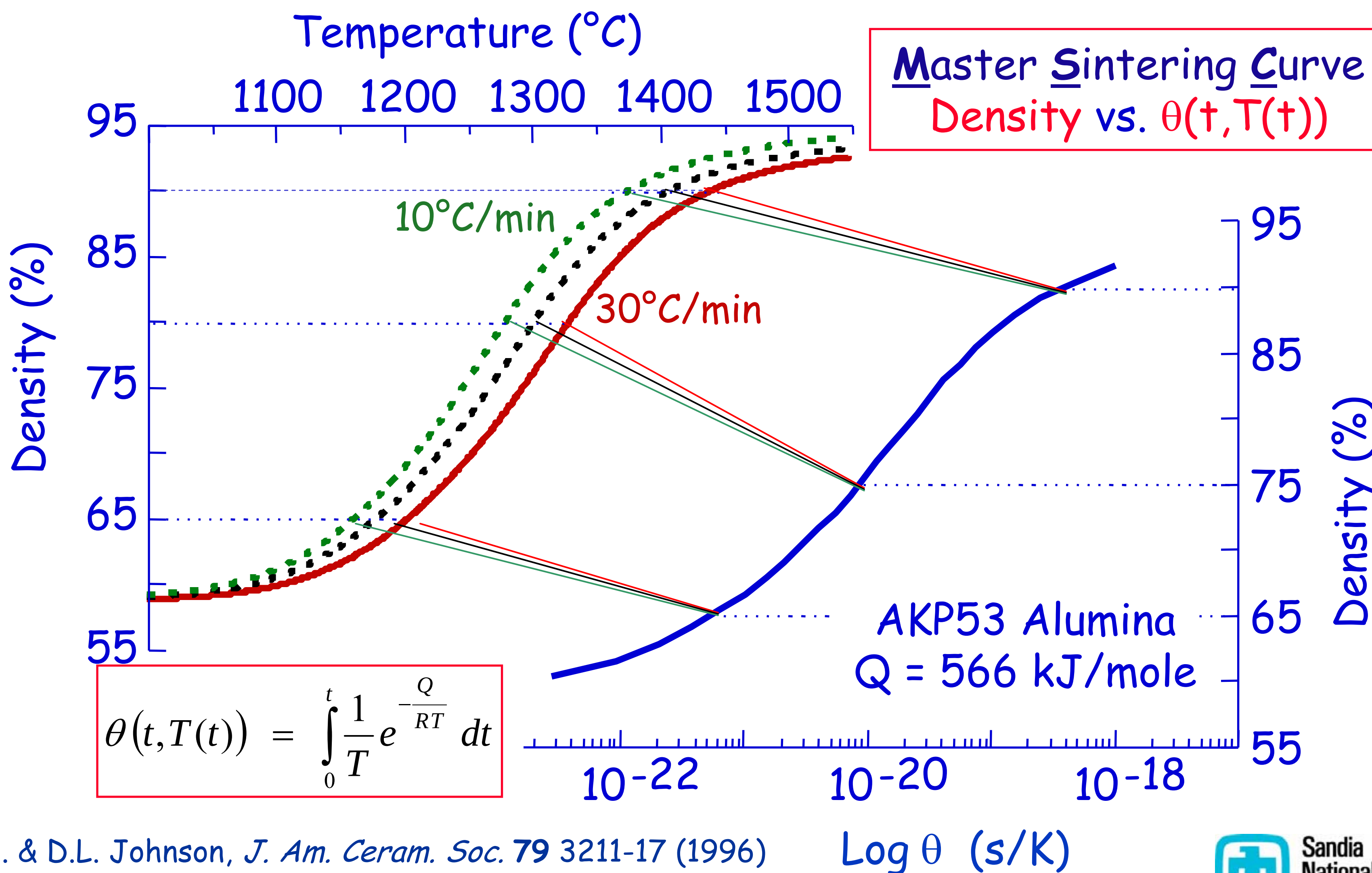
The MSC Can Be Used To Predict And Control Densification



Master Sintering Curve
Density vs. θ(t,T(t))

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

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

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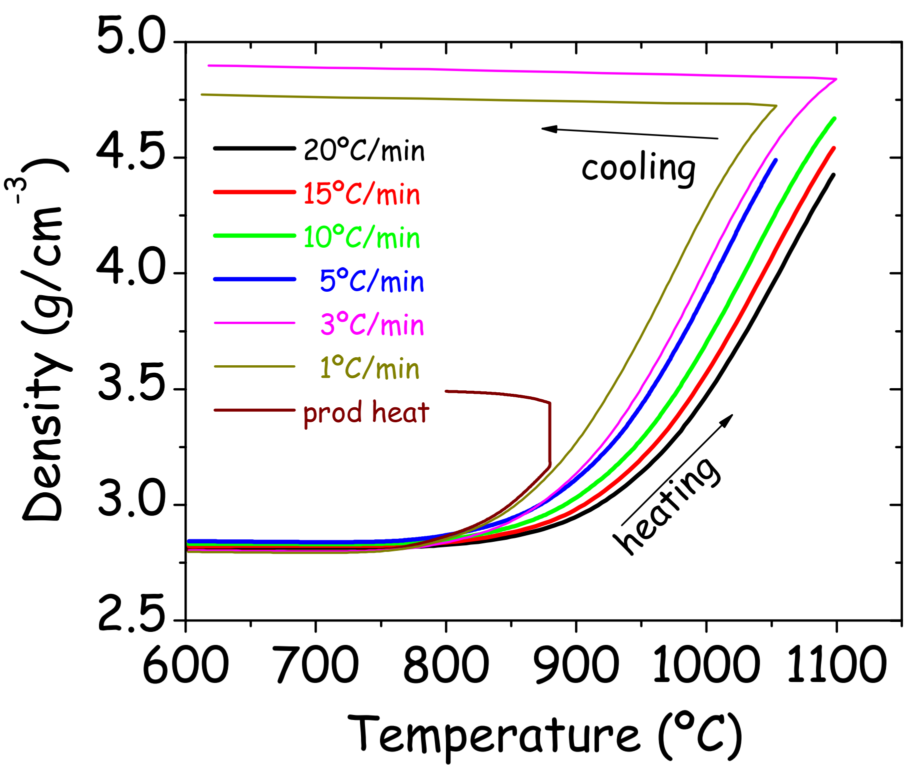
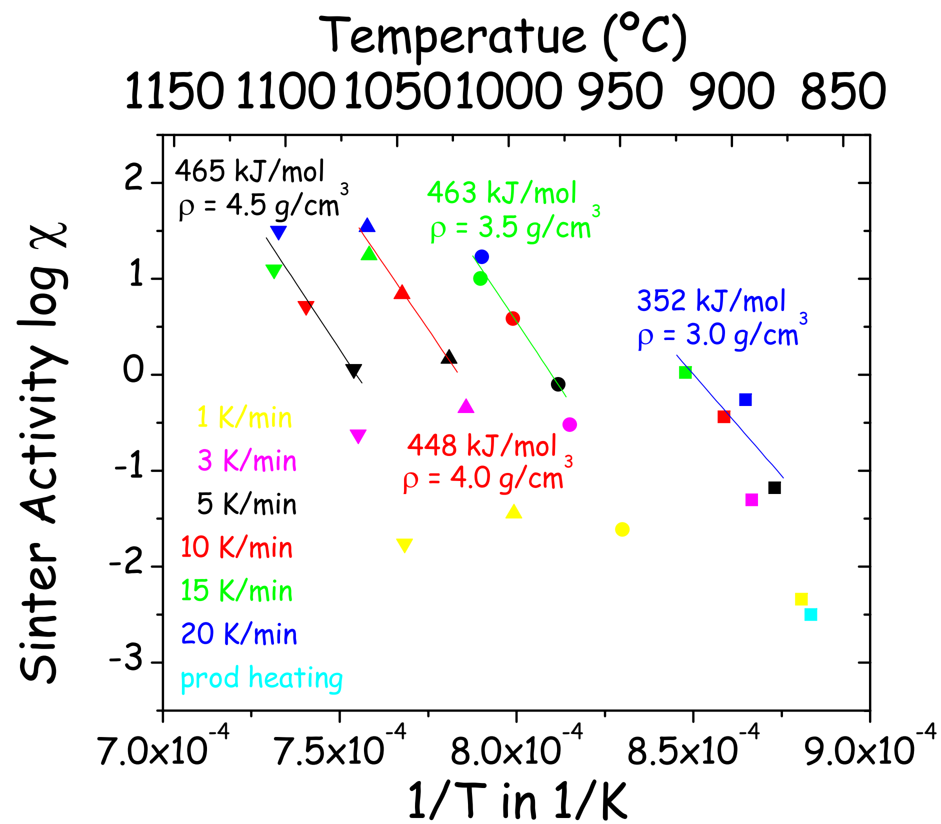
The Activation Energy Was Determind From The Sintering Data

An activation energy (Q) of 394 kJ/mole was calculated for densification of the mixed-oxide (M-O) varistor

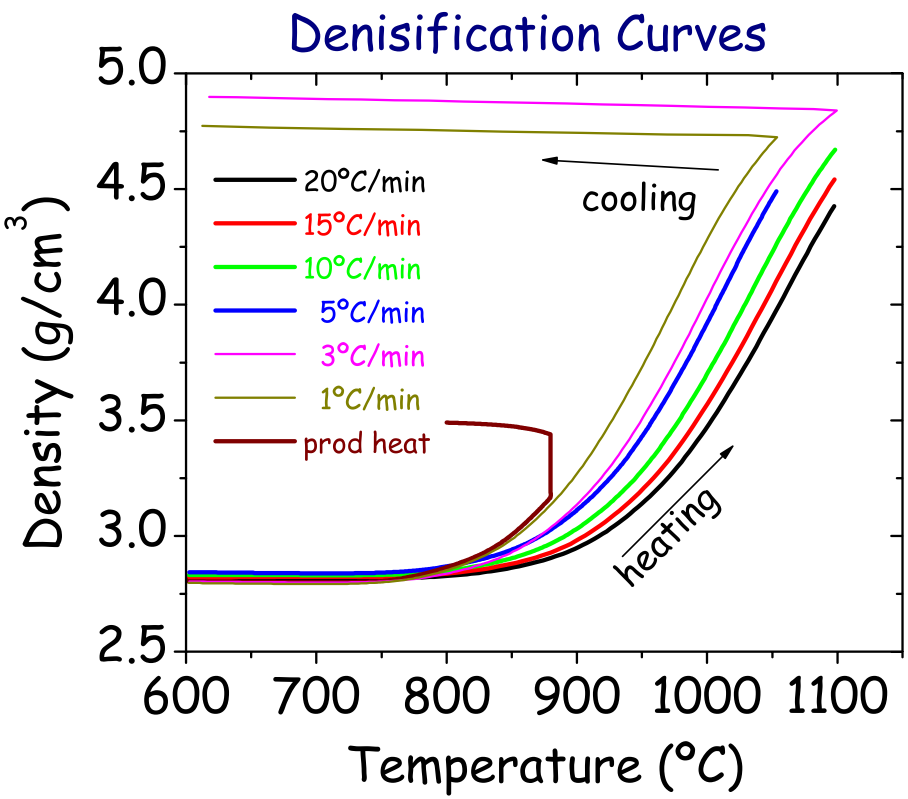
MO Varistor Denisification

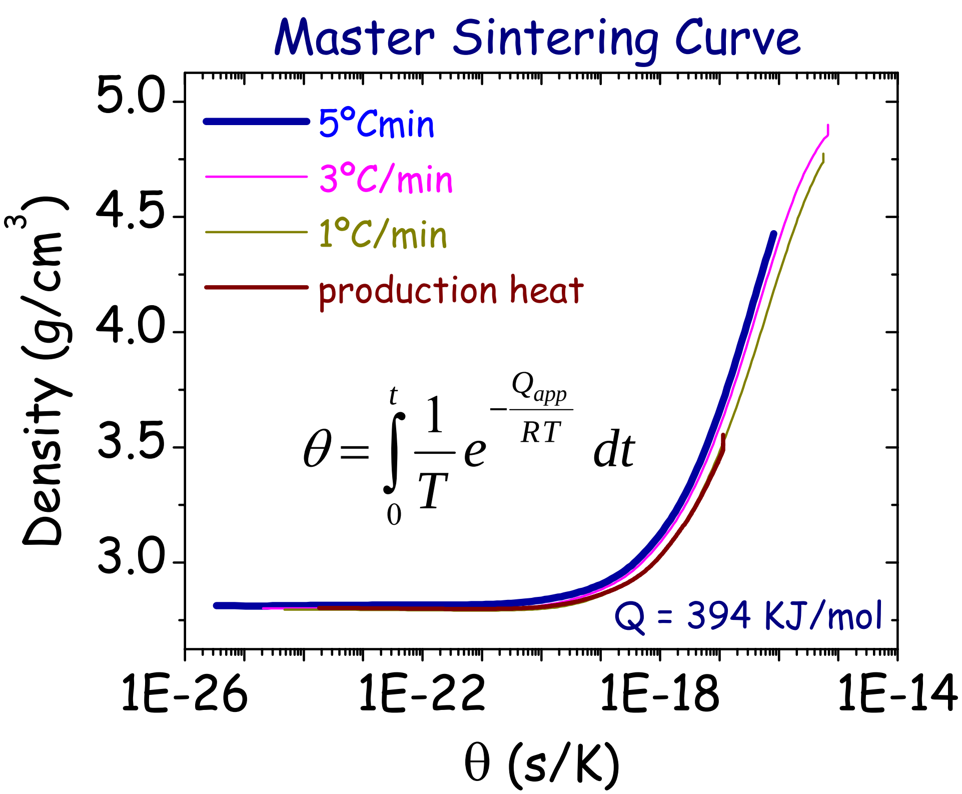




A Master Sintering Curve Was Constructed For The M-O Varistor

The 5-20°C/min shrinkage data collapse onto a MSC





Heating rates <5°C/min do <u>NOT</u> fall on the MSC

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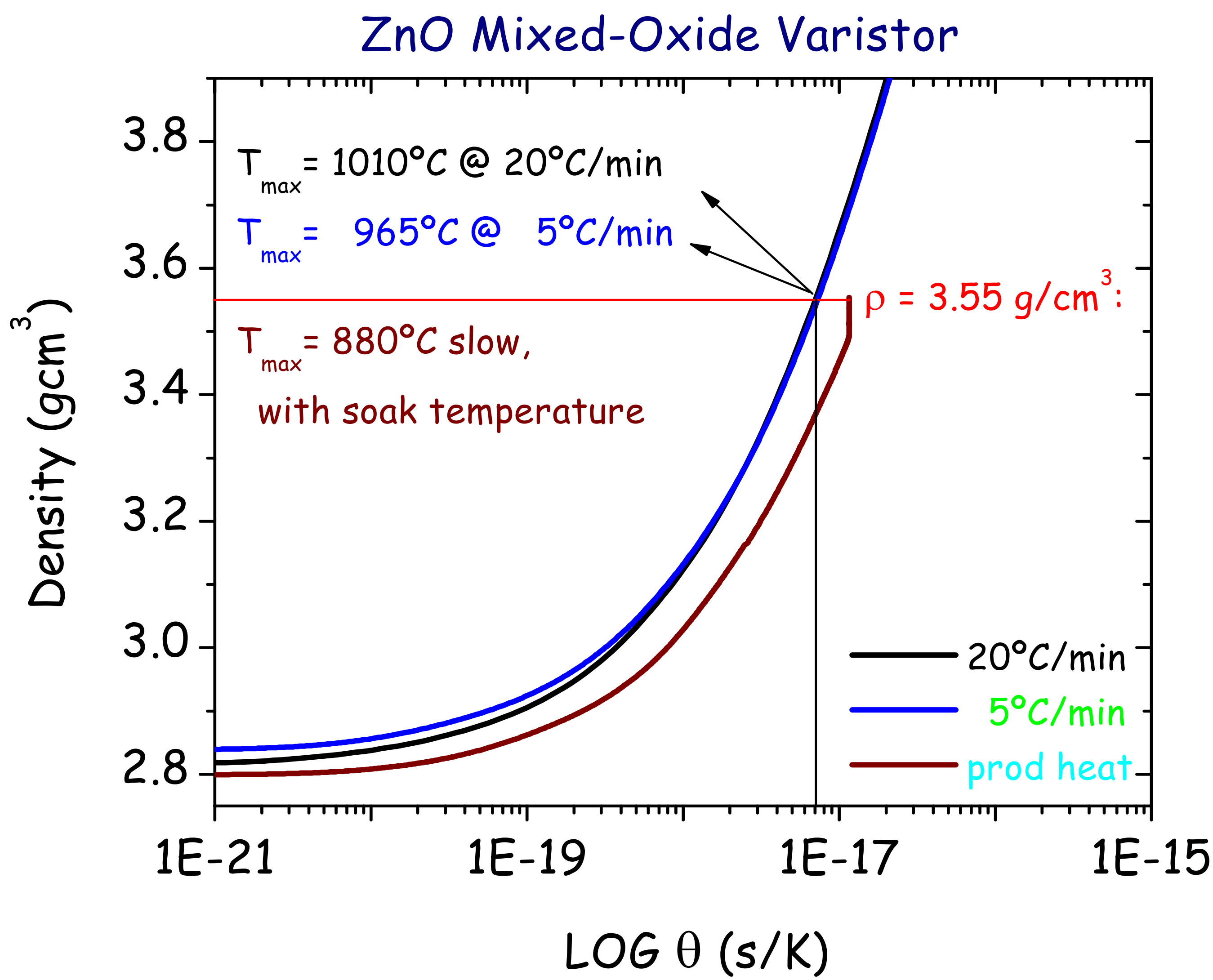
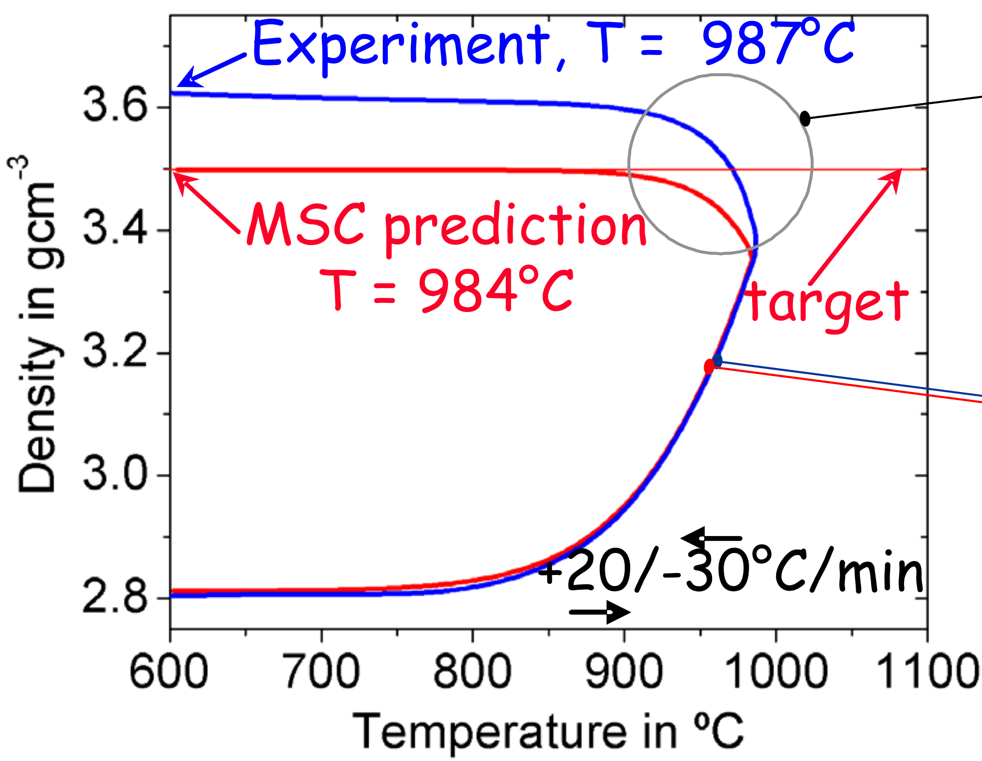
MSC Derived Temperature-time Sintering Profiles Were Designed



MSC Predictions Reveal A Sensitive Sintering Process

ZnO Mixed-Oxide Varistor

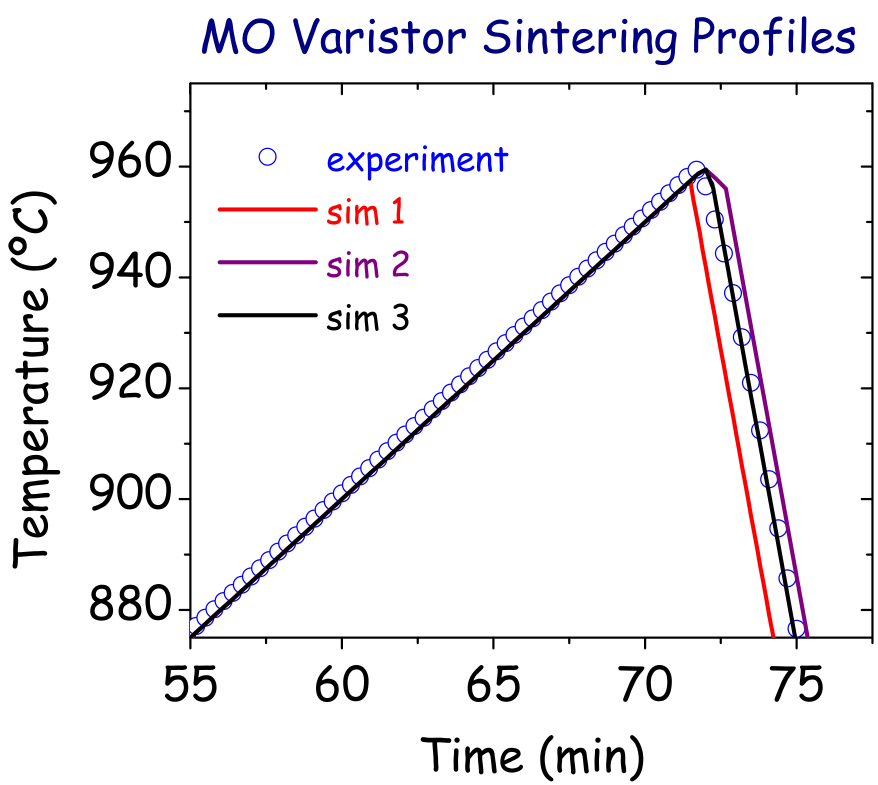


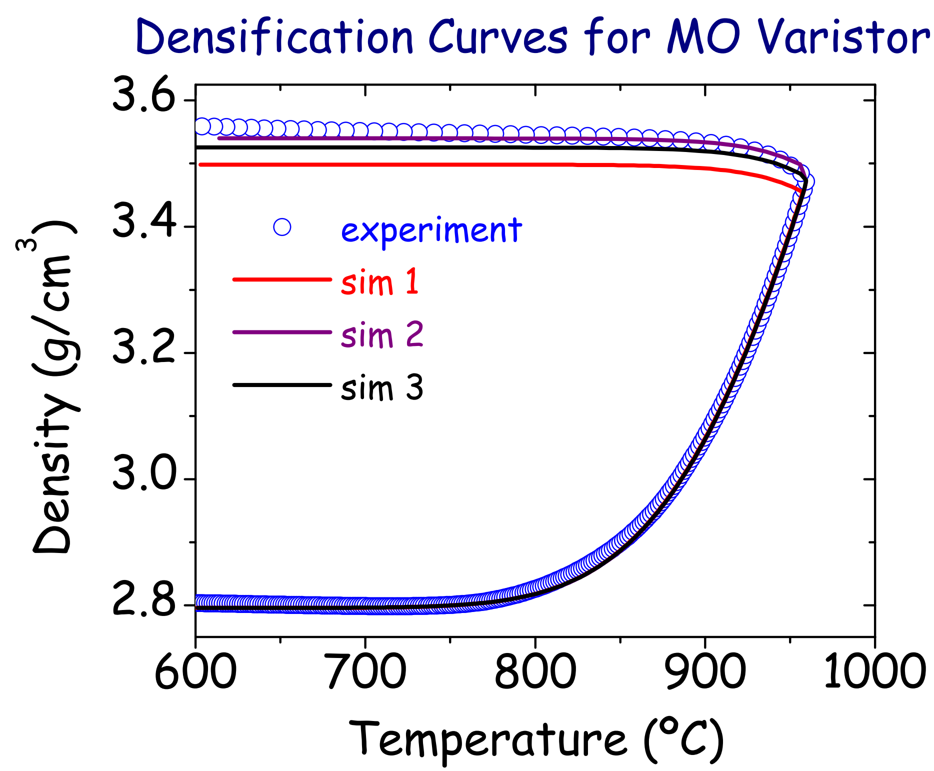
- Modeling varistor firing revealed process sensitivity
- Predictive modeling was used to design & control varistor firing

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

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

MSC predictions are validated by experimental results





The MSC accurately predicts densification

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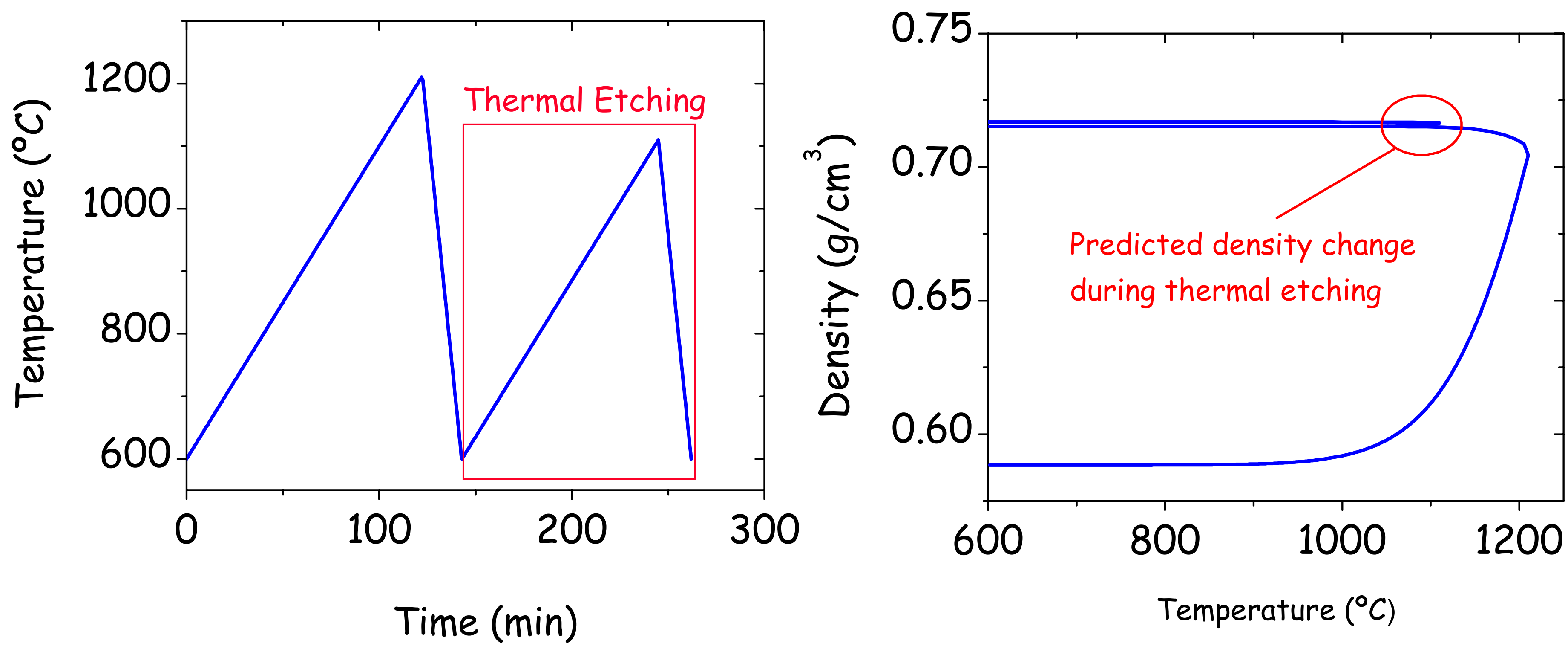
Quantitative Microstructure Analysis Was Aided By MSC-Based Calculations

MSC derived T-t profiles allow for thermal etching without changing the density and microstructure



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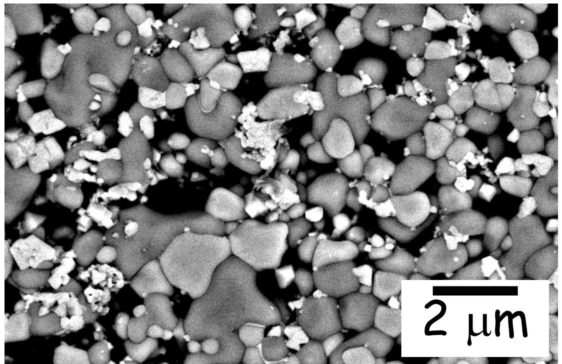
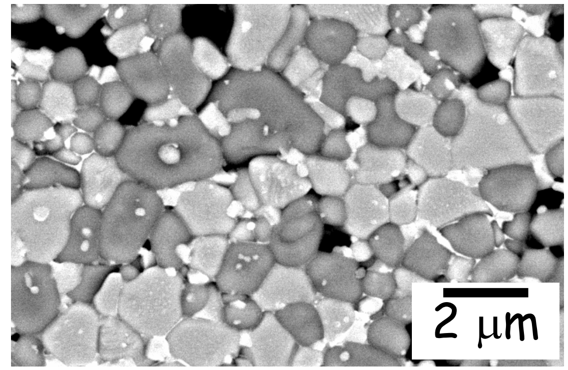
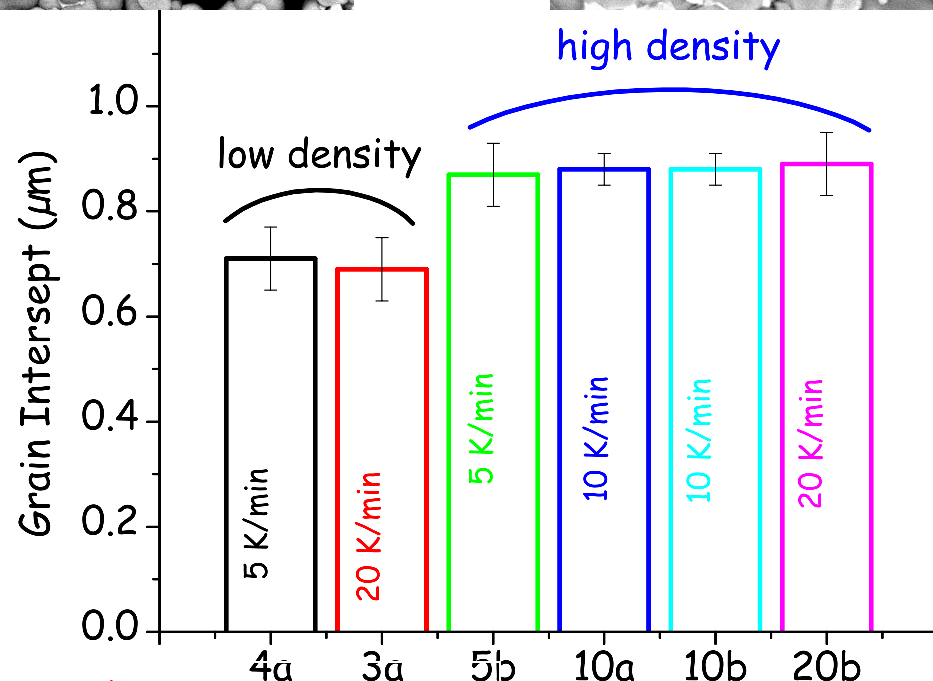
MSC T-t Profiles Produce The Same Microstructure At The Same Density







The MSC facilitates the processing of controlled microstructure ceramics

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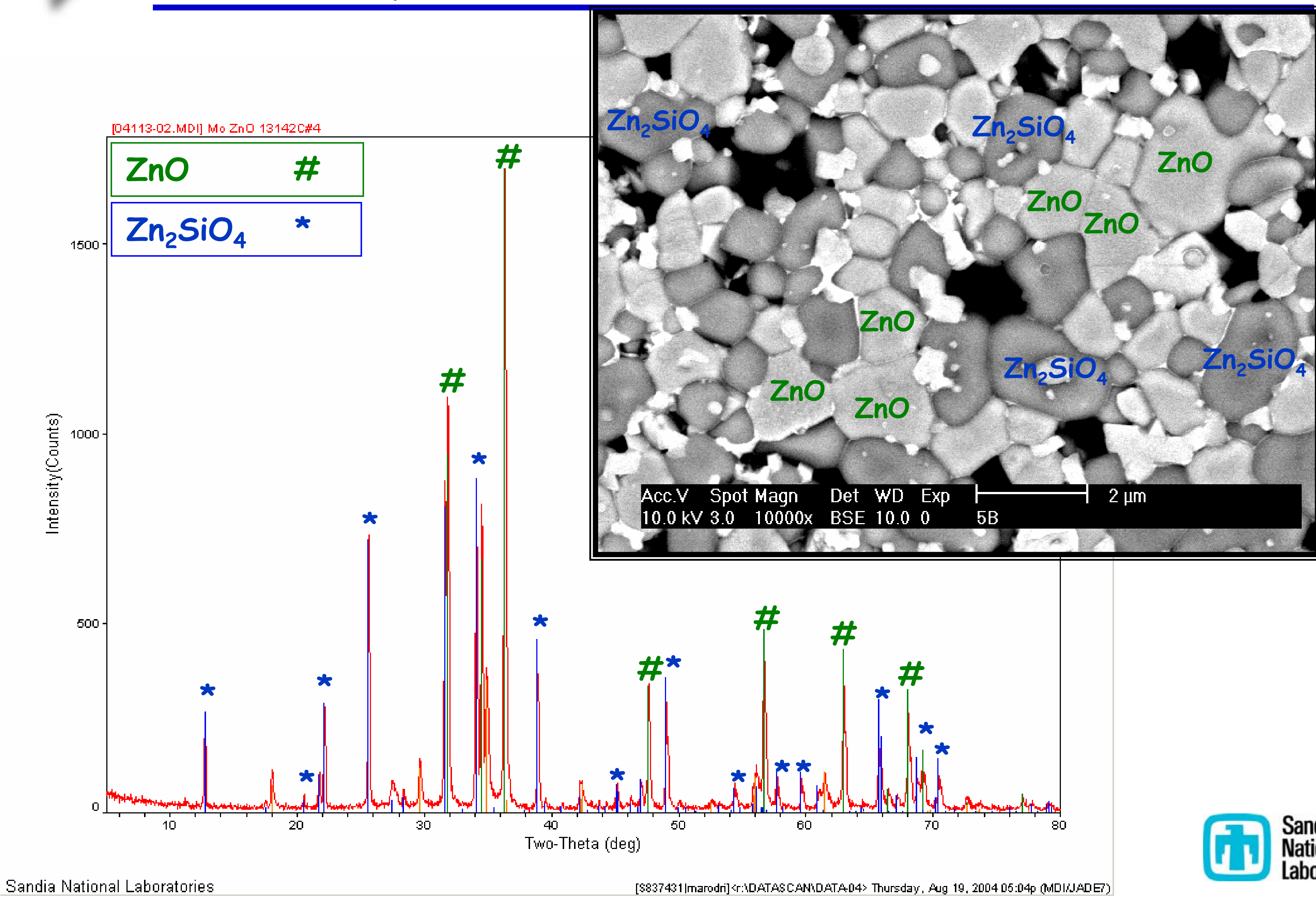
XRD Analysis Reveals Two Major Crystalline Phases – ZnO & $ZnSiO_4$



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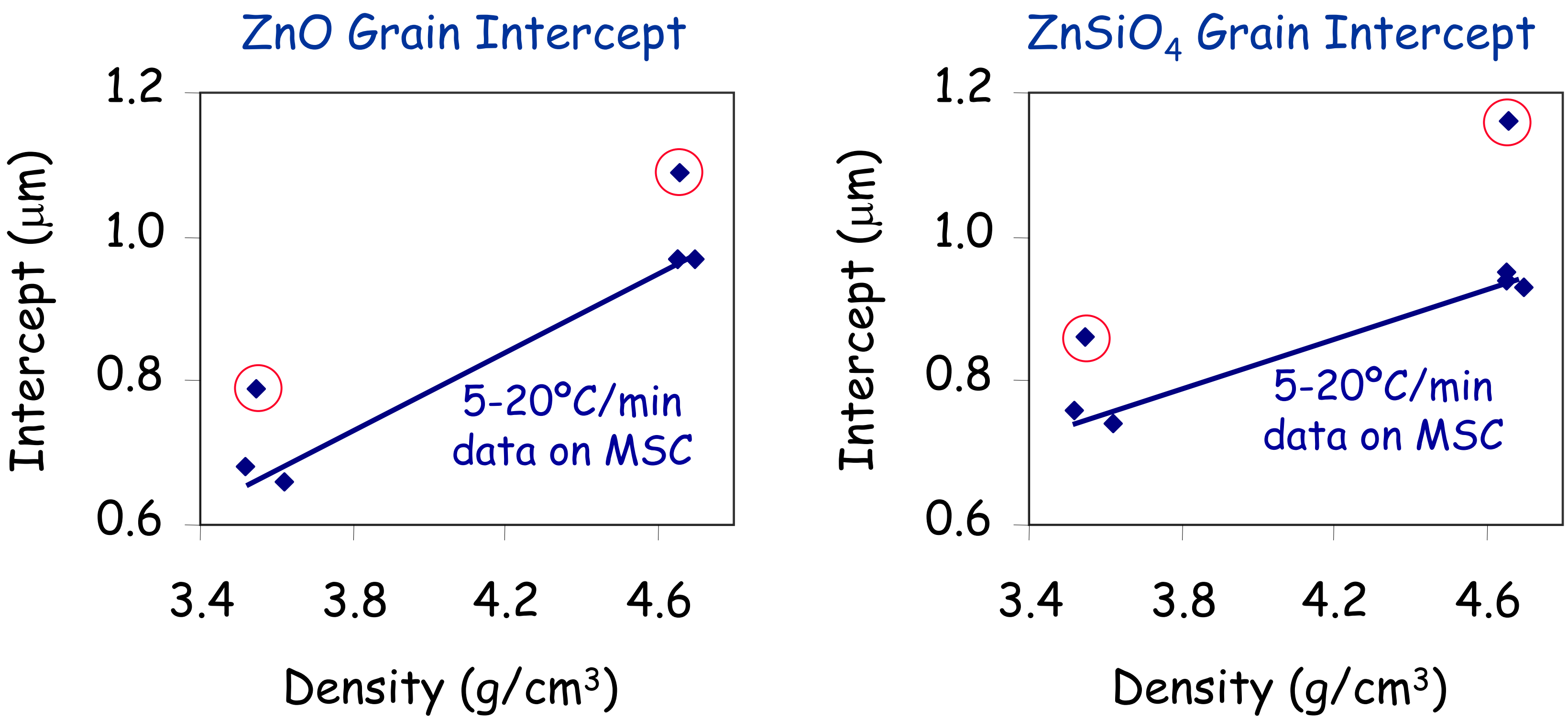
Varistors Sintered To The Same MSC Density Have The Same Grain Size

Sintered ZnO Mixed-Oxide Varistor Microstructure

MSC Densities

Sample	Density (g/cc)	ZnO Avg. Grain Intercept (μm)	$ZnSiO_4$ Avg. Grain Intercept (μm)
Production Heat ~0.5°C/min to 880°C	3.55	0.74±0.08	0.81±0.03
4a: 5°C/min to 960°C	3.52	0.63±0.06	0.71±0.06
3a: 20°C/min to 985°C	3.62	0.61±0.05	0.69±0.06
10b: 10°C/min to 1100°C	4.65	0.92±0.06	0.90±0.09
20b: 20°C/min to 1100°C	4.65	0.92±0.04	0.89±0.06
10a: 10°C/min to 1100°C	4.70	0.92±0.06	0.88±0.03
1a: 1°C/min to 1055°C	4.66	1.04±0.08	1.11±0.06

The Results Support A Master Density-Microstructure Trajectory



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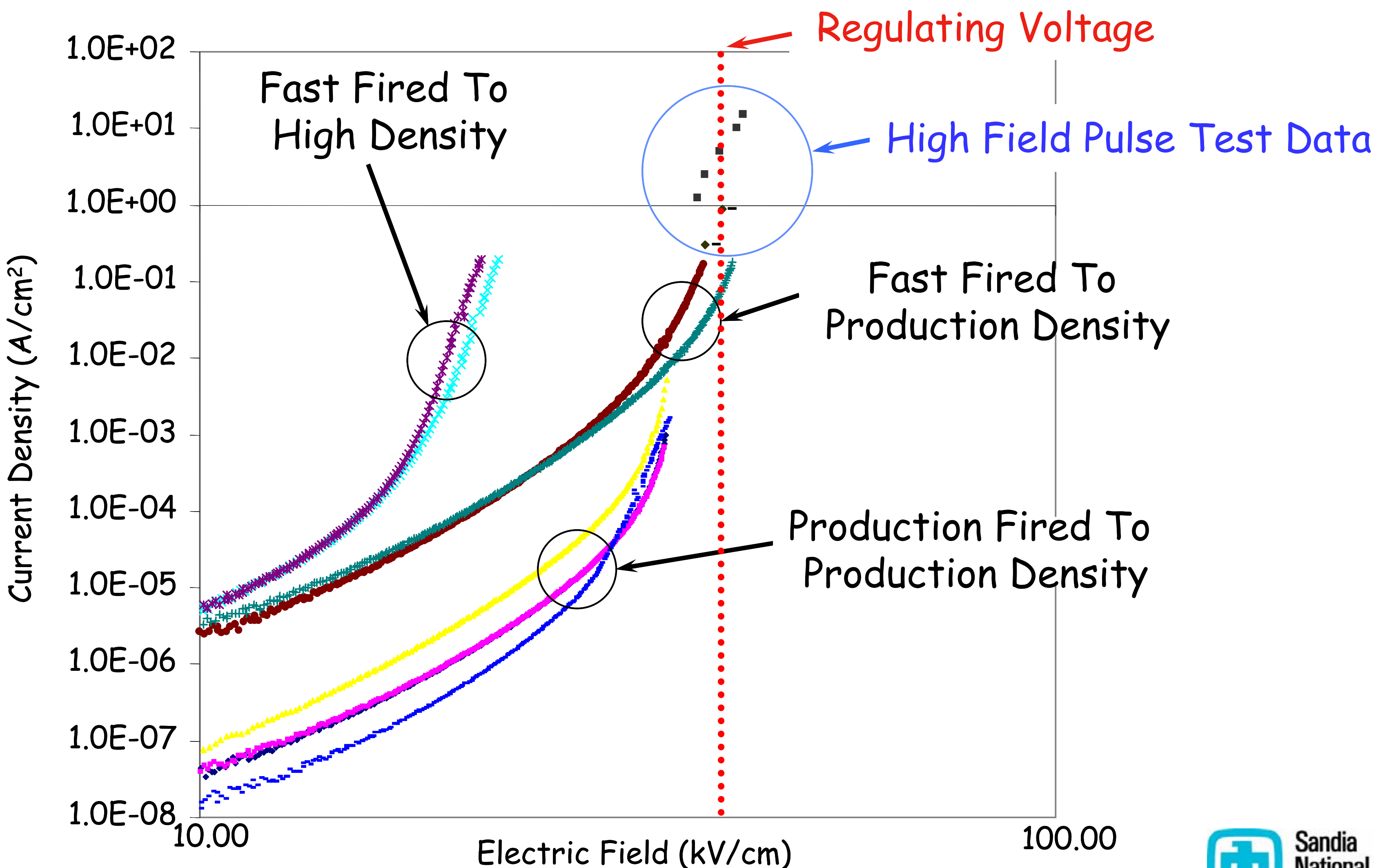
Comparable Density & GS Varistors Have The Same Regulating Voltage



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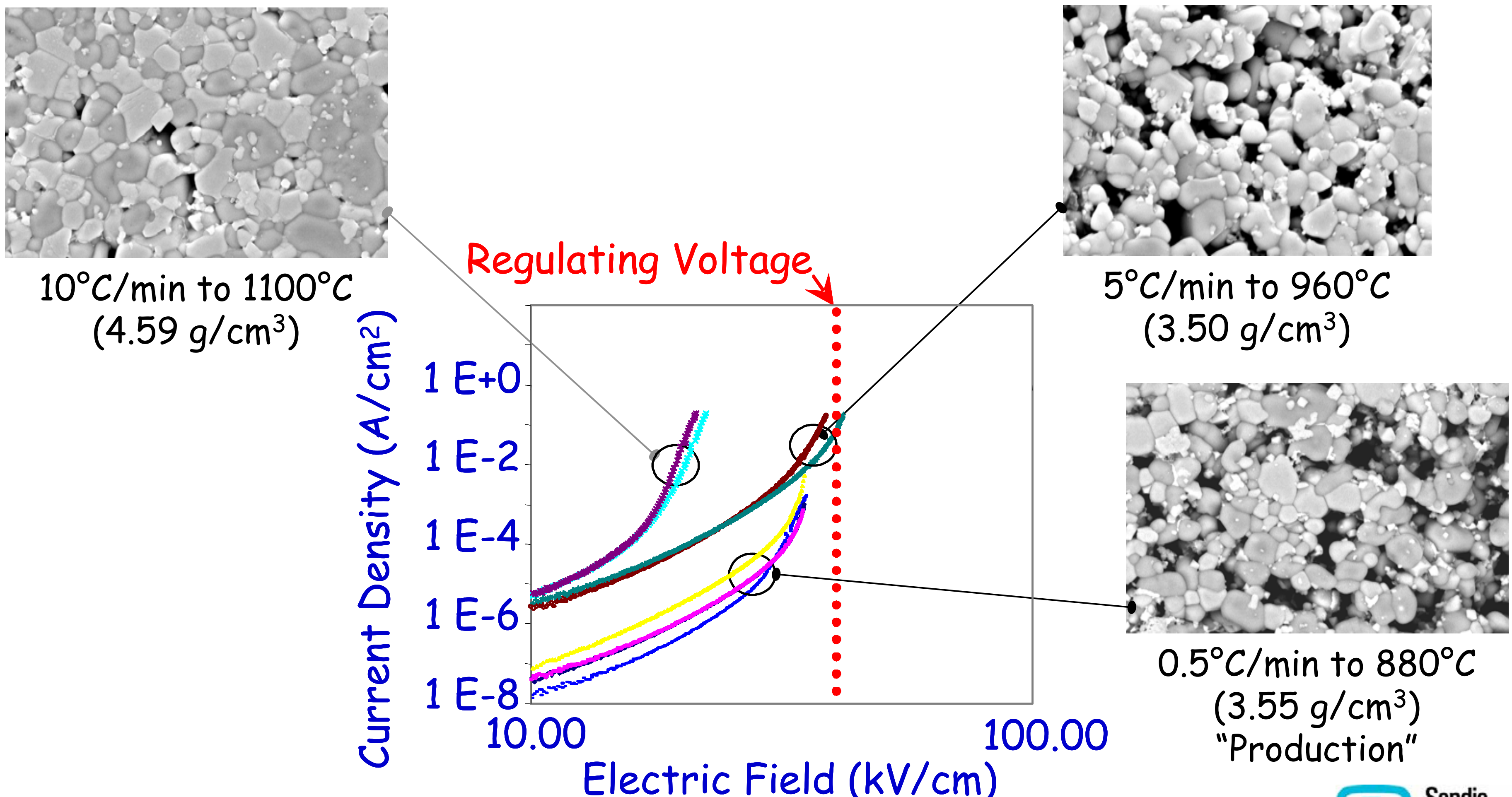
Controlled Microstructure And Property Varistors Were Produced

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



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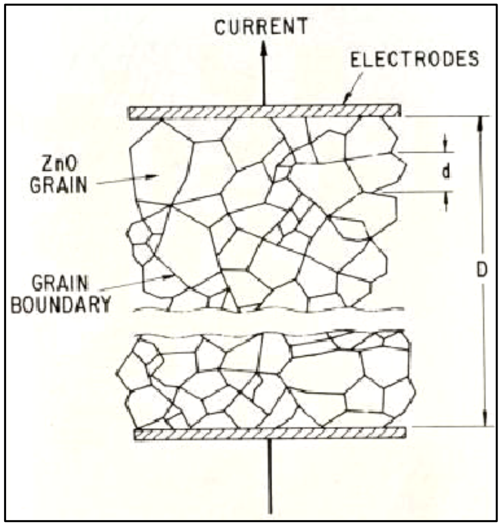
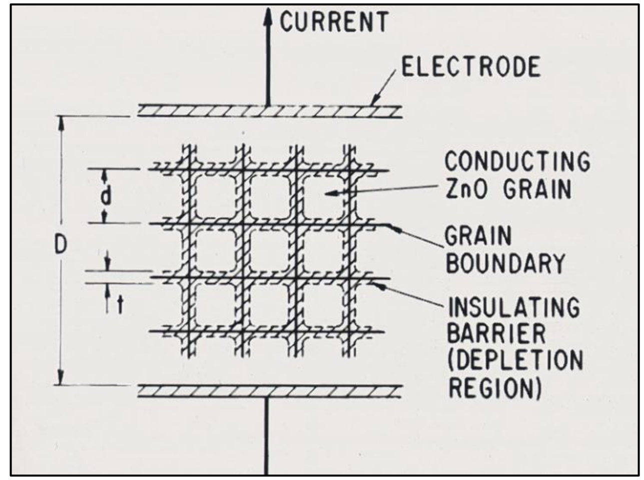
A “Block” Model Was Used To Calculate Electrical Parameters





“Block” model microstructure

» Conducting ZnO cubes in an insulating barrier matrix

» $V_{Barrier} = E_{Breakdown} * d$ = Volts / Barrier

» $V_{Breakdown} = n * V_{Barrier} = (D * V_{Barrier}) / d$

Empirical Power Law Equation:

» $J_1/J_2 = (E_1/E_2)^{\alpha}$

Levinson, L. M., Amer. Ceram. Soc. Bull., Vol. 65, NO. 4 (1986)

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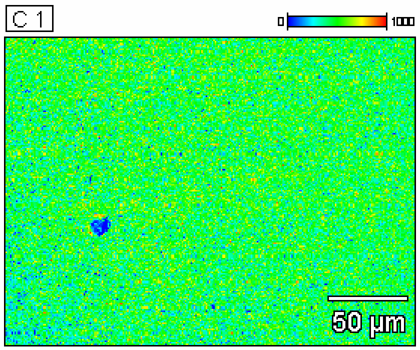
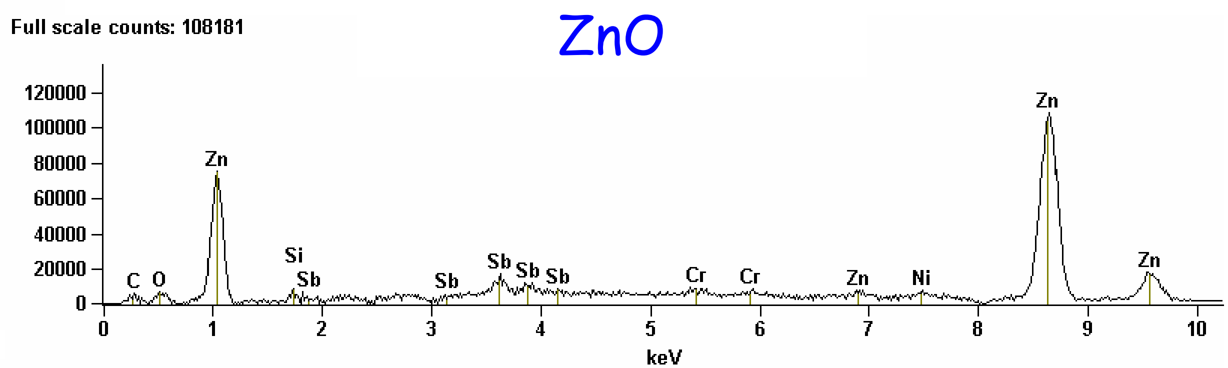
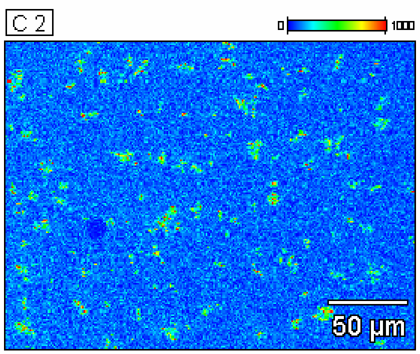
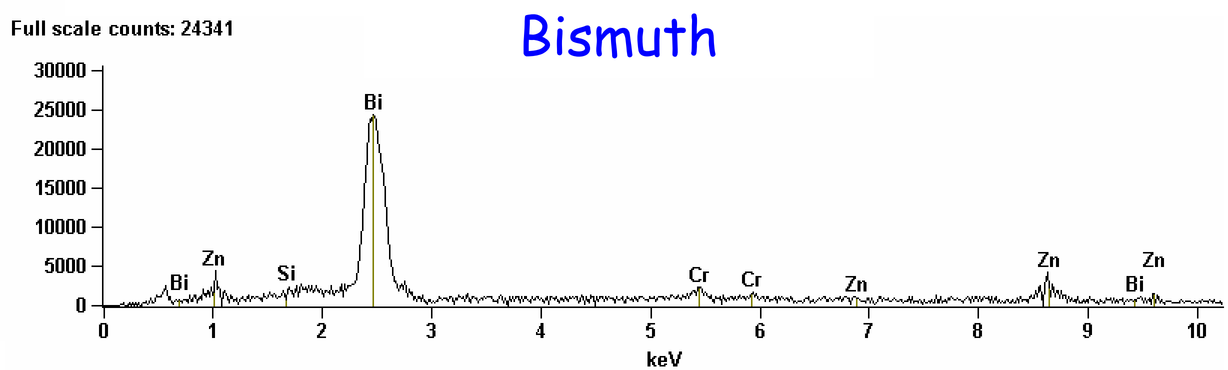
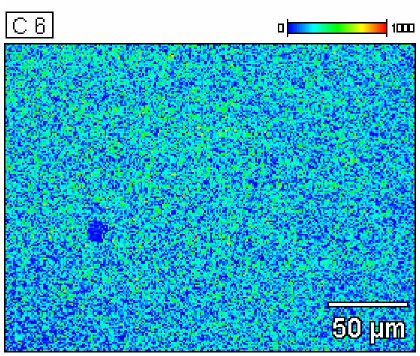
EDS-Spectral Imaging Maps Reveals A Three Component System

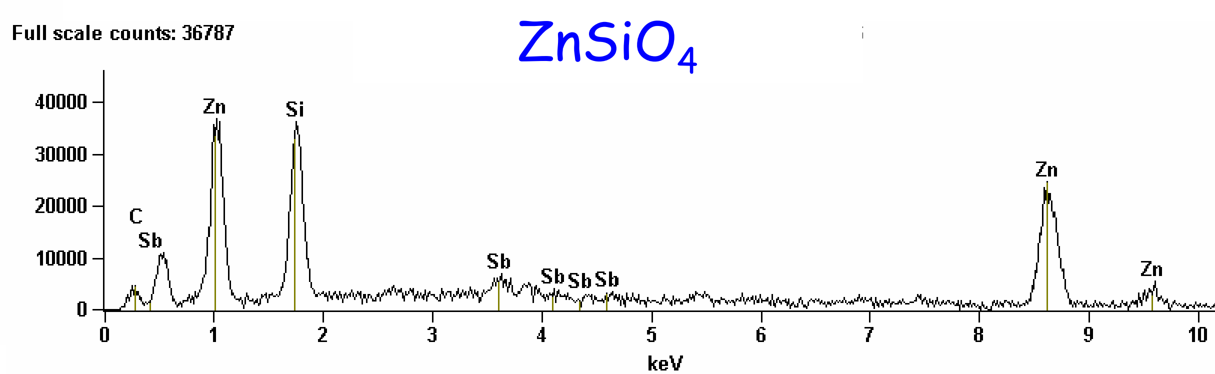












Model Calculations Confirm The Microstructure - Properties Link

Sample Set	$E_{Breakdown}$ Breakdown Field @ 5 Amps/cm^2 (kV/cm)	Alpha (5-10 Amps/cm^2)	$V_{Barrier}$ Macroscopic Barrier Voltage (Volts/Barrier)
SS #1 69.0±1 g/cc 5^{o}C/min to 950^{o}C	47.90	19.30	4.52
SS #2 70.50±1 g/cc 20^{o}C/min to 980^{o}C	48.57	19.90	4.44
SS #3 91.50±1 g/cc 20^{o}C/min to 1100^{o}C	27.75	21.03	3.83

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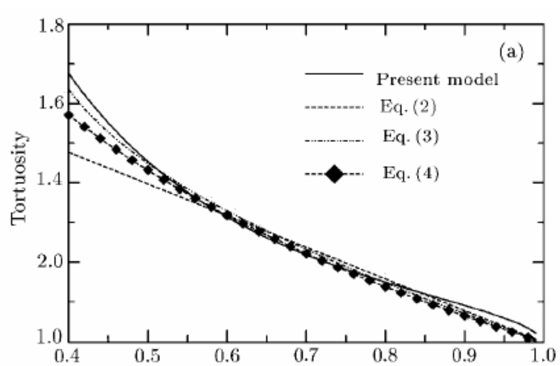
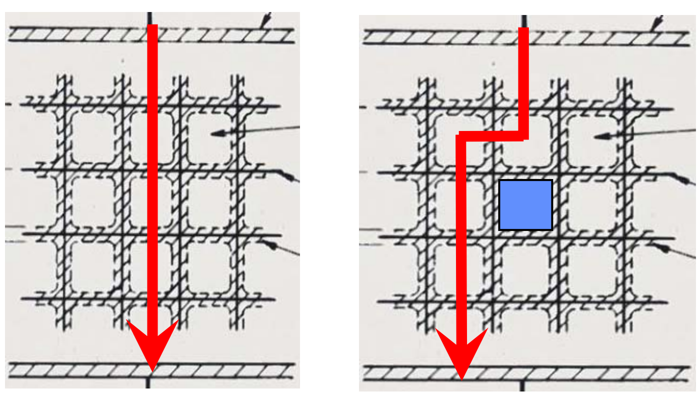
"Tortuosity & Percolation" Theory Were Used to Correct for Porosity

Tortuosity & Percolation Theory

Geometric Model for Flow Path in a Porous Media

- Tortuosity = $\tau = L_{actual}/L$





$V_{Barrier}$ - Macroscopic Barrier Voltage (Volts/Barrier)

Sample Set	Calculated	Tortuosity Factor	Corrected
Theoretical 0% Porosity	3.63	1.000	3.63
SS #1	4.52	1.234	3.67
SS #2	4.44	1.220	3.64
SS #3	3.83	1.056	3.63

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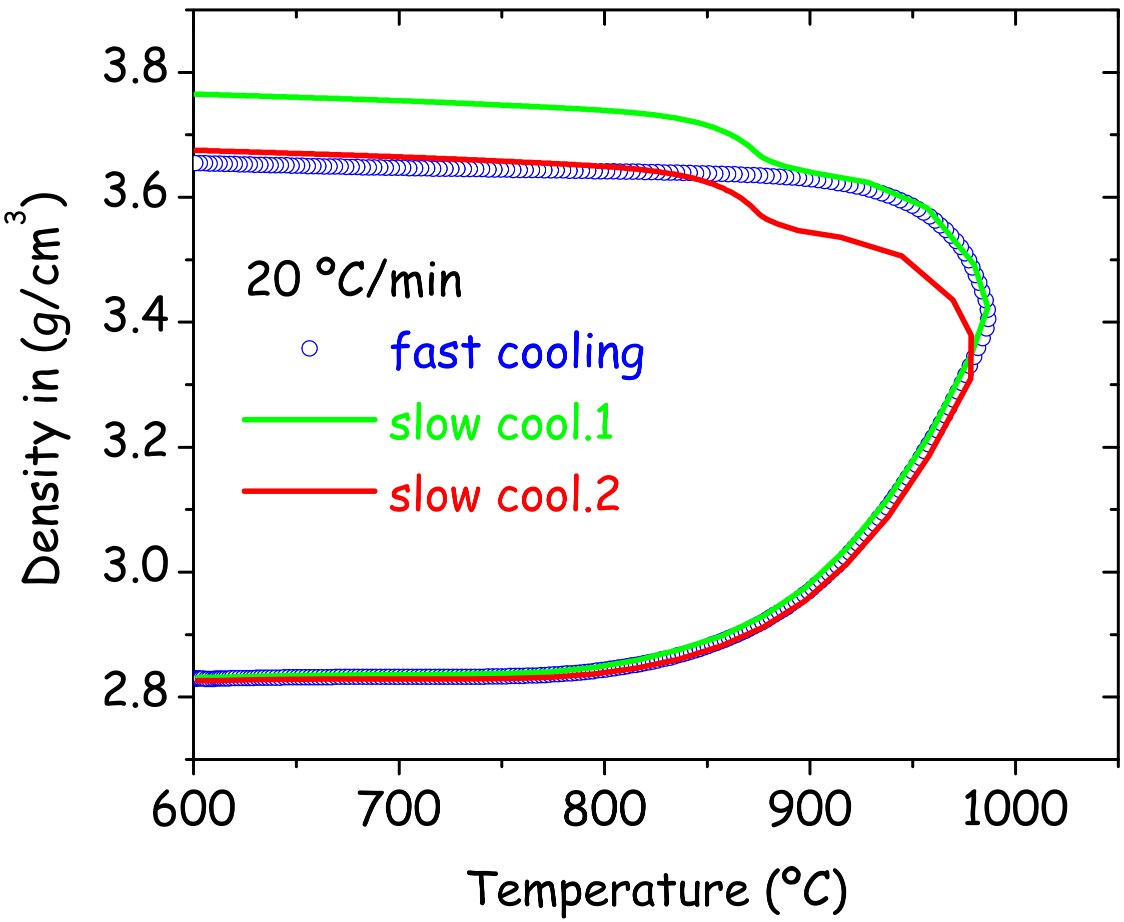
*Bo-Ming, Y. and Jian-Hua, L. "A Geometry Model for Toruosity of Flow Path in Porous Media", Chin. Phys. Lett., 21 [8] 1569-1571 (2004)

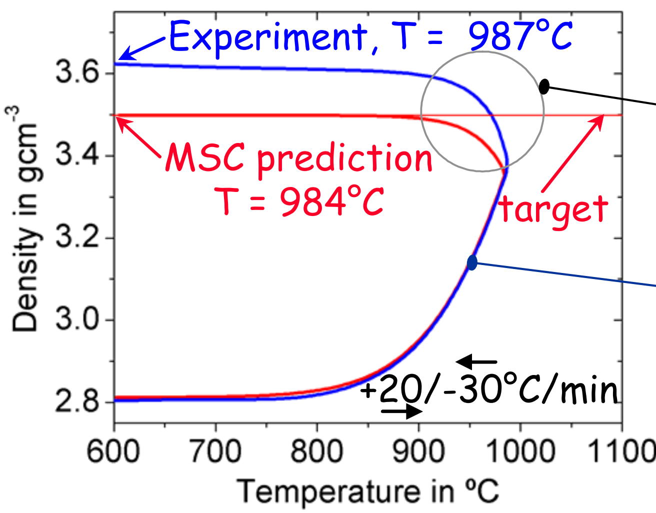
MSC Derived T-t Profiles Predict Densification During Slow Cooling

MO ZnO Varistor Densification Curves



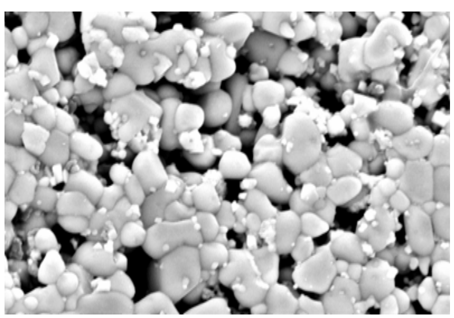
Leakage current is reduced by maturating
the grain boundary phase during slow cooling

The MSC Ties Processing, Microstructure, & Properties Together

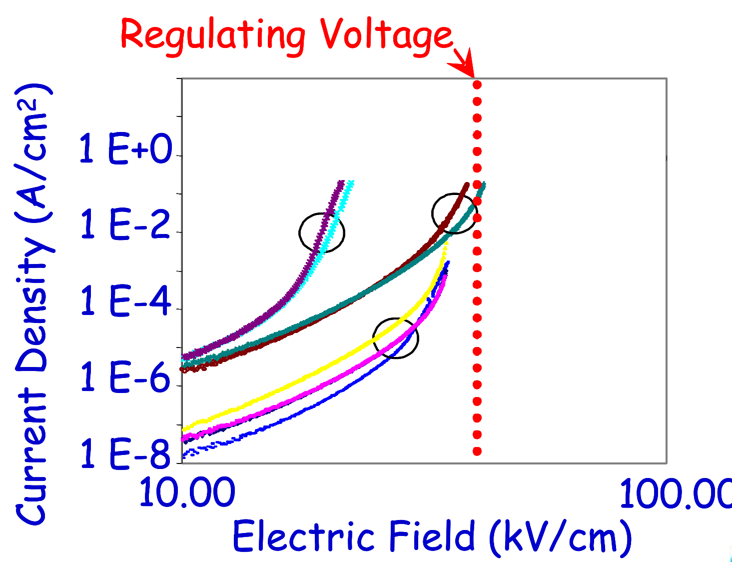


Modeling was used to assess process sensitivity, and optimize processing

The MSC was used to predict, design, and control varistor processing, microstructure, and properties



5°C/min to 960°C
(3.50 g/cm^3)



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