



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

K.G. Ewsuk

M.W. Reiterer, and C.B. DiAntonio

Sandia National Laboratories, Albuquerque, NM 87185-1340

I. Nettleship

University of Pittsburgh, Pittsburgh, PA

ICCCI 2006

Kurashiki, Japan, September 6-9, 2006

The Second International Conference on the Characterization
and Control of Interfaces for High Quality Advanced Materials, and
Joining Technology for New Metallic Glass and Inorganic Materials

*Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed
Martin company, for the United States Department of Energy's National
Nuclear Security Administration under contract DE-AC04-94AL85000*





Acknowledgements

Sandia National Laboratories

Denise Bencoe
Dick Grant
Joanetta Hanlon
Alice Kilgo
Steve Lockwood
Julie Marquez
Bonnie McKenzie
Don Susan

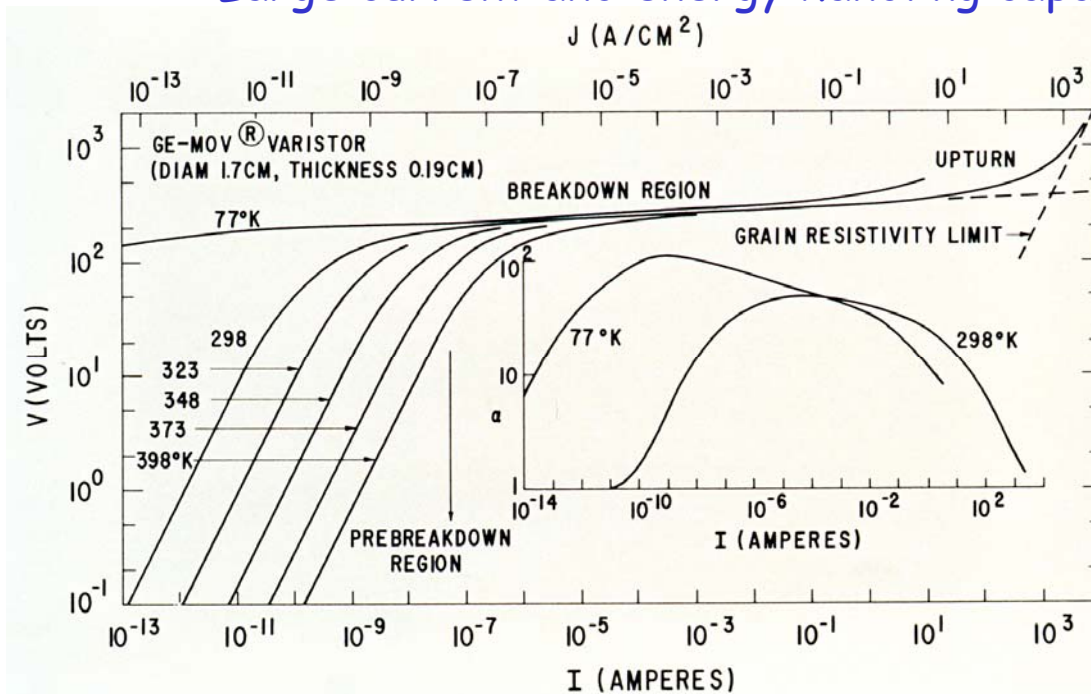
University of Pittsburgh

Tienden Chen

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%
- Bi₂O₃ 2.43 mol%
- CoO 0.87 mol%
- MnO₂ 0.45 mol%,
- Sb₂O₃ 3.04 mol %
- Cr₂O₃ 0.79 mol%
- SiO₂ 9.84 mol%
- NiO 0.78 mol%
- H₃BO₃ 0.13 mol%
- BaCO₃ 0.21 mole
- Al 0.01 mol%

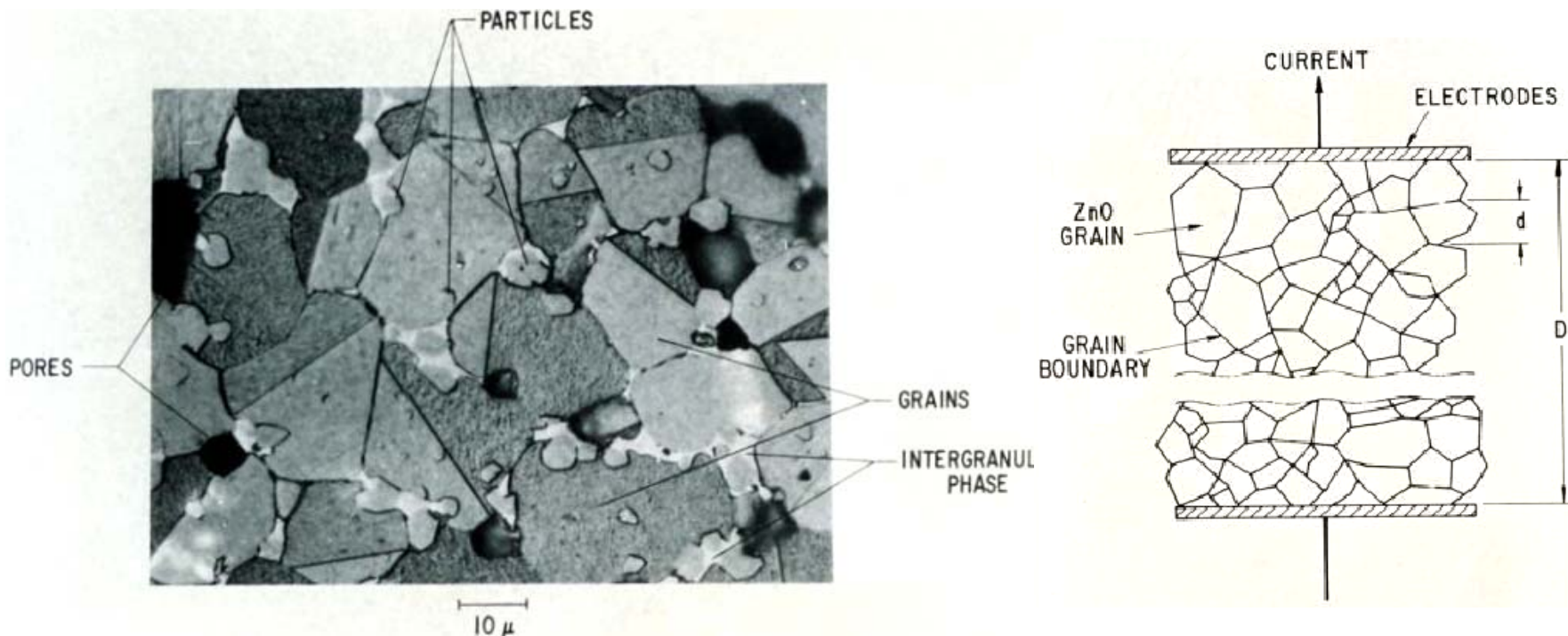
Typical Role of Dopant

- 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

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)



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:

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

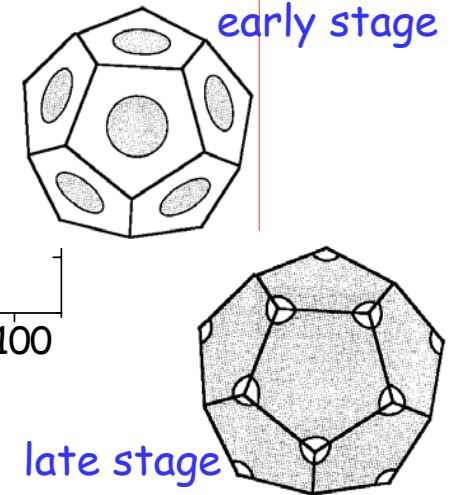
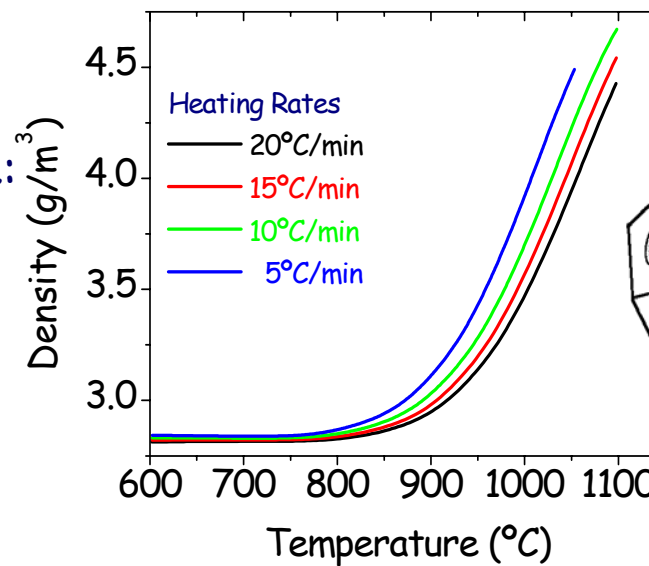
Microstructure & Properties:

$$\Phi(\rho) = \frac{k}{\gamma_s \Omega D_0} \int_{\rho_0}^{\rho} \frac{G((\rho))^n}{3\rho\Gamma(\rho)} d\rho \quad \equiv$$

time-Temperature profile:

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

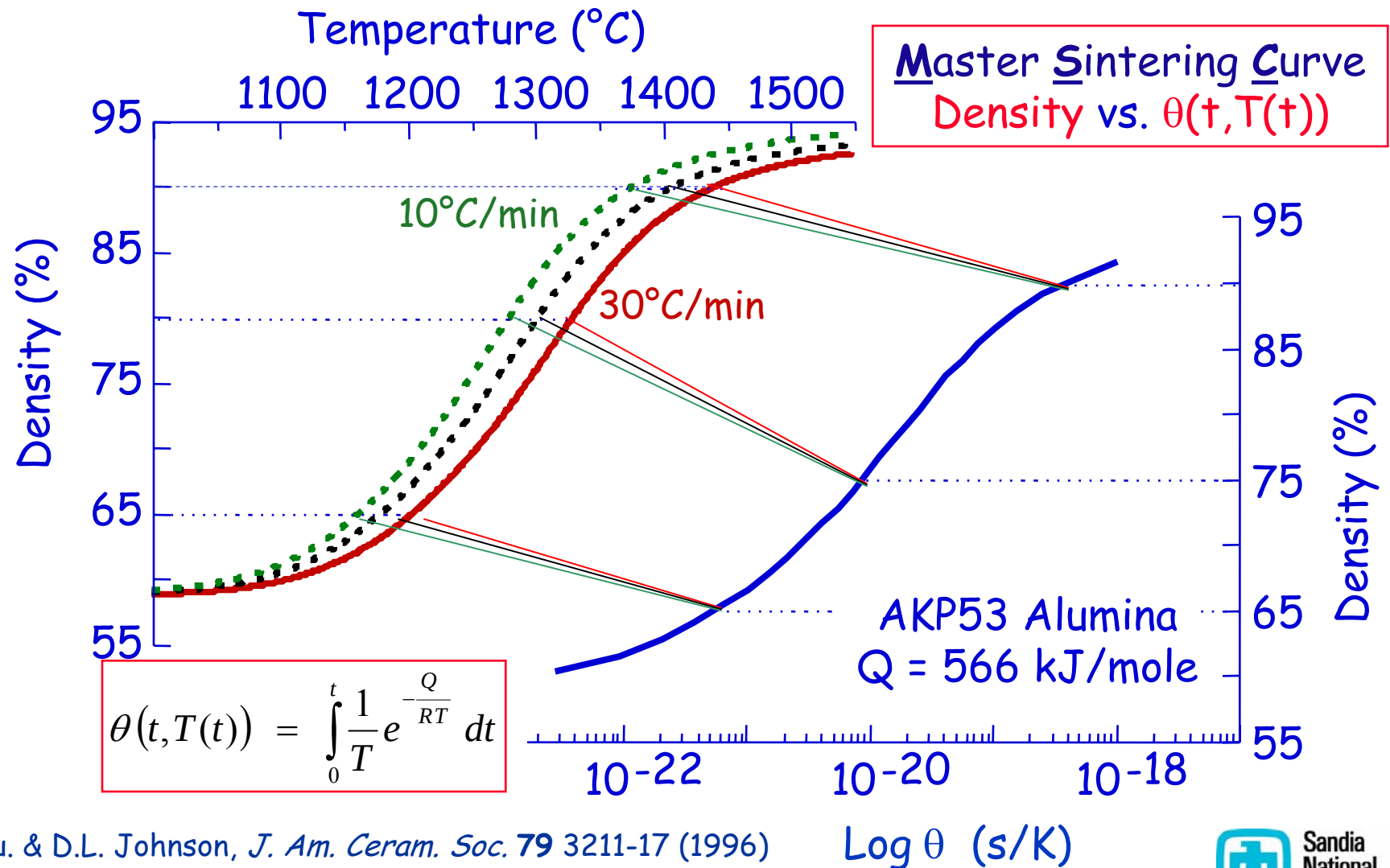
Varistor Densification Curves



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



The MSC Can Be Used To Predict And Control Densification



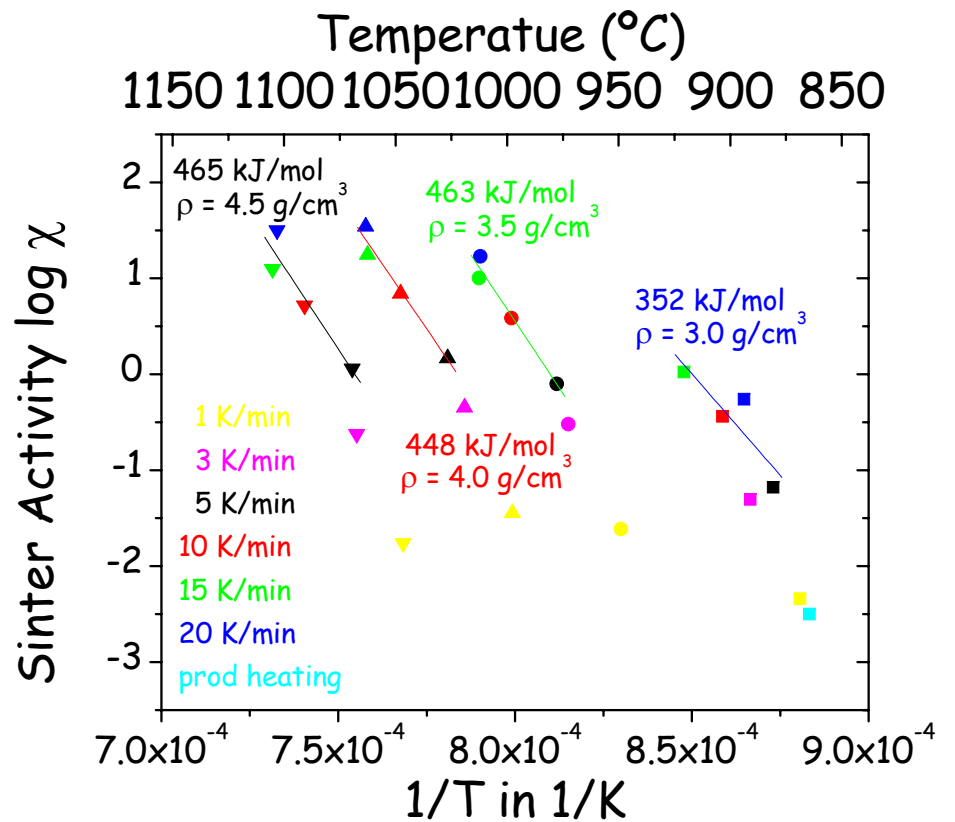
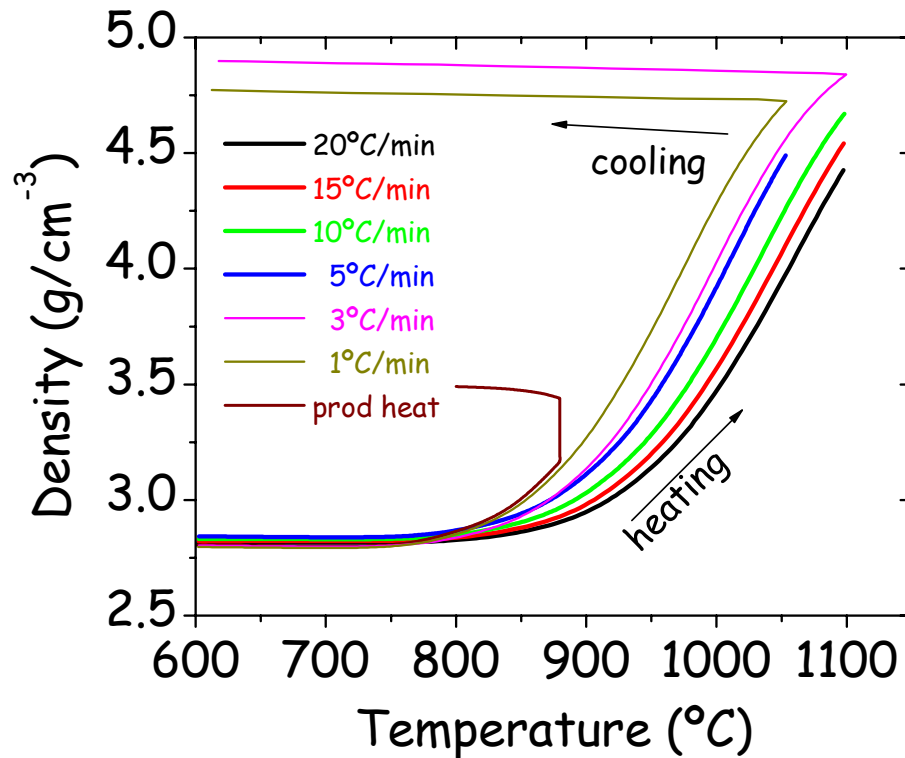
H. Su. & D.L. Johnson, *J. Am. Ceram. Soc.* **79** 3211-17 (1996)
"Master Sintering Curve: A Practical Approach to Sintering"



The Activation Energy Was Determined From The Sintering Data

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

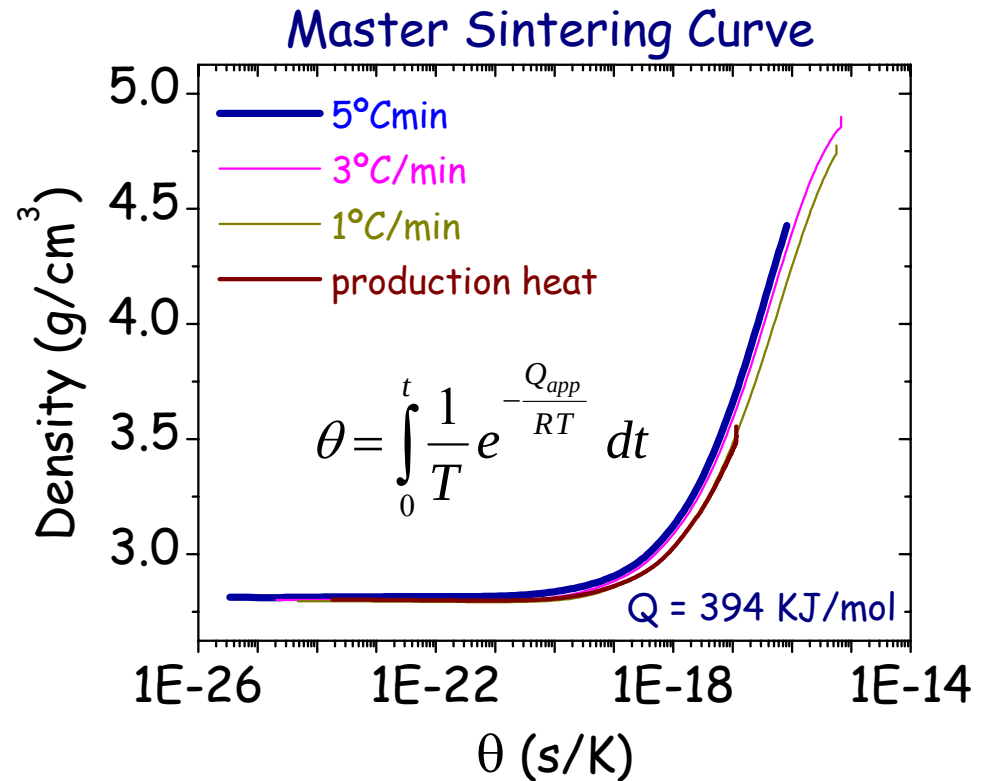
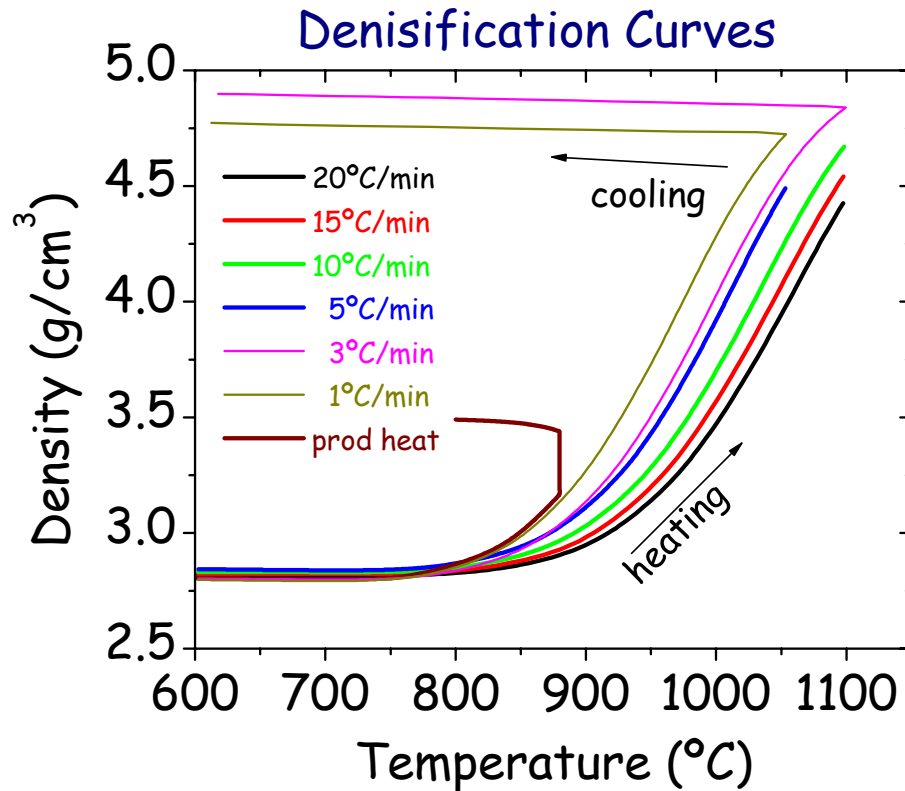
MO Varistor Densification





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

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

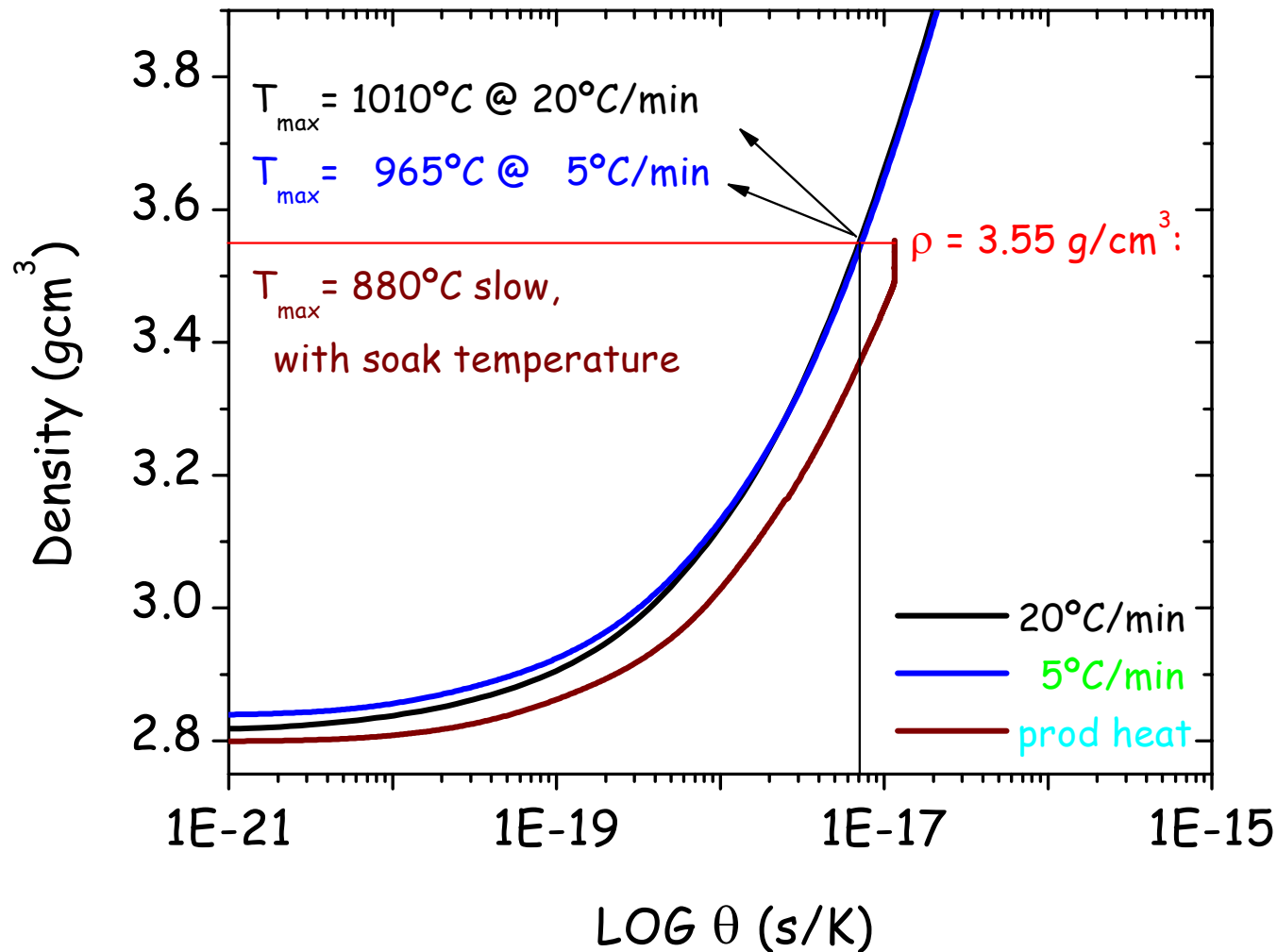


Heating rates <5°C/min do NOT fall on the MSC



MSC Derived Temperature-time Sintering Profiles Were Designed

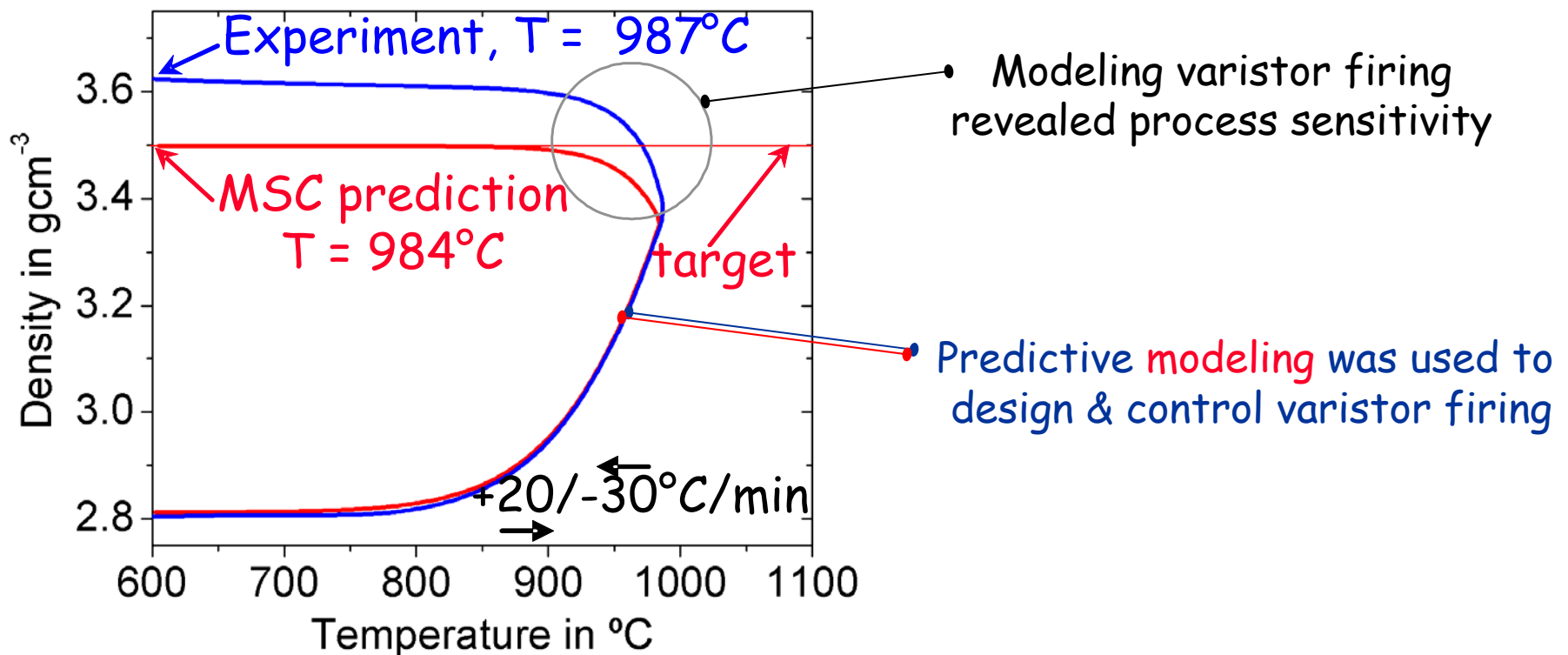
ZnO Mixed-Oxide Varistor





MSC Predictions Reveal A Sensitive Sintering Process

ZnO Mixed-Oxide Varistor



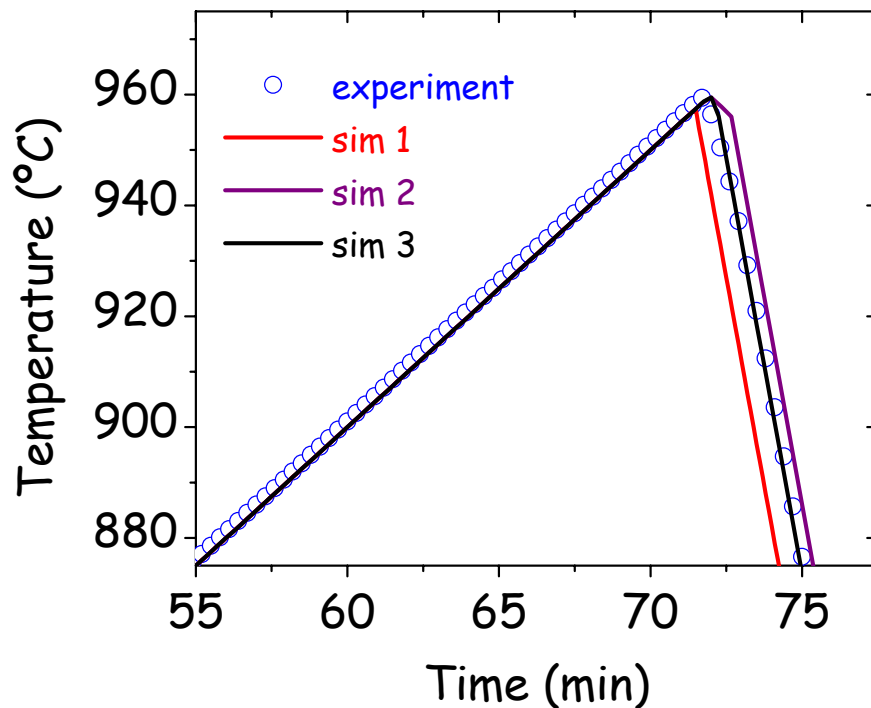
The sensitivity of varistor density (and microstructure) to minor deviations in sintering time & Temperature can contribute to variability in varistor performance.



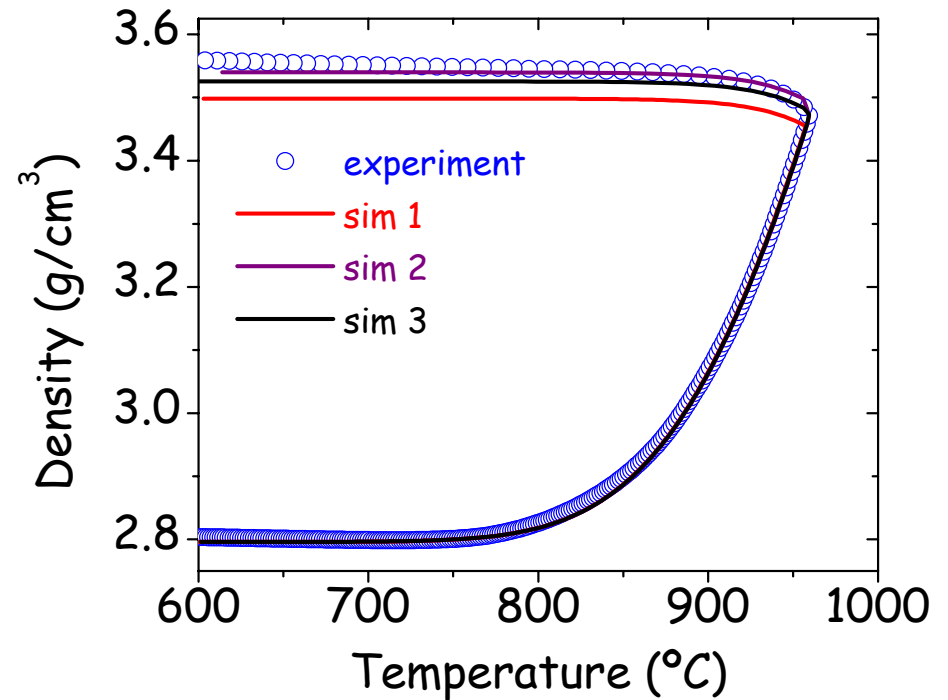
MSC-Based T-t Profiles Predict The Densification Observed Experimentally

MSC predictions are validated by experimental results

MO Varistor Sintering Profiles



Densification Curves for MO Varistor

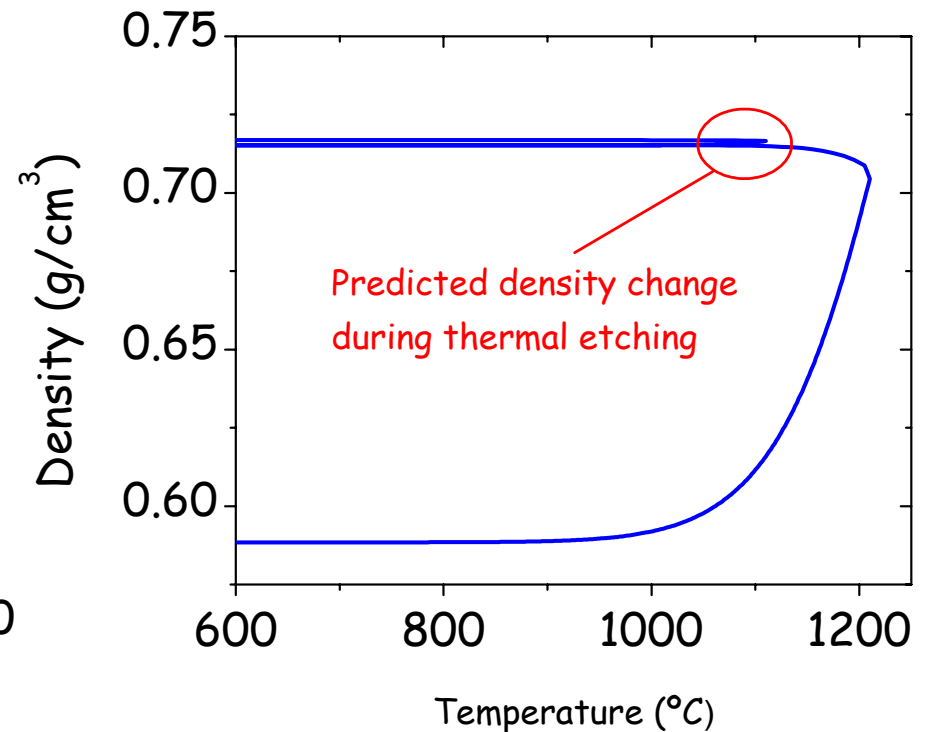
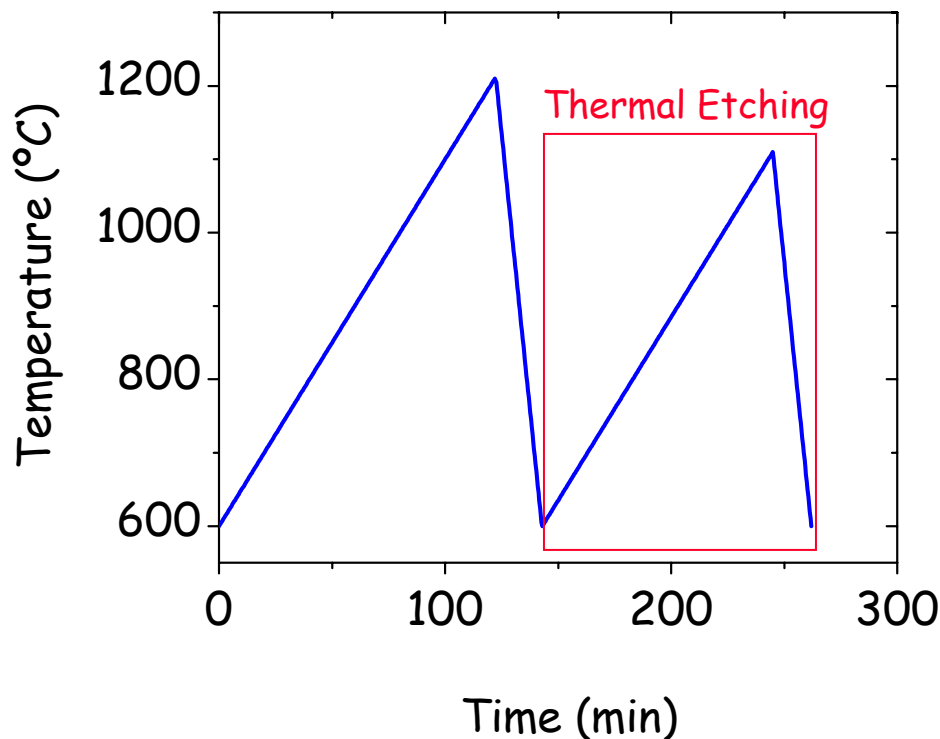


The MSC accurately predicts densification

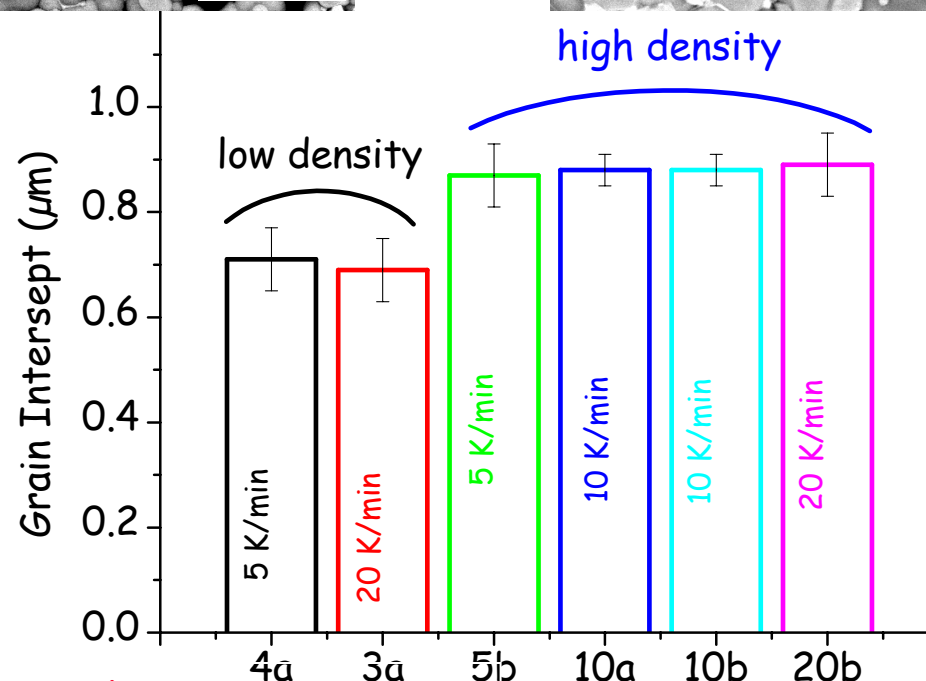
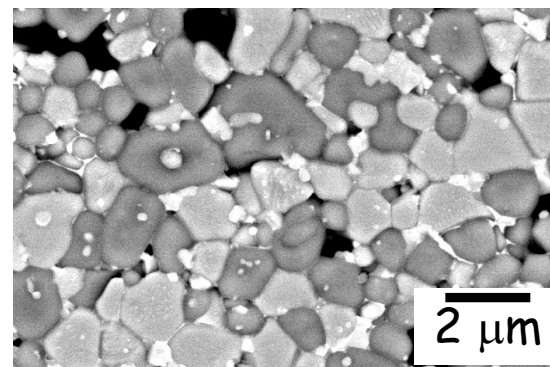
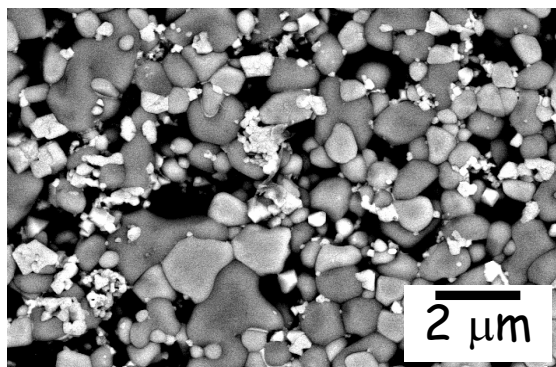


Quantitative Microstructure Analysis Was Aided By MSC-Based Calculations

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

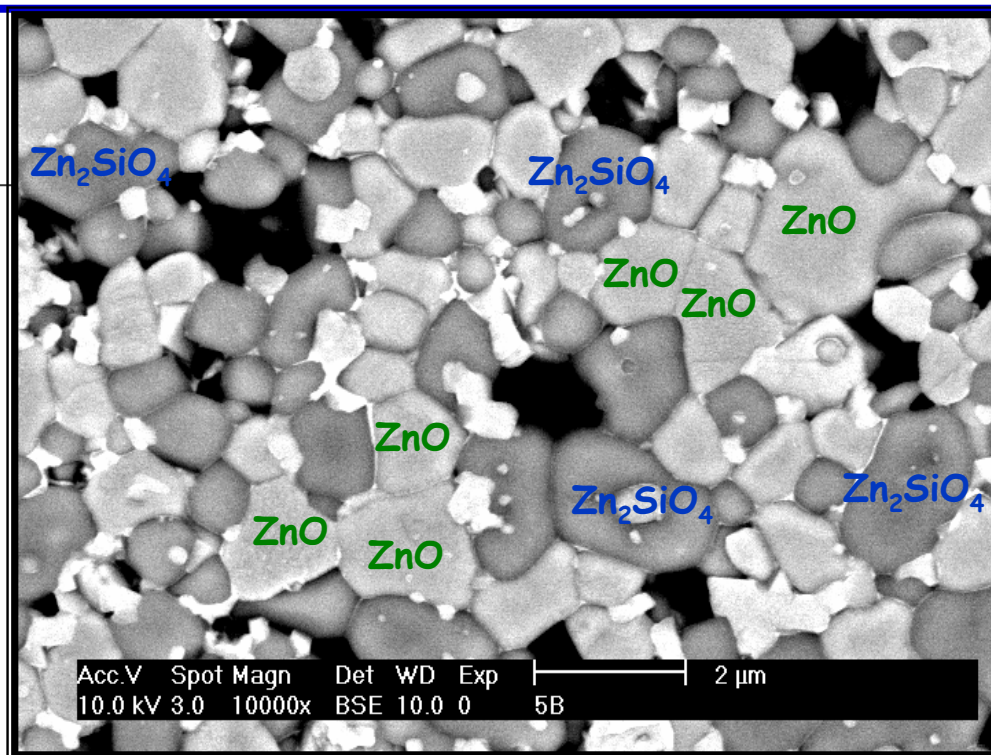
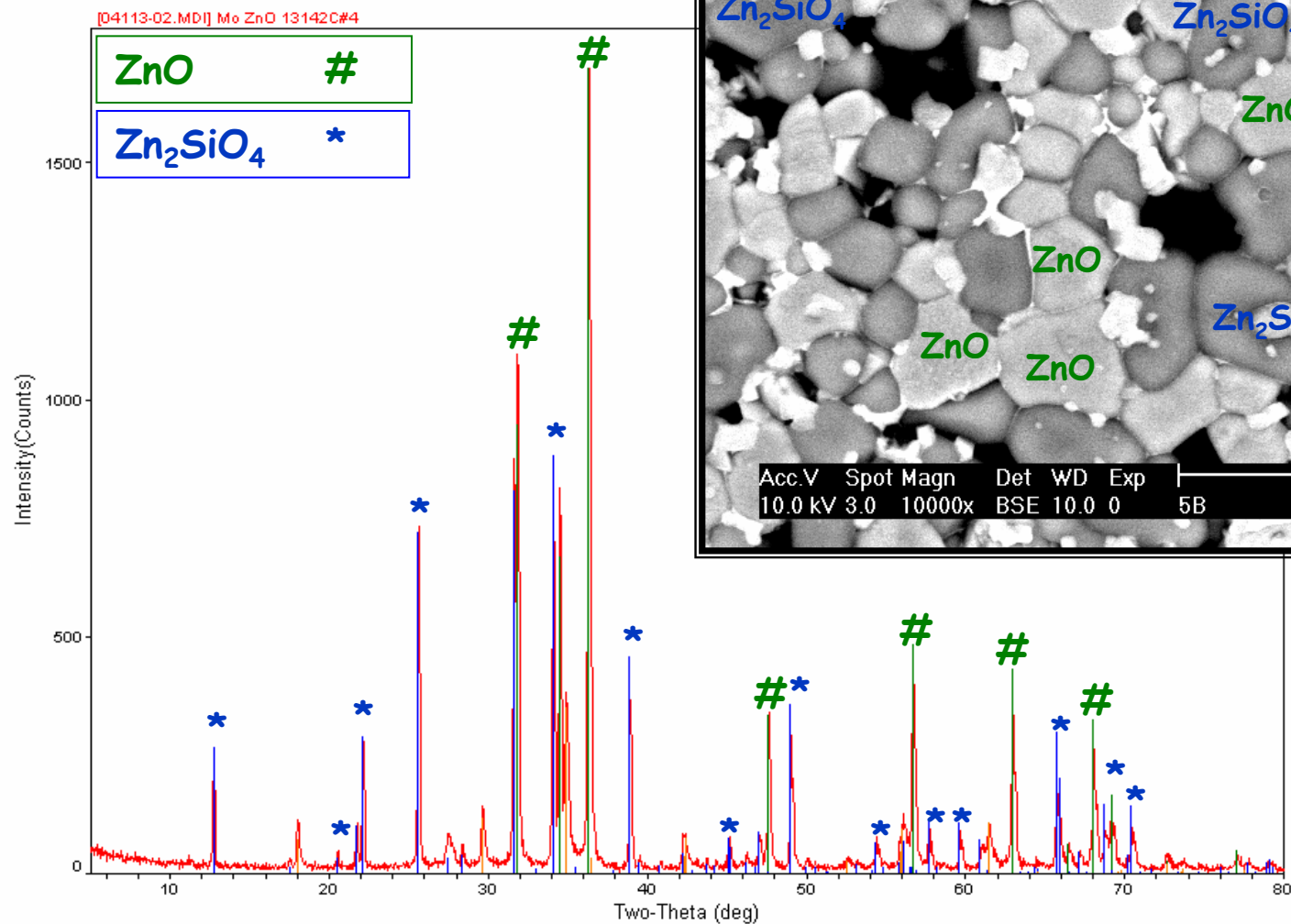


MSC T-t Profiles Produce The Same Microstructure At The Same Density



The MSC facilitates the processing of controlled microstructure ceramics

XRD Analysis Reveals Two Major Crystalline Phases - ZnO & ZnSiO₄





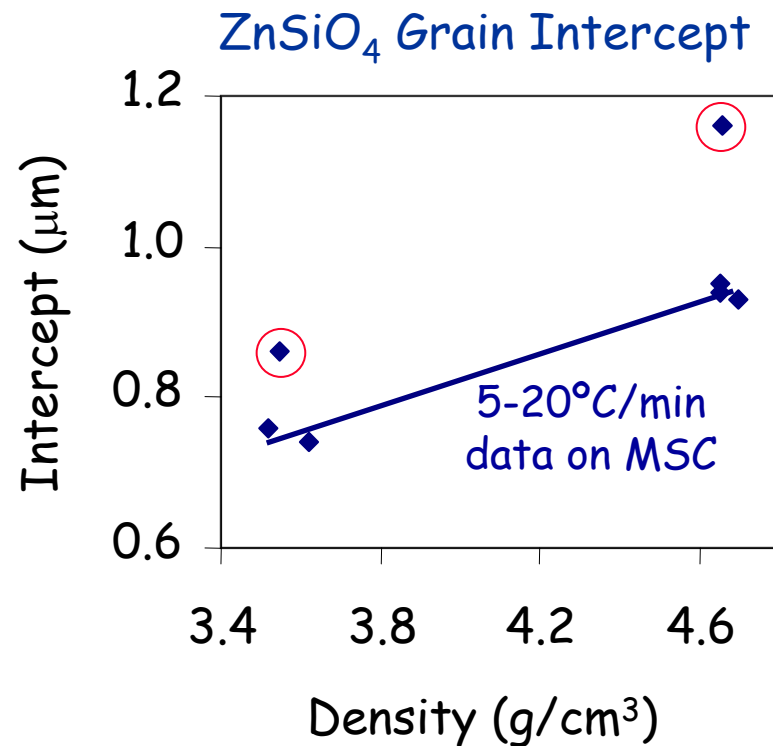
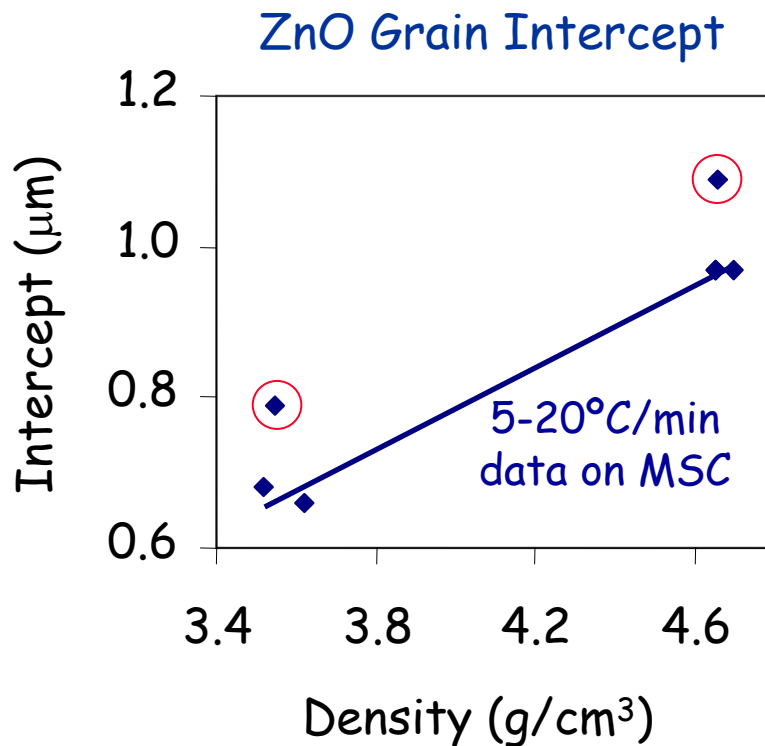
Varistors Sintered To The Same MSC Density Have The Same Grain Size

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

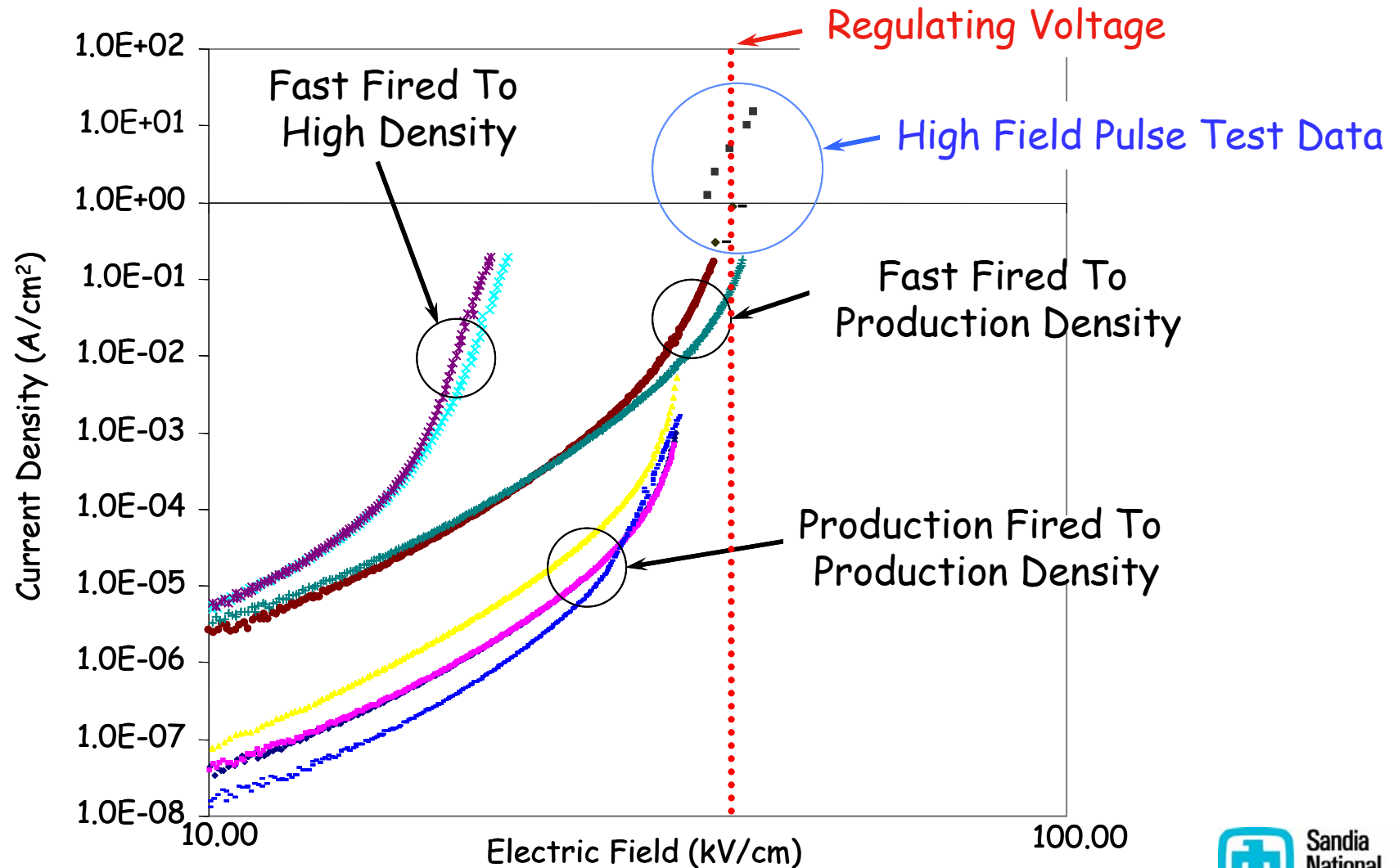


The Results Support A Master Density-Microstructure Trajectory



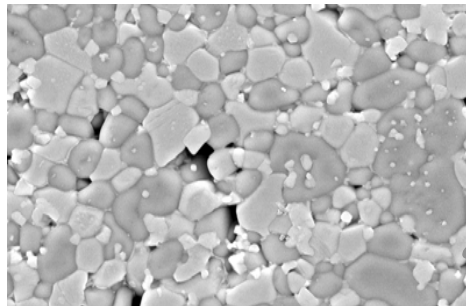


Comparable Density & GS Varistors Have The Same Regulating Voltage

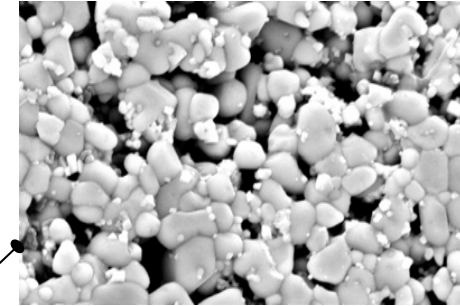


Controlled Microstructure And Property Varistors Were Produced

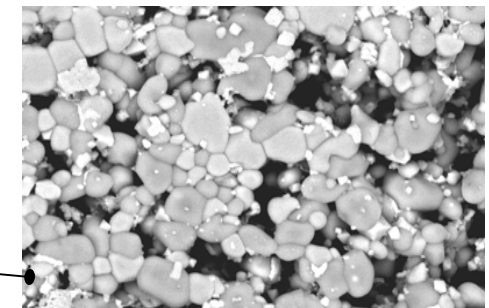
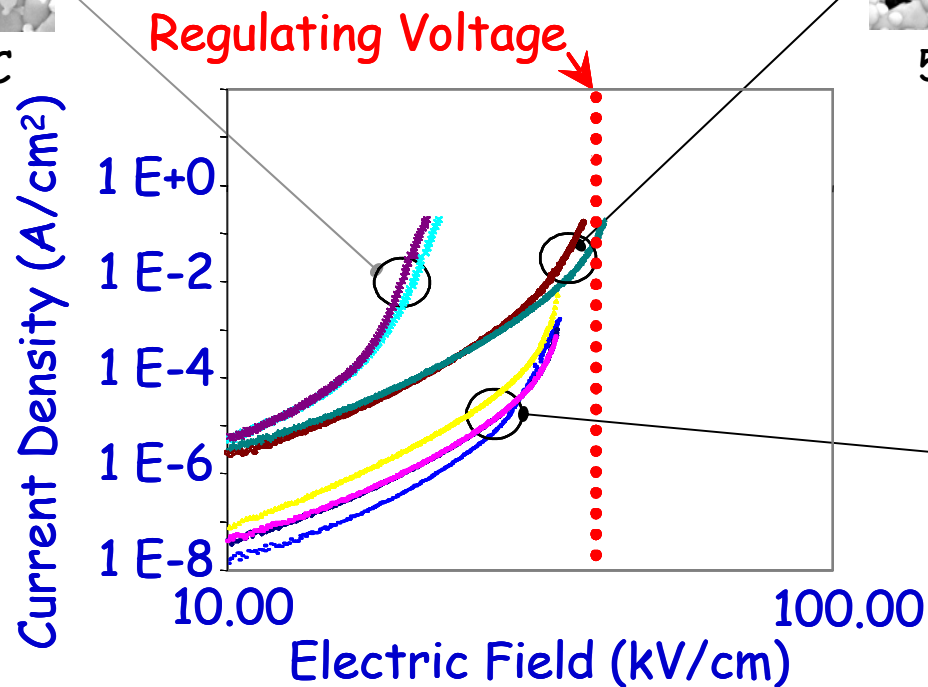
Model-derived sintering profiles were used to control processing to systematically control the density, microstructure, & electrical properties of ZnO varistors.



10°C/min to 1100°C
(4.59 g/cm³)



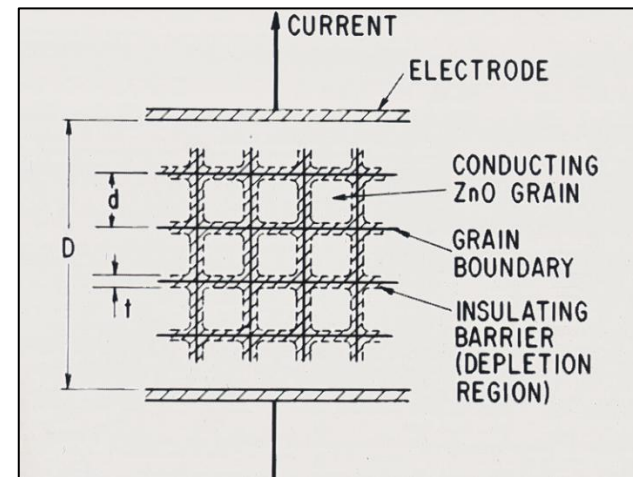
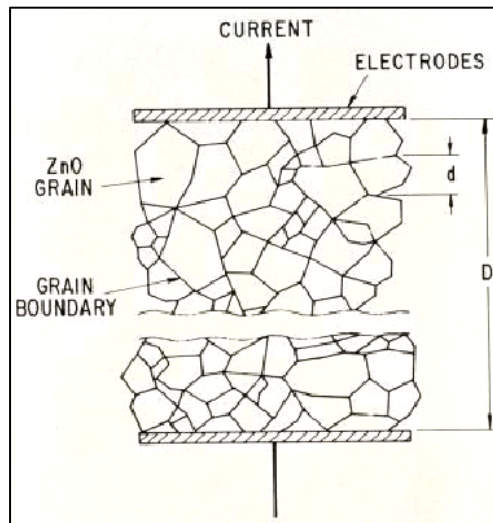
5°C/min to 960°C
(3.50 g/cm³)



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



A "Block" Model Was Used To Calculate Electrical Parameters



"Block" model microstructure

» Conducting ZnO cubes in an insulating barrier matrix

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

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

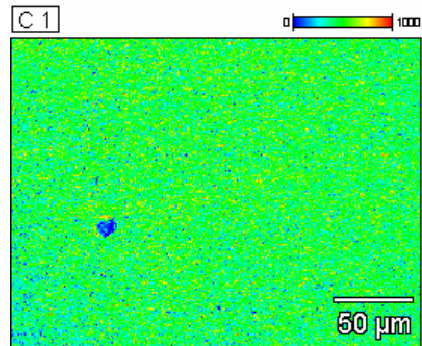
Empirical Power Law Equation:

» $J_1/J_2 = (E_1/E_2)^\alpha$

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

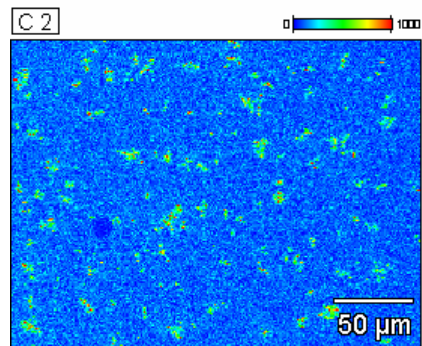
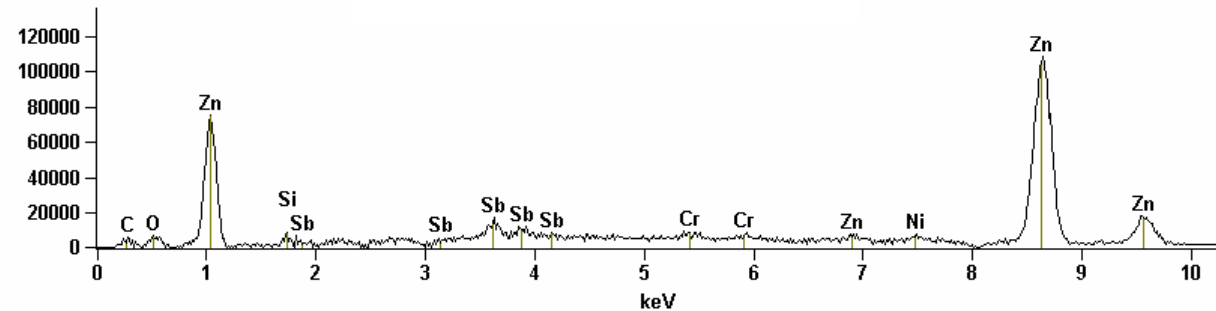


EDS-Spectral Imaging Maps Reveals A Three Component System



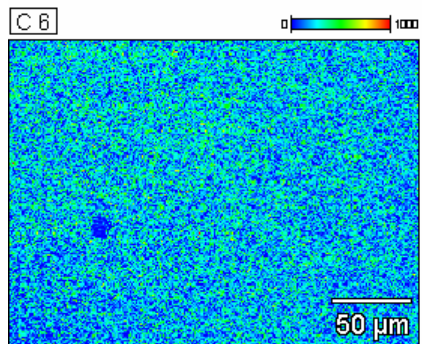
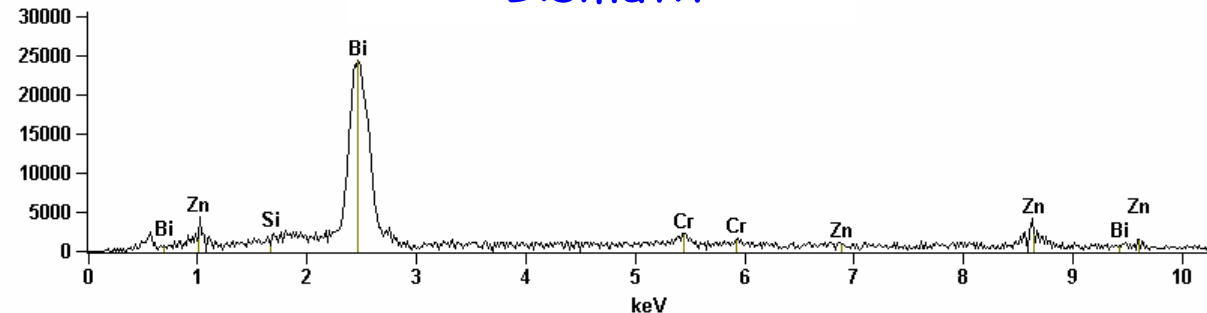
Full scale counts: 108181

ZnO



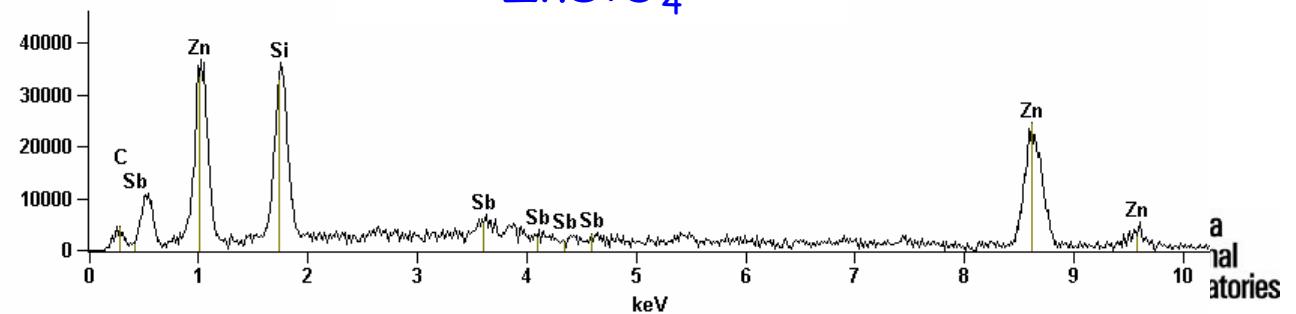
Full scale counts: 24341

Bismuth



Full scale counts: 36787

ZnSiO₄





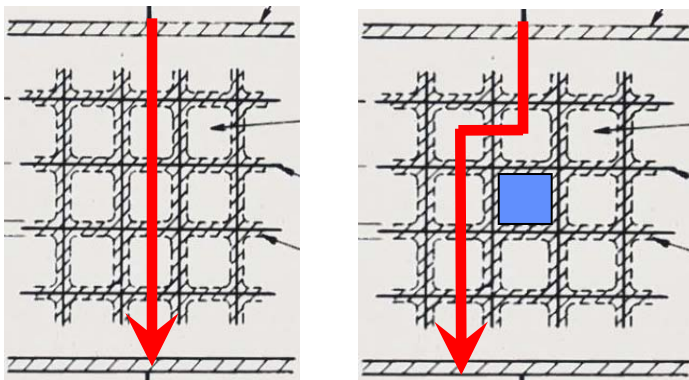
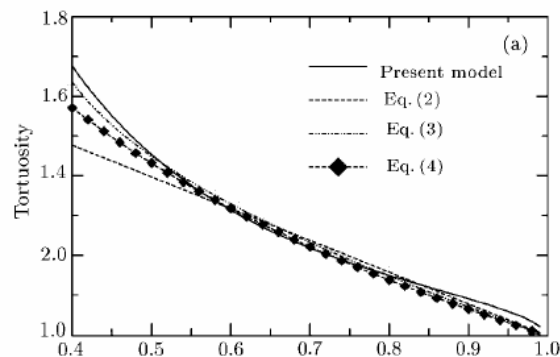
Model Calculations Confirm The Microstructure - Properties Link

Sample Set	$E_{\text{Breakdown}}$ 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°C/min to 950°C	47.90	19.30	4.52
SS #2 70.50±1 g/cc 20°C/min to 980°C	48.57	19.90	4.44
SS #3 91.50±1 g/cc 20°C/min to 1100°C	27.75	21.03	3.83



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

Tortuosity & Percolation Theory
Geometric Model for Flow
Path in a Porous Media
- Tortuosity = $\tau = L_{\text{actual}}/L$

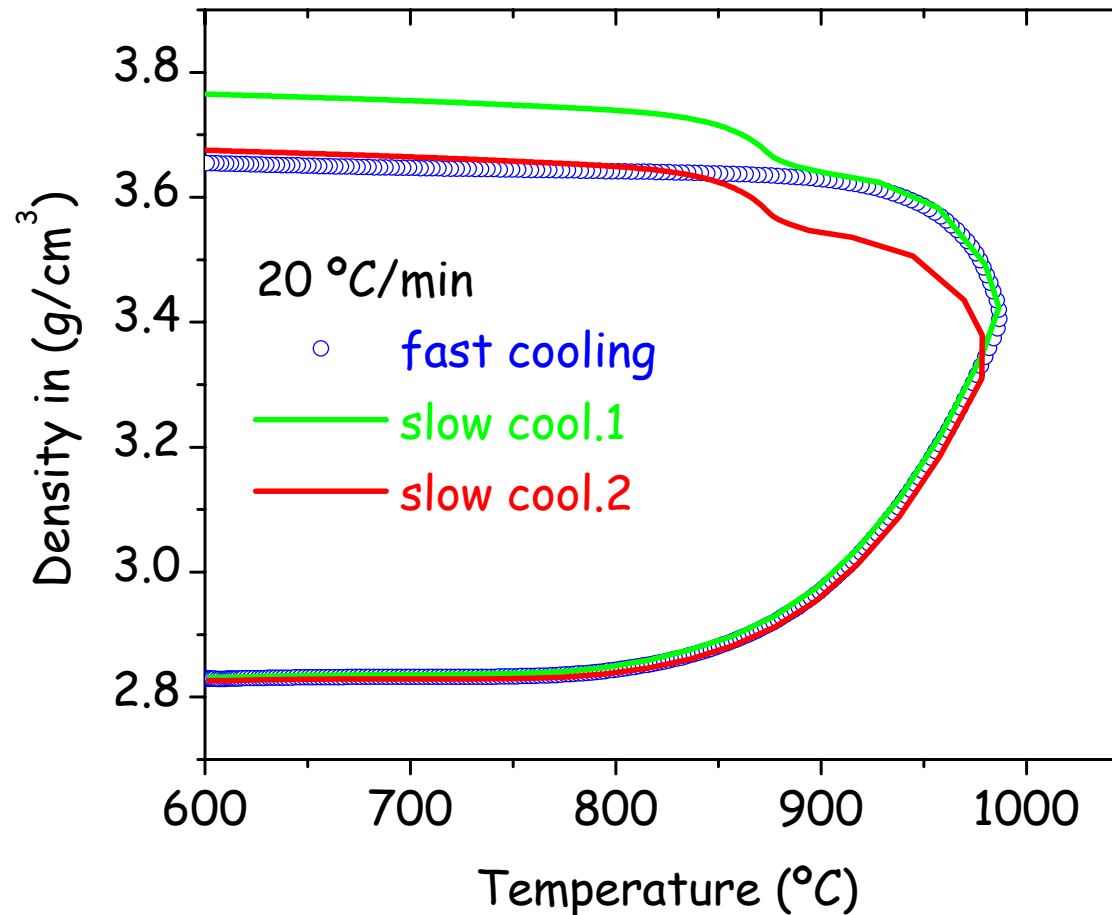


V_{Barrier} - Macroscopic Barrier Voltage (Volts/Barrier)			
Sample Set	Calculated	Tortuosity Factor	Corrected
Theoretical 0% Porosity	3.63	1.000	3.63
SS #1	4.52	1.234	3.67
SS #2	4.44	1.220	3.64
SS #3	3.83	1.056	3.63



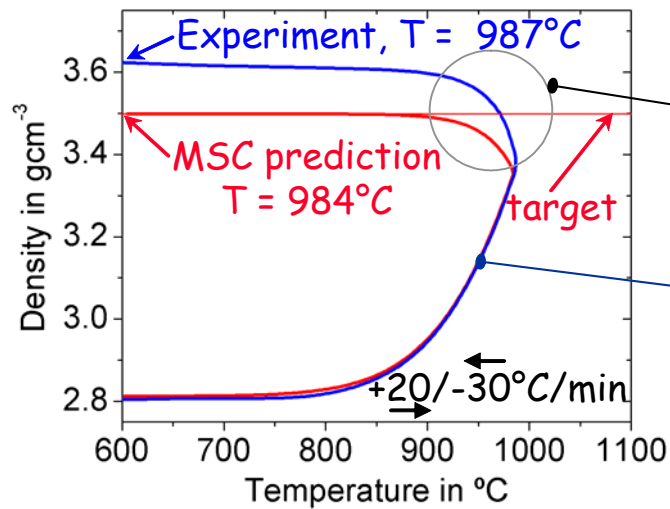
MSC Derived T-t Profiles Predict Densification During Slow Cooling

MO ZnO Varistor Densification Curves



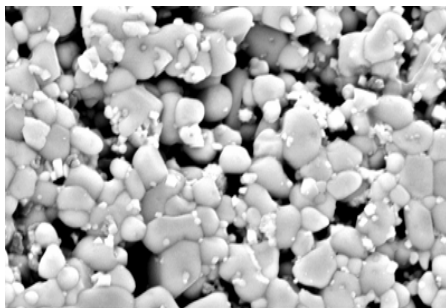
Leakage current is reduced by maturing
the grain boundary phase during slow cooling

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 $^{\circ}\text{C}/\text{min}$ to 960 $^{\circ}\text{C}$
(3.50 g/cm^3)

