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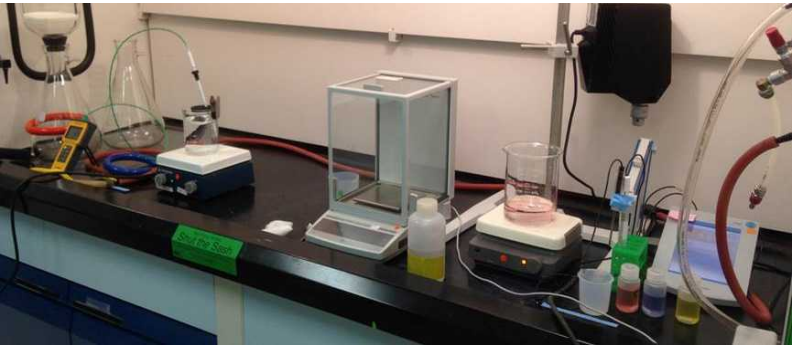

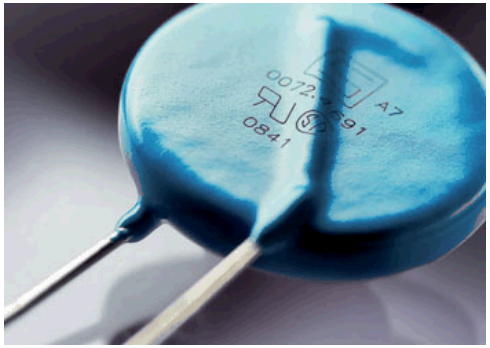

The Effects of Calcination and Milling on Powder Characteristics and Electrical Behaviour of ZnO Varistor Materials

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Introduction

Brief overview of varistors

- Voltage dependent resistor
  - Non-linear I-V curve
- Microstructure
  - Typically doped ZnO grains surrounded by thin (nm thick) grain boundary Bi_2O_3 phase
- Applications
  - Placed in parallel with critical features of circuit
  - Power stacks, surge protectors, etc.

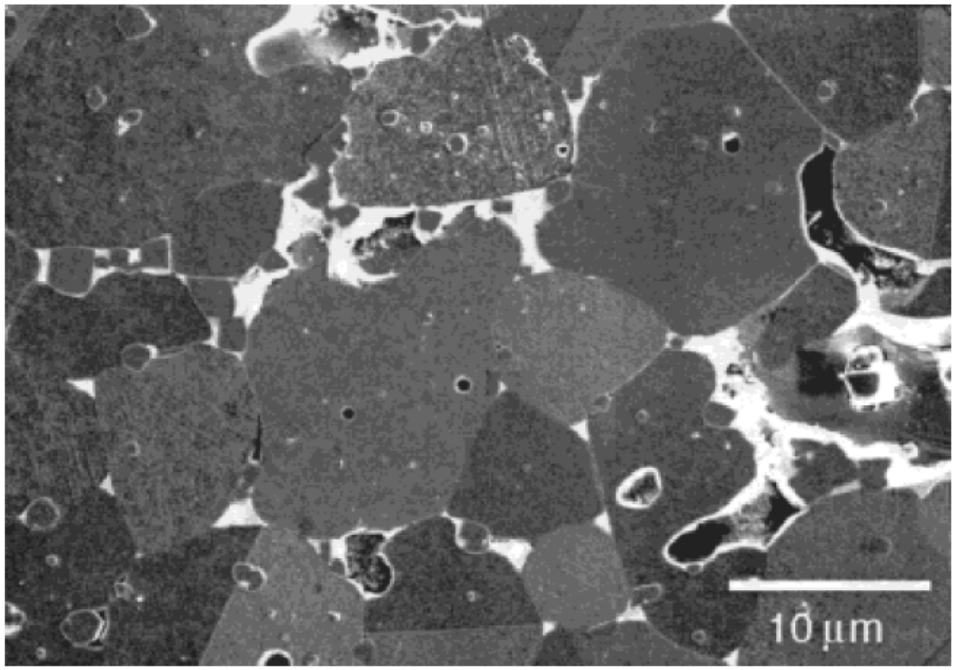


Image: Clarke, D. R. *Journal of the American Ceramic Society*, (1999) **82** (3), 485-500.

Important Characteristics

- Leakage current
  - Affected by grain boundary
- E_b, switching field
  - Affected by grain size
- α
  - Affected by dopants (which dopants and amounts)
- Porosity

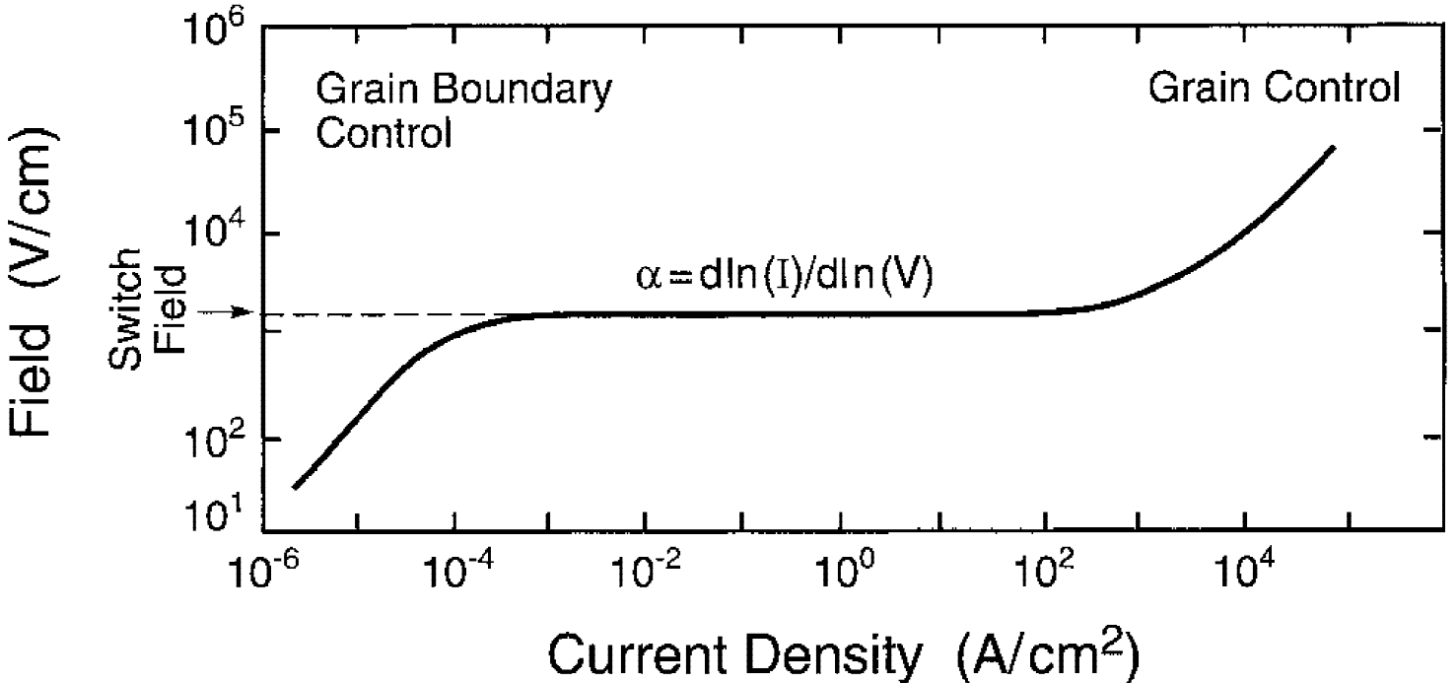


Image: Clarke, D. R. *Journal of the American Ceramic Society*, (1999) **82** (3), 485-500.

Physical Basis for Varistors

- Modeled by double Schottky barrier across two grains
- “Breakdown” mechanisms
- ~3.5V/grain boundary [1]

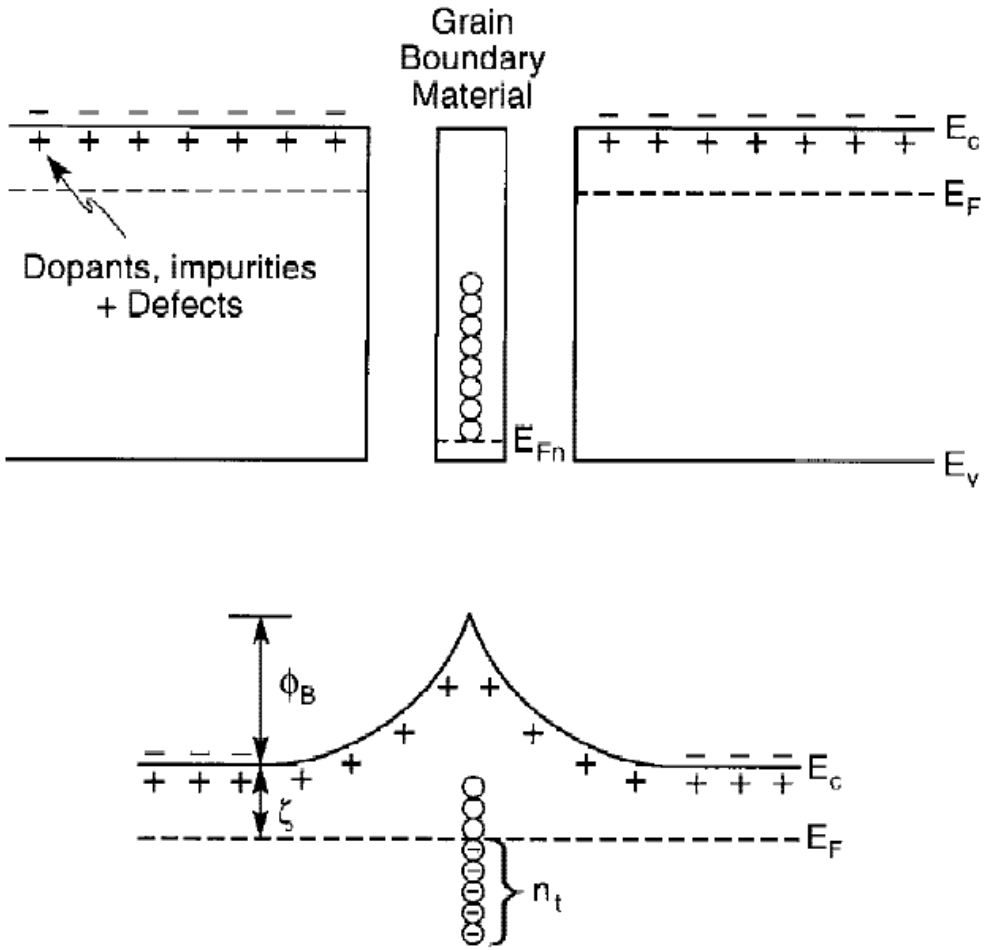
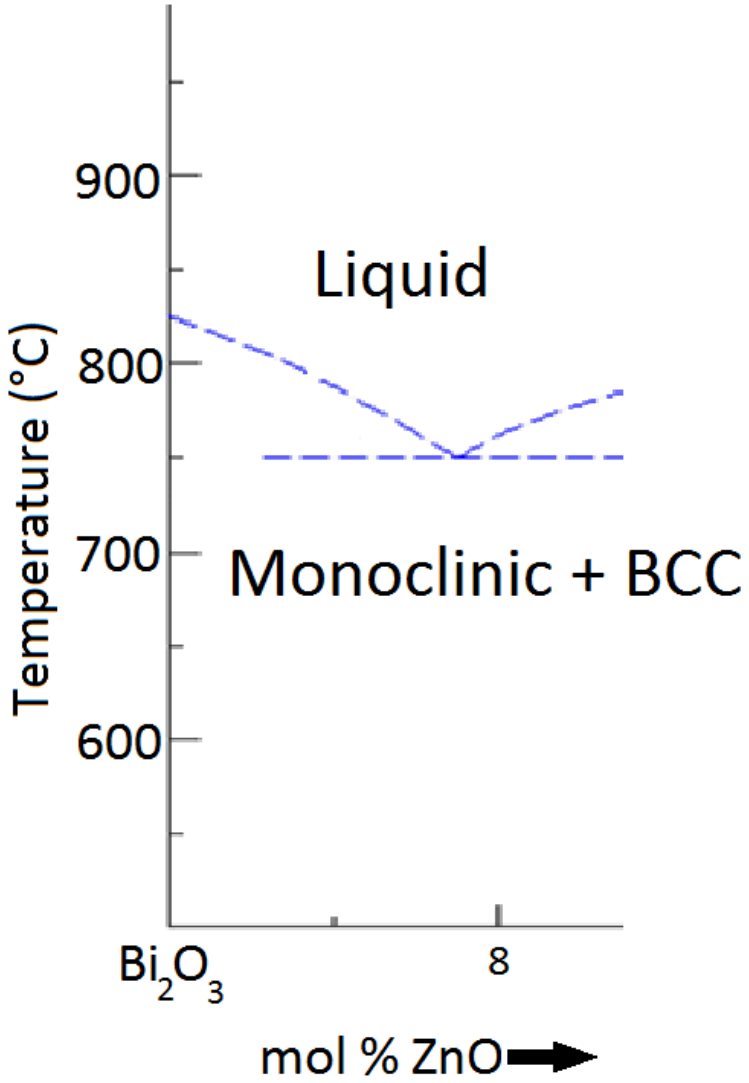


Image: Clarke, D. R. *Journal of the American Ceramic Society*, (1999) **82** (3), 485-500.

Common Dopants in ZnO Varistors

- Bi_2O_3
  - Used for setting up electrostatic barrier, liquid phase sintering
- Sb_2O_3
  - Also establishes electrostatic barrier
- CoO, MnO
  - Modify grain conductivity
- Al_2O_3, Na_2O
  - Can modify grain conductivity, affect grain growth



Motivation from Literature

- M. Peiteado et al. perform diffusion couple for ZnO-CoO [2]
- Oxidation state of Co_xO is temperature dependent

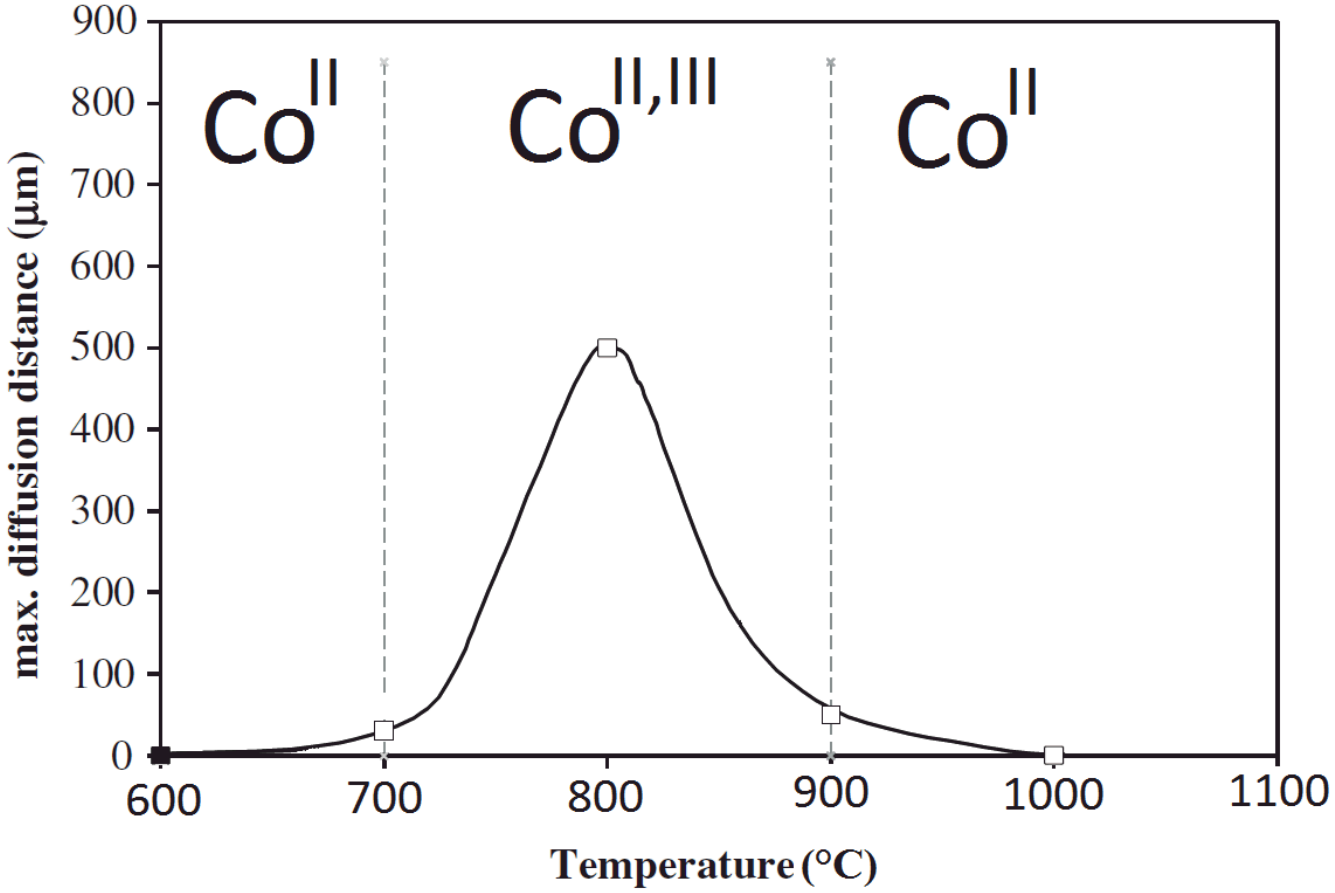
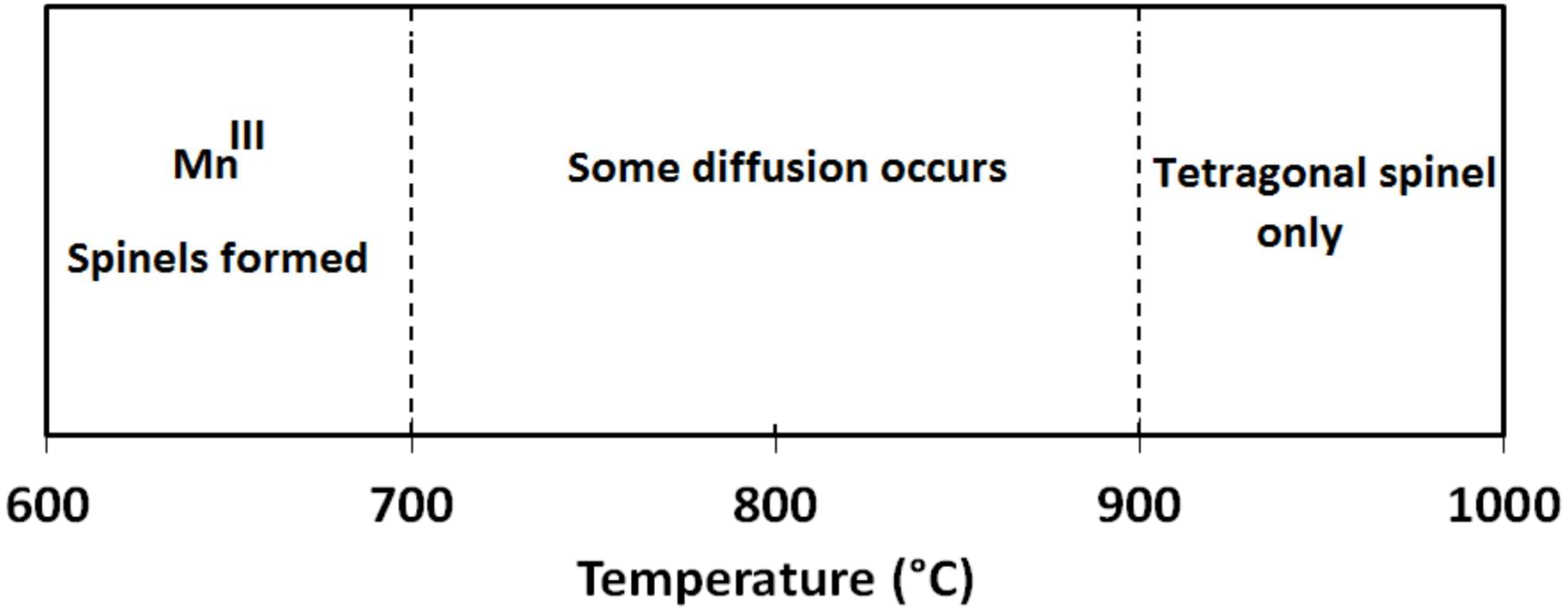


Image modified from: Peiteado, M. et al., *J. Solid State Chemistry*, (2008) **181**, 2456-2461.

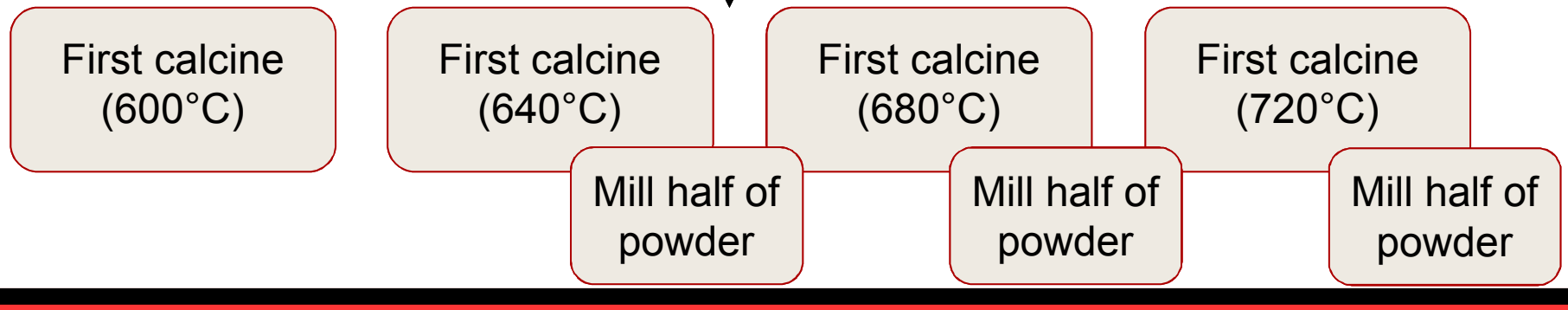
Motivation from Literature

- M. Peiteado et al. perform similar diffusion couple for ZnO-MnO_2 [3]
- Mn^{IV} too small, Mn^{III} sits on intersticies of wurtzite structure
- Mn_2O_3 does not significantly diffuse into ZnO, but reacts at surface



Peiteado, M. et al., *J. Solid State Chemistry*, (2007) **180**, 2459-2464.

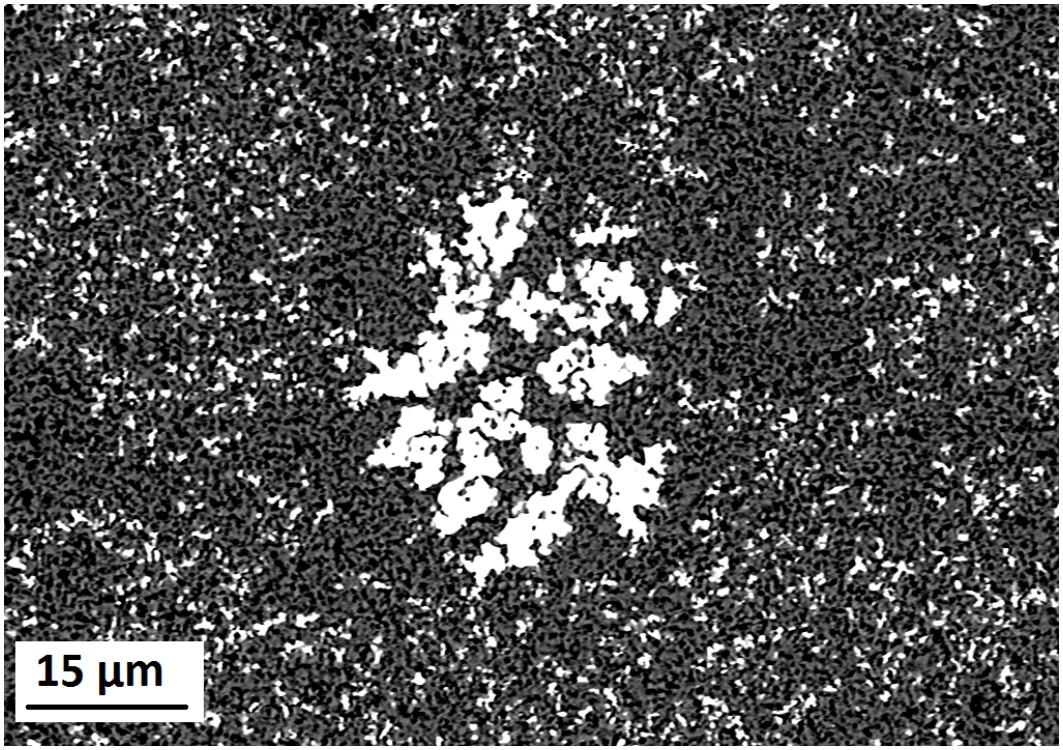
Powder Synthesis



Process learned from Dani McCade, Julie Gibson, Mike Hutchinson

Characterization to Perform

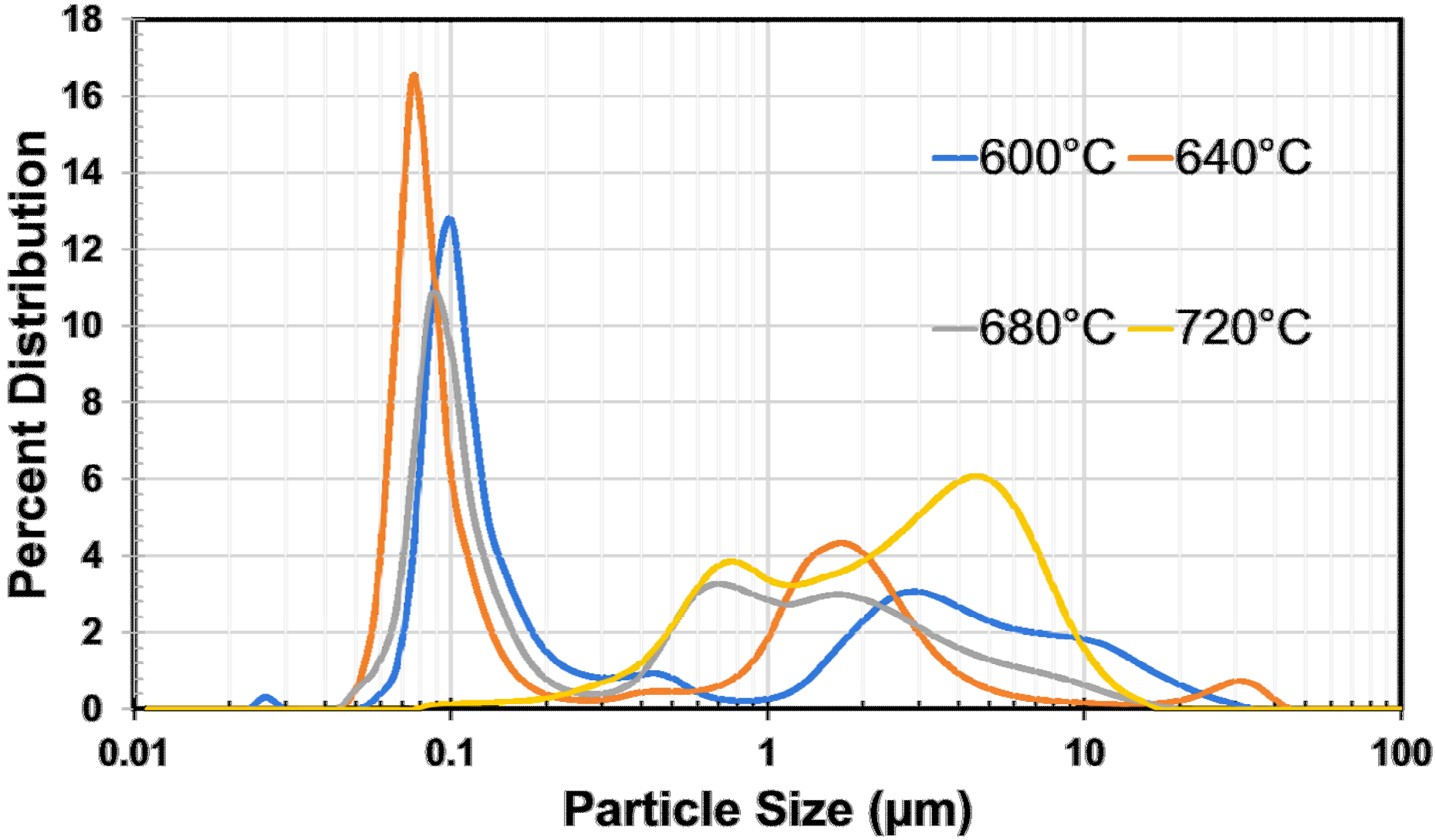
- Powder: after first calcine
  - Particle size analysis (compare milling)
  - UV-Vis analysis
- Sintered pellet
  - SEM
  - EDXS
  - Electric testing
  - Archimedes density



A “Bismuth flower” that results after sintering

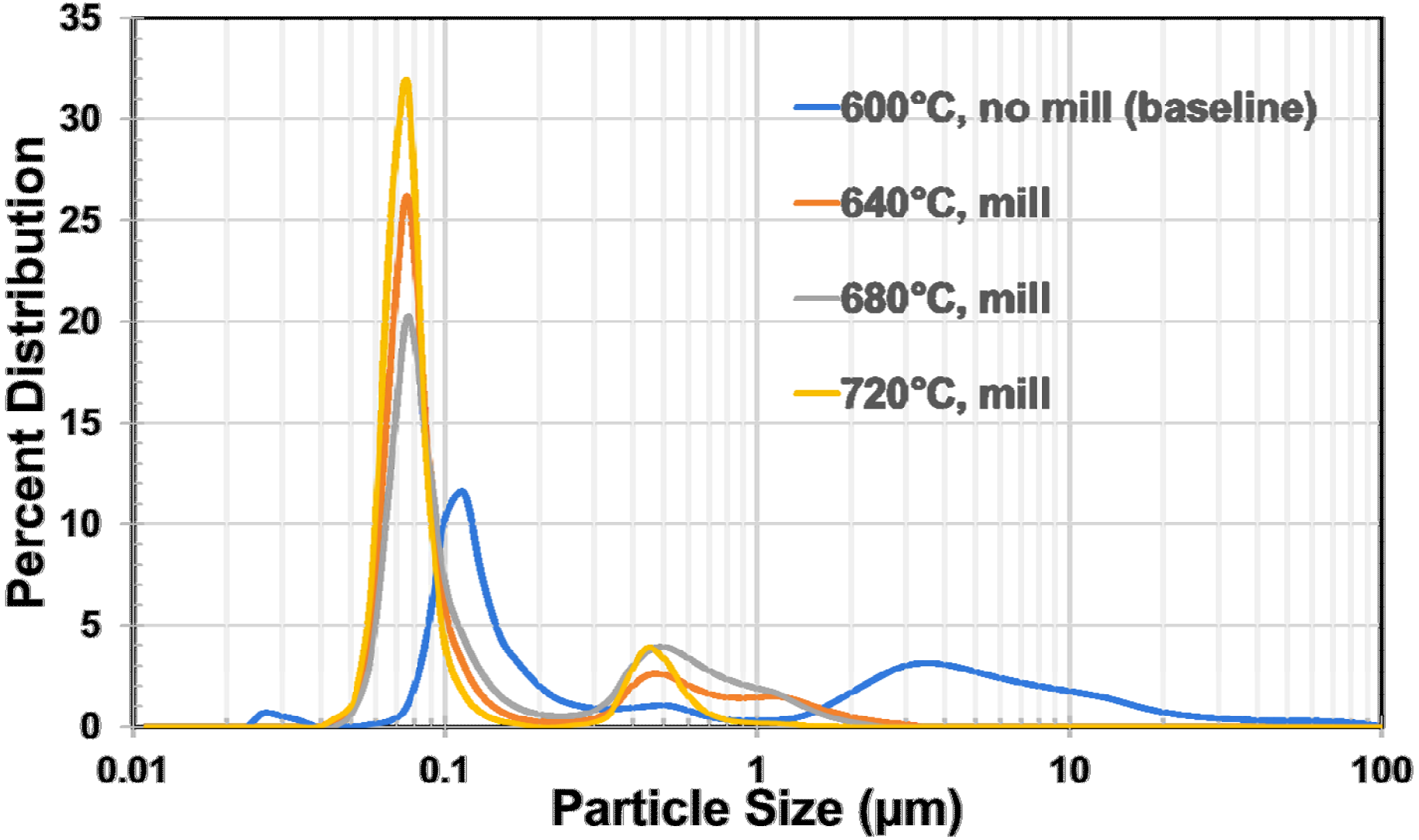
SEM image taken by Amy Allen

Post Calcination

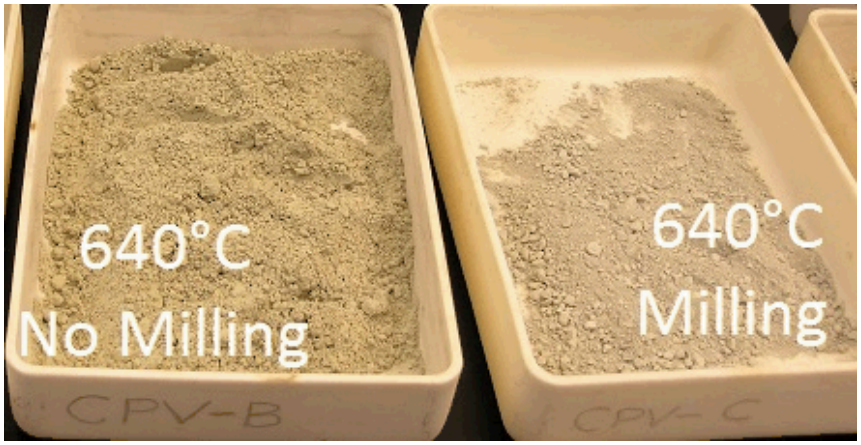


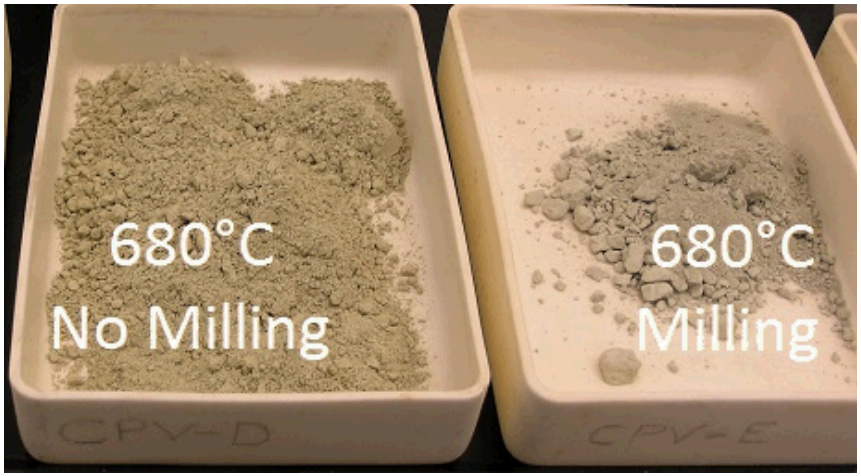
No significant difference except at 720°C.

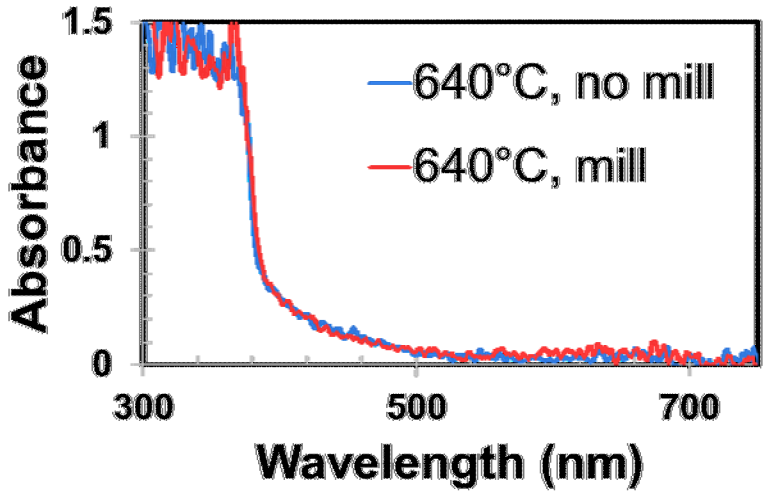
Post Milling

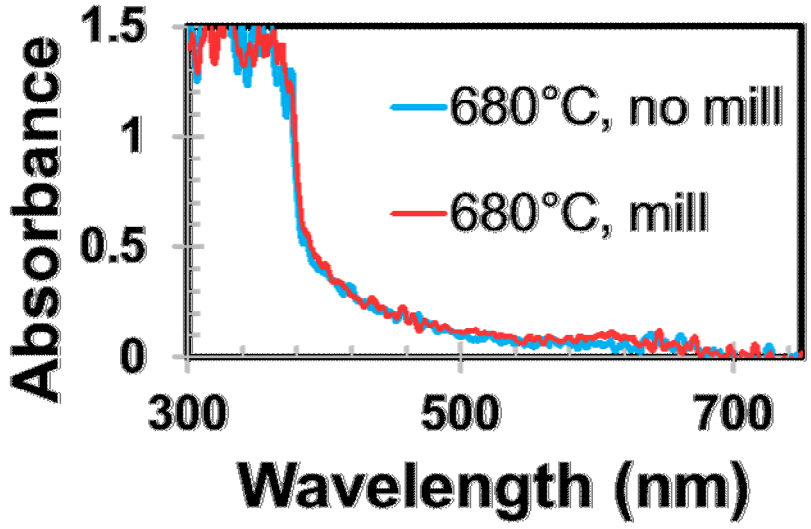


Color Differences Observed

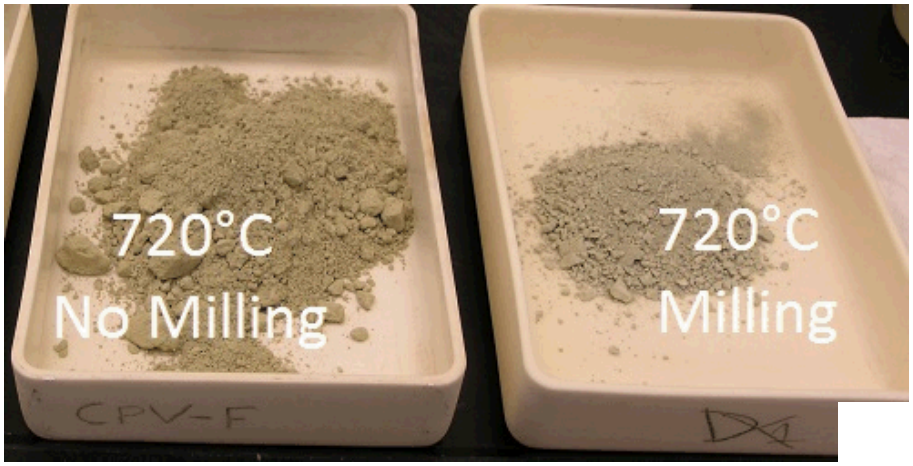


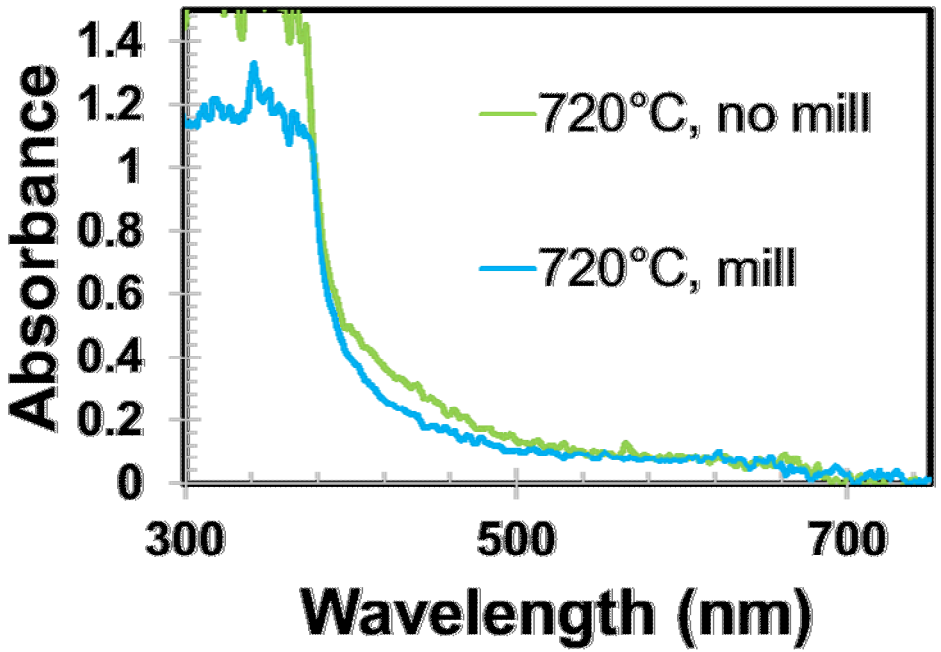




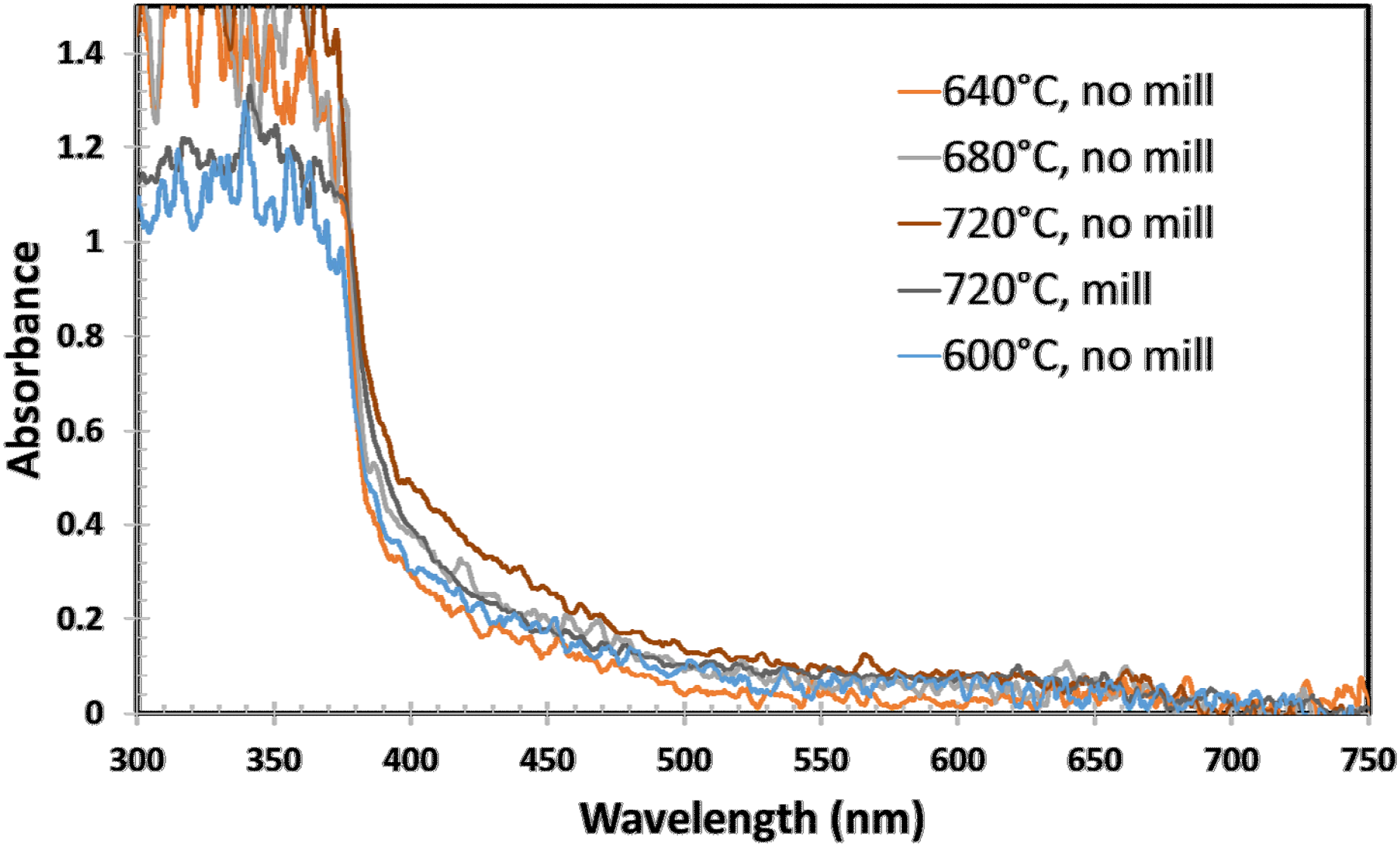


Color Differences Observed

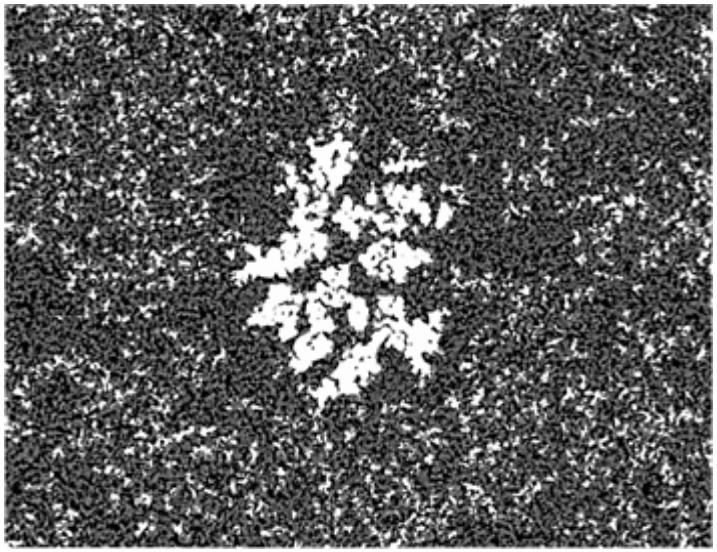


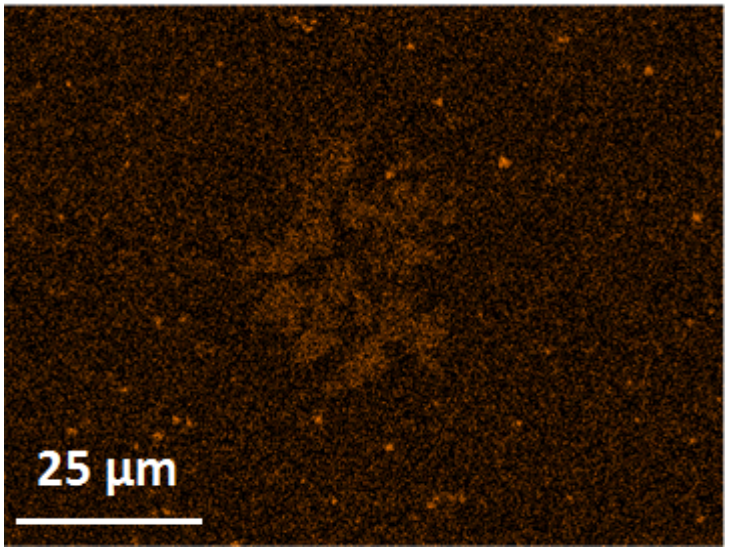


Processing Effect on Band Structure

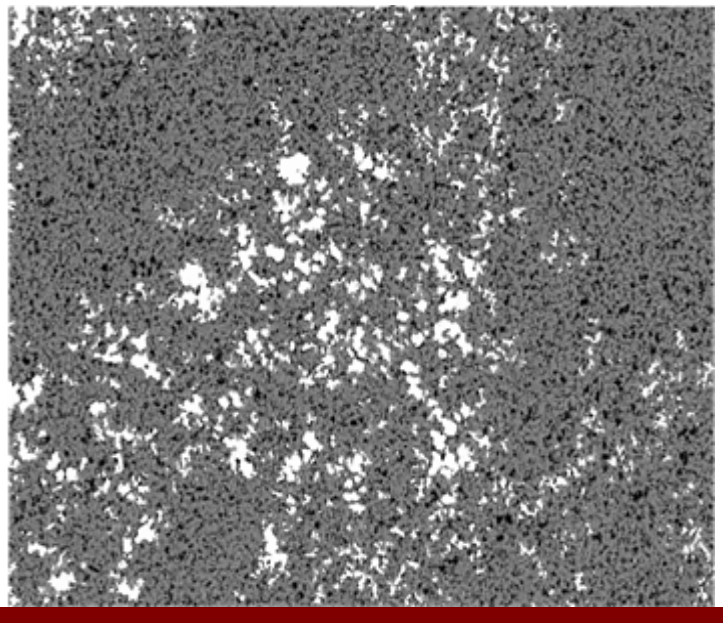


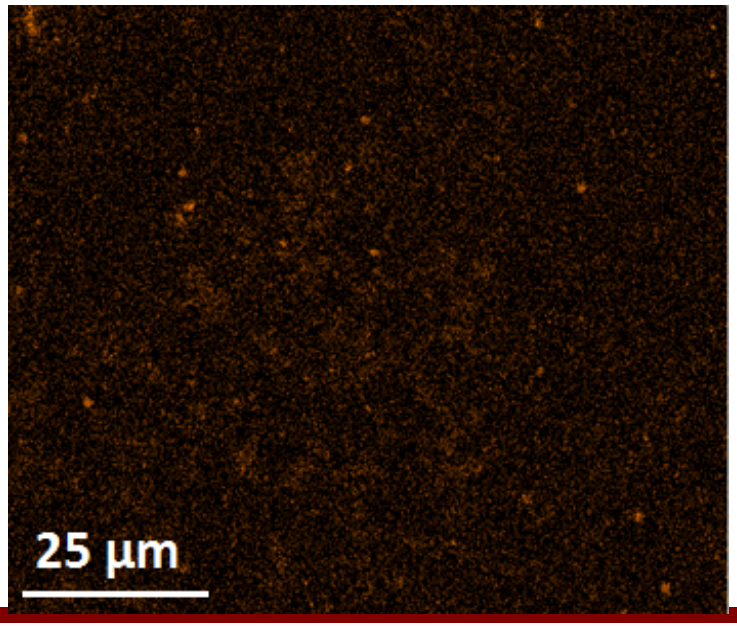
EDXS-Mn mapping





600°C
No mill

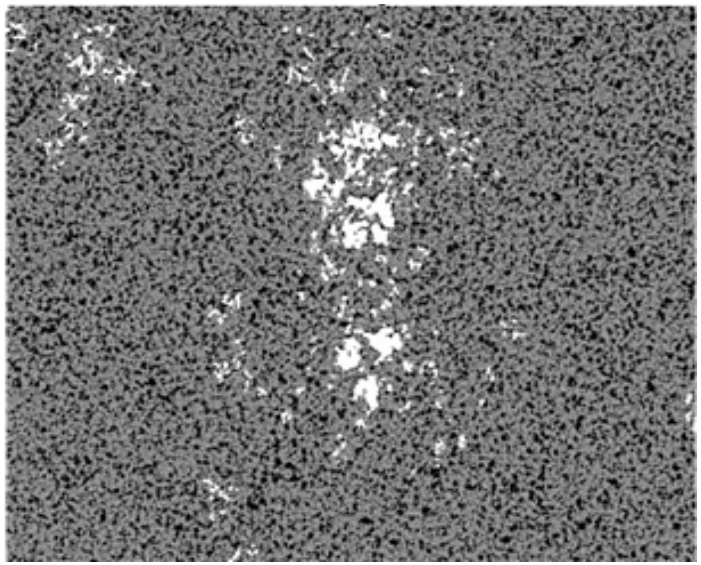


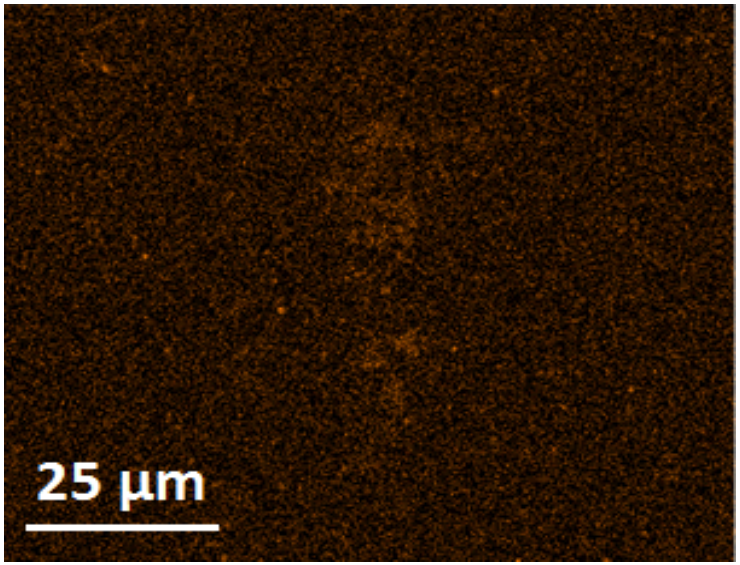


640°C
mill

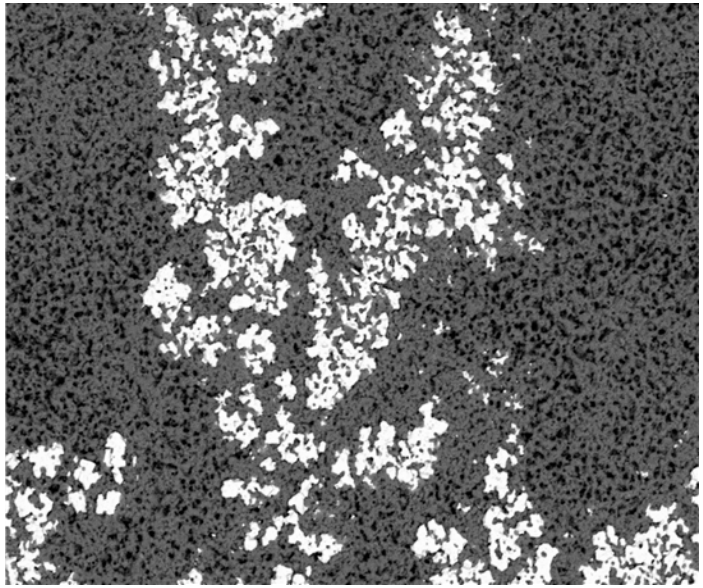
SEM images taken by Amy Allen

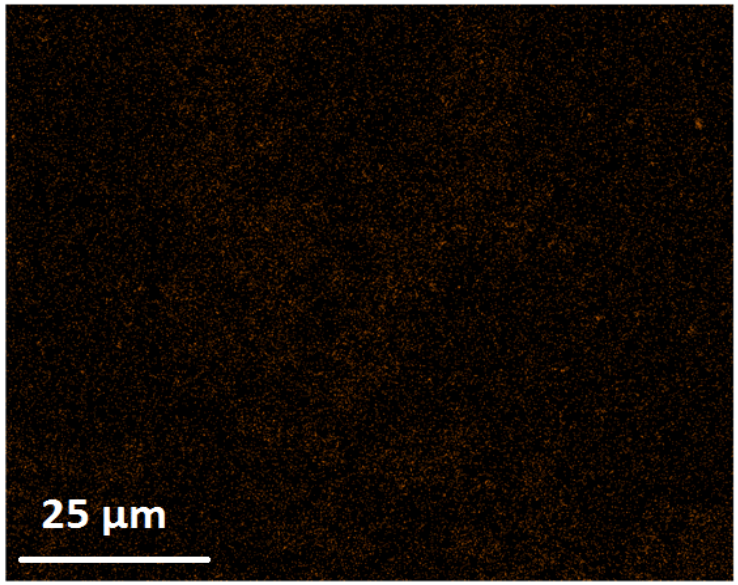
EDXS-Mn mapping





680°C
mill

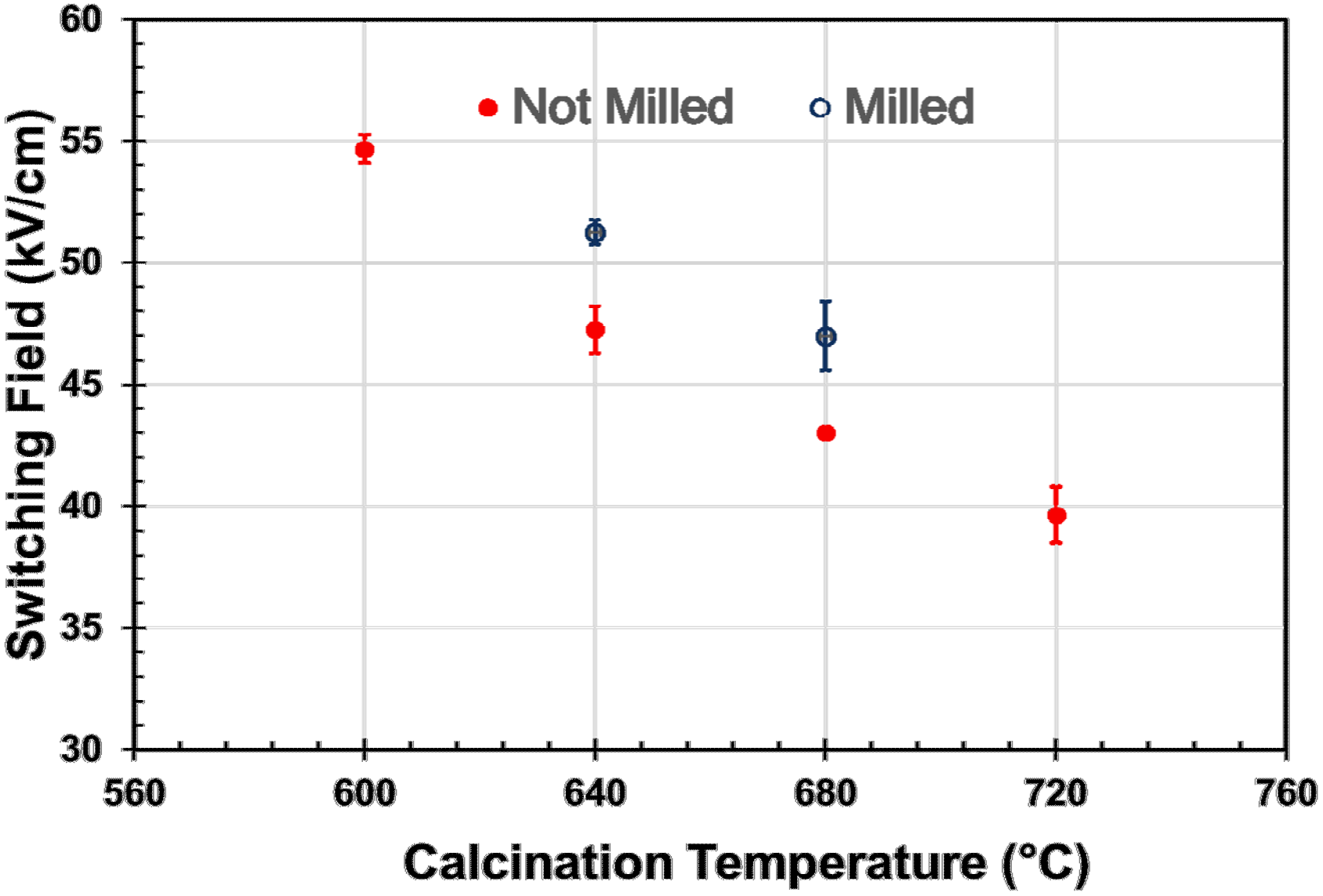




720°C
mill

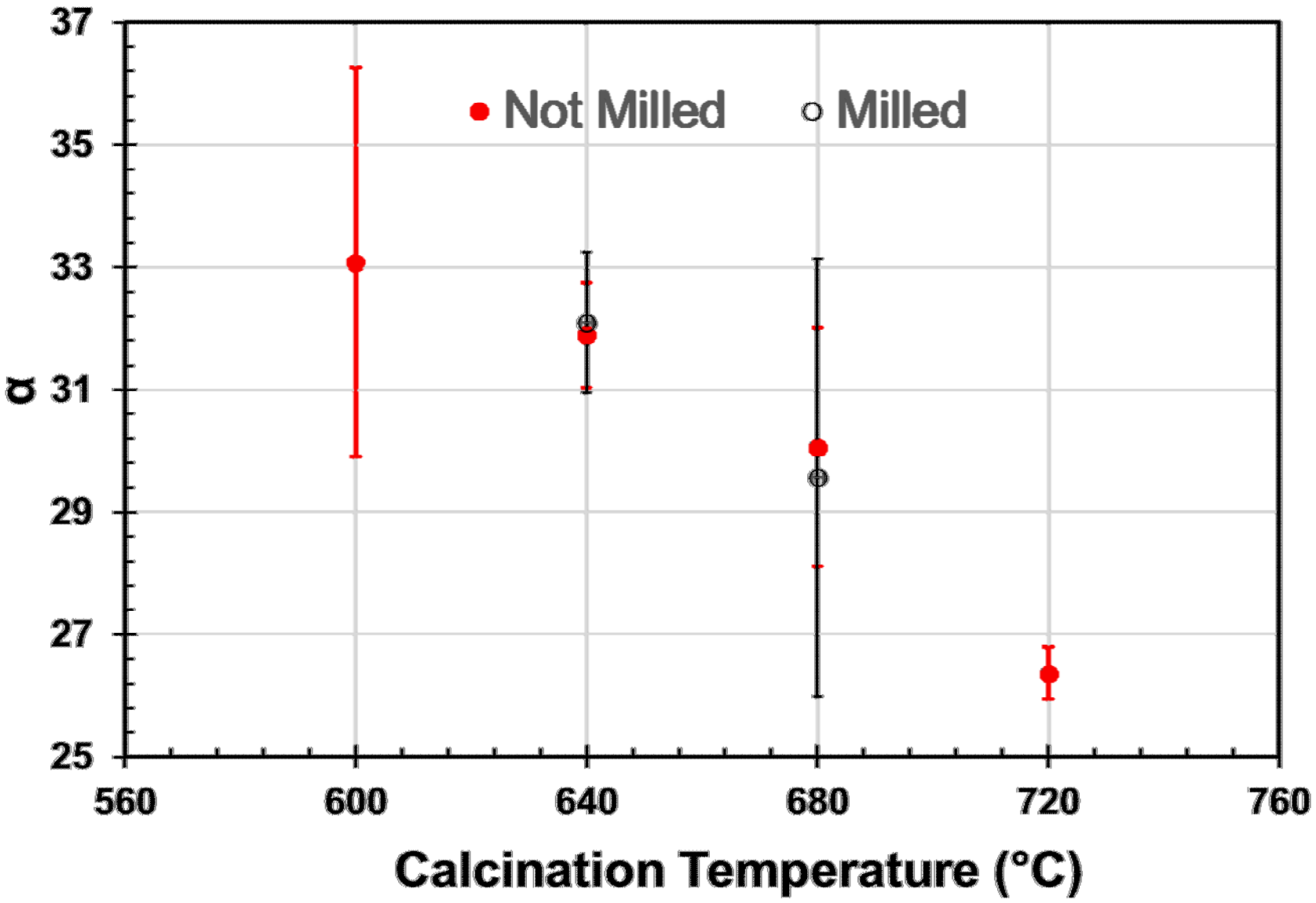
SEM images taken by Amy Allen

Switching Field



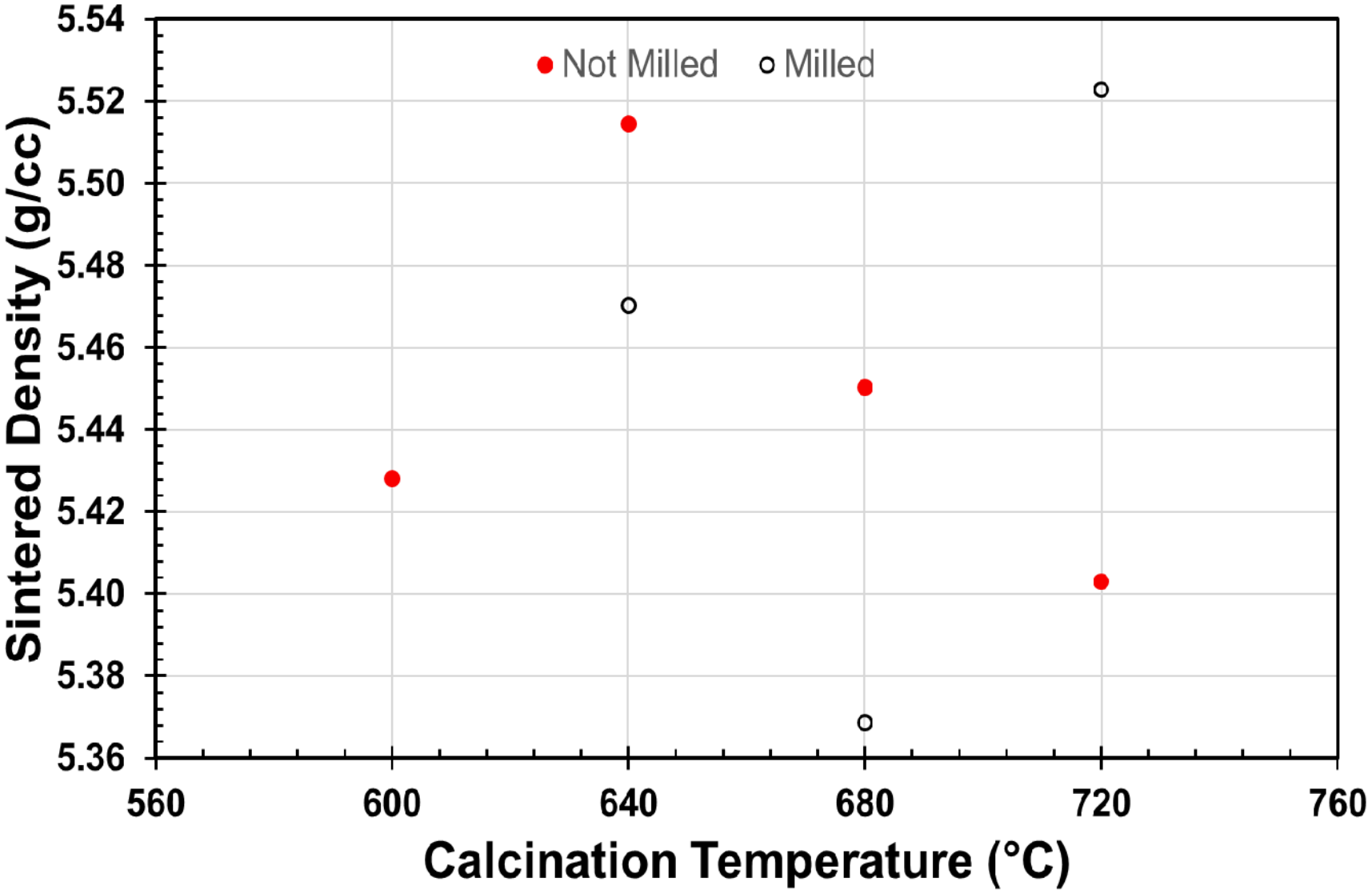
I-V testing performed by Kristin Meyer

α



I-V testing performed by Kristin Meyer

Archimedes Density



Conclusions

- Color differences observed among powder samples likely due to light scattering
- Apparent heterogeneous distribution of Co, Mn results in higher α
- Milling increases E_b, no statistical effect on α

Electroding ¼” sintered pellets in preparation for I-V testing

Path Forward

Future Work

- Repeat experiment to verify observation (in progress)
- ZnO Varistors doped with CoO or MnO (in progress)
- Effect of spinel phase(s) on varistor electrical performance

Acknowledgments

Team

Tom Chavez, Mya Hartley, Chris DiAntonio, Mike Winter

Thank you!

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Questions?

References

- [1] D. R. Clarke, “Varistor Ceramics,” *J. Am. Cerm. Soc.,* vol. 82, pp 485-502, 1999
- [2] M. Peiteado et al., “Influence of crystal structure on the CoII diffusion behavior in the Zn1-xCoxO system,” *J. Solid State Chemistry,* vol. 181, pp. 2456-2461, June, 2008.
- [3] M. Peiteado et al., “Diffusion and reactivity of ZnO-MnOx system,” *J. Solid State Chemistry*, vol. 180, pp. 2459-2464, July 2007
- [4] R. G. Dosch and K. M. Kimball , " Chemical Preparation of High Field Zinc Oxide Varistors," Sandia Report, SAND85-0195, Sandia National Laboratories , Albuquerque, NM, Printed September 1985, 100 pages.