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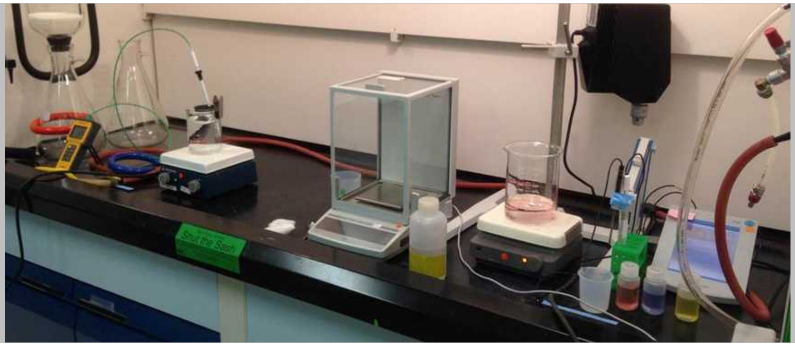

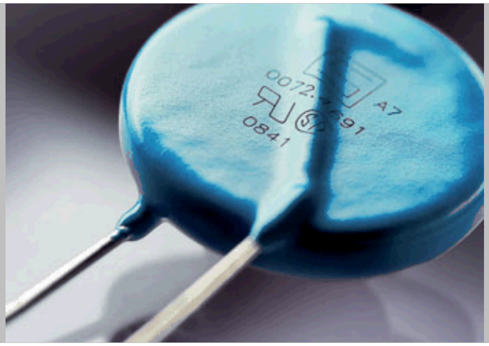

High Doping of ZnO Varistor Powder and Manganese pH Speciation Experiments

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Varistor Introduction

Varistor: variable resistor

- Typically used in parallel with circuits to protect from voltage surges
- When switch voltage is exceeded, becomes highly conducting which draws current away from circuit usually to ground
- Follows ohmic behavior except for switching region which follows the power-law: $I \propto V^{\alpha}$
- Switching time occurs in nanoseconds

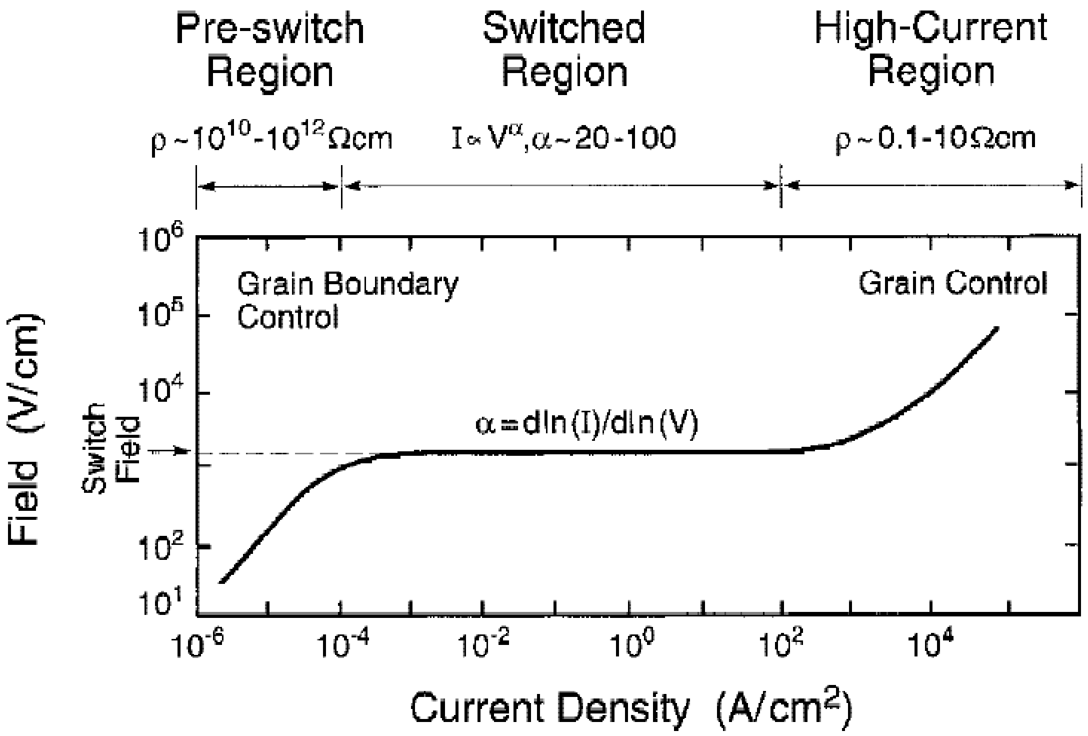


Image: Clarke, D. R. *Journal of the American Ceramic Society*, (1999) **82** (3), 485-500.

Varistor Dopants

Dopants play three main roles: affect grain growth during sintering, affect dewetting characteristics of liquid phase on cooling, control electronic defect states

- Bi_2O_3- provides nm thick electrostatic barrier on grain boundary while enhancing densification by liquid phase sintering
- MnO_x, CoO_x- modify nonlinearity (α), controls grain growth
- Al_2O_3 - enhance grain conductivity, controls grain growth
- Sb_2O_3 – establishes electrostatic barrier and controls grain growth
- Si- inhibit grain growth
- Li- inhibits grain growth in aluminum-doped varistors

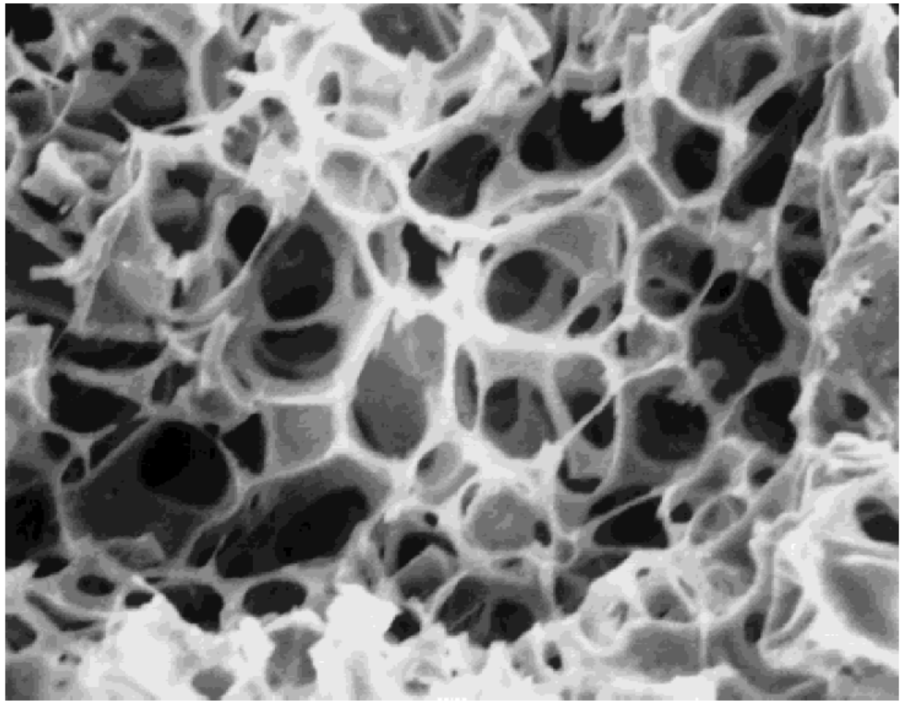


Fig. 5. Etched microstructure of a varistor revealing the continuous, interconnected bismuth-rich phase that percolates through the body of the varistor. (Courtesy of T. Gupta.)

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

Introduction

Low concentration dopants hard to find using characterization techniques

- High Dope
    - 5 mol % Co
    - 5 mol % Mn
    - 2.5/2.5 mol % Co/Mn
- Processed (Pyrolized 450 C samples)
- Pressed
    - 7/8” pellets
    - 1/4” pellets

Experimental Setup

Batch and Synthesis Details

Co-precipitation of oxalates from metal salt solutions

↓

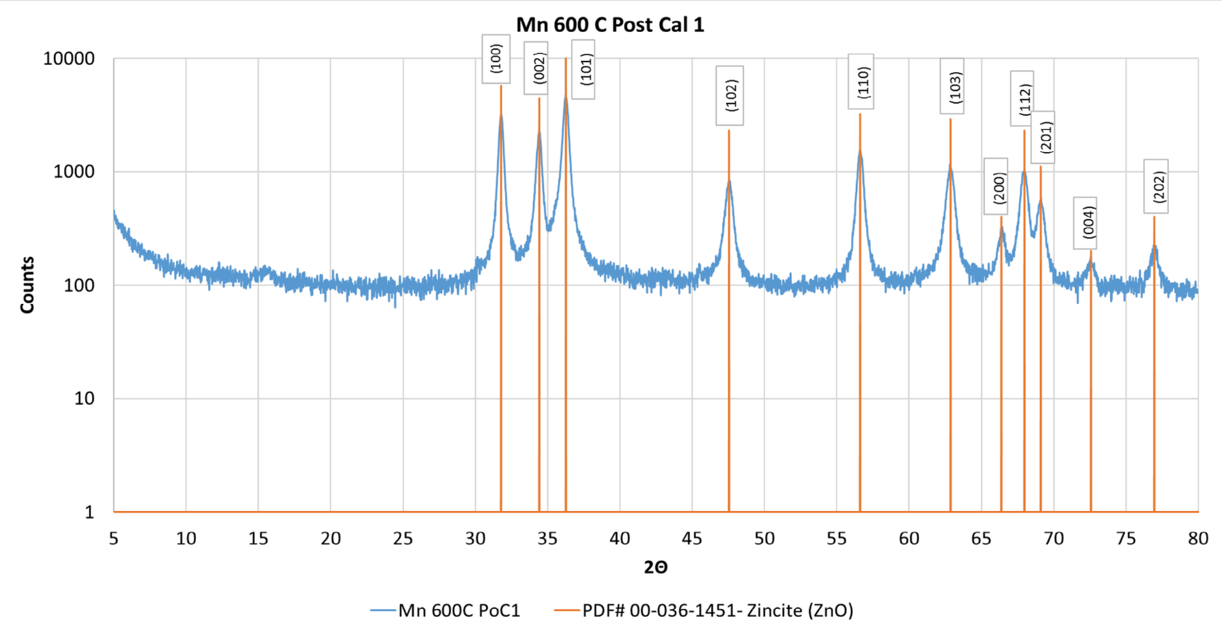
First calcine (600°C)

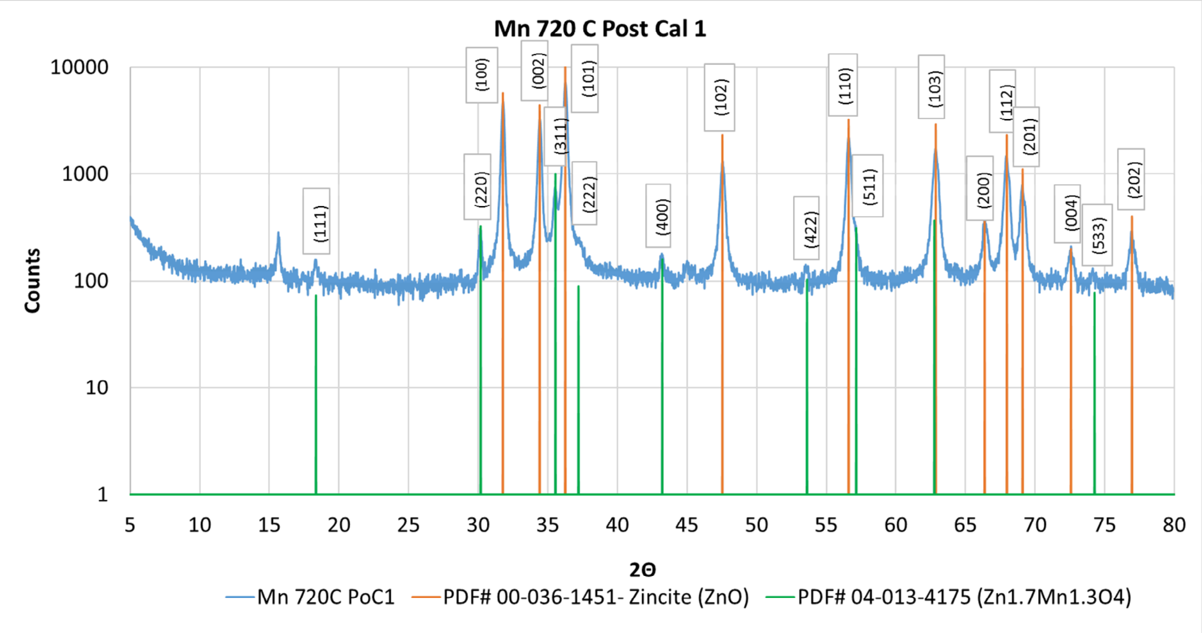
↓

Two doping stages (each with calcine at 400°C)

Image taken by Dani McCade

Characterization





XRD (X-ray Diffraction)

- Patterns taken at Post Cal 1 and Post Cal 3
- Unlike typical composition, Post Cal 1 shows some unique phases in Mn
- Spinels form

Characterization

ESR (Electron Spin Resonance)

- Powerful and sensitive technique to characterize electronic structure of materials with unpaired electrons
- Allows probing of oxidation states of the transition metals doped at low concentrations

8: Mn High Dope 600c no Bi

9: Mn High Dope 720C no Bi

<no Result>

<no Qualifier>

Dataset saved: /home/xuser/xeprFiles/Data/USER DATA/AFRL/cobalt high doped 600C no Bi

Freq. [GHz]: 9.809

Power [mW]: 0.01616

Atten. [dB]: 33

Q: 8300

Field [G]: 50.000

Diode Current [uA]: 0

Lock Offset [%]: 1,183

Receiver Level [%]: -1,961

Image taken by Dani McCade

Wertz, John, and James Bolton. Electron Spin Resonance: Elementary Theory And Practical Applications. Springer Science+Business Media, 2012. Web.

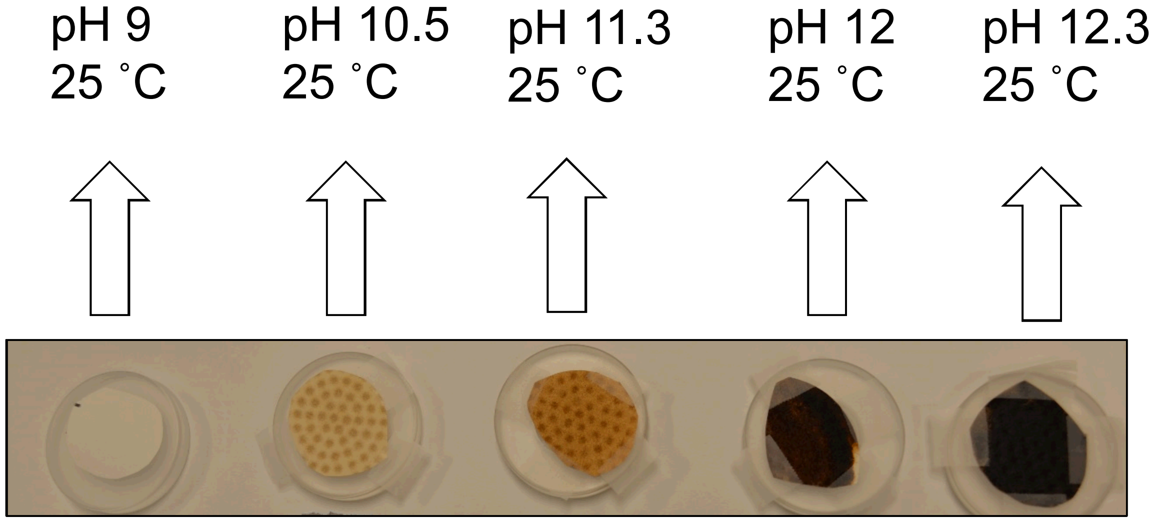
Manganese Speciation pH Experiments

Why?

- Behaves differently depending on oxidation state
- Identify which states provide best results
- Identify pH needed for best results

Experimental Setup

- Fixed pH using NaOH in DI water
- $MnCl_2$ concentration same as 50g batch
- Mixed for 2 mins and filtered
- Temperature (60 ˚C)

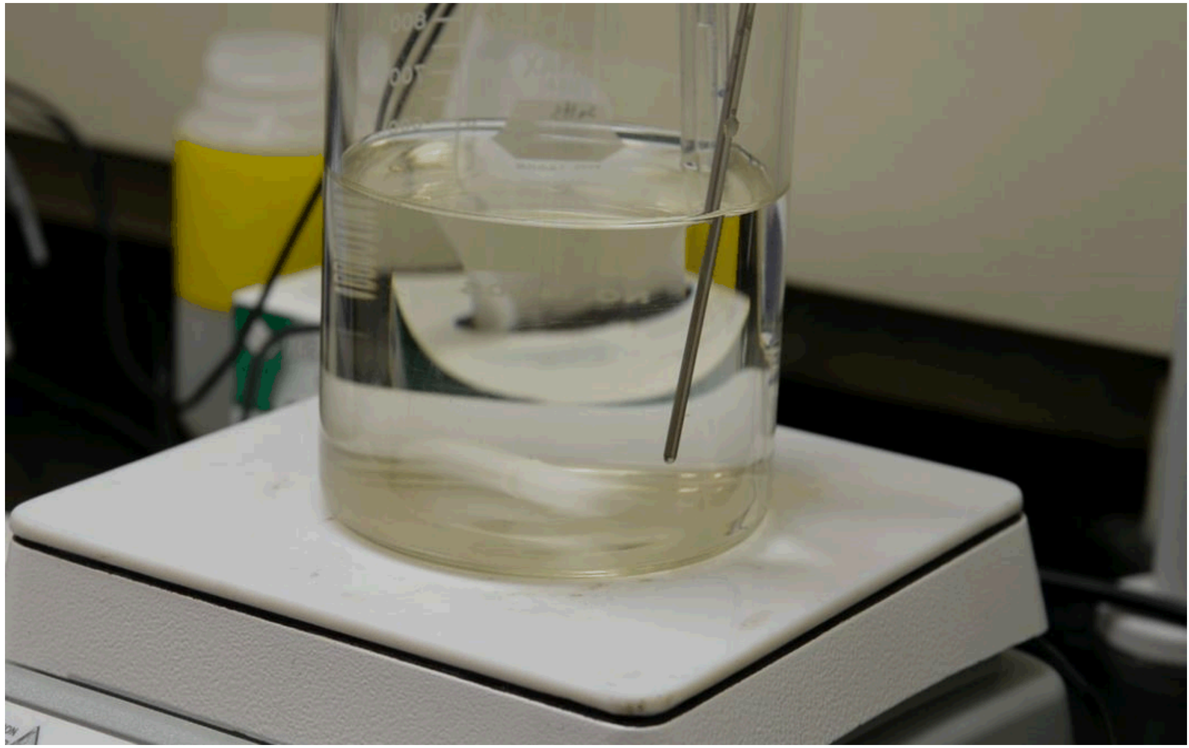


From left to right: increasing pH when manganese chloride added increases amount of precipitate formed

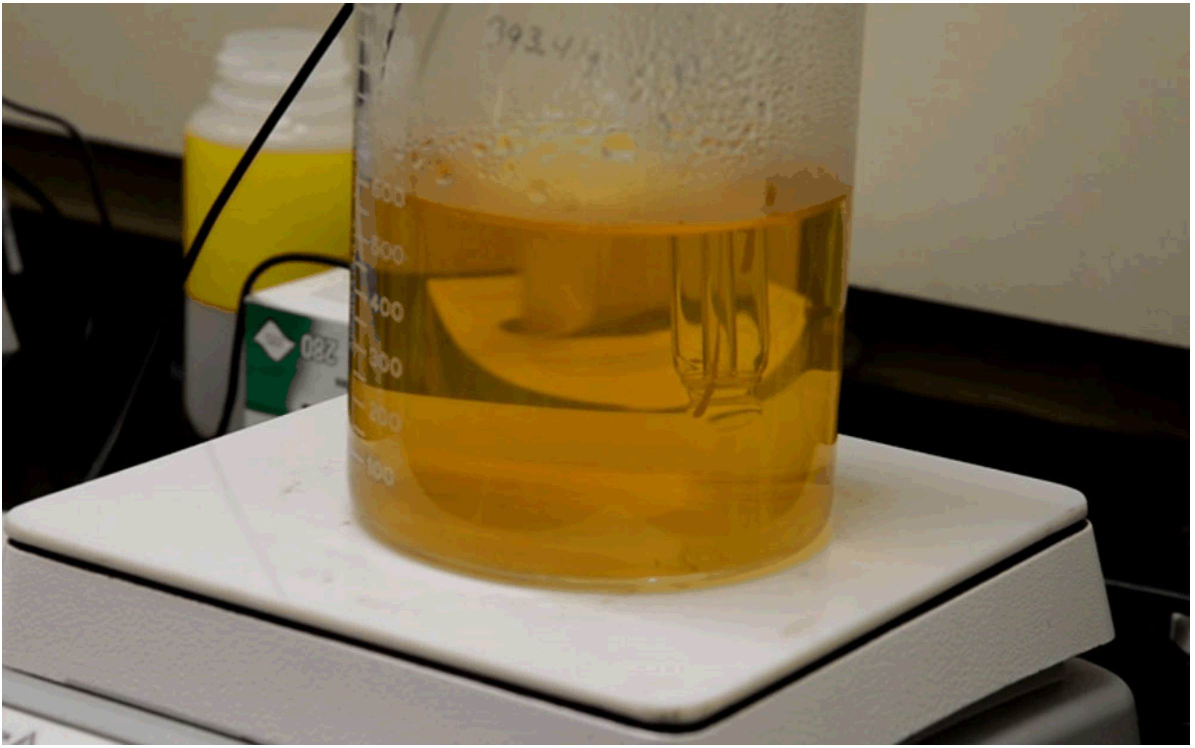
Photo by Michael Hahn

Mn Experiments End Photo

pH 10, 25 ˚C

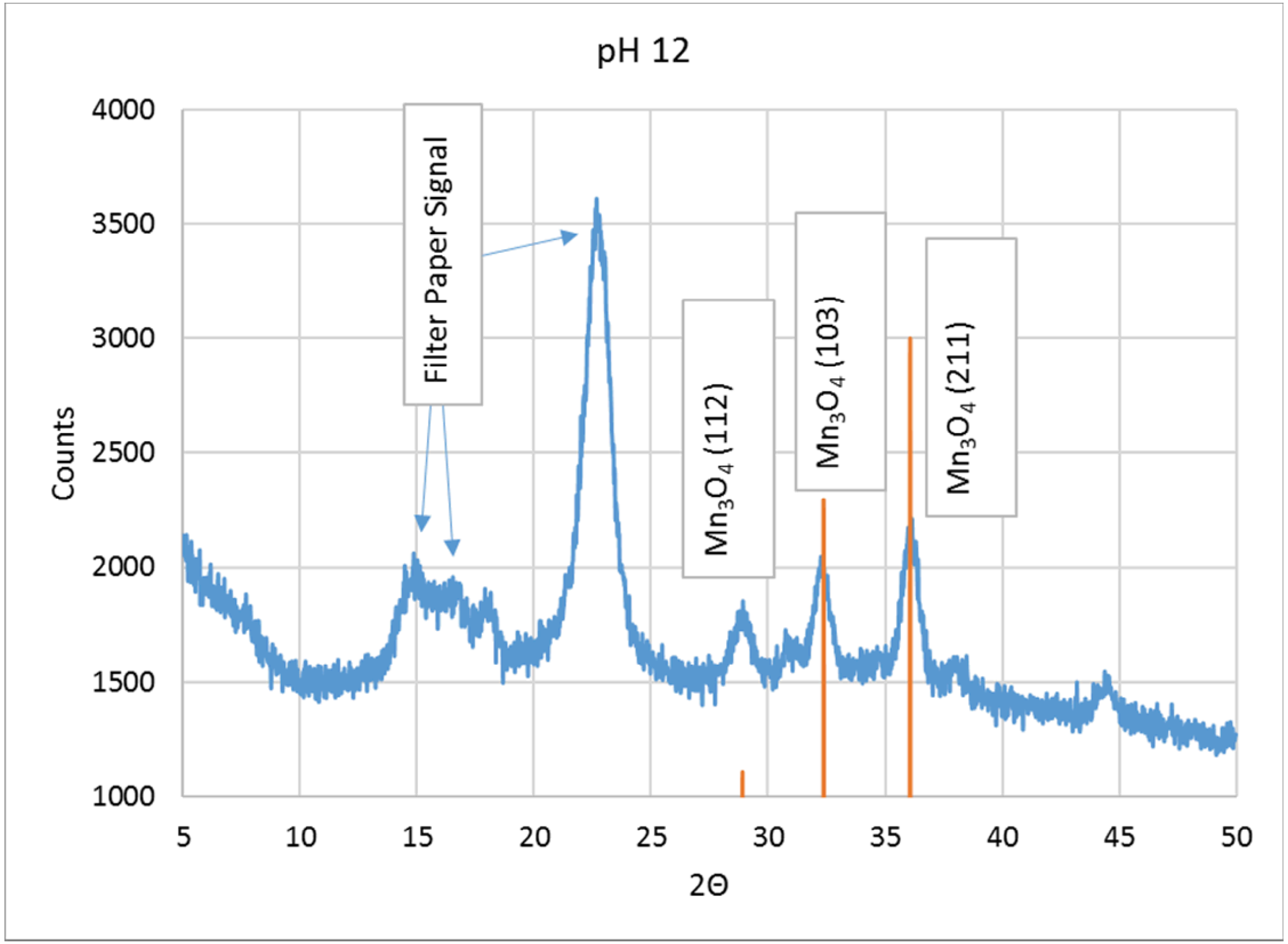


pH 10, 60 ˚C

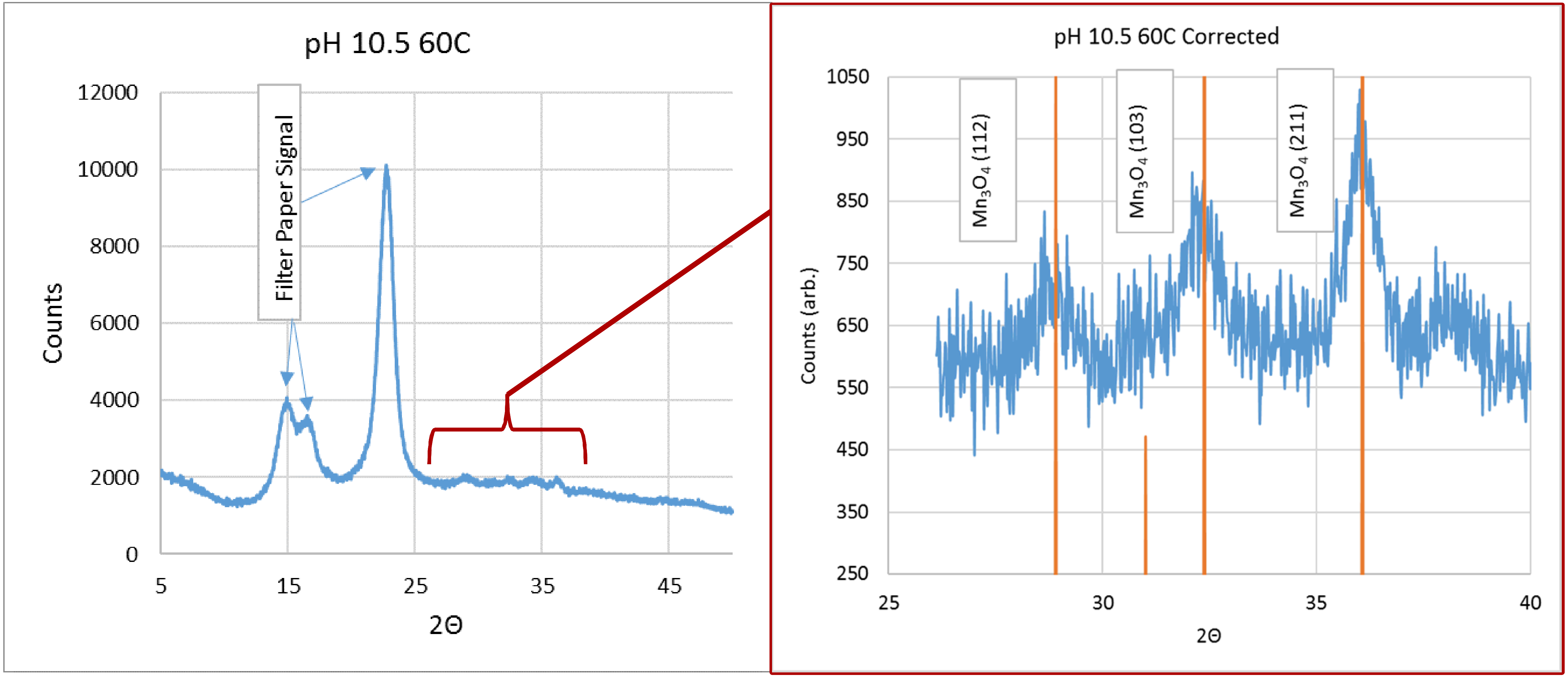


Results

- Only Mn_3O_4 has been detected
- At lower pH, filter paper must be subtracted out with small amount of precipitate present

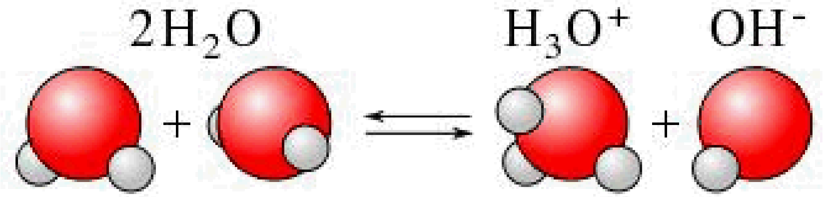


Results (cont.)



Results

- pH related with temperature affects readings
- ~10x times more base required for equal pH at 60 ˚C at 10.5 pH



bath temp (°C)	pH + pOH	terminal pH	$[OH^-]$
10	14.5	8	3.2E-07
45	13.3	8	5.0E-06
50	13.2	7.53	2.1E-06
60	12.8	7.51	5.1E-06
70	12.6	7.23	4.3E-06

Tawa, Gregory J., and Lawrence R. Pratt. "Theoretical Calculation Of The Water Ion Product KW". *Journal of the American Chemical Society* 117.5 (1995): 1625-1628. Web.

References

- [1] D. R. Clarke, “Varistor Ceramics,” *J. Am. Cerm. Soc.,* vol. 82, pp 485-502, 1999. Web.
- [2] Wertz, John, and James Bolton. Electron Spin Resonance: Elementary Theory And Practical Applications. Springer Science+Business Media, 2012. Web.
- [3] Tawa, Gregory J., and Lawrence R. Pratt. "Theoretical Calculation Of The Water Ion Product KW". *Journal of the American Chemical Society* 117.5 (1995): 1625-1628. Web.

Acknowledgments

Tom Chavez, Mya Hartley, Chris DiAntonio, Mike Winter

Thank you!