SAND2017-7697D

Mn Speciation and High Doping of ZnO Varistor Powder Experiments

Michael Hahn
Sandia National Laboratories, Albuquerque, NM
Missouri University of Science and Technology, Ceramic Engineering, May 2018
Manager: Mike Winter, 2568
7/26/2017
Collaborators: Pin Yang, Erik Spoerke, Dani McCade, Josh Nordlander

Background

Varistor materials are commonly used in electrical surge protection applications. They are formed by making ceramic powders and sintering. Dopants are used to enhance their electrical properties and allow for high sintered densities. Very small amounts of dopants are needed to achieve the best electrical results.

Motivation

- Difficult to find dopants due to very low amounts used
- Hard to characterize their phases and oxidation states which affect electrical properties
- Particularly Mn has multiple oxidation states (2^+, 3^+, 4^+) which changes during processing

Experimental Setup and Procedure

Standard Synthesis via Chemical Precipitation

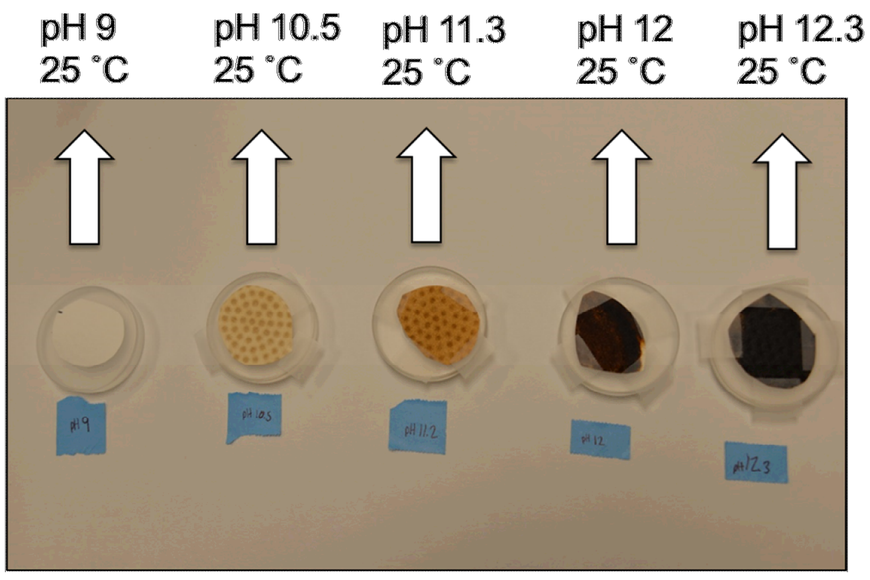
Co-precipitation of oxalates from metal salt solutions → First calcine (600°C) → Two doping stages (each with calcine at 400°C)

Experiment

Addition of only $MnCl_2$ into basic aqueous solution → Precipitation of only Mn_3O_4 → Filtered and collected after two minutes to analyze

Results

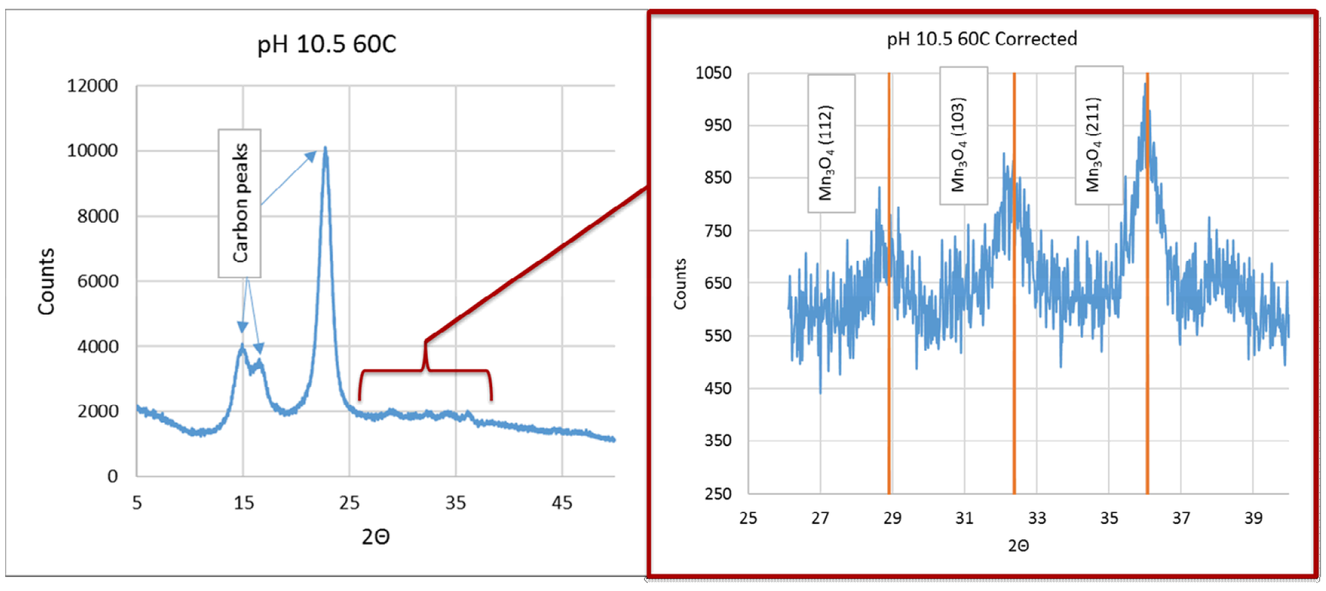
- Throughout the studied pH range, only Mn_3O_4 was identified as forming
- The amount of precipitate that was collected depended on the pH
- Temperature was shown to directly affect the pH reading due to water dissociation



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

X-Ray Diffraction (XRD)

- For higher pH, plenty of precipitate allows easy identification of Mn_3O_4
- For lower pH, a filter paper control pattern is subtracted out to allow more confidence in Mn_3O_4 identification shown on the right



Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

SAND No. 2011-XXXXP

Experiment Setup and Procedure

- A composition was doped with high amounts of Mn
- Processed through bismuth and sodium dope including calcinations as shown above in standard synthesis graphic
- Using this powder, XRD and ESR data may be collected

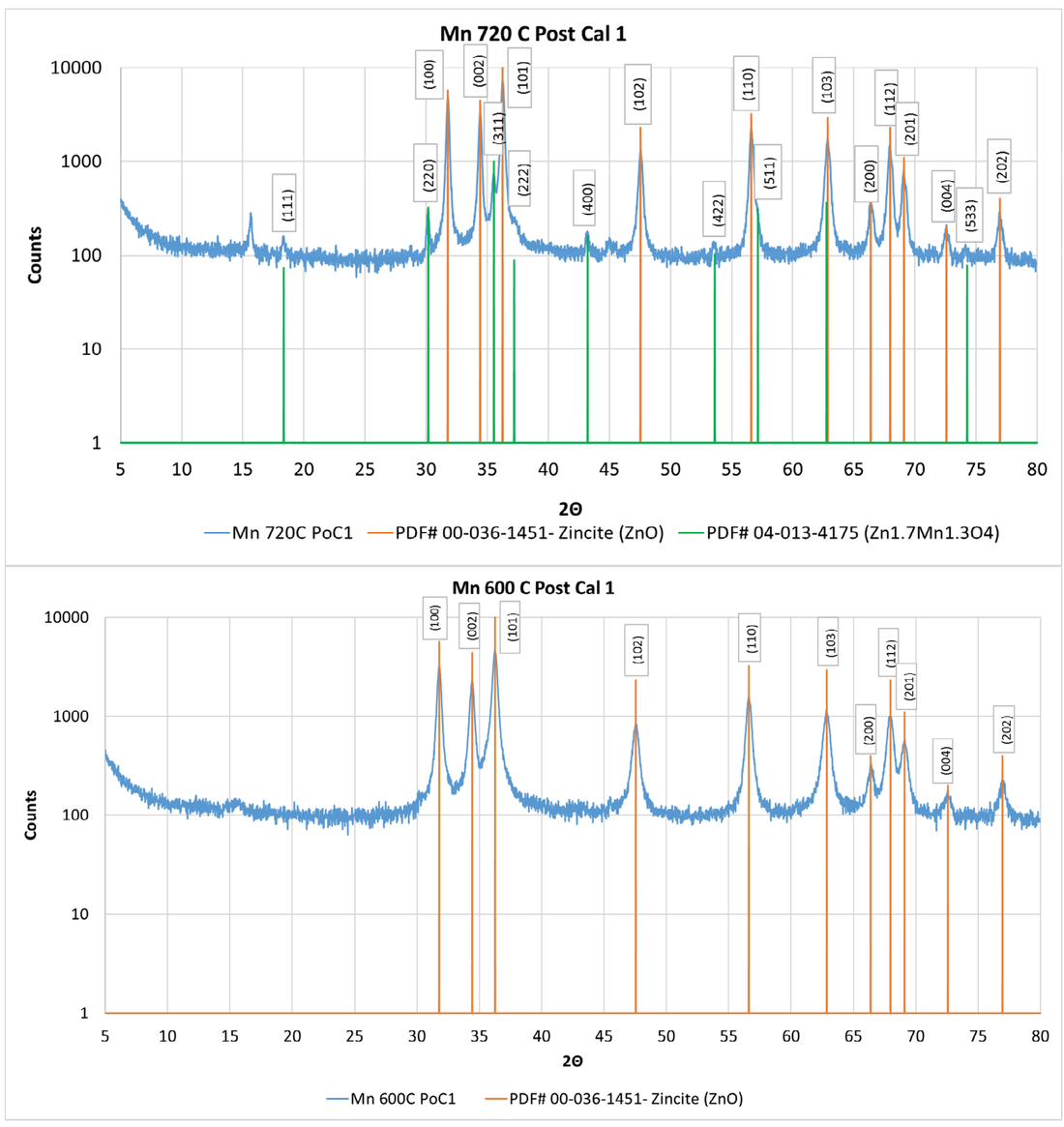
Electron Spin Resonance (ESR)

- 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

Example shows raw data of two different powders calcined differently with high amounts of Mn: green corresponds to Mn^{2+}, red is unknown. The fact that both patterns are different tells us that Mn is behaving differently during calcinations

XRD

- Patterns taken after the first and third calcination
- Mn pattern at 720 ˚C shows spinel phase, $Zn_{1.7}Mn_{1.3}O_4$, which is either undetectable or absent in the 600 ˚C sample



Future Work

- High dope Mn powder showed spinel phase at 720 ˚C vs none at 600 ˚C and differences in ESR patterns suggest a change in oxidation state that needs to be verified and understood
- Mn_3O_4 is produced in the pH speciation experiments, but this is isolating the Mn from a standard reaction. We want to see what happens if $ZnCl_2$ and $MnCl_2$ are added together.

U.S. DEPARTMENT OF ENERGY

National Nuclear Security Administration

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

SAND No. 2011-XXXXP