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Synthesis, Development and Characterization of Novel Nanoparticle Ferrite Materials

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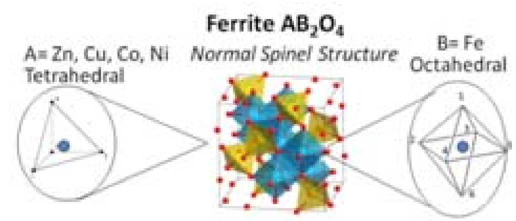

Tom Chavez, Bernadette A. Hernandez-Sanchez
Sandia National Laboratories, Albuquerque, New Mexico

The 25th Annual Rio Grande Symposium on Advanced Materials
October 7, 2013
Albuquerque, New Mexico

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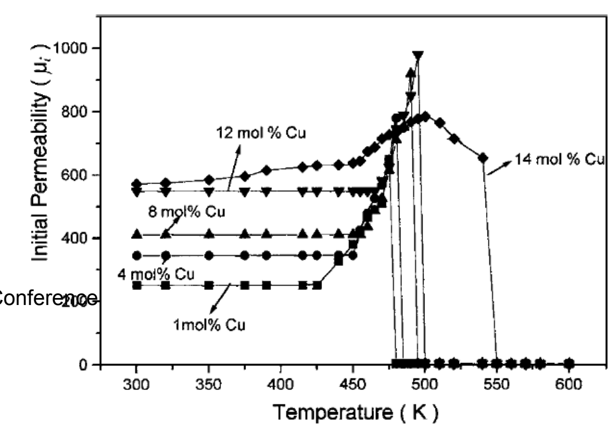
Objective Details

- **Single greatest technology gap limiting further reduction in size and cost of ferrite based microsystems/microdevices lies with the material system**
  - This research focuses specifically on novel and enhanced ferrite materials
- **Development of novel LTCC ferrite material(s) with significantly improved magnetic performance**
  - Increase saturation by 60% (goal – 5 kG), permeability by 40% (goal – 550), and insulation resistance 3-fold (goal – 10^{13} Ω•cm)
- **Explore novel designs that reduce leakage inductance (e.g., use of leakage shorting coils) and marry them with the new ferrite** – allowing for significantly higher output voltages within a fixed design volume

- **Direction: Optimized novel ferrite composition**
  - ➢ Initiation point based on literature*: $Ni_{0.65-x}Cu_xZn_{0.35}Fe_{2-x}O_4$
    - o Materials performance for x = 12 mol% (3.31-3.35 wt% Cu) with B_{sat} = 0.61T, grain size of 2.5 µm and μ_r= 615 for 900 °C sintering
    - o Curie temperature of 500 K (227 °C) for this formulation which is substantially higher than the existing ferrite tape (T_C ~120 °C)
    - o Insulation resistance (1.82x10^{14} Ω·cm) also ~50X higher (3.58x10^{12} Ω·cm)
    - o Increase Tc – more stable performance
  - ➢ Sintering aids or fluxes, decrease sintering temperature, enlarge sintering window while minimizing the reduction of volume of the magnetic phase

T_s (°C)	d_x (g/cm^3)	D_m (µm)	μ_i (1 MHz)	B_s (Tesla)	ρ (Ω cm)	Q (At 1 MHz)
850	4.146	5.8	490	0.25	8.8×10^{13}	103
860	4.312	5.5	520	0.30	12.5×10^{13}	113
870	4.525	5.2	560	0.35	13.4×10^{13}	124
880	4.715	4.8	580	0.48	14.5×10^{13}	124
890	4.925	3.5	590	0.54	15.8×10^{13}	128
900	5.256	2.5	615	0.61	18.2×10^{13}	132
910	5.285	3.8	510	0.48	14×10^{13}	85
920	5.315	5.4	450	0.31	12.5×10^{13}	72
930	5.384	6.2	415	0.22	8.5×10^{13}	65



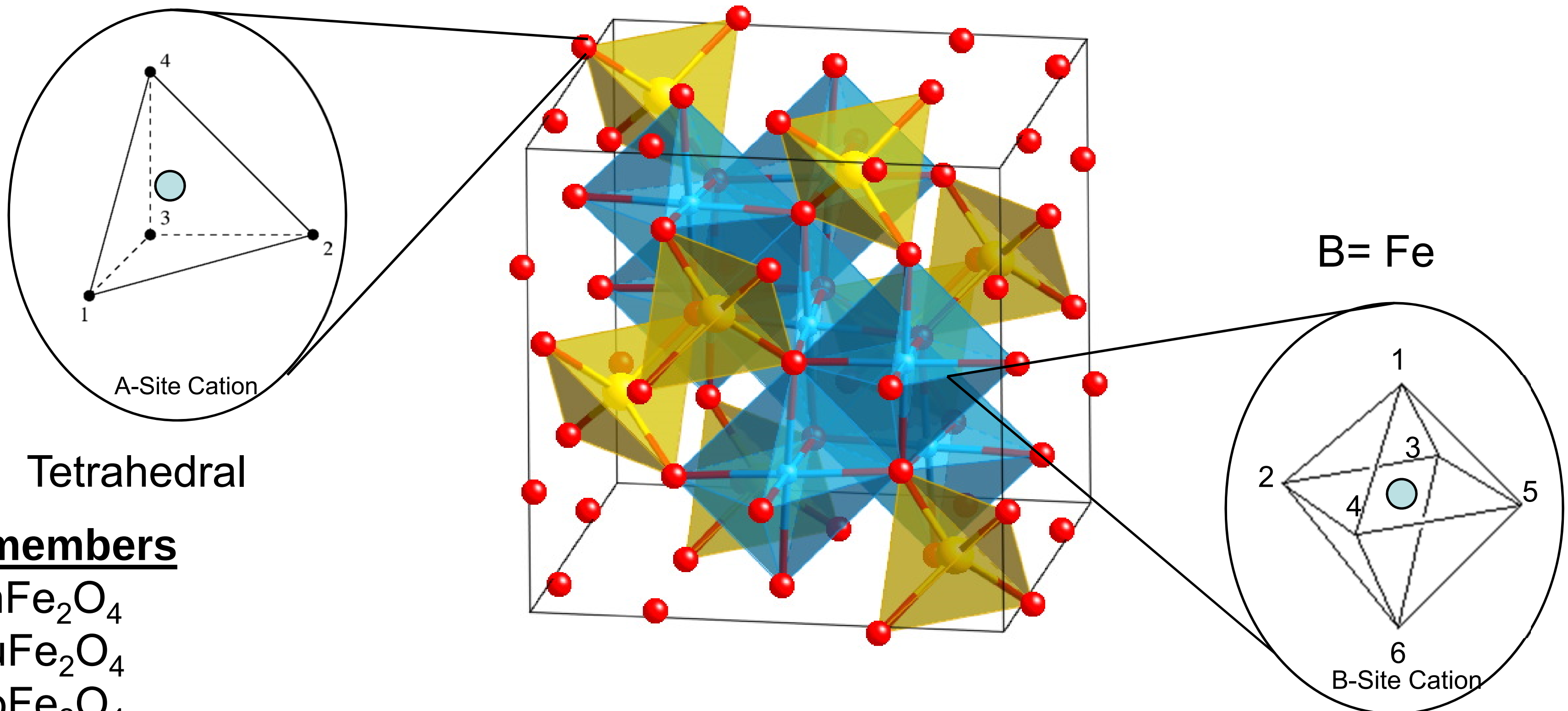
Materials Science & Technology 2012 Conference
October 07-11, 2012
Pittsburgh, Pennsylvania

*Murthy, S.R., "Low temperature sintering of NiCuZn ferrite and its electrical, magnetic and elastic properties," *Journal of Materials Science Letters*, Vol. 21, No. 8 (2002), pp. 657-660.

Ferrite AB_2O_4

A= Zn, Cu, Co, Ni

Normal Spinel Structure



Tetrahedral

B= Fe

Octahedral

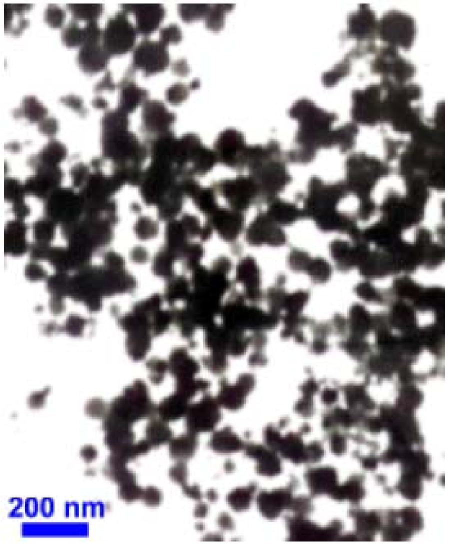
<u>Endmembers</u>

$ZnFe_2O_4$
$CuFe_2O_4$
$CoFe_2O_4$
$NiFe_2O_4$

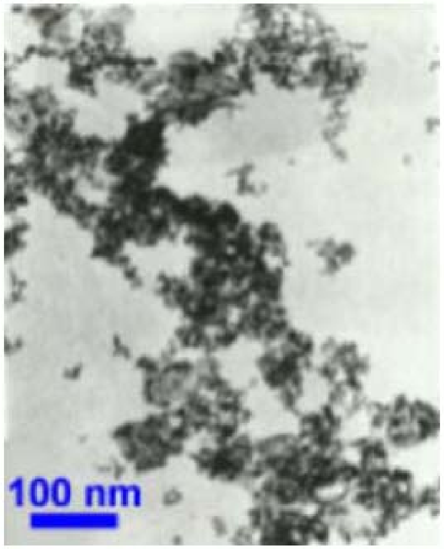
Raw materials and characterization

- Procured initial set of raw materials for development of novel and baseline ferrite formulations from ‘solid-state/mixed oxide’ synthesis route and initiated scoping studies for chemical synthesis route
  – Suppliers - Inframat and MTI Xrstal
- Characterization of initial set of raw materials is complete:
  – Helium pycnometry (density), BET (specific surface area), Laser Scattering (Particle size distribution), SEM/TEM (size and morphology), XRD (crystalline phase and nanostructure)

Gamma-Fe_2O_3, 20nm, $30m^2/gr$



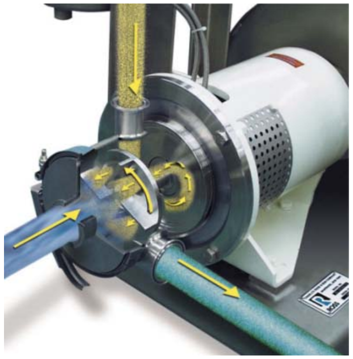
NiO, 30nm, $65m^2/gr$

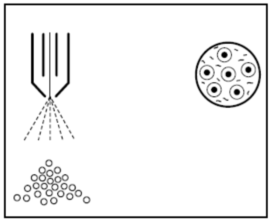


ZnO, 50nm, $7m^2/gr$

Synthesizing/processing ferrite powder and forming test samples

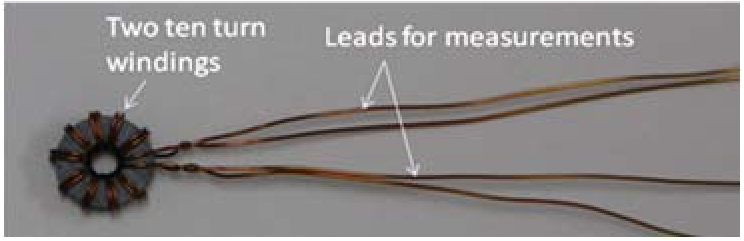
- Mapping processing parameters and routes on the resultant ferrite formulation/composition development
  - Raw materials, dispersion-mixing-milling-drying and calcination techniques



- Baseline samples from standard compositions have been fabricated as toroids and test discs



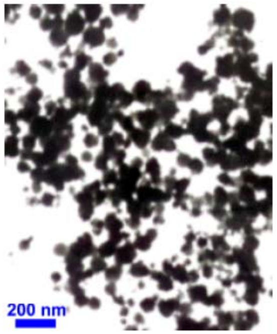



- Magnetometry of test samples has been initiated – Magnetic property measurement system (SQUID - Superconducting Quantum Interference Device)

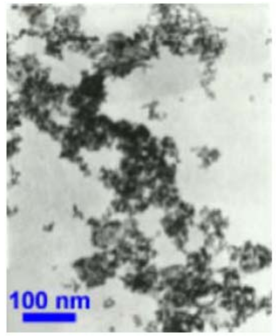
Synthesizing/processing ferrite powder and forming test samples

- Nanoparticle materials dispersed and mixed in a high speed disperser utilizing a Solid/Liquid Injection Manifold and then spray dried to final formulation

Gamma-Fe_2O_3, 20nm, 30m^2/gr

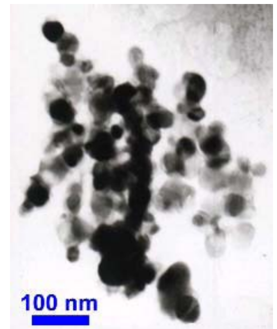


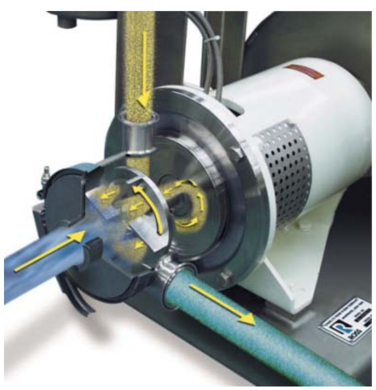
NiO, 30nm, 65m^2/gr



ZnO, 30nm, 35m^2/gr

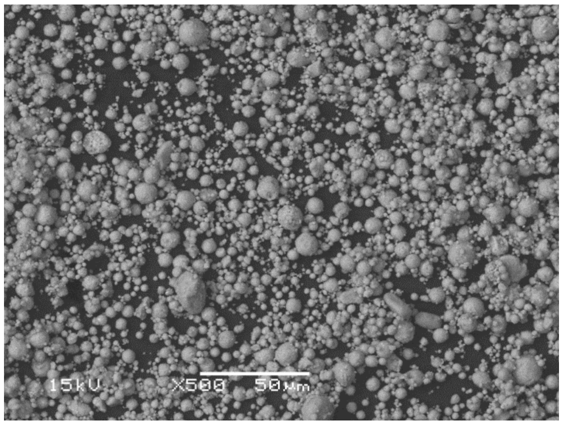
CuO, 50-80nm, 13m^2/gr

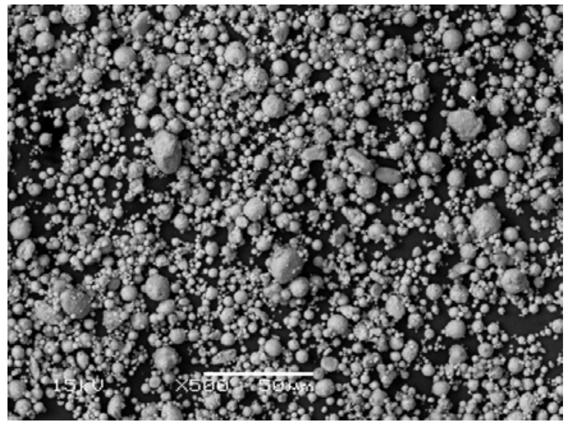


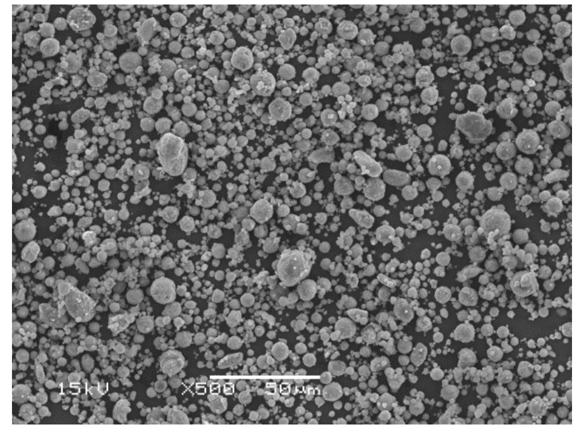


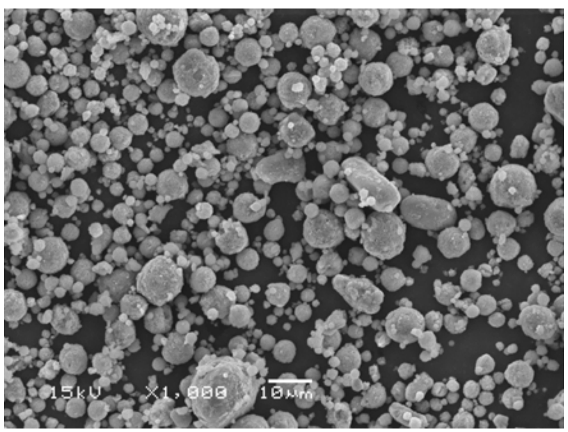
SEM-EDS analysis of ‘as-synthesized’ ferrite powder

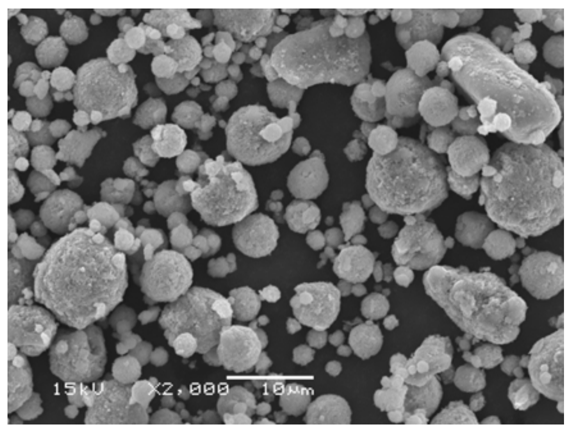
- SEM-EDS analysis provides qualitative evidence for a homogeneous synthesis procedure

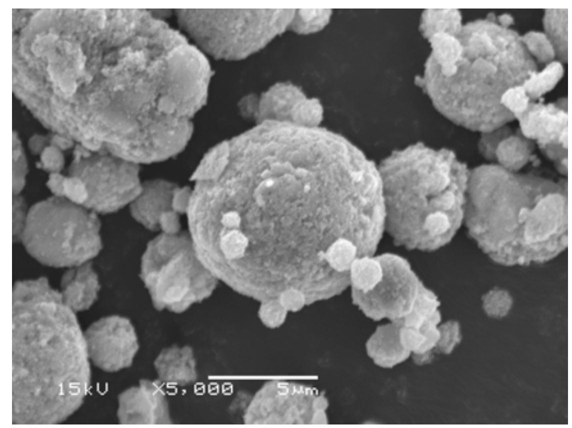












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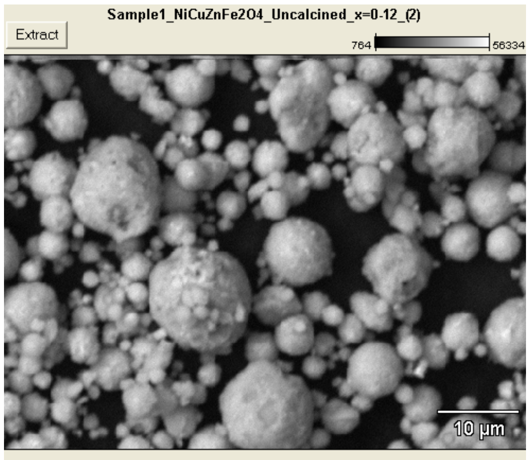
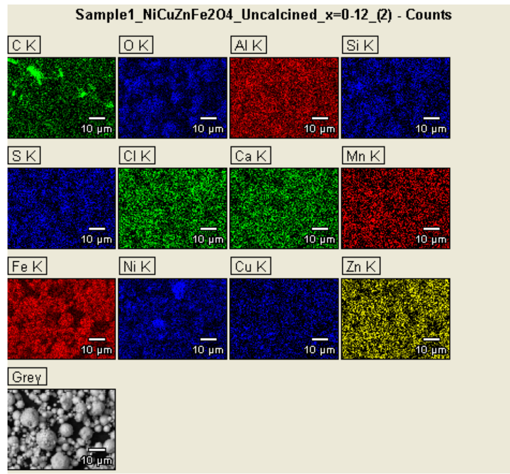
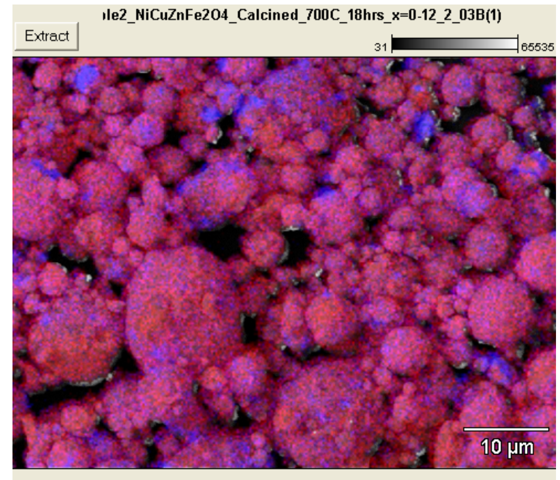
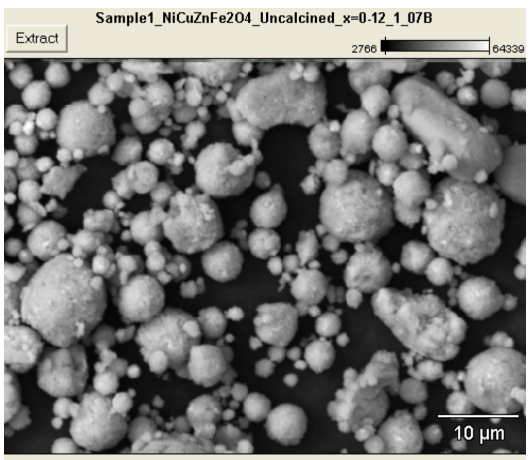
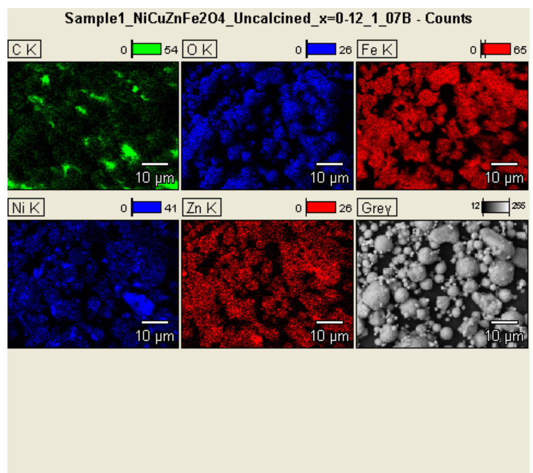
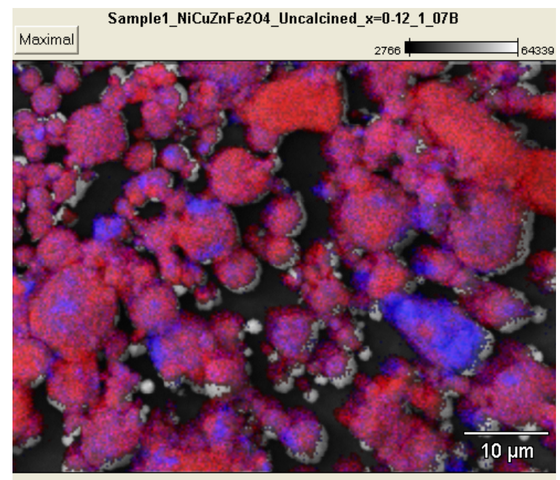






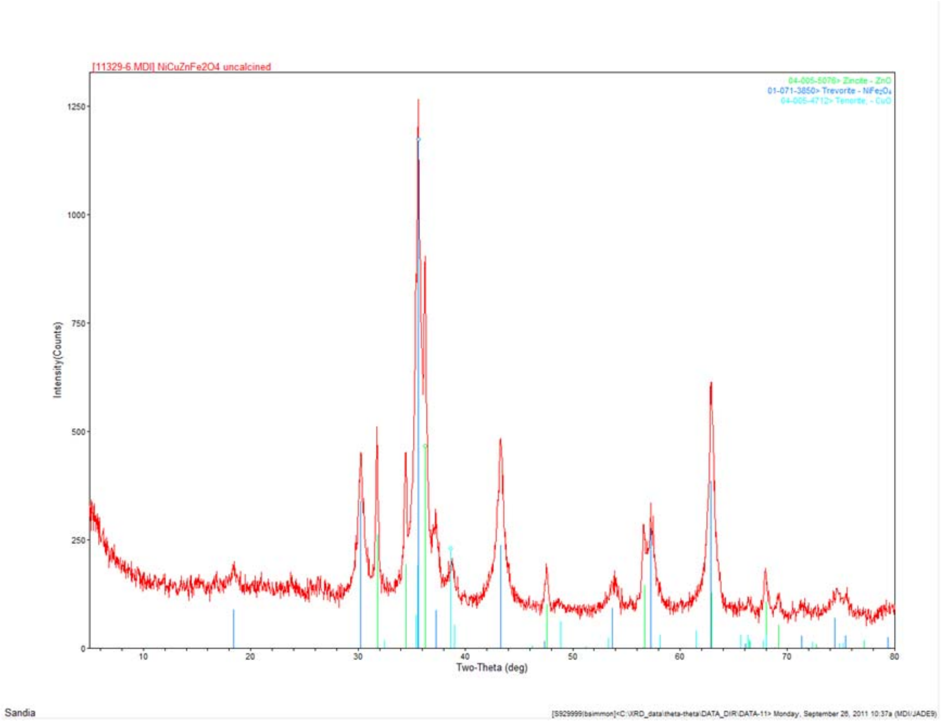




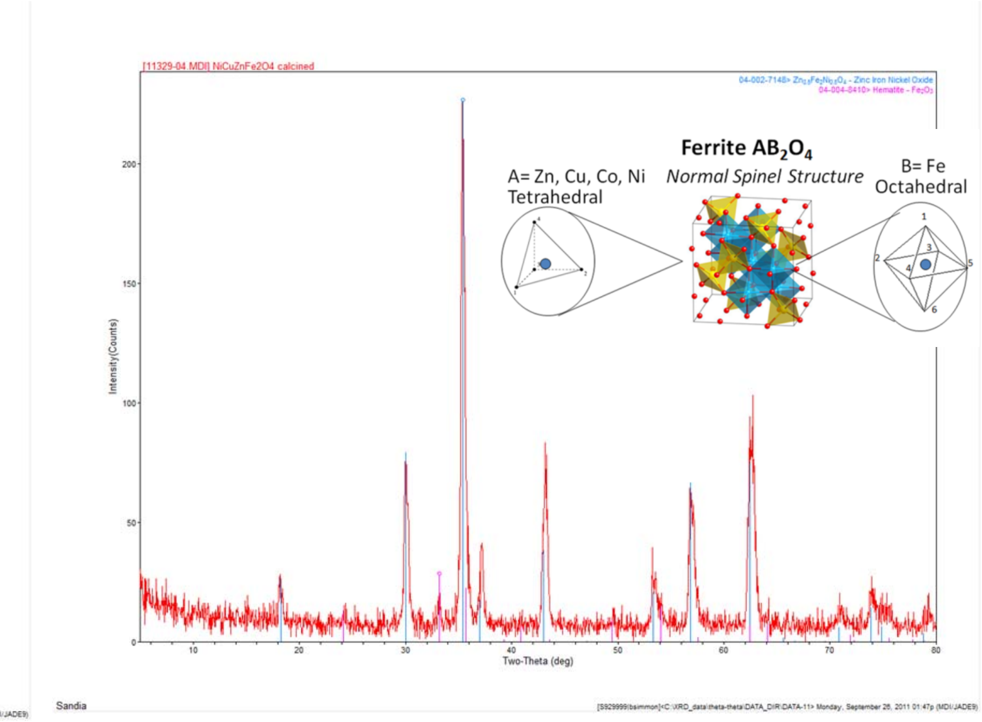


Initial X-Ray Diffraction Results

- Pre-calcined, pre-pyrolysis $Ni_{0.53}Zn_{0.35}Cu_{0.12}Fe_{1.88}O_{3.82}$ spray dried powder

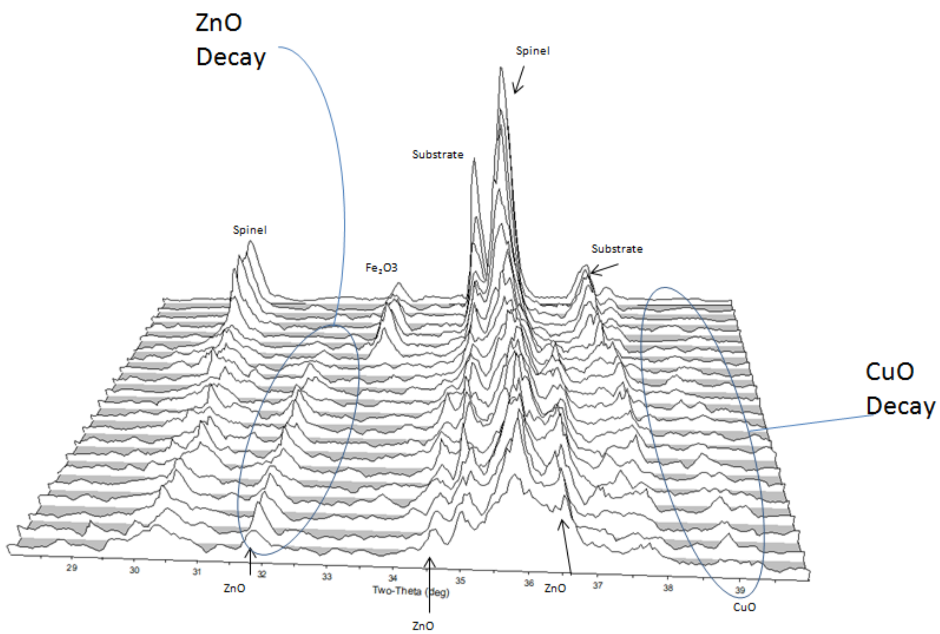


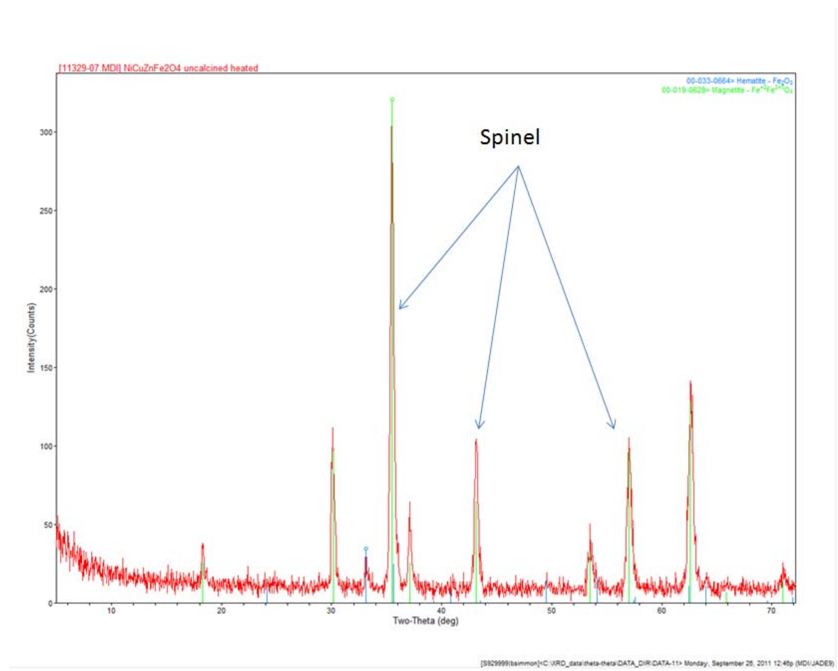
- Calcined, pyrolyzed $Ni_{0.53}Zn_{0.35}Cu_{0.12}Fe_{1.88}O_{3.82}$ powder
  - Hematite phase: Fe_2O_3
  - Prototype phase: $Ni_{0.50}Zn_{0.50}Fe_2O_4$



Initial X-Ray Diffraction Results

- High Temperature X-Ray Diffraction Analysis of Pre-calcined $Ni_{0.53}Zn_{0.35}Cu_{0.12}Fe_{1.88}O_{3.82}$ powder
  - Decay of CuO and ZnO diffraction
  - Formation of Fe_2O_3 and Spinel (magnetite, $Fe^{+2}Fe^{+2,+3}O_4$)





Initial X-Ray Diffraction Results

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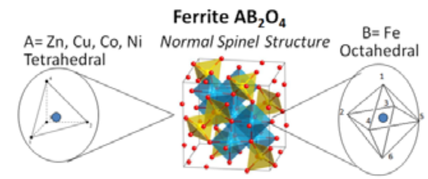
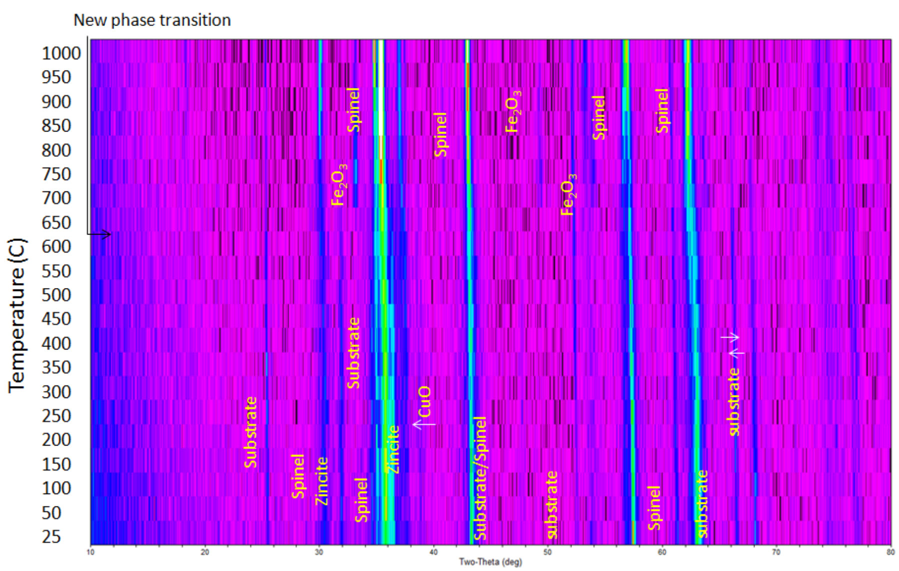
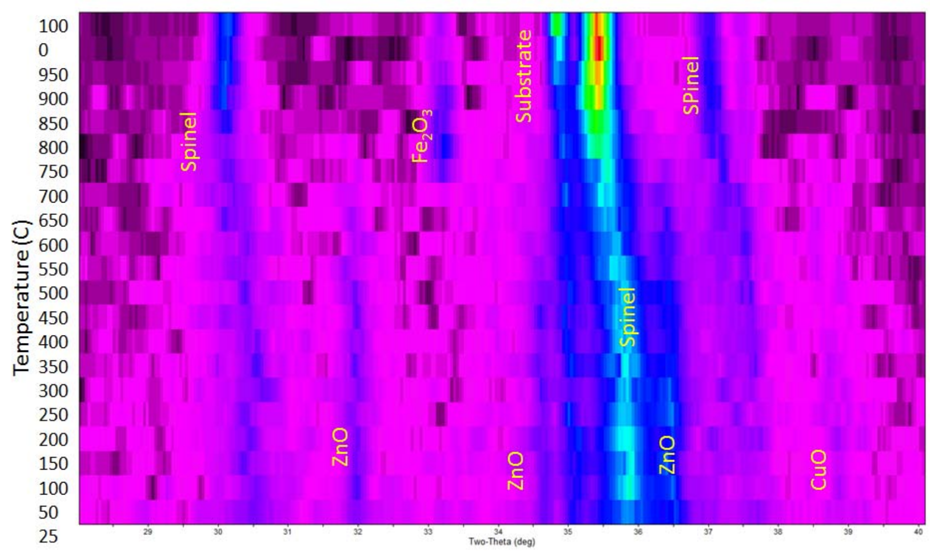
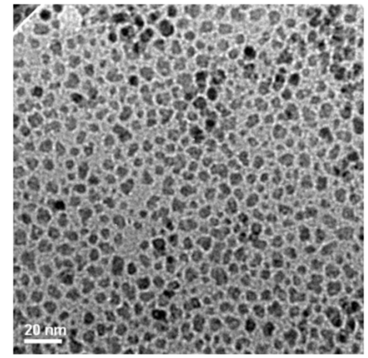






Ferrite powder chemical synthesis

- Ferrite Chemical Synthesis – Evaluations include both co-precipitation and psuedo-hydrothermal routes.



•***Co-precipitation was first investigated using commercially available metal nitrates using 'targeted' composition:***

General aqueous route:

(1) $M(MO_3)_2 + 2\ NaOH \longrightarrow M(OH)_2 + 2\ NaNO_3$

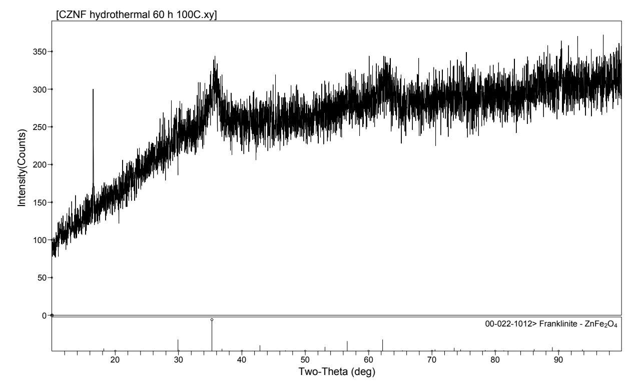
(2) $M(MO_3)_2 + H_2O_2C_2 \longrightarrow M(Ox)_2 + 2\ HNO_3$

•Difficult to co-precipitate all the cations at the same time (both oxalate and hydroxide)

•Hydroxide powders were "hydrothermally" heat-treated using reflux method at STP (have XRD)

•Hydroxide powders are being heat treated Hydrothermally at 200C 24h (XRD underway)

•Oxalate and Hydroxide powers are being calcined (XRD underway)

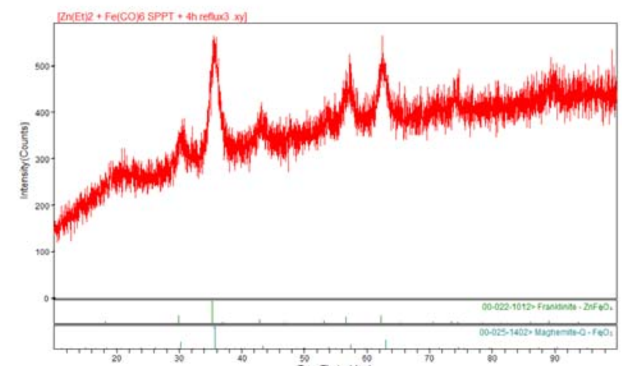


•***Nanoparticle Solution Precipitation Route:***

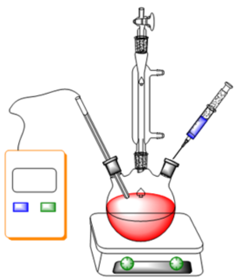
$2\ Fe(CO)_6 + Zn(Et)_2 \longrightarrow$ ZnFe2O4

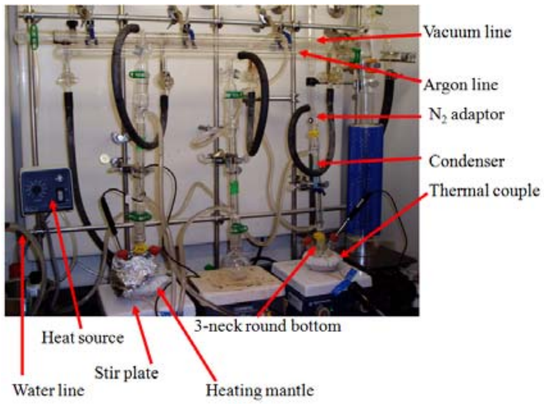
•XRD pattern shows broad peaks maybe associated with ferrite.

•TEM and EDS are underway to confirm

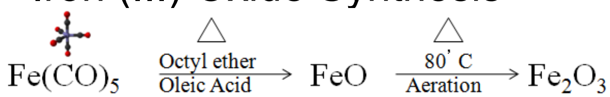


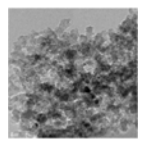
Ferrite powder chemical synthesis



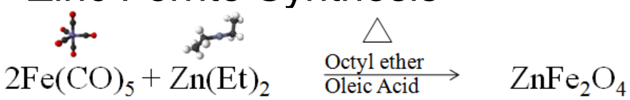


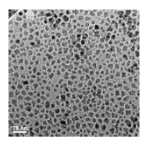
- Iron (III) Oxide Synthesis

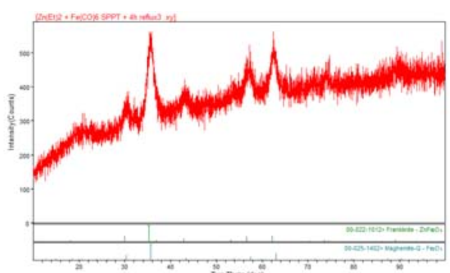


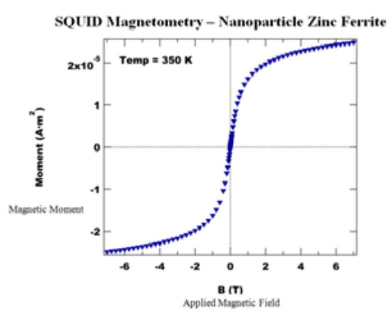


- Zinc Ferrite Synthesis

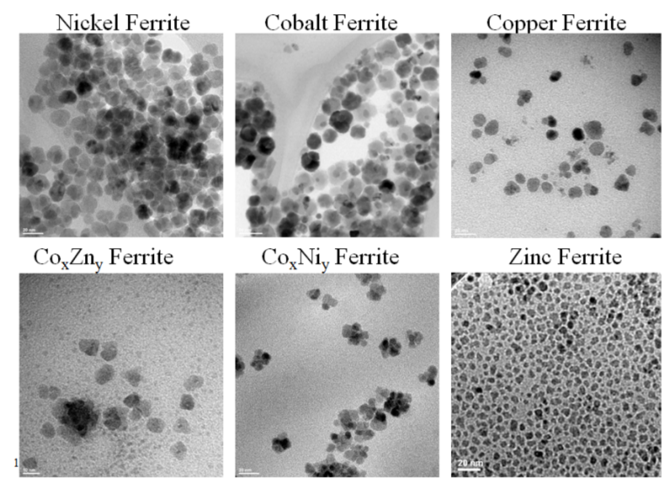


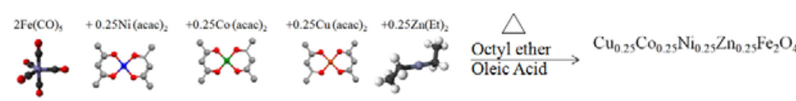






Precursors	Solvents	Solution
$2Fe(CO)_5 + Zn(Et)_2$	Oleic Acid & Oleylamine	$ZnFe_2O_4$
$2Fe(CO)_5 + Zn(Et)_2$	Oleic Acid	$ZnFe_2O_4$
$2Fe(CO)_5 + (CH_3COCHCOCH_3)_2Cu$	Oleic Acid & Octyl Ether	$CuFe_2O_4$
$2Fe(CO)_5 + (CH_3COCHCOCH_3)_2Cu$	Oleic Acid & Oleylamine	$CuFe_2O_4$
$2Fe(CO)_5 + Cu(CH_3COO)_2$	Oleic Acid & Oleylamine	$CuFe_2O_4$
$2Fe(CO)_5 + (CH_3COCHCOCH_3)_2Co$	Oleic Acid & Octyl Ether	$CoFe_2O_4$
$2Fe(CO)_5 + (CH_3COCHCOCH_3)_2Ni$	Oleic Acid & Octyl Ether	$NiFe_2O_4$
$2Fe(CO)5 + 0.5(CH_3COCHCOCH_3)_2Cu + 0.5Zn(Et)_2$	Oleic Acid & Octyl Ether	$Cu_xZn_yFe_2O_4$
$2Fe(CO)5 + 0.5(CH_3COCHCOCH_3)_2Co + 0.5(CH_3COCHCOCH_3)_2Ni$	Oleic Acid & Octyl Ether	$Co_xNi_yFe_2O_4$
$2Fe(CO)5 + 0.5(CH_3COCHCOCH_3)_2Co + 0.5(CH_3COCHCOCH_3)_2Cu$	Oleic Acid & Octyl Ether	$Co_xCu_yFe_2O_4$
$2Fe(CO)5 + 0.33(CH_3COCHCOCH_3)_2Co + 0.33(CH_3COCHCOCH_3)_2Cu + 0.33(CH_3COCHCOCH_3)_2Ni$	Oleic Acid & Octyl Ether	$Ni_xCo_yCu_zFe_2O_4$

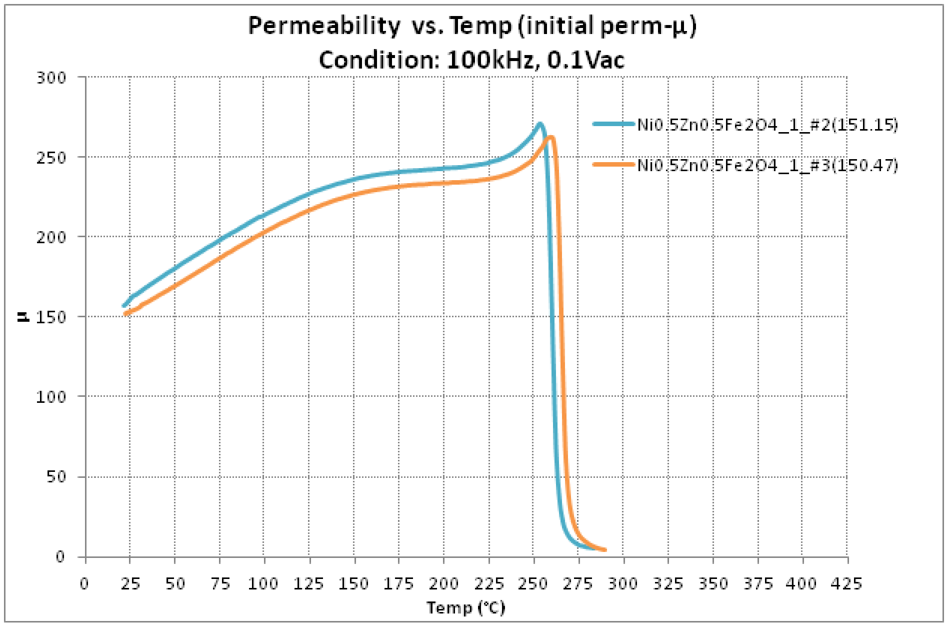


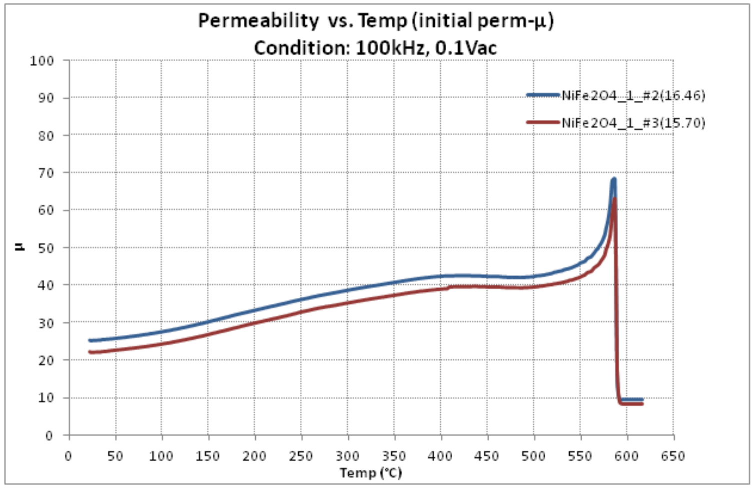


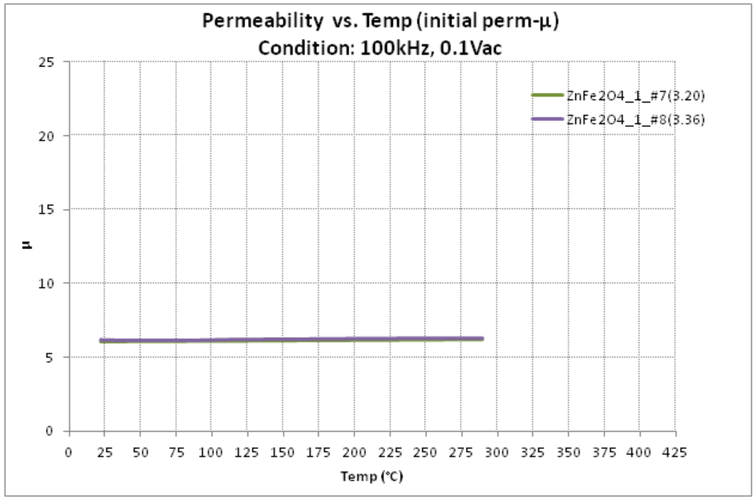
Magnetic property characterization - Toroid magnetic properties

- Initial Permeability (100kHz, 23^{o}C), Permeability vs. Temperature (100kHz, 0.5V_{AC}) and Coreloss (100kHz, 200mT, 23^{o}C) Measurements

Toroid #	$\mu_{initial}$	P (mw)	L (µH)	µ	Coreloss P (w/cm^3)	Bsat
NiFe2O4_1_#2	16.46	2517.1	2.94	75.35	21.23	93.49
NiFe2O4_1_#3	15.7	2807.6	3.08	75.73	22.19	92.31
ZnFe2O4_1_#7	3.2	Too High		0	NA	-
ZnFe2O4_1_#8	3.36	Too High		0	NA	-
Ni0.5Zn0.5Fe2O4_1_#2	151.15	467.25	25.43	614.12	3.36	284.77
Ni0.5Zn0.5Fe2O4_1_#3	150.47	476.96	26.61	614.96	3.39	282.85

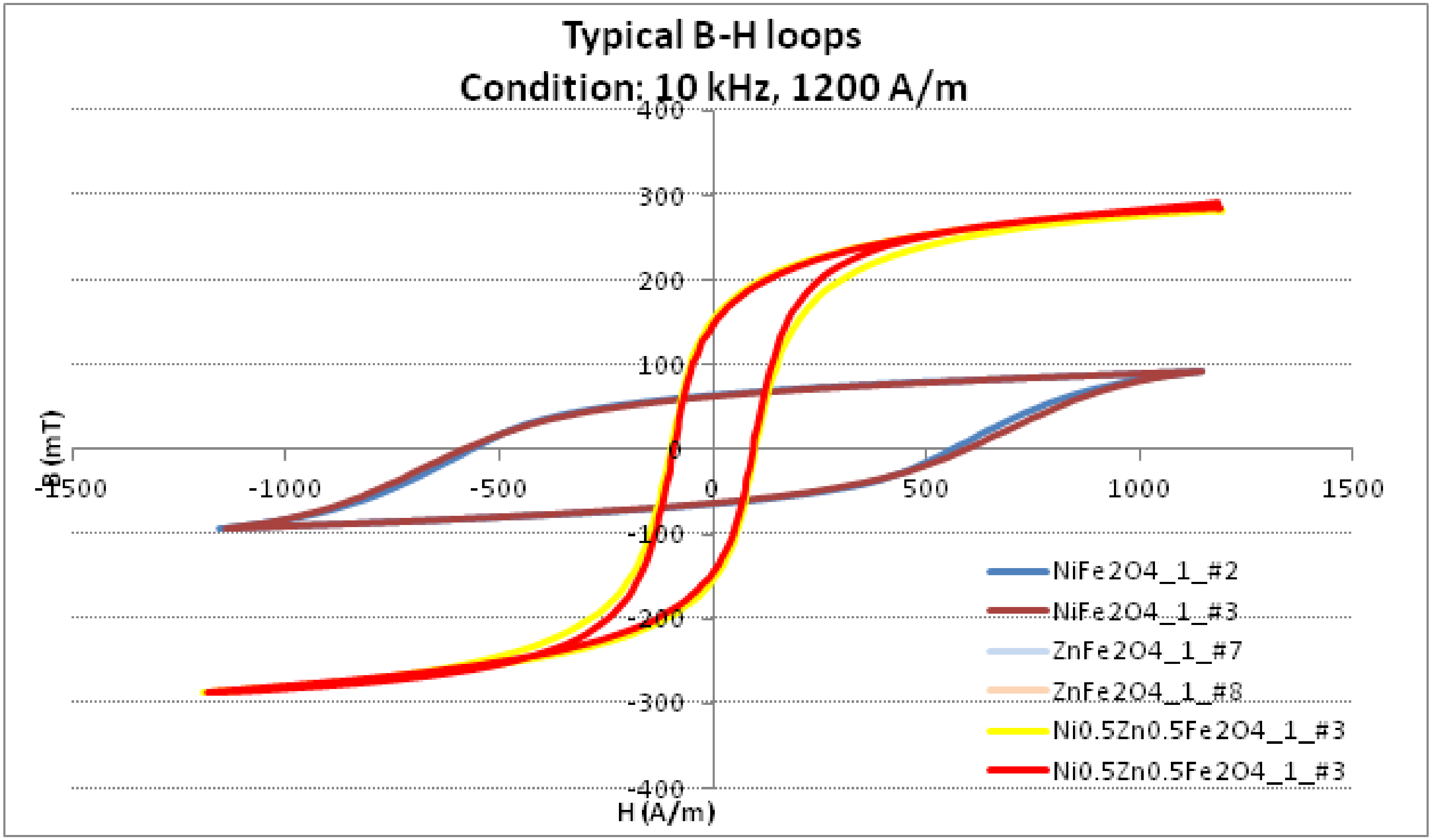






Magnetic property characterization - Toroid magnetic properties

- B-H Hysteresis Loop Characterization – 10kHz and 1200A/m

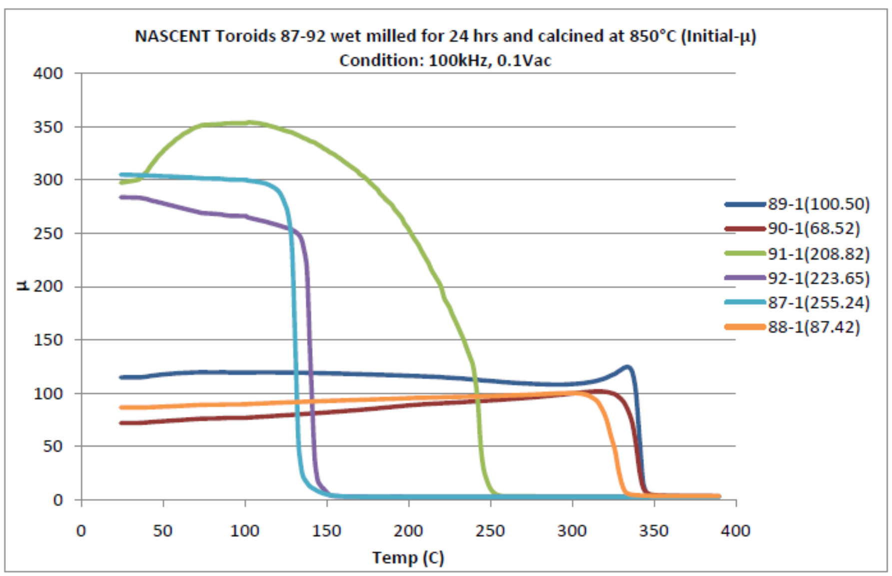


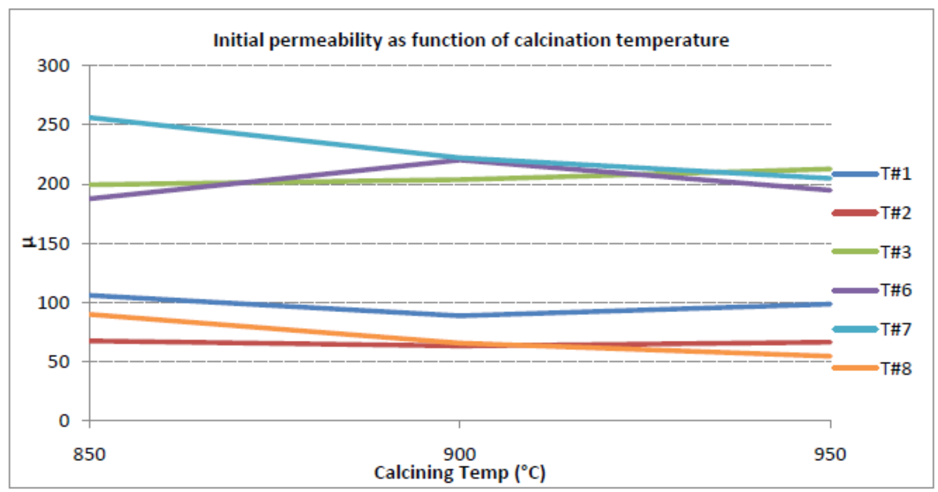
NASCENTechnology Inc. collaboration efforts

- Initiated collaboration with NASCENTechnology Inc – Reviewed several interim reports providing a summary of results

S. No	Powder type	Composition/Formula	Paper
1	T#1	$Ni_{0.3}Cu_{0.1}Zn_{0.3}Mg_{0.3}Fe_2O_4$	N. Varalaxmi et al[6]
2	T#2	$Ni_{0.53}Cu_{0.12}Zn_{0.35}Fe_{1.88}O_4$	S. R. Murthy[5]
3	T#3	Fe_2O_3(49.5%)+ZnO(24%)+NiO(13.9%)+CuO(12%)+MnO_2(0.6%)	Y. Matsuo et al[7]
4	T#6	$Ni_{0.26}Cu_{0.16}Zn_{0.6}Fe_{1.96}O_{3.96}$	J. Topfer et al[3]
5	T#7	$Ni_{0.2}Cu_{0.2}Zn_{0.62}Fe_{1.98}O_{3.99}$	J. Jeong et al[8]
6	T#8	$Ni_{0.41}Cu_{0.24}Zn_{0.35}Fe_{1.76}O_4$	S. R. Murthy[5]

*percentages are in mole percent.

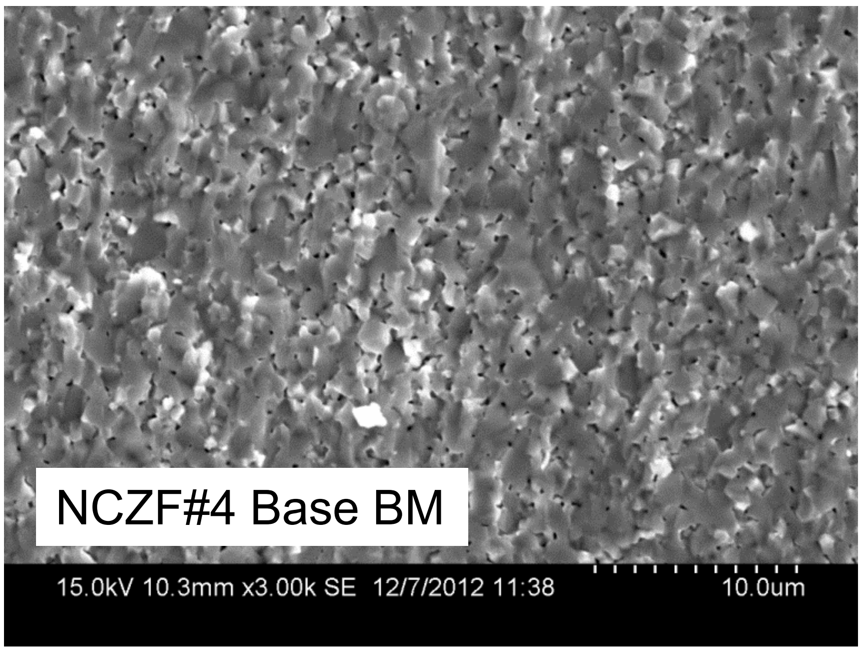


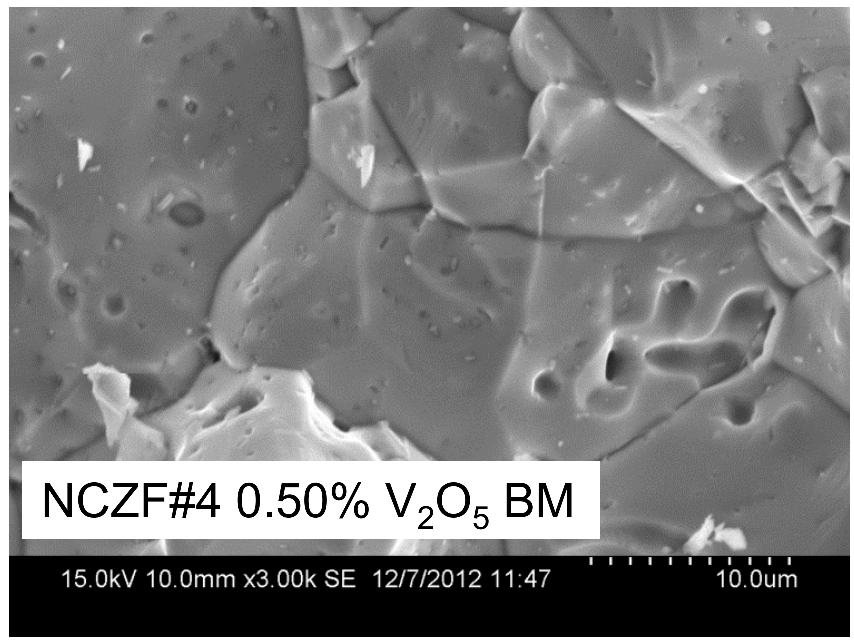


Processing–Microstructure-Performance

- NZCF #4: $Ni_{0.204}Zn_{0.612}Cu_{0.204}Fe_{1.98}O_{3.99}$

SNO	Toroid #	Description	Sintering profile	Initial permeability
1	NCZF#4 Base BM	Original/base formulation	Fired at 975°C	297.9
2	NCZF#4 0.5 V BM	0.5% V2O5	Fired at 923°C	372.78
3	NCZF#4 0.75 V BM	0.75% V2O5	Fired at 923°C	308.71
4	NCZF#4 Bi BM	Bismuth	Fired at 923°C	190.88





Processing–Microstructure-Performance

- NZCF #4: $Ni_{0.204}Zn_{0.612}Cu_{0.204}Fe_{1.98}O_{3.99}$

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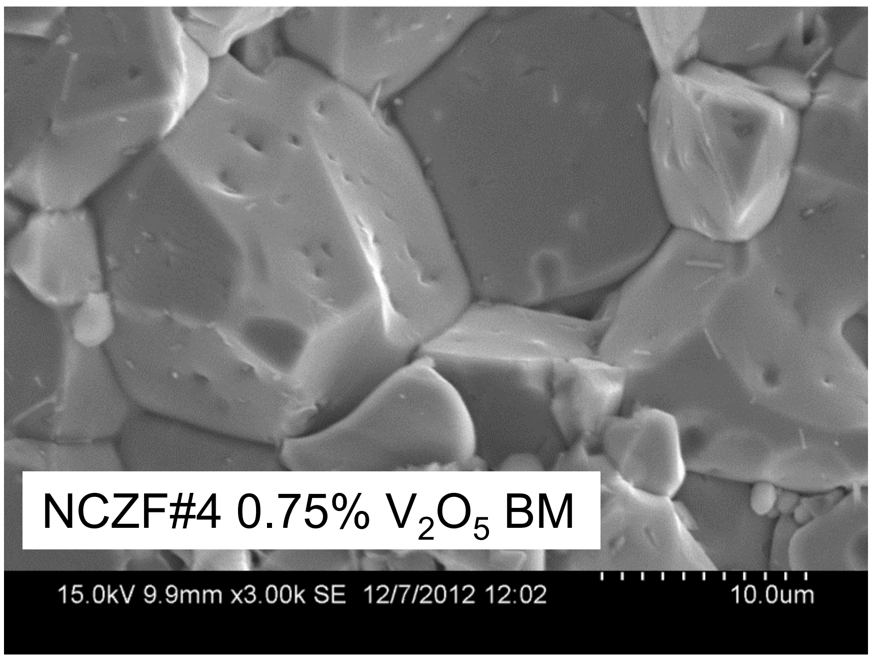
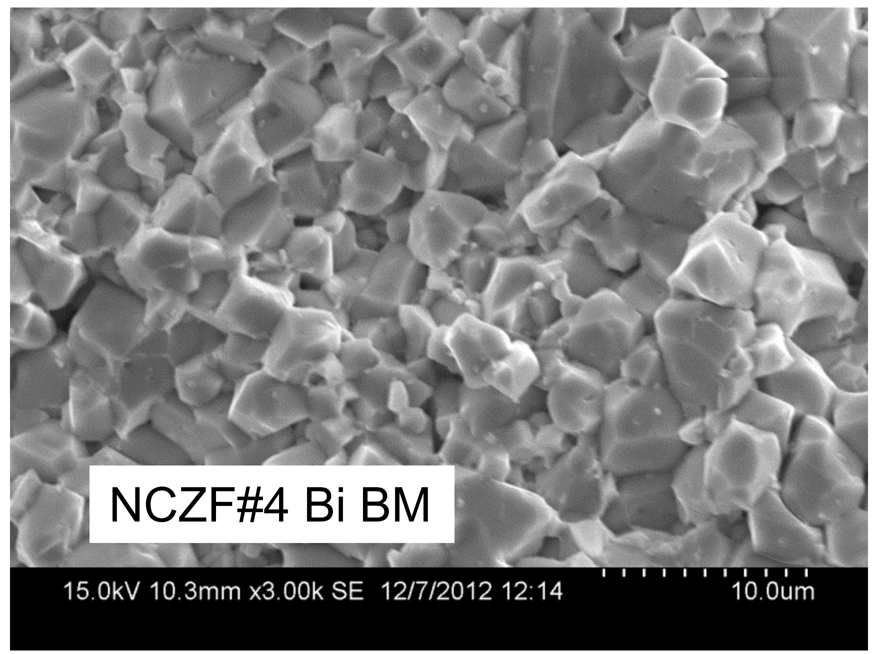
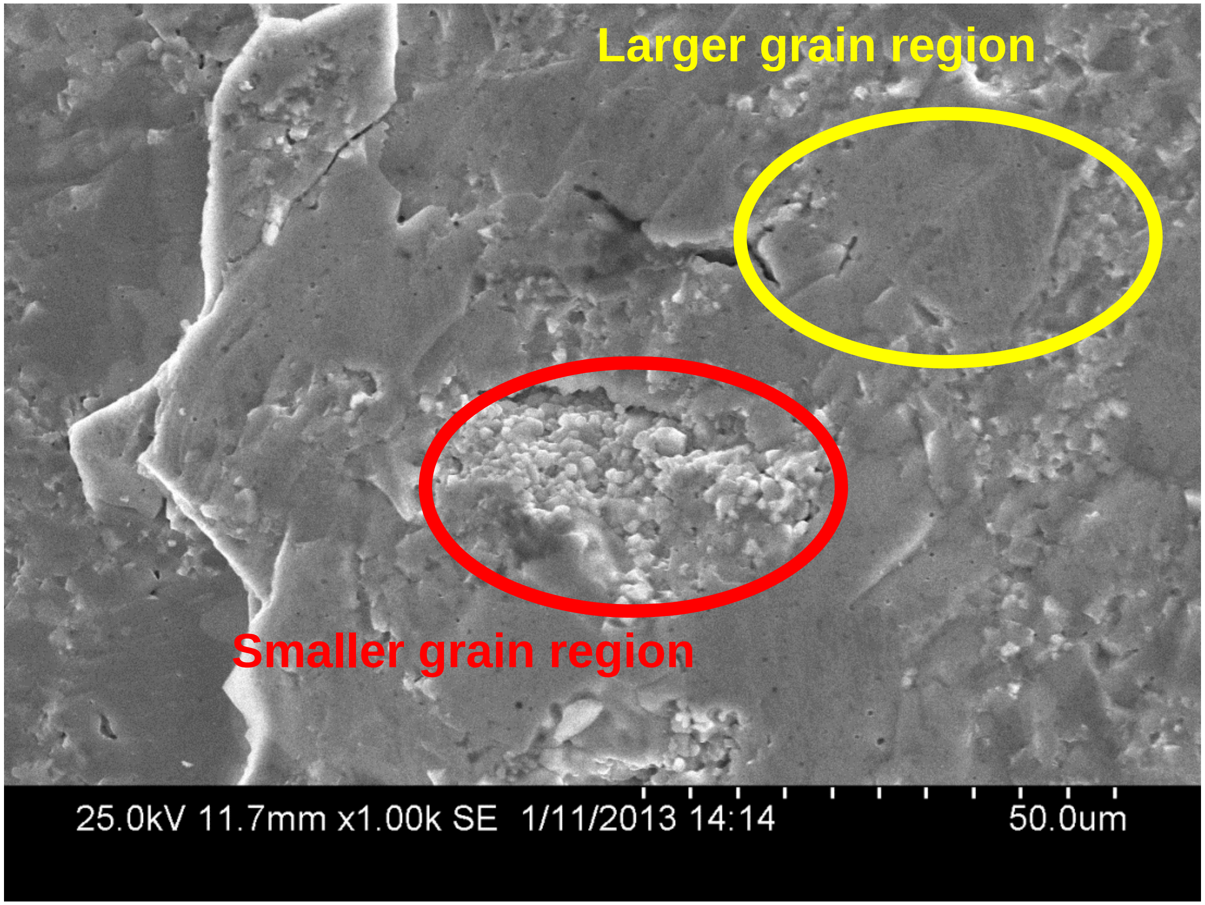


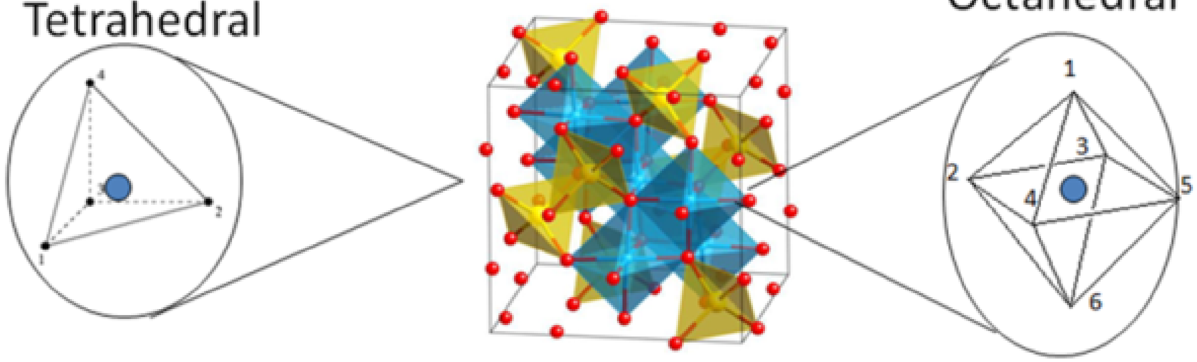


Processing–Microstructure-Performance

- **NZCF: $Ni_WZn_XCu_YFe_ZO_{(W+X+Y+3Z)}$:**
- NZCF #4: $Ni_{0.204}Z_{0.612}Cu_{0.204}Fe_{1.98}O_{3.99}$
- SEM image of NZCF#4 attrition milled and sintered to 1050oC for 2 hours
- Inhomogeneous microstructure
- Areas of smaller and larger grains



NZCF - Ferrite Formulations



- **NZCF: $Ni_W Zn_X Cu_Y Fe_Z O_{(W+X+Y+3Z)}$**

1) NZCF #1: $Ni_{0.530}Zn_{0.350}Cu_{0.120}Fe_{1.88}O_{3.82}$
2) NZCF #2: $Ni_{0.510}Zn_{0.350}Cu_{0.140}Fe_{1.86}O_{3.76}$
3) NZCF #3: $Ni_{0.490}Zn_{0.350}Cu_{0.160}Fe_{1.84}O_{3.76}$
4) NZCF #4: $Ni_{0.204}Zn_{0.612}Cu_{0.204}Fe_{1.98}O_{3.99}$
5) NZCF #5: $Ni_{0.170}Zn_{0.640}Cu_{0.200}Fe_{1.98}O_{3.98}$

Results summary

1) Procured initial set of raw materials for development of novel and baseline ferrite formulations from ‘solid-state/mixed oxide’ synthesis route and initiated scoping studies for chemical synthesis route
   - Suppliers - Inframat and MTI Xrstal
2) Characterization of initial set of raw materials is complete:
   - Helium pycnometry (density), BET (specific surface area), Laser Scattering (Particle size distribution), SEM/TEM (size and morphology), XRD (crystalline phase and nanostructure)
3) Mapping processing parameters and routes on the resultant ferrite formulation/composition development
   - Raw materials, dispersion-mixing-milling-drying and calcination techniques
   - Synthesized $Ni_{0.53}Zn_{0.35}Cu_{0.12}Fe_{1.88}O_{3.82}$ powder
4) Baseline samples and $Ni_{0.53}Zn_{0.35}Cu_{0.12}Fe_{1.88}O_{3.82}$ powder have been fabricated as toroids and test discs
5) Characterizing the reaction (STA/DSC) and sintering (Dilatometry) behavior
6) Magnetometry of test samples has been initiated and ongoing – Magnetic property measurement system (SQUID)
7) Collaboration with NASCENTechnology Inc – Reviewed several interim reports providing a summary of results