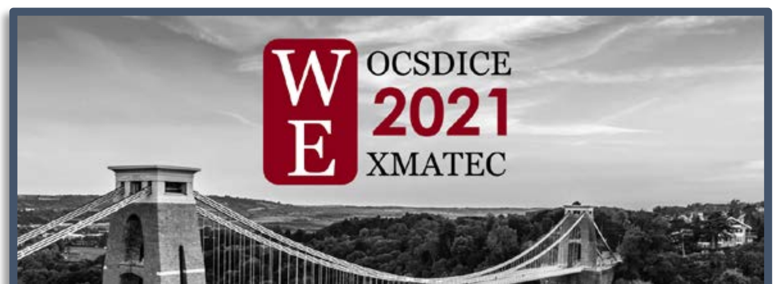
Electrical properties of Mn-Ni-Zn spinel oxides alloys

D. Katerinopoulou, C. Papakonstantinopoulos, E. C. P. Smits, P. Zalar, G. H. Gelinck, G. Kiriakidis and E. Iliopoulos



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Outline

- Aim
- Introduction
- Methods
- Results
- Conclusions

Aim

Type/Characteristics	Active material	T range (°C)	Sensitivity	Accuracy
Thermocouples	Dissimilar metals	-270 to +2300	~1-80 μV/°C	0.5 - 5
RTDs	Platinum	-200 to +650	~ 0.4%/°C	0.001 - 1
ICs	Si/Ge	-55 to +150	7.3%/°C (Si)	1
Thermistors	Ceramic	-50 to +1000	-2%/°C to -6%/°C	0.001 - 1

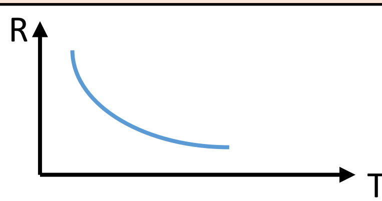
Source: J. Am. Ceram. Soc., 92 [5] 967–983 (2009)

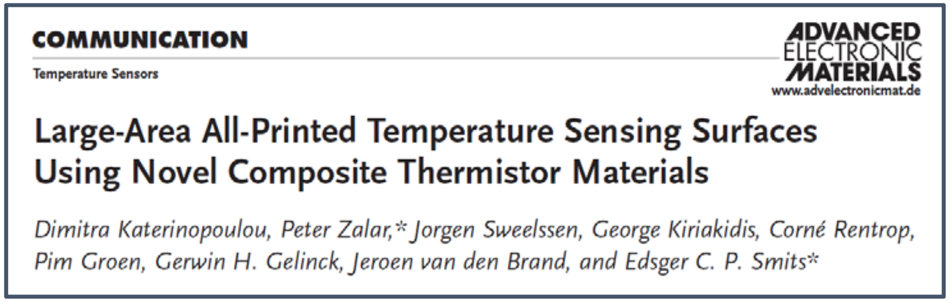
Thermistor : **Therm**al + Res**istor**

NTC

Negative **T**emperature **C**oefficient

↓R with↑T

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Dimitra Katerinopoulou, Peter Zalar, Jorgen Sweelssen, George Kiriakidis, Corné Rentrop, Pim Groen, Gerwin H. Gelinck, Jeroen van den Brand, and Edsger C. P. Smits**

A complex spinel oxide system

($Mn_{1.71}Ni_{0.45}Co_{0.15}Cu_{0.45}Zn_{0.24}O_4$)

Understand the transport mechanism of a quaternary system:

Mn – Zn – Ni - O

What is Spinel oxide?

General formula: **AB_2O_4**

- A^{2+} = divalent cation
- B^{3+} = trivalent cation

Types:

a) Normal spinels

$(A^{2+})[B^{3+}]_2O_4$

b) Inverse spinels

$(B^{3+})[A^{2+}B^{3+}]O_4$

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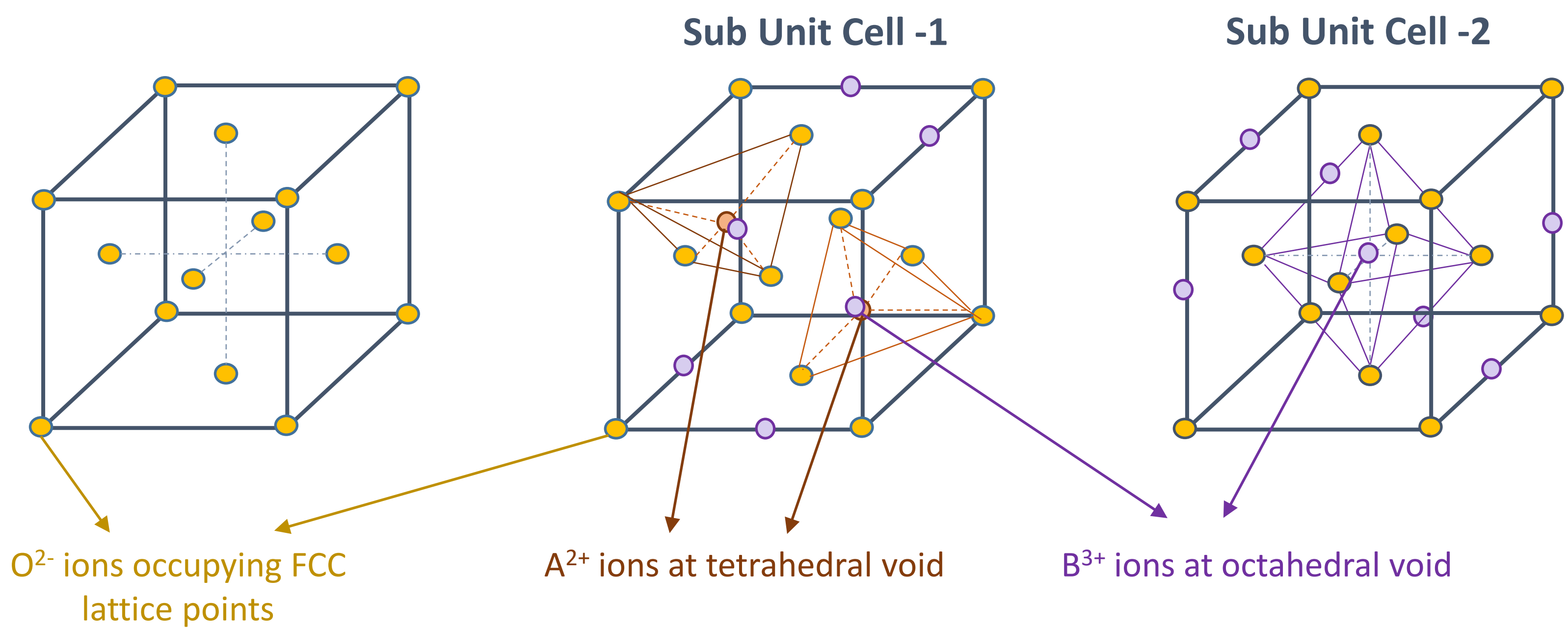

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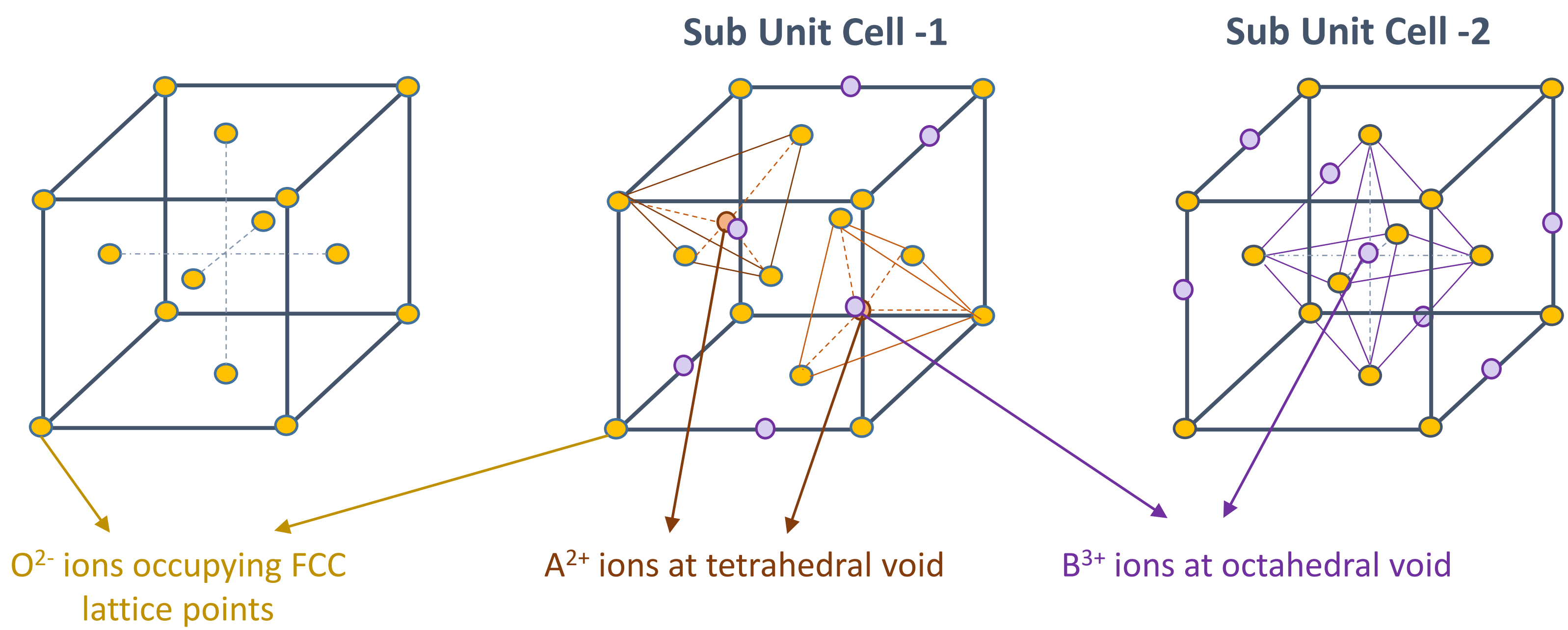
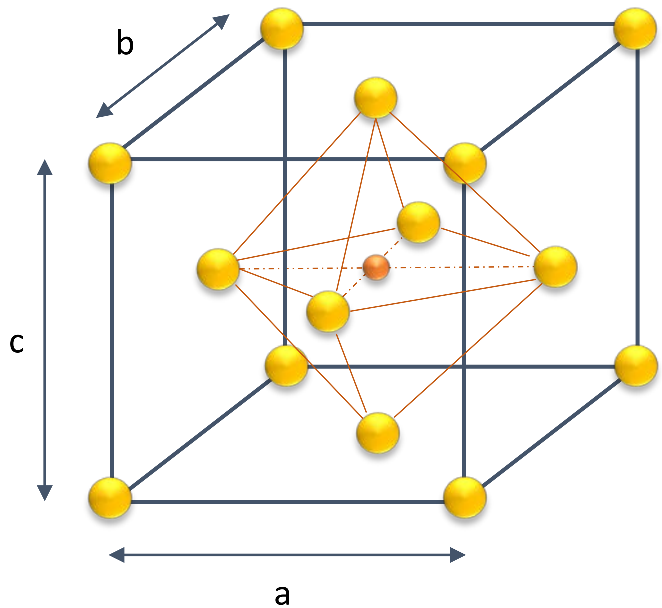
Conduction is attributed to the mixed valence states of different cations → electrical properties are affected by cation distribution in tetrahedral & octahedral sites



Crystal structure of Spinel

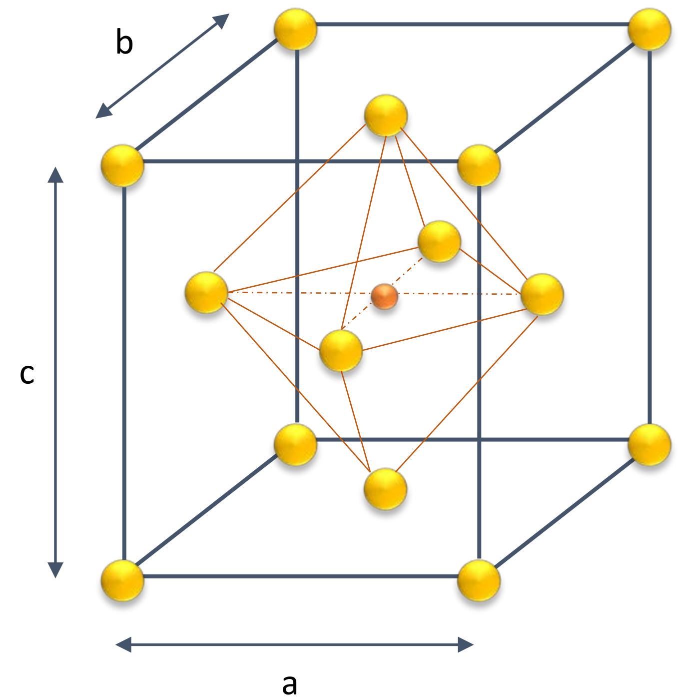
- Crystal structure: **Cubic** / Tetragonal (Jahn-Teller distortion)

Cubic



a = b = c

Tetragonal



a = b ≠ c

Samples preparation

- Mn-based spinel oxides with different compositions.

$Mn_{2.5-x}Zn_{0.5}Ni_xO_4$						
x	0	0.25	0.5	0.75	1.0	1.25

- Classical solid state reaction method, as followed:

Powder mixing → Calcination → Pellets → Sintering → Air cooled / Quenched

Diameters: 5 x 1 mm
Contacts: Au (both sides)

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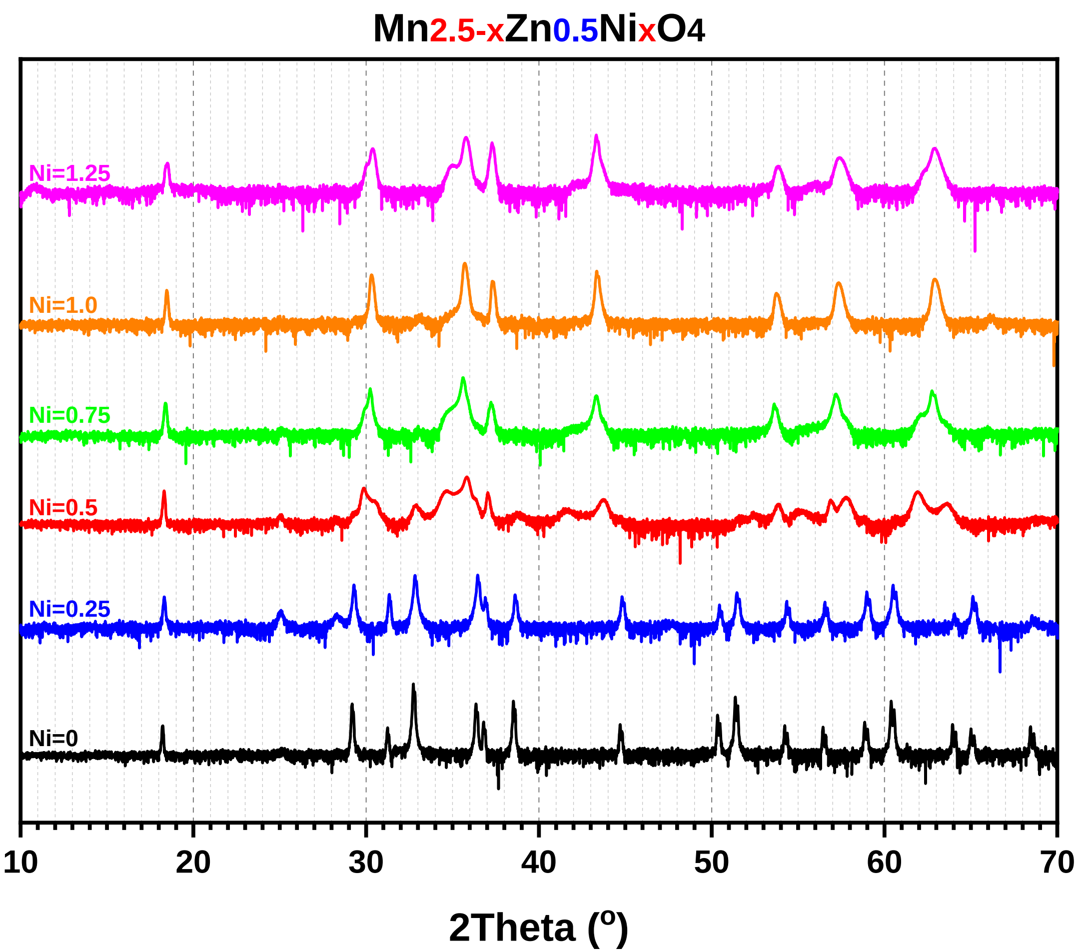
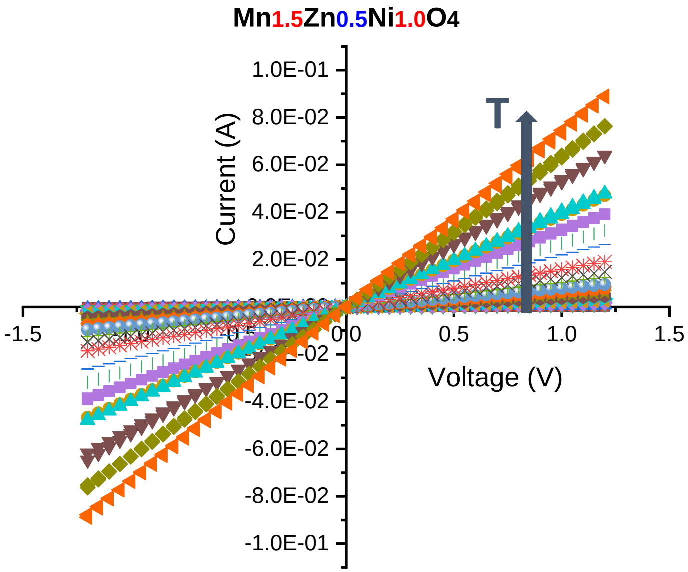
Structural characterization

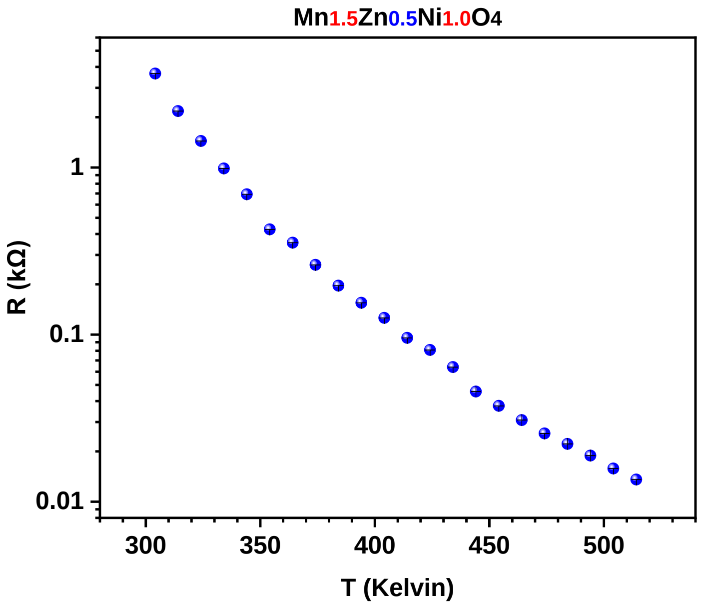


x	Lattice parameters	Space group
1.25	a = b = c = 8.34Å	Fd-3m
1.0	a = b = c = 8.34Å	Fd-3m
0.75	a = b = c = 8.35Å	Fd-3m
0.5	Mixed phase	-
0.25	Mixed phase	-
0	a = b = 5.72Å c = 9.26Å	I41/amd

Ref. code: 00-036-0083 (cubic)
Ref. code: 00-024-1133 (tetragonal)

Electrical characterization





<u>Measurements settings:</u>

Set up: oil bath (home made)

V range: ± 1.2V

T range: RT up to 240°C

- No hysteresis back and front at applied voltages.
- Scale with the T.
- No deviations upon heating and cooling.
- As the T ↑ the R↓ → **NTC** behavior.

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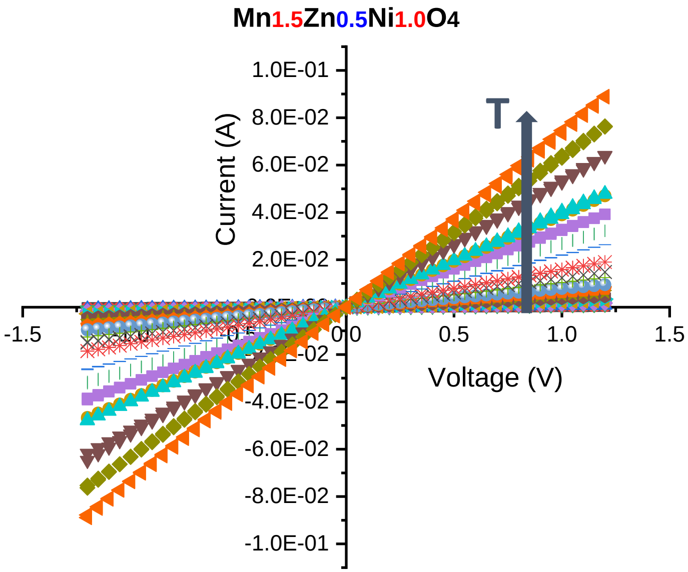
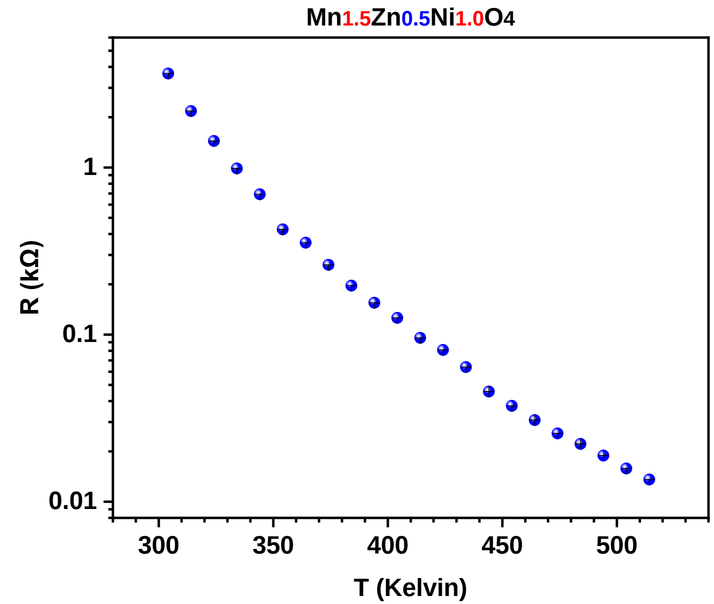
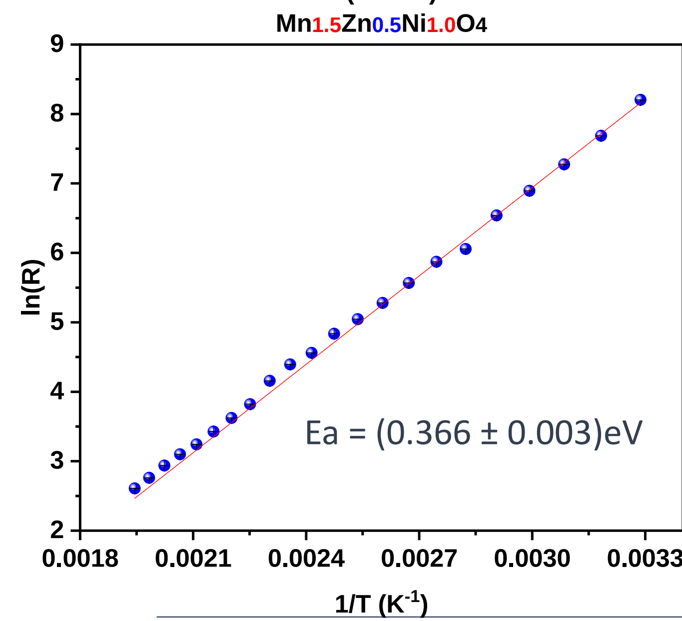
Electrical characterization







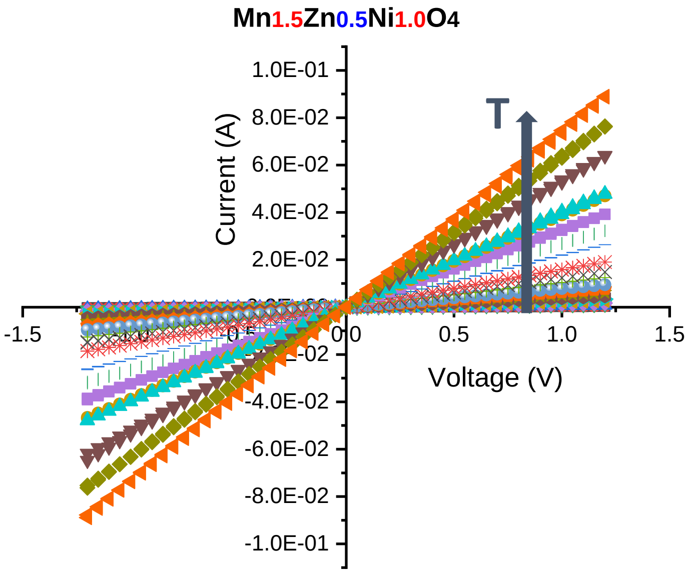
Temperature dependence of resistance:

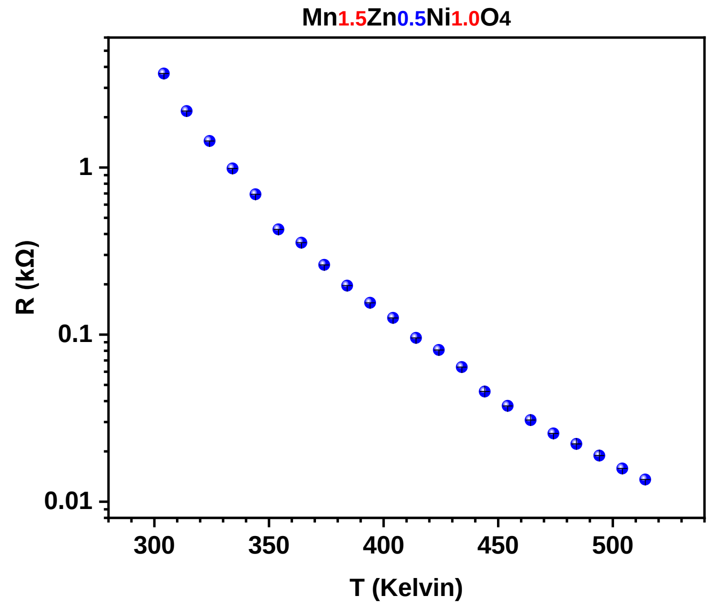
$$R = R_0 e^{\left(E_a/k_B T\right)}$$

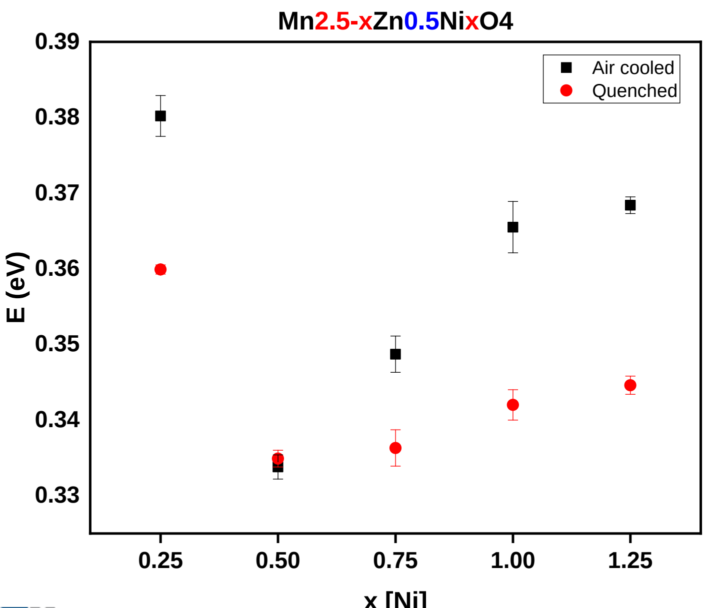
$\frac{E_a}{k_B} = B \rightarrow$ material constant

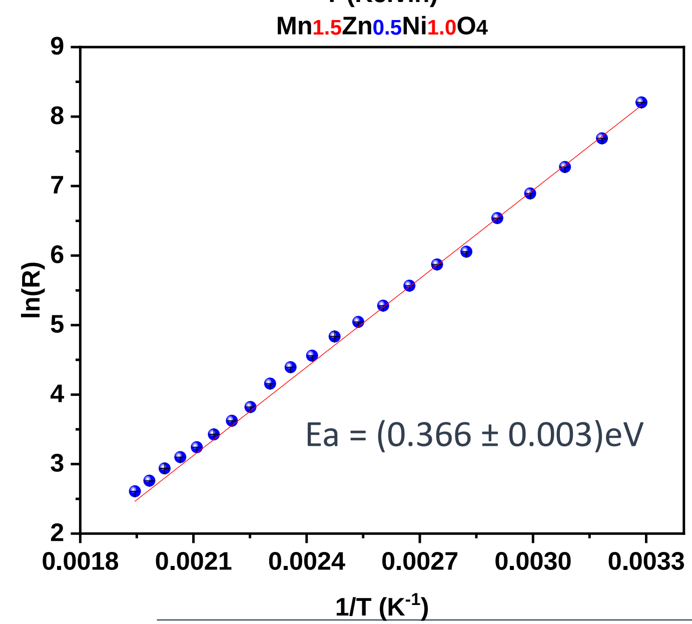
For bulk NTCs ceramics: 2000 K < B < 5000 K

Electrical characterization









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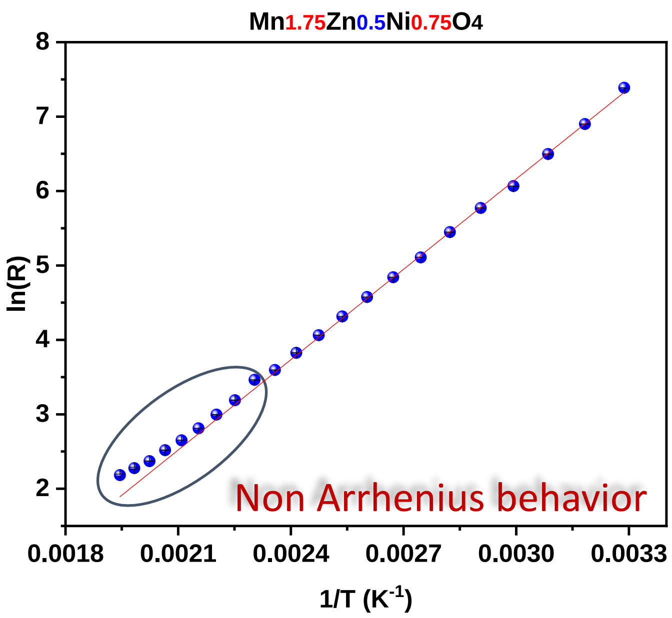
Electrical characterization

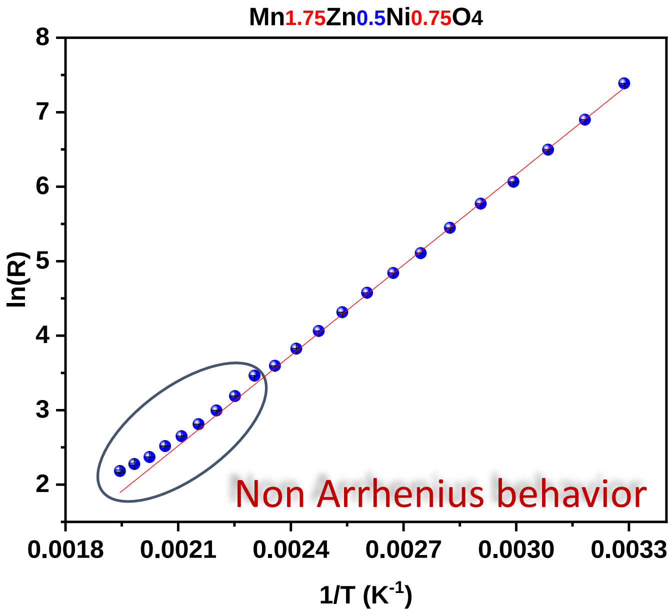


Small polaron hopping

$$\rho(\mathrm{T}) = CT^{a} exp\left(-\frac{T_0}{T}\right)^{\rho}$$

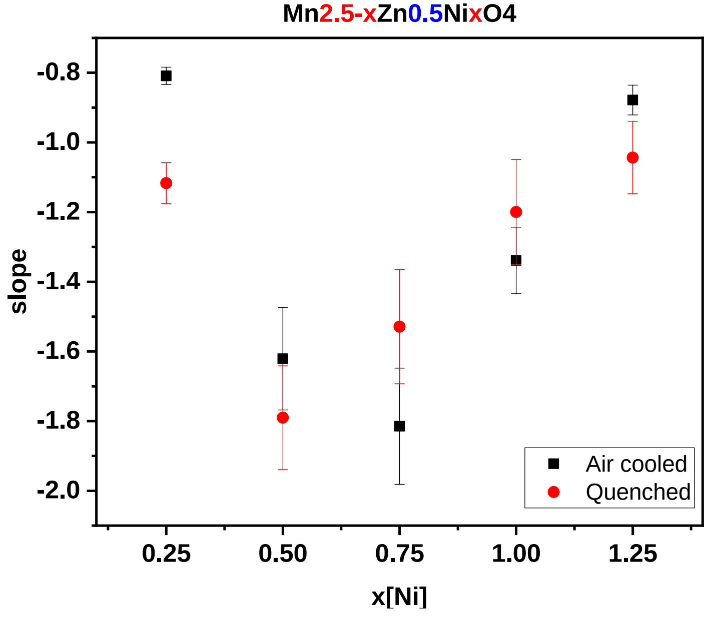
- VRH → $0.25 < \rho < 0.5$
- NNH → $\rho = \alpha = 1$

Electrical characterization



Shklovskii - Efros

$$W = \frac{1}{T}\frac{d(\ln \rho)}{d(T^{-1})} \approx -\rho\left(\frac{T_0}{T}\right)^{\rho}$$



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- VRH → 0.25 < ρ < 0.5
- NNH → ρ = α = 1

Conclusions

- ✓ **Ni = 0** tetragonal, **Ni ≥ 1.0** cubic, **0 < Ni < 1.0** mixed phase
- ✓ NTC behavior
- ✓ No hysteresis
- ✓ High B Coefficient → high sensitivity
- ✓ Air cooled and quenched same trend

Future plans

- Separation bulk & grain boundaries contribution to the conduction
- Theoretical study (electrons configuration etc.)
- Optical properties (Raman spectroscopy)
- Print on flexible substrates

Acknowledgments

Thank you for your attention

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