# Thermoelectric Properties in the $TiO_2/SnO_2$ System

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Nanotechnology has provided a new interest in thermoelectric technology.
A thermodynamically driven process is one approach in achieving nanostructures in bulk materials. TiO2/SnO2 system exhibits a large spinodal region with exceptional stable phase separated microstructures up to 1400 °C. Fabricated TiO2/SnO2 nanocomposites exhibit n-type behavior with Seebeck coefficients greater than -300 ⌠V/K. Composites exhibit good thermal conductance in the range of 7 to 1 W/mK. Dopant additions have not achieved high electrical conductivity (<1000 S/m). Formation of oxygen deficient composites, TixSn1-xO2-y, can change the electrical conductivity by four orders of magnitude. Achieving higher thermoelectric ZT by oxygen deficiency is being explored. Seebeck coeffcient, thermal conductivity, electrical conductance and microstructure will be discussed in relation to composition and doping.

# Thermoelectric Properties in the $TiO_2/SnO_2$ System


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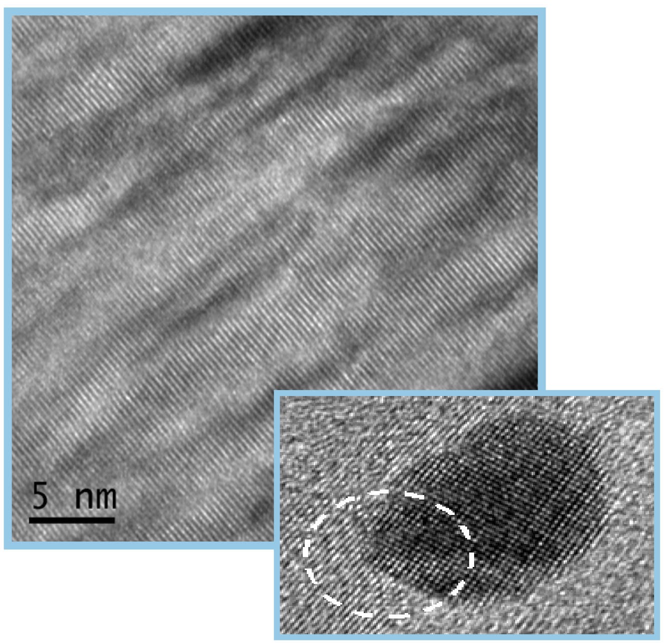



**NASA-IVHM**

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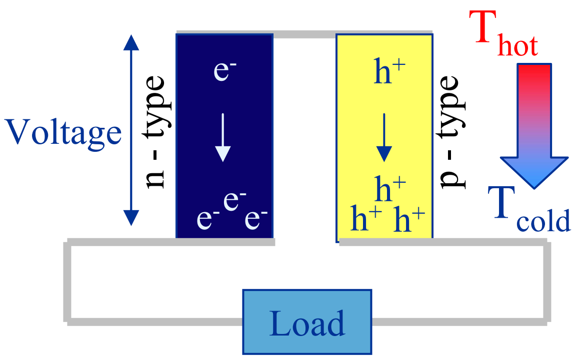
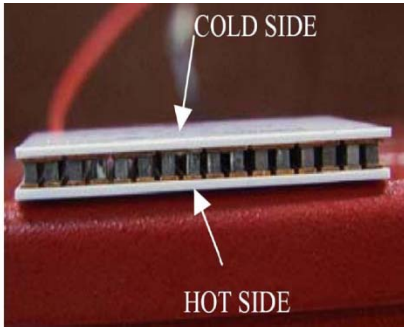
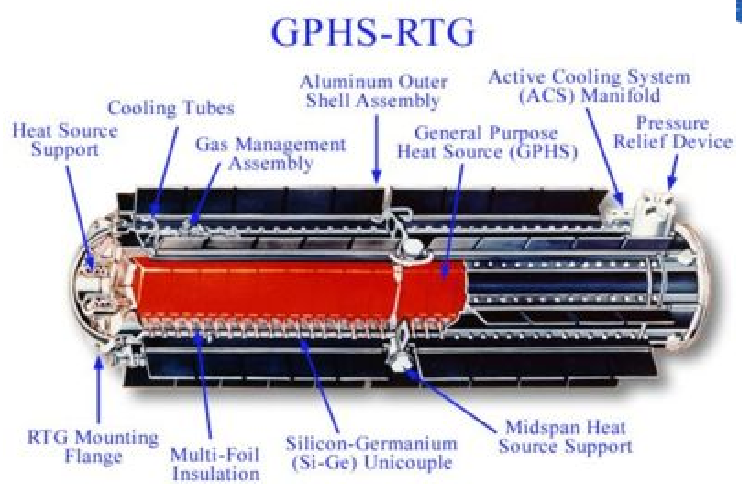
**NASA-Hypersonics (NNX08AB34A)**

# Heat to Electric Power Generation



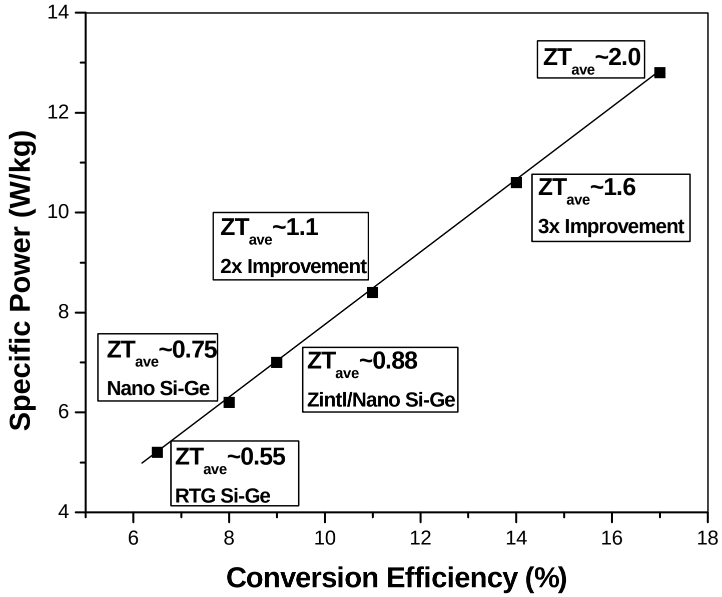




**Objective:** High Conversion Efficiency

- Reduces Mass, Volume & Cost

## Space Power Generation




## Waste Heat to Power

- Waste Heat is a under utilized energy resource
- U.S.-energy consumption ~29 tera-kWh ($10^{12}$)
  Barrels of Oil – 170 giga-barrels ($10^9$)
- World-energy consumption ~120 tera- kWh ($10^{12}$)
- 20-65 percent is lost in the form of heat
- Maximizes efficiency
- Reduces $CO_2$ emission

- High temperature -Low mass
- Oxidizing environment -Low cost

# Nanotechnology

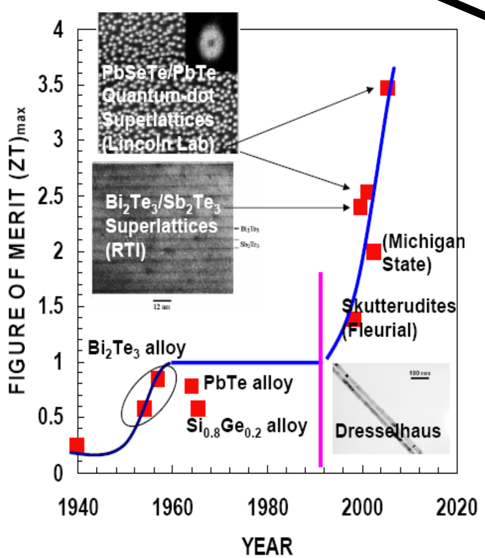
## Figure of Merit

$$ZT = \frac{S^2\sigma}{\kappa}T$$

S - Seebeck coefficient
σ – electrical conductivity
κ– thermal conductivity

## Efficiency

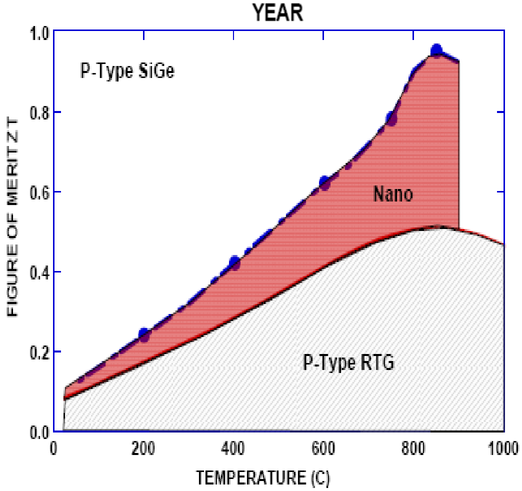
$$\eta_{\max} = \frac{\Delta T}{T_{hot}} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+T_{cold}/T_{hot}}$$

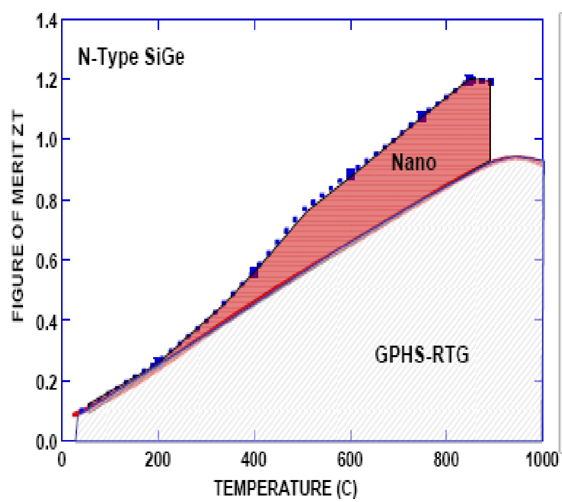


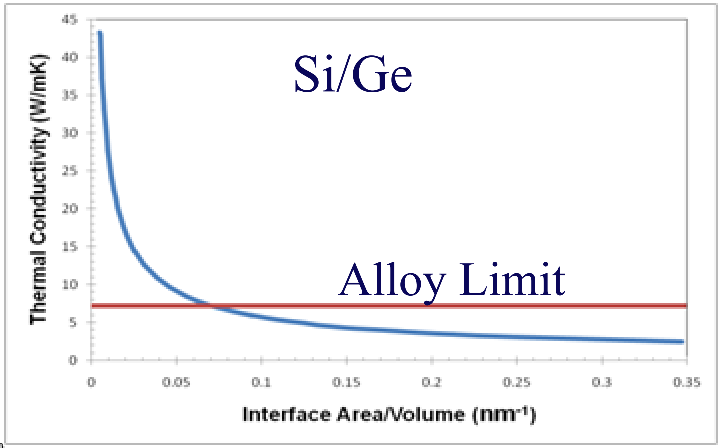

**Phonon Scattering:**

- Atom disorder
- Alloying
- Anharmonic vibrations
- **Superlattices**
- **Crystal Structures**
- **Nano-technology**

Fleurial/Chen – JPL/MIT



# Spinodal Decomposition

## $TiO_2 – SnO_2$

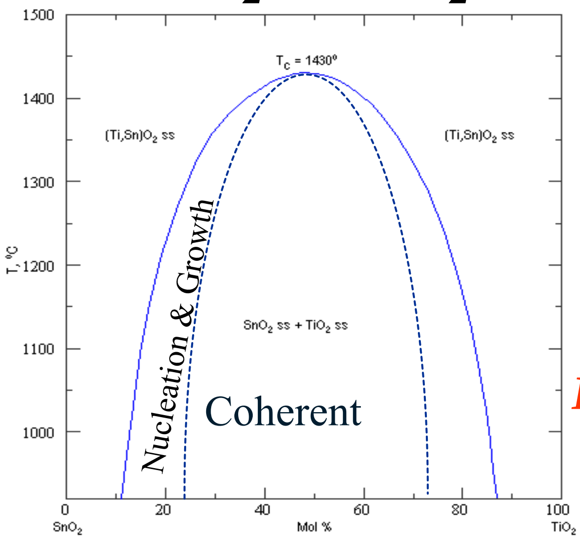




Fig. 10. TEM image of $(Ti_{0.5}/Sn_{0.5})O_2$ ceramics annealed for 48 h.

Shultz & Stubican, JACS, 53, 1970

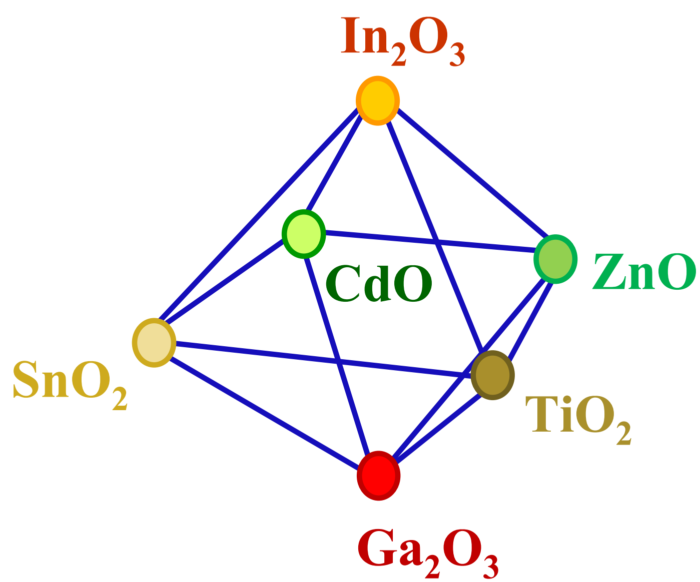
**Desired Features**

- ~50 nm grains
- High Temperature Stability
- Wide Composition Range
- Large Δ Mass

## Transparent Conducting Oxides

*Insulator/Semiconductor/Conductor*

- Large Bandgap 2.4-3.8 ev
- N-type –Degenerate Semiconductor



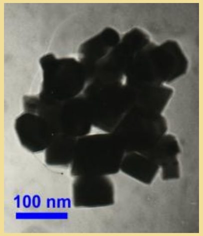

## Electrical Conductivity

| TCO | σ(S/m) @ RT |
|---|---|
| ITO | $8x10^5$ |
| $In_2O_3$ | $1x10^6$ |
| $SnO_2$ | $2.5x10^5$ |
| ZnO | $8.3x10^5$ |
| ZnO:Al | $7.7x10^4$ |
| $CdSnO_2$ | $7.7x10^5$ |
| CdO:In | $1.7x10^6$ |

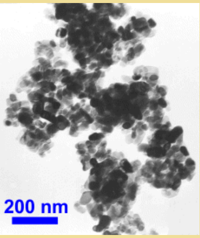
ZnO:Al
ZT~0.6 @ 1000 °C

# Experimental

$SnO_2$
Purity: 99.9%
APS: 50 nm
SSA: 14.2 $m^2/g$




$TiO_2$ Rutile
Purity: 99.99 %
APS: 20 nm,
SSA: > 30 $m^2/g$




Dopants
CoO, $MnO_2$
$Ta_2O_5$, $In_2O_3$

$TiO_2/SnO_2$
50/50 mol %
75/25 mol %
25/75 mol %

Powder Mixing

Compaction Die Press

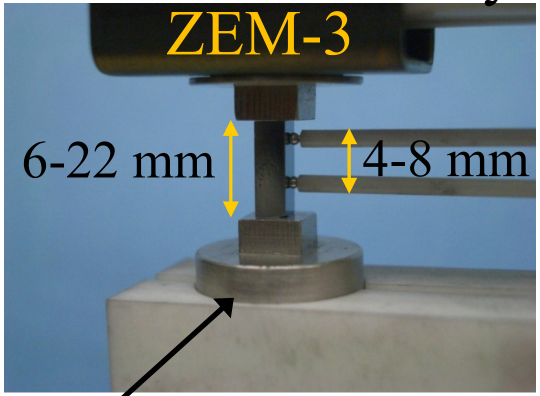
Reactive Sintering 1250-1550 $^oC$

Anneal 72 Hrs

## Thermal Conductivity

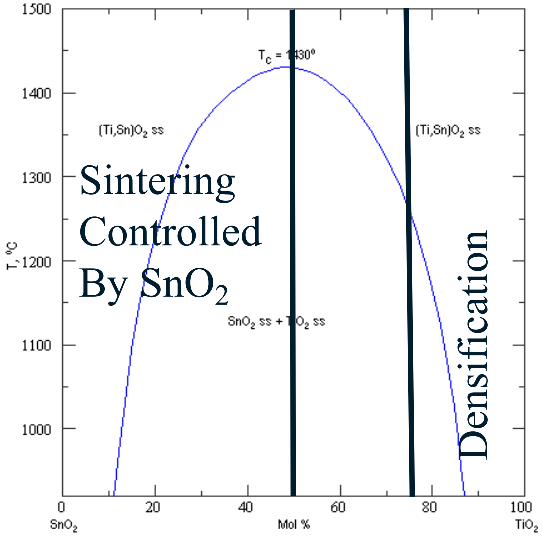
- **Laser Flash Method- Thermal Diffusivity**
- **Standard**
- **Specific Heat- $C_p$ - Laser Flash**
- **Thermal Conductivity ($K = \alpha\rho C_p$)**

## Seebeck/Resistivity

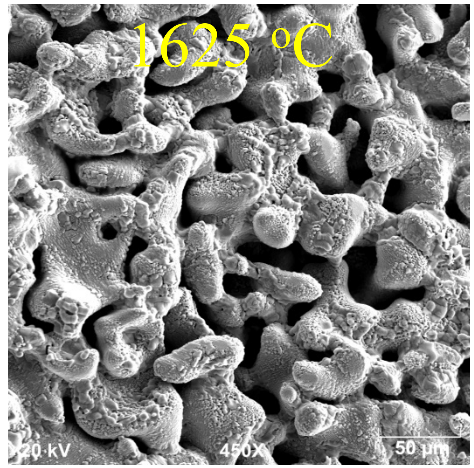



$\Delta T$ 0-50 $^oC$/Furnace RT-1000 $^oC$

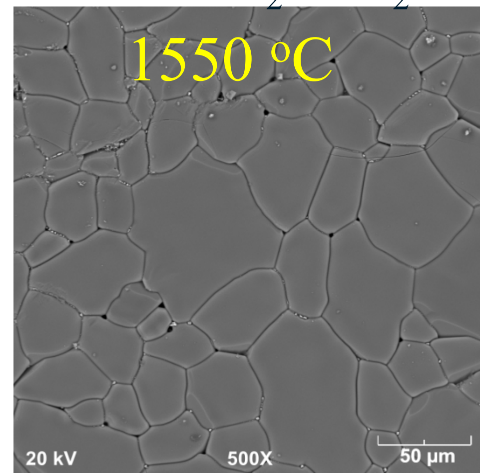
# Sintering




50/50 $TiO_2/SnO_2$




75/25 $TiO_2/SnO_2$




## $SnO_2$ Sintering-Inhibited

- Surface Diffusion <1100 °C
- Evaporation >1100 °C

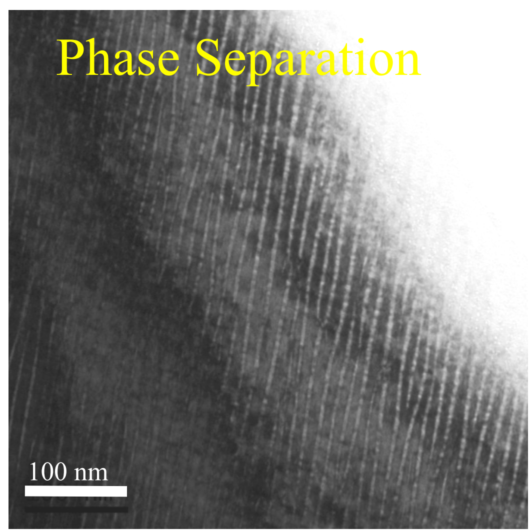
$SnO_2 \rightarrow SnO + \frac{1}{2}O_{2\,(g)}$

## Sintering Aids-$SnO_2$

- MnO, CoO, CuO, ZnO

$$CoO \rightarrow Co''_{Ti,Sn} + V_O^{\bullet\bullet}$$

50/50 $TiO_2/SnO_2$

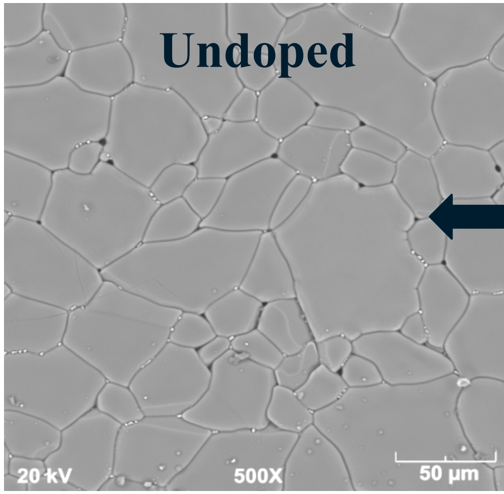



$Ta_2O_5$ & $In_2O_3$
Ineffective Sintering Aids

$$Ta_2O_5 \rightarrow 2Ta^{\bullet}_{Ti,Sn} + 2e' + \frac{1}{2}O_2$$

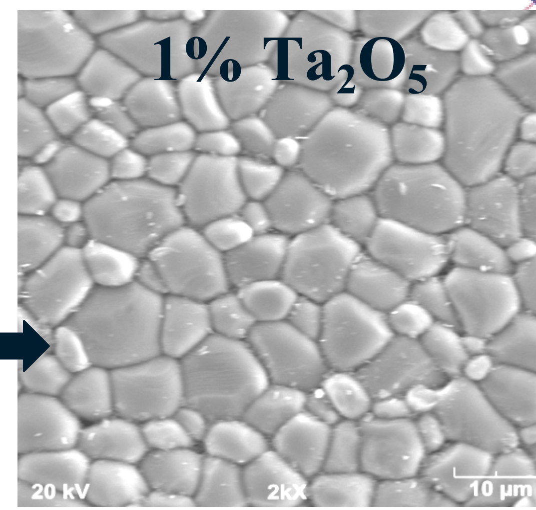
$$In_2O_3 \rightarrow 2In'_{Ti,Sn} + 2V_O^{\bullet}$$

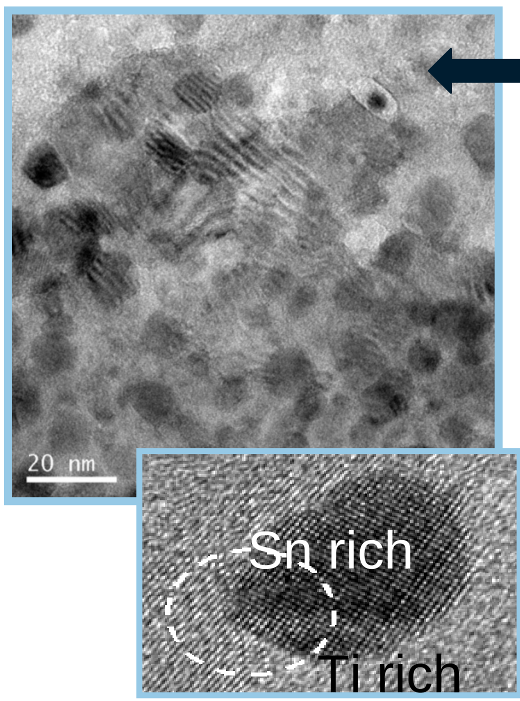
# 75/25 $TiO_2/SnO_2$




Large Grain

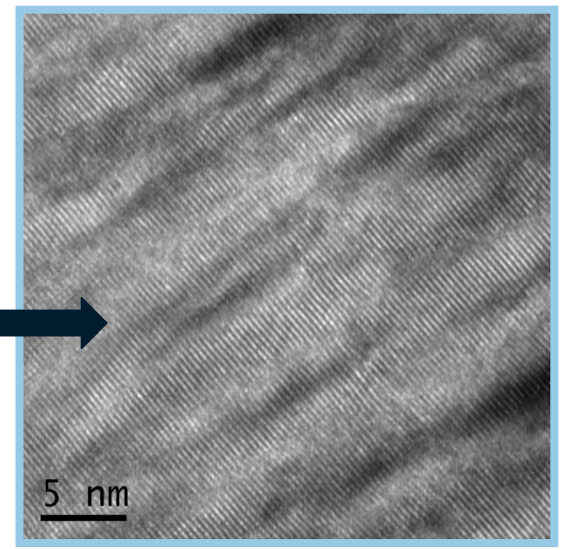
Small Grain



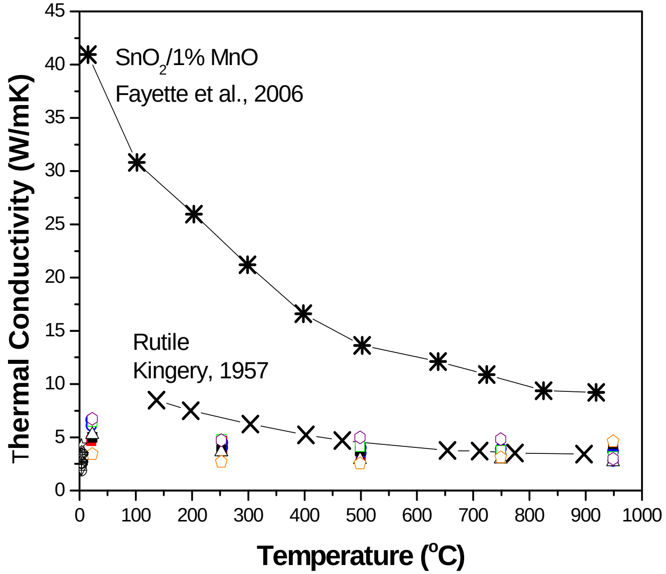



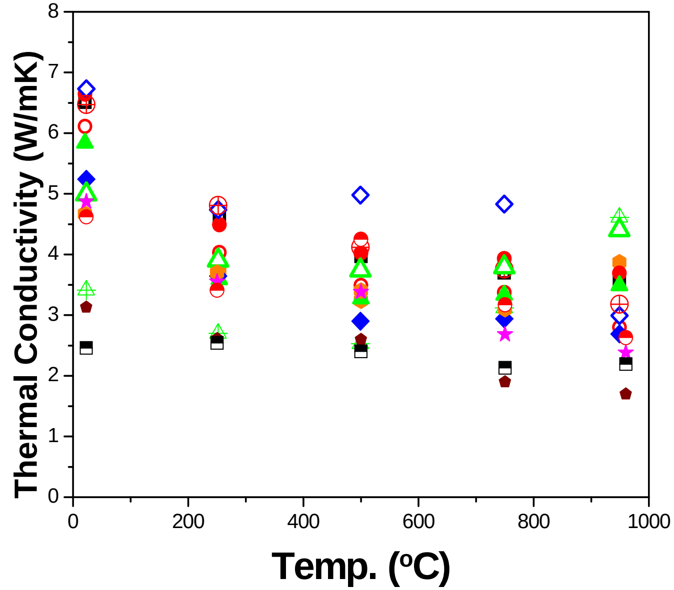

Nano-ppts

Diffuse
Composition
Fluctuation



# Thermal Conductivity



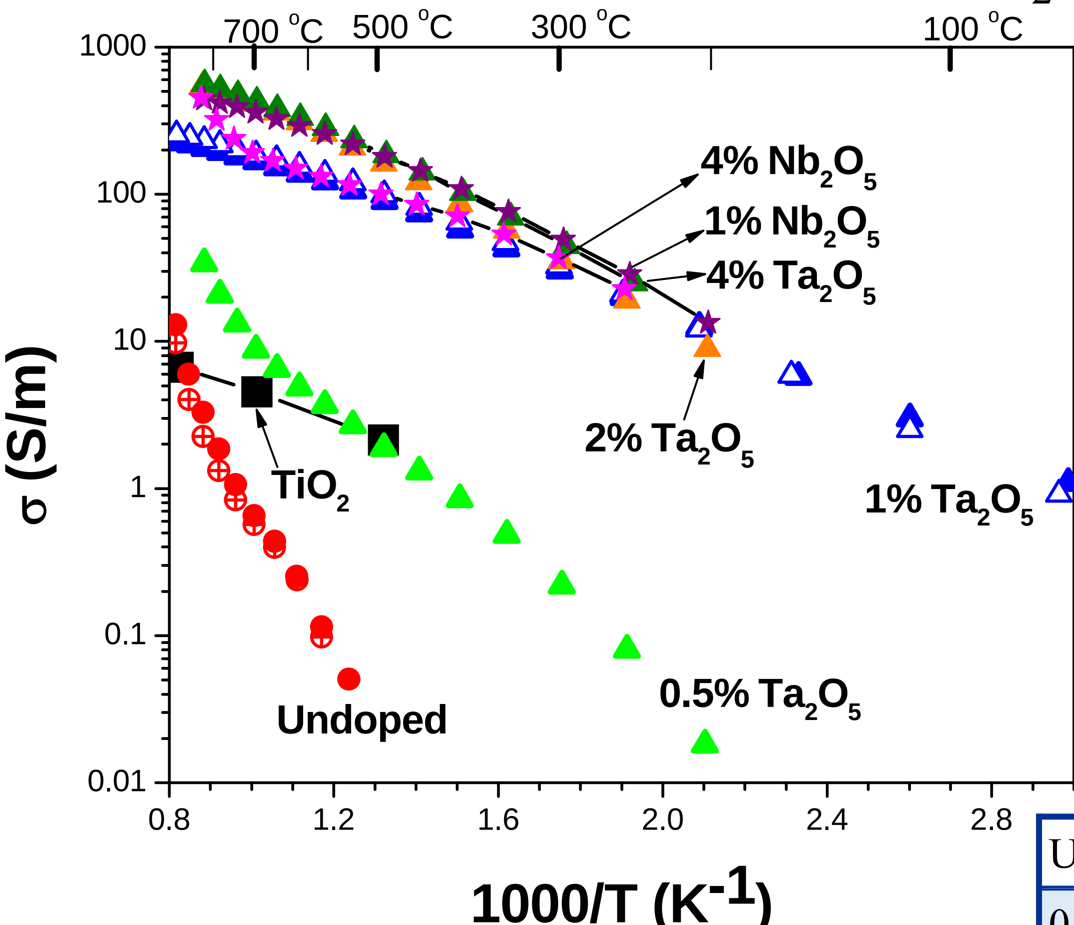

Compositions

1% MnO-50 $TiO_2$
1% CoO-50 $TiO_2$
1% MnO-75 $TiO_2$
1% CoO-75 $TiO_2$
1% MnO-25 $TiO_2$
1% CoO- 25$TiO_2$
1%$Ta_2O_5$/0.5% CoO-25 $TiO_2$

- •Compositions exhibit low κ – 1.7 to 6.8 W/mK
- •Observe no dependence on composition or post treatments
- •Spinodal Decomposition – κ reduction ?
- •Best ZT ~ 0.05

# Electrical Conductivity

## 75/25 $TiO_2/SnO_2$




- $Ta_2O_5$ & $Nb_2O_5$ - Increases σ

$$M_2O_5 = 2M^{\bullet}_{Ti,Sn} + \boxed{2e'} + \tfrac{1}{2}O_2 + 4O_O^X$$

- No further σ increase above 2% dopant.
- $In_2O_3$, MnO & CoO – No σ increase

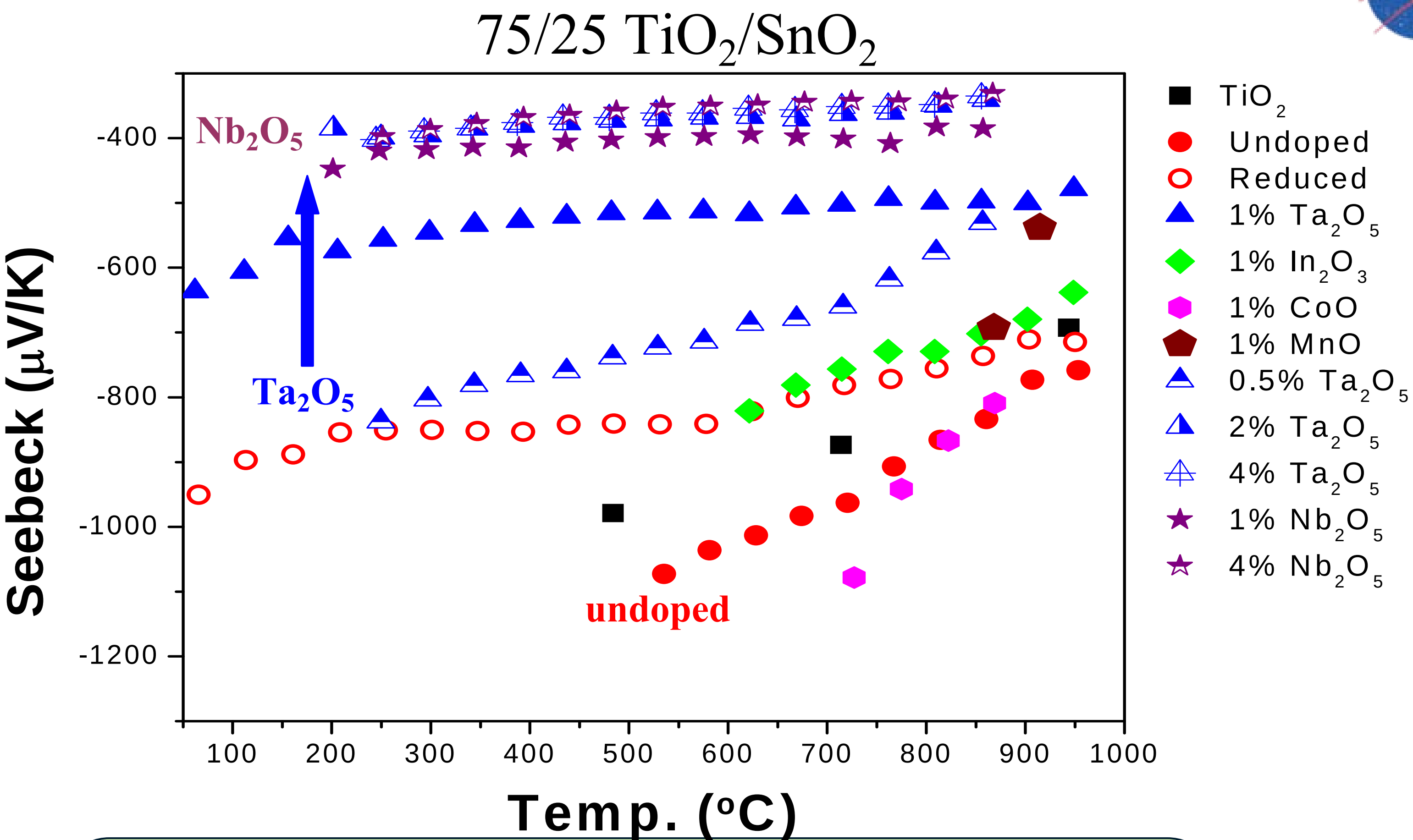
$$ZT = \frac{S^2\sigma}{\kappa}T$$

σ to low

Activation Energy

| | | | |
|---|---|---|---|
| Undoped | 0.97 ev | 1% $Nb_2O_5$ | 0.25 ev |
| 0.5% $Ta_2O_5$ | 0.49 ev | 4% $Nb_2O_5$ | 0.20 ev |
| 1% $Ta_2O_5$ | 0.22 ev | 1% $In_2O_3$ | 0.99 ev |
| 2% $Ta_2O_5$ | 0.30 ev | 1% CoO | 1.6 ev |
| 4% $Ta_2O_5$ | 0.26 ev | 1% MnO | 7.9 ev |

# Seebeck Coefficient

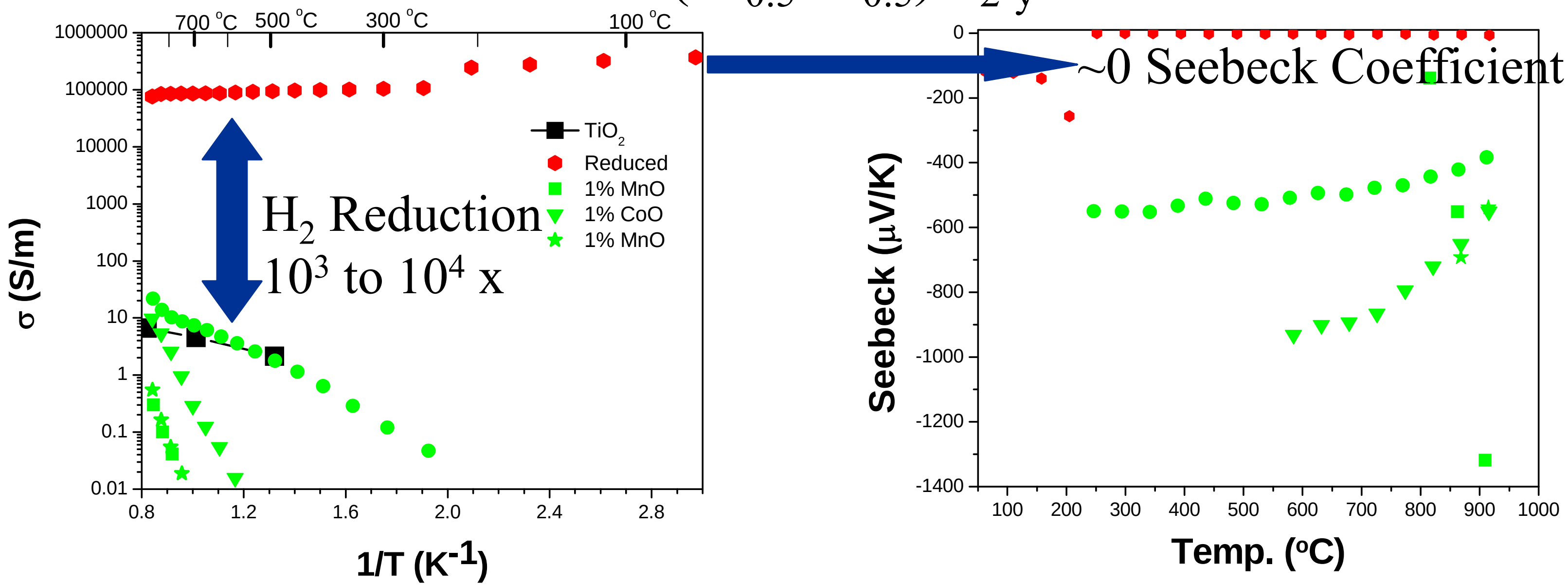



- N-type
- Large Seebeck coefficients at low σ
- Increase $Ta_2O_5$ conc. reduces Seebeck coefficient
- $Nb_2O_5$ doping most effective in Seebeck reduction

# Semiconductor

- Improve electrical conductivity by forming oxygen deficient material $(Ti_xSn_{1-x})O_{2-y}$

$(Ti_{0.5}Sn_{0.5})O_{2-y}$

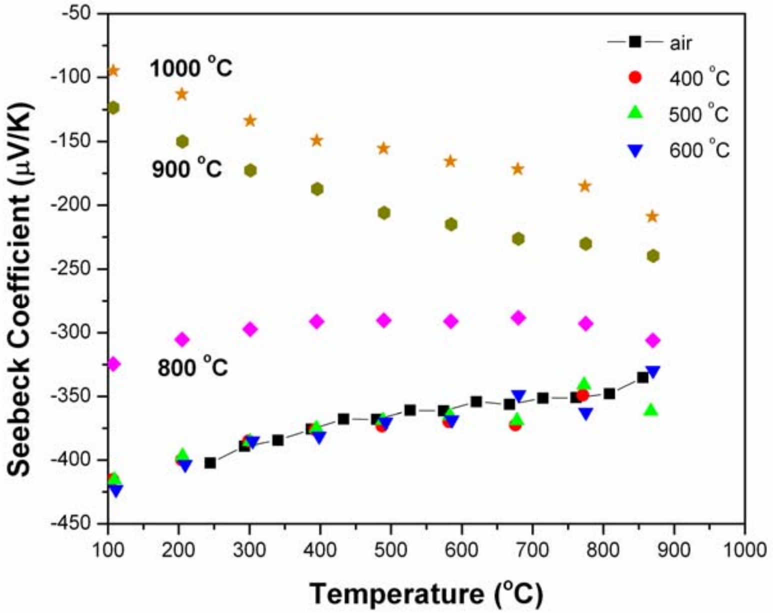


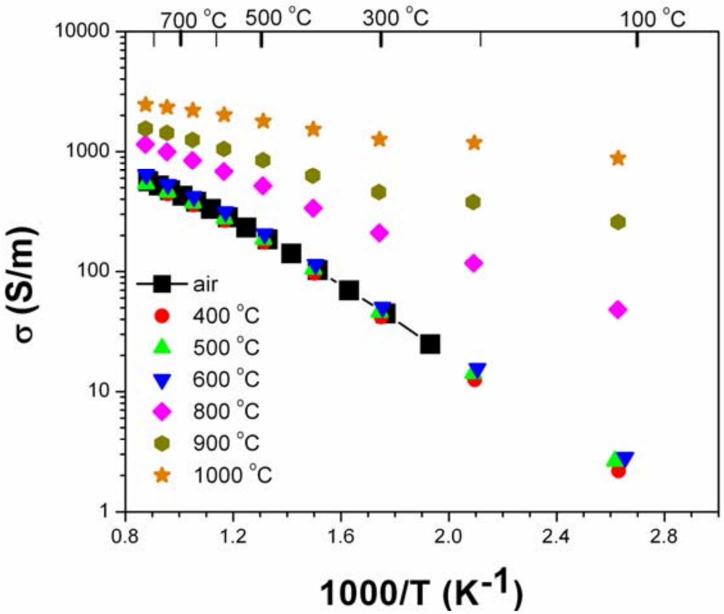

- Control the oxygen stoichiometry to increase σ and maintain a good Seebeck coefficient?

# Effects of reducing conditions

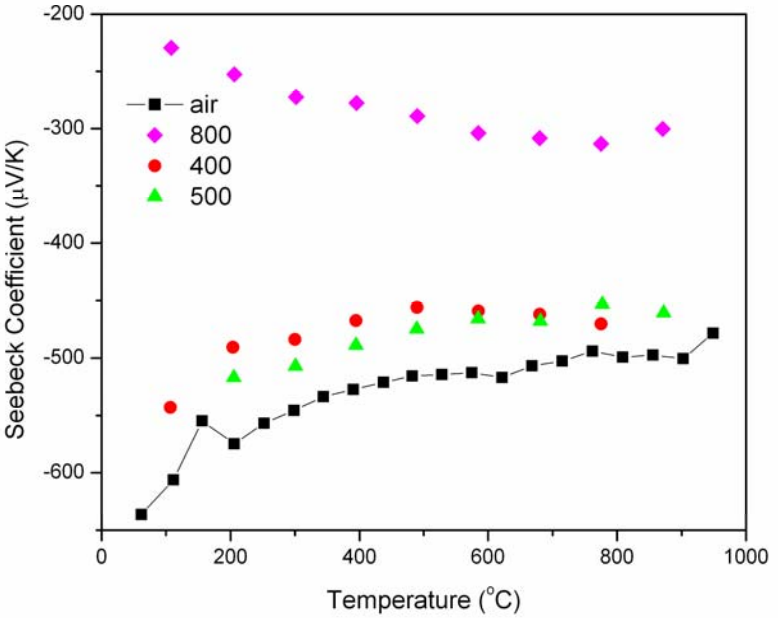
## $(Ti_{0.75}Sn_{0.25})O_{2-x}$

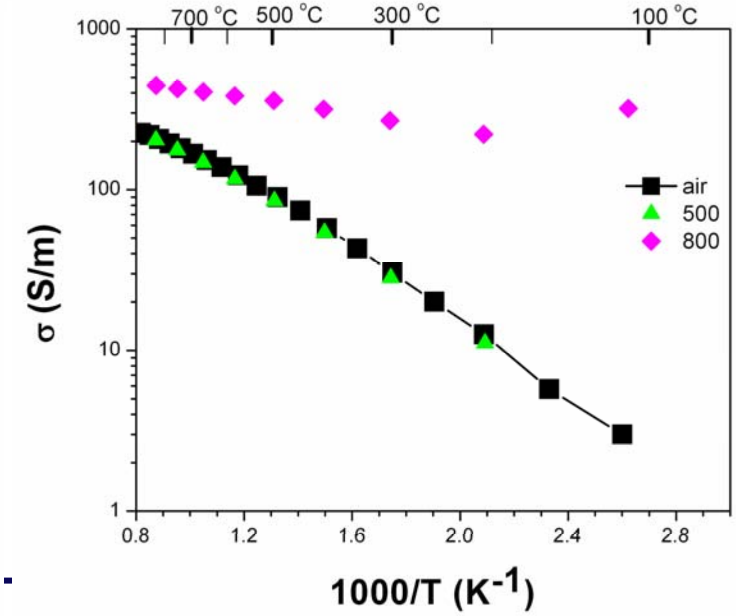
4% Ta




1% Ta



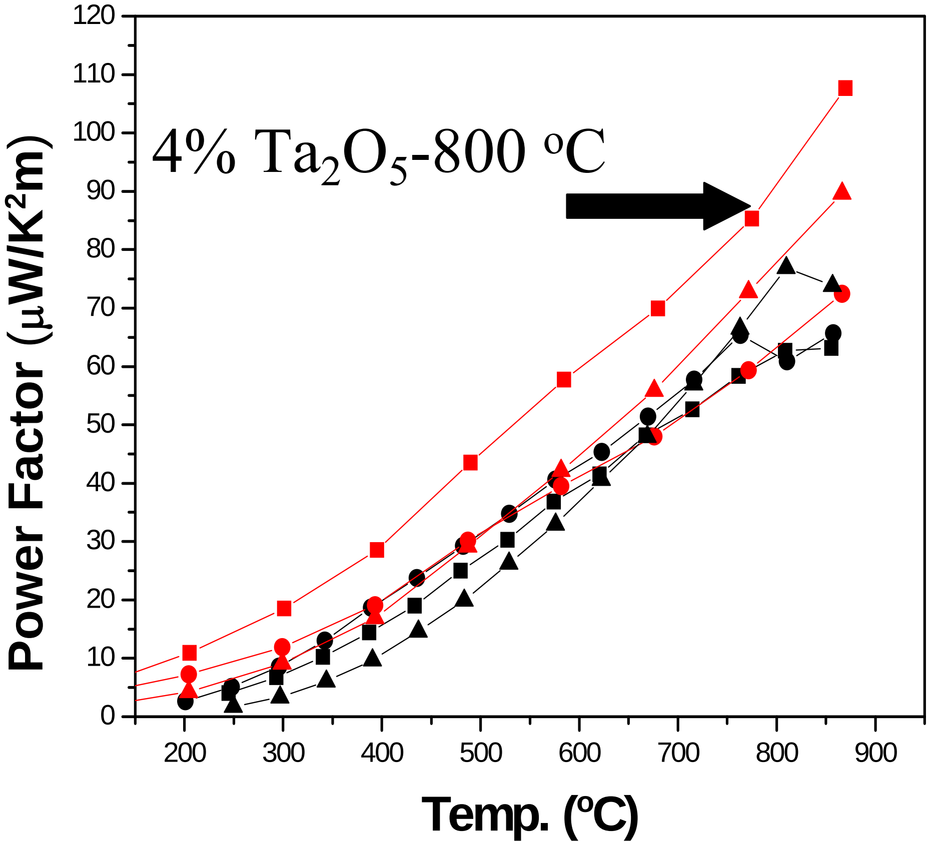
# Mechanical Robustness

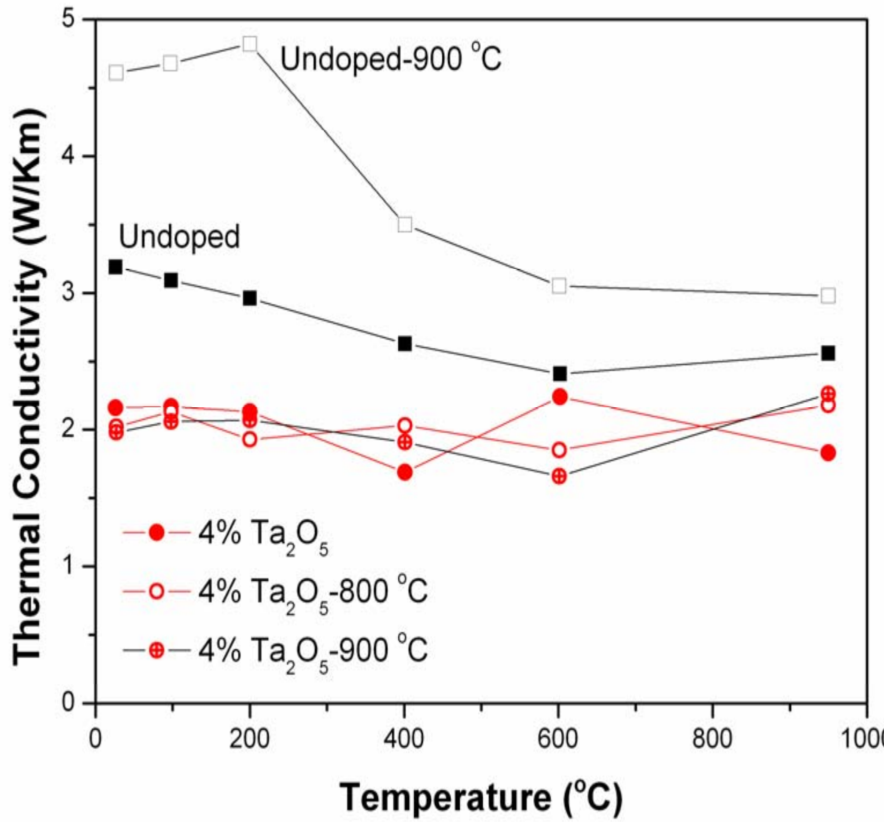
Undoped – 800 $^{o}$C

1% Ta doped – 900 $^{o}$C

4% Ta doped – 900 $^{o}$C

# Power Factor and Thermal conductivity




$$\boxed{PF = S^2\sigma}$$

# In Summary

•$TiO_2/SnO_2$ compositions exhibit low thermal conductivity. Nanostructured phases are observed.

•Improved electrical conductivity is observed for $Ta_2O_5$ doped $(Ti_{0.75}Sn_{0.25})O_{2-x}$ reduced at 800 $^oC$.

• Reduction of doped samples retained a low thermal conductivity (≈2W/mK).

•800 $^oC$ reduction increases the power factor by 1.69 – 2.76 for 4% $Ta_2O_5$ doping. However, ZT is <0.1.

Dense specimens with Sn-rich compositions need to be evaluated

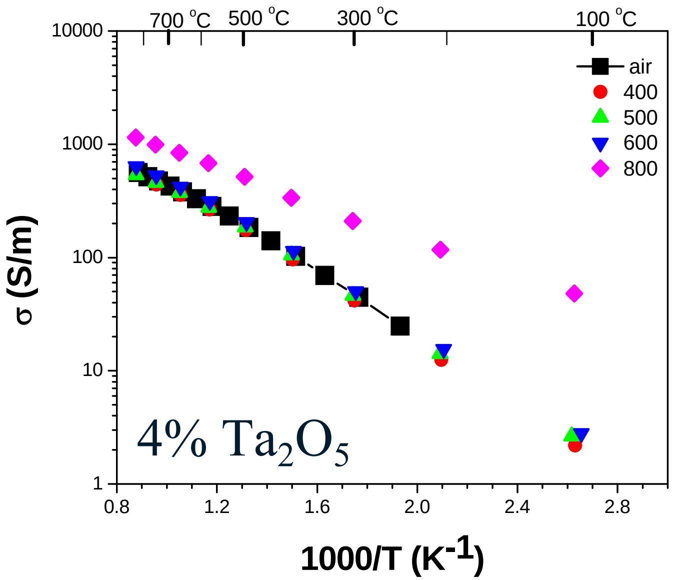
## Acknowledgements

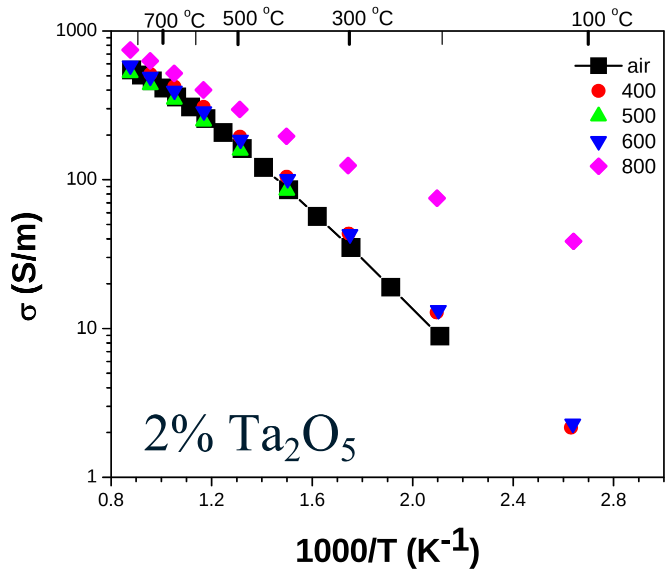
Thomas Sabo

Raymond Babuder

# Electrical Conductivity

## $(Ti_{0.75}Sn_{0.25})O_{2-x}$




- ≥800 °C treatment is Required to enhance σ.
- 4% $Ta_2O_5$ produces the highest σ.
- Significant effect on low temperature σ.