

# Transparent Conductors: Part I

Prof. Tom Mason

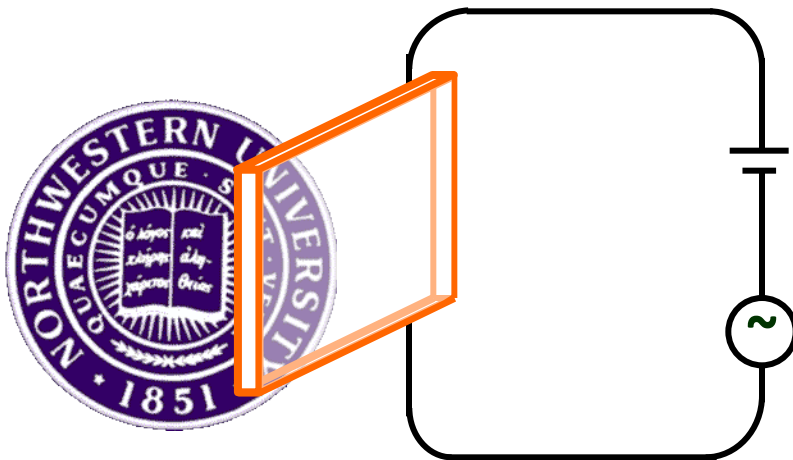
Northwestern University

Materials Science & Engineering

# An Introduction to TCOs

Transparency

(> 80% through visible spectrum for  
typical 1  $\mu\text{m}$  thin film)



Conductivity (>  $10^3$  S/cm)

- Some History and Applications
- Basic requirements for TCOs
- Role of Crystal Structure
- Phase Diagrams
- Bulk Experimental Methods:
  - Synthesis
  - Characterization
- Defect Chemistry

# TCO History and Applications

# The First Transparent TCO

CdO

"a brown/black powder"

$$\sigma = 37 \text{ S/cm}$$

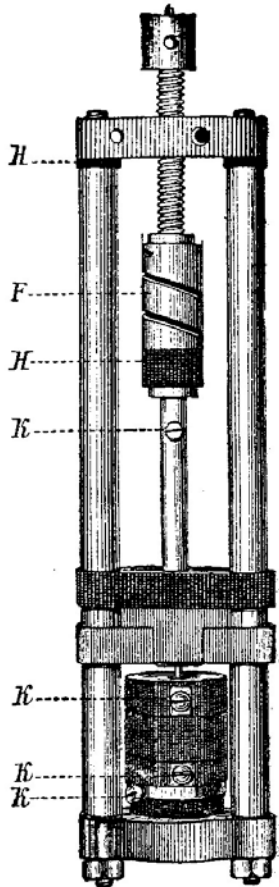


Fig. 1.

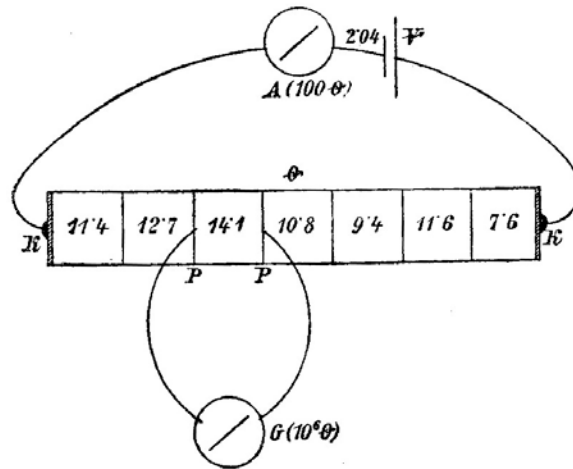


Fig. 2.

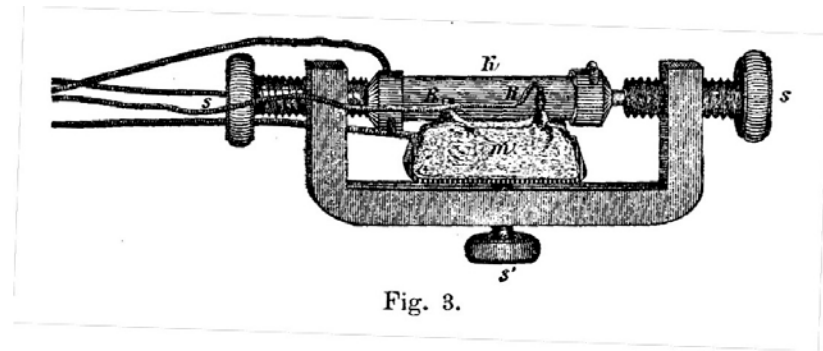


Fig. 3.

*F. Streintz, Ann. Phys. (Leipzig) 9, 854 (1902)*

# The First Thin Film TCO

thermal oxidation of sputtered Cd films  
on glass  $\sigma = 870 \text{ S/cm}$  (106 nm thick)  
with orange/gold color

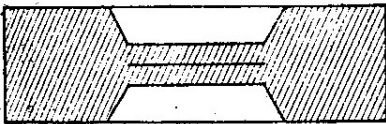


Fig. 2.

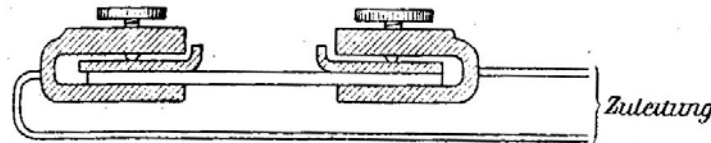


Fig. 1.

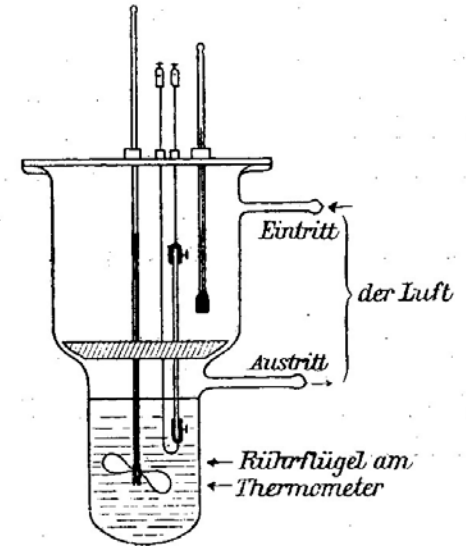
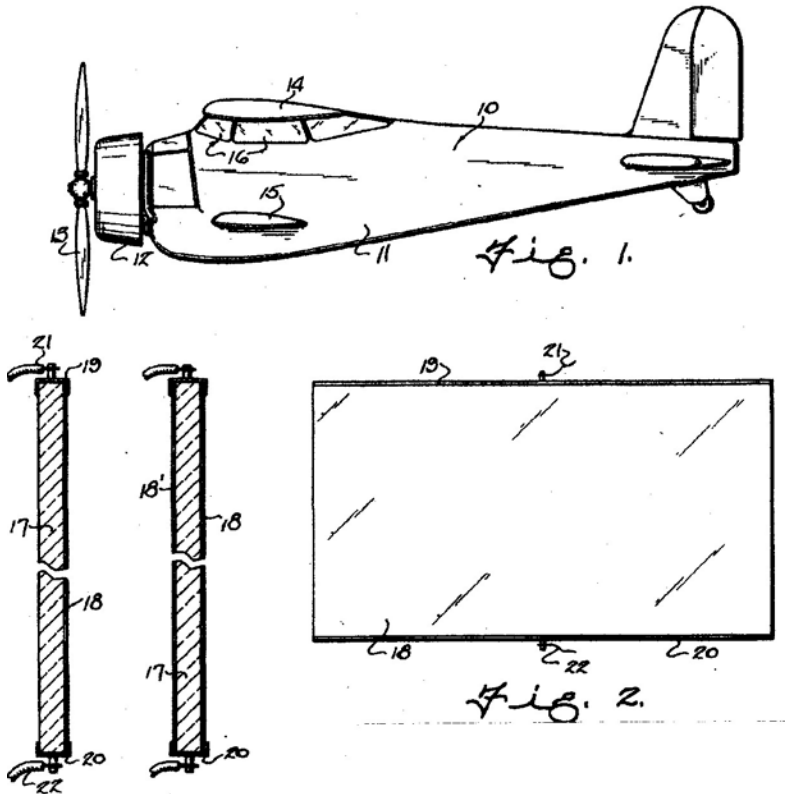


Fig. 3.

*K. Bädeker, Ann. Phys. (Liepzig) 22, 749 (1907)*

# Mid-20<sup>th</sup> Century Developments



- 1930s-1940s: conductive SnO<sub>2</sub> film patents (various glass companies)
- 1951: first ITO patent (Corning) → Sn-doped In<sub>2</sub>O<sub>3</sub>
- 1959: key dissertation on ZnO properties
- 1971: ZnO varistor and TCO film patents (Japan)

*SnO<sub>2</sub>-based windshield de-icer*

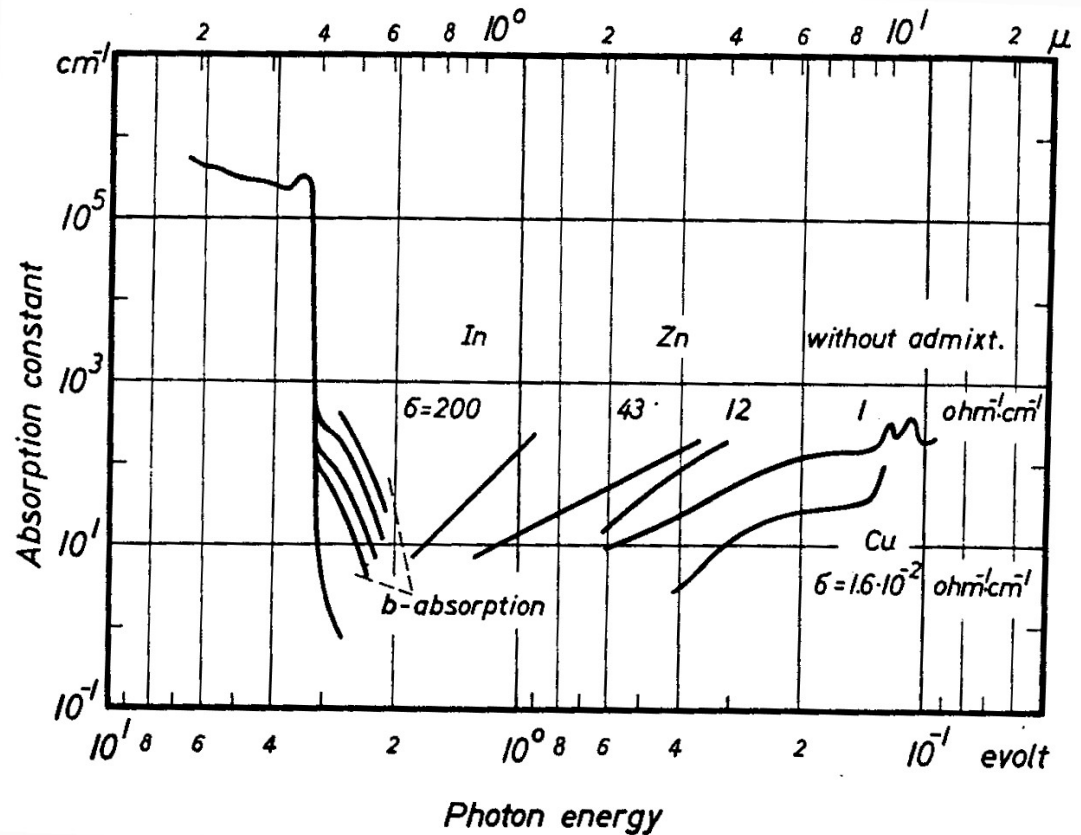
# Early TCO Science: In-doped ZnO

Single crystal data:

E. Scharowsky, A. Physik,  
135, 318 (1953)

R. Arneth, PhD thesis,  
U. Erlangen (1959)

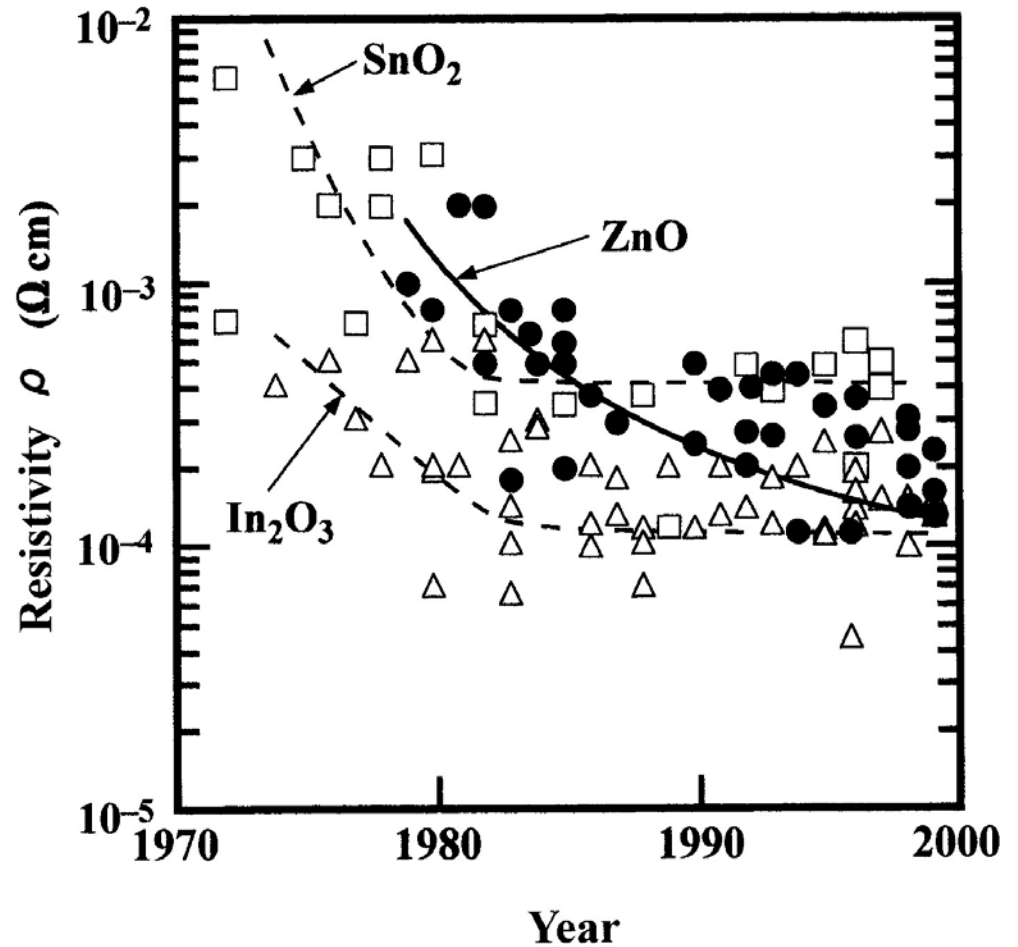
(taken from: G. Heiland,  
E. Mollwo and F. Stockmann,  
in Solid State Physics, Vol. 8,  
ed. By F. Seitz and D.  
Turnbull, 1959)



# TCO Development (1970-2000)

Source:  
*T. Minami,*  
*MRS Bulletin,*  
*August, 2000*

-data for pure and  
doped host oxides.





# Why the Surge of Interest?

- Novel complex oxide/solid solution TCOs discovered in the 1990s
- Discovery of p-type TCO materials since the late 1990s
- Development of amorphous n-type TCOs since 2004
- Large area applications (organic LEDs, solar cells) require ITO-alternatives (chemical, electrical, cost issues)
- Development of Transparent Oxide Semiconductors (oxide-based thin film transistors-TTFTs)

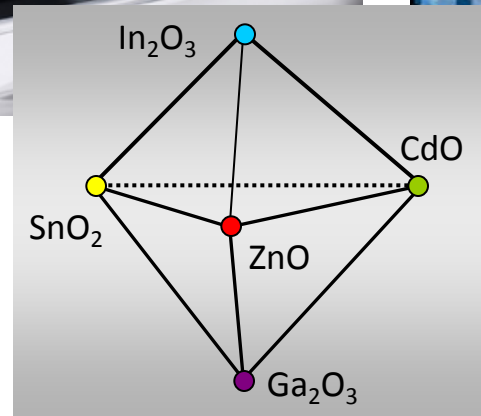
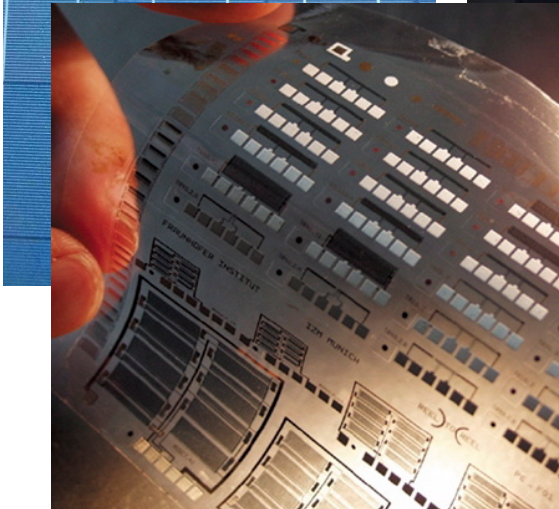
# A Wide Array of TCO Applications

- Low-emissivity windows
- Transparent front electrodes for flat-panel displays
- Transparent top electrodes for photovoltaic cells
- Defrosting windows (freezers, cockpits)
- Electrochromic mirrors and windows
- Oven window coatings
- Static charge dissipation coatings
- Touch-panel controls
- Electromagnetic shielding
- Invisible security circuits
- Organic light-emitting diodes

*- R. Gordon, MRS Bulletin, August 2000.*

# Large-Area Applications

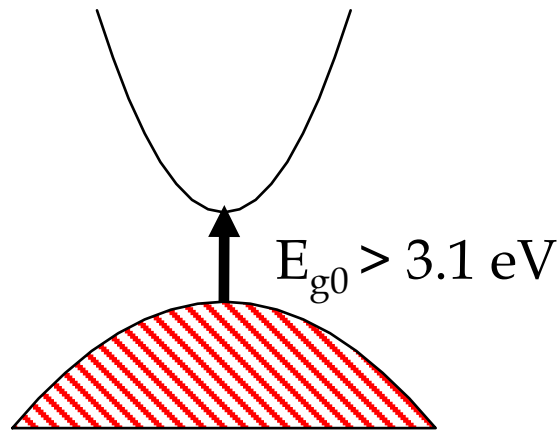
- High electrical conductivity ( $>1000$  S/cm)
- High optical transparency in visible region ( $>80\%$ )
- Industry standards: ITO,  $\text{SnO}_2$



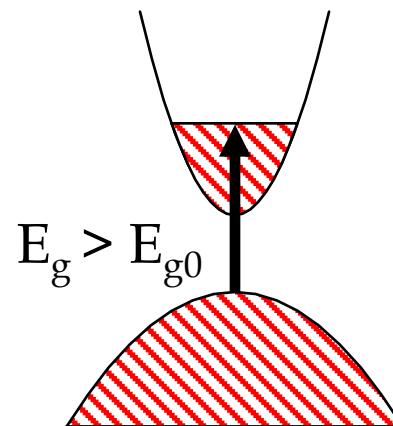
# Basic TCO Requirements

# Basic TCO Requirements

Insulating Parent Compound



N-type Degenerate Doping



- Parent oxide with relatively wide band gap
- Interband transitions  $> 3.1 \text{ eV}$  (cations with filled d-shells)
- Highly dispersed conduction (or valence) band (high mobility)
- Ability to donor- or acceptor-dope to  $\sim 10^{21}/\text{cm}^3$

*I. Hamberg and C. G. Grandqvist, J. Appl. Phys., 60, R123 (1986).*

# TCO-Active Species: $d^{10}$ Cations

valence state  $\longrightarrow$  +1      +2      +3      +4

Cu	Zn	Ga	
Ag	Cd	In	Sn



= p-type



= n-type

# Typical Parameters:

- Large electron populations in the  $10^{20}$  to  $10^{21}$   $\text{cm}^{-3}$  range (highly degenerate)
- High electron mobilities in the 30-70  $\text{cm}^2/\text{V-s}$  range
- Large conductivities (in excess of 1000 S/cm)
- Low absorption in the visible ( $\alpha < 10^4 \text{ cm}^{-1}$ )
  - 100nm film 90% transparent in the visible
  - 500nm (0.5 $\mu\text{m}$ ) film 60% transparent in the visible

# Role of Crystal Structure



# Shannon's n-type TCO Maxim

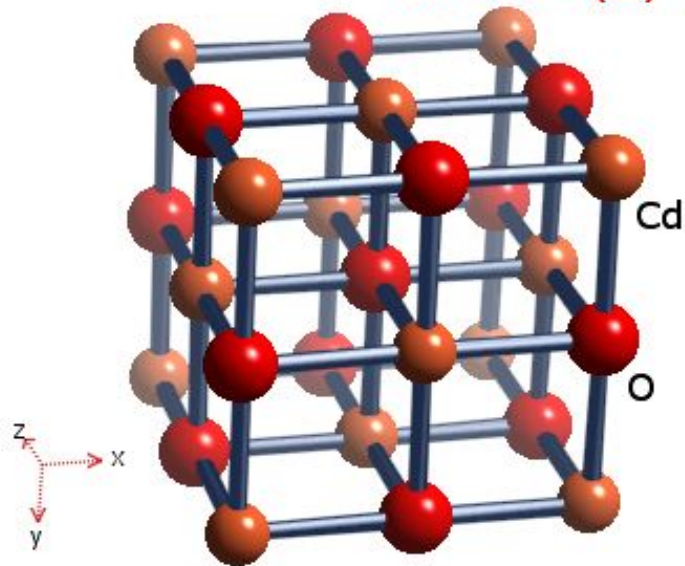
*“...continuous edge-sharing of  $Cd^{2+}$ ,  $In^{3+}$  and  $Sn^{4+}$  octahedra is a necessary criterion for the formation of an n-type transparent conductor.”*

*-R. D. Shannon et al., J. Phys. Chem. Solids, 38, 877 (1977).*

# Octahedral Cation TCO Family



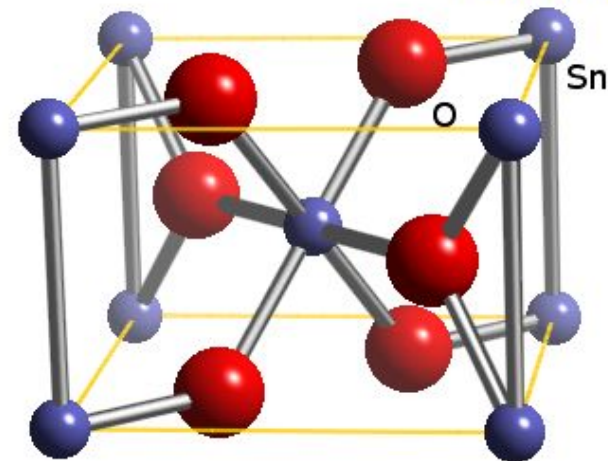
cadmium (II) oxide



rocksalt structure

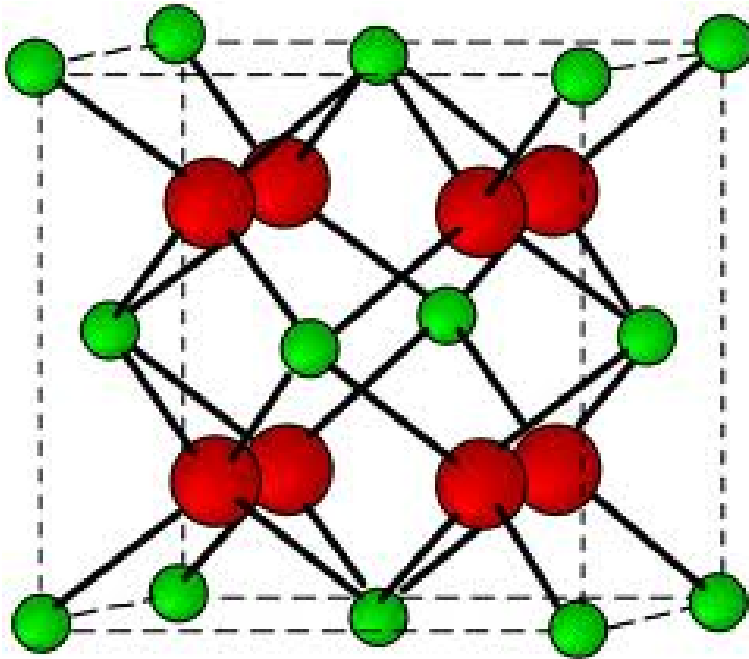


tin(IV) oxide



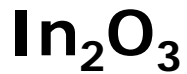
rutile structure

# Bixbyite: a Fluorite-Derivative

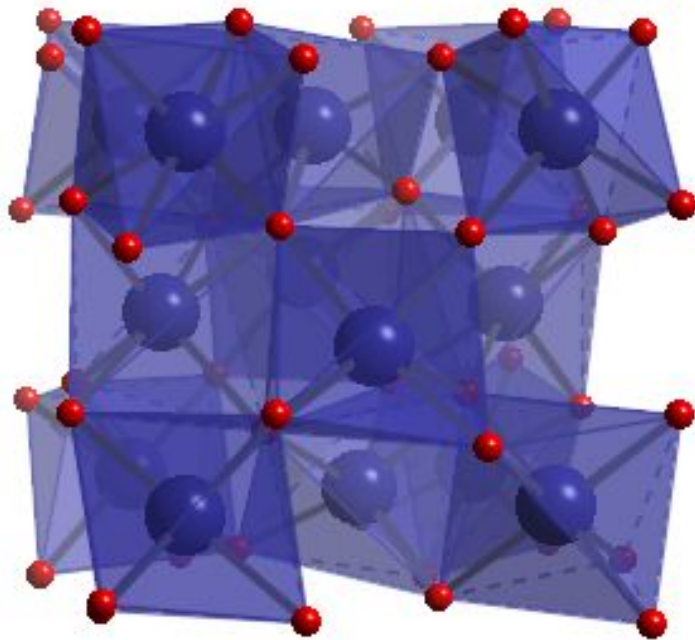


- Double  $\text{ZrO}_2$  to  $\text{Zr}_2\text{O}_4$
- If In-oxide were a fluorite, it would be  $\text{In}_2\text{O}_4$
- But  $\text{In}^{3+}$  rather than  $\text{In}^{4+}$
- For charge balance, remove  $\frac{1}{4}$  of O-ions
- Get  $\text{In}_2\text{O}_3$

# Octahedral Cation TCO Family



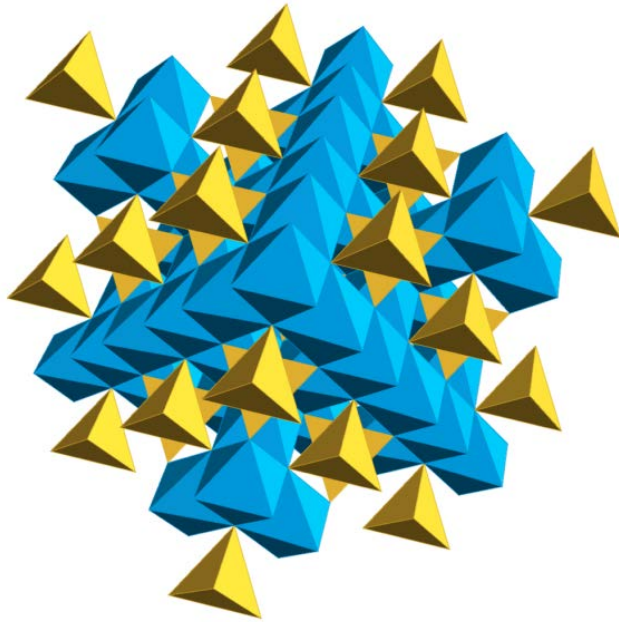
indium(III) oxide



bixbyite structure

- Edge-shared octahedra
- The octahedra are distorted (hints at why amorphous TCOs also conduct)
- Can be readily doped (e.g.,  $\text{Sn}^{4+}$ ) and co-doped ( $\text{Zn}^{2+}/\text{Sn}^{4+}$  and  $\text{Cd}^{2+}/\text{Sn}^{4+}$ )
- The basis of a rich family of complex oxide solid solutions

# Octahedral Cation TCO Family



**Yellow:**  
**Tetrahedral ( $T_d$ )**

**Blue:**  
**Octahedral ( $O_h$ )**

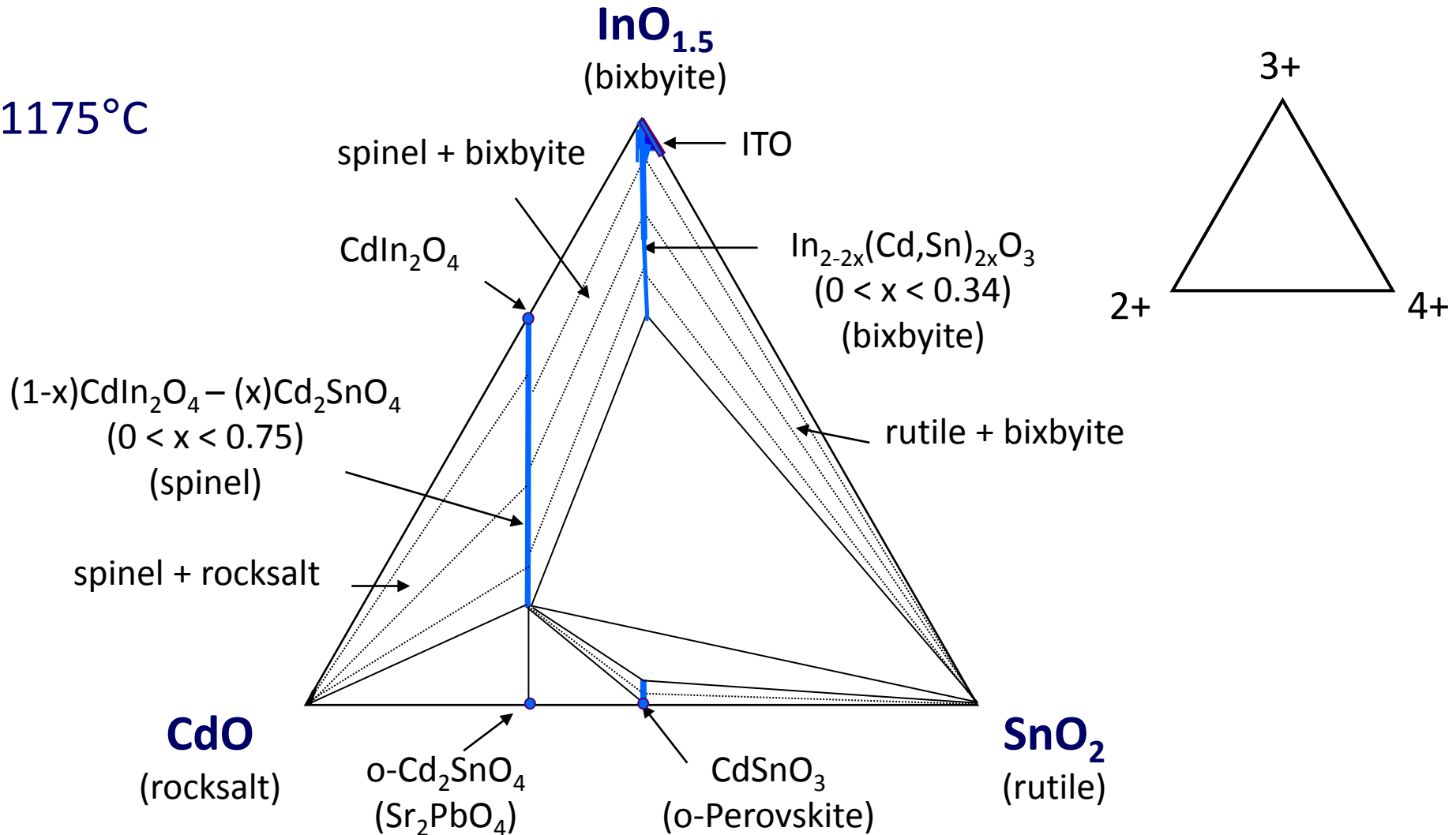
spinel structure

- Spinel =  $MgAl_2O_4$
- 1/2 octahedral interstices occupied: octahedral sites
- 1/8 of tetrahedral interstices occupied: tetrahedral sites
- Arrays of edge-shared cation octahedra
- Spinel is well-known for exhibiting extended solid solutions

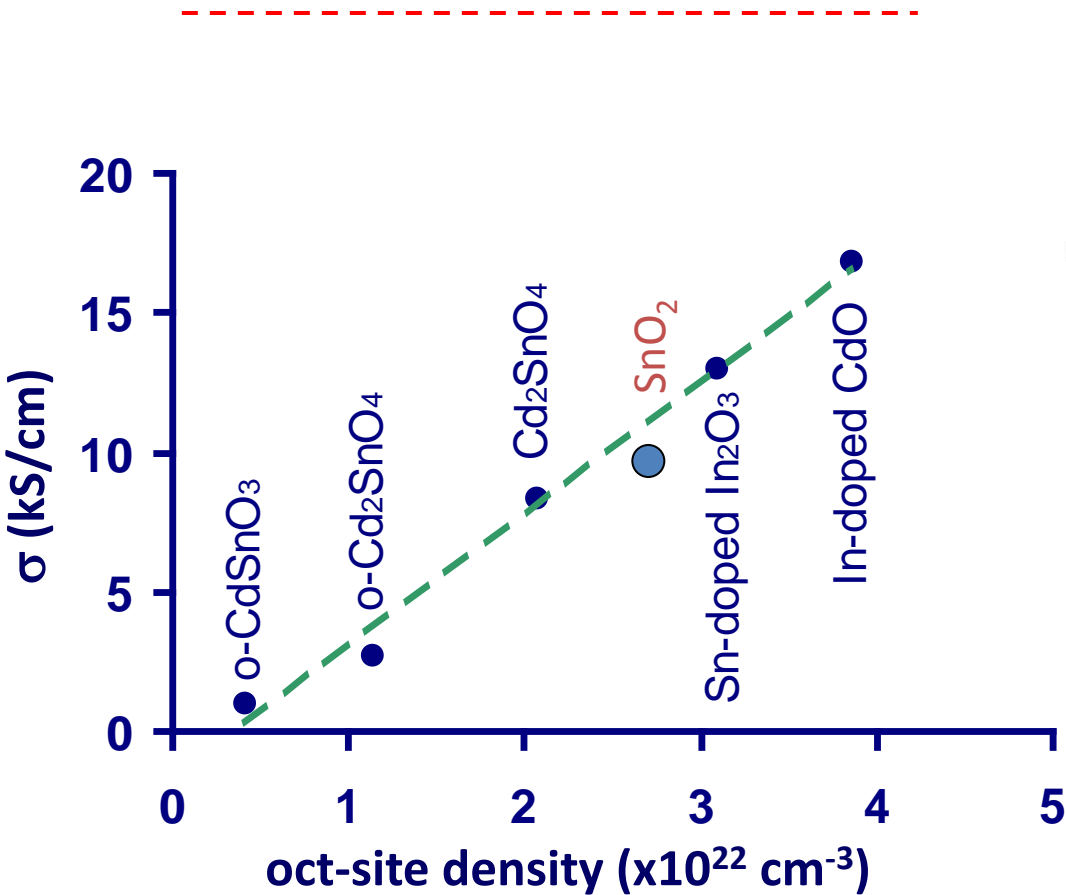
# The Importance of Phase Diagrams

# The Cd-In-Sn-O (CITO) System

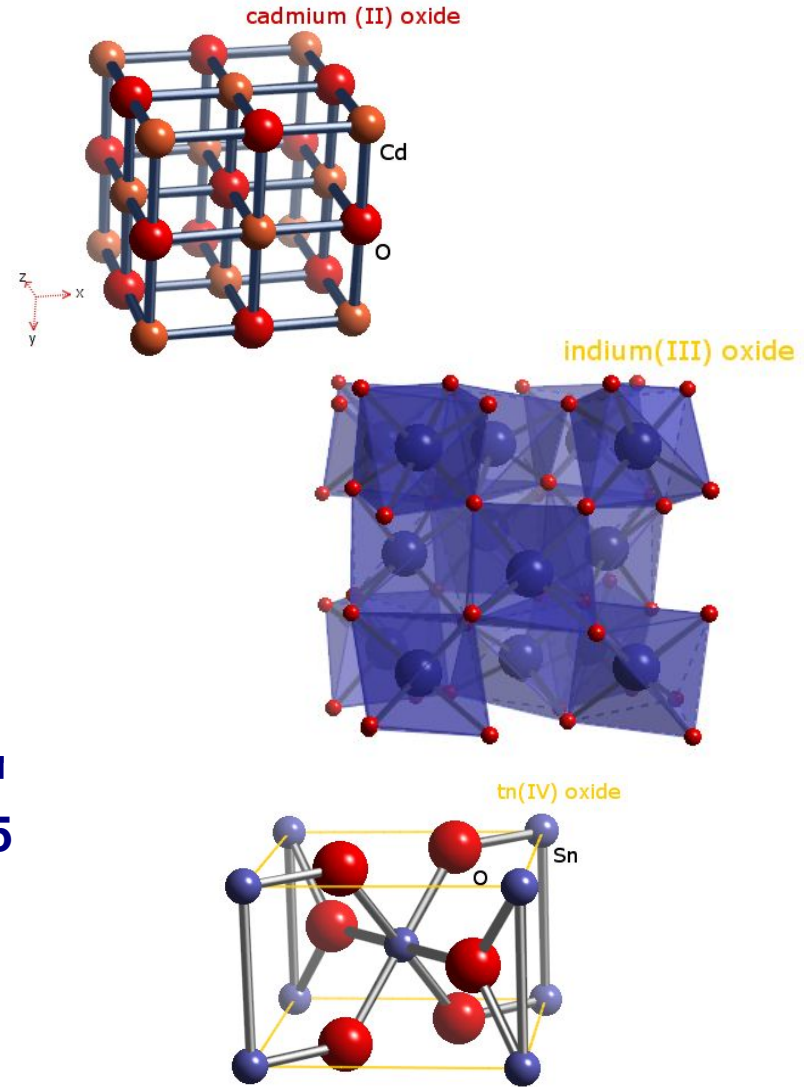
1175°C



# Optimized conductivity vs. OSD



Bellingham et al. (1991) predicted the maximum TCO conductivity = 25,000 S/cm





# Shannon's n-type TCO Maxim

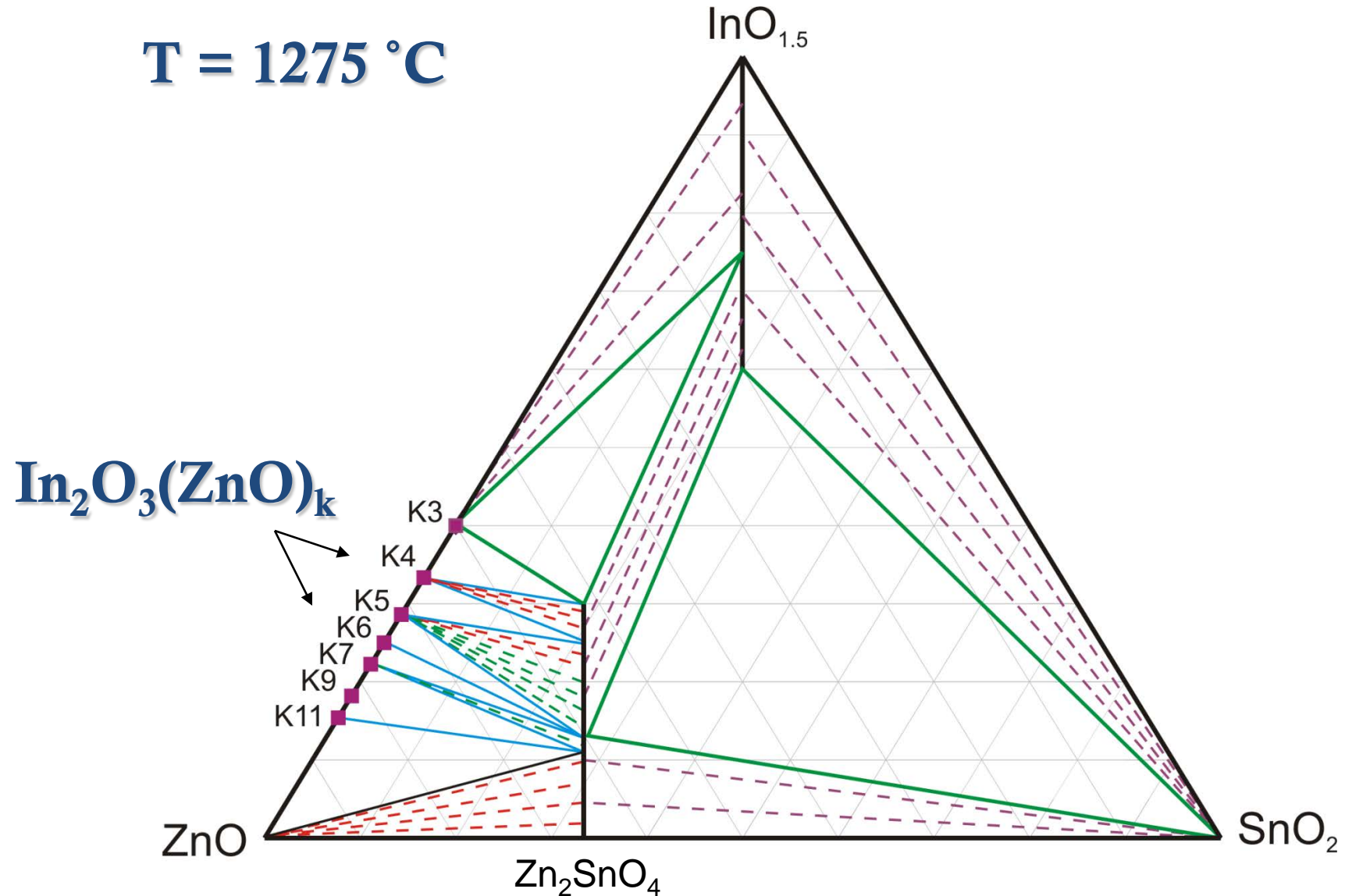
*“...continuous edge- **or corner-** sharing of  $\text{Cd}^{2+}$ ,  $\text{In}^{3+}$  and  $\text{Sn}^{4+}$  octahedra is a necessary criterion for the formation of an n-type transparent conductor.”*

*-R. D. Shannon et al., J. Phys. Chem. Solids, 38, 877 (1977).*

*What about  $\text{Zn}^{2+}$ ?*

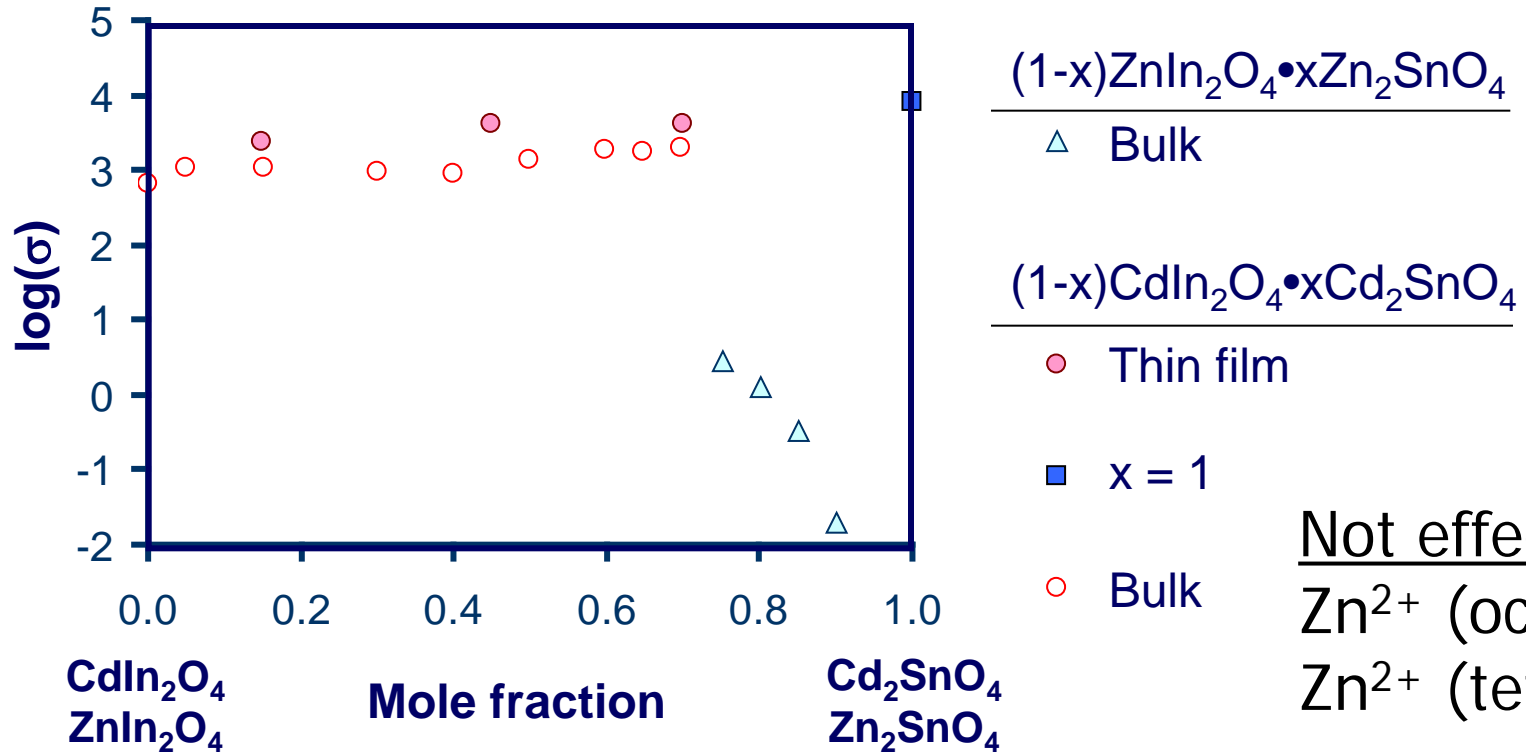
# The Zn-In-Sn-O System

$T = 1275\text{ }^\circ\text{C}$



# What About Zn<sup>2+</sup> ?

## spinel conductivities



△ G.P. Palmer, K.R. Poeppelmeier, and T.O. Mason. J Solid State Chem 134. 192 (1997)

○ D.R. Kammler, T.O. Mason, D.L. Young, and T.J. Coutts. J App Phys 90. 3263 (2001)

■ X. Wu, T.J. Coutts, and W.P. Mulligan, J Vac Sci Tech A15. 1057 (1997)

○ D.R. Kammler, T.O. Mason, and K.R. Poeppelmeier. Chem Mater 12. 1954. (2000)

# Shannon's n-type TCO Maxim

*“...continuous edge- **or corner-** sharing of  $\text{Cd}^{2+}$ ,  $\text{In}^{3+}$  and  $\text{Sn}^{4+}$  octahedra is a necessary criterion for the formation of an n-type transparent conductor.”*

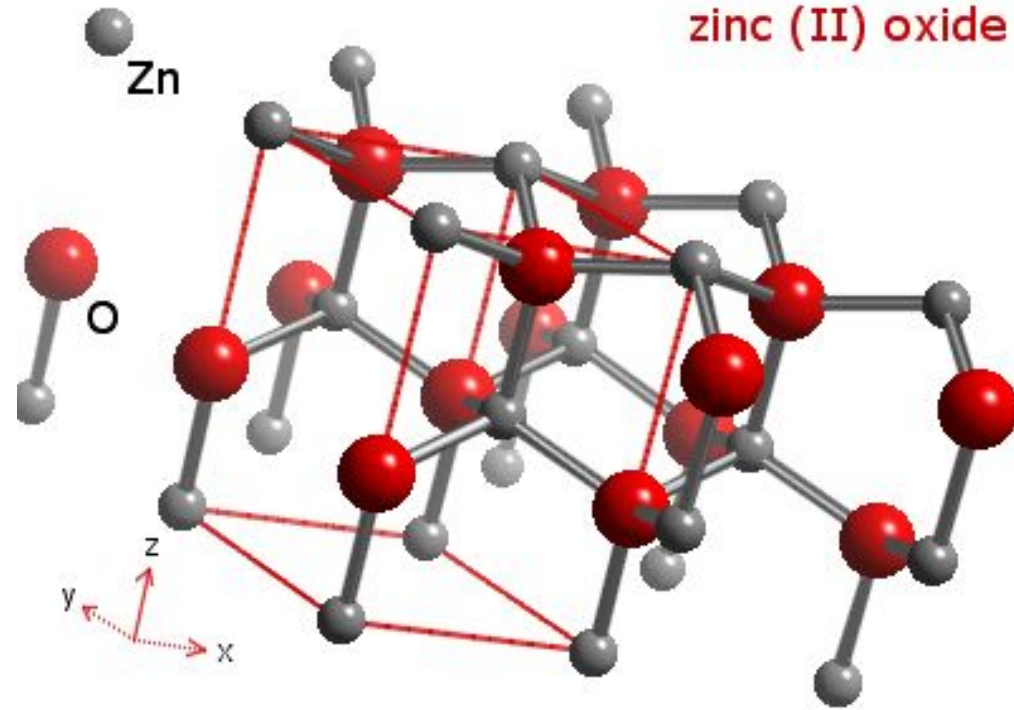
*-R. D. Shannon et al., J. Phys. Chem. Solids, 38, 877 (1977).*

*What about ZnO?*

# Tetrahedral Coordination TCO

ZnO

zinc (II) oxide



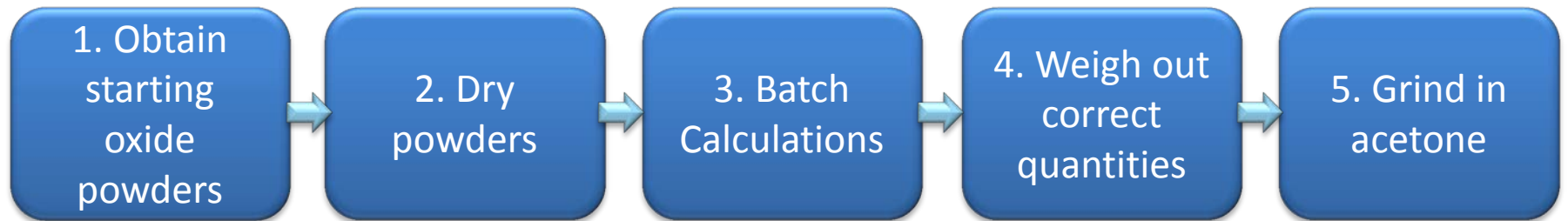
wurtzite structure

- ZnO is the only TCO with exclusively tetrahedral coordination
- In other crystal structures/CNs Zn is not as strong a contributor to TCO behavior
- Zn cations play an important role in stabilizing amorphous n-type TCOs

# Bulk Experimental Methods

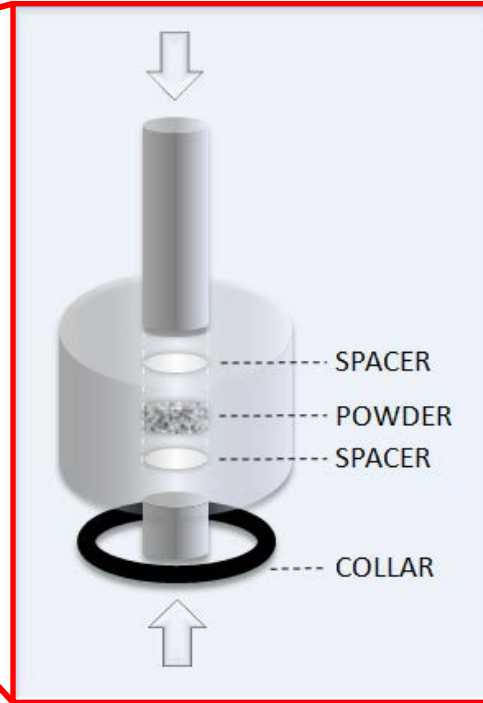
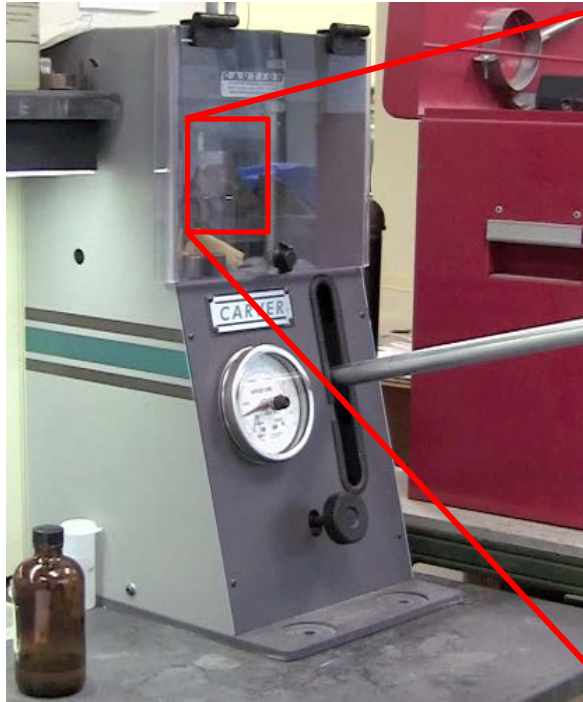
# Solid State Reactions

- Batch calculations of precursors (usually constituent oxides)
- Weighing and mixing of precursors



# Pellet Pressing

## Cold pressing



- Typically ~130 MPa with steel dies
- Can add binder/ pressing aid
- 0.25" to 1.5" pellets

## Hot pressing



- $\text{Al}_2\text{O}_3$  dies prevent reduction
- 67 – 774 MPa max
- 0.5" to 1.7" pellets

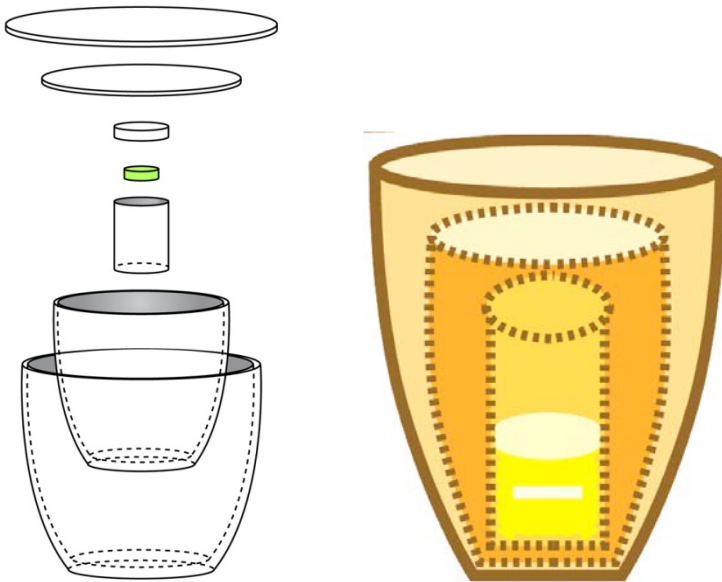


# Solid State Reaction/Sintering

- Up to  $\sim 1400^{\circ}\text{C}$
- In fume hoods when needed
- **Nested crucibles minimize preferential evaporation (e.g. Zn)**
- **Sacrificial powder minimizes contamination**

- **Quenching preserves high temperature phase**

Limitation: thermal shock

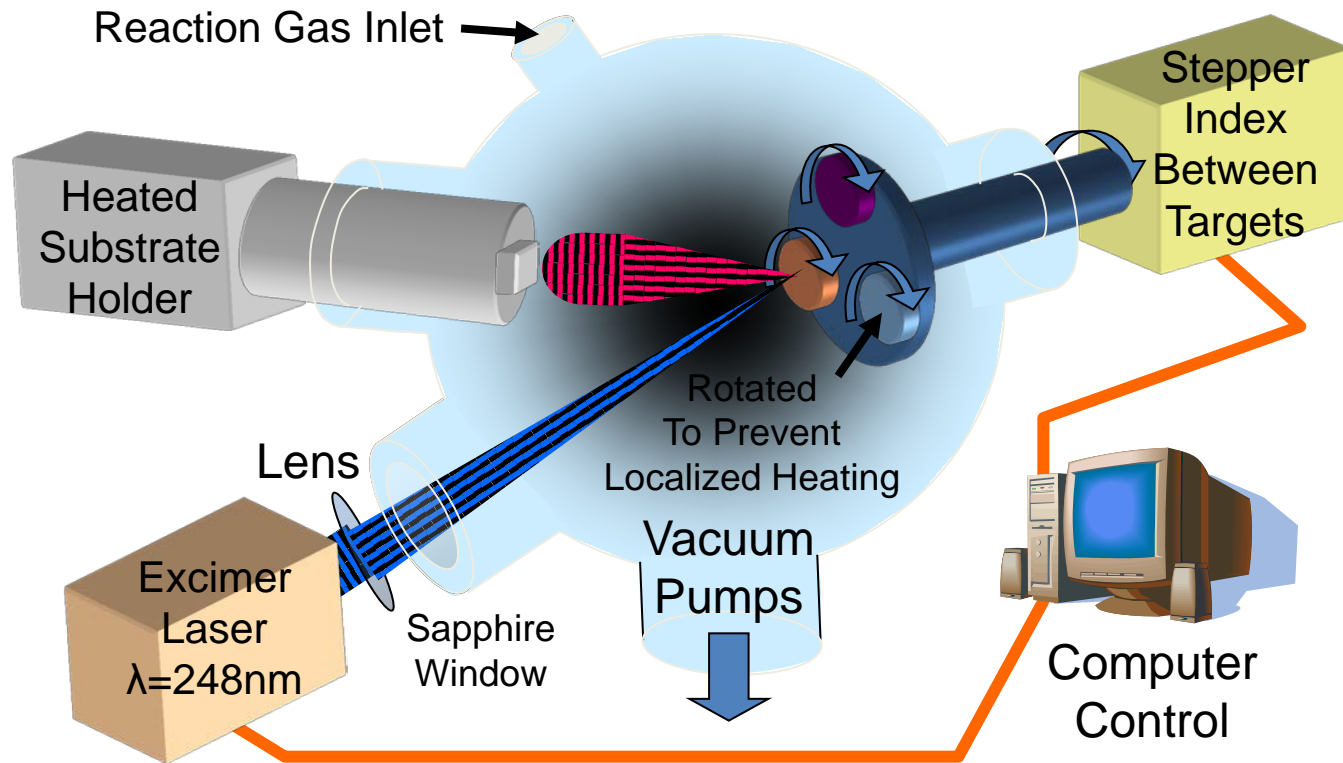


Time frame: 1 day – 2 weeks

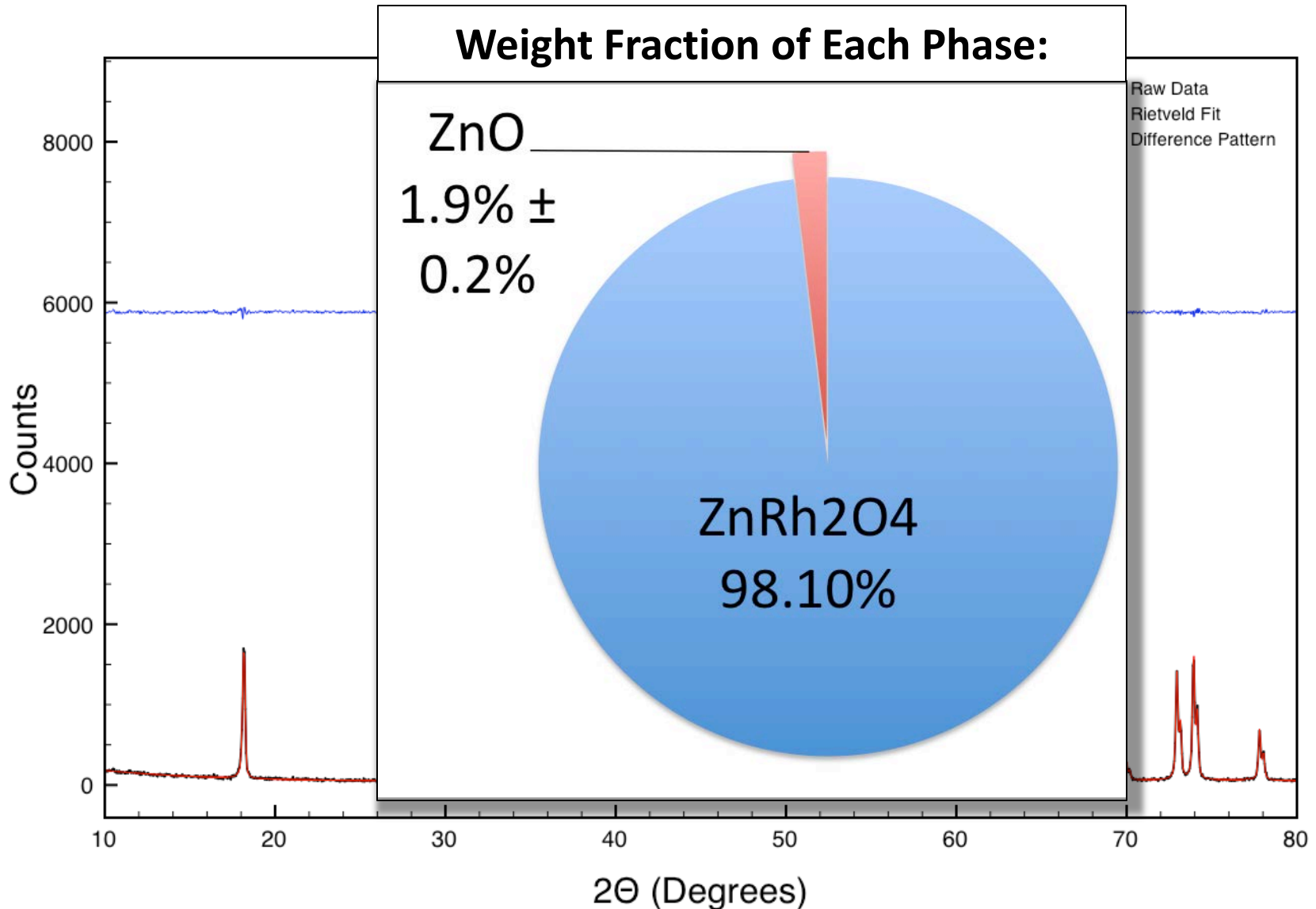


# Multi-target Pulsed Laser Deposition

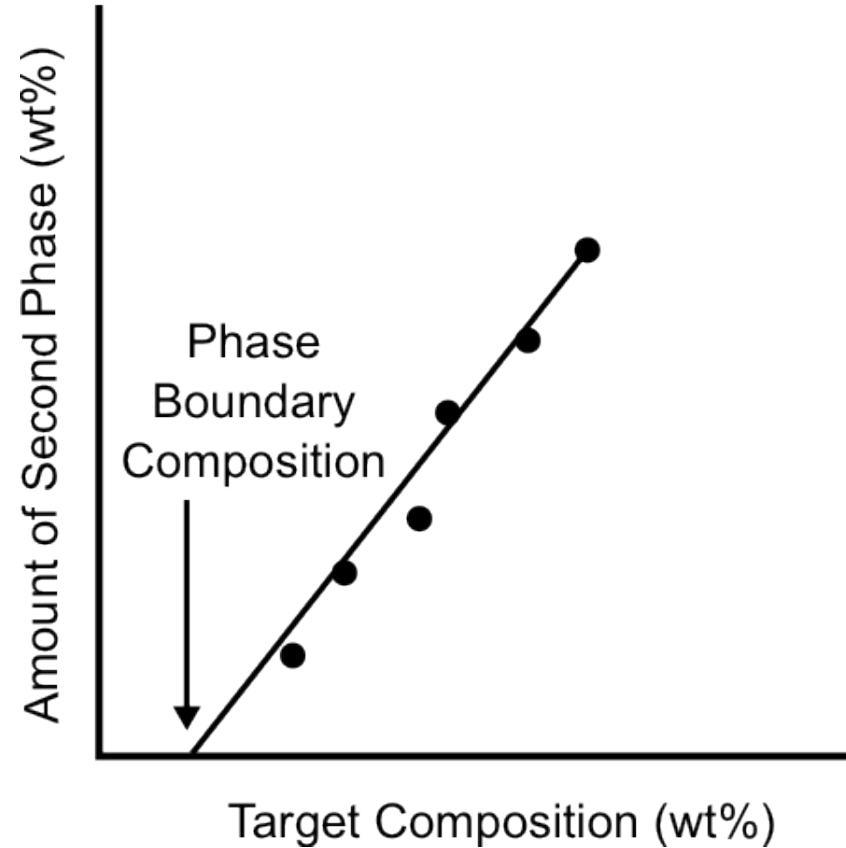
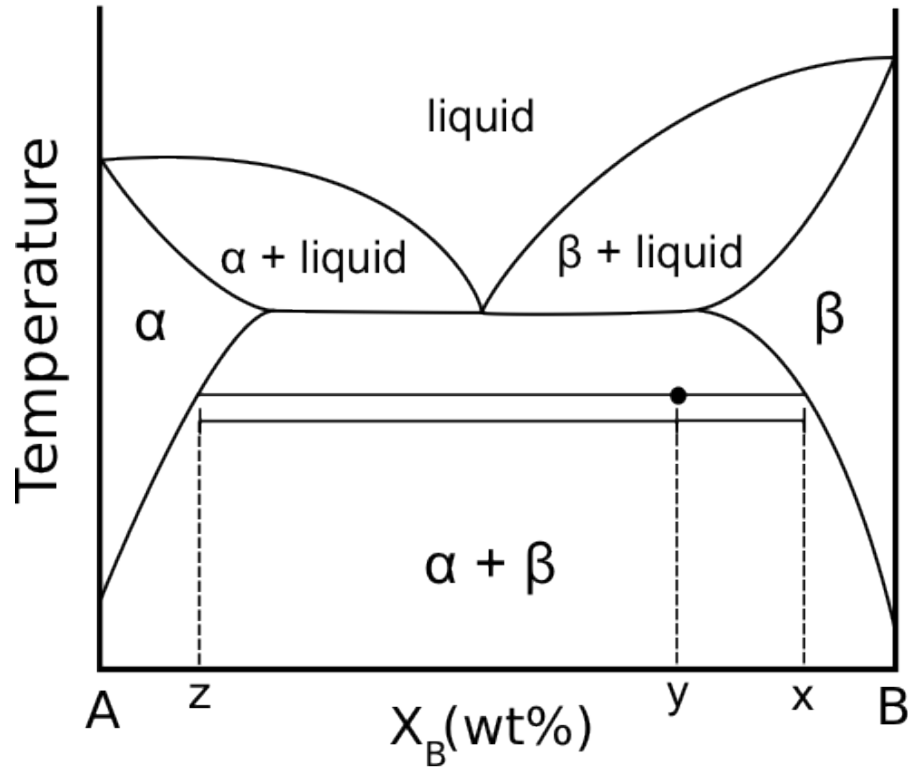
(collaboration with Prof. Chang, Dr. Buchholz)



# Rietveld Analysis

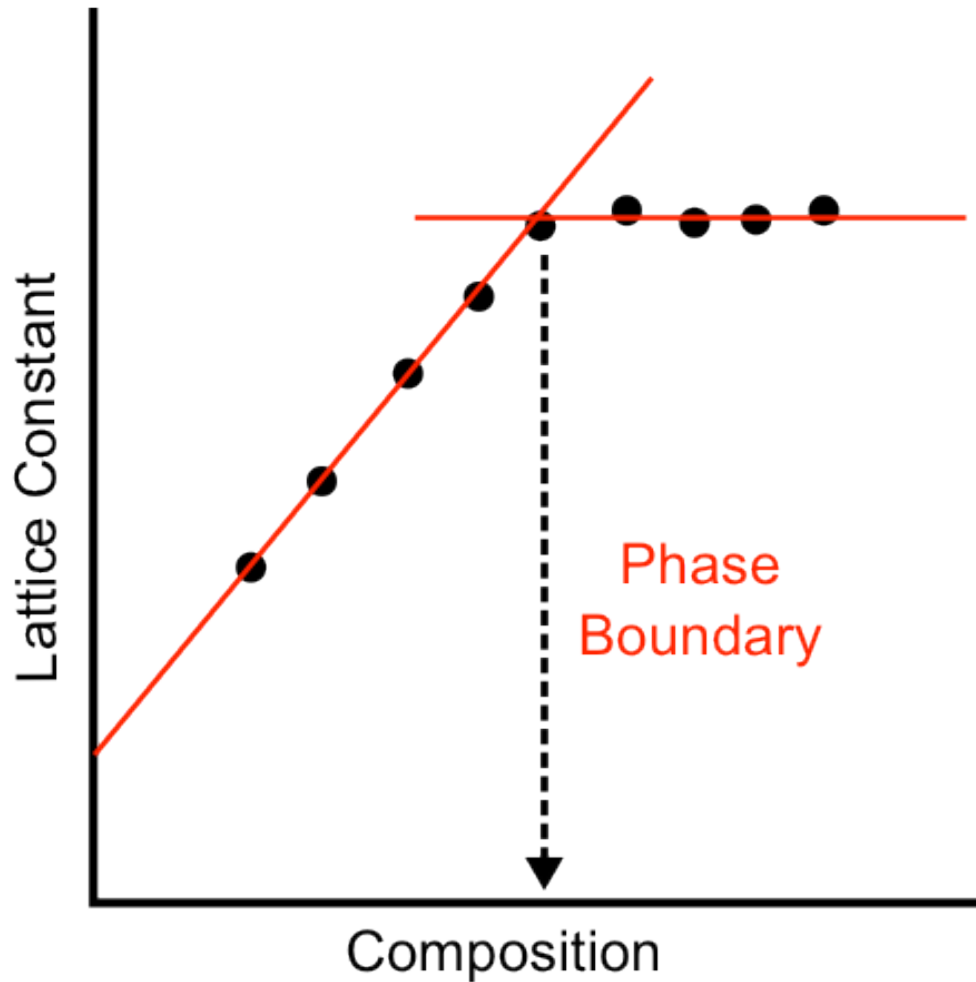


# Determining Phase Boundaries



Lever Rule:  $f_{\beta} = (y-z)/(x-z)$  Disappearing Phase Method

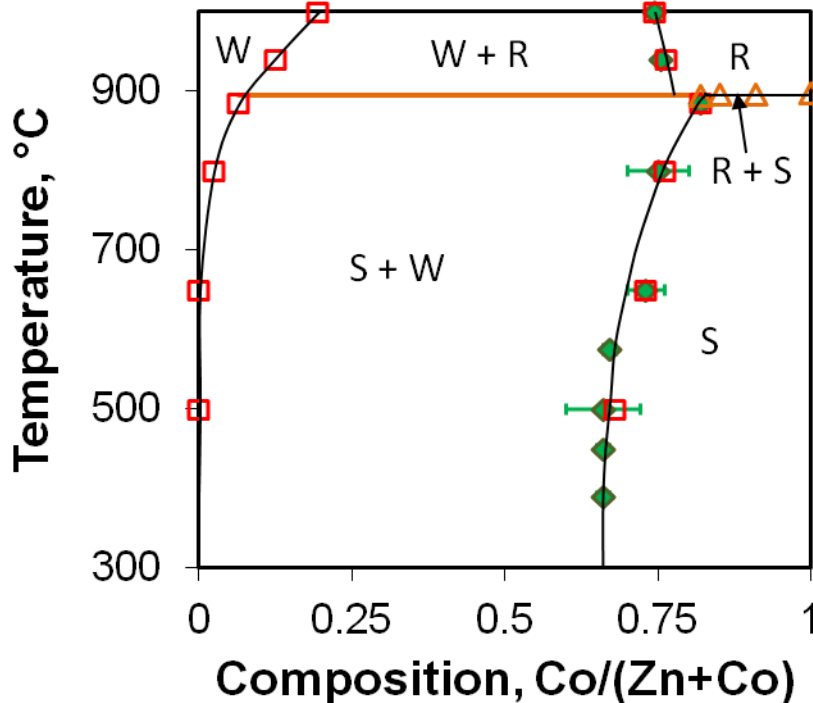
# Phase Boundaries: Vegard's Law



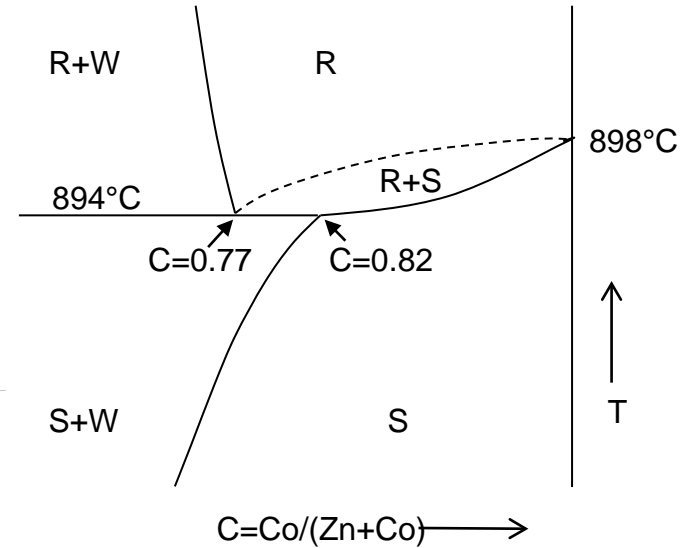
- Lattice constant changes linearly with composition until the solubility limit is reached.
- Can use Rietveld refinement with internal silicon standard to accurately measure the lattice constant.

# The Zinc Oxide – Cobalt Oxide System

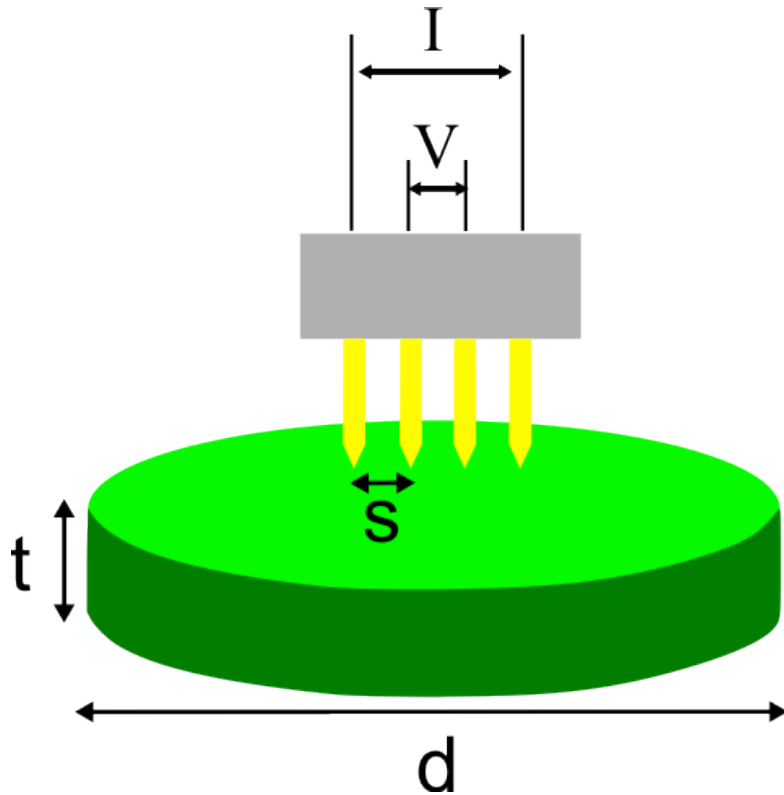
**T-X Phase Diagram  
in Air**



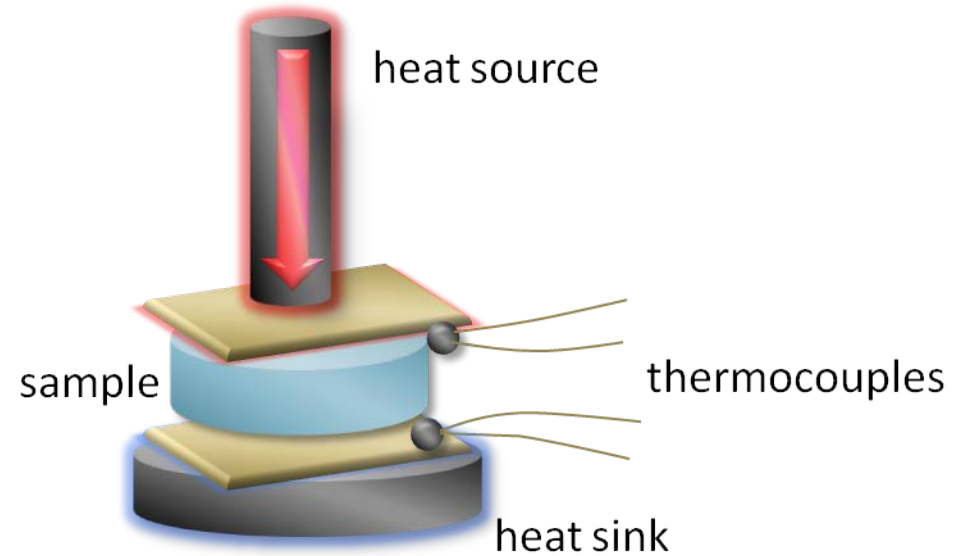
- ◆ Lever Rule
- Disappearing Phase
- △ Electrical Measurements
- Electrical Measurements



# 4-Point Conductivity and Thermopower



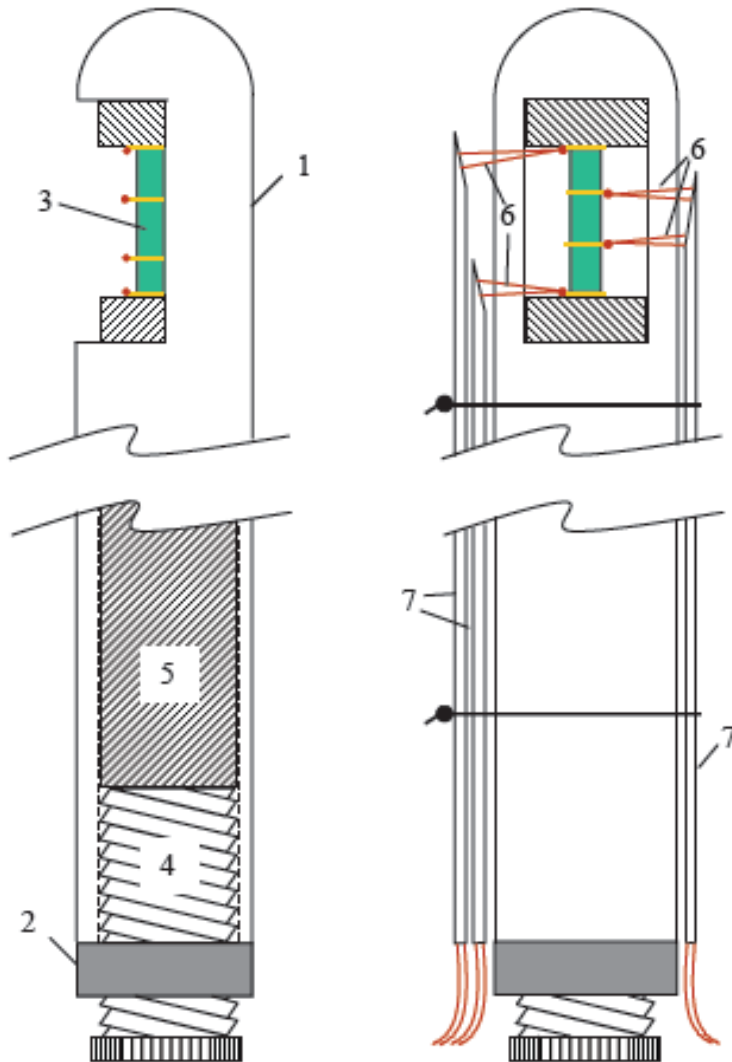
$$\rho = \frac{V}{I} \cdot t \cdot C \left( \frac{d}{s} \right) \cdot F \left( \frac{t}{s} \right)$$



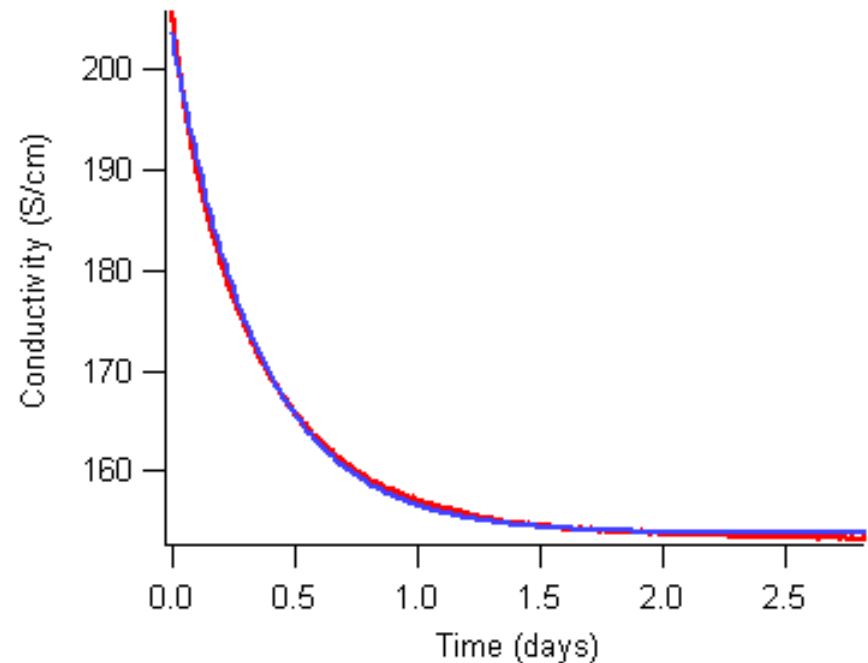
$$Q = - \lim_{\Delta T \rightarrow 0} \frac{\Delta V}{\Delta T}$$

# In situ bulk electrical measurements

Controlled atmosphere electrical measurements performed for a sample of c-ZITO ( $\text{In}_{1.2}\text{Sn}_{0.40}\text{Zn}_{0.40}\text{O}_3$ )

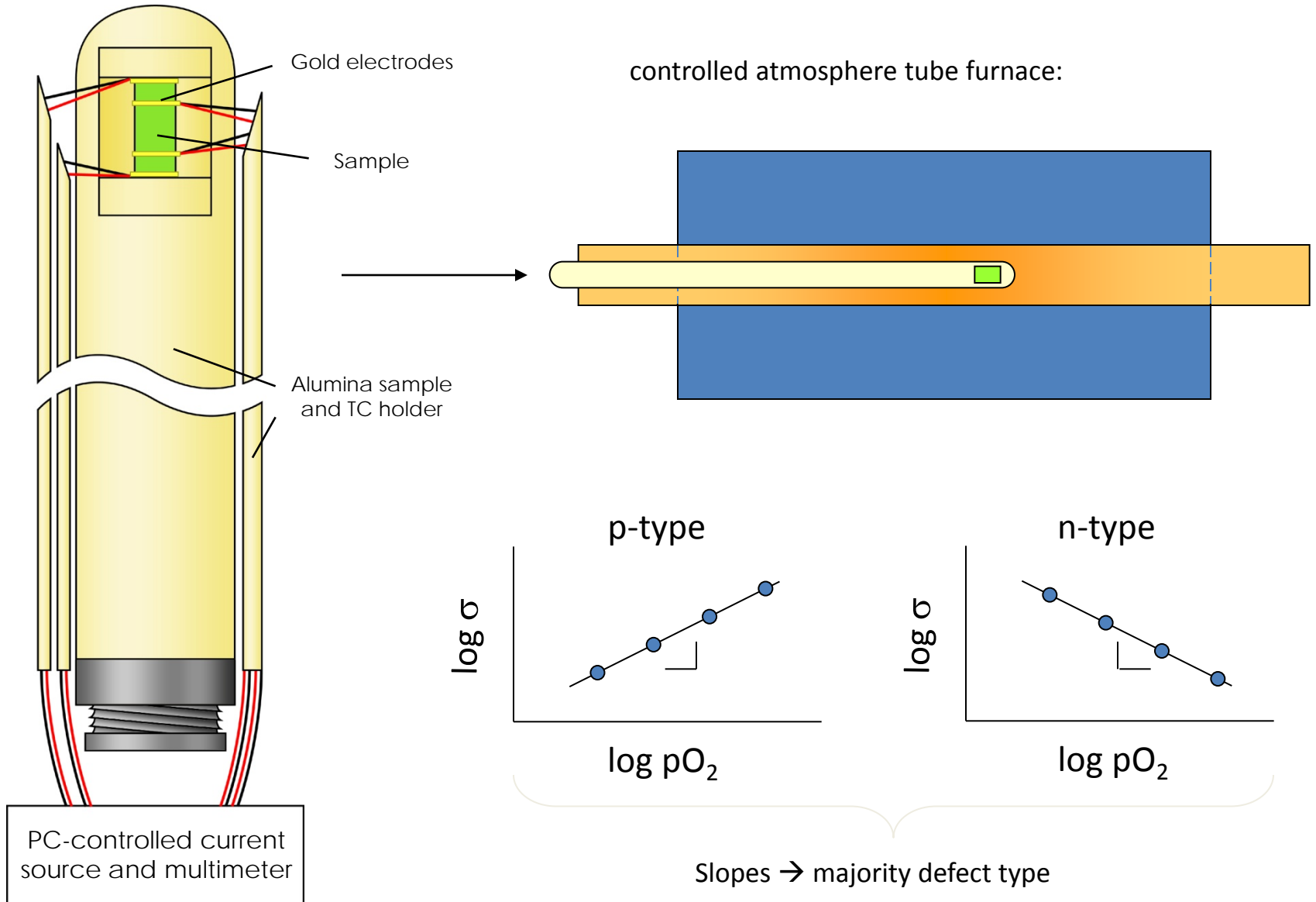


Conductivity vs. time for change of  $p\text{O}_2$  (from 1000ppm to 1% $\text{O}_2$ ) at 750°C





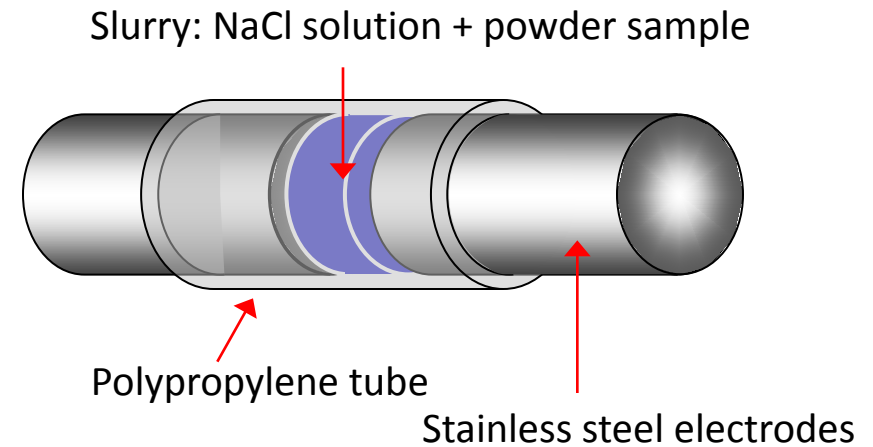
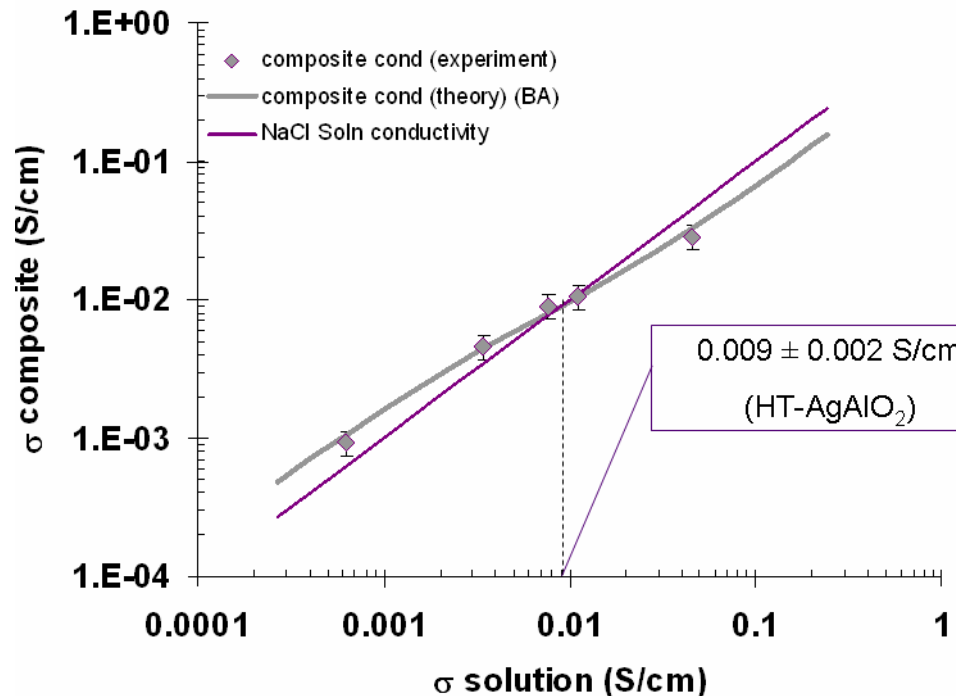
# Brouwer Analysis for Determining Point Defect Mechanism



# Powder-Solution-Composite Method

**Motivation:** Measurement of low-temperature derived materials in powder form.

**Technique:** Based on impedance spectroscopy of composite materials



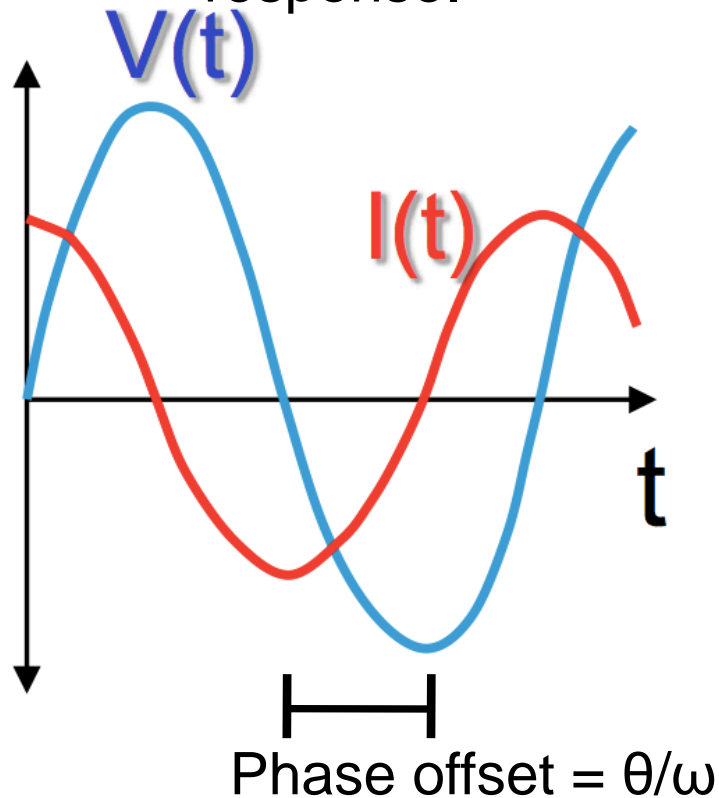
Comparison of slurry composite conductivity to matrix (plain NaCl solution) conductivity:

Cross over point corresponds to bulk value for powder in question.

Use effective medium theory to fit the data.

# AC Impedance Spectroscopy (AC-IS)

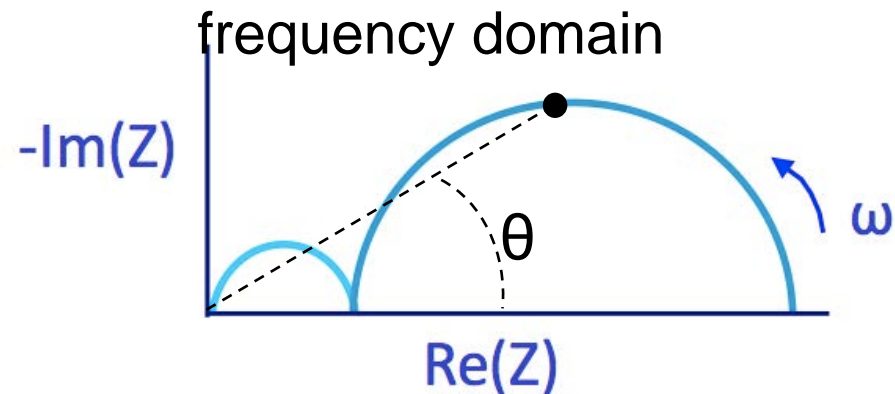
Apply oscillating voltage,  
measure current  
response.



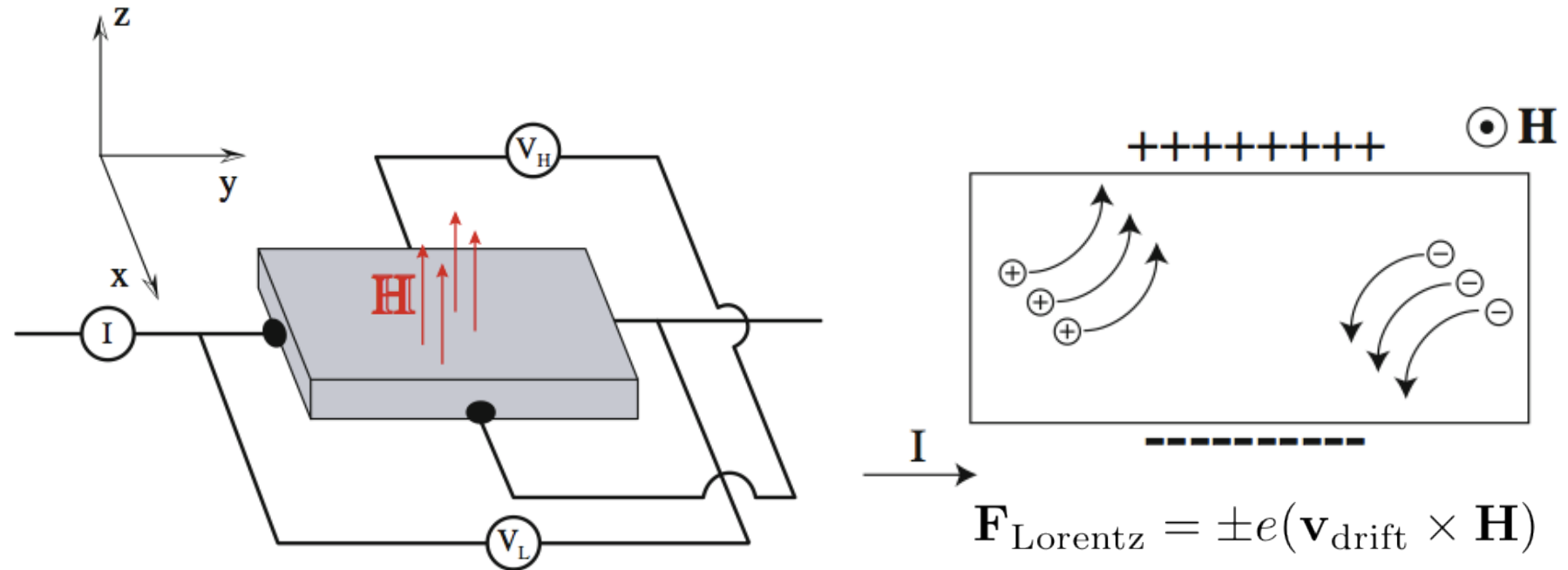
Ratio is the complex  
impedance, which depends on  
frequency.

$$Z(\omega) = V(t) / I(t)$$

Nyquist plot can illustrate  
different processes in  
frequency domain



# Hall Effect



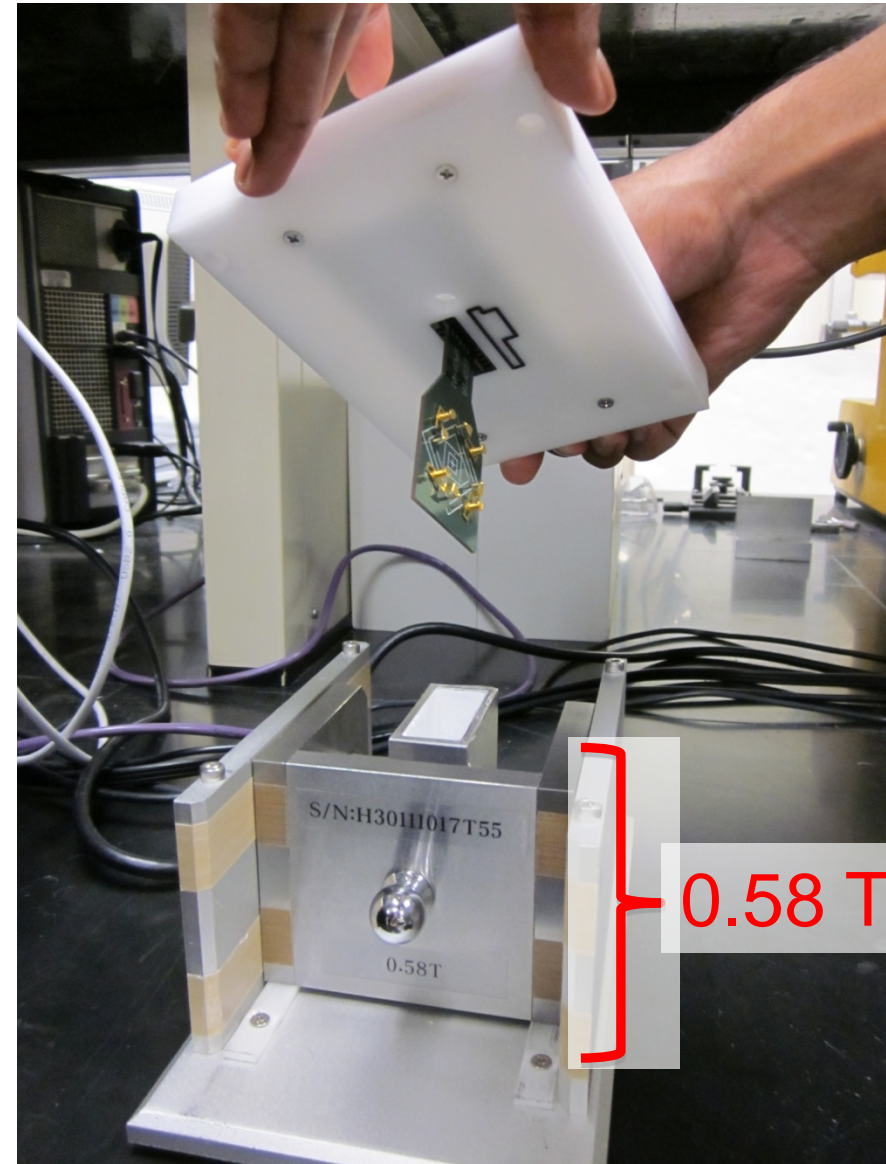
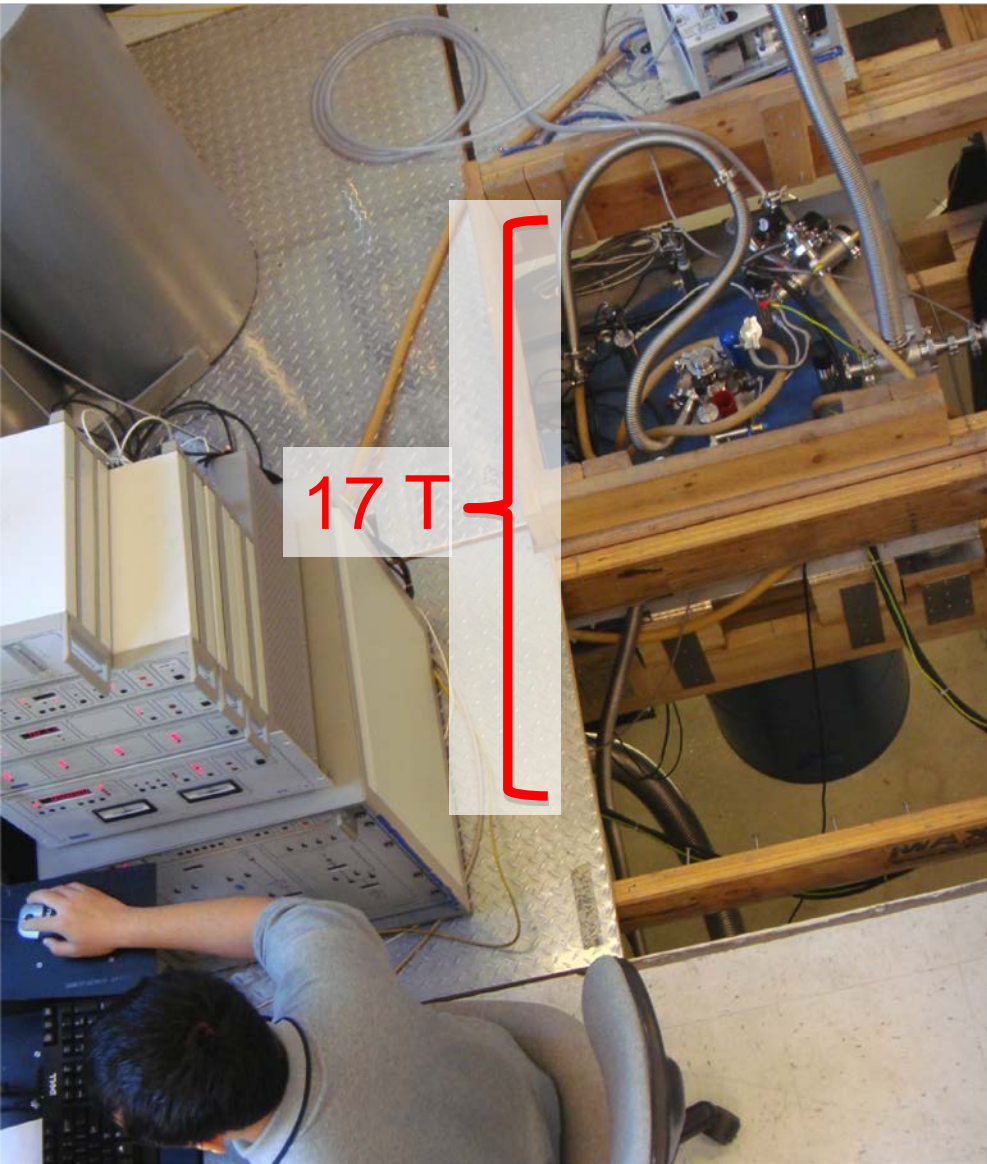
$R_H = \text{Hall coefficient}$

$$V_H = \left( \frac{1}{pe} \right) \frac{1}{d} I H_z$$

Hall Mobility:

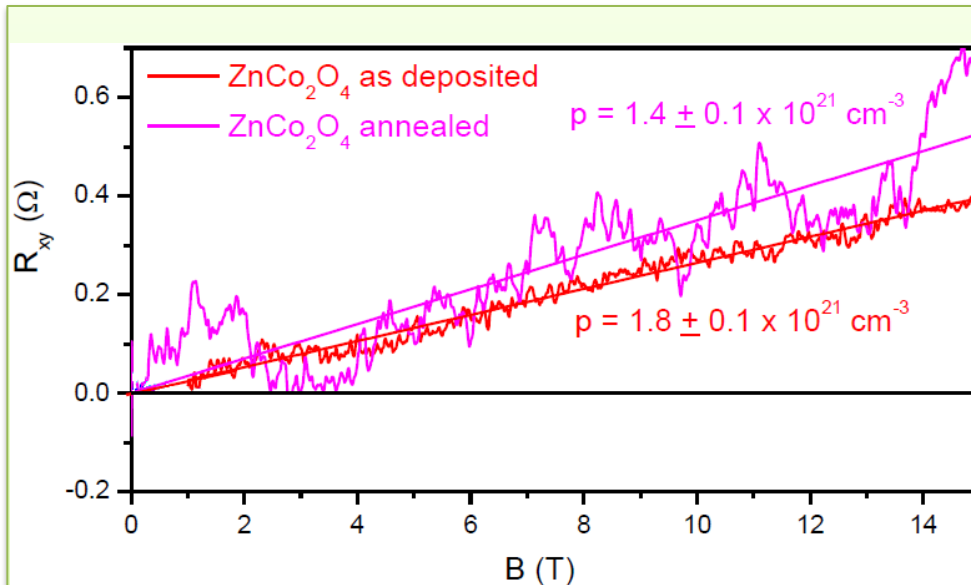
$$\mu_H = \frac{\sigma}{pe} = \sigma R_H$$

# Hall Effect: 17 T and 0.58 T

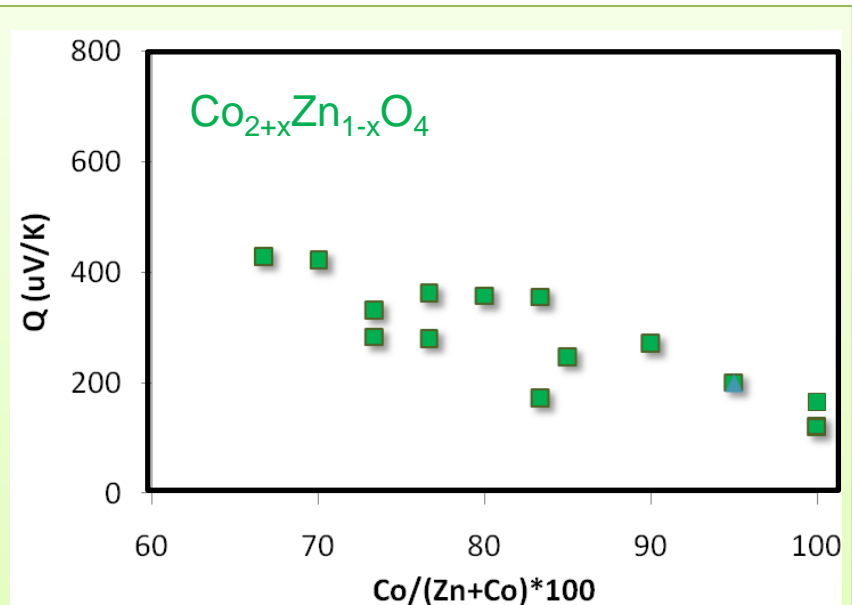


# Experiment: Confirms Robust P-type Character

Both Hall resistance and Seebeck coefficient are positive

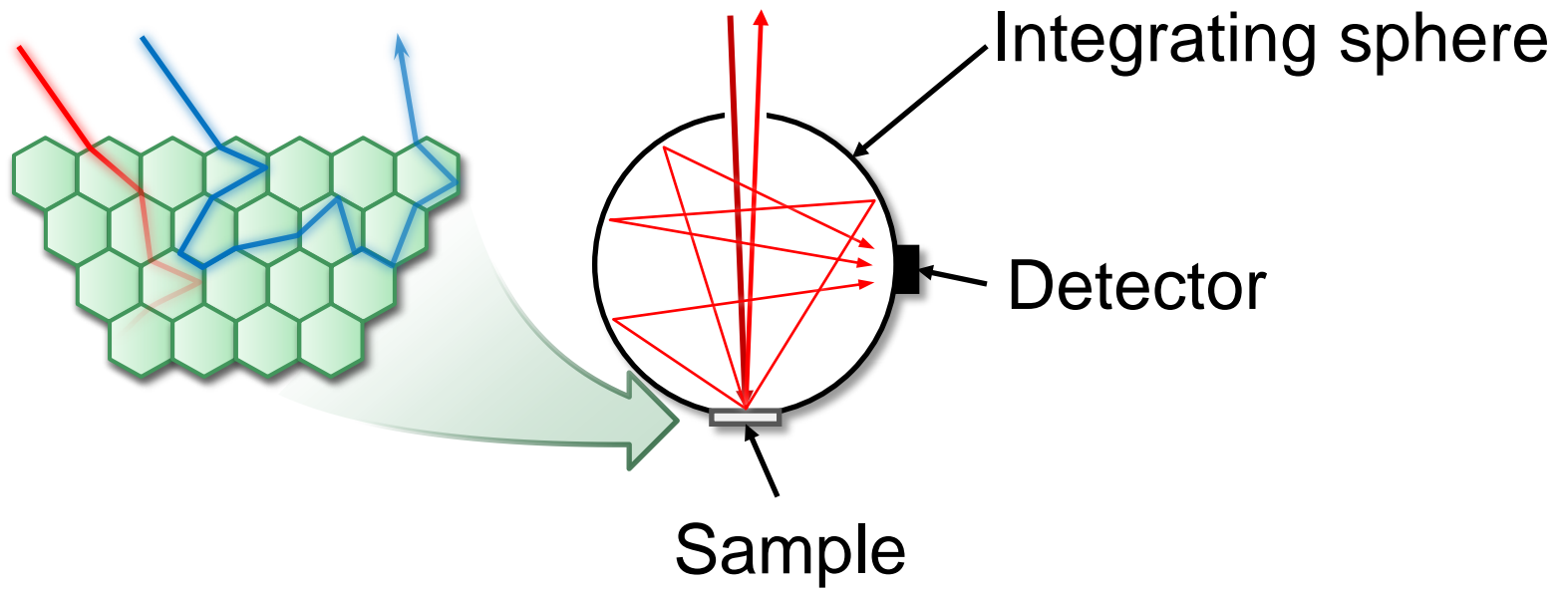


$$R_{xy} = + \frac{B}{ped}$$



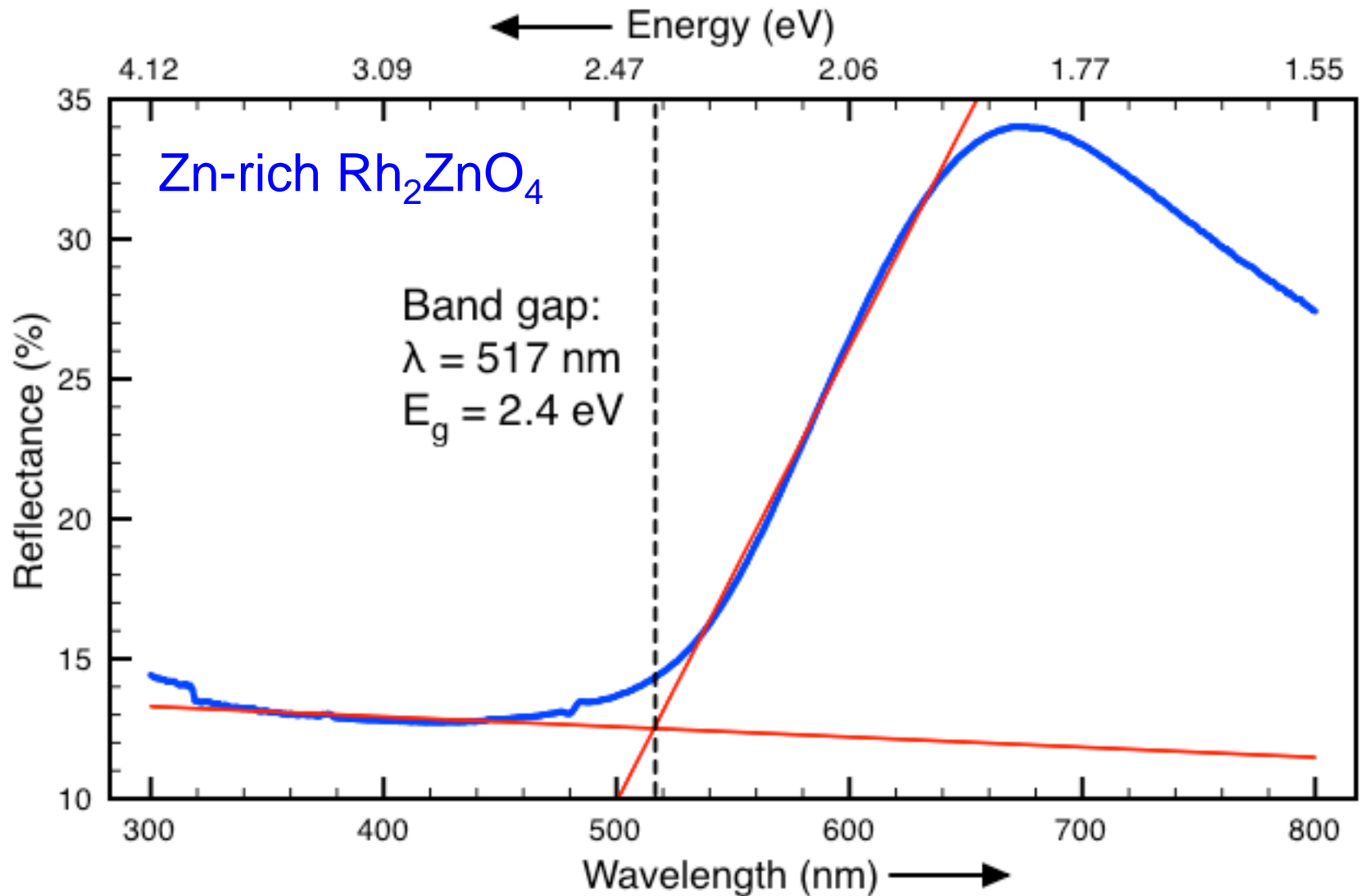
$$Q = + \frac{k}{e} \left[ \text{Ln} \left( \frac{N_v}{p} \right) + A \right]$$

# Diffuse Reflectance Spectroscopy





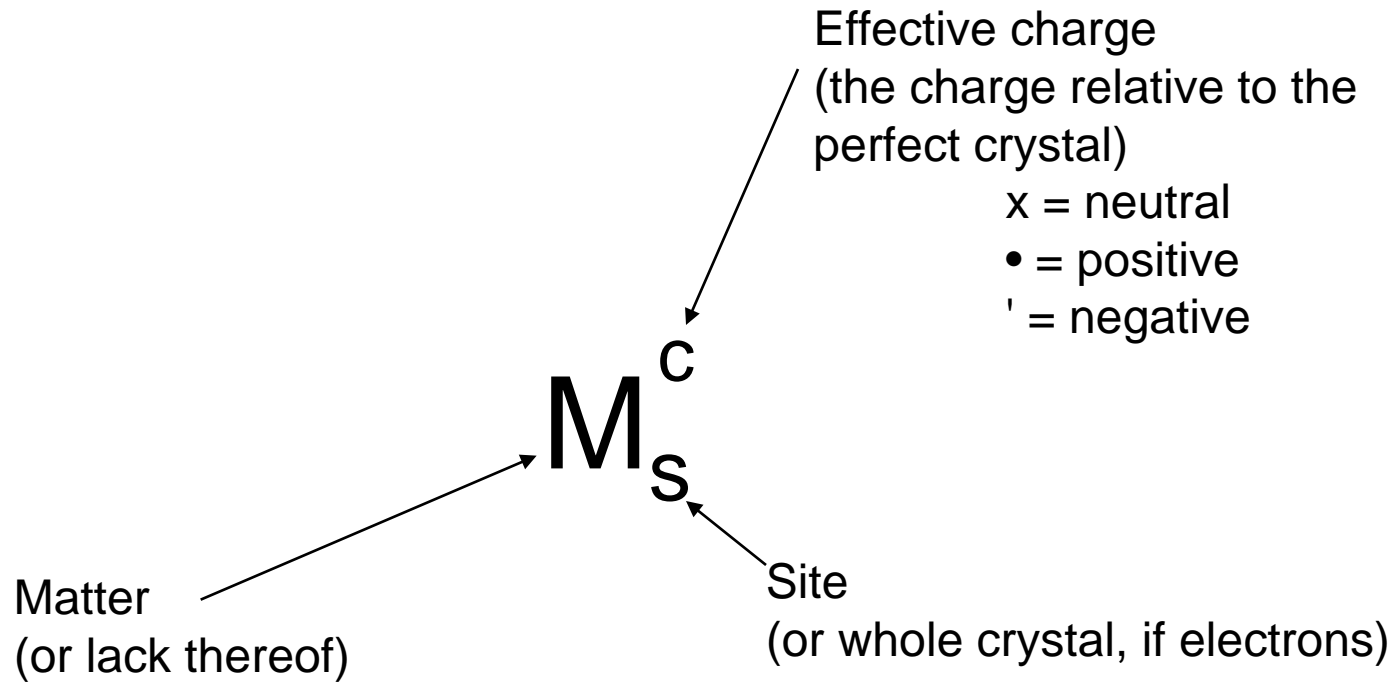
# Diffuse Reflectance Spectroscopy



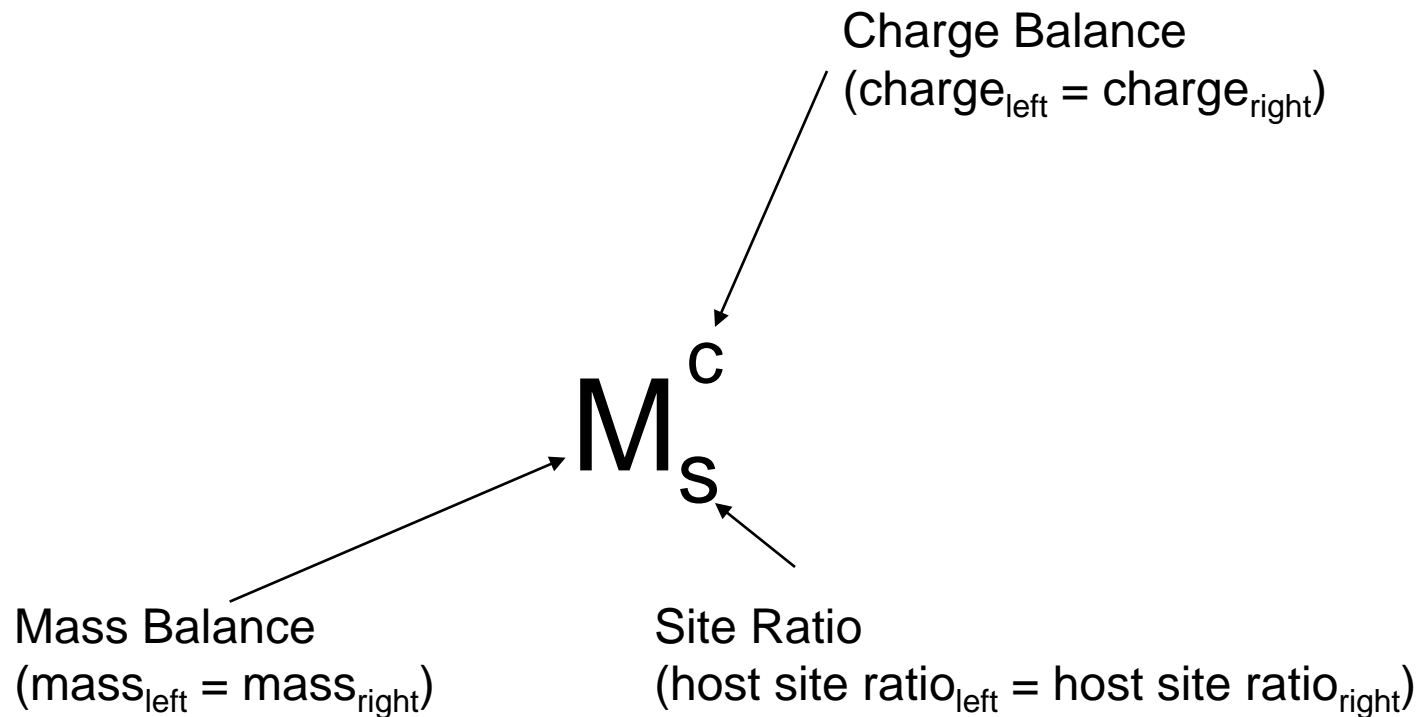


# Defect Chemistry of n-type TCOs

# Kröger-Vink Notation:

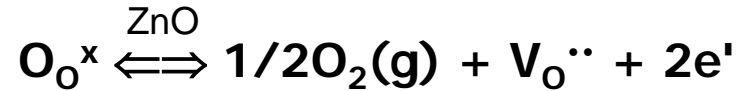


# Writing Balanced Defect Reactions:



Note: sites can be created or destroyed, but only in the stoichiometric ratio of the host!

# An Example Point Defect Reaction

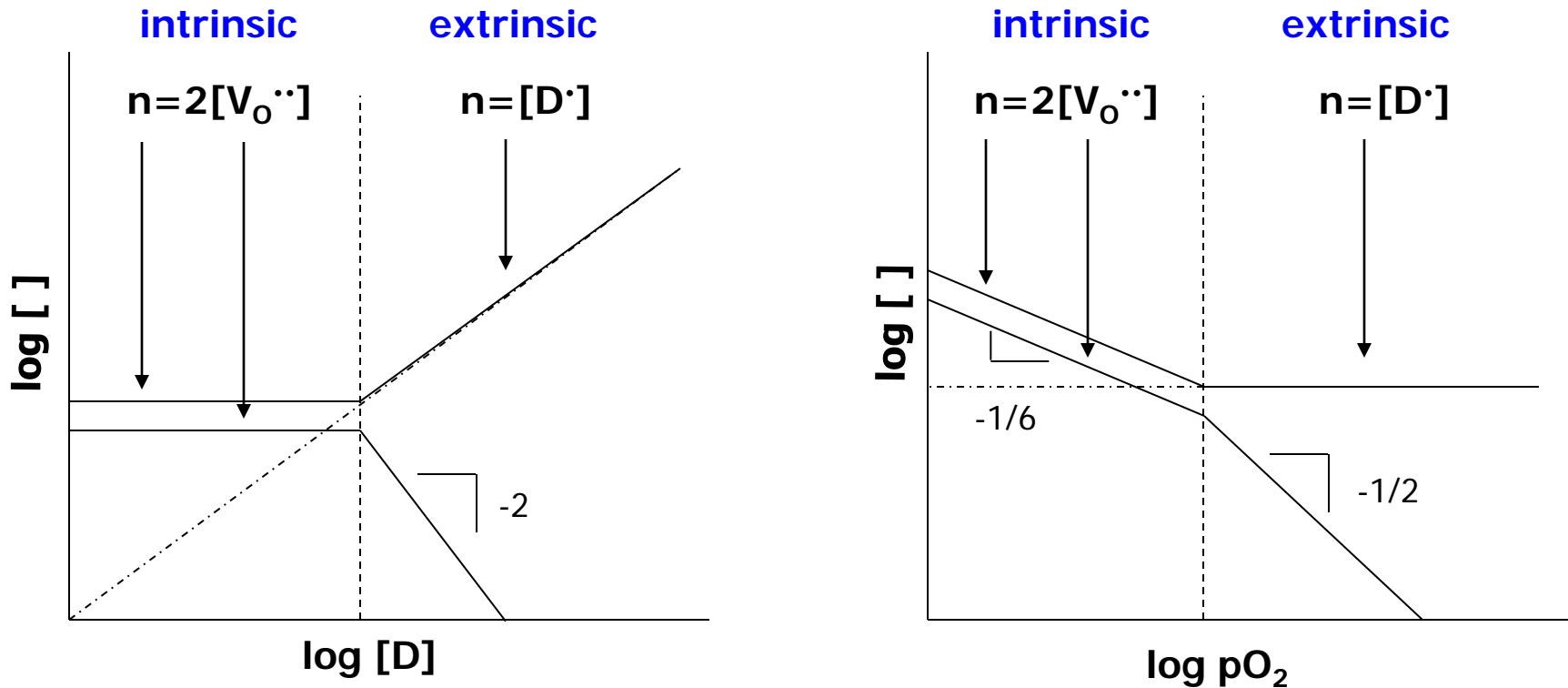


$$K_{\text{red}} p\text{O}_2^{-1/2} = [\text{V}_\text{O}^{\bullet\bullet}] n^2$$

$$n = 2 [\text{V}_\text{O}^{\bullet\bullet}] \text{ or } [\text{V}_\text{O}^{\bullet\bullet}] = n/2$$

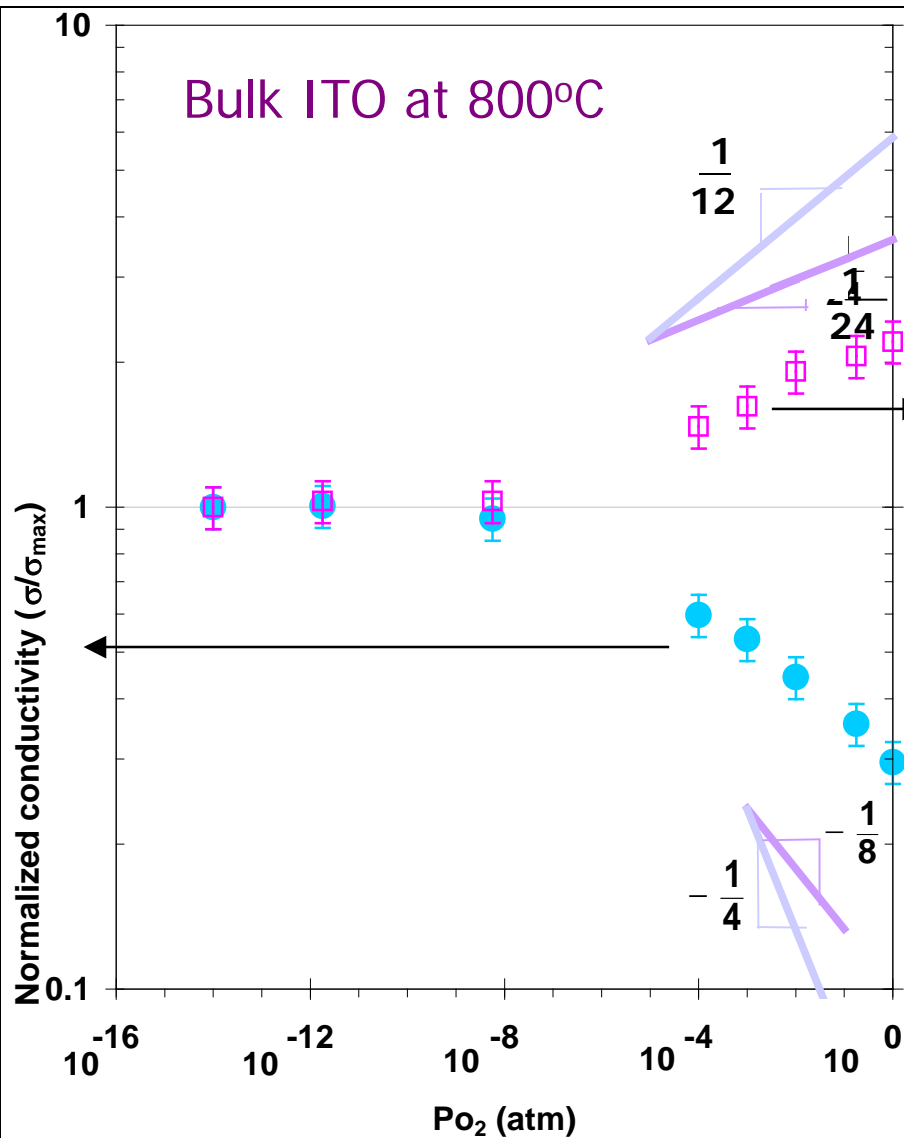
$$n = (2K_{\text{red}})^{1/3} p\text{O}_2^{-1/6}$$

# Point defects in n-type TCOs



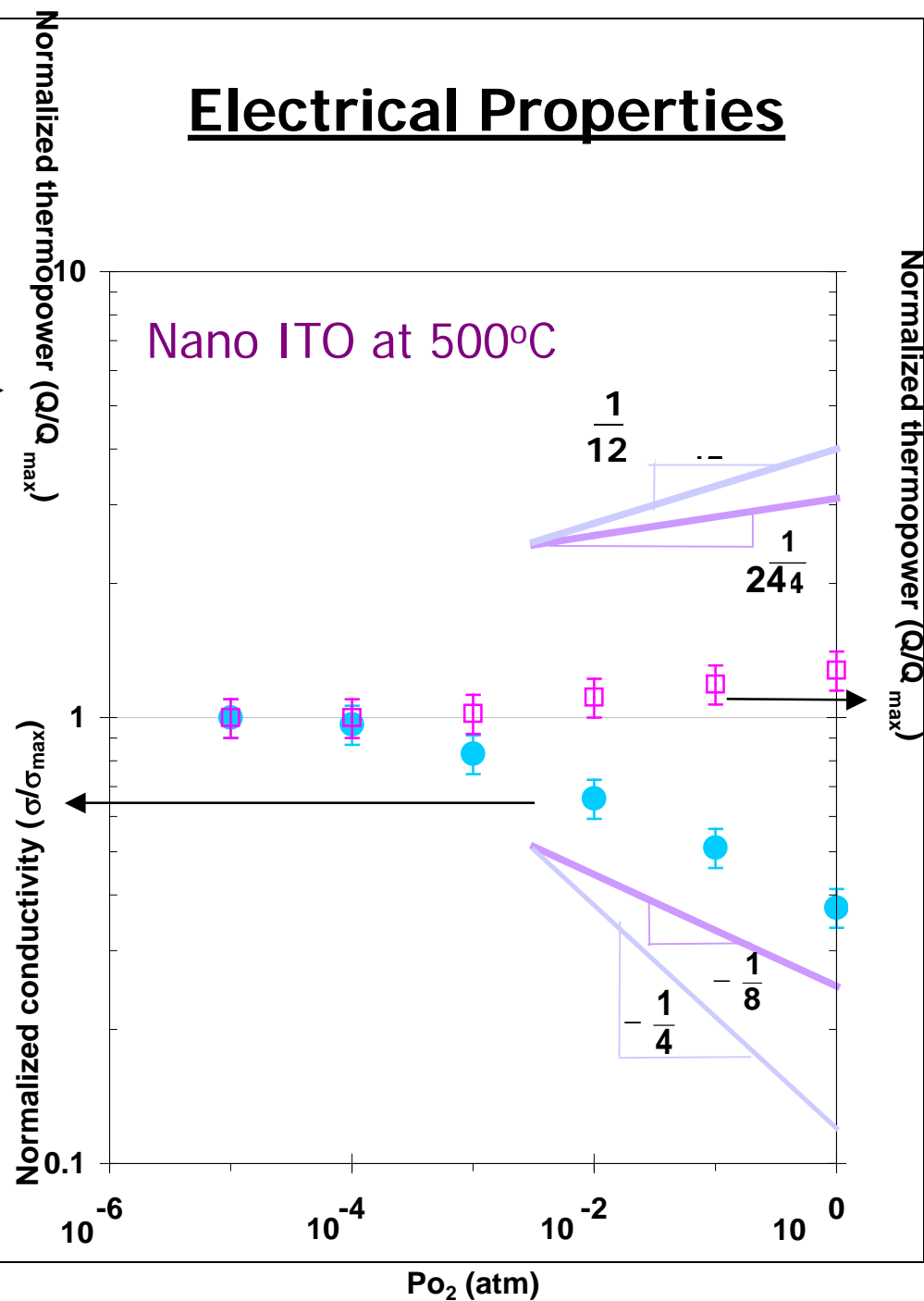
***Is this the whole story?***

# Electrical Properties



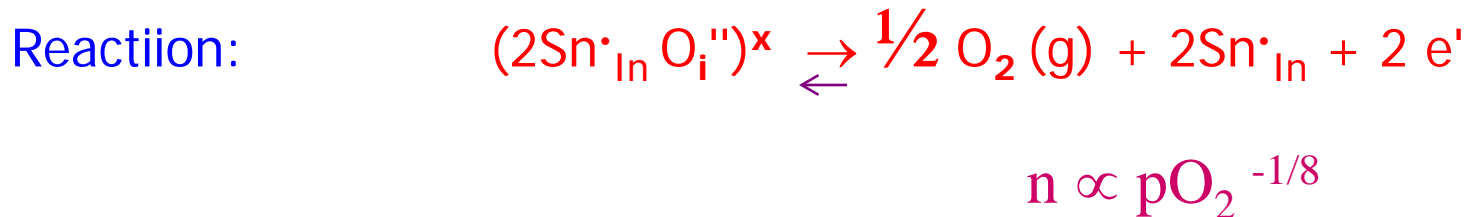
$$Q \propto m^*/n^{2/3}; m^* \propto n^{1/3}$$

$$Q \propto n^{-1/3}$$



# The Frank-Köstlin Cluster

Formation of point defect associates:



*Kröger-Vink notation*

$\text{Sn}_{\text{In}}^{\bullet}$  represents a tin (on an indium site) with 1+ charge

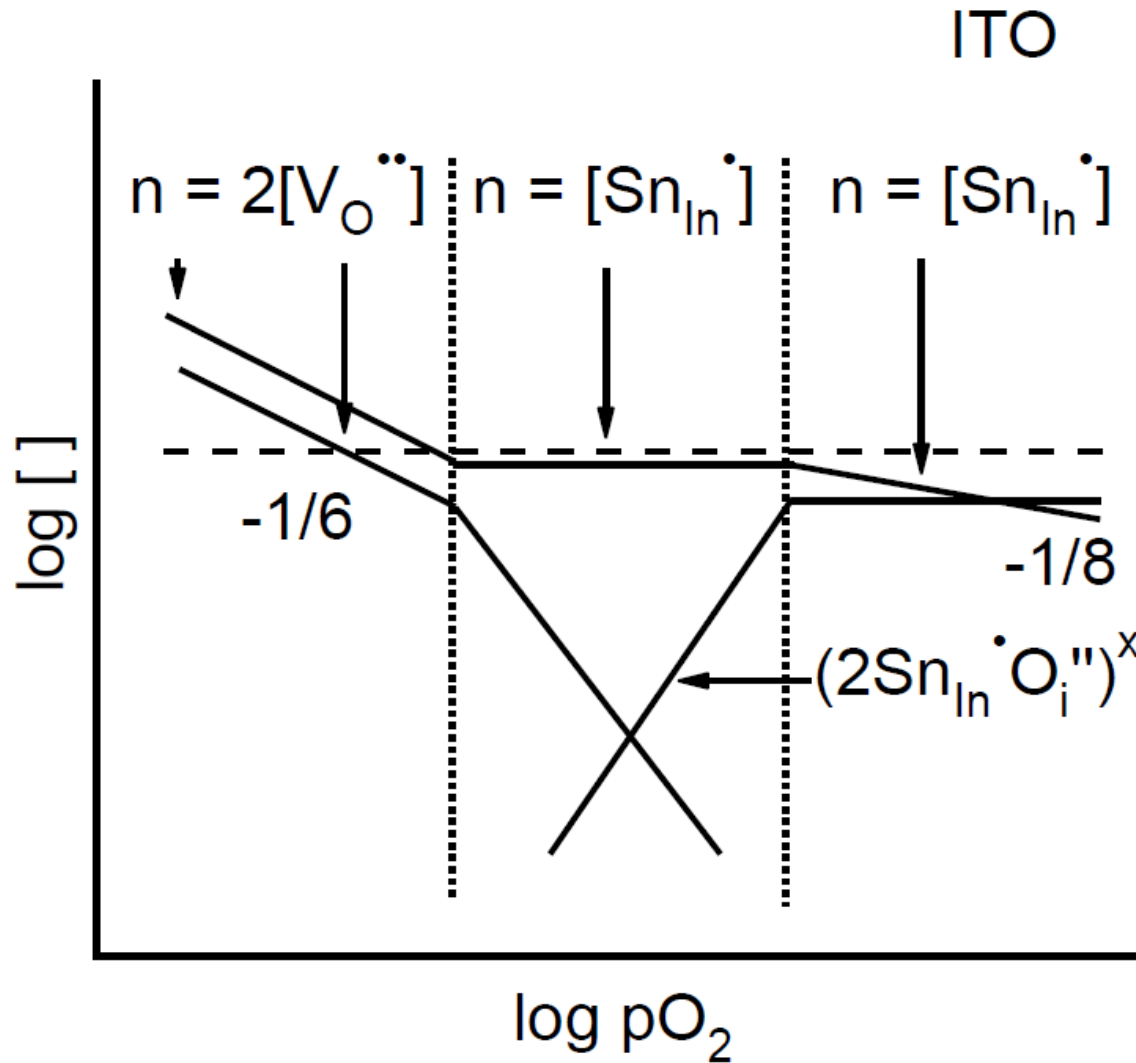
$\text{O}_{\text{i}}^{2-}$  represents an oxygen interstitial with 2- charge

$\text{O}_{\text{O}}$  represents an oxygen (on an oxygen site)

$( )^{\times}$  represents a neutral defect

<sup>1</sup> G Frank and H Köstlin, *Appl Phys A*, **27** (1982), 197

# ITO Defect Chemistry

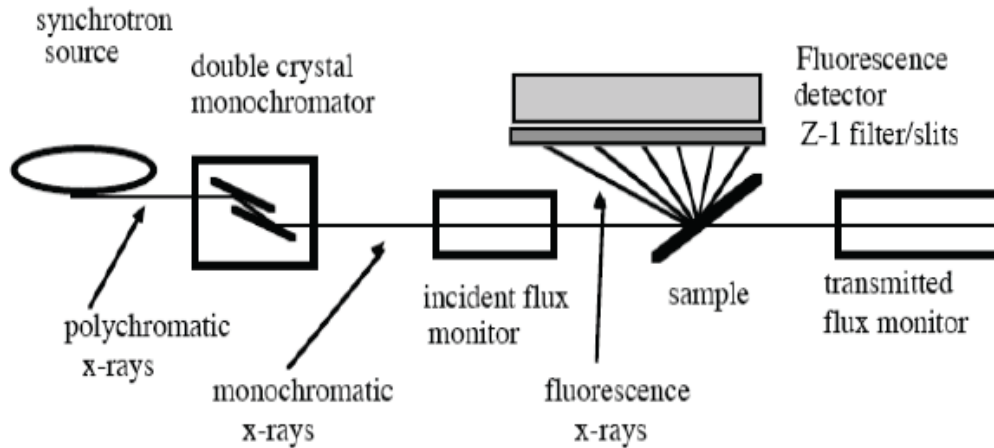




# Evidence for Defect Associates in ITO

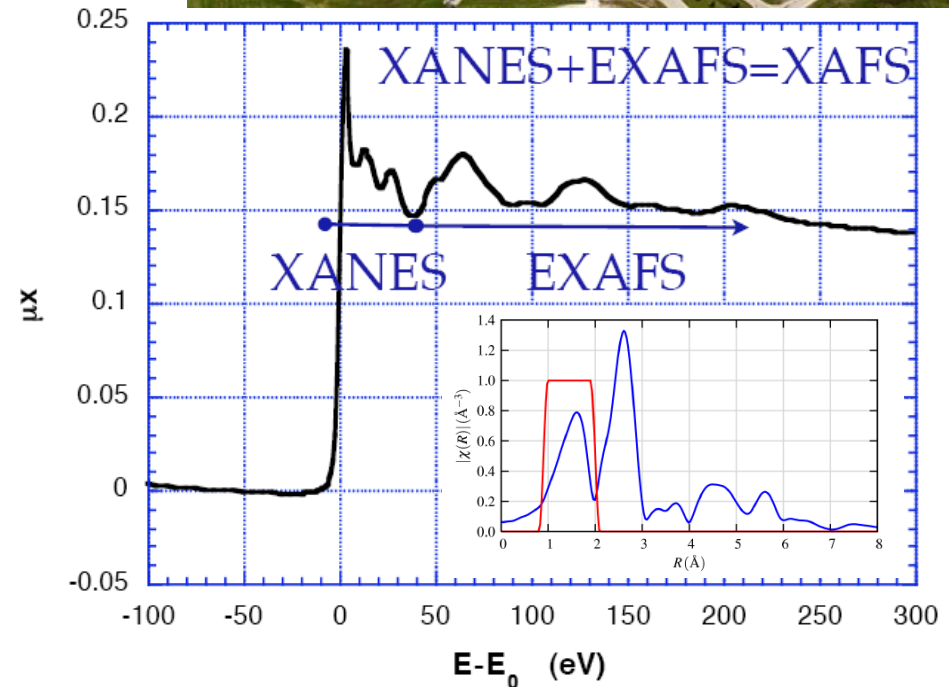
- Rietveld analysis of combined neutron and X-ray diffraction patterns (bulk and nano ITO)
  - Sn-to-oxygen interstitial ratio  $\sim 2:1$
- EXAFS studies of bulk and nano ITO specimens
  - Sn coordination number  $> 6$
  - First near neighbor distances of Sn similar to that in  $\text{SnO}_2$

# X-ray Absorption Fine Structure



$$I = I_0 e^{-\mu t} \Rightarrow \mu(x) \propto I/I_0$$

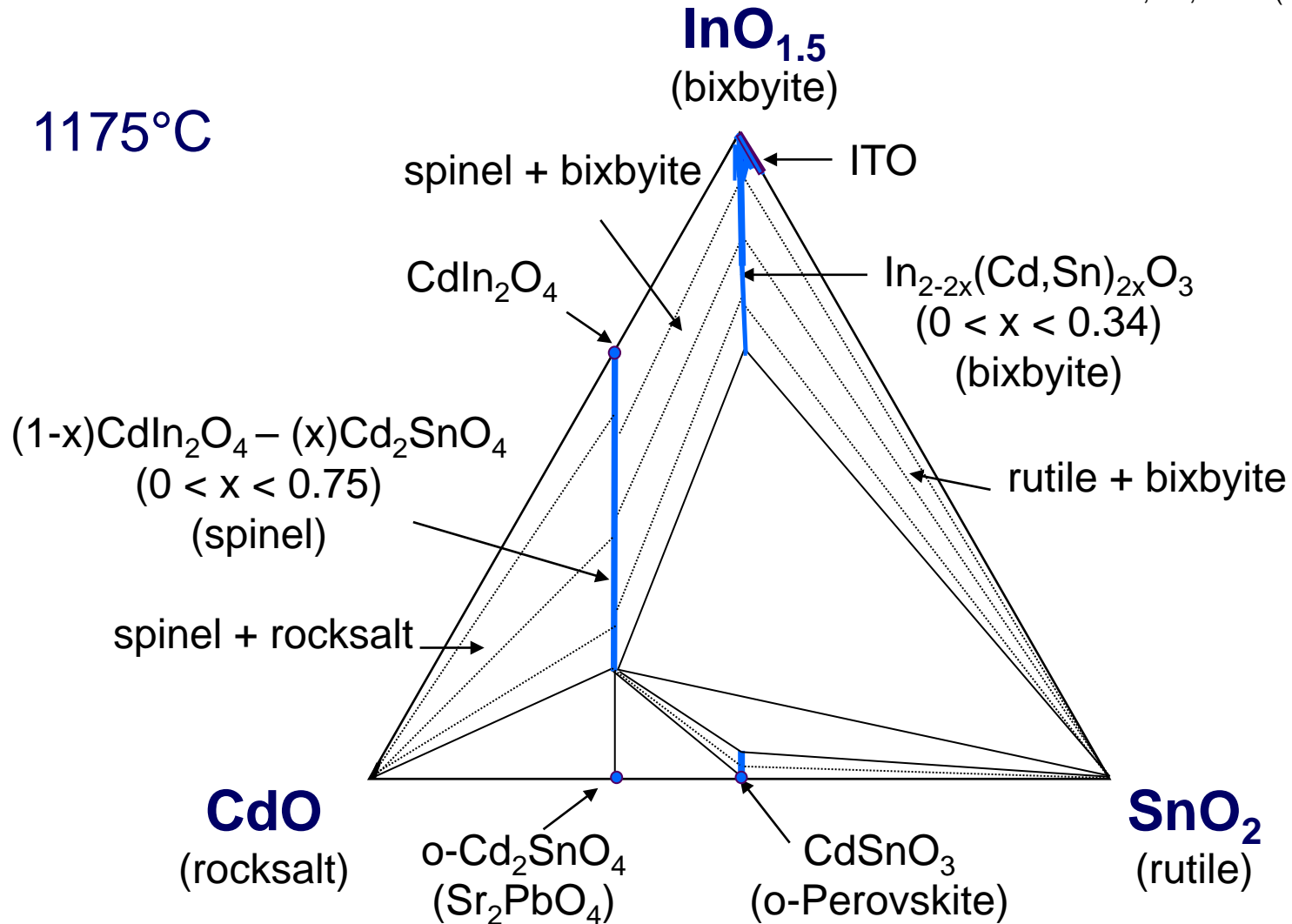
- ✓ Determines:
  - ✓ Oxidation/charge state
  - ✓ Local structure
    - ✓ Atomic distances
    - ✓ Coordination numbers
- ✓ Element specific
- ✓ Sensitive at low concentrations



# Defect Chemistry of n-type TCOs (Cont'd)

# The Cd-In-Sn System

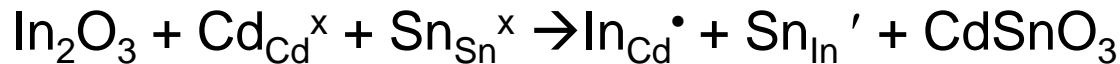
D. R. Kammler, T. O. Maosn, K. R. Poeppelmeier,  
 J. Am. Ceram. Soc., 84, 1004 (2001)



# Extended Solubility Ranges

<u>Compound</u>	<u>Structure</u>	<u>Solubility</u>
CdSnO <sub>3</sub>	o-Perovskite	4.5%
In <sub>2</sub> O <sub>3</sub>	Bixbyite	34%
CdIn <sub>2</sub> O <sub>4</sub>	Spinel	75%

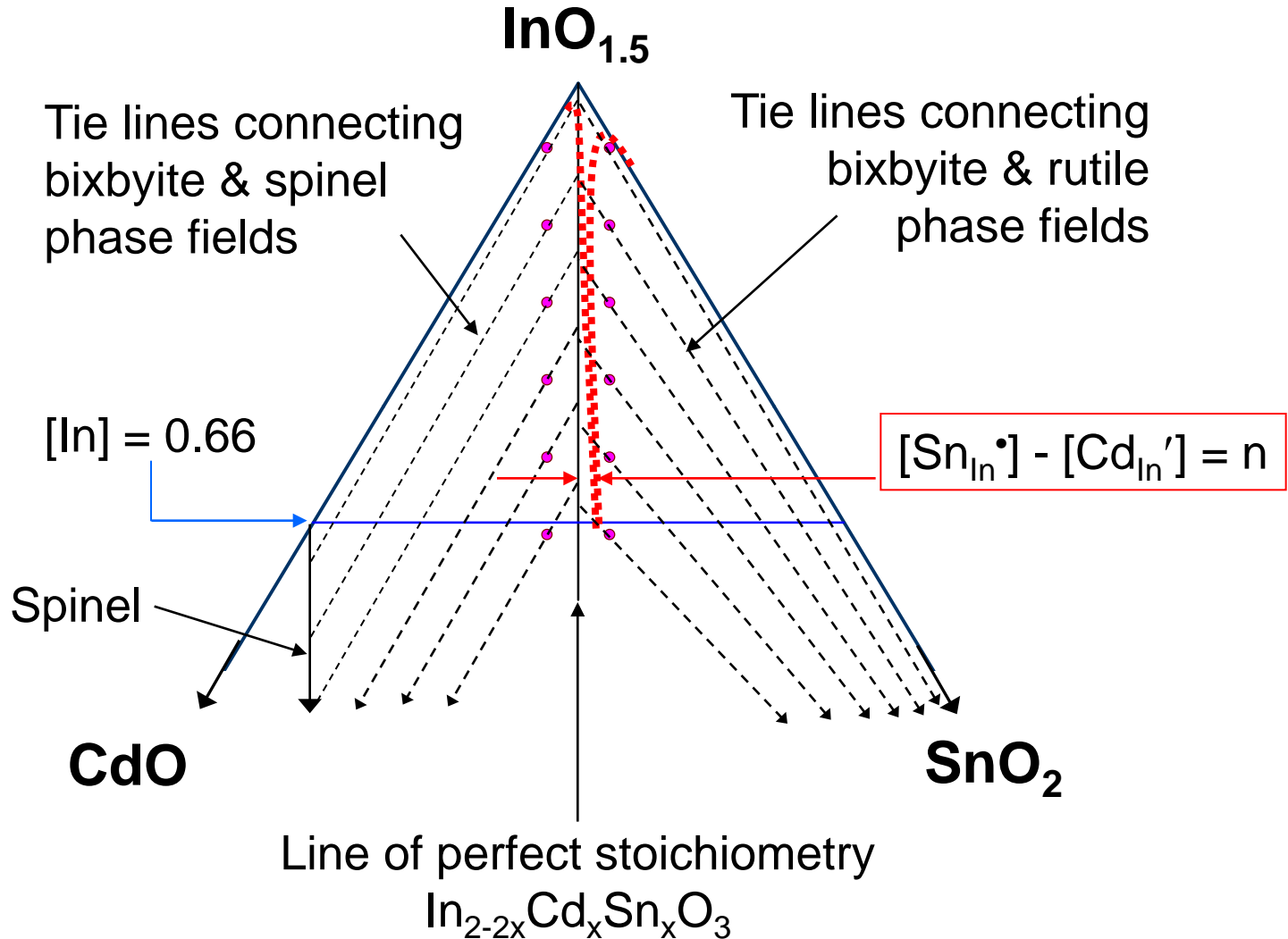
Isovalent substitutions: [D•] = [A']



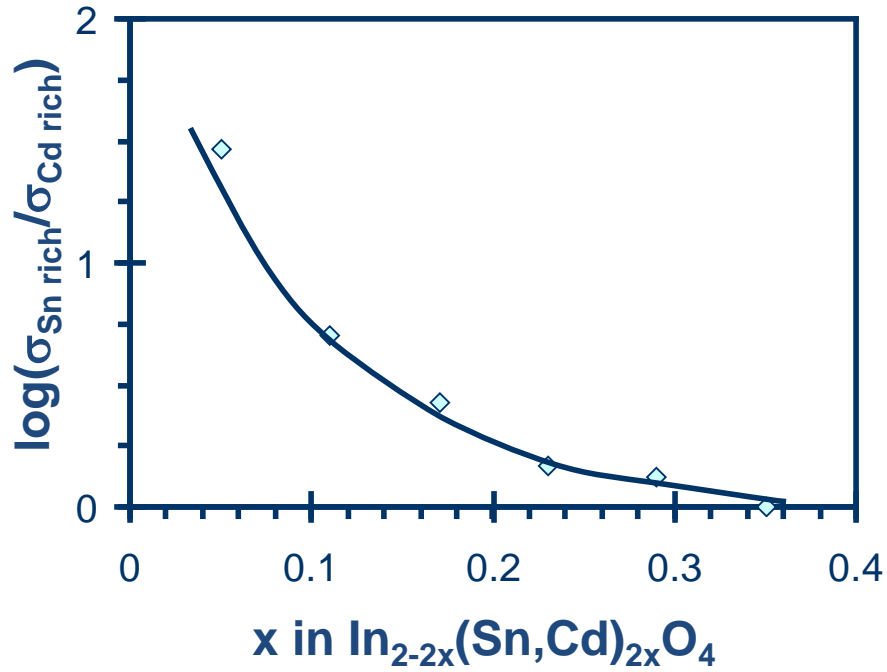
Size-matched substitutions:

$$r_{\text{In}^{3+}} = 0.80 \text{ \AA} \approx \frac{r_{\text{Cd}^{2+}} + r_{\text{Sn}^{4+}}}{2} = \frac{0.95 \text{ \AA} + 0.69 \text{ \AA}}{2} = 0.82 \text{ \AA}$$

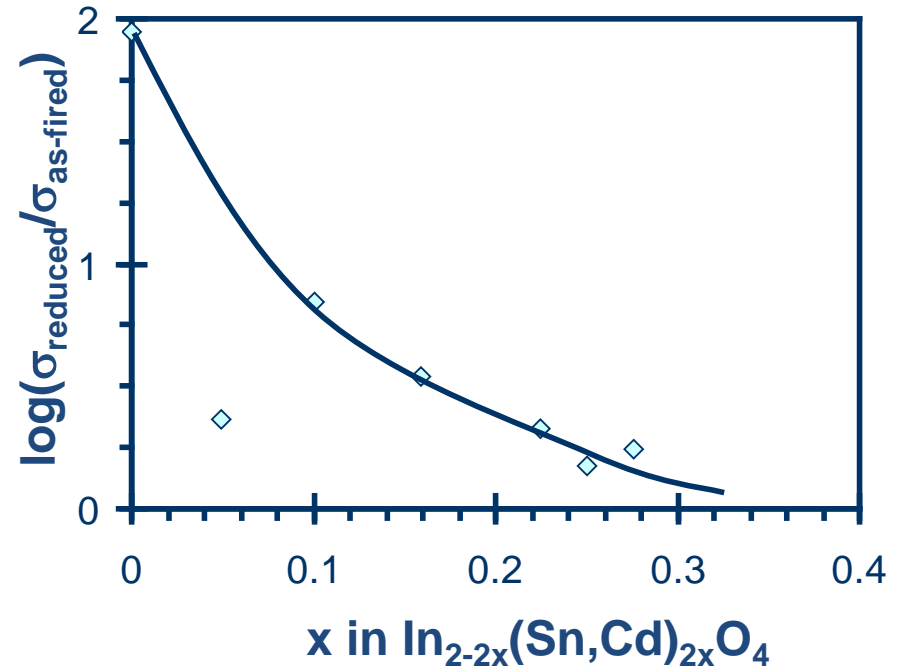
# Biphasic Studies



# Conductivity Variations

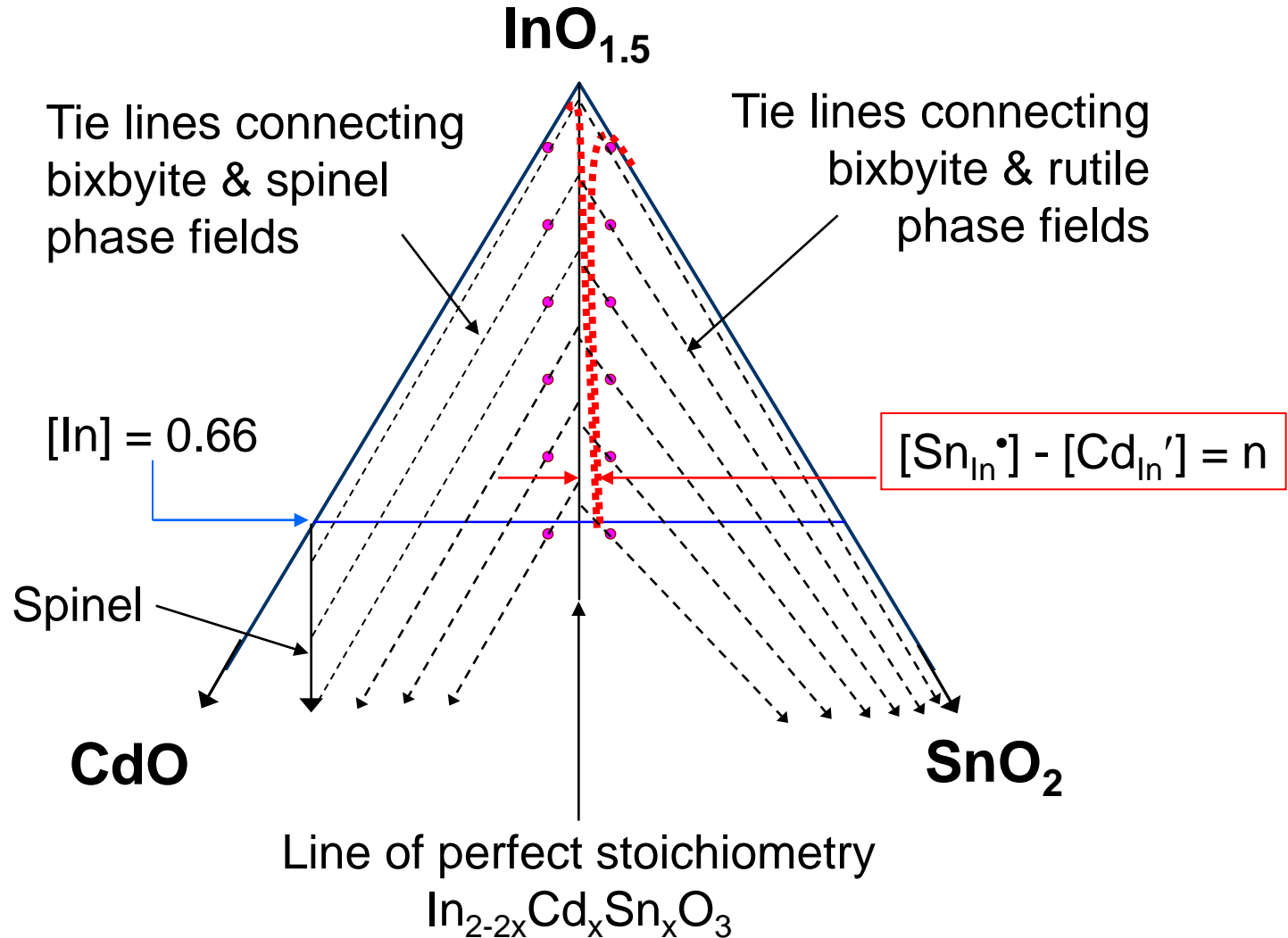


phase field width



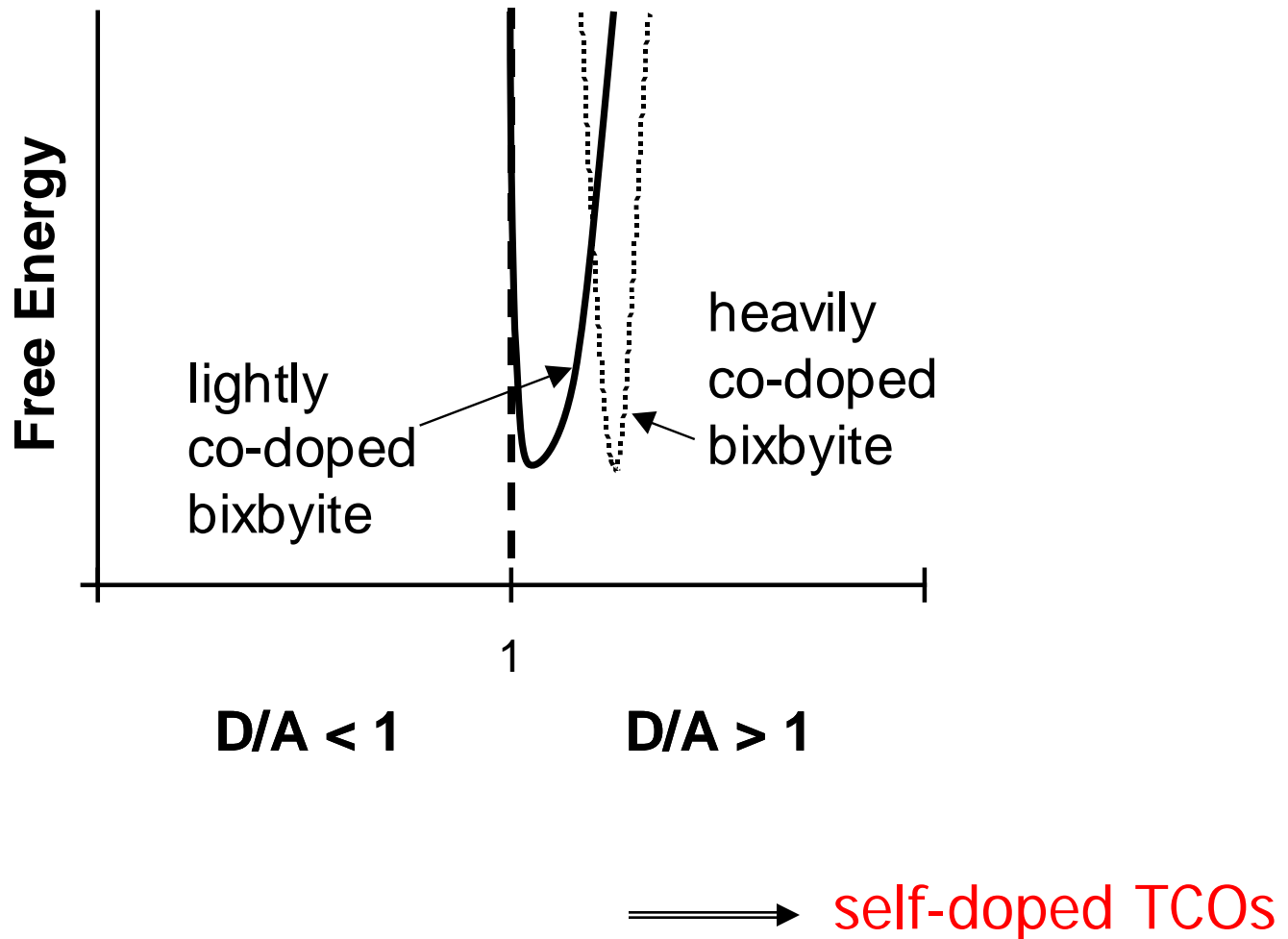
sensitivity to reduction

# Self-Doped Materials



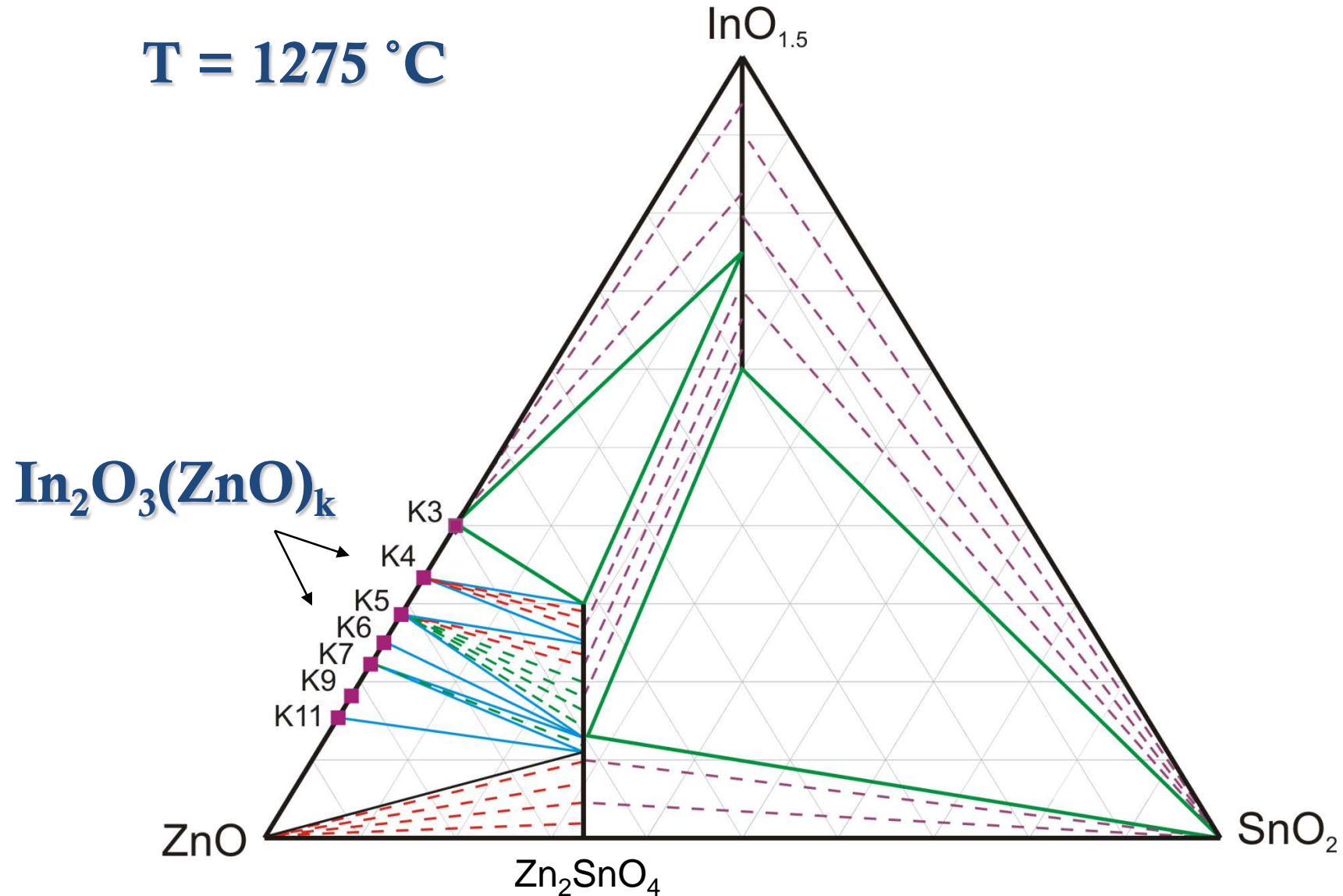


# Inherent Off-Stoichiometry



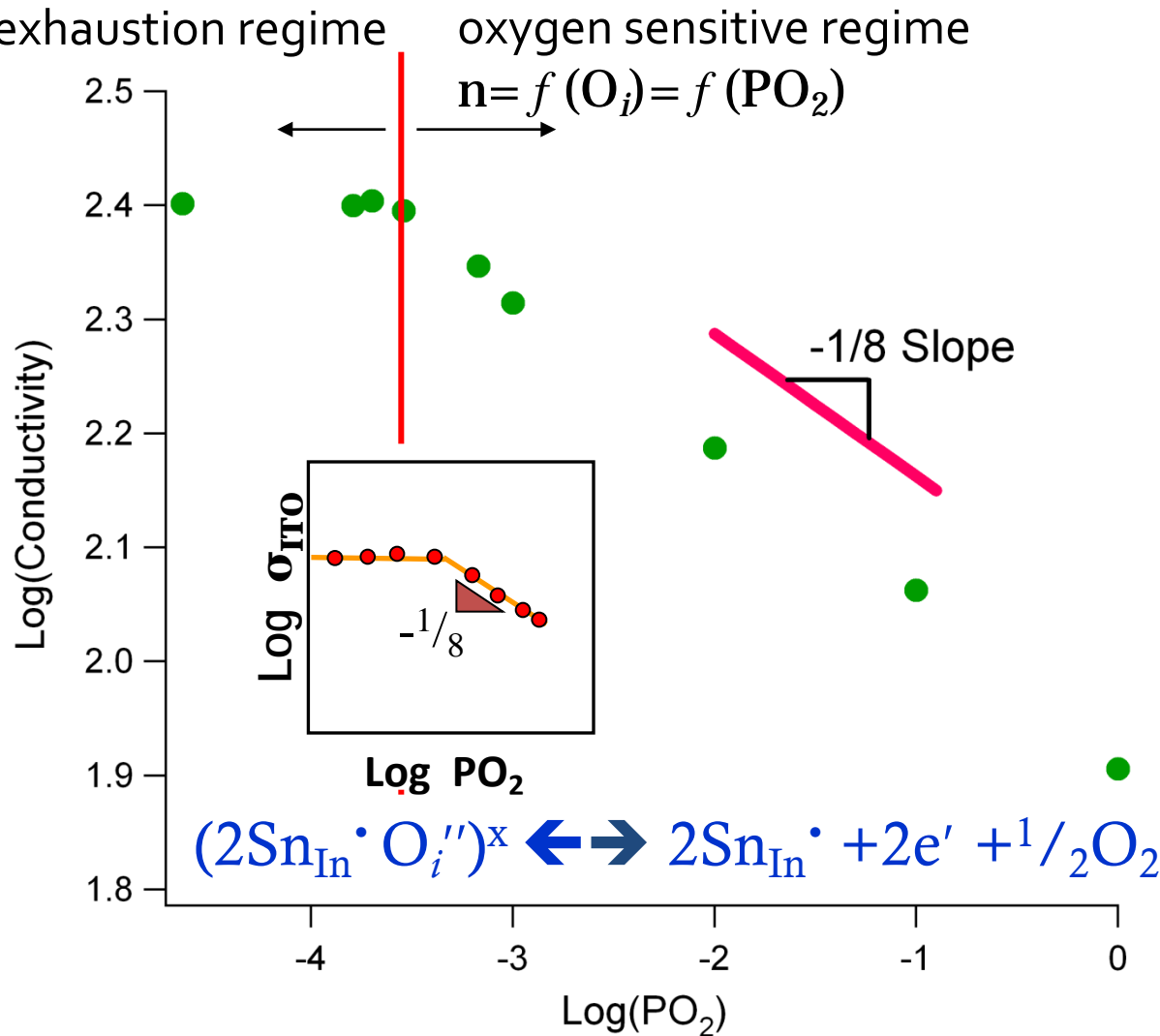
# The Zn-In-Sn-O System

$T = 1275\text{ }^{\circ}\text{C}$



# In Situ Conductivity: $\text{In}_{1.2}\text{Zn}_{0.4}\text{Sn}_{0.4}\text{O}_3$

**750 °C**



$\text{In}_{1.2}\text{Sn}_{0.40}\text{Zn}_{0.40}\text{O}_3$   
 or ZITO40 co-doped  $\text{In}_2\text{O}_3$

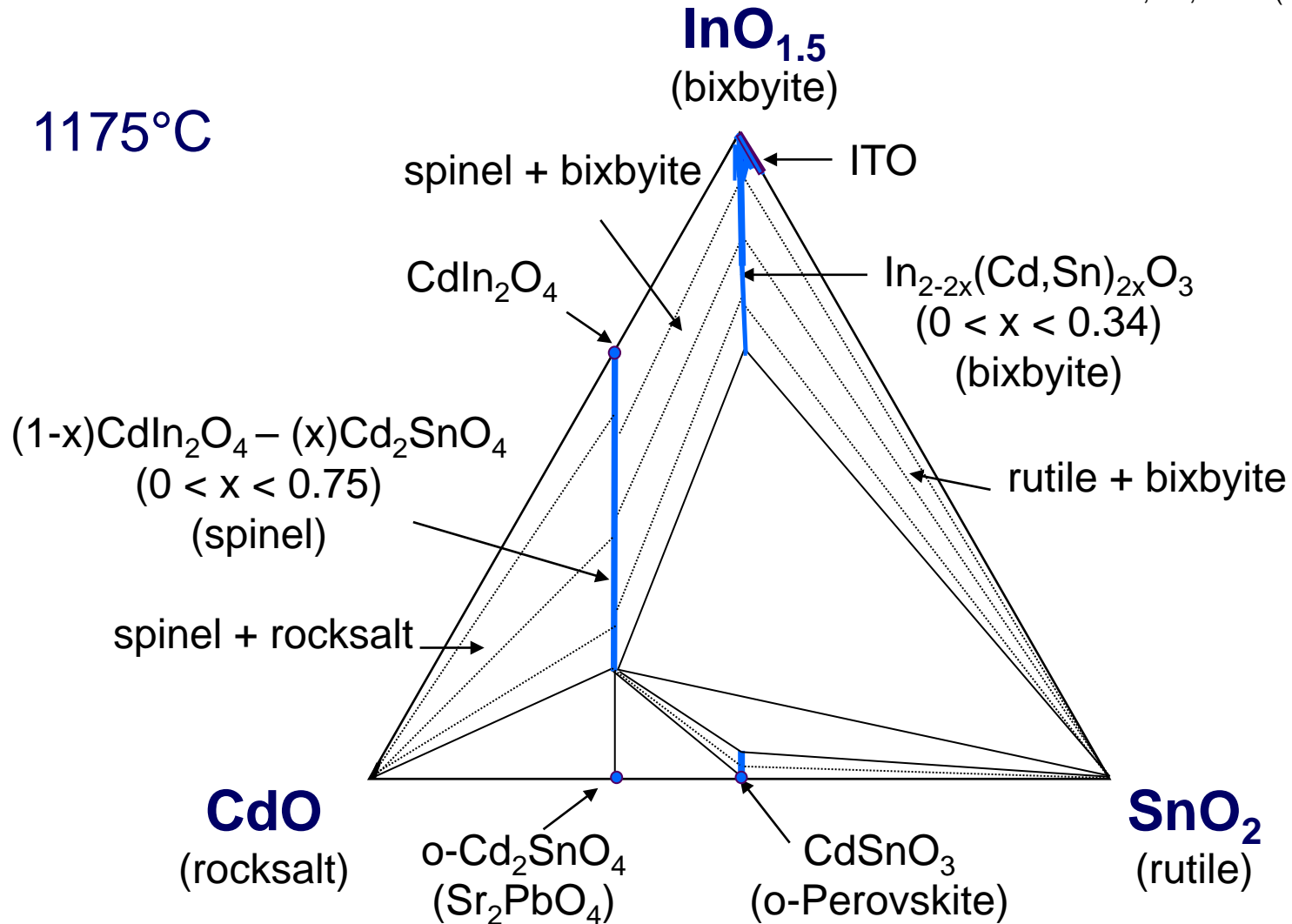
Bixbyite structure

The -1/8 slope attributable  
 to  $(2\text{Sn}_{\text{In}} \cdot \text{O}_i'')^x$  complex

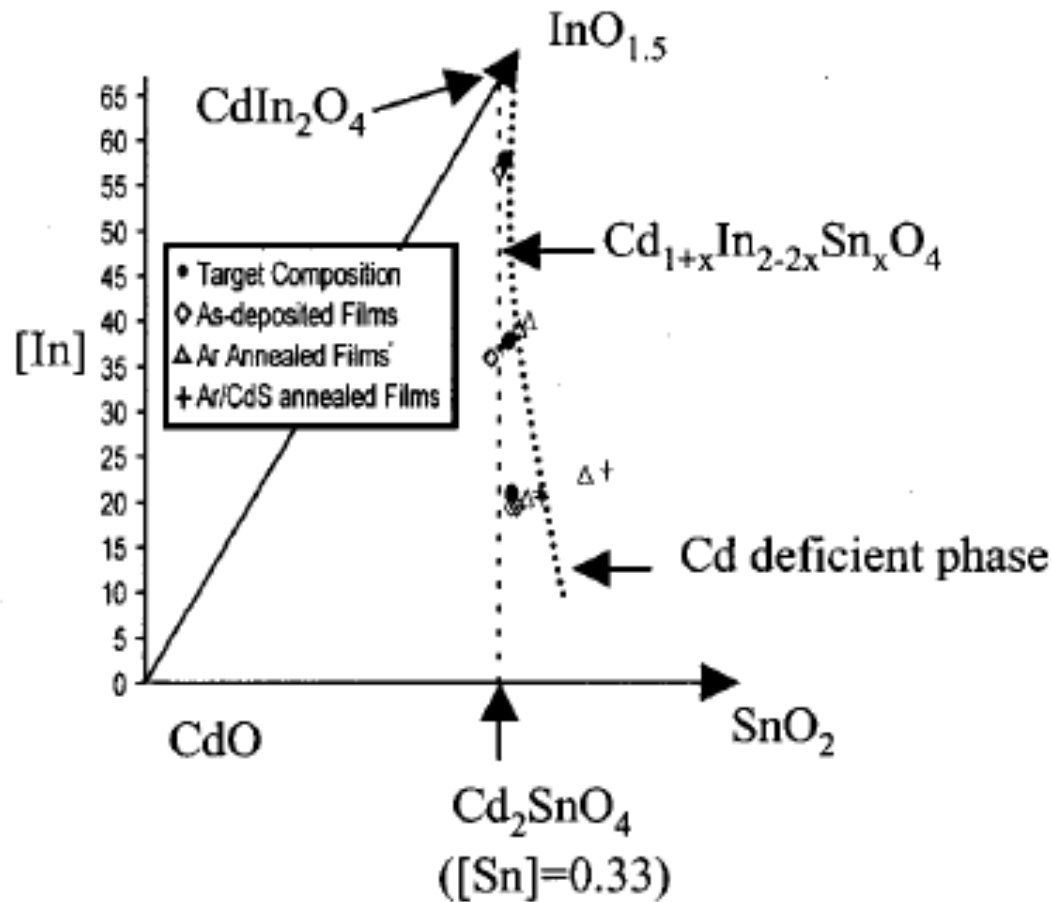
$\text{In}_{1.2}\text{Sn}_{0.40}\text{Zn}_{0.40}\text{O}_3$   
 or ZITO40

# The Cd-In-Sn System

D. R. Kammler, T. O. Maosn, K. R. Poeppelmeier,  
 J. Am. Ceram. Soc., 84, 1004 (2001)



# Evidence for D/A Excess in Spinel



# $\text{Cd}_2\text{SnO}_4$ Theory Predictions

- n-type character *not* attributable to typical intrinsic donors:
  - $V_{\text{O}}$  has a small  $\Delta H_{\text{f}}$ , but lies deep in the gap
  - $\text{Cd}_i$  is a shallow donor, but  $\Delta H_{\text{f}}$  is large
- Antisite defects are shallow donors ( $\text{Sn}_{\text{Cd}}^{\bullet}$ ) and acceptors ( $\text{Cd}_{\text{Sn}}'$ ), but the former has a lower  $\Delta H_{\text{f}}$
- The net result:  $[\text{Sn}_{\text{Cd}}^{\bullet}] > [\text{Cd}_{\text{Sn}}']$ ;  $\text{Cd}_2\text{SnO}_4$  is consistently n-type

What About p-Type TCOs?  
Stay tuned...

# Conclusions

- With the exception of ZnO, the best TCOs are high octahedral site density crystal structures
- They are n-type only
- The “basis” cations are In, Sn, Zn, Cd and Ga
- Their defect chemistries can be complicated (not just oxygen vacancies)
- Phase diagrams play an important role
- If you can make a comparable p-type TCO...