

# SOLID ION CONDUCTORS

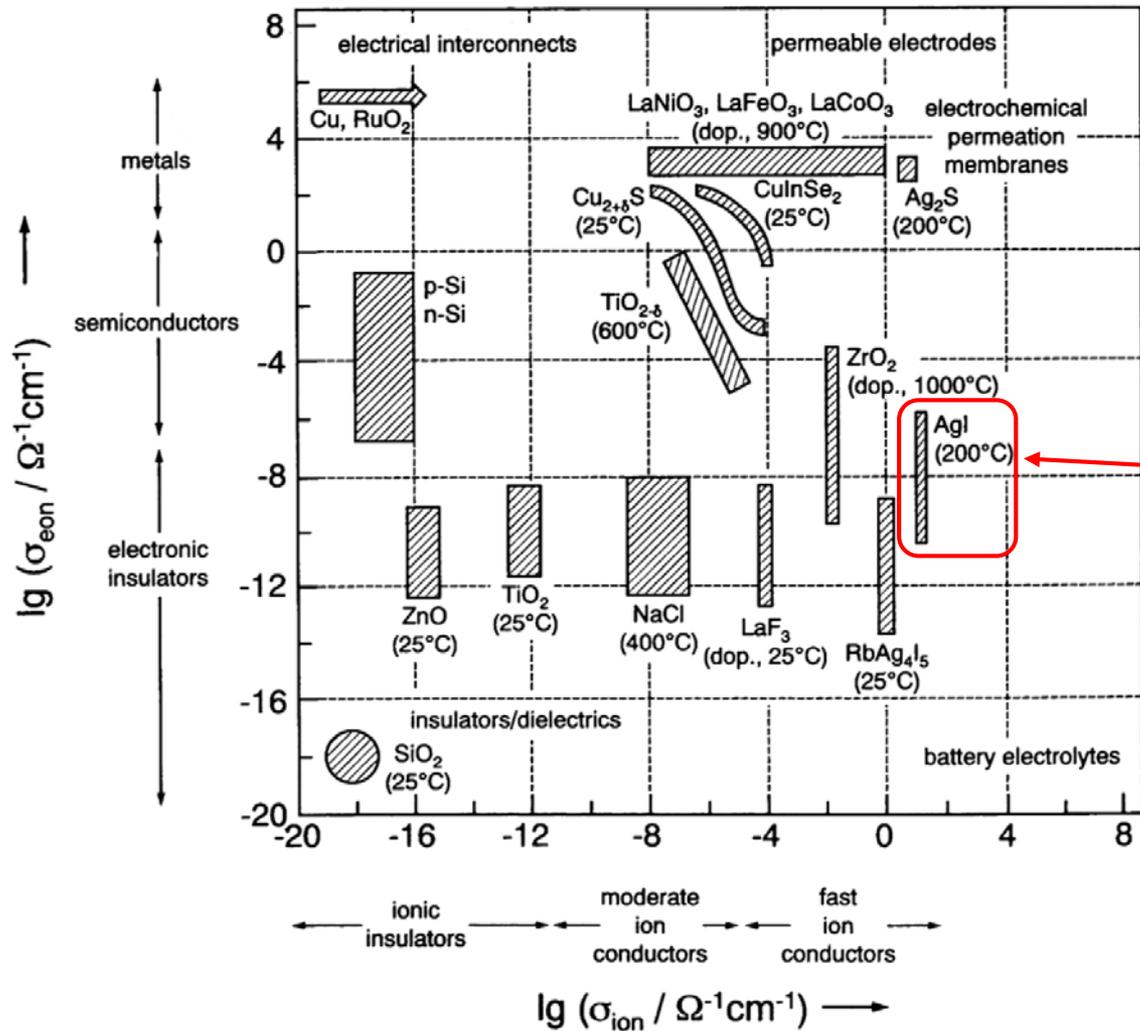
SOSSINA M. HAILE

Northwestern University

# Classes of “Hard” Ionic Conductors

- Defective Crystalline Materials:  $\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_{1.96}$ 
  - Dopants fix concentration of mobile carriers
  - Carriers move through periodic energy landscape
- Disordered Crystalline Materials:  $\text{AgI}$ ,  $\text{CsH}_2\text{PO}_4$ 
  - Crystal chemistry fixes concentration of mobile carriers
  - Carriers move through periodic energy landscape
- Amorphous Materials:  $\text{Li-P-O-N}$  glass
  - Variable mobile carrier concentration
  - Aperiodic, irregular energy landscape

# Range of Properties (xtalline)

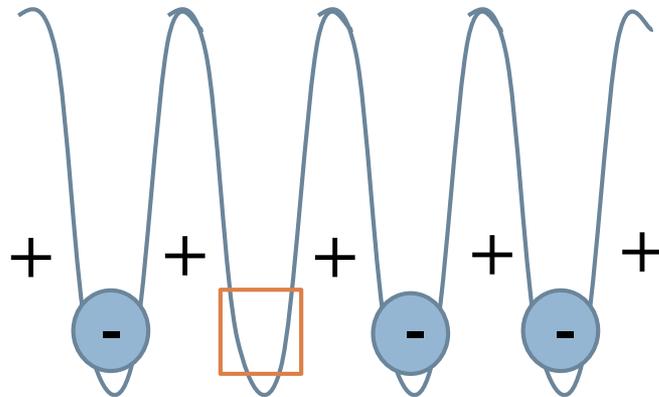


Highest value:  
 $\sim 10 \Omega^{-1}\text{cm}^{-1}$

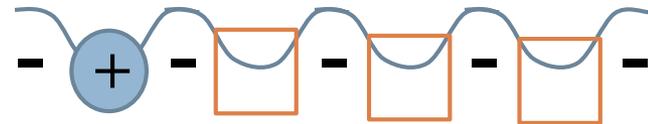
Disordered AgI  
 200 °C

# Potential Energy Landscapes

Defective anionic vacancy conductor

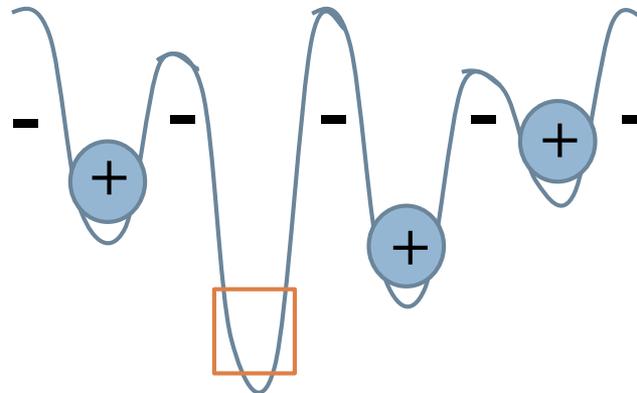


Disordered crystalline cationic conductor



Simultaneous vacancy/interstitial mechanism

Amorphous cationic conductor



# Diffusion and Ionic Conductivity

## □ (Defective) Crystalline Materials

$$D = D_0 \exp\left(\frac{-\Delta H}{k_b T}\right) \quad \Delta H = \Delta H_{\text{migration}} \quad \text{or} \quad \Delta H = \Delta H_{\text{migr}} + \Delta H_{\text{def\_gen}}$$

## □ Disordered Crystalline Materials

$$\Delta H = f(T) \quad \leftarrow \text{as transition temperature is approached}$$

## □ Amorphous Materials

$$D = D_0 \exp\left(\frac{B}{T - T_0}\right)$$

### Nernst-Einstein Relation

$$\sigma_i = \frac{c_i D_i (e z_i)^2}{k_b T}$$

# Diffusion in Crystalline Solids

□ Can show:  $D = \gamma \cdot a_o^2 \cdot P \cdot [N] \cdot \omega$

Annotations:

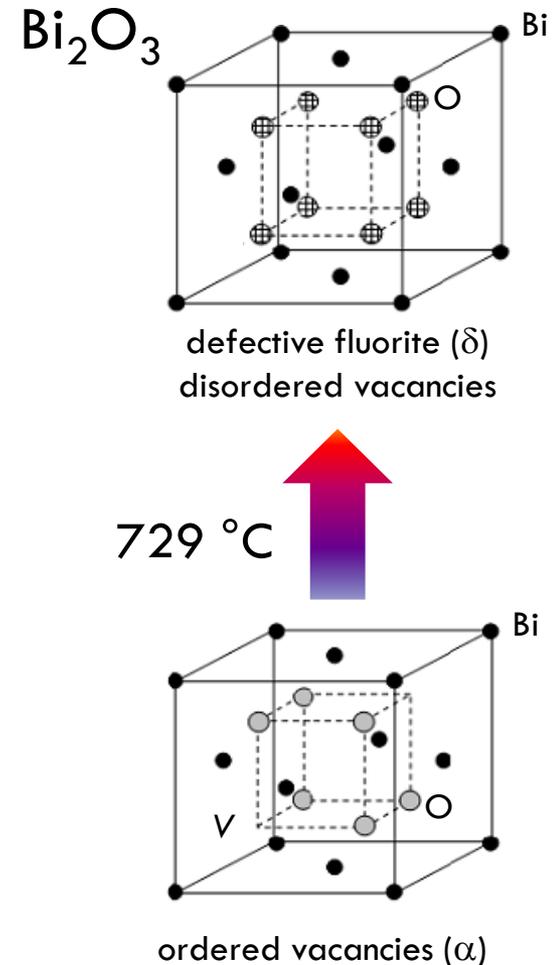
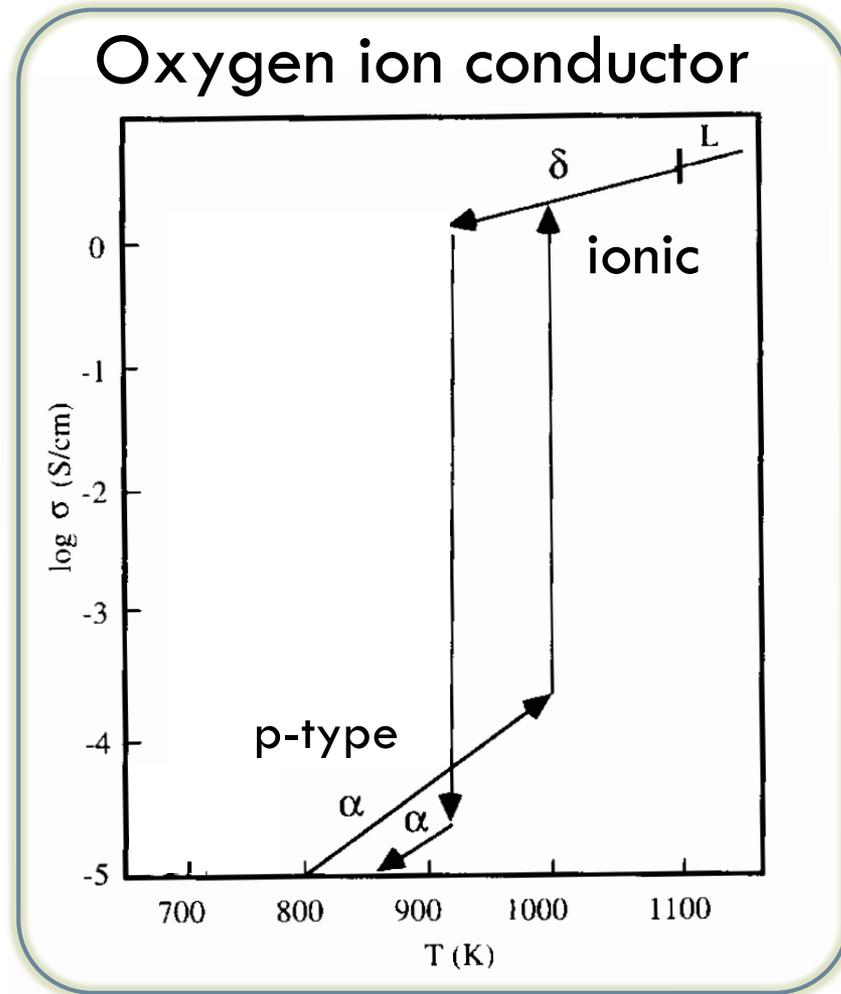
- jump distance (points to  $a_o$ )
- fraction of atoms that participate (points to  $[N]$ )
- probability that an atom will jump into an available site (points to  $\omega$ )
- geometric constant  $\sim 1/(\# \text{ nearest neighbor sites})$  (points to  $\gamma$ )
- probability that a nearest neighbor site is vacant (available) for jumping into (points to  $P$ )

□ Gives rise to:

$$D = D_0 [N] \exp\left(\frac{-\Delta H_m}{k_b T}\right)$$

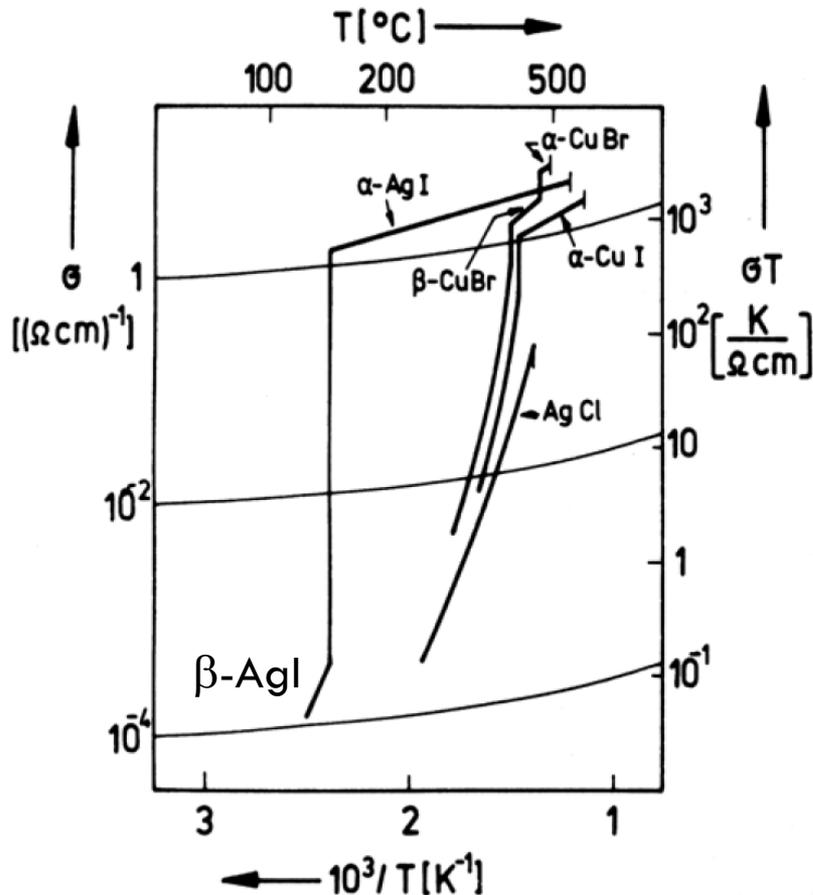
Do these relationships imply a limit to  $\sigma_{ion}$ ?? Particularly via point defects?

# Disordered Crystalline Conductors



# Disordered Crystalline Solids

## Cation (Ag, Cu) conductors



AgI (CuI, CuBr)

BCC array of I (2/unit cell)  
2 Ag distributed over 36 sites ( $\alpha$ )

$147^{\circ}\text{C}$

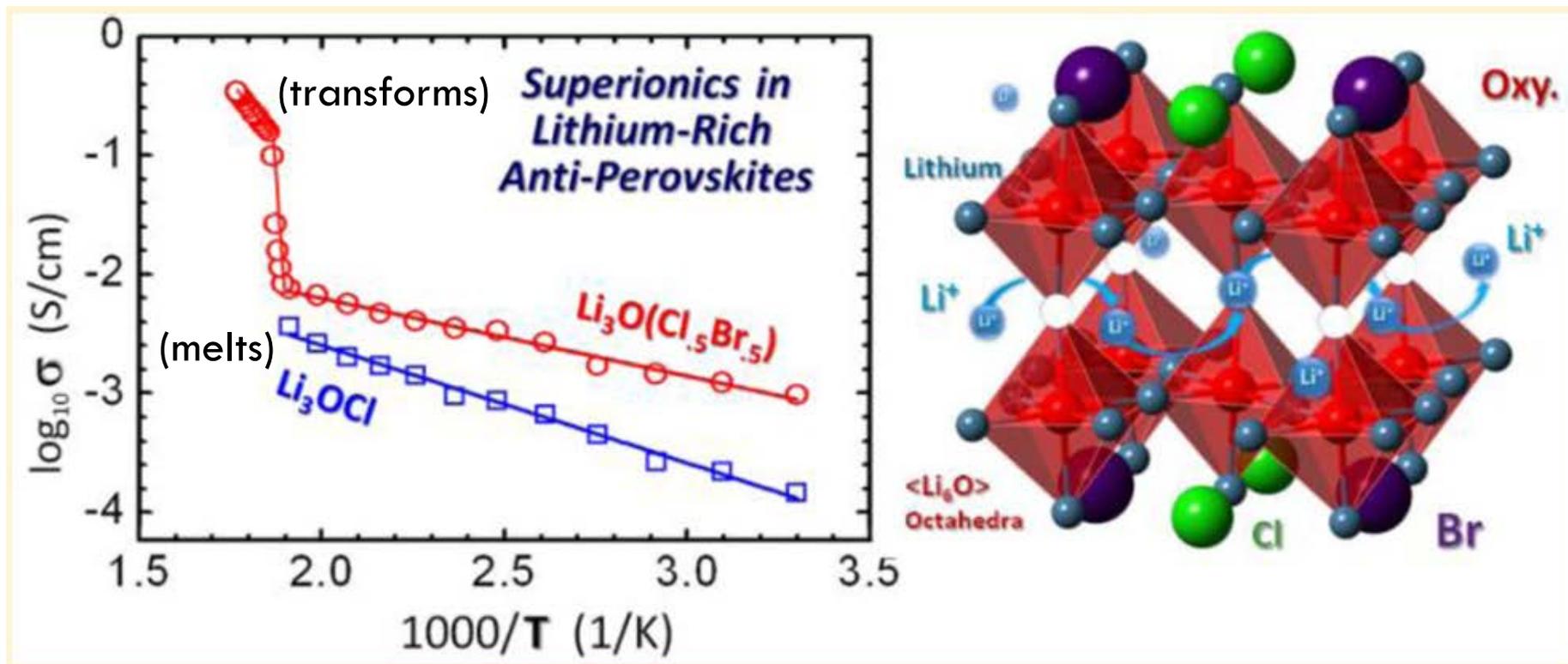


Wurtzite structure type ( $\beta$ )

Tubandt and Lorenz *Z. Phys. Chem. B* (1914)  
Funke, *Sci. Technol. Adv. Mater.* (2013)

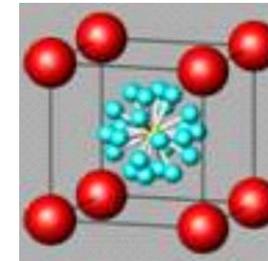
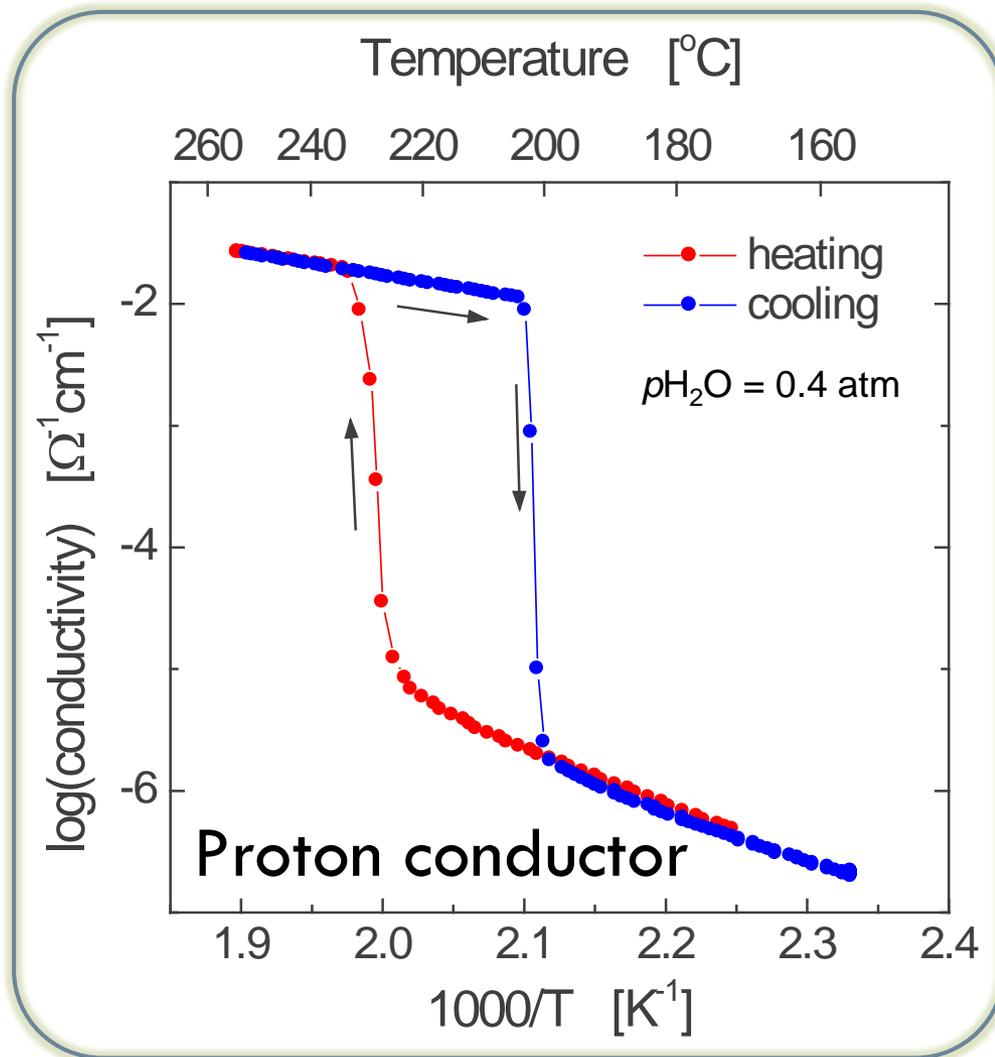
# Disordered Crystalline Solids

## Lithium ion conductors



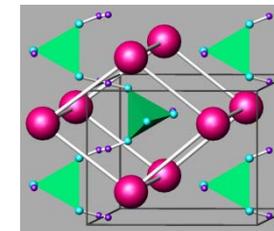
Zhao & Daemen, *JACS* (2012)

# Disordered Crystalline Solids



cubic  
CsCl-type

229 °C



monoclinic

Haile et al., *Faraday Discussions* (2007).  
Baranov et al., *Ferroelectrics* (1988).

# Lessons from Crystalline Materials

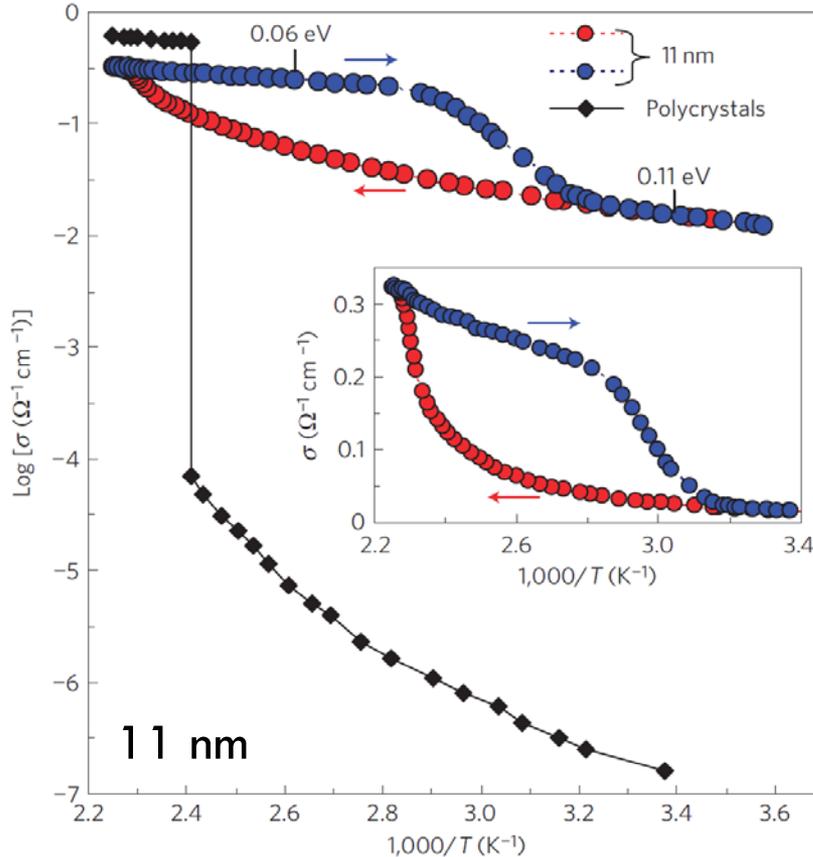
- Conductivity disordered  $>$  conductivity defective
  - ▣  $\sigma_s \sim 10 \text{ S cm}^{-1}$  some sort of limit?
- Conductivity of disordered materials often drops on melting (AgI)
- The superionic transition itself is not of interest, the high conductivity phase is
  - ▣ Has motivated extensive efforts to stabilize the disordered phase over wider temperature range
  - ▣ Often the target is lower temperature
- Other properties also matter (e.g., transference #)

# Stablizing Superionic Phases

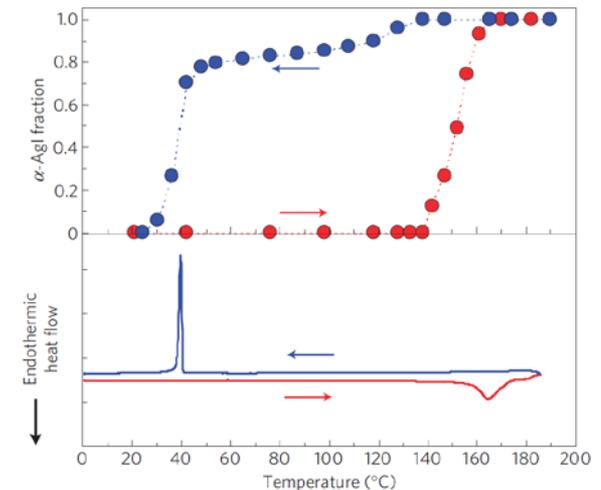
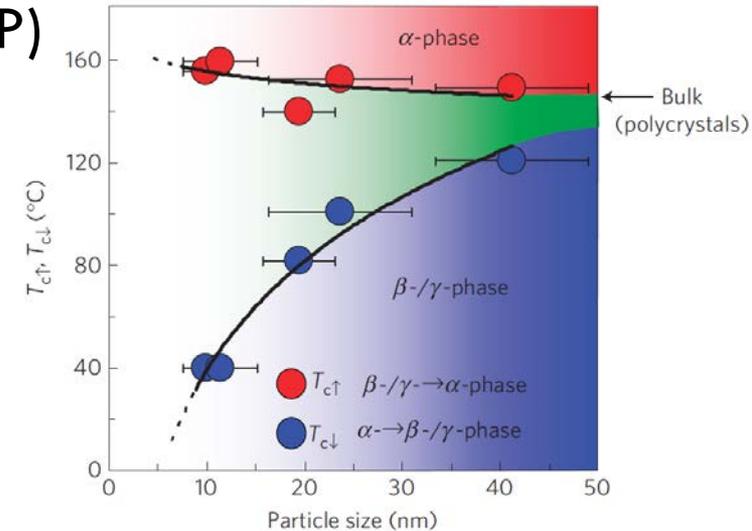
- Nano-confinement
  - ▣ A relatively recent approach
- Lattice matching (?)
  - ▣ No explicit examples
  - ▣ Leads into a controversial topic: conductivity enhancement in ultra thin films and multi-layers
- Chemical substituents
  - ▣ Traditional materials chemist approach

# Nanoconfinement of AgI

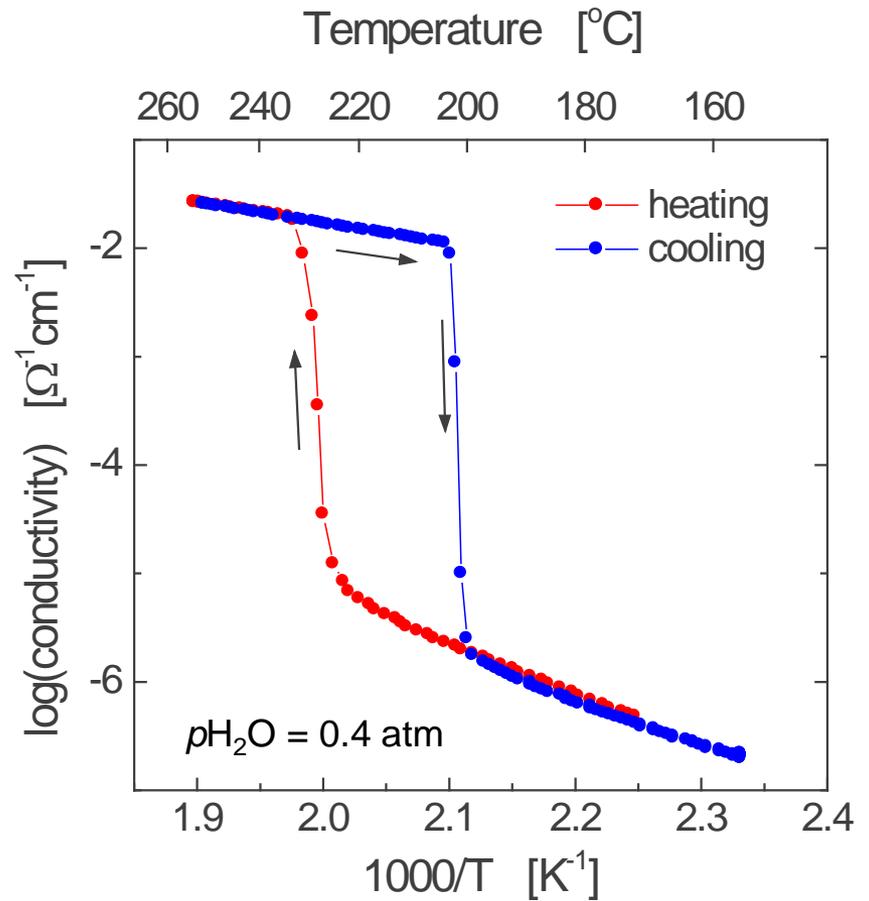
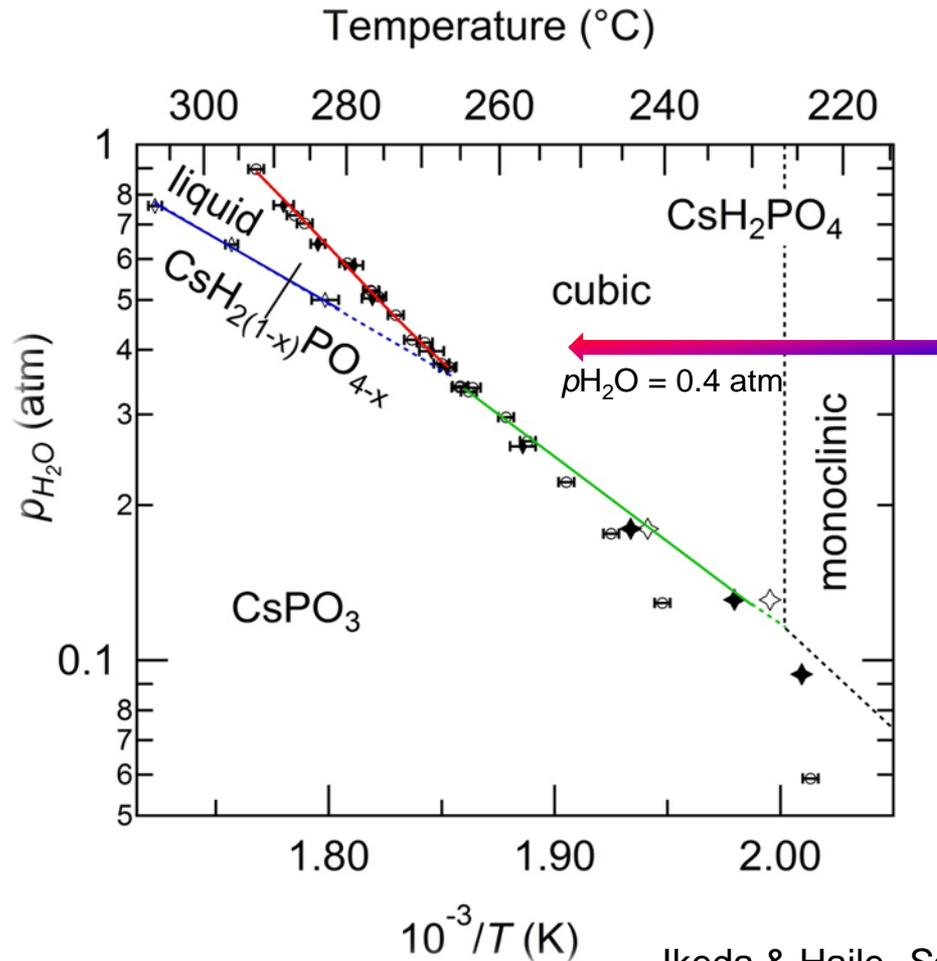
Encapsulated in polyvinylpyrrolidone (PVP)



Makiura et al., *Nat. Mat.* (2009)



# Chemical Substituents: $\text{CsH}_2\text{PO}_4$



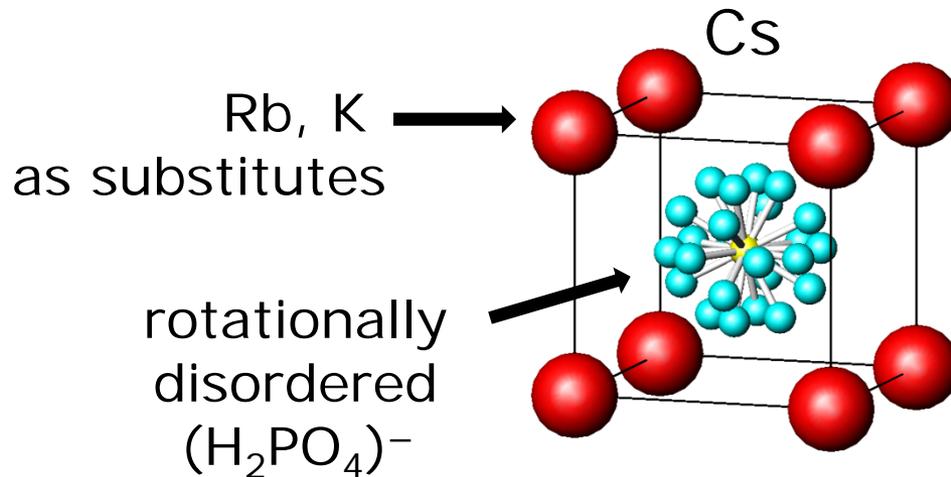
Ikeda & Haile, *Solid State Ionics* (2012).

Target(s): decrease humidification requirement; lower transition temperature

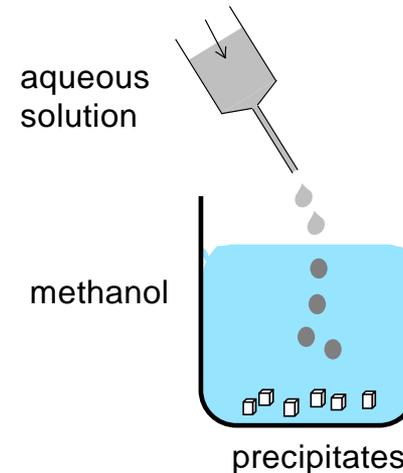


# Improve properties by substitution?

$$r_{\text{Rb}}/r_{\text{Cs}} = 0.92 \quad r_{\text{K}}/r_{\text{Cs}} = 0.86$$



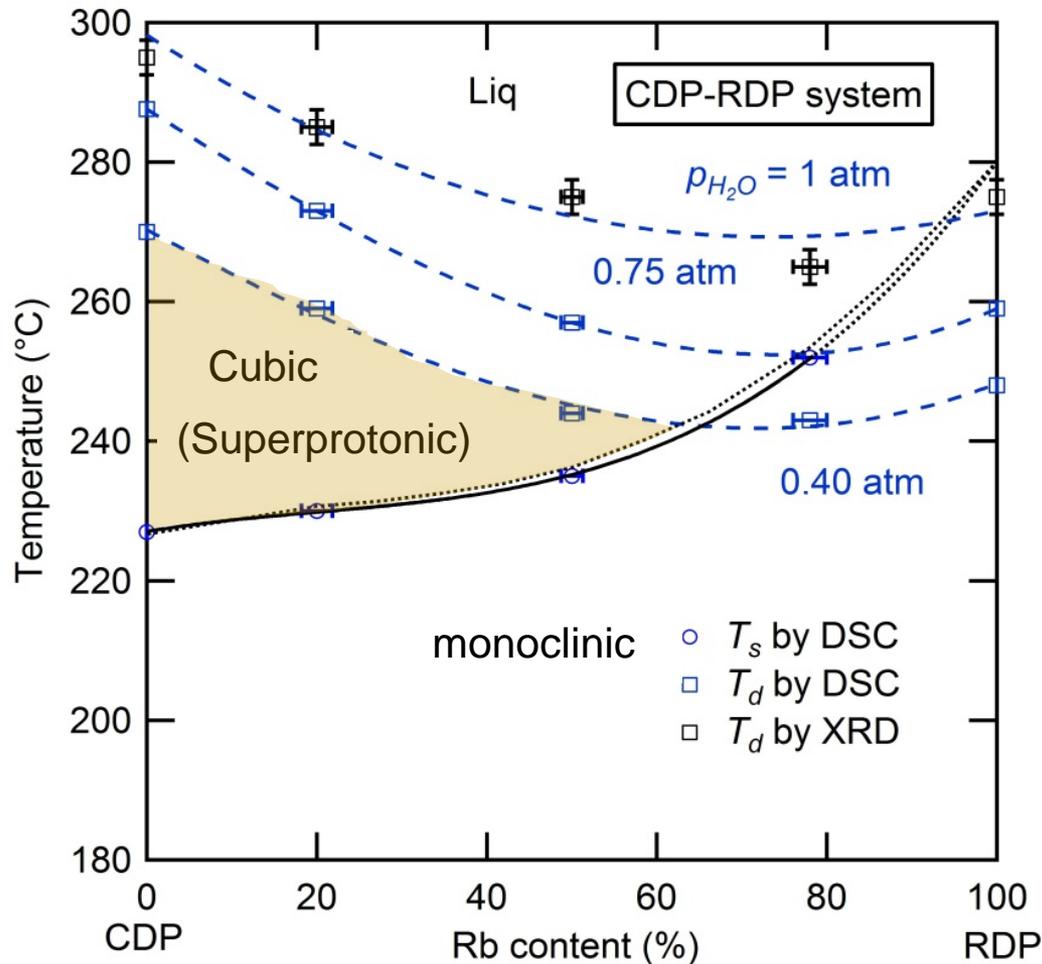
Distinct structures



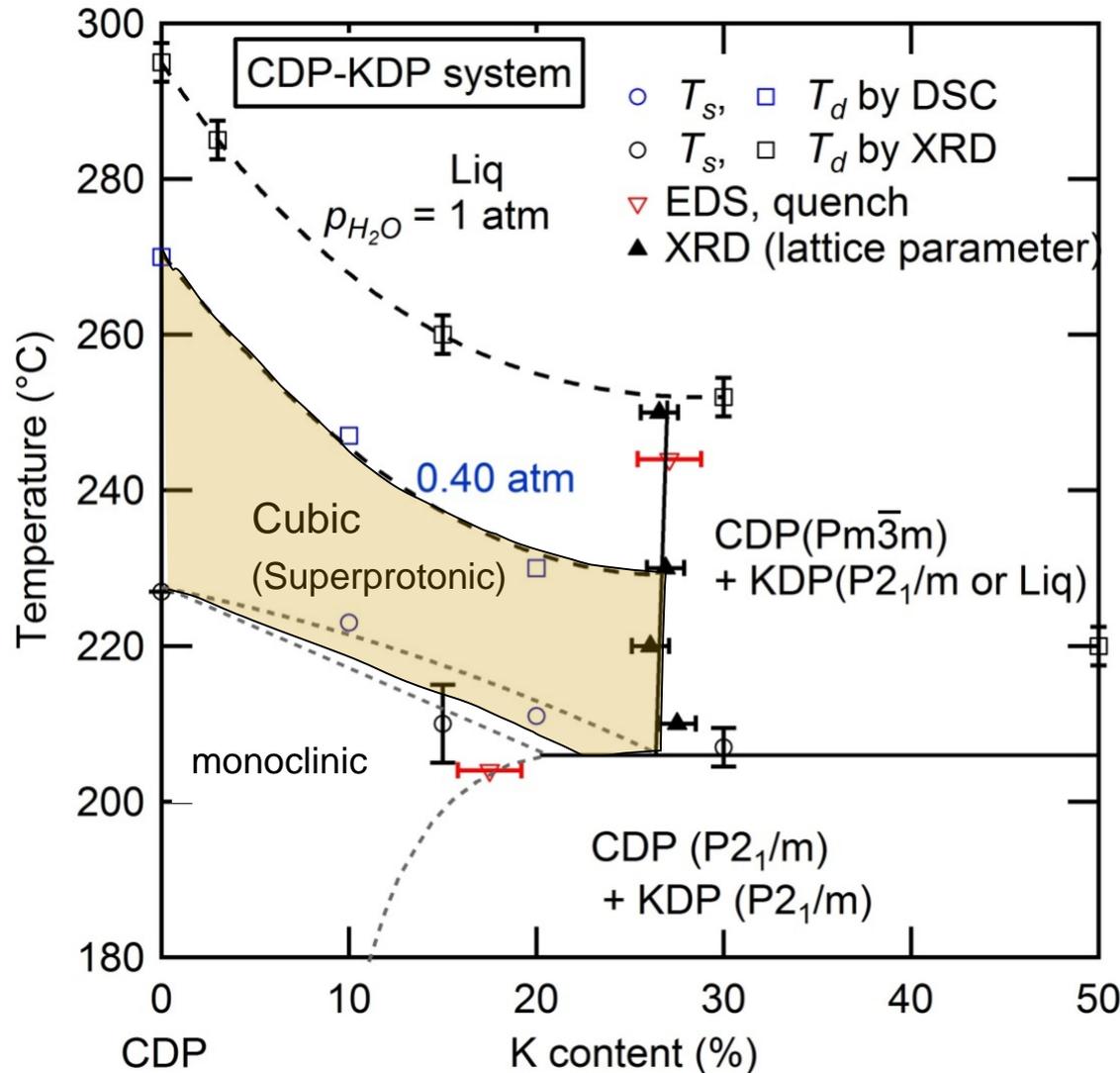
- $T_{sp}$ : superprotonic temp. – lower (228°C)
- $T_d$ : dehydration temp. – higher (270°C, 0.4  $p\text{H}_2\text{O}$ )
- $\sigma$ : conductivity – higher ( $2.2 \times 10^{-2}$  S/cm, 240°C)
- $a$ : lattice parameters – better cubic/monoclinic compatibility

# CsH<sub>2</sub>PO<sub>4</sub>-RbH<sub>2</sub>PO<sub>4</sub> Phase diagram

$$r_{\text{Rb}}/r_{\text{Cs}} = 0.92$$



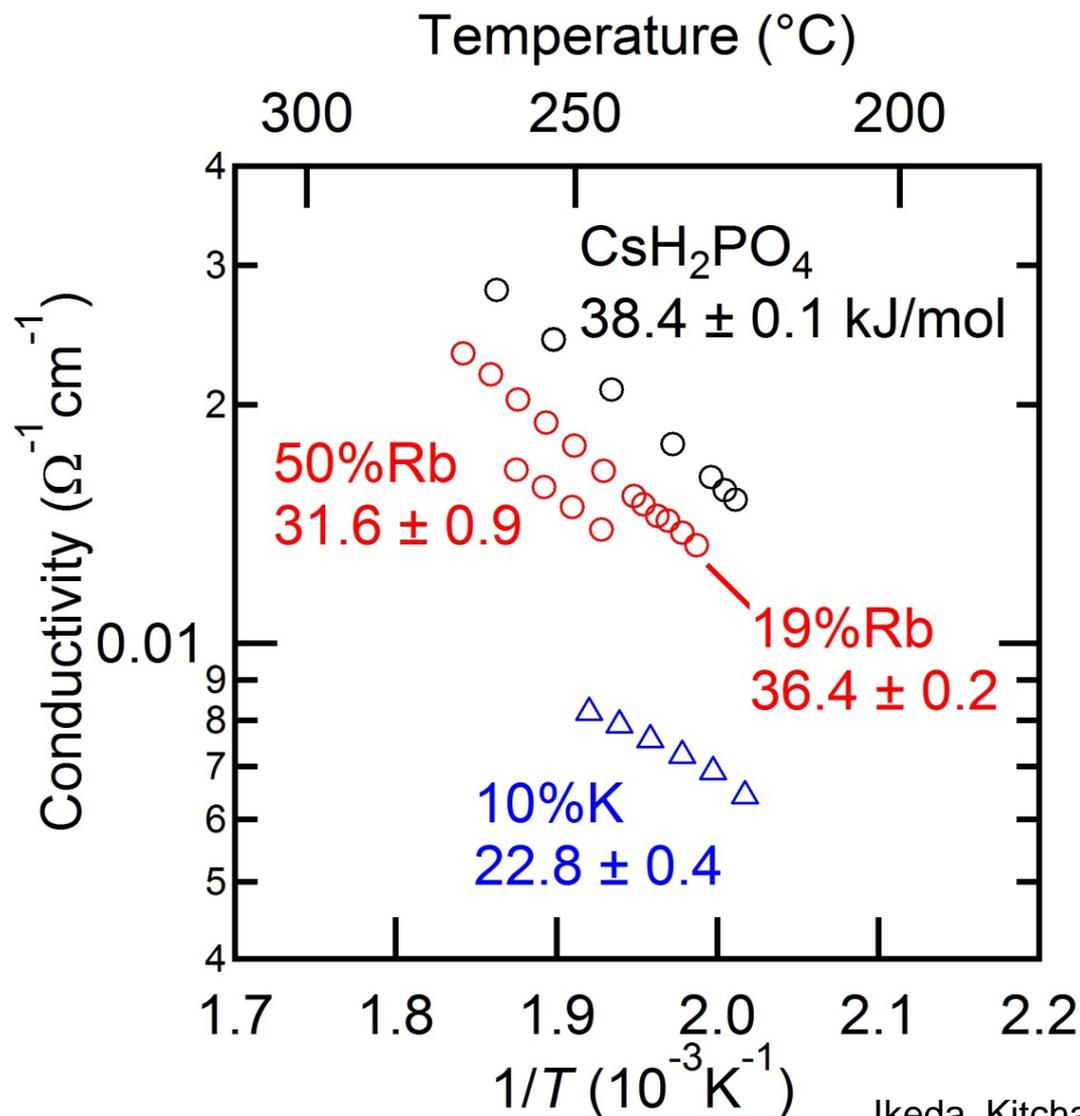
# CsH<sub>2</sub>PO<sub>4</sub>-KH<sub>2</sub>PO<sub>4</sub> Phase diagram



$$r_K/r_{Cs} = 0.86$$



# Conductivity



$\sigma$  decreases dramatically on doping



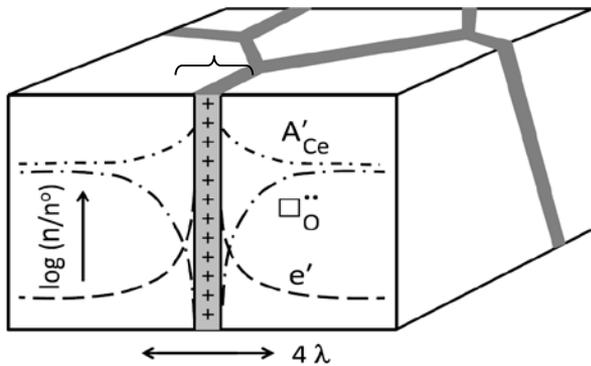
Remarkably, so does  $E_a$

Why... (another day)



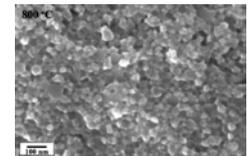
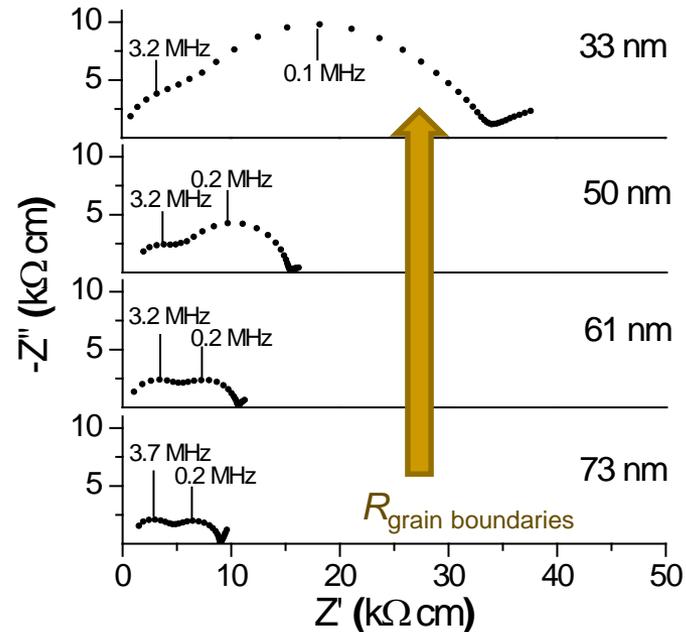
# Comments on Internal Interfaces

Space charge region

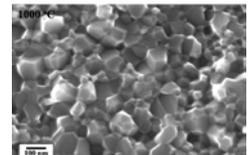


cation excess at grain boundary core

Vacancy depletion in sp.ch. region  
 ⇒ reduced conductivity



$T_{\text{sinter}} \uparrow$



Souza et al., *J. Electrochem. Soc.* (2012)

Engineer to reverse sign of space charge??

Funke, *Sci. Technol. Adv. Mater.* (2013)



# Can We Get There Faster?

- High throughput computation
- High throughput experimentation



# Summary

- Disordered crystalline solids have exceptional ionic conductivity
- Pathway to greater than 10 S/cm unclear
- Stabilization for utility over wider temperature range likely possible
- Chemical stabilization proven
  - YSZ, doped-Bi<sub>2</sub>O<sub>3</sub>, K-substituted CDP
- Newer approaches have yet to pass the test of time
- Defective solids amenable to gb engineering?
- High throughput is required



# Acknowledgements

- Ayako Ikeda
  - $\text{CsH}_2\text{PO}_4$  and derivatives
- Rob Usiskin
  - High throughput instrumentation
- Funding
  - ARO (MURI), NSF (MRSEC)

