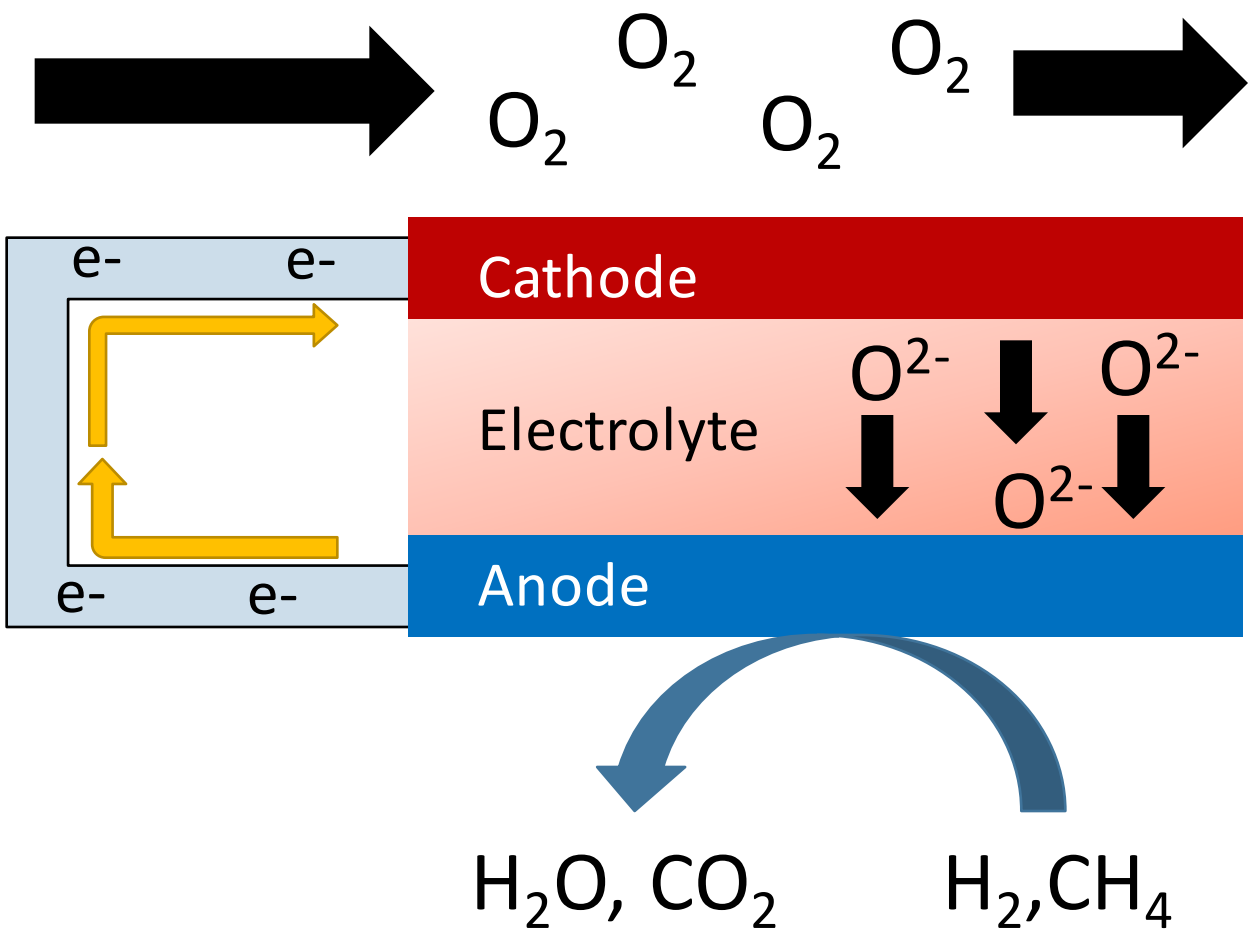
High Conductivity Oxides for Solid Oxide Fuel Cells

ABEL FERNANDEZ

MATERIALS 286G

JUNE 2016

How do Solid Oxide Fuel Cells Work?

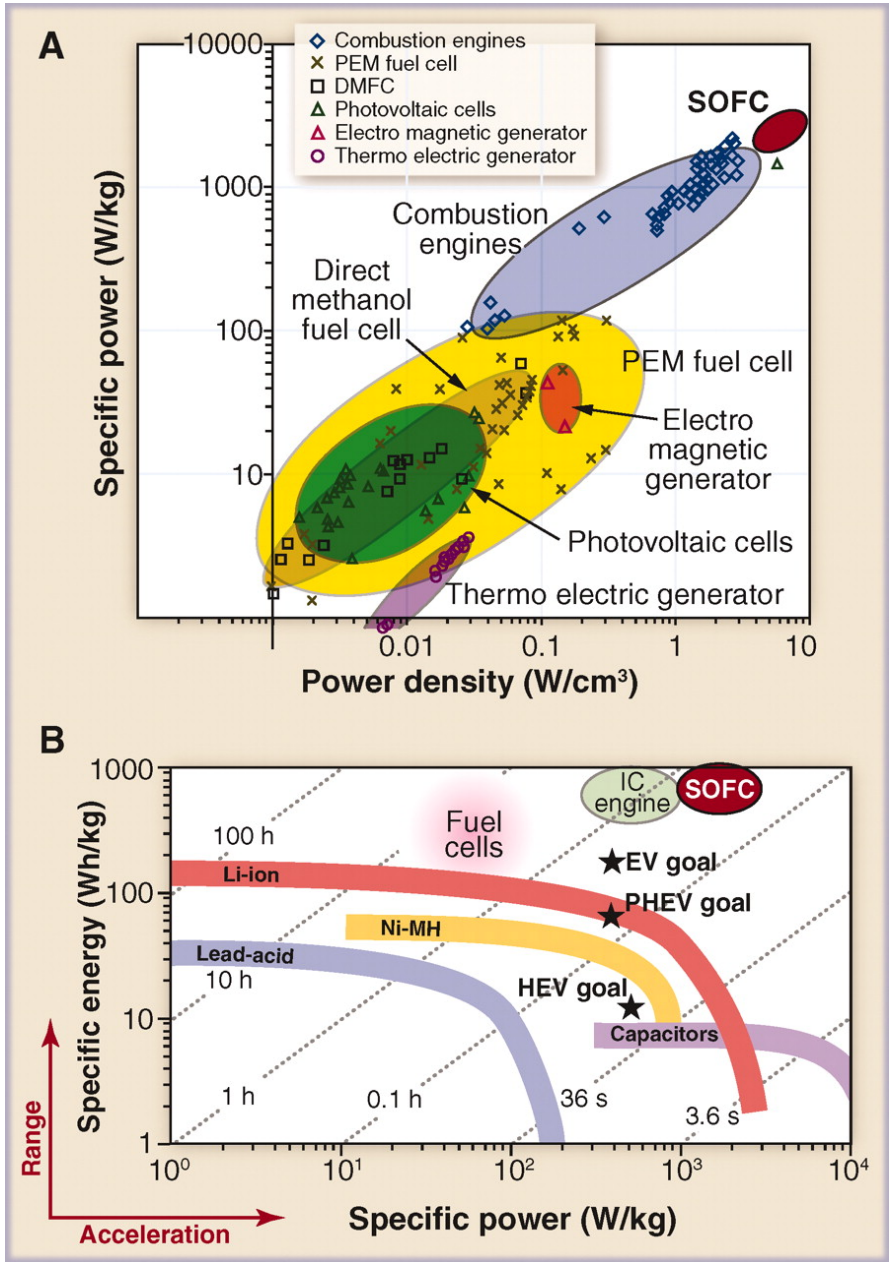


Porous cathode reduces O_2 from flowing air, currently $LaMnO_3$, $La_{1-x}Sr_xMnO_3$

Reduced O^{2-} conducts through ionic conducting electrolyte, currently yttria-stabilized-zirconia (YSZ)

Fuel is oxidized at anode, releasing electrons to circuit, currently Ni-YSZ

Operating Temps: 650-800°C

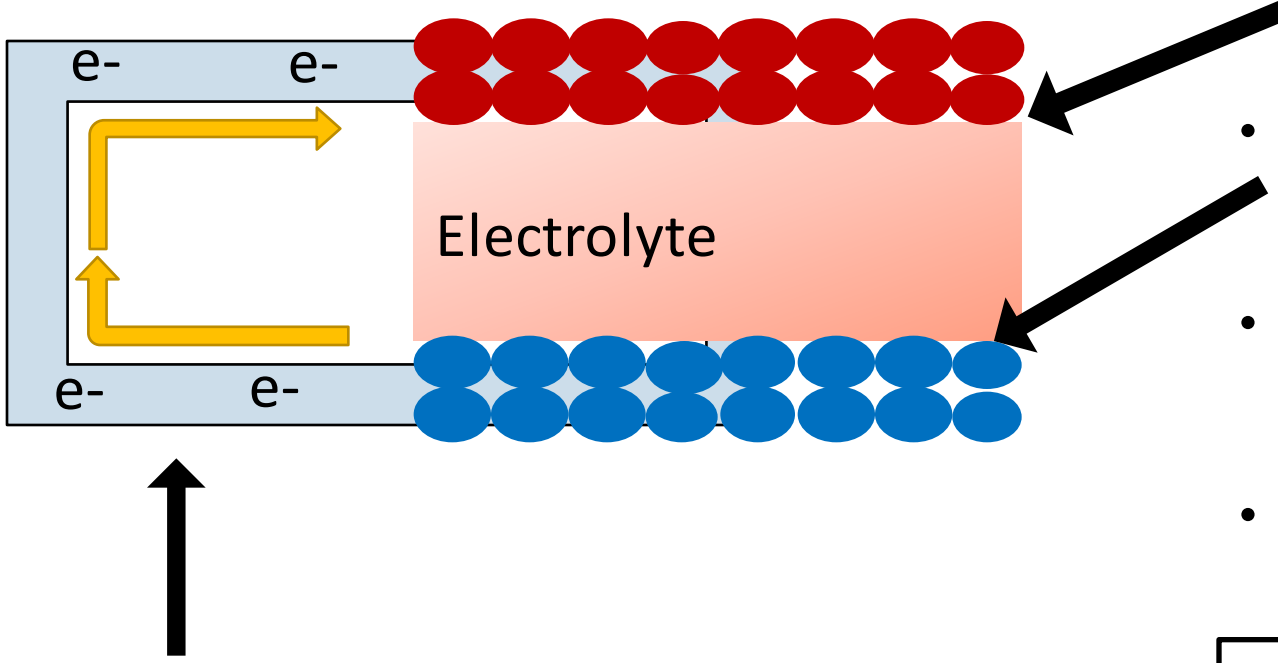


SOFCs will solve the energy crisis

- Stand-alone chemical-to-electrical efficiency between 45-65%, twice that of internal combustion engines
- Can be used in combined heat power applications for higher efficiency ~75%
- Facilitate the transition from fossil fuel economy to hydrogen based economy

Wachsman, E.D., Lee, K.T., "Lowering the Temperature of Solid Oxide Fuel Cells", *Science*, **2011**, *334*, 6058, 935-939

SOFCs still face obstacles

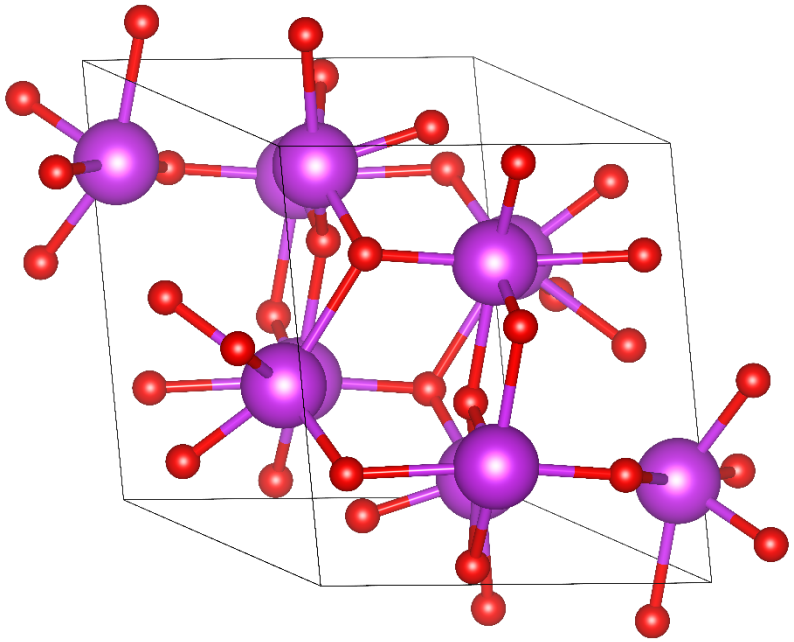


- Electrodes must be porous to make up for poor conductivity, reactions happen at triple phase boundary
- Electrodes must be chemically compatible at electrode/electrolyte interface
- Electrodes sinter at high temperature, ruin porosity
- Need matching CTE for mechanical durability
- Interconnect must be stable at high temperature, as well oxidizing and reducing environments

To lower operating temperature, need better electrolyte

High-temperature Bi_2O_3 (>730°C) has potential as new electrolyte, higher conductivity than currently used YSZ electrolyte

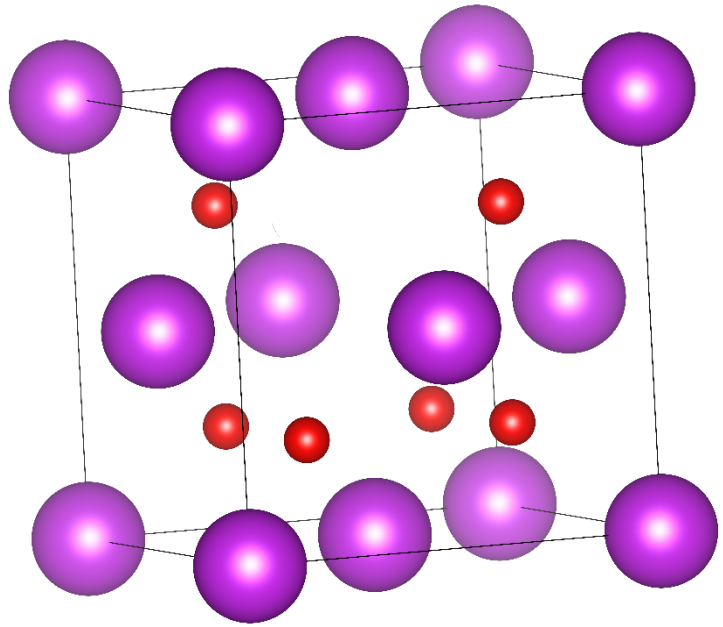
α-Bi_2O_3



- Naturally occurring mineral *bismite*
- Complicated monoclinic structure
- Exhibits no ionic conductivity

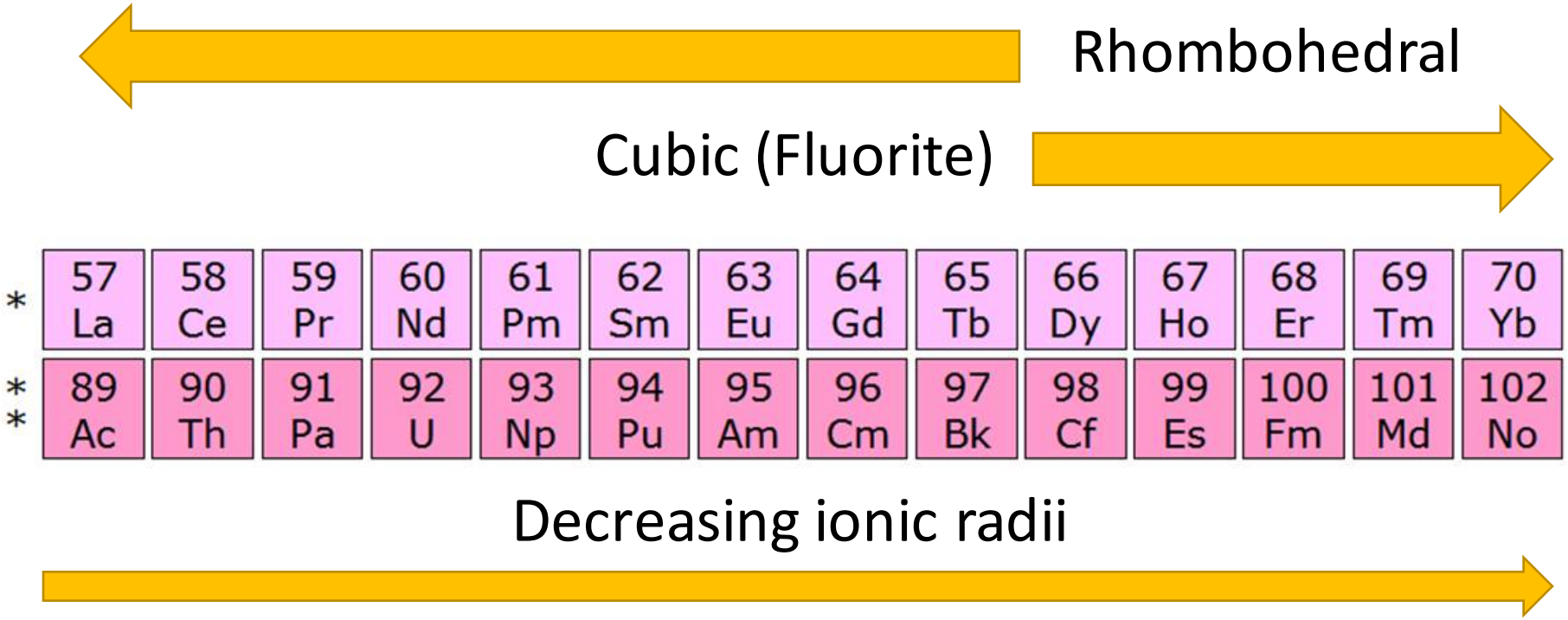
730°C

δ-Bi_2O_3



- Defect fluorite structure with 25% of anion sites vacant
- High ionic conductivity due to large concentration of vacancies
- Bi^{3+} in a fluorite lattice

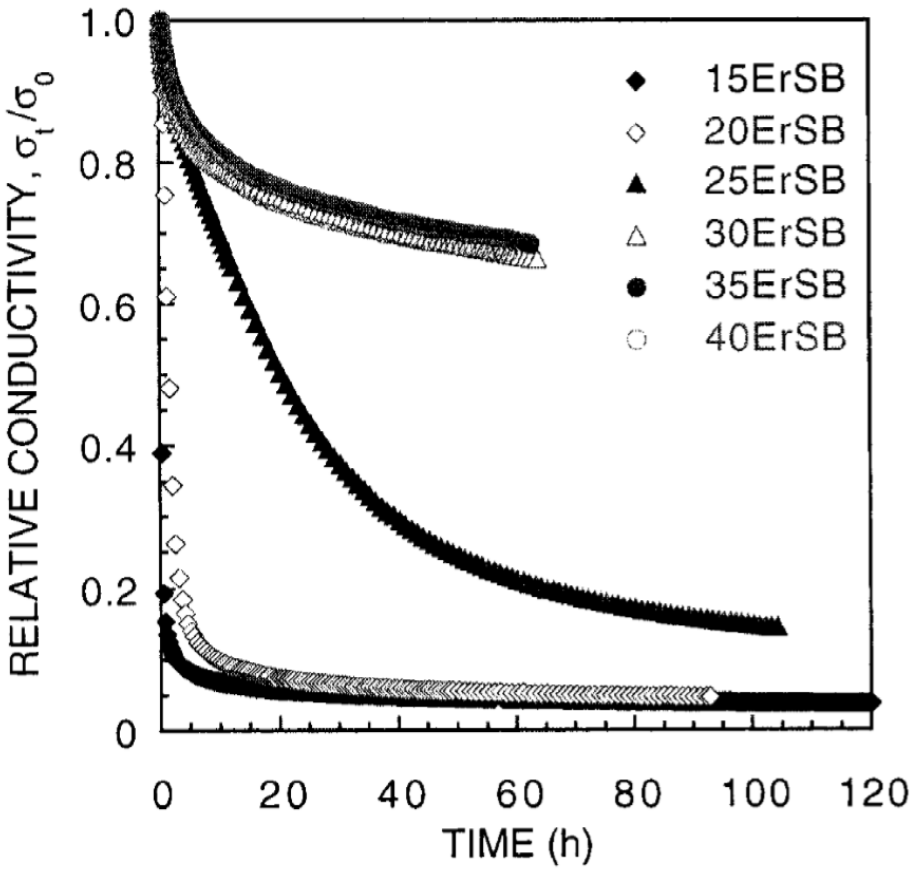
Isovalent lanthanide-doping stabilizes the δ-Bi_2O_3 structure to lower temperature (~500°C)

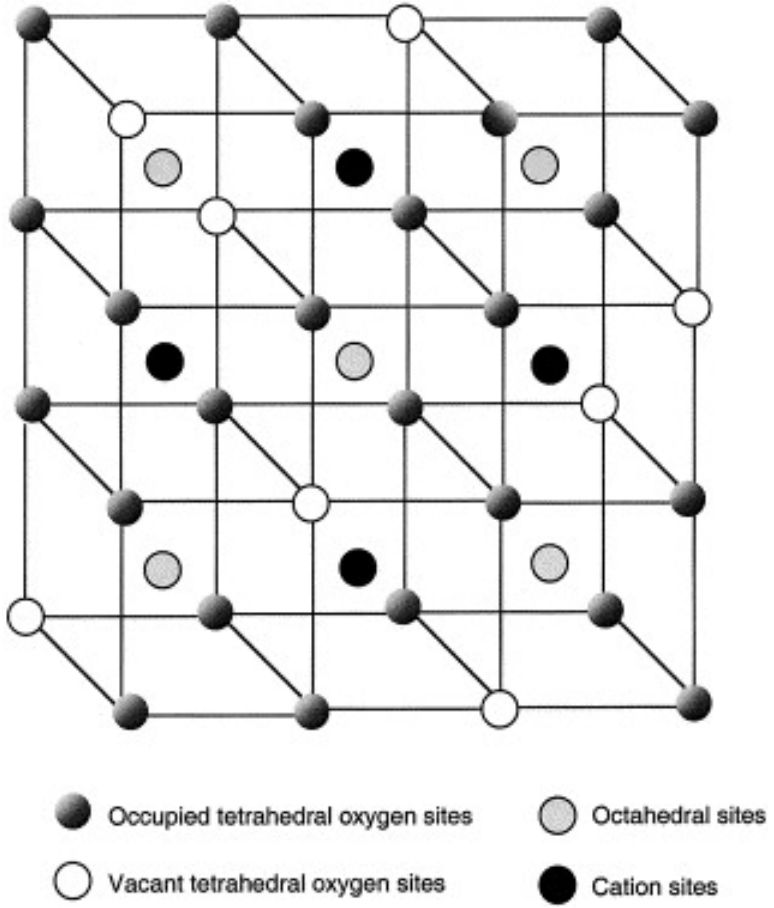


- Larger cationic radii destabilizes cubic structure at lower temperatures (similar to Bi^{3+})

https://en.wikipedia.org/wiki/Periodic_table#/media/File:14LaAc_periodic_table_IIb.jpg

Oxygen vacancy ordering below 600°C decreases conductivity

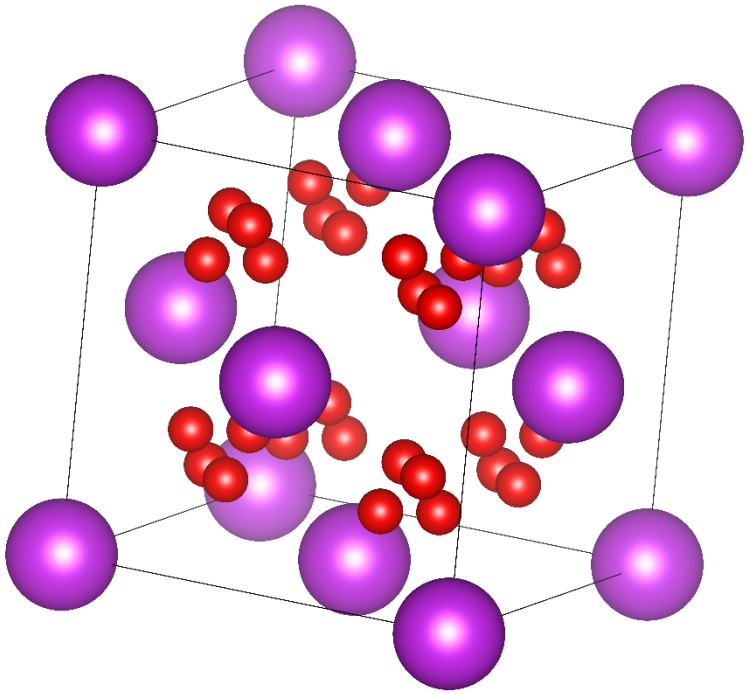


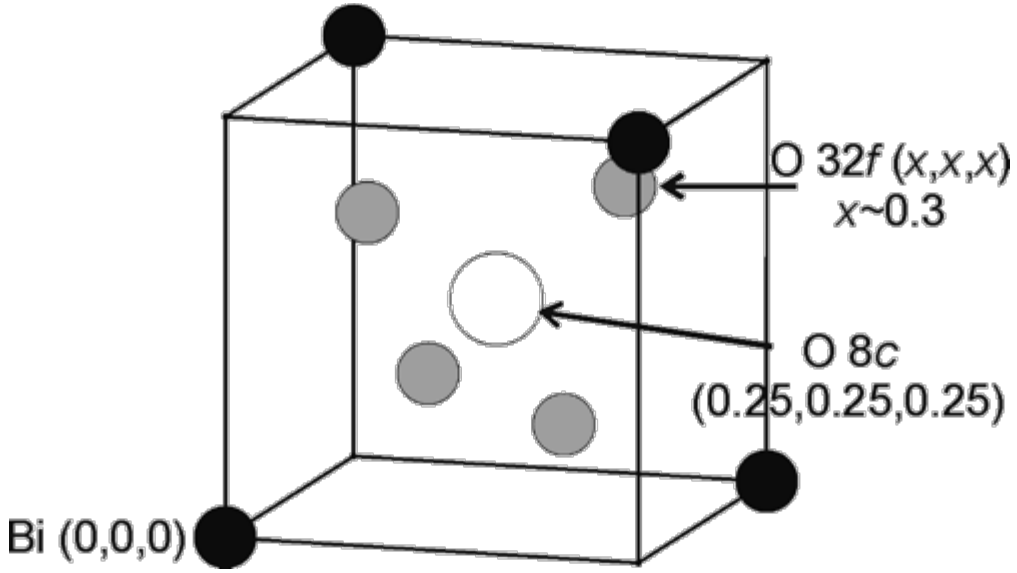


- Oxygen vacancies order along body diagonal, <111>, across octahedral sites, and <110> next to Bi cations due to lone pair, high polarizability
- Higher concentrations of dopant increasing aging effect

Boyapati, S., Wachsman, E.D., Jiang, N., "Effect of oxygen sublattice ordering on interstitial transport mechanism and conductivity activation energies in phase-stabilized cubic bismuth-oxides", *Solid State Ionics*, **2001**, *140*, 149-160; Jiang, N., Wachsman, E.D., "Structural Stability and Conductivity of Phase-Stabilized Cubic Bismuth Oxides", *J. Am. Ceram. Soc.*, **1999**, *82*, 3057-3064

Vacancy ordering is accompanied by oxygen anion positional ordering in 32f interstitial sites

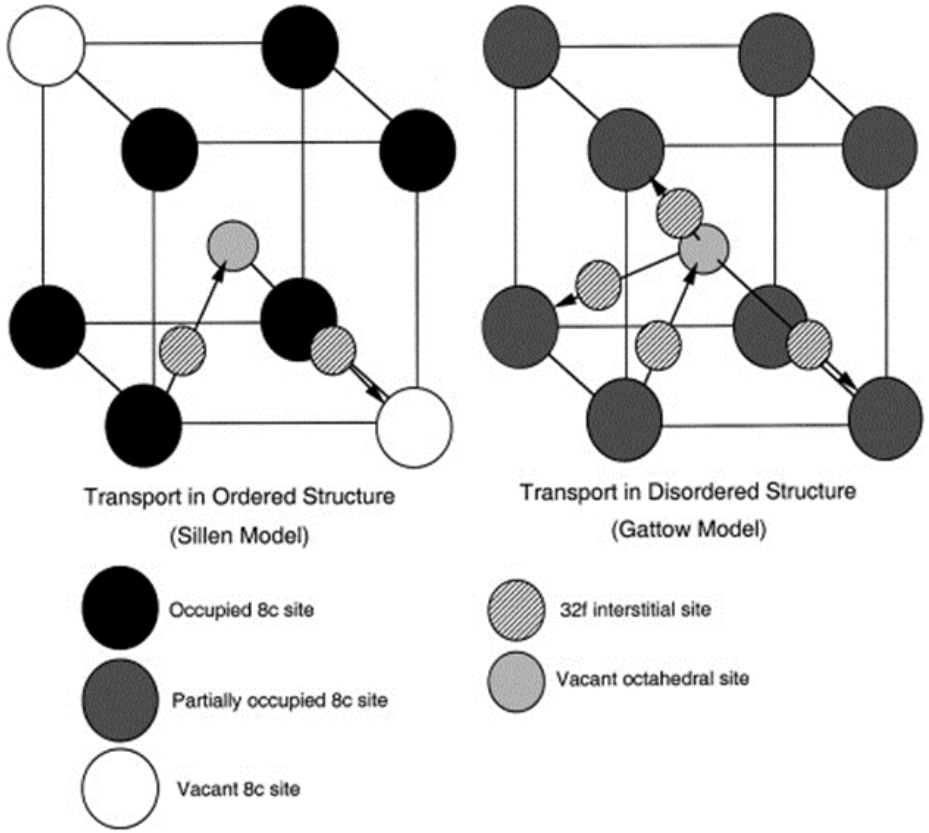


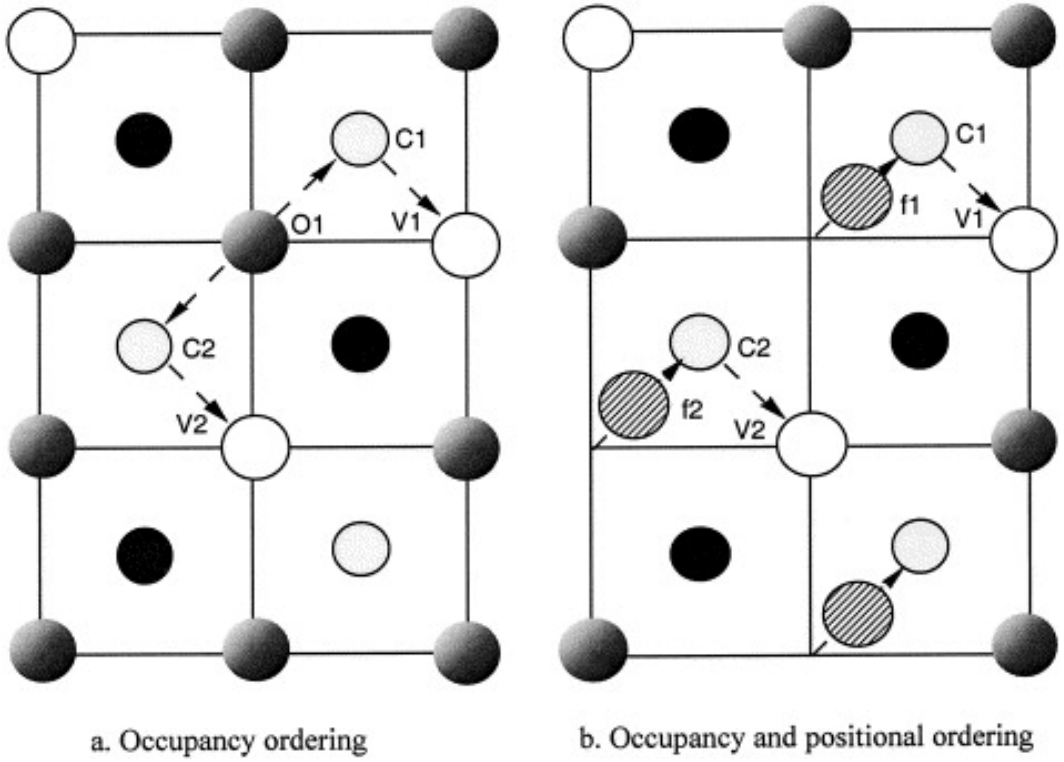


- In ordered structure oxygen ions have high occupancy of 32f interstitial sites along <111> direction towards empty octahedral site (center of unit cell)
- Observed in TEM diffraction, neutron diffraction

Punn, R., Feteira, A.M., Sinclair, D.C., Greaves, C. "Enhanced Oxide Ion conductivity in Stabilized δ-Bi_2O_3", *J. Am. Chem. Soc.*, **2006**, *128*, 15386-15387

Ion conduction occurs through empty octahedral site, limited by interstitial occupancy and anion ordering





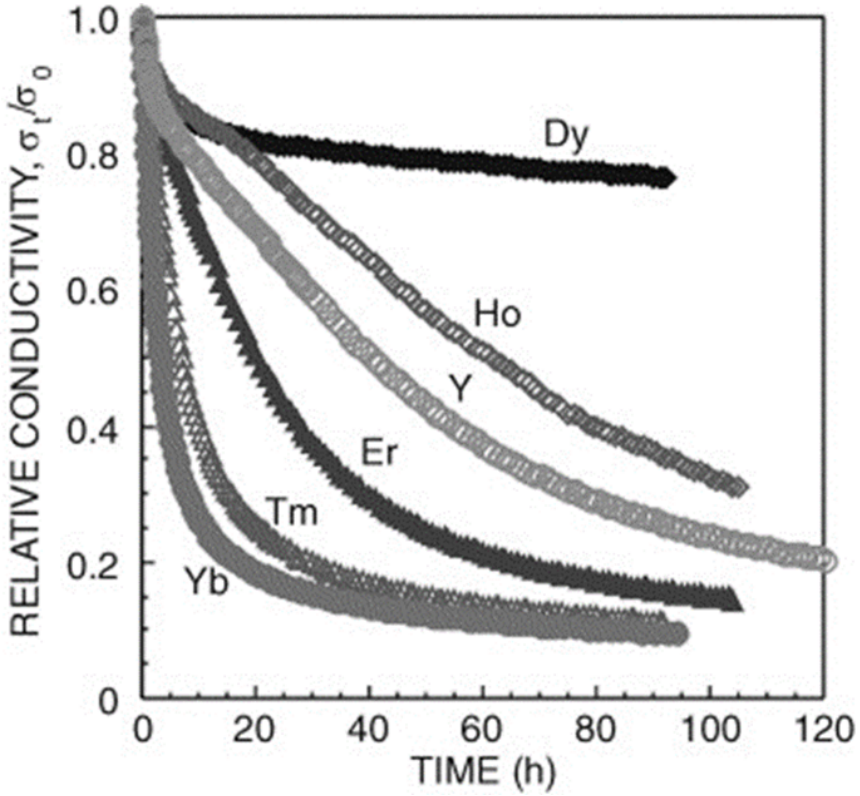
a. Occupancy ordering

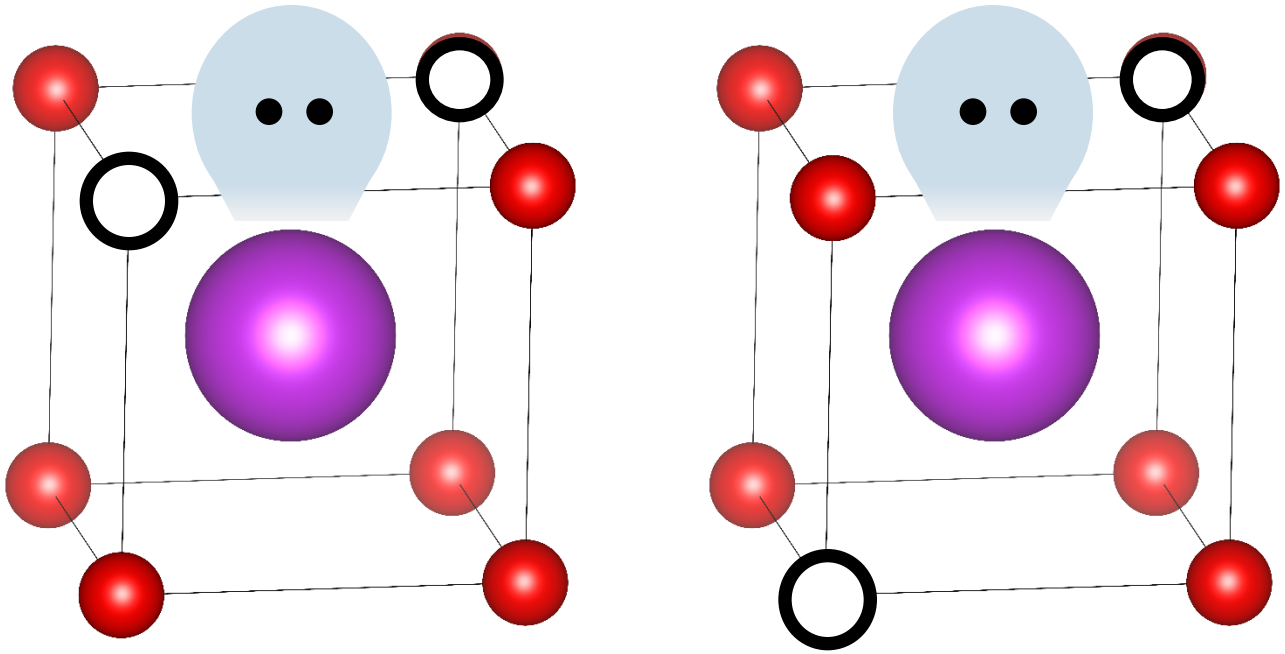
b. Occupancy and positional ordering

- Disordered structure has more jump directions, 8c site is unstable, interstitials can only jump to octahedral site
- Occupation of interstitial sites decreases activation energy

Boyapati, S., Wachsman, E.D., Jiang, N., "Effect of oxygen sublattice ordering on interstitial transport mechanism and conductivity activation energies in phase-stabilized cubic bismuth-oxides", *Solid State Ionics*, **2001**, *140*, 149-160

Oxygen sublattice ordering is limited by polarizability of cations



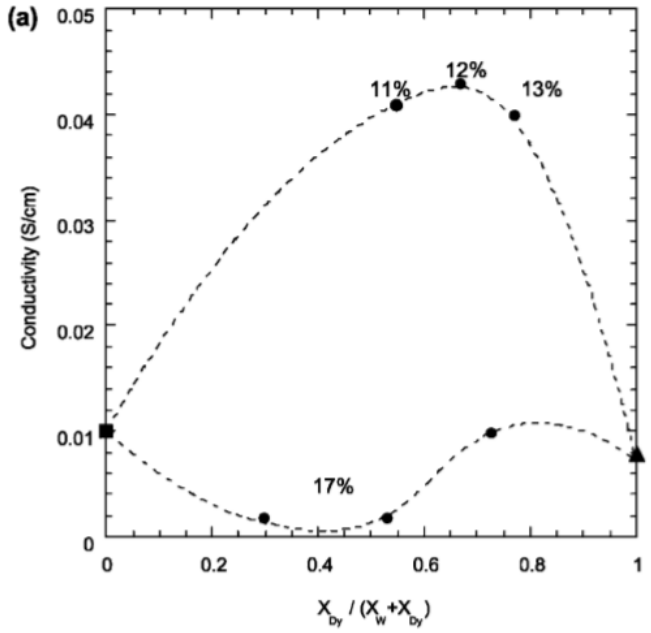


- Larger atomic radius higher polarizability, Bi^{3+} has lone pair, destabilizes <111> ordering of vacancies
- Dy has lowest occupancy of 32f sites, maintains disorder after annealing at 500°C
- Lower concentration of dopant cations allows for structure more similar to δ-Bi_2O_3, higher conductivities

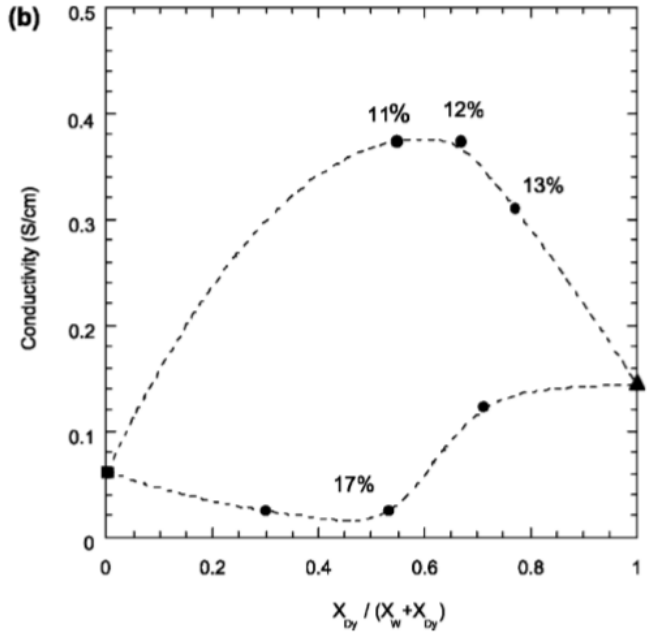
Jiang, N., Wachsman, E.D., "Structural Stability and Conductivity of Phase-Stabilized Cubic Bismuth Oxides", *J. Am. Ceram. Soc.*, **1999**, *82*, 3057-3064

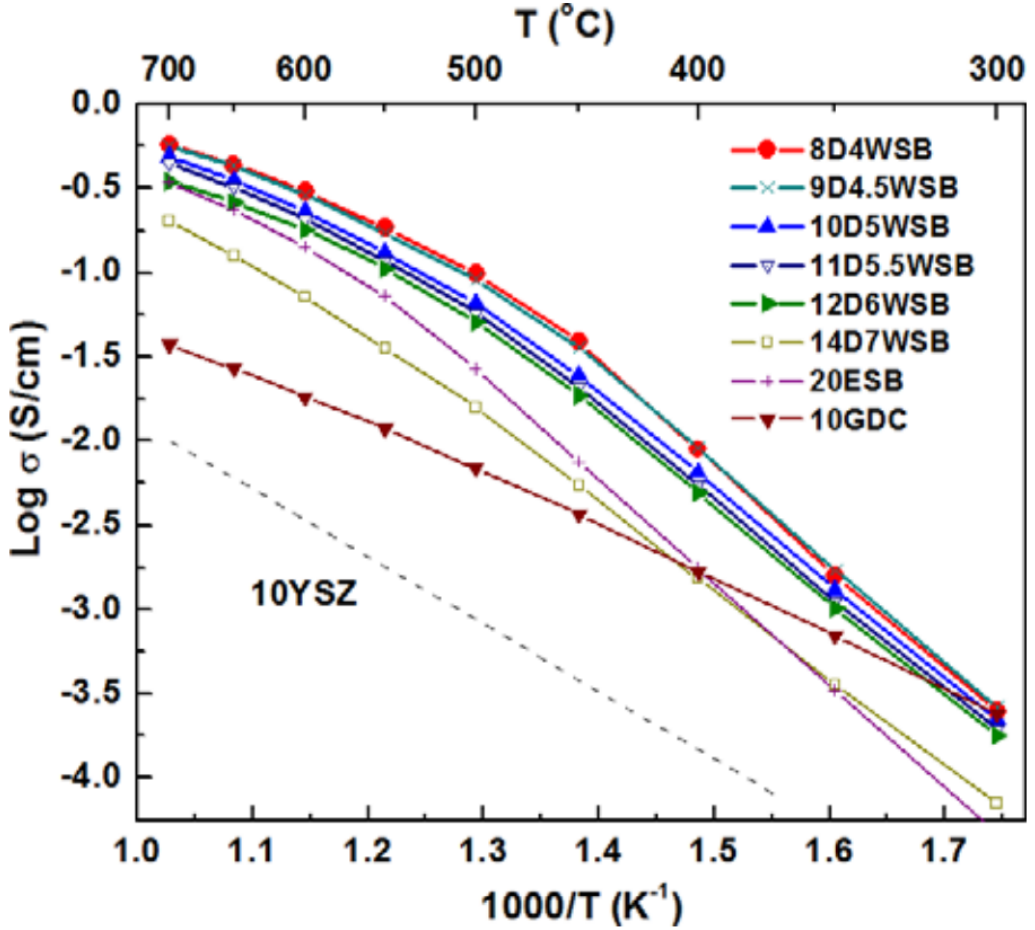
Use of two dopants allows for lower dopant concentration, higher conductivities

500°C



700°C





Jung, D.W., Duncan, K.L., Wachsman, E.D., "Effect of total dopant concentration and dopant ratio on conductivity of $(DyO_{1.5})_x$-$(WO_3)_y$-$(BiO_{1.5})_{1-x-y}$",. *Acta Materialia*, **2010**, *58*, 355-363; Jiang, N., Wachsman, E.D., "A higher conductivity Bi_2O_3-based electrolyte ", *Solid State Ionics*, **2002**, *150*, 347-353

Conclusions

- δ-Bi_2O_3 promises very high conductivities, need to stabilize the high temperature structure below transformation temperature
- Structure experiences anion vacancy ordering at low temperatures, which can be limited by a low concentration of large radii dopant
- Double-doping allows for reduced concentration of dopant necessary to stabilize cubic structure
- Highest conductivity of ceramic electrolyte achieved with $Dy_{0.08}W_{0.04}Bi_{0.88}O_{1.56}$