Engineering Density of States of Earth Abundant Semiconductors for Enhanced Thermoelectric Power Factor

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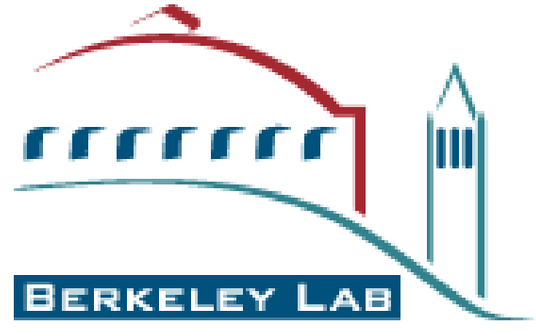


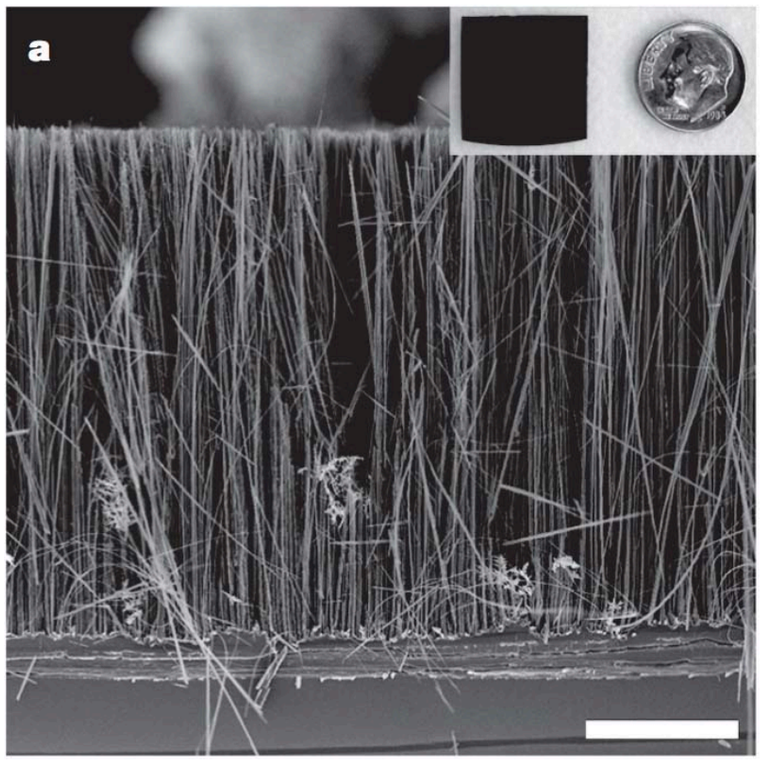
Enhancing ZT by reducing thermal conductivity

$$ZT = \frac{S^2 \sigma T}{\kappa_l + \kappa_e}$$

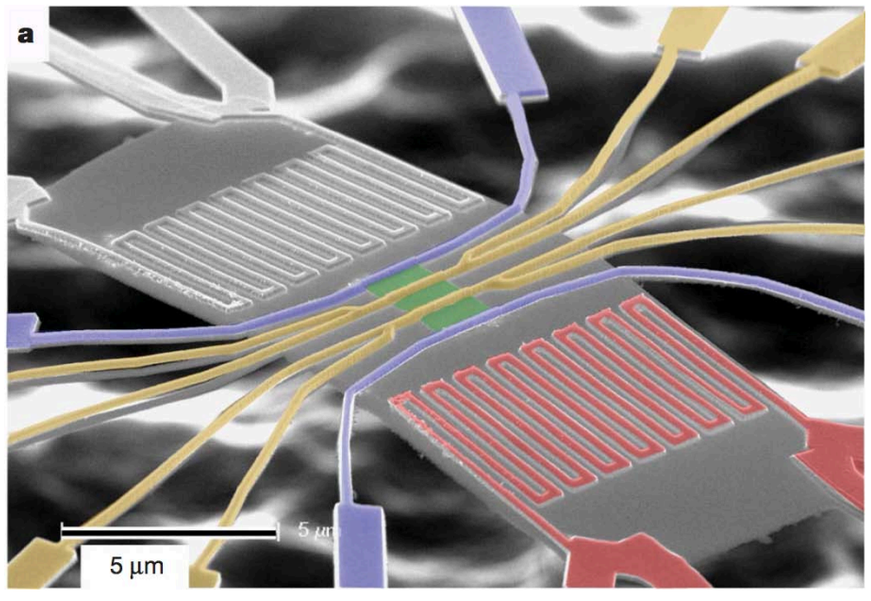
Reducing κ_l through nanostructuring

- Bi_2Te_3/Sb_2Te_3 thin-film SLs (Nature **413**, 597 (2001))
- $Ag(Pb_{1-x}Sn_x)_mSbTe_{2+m}$ NCs (Adv. Mater. **18**, 1170 (2006))
- PbSeTe/PbTe-based QDSLs (Science **297**, 2229 (2002))

Si NW

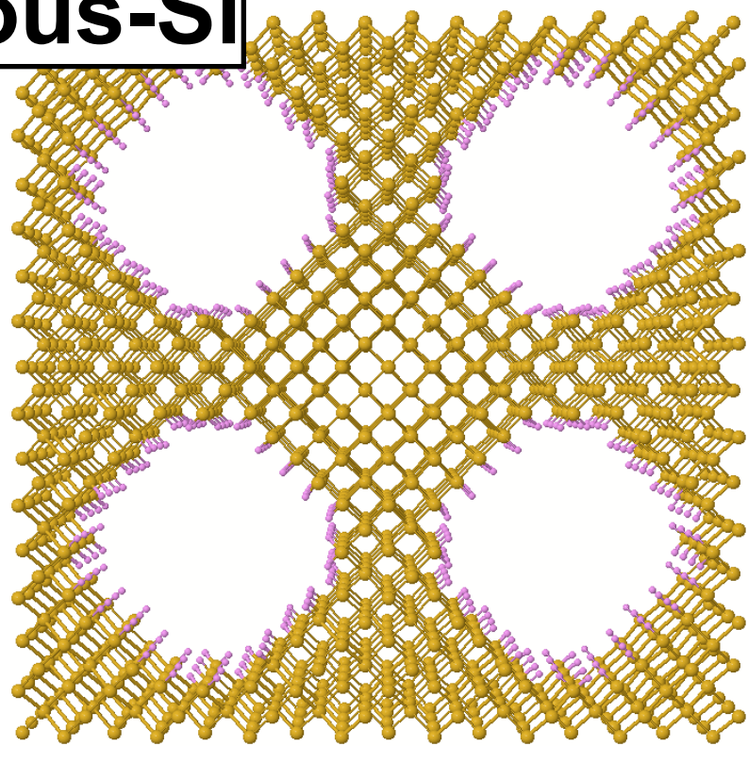


(Hochbaum *et al*., Nature **451**, 163 (2008))



(Boukai *et al*., Nature **451**, 168 (2008))

porous-Si



(Lee *et al*., Nano Lett. **8**, 3750 (2008))

Enhancing ZT by enhancing power factor

$$ZT = \frac{S^2 \sigma T}{\kappa_l + \kappa_e}$$

Increasing $S^2\sigma$ through DOS engineering

If E_F is tuned to near a peak in DOS, $S^2\sigma$ would be sharply increased (PNAS 93, 7436 (1996))

- $\sigma(\varepsilon) = D(\varepsilon)\, f(\varepsilon)\mu(\varepsilon)$
- $D(\varepsilon)$: density of states
- $f(\varepsilon)$: Fermi function
- $\mu(\varepsilon)$: carrier mobility

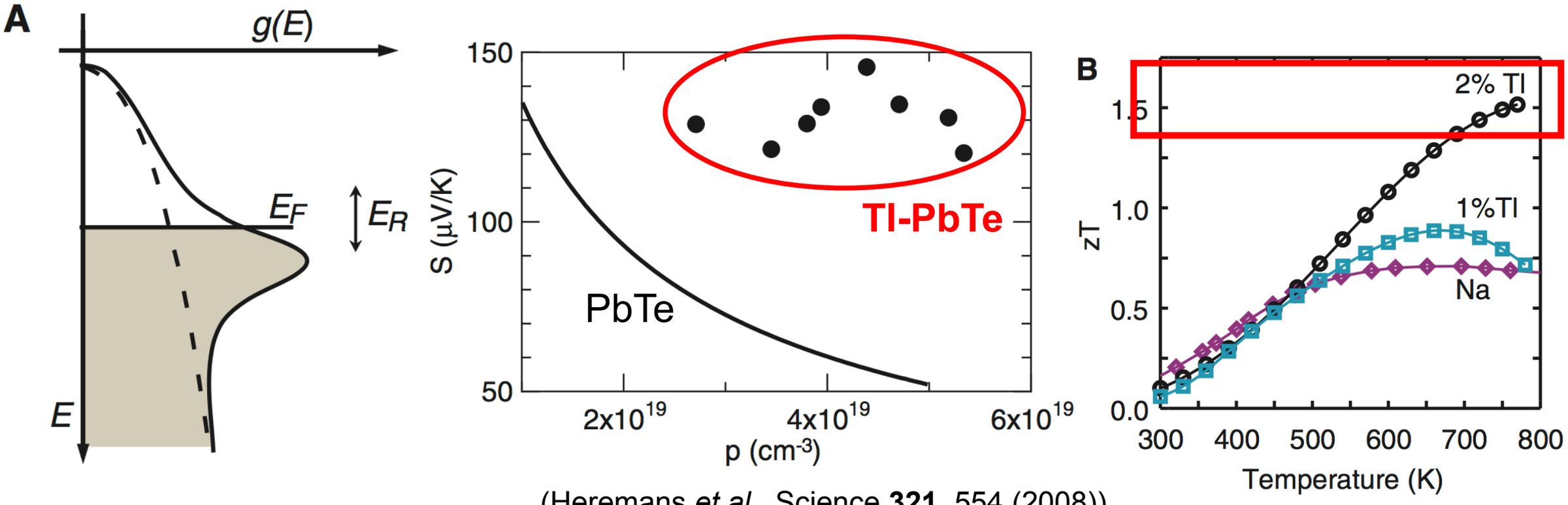
$$\begin{aligned} S &= \frac{\pi^2 k_B^2 T}{3q}\left[\frac{d(\ln(\sigma(\epsilon)))}{d\epsilon}\right]_{\epsilon=\epsilon_F} \\ &= \frac{\pi^2 k_B^2 T}{3q}\left[\frac{1}{D}\frac{dD(\epsilon)}{d\epsilon} + \frac{1}{f}\frac{df(\epsilon)}{d\epsilon} + \frac{1}{\mu}\frac{d\mu(\epsilon)}{d\epsilon}\right]_{\epsilon=\epsilon_F} \end{aligned}$$

Enhancing ZT

$$ZT = \frac{S^2 \sigma T}{\kappa_l + \kappa_e}$$

Increasing $S^2\sigma$ through DOS engineering

We seek to engineer DOS in earth-abundant materials



(Heremans *et al.*, Science **321**, 554 (2008))

How to control DOS?

Highly-mismatched alloys (HMAs)

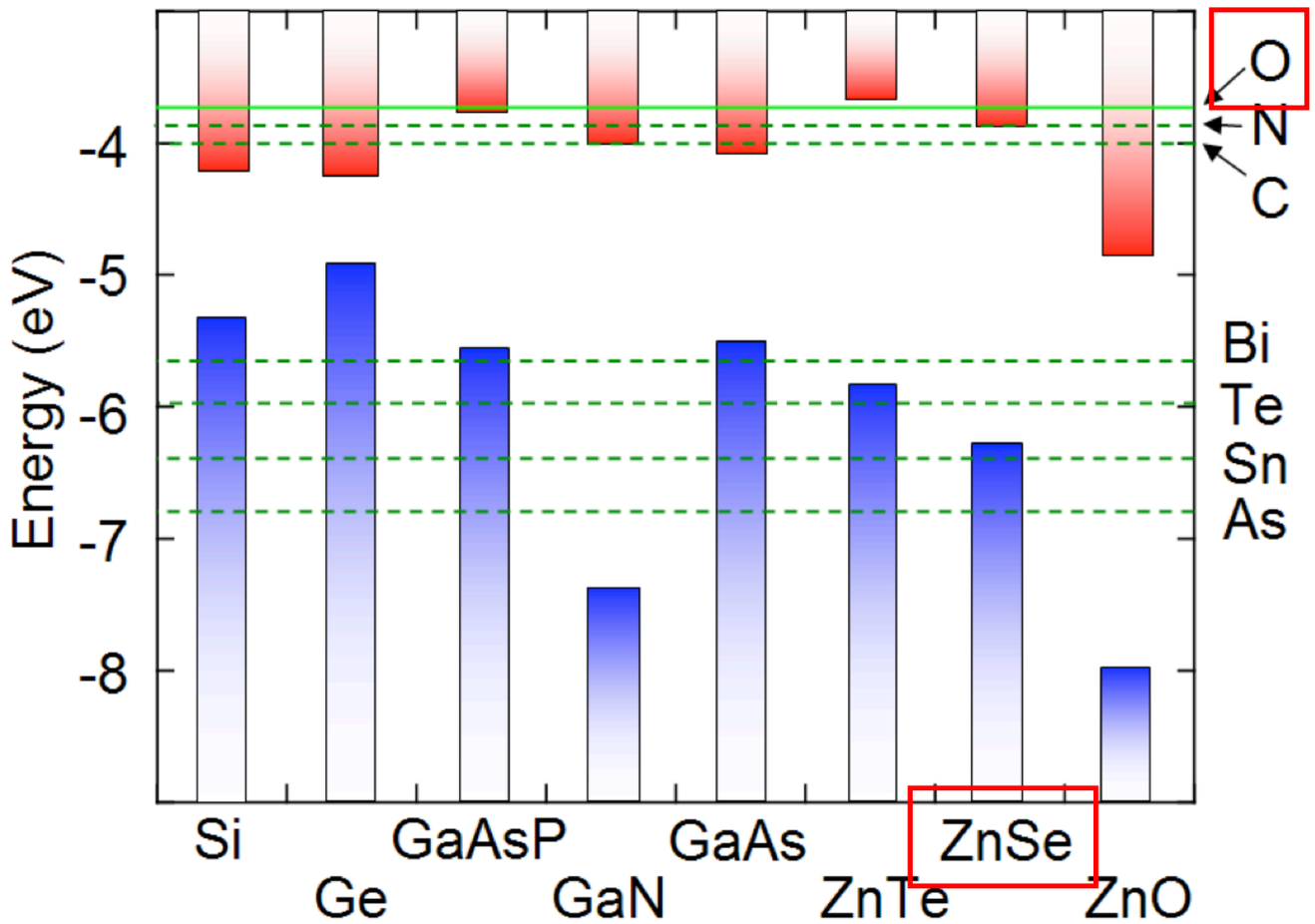
- Isovalent, but electronegativity-mismatched constituents

  ® control over electronic structure and DOS

- Studied for optoelectronic applications

  $Ge_{1-x}Sn_x$ (PRB 77, 073202 (2008)),
  $GaN_{1-x}As_x$ (PRB 70, 115214 (2004)),
  $ZnTe_{1-x}Se_x$ (PRL 85, 1552 (2000)),
  review (Semi.Sci.Tech, 17, 860(2002)

- Few study on thermoelectric applications

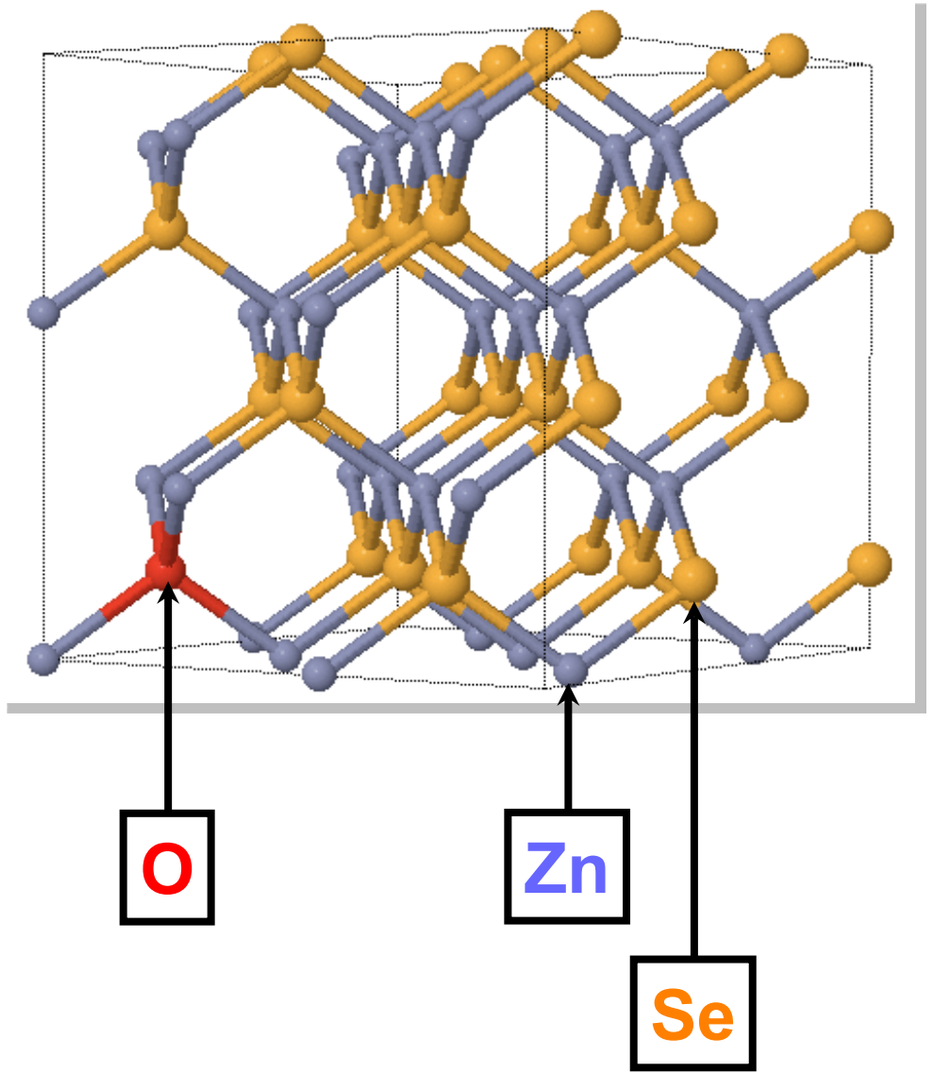


$ZnSe_{1-x}O_x$

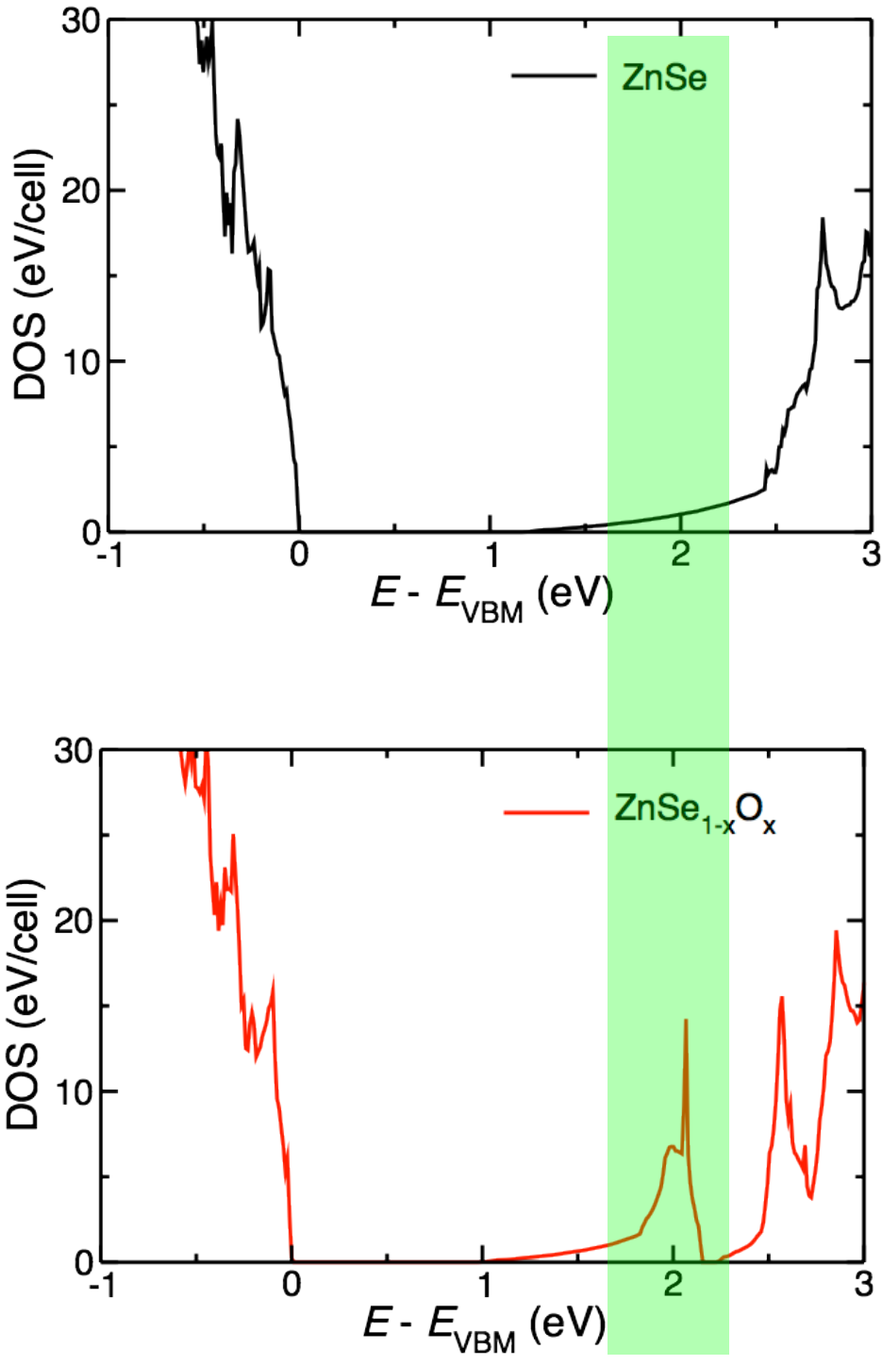
First-Principles Computation

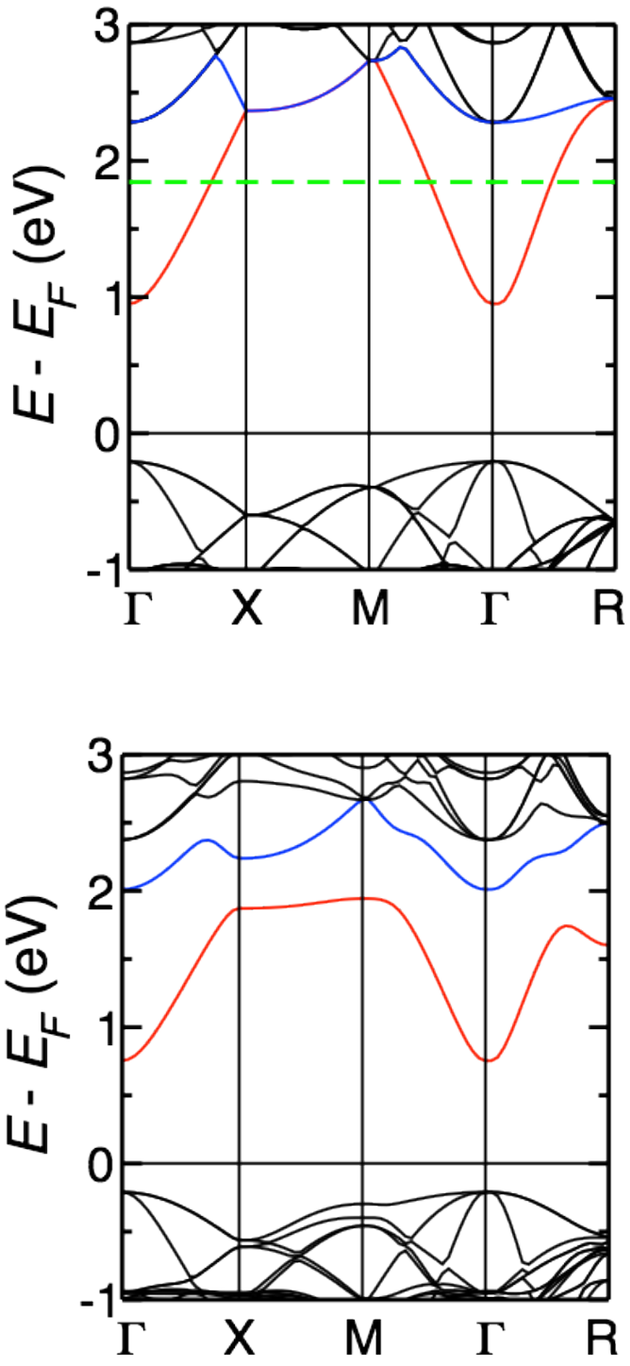
Calculate S and σ for $ZnSe_{1-x}O_x$

- Density functional theory + Boltzmann transport equation (constant relaxation time approximation)
- 64 atoms/cell
- a or 2 O atoms/32 Se atoms (x~3 or 6%)
- 600 eV plane wave cutoff
- Generalized Gradient Approx. for E_{xc}
- 120 irreducible k-points



$ZnSe_{1-x}O_x$: DOS and bands





ZnSe

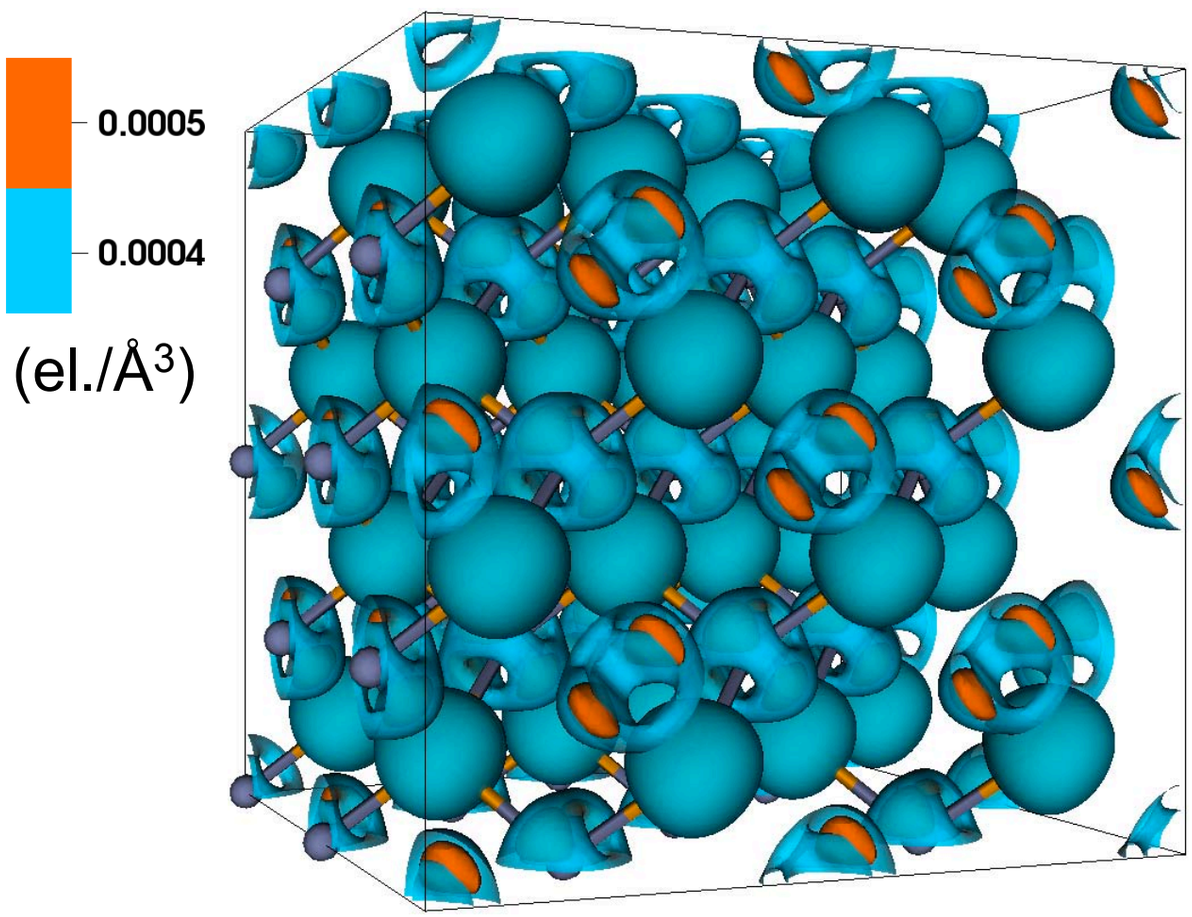
$ZnSe_{1-x}O_x$

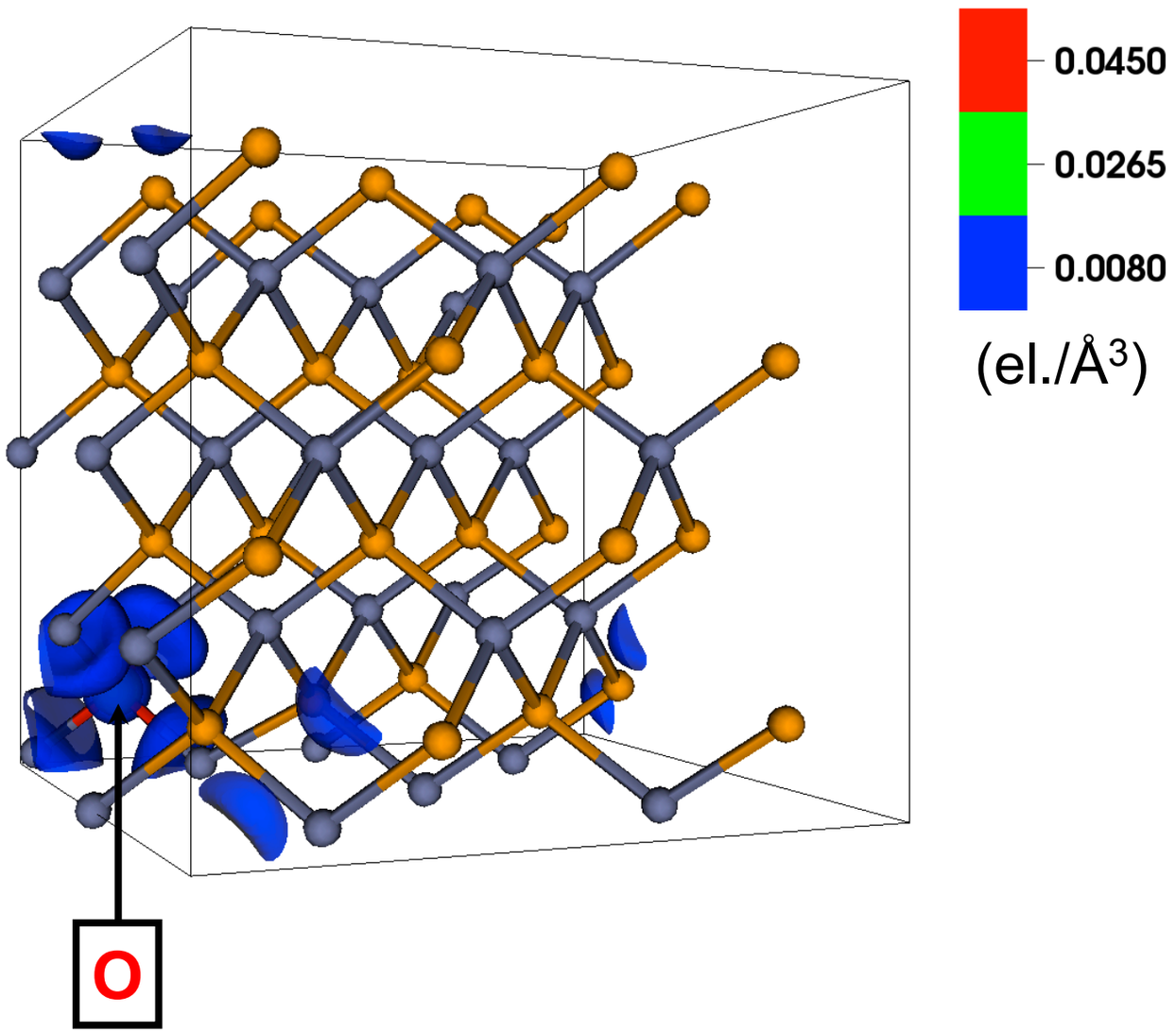
(Lee, Wu and Grossman, Phys. Rev. Lett., 104, 016602 (2010))

$ZnSe_{1-x}O_x$: Charge density near DOS peak

ZnSe

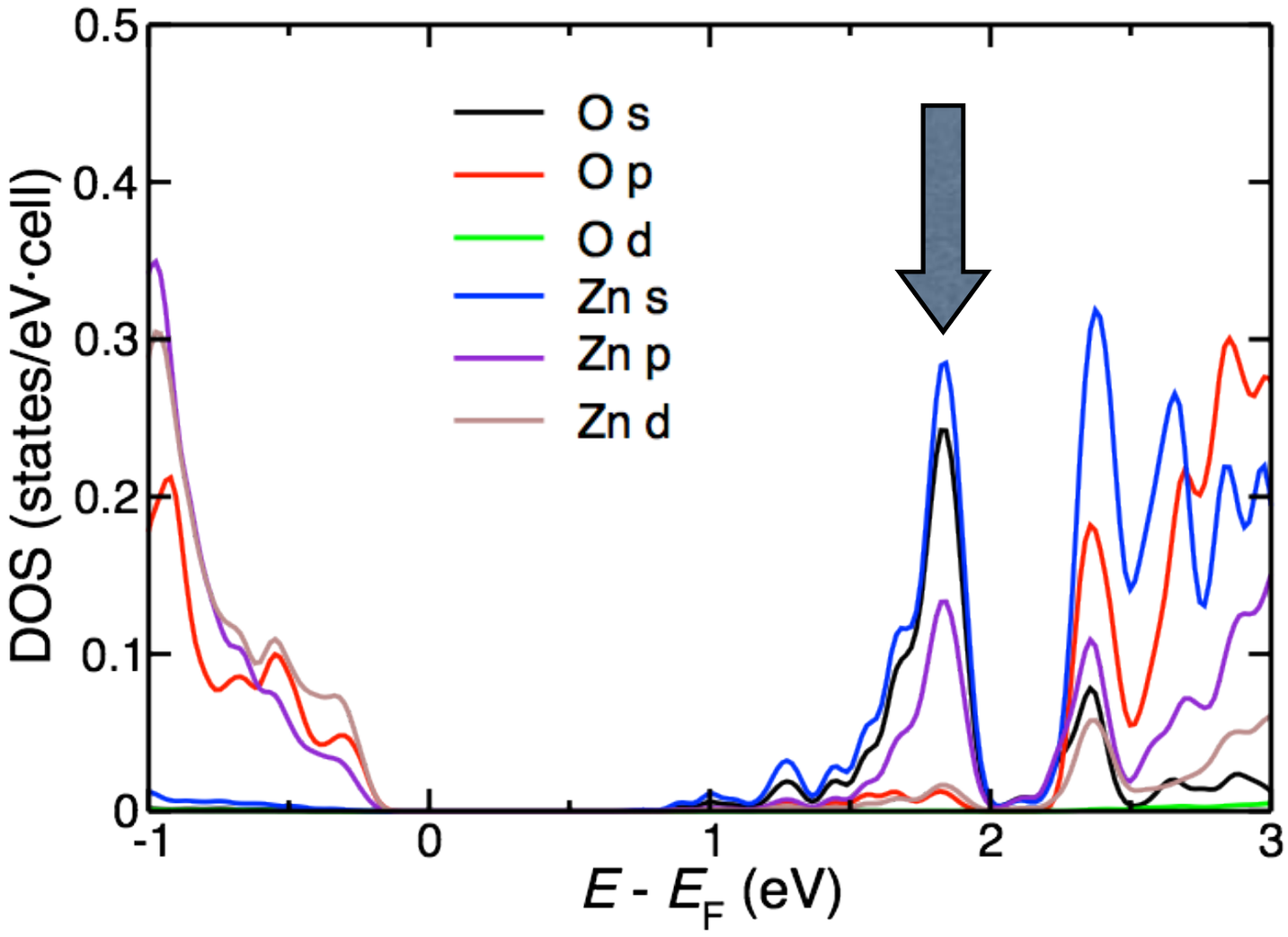
$ZnSe_{1-x}O_x$





$ZnSe_{1-x}O_x$: Why peak occurs?

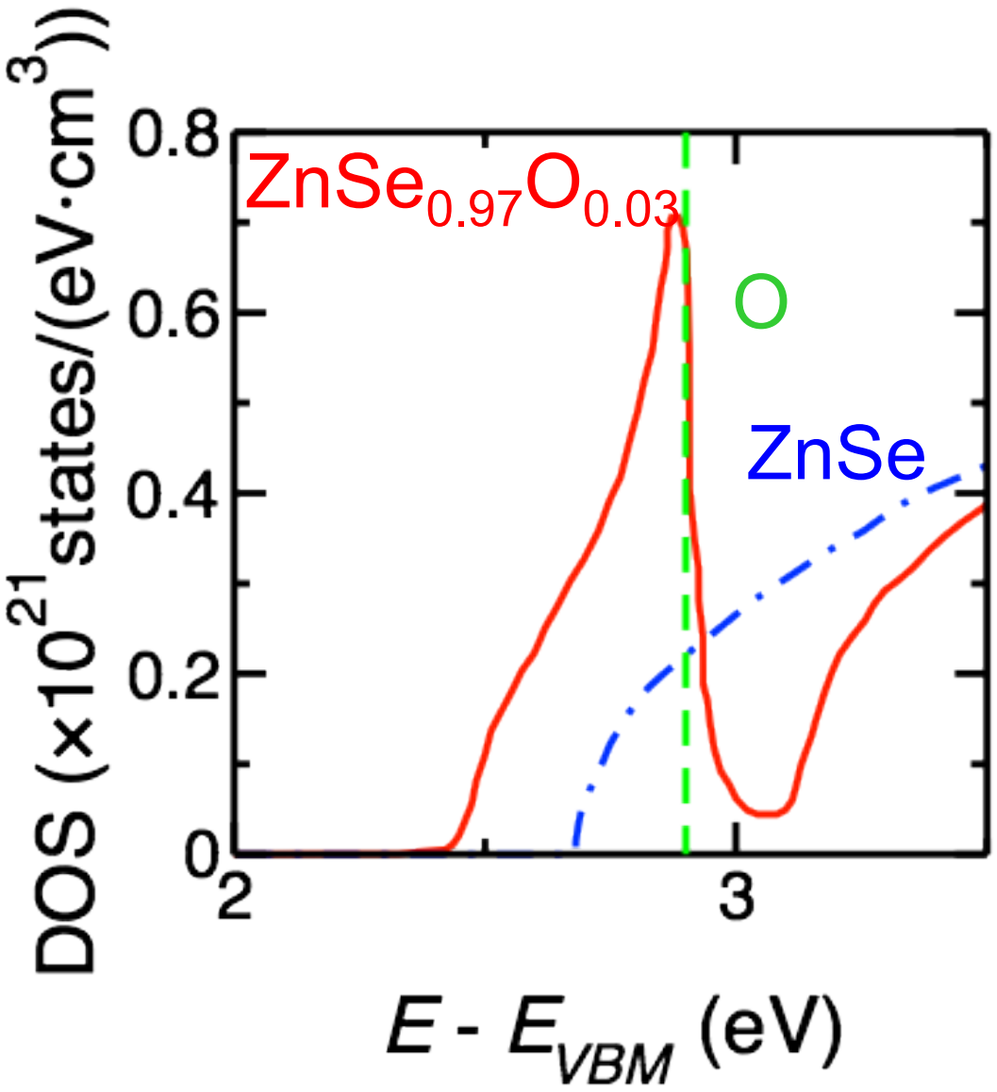
Projected DOS

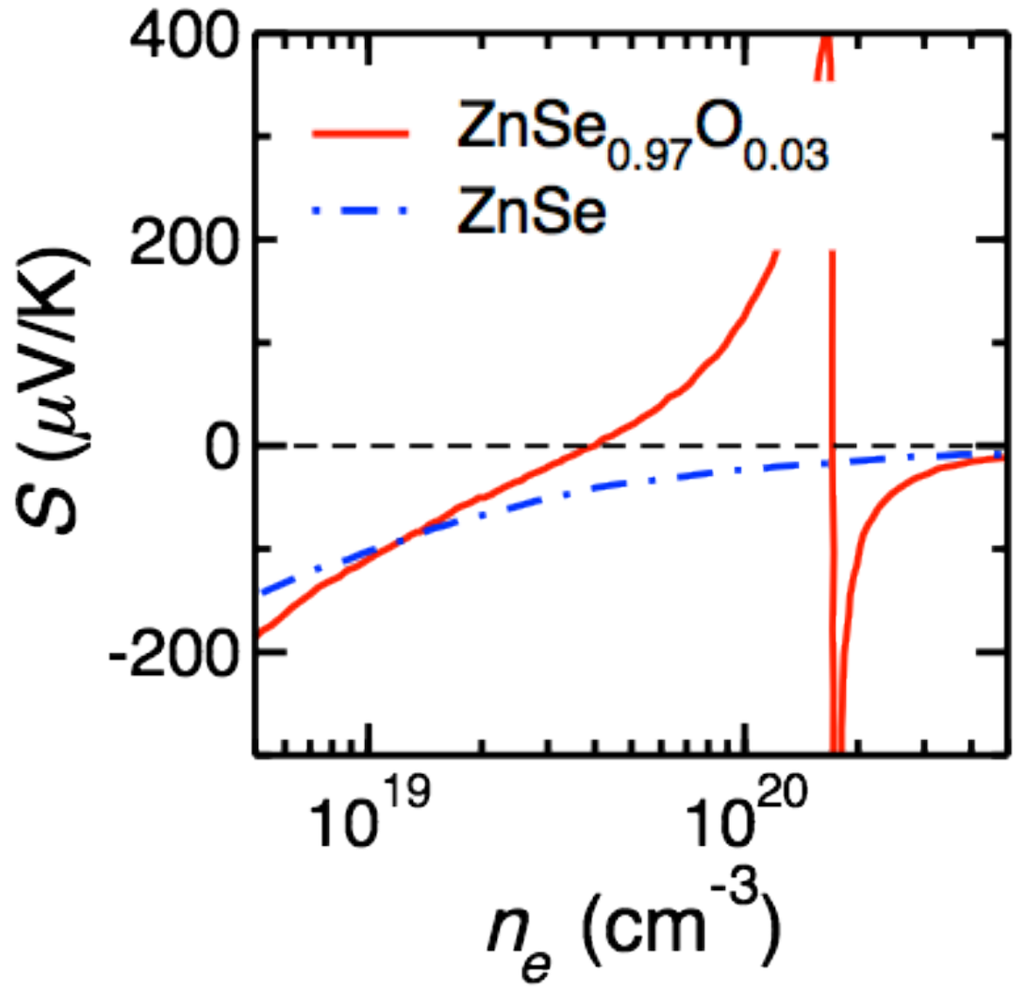


Hybridization mainly between O-s and Zn-p states

$ZnSe_{1-x}O_x$: Seebeck coefficient and power factor

- |S| is up to 30 times increased from that of pure ZnSe under optimal doping.
- $S^2\sigma$ is estimated to be enhanced ~180 times compared to that of ZnSe (extended states are mixed into the O-derived states by hybridization).

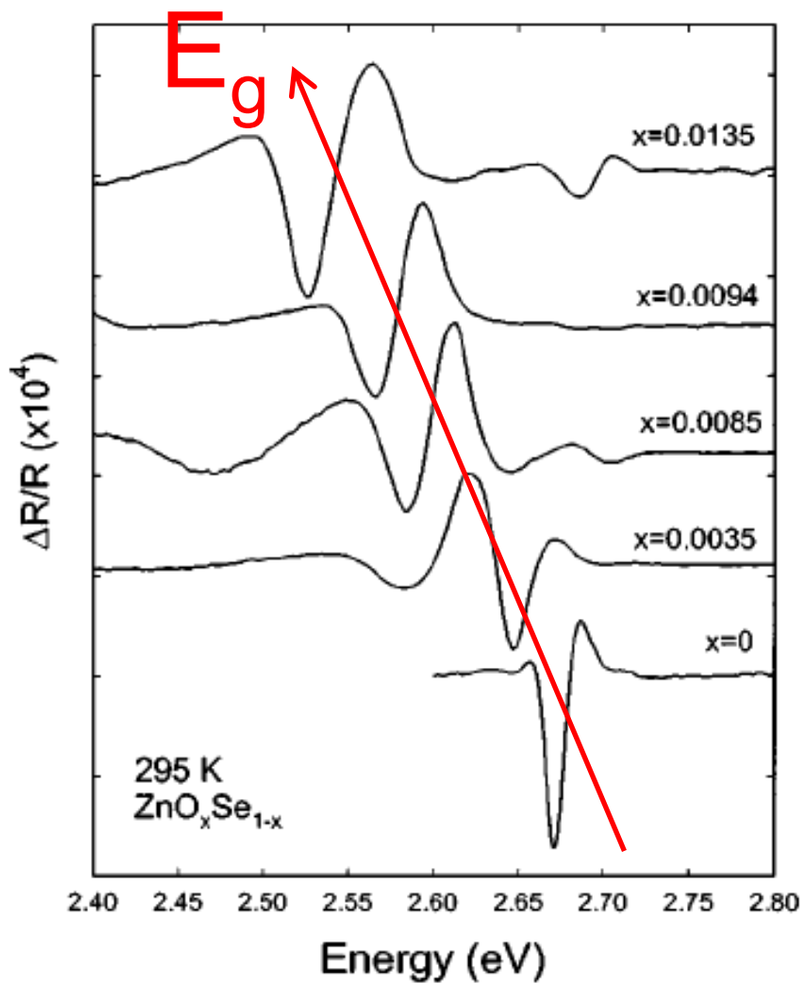


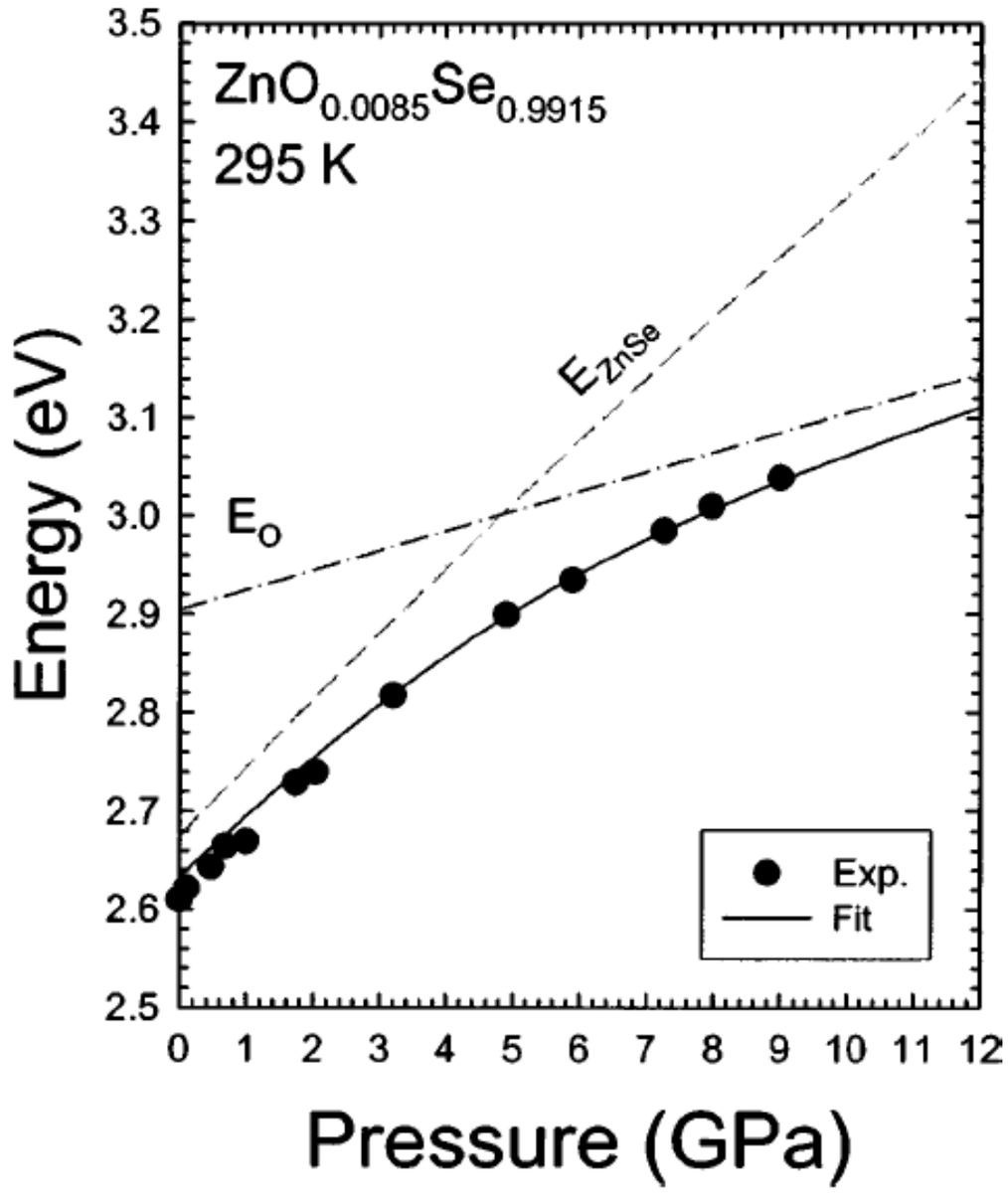


(Lee, Wu and Grossman, Phys. Rev. Lett., 104, 016602 (2010))

Synthesizing and doping HMAs - challenges

- These materials are immiscible alloys, - requiring highly non-equilibrium synthesis techniques
- These alloys are all isoelectronic, - additional dopant doping is needed to introduce free carriers





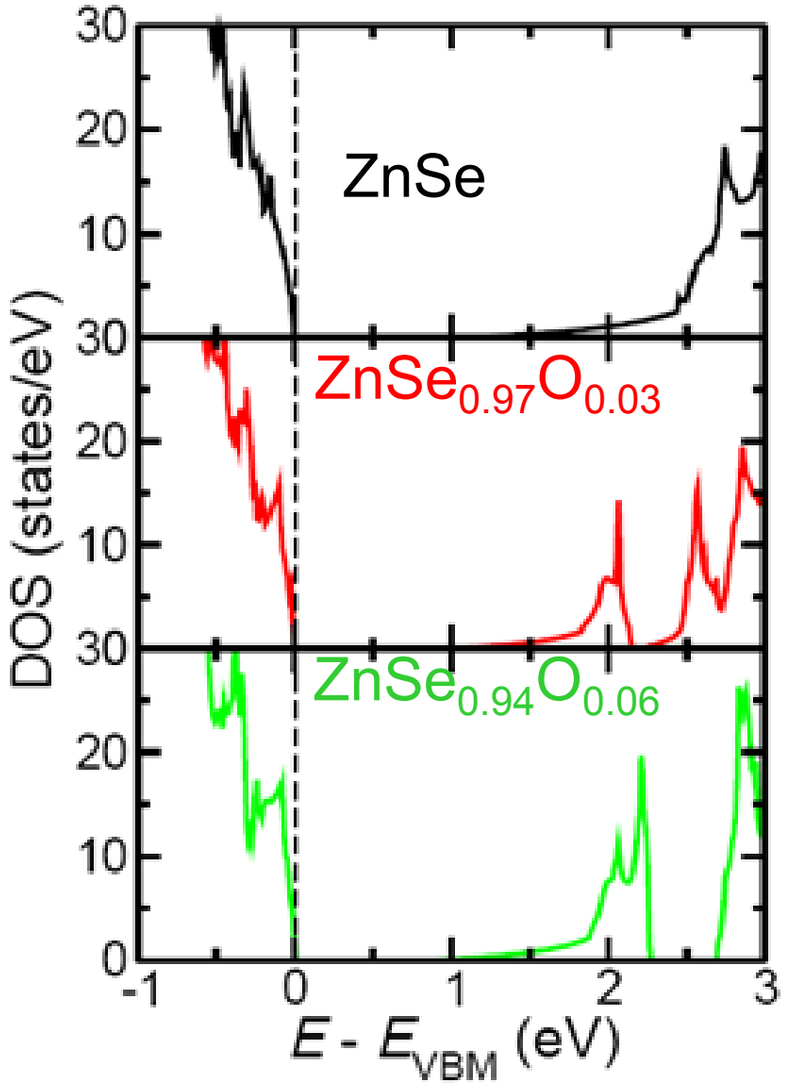
APL, 83, 299(2003); APL 95, 151907(2009)

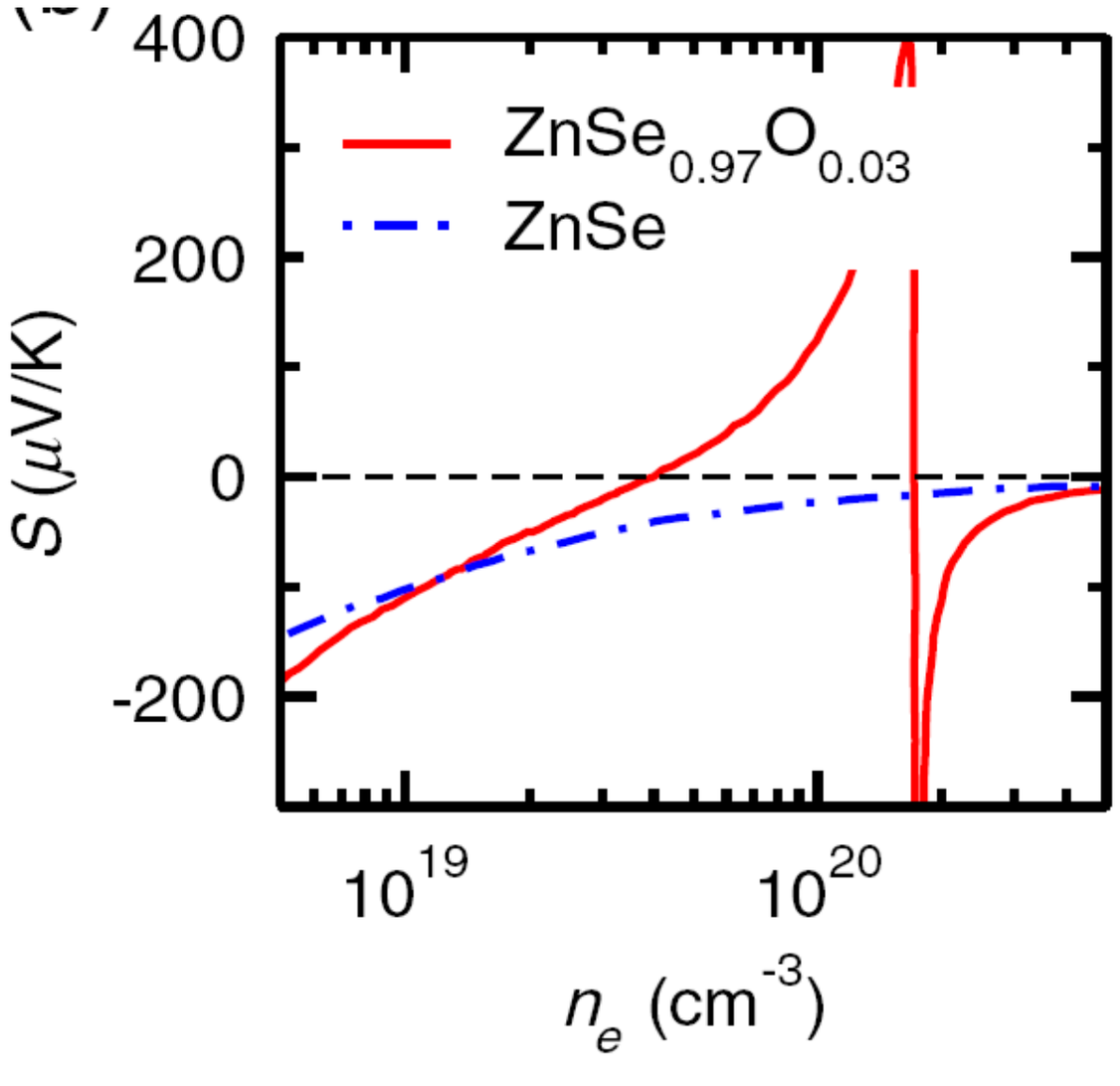
Summary

- DOS in earth-abundant semiconductors can be engineered to enhance thermoelectric thermopower and power factor.
- Example: in dilute $ZnSe_{1-x}O_x$ alloys, a peak forms in the DOS via hybridization of O-s with Zn-p states.
- Under optimal doping, |S| is predicted to increase by 30 times, and $S^2\sigma$ by ~180 times.
- Similar effect exists in a wide range of group IV, III-V and II-VI highly mismatched alloys (HMAs) as a new class of abundant thermoelectric materials (both n and p).

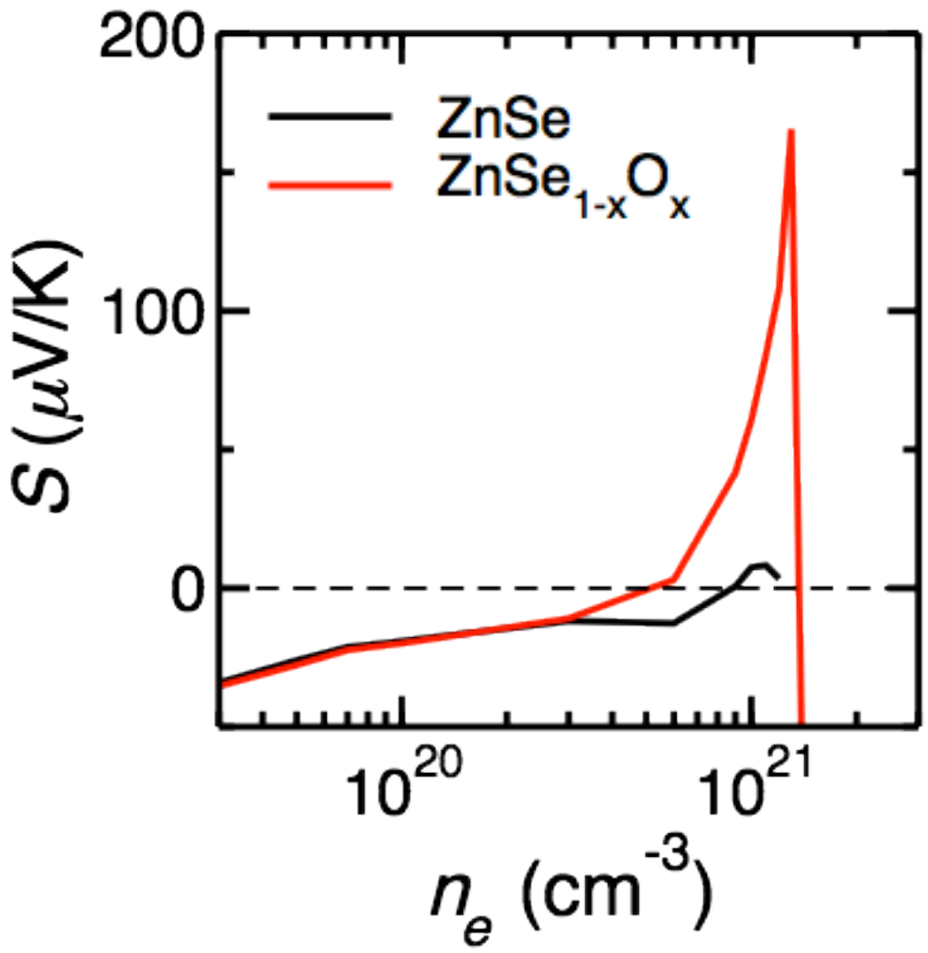
Work supported by NSF and DOE.

Lee, et al, Phys. Rev. Lett., 104, 016602 (2010)
Yu, et al, Phys. Rev. Lett., 91, 246403 (2003)
Wu, et al, Phys. Rev. B, 65, 233210 (2002)

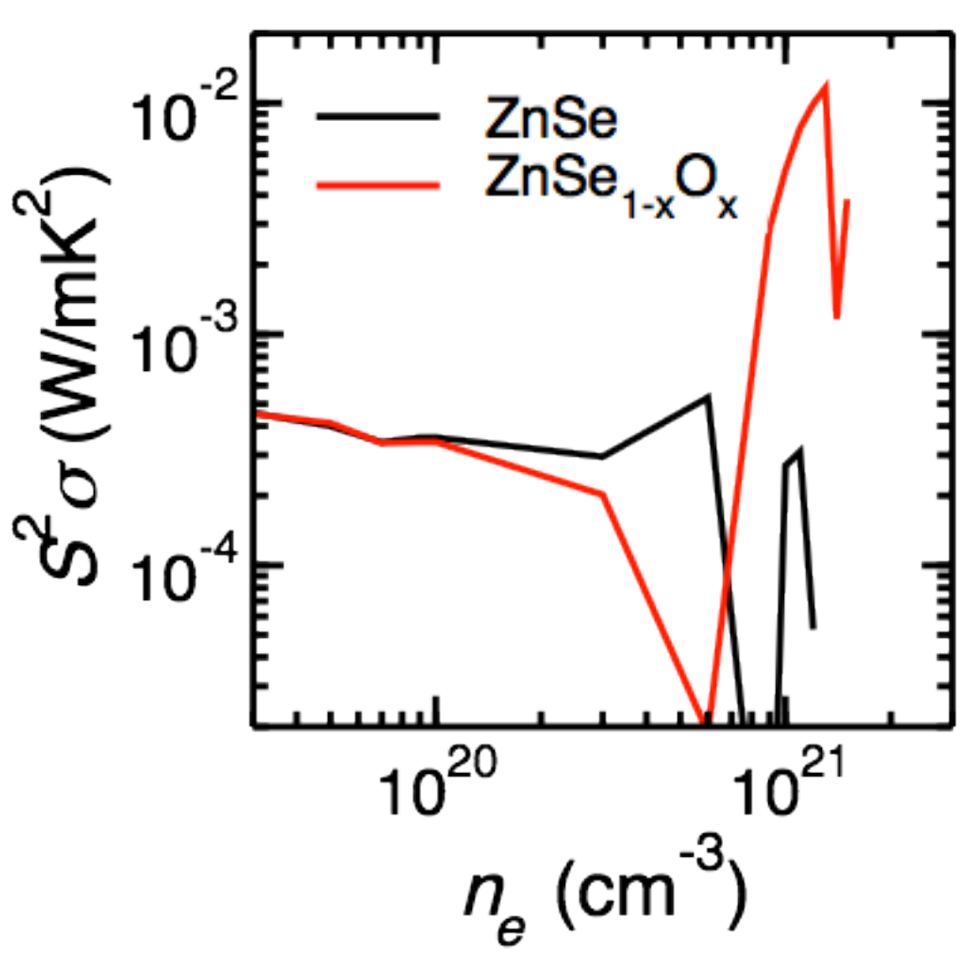

ZnSe
$ZnSe_{0.97}O_{0.03}$
$ZnSe_{0.94}O_{0.06}$
DOS (states/eV)
E - E_{VBM} (eV)


$ZnSe_{0.97}O_{0.03}$
ZnSe
S (μV/K)
n_e (cm^{-3})

Seebeck coefficient

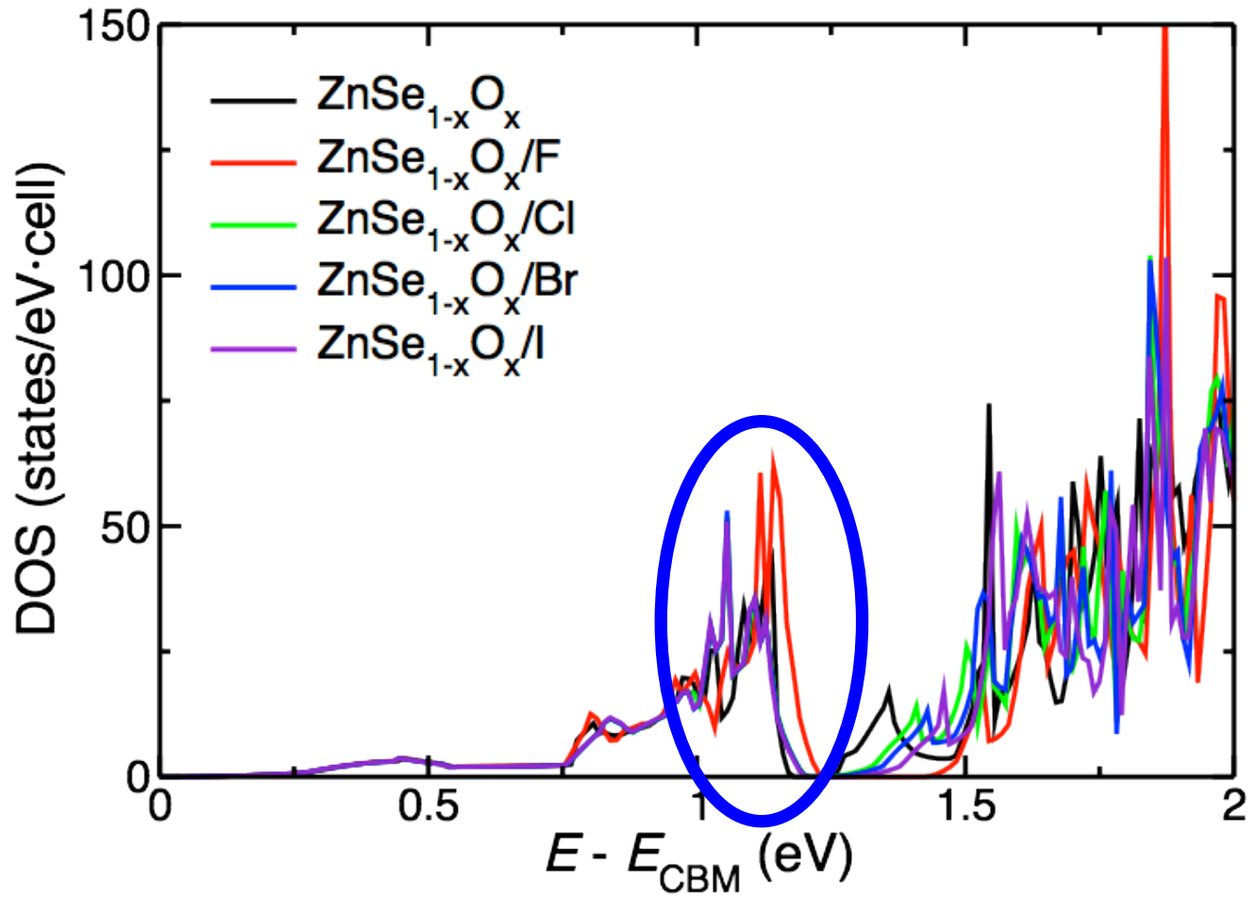


Power factor



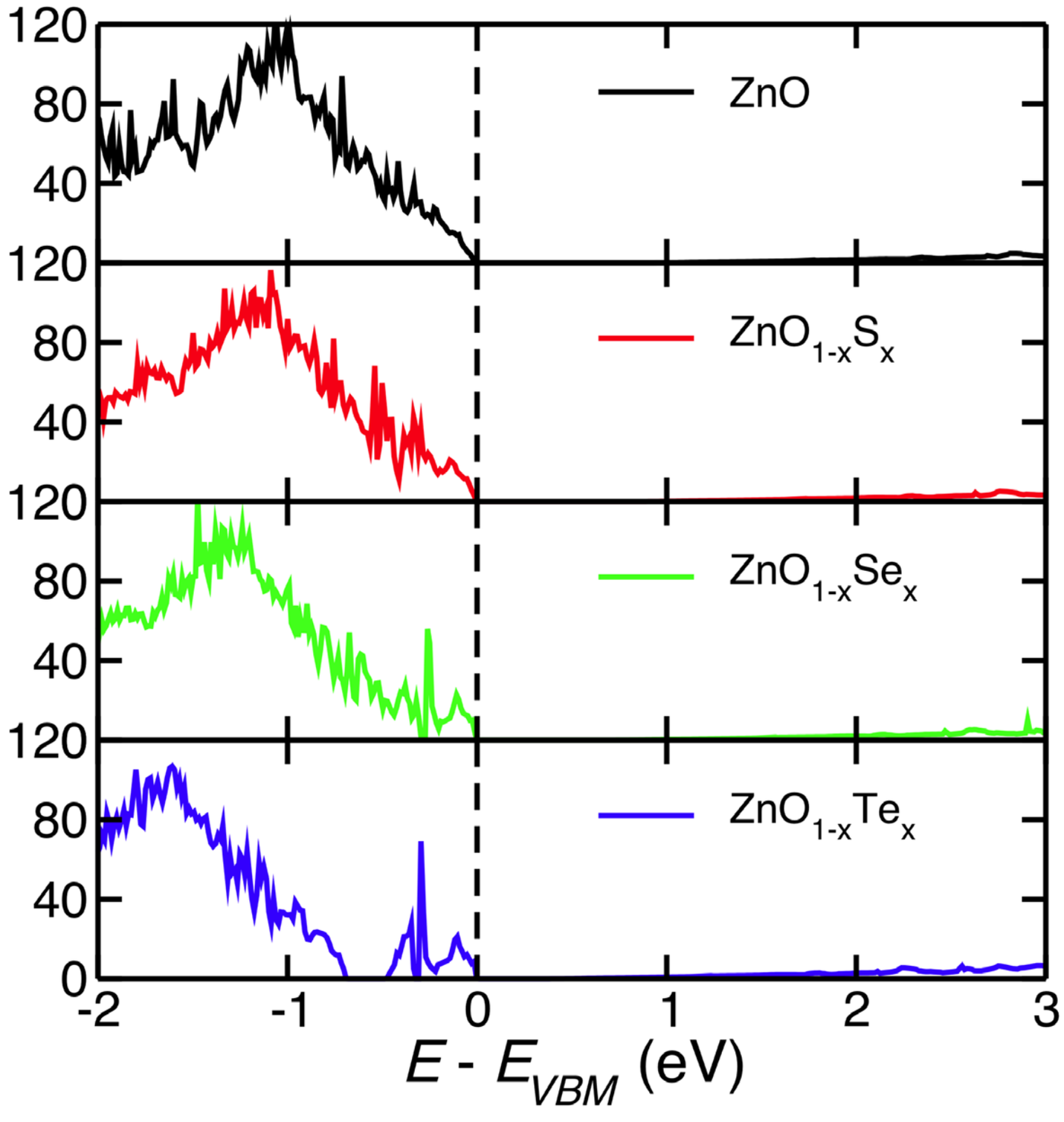
$ZnSe_{1-x}O_x$: Doping effect

- Effect of doping on DOS
  - Supercell with 128 Zn, 123 Se, 4 O and 1 halogen atoms
  - This would correspond to $1.7\times10^{20}/cm^3$ of carrier concentration.



DOS changes little even after free-carrier doping

VB-DOS of ZnO-based HMAs



DOS of GaN-based HMAs