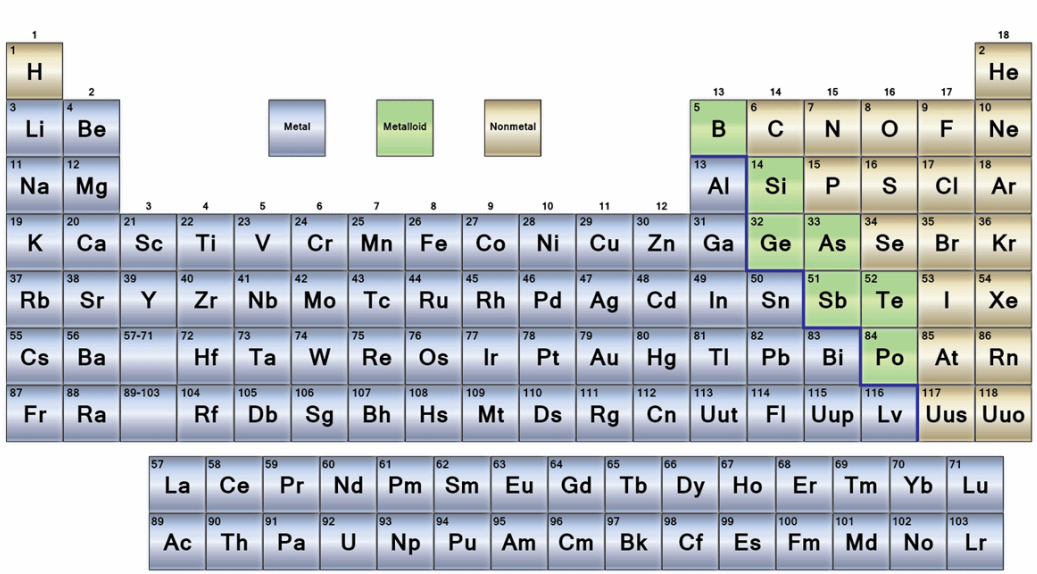
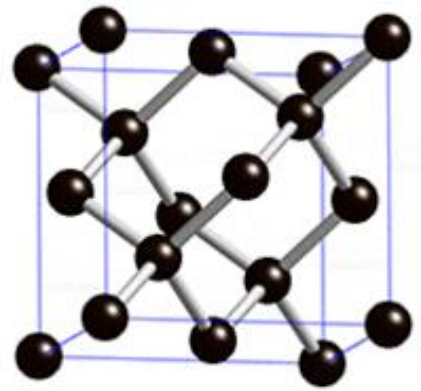
# What is a semiconductor

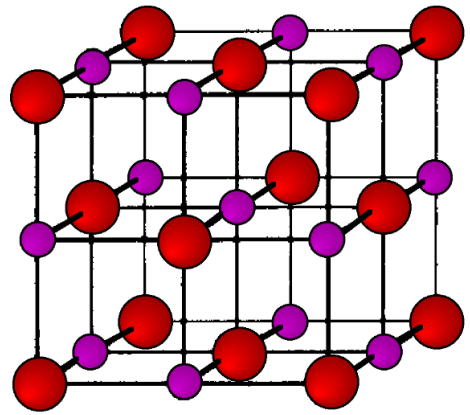



| IB | IIB | IIIA | IVA | VA | VIA | VIIA | VIIIA |
|---|---|---|---|---|---|---|---|
| | | | | | | | 2 He 4.003 |
| | | 5 B 10.811 | 6 C 12.011 | 7 N 14.007 | 8 O 15.999 | 9 F 18.998 | 10 Ne 20.183 |
| | | 13 Al 26.982 | 14 Si 28.086 | 15 P 30.974 | 16 S 32.064 | 17 Cl 35.453 | 18 Ar 39.948 |
| 29 Cu 63.54 | 30 Zn 65.37 | 31 Ga 69.72 | 32 Ge 72.59 | 33 As 74.922 | 34 Se 78.96 | 35 Br 79.909 | 36 Kr 83.80 |
| 47 Ag 107.870 | 48 Cd 112.40 | 49 In 114.82 | 50 Sn 118.69 | 51 Sb 121.75 | 52 Te 127.60 | 53 I 126.904 | 54 Xe 131.30 |
| 79 Au 196.967 | 80 Hg 200.59 | 81 Tl 204.37 | 82 Pb 207.19 | 83 Bi 208.980 | 84 Po (210) | 85 At (210) | 86 Rn (222) |

Diamond structure



Rock-salt structure



*Elemental semiconductors*

*C, Si,Ge*

*Compound semiconductors*

*III-V: GaAs*

*II-VI: CdTe*

*IV-VI: PbTe*

*Complex semiconductors*

*I-III-VI: $AgGaSe_2$*

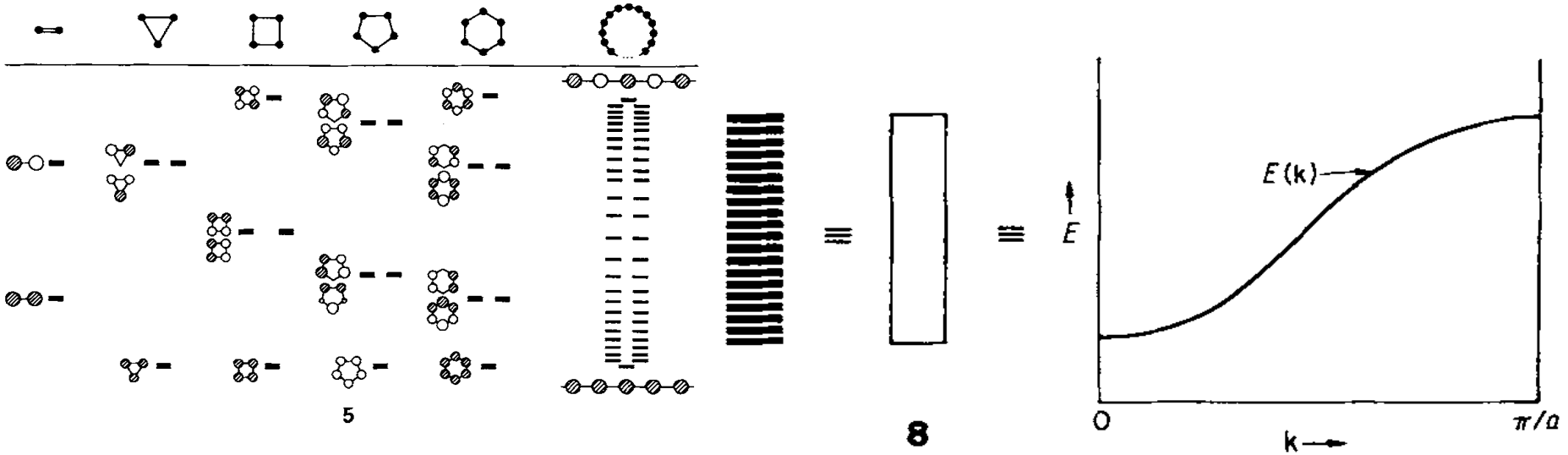
*II-IV-V: $ZnGeP_2$*

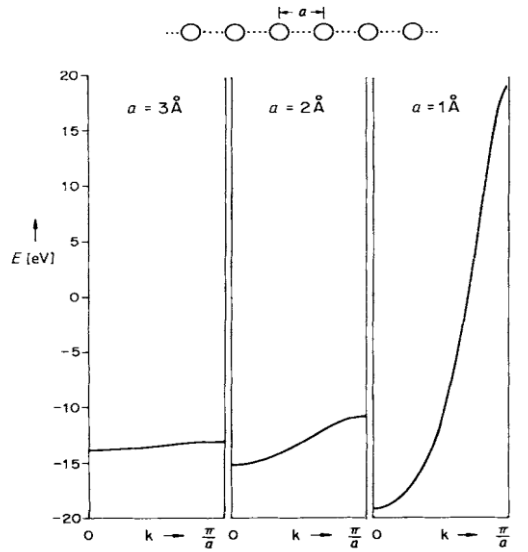
# From molecules to the solid state

Molecules

Solid state

α is the interatomic distance




HOMO and LUMO frontier orbitals

Valence and Conduction bands

α defines the band dispersion in k-space

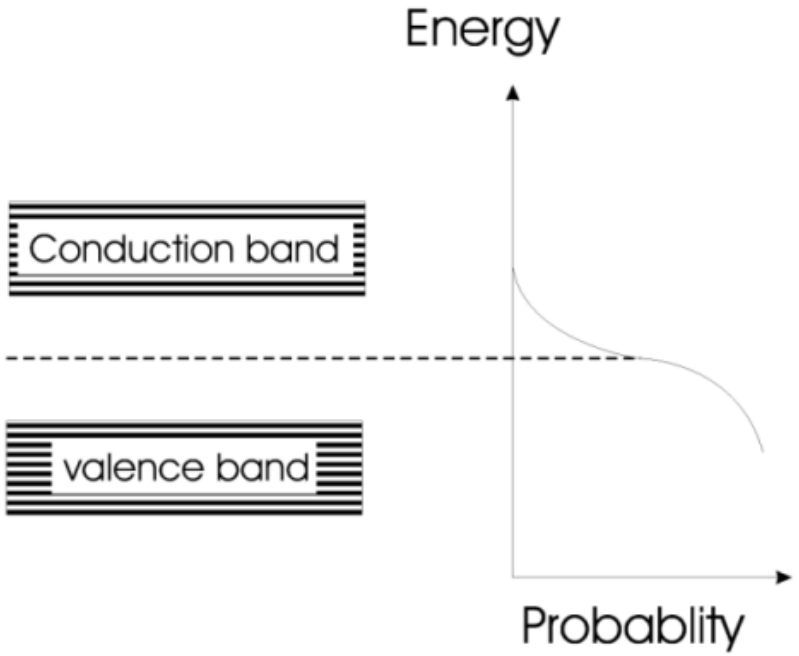
*In the solid state*, α relates to the unit cell parameters in k-space (reciprocal space)

The k-vector denotes the momentum of the electrons moving along the bands (Bloch states)

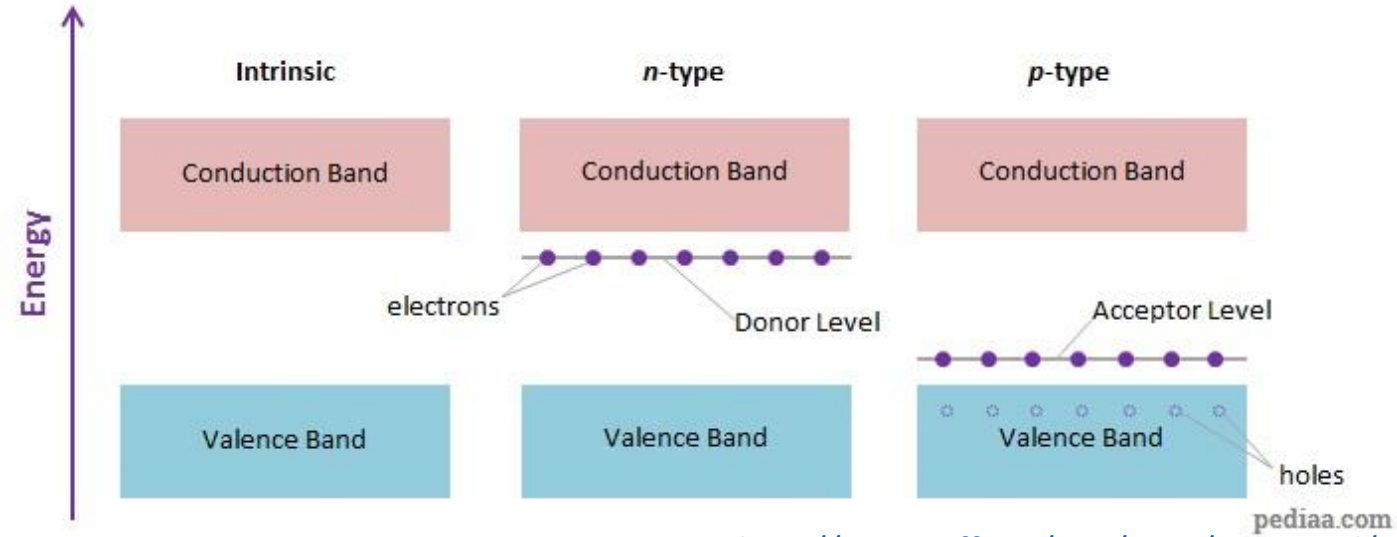
R. Hoffman ***Angew. Chem. Int. Ed.*** *26* ***(1987)*** *846*

# Doped semiconductors and thermally activated behavior of electrons

https://en.wikibooks.org/wiki/Semiconductors/PN_Junctions

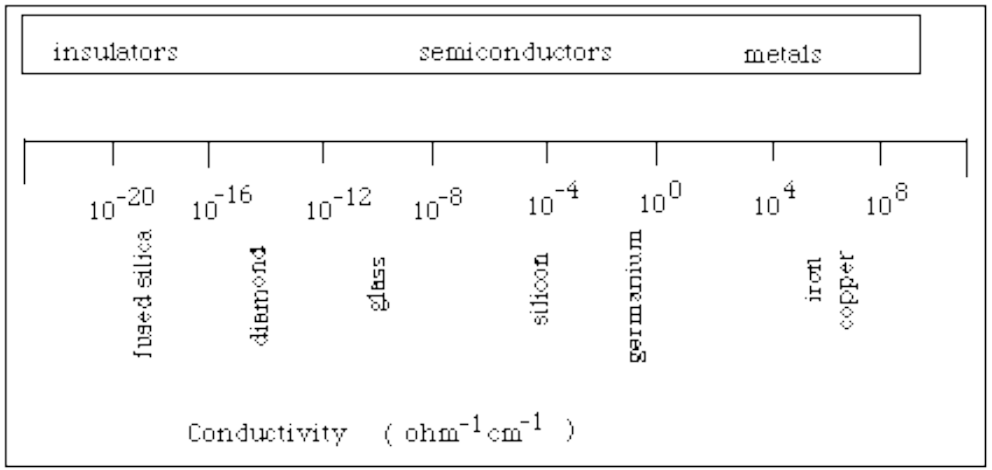



http://pediaa.com/difference-between-p-type-and-n-type-semiconductor/




http://www.ioffe.ru/SVA/NSM/Semicond/index.html

http://matse1.matse.illinois.edu/sc/prin.html




$$\mu = \sigma / ne$$

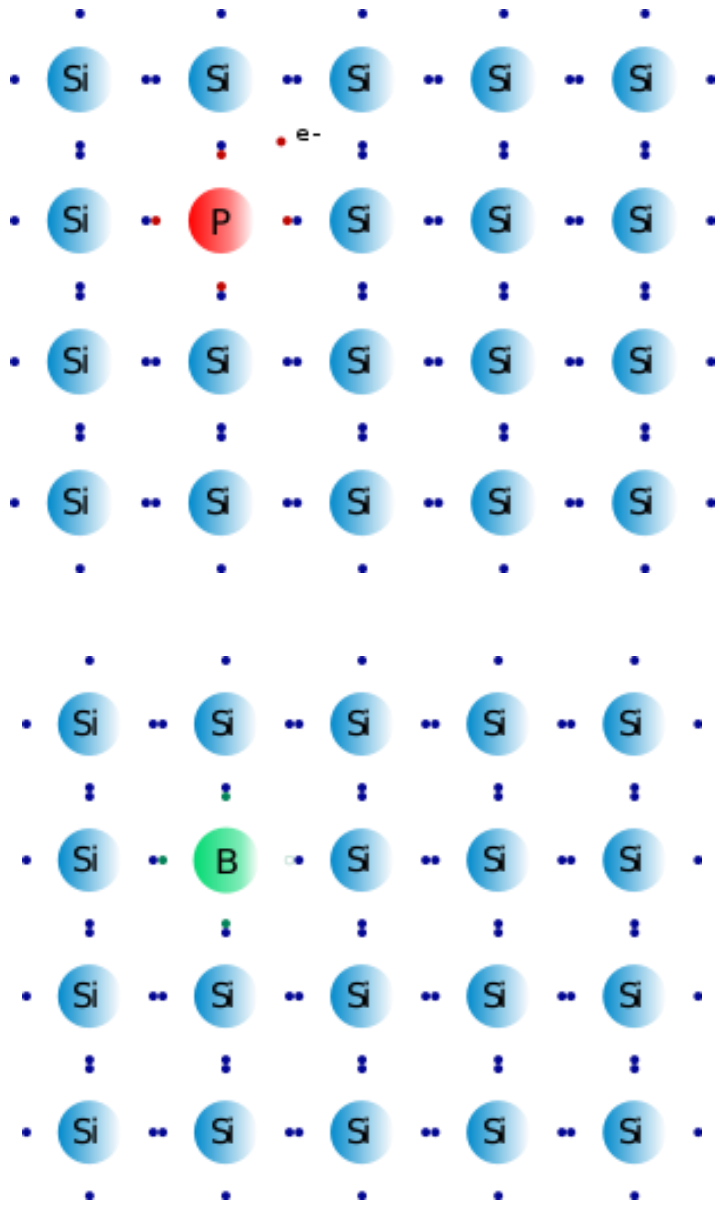
$\mu$ = electron mobility ($cm^2/Vs$)
$\sigma$ = conductivity ($1/\Omega \cdot cm$) = $1/\rho$
$n$ = carrier density ($1/cm^3$)
$e = 1.609 \cdot 10^{-19}$ C

$$n_E = ne^{-(Eg/kT)}$$

*Typical intrinsic semiconductors*

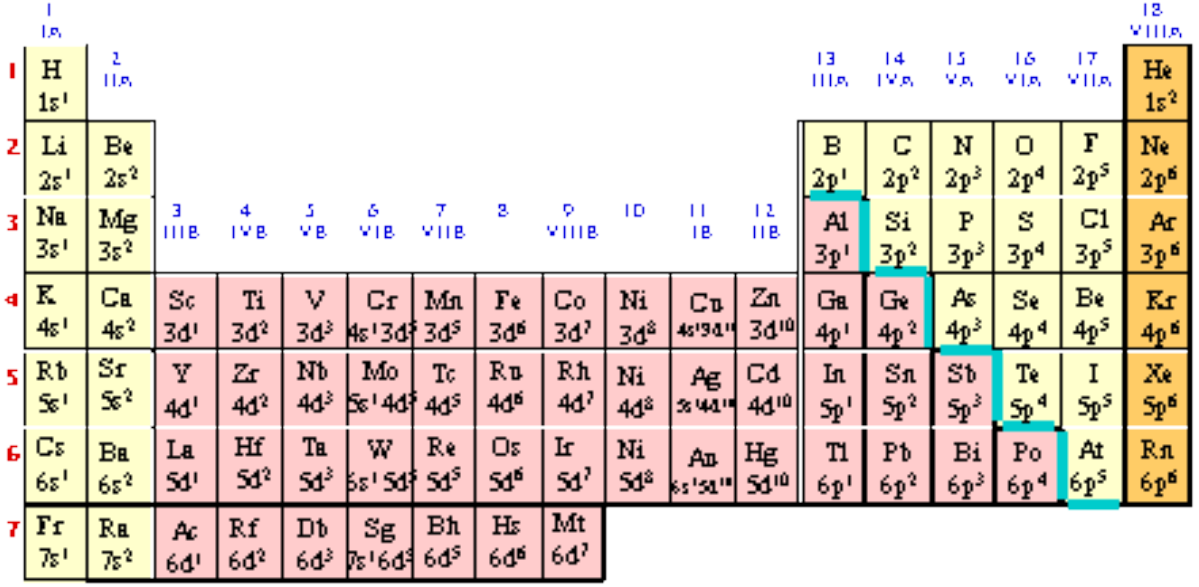
| | | |
|---|---|---|
| GaN: | $n = 0\ cm^{-3}$; | $E_g = 3.20$ eV |
| GaP: | $n = 2 \cdot 10^0\ cm^{-3}$; | $E_g = 2.26$ eV |
| GaAs: | $n = 2 \cdot 10^6\ cm^{-3}$; | $E_g = 1.42$ eV |
| GaSb: | $n = 2 \cdot 10^{12}\ cm^{-3}$; | $E_g = 0.73$ eV |
| PbTe: | $n = 2 \cdot 10^{18}\ cm^{-3}$; | $E_g = 0.30$ eV |

# Examples of doped semiconductors




$TiO_{2-x}$

Excess of electrons:
n-type

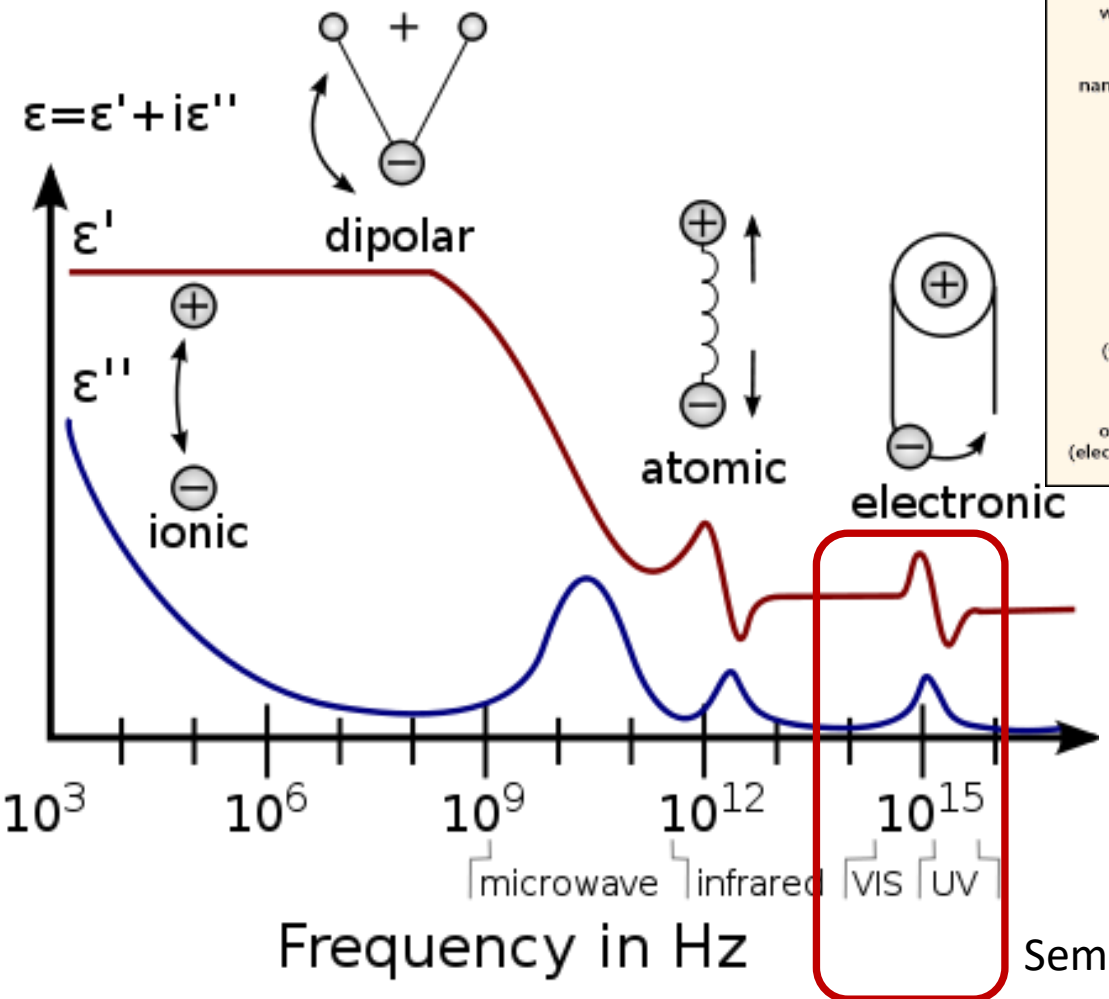



Deficit of electrons:
p-type

$Sn_{1-x}Te$

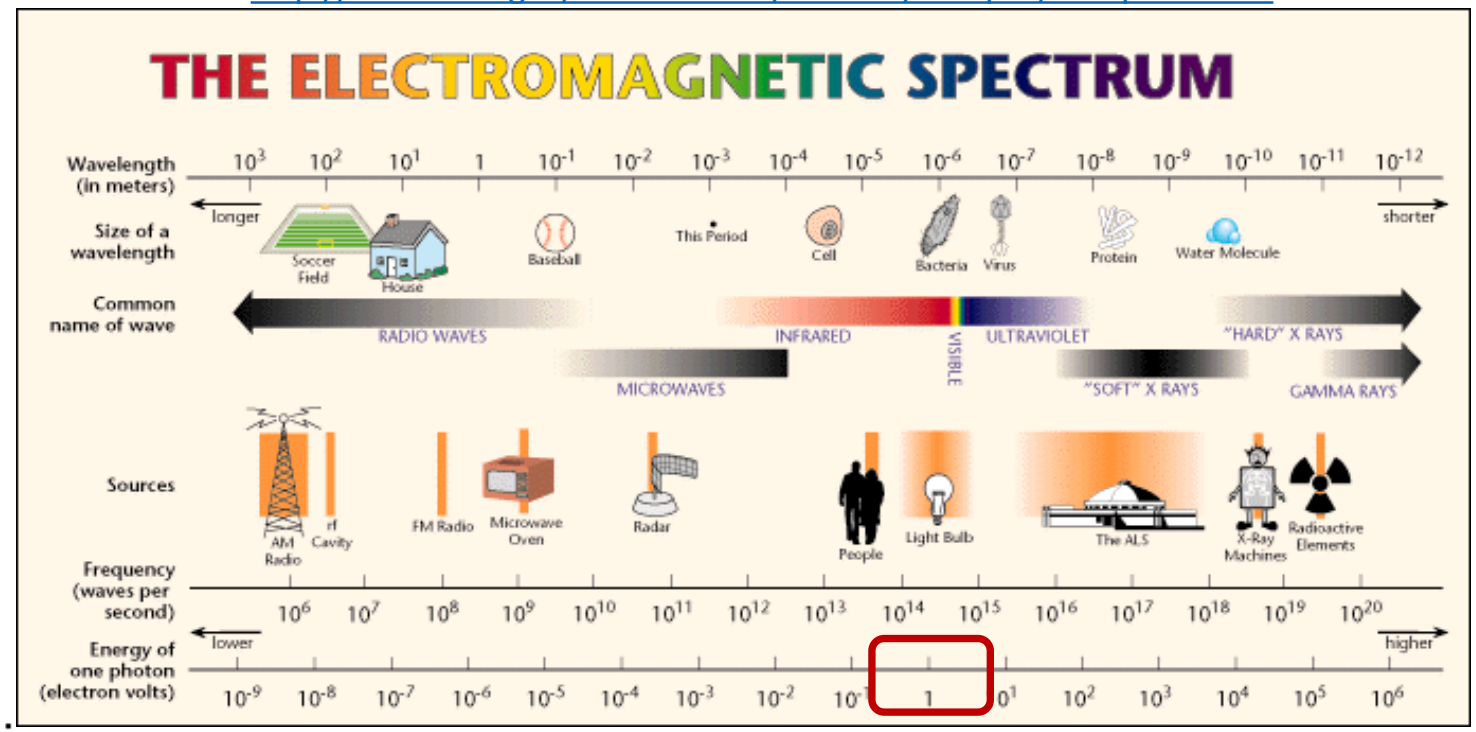
# The electromagnetic spectrum

https://en.wikipedia.org/wiki/Permittivity




Semiconductors

http://www2.lbl.gov/MicroWorlds/ALSTool/EMSpec/EMSpec2.html




Semiconductors

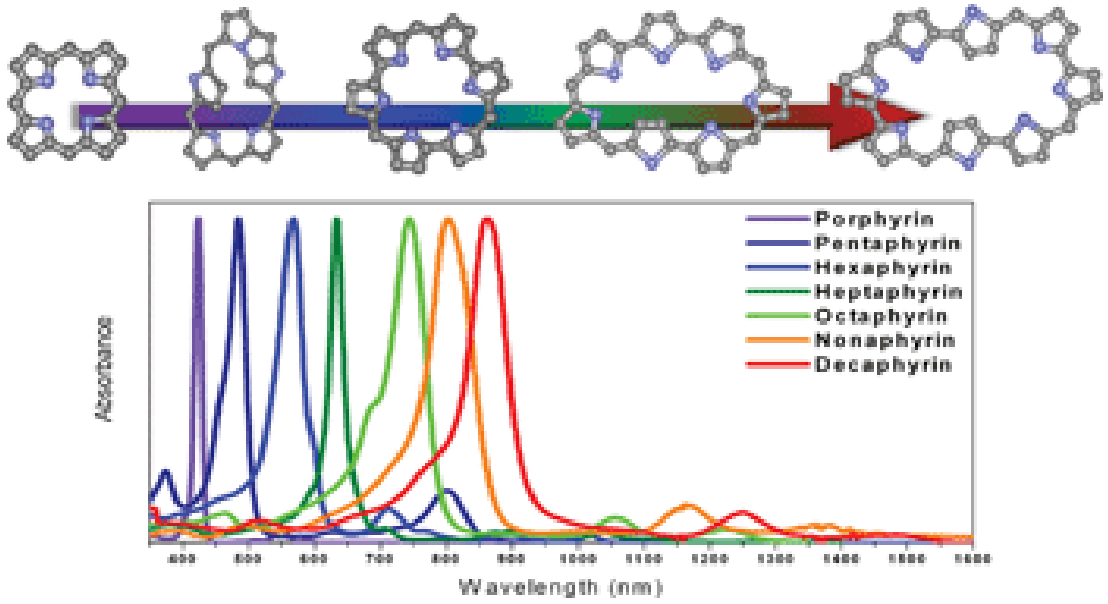
Relationship between the band gap and the dielectric constant

$$\varepsilon^2 E_g = 95 \text{ eV}$$

N. M. Ravindra et al. *Infr. Phys. Tech.* 50 (2007) 21

# Molecular versus solid state optical absorption

## In a molecule

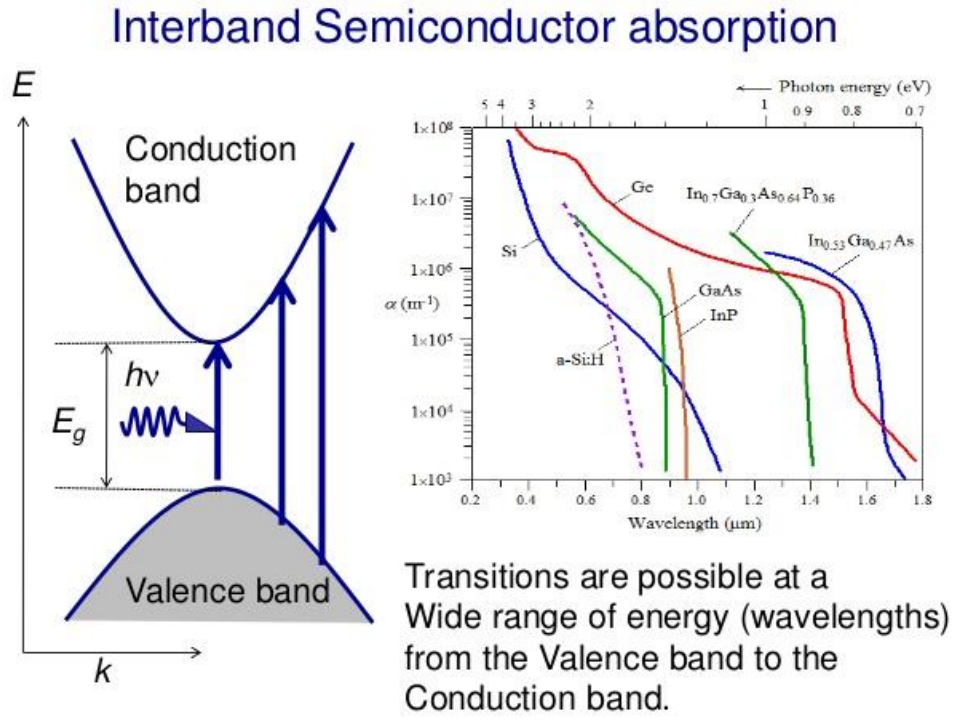



http://pubs.rsc.org/en/content/articlelanding/2008/cc/b810718a#!divAbstract

Discrete energy levels

Absorption maxima

## In the solid-state



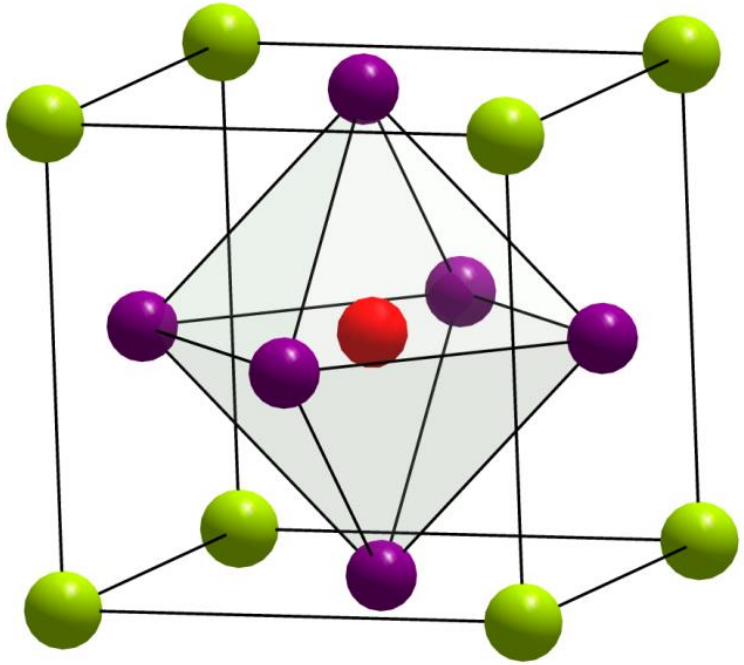

http://www.slideshare.net/cdtpv/optical-spectroscopy-56823999

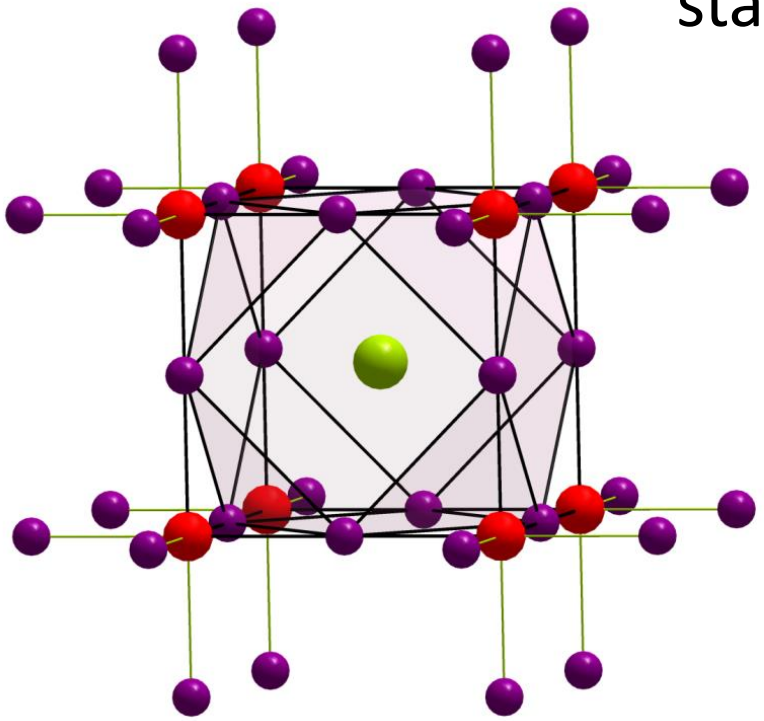
Bands made up of $N_A$ molecular orbitals

Absorption Edges

# Halide perovskite structure

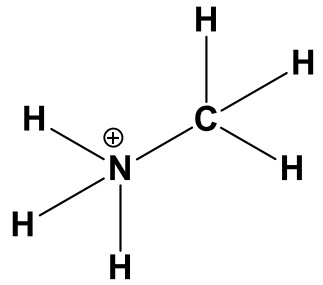
$A^{+}M^{2+}X^{-}_{3}$



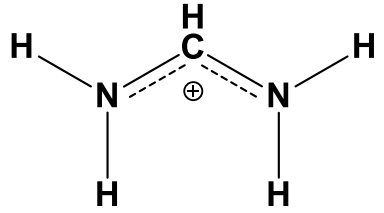


Only 3 cations can stabilize the halide perovskite

$Cs^{+}$



Methylammonium (MA)



Formamidinium (FA)

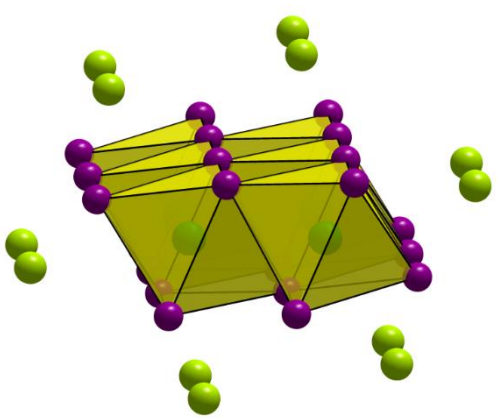


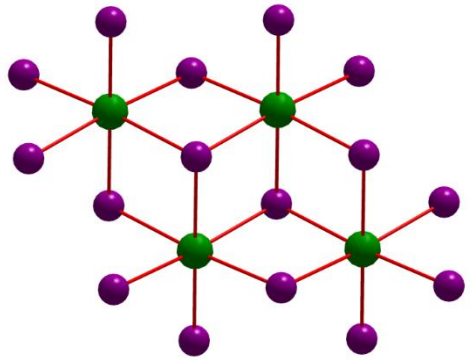
C. C. Stoumpos, M. G. Kanatzidis, *Acc. Chem. Res.* **2015**, *48*, 2791.

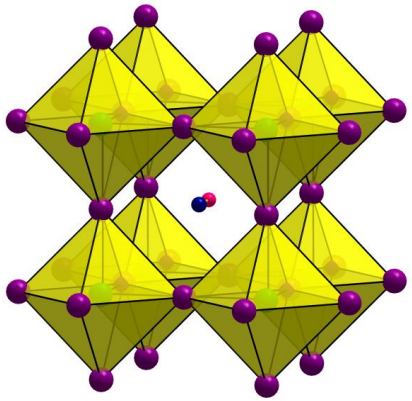
# Perovskite stabilization conditions

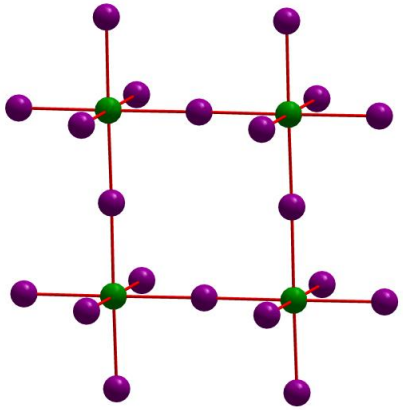
$$t = (r_A + r_X)/\sqrt{2}(r_M + r_X)$$

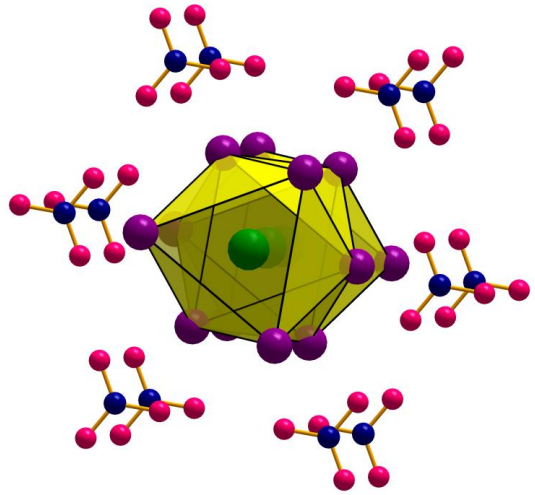
| t < 0.8 | 0.8 < t < 1.0 | t > 1.0 |
|---|---|---|
| $NH_4CdCl_3$-type | $CaTiO_3$-type | $CsNiBr_3$-type |

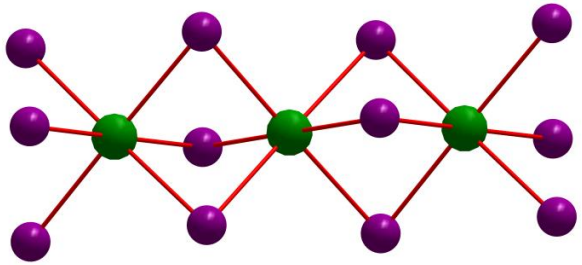










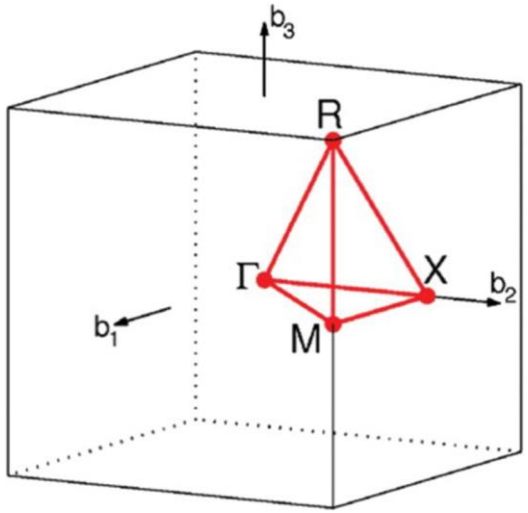


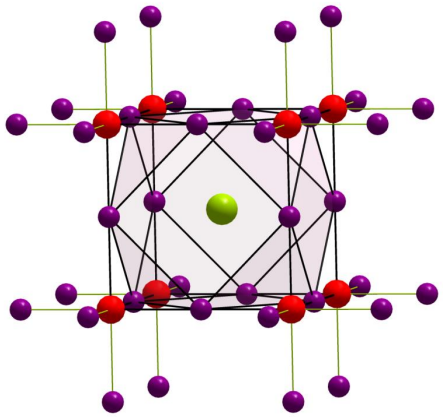


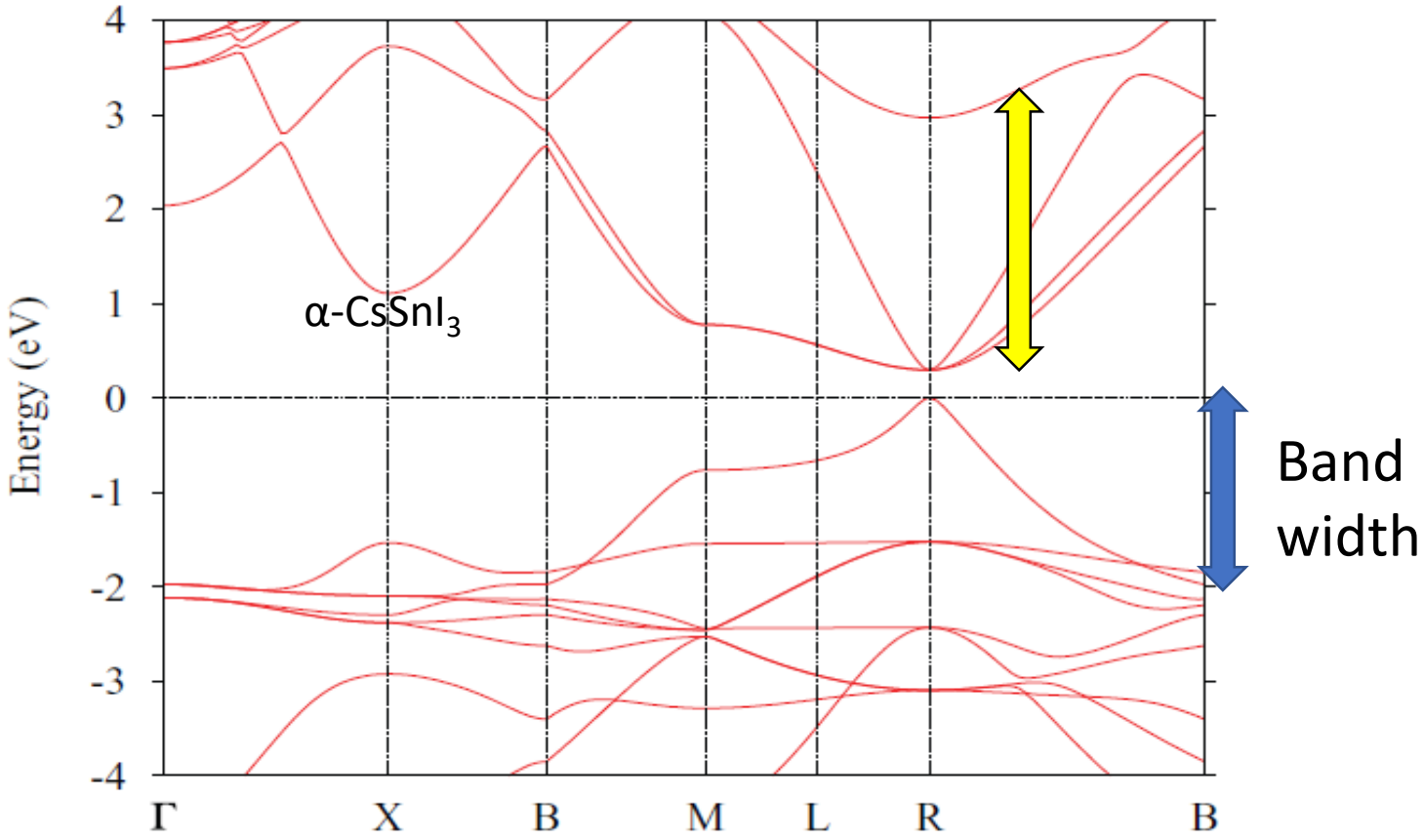
C. C. Stoumpos, M. G. Kanatzidis, *Acc. Chem. Res.* **2015**, *48*, 2791.

# $ASnI_3$: Direct band gap semiconductors

**The electronic structure suggest high-mobilities for both $e^-$ and $h^+$**






Band width

**CBM**
Metal $np^0$ orbitals

**VBM**
Halide $np^6$ orbitals
Metal $ns^2$ orbitals

L.-Y. Huang, R. L. Lambrecht *Phys. Rev. B* **2013** *88* 165203

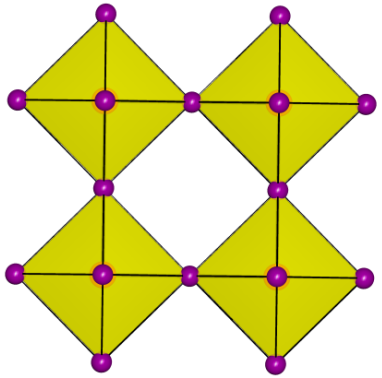
# Halide perovskite phase transitions

$Cs^+$ $CH_3NH_3^+$ $HC(NH_2)_2^+$

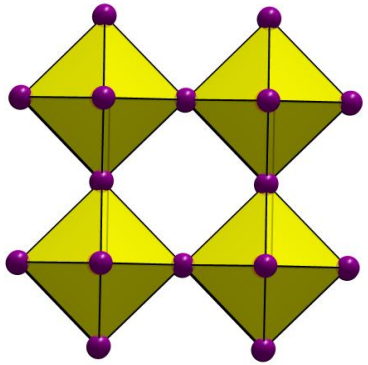
## Undistorted α-phases

Sn Pb

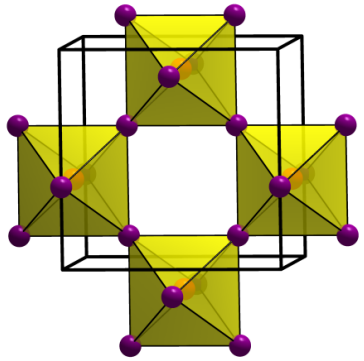
a x a x a



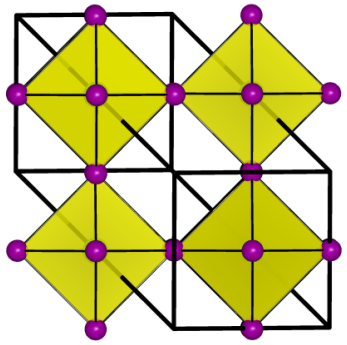
a x a x a’



√2a x √2a x a

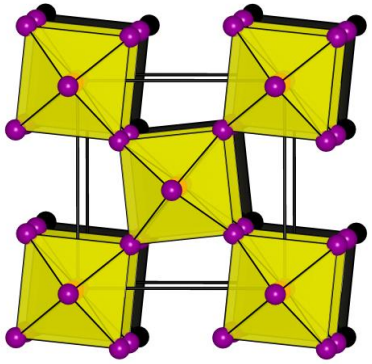


√2a x √2a x √3a

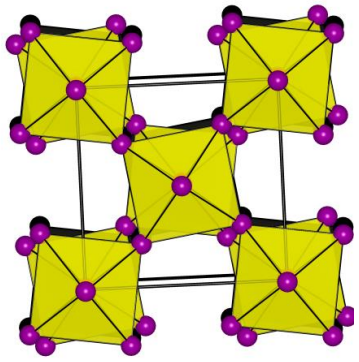


## Distorted β-phases

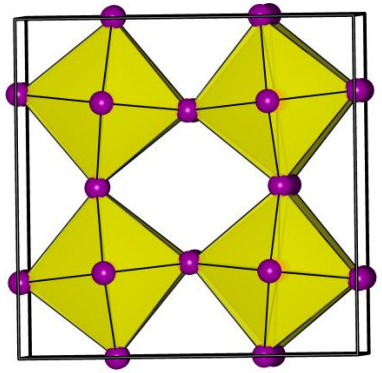
√2a x √2a x a
(in-phase)



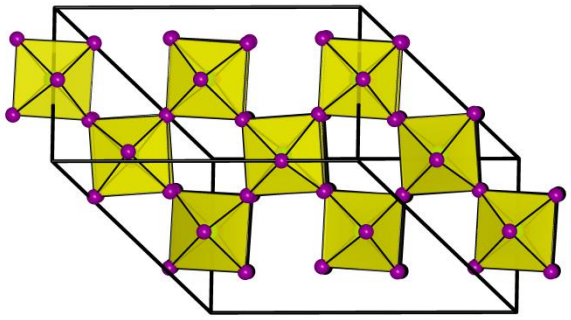
√2a x √2a x 2a
(out-of-phase)



2a x 2a x 2a
(in-phase)



2√2a x 2√2a x √3a
(in-phase)

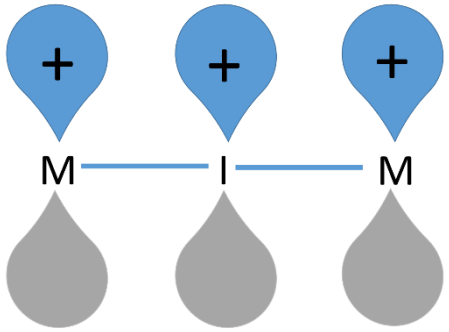




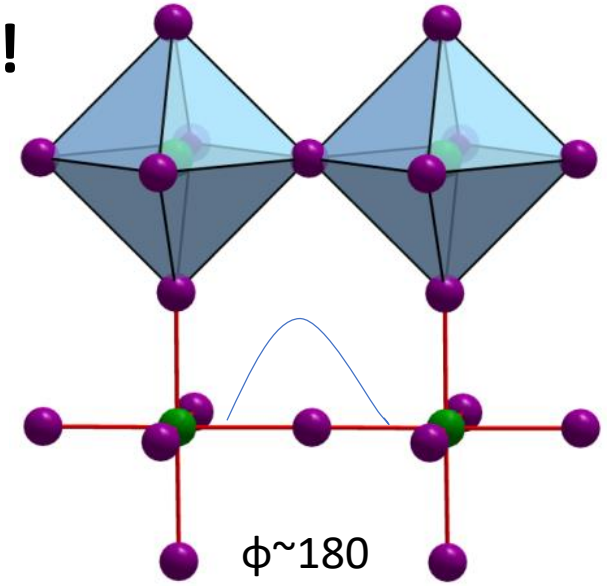
C. C. Stoumpos, M. G. Kanatzidis, *Acc. Chem. Res.* **2015**, *48*, 2791.

# Tilting of the octahedra increases bandgap

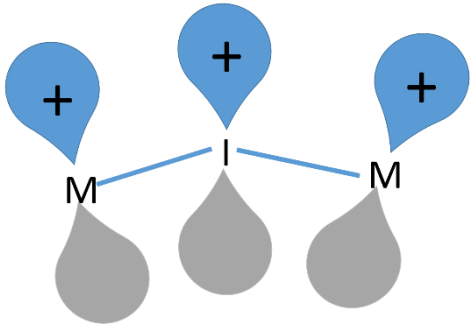
## M-I-M angle matters!



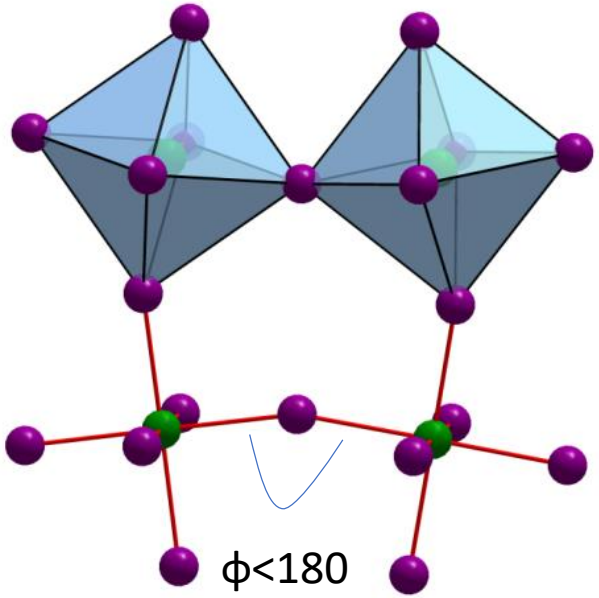

ϕ=180 deg



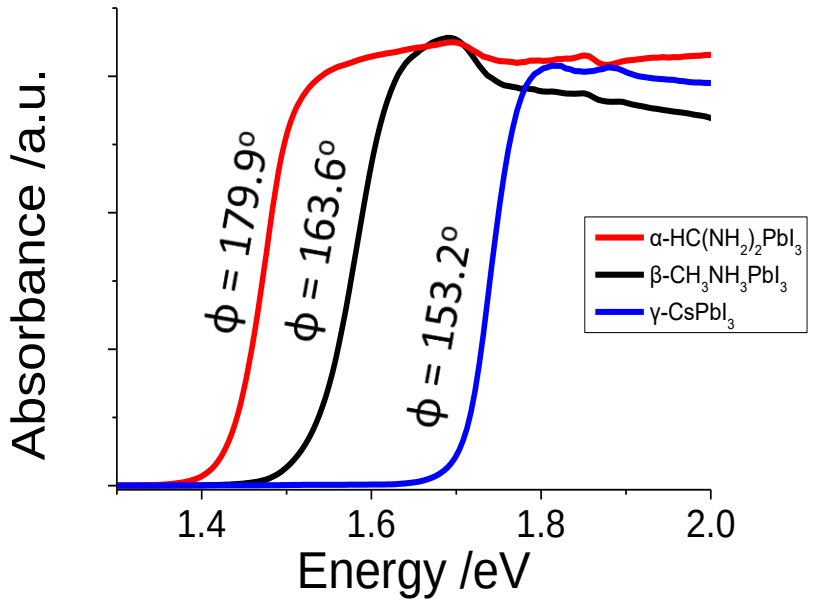
ϕ~180

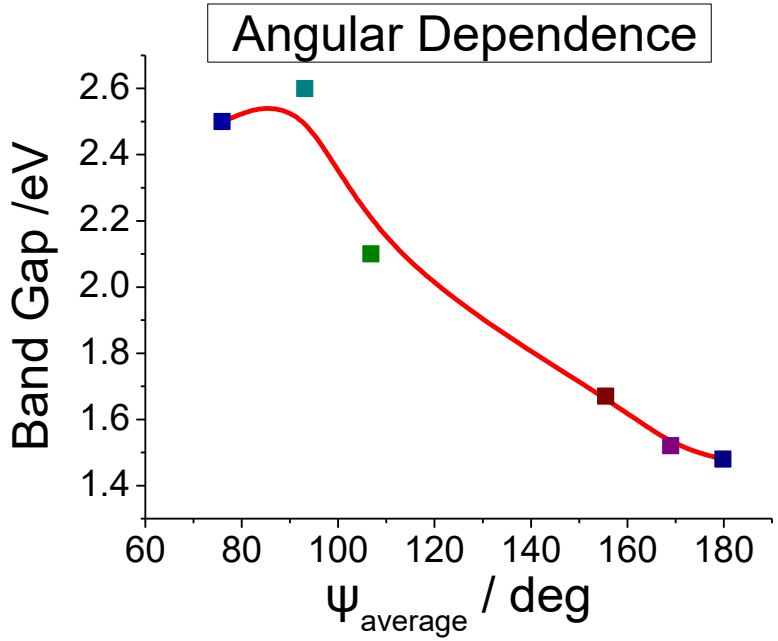



ϕ<<180 deg



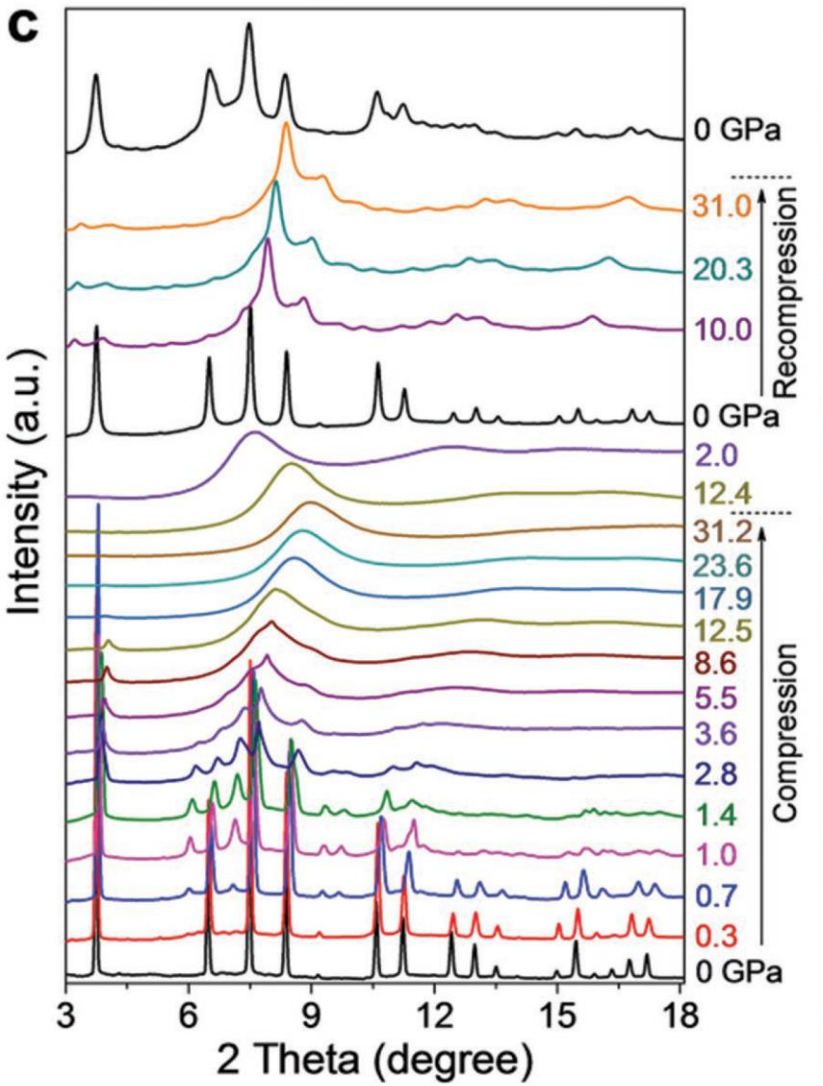
ϕ<180

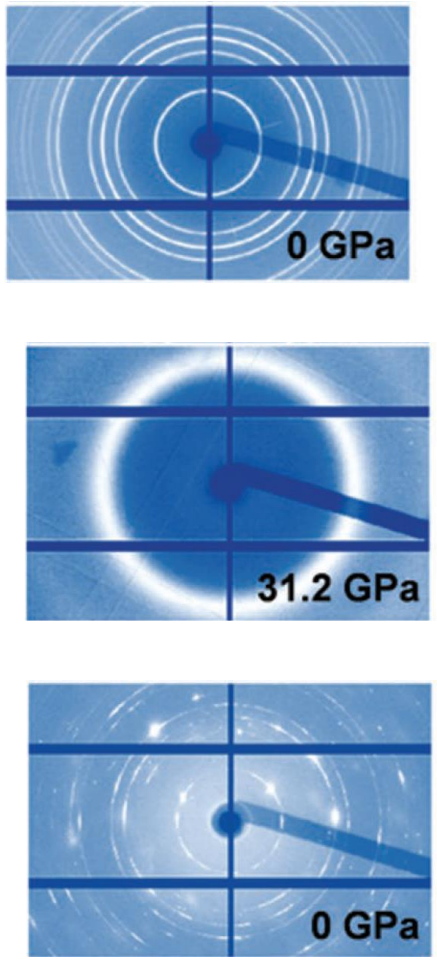


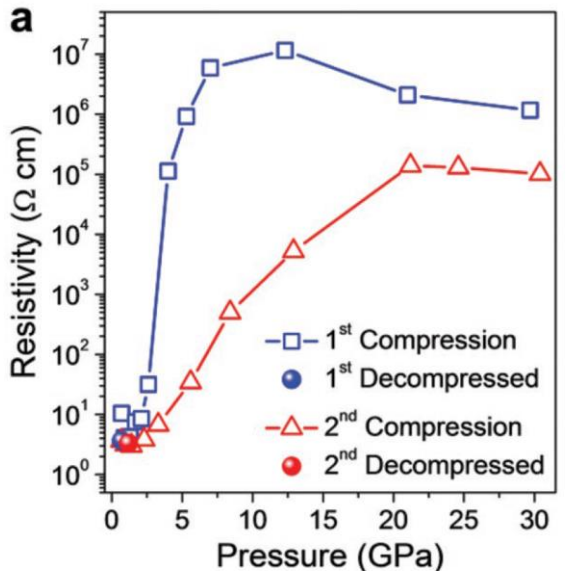



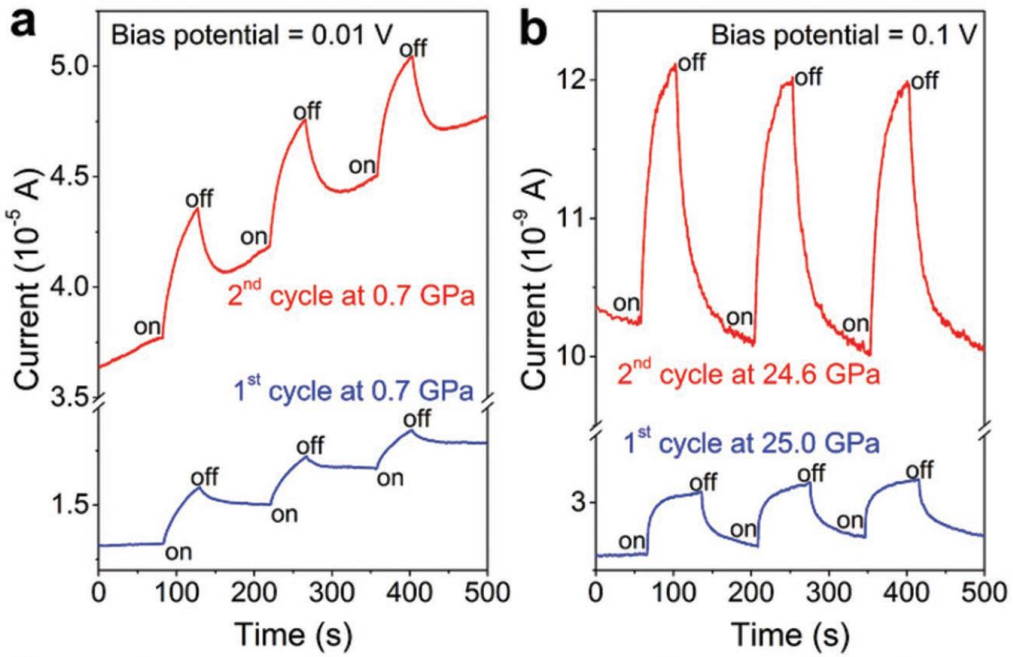

C. C. Stoumpos, M. G. Kanatzidis, *Acc. Chem. Res.* **2015**, *48*, 2791.

# $ASnI_3$ : Photoconductivity under pressure



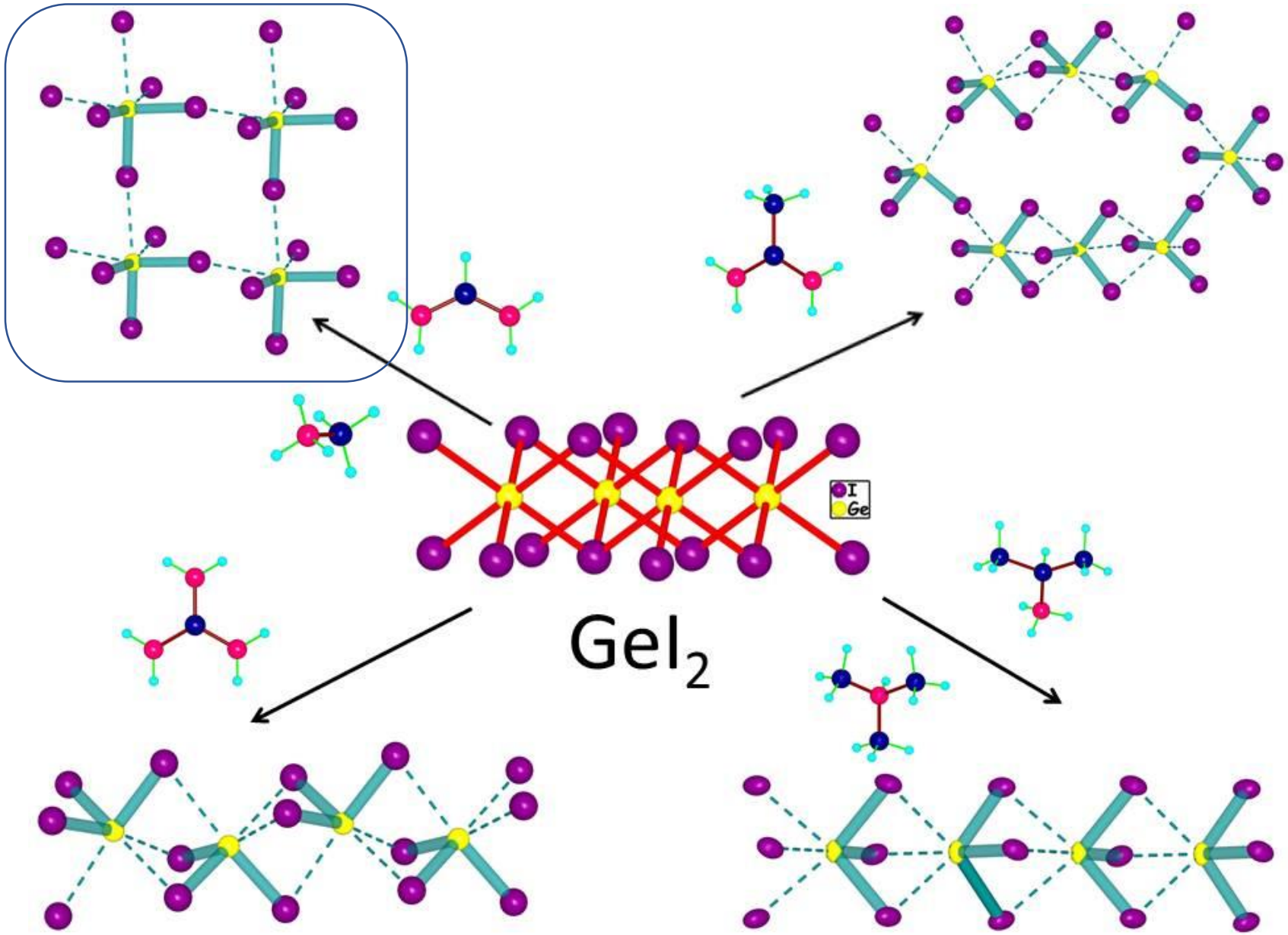



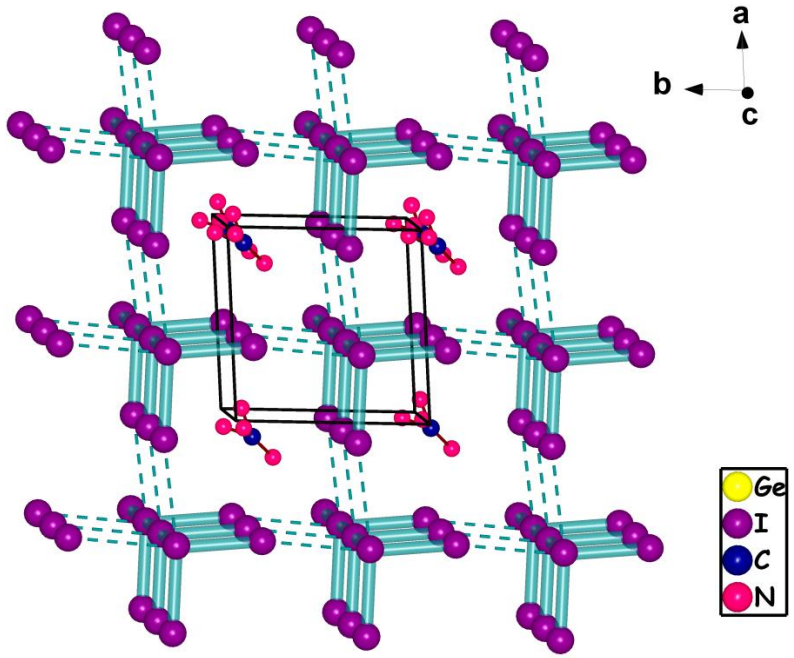

Lü, X.; Wang, Y.; Stoumpos, C. C.; Hu, Q.; Guo, X.; Chen, H.; Yang, L.; Smith, J. S.; Yang, W.; Zhao, Y.; Xu, H.; Kanatzidis, M. G.; Jia, Q. *Adv. Mater.* **2016** *in press*

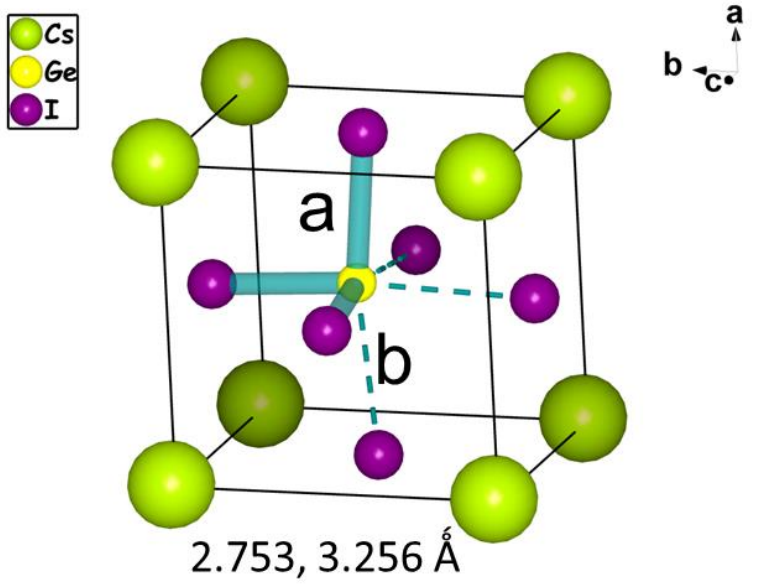
# Structural Diversity: the case of Germanium Perovskites

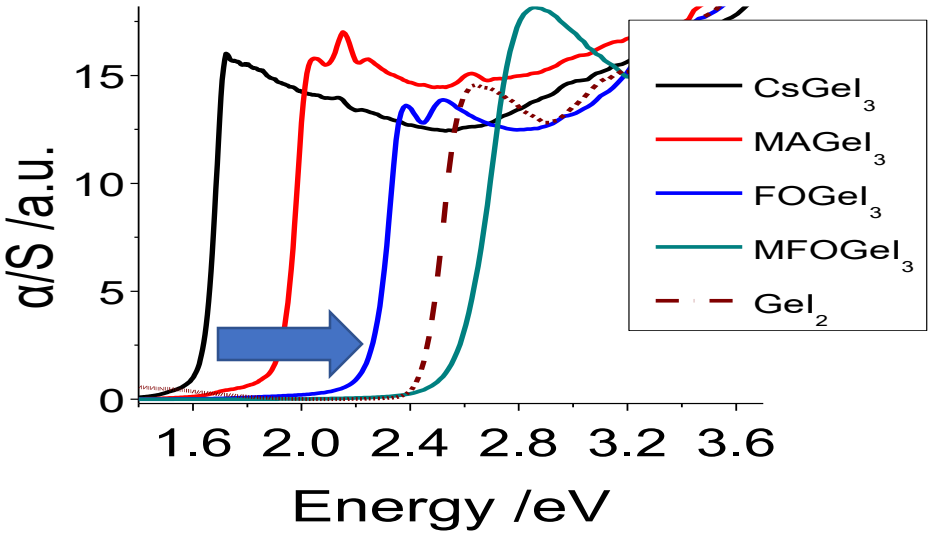



C. C. Stoumpos, L. Frazer, D. J. Clark, Y. S. Kim, S. H. Rhim, A. J. Freeman, J. B. Ketterson, J. I. Jang, M. G. Kanatzidis, *J. Am. Chem. Soc*. **2015**, *137*, 6804.

# Ferroelectric Halide Perovskites

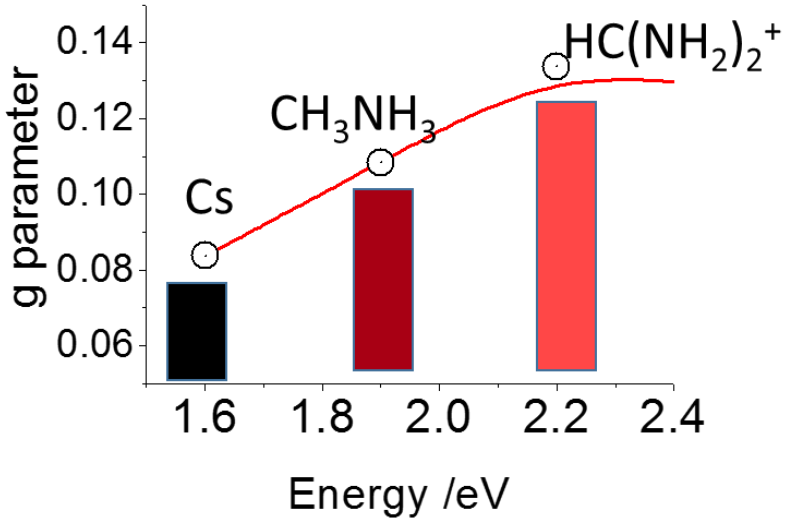



The distortion parameter g = (a-b)/(a+b)

Controls the bandgap

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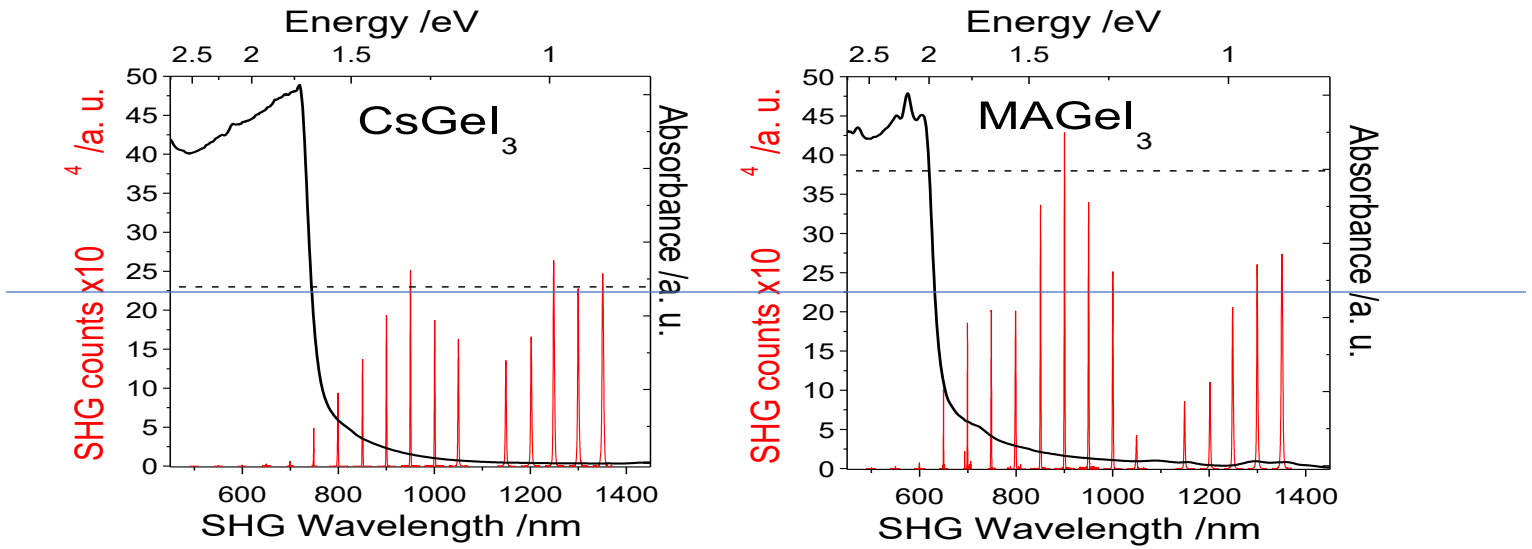
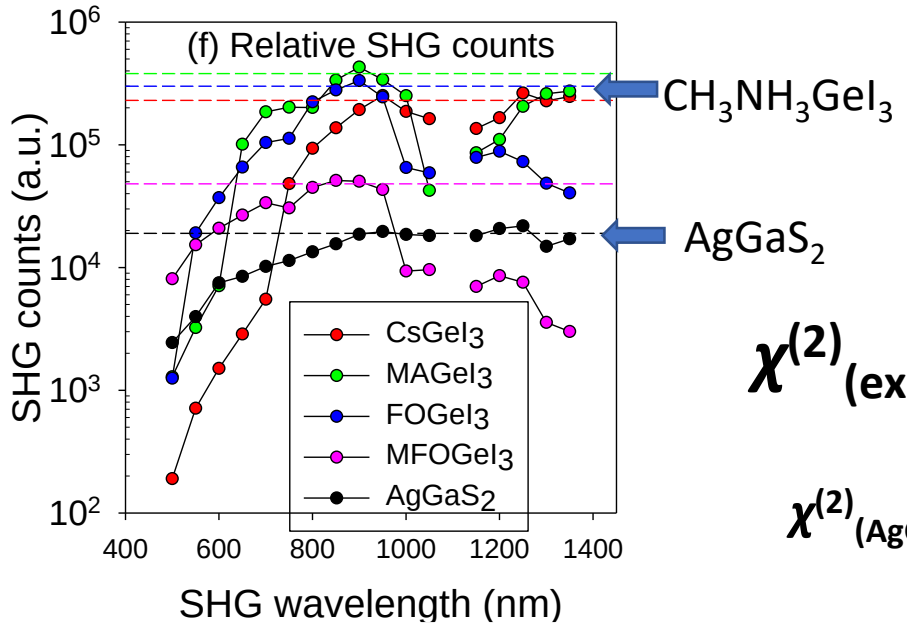
# Huge Nonlinear optical second harmonic generation




$CH_3NH_3GeI_3$

$AgGaS_2$

$\chi^{(2)}_{(exp)}$ (pm/V) = 120-161 pm/V

$\chi^{(2)}_{(AgGaS2)}$ (pm/V) = 13 pm/V

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