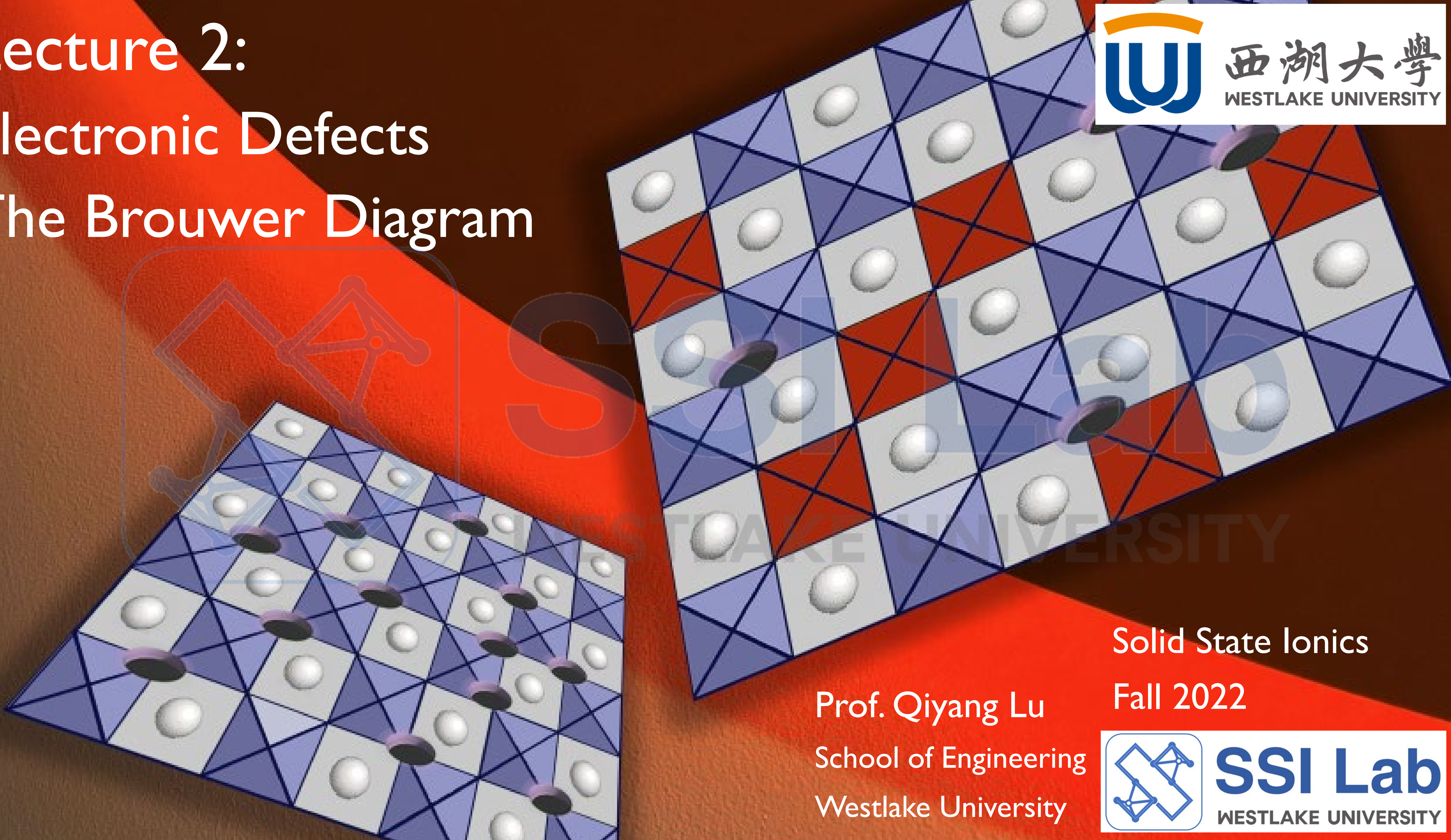
Lecture 2:
Electronic Defects
The Brouwer Diagram



Solid State Ionics

Fall 2022

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Things we will discuss in this lecture

Electronic defects:

- What is the difference between electronic and ionic defects?
- A brief review on basic semiconductor physics: how to write the charge neutrality equation by using Kröger-Vink notations?

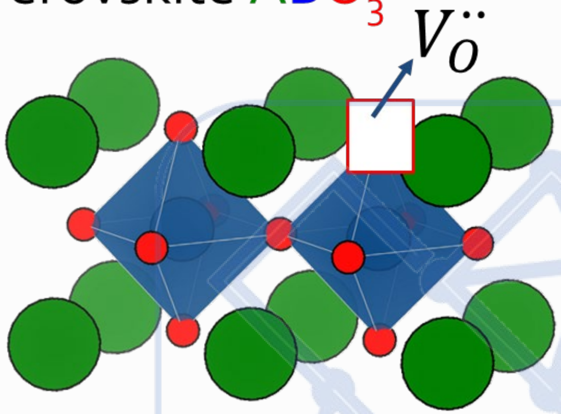
Brouwer diagrams:

- What question are we trying to solve by using the Brouwer diagram?
- What is the key assumption of Brouwer diagram (so-called Brouwer condition)?
- How does a typical Brouwer diagram for metal oxides look like? How can it be used to predict/understand the conductivity of materials?

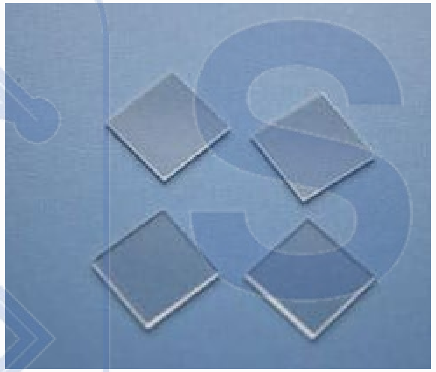
Goal of this lecture: you should be able to answer the questions above by the end of this lecture :)

Ionic *vs.* Electronic defects

Perovskite ABO$_3$



SrTiO$_{3\text{-}\delta}$ (STO)



Compare ***mobilities*** of ionic and electronic defects

Ionic (oxygen vacancy)	$\mu_V = 1.0\times10^4(T^{-1}/K^{-1}) \times \exp\left(-\frac{0.86\ eV}{k_B T}\right) cm^2V^{-1}s^{-1}$
Electronic (electrons & holes)	$\mu_n = 4.5\times10^5(T/K)^{-2.2}cm^2V^{-1}s^{-1}$ $\mu_p = 8.9\times10^5(T/K)^{-2.36}cm^2V^{-1}s^{-1}$

Guo, Fleig & Maier, ***SSI***, 2002

Perovskite ABO$_3$ structure; Cubic (ideal tolerance factor);

("Si for perovskite oxides")

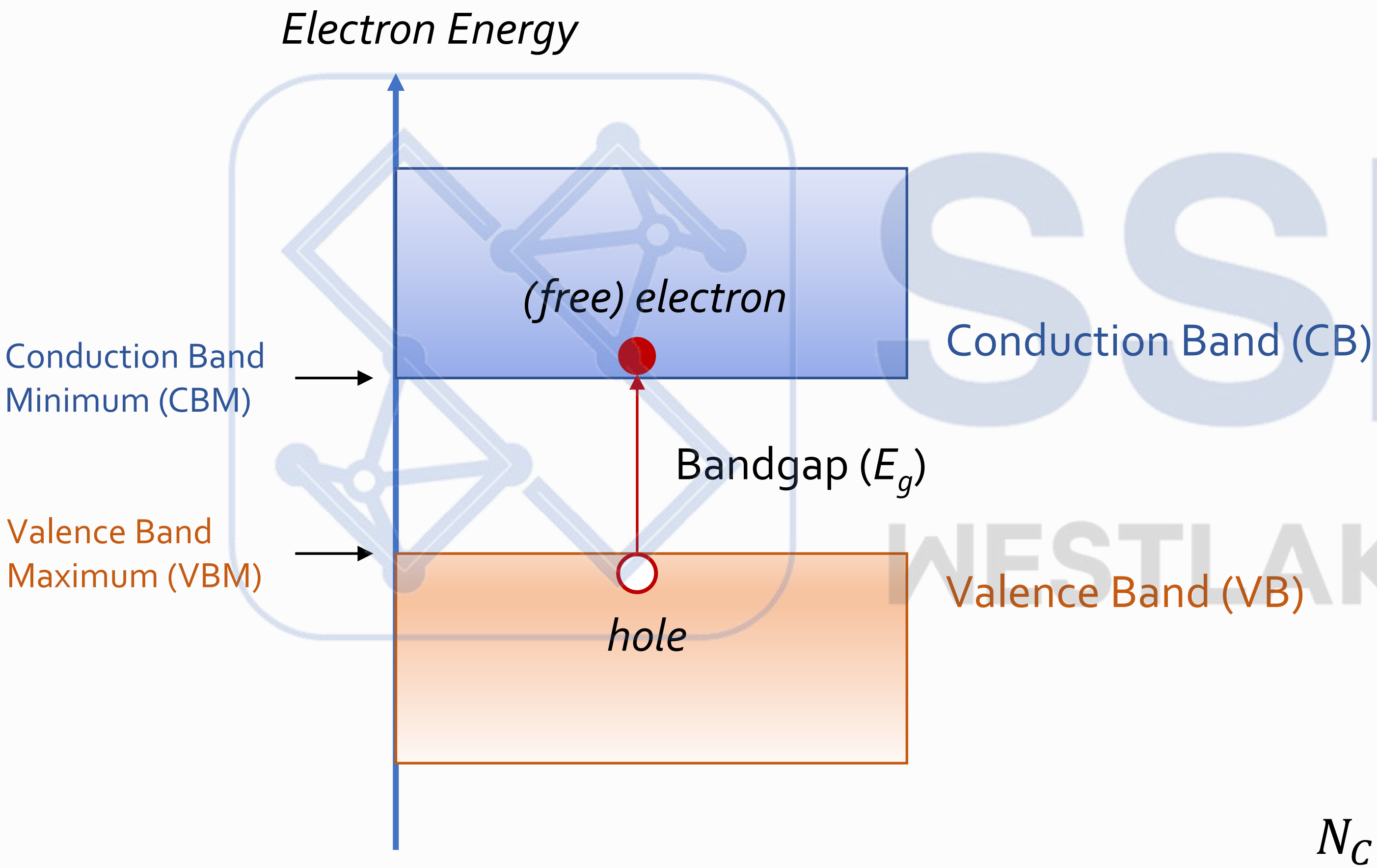
At RT (300 K): $\mu_V = 1.43\times10^{-13}cm^2V^{-1}s^{-1}$ (*almost negligible*);

$\mu_n = 1.60\ cm^2V^{-1}s^{-1}$; $\mu_p = 1.27\ cm^2V^{-1}s^{-1}$

At 500°C (773 K): $\mu_V = 3.19\times10^{-5}cm^2V^{-1}s^{-1}$(*still very low, but can sustain ion motion*);

$\mu_n = 0.20\ cm^2V^{-1}s^{-1}$; $\mu_p = 0.14\ cm^2V^{-1}s^{-1}$

Review of semiconductor physics: intrinsic semiconductors



Electron Energy

(free) electron

Conduction Band Minimum (CBM)

Conduction Band (CB)

Bandgap (E_g)

Valence Band Maximum (VBM)

Valence Band (VB)

hole

"Band-to-band" excitation:

$$\boxed{\mathrm{null} \rightleftharpoons e' + h^{\cdot}}$$

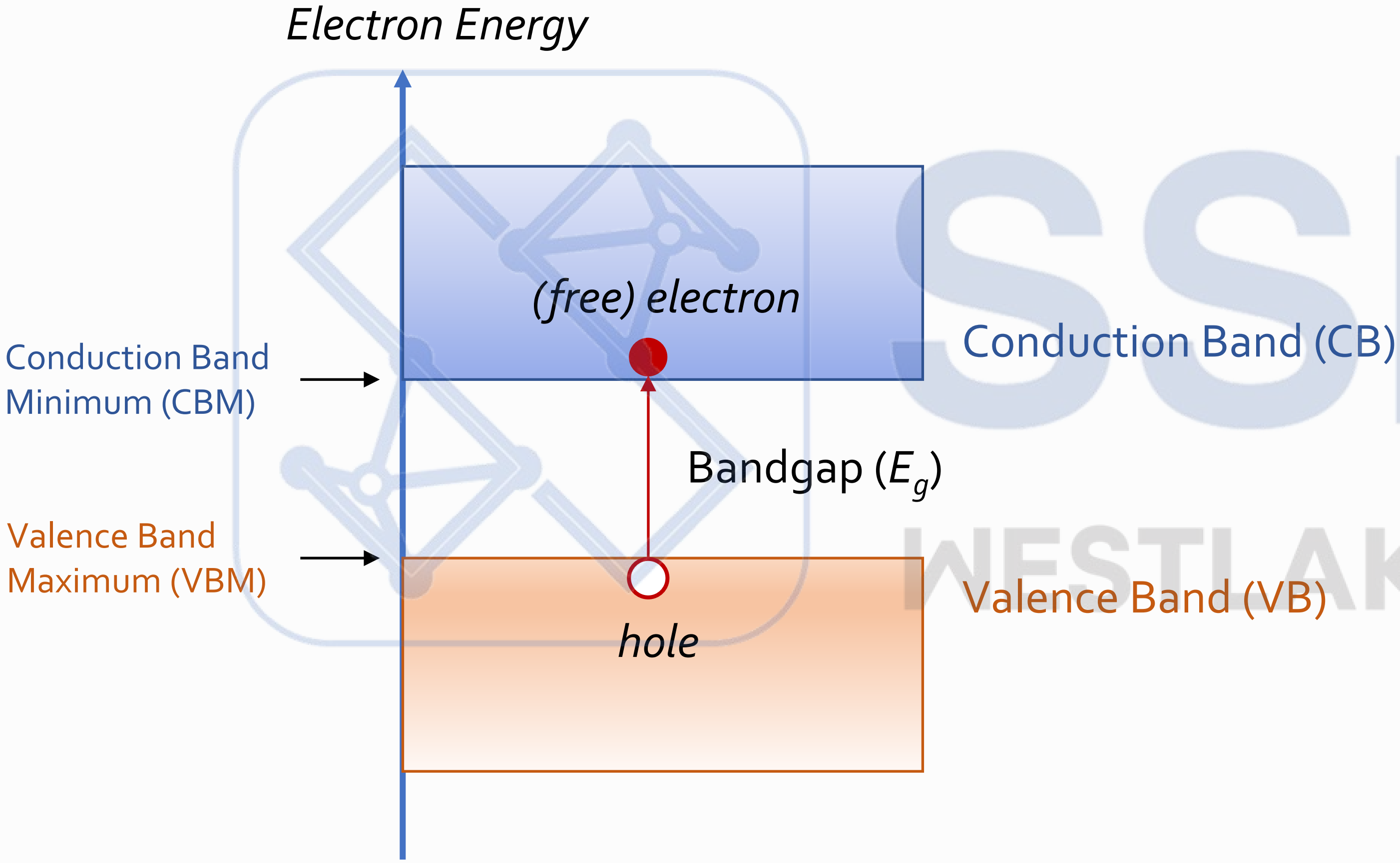
(free) electron *hole*

$$\boxed{K_{el} = [e'][h^{\cdot}] = n\,p}$$

$$\boxed{K_{el} = N_C N_V \exp(-\frac{E_g}{k_B T})}$$

N_C: effective density of state (DOS) at CBM
N_V: effective density of state (DOS) at VBM

Review of semiconductor physics: intrinsic semiconductors, cont'd



"Band-to-band" excitation:

$$\boxed{\text{null} \rightleftharpoons e' + h^{\cdot}}$$

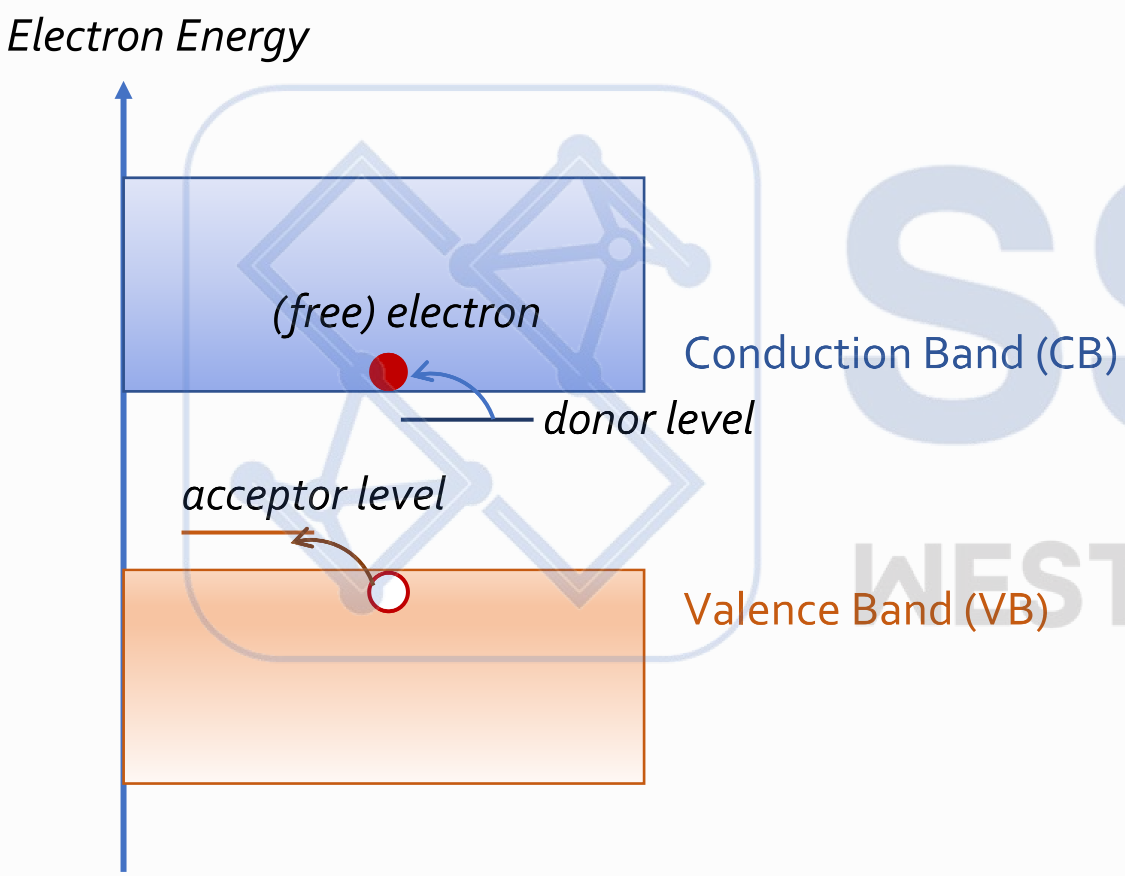
(free) electron *hole*

$$\boxed{K_{el} = [e'] \, [h^{\cdot}] = n \, p}$$

Intrinsic semiconductors:

$$\boxed{[e'] = [h^{\cdot}] = \sqrt{K_{el}} \propto \exp(-\frac{E_g}{2k_B T})}$$

Review of semiconductor physics: doped semiconductors



***Doping*—**charge neutrality condition:

$$\boxed{[A'] + [e'] = [D^{\cdot}] + [h^{\cdot}]}$$

$D^{\cdot}$: donor, *e.g.*, $P_{Si}^{\cdot}$;
A': acceptor, *e.g.*, B_{Si}';

Intrinsic semiconductors:

$$[e'] \approx [h^{\cdot}] \gg [A'] \quad (\gg [D^{\cdot}])$$

p-type semiconductors:

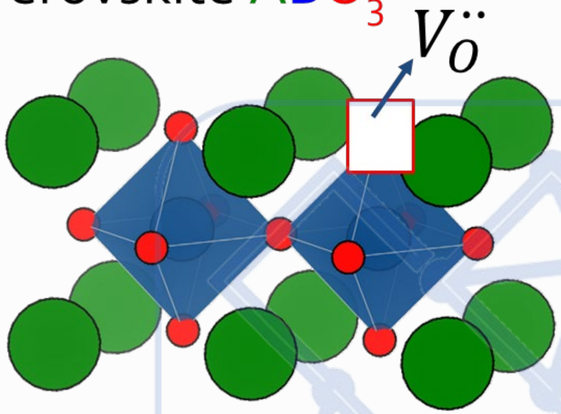
$$[A'] \approx [h^{\cdot}] \gg [e'] \quad ([D'] \approx 0)$$

n-type semiconductors:

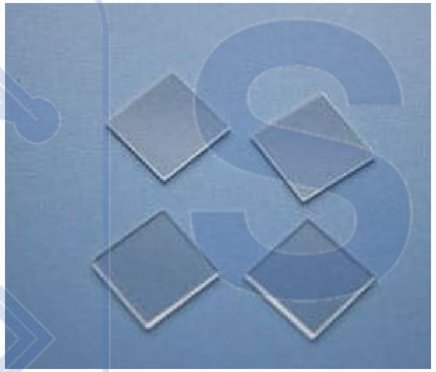
$$[D^{\cdot}] \approx [e'] \gg [h^{\cdot}] \quad ([A'] \approx 0)$$

Charge neutrality considering both ionic and electronic defects

Perovskite ABO_3



$SrTiO_{3-\delta}$ (STO)



Note: even un-doped "pure" $SrTiO_3$ single crystal contains *acceptor dopants* such as Mn, Al, Fe, Mg *etc.* (usually on the level of ~100 ppm, *e.g.* $\mathrm{Al}_{\mathrm{Ti}}'$, $\mathrm{Mg}_{\mathrm{Ti}}''$)

Electronic defects: $[e']$, $[h^\cdot]$

(Intrinsic) ionic defects: $[V_O^{\cdot\cdot}]$, $[O_i'']$ (uncommon), $[Ti_i^{\cdot\cdot\cdot\cdot}]$(uncommon), $[V_{Sr}'']$,$[Sr_{Ti}'']$ (anti-site defects)

(Extrinsic) ionic defects: $[\mathrm{Al}_{\mathrm{Ti}}']$, $[\mathrm{Mg}_{\mathrm{Ti}}'']$

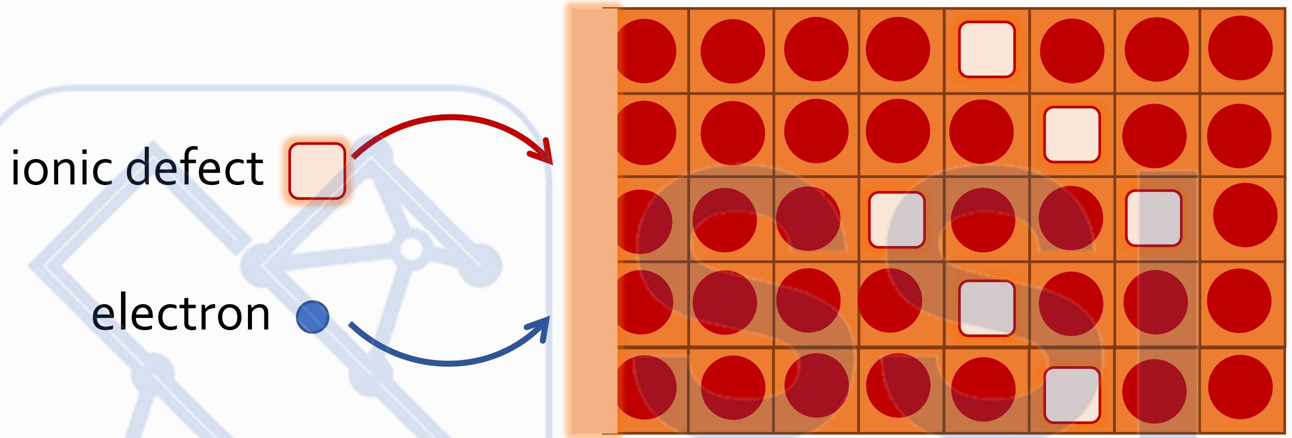
Charge neutrality considering both ionic and electronic defects:

$$\boxed{[e'] + 2[V_{Sr}''] + 2[Sr_{Ti}''] + 2[O_i''] = [h^\cdot] + 2[V_O^{\cdot\cdot}] + 4[Ti_i^{\cdot\cdot\cdot\cdot}]}$$

- Usually, it is very difficult to solve the equation w/ these many unknowns.
- The common practice is to ignore some defects with very low concentrations by dividing the chemical potential range into different regimes.

How to tune defect concentration?

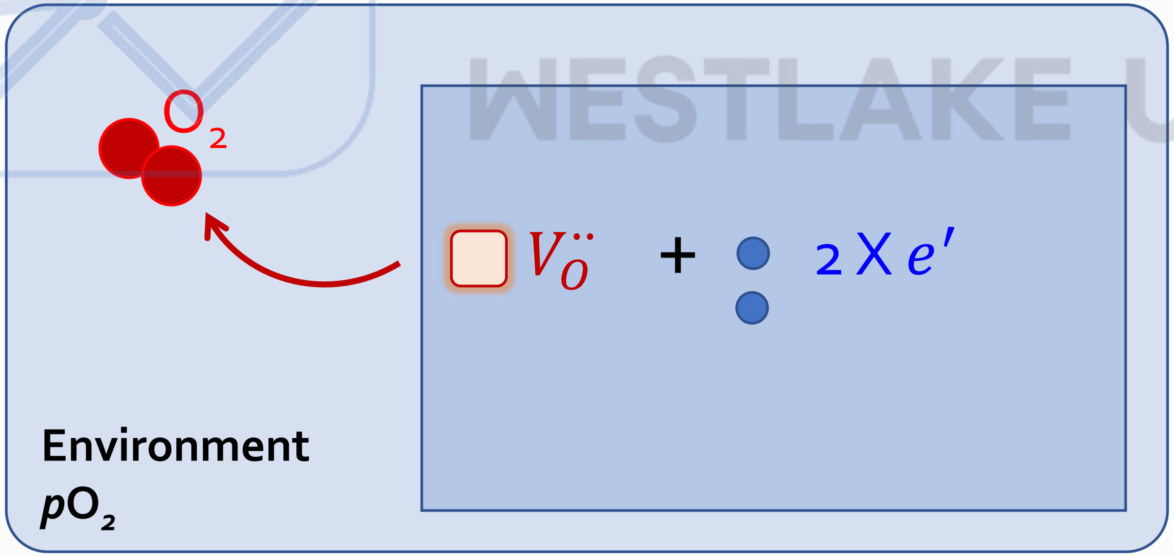
Surfaces/Interfaces



🟧 = *lattice site*

▢ = *ionic defect* (*e.g.*, oxygen vacancy, lithium ion vacancy…)

Example:



Environment
p**O₂**

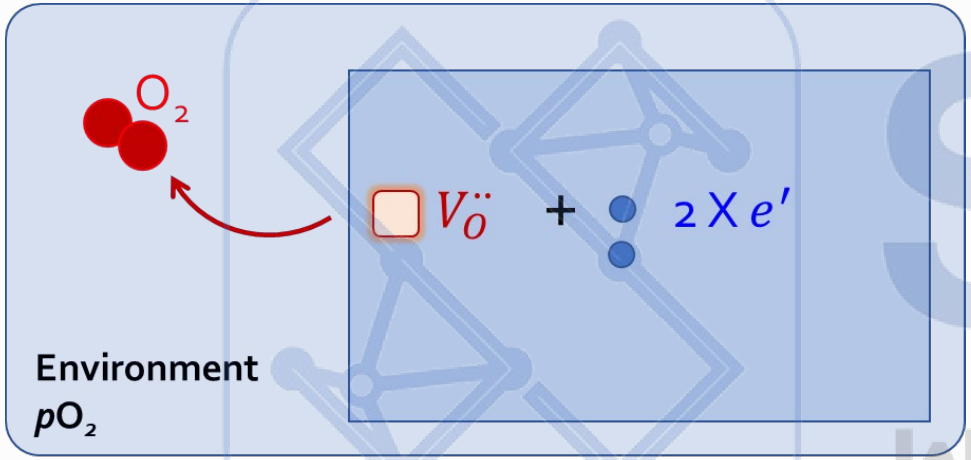
Metal Oxide
MO*₁₋ₓ*

$$O_O^{\times} \rightleftharpoons V_O^{\cdot\cdot} + 2e' + 1/2O_2$$

$$\mu_O = 1/2\,\mu_{O_2}$$
$$\mu_{O_2} = \mu_{O_2}^0 + RT\ln(p_{O_2}/p_{O_2}^0)$$

Summary of defect chemical reactions

Example: Metal Oxide **MO_{1-x}**



Assumption: metal cations (**M**) are immobile (usually true, since the migration of cations is much more difficult compared with anions)

Defect reactions and mass action laws:

Frenkel pair $null \rightarrow O_i'' + V_O^{\cdot\cdot}$ $K_F = [O_i''][V_O^{\cdot\cdot}]$

"Band-to-band" $null \rightarrow e' + h^{\cdot}$ $K_{el} = [e'][h^{\cdot}]$

Oxygen Exchange $O_O^{\times} \leftrightharpoons V_O^{\cdot\cdot} + 2e' + 1/2O_2$ $K_O = \dfrac{{p_{O_2}}^{1/2}[V_O^{\cdot\cdot}][e']^2}{[O_O^{\times}]}$

Electroneutrality also applies $[e'] + 2[O_i''] = [h^{\cdot}] + 2[V_O^{\cdot\cdot}]$

In principle, one can solve for four unknowns using these four equations, but it is much easier to ***ignore the minority defects*** with low enough concentration. ***Brouwer condition***: *only two majority defects with opposite charges matter*.

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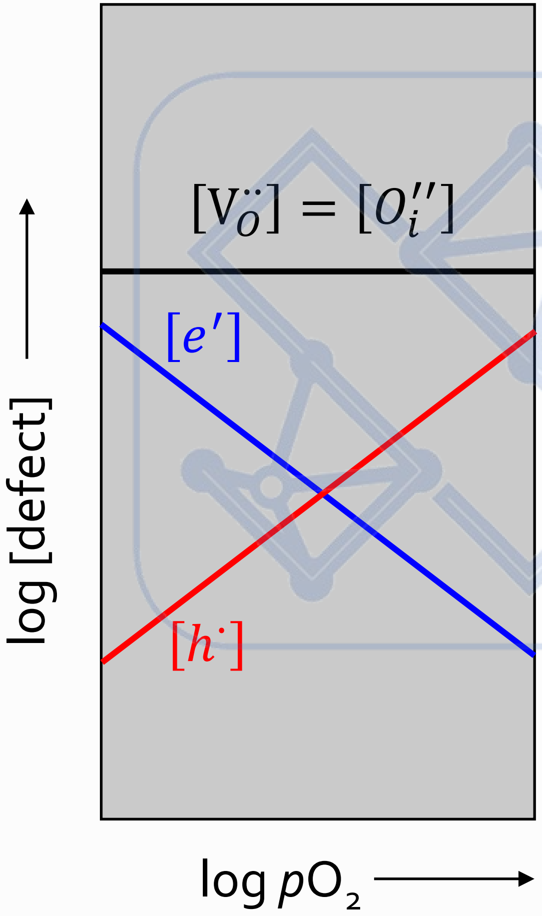
The Brouwer diagram: the *log*[ ]~ *log* pO_2 plot



<u>Regime I: "Intrinsic" regime</u>

The majority charge carriers are ionic defects

$$[V_O^{\cdot\cdot}] \gg [h^{\cdot}],\ [O_i''] \gg [e']$$

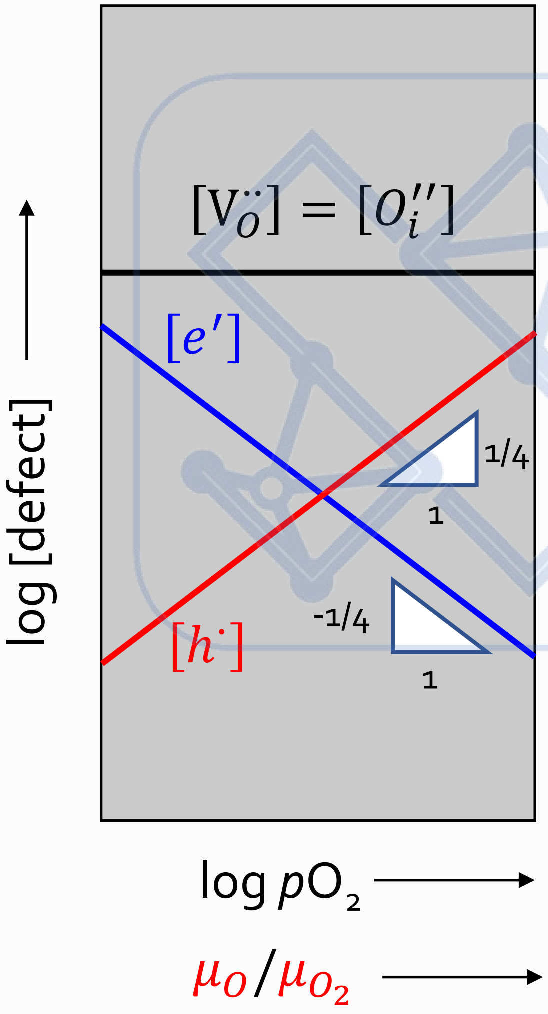
Electroneutrality $$[\cancel{e'}] + 2[O_i''] = [\cancel{h^{\cdot}}] + 2[V_O^{\cdot\cdot}]$$

$$null \rightarrow O_i'' + V_O^{\cdot\cdot},\ K_F = [O_i''][V_O^{\cdot\cdot}] \longrightarrow [O_i''] = [V_O^{\cdot\cdot}] = \sqrt{K_F}$$

$$\boxed{O_O^{\times} \leftrightharpoons V_O^{\cdot\cdot} + 2e' + 1/2O_2} \quad K_O = \frac{{p_{O_2}}^{1/2}[V_O^{\cdot\cdot}][e']^2}{[O_O^{\times}]}$$

$$[e'] = \sqrt{\frac{K_O}{{p_{O_2}}^{1/2}[V_O^{\cdot\cdot}]}} = {p_{O_2}}^{-1/4}{K_O}^{1/2}{K_F}^{-1/4} \propto {p_{O_2}}^{-1/4}$$

Regime I:“Intrinsic” regime



Regime I: “Intrinsic” regime

The majority charge carriers are ionic defects

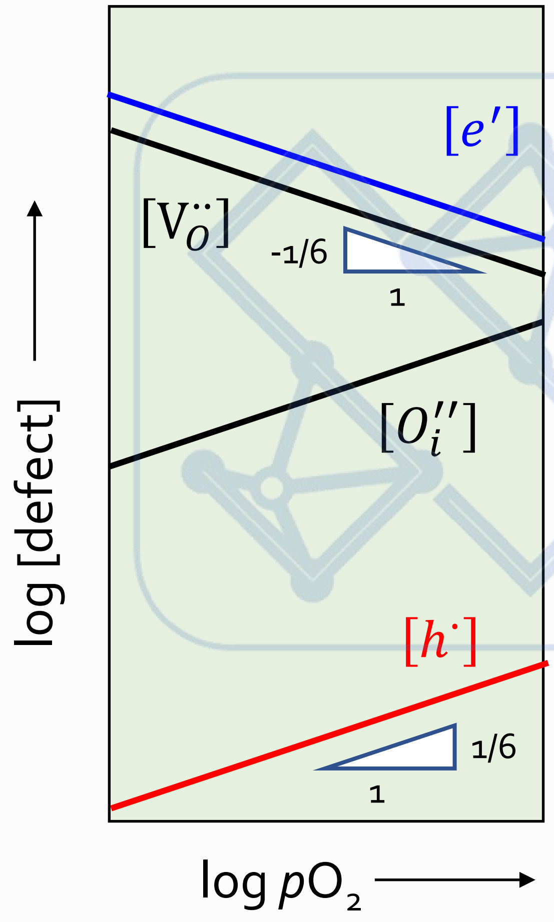
$$[e'] = \sqrt{\frac{K_O}{p_{O_2}{}^{1/2}[V_O^{\cdot\cdot}]}} = p_{O_2}{}^{-1/4} K_O{}^{1/2} K_F{}^{-1/4} \propto p_{O_2}{}^{-1/4}$$

$$null \rightarrow e' + h^{\cdot},\ K_{el} = [e'][h^{\cdot}] \longrightarrow [h^{\cdot}] \propto p_{O_2}{}^{1/4}$$

Notes:

- A “small” change of oxygen chemical potential can lead to ***a large change in the concentration of electronic defects***;
- ***n-type to p-type*** transition can be triggered by changing pO_2

Regime II: Oxygen-poor



Regime II: "oxygen-poor" regime

The majority charge carriers are $[V_O^{\cdot\cdot}]$ & $[e']$

$[V_O^{\cdot\cdot}] \gg [h^\cdot]$, $[e'] \gg [O_i'']$

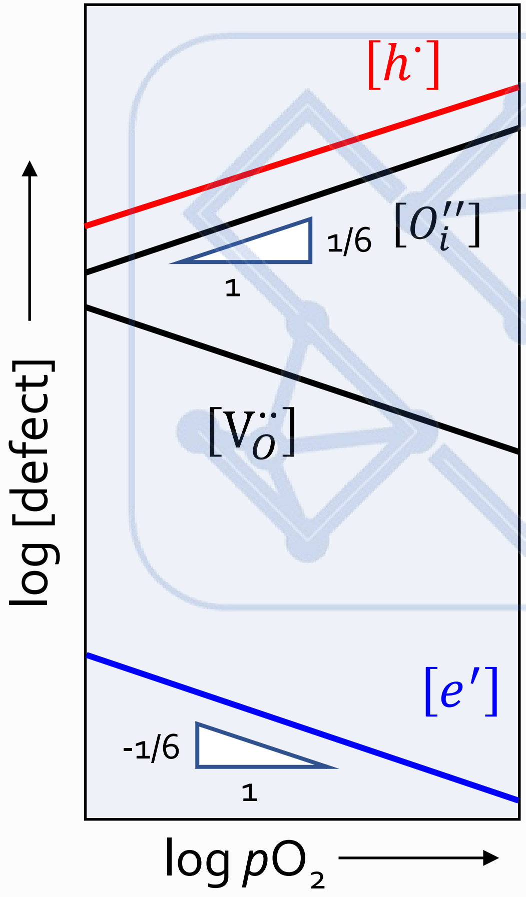
Electroneutrality $\quad [e'] + 2\cancel{[O_i'']} = \cancel{[h^\cdot]} + 2[V_O^{\cdot\cdot}]$

$$K_O = \frac{{p_{O_2}}^{1/2}[V_O^{\cdot\cdot}][e']^2}{[O_O^\times]} \Rightarrow \quad [V_O^{\cdot\cdot}] \propto {p_{O_2}}^{-1/6},\ [e'] \propto {p_{O_2}}^{-1/6}$$

$$K_{el} = [e'][h^\cdot] \quad \Rightarrow \quad [h^\cdot] \propto {p_{O_2}}^{1/6}$$

$$K_F = [O_i''][V_O^{\cdot\cdot}] \quad \Rightarrow \quad [O_i''] \propto {p_{O_2}}^{1/6}$$

Regime III: Oxygen-rich



Regime III: "oxygen-rich" regime

The majority charge carriers are $[O_i'']$ & $[h^{\cdot}]$

$$[h^{\cdot}] \gg [V_O^{\cdot\cdot}],\ [O_i''] \gg [e']$$

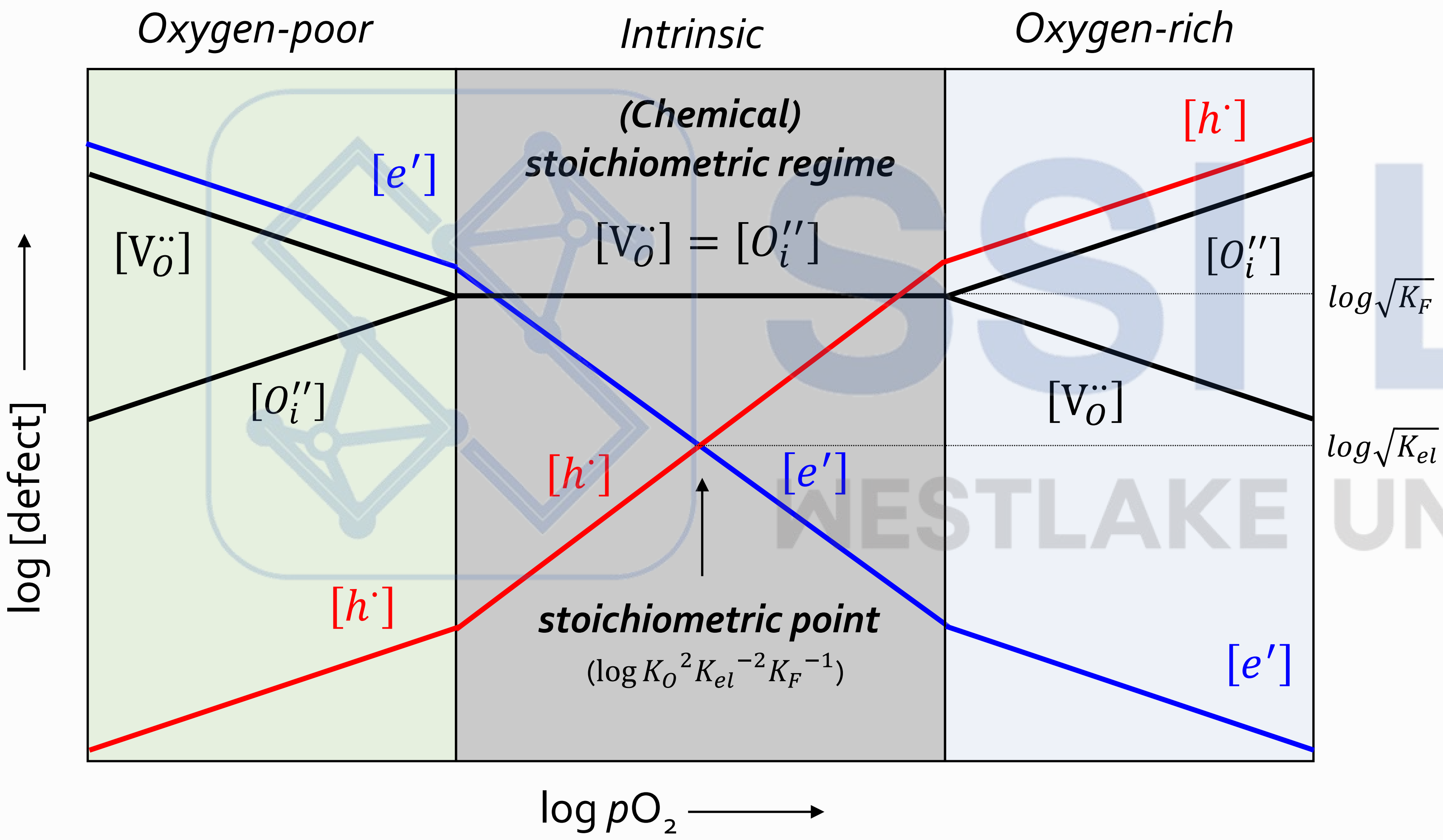
Electroneutrality $\quad \cancel{[e']} + 2[O_i''] = [h^{\cdot}] + 2\cancel{[V_O^{\cdot\cdot}]}$

It is more convenient to rewrite the oxygen incorporation reaction in this case:

$$\boxed{\frac{1}{2}O_2 \leftrightharpoons O_i'' + 2h^{\cdot}} \qquad K_O = \frac{[O_i''][h^{\cdot}]^2}{p_{O_2}{}^{1/2}} \Rightarrow [O_i''] \propto p_{O_2}{}^{1/6} \quad [h^{\cdot}] \propto p_{O_2}{}^{1/6}$$

$$K_{el} = [e'][h^{\cdot}] \Rightarrow [e'] \propto p_{O_2}{}^{-1/6} \qquad K_F = [O_i''][V_O^{\cdot\cdot}] \Rightarrow [V_O^{\cdot\cdot}] \propto p_{O_2}{}^{-1/6}$$

Combine the three regimes together: a prototypical Brouwer diagram of metal oxides



Note:

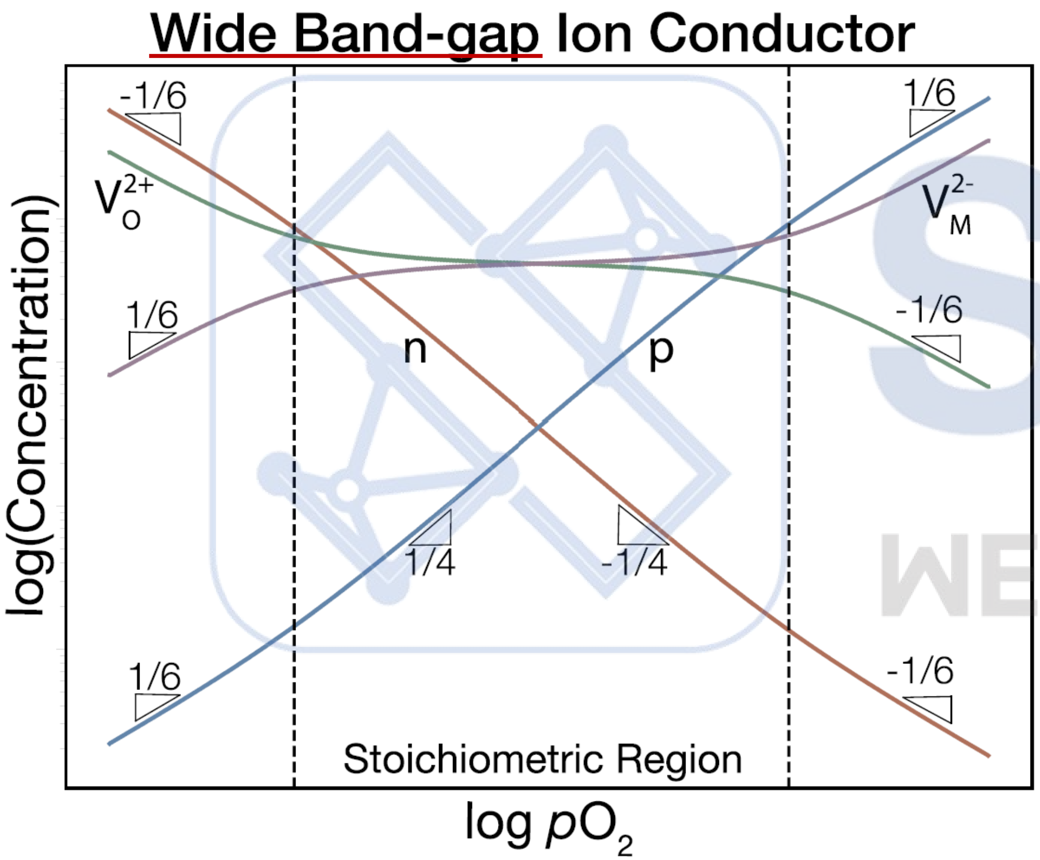
- We only considered intrinsic Frenkel pairs → can be extended to ***extrinsic ionic defects*** or ***Schottky pairs*** $(V_O^{\cdot\cdot} + V_M'')$;
- The ***x***-axis can be expressed by either log pO_2 or chemical potential of oxygen gas/neutral oxygen;
- The existence of a ***stoichiometric point***.

Metal Oxide $\mathbf{MO_{1-\delta}}$

$$\boxed{\delta = [O_i''] - [V_O^{\cdot\cdot}]}$$

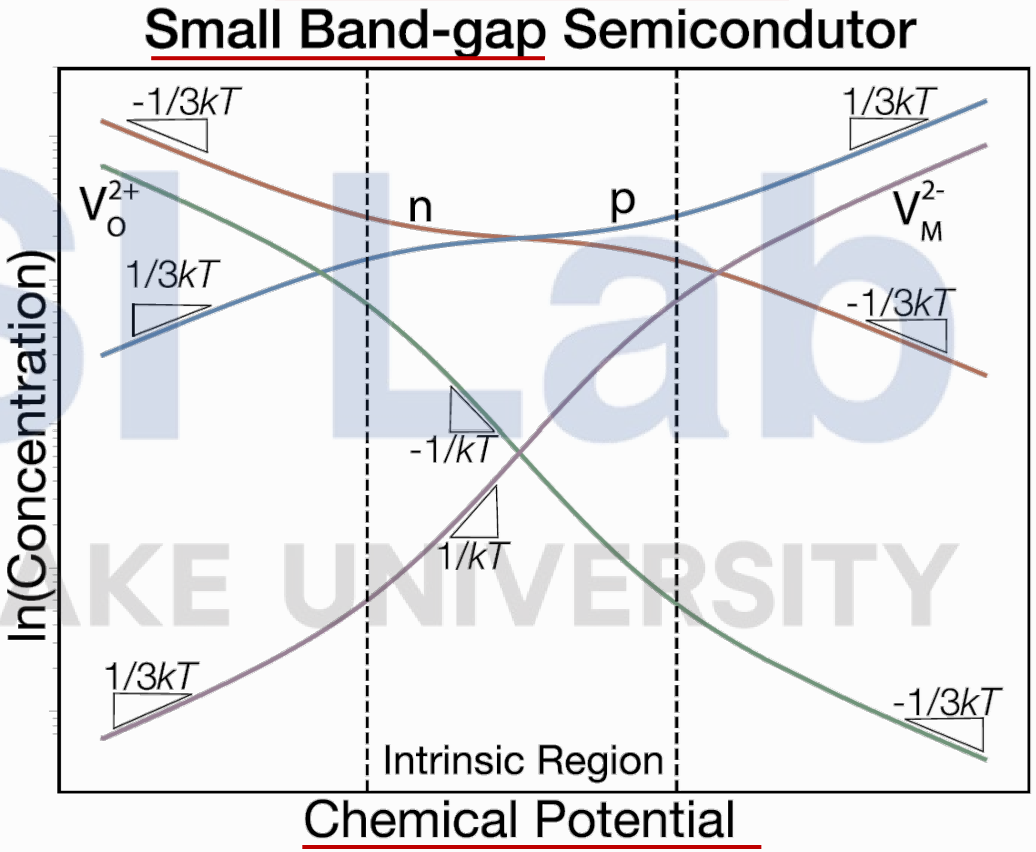
More “realistic” Brouwer diagram w/ Schottky pairs or extrinsic ionic defects

$K_{el} \ll K_S\ (E_g > \Delta G^0_{Sch}\ )$



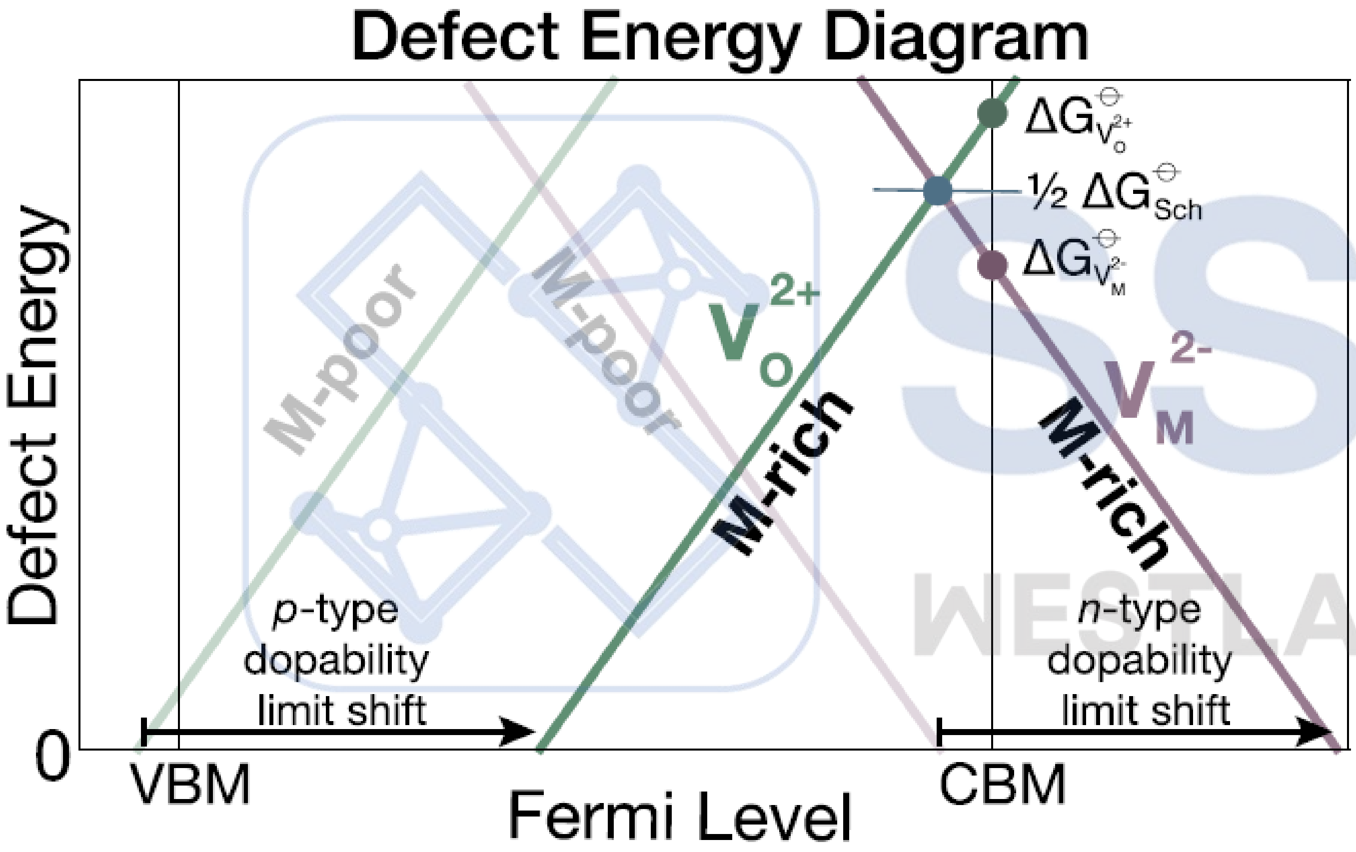
Anand, Haile, Snyder *et al.*, ***Acc. Mater. Res.***, 2022

$K_{el} \gg K_S\ (E_g < \Delta G^0_{Sch}\ )$



$$\mu_O = 1/2\ \mu_{O_2}$$
$$\mu_{O_2} = \mu^0_{O_2} + RTln(pO_2/pO_2{}^0)$$

Another way of expressing formation of defects



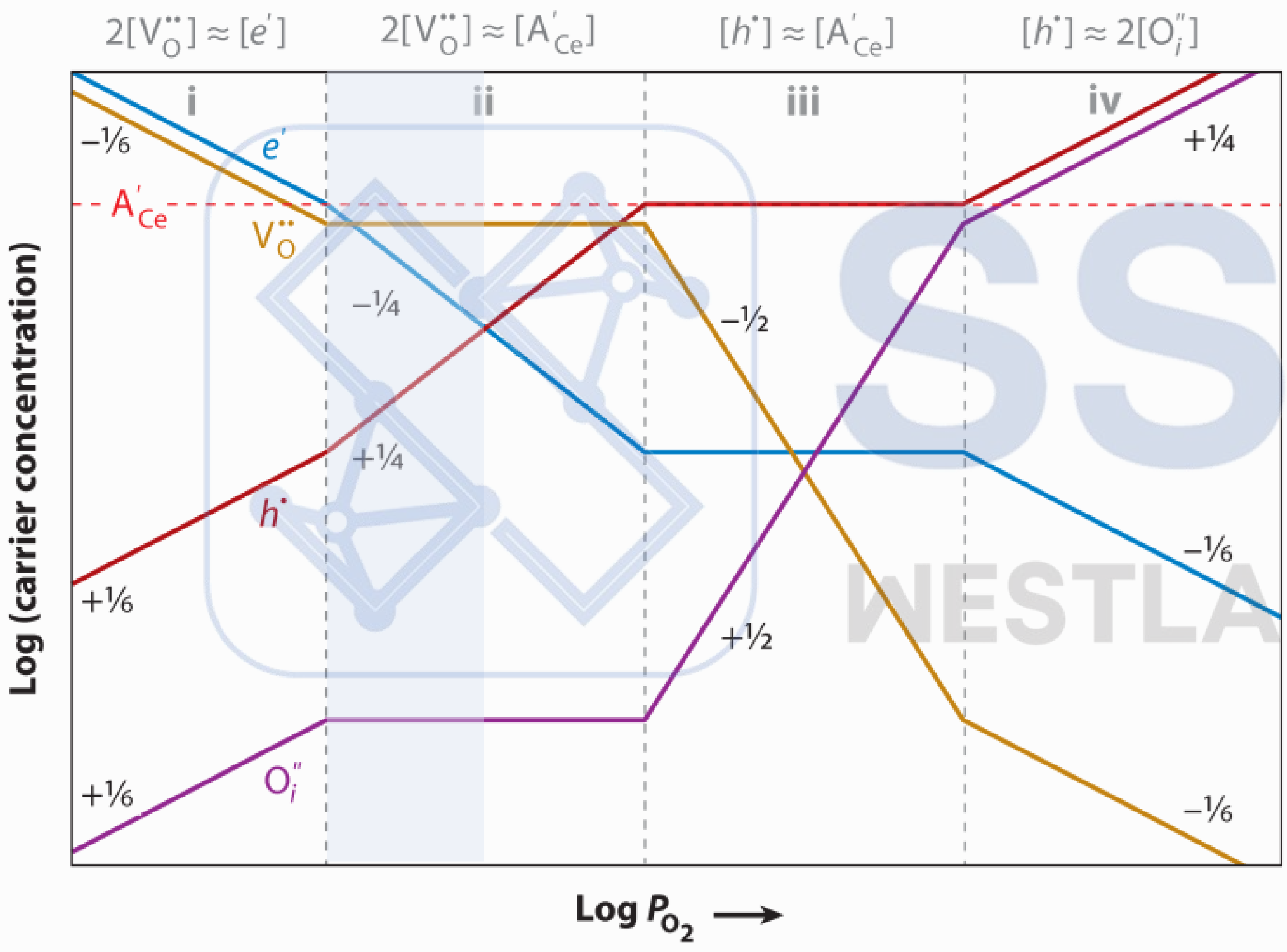
Anand, Haile, Snyder *et al.*, ***Acc. Mater. Res.***, 2022

$$\Delta E_d = E_{def} - E_{perfect} + qE_F - \sum_i \Delta N_i \mu_i$$

Fermi level

- Very commonly used by semiconductor physicists, especially those who do DFT calculations, since E_F can be used as a tuning parameter;
- Can be used to ***construct/convert to Brouwer diagrams***.

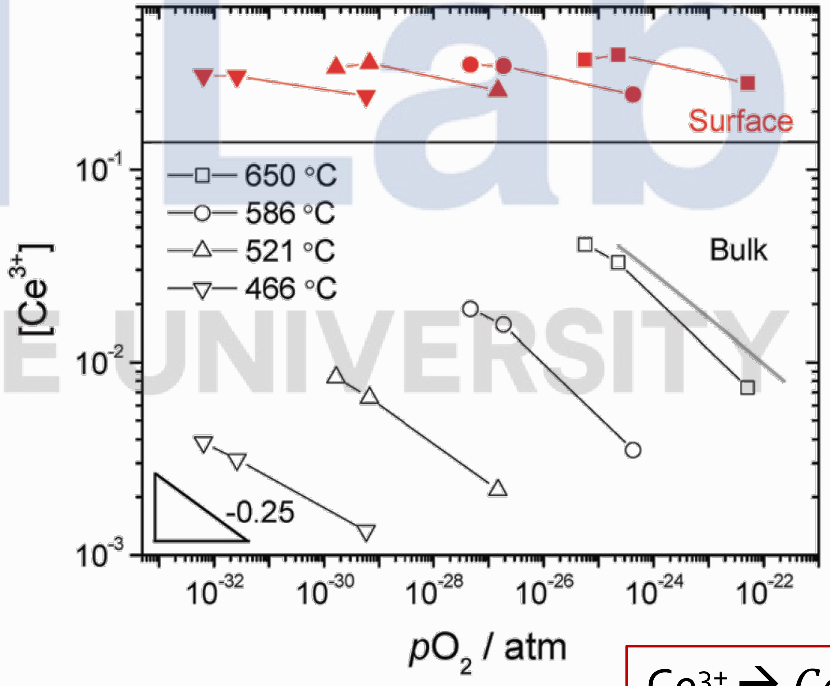
More “realistic” Brouwer diagram w/ Schottky pairs or extrinsic ionic defects



Acceptor-doped $CeO_{2-x-\delta}$

e.g., $Sm_{0.2}Ce_{0.8}O_{1.9-\delta}$

Sm^{3+} replacing Ce^{4+} → Sm'_{Ce}



Chueh *et al.*, ***Chem. Mater.***, 2012

Ce^{3+} → Ce'_{Ce} → e'

“small polaron”

Tuller and Bishop, ***Annu. Rev. Mater. Res.***, 2011

Defect concentration → ionic and electronic conductivity

- Direct measurement of defect concentration can be rather difficult;
- The most common practice is to measure the ***conductivity*** of materials.

Expression of ***conductivity***:

$$\sigma = n \cdot ze \cdot \mathrm{M} = cN_A \cdot ze \cdot \mathrm{M} = czFM$$

σ : Conductivity
c : Charge carrier concentration; N_A: Avogadro constant; F: Faraday constant
ze : Electric charge, for Li^+, $z = 1$
M: Mobility (usually denoted as μ, but not to be confused with chem. potential)

If we assume that the mobility stays constant within a range of chemical potential, then: $\boxed{\sigma \propto c_{def}}$

Usually, what we measure is the ***total*** conductivity σ_{tot}:

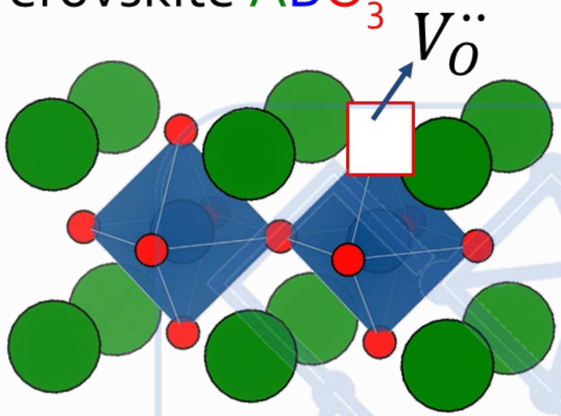
$$\boxed{\sigma_{tot} = \sigma_{el} + \sigma_{ion}}$$

$$\boxed{\sigma_{el} = n_e e M_e + n_p e M_h}$$

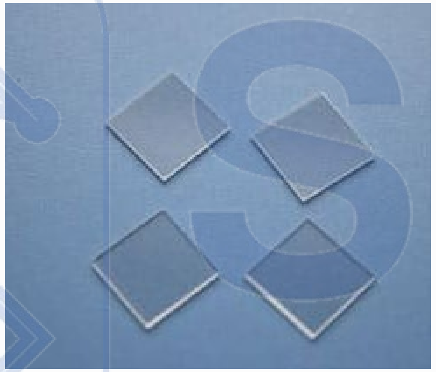
$$\boxed{\sigma_{ion} = n_{ion} z_{ion} e \, M_{ion}}$$

SrTiO$_3$ serves as a perfect example to show the log σ ~ log pO_2 plot

Perovskite ABO$_3$



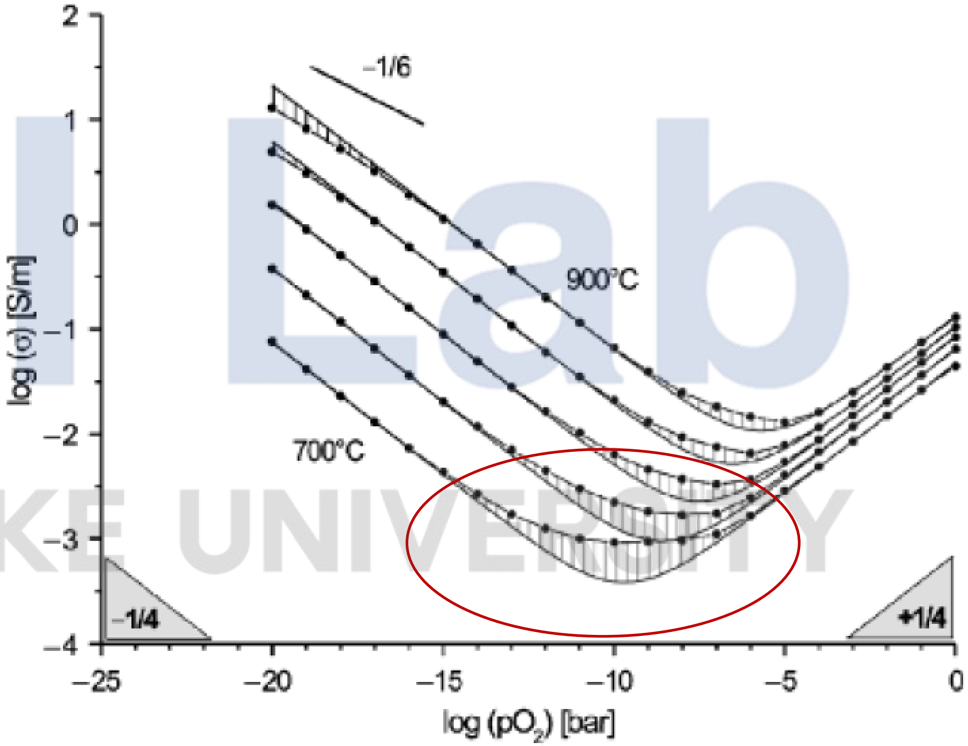
SrTiO$_{3-\delta}$ (STO)



Perovskite ABO$_3$ structure; Cubic (ideal tolerance factor);

("Si for perovskite oxides")

log σ_{tot} ~ log pO_2 plot

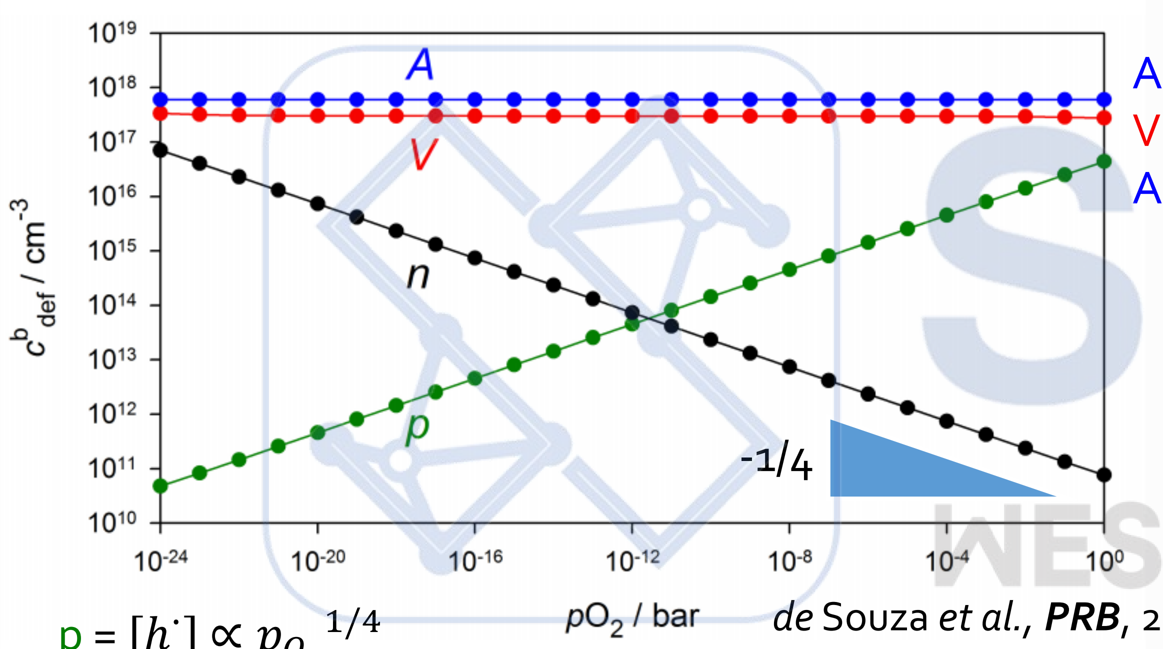


Ohly *et al.*, ***J. Am. Ceram. Soc.***, 2006

We want to understand:

- What do the different slopes tell us about ionic and electronic defect equilibrium?
- What does the shaded area mean?

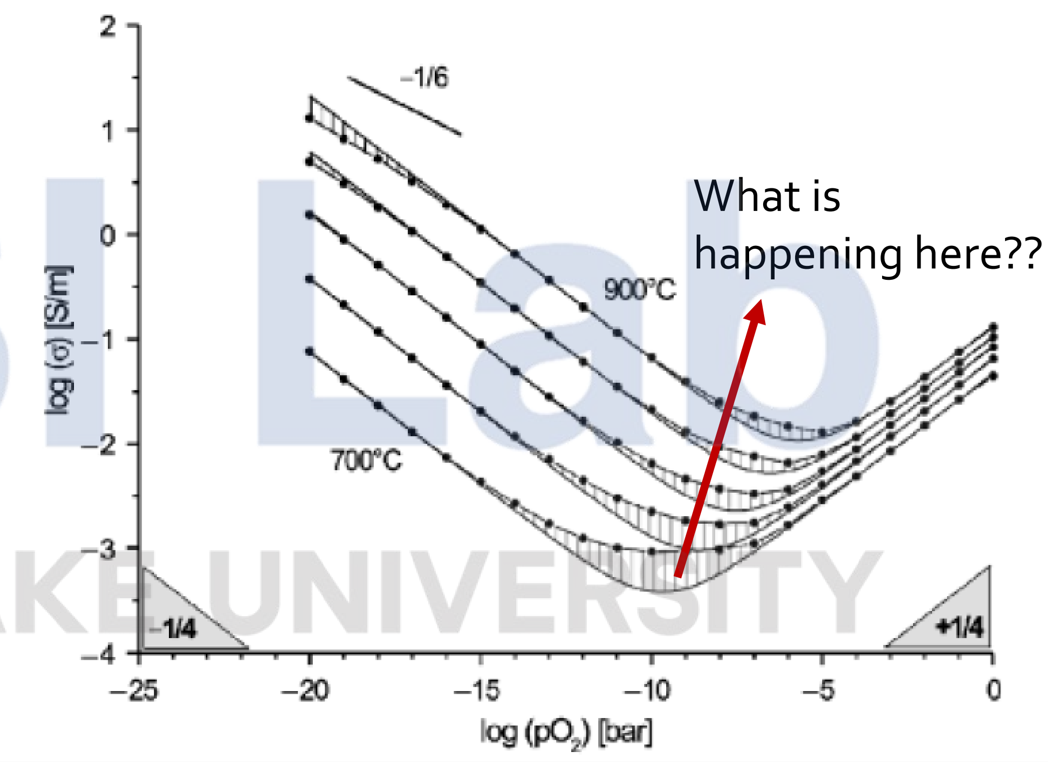
Ionic and electronic conductivity of $SrTiO_3$



A = $[A'_{Ti}]$
V = $[V_O^{\bullet\bullet}]$
A ≈ 2V

p = $[h^{\bullet}] \propto {p_{O_2}}^{1/4}$
n = $[e'] \propto {p_{O_2}}^{-1/4}$

de Souza *et al.*, ***PRB***, 2014



What is happening here??

Ohly *et al.*, ***J. Am. Ceram. Soc.***, 2006

$$\sigma_{tot} = ne\mu_e + pe\mu_h + V(Z_V e)\mu_V$$

At ~973 K for $SrTiO_3$:
μ_e, μ_h ~ 0.1 cm²/(V·s) vs. μ_V ~ 4 x 10^{-4} cm²/(V·s)

Brouwer diagram for lithium storage materials

For a lithium-storage material ***LiX*** that can tolerate both ***Li-excess and Li-deficiency***, we consider four point defects: Li_i', $V_{Li}^{\cdot}$, e', $h^{\cdot}$

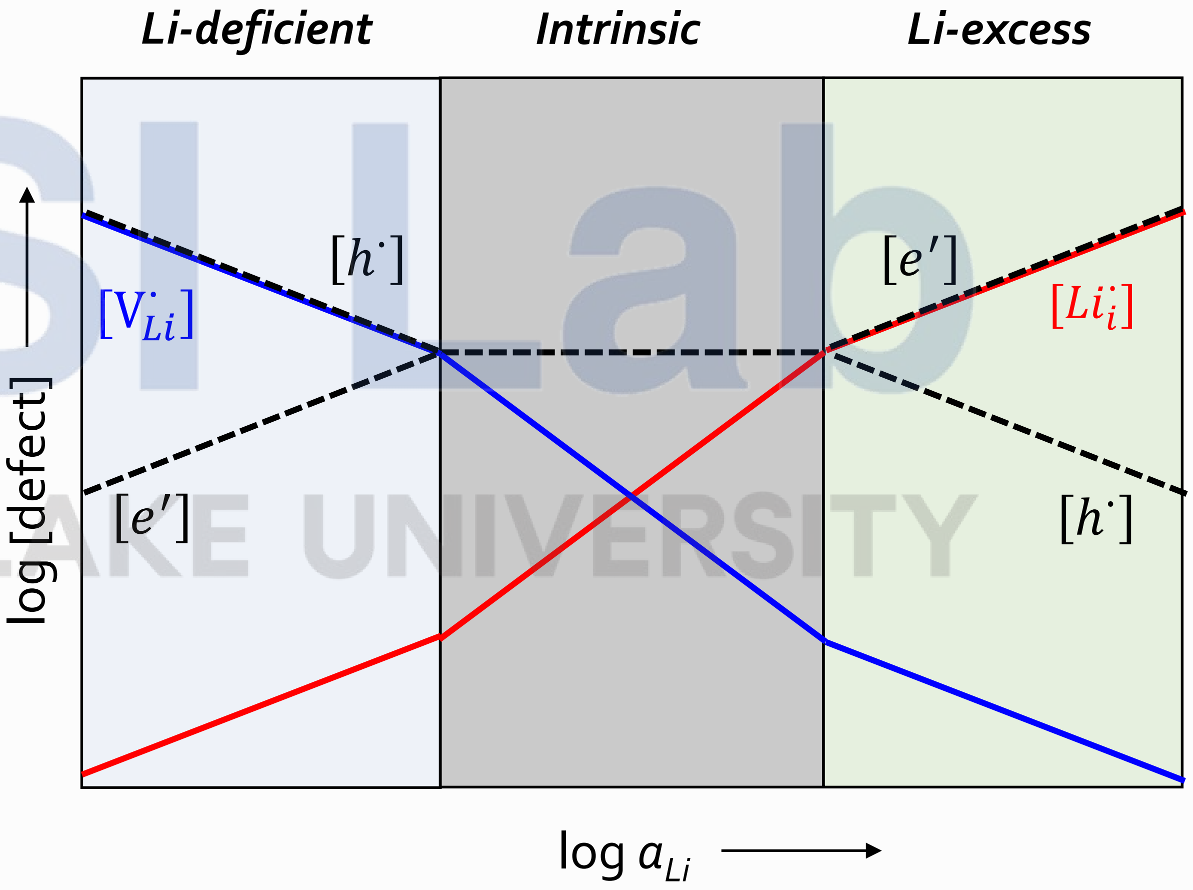
Frenkel pair $\quad null \leftrightharpoons Li_i^{\cdot} + V_{Li}' \quad K_F = [Li_i'][V_{Li}^{\cdot}]$

"Band-to-band" $\quad null \leftrightharpoons e' + h^{\cdot} \quad K_{el} = [e'][h^{\cdot}]$

Li intercalation $\quad Li \leftrightharpoons Li_i^{\cdot} + e' \quad K_{Li} = \frac{[Li_i^{\cdot}][e']}{a_{Li}}$

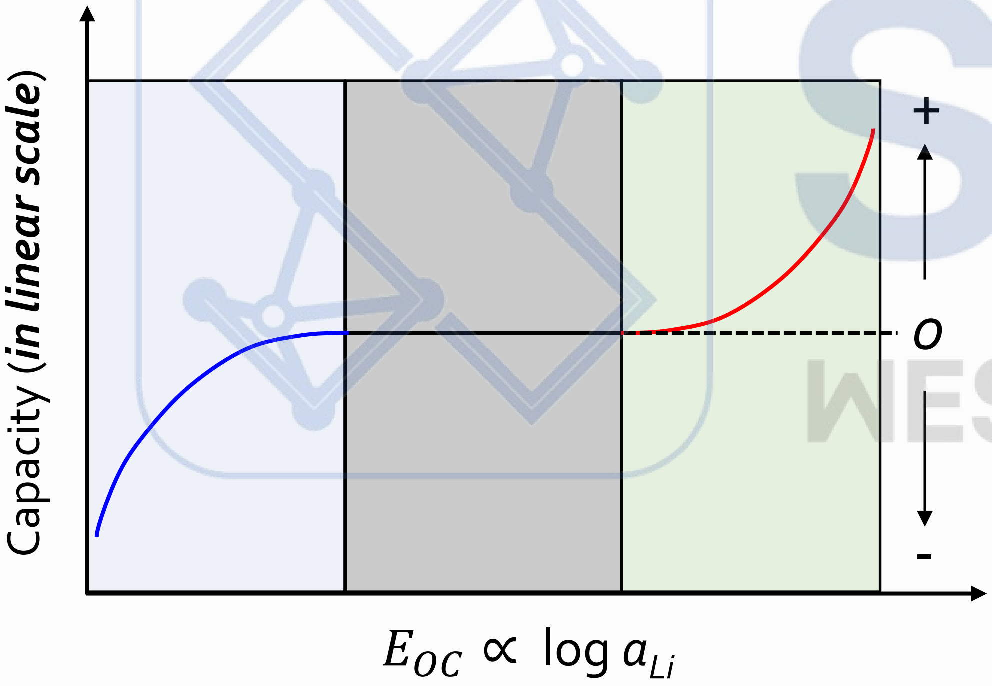
$$\boxed{\mu_{Li} = \mu_{Li}^0 + RTlna_{Li}}$$

We assume $K_{el} \gg K_F$ (small bandgap)

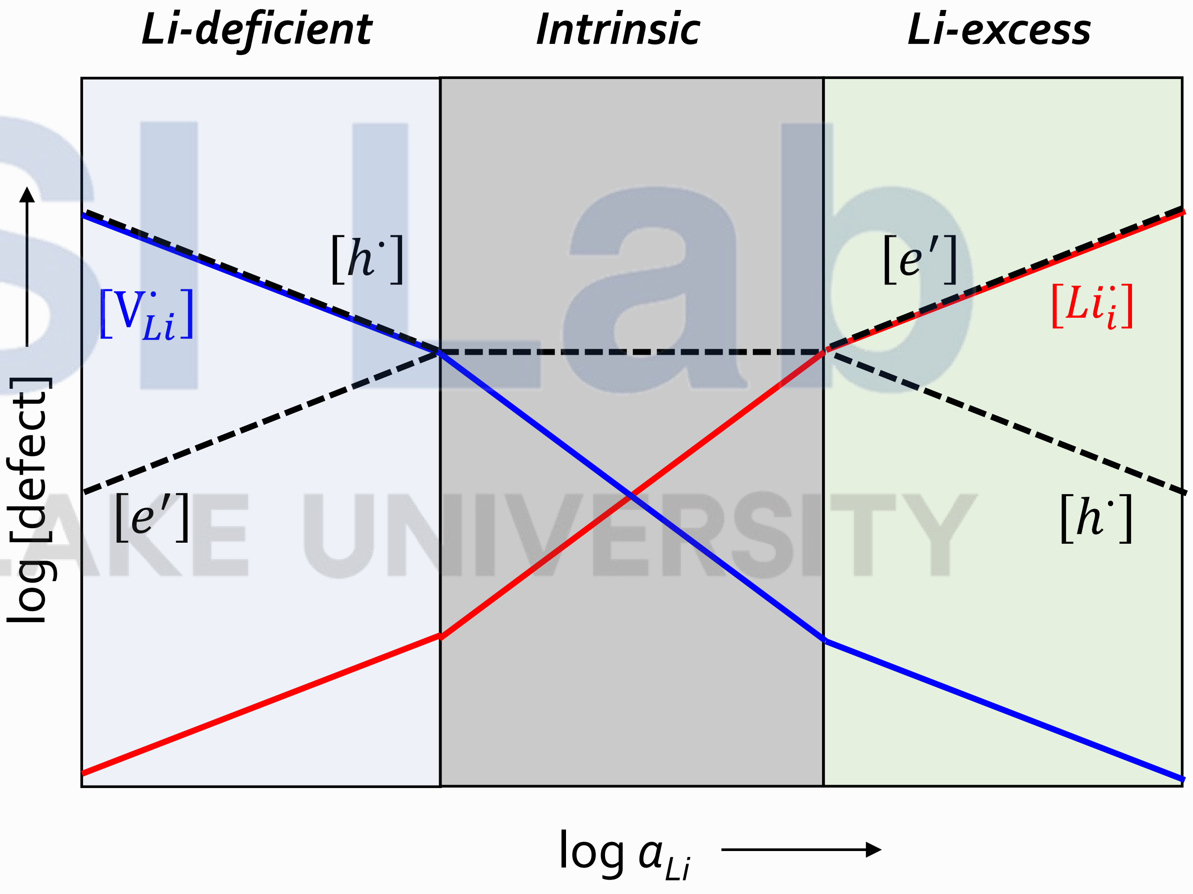


What can we get from such a Brouwer diagram?

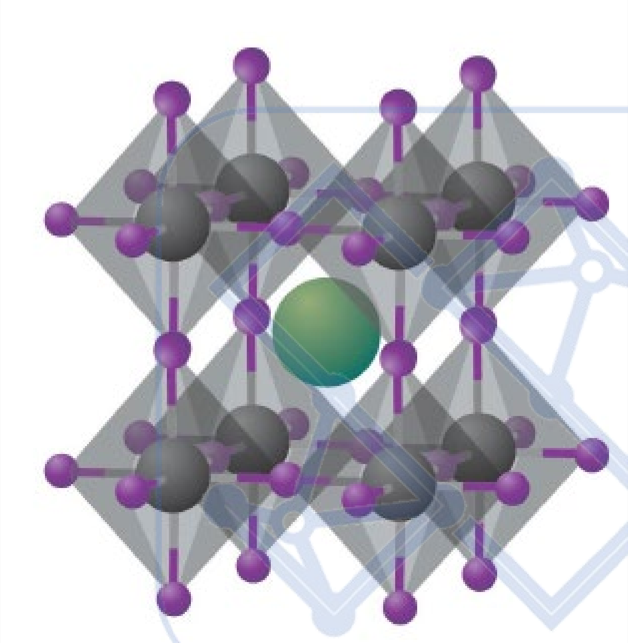
For Li-ion battery materials, we have:
Charge stored: $Q \propto |[Li_i^{\cdot}] - [V_{Li}^{\cdot}]|$
Open-circuit potential: $E_{OC} \propto \mu_{Li} \propto \ln a_{Li}$



Simulated battery charge/discharge curves (!)



Brouwer diagrams for halide perovskites



● A ● B ● X

e.g. Methylammonium lead iodide
$CH_3NH_3PbI_3$ ($MAPbI_3$)

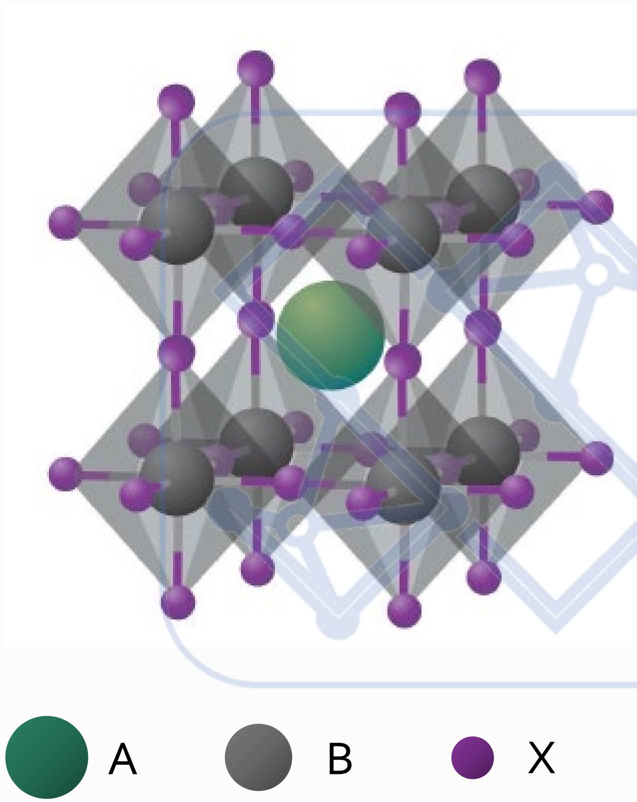
Why do halide perovskites attract so much attention?

- Wide range in composition design: from inorganic compound (*e.g.* $CsPbI_3$) to organo-metallic compound (*e.g.* $MAPbI_3$);
- High light absorption coefficient + very long diffusion length of electrons and holes (*i.e.*, very low charge recombination rate)

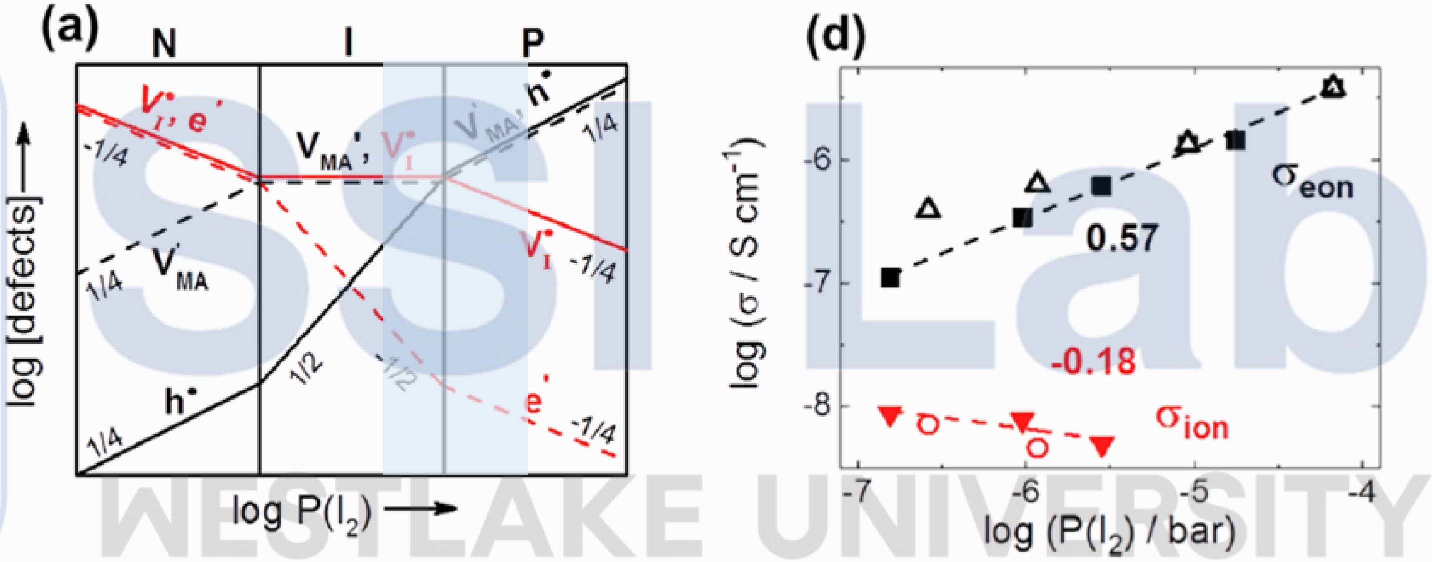
Since halide perovskites are called "*ionic semiconductors*", we should be able to understand from the perspective of defect chemistry:

- Halide perovskites are ***mixed ionic-electronic conductors.*** Therefore, it is important to differentiate ionic and electronic conductivities;
- Peculiar ion transport behavior under illumination. Ionic conductivity is shown higher under light compared with dark condition.

Brouwer diagrams for halide perovskites: *Intrinsic*



$$\frac{1}{2}I_{2(g)} + \mathrm{V}_{\mathrm{I}}^{\cdot} \rightarrow \mathrm{I}_{\mathrm{I}}^{\times} + h^{\cdot}$$



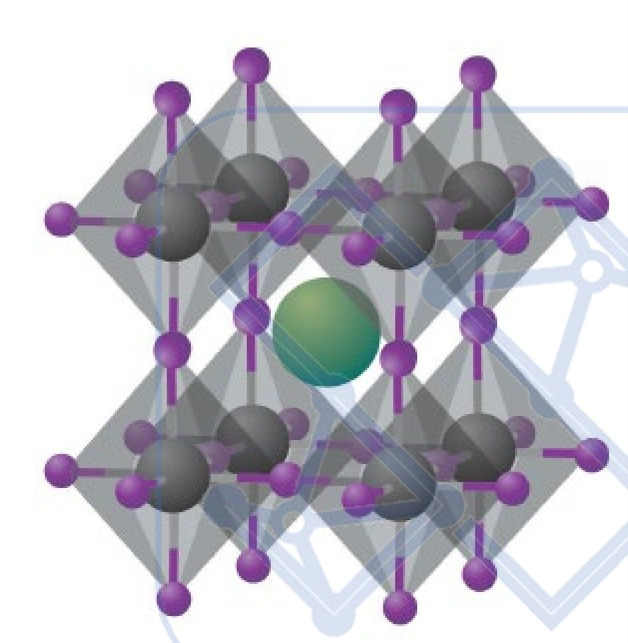
Senocrate and Maier, *J. Am. Chem. Soc.*, 2019

Brouwer diagram of MAPbI$_3$
Measure ionic (σ_{ion}) and electronic (σ_{eon}) conductivity as a function of *p*I$_2$

Conclusions:

1. The tested *p*I$_2$ range is within the **I-P** transition region in the Brouwer diagram; (The measured slope has some uncertainties)
2. The dominate ionic mobile defects are the ***iodine vacancies***

Brouwer diagrams for halide perovskites: *Intrinsic*

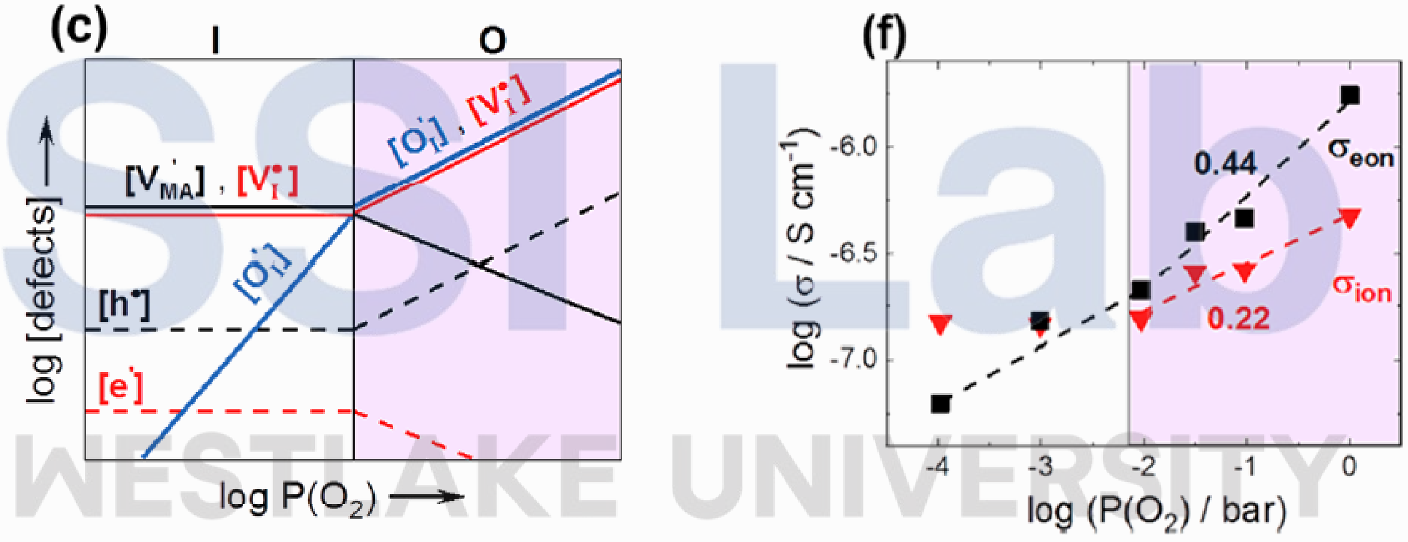


● A ● B ● X

Brouwer diagram of $MAPbI_3$

Measure ionic (σ_{ion}) and electronic (σ_{eon}) conductivity as a function of pO_2

$$\frac{1}{2}O_{2(g)} + I_I^{\times} \rightarrow O_I' + V_I^{\cdot}$$



Senocrate and Maier, *J. Am. Chem. Soc.*, 2019

Conclusion:

Incorporated O ions act as accept dopants, which increases the electronic conductivity.

Things we have discussed in this lecture

Electronic defects:

- What is the difference between electronic and ionic defects?
- A brief review on basic semiconductor physics: how to write the charge neutrality equation by using Kröger-Vink notations?

Brouwer diagrams:

- What question are we trying to solve by using the Brouwer diagram?
- What is the key assumption of Brouwer diagram (so-called Brouwer condition)?
- How does a typical Brouwer diagram for metal oxides look like? How can it be used to predict/understand the conductivity of materials?

Goal of this lecture: you should be able to answer the questions above now (hopefully) :)

西湖大學
WESTLAKE UNIVERSITY

End of Lecture 2
Solid State Ionics Fall 2022

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