Functional Inorganic Materials
Fall 2023

Mondays: 10.15 - 12.00
Thursdays: 10.15 - 12.00

Lecture hall locations: U7 in Otakaari 1 / U-wing
Ke1 in Kemistintie 1 (CHEM building)

You can use https://usefulaaltomap.fi/ to see the exact location of U7.

#	Date	Place	Who	Topic
1	Mon 4.9.	U7 (U135a)	Maarit	Introduction + **Materials design**
2	Thu 7.9.	Ke1 (A305)	Antti	Introduction + Computational materials design
3	Mon 11.9.	U7 (U135a)	Maarit	Superconductivity: High-T_c superconducting Cu oxides
4	Thu 14.9.	Ke1 (A305)	Maarit	Magnetic oxides
5	Mon 18.9.	U7 (U135a)	Maarit	Ionic conductivity (Oxygen): Oxygen storage and SOFC
6	Thu 21.9.	Ke1 (A305)	Maarit	Ionic conductivity (Lithium): Li-ion battery
7	Mon 25.9.	U7 (U135a)	Antti	Thermal conductivity
8	Thu 28.9.	Ke1 (A305)	Antti	Thermoelectricity
9	Mon 2.10.	U7 (U135a)	Antti	Piezoelectricity
10	Thu 5.10.	Ke1 (A305)	Antti	Pyroelectricity and ferroelectricity
11	Mon 9.10.	U7 (U135a)	Antti	Luminescent and optically active materials
12	Thu 12.10.	Ke1 (A305)	Maarit	Hybrid materials

LECTURE 1: Materials Design Concepts

- **EXAMPLE: Electrical conductivity & Charge carrier concentration**
- **n-type (electrons) & p-type (holes) conductivity**
- **Doping & Substitution**
- **Aliovalent Substitution (vs. isovalent subst.) & Mixed Valency**
- **Nonstoichiometry: Vacancies (deficiency) & Interstitials (excess)**
- **Relative Ion Sizes & Tolerance Parameter**
- **OTHER KEYWORDS:**
  Band structure, Crystal field splitting & Jahn-Teller distortion

We first recall the doping scheme in elemental semiconductors (Si) which you have learned in your basic studies.

Then, we have a look on how the situation is similar/different for chemical compounds (of major focus in this course),

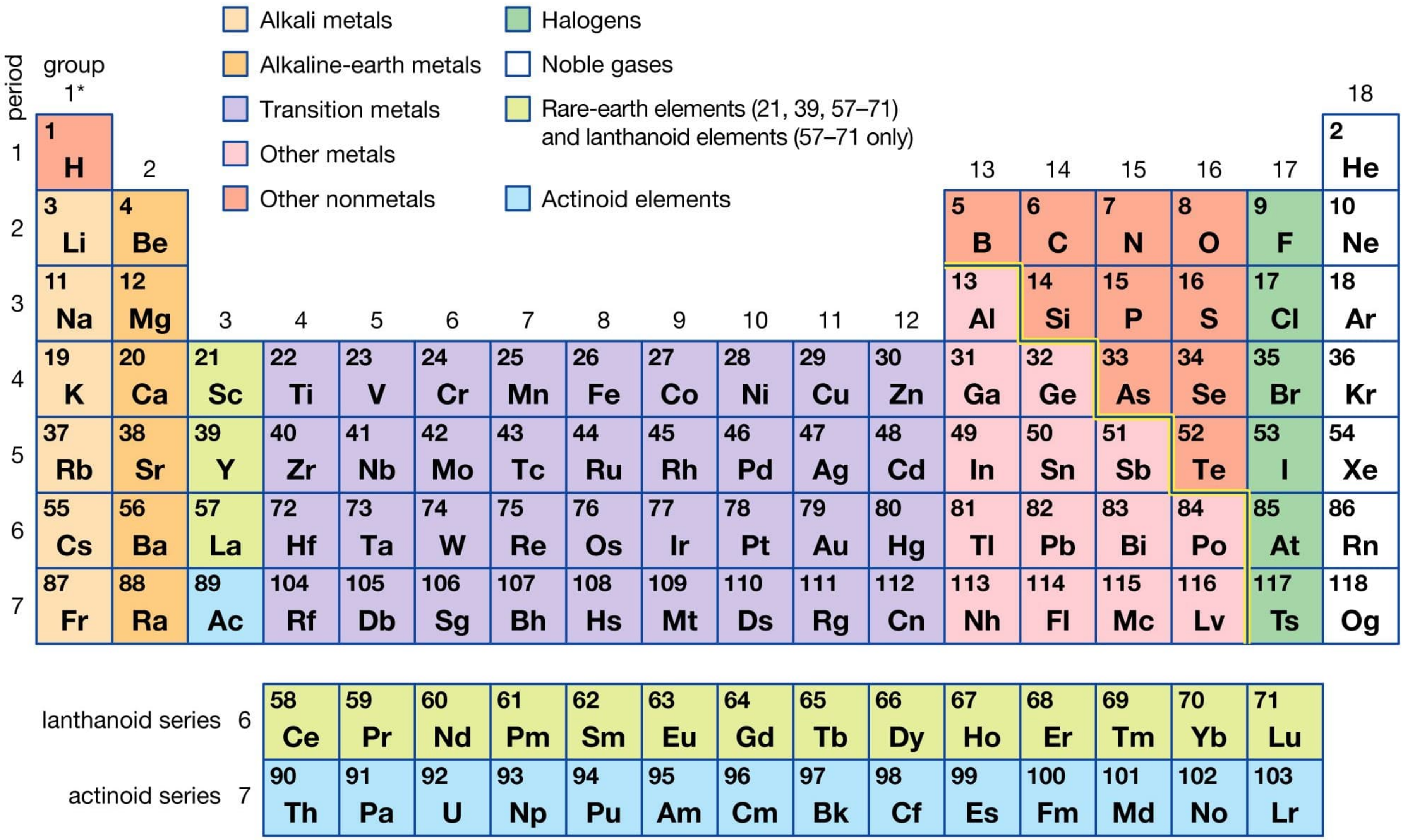
using ZnO and perovskite metal oxides as examples.

LECTURE EXERCISE 1

1. **Discuss in a comparative manner the doping schemes in Si (elemental semiconductor), ZnO (simple metal oxide) and complex transition metal oxides (perovskites).**
2. **Assign the type of doped carriers (n-type or p-type) for the following materials, and rationalize your answers: Al-doped Si, Al-doped ZnO, $(Pb_{0.98}Na_{0.02})Te$, $(La_{0.9}Sr_{0.1})_2CuO_{4.0}$, $La_2CuO_{4.1}$.**
3. **Calculate tolerance parameters for the following perovskite compounds (using ionic radius values given below), and judge whether the compounds are feasible. Also, predict in which of them it is most easy to create oxygen vacancies; explain why: $LaMnO_3$, $LaCoO_3$, $LaNiO_3$, $LaCuO_3$.**

IONIC RADII:		
	La^{3+}	1.36 Å
	Mn^{3+}	0.65 Å
	Co^{3+}	0.61 Å
	Ni^{3+}	0.60 Å
	Cu^{3+}	0.54 Å
	O^{2-}	1.40 Å

Periodic table of the elements



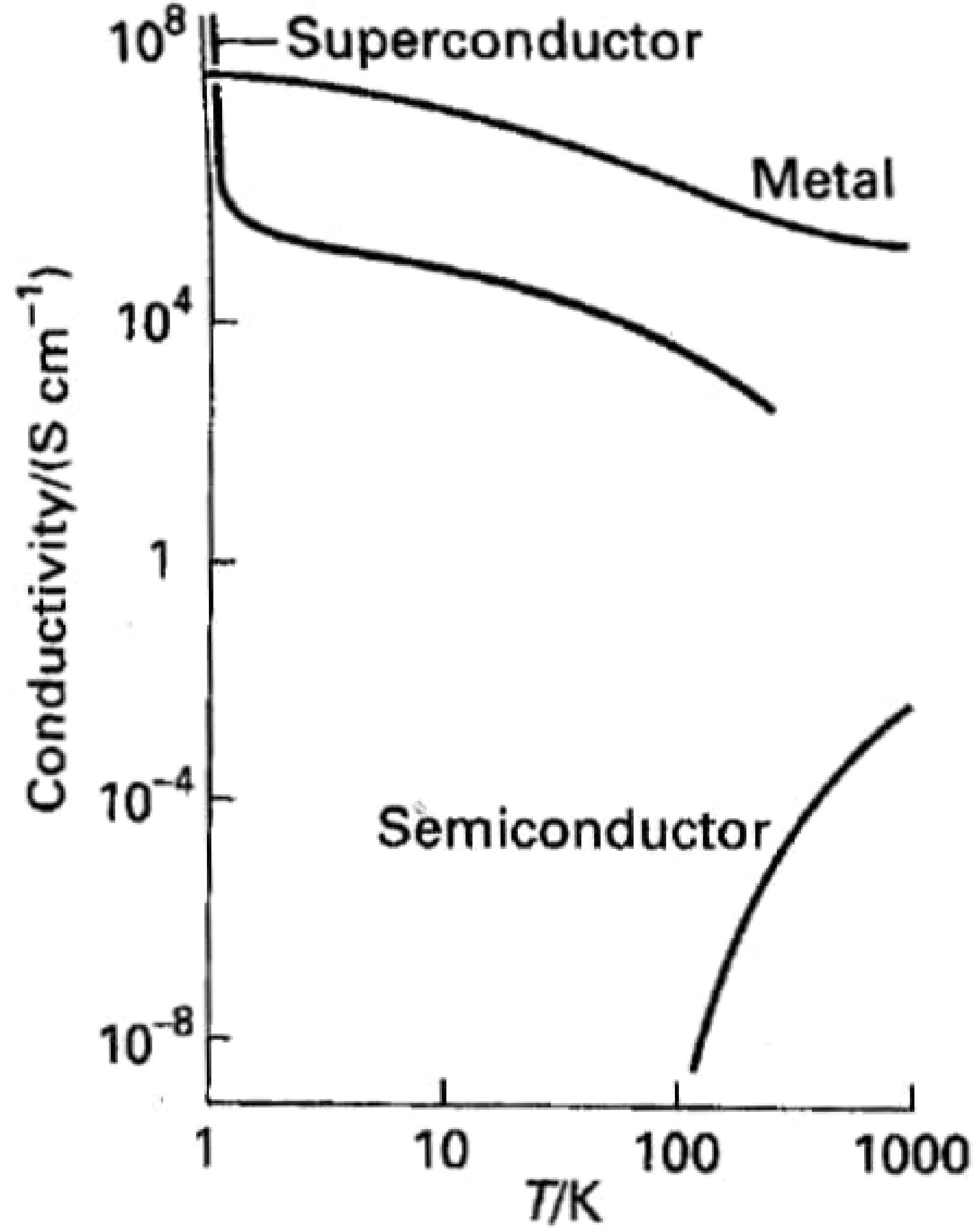
- ☐ Alkali metals
- ☐ Alkaline-earth metals
- ☐ Transition metals
- ☐ Other metals
- ☐ Other nonmetals
- ☐ Halogens
- ☐ Noble gases
- ☐ Rare-earth elements (21, 39, 57–71) and lanthanoid elements (57–71 only)
- ☐ Actinoid elements

period \ group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

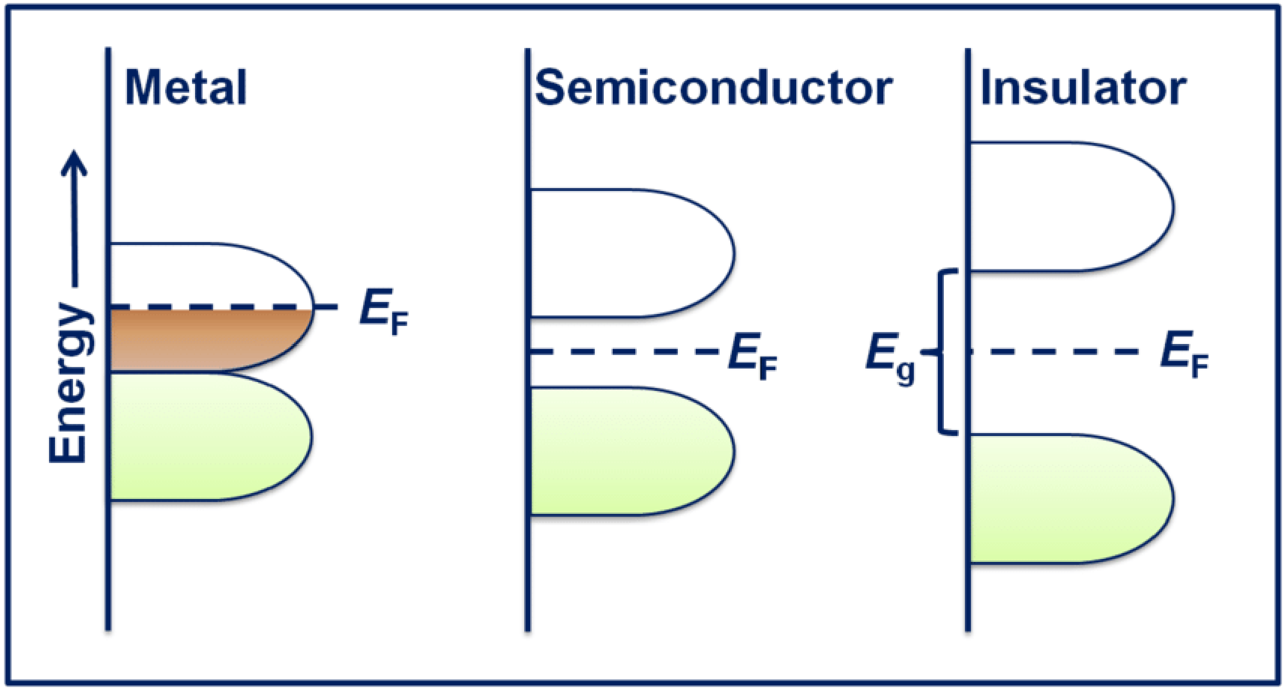
lanthanoid series 6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
actinoid series 7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

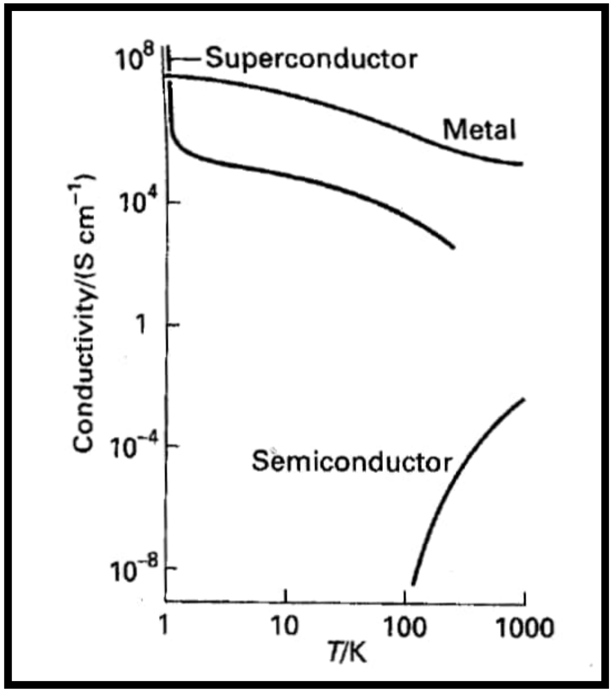
*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

ELECTRICAL CONDUCTIVITY

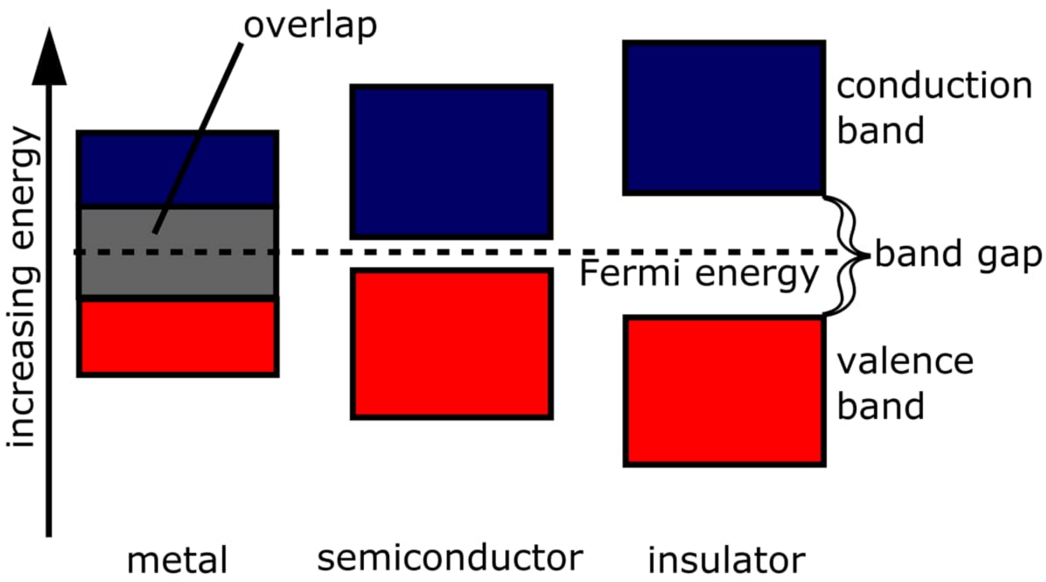


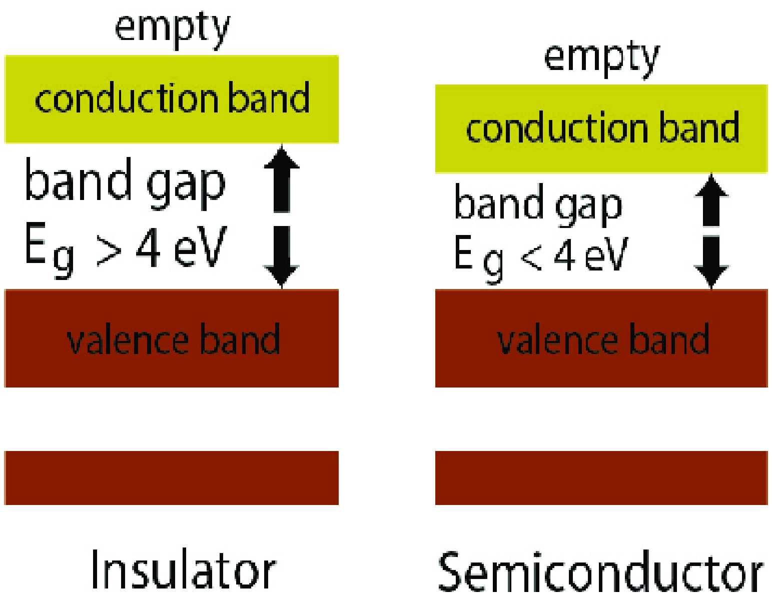
Schematic Band Structures

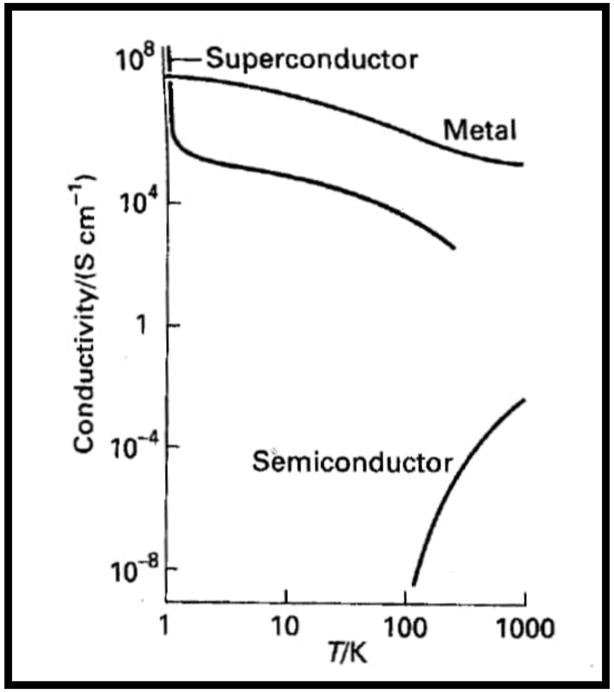




- Recall the meanings of E_F and E_g
- What is the x-axis ?
- How large is E_g for a semiconductor / an insulator ?
- Can you explain the different temperature dependencies of electrical conductivity for metals and semiconductors ?

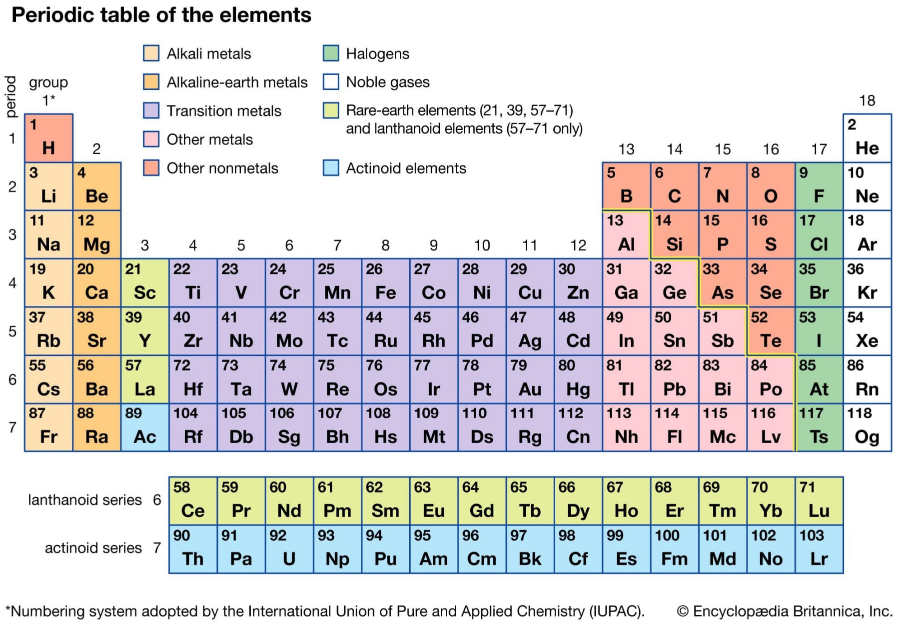

overlap
increasing energy
conduction band
band gap
Fermi energy
valence band
metal
semiconductor
insulator


empty
conduction band
band gap
$E_g > 4$ eV
valence band
Insulator
empty
conduction band
band gap
$E_g < 4$ eV
valence band
Semiconductor


Superconductor
Metal
Semiconductor
Conductivity/(S cm^{-1})
10^8
10^4
1
10^{-4}
10^{-8}
1
10
100
1000
T/K

n-type: donor

p-type: acceptor



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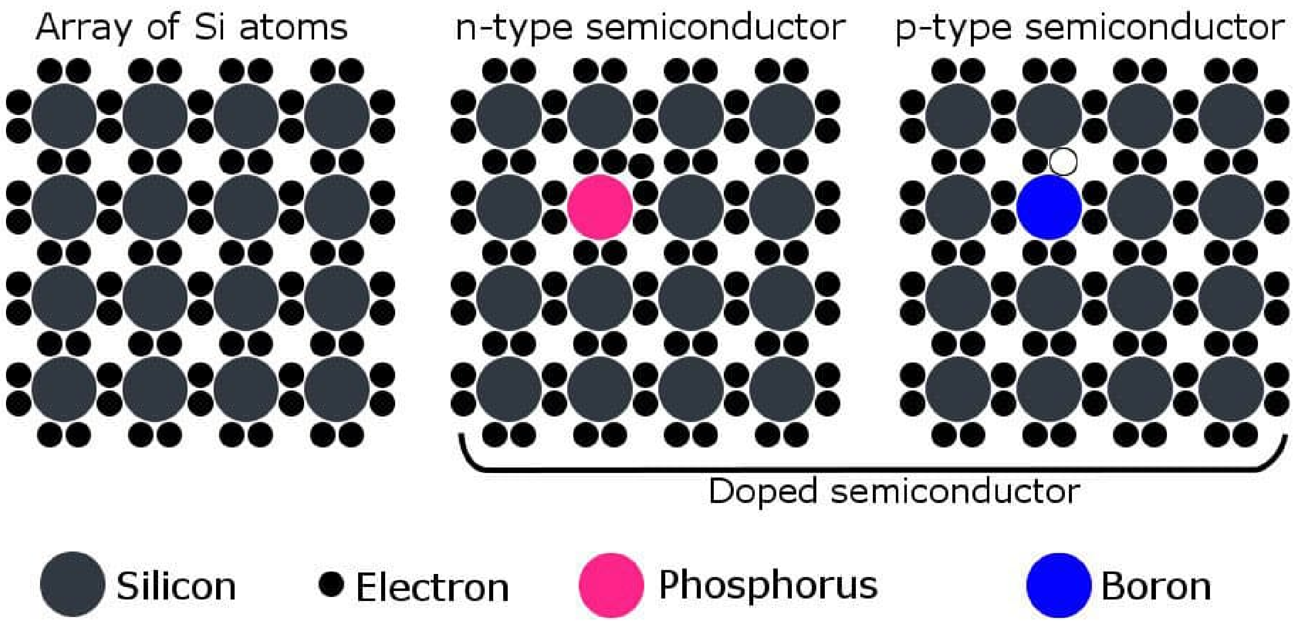
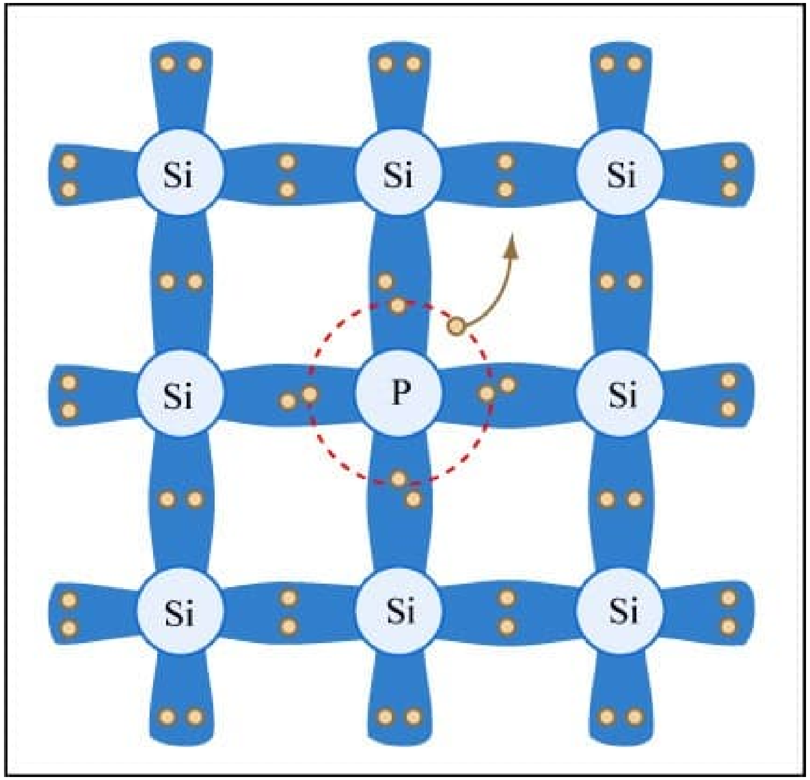
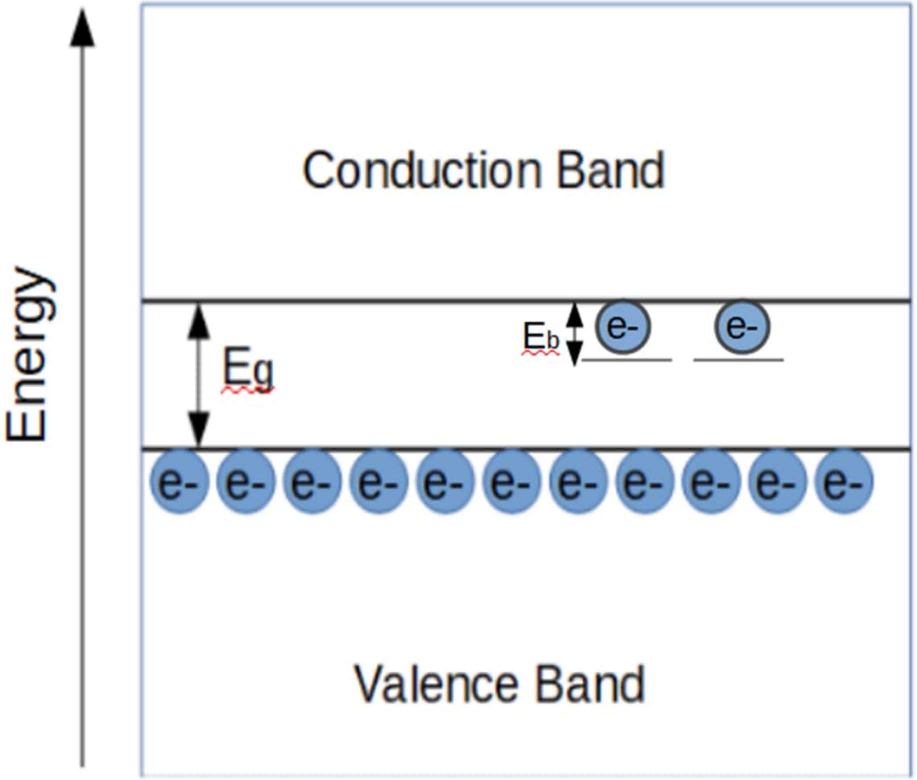
Doping in Semiconductors



n-type doping:

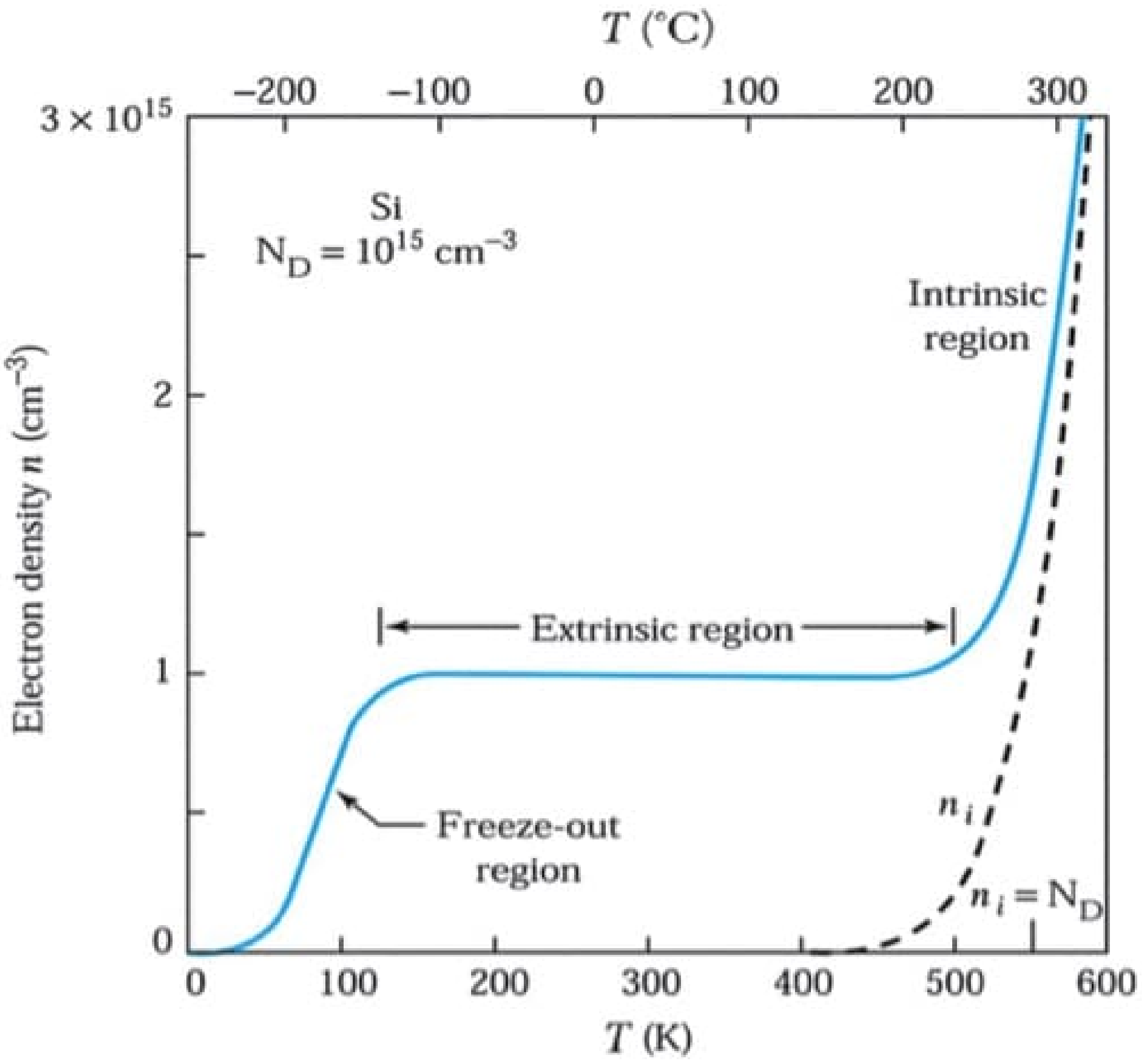
- Si: 4 valence electrons
- P: 5 valence electrons (= 1 extra)

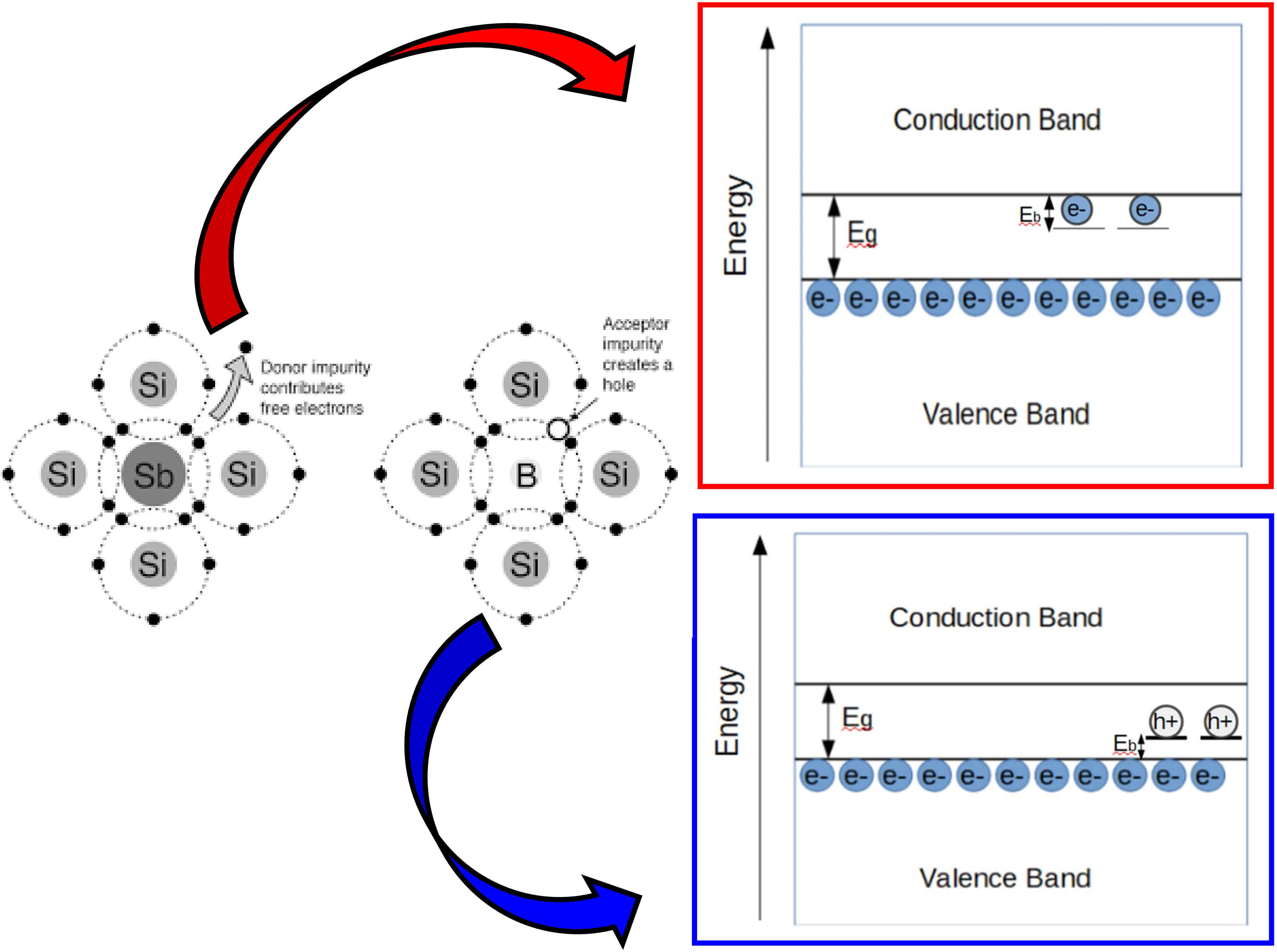




Si atoms: $5 \cdot 10^{22}$ cm^{-3}

Dopant atoms: 10^{15} cm^{-3}




Si
Si
Sb
Si
Si
Donor impurity contributes free electrons
Si
Si
B
Si
Si
Acceptor impurity creates a hole
Energy
Conduction Band
Eg
Eb
e-
e-
e-
e-
e-
e-
e-
e-
e-
e-
e-
e-
e-
Valence Band
Energy
Conduction Band
Eg
h+
h+
Eb
e-
e-
e-
e-
e-
e-
e-
e-
e-
e-
e-
Valence Band

ALIOVALENT SUBSTITUTION

n-type doping: “higher valent”

e.g. P(V) e.g. for Si(IV)

p-type doping: “lower valent”

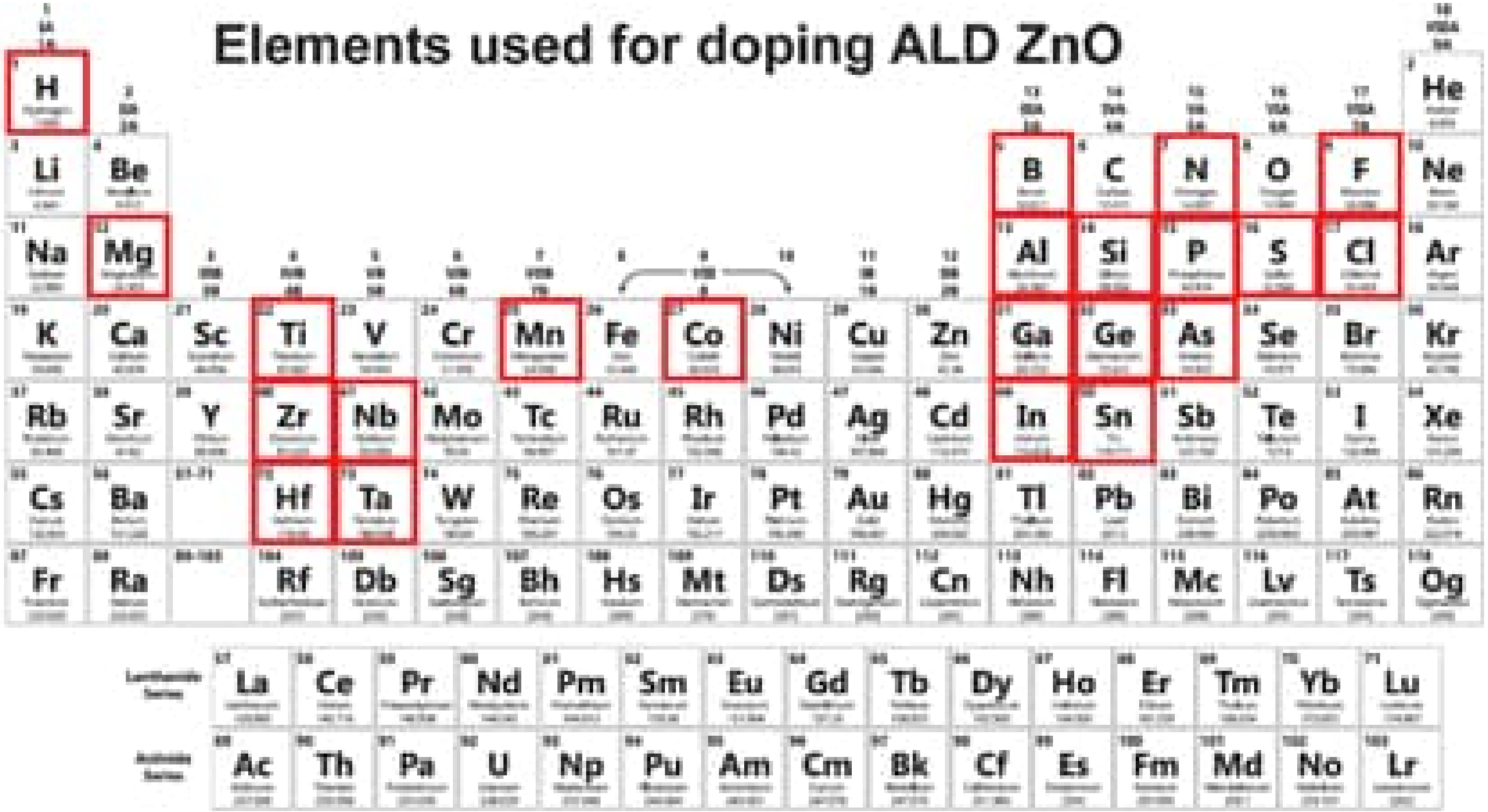
e.g. B(III) for Si(IV)

Simple metal oxide semiconductor: ZnO

- Intrinsically n-type: “native” or “unintentionally occurring” defects;
  What kind of defects could be responsible for n-type doping ?
    - n-type: “higher positive valence”
    - Slight excess of Zn(II) (at interstitial sites)
    - Proton (H^+) interstitials

- Intentional n-type doping: typically Al(III) for Zn(II)

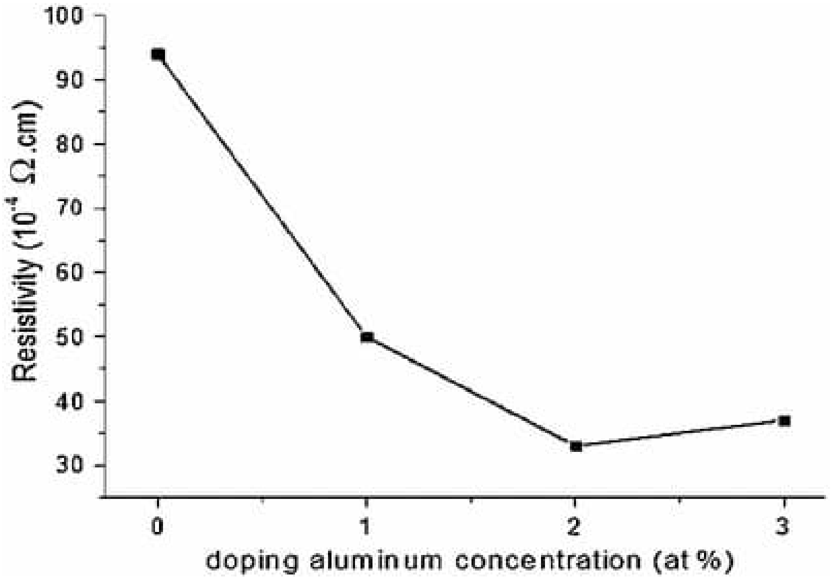
- p-type doping very much desired but has turned out to be difficult

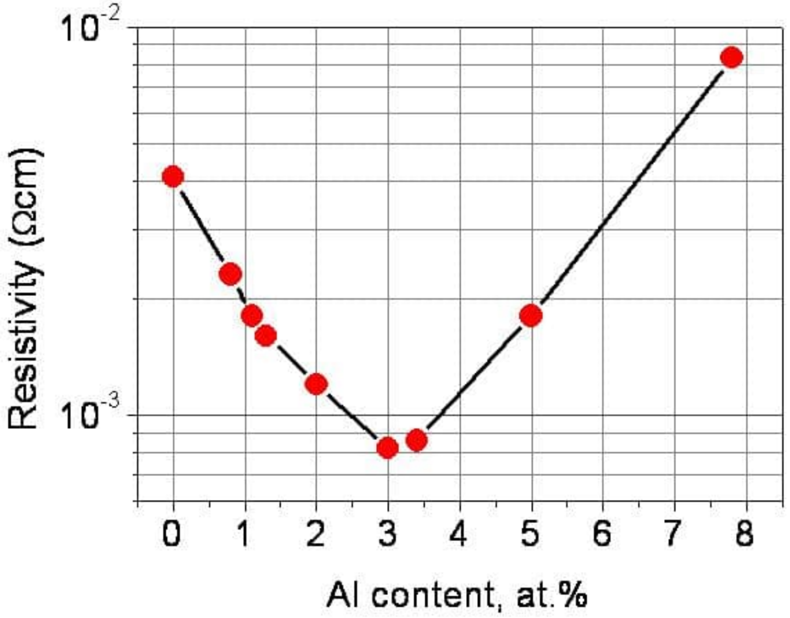


Zhengning Gao *and* Parag Banerjee, Review Article: Atomic layer deposition of doped ZnO films, Journal of Vacuum Science & Technology A **37**, 050802 (2019); https://doi.org/10.1116/1.5112777

INTENTIONAL DOPING: typical substitution level ?

Typical aluminum substitution level in ZnO ?





Perovskite – Multifunctional structure

Perovskite

ABO_3

Ion conductor
$La(Co,Ga)O_3$

Electric insulator
$SrTiO_3$

Superconductor
$CuBa_2YCu_2O_{6+z}$

Magnetoresistor
$LaMnO_3$

Record-high melting point
$Ba_3MgTa_2O_9$

Major constituent of earth
$MgSiO_3$

Catalyst
$La(Co,Mn)O_3$

Metallic conductor
$LaCrO_3$

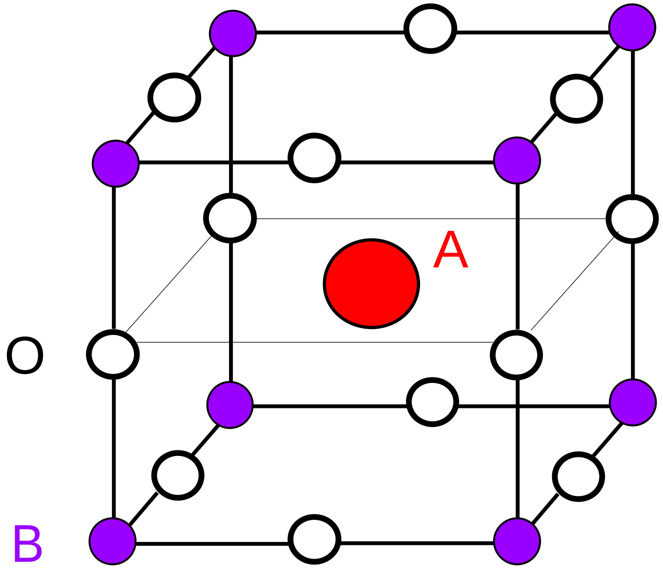
Piezoelectric material
$Pb(Zr,Ti)O_3$

Capasitor
(high dielectric constant)
$BaTiO_3$

PEROVSKITE STRUCTURE

General formula: $ABO_{3-\delta}$

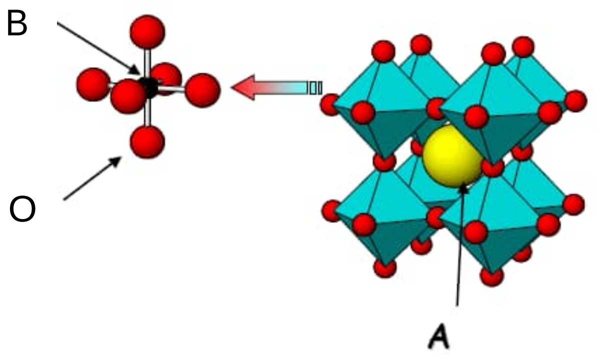
A: large cation
B: small cation (transition metal)
O: oxygen (sometimes halogen)



$V(A) + V(B) = 6$

e.g. $La^{III}Sc^{III}O_3$, $Sr^{II}Ti^{IV}O_3$, $Na^{I}Nb^{V}O_3$

$CN(A)=12$, $CN(B)=6$, $CN(O)=6$



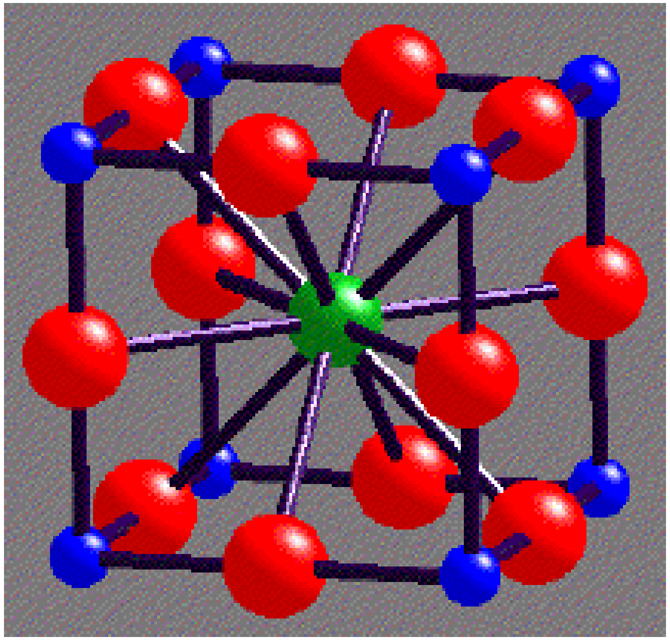
Mineral Perovskite: $CaTiO_3$

- **Named after Russian mineralogist, Count Lev Aleksevich von Perovski**
- **Discovered by Gustav Rose in 1839 from samples found in Ural Mountains**

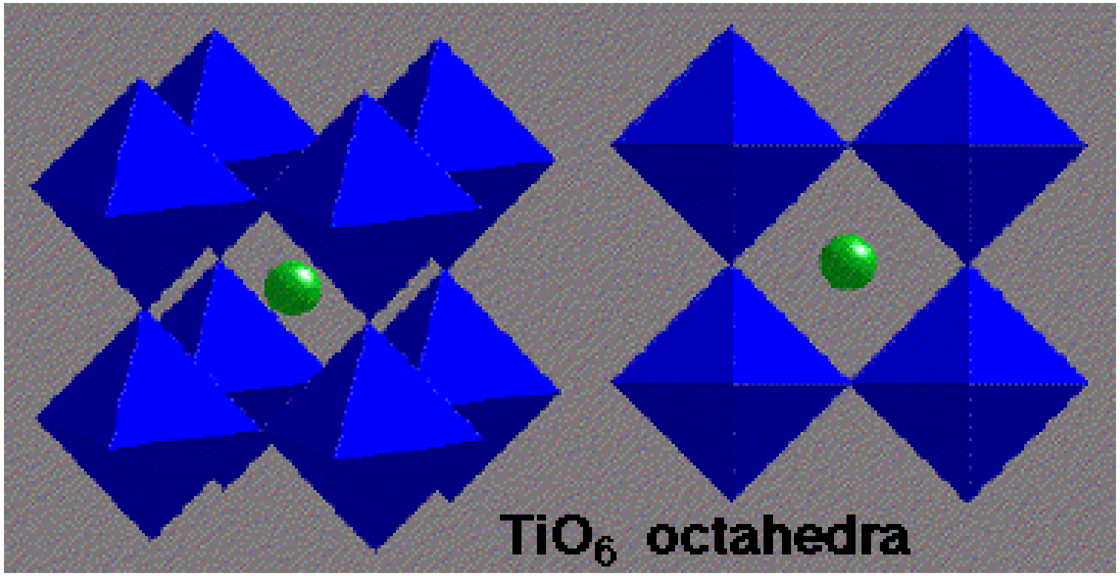
Perovskite

$CaTiO_3$

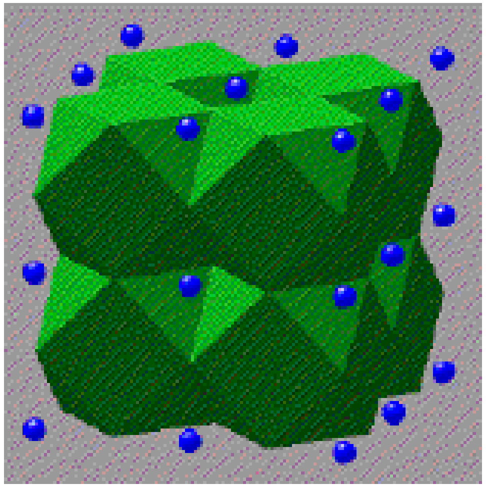
● Ca ● Ti ● O



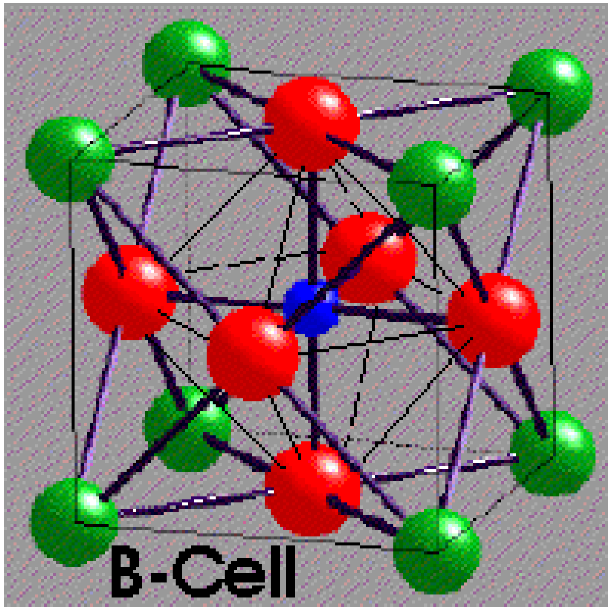
A-Cell



TiO_6 octahedra

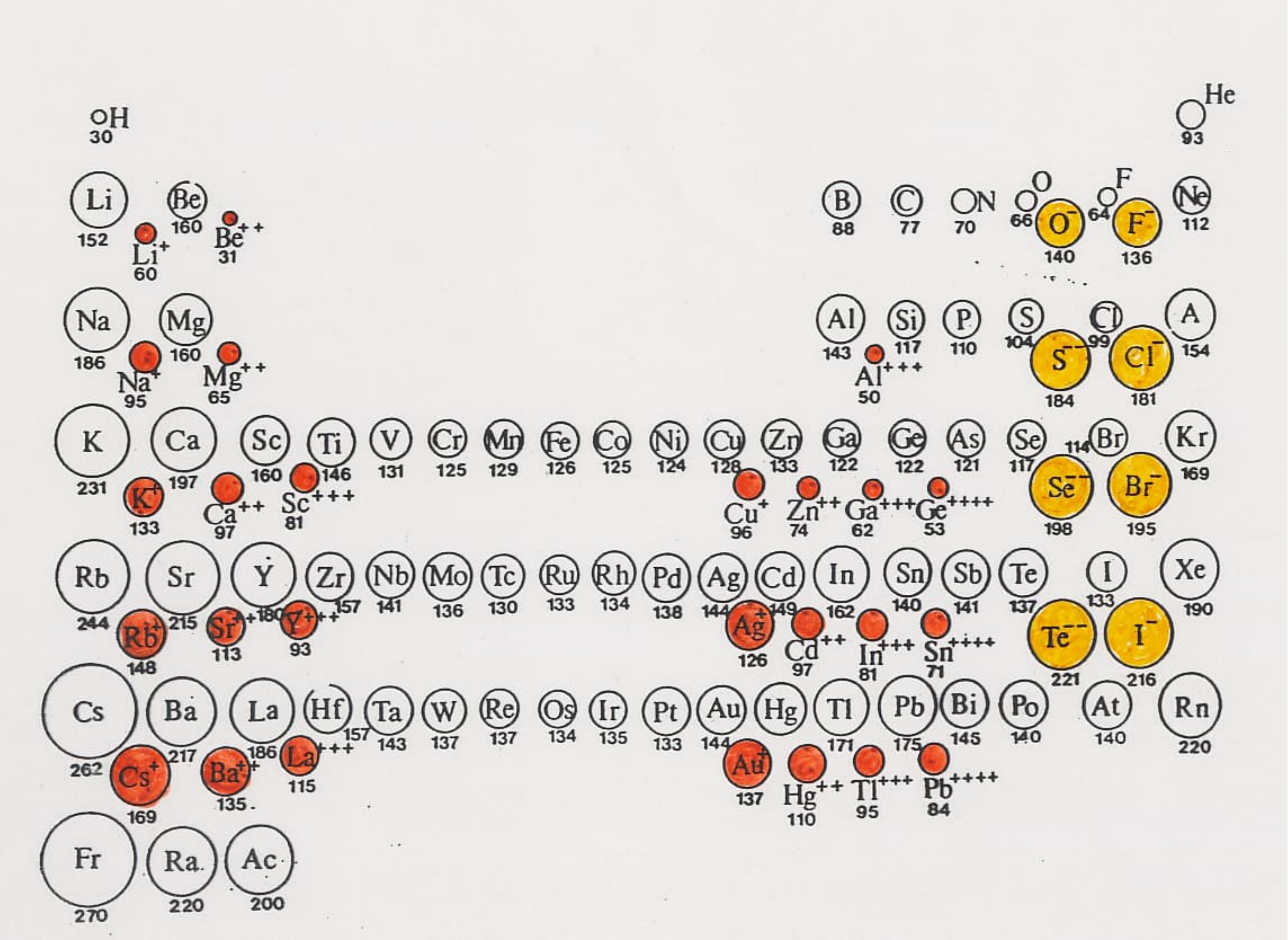


CaO_{12} cuboctahedra



B-Cell

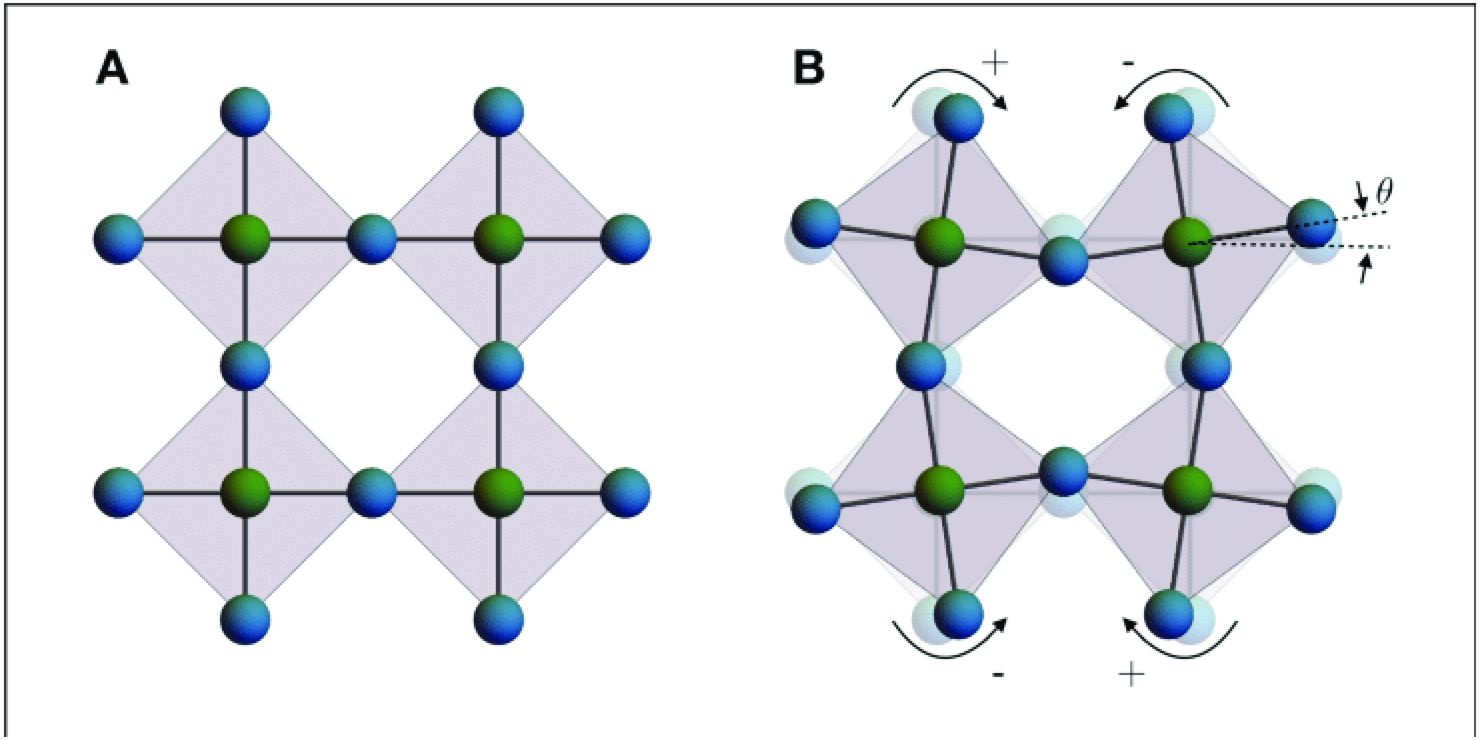
SIZES of ATOMS & IONS !!!



Ox. state	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+II	0.86	0.79	0.80	0.83	0.78	0.75	0.69	0.73	0.74
+III	0.67	0.64	0.62	0.65	0.65	0.61	0.60	0.54	-
+IV	0.61	0.58	0.55	0.53	0.59	0.53	0.48	-	-

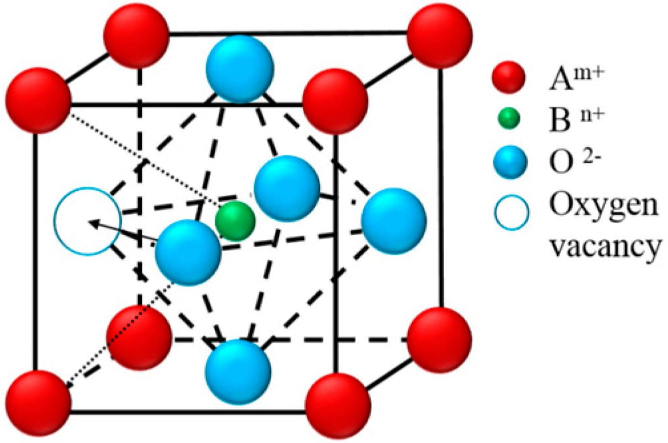
DISTORTIONS in ABO_3

- Atoms (typically oxygen atoms) are often slightly displaced from their ideal positions
- This ends up with tilting of the BO_6 octahedra
- These **distortions affect many properties** (magnetic, ferroelectric, etc.)

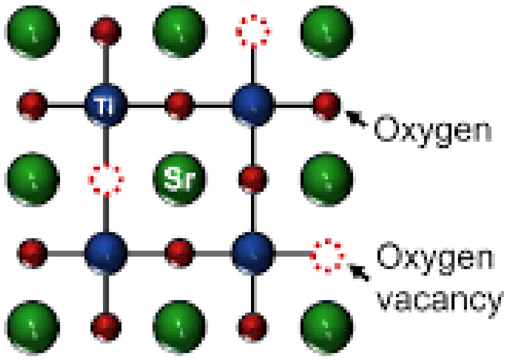


OXYGEN DEFICIENCY in $ABO_{3-\delta}$

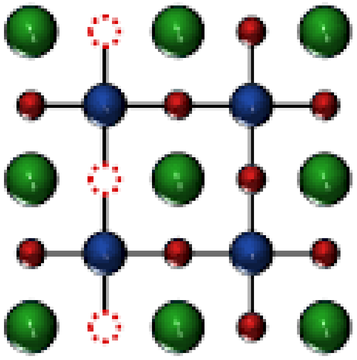
- Oxygen deficiency even up to $\delta = 0.5$ is common for perovskite compounds
- **Oxygen content controls metal valences → properties**
- Location of oxygen vacancies: random or ordered

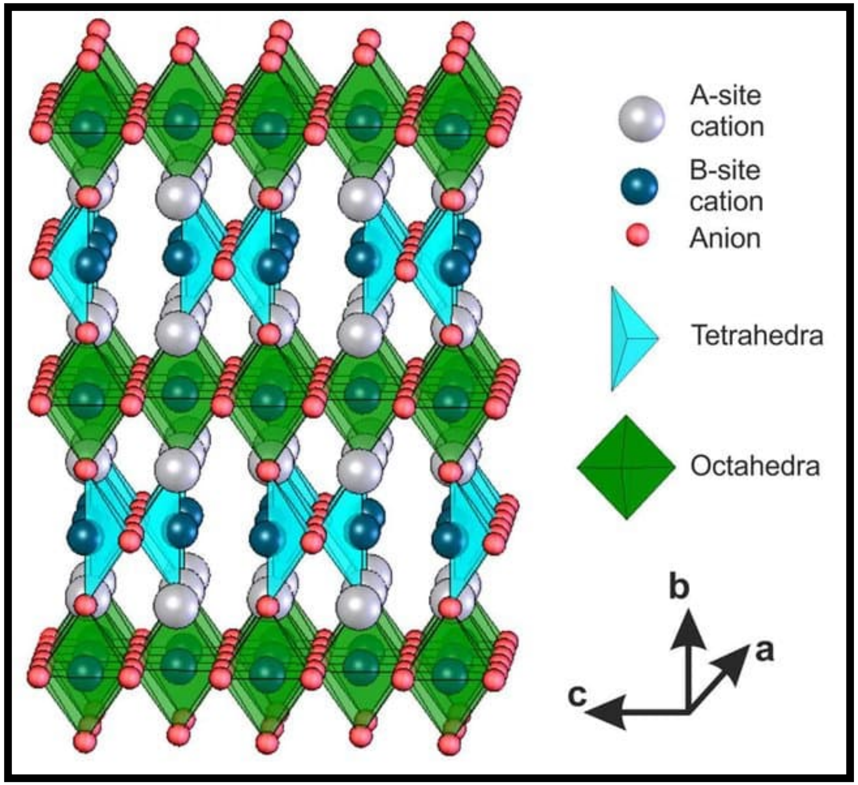


Random

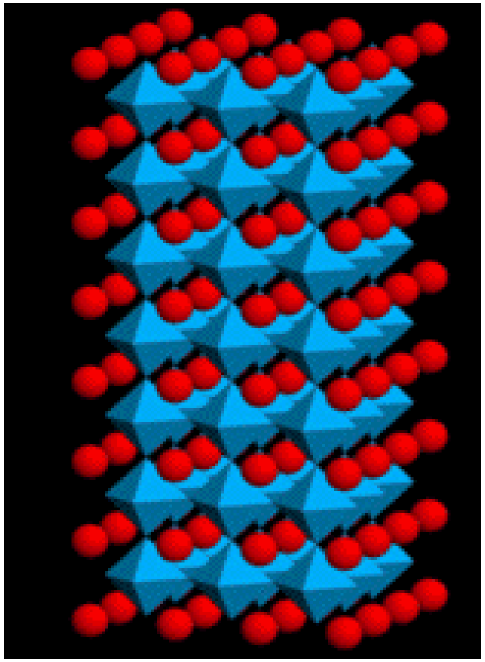


Ordered

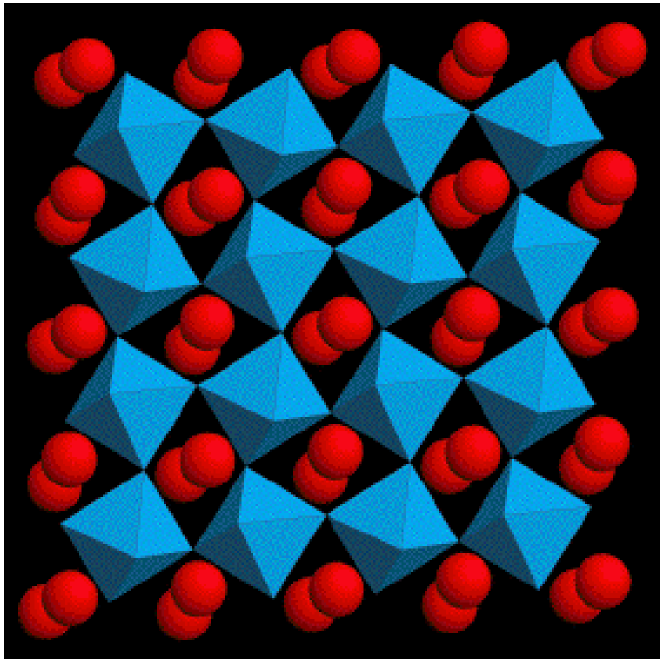




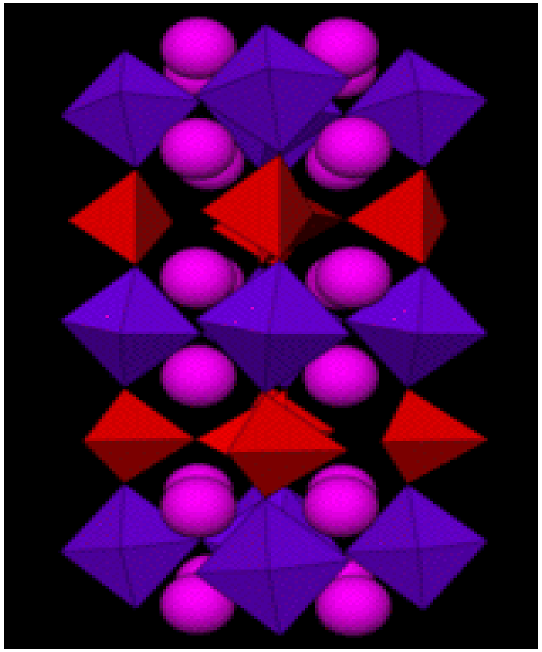
Distortions and deficiencies in Perovskite Structure:
- often the source of the desired properties



IDEAL



Changes in atomic positions



Oxygen deficiency

Let’s talk more about these distortions/deficiences

Victor Moritz Goldschmidt
(1888-1947)

TOLERANCE FACTOR (t)

- 1926 Goldschmidt

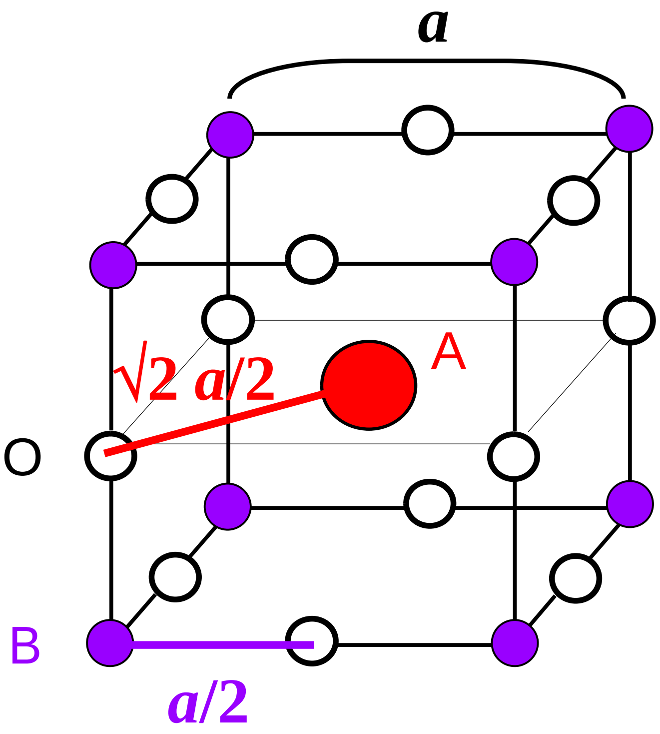
  V.M. Goldschmidt , “Geochemische Vertailungsgesetze der Elemente”, Skrifter Norske Videnskaps-Akad, Oslo, I. Mat-Naturr. K1 (1926)

- t: measure for the degree of mismatch between two different atomic layers
- Calculated from preferred bond lengths
- Preferred bond lengths are estimated from ionic radii

  R.D. Shannon, Acta Cryst. A 32, 751 (1976)

Tolerance factor for ABO_3 perovskite

$$\boxed{t = \frac{(r_A + r_O)}{\sqrt{2}\,(r_B + r_O)}}$$



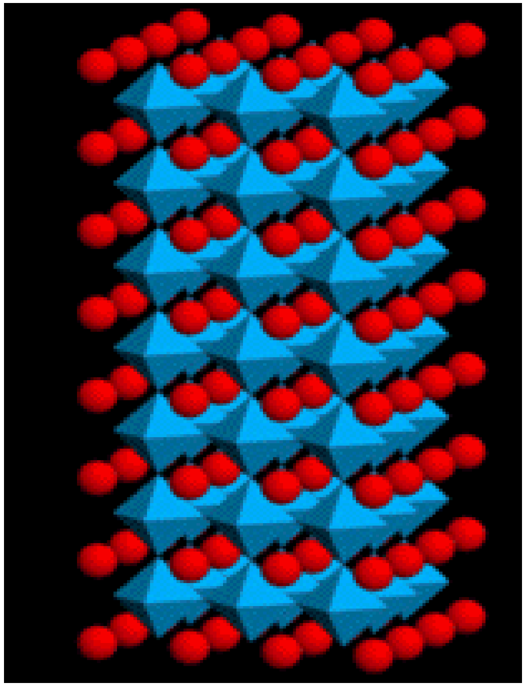
$t = 1$: ideal matching (0.80 < t < 1.05 possible)

$t < 1$: A is too small → change in oxygen position

$t > 1$: B is too small → B reduced → oxygen vacancies

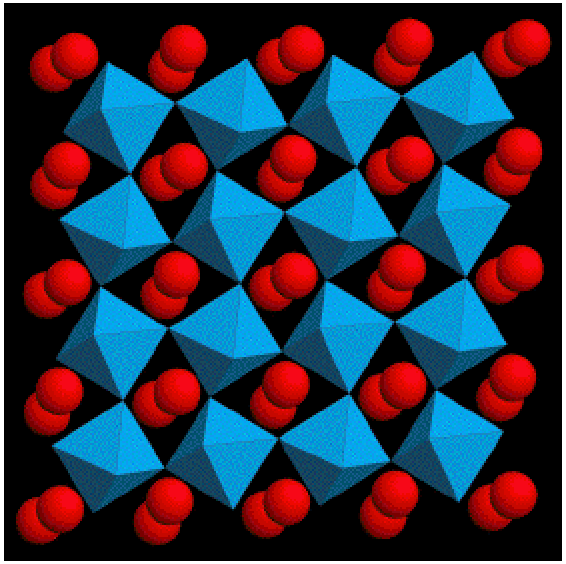
$$t = \frac{(r_A + r_O)}{\sqrt{2}\,(r_B + r_O)}$$

***t* = 1**



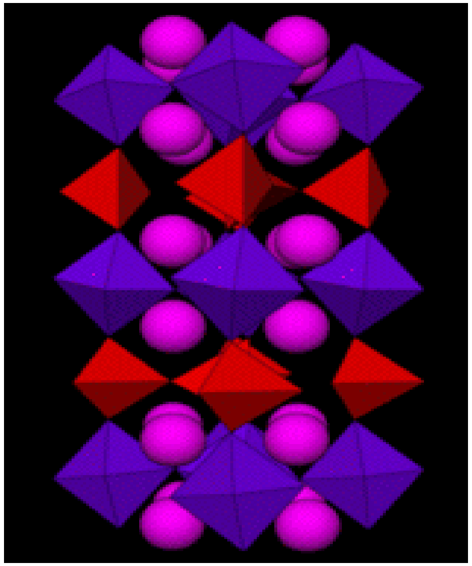
Ideal perovskite

***t* < 1**



Changes in
atomic positions

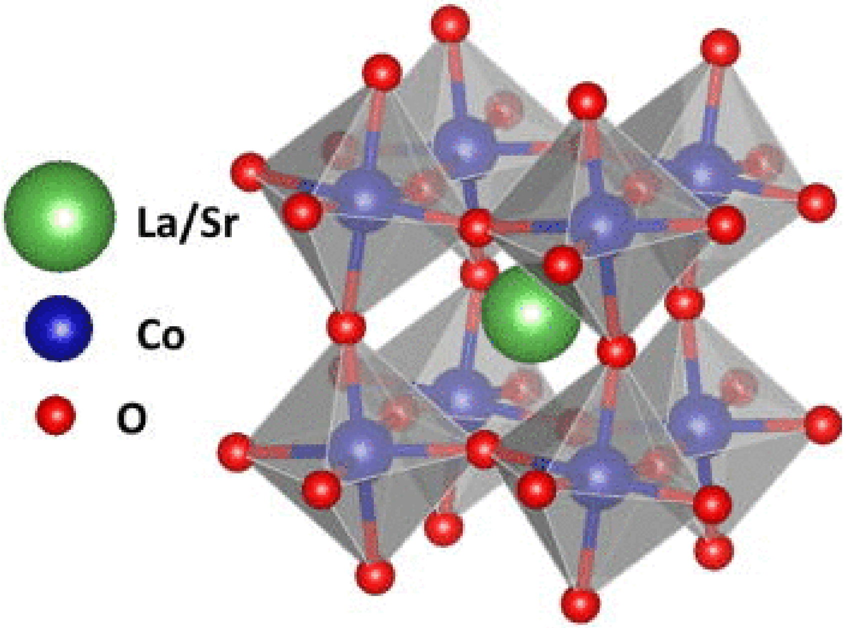
***t* > 1**



Oxygen deficiency

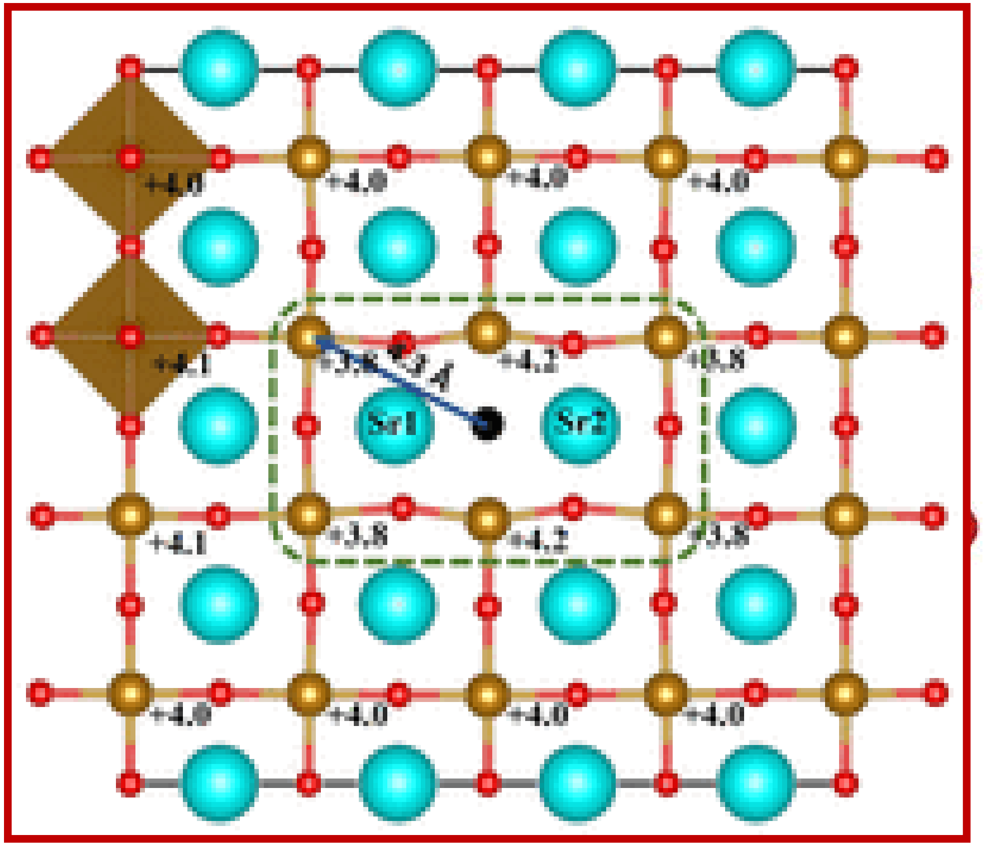
ALIOVALENT SUBSTITUTIONS in PEROVSKITES

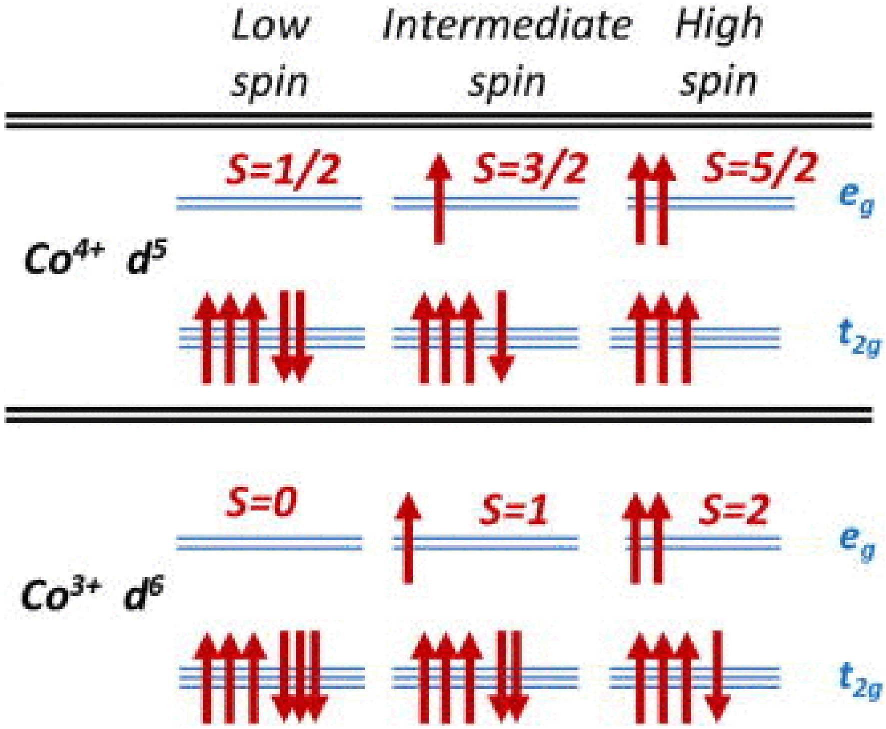
- **“Doping”: creates mixed valency**
- **For example: Sr^{2+}-for-La^{3+} substitution in $(La,Sr)CoO_3$**
- **Type of doping ? Typical substitution level ?**
- **Effect on Co valence ?**
- **What else may happen ?**



ALIOVALENT SUBSTITUTION in $(La^{3+},Sr^{2+})CoO_{3-\delta}$

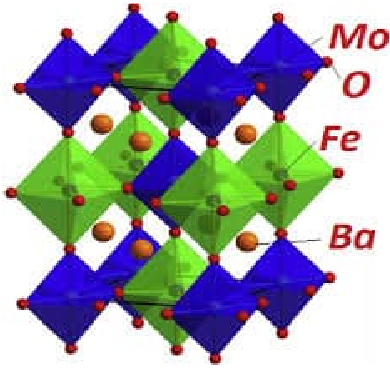
- Cobalt partly oxidized: $Co^{3+} \rightarrow Co^{4+}$
- Oxygen vacancies created
- Balance: metal redox versus oxygen vacancies
- Possible chemical pressure effects (c.f. isovalent substitution)
- Effects on electrical cond., ionic cond. & magnetic properties ?

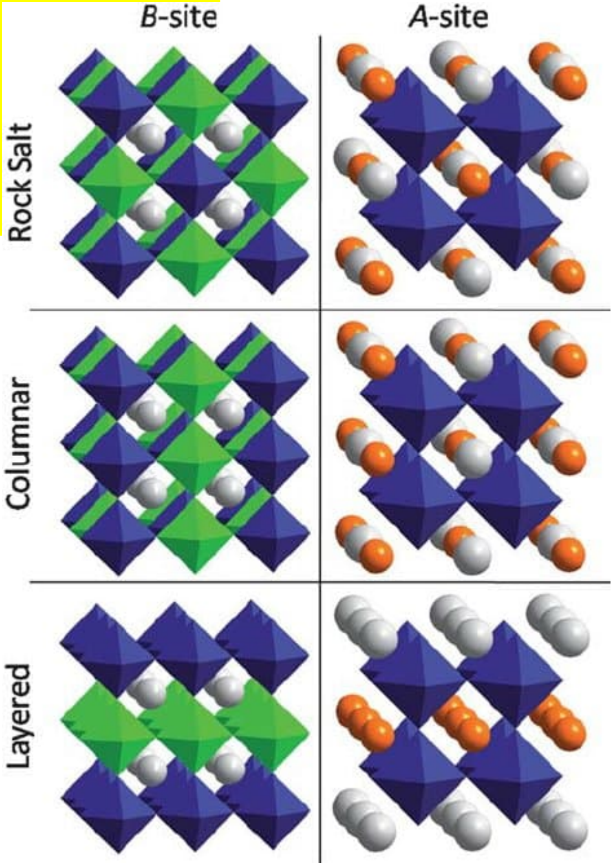


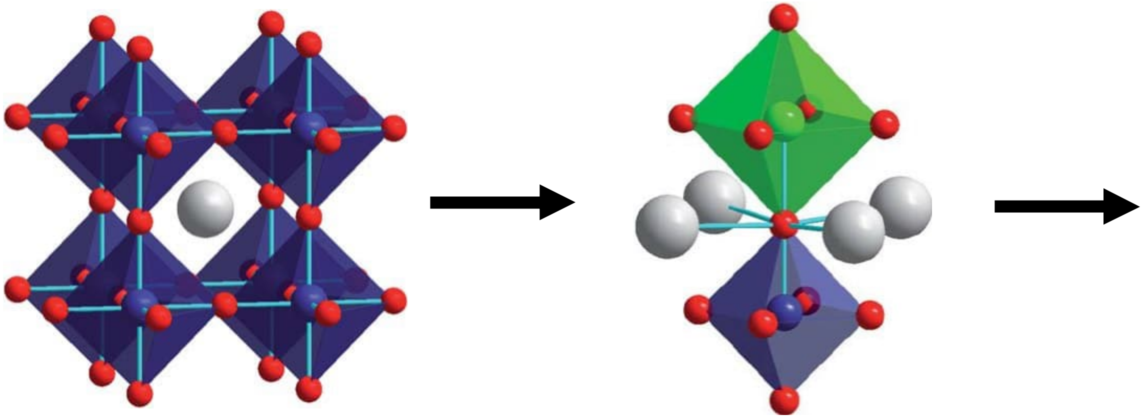


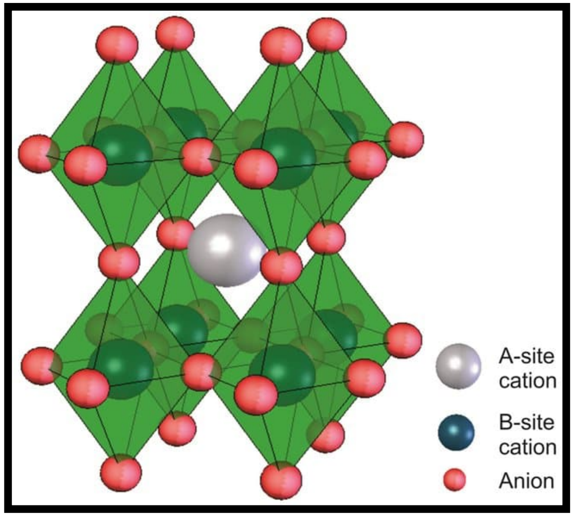
DOUBLE & TRIPLE PEROVSKITES

- FOR EXAMPLE: Two different cations (**B'** and **B''**) occupy the B-site with 50%/50% ratio and in an ordered manner → B-site ordered double perovskite
- Example of B-site ordered double perovskites: Sr_2FeMoO_6 (ferrimagnetic halfmetal)
- Similarly, there are A-site ordered double perovskites
- There are also triple perovskites, e.g. $A'A''_2B_3O_9$
- Example of (oxygen-deficient) triple perovskites: $YBa_2Cu_3O_7$ (high-T_c superconductor)









Perovskite ABO_3

- No space for interstitial oxygen

Ruddlesden-Popper $A_{n+1}B_nO_{1+3n}$

- Enough space for interstitial oxygen