Functional Inorganic Materials
Fall 2022

Tuesdays: 12.15 - 14.00 (U8)
Thursdays: 10.15 - 12.00 (Ke1)

#	Date	Who	Topic
1	**Mon 5.9.**	**Maarit**	**Introduction + Materials design concepts**
2	Thu 8.9.	Antti	Introduction + Computational materials design
3	Tue 13.9.	Maarit	Superconductivity: High-T_c superconducting Cu oxides
4	Thu 15.9.	Maarit	Magnetic oxides
5	Tue 20.9.	Maarit	Ionic conductivity (Oxygen): Oxygen storage and SOFC
6	Thu 22.9.	Maarit	Ionic conductivity (Lithium): Li-ion battery
7	Tue 27.9.	Antti	Thermal conductivity
8	Thu 29.9.	Antti	Thermoelectricity
9	Tue 4.10.	Antti	Piezoelectricity
10	Thu 6.10.	Antti	Pyroelectricity and ferroelectricity
11	Tue 11.10.	Maarit	Hybrid materials
12	Thu 13.10.	Antti	Luminescent and optically active materials

LECTURE 1: Materials Design Concepts

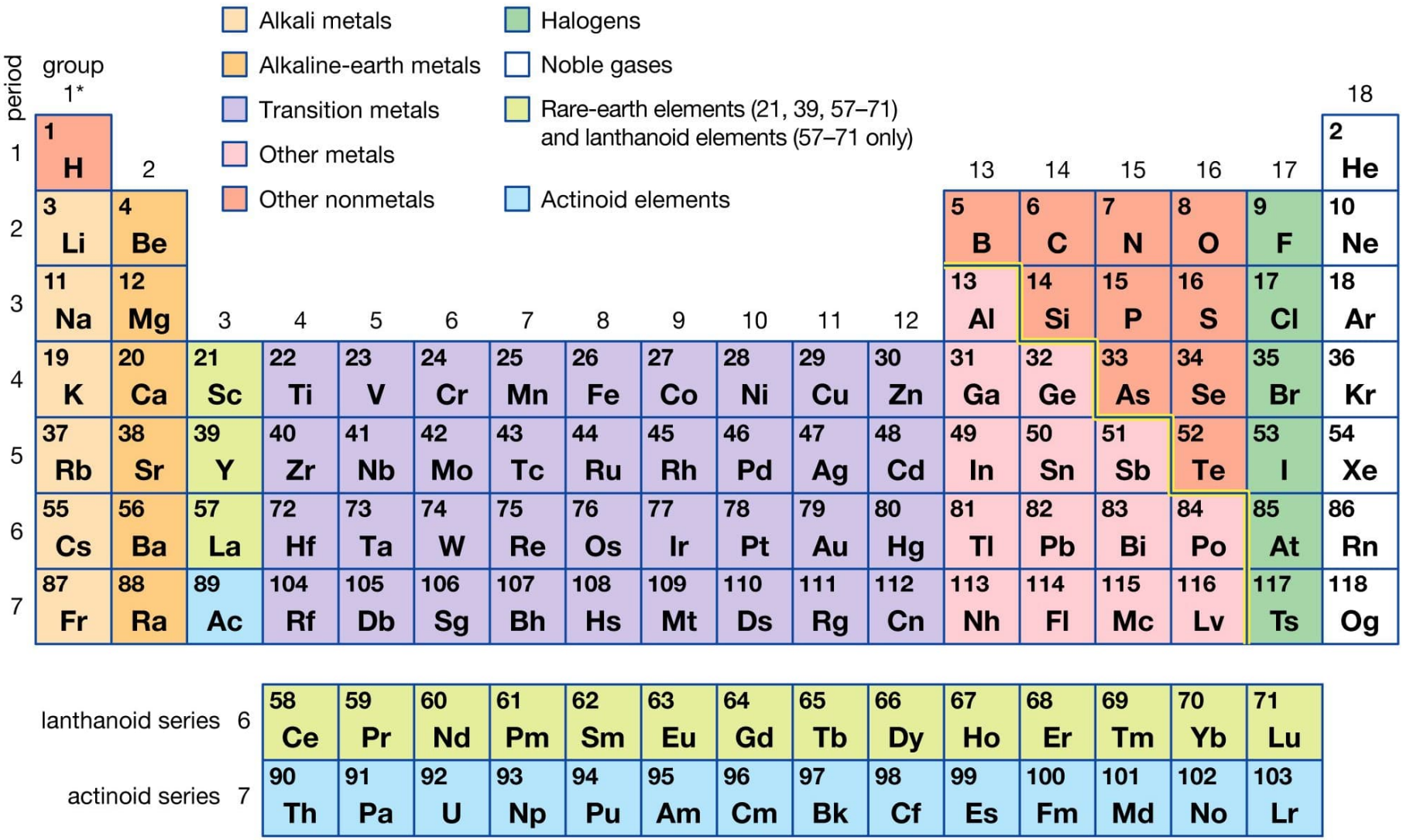
- **FOR: Electrical conductivity**
- **Doping & Substitution**
- **Aliovalent Substitution**
- **Mixed Valency**
- **Vacancies & Interstitials**
- **Relative Ion Sizes & Tolerance Parameter**

We first recall the doping scheme in elemental semiconductors (Si),

and then 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.

Periodic table of the elements



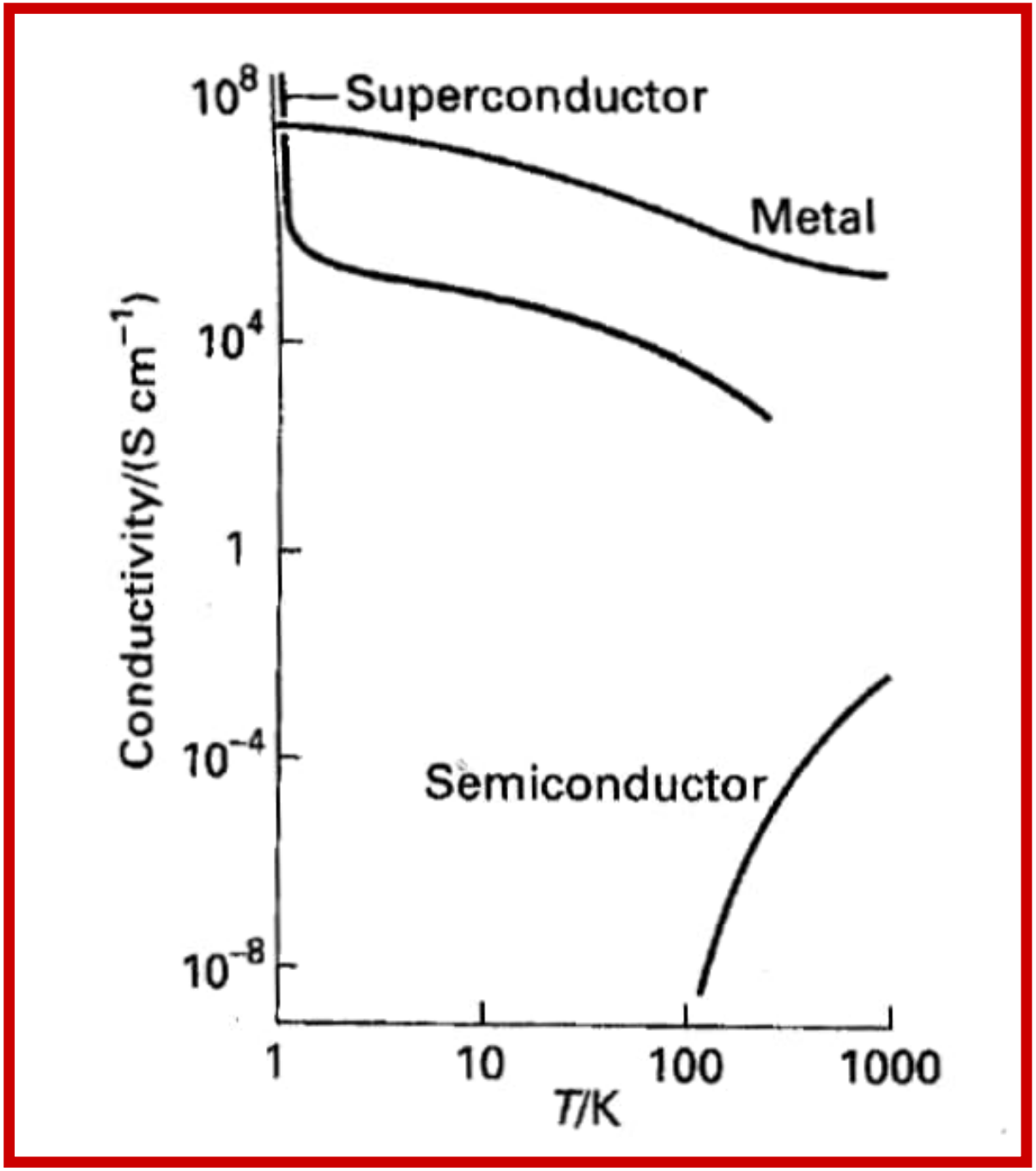
*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

LECTURE EXERCISE 1

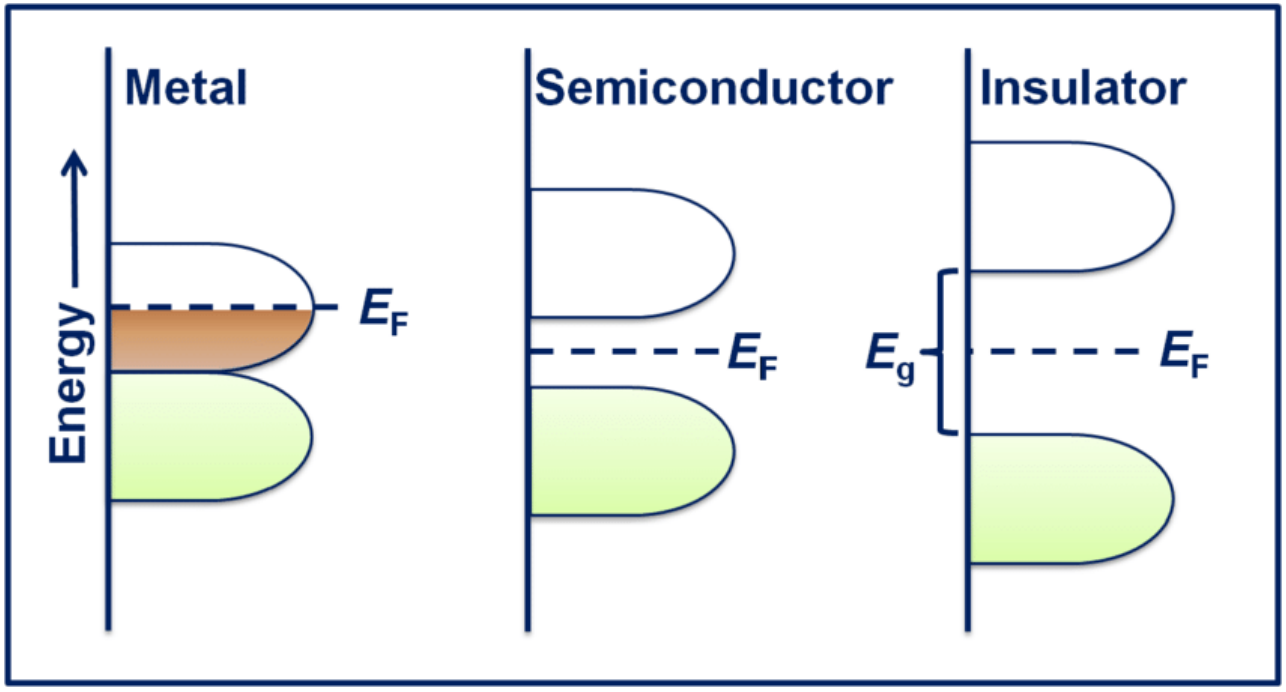
1. **Discuss shortly the doping levels in elemental semiconductors (Si), simple metal oxides (ZnO) and in complex transition metal oxides (perovskites).**
2. **Assign the type of doped carriers (n-type or p-type) for the following materials (rationalize your answers !): Al-doped Si, $(Zn_{0.98}Al_{0.02})O$, $(Pb_{0.98}Na_{0.02})Te$, $(La_{0.9}Sr_{0.1})_2CuO_{4.0}$, $La_2CuO_{4.1}$.**
3. **Calculate the tolerance parameter for the following perovskite compounds (assuming the 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 (and explain why !): $LaMnO_3$, $LaCoO_3$, $LaNiO_3$, $LaCuO_3$.**

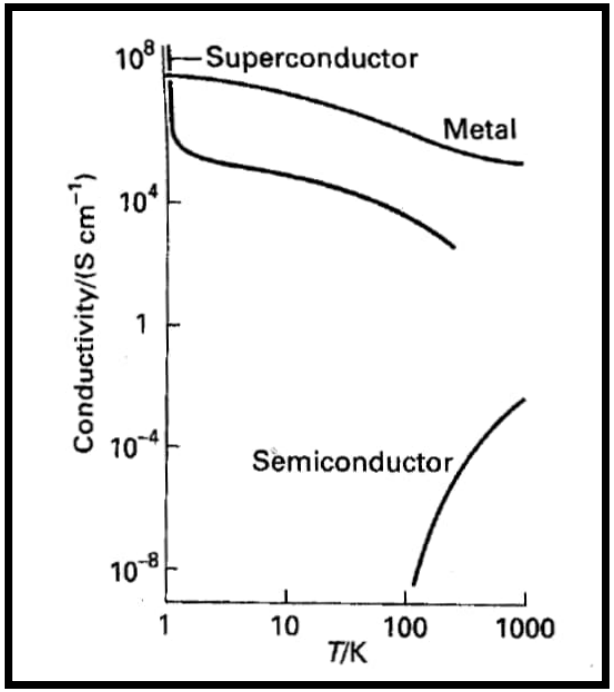
IONIC RADII:		
	La^{3+}	1.36 Å
	Mn^{3+}	0.65 Å
	Co^{3+}	0.61 Å
	Ni^{3+}	0.60 Å
	Cu^{3+}	0.54 Å
	O^{2-}	1.40 Å

ELECTRICAL CONDUCTIVITY

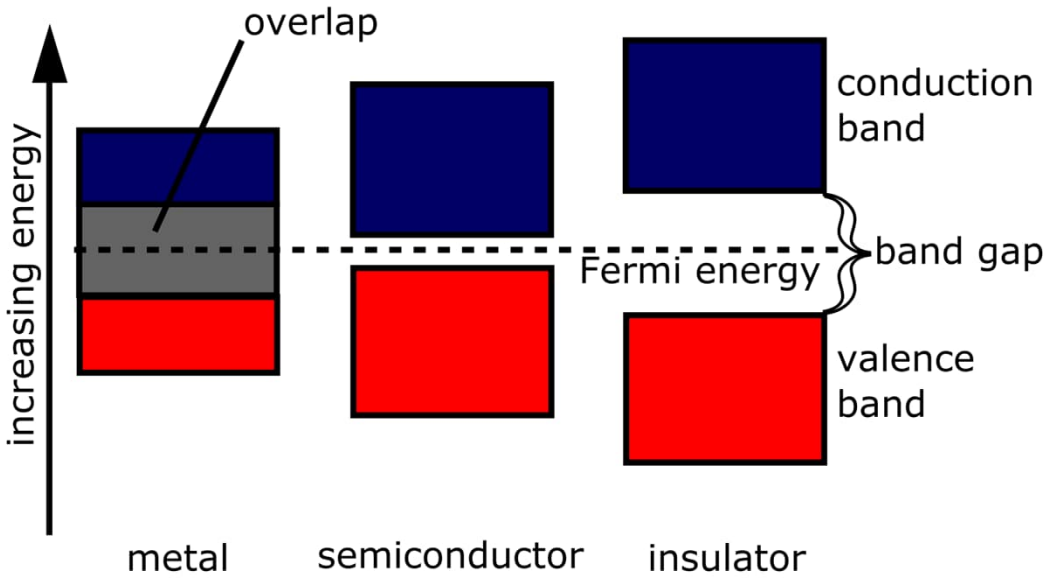


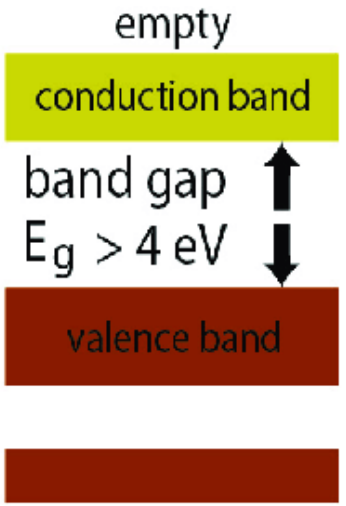
Schematic Band Structures

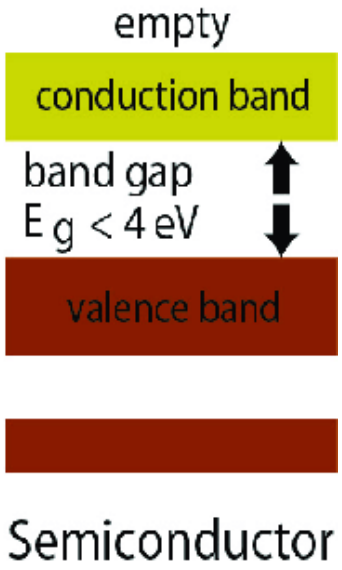


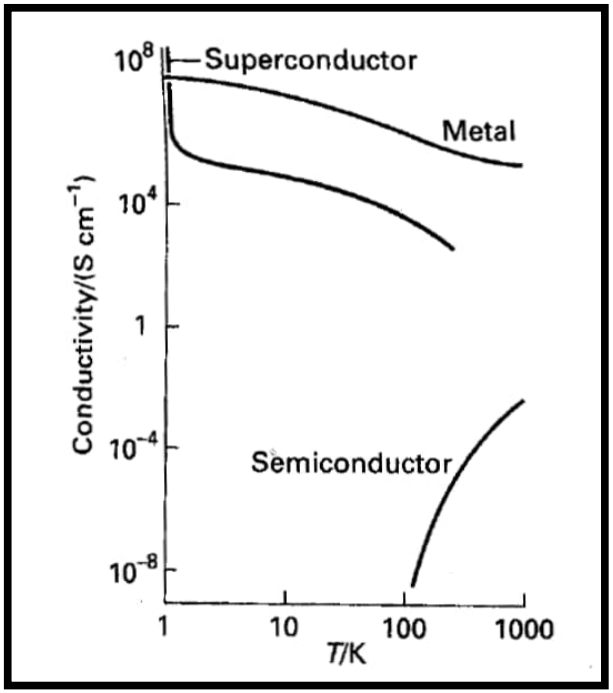


- What are: E_F and E_g ?
- What is the x-axis ?
- How large is E_g for a semiconductor / an insulator ?
- Can you explain the different temperature dependencies of electrical conductivity for metals and semiconductors ?


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

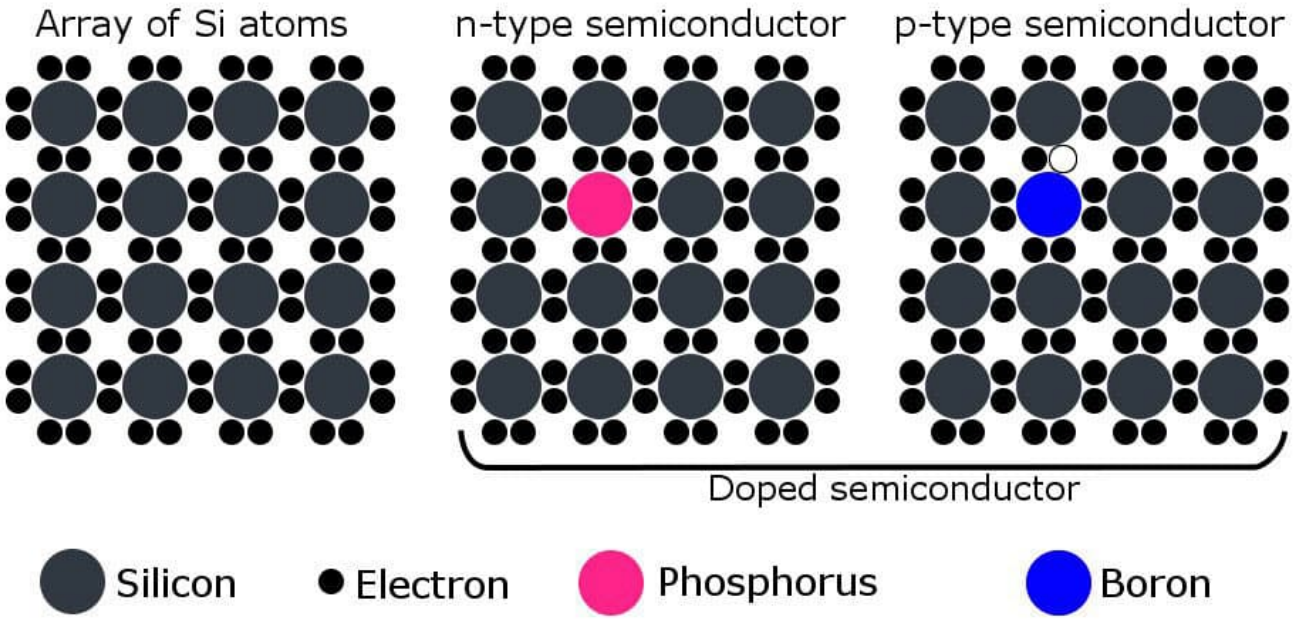
Periodic table of the elements

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	

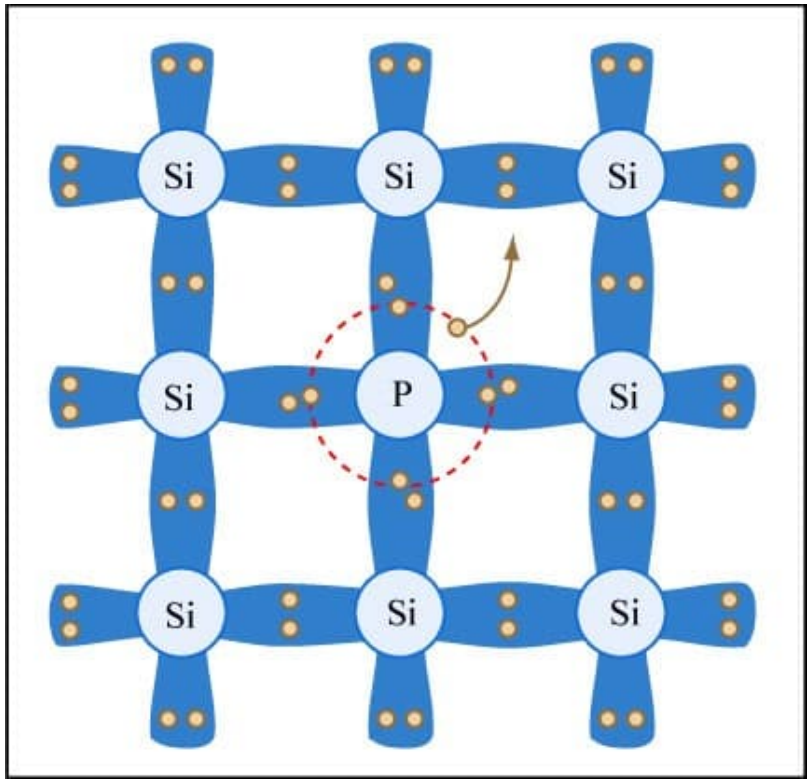
*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

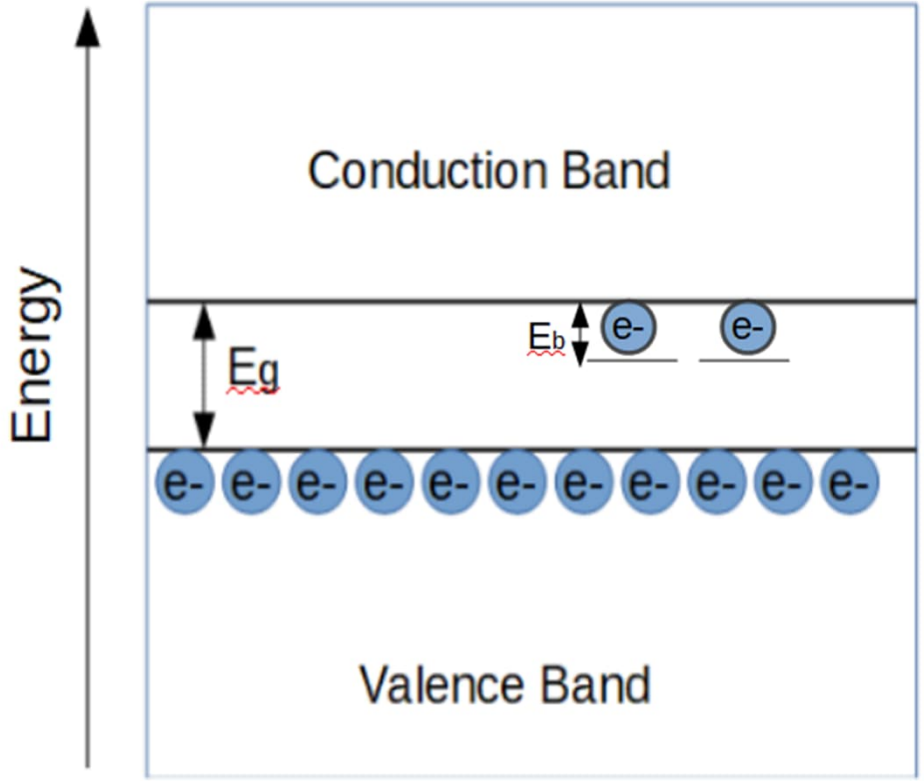
Doping in Semiconductors



n-type doping:

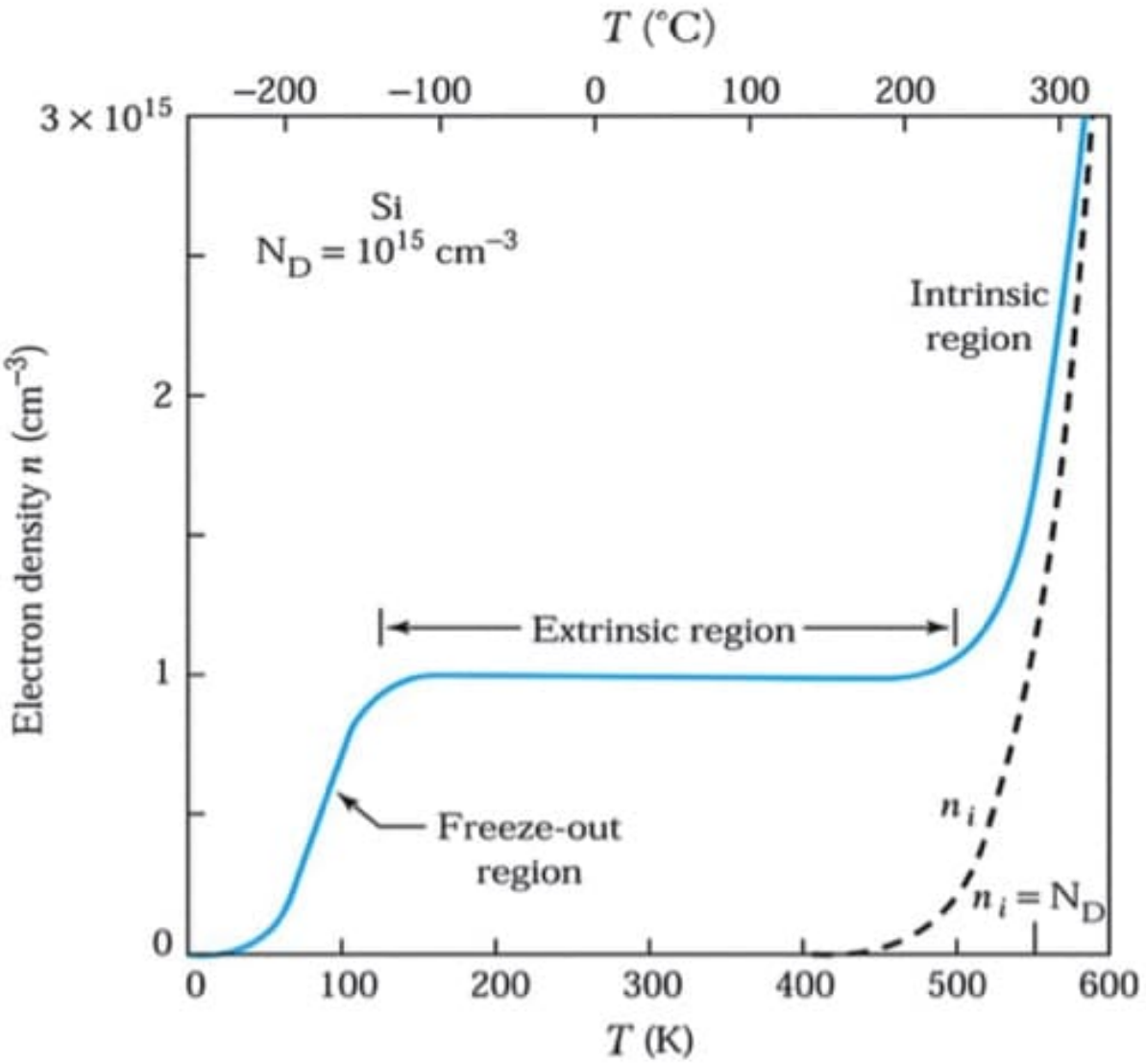
- Si: 4 valence electrons
- P: 5 valence electrons (= 1 extra)

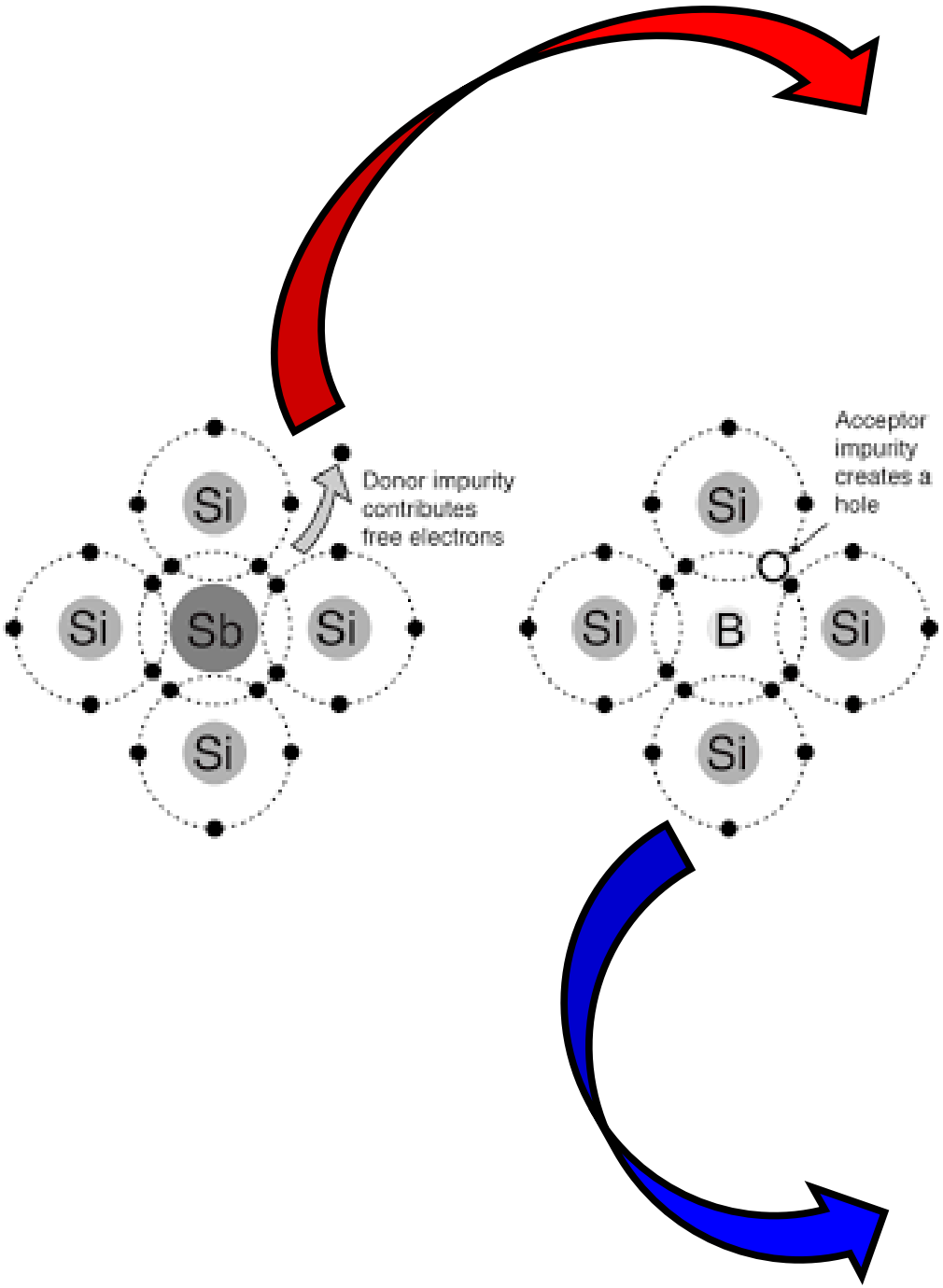


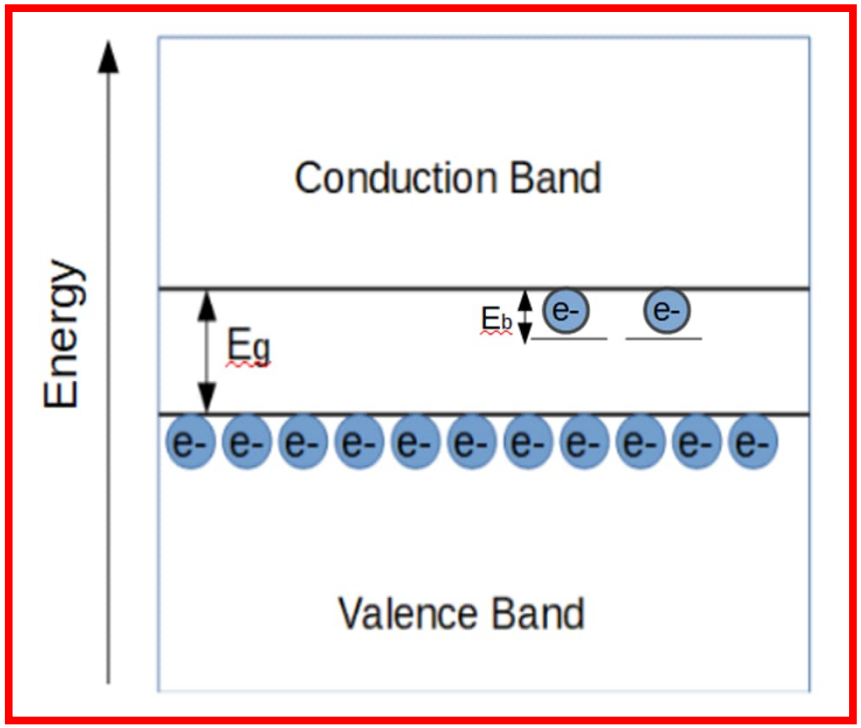


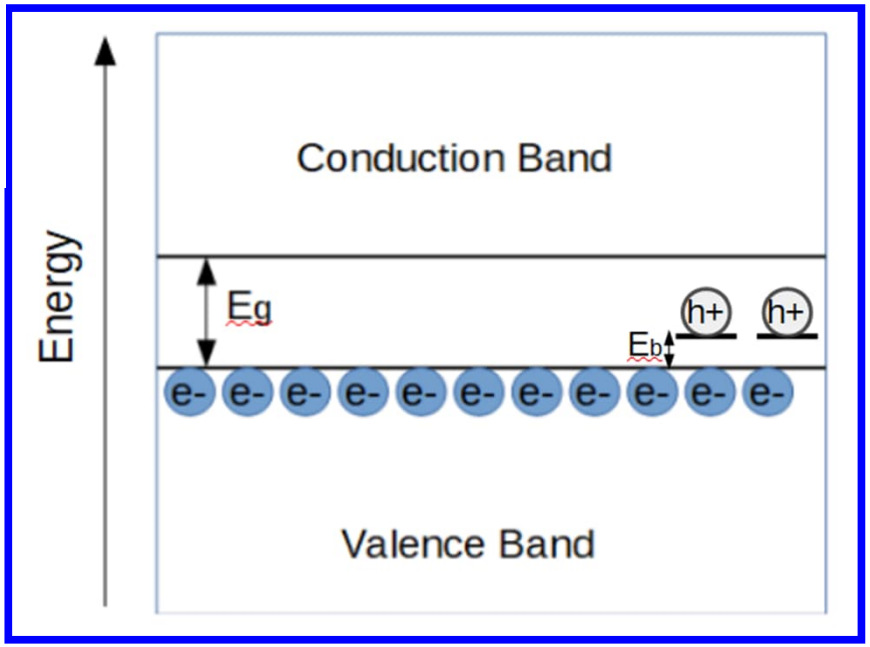
Si atoms: $5 \cdot 10^{22}$ cm^{-3}

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



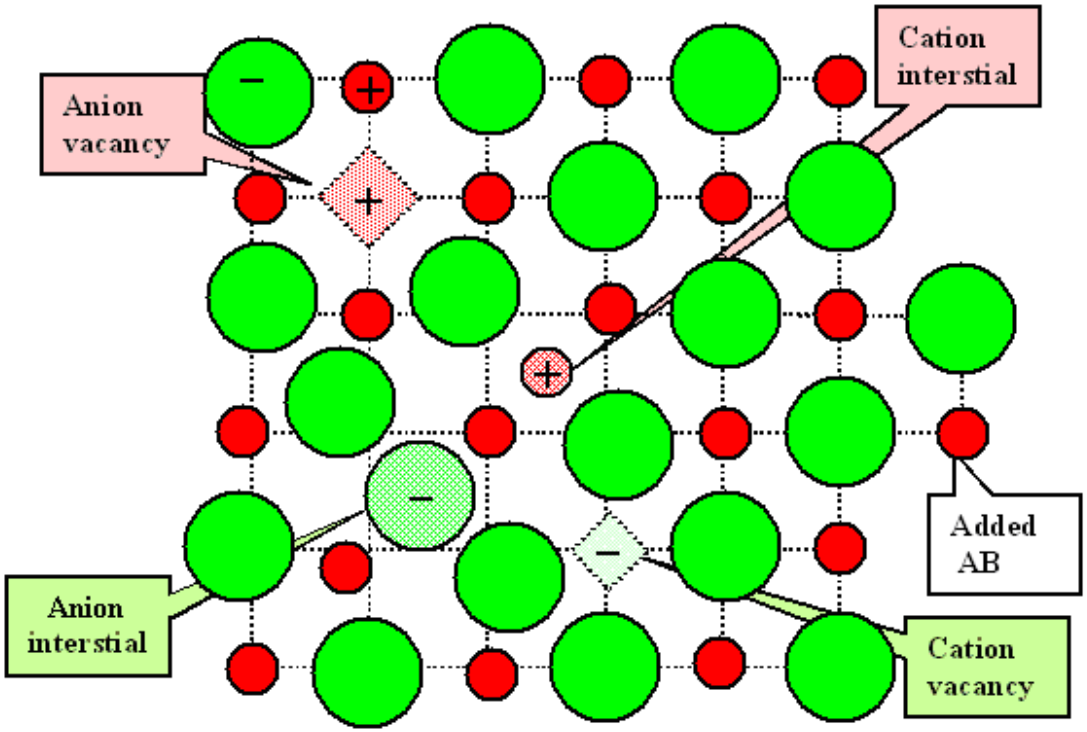

Si
Sb
Si
Si
Donor impurity
contributes
free electrons
Si
B
Si
Si
Acceptor
impurity
creates a
hole

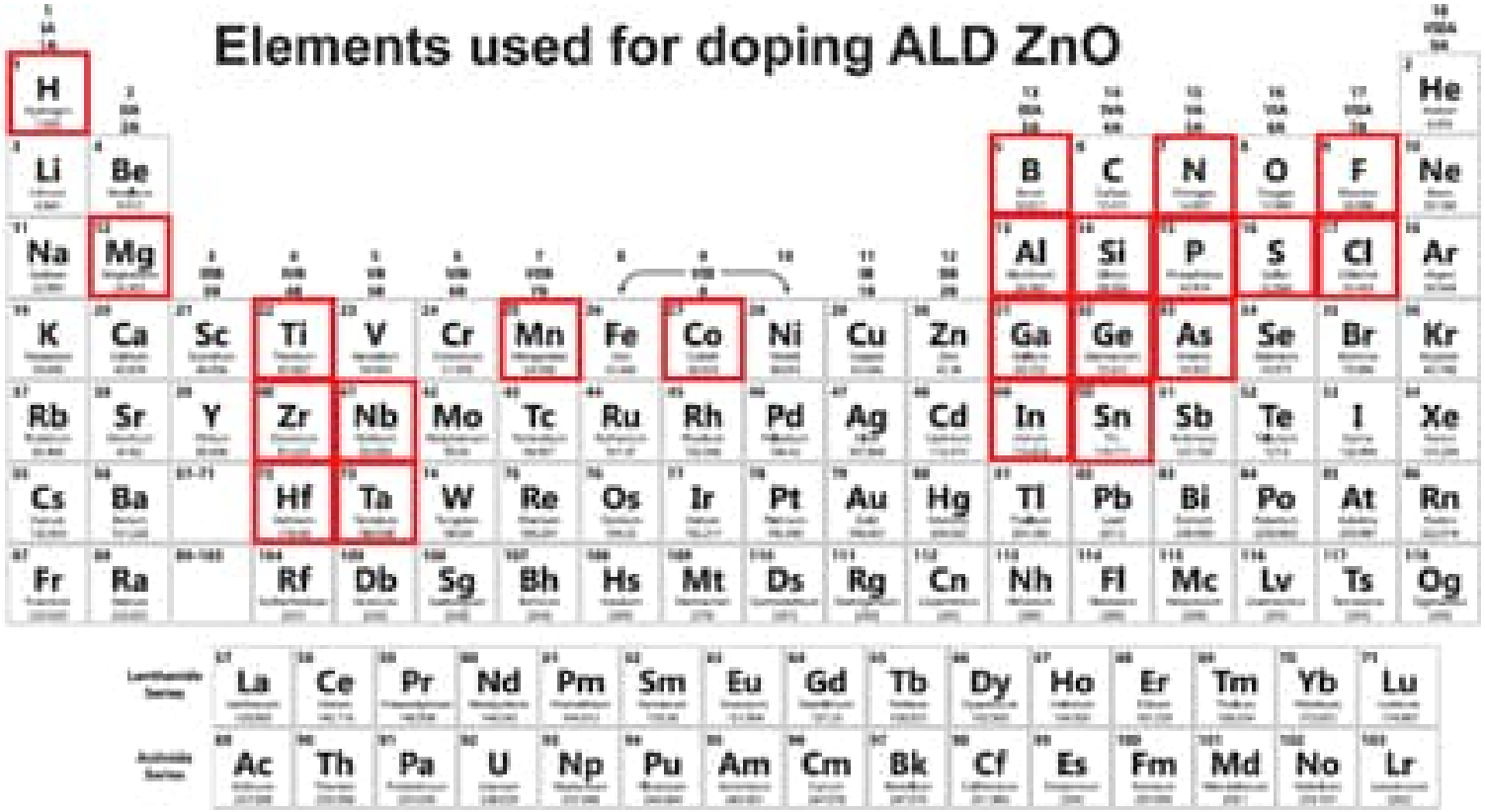

Energy
Conduction Band
Eg
Eb
e-
e-
Valence Band


Energy
Conduction Band
Eg
h+
h+
Eb
Valence Band

Simple metal oxide semiconductor: ZnO

- Intrinsically n-type (due to native defects)
- What kind of native defects could be responsible for n-type doping ?
  - n-type → slight off-stoichiometry which makes Zn “reduced”
  - Oxygen vacancies
  - Zn interstitials
  - Proton (H^+) interstitials

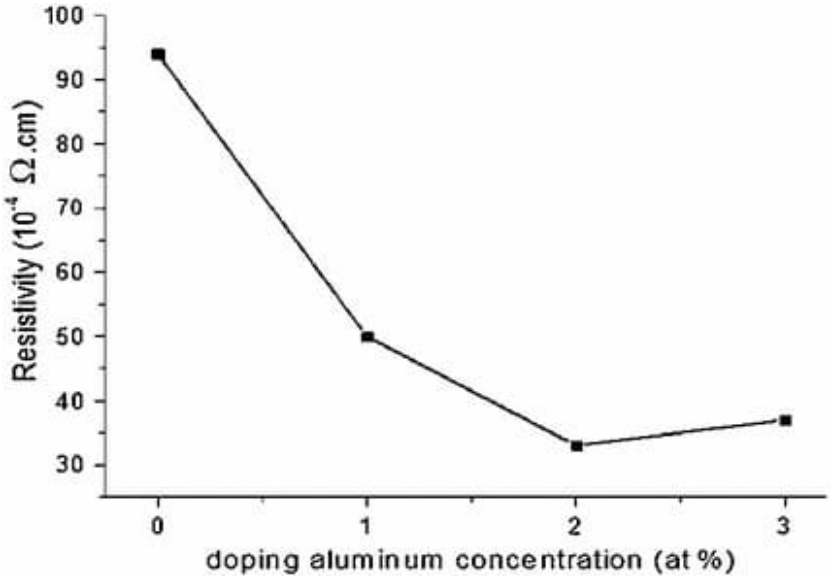


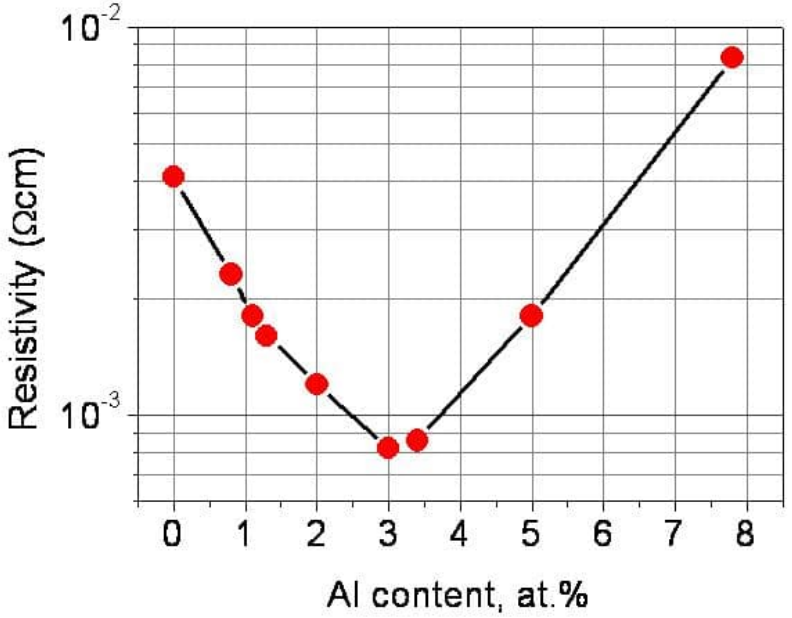


Zhengning Gao *and* Parag Banerjee, Review Article: Atomic layer deposition of doped ZnO films, Journal of Vacuum Science & Technology A **37**, 050802 (2019); https://doi.org/10.1116/1.5112777

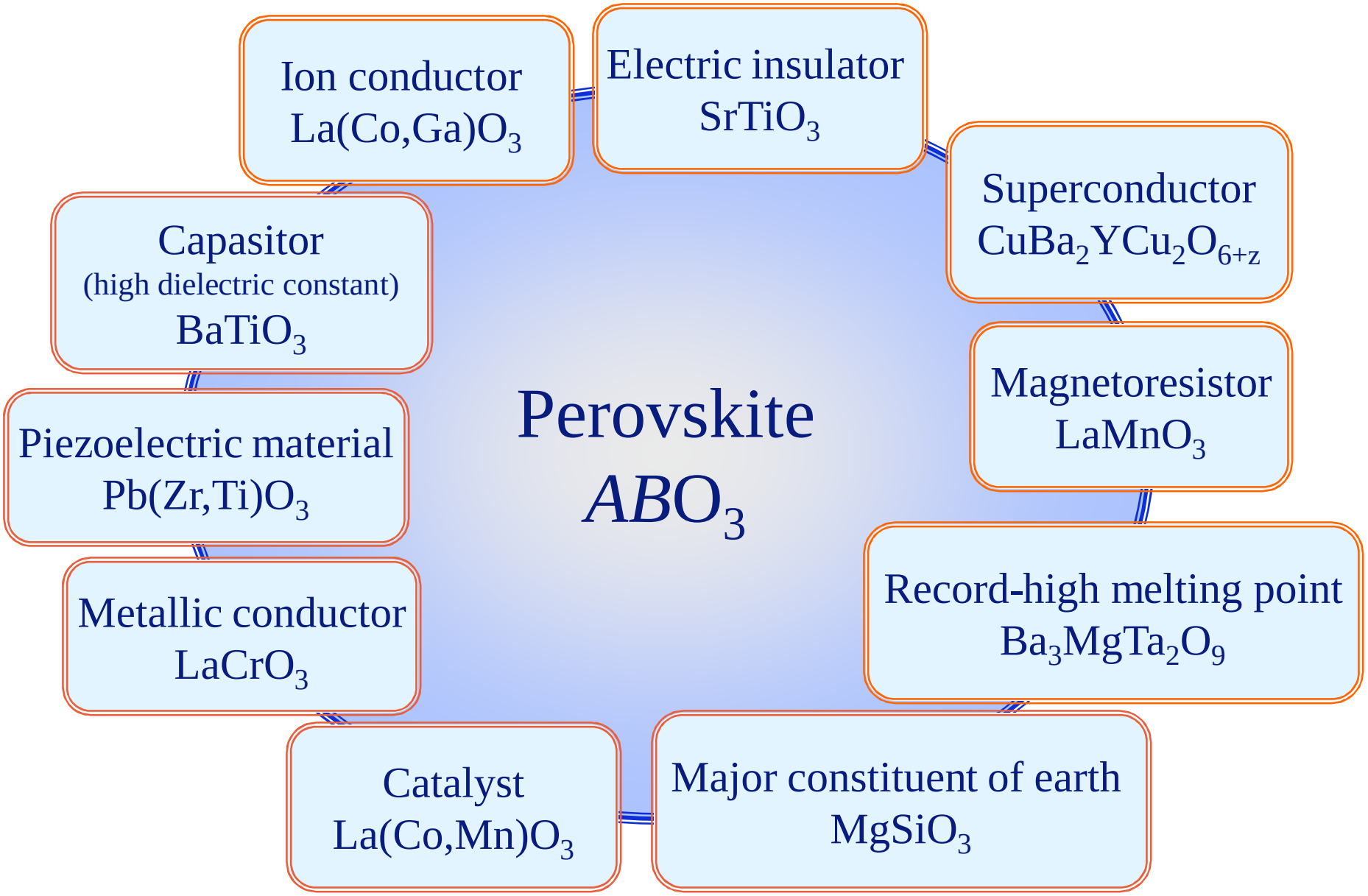
INTENTIONAL DOPING: typical substitution level ?

Typical aluminum substitution level in ZnO ?





Perovskite – Multifunctional structure



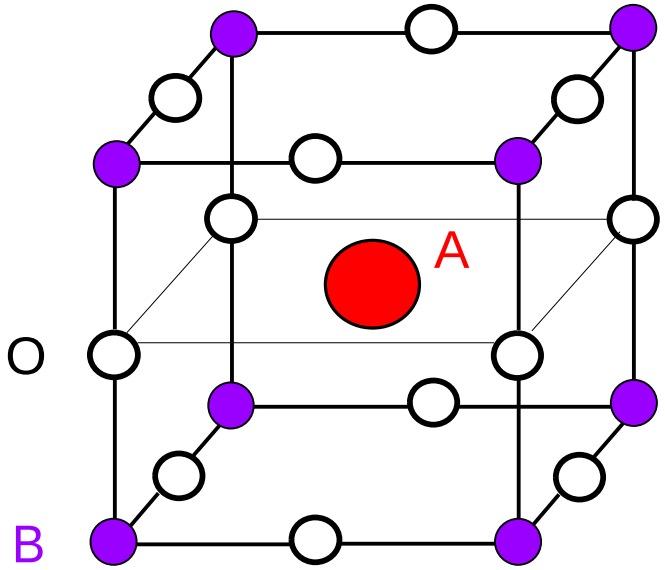
PEROVSKITE STRUCTURE

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

A: large cation

B: small cation (transition metal)

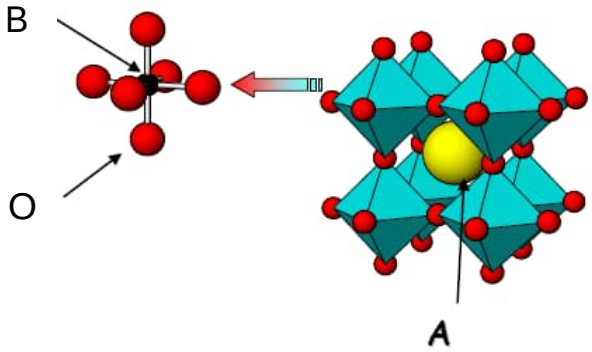
O: oxygen (sometimes halogen)



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

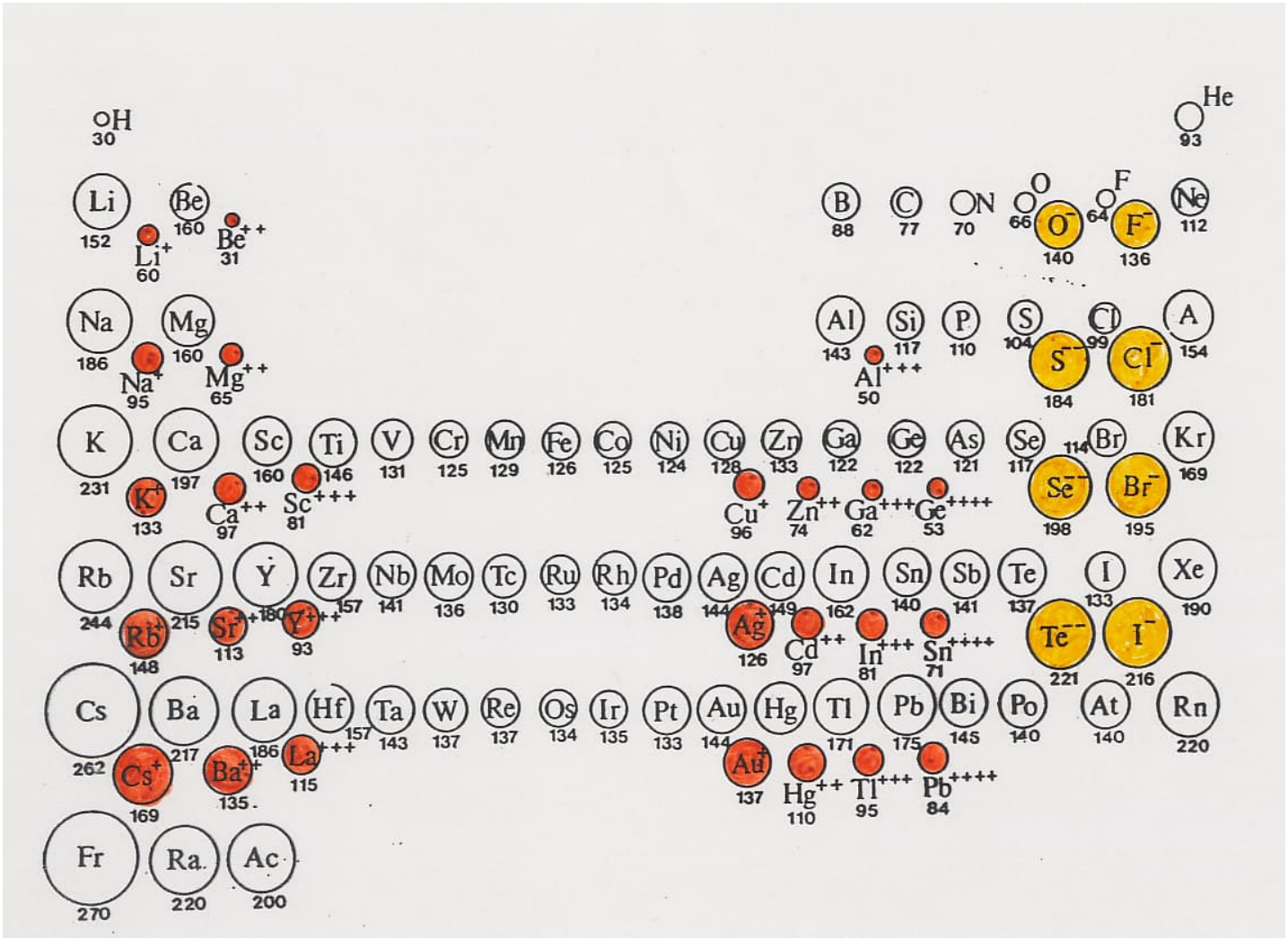


Mineral Perovskite: $CaTiO_3$

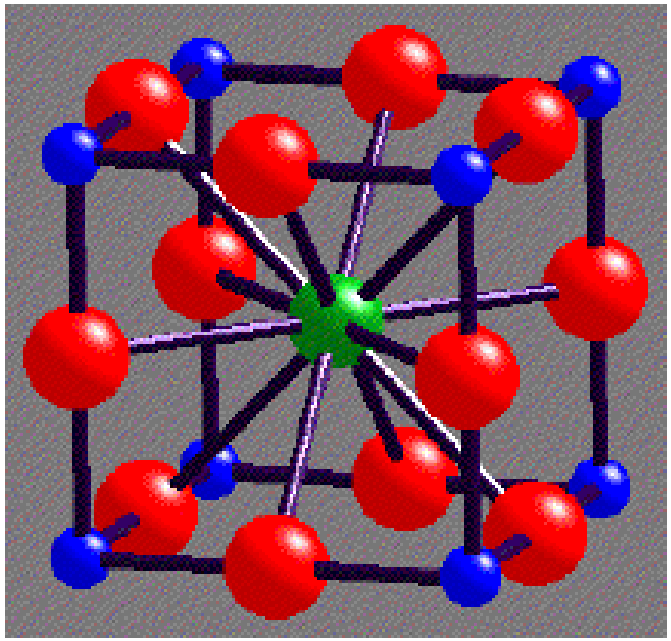
- Named after Russian mineralogist, Count Lev Aleksevich von Perovski

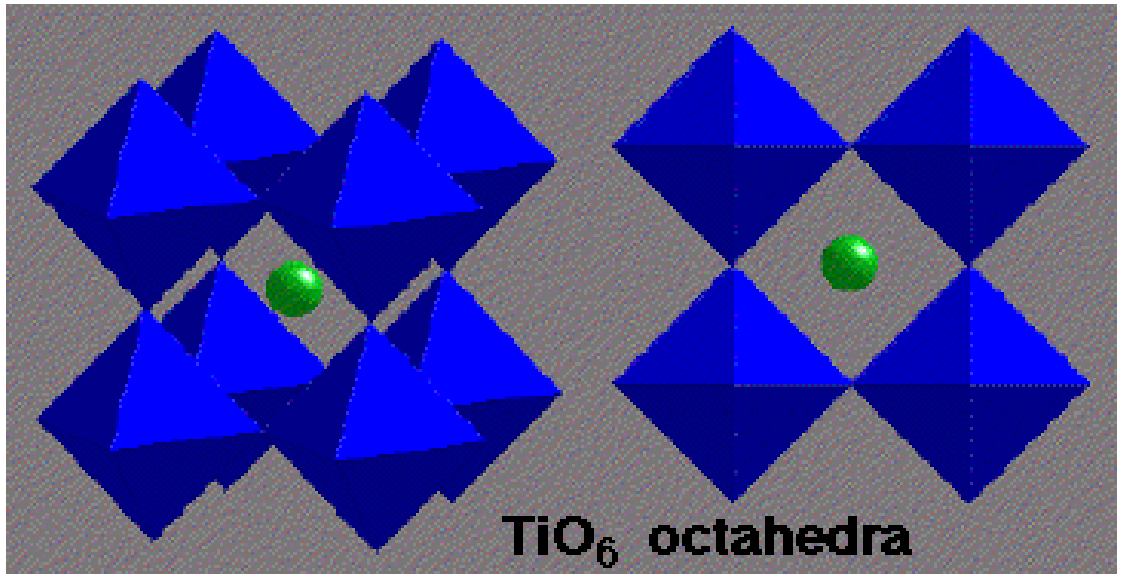
- Discovered by Gustav Rose in 1839 from samples found in Ural Mountains

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	-	-



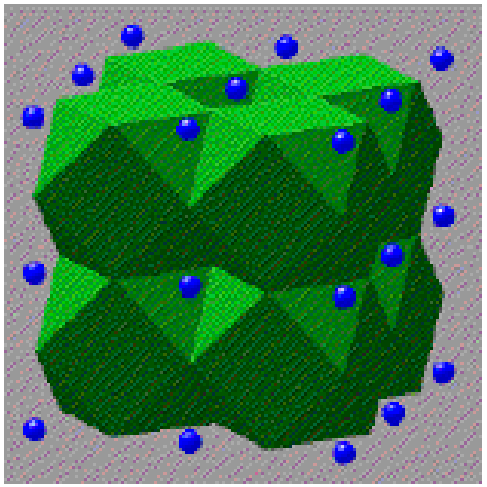


Perovskite

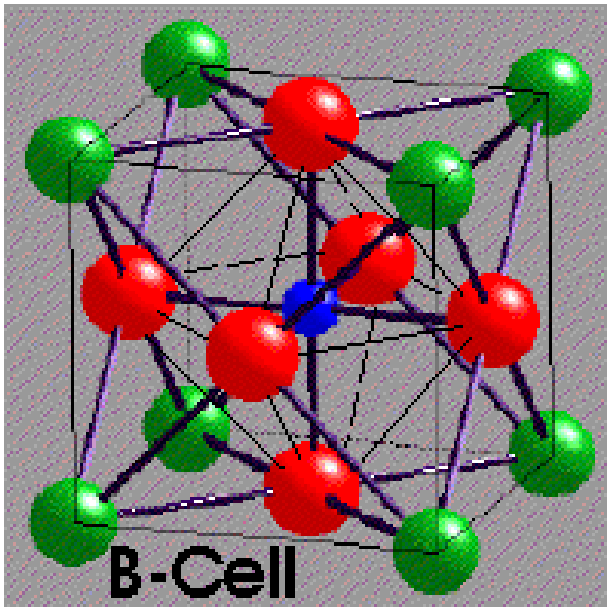
$CaTiO_3$

Ca Ti O

A-Cell

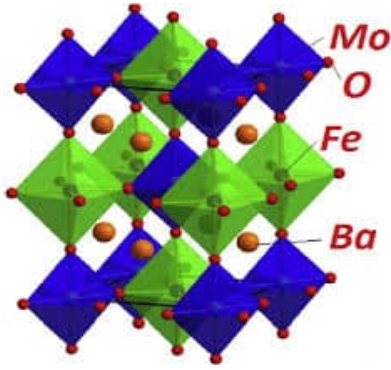


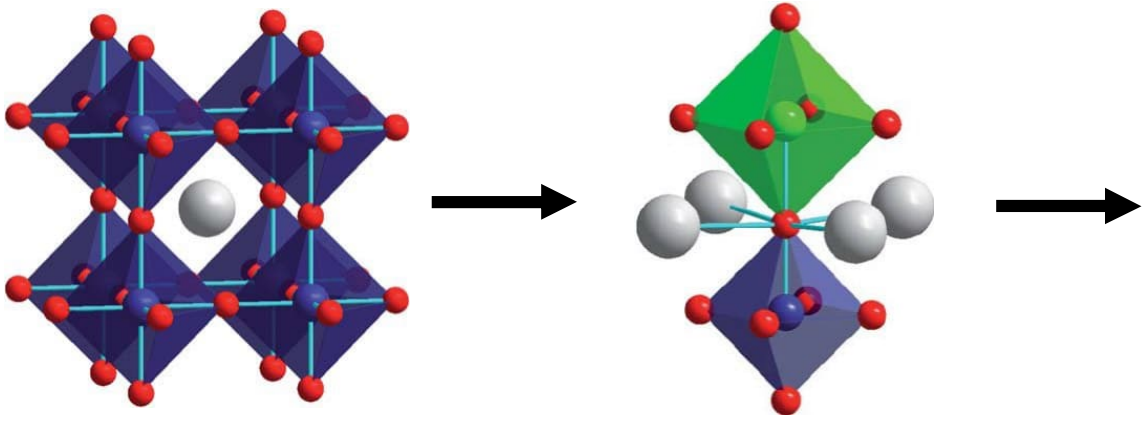
CaO_{12} cuboctahedra

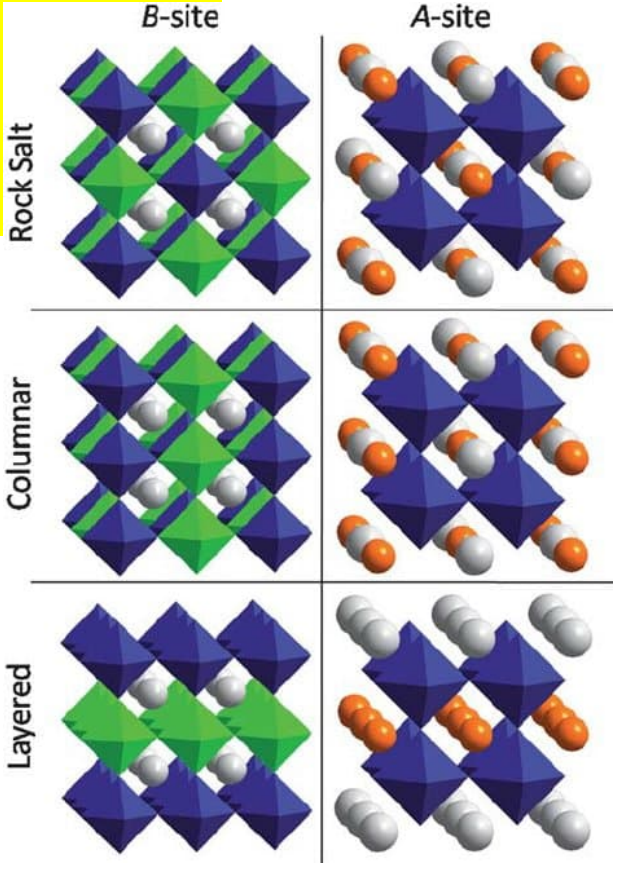


DOUBLE & TRIPLE PEROVSKITES

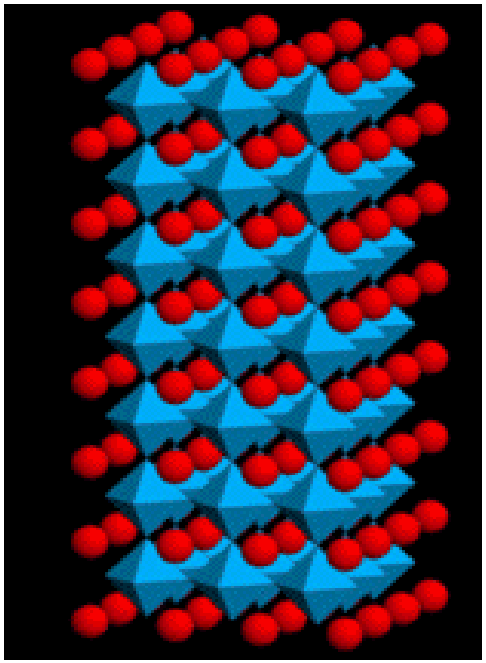
- FOR EXAMPLE: Two different cations (**B'** and **B''**) occupy the B-site with 50%/50% ratio and in an ordered manner → B-site ordered double perovskite
- Example of B-site ordered double perovskites: Sr_2FeMoO_6 (ferrimagnetic halfmetal)
- Similarly, there are A-site ordered double perovskites
- There 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)



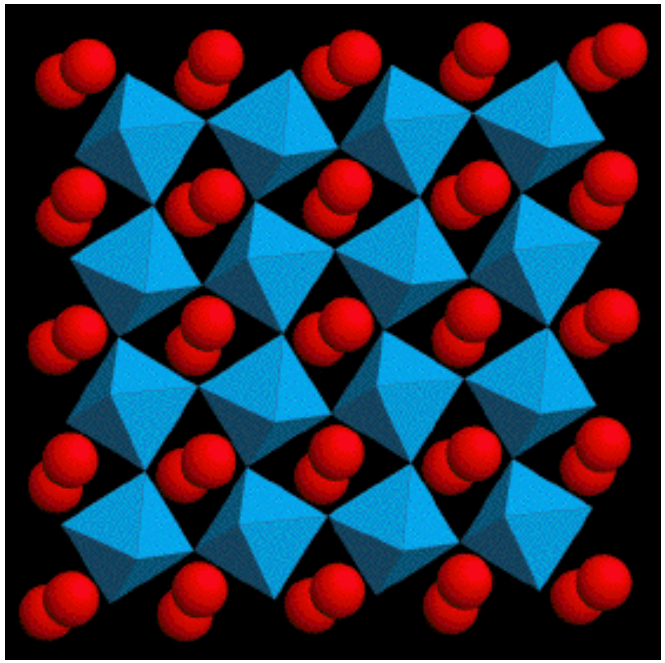




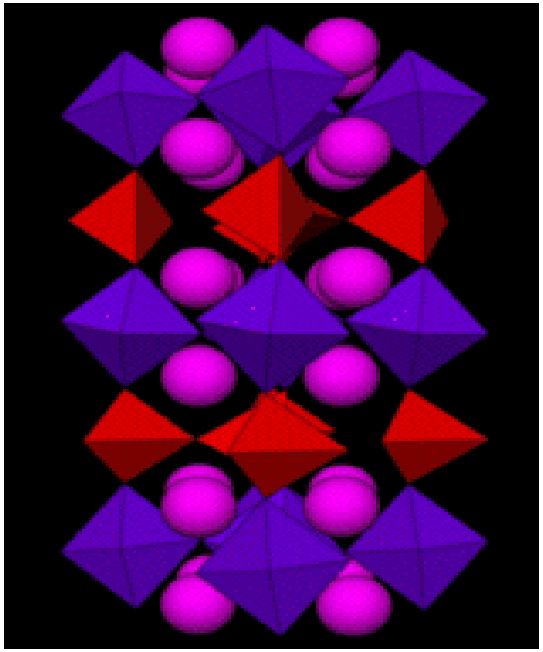
Distortions and deficiencies in Perovskite Structure: - often the source of the desired properties



IDEAL



Changes in atomic positions

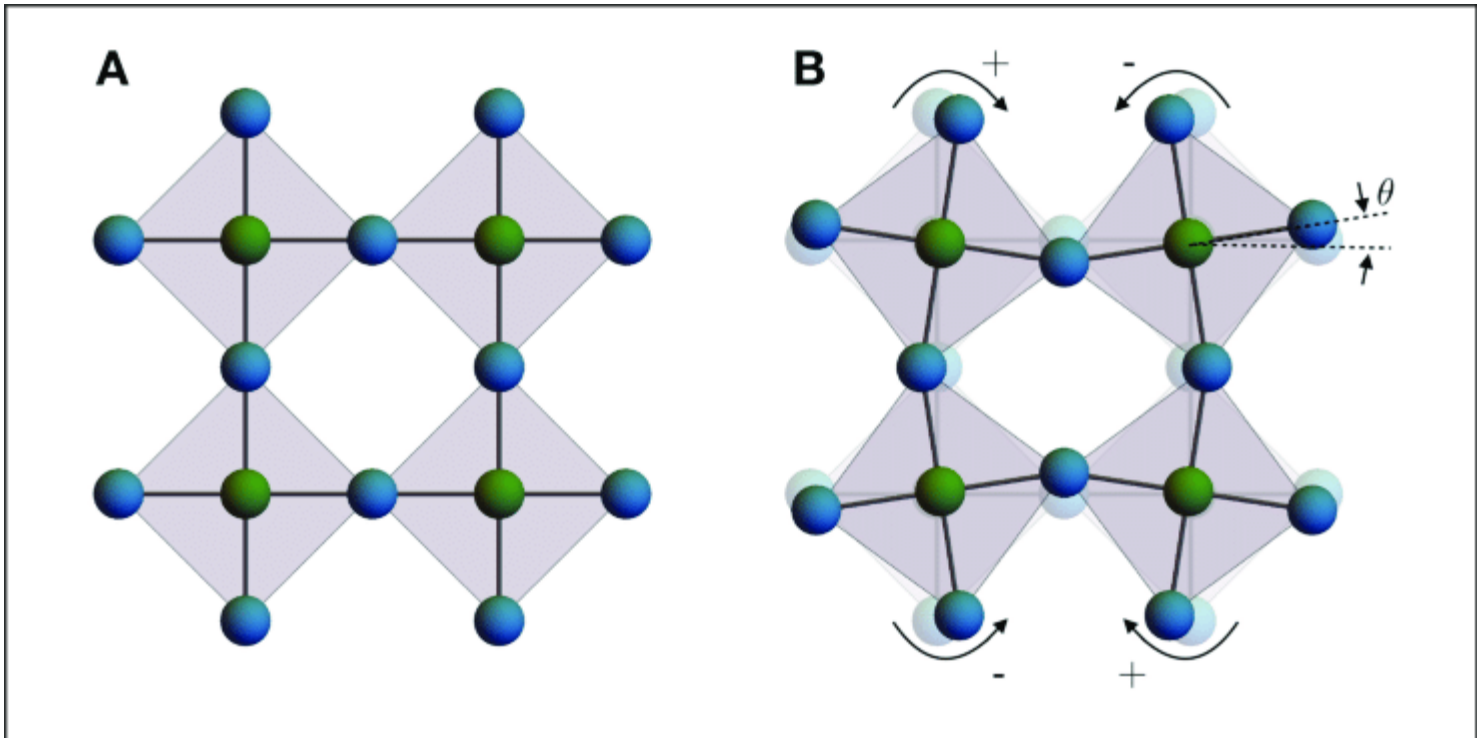


Oxygen deficiency

Let’s talk more about these distortions/deficiences

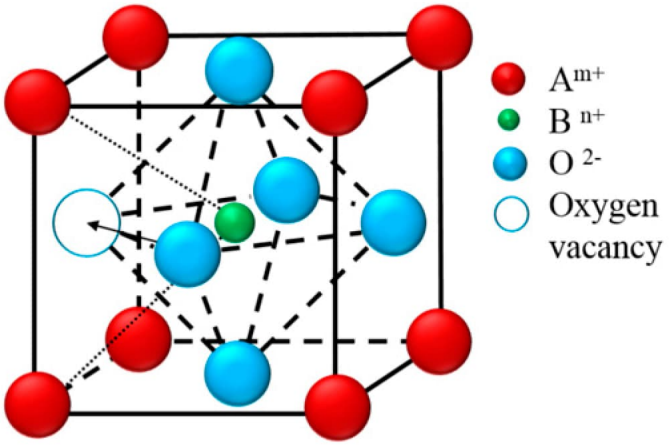
DISTORTIONS in ABO_3

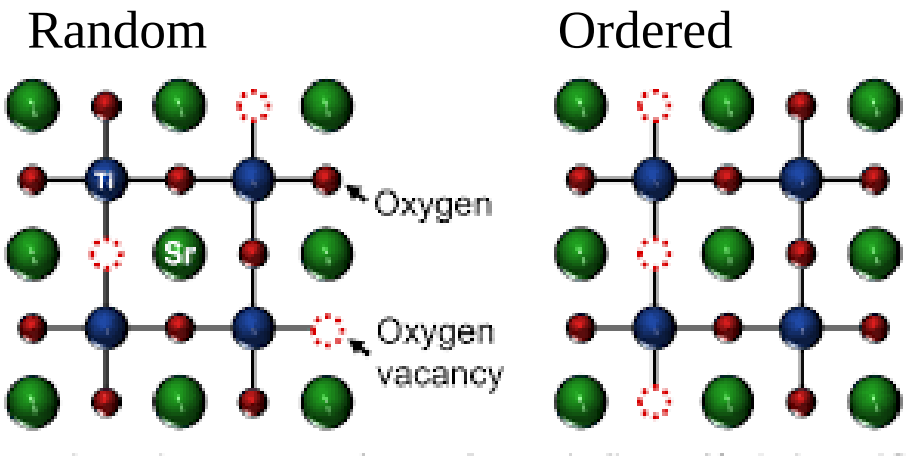
- Atoms (typically oxygen atoms) are often slightly displaced from their ideal positions
- This ends up with tilting of the BO_6 octahedra
- These **distortions affect many properties** (magnetic, ferroelectric, etc.)

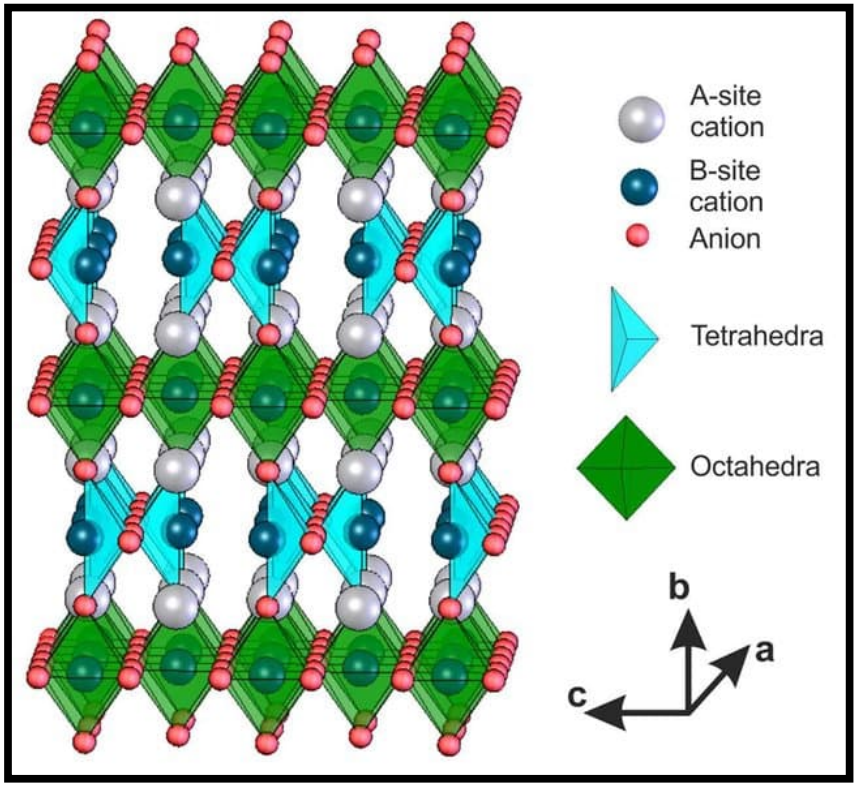


OXYGEN DEFICIENCY in $ABO_{3-\delta}$

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







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

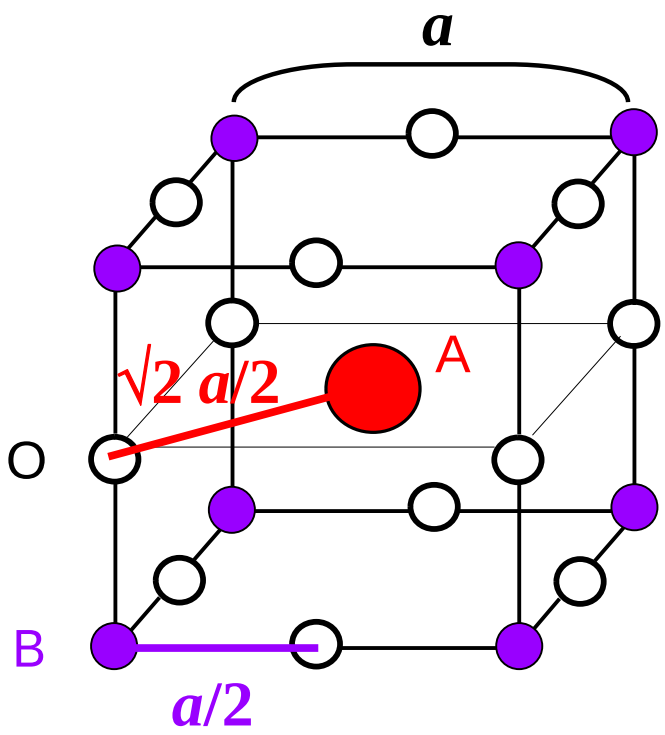
- Calculated from preferred bond lengths

- Preferred bond lengths are estimated from ionic radii

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

Tolerance factor for ABO_3 perovskite

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



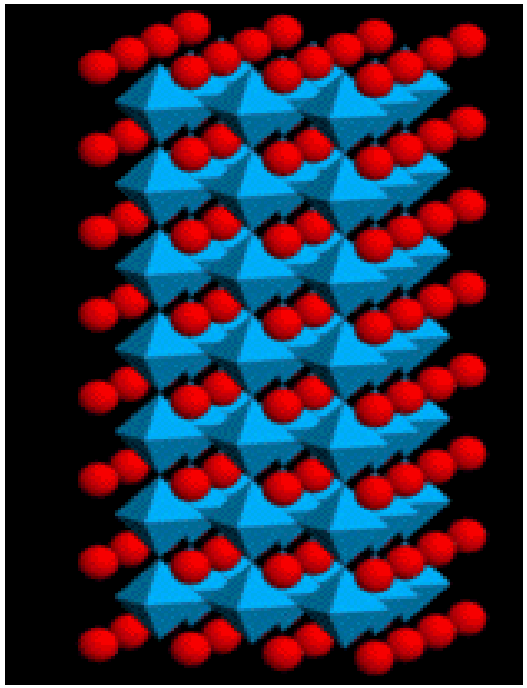
$t = 1$: ideal matching (0.80 < t < 1.05 possible)

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

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

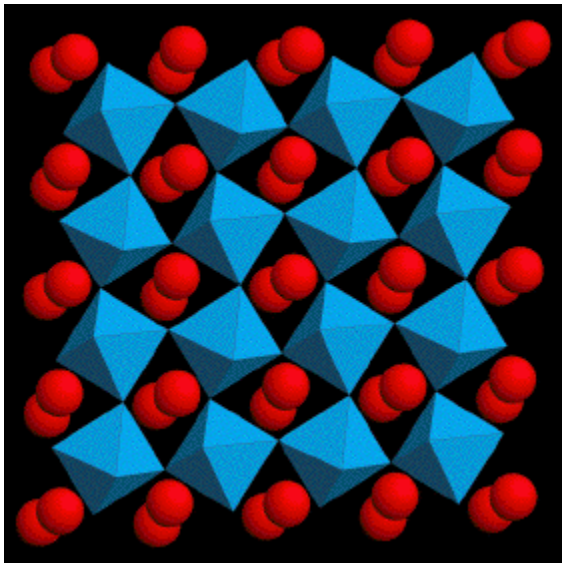
$$t = \frac{(r_A + r_O)}{\sqrt{2}\,(r_B + r_O)}$$

***t* = 1**



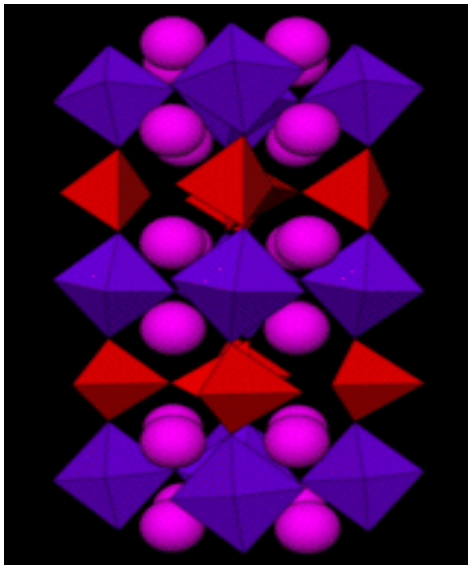
Ideal perovskite

***t* < 1**



Changes in
atomic positions

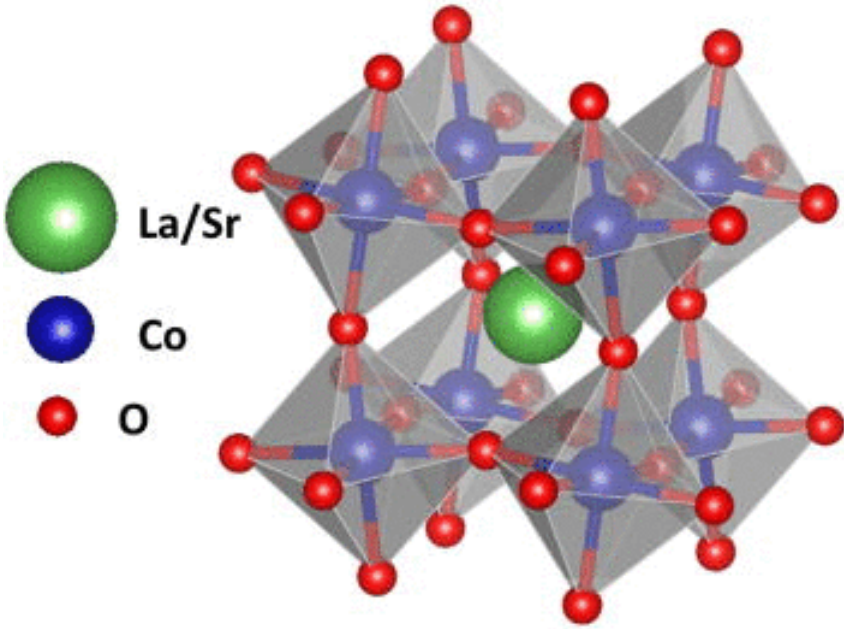
***t* > 1**



Oxygen deficiency

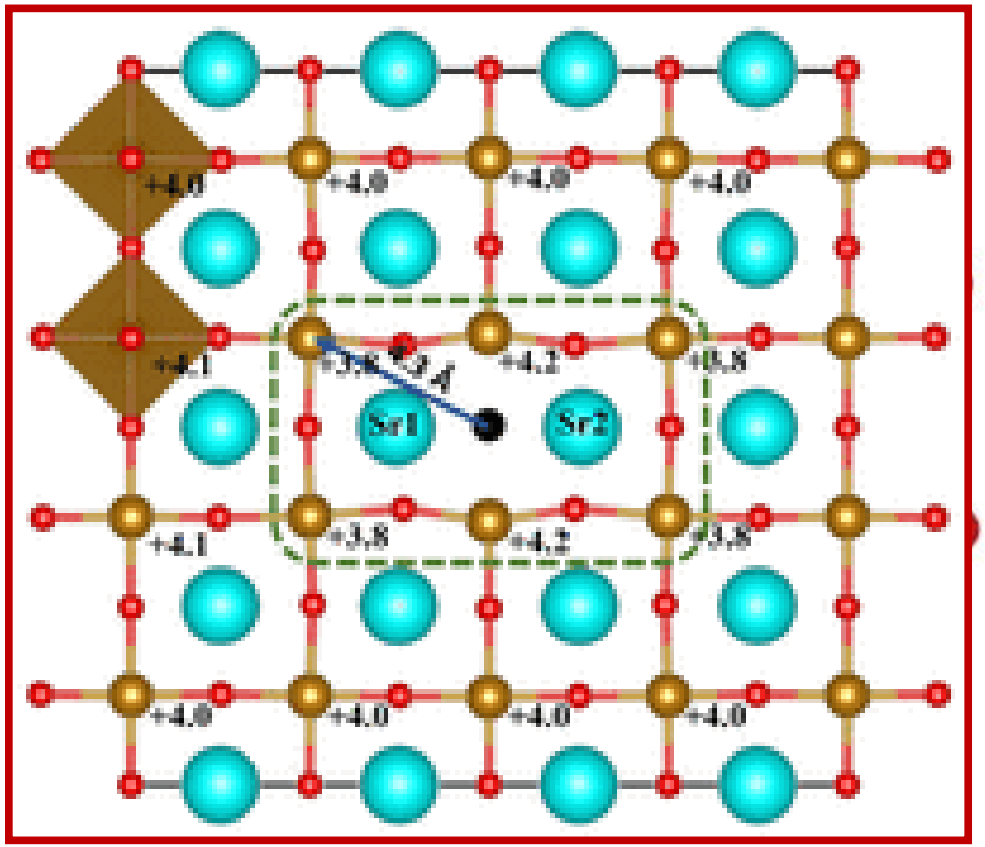
ALIOVALENT SUBSTITUTIONS in PEROVSKITES

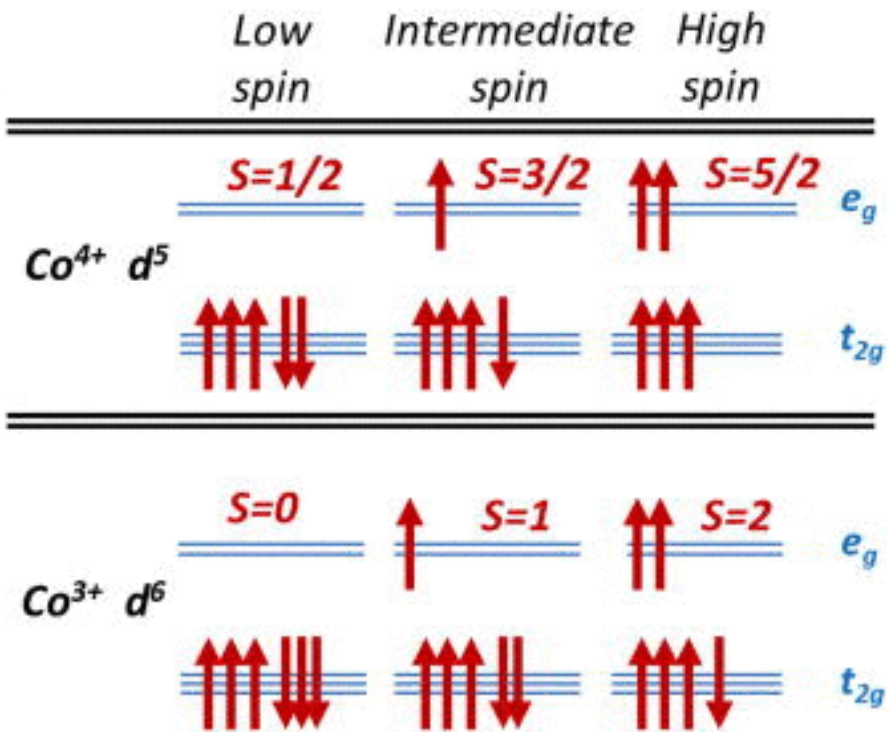
- "Doping": creates mixed valency
- For example: Sr^{2+}-for-La^{3+} substitution in $(La,Sr)CoO_3$
- Type of doping ? Typical substitution level ?
- Effect on Co valence ?
- What else may happen ?

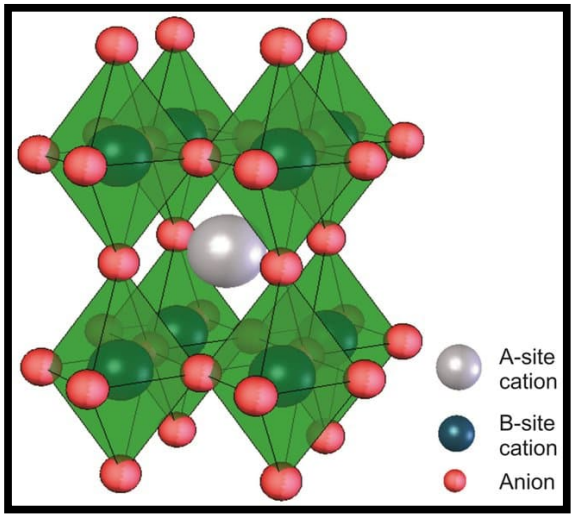


ALIOVALENT SUBSTITUTION in $(La^{3+},Sr^{2+})CoO_{3-\delta}$

- 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 ?







Perovskite ABO_3

- No space for interstitial oxygen

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

- Enough space for interstitial oxygen