# Functional Inorganic Materials
# Fall 2021

Tuesdays: 14.15 - 16.00
Thursdays: 12.15 - 14.00
Remote Zoom lectures

| # | Date | Who | Topic |
|---|---|---|---|
| s | Tue 02.11. | Maarit | Introduction + Materials design |
| 2 | Thu 04.11. | Antti | Computational materials design |
| 3 | Tue 09.11. | Maarit | Superconductivity: High-$T_c$ superconducting Cu oxides |
| 4 | Thu 11.11. | Maarit | Ionic conductivity (Oxygen): Oxygen storage and SOFC |
| 5 | Tue 16.11. | Maarit | Ionic conductivity (Lithium): Li-ion battery |
| 6 | Thu 18.11. | Antti | Thermal conductivity |
| 7 | Tue 23.11. | Antti | Thermoelectricity |
| 8 | Thu 25.11. | Maarit | Hybrid materials |
| 9 | Tue 30.11. | Maarit | Luminescence and optically active materials |
| 10 | Thu 02.12. | Antti | Piezoelectricity |
| 11 | Tue 07.12. | Antti | Pyroelectricity and ferroelectricity |
| 12 | Thu 09.12. | Antti | Magnetic and multiferroic oxides |

# LECTURE 1: Materials Design

- Doping & Substitution
- Aliovalent Substitution
- Mixed Valency
- Vacancies & Interstitials
- Electronic & Ionic Conductivity
- Oxygen Engineering
- Relative Ion Sizes & Tolerance Parameters

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 H | | | | | | | | | | | | | | | | | 2 He |
| 3 Li | 4 Be | | | | | | | | | | | 5 B | 6 C | 7 N | 8 O | 9 F | 10 Ne |
| 11 Na | 12 Mg | | | | | | | | | | | 13 Al | 14 Si | 15 P | 16 S | 17 Cl | 18 Ar |
| 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 |
| 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 |
| 55 Cs | 56 Ba | 57 to 71 | 72 Hf | 73 Ta | 74 W | 75 Re | 76 Os | 77 Ir | 78 Pt | 79 Au | 80 Hg | 81 Ti | 82 Pb | 83 Bi | 84 Po | 85 At | 86 Rn |
| 87 Fr | 88 Ra | 89 to 103 | 104 Rf | 105 Ha | 106 Sg | 107 Ns | 108 Hs | 109 Mt | | | | | | | | | |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 57 La | 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 |
| 89 Ac | 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 |

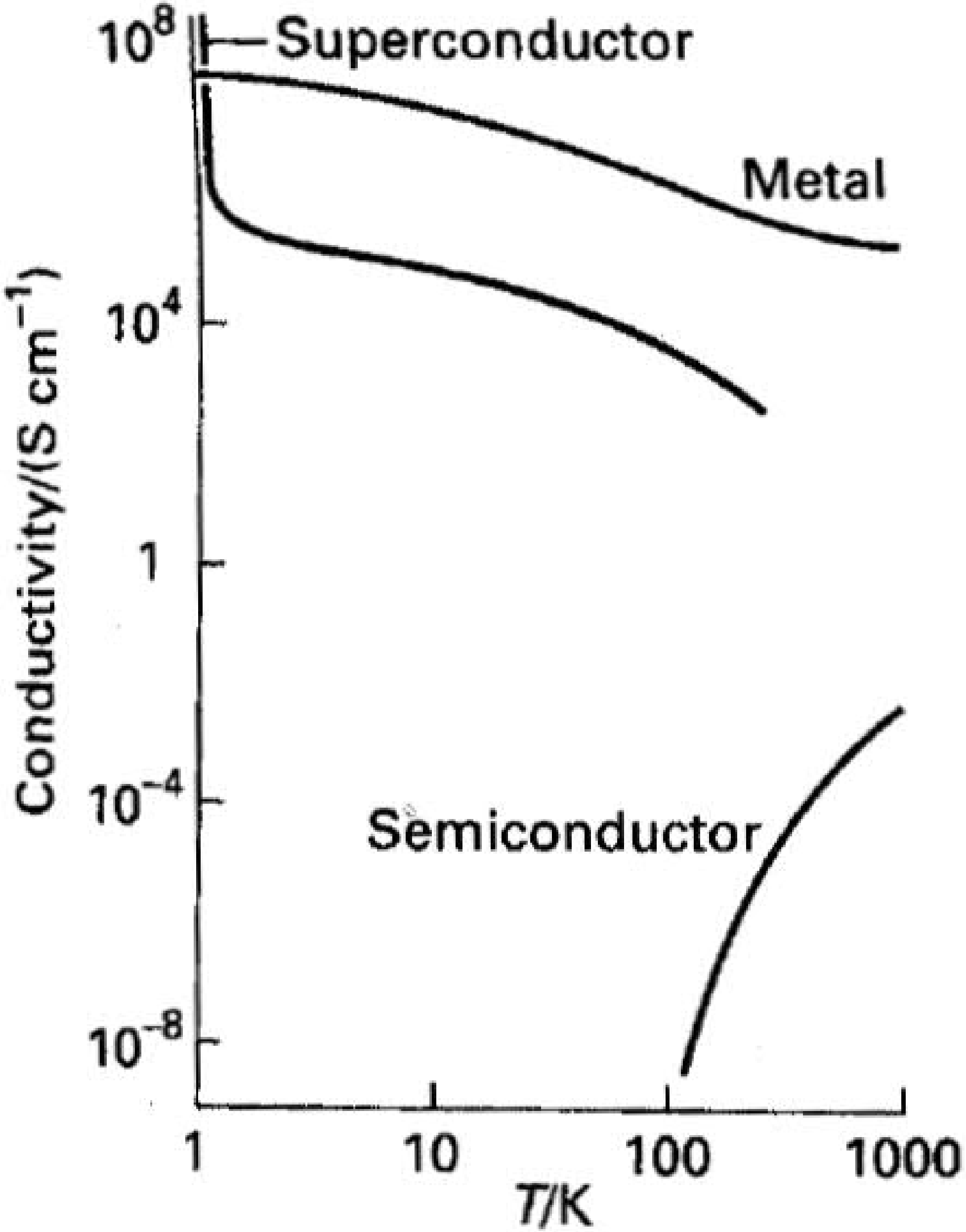
# LECTURE EXERCISE 1

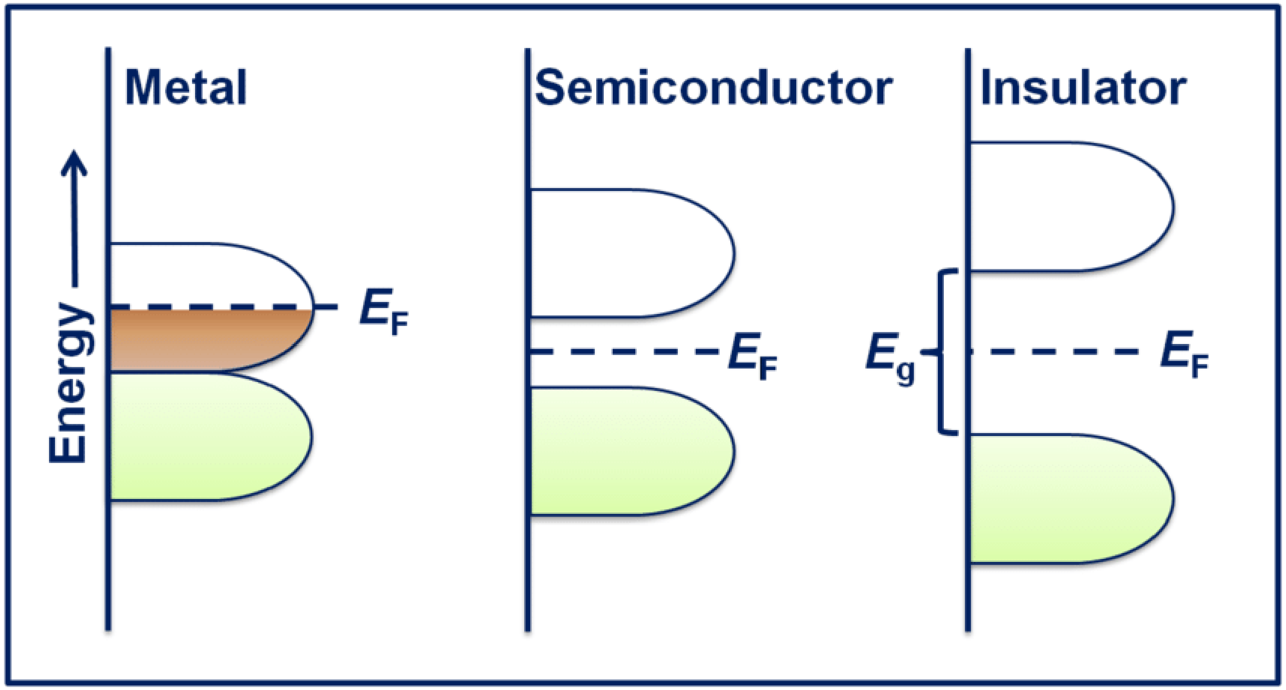
1. **Assign the type of doped carriers (n-type or p-type) for the following materials (rationalize your answers!): Al-doped Si, $(Zn_{0.98}Al_{0.02})O$, $(Pb_{0.98}Na_{0.02})Te$, $(La_{0.9}Sr_{0.1})_2CuO_4$, $La_2CuO_{4.1}$.**

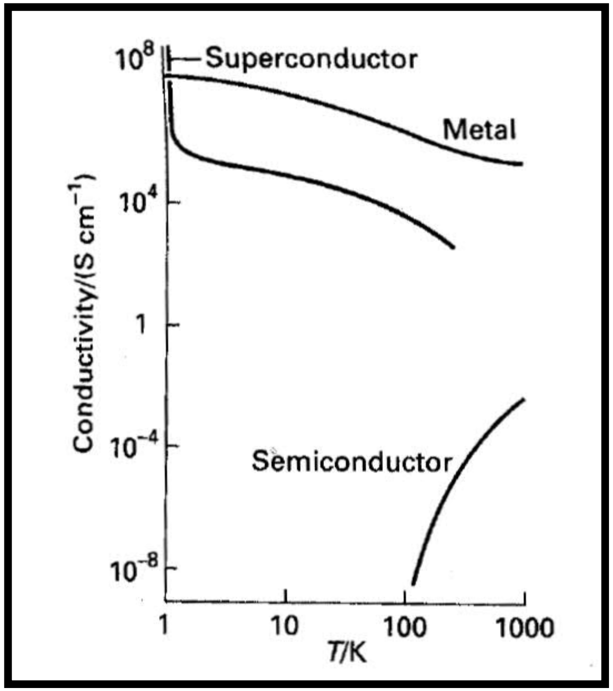
2. **Calculate the tolerance parameter for the following perovskite compounds (assuming the ioniv radius values given below), and judge are them feasible. Also, predict which of them is most easily reduced; most importantly, explain why: $LaMnO_3$, $LaCoO_3$, $LaNiO_3$, $LaCuO_3$.**

| 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 |

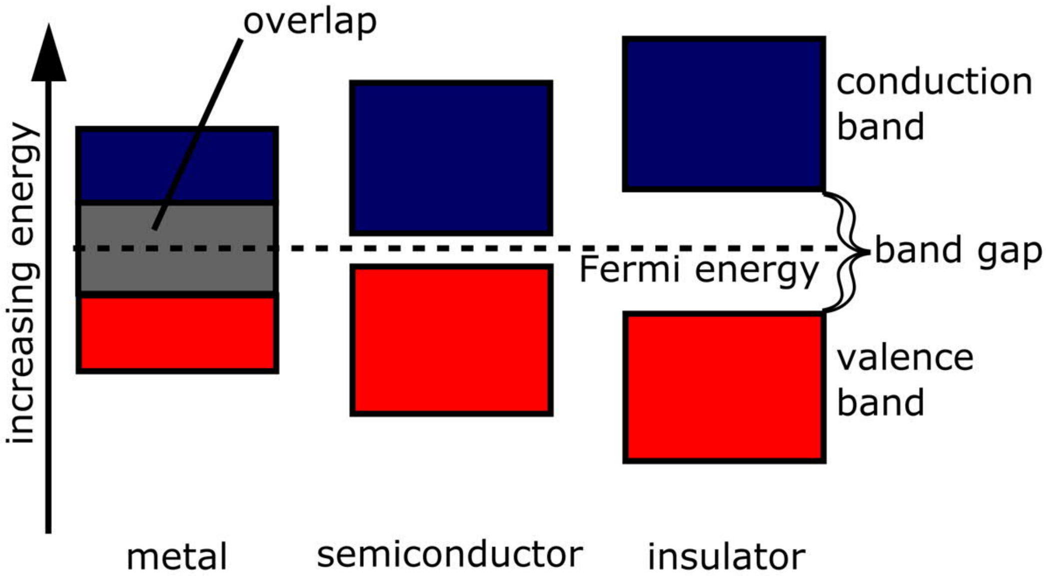
# ELECTRICAL CONDUCTIVITY



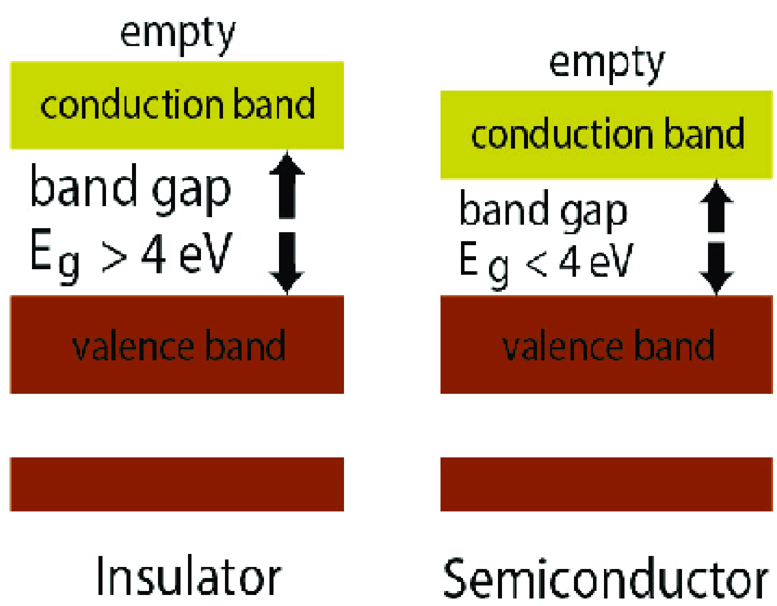


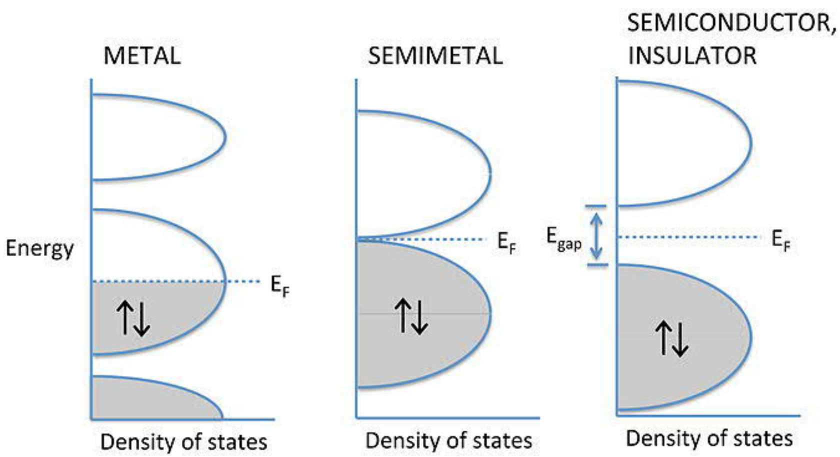

- What are: $E_F$ and $E_g$ ?
- How large is $E_g$ for a semiconductor / an insulator ?
- Can you explain the different temperature dependencies of electrical conductivity for metals and semiconductors ?



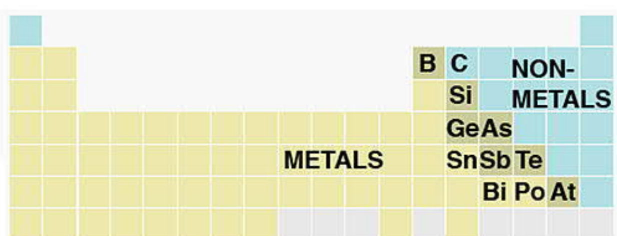
overlap
increasing energy
conduction band
band gap
Fermi energy
valence band
metal
semiconductor
insulator

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

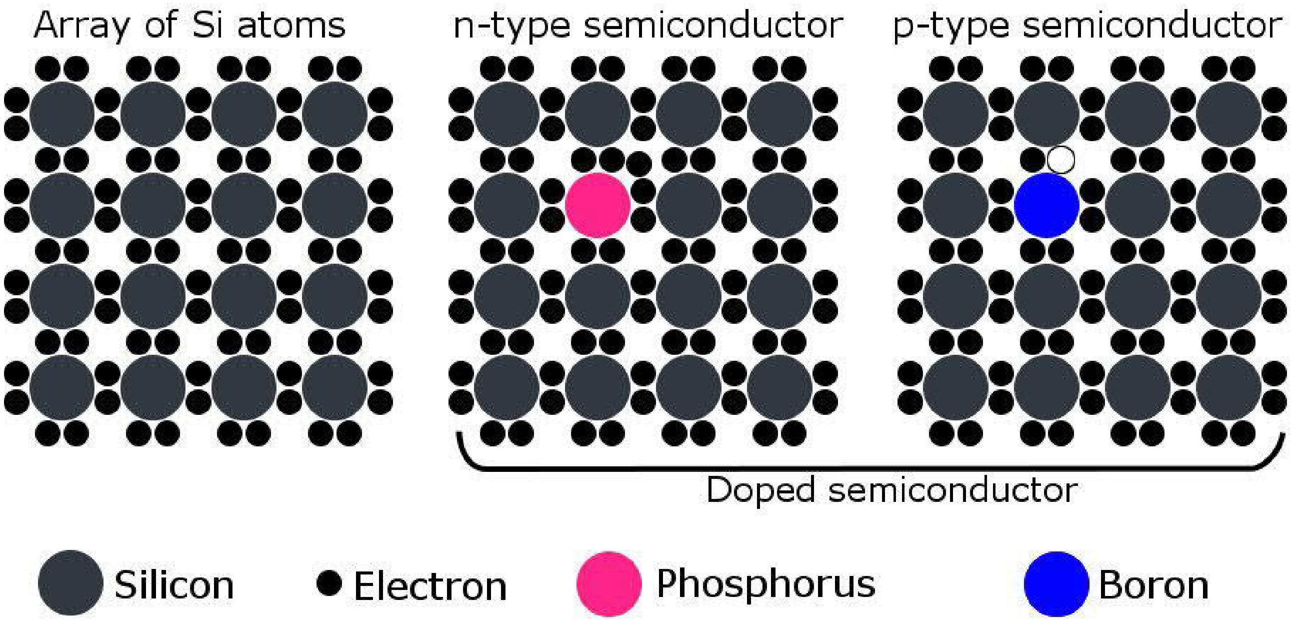



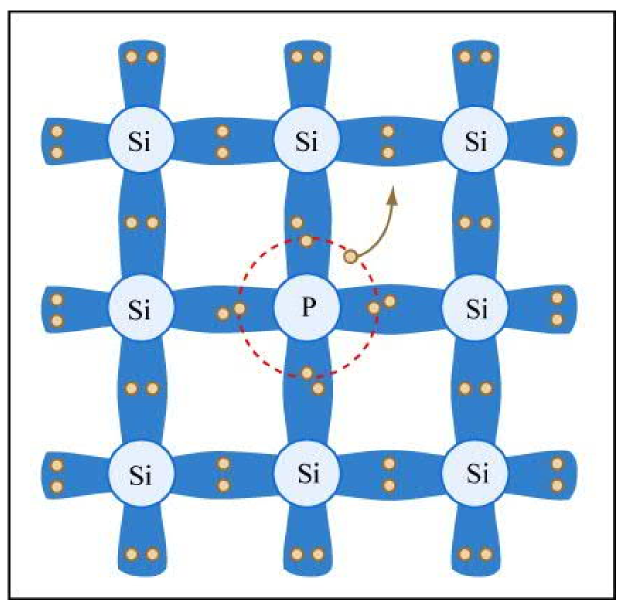
METAL
SEMIMETAL
SEMICONDUCTOR, INSULATOR
Energy
$E_F$
$E_{gap}$
Density of states
Density of states
Density of states

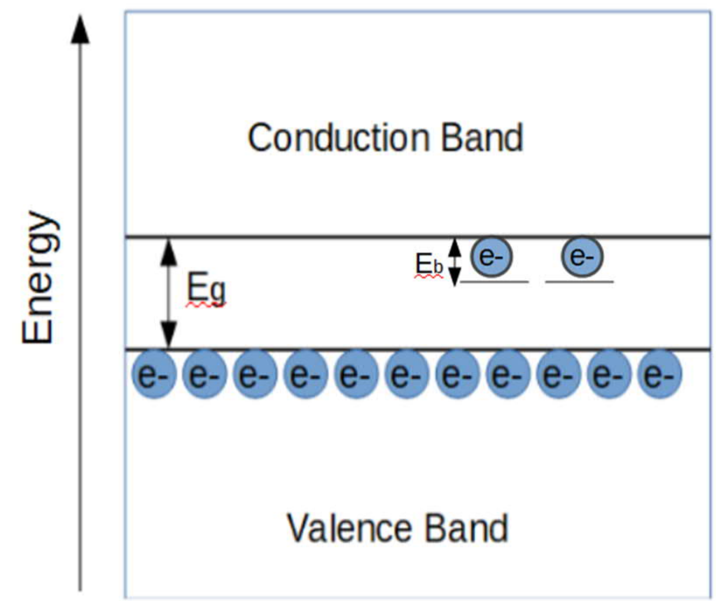



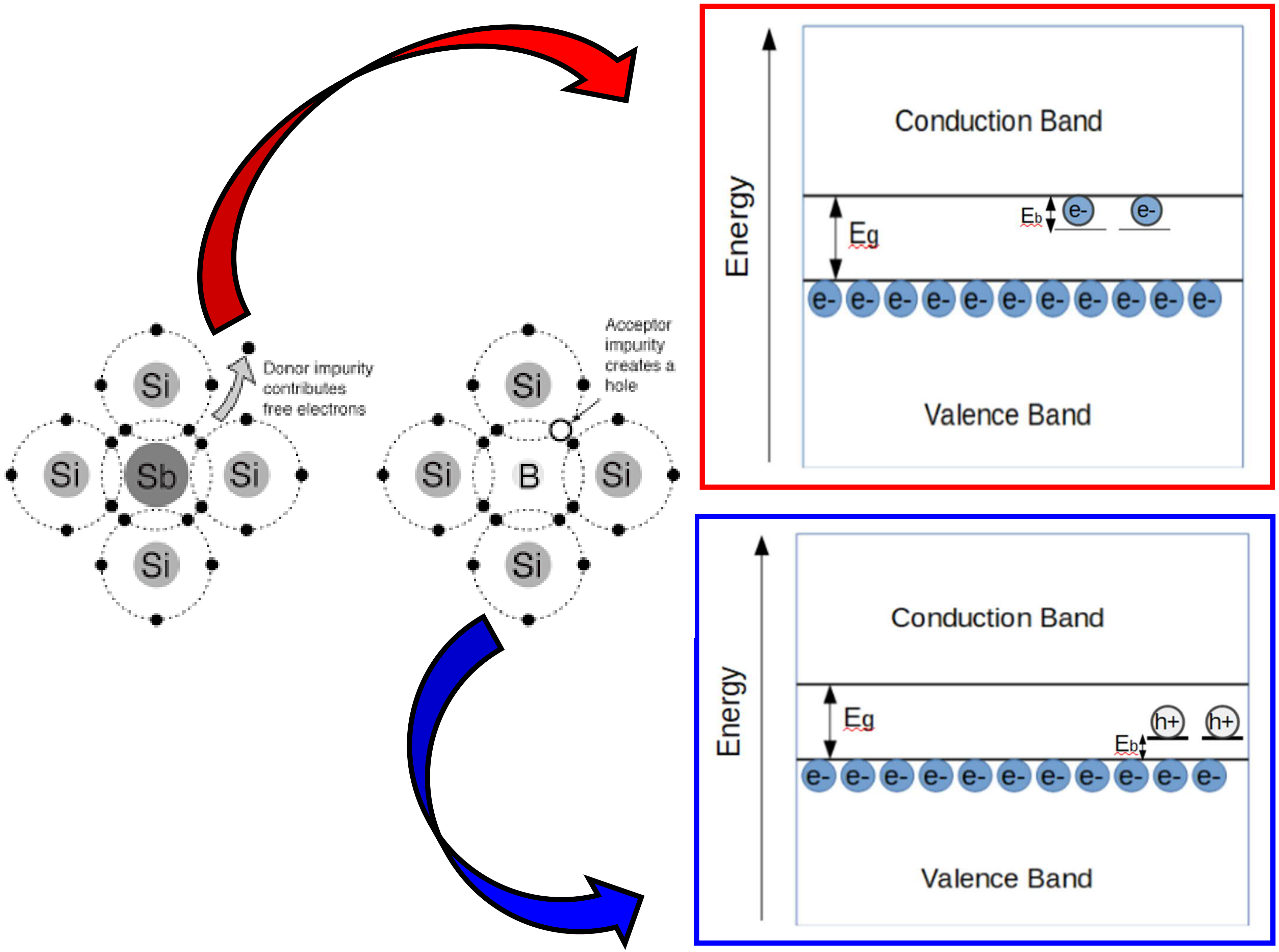
B
C
Si
Ge
As
Sn
Sb
Te
Bi
Po
At
NON-METALS
METALS

# Doping in Semiconductors

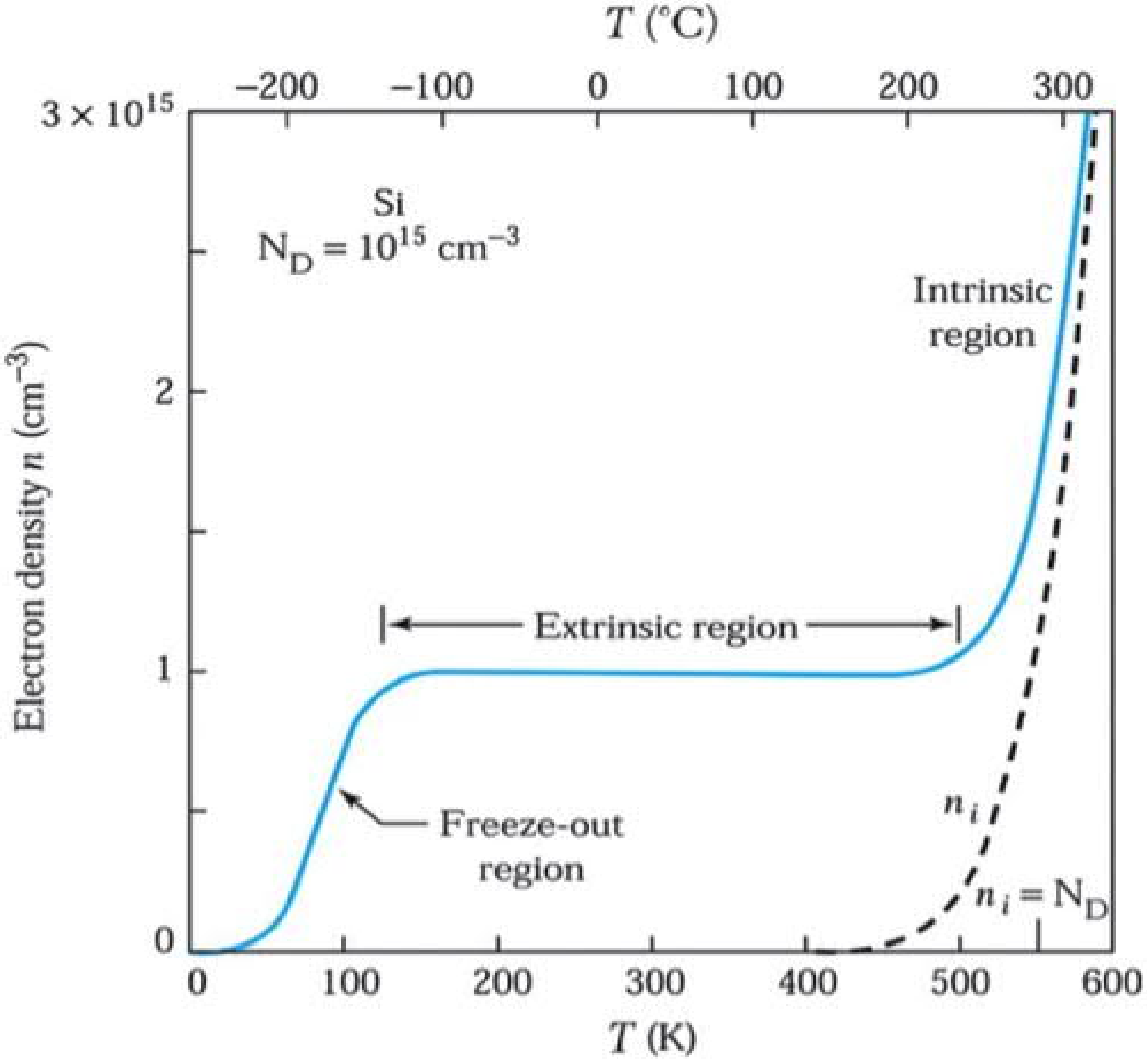


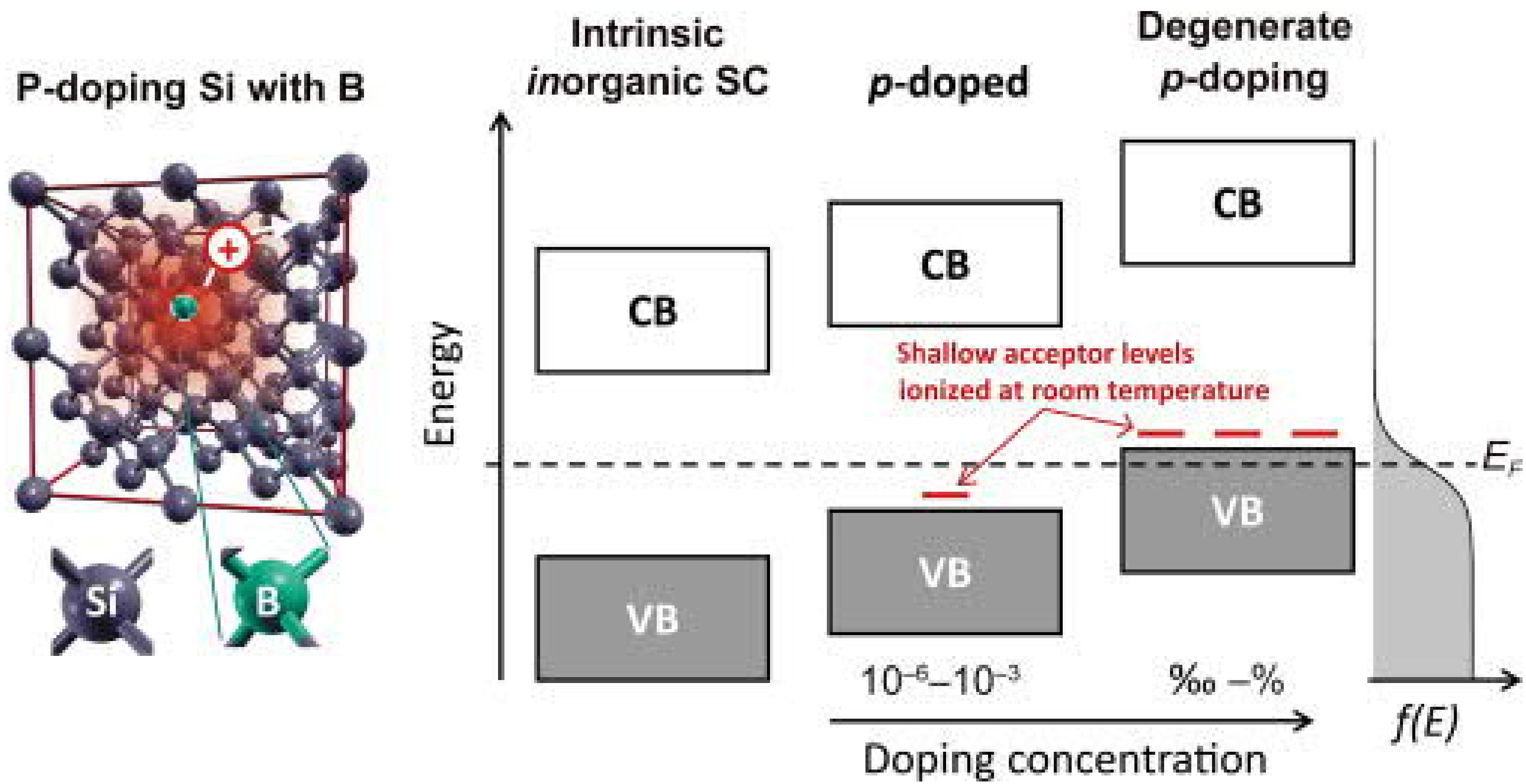




Si
Sb
B
Donor impurity contributes free electrons
Acceptor impurity creates a hole
Energy
Conduction Band
Valence Band
Eg
Eb
e-
h+

If density of donor atoms is $10^{15}$ atoms /cm$^3$ and intrinsic carrier density in Si is given by a curve that was given by Fig 1.18. Regenerate the following figure for temperatures higher than 180 K.



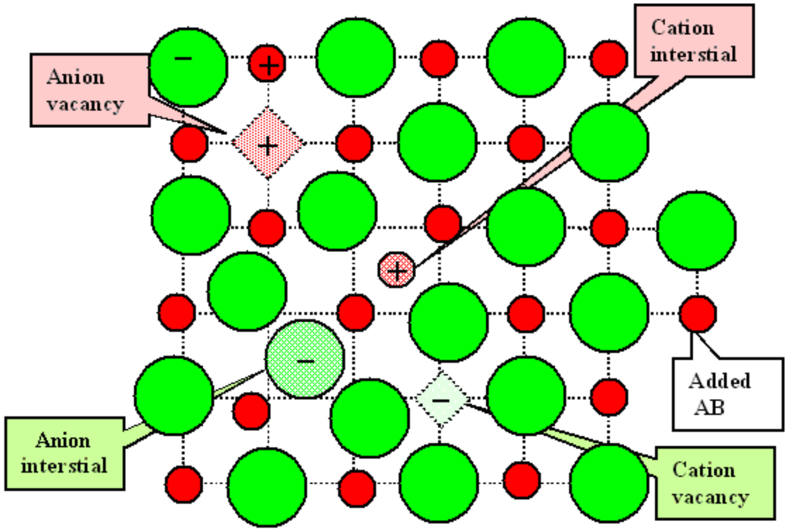


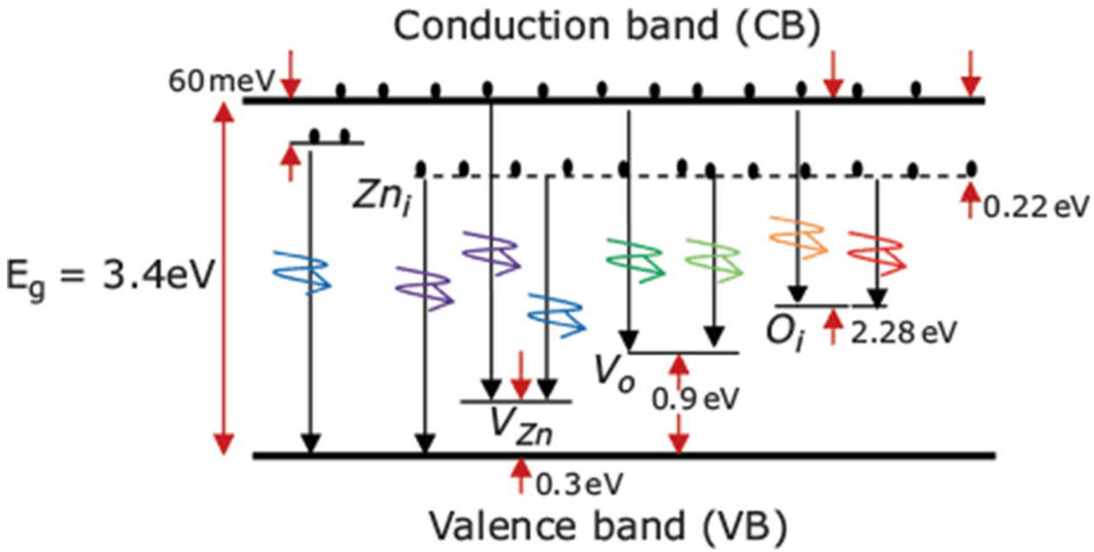

# What is the dopant concentration ? !

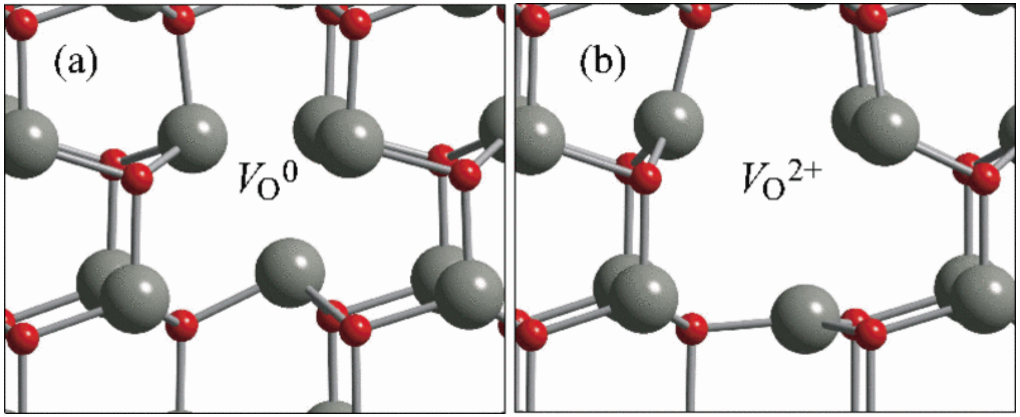
# Simple metal oxide semiconductor: ZnO

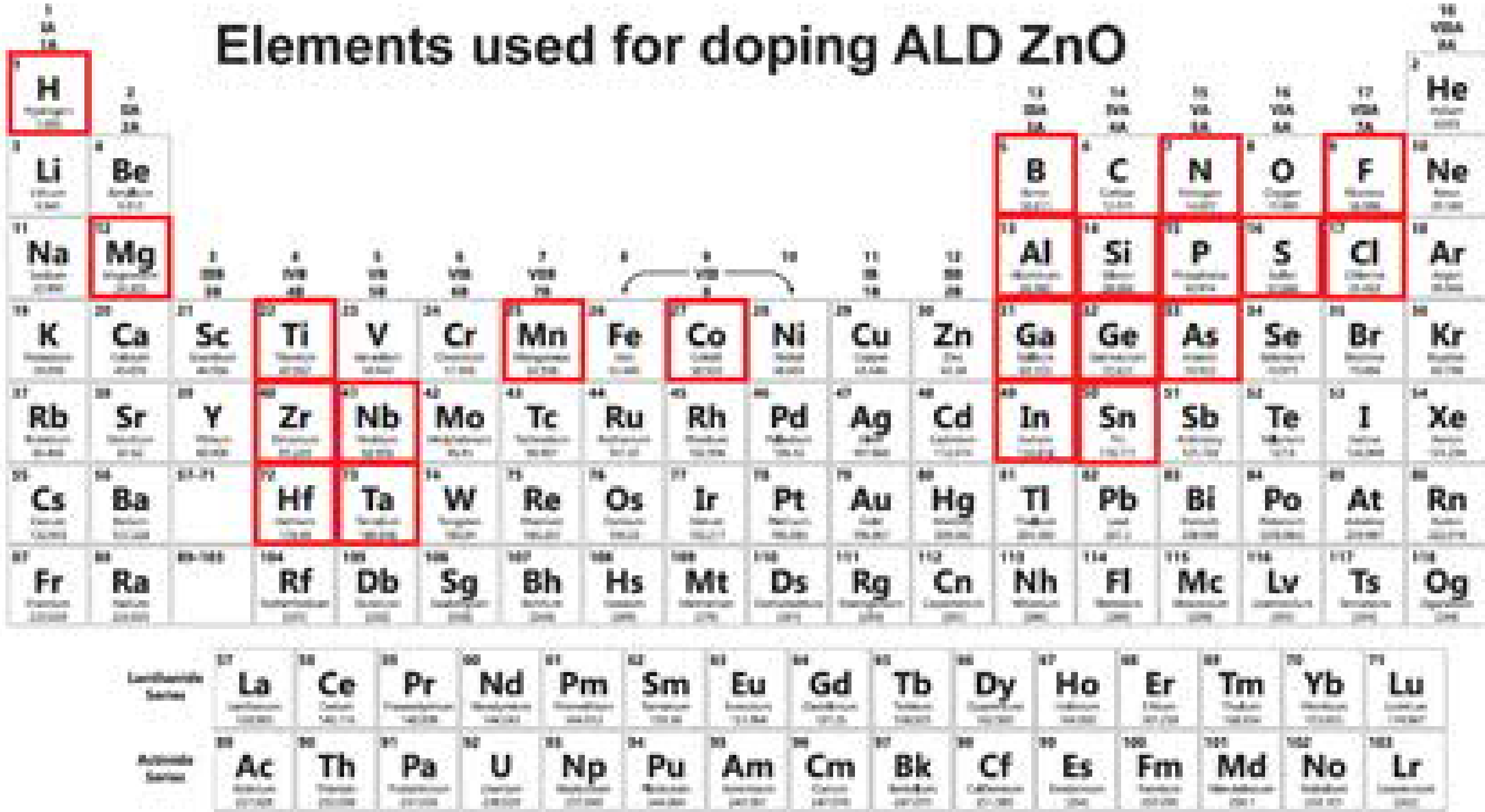
# - Intrinsically n-type

# - What kind of native defects ?



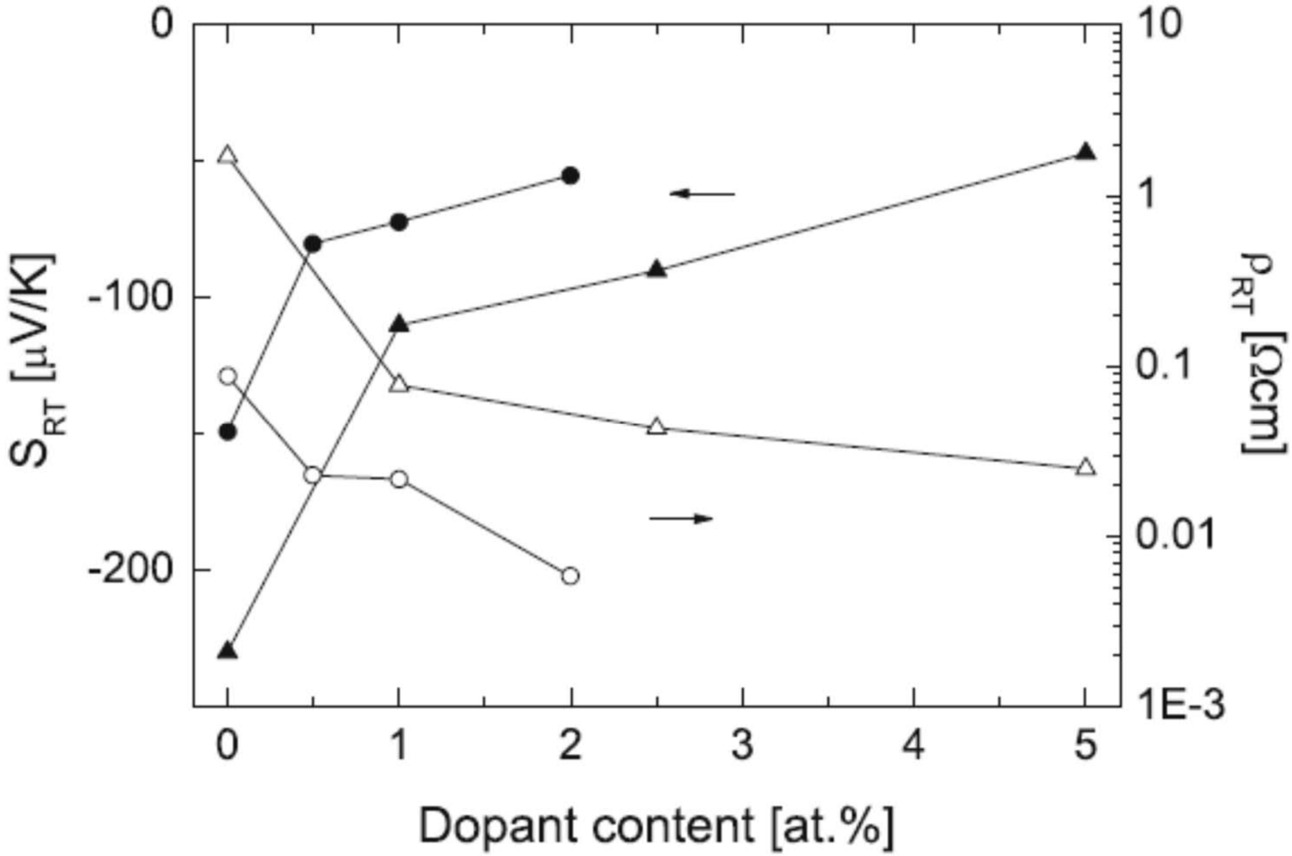





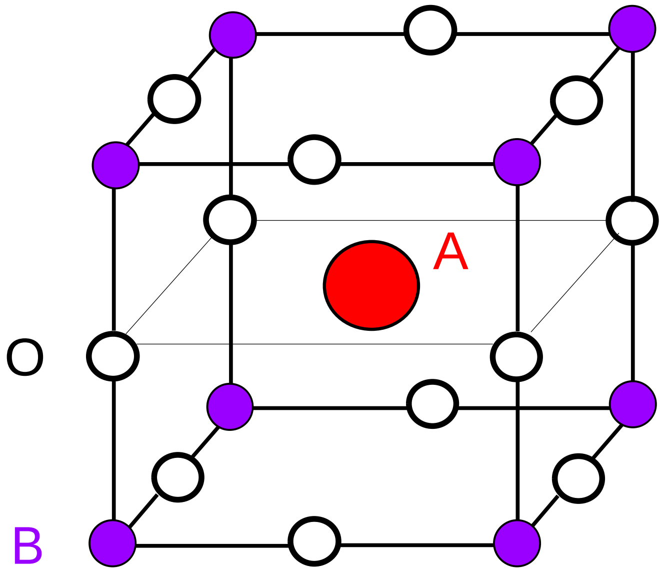

Zhengning Gao *and* Parag Banerjee, Review Article: Atomic layer deposition of doped ZnO films, Journal of Vacuum Science & Technology A **37**, 050802 (2019); https://doi.org/10.1116/1.5112777

# What is the substitution level ?




T. Tynell, R. Okazaki, I. Terasaki, H. Yamauchi & M. Karppinen,
Electron doping of ALD-grown ZnO thin films through Al and P substitutions,
*Journal of Materials Science* **48**, 2806 (2013).

# PEROVSKITE STRUCTURE

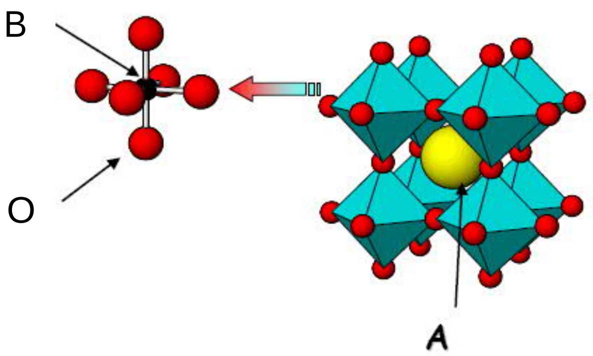



**General formula: A B O$_{3-\delta}$**

A: large cation

B: small cation (transition metal)

O: oxygen (sometimes halogen)




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

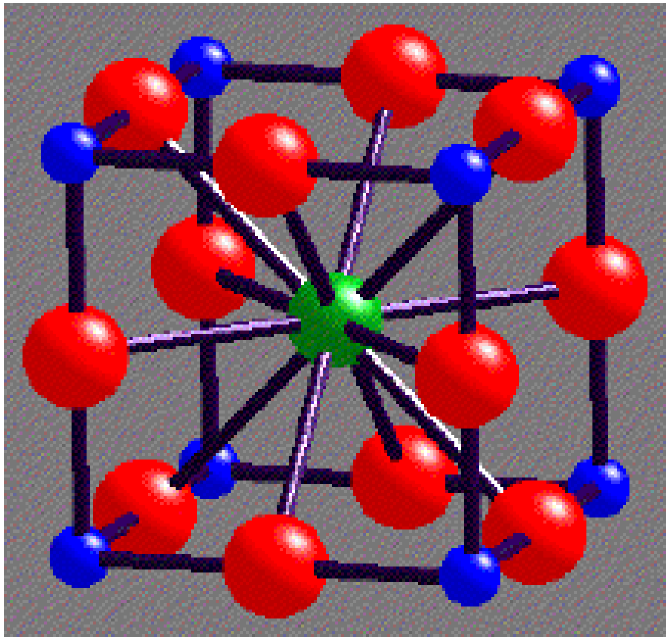
e.g. $La^{III}Sc^{III}O_3$, $Sr^{II}Ti^{IV}O_3$, $Na^{I}Nb^{V}O_3$

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

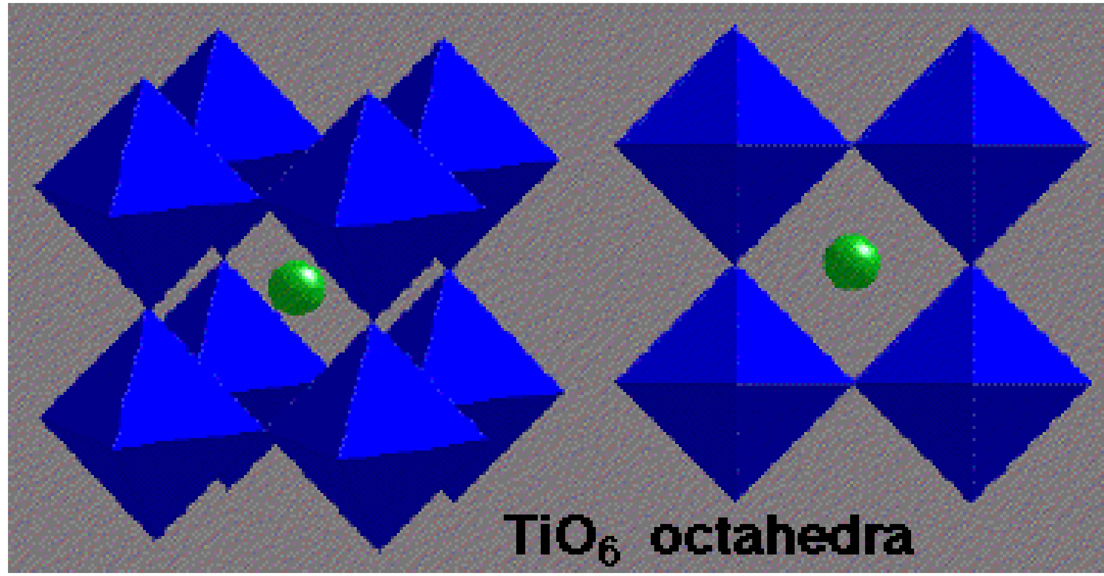
**Mineral Perovskite: $CaTiO_3$**

**- Named after Russian mineralogist, Count Lev Aleksevich von Perovski**

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

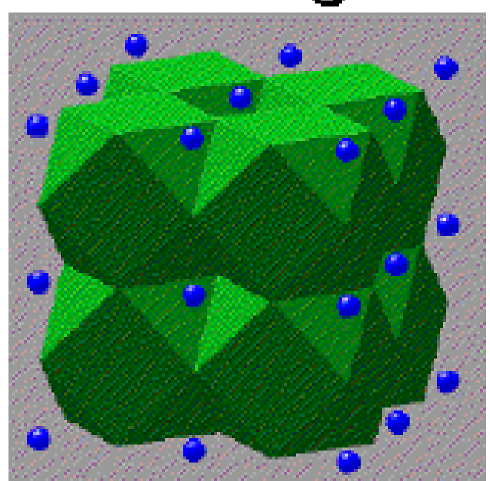


A-Cell

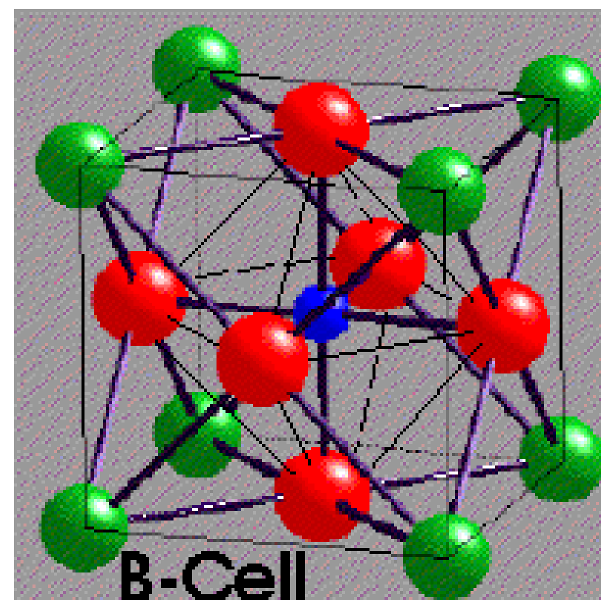



# Perovskite
## $CaTiO_3$

Ca Ti O



$CaO_{12}$ cuboctahedra



# 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
$La(Co,Mn)O_3$

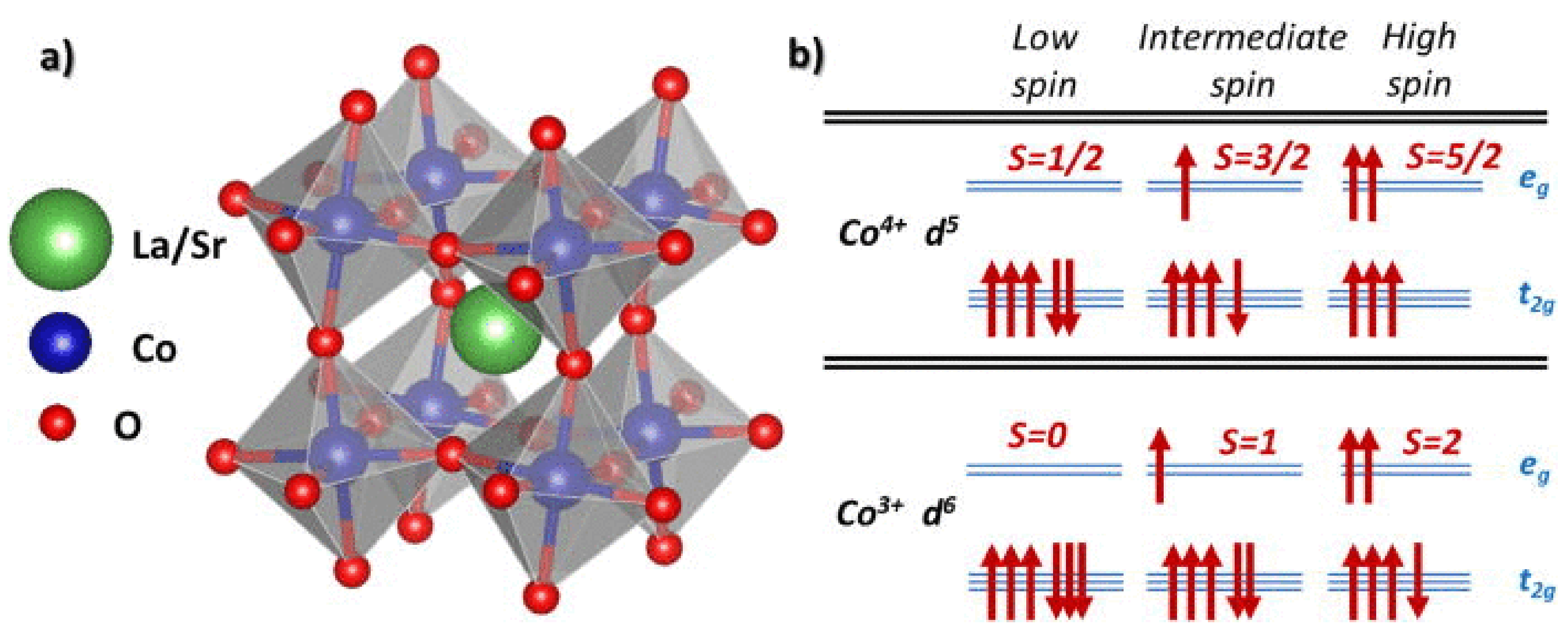
Metallic conductor
$LaCrO_3$

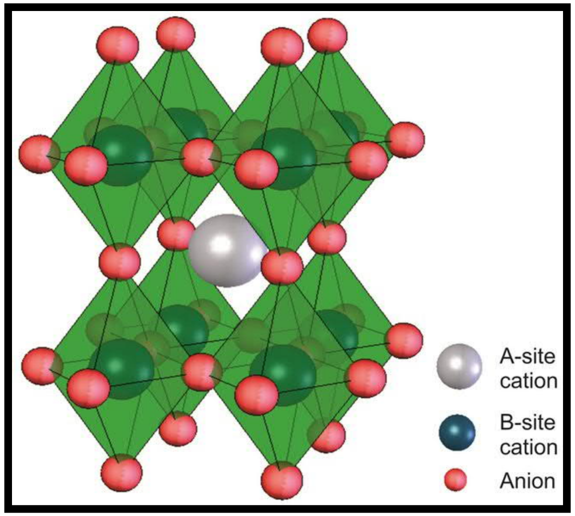
Piezoelectric material
$Pb(Zr,Ti)O_3$

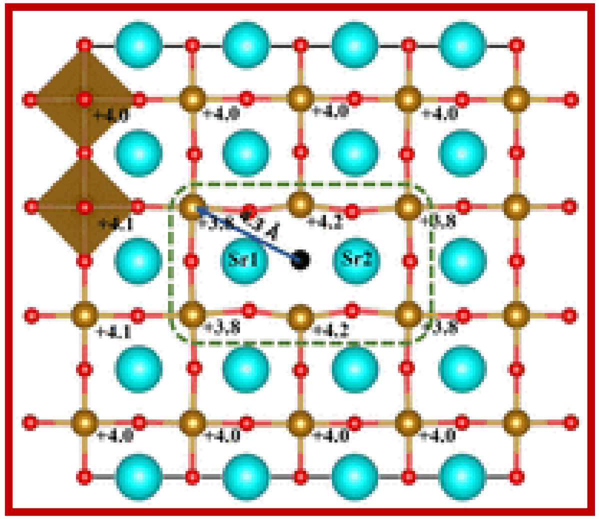
Capasitor
(high dielectric constant)
$BaTiO_3$

## ALIOVALENT SUBSTITUTIONS: Perovskite $(La^{3+},Sr^{2+})CoO_3$

- **Effect on Co valence ?**
- **Typical substitution levels ?**
- **What else may happen ?**

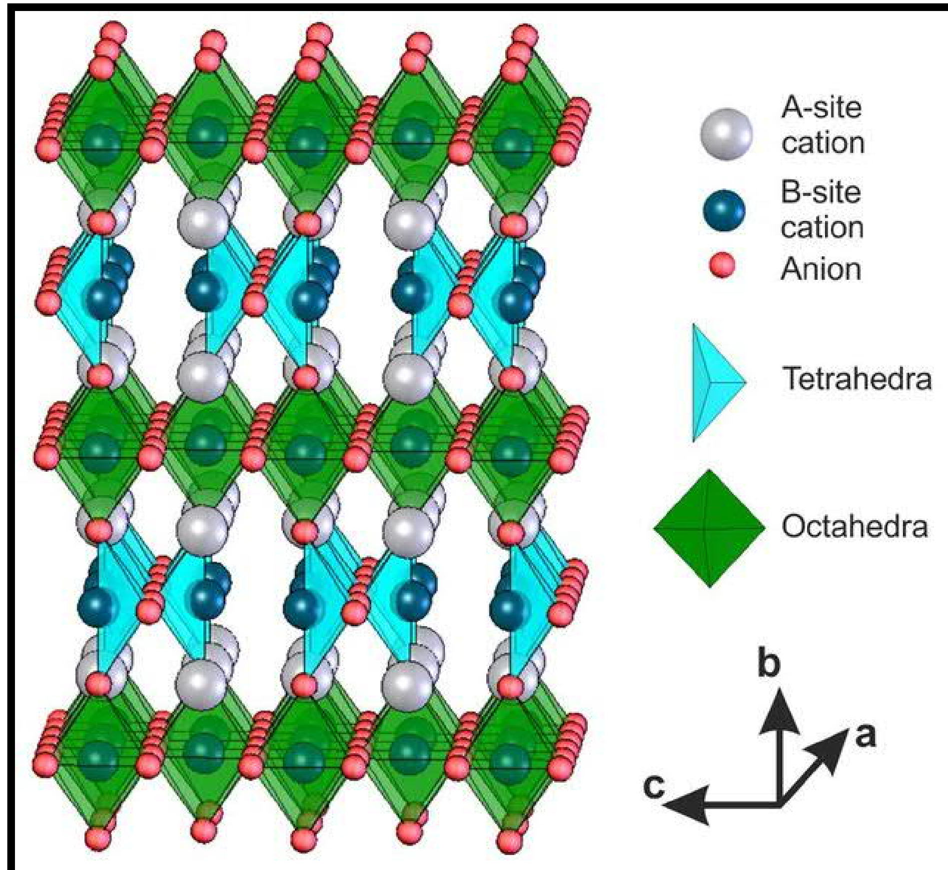


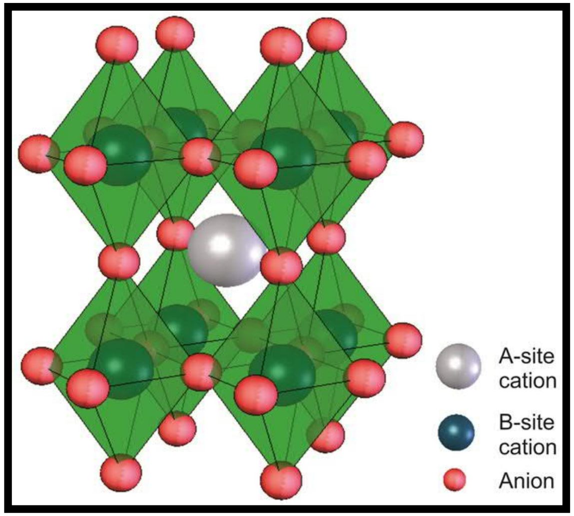



**OXYGEN NONSTOICHIOMETRY: $(La^{3+},Sr^{2+})CoO_{3-\delta}$**

- **Oxygen vacancies**
- **Random or Ordered**
- **Balance: redox versus vacancies**



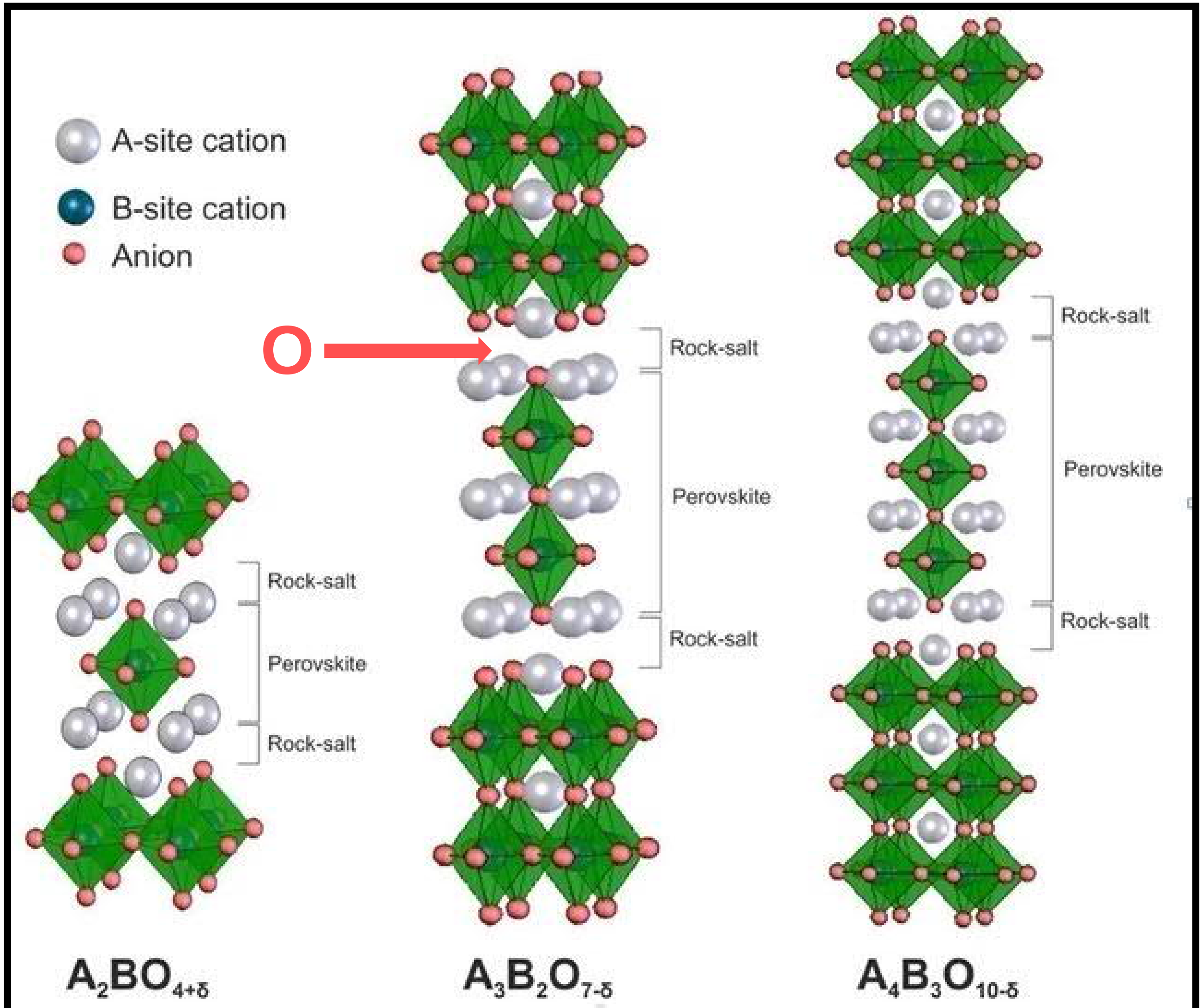



## Perovskite $ABO_3$

- No space for interstitial oxygen

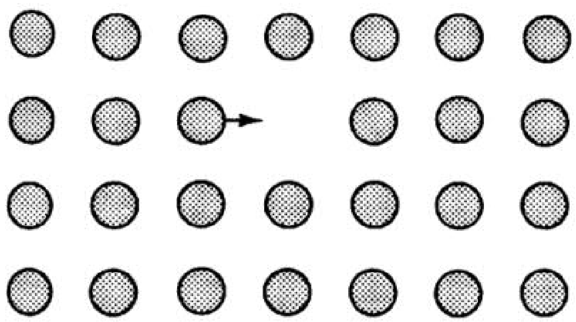
## Ruddlesden-Popper $A_{n+1}B_nO_{1+3n}$

- Enough space for interstitial oxygen

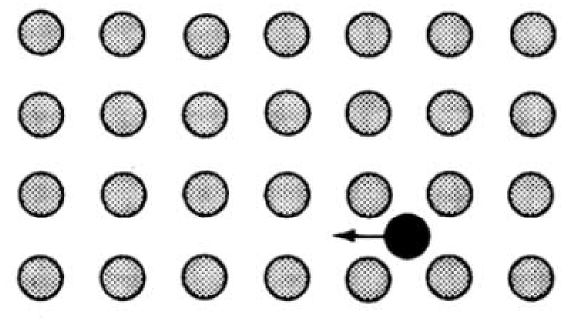


# IONIC CONDUCTIVITY

- **Mobile Vacancies or Interstitials**



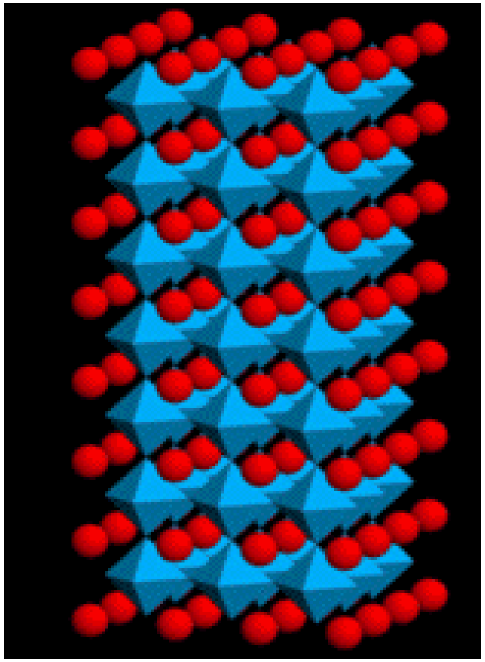
mobile vacancy



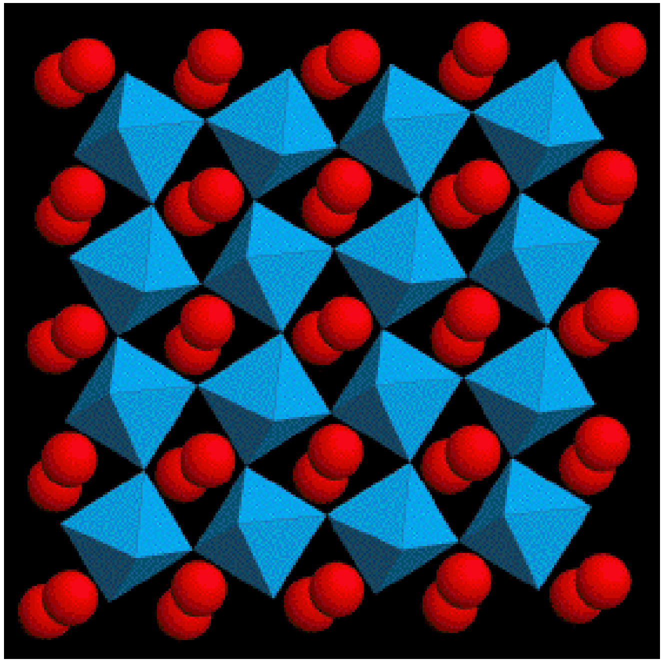
mobile interstitial

| | Material | Conductivity (S m$^{-1}$) |
|---|---|---|
| **Ionic conductors** | Ionic crystals | $< 10^{-16} – 10^{-2}$ |
| | Solid Electrolytes | $10^{-1}$-$10^{3}$ |
| | Liquid electrolytes | $10^{-1}$-$10^{3}$ |
| **Electronic conductors** | Metals | $10^{3}$-$10^{7}$ |
| | Semiconductors | $10^{-3}$-$10^{4}$ |
| | Insulators | $< 10^{-10}$ |

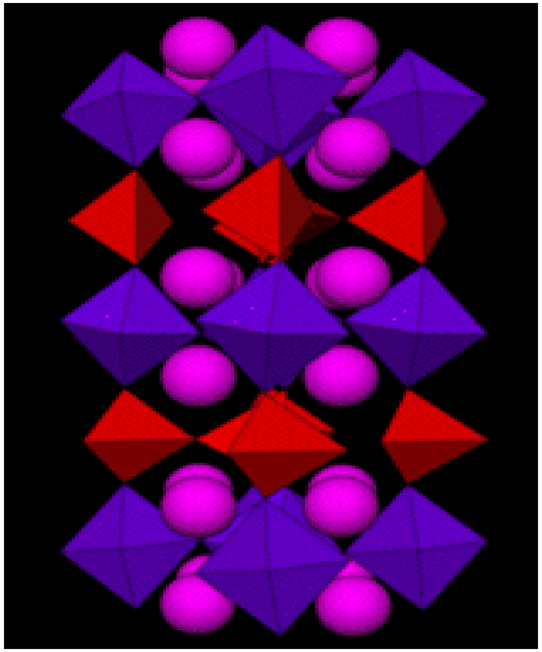
## Distortions and Imperfections in Perovskite Structure: - often the source of the desired properties



IDEAL



Changes in atomic positions

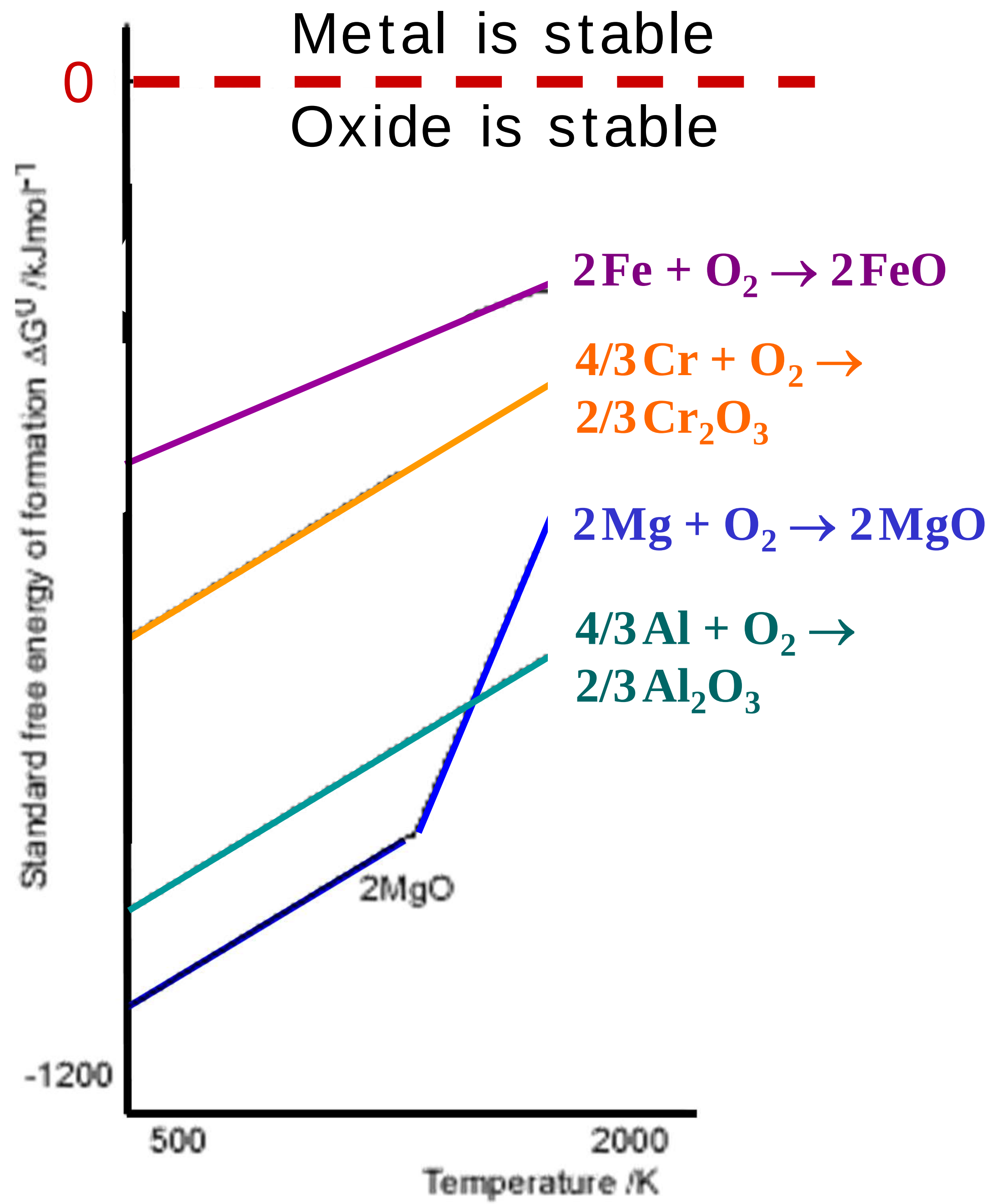


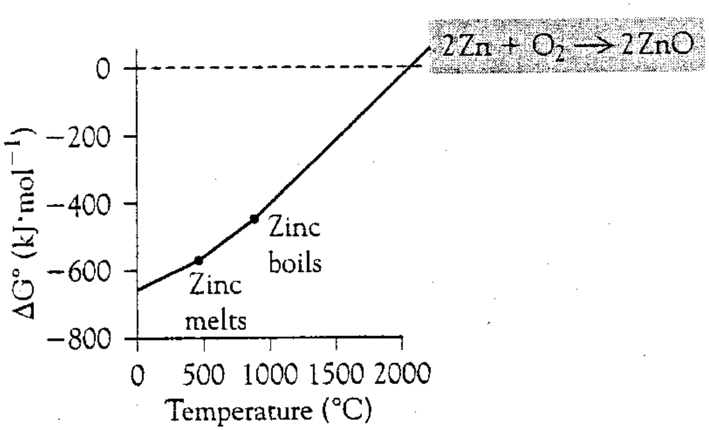
Oxygen deficiency

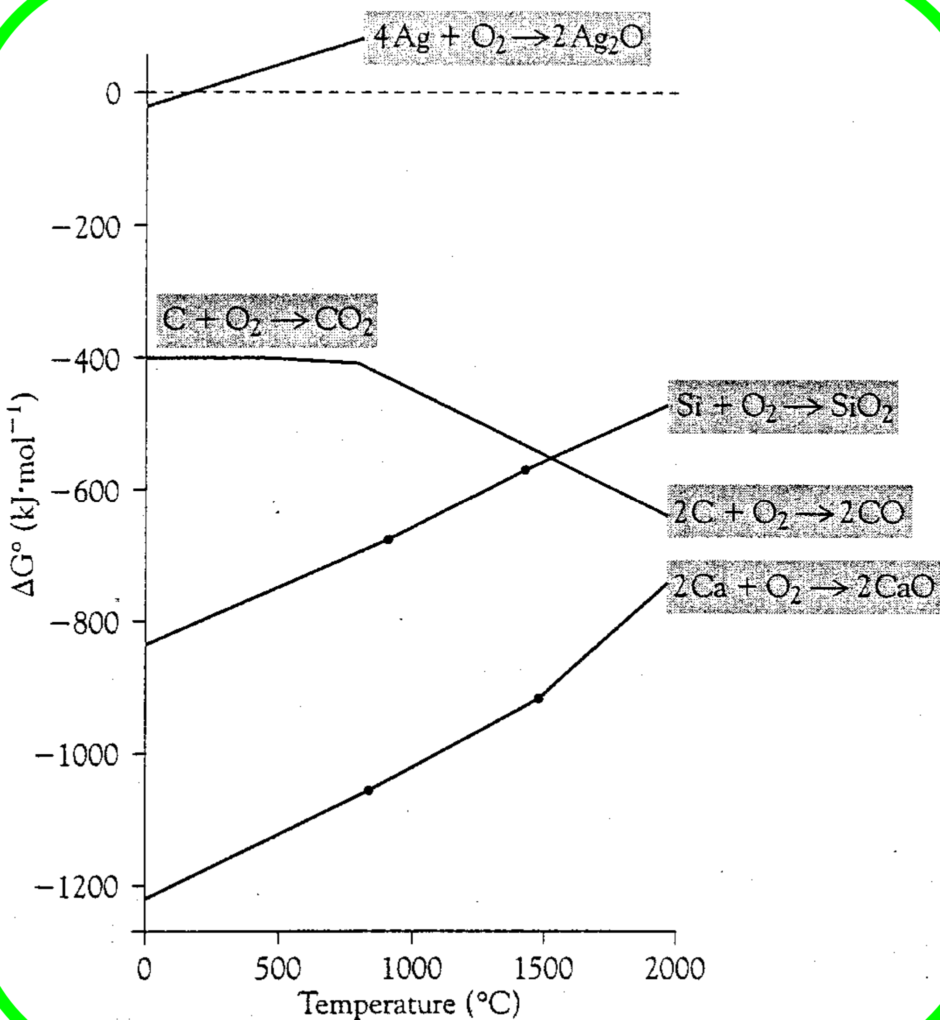
**Let's talk more about oxygen (non)stoichiometry ⟶**

# Ellingham diagram

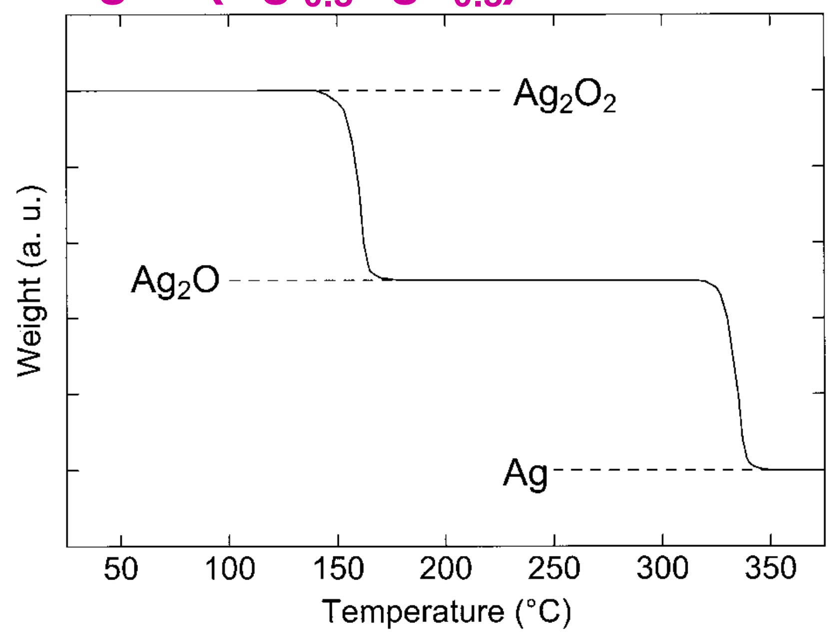
- (Gibb's) free energy of formation versus temperature for metal oxides
- Temperature at which a metal oxide is spontaneously reduced to a metal



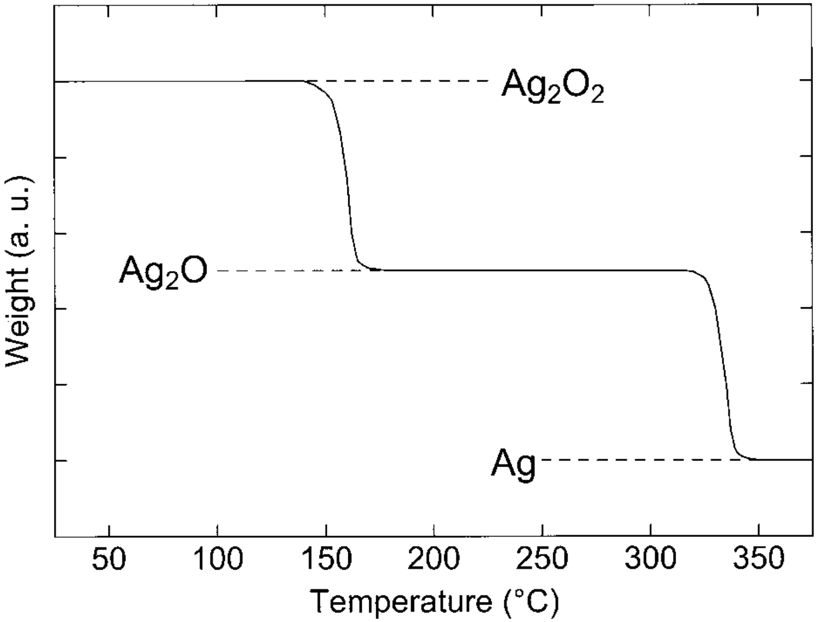





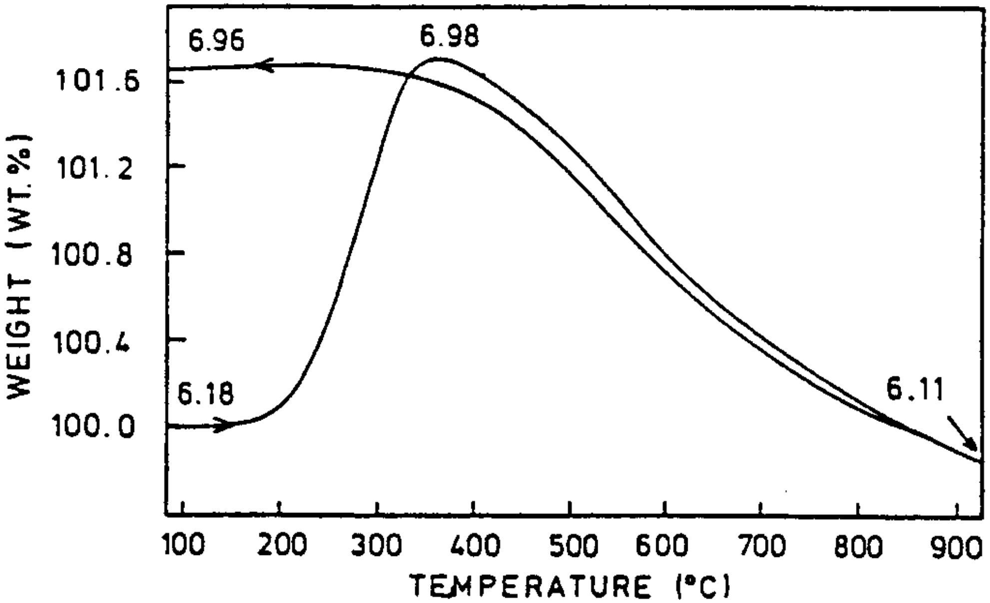

**AgO: $(Ag^{I}_{0.5}Ag^{III}_{0.5})O$**



## TG of AgO in air

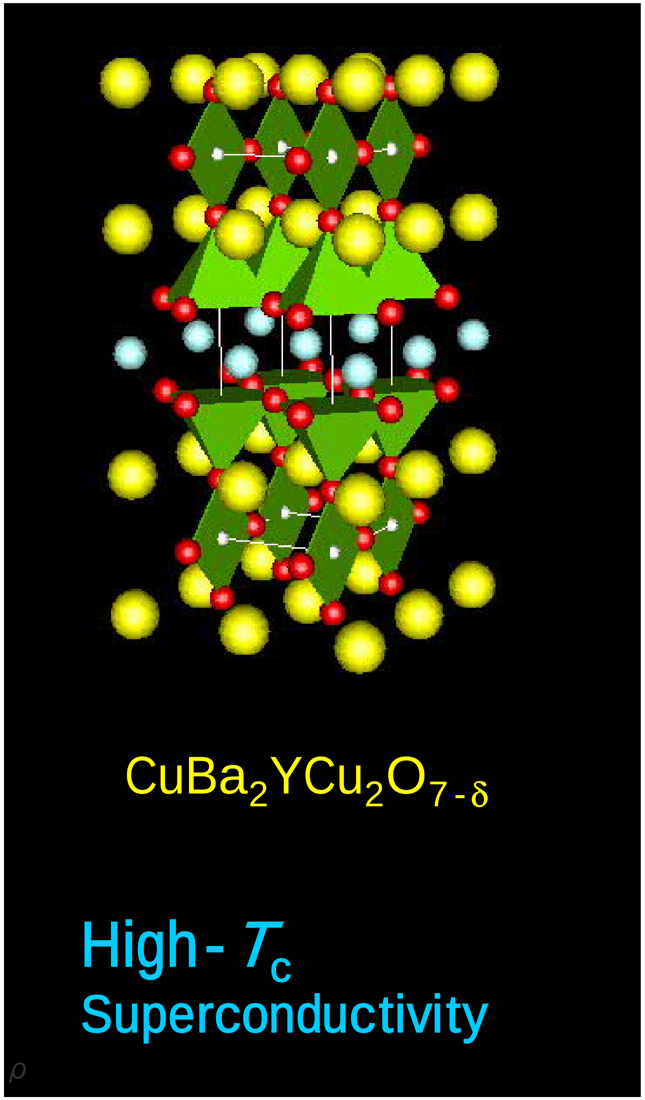


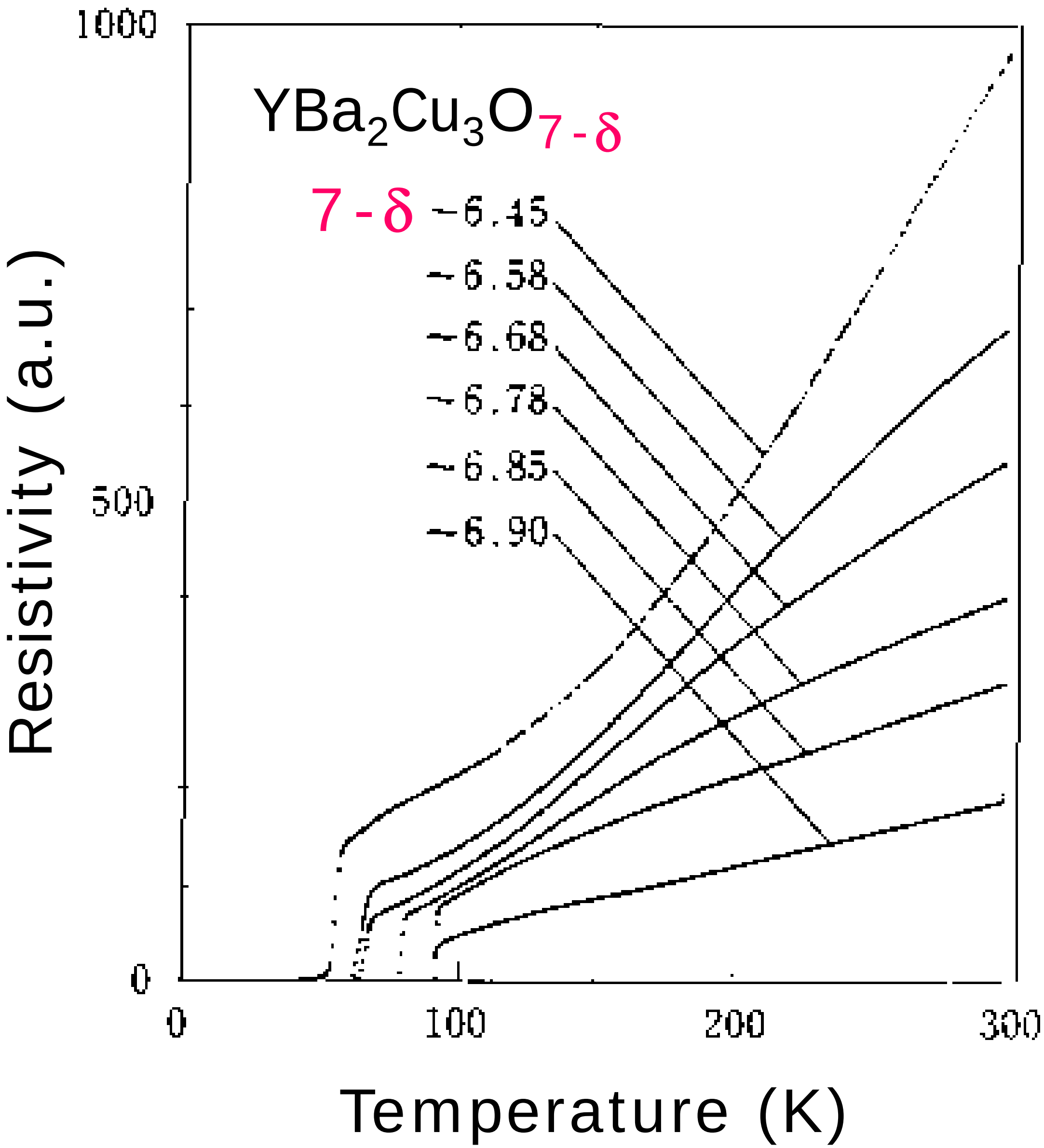

## TG of $YBa_2Cu_3O_{7-\delta}$ in air

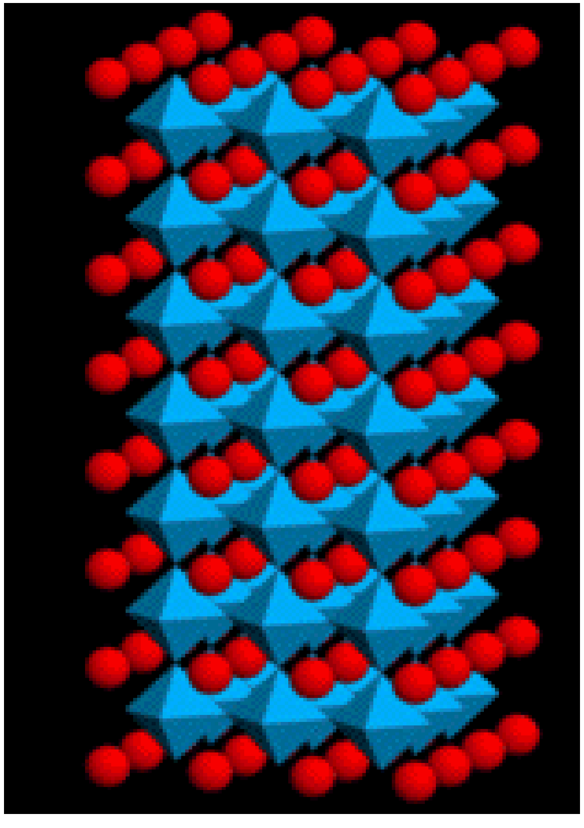
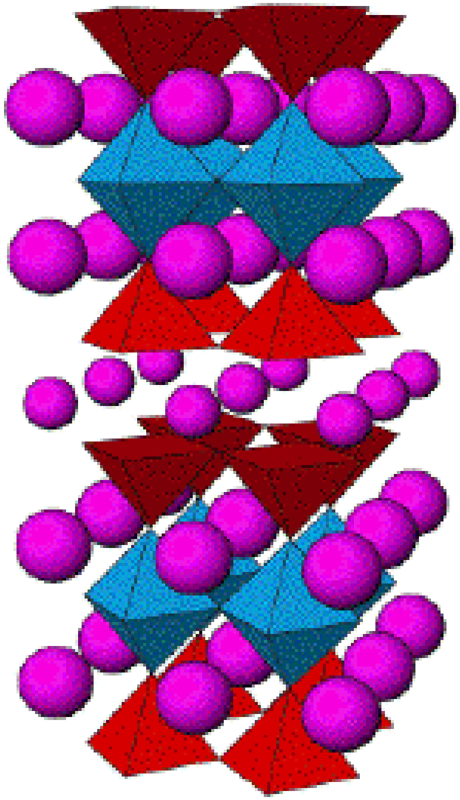



**Gradual oxygen loss**
**→ Mixed-valent Cu**

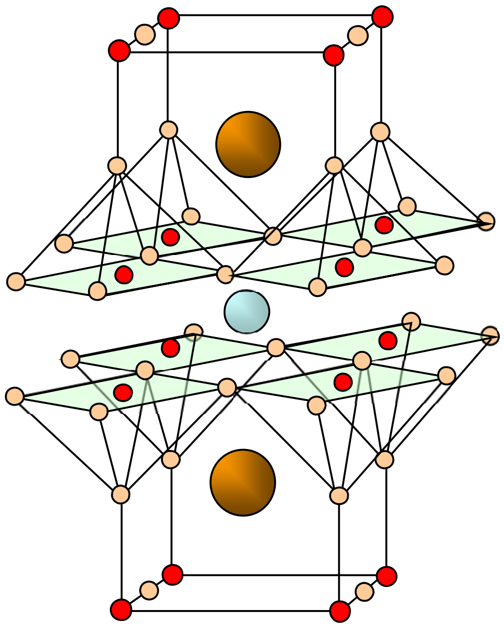
# SUPERCONDUCTIVITY depends on OXYGEN CONTENT

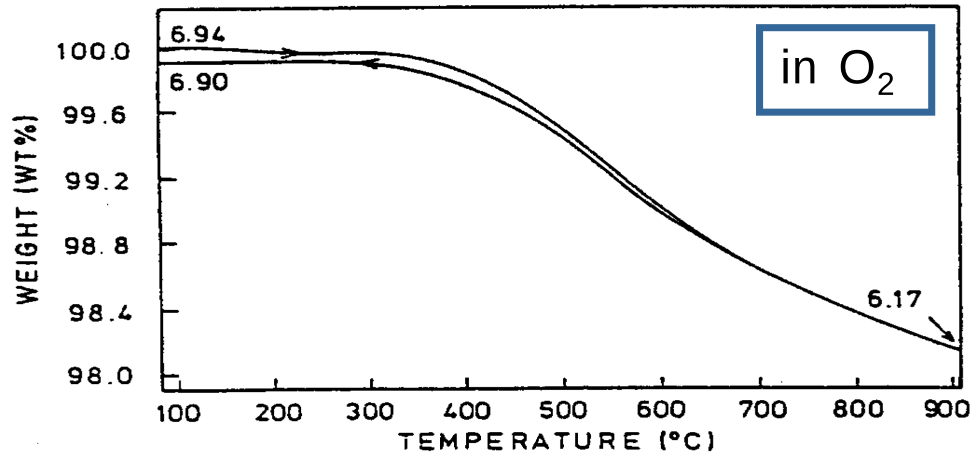


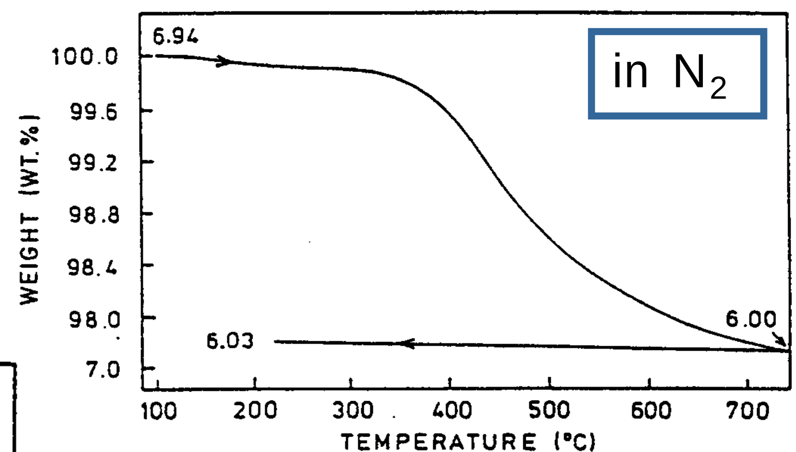



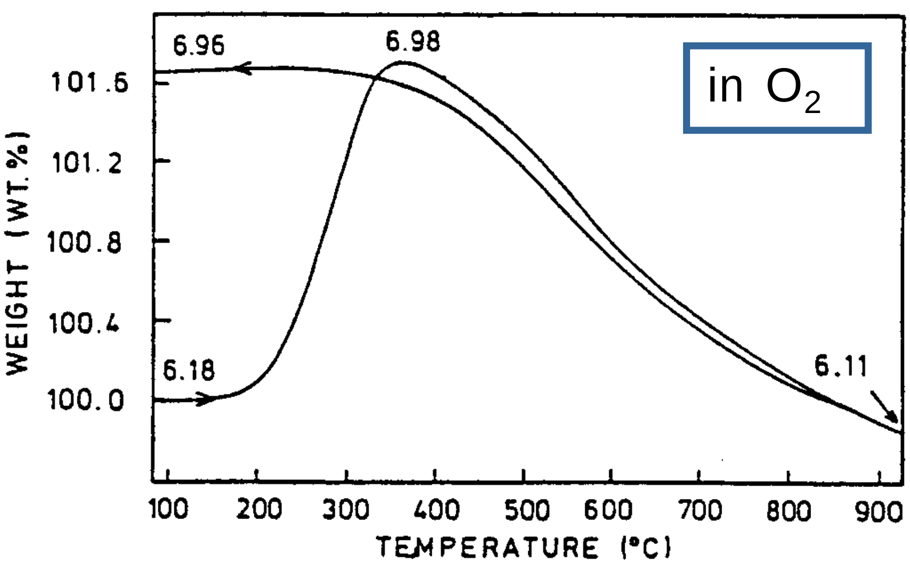



# $YBa_2Cu_3O_{7-\delta}$

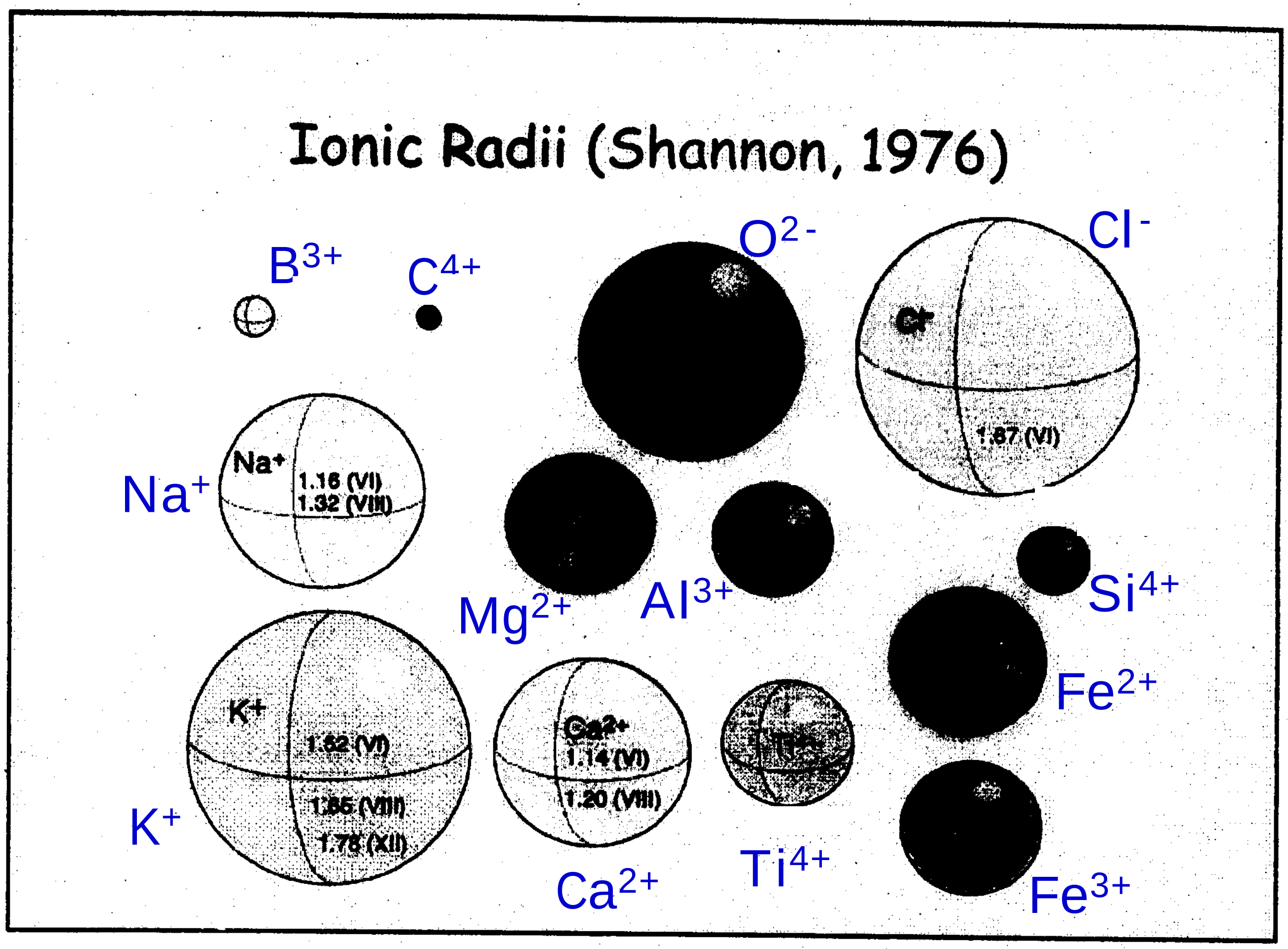


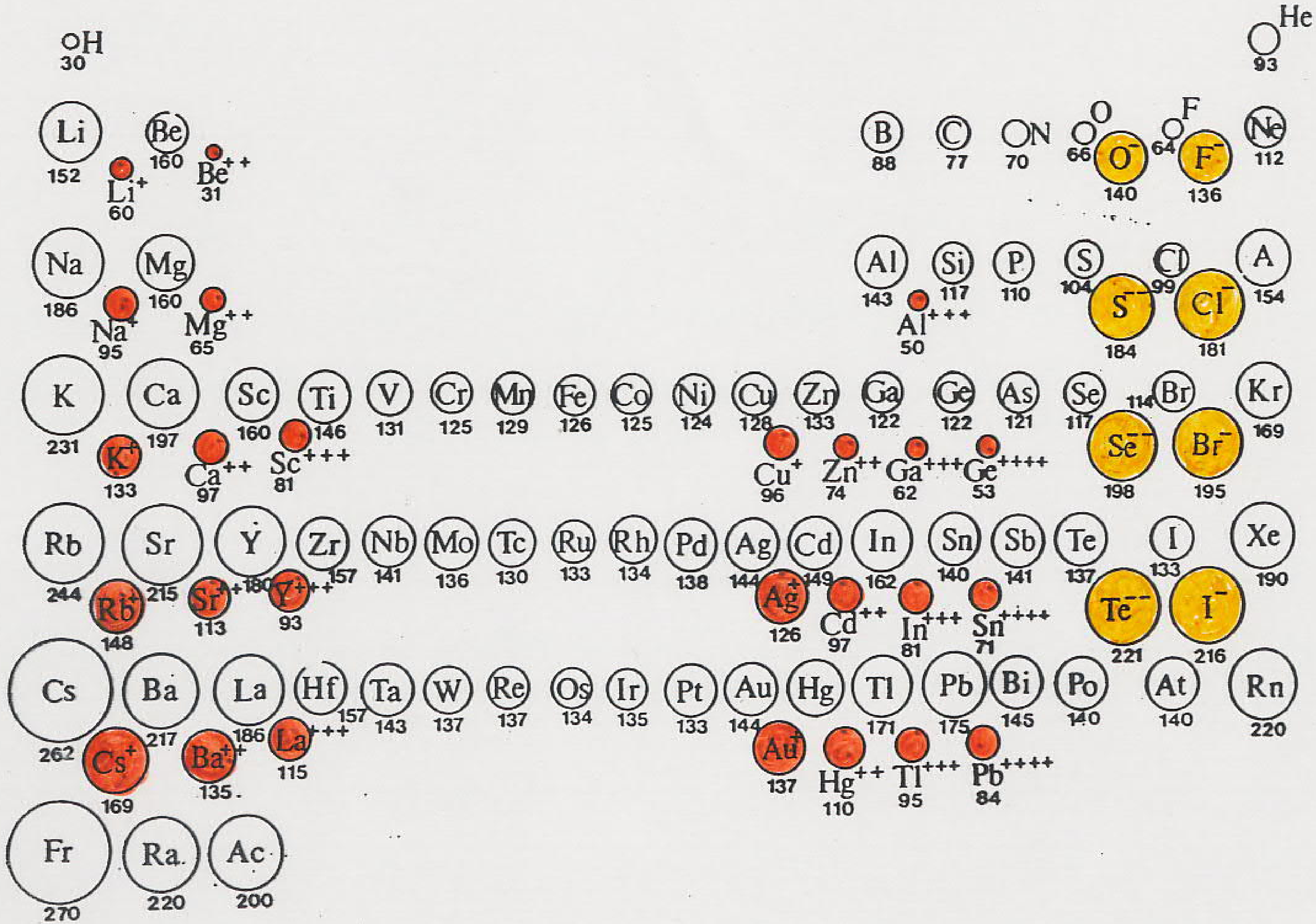


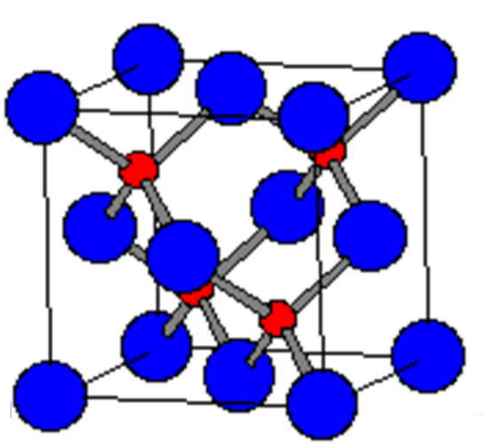
# MATCHING of IONIC RADIUS values important for the formation of the CRYSTAL STRUCTURE → NEW-MATERIAL DESIGN TOOL



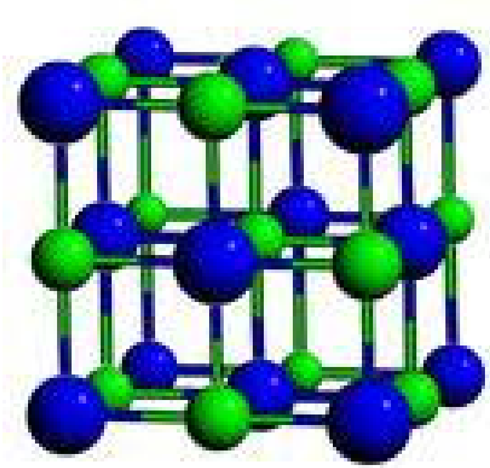


H
30
He
93
Li
152
Li+
60
Be
160
Be++
31
B
88
C
77
N
70
O
66
O-
140
F
64
F-
136
Ne
112
Na
186
Na+
95
Mg
160
Mg++
65
Al
143
Al+++
50
Si
117
P
110
S
104
S--
184
Cl
99
Cl-
181
A
154
K
231
K+
133
Ca
197
Ca++
97
Sc
160
Sc+++
81
Ti
146
V
131
Cr
125
Mn
129
Fe
126
Co
125
Ni
124
Cu
128
Cu+
96
Zn
133
Zn++
74
Ga
122
Ga+++
62
Ge
122
Ge++++
53
As
121
Se
117
Se--
198
Br
114
Br-
195
Kr
169
Rb
244
Rb+
148
Sr
215
Sr++
113
Y
180
Y+++
93
Zr
157
Nb
141
Mo
136
Tc
130
Ru
133
Rh
134
Pd
138
Ag
144
Ag+
126
Cd
149
Cd++
97
In
162
In+++
81
Sn
140
Sn++++
71
Sb
141
Te
137
Te--
221
I
133
I-
216
Xe
190
Cs
262
Cs+
169
Ba
217
Ba++
135
La
186
La+++
115
Hf
157
Ta
143
W
137
Re
137
Os
134
Ir
135
Pt
133
Au
144
Au+
137
Hg
Hg++
110
Tl
171
Tl+++
95
Pb
175
Pb++++
84
Bi
145
Po
140
At
140
Rn
220
Fr
270
Ra
220
Ac
200

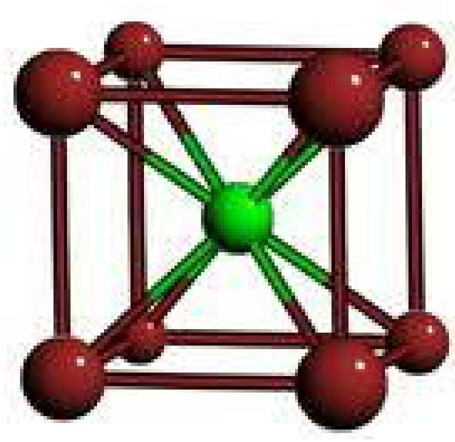
# Binary AB compounds



ZnS



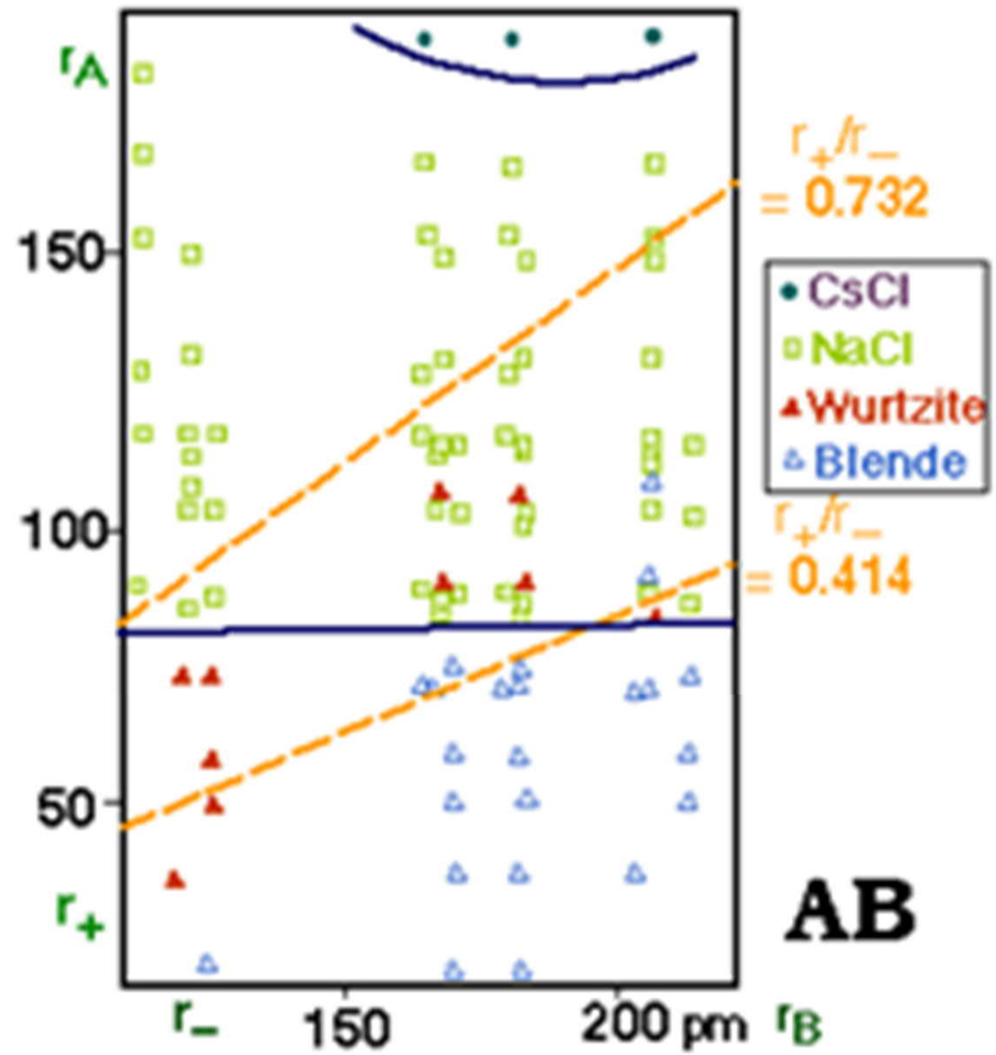
NaCl



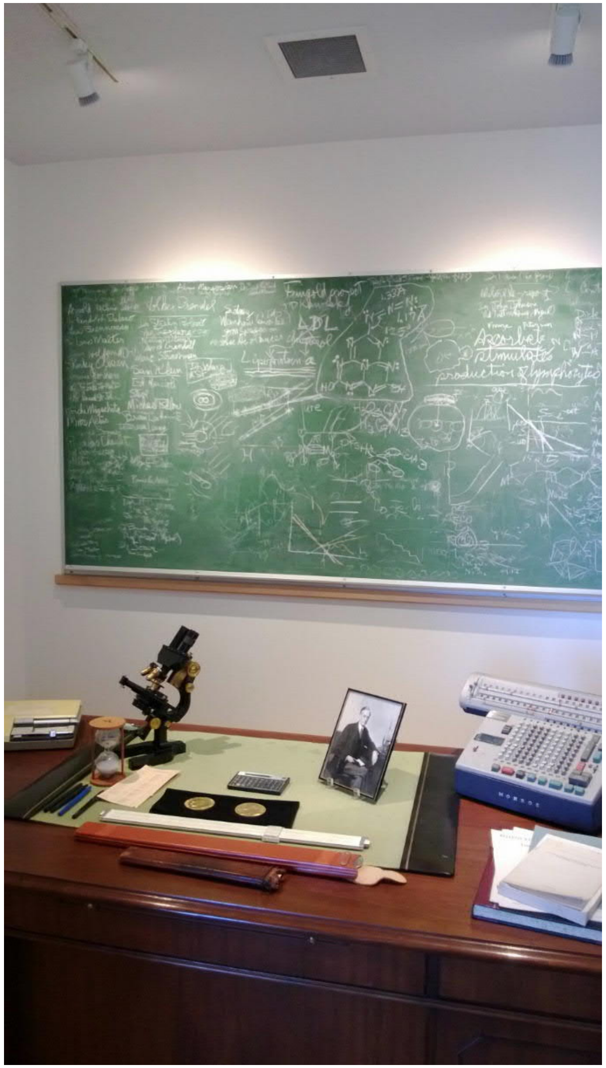
CsCl

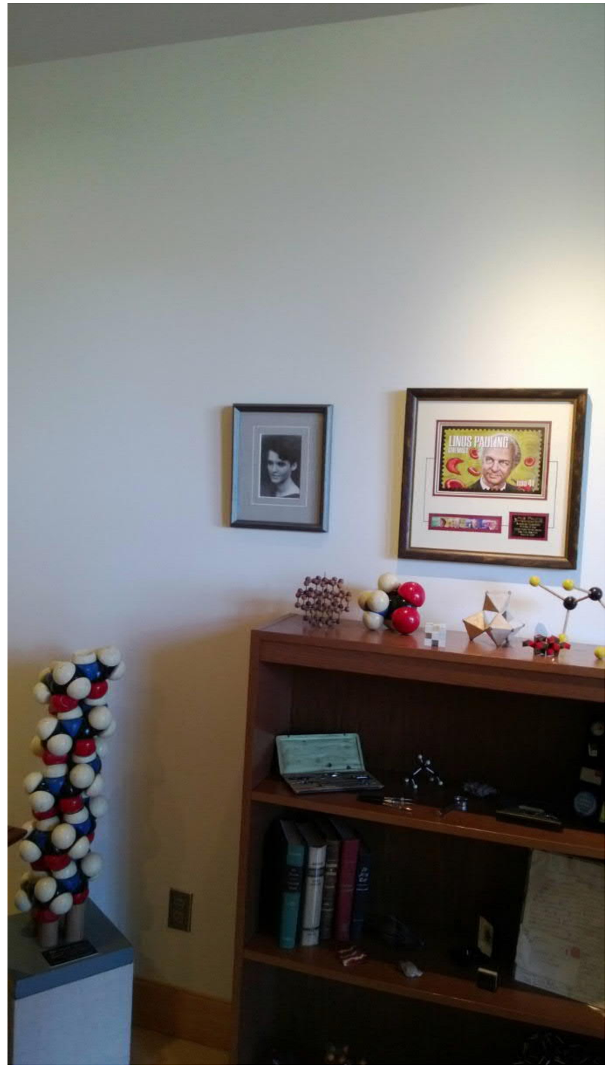
## Pauling's Rule

| | |
|---|---|
| $r_C/r_A < 0.155$ | CN = 2 |
| $0.155 < r_C/r_A < 0.225$ | CN = 3 |
| $0.225 < r_C/r_A < 0.414$ | CN = 4 |
| $0.414 < r_C/r_A < 0.732$ | CN = 6 |
| $0.732 < r_C/r_A < 1.00$ | CN = 8 |
| $r_C/r_A > 1.00$ | CN = 12 |



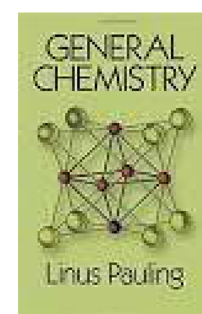
r_A
r_+
150
100
50
r_−
150
200 pm
r_B
r_+/r_−
= 0.732
r_+/r_−
= 0.414
CsCl
NaCl
Wurtzite
Blende
AB





**Linus Pauling** (1901–1994)

- American chemist, quantum chemist, biochemist and peace activist
- Graduated from Oregon State University
- 1939: “The Nature of the Chemical Bond”
- 1954: Nobel Prize in Chemistry
- 1962: Nobel Peace Prize




...

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

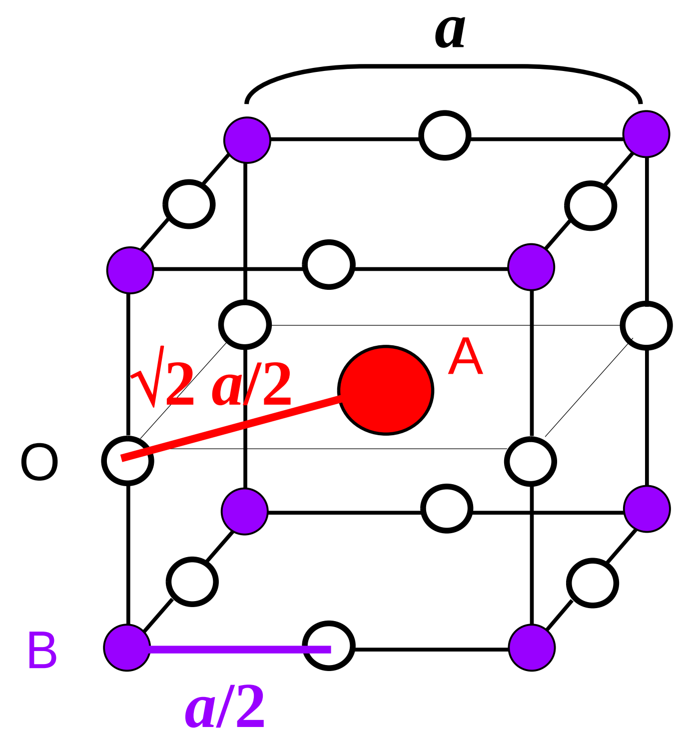
- Calculated from preferred bond lengths

- Preferred bond lengths are estimated from ionic radii

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

# Tolerance factor for $ABO_3$ perovskite

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



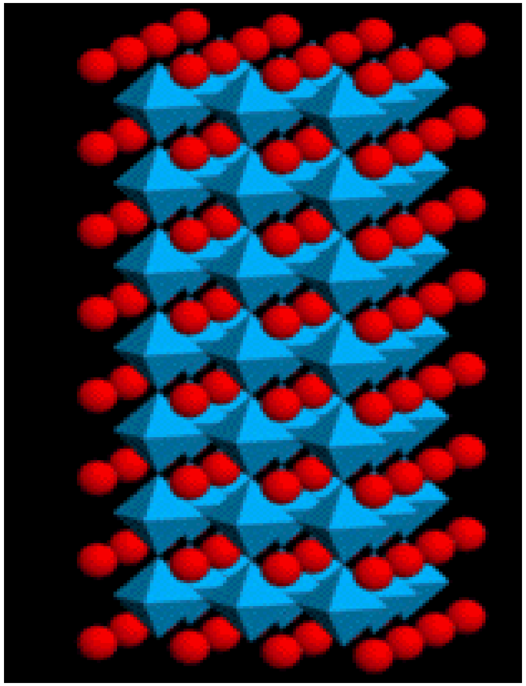

$t = 1$ : ideal matching (0.80 < t < 1.05 possible)

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

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

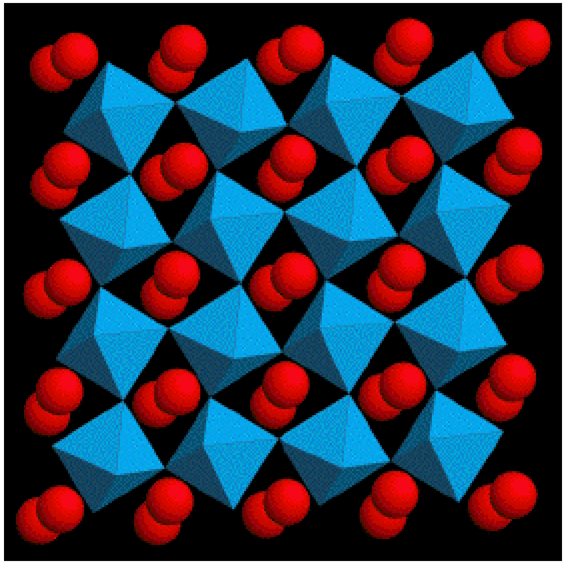
$$t = \frac{(r_A + r_O)}{\sqrt{2}\,(r_B + r_O)}$$

***t* = 1**



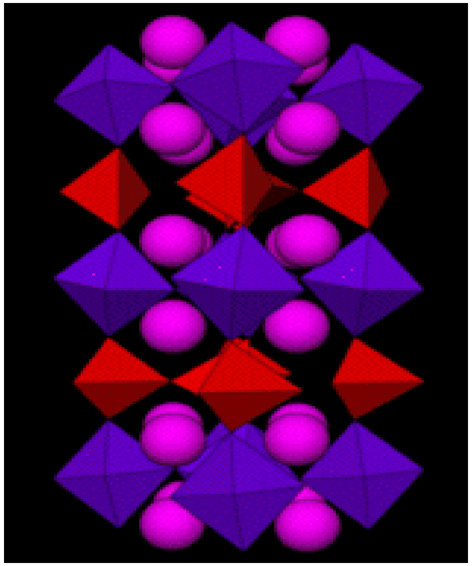
Ideal perovskite

***t* < 1**

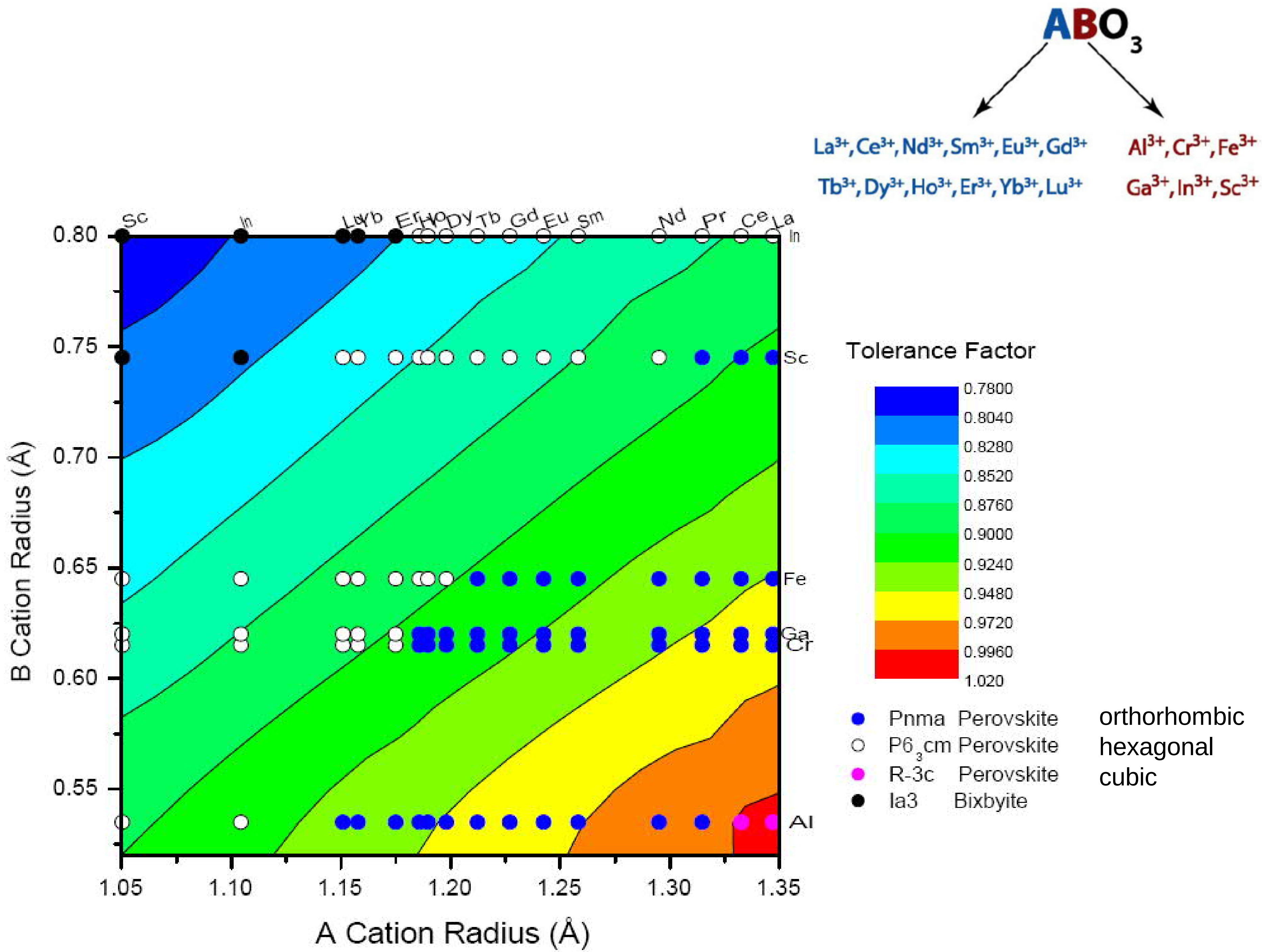


Changes in atomic positions

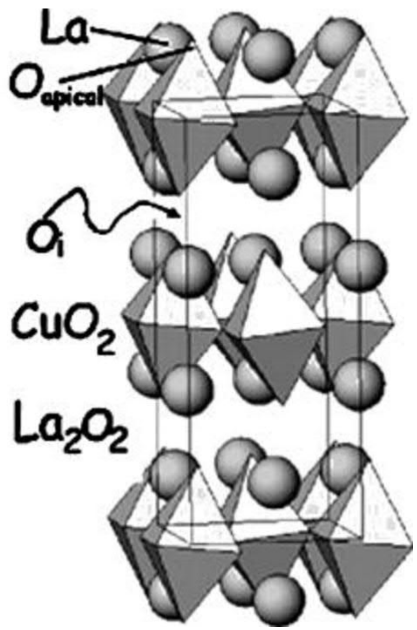
***t* > 1**



Oxygen deficiency



ABO3
La3+, Ce3+, Nd3+, Sm3+, Eu3+, Gd3+
Tb3+, Dy3+, Ho3+, Er3+, Yb3+, Lu3+
Al3+, Cr3+, Fe3+
Ga3+, In3+, Sc3+
Sc
In
Lu
Yb
Er
Ho
Dy
Tb
Gd
Eu
Sm
Nd
Pr
Ce
La
In
Sc
Fe
Ga
Cr
Al
0.80
0.75
0.70
0.65
0.60
0.55
B Cation Radius (Å)
1.05
1.10
1.15
1.20
1.25
1.30
1.35
A Cation Radius (Å)
Tolerance Factor
0.7800
0.8040
0.8280
0.8520
0.8760
0.9000
0.9240
0.9480
0.9720
0.9960
1.020
Pnma Perovskite
P6_3cm Perovskite
R-3c Perovskite
Ia3 Bixbyite
orthorhombic
hexagonal
cubic




# EFFECT OF COORDINATION SPHERE