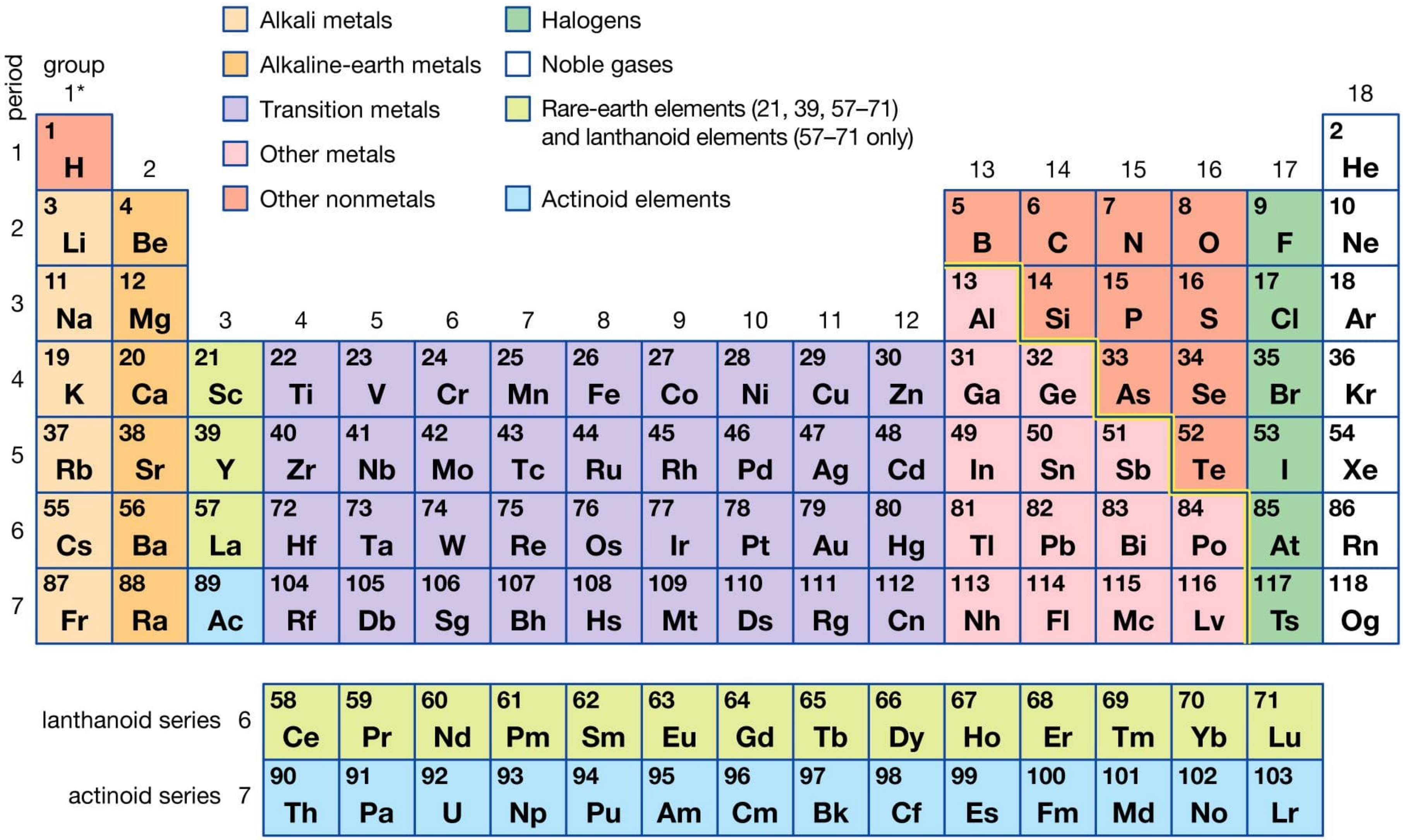
SCHEDULE

	Date		Topic
1.	Wed	01.03.	Lec-1: Introduction
2.	Mon	06.03.	Lec-2: Crystal Chemistry & Tolerance parameter
3.	Mon	06.03.	EXERCISE 1
4.	Wed	08.03.	Lec-3: Crystal Chemistry & BVS
5.	Fri	10.03.	Lec-4: Symmetry & Point Groups
6.	Mon	13.03.	EXERCISE 2
7.	Wed	15.03.	Lec-5: Crystallography & Space Groups (Linda)
8.	Fri	17.03.	Lec-6: XRD & Reciprocal lattice (Linda)
9.	Mon	20.03.	EXERCISE 3 (Linda)
10.	Fri	31.03.	Lec-7: Rietveld (Linda)
11.	Mon	03.04	EXERCISE 4: Rietveld (Linda)
12.	Wed	12.04.	Lec-8: ND & GI-XRD
13.	Fri	14.04.	Lec-9: XRR (Topias)
14.	Mon	17.04.	EXERCISE 5: XRR (Topias)
15.	Wed	19.04.	Lec-10: Synchrotron radiation & XAS & EXAFS
16.	Fri	21.04.	Mössbauer
17.	Fri	21.04.	EXERCISE 6
18.	Thu	27.04.	Seminars: XPS, FTIR, Raman
19.	Fri	28.04.	Seminars: ED, HRTEM, SEM, AFM
EXAM			

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).

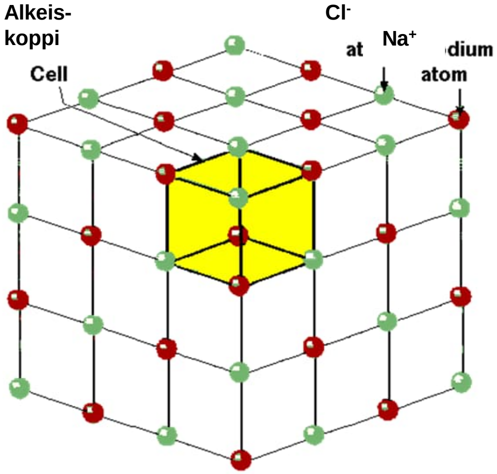
LECTURE 2: CRYSTAL CHEMISTRY

- **Learn to ”read” different types of crystal structure representations**
- **Concepts of coordination number (CN) and coordination polyhedron (= spatial arrangement of nearest-neighbour atoms)**
- **Ionic radius: dependence on CN and valence (V)**
- **Tolerance factor concept and utilization**

EXAMPLES of ”everyday” crystals/structures

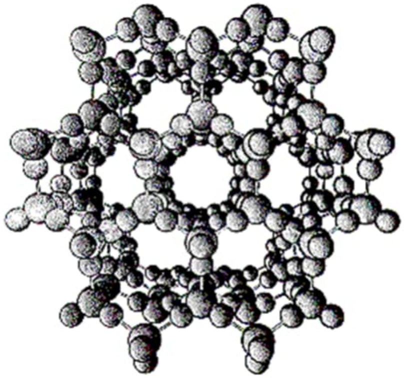
Rock salt (NaCl)

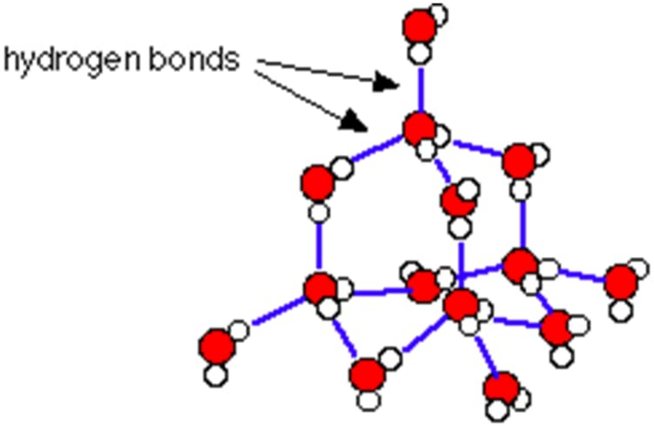
NaCl single crystal



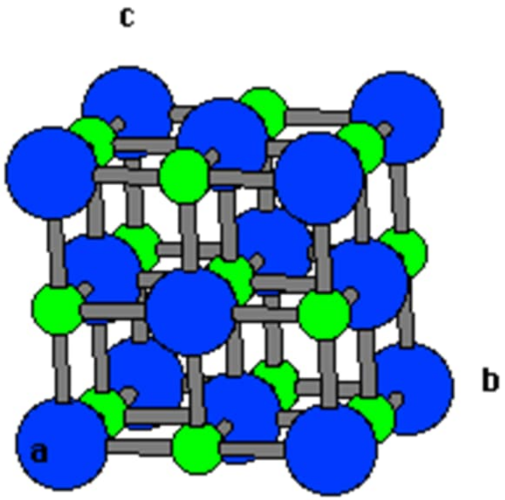
Cubic crystal structure:
high symmetry, ionic bonds
→ extremely stable

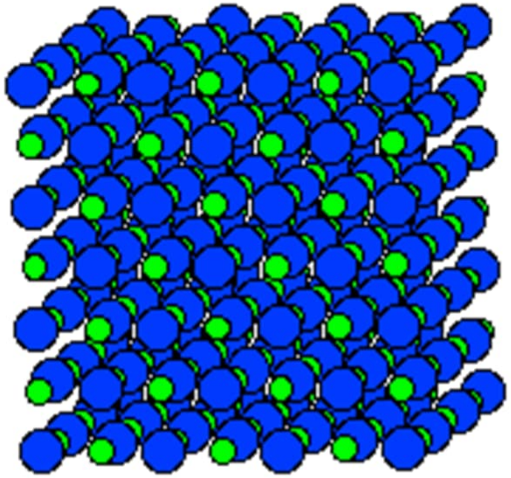
Snow flake:
hexagonal

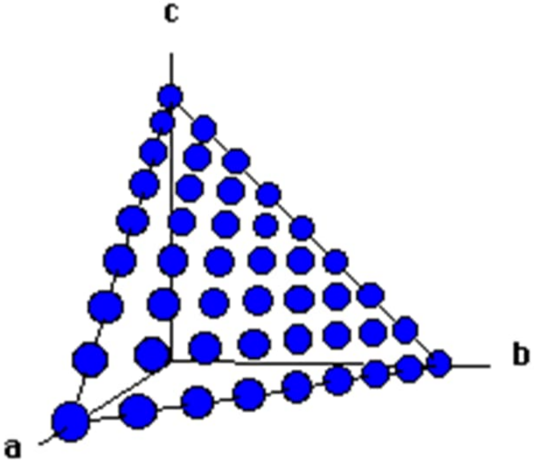


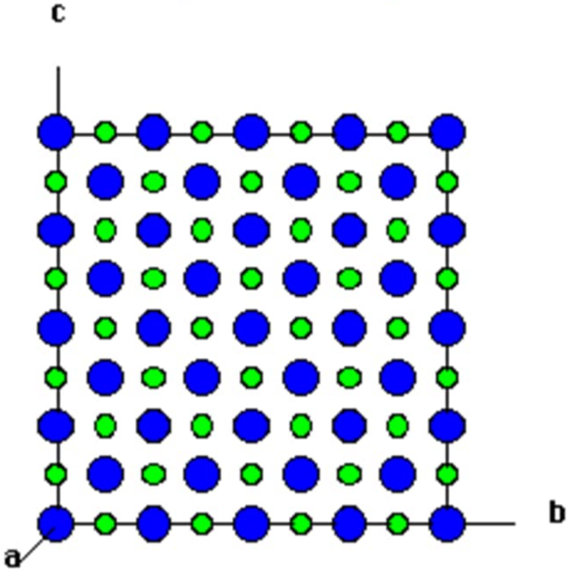


The same (NaCl) crystal structure can be presented in multiple ways



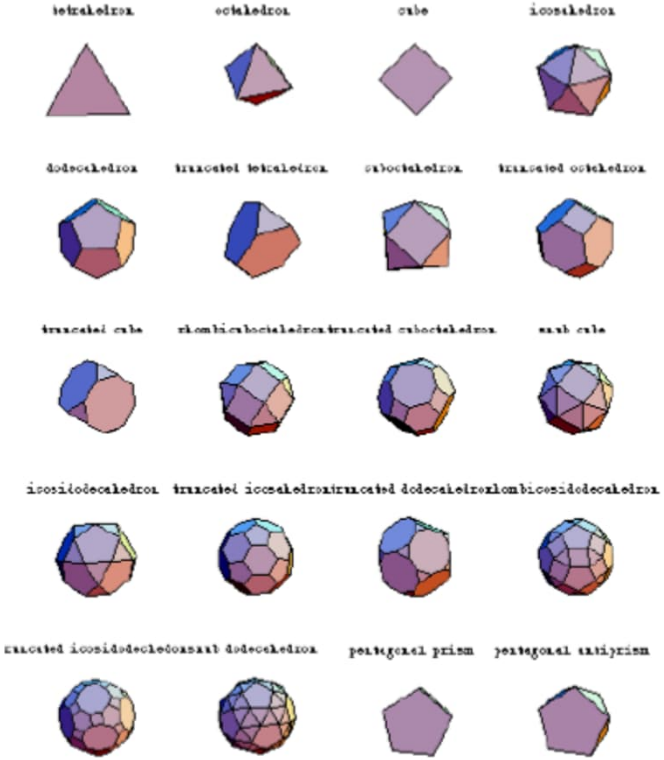


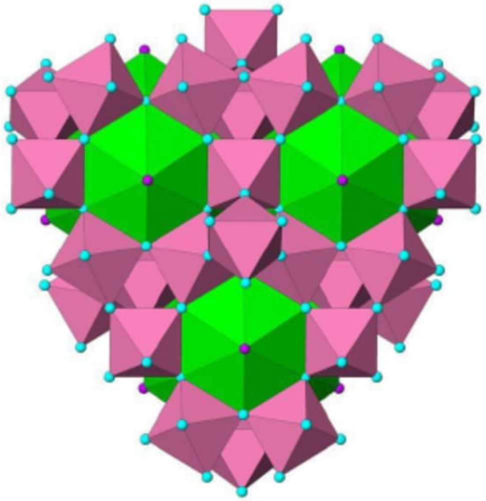




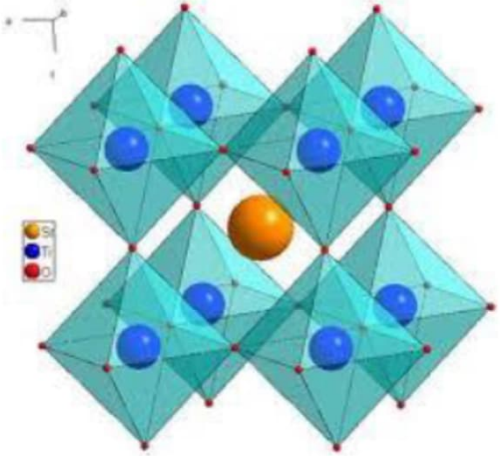
Polyhedra

Generally metal in centre and oxide or halide at vertices

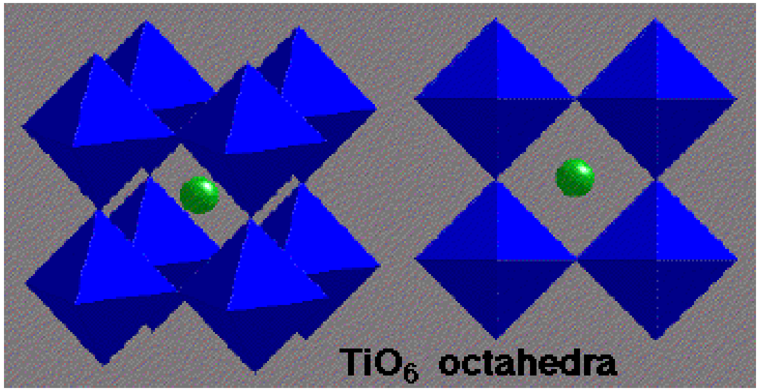




Pyrochlore



Perovskite

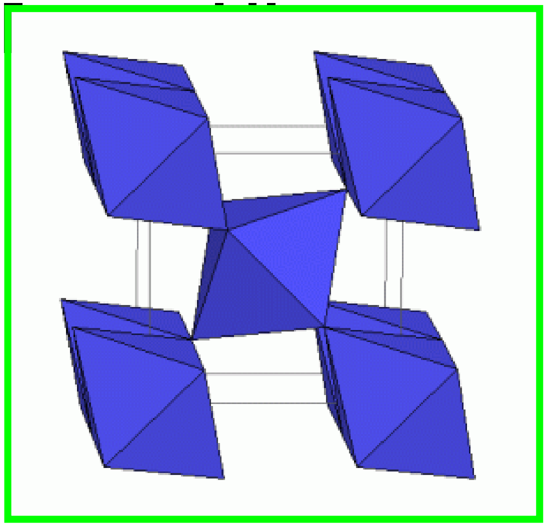


PEROVSKITE $CaTiO_3$

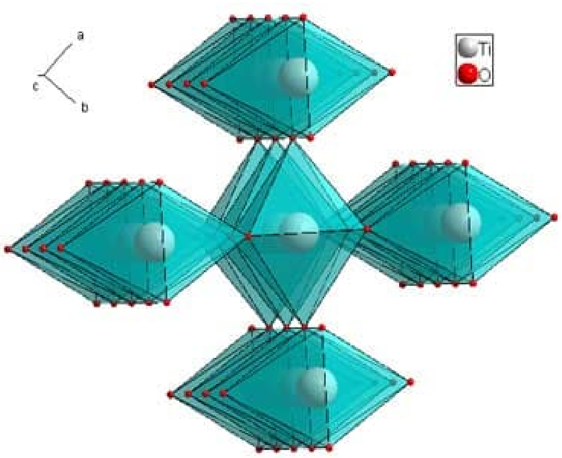
Examples

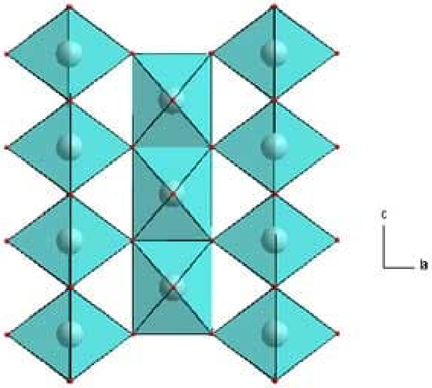
of related crystal structures:

- Coordination numbers?

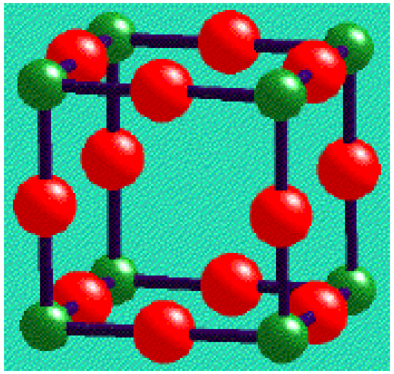


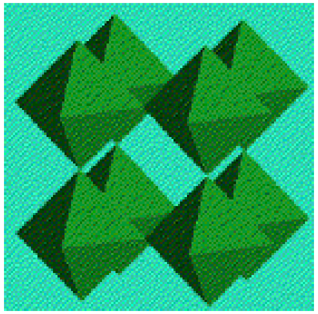
RUTILE TiO_2





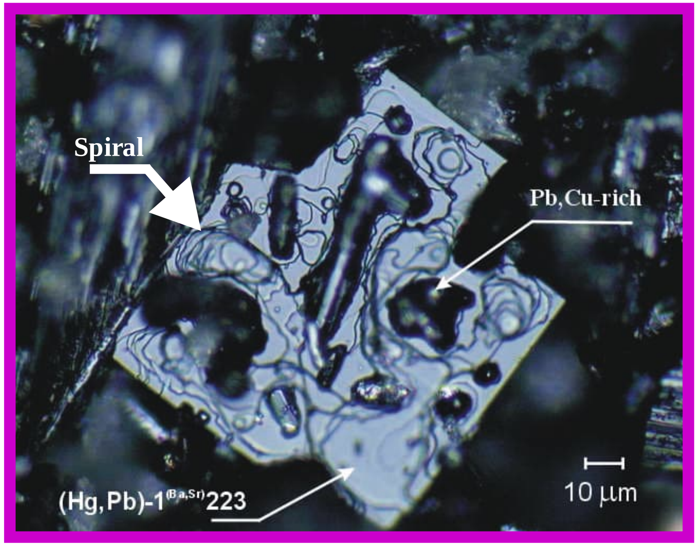
ReO_3

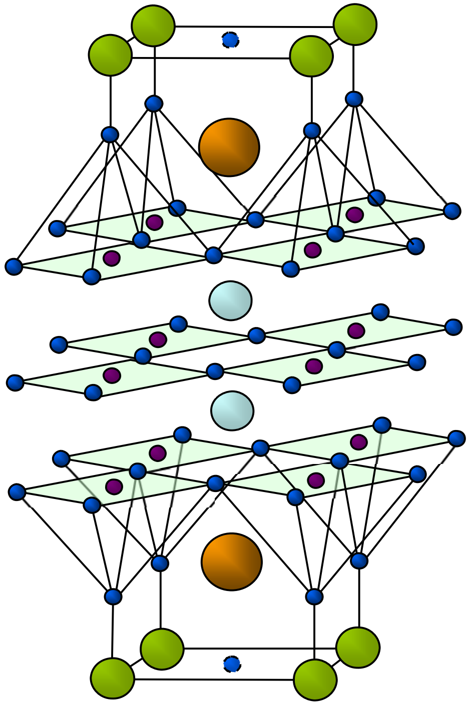




CRYSTAL

- Regularity of small building units in crystalline solids was predicted already in 17th century based on the beautifully symmetric shapes of macroscopic crystals
- Experimentally this was verified in 1912 by showing that crystals work as 3D diffraction gratings for X-rays (with wavelength of the same order as the distances of atoms in crystals)
- Interatomic distances in crystals are of Ångström-scale: $1\ \text{Å} = 10^{-10}\ \text{m} = 0.1\ \text{nm}$
- On the right, the tiny crystal (grown from flux by my students) is a single crystal of the record-high T_c (135 K) Hg-Ba-Ca-Cu-O superconductor; crystal structure shown below





WHAT WE LIKE TO KNOW ABOUT THE CRYSTAL STRUCTURE

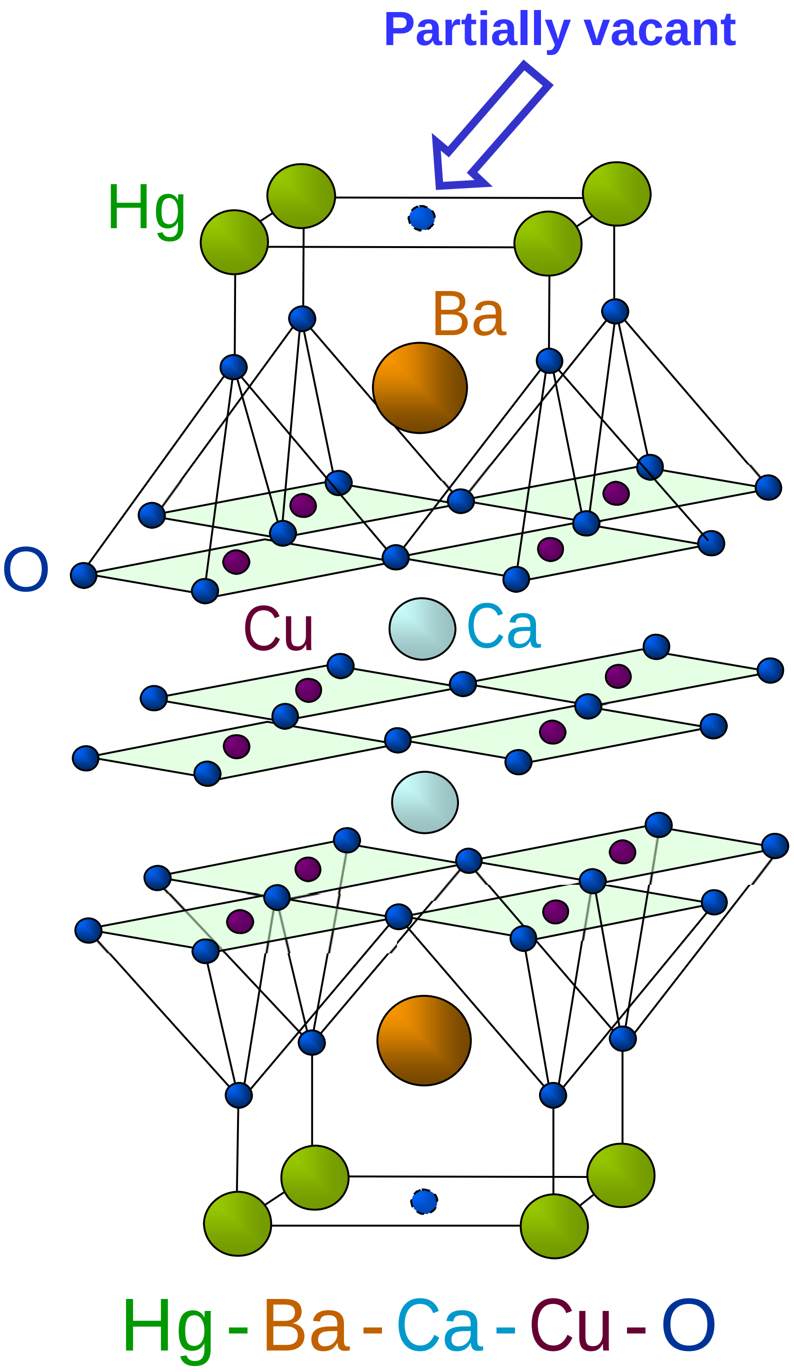
CRYSTALLOGRAPHY

- unit cell
- lattice parameters
- symmetry
- space group
- number of formula units in unit cell
- etc.

CRYSTAL CHEMISTRY

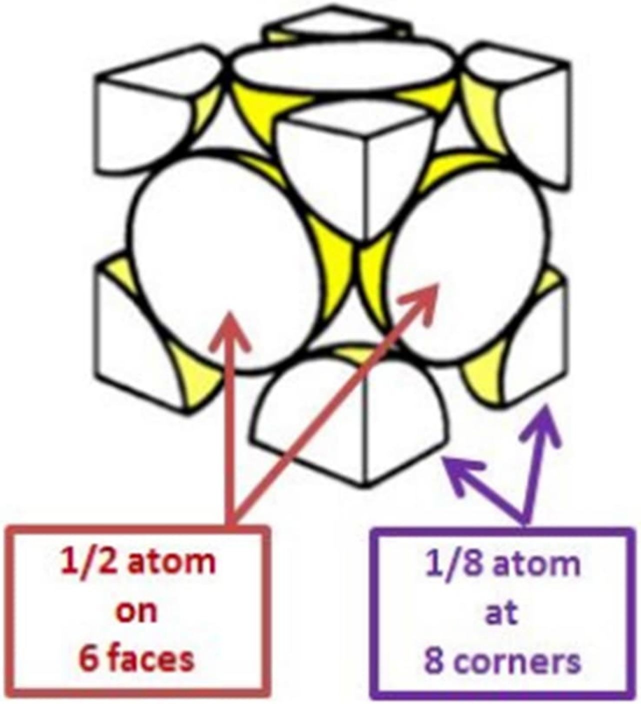
- coordination numbers
- coordination polyhedra
- bond lengths/angles
- occupancy factors
- etc.

This lecture is of crystal chemistry !



NUMBER of ATOMS in UNIT CELL

- **atom inside unit cell: belongs only to one unit cell → 1**
- **atom on unit cell face: belongs to two unit cells → 0.5**
- **atom on unit cell edge: belongs to four unit cells → 0.25**
- **atom on unit cell corner: belongs to eight unit cells → 0.125**



How the atoms are located in the structure depends on:

- **relative sizes of atoms/ions**
- **charges (oxidation states) of ions**
- **nature of chemical bonds (involvement of different orbitals)**

NEXT WE BRIEFLY RECALL & DISCUSS:

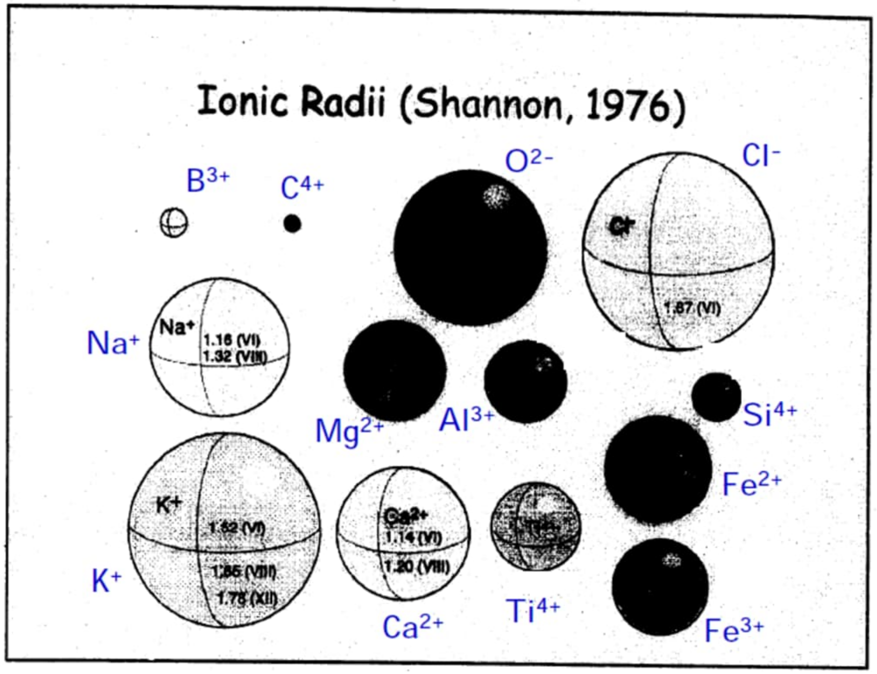
- Ion size (ionic radius) and how it affects the structure

Theorists are always predicting new structures that we (experimentalists) can’t make. But we keep making structures they can’t predict.

Prof P.D. Battle

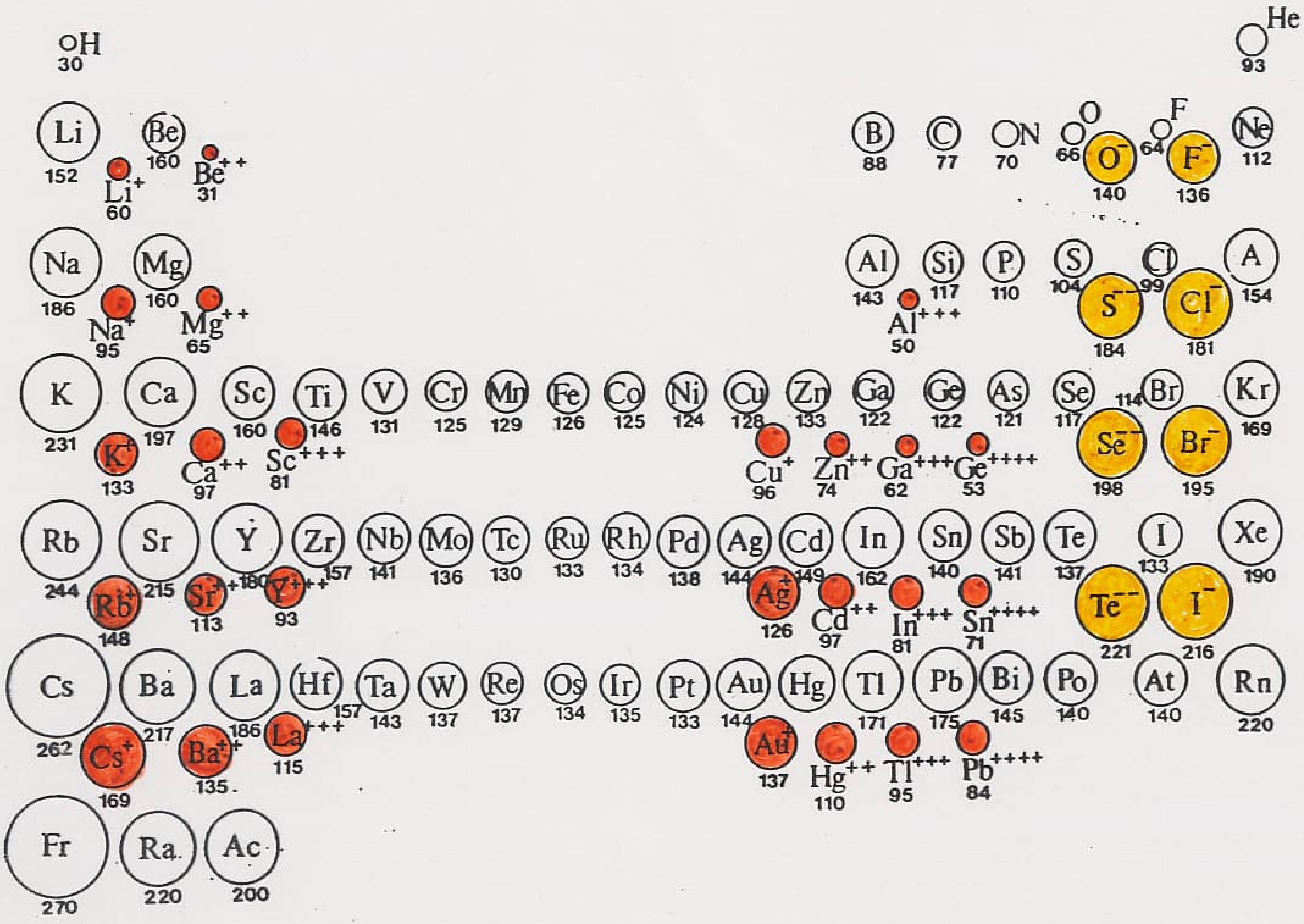
IONIC RADIUS

- It is not possible to measure ionic radius values directly
- The values are estimated (using statistical techniques) for each ion from a large experimental data set for bond lengths between many pairs of two different elements in different (ionic) compounds
- These are tabulated; there are several different ionic radius tables; the most commonly used one is: R.D. Shannon, Acta Cryst. A 32, 751 (1976)
- There are relatively large diffrences in ionic radii among different ions
- For the same element, ionic radius depends on the oxidation state and coordination number



Ionic Radii - Notable Trends

- The radius increases as you move down a column.
  - Al^{+3} = 0.675 Å, Ga^{+3} = 0.760 Å, In^{+3} = 0.940 Å, Tl^{+3} = 1.025 Å
- The radius decreases as you move across a period.
  - La^{+3} = 1.172 Å, Nd^{+3} = 1.123 Å, Gd^{+3} = 1.078 Å, Lu^{+3} = 1.001 Å
- The 4d & 5d metals have similar radii due to the lanthanide contraction.
  - Nb^{+5} = 0.78 Å, Ta^{+5} = 0.78 Å, Pd^{+4} = 0.755 Å, Pt^{+4} = 0.765 Å
- The cation radius decreases as you increase the oxidation state.
  - Mn^{+2} = 0.810 Å, Mn^{+3} = 0.785 Å, Mn^{+4} = 0.670 Å
- The radius increases as the coordination number increases.
  - Sr^{+2}: CN=6 → 1.32 Å, CN=8 → 1.40 Å,
    CN=10 → 1.50 Å CN=12 → 1.58 Å

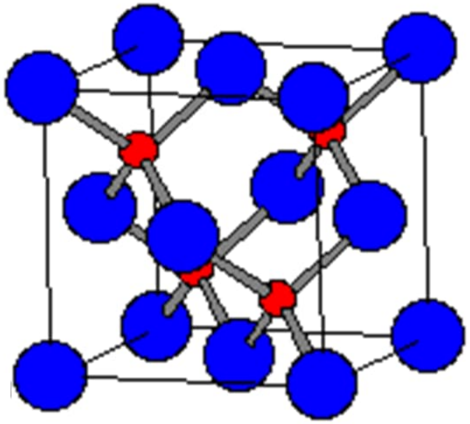

H 30
He 93
Li 152
Be 160
Li+ 60
Be++ 31
B 88
C 77
N 70
O 66
F 64
O− 140
F− 136
Ne 112
Na 186
Mg 160
Na+ 95
Mg++ 65
Al 143
Si 117
P 110
S 104
Cl 99
A 154
Al+++ 50
S−− 184
Cl− 181
K 231
Ca 197
Sc 160
Ti 146
V 131
Cr 125
Mn 129
Fe 126
Co 125
Ni 124
Cu 128
Zn 133
Ga 122
Ge 122
As 121
Se 117
Br 114
Kr 169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

Linus Pauling was the first to predict crystal structures based on relative (cation versus anion) ionic radii

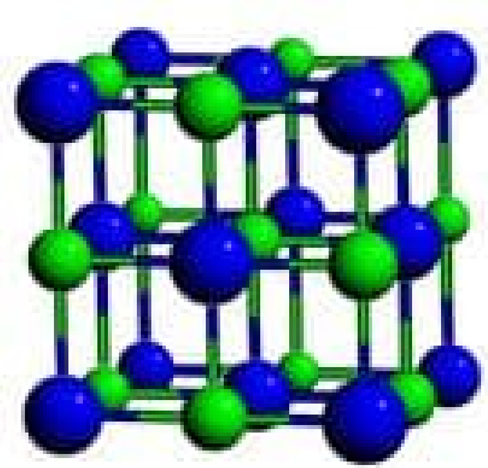
Pauling’s Rule for binary AB compounds

$r_C / r_A < 0.155$	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

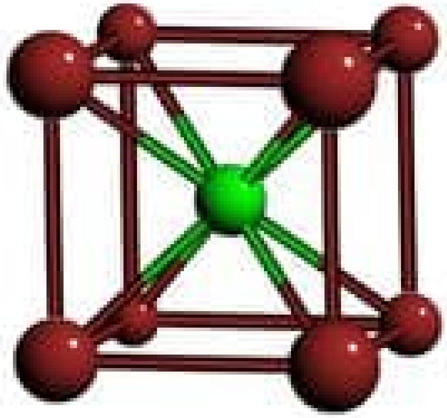
QUESTION: what are the coordination numbers (CN) in ZnS, NaCl and CsCl ?



ZnS



NaCl



CsCl

Victor Moritz Goldschmidt
(1888-1947)

Another approach:

TOLERANCE FACTOR (t)

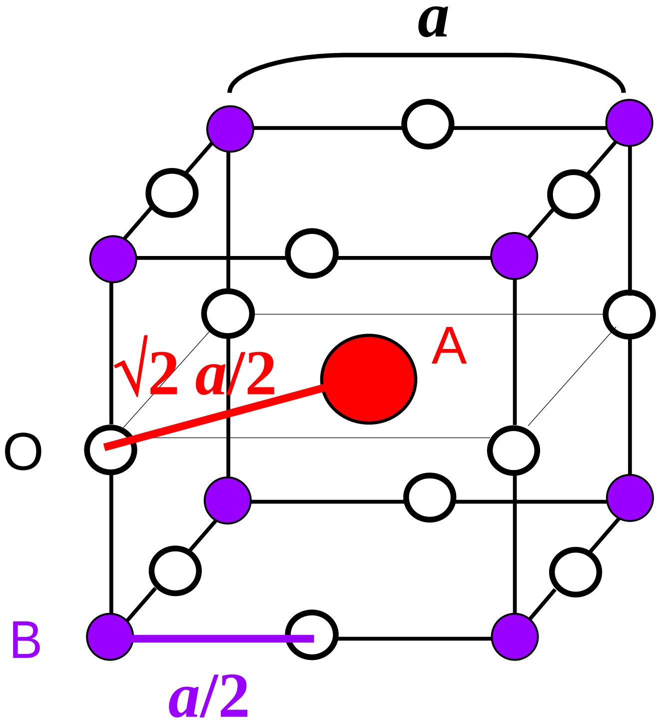
- **1926 Goldschmidt**

  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: at t = 1, perfect match
- Calculated from preferred bond lengths
- Preferred bond lengths are estimated from ionic radii (Shannon)
- Developed first for the perovskite structure, later extended to other structures as well
- To understand the stability of the structures and the creation of different distortions/defects (e.g. oxygen vacancies)

Tolerance factor for ABO_3 perovskite

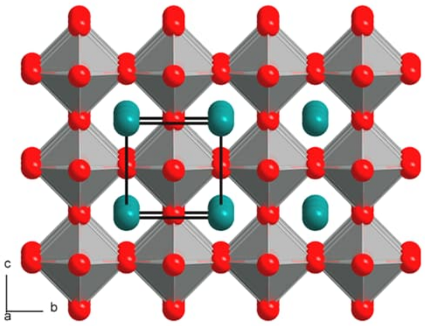
$$t = \frac{(r_A + r_O)}{\sqrt{2}\,(r_B + r_O)}$$



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

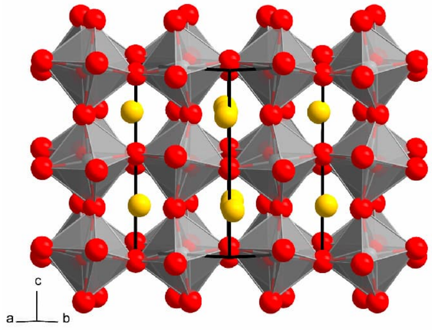
$t < 1$: **A is too small → changes in oxygen position**

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



$t = 1$

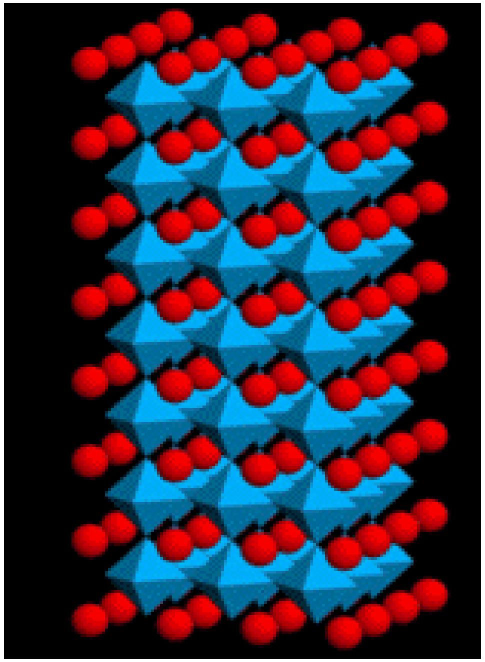
$t < 1$



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

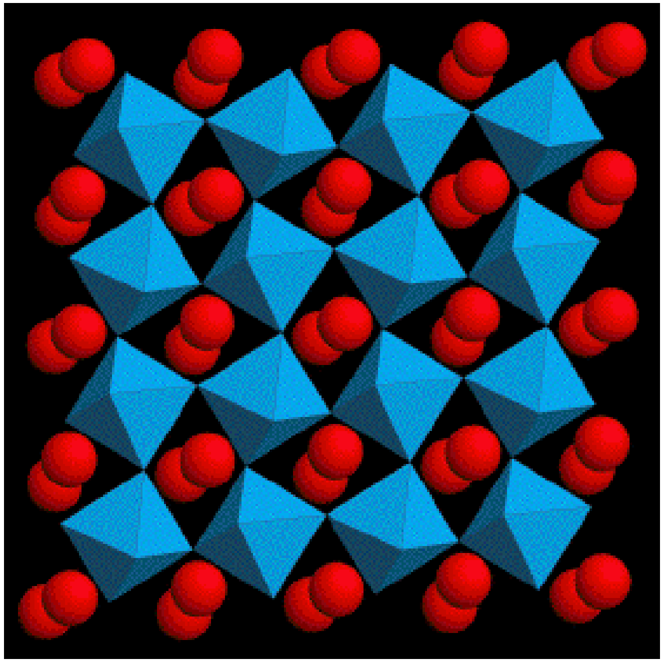
NOTE:
Oxygen vacancies can be random or ordered (as below)

***t* = 1**



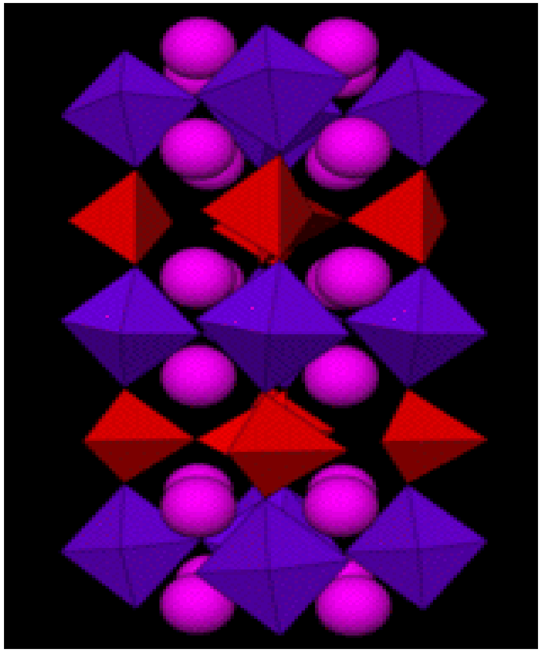
IDEAL

***t* < 1**



Changes in atomic positions

***t* > 1**



Oxygen deficiency

FOR METAL OXIDES,
defects are usually discussed in terms of oxygen nonstoichiometry, but this is not always exactly true

(1) Interstitial oxygen atoms

- $La_2CuO_{4+\delta}$

(2) Cation vacancies

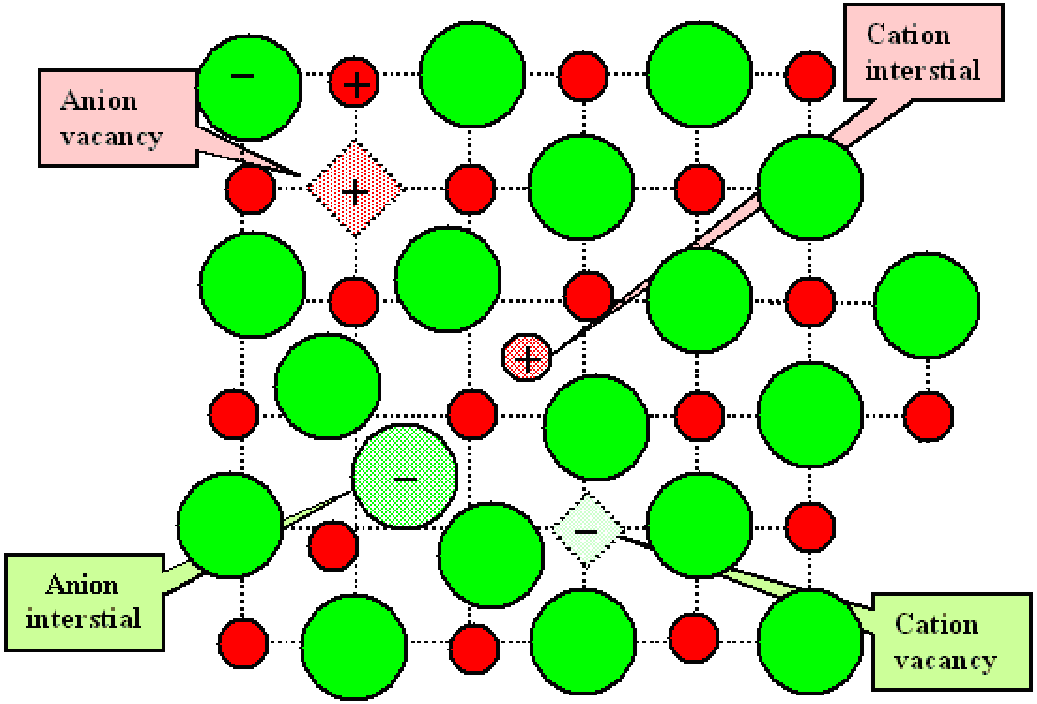
- $La_{1-x}Mn_{1-x}O_3$

(3) Oxygen vacancies

- $YBa_2Cu_3O_{7-\delta}$

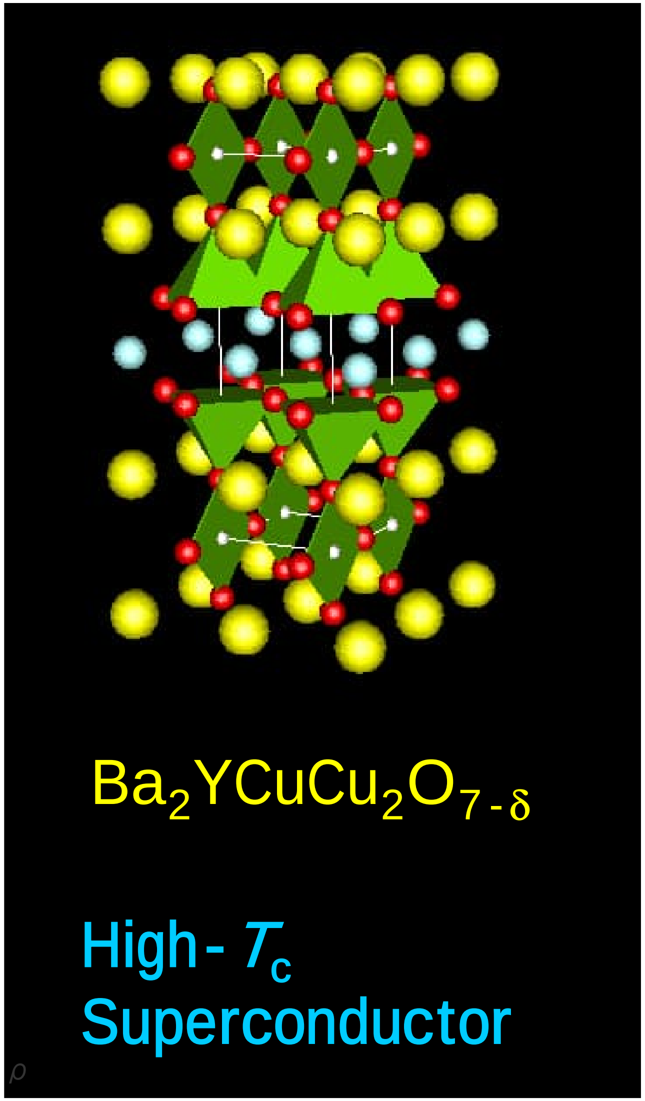
(4) Interstitial cations

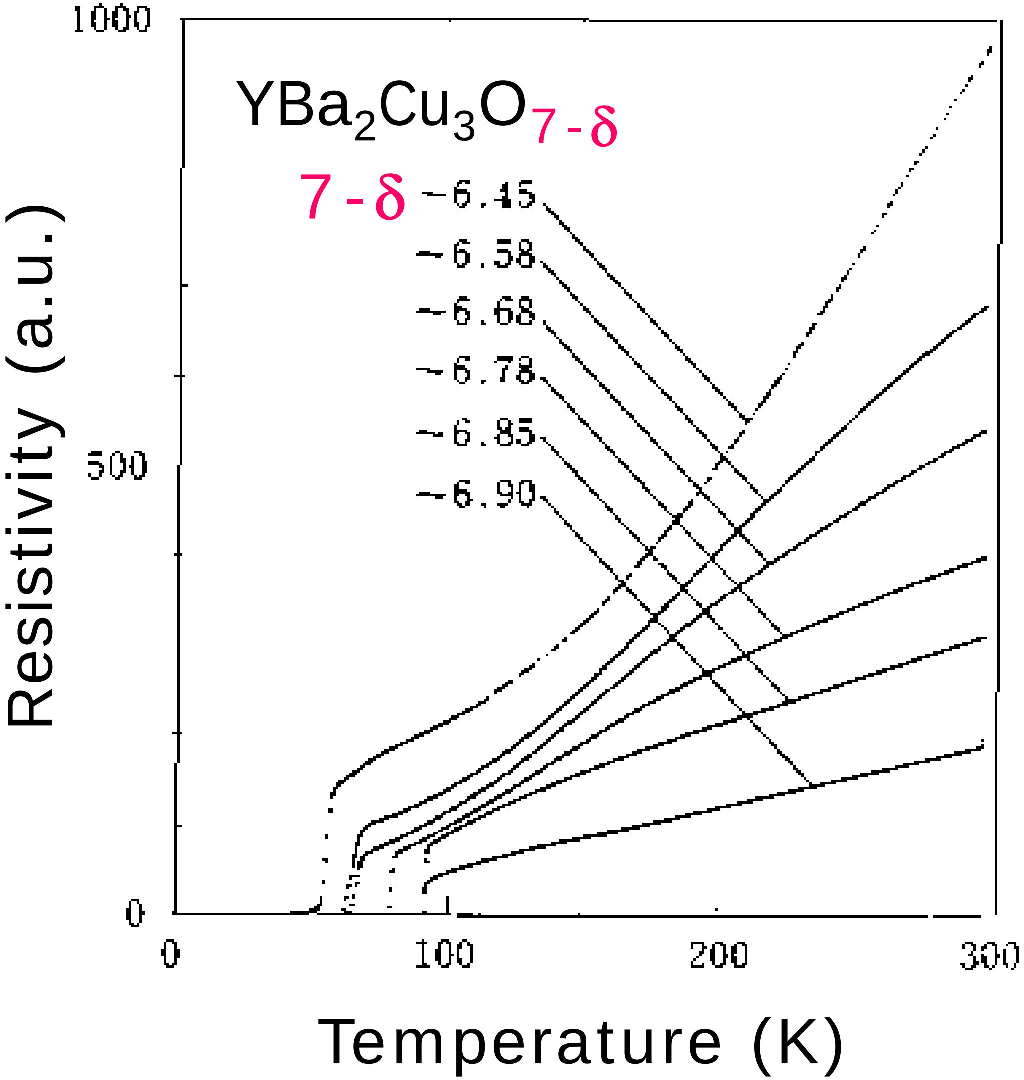
- $Zn_{1+x}O$



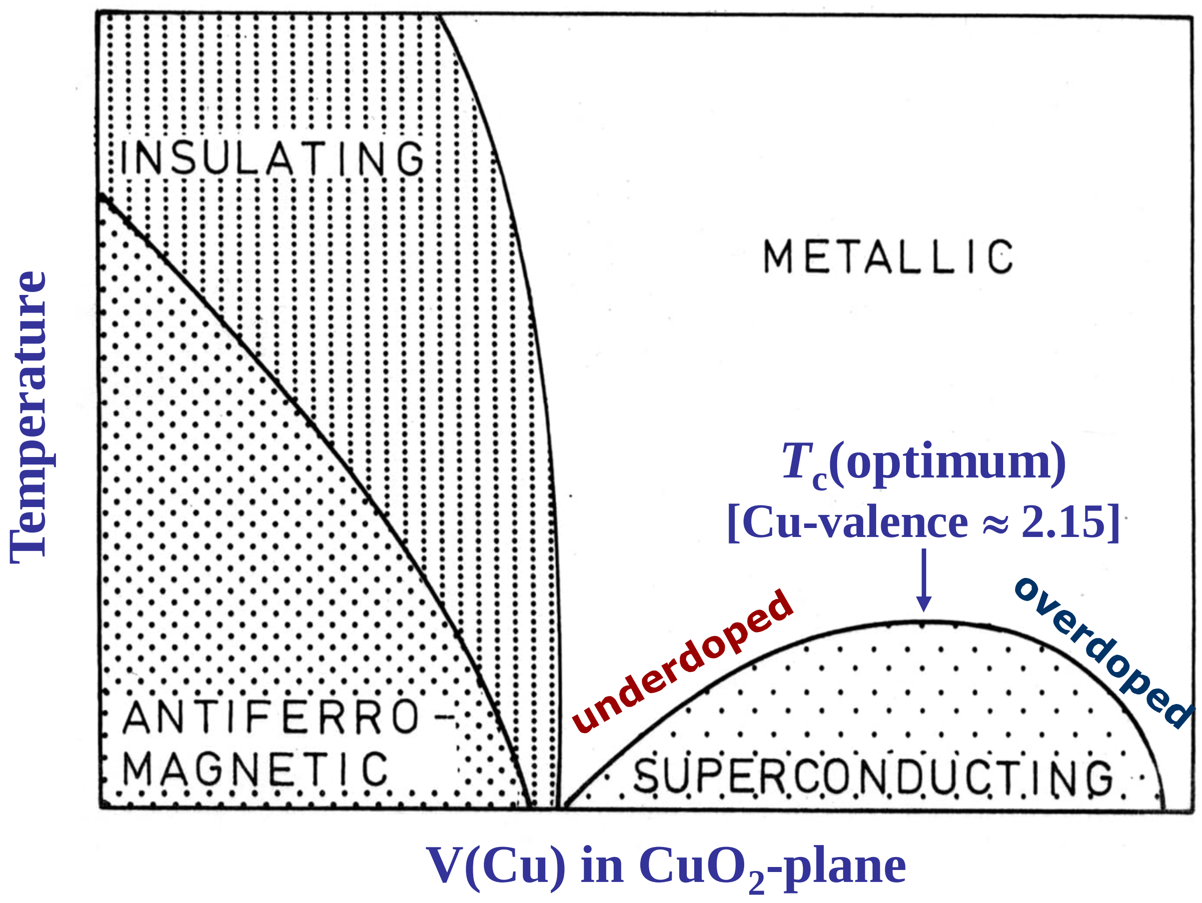
$YBa_2Cu_3O_{7-\delta}$ (or $Ba_2YCu(1)Cu(2)_2O_{7-\delta}$ to more properly reflect the structure) **is a notorious example of the huge impact of oxygen (non)stoichiometry.**

In the next lecture we will use BVS technique to look at this more presicely





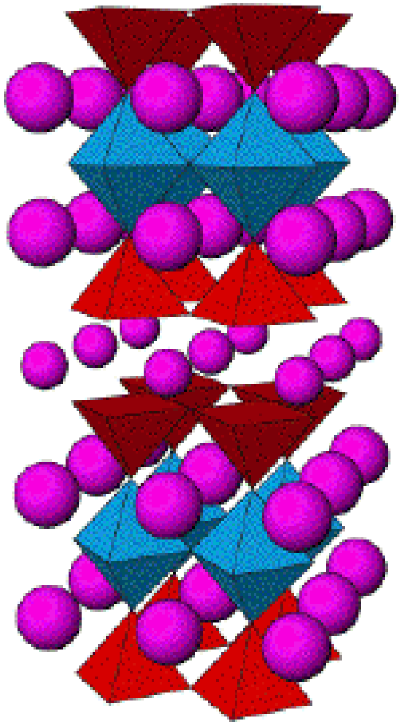
Simplified Phase Diagram of High-T_c Superconductors

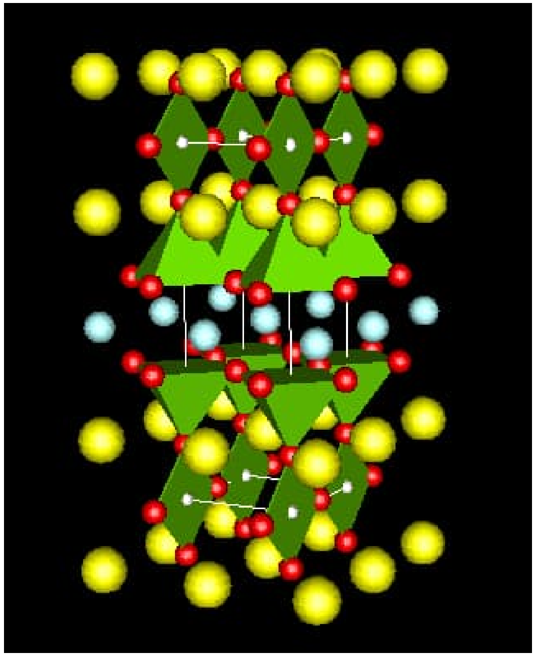


Oxygen content in $YBa_2Cu_3O_{7-\delta}$ controls the valence state of copper, and thereby the superconductivity (T_c value)

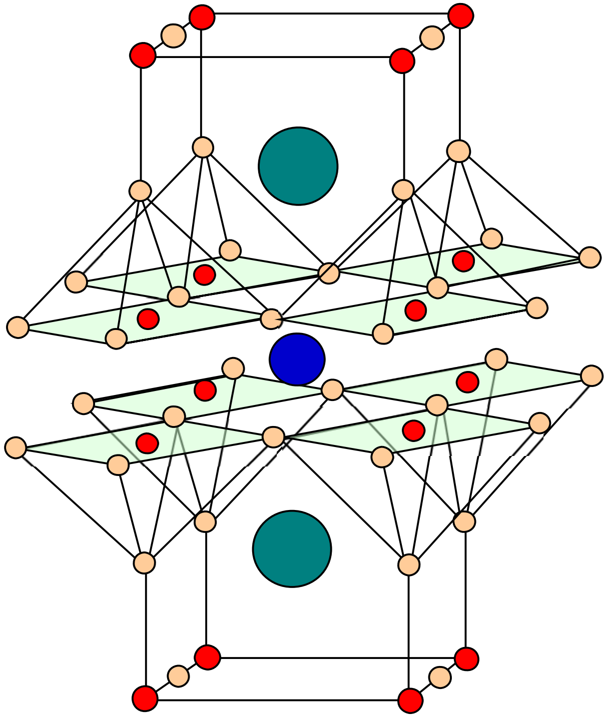
Illustration how the $YBa_2Cu_3O_{7-\delta}$ structure is derived from the perovskite structure through cation ordering and ordered oxygen vacancies

A-site ordered &
oxygen-vacancy ordered
TRIPLE PEROVSKITE
$A'_2A''B_3O_8$ (= 9-1)





$Ba_2YCu(1)Cu(2)_2O_7$ (= 9-2)



Cu(1)O chain

$Cu(2)O_2$ planes

$Ba_2YCu(1)Cu(2)_2O_7$

EXERCISE 1.1.

A. Describe shortly by words and/or drawings the following terminologies: oxygen vacancy, oxygen vacancy ordering, and occupancy factor
B. Describe shortly by words and/or drawings the following terminologies: double perovskite and antisite defect.
C. Why the same transition metal is smaller as a trivalent cation than as a divalent ion? Give an example with actual numbers for a transition metal of your choice.
D. Familiarize yourself with the units: Å and nm

You can find ionic radius values at:
http://abulafia.mt.ic.ac.uk/shannon/ptable.php

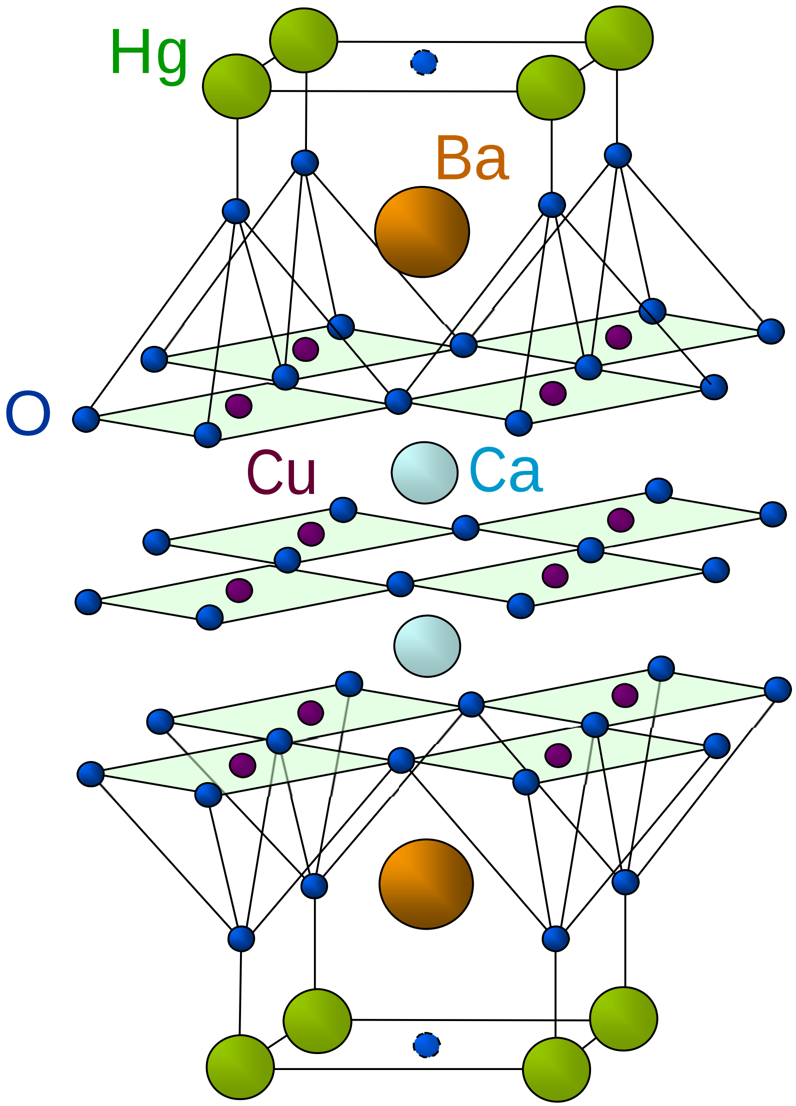
EXERCISE 1.2.

Here is the crystal structure of the highest T_c superconductor Hg-Ba-Ca-Cu-O.

A. From this structure, derive the chemical formula of the compound. (Please explain how you ended up with the formula!)

B. Do you expect fractional occupancies for any of the cation/anion sites in this structure? (Explain!)

C. Do the sizes of the balls properly reflect the ionic sizes of the different cations and anions in the structure?



Hg-Ba-Ca-Cu-O

EXERCISE 1.3.

A. Search for the ionic radius values for Ca^{2+}, Ti^{4+} and O^{2-} ions, relevant to the perovskite structure (HINT: take into account the coordination numbers).

B. Calculate the "tolerance factor" for the mineral perovskite $CaTiO_3$.

C. How well Ca and Ti match size-wise with each other considering the ideal cubic perovskite structure?

D. To improve the match, you could as a chemist consider different modifications, for example, to control the oxygen content or to replace Ca (partly) with other alkaline earth metals. Which option you would select and why?

You can find ionic radius values at:
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EXERCISE 1.4.

A. Calculate the “tolerance factor” for the perovskite $LaMnO_3$.

B. Based on this value, do you expect that Mn in this compound has a tendency to be reduced or oxidized? Explain!

C. How do you think this predicted tendency could be realized in this compound? Explain!

You can find ionic radius values at:
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