

CHEM-E4205 (5 cr):

Crystallography Basics & Structural Characterization

The course deals with **crystal chemistry** concepts and structural **characterization** techniques of **inorganic materials** and covers also the basics of **crystallography**. The emphases are on the various diffraction and spectroscopic methods used for phase identification, **crystal structure** determination and studies of **chemical environment**.

Time Slots	Mon 14–16 Ke4; Wed 14-16 Ke3 (Thu 12-14 Ke3); Fri 12–14 Ke4 28.2. – 30.5.2024
Lectures	Wednesdays (Thursdays) and Fridays Lecture slides and additional reference material (if needed) provided in MyCourses before the start of each lecture.
Exercises	Mondays (assignments given on Fridays) Mostly "free time" to discuss the homework & get some guidance. Exercise answers returned to MyCourses by Wed. 1 pm.
Seminars	Given individually/in a group of two students on an assigned topic
Teachers:	Maarit Karppinen Linda Sederholm (XRD) Topias Jussila (XRR)

GRADING (max 100 points)

- Exam: 0 – 44 points
- Exercises: = 0 – 36 (= 6 x 6) points
- Seminar (mandatory): 10 – 20 points

SCHEDULE

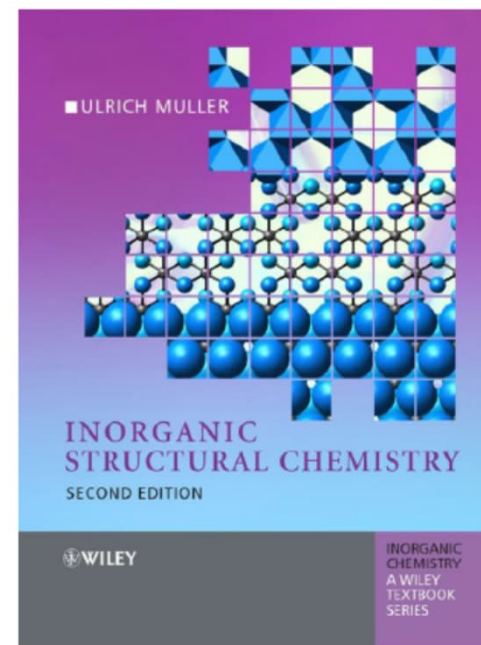
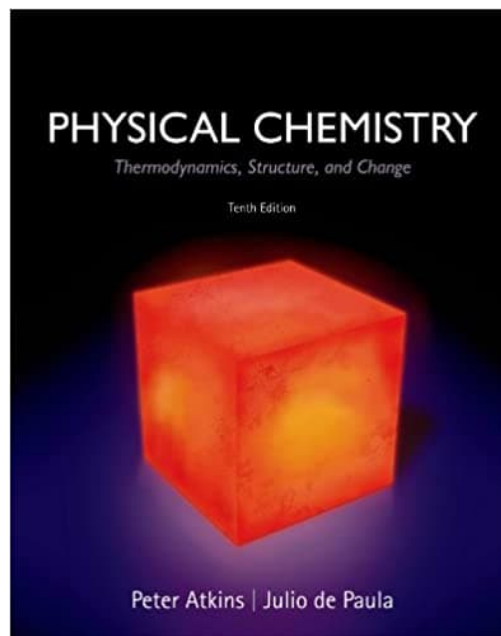
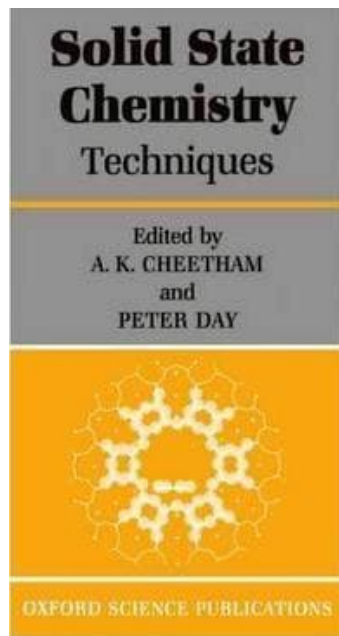
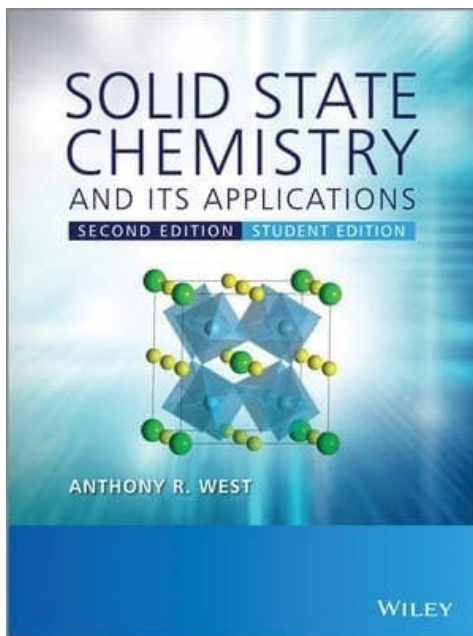
	Date	Topic
1.	Wed 28.02.	Lec-1: Introduction
2.	Mon 04.03.	Lec-2: Crystal Chemistry & Tolerance parameter
3.	Mon 04.03.	EXERCISE 1
4.	Wed 06.03.	Lec-3: Crystal Chemistry & BVS
5.	Fri 08.03.	Lec-4: Symmetry & Point Groups
6.	Mon 11.03.	EXERCISE 2
7.	Wed 20.03.	Lec-5: Crystallography & Space Groups (Linda)
8.	Fri 22.03.	Lec-6: XRD & Reciprocal lattice (Linda)
9.	Mon 25.03.	EXERCISE 3 (Linda)
10.	Thu 04.04.	Lec-7: Rietveld (Linda)
11.	Fri 05.04.	EXERCISE 4: Rietveld (Linda)
	Mon 08.04.	EXERCISE 4: Rietveld (Linda)
12.	Thu 11.04.	Lec-8: ND & GI-XRD
13.	Fri 12.04.	Lec-9: XRR (Topias)
14.	Mon 15.04.	EXERCISE 5: XRR (Topias)
	Wed 17.04.	EXERCISE 5: XRR (Topias)
15.	Mon 22.04.	Lec-10: Synchrotron radiation & XAS & EXAFS
16.	Wed 24.04.	Mössbauer (to 25.10)
17.	Fri 26.04.	EXERCISE 6
18.	Mon 29.04.	Seminars:
19.	Fri 03.05.	Seminars:
20.	Mon 06.05.	ADDITIONAL DISCUSSION/QUESTION POSSIBILITY

INSTRUCTIONS for SEMINAR PRESENTATION

- Topics: **IR, Raman, XPS, SEM, AFM, HRTEM, ED, EELS**
- Seminar presentation is mandatory
- Given individually or in a group of two students
- Evaluated in the scale: 10 ~ 20 points
- Presentation is given in English, and the slides will be put up in MyCourses afterwards
- Presentation: 25+5 minutes
- Rough content of the presentation:
 - principle of the technique(s)
 - type of information gained
 - interpretation of the measured data
 - pros & cons
 - **two to four research examples**
(you will be given some relevant research papers for an example)

TEXT BOOKs & Background Knowledge

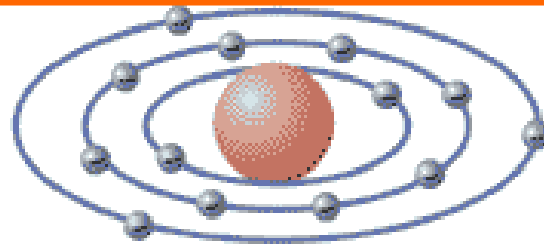
- ❖ This course does not follow any specific text book; no text book fully covers the topics included; below are examples of text books which could be useful reference/background books for many of the course topics.
- ❖ The following two courses (or similar studies) are mandatory prerequisites. It is difficult to follow this course without a similar basic background knowledge on inorganic (materials) chemistry and solid state chemistry:
- ❖ CHEM-E4130: Chemistry of Elements (Maarit Karppinen)
- ❖ CHEM-E4155: Solid State Chemistry (Antti Karttunen)



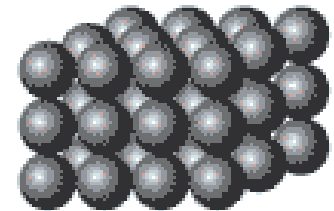
Structure of materials (in different levels)

- (a) Single atom: electron/spin configuration => valence/oxidation state & spin state
 - (+) Local structure: bonding structure/coordination sphere
- (b) Crystal structure: (periodic) locations of different atoms in regular crystal lattice
 - (+) Magnetic structure (periodic) ordering of spins
- (c) Microstructure: e.g. particle size/shape, grain boundaries
- (d) Phase/macroscale structure

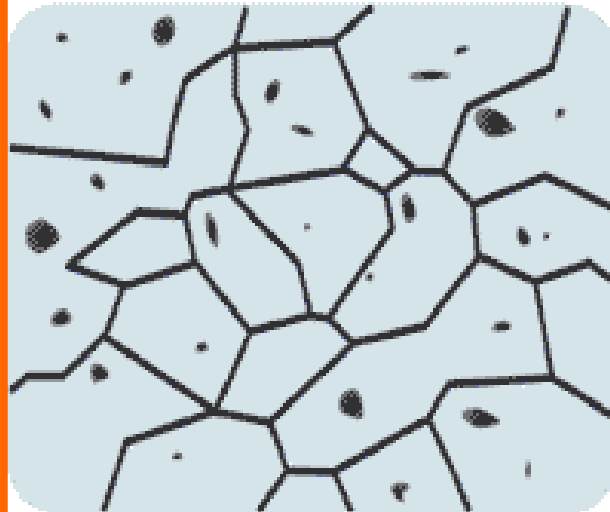
All these levels of material's structure significantly affect the material's properties



(a)



(b)



(c)



(d)

LECTURE 1: INTRODUCTION

- **Different types of crystal structure representations**
- **Coordination number (CN) & Coordination polyhedron**
- **Perovskite structure**
- **Cation ordering**
- **Distortions**
- **Nonstoichiometry**
- **Oxygen-vacancy ordering**
- **Antisite defects**

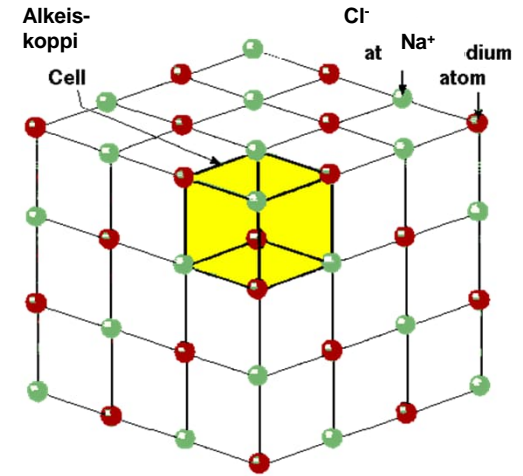
EXAMPLES of "everyday" crystals/structures



Rock salt (NaCl)



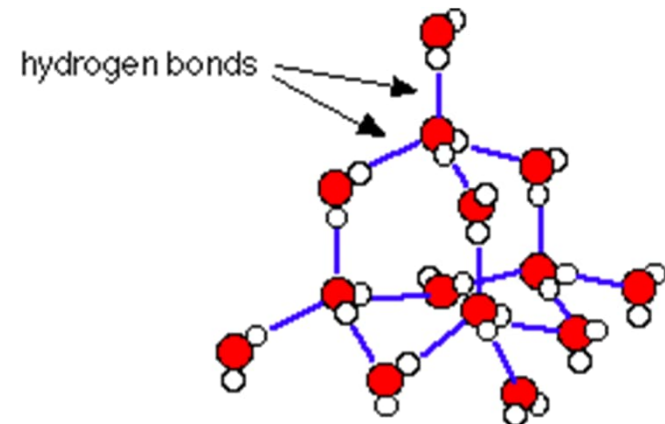
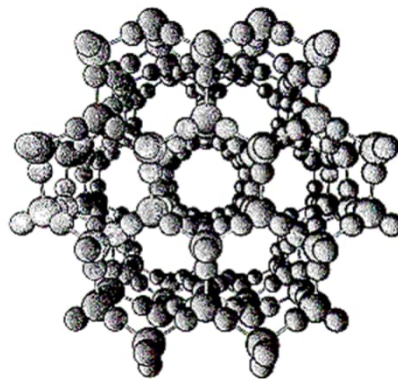
NaCl single crystal



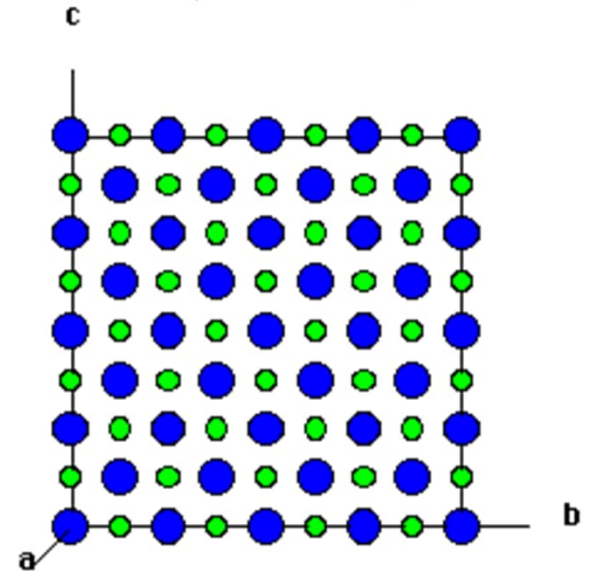
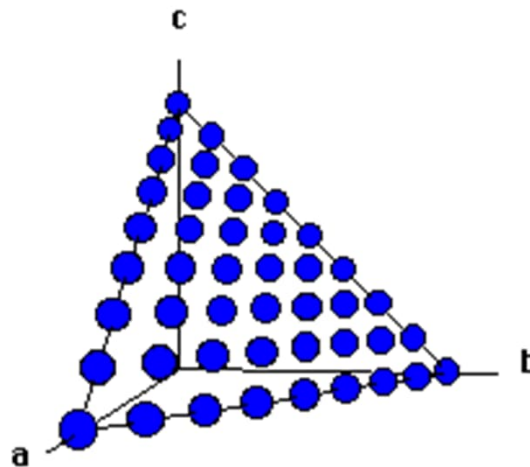
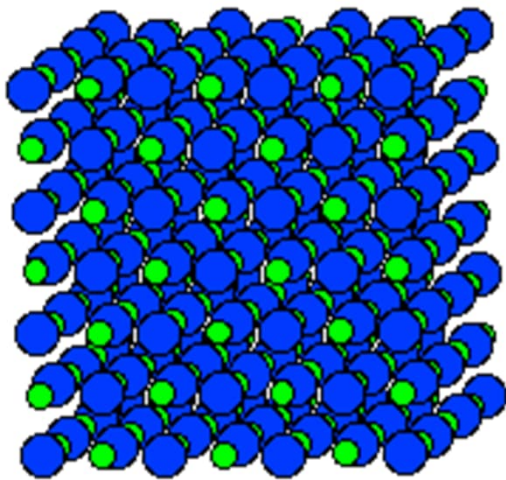
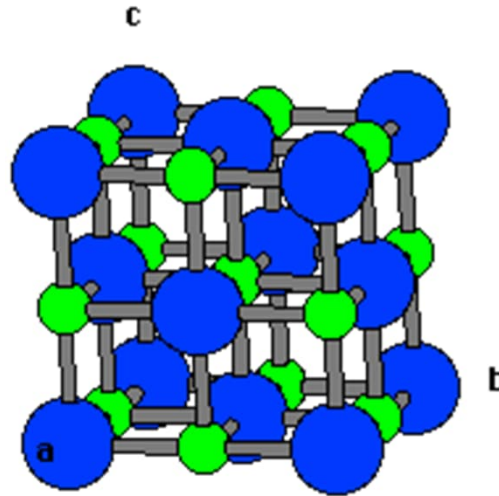
Cubic crystal structure:
high symmetry, ionic bonds
→ extremely stable



Snow flake:
hexagonal

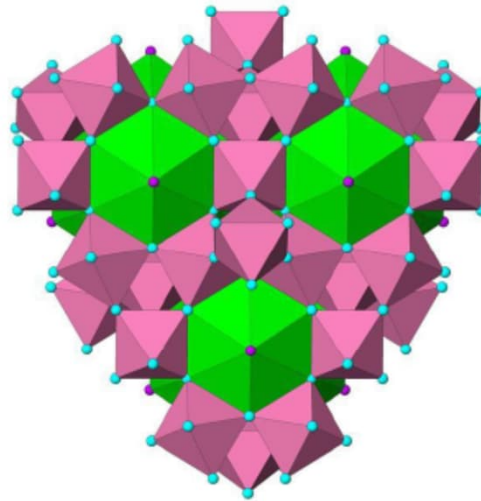
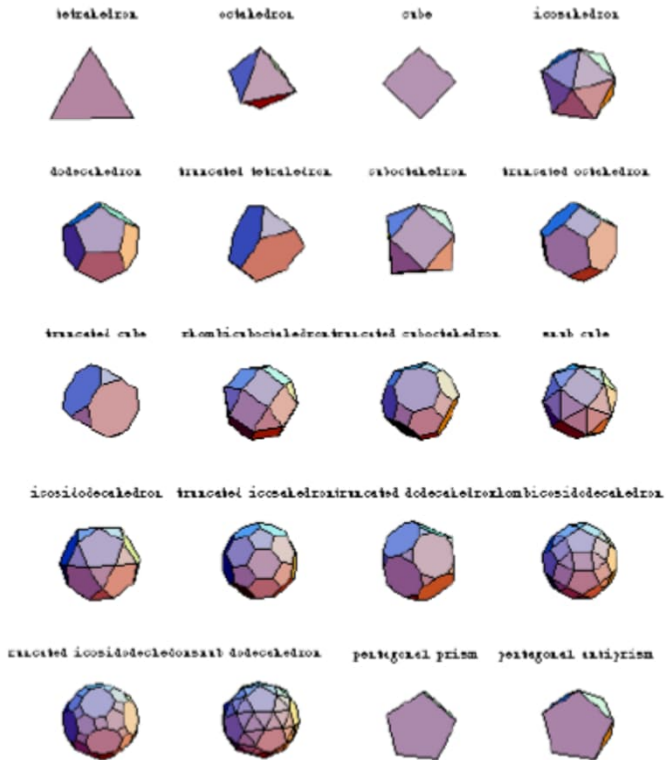


The same (NaCl) crystal structure can be presented in multiple ways

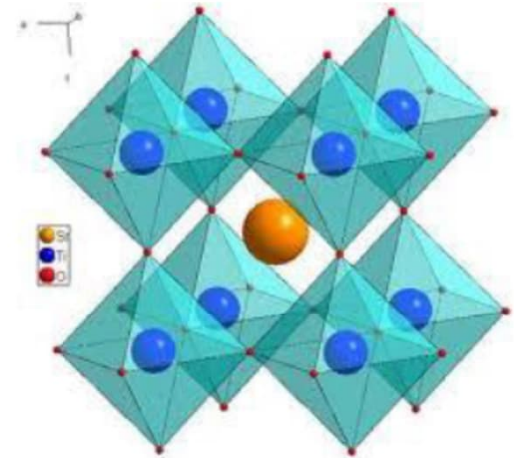


Polyhedra

Generally metal in centre and oxide or halide at vertices



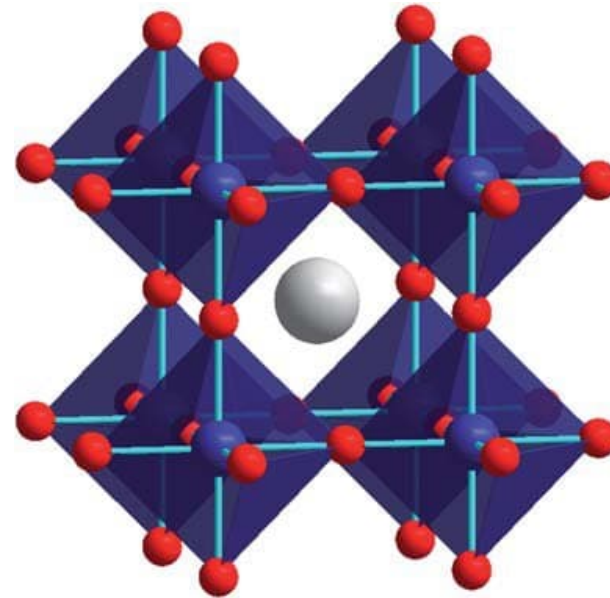
Pyrochlore

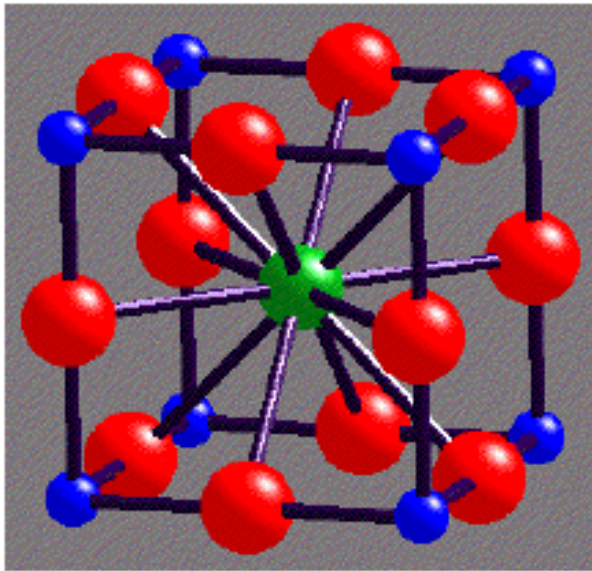


Perovskite

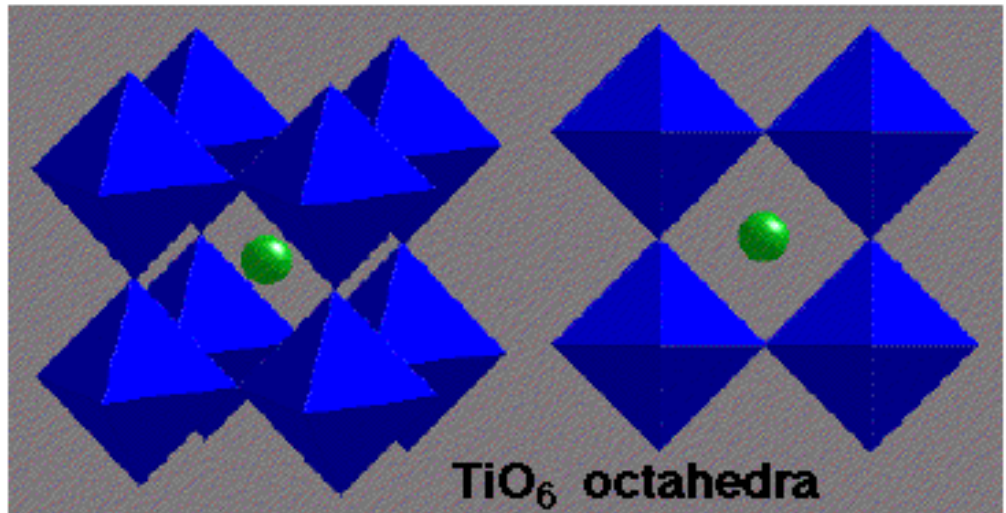
(Inorganic) PEROVSKITE ABO_3

- Thousands of perovskite compounds known
- Structure named after the mineral Perovskite $CaTiO_3$
- Mineral found in Ural Mountains, named in 1839 after Russian mineralogist, Von Perovski
- Components: - **A**: large metal
 - **B**: small (transition) metal
 - **O**: oxygen (can also be halogen)
- Oxygen deficiency (very common): $ABO_{3-\delta}$
- Because of these possibilities of chemical composition tuning, perovskite compounds can be tailored to a wide variety of functional properties
- Ideal perovskite has cubic unit cell; coordination numbers: $CN(A)=12$, $CN(B)=6$, $CN(O)=6$
- Valences: $V(A) + V(B) = 6$,
e.g. $La^{III}Sc^{III}O_3$, $Sr^{II}Ti^{IV}O_3$, $Na^{I}Nb^{V}O_3$
- Tuning the chemical composition controls redox chemistry (metal valences) and tiny crystal structure distortions (in CNs, bond lengths, bond angles)
- Metal valences and structural distortions control the functional properties





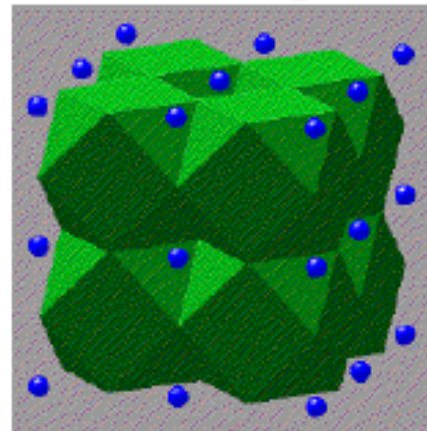
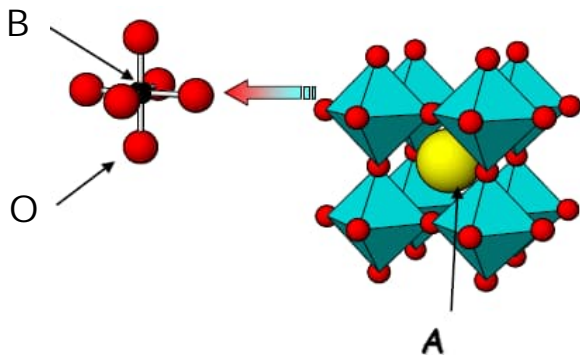
A-Cell



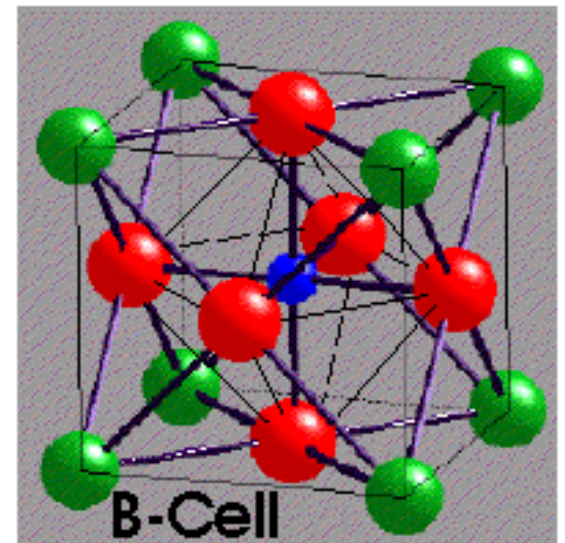
TiO₆ octahedra

Perovskite CaTiO₃

● Ca ● Ti ● O



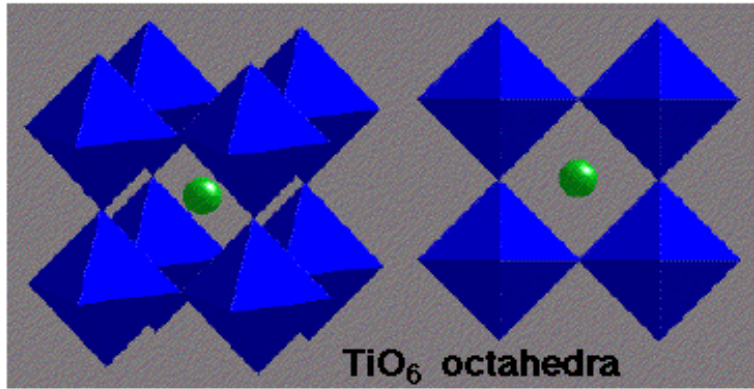
CaO₁₂ cubooctahedra



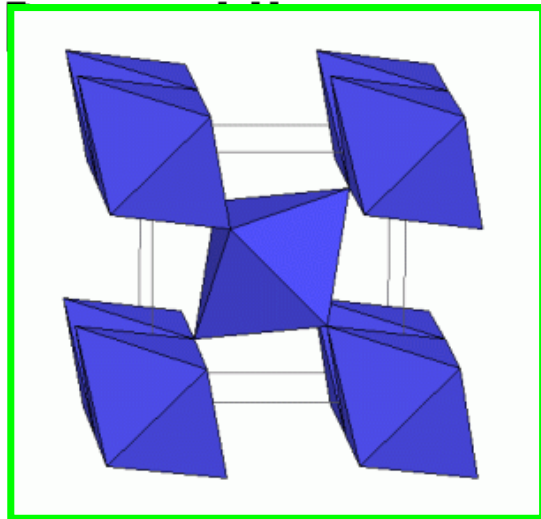
B-Cell

Different presentations of the perovskite structure

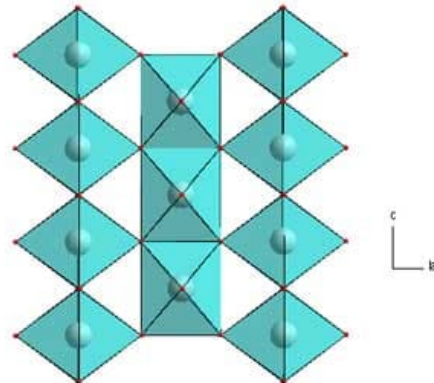
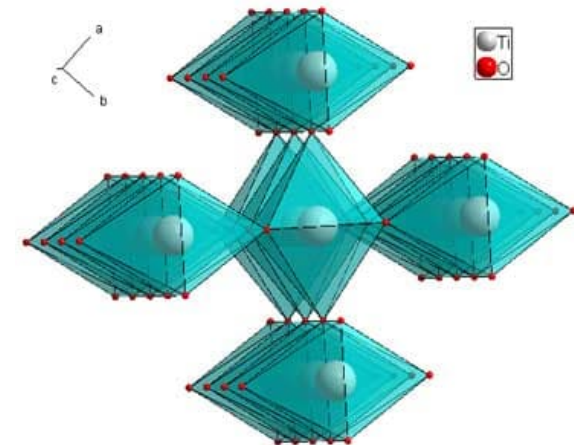
PEROVSKITE CaTiO_3



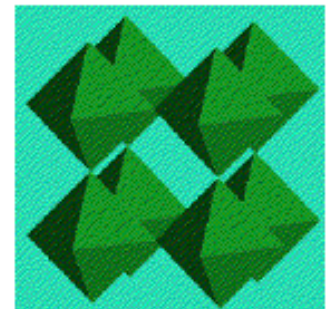
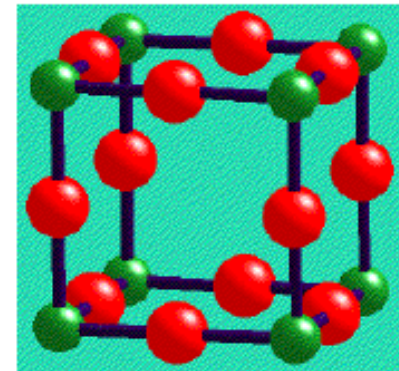
Examples
of related crystal structures:
- Coordination numbers?



RUTILE TiO_2



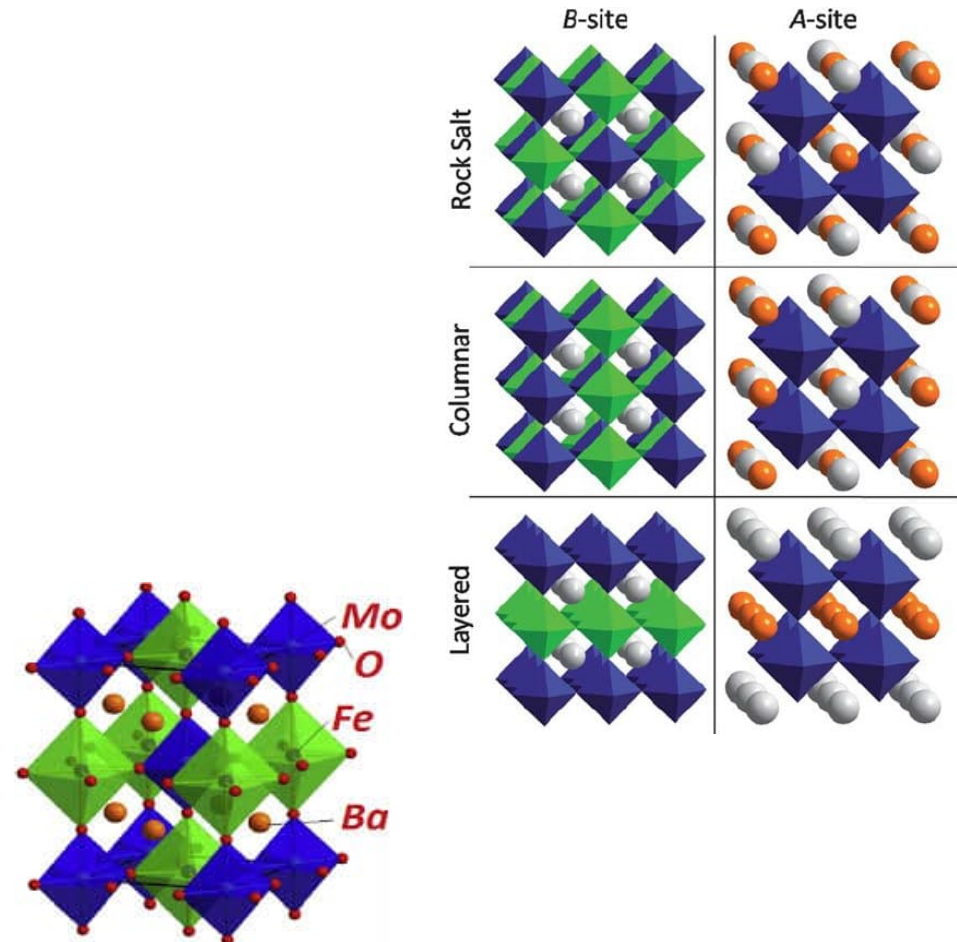
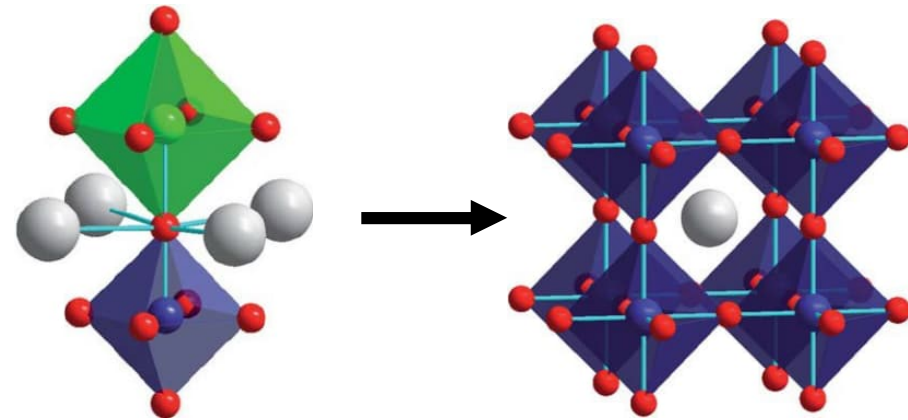
ReO_3



CATION ORDERING

DOUBLE PEROVSKITES

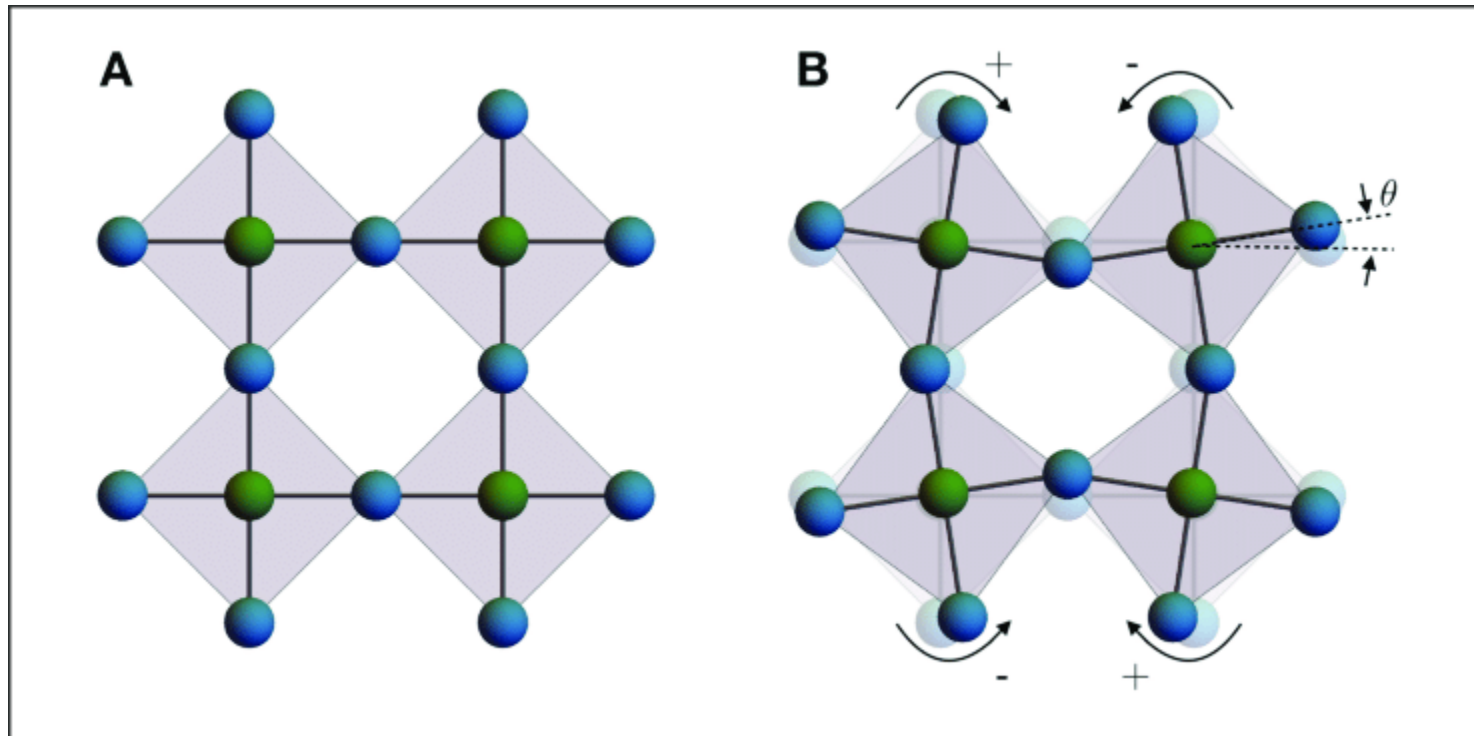
- Two different cations (**B'** and **B''**) occupy the B-site with 50%/50% ratio and in an ordered manner → B-site ordered double perovskite
- Two different cations (**A'** and **A''**) occupy the A-site with the 50%/50% ratio and in an ordered manner → A-site ordered double perovskite
- For both cases, there are multiple different ordering patterns
- Many double perovskite compounds show exciting functional properties, e.g. the B-site ordered halfmetallic $\text{Sr}_2\text{FeMoO}_6$ (simultaneously ferromagnetic and electrically conducting → magnetic-field control of conductivity → spintronics)



DISTORTIONS: atom displacements

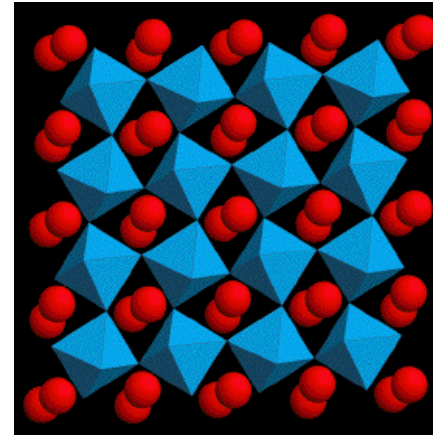
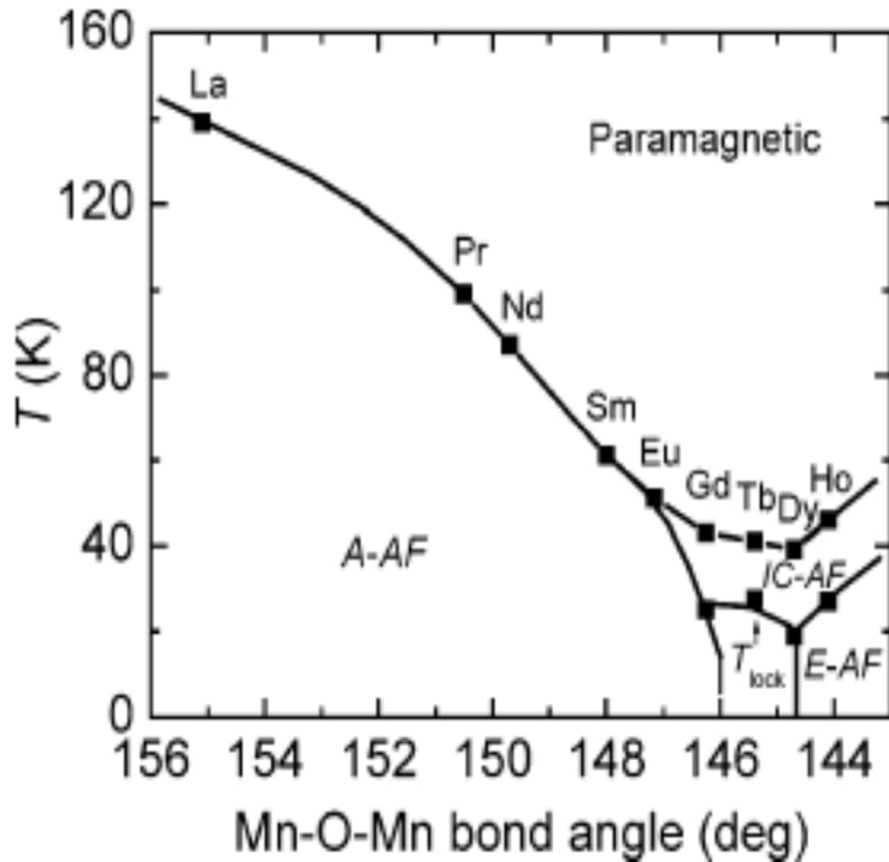
COMMON EXAMPLE OF DISTORTIONS in ABO_3

- Oxygen atoms often move from their ideal positions such that the BO_6 octahedra e.g. get tilted
- There are many other ways for oxygen atoms to get displaced
- These **distortions affect many properties** (magnetic, ferroelectric, etc.)



ANTIFERROMAGNETIC (AF) LnMnO_3 PEROVSKITES

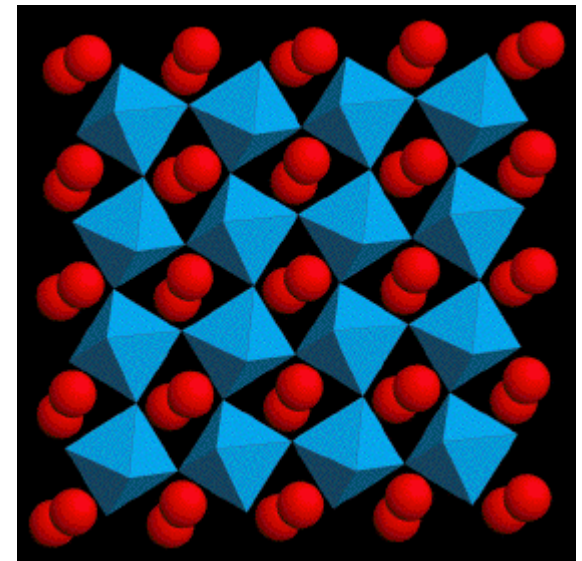
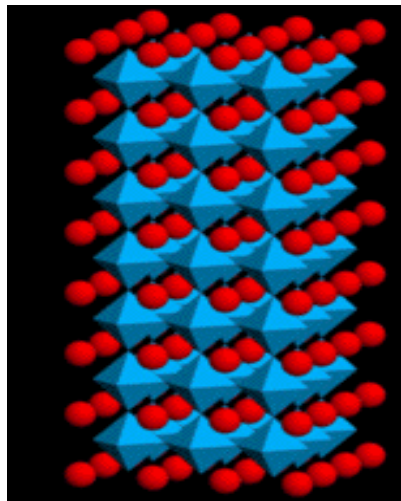
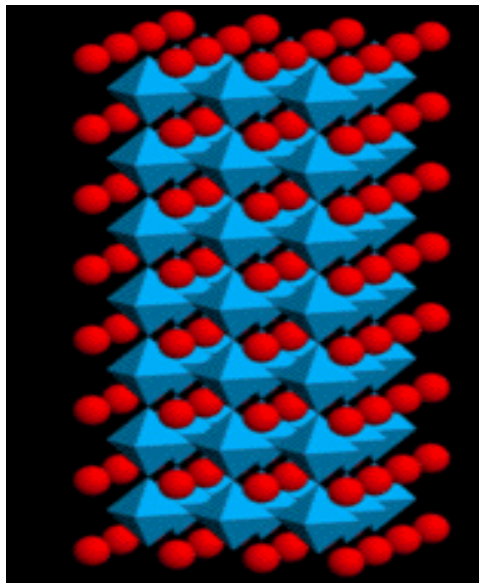
- Magnetic transition temperature increases with:
 - decreasing Mn-O-Mn bond length
 - increasing Mn-O-Mn bond angle (closer to 180°)



Y.H. Huang, H. Fjellvåg, M. Karppinen, B.C. Hauback, H. Yamauchi & J.B. Goodenough, *Chem. Mater.* **18**, 2130 (2006).

HYPOTHETICAL EXAMPLE: Ferromagnetic (Ba/Sr/Ca)BO₃

- Ferromagnetic transition temperature (T_C) highest when strong B-O-B interactions: short bond length and non-tilted bonding
- LEFT: with the largest **A = Ba** cation, ideal perovskite structure, **B-O-B** bond angle 180 °C, but **B-O** bond length long $\rightarrow T_C = 320$ K
- MIDDLE: with the intermediate-sized **A = Sr** cation, ideal perovskite structure, **B-O-B** bond angle 180 °C, and **B-O** bond length shorter $\rightarrow T_C = 400$ K
- RIGHT: with the smallest **A = Ca** cation, tilted perovskite structure, **B-O** bond length short, but the **B-O-B** bond angle < 180 °C $\rightarrow T_C = 370$ K



NON-STOICHIOMETRY: vacancies & interstitials

(1) Interstitial oxygen atoms



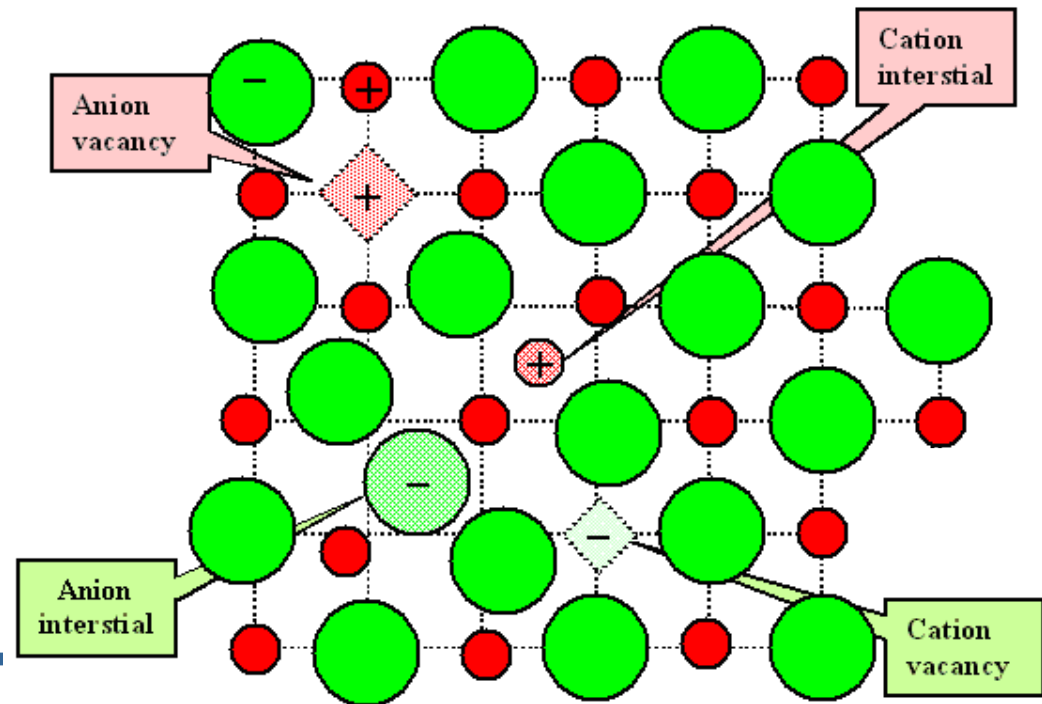
(2) Cation vacancies



(3) Oxygen vacancies

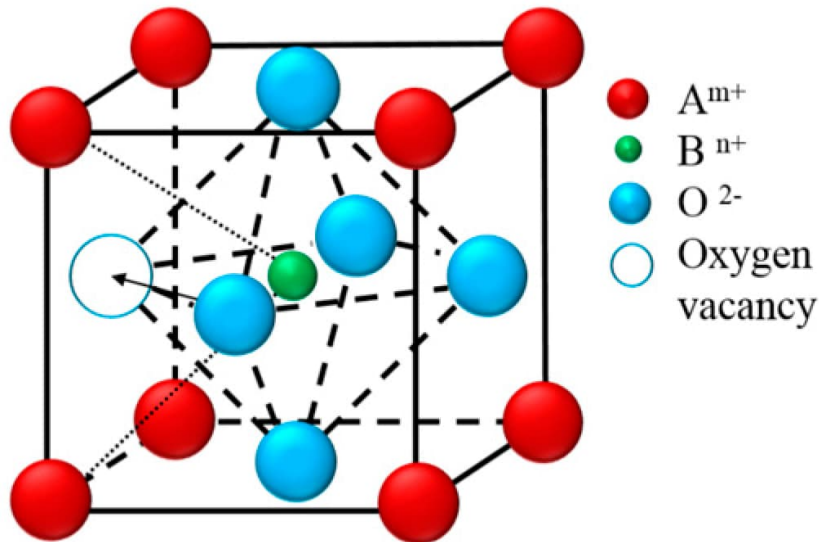


(4) Interstitial cations



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

- Oxygen nonstoichiometry, even within the wide range of $0 < \delta < 0.5$, is very common among perovskite compounds
- **Oxygen content controls the metal valences and thereby the properties**
- Oxygen vacancies can be randomly located or ordered along different patterns



OXYGEN ORDERING

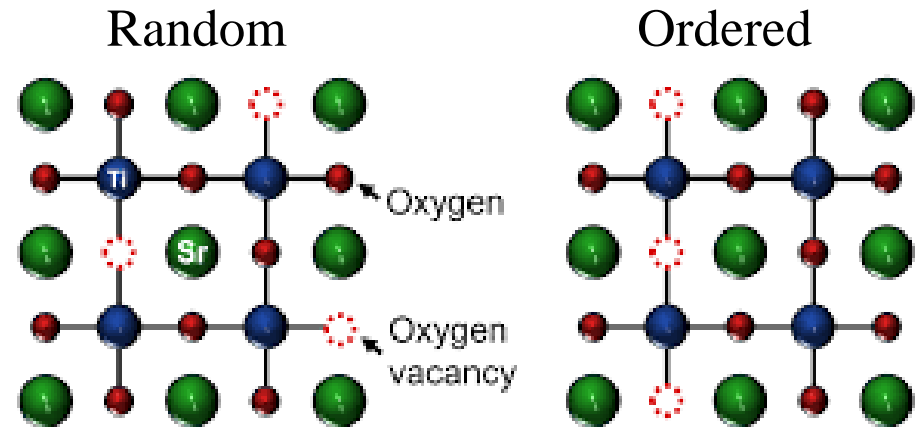
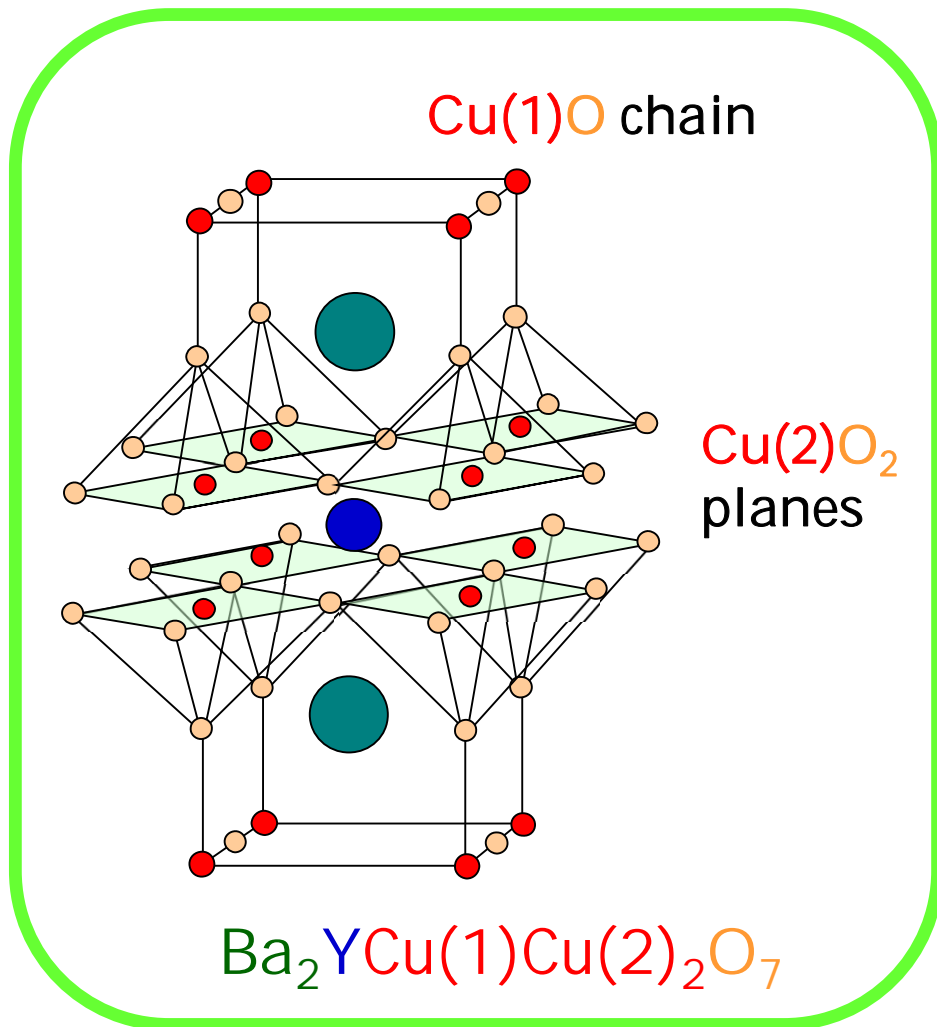
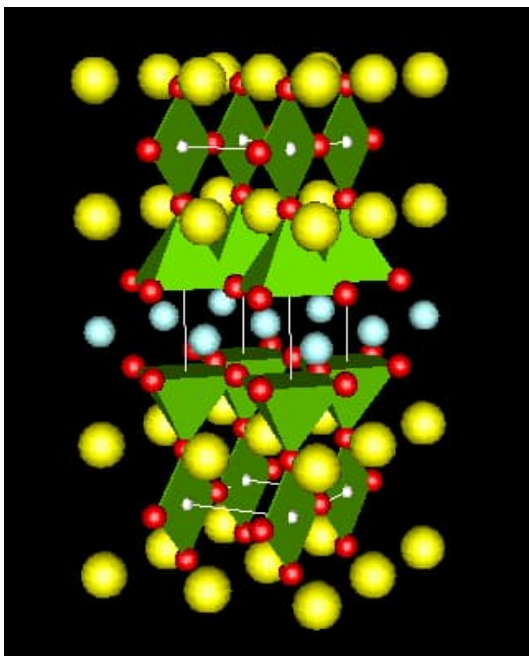
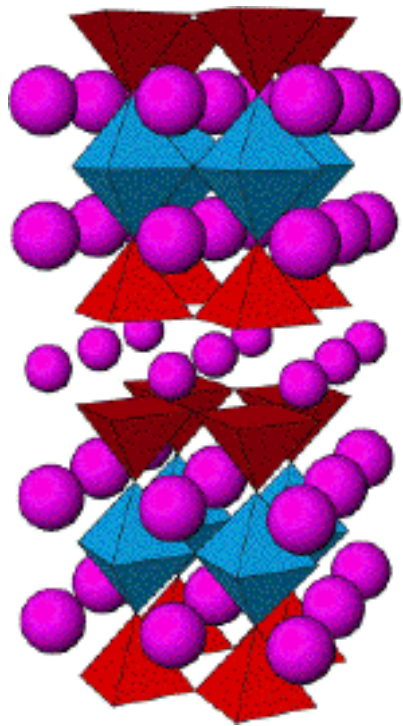
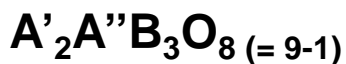
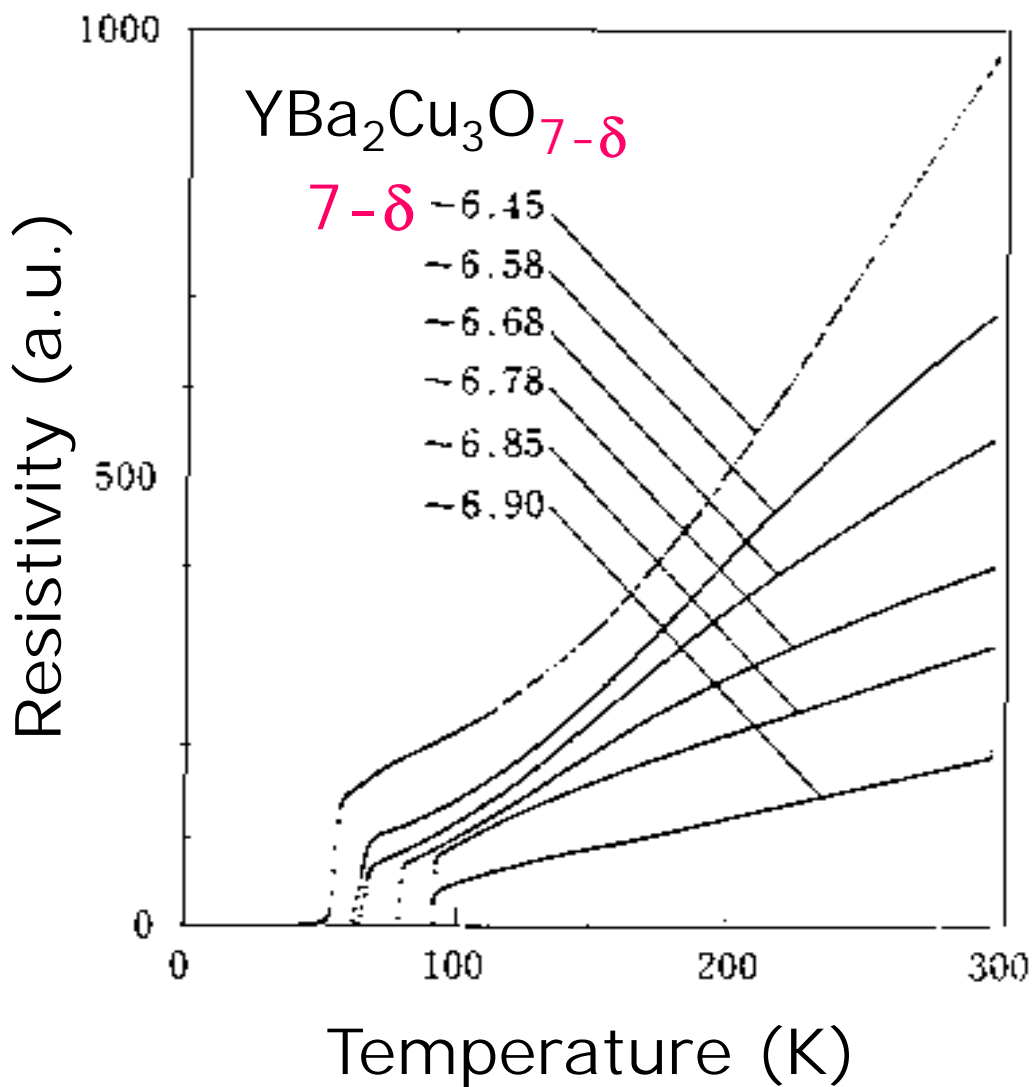
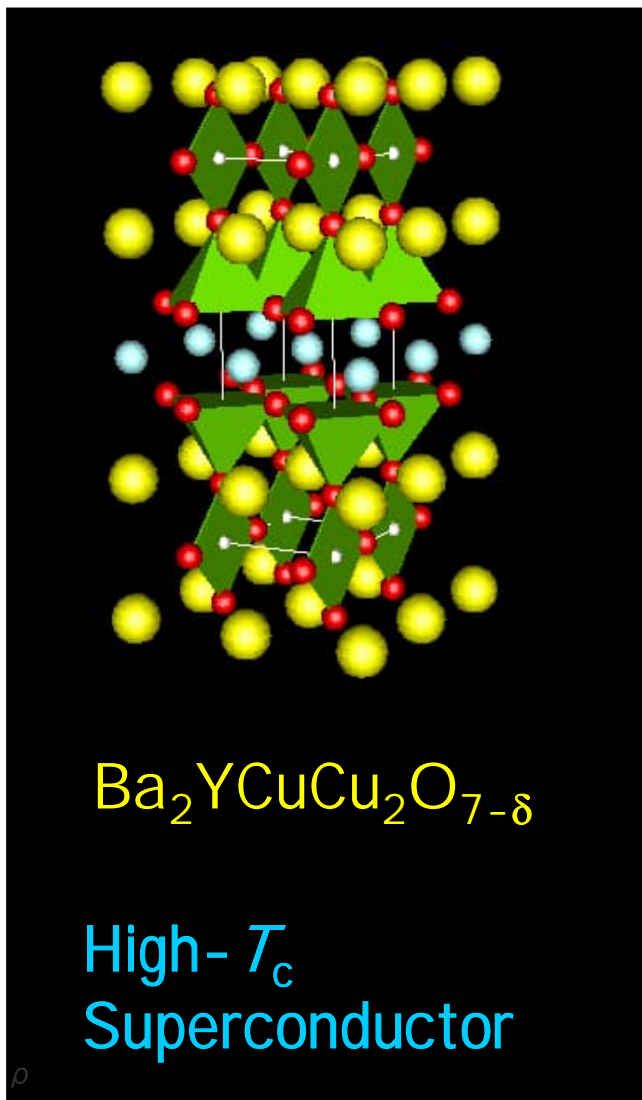


Illustration how the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ structure is derived from the perovskite structure through cation ordering and ordered oxygen vacancies

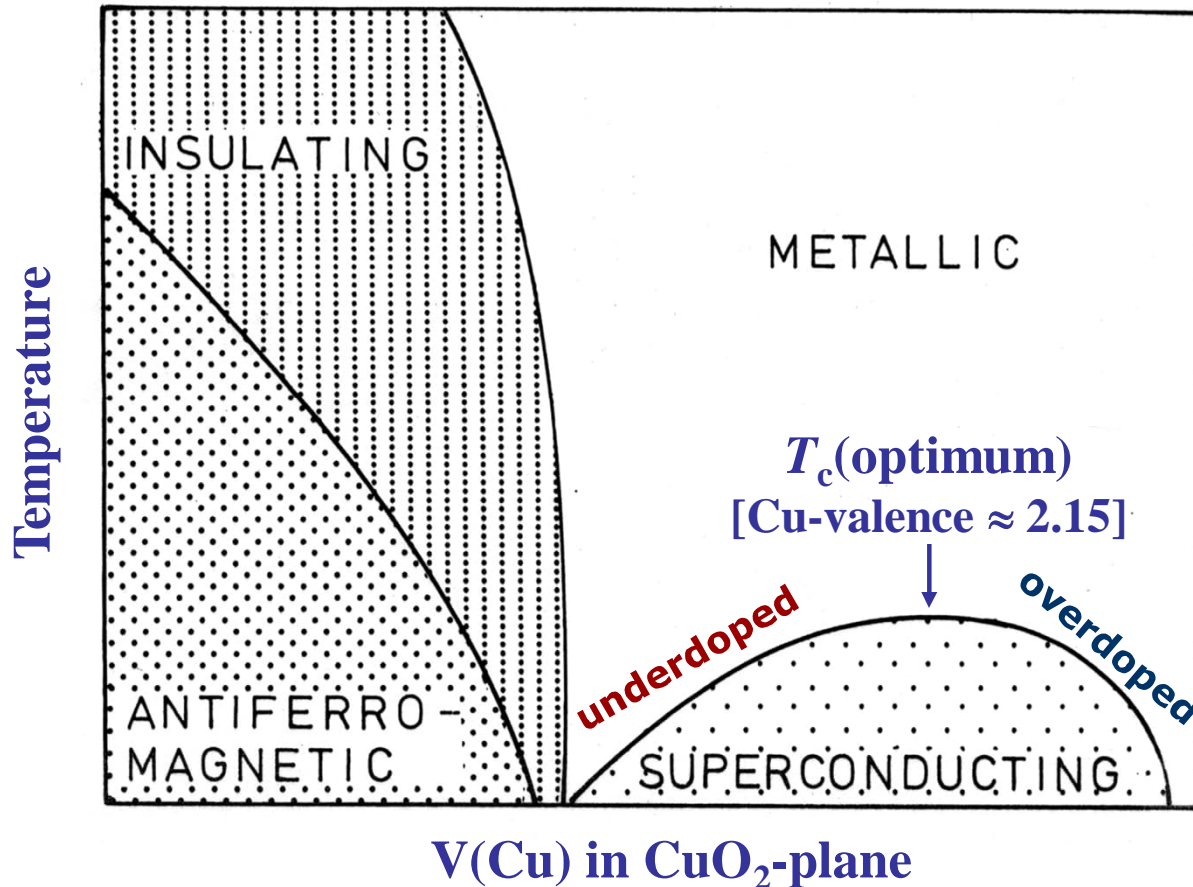
A-site ordered &
oxygen-vacancy ordered
TRIPLE PEROVSKITE



$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (or $\text{Ba}_2\text{YCu(1)Cu(2)}_2\text{O}_{7-\delta}$ 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 precisely



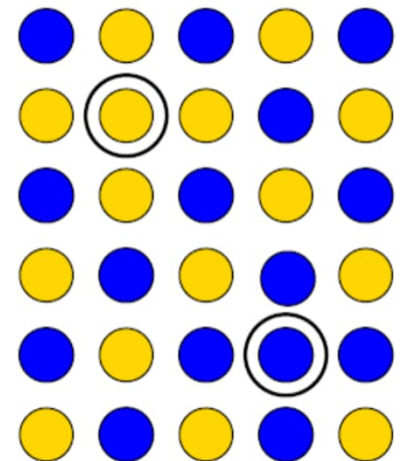
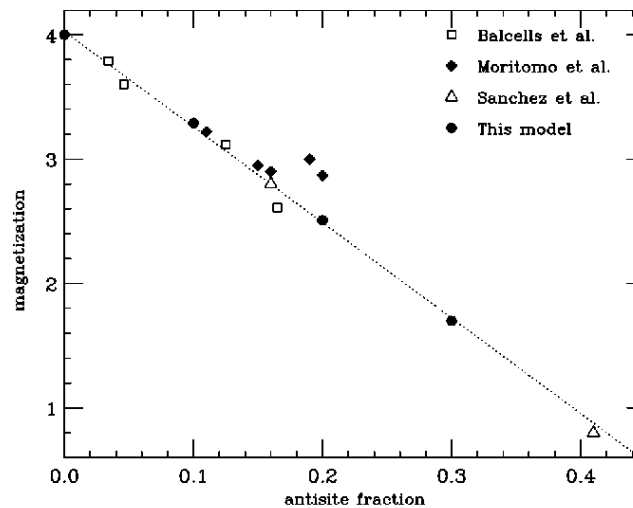
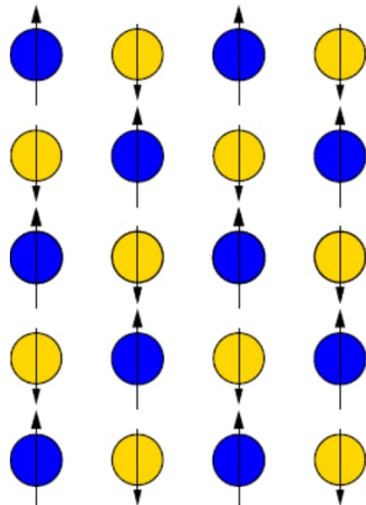
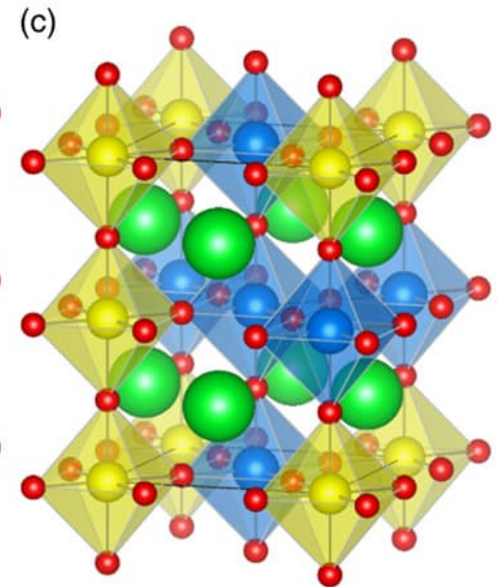
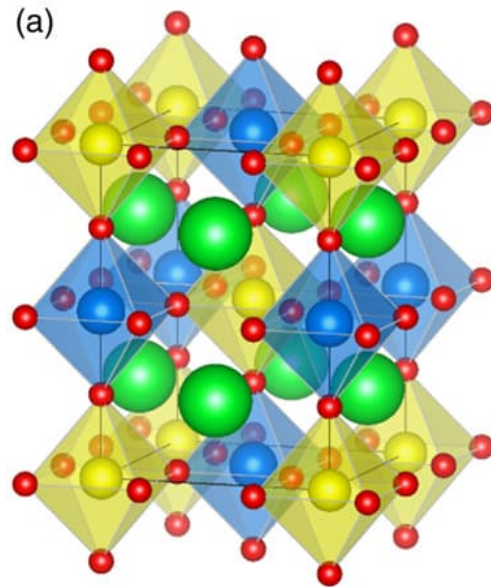
Simplified Phase Diagram of High- T_c Superconductors

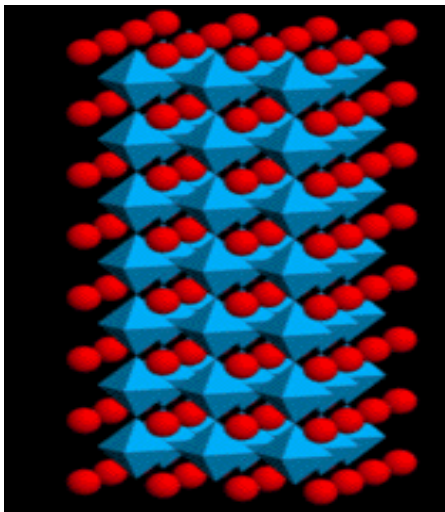


Oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ controls the valence state of copper, and thereby the superconductivity (T_c value)

ANTISITE DEFECTS in $A_2B'B''O_6$

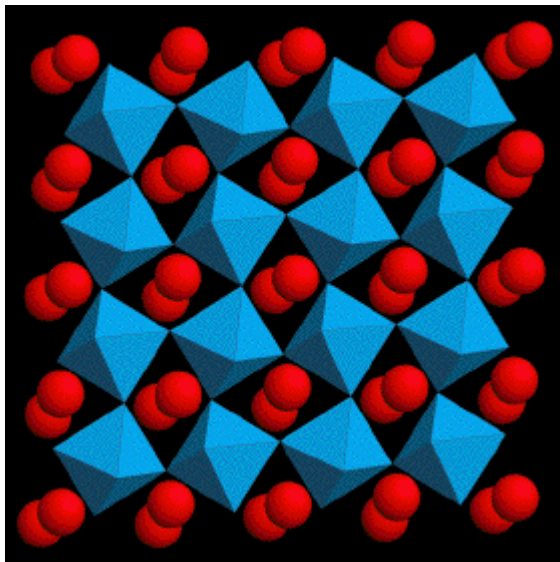
- Ordering of B' and B'' is not always perfect
- Antisite (=defected) atom is B' cation at the B'' site, and vice versa



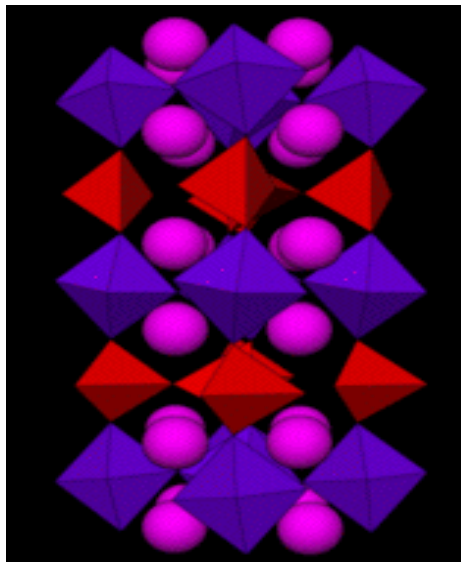


“Distortions and Imperfections” in Perovskite Structure

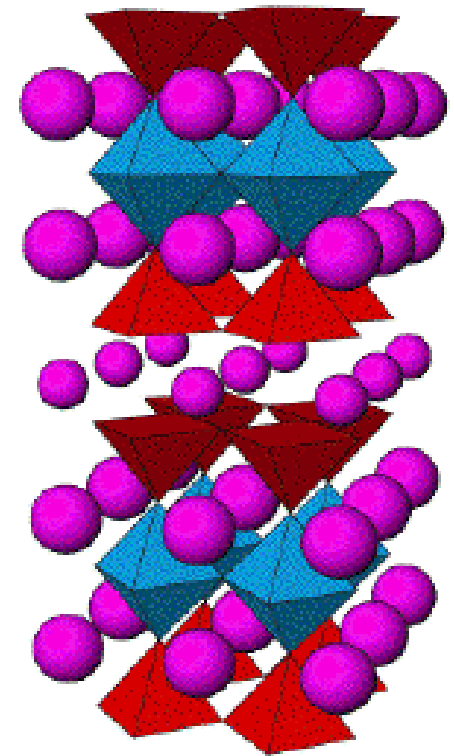
- often the source of the desired properties



Changes in
atomic positions



Oxygen deficiency



Ordering of cations
→ Layered structure