# 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.

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|---|---|
| Time Slots | Monday 14–16 (Ke4), Wednesday 14-16 (Ke3) & Friday 12–14 (Ke4) |
| Lectures | Wednesdays and Fridays<br>Lecture slides and additional reference material (if needed) provided in MyCourses before the start of each lecture. |
| Exercises | Mondays (assignments given on Fridays)<br>Mostly ”free time” to discuss the homework & get some guidance.<br>Exercise answers returned to MyCourses by Wed. 1 pm. |
| Seminars | Given in a group of two students on an assigned topic |
| Teachers: | Maarit Karppinen<br>Linda Sederholm (XRD)<br>Eeva Rautama (Rietveld)<br>Topias Jussila (XRR) |

# SCHEDULE (tentative)

| | Date | | Topic |
|---|---|---|---|
| 1. | Wed | 01.03. | Lec-1: Introduction |
| 2. | Fri | 03.03. | 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 | | | |

# GRADING (max 100 points)

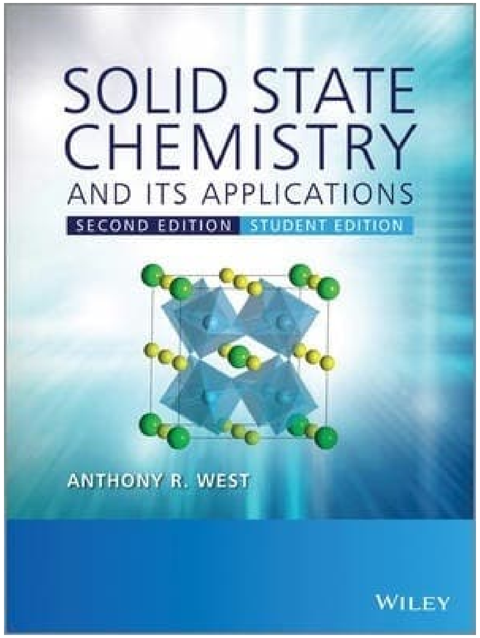
- Exam:  0 – 44 points
- Exercises: = 0 – 36 (= 6 x 6) points
- Seminar (mandatory): 10 – 20 points

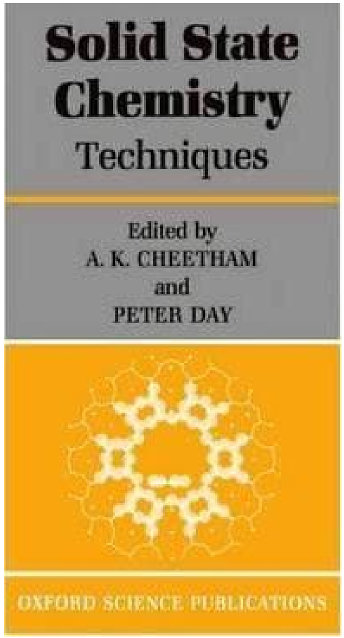
# INSTRUCTIONS for SEMINAR PRESENTATION

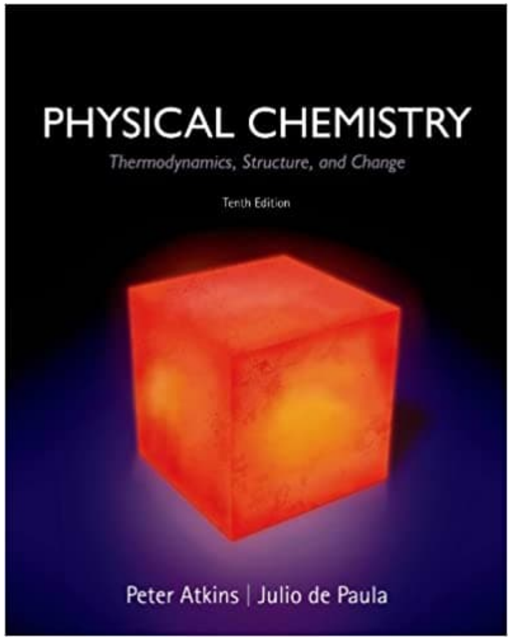
- Topics: **IR, Raman, XPS, SEM, AFM, HRTEM, ED, EELS**
- Seminar presentation is mandatory
- Given in a group of two students
- Evaluated in the scale: 10 ~ 20 points
- Presentation is given in English, and the slides will be put up in MyCourses afterwards
- Presentation: 25+5 minutes
- Rough content of the presentation/report:
    - 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)

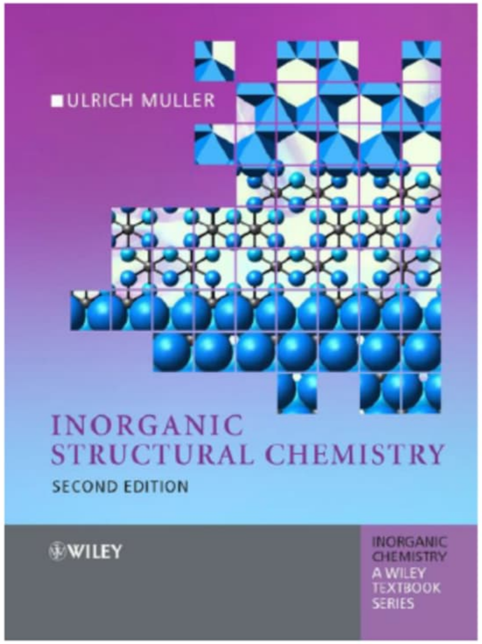
# TEXT BOOKs & Background Knowledge

- 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)





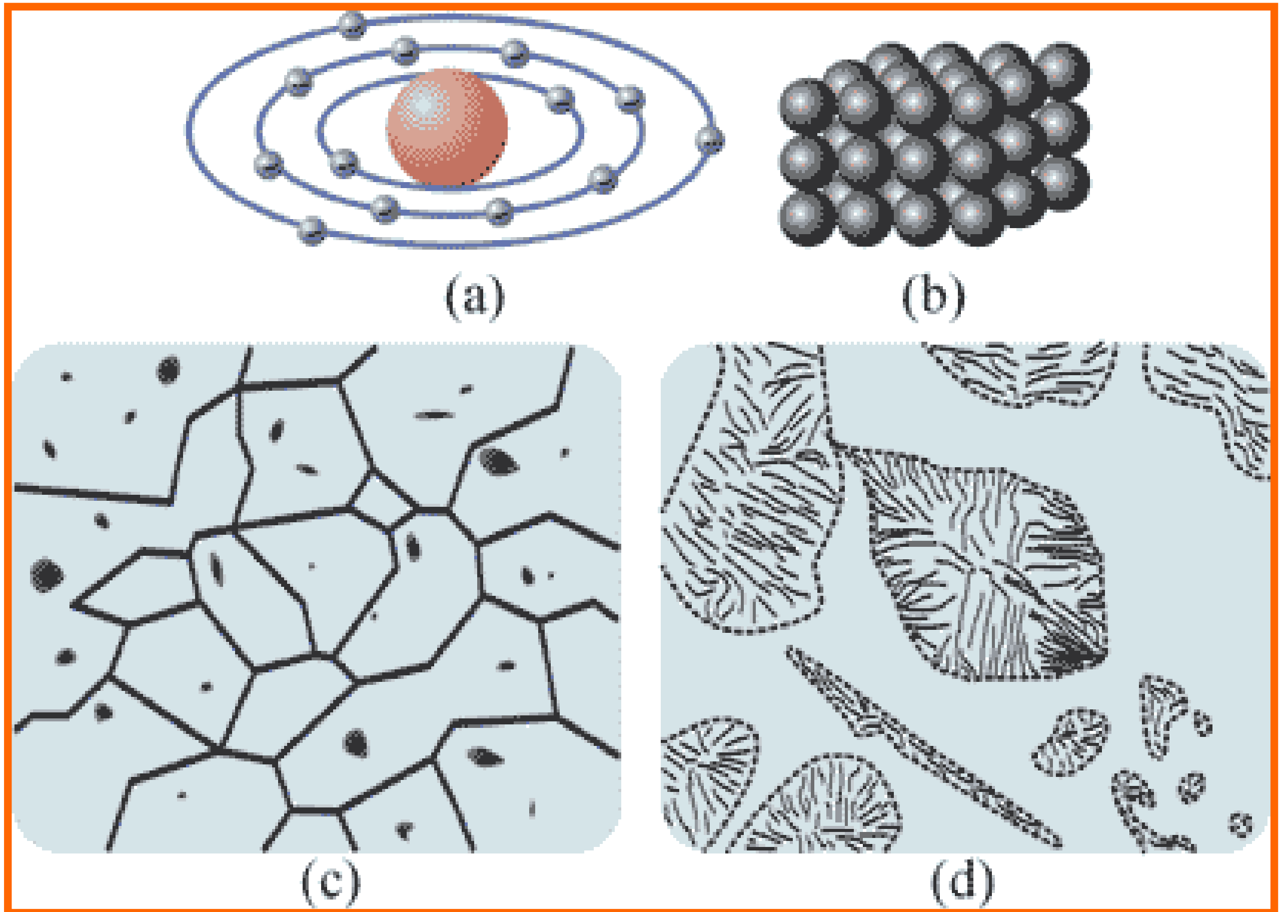




# Structure of materials (in different levels)

(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/macroscopic structure

**All these levels of material’s structure significantly affect the material’s properties**

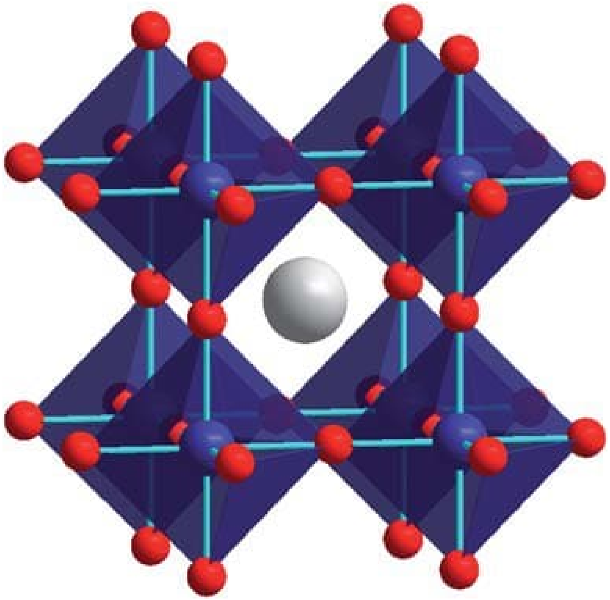


# LECTURE 1: INTRODUCTION

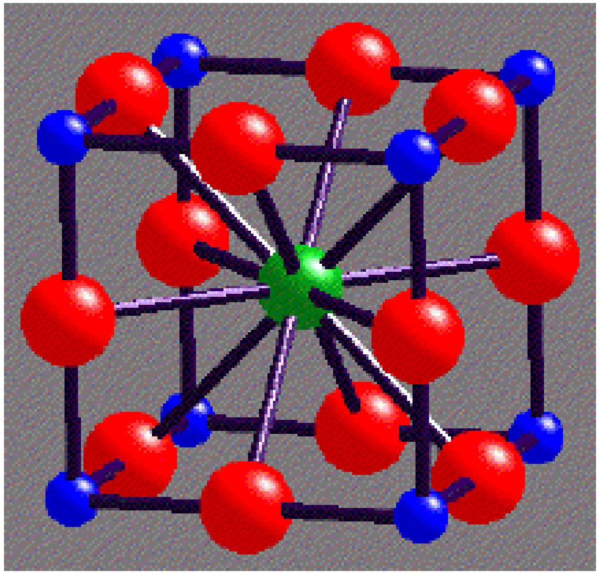
The course deals with structural characterization techniques of inorganic materials and covers also the basics of crystallography. The emphases are on the various diffraction and spectroscopic methods used for phase identification, **crystal structure** determination and studies of **chemical environment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

- Important: relations between crystal structure, chemical environment (coordination and valence) and material properties
- To get the full picture, a wide arsenal of different characterization techniques are needed for: crystal structure (XRD, ND, ED, HRTEM, EXAFS, RIXS), morphology (SEM, TEM, AFM), chemical environment (EXAFS, XANES, Mössbauer, XPS, IR, Raman) and properties (e.g. ND, Mössbauer for magnetic properties)
- Information needed in particular for: small distortions, different defects (vacancy, interstitial, antisite, etc.), mixed metal valences, magnetic structures, etc.
- For thin film characterization, specific techniques are needed (GIXRD, XRR)
- **Perovskite structure** is often used as a model/example case;
  however, all the issues discussed in the context of the perovskite structure
  are directly transferable to many other inorganic materials

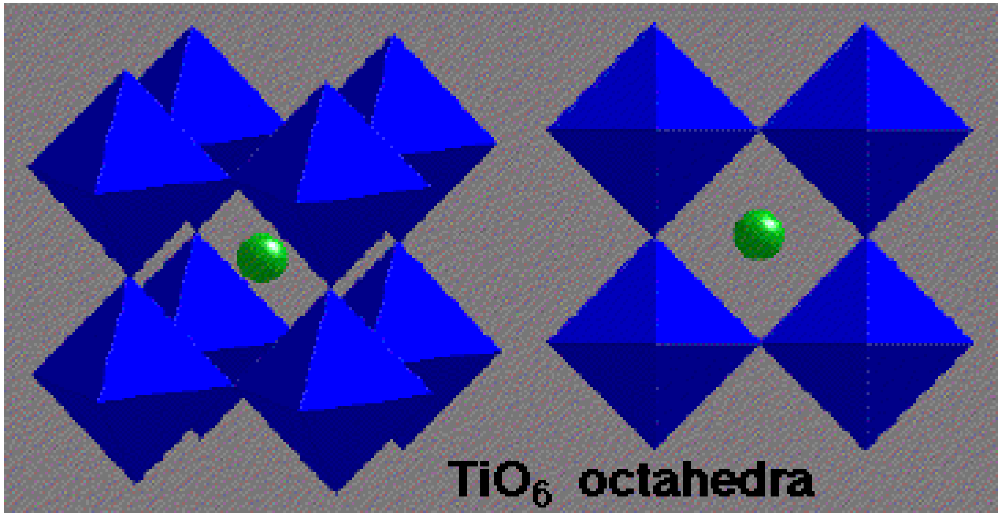
# (Inorganic) PEROVSKITE $ABO_3$



- 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**

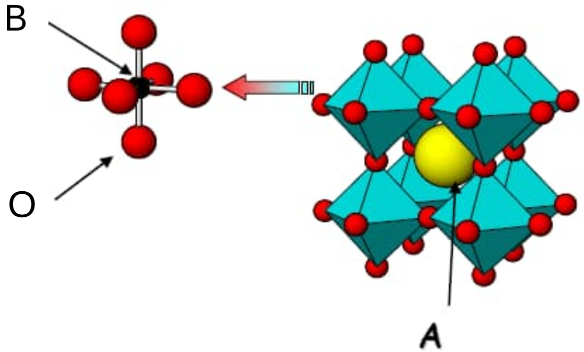


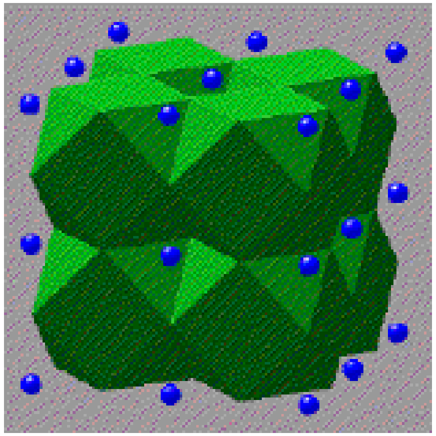
$TiO_6$ octahedra

# Perovskite

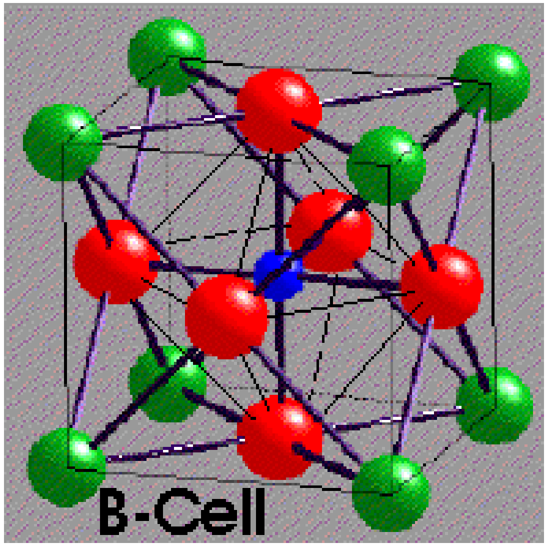
## $CaTiO_3$

● Ca ● Ti ● O





$CaO_{12}$ cuboctahedra



**B-Cell**

**Different presentations of the perovskite structure**

# 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
$La(Co,Mn)O_3$

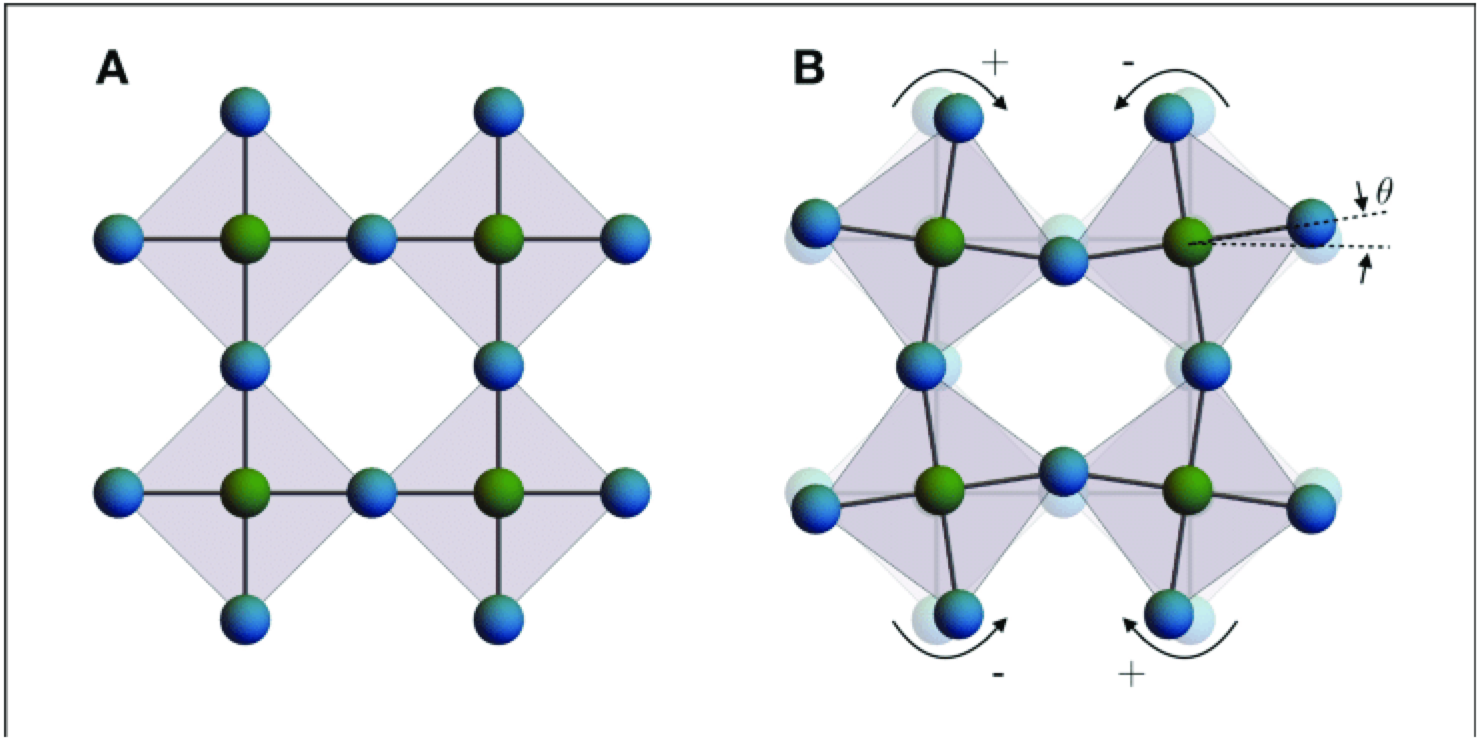
Metallic conductor
$LaCrO_3$

Piezoelectric material
$Pb(Zr,Ti)O_3$

Capasitor
(high dielectric constant)
$BaTiO_3$

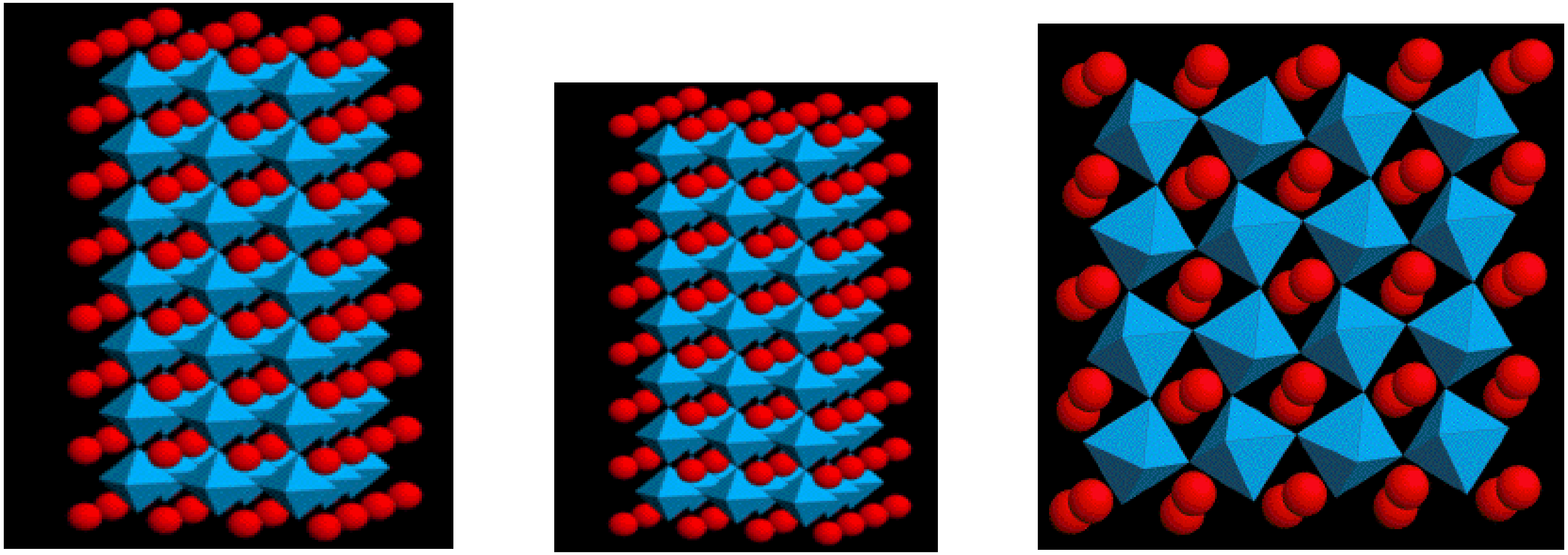
# COMMON EXAMPLE OF DISTORTIONS in $ABO_3$

- 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.)



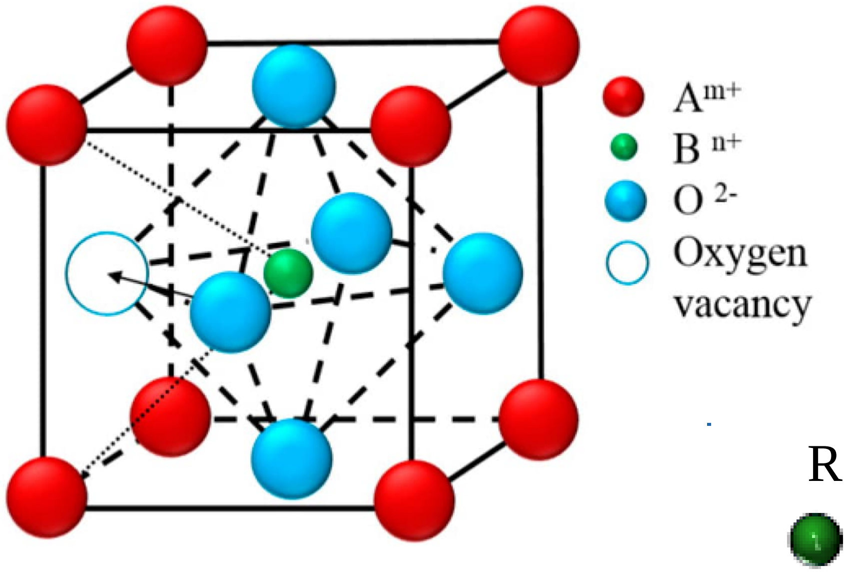
# HYPOTHETICAL EXAMPLE: Ferromagnetic (Ba/Sr/Ca)$BO_3$

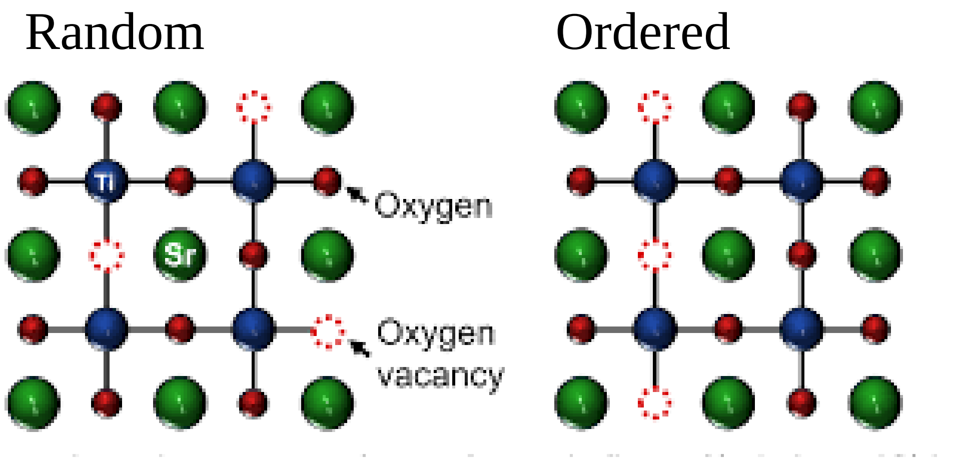
- Ferromagnetic transition temperature ($T_C$) highest when strong B-O-B interactions: short bond length and non-tilted bonding
- LEFT: with the largest **A = Ba** cation, ideal perovskite structure, **B-O-B** bond angle 180 $^{o}$C, but **B-O** bond length long → **$T_C$ = 320 K**
- MIDDLE: with the intermediate-sized **A = Sr** cation, ideal perovskite structure, **B-O-B** bond angle 180 $^{o}$C, and **B-O** bond length shorter → **$T_C$ = 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 $^{o}$C → **$T_C$ = 370 K**



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

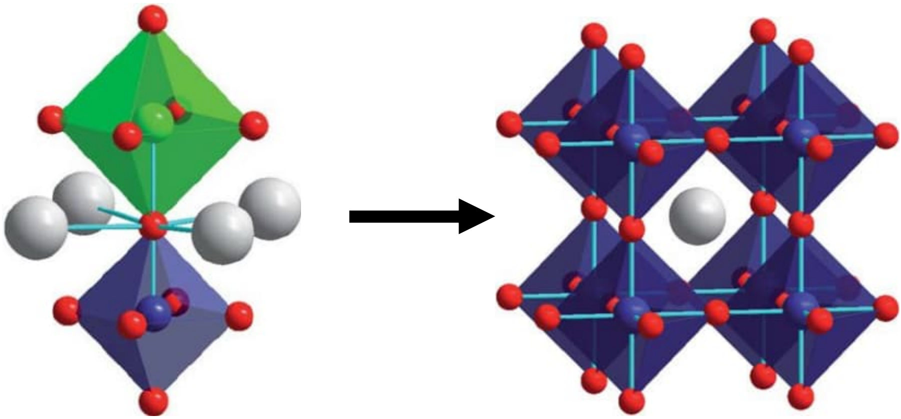
- Oxygen nonstoichiometry, even within the wide range of $0 < \delta < 0.5$, is very common among perovskite compounds
- **Oxygen content controls the metal valences and thereby the properties**
- Oxygen vacancies can be randomly located or ordered along different patterns

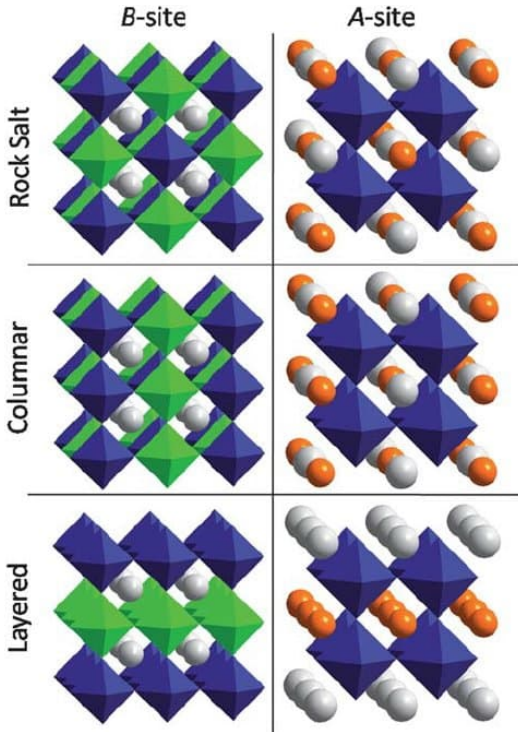


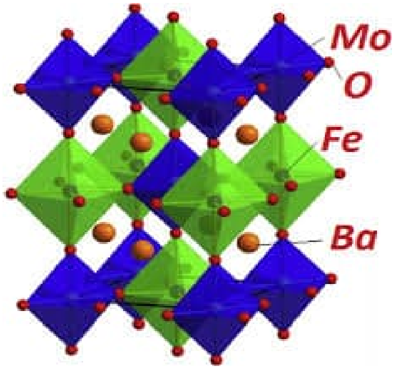


# DOUBLE PEROVSKITES

- 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 $Sr_2FeMoO_6$ (simultaneously ferromagnetic and electrically conducting → magnetic-field control of conductivity → spintronics)

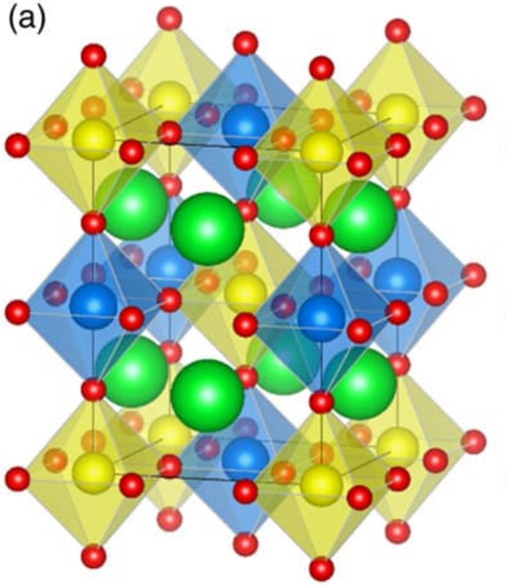


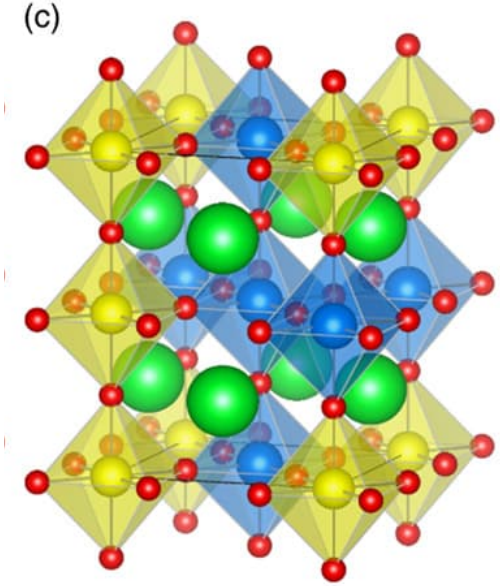


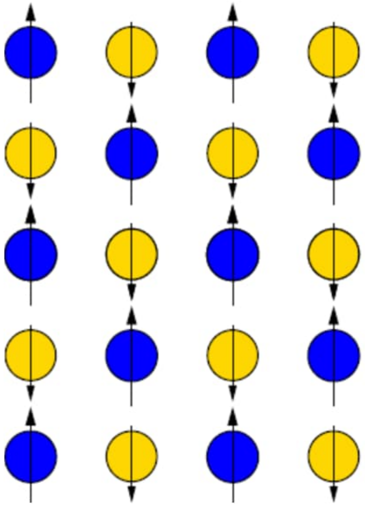


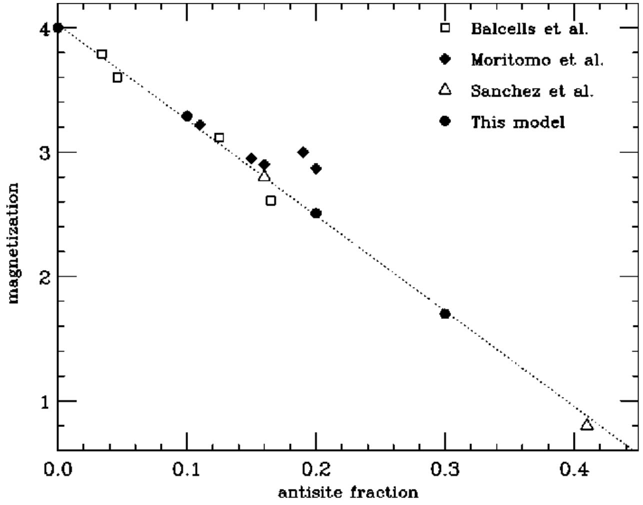
# ANTISITE DEFECTS in $A_2B'B''O_6$

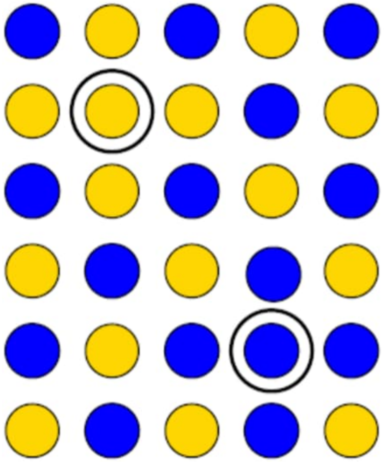
- Ordering of **B’** and **B”** is not always perfect
- Antisite (=defected) atom is B’ cation at the B” site, and vice versa

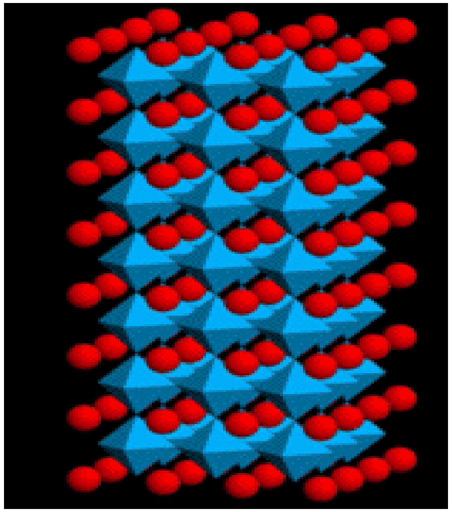






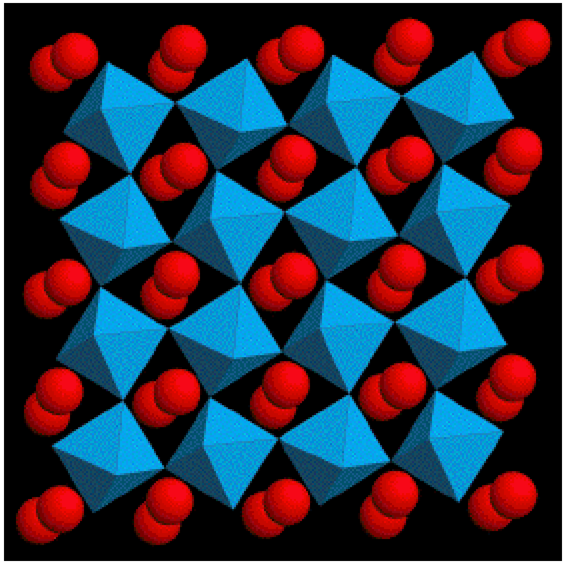




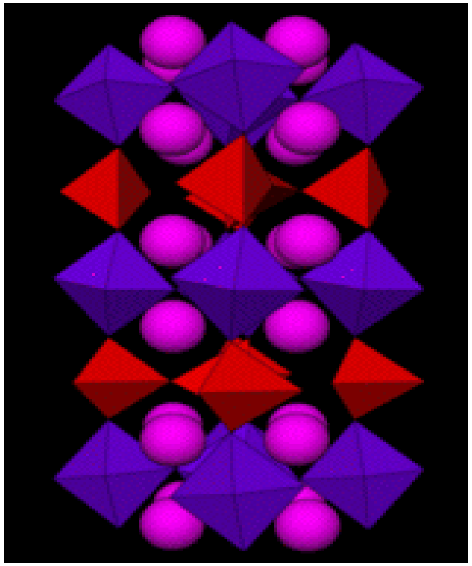


# “Distortions and Imperfections” in Perovskite Structure

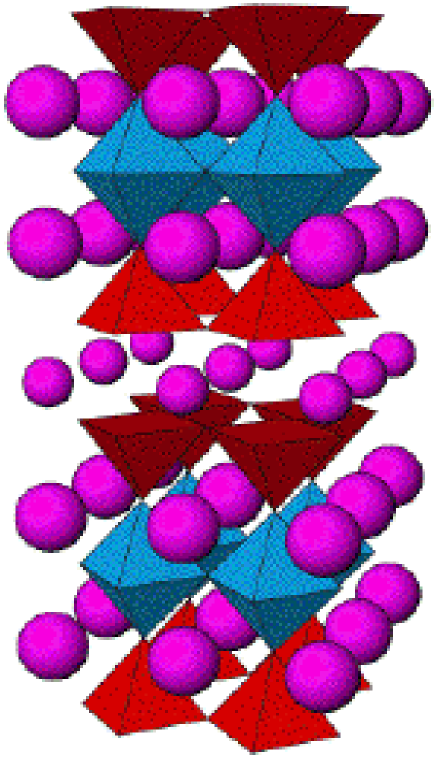
- often the source of the desired properties



Changes in
atomic positions



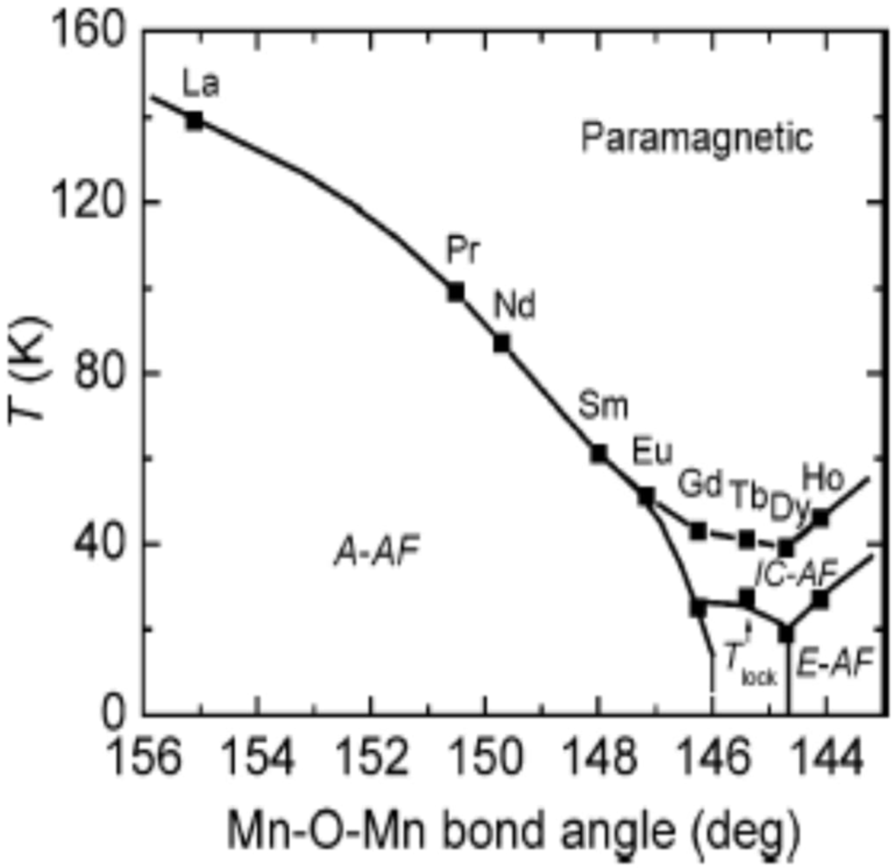
Oxygen deficiency

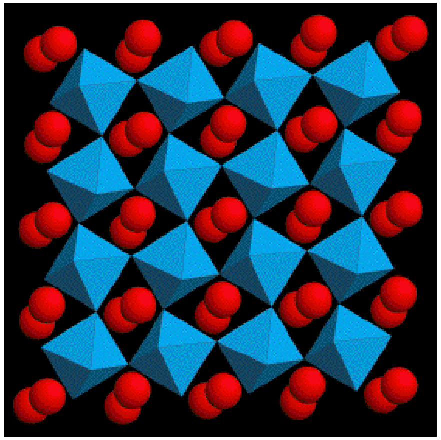


Ordering of cations
→ Layered structure

# 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 º)**





**$LnMnO_3$**

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

- **The International Union of Crystallography (IUCr):** https://www.iucr.org/
- A crystallography promo video from IUCr: https://www.youtube.com/watch?v=m2maeeA9z84&list
- Very nice introduction to crystallography: http://www.xtal.iqfr.csic.es/Cristalografia/cascara-en.html
- **The Crystallography Open Database** http://www.crystallography.net/cod/
- **Vesta** a small but very nice program to depicture crystal structures (e.g. load .cif files from the database and look at them with vesta): http://jp-minerals.org/vesta/en/