

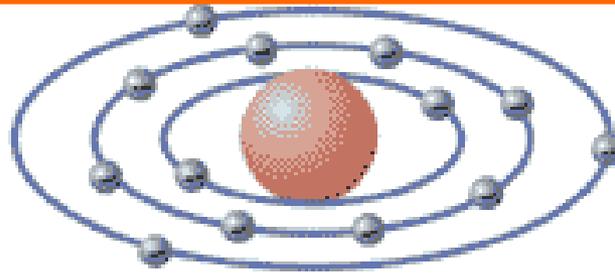
LECTURE 1: INTRODUCTION

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**.

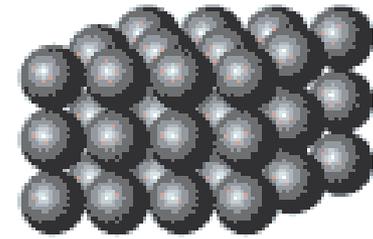
- An important goal is to understand the relations between basic crystal structure, defects, chemical environment (coordination and valence) and material properties
- For this target, we need a wide arsenal of different characterization techniques for the crystal structure (XRR, ND, ED, HRTEM, EXAFS), morphology (SEM, HRTEM, AFM), chemical environment (EXAFS, XANES, Mössbauer, XPS, IR, Raman), and properties (e.g. ND, Mössbauer for magnetic properties)
- One of the challenges: how to detect/investigate small distortions, different defects (vacancy, interstitial, antisite, etc.), mixed metal valences, magnetic structures, etc.
- We will also need techniques specific for thin-film characterization (GIXRD, XRR)
- We will often use the perovskite structure as a model/example case; however, it should be remembered that the issues discussed in the context of the perovskite structure are mostly transferable to many other inorganic materials

Structure of materials

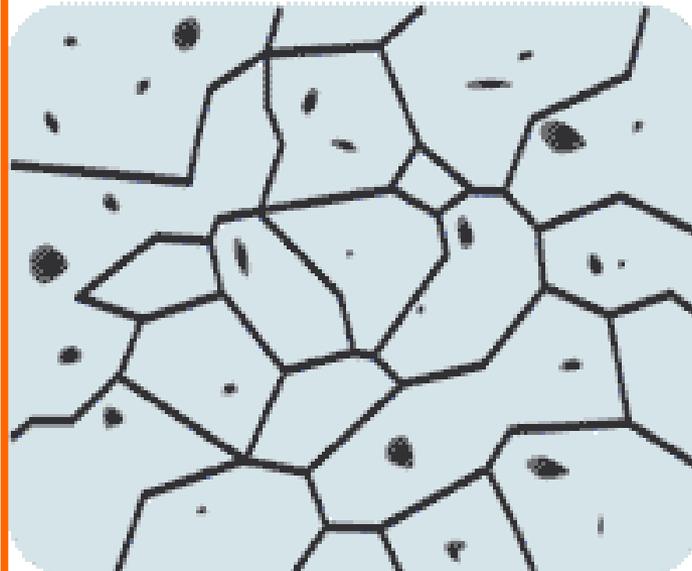
- (a) Single atoms (electron/spin configuration/structure = valence & magnetic moments)
- (b) Crystal structure (location of atoms in the crystal lattice)
- (c) microstructure (e.g. raerajat)
- (d) Phase/macrosopic structure



(a)



(b)



(c)

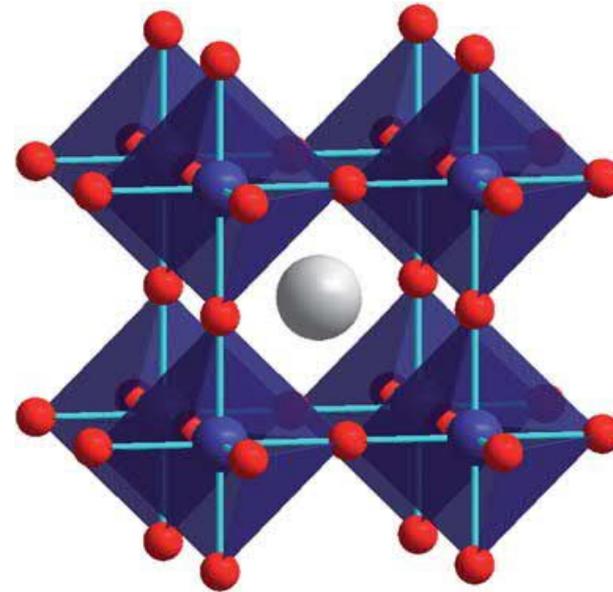


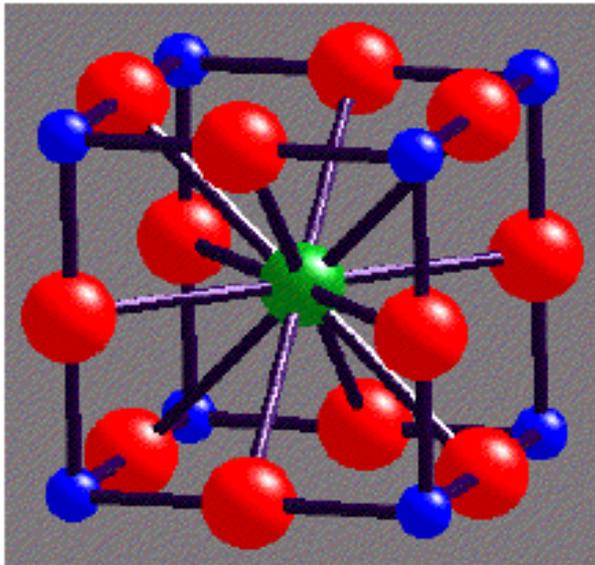
(d)

In all these levels
the material's
structure
significantly
affects
the material's
properties

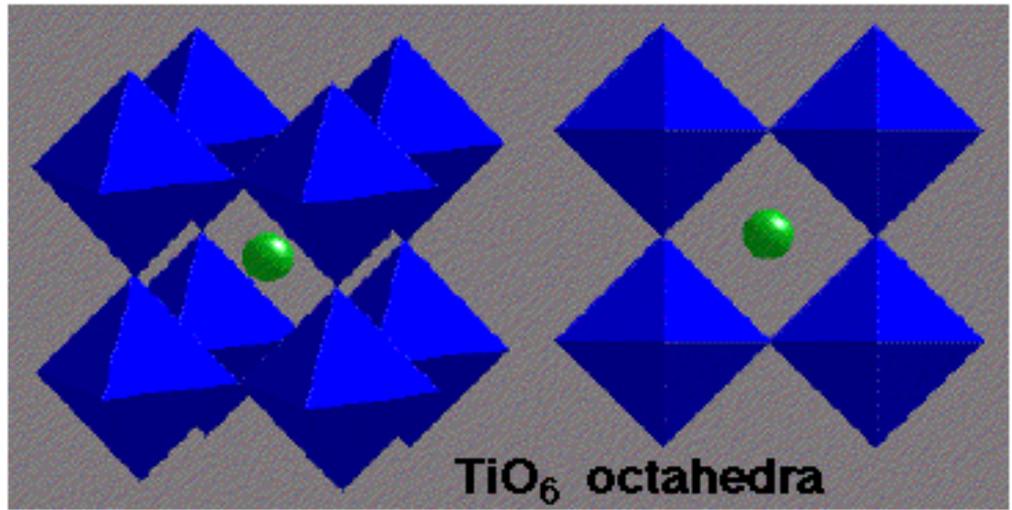
PEROVSKITE ABO_3

- 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





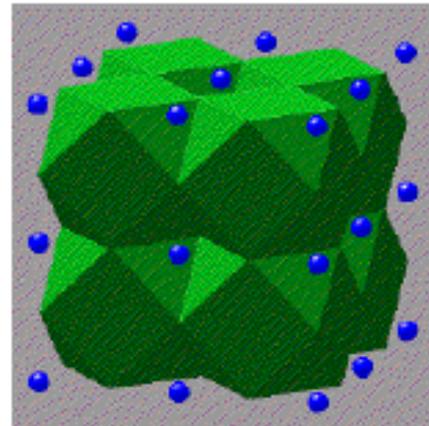
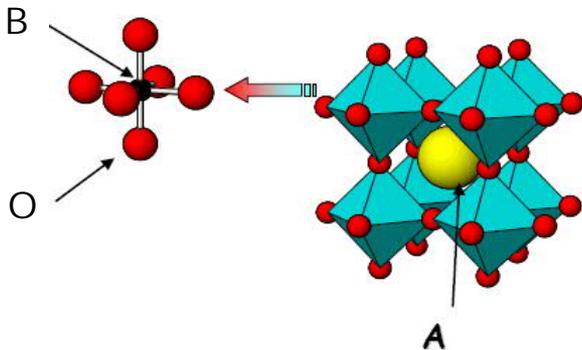
A-Cell



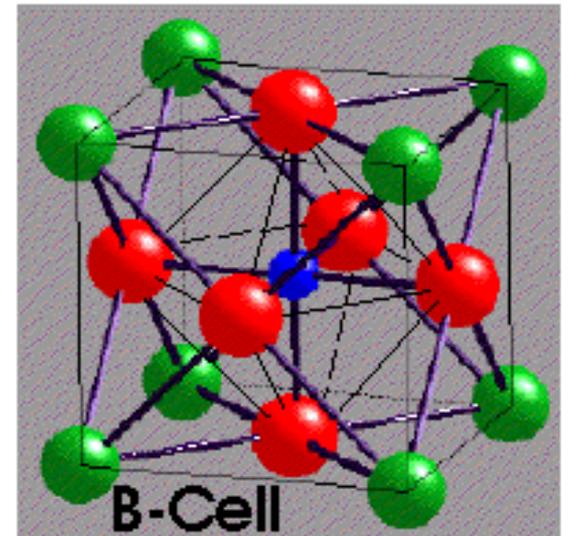
TiO₆ octahedra

Perovskite CaTiO₃

● Ca ● Ti ● O



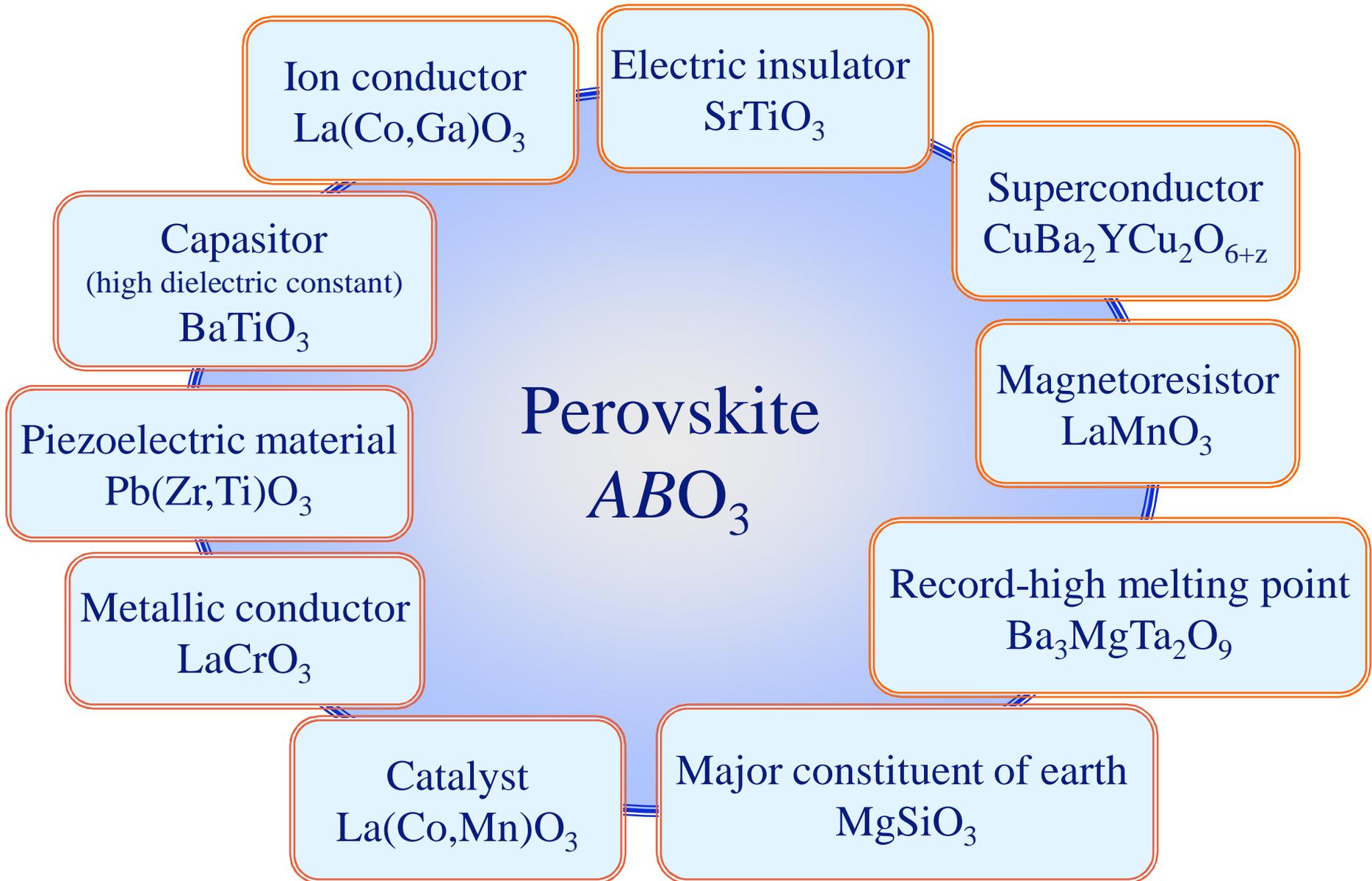
CaO₁₂ cubooctahedra



B-Cell

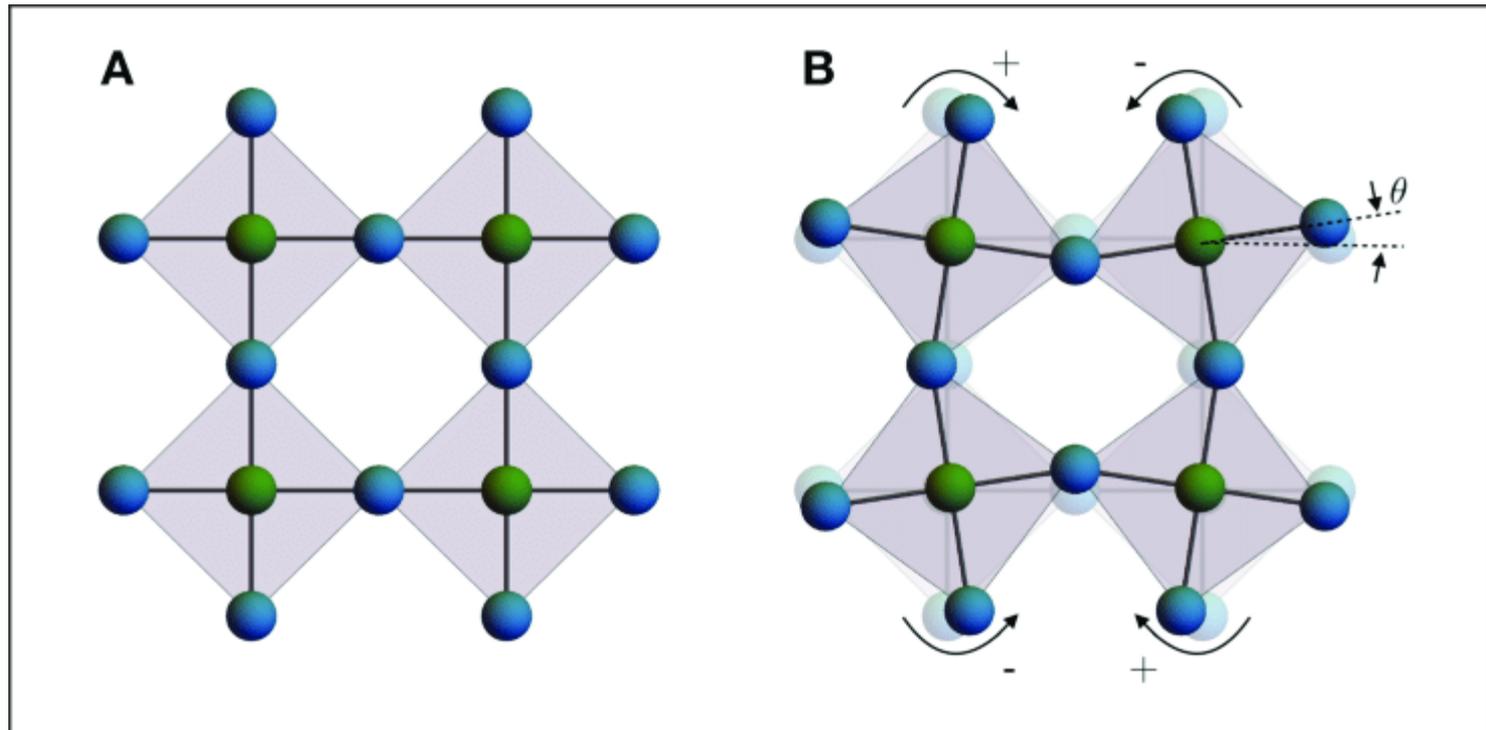
Different presentations of the perovskite structure

Perovskite – Multifunctional structure



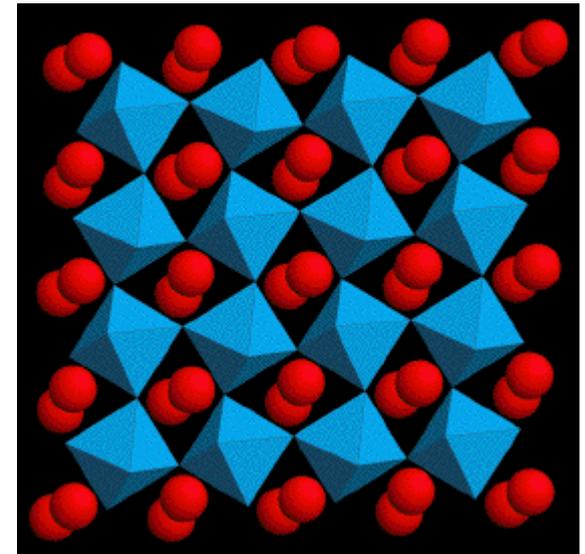
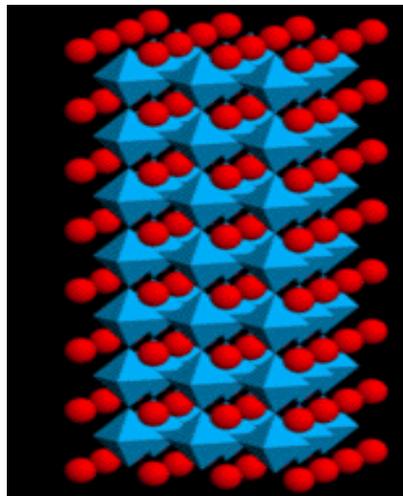
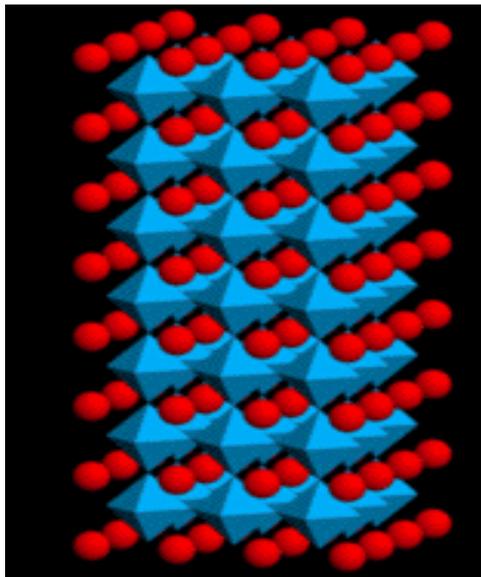
COMMON EXAMPLE OF DISTORTIONS in ABO_3

- 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.)



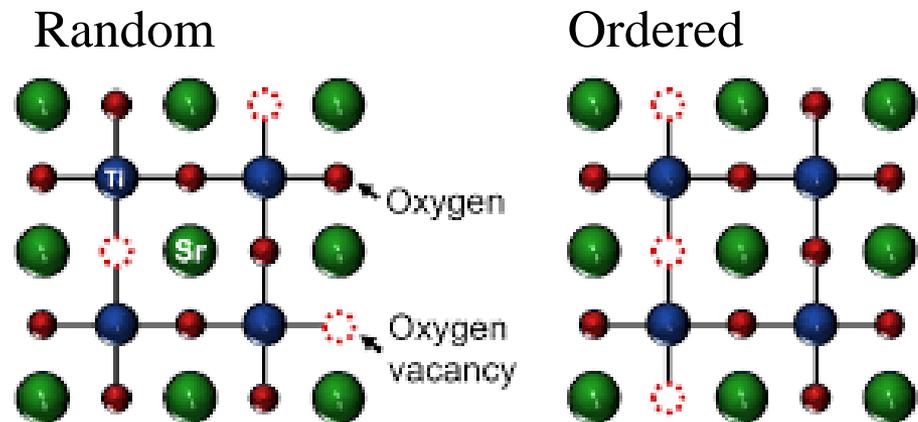
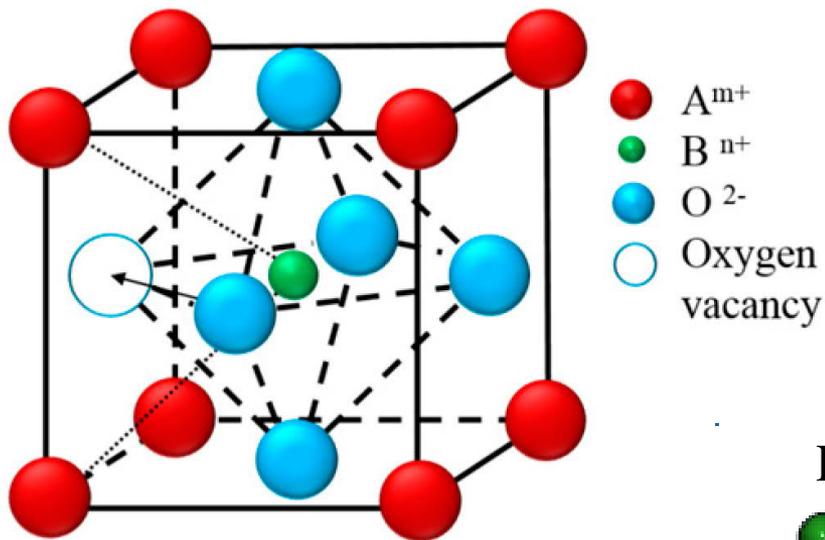
HYPOTHETICAL EXAMPLE: Ferromagnetic (Ba/Sr/Ca)BO₃

- 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



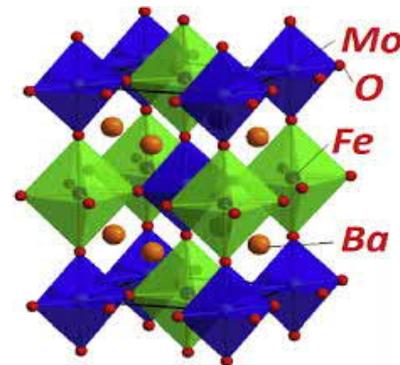
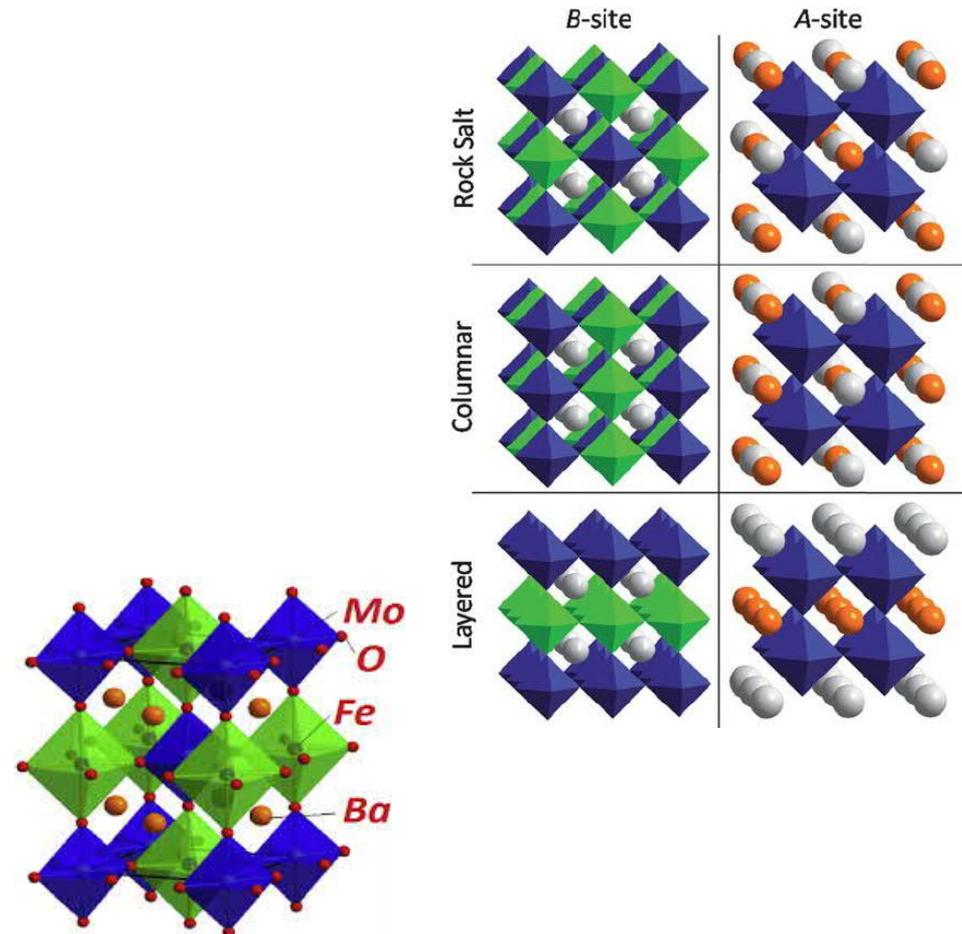
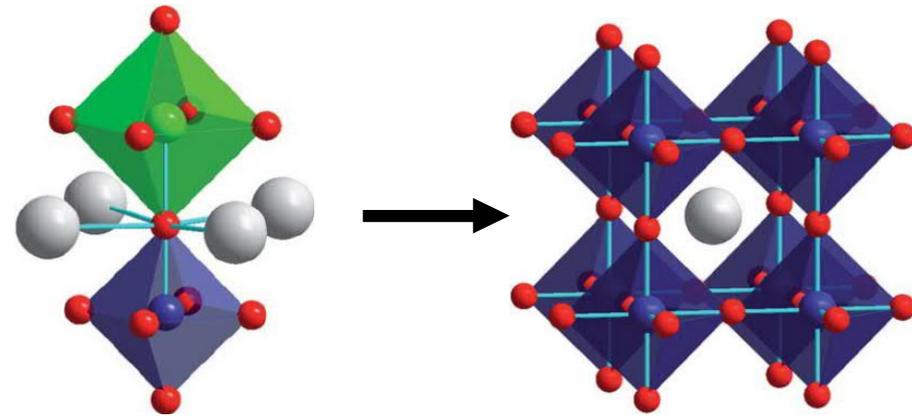
OXYGEN DEFICIENCY in $ABO_{3-\delta}$

- 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



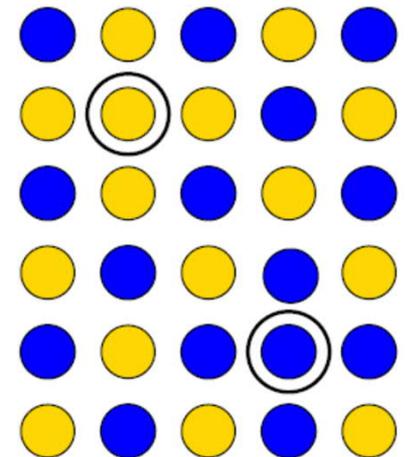
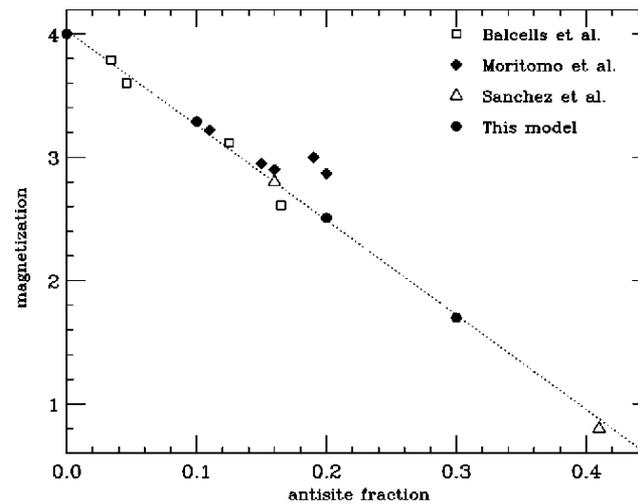
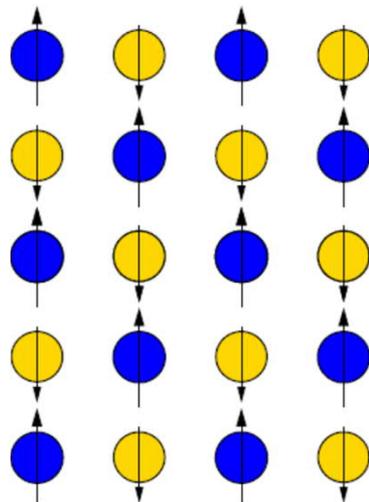
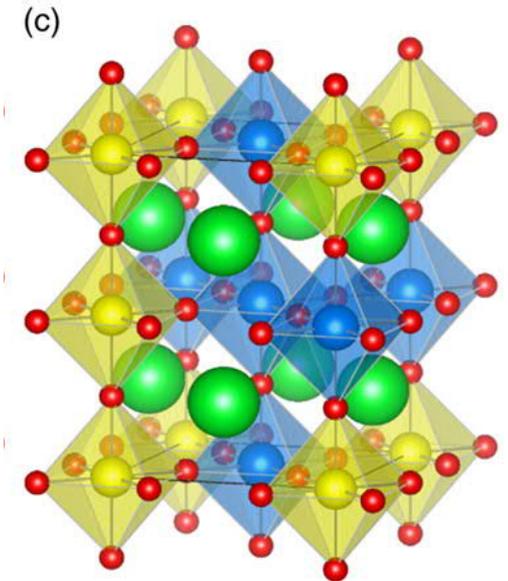
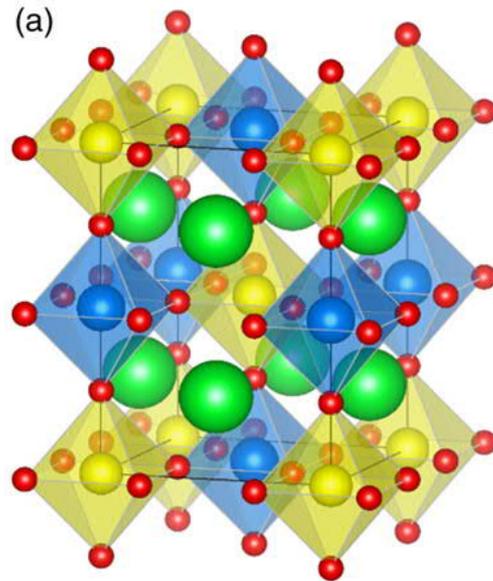
DOUBLE PEROVSKITES

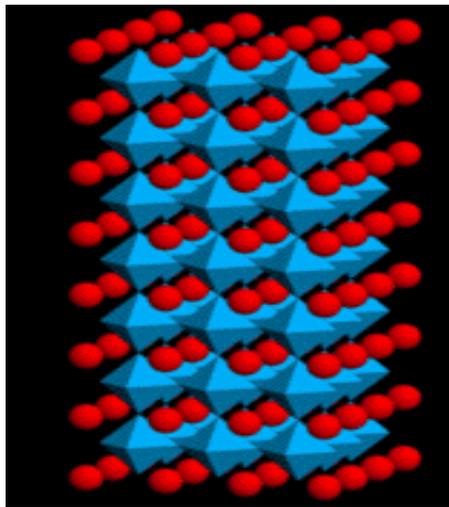
- Two different cations (**B'** and **B''**) occupy the B-site with 50%/50% ratio and in an ordered manner → B-site ordered double perovskite
- Two different cations (**A'** and **A''**) occupy the A-site with the 50%/50% ratio and in an ordered manner → A-site ordered double perovskite
- For both cases,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



ANTISITE DEFECTS in $A_2B'B''O_6$

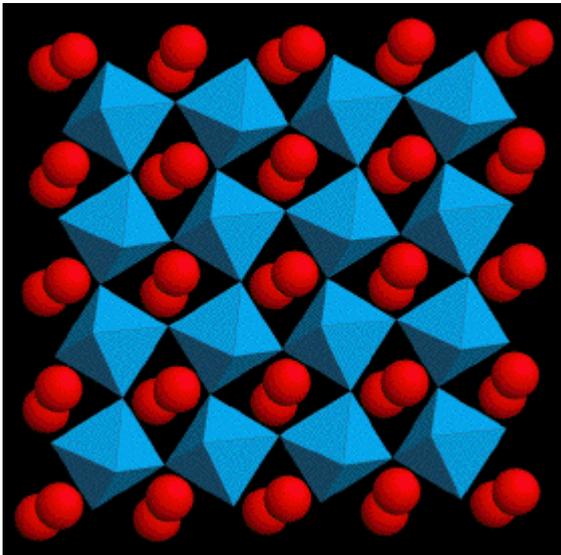
- Ordering of B' and B'' is not always perfect
- Antisite (=defected) atom is B' cation at the B'' site, and vice versa



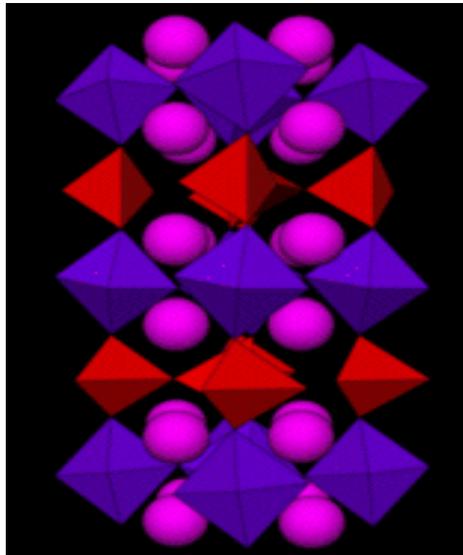


“Distortions and Imperfections” in Perovskite Structure

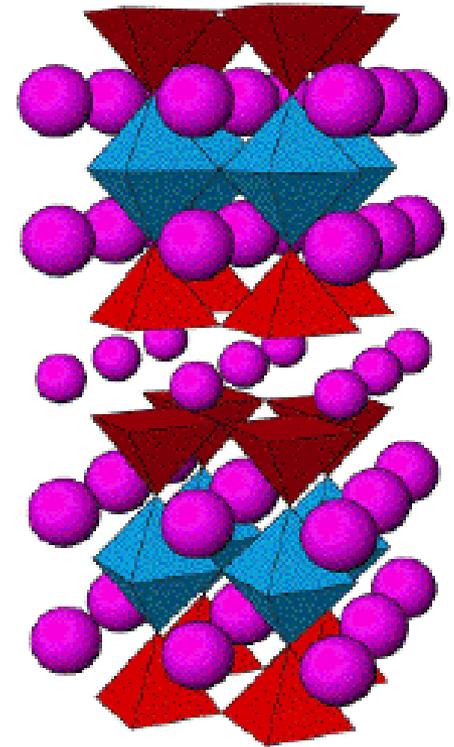
- often the source of the desired properties



Changes in
atomic positions



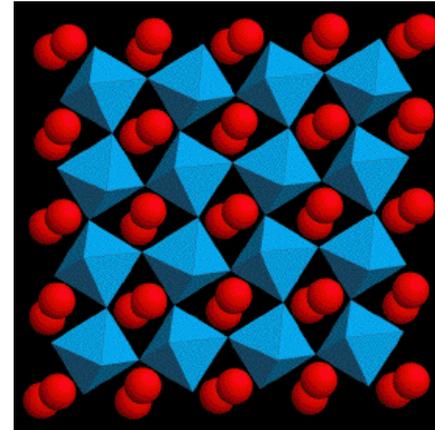
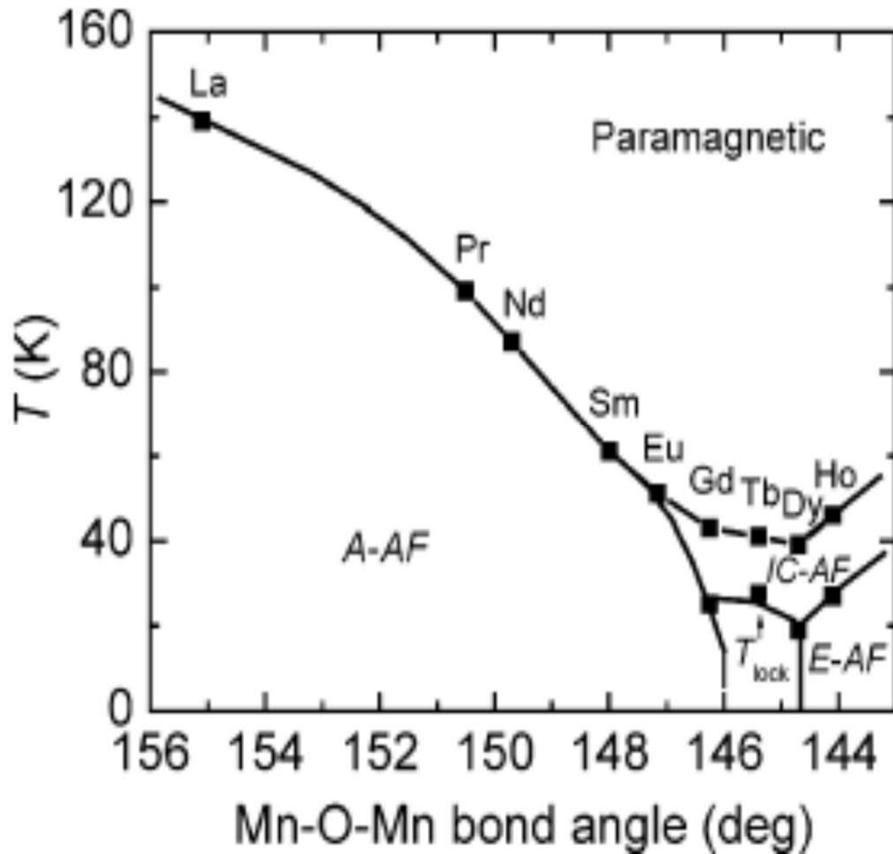
Oxygen deficiency



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°)



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 depict crystal structures (e.g. load .cif files from the database and look at them with vesta): <http://jp-minerals.org/vesta/en/>