Rutile or C4 Crystal Structure
(TiO$_2$ prototype)

- Not all structures have to be cubic or hexagonal lattices in order to be close packed.
- Rutile is an example of a non-cubic close packed structure. It’s tetragonal close packed.
- How many formula units?

- Since the ratio of Ti$^{4+}$ to O$^{2-}$ is 1:2 and there is one octahedral site per O$^{2-}$ ion, only one-half of the octahedral (O) sites will be occupied by Ti (filling every other row along [100]).

- Other compounds with rutile structure: CrO$_2$, GeO$_2$, MoO$_2$, TaO$_2$, WO$_2$, MgF$_2$, ZnF$_2$, NiF$_2$, etc.

- Filled rows are staggered in every other layer.
- Octahedra are linked in bands by sharing horizontal edges.
- Octahedra of neighboring chains share corners.

Analogous to: p. 680(585) in DeGraef
Rutile (TiO$_2$) Structure (continued)

Ti:CN=6 based on $\rho$; thus O:CN=3

- The Ti ions occupy half of the O$_H$ sites by filling every other row along [100].
- The filled rows are staggered in every other layer.

- Octahedra of neighboring chains share corners.
- Octahedra are linked in bands by sharing horizontal edges.

Projection down the [010]:

- The Ti ions occupy half of the O$_H$ sites by filling every other row along [100].
- The filled rows are staggered in every other layer.
Perovskite or $E2_1$ Crystal Structure
(BaTiO$_3$ prototype)

• Example that cations and anions can mix on eutactic sites.
• For BaTiO$_3$, an important ferroelectric, it’s a combination of Ba and O that form the cubic close packed framework. (O ions occupy $\frac{3}{4}$ of the CCP sites and the Ba ions occupy the remaining $\frac{1}{4}$).

• How many formula units?
• Ti: 6 coordinated to oxygen (octahedron): TiO$_6$ octahedron
• Ba: 12 coordinated to oxygen (ccp): BaO$_{12}$ cuboctahedron
• O: 4 coordinated to Ba and 2 coordinated to Ti (⇒ at any O site, 2 octahedra and 4 cuboctahedra are shared)

Share corners
2 x 2 x 2 unit cells
Share square faces

TiO$_6$ octahedron

BaO$_{12}$ cuboctahedron

Ti$^{4+}$ Ba$^{2+}$ O$^{2-}$

p. 672/578 in DeGraef
A cuboctahedron has 12 identical vertices, with two triangles and two squares meeting at each, and 24 identical edges, each separating a triangle from a square.

Another example: \( \text{Ca}_{1-x} \text{Y}_x \text{F}_{2+x} \) \((0 < x < 0.32)\): mineral Tveitite \((x=0.25-0.27)\), which contains an ordered calcium yttrium-fluoride phase with excess fluoride ions located in cuboctahedron clusters.
• Instead of Ti at the center, the Ti can also be at cell vertices and the Ba in the center site.
• Oxygen is now on midpoint of cell edges.
• Still maintain 1 formula unit/unit cell
• Nothing changes in terms of CN:
  • Ti: 6 coordinated to oxygen (octahedron): 8 corner sharing TiO$_6$ octahedrons at cell vertices.
  • Ba: 12 coordinated to oxygen (ccp): BaO$_{12}$ cuboctahedron in center (central cavity) of unit cell formed by the 8 connected TiO$_6$ octahedra.
• O: 4 coordinated to Ba and 2 coordinated to Ti
Experimental Evidence of Perovskite Structure


Chun-Lin Jia,$^{1,2,3,*}$ Juri Barthel,$^{2,4}$ Felix Gunkel,$^1$ Regina Dittmann,$^1$ Susanne Hoffmann-Eifert,$^1$ Lothar Houben,$^{1,2}$ Markus Lentzen,$^{1,2}$ and Andreas Thust$^{1,2}$

$^1$Peter Grünberg Institute (PGI), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany
$^2$Ernst Ruska-Centre (ER-C) for Microscopy and Spectroscopy with Electrons, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany
$^3$International Centre for Dielectric Research, Xi’an Jiaotong University, 710049 Xi’an, China
$^4$Central Facility for Electron Microscopy (CFE), Aachen University (RWTH), 52074 Aachen, Germany


Figure 3. a: HRTEM image of the nominally single unit cell layer of LAO embedded in STO, which was recorded at 300 kV accelerating voltage along the [110] direction of STO using the NCSI technique on an aberration-corrected TEM. The arrow denotes the nominally single LaO plane. b: Refined simulated image with the best match to the experimental image. Note that the experimental image (a) and the best fitting simulated image (b) are displayed here within the same range of the absolute image contrast.