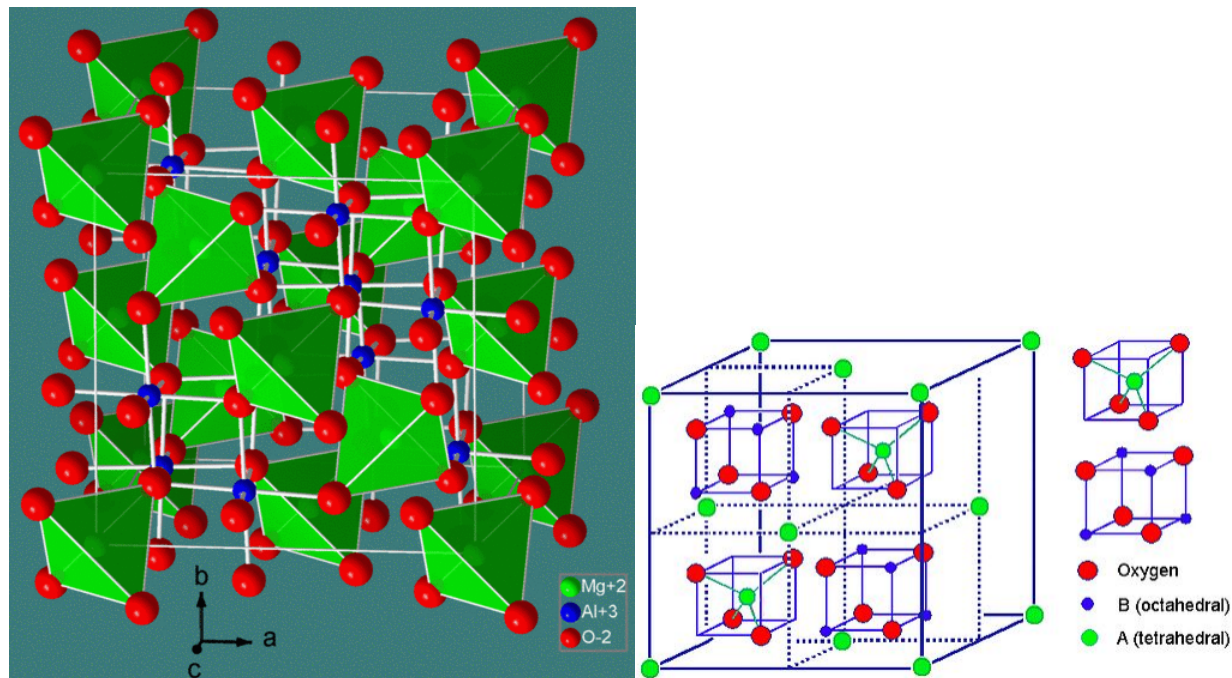


8.7: Spinel, Perovskite, and Rutile Structures

There are three more structures, which are derived from close-packed lattices, that are particularly important because of the material properties of their compounds. These are the **spinel** structure, on which ferrites and other magnetic oxides are based, the **perovskite** structure, which is adopted by ferroelectric and superconducting oxides, and the **rutile** structure, which is a common binary 6:3 structure adopted by oxides and fluorides.



The **spinel structure** is formulated MM'_2X_4 , where M and M' are tetrahedrally and octahedrally coordinated cations, respectively, and X is an anion (typically O or F). The structure is named after the mineral $MgAl_2O_4$, and oxide spinels have the general formula AB_2O_4 .

In the **normal spinel** structure, there is a close-packed array of anions. The A-site cations fill 1/8 of the tetrahedral holes and the B-site cations fill 1/2 of the octahedral holes. A polyhedral view of the normal spinel unit cell is shown at the left, and a simplified view (with the contents of the back half of the cell removed for clarity) is shown above. Each unit cell contains eight formula units and has a composition $A_8B_{16}O_{32}$.

Inverse spinels have a closely related structure (with the same large unit cell) in which the A-site ions and half of the B-site ions switch places. Inverse spinels are thus formulated $B(AB)O_4$, where the AB ions in parentheses occupy octahedral sites, and the other B ions are on tetrahedral sites. There are also mixed spinels, which are intermediate between the **normal** and **inverse** spinel structure.

Some spinel and inverse spinel AB combinations are:

$A^{2+}B^{3+}$, e.g., $MgAl_2O_4$ (normal spinel)

$A^{4+}B^{2+}$, e.g., $Pb_3O_4 = Pb^{II}(Pb^{II}Pb^{IV})O_4$ (inverse spinel)

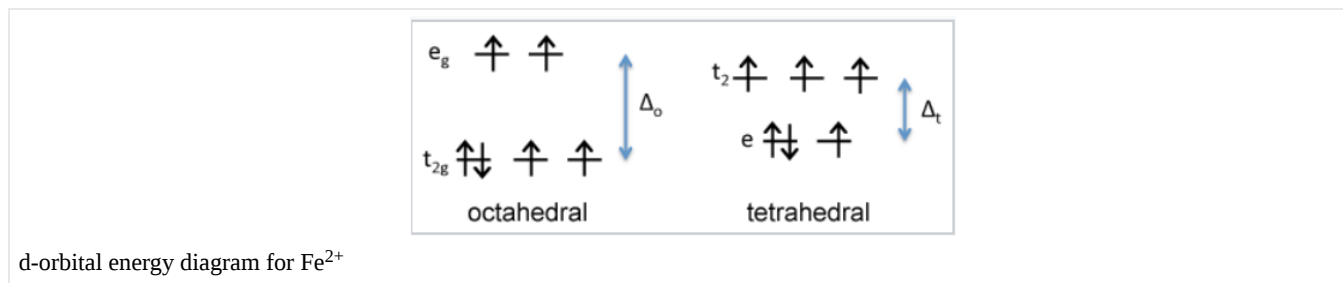
$A^{6+}B^{+}$, e.g., Na_2WO_4 (normal spinel)

Many magnetic oxides, such as Fe_3O_4 and $CoFe_2O_4$, are spinels.

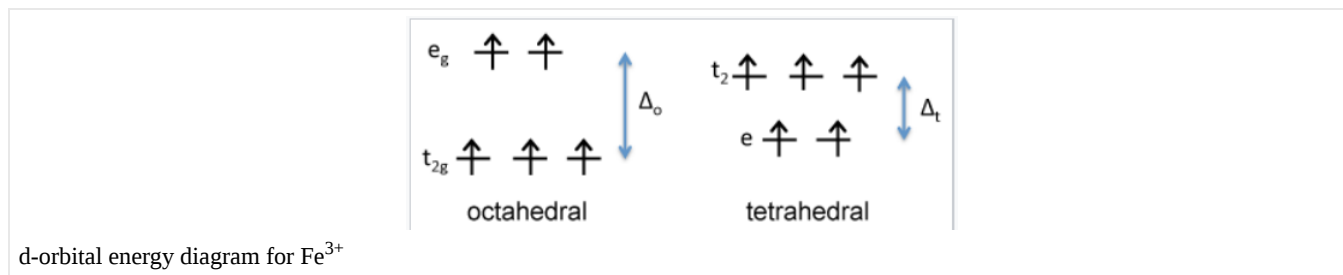
Normal vs. inverse spinel structure

For transition metal oxide spinels, the choice of the normal vs. inverse spinel structure is driven primarily by the **crystal field stabilization energy** (CFSE) of ions in the tetrahedral and octahedral sites. For spinels that contain 3d elements such as Cr, Mn, Fe, Co, and Ni, the electron configuration is typically **high spin** because O^{2-} is a **weak field ligand**.

As an example, we can consider magnetite, Fe_3O_4 . This compound contains one Fe^{2+} and two Fe^{3+} ions per formula unit, so we could formulate it as a normal spinel, $\text{Fe}^{2+}(\text{Fe}^{3+})_2\text{O}_4$, or as an inverse spinel, $\text{Fe}^{3+}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4$. Which one would have the lowest energy?



First we consider the crystal field energy of the Fe^{2+} ion, which is d^6 . Comparing the tetrahedral and high spin octahedral diagrams, we find that the CFSE in an **octahedral** field of O^{2-} ions is $[(4)(\frac{2}{5}) - (2)(\frac{3}{5})]\Delta_o - P = 0.4\Delta_o - P$. In the **tetrahedral** field, the CFSE is $[(3)(\frac{3}{5}) - (3)(\frac{2}{5})]\Delta_t - P = 0.6\Delta_t - P$. Since Δ_o is about 2.25 times larger than Δ_t , the octahedral arrangement has a larger CFSE and is preferred for Fe^{2+} .



In contrast, it is easy to show that Fe^{3+} , which is d^5 , would have a CFSE of zero in either the octahedral or tetrahedral geometry. This means that Fe^{2+} has a preference for the octahedral site, but Fe^{3+} has no preference. Consequently, we place Fe^{2+} on octahedral sites and **Fe_3O_4 is an inverse spinel**, $\text{Fe}^{3+}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4$.

Ferrites are compounds of general formula $\text{M}^{\text{II}}\text{Fe}_2\text{O}_4$. We can see that magnetite is one example of a ferrite (with $\text{M} = \text{Fe}$). Other divalent metals ($\text{M} = \text{Mg}, \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$) also form ferrites. Ferrites can be normal or inverse spinels, or mixed spinels, depending on the CFSE of the M^{II} ion. Based on their CFSE, Fe^{2+} , Co^{2+} , and Ni^{2+} all have a strong preference for the octahedral site, so those compounds are all inverse spinels. ZnFe_2O_4 is a normal spinel because the small Zn^{2+} ion (d^{10}) fits more easily into the tetrahedral site than Fe^{3+} (d^5), and both ions have zero CFSE. MgFe_2O_4 and MnFe_2O_4 , in which all ions have zero CFSE and no site preference, are mixed spinels. **Chromite** spinels, $\text{M}^{\text{II}}\text{Cr}_2\text{O}_4$, are always **normal spinels** because the d^3 Cr^{3+} ion has a strong preference for the octahedral site.

Examples of normal and inverse spinel structures:

MgAl_2O_4 is a normal spinel since both Mg^{2+} and Al^{3+} are non-transition metal ions and thus $\text{CFSE} = 0$. The more highly charged Al^{3+} ion prefers the octahedral site, where it is surrounded by six negatively charged oxygen atoms.

Mn_3O_4 is a normal spinel since the Mn^{2+} ion is a high spin d^5 system with zero CFSE. The two Mn^{3+} ions are high spin d^4 with higher CFSE on the octahedral sites ($3/5 \Delta_o$) than on the tetrahedral site ($2/5 \Delta_t \sim 1/5 \Delta_o$).

Fe_3O_4 is an inverse spinel since the Fe^{3+} ion is a high spin d^5 system with zero CFSE. Fe^{2+} is a high spin d^6 system with more CFSE on an octahedral site than on a tetrahedral one.

NiFe_2O_4 is again an inverse spinel since Ni^{2+} (a d^8 ion) prefers the octahedral site and the CFSE of Fe^{3+} (a d^5 ion) is zero.

FeCr_2O_4 is a normal spinel since Fe^{2+} is high spin d^6 ion with $\text{CFSE} = [4(\frac{2}{5}) - 2(\frac{3}{5})]\Delta_o = \frac{2}{5}\Delta_o$ on an octahedral site, and Cr^{3+} is a d^3 ion with $\text{CFSE} = 3(2/5) \Delta_o = 6/5 \Delta_o$. Hence it is more energetically favorable for Cr^{3+} to occupy both of the octahedral sites.

Co_3O_4 is a normal spinel. Even in the presence of weak field oxo ligands, Co^{3+} is a low spin d^6 ion with very high CFSE on the octahedral sites, because of the high charge and small size of the Co^{3+} ion. Hence the Co^{3+} ions occupy both octahedral

sites, and Co^{2+} occupies the tetrahedral site.

Magnetism of ferrite spinels

Ferrite spinels are of technological interest because of their magnetic ordering, which can be ferrimagnetic or antiferromagnetic depending on the structure (normal or inverse) and the nature of the metal ions. Fe_3O_4 , CoFe_2O_4 , and NiFe_2O_4 are all inverse spinels and are ferrimagnets. The latter two compounds are used in magnetic recording media and as deflection magnets, respectively.

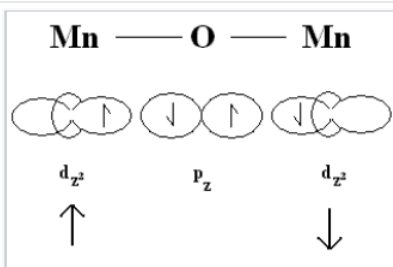
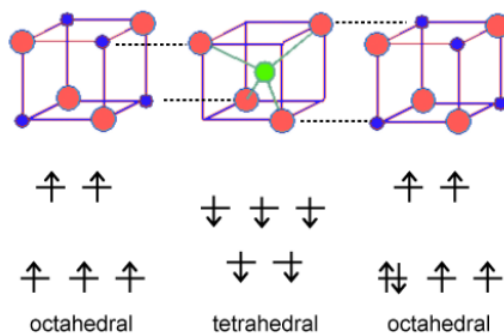


Illustration of antiferromagnetic superexchange between two transition metal cations through a shared oxygen atom.

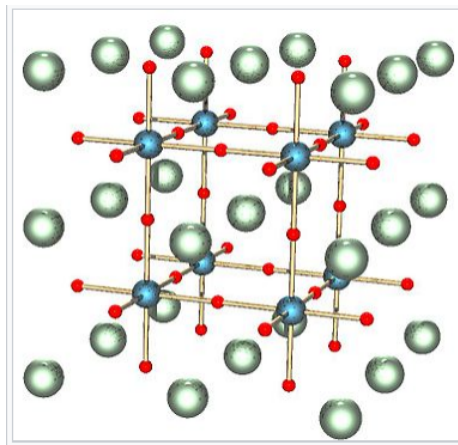
In order to understand the magnetism of ferrites, we need to think about how the unpaired spins of metal ions are coupled in oxides. If an oxide ion is shared by two metal ions, it can mediate the coupling of spins by superexchange as shown at the right. The coupling can be antiferromagnetic, as shown, or ferromagnetic, depending on the orbital filling and the symmetry of the orbitals involved. The **Goodenough-Kanamori rules** predict the local magnetic ordering (ferromagnetic vs. antiferromagnetic) that results from superexchange coupling of the electron spins of transition metal ions. For ferrites, the strongest coupling is between ions on neighboring **tetrahedral and octahedral sites**, and the ordering of spins between these two sites is reliably **antiferromagnetic**.



Because all the tetrahedral and octahedral sites in a spinel or inverse spinel crystal are coupled together identically, it works out that ions on the tetrahedral sites will all have one orientation (e.g., spin down) and ions on all the octahedral sites will have the opposite orientation (e.g., spin up). If the number of spins on the two sites is the same, then the solid will be antiferromagnetic. However, if the **number of spins is unequal** (as in the case of Fe_3O_4 , CoFe_2O_4 , and NiFe_2O_4) then the solid will be **ferrimagnetic**. This is illustrated above for Fe_3O_4 . The spins on the Fe^{3+} sites cancel, because half of them are up and half are down. However, the four unpaired electrons on the Fe^{2+} ions are all aligned the same way in the crystal, so the compound is ferrimagnetic.

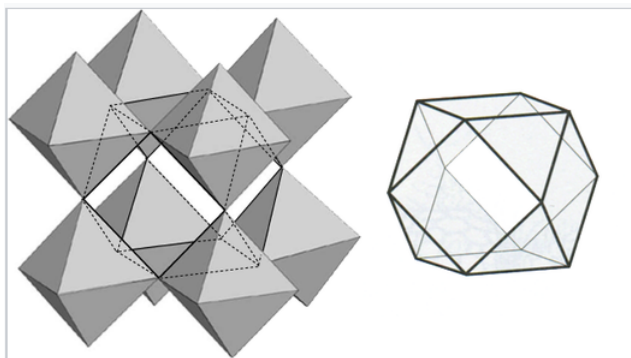
Perovskites are **ternary oxides** of general formula ABO_3 . More generally, the perovskite formula is ABX_3 , where the anion X can be **O, N, or halogen**. The A ions are typically large ions such as Sr^{2+} , Ba^{2+} , Rb^+ , or a lanthanide 3+ ion, and the B ions are smaller transition metal ions such as Ti^{4+} , Nb^{5+} , Ru^{4+} , etc. The mineral after which the structure is named has the formula CaTiO_3 .

The perovskite structure has simple cubic symmetry, but is related to the fcc lattice in the sense that the A site cations and the three O atoms comprise a fcc lattice. The B-site cations fill 1/4 of the octahedral holes and are surrounded by six oxide anions.



ABX₃ perovskite structure. A, B, and X are white, blue, and red, respectively.

The coordination of the A ions in perovskite and the arrangement of BO₆ octahedra is best understood by looking at the ReO₃ structure, which is the same structure but with the A-site cations removed. In the polyhedral representation of the structure shown at the right, it can be seen that the octahedra share all their vertices but do not share any octahedral edges. This makes the ReO₃ and perovskite structures flexible, like three-dimensional wine racks, in that the octahedra can **rotate and tilt cooperatively**. Eight such octahedra surround a large **cuboctahedral cavity**, which is the site of the A ions in the perovskite structure. Cations in these sites are coordinated by 12 oxide ions, as expected from the relationship between the perovskite and fcc lattices.



Polyhedral representation of the ReO₃ structure showing the large cuboctahedral cavity that is surrounded by 12 oxygen atoms

Because the A-site is empty in the ReO₃ structure, compounds with that structure can be reversibly **intercalated** by small ions such as **Li⁺ or H⁺**, which then occupy sites in the cuboctahedral cavity. For example, smart windows that darken in bright sunlight contain the **electrochromic** material WO₃, which has the ReO₃ structure. In the sunlight, a photovoltaic cell drives the reductive intercalation of WO₃ according to the reaction:

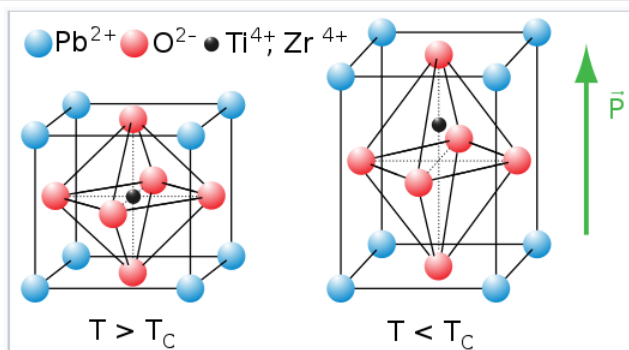


WO₃ is a light yellow compound containing d⁰ W(VI). In contrast, H_xWO₃, which is mixed-valent W(V)-W(VI) = d¹-d⁰, has a deep blue color. Such coloration is typical of mixed-valence transition metal complexes because their d-electrons can be excited to delocalized conduction band levels by red light. Because the electrochemical intercalation-deintercalation process is powered by a solar cell, the tint of the windows can adjust automatically to the level of sunlight.

Ferroelectric perovskites

The flexibility of the network of corner-sharing BO₆ octahedra is also very important in ferroelectric oxides that have the perovskite structure. In some perovskites with small B-site cations, such as Ti⁴⁺ and Nb⁵⁺, the cation is too small to fit symmetrically in the BO₆ octahedron. The octahedron distorts, allowing the cation to move off-center. These distortions can be **tetragonal** (as in the example shown at the right), **rhombohedral**, or **orthorhombic**, depending on whether the cation moves towards a vertex, face, or edge of the BO₆ octahedron. Moving the cation off-center in the octahedron creates an **electric dipole**. In

ferroelectrics, these dipoles align in neighboring unit cells through cooperative rotation and tilting of octahedra. The crystal thus acquires a net electrical polarization.



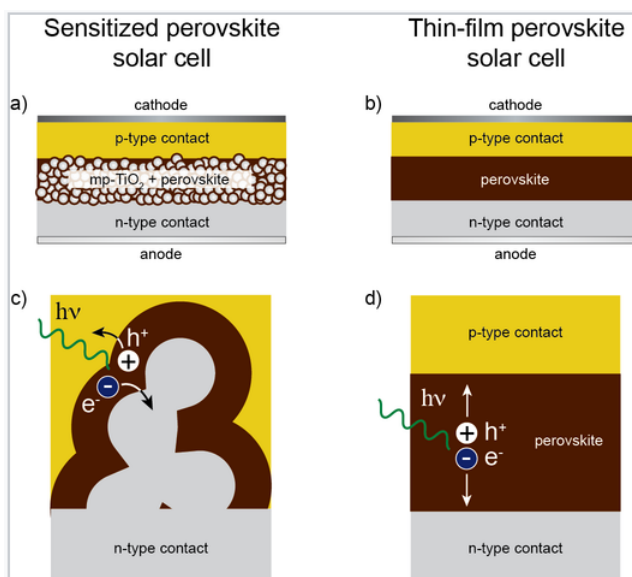
Tetragonal distortion of the perovskite unit cell in the ferroelectric oxide PZT, $\text{PbTi}_x\text{Zr}_{1-x}$

Ferroelectricity behaves analogously to **ferromagnetism**, except that the polarization is electrical rather than magnetic. In both cases, there is a **critical temperature** (T_c) above which the **spontaneous polarization** of the crystal disappears. Below T_c , the electric polarization of a ferroelectric can be switched with a coercive field, and hysteresis loop of polarization vs. field resembles that of a ferromagnet. Above T_c , the crystal is **paraelectric** and has a high dielectric permittivity.

Ferroelectric and paraelectric oxides (along with piezoelectrics and pyroelectrics) have a wide variety of applications as switches, actuators, transducers, and dielectrics for capacitors. **Ferroelectric capacitors** are important in memory devices (FRAM) and in the tuning circuits of cellular telephones. **Multiferroics**, which are materials that are simultaneously ferroelectric and ferromagnetic, are rare and are being now intensively researched because of their potential applications in electrically addressable magnetic memory.

Halide perovskites (ABX_3 , $\text{X} = \text{Cl}, \text{Br}, \text{I}$) can be made by combining salts of monovalent A ions ($\text{A}^+ = \text{Cs}^+, \text{NH}_4^+, \text{RNH}_3^+$) and divalent metal salts such as PbCl_2 or PbI_2 . These compounds have sparked recent interest as light absorbers for **thin film solar cells** that produce electricity from sunlight. Lead and tin halide perovskites can be grown as thin films from solution precursors or by thermal evaporation at relatively low temperatures. In some lead halide perovskites, the mobility of electrons and holes is very high, comparable to that of more expensive III-V semiconductors such as GaAs, which must be grown as very pure single crystals at high temperatures for use in solar cells. Because of their high carrier mobility, some lead halide perovskites are also electroluminescent and are of interest as inexpensive materials for light-emitting diodes (LEDs).

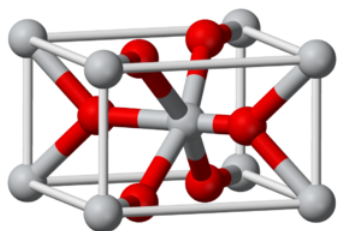
Tin and lead halide perovskites were first studied in the 1990s as materials for thin film electronics,^[4] and more recently as light absorbers in dye-sensitized solar cells. Soon after the results on dye-sensitized perovskite cells were reported, it was discovered that halide perovskites could also be used in thin film solid state solar cells. The structures of these solar cells are shown schematically at the right. The highest reported solar power conversion efficiencies of perovskite solar cells have jumped from 3.8% in 2009^[5] to 10.2% in 2012^[6] and a certified 20.1% in 2014.^[7] The highest performing cells to date contain divalent lead in the perovskite B cation site and a mixture of methylammonium and formamidinium ions in the perovskite A cation site.



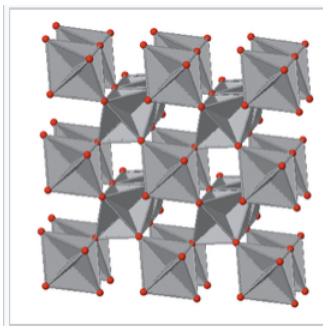
a) Solar cell architecture in which a lead halide perovskite absorber coats a layer of nanocrystalline anatase TiO₂. b) Thin-film solar cell, with a layer of lead halide perovskite sandwiched between two selective contacts. c) Charge generation and extraction in the sensitized architecture and d) in the thin-film architecture.

Despite their very impressive efficiency, perovskite solar cells are stable for relatively short periods of time and are sensitive to air and moisture. Current research is focused on understanding the degradation mechanisms of these solar cells and improving their stability under operating conditions.

The **rutile structure** is an important MX₂ (X = O, F) structure. It is a 6:3 structure, in which the cations are octahedrally coordinated by anions, and as such is intermediate in polarity between the CaF₂ (8:4) and SiO₂ (4:2) structures. The mineral rutile is one of the polymorphs of TiO₂, the others (anatase and brookite) also being 6:3 structures.



The rutile structure can be described as a distorted version of the NiAs structure with half the cations removed. Recall that compounds with the NiAs structure were typically metallic because the metal ions are eclipsed along the stacking axis and thus are in relatively close contact. In rutile, the MO₆ **octahedra share edges** along the tetragonal c-axis, and so some rutile oxides, such as **NbO₂, RuO₂ and IrO₂**, are also **metallic** because of **d-orbital overlap** along that axis. These compounds are important as electrolyzer catalysts and catalyst supports because they combine high catalytic activity with good electronic conductivity.



View down the tetragonal c-axis of the rutile lattice, showing edge-sharing MO_6 octahedra.

Rutile TiO_2 , because of its high refractive index, is the base pigment for white paint. It is a wide bandgap semiconductor that has also been extensively researched as an electrode for water splitting solar cells and as a photocatalyst (primarily as the anatase polymorph) for degradation of pollutants in air and water. Self-cleaning glass exploits the photocatalytic properties of a thin film of TiO_2 to remove oily substances from the glass surface and improve the wetting properties of the glass.

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