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’₂X₄, 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 Mg₆Al₂O₄, and oxide spinels have the general formula AB₂O₄.

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 A₈B₁₆O₃₂.
**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$_2$O$_4$ (normal spinel)
- $A^{4+}B^{2+}$, e.g., Pb$_3$O$_4 = Pb^{II}(Pb^{II}Pb^{IV})O_4$ (inverse spinel)
- $A^{6+}B^+$, e.g., Na$_2$WO$_4$ (normal spinel)

Many magnetic oxides, such as Fe$_3$O$_4$ and CoFe$_2$O$_4$, are spinels.

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**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$_3$O$_4$. This compound contains one Fe$^{2+}$ and two Fe$^{3+}$ ions per formula unit, so we could formulate it as a normal spinel, Fe$^{2+}(Fe^{3+})_2$O$_4$, or as an inverse spinel, Fe$^{3+}(Fe^{2+}Fe^{3+})O_4$. Which one would have the lowest energy?

The d-orbital energy diagram for Fe$^{2+}$ shows the splitting of the d orbitals into tetrahedral and octahedral orbitals.

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 $\Delta_o = (4)(\frac{2}{5}) - 2(\frac{3}{5}) = 0.4\Delta_o - P$. In the tetrahedral field, the CFSE is $\Delta_t = (3)(\frac{3}{5}) - 3(\frac{2}{5}) = 0.6\Delta_t - P$. Since $\Delta_o$ is about 2.25 times larger than $\Delta_t$, 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\(_3\)O\(_4\) is an inverse spinel, Fe\(^{3+}\)(Fe\(^{2+}\)Fe\(^{3+}\))O\(_4\).

**Ferrites** are compounds of general formula M\(_{II}\)Fe\(_2\)O\(_4\). We can see that magnetite is one example of a ferrite (with M = Fe). Other divalent metals (M = Mg, Mn, Co, Ni, 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\(_2\)O\(_4\) 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\(_2\)O\(_4\) and MnFe\(_2\)O\(_4\), in which all ions have zero CFSE and no site preference, are mixed spinels. Chromite spinels, M\(_{II}\)Cr\(_2\)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\(_2\)O\(_4\) is a normal spinel since both Mg\(^{2+}\) and Al\(^{3+}\) are non-transition metal ions and thus CFSE = 0. The more highly charged Al\(^{3+}\) ion prefers the octahedral site, where it is surrounded by six negatively charged oxygen atoms.

Mn\(_3\)O\(_4\) 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\(_3\)O\(_4\) 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\(_2\)O\(_4\) 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\(_2\)O\(_4\) is a normal spinel since Fe\(^{2+}\) is high spin d\(^6\) ion with \(\text{CFSE} = 4\left\langle \frac{2}{5}\right\rangle - 2\left\langle \frac{3}{5}\right\rangle\Delta_o\) \(\sim 6/5 \Delta_o\) on an octahedral site, and Cr\(^{3+}\) is a d\(^3\) ion with 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.
**Co₃O₄** is a normal spinel. Even in the presence of weak field oxo ligands, Co³⁺ is a low spin d⁶ ion with very high CFSE on the octahedral sites, because of the high charge and small size of the Co³⁺ ion. Hence the Co³⁺ ions occupy both octahedral sites, and Co²⁺ occupies the tetrahedral site.

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**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. Fe₃O₄, CoFe₂O₄, and NiFe₂O₄ 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.](image)

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$_3$O$_4$, CoFe$_2$O$_4$, and
NiFe$_2$O$_4$) then the solid will be ferrimagnetic. This is illustrated above for Fe$_3$O$_4$. 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.
ABX$_3$ perovskite structure. A, B, and X are white, blue, and red, respectively.

The coordination of the A ions in perovskite and the arrangement of BO$_6$ octahedra is best understood by looking at the ReO$_3$ 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 ReO$_3$ 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 ReO$_3$ structure showing the large cuboctahedral cavity that is surrounded by 12 oxygen atoms.
Because the A-site is empty in the ReO$_3$ 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 WO$_3$, which has the ReO$_3$ structure. In the sunlight, a photovoltaic cell drives the reductive intercalation of WO$_3$ according to the reaction:

\[
\text{\ce{xH^+ + xe^{-} + WO3 \leftrightharpoons H$_x$WO3}}\]

WO$_3$ is a light yellow compound containing d$^0$ W(VI). In contrast, H$_x$WO$_3$, which is mixed-valent W(V)-W(VI) = d$^1$-d$^0$, 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 BO$_6$ octahedra is also very important in ferroelectric oxides that have the perovskite structure. In some perovskites with small B-site cations, such as Ti$^{4+}$ and Nb$^{5+}$, the cation is too small to fit symmetrically in the BO$_6$ 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 BO$_6$ 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.

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 adressable magnetic memory.

**Halide perovskites** (ABX₃, X = Cl, Br, I) can be made by combining salts of monovalent A ions (A⁺ = Cs⁺, NH₄⁺, R⁢N⁢H₃⁺) and divalent metal salts such as PbCl₂ or PbI₂. 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.

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![Diagram](image)

**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.
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.