Lecture 26 - The Solid State - Perovskites and Spinels

1. Perovskites and spinels.
2. Practice exam questions.

5. Perovskites and spinels

Perovskites - formula $\text{A}^{2+}\text{B}^{4+}\text{O}_3$

i.e. $\text{Ca}^{2+}\text{Ti}^{4+}\text{O}_3$

Structure - Ti $^{4+}$ ions are at the corners of the cube,
Ca$^{2+}$ ion in the centre of the cube
O$^{2-}$ at the edge of the cube faces.

The $^{4+}$ ion size must be between 0.414rO$^{2-}$ and 0.732rO$^{2-}$
i.e. The $^{4+}$ ion size 52-92 pm for Octahedral Coordination
and the $^{2+}$ ion must be 100 pm or greater.

Both of these conditions must be met for $\text{ABO}_3$ to be a perovskite.
- Representation of a unit cell that is perovskite. The cell is cubic, with Ti$^{4+}$ centres at the corners of the cube, and O$^{2-}$ ions at the 12 edge sites. The 12-coordinate Ca$^{2+}$ ion lies at the centre of the unit cell. Each Ti$^{4+}$ centre is six-coordinate, and this can be appreciated by considering the assembly of adjacent unit cell in the lattice.

- Perovskites are a large family of crystalline ceramics that derive their name from a specific mineral known as perovskite (CaTiO$_3$) due to their crystalline structure.
- The mineral perovskite, which was first described in the 1830's by the geologist Gustav Rose, who named it after the famous Russian mineralogist Count Lev Aleksevich von Perovski, typically exhibits a crystal lattice that appears cubic, though it is actually orthorhombic in symmetry due to a slight distortion of the structure.
- Members of the class of ceramics dubbed perovskites all exhibit a structure that is similar to the mineral of the same name.
- The characteristic chemical formula of a perovskite ceramic is ABO$_3$, with the A atom exhibiting a +2 charge and the B atom exhibiting a +4 charge. The atoms of the unusual material are generally arranged so that 12 coordinated A atoms mark the corners of a cube, octahedral O ions are featured on the faces of that cube, and octahedral B ions are located in the center of the structure.
Superconductivity, a phenomenon characterized by the disappearance of electrical resistance in various metals, alloys, and compounds when they are cooled to very low temperatures, was first observed in 1911 by Heike Kamerlingh Onnes.

In Onnes’ early studies, he noted that the resistance of a frozen mercury rod abruptly dropped to zero when cooled to the boiling point of helium, 4.2 Kelvin. He also discovered that a material in a superconducting state can be returned to its standard, nonsuperconducting condition through exposure to a strong magnetic field of a certain critical value or by passing a large current through it.

Though such findings were considered important, and Onnes was even awarded the Nobel Prize for Physics in 1913, the extremely cold temperatures required to instigate superconductivity necessitated the use of liquid helium, which made it cost prohibitive to utilize traditional superconductors for many applications.

The discovery of perovskite superconductors revolutionized this field, however, and by 1987, superconductivity in these materials could be induced above 77K, the boiling point of liquid nitrogen.

This significant advance made superconductors cheaper to cool to their critical temperature, since liquid nitrogen is considerably less costly than liquid helium.
The first superconducting perovskite was discovered by IBM researchers Bednorz and Mueller, who were examining the electrical properties of a family of materials in the Ba-La-Cu-O system.

One of the materials they were studying was reported to have a critical temperature of approximately 35 Kelvin, which was a benchmark in field of superconductivity at the time.

For their discovery, which opened up an entirely new area of study since their high-temperature superconductors did not conform to the BCS theory widely believed to govern the activity of all superconductors known up to that time, Bednorz and Mueller were awarded the Nobel Prize for Physics in 1987.

Meanwhile, between 1986 and 1988 the critical temperature for superconductivity in perovskite ceramics was raised by more than 100 Kelvin, but in recent years only several degrees have been added to this remarkable elevation.

Many of these minor increases in the critical temperatures of ceramic superconductors have stemmed from the utilization of increasingly exotic elements in the base perovskite.

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**Spinels** – formula $AB_2O_4$

- Octahedral and tetrahedral coordination occurs
- A and B size must be compatible with octahedral coordination by the oxygens.
- i.e. the radii must be between 52pm and 92pm.

The mineral Spinel $\text{MgAl}_2\text{O}_4$, Magnesium Aluminum Oxide
Uses: as a gemstone
Spinel is a very attractive and historically important gemstone mineral. Its typical red color, although pinker, rivals the color of ruby.

In fact, many rubies, of notable fame belonging to crown jewel collections, were found to actually be spinels.

Perhaps the greatest mistake is the Black Prince’s Ruby set in the British Imperial State Crown.

Whether these mistakes were accidents or clever substitutions of precious rubies for the less valuable spinels by risk taking jewelers, history is unclear.

The misidentification is meaningless in terms of the value of these gems for even spinel carries a considerable amount of worth and these stones are priceless based on their history, let alone their carat weight and pedigree.

Today, expensive rubies are still substituted for by spinel in much the same way a diamond is substituted by cubic zirconia. Not to commit a fraud or theft but to prevent one. Spinels may take the place of a ruby that would have been displayed in public by an owner who is insecure about the rubies safety.

The spinel probably is still valuable but better to lose a $100,000 dollar spinel than a $1 million dollar ruby.

Spinel and ruby are chemically similar.

Spinel is magnesium aluminum oxide and ruby is aluminum oxide. This is probably why the two are similar in a few properties. Not surprisingly, the red coloring agent in both gems is the same element, chromium.

Spinel and Ruby also have similar luster (refractive index), density and hardness. Although ruby is considerably harder (9) than spinel, spinel’s hardness (7.5 - 8) still makes it one of the hardest minerals in nature.
The Mineral Franklinite

- Chemical Formula: (Zn, Fe, Mn)(Fe, Mn)\(_2\)O\(_4\), Zinc Iron Manganese Oxide
- Class: Oxides and Hydroxides
- Group: Spinel
- Uses: Important ore of zinc and manganese
- Franklinite is one of the minerals found at Franklin, New Jersey, a world famous locality that has produced many formerly unknown and exotic mineral species. It is found in large enough quantity to serve as an ore of zinc and manganese, two important strategic and industrial metals. It forms octahedral crystals that are typical of the spinel group of minerals. Specimens from Franklin often contain the rounded black grains of franklinite surrounded by white calcite and/or greenish willemite with a sprinkling of red zincite. Specimens of this exotic and interesting mineral are truly valued by mineral collectors.

The Mineral Magnetite

- Chemical Formula: Fe\(_3\)O\(_4\), Iron Oxide
- Class: Oxides and Hydroxides
- Group: Spinel
- Uses: Major ore of iron
- Magnetite is a natural magnet, hence the name, giving it a very nice distinguishing characteristic. Magnetite is a member of the spinel group which has the standard formula A(B)\(_2\)O\(_4\). The A and B represent usually different metal ions that occupy specific sites in the crystal structure. In the case of magnetite, Fe\(_3\)O\(_4\), the A metal is Fe\(^{+2}\) and the B metal is Fe\(^{+3}\); two different metal ions in two specific sites. This arrangement causes a transfer of electrons between the different irons in a structured path or vector. This electric vector generates the magnetic field.
Magnetite, a magnetic compound is present in homing pigeons, migratory salmon, dolphins, honeybees, and bats. Hence the term “animal magnetism.” Magnetite helps orientation and direction finding in animals. It is thought to help certain migratory species migrate successfully by allowing them to draw upon the earth’s magnetic fields.

The topic of bird migration is complex and not fully elucidated, but magnetite as a magnetic compass has been proposed to aid in navigation in certain families of birds.

Magnetite was nicknamed lodestone and used by early navigators to locate the magnetic North Pole. William Gilbert published De Magnete, a paper on magnetism in 1600, about the use and properties of Magnetite.

Magnetic Compass

The magnetic compass is an old Chinese invention, probably first made in China during the Qin dynasty (221-206 B.C.). Chinese fortune tellers used lodestones to construct their fortune telling boards. Eventually someone noticed that the lodestones were better at pointing out real directions, leading to the first compasses. They designed the compass on a square slab which had markings for the cardinal points and the constellations.

The pointing needle was a lodestone spoon-shaped device, with a handle that would always point south.

Magnetized needles used as direction pointers instead of the spoon-shaped lodestones appeared in the 8th century AD, again in China, and between 850 and 1050 they seem to have become common as navigational devices on ships.
2. Practice Exam Questions

1. (15 Marks) Consider the oxides of the following ions: Ca\(^{2+}\), S\(^{6-}\), Ti\(^{4+}\), Co\(^{3+}\), Zn\(^{2+}\). Answer the following questions. Note that a particular oxide may be used more than once or may not be used at all in answer to these questions.

   (a) Give the formula of the oxide most likely to give an acidic solution when dissolved in water. Write an equation for the reaction.

   (b) Give the formula of the oxide most likely to be colored. Why is it colored?

   (c) Give the formula of the oxide most likely to be amphoteric. Write an equation for its reaction with an acid with a base.

   (d) Give the formula of the oxide most likely to occur as gaseous molecules. Draw its Lewis structure.


2. (7 marks)

   (a) What is meant by the acidity of a metal cation? Explain with a chemical equation.

   (b) Arrange the following cations in order of their acidity: Mg\(^{2+}\), Al\(^{3+}\), K\(^{+}\), Zn\(^{2+}\), C\(^{+}\). Briefly explain how you arrived at the order.