SPINELS

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→ any class of minerals having general formulation of $(A^{+}_{2}B^{+}_{3}2O_{2-4})$. crystallise in the cubic crystal system.

Such that the oxide anions are arranged in a cubic closely-packed lattice and some or all of the cations A and B are arranged at the octahedral and tetrahedral sites in the lattice.

→ The cations A and B charges in a prototypical spinel is +2 and +3. Other combinations incorporating divalent, trivalent and tetravalent cations including aluminium, iron, magnesium, manganese, chromium e.t.c.

→ The A and B can be same with different valencies. As in the Fe_3O_4 as $(Fe_2+Fe_3+2O_{2-4})$ is a stable spinel.

→ The spinel is separated in different groups based upon B cation.

As;

GROUPS. (example)

- Aluminium Spinel → • $MgAl_2O_4$ → mineral spinel
- Gahnite → $ZnAl_2O_4$ • $BeAl_2O_4$ → chrysoberyl

Iron Spinel. Magnetite → Fe_3O_4
magnesioferrite → $MgFe_2O_4$

Chromium spinel, $FeCr_2O_4$ → chromite.

→ Spinels having composition based upon

- ferrous and magnesium
  - ↓ heterogenous
- ferrite + aluminium
  - ↓ homogenous

→ STRUCTURE:

- Normal spinels structure
- Inverse spinels structure

Normal spinels structure

↳ have close-packed cubic structure

- two tetrahedral sites
- one octahedral site

per formula unit.

↳ tetrahedral sites having smallere space as compared to octahedral sites.

↳ half of the octahedral holes occupied by B^{3+} cations.

- 1/8th of tetrahedral holes occupied by A^{2+} cations

e.g. $MgAl_2O_4$

Inverse spinels structure

↳ In this all A^{2+} cations and half of the B^{3+} cations occupies octahedral sites. Other half of B^{3+} cations occupy tetrahedral sites.

e.g. Fe_3O_4

if Fe^{2+} ions are d^6 high spin and Fe^{3+} ions are d^5 high spin.

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To explain distribution of cations →

CFSE was used as for transitions metals.

→ It tells if a large number of A^{2+} cations show high preference for octahedral sites than half of the B^{3+} ions moves to tetrahedral site.

→ Similarly if B^{3+} ions show high preference for tetrahedral sites it leaves octahedral site for A^{2+} completely.

Relative sizes of S and p orbitals.

Where the CFSE was not applying then Burdett and his coworkers used sizes of s and p orbitals to explain the distribution of cations in different sites.

→ Spinels in which both the cations are similar atoms are more stable and more particular. They show fractional oxidation ~~states~~ number due to same metal in same compound having two different oxidation states. e.g. Mg_3O_4, Fe_3O_4, Co_3O_4

• These are dark black and much darker in colour due to charge transfer transitions.

They show two important magnetic properties:

- **Ferromagnetism** → shown by Fe_3O_4 only
  that's why used in magnetic storage devices
  due to its property of ferromagnetism above room temperature.
- **Antiferromagnetism** → shown by Mg_3O_4 and Co_3O_4.

spinels are generally used in solid state electronics industry.

PEROVSKITES

- Another class of mixed metal oxides.
- An unusual closely packed cubic lattice
- General formulation ABO_3.
  e.g. $CaTiO_3$.
- The smaller Ti^{+4} occupies octahedral holes.
- **Other perovskites structures:-** can be formed from the structure of $CaTiO_3$ with the help of isomorphous substitution.
- In this the Ca^{++} and Ti^{+4} ions are replaced by ions of similar sizes.
- It does not matter if the ions which are replacing old ones should have same charge

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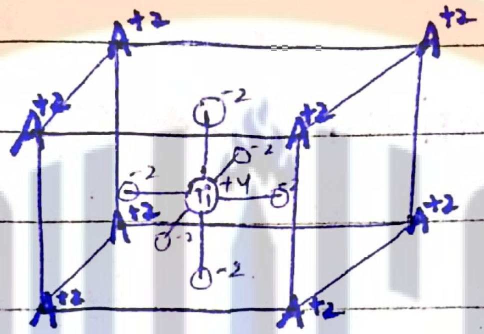
as their sum should be same.

- The total charge of the replacing ions must be same to the replaced ones.

As;



- **Total charge:**

Total charge of perovskites must be +6.

As; $\overset{+1}{Li}\overset{+5}{Nb}O_3$

- **Ferroelectrics:**

When the perovskites are not at high temp. the Ti^{+4} ion tends to move somewhat away from the center unit of the lattice which give rise to an electric charge separation or dipole called as ferroelectrics.

- **Peizoelectrics:**

When a mechanical pressure is applied on perovskites the Ti^{+4} migrates from center due to which an electric current is produced which cause mechanical motion of ions. This is Piezoelectric property of perovskites to convert ~~els~~ mechanical energy to electrical energy.

APPLICATIONS:

- Used in sonars, radiation sensor.
- In sonic and ultrasonic transducers, loud speakers and headphones the property of converting electrical energy to mechanical energy is used.

Na_xWO_3:

It is formed by reducing sodium tungstate and it is perovskite like. In this electrical conductivity is due to movement of electrons in MO's.

- Conductivity in this does not depends upon valency numbers but it depends upon energy states. more the energy state more the conductivity.

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PARAMAGNETISM

- Atoms, ions or molecules having unpaired electrons are when placed in a magnetic field strongly attracted towards it by a force proportional to field strength.
- When an electron spins in an axis then according to classical electromagnetism it produces a magnetic moment.
- As when current flows in a loop of wire it produces magnetic moment.
- There are magnetic moments present in paramagnetic substance such as spin magnetic moment and orbital magnetic moment by which we can determine the magnetic properties of atom, ions or molecules.
- Magnetic moment unit is BM
  ↓
  Bohr's magneton
  ↓
  $BM = \frac{eh}{4\pi mc}$

- Formula, spin magnetic moment

$$\mu_s = g\sqrt{S(S+1)}$$

$g = 2$, $S = \frac{1}{2}$

then calculate.

c - speed of light

e - electronic charge

h - planck's constant

m - mass of electron

DIAMAGNETISM.

↳ shown by all forms of matter

- Diamagnetism is shown by substances having paired electrons. These substances repell the magnetic field.
- The repulsion is not due to spin magnetic moment it is due to orbital magnetic moments.
- As when a diamagnetic substance is placed in a magnetic field the planes of orbitals are deviated from their equilibrium which repels the magnetic field.

• As orbital magnetic moment is,

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$$

• In this spin magnetic moments are cancelled out.

FERRIMAGNETIC:

In ferrimagnetism the antiparallel aligned moments do not cancel each other and a little magnetism remained.

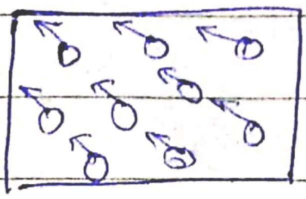
Para and Diamagnetism → for individual atoms or molecules.

FERROMAGNETISM.

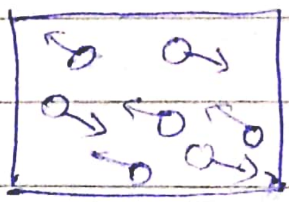
Ferromagnetism is a property of magnetism that exists b/w group of atoms, ions or molecules.
In this the electron spins of neighbouring atoms coupled in parallel alignment and the magnetic moment is very large and remain locked below (T_c) curie temp.
When ferromagnetic substances are placed in a magnetic field they become magnet and remain as a permanent magnet if the field is removed.

ANTIFERROMAGNETIC.

Antiferromagnetism involved coupling of spins of neighbouring atoms into an antiparallel alignment such that very low magnetic moment. A paramagnetic substance changes to antiferromagnetic substance by cooling it at very low temp. (Neel temp).



Ferromagnetism



Anti-

Pairing or coupling may occur in f and d-block electron

• **Magnetic Suceptibility:**

" The ability of a material to be effected by a magnetic field".

$B = H + 4\pi I \rightarrow$ intensity of magnetization.

B ↙ density of magnetic lines

H ↓ magnetic field strength

• **Curie Temperature:**

The temp. below which the spontaneous ~~mag~~ polarization occurs due to the disturbance in the symmetry of unit cell in pervoskite crystal. The change in ions unit cell's high symmetry sites leads to polarization.

• **Neel Temp:**

The Temp below which paramagnetic substance changes to antiferromagnetic.

Mixed Metal Oxides.

"Mixed metal oxides are the oxides that have cations of more than one type of element or same element with different oxidation states."

- They are highly conducting with less corrosion. (mostly used as anodes in electrolysis) e.g. spinels, perovskites.

High Temperature Super Conductors

- **Superconductors:**

Substances or metallic alloys that show zero electrical resistance when cooled near an absolute zero are called as super conductors. They allows electrical current to pass through them without any energy loss.

- **Superconductivity:**

The phenomenon in which an element exhibits zero electrical resistance and expulsions of magnetic fields of a certain substance at a certain critical temperature.

- **HIGH TEMP SUPERCONDUCTORS.**

High temperature superconductors are those that show superconductivity at an unusual high temperature. (HTS). **TRANSITION Temp.**

↳ The temperature at which ordinary or metallic elements behaves as superconductor usually → 30K (-243.2°C)

- HT Superconductors have temp as high as 138K (-135°C)

EXAMPLE:

cupper and oxygen elements as (cuprates) are example of **(HTS).**

As; Bismuth Strontium ~~barium~~ calcium copper oxide

Ytterbium barium copper oxide (YBCO)
↓
first to achieve superconductivity above the boiling point of liq N_2.

CLASSIFICATION:

- cuprates
- Iron based superconductors high Temp (SC.)
- low temp superconductors

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CUPRATES.

- quasi two dimensional materials whose properties of super conding conducting is determined by the weakly coupled layers of CuO_2. These are stabilized by the neighbouring ions such as lanthanum strontium or barium.
- It has perroskite structure.
- It has checkerboard lattice.
- The chemical formula of uprate super conductors based on fractional numbers depends upon dopping required for superconduction.
- The cuprates are classified on the basis of similarities and differences of
  - electron dopped (SC)
  - hole dopped (SC)

e.g: Ytterbium barium copper oxide (YBCO)

~~Barium~~ Bismuth strontium calcium copper oxide. (BSCCO)

IRON BASED SUPER CONDUCTORS.

Super conductors based upon iron and

certain chalcinogens or arsenic, phosphorus are iron based superconductors.

- They are undopped superconductors.
- They have tetrahedral orthorhombic structure.

They are second best in superconducting after cuprates.

(K, Ba) Fe_2As_3 having 38K (critical temp) or (transition temp)

Metallic low temperature (SC).

(lead or mercury) (alloy of tin are high temp SC)

- These are super conductors at low (T_c) - They should have ~~high~~ correct strength of interaction b/w valence electrons and the lattice structure within the metallic bond.
- If the strength is high then the electrons cannot move freely and conduction lowers.
- If the strength is lower then the electrons can interact with the nearby ions.

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- **High temp. superconductors:-**

Magnesium bromide with ($T_c = 39K$) are high temp superconductors with relative fermi energy

APPLICATIONS OF METAL OXIDES

AS HIGH TEMPERATURE SUPERCONDUCTORS:-

- **Transportation:-**

Transport vehicles as train "floats" on ~~magnetic~~ superconducting magnets by climiting ~~[illegible]~~ the friction b/w train and its track.

- **MRI:-**

Used in magnetic resonance imaging.

super ~~used in elect.~~

- **Electrical generators:** Super conducting wires used in electrical generators are more effecient than conventional generators.

- **In D-SMES:-** In Distributed superconducting magnetic energy storage system the metal oxides are used. One of the 6 D-SMES can store ~~a~~ 3 million watts which can be retrieved when needed for the maintenance of disturb power grids by providing needed voltage lines.

Hazardous Effects Of Volatile Oxides:

The volatile oxides are as;

→ CO:

→ Carbon monoxide is a colorless, ordour less, tasteless gas.

→ It is a green house gas.

→ It contributes in smog, ozone depletion and global warming, acidification.

Sources:

- fossil fuel combustion
- incomplete combustion
- vehicular emissions

Effects:

- lowers oxygen carrying capacity of hemoglobin by combining to it.
- This leads to damage of tissues of heart or brain leads to death.
- It increase oxygen demand.

→ **NO_2:** NO_2 is a class of important oxides of nitrogen. It can be found in form of nitric acid. It plays important role in formation of land ozone.

Sources:

- combustion of fuels, • vehicular emission

Effects:

short term exposure causes respiratory disorders such as asthma, bronchitis or emphysema.

long term exposure → death due to suffocation

→ **SO_2:** a volatile oxide found in the form of SO_2 mostly in atmosphere.

→ In acid rain plays important role as H_2SO_4.

Sources:

- vehicular emissions
- volcanic eruptions
- industrial emissions (20%)
- fossil fuel combustion at power plants (73%)

Effects:

Causes diseases like bronchitis constriction and respiratory damage.

OsO_4 : (Osmium tetraoxide)

a poisonous volatile oxide that a little exposure to it can cause pulmonary edema and leads to death.

Effects.

- It blurs or pollutes the cornea of human eye, causes blindness.
- → It can penetrate through plastic therefore kept at low temperature in glass.

Ruthenium tetra Oxide RuO_4.

- a diamagnetic tetrahedral (RuO_4).
- change neutral symmetrical oxide

Rhenium Oxide RhO_2.

→ It is greyish to black crystalline oxide in colour → As laboratory reagent used as enzyme. / ~~forms rhenium~~

→ It forms rhenates by combining rhenium oxides with alkaline hydrogen peroxides

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Technitium oxides: (Tc_2O_7)

→ yellow volatile solid

→ molecular binary metal oxide

→ **Uses of MgO and TiO_2 in industry:**

TiO_2:

→ Because of its whitening or bright whiteness it is used in

- paints
- coatings
- papers
- inks
- toothpaste
- face powder and food colouring.

→ used in ~~cos~~ cosmetics such as sunscreen.

MgO:

- High temp. dehydrating agent used for the production of silicon steel sheet, electronic industry material, adhesive and additive in the chemical raw material
- Electric insulating material for smelter, electrode bar and electrode sheet.