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Chemistry of materials

The formation of bulk material

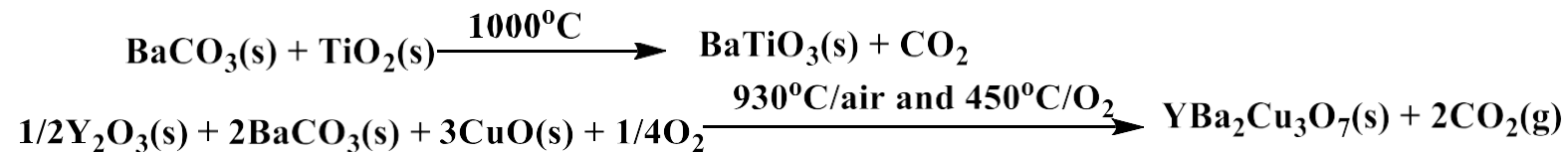
New materials can be obtained by two main methods.

- a. One is the direct reaction of two or more solids.
- b. Reaction via solution method.

(a) Methods of direct synthesis

Many complex solids can be obtained by direct reaction of the components at high temperatures.

Ternary oxides, such as BaTiO_3 , and quaternary oxides, such as $\text{YBa}_2\text{Cu}_3\text{O}_7$, are synthesized by heating together the following mixtures for several days:

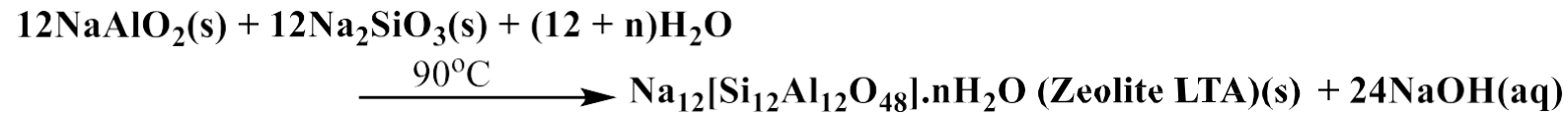
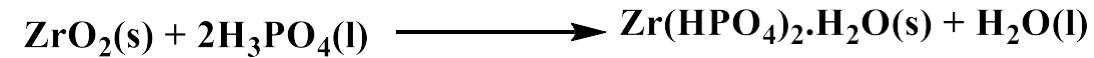


High temperatures are used in these syntheses to accelerate the slow diffusion of ions in solids and to overcome the high Coulombic attractions between the ions.

(b) Solution methods

Many inorganic materials, especially framework structures, can be synthesized by crystallization from solution.

The following are typical reactions that occur in water:

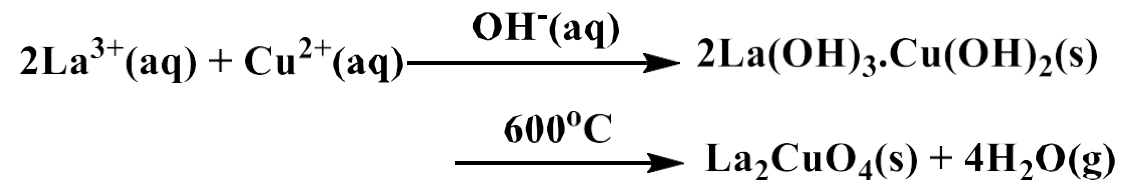


Solution methods are extended by using **hydrothermal techniques**, in which the reacting solution is heated above its normal boiling point in a sealed vessel. Such reactions are important for the synthesis of open-structure aluminosilicates (zeolites), analogous porous structures based on linked oxo-polyhedra and related **metal-organic frameworks** (MOF) in which metal ions are linked by coordinating organic species, such as carboxylates.

- MOFs are porous structures and are often thermodynamically metastable with respect as conversion to denser structure types so they cannot be made by direct high-temperature reactions.
- For example, the sodium aluminosilicate zeolite $\text{Na}_{12}[\text{Si}_{12}\text{Al}_{12}\text{O}_{48}].n\text{H}_2\text{O}$ formed in solution converts on heating above 800°C to the dense aluminosilicate NaSiAlO_4 .
- More recently, other solvents such as liquid ammonia, supercritical CO_2 , and organic amines have been used in so-called **solvothermal reactions**.

The advantages of starting with solutions is that the reactants are mixed at the atomic level, so overcoming the problems associated with the direct reaction of two or more solid phases consisting of micrometre-sized particles.

One example is



Chemical deposition

- **Chemical vapour deposition** (CVD) is a method in which a volatile inorganic compound is decomposed above the substrate.
- When the compound is a metallo-organic complex (that is, a complex of a metal atom with organic ligands), this route is known as **metallo-organic chemical vapour deposition** (MOCVD).
- Me_2Zn can react with H_2S above a substrate to generate the Group 12/16 (II/VI) semiconductor ZnS (and methane).

Defects and ion transport

Atom and ion diffusion

- Diffusion of atoms or ions in solids is in fact very important in many areas of solid-state technology, such as semiconductor manufacture, the synthesis of new solids, fuel cells, sensors, metallurgy, and heterogeneous catalysis.

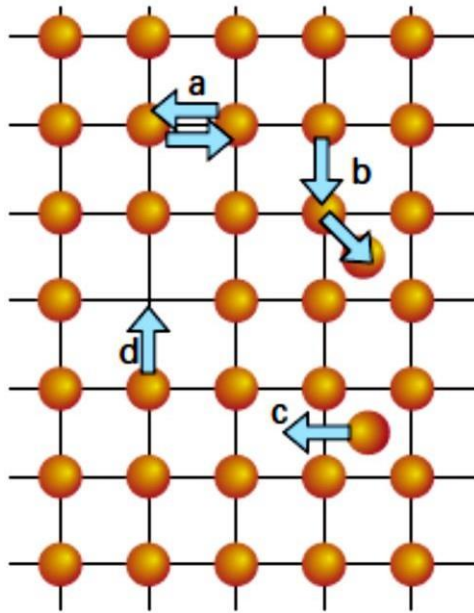


Fig 1. Some diffusion mechanisms for ions or atoms in a solid: (a) two atoms or ions exchange positions, (b) an ion hops from a normally occupied site in the structure to an interstitial site, which produces a vacancy which can then be filled by movement of an ion from another site, (c) an ion hops between two different interstitial sites and (d) an ion or atom moves from a normally occupied site to a vacancy, so producing a new vacant site.

Materials that show high rates of diffusion at moderate temperatures have the following characteristics:

- **Low-energy barriers:** so temperatures at (or a little above) 300 K are sufficient to permit ions to jump from site to site.
- **Low charges and small radii:** so, for example, the most mobile cation (other than the proton) and anion are Li⁺ and F⁻. More highly charged ions develop stronger electrostatic interactions and are less mobile.
- **High concentrations of intrinsic or extrinsic defects:** defects typically provide a low energy pathway for diffusion through a structure.
- Mobile ions are present as a significant proportion of the total number of ions.

Solid electrolytes

- Any electrochemical cell, such as a battery, fuel cell, electrochromic display, or electrochemical sensor, requires an electrolyte. There is considerable interest in the development of solid electrolytes over the liquid phase electrolytes.
- **Two important and thoroughly studied solid electrolytes with mobile cations are**
 - a. silver tetraiodomercurate(II), Ag_2HgI_4 , and
 - b. sodium –alumina with the composition $\text{Na}_{1-x}\text{Al}_{11}\text{O}_{17+x/2}$.
- Other recently developed fast-cationic conductors include **NASICON** (a name formed from the letters in sodium, Na, Superionic Conductor)

Solid cationic electrolytes

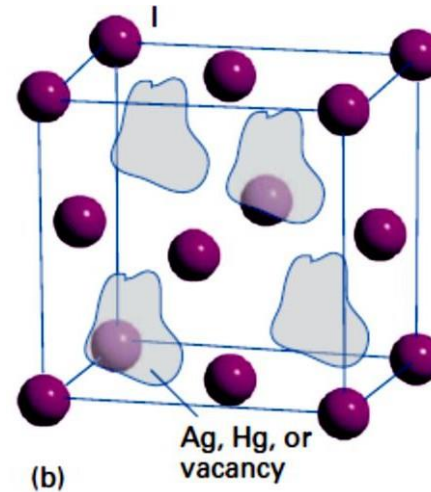
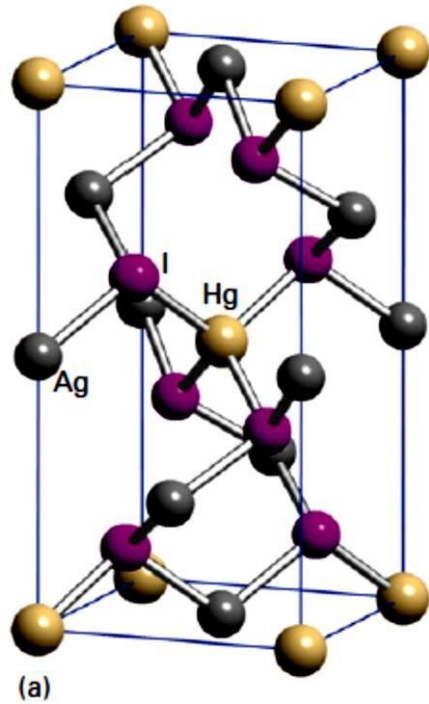


Fig 2. (a) Low-temperature ordered structure of Ag_2HgI_4 . (b) High-temperature disordered structure showing the cation disorder. Ag_2HgI_4 is an Ag^+ ion conductor in the high temperature form.

- **Below 50°C**, Ag_2HgI_4 has an ordered crystal structure in which Ag^+ and Hg^+ ions are tetrahedrally coordinated by I^- ions and there are unoccupied tetrahedral holes (Fig 2a). At this temperature **its ionic conductivity is low**.
- **Above 50°C**, the Ag^+ and Hg^{2+} ions are randomly distributed over the tetrahedral sites (Fig. 2b). At this temperature the **material is a good ionic conductor**, largely on account of the mobility of the Ag^+ ions between the polarizable I^- ions.

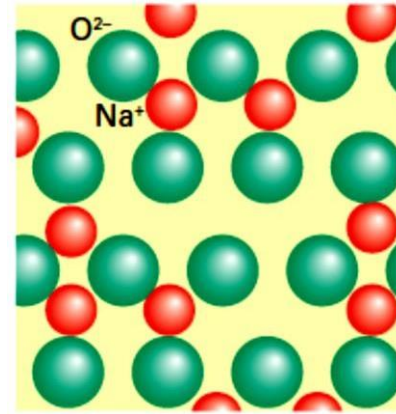
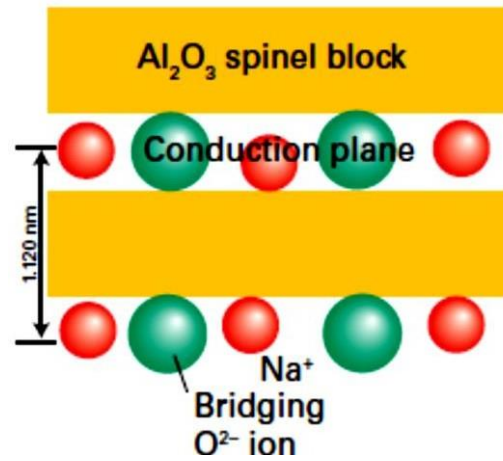


Fig 3. (a) Schematic side view of β -alumina showing the Na_2O conduction planes between Al_2O_3 slabs. The O atoms in these planes bridge the two slabs. (b) A view of the conduction plane.

- Sodium β -alumina is an example of a mechanically hard material that is a good ionic conductor.
- In this case, the rigid and dense Al_2O_3 slabs are bridged by a sparse array of O^{2-} ions (Fig.3).
- The plane containing these bridging ions also contains Na^+ ions, which can move from site to site.
- Many similar rigid materials having planes or channels through which ions can move are known; they are called **framework electrolytes**.

- The material NASICON is a nonstoichiometric, solid-solution system with a framework constructed from ZrO_6 octahedra and PO_4 tetrahedra, corresponding to the parent phase of composition $\text{NaZr}_2\text{P}_3\text{O}_{12}$ (Fig 4).
- A solid solution can be obtained by partially replacing P by Si to give $\text{Na}_{1-x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ with an increase in the number of Na ions for charge balance.

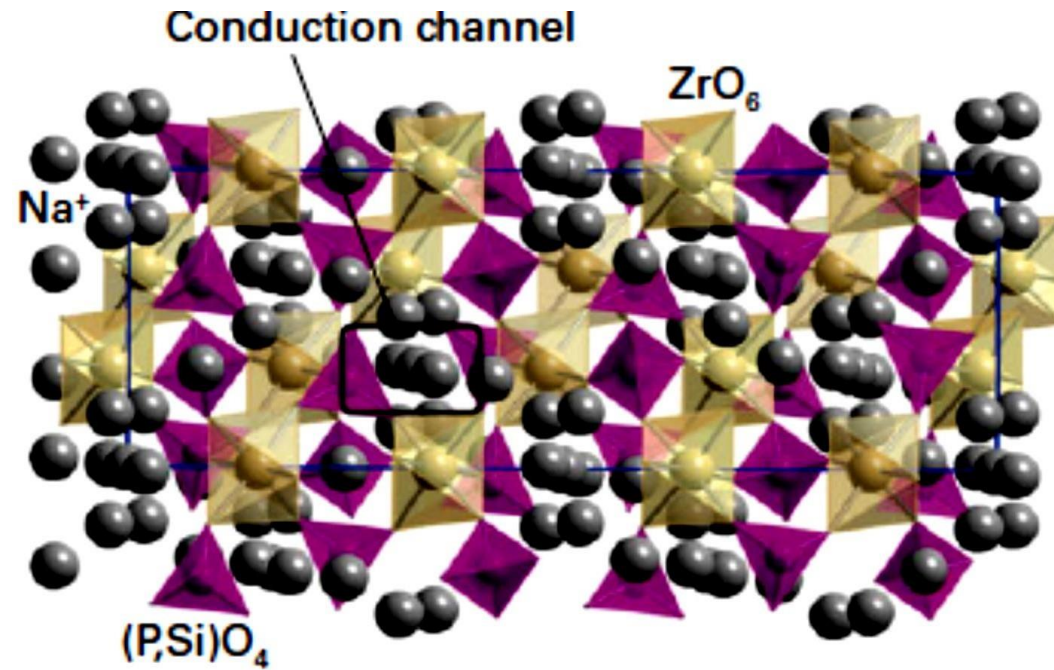


Fig 4. The $\text{Na}_{1-x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ (NASICON) structure shown as linked $(\text{P,Si})\text{O}_4$ tetrahedra and ZrO_6 .

Metal oxides, nitrides, and fluorides

Monoxides of the 3d metals

The monoxides of most of the 3d metals adopt the rock-salt structure.

Compound	Structure	Composition, x	Electrical character
CaO_x	Rock-salt	1	Insulator
TiO_x	Rock-salt	0.65–1.25	Metallic
VO_x	Rock-salt	0.79–1.29	Metallic
MnO_x	Rock-salt	1–1.15	Semiconductor
FeO_x	Rock-salt	1.04–1.17	Semiconductor
CoO_x	Rock-salt	1–1.01	Semiconductor
NiO_x	Rock-salt	1–1.001	Insulator
CuO_x	PtS (linked CuO_4 square-planes)	1	Semiconductor
ZnO_x	Wurtzite	Slight Zn excess	Wide band gap n-type semiconductor

(a) Electronic properties

- **The 3d-metal monoxides MnO, FeO, CoO, and NiO are semiconductors; TiO and VO are metallic conductors.**
- The electron or hole migration in MnO, Fe_{1-x}O , CoO, and NiO is attributed to a hopping mechanism.
- The metallic conductivity persists over a broad composition range from highly oxygen-rich Ti_{1-x}O to metal-rich TiO_{1-x} . In these compounds, a conduction band is formed by the overlap of the t_{2g} orbitals of metal ions in neighbouring octahedral sites that are oriented towards each other (Fig.5 and 6).

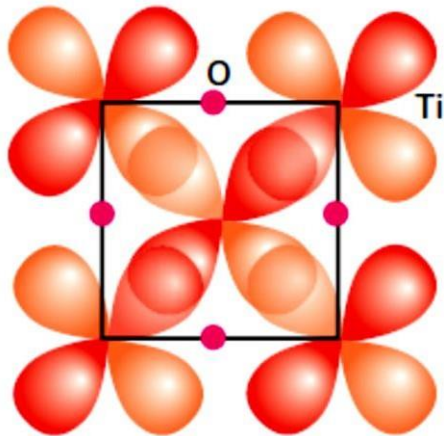


Fig. 5 Overlap of the d_{zx} orbitals in TiO to give a t_{2g} band. In the perpendicular directions the d_{yx} and d_{zy} orbitals overlap in an identical manner.

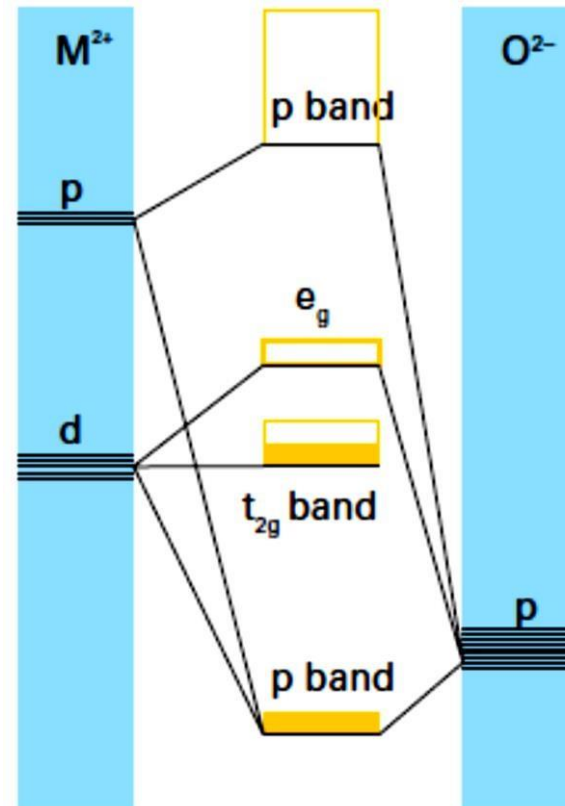


Fig. 6 Molecular orbital energy level diagram for early d-metal monoxides. The t_{2g} band is only partly filled and metallic conduction results.

(b) Magnetic properties

- The 3d-metal monoxides MnO, FeO, CoO, and NiO order antiferromagnetically with Neel temperatures that increase from Mn to Ni.
- The Neel temperatures (T_N , the temperature of the paramagnetic/antiferromagnetic transition) of the series of d-metal oxides are as follows:

MnO	FeO	CoO	NiO
122 K	198 K	271 K	523 K

- These values reflect the strength of the superexchange spin interactions along the M-O-M directions, which in the rock-salt type structure propagate in all three unit cell directions.
- As the size of the M^{2+} ion decreases from Mn to Ni, the superexchange mechanism becomes stronger due to the increased metal–oxygen orbital overlap and T_N increases.

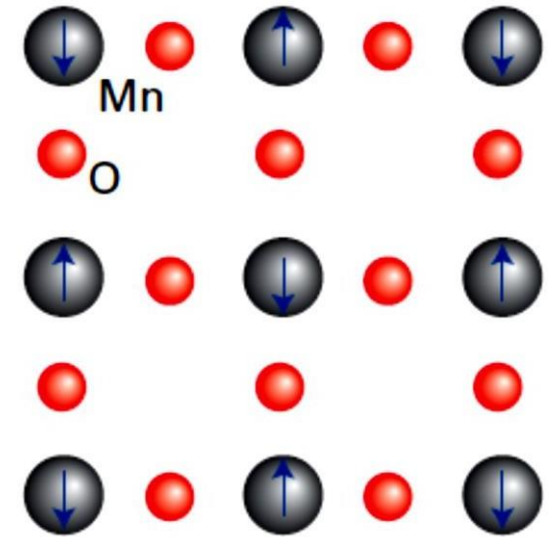


Fig. 7 The arrangement of electron spins on the Mn^{2+} ions in the antiferromagnetic state of MnO.

Higher oxides and complex oxides

- Binary metal oxides that do not have a 1:1 metal:oxygen ratio are known as **higher oxides**.
- Compounds containing ions of more than one metal are often termed **complex oxides** or **mixed oxides** and (for instance, LaFeO_3 and $\text{YBa}_2\text{Cu}_3\text{O}_7$).
- **α -Aluminium oxide (the mineral *corundum*)** adopts a structure that can be modelled as a hexagonal close-packed array of O^{2-} ions with the cations in two-thirds of the octahedral holes (Fig. 8).
- The corundum structure is adopted by many oxides of the stoichiometry M_2O_3 , including Cr-doped aluminium oxide (ruby).

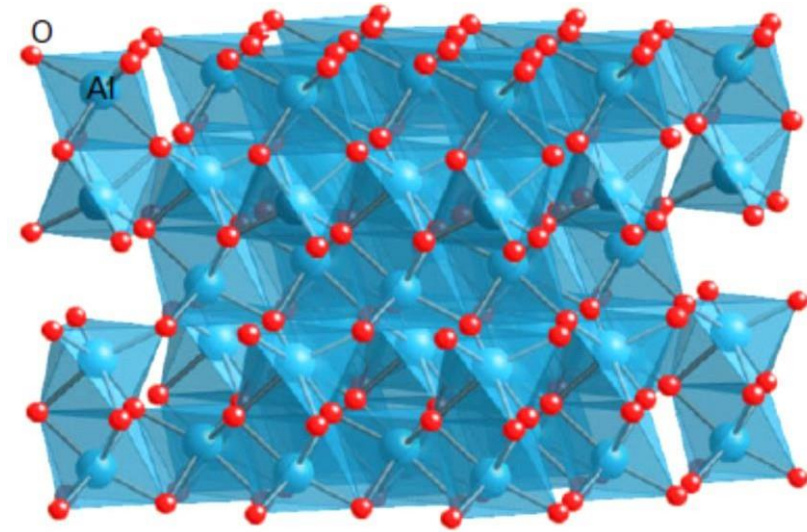


Fig. 8 The *corundum* structure

(a) Spinel

- The d-block higher oxides Fe_3O_4 , Co_3O_4 , and Mn_3O_4 all adopt the structural type of the **mineral spinel**, **MgAl_2O_4** , and have the general formula AB_2O_4 . Most oxide spinels are formed with a combination of A^{2+} and B^{3+} cations.
- **The spinel structure consists of an fcc array of O^{2-} ions in which the A ions reside in one-eighth of the tetrahedral holes and the B ions inhabit half the octahedral hole**; this structure is commonly denoted $\text{A}[\text{B}_2]\text{O}_4$, where the atom type in the square bracket represents that occupying the octahedral sites.
- In the inverse spinel structure, the cation distribution is $\text{B}[\text{AB}]\text{O}_4$, with the B-type cation distributed over both coordination geometries.
- **The occupation factor, λ , of a spinel is the fraction of B atoms in the tetrahedral sites: $\lambda = 0$ for a normal spinel and $\lambda = 1/2$ for an inverse spinel, $\text{B}[\text{AB}]\text{O}_4$.**

(b) Perovskites and related phases

- The perovskites have the general formula ABX_3 , in which the 12-coordinate hole of BX_3 (as in ReO_3) is occupied by a large A ion (Fig. 9). The X ion is most frequently O^{2-} or F^- (as in $NaFeF_3$).
- **Barium titanate, $BaTiO_3$** has a perfect cubic perovskite structure at temperatures above $120^\circ C$.
- The temperature at which certain magnetic materials undergo a sharp change in the magnetic properties is known as the **Curie temperature (T_C)**. For $BaTiO_3$, $T_C = 120^\circ C$.

(c) **Piezoelectricity** is the generation of an electrical field when the crystal is under stress or the change in dimensions of the crystal when an electrical field is applied.

- Piezoelectric materials are used for a variety of applications, such as pressure transducers, ultramicromanipulators (where very small movements can be controlled), sound detectors. Examples are $BaTiO_3$, $NaNbO_3$, $NaTaO_3$, and $KTaO_3$.

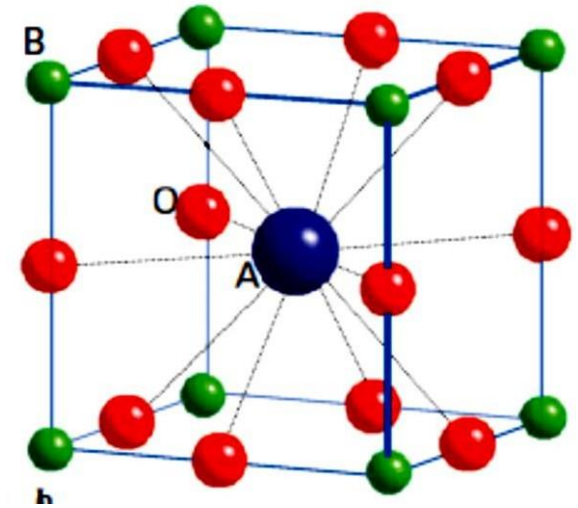


Fig. 9 Views of the perovskite (ABO_3) structure (a) emphasizing the 12-fold coordination of the larger A cation

(d) **High-temperature superconductors**

Most of the high temperature superconductors (which were first reported in 1986) can be viewed as variants of the perovskite structure.

Superconductors have two striking characteristics.

- a. Below a critical temperature, T_c (not to be confused with the Curie temperature of a ferroelectric, T_C), they enter the superconducting state and have zero electrical resistance.
- b. In this superconducting state they also exhibit the **Meissner effect**, the exclusion of a magnetic field. Because of the Meissner effect, a pellet of superconductor levitates above a magnet. It is also the basis for a number of potential applications of superconductors that include magnetic levitation, as in MAGLEV trains.

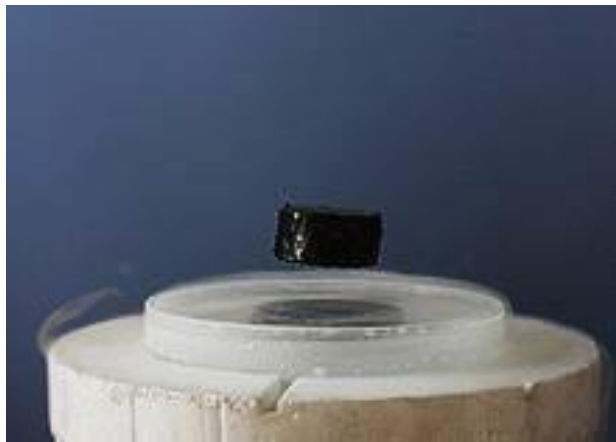


Fig. 10 A magnet levitating above a high-temperature superconductor, cooled with liquid nitrogen. Persistent electric current flows on the surface of the superconductor, acting to exclude the magnetic field of the magnet (Faraday's law of induction). This current effectively forms an electromagnet that repels the magnet.

- Mercury is a superconductor below 4.2 K. Magnesium diboride is superconducting below 39 K.
- In 1986, the first **high-temperature superconductor** (HTSC) was discovered.
- Two types of superconductors are known:

Type I show abrupt loss of superconductivity when an applied magnetic field exceeds a value characteristic of the material.

Type II superconductors, which include high-temperature materials, show a gradual loss of superconductivity above a critical field denoted H_c .

- The first HTSC reported was $\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_4$ ($T_c = 35 \text{ K}$), which is a member of the solid-solution series $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ in which Ba replaces a proportion of the La sites in La_2CuO_4 .
- One of the most widely studied HTSC oxide materials is $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ($T_c = 93 \text{ K}$) Fig. 11.

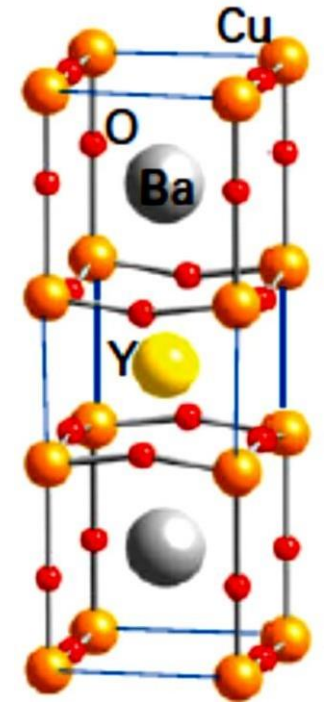


Fig. 11 The unit cell of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconductor.

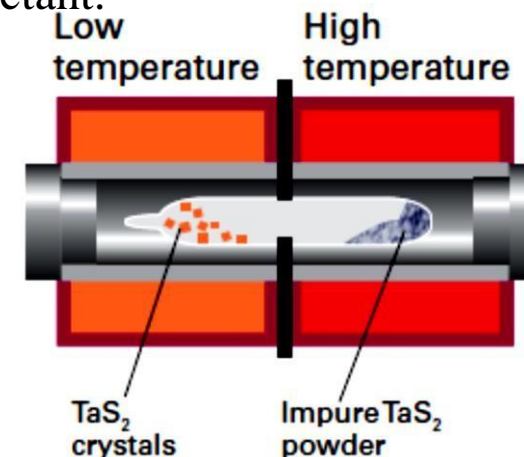
Chalcogenides, intercalation compounds, and metal-rich phases

Chalcogenides are compounds formed principally from chalcogen element atoms, for example, sulfur, selenium or tellurium and at least one more electropositive element. Eg. TaS_2 , CdS_2

(a) Synthesis and crystal growth

- d-Metal disulfides are synthesized by the direct reaction of the elements in a sealed tube and purified by using chemical vapour transport with iodine.
- In a typical procedure, the crude material is loaded into one end of a borosilicate or fused quartz tube. The impure metal chalcogenide is vaporized at one end and redeposited as pure crystals at the other (Fig. 12). The technique is called chemical vapour *transport*.
- The CVT agent, which is often a halogen, produces an intermediate volatile species, such as a metal halide and after crystal formation it is released and diffuses back to pick up more reactant.
- For example, TaS_2 can be transported with I_2 in a temperature gradient.

Fig. 12 Vapour transport crystal growth and purification of TaS_2 . A small quantity of I_2 is present to serve as a transport agent.

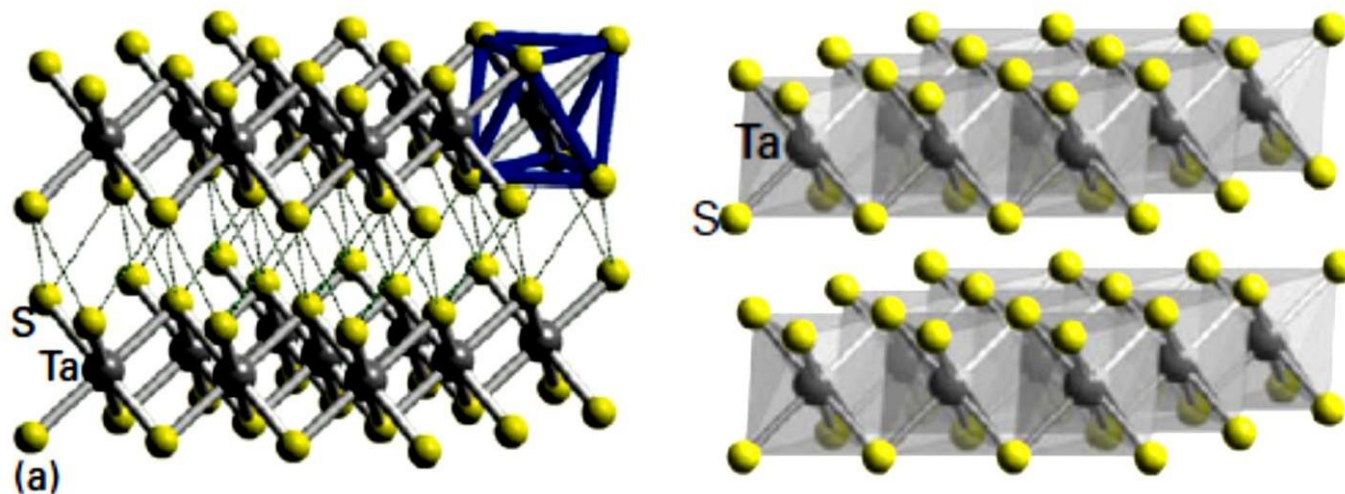


(b) Structure

Elements on the left of the d block form sulfides consisting of sandwich-like layers of the metal coordinated to six S ions; the bonding between the layers is very weak.

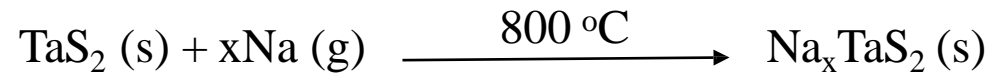
- In TaS_2 and many other layered disulfides, the d-metal ions are located in octahedral holes between close-packed AB layers (Fig. 13a).
- The Ta ions form a close-packed layer denoted X, so the metal and adjoining sulfide layers can be portrayed as an AXB sandwich.
- These sandwich-like slabs form a three-dimensional crystal by stacking in sequences such as AXBAXBAXB..., where the strongly bound AXB slabs are held to their neighbours by weak dispersion forces.
- An alternative view of these MS_2 structures, which have the metal ions in octahedral holes, is as MS_6 octahedra sharing edges (Fig. 13b).

Fig. 13 (a) The structure of TaS_2 (CdI_2 -type). The Ta atoms reside in octahedral sites between the AB layers of S atoms. (b) The metal disulfide structures drawn as layers of MS_6 octahedra sharing edges in TaS_2 .



(c) Intercalation and insertion

- Insertion compounds can be formed from the d-metal disulfides either by direct reaction or electrochemically; insertion compounds can also be formed with molecular guests.
- Reactions in which the structure of one of the solid starting materials is not radically altered are called **topotactic reactions**. For example, hydration, dehydration, and ion exchange reactions may also be topotactic.
- The insertion of alkali metal ions into host structures can be achieved by direct combination of the alkali metal and the disulfide:



with $0.4 < x < 0.7$. Insertion may also be achieved by using a highly reducing alkali metal compound, such as butyllithium, or the electrochemical technique of **electrointercalation** (Fig. 20).

- One advantage of electrointercalation is that it is possible to measure the amount of alkali metal incorporated by monitoring the current (I) passed during the synthesis (using $n_e = It/F$).

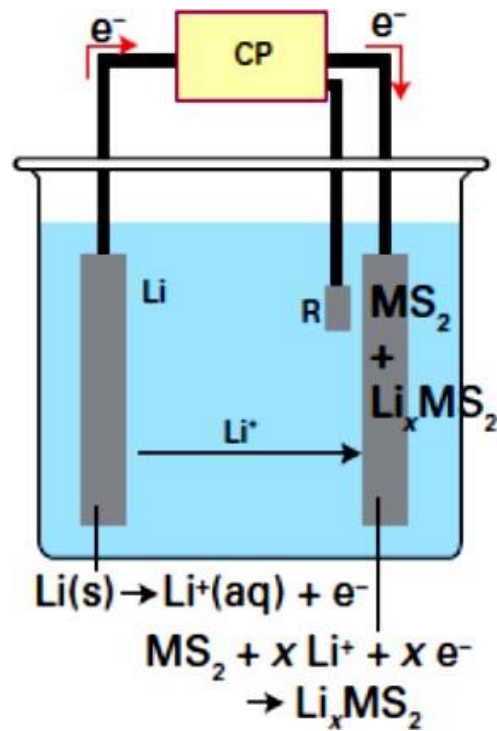


Fig. 14 Schematic experimental arrangement for electrointercalation. A polar organic solvent (such as polypropylene carbonate) containing an anhydrous lithium salt is used as an electrolyte. R is a reference electrode and CP is a coulometer (to measure the charge passed) and a potential controller.

- Insertion compounds are examples of mixed ionic and electronic conductors. The insertion process can be reversed either chemically or electrochemically. This reversibility makes it possible to recharge a lithium cell by removal of Li from the compound.
- Insertion compounds also can be formed with molecular guests. The most interesting guest is the metallocene Co(η^5 -Cp)₂, where Cp = C₅H₅, which can be incorporated into a variety of hosts with layered structures, such as TiS₂, TiSe₂, and TaS₂.

Inorganic pigments

- Pigments were originally developed from naturally occurring compounds such as hydrated iron oxides, manganese oxides, lead carbonate, vermilion (HgS), orpiment (As_2S_3), and copper carbonates.

(a) White pigments

- **Titanium dioxide is used almost universally as a white pigment.** Other examples of white pigment include ZnO , and ZnS , lead(II) carbonate.
- Uses of titanium dioxide, include paints, coatings, and printing ink, fibres, paper, white cements, and even foodstuffs (where it can be added to icing sugar, sweets, and flour to improve their brightness).

(b) Black, absorbing, and specialist pigments

- The most important black pigment is *carbon black*, which is industrially manufactured form of soot. Carbon black is obtained by partial combustion or pyrolysis (heating in the absence of air) of hydrocarbons.
- $\text{Bi}_2\text{Mn}_4\text{O}_{10}$ absorb in the visible region but reflect infrared wavelengths.
- Examples of more specialist inorganic pigments are magnetic pigments based on coloured ferromagnetic compounds such as Fe_3O_4 and CrO_2 , and anticorrosive pigments such as zinc phosphates.

Fullerides

- Solid C_{60} can be considered as a close-packed array of fullerene molecules interacting only weakly through van der Waals forces; holes in arrays of C_{60} molecules may be filled by simple and solvated cations and small inorganic molecules(Fig. 15)

Fig. 15 The arrangement of C_{60} molecules in a face-centred cubic lattice in the crystalline material.

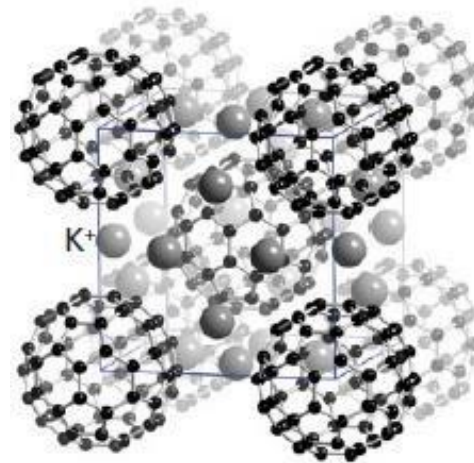
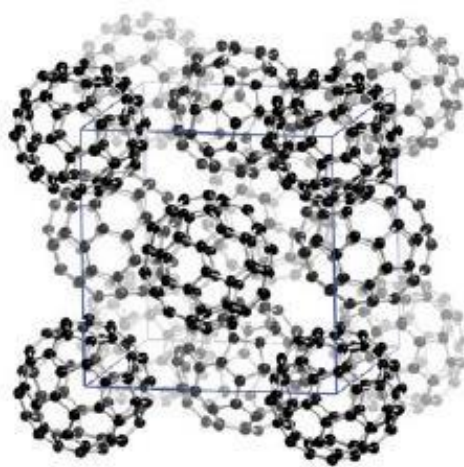


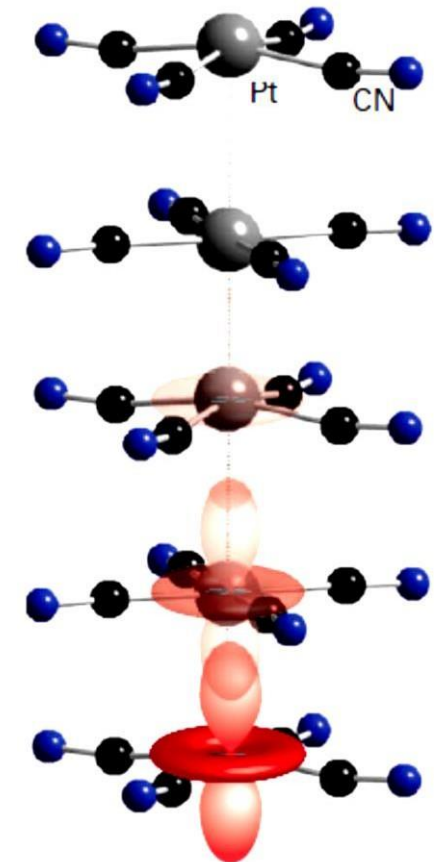
Fig.16 The structure of K_6C_{60} with a body-centred cubic unit cell with C_{60}^{6-} molecular ions at the cell corners and body centre, and K^+ ions occupying half of the sites in the faces of the cell which have approximate tetrahedral coordination to four C_{60} molecular ions.

- With excess alkali metal, compounds of composition M_6C_{60} , M K, Rb, Cs, and sometimes Na and Li, are formed. The structure of K_6C_{60} is body-centred cubic(Fig. 16).
- Of most interest are the compounds with the stoichiometries M_3C_{60} , which become superconducting in the temperature range 10–40 K depending on the type of metal. **K_3C_{60} becomes superconducting on cooling to 18 K.**

Molecular materials chemistry

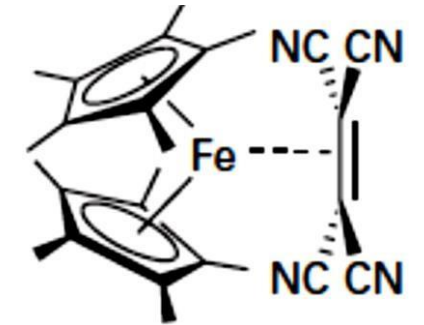
(a) One-dimensional metals

- A one-dimensional metal is a material that exhibits metallic properties along one direction in the crystal and nonmetallic properties orthogonal to that direction. Such properties arise when the orbital overlap occurs along a single direction in the crystal (as in VO_2).
- In such materials, the structural requirements for a one-dimensional metal are satisfied by the presence of square-planar complexes that stack one above another (Fig. 17).
- Square-planar complexes are commonly found for metal ions with d^8 configurations, and the overlap of orbitals between d^8 species is greatest for the heavy d metals of Period 6 (which use 5d orbitals). Hence the compounds of interest are mainly associated with Pt(II) and Ir(I), where a band is formed from overlapping d_{z^2} and p_z orbitals.
- The first one-dimensional metal Pt complex was made in 1846 by oxidation of a solution of $\text{K}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$ with bromine, which on evaporation gave crystals of $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 3\text{H}_2\text{O}$, known as KCP

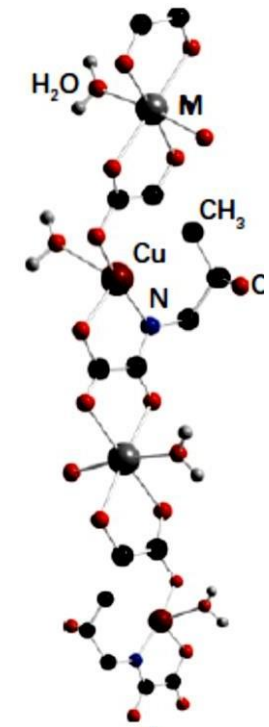


(b) Molecular magnets

- Molecular solids containing individual molecules, clusters, or linked chains of molecules can show bulk magnetic effects such as ferromagnetism.
- Examples of ferromagnetic molecular inorganic compounds are decamethylferrocene tetracyanoethenide (TCNE), $[\text{Fe}(\eta^5\text{-Cp}^*)_2(\text{C}_2(\text{CN})_4)]$ (**1**, $\text{Cp}^* = \text{C}_5\text{Me}_5$). These materials, which have structures based on chains of alternating $[\text{M}(\eta^5\text{-Cp}^*)_2]$ and TCNE ions, show ferromagnetism along the chain direction below $T_C = 4.8$ K (for $\text{M} = \text{Fe}$) and 6.2 K (for $\text{M} = \text{Mn}$).
- An alternative approach to molecular based compounds exhibiting magnetic ordering consists of assembling chains of magnetically interacting centres. For example, $\text{MnCu}(\text{2-hydroxy-1,3-propenebisoxamato}) \cdot 3\text{H}_2\text{O}$ consists of chains of alternating $\text{Mn}(\text{II})$ and $\text{Cu}(\text{II})$ ions bridged by the ligand.
- The magnetic moments on the metal ions in the chains order ferromagnetically below 115 K.



1 (TCNE), $[\text{Fe}(\eta^5\text{-Cp}^*)_2(\text{C}_2(\text{CN})_4)]$



(c) Inorganic liquid crystals

- Inorganic metal complexes with disc- or rod-like geometries can show liquid crystalline properties.
- Liquid crystalline, or **mesogenic**, compounds possess properties that lie between those of solids and liquids and include both. For instance, they are fluid, but with positional order in at least one dimension.
- The molecules that form liquid crystalline materials are generally **calamitic** (rod-like) or **discotic** (disc-like), and these shapes lead to the ordered liquid-type structures in which the molecules align in a particular direction (Fig. 19).

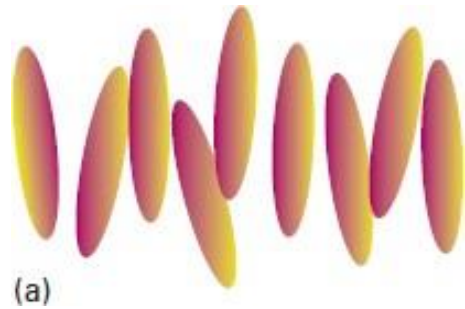


Fig. 19 Schematic diagram of liquid crystalline materials based on (a) calamitic (rod-like) or (b) discotic (disc-like) molecules

The conductivities of inorganic solids

- Electronic conduction is also a characteristic of semiconductors. The criterion for distinguishing between a metallic conductor and a semiconductor is the temperature dependence of the electric conductivity:
- A **metallic conductor** is a substance with an electric conductivity that *decreases* with increasing temperature.
- A **semiconductor** is a substance with an electric conductivity that increases with increasing temperature.
- A solid **insulator** is a substance with a very low electrical conductivity.
- **Superconductors** are a special class of materials that have zero electrical resistance below a critical temperature.

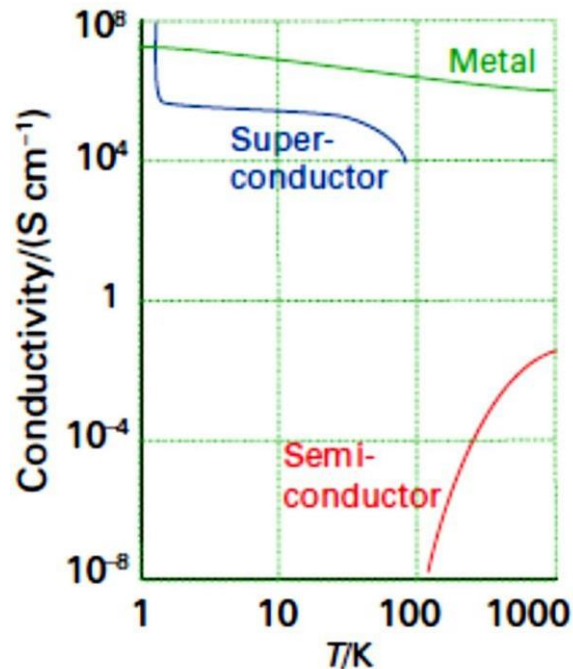


Fig. 20 The variation of the electrical conductivity of a substance with temperature is the basis of the classification of the substance as a metallic conductor, a semiconductor, or a superconductor.

Reference:

1. Peter Atkins, Tina Overton, Jonathan Rourke, Mark Weller, Fraser Armstrong, Mike Hagerman; Shriver & Atkins' Inorganic Chemistry, 5th Ed. 2012, OXFORD UNIVERSITY PRESS-NEW DELHI.