A diverse array of methods are available to synthesize solid compounds and materials.

**Care must be taken:**
- stoichiometric quantities (no purification possible)
- pure starting materials (99%, 99.95%, 99.99%, 99.998%, etc.)
- ensure the reaction has gone to completion (no purification possible)

**Solids may need to:**
- be highly pure → silica glass for fiber optics (99.99999%)
- be less highly pure → laboratory glassware
- be in unusual oxidation states → hydrothermal
- be a fine powder
- be a large single crystal

**Solid-State or Ceramic Method**

Consists of heating two non-volatile solids which react to form the required product.

- The solid-state method can be used to prepare a whole range of materials including mixed metal oxides, sulfides, nitrides, aluminosilicates, etc.

\[
\text{ZrO}_2(s) + \text{SiO}_2(s) \rightarrow \text{ZrSiO}_4(s) \quad \text{heat to 1300°C}
\]

- The method can be used to prepare an extremely large number of compounds.

**Disadvantages**

- High temperatures are generally required (500-2000°C), because it takes a significant amount of energy to overcome the lattice energy so a cation or anion can diffuse into a different site.
- The desired compound may decompose at high temperatures.
- The reaction may proceed very slowly, but increasing the temperature speeds up the reaction since it increases the diffusion rate.
- Generally, solids are not raised to their melting point, so reactions take place in the solid state (subsolidus).
Solid State Reactions

- Diffusion controlled: Fick’s 1st Law
  \[ J = -D \frac{dc}{dx} \]
- Small particle sizes that are well mixed are needed to maximize the surface contact area.
- Tamman’s Rule suggests a temperature of about two-thirds of the melting point (K) of the lower melting reactant is needed to have reaction to occur in a reasonable time.

• Thorough grinding is necessary to achieve a homogenous mixture of reactants.
• The number of crystallites in contact may be increased by pelletizing the powders using a hydraulic press.
• The reaction mixture is typically removed and reground to bring fresh surfaces in contact, which speeds up the reaction.
• Reaction times are sometimes hours, but may range into several days or weeks for a complete reaction, with intermediate grinding.
• Sample purity is typically examined using powder X-ray diffraction.
• Furnaces use resistance heating with metal, SiC, or MoSi2 heating elements.
• Conversion of electrical energy into heat (to 2300 K). An electrical arc directed at the sample may achieve 3300 K. A CO2 laser can give temperatures up to 4300 K.
• Containers for the reaction (crucibles) must be able to withstand high temperatures and be sufficiently inert to the reactants. Common crucibles are silica (to 1430 K), alumina (to 2200 K), zirconia (to 2300 K), or magnesia (2700 K). Platinum (m.p. 2045 K) and silver (m.p. 1235 K) are also used for some reactions.
Sealed Tube Methods

If reactants are volatile or air sensitive, then heating in an open atmosphere is inappropriate. Evacuated tubes are used when the products or reactants are sensitive to air or water, or are volatile.

$$\text{Sm} (s) + \frac{1}{8} \text{S}_8 (s) \rightarrow \text{SmS}$$

Sulfur has a low boiling point (717 K), so the reaction mixture is placed in an evacuated tube to prevent it from boiling off and being lost.

The tube is often made of Pyrex or silica, since these are fairly inert and can be flame sealed with a Pyrex vacuum system. Usable to about 1000-1100 K.

The sample might be ground, then heated in a tantalum tube for high temperature reactions (to 2300 K).

The Ta tube must be sealed by welding the tube. An electric current is passed through the tube, generating high pressures and temperatures. Safety precautions must be taken in case of tube rupture.

Special Atmosphere

Synthesis of some compounds must be carried out under a special atmosphere.

- an noble gas, argon, may be used to prevent oxidation to higher oxidation state.
- an oxidizing gas, oxygen, might be used to form a high oxidation state.
- a reducing gas, hydrogen, might be used to form a low oxidation state.

Reactions usually take place in a small boat crucible placed in a tube in a horizontal tube furnace.

- Gas is passed of a period of time to expel all air from the apparatus, then continues to flow during the heating and cooling cycle. A bubbler is used to ensure positive pressure is maintained.
Polycrystalline samples might have particle sizes from 1-10 μm. With significant grinding, particles sizes of near 0.1 μm may be obtained. Diffusion is taking place over between 100 and 10,000 unit cells. Many methods, both physical and chemical, have been developed to improve mixing and particle size to reduce the diffusion path length.

**Spray-Drying:**
Reactants are dissolved in a suitable solvent and sprayed as fine droplets into a hot chamber. The solvent evaporates and leaves a mixture of the solids as a fine powder which can be heated to give the product.

**Freeze-Drying:**
Reactants are dissolved in a suitable solvent and frozen to liquid nitrogen temperatures (77 K). The solvent is removed by pumping to leave a fine powder.

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**Co-precipitation and precursor methods.**

Precursors such as nitrates and carbonates can be used as starting materials instead of oxides.

**Co-precipitation** involves taking a stoichiometric mixture of soluble salts of the metal and precipitating them as hydroxides, citrates, oxalates, or formates. The mixture is filtered, dried, and then heated to give the final product.

**Precursor method** involves atomic level mixing by forming a solid compound (precursor) in which the metals of the desired compound are present in the proper stoichiometry. For example, a mixed salt of an oxyacid (e.g. acetate) containing M and M’ in the ratio of 1:2 is formed in the case of formation of MM’\(_2\)O\(_4\).

- the precursor is heated to decompose it to the desired product.
- homogeneous products are formed at relatively low temperatures.
- it is not always possible to find a suitable precursor
Precursor method example

\[
\text{Ti(OBu)}_4(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) \rightarrow \text{Ti(OH)}_4(\text{s}) + 4\text{BuOH}(\text{aq})
\]
Excess oxalic acid redissolves the precipitate.

\[
\text{Ti(OH)}_4(\text{s}) + (\text{COO})_2^{2-}(\text{aq}) \rightarrow \text{TiO}((\text{COO})_2)(\text{aq}) + 2\text{OH}^{-}(\text{aq}) + \text{H}_2\text{O}(\text{l})
\]

\[
\text{Ba}^{2+}(\text{aq}) + (\text{COO})_2^{2-}(\text{aq}) + \text{TiO}((\text{COO})_2)(\text{aq}) \rightarrow \text{Ba}[\text{TiO}((\text{COO})_2)](\text{s})
\]
Decomposition by heating (920 K) gives the desired oxide phase.

\[
\text{Ba}[\text{TiO}((\text{COO})_2)](\text{s}) \rightarrow \text{BaTiO}_3(\text{s}) + 2\text{CO}_2(\text{g}) + 2\text{CO}(\text{g})
\]

Decomposition of oxalates is also used to form ferrites (\text{MFe}_2\text{O}_4).
Products from precursor methods often contain small particles with a large surface area, which is desired for certain applications.

---

**Sol-Gel Method**

A concentrated solution or colloidal solution of the reactants, the ‘sol’, is prepared and then further concentrated to form the gel.

- The gel is heat-treated to form the product.

A **sol** is a colloidal suspension of particles in a liquid (~1-100 nm diameter)

A **gel** is a semi-rigid solid in which the solvent is contained in a framework of material that is either colloidal or polymeric.

A **dispersal** stage may involve oxides or hydroxides in water with a specific pH so the solid particles remain in suspension rather than ppt.

A **hydrolysis** may involve addition of metal alkoxides to water, which are hydrolyzed to give the oxide as a colloidal product.

The sol forms a gel by dehydrating or polymerizing.

The gel forms the product by heating to decompose the alkoxides or carbonates to give the oxide. Time and temperature is reduced compared to the conventional methods.
Sol-Gel Preparation of LiNbO₃

Preparation by solid-state method may lead to secondary phases at the higher temperatures needed for reaction.

LiNbO₃ may be prepared by the sol-gel method by starting with lithium ethoxide (LiOC₂H₅) and niobium ethoxide [Nb₂(OE₂H₅)₁₀].

• Each ethoxide may be dissolved in absolute EtOH and mixed.
• Addition of water leads to partial hydrolysis giving hydroxy-alkoxides.

\[
\text{Nb}_2(\text{OC}_2\text{H}_5)_5 + 2\text{H}_2\text{O} \rightarrow 2\text{Nb}(\text{OEt})_4(\text{OH}) + 2 \text{EtOH}
\]

• Hydroxy-alkoxides condense to form a polymeric gel with metal-oxygen-metal links.
• LiNbO₃ is formed when the gel is heated – the remaining ethanol and water is evaporated and any remaining ethyl groups are pyrolysed (forming CO₂ and H₂O).

Sol-Gel Preparation of doped SnO₂

Conductivity of SnO₂ may be increased by the addition of dopants such as Sb³⁺, forming an oxygen deficient n-type semiconductor,

• Sol-gels are suitable for the preparation of materials with a large surface area with a controlled distribution of dopants.
• Titanium doped SnO₂ may be prepared by adding titanium butoxide, Ti(OEt₄)₄, to a solution of SnCl₂•2H₂O in absolute EtOH.
• The tin(II) salt is easily hydrolyzed to give hydroxyl complexes and can be oxidized to tin(IV) by oxygen in air.
• Leaving the sol in an open container, a gel will be formed in about five days.
• Heating (333 K) at reduced pressure for two hours dries the gel.
• Heating (600 K) for 10 minutes produces a layer of SnO₂ doped with Ti⁴⁺.
Optical fibers need to be free from metallic impurities.

- use of volatile compounds of silica, liquid silicon alkoxide \[\text{Si(OR)}_4\] are more easily purified than solid silica \((\text{SiO}_2)\).

\[
\text{Si(OR)}_4 + 4 \text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4 \text{ROH}
\]

\[
\text{Si(OH)}_4 + \text{Si(OH)}_2 = (\text{OH})_3\text{Si-O-Si(OH)}_3 + \text{H}_2\text{O}
\]

\[
(\text{OH})_3\text{Si-O-Si(OH)}_3 + 6\text{Si(OH)}_3 =
\]

Fibers can be pulled as gelation occurs, then heated 1300 K to increase density.

A sol-gel may be used to create a biosensor.

- A biosensor, often an enzyme, is often very specific.
- One limitation includes denaturing, if the enzyme is removed from the aqueous environment or the pH is altered.
- An approach to minimize this problem is to trap the enzyme with its microenvironment in a silica gel.
- A sol of silica may prepared by acid hydrolysis of \(\text{Si(OMe)}_4\).
- The sol is buffered at a suitable pH for the enzyme and the enzyme is added.
- As the sol forms a gel by condensing, the enzyme is trapped in the cavities in the gel and is surrounded by an aqueous medium of the correct pH.

http://biomaterials.kaist.ac.kr/research/research.htm
In a liquid or solid, the molecules of ions are not free to rotate. The alternating electric field of the radiation:

1. If charged particles are present, these move under the influence of the field and produce an oscillating electric current. Resistance to the movement causes energy to be transferred to the surroundings as heat, known as conduction heating.

2. If no particles are present that can move freely, but molecules or units with dipole moments are present, then the electric field acts to align the dipole moments. This is dielectric heating. This is the type of heating that acts on water molecules in food.

The electric field of the microwave radiation is oscillating at the frequency of the radiation, but the electric dipoles in solids do not change their alignment instantaneously, but with a characteristic time, \( \tau \).

The oscillating electric field changes its direction rapidly so that the time between changes is much smaller than \( \tau \), then the dipoles cannot respond fast enough and do not realign (lags behind).

The solid absorbs some of the microwave radiation and the energy is converted to heat.

Depends on the dielectric constant and the dielectric loss.

To use microwave heating, at least one component of the reaction mixture must absorb microwave radiation.
Microwave irradiation raises the temperature of the whole volume simultaneously (i.e. bulk heating).

High Temperature Superconductor \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \)

Conventional method takes about 24 hours to complete, whereas it takes approximately 2 hours using microwave synthesis.

- A stoichiometric mixture of \( \text{CuO}, \text{Ba(NO}_3)_2, \text{Y}_2\text{O}_3 \) are placed in a modified microwave oven that allows the safe removal of nitrogen oxides formed during the reaction.
- The reaction mixture is treated with 500 watts of microwave radiation for five minutes, then reground and exposed to microwave radiation between 130-500 watts for 15 minutes. The reaction mixture is ground again and exposed to microwave radiation for 25 minutes.
- The microwaves couple to the \( \text{CuO} \).
- A 5 to 6 g sample of \( \text{CuO} \) exposed to 500 W of microwave radiation for 30 seconds attained a temperature of 1074 K.
- Other oxides that strongly absorb microwave radiation include \( \text{ZnO}, \text{V}_2\text{O}_5, \text{MnO}_2, \text{PbO}_2, \text{Co}_3\text{O}_4, \text{Fe}_2\text{O}_4, \text{NiO}, \text{and WO}_3 \). Carbon, \( \text{SnCl}_2 \), and \( \text{ZnCl}_2 \) are also strong absorbers.
- A 5 to 6 g sample of \( \text{CaO} \) exposed to 500 W of microwave radiation for 30 minutes attained a temperature of 356 K.
- Microwave synthesis does not solve the problem of chemical inhomogeneity.
- The reaction temperatures are high, and relatively difficult to precisely control.
- One advantage is less problems with cracking, since heating is from inside.

http://www.nature.com/nrd/journal/v5/n1/fig_tab/nrd1926_F1.html
Combustion synthesis is a self-propagating high temperature synthetic method that has been developed as an alternative to the standard method.

- Combustion synthesis uses highly exothermic ($\Delta H < -170$ kJ/mol) and even explosive reactions to maintain a self-propagating high reaction temperature.
- The method has been used to prepare many refractory materials including borides, nitrides, oxides, silicides, intermetallics, and ceramics.
- Reactants are mixed together, formed into a pellet, and ignited (laser, electric arc, heating coil) at high temperature.
- Once ignited, the reaction propagates as a synthesis wave, the reaction must lose less heat than it generates, or it will quench.
- Temperatures up to 3000 K are maintained during the fast reaction.
- Self ignition can sometimes be achieved by ball milling.
- In some cases, the presence of a magnetic field will make the reaction proceed faster and with a higher temperature wave.

Combustion synthesis production of $\text{BaFe}_{12}\text{O}_{19}$ from $\text{Fe}$, $\text{Fe}_2\text{O}_3$, and $\text{BaO}_2$. The solid flame propagates from left to right in a silica tube with a constant flow of oxygen.
Compounds prepared using self-propagating high temperature synthesis:

- Hydrides for hydrogen storage (e.g. MgH$_2$)
- Borides for abrasives and cutting tools (e.g. TiB$_2$)
- Carbides for abrasives and cutting tools (e.g. SiC and TiC)
- Nitrides for high strength, heat resistant ceramics (e.g. Si$_3$N$_4$)
- Oxides for high temperature superconductors (e.g. cuprates)
- Silicides for high temperature heating elements (e.g. MoSi$_2$)
- Composites have been used to coat the inside of steel pipes with an inner layer of Fe and a surface layer of Al$_2$O$_3$.

\[
3\text{Fe}_3\text{O}_4 + 8 \text{Al} \rightarrow 4 \text{Al}_2\text{O}_3 + 9 \text{Fe}
\]
1. high solvent pressure in an autoclave – known as the hydrothermal method
2. using a high pressure of a reactive gas
3. directly applied hydrostatic pressure on solids
4. Detonation
5. Ultrasound

The hydrothermal method involves heating the reactants in a closed vessel (an autoclave).

- An autoclave is constructed from thick stainless steel and fitted with safety valves.
- Typically lined with a non-reactive material such as teflon.
- The autoclave is heated to above its normal boiling point, the pressure is increased and is called ‘super heated water’.
- These hydrothermal conditions also exist in nature and many minerals are formed in this process (e.g. zeolites, emeralds, etc.)
- Low temperatures are one advantage of the method.
- Unusual oxidation states may be stabilized.
- Superheated water may dissolve some metal oxides that are insoluble under ambient conditions.

Hydrothermal synthesis of quartz

Uses a temperature gradient to dissolve the reactant at higher temperature, which is transported up the reaction tube by convection, then crystallizes out at a lower temperature.
Hydrothermal synthesis of \( \text{CrO}_2 \)

\( \text{Cr}_2\text{O}_3 \) is the stable oxide of chromium at normal conditions.

\[
\begin{align*}
\text{Cr}_2\text{O}_3 + \text{CrO}_3 & \rightarrow 3\text{CrO}_2 \\
\text{CrO}_3 & \rightarrow \text{CrO}_2 + \frac{1}{2} \text{O}_2
\end{align*}
\]

\[
3 \text{CrO}_3 + \text{Cr}_2\text{O}_3 \rightarrow 5 \text{CrO}_2 + \text{O}_2
\]

Hydrothermal synthesis of zeolite A, \( \text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]\cdot27\text{H}_2\text{O} \).

• Hydrated alumina, \( \text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O} \) is dissolved in concentrated \( \text{NaOH} \).
• The cooled solution is mixed with sodium metasilicate, \( \text{Na}_2\text{SiO}_3\cdot9\text{H}_2\text{O} \) and a thick white gel forms.
• The gel is placed in a closed teflon bottle and heated to 363 K over 6 hours.
• Changes in the form of alumina, pH of the solution, type of base used, and proportions of alkali, aluminum compound, and silica lead to the production of different zeolites.
Microporous and Mesoporous Solids

Large cations, e.g. tetramethylammonium (NMe₄⁺) and tetrapropylammonium (N(C₃H₇)₄⁺), may be used as a template around which the aluminosilicate framework crystallizes with large cavities to accommodate the ion.

• upon later heating the cation is pyrolyzed, but the structure retains the cavities.

• these structures are known as microporous, with a pore size of between 200 and 2000 pm.

Zeolites with pore sizes of 2000-10000 pm are known as mesoporous solids. Liquid crystal templating is a technique to prepare mesoporous solids.

![Micelle, Micellar rod, Hexagonal array, Silicate, MCM-41](image)

Yttrium Aluminum Garnet

Starting materials have very different solubilities.

• Y₂O₃ is placed in a cooler section of the autoclave and Al₂O₃ (sapphire) in the hotter section to increase the solubility.

• Y₃Al₅O₁₂ forms where the two zones meet.

\[ 3Y₂O₃ + 5 Al₂O₃ \rightarrow 2Y₃Al₅O₁₂ \]
Application of high pressure and temperatures can induce reactions and phase changes that are not possible under ambient conditions.

- High pressure tends to decrease volume and improve packing efficiency in ionic compounds, thereby increasing the coordination numbers.

A **piston and cylinder** allows pressures up to 5 GPa (50,000 atm) and 1800 K.

A **belt apparatus** uses two opposing tungsten carbide cylinders to reach 15 GPa and 2300 K.

- Can be used to make synthetic diamonds.

A **diamond anvil** uses to directly opposed diamonds, four tetrahedrally opposed, or six in an octahedral configuration.

- Only mg amounts of samples can be prepared or examined (phase transitions).

**Synthetic Diamond**

Diamonds are used for many purposes, including jewelry, machinery, etc.

- In order to synthesize diamonds, the geothermal conditions that produce natural diamonds must be imitated.

- Crystals up to 1 mm in length may be prepared by dissolving graphite in a molten metal such as Ni, Co, or Ta in a vessel, then subjecting the graphite to pressures of 6 GPa and temperatures of 2300 K until diamond crystals form.

- Molten metal lowers the working temperature and pressure.

- Gemstone quality diamonds may also be made.

- Diamond has high thermal conductivity, which through isotopic substitution ($^{12}$C) may be further increased.

- Above 8 GPa and 700 K, C$_{60}$ forms two amorphous phases which are harder than diamond. The phases have a lower density than diamond and are semiconducting.
In CVD, powders and microcrystalline products are prepared from reactants in the vapor phase, then can be deposited on a substrate to form single crystal films for devices.

- Volatile starting materials are heated to form vapors, then mixed at a suitable temperature and transported to the substrate by carrier gas.
- Typical starting materials include hydrides, halides, and organometallic compounds, since these tend to be volatile.
- When an organometallic precursor is used, it is called MOCVD (Metal Organic Chemical Vapor Deposition).

**Chemical Vapor Deposition**

\[
\begin{align*}
\text{AsCl}_3 + \text{Ga} + \frac{3}{2} \text{H}_2 & \rightarrow \text{GaAs} + 3 \text{HCl} \\
\text{SiCl}_4 + 2 \text{H}_2 & \rightarrow \text{Si} + 4 \text{HCl} \\
\text{SiH}_4 & \rightarrow \text{Si} + 2 \text{H}_2
\end{align*}
\]

**Diamond Films**

- Diamond films are made by CVD at low pressure and below 1300 K by heating gas mixtures (methane or acetylene and hydrogen), or by breaking down the mixtures with microwaves.
- The carbon atoms and carbon containing radicals are deposited onto a substrate.
- It is also possible to deposit monocrystalline layers onto a seed diamond, building a larger diamond layer by layer.
- Used to deposit non-scratch optical coatings, coatings on knives and scalpels so they retain their sharpness, and as a wear resistant coating on moving parts.
• Sol-gel method uses lithium and niobium alkoxides, but lithium alkoxides are less volatile than niobium alkoxides.
• Compounds of similar volatility are preferred for good films.
• A more volatile compound of lithium, a β-diketonate of Li from 2,2,6,6-tetramethylheptan-3,5-dione is used.
• The lithium compound is heated to 520 K and niobium pentamethoxide at 470 K is in a stream of Ar containing O$_2$.
• LiNbO$_3$ was successfully deposited on the reaction vessel when heated to 720 K.

Epitaxy methods:

**Vapor Phase Epitaxy** – possible to prepare high purity thin films. The epitaxial growth, a precursor is decomposed in the gas phase and a single crystal is built up layer by layer.

**Gallium Arsenide (GaAs)**

\[2\text{Ga}(g) + 2\text{AsCl}_3(g) \rightarrow 2\text{GaAs}(s) + 3\text{Cl}_2(g)\]

or

\[\text{Ga(CH}_3)_3(g) + \text{AsH}_3(g) \rightarrow \text{GaAs} + 3\text{CH}_4(g)\]

**Mercury Telluride (HgTe)**

\[(\text{C}_2\text{H}_5)_2\text{Te}(g) + \text{Hg}(g) \rightarrow \text{HgTe}(s)\]

Substrate temperature = 470 K, about 200 °C lower than thermal decomposition temperature.
Molecular Beam Epitaxy

- A narrow stream of molecules is formed by heating a compound in an oven with a hole which is small compared to the mean free path of the gaseous molecules.
- Thin layers are built up by directing the beam onto the substrate.
- The relative pressure of the beams are adjusted to achieve the desired composition.

![Diagram of layers of different materials.](image)

The layers of an active region of a quantum cascade laser.

Chemical Vapor Transport

In CVT, a solid or solids interact with a volatile compound and a solid product is deposited in different part of the apparatus.

![Diagram of growth of magnetite crystals.](image)

Growth of magnetite crystals using chemical vapour transport

\[
\text{Fe}_3\text{O}_4(s) + 8\text{HCl}(g) \rightarrow \text{FeCl}_2(g) + 2\text{FeCl}_3(g) + 4\text{H}_2\text{O}(g)
\]

The reaction is endothermic, so the equilibrium moves to the right as the temperature is raised. At the cooler end of the tube, the equilibrium shifts to the left and magnetite is deposited.
Silicon for the electronics industry has to have low levels of impurities, less than one impurity atom in $10^{10}$ Si.

$\text{SiHCl}_3$ is highly volatile and distilled and decomposed as polycrystalline material onto rods of high purity silicon at 1300 K.

Large single crystals are made by the Czochralski process.

- The silicon is melted in an atmosphere of Ar, then a single crystal seed rod is used as a seed which is dipped into the melt.
- The crystal is slowly withdrawn, pulling an ever lengthening single crystal in the same orientation as the original seed.

**Czochralski Process**

**Float-zone** process – uses a moving heater to produce a single crystal as it moves.

**Zone-refining** – impurities tend to stay dissolved in the melt, so those are swept to the end of the crystal and rejected.

**Bridgman and Stockbarger** and related temperature gradient methods.
Verneuil method – a powdered sample is melted to high temperature in a high temperature oxy-hydrogen flame (or plasma torch) and droplets are allowed to fall on to a seed crystal.

Skull Melting – grow large single crystals of refractory oxides.

Uses up to 50 kW, 4 MHz radio frequency that is transferred to a coil wrapped around the skull crucible (Cu) cooled by water.

The container can be evacuated and filled with an appropriate atmosphere and temperatures up to 3600 K may be achieved.

Crystal Growth - Solution Methods

Crystals have been traditionally grown from saturated solutions. Various techniques to induce crystallization:

- evaporating solvent
- freezing solvent
- addition of other components to reduce solubility

Oxides are very insoluble in water, so these may be dissolved in melts of borates, fluorides, or even metals.

- These solvents are known as a flux as it brings down the melting temperature of the solute.
- The melt is then cooled slowly until the crystals form, and the flux is poured or dissolved away.

liquid diffusion method

vapor diffusion method
Solids produced by the reversible insertion of guest molecules into lattices are known as intercalation compounds.

**Graphite intercalation compounds**

- Many layered solids form intercalation compounds, where a neutral molecule is inserted between weakly bonded layers.
- KC₈ has potassium ions that sit between the graphite layers, with a resulting increase in the interlayer spacing of 200 pm.
- The K donates an electron to the graphite (forming K⁺) and the conductivity of the graphite increases.
- Graphite electron-acceptor intercalation compounds have been made with NO₃⁻, CrO₃, Br₂, FeCl₃, AsF₅.

**Titanium Disulfide**

- Layered sulfide are also found for many oxides and sulfides of transition metals.
- Forming intercalation compounds with electron donors can greatly increase the conductivity.

\[ xC_4H_9Li + TiS_2 \rightarrow Li_xTiS_2 + (x/2)C_8H_{18} \]

---

• Mechanical grinding using **high-energy milling** can be used to form nanoparticles from bulk solids.

• Mechanical attrition can be used to produce uniformly sized particles.

• In micronizing milling, cylindrical grinding media is arranged in a container and shaken.

• In ball milling, the solid is rotated in a cylindrical container with a grinding medium such as ceramic or metal balls.

• Reduces grinding time compared to conventional grinding by hand.

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[Image of a milling process]

[Link to a research page: http://sciences.ucf.edu/physics/blair-research/]