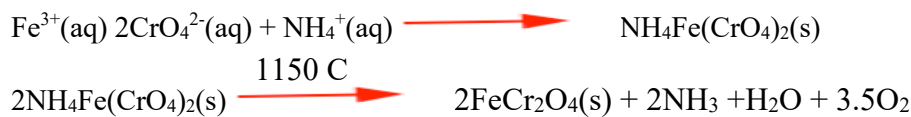## H. Synthesis of solid-state compounds continued…..

A. Spray drying: Reactants are dissolved in a common solvent and then are typically either sprayed into a hot chamber where the solvent instantaneously evaporates.

B. Solvation of metal salts: Two metal salts are dissolved in a solvent. Then the solvent is evaporated leaving behind the solid residue that is mixed on a much more intimate level. They key is that the salts have to have similar solubility because if you get one crashing out before the other then you get again an inhomogeneous mixture.

C. Co-precipitation:

Mixed ions in solution are placed with some complexing agent like oxalic acid, ammonia, catechols.

Here are two examples:

$$Zn^{2+}(aq) + 2Fe^{2++}(aq) + 3C_2O_4^{2-+}(aq) \xrightarrow{\hspace{2cm}} ZnFe_2(C_2O_4)*6H_2O(s) \xrightarrow{800\ C}$$
$ZnFe_2O_4$ spinel

You heat the precipitate at 800C. The problem is that you have to be sure that the correct ratio of ions precipitate

$$Fe^{3+}(aq)\ 2CrO_4^{2-}(aq) + NH_4^+(aq) \xrightarrow{\hspace{2cm}} NH_4Fe(CrO_4)_2(s)$$

$$2NH_4Fe(CrO_4)_2(s) \xrightarrow{1150\ C} 2FeCr_2O_4(s) + 2NH_3 + H_2O + 3.5O_2$$

D. Sol-gel: Similar to previous methods but instead forms an amorphous gel. Is a method where a solution containing the cation ingredients is first made. The solution is gradually dried and then forms a viscous, amorphous gel. The resulting gel is fired at high temperatures to remove all volatile components trapped in the gel pores or chemicall bound organic groups and then the material crystallizes.

The method is often used for the formation of metal-organic compounds like alkoxides, MOR, such as:

tetraethyl orthosilicate (TEOS) Si(OCH2CH3)4 as a source of SiO_2
Titanium isopropoxide (Ti(OPr)4 as a source of TiO_2,
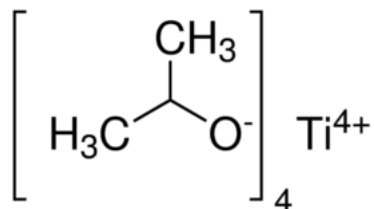
Aluminium t-butoxide, Al(OtBu)$_3$ as a source of Al_2O_3

These are usually mixed with alcohol and water. The alcohol aids the miscibility of the alkoxide in water. The water hydrolyses the alkoxide.

Ex)

1)Hydrolosis

$Si(OCH_2CH_3)_4 + H_2O \longrightarrow Si(OCH_2CH_3)_3(OH)$

2) Condensation polymerization

$(RO)_3\text{-}Si\text{-}OH \quad HO\text{-}Si(OR)_3 \longrightarrow (RO)_3\text{-}Si\text{-}O\text{-}Si\text{-}(OR)_3 + H_2O(g)$

You can imagine that this can happen 3-dimensionally. I am only showing one link…but you actually form an amorphous polymer.
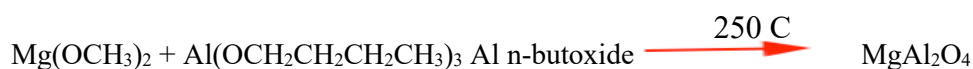

The hydrolosis step can be base or acid catalyzed:

$Cl\text{-} + H\text{+} + ROSi(OR)3 \longrightarrow HOSi(OR)3 + RCl$

Or base catalyzed

$OH\text{-} + Si(OR)_4 \longrightarrow HO(Si(OR)3 + \text{-}OR$

Used to synthesize the following:

MgAl2O4:
Just as an example, the reaction we studied earlier to form the spinel MgAl2O4

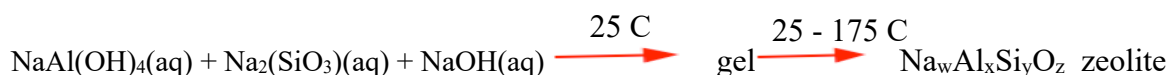$Mg(OCH_3)_2 + Al(OCH_2CH_2CH_2CH_3)_3 \text{ Al n-butoxide} \xrightarrow{250\ C} MgAl_2O_4$

Note that the temperature is significantly lower than 1500 C required for ceramic methods.

Sn-doped In_2O_3 (ITO) Used to put thin coatings of ITO on surfaces Indium tin oxide which is used as an electrode and also for energy control in buildings. The material transmits in the visible regime giving transparent windows, but it reflects in the Infrared regime not permitting heat to pass. You will find that are conductive materials now change absorption with appliec potential. So this is refered to as a electrochromic effect and is important for smart buildings you can change when windows absorb and reflect infrared radiation for instance.

Silica glass, alumina fibers, YSZ ceramics (yittria-stabilized zirconia) used in solid oxide fuel cells and gas sensors.

Synthesis of zeolites: microporous aluminosilicates

$NaAl(OH)_4(aq) + Na_2(SiO_3)(aq) + NaOH(aq) \xrightarrow{25\ C} gel \xrightarrow{25\ \text{-}\ 175\ C} Na_wAl_xSi_yO_z \text{ zeolite}$

The zeolite that forms depends on the starting composition, teperature, and pressure. For instance the higher the Al content the larger the numbero fo charge balancing cations needed. Also sometimes templates are used, usually an alkylammonium cation $(RNH_4)^+$ around which the porous structure crystallizes. You can imagine the templaeting agents can help in the formation of large pores. Templates must be removed at 300 to 400 C

While they are not thermodynamically stable, they are kinetically stable up to 300 to 400 C and so they are used as molecular sieves and a variety of catalytic applications.

E. Hydrothermal synthesis: referred to as solvothermal when water is replaced by some other pressure transmitting medium (solvent). Reactants are placed in water/steam at high pressures and temperatures. Reactants are placed in a Teflon lined cylinder or bomb that is sealed. It can or cannot be connected to an external pressure control. Keep in mind you can also control pressure by the fill volume.

For the last step of zeolite synthesis, the materials are heated hydrothermally to induce crystallization.

F. Intercalation and Deintercalation, these reactions involve the addition or removal of ions. In order to maintain charge balance, you must then add or remove electrons. You can refer to these reactions as topotactic because the overall architecture remains the same.

These have been used for the intercalation of H+ ions into tungsten bronzes (WO_3) used in electrochromic applications

Intercalation of Lithium into $LiMn_2O_4$ or Li_xCoO_2 cathode materials used in Lithium ion batteries

Intercalation of O into $TBa_2Cu_3O_x$ and other copper perovskites in order to tune the superconductivity.

Example:

Intercalation:

$$Ti^{4+}O_2 + \text{n-Bu-Li} \longrightarrow Li_xTi^{4+}_{1-x}Ti^{3+}_x O_{2 + x/2} \text{ octane}$$

Deintercalation:

$$LiCo^{3+}O_2 + I_2 \text{ in } CH_3CN \longrightarrow Li_xCo^{3+}_xCo^{4+}_{1-x}O_2 + LiI$$

Intercalation and Deintercalation reactions can also be carried out in graphite

G. Vapor Phase Transport: often used for the growth of single crystals or the purification of a compound or the synthesis of ternary or quaternary compounds.

A	B gas	

A reactants	AB gas	A crystals

T2		T1
	K	

Equilibrium is A(s) + B(g) $\longrightarrow$ $\longleftarrow$ AB(g)
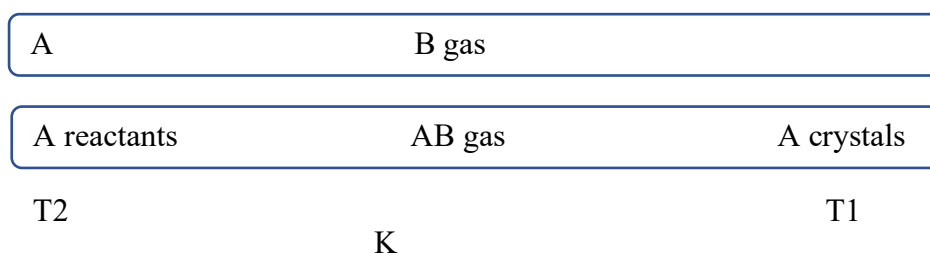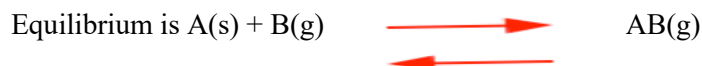
The tube is placed in a tube furnace so that the temperature gradient is between 50 and 100 C over the length of the tube. A reacts with B to form AB gas, which then decomposes at another point in the tube. I2 crystals are usually sealed in a tube and they readily sublime. This is referred to as the van Arkel method. You can also use reactants like O2 and HCl.
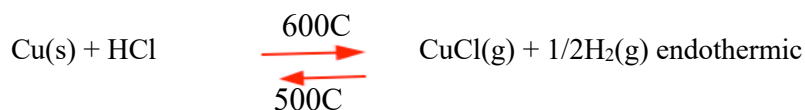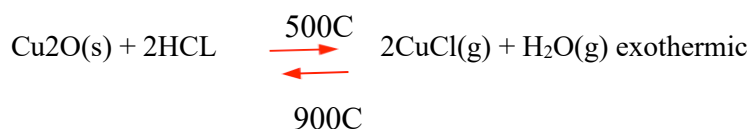
Vapor phase transport. The method depends on a reversible equilibrium shown above.

You want the equilibrium constant to be small. If the equilibrium constant K is zero AB does not form. If very large then AB is super stable and does not decompose.

If the rxn is endothermic then reactants are at the hot end. This means the reaction is pushed to the right at higher temperature. Then you are pushing the equilibrium towards AB.
So T2 >T1 in the above diagram

If the rxn is exothermic then reactants are at the cold end. T1 >T2

If we have a mixture of Cu and Cu2O and we want to separate the two….

$Cu_2O(s) + 2HCL$ $\xrightarrow{500C}$ $\xleftarrow{900C}$ $2CuCl(g) + H_2O(g)$ exothermic

$Cu(s) + HCl$ $\xrightarrow{600C}$ $\xleftarrow{500C}$ $CuCl(g) + 1/2H_2(g)$ endothermic

If T1 >T2 then Cu2O is transported to T2 because reactants are at the cold end.
If T2>T1 then Cu is transported to T2 because reactants are at the hot end.

Preparation of other compounds:

$2CaO + SnO_2$ $\longrightarrow$ Ca_2SnO_4

In the presence of CO the reaction speeds up because

$SnO_2(s) + CO(g)$ $\longrightarrow$ $SnO(g) + CO_2(g)$

The gaseous SnO is transported to the CaO, where it reacts. The gases react more quickly than those in the solid state becaseu the mobility is significantly improved. Likewise the presence of gases can help in normal solid state reactions as you can see above how it helps to transport reactants to the interface.

H. CVD (chemical vapor deposition) commonly used to make industrial coatings and thin films, especially for electronics. In this method you have precursor molecules that have the elements of interest. The molecules are decomposed in the gas phase and then then the resulting products from the decomposition are deposited on the surface of everything in the near vicinity. You can imagine that when you are depositing a single phase like Si you can use SiH4 or for Al Al(CH3)3. But when you get to the point that you want binary compounds like GaAs then you need a mixture of precursors or you need to make single precursors that contain all elements of interest and in the correct composition. And the latter has been an area of intense study, to make single precursors with interesting compositions of use for CVD.

This has brought about the synthesis of exotic organometallic molecules with clean decomposition towards a desired product.

MOCVD metal-organic which signifies the nature of the precursors.

Examples of CVD reactions include the following:
1. $Si(CH_2CH_3)_4$ SiO_2
2. $CrCl_2 + H_2$ $Cr + 2HCl$
3. $Ga(CH)_3 + AsH_3$ $GaAs + 3CH_4$
4. $SiH_4 + NH_3$ Si_3N_4 $_{650\ to\ 750\ C}$

General problems with the methods
1. Pyrophoric alkyls
2. Water sensitivity of alkyls leading to O impurity into the resulting film
3. Toxicity of hydrides
4. Nucleation of reaction products inside the reaction chamber prior to deposition referred to as a snowing effect results from the coord. Unsaturated Lewis acids metals (result from removal of alkyls) react with e- pair donors, Lewis bases, Group V and IV hydrides
5. Controlling homogeneity
6. Variations in the volatility or reactivity of reactants

Reasons to use complex single source precursors:
➢ Snowing is less of a problem
➢ Maybe you can reduce toxicity
➢ Ligands less reactive towards O2 and water bc they are less coordinatively unsaturated than metal alkyls.
➢ You can design complexes with stable ligands that avoid charring. This means metal ligand bond can be pyrolyzed cleanly to results in the evolution of ligands that remain in the gas phase and do not form carbons that change the composition of the resulting film.

Characterization

Depending on the type of material you make there are a variety of different, general characterization techniques that one can use to determine the chemical and physical properties of solid materials. However, there are some basic types of characterization that are used for most solid materials.

The principle methods used to characterize crystalline solids are typically

1). Elemental analysis allows one to determine composition
Inductively coupled plasma Optical emission spectroscopy (ICP-OES), Inductively coupled plasma Mass spectrometry (ICP-MS), Prompt gamma activation analysis (PGAA), Energy dispersive x-ray analysis (EDX), Combustion analysis (C, N, O, S)
2). Thermal analysis to look at stability, reactivity, and phase changes.
Examples include TGA, DTA, DSC
3). Microscopy to look at morphology of crystallites, particularly in polycrystalline materials
Examples include SEM and TEM
4). Spectroscopic techniques can give valuable insight into the structure of molecular materials and also the optical properties of materials, for instance the size of the band gap and give insight into the origin of color of materials.

Examples include NMR - is particularly good to look at organic structures. There is also solid state NMR that is used to understand the structures of inorganic materials. Infrared (IR), Diffuse reflectance Infrared fourier transform spectroscopy (DRIFTS), and Raman is used for instance to look at certain vibrational modes and UV/Vis is often used to assess optical properties of materials.

5). X-ray and neutron spectroscopies

Inelastic neutron scattering (INS) and quasielastic neutron scattering (QENS) for neutrons and X-ray absorption or emission spectroscopy (XAS and XES) for x-rays.

6). Single crystal and powder x-ray diffraction allow one to study the structure of crystalline materials. Neutrons, x-rays, and electrons can be used as a source.

While spectroscopy can be used to determine the structure of organic molecules, for inorganic materials in particular the structures as you have seen are much more diverse with regard to coordination numbers and geometries. As such, diffraction is required. Further, spectroscopy doesn't give you any clue about how molecules are arranged in 3-D space in solid form, so even for organic molecules diffraction is the technique you use to see precise interatomic distances and angles as well as how the molecules are arranged in space.

X-ray Diffraction

The general things that we obtain form diffraction:

      a). Identify structure of unknown materials

      -Crystal System (triclinic, monoclinic, etc….)
      -Lattice Type (P, I, F, or C)
      -Symmetry and hence the space group
      -Unit Cell dimensions (parameters) and volume
      - Offers a precise determination of atomic positions in solid materials and the types of atoms.
      - Particularly of importance is being able to determine the distances between atoms and angles which give insight into oxidation states

The structure solutions for a number of different materials are placed in what are called crystallographic information files .cif and these are reported to structural databases like, Cambridge Structural Database and then the data can be downloaded by any researcher if you simply have the deposition number that is reported inside a manuscript for instance.

      b). Allow you to simply determine if what you have made already exists or if you made what you wanted to make.

Most x-ray diffractometers come with software that can use an x-ray powder pattern to look for specific phases already reported in a database. So, using this software you can often rapidly determine whether the material you have made is new or existing.

      c). Size distribution of crystallites in polycrystalline powders

      d). Can provide us with valuable insight into the structure-derived function of materials

      e). Determine phase purity (from powder diffraction) as long as the secondary crystalline phase is above approximately 3% on average.

If it is below 3% it might be drowned in the background noise. You can simulate the powder pattern of an existing structure and compare it with the powder pattern you have obtained from your sample and by overlaying them you can see if there are any extra peaks from impurity crystalline phases. You can use refinement software in order to determine how much of each crystalline impurity is present.

X-ray generation

X-rays are produced when high energy charged particles like electrons are accelerated (via an accelerating voltage, typically 30kV) and then collide with a target. The resulting x-ray spectrum will be in one of two forms:

(1) A broad spectrum of x-rays that means of many different wavelengths referred to as white radiation
(2) Or monochromatic, a single wavelength

While there are a broad spectrum of ways x-rays are produced I will describe the most common, which is done for lab based x-ray source that results in monochromatic wavelength that is usually 1.5418 Å for Cu. For this a tungsten filament is heated and the resulting electron beam is accelerated via an accelerating voltage of 30 kV which are then allowed to strike a metal target fixed to the anode. It is this metal target that dictates what the resulting wavelength is. For lab-based powder x-ray sources this is usually copper while for single crystal this is usually Molybdenum (but also at times can also be copper). Wavelengths used in diffraction experiments range from 0.6 to 2.3 Å.
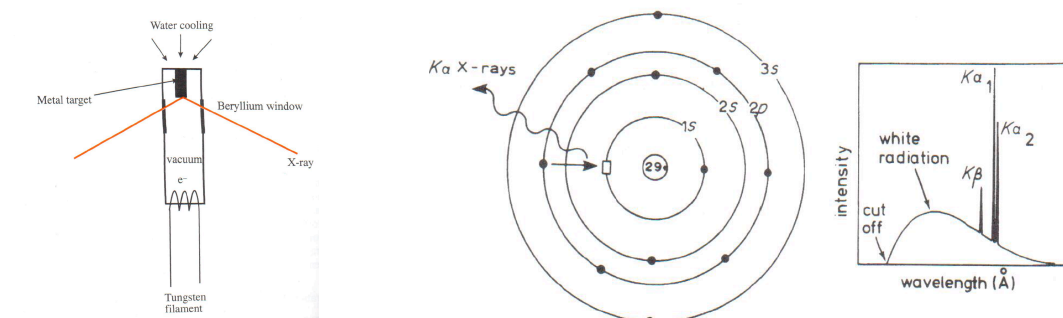
The anode is cooled continuously during x-ray production because not all of the energy is converted into x-rays, much of it is converted into heat and the anode would melt otherwise.

They typical source is Cu. You see the structure of the Cu atom in the middle above. The ionizing electrons strike the Cu, ejecting an electron from the 1s core orbital and then an electron from the 2p orbital falls down into the spot giving off an x-ray that is characteristic of the energy difference between the two states. You can see the emission spectrum in the right. The most intense wavelength is known as the K alpha radiation.

K refers to a transition from n = 2 energy level to an n = 1 energy level. And alpha refers to the 2p to 1s transition. Beta refers to the 3p to 1s transition.

For transitions the orbital angular moment quantum number l must change by + or – 1 in order for a transition to be allowed. For s, p, d, and f orbitals l = 1, 2, 3, and 4, respectively. So, you can have transitions between s and p for instance.

You can filter out the $k\beta$ (1.3922 Å) radiation by adding a filter. This is done by using an element with a slightly lower atomic number, like Ni. The $k\beta$ wavelength is enough to ionize the 1s electron of Ni (requires a wavelength of 1.488Å for ionization of the 1s e- of Ni) and it permits the lower energy wavelength $k\alpha$ to go through. At the same time, Ni can also absorb most of the white radiation as well.

The wavelengths of some common sources are shown below:

Table 3.2   X-ray wavelengths ($\mathring{A}$) of commonly used target materials

Target	$K\alpha_1$	$K\alpha_2$	$K\bar{\alpha}^*$	Filter
Cr	2.2896	2.2935	2.2909	V
Fe	1.9360	1.9399	1.9373	Mn
Cu	1.5405	1.5443	1.5418	Ni
Mo	0.7093	0.7135	0.7107	Nb
Ag	0.5594	0.5638	0.5608	Pd

* $\bar{\alpha}$ is the intensity-weighted average of α_1 and α_2.

In some experiments the $k\alpha_2$ is filtered out but in most the two peaks are not well resolved due to the similarities in wavelength as so the average in the 4th column is instead used.