Synthesis and Characterization of Solid

PG Semester I
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Lecture 6-7

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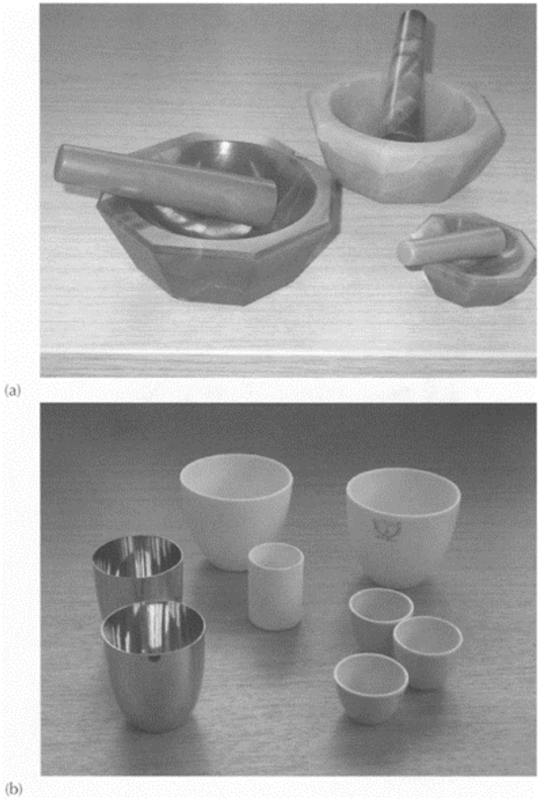
Contents

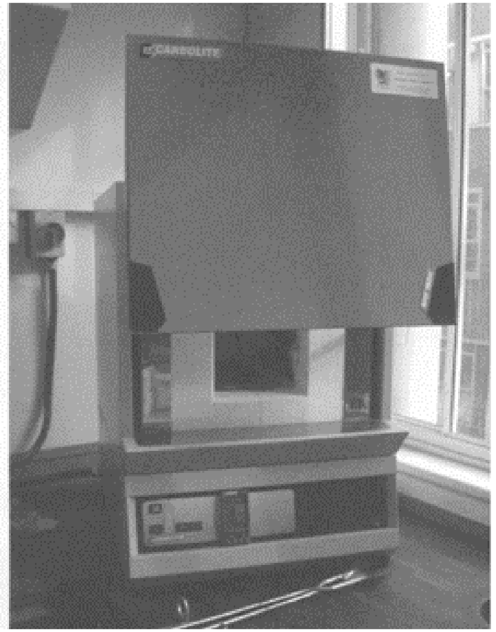
Ceramic Method

- This is the simplest and most common used method for preparation of solids.
- In this method two solids which react to form the required product are heated together either in an ambient condition or in an evacuated vessel. Evacuated vessels are required when the reactant or product is air or water sensitive and volatile.
- This method is used widely both industrially and in the laboratory
- This method can be used to synthesize a whole range of materials such as mixed metal oxides, sulfides, nitrides, aluminosilicates and many others.
- The first high-temperature superconductors were made by ceramic method.
- Zircon ($ZrSiO_4$) is prepared by the direct reaction of zirconia, ZrO_2, and silica, SiO_2 at 1300°C:

$$ZrO_2\ (s) + SiO_2\ (s) \rightarrow ZrSiO_4$$

- It is used in the ceramics industry as the basis of high temperature pigments to color the glazes on bathroom china
- The stoichiometric amounts of the binary oxides is grinded in a pestle and mortar to give a uniform small particle size, and then heated in a furnace for several hours in an alumina crucible





The basic apparatus for the ceramic method: (a) pestles and mortars for fine grinding; (b) a selection of porcelain, alumina, and platinum crucibles; and (c) furnace

- $PbTiO_3$ can be prepared by direct reaction of PbO with TiO_2 at high (900 °C) temperarture.

  $PbO + TiO_2 \rightarrow PbTiO_3$

- Protocol: Grind/mix the powdered reactants, press into a pellet and heat
- Requires high temperature because reaction is diffusion limited
- Reaction occurs in solid state

Disadvantages

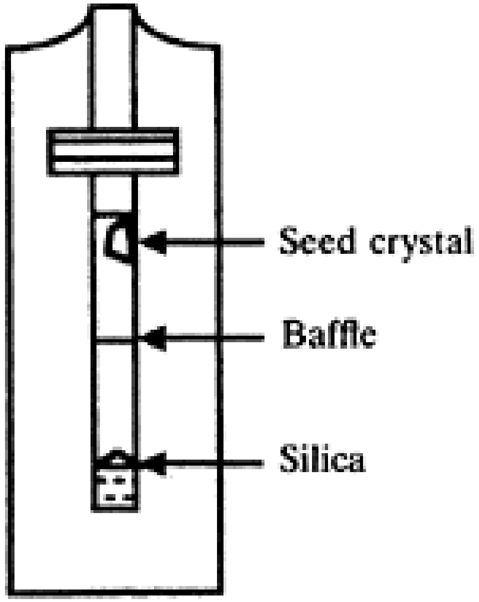
- High temperatures are generally required (between 500-2000°C), because it takes a significant amount of energy to overcome the lattice energy so a cation or anion can diffuse into a different site.
- In addition, the desired compound may be unstable or decompose at such high temperatures.
- Can be expensive
- May give incomplete reaction
- May give compositionally inhomogeneous product

See books for all preparation

Hydrothermal synthesis

- Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure.
- The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave, in which a nutrient is supplied along with water.
- A temperature gradient is maintained between the opposite ends of the growth chamber.
- At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal.
- Advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapor pressure near their melting points can be grown by the hydrothermal method. The method is also particularly suitable for the growth of large good-quality crystals while maintaining control over their composition.

Autoclave.



Growth of quartz crystals in an autoclave under hydrothermal conditions.

- Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows if a steel tube is used. There are autoclaves made out of thick walled glass, which can be used up to 300 °C and 10 bar.

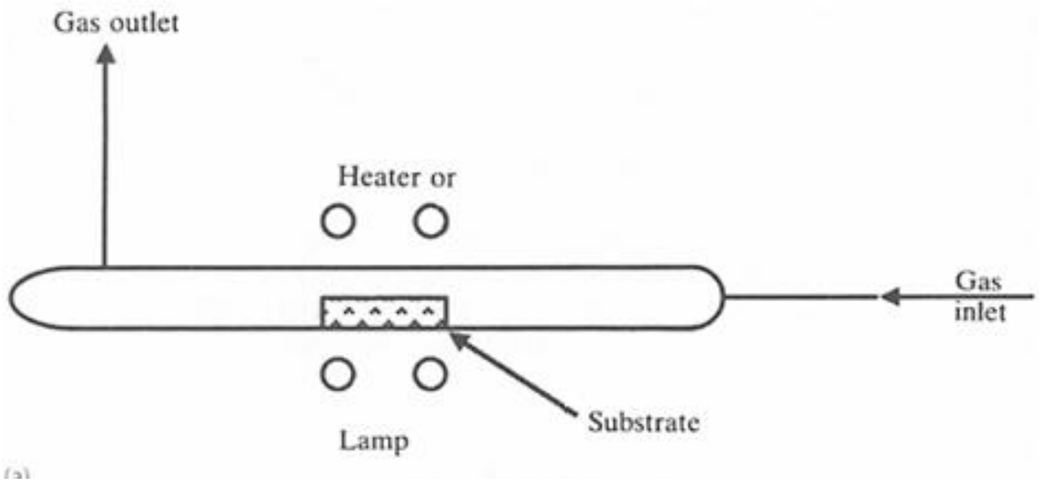
Uses

- Large number of compounds belonging to practically all classes have been synthesized under hydrothermal conditions: elements, simple and complex oxides, tungstates, molybdates, carbonates, silicates, germanates etc.
- Hydrothermal synthesis is commonly used to grow synthetic quartz, gems and other single crystals with commercial value.
- Some of the crystals that have been efficiently grown are emeralds, rubies, quartz, alexandrite and others.
- The method has proved to be extremely efficient both in the search for new compounds with specific physical properties and in the systematic physicochemical investigation of intricate multicomponent systems at elevated temperatures and pressures.

Chemical vapor deposition (CVD)

- CVD is a vacuum deposition method used to produce high quality, and high-performance, solid materials.
- The process is often used in the semiconductor industry to produce thin films.
- In typical CVD, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit.
- Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber.
- Microfabrication processes widely use CVD to deposit materials in various forms, including: monocrystalline, polycrystalline, amorphous, and epitaxial.
- These materials include: silicon (dioxide, carbide, nitride, oxynitride),carbon(fiber, nanofibers, nanotubes, diamond and graphene), fluorocarbons, filaments, tungsten, titanium nitride and various high-k dielectrics.
- CVD is practiced in a variety of formats. These processes generally differ in the means by which chemical reactions are initiated

- The advantages of the method are that reaction temperatures are relatively low, the stoichiometry is easily controlled, and dopants can be incorporated.



Chemical-vapour deposition reactor

Classification

Classified by operating conditions:

- Atmospheric pressure CVD (APCVD) – CVD at atmospheric pressure.
- Low-pressure CVD (LPCVD) – CVD at sub-atmospheric pressures. Reduced pressures tend to reduce unwanted gas-phase reactions and improve film uniformity across the wafer.
- Ultrahigh vacuum CVD (UHVCVD) – CVD at very low pressure, typically below 10^{-6} Pa ($\approx 10^{-8}$ torr).
- Sub-atmospheric CVD (SACVD) – CVD at sub-atmospheric pressures. Uses tetraethyl orthosilicate (TEOS) and Ozone to fill high aspect ratio Si structures with silicon dioxide (SiO_2).

Most modern CVD is either LPCVD or UHVCVD

Classified by physical characteristics of vapor:

- Aerosol assisted CVD (AACVD) – CVD in which the precursors are transported to the substrate by means of a liquid/gas aerosol, which can be generated ultrasonically. This technique is suitable for use with non-volatile precursors.
- Direct liquid injection CVD (DLICVD) – CVD in which the precursors are in liquid form (liquid or solid dissolved in a convenient solvent). Liquid solutions are injected in a vaporization chamber towards injectors (typically car injectors). The precursor vapors are then transported to the substrate as in classical CVD. This technique is suitable for use on liquid or solid precursors. High growth rates can be reached using this technique.

Classified by type of substrate heating:

- Hot wall CVD – CVD in which the chamber is heated by an external power source and the substrate is heated by radiation from the heated chamber walls.
- Cold wall CVD – CVD in which only the substrate is directly heated either by induction or by passing current through the substrate itself or a heater in contact with the substrate. The chamber walls are at room temperature.

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Plasma methods

- Microwave plasma-assisted CVD (MPCVD)
- Plasma-enhanced CVD (PECVD) – CVD that utilizes plasma to enhance chemical reaction rates of the precursors. PECVD processing allows deposition at lower temperatures, which is often critical in the manufacture of semiconductors. The lower temperatures also allow for the deposition of organic coatings, such as plasma polymers, that have been used for nanoparticle surface functionalization.
- Remote plasma-enhanced CVD (RPECVD) – Similar to PECVD except that the wafer substrate is not directly in the plasma discharge region. Removing the wafer from the plasma region allows processing temperatures down to room temperature.
- Low-energy plasma-enhanced chemical vapor deposition (LEPECVD) - CVD employing a high density, low energy plasma to obtain epitaxial deposition of semiconductor materials at high rates and low temperatures.

- Atomic-layer CVD (ALCVD) – Deposits successive layers of different substances to produce layered, crystalline films.
- Combustion chemical vapor deposition (CCVD) – Combustion Chemical Vapor Deposition or flame pyrolysis is an open-atmosphere, flame-based technique for depositing high-quality thin films and nanomaterials.
- Hot filament CVD (HFCVD) – also known as catalytic CVD (Cat-CVD) or more commonly, initiated CVD, this process uses a hot filament to chemically decompose the source gases. The filament temperature and substrate temperature thus are independently controlled, allowing colder temperatures for better absorption rates at the substrate and higher temperatures necessary for decomposition of precursors to free radicals at the filament.
- Hybrid physical-chemical vapor deposition (HPCVD) – This process involves both chemical decomposition of precursor gas and vaporization of a solid source.
- Metalorganic chemical vapor deposition (MOCVD) – This CVD process is based on metalorganic precursors.
- Rapid thermal CVD (RTCVD) – This CVD process uses heating lamps or other methods to rapidly heat the wafer substrate. Heating only the substrate rather than the gas or chamber walls helps reduce unwanted gas-phase reactions that can lead to particle formation.

- Vapor-phase epitaxy (VPE)
- Photo-initiated CVD (PICVD) – This process uses UV light to stimulate chemical reactions. It is similar to plasma processing, given that plasmas are strong emitters of UV radiation. Under certain conditions, PICVD can be operated at or near atmospheric pressure.
- Laser chemical vapor deposition (LCVD) - This CVD process uses lasers to heat spots or lines on a substrate in semiconductor applications. In MEMS and in fiber production the lasers are used rapidly to break down the precursor gas-process temperature can exceed 2000°C-to build up a solid structure in much the same way as laser sintering based 3-D printers build up solids from powders.

Uses

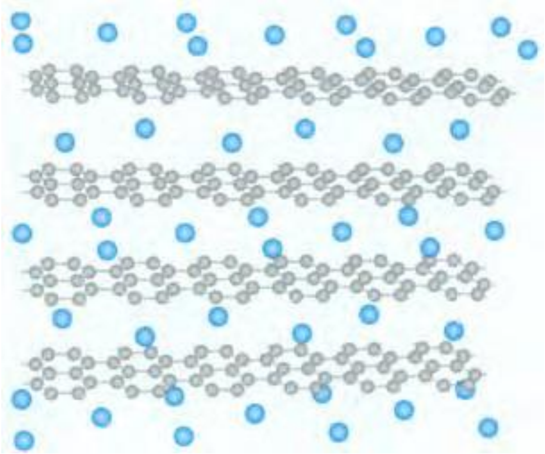
- CVD is commonly used to deposit conformal films and augment substrate surfaces in ways that more traditional surface modification techniques are not capable of.
- CVD is extremely useful in the process of atomic layer deposition at depositing extremely thin layers of material. A variety of applications for such films exist. Gallium arsenide is used in some integrated circuits (ICs) and photovoltaic devices. Amorphous polysilicon is used in photovoltaic devices. Certain carbides and nitrides confer wear-resistance.
- Polymerization by CVD, perhaps the most versatile of all applications, allows for super-thin coatings which possess some very desirable qualities, such as lubricity, hydrophobicity and weather-resistance to name a few.
- CVD of MOFs, a class of crystalline nanoporous materials, has recently been demonstrated. Recently scaled up as an integrated cleanroom process depositing large-area substrates, the applications for these films are anticipated in gas sensing and low-k dielectrics.
- CVD techniques are advantageous for membrane coatings as well, such as those in desalination or water treatment, as these coatings can be sufficiently uniform (conformal) and thin that they do not clog membrane pores.

Intercalation

- 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.
- KC_8 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 NO_3^- , CrO_3, Br_2, $FeCl_3$, AsF_5.



The structure of KC_8. K, blue; C, grey.

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.

$$xC_4H_9\,Li + TiS_2 \rightarrow Li_xTiS_2 + (x/2)C_8H_{18}$$

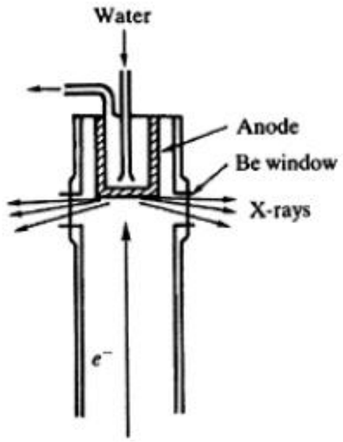
Characterization of Solids

- A vast array of physical methods are used to investigate the structures of solids, each technique with its own strengths and weaknesses—some techniques are able to investigate the local coordination around a particular atom or its electronic properties, whereas others are suited to elucidating the long-range order of the structure.
- Single crystal X-ray diffraction is used to determine atomic positions precisely and therefore the bond lengths (to a few tens of picometres) and bond angles of molecules within the unit cell.
- It gives an overall, average picture of a long-range ordered structure, but is less suited to giving information on the structural positions of defects, dopants, and non-stoichiometric regions.
- It is often very difficult to grow single crystals, but most solids can be made as a crystalline powder.
- Powder X-ray diffraction is probably the most commonly employed technique in solid state inorganic chemistry and has many uses from analysis and assessing phase purity to determining structure.

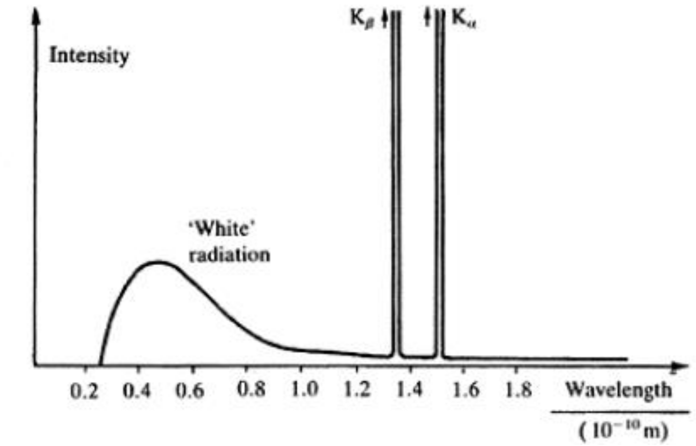
X-ray diffraction

Generation of X-rays

- An electrically heated filament, usually tungsten, emits electrons, which are accelerated by a high potential difference (20-50 kV) and allowed to strike a metal target or anode which is water cooled (a).
- The anode emits a continuous spectrum of 'white' X-radiation but superimposed on this are sharp, intense X-ray peaks (K_{α}, K_{β}) (b)
- The frequencies of the K_{α} and K_{β} lines are characteristic of the anode metal; the target metals most commonly used in X-ray crystallographic studies are copper and molybdenum, which have K_{α} lines at 154.18 pm and 71.07 pm, respectively.
- Normally in X-ray diffraction, monochromatic radiation is required (K_{α} line is selected and the K_{β} line is filtered out)



(a) Section through an X-ray tube



(b) an X-ray emission spectrum.

Diffraction of X-rays

- Max von Laue used a crystal of copper sulfate as the diffraction grating: the Nobel Prize for Physics in 1914.
- Crystalline solids consist of regular arrays of atoms, ions or molecules with interatomic spacings of the order of 100 pm. For diffraction to take place, the wavelength of the incident light has to be of the same order of magnitude as the spacings of the grating.
- Because of the periodic nature of the internal structure, it is possible for crystals to act as a three-dimensional diffraction grating to light of a suitable wavelength.
- W. H. and W. L. Bragg (father and son), first determined the crystal structure of NaCl using X-ray crystal diffraction 1913
- W. L. (Lawrence) Bragg noted that X-ray diffraction behaves like ‘reflection’ from the planes of atoms within the crystal and that only at specific orientations of the crystal with respect to the source and detector are X-rays ‘reflected’ from the planes. It is not like the reflection of light from a mirror, as this requires that the angle of incidence equals the angle of reflection, and this is possible for all angles. With X-ray diffraction, the reflection only occurs when the conditions for constructive interference are fulfilled.

Read from Smart and Moore’s Book: Just basic things

Ask Chayanika Mam to share the notes of PG Sem III

1. Single Crystal XRD
2. Powder-XRD
3. SEM
4. TEM
5. DTA
6. TGA