Solid State Chemistry

6th week

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Synthesis, Processing and Fabrication Methods

- Non-molercular inorganic solids can also be prepared in various forms, as fibres, films, forma, ceramics, powders, nanoparticles and single crystals

- Synthesis is not the problem; instead, it is optimisation of the processing and fabrication procedures that is crucially important

1) solid state reaction
2) low temperature methods
3) gas-phase methods
4) high pressure methods
5) crystal growth
6) chemical methods

Bulk Materials

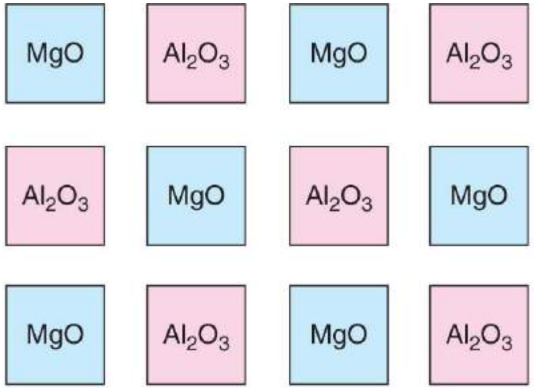
Solid state synthesis
Chemical vapour transport
Sol gel synthesis
Melt growth

Thin Films

Chemical vapour deposition
Laser ablation
Sputtering
Molecular beam epitaxy
Atomi layer deposition

Solid State Reaction

- The oldest, simplest and still most widely used method to make inorganic solids
- Mix together powdered reactants, perhaps them into pellets or some other shape and then heat in a furnace for prolonged periods
- Intrinsically slow process because, although the reactants may be well mixed at the level of individual particles (e.g. on a scale of 1 μm or 10^{-3} mm), on the atomic level they are very inhomogeneous
- At every *interface between contacting grains* of MgO and Al_2O_3, all the ingredients to form the $MgAl_2O_4$ product is present



Ideal mixture composed of grains of MgO and Al_2O_3

Solid State Reaction

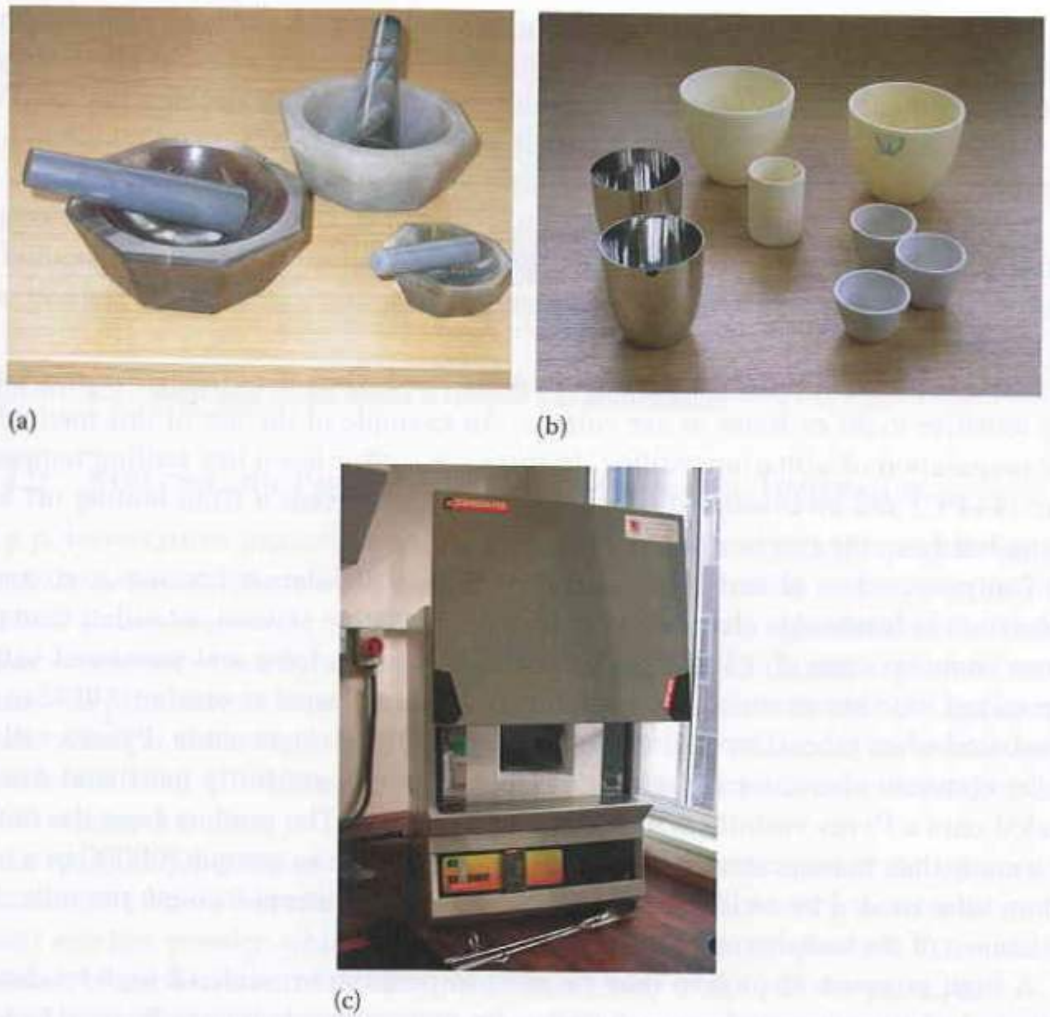


FIGURE 3.1 The basic apparatus for the ceramic method: (a) pestles and mortars for fine grinding; (b) a selection of porcelain, alumina and platinum crucibles; and (c) a furnace.

Adopted from Solid State Chemistry: An Introduction, 4th Ed., CRC (L. E. Smart)

Solid State Reaction

- The 1st stage is *nucleation* of small crystals with the spinel stoichiometry and structure

- The *critical size* of nuclei represents a balance btw the -ve free energy of formation of the spinel product and the +ve surface energy of the nuclei

- Nucleation is greatly facilitated if it is *heterogeneous* and the product nuclei are able to form on the surface of an existing structure, especially if there is some similarity in the two structures.

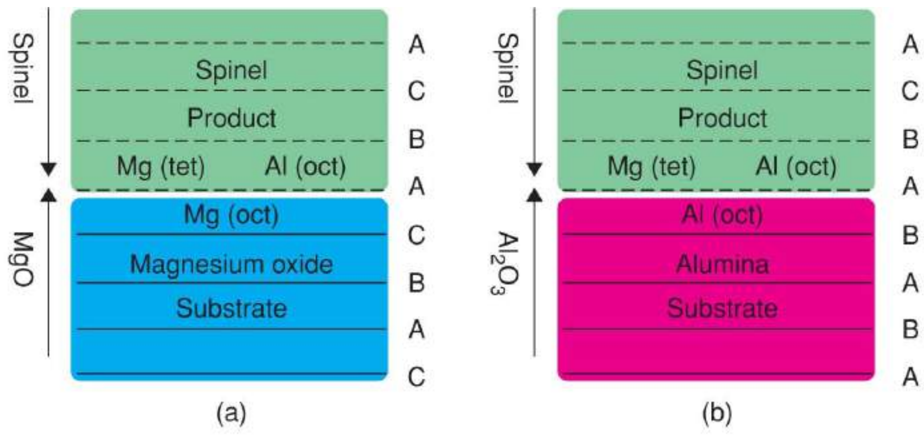
- Good lattice matching : *coherent interface*
- Bad lattice matching : large strains rapidly develop and the coherency of the interface is lost and the nucleus becomes detached from the substrate

Topotaxy

Epitaxy

Spinel structure (*ccp*)

Rock salt structure (*ccp*)



Spinel structure (*ccp*)

stacking fault

hcp structure

Figure 4.2 ***Nucleation of $MgAl_2O_4$ spinel on (a) MgO and (b) Al_2O_3. Letters A, B, C refer to close-packed layers of oxide ions.***

Solid State Chemistry and its Applications, Second Edition, Student Edition. Anthony R. West.

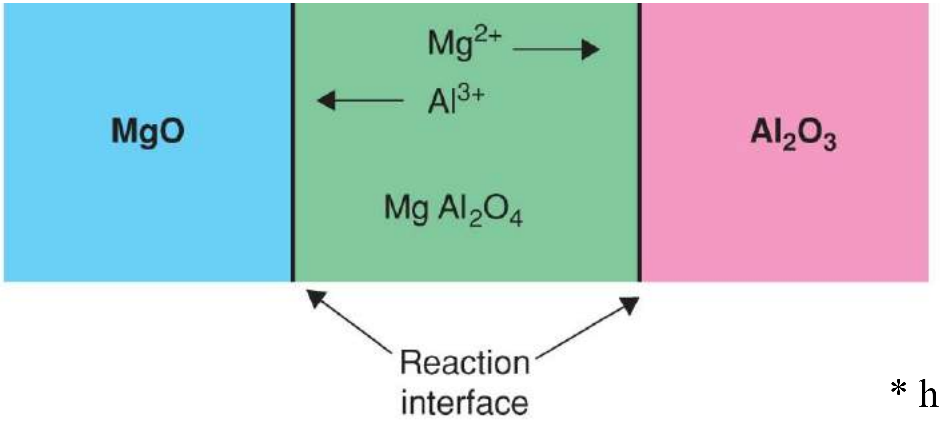
Companion Website: http://www.wiley.com/go/west/solidstatechemistrystudent

Solid State Reaction

- Although the first few atomic layers of product may form easily, subsequent growth or thickening of the product is more difficult because, effectively, the two reactants, MgO and Al_2O_3, are no longer in contact but are separated by a rather impenetrable spinel layer.

- A complex *counter-diffusion process* is then required in which Mg^{2+} ions diffuse away from, and Al^{3+} ions diffuse towards, the $MgO/MgAl_2O_2$ interface, and vice versa for the $MgAl_2O_4/Al_2O_3$ interface

$$2Al^{3+} - 3Mg^{2+} + 4MgO \longrightarrow MgAl_2O_4$$



$$3Mg^{2+} - 2Al^{3+} + 4Al_2O_3 \longrightarrow 3MgAl_2O_4$$

Defects in both reactants and product are required, particularly, vacant sites for adjacent ions to hop into.

* heating for 1 week at 1500 °C

Figure 4.4 ***Spinel product layer separating MgO and Al_2O_3 reactant grains.***

Solid State Chemistry and its Applications, Second Edition, Student Edition. Anthony R. West.

Companion Website: http://www.wiley.com/go/west/solidstatechemistrystudent

Low Temperature Methods

* *Sol-gel Methods*

- prepare a homogeneous solution containing all the cationic ingredients
- gradually dried without precipitation of any crystalline phases
- fired at high temperature
- numerous elements of the Periodic Table with *intermediate electronegativity* also show complex aqueous solution chemistry

- Hydrolysis : (1) replacement of -OR groups by -OH

$$Si(OCH_2CH_3)_4 \longrightarrow Si(OCH_2CH_3)_3OH + Si(OCH_2CH_3)_2(OH)_2 + \text{etc.}$$

(2) condensation polymerization with elimination of H_2O

$$(RO)_3Si\text{-}OH + OH\text{-}Si(OR)_3 \longrightarrow (RO)_3Si\text{-}O\text{-}Si(OR)_3$$

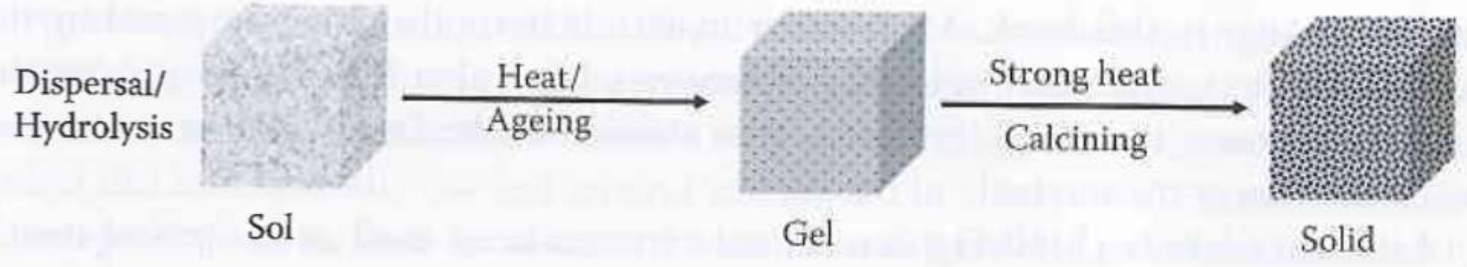


FIGURE 3.3 The steps in the sol–gel synthesis route.

Adopted from Solid State Chemistry: An Introduction, 4th Ed., CRC (L. E. Smart)

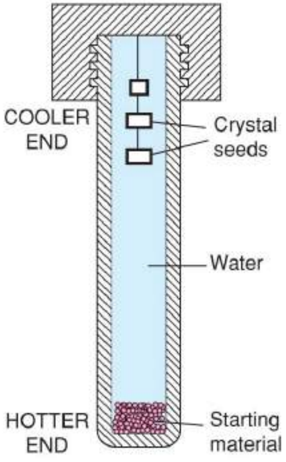
Low Temperature Methods

* *Hydrothermal Synthesis*

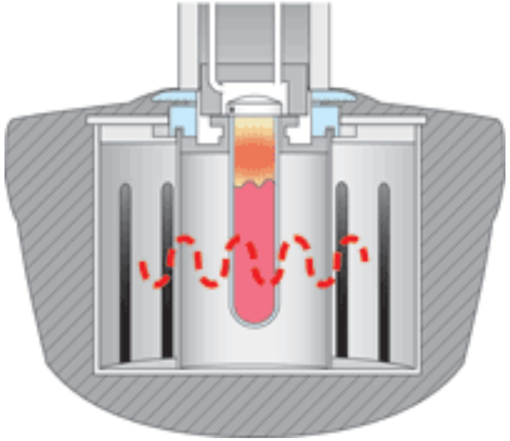
- heating reactants in water/steam at high pressures and temperatures

* *Microwave Synthesis*

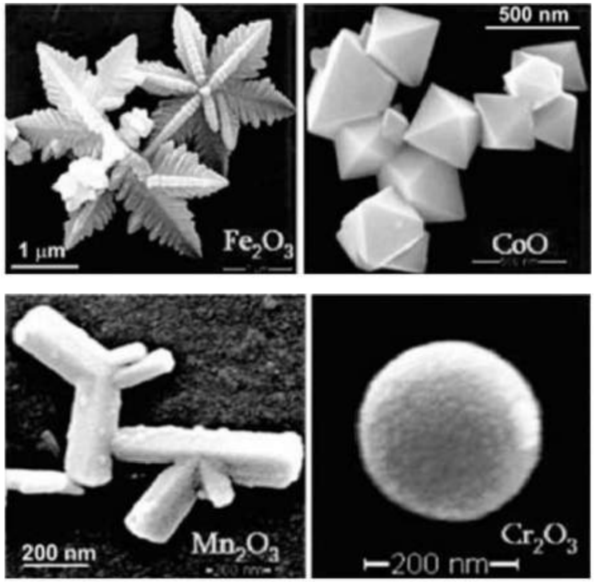
- reaction times are ordered of magnitude less than required for solid state reaction and side reactions are less problematic



hydrothermal



microwave



Adopted from Solid State Chemistry: An Introduction, 4th Ed., CRC (L. E. Smart)

Low Temperature Methods

* *Intercalation and Deintercalation*

- A very elegant way to synthesize new materials is to take an existing crystalline solid and either introduce new atoms into empty sites or selectively remove certain atoms, while keeping the overall original structure intact

- Intercalation species (guests) can be either ions or molecules (commonly Li^+, Na^+, H^+, O^{2-})

- Since the intercalation process involves addition or removal of ions, electrons must also be added or removed to preserve charge balance

- Most intercalation hosts are layered structures with strong intralayer bonds but weak interlayer bonds

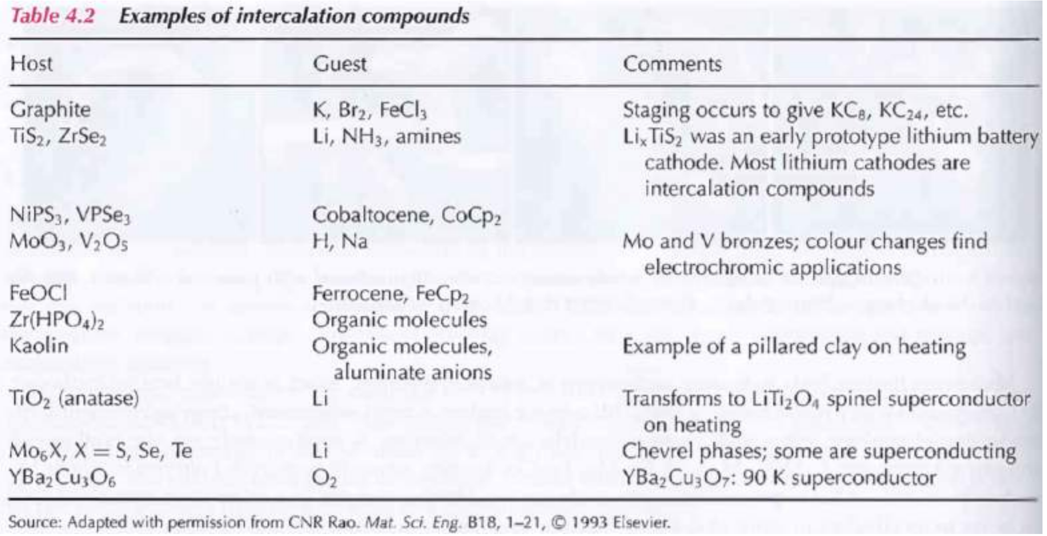


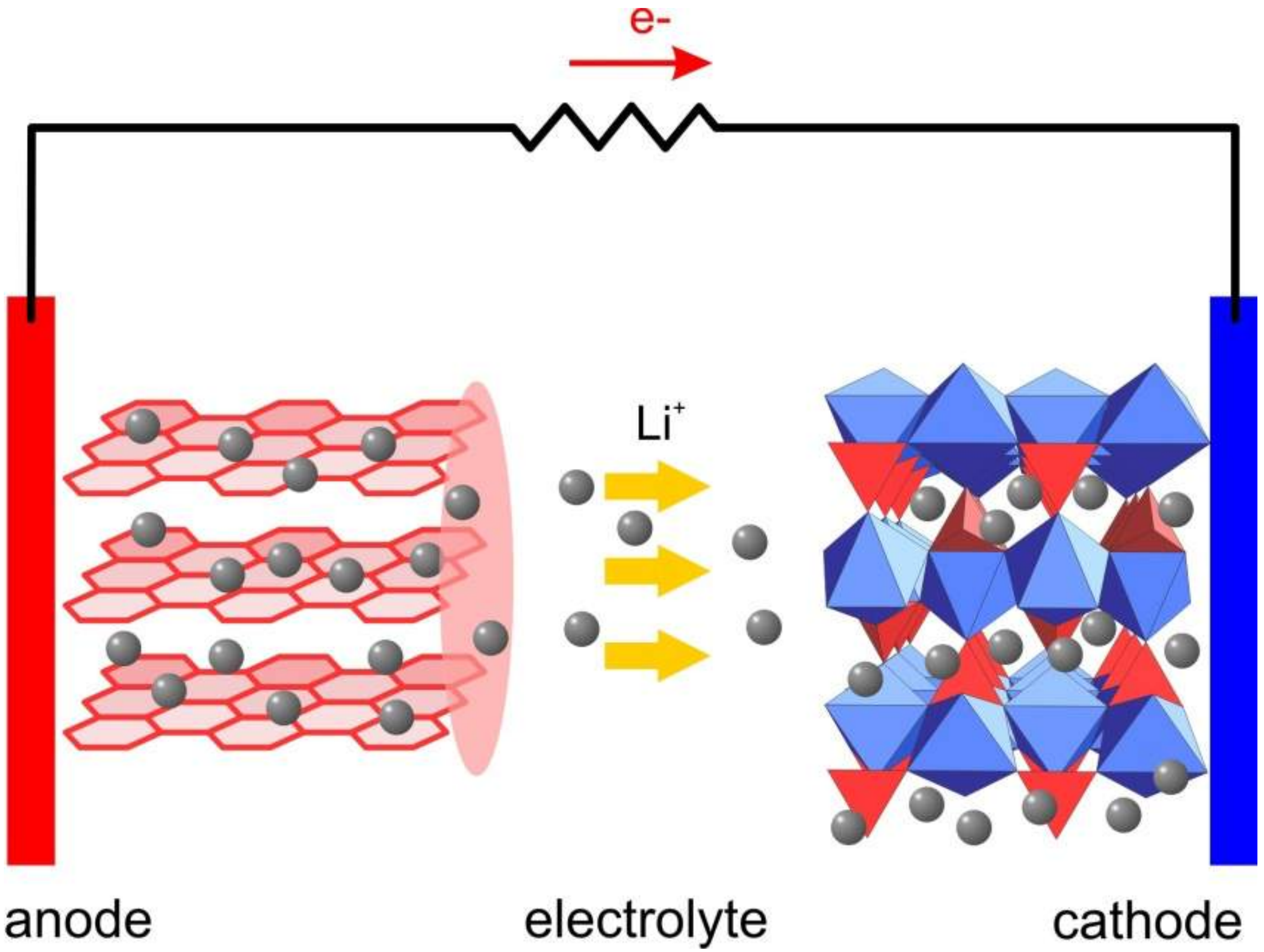
Table 4.2 ***Examples of intercalation compounds***

Host	Guest	Comments
Graphite	K, Br_2, $FeCl_3$	Staging occurs to give KC_8, KC_{24}, etc.
TiS_2, $ZrSe_2$	Li, NH_3, amines	Li_xTiS_2 was an early prototype lithium battery cathode. Most lithium cathodes are intercalation compounds
$NiPS_3$, $VPSe_3$	Cobaltocene, $CoCp_2$	
MoO_3, V_2O_5	H, Na	Mo and V bronzes; colour changes find electrochromic applications
FeOCl	Ferrocene, $FeCp_2$	
$Zr(HPO_4)_2$	Organic molecules	
Kaolin	Organic molecules, aluminate anions	Example of a pillared clay on heating
TiO_2 (anatase)	Li	Transforms to $LiTi_2O_4$ spinel superconductor on heating
Mo_6X, X = S, Se, Te	Li	Chevrel phases; some are superconducting
$YBa_2Cu_3O_6$	O_2	$YBa_2Cu_3O_7$: 90 K superconductor

Source: Adapted with permission from CNR Rao. *Mat. Sci. Eng.* B18, 1–21, © 1993 Elsevier.

Low Temperature Methods

* *Intercalation and Deintercalation in Li ion Batteries*



Gas-Phase Methods

* *Vapour-Phase Transport*

- The essential feature of this method is the formation of a ***volatile, unstable intermediate*** that contains at least one of the elements in the desired final product
- It involves chemical transport along a temperature gradient via the vapour phase
- The method consists of a tube (usually silica glass) with the reactants, which are sealed either under vacuum or with a small amount of the transporting agent
- The tube is placed in a furnace such that a temperature gradient of e.g. 50-100 °C exists

$$A(s) + B(g) \overset{K}{\rightleftharpoons} AB(g)$$

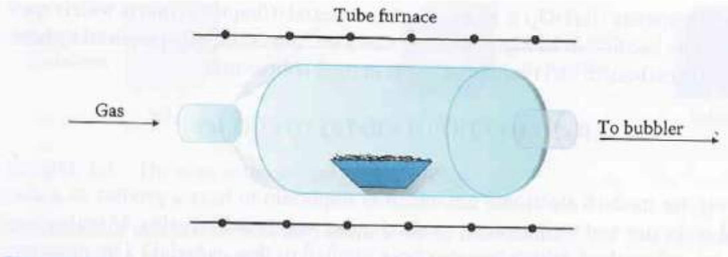


FIGURE 3.2 Reacting solids under a special gas atmosphere

at T_2:	$A(s) + B(g) \longrightarrow AB(g)$		$SnO_2(s) + CO \longrightarrow SnO(g) + CO_2$		
at T_1:	$AB(g) + C(s) \longrightarrow AC(s) + B(g)$		$SnO(g) + CaO(s) \longrightarrow Ca_2SnO_4$		
overall:	$A(s) + C(s) \longrightarrow AC(s)$		$2CaO + SnO_2 \longrightarrow Ca_2SnO_4$		

Gas-Phase Methods

* *Chemical Vapour Deposition (CVD)*

- formation of high purity thin films and coatings for industrial applications, especially in electronics, and also for fundamental scientific research

- precursor molecules containing the elements of interest are decomposed in the gas phase and the products deposit as thin films on every available object in the vicinity

- MOCVD refers to the *melt-organic* nature of the precursors. The precursors can be decomposed in various ways, by the action of heat or by irradiation

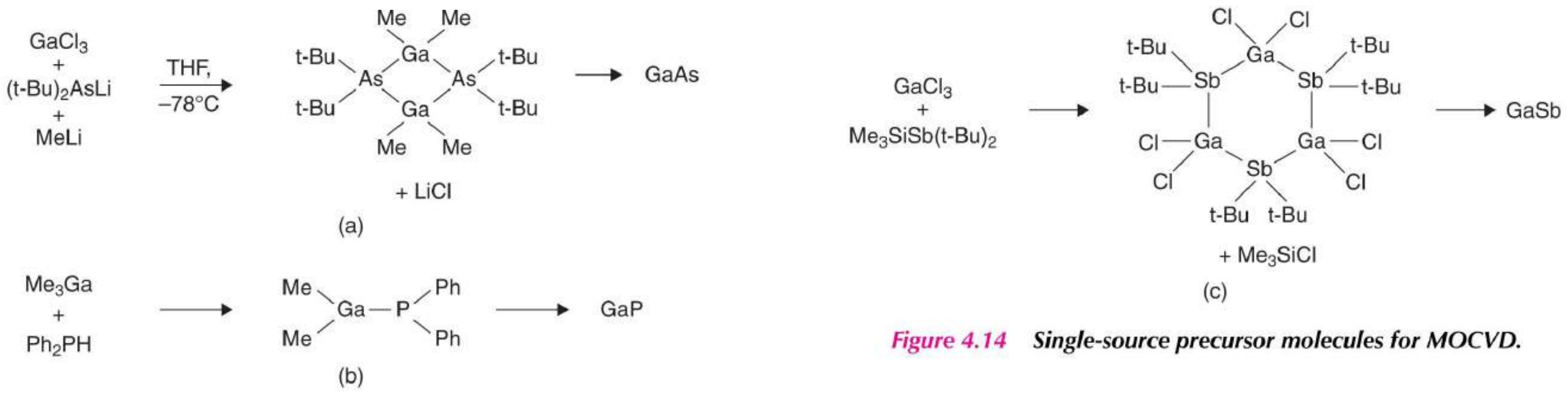


Figure 4.14 ***Single-source precursor molecules for MOCVD.***

* precursor: a compound that participates in a chemical reaction that produces another compound

Gas-Phase Methods

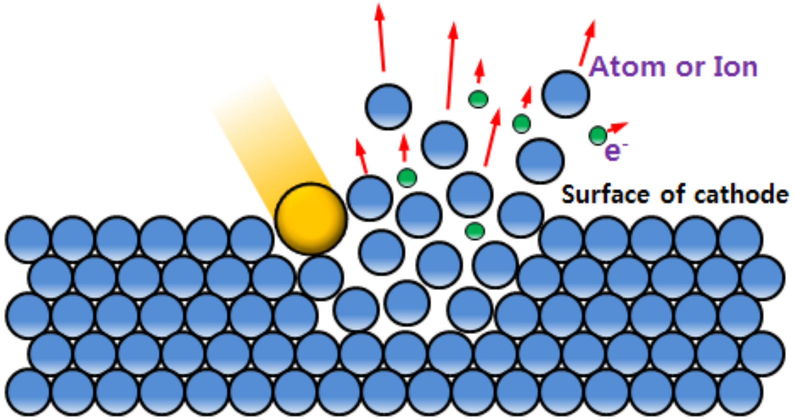
* *Chemical Vapour Deposition (CVD)*

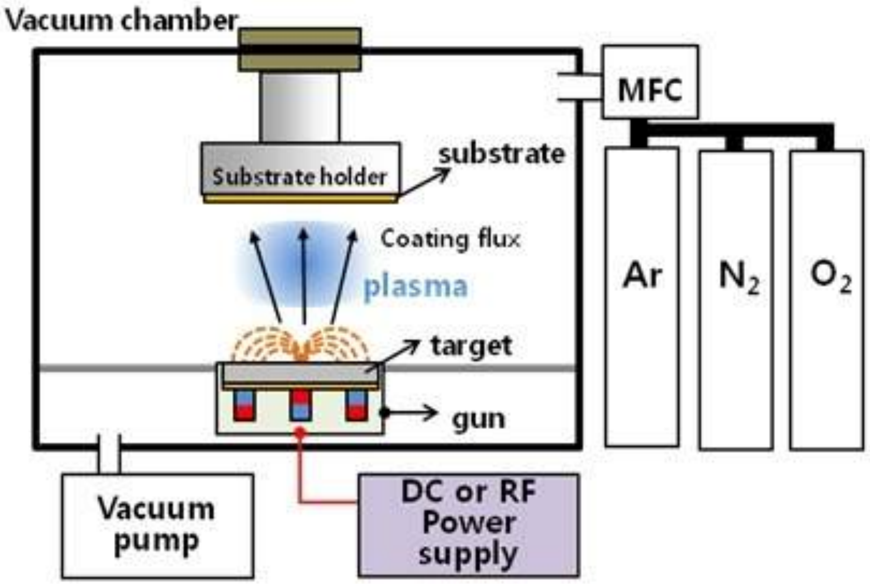
Gas-Phase Methods

* *Sputtering*

- The mechanism of sputtering involves the transfer of momentum from the gaseous ions to the cathode in such a way that atoms or ions are ejected from the cathode
- at reduced pressure, 10^{-1} - 10^{-2} Torr of inert gas (Ar)
- a potential drop of several kVs, creating a glow discharge from which positive ions are accelerated towards the cathode (target)

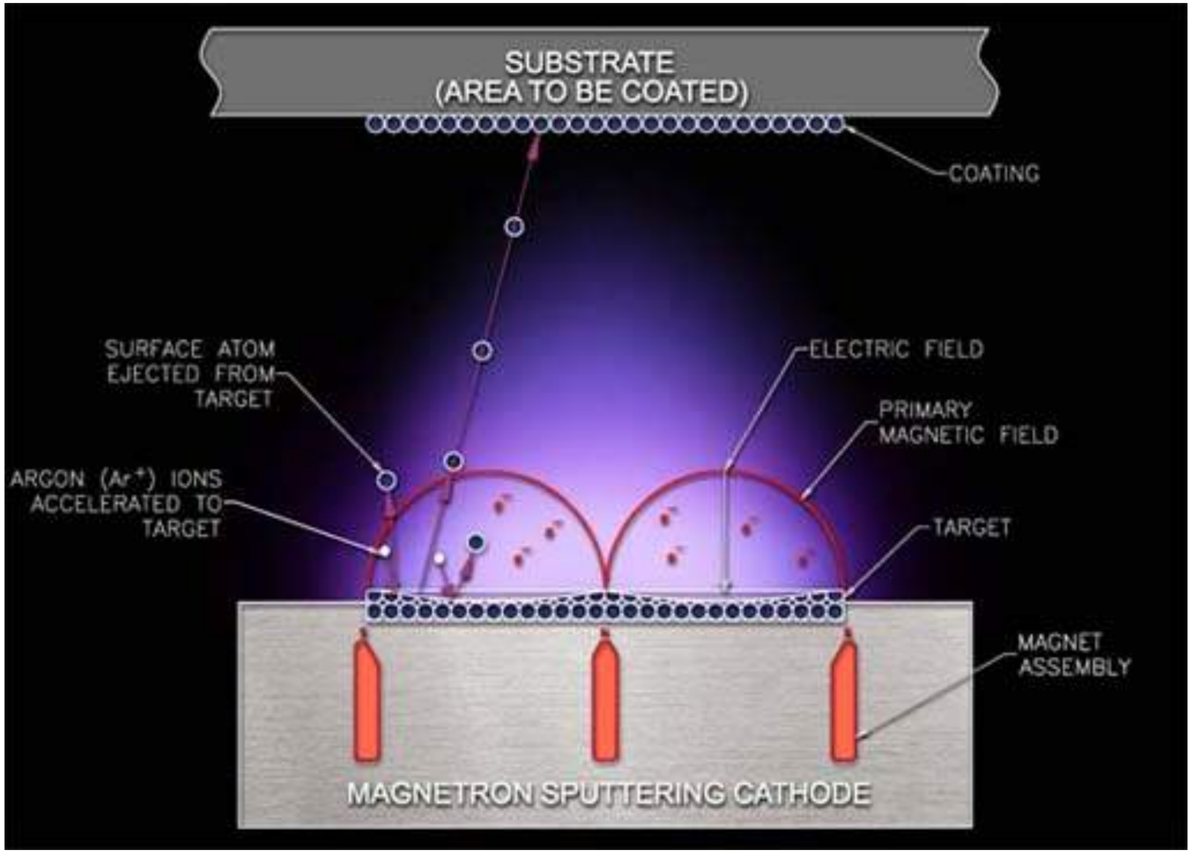
* 1 torr = 1/760 atm





Gas-Phase Methods

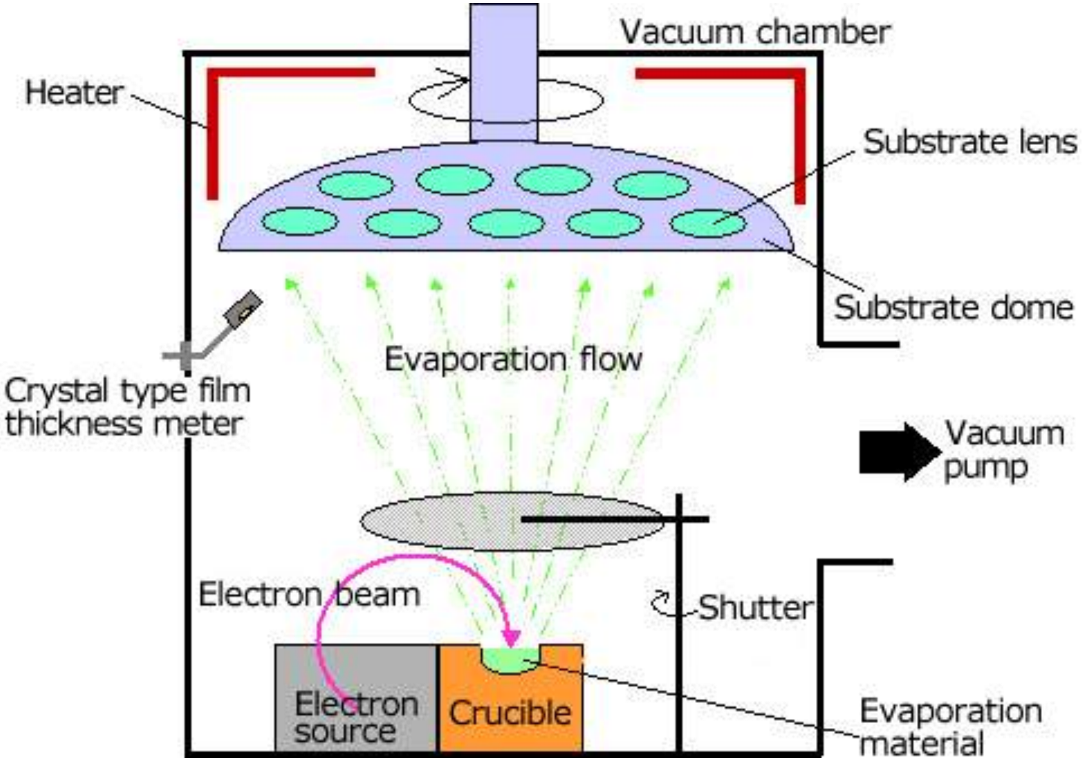
* *Sputtering*



Gas-Phase Methods

* *Evaporation*

- Material from the evaporation source is converted into the gaseous phase by heating or electron bombardment under high vacuum ~ 10^{-6} Torr or better



Gas-Phase Methods

* *Atomic Layer Deposition (ALD)*

- formation of nanometer thick conformational films, particularly for microelectronics applications
- two self-limiting and complementary reactions are used sequentially to build up films slowly one monolayer at a time
- temperature control is important to achieve single-layer deposition in one cycle
- since film thickness depends only on the number of reaction cycles, it can be controlled accurately in a way that is not possible with other CVD processes

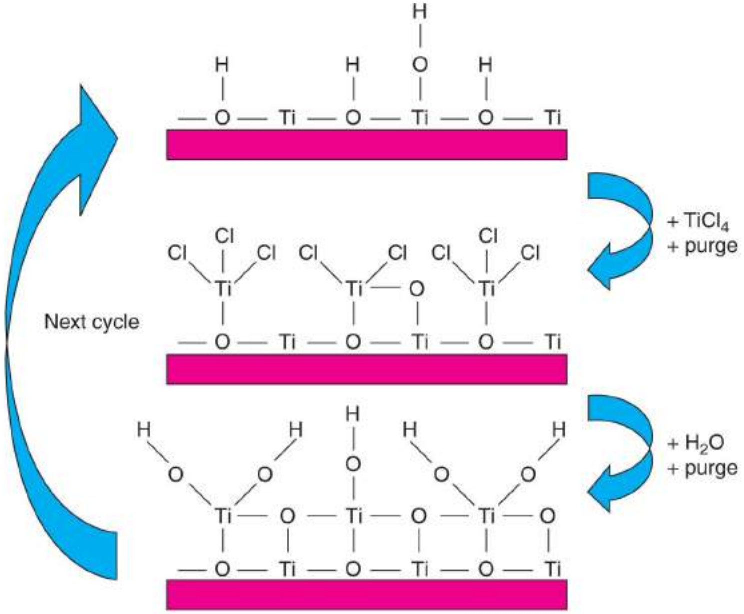


Figure 4.18 ***Deposition of TiO_2 films by ALD. Adapted with permission from M. Leskelä and M. Ritala, Angew. Chem., Int. Ed., 42, 5548, © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.***

Gas-Phase Methods

* *Atomic Layer Deposition (ALD)*

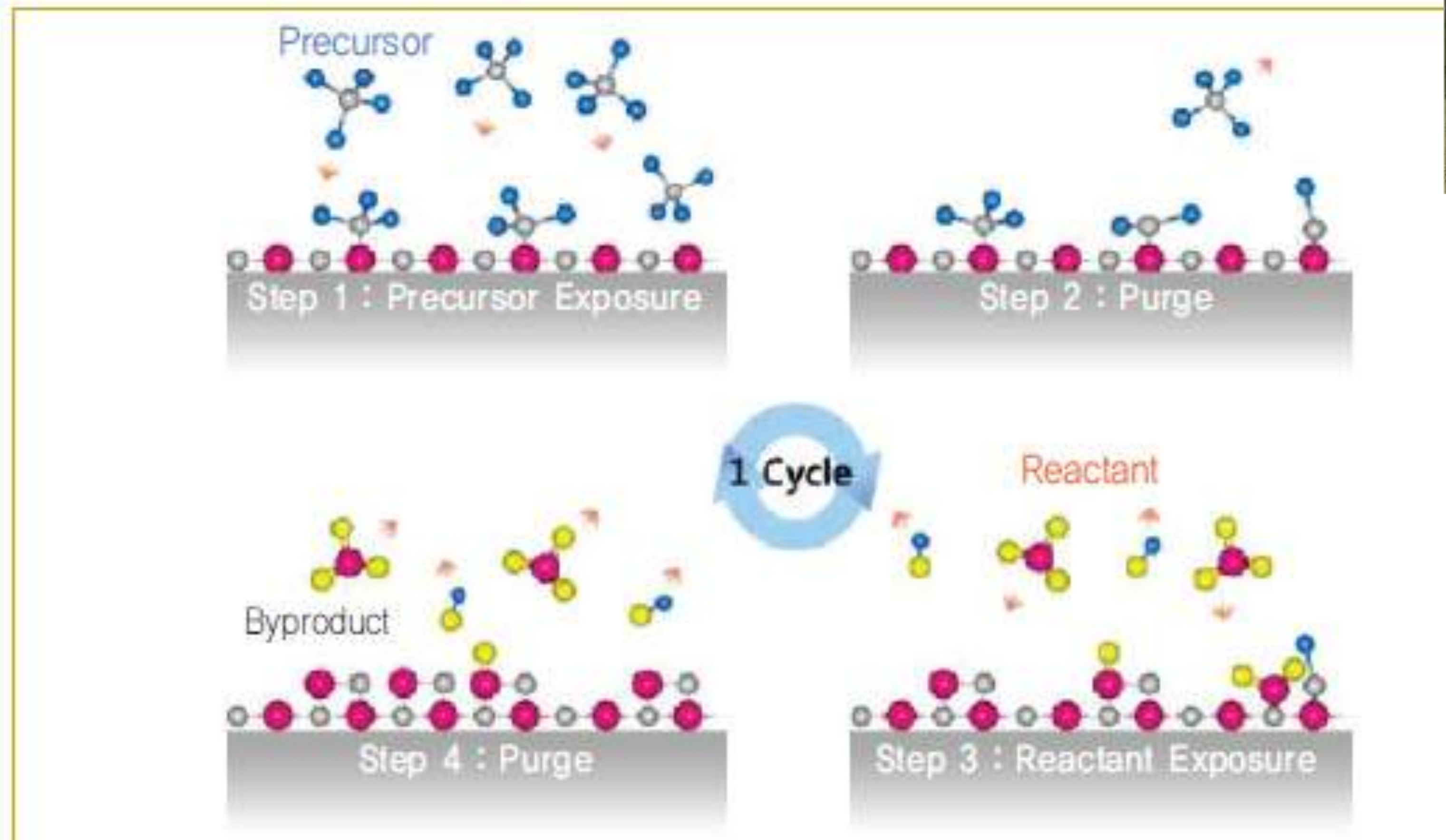
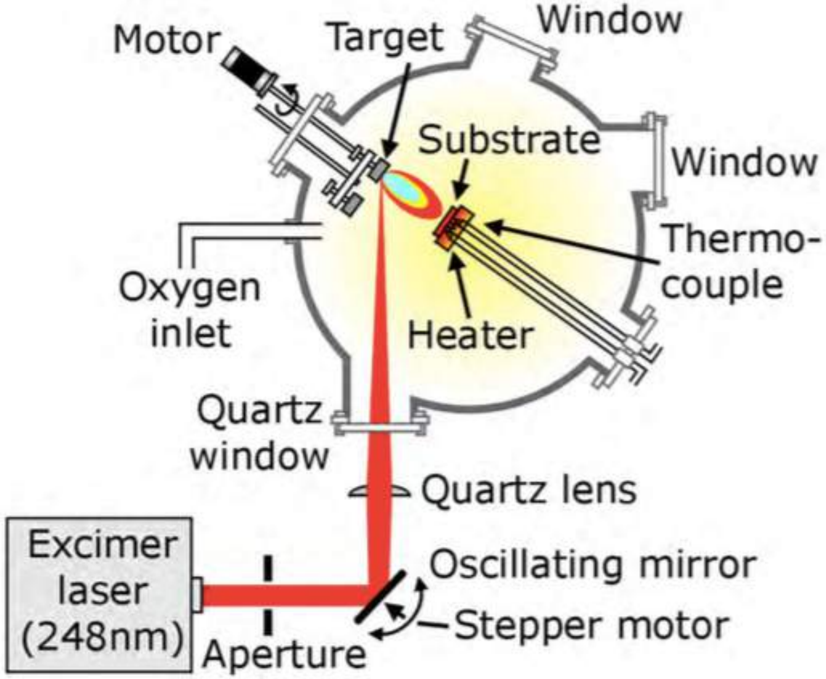


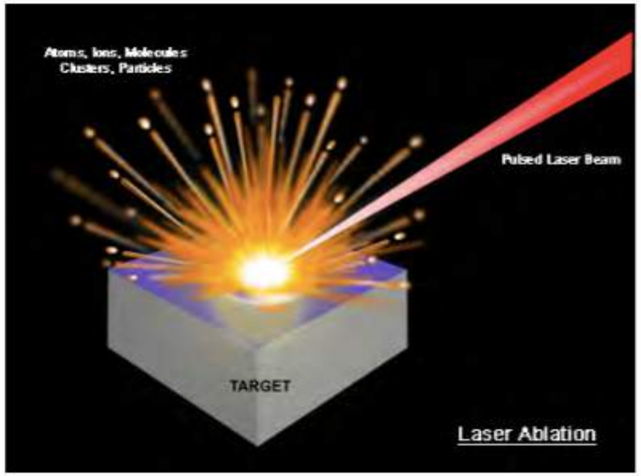
그림 1 원자층 증착의 성장 과정을 보여주는 개략도

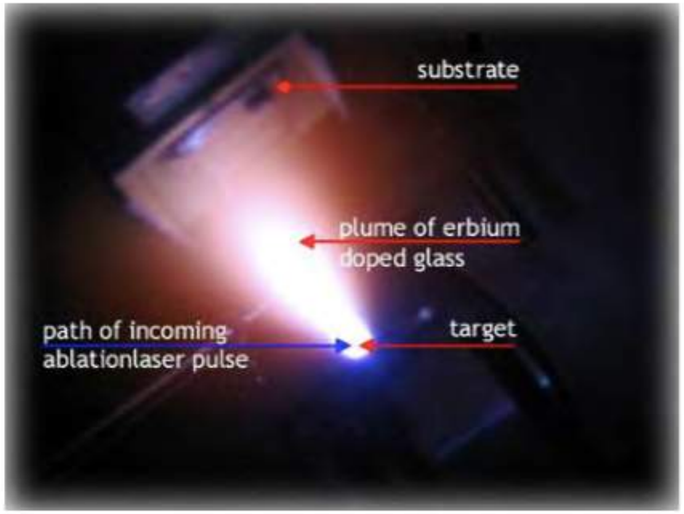
Gas-Phase Methods

PULSED LASER DEPOSITION (PLD)

Stoichiometric mass transfer by ablation of a solid target using a pulsed laser in HV or UHV.





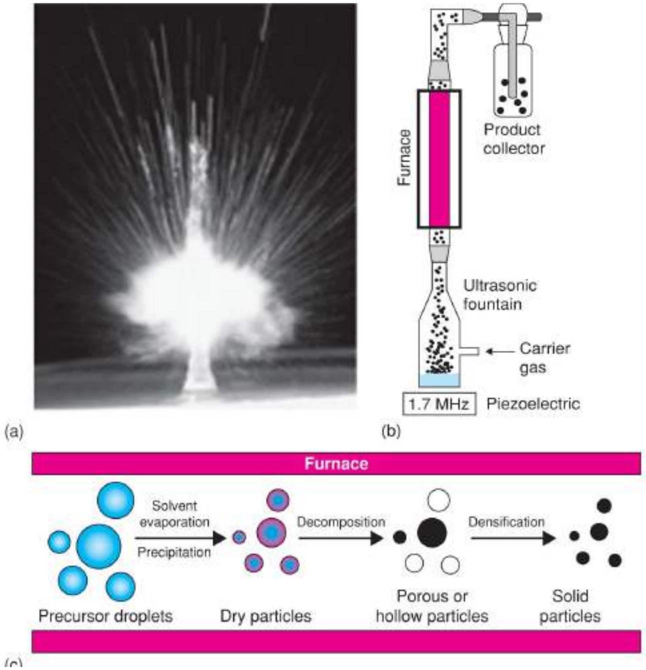


good for materials of complex stoichiometry

Gas-Phase Methods

* *Aerosol Synthesis and Spray Pyrolysis*

- an important method for the preparation of fine powders and thin-film deposition in industry is spray pyrolysis
- the method generates aerosols, which are solid or liquid droplets suspended in a gas, in a nebuliser and are carried in a gas flow to a furnace where they are pyrolysed



* nebuliser

* pyrolysis: a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen