Solid state reactions

Often defined as reactions between two solids

Here the definition is extended to any reaction involving a solid:

•**Solid/solid**

•**Solid/gas (Reaction, decomposition)**

•**(Solid/liquid)**

•**Intercalation**

2   Solid-State Reactions

2.1   Reactions Between Solid Compounds
2.1.1 Ceramic Method
2.1.2 Carbothermal Reduction
2.1.3 Combustion Synthesis
2.1.4 Sintering

2.2   Solid–Gas Reactions

2.3   Decomposition and Dehydration Reactions

2.4   Intercalation Reactions
2.4.1 General Aspects
2.4.2 Preparative Methods
2.4.3 Pillaring of Layered Compounds

Ceramic method

Direct reaction of solids to form the final product
In principle no decomposition is involved.

Solids do not react with solids at room temperature even of thermodynamics is favorable.

High temperature must be used.

Solid-solid reactions are simple to perform, starting materials are often readily available at low cost and reactions are "clean" i.e. do not involve other chemical elements.

Disadvantages include the need for high temperatures, the possibility of non-homogeneity, contamination from containers etc. etc.

Synthesis of YBCO, $YBa_2Cu_3O_{7-x}$
Direct reaction between Y_2O_3, BaO_2, CuO
(Reaction between **three** solid components)
Grind to obtain large surface area
Press into pellets (contact)
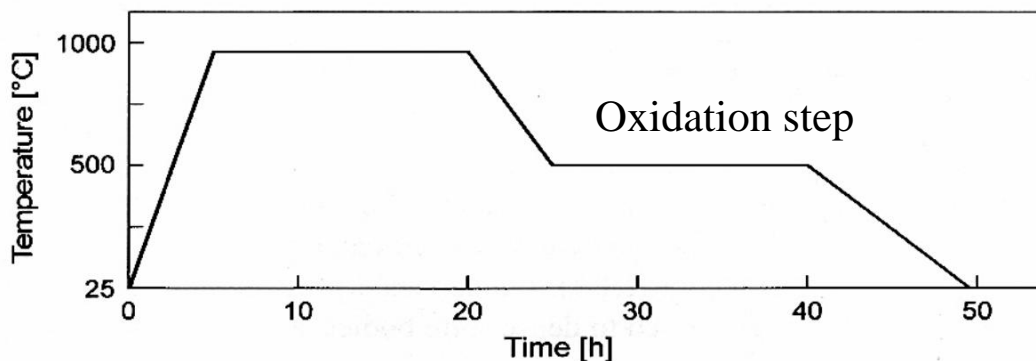Heat in alumina boat, temperature profile:

Figure 2-1. Heating protocol for the preparation of $YBa_2Cu_3O_{6.9}$ (see text).

Other precursors may be used, e.g. $BaCO_3$, which may be decomposed to fine grained BaO during the reaction.
(+ nitrates etc.)
Decomposition must be performed in a controlled manner in order to avoid violent decomposition
(i.e. choosing an appropriate temperature)

Many other ways of synthesizing YBCO:
Precursor methods
Sol/gel
Flux
Many melt-texturing methods
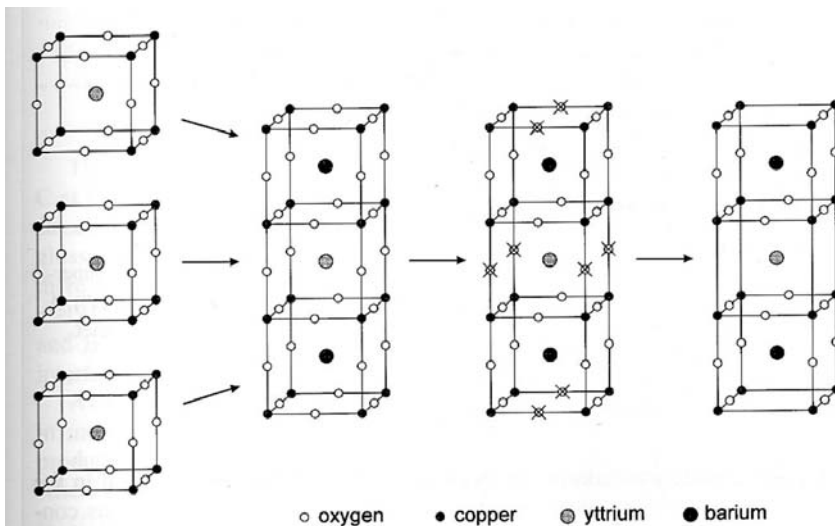including partially melting/fluxing

o oxygen   • copper   ⊚ yttrium   • barium

Figure 2-2. Deduction of the unit cell of $YBa_2Cu_3O_7$ (right) from the perovskite structure. Three perovskite unit cells (left) are stacked above each other. Then the oxygen atoms marked by an x are removed.
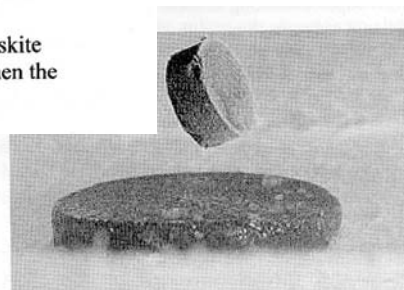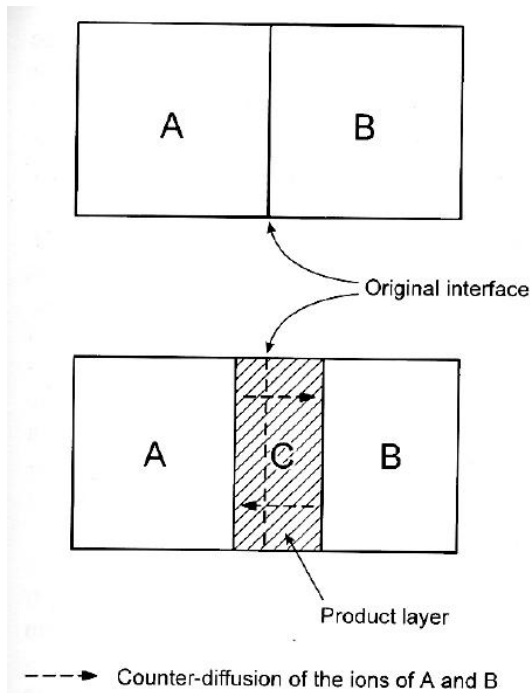

Figure 2-3. In 1933, Walter Meissner and Robert Ochsenfeld discovered that a super-conducting material will repel a magnetic field (the "Meissner–Ochsenfeld effect"). A body made of a superconducting material thus floats above the surface of a magnet.

Solid state reactions, general aspects

Figure 2-4. Reaction of two crystals (A and B) sharing one face. After initial formation of a product layer C, ions from A and B have to counter-diffuse through the product layer to form new product at the interfaces A/C and B/C.

- Nucleation at the interface (depends on the degree of structural rearrangement involved)
- Formation of product layer, two reaction interfaces
- Diffusion/counter diffusion through the product layer

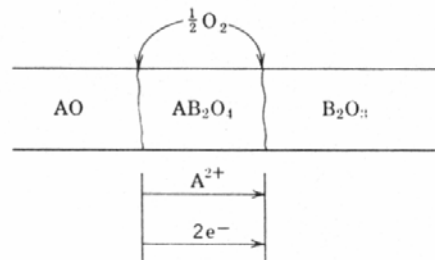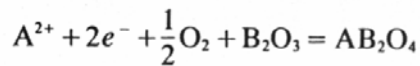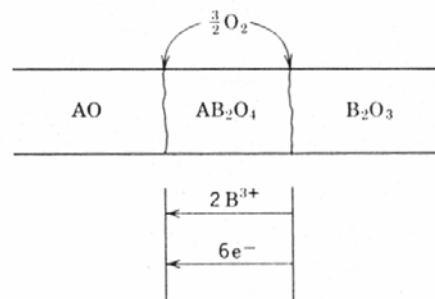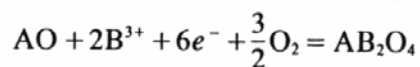Longer diffusion paths, slower reaction rate. Simple case: lattice diffusion through a planar layer:

$$dx/dt = k * x^{-1}$$

Reactions often involve other reactions and transport mechanisms. Electrons, gaseous species, oxygen ions, defects …

Reaction occurs at AB_2O_4–B_2O_3 interface: oxygen gas phase transport with A^{2+} ion and electron transport through AB_2O_4:

$$A^{2+} + 2e^- + \frac{1}{2}O_2 + B_2O_3 = AB_2O_4$$

Reaction occurs at AO–AB_2O_4 interface: oxygen gas phase transport with B^{3+} ion and electron transport through AB_2O_4:

$$AO + 2B^{3+} + 6e^- + \frac{3}{2}O_2 = AB_2O_4$$
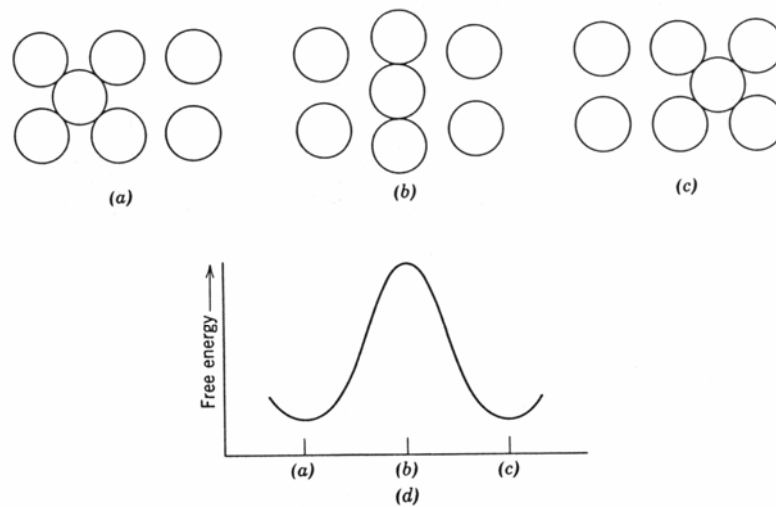
Diffusion is a thermally activated process

Fig. 6.8. (a), (b), and (c) are schematic drawings showing the sequence of configurations involved when an atom jumps from one normal site to a neighboring one. (d) shows how the free energy of the entire lattice would vary as the diffusing atom is reversibly moved from configuration (a) to (b) to (c).

Transport: Diffusion in a gradient
(i.e. chemical potential gradient, Δμ)

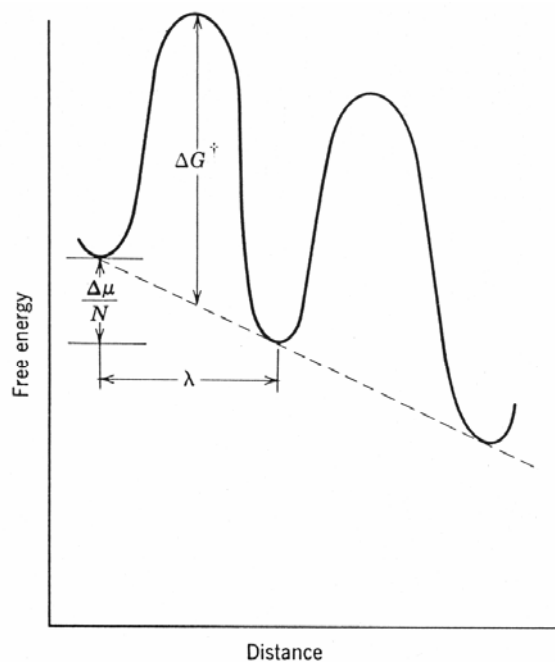Fig. 6.9. Diffusion in a potential gradient $\Delta\mu$; $\Delta G^{\dagger}$ is the activation energy and λ the jump distance.

Mass transport in an ionic solid is often achieved by transport of a charged species and counter transport of a differently charged ion or defect in the opposite direction.

Then the electrochemical potential is the driving force, and not the chemical potential or the concentration gradient.

The electrochemical potential (η_i) of species i is the sum of the chemical potential and electrostatic potential ϕ:

$$\eta_i = \mu_i + Z_i F \phi$$

Where Z_i is the effective charge and F is the Faraday constant.

The flux is given by:

$$j_i = c_i v_i = -c_i B_i \frac{\partial \eta_i}{\partial x} = -c_i B_i \left[\frac{\partial \mu_i}{\partial x} + Z_i F \frac{\partial \phi}{\partial x} \right]$$

Implications of the expression for flux:

● The effect of the terms may pull in opposite directions (i.e. a concentration gradient may be countered by an electrical field gradient)

● A different type of effect may occur due to the local electrical field between oppositely charged species. This may affect the transport of an ion relative to other(s). This coupling results in e.g. that both Al^{3+} and O^{2-} move in Al_2O_3 (in contrast one would normally expect O^{2-} to by fairly immobile due to the large ionic size)
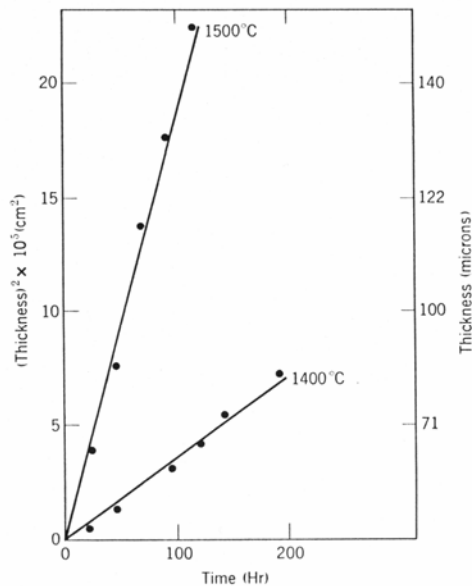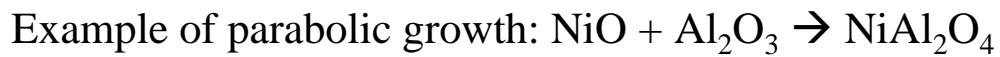
Example of parabolic growth: $NiO + Al_2O_3 \rightarrow NiAl_2O_4$

Fig. 9.7. Thickness of NiAl$_2$O$_4$ formed in NiO–Al$_2$O$_3$ couples as a function of time for couples heated in argon at 1400 and 1500°C. From F. S. Pettit et al., *J. Am. Ceram. Soc.*, **49**, 199 (1966).
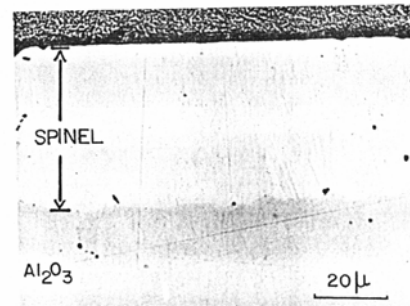
Fig. 9.8. Cross-sectional view of a typical NiAl$_2$O$_4$ layer formed in an NiO–Al$_2$O$_3$ couple after 73 hr at 1400°C. From F. S. Pettit, et al., *J. Am. Ceram. Soc.*, **49**, 199 (1966).

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Ions in solids are not mobile at low temperatures.
High temperatures, as a rule of thumb, at 2/3 of the melting temperature (of one component) the diffusion is sufficient to achieve solid state reactions.

Formation of $BaTiO_3$ by reacting $BaCO_3$ and TiO_2 is an example of a seemingly simple reaction is more complex than expected.
$BaTiO_3$ is an important electroceramic, (Thermistors, capacitors, optoelectronic devices, DRAMs)

$BaCO_3$ is decomposed to reactive BaO: (Rock salt, ccp of the oxide anions, Ba^{2+} in octahedral sites),
TiO_2 (Rutile, hcp of oxide ions, Ti^{4+} in half of the octahedral sites)
At least three stages are involved in formation of $BaTiO_3$ from BaO and TiO_2.

- **BaO react with the surface of TiO_2, forming nuclei and a surface layer of $BaTiO_3$.**

- **Reaction between BaO and $BaTiO_3$ to form Ba_2TiO_4. NB! This is a necessary phase for increasing migration of Ba^{2+} ions.**

- **Ba^{2+} ions from the Ba-rich phase migrate into the TiO_2 phase and form $BaTiO_3$.**
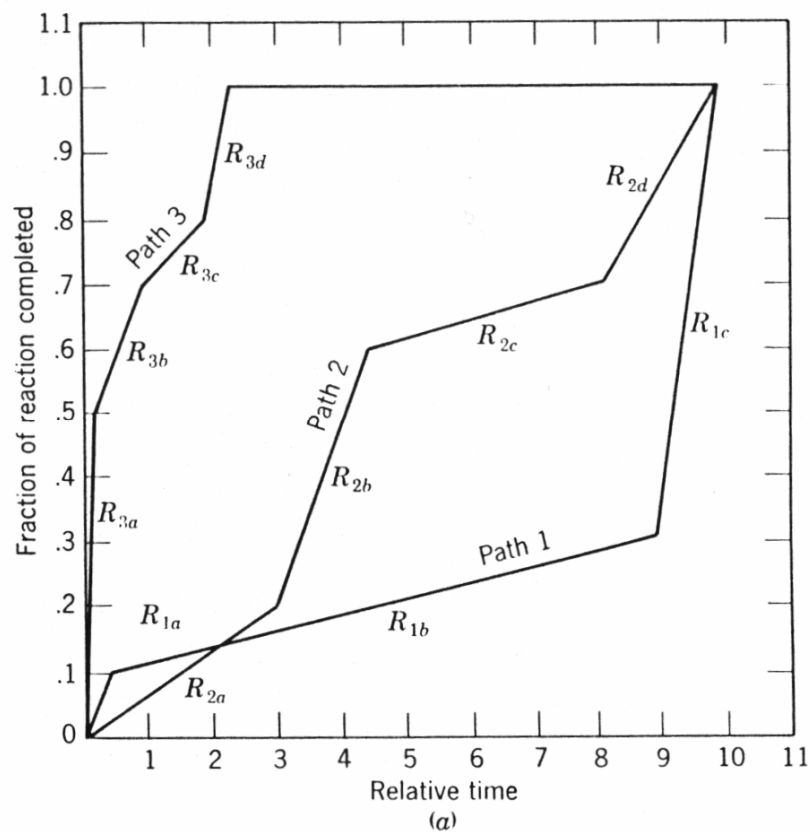
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Reactions between two solids:

Reaction rates depends on:

- **Area of contact between the reacting solids, i.e. surface area and "density"**
- **The rate of nucleation**
- **Rates of diffusion of ions (and other species)**

Disadvantages, e.g.:

•Nucleation and diffusion related problems (high temperature)
•Formation of undesired phases (reaction paths) (e.g. $BaTi_2O_5$)
•Homogeneous distribution, especially for dopants, is difficult
•Difficult to monitor the reaction directly, in-situ…??
•Separation of phases after synthesis is difficult
•Reaction with containers/crucibles
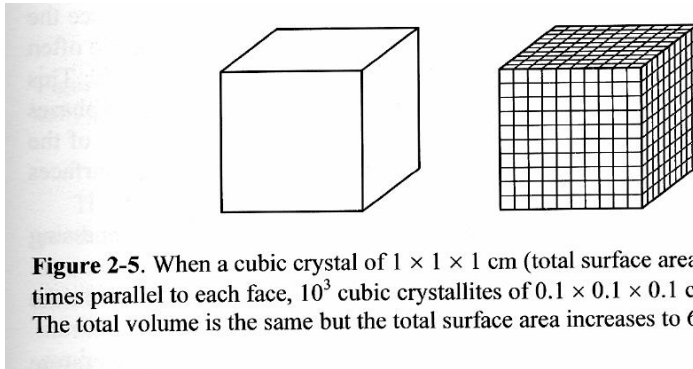•Volatility of one or more of the components

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(a)

Surface area:
Surface area is increased by crushing/milling

1 cm3 cube: surface area 6 cm^2
1 mm cubes: surface area 60 cm^2
10µm cubes: surface area 6000 cm^2
10 nm cubes: surface area 6000000 cm^2 (600m^2)

Figure 2-5. When a cubic crystal of $1 \times 1 \times 1$ cm (total surface area 6 cm^2) is cut ten times parallel to each face, 10^3 cubic crystallites of $0.1 \times 0.1 \times 0.1$ cm are obtained. The total volume is the same but the total surface area increases to 60 cm^2.

Increase diffusion rates (decrease diffusion lengths)

Small particles by grinding, ball milling, spray drying, freeze drying, spray pyrolysis etc. Cooling and regrinding may be necessary
Intimate mixture of reactants by coprecipitation, sol-gel processes, spray pyrolysis etc.
Reduction of diffusion distances by incorporating the cations in the same solid precursor.
Solid state reactions involving melts, molten fluxes or high temperature solvents.

Nucleation

Nucleation limited reactions may be described by the Avrami-Erofeyev equation:

$$x(t) = 1 - \exp(-kt^n) \quad \{or \quad x(t) = 1 - \exp(-(kt)^n)\}$$

N is a real number, usually between 1 and 3 (n>4 is often interpreted as autocatalytic nucleation)

For n > 1 the curve is sigmoidal

Note: This is more empirical for most solid state reactions. It is difficult to talk about reaction order and activation energy for these reactions.
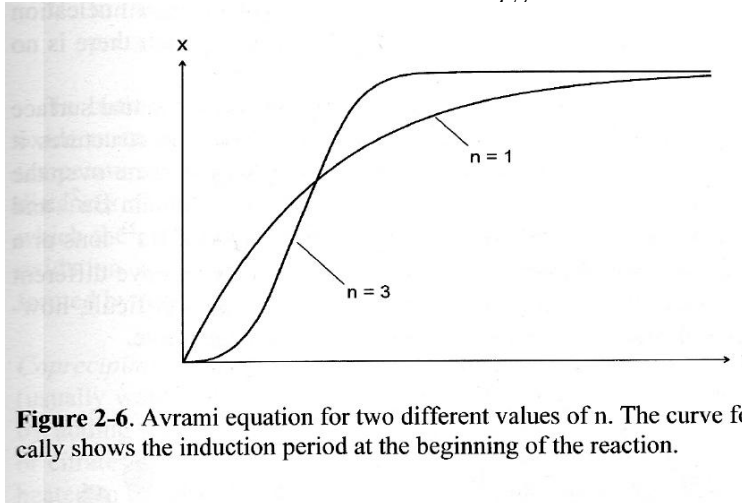

Figure 2-6. Avrami equation for two different values of n. The curve for n = 3 graphically shows the induction period at the beginning of the reaction.

Nucleation may be facilitated by structural similarity between the reacting solids, or products.

In the reaction between MgO and Al_2O_3, MgO and spinel have similar oxide ion arrangements. Spinel nuclei may then easily form at the MgO surfaces.

There is often a structural orientational relationship between the reactant, nuclei and product.

The lattice spacing (e.g. distance between oxide ions) should not be too different for oriented nucleation.

Epitactic and topotactic reactions

Epitactic: structural similarity restricted to the surface / interface between two crystals layer
Topotactic: Structural similarity through the crystal

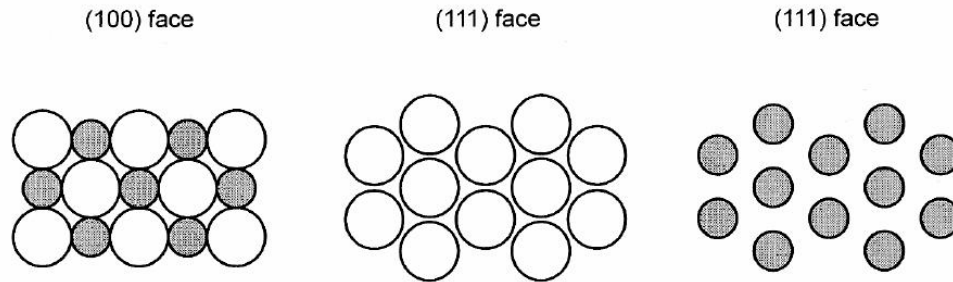The ease of nucleation depends also on the actual surface structure of the reactants.

Figure 2-7. Different planes of the BaO (rock salt) structure. The open circles represent the oxygen atoms, the smaller dark circles the metal atoms.