<u>Lecture: Solid State Chemistry WP I/II</u> H.J. Deiseroth, B. Engelen, SS 2011

Chapter 3: Chemical preparation and crystal groth

- 3.1 Possible reaction paths of solid state reactions
- 3.2 Chemical transport reactions
- 3.3 Crystal refinement by floating zone melting
- 3.4 Growth of single crystals
- 3.5 Chemical Vapor Deposition (CVD)

3.6 High pressure syntheses

3.1 Possible reaction paths between two solid grains A and B



3.1 Importance of the surface aerea for solid state reactions

The common surface of reacting grains influences strongly the reaction rate



Enlargement of the surface aerea by a factor of 10³

3.1 Velocity of diffusion of particles (ions, atoms ...) in a solid

- mass transport and concentration gradient for a given point in a solid!

 $J_i = -D_i \bullet \delta c_i / \delta x$ [mol cm⁻² s⁻¹]

(1st law of Fick)

- Typical diffusion coefficients D_i for ions (atoms) in a solid at room temperature are about 10⁻¹³ cm² s⁻¹.
- In solid state ionic conductors (e.g. Ag-ions in α -AgI) the values are greater by orders of magnitude (\approx 10⁻⁶ cm² s⁻¹)

3.1 Diffusion coefficients show an exponential temperature dependence (Arrhenius type)

 $D = D_{\infty} \exp(-Q/kT)$ (D_{∞} : D für $T \rightarrow \infty$, Q: activation energy of diffusion, k: Boltzmann-faktor)



The logarithmic representation of D verus 1/T is linear, the slope corresponds to the activation energy and the intercept to D_{∞} .

3.1 Model for a classical solid-solid reaction (below melting point !): Planar interface between two crystals

Assumed: single crystals and volume diffusion only (see transparency 1)

$$MgO + Al_2O_3 \rightarrow MgAl_2O_4 \text{ (spinell)}$$



3.1 Gibbs free enthalpy for the first steps of the formation of seeds (nucleation)



r: radius of spheric seed
r*: critical radius
(r>r* seed grows by itself)

 $\Delta G: \underline{\text{total}} \text{ free energy change} \\ \Delta G_s: \underline{\text{surface}} \text{ free energy change} \\ \Delta G_v: \underline{\text{volume}} \text{ free energy change} \\ \end{bmatrix}$

($\Delta G = \Delta G_s 4\pi r^2 + \Delta G_v 4/3\pi r^3$)

3.1 Container materials for solid state reactions

a) glasses b) ceramics c) metals

- depends on the maximum reaction temperature and/or the type of reacting material (e.g. quartz is an "acidic" solid unsuitable for "basic" reactands)

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a) types of glasses:
PYREX (DURAN): borosilicate glass (76% SiO<sub>2</sub>, 16% B<sub>2</sub>O<sub>3</sub>, BaO ...) T<sub>max.</sub> ~ 400 °C,
QUARTZ: Pure amorphous SiO_2, T_{max} \sim 1100 °C
b) ceramics
Al-silicates: T_{max} ~ 1700 °C Corundum (\alpha-Al<sub>2</sub>O<sub>3</sub>): T_{max} ~ 1900 °C
MgO: T<sub>max</sub> ~ 2200 °C BN: ~ 2900 °C
c) metals
Steel: ~ 1400 °C (under inert gas) Pt: ~ 1600 °C (PtO↑), Mo: ~ 2000 °C
          Ta: ~ 2500 °C
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3.2 Chemical transport reaction

A <u>solid</u> ist <u>dissolved</u> in the <u>gas phase</u> at one place (T=T1) by reaction with a <u>transporting agent</u> (e.g. I_2).

At another place (T=T2) the solid is <u>condensed</u> again.

Whether T1 < T2 or T1 > T2 depends on the <u>thermochemical</u> <u>balance</u> of the reaction !

Transport can proceed from <u>higher to lower</u> or from <u>lower to</u> <u>higher</u> temperature



3.2 Transport direction and examples for chemical transport reactions

Transport direction hot \rightarrow cold or cold \rightarrow hot depends on the enthalpy of the transport reaction $A_{(solid)} + B_{(gas)} \leftrightarrow AB_{(gas)} \Delta H = ???$ $\Delta H > 0$ (endothermic): hot \rightarrow cold $\Delta H < 0$ (exothermic): cold \rightarrow hot

Some examples for transport reactions: $T1/T2 \circ C$ $W + 3Cl_{2} \leftrightarrow WCl_{6} \qquad 400/1400 \quad (exo)$ $Ni + 4CO \leftrightarrow Ni(CO)_{4} \qquad 50/190 \quad (exo)$ $2Al + AlCl_{3} \leftrightarrow 3 AlCl \qquad 1000/600 \quad (endo)$ $4Al + Al_{2}S_{3} \leftrightarrow 3Al_{2}S \qquad 1000/900 \quad (endo)$

<u>Main application:</u> crystallisation and purification of solids

3.2 Estimation of ΔH for a transport reaction e.g.:

$$\begin{aligned} \mathsf{ZnS}_{(s)} + \mathbf{I}_{2(gas)} \leftrightarrow \mathsf{ZnI}_{2(gas)} + \mathsf{S}_{gas} & \Delta \mathsf{H} = ?? \\ \mathsf{Zn}_{(s)} + \mathbf{I}_{2(g)} \leftrightarrow \mathsf{ZnI}_{2(gas)} & \Delta \mathsf{H} = -88 \text{ kJ mol}^{-1} \\ & \mathsf{ZnS}_{(s)} \leftrightarrow \mathsf{Zn}_{(s)} + \mathsf{S}_{(g)} & \Delta \mathsf{H} = +201 \text{ kJ mol}^{-1} \\ \hline & \mathsf{ZnS}_{(s)} + \mathbf{I}_{2(gas)} \leftrightarrow \mathsf{ZnI}_{2(gas)} + \mathsf{S}_{gas} & \Delta \mathsf{H} = +113 \text{ kJ mol}^{-1} \\ & \text{transport from hot to cold (normal conditions provided)!} \end{aligned}$$

3.2 Application of chemical transport: halide lamp !



3.2 A further application of chemical transport: \rightarrow purification of Ti

transport reaction: Ti + $2I_2 \rightarrow TiI_4 \quad \Delta H = -376 \text{ kJ mol}^{-1}$ (exothermic: transport from <u>cold to hot</u>)



3.3 Crystal refinement by floating zone melting



3.4 Growth of single crystals: Bridgman-Stockbarger-process (moving temperature gradient, vertical or horizontal)







3.4 Groth of single crystals: Bridgman-Stockbarger-process

\rightarrow preferably: crystal growth of <u>congruently</u> <u>melting</u> compounds

crystal	mp (°C)	velocity of grad.	container material
Al ₂ O ₃	2037	2-8 mm h ⁻¹	Мо
FeAl ₂ O ₄	1790	5-10	Ir
Cu	1083	6-60	graphite
AgBr	434	1-5	Pyrex
Ar (!)	-189	0,5-1,5	Mylar

3.4 Groth of single crystals: Czochralski process: Si (!)

- a rotating seed crystal is raised slowly from a melt with equal composition





3.4 Further treatment of Si single crystal



(a)

(b)

The single crystal is ground to a precision diameter and then sliced into wafers 1 mm thick. The wafers are then chemically etched and polished with successively finer polishing abrasives until a defect free mirror finish is achieved.

3.4 Groth of single crystals: Verneuil process

- preferably for high melting oxides (T > 2000 K)
- powdered sample is blown into a oxyhydrogengas burner



Synthetic corundum crystals obtained by the Verneuile process





3.4 Groth of single crystals: Hydrothermal synthesis

Chemical transport in supercritical aquous solution (H_2O : T_k = 374 °C, p_k = 217,7 atm)

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Autoclave for the growth of SiO_2 single crystals (1 m NaOH, 1500 bar,
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T- gradient 400 \rightarrow 380 °C

- 1: nutrient (powder), 2: seed crystal,
- 3: mechanical fixing of crystal
- 4: product crystal

Lit.: Die Rolle der Hydrothermalsynthese in der präparativen Chemie, A. Rabenau, Angew. Chem. *97* (1985) 1017







3.5 Chemical Vapor Deposition (CVD)

General term for a variety of methods (including epitaxy and sputtering) to deposit a range of inorganic materials for use in semiconducting devices, ceramic coatings, electrooptic devices etc.



3.5 Physical and chemical methods to produce thin layers of chemical compounds or to clean surfaces

- <u>"Sputtering</u>": (to sputter: zischen, brutzeln, spritzen ...)

 <u>originally</u>: method to clean surfaces, Ar⁺-ions ar accelerated in an electrical field and "hit" the target that has to be cleaned; as a consequence surface atoms or molecules are removed from the surface
- <u>Epitaxy</u>: "Thin" oriented layers (thickness of some μm or nm) are deposited on a "substrate with the same or a similar crystal structure. The deposition starts from gaseous precursors, which condensate or decompose on the surface of the substrate.



3.6 High pressure syntheses

Diamond anvil cell

about 1000 kbar (100 GPa) (1 bar = 10⁵ Pascal) Starting mixture is encapsulated and heated under pressure!

By rapid pressure release and quenching metastable products are eventually stabilized

In general the high pressure phase has a higher density and the coordination numbers (and interatomic distances!) of corresponding atoms are higher than in the low pressure phase, e.g.

SiO₂ (Si: CN=4) \rightarrow SiO₂ (Si: CN=6) (quartz) (Stishovit, rutile structure)

 \rightarrow "pressure-distance-paradoxon"

3.6 High pressure syntheses: limitations of the reactive volume

