Exercises: Syntheses Techniques

1) Give an example for a binary, ternary, and quaternary oxide! Give also an example for such sulphides, nitrides and fluorides!

2) Calculate the specific surface area of an Y_2O_3 sample (density = 5.0 g/cm^3), which comprises out of monodisperse spherical particles (particle diameter = 100 nm)!

3) Which is the basic physical process of solid state reactions? Give an example!

4) Describe by simple chemical reaction equations the principle of the precursor process!

5) By which three main factors is the speed of a solid state reaction determined?

6) Propose a synthesis route for the following solid state compounds! Which flux would you apply?
a) $Gd_3Ga_5O_{12}$
b) $BaMgAl_{10}O_{17}$
c) YBO_3
d) $Y_4Al_2O_9$
e) $SrLi_2SiO_4$

7) Explain the technique ”Carbothermal Synthesis” by means of an example!

8) Propose a synthesis route starting from oxides/carbonates for the preparation of the following solid-state compounds! Balance all reaction equations!
a) $GdMgAl_{11}O_{19}$
b) Ba_2GdTaO_6
c) $YBa_2Cu_3O_7$
d) $LiEuMo_2O_8$

9) Write balanced equations for the following reactions !
a) Al_2O_3 and Tb_4O_7 to give $TbAlO_3$
b) Cu_2O and HCl to give CuCl and H_2O
c) CaO and SnO_2 to give Ca_2SnO_4
d) Lu_2O_3 and alumina to give $Lu_3Al_5O_{12}$

10) Please complete the following reaction equations!
a) $(Y_{1-x}Eu_x)_2(C_2O_4)_3 \rightarrow$:1600 °C, air
b) $Eu_2(CO_3)_3 + 5\ Al_2O_3 + MgO \rightarrow$:1200 °C, N_2/H_2
c) $La_2O_3 + WO_3 \rightarrow$:1000 °C, air

11) Balance the following reaction equations!
a) $SrO + C + N_2 + Si_3N_4 \rightarrow Sr_2Si_5N_8 + CO$
b) $SrCO_3 + H_3BO_3 \rightarrow SrB_4O_7 + H_2O + CO_2$
c) $La_2O_3 + MgO + H_3BO_3 \rightarrow LaMgB_5O_{10} + H_2O$
d) $NH_4H_2PO_4 + Y_2O_3 \rightarrow YPO_4 + H_2O + NH_3$
e) $Eu_2O_3 + C + H_2O + Si_3N_4 \rightarrow EuSi_2N_2O_2 + CO + NH_3$

12) Chemical transport reactions:
a) Please sketch the basic steps of a chemical transport reaction!
b) What is the driving force for a chemical transport reaction?
c) Please give 2 examples for a chemical transport reaction and the respective reaction equations!

13) Complete the following equations of chemical transport reactions!
a) $W + O_2 + I_2 \leftrightarrow$
b) $Ni + CO \leftrightarrow$
c) $Ti + I_2 \leftrightarrow$
Which technical processes make use of these reactions?

14) Which metals can be purified by chemical transport reactions? Give three examples! Is the purification of noble metals possible by CVT reactions?

15) Please sort the following compounds according to their band gap!
a) GaAs, InAs, AlAs, GaP, GaN
b) $MgCl_2$, MgO, MgF_2, $MgBr_2$
(Please explain the physical basis of your chosen series)!

16) Please sketch the main components of a FB-CVD reactor? Which typical precursors are used in a FB-CVD experiment? Please give an example for the application of a FB-CVD reactor!

17) Sketch the relative course of the band gaps of the solid solutions $(Ga_{1-x}In_x)N$ and $(Ga_{1-x}In_x)P$? Which solid solution has the higher band gap?

18) Which type of dopants do you need to obtain
a) p-type Si
b) n-type Si
c) p-type GaN
d) n-type GaN?

19) Which methods exist to prepare artificial diamond? How can you distinguish between natural and artificial diamond?

20) Give an example of a volatile Cu and Y compound, which can be used as precursor in chemical vapour deposition experiments!

21) Which products do you expect for the following reactions?
a) $WF_6 + H_2 \rightarrow$
b) $Si(C_2H_5)_4 + O_2 \rightarrow$
c) $Ga(CH_3)_3 + NH_3 \rightarrow$
d) $In(CH_3)_3 + PH_3 \rightarrow$

22) Sketch a simple picture to illustrate the reaction pathway of a chemical vapour deposition reaction (use the deposition of ZnS from $ZnCl_2$ and H_2S as an example)!

23) Which applications of solvothermal processes are known to you?

24) Give the reaction equation for the hydrothermal single crystal growth of the following compounds:
a) SiO_2
b) Al_2O_3:Cr

25) Explain the expressions “Sol” and “Gel”! Describe two methods to generate a Gel starting from
a) biopolymers, e.g. gelatine, agar-agar, or pectin
b) inorganic colloidal particles, e.g. an SiO_2-Sol

26) Sol-Gel-Chemistry: Please sort the following compounds with respect to their reactivity towards hydrolysis!
a) $Y(OCH_3)_3$, $Y(OC_2H_5)_3$, $Y(OC_3H_7)_3$
b) $Lu(OCH_3)_3$, $La(OCH_3)_3$, $Y(OCH_3)_3$

27) Propose starting compounds and a synthesis method to prepare zeolites!

28) Sketch the Pechini method for the synthesis of nanoscale particles!

29) Give three examples for methods to
a) to determine the particle size distribution of solid state particles
b) to separate micro from nanoparticles!

30) Please propose a technique for the preparation of nanoparticles of the following compounds!
a) $LaPO_4$
b) Cr_2O_3
c) TiO_2
d) Y_2O_3
e) SiO_2
f) AgBr

31) Please calculate the percentage of atoms, which are located at the surface of a metal cluster, if the coordination number of the atoms is 12 (cubic close packaging) and the cluster comprises n shells. The amount of atoms in shell n is $10 \cdot n^2 + 2$ (i.e. 0. shell = 1 atom, 1. shell = 12 atoms, and so on)!
a) Cluster with n = 3
b) Cluster mit n = 5
c) How can you prepare Au-Cluster in water?

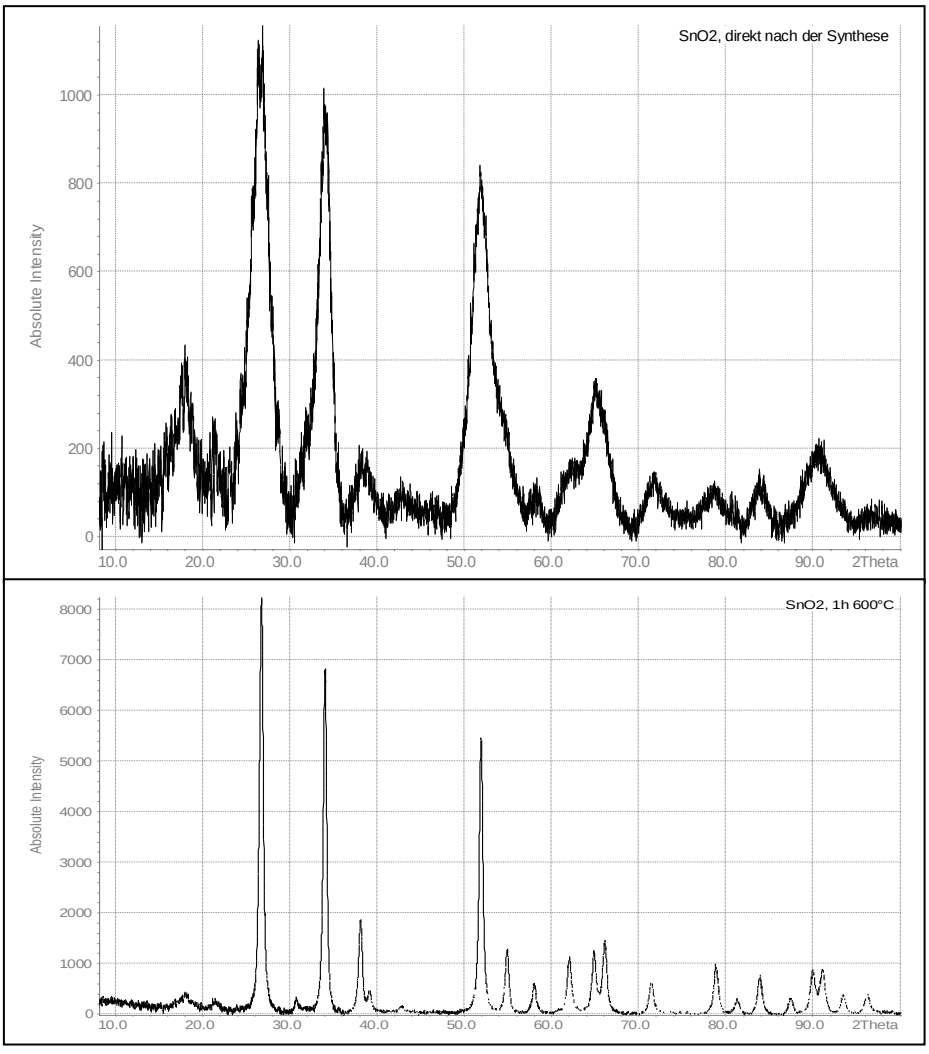
32) Sketch the procedure for the synthesis of CdS nanoparticles by the micro-emulsion technique!

33) Scherer studied the influence of the particle size on the line width of x-ray interferences. The line width at half maximum is given by the so-called Scherrer equation:

$$\beta_{1/2} = \frac{57.3K\lambda}{D\cos\vartheta}$$

K is a constant (form factor), which is a function of the particle shape and is usually between 0.89 and 1.39. For spherical particles one can work with K = 1.
D – average particle size perpendicular to the refractive net layer
ϑ - refraction angle
λ - applied x-ray wavelength Cu K_α = 1.540598 Å
57.3 – transformation factor, if $ß_{1/2}$ is measured in degrees

Determine the particle (crystallite) size of spherical nanoscale particles of SnO_2, which were made by the polyol method (top XRD pattern)! Which influence has an additional annealing step for 2 h at 600 °C (bottom XRD pattern) on the particle (crystallite) size?



34) Please give five application areas and examples of inorganic pigments!

35) The doping of SiO_2 by Ti^{3+} ([Ar]$3d^1$) yields crystals having a rose colour, while doping of Al_2O_3 results in light blue sapphire.
At which wavelength range are the absorption bands of Ti^{3+}? Please explain the origin of the difference in the position of the absorption bands!

36) A 100 g sample of $BaMgAl_{10}O_{17}$:Eu ($\rho(BaMgAl_{10}O_{17}) = 3.8$ g/cm^3), which consists of monodisperse spherical particles with a diameter of 5 µm shall be coated by MgO. Calculate the required amount of MgO to coat all particles by a dense and 50 nm thick coating layer ($\rho(MgO) = 3.58$ g/cm^3). How much $Mg(NO_3)_2$ is required as precursor for the $Mg(OH)_2$ precipitation?

37) Propose suitable precursor materials for the coating of a microscale powder by Al_2O_3 by the following processes!
a) Wet-chemical coating
b) Chemical vapour phase deposition

38) Quote the chemical formula of 5 technically important colour pigments! Which type of electronic transition causes the colour of these pigments?

39) Give three mechanisms, which can cause the degradation of colour or luminescent pigments!

40) Propose a synthesis for the luminescent pigment $(La_{0.8}Ce_{0.1}Tb_{0.1})PO_4$. Calculate the amount of required starting materials to synthesise 100 g of the pigment!

41) Imagine you have prepared a water-sensitive inorganic pigment. By which measure can you improve its stability? Propose a process to apply your idea!

42) Which chemical and physical properties must a material show to be applicable as a particle coating?

43) Explain by a simplified sketch the principle of contrast enhancement by inorganic pigments!

44) Give two examples for catalytic pigments and describe by simple reaction equations the catalytic process!

45) Explain the origin of the following physical phenomena!
a) Diamagnetism
b) Paramagnetism
c) Ferromagnetism
d) Antiferromagnetism
e) Ferrimagnetism

46) Which materials could you apply as a photosensor in a light meter for a black/white camera and for an IR camera?

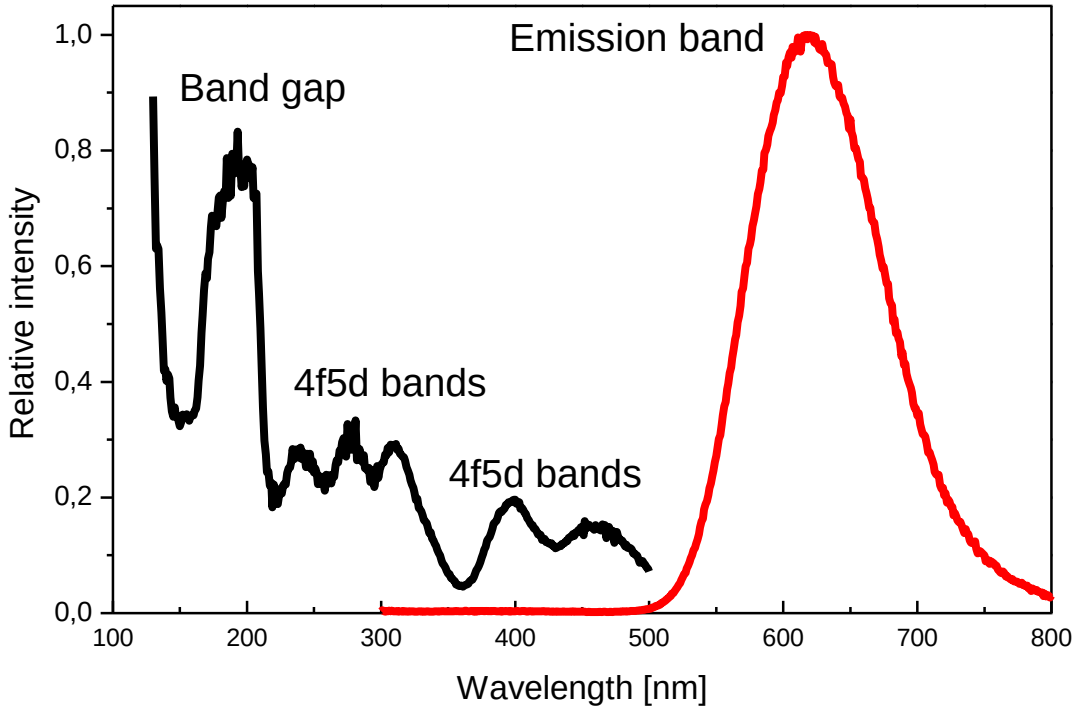
47) Alkaline halides are transparent to visible light. Calculate the wavelength at which they become transparent by using the band gap data from the following table!
(1 eV = $1.602 \cdot 10^{-19}$ J ~ 8050 cm^{-1})

Compound	band gap [eV]
LiF	11.0
LiCl	9.5
NaF	11.5
NaCl	8.5
NaBr	7.5
KF	11.0
KCl	8.5
KBr	7.5
KI	5.8

48) Quote four inorganic materials, which are applied as solid ion conductors! Which of these materials are cation and which are anion conductors?

49) Which causes are responsible for the fact that luminescent pigments show quantum efficiency smaller than unity? Which conclusions can be drawn from this for the synthesis planning of high-quality luminescent pigments?

50) The excitation and emission spectrum of $SrSi_2N_2O_2$:Yb is given below.



Determine the energy gap between the valence and conduction band and sketch a band gap diagram, which comprises the relative location of the excited states of the Yb^{2+} activator relative to the ground state level (electron configuration [Xe]$4f^{14}$].