Part One
Rational Design and Related Physical Properties

1
From Solid-State Chemistry to Soft Chemistry Routes

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1.1
Introduction

As a recent report on the future directions in solid-state chemistry points out, "Synthesis . . . is the essence of chemistry because it provides the objects of any further studies" [1]. Without synthesis we have nothing to work on experimentally, we cannot develop new compounds with new or improved properties, sometimes for previously unknown or even unforeseen applications.

Synthesis can be carried out on exploratory (serendipity) or directed bases. To obtain a given highly pure solid is not enough in some cases, as precise morphology, size, and so on are needed for a given application; obtention of amorphous or a microcrystalline powder or single crystals might require specific procedures. For this reason, it is more convenient to speak about *preparation* when all these requirements (composition, purity, crystalline phase, morphology, particle size, etc.) are fulfilled, and about *synthesis* when simply the pure compound is pursued.

Even for known compounds, the preparation procedure has changed along history, aiming to reduce time and energy consumption. Current concern on environment has also led to search for more environment-friendly procedures. The procedure also depends on the scale production, for instance, formation of toxic by-products or using expensive reagents will be less important when producing a few grams than when producing several kilograms or tons.

This chapter describes the main methods used to prepare metal oxides. They have been classified according to the state of the starting reactants: solids, liquids (melts or solutions), or gases and vapors. Brief sections on single crystals, films, and nanoparticles are also included. Within each section we proceed from the most energy-demanding processes, usually at high temperatures, to those that can undergo at lower temperatures.

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1.2
Processes Involving Solids

1.2.1
The Ceramic Method

The ceramic method *simply* implies the direct reaction between solids to yield the final product. The reaction is very low at room temperature and thus high temperatures are required; the reaction can be completed if the reaction temperature reaches two-thirds of the melting point of one of the solid reactants [2]. As an advantage, the reaction is simple to perform, the starting materials are usually available, and no solid by-products are formed. Increasing the reaction temperature might have some disadvantages: No reactant easily forming volatile species can be used, metastable phases cannot be obtained, and high oxidation states are usually unstable at high temperatures. In addition to the need for high temperatures, it is difficult to obtain completely homogeneous products, and contamination from the crucible or container is common. The reaction takes place through diffusion of the reactants (their ions, actually) through the interface and in many cases rearrangement of the ions forming the lattice. For instance, in the reaction between MgO (fcc lattice) and α-Al_2O_3 (hcp lattice) to form the $MgAl_2O_4$ spinel (fcc lattice), all oxide anions should rearrange to a fcc structure, octahedrally coordinated Mg^{2+} ions should diffuse to tetrahedral sites, and an ordered occupation of 50% of the octahedral sites by Al^{3+} ions should be reached.

The reaction rate increases by using powdered reactants with large specific surface area (SSA) and high contact area between their particles; the diffusion lengths are also reduced. The SSA of a nonporous solid increases as the size of the particle decreases; assuming homogeneous, nonporous, spherical particles, the relationship $\mathrm{SSA}\cdot r\cdot\delta = 3$ holds, where r stands for the radius of the particle and δ for its density.

Other important aspects are the *nucleation* rate of the new phase and the *diffusion* of the ions. Nucleation is easy if structural similarities exist between the reagents (or one of them) and the products. In the case of spinel, this and MgO have the same oxide arrangement (fcc), facilitating formation of spinel nuclei at the surface of the MgO crystallites. In the simplest case of diffusion through a planar layer, it is governed by a parabolic rate law $x = kt^{1/2}$, where x is the thickness of the growing layer, t is the time, and k is a constant. The diffusion rate decreases as the layer of the new phase is formed in the interface of the two reactants. To increase the diffusion rate, defects can be generated by using reactants that decompose prior to or during the reaction (e.g., nitrates or carbonates), or the length of the diffusion path should be decreased. This can be achieved by modifying the conventional ceramic method (shake and bake).

The reactants should be powdered and intimately and stoichiometrically mixed and heated. Then they should be thoroughly pulverized and heated a second or even a third time; the advance of the reaction can be checked from the powder X-ray diffraction diagram, although the method is of low accuracy for poorly crystallized solids. Containers used can be quartz or alumina tubes in tubular furnaces (for an easy control of the atmosphere) or crucibles; sometimes the reaction is carried out under vacuum or in sealed tubes. The heating procedure depends on the temperature to be reached: electrical furnaces (up to 2000 °C), arc devices (3000 °C) [3], or lasers (4000 °C) should be used.

Koshy and coworkers [4] have prepared $Ba_{2-x}Sr_xEuSbO_6$ perovskites by mixing stoichiometric amounts of Eu_2O_3, $BaCO_3$, $SrCO_3$, and Sb_2O_3 thoroughly ground in acetone; the mixture was pressed into pellets and calcined in air at 1000 °C for 36 h with two intermediate grindings. The calcined material was then ground and pelletized at $5\,t/cm^2$ and sintered in air at 1500–1550 °C for 16 h.

The specific nature of the reactants can permit lower reaction temperatures. So, Alikhanzadeh-Arani and Salavati-Niasari [5] have reported the preparation of YBaCuO at 870 °C, a temperature somewhat lower than that required in the conventional ceramic method, when starting from [tris(2-hydroxyacetophenato) triaqua yttrium(III)] instead of $Y_2(CO_3)_3$.

1.2.2
Microwave Synthesis

This is not exactly referring to a synthesis procedure, as the role of microwaves (MW) is merely to increase the rate of the solid–solid reaction and the diffusion rate; no other difference exists with the conventional ceramic method.

Electromagnetic MW (typical wavelength $\approx$ 1 cm) may be reflected, transmitted, or absorbed by condensed matter. Absorbing materials (dipolar liquids and dielectric or polar materials as ferroelectrics with high dielectric permittivity) transform the electromagnetic energy into heat; dielectric permittivity and dielectric losses determine the absorption of MW by a material, those with dielectric losses between 10^{-2} and 5 being the best candidates for MW heating. The dielectric permittivity describes the polarizability, and polarization depends on the frequency of the applied electric field (2.45 GHz in the so-called MW ovens).

When using MW, heat energy is directly transferred to the material through the interaction with the electromagnetic field at the molecular level. MW reduce the processing time, but can lead to formation of hot spots, with nonhomogeneous temperature profiles. Not all materials are sensitive to microwaves, but these can heat selectively a given material within a mixture of several components.

Direct MW irradiation of solid reactants has been used to prepare solids. MW can also be used as an aging source in hydrothermal synthesis (see below). MW heating can also be combined with other synthesis procedures, for instance, with sol–gel procedures to prepare solid oxide fuel cells such as $La_{1-x}Sr_xFeO_{3+\delta}$ and $La_{1-x}Sr_xFe_xCo_{1-y}O_{3+\delta}$ [6], or in a MW-induced autocombustion to produce $LaMnO_3$ [7]. The application of MW to synthesize perovskites has been recently reviewed [8]. MW-assisted synthesis of $YBa_2Cu_3O_{7-x}$ can be achieved by intimately mixing CuO, $Ba(NO_3)_2$, and Y_2O_3 in stoichiometric amounts; after 5 min under 500 W irradiation with MW, grinding, exposure for 15 min at 500 W, and grinding and exposure for further 25 min, the mixed oxide is formed [9].

In all cases, at least one of the components of the mixture should be sensitive to MW, as CuO in the case of $YBa_2Cu_3O_{7-x}$. Other absorbing oxides are ZnO, V_2O_5, MnO_2, PbO_2, Co_2O_3, Fe_3O_4, NiO, and so on, while CaO, TiO_2, CeO_2, Fe_2O_3, Pb_3O_4, SnO, Al_2O_3, and so on are poor absorbers.

1.2.3
Self-Propagating High-Temperature Synthesis (SHS)

In this process, combustion waves (solid flames) are used; it is also known as *combustion synthesis*, and has been applied to prepare refractory materials [10]. The reactions are driven by their reaction enthalpy [11] and its dynamics in layer models has been studied [12]. A compressed powder mixture is ignited producing a chemical reaction, which is self-sustained by the heat released. It can be carried out in two modes, propagating or bulk, and temperatures above 2000 °C are easily reached. For instance, Cr_2C_3-Al_2O_3 and TiC-Al_2O_3 composites are formed at 6500 and 2300 K, respectively [11]. The extremely high temperatures vaporize volatile contaminants and highly pure products result; as the cooling rate is also very high, metastable, highly reactive phases can be formed. High-temperature furnaces are not required and the process takes seconds instead of hours or days, with important savings in energy and time. The major difficulty is to achieve a high product density and tight control over the reaction. When carried out under intense magnetic fields, the nature and properties of the products can be drastically changed. Pankhurst and coworkers [13] have prepared $BaFe_{12}O_{19}$ after SHS sintering (1200 °C for 2 h, fast heating, and sintering at 20 °C/min) a mixture of BaO_2, Fe_2O_3, and Fe. The coercivity of the final product depends on the magnitude of the field applied (up to 15 T) during combustion. The method can be modified, for example, combining it with mechanical activation or carrying out the reaction in the presence of additives to prepare nanomaterials; it has been recently reviewed by Aruna and Mukasyan [14].

1.2.4
The Precursor Method

It is a minor (but significant) modification of the ceramic method to improve diffusion of the reactants: While the average size of a chemical bond is 1–2 Å, solid particles have an average size on the order of micrometers, about 10^4 larger. The idea is mixing intimately the cations in a single-solid precursor, which upon heating will form the final solid. We can distinguish between *ordered* precursors, with defined stoichiometry and crystal structure, and *disordered* precursors, amorphous phases containing the desired elements in the appropriate stoichiometry [15].

For instance, synthesis of $Ni_{1-x}Mg_xO$ from NiO and MgO by the ceramic procedure requires very high temperatures. But starting from an aqueous solution of Ni^{2+} and Mg^{2+} cations (in the desired molar ratio) and crystallizing or precipitating a mixed salt in a *single* crystallographic phase (this point is essential) with the required stoichiometry [16], the Ni^{2+} and Mg^{2+} cations will be close to each other. Heating to decompose the salt (carbonate, oxalate, hydroxide, etc.) will lead to the mixed oxide at lower temperatures than that required in the pure ceramic method. Advantages can be summarized as follows: lower reaction temperature, stabilization of metastable phases, absence of intermediate impurity phases, and formation of smaller crystallites with a larger SSA. The main disadvantage can be the lack of a suitable precursor fulfilling the required properties or markedly different precipitation rates of the species forming the precursor. Chromites (MCr_2O_4) can thus be easily prepared by heating at 1100–1200 °C the corresponding chromate or dichromate salts, for example, $FeCr_2O_4$ from $(NH_4)Fe(CrO_4)_2$ at 1150 °C or $MnCr_2O_4$ from $MnCr_2O_7{\cdot}4py$ at 1100 °C [17]; the ceramic method requires temperatures between 1400 and 1700 °C.

Examples of ceramic (1.1 and 1.3) and precursor (1.2 and 1.4) reactions to produce some mixed oxides are as follows:

$$BaCO_3(s) + TiO_2(s) \rightarrow BaTiO_3(s) + CO_2(g) \tag{1.1}$$

$$BaTiO(C_2O_4)_2(s) + O_2(g) \rightarrow BaTiO_3(s) + 2CO_2(g) \tag{1.2}$$

$$La_2O_3(s) + CO_2O_3(s) \rightarrow LaCoO_3(s) \tag{1.3}$$

$$La[Co(CN)_6]{\cdot}6H_2O(s) \rightarrow LaCoO_3(s) + 6H_2O(v) + 6CO_2(g) + 3N_2(g) \tag{1.4}$$

1.2.5
Hydrothermal Synthesis

The reaction is carried out in water, but the reagents are solids. A solid is precipitated and by reaction with other components of the solid mixture or with dissolved species it is transformed into a new solid. The reaction takes place in a closed vessel (a hydrothermal bomb) usually built in stainless steel lined with Teflon. The reaction takes place at 150–500 °C (depending on the liner used) and high autogenous pressures. Water acts as a pressure transmitter and as a solvent. Seed crystals and a temperature gradient are sometimes used for crystal growth. Under these conditions, solubilization of very insoluble species (e.g., silica) takes place, and the reaction proceeds; for instance:

$$6CaO + 6SiO_2 + H_2O \rightarrow Ca_6Si_6O_{17}(OH)_2 \tag{1.5}$$

The crystal size generally increases as a result of Ostwald ripening: small particles dissolve faster than the large ones and dissolved small particles dynamically and reversibly contribute to growing of the large ones. The process proceeds until the solubilities of the large and the small particles are very close to each other.

This procedure is generally used to prepare zeolites. A gel is formed by hydrothermal treatment (<200 °C) of an aqueous solution of NaOH, $NaAl(OH)_4$, and Na_2SiO_3 (a structure-director agent (SDA) can be added). Depending on the reactants nature and ratio, the SDA used, and the specific experimental conditions (temperature, pH, time, etc.), different structures can be formed.

The garnet $Y_3Al_5O_{12}$ (YAG) can be prepared from Y_2O_3 and sapphire (a form of Al_2O_3) in two zones of an autoclave at different temperatures; YAG is formed where the two zones meet [9]:

$$3Y_2O_3(s) + 5Al_2O_3(s) \rightarrow 2Y_3Al_5O_{12}(s) \tag{1.6}$$

Microwaves can be used as an energy source for heating in hydrothermal processes. More crystalline phases, with larger SSA development, are formed, probably via Ostwald ripening removing small particles blocking the pores, which are dissolved and reprecipitated increasing the size of the large crystals [18].

1.2.6
High-Pressure Methods

Solids or mixed solids are compressed in flexible compressible containers and on applying a high pressure, dense, high coordination number phases are formed. Depending on the geometry of the device, different techniques have been applied [3]: *piston–cylinder press* can achieve 50 kbar and 1800 K; *multianvil press* up to 200 kbar and above 2000 K; and *belt design* up to 150 kbar and 2300 K.

1.2.7
Mechanochemistry

As early as in the fourth century BC, “native cinnabar was rubbed with vinegar in a copper mortar with a copper pestle yielding the liquid metal,” that is, mercury [19]. This is probably the most ancient documented chemical recipe and describes a mechanochemical reaction, “a chemical reaction that is induced by the direct absorption of mechanical energy” [20]. A small amount of liquid accelerates or even enables mechanochemical reactions between solids. Mechanical treatment provides energy to break chemical bonds, or facilitates “grinding” reactions, which proceed due to an increase of the contact area between the solid reactants.

The procedure for oxides is similar to the ceramic method, but using mechanical energy instead of heat; despite the small thermodynamic driving force involved, numerous compounds, such as $CrVO_4$, $LaCrO_3$, $MnFe_2O_4$, and so on, have been prepared [21], with grinding times between 2 and 24 h. Mechanical activation (probably developing highly reactive defects) permits preparation of $ZrTiO_4$ at 1100 °C instead of 1400 °C without pregrinding [22]. A thermodynamic driving force can be involved by introducing a reducing metal, to be included in the final solid; for example, the presence of Ti favors the formation of $FeTiO_3$ or Fe_2TiO_4 [23].

Formation of a mixture of products is not a disadvantage if the desired product and the by-products have different solubilities; this is the situation in displacement reactions, as between $ZnCl_2$ and $Ca(OH)_2$, to produce ZnO nanoparticles in a $CaCl_2$ matrix, which is removed by washing with water [24]. Alkaline and alkaline-earth cations are usually introduced by using carbonates, that is, to prepare $CaTiO_3$ [25].

Preparation of photoactive TiO_2 has been achieved by mechanochemical decomposition of $TiOSO_4 \cdot xH_2O$ using NaCl diluents, reaction between $TiCl_4$ and $(NH_4)_2CO_3$, or displacement reaction between $TiOSO_4 \cdot xH_2O$ and Na_2CO_3 [21].

1.2.8
Other Methods Starting from Solids

Oxides can be prepared by *dehydration* or *dehydroxylation* of hydroxides, whose preparation is usually the critical step. Medium temperatures are used and the process may lead to formation of metastable species; for instance, TiO_2-B can be prepared by calcination of $Ti_4O_7(OH)_2 \cdot nH_2O$ at 500 °C in air.

In *ion exchange*, ions are exchanged between two different environments; so, zeolites, hydrotalcite-like materials, and clays can exchange nonframework ions when suspended in aqueous solutions of other ions; in some cases, the process can also be performed in molten salts at moderate temperatures. Sodium/silver substitution in β-alumina takes place at 300 °C according to the reaction:

$$NaAl_{11}O_{17} + AgNO_3 \rightarrow AgAl_{11}O_{17} + NaNO_3 \tag{1.7}$$

An alternative method to prepare TiO_2-B consists of combining ion exchange and dehydration:

$$\text{ceramic reaction at } 900\,^{\circ}\text{C}: \quad 2KNO_3 + 4TiO_2 \rightarrow K_2Ti_4O_9 \tag{1.8}$$

$$\text{ion exchange at room temperature}: \; K_2Ti_4O_9 + HNO_3(aq) \rightarrow H_2Ti_4O_9 \cdot H_2O \tag{1.9}$$

$$\text{topotactic dehydration at } 500\,^{\circ}\text{C} \quad H_2Ti_4O_9 \cdot H_2O \rightarrow TiO_2\text{-B} + 2H_2O \tag{1.10}$$

Other methods, like *insertion* reactions and *intercalation*, are scarcely used to prepare or to modify oxides.

1.3
Processes Involving Liquids

1.3.1
Flux Method

The reactants are dissolved in an inert material with a low melting point (*flux*) where they mix intimately and react. If a low cooling rate is used, large crystals can be formed and the method can be used to prepare single crystals from a preexisting compound dissolved in the flux. The flux is finally removed by dissolving it in a conventional medium (acid, water, etc.).

The flux is selected depending on the nature of the reactants and the expected products. For essentially ionic oxides, other oxides should be used as fluxes, for example, B_2O_3 (mp 480 °C), Bi_2O_3 (mp 817 °C), PbO (mp 888 °C), or hydroxides such as KOH (mp 406 °C) or NaOH (mp 318 °C). PbO has been used to prepare magnetic garnets ($A_3Fe_5O_{12}$, A = Y, Sm, Er, Gd) [26]; the melting point can be lowered by using eutectics; for instance, the 50:50 PbO/PbF_2 eutectic melts at about 500 °C; the performance for preparation of garnets is even improved if B_2O_3 is added to the $PbO–PbF_2$ mixture [27]. The KOH/NaOH eutectic (41 wt% NaOH, mp 70 °C) has been used to prepare superconductors: NaOH, KOH, and $Ba(OH)_2$ were first heated under wet O_2 for 1 h at 475 °C; stoichiometric amounts of CuO and Eu_2O_3 were added and crystalline $EuBa_2Cu_4O_8$ was formed [28]. $BaMO_4$ (M = Mo, W) have been prepared using alkaline metal nitrates as fluxes at 400–550 °C; nice rhombic-shaped crystals with a size of 50 µm and mostly exposing (111) faces were formed (Figure 1.1) [29]; the crystal size can be controlled through the reaction temperature and the time and nature of the alkaline metal nitrate flux. A low temperature phase of $BiNbO_4$ using a $Bi_2O_3–B_2O_3$ eutectic flux was prepared by Maruyama *et al.* [30] at 800 °C, 100 °C below the temperature required in the conventional ceramic method; the particles were also more crystalline.

1.3.2
Molten Salt Electrolysis

A conducting melt is electrolyzed forming crystals of the desired reduced product on the surface of an electrode. It is an isothermal process that may lead to single crystals whose growth can be electrochemically controlled; the reaction takes place in relatively short periods of time and the equipment needed is not expensive. But it is sometimes difficult to find suitable solvents, to avoid impurification by the container, and not all substances possess favorable electrode potentials. The method can be used to prepare tungsten bronzes (Na_xWO_3), superconducting materials, and so on. It is rather restricted to mixed oxides containing Mo, because of their relatively low melting point.

1.3.3
Sol–Gel

The method consists of preparation of a sol (colloidal suspension of solid particles with size in the 1–1000 nm range, dispersed in a liquid), its gelation, and removal of the entrapped solvent molecules. Dispersion of a hydroxide $M(OH)_n$ is not a suitable method to prepare a sol, as the particles do not disperse sufficiently and precipitation occurs; formation of the hydroxide *in situ* by increasing the pH of a solution of the metal cation is not valid. Usually the sol is formed by

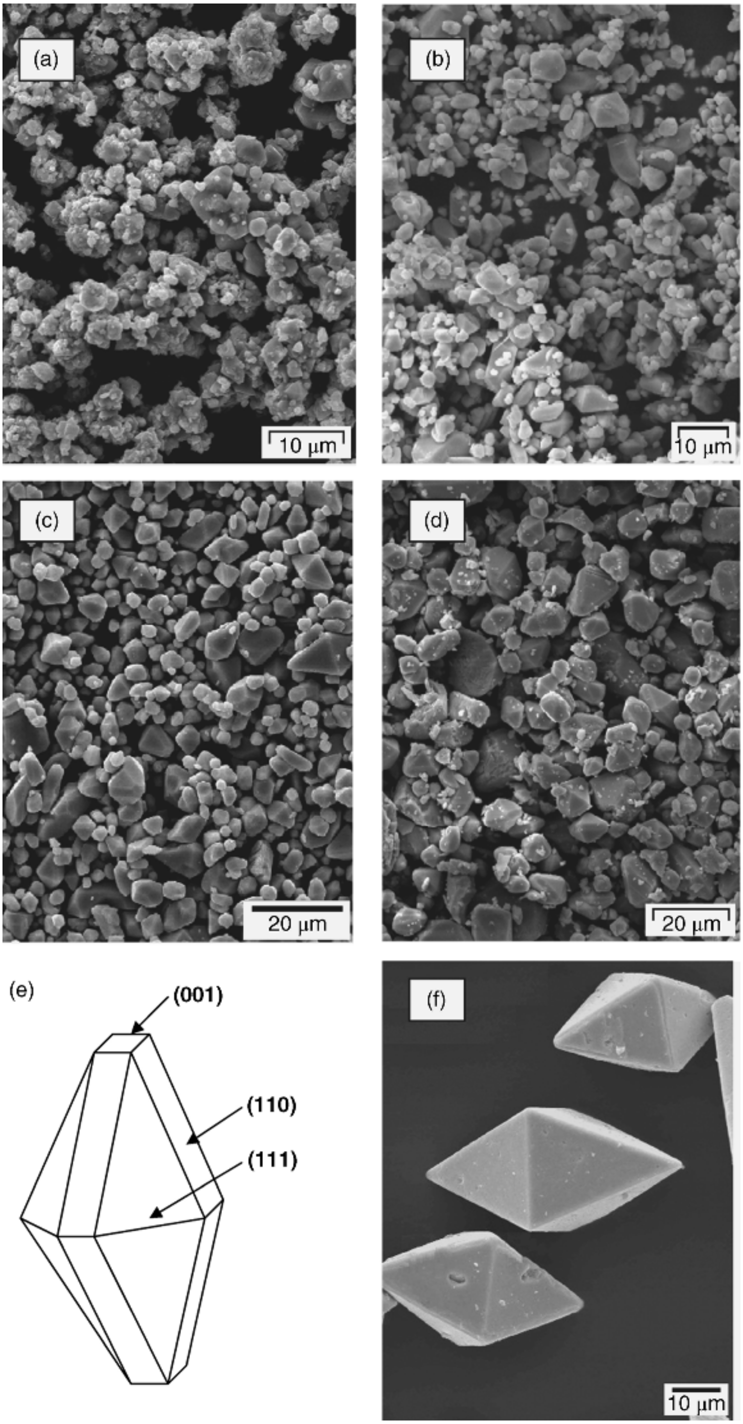

Figure 1.1 SEM images of $BaMoO_4$ crystals obtained in (a) KNO_3 at 673 K; (b) $NaNO_3$ at 673 K; (c) $NaNO_3$ at 773 K; (d) $NaNO_3$ at 823 K; (e) Scheelite crystal shape, showing the planes observed in the molten salt preparation; and (f) SEM image of $BaWO_4$ crystals obtained in $NaNO_3$ at 773 K. Reprinted from Ref. [29] with permission from Elsevier. Copyright 2007.

hydrolysis of an alkoxide or by *homogeneous precipitation*, addition of urea to a M^{n+} aqueous solution, and heating. Decomposition of urea increases the pH simultaneously in all the solution and thus very small particles (a sol) are formed. Aging (usually at room temperature) without agitation leads to formation of the gel phase (a semirigid solid with solvent molecules entrapped in its structure). Finally, drying and calcination steps are needed: (i) to remove the solvent and entrapped anions or to transform them into oxide species (e.g., burning organic anions evolving CO_2 and H_2O), and (ii) to obtain a crystalline phase. The final shape of the solid obtained critically depends on the drying steps: By conventional drying, a xerogel whose pore structure collapses due to surface tension is formed; with supercritical CO_2 drying, the solvent is extracted and the porous structure is preserved. On shortening the gelation step, fibers can be obtained; if the solvent is evaporated from the sol before gelation, a xerogel film can be extended on a support, leading to a dense film on heating [31], a cheaper method than CVD (see below).

The method produces well-mixed amorphous materials, whose crystallinity can be improved by annealing. Diffusion of species is not the determining step, and hence lower temperatures and shorter times are required than with the ceramic method, thus permitting as well preparation of metastable phases. Additionally, small particles in the nanoscale can be prepared. As a disadvantage, the method is experimentally complex and the starting alkoxides can be expensive.

SiO_2 for optical fibers can be prepared by this procedure (Eq. (1.11)) through successive oligomerization and branching steps, and residual hydroxyl groups are removed by annealing at 1000 °C:

$$\begin{aligned} &\mathrm{Si(OMe)_4 + 4H_2O \rightarrow \text{“}Si(OH)_4\text{”} \rightarrow (OH)_3Si\text{-}O\text{-}Si(OH)_3} \\ &\mathrm{(OH)_3Si\text{-}O\text{-}Si(OH)_3 + 6\text{“}Si(OH)_4\text{”} \rightarrow (OH)_3Si\text{-}O\text{-}Si[OSi(OH)_3]_2} \\ &\qquad\qquad \mathrm{\text{-}O\text{-}Si[OSi(OH)_3]_2\text{-}O\text{-}Si(OH)_3 \rightarrow colloid \rightarrow sol{-}gel} \end{aligned} \tag{1.11}$$

Birnessite, $K_xMnO_2{\cdot}nH_2O$, consists of infinite layers of edge-sharing $[MnO_6]$ octahedra where Mn ions are in +4, +3, and +2 oxidation states. Electrical balance is achieved by intercalation of hydrated K^+ cations. It can be prepared by mixing solutions of $KMnO_4$ and glucose at room temperature; stirring for a few seconds leads to formation of a brownish sol. After 30 min without stirring, a gel is formed. Drying at 100 °C and calcination at 400 °C lead to formation of the final compound. During this process, permanganate is reduced by glucose and the excess of filamentous glucose molecules entrap the K and reduced Mn cations, as well as hydroxyl groups, forming the amorphous gel [32].

The variables on which one can act in sol–gel processes are the nature of the metal precursor and the alkoxide groups (e.g., branching degree), the water/alkoxide ratio, the presence of acid or base (which lead to highly branched polymers) catalysts, the precursor concentration, the nature of the solvent, and the temperature. An example of the effect of using different chelating agents and calcination temperatures on the crystal parameters of $LiCoO_2$ is shown in Table 1.1.

Table 1.1 Effect of the chelating agent and the calcination temperature on the lattice parameters of $LiCoO_2$ obtained by sol–gel [33].

Chelating agent	Temperature (°C)	*a* (Å)	*c* (Å)	*c*/*a*
Acrylic acid	800	2.815	14.046	4.989
Citric acid	800	2.806	14.037	5.002
Oxalic acid	800	2.805	14.004	4.992
Triethanolamine	400	2.828	13.862	4.901
Triethanolamine	550	2.820	13.871	4.918
Triethanolamine	800	2.817	14.041	4.984

The *Pechini method* is a modification of the sol–gel procedure. Originally developed to prepare titanates [34], it consists of forming poly-citrate chelates of the metal cations; polyesterification with a polyol occurs at 150 °C, forming a polymeric precursor resin with dispersed cations. Burning at 400 °C removes the organic species and forms a char with a controlled cation stoichiometry; heating at higher temperatures leads to formation of the mixed oxide. The method was used to prepare Mg-doped lanthanum gallate from the metal nitrates, citric acid, and ethylene glycol; the mixed solution was heated (100 °C overnight) until a dark brown resin was formed, which was then hand ground and calcined up to 1400 °C [35]. The method has been modified and optimized by changing the nature of the chelating agent, using EDTA in some cases [36].

1.3.4
Spray Drying (SD) and Related Methods

A powder is formed through fast drying (using air or nitrogen) of a solution or a slurry. The method has been used to prepare catalysts, ceramic materials, or ceramic pigments with a narrow particle size distribution, and also to dry pharmaceuticals and food. The procedure is as follows: A solution of salts of the metal cations is prepared and dispersed with an atomizer or a spray nozzle, controlling the size of the droplets. These are directed against a high-temperature heated surface; the solvent is instantaneously evaporated and the solid residue reacts and decomposes on the hot surface forming spherical or hollow particles. On controlling the concentration of the starting solution and the size of the droplets, the amount of precursor in a droplet and thus the size of the final oxide can be controlled. For instance, magnetite can be easily formed starting from a mixture of Fe^{2+} and Fe^{3+} chlorides. Rivas-Murias *et al.* [37] have reported the preparation of multimetallic (Bi, Ca, and Co; La, alkaline-earths, and Co or Mn) oxides: Stock solutions of the metal cations in acetic acid were prepared and spray dried using a cocurrent (the sprayed solution and hot airflow in the same direction) atomizer at 145–150 °C. The powders were heated at 600 °C for 2 h in air and calcined at higher temperatures.

Scale-up is easy using a drying chamber with countercurrent flows of droplets from the top and hot air from the bottom; contacting both flows dries the droplets and the powder is collected at the bottom [38].

1.3.4.1 **Freeze-Drying**

Freeze-drying (FD), also known as *lyophilization*, is also used to preserve food and fine chemicals. For preparing oxides at a laboratory scale, a solution of the salts of the cations in the required stoichiometry is first prepared. This solution is dropwise added to liquid nitrogen, where it is instantaneously frozen and the cations are disordered as in the dissolved phase. The solid is transferred to a shell freezer at −40 °C, where medium vacuum (residual pressure $\sim 10^{-2}$ mbar) is applied. The solvent sublimates without heating and dry, porous solids with low apparent density are formed; calcination leads to the final solids. High magnetoresistant, micrometric, $La_{1-x}K_xMnO_{3+\delta}$ perovskites have been prepared starting from metal acetates [39,40] and calcining at 600 °C, with further sintering at 1000 °C. Nanostructured $Co_{1-x}Ni_xMoO_4$ catalysts have also been prepared by this method starting from Co and Ni nitrates and ammonium heptamolybdate and calcining at 300–700 °C [41].

1.3.4.2 **Spray–Freeze-Drying**

Spray–freeze-drying (SFD) is a combination of SD and FD to produce spherical porous particles. The starting solution is spray dried with a hot airflow and immediately directed to a cryogenic liquid (N_2, −196 °C) or chilled organic liquids (e.g., *n*-hexane, mp −95 °C) for freezing. The slurry of frozen particles formed is submitted to conventional FD. The shape and size of the granules are controlled by the solution rheology, spray flow rate, and gas pressure in the atomizer. Highly porous, temperature-resistant magnesia ceramics were obtained by spraying aqueous magnesium sulfate into *n*-hexane [42]. A citrate precursor was used [43] to prepare $LaCoO_3$ perovskites by SFD and using a calcination temperature much lower than in other conventional methods, resulting in a larger specific surface (23.7 instead of 5 m^2/g).

1.3.5
Molecular Self-Assembling

Templates or SDAs formed by a single molecule or ion can be used in hydrothermal methods to shape the final products. An assembly of molecules can also act as a template to direct the formation of new materials. The well-known silica MCM-41, with a unidimensional structure of hexagonal pores, is a good example. A surfactant (e.g., NR_4^+ cations) is used as SDA, TEOS or a similar compound as a silicon source, and water as a solvent; a catalyst (acid or basic) is also added. At concentrations above the critical micellar concentration, the surfactant molecules are ordered in micelles (layers, spheres, cylinders, etc.), where the molecules are weakly bonded by van der Waals or hydrogen bonds. Supramicellar interactions lead to a liquid crystal (LC) structure, on whose walls the inorganic species are formed, oligomerized, and finally polymerized [44].

Formation of the LC structure has been discarded by Davis and coworkers [45], who claimed that silicate species form a few layers of silica on the surface of the randomly oriented cylindrical micelles; condensation of the particles thus formed leads to the characteristic hexagonal structure of MCM-41.

1.3.6
Other Methods Starting from Liquid Reactants or Solutions

Preparation of TiO_2 has been taken as an example in all cases [46].

1.3.6.1 Ionic Liquids

Ionic liquids have been used to prepare pure anatase by mixing [BMIM][PF_6] and tetra-*n*-butyl titanate [47]; addition of water and stirring at 80 °C produced nanoparticles of anatase with a size close to 5 nm.

1.3.6.2 The Gel Combustion Method

The gel combustion method consists of the addition of an organic reactant or a polymer to the liquid medium containing the precursor and calcining the gel formed. For instance, $TiO(NO_3)_2$ was mixed in water with oxalyldihydrazide and heated at 350 °C; after dehydration and frothing sparks appear, leading to titania formation:

$$\begin{aligned} \mathrm{TiO(NO_3)_2(aq) + H_2NNHCOCONHNH_2(aq)} &\rightarrow \mathrm{TiO_2(s) + 3N_2(g)} \\ &\quad + \mathrm{2CO_2(g) + 2H_2O(v)} \qquad (1.12) \end{aligned}$$

The high temperatures reached last for a very short period of time, and anatase, with minimum amounts of rutile and brookite, is formed [48].

1.3.6.3 Sonication

Sonication is an easy method to prepare highly dispersed oxides. *Cavitation* develops when ultrasounds are applied to a liquid: The traveling sound wave causes high pressures, compressing the liquid, followed by low pressure and sudden expansion, forming very small bubbles, which expand and collapse. Such expansion/collapsing of the bubbles creates hot spots (up to 5000 °C) with high pressures (1000 atm), and the reaction proceeds.

Sonication for 50 min of titanium tetraisopropoxide mixed with acetone and methanol produced a solid after evaporation of the solvent at 150 °C [49]; calcination at 400 °C led to the formation of anatase (6.4 nm crystallite size), changing to rutile at 900 °C. When the same titanium precursor was dissolved in a water–acetic acid mixture and sonicated for 3 h in air, an amorphous solid was formed, but anatase crystallized even at 75 °C; a detailed study of the effect of different water/acetic ratios or temperatures has been reported [50].

1.3.6.4 Reverse Microemulsion

Reverse microemulsion, a rather soft method, has been used to prepare hollow titania microspheres [51]: $TiCl_4$ was dissolved in HCl-acidified water and added to a solution of TX-100 in cycloheptane; after addition of ammonia and stirring for 1 h at room temperature, addition of acetone led to precipitation of TiO_2 particles.

1.4
Processes Involving Gases or Vapors

There are rather few methods within this category, as only low-boiling-point covalent precursors can be used.

1.4.1
Gas Flame Combustion

The idea is to feed the vaporized metal precursor into a flame in the presence of oxygen; the heat evolved by combustion of the fuel decomposes the precursor, forming the oxide. For instance, nitrogen saturated with $TiCl_4$ at 90 °C is mixed with air and fed into a H_2–O_2 coflow diffusion flame, producing titania particles [52]; by using different O_2 partial pressures (N_2–O_2 mixtures), particles with different properties (anatase content, crystallite size, SSA, etc.) can be prepared [53].

In the *flame spray pyrolysis method* [54], the metal precursor (titanium tetraisopropoxide) was diluted with a mixture of xylene and acetonitrile [54] or N_2 [55] and fed into a reactor, simultaneously with O_2 and methane (fuel), producing titania particles.

1.4.2
Chemical Vapor Deposition (CVD)

The reactants are mixed and react in the vapor phase producing a powder or a microcrystalline solid; single crystals or films can also be prepared. Volatile starting precursors (e.g., expensive organometallic compounds and acetylacetonates) are vaporized, mixed at a given temperature, and react producing the solid. By-products are usually vapors or gases and are easily eliminated. $LiNbO_3$ can be prepared starting from a β-diketonate of Li and $Nb(OCH_3)_5$; the mixture is heated at 200–250 °C in a $Ar+O_2$ stream; the product is deposited on the walls of the reaction vessel upon heating at 450 °C [9]. Heating can be made using a furnace, or be plasma enhanced (PECVD) or laser enhanced (LCVD), depending on the temperature required. The name metal organic chemical vapor deposition (MOCVD) is applied when metalorganic precursors are used.

1.5
Single Crystals

Single crystals are essential in some cases or to study anisotropic properties; fields as semiconductors and optics require large-size, highly pure, defect-free, single crystals. They are generally grown from more easily prepared polycrystalline samples. Some of the growth methods are outlined below.

In the *Czochralski method*, the material is heated in a crucible just above its melting point. A seed crystal is immersed in the melt and it is slowly pulled out (5 mm/min) from the melt vertically while being slowly twisted (2–20 rpm), resulting in continuous growth at the interface. The system is within a chamber with argon to avoid contamination.

In the *Kyropoulos method*, the crystal–liquid interface moves into the melt as crystallization proceeds [3].

In the *Bridgman–Strockbarger method*, the crucible is displaced along a furnace with a temperature gradient: the temperature is higher at the top; when it moves downward, the melt becomes solidified at the bottom of the crucible, which is conic-shaped to decrease the number of nuclei.

In the *floating zone* method, a rod-shaped starting material is oriented vertically and heated by a ring-shaped furnace moving along the rod; the material melts and recrystallizes if a seed crystal is put on one end of the rod. This method can be used to purify the solid, as the solubility of the impurities is usually different in the solid or in the melted state.

In the *flame fusion method (Verneuil)*, the powder falls onto an O_2–H_2 flame and the melt drops on a seed crystal, which is slowly lowered as the crystal grows. The method has been applied to grow high-melting-point oxides (ruby and sapphire). The starting powder is usually placed on a gently hopped mesh to get a continuous flow of solid particles of the same size.

Other methods, already described here to prepare solids, can be used too to obtain single crystals. The *flux method* has been modified by Scheel [56] to produce $GaAlO_3$ from a PbO-PbF_2-B_2O_3 solution by the accelerated crucible rotating technique (ACRT), which allows fast solution flow rates at the growing crystal faces. The *hydrothermal method* is successfully used to grow emerald crystals using powder from the emerald cutting and polishing industry.

Chemical vapor transport (CVT) is used not only to grow single crystals but also to purify them. The idea is rather simple: A gas reacts with a solid forming volatile products and the single crystal is recovered from these by slow crystallization. The method can be used to grow Fe_3O_4 crystallites from magnetite (precipitated in an aqueous medium with $NaOH_{aq}$). The calcined, precipitated, microcrystalline magnetite will probably contain some sodium oxide. If this mixture is put on one end of a closed tube containing a low pressure of HCl and heated, the following reaction will take place:

$$Fe_3O_4(s) + HCl(g) \rightarrow FeCl_3(v) + FeCl_2(v) + H_2O(v) \qquad (1.13)$$

The vapor will diffuse to the other end of the tube, kept at a lower temperature, where the reverse reaction will take place, forming larger magnetite crystals. Even if HCl reacts with solid Na_2O, the highly ionic NaCl will not be vaporized.

Growing of very insoluble solids is rather difficult, as instantaneous precipitation of the product takes place when starting solutions are mixed. In this case, the *gel method* (*not* the sol–gel method) is used: a U-shaped tube is filled with a gel; the dissolved reagents (e.g., Na_2SO_4 and $BaCl_2$ to prepare $BaSO_4$) are slowly poured into each arm of the tube, and slowly diffuse toward one another. On mixing, nuclei are formed and grow to yield larger crystals. The method has been used [57] to prepare $CaWO_4$.

The main advantage of the methods using aqueous solutions is that unusual oxidation states and low-temperature stable or metastable phases can be obtained.

1.6
Nanoparticles

The interest in preparing nanoparticles (size in the 0.1–100 nm range) has increased since it has been realized that they develop quantum and particle size effects, changing drastically their catalytic properties. Other properties change as well when the size of the particles is in the nanorange; for instance, silver (mp = 960 °C) melts at 100 °C when it forms particles of 2 nm [58].

Many of the methods described above can be used to prepare nanoparticles if the experimental details are fixed to specific values. The methods are named as "top-down" methods when bulk materials are first prepared and then are manipulated to the size and morphology required, and "bottom-up" procedures, when a structure is built atom by atom.

Within the *top-down methods*, mechanochemical synthesis can be used to produce nanoparticles embedded in a matrix that avoids agglomeration and is subsequently washed away; the method has been successfully applied to prepare different oxides, such as Al_2O_3, ZrO_2, Cr_2O_3, SnO, ZnO, and so on.

Microemulsions have been used to prepare $SrTiO_3$, $SrZrO_3$, CeO_2, and SnO_2 as well as magnetic particles and YBaCuO superconductors.

Among the *bottom-up methods*, sol–gel, hydrothermal, CVD, ultrasounds, and so on can be mentioned, but also scanning tunneling microscopy can be used: If the tip is sufficiently close to the surface, the interactions increase and the repulsive forces generated can push the molecules across the surface.

Porous solids and membranes can be used as templates to prepare nanoparticles: Porous solids with nanosize cavities are first prepared and impregnated with solutions of the reactants, filling the cavities, where the particles are formed; then the template is destroyed by reaction or dissolution. For instance, a silica xerogel has been used to prepare Fe_2O_3 nanoparticles or nanostructures [59]. Anodization of aluminum film produces nanoporous Al_2O_3, which has been used as a template to prepare CuO, MnO_2, ZnO, or TiO_2. Other substrates able to be used as templates include organic surfactants or biological structures, such as DNA, peptides, pollen grains, and so on; these last ones have been used to prepare replica porous TiO_2 [60].

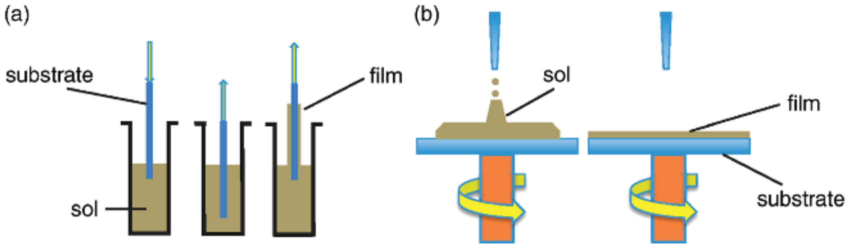

Figure 1.2 Schemes showing the (a) dip and (b) spin-coating techniques.

1.7
Films

Preparation of thin films is an important step for semiconductors and related devices. These films can be prepared following some of the techniques described, such as CVD and its variants (PECVD, LEPVD, MOCVD, etc.). Some methods (e.g., sputtering, evaporation, and molecular beam epitaxy) have been mostly developed to prepare metal films or III–V semiconductors, and will not be discussed here. Other methods are more versatile and can be used to prepare metal oxide films.

Dip coating. A solution or a sol dispersion of the precursor is first prepared. Then the substrate is vertically introduced in the solution or dispersion and slowly pulled out; the covered substrate is then dried and the film formed upon calcination. The method has been used to prepare anatase, brookite, or rutile films [61]. The width of the film depends on the pulling rate, viscosity, and density of the liquid medium, its concentration, the liquid–vapor surface tension, and the temperature.

Spin coating. In this method, a flat substrate rotates at a high speed. The solution of the precursor salt is dropped on the center of the rotating surface and is homogeneously dispersed by centrifugation. Upon drying and calcination, the solid film is formed. Schemes showing these two techniques are included in Figure 1.2.

1.8
Conclusions

This is not a complete description of *all* methods available to prepare solids. They intend to be a series of the most popular and more widely used methods.

But the question remains: Is there an optimum method to prepare a solid? The answer is simple: “No.” There is no such sort of *panacea* to prepare any solid.

Different methods can be followed to prepare a given solid. The questions arise: Which one for my solid? In which form I want the solid to be in? Energy demanding of the process? Contamination effects? Then the availability of reactants, their suitability (volatile or not, MW-sensitive or not, etc.), their price (whose importance will depend on the production scale), the required purity, and the price of the equipment are other factors that are taken into account to select not the optimum method, but the most suitable (or less unsuitable) method to prepare a given solid.

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