



HAL
open science

Back to basics: synthesis of metal oxides

Clement Nicollet, Alfonso Carrillo

► **To cite this version:**

Clement Nicollet, Alfonso Carrillo. Back to basics: synthesis of metal oxides. Journal of Electroceramics, 2023, <10.1007/s10832-023-00340-y>. <hal-04330539>

HAL Id: hal-04330539

<https://hal.science/hal-04330539v1>

Submitted on 8 Dec 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Back to basics: Synthesis of metal oxides

Clement Nicollet¹*, Alfonso J. Carrillo²

¹ Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, F-44000 Nantes, France

² Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas, Avenida Los Naranjos s/n, 46022 Valencia, Spain

* Corresponding author: clement.nicollet@cnrs-immn.fr

Abstract: *Synthesis of metal oxides is typically the first step of any materials science research in a field or application involving oxides materials. However, the synthesis is rarely the prime focus in materials science, which usually describe properties and characterizations of said materials. Consequently, synthesis protocols are often given too little attention in the literature and hence poorly described. For scientists starting in the field, it becomes confusing to make the right choice of synthesis route and conditions to successfully prepare what will be the base of their research, which is a pure, single phase, complex oxide powder. With this tutorial article, we are giving basic knowledge on the underlying chemistry of oxide synthesis, and simple explanations on what motivates the need of various synthesis routes. Then, four main synthesis routes are described, namely the solid state reaction route, the Pechini route, the combustion route, and the precipitation route. For each routes, the approach is described, and the relevant parameters to be considered are developed. Finally, a step by step general protocol for each route is proposed, which can serve as a solid foundation for unexperienced researchers to become more confident when approaching metal oxide synthesis.*

Part of the Back-to-Basics Tutorial Series:

In this **Back-to-Basics** article series, we aim to lower the entrance barrier for researchers carrying out measurements in a given technique for the first time by establishing a series of tutorials, each on a specific experimental technique or method applied to electroceramic materials. Each article will impart a basic understanding and provide practical guidelines for the beginner. Through the **Back-to-Basics** series, we hope to collectively gather the community's experience on experimental research in a way that will ultimately serve the needs of as broad as audience as possible.

1 Introduction

Oxide ceramics are used in countless applications and widely studied in the lab for their unique properties. Oftentimes, the property of the oxide material is the prime focus of the published literature, and the protocol with which the oxide is prepared remains secondary and therefore poorly described. This is particularly true when the synthesis and processing technique used is considered “standard”, because authors do not feel the need to extensively explain how the samples were prepared. However, many properties studied require a training in physics (electronic transport, magnetism, etc.), while syntheses and processing techniques falls more into the expertise of researchers trained in chemistry. The consequence of this plurality of expertise and poor description of experimental protocols is that most often new researchers such as PhD students in materials science, will likely be lost when it comes to choosing the appropriate synthesis and processing protocol to be used to prepare the oxides samples needed for their studies. The following text aims at providing the essential fundamental background to better understand why several synthesis and processing routes exist for a given material, and how to choose the route that best fits one's needs. Then, the most commonly used protocols will be extensively described, emphasizing on the potential pitfalls one should be aware of.

2 Physics of oxide synthesis and ceramic processing

Generally speaking, the preparation of oxide samples for further characterization of their properties can follow a two-step protocol: the synthesis of the material in powder form, and the processing of this powder into the desired shape (dense body, porous layers, *etc.*). Of course, some measurements can be performed directly on powder samples, in which case the characteristics of the synthesized powder will be of importance. This point will be developed later in this paper. From scratch, when considering the synthesis of an oxide powder, one should first search in the literature if the desired compound is already reported. This is to ensure that the desired compound exists! Or that it is at least thermodynamically possible. We will restrict the description of the powder synthesis to the case of people trying to prepare material that has already been reported, and to those who want to make compositional variation of an already reported compound (different dopant or doping level in a perovskite, for example).

2.1 Synthesis of oxide materials

2.1.1 Thermodynamic and structural considerations.

For synthesizing a complex oxide, the first task is to assess whether or not the thermodynamics are favorable, *i.e.* that the Gibbs free energy of reaction is negative. The Gibbs free energy of reaction is the difference of the enthalpy of reaction and the product of temperature and entropy of reaction such as

$$\Delta G_r^0 = \Delta H_r^0 - T \cdot \Delta S_r^0 \quad (1)$$

The Gibbs free energy of reaction can be readily determined experimentally or computationally, but this is out of the scope of this tutorial. Here, the emphasis is put on the conceptualization of the parameters influencing this quantity, so that one can assess with rules of thumbs whether the attempted synthesis is likely to succeed or not. As stated in equation (1), the Gibbs free energy includes a enthalpy term and an entropic term, which are detailed in the following section.

Enthalpy of reaction

The first consideration to take is that the standard enthalpy of formation of ABO_3 $\Delta_f H^0$ should be negative for the phase to form. For a perovskite with the general formula ABO_3 one could write



with A_2O_3 a typical rare earth oxide and BO a typical transition metal oxide. Although the formation enthalpy is easy to find in the literature for well-known perovskites, it is less so for more exotic compositions. Fortunately, for perovskites and related compounds (Ruddlesden-Popper phases, double perovskites) it was shown that the enthalpy of formation scales linearly with a tolerance factor called the Goldschmidt factor¹, which can be readily calculated from the ionic radii of the constituent ions. The Goldschmidt tolerance factor is calculated following equation (3)

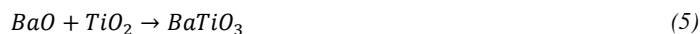
$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_A)} \quad (3)$$

with r_A , r_B , and r_O the ionic radii of the ions A, B, and O, respectively. If the tolerance factor for the targeted composition lies between 0.7 and 1, there is a good chance that the perovskite will be formed during the synthesis. This tool is valuable for beginners, because it only requires ionic radii, available in Shannon tables for example², to get started on planning a new synthesis. It is also easy to adapt to new compositions and doping levels, since the dopant on each site can simply be included to the calculation using a linear mean value of radii and stoichiometric quantities. For a perovskite with general formula $A_xA'_{1-x}B_yB'_{1-y}O_3$, with A' and B' the potential dopants on their respective sites, the extended equation for the tolerance factor becomes

$$t = \frac{(x \cdot r_A + (1-x)r_{A'}) + r_O}{\sqrt{2}((y \cdot r_B + (1-y)r_{B'}) + (x \cdot r_A + (1-x)r_{A'}))} \quad (4)$$

However, negative standard enthalpy of formation or good tolerance factor does not mean that the synthesis of a new composition will be successful. Moreover, tolerance factor will not be helpful for non-perovskite systems like spinels, fluorite-type phases *etc.* However, the approach of using ionic radii can be extended to these non-perovskite structures. For examples, spinels accommodate cations of roughly the same sizes in their sites, which can be used as a rule of thumb to predict whether a dopant is likely to enter the structure. Then, because spinels mainly involve transition metals, bigger cations such as rare earths or alkaline earths are not likely to be soluble in the spinel structure. Another example is fluorite type oxides such as ZrO_2 or CeO_2 , which only have one large cation site. Those phase are the opposite of spinels, in that they will preferentially accommodate bigger cations, and smaller transition metals cations will only have limited solubility in the structure.

Once the enthalpy of formation of the targeted phase is estimated, it is possible to estimate whether the enthalpy of reaction for a synthesis is favorable by subtracting the formation enthalpy of the reactants to that of the products. For most simple compounds, enthalpies of formations are available in thermochemical tables. However, without getting into calculations of reaction enthalpies, and with a bit of chemical knowledge, one can make an educated guess on whether a reaction enthalpy will be favorable or not, depending on the precursors considered. Let us consider the example of the synthesis of barium titanate $BaTiO_3$. For this phase, the most obvious reaction would be to use the oxides of barium and titanium as precursors, such as



However, another potential precursor for barium is $BaCO_3$. In this case, the reaction yields



For reaction (5), it is notorious that barium oxide is poorly stable, which means that its formation enthalpy is likely high. This is actually favorable for our reaction because BaO will more readily react with TiO_2 to form $BaTiO_3$, *i.e.* the enthalpy of reaction will be low. On the contrary, for reaction (6), $BaCO_3$ is known to be a very stable compound, which means that its enthalpy of formation is likely low. That means that the reaction enthalpy for reaction (6) will be less favorable than that of reaction (5). This is to illustrate that the choice of precursor can have a decisive impact on the synthesis. However, favorable enthalpy of reaction is not a sufficient condition for whether a synthesis is possible or not. Additionally, entropic effects have to be considered.

Entropic consideration

Without getting into the details of the thermodynamics of entropy, it is important to conceptualize what are the possible entropic variations that can influence the synthesis of complex oxides. Simply speaking, entropy variations during a chemical reaction boils down to two main effects: changes of the number of phases/constituents, and changes of state (solid, liquid, and gas). Chemical reactions that have a positive ΔS are additionally favored because, due to the entropy term $-T\Delta S$ in equation (1), their ΔG becomes more negative. From there, it is easy to predict whether a synthesis of complex oxide will be favored or inhibited by entropic effects. Taking our first example in equation (2), one can easily see that going from three reactants to one products will reduce the entropy, thus pushing the equilibrium towards the reactants. Additionally, the reaction will consume a gaseous reactant and only form a solid product, which is also a reduction of entropy.

More effects can yield entropy changes during the reaction, for example the entropy of mixing, which will increase if more precursors are mixed together. In some cases, entropy of mixing can be so important that they can compensate a positive enthalpy of reaction, yielding a negative ΔG (favorable reaction).

This is the case for example for high entropy oxides, which are studied in a variety of field of electroceramics.

Coming back to the synthesis of BaTiO₃, entropy considerations can also help choosing precursors for the reaction. Reaction (5) involve two solid reactants and yield one solid product, which means that the entropy will decrease and that the reaction will not be favored by entropy. On the contrary, reaction (6) involve the formation of gaseous CO₂ as product, which will increase the entropy significantly, and in turn favor the formation of BaTiO₃. To summarize this example, reaction 4 will be favored by enthalpy, while reaction (6) will be favored by entropy. As the effect of entropy on the reaction equilibrium is enhanced by temperature, it is then easy to predict that reaction 5 will become more and more favorable as temperature increases, whereas the equilibrium of reaction (5) will be less affected by temperature.

These concepts can be used as rules of thumb to plan a new experiment: by comparing Gibbs energy of reaction for synthesis routes involving different precursors, one can determine which strategy is the most favorable thermodynamically. Even when the Gibbs free energy is not available in the literature, knowing those implications will facilitate decision making for new syntheses, ultimately increasing their chances of success.

Phase competition

In some cases, the formation of the targeted complex oxide will compete with the formation of other oxides containing the same cations. For known systems, there is a chance that Gibbs free energies of formation of a number of phases were already measured in the past, and that their phase diagrams are available in the literature. Those are useful to choose experimental parameters (*e.g.* calcination temperature) for a successful synthesis of complex oxides. As an example, let us look at the lanthanum-nickel-oxygen system. In this system, a series of phases can form, namely the Ruddlesden-Popper series, which corresponds to the general formula La_{n+1}Ni_nO_{3n+1}. Consequently, in the La-Ni-O system, mainly 4 phases of this series can form: La₂NiO₄ (n = 1), La₃Ni₂O₇ (n = 2), La₄Ni₃O₁₀ (n = 3), and the perovskite LaNiO₃ (n = ∞). For this system, Zinkevich *et al.*³ have measured Gibbs free energies for each phase and proposed a phase diagram, shown in Figure 1.

With such phase diagram, it becomes easy to choose parameters of temperature and oxygen pressure to target each phase of the system. For example, for La₂NiO₄, it will be more favorable to choose high temperatures and low oxygen pressure to avoid the formation of higher terms of the Ruddlesden-Popper series. On the contrary, the perovskite LaNiO₃ will be favored at lower temperature and higher oxygen pressure. If the *p*O₂ cannot be controlled (in a typical muffle furnace for example), then a line can be drawn on the phase diagram at ambient *p*O₂ (dashed line in Figure 1), and the temperature can be tuned to obtain the desired phase. Consequently, for this system, it becomes obvious that La₂NiO₄ will not form in air at temperatures below 1200 °C, so any annealing under this temperature will yield a mixture of phases.

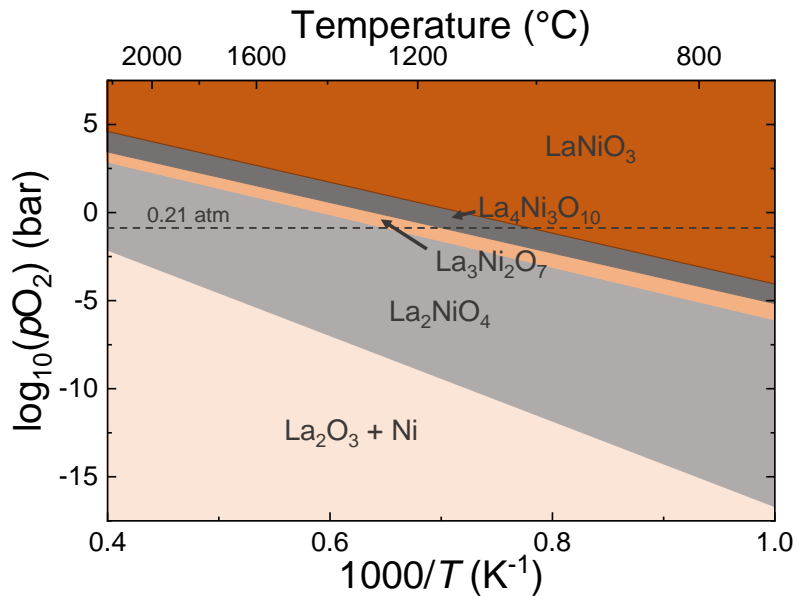


Figure 1: Phase diagram of the La-Ni-O system, created with data from Zinkevich et al.³ The dashed line represents the pO_2 of the ambient atmosphere.

2.1.2 General principle of the synthesis of oxides materials.

Oxide powder synthesis follow the same principle as essentially any chemical reaction. First, the reactants should be mixed together, as intimately as possible. Second, some energy should be brought to the system to activate the reaction and produce the desired product, at a rate defined by the reaction parameters. However, some features specific to solid-state reactants and products complicate this oversimplified picture. Indeed, when trying to react two solids together, the intimate mixing is not straightforward, and careful attention has to be taken to ensure that it is correctly achieved. Additionally, products in the solid form are usually rather hard to separate from impurities, leftover reactants, etc. Then, the reactants must be introduced in stoichiometric quantities, and each step of the synthesis should be managed to avoid introduction of external impurities, because separation/purification steps are not cost-effective, requires high energy inputs and multistep protocols for small gains in purity.

As to the activation part, the energy required to synthesize the desired oxide is usually provided through heating, because oxides are, for the most part, stable at relatively high temperature. This thermal energy serves mainly one purpose: activating mass transport through diffusion, so that elements from the precursors can meet and re-organize into a new crystalline structure: the targeted oxide material. However, for some specific case, heat treatment will also achieve additional task: for example, some route requires the decomposition of a precursor to remove the counter ion of the desired cation. This is the case when the precursor is not directly the oxide, *e.g.* carbonate, acetates, nitrates, hydroxides, *etc.* In that case the synthesis will require a calcination step. In other cases, like precipitation synthesis, heat treatments can also assist nucleation and growth kinetics of nanoparticles, to achieve the desired powder morphology⁴.

Then, when first searching for a synthesis protocol that best fits a new project, anyone would come to the realization that there are just as many synthesis options as human imagination can create. However, one should not give up into finding the right one just yet. Indeed, all the varieties of synthesis routes come down to one single purpose: intimate and homogeneous mixing of constituent element of the desired oxide. Indeed, the better the initial mixing of element, the lower the energy needed for reacting them together and form the targeted oxide. This is simply due to elements having to diffuse a shorter distance to react together. Hence, for most cases, the only consequence of choosing the “wrong” synthesis route is the requirement for increased final annealing temperature/time forming the right phase.

For some cases this is not an issue (refractory materials), for others, it is (temperature sensitive materials). The next section will describe the main synthesis routes and their characteristics, and will briefly introduce which cases they are best suited for.

2.2 Most common routes for oxide synthesis

Before listing and describing all the available routes for preparing oxides, a little bit of history is necessary to understand how the community came about developing them. As mentioned in the previous section, the most straightforward way of doing this is to mix solid precursors and anneal them at high temperature to obtain the desired complex oxides. This “historical” approach is the so-called solid state reaction synthesis, and even though it is simple, it is still widely used in the community.

Then, as chemists realized that the solid state route was not optimum for realizing an intimate mixture of precursors, new protocols appeared. They are mostly involving a dissolution of precursor in a liquid phase, and turning that solution into an oxide powder through various techniques that are described in the following sections. Those new protocols are commonly referred to as “wet chemistry routes”, in contrast with the historical solid state route.

For all of the wet chemistry routes, the trick is to be able to maintain the homogenous distribution of elements achieved in solution to a solid state, without demixing, segregation *etc.* In principle, this guarantees homogeneous distribution of the precursors at the atomic scale, thereby making the reaction much more favorable. Thus, the wet chemistry routes should require, again in principle, much lower energy, as diffusion pathways are much shorter.

In the following sections, most common synthesis routes are described. As their main purpose is to mix elements together, their description will focus on this, while the annealing part, common to all syntheses, will be described in a separate section (2.2.5).

2.2.1 Solid State Synthesis

As mentioned in the previous section, the solid state synthesis is the most straightforward way of preparing complex oxides. In general, one would start by choosing commercially available single oxides of the elements constituting the desired complex oxide. However, this is not possible for every element, because some cations do not form stable oxides in atmospheric conditions. This is the case for example for alkaline and alkaline earth elements, which form very stable carbonates by reaction with the ambient CO₂. Some other elements, like rare earths, form hygroscopic oxides, which will slowly turn to hydroxides by reaction with ambient humidity. In this case, using carbonates and hydroxides as precursors is possible, because the subsequent heat treatment used to form the complex oxide will also serve to decompose carbonates and hydroxides into oxides, as they are usually not stable at high temperature.

Once precursors are selected, they should be mixed together as homogeneously as possible. This is usually achieved by grinding the precursor powders together. This can be done in a simple mortar, in which case the quality of the mixture strongly depends on the experimentalist: mortar mixing is tedious, and homogeneity of the mixture strongly depends on the researchers’ patience! Depending on the lab capabilities, mixing precursors can be more readily achieved in a ball mill. Then, the mixture is annealed at high temperature to activate diffusion between particles and crystallize the new complex oxide phase. As the main mechanism to form a new phase is mass transport through diffusion, the formation of the complex oxide, free of leftover reactants, is closely linked to the length of the diffusion pathways. This means that the morphology of the starting powders and how well they are mixed together will have a decisive impact on whether or not a pure complex oxide can be obtained. Figure 2 illustrates three cases. In the first scenario (Figure 2a), the precursor powders are coarse, which means that the diffusion distance from one phase to the other is long. In that case, the time needed for both reactants to diffuse, meet and form the product is long (extended heat treatment duration required). In the second scenario (Figure 2b), the precursors powders are finer, which is in principle better than coarse powders, but they

are not mixed homogeneously. In that case, the diffusion distance to react precursors is also long and the reaction is not favored. The third case (Figure 2c) is the ideal case where fine precursor powders are thoroughly mixed together so that a homogeneous mixture is obtained. In that case, the diffusion distances between precursors are short and the reaction is favored.

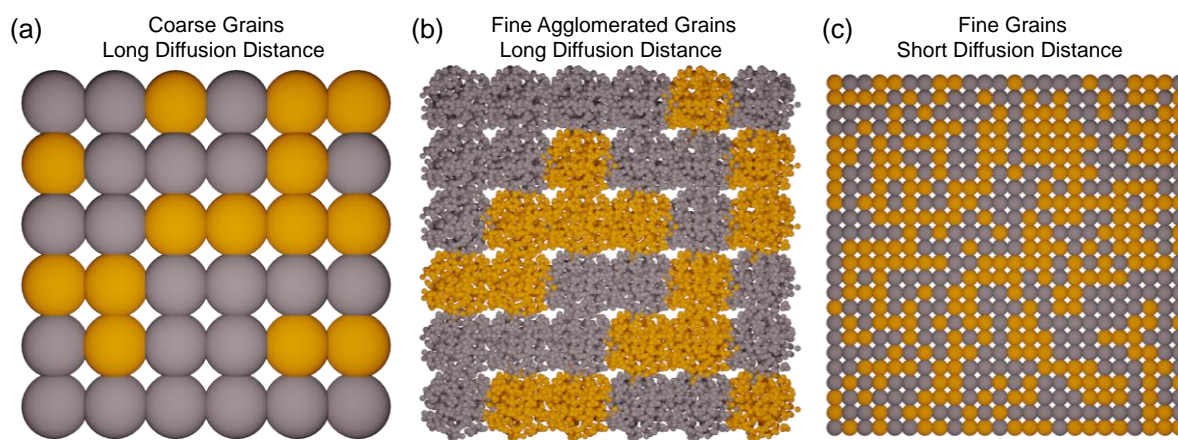


Figure 2: Illustration of three cases for solid state synthesis: a) coarse grains, b) agglomerated fine grains, and c) fine grains. The diffusion distance corresponds to the length that cations need to diffuse for the reaction to take place.

One can also note that one driving force for diffusion, especially surface diffusion, is the reduction of the excess energy of surface atoms (arising from missing bounds). As fine powders have higher specific areas than coarse powders, the driving force for diffusion is higher, which results in faster diffusion. Then, using fine precursor powders has a double benefit for the reaction kinetics: faster diffusion and shorter diffusion distances.

2.2.2 Complexing/Polymerization or “Pechini” synthesis

The so-called Pechini route, named after his inventor Maggio Pechini⁵, is an alternative route to the solid state synthesis that takes advantage of the homogeneity of solution to prepare complex oxides. Also considered to be a ‘sol-gel’ synthesis, the principle is to use a polymerization reaction between an organic acid and an alcohol to “trap” the cations of the solution and maintain their distribution while solidifying the mixture. Indeed, the polymerization forms a solid resin that keeps the homogeneous distribution of cations, thereby facilitating the subsequent formation of the complex oxide (Figure 3).

The cation precursors can be of any type, as long as they are soluble in the considered solvent. The solvent is usually water, and common precursors for cations can be nitrates, acetates, chlorides, *etc.* However, some counter ions such as chlorides can substitute oxygen atoms in the final oxide and become difficult to remove after annealing, which should be considered when choosing the suitable precursors. The acid is usually citric acid, which has three carboxylic functions: two are used in the polymerization reaction, and the third one serves as chelating group to maintain the cation distribution. The alcohol is usually ethylene glycol, which has two hydroxide groups necessary for polymerization. A comprehensive review of the technique was published by Danks *et al.*⁶, from which the illustration of the reaction shown in Figure 3 was reproduced.

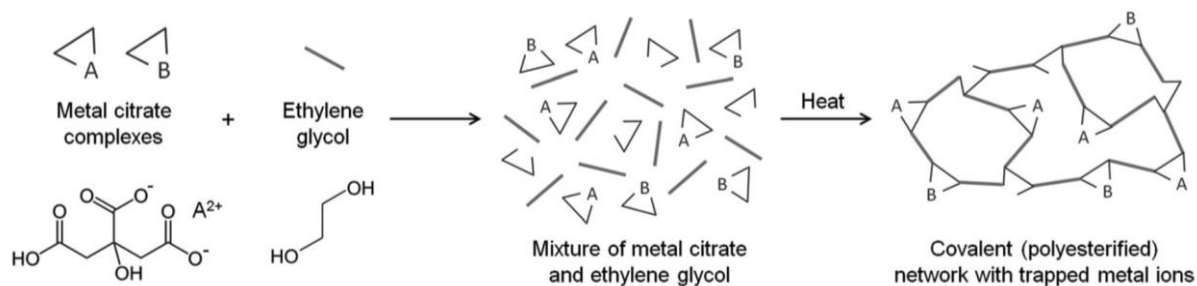


Figure 3: Polyesterification between citric acid and ethylene glycol used in the Pechini route, reproduced from Danks *et al.*⁶ with permission from the Royal Society of Chemistry.

The Pechini route has gained popularity mainly because of its versatility: the protocol can be applied to the synthesis of about any complex oxide, as long as their constitutive elements exist as soluble precursors. The Pechini route also produces nanometric scale powders after calcination of the polymer matrix (10-100 nm) but generally yields an amorphous oxide, which has to be annealed subsequently to crystallise the desired oxide. Because the amorphous powder is nanometric, it tends to agglomerate in micrometric clusters of nanoparticles. These clusters can readily sinter during the annealing step, resulting in a micrometric powder rather than keeping the nanoscale grains. Another drawback of the Pechini method is that its atom efficiency is low, which makes a potential scale up expensive. These are the main drawbacks of this technique, and one has to decide whether or not it is a problem for their application.

2.2.3 Combustion synthesis

If grain size is indeed important, the Pechini route will not be suitable to prepare nanoscale powders of complex oxides. Instead, the combustion synthesis might be a better option. The combustion route can appear very similar to the Pechini route in that it involves similar chemicals (nitrates and citric acid for example) and steps (gel formation and calcination), but is actually a complete family of syntheses very different from the Pechini route! Indeed, the combustion route does not involve a polyesterification reaction, and can be achieved with a wide variety of reagents.

The principle of the combustion route is to trigger a highly exothermic reaction from a solution of precursors, which will bring enough energy to directly crystallize the desired complex oxide. Those reactions are inspired by the propellant chemistry, which aim at releasing high amounts of energy in short times. Typical reactions that can achieve this are redox reactions between a strong oxidizer such as nitrates and a reducing agent such as citric acid, glycine, urea, etc. The latter is often referred to as fuel, while the former is the combustive. In a typical combustion synthesis of metal oxides, the cations precursors are nitrates, so that the counter ions NO_3^- can act as the combustive (or oxidizer). The selection of the fuel will be described in the practical guidelines section (3). Once all precursors and fuel are fully dissolved in water, the solvent (water) is slowly evaporated in order to form a dry mixture. Indeed, the combustion reaction not only is favored with a dry mixture, but also any leftover water will consume part of the heat of reaction to evaporate during the combustion, thereby decreasing the energy available for the crystallization of the complex oxide.

Because the combustion reaction is usually fast, the crystallization of the complex oxide can happen without leaving any time for grain growth and sintering, which makes this route interesting for producing nanoscale powders of complex oxides with high surface area. A comprehensive review about combustion synthesis was published by Varma *et al.*⁷ and gives a more extensive description of the technique.

2.2.4 Precipitation synthesis

Another way of quickly turning a solution of metal precursors into an oxide powder is the precipitation technique. As the name suggests, the idea is to trigger a precipitation of solid particles from a solution of initially soluble precursors. In the vast majority of cases, the strategy is to take advantage of the insolubility of hydroxide of most metals into aqueous solutions. Typically, a metal cation in an aqueous solution is stable in acidic pH , but will form a solid hydroxide precipitate when the pH is increased above a defined value, given by their thermochemical properties. The precipitation pH is easily accessible by looking at so-called Pourbaix diagrams (E - pH diagrams).

Consequently, the strategy of the precipitation synthesis is to dissolve the desired metal precursors into an acidic aqueous solution, and then rapidly change the pH by pouring a strong base into the solution, such as ammonia. This will trigger the precipitation of hydroxides, which should be filtered, washed, and dried. The obtained powder is usually fine (10-100 nm), but require a subsequent annealing treatment to burn the hydroxide groups and form the final oxide.

Just like in the Pechini method, this annealing step is critical because it can trigger a dramatic grain growth, especially if the hydroxide powder is highly agglomerated. Then, the most sensitive step of this technique will be to limit agglomeration of the precipitate, and limit the grain growth during the annealing treatment.

Another factor that one has to keep in mind, is that for preparing complex oxides by precipitation, the precipitation pH values for all constituent cation have to be in a relatively narrow window, to avoid segregation of each cation, thus losing the benefit of the wet chemistry approach. With this consideration, it appears that the precipitation technique is often well suited for phases containing only cations of similar nature. For example, doped ceria, which uses only rare earth cations, is well suited for this technique, because all rare earths will form hydroxides at similar pH . Another example is the $\text{Li}(\text{Ni},\text{Mn},\text{Co})\text{O}_2$ phases used as cathodes of Li-ion batteries, in which the three transition metal cations precipitate in a narrow pH window^{8,9}, while lithium is added in a post processing step.

This manuscript covers only the most straightforward way of exploiting precipitation chemistry to synthesize oxides powder, *i.e.* a pH change. However, one should be aware that a wealth of other precipitation approaches exists, and new ones are constantly developed by researchers around the world. The basis of such research will be mainly focused on complexation chemistries, which can extend the technique to a wider variety of metal precursors, solvents, and cation combinations. More details about the precipitation technique can be found in a review published by Cushing *et al.*¹⁰.

2.2.5 Calcination and annealing treatments

As mentioned earlier, all synthesis routes require thermal treatments, whether it is for calcination of synthesis leftover organics, or for annealing the produced powder and form the desired complex oxide in its pure, crystallized form. Indeed, depending on the chosen synthesis route, the powder obtained from the synthesis can still contain unreacted precursors, form other stable compounds like hydroxides and carbonates, or be amorphous. This section introduces the final step of every oxide synthesis, and what is the general philosophy behind choosing the right heat treatment to obtain a pure oxide powder.

For calcination treatments, the best practice is to run a thermogravimetric analysis of the reaction products to assess the minimum temperature to eliminate all species but the final oxide product. Calcination treatments are usually performed at intermediate temperatures (400 - 800 °C) to avoid premature sintering. For annealing treatment, in theory one could define the ideal heat treatment for a given system to form the pure complex oxide, taking into account the thermodynamics (formation enthalpy, *etc.*) and the kinetics (diffusion of species). In practice, such a calculation would have to take into account too many parameters and is not at all easy to achieve. Instead, the easiest way to define the good annealing treatment for a given synthesis will most readily be found by trial and error. As a starting

point, one can first look at synthesis protocols for similar compositions in the literature, and build an array of heat treatment around this. That being said, the experimentalist needs to be aware of a few key parameters affecting the annealing treatment before starting.

1) **The annealing treatment depends on the chemical composition.** When attempting to prepare a known phase but varying the concentration of various dopants, one would be tempted to reproduce the same heat treatment that was reported for the parent phase. This is not a guaranteed success, because dopants can greatly modify diffusion kinetics of cations, which is the key parameter controlling the energy needed to successfully anneal a powder to a pure, crystallized, single phase oxide. Also, a doped phase could be less thermodynamically favorable, which means that its enthalpy of formation will be higher, thereby requiring a higher temperature annealing.

2) **The annealing treatment depends on the morphology of the powder.** As mentioned earlier, a finer powder means that constituents of the desired complex oxides are intimately mixed together, which facilitates the interdiffusion required to react precursors and crystallize the complex oxide. This means that depending on the morphology of the powder obtained from various routes, the heat treatment required to crystallize the pure single phase oxide will vary.

3) **Annealing at higher temperature does not necessarily work better.** Once stated that crystallizing a pure single phase oxide is a matter of activating diffusion, one could believe that the higher the temperature, the better. Although it is true that diffusion will be faster at higher temperature, annealing at higher temperatures can create new problems that will make this strategy counterproductive. As mentioned in section 2.1.1, some systems will face the issue of phase competition, *i.e.* that several complex oxides with similar composition can form. This means that the desired phase will only be favorable in the defined range of temperature, whereas being out of this range will favor the undesired phase. For example, perovskites ABO_3 often compete with other terms of the Ruddlesden-Popper Series $A_{1+n}B_nO_{3n+1}$ of the same system. In the (La, Ni, O) system discussed in the section 2.1.1, $LaNiO_3$, La_2NiO_4 , and $La_4Ni_3O_{10}$ will preferentially form in different temperature ranges: $LaNiO_3$ and $La_4Ni_3O_{10}$ are more favorable at low temperature, whereas La_2NiO_4 is more favorable at high temperature³. Higher temperatures can also favor evaporation of volatile elements, thereby modifying the stoichiometry of the powder. This is typically true for lithium conductors such as garnets $Li_7La_3Zr_2O_{12}$, or perovskites $Li_{3x}La_{(2/3)-x}TiO_3$, for which Li can readily evaporate and prevent the desired phase to form. For garnet, this Li evaporation ultimately leads to the formation of the pyrochlore $La_2Zr_2O_7$, which is so stable that it becomes impossible to react it with more Li to form the garnet again. For some oxides, it is also important to be aware of the melting point, that can sometimes be in the same range as the targeted annealing temperatures.

4) **The atmosphere of the annealing treatment is important.** Often neglected, the atmosphere in which the annealing is done can have a dramatic influence on whether or not a single phase is obtained. This is mainly due to two factors: the affinity of some element with impurities in the gas phase like CO_2 and H_2O , and the oxidation state of transition metals. The former is a recurrent issue when performing annealing treatments in a furnace opened to room atmosphere, which is the case for most high-temperature furnaces. Some cations like alkaline earths tend to form very stable carbonates when in contact with CO_2 , and these carbonates will not react as readily to form the desired complex oxide than their oxide counterpart. For example, barium zirconate and barium cerates $BaZrO_3$ and $BaCeO_3$ can suffer from barium segregation out of the structure, which is in part activated by the favorable formation of $BaCO_3$ in presence of CO_2 . This segregation makes the phase under-stoichiometric in the A-site cation, and the presence of $BaCO_3$ can inhibit the cation diffusion and make the subsequent sintering harder. This is also a known issue for lithium conducting oxides, for which H_2O and CO_2 in the atmosphere can activate the segregation and evaporation of lithium mentioned earlier.

When complex oxides include a transition metal cation, they are not necessarily at the same oxidation state as that of their stable single oxide. This means that the annealing of the synthesized powder will

also serve to reduce or oxidize the transition metal cation into its final oxidation state, *i.e.* the one that is most stable in the complex oxide. In this case, it is often a good idea to think this beforehand and change the annealing atmosphere to a reducing or oxidizing one, rather than simply perform annealing in ambient air. For example, when trying to synthesize $(\text{La,Sr})\text{CoO}_{3-\delta}$, one would often find that a persistent impurity appears after annealing. This impurity is the Ruddlesden-Popper phase LaSrCoO_4 that has Co at a lower oxidation state than that of the perovskite ($2+/3+$ for the Ruddlesden-Popper phase, and $3+/4+$ for the perovskite). This is because the oxidation state of the stable single oxides for cobalt are mainly $2+$ (CoO) or $2+/3+$ (Co_3O_4). Then, it is easy to understand that the Ruddlesden-Popper phase with the same oxidation state as the cobalt precursor can be more favorable than the perovskite, which requires an additional oxidation of cobalt. In this specific case, performing the annealing treatment in oxidizing atmosphere, *i.e.* pure oxygen, makes the formation of the pure single phase perovskite much easier than simple ambient air heat treatments. On the contrary, when trying to prepare Ruddlesden-Popper phases like $\text{Pr}_2\text{NiO}_{4+\delta}$, Pr has to be reduced into Pr^{3+} for the phase to form¹¹, and Ni has to be mainly $2+$. The stable oxide for praseodymium being Pr_6O_{11} (mixed $3+/4+$ valence state), a treatment in mildly reducing conditions can be favorable and make the pure single phase $\text{Pr}_2\text{NiO}_{4+\delta}$ form at lower temperature¹².

Those examples illustrate that finding the right treatment on the first try will likely be a lucky shot, rather than a smart choice! Instead, one must define a temperature window that could be relevant for their system, considering all points mentioned above, and try an array of heat treatments to increase their chances of obtaining a single phase.

3 Guidelines to oxide synthesis from scratch

This section will provide guidance to anyone who is given the task of preparing an oxide powder with no information other than the chemical formula of the said oxide. It serves to reassure the lost chemist and shows that just a formula, some internet searching and a bit of motivation can go a long way!

We give a general strategy on how to choose the right synthesis route first, and then how to carry on with the synthesis, with simple equipment available in every materials science lab.

3.1 How to choose the appropriate route?

Before starting any laboratory work, one has to decide which route is most appropriate for the targeted materials and application. Table 1 is meant to rapidly visualize which route will fit best with someone's requirement.

Table 1 : Advantages and drawbacks of each synthesis route. Dashes represent the case where the route could be considered but may not be optimum.

	Solid State Synthesis	Pechini Method	Combustion Method	Precipitation
Suitable for larger quantities	✓	✗	✗	✓
High surface area required	✗	✓	✓	—
Porosity required	✗	✓	—	—
Good control over particle size	✗	—	✓	✓
Nitrate precursors unavailable	✓	✗	✗	✗
Cations of same nature	—	—	—	✓
Densification needed	✓	—	—	—
High degree of homogenization	—	✓	✓	✓

3.2 Choosing and weighing precursors

The first step of a synthesis, regardless of the chosen route, is to choose the suitable precursors and weigh the appropriate amount for each constituent cation. Needless to say that the right stoichiometric amount has to be properly calculated. However, even without calculation errors, there is a number of parameters that can lead to improper amount of precursors being added to the reaction mixture, and that will cause a failed synthesis. Here, typical causes of weighing errors are described for two classes of precursors, *i.e.* ceramic powders or salts.

3.2.1 Ceramics (oxides, carbonates, *etc.*)

In solid state synthesis, the precursors are oxides, hydroxides, or carbonates of the constituent metal ions. In principle, one can calculate the weight of precursor needed for the desired amount of metal ion in the targeted oxide. However, for ceramic precursors there are two main sources of errors that can come from weighing precursors: hydration level of the precursor, and non-stoichiometry of oxide precursors.

Hydrated oxides and carbonates

Some metal oxides and carbonates are hygroscopic, which means that they will take up water from the humidity in the atmosphere. Depending on the oxide (or carbonate), the water can simply be adsorbed at the surface, or in some cases react and form hydroxides. Some oxides can also react with CO₂ and form carbonates, especially for basic compounds such as alkaline-earth oxides. In all cases, these interactions with reactive gases present in the atmosphere will cause errors in weighing the stoichiometric amount of precursors, and different strategies need to be considered to limit the errors. In general, it is good practice to perform, if possible, basic characterizations of the precursors, by X-ray diffraction and thermogravimetric analysis, to assess their purity, and potential degree of hydroxides/carbonates/water content present in the precursor powder.

For most transition metals (d block in the periodic table), heavy metals and semi metals, the oxide is stable and weakly hygroscopic, which means that water will simply adsorb at their surface and induce a small error in the weighed mass. To avoid this error, the oxides should be dried in an oven set to a temperature over 100 °C to remove the adsorbed water. Good practice is to put the required amount of precursor in the oven the day before weighing them to let them dry overnight. Alternatively, proper storage of the precursors in inert atmospheres (*e.g.* glove box) or at least in desiccators is recommended.

For rare earth elements (f block in the periodic table), the sesquioxides RE_2O_3 are very hygroscopic, and they will turn into hydroxides $\text{RE}(\text{OH})_3$ over time. For example, La_2O_3 is a typical precursor for lanthanum based oxides, but it reacts and forms hydroxide in a matter of hours. Cerium oxide is an exception because its stable oxide is the Ce^{4+} CeO_2 fluorite type oxide. In this case, a simple oven drying overnight is enough to remove the adsorbed water. The reaction of sesquioxides with water is relatively slow (one day to several days), which means that the oxide can be directly used as precursor if the hydroxide is not formed yet. This means that rare earth oxides have to be annealed at high temperature prior to weighing, to decompose the hydroxides and make sure that only the oxide is present in the precursors. The decomposition temperature depends on the rare earth element, but a treatment at 900°C for several hours will be sufficient in most cases to decompose the hydroxide. Here, it is paramount to quench the oxide to avoid the formation of hydroxides upon cooling. Additionally, the oxide precursor should be weighed right after taking it out of the furnace. A second strategy is to directly use hydroxides as precursors, which has the advantage of avoiding the thermal treatment step. However, forming a complex oxide from a hydroxide will require additional energy during the annealing treatment to decompose the hydroxide.

For alkaline and alkaline earth elements, which are very electropositive, the oxide form is usually poorly stable and will react easily with the atmosphere to form carbonates or hydroxides. Because the reaction of these oxides with CO_2 is much faster than that of RE oxides with water, it is not a good idea to use them as precursors even after thermal decomposition of the carbonate. Instead, these elements should be weighed as carbonate precursors directly. The carbonates should be dried in an oven overnight prior to being weighed, like transition metal oxides.

Non stoichiometric oxides

Regardless of reaction with the atmosphere, some oxide precursors of transition metals and rare earths can be non-stoichiometric, which means that their oxygen content will be ill-defined. This non-stoichiometry can induce significant weighing errors if not properly considered. This is the case for NiO, for Pr_6O_{11} , or for WO_3 for example. In this case, it is good to perform a thermogravimetric analysis on those precursors to determine their stoichiometry, and avoid weighing errors.

3.2.2 Salts (nitrates, chlorides, acetates etc.)

Synthesis routes that involve a dissolution of precursors in a solution will typically involve metal salts, because they readily dissolve in water. Most current metal salts are nitrates, chlorides, or acetates. The main difficulty when using metal salts is that they bond strongly with water to form stable hydrates. This hydration is not necessarily constant, and not knowing how the salt is hydrated can lead to significant errors in weighing stoichiometric amounts of metal ions for the synthesis. In general, the hydration of a salt will happen because the metal cation completes its coordination sphere with water molecules, which results in a crystal field stabilization and the formation of a hydrated metal complex. For example, nickel nitrate anhydride is a Ni^{2+} cation bonded with two NO_3^- ligands, which neutralizes its charge. However, the crystal field stabilization theory tells that Ni^{2+} can lower its energy when in an octahedron coordination sphere, because of the splitting of the d orbitals. Then, Ni nitrate anhydride will naturally fix six water molecules from the ambient humidity to satisfy its octahedron configuration, while the two nitrate ions will be loosely bound to the Ni water complex. Therefore, the most stable form of nickel nitrate is the hexahydrate form. However, upon heating and evaporating water, the two nitrate ligands can replace water molecules to form a tetra hydrate and still maintain the octahedron configuration. Then, one can think that weighing metal salts is as simple as taking into account the hydration molecules in the calculation. This is true in theory, and will work for some metals, but it is not a valid general strategy. First, some metals nitrates can form several stable hydrates, which means that the hydration sphere can vary from one crystal to another, resulting in an ill-defined hydration level. In commercial salts, this is usually mentioned to as $\text{X H}_2\text{O}$ in the general formula. Second, even when only one stable hydrate exists, the salts remain highly hygroscopic, and can fix more water than their coordination

sphere. The visualization of this is easy in some old bottles of metal salts, in which it is common to see partially dissolved crystals and the formation of drops on the bottle!

Unlike with oxides and carbonates, it is usually not a good idea to dehydrate a salt in an oven, because it is in practice complicated to dehydrate the salt to a defined water content. Instead, the best strategy to accurately weight metal salts is to dissolve them into large batches of stock solutions. Indeed, stock solutions can be stored in a fridge and their concentration is far more stable than the water content in nitrate crystals. The exact concentration of the stock solution can be determined by various methods, but the easiest if the metal yield a stoichiometric oxide is to burn a known volume of the solution in a tared crucible, until the formation of the oxide. The weight of the resulting oxide powder is a measure of the metal concentration in the stock solution. Once the concentration of the stock solution is known, the stoichiometric amount of metal ions for the desired oxide composition can be determined with the concentration and the volume of solution to be added to the reaction. For transition metal oxides, complexometric titrations are also possible, and the protocol is adapted for each cation. For other cation, an ICP titration is also suitable, although less accessible depending on the lab capabilities.

3.3 Dissolving precursors (wet routes)

For all wet chemistry route, the weighed precursors have to be dissolved in the reaction solvent prior to the synthesis.

In most cases, the precursors are chosen to be easily dissolved in the considered solvent (most of the time water), and the dissolution is straightforward. However, there are a few pitfalls that one should be aware of so they can be easily avoided. First, the saturation limit of the solution. A given salt has a saturation limit in a solvent, which means that adding more salt than this limit will not yield full dissolution. An important point is that the saturation limit changes depending on the type and number of salts to be added to the solution. For typical perovskite oxides, often requiring three cations salts, the total saturation of the solution will be influenced by the three salts. This can be easily avoided by diluting the precursor solution in more solvent, if the concentration is not critical (which is the case for combustion or Pechini route). A rule of thumb is that saturation issues could appear with concentrations above 1 mol.L^{-1} . Targeting concentrations around 0.1 mol.L^{-1} is a safe bet to avoid saturation problems.

Some precursors, even if they are in principle soluble in the considered solvent, can have slow dissolution kinetics, which will appear to the experimentalist as a non-soluble product. This can be simply overcome by heating the solution (below the boiling point to avoid excessive evaporation) to accelerate the dissolution kinetics.

3.4 Mixing/grinding solid precursors

For solid state synthesis, solid precursors have to be mixed together as homogeneously as possible to favor reaction. There are mainly two options to achieve this homogeneous mixing: manual grinding in a mortar and ball milling. As often, more is not necessarily better, because long and intensive grinding can introduce impurities to the solid mixture.

With manual grinding with a mortar and pestle, homogeneous mixing mainly depends on two factors: time and force applied. Because force may vary significantly from one experimentalist to another, it is good practice to compensate potential inconsistencies in force with longer grinding time. Indeed, with manual grinding, the issue of introducing impurities into the mixture is less problematic than for ball milling, which is usually much more energetic. The grinding time would depend strongly on the quantity of precursor considered, but it should be in the order of tens of minutes, rather than a few minutes of grinding! If the precursors are stable in common solvents like ethanol, adding solvent in the mortar will facilitate mixing and yields more homogeneous reaction media. The drawback of the solvent addition is that a drying step has to be added to the synthesis protocol to remove the solvent prior to annealing treatment.

In case of mixing in a ball mill, the homogeneity of the media will depend on more parameters, and their optimization of precursor mixing can quickly become time consuming. Indeed, one can modify the milling time, the speed, the size and number of balls, the addition of solvent, the solvent/powder/ball volume ratio, the materials of the jars and balls *etc.* Strictly speaking, ball mills are intended for a variety of uses from component mixing, to particle size reduction, or mechanosynthesis of various compounds. They are also used for almost any materials classes from soft polymer to hard ceramics. Because of this versatility of use, choosing starting parameters for milling can be a daunting task. The best practice to make the right choice in starting parameters is simply to ask the ball milling manufacturer, because they have experience with wide variety of uses for their products and are probably aware of suitable parameters for powder mixing similar to the targeted synthesis. It is important to remember that mixing two powder precursors homogeneously does not require very energetic grinding conditions, so it is good practice to keep the speed and duration of milling as small as possible until a desired homogeneity is achieved. For example, a planetary ball milling at 500 rpm for 1 h can be used as a starting point, and can be optimized further later. That is, again, to prevent impurities from the grinding media to be accidentally carried over to the powder. Of the precursor powders are coarse, the ball milling

3.5 After synthesis – powder processing after mixing

For all wet chemistry routes, after precursors mixing the reaction takes place and yields a powder, which will be further annealed to obtain the desired crystalline phase. However, some intermediate steps must be considered to ensure that the annealing step is effective. Because wet chemistry routes use organics, solvents and other chemicals that are not constituent of the final oxide, all those compounds have to be eliminated prior to the annealing treatment. That is why it is often mandatory to include a calcination step at moderate temperature to ensure that the powder before annealing is strictly composed of metal oxides. This will be indeed the most favorable situation for a successful annealing.

The calcination step should be done at the lowest possible temperature, to avoid the activation of particle sintering and grain growth. A rule of thumb is that calcination steps should be limited to the temperature range 400-600 °C, which is sufficient to decompose most organic, and nitrate based compounds. Some cases could be at slightly higher temperature, for example, $\text{Ca}(\text{NO}_3)_2$ fully decomposes at 650 °C so a synthesis involving calcium could require a calcination step at higher temperature.

After the calcination step, it is important to manually grind the powder in a mortar prior to annealing. This step is to break agglomerates, or sub grain microstructures that can be form during the reaction. For combustion synthesis for example, the reaction usually forms highly porous foam-like powders with a wide distribution of pore and agglomerate sizes, while the actual crystallite size is rather small. A manual grinding step eliminates those structures and ensures a more homogeneous, fine powder, which is more suitable for further processing. On the contrary, performing the annealing step directly on agglomerated powders (precipitation) or foam-like powder, will irreversibly sinter those sub grain structure, making them much harder to process afterward.

One last step to consider before the annealing treatment is whether the powder should be pressed into pellets or not. For solid state synthesis, this step is mandatory, because the distribution of reactant is only at the scale of grains. This means that reaction has to take place between different grains, so pressing the powder into a pellet will reduce the distance between grains, thereby favoring the reaction. For wet chemistry route, pressing the powder into a pellet is not always necessary, because the reactants are distributed homogeneously at the atomic scale. Moreover, pressing the powder into a pellet will favor sintering, so if the application requires a fine powder with high specific surface area, it might be wise to avoid pressing the powder into a pellet.

3.6 Route specific pitfalls and tips

Having covered most general considerations for oxide synthesis in the previous section, we will now give practical tips for each routes, and the common pitfalls that are good to be aware of in order to successfully synthesize an oxide powder.

3.6.1 Solid state reaction

Required hardware: scale, mortar and pestle, crucibles, high temperature furnace

Optional hardware: Planetary ball mill

The solid state synthesis is the most straightforward synthesis to achieve for a beginner chemist, in that only a few steps are required. This makes it relatively foolproof, and is often appreciated by beginners for this very reason. The protocol is illustrated in Figure 4. There are two potential pitfalls that one should be aware of. First, because the mixing/grinding steps in a mortar or a planetary ball mill are long for this route, the synthesis is very sensitive to potential cross contamination from the grinding media. For mortar and pestle, if they are used for other syntheses, it is advised to thoroughly clean them before use. Oftentimes, simple water or alcohol sweep is not enough to remove all contaminants. In this case, using dilute nitric acid is effective for removing potential residue from previous syntheses. Leaving the dilute acid in the mortar for a minute and washing it off with distilled water is usually enough to remove most contaminants from the mortar. However, some contaminants (TiO_2 , ZrO_2 , etc.) are not soluble in common acids, in which case a mechanical cleaning will be more appropriate. Mechanical cleaning is usually done by simply grinding sea sand and a solvent in the mortar to scrub the impurities before washing.

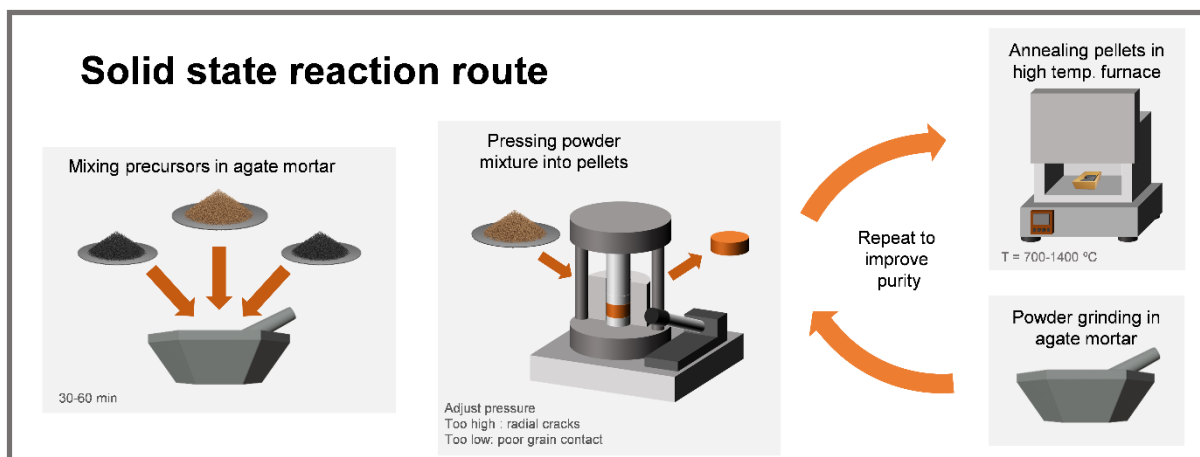


Figure 4: Illustration of the steps involved in the solid state reaction route.

Second, solid state synthesis can yield, after annealing, powders with significant amount of unreacted precursors, especially if the mixing step was not done thoroughly enough. In this case, the experimentalist would be tempted to put the powder in the furnace again and anneal it a second time to “finish” the reaction. Or even anneal the powder at higher temperature, for the same reason. This generally not a good idea, because it will not make much difference. Indeed, the powder after a long treatment at high temperature usually reaches a state where diffusion kinetics become sluggish, which means that unreacted precursors will not react further. The best way to increase the chances of “finishing” the reaction is to add an additional grinding step before the second annealing treatment. The grinding step acts to “break” the equilibrium state, redistribute the unreacted precursor, and potentially reduce the grain size of the powder. Since the additional surface area is a driving force for diffusion, the grinding step will favor cation motion during annealing and increase the chances of reaction the leftover precursors. Then, for solid state synthesis, grinding and annealing steps always go hand in hand. They can both be repeated several times to completely react all the precursors and yield the desired complex oxide as a pure single phase compound.

3.6.2 Pechini method

Required hardware: large volume beakers (400mL), magnetic stirrer, hotplate, crucibles, high temperature furnaces, mortar and pestle

Optional hardware: If a hot plate reaching temperatures between 200 - 400 °C is not available, the gelification and/or gel drying process can be carried overnight in an oven at 200 - 220 °C.

The protocol for the Pechini route is illustrated in Figure 5. Conventionally, although this may vary, citric acid together with stoichiometric amounts of nitrate precursors are dissolved in deionized water at room temperature in a defined citric acid to metal molar ratio. This ratio can be adjusted according to desired textural properties. Afterward, the aqueous solution is heated up to 60-80 °C under constant stirring, followed by addition of ethylene glycol in a fixed (*e.g.* 2 to 3) weight ratio. Continuing the stirring and keeping the temperature at 80 °C, water is evaporated until a gel is formed. The gel is then dried on a heating plate at 200 °C for 2 h followed by calcination for 1 h at 400 °C. The calcined gel is then ground to fine powders in an agate mortar. Finally, the powders are transferred to an alumina crucible, and then heat-treated inside a high-temperature furnace at the required temperature to obtain a pure phase.



Figure 5: Illustration of the steps involved in the Pechini route

As previously described in section 2.2.2, this route encompasses a series of modifications of the original synthesis protocol patented by Maggio Pechini. As such, over the last decades, researchers have adjusted this method to favor the homogeneity of the oxides produced, or to induce alterations on the solid textural properties, such as porosity or increased specific surface area. Most of these modifications have consisted of replacing citric acid and ethylene glycol by other carboxylic acids or polyols. For instance, for the synthesis of some oxides EDTA (ethylenediaminetetraacetic acid) was used instead of citric acid to favor phase purity of the multication system. This has been ascribed to a delayed decomposition of the EDTA mixture with ethylene glycol if compared to citric acid⁶. This in turn could favor the homogeneity of the final product due to a longer time of intermixing. In line with this, it is important to take into account that the resin formed during the gelification process must be entirely burned in order to completely remove any organic residues present in the solid. Generally, the high annealing temperatures used in the synthesis of perovskite oxides will already help in this process. However, when synthesizing other oxides, *e.g.* binary oxides such as Mn_2O_3 or Co_3O_4 , lower temperatures are required to obtain the desired phase, which might indeed suppose the presence of some organic leftovers. These organic residues can be detrimental for several reasons. For instance, they alter the sample mass, since not all the solid will be oxide. This is quite important for the preparation of composites, in which two oxides are mixed using a mass ratio, or heterogeneous catalysis where the sample mass is required to normalized the production results. Importantly, if the solid with remaining organics is treated in inert atmospheres afterwards can lead to organic pyrolysis, which might alter the oxide surface, morphology or the expected process results. Thus, it is suggested to perform a thermogravimetric analysis in air of the resin in order to assess the decomposition temperature of all the organic matter present in the solid, thereby assuring that the oxide is free of organic residues.

Continuing with the possible modifications, several studies have demonstrated the possibilities of tuning the morphology and textural properties by adapting the molar ratios of citric acid (CA), ethylene glycol (EG) and the total metal ions (TMI)¹³. With a fine tuning of the CA:EG:TMI ratios different shapes such as spheres can be obtained. Some authors have also incorporated PMMA (polymethylmethacrylate) microspheres during the process as a template for the formation of nanoporous structures. Besides, control of the aqueous solution pH is paramount for the synthesis of some oxides in which the cation precursors can precipitate during the sol-gel process at high pH's. This is obviously something to avoid, since these cations will not then be embedded in the polymeric matrix. In practical terms it is important to choose adequately the volume of the beaker that is going to be used during the synthesis, since during the initial steps of drying process the gel formed normally grows into a porous solid that can overflow the beaker. Alternatively, putting the beaker into a larger glass container could help to collect any powder that left the beaker during such process. And of course, do not forget to remove the magnetic stirrer from the beaker before this initial heating process! For high purity synthesis, a quartz beaker can be used to limit contaminants from usual borosilicates beakers being released at high temperature into the powder. The Teflon stir bar can also release fluorine in the sample, so using a simple quartz rod to manually stir the solution can be a better option if high purity is targeted. Finally, it is important to keep the adequate safety protocols during the synthesis and carry out this route in a fume hood, since toxic gases *e.g.* NO_x, are released during the process.

3.6.3 Combustion

Required hardware: large volume beakers (400mL), magnetic stirrer, hotplate, crucibles, high temperature furnaces

Optional hardware: A combustion vessel with a top filter to retain the powders while evacuating fumes. A calcination furnace for more homogeneous heating during combustion

For combustion synthesis, the first thing to determine is what fuel will be used, and in what ratio as compared to the oxidizer, *i.e.* the NO₃⁻ ions of the metal nitrate precursors¹⁴. There is a wide range of fuel that can be used, the most common being glycine, citric acid, and urea. Although choosing the adequate fuel is critical, there is no clear rule on how to do so. Degalleno and Tyagi have described some useful point for choosing fuel in various cases¹⁵. In general, the experimentalist should find protocols for synthesis of similar oxides in the literature and choose the same fuel as what was already reported.

It can also be a good idea to try a few, and select the one that yield the best phase purity. Then, the fuel to oxidizer ratio will be the next critical parameter to consider. Again, there are many parameters that the fuel/oxidizer ratio will affect, and it is not possible to give general guidelines for it. However, one can plan at least three experiments to clarify the effect of fuel/oxidizer ratio on their system: a fuel lean ratio, a fuel rich ratio, and the stoichiometric point, and compare which one gives the best results in terms of morphology and phase purity.

The protocol is illustrated in Figure 6. In a typical combustion synthesis, the metal nitrates are first weighed and dissolved in water. Metal or oxides that dissolve in HNO₃ are also a good choice here, since it will yield the same solution. The water content does not matter, since it will be evaporated before the ignition of the reaction. Some precursors can take some time to dissolve, in which case it is possible to heat (80 °C) and stir the solution. After the cations nitrates are fully dissolved, the fuel can be added to the solution. When all reactants are dissolved, the solution can be heated above the boiling point of water (100 °C) to evaporate as much water as possible. This drying step is critical, since any water leftover will consume some of the heat of the reaction to evaporate during the combustion, which will decrease the flame temperature. If the water content at ignition is not consistent from one batch to another, then the purity and morphology will not be reproducibly vary. A good practice is to heat the solution at 110 °C overnight, which leave enough time to completely dry the reaction media. It is sometimes tempting

to increase the temperature to accelerate the drying process. This is not advised, because higher temperatures can partially decompose some of the fuel and nitrate ions during the drying step, which will change the fuel to oxidizer ratio for the subsequent combustion step.

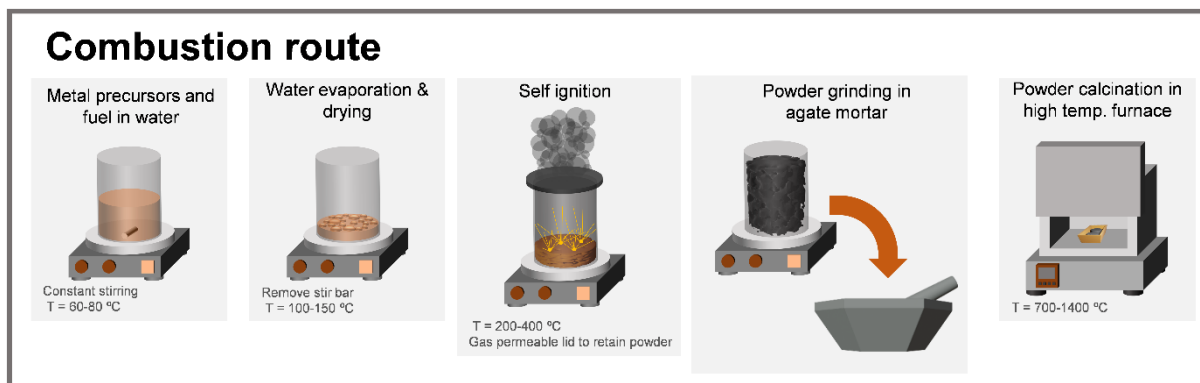


Figure 6: Illustration of the steps involved in the combustion route.

After drying, the ignition has to be triggered to finish the reaction. This step is the most dangerous, because it can be vigorous. It is mandatory to perform the ignition step in a safe environment, usually under a fume hood. The fume hood is also important since the reaction often release toxic gases like CO and NO_x. The ignition step is usually done on a hot plate set to the max temperature (300-400 °C). Using some gas permeable cover on top of the reaction media is advised, because in some cases the reaction is vigorous enough to blow the produced powder along with the released gases. A stainless steel mesh filter is a good way to achieve this, but the mesh can strongly oxidize with acid fumes after repeated use. Then, it is necessary to control the quality of the mesh beforehand to avoid oxide scales crumbling into the powder. If possible, using quartz beakers instead of borosilicates is even more relevant here than for Pechini Synthesis, since the combustion can reach temperature above 1000 °C, which can readily activate the diffusion of cations from the glass beaker into the powder.

Because the reaction can be explosive in some cases, the experimentalist should always start the synthesis of a new composition in small batches: *max.* 2 grams, which limit the risks of uncontrolled reaction.

After the combustion, the powder can be collected. Here it is advised to wear a mask suited for manipulating nanopowders, because the synthesis produces fine ashes that easily fly around. The powder is collected and crushed in a mortar, mostly to break foam-like structures that increases the volume of the powders. From this step, there are two cases: the experimentalist can take X-ray diffraction measurement to control whether a single phase was obtained straight from the combustion. The second case is to directly perform a calcination treatment on the powder to eliminate potential unburnt species like hydrocarbons, nitrates *etc.* The calcination should be done at the lowest temperature needed to burn the precursors i.e. usually between 400 and 600 °C depending on the cations. Avoiding high temperature calcination limit premature grain coarsening of the powder, which is critical in two cases: if the surface area of the powder is important for the application, and if the powder will be sintered into dense ceramics (for which small particles sinter better than coarse particles).

3.6.4 Precipitation

Required hardware: large volume beakers (400mL), magnetic stirrer, hotplate, crucibles, oven, high temperature furnaces, burette, Buchner flask and funnel, filters.

Optional hardware: pH meter to control pH, syringe pump as alternative to burette

The protocol is illustrated in Figure 7. First, solutions of metal precursors are prepared dissolving the metal nitrates, chlorides or other compounds in deionized water. After stirring the solution during 30min, the precipitates are formed when a certain volume (e.g. 50 ml) of precipitation agent solution (e.g. ammonia, 2.5 M) is slowly added dropwise to the precursor solution with continuous stirring. When the addition of the ammonia is finished, the solution is then aged at room temperature during a certain period of time that can vary given the final properties desired (it can last from 1 h to overnight). Afterwards, the obtained solids are filtered and washed with distilled water several times and finally dried at around 100 °C overnight. The dried material is then ground to fine powders using an agate mortar and calcined at a given temperature (and heating rate) to obtain a mixed oxide pure phase

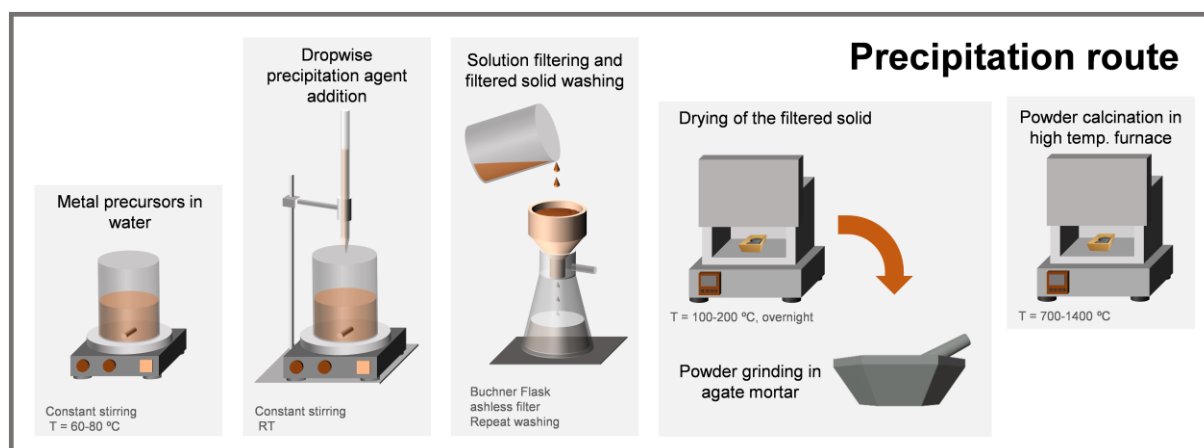


Figure 7: Illustration of the steps involved in the precipitation route

In precipitation, and especially, co-precipitation there is a long list of possible pitfalls that one should be aware of before performing the synthesis. Opposite to Pechini method, in which almost all the fabrication route occurs in one pot, precipitation routes encompass a series of steps (precipitation, filtering, drying...) in which several laboratory equipment is used. Here it is key to guarantee that each step is performed efficiently, avoiding, for instance, that precipitates are not adequately filtered, since it will imply that part of the synthesized material will be lost in the washing solution. Thus, one important aspect is the right choice of filter, which depends on the particle size of the precipitates. This value in turn can be modulated by carefully selecting the molar concentrations of the precursors and/or precipitation agent solutions. As an example, Carrillo et al.¹⁶ showed that Mn_2O_3 particle size could be varied from 65 to 266 nm by increasing the manganese nitrate solution from 0.025 to 1 M. Therefore, even if the precipitates will be agglomerated, filter mesh specification should be taken into account especially when synthesizing oxide nanoparticles. Filtering is indeed one of the most critical steps in this route. Besides trying to guarantee the highest filtering efficiency possible, it is the step in which the precipitates are washed to remove surface species formed during the precipitation process. The nature and amount of the species obviously depends on the choice of precipitation agent or metal precursor solution (e.g. sodium carbonate, ammonium hydroxide, and metal nitrates or chlorides) and its molar concentration, which as aforementioned can have profound implications in the particle size of the solids obtained. Thus, it is important to assure that the solid precipitate is washed several times until the removal of possible surface contaminants is guaranteed. Filtering is a crucial process since, if not carried properly, can result in lower amounts of precipitates extracted and possible surface contaminations that can affect negatively the electrocatalytic activity of the solids, changing the acidity/basicity of the oxide¹⁷. Alternatively, centrifugation can also be considered for small quantities, which can accelerate the separation process.

Besides filtering, careful control of the precipitation is key for assuring high process homogeneity, in terms of nanoparticle size distribution, or in the case of co-precipitation more homogenous solid solutions. Here, it is recommended to control the addition of the precipitation agent solution into the

metal precursor aqueous one (or viceversa) dropwise under constant stirring. This process is normally carried out with a burette or syringe pump assuring control over the rate of solution addition. During this step it is important to control the pH of the precursor solution especially during co-precipitation of multielemental oxides in which the precipitation pH 's of the targeted cations differ. If this step is not carefully controlled, it can result in multiphasic oxide precipitation in which cations are not replaced in the oxide lattice and resulting in severe phase segregation. Additionally, by proper adjustment of the solution pH it will be guaranteed that all the precursor cations precipitate. Some literature protocols recommend that the solution is aged under constant stirring after the precipitation process during several hours or overnight to further assure the homogenization. Regarding homogenization, it is important to grind the dried precipitates before the calcination process, as commented in section 3.5. Hydrothermal treatment of the precipitate can also be a good option to accelerate the aging process or even form the desired phase.

3.6.5 Annealing treatments

Annealing treatment of oxides are usually done in a laboratory furnace that can reach temperatures as high as 1600-1700 °C. There are mainly two types of furnaces available to the experimentalist: box (or muffle) furnaces, and tube furnaces. The tube furnaces have the advantage of allowing gas flows or vacuum to control the atmosphere. Box furnaces, on the other hand, generally have a bigger heated volume, which is suitable for heating larger batches of powder. There are four main concerns to be aware of when performing heat treatments in a high temperature furnace: potential pollutions, furnace calibration, heating and cooling ramps, and atmosphere control.

At elevated temperature, cross diffusion between the powder sample and the crucible is readily activated, and should be managed. The most common crucibles material is alumina, because it is cheap and relatively inert with a lot of materials. However, it should be kept in mind that alumina crucibles are not the only option for annealing a powders. If the targeted oxide is known to react with aluminum, which is the case for example with lithium garnets, other crucible materials can be used like MgO or ZrO₂. However, those crucibles are markedly more expensive. If cost is an issue, one can also prepare MgO or ZrO₂ lids by pressing powders of those materials and sintering them. Then, the lid can be placed between the sample and the alumina crucible to stop interdiffusion. In some case, platinum crucibles can also be used because Pt is also inert to a lot of compounds. It should be kept in mind that the higher the temperature, the worse interdiffusion gets, so one should be particularly mindful of those issues at temperatures of 1300 °C and above.

When working with tube furnaces in a lab with many users, it is not easy to know exactly if previous treatments have left pollutions on the inner walls of the tube. Indeed, some compounds are volatile at high temperature and redeposit on the cold part of the furnace, making it a potential source of cross contamination from one user to another. An example of this is chromium based oxides, that can release Cr+VI volatile species that will contaminate subsequent samples. To avoid cross contamination between users, the best practice is to use a second alumina tube (of smaller diameter) inside the tube furnace, which will be used only for treatments on the same materials. Then, the inner tube can easily be swapped with another when the sample changes, and the users can track exactly the history of their dedicated tubes, to suppress risks of contamination. When working with box furnaces, the refractories used for the chamber can be crumbly, which adds the risk of refractory particles dropping in the powders sample and contaminating them. A simple way to avoid this is to cover the crucible containing the powder sample with an alumina lid.

When using a furnace for a heat treatment, the user should be aware of whether or not the furnace has been calibrated, and when was the last calibration done. Indeed, the temperature on the sample is not necessarily the same as the temperature measured by the furnace thermocouple (which is located outside of the refractory tube). For tube furnace, especially when using additional inner tubes, the temperature difference between the furnace thermocouple and the sample can be as high as 50 °C, which is enough

to completely change the powder crystallization. Then, the user should plan on performing temperature calibration regularly (every 6 months for example) and more particularly systematically after a modification was made to the furnace (replacement of parts, displacement of the inner tube, displacement of the furnace itself, *etc.*). For tube furnaces, the calibration can be done using a second thermocouple placed where the sample sits, in the hot zone. The temperature is measured for a range of setpoints covering the typical utilization range of the furnace, and the data can be used as reference for future treatments. For box furnaces, the control thermocouple is located directly inside the chamber where the sample sits, so in principle those furnaces are less sensitive to ill-defined temperatures, and a calibration is less critical. However, if the thermocouple is old some drift in measured temperature can appear. In practice, it is difficult to introduce another thermocouple in the chamber, since it would block the furnace door from being closed shut. Instead, one can use a process temperature control ring (PTCR) (available commercially). Those rings are ceramics of calibrated diameter, for which the shrinkage as a function of the process temperature is available.

Although the temperature and duration of the heat treatment are the most relevant parameters for controlling the formation of an oxide phase, heating and cooling rates can also have an impact on the final product. For heating rates, it is generally a good idea to reach the targeted temperature fast, since dwelling too long at intermediate temperatures could favor the formation of alternative phases, as illustrated in Figure 1. For cooling rates, it is case specific and should be adapted depending on the material. The rule of thumb is that fast cooling rates can induce thermal stress to the materials, while slow cooling rates can re-stabilize intermediates compounds. For non-stoichiometric oxides, it should be kept in mind that the oxygen concentration of the oxide depends on the pO_2 and temperature. Then, cooling rates will have an impact on the stoichiometry at room temperature, after the annealing treatment. This is a reversible process, but the experimentalist should be mindful of it, since the non-stoichiometry affects a wide range of properties of the oxide.

The last parameter that should be controlled is the atmosphere. Although some phases will readily form with treatments in ambient air, it is always a good idea to question whether a controlled atmosphere can help the phase formation. For that, a tube furnace can be equipped with flanges and fittings to connect it to various gas cylinders. For oxides, the most important parameter to control is the oxygen partial pressure. Experimentalists should be mindful of oxygen partial pressure in their furnaces, and below are a few tips to avoid making mistakes when using controlled atmospheres. First, a supposedly inert gas like argon is not free of oxygen, a typical argon cylinder will have a pO_2 in the range of 10^{-4} - 10^{-6} atm. Second, the final pO_2 in the furnace strongly depends on the gas tightness of the whole setup. Small leaks result in oxygen entering the system, and can modify the pO_2 by several orders of magnitude. If possible, the best practice is to use an oxygen sensor at the outlet of the furnace to measure the actual pO_2 during the treatment. Third, it is often necessary to flush the furnace with the desired gas for some time before starting the heater, since the new atmosphere must remove all the ambient air from the chamber to make sure that the pO_2 is the intended one. The time needed to flush the chamber will depend on its size and on the gas flow rates, so the best practice is again to monitor the pO_2 with a sensor. To reach very low pO_2 (10^{-10} and below), there are two gas mixture options: CO-CO₂, and H₂-H₂O. choosing either of those will depend on the sample sensitivity to those gases. Also, handling CO lines requires caution because of its toxicity.

4 Conclusion

The synthesis of complex oxide powders is often the very first step to any research in materials science. The wide variety of synthesis routes, parameters and experimental details that one needs to be aware of before starting experimental work can be daunting. In this tutorial article, we have introduced the basics of oxide synthesis, and detailed the key parameters to be aware of in order to plan a synthesis from scratch. Then, four main synthesis routes were described, namely the solid state reaction, the combustion, the Pechini, and the precipitation route. As any synthesis protocol has their pros and cons,

a guiding table is proposed to help the experimentalist on how to choose the route that will best suit their needs. An effort was made to introduce each steps of every routes with simple explanation of the underlying physics, so that the reader can make more sense of why the protocols are constructed in such way. The last part of this tutorial aimed at listing current pitfalls that can easily be avoided once the experimentalist is aware of them.

This article does not encompass all of the possible synthesis routes available from the literature, as many variations of each routes, and additional routes can also be found in the literature. Instead, our intention is that it will give a sound background to inexperienced scientists to be able to start their research, especially when the synthesis part is not the core topic of their research. However, such base knowledge can be a strong foundation on which scientists can develop more exotic protocols if they feel the need.

5 Further reading

5.1 Book on ceramic synthesis

Below are a few general books on metal oxides that include chapters on synthesis:

- Kinetics of processes in the solid state - House¹⁸
- Comprehensive inorganic chemistry II: from elements to applications - M. Hayward Pages ¹⁹
- Complex Oxides: Materials Physics, Synthesis, Characterization and Applications - Jan Seidel²⁰
- Metal Oxide Chemistry and Synthesis: From Solution to Solid State - Jean-Pierre Jolivet²¹
- Chapter 4 of Solid State Chemistry and its Applications, 2nd Edition - Anthony R. West²²
- Transition Metal Oxides: Structure, Properties, and Synthesis of Ceramic Oxides, 2nd Edition - C. N. R. Rao, B. Raveau²³

5.2 Reviews on specific routes

- General review on solution based synthesis routes¹⁰
- A review on synthesis of hydroxides by precipitation that have valuable information on precipitation synthesis in general²⁴
- A comprehensive review on sol gel synthesis, that include Pechini ⁶
- A detailed review on Combustion synthesis⁷

6 Declarations

The authors declare no competing interests

7 References

1. Laberty, C., Navrotsky, A., Rao, C. N. R. & Alphonse, P. Energetics of Rare Earth Manganese Perovskites $A_{1-x}A'_xMnO_3$ (A=La, Nd, Y and A'=Sr, La) Systems. *Journal of Solid State Chemistry* **145**, 77–87 (1999).
2. Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst A* **32**, 751–767 (1976).
3. Zinkevich, M., Solak, N., Nitsche, H., Ahrens, M. & Aldinger, F. Stability and thermodynamic functions of lanthanum nickelates. *Journal of Alloys and Compounds* **438**, 92–99 (2007).
4. Besenhard, M. O. *et al.* Co-precipitation synthesis of stable iron oxide nanoparticles with NaOH: New insights and continuous production via flow chemistry. *Chemical Engineering Journal* **399**, 125740 (2020).
5. Pechini, M. Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor, US Patent, 3330697A, 1967.

6. Danks, A. E., Hall, S. R. & Schnepf, Z. The evolution of ‘sol–gel’ chemistry as a technique for materials synthesis. *Mater. Horiz.* **3**, 91–112 (2016).
7. Varma, A., Mukasyan, A. S., Rogachev, A. S. & Manukyan, K. V. Solution Combustion Synthesis of Nanoscale Materials. *Chem. Rev.* **116**, 14493–14586 (2016).
8. Cho, T. H., Park, S. M., Yoshio, M., Hirai, T. & Hideshima, Y. Effect of synthesis condition on the structural and electrochemical properties of Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O₂ prepared by carbonate co-precipitation method. *Journal of Power Sources* **142**, 306–312 (2005).
9. Kim, M.-H., Shin, H.-S., Shin, D. & Sun, Y.-K. Synthesis and electrochemical properties of Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O₂ and Li[Ni_{0.8}Co_{0.2}]O₂ via co-precipitation. *Journal of Power Sources* **159**, 1328–1333 (2006).
10. Cushing, B. L., Kolesnichenko, V. L. & O’Connor, C. J. Recent Advances in the Liquid-Phase Syntheses of Inorganic Nanoparticles. *Chem. Rev.* **104**, 3893–3946 (2004).
11. Ogier, T. *et al.* In-situ study of cationic oxidation states in Pr₂NiO_{4+δ} using X-ray absorption near-edge spectroscopy. *Chemical Physics Letters* **727**, 116–120 (2019).
12. Nicollet, C. *et al.* Preparation and characterization of Pr₂NiO_{4+δ} infiltrated into Gd-doped ceria for SOFC cathode. *J. Solid State Electrochem.* **20**, 2071–2078 (2016).
13. Rudisill, S. G., Hein, N. M., Terzic, D. & Stein, A. Controlling Microstructural Evolution in Pechini Gels through the Interplay between Precursor Complexation, Step-Growth Polymerization, and Template Confinement. *Chem. Mater.* **25**, 745–753 (2013).
14. Shao, Z., Zhou, W. & Zhu, Z. Advanced synthesis of materials for intermediate-temperature solid oxide fuel cells. *Progress in Materials Science* **57**, 804–874 (2012).
15. Deganello, F. & Tyagi, A. K. Solution combustion synthesis, energy and environment: Best parameters for better materials. *Progress in Crystal Growth and Characterization of Materials* **64**, 23–61 (2018).
16. Carrillo, A. J., Serrano, D. P., Pizarro, P. & Coronado, J. M. Thermochemical heat storage based on the Mn₂O₃/Mn₃O₄ redox couple: influence of the initial particle size on the morphological evolution and cyclability. *J. Mater. Chem. A* **2**, 19435–19443 (2014).
17. Nicollet, C. *et al.* Acidity of surface-infiltrated binary oxides as a sensitive descriptor of oxygen exchange kinetics in mixed conducting oxides. *Nat Catal* **3**, 913–920 (2020).
18. House, J. E. *Kinetics of processes in the solid state*. (Elsevier, 2023).
19. *Comprehensive inorganic chemistry II: from elements to applications*. (Elsevier, 2013).
20. Seidel, J. *Complex oxides: materials physics, synthesis, characterization and applications*. (De Gruyter, 2015).
21. Jolivet, J.-P., Henry, M., Livage, J. & Jolivet, J.-P. *Metal oxide chemistry and synthesis: from solution to solid state*. (Wiley, 2000).
22. West, A. R. *Solid state chemistry and its applications*. (Wiley, 2014).
23. Rao, C. N. R. & Raveau, B. *Transition metal oxides: structure, properties, and synthesis of ceramic oxides*. (Wiley, 1998).
24. Theiss, F. L., Ayoko, G. A. & Frost, R. L. Synthesis of layered double hydroxides containing Mg²⁺, Zn²⁺, Ca²⁺ and Al³⁺ layer cations by co-precipitation methods—A review. *Applied Surface Science* **383**, 200–213 (2016).