

Modified Pechini Synthesis of Oxide Powders and Thin Films

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Abstract

The **modified Pechini** method has become one of the most popular synthesis methods for complex oxide materials due to its simplicity and versatility. The method can be applied to synthesize nano-crystalline powders, bulk materials as well as oxide thin films. Here, we present a comprehensive review of the method with focus on the chemistry through the three stages of the process; preparation of stable aqueous solution, poly-esterification to form a solid polymeric resin and finally decomposition/combustion of the resin to form an amorphous oxide followed by crystallization of the desired oxide phase. The review includes several examples of important technical oxide materials where the method has been successfully applied to prepare **oxide powders**, bulk or **thin films**.

INTRODUCTION

Oxide materials in form of particles, bulk or thin films are continuously becoming more important and thereby have also synthesis methods of oxides grown to be an important research field including solution based routes. **Pechini** described in a patent from 1967 (Pechini 1967) how films of titanate and niobate dielectrics could be prepared by utilizing the ability of certain alpha-hydroxycarboxylic acids, such as citric, lactic and glycolic acids, to form polybasic acid chelates with different cations. The chelates underwent **polyesterification** when heated in a polyhydroxy alcohol solution resulting in a transparent solid resin, which maintains the desired **homogeneity** of the cation distribution from the solution. Upon calcination of the resin the organics are removed leaving the desired oxide ceramic composition as the residue. The precursors Pechini suggested were oxides, hydroxides, alkoxides and carbonates. The synthesis method first described in the Pechini patent has further been modified by several authors. Marcilly (Marcilly et al. 1967; Marcilly et al. 1970; Courty et al. 1973) proposed the same year as Pechini a similar approach where the polyol (**ethylene glycol**) was completely replaced with water forming an amorphous gel-like matter instead of the polymer. This process is termed amorphous-citrate or metal complex method. An advantage with this process was the lower amount of organics, but the homogeneity of the resulting oxide seemed to be lower than the original Pechini route. The following development led to the use of other precursors, e.g. nitrates containing crystallization water, like in the synthesis of $\text{LaMnO}_{3+\delta}$ using the polymerizable complex route and nitrate salt precursors (Kakihana et al. 1999). Focus on reducing the amounts of organics occurred in the

following years and water was introduced as a solvent for the precursors. One of the first publications using the water based approach was a study of superconducting film formation (Chiang et al. 1991). The term “modified Pechini process” is today mostly used for a process where aqueous solutions are used as precursors and this can be defined in the following way: *The modified Pechini type of synthesis process to oxide materials starts with a homogeneous aqueous solution containing the desired cation precursors in stoichiometric ratio and selected additives, which by evaporation and reactions is converted to a rigid cross-linked polymer hindering segregation of the cations. The polymer is further converted to a homogeneous oxide powder or film by heat treatment.*

The modified Pechini synthesis method is simple and does not need sophisticated laboratory infrastructure facilities. Aqueous processing routes to oxides are also attractive related to environmental concerns. The synthesis can be performed in a simple beaker using a hot plate and the heat-treatment can be done in a regular laboratory furnace. The modified Pechini process is hence a robust and versatile synthesis method used for many different applications. Due to the fact that the homogeneity from the aqueous solution is maintained through the polymeric resin into the final oxide material, the method is well suited for the preparation of the wide range of homogeneous multicomponent oxide materials. The method can easily be extended to chemical solution deposition of thin films or coatings. There are in principle no restrictions to the number of cations in the solutions, and this simple method actually becomes more attractive the more complex the product is.

Here we provide a detailed review of the chemistry related to the modified Pechini process to oxide powders and films. We focus on the three different steps of the synthesis process including solutions to challenges that might appear using the method. Finally, the applicability of the process is illustrated by describing several selected examples of important technical oxides where the synthesis is applied with success.

WHAT IS THE MODIFIED PECHINI SYNTHESIS?

The three major steps of the modified Pechini process to achieve a homogeneous oxide powder or film is illustrated in Figure 1. In the following a thorough description of the chemistry related to these three steps is provided.

Figure 1. Flowsheet showing the different steps of the modified Pechini process producing a complex oxide from an aqueous solution of precursors and additives.

Step 1) Aqueous solution of precursors

A stable aqueous chelated solution with the cation precursors is paramount for a successful wet chemical synthesis. The complexing agent polybasic hydroxy carboxylic acid forms the polybasic carboxylic acid chelates. The solution needs to be stable over time preventing precipitation, as this will introduce inhomogeneities in the resulting material. The cation precursors should be soluble in water or in aqueous solutions with the chelating agents, hence typical precursors can be hydroxides, alkoxides, acetates, chlorides, citrates and nitrates. The most economically, abundant and highly soluble precursor for most metals is their nitrates. Concentration of the cations will normally be in the range from 0.1 to 1.0 M. It is of imperative importance that the cations are mixed in the correct stoichiometric ratio. Thermogravimetric analysis or ICP is normally performed on each stock solution of cation precursors to determine and control the exact concentration.

The most common polybasic hydroxyl carboxylic acid used is **citric acid**. The molecular structures of citric acid together with some other relevant polybasic hydroxyl carboxylic acids are given in Figure 2.

Figure 2. Structure of relevant polybasic hydroxyl carboxylic acids frequently used during the modified Pechini synthesis.

The middle carboxylic acid group of citric acid is the most acidic due to the electron withdrawing power of the alpha -OH group and hence this carboxylic acid group will form the strongest complexes. The degree of protonation of citric acid is dependent on the pH with the three pKa values being 3.13, 4.76 and 6.39.

Most transition metals form stable complexes with the citric acid and other similar chelating agents which is common for all acidic cations. However, basic cations like the alkaline earths form weak complexes. The stability of the complexes is dependent on pH and concentration and the stability of several important cations can be found from data provided by standard databases (The IUPAC Stability Constants Database, Academic Software). Basic cations are found in the lower left corner of the periodic table while the more acidic ones are found in the right upper part of the periodic table. The cation charge, cation size as well as number of valence electrons are important factors determining the acidity or basicity of cations and hence the stability of **chelate complexes**. For the most basic cations like Ba it has been found necessary to add EDTA as an additional complexing agent (Sletnes et al. 2016). Normally the carboxylic acid like citric acid is added in excess, typically with a molar ratio citric acid:cations from 1 to 3, and this ratio is important for the success of the synthesis as will be demonstrated in some of the examples provided (Fontaine et al. 2004; Nityanand et al. 2011). The order of mixing of the cations and chelating agents has been studied in a few examples and it is normal to add the cation forming the most stable chelate first followed by the cations forming less stable **chelates** (Sletnes et al. 2016).

The structure of the chelate complexes has been revealed in some cases, but this is not a topic that has gained much focus in the literature. For a few materials, like BaTiO₃ and Y₂Ti₂O₇, it has actually been indicated that heterometallic chelate complexes can be formed, where both cations are bound with a stoichiometric ratio in the same complex (Arima et al. 1996; Kakihana et al. 1996). This gives a very high degree of homogeneity, which is beneficial for the preparation of these compounds. The size of the polybasic acid as well as the ratio between the acid and cations have shown to be of importance as more organics has to be burned off, influencing on the local temperature as well as the partial pressure of oxygen (Selbach et al. 2007). In a synthesis protocol closely related to the modified Pechini synthesis, a polymer (PVA or PEG) is used to physically stabilize the cations by a proposed entanglement around the cations. By this polymer-complex solution method, less amount of organics is used and for the synthesis of CaAl₂O₄ a phase pure material was prepared with a higher amount of cations than the number of functional groups in the polymer (Gülğün et al. 1999)

For some specific cations it has more recently been observed that complexing agents with –OH groups like ethylene glycol and polyvinyl alcohol (PVA) are better compounds to promote homogeneity of the final oxide than carboxylic acids. This has empirically been found to be of great advantage for amphoteric cations like In³⁺, Sn⁴⁺ and Bi³⁺ in the preparation of indium tin oxide (Kundu and Biswas 2008; Sunde et al. 2012) and BiFeO₃ (Selbach et al. 2007; Liu et al. 2010). An amino carboxylic acid, e.g. glycine, has also been used as a **complexing agent** and fuel in a related synthesis route; glycine-nitrate method (Chick et al. 1990).

To promote the polymerization into a resin, a polyalcohol is added, normally ethylene glycol, to promote polymerization with the polybasic carboxylic group giving a polyester, according to the chemical reaction given in Figure 3. The amount of ethylene glycol added should at least be the minimum amount necessary with respect to the esterification reaction. The role of the polyalcohol is questioned in the literature and historically a large excess was used (Pechini 1967; Kakihana et al. 1996), but now it is common to add polyalcohol in the same molar ratio as the **carboxylic acid**. The amount of ethylene glycol has been shown to be important for the morphology of ZnO powder produced by the method (Farbun et al. 2013). The polyesterification reaction is dependent on the presence of protonated carboxylic groups and hence the pH of the solution (Tai and Lessing 1992a; Kakihana and Yoshimura 1999). Sometimes an acid (typically nitric acid) has to be included in the solution to catalyze the polymerization dependent on the original pH. On the other hand, the addition of a base (typically ammonium hydroxide) to increase the pH can sometimes be necessary to avoid precipitations of for instance barium nitrate (Chu and Dunn 1987).

Figure 3. Illustration of the chemical reaction between a polybasic carboxylic acid chelate and ethylene glycol during the formation of a complex perovskite oxide (Kakihana and Yoshimura 1999). In the modified Pechini process water has to be evaporated in order to form the polymeric resin. Figure reprinted with permission from Bull. Chem. Soc. Japan.

Step 2) Drying and heating of the solution obtained and formation of a polymeric resin

The stable aqueous solution of the cation precursors and the chelating agents prepared in step 1) is further dried at temperatures in the range 110-150 °C to remove water. As the amount of water decreases it is important to completely prevent **precipitation** of salts as this will be detrimental to the homogeneity of the final material. The viscosity is increasing during the evaporation of water and the solution is finally turned into a polymeric-like resin without any precipitates. Basic cations might precipitate as nitrates, chlorides, acetates as well as citrates from the chelating agent during evaporation of water. Possible precipitation reactions should be carefully considered during the initial design of the synthesis.

Upon further heating of the polymeric resin, a large increase in volume (foaming) occurs due to release of water from hydrated chelates, **decomposition** of complex anions from the precursors as well as decomposition of the organics. The foaming reduces segregation of cations during the process due to the formation of long diffusion paths in the very fine foam formed by the gas development. After drying and reactions, the aqueous precursor solution is turned into a brittle voluminous spongy-like precursor material.

Step 3) Decomposition of the precursor material to obtain an oxide powder

The third step is thermal decomposition of the precursor material to remove the organic part of the resin. Thermal decomposition of the resin usually occurs below 400 °C. The decomposition products are normally not identified and not well described in relevant literature. The spongy-like precursor material is first turned into an amorphous material that is further crystallized into a single phase target material (Tai and Lessing 1992a; Sletnes et al. 2016). The **crystallization** temperature is dependent on the system but can be as low as 400 °C as for example in ITO (Sunde et al. 2012). The decomposition is exothermic, sometimes causing the decomposition and crystallization to occur simultaneously, thereby making it challenging to identify the real crystallization temperature (Sunde et al. 2012).

Metastable oxide phases may also crystallize from the homogeneous amorphous oxide due to the low crystallization temperature of the precursor. This is an interesting aspect with this synthesis approach. Upon further heating the metastable phase will be transformed to the thermodynamically stable phase (Schumm et al. 2011; Sunde et al. 2012). During preparation of oxides with very basic cations, the formation of intermediate carbonates might occur due to the availability of CO₂ from the decomposition of the organics. These carbonates will decompose upon further heating forming the target phase. Several authors also claim that carbonates are not formed during synthesis of for example BaTiO₃ and SrTiO₃ and that the homogeneity is maintained throughout the synthesis (Cho et al. 1990; Arima et al. 1996; Kakihana and Yoshimura 1999).

Film deposition

The aqueous chelated solution developed under Step 1) can also be utilized for deposition of thin films by the modified Pechini process. The film is then deposited on a substrate by spin coating or dip coating, and the necessary equipment is significantly simpler and less expensive than for physical deposition techniques. This precursor film is dried on a hot plate, pyrolyzed (heat treated) to decompose organic additives and complex anions from the precursors and crystallized. The two latter steps are often combined in a single heat treatment step, normally performed by rapid thermal processing. The microstructure of the resulting film is very dependent on the type of nucleation, being dependent on the pyrolysis temperature, heating rate and crystallization temperature (Schwartz et al. 2004). The thickness of each deposited film can be tailored from a few to a few hundred nanometers by varying the cation concentration and viscosity of the solution, or by changing the spinning or dipping speed (Bernardi et al. 2002; Sunde et al. 2014). The total thickness of the film can also be increased by repeating the deposition procedure.

Health and safety concerns

The Pechini process is a low temperature, simple and robust method for making oxide materials, however there are some HSE issues that should be considered. Starting with precursors containing a strong oxidation agent like the nitrate ion could actually lead to ignition of the organic material during drying and heating giving a combustion reaction. Care should therefore be taken when using these precursors by testing a small batch of the synthesis. The drying and heat treatments in this case should be under controlled conditions. Poisonous gases might also evolve during the decomposition of the precursor anions, e.g. nitrous gases from the decomposition of nitrates, which should be used under proper ventilation. Moreover, during the drying of the solution a large volume increase will occur due to foaming caused by gas evolution. It is important to use large enough container to take this into consideration. Using a polybasic amino carboxylic acid as complexing agents and fuel as in the glycine nitrate method might lead to a combustion dependent on the nitrate/glycine ratio. Special care must be taken in doing this synthesis and only small amount can be made in each batch. Finally, it should also be emphasized that the use of water as a solvent in contrast to toxic and/or expensive organic solvents is beneficial with respect to environmental as well as economic concerns. Most of the precursors are also environmentally friendly.

Solutions to frequent challenges

Correct stoichiometry not obtained: The cation concentration and ratio in the solution has to be accurate, especially for line compounds with very limited solid solubility. Several cation

precursors like nitrates contain uncertain amount of crystal water and calibration of the cation content in the solution has to be carried out. Solid precursors (alkali nitrates, oxides) also contain adsorbed water and needs to be dried before use. For cations forming volatile species, evaporation below the polymeric resin decomposition/burning may result in incorrect **stoichiometry**.

Precipitation of crystalline phases before the formation of the polymeric resin: Make sure that complexation of the less-soluble salts is taken into account to prevent precipitates like nitrates, oxalates, citrates, acetates or tartrates especially in case of basic cations. If this is the case change the cation precursor or the chelating agent.

Inhomogeneities in the oxide powder/film: Carbonates might form during the heat treatment especially of basic cations like Ba. These carbonate phases will disappear at higher temperature due to reaction with the residual oxides, but a single phase product might be challenging to obtain due to the initial formation of several phases. In some cases the formation of thermodynamically stable inert compound might occur e.g. formation of parasitic pyrochlore formation instead of the desired perovskite phase (Rørvik et al. 2009). Red-ox reactions between the cations and the organics may also in some cases give elemental metal like for e.g. Bi (Leonard et al. 2002), which may be prevented by changing in the type of cation precursors or complexing agents.

POWDERS

Bismuth ferrite

Bismuth ferrite, BiFeO_3 , is a **multiferroic** material due to the coexistence of ferroelectricity and antiferromagnetism. The material has received considerable attention the last decade due to potential applications in data storage, sensors and devices for spintronics (Wang et al. 2003). BiFeO_3 is known for being difficult to prepare by solid state reactions due to its relatively low melting point (incongruently melting at 934 °C) and preferential evaporation of Bi_2O_3 at high temperatures. Even small offsets in stoichiometry can lead to secondary phases of $\text{Bi}_{25}\text{FeO}_{40}$ and $\text{Bi}_2\text{Fe}_4\text{O}_9$ (Selbach et al. 2009).

A variety of **wet chemical synthesis routes** have been reported (Kim et al. 2005), but in most reports only nearly phase-pure materials were prepared (Shetty et al. 2002). Several modified Pechini-related synthesis routes have been used, with different polybasic carboxylic acids as complexing agents with and without the addition of EG as polymerization agent (Selbach et al. 2007). Here, phase-pure BiFeO_3 was obtained by tartaric and malic acid, with and without EG, and maleic acid with EG. It was proposed that a requirement for the formation of phase-pure materials was the presence of both COOH groups for complexing Bi^{3+} and Fe^{3+} and OH groups for polyesterification. A literature review from Liu et al. (Liu et al. 2010) noted that it appeared that the presence of the OH -group is critical for the formation of phase-pure BiFeO_3 , while the presence of the COOH -groups does not seem to be significant, as can be seen from Table 1. Synthesis routes with PVA and EG have been successful, while synthesis routes with maleic, succinic, malonic and oxalic acids (acids with no OH -groups) were not. Even the utilization of EDTA, known as a very strong complexing agent with four carboxylic acid groups, was unsuccessful (Liu et al. 2010). It is interesting to note that the classical Pechini synthesis route (Pechini 1967) with citric acid and ethylene glycol has been reported both to give phase-pure (Popa et al. 2007) materials and to give secondary phases (Ghosh et al. 2005a). However, in the successful experiment, EG was used as a solvent, i.e. in much larger quantities than when it is only added in smaller amounts as a polymerization agent to an aqueous solution.

TABLE 1. LITERATURE REVIEW OF MODIFIED PECHINI SYNTHESSES WHERE DIFFERENT COMPLEXING AGENTS HAVE BEEN USED FOR THE PREPARATION OF BiFeO₃. MODIFIED FROM (LIU ET AL. 2010).

	# of OH	# of COOH	Phase-purity		Reference
PVA	X	0	✓		(Liu et al. 2010)
EG	2	0	✓		(Park et al. 2007)
			Without EG	With EG	
Tartaric	2	2	✓	✓	(Ghosh et al. 2005a)
Malic	1	2	✓	✓	(Selbach et al. 2007)
Citric	1	3	×	✓	(Jiang et al. 2006; Popa et al. 2007)
Maleic	0	2	×	✓	(Selbach et al. 2007)
Succinic	0	2	×	×	(Selbach et al. 2007)
Malonic	0	2	×	×	(Selbach et al. 2007)
Oxalic	0	2	×	?	(Ghosh et al. 2005b)
EDTA	0	4	?	×	(Liu et al. 2010)

✓: phase-pure; ×: not phase-pure; ?: not reported

The majority of works use nitrates of bismuth and iron as cation precursors (Selbach et al. 2007)). The choice of precursors and amount of organic additives can be important. Hardy et al. reported a Pechini-like synthesis where nitrates and citrates were used as precursor (Hardy et al. 2009). This combination can lead to a self-combustion of the gel during **calcination**, in combination with the evaporation of large amounts of decomposition gases, like CO (Hardy et al. 2005). This can locally create quite high temperatures and a reducing atmosphere, which again can lead to the formation of metallic bismuth. This phase segregation implies a loss of homogeneity during calcination which will be a disadvantage, even if the metal is readily oxidized in the later stages of calcination.

Indium tin oxide

Tin-doped indium oxide, known as **indium tin oxide** (ITO) has been the most widely used **transparent conducting oxide** to date (Ginley and Perkins 2011). Due to excellent properties ITO has found numerous technological applications such as flat panel displays, touch panels, energy-efficient windows and solar cells. ITO thin films are industrially prepared by sputtering, where targets with high density are required (Gehman et al. 1992). It has been known for decades that it is difficult to obtain In₂O₃ and ITO with high density (Vojnovich and Bratton 1975; Nadaud et al. 1994), which has caused a considerable interest in the synthesis and sintering of nano-crystalline In₂O₃ and ITO.

In most of these studies, nano-crystalline In₂O₃ and ITO were prepared by co-precipitation (Kim et al. 2002; Kim et al. 2006), although a few reports with modified Pechini-methods exist (Sunde et al. 2012). The modified Pechini methods avoid the simultaneous precipitation of both indium and tin hydroxides, which ruins the homogeneity on the atomic scale using co-precipitation. Indium nitrate and tin chloride are the most commonly used precursors (Psuja et al. 2007), although alternatives like tin acetate has also been applied (Sunde et al. 2012). Abbas et al. prepared ITO powder from an aqueous solution with CA and EG (Abbas et al. 2014). CA was used with a molar ratio of 2:1 compared to the cations while (EG) was added with a ratio of CA:EG of 80:20, 70:30 or 60:40. Powders prepared with the 80:20 ratio had the best sintering properties, possibly due to less agglomeration. Sunde et al. performed a series of experiments with a cation concentration of 0.5 M and different complexing agents, applied alone or in combination, namely acetic acid, ethanol, ethylene glycol, succinic acid and tartaric acid (Sunde et al. 2012). Here, it was observed that precipitations of organometallic salts occurred for almost all syntheses during the drying of the gel. **Amorphous gels** were only be obtained in the synthesis with EG and tartaric acid and EG in

combination. This is an indication that the ROH-group is more efficient at chelating indium and tin cations than the RCOOH group. In another work, phase pure ITO was prepared by a citrate-combustion method, without ROH groups, (Wang et al. 2010) indicating that also the carboxylic acid group can also effectively chelate these cations when the experimental conditions are favorable.

The organics in the obtained amorphous gels will decompose upon calcination, and the exothermic nature of the reaction causes the decomposition and crystallization to occur simultaneously already at 400 °C (Wang et al. 2010). In some cases also the metastable rhombohedral polymorph of ITO can be obtained during calcination at these low temperatures. This has been observed both when smaller organic complexing agents were used, giving less reducing atmospheres during calcination (Sunde et al. 2012) and when ZrO₂ was used as a dopant (Abbas et al. 2014). An indication of the excellent homogeneity provided by the modified Pechini method is that phase pure ITO powders can be prepared with significantly higher amounts of tin doping than the thermodynamic solubility limit (Sunde et al. 2013). The phase-purity will remain until the temperature is high enough to activate cation mobility to give phase segregation. This can be seen in Figure 4, where the material is phase-pure up to 800 °C and a secondary phase of SnO₂ appears at temperatures above 1000 °C.

Figure 4. XRD of ITO powders with 100 cation% tin-doping prepared from a modified Pechini synthesis after heat treatment at different temperatures. The material is phase pure at low temperatures, but an exsolution of SnO₂ is observed from 1000 °C and upwards (diffraction lines from SnO₂ marked by *). From (Sunde et al. 2013).

Phosphors

Phosphors are materials which can emit light, and one of their emerging applications is as white light-emitting diodes (WLED), with the potential to significantly reduce the energy consumption of illumination (Shur and Žukauskas 2005). The phosphors often consist of host materials with complex composition doped with small amounts of the active light-emitting species, and are sensitive to phase-purity, crystallinity and impurities (Smet et al. 2011). Hence, wet chemical synthesis methods are highly applicable for their synthesis (Gai et al. 2014). The literature on phosphors prepared by modified Pechini methods is extensive, including host materials such as CaIn₂O₄ (Liu et al. 2007), Ca₈La₂(PO₄)₆O₂ (Shang et al. 2012), YVO₄ (Serra et al. 2000), YNbO₄ (Lü et al. 2015) and SrZrO₃ (Zhang et al. 2008). In some of these reports the materials are also prepared by solid-state reactions for comparison, and the modified Pechini-powders are shown to have equal or better properties (Wang et al. 2008b).

A much studied group of novel red phosphor materials for WLED are Eu³⁺-doped oxides of Mo and W, including compounds such as NaLa(WO₄)(MoO₄) (Li et al. 2013), La₂(WO₄)₃ (Kodaira et al. 2003) and double perovskites within the (Sr,Ba)₂Ca(W,Mo)O₆ series (Ye et al. 2011). The most common synthesis method of these materials is solid state reaction, but there are several reports of modified Pechini synthesis being used (Zalga et al. 2011). However, it is not trivial to obtain phase pure materials and parameters such as choice of complexing agent, pH and calcination temperature must be optimized.

In most of the reports, CA and EG are used as complexing and polymerization agents (Kodaira et al. 2003; Wang et al. 2008b), but other complexing agents have also been used. In a work by Sletnes et al., NaLa(WO₄)(MoO₄) was synthesized by using malic and tartaric acid, with and without EG (Sletnes et al. 2016). All of the syntheses yielded phase-pure materials

after calcination at 600 °C, but when malic acid was used alone precipitation of a salt was observed in the gel. Although crystallization occurred already at 400 °C, 600 °C was necessary to completely oxidize and remove the organic residue. Increasing the calcination temperature increased the crystallinity and particle size, which often improves the optical properties. Interestingly, the best optical properties of the powder were obtained after calcination at 600 °C, possibly due to some finite size effects.

The same work also showed how phase-pure $\text{Ba}_2\text{CaMoO}_6$ could be synthesized by the utilization of CA and EDTA as complexing agent. Preliminary experiments with MA, TA, CA, EDTA and DTPA, with or without EG, demonstrated the challenges related to the synthesis of this material, mostly due to precipitation of $\text{Ba}(\text{NO}_3)_2$ in the gel. Precipitations were observed when MA, TA and EDTA were used, which further lead to secondary phases of $\text{Ba}_{1-x}\text{Ca}_x\text{CO}_3$ and BaMoO_4 after calcination. Amorphous gels, indicating a good homogeneity, were obtained by using CA, DTPA or EDTA and CA in combination. Among these, phase pure materials were only obtained by the latter two routes at calcination temperatures higher than 800 °C. Of the two routes, the one with EDTA and CA was deemed most promising, due to the suspected toxicity of DTPA. There are several modified Pechini syntheses of perovskites reported in the literature in which EDTA and CA are used in combination, and many of them involve basic cations, such as Sr, Ba and La (Ding et al. 2008; Patra et al. 2011). The application of these two complexing agents in combination is clearly favorable, but the actual mechanism is not understood. It might be related to their favorable complexing, but also that the combination is a good combustion reagent, which increases the local temperature and the reaction rate.

The difference in the required complexing agents for the synthesis of the two materials can be partly explained by the solubility of the precursors and the stability of the cation complexes. The stability constants for complexes with Ca^{2+} , Ba^{2+} , Na^+ and La^{3+} are plotted in Figure 5. The stability constants are significantly higher for EDTA and DTPA than for MA, TA and CA, and the stability increases in the order $\text{Na}^+ < \text{Ba}^{2+} < \text{Ca}^{2+} < \text{La}^{3+}$. For NaNO_3 , the solubility is so high that strong complexation might not be necessary to achieve phase pure materials. For $\text{Ba}(\text{NO}_3)_2$, on the other hand, strong complexing agents like EDTA should be used.

Figure 5. Stability constants (log K) of complexes of Ca^{2+} , Ba^{2+} , Na^+ and La^{3+} with malic acid, tartaric acid, citric acid, EDTA and DTPA. From (Sletnes et al. 2016).

Lanthanum transition metal perovskite oxides for energy technology

Several transition metal perovskites with lanthanum/strontium on the A-site have been extensively investigated as electrodes for **solid oxide fuel cells** (SOFC) (Tao and Irvine 2004; Baumann et al. 2006; Jiang 2008), such as $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ (LSC), $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM), $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) and $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF). Doped LaCrO_3 has also received considerable attention as an interconnect material for SOFCs (Zhu and Deevi 2003). Tailoring the stoichiometry, microstructure and phase purity of the powders is vital in order to optimize their performance and powders of high quality is an essential prerequisite for these applications.

The typical cation precursors for these perovskites are nitrates (Magnone et al. 2007), occasionally prepared by dissolving the parent oxide in HNO_3 (da Conceição et al. 2009), although sometimes carbonates are used for the more basic cations (Fan and Liu 2009). Gupta and Whang also did a series of experiments where they changed between nitrates and acetates

as precursors for the preparation of $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.85}\text{Fe}_{0.05}\text{Co}_{0.05}\text{Ni}_{0.05}\text{O}_{3-\delta}$ (Gupta and Whang 2007). They observed that using acetates gave less secondary phases, and discussed this in relation to the pH in the solution and its influence on the chelating ability of CA. Several complexing agents have been used, but the most typical is CA, both with (Gaudon et al. 2002) and without (Fan and Liu 2009) addition of EG as a polymerization agent. The ratio between CA and metal cations has been demonstrated to be an important parameter. For ratios less than three, precipitations of unidentified phases was observed, both for LSM (Da Conceição et al. 2011) and LSCF (Nityanand et al. 2011). On the other hand, by adding ammonia to adjust the pH to 8, Fan et al. prepared phase-pure LSCF with a CA:cation ratio of only 1.5 (Fan and Liu 2009). Strontium carbonate has been observed as a secondary phase for calcination at temperatures of 500-600 °C due to the high stability of SrCO_3 , but phase-pure materials are obtained by increasing the calcination temperatures (Shao et al. 2009). This is illustrated by the XRD diffractograms in Figure 6. It is interesting to note that lanthanum manganite typically can be made phase-pure at lower temperatures than lanthanum strontium manganite, because the possible formation of SrCO_3 can be avoided (Kakihana et al. 1999). The necessity of adding EG as a polymerization agent is also not clear. Phase-pure LSCF has been prepared by the amorphous citrate synthesis, without the use of EG (Magnone et al. 2007; Fan and Liu 2009). On the other hand, Kakihana et al. demonstrated that the polymerization was crucial in order to avoid secondary phases during the synthesis of lanthanum manganite (Kakihana et al. 1999). It appears that the polymerization is not essential, but it improves the homogeneity during the synthesis, thereby enabling the formation of phase-pure materials at lower temperatures. This can be important if a high surface area of the powder is desirable, for instance to provide a large surface area of a cathode material or enhance the sintering properties.

Figure 6. XRD diffractograms of LSCF prepared with CA and EDTA as complexing agents after calcination at different temperatures. From (Shao et al. 2009).

Shao et al. performed an interesting series of experiments to shed light on the chelating of the precursors of LSCF (Shao et al. 2009). Here, CA, EDTA or the combination of the two were used in experiments with all four cations of LSCF together and for the individual cations alone. Based on visual observations of precipitations and FTIR and XRD experiments they observed that CA could form complexes with all four cations, but could not totally coordinate them (a molar ratio of 1.5 compared to the cations was used). On the other hand, EDTA could only form stable complexes with Co and Fe, not with La and Sr (molar ratio of 0.5). The best results were obtained by using both complexing agents together. The infrared spectrum of the LSCF complex precursor with CA and EDTA was not a pure superposition of the spectra of the individual cation complexes indicating a strong interaction between the cations during the chelation. Similar observations have been reported in the synthesis of BaTiO_3 (Kakihana and Yoshimura 1999) and $\text{La}_2\text{Mo}_2\text{O}_9$ (Rocha and Muccillo 2003) using modified Pechini syntheses.

In the early 1990s, Tai and Lessing performed a thorough fundamental investigation of the synthesis of $\text{La}_{0.85}\text{Sr}_{0.15}\text{CrO}_3$ by the modified Pechini method (Tai and Lessing 1992a; Tai and Lessing 1992b) where the ratio between CA and EG, the ratio between the organic additives and cations as well as the amount of excess water were investigated. The optimal ratio between CA and EG in order to get a polymerization is between 40 and 57 % CA. Three drops of nitric acid was added for each 100 mL of water, in order to catalyze the esterification reaction. The CA and EG should be mixed together before adding the cation precursors. If not, they could observe precipitations of strontium nitrate. If the ratio between organics and cations is too high, > 4, fierce ignition of the gel occurred during calcination, thereby

increasing the temperature and creating hard agglomerates. It is also desirable to keep the amount of added organics low from an economic perspective. However, if the ratio was too low, < 0.5 , the complexation was not sufficient to avoid secondary phases. A total of 150 mL water was necessary to aid the dissolution of CA when 1 mole of CA and 1 mole of EG were used. Excess water beyond this had two drawbacks. First, the evaporation of water also removed some quantities of the polymeric substance out from the boiling solution. And second, the formation of energetic water vapor during the evaporation could break the polymeric network that was already forming in the solution.

High-temperature superconductors

Superconductors are materials which exhibit zero electrical resistance and expulsion of magnetic fields below a critical temperature, T_c . The discovery of **high-temperature superconductors** in copper oxide-based material systems with a T_c above 77 K (can be cooled by liquid nitrogen) in the late 1980s created enormous excitement and these materials were intensively investigated (Bednorz and Müller 1986). Particularly oxides in the Y-Ba-Cu system (**YBCO**), like $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, received a significant amount of interest (Wu et al. 1987).

There are numerous reports on different synthesis routes to prepare YBCO powder, as reviewed by Kakihana and Pathak and Misra (Kakihana 1996; Pathak and Mishra 2005). The powder characteristics, like homogeneity, phase-purity and particle size, will have a large influence on the properties of the final device, and both solid-state (Cava et al. 1987) and wet chemical synthesis routes (Kamat et al. 1991), have been employed for the synthesis of YBCO. Different **sol-gel** syntheses to prepare YBCO have been applied and they are argued to give better homogeneity and be less complicated than other wet chemical methods, such as co-precipitation (Kakihana et al. 1989).

The cation precursors used in modified Pechini syntheses for YBCO can either be nitrates (Kakihana et al. 1991) or Y_2O_3 and CuO dissolved in HNO_3 together with BaCO_3 (Lee et al. 1989). A possible precipitation of $\text{Ba}(\text{NO}_3)_2$ could be avoided by adding ammonia to adjust the pH to about 6 (Chu and Dunn 1987). In all of the reports CA and EG were employed as complexing and polymerization agents. The ratio between metal cations and CA varied from 1:0.33 (Kakihana et al. 1991) to 1:6.5 (Shiomi et al. 1993). After evaporation of the solvent, the gels were calcined and phase-pure YBCO was obtained at around 900 °C (Mazaki et al. 1991). Sometimes BaCO_3 could be detected after calcination at lower temperatures (Lee et al. 1989). The resistivity of YBCO prepared with CA and EG is shown in Figure 7, demonstrating the superconducting transition. The narrow transition temperature interval is an indication that YBCO with high purity and structural homogeneity could be prepared (Kakihana et al. 1991) by this method.

Figure 7. Resistivity as a function of temperature for a polycrystalline sample of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ prepared by a modified Pechini method with CA and EG. From (Kakihana et al. 1991).

In addition to the modified Pechini routes, there are also several reports on amorphous citrate-syntheses to prepare YBCO (Yang et al. 1989) without the use of EG. Also oxalic acid has been used as the complexing agent (Sanjines et al. 1988). In some of these reports, Y_2O_3 , together with barium and copper carbonate, was dissolved directly in citric acid, without the use of HNO_3 (Karen and Kjekshus 1994). The molar ratio between cations and CA was typically 1:2 (Sanjines et al. 1988). Also in these syntheses the pH was often increased to prevent precipitation of $\text{Ba}(\text{NO}_3)_2$. Liu et al. argued that it was advantageous to use ethylenediamine to adjust the pH instead of ammonia, as it could react with nitric acid and thereby further prevent precipitation of $\text{Ba}(\text{NO}_3)_2$ (Liu et al. 1989). Another reported way to

mitigate the issue with $\text{Ba}(\text{NO}_3)_2$ precipitation is to employ a combination of CA and EDTA as complexing agents (Van der Biest et al. 1991). Here, one solution is prepared where Y^{3+} and Cu^{2+} are complexed by CA and another with Ba^{2+} complexed by EDTA. After mixing the two solutions and adjusting pH to 7, the precipitation could be avoided (Niou et al. 1992).

Cathode materials for Li ion batteries

Lithium ion batteries have become increasingly important and have been at the focus of intense research the last decades. They are today routinely used in portable electronic devices and also show great promise for storage of energy from renewable sources and their use in electronic vehicles (Bruce et al. 2008; Goodenough and Kim 2010). The anode is typically graphite, whereas the cathode traditionally was LiCoO_2 (Mizushima et al. 1980). Later a variety of potential cathode materials has received interest, among them several materials based on manganese oxide (LiMn_2O_4 , $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$, $\text{Li}(\text{Mn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3})\text{O}_2$), phosphates (LiFePO_4) and silicates ($\text{Li}_2\text{FeSiO}_4$) (Tarascon et al. 1991; Padhi et al. 1997; Nytén et al. 2005). It has been shown for many of these materials that their performance is highly dependent on the synthesis method (Li et al. 2004), and indeed, the modified Pechini process has proven very useful (Liu et al. 1996).

The choice of cation precursors for Li ion battery cathodes are typically nitrates and sometimes acetates (Predoana et al. 2015). Some exceptions exist, for instance was SiO_2 particles used in the synthesis of $\text{Li}_2\text{FeSiO}_4$ (giving a colloidal suspension) (Dominko et al. 2008) and tetra-n-butyl titanate was used to dope LiMn_2O_4 with titanium (Xiong et al. 2012). In the latter case lactic acid was used to stabilize the titanium solution. The first report of Pechini synthesis of LiMn_2O_4 used EG as a solvent (Liu et al. 1996), but it has since become increasingly common to use aqueous solutions (Kunduraci and Amatucci 2006; Predoana et al. 2015).

The most commonly used complexing agents are, as in Pechini's original patent, CA and EG (Zhao et al. 2013). There are a few reports where the amount of EG has been optimized (Han and Kim 2000). Kunduraci and Amatucci prepared $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ with a 1:1 ratio between cations and CA and an accompanying ratio of EG varying between 0, 2, 4 and 7 (Kunduraci and Amatucci 2008). Interestingly, it was found that the presence of EG had a large influence on the obtained microstructure after calcination. The materials prepared with EG had smaller particles and also a more mesoporous structure, as can be seen in Figure 8. Both of these factors had a large impact on the electrochemical performance of the cathode material, and the optimal ratio between CA and EG was found to be 1:4. Other authors have applied only CA (Predoana et al. 2015) or a combination of CA and EDTA (Liu et al. 2014). Duncan et al. used EG without a carboxylic acid for the preparation of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (Duncan et al. 2010). Here, an ester reaction occurred between EG and the acetate precursors, however, a polymer network will not form as the acetate has only one functional group.

Figure 8. Scanning electron microscopy images of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ prepared by a modified Pechini method with a 1:4 ratio between CA and EG (a) and without EG (b). From (Kunduraci and Amatucci 2008).

The calcination temperature has been shown to be an important parameter to optimize the electrochemical properties of the cathode materials. First of all, the volatility of Li at high temperatures is well known (Rossen et al. 1993), and sometimes an excess of Li is used in the solution to compensate for this (Predoana et al. 2015). Furthermore, a low calcination temperature will give smaller particle sizes, giving a high discharge capacity, however, the crystallinity of the particles can often be impaired, leading to fast capacity fading (Zhao et al.

2013). Typically a compromise must be found between these two aspects. A similar contradiction was encountered in the preparation of the layered material $\text{Li}(\text{Mn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3})\text{O}_2$ (Xia et al. 2009). Again, a low calcination temperature favorably produced smaller particles. However, in this case it also resulted in cation disorder, where Li goes into the transition metal layers, which in turn significantly reduced the lithium mobility.

Finally, most of these cathode materials suffer from inherently poor electron conductivity. A carbon coating on the particle surfaces is typically necessary to mitigate this issue (Dominko et al. 2005). Sometimes this is obtained by adding a polymer, like polyethylene glycol, to the solution, followed by a heat treatment in reducing atmosphere (Mei et al. 2012). However, interestingly, when the modified Pechini method is used this layer can be formed without the use of additives, simply from carbonization of the complexing agents CA and EG (Dominko et al. 2008). This carbon layer provides the necessary conductivity, but also serves to prevent particle growth and agglomeration (Moskon et al. 2007). Zhang et al. used a modified Pechini route to prepared a composite cathode material of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and graphene (Zhang et al. 2013). Here, the complexing agents, CA and EG, were not only used to chelate the precursors, but also to attach the phosphate to functional groups on graphene oxide. In the following reducing heat treatment CA and EG decomposed to coat the surface of the phosphate particles with a carbon layer and the graphene oxide was reduced to graphene. A schematic depiction of this process is given in Figure 9.

Figure 9. A schematic depiction of how a composite cathode of graphene and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) was prepared from a modified Pechini process. From (Zhang et al. 2013).

THIN FILMS

Superconducting thin films

Superconducting thin films have been an important part of the science of superconductivity for more than six decades (Lin et al. 2015). Potential applications for high-temperature superconducting films include high-frequency electronics, microwave communications and magnetic field detectors (Norton 2003). Different substrates are used for different application, and lattice match to give epitaxy and chemical compatibility are among the important considerations. Special attention has also been directed towards the preparation of superconducting wires, typically consisting of a metallic tape with a superconducting coating, which can enable large-scale applications for electric-power and magnetic applications (Larbalestier et al. 2001; Rupich et al. 2004; Kang et al. 2006). Here, a buffer layer between the metal substrate and the superconducting layer is needed to protect the metal substrate from oxidation and to give **epitaxial** growth of the superconducting film (Obradors et al. 2004). **Chemical solution deposition** has emerged as a highly competitive method for the preparation of YBCO **coatings**, both in the shape of wires and films, where high quality films can be prepared cost-effectively with high speed without the need for vacuum (Obradors et al. 2006).

A highly successful route for the preparation of superconducting films is the trifluoroacetate (TFA) route (Iguchi et al. 2002). The advantage of this synthesis method is that it avoids the formation of BaCO_3 , which can precipitate at the grain boundaries and limit the performance. However, there are some drawbacks from using fluorine, most notably the evolution of highly corrosive and dangerous hydrofluoric gas, making it less suitable for industrial upscaling (Cui et al. 2009). As a consequence, several modified Pechini routes have been developed as alternatives (Bubendorfer et al. 2003), where the formation of barium carbonate can also be avoided (Cui et al. 2009). The typical cation precursors are nitrates or acetates, but there is a larger variety in the choice of complexing agents, with CA and EG (Cui et al. 2009), EDTA

(Brylewski and Przybylski 1993), triethanolamine and acetic acid (Thuy et al. 2009) and trimethylacetate and propionic acid (Shi et al. 2004) all being applied. Bubendorfer et al. investigated several organic acid, such as lactic, tartaric, glycolic, malonic and diglycolic acid, but found that malic acid was the best choice, due to its superior ability to chelate Y^{3+} (Bubendorfer et al. 2003). Wang et al. used the addition of polymers, such as PVB, PEG and PVP to improve the wettability and viscosity of the solution (Wang et al. 2008a). Solutions with a very long shelf life can be prepared (Thuy et al. 2009). By spin or dip coating on substrates such as strontium titanate or lanthanum aluminate films with a preferential orientation can be prepared, as can be seen in the diffractogram in Figure 10.

Figure 10. XRD of an YBCO thin film with preferential orientation deposited by spin coating on a strontium titanate substrate. The solution was prepared with malic acid and glycerol as complexing agents. From (Bubendorfer et al. 2003).

Transparent conducting oxides

Powder synthesis and preparation of bulk materials, as described for ITO above, are important for the preparation of high quality sputtering targets, but the materials are used as transparent thin films in their final application. Several physical deposition techniques for the preparation of TCOs exist, but chemical solution based techniques offers several advantages. TCO thin films of In_2O_3 (Legnani et al. 2007), SnO_2 (Sladkevich et al. 2011) and ZnO (Lima et al. 2007) have all been prepared by the modified Pechini method, both by spin coating (Sunde et al. 2012) and dip coating (Kundu and Biswas 2008).

The most common synthesis route is to dissolve nitrate or chloride precursors in water with the addition of CA and EG (Legnani et al. 2007). For the deposition of ZnO thin films, He et al. used a mixture of water and ethanol as solvent. In some cases it was shown that an additive, like PVA, was necessary in order to increase the viscosity of the solution and improve the wettability on the substrate (Kundu and Biswas 2008; Sunde et al. 2014). The thickness of the films were tailored by the number of depositions, but also by varying the cation concentration and viscosity of the solution and by changing the spinning or dipping speed (Sunde et al. 2014). Layers ranging from 10 to several hundreds of nm could be prepared. Bernardi et al. prepared films of antimony-doped tin oxide (ATO) with varying thickness by changing the viscosity by carefully adding or evaporating water before dip coating (Bernardi et al. 2002). Two films with the same total thickness, consisting of seven and one layers, respectively, are shown in Figure 11. They found that the highest density and best optical and electrical properties were obtained in the film made by several depositions.

Figure 11. SEM micrographs obtained at 45° inclination of ATO films prepared by dip coating of a modified Pechini solution. The top film (a) is prepared by 7 layers from a solution with a viscosity of 4 cP. The bottom film (b) is a single layer from a solution with 20 cP. From (Bernardi et al. 2002)

The TCO films are typically deposited on glass slides, but more refractory substrates, like sapphire or YSZ, are necessary if the calcination temperature is higher than about $500^\circ C$. Sladkevich et al. also prepared ATO films on sheet-like clay particles, thereby demonstrating the flexibility of the modified Pechini process (Sladkevich et al. 2011). Also **patterning**, which is important for TCOs used in photovoltaic devices has been demonstrated by the modified Pechini process. Sladkevich et al. prepared films of Cd_2SnO_4 by spin coating of an aqueous solution with CA and EG. By using a lithographic nanoimprint technique a pattern was made in the as-spun polymeric precursor film, which remained in the film after calcination (Schumm et al. 2011). Here, it was also demonstrated that they could obtain the metastable

cubic phase of Cd_2SnO_4 in the thin film, which cannot be obtained in bulk materials, by optimizing the calcination procedure. Finally, the calcination temperature and atmosphere have been shown to be very important for the electrical properties of the TCOs (Choppali and Gorman 2008). After heat treatment at high temperatures and in reducing atmospheres, ITO thin films with excellent properties have been obtained. With a specific resistance down in the $10^{-4} \Omega \cdot \text{cm}$ -range, the films prepared by the modified Pechini method are comparable to the best values from physical deposition techniques (Sunde et al. 2014).

Thin film phosphors

Thin films of **luminescent materials** are attractive for many technological applications, especially related to display technology (Yu et al. 2005), but also for light-conversion layers for photovoltaics (Huang et al. 2013) and optical waveguides (Chae et al. 2013). Already in 1980 Robertson and van Tol demonstrated that epitaxial luminescent films of rare earth-doped garnets could withstand much higher power densities in cathode ray tubes without degradation than their powder counterparts (Robertson and Van Tol 1980). Since then, thin film phosphor materials have received significant attention (Choe et al. 2001; Garskaite et al. 2010). The uniform thickness and smoother surface of the thin films makes it possible to define smaller pixels, thereby giving a higher resolution. Thin films prepared by the modified Pechini method can also be patterned, which can be achieved by relatively simple and inexpensive soft-lithography techniques (Pang et al. 2003). A demonstration of such patterning is given in Figure 12. These patterns were prepared by the micromolding in capillaries technique. Here, a droplet of the modified Pechini solution, containing the cation precursors and complexing agents, is deposited next to a micromold, upon which capillary forces will pull the solution into the mold. After drying the mold can be removed, and the patterned oxide thin film remains after calcination (Lin et al. 2007).

Figure 12. Optical photographs of patterned thin films of LaPO_4 doped with Ce^{3+} and Tb^{3+} prepared by the modified Pechini process and the micromolding in capillaries technique. Modified from (Lin et al. 2007). Reprinted with permission from Lin et al. Copyright 2007 American Chemical Society.

Phosphors made up from monodisperse, small and spherical particles are attractive due to the possibility of a low light-scattering and a high packing density, leading to good resolution (Martinez-Rubio et al. 2001). In this regard, the flexibility of the modified Pechini method can be utilized to produce **core-shell** structures. Here, monodisperse and spherical silica particles are typically produced by the Stöber method (Stöber et al. 1968). These particles are added to a modified Pechini solution, containing the chosen cations in the desired stoichiometry together with complexing agents, typically CA and PEG (Wang et al. 2005). The silica particles contain OH-groups, which the chelated cations can bond to, thereby producing a thin coating after calcination. By using a silica core the total cost of the phosphor particle is significantly reduced. The optical properties of the core-shell particles can be tuned by the number of coatings, the calcination temperature and the size of the silica particle. The crystallinity of the coating improves with increasing annealing temperature, however if the temperature is too high a reaction between the core and the shell can occur (Lin et al. 2007).

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