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Enhancement of LaPO4 and Sr-doped LaPO4 Direct Precipitation Synthesis

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Enhancement of LaPO$_4$ and Sr-doped LaPO$_4$ Direct Precipitation Synthesis

THESIS
submitted in partial satisfaction of the requirements
for the degree of
MASTER OF SCIENCE
in Chemical and Biochemical Engineering

by

Neshat Jalali Heravi

Thesis Committee:
Professor Martha L. Mecartney, Chair
Professor Daniel R. Mumm
Professor Mikael Nilsson

2015
Dedication

To mom and dad, and my precious siblings

Shadi, Mojdeh, and Navid for their endless

love and support
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Abstract of the Thesis

Enhancement of LaPO$_4$ and Sr-doped LaPO$_4$ Direct Precipitation Synthesis

By

Neshat Jalali Heravi

Master of Science in Chemical and Biochemical Engineering

University of California, Irvine, 2015

Professor Martha L. Mecartney, Chair

Monoclinic LaPO$_4$ (monazite) is a chemically stable compound with a high melting temperature, high radiation damage resistivity, and very low solubility in water; it has various applications arising from its unique structure. Low temperature solution synthesis usually results in formation of a hexagonal hydrate, LaPO$_4$·$\frac{1}{2}$H$_2$O (rhabdophane). The presence of rhabdophane in the compound results in formation of a liquid phase at high temperatures due to availability of excess phosphorus, thus making monazite less applicable. In this study, different batches of LaPO$_4$ were synthesized at different temperatures using the direct precipitation synthesis method. The synthesis technique in this study coupled with washing and ball-milling the samples yields monoclinic monazite without the formation of rhabdophane, as confirmed via XRD.

Monoclinic LaPO$_4$ doped with divalent elements such as strontium (Sr$^{2+}$) is a material candidate for electrolytes in intermediate temperature proton conducting solid oxide fuel cells. Synthesis of monoclinic monazite usually results in the production of rhabdophane. Availability of liquid phase at high temperatures detrimentally scavenges Sr from the doped monazite. Here, monoclinic LaPO$_4$, with up to 30% Sr doping, has been synthesized using a direct precipitation synthesis, without any formation of rhabdophane, as investigated by XRD.
The solubility limit of Sr in LaPO₄ structure was determined to be around 30% via measuring Sr concentration through EDS. The XRD results showed that Sr(PO₃)₂ was formed when Sr-doped LaPO₄ powders were annealed in air, and Sr₂P₂O₇ phase was formed when powders were sintered in water.
Chapter I. Enhancement of LaPO₄ Direct Precipitation Synthesis

1.1 Introduction

1.1.1 Rare-earth Orthophosphates (RE(PO₄))

The rare-earth (RE; considered as lanthanides plus Y) phosphates, RE(PO₄), exist in nature as the phases monazite and xenotime. Monazite preferentially incorporates the larger, light rare-earth elements (La-Gd) whereas xenotime tends to incorporate the smaller, heavy rare-earth elements (Tb-Lu,Y) \[^{[1]}\]. Both monazite and xenotime are dimorphs. Monazite is monoclinic, and xenotime is tetragonal. Due to the crystal-chemical similarity between the lanthanides and actinides, monazite has been investigated for use as a solid-state repository for radioactive waste \[^{[1]}\].

1.1.2 La-Monazite (LaPO₄)

LaPO₄ has a monoclinic structure (a = 6.825 Å, h = 7.057 Å, c = 6.482 Å, p = 103.21°), with 9-fold oxygen coordination around La sites, and phosphorus is 4-coordinated in a distorted tetrahedral environment as shown in Figure 1.1. The density of LaPO₄ is 5.13 g/cm³ \[^{[2]}\]. LaPO₄ exhibits unique properties such as high melting temperature (~2000K), low solubility in water and acids, and high resistance to radiation damage \[^{[3][4][5]}\].

Monazite is suitable for many varieties of applications. Layers of LaPO₄ is used as the soft, self-lubricant phase in the diphase abradable coatings \[^{[6]}\]. In fiber coatings and ceramic reinforced oxide composites, monazite is used in multilayered composites to create a weakly
bonded interface to support toughening \cite{6}. Since single phase LaPO\textsubscript{4} is easily machinable, it has been dispersed in Al\textsubscript{2}O\textsubscript{3} and ZrO\textsubscript{2} ceramic matrices to improve machinability \cite{7}. In the field of advanced nuclear technologies, LaPO\textsubscript{4} is used in multiphase inert ceramic matrix as nuclear fuel to stabilize the structure under irradiation \cite{8}. It is also proposed as a material used for nuclear spent fuel management due to its stability against radiation, recrystallization at low temperatures, and low solubility in water and acid \cite{9,10}. The lanthanum sites can accommodate nuclear waste fission byproducts such as actinides and lanthanides, Sr, Ba and Ca \cite{11,12}.

To meet the set of requirements for some of the monazite applications, stoichiometric LaPO\textsubscript{4} is a necessity. Presence of excess phosphorus in a LaPO\textsubscript{4} containing system makes La-monazite less suitable by changing some of its key properties. For example, stoichiometric monazite bonds weakly to alumina, thus it is a suitable interphase for alumina composites, to avoid creep and prevent crack growth from monazite to alumina in coatings on alumina fibers \cite{13}. Thus, the debonding property of monazite mainly depends on its stoichiometry. Previous studies have also shown that small amounts of excess P in polycrystalline LaPO\textsubscript{4} can have a vast influence on its micro-structural stability and creep at high temperature \cite{14}. It has been shown that regardless of LaPO\textsubscript{4} and Al\textsubscript{2}O\textsubscript{3} compatibility in air at temperatures as high as 1600°C, availability of excess P can result in formation of AlPO\textsubscript{4}, and excess La can result in formation of LaAl\textsubscript{11}O\textsubscript{18} (at \textasciitilde1400°C) \cite{14}.

\textbf{1.1.3 Issues with Available LaPO\textsubscript{4} Synthesis Methods}

La\textsubscript{2}O\textsubscript{3}/P\textsubscript{2}O\textsubscript{5} phase diagram shown in Figure 1.2 suggests that even with small amount of excess phosphorus, a peritectic liquid is formed around 1235°C \cite{15}. Also, previous studies show that giant grain-growth occurs above 1235°C \cite{15}. The formation of intergranular phases at high temperatures, due to availability of excess P in the monazite or rhabdophane powders
used in the system, should be of great concern specially when dealing with radionuclides. In the process of nuclear waste storage, acid water can dissolve the intergranular phase and carry away the radionuclides. The intergranular phases can also leach out substitutional cations at high temperatures, which is detrimental for applications.

Figure 1.2 \( \text{La}_2\text{O}_3/\text{P}_2\text{O}_5 \) phase diagram\(^{[15]}\).

Monazite has been synthesized using various methods such as wet chemical method \(^{[16]}\), solgel \(^{[17]}\), high temperature solid state reactions \(^{[18]}\), crystallization from phosphoric acid solution \(^{[19]}\), and aqueous precipitation using \( \text{LaCl}_3 \)\(^{[20]}\). However, current methods to form \( \text{LaPO}_4 \) result in excess \( \text{PO}_4 \)\(^{[21]}\). A vast majority of the synthesis procedures currently available incorporate extra steps; such as filtration, heat treatment (above 400°C), handling unwanted byproducts such as HCl, and long ripening time to produce stoichiometric \( \text{LaPO}_4 \) wherein the \( \text{La/P} \) ratio nears unity\(^{[17][20][16]}\). To get rid of the excess P the powders have to be washed repeatedly with toxic chemicals \(^{[13]}\). Furthermore, just heat-treating the commercial rhabdophane powders is not enough for making single phase \( \text{LaPO}_4 \) of high purity, due to the excess P in such powders. Synthesis of monoclinic monazite by solution routes usually results in the production of a hexagonal hydrate, rhabdophane \( (\text{LaPO}_4\cdot \frac{1}{2}\text{H}_2\text{O}) \) which engenders liquid
phase formation within the samples at high temperatures due to excess P trapped in its needle-like particle morphology\textsuperscript{[14]}. Schatzmann \textit{et al.} introduced the method of direct precipitation of monazite. This method is desirable since it prevents formation of rhabdophane in the sample, and it is more economically feasible in comparison to the other available methods\textsuperscript{[21]}. In this research several batches of LaPO\textsubscript{4} were synthesized by the direct precipitation method at different temperature ranges. In this research several batches of LaPO\textsubscript{4} were synthesized by the direct precipitation method at different temperature ranges. Herein, an enhancement of the direct precipitation method for synthesis of high purity LaPO\textsubscript{4} has been studied, and methods for preventing the formation of the P-rich secondary phase in the La-monazite powders have been proposed.

\textbf{1.2 Experimental Methods}

\textit{1.2.1 Synthesis and Characterization of LaPO\textsubscript{4}}

Lanthanum nitrate hexahydrate (La (NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O\textsubscript{(s)}) crystalline (Alfa Aesar, 99.9\%) was dissolved in deionized water. Eighty five percent (85\%) pure phosphoric acid (H\textsubscript{3}PO\textsubscript{4(l)}) (J.T. Baker) was heated to 150°C and kept below its boiling point (duration depends on the volume of the system) to ensure that there was no water in the acid. Then, the temperature of the hot plate was brought down to the desired range. The experiment was carried out at various temperature ranges; 155°C, 145°C, 135°C, 125°C, 115°C, 105°C, and also at lower temperature ranges of 95°C, 75°C, and 55°C. The temperature control of the hot plate used is accurate to ±5°C.

The lanthanum nitrate hexahydrate solution was added drop wise to the heated phosphoric acid. Thereby, ensuring the evaporation of any free water present at temperatures above the water boiling point and also inhibiting the formation of rhabdophane during the
precipitation process. NO\textsubscript{x} gas was released when the drops came in contact with the heated phosphoric acid. Adding the solution drop wise was conducted slowly at the beginning of the procedure. After obtaining the milky precipitation (after nucleation occurs), the rate of adding the solution was increased.

The pH of the product was measured to be around 2 (BDH pH Test 0-14, VWR International Radnor, PA USA). The precipitated powders were then washed with deionized water until the pH reached 7, in order to eliminate the phosphoric acid on the surface of the particles. Water has higher surface tension than alcohol and acetone, leading to higher capillary forces and hard agglomeration in water washed powders can occur. To prevent agglomeration the powders were washed with ethanol and acetone respectively\textsuperscript{[22]}. 

The geometric densities of the dried synthesized powders and sintered samples were measured. The crystal chemistry and presence of rhabdophane in the samples synthesized with both methods were evaluated via powder X-ray Diffraction using Rigaku Smartlab diffractometer, and Rietveld analysis with Cu-K\textsubscript{α} x-ray source (\(\lambda=1.5418\ \text{Å}\)). The change in morphology and the secondary phase formed in the sintered samples were studied via secondary electron microscopy (SEM) imaging analysis using FES Magellan (400 XHR SEM). The SEM analysis was performed using an accelerating voltage range of 3-20 keV. Both powders and sintered samples were mounted on adhesive carbon tape, and were sputter coated with a thin layer of Iridium (Ir) to prevent charging during the imaging processes.
1.2.2 Sintering LaPO$_4$

The LaPO$_4$ green body samples were made using cold isostatic press (CIP) in a mold. Then, they were sintered at 1300°C for 2 hours and polished. They were examined using SEM. If there were an excess of phosphorus from synthesis, a liquid phase would form at high temperatures.

The area fraction percentage of grains, pores, and intergranular phase were quantified using the ImageJ (Image Processing and Analysis in Java) software. ImageJ performs based on the contrast in the SEM images to compare the amount of P-rich intergranular phase in samples synthesized at different temperatures and sintered in air at 1300°C for 2 hours. Each point on the graph generated by ImageJ is generated by taking the average of the area fraction percentage values generated from 5 to 7 SEM images of the cross-sectional areas of each sintered sample.

1.2.3 Excess Phosphorus Removal from the Particles

To remove any possible trapped excess phosphorus in the LaPO$_4$ florets, the powders were ball-milled in diluted ammonia with deionized water and with zirconia media. Figures 1.3 and 1.4 show the effect of washing and ball-milling on the powders.

![Figure 1.3 Washing and ball-milling the powder. Purple indicates excess phosphorus.](image-url)
Another method used for removing the excess phosphorus was annealing the powders at 800°C in flowing water vapor at 20 kPa. The flowing water vapor washed away the phosphorus on the surface of the samples. Figure 1.5 shows the setting of this section.

Also, in the case of Sr-doped LaPO₄ this method (annealing in the presence of water vapor) is primarily used, as it is important to keep the protons within the structure. Thereby, keeping the strontium doped. More details are provided in Chapter 2.
1.3 Results and Discussions

1.3.1 Crystal structure of LaPO₄ Synthesized at Different Temperature

X-Ray diffraction was performed for samples synthesized at different temperatures. The results are shown in Figure 1.6.

X-Ray powder diffraction patterns confirm that monoclinic monazite is synthesized at temperatures above 100°C. However, at temperatures below 100°C rhabdophane is formed. The formation of the hydrate form at lower temperatures is due to availability of excess water in the system. At synthesis temperatures at or above 100°C (temperature of heated acid) the water in the solution instantly evaporates as it comes into contact with the heated acid. However, at lower temperatures the water stays in the solution, which results in the formation of rhabdophane. Moreover, the peak broadening at temperatures 75°C and 55°C suggest poor crystallization of monazite and finer particle size at lower temperatures.

Based on the results shown in Figure 1.6, the samples synthesized at all temperatures between 100-150°C have the monoclinic structure, and no rhabdophane peaks were observed. However, at temperatures below 100°C a broad peak around 20 degrees can be observed, indicating that at temperature ranges below the water boiling point the hexagonal hydrate form of LaPO₄ is formed.

Figure 1.6 X-ray diffraction patterns of LaPO₄ precipitate at different temperatures.
1.3.2 Morphology and Particle Size Dependence on Synthesis Temperature

SEM images of the synthesized LaPO$_4$ at 150-160°C is shown in Figure 1.7. The LaPO$_4$ particles synthesized using the direct precipitation method have floret shape as was originally shown by Schatzmann et al for LaPO$_4$ synthesized at 150-160°C $^{[21]}$.

![SEM images of LaPO$_4$ floret-like particles synthesized at 150-160°C.](image)

Figure 1.7 SEM of LaPO$_4$ floret-like particles synthesized at 150-160°C.

At synthesis temperatures below 100°C, the LaPO$_4$ hydrate (rhabdophane) is also formed. Figure 1.8 shows the SEM images of a sample synthesized at 90-100°C using the direct precipitation method.

![SEM images of samples synthesized at 90-100°C](image)

Figure 1.8 SEM images of samples synthesized at 90-100°C
XRD of this sample (Figure 1.6) confirms the coexistence of monoclinic LaPO$_4$ and its hexagonal hydrate, rhabdophane. The morphology of this sample can be described as packs of straws. Rhabdophane has a needle-like structure, but the XRD results show primarily monazite.

SEM images of LaPO$_4$ synthesized at different temperatures are shown in Figure 1.9. More SEM images are presented in Appendix A.1-7.

Figure 1.9 SEM of monoclinic LaPO$_4$ at different synthesis temperatures. Morphology becomes more rounded as synthesis temperature decreases.
It is shown that the particles size decreased with decrease in synthesis temperature and particle morphology became more rounded. For synthesis temperatures between 150-100°C, as the temperature decreased-the precipitation occurred faster but it took longer for the precipitates to settle after the synthesis was done due to the decrease in particle size of the powders. However, for temperatures below 100°C the precipitation took a longer time. For lower synthesis temperatures, the change in color of the acid solution was observed later (from clear to milky) compared to synthesis temperatures above 100°C. At synthesis temperature of 50-60°C the precipitation started after 8 hours, and it took 24 hours for the precipitates to settle. In contrast to synthesis temperature of 150-160°C where the precipitation started within 30 minutes and it settled within minutes after the process was done. For lower temperatures the powders were settled and washed using a centrifuge.

1.3.3 Intergranular Phase Fraction with Respect to Particle Size

To investigate the amount of intergranular phase forming at different temperatures, LaPO₄ samples synthesized at 145°C, 135°C, 125°C and 115°C were sintered in air at 1300°C for 2 hours. Figure 1.10 shows the SEM images of the sintered samples synthesized at different temperatures, and a close comparison of as synthesized and sintered LaPO₄ at 140-150°C and 100-110°C is shown in Figure 1.11.
Figure 1.10 SEM of LaPO$_4$ synthesized at different temperatures, sintered in air at 1300°C for 2 hrs. Dark grey areas are the P rich intergranular phase formed at high temperatures.

Figure 1.11 SEM of LaPO$_4$: a) as synthesized at 140-150°C (left) and 100-110°C (right) b) Sintered at 1300°C in air for 2 hrs.
It is shown that as synthesis temperature decreased from 150°C to 100°C there is less intergranular phase formed when samples were sintered in air at 1300°C for 2 hours. This can be explained by the change in particle size of the samples. Washing off the excess phosphorus (without milling) in the LaPO₄ powders with smaller particle size can be more effective. Thus, less P-rich intergranular phase is formed when sintering the powders with less excess P contamination. The actual densities of the sintered samples are presented in Table 1.1.

Table 1.1 Actual densities of samples sintered in air (1300°C for 2 hrs)

<table>
<thead>
<tr>
<th>Sample's Synthesis Temperature</th>
<th>Actual Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>145°C ±5°C</td>
<td>3.97</td>
</tr>
<tr>
<td>135°C ±5°C</td>
<td>4.19</td>
</tr>
<tr>
<td>125°C ±5°C</td>
<td>4.14</td>
</tr>
<tr>
<td>115°C ±5°C</td>
<td>4.40</td>
</tr>
<tr>
<td>105°C ±5°C</td>
<td>4.11</td>
</tr>
</tbody>
</table>

Moreover, ImageJ (Image Processing and Analysis in Java) software was used to compare the amount of P-rich intergranular phase in samples synthesized at different temperatures and sintered in air at 1300°C for 2 hours. The results are shown in Figure 1.12.

It is shown that at lower synthesis temperatures, such as 110-120°C, there is less intergranular phase (liquid phase formed while sintering) formed compared to the samples synthesized at higher temperatures. This can be the result of different morphology of the samples at lower synthesis temperatures. It was shown...
that as synthesis temperature decreases the morphology become more rounded. Thus, the process of washing to remove excess P seems to be more effective for these samples.

1.3.4 Effectiveness of Excess Phosphorus Removal Processes

LaPO$_4$ synthesized at 100-110°C was chosen for this section since lesser intergranular phase was observed in this sample after being sintered in air at 1300°C compared to other samples. The effect of milling in ammonia and annealing in the water vapor on further eliminating the excess phosphorus were examined on this sample. Figure 1.13 shows the SEM of LaPO$_4$ synthesized at 100-110°C and sintered in air at 1500°C for 2 hours, after being milled in ammonia and annealed in water vapor at 800°C.

Figure 1.13  LaPO$_4$ synthesized at 100-110°C; milled in ammonia (left), or annealed with water vapor at 800°C for 1000 min (right), then sintered at 1500°C for 2 hours

LaPO$_4$ milled with ammonia before sintering at 1500°C in air has even less intergranular phase. Annealing with water vapor at 800°C for 1000 minutes prior to sintering at 1500°C was even more effective in removing excess phosphorus by volatilization. The densities of the sintered samples were 82% for LaPO$_4$ milled in ammonia and 85% when annealed in water vapor. It is shown that both methods are fairly efficient in removing the excess phosphorus from LaPO$_4$ powders. Thus, using the optimum synthesis temperature (100-
110°C) coupled with milling in ammonia or annealing in water vapor can result in single phased monoclinic LaPO$_4$ of high purity.

### 1.4 Conclusions

In this study, different batches of LaPO$_4$ were synthesized at different temperatures using the direct precipitation method. The morphologies and the possible presence of excess phosphorus were studied using SEM imaging. It was shown that morphology of the particles becomes more rounded and the particle size decreases as synthesis temperature decreased. Also, it was discovered that the synthesis technique used in this study coupled with washing (DI water, ethanol and acetone) and ball-milling the powders in ammonia, or annealing the samples in water vapor yielded monoclinic monazite without the formation of rhabdophane; negligible liquid phase was formed during sintering at 1500°C for 2 hours. Eliminating the excess phosphorus by ball-milling the powders in the dilute ammonia was found to be most effective, since annealing the powders in presence of water vapor can result in contamination of the furnace with phosphorus.

It was further demonstrated via ImageJ software analysis, that reducing the synthesis temperature by 50°C (from 150°C to 100°C) reduced intergranular phase formation by about 40% after sintering. However, the XRD result showed that at synthesis temperatures below 100°C, rhabdophane was formed. Thus, the optimal temperature range for direct precipitation synthesis of pure monoclinic monazite was confirmed to be between 100-110°C via XRD.

The synthesis of LaPO$_4$ via the direct precipitation method involves simple steps, without the need for a controlled processing environment -such as high temperatures or pressures. This makes the procedure not only more effective, but also efficient. Unlike other available methods, production of pure LaPO$_4$ using the direct precipitation method does not
require filtration, calcination, or long ripening time. In this method, the phosphoric acid used during synthesis can be recycled after the LaPO$_4$ particles have settled, and can be reused towards the same purpose. The fine LaPO$_4$ particles that are still present in the used phosphoric acid after synthesis, can act as seeds for the next synthesis rounds. The enhanced synthesis techniques that have been presented in this study have vast potential for scale up - as continuous processing methods for producing stoichiometric LaPO$_4$. However, further investigation would be required in order to evaluate and improve the method of producing stoichiometric LaPO$_4$ in large scales.
Chapter II. Sr-Doped LaPO$_4$

2.1 Introduction

2.1.1 Doped Monazite

Many different rare-earth elements with relatively large ionic radii can be incorporated in LaPO$_4$ due to its 9-fold oxygen coordination \[^{[1]}\]. For example, rare-earth elements such as Europium (Eu$^{3+}$) exhibit strong and defined luminescence, and have been investigated for their use in optical applications such as LEDs \[^{[23]}\]. When LaPO$_4$ is doped with divalent elements such as strontium (Sr$^{2+}$), it becomes a good candidate for intermediate temperature proton conduction for fuel cells \[^{[24][25][26]}\]. The stoichiometry will be La$_{1-x}$Sr$_x$PO$_4$$_x$(OH)$_x$, with x% of Sr replacing La \[^{[21]}\]. In this case, the process of allovalent doping occurs - as there is a difference in valency between the foreign atoms (Sr$^{2+}$) and the native atom, it replaces (La$^{3+}$). Their effective charge will affect the electron neutrality condition. Hence, the Sr-doped LaPO$_4$ can potentially be used in proton conducting systems.

2.1.2 Issue with Available Sr-doped LaPO$_4$ Synthesis Methods

Several methods are available for the synthesis of Sr-doped LaPO$_4$ - homogeneous precipitation, hydrothermal, and calcination methods to name a few \[^{[27][28][29]}\]. Heat treatment is a vital step in the processing of Sr-doped LaPO$_4$ so as to convert Sr-doped rhabdophane to doped monazite. However, sintering Sr-doped LaPO$_4$ in air can result in the segregation of Sr as a secondary phase, thus reducing the Sr concentration in the LaPO$_4$ structure \[^{[27]}\]. Previous work has shown that even heating Sr-doped LaPO$_4$ at 800°C in a (nitrogen environment) can lead to a decrease in the unit cell volume \[^{[27]}\]. The ionic radius of La is 1.22 Å and that of Sr is 1.31 Å with 9-fold coordination \[^{[30]}\]. Therefore, the shrink in the unit cell volume can be a result of segregation of Sr out of the structure. Other reports also mention the segregation of Sr,
as a secondary phase and the volatilization of H₂O at high temperatures \(^{[31]}\). Consequently, it is proposed herein, to keep the protons within the structure, and to carry out all the heat treatment processes required for the Sr-doped LaPO₄ in a humid environment.

As mentioned earlier, monoclinic monazite synthesis by solution routes usually results in formation of rhabdophane. Rhabdophane engenders liquid phase formation within samples during sintering at high temperatures due to the presence of excess phosphorus. Availability of a liquid phase at high temperatures detrimentally scavenges Sr\(^{2+}\) from the doped monazite. The direct precipitation method results in Sr-doped LaPO₄ directly without any further heat treatment. To date, only 4\% Sr-doped LaPO₄ has been reported using this method \(^{[21]}\).

Increasing the Sr concentration in the structure can directly increase the number of protons, which can lead to higher ionic conductivity. Thus, to increase the protonic conductivity efficiency, increasing Sr concentration in LaPO₄ structure should be considered. Here, Sr-doped LaPO₄ with different Sr concentrations was synthesized by the direct precipitation method. Monoclinic LaPO₄, with up to 30\% Sr-doping, has been synthesized using the direct precipitation synthesis method, without any formation of rhabdophane, as investigated by XRD. The morphology of the precipitated powders, under differing conditions of doping was seen using SEM. The solubility limit of Sr in LaPO₄ structure was determined by measuring Sr concentration through EDS. Also, the ionic conductivity of Sr-doped LaPO₄ with different Sr concentrations, were measured via Electrochemical Impedance Spectroscopy (EIS).
2.2 Experimental Methods

2.2.1 Synthesis of Doped LaPO$_4$

The Sr$^{2+}$ doped LaPO$_4$ was synthesized using the direct precipitation method at the temperature range of 150-160°C. Strontium nitrate Sr(NO$_3$)$_3$ was chosen as the Sr$^{2+}$ source. Also, the calculations were performed such that the composition includes x% atom substitution of strontium for lanthanum to get La$_{1-x}$Sr$_x$PO$_4$$_x$OH$_x$. For example, a 10% atom substitution of strontium for lanthanum results in (La$_{0.9}$Sr$_{0.1}$PO$_{3.9}$OH$_{0.1}$). EDS analysis was performed to examine the effectiveness of doping.

Eight five percent (85%) pure phosphoric acid (H$_3$PO$_4$(l)) was heated to 150°C and kept below its boiling point (duration depends on the volume of the system) to ensure that there was no water in the acid. For this set of experiments, the temperature of synthesis (temperature of acid) was held at 150-160°C and only Sr concentration was varied. The setting of the experiment was the same as the synthesis process described in section 1.2.1, except that here strontium nitrate and lanthanum nitrate hexahydrates solution was added drop wise to the heated phosphoric acid. Again, adding the solution drop wise was carried out slowly, till a milky precipitation was observed. The powders were washed with DI water till their pH reached 7. The powders were then washed with ethanol and acetone to reduce agglomeration, followed by drying, before being compressed by CIP. The pressed powders were then sintered in 20kPa water vapor at 1200°C for 1000 minutes.

2.2.2 Characterization of Sr-doped LaPO$_4$ Samples

Sr-doped LaPO$_4$ with 10%, 20%, 30%, 40%, 50%, and 100% nominal Sr concentration is made using this synthesis method. Different nominal Sr concentrations are based on Equation 1, where [Sr] and [La] are respectively the Sr and La starting concentrations in the
solution. Crystal structure and morphology of each sample was examined using XRD and SEM with the same instrumental parameters mentioned in Chapter 1. EDS analysis was carried out to measure the actual Sr concentrations of the compressed powders.

\[
\frac{100 \times [\text{Sr}]}{[\text{Sr}] + [\text{La}]} 
\]

(1)

Ionic conductivity measurements of the compressed sample powders (both sintered and non-sintered) with Pt coatings were carried out both in air and water vapor at 300°C to 500°C via EIS and the results were converted by Zview. During EIS measurements, the temperature was ramped up at a 25°C/hour ramp rate. XRD analysis was performed after the EIS measurements were completed.

2.3 Results and Discussion

2.3.1 Crystal Structure of Sr-doped LaPO₄ with Varied Sr Concentrations

X-Ray diffraction was performed for Sr-doped samples synthesized with different Sr concentrations. The results are shown in Figure 2.1. X-Ray powder diffraction patterns confirm that monoclinic monazite is synthesized for 10-40% Sr samples. However, extra peaks are observed for samples with higher Sr concentrations.
A single phase of LaPO$_4$ was obtained for samples with up to 40% nominal Sr concentration. However, with 50% Sr concentration in the starting solution (50% Sr replacing La), both Sr(H$_2$PO$_4$)$_2$ and LaPO$_4$ phases are formed. To study the segregation of Sr in the samples, only Sr(NO$_3$)$_2$·6H$_2$O solution was added drop wise to phosphoric acid (is indicated as Sr100% in Fig. 2.1). It should be noted that the resultant Sr(H$_2$PO$_4$)$_2$ phase was very soluble in water, and thus washing the samples with DI water resulted in dissolving the Sr(H$_2$PO$_4$)$_2$ precipitates. Therefore, the sample with 100% nominal Sr concentration was washed with ethanol and acetone only, and then dried after the synthesis process to investigate the secondary phase by XRD.

2.3.2 Morphology of Sr-doped LaPO$_4$ with Different Sr Concentrations

SEM analysis was used to study the change in morphology and particle size with respect to change in Sr concentration. The SEM images of Sr-doped LaPO$_4$ precipitates with
different nominal Sr concentrations are shown in Figure 2.2. The sample that is referenced 100% in Fig. 2.2 represents Sr(H₂PO₄)₂, meaning Sr:La is 100:0. More SEM images of this sample are presented in Appendix B. The SEM results suggest that the morphology of Sr-doped LaPO₄ becomes more rounded as nominal Sr concentration increases.

![SEM images of Sr-doped LaPO₄ with varied nominal Sr concentrations](image)

Figure 2.2. SEM of Sr-doped LaPO₄ with varied nominal Sr concentrations (e.g. 10% means Sr:La = 10:90)

The 10-50% Sr-doped LaPO₄ precipitates were washed with DI water, ethanol and acetone prior to SEM imaging. Hence, the Sr(H₂PO₄)₂ which is very soluble in water was hypothetically washed off of these samples. However, the Sr(H₂PO₄)₂ phase that was formed through direct precipitation Sr(NO₃)₃ solution was added drop wise to phosphoric acid ) was washed with ethanol and acetone only, to prevent dissolution of the precipitates. Also, it is shown that Sr(H₂PO₄)₂ has completely different morphology in the last case as compared to the earlier cases (10-50%). More SEM images of this sample are available in Appendix B.

### 2.3.3 The EDS Analysis on Sr doped-LaPO₄

To examine the actual Sr concentrations within the Sr-doped LaPO₄ particles EDS analysis was performed, and the results are shown in Table 2.1. Since all the samples were
washed with DI water prior to being isostatically pressed (cold), it is safe to say that the Sr concentration measured is not from the Sr(H$_2$PO$_4$)$_2$ phase but from Sr within or on the surface of LaPO$_4$ particles.

<table>
<thead>
<tr>
<th>Sr/(Sr+La) atom% in particles</th>
<th>Nominal Sr%</th>
<th>Measured by EDS%</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>9.8±0.33</td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>18±0.27</td>
<td></td>
</tr>
<tr>
<td>30%</td>
<td>22±0.51</td>
<td></td>
</tr>
<tr>
<td>40%</td>
<td>28±0.31</td>
<td></td>
</tr>
<tr>
<td>50%</td>
<td>29±0.35</td>
<td></td>
</tr>
</tbody>
</table>

It should be noted that EDS analysis cannot distinguish between the Sr on the surface or within the structure of LaPO$_4$ particles. With that said, the EDS results indicate that 10% nominal Sr concentration has almost 10% actual (measured by EDS) Sr concentration in LaPO$_4$ particles. However, with higher than 30% nominal Sr concentrations, the actual Sr concentrations of the compressed powders were lower than the nominal concentrations. The highest Sr concentration measured by EDS is around 30% with 50% nominal Sr concentration. Thus far in the literature, the highest percentage of Sr solubility in LaPO$_4$ has been reported to be 20.1% at temperatures around 600°C, and it has been predicted that it would be considerably lower at 1200°C [27]. Here, it is shown that up to 30% Sr can be doped in LaPO$_4$ at synthesis temperatures as low as 150°C. Also based on the EDS results, the solubility limit of Sr in LaPO$_4$ is around 30%.

2.3.4 High Temperature Stability of Sr-doped LaPO$_4$ in Air and Water Vapor

The high temperature stability of 10-30% nominal Sr-doped LaPO$_4$ powders was evaluated by XRD in air and in the presence of 20% partial pressure water vapor. The results are shown in Figure 2.3.
Figure 2.3. XRD of heat treated Sr-doped LaPO$_4$; annealed in air at 800°C for 10 hrs (left), and sintered in presence of 20% partial pressure water vapor at 1200°C for 10 hrs (right).

The XRD results from the heat treated 10-30% Sr-doped LaPO$_4$ powders, in air and in presence of water vapor, indicate that a secondary phase is formed in both cases. The amount of each secondary phase formed increased with increasing nominal Sr concentration. The XRD results show that Sr(PO$_3$)$_2$ is formed when powders were annealed in air at 800°C for 10 hours. Moreover, a Sr$_2$P$_2$O$_7$ phase was formed when Sr-doped LaPO$_4$ powders were sintered in water vapor (20% partial pressure) at 1200°C for 10 hours. Further, the densities of sintered samples were only 50-60% of the theoretical density. Besides the instability at high temperatures, the low densities can be an issue when using this material as proton conducting electrolytes in SOFCs.
2.3.5 Sr-doped LaPO$_4$ Ionic Conductivity Measurements

The ionic conductivity of 10-30% nominal Sr-doped LaPO$_4$ was measured via EIS under water vapor pressure, for both compressed samples and the ones sintered in air at 1200°C for 10 hours. The samples were coated with Pt, since the sample holder sheaths of the instrument are coated with Pt paint on the outer side, coating the samples with Pt provides the required electrical screening. The densities of the samples were in the range of 60% of the theoretical density. The EIS measurement results and their comparison with work done by another group are presented in Figure 2.4. The referenced data has been reported by Amezawa et al [32]. Based on their report, the EIS data was generated from 1-7% Sr-doped LaPO$_4$ samples sintered in air at 1200°C or 1350°C. The densities of their samples were stated as 95%, relative to the theoretical density [32]. The ionic conductivity of sintered samples was in range with results from previous work done by Amezawa et al [32]. However, cold isostatically pressed samples with similar densities that were not sintered showed a higher ionic conductivity at low temperatures, indicating the intrinsic conductivity of Sr-doped LaPO$_4$. The conductivity of compressed samples also dropped at around 500°C due to degradation of the Pt coating. Also, the ionic conductivity of sintered Sr-doped LaPO$_4$ did not increase with increasing Sr concentration. Further, the conductivity of 30% doped Sr was lower than that of the 10% doped sample, for compressed samples. This can be a result of the formation of a

Figure 2.4. EIS measurement of sintered and compressed powders of 10-30% Sr-doped LaPO$_4$ with Pt coating in water vapor at 300°C-500°C
secondary phase during the EIS measurements. In the previous section, it is shown via XRD results that the amount of each secondary phase formed during sintering of the Sr-doped LaPO$_4$ samples increased, with increasing the nominal Sr concentration. Thus, 30% Sr-doped LaPO$_4$ formed more of the secondary phase during the EIS conductivity measuring process than 10% Sr-doped LaPO$_4$. Consequently, less Sr was present in the structure, which resulted in lower protonic conductivity. The decrease in conductivity around 500°C can be attributed to the degradation of the Pt coating at that temperature.

Furthermore, density of the samples can have a huge effect on the ionic conductivity. The compressed samples had relative theoretical densities around 40%. To be able to account for the porosity of the material and have more accurate conductivity measurements, Bruggeman’s model can be used$^{[33]}$. Thus, further evaluation is required in this respect.

Both XRD and EDS results from the compressed samples after the EIS measuring process confirmed formation of secondary phases which resulted in leaching out the Sr from the grains. The XRD of the samples after the EIS is shown in Figure 2.5, and the EDS analysis is presented in Table 2.2.

![Figure 2.5. XRD of compressed 10% and 30% Sr-doped LaPO$_4$ after EIS conductivity measurements.](image)
After the EIS conductivity measurements in water vapor at 300-500°C it was learnt that although the 10% Sr-doped sample stays monoclinic, the $\text{Sr}_2\text{P}_2\text{O}_7$ secondary phase is formed for the compressed sample with 30% nominal Sr concentration. Since the Sr leached out of the grains and formed $\text{Sr}_2\text{P}_2\text{O}_7$, there was a decrease in protonic conductivity for the compressed 30% Sr doped LaPO$_4$ compared to the 10% doped sample.

Table 2.2 Sr concentration in sintered samples measured by EDS after EIS

<table>
<thead>
<tr>
<th>Sr/(Sr+La) atom% in grains</th>
<th>Nominal</th>
<th>Measured by EDS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>8.046±2.7</td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>17.32±1.8</td>
<td></td>
</tr>
<tr>
<td>30%</td>
<td>21.72±4.8</td>
<td></td>
</tr>
</tbody>
</table>

The EDS analysis of the sintered Sr-doped LaPO$_4$ samples after the EIS conductivity measurements indicated that Sr had leached out of the grains after being sintered at 1200°C in air. Therefore, from both XRD and EDS results, formation of the $\text{Sr}_2\text{P}_2\text{O}_7$ as the secondary phase in the structure is the primary cause of the decrease in conductivity at the 300-500°C temperature range.

2.4 Conclusions

Monoclinic LaPO$_4$ doped with divalent elements such as strontium ($\text{Sr}^{2+}$) is a good material candidate for use as electrolytes in intermediate temperature proton conducting solid oxide fuel cells (SOFC). Producing Sr-doped LaPO$_4$ with current synthesis methods requires heat treatment of the material. However, heat-treating can result in segregation of the Sr and thus formation of a secondary phase, which can reduce the protonic conductivity of this
material. Sr-doped LaPO$_4$ can be produced via direct precipitation method without any heat treatment.

Here, Sr-doped LaPO$_4$ with up to 50% nominal and around 30% actual Sr concentration has been synthesized using the direct precipitation method. XRD and SEM analysis was used to examine the crystal structure and change in morphology of samples with 10-50% nominal Sr concentrations. Also, the protonic conductivity of the 10-30% Sr-doped LaPO$_4$ has been measured with EIS in water vapor and at 300-500°C. It is shown that, a single phase of LaPO$_4$ was detected by XRD for samples with up to 40% nominal Sr concentration. However, with 50% Sr concentration, both Sr(H$_2$PO$_4$)$_2$ and LaPO$_4$ phases are obtained. The XRD results also showed that Sr(PO$_3$)$_2$ was formed when powders were annealed in air at 800°C for 10 hours, and Sr$_2$P$_2$O$_7$ phase was formed when Sr-doped LaPO$_4$ powders were sintered in water vapor (20% partial pressure) at 1200°C for 10 hours. In both cases, the amount of the secondary phase formed increased with increasing Sr concentration. Moreover, the SEM images of the samples showed that the morphology became more rounded as the Sr concentration increased. Based on EDS analysis, up to 30% Sr can be doped in LaPO$_4$ at synthesis temperatures as low as 150°C, and the solubility limit of Sr in LaPO$_4$ is around 30%.

The ionic conductivity measurements were the highest for compressed (non-sintered) sample with 10% Sr concentration. The XRD and EDS analysis of samples after the EIS ionic conductivity measurements in water vapor showed that Sr leached out of the grains and formed Sr$_2$P$_2$O$_7$, which in turn reduced proton conductivity. To improve the ionic conductivity of this material further evaluations and porosity correction calculations are required.

Doping high Sr concentrations in LaPO$_4$ is possible through the direct precipitation method. However, the lower stability of Sr-doped LaPO$_4$ at higher temperatures, results in the
formation of a secondary phase, which hampers any further density improvements in the samples (as the material is not stable at higher temperatures), thus making this material less suitable for use as an electrolyte in solid oxide fuel cells. Hence, a breakthrough improvement is required in order to make this material suitable for the proposed application. To improve the ionic conductivity of Sr-doped LaPO$_4$, the synthesis method should be enhanced in such a manner so as to prevent the formation of the liquid phase, and also the segregation of Sr out of the LaPO$_4$ grains at higher temperatures. It is important that different methods such as flash sintering be investigated in an effort towards increasing the densities of this material.
References


31. Frode Tyholdt, Jens Anton Horst, Sissel Jorgensen, Thomas Ostvold, and Truls Norby.

32. K. Amezawa, H. Maekawa, Y. Tomii, & N. Yamamoto, "Protonic conduction and

33. V. D. Bruggeman, "Calculation of various physics constants in heterogenous
substances I Dielectricity constants and conductivity of mixed bodies from isotropic
Appendices

Appendix A. SEM Images of LaPO$_4$ Particles

A.1 SEM images of LaPO$_4$ particles synthesized 140-150°C
A.2 SEM images of LaPO$_4$ particles synthesized 130-140°C
A.3 SEM images of LaPO$_4$ particles synthesized 120-130°C

A.4 SEM images of LaPO$_4$ particles synthesized 110-120°C
A.5 SEM images of LaPO₄ particles synthesized 100-110°C
A.6 SEM images of LaPO$_4$ particles synthesized 90-100°C
A.7 SEM images of LaPO$_4$ particles synthesized 50-60°C
Appendix B. SEM images of Sr(H$_2$PO$_4$)$_2$