Preparation and characterization of perovskite structure lanthanum gallate and lanthanum aluminate based oxides

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Department of Materials Science and Engineering
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and lanthanum aluminate based oxides

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ABSTRACT

The present work was initiated to study the synthesis and properties of lanthanum gallate based oxides as intermediate temperature electrolyte for solid oxide fuel cells. The wet chemical method, polymer complexing route, was used to prepare the precursor powders. To further investigate the polymer complexing method, it was also applied to the preparation of lanthanum aluminate based oxides.

Single perovskite phase $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$ can be prepared by the polymer complexing method using PVA as complexing agent. The thermal decomposition of the precursor powder undergoes three stages. While complete decomposition of the precursor is obtained at 1000°C. Further investigation of $\text{LaGaO}_3$ doped with various amounts Sr or/and Mg was conducted. Three secondary phases were identified by X-ray diffraction, e.g. $\text{LaSrGaO}_4$, $\text{LaSrGa}_3\text{O}_7$ and $\text{La}_4\text{Ga}_2\text{O}_9$. The relative amount of these secondary phases depends on the doping compositions. Sr doping produced more Sr rich secondary phases with increasing content, while enhanced solid solubility was observed with Mg addition. Sintered samples showed dense microstructures with well-developed equiaxed grains, and the secondary phases were mainly in the grain boundaries. The oxygen ionic conductivity was enhanced by doping with Sr and Mg. Mg doping showed the increased activation energy of conductivity.

Preliminary study showed that the lanthanum gallate and ceria composite electrolyte is mainly fluorite $\text{CeO}_2$ phase after sintering. The minority secondary phase, $\text{Sm}_3\text{Ga}_5\text{O}_{12}$, was also detected by XRD. The composite electrolyte showed superior electrical performance. It exhibited the highest conductivity in the temperature range of 250–600°C, compared with lanthanum gallate and ceria specimens.

The phase pure perovskite $\text{La}_{0.9}\text{Sr}_{0.1}\text{Al}_{0.85}\text{Mg}_{0.1}\text{Co}_{0.05}\text{O}_{2.875}$ powders can easily be obtained by the polymer method using PVA as complexing agent. No secondary phase was detected after calcination at various temperatures (500–1100°C). The fully crystallized $\text{LaAlO}_3$ phase was prepared after calcination at 900°C. Meanwhile the secondary phases were difficult to eliminate in the Sr- and Mg- doped $\text{LaGaO}_3$ powder prepared by the same polymer method. It is thus concluded that the polymer, PVA in this work, provides more homogeneous mixing for cations of lanthanum aluminate based oxides, compared with the one for doped lanthanum gallate.

The influence of different complexing agents, e.g. PVA and PEG, was investigated in the synthesis of lanthanum aluminate powders. Minority impurity $\text{La}_2\text{O}_3$ existed in the PEG powder, but it could be eliminated after sintering at high temperatures. Although the pure phase $\text{LaAlO}_3$ can be easily obtained in PVA powders calcined at 950°C, more seriously aggregated particles existed. PEG showed advantages over PVA in terms of better densification and microstructure control in the sintered products. To select proper polymers in complex oxide synthesis, the agglomeration and morphology of the powder are the most important factors to be considered.

Key words: Lanthanum gallate, lanthanum aluminate, ceria, composite, solid oxide fuel cell, electrolyte, polymer complexing.
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Shuai Li (李帅)

Stockholm, April 2009
SUPPLEMENTS

The thesis is based on the following papers:

Supplement 1  “Doping effect on secondary phases, microstructure and electrical conductivities of LaGaO$_3$ based perovskites”
Shuai Li, Bill Bergman

Supplement 2  “Preparation and characterisation of perovskite La$_{0.8}$Sr$_{0.2}$Ga$_{0.83}$Mg$_{0.17}$O$_{2.815}$ electrolyte using a poly(vinyl alcohol) polymeric method”
Shuai Li, Bill Bergman, Zhe Zhao
Submitted to *Solid State Ionics*, 2009

Supplement 3  “Synthesis of La$_{0.9}$Sr$_{0.1}$Al$_{0.85}$Mg$_{0.1}$Co$_{0.05}$O$_{2.875}$ using a polymeric method”
Shuai Li, Bill Bergman, Zhe Zhao

Supplement 4  “Synthesis and characterisation of lanthanum aluminate powders via a polymer complexing plus combustion route”
Shuai Li, Zhe Zhao, Bill Bergman
Submitted to *Materials Chemistry and Physics*, 2009

Supplement 5  “Lanthanum gallate and ceria composite as electrolyte for solid oxide fuel cells”
Shuai Li, Zhicheng Li, Bill Bergman
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The author’s contribution to the supplements in the thesis:

Supplement 1: Literature survey, experimental work, data analysis, major part of writing.

Supplement 2: Literature survey, experimental work, data analysis, major part of writing.

Supplement 3: Literature survey, experimental work, data analysis, major part of writing.

Supplement 4: Literature survey, experimental work, data analysis, major part of writing.

Supplement 5: Literature survey, experimental work, data analysis, major part of writing.
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INTRODUCTION

Solid oxide fuel cells (SOFCs) provide efficient and clean energy conversion from chemical energy of fuels to electrical power.\(^1\)\(^-\)\(^3\) A fuel cell consists of anode, cathode and electrolyte. The construction of a solid oxide fuel cell is shown in Fig. 1.1. In the SOFC, fuel is in the anode side, gets oxidized and releases electrons. These electrons travel through the outer circuit and then come to the cathode side. Oxidant at the cathode accepts electrons and gets reduced into oxygen anions. The electrolyte provides a path for the travelling of oxygen anions, and meanwhile separates fuels and oxidants.

![Fig. 1.1 Schematic diagram of solid oxide fuel cells.](image)

The traditional SOFCs with yttria-stabilized zirconia (YSZ) electrolyte need high operating temperatures (800–1000°C) to obtain a high enough ionic conductivity. The high operating temperature improves reaction kinetics, allows reforming of hydrocarbon fuels, e.g. methane or natural gas, within the fuel cells and produces byproduct heat for cogeneration.\(^1\)\(^,\)\(^2\) On the other hand, it also exerts harsh requirements on the materials. First of all, the components in SOFC should be stable at high temperatures, in the aspects of chemical, phase, microstructure and so on. Secondly, chemical stability and thermal match between different components should also be considered at elevated temperatures. Therefore, the development of novel electrolyte which can operate at intermediate temperatures (500–800°C) has attracted enormous attention in recent years. To reduce the operating temperature to such a low temperature, the reduction of resistance of electrolyte should be considered first. One approach is to use thin film YSZ electrolyte.\(^4\) Another alternative is to use a solid electrolyte with higher ionic conductivity, such as the stabilized Bi\(_2\)O\(_3\) and CeO\(_2\). Although the stabilized Bi\(_2\)O\(_3\) has higher ionic conductivity at comparable temperatures than other electrolytes, the application of this material has a problem of chemical stability under low oxygen partial pressures.\(^1\)\(^,\)\(^5\) Bi\(_2\)O\(_3\) is easily reduced and decomposes to metallic bismuth even at moderately low oxygen partial pressure.\(^5\) Ceria based oxides show higher conductivity at intermediate temperatures when compared with YSZ, however, the materials are mixed conductor at low oxygen partial pressures, because of the reduction of Ce\(^{4+}\) to Ce\(^{3+}\).\(^6\) The perovskite lanthanum gallate based oxides were recently reported to be a high conductive electrolyte. In 1994, Ishihara et al.\(^7\) and Feng and Goodenough\(^8\) reported that the perovskite LaGaO\(_3\)
doped with Sr and Mg had an oxide ion conductivity $\sigma > 0.10$ S/cm at 800°C, which exceeded those of YSZ by a factor of about three. Moreover, the materials had a near unity transference number in the oxygen partial pressure region from $10^{-22}$ to 1 atm and showed a stable performance over long operation time. These superior electrical and chemical properties make the LaGaO$_3$ based oxide one of the most promising candidates as intermediate temperature electrolytes for SOFCs.

The synthesis of phase pure LSGM ceramics is rather difficult, and the secondary phases depend strongly on the synthesis methods. The common secondary phases found in LSGM are LaSrGaO$_4$ and LaSrGa$_3$O$_7$. While in a phase diagram study by Majewski et al., further secondary phases exist in the quaternary system La$_2$O$_3$-SrO-MgO-Ga$_2$O$_3$, e.g. LaSrGaO$_4$, LaSrGa$_3$O$_7$, MgO, Ga$_2$O$_3$, and MgGa$_2$O$_4$. Moreover, the amounts of secondary phases in LSGM may not only relate to the synthesis route, but also depend on the dopants. For example, when Sr and Mg were present together, it was found that the solubility of Sr and Mg in LaGaO$_3$ increased significantly. Polini reported that the amount of secondary phases decreased with the increase of Mg at a given Sr content, while increased with the Sr content at a given Mg content. The LaGaO$_3$ based oxides are normally produced by the solid state reaction method. Although the method is used for its simplicity, the process is not satisfactory due to drawbacks such as impurities introduced by milling, high reaction temperature, coarse grains and low chemical homogeneity. Therefore, wet chemical methods were developed to prepare these LSGM oxides, such as sol-gel, Pechini, combustion, and polymer complexing route. The wet chemical methods are believed to mix the component cations homogeneously at atomic level. The homogeneous mixing therefore can result in a better powder compared with the solid state reaction method. The powder has better morphology, in the aspects of grain size, grain size distribution and agglomeration. In the present work, we chose a simple and cost-effective wet chemical method, the polymer complexing method, to prepare the doped lanthanum gallate powders. The method is characterized with stabilization of cations in liquid through either chemical binding between functional groups in polymer chains and cations or steric entrapment of cations into the polymer network. This stabilization process prevents precipitation and thus ensures a homogeneous mixing of components at atomic level.

To further investigate the polymer complexing method, lanthanum aluminate based oxides was also prepared. LaAlO$_3$ ceramics can be used as resonators in microwave filter application due to its favourable microwave dielectric properties. Lanthanum aluminate has a perovskite structure, similar as lanthanum gallate. This material has small lattice and thermal mismatches with perovskite materials, and thus has emerged as one of the most favoured high-temperature superconducting (HTS) substrates or buffer layers for depositing ferroelectric films. Because lanthanum aluminate has a similar perovskite structure as lanthanum gallate, it is expected that the behaviour of synthesis of lanthanum aluminate is comparable to the one of lanthanum gallate.

The application of lanthanum gallate based oxides was further examined by the lanthanum gallate and ceria composite electrolyte. This composite electrolyte has been shown to have promising electrical performance by Xu et al. As a matter of fact, the extraordinary electrical properties of the composite electrolyte have been known for decades. In 1973, Liang reported a substantial increase of ionic conductivity of lithium iodide with the incorporation of the inert phase, aluminum.
oxide. Mishima et al.\textsuperscript{25} investigated the CSO-YSZ composite electrolyte. The addition of CSO demonstrates an improvement of electrical conductivity of the composite electrolyte. Meanwhile, the electronic conduction of CSO is successfully blocked in the composite electrolyte, as the composite possesses a microstructure with CSO particles well dispersed in the YSZ matrix.

In the present work, a systematic investigation on the synthesis and characterization of perovskite structured oxides, particularly lanthanum gallate and lanthanum aluminate based oxides was performed, by using a polymer complexing method. In addition, a composite electrolyte, lanthanum gallate and ceria composite, was also investigated as a promising process for fuel cell electrolyte. Through the thesis, $\text{La}_{1-x}\text{Sr}_{x}\text{Ga}_{1-y}\text{Mg}_{y}\text{O}_{3-\delta}$ composition is referred to LSGM with numbers denoting contents of Sr and Mg. For example, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.9}\text{Mg}_{0.1}\text{O}_{2.85}$ is denoted as LSGM2010.
2 OXYGEN CONDUCTION

Oxides with high ionic conductivity normally have open structure, such as fluorite and perovskite. The ideal perovskite structure (ABO₃) is shown in Fig. 2.1. The perovskite structure oxides have high tolerance to changes of the radii of A and B cations and can thus easily accept dopant cations. The addition of dopants gives rise to oxygen vacancies, which are essential for the oxygen conduction in oxygen ionic conductors. The theoretical consideration of oxygen conduction in perovskite is illustrated in this chapter.⁶,²⁶,²⁷

Fig. 2.1 The ideal perovskite structure ABO₃.

2.1 Oxygen vacancy migration

Let us consider first a crystal with \( N \) oxygen sites per unit volume, \( \left[ V_o^- \right] \) is the oxygen vacancy fraction, and \( 1 - \left[ V_o^- \right] \) is the fraction of oxygen atoms in oxygen sites. The diffusion coefficient for oxygen vacancies is expressed in the following general form,

\[
D = a_0^2 \nu_0 \exp\left( -\frac{\Delta G_m}{kT} \right) \quad (2.1)
\]

where \( a_0 \) is the jump distance of oxygen vacancy, \( \nu_0 \) is the characteristic lattice vibration frequency and \( \Delta G_m \) is the free energy of migration.

\[
\Delta G_m = \Delta H_m - T \Delta S_m \quad (2.2)
\]

\( \Delta H_m \) is the migration enthalpy, \( \Delta S_m \) is the migration entropy. Substituting the Eq. 2.2 into Eq. 2.1 gives

\[
D = a_0^2 \nu_0 \exp\left( \frac{\Delta S_m}{k} \right) \exp\left( -\frac{\Delta H_m}{kT} \right) \quad (2.3)
\]

According to the Nernst-Einstein relation, the mobility \( \mu \) of charged ions is expressed with the corresponding diffusion coefficient.
The oxygen ionic conductivity is obtained from following,

$$\sigma = nq\mu$$  \hspace{1cm} (2.5)

where \(n\) is the number of oxygen vacancies per unit volume and it is given by \(N_{OV}\), \(q\) is the charge of oxygen vacancy.

Substituting Eqs. 2.3 and 2.4 into Eq. 2.5 gives

$$\sigma T = \frac{q^2}{k}Na_i^2\nu_0[V_o^-] \exp\left(\frac{\Delta S_m}{k}\right) \exp\left(-\frac{\Delta H_m}{kT}\right)$$  \hspace{1cm} (2.6)

This equation is comparable with the empirical Arrhenius equation, which is used to describe the temperature dependence of the electrical conductivity.

$$\sigma T = A \ln\left(\frac{E}{kT}\right)$$  \hspace{1cm} (2.7)

In Eq. 2.7, \(A\) is the pre-exponential factor and \(E\) is the activation energy of conductivity. The factor \(A\) increases with the fraction of oxygen vacancies, and the activation energy \(E\) can be seen dependent on the migration enthalpy of oxygen vacancies.

2.2 Defect association

So far, we assumed that defects are independent and do not influence each other. However, opposite charges form associates to keep the electrical neutrality when one kind of charged defects is introduced. There is always possibility of electrostatic attraction between the oppositely charged defects. Thus, it is reasonable to assume that the defects in crystal can form defect associates. Take for example the Mg-doped LaGaO\(_3\), where Mg atoms substitute Ga atoms.

$$[\{\text{Mg}_{Ga}^-V_o^+\}] = \text{Mg}_{Ga}^+ + V_o^-$$  \hspace{1cm} (2.8)

Applying the law of mass action to this reaction gives

$$\left[\text{Mg}_{Ga}^-\right]\left[V_o^-\right]/\left[\{\text{Mg}_{Ga}^-V_o^+\}\right] = K_a(T)$$  \hspace{1cm} (2.9)

Considering the electrical neutral condition in the crystal, we have

$$\left[\text{Mg}_{Ga}^-\right] = 2\left[V_o^-\right] + \left[\{\text{Mg}_{Ga}^-V_o^+\}\right]$$  \hspace{1cm} (2.10)

If we assume the extreme case of full association of defects, it gives
\[
\left[ \{\text{Mg}_{Ga}^+ V_O^-\}^+ \right] \gg \left[ V_O^- \right], \left[ \{\text{Mg}_{Ga}^+ V_O^-\}^+ \right] = C_{Mg} \tag{2.11}
\]

where \(C_{Mg}\) is the concentration of Mg in LaGaO\(_3\). The equilibrium constant \(K_a(T)\) has the following form,

\[
K_a = K_a^0 \exp\left(\frac{\Delta S_a}{k}\right) \exp\left(-\frac{\Delta H_a}{kT}\right) \tag{2.12}
\]

\(K_a^0\) is a pre-exponential constant. The fraction of oxygen vacancies is given by substituting Eqs. 2.10, 2.11 and 2.12 into Eq. 2.9,

\[
\left[ V_O^- \right] = K_a^0 \exp\left(\frac{\Delta S_a}{k}\right) \exp\left(-\frac{\Delta H_a}{kT}\right) \tag{2.13}
\]

Then we have the following equation, similar as Eq. 2.7.

\[
\sigma T = A \exp\left(-\frac{\Delta H_m + \Delta H_m}{kT}\right) \tag{2.14}
\]

\[
A = \frac{q^2}{k} N_{o^2} K_a^0 \exp\left(\frac{\Delta S_m}{k}\right) \exp\left(\frac{\Delta S_m}{k}\right) \tag{2.15}
\]

In the case where there are defect associates, the activation energy \(E\) then depends on the association enthalpy and migration enthalpy of oxygen vacancies.
3 EXPERIMENTAL

3.1 Powder preparation

The chemical reagents used for the powder preparation are listed in Table 3.1.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Chemical formula</th>
<th>Purity</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lanthanum nitrate</td>
<td>La(NO₃)₃·6H₂O</td>
<td>99.99%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Strontium nitrate</td>
<td>Sr(NO₃)₂</td>
<td>99.97%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Gallium nitrate*</td>
<td>Ga(NO₃)₃·xH₂O</td>
<td>99.9%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Magnesium nitrate</td>
<td>Mg(NO₃)₂·6H₂O</td>
<td>99.97%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Aluminium nitrate</td>
<td>Al(NO₃)₃·9H₂O</td>
<td>98%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Cobalt nitrate</td>
<td>Co(NO₃)₂·6H₂O</td>
<td>&gt;98.0%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Poly(vinyl alcohol) (PVA)</td>
<td>−(CH₂−CHOH)_n−</td>
<td>NA</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Poly(ethylene glycol) (PEG)</td>
<td>H−(O−CH₂−CH₂)_n−−OH</td>
<td>NA</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Lanthanum oxide</td>
<td>La₂O₃</td>
<td>99.99%</td>
<td>KEBO</td>
</tr>
<tr>
<td>Gallium oxide</td>
<td>Ga₂O₃</td>
<td>99.999%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Strontium carbonate</td>
<td>SrCO₃</td>
<td>99.99%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Magnesium oxide</td>
<td>MgO</td>
<td>99.95%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Cerium oxide</td>
<td>CeO₂</td>
<td>99.9%</td>
<td>Rare Earth Co.</td>
</tr>
<tr>
<td>Samarium oxide</td>
<td>Sm₂O₃</td>
<td>99.9%</td>
<td>Baotou Inst. Rare Earth</td>
</tr>
<tr>
<td>Ammonia solution</td>
<td>NH₃</td>
<td>25%</td>
<td>Merck</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO₃</td>
<td>65%</td>
<td>Merck</td>
</tr>
</tbody>
</table>

Note: * The x value in the formula of gallium nitrate is determined to be 9 using a thermogravimetric analysis.

3.1.1 Polymer complexing route

![Flow chart](image)

Fig. 3.1 Flow chart for the powder preparation using a polymer complexing route.
Fig. 3.1 shows the flow chart of the polymer complexing process for preparing oxide powders. The lanthanum gallate and lanthanum aluminate based oxide powders were prepared by using PVA or PEG as complexing agents. The comprising nitrate salts were dissolved in distilled water in stoichiometric proportions. The polymer solution was made by dissolving PVA or PEG in distilled water. The as prepared solutions were then mixed together in a glass beaker. The proportion of PVA or PEG to nitrate salts was adjusted according to the required ratio. The precursor solution was homogenized for 1 h at room temperature, and then heated to evaporate water while stirring. No precipitation was observed as water evaporated. A crisp gel was finally formed. The obtained crisp gel was grounded with an agate mortar, and then calcined in air atmosphere.

3.1.2 Coprecipitation route

![Flow chart of the coprecipitation route](image)

The coprecipitation method was also used to prepare the oxide powders. The flow chart for the coprecipitation route is shown in Fig. 3.2. Stoichiometric amounts of comprising oxides and/or carbonates were first dissolved in nitric acid solution by stirring on a hot plate. After the complete dissolution of these component oxides and/or carbonates, this solution was added dropwise into a stirred ammonia solution at 80°C. A white precipitate was formed at a pH value around 9. The resulting precipitate was then aged for 24 h on the hot plate and evaporated in the oven at 150°C. Calcination was subsequently carried out for the dry precursor powder.

3.2 Characterization

The phases in calcined and sintered samples were examined by powder X-ray diffraction (XRD) (X’Pert Pro, PANalytical) with Cu Kα radiation (45 kV, 40 mA).
The amount of secondary phases is estimated by the integrated intensity of the most intense peaks of comprising phases in specimen. This is a semi quantitative estimation of XRD patterns and reflects the relative amount of phases. To calculate the lattice parameters, all diffraction peaks are evaluated by means of the UNIT-CELL program. The average grain size of the powder is estimated using the Scherrer’s formula:

\[ d = \frac{0.9 \lambda}{\beta \cos \theta} \]  

(3.1)

where \( d \) is the average grain size, \( \lambda \) is the wavelength of Cu K\( \alpha \), \( \beta \) is the full width at half maximum intensity, and \( \theta \) is the Bragg’s angle.

Thermal analysis was used to characterize the thermal decomposition behaviour of precursor powders. Thermogravimetric analysis (TG) (TAG 24, SETARAM) and differential thermal analysis (DTA) (TG-DTA 1600, Labsys) were used in our work. The powder was heated up to 1200°C with air flow at a heating rate of 10°C/min. Al\( \text{2O}_3 \) powder was used as reference material in the DTA measurements.

Fourier transform infrared (FTIR) (IFS 55, Bruker) was performed to analyze the chemical structures in specimens. The wave number was in a range of 400–4000cm\(^{-1}\). The powder was mixed with dry KBr to form pellet for the FTIR measurement.

The morphology of powders and pellets was studied by scanning electron microscope (SEM). To illustrate the morphology of LSGM pellet surface, pellets were first polished and then thermally etched at 1350°C for 0.5 h. While for the fracture surface, such a thermal etching process is not necessary. To avoid the electronic charging, powders and pellets were Pt/Au or carbon coated. The density of sintered pellets was measured by the Archimedes method.

![Fig. 3.3 The schematic setup of sample holder for the impedance measurements at high temperatures.](image)

The electrical characterization of specimens was carried out by impedance spectroscopy. Sintered pellets were first wet-ground to remove the surface layer. Gold paste or platinum paste was then applied on both sides of the pellets and cured at 730°C for 2 h or 1100°C for 0.5 h. The setup of sample holder for the impedance measurement at high temperatures is shown in Fig. 3.3. Impedance from cables, leads
and sample holders obtained by measuring a blank cell was subtracted from the sample impedance spectra.
4 RESULTS AND DISCUSSIONS

4.1 Lanthanum gallate based oxides

In this section, it is focused on the preparation and characterization of lanthanum gallate based oxides. In general, the properties of the sintered pellets, such as phase purity, morphology and electrical properties etc., strongly depend on the processing route. The lanthanum gallate based oxides were prepared by the polymer complexing method using PVA as a complexing agent.

4.1.1 Characterization of precursor powders

4.1.1.1 Thermal analysis

![Fig. 4.1 TG/DTA curves showing the thermal decomposition of the LSGM2017 precursor powder.](image)

The thermal decomposition behaviour of the LSGM2017 precursor powder was characterized by TG and DTA, as shown in Fig. 4.1. The DTA curve exhibits a weak and broad endothermic peak at around 100°C, which is followed by two pronounced exothermic peaks at 366°C and 615°C. While, the TG curve shows the thermal weight loss as a function of temperature, corresponding to the DTA peaks. Clearly, most of the organics in the precursor powder decompose at temperature <760°C, yielding a weight loss of 23.6% in the TG curve. Furthermore, the thermal decomposition can be divided into three stages according to Fig. 4.1. The first stage happens below 290°C, with a weight loss of 2.5% related to the weak endothermic peak at 100°C. This weight loss is ascribed to the desorption of the absorbed water. In addition, the dehydration and depolymerisation of the polymeric residual in precursor could be another reason for this weight loss. The second stage occurs at the temperature range of 290–760°C with a weight loss of 21.1%, which is explained by the complex decomposition reactions of organics and nitrates. The carbonates, such as SrCO₃ or MgCO₃, are believed to be present in this stage as well. In the third stage over a temperature range of 760–1000°C, a slight 2.0% weight loss is observed. This weight loss could be due to the decomposition of carbonate intermediates. There is no
evidence of more weight loss above 1000°C, and this means a complete decomposition for the precursor powder.

4.1.1.2 IR spectra

![FTIR spectra of LSGM2017 powders calcined at different temperatures.](image)

Fig. 4.2 FTIR spectra of LSGM2017 powders calcined at different temperatures.

The chemical structure of the calcined LSGM2017 powders was examined by FTIR. Fig. 4.2 shows the FTIR spectra for these powders heated between 250°C and 1100°C. The spectrum for the 250°C calcined powder exhibits extensive absorption peaks. The broad band at 3200–3600 cm\(^{-1}\) is due to O–H stretching vibration. The presence of -CH\(_2\) groups is detected by a weak broad band at 2900 cm\(^{-1}\), which is assigned as C-H stretching vibration. The weak peak at 2211 cm\(^{-1}\) may indicate the presence of C≡C in the 250°C calcined powder; the peak disappears with increasing temperature. PVA dehydrates to polyenes during pyrolysis, and the presence of these polyenes is indicated by the medium bands located at 1653 cm\(^{-1}\) (stretching vibration of C=C) and 816 cm\(^{-1}\) (bending of C–H). Double bands, produced by acetate groups, are observed at 1558 cm\(^{-1}\) (asymmetrical stretching vibration of COO\(^{-}\)) and 1436 cm\(^{-1}\) (symmetrical stretching vibration of COO\(^{-}\)). Remaining nitrate salts in the LSGM2017 powders are also found with the bands from NO\(_3\), located at 1380 cm\(^{-1}\) (asymmetrical stretching vibration) and 736 cm\(^{-1}\) (in plane bending). In addition, the medium bands at 1070 cm\(^{-1}\) and 860 cm\(^{-1}\) can be attributed to the stretching vibration of CO\(_3\)^2\(^{-}\), which confirms the carbonates generated by the decomposition of organics and nitrates from the above thermal analysis. The two peaks located at 2360 cm\(^{-1}\) and 2340 cm\(^{-1}\) come from the atmospheric CO\(_2\).

With increasing temperature, the FTIR spectrum shows significant changes for the bands of C=C and NO\(_3\), while only little decrease of the O–H band is observed. At 500°C, the band at 1653 cm\(^{-1}\) for C=C disappears in the powder, indicating that the polyene has decomposed at this stage. Besides, the band at 1487 cm\(^{-1}\) is due to the
The stretching vibration of $\text{CO}_3^2$, which means carbonate salts still remain in the powder. Further increase of temperature to 700°C shows apparent decrease of $\text{NO}_3^-$ band intensity; the residual nitrate salts gradually decompose as temperature increases. The 900°C calcined powder shows traceable vibrations from carbonates, and most organics vanish. The powders calcined at above 1000°C have low frequency bands besides bands from $\text{CO}_2$. These low frequency bands are characteristic of metal oxygen vibrations. This indicates a complete decomposition of precursor powder.

4.1.1.3 Phase evolution with increasing calcination temperatures

Fig. 4.3 XRD patterns showing phase evolutions for the calcined LSGM2017 powders, (O) $\text{Sr(NO}_3\text{)}_2$; (△) $\text{SrCO}_3$; (Δ) $\text{LaSrGa}_3\text{O}_7$; (+) $\text{La}_4\text{Ga}_2\text{O}_9$; (×) $\text{LaSrGaO}_4$.

Fig. 4.3 shows the XRD patterns for LSGM2017 powders calcined at various temperatures. The XRD spectrum for the powder calcined at 250°C has a broad arc-shaped continuum over $2\theta$ range of 25°–30°. It indicates that the powder is mainly amorphous. The FTIR results show that nitrates and carbonates exist in powders calcined in the temperature range of 250–900°C, and this finding is also observed in XRD patterns. The two weak diffraction peaks of the 250°C calcined powder could be indexed as $\text{Sr(NO}_3\text{)}_2$. With increasing calcination temperature to 500°C, no significant change is observed for the XRD spectrum; there is still trace amount of $\text{Sr(NO}_3\text{)}_2$ in the amorphous powder, with no evidence of other crystalline phases. The powder consists of amorphous phase after calcination at 700°C, however, no $\text{Sr(NO}_3\text{)}_2$ is found but weak peaks from $\text{SrCO}_3$ and $\text{LaSrGa}_3\text{O}_7$ instead. The nitrate salts vanish as temperature increases, corresponding well with FTIR. At 900°C, fully crystallized powder is formed since the arc-shaped continuum has disappeared from the XRD pattern. Furthermore, strong diffraction peaks from perovskite $\text{LaGaO}_3$ are observed, which means that perovskite $\text{LaGaO}_3$ phase is essentially formed after calcination at 900°C. Thus, it can be concluded that the formation of $\text{LaGaO}_3$ undergoes intermediate stages but is not directly completed from the amorphous precursor.

The secondary phases in calcined powders are shown in the XRD patterns in Fig. 4.3. These secondary phases are identified as $\text{La}_4\text{Ga}_2\text{O}_9$, $\text{LaSrGa}_3\text{O}_7$ and $\text{LaSrGaO}_4$. All
the calcined powders have secondary phases, and the LSGM2017 powder could not be obtained as phase pure even after calcination at 1100°C. The amount of secondary phases is estimated from the XRD pattern. The fractions of secondary phases are 42.8%, 36.1%, and 31.0% in powders calcined at 900°C, 1000°C and 1100°C, respectively. Therefore, it can be concluded that the amount of these secondary phases decreases with increasing calcination temperature.

4.1.2 Characterization of sintered specimens

4.1.2.1 The influence of sintering temperature and holding time on phases

![XRD patterns of sintered LSGM2017 pellets.](image)

Fig. 4.4 XRD patterns of sintered LSGM2017 pellets.

The phase evolution with various sintering temperature and holding time was investigated on LSGM2017. Fig. 4.4 shows the XRD patterns for sintered LSGM2017 pellets. The pure perovskite LaGaO$_3$ phase could be obtained after sintering at 1450°C for 10 h. All sintered pellets show mainly cubic perovskite LaGaO$_3$. The secondary phases, LaSrGa$_3$O$_7$ and LaSrGaO$_4$, can still be detected in sintered pellets. However, the La$_4$Ga$_2$O$_9$ in the calcined powder is eliminated by the sintering process. The increasing temperature thus promotes the dissolution of the secondary phases. In addition, prolonged sintering time can also decrease the amount of secondary phases, as shown in Fig. 4.4. The LSGM2017 pellet has a high relative density of 97% (theoretical density: 6.56 g/cm$^3$) after sintering at 1450°C for 10 h.

4.1.2.2 The influence of doping composition on the phases

Different doping composition can also substantially influence the phases in specimen. Fig. 4.5 shows the XRD patterns of the 1470°C sintered LSGM pellets with changing doping amount of strontium and magnesium. Apparently, all sintered pellets contain mostly perovskite LaGaO$_3$ phase. Secondary phases in sintered samples are demonstrated in the XRD patterns. These secondary phases are identified to be La$_4$Ga$_2$O$_9$, LaSrGa$_3$O$_7$ and LaSrGaO$_4$. Surprisingly, all the sintered samples of La$_{1-x}$Sr$_x$Ga$_{0.95}$Mg$_{0.05}$O$_{3-\delta}$ with $x = 0.05 - 0.25$ have secondary phases (Fig. 4.5(a)). Trace amount of secondary phases is detected in La$_{1-x}$Sr$_x$Ga$_{0.95}$Mg$_{0.05}$O$_{3-\delta}$ with $x =$
0.05 – 0.20, while La$_{0.75}$Sr$_{0.25}$Ga$_{0.95}$Mg$_{0.05}$O$_{3-\delta}$ shows quite a lot of secondary phases. The solubility of Sr in LaGaO$_3$ is 10–20 at% when the Mg content is 5 at%, as reported by various researchers. So the solubility limit of Sr in LaGaO$_3$ does not reasonably explain the presence of these secondary phases. One of the possible reasons for the trace amount of secondary phases may be the short calcination time, 3 h in this work. It is believed that a higher calcination temperature or prolonged holding time may result in a pure sintered pellet. For instance, Tas et al. found that LSGM2017 prepared by a Pechini method contained 4–5 wt% secondary phases even after calcination at 1400°C for 6 h. It was reported that the increasing calcination time or increasing firing temperature could remove these secondary phases effectively. It is seen in Fig. 4.5(b) that the secondary phases are also found in La$_{0.8}$Sr$_{0.2}$Ga$_{1-y}$Mg$_{y}$O$_{3-\delta}$ with $y = 0.05 – 0.2$, LaSrGa$_3$O$_7$ and LaSrGaO$_4$. However, as the Mg content increases, the amount of secondary phases decreases, and in particular, no secondary phase is detected in LSGM2015 and LSGM2020.

![Fig. 4.5 XRD patterns of sintered specimens, (a) La$_{1-x}$Sr$_x$Ga$_{0.95}$Mg$_{0.05}$O$_{3-\delta}$ pellets ($x = 0.05 – 0.25$); (b) La$_{0.8}$Sr$_{0.2}$Ga$_{1-y}$Mg$_{y}$O$_{3-\delta}$ pellets ($y = 0.05 – 0.20$).](image)

The amount of secondary phases in LSGM with different doping compositions was estimated by the most intense peaks of the phases. Table 4.1 shows the change of the amount of secondary phases in calcined and sintered samples. All the powders have secondary phases after calcination at 1300°C. Except for low dopant specimens, LSGM0505 and LSGM1005, calcined powders contain much secondary phases, >20% as shown in Table 4.1. The sintering process can substantially reduce the amount of these secondary phases. The amount change of secondary phases in the sintered pellets with doping content is illustrative. At an Mg content of 5 at%, the amount of secondary phases, such as LaSrGa$_3$O$_7$ and LaSrGaO$_4$, increases when the content of Sr increases. LaSrGa$_3$O$_7$ and LaSrGaO$_4$ are Sr rich compounds, so it is believed that excessive addition of Sr is compensated by formation of Sr rich
secondary phases with increasing \( x \) value in \( \text{La}_{1-x}\text{Sr}_{x}\text{Ga}_{0.95}\text{Mg}_{0.05}\text{O}_{3-\delta} \). On the other hand, when Sr is fixed at 20 at%, there is a fast decrease of the amount of Sr containing secondary phases as the Mg content increases. The solubility of Sr could be extended by the addition of Mg.

Table 4.1 Estimation of the amount of secondary phases in LSGM.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>( \text{LaSrGa}_3\text{O}_7 ) (%)</th>
<th>( \text{LaSrGa}_4\text{O}_4 ) (%)</th>
<th>( \text{La}_4\text{Ga}_2\text{O}_9 ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSGM0505</td>
<td>1.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LSGM1005</td>
<td>5.1</td>
<td>2.0</td>
<td>0</td>
</tr>
<tr>
<td>LSGM1505</td>
<td>10.9</td>
<td>0.0</td>
<td>5.8</td>
</tr>
<tr>
<td>LSGM2005</td>
<td>15.3</td>
<td>4.0</td>
<td>8.9</td>
</tr>
<tr>
<td>LSGM2505</td>
<td>25.6</td>
<td>14.1</td>
<td>14.1</td>
</tr>
<tr>
<td>LSGM2010</td>
<td>16.1</td>
<td>3.0</td>
<td>10.9</td>
</tr>
<tr>
<td>LSGM2015</td>
<td>13.5</td>
<td>0.0</td>
<td>11.0</td>
</tr>
<tr>
<td>LSGM2020</td>
<td>9.2</td>
<td>0.0</td>
<td>14.3</td>
</tr>
</tbody>
</table>

4.1.2.3 Microstructure of sintered specimens

The SEM microstructures of \( \text{La}_{1-x}\text{Sr}_{x}\text{Ga}_{0.95}\text{Mg}_{0.05}\text{O}_{3-\delta} \) \((x = 0.05 - 0.25)\), polished and thermally etched at 1350°C, are shown in Fig. 4.6. An equiaxed microstructure with no abnormal grain growth is shown. The pellets are dense and with few pores. Increasing Sr content results in bigger grains, but this is not apparent at high Sr doping content. However, SEM illustrates increasing grain sizes for \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta} \) \((y = 0.10 - 0.20)\) pellets. The reason for the larger average grain size \((20 - 26 \mu\text{m})\) in LSGM2015 and LSGM2020 could be due to less secondary phases (Table 4.1). The density of all sintered pellets is larger than 97% of theoretical density. Moreover, it is noticed that few and uniformly distributed pores can be seen in the SEM microstructure. Detailed examination shows that the pores are mainly accumulated along grain boundaries. However, in LSGM2015 and LSGM2020, more pores are found and they are in both grain boundaries and grain bulk. Considering the much bigger grain size in these two pellets, the reason for this could be that these pores are trapped in the grains during the grain growth.

Secondary phases could be easily distinguished from the matrix perovskite phase in the microstructures as shown in Fig. 4.6 and Fig. 4.7. The dark grains accumulated along grain boundaries are secondary phases, \( \text{LaSrGa}_3\text{O}_7 \) or \( \text{La}_4\text{Ga}_2\text{O}_9 \), demonstrated by energy dispersive spectroscopy (EDS). Although LSGM2015 is found to be single \( \text{LaGaO}_3 \) perovskite by XRD, two secondary phases are clearly visible in the SEM microstructures, Fig. 4.7(b). The small amount of secondary phases is apparently beyond the detection limit of XRD. The dark intragranular secondary phase is found to be \( \text{LaSrGa}_3\text{O}_7 \) by EDS. While for the bright plate-like phase protruding from grain surface, the region is too small for EDS analysis. Similar phenomenon was also reported by Abram et al. in a study of LSGM2017.\(^{30}\) The authors attribute this plate-like phase to be \( \text{LaSrGa}_4\text{O}_4 \). This should not be the case here, because no such bright plate-like phase could be detected by SEM in the other samples containing \( \text{LaSrGa}_4\text{O}_4 \) as determined by XRD. Therefore, no \( \text{LaSrGa}_4\text{O}_4 \) could be found in the microstructure, even when it is detected by XRD. It has been reported that \( \text{LaSrGa}_4\text{O}_4 \) has a low melting point, ~1400°C,\(^{11}\) and should be in a liquid state at the sintering temperature.
of 1470°C. The liquid phase LaSrGaO$_4$ may wet over grains, thus no detectable LaSrGaO$_4$ could be found in the microstructure. On the other hand, secondary phases, such as LaSrGa$_3$O$_7$ and La$_4$Ga$_2$O$_9$ have higher melting points, >1600°C and ~1700°C, respectively. They do not melt at the sintering temperature 1470°C, and thus remain along grain boundaries. LSGM2020 has no secondary phase in the microstructure observation, which corresponds to the XRD analysis.

Fig. 4.6 SEM showing microstructure and secondary phases of La$_{1-x}$Sr$_x$Ga$_{0.95}$Mg$_{0.05}$O$_{3-d}$, where $x = 0.05 - 0.25$, (a) LSGM0505; (b) LSGM1005; (c) LSGM1505; (d) LSGM2005; (e) LSGM2505.
Fig. 4.7 SEM showing microstructure and secondary phases of La$_{0.8}$Sr$_{0.2}$Ga$_{1-y}$Mg$_y$O$_{3-\delta}$, where $y = 0.10 – 0.20$, (a) LSGM2010; (b) LSGM2015; (c) LSGM2020.

4.1.3 Electrical properties

4.1.3.1 Impedance spectroscopy

Fig. 4.8 illustrates the change of the impedance spectrum with temperature for the LSGM2017 pellets sintered at 1450°C for 10 h. At 350°C, the impedance spectrum can resolve two semicircles, corresponding to bulk and grain boundary responses. When the temperature goes up to 400°C, the two semicircles still exist, however, the frequency limit is found to move to the higher end, as illustrated in Fig. 4.8. Further increasing the temperature to 500°C results in total disappearance of the bulk semicircle in the spectrum. The resistance ($R$) and capacitance ($C$) follow the relationship

$$\omega_{\text{max}} RC = 1$$

where $\omega_{\text{max}} = 2\pi f_{\text{max}}$ is the angular frequency at the semicircle maximum. For temperatures $\geq$450°C, the dielectric relaxation time $\tau = RC$ becomes too small ($\tau < 10^{-8}$) for $\omega_{\text{max}}$ to fall into the high frequency limitation. Only the electrode process arc can be detected in the impedance spectrum when the measuring temperature is higher than 600°C. Therefore, for impedance spectrum without apparent bulk and grain boundary response, the interception between the real axe and spectrum is taken as the total resistance for the pellet.
4.1.3.2 Composition dependence of conductivity

The total resistance could be obtained for the LSGM specimens from the impedance spectra in Fig. 4.8. The conductivity is then calculated using the following equation:

$$\sigma = \frac{1}{R} \cdot \frac{l}{S}$$  \hspace{1cm} (4.2)

where $R$ is the total resistance, $l$ is the thickness of specimen, $S$ is the cross-sectional area.

The composition dependence of conductivity of LSGM specimens is illustrated in Fig. 4.9 and Fig. 4.10. Fig. 4.9 shows the total conductivity of $La_{1-x}Sr_xGa_{0.95}Mg_{0.05}O_3$ ($x = 0.05 - 0.25$) at 600°C, 700°C and 800°C, respectively. At an Mg level of 5 at%, the conductivity increases with Sr content to a maximum at $x = 0.15$ for 600°C and $x = 0.20$ for 700°C and 800°C. This obviously reflects a different dependence of conductivity activation energy on composition. LSGM2505 has an inferior electrical conductivity, which most probably is due to the large amount of secondary phases in the sintered pellet (see Table 4.1). As shown in Fig. 4.10, the ionic conductivity...
increases with increasing Mg content initially, and decreases after reaching a maximum. LSGM2010 has the highest conductivity at 800°C, \( \sigma = 0.128 \text{ S/cm} \), which is comparable to literature values.\(^8,9\) According to Huang et al., the highest conductivity at 800°C (\( \sigma = 0.17 \text{ S/cm} \)) was observed for LSGM2017 prepared by a solid state reaction method.\(^10\) However, it was reported that LSGM with \( x + y = 0.35 \) had the highest conductivity in another work.\(^9\) This discrepancy is maybe caused by the different processing methods, microstructures and crystal structures of LSGM oxides. It should be pointed out that LSGM2010 pellet has trace amount of secondary phases according to the XRD analysis, although it has the highest ionic conductivity at 800°C. So it is reasonable to expect that the conductivity might be higher if purer perovskite phase could be obtained for LSGM2010. LSGM2015 and LSGM2020 have inferior ionic conductivities, in spite of the purer perovskite phase. As shown in the microstructures (see Fig. 4.7), the amount of pores in these two samples is found to be higher than in other specimens, and this may block the oxygen ion migration as

Fig. 4.9 The conductivity of La\(_{1-x}\)Sr\(_x\)Ga\(_{0.95}\)Mg\(_{0.05}\)O\(_{3-\delta}\) as a function of Sr content.

Fig. 4.10 The conductivity of La\(_{0.8}\)Sr\(_{0.2}\)Ga\(_{1-y}\)Mg\(_y\)O\(_{3-\delta}\) as a function of Mg content.
discussed above. The pores may thus have a deteriorating effect on the ionic conductivity for LSGM2015 and LSGM2020. Meanwhile, LSGM2015 and LSGM2020 microstructures show a thickening of the grain boundaries, Fig. 4.7. This indicates the formation of a liquid phase wetting the grains. This grain boundary thickening is probably amorphous and might be another reason for the inferior conductivity of LSGM2015 and LSGM2020.

4.1.3.3 Arrhenius plots of conductivity

![Arrhenius plots of conductivity](image)

Fig. 4.11 Arrhenius plots of total conductivity of LSGM2017 sintered pellets.

The temperature dependence of the conductivity of LSGM2017 specimen is shown in Fig. 4.11. The pellet sintered at 1450°C for 10 h has the highest conductivity over all the measured temperature range, while an inferior performance is shown for the pellet sintered at 1400°C for 10 h. Obviously, the secondary phases in the pellets exert a weakening effect on the electrical performance. The amount of secondary phases decreases with increasing sintering temperature or prolonged sintering time. The secondary phases, LaSrGa$_3$O$_7$ and LaSrGaO$_4$, have low ionic conductivity, and they block the oxygen ion migration.$^{11}$

The dependence of conductivity with temperature in electrolyte can be expressed by Arrhenius equation, $\sigma T = A \exp(-E/kT)$. It is observed in Fig. 4.11 that the slope of the curve changes at about 600°C. The plotted curves are straight lines and parallel to each other at the temperature range of 250–550°C, which indicates a similar activation energy at the temperature range. However, there is pronounced difference between the high temperature (600–800°C) curves, suggesting a different activation energy.

4.1.3.4 Activation energy of conductivity

In Table 4.2 the electrical properties of sintered LSGM samples at various compositions are compared. Activation energies ($E$) for conductivities at the temperature range 500–800°C are also listed in Table 4.2. The activation energy values are lower than the reported literature values.$^{9,10}$ The activation energy of
conductivity consists of an association energy \((E_a)\) and a migration energy \((E_m)\), where \(E_a\) is the energy needed for dissociation of oxygen vacancies from their cation atmosphere, and \(E_m\) is the migration energy of oxygen vacancies. At low temperatures both processes are present, but with increasing temperatures, only the migration energy remains at elevated temperatures. At the temperature range of 500–800°C, it is thus reasonable to attribute the activation energy \((E)\) to the migration energy \((E_m)\). The lower activation energy values could be explained by a lower migration energy. And the reason for this difference is probably related to lattice strain or mismatch introduced by different synthesis methods.

Table 4.2 Electrical properties of LSGM pellets.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Bulk conductivity (S/cm)</th>
<th>(600^\circ\text{C})</th>
<th>(700^\circ\text{C})</th>
<th>(800^\circ\text{C})</th>
<th>(\ln A)</th>
<th>(E) (eV)</th>
<th>(E) (eV)*</th>
<th>(E) (eV)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSGM0505</td>
<td>0.016</td>
<td>0.029</td>
<td>0.056</td>
<td>9.908</td>
<td>0.547</td>
<td>N/A</td>
<td>0.634</td>
<td></td>
</tr>
<tr>
<td>LSGM1005</td>
<td>0.021</td>
<td>0.044</td>
<td>0.081</td>
<td>10.875</td>
<td>0.597</td>
<td>0.87</td>
<td>0.642</td>
<td></td>
</tr>
<tr>
<td>LSGM1505</td>
<td>0.030</td>
<td>0.053</td>
<td>0.085</td>
<td>10.218</td>
<td>0.524</td>
<td>0.918</td>
<td>0.624</td>
<td></td>
</tr>
<tr>
<td>LSGM2005</td>
<td>0.027</td>
<td>0.058</td>
<td>0.102</td>
<td>11.275</td>
<td>0.609</td>
<td>0.874</td>
<td>0.602</td>
<td></td>
</tr>
<tr>
<td>LSGM2505</td>
<td>0.017</td>
<td>0.038</td>
<td>0.057</td>
<td>10.565</td>
<td>0.590</td>
<td>N/A</td>
<td>0.615</td>
<td></td>
</tr>
<tr>
<td>LSGM2010</td>
<td>0.033</td>
<td>0.079</td>
<td>0.128</td>
<td>11.588</td>
<td>0.614</td>
<td>0.950</td>
<td>0.789</td>
<td></td>
</tr>
<tr>
<td>LSGM2015</td>
<td>0.029</td>
<td>0.060</td>
<td>0.101</td>
<td>11.384</td>
<td>0.617</td>
<td>1.06</td>
<td>0.785</td>
<td></td>
</tr>
<tr>
<td>LSGM2020</td>
<td>0.019</td>
<td>0.042</td>
<td>0.093</td>
<td>12.556</td>
<td>0.739</td>
<td>1.15</td>
<td>0.837</td>
<td></td>
</tr>
</tbody>
</table>

* Ref. 9
** Ref. 10

Fig. 4.12 compares the activation energies of all samples. It is shown that the activation energy increases with increasing content of Mg. However, there is no obvious trend with increasing Sr content. This may indicate that the Mg addition increases the migration energy, while the Sr addition has no specific effect on the migration energy. Earlier calculations on the perovskite type oxides demonstrated that vacancy migration takes place along the \(<1 1 0>\) edge of the anion octahedron. In \(\text{LaGaO}_3\), an oxygen atom forms two bonds both with Ga and La. Significant binding

![Fig. 4.12 The conductivity activation energy of LSGM as a function of dopant content.](image-url)
energy between Mg and oxygen vacancy was found compared with the near-zero binding energy for Sr and oxygen vacancy using a computer simulation. This means that an oxygen vacancy is more strongly trapped by Ga-O-Mg pair than by the La-O-Sr pair. Therefore, the addition of Mg has more effect on the migration energy than Sr.

4.2 Lanthanum aluminate based oxides

Although the polymer complexing method can produce relatively satisfactory LSGM powders, the powders still contain secondary phases even after high temperature calcination. However after sintering the pellets are phase pure. Lanthanum aluminate is also a perovskite structure oxide. As a comparison, lanthanum aluminate based oxide powders were also prepared by the polymer complexing method.

4.2.1 Thermal decomposition of precursor powders

The perovskite La$_{0.9}$Sr$_{0.1}$Al$_{0.85}$Mg$_{0.1}$Co$_{0.05}$O$_{2.875}$ (LSAMC) powder was prepared by the polymer complexing method using PVA as complexing agent. The thermal decomposition behaviour of the precursor was first investigated using thermal analysis. Fig. 4.13 shows the TG/DTA curves of the LSAMC precursor powder. It can be seen that there are pronounced exothermic peaks around 215°C, 400°C, and 790°C and an endothermic peak around 75°C. TG analysis shows that most of the organics and nitrates decompose at temperatures <700°C. The decomposition of LSAMC precursor powder shows three stages, which may be overlapping. In the first stage below 160°C, the weight loss (4%) is due to evaporation of free water, corresponding to the endothermic peak around 75°C. The second stage occurs over the temperature range of 160–700°C, where complex decomposition of organics and nitrates happens and corresponds to the exothermic peaks at 215°C and 400°C in the DTA curve and with a weight loss of 24%. The third stage shows a slight weight loss of 4.5% in temperature range of 700–800°C. This weight loss could be due to the decomposition of carbonate intermediates, and the exothermic peak at 790°C corresponds to this process.

Fig. 4.13 TG/DTA curves of the LSAMC precursor powder at a heating rate of 10°C/min.
4.2.2 Phase evolution

4.2.2.1 Phase evolution with increasing temperature

Fig. 4.14 shows the XRD patterns of the LSAMC powders calcined at various temperatures for 6 h and pellet sintered at 1450°C for 5 h. Fig. 4.14 reveals that the amorphous phase starts to crystallize around 500°C, since the diffraction peaks from LaAlO$_3$ perovskite phase could be first detected at this temperature. At a calcination temperature of 700°C, it is seen that mainly crystalline LaAlO$_3$ is formed in the powder. Fully crystallized LaAlO$_3$ perovskite phase is obtained in the powders after calcination at 900°C and 1100°C, and no amorphous phase could be found. The 1450°C sintered pellet shows a rhombohedral LaAlO$_3$ perovskite phase, with lattice parameters of $a = 5.36301$ Å and $c = 13.12887$ Å, which is in good agreement with the previously reported values.$^{33,34}$

![Fig. 4.14 XRD patterns of calcined LSAMC powders and sintered pellet.](image)

Furthermore, it is shown in Fig. 4.14 that no diffraction peaks from impurity phases could be detected in the XRD patterns after calcination. It implies a homogeneous mixing of the cations in the LSAMC precursor by PVA in the polymer complexing method. The different mixing ability is demonstrated for the polymer when preparing lanthanum gallate based and lanthanum aluminate based oxides. More impurities exist during the preparation of LSGM ceramics (see Fig. 4.5), since it is not possible to obtain a phase pure LSGM powder even after calcination at 1000°C. However, the phase pure LSAMC powder can easily be prepared by the similar polymer complexing route. It is believed that homogeneous mixing of cations in the precursor is of great importance to enhance purity, reactivity and homogeneity of powders.$^{35}$ In the polymer complexing route, the floating metal ions are not only stabilized around the polymer by the complexation between cations and the hydroxyl groups (–OH), but also entrapped by the polymer network.$^{35}$ It can be expected that the PVA provides a better and more homogeneous mixing and distribution for the cations of LSAMC oxides than for the cations of LSGM.
4.2.2.2 Influence of different complexing polymers

The different complexing ability of PVA and PEG is also investigated through the synthesis of undoped lanthanum aluminate (LAO). The XRD patterns of calcined LAO powders are shown in Fig. 4.15. The PVA powder is essentially phase pure after calcination at 950°C for 6 h. As shown in Fig. 4.15(a), no secondary phase is found in this PVA powder, and all the diffraction peaks can be indexed with perovskite LaAlO$_3$ phase. The PEG sample shows mainly perovskite LaAlO$_3$ phase after calcination. However, small amount of secondary phase, namely La$_2$O$_3$, is detected as shown in Fig. 4.15(b). The fraction of La$_2$O$_3$ is estimated to be 6% by the XRD pattern.

![Fig. 4.15 XRD patterns of calcined LAO powders, (a) PVA powder; (b) PEG powder.](image)

The homogeneous mixing of cations in the precursor is of great importance to enhance homogeneity and thus the purity of obtained powders. The XRD results illustrate a different stabilization capacity of mixing cations for these two polymers. Apparently, PVA can guarantee a chemical homogeneity in the solution during the process, and thus result in calcined phase pure powder. However, all the sintered samples (1450°C, 1500°C and 1600°C) from both calcined PEG and PVA powders only show single LaAlO$_3$ phase in the XRD spectrum (Fig. 4.16(a) and (b)). The minor impurity of La$_2$O$_3$ in the PEG powder can be further consumed to form LaAlO$_3$.

![Fig. 4.16 XRD patterns of sintered LAO specimens, (a) PVA pellets; (b) PEG pellets.](image)
during the high temperature heat treatment. Although the PEG method suffers from the shortcoming of a trace amount of impurity after calcination, both methods can successfully produce single phase sintered pellets. Therefore, the impurity in LaAlO₃ powders does not influence the final sintered samples in terms of phase purity.

4.2.3 Morphology of powders

The nanometer sized particles in the calcined powders are shown in the SEM images in Fig. 4.17. Fine particles with an average grain size of ~150 nm are obtained in the PVA powder. However, these PVA powders are found to have severe hard aggregates with sintered necks between grains. The agglomerated grains tend to form a sheet-like network as shown in Fig. 4.17(a). In the PEG powder, the particles, which have a size around 100 nm, have a rather regular spherical shape and are only weakly agglomerated.

Generally, the morphology of agglomerates is independent of chemical composition, and more linked to the gel characteristics. PVA provides a continuous chemical binding position of hydroxyl groups along the polymer chain. The distance between cations is extremely small. Therefore, it is possible to obtain a strong driving force to form the chain shaped powder when the precursor is calcined in air. The intrinsic entangled conformation of PVA will further facilitate the formation of a sheet-like network in the final powder. On the contrary, each PEG molecule only provides two hydroxyl groups on the two ends for the chemical binding between the polymer and the cations. Most of the cations are stabilized by a physical entrapment process in the entangled PEG chains. The larger distance between the cations offers less possibility to have a close contact between newly formed oxide particles during the heat treatment. Duran et al. reported a stronger agglomeration in PVA powder than in PEG powder in the synthesis of CeO₂ when the same polymer complexing route was used. The green pellets prepared from PVA powders obtained obvious density gradients during dry-press process, which leads to the inferior densification.

![Fig. 4.17 Typical morphology of calcined powders, (a) PVA method; (b) PEG method.](image)

To break up agglomerates in the as-calcined powders, ball milling was used. The morphology of powders after ball milling for 2 h is shown in Fig. 4.18. Most of the sheet structures in the PVA powder disappear after the milling process. However, hard agglomerates still exist with sintered necks between several nearby particles,
which implies that the milling process is only efficient to break the big network but not the local sintered necks (Fig. 4.18(a)). While in the PEG powder, former agglomerated particles are reduced to a smaller size and with only a weak agglomeration due to van der Waals' forces, since only physical contacts between primary particles were indicated from the morphology observation.

Fig. 4.18 SEM showing the morphology of powders after ball milling for 2 h, (a) PVA method; (b) PEG method.

4.2.4 Microstructure of sintered pellets

To compare the sintering performance of these as-prepared powders, pellets were sintered at 1450°C, 1500°C and 1600°C for 5 h. The sintering behaviour of the two powders is compared in Fig. 4.19, where the relative density is plotted as a function of sintering temperature. The theoretical density of 6.52 g/cm³ is used for calculating the relative density. The PVA samples show a sharp increase in relative density when the sintering temperature increases from 1450°C to 1500°C. However, the densification is rather limited above 1500°C, with a minor increase when the temperature goes up to 1600°C, where the relative density only increases from 96.5% to 96.8%. While for PEG samples, the relative density increases with increasing sintering temperature and

Fig. 4.19 Change of the relative density as a function of sintering temperature.
this implies a continuous densification process. The highest relative density of 97.0% is obtained for the PEG pellet sintered at 1600°C for 5 h. This result is comparable to those reported by other researchers.\textsuperscript{38-40} The existence of a small amount of La\textsubscript{2}O\textsubscript{3} does not seem to be so detrimental for the sintering, especially for the densification process. Nevertheless, it is still highly preferred to remove such a minor impurity to improve the stoichiometry precision. Considering the slightly smaller particle size in PEG powder, it is quite logical to expect a higher driving force and thus a higher relative density of the sintered samples at the low temperature of 1450°C. However, a reversed sequence for densities of PVA and PEG 1500°C sintered samples is observed in Fig. 4.19, which suggests that further factors influencing densification process need to be analyzed.

![SEM images of fracture surface](image)

Fig. 4.20 shows the SEM images of the fracture surface of the sintered pellets. The images reveal that intergranular fracture mode dominates in all the LaAlO\textsubscript{3} pellets. When sintering temperature increases from 1450°C to 1600°C, both PVA and PEG samples show an increase of grain size. Although particle size is comparable in PVA and PEG powders (Fig. 4.17), the grain sizes of the sintered PVA samples are much larger than those of PEG samples. Even at a higher temperature of 1600°C, the grain size in the PEG pellet is still between 2 – 3 µm while the grain size is larger than 6 µm in the PVA sample. Intergranular pores can be found in all samples, but the characteristics of the pores are rather different in PEG and PVA samples. Firstly, a noticeable difference in the pore size development can be easily identified in all the
samples shown in Fig. 4.20. For samples sintered at 1500°C and 1600°C respectively, the pore size in PEG pellets is much smaller than in PVA pellets. There is no obvious change of the maximum pore size in the PEG pellets (indicated by the arrows in Fig. 4.20) when sintering temperature increases from 1500°C to 1600°C, while the PVA pellets show definitive increase in both average pore size and maximum pore size in Fig. 4.20. Secondly, for PVA samples, there is a clear difference in the pore surface when the sintering temperature increases from 1500°C to 1600°C, where the well developed fringes can be found in the 1600°C samples. Such a fringe can only be formed by strong surface diffusion during the sintering process. Thus, PVA samples undergo an extraordinary final sintering stage where surface diffusion is as active as other diffusion processes. If only the surface energy is considered, the concave grain surface around the pores found in PVA samples should introduce a tendency of pore shrinkage. But the further pore growth indicates that more factors need to be considered. Based on the solid state sintering theory, the numbers of grains around the pore can be expressed as a function of pore to grain size ratio. The pore growth will occur when the pore size is larger than a critical size if the dihedral angle is kept constant. The large pore size formed at lower temperature should be the reason for the pore growth at 1600°C in PVA samples. Once the surface diffusion dominates the mass transport in the sintering process, there will be no further densification and only substantial grain growth happens in polycrystalline solids. Therefore, the big difference in grain size between PEG and PVA pellets should be attributed to the active surface diffusion in the PVA samples sintered at high temperatures. Such a difference in the diffusion mechanism is highly linked with the morphology of the starting powder. PVA powder shows strongly sintered neck which leads to difficulties in removing the large pores by grain boundary diffusion during sintering. Therefore, the pore size in PVA pellets is much larger than that in PEG pellets, even if a similar density was obtained at 1500°C and 1600°C. This further indicates that PEG pellet can obtain a higher density if the starting powder can be improved in the future. Although phase purity in the PEG powder synthesis is of worse performance, the normal sintering process without active surface diffusion process gives PEG powder strong advantages over PVA powder in terms of densification and grain size control in the final product. Therefore, it can be concluded that the polymer complexing route using PEG as complexing agent can provide much better densification and microstructure control in the synthesis of complex oxides.

4.3 Lanthanum gallate and ceria composite

The composite electrolyte is an interesting alternative to obtain highly conductive electrolytes. The composite electrolyte may combine the advantages of different phases. In this work, we have prepared and investigated the doped lanthanum gallate (La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}, LSGM) and doped ceria (Ce_{0.8}Sm_{0.2}O_{1.9}, CSO) composite as electrolyte for fuel cells.

4.3.1 XRD phases

Fig. 4.21 shows the XRD diffraction pattern of the sintered LSGM-CSO composite. The XRD patterns of LSGM and CSO are included as a reference. It is found that the composite mainly has fluorite CeO_{2} phase after sintering at 1450°C. However, diffraction peaks from a minority phase, Sm_{3}Ga_{5}O_{12}, were also observed. This means that a reaction between CSO and LSGM occurs during the heat-treatment. Lanthanum and strontium have similar ionic radius as cerium, and thus La^{3+} and Sr^{2+} cations can
be dissolved into the ceria lattice.\textsuperscript{6,41} Diffusion of La\textsuperscript{3+} and Sr\textsuperscript{2+} cations into the CSO lattice leads to deficiency of A-sites in the LSGM phase. Therefore, formation of Sm\textsubscript{3}Ga\textsubscript{5}O\textsubscript{12} as a compensation can be expected to occur at the interface between the two phases, CSO and LSGM. Moreover, the coprecipitation method produces fine particles and an intimate mix of the component oxides, which leads to a large contacting interface between CSO and LSGM. It can therefore be expected that an impurity phase is formed at the interface of the contacting two phases. The inter-diffusion and reaction rate depend strongly on the particle morphology. The powder processing for preparation of LSGM-CSO composite should be controlled carefully to avoid potential reactions or diffusion among the phases. Further analysis of XRD pattern of LSGM-CSO composite shows no evidence of LaGaO\textsubscript{3} phase. LSGM reacts with CSO at the interface to form Sm\textsubscript{3}Ga\textsubscript{5}O\textsubscript{12} in the composite electrolyte, and thus the amount of remaining LSGM is too small to be detected. When Xu \textit{et al.}\textsuperscript{23} investigated the LSGM-CSO composite with 10 wt\% of LSGM added, they also did not observe any LaGaO\textsubscript{3} phase. It is suggested that LSGM in the composite is distributed along grain boundaries as a glass phase, and thus cannot be detected by XRD.

Fig. 4.21 XRD patterns showing the phases in pellets sintered at 1450°C for 5 h.

4.3.2 Electrical properties

4.3.2.1 Impedance spectra

Fig. 4.22 shows the impedance spectra of the sintered specimens measured at 250°C. The LSGM-CSO composite electrolyte has a better electrical performance. Its impedance spectrum shows a small grain boundary response and a relatively perfect grain boundary semi-circle. Compared with LSGM-CSO and LSGM, the CSO sample demonstrates the highest grain boundary response, although the CSO sample shows a pure fluorite phase as detected in the XRD pattern. The large grain boundary resistance is normally due to the microstructure defects such as impurity phases and/or pores. The density of sintered CSO pellet measured by Archimedes method was 86\% of theoretical density (7.15 g/cm\textsuperscript{3}). The CSO pellet thus contains pores
and/or defects along grain boundaries. The LSGM shows a smaller grain boundary influence than that of the CSO. However, a depressed grain boundary semicircle for LSGM pellet was found, and this indicates that a constant phase element (CPE) exists along the grain boundaries. CPE is believed to be dependent on the impurities. A more general explanation for CPE is the distortion introduced by local inhomogeneities, e.g., two- or three-phase regions, local charge inhomogeneity, and variations in composition and stoichiometry.

![Impedance spectra of sintered pellets measured at 250°C](image)

Fig. 4.22 Impedance spectra of sintered pellets measured at 250°C, (a) CSO; (b) LSGM; (c) LSGM-CSO composite.

The LSGM-CSO electrolyte has the smallest grain boundary response and a relatively perfect grain boundary semi-circle spectrum. This may be due to the space charge layer formed at the phase interfaces. It is generally accepted that the space charge layer exists in the two-phase system. The enhancement of the concentration of vacancies or interstitials is expected if the second phase is surface reactive. As discussed earlier, the LSGM in the composite electrolyte may exist along grain boundaries, and thus provide a space charge layer at the interfaces. This space charge layer can explain the better electrical performance of the LSGM-CSO composite electrolyte.

### 4.3.2.2 Conductivity

Fig. 4.23 shows Arrhenius plots of the total conductivity as a function of temperatures. It is found that the LSGM-CSO composite has the highest conductivity within the measured temperature range of 250–600°C. While, the conductivity of LSGM is higher than those of the other two specimens in the temperature range 650–750°C. The LSGM-CSO composite has a lower conductivity than LSGM at this high
temperature range, but the conductivity difference between these two pellets is relatively small. Although sintered CSO is phase pure as shown in Fig. 4.21, the specimen has a lower electrical performance. This inferior conductivity may result from the pores and defects in the grain boundaries in the CSO pellets as discussed before. Furthermore, the sintered pellets have a different temperature dependence of the conductivity, and thus a different activation energy. The activation energies ($E$) of conductivity are calculated from the Arrhenius plots in Fig. 4.23 and listed in Table 4.3. The activation energy at temperatures 250–600°C for LSGM is 1.06 eV, agreeing well to the literature values.\textsuperscript{8,9} Moreover, it is shown that the activation energies of LSGM-CSO composite electrolyte are lower than those for the LSGM and CSO at both temperature ranges of 250–600°C and 600–750°C. This reveals that the electrical conduction in the composite electrolyte has a lower energy barrier than in the other two specimens.

Table 4.3 Total conductivity and activation energy for sintered pellets.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>LSGM</th>
<th>CSO</th>
<th>Composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity at 750°C (S/cm)</td>
<td>0.030</td>
<td>0.020</td>
<td>0.026</td>
</tr>
<tr>
<td>$E$ at 250–600°C (eV)</td>
<td>1.06</td>
<td>0.98</td>
<td>0.90</td>
</tr>
<tr>
<td>$E$ at 650–750°C (eV)</td>
<td>0.76</td>
<td>0.78</td>
<td>0.72</td>
</tr>
</tbody>
</table>

From the above results, it can be seen that the LSGM-CSO composite electrolyte has a reasonable electrical performance. Although the present work did not analyze the transport number of the composite materials, it is reported that the LSGM-CSO composite electrolyte is an ionic conductor based on the open-circuit voltage test.\textsuperscript{23} Therefore, it can be expected that the composite process as reported here is a promising method for the improvement the conductivity of electrolytes for SOFC.
5 CONCLUSIONS

The LSGM2017 ceramics were prepared by a polymer complexing method. The thermal analysis shows that the decomposition of the precursor powder has three stages. Desorption of water and depolymerisation of residual polymer in the precursor powder happen below 290°C. The complex decomposition of polymer, nitrates and carbonates occurs in the temperature range of 290–760°C. The elimination of residual carbonates in the powder is completed in the temperature range of 760–1000°C. Three secondary phases are detected in the calcined LSGM2017 powders, $\text{La}_6\text{Ga}_2\text{O}_{12}$, $\text{LaSrGa}_3\text{O}_7$ and $\text{LaSrGaO}_4$. Phase pure and highly densified LSGM2017 pellet is obtained after sintering at 1450°C for 10 h.

LSGM ceramics with various dopant contents were further investigated. The fraction of secondary phases in sintered specimens is found to depend on dopant contents. The amount of Sr rich secondary phases, $\text{LaSrGaO}_4$ and $\text{LaSrGa}_3\text{O}_7$, increases with increasing Sr content, while enhanced solubility is observed when doping with Mg. SEM observation showed equiaxed grains in sintered samples. The activation energy increases with increasing content of Mg, while there is no specific trend with change of the Sr content.

The similar polymer complexing method was used to synthesize LSAMC powders. The fully crystallized $\text{LaAlO}_3$ phase is obtained after calcination at 900°C. Moreover, the XRD pattern showed no trace of impurity phases after various calcination temperatures. It can thus be concluded that PVA provides more homogeneous mixing for cations of LSAMC than for cations of LSGM, since the LSGM powder contains impurity even after calcination at 1000°C.

Different complexing agents, e.g., PVA and PEG, were compared to prepare $\text{LaAlO}_3$ powders in the aspects of phase purity, morphology and sintering performance. Small amount of $\text{La}_2\text{O}_3$ is detected in the PEG powder, but it could be eliminated after sintering. Although the PVA powder is phase pure after calcination at 950°C, it contains more seriously aggregated particles. The morphology of the starting powder has dramatic influence on the sintering performance in aspects of both densification and microstructure control. PEG shows advantages over PVA due to much less degree of agglomeration state in the synthesized powder. High density and homogeneous fine microstructure can be obtained for the PEG pellet after sintering at 1600°C for 5 h. The powders with appropriate morphology and less agglomeration are preferable for the synthesis of complex oxides.

The LSGM-CSO composite was investigated as an alternative approach for electrolytes. The composite contains a small amount of an impurity phase after sintering at 1450°C, namely $\text{Sm}_3\text{Ga}_5\text{O}_{12}$, besides the main phase fluorite $\text{CeO}_2$. $\text{La}^{3+}$ and $\text{Sr}^{2+}$ cations may diffuse into the ceria lattice, and the impurity phase is believed to form at the interface between the phases as a result of inter-diffusion of phase components. The LSGM-CSO specimen shows smaller and more perfect semi-circle grain boundary response in the impedance spectrum compared with the CSO and LSGM specimens. This is explained by the space charge layer formed at interfaces between different phases. The composite electrolyte shows the highest conductivity at temperatures 250–600°C. The composite process is a promising method for the improvement the conductivity of electrolyte for SOFC.
6 FUTURE WORK

Preparation of the phase pure LSGM powder by the polymer complexing method should be further investigated. The knowledge of chemical binding behaviour of polymer to the cations in the precursor solution is still lacking. It would be interesting to study the chemical binding ability of polymer to different cations and the distribution of these cations in solutions with more detail.

The lanthanum aluminate powder prepared by the PEG method is satisfactory in the sense of powder morphology and phase purity of the final sintered product. The synthesis of phase pure LaAlO$_3$ powder by the polymer complexing method still needs more investigation.

Primary study of the lanthanum gallate and ceria composite electrolyte showed promising results in the aspect of electrical performances. Further study of the preparation of this composite material without secondary phase is necessary in the future.
LIST OF SYMBOLS

\[ V_o \] Oxygen vacancy fraction

\( D \) Diffusion coefficient

\( a_0 \) Jump distance of oxygen vacancy

\( \nu_0 \) Characteristic lattice vibration frequency

\( \Delta G_m \) Free energy of migration

\( \Delta H_m \) Migration enthalpy

\( \Delta S_m \) Migration entropy

\( k \) Gas constant

\( T \) Absolute temperature

\( \mu \) Mobility of charged ions

\( \sigma \) Ionic conductivity

\( E \) Activation energy of conductivity

\( K_a(T) \) Equilibrium constant

\( \Delta H_a \) Association enthalpy

\( \Delta S_a \) Association entropy

\( R \) Resistance

\( C \) Capacitance

\( \omega \) Angular frequency

\( \tau \) Dielectric relaxation time
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Supplement 1

“Doping effect on secondary phases, microstructure and electrical conductivities of LaGaO$_3$ based perovskites”

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Doping effect on secondary phases, microstructure and electrical conductivities of LaGaO₃ based perovskites

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Abstract

The intermediate temperature electrolytes La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-δ} (LSGM, where δ = (x + y)/2) with perovskite structure were prepared using a poly(vinyl alcohol) (PVA) solution polymerization method. Three secondary phases were identified by X-ray diffraction, LaSrGaO₄, LaSrGa₃O₇ and La₄Ga₂O₉. The relative amount of these secondary phases depended on the doping compositions. Sr doping produced more Sr rich secondary phases with increasing content, while enhanced solid solubility was observed with Mg addition. Sintered samples showed dense microstructures with well-developed equiaxed grains, and the secondary phases were mainly in the grain boundaries. LaSrGaO₄ could not be detected by SEM for the sintered pellets. The oxygen ionic conductivity was enhanced by doping with Sr and Mg. Mg doping showed the increased conductivity activation energy. La₀.₈Sr₀.₂Ga₀.₉Mg₀.₁O₂.₈₅ had the highest ionic conductivity σ = 0.128 S/cm at 800 °C in this work.

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Keywords: Perovskite; Lanthanum gallate; Secondary phases; Microstructure; Ionic conductivity

1. Introduction

Solid oxide fuel cells (SOFCs) convert chemical energy of the fuel directly to electrical energy with high efficiency and are environmentally friendly. Typical SOFCs with yttria-stabilized-zirconia (YSZ) electrolytes require high operating temperatures (800–1000 °C). The high temperature may cause serious problems for sealing materials, thermal mismatches and reaction between interface materials, leading to higher manufacturing cost and application limitation. Therefore, effect has been focused on developing and designing novel oxide electrolytes which can operate at intermediate temperatures (500–800 °C). Stabilized Bi₂O₃ and doped CeO₂ show higher conductivity than YSZ at low temperatures and should thus be interesting alternatives. But later works showed that CeO₂ and Bi₂O₃ based oxides become mixed electronic/oxide-ion conductors in the reducing atmosphere. In 1994, Ishihara et al. and Feng and Goodenough reported that the perovskite LaGaO₃ doped with Sr and Mg had an oxide ion conductivity σ > 0.10 S/cm at 800 °C, which exceeded those of YSZ by a factor of about three. Moreover, the materials had a near unity transference number in the oxygen partial pressure region from 10⁻²² to 1 atm and showed a stable performance over long operation time. These superior electrical and chemical properties make the LaGaO₃ based oxide one of the most promising candidates as intermediate temperature electrolytes for SOFCs.

LSGM ceramics were mostly prepared by the conventional solid state reaction method. The method suffers from time-consuming grinding and high temperature firing; and the synthesized powder is not chemically homogeneous and the particle size is large. LSGM ceramics have also been synthesized by other methods, such as sol–gel method, Pechini method and combustion method. Recently, Li et al. studied the preparation of La₀.₈₅Sr₀.₁₅Ga₀.₈₅Mg₀.₁₅O₂.₈₅ by a PVA solution polymerization method and compared it with the solid state reaction method. The method involves a mechanism of steric entrapment of cations into the polymer network, which prevents precipitation and thus ensures a homogeneous mixing at atomic level. It was concluded that the PVA method was effective and efficient with pure perovskite phase produced at a much lower sintering temperature than the conventional ceramic
method, and this was attributed to the fine and homogeneous powders produced by the PVA method.

However, the secondary phases and microstructure of LSGM ceramics depend strongly on the synthesis methods and doping compositions, and as a matter of fact, the synthesis of single perovskite phase is rather difficult. According to Huang et al., secondary phases, namely LaSrGaO₄ and LaSrGa₃O₇, were identified in the sintered samples prepared by solid state reaction method. While in a phase diagram study by Majewski et al., further secondary phases exist in the quaternary system La₂O₃–SrO–MgO–Ga₂O₃, e.g. LaSrGaO₄, LaSrGa₃O₇, MgO, Ga₂O₃, and MgGa₂O₄. Moreover, the amounts of secondary phases in LSGM may not only relate to the synthesis route, but also depend on the dopants. For example, when Sr and Mg were present together, it was found that the solubility of Sr and Mg in LaGaO₃ increased significantly. Polini reported that the amount of secondary phases decreased with the increase of Mg at a given Sr content, while increased with the Sr content at a given Mg content. The LSGM ceramics were mostly reported to have a microstructure with equiaxed grains. Secondary phases, such as LaSrGa₃O₇ and MgO, could easily be identified in the SEM microstructures and were primarily accumulated along the grain boundaries. However, in a microstructure study of LaGaO₃ based electrolytes by Liu et al., secondary phases such as LaSrGa₃O₇ and LaSrGaO₄ existed with a rod shape in the perovskite phase matrix.

In this work, we report a systematic study in which the relationship between doping composition and the secondary phases and microstructure was further investigated. To study the effect of Sr and Mg separately, La₁₋ₓSrₓGa₀.₉₅Mg₀.₀₅O₃₋ₓ (x = 0.05–0.25) and La₀.₈Sr₀.₂Ga₁₋ₓMgₓO₃₋ₓ (y = 0.05–0.20) were prepared by the PVA method. In order to get as pure perovskite phase as possible, the powders were calcined at temperature of 1300 °C. The sintered pellets were characterised by X-ray diffraction, scanning electron microscope, as well as ac impedance spectroscopy. We also discuss the effect of doping content on the electrical properties of LSGM electrolytes, such as ionic conductivity and activation energy.

2. Experimental

2.1. Materials and preparation

The powders were synthesized using the following nitrate salts as cation sources: La(NO₃)₃·6H₂O (99.99%), Sr(NO₃)₂ (99.97%), Ga(NO₃)₃·xH₂O (99.9%) and Mg(NO₃)₂·6H₂O (99.97%) (all of them were from Alfa Aesar, a Johnson Matthey Company). The x value in the formula of gallium nitrate was determined to be 9 using a thermogravimetric analysis (TGA). Stoichiometric amounts of the given nitrate salts were mixed initially in distilled water and homogenized in a glass beaker. This solution was then mixed together with PVA solution in a glass beaker. The PVA solution was made by dissolving appropriate amount of PVA (–(CH₂–CHOH)ₙ, molecular weight of 57,000–66,000, Alfa Aesar) into distilled water and stirring on a hot plate at 150 °C. The proportions of PVA to nitrate salts were adjusted in such way that the ratio of positively charged valences from metal cations to hydroxyl group of PVA is 1:1. For example, in the case of 1 mol La₀.₉Sr₀.₁Ga₀.₉₅Mg₀.₀₅O₂.₉₂₅, total positively charged valences are 5.85 mol, and then the amount of PVA corresponding to 5.85 mol hydroxyl group is needed. The resulting precursor solution was stirred and homogenized on a hot plate for 1 h at room temperature. The solution was then heated at 250°C to evaporate water while stirring. Black crisp char was finally formed and dried in an oven at 250 °C overnight. The char was ground into fine powder with an agate mortar and pestle. Calcination was subsequently performed in an air atmosphere in a tube furnace at 1300 °C for 3 h.

The as calcined powder was mixed with 1 wt.% PVA solution for binder and ground with an agate mortar and pestle. This powder was uniaxially pressed into pellets with 11 mm diameter and 2 mm thickness. The pressure was 200MPa. Green pellets were sintered at a temperature of 1470 °C for 20 h in air in a muffle furnace.

2.2. Characterisation

The phases in specimens were identified using X-ray Diffraction (XRD) (X’Pert Pro, PANalytical) with Cu Kα radiation. For the sintered samples, pellets were crushed into powders and then examined. The operating conditions for XRD were 45 kV, 40 mA at room temperature. Scans were taken in a 2θ range of 20–80° with a step size of 0.02°.

Fig. 1. XRD patterns of sintered La₁₋ₓSrₓGa₀.₉₅Mg₀.₀₅O₃₋ₓ pellets (x = 0.05–0.25).
Fig. 2. (a) XRD patterns of sintered La$_{0.8}$Sr$_{0.2}$Ga$_{1-y}$Mg$_y$O$_{3-\delta}$ pellets ($y=0.05–0.20$). (b) Enlarged XRD pattern portion around $2\theta=40^\circ$ showing a change from orthorhombic to cubic symmetry.

The microstructures of sintered pellets were studied by scanning electron microscope (SEM) (JSM-840, JEOL). The pellets were wet-ground, polished and thermally etched at 1350 °C for 0.5 h. Chemical compositions were determined by an X-ray energy dispersive spectrometer (EDS) (Link, Oxford) attached to the SEM.

The ac conductivity of sintered pellets was obtained using two-probe impedance spectroscopy. Pellets were wet-ground to a thickness of about 1 mm. Gold paste (Agar Scientific) was applied on both sides of pellets and fired at 730 °C for 2 h. Measurements were made using electrochemical impedance spectroscopy (EI300, Gamry Instruments) over a frequency range of 300 kHz to 1 Hz in air. The temperature range was 500–800 °C at an interval of 50 °C. Pellets were kept at each temperature for at least 40 min to allow thermal equilibrium. Impedance from cablings, leads and sample holders were obtained by measuring a blank cell.

In this paper, La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-\delta}$ composition is referred to LSGM with numbers denoting contents of Sr and Mg. For example, La$_{0.8}$Sr$_{0.2}$Ga$_{0.9}$Mg$_{0.1}$O$_{2.85}$ is denoted as LSGM2010.

### Table 1

<table>
<thead>
<tr>
<th>Specimen</th>
<th>LaSrGa$_3$O$_7$ (%)</th>
<th>LaSrGaO$_4$ (%)</th>
<th>La$_4$Ga$_2$O$_9$ (%)</th>
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<td>6.1</td>
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<tr>
<td>LSGM1005</td>
<td>5.1</td>
<td>2.0</td>
<td>1.3</td>
</tr>
<tr>
<td>LSGM1505</td>
<td>10.9</td>
<td>3.2</td>
<td>3.3</td>
</tr>
<tr>
<td>LSGM2005</td>
<td>15.3</td>
<td>4.0</td>
<td>2.5</td>
</tr>
<tr>
<td>LSGM2505</td>
<td>25.6</td>
<td>14.1</td>
<td>9.3</td>
</tr>
<tr>
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<td>1.7</td>
</tr>
<tr>
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<td>11.0</td>
<td>0.0</td>
</tr>
<tr>
<td>LSGM2020</td>
<td>9.2</td>
<td>14.3</td>
<td>0.1</td>
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</table>

### Results and discussion

#### 3.1. X-ray diffraction patterns

Fig. 1 shows the XRD patterns of the sintered La$_{1-x}$Sr$_x$Ga$_{0.95}$Mg$_{0.05}$O$_{3-\delta}$ ($x=0.05–0.25$) pellets. Diffraction peaks from the perovskite phase are found in the LSGM pellets, illustrating that LaGaO$_3$ perovskite is essentially formed after sintering. The peak splitting at around $2\theta=40^\circ$ shows the structure to be noncubic and the samples could be indexed with the orthorhombic LaGaO$_3$ (JCPDS 24-1102). Fig. 2 shows the XRD patterns from sintered La$_{0.8}$Sr$_{0.2}$Ga$_{1-y}$Mg$_y$O$_{3-\delta}$ ($y=0.05–0.20$) pellets. These samples are also characterised with perovskite phase after sintering. However, it is interesting to note that the sintered samples with a fixed Sr content of 20 at.% have a structure change from orthorhombic to cubic with increasing Mg content. The enlarged portion of XRD patterns around $2\theta=40^\circ$ for these samples are shown in Fig. 2(b). Sintered LSGM2005 has an orthorhombic symmetry, which is verified in Fig. 2(b) where two reflection peaks are identified. But the samples LSGM2015 and LSGM2020 have a cubic symmetry which is confirmed by the well defined (1 1 1) reflection peak. The peak splitting for sample LSGM2010 is not as much for sample LSGM2005, and this might reveal the
Fig. 3. SEM showing microstructures and secondary phases of La$_{1-x}$Sr$_x$Ga$_{0.95}$Mg$_{0.05}$O$_{3-\delta}$, where $x = 0.05$–$0.25$: (a) LSGM0505, (b) LSGM1005, (c) LSGM1505, (d) LSGM2005, (e) LSGM2505.

The fact that the sample has a mixture of orthorhombic and cubic structure. The crystal structure of LSGM strongly depends on the doping content and temperature. There are contradictory reports about the crystal structure of Sr and/or Mg doped LaGaO$_3$ perovskite.\textsuperscript{5,6,7,18} Huang et al. reported a primitive cubic structure of LaGaO$_3$ at all doping levels of Sr and Mg.\textsuperscript{7}

However, it was found in other works that the structure could change from orthorhombic to cubic with increasing content of dopants\textsuperscript{6,18}. For example, Datta reported an orthorhombic structure for samples with total dopant content $x+y<0.25$, whereas a cubic symmetry for $x+y>0.35$ with either $x$ or $y>0.2$. It is generally believed that the higher symmetry of the
crystal structure gives a better oxide ion conductivity and thus is preferable.19

Secondary phases in sintered samples are demonstrated in the XRD patterns in Figs. 1 and 2. These secondary phases are identified to be La2Ga2O9 (JCPDS 53-1108), LaSrGa3O7 (JCPDS 45-0637) and LaSrGaO4 (JCPDS 24-1208). Surprisingly, all the sintered samples of \( \text{La}_{1-x}\text{Sr}_{x}\text{Ga}_{0.95}\text{Mg}_{0.05}\text{O}_{3-\delta} \) with \( x = 0.05-0.25 \) have secondary phases (Fig. 1). Trace amount of secondary phases are detected in \( \text{La}_{1-x}\text{Sr}_{x}\text{Ga}_{0.95}\text{Mg}_{0.05}\text{O}_{3-\delta} \) with \( x = 0.05-0.20 \), while \( \text{La}_{0.75}\text{Sr}_{0.25}\text{Ga}_{0.95}\text{Mg}_{0.05}\text{O}_{3-\delta} \) shows quite a lot of secondary phases. The solubility of Sr in LaGaO3 is 10–20 at.% when Mg content is kept 5 at.%, as reported by various researchers.6,7,16 So the solubility limit of Sr in LaGaO3 does not reasonably explain the presence of these secondary phases. One of the possible reasons for the trace amount of secondary phases is maybe the short calcination time (3 h). It is believed that a higher calcination temperature or prolonged holding time may result in a pure sintered pellet. For instance, Tas et al. found that LSGM2017 prepared by a Pechini method contained 4–5 wt.% secondary phases even after calcination at 1400 °C for 6 h. It was reported that increasing calcination time or increasing firing temperature could remove these secondary phases effectively.10 It is seen in Fig. 2 that the secondary phases are also identified in \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{1-y}\text{Mg}_{y}\text{O}_{3-\delta} \) with \( y = 0.05-0.2 \), \( \text{LaSrGa}_3\text{O}_7 \) and \( \text{LaSrGaO}_4 \). However, as the Mg content increases, the amount of secondary phases decreases, and in particular, no secondary phase is detected in LSGM2015 and LSGM2020.

The amount of secondary phases is estimated by the ratio of the integrated intensity of the most intense peaks of the secondary phase over the perovskite LaGaO3. This is a semi quantitative estimation of XRD patterns and reflects the relative amount of the secondary phases. Table 1 shows the amount change of secondary phases in calcined and sintered samples. All the powders suffer from secondary phases after calcination at 1300 °C. Except for low doping specimens, LSGM0505 and LSGM1005, calcined powders contain much secondary phases, >20% as shown in Table 1. The sintering process can the substantially reduce these secondary phases. The amount change of secondary phases in the sintered pellets with doping content is illustrative. At a Mg content of 5 at.%, the amount of secondary phases, such as \( \text{LaSrGa}_3\text{O}_7 \) and \( \text{LaSrGaO}_4 \), increases when the content of Sr increases. \( \text{LaSrGa}_3\text{O}_7 \) and \( \text{LaSrGaO}_4 \) are Sr rich compounds, so it is believed that excessive addition of Sr is compensated by formation of Sr rich secondary phases with increasing \( x \) value in \( \text{La}_{1-x}\text{Sr}_{x}\text{Ga}_{0.95}\text{Mg}_{0.05}\text{O}_{3-\delta} \). On the other hand when Sr is fixed to 20 at.%, there is a fast decrease of amount of Sr containing secondary phases as the Mg content increases. The solubility of Sr could be extended by the addition of Mg.

3.2. Microstructure

The SEM microstructures of \( \text{La}_{1-x}\text{Sr}_{x}\text{Ga}_{0.95}\text{Mg}_{0.05}\text{O}_{3-\delta} \) (\( x = 0.05-0.25 \)), polished and thermally etched at 1350 °C, are shown in Fig. 3. Equiaxed microstructure with no abnormal grain growth is demonstrated. The pellets are dense and with few pores. Increasing Sr content results in bigger grains, but this is not apparent with high Sr doping content. However, SEM illustrates increasing grain sizes for \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{1-y}\text{Mg}_{y}\text{O}_{3-\delta} \) (\( y = 0.10-0.20 \)) pellets, as shown in Fig. 4. The reason for the larger average grain size (20–26 μm) in LSGM2015 and LSGM2020 could be the less secondary phases (Table 1).
Density of all sintered pellets, as determined by the Archimedes method, is larger than 97% of theoretical density.

Secondary phases could be easily distinguished from the matrix perovskite phase in the microstructures as shown in Figs. 3 and 4. The dark grains accumulated along grain boundaries are secondary phases, LaSrGa$_3$O$_7$ or La$_4$Ga$_2$O$_9$, demonstrated by energy dispersive spectroscopy. Although LSGM2015 is found to be single LaGaO$_3$ perovskite by XRD, two secondary phases are clearly visible in the SEM microstructures, Fig. 4(b). The small amount of secondary phases is apparently beyond the detection limit of XRD. The dark intragranular secondary phase is found to be LaSrGa$_3$O$_7$ by EDS. While for the bright plate-like phase protruding from grain surface, the region is too small to perform EDS. Similar phenomenon was also reported by Abram et al. in a study of LSGM2017.$^{20}$ The authors attribute this plate-like phase to be LaSrGa$_4$O$_4$. This should not be the case in this work, because no such bright plate-like phase could be detected by SEM in those other samples containing LaSrGa$_4$O$_4$, as determined by XRD. Therefore, no LaSrGa$_4$O$_4$ could be found in the microstructures, even when it is detected by XRD. LaSrGa$_4$O$_4$ has a low melting point, $\sim$1400°C,$^8$ and should be in a liquid state at the sintering temperature of 1470°C. The liquid phase LaSrGa$_4$O$_4$ may wet over grains, thus no detectable LaSrGa$_4$O$_4$ could be found in the microstructure. On the other hand, secondary phases, such as LaSrGa$_3$O$_7$ and La$_4$Ga$_2$O$_9$ have higher melting points, $>$1600°C and $\sim$1700°C, respectively. They do not melt at the sintering temperature, and thus remain along grain boundaries. LSGM2020 has no secondary phase in the microstructure observation, which corresponds to the XRD analysis.

Few and uniformly distributed pores can be seen through the SEM microstructure. Detailed examination shows that the pores are mainly accumulated along grain boundaries. However, in LSGM2015 and LSGM2020, more pores are found and they are in both grain boundaries and grain bulks. Considering the much bigger grain sizes in these two pellets, the reason for this could be that these pores are trapped in the grains during the grain growth. The pores, whether in grain boundaries or grains, may deteriorate the electrical properties. They block the oxide ion migration, and thus decrease the ionic conductivity.

### 3.3. Electrical properties

Electrical properties of sintered samples are characterised using ac impedance spectroscopy (IS). Generally, impedance spectroscopy allows separation of bulk, grain boundary, and electrode processes of the ceramics.$^{21}$ A typical impedance spectroscopy of ceramics normally resolves three parts, a bulk semicircle, a grain boundary semicircle, and an electrode arc. Huang et al. investigated the grain boundary effect in LSGM using impedance spectroscopy.$^8$ It was reported that LaSrGa$_3$O$_7$ along the grain boundary is oxide ion insulating and contributes a depressed grain boundary semicircle in the impedance spectroscopy. While Abram et al. discussed the effect from LaSrGa$_4$O$_4$ secondary phase within LSGM2017 grains, using a more quantitative approach to model the IS data with equivalent electrical circuit.$^{20}$ The equivalent circuit is rather difficult to assess, and the authors demonstrated the importance of correct equivalent circuit to extract physically significant parameters.

In this work, simple hand fitting procedure to measure total resistance from impedance complex plane ($Z'$ vs $Z''$) is used.

Fig. 5 shows the total conductivity of La$_{1-x}$Sr$_x$Ga$_{0.95}$Mg$_{0.05}$O$_{3-\delta}$ ($x = 0.05$–$0.25$) at 600°C, 700°C and 800°C, respectively. At a Mg level of 5 at.%, the conductivity increases with Sr content to a maximum at $x = 0.15$ for 600°C and $x = 0.20$ for 700°C and 800°C. At different temperatures, the highest conductivity occurred at different contents. This reflects a different dependence of conductivity activation energy on composition. LSGM2505 has an inferior electrical conductivity, which apparently has much to do with the large amount of secondary phases in the sintered pellets (see Table 1). As shown in Fig. 6, the ionic conductivity increases with increasing Mg content initially, and decreases after reaching a maximum. LSGM2010 has the highest conductivity at 800°C, $\sigma = 0.128$ S/cm, which is comparable to literature values.$^{5,6}$ According to Huang et al., the highest conductivity at 800°C ($\sigma = 0.17$ S/cm) was observed for LSGM2017 prepared by a solid state reaction method.$^7$ However, it was reported that LSGM with $x + y = 0.35$ had the highest conductivity in another
Table 2
Electrical properties of LSGM pellets

<table>
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<tr>
<th>Pellet</th>
<th>Total conductivity (S/cm)</th>
<th>lnA</th>
<th>E (eV)</th>
<th>E (eV)*</th>
<th>E (eV)**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>600 °C</td>
<td>700 °C</td>
<td>800 °C</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.029</td>
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<td>9.908</td>
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<tr>
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<td>0.044</td>
<td>0.081</td>
<td>10.875</td>
<td>0.597</td>
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<tr>
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<td>0.093</td>
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<td>0.739</td>
</tr>
</tbody>
</table>

* Ref. 6.
** Ref. 7.

work.6 This discrepancy is maybe caused by the different synthesis methods, microstructures and crystal structures of LSGM oxides. It should be pointed out that LSGM2010 pellet has trace amount of secondary phases according to the XRD analysis, although it has the highest ionic conductivity at 800 °C. So it is reasonable to expect that the conductivity could be higher if purer perovskite phase can be obtained for LSGM2010. LSGM2015 and LSGM2020 have inferior ionic conductivities, and even they are found to have purer perovskite phase. As shown in the microstructures (see Fig. 4), the amount of pores in these two samples is found to be higher than in other specimens, and they may block the oxygen ion migration as discussed above. The pores may thus be a deteriorating effect on the ionic conductivity for LSGM2015 and LSGM2020. Meanwhile, LSGM2015 and LSGM2020 microstructures show apparent thickening of grain boundaries, Fig. 4. This indicates a molten composition forms and wet over grains. This grain boundary thickening is probably amorphous and could be another reason for the inferior conductivity of LSGM2015 and LSGM2020.

Table 2 compares the electrical properties of sintered LSGM samples with various compositions. The Arrhenius plots for La_{0.8}Sr_{0.2}Ga_{1−y}Mg_{y}O_{3−δ} in the temperature range 500–800 °C are shown in Fig. 7. A linear relationship of conductivity with temperature was found. The conductivities of other samples are found to follow a similar linear relationship. Activation energies (E) for conductivities of all pellets are calculated from the Arrhenius plots and are listed in Table 2. The activation energy values are lower than the reported literature values.6,7 The activation energy for LSGM consists of association energy (E_a) and migration energy (E_m), where E_a is the energy needed for dissociation of oxygen vacancies from their cation atmosphere, and E_m is the migration energy or mobility barrier for oxygen vacancies. At low temperatures both are present, but with increasing temperatures, there is an order–disorder transition at a critical temperature T* and only the migration energy remains at elevated temperatures. Huang et al. reported the critical temperature to be 599 ± 49 °C.7 It is thus reasonable to attribute the activation energy (E) to the migration energy (E_m) in our case. Therefore, the lower activation energy values in our work could be explained by a lower migration barrier. And the reason for this difference is probably related to lattice strain or mismatch introduced by different synthesis methods. The issue is complex and there is not yet a definite explanation to it. It is seen that further work is required to get a complete understanding of this phenomenon. Fig. 8 compares the activation energies of all samples. It is revealed that the activation energy increases with increasing content of Mg. However, there is no obvious trend with the increase of Sr content. This indicates that...
the Mg addition increases the migration energy, while the Sr addition has no specific effect on the migration energy. Earlier calculations on the perovskite type oxides demonstrated that vacancy migration take place along the (1 1 0) edge of the anion octahedron.22,23 In LaGaO₃, an oxygen atom forms two bonds both with Ga and La. Significant binding energies between Mg and oxygen vacancy was found compared with the near-zero binding energy for Sr and oxygen vacancy using a computer simulation.25 This means that an oxygen vacancy is more strongly trapped by Ga–O–Mg pair than by the La–O–Sr pair. Therefore, addition of Mg has more effect on the migration barrier than Sr.

4. Conclusions

LSGM ceramics with various dopant contents were prepared using a PVA solution polymerization method. The crystal structure of the LaGaO₃ perovskite changes with increasing dopant content. LaₓSrₓGa₀.₉₅₋ₓMg₀.₅₀O₃₋ₖ (x = 0.05–0.25) pellets could be characterised with orthorhombic symmetry. However, the sintered samples with fixed Sr content of 20 at.% showed a structure change from orthorhombic to cubic with the increase of Mg content. A cubic symmetry was observed for La₀.₈₀Sr₀.₂₀Ga₀.₈₅₋ₓMgₓO₃₋ₖ with y ≥ 15 at.%. The secondary phases in pellets were mainly LaSrGaO₄, LaSrGa₃O₇ and La₄Ga₂O₉ as revealed by XRD analysis. The relative amount of these secondary phases was found to depend on dopant contents. The amount of Sr rich secondary phases, LaSrGaO₄ and La₂SrGa₃O₇, increased with increasing Sr content, while enhanced solubility was observed when doping with Mg. SEM observation showed equiaxed grains in sintered samples. Secondary phases, such as LaSrGa₃O₇ and La₄GaO₂₉, were confirmed by EDS and they were found to accumulate along grain boundaries. Because of the lower melting point of LaSrGaO₄, it was liquid at the sintering temperature of 1470 °C and wetting the grains. Thus no LaSrGaO₄ was detected in the SEM microstructures for all sintered pellets. Oxygen ionic conductivities were enhanced by doping with Sr and Mg. The activation energy increased with increasing content of Mg, while there was no specific trend with the Sr content. The highest ionic conductivity value σ = 0.128 S/cm at 800 °C was found for LSGM2010.

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References

Supplement 2

“Preparation and characterisation of perovskite La$_{0.8}$Sr$_{0.2}$Ga$_{0.83}$Mg$_{0.17}$O$_{2.815}$ electrolyte using a poly(vinyl alcohol) polymeric method”

Shuai Li, Bill Bergman, Zhe Zhao

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Preparation and characterisation of perovskite La$_{0.8}$Sr$_{0.2}$Ga$_{0.83}$Mg$_{0.17}$O$_{2.815}$ electrolyte using a poly(vinyl alcohol) polymeric method

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Abstract

The perovskite La$_{0.8}$Sr$_{0.2}$Ga$_{0.83}$Mg$_{0.17}$O$_{2.815}$ (LSGM) fuel cell electrolyte was prepared by a polymeric method using poly(vinyl alcohol) (PVA). The LSGM precursor powder was examined by thermal analysis (TG/DTA) and Fourier transform infrared (FTIR) spectroscopy. It was found that thermal decomposition of the LSGM precursor powder occurs in a number of different stages, and complete decomposition of the precursor is obtained at 1000°C. X-ray diffraction showed that calcined powders contain three secondary phases, namely La$_4$Ga$_2$O$_9$, LaSrGa$_3$O$_7$ and LaSrGaO$_4$, even after calcination at 1100°C. Furthermore, the fraction of secondary phases decreases with increasing calcination temperature. Single phase perovskite LSGM pellets with a relative density of 97% were obtained after sintering at 1450°C for 10 h. It is therefore shown that the powders prepared by the simple PVA method are fine, highly reactive and sinterable. The electrical properties of LSGM pellets were characterised by impedance spectroscopy. The conductivity of the LSGM pellet sintered at 1450°C for 10 h is 8.24$\times$10$^{-2}$ S/cm at 800°C.

Keywords: Lanthanum gallate; perovskite; polymeric method; ionic conductivity

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1. Introduction

The perovskite lanthanum gallate doped with Sr and Mg (La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-\delta}$, LSGM) has gained much attention in recent years for its high oxygen ionic conductivity at intermediate temperatures (500 – 800°C) [1-5]. In 1994, Ishihara et al. [2] studied the effect of different dopants on the electrical properties of perovskite LaGaO$_3$, and for the first time it was demonstrated that LaGaO$_3$ doped with Sr and Mg is a promising ionic conductor with its high conductivity. Feng and Goodenough [3] further reported that La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.85}$ has an ionic conductivity $\sigma > 0.10$ S/cm at 800°C, and that the electrolyte was a pure oxygen ion conductor over a wide oxygen partial pressure range of $10^{-22} < p_{O_2} < 0.4$. The chemical stability of the material was also tested and it was reported that the doped LaGaO$_3$ showed a stable performance over a long operation time [2,5]. The electrical properties of LSGM ceramics with different compositions were investigated by Huang et al [5]. The highest ionic conductivity of $\sigma = 0.17$ S/cm was obtained for La$_{0.8}$Sr$_{0.2}$Ga$_{0.83}$Mg$_{0.17}$O$_{2.815}$ at 800°C. Thus the Sr- and Mg- doped LaGaO$_3$ is a promising material as an electrolyte in solid oxide fuel cells.

The LaGaO$_3$ based oxides are normally produced by solid state reaction [2-8]. Although the method is used for its simplicity, the process is not satisfactory due to drawbacks such as impurities introduced by milling, high reaction temperature, coarse grains and low chemical homogeneity. Thus, wet chemical approaches are widely used to prepare the LSGM ceramics: sol-gel [9,10], Pechini [11-13], combustion [14] and hydrothermal [15]. Huang and Goodenough [10] successfully prepared La$_{0.8}$Sr$_{0.2}$Ga$_{0.83}$Mg$_{0.17}$O$_{2.815}$ powders by a coprecipitation method using ammonia to peptize an acetate solution of the cations. Ultrafine powders with nanosized particles were obtained after calcination, however, the process needs expensive acetate salts; and
the reaction mechanism is difficult to control. The Pechini method was also used to synthesize LSGM ceramics [11]. This route involves the chelation process between citric acid and metal cations, and polymerization of these chelates [16]. As reported, the metal cations disperse uniformly at atomic level in the polymer network, which may ensure a homogeneous and fine powder. In addition, the glycine nitrate combustion method and hydrothermal route have also been developed by Cong et al. [14] and Chen et al. [15]. However, the phase purity and microstructure may strongly depend on the synthesis route, and the preparation of pure perovskite phase is rather difficult. It has been reported in various works that secondary phases such as LaSrGa₃O₇, LaSrGaO₄ or MgO are found after high temperature treatment of LSGM samples [11-14]. Tas et al [11] further suggested that prolonged calcination time and increasing sintering temperature (e. g. 1470 – 1500°C) could remove these secondary phases. Nevertheless, a simple method to synthesize purer LSGM ceramics at lower temperatures is desirable.

The PVA polymeric route is an attractive method to prepare multicomponent oxides. According to Kriven et al. [17-19], the method mainly involves steric entrapment of metal cations in the polymer network, and thus offers a homogeneous dispersion of components. Ultrafine, homogeneous and highly reactive oxide powders have successfully been prepared by using the PVA method. Phase pure LSGM pellets were obtained when this PVA method was investigated by Li et al [20] and Zhai et al [21], respectively. Furthermore, the method does not need high temperatures. For example, the sintering temperature for the La₀.₈₅Sr₀.₁₅Ga₀.₈₅Mg₀.₁₅O₂.₈₅ pellets prepared by PVA method was 50 – 100°C lower, compared with the solid state method [20]. Although the method has been successfully applied to the preparation of LSGM ceramics, there is still a need for detailed investigation of the thermal decomposition process for the
LSGM precursor powders prepared through this PVA method and the resulting electrical properties of sintered pellets. In this work, we report a systematic study on the preparation of LSGM ceramics by the PVA method. The calcined powder was characterised by TG/DTA, FTIR and XRD. We also measured and discuss the impedance spectra for the sintered LSGM pellets.

2. Experimental

2.1 Materials preparation

Nitrate salts were used for the synthesis of LSGM: La(NO$_3$)$_3$·6H$_2$O (99.99%), Sr(NO$_3$)$_2$ (99.97%), Ga(NO$_3$)$_3$·$x$H$_2$O (99.9%, $x$ was determined to be 9 using thermogravimetric analysis) and Mg(NO$_3$)$_2$·6H$_2$O (99.97%) (Alfa Aesar). These nitrate salts were dissolved in distilled water in stoichiometric proportions and homogenized by stirring on a hot plate. To obtain the PVA solution, an appropriate amount of PVA (–(CH$_2$–CHOH)$_n$–, molecular weight of 57,000 – 66,000, Alfa Aesar) was added to distilled water, and stirred at 150°C until completely dissolved. Then the prepared solutions were mixed in a glass beaker. The proportion of PVA to nitrate salts was adjusted in such a way that the ratio of positively charged valences from the metal cations to the hydroxyl groups from the PVA is 1.5:1. The precursor solution was homogenized for 1 h at room temperature, and then heated to 250°C to evaporate water. No precipitation was observed as water evaporated. A foam-like aerogel was finally formed. The foam was formed from the NO$_x$ gas evolved during the decomposition of nitrates [17]. The aerogel obtained was ground in an agate mortar, and then calcined over a temperature range of 250 – 1100°C for 6 h.

To break up the agglomerates, the 1000°C calcined powder was ball milled for 1 h using a planetary mill. ZrO$_2$ balls (diameter: 5 mm) were used as the milling media, and
ethanol as a solvent. The milled and dried powder was then uniaxially pressed into pellets with a compaction pressure of 200 MPa. Green pellets were sintered at temperatures in the range of 1350 – 1450°C with a heating rate of 5°C/min.

2.2 Characterisation

Phase evolution in the samples was investigated by means of powder X-ray diffraction (XRD) (X’Pert Pro, PANalytical) using Cu Kα radiation (45 kV, 40 mA). Scans were taken in the 2θ range of 20° – 80° with a step size of 0.017°. Lattice parameters were evaluated from all the diffraction peaks, using the UNIT-CELL program [22].

The thermal decomposition process of the LSGM precursor powder was examined by thermogravimetric analysis (TG) (TAG 24, SETARAM) and differential thermal analysis (DTA) (TG-DTA 1600, Labsys). The powder was heated to 1200°C with air flow at a heating rate of 10°C/min. Al₂O₃ powder was used as reference material in the DTA test.

Fourier transform infrared (FTIR) (IFS 55, Bruker) spectroscopy was performed to analyze the chemical structures in the calcined powders. Measurements were made in the range 400 – 4000 cm⁻¹. The powder was mixed with dry KBr to form pellets for the FTIR.

The impedance spectra of sintered pellets were measured by impedance spectroscopy (SI 1260 impedance/Gain-phase analyzer, Solartron). Sintered pellets were first wet-ground to a thickness of about 1 mm. Platinum paste (ChemPur) was applied on both sides of the pellets and cured at 1100°C for 0.5 h. Impedance measurements were made on cooling from 800°C to 250°C at intervals of 50°C in the frequency range from 10 MHz to 0.1 Hz with an ac amplitude of 80 mV. The impedance spectrum was analyzed
using the ZView 2 software. Impedance from cables, leads and sample holders obtained by measuring a blank cell was subtracted from the sample impedance spectra.

3. Results and discussion

3.1 Thermal analysis

The thermal decomposition behavior of the LSGM precursor powder prepared by the PVA method was characterised by TG and DTA, as shown in Fig. 1. The DTA curve exhibits a weak and broad endothermic peak at around 100°C, which is followed by two pronounced exothermic peaks at 366°C and 615°C. The TG curve shows the thermal weight loss as a function of temperature, corresponding to the DTA peaks. Clearly, most of the organics in the precursor powder decompose at temperatures <760°C, yielding a weight loss of 23.6% (from the TG curve). Furthermore, the thermal decomposition can be divided into three stages as shown in Fig. 1. The first stage occurs below 290°C, with a weight loss of 2.5% related to the weak endothermic peak at 100°C. This weight loss is ascribed to the desorption of absorbed water. The PVA decomposes to polyenes and water through dehydration at the start of pyrolysis [18], so dehydration and depolymerisation of the polymeric residual from the precursor could be another reason for this weight loss. The second stage occurs in the temperature range of 290 – 760°C with a weight loss of 21.1%, which is explained by the complex decomposition reactions of organics and nitrates. Carbonates, such as SrCO₃ or MgCO₃, are also believed to be present at this stage. In the third stage, at temperatures in the range of 760 – 1000°C, a slight 2.0% weight loss is observed. This weight loss could be due to the decomposition of carbonate intermediates [18, 21]. There is no evidence of additional weight loss above 1000°C, which indicates the LSGM precursor powder has completely
decomposed. The small peaks shown in the DTA curve above 800°C are believed to be the background noise.

3.2 IR spectra

The chemical structure of the calcined LSGM powders was further examined by FTIR. Fig. 2 shows the FTIR spectra for these powders heated between 250°C and 1100°C. The spectrum for the 250°C calcined powder exhibits extensive absorption peaks, as shown in Fig. 2. The broad band at 3200 – 3600 cm$^{-1}$ is due to O–H stretching vibration. The presence of –CH$_2$ groups is detected by a weak broad band at 2900 cm$^{-1}$, which is assigned to C–H stretching vibration. The weak peak at 2211 cm$^{-1}$ may indicate the presence of C≡C in the 250°C calcined powder; the peak disappears with increasing temperature. As mentioned above, PVA dehydrates to polyenes during pyrolysis, and the presence of these polyenes is indicated by the medium bands located at 1653 cm$^{-1}$ (stretching vibration of C=C) and 816 cm$^{-1}$ (bending of C–H). Double bands, produced by acetate groups, are observed at 1558 cm$^{-1}$ (asymmetrical stretching vibration of COO$^-$) and 1436 cm$^{-1}$ (symmetrical stretching vibration of COO$^-$) [10]. Remaining nitrate salts in the LSGM powders are also found with the bands from NO$_3^-$, located at 1380 cm$^{-1}$ (asymmetrical stretching vibration) and 736 cm$^{-1}$ (in plane bending). In addition, the medium bands at 1070 cm$^{-1}$ and 860 cm$^{-1}$ can be attributed to the stretching vibration of CO$_3^{2-}$, which confirms the carbonates generated by the decomposition of organics and nitrates from the above thermal analysis. Moreover, there are two peaks located at 2360 cm$^{-1}$ and 2340 cm$^{-1}$ that can not be identified. They may come from the atmospheric CO$_2$ according to the literature [11].

With increasing temperature, the FTIR spectrum shows significant changes in the C=C and NO$_3^-$ bands, while only a slight decrease of the O–H band is observed. At
500°C, the band at 1653 cm\(^{-1}\) for C=C disappears in the powder, indicating that the polyene has decomposed at this stage. The band at 1487 cm\(^{-1}\) is due to the stretching vibration of CO\(_3^{2-}\), which shows carbonate salts still remain in the powder. Further increase in temperature to 700°C shows an apparent decrease of the NO\(_3^-\) band intensity; and the residual nitrate salts gradually decompose as temperature increases. The 900°C calcined powder shows traceable vibrations from carbonates, and most organics vanish. The powders calcined at above 1000°C have low frequency bands in addition to bands from CO\(_2\). These low frequency bands are characteristic of metal-oxygen vibrations, which indicates a complete decomposition of the precursor powder has occurred, consistent with the result in Fig. 1.

3.3 Phase analysis

Fig. 3 shows the XRD patterns for LSGM powders calcined at various temperatures. The XRD spectrum for the powder calcined at 250°C has a broad arc-shaped continuum over 2\(\theta\) range of 25° – 30°. This indicates that the powder is mainly amorphous. The FTIR results show that nitrates and carbonates exist in powders calcined in the temperature range of 250 – 900°C, and this finding is also observed in XRD patterns. The two weak diffraction peaks of the 250°C calcined powder were indexed as Sr(NO\(_3\))\(_2\) (JCPDS 25-0746). With increasing calcination temperature to 500°C, no significant change is observed for the XRD spectrum; and there is still a trace amount of Sr(NO\(_3\))\(_2\) in the amorphous powder, with no evidence of other crystalline phases. The powder consists of an amorphous phase after calcination at 700°C, however, no Sr(NO\(_3\))\(_2\) is found but weak peaks from SrCO\(_3\) (JCPDS 05-0418) and LaSrGa\(_3\)O\(_7\) (JCPDS 45-0637) were seen. The nitrate salts vanish as the calcining temperature increases, corresponding well with FTIR. At 900°C, fully crystallized powder is formed.
since the arc-shaped continuum has completely disappeared from the XRD pattern. Furthermore, strong diffraction peaks from perovskite LaGaO₃ are observed, which means that perovskite LaGaO₃ phase is essentially formed after calcination at 900°C. Thus, it can be concluded that the formation of LaGaO₃ occurs through intermediate stages and not directly from the amorphous precursor.

The secondary phases in calcined powders are seen in the XRD patterns in Fig. 3. These secondary phases are identified as La₄Ga₂O₉ (JCPDS 53-1108), LaSrGa₃O₇ (JCPDS 45-0637) and LaSrGaO₄ (JCPDS 24-1208). All calcined powders have secondary phases, and the LSGM powder could not be obtained as phase pure even after calcination at 1100°C. The fraction of secondary phases was estimated by calculating the ratio of the integrated intensity of the most intense peaks of the secondary phase to the perovskite LaGaO₃ peak intensity. The fraction of secondary phases are estimated to be 42.8%, 36.1%, and 31.0% in powders calcined at 900°C, 1000°C and 1100°C, respectively. Therefore, it can be concluded that these secondary phases decrease with increasing calcination temperature, as reported in previous works [13,20].

The phases in the sintered pellets were examined by XRD on the polished surface, as shown in Fig. 4. The pure perovskite LaGaO₃ phase could be obtained after sintering at 1450°C for 10 h. All sintered pellets show cubic perovskite LaGaO₃ (JCPDS 24-1102). The diffraction data for the LSGM pellet sintered at 1450°C for 10 h is given in Table 1. The lattice parameter obtained for this pellet was calculated to be \(a = 3.9077\) Å. The secondary phases, namely LaSrGa₃O₇ and LaSrGaO₄, can still be detected in sintered pellets. However, the La₄Ga₂O₉ present in the calcined powder is eliminated by the sintering process. The fraction of secondary phases in sintered pellets, estimated from the XRD pattern, is shown in Table 2. The increasing temperature could apparently
promote the dissolution of secondary phases in the sintered pellet. In addition, prolonged sintering times can also decrease the fraction of secondary phases, as shown in Table 2. LSGM pellets were prepared phase pure after sintering at 1450°C for 10 h. Although the formation of single phase LaGaO₃ can also be obtained using the solid state reaction method, this usually needs a higher sintering temperature (e.g. >1500°C) and much longer duration [5,23]. Compared with this traditional ceramic method, the sintering temperature for powder prepared by the PVA method is reduced by least 50°C. Synthesis of single phase perovskite has been a basic requirement for LaGaO₃ based oxides, but lowering the sintering temperature is also desirable. A high sintering temperature may result in severe coarsening of grains and potential Ga evaporation. Stevenson et al. [24] have previously demonstrated that Ga evaporation in the form of Ga₂O could occur for LSGM sintered at 1500°C.

The density of sintered pellets, measured using Archimedes’ method, is shown in Table 2. The theoretical density of LSGM is calculated to be 6.56 g/cm³, using the lattice parameter, 3.9077 Å. The LSGM pellet sintered at 1450°C for 10 h has a high relative density of 97%, showing that the LSGM powder prepared by the PVA method has a high sinterability. Therefore, it can be concluded that the PVA method can prepare phase pure and high density LSGM ceramics at a lowering sintering temperature.

3.4 Impedance spectra

Impedance spectroscopy was used to characterise the electrical properties of sintered LSGM pellets. The impedance spectrum normally separates bulk, grain boundary, and electrode processes of the ceramics. The high frequency semicircle in the impedance complex plane comes from the bulk conduction and dielectric process; the intermediate frequency semicircle is due to the grain boundary response, and the low frequency arc is
attributed to electrode processes [6,8,9]. The impedance data can be analyzed by a simple hand fitting process [6], while a more quantitative approach uses an electrical equivalent circuit to model the spectrum and extract parameters [8]. Abram et al. [8] compared various equivalent circuits to model the impedance response of the LSGM ceramic. It is suggested that a suitable equivalent circuit is necessary in order to obtain parameters with physical significance. In the present work, the equivalent circuit approach was used to analyze the impedance spectrum of the sintered pellets.

Fig. 5 shows the typical impedance spectrum for the LSGM pellets made by the PVA method. The spectrum has two semicircles, and they correspond to bulk and grain boundary responses, respectively. In addition, it is found that the bulk semicircle is slightly depressed, which means a constant phase element (CPE) existing parallel to $R_b$ (a bulk resistor) and $C_b$ (a bulk capacitor). The CPE can be written as follows:

$$Z_{CPE} = Q^0 (j\omega)^n$$

where $Q^0$ is a constant, $n$ is the depressed exponent, and $\omega$ is the angular frequency. As shown in Fig. 5, the grain boundary semicircle for LSGM pellet is perfect, and thus consists of a parallel $R_{gb}$ (grain boundary resistor) and $C_{gb}$ (grain boundary capacitor) circuit. The equivalent circuit, given in Fig. 5, is used to fit the impedance data of LSGM pellets. In addition, corresponding complex formalisms are used to check the fitting parameters: impedance, modulus, admittance and permittivity.

The fitting data for the impedance spectroscopy data is given in Fig. 5. Clearly, the equivalent circuit gives a good fit. This is further proved by Fig. 6, where fitting data provide a satisfactorily model for the real and imaginary parts of the four formalisms over the frequency range. The fitted values are $R_b=62.9$ k$\Omega$, $C_b=5.2$ pF, $Q^0=3.65 \times 10^{-10}$ S$\cdot$s$^n$ and $n=0.81$ for CPE; $R_{gb}=4.4$ k$\Omega$, $C_{gb}=108$ nF.
The depressed exponent of CPE is 0.81 for the pellet measured at 250°C (Fig. 5). For a R–C combination CPE, the value of $n$ is $0 \leq n \leq 1$ [6]. The CPE represents a resistor for $n = 0$, and a capacitor for $n = 1$. Thus, the closeness of $n$ to 1 in the LSGM pellet may indicate a greater capacitance component in the grain bulk. The depressed exponent for CPE is believed to be dependent on the secondary phases in LSGM pellets [6]. However, a more common explanation for CPE is the distortion introduced by local inhomogeneities [25]. In general, the microscopic properties are often distributed, for example, the ceramic contains two- or three-phase regions, local charge inhomogeneity, and variations in composition and stoichiometry. The capacitance and CPE depressed exponent for the pellet measured at different temperatures were also estimated. They were found to be insensitive to the measuring temperature, in good agreement with previous reports [6, 8].

Fig. 7 illustrates the change of the impedance spectrum with measurement temperature for the LSGM pellet sintered at 1450°C for 10 h. At 350°C, the impedance spectrum can be resolved into two semicircles, corresponding to the bulk and grain boundary responses. When the temperature is increased to 400°C, the two semicircles still exist, however, the frequency limits are found to move to the higher end, as illustrated in Fig. 7. Further increase in temperature to 500°C results in the total disappearance of the bulk semicircle in the spectrum. The resistance ($R$) and capacitance ($C$) follow the relationship, $\omega_{\text{max}}RC = 1$, where $\omega_{\text{max}} = 2\pi f_{\text{max}}$ is the angular frequency at the semicircle maximum. For temperatures $\geq 450°C$, the dielectric relaxation time $\tau = RC$ becomes too small ($\tau < 10^{-8}$) for $\omega_{\text{max}}$ to fall within the high frequency limit. Only the electrode process arc can be detected in the impedance spectrum when the measurement temperature is higher than 600°C. Therefore, for temperatures higher than
600°C, the intercept between the real axis and spectrum is taken as the total resistance for the pellet.

3.5 Conductivity

The temperature dependence of conductivity is shown in Fig. 8. The pellet sintered at 1450°C for 10 h has the highest conductivity over all the measured temperature range, while inferior performance is demonstrated for the pellet sintered at 1400°C for 10 h. Porosity may hinder oxygen ion migration and reduce the conductivity. However, porosity is not thought to be the reason for the low conductivity measured, since the sintered pellets have a relative density higher than 97%, as shown in Table 2. It is thought that secondary phases in the pellets exert a negative effect on the electrical conductivity. The fraction of secondary phases decreases with increasing sintering temperature or prolonged sintering time (Table 2). The secondary phases identified, LaSrGa₃O₇ and LaSrGaO₄, have low ionic conductivity, and thus block oxygen ion migration [6]. The phase pure LSGM pellet sintered at 1450°C for 10 h has the highest total conductivity of 0.08 S/cm.

The dependence of conductivity on temperature in the electrolyte can be expressed by the Arrhenius equation:

$$\sigma T = A \exp\left(\frac{-E}{kT}\right)$$

where $A$ is a pre-exponential factor and $E$ is the activation energy. It is observed in Fig. 8 that the curvature for the curve changes at 600°C. Feng and Goodenough [3] reported a similar phenomenon in La₀.₉Sr₀.₁Ga₀.₈Mg₀.₂O₃₋δ, which they attributed to the order-disorder transition associated with short range ordering of the oxygen vacancies around 600°C. An alternative explanation in another work attributes the effect to dopants, such as Sr and Mg, for isolated oxygen vacancies [5]. Dopants act as nucleation centers for
the formation of ordered-vacancy clusters below the critical temperature $T^*$ while above this temperature the clusters dissolve into the oxygen sites. As shown in Fig. 8, the plotted curves are straight lines and parallel to each other over the temperature range 250 – 550°C, which indicates a similar activation energy (in this temperature range). However, there is apparent difference between the high temperature (600 – 800°C) curves, suggesting a different activation energy. The activation energies calculated are shown in Table 3. The Arrhenius plots of LSGM sintered at 1450°C for 10 h give an activation energy of 1.078 eV in the temperature range 250 – 550°C, which compares well with the literature value of 1.07 eV [3,5].

4. Conclusions

Single phase LSGM ceramics can be prepared by the PVA polymeric method. The thermal analysis (TG/DTA) shows that the decomposition of the LSGM precursor powder occurs several stages. Desorption of water and depolymerisation of residual polymer in the precursor powder takes place below 290°C. The complex decomposition of the polymer, nitrates and carbonates occurs in the temperature range of 290 – 760°C. FTIR and XRD analysis further demonstrate the presence of nitrates and carbonates at this stage. The elimination of residual carbonates in the powder is completed in the range 760 – 1000°C. Furthermore, XRD analysis shows that the LaGaO$_3$ phase forms at a calcination temperature of 900°C. Three secondary phases are detected in the calcined LSGM powders, namely La$_4$Ga$_2$O$_9$, LaSrGa$_3$O$_7$ and LaSrGaO$_4$; the fraction of these secondary phases depends on the calcination temperature. Higher sintering temperatures or longer sintering times further decrease the fraction of secondary phases. Phase pure and high density LSGM can be obtained by sintering at 1450°C for 10 h. Impedance spectroscopy reveals a depressed grain bulk semicircle for LSGM pellets, indicating the
presence of constant phase element (CPE) in the grains. The CPE is believed to be related to the distortion introduced by local inhomogeneities in sintered LSGM. A high conductivity, $\sigma = 8.24 \times 10^{-2}$ S/cm at 800°C, is obtained for the phase pure LSGM pellet sintered at 1450°C for 10 h.

Acknowledgement

The authors would like to thank Prof. Zhicheng Li from the School of Materials Science and Engineering at Central South University (Hunan, China) for the helpful discussions and suggestions on this work.

References


Figure captions:

Fig. 1 TG/DTA curves showing the thermal decomposition of the LSGM precursor powder.

Fig. 2 FTIR spectra of LSGM powder calcined at different temperatures.

Fig. 3 XRD patterns showing phase evolutions for the calcined LSGM powders, (○) Sr(NO₃)₂; (△) SrCO₃; (Δ) LaSrGa₃O₇; (+) La₄Ga₂O₉; (×) LaSrGaO₄.

Fig. 4 XRD patterns for sintered LSGM pellets.

Fig. 5 Impedance spectrum for the LSGM pellet sintered at 1450°C for 10 h, measured at 250°C; and the equivalent circuit for impedance spectrum. (Open circle for the observed impedance data, and cross for the fitting data from the equivalent circuit.)

Fig. 6 Spectroscopic plots of the real and imaginary parts of (a) impedance, Z; (b) modulus, M; (c) admittance, Y; (d) relative permittivity, ε, and the fitted plots from equivalent circuit.

Fig. 7 Impedance spectra for the LSGM pellet sintered at 1450°C for 10 h, measured at 350 – 800°C (the arrow in the spectrum indicates the measuring frequency in Hz for the point).

Fig. 8 Arrhenius plots of total conductivity for LSGM sintered pellets.

Table captions:

Table 1 The XRD diffraction data of LSGM pellet sintered at 1450°C for 10 h.

Table 2 Estimation of the fraction of secondary phases and density of LSGM pellets.

Table 3 Total conductivity and activation energy for different LSGM pellets.
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Table 2 Estimation of the amount of secondary phases and density of LSGM pellets.

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<tr>
<th>Specimen</th>
<th>LaSrGa₃O₇</th>
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<td>2.3%</td>
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<td>0</td>
<td>0</td>
<td>6.37</td>
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Table 3 Total conductivity and activation energy for different LSGM pellets.

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<th>700°C (S cm⁻¹)</th>
<th>800°C (S cm⁻¹)</th>
<th>ln A₁</th>
<th>E₁</th>
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<th>E₂</th>
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* ln A₁ and E₁ are calculated in the temperature range of 250 – 550°C.
** ln A₂ and E₂ are calculated in the temperature range of 600 – 800°C.
Supplement 3

“Synthesis of $\text{La}_{0.9}\text{Sr}_{0.1}\text{Al}_{0.85}\text{Mg}_{0.1}\text{Co}_{0.05}\text{O}_{2.875}$ using a polymeric method”

Shuai Li, Bill Bergman, Zhe Zhao

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Synthesis of La$_{0.9}$Sr$_{0.1}$Al$_{0.85}$Mg$_{0.1}$Co$_{0.05}$O$_{2.875}$ using a polymeric method

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Abstract

Nanocrystalline La$_{0.9}$Sr$_{0.1}$Al$_{0.85}$Mg$_{0.1}$Co$_{0.05}$O$_{2.875}$ (LSAMC) powders were synthesized via a polymeric method using poly(vinyl alcohol) (PVA). The effect of PVA content on the synthesized powders was studied. When the ratio of positively charged valences (M$^{n+}$) to hydroxyl groups (―OH) is 1.5:1, crystalline LaAlO$_3$ could be obtained at such a low calcination temperature as 700 $^\circ$C. While at 900 $^\circ$C the ratio is of less importance, since pure LaAlO$_3$ perovskite could be formed for all powders after calcination at 900 $^\circ$C. Thermal analysis (TG/DTA) was utilized to characterize the thermal decomposition behaviour of precursor powders. The chemical structure of the calcined powder was studied by Fourier transform infrared (FTIR) spectroscopy. The powder morphology and microstructure were examined by SEM. Dense pellets with well-developed submicron microstructures could be formed after sintering at 1450 $^\circ$C for 5 h. Compared with the solid-state reaction method, the sintering temperature is substantially lower for powder prepared by the PVA method. This is due to the ultrafine and highly reactive powder produced.

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Keywords: Nanocrystalline; Lanthanum aluminate; Perovskite; Polymeric method

1. Introduction

Solid oxide fuel cells (SOFCs) offer a clean, highly efficient and environmentally friendly alternative energy solution to convert chemical energy of the fuel directly to electrical energy. The most commonly used electrolytes in SOFCs are zirconia-based oxides, which need to be operated at high temperatures (1000 $^\circ$C). The high operation temperature may lead to serious problems for sealing materials, such as thermal mismatches and reaction between interface materials. Novel oxide electrolytes, which can operate at intermediate temperatures (500–800 $^\circ$C), have thus attracted intensive research interests. The perovskite structure oxides (ABO$_3$) have been extensively investigated for their different allotropic structures and easy accommodation for doping cations. It was reported that the Sr- and Mg-doped LaGaO$_3$ (LSGM) have high ionic conductivity at 800 $^\circ$C over a wide range of oxygen partial pressures, 10$^{-20}$ < $P_{O_2}$ < 1 atm.$^{2,3}$ Huang et al. reported an ionic conductivity of 0.17 S/cm at 800 $^\circ$C for La$_{0.8}$Sr$_{0.2}$Ga$_{0.83}$Mg$_{0.17}$O$_{3-\delta}$ samples, which remained stable over a week-long test.$^4$ The superior electrical conductivity has made LSGM one of the most promising candidates as intermediate temperature electrolytes for SOFCs.

However, there are still problems associated with the applications of LSGM electrolytes, such as high cost of gallium, poor mechanical performance,$^5,6$ and chemical stability problems with the Ni–ceramic anode.$^7$ Therefore, replacement of Ga with the low cost Al is highly desirable. Nguyen and Dokiya reported a strengthening effect of mixing LaAlO$_3$ into LSGM, and the chemical stability of Sr-doped LaAlO$_3$ was also confirmed.$^7$ The obstacles for the use of LaAlO$_3$-based electrolytes are the low ionic conductivity and the mixed conduction mechanism at high oxygen partial pressures.$^8$ Nomura reported that the La$_{0.9}$Sr$_{0.1}$AlO$_{2.95}$ has a conductivity about one order of magnitude lower than that of La$_{0.9}$Sr$_{0.1}$GaO$_{2.95}$ at 1000 $^\circ$C, and explained it by the balance between crystallographic free volume and Goldschmidt tolerance factor.$^8$ Chen also found a significantly lower conductivity of doped LaAlO$_3$ compared with doped LaGaO$_3$, which is attributed to the much higher bonding strength of Al–O and thus the higher formation energy of intrinsic oxygen vacancies.$^{13}$ Besides, the LaAlO$_3$-based ceramics are p-type conductors at high oxygen

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partial pressures. Park observed that La0.9Sr0.1Mg0.85Al0.15O2.875 was a pure ionic conductor only at oxygen partial pressure $P_{O_2} < 10^{-10}$ atm.\(^9\) However, the LaAlO3 ceramics may become good ionic or mixed conductors with suitable dopants. With double-doping of Sr and Mg in LaAlO3 materials, the conductivity of LaAlO3 is sharply enhanced within the solubility limit.\(^13\) Similar enhancement from dopants was also reported by other researchers.\(^7,9,10\) Recently, Basu et al. reported that Co doping could increase the conductivity of LaAlO3-based electrolytes. The La0.9Sr0.1Al0.85Mg0.1CO0.05O2.875 sample showed a conductivity of 2.4 $\times$ 10$^{-2}$ S/cm at 1000$^\circ$C compared with 4.9 $\times$ 10$^{-3}$ S/cm for La0.9Sr0.1Al0.85Mg0.15O2.875.\(^14\) By adding Sr and Mg to LaAlO3, the conductivity as well as the oxygen partial pressure range for pure ionic conduction was enhanced, e.g., from $P_{O_2} < 10^{-13}$ atm for LaAlO3 to $P_{O_2} < 10^{-6}$ atm for La0.8Sr0.2Al0.95Mg0.05O2.875.\(^10\) Therefore, LaAlO3-based ceramics are promising oxygen ion conductors at high temperature and low $P_{O_2}$.

The LaAlO3-based ceramics were primarily prepared by the conventional solid-state reaction method.\(^7–11,13\) The method involves high firing temperatures and time consuming regrinding process. The synthesized powders suffer from inhomogeneous composition distribution, coarse particles, and undesired impurities. Other methods, such as glycine–nitrate method,\(^12\) Pechini process,\(^14\) sol–gel process\(^15\) and coprecipitation,\(^16\) have also been used to synthesize LaAlO3-based ceramics. It was reported by Kriven and her colleagues that a polymeric route, using the PVA as the polymeric carrier, is an effective method to synthesize fine and homogeneously mixed oxide powders.\(^17–19\) Unlike the Pechini route, which involves chelation and polymerization, the PVA method involves mainly steric entrapment of cations into the polymer network. The cations are entangled in the polymer network, which prevents precipitation, and thus ensures a homogeneous mixing at atomic level. In the present work, we report a systematic study on the synthesis of LSAMC using the PVA polymeric route. The LSAMC powder calcined in the temperature range of 250–1100$^\circ$C was characterized by XRD, TG/DTA, Fourier transform infrared (FTIR) and SEM.

2. Experimental

2.1. Materials preparation

The powders were synthesized using the following chemicals: La(NO3)3·6H2O (99.99%), Sr(NO3)2 (99.97%), Al(NO3)3·9H2O (98%), Mg(NO3)2·6H2O (99.97%) and Co(NO3)2·6H2O (98.0–102.0%) (All of them are from Alfa Aesar, a Johnson Matthey Company). To prepare the polymeric precursor for LSAMC, stoichiometric amounts of nitrate salts were mixed with the 5 wt.% PVA ($\sim$(CH2–CHOH)$_n$ molecular weight of 57,000–66,000, Alfa Aesar) solution. The nitrate salts were mixed in distilled water. This solution was then added to the PVA solution, which was made by dissolving appropriate amount of PVA into distilled water and stirring on a hot plate at 150$^\circ$C. The proportions of PVA to nitrate salts were adjusted in such way that the ratios of positively charged valences to hydroxyl groups (M$^{n+}$/–OH) of PVA were 1:1, 1.5:1 and 2:1, respectively. For example, in the case of 1.5:1 for 1 mol of LSAMC, total metal valences are 5.75 mol, and then the amount of PVA corresponding to 3.83 mol hydroxyl groups is needed. The resulting precursor solution was stirred and homogenized on a hot plate for 1 h at room temperature. The solution was then heated up to 250$^\circ$C to evaporate water while stirring. No precipitation was observed during the evaporation. Black crisp char was finally formed and dried in an oven at 200$^\circ$C overnight. The char was grounded into fine powders and calcined over a temperature range of 250–1100$^\circ$C in air for 6 h.

To break the hard agglomerates of the calcined powders, the 900$^\circ$C calcined powders was subjected to ball milling using a planetary mill for 1 h. ZrO2 balls (diameter: 5 mm) were used as the milling media, and ethanol as a solvent. The 900$^\circ$C calcined and ball milled powders were uniaxially pressed into pellets with a compaction pressure of 300 MPa. Green pellets were sintered at 1450$^\circ$C for 5 h in air with a heating rate of 5$^\circ$C/min.

2.2. Characterization

The phases in calcined and sintered samples were analysed using powder X-ray diffraction (XRD) (X’Pert Pro, PANalytical) with Cu Kα radiation (45 kV, 40 mA). Scans were taken in a 2θ range of 20–80$^\circ$ with a step size of 0.017$^\circ$. Lattice parameters were evaluated from all the diffraction peaks, by means of the UNIT-CELL program.\(^20\) The average grain size of the powder is estimated using the Scherrer’s formula:

$$d = \frac{0.9 \lambda}{\beta \cos \theta}$$

where $d$ is the average grain size, $\lambda$ is the wavelength of Cu Kα, $\beta$ is the full width at half maximum intensity, and $\theta$ is the Bragg’s angle.

The pyrolysis and decomposition behaviour of the LSAMC precursor powders was analyzed using thermogravimetric analysis (TG) (TAG 24, SETARAM) and differential thermal analysis (DTA) (TG-DTA 1600, Labsys) up to 1200$^\circ$C with air flow at a heating rate of 10$^\circ$C/min. Al2O3 powder was used as reference materials in the DTA test. To analyze the structure and chemistry of the calcined powders, FTIR (IFS 55, Bruker) was performed in a range of 400–4000 cm$^{-1}$. Dry KBr was used to form pellets for the FTIR tests. The morphology of powders and pellets was studied by scanning electron microscope (SEM) (JSM-840, JEOL). To avoid the electrical charging, powders and pellets were Pt/Au coated. The density of as sintered pellets was measured using the Archimedes method.

3. Results and discussion

3.1. Phase analysis

The XRD patterns of LSAMC powders with different M$^{n+}$/–OH ratios calcined at 700$^\circ$C for 6 h are shown in Fig. 1. As indicated in Fig. 1, all the diffraction peaks are from the perovskite LaAlO3 phase (JCPDS 31-0022). A broad arc-shaped continuum could be detected in the range of 25–33$^\circ$ besides the sharp diffraction peaks from LaAlO3 perovskite in powders.
Fig. 1. XRD patterns of LSAMC powders with different Mn+/OH ratios calcined at 700 °C for 6 h.

with Mn+/OH ratios of 1:1 and 2:1. The arc-shaped continuum is believed to result from the amorphous phase, which remains in these two powders after calcination at 700 °C. While the LSAMC powder with 1:1 ratio shows a flat background, and mainly crystalline LaAlO3 is obtained at such a low calcination temperature. This implies that the powder crystallizes more easily from the amorphous precursor powder than the other two powders.

Fig. 2 shows the XRD patterns of LSAMC powders calcined at 900 °C for 6 h. Single LaAlO3 perovskite phase is obtained for all three powders after calcination at 900 °C. Since the weak broad arc-shaped continuum has disappeared, it clearly implies the complete transformation of the amorphous phases into a pure LaAlO3 perovskite. Therefore, it can be concluded that the Mn+/OH ratio is of less importance when the calcination temperature is increased to 900 °C. Although the amount of PVA has no apparent effect on the phase purity of powders calcined at 900 °C, the larger amount of crystalline phase appeared in LSAMC powders with Mn+/OH ratio of 1:5:1 calcined at 700 °C points out that the ratio is the optimum to produce homogeneous powders. Thus, in the following study LSAMC powders synthesized in this ratio are used.

Fig. 3 shows the XRD patterns of the LSAMC powders with Mn+/OH ratio of 1.5:1 calcined at various temperatures for 6 h and pellet sintered at 1450 °C for 5 h. Fig. 3 reveals that the amorphous phase starts to crystallize around 500 °C, since the diffraction peaks from LaAlO3 perovskite phase could be first detected at this temperature. At a calcination temperature of 700 °C, it can be illustrated that mainly crystalline LaAlO3 is formed in the powder. Fully crystallized LaAlO3 perovskite phase is obtained in the powders after calcination at 900 and 1100 °C, and no amorphous phase could be found. The 1450 °C sintered pellet shows a rhombohedral LaAlO3 perovskite phase, with lattice parameters of $a = 5.36301 \text{ Å}$ and $c = 13.12887 \text{ Å}$, which is in good agreement with the previously reported values.8,12

Furthermore, it is illustrated in Fig. 3 that no diffraction peaks from impurity phases could be detected in the XRD patterns during the firing process. It implies a perfect mixing of the constituent cations in the precursor powders prepared by the PVA process. It is believed that homogeneous mixing of cations in the precursor is of great importance to enhance purity, reactivity and homogeneity of powders.17 In the PVA process, the floating metal ions are not only stabilized around the polymer by the complexation between cations and the hydroxyl groups (–OH), but also entrapped by the polymer network.17–19 The metal cations mix homogeneously at an atomic level and thus results in fine powders. Therefore, the PVA process offers the advantage of preparing homogeneous and highly reactive LSAMC powders through a much more simplified procedure. The solid-state reaction method could produce pure phase and dense LaAlO3 ceramics,7–11,13 however, it suffers from tedious regrinding of powders, high sintering temperature and long firing time. As a matter of fact, synthesis of doped LaAlO3 materials using solid-state reaction method can easily be affected by the presence of impurities. Kakihana and Okubo found unreacted La2O3 even after the powders were calcined at 1700 °C.21 La4Al2MgO10 and LaSrAlO4 were observed in LaAl0.9Mg0.1O2.95 after firing at 1500 °C for 3 h.13 Moreover, Nguyen et al. reported impurities such as SrAl2O4 and (La and Al) oxides in sintered La0.9Sr0.1Al0.9Mg0.1O2.9 pellets.10 Thus, the PVA method

Fig. 2. XRD patterns of LSAMC powders with different Mn+/OH ratios calcined at 900 °C for 6 h.

Fig. 3. XRD patterns of calcined LSAMC powders and sintered pellet.
is quite effective at preparing phase pure LSAMC materials, compared with the conventional solid-state reaction method.

3.2. Thermal behaviour

Fig. 4 shows the TG/DTA curves of the LSAMC precursor powder (Mn+/OH = 1.5:1). It can be seen from the DTA curve that there are pronounced exothermic peaks around 215, 400, and 790°C and an endothermic peak around 75°C. TG analysis shows that most of the organics and nitrates decompose at temperatures <700°C. The decomposition of LSAMC precursor powder shows three stages, which may be overlapping. In the first stage below 160°C, the weight loss (4%) is due to evaporation of free water, corresponding to the endothermic peak around 75°C. The second stage occurs over the temperature range of 160–700°C, where complex decomposition of organics and nitrates happens and corresponds to the exothermic peaks at 215 and 400°C in the DTA curve and with a thermal weight loss of 24%. The third stage shows a slight weight loss of 4.5% in temperature range of 700–800°C. This weight loss could be due to the decomposition of carbonate intermediates, and the exothermic peak at 790°C corresponds to this process.

3.3. IR spectra

FTIR spectra of the LSAMC powder as a function of calcination temperature are given in Fig. 5. The broad band at 3200–3700 cm\(^{-1}\) is due to the stretching vibration of the free hydroxyl group. The presence of CO\(_2\) is clearly observed in all these calcined powders. The dissolved or atmospheric CO\(_2\) is detected by the band located at 2345 cm\(^{-1}\). The presence of structural CO\(_3^{2-}\) is detected by the double bands at 1420 and 1500 cm\(^{-1}\), as well as at 1065 cm\(^{-1}\). The existence of NO\(_3^-\) is indicated by the band located at 845 cm\(^{-1}\). As illustrated by the XRD patterns in Fig. 3, there is only amorphous phase besides the crystalline perovskite LaAlO\(_3\) phase in LSAMC powders calcined below 700°C. And thus it can be concluded that the carbonate and nitrate compounds must be in an amorphous state. The lower wave number under 690 cm\(^{-1}\) is due to the complex metal oxygen vibrations. As shown in Fig. 5, the hydroxyl group, carbonate and nitrate ions remain in the LSAMC powder calcined below 700°C. After calcination at 900°C, there are only CO\(_2\) and metal oxygen vibrations left in the curve, which implies that most of the organic, nitrate and carbonate intermediate compounds are completely decomposed at this stage. This result is consistent with the XRD patterns and TG analysis (see Figs. 3 and 4).

3.4. Powder morphology and microstructure

Fig. 6 shows the SEM morphology of 900°C calcined LSAMC powders. As discussed above, the crystallization and thermal decomposition process are complete for LSAMC powders calcined at 900°C. Ultrafine powders with primary particle sizes of 50–100 nm could be demonstrated in the calcined powder from Fig. 6. The average grain size of these powders estimated from the X-ray diffraction pattern (see Fig. 3) is 60 nm, in good agreement with the SEM observation.

Furthermore, Fig. 6 shows that the small particles sintered into big hard agglomerates at calcination temperature of 900°C. The presence of hard agglomerates may seriously deteriorate the density of the final sintered ceramics. Huang et al. reported a sol–gel method to prepare doped lanthanum gallate powders, and...
found that the density of sol–gel prepared samples was generally lower than the traditional ceramic method produced ones.\(^{22}\)

A 85% relative density of lanthanum gallate pellets produced by the Pechini method was reported by Tas et al.\(^{23}\) Although ultrafine calcined powders were prepared in both cases, the densification of the sintered pellets was apparently not satisfactory. The reason is attributed to the agglomeration of the super fine particles, and it is suggested that the milling process may be a possible way to reduce agglomeration. In a crystallization and densification study of nano-size cordierite powder by Lee, it was found that mechanical milling was needed to break up the agglomerates, and finally a nearly full densification was obtained after sintering.\(^{17}\) Therefore, planetary ball milling was introduced to the 900 °C calcined powders in order to break up the agglomerates and enhance the densification. The SEM morphology of 900 °C calcined LSAMC powders after planetary ball milling is shown in Fig. 7. Compared with the un-milled powder (see Fig. 6), the powder shows fine and loosely packed particles instead of the hard agglomerates.

Fig. 8 illustrates the SEM microstructures of the fracture surface of a pellet after sintering at 1450 °C for 5 h. The fracture surface morphology reveals that an intergranular fracture behaviour dominates in the LSAMC sintered pellets. Further study of the SEM microstructure illustrates that the sintered LSAMC ceramics have uniform isotropic grain morphology, and the grain size is around 0.6 μm. The density of the sintered pellet is 5.98 g/cm\(^3\), measured by the Archimedes method, and is 95% of the theoretical density. Actually, formation of single-phase perovskite is a basic issue in the processing of LaAlO\(_3\)-based ceramics, but to lower the synthesis temperature using an alternative route is also rather necessary. Because the sinterability of LaAlO\(_3\)-based ceramics is rather poor, the sintering temperature for the solid-state reaction method prepared powders is raised to around 1600–1700 °C. Thus, the PVA method shows advantages to prepare dense doped LaAlO\(_3\) ceramics with well-developed submicron microstructures at a lower firing temperature. It has been discussed above that the PVA method can provide ultrafine and homogeneous powders with a particle size below 100 nm. Besides, the milling process introduced to the calcined powders is also found to be effective to break up the hard agglomerates evolved during calcination. Therefore, it is reasonable to conclude that this enhanced densification to get dense LSAMC ceramics at relatively lower sintering temperature is due to the fine powders and milling process.

**4. Conclusions**

A PVA complexing method was used to synthesize LSAMC powders. It was found that mainly crystalline LaAlO\(_3\) was formed for powder with 1.5:1 M\(^{3+}\)/OH ratio after calcination at 700 °C. The fully crystallized LaAlO\(_3\) phase is obtained after calcination at 900 °C. Moreover, the XRD pattern revealed no trace of impurity phases during the heating process of LSAMC powders, which reflects the perfect mixing of metal ions in precursor powders. SEM showed that the powders calcined at 900 °C consist of fine nanocrystalline powders, although hard agglomerates are also demonstrated. The ball milling process is effective to break up the hard agglomerates and finally results in fine and loosely packed particles. The 1450 °C sintered pellet is dense and has a uniform and well-developed submicron microstructure as shown by SEM. Compared with the conventional solid-state reaction method, the PVA method is found to be effective to substantially lower the sintering temperatures. The density of the sintered pellet is 5.98 g/cm\(^3\), 95% of the theoretical density.

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Supplement 4

“Synthesis and characterisation of lanthanum aluminate powders via a polymer complexing plus combustion route”

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Synthesis and characterisation of lanthanum aluminate powders via a polymer complexing plus combustion route

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Abstract

Lanthanum aluminate powders were prepared by a simple polymer complexing plus combustion method using PVA or PEG as complexing agent. The influence of different polymers on the phase purity, morphology of product and sintering performance were investigated. Minority impurity La\textsubscript{2}O\textsubscript{3} exists in the PEG powder, but it could be eliminated after sintering at high temperatures. Although the pure phase LaAlO\textsubscript{3} can be easily obtained in PVA powders calcined at 950\textdegree C, more seriously aggregated particles exist. PEG shows advantages over PVA in terms of better densification and microstructure control in the sintered products. The high relative density of 97.0\% and homogeneous fine microstructure with grain size < 3 \(\mu\)m can be obtained for the PEG pellet sintered at 1600\textdegree C for 5 hrs. To select proper polymers in complex oxide synthesis, the agglomeration and morphology of the powder are the most important factors to be considered.

Key words: Lanthanum aluminate; perovskite; PVA; PEG.

1. Introduction

Lanthanum Aluminate (LaAlO\textsubscript{3}) has gained much attention in the last decade for its dielectric properties and perfect lattice matching to many materials with perovskite
structure. LaAlO$_3$ ceramics can be used as resonators in microwave filter application due to its favourable microwave dielectric properties [1]. In addition, the material offers small lattice and thermal mismatches with perovskite materials, and thus it has emerged as one of the most favoured high-temperature superconducting (HTS) substrates or buffer layers for depositing ferroelectric films [2–4]. Generally, the performance of polycrystalline LaAlO$_3$ ceramics in the above-mentioned applications is dependent on the microstructure defects, e.g. residual porosity, impurity etc.

As the bases of making LaAlO$_3$ ceramic, LaAlO$_3$ powder is normally synthesized by solid state mixing and reaction method in the temperature range of 1500 – 1700°C [5,6]. Although the method has the advantage of simplicity, it requires repeated and prolonged heat treatment and grinding process. The synthesized powders may suffer the drawbacks of chemical inhomogeneity, low sinterability with large particle size, and undesired impurities. In order to prepare high performance LaAlO$_3$ ceramics, several wet chemistry methods have been developed to overcome the drawbacks in solid state reaction route. In order to have small particle size for better densification, low heat treatment temperature is always regarded as the key point. Taspinar and Tas [7] reported a successful conversion of precursor to pure LaAlO$_3$ powder at 750°C for 16 hrs using the self propagating combustion, however heavily agglomerated particles were obtained. Li [8] and Kuo [9] implemented the same co-precipitation method, where the reaction between diluted ammonia and nitrate salts leads to fine precursors. The nanocrystalline LaAlO$_3$ powders with a particle size less than 50 nm were obtained by calcination at 700°C. Recently, pure and well developed LaAlO$_3$ cubic-shaped particles with size < 3 μm were even successfully synthesized at temperature of 630°C using a molten salt method, which is the lowest synthesis temperature so far [10]. Considering the
application for ceramic production, the highest relative density of LaAlO₃ ceramics obtained by conventional sintering with is 98.7% [9], which is still not perfect for the applications as substrates and microwave components where zero porosity is highly preferred. There is still a need to find simple and reliable methods to prepare fine and homogeneous powder with excellent sintering properties.

The polymer complexing plus combustion route is regarded as a simple and cost-effective gel method [11]. The method is characterized with stabilization of cations in liquid through either chemical binding between functional groups in polymer chains and cations or steric entrapment of cations into the polymer network. This stabilization process prevents precipitation and thus ensures a homogeneous mixing of components at atomic level. Various complex oxides have been successfully prepared with this method using water soluble polymers such as poly(vinyl alcohol) (PVA) [12,13] or poly(ethylene glycol) (PEG) [14–16]. The properties of polymer play important roles for the final powder properties. Simply considering the available sites in single PVA and PEG chain, PVA is more efficient to combine more cations in a single molecule. But there is no clear evidence to show how the different polymers influence the synthesis and properties of the final complex oxides. In this study, we report a comparative synthesis study of LaAlO₃ powders by using PVA or PEG as complexing agent. The difference between powders prepared by these two complexing agents is compared in terms of phase purity, morphology and sintering performance.

2. Experimental

The powder was synthesized using the following starting materials, supplied by Alfa Aesar: La(NO₃)₃·6H₂O (99.9%), Al(NO₃)₃·9H₂O (98%), PVA (98 – 99%, molecular weight of 57,000 – 66,000) and PEG (molecular weight of 1500).
The PVA-metal nitrate precursor for LaAlO$_3$ was prepared as follows. The PVA solution was made by dissolving weighed amount of PVA in distilled water and stirring on a hot plate at 150°C. Stoichiometric amounts of nitrate salts were then added to the PVA solution. The molar ratio of PVA monomers to the total metal cations was 2:1. The PVA-metal nitrate solution was stirred to homogenize for 1 h at room temperature. Then the solution was heated at 80°C to evaporate water while stirring for 5 hrs. No precipitation was observed as water evaporated, and finally a crisp gel was obtained. The obtained gel was grounded and calcined at 950°C for 6 hrs (10°C/min heating rate).

A similar preparation route was used for PEG-metal nitrate precursor. Stoichiometric amounts of nitrate salts were dissolved in the PEG solution. The PEG solution was prepared by adding PEG in distilled water, with 2:1 molar ratio of PEG monomers to metal cations. The resulting PEG-metal nitrate solution was stirred for 1 h at room temperature and then evaporated at 80°C to obtain the crisp gel. The crisp gel was calcined in air at 950°C for 2 hrs (10°C/min heating rate).

The as-calcined powders were milled for 2 hrs using planetary mill with zirconia balls (Φ5 mm) and isopropanol as the milling media. These powders were dry-pressed into pellets with a compaction pressure of 200 MPa. Green pellets were sintered at temperatures in range of 1450 – 1600°C for 5 hrs in air with a heating rate of 5°C/min.

The phases in the samples were investigated using powder X-ray diffraction (XRD) (X’Pert Pro, PANalytical) with Cu Kα$_1$ radiation (45 kV, 40 mA). Scans were taken in the 2θ range of 20 – 80° with a step size of 0.017°. The morphology of powders and microstructure in the sintered pellets was studied by scanning electron microscope (SEM) (JSM–7000, JEOL). To avoid the electronic charging, powders and pellets were
carbon coated. The density of sintered specimen was measured using the Archimedes method.

3. Results and discussions

The XRD patterns of calcined powders and sintered pellets are shown in Fig. 1. The PVA powder is essentially phase pure after calcination at 950°C for 6 hrs. As shown in Fig. 1a, no secondary phase is found in this PVA powder, and all the diffraction peaks can be indexed with perovskite LaAlO$_3$ phase (JCPDS 31-0022). The PEG sample shows mainly perovskite LaAlO$_3$ phase after calcination. However, small amount of secondary phase, La$_2$O$_3$ (JCPDS 05-0602), is detected as shown in Fig. 1b. The fraction of La$_2$O$_3$ is estimated to be 6%, by a semi quantitative calculation using the most intensive peaks of phases. It is believed that a homogeneous mixing of cations in the precursor is of great importance to enhance homogeneity and thus the purity of obtained powders. The XRD results illustrate a different stabilization capacity of mixing constituent cations for these two polymers. Apparently, PVA can guarantee a chemical homogeneity in the solution during the process, and thus result in phase pure calcined powder. However, all the sintered samples (1450°C, 1500°C and 1600°C) from both PEG and PVA powders calcined at 950°C only show single LaAlO$_3$ phase in the XRD spectrum (Fig. 1c and Fig. 1d). The minor impurity of La$_2$O$_3$ in the PEG powder can be further consumed to form LaAlO$_3$ during the high temperature heat treatment. Although the PEG method suffers from the shortcoming of a trace amount of impurity after calcination, both methods can successfully produce single phase sintered pellets. Therefore, the impurity in LaAlO$_3$ powders does not influence the final sintered samples in terms of phase purity.
The nanometer sized particles in the calcined powders are shown in the SEM images in Fig. 2. Fine particles with an average grain size of ~150 nm are obtained in the PVA powder. However, these PVA powders are found to have severe hard aggregates with sintered necks between grains. The agglomerated grains tend to form a sheet-like network as shown in Fig. 2a. In the PEG powder, the particles, which have a size around 100 nm, have a rather regular spherical shape and are only weakly agglomerated. Generally, morphology of agglomerates is independent of chemical composition, and more linked to the gel characteristics [13,17]. PVA provides a continuous chemical binding position of hydroxyl groups along the polymer chain. The distance between cations is extremely small. Therefore, it is possible to obtain a strong driving force to form the chain shaped powder when the precursor is calcined in air. The intrinsic entangled conformation of PVA will further facilitate the formation of a sheet-like network in the final powder. On the contrary, each PEG molecule only provides two hydroxyl groups on the two ends for the chemical binding between the polymer and cations. Most of the cations are stabilized by a physical entrapment process in the entangled PEG chains. The larger distance between the cations offers less possibility to have a close contact between newly formed oxide particles during the heat treatment. Duran et al. [18] reported a stronger agglomeration in PVA powder than PEG powder in the synthesis of CeO₂ when the same polymer complexing route was used; the green pellets prepared from PVA powders were subjected to obvious density gradients during the dry-press process, which leads to the inferior densification.

To break up agglomerates in the as-calcined powders, ball milling was used. The morphology of powders after ball milling for 2 hrs is shown in Fig. 3. Most of the sheet structures in the PVA powder disappear after the milling process. However, hard
agglomerates still exist with sintered necks formed between several nearby particles, which implies that the milling process is only efficient to break the big network but not the local sintered necks (Fig. 3a). While in the PEG powder, former agglomerated particles are reduced to smaller size and with only the weak agglomeration; physical contacts between primary particles were indicated from the morphology observation.

To compare the sintering performance of these as-prepared powders, green pellets were sintered at 1450°C, 1500°C and 1600°C for 5 hrs. The sintering behaviour of the two powders is compared in Fig. 4, where the relative density is plotted as a function of sintering temperature. The theoretical density of 6.52 g/cm³ is used for calculating the relative density. The PVA samples show a sharp increase in relative density when the sintering temperature increases from 1450°C to 1500°C. However, the densification is rather limited after 1500°C, with a minor increase when the temperature goes up to 1600°C, where the relative density only increases from 96.5% to 96.8%. While for PEG samples, the relative density increases with increasing sintering temperature and this implies a continuous densification process. The highest relative density of 97.0% is obtained for the PEG pellet sintered at 1600°C for 5 hrs. This result is comparable to those reported by other researchers [8,9,19]. The existence of small amount of La₂O₃ does not seem to be so detrimental for the sintering, especially for the densification process. Nevertheless, it is still highly preferred to remove such a minor impurity to improve the stoichiometry precision. This is under further investigation by improving the gel-forming process in the PEG method. Considering the slightly smaller particle size in PEG powder, it is quite logic to expect a higher driving force and thus a higher relative density of sintered samples at low temperature of 1450°C. However, a reversed
sequence for densities of PVA and PEG 1500°C sintered samples is observed in Fig. 4, which suggests that further factors influencing densification process need to be analyzed.

Fig. 5 shows the SEM images of the fracture surface of the sintered pellets. The images reveal that intergranular fracture mode dominates in all the LaAlO$_3$ pellets. When sintering temperature increases from 1450°C to 1600°C, both PVA and PEG samples show an increase of grain size. Although particle size is comparable in PVA and PEG powders (Fig. 2), the grain sizes of the sintered PVA samples are much larger than those of PEG samples. Even at a higher temperature of 1600°C, the grain size in the PEG pellet is still between 2 – 3 µm while the grain size is larger than 6 µm in the PVA sample. Intergranular pores can be found in all samples, but the characteristics of the pores are rather different in PEG and PVA samples. Firstly, a noticeable difference in the pore size development can be easily identified in all the samples shown in Fig. 5. For samples sintered at 1500°C and 1600°C respectively, the pore size in PEG pellets is much smaller than in PVA pellets. There is no obvious change of the maximum pore size in the PEG pellets (indicated by the arrows in Fig. 5) when the sintering temperature increases from 1500°C to 1600°C, while the PVA pellets show definitive increase in both average pore size and maximum pore size in Fig. 5. Secondly, for PVA samples, there is a clear difference in the pore surface when the sintering temperature increases from 1500°C to 1600°C, where the well developed fringes can be found in the 1600°C samples. Such a fringe can be only formed by strong surface diffusion during the sintering process. Thus, PVA samples undergo an extraordinary final sintering stage where surface diffusion is as active as other diffusion processes. If only the surface energy is considered, the concaved grain surface around the pores found in PVA samples should introduce a tendency of pore shrinkage. But the further pore growth
indicates that more factors need to be considered. Based on the solid state sintering theory, the numbers of grains around the pore can be expressed as a function of pore to grain size ratio. The pore growth will occur when the pore size is larger than a critical size if the dihedral angle is kept constant. The large pore size formed at lower temperature should be the reason for the pore growth at 1600°C in PVA samples. Once the surface diffusion dominates the mass transport in the sintering process, there will be no further densification and only substantial grain growth happens in polycrystalline solids. Therefore, the big difference in grain size between PEG and PVA pellets should be attributed to the active surface diffusion in the PVA samples sintered at high temperatures. Such a difference in the diffusion mechanism is highly linked with the morphology of the starting powder. PVA powder shows strongly sintered neck which leads to difficulties in removing big pores through grain boundary diffusion during sintering. Therefore, the pore size in PVA pellets is much larger than that in PEG pellets, even if the similar density was obtained at 1500°C and 1600°C. This further indicates that PEG pellet can be obtained a higher density if the starting powder can be improved in the future. Although phase purity in the PEG powder synthesis is of worse performance, the normal sintering process without active surface diffusion process gives PEG powder strong advantages over PVA powder in terms of densification and grain size control in the final product. Therefore, it can be concluded that the polymer route using PEG as complexing agent can provide much better densification and microstructure control in the synthesis of complex oxides.

4. Conclusions

A simple polymer complexing and combustion method is used to prepare nanocrystalline LaAlO₃ powders. The influence of different polymers on the phase
purity, morphology of product and sintering performance is compared using different complexing agents, namely PVA and PEG. Small amount of \( \text{La}_2\text{O}_3 \) is detected in the PEG powder, but it could be eliminated after sintering. Although the PVA powder is phase pure after calcination at 950°C, it contains more seriously aggregated particles. The morphology of the starting powder has dramatic influence on the sintering performance in aspects of densification and microstructure control. PEG shows strong advantages over PVA due to much less degree of agglomeration state in the synthesized powder. High density of 97.0% and homogeneous fine microstructure with grain size < 3 \( \mu \text{m} \) can be obtained for the PEG pellet after sintering at 1600°C for 5 hrs. It is more important to get powders with desirable morphology and less agglomeration when different polymers can be selected for the synthesis of complex oxides.

References


Figures captions:

Fig. 1 XRD patterns of (a) PVA powder; (b) PEG powder; (c) PVA pellets; (d) PEG pellets.

Fig. 2 Typical morphology of calcined powders: (a) PVA method; (b) PEG method.

Fig. 3 SEM showing the morphology of powders after ball milling for 2 hrs: (a) PVA method; (b) PEG method.

Fig. 4 Change of relative density as a function of sintering temperature.

Fig. 5 Microstructures of the fracture surface of sintered pellets: (a) PVA method, 1500°C; (b) PVA method, 1600°C; (c) PEG method, 1500°C; (d) PEG method, 1600°C.
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Supplement 5

“Lanthanum gallate and ceria composite as electrolyte for solid oxide fuel cells”

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Lanthanum gallate and ceria composite as electrolyte for solid oxide fuel cells

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Abstract

The composite of doped lanthanum gallate (La0.9Sr0.1Ga0.8Mg0.2O2.85, LSGM) and samaria-doped ceria (Ce0.8Sm0.2O1.9, CSO) was investigated as an electrolyte for solid oxide fuel cell (SOFC). The LSGM-CSO composite was examined by X-ray diffraction (XRD) and impedance spectroscopy. It was found that the sintered LSGM-CSO composite contains mainly fluorite CeO2 phase, and with a minority impurity phase, Sm3Ga5O12, detected by XRD. The LSGM-CSO composite electrolyte shows a small grain boundary response in the impedance spectroscopy as compared to LSGM and CSO pellets. The composite electrolyte exhibits the highest conductivity in the temperature range of 250–600°C, comparing with LSGM and CSO specimens. The LSGM-CSO composite electrolyte can be expected to be an attractive intermediate temperature electrolyte material for solid oxide fuel cells.

Key words: lanthanum gallate, ceria, composite, phase evolution, conductivity.

1. Introduction

Solid oxide fuel cells (SOFCs) allow efficient and clean conversion of chemical energy of fuels to electricity. In general, the traditional SOFCs with yttria-stabilized zirconia (YSZ) as electrolyte need high operating temperatures, e.g. 800–1000°C, to obtain a high enough ionic conductivity. The high temperature exerts harsh requirements on the sealing materials and interconnects, such as thermal matching and
chemical stability, *etc.* [1]. Thus alternative electrolyte materials for intermediate temperature solid oxide fuel cell (IT-SOFC) operated at 500–800°C have attracted much attention in recent years [2]. The fluorite structure ceria based oxides are promising alternative electrolyte materials for IT-SOFC [2-5]. The material has a higher conductivity than the YSZ electrolyte, especially at low temperatures. However, the doped ceria shows some electronic conductivity at low oxygen partial pressures due to the reduction of Ce$^{4+}$ to Ce$^{3+}$ [4,5]. The Sr- and Mg-doped LaGaO$_3$ electrolyte has a superior conductivity and remains as ionic conductor over wide range of oxygen partial pressures, $10^{-20} < P_{O_2} < 1$ atm [6-8]. Nevertheless the material has the disadvantage of expensive gallium, poor mechanical performance [9], and chemical stability problems with electrode materials [2].

Composite electrolytes have been identified as interesting alternative electrolyte material because of their extraordinary electrical properties [10-11]. Already in 1973, Liang reported a substantial increase of ionic conductivity of lithium iodide with the incorporation of the inert phase, aluminum oxide [12]. Mishima *et al.* investigated the CSO-YSZ composite electrolyte [10]. The addition of CSO demonstrates an improvement of electrical conductivity of the composite electrolyte. Meanwhile, the electronic conduction of CSO is successfully blocked in the composite electrolyte, as the composite has a microstructure with CSO particles well dispersed in the YSZ matrix. Recently, the LSGM-CSO composite was investigated by Xu *et al.* [13]. The results suggested that 10 wt% of LSGM addition in the composite is the optimum and a higher conductivity was obtained at temperatures 500–700°C as compared with the LSGM pellet. However, the problem of inter-diffusion and reaction may arise due to the presence of interfaces between different phases, especially for the intimate mixture [4,10,14]. The lanthanum and strontium cations can diffuse into the fluorite
ceria lattice [4]. Kharton et al. reported a formation of low ionic conductive layers caused by the diffusion of lanthanum and strontium into the ceria lattice [14]. In addition, information on the electrical properties of the LSGM-CSO composite is still quite limited. In this work, we investigate the LSGM-CSO composite electrolyte prepared by coprecipitation method. LSGM and CSO are prepared as a comparison. X-ray diffraction and impedance spectroscopy are used to characterize the materials.

2. Experimental

2.1 Materials preparations

The coprecipitation method was used to prepare La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.85}$ (LSGM) precursor. Stoichiometric amounts of La$_2$O$_3$ (99.99%), SrCO$_3$ (99.99%), Ga$_2$O$_3$ (99.999%) and MgO (99.95%) were first dissolved in nitric acid solution by stirring on a hot plate. After the complete dissolution of the component oxides, this solution was added dropwise into a stirred ammonia solution at 80°C. White precipitate was formed at the pH value around 9. The resulting precipitate was then aged for 24 h on a hot plate and evaporated in the oven at 150°C. Calcination was subsequently carried out for the dry LSGM precursor at 800°C for 0.5 h.

The preparation of Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ (CSO) precursor followed the same route as for LSGM. The starting materials are CeO$_2$ (99.9%) and Sm$_2$O$_3$ (99.9%). The CSO precursor was calcined at 600°C for 0.5 h.

The LSGM-CSO composite was prepared with a LSGM to CSO weight ratio of 1:9. The CSO precipitate was initially prepared as above mentioned. A solution with completely dissolved stoichiometric amounts of La$_2$O$_3$, SrCO$_3$, Ga$_2$O$_3$ and MgO was then slowly dripped into the CSO precipitate solution while stirring and, at the same time, ammonia solution was also added to keep the mixture at a pH of 9.
obtained mixture was aged for 24 h on a hot plate and dried at 150°C afterward. The obtained dry precursor was calcined at 600°C for 0.5 h.

All calcined powders were ground in an agate mortar and then dry pressed into pellets with a compaction pressure of 200MPa. The green pellets were sintered at 1450°C for 5 h at a heating/cooling rate of 5°C/min.

2.2 Characterization

X-ray diffraction patterns of the samples were examined by using powder X-ray diffraction (XRD) (X’Pert Pro, PANalytical) with Cu Ka radiation (45 kV, 40 mA). Scans were taken in a 2θ range of 20 – 80° with a step size of 0.017°.

The electrical characterisation of sintered pellets was carried out by impedance spectroscopy (SI 1260, Solartron). Sintered pellets were first wet-ground to remove the surface layer. Gold paste (Agar Scientific) was then applied on both sides of the pellets and cured at 730°C for 2 h. Impedance measurements for these pellets were made from 250°C to 750°C at intervals of 50°C in the frequency range from 10 MHz to 0.1 Hz. The impedance spectrum was analyzed using the ZView 2 software. Impedance from cables, leads and sample holders obtained by measuring a blank cell was subtracted from the sample impedance spectra.

3. Results and discussions

3.1 XRD diffraction patterns

Fig. 1 shows the XRD diffraction pattern of the sintered LSGM-CSO composite. The XRD patterns of LSGM and CSO are included as a reference. It is found that the composite mainly has fluorite CeO₂ phase after sintering at 1450°C. However, diffraction peaks from a minority phase, Sm₃Ga₅O₁₂, were also observed. This means that a reaction between CSO and LSGM occurs during the heat-treatment. Lanthanum and strontium have similar ionic radius as cerium, and thus La³⁺ and Sr²⁺ cations can
be dissolved into the ceria lattice \([4,5]\). Diffusion of \(La^{3+}\) and \(Sr^{2+}\) cations into the CSO lattice leads to deficiency of A-sites in the LSGM phase. Therefore, formation of \(Sm_3Ga_5O_{12}\) as a compensation can be expected to occur at the interface between the two phases, CSO and LSGM. Moreover, the coprecipitation method produces fine particles and an intimate mix of the component oxides, which leads to a large contacting interface between CSO and LSGM. It can therefore be expected that an impurity phase is formed at the interface of the contacting two phases. The inter-diffusion and reaction rate depend strongly on the particle morphology. The powder processing for preparation of LSGM-CSO composite should be controlled carefully to avoid potential reactions or diffusion among the phases. Further analysis of XRD pattern of LSGM-CSO composite shows no evidence of \(LaGaO_3\) phase. LSGM reacts with CSO at the interface to form \(Sm_3Ga_5O_{12}\) in the composite electrolyte, and thus the amount of remaining LSGM is too small to be detected. When Xu et al. [13] investigated the LSGM-CSO composite with 10 wt% of LSGM added, they also did not observe any \(LaGaO_3\) phase. It is suggested that LSGM in the composite is distributed along grain boundaries as a glass phase, and thus can not be detected by XRD.

3.2 Electrical properties

3.2.1 Impedance spectra

All the sintered pellets were characterised by impedance spectroscopy. The impedance spectrum generally separates bulk, grain boundary, and electrode processes of the ceramics [15]. Fig. 2 shows the impedance spectra, Nyquist plot, of the sintered specimens measured at 250°C. The LSGM-CSO composite electrolyte has a better electrical performance. Its impedance spectrum shows a small grain boundary response and a relatively perfect grain boundary semi-circle. Compared
with LSGM-CSO and LSGM, the CSO sample demonstrates the highest grain boundary response, although the CSO sample shows a pure fluorite phase as detected in the XRD pattern. The large grain boundary resistance is normally due to the microstructure defects such as impurity phases and/or pores. The density of sintered CSO pellet measured by Archimedes method was 86% of theoretical density (7.15 g/cm³). The CSO pellet thus contains pores and/or defects along grain boundaries. The LSGM shows a smaller grain boundary influence than that of the CSO. However, a depressed grain boundary semicircle for LSGM pellet was found, and this indicates that a constant phase element (CPE) exists along grain boundaries. CPE is believed to be dependent on the impurities in LSGM pellets [16]. A more general explanation for CPE is the distortion introduced by local inhomogeneities, e.g. two- or three-phase regions, local charge inhomogeneity, and variations in composition and stoichiometry [15].

The LSGM-CSO electrolyte has the smallest grain boundary response and a relatively perfect grain boundary semi-circle spectrum. This may be due to the space charge layer formed at the phase interfaces. It is generally accepted that the space charge layer exists in the two-phase system [11]. The enhancement of the concentration of vacancies or interstitials is expected if the second phase is surface reactive. As discussed earlier, the LSGM in the composite electrolyte may exist along grain boundaries, and thus provides a space charge layer at the interfaces. This space charge layer can explain the better electrical performance of the LSGM-CSO composite electrolyte.

3.2.2 Conductivity

Fig. 3 shows Arrhenius plots of the total conductivity as a function of temperatures. It is found that the LSGM-CSO composite has the highest conductivity at the
measuring temperature range of 250 – 600°C. While, the conductivity of LSGM is higher than those of the other two specimens in the temperature range 650 – 750°C. The LSGM-CSO composite has a lower conductivity than LSGM at this high temperature range, but the conductivity difference between these two pellets is relatively small. Although sintered CSO is phase pure as shown in Fig. 1, the specimen shows a lower electrical performance. This inferior conductivity may result from the pores and defects along grain boundaries in the CSO pellets as discussed before. Furthermore, the sintered pellets have different temperature dependence of conductivity, and thus a different activation energy of conductivity. The activation energies ($E_a$) of conductivity are calculated from the Arrhenius plots in Fig. 3 and listed in Table 1. The activation energy at temperatures 250 – 600°C for LSGM is 1.06 eV, corresponding well to the literature values [7,8]. Moreover, it is shown that the activation energies of LSGM-CSO composite electrolyte are lower than those for the LSGM and CSO at both temperature ranges of 250 – 600°C and 600 – 750°C. This reveals that the electrical conduction in the composite electrolyte has a lower barrier energy than in the other two specimens.

From the above results, it can be seen that the LSGM-CSO composite electrolyte has a reasonable electrical performance. Although we in the present work did not analyze the transport number of the composite materials, it is reported that the LSGM-CSO composite electrolyte is an ionic conductor based on the open-circuit voltage test [13]. Therefore, it can be expected that the composite process as reported here is a promising method for the improvement the conductivity of electrolytes for SOFC. Further investigation is necessary to optimize the processing conditions of the composite and to reduce the interaction between the phases.

4. Conclusions
The LSGM-CSO composite was investigated as an alternative material for SOFC electrolyte. The composite contains a small amount of impurity phase after sintering at 1450°C, namely Sm$_3$Ga$_5$O$_{12}$, besides the main phase fluorite CeO$_2$. La$^{3+}$ and Sr$^{2+}$ cations may diffuse into the ceria lattice, and the impurity phase is believed to form at the interface between phases as a result of the inter-diffusion of phase components. The LSGM-CSO shows smaller and more perfect semi-circle grain boundary response in the impedance spectrum compared with the CSO and LSGM specimens. This is explained by the space charge layer formed at interfaces between different phases. The composite electrolyte exhibits highest conductivity at temperatures 250–600°C. Therefore, the composite process is a promising method for the improvement the conductivity of electrolyte for SOFC.

References


Figures captions:

Fig. 1 XRD diffraction patterns showing the phases in pellets sintered at 1450°C for 5 h.

Fig. 2 Impedance spectra of sintered pellets measured at 250°C, (a) CSO; (b) LSGM; (c) LSGM-CSO composite.

Fig. 3 Arrhenius plots of the total conductivity of sintered pellets.

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<tr>
<th>Specimens</th>
<th>LSGM</th>
<th>CSO</th>
<th>Composite</th>
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<td>Conductivity at 750°C (S/cm)</td>
<td>0.030</td>
<td>0.020</td>
<td>0.026</td>
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<td>$E_a$ at 250 – 600°C (eV)</td>
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<td>$E_a$ at 650 – 750°C (eV)</td>
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<td>0.78</td>
<td>0.72</td>
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