ELABORATION AND IONIC CONDUCTION OF APATITE-TYPE RARE EARTH OXIDES

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ABSTRACT

We synthesized lanthanoid silicates and germanates with the apatite structure such as La_{10-x}AE_xSi_{6}O_{27-3x/2} with AE = Ca and Sr, La_{10-x}Y_xSi_{6}O_{27} and La_{10-x}Ge_{6}O_{27-3x/2}, with a view to the development of new electrolytes having good oxide-ion conductivities under 800°C for intermediate operating temperature solid oxide fuel cells (SOFCs). These ceramics were prepared by the mixed oxide route. Densities above 95% of the theoretical density were obtained. X-ray diffraction spectra evidenced a hexagonal apatite structure as a major phase. Conductivities as high as 1.4 \times 10^{-2} \text{ S.cm}^{-1} were measured at 700°C.

INTRODUCTION

One of the most important tasks in solid oxide fuel cell (SOFC) research is the reduction of operating temperature down to 700°C. The benefits include wider choice of cell materials, longer cell life, reduced thermal stresses, improved reliability, and reduced fuel cell costs. Operating temperatures of 800°C and lower can be achieved by using an extremely thin and dense \text{Y}_2\text{O}_3*\text{stabilised ZrO}_2 (YSZ) electrolyte or by using new oxide ion conductors with improved properties. So far, high oxide ion mobility has been reported in a small number of structural families, such as fluorite (doped cerium oxides) and perovskites (lanthanum gallates) (1-3), but these materials also exhibit too high an electronic conductivity in reducing atmospheres and strong reactivity toward standard electrode materials (4-7). Rare earth-based apatites have recently attracted considerable attention because of their high ionic conductivity and the well known chemical stability of the apatite structure. Conductivities as high as 0.01 \text{ S.cm}^{-1} have been reported for La_{10}Si_{6}O_{27} at 700°C by Nakayama et al. (8-11). Arikawa et al. (12) have subsequently reported that the strontium doped silicate La_{9.75}Sr_{0.25}Si_{6}O_{26.75} and the germanium analogue La_{9}Sr_{1}Ge_{6}O_{26.5} exhibit even higher conductivities. The apatite structure \text{A}_{10}(\text{MO}_4)_6\text{O}_2 consists of isolated MO_4 tetrahedra with the A cations located in two sites, one 7 coordinated (6h) and one 9 coordinated (4f), and the 2 extra oxide ions occupying 2a sites in channels along the c axis in which they can diffuse.

The present work focused on the synthesis, the physico-chemical, and electrochemical characterization of polycrystalline ceramics in the Si-based system La_{10}Si_{6}O_{27} ("oxygen-excess" compositions), with substitutions by calcium, strontium and yttrium on the La site according to the compositions La_{10-x}AE_xSi_{6}O_{27-3x/2} and La_{10-x}Y_xSi_{6}O_{27}, where x = 0.5, 0.75, 1.0, 1.5, and 4 for Ca, x = 0.5 and 1 for Sr, and x = 1, 2, and 4 for Y. Some compositions in the Ge-based system La_{10-x}Ge_{6}O_{27-3x/2} were also studied. Composition La_{9.33}Si_{6}O_{26} was also prepared as a reference composition.

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Calcium and strontium substitutions on the La sites are expected to induce the formation of $x/2$ anionic vacancies on the oxygen 2a site, according to the formula $\text{La}_{10-x}\text{AE}_x(\text{SiO}_4)_6\text{O}_3x/2$. Oxygen diffusion within the channels should be enhanced compared to pure $\text{La}_{10}\text{Si}_6\text{O}_{27}$ compound. Moreover, $\text{Ca}^{2+}$ cations, with a small ionic radius of 1.0 Å, are expected to occupy the La 7 coordinated site (6h) near the oxygen 2a site, whereas $\text{Sr}^{2+}$ cations, with a larger ionic size (1.26 Å), are expected to occupy the La9 coordinated site (4f); these substitutions should modify channels dimensions and electrostatic interactions with the oxygens in the 2a site. $\text{Y}^{3+}$ cations are expected to substitute to $\text{La}^{3+}$ cations in the 6h site with no modification of anionic vacancies concentration.

**EXPERIMENTAL**

High-purity $\text{La}_2\text{O}_3$, $\text{SiO}_2$, $\text{GeO}_2$, $\text{Y}_2\text{O}_3$, $\text{CaCO}_3$ and $\text{SrCO}_3$ powders were used as starting materials. The raw materials were ball-milled in ethanol, dried, and calcined in air between 1000° and 1200°C for Ge-based materials and at 1500°C for Si-based materials. Discs were prepared by uniaxial pressing with a pressure of 200 MPa. Sintering temperatures between 1350° and 1700°C in air were investigated to optimize ceramics microstructures and densities. The purity of these materials was studied by X-ray diffraction. Lattice parameters were evaluated to control cationic substitutions on the La sites and to determine theoretical densities. The hydrostatic density was measured on materials sintered at different temperatures. Dilatometry experiments were performed to study Ca, Sr, and Y doping influence on the sintering behavior. Conductivity measurements were made using AC impedance spectroscopy between 600° and 950°C under air, in the frequency range $10^6$ to $10^{-1}$ Hz. Both sides of the pellets were coated with a Pt paste and baked at 900°C to act as electrical contacts for the measurements.

**RESULTS**

**Physico-Chemical Characterizations**

X-ray diffraction was used to analyze phase purity in the calcined apatite powders as a function of the calcination temperature. Lattice parameters of the apatite phase were also determined for all compositions. The observation of Table 1 leads to the following conclusions:

1. **Si-based compositions**
   a. The apatite phase is formed after calcination at 1500°C without secondary phases for all compositions except for Y-doped compositions where secondary phase $\text{La}_8\text{Si}_4$ and residual starting material $\text{Y}_2\text{O}_3$ are observed.
   b. Lattice parameters $a$ and $c$ decrease linearly with calcium concentration.
   c. Lattice parameter $a$ decreases linearly with strontium concentration, whereas lattice parameter $c$ increases.

2. **Ge-based compositions**
   a. A calcination at 1000°C leads to the formation of secondary phases, which are eliminated at 1200°C.
   b. Lattice parameters are larger than those of the Si-based system, probably due to the larger ionic size of $\text{Ge}^{4+}$ (0.54 Å) compared to $\text{Si}^{4+}$ (0.40 Å).
Table 1. Crystalline Phases in the Si- and Ge-Based Apatite Materials Evidenced by X-ray Diffraction as a Function of Calcination Temperature and Doping Levels.

| Composition                | Calcination temperature (°C) | Main phase (apatite, hexagonal) | Secondary phase | a (Å)   | c (Å)   |
|----------------------------|-----------------------------|---------------------------------|-----------------|--------|--------|
| La₉₃₃Si₆O₂₆                 | 1500                        | La₉₃₃Si₆O₂₆                    | -               | 9.7128 | 7.1858 |
| La₉₃₃Ca₀.₅Si₆O₂₆.₇₅       | 1500                        | La₉₃₃Si₆O₂₆                    | -               | 9.703  | 7.179  |
| La₉₂₂₅Ca₀.₇₅Si₆O₂₆.₆₂₅     | 1500                        | La₉₃₃Si₆O₂₆                    | -               | 9.69   | 7.16   |
| La₉CaSiO₂₆.₇₅             | 1500                        | La₉₃₃Si₆O₂₆                    | -               | 9.651  | 7.155  |
| La₉₅CaSiO₂₆.₂₅            | 1500                        | La₉₃₃Si₆O₂₆                    | -               | 9.66   | 7.15   |
| La₆Ca₅Si₆O₂₆              | 1500                        | La₉₃₃Si₆O₂₆                    | -               | 9.67   | 7.15   |
| La₉₅S₉₀.₅Si₆O₂₆.₇₅        | 1500                        | La₉₃₃Si₆O₂₆                    | -               | 9.697  | 7.207  |
| La₉₅S₉₅O₂₆.₅             | 1500                        | La₉₃₃Si₆O₂₆                    | -               | 9.68   | 7.207  |
| La₉₉Si₆O₂₆                | 1500                        | La₉₃₃Si₆O₂₆                    | -               | 9.7    | 7.14   |
| La₉₉Si₆O₂₆                | 1500                        | La₉₃₃Si₆O₂₆                    | -               | 9.67   | 7.11   |
| La₉₉Si₆O₂₆                | 1500                        | La₉₃₃Si₆O₂₆                    | -               | 9.62   | 7.01   |
| La₉₃₃Ge₆O₂₆               | 1000                        | La₉₃₃Ge₆O₂₆                    | La₉₂Ge₂O₇,     | 9.907  | 7.27   |
| La₉₃₃Ge₆O₂₆               | 1200                        | La₉₃₃Ge₆O₂₆                    | La₉₂Ge₂O₅,     | 9.931  | 7.291  |
| La₉₆Ge₆O₂₆.₄             | 1000                        | La₉₃₃Ge₆O₂₆                    | La₉₂Ge₂O₇,     | -      | -      |
| La₉₆Ge₆O₂₆.₄             | 1200                        | La₉₃₃Ge₆O₂₆                    | La₉₂Ge₂O₅      | -      | -      |

The variations of the relative density as a function of the sintering temperature are given in Figures 1 and 2, respectively for Ca/Si-based and Sr-Y/Si-based apatites. Densities greater than 95% of the theoretical density are obtained for all Si-based apatites above 1600°C, except for Y-doped compositions. The presence of secondary phases in Y-doped apatites may explain these lower densities. Calcium and strontium doping enhance the densification of Si-based apatites at high temperatures.

Densities greater than 97% are obtained for Ge-based samples with an optimum sintering temperature of 1500°C. A de-densification is observed above 1550°C. The sintering of Ge-based apatites occurs at lower temperatures than Si-based apatites.

The effects of the doping elements on the densification were confirmed by dilatometry experiments (Figure 3). The presence of Ca and Sr activates sintering mechanisms at lower temperatures, which results in greater final shrinkage values.

Conductivity Measurements

Conductivity measurements were performed on the most densified ceramics. Results were compared to those reported in references (8-12). Table 2 summarizes the corresponding values of conductivities and activation energies.

As can be observed from Table 2, Ge-based electrolytes exhibit the highest conductivities (1.4 x 10⁻² S.cm⁻¹ for La₉₆Ge₆O₂₆.₄ at 700°C) (see Figure 4). Similar materials were previously studied, such as La₁₀Ge₆O₂₇. Nakayama et al. (11) reported weaker...
Table 2. Conductivities (S.cm⁻¹) and Activation Energies of Ge and Si-Based Apatite Materials as a Function of Temperature.

| Temperature (°C) | 700  | 750  | 800  | \(E_a/\text{kJ.mol}^{-1}\) |
|------------------|------|------|------|---------------------------|
| \(\text{La}_{9.33}\text{Si}_6\text{O}_{26}\) | 4.2 10⁻⁴ | 6.2 10⁻⁴ | 8.7 10⁻⁴ | 64.8 |
| \(\text{La}_{9.5}\text{Ca}_{0.5}\text{Si}_6\text{O}_{26.75}\) | 4.9 10⁻³ | 1.0 10⁻² | 1.1 10⁻² | 67.2 |
| \(\text{La}_{9.25}\text{Ca}_{0.75}\text{Si}_6\text{O}_{26.625}\) | 9.2 10⁻³ | 1.1 10⁻² | 1.4 10⁻² | - |
| \(\text{La}\text{Ca}_6\text{Si}_6\text{O}_{26.5}\) | 7.7 10⁻³ | 1.2 10⁻² | 1.8 10⁻² | 70.5 |
| \(\text{La}_{8.5}\text{Ca}_{1.5}\text{Si}_6\text{O}_{26.25}\) | 3.0 10⁻³ | 5.1 10⁻³ | 7.6 10⁻³ | 75.0 |
| \(\text{La}_{6}\text{Ca}_4\text{Si}_6\text{O}_{25}\) | 3.5 10⁻⁵ | - | 4.9 10⁻⁵ | - |
| \(\text{La}_{9.5}\text{Sr}_{0.5}\text{Si}_6\text{O}_{26.75}\) | 4.6 10⁻³ | 6.8 10⁻³ | 9.5 10⁻³ | 61.7 |
| \(\text{La}\text{Sr}_1\text{Si}_6\text{O}_{26.5}\) | 1.2 10⁻² | 1.4 10⁻² | - | 26.4 |
| \(\text{La}\text{Y}_1\text{Si}_6\text{O}_{27}\) | 3.9 10⁻³ | 4.5 10⁻³ | 6.3 10⁻³ | 59.4 |
| \(\text{La}\text{Y}_2\text{Si}_6\text{O}_{27}\) | 3.3 10⁻³ | 4.5 10⁻³ | 6.5 10⁻³ | 62.2 |
| \(\text{La}_{9.33}\text{Ge}_6\text{O}_{26}\) | 9.7 10⁻³ | 1.6 10⁻² | 2.3 10⁻² | 74.8 |
| \(\text{La}_{9.6}\text{Ge}_6\text{O}_{26.4}\) | 1.4 10⁻² | 2.2 10⁻² | 3.3 10⁻² | 68.5 |

Conductivities while Arikawa et al. (12) announced values close to 1.08 \(10^{-2}\) S.cm⁻¹ at 700°C. We can also notice that our samples, compared to \(\text{La}_{10}\text{Ge}_6\text{O}_{27}\) from reference 12, have a strong different behavior regarding to temperature (see Figure 4). If the activation energies are comparable for temperatures above 800°C, material from Arikawa et al. (12) has much more important activation energy for temperatures below 800°C. However, our composition is different since our material contains less La atoms and less than 3 oxygen atoms in channels.

Undoped Si-based apatites showed relatively poor performances, which is in good agreement with previous studies (8-10). However, the doping of these materials leads to a significant enhancement of conducting properties, especially for Sr- and Ca-doped compositions (see Figure 5). At 700°C, \(\text{La}\text{Sr}_1\text{Si}_6\text{O}_{26.5}\) reaches 1.2x10⁻² S.cm⁻¹, which is comparable to values measured for Ge-based materials at the same temperature. Activation energy is low (under 30 kJ.mol⁻¹), which means that these materials are promising candidates for an application as electrolyte for intermediate SOFC. Concerning Ca doping, at 700°C it seems that an optimum can be observed for a doping level close to 0.75. We can also notice that in the 700-800°C temperature range, for identical doping levels, Sr doping leads to better conductivities than Ca doping, probably because of the larger ionic radius of \(\text{Sr}^{2+}\): the size of the channels in which oxide ions are migrating may therefore be greater and allow an easier diffusion of oxide ions on 2a sites.

Measurements conducted on yttrium-doped apatites seem to support this assumption. We found poor conductivities compared with those obtained with Sr- and Ca-doped materials. A possible explanation is the ionic radius of \(\text{Y}^{3+}\), which is smaller than that of \(\text{La}^{3+}\text{Y}^{3+}\), located on 6h site, that could lead to a shrinkage of the diffusion channel for oxide ions. Nevertheless, these results have to be checked because of the presence of secondary phases in every Y-doped sample (Table 1). The presence of secondary phases...
such as $Y_2O_3$ in sample $La_6Y_4O_{27}$ could also explain that it was not possible to record convenient impedance spectra, suggesting that the material has very poor conductivity.

CONCLUSIONS

This investigation on the conducting properties of Si- and Ge-based apatite materials showed that they could compete with the traditional $Y_2O_3$-stabilised $ZrO_2$ electrolyte in intermediate temperature SOFCs. Conductivities as high as $9.2 \times 10^{-3}$ S.cm$^{-1}$, $1.2 \times 10^{-2}$ S.cm$^{-1}$, and $1.4 \times 10^{-2}$ S.cm$^{-1}$ were obtained, respectively, for Ca/Si, Sr/Si-based apatites ($La_{9.25}Ca_{0.75}Si_6O_{26.625}$ and $La_{9.0}Sr_{1.0}Si_6O_{26.5}$), and Ge-based apatites ($La_{9.6}Ge_6O_{26.4}$).

Much work still needs to be done to confirm and improve these promising results. Further investigations will be performed to optimize phase purity and ceramics microstructures and to correlate the conducting properties (i) to the nature and concentration of the doping elements (ii) to the elaboration parameters and (iii) to the morphology of the materials. We also intend to measure the conductivity in reducing atmospheres to check the absence of electronic conduction in the materials.

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Figure 1. Influence of Ca doping on the variations of the relative density of Si-based materials as a function of sintering temperature.

Figure 2. Influence of Sr and Y doping on the variations of the relative density of Si-based materials as a function of sintering temperature.

Figure 3. Influence of Ca and Sr doping on the dilatometric behavior of Si-based apatites.
Figure 4. Arrhenius plots of the electrical conductivity of Ge-based apatites.

Figure 5. Arrhenius plots of the electrical conductivity of Sr doped Si-based apatites.