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Effect of Sr and Al or Fe co-doping on the sinterability and conductivity of lanthanum silicate oxyapatite electrolytes for solid oxide fuel cells

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ABSTRACT

The effect of co-doping of Sr and Al or Fe on the microstructure, sinterability and oxide-ion conductivity of lanthanum silicate oxyapatites is investigated in detail at 300–800 °C by the electrochemical impedance spectroscopy. The oxide-ion conductivity is $1.46 \times 10^{-2} \text{ S cm}^{-1}$ for $\text{La}_{9.5}\text{Sr}_{0.5}\text{Si}_{5.5}\text{Fe}_{0.5}\text{O}_{26.5}$ (LSSFo) and $1.34 \times 10^{-2} \text{ S cm}^{-1}$ at 800 °C for $\text{La}_{9.5}\text{Sr}_{0.5}\text{Si}_{5.5}\text{Al}_{0.5}\text{O}_{26.5}$ (LSSAO), respectively, which is one order of magnitude higher than $6.16 \times 10^{-3} \text{ S cm}^{-1}$ measured on $\text{La}_{9.67}\text{Si}_6\text{O}_{26.5}$ (LSO) oxyapatite under the identical test conditions. The grain bulk and grain boundary resistances of co-doped oxyapatite are significantly smaller than that of LSO oxyapatite, and decrease significantly with the increase of the sintering temperature. LSSFo and LSSAO also show significantly higher density as compared to that of LSO. The results indicate that co-doping of Sr and Al or Fe significantly improves the densification, sinterability and oxide-ion conductivity of lanthanum silicate oxyapatites.

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Introduction

Solid oxide fuel cells (SOFCs) have attracted considerable attention as efficient power-generating systems with high fuel flexibility, low greenhouse gas emission and high efficiency [1–6]. Yttria-stabilized zirconia (YSZ) is the most common electrolyte for SOFCs [7–9]. However, the ionic conductivity of YSZ electrolytes decreases rapidly with the reduction in operation temperatures, which significantly limits its application in the intermediate to low temperature SOFCs [10].

Recently, a range of rare-earth apatite materials have been proposed as alternative solid electrolyte materials following the observations of fast oxide-ion conductivity in the silicate-based systems [11–18]. The general formula for the apatite-type materials can be written as $\text{RE}_{10-x}\text{Si}_6\text{O}_{26 \pm \delta}$, where RE = rare earth. As the best conductivities were obtained for RE = La, the initial studies on oxyapatites were focused on the La containing system ($\text{La}_{9.33+x}(\text{SiO}_4)_6\text{O}_{2+3x/2}$) [12,19–21]. The results showed that nonstoichiometry in the form of either cationic vacancies or oxygen excess is required to achieve good oxide-ion conductivity. To further optimize the

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conductivities of apatite-type lanthanide silicates, extensive studies on the effect of doping on the oxygen ion conductivity of oxyapatites have been reported [22–27].

The computer modeling studies have indicated the importance of the silicate substructure in aiding the motion of the oxide ions down the channels in the apatite-type oxide ion conductors. La-site vacancies, particularly in positions enveloping oxygen channels, obviously affect the ionic transport in the apatite lattice. The La-site deficiency influences the SiO_4 tetrahedra relaxation and may cause displacement of the anions from channels into new interstitial sites, thus creating vacancies at fixed oxygen content [12,20,28,29]. Detailed studies of the Al-doped lanthanum silicate oxyapatite systems have been reported by Shaula and Abram et al. [12,30,31]. For $\text{La}_{9.33+x/3}\text{Si}_6-x\text{Al}_x\text{O}_{26}$ oxyapatites with cation nonstoichiometry, doping lower valent Al^{3+} on the Si^{4+} site is compensated by La-site vacancies without oxygen content variations, with a maximum value for $x = 1.5$ ($\text{La}_{9.83}\text{Si}_{4.5}\text{Al}_{1.5}\text{O}_{26}$). On the other hand, Al-doped oxyapatites containing oxygen excess, e.g. $\text{La}_{10}\text{Si}_{5.5}\text{Al}_{0.5}\text{O}_{26.75}$, exhibits high oxide-ion conductivity. The oxide-ion conductivity of $\text{La}_{9.83}\text{Si}_{5.5}\text{Al}_{0.5}\text{O}_{26.5}$ with cationic vacancies and oxygen excess is significantly higher than $\text{La}_{9.83}\text{Si}_{4.5}\text{Al}_{1.5}\text{O}_{26}$ with the same cationic vacancies. These results show that oxygen excess is more important than cationic vacancies to achieve good oxide-ion conductivity of lanthanum silicate oxyapatite. For $\text{La}_{10-x}\text{Si}_6-y\text{Al}_y\text{O}_{27-3x/2-y/2}$ oxyapatites with oxygen excess, the conductivities are shown to have a maximum value at $y = 0.5$, and then decrease up to $y = 1.5$. Kharton et al. [32–34] studied the Fe-doped lanthanum silicate oxyapatites and showed that Fe doping could improve the sinterability and oxide ion conductivity of lanthanum silicate oxyapatites. The conductivity of the fully stoichiometric $\text{La}_{10}\text{Si}_4\text{Fe}_2\text{O}_{26}$ is significantly lower than that of the samples with lower doping levels in agreement with Al-doped oxyapatites.

Various cationic substitutions were studied on the La site with Mg, Ca, Sr and Ba. The fully stoichiometric compositions $\text{La}_8\text{M}_2(\text{SiO}_4)_6\text{O}_{26}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) [20,28,35] exhibit a much lower conductivity and higher activation energy than compositions containing either cationic vacancies or oxygen excess [35,36]. In contrast, alkaline earth (Ca, Sr, Ba) doped samples containing oxygen excess all exhibited high oxide conductivities (e.g. σ at $700^\circ\text{C} = 8.74 \times 10^{-3} \text{ S cm}^{-1}$ for $\text{La}_9\text{Sr}(\text{SiO}_4)_6\text{O}_{2.5}$, versus $3.26 \times 10^{-4} \text{ S cm}^{-1}$ for $\text{La}_{9.33}\square_{0.67}\text{Si}_6\text{O}_{26}$) [22]. These results also show that oxygen excess is more important than cationic vacancies to achieve good oxide-ion conductivity of lanthanum silicate oxyapatite.

The doping results as shown above indicate clearly that oxygen over-stoichiometry is responsible for the good oxide-ion conductivity. The highest conductivity is characteristic of lanthanum silicate oxyapatite containing 26.25–26.75 oxygen atoms per formula unit [31]. Thus, co-doped lanthanum silicate oxyapatites with compositions $\text{La}_{9.5}\text{Sr}_{0.5}\text{Si}_{5.5}\text{A}_{0.5}\text{O}_{26.5}$ with $\text{A} = \text{Al}, \text{Fe}$ were selected in this study. Here, $\text{La}_{9.5}\text{Sr}_{0.5}\text{Si}_{5.5}\text{A}_{0.5}\text{O}_{26.5}$ with $\text{A} = \text{Al}, \text{Fe}$ were synthesized by the high-temperature solid state reaction process. The undoped $\text{La}_{10}\text{Si}_6\text{O}_{26.5}$ oxyapatite containing 26.5 oxygen atoms per formula unit was also studied under identical conditions. The effect of co-doping of Sr and Al or Fe on the microstructure, sinterability and oxide-ion conductivity of lanthanum silicate

oxyapatite was studied by SEM and electrochemical impedance spectroscopy techniques. The results show that co-doping of Sr and Al or Fe benefits significantly the sintering and densification process. Moreover, the co-doped lanthanum silicate oxyapatite shows a significant enhancement of the oxide-ion conductivity.

Experimental

Synthesis of LSO, LSSAO and LSSFO powders

The powders were synthesized by a conventional solid state reaction process using high purity La_2O_3 , SiO_2 , SrCO_3 , Al_2O_3 and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (all from Sigma–Aldrich) as the raw materials without further treatment. The raw materials were weighed in appropriate ratio to elaborate the compounds with

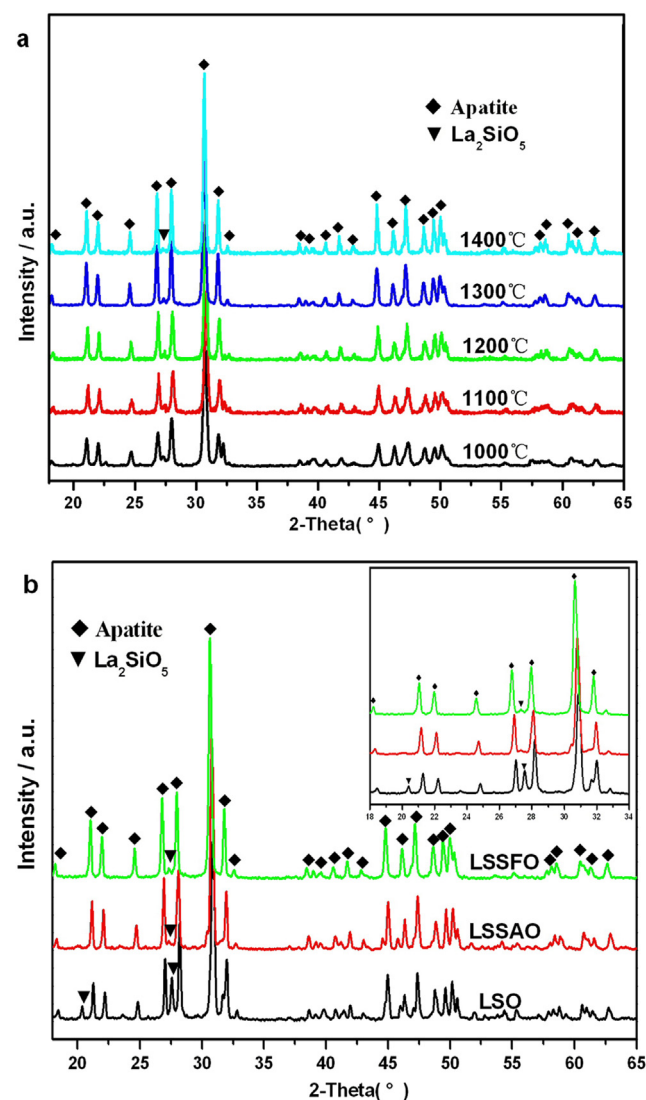


Fig. 1 – XRD patterns of (a) LSSFO powders calcined at 1000, 1100, 1200, 1300 and 1400 °C for 10 h in air, and (b) LSO, LSSAO and LSSFO powders calcined at 1300 °C for 10 h in air.

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