Materials Research Bulletin 47 (2012) 719–723

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Electrical properties and thermal expansion of cobalt doped apatite-type lanthanum silicates based electrolytes for IT-SOFC

Qingle Shi, Lihua Lu, Hongjian Jin, Hua Zhang *, Yanwei Zeng

College of Materials Science and Engineering, Nanjing University of Technology, No.5 Xinmofan Road, Nanjing, Jiangsu, PR China

ARTICLE INFO

Article history:
Received 14 January 2011
Received in revised form 21 November 2011
Accepted 8 December 2011
Available online 17 December 2011

Keywords:
A. Oxides
B. Sol–gel chemistry
C. Impedance spectroscopy
D. Ionic conductivity
D. Thermal expansion

ABSTRACT

The thermal expansion and conductivities have been investigated for Co^{3+} doped lanthanum silicates. The apatite-type lanthanum silicates with formula $La_{10}Si_{6-x}Co_xO_{27-x/2}$ ($x = 0.2, 0.4, 0.6, 0.8, 1.0, 1.5$) were synthesized by sol–gel process. The thermal expansion coefficient (TEC) of $La_{10}Si_{6-x}Co_xO_{27-x/2}$ was improved with increasing cobalt content because of the lower valence and larger radius of Co^{3+} ion compared to Si^{4+}. Analysis of AC impedance spectroscopy showed that conductivity increased first and then decreased with increasing cobalt content. There is an optimum doping amount of cobalt and $La_{10}Si_{5.2}Co_{0.8}O_{26.6}$ exhibits the highest conductivity of 3.33×10^{-2} S/cm at 800 °C. When $x \leq 0.8$, the local distortion caused by doping with Co^{3+} can significantly affect the oxygen channels and assist the migration of the interstitial oxide ions, resulting in the improvement of ionic conductivity. However, excess Co^{3+} dopant ($0.8 < x \leq 1.5$) reduced the number of interstitial oxide ions and decreased the conductivity.

1. Introduction

As a key component of intermediate temperature solid oxide fuel cells (IT-SOFCs), the solid electrolyte should possess high ionic conductivity and a moderate thermal expansion coefficient (TEC). The apatite-type lanthanum silicates with formula $La_{10-x}Si_6O_{27-1.5x}$ is a type of solid electrolyte. It exhibited high ionic conductivities at intermediate temperatures as reported by Nakayama [1]. The structure of the apatite-type lanthanum silicates consists of isolated SiO_4 tetrahedral units with La^{3+} located in cavity sites. Extra oxide ions occupy the channels with a non-liner (sinusoidal-like) pathway along the *c*-axis in the structure, which benefits the ionic conductivity [2,3]. The interstitial conduction mechanism suggests that the conductivity could be enhanced by the La content associated with extra oxide ions. For $x = 0.67$, the lanthanum silicate $La_{9.33}Si_6O_{26}$ is found to be cation deficiency and oxygen stoichiometry. The conductivities of $La_{9.33}Si_6O_{26}$ were 2×10^{-4} S/cm at 700 °C and 2×10^{-3} S/cm at 800 °C, respectively [4,5]. As the La content increases, extra oxide ions at an interstitial site should be introduced. Yoshioka [6] reported that the oxide ionic conductivity of apatite-type lanthanum silicates increased with increasing La content from $y = 9.29$ to 9.92 in $La_ySi_6O_{1.5y+12}$. $La_{10}Si_6O_{27}$ showed higher conductivity (1.08×10^{-2} S/cm at 700 °C) than $La_{9.33}Si_6O_{26}$ [7]. However, the conductivity of the apatite-type lanthanum silicates is insufficient for IT-SOFC electrolytes. The improvement of the ionic conductivity for the apatite-type lanthanum silicates was made by several research groups [8–21]. It was reported that Co doping greatly improved the conductivity and the conductivity of $La_{10}Si_{4.5}Co_{1.5}O_{26.25}$ was 1.3×10^{-2} S/cm at 800 °C [8]. A further consideration is the matching of the thermal expansion coefficient (TEC) for the SOFC components. The average thermal expansion coefficient of lanthanum silicates is around 9×10^{-6} K^{-1}[3,10,12,22,23], which is lower than that of the common electrode material such as LSM ($10–13 \times 10^{-6}$ K^{-1}). Thereby, it is necessary to enhance the TEC of the apatite-type lanthanum silicates.

To improve the conductivities and TECs of the lanthanum silicates, a batch of lanthanum silicates with formula $La_{10}Si_{6-x}Co_xO_{27-x/2}$ ($x = 0.2, 0.4, 0.6, 0.8, 1.0, 1.5$) were synthesized via sol–gel process. The effects of doping with cobalt on the thermal expansion and conductivity were investigated. Moreover, the dependence of conductivity on $p(O_2)$ was discussed.

2. Experimental

The analytical reagents (AR) tetraethyl orthosilicate (TEOS), lanthanum nitrate hexahydrate $La(NO_3)_3 \cdot 6H_2O$ and cobalt nitrate hexahydrate $Co(NO_3)_3 \cdot 6H_2O$ were used in sol–gel synthesis. Stoichiometric quantities of $La(NO_3)_3 \cdot 6H_2O$ and $Co(NO_3)_3 \cdot 6H_2O$ was dissolved in the mixture of ethanol, acetic acid and distilled

---

* Corresponding author. Tel.: +86 25 83587259; fax: +86 25 83587216.
E-mail addresses: huazhang@njut.edu.cn, llh0727@163.com, shiqingle1219@163.com (H. Zhang).

0025-5408/$ – see front matter.
doi:10.1016/j.materresbull.2011.12.015

water. Then an appropriate amount of TEOS was added, with continuous stirring until a clear sol formed. After refluxing (80 °C/1–2 h), the sol was converted into a clear gel, followed by drying at 100 °C for 20 h.

In order to remove the water and organic components, the gel was heated at 600 °C for 4 h. The resulted precursor was then calcined at 1000 °C for 4 h to get the desired phase. The phase purity was examined by X-ray powder diffraction (XRD) (ARL X'TRA) using Cu K_α radiation (λ = 1.5406 Å). For TEC and conductivity measurements, the powders were pressed into pellets and bars and then sintered (1500–1550 °C/4 h). The density of the sintered samples was determined by Archimede's method. The TEC was measured in air with a RPZ-03P dilatometer from room temperature to 800 °C with a heating rate of 10 °C/min. For conductivity measurements, Pt wire was affixed to the pellets using Pt paste and fired (500 °C/60 min followed by 850 °C/30 min) to give good electrical contact between the sample and electrode. The conductivity measurements were performed by AC impedance spectroscopy in the frequency range of 0.1 Hz to 1 MHz using electrochemical workstation (PARSTAT 2273).

3. Results and discussion

XRD patterns of the synthesized samples are shown in Fig. 1. The analysis of the X-ray data confirms that the pure apatite phase is formed at 1000 °C and there is no second phase formed after the samples were sintered at 1550 °C, which suggests that the samples are stable at the high temperature. The phase formation temperature of lanthanum silicates synthesized by sol–gel process decreased about 350 °C compared to solid state reaction. The structural parameters have been refined by Rietveld analysis. Fig. 2 shows the fitted XRD data for $La_{10}Si_{5.2}Co_{0.8}O_{26.6}$ and the dependence of the cell-unit volumes on the cobalt content. The XRD patterns of $La_{10}Si_{6-x}Co_xO_{27-x/2}$ are consistent with a powder XRD pattern corresponding to the hexagonal $P6_3/m$ appetites and the confidence factors are R_{wp} = 8.89%, R_p = 7.31%, and χ^2 = 2.239. The cell parameters and the unit volumes of $La_{10}Si_{6-x}Co_xO_{27-x/2}$ (x = 0.2, 0.4, 0.6, 0.8, 1.0, 1.5) are listed in Table 1. Co^{3+} doping results in an increase of the unit volume because the ionic radius of Co^{3+} (0.54 Å) is larger than that of Si^{4+} (0.26 Å). The dependence of a-parameter on the cobalt content is shown in Fig. 3. The cell-unit volume and a-parameter increase with increasing cobalt content, which indicates that Co is entering structure. The curves of cell-unit volume are approximately linear from x = 0.2 to 1.0. However, Co^{3+} doping may reduce the number of interstitial oxygen anion, causing the shrinkage of unit volume. This effect emerges at $x \geq 1.0$ and the increasing rate of the unit volume becomes slower. Therefore, the increase of cell-unit volume deviates from the linear relationship when $x \geq 1.0$.

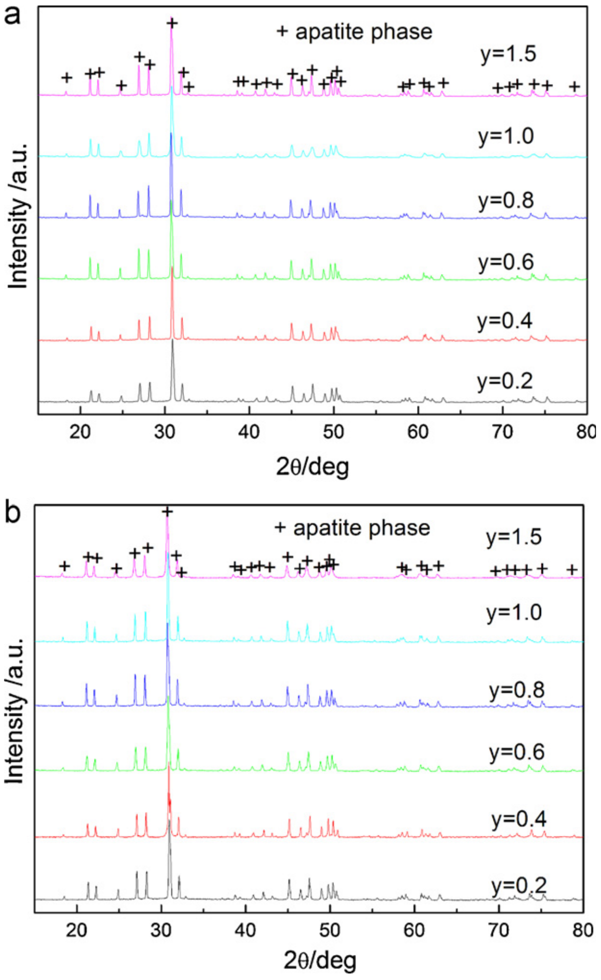

Fig. 1. XRD patterns of $La_{10}Si_{6-x}Co_xO_{27-x/2}$ (a) calcined at 1000 °C; and (b) sintered at 1550 °C.

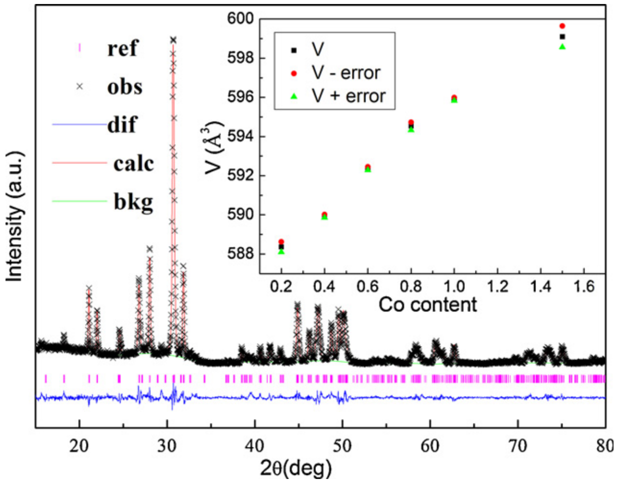

Fig. 2. Fitted XRD data for $La_{10}Si_{5.2}Co_{0.8}O_{26.6}$. The inset shows the cell-unit volumes of $La_{10}Si_{6-x}Co_xO_{27-x/2}$ vs Co content.

As an electrolyte, $La_{10}Si_{6-x}Co_xO_{27-x/2}$ should be dense to avoid the gas permeation. 1500 °C, 1530 °C and 1550 °C were selected as sintering temperature for $La_{10}Si_{6-x}Co_xO_{27-x/2}$ (x = 0.2, 0.4, 0.6, 0.8, 1.0, 1.5) pellets and bars to obtain the dense samples. The densities measured by Archimedes method are listed in Table 2. It can be seen that Co^{3+} doping facilitates sintering of $La_{10}Si_{6-x}Co_xO_{27-x/2}$ and improves the density. The relative density of $La_{10}Si_{6-x}Co_xO_{27-x/2}$ increases with increasing cobalt content. The value of the relative density is more than 98% for $La_{10}Si_{6-x}Co_xO_{27-x/2}$ sintered at 1550 °C. Therefore, the samples sintered at 1550 °C have been chosen to measure the TEC and conductivity.

Table 1
Lattice parameters of $La_{10}Si_{6-x}Co_xO_{27-x/2}$ calcined at 1000 °C.

Sample composition	Structure	Lattice parameters		Cell volume V (Å^3)
		a (Å)	c (Å)	
$La_{10}Si_{5.8}Co_{0.2}O_{26.9}$	$P6_3/m$	9.726(2)	7.182(1)	588.3(3)
$La_{10}Si_{5.6}Co_{0.4}O_{26.8}$	$P6_3/m$	9.7294(5)	7.1965(5)	589.94(8)
$La_{10}Si_{5.4}Co_{0.6}O_{26.7}$	$P6_3/m$	9.7330(8)	7.221(1)	592.37(8)
$La_{10}Si_{5.2}Co_{0.8}O_{26.6}$	$P6_3/m$	9.737(1)	7.240(1)	594.5(2)
$La_{10}Si_5CoO_{26.5}$	$P6_3/m$	9.7409(5)	7.2520(5)	595.91(8)
$La_{10}Si_{4.5}Co_{1.5}O_{26.25}$	$P6_3/m$	9.755(3)	7.270(3)	599.1(5)