Preparation and Characterization of Gd and Zn Doped Apatite Lanthanum Silicate Electrolyte

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Abstract: Apatite lanthanum silicate is an oxygen ionic conductor with high conductivity. In this paper, research the effects of Gd and Zn double doping in La_{9.33}Si_{6}O_{26+x}^{2-}. Synthesis La_{9.33}Gd_{x}Si_{5}ZnO_{25+3x/2} (x = 0.2, 0.4, 0.6, 0.8) by Sol-gel Self combustion method, Characterization of the synthesized phase and electrical properties by X-ray diffraction, Scanning electron microscopy and Electrochemical workstations. The results show that doping can effectively improve the conductivity, La_{9.33}Gd_{0.2}Si_{5}ZnO_{25.3} has best conductivity that reach 1.49×10^{-3}S/cm in 500°C.

1. Introduction

Solid electrolyte is the key component of solid oxide fuel cells (SOFCs), it plays an important role in isolating reaction gases and transporting oxygen ions, and its conductivity directly affects the performance of solid oxide fuel cells [1-3].

The traditional YSZ solid electrolyte, because it works at high temperature, leads to slow decomposition and corrosion of materials, interphase diffusion, complex preparation process and high cost, which restricts its large-scale application [4-6]. Later, fluorite (e.g. CeO_{2},Bi_{2}O_{3}) and perovskite electrolytes with high ionic conductivity appeared one after another at medium and low temperatures [7,8]. But the working temperature range of CeO_{2}-based and doped Bi_{2}O_{3}-based electrolyte materials is narrow, electrical conductance of short-circuit channel is easily produced in low oxygen partial pressure and reduction atmosphere, perovskite electrolyte materials have some problems, such as poor sintering performance and poor compatibility between electrolyte and electrode materials.

Apatite lanthanum silicate has low activation energy and high oxygen Ion conductivity at medium and low temperatures. As a new solid electrolyte, it was first reported by Nakayama et al [9,10], this has aroused widespread concern. It is reported that apatite-type lanthanum silicate belongs to hexagonal system and its space group is P6_3/m, it has six [SiO_{4}]^{4-} tetrahedrons and two extra O^{2-} in a unit cell. La cations are situated at seven-coordinated sites (6h) and nine-coordinated sites (4f), La cations connect [SiO_{4}]^{4-} tetrahedrons to form the oxygen ion transport channel and the extra O^{2-} located in the channel as an important factor to determine the conductivity of electrolyte. The conduction mechanism of apatite lanthanum silicate is interstitial oxygen ion conduction, the interstitial oxygen ions migrate in the conduction channels along the c-axis via a complex sinusoidal pathway [11]. In this process, interstitial oxygen ions are constantly changing direction and shiftability is improved, so it has high conductivity.

Conductivity can be improved by increasing the amount of interstitial oxygen, interstitial oxygen can be introduced by doping. In this paper, we study the effect of Gd and Zn double doping on lanthanum silicate, because have research shows doped amount of Zn less than 1, it would cause grain incomplete growth of sintering, if doped amount of Zn more than 1 would cause overburn and grain
boundary melting. So that decide the doped amount of Zn is 1. Use sol-gel methodsynthesis 
$La_{9.33}Gd_xSi_5ZnO_{25+3x/2}$, and study the effect of double-site doped for conductivity.

2. Experiment

The $La_{9.33}Gd_xSi_5ZnO_{25+3x/2}$ was prepared by sol-gel method. $La_2O_3$ (99.99%), $Gd_2O_3$ (99.99%), $ZnO$ (99.99%) and TEOS (99.99%) were the starting materials. $La_2O_3$, $Gd_2O_3$, and $ZnO$ were dissolved in a mixed solution of nitric acid and anhydrous ethanol in stoichiometric ratio. Heated and stirred in water bath at 35°C, then adequate ammonia were applied to adjust pH value to 5–6 stirred until the solution was completely clarified, after added TEOS in stoichiometric ratio as silica source and urea was introduced as fuel, continuous stirred for solution clarification got sol, then the sol was placed in 80°C water bath, after 2h it transformed into transparent gel. The gel was dried 12h at 100°C to remove moisture from the gel, then loose lanthanum silicate foam was got by combustion for 5min at 600°C, grinding the foam to fine powders and calcined at 800°C for 12h to promote the crystallization of the powders. The calcined powder is weighed at 0.8g placed in a 13mm diameter mould, and pressed on a disc under 300MPa pressures got sample, sintered the sample of 1300°C, 1400°C and 1500°C for 3h.

The phase purity of the powders was examined by X-ray diffraction (Bruker D8 ADVANCE, Germany) using Cu $K_α$ radiation ($λ=0.15418nm$), working voltage is 40 kV, working current is 30 mA, scanning speed is 4°/min and scanning angle is 10° to 70°. Scanning electron microscopy was used to observe the microstructure of sintered at 1300°C, 1400°C and 1500°C for 3h. And then, coated with silver paste as electrode and conductivity of the sintered body was measured by the AC impedance techniques.

![Figure 1. XRD pattern of $La_{9.33}Gd_xSi_5ZnO_{25+3x/2}$ (x=0.2, 0.4, 0.6, 0.8) calcined at 800°C for 12h.](image)

3. Results and discuss

3.1 Phase analysis

Figure 1 is XRD pattern of $La_{9.33}Gd_xSi_5ZnO_{25+3x/2}$ (x=0.2, 0.4, 0.6, 0.8) calcined at 800°C for 12h, compared with standard card the characteristic peaks of doped samples shifted to low angle, this is
because the doped elements into the lattice and make the lattice expansion. And the presence of no impurity phases in the sample showed that the pure apatite phase can be obtained by sol-gel method. Table 1 is cell parameters of La$_{9.33}$Gd$_x$Si$_5$ZnO$_{25+3x/2}$ ($x=0.2, 0.4, 0.6, 0.8$) calcined at 800°C for 12h, it can be seen that the cell parameters had variety after doped, indicating that doped elements had entered the cell.

| Samples composition          | Lattice parameters |
|------------------------------|--------------------|
|                              | a(Å)   | c(Å)   |
| La$_{9.33}$Si$_6$O$_{26}$    | 9.7128 | 7.1858 |
| La$_{9.33}$Gd$_{0.2}$Si$_5$ZnO$_{25.3}$ | 9.7363 | 7.1835 |
| La$_{9.33}$Gd$_{0.4}$Si$_5$ZnO$_{25.6}$ | 9.7408 | 7.2259 |
| La$_{9.33}$Gd$_{0.6}$Si$_5$ZnO$_{25.9}$ | 9.7479 | 7.2082 |
| La$_{9.33}$Gd$_{0.8}$Si$_5$ZnO$_{26.2}$ | 9.7515 | 7.2314 |

3.2 Microstructure analysis
Figure 2 is SEM of La$_{9.33}$Gd$_{0.2}$Si$_5$ZnO$_{25.3}$ sintered for 3h at different temperatures, (a) is SEM diagrams sintered at 1300°C for 3h, it can observe that the sintered samples have high porosity, low density and particle size is nonuniform, this is due to the low sintered temperature lead to the incomplete grain growth, (b) is SEM diagrams sintered at 1400°C for 3h, it can see the sintered sample have no pore, closely packed particles, size is uniform and can observe obvious grain boundary, shows good sintering effect, (c) is SEM diagrams sintered at 1500°C for 3h, the high density of the sample can be observed and have partially particle overgrowth makes the particle size nonuniform, this will have an impact on electrical performance.

Figure 2 is SEM of La$_{9.33}$Gd$_{0.2}$Si$_5$ZnO$_{25.3}$ sintered for 3h at different temperatures, (a) is sintered at 1300°C for 3h, (b) is sintered at 1400°C for 3h, (c) is sintered at 1500°C for 3h.

3.3 Conductivities
Figure 3 is conductivity diagram of La$_{9.33}$Gd$_x$Si$_5$ZnO$_{25+3x/2}$ ($x=0.2, 0.4, 0.6, 0.8$) at different temperatures, it can be seen that the maximum conductivity are obtained when the doping content is 0.2, the conductivity is 6.91 x 10$^{-3}$S/cm at 650°C. With the increase of doping amount, the conductivity shows a downward trend, which is due to dope can introduction of interstitial oxygen ions to improve conductivity, but with the increase of doping amount, interstitial oxygen ion channels will be squeezed. The results show that a proper amount of double-site doping can increase interstitial oxygen and improve the conductivity, excessive doping can introduce more interstitial oxygen but also squeeze interstitial oxygen channels reduce interstitial oxygen percent of pass lead to decrease in conductivity.
4. Conclusions

Gd and Zn double doped La$_{9.33}$Si$_{6}$O$_{26}$ are prepared by sol-gel method, the characterization of XRD indicates Gd and Zn doped into La$_{9.33}$Si$_{6}$O$_{26}$ and the crystal structure of La$_{9.33}$Si$_{6}$O$_{26}$ has not been destroyed. Microstructure of samples sintered at different temperatures is observed by scanning electron microscopy, the optimum sintering temperature is 1400°C. La$_{9.33}$Gd$_{0.2}$Si$_{5}$ZnO$_{25.3}$ has the higher conductivity than others doped amount, it conductivity is 6.91×10$^{-3}$ S/cm at 650°C. The double doping of Gd and Zn introduces interstitial oxygen ions, which are the main carriers, increasing the number of interstitial oxygen ions can improve its percent of pass in oxygen ion channels, so that the conductivity can be improved.

Acknowledgments

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