Preparation of praseodymium-doped La$_{9.33}$(SiO$_4$)$_6$O$_2$ apatite-type solid electrolytes and analysis of the conductivity mechanism

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Abstract: In order to improve the electrical conductivity of lanthanum silicate oxide electrolyte (LSO), La$_{9.33}$Pr$_x$Si$_6$O$_{26+1.5}$x (LPSO) solid electrolyte powder doped with praseodymium was synthesized at 600 ºC by urea-nitrate combustion method with lanthanum oxide (La$_2$O$_3$) and Praseodymium nitrate hexahydrate (Pr(NO$_3$)$_3$·6H$_2$O) as raw materials. It is shown that the Pr-doped LSO still have the typical apatite structure and occupy the La II cation vacancy at the 6h position. Optimal sintering temperature is 1550 ºC. La$_{9.33}$Pr$_{0.5}$Si$_6$O$_{26.75}$ reaches the highest conductivity (4.80×10$^{-4}$ S·cm$^{-1}$ at 600 ºC). The main factor that Pr-doped improves the performance of LSO is that Pr-doped that introduced more interstitial oxygen ions Oi* and increased lattice volume, so improved the transport efficiency of interstitial oxygen. The secondary factor is the decrease in the concentration of cation vacancy after Pr-doped, which reduced the negative defect stacking centers. Thereby, decreases space drag of interstitial oxygen transport which increases conductivity of LSO. The praseodymium doped to enhancement LSO conductivity mechanism that interstitial oxygen concentration-cation vacancies concentration-lattice volume composite enhancement mechanism was proposed.

1. Introduction

The apatite type lanthanum silicate (LSO) electrolyte ceramics have the advantages of low price, high ionic conductivity and good performance at low temperature [1,2]. It is widely used in fuel cells. LSO has a p6$_3$/m apatite crystal structure. In this crystal structure, the connection between La II with seven-coordinated and tetrahedron [SiO$_4$]$^4$ makes up the hexagonal 6$_1$ conduction channel that parallels to the C axis. Interstitial oxygen is the carrier of oxygen ion transport in the channel. As a result, it has better migratory ability than free oxygen ion. The generally accepted conduction mechanism of LSO is interstitial oxygen conduction [3-6]. At present, LSO electrolytes doped with different cations can increase the interstitial oxygen in order to enhance the conductivity. At present, there have been abundant studies on doped at Si sites to improve conductivity of LSO, such as B, Fe, Zn, Ge, Ga, Mg, Al, Ti, Co, Cu, Mn, In, Nb, Sn and so on [3, 4, 7-9]. However, there are few studies on the enhancement of conductivity by doping at La sites, especially improving conductivity by generating more interstitial oxygen ions Oi* and reducing the negative defect stacking centers.

In this paper, we try to use low valence small radius Pr$^{3+}$ ion doping to occupy the cation vacancies at the La site, which makes the concentration of cation vacancies decrease so that the negative defect

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stacking center is reduced and the spatial site resistance of interstitial oxygen ion transport is decreased, at the same time, the concentration of interstitial oxygen ions (Oi\(^{\ast}\)) is increased and the lattice volume is increased, so that the transport efficiency of interstitial oxygen ions is improved. Thus, the enhancement of conductivity by praseodymium doping of rare earth elements is proposed as a composite enhancement mechanism of interstitial oxygen concentration—cation vacancy concentration—lattice volume. Based on the study of the structural evolution and conductivity properties of Pr-doped LSO, the mechanism of conductivity enhancement by doping with small radius ions of low valence at the La position is revealed.

2. Experiment

First, weighed quantitative La\(_2\)O\(_3\) and Pr(NO\(_3\))\(_3\)·6H\(_2\)O successively, dissolved them in a mixture of nitric acid and absolute ethyl alcohol, heated and stirred in the water bath at 35 \(^\circ\)C, then added ammonia to regulate pH to 2-4. After the solution was clarified, the precursor sol was prepared by adding urea (as incendiary agent) and TEOS (silicon source) according to stoichiometric proportion. The precursor wet gel was obtained by heating the precursor sol in a water bath at 80 \(^\circ\)C for 2 h, and dried the precursor wet gel at 100 \(^\circ\)C for 12 h to obtain the precursor xerogel. The precursor xerogel was ignited in a muffle furnace at 600 \(^\circ\)C and combusted 5-7 min to form the amorphous LPSO powders. Subsequently, the product was ground into fine powders and calcined for 12 h at 800 \(^\circ\)C to form crystalline powders. Weighted 0.6 g crystallized LPSO powders into a mould with 13 mm diameters, and pressed them for 300 MPa to get the green body. Then, sintered the green body at 1400 \(^\circ\)C, 1450 \(^\circ\)C, 1500 \(^\circ\)C, 1550 \(^\circ\)C, 1600 \(^\circ\)C (heating rate is 4 \(^\circ\)/min) and kept warm for 5 h to obtain LPSO electrolyte ceramics.

X-ray diffraction (XRD) (Bruker D8 ADVANCE, Germany) was performed for structure analysis on the LPSO with different content. Test parameters: copper target, operating voltage was 30 kV, x-ray wavelength was 0.15406 nm, operating current was 30 mA, scanning speed was 4 \(^\circ\)/min, scanning angle was 10-80 \(^\circ\), and step width was 0.02. Intelligent Fourier transform infrared spectrometer (FT-IR) (ThermoNicolet Nexus, USA) was characterized on molecular structure of the LPSO. The range of measurement was 4000-400 cm\(^{-1}\). Scanning electron microscope (SEM) (JEOLJSM5510LV, Japan) was used to observe the morphology of LPSO. The AC impedance (400-600 \(^\circ\)C) was measured by Shanghai Chenhua electrochemical workstation (CHI650C), and by means of calculating to get the correspondent conductivity.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of La\(_{9.33}\)Pr\(_x\)Si\(_6\)O\(_{26+1.5}\) electrolyte ceramics are shown in figure 1. The Pr-doped La\(_{9.33}\)Pr\(_x\)Si\(_6\)O\(_{26+1.5}\) is completely consistent with the chart shape of standard card (JCPDS49-0443), that indicates the doping of Pr\(^{3+}\) hasn't destroyed the apatite-type crystal structure(p6\(_3\)/m). There were no common impurity phases have been found, which indicates the high purity of the samples. The Pr and La are both lanthanides so that the ionic radius and the electronegativities are similar, so it is easier to dope the Pr at the La position, and it will not have a large impact on the lattice of LSO.

As shown in table 1, comparing the Pr-doped La\(_{9.33}\)Pr\(_x\)Si\(_6\)O\(_{26+1.5}\) (x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.67) with undoped LSO, it is found that the lattice volume gradually increase. For rare earth elements with the same coordination number, their ionic radius decreases with increasing atomic number, and the ionic radius of La is the largest, so the reason for the increase of its lattice volume is the existence of 0.67 cation vacancies at the La position in LSO, and with the doping of praseodymium, it occupies the cation vacancies in LSO, which makes the lattice volume increase. Thus, it is tentatively judged that the praseodymium element has been successfully doped in the La site of LSO.
3.2. IR analysis
The $\nu_{\text{Si}-\text{O}}$ in the doped La$_{9.33}$Pr$_x$Si$_2$O$_{26+1.5x}^+$ ($x = 0.4, 0.5, 0.6$) exhibit a feeble decrease on increasing $x$, which can be depicted as when the Pr-doped in the LSO, the Pr$^{3+}$ occupies the cation vacancy of La and its lattice volume expands, then Pr-O bond is formed at the original cation vacancy, and the formation of Pr-O bond increases the bond length of O-Si bond. According to equation (1) and equation (2) know that as the bond length increases its force constant $K$ decreases, the vibration frequency also decreases. the $\nu_{\text{Si}-\text{O}}$ in the doped La$_{9.33}$Pr$_x$Si$_2$O$_{26+1.5x}^+$ ($x = 0.4, 0.5, 0.6$) exhibit show a feeble increase on increasing $x$, which can be depicted as there are two chemical environments of Si-O bonds in LSO, and as the bond energy of O-Si bonds in one environment decreases, the Si-O bonds in the other chemical environment increase their bond energy. The $B_{\text{Si}-\text{O}}$ and $B_{\text{Si}-\text{O}}$ have the same phenomenon. It further confirms that praseodymium enters the LSO.

$$K = aN(X_A X_B / d^2)^{3/4} + b$$  \hspace{1cm} (1)

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$  \hspace{1cm} (2)

Where $K$ is force constant, $N$ is bond order, $X_A$ and $X_B$ are electronegativities, $a$ and $b$ are constant, $d$ is bond length, $\nu$ is vibration frequency, $c$ is speed of light, $\mu$ is reduced mass.

![Figure 1. XRD diffractograms of the La$_{9.33}$Pr$_x$Si$_2$O$_{26+1.5x}$ ($x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.67$) ceramics.](image)

**Table 1.** Lattice parameters of La$_{9.33}$Pr$_x$Si$_2$O$_{26+1.5x}$ ($x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.67$).

| Sample          | Lattice parameters | Lattice volume($\text{Å}^3$) |
|-----------------|--------------------|------------------------------|
|                 | $a=b$(Å) | $c$(Å) |                 |
| La$_{9.33}$Si$_2$O$_{26}$ | 9.7149   | 7.1817 | 587.00 |
| La$_{9.33}$Pr$_{0.1}$Si$_2$O$_{26.15}$ | 9.7102   | 7.1892 | 587.04 |
| La$_{9.33}$Pr$_{0.2}$Si$_2$O$_{26.30}$ | 9.7154   | 7.1836 | 587.22 |
| La$_{9.33}$Pr$_{0.3}$Si$_2$O$_{26.45}$ | 9.7148   | 7.1853 | 587.28 |
| La$_{9.33}$Pr$_{0.4}$Si$_2$O$_{26.60}$ | 9.7179   | 7.1816 | 587.36 |
| La$_{9.33}$Pr$_{0.5}$Si$_2$O$_{26.75}$ | 9.7135   | 7.1900 | 587.51 |
| La$_{9.33}$Pr$_{0.6}$Si$_2$O$_{26.90}$ | 9.7196   | 7.1933 | 587.58 |
| La$_{9.33}$Pr$_{0.67}$Si$_2$O$_{27.005}$ | 9.7213   | 7.1962 | 587.83 |
**Figure 2.** Infrared spectra of the La$_{9.33}$Pr$_x$Si$_6$O$_{26+1.5x}$ ($x = 0, 0.4, 0.5, 0.6$) ceramics.

**Table 2.** Wavenumber, model of vibration and type of tetrahedral of La$_{9.33}$Pr$_x$Si$_6$O$_{26+1.5x}$ ($0, 0.4, 0.5, 0.6$).

| Sample composition | Wavenumber (cm$^{-1}$) | Model of vibration | Type of tetrahedral |
|--------------------|------------------------|---------------------|---------------------|
| La$_{9.33}$Si$_6$O$_{26}$ | 989.02, 909.28 | $\nu_{\text{Si-O}}$ stretching vibration | $[\text{SiO}_4]$ |
|  | 540.12, 496.48 | $\beta_{\text{Si-O}}$ bending vibration |  |
| La$_{9.33}$Pr$_x$Si$_6$O$_{26+1.5x}$ (0, 0.4, 0.5, 0.6) | 985–987, 910–913 | $\nu_{\text{Si-O}}$ stretching vibration |  |
|  | 540–542, 495–497 | $\beta_{\text{Si-O}}$ bending vibration |  |

3.3. **Sintering temperature and morphology of LPSO electrolyte ceramics**

**Figure 3.** Linear shrinkage and relative density of different Pr-doped content and sintered temperature. (a) different temperature sintered for 5h when Pr-doped content is 0.5; (b) different Pr-doped content at 1550 °C sintered for 5 h.

As shown in figure 3(a), the relative densities reached 77% after sintering at 1400 °C and reached 82.5% after sintering at 1550 °C, but there was only a small increase in the relative densities after sintering at 1600 °C when the Pr-doped was 0.5. The changes of the line shrinkage and relative density were
similar, indicating that 1550 °C was the optimum sintering temperature. The effect of different doping content on the relative density and linear shrinkage can be seen in figure 3(b), the relative density and linear shrinkage of LSO did not change significantly due to Pr-doped, which indicates that Pr-doped does not have a significant effect on the sintering of LSO.

Figure 4. SEM image of La_{9.33}Pr_{0.5}Si_{6}O_{26.75} sintered at different temperature for 5 h.

The SEM images of La_{9.33}Pr_{0.5}Si_{6}O_{26.75} sintered at 1500 °C, 1550 °C, and 1600 °C for 5 h are shown in figure 4. When La_{9.33}Pr_{0.5}Si_{6}O_{26.75} sintered at 1500 °C, the grain size is small, but the grain boundaries between the grains are obvious, and the relative density of the sintered body is 81.03%. When La_{9.33}Pr_{0.5}Si_{6}O_{26.75} sintered at 1550 °C, the grain growth is good, the grain size is relatively average, the grain boundaries are clear, and the relative density is 82.56%. When La_{9.33}Pr_{0.5}Si_{6}O_{26.75} sintered at 1600 °C, the sintered body has obvious grain boundaries and the grains are closely arranged, and the relative density is 83.03%.

3.4. Conductivity and enhancement mechanism of Pr-doped LPSO electrolyte ceramics

It can be seen from figure 5, Pr-doped reduces the impedance of LSO, and with the increase of doping amount, the impedance changes show a trend of decreasing first and then increasing, indicating that Pr-doped improves the conductivity of LSO. When the doping amount of Pr reaches a certain level, the peak conductivity of LPSO will continue to increase, which will lead to the decline of the conductivity of LPSO. The optimal doping amount of Pr is 0.5. When the doping amount of Pr is greater than 0.5, its impedance increases. Therefore, a certain doping amount of Pr can effectively improve the conductivity of LSO.

\[
\ln(\sigma T) = \ln \sigma_0 - \frac{E_a}{k} \cdot \frac{1}{T}
\]

where \(\sigma\) is the conductivity, \(\sigma_0\) is the pre-exponential factor, \(E_a\) is the interstitial oxygen transport energy, \(k\) is the Boltzmann constant, and \(T\) is the absolute temperature.
Figure 6 shows the Arrhenius plot for La$_{9.33}$Pr$_x$Si$_6$O$_{26+1.5x}$ ($x = 0, 0.4, 0.5, 0.6$). According to the Arrhenius empirical formula (equation (1)), the ln(σT) of sintered LPSO ceramics has a good linear relationship with 1000/T (figure 6). The Activation energy (Ea) of the La$_{9.33}$Pr$_x$Si$_6$O$_{26+1.5x}$ ($x = 0, 0.4, 0.5, 0.6$) are calculated by the slope of the straight lines in figure 6. Table 3 presents the conductivity and activity energy of La$_{9.33}$Pr$_x$Si$_6$O$_{26+1.5x}$ ($x = 0, 0.4, 0.5, 0.6$) at 600 °C. From the analysis of the experimental data, the Activation energy (Ea) of Pr-doped La$_{9.33}$Pr$_x$Si$_6$O$_{26+1.5x}$ ($x = 0, 0.4, 0.5, 0.6$) are lower than that of undoped LSO. The conductivity of Pr-doped La$_{9.33}$Pr$_x$Si$_6$O$_{26+1.5x}$ ($x = 0, 0.4, 0.5, 0.6$) are significantly improved, which is related to the reduction of activation energy of LSO after praseodymium doping, and also related to the introduction of more interstitial oxygen ions Oi* after praseodymium doping. Because the conduction of LSO is dominated by the conduction of interstitial oxygen ions, the introduction of more interstitial oxygen ions by Pr doping has an important role in the improvement of its conductivity performance.

| Sample composition | Electrical conductivity (S·cm$^{-1}$) | Activation energy (eV) |
|--------------------|--------------------------------------|------------------------|
| La$_{9.33}$Si$_6$O$_{26}$ | 5.42×10$^{-5}$ | 0.92 |
| La$_{9.33}$Pt$_{0.4}$Si$_6$O$_{26.60}$ | 1.33×10$^{-4}$ | 0.89 |
| La$_{9.33}$Pt$_{0.5}$Si$_6$O$_{26.75}$ | 4.80×10$^{-4}$ | 0.82 |
| La$_{9.33}$Pt$_{0.6}$Si$_6$O$_{26.90}$ | 2.29×10$^{-4}$ | 0.84 |

Since the cation vacancies and the interstitial oxygen ions are negatively charged, and in the channel of interstitial oxygen ions, the cation vacancies with the interstitial oxygen ions form a negative defect stacking center, which creates a certain obstruction to the transport of interstitial oxygen ions. When Pr is doped the LSO, it occupies the cation vacancies at the 6h position La$_{II}$, which reduces the concentration of cation vacancies and makes the negative defect stacking centers decrease, thus reducing the activation energy.

In addition, Pr-doped adds a small amount of interstitial oxygen ions. Since the conductivity of LSO is dominated by the conduction of interstitial oxygen ion, increasing the amount of interstitial oxygen ions, and the conductivity of LSO will be increased as a result. The Pr-doped occupies cation vacancies to increase the lattice volume, which expands the interstitial oxygen ion transmission space,
increases the interstitial oxygen ion transmission efficiency, so increases the conductivity. However, the conductivity of LSO shows a trend of increasing and then decreasing with the amount of Pr-doped increase, because the electrostatic attraction of 6h-site cation to interstitial oxygen ion increases when praseodymium is overdoped, which increases the spatial resistance of interstitial oxygen ion transport. In summary, the praseodymium doped to enhance LSO conductivity mechanism that interstitial oxygen concentration-cation vacancies concentration-lattice volume composite enhancement mechanism was proposed.

4. Conclusion
FT-IR characterization was performed, and the results showed that praseodymium was successfully doped at the La site of LSO, and Pr$^{3+}$ occupied the cation vacancy at the 6h site and led to lattice expansion. XRD analysis showed that LPSO had a typical $p6_3/m$ apatite type structure. The AC impedance spectrum test showed that: The conductivity of LPSO shows a trend of increasing and then decreasing with the increase of Pr-doped, and the conductivity of LPSO doped with Pr$^{3+}$ increases obviously compared with that of undoped LSO. When the doping amount was 0.5, the maximum conductivity was $4.80\times10^4 \text{ S cm}^{-1} (t = 600 \text{ °C})$. However, as the Pr$^{3+}$ content ($x > 0.5$) increased continuously, the conductivity of LPSO decreased. Pr-doped adds the concentration of interstitial oxygen ion and expands the lattice volume, it improves the interstitial oxygen ion transmission efficiency and decreases the concentration of cation vacancies and the spatial resistance of interstitial oxygen ions transport. So, the praseodymium doped to enhance LSO conductivity mechanism that interstitial oxygen concentration-cation vacancies concentration-lattice volume composite enhancement mechanism was proposed.

Acknowledgements
The authors are grateful to the National Natural Science Foundation of China (51374155, 51242010) and the Hubei Province Key Technology R&D Program (2014BCB034) for supporting this work.

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