

# Influence of sintering parameters on microstructure and electrical conductivity of $\text{La}_{10}\text{Si}_6\text{O}_{27}$ ceramics

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## Abstract

$\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics powders were synthesized via the high temperature solid state reaction, and were then pressureless-sintered to obtain dense bulk ceramics by adjusting the sintering parameters. Crystal structure and electrical conductivity of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics were investigated by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, Raman spectroscopy and complex impedance analysis.  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics obtained at sintering parameters of 1923 K and 10 h has the highest electrical conductivity of  $1.28 \times 10^{-2} \text{ S cm}^{-1}$  at test temperature of 1073 K. Sintering temperature have a distinct effect on the bulk density of samples and the content of  $\text{La}_2\text{SiO}_5$  second phase. The content of  $\text{La}_2\text{SiO}_5$  second phase is inversely proportional to electrical conductivity of as-sintered samples, while the bulk density is directly proportional to electrical conductivity of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics.

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**Keywords:** B. Microstructure; C. Electrical conductivity; Lanthanum silicate; Oxy-apatite; Sintering temperature

## 1. Introduction

Oxy-apatite lanthanum silicates are the most attractive candidates for intermediate temperature electrolytes of solid oxide fuel cells (SOFCs) applications due to low operating temperatures of less than 873–1073 K, low activation energy, excellent long-term stability, a wide range of materials selection and relatively low processing cost [1–5]. Recently, many researchers reported high oxide-ionic conductivity of oxy-apatite lanthanum silicates [6–10]. Rather than traditional SOFC electrolytes of fluorite and perovskite structures with the anion-vacancy conduction mechanism, oxy-apatite silicates are novel electrolytes with a conduction mechanism of interstitial oxide-ion migration [11–20].

The crystal structure of lanthanum silicates is hexagonal oxy-apatite structure with a space group  $P6_3/m$ , which is constituted of covalent and isolated silicate tetrahedra ( $\text{SiO}_4$ ). The La cations are situated at seven-coordinated sites named 6h and nine-coordinated sites named 4f. In lanthanum silicates,

interstitial oxide ions are demonstrated to migrate in the conduction channels along the  $c$ -axis via a complex sinusoidal pathway, hence the conductivity is much higher parallel to the  $c$ -axis than perpendicular to this direction [21]. The interstitial oxide ions neighboring the silicate units were well evidenced by nuclear magnetic resonance (NMR) and Raman spectroscopy [22–24].

However, the influence of sintering parameters on structure and electrical conductivity of oxy-apatite lanthanum silicates remains unclear in the open literature. Therefore, in the present work, the crystal structure and electrical conductivity of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics were investigated by tailoring the sintering parameters.

## 2. Experimental procedures

$\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics were synthesized via the high temperature solid state reaction process. Ultrapure  $\text{La}_2\text{O}_3$  powder (Griem Advanced Materials Co. Ltd., Beijing, China; purity  $\geq 99.9\%$ ) and  $\text{SiO}_2$  powder (Huijing New Materials Ltd., Shanghai, China; purity  $\geq 99.9\%$ ) were used as original materials. In order to attain complete decarbonation and

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dehydroxylation, precalcining of  $\text{La}_2\text{O}_3$  powder was performed at 1173 K for 2 h before weighing. These powders in appropriate ratios were mechanically ball-milled in analytically pure ethanol for 24 h with zirconia balls at 400 rpm, and were dried at 373 K. These powder mixtures were then calcined at 1623 K for 10 h. The as-calcined powders were uniaxially compacted in a steel mold at 20 MPa, and were then cold isostatically pressed under a pressure of 260 MPa for 8 min. After that, the compacts were pressureless-sintered under the condition of designed sintering parameters as shown in Table 1.

The as-sintered samples were characterized using X-ray diffraction (XRD, Rigaku D/Max-rB, Japan) with monochromatized  $\text{Cu K}\alpha$  radiation in a  $2\theta$  range of  $10\text{--}70^\circ$  at a scanning rate of  $4\text{ deg min}^{-1}$ . Surface morphologies of sintered samples were determined by a scanning electron microscope (SEM, Helios Nanolab 600i, USA). The samples were polished and thermally etched at a temperature, which is 50 K lower than the sintering temperature for 30 min. Thermally etched surfaces of samples were covered with a thin gold coating for a better image definition. The bulk densities of all the sintered samples were measured by the Archimedes method with an immersion medium of deionized water. Microstructure of sintered samples was observed by transmission electron microscopy (TEM, FEI Tecnai G2 F30, USA). For TEM observations, the specimens were first ground down to a thickness of 50  $\mu\text{m}$ , and were then prepared by ion beam thinner in argon. Raman spectra were recorded by Raman microscope (LabRAM HR800, Horiba Jobin Yvon, France). The measurement was performed with a 458 nm line of an argon ion laser at room temperature. The laser power was selected to be 20 mW, and the spot diameter was 1  $\mu\text{m}$ . The Raman shift range was from 100 to 1000  $\text{cm}^{-1}$ .

The AC impedance/gain-phase analyzer (Solartron<sup>TM</sup> SI 1260, UK) combined with electrochemical interface (Solartron<sup>TM</sup> SI 1287, UK) was used to measure the impedance of

$\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics in air. Platinum pastes were painted on both surfaces of the specimens with a diameter of 8 mm and a thickness of 1 mm as the electrodes, which were heated to 1273 K for 2 h in air in order to adhere to the specimen surfaces. For the measurements of the impedance plots, the specimens were heated from 673 to 1173 K at a heating rate of  $5\text{ K min}^{-1}$ . The temperature interval was 50 K and the stabilization time was 15 min between continuous measurements. The measurement frequency was in the range of 20 Hz to 20 MHz and the AC signal strength was 50 mV. The Zview software was used to analyze the results.

### 3. Results and discussion

#### 3.1. Sintering parameters on microstructures for $\text{La}_{10}\text{Si}_6\text{O}_{27}$ ceramics

XRD patterns of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics under different sintering conditions are shown in Fig. 1. The main diffraction peaks of all the specimens under different sintering parameters are in agreement with the standard XRD spectrum of  $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$  (JCPDS no. 53-0291), which belongs to hexagonal apatite structure with a space group  $P63/m$ . From Fig. 1, no starting powders are found in sintered samples. However, all the specimens also contain a small amount of second phase  $\text{La}_2\text{SiO}_5$  (JCPDS no. 40-0234), which belongs to monoclinic structure with a space group  $P21/c$ . The ionic ratio of  $\text{La}^{3+}$  to  $\text{Si}^{4+}$  is 1.67:1 in  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics prepared by high temperature solid state reaction, which is close to 2:1, so it is easy to form the second phase  $\text{La}_2\text{SiO}_5$ .

XRD patterns of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics sintered at different temperatures for 10 h are shown in Fig. 1(a). With increasing the sintering temperature from 1873 K to 1923 K, the diffraction peaks of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics are clearly more incisive, while the peaks of  $\text{La}_2\text{SiO}_5$  second phase are very lower. The higher the sintering temperature, the lower content the second phase  $\text{La}_2\text{SiO}_5$ . However, when the sintering temperature increases to 1973 K,  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics becomes melted completely. In the present work, the melting points of  $\text{La}_2\text{O}_3$  and amorphous  $\text{SiO}_2$  starting powders are 2490 K and 1983 K, respectively. When the sintering temperature is selected at 1923 K,  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics exhibits uniform grains and a lowest content of second phase  $\text{La}_2\text{SiO}_5$ .

Table 1  
Sintering parameters of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics.

Sintering temperature (K)	Sintering time (h)		
1873	5	10	15
1923	5	10	15
1973	5	10	15

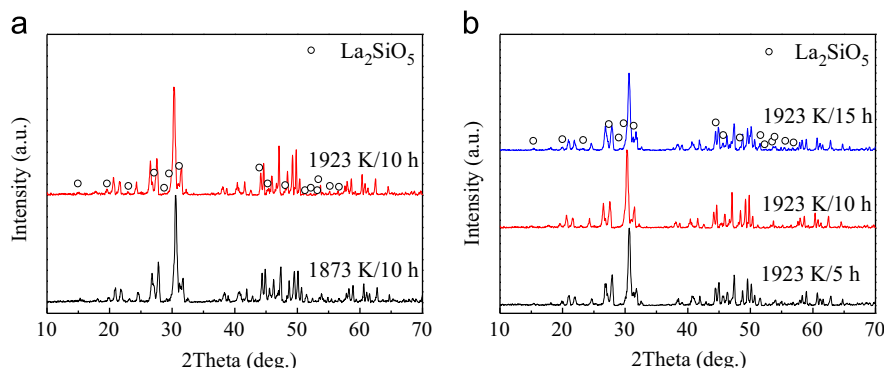


Fig. 1. XRD patterns of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics under different sintering conditions: (a) different sintering temperatures; and (b) different sintering time.

Fig. 1(b) shows XRD patterns of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics sintered at 1923 K for different time. When the sintering time is 10 h,  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics exhibits strong diffraction peaks. However, these peaks become broadening when the sintering time is prolonged to 15 h, which may overheat the  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics and result in partial melting. In addition, when the sintering time increases from 5 h to 10 h, the peak intensities of  $\text{La}_2\text{SiO}_5$  second phase are distinctly reduced.

Microstructures of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics sintered at different temperatures are shown in Fig. 2. Obviously, the grains grow well on the surfaces of all these specimens, and the grain size is between 3 and 10  $\mu\text{m}$ . The grain boundary is very clean, and the bulk density is quite high. From Fig. 2(a), the grain size is relatively small when the sintering temperature is 1873 K. However, the grain size increases obviously with increasing the sintering temperature to 1923 K (Fig. 2(b)–(d)). Comparing with the microstructures in previous literatures [25–28], we know that the regions pointed by arrows are the partial melting area, which is caused by the use of the amorphous silica as raw powders in this work.

Fig. 3 shows the bulk density of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics obtained under different sintering conditions. Theoretical density of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics is  $5.614 \text{ g cm}^{-3}$  by the criterion PCPDF from XRD. With increasing the sintering temperature, the bulk density of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics decreases distinctly, as shown in Fig. 3(a). The sintering temperature is one of the most important influencing factors to the densification process. However, too high sintering temperature will result in abnormal growth of grains and partial melting phenomenon easily. When the sintering temperature is 1923 K, and the densification process is almost complete. At

1973 K,  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics is completely melted into the crucible. Therefore, the sintering temperature of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics is optimized to be 1923 K. Fig. 3(b) shows the bulk density of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics at 1923 K for different sintering time. Clearly, the bulk density decreases gradually with increasing the sintering time from 5 h to 15 h.

Fig. 4 shows TEM micrographs and the corresponding zone axis selected area electron diffraction (SAED) patterns of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics sintered at 1923 K for 10 h. From Fig. 4(a), the grain boundary is very clean, and no impurity phase is found at grain boundary. Fig. 4(b)–(d) shows the SAED patterns at different locations of A, B and C as marked in (a), respectively. These patterns indicate that  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics are well crystallized. The SAED pattern of the grain A corresponds to [111] zone axis, with a hexagonal structure of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics; The SAED patterns of the grains B and C correspond to [100] and  $[\bar{2}1\bar{1}]$  zone axis, respectively, with a monoclinic structure of  $\text{La}_2\text{SiO}_5$ . The SAED patterns in Fig. 4(b)–(d) only contain these two crystal lattices of hexagonal  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  and monoclinic  $\text{La}_2\text{SiO}_5$ , no other phases are found, which is consistent with the above XRD results.

### 3.2. Raman analysis of $\text{La}_{10}\text{Si}_6\text{O}_{27}$ ceramics

Fig. 5 shows microstructures and Raman spectra of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics at different sintering temperatures. Fig. 5(c) corresponds to D, E, and F regions of (a), while Fig. 5(d) corresponds to G, H, and I regions of (b). Microstructures of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics obtained at different sintering temperatures contain three kinds of different morphologies,

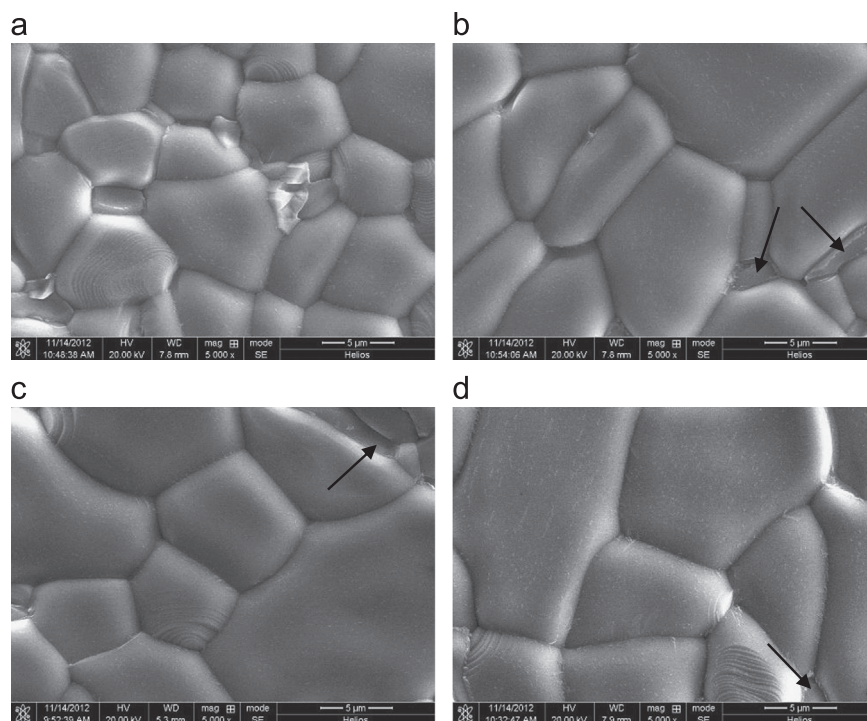


Fig. 2. Microstructures of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics under different sintering conditions: (a) 1873 K for 10 h; (b) 1923 K for 10 h; (c) 1923 K for 5 h; and (d) 1923 K for 15 h.

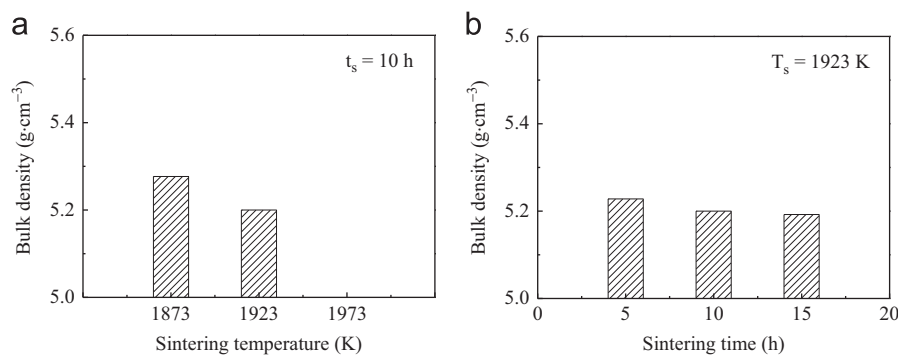


Fig. 3. Bulk density of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics under different sintering conditions: (a) bulk density vs. sintering temperature; and (b) bulk density vs. sintering time.

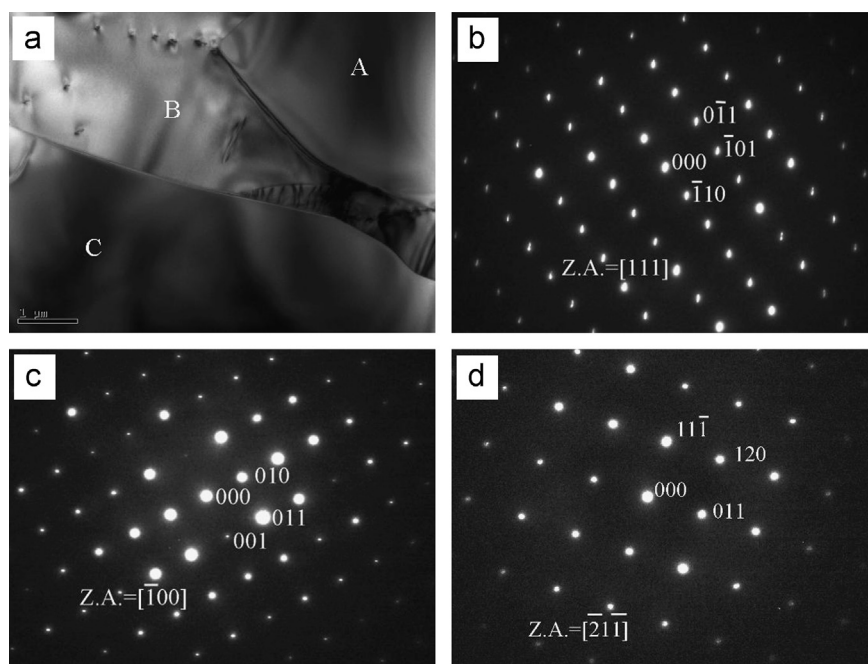


Fig. 4. TEM micrographs and the corresponding zone axis selected area electron diffraction patterns of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics sintered at 1923 K for 10 h: (a) TEM micrograph of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics; (b), (c) and (d) selected area electron diffraction patterns at different locations of A, B and C in (a), respectively.

including polygonal, lathy and plicated grains. As shown in Fig. 5(c) and (d), Raman spectra recorded from different spots of each specimen are almost the same, such as band position, band relative intensity and band half-width. In the present work, major bands positions of Raman spectra in the range of 100–1000  $\text{cm}^{-1}$  obtained at both sintering temperatures of 1873 K and 1923 K corresponds to those reported in previous studies related to oxy-apatites [29,30]. The integral range can be divided at 350  $\text{cm}^{-1}$  into two distinctly different areas. The bands above 350  $\text{cm}^{-1}$  can be assigned to internal modes of the pseudo tetrahedral  $\text{SiO}_4$  units at frequencies closely related to those of the free species. The band in the range of 370–390  $\text{cm}^{-1}$  can be assigned to the symmetric bending mode  $\nu_2$ , the band around 525  $\text{cm}^{-1}$  can be due to the asymmetric bending mode  $\nu_4$ , the band at 850  $\text{cm}^{-1}$  and 920  $\text{cm}^{-1}$  can correspond to the symmetric stretching mode  $\nu_1$  and asymmetric stretching mode  $\nu_3$  of  $\text{SiO}_4$  tetrahedra. However, the external bands below 350  $\text{cm}^{-1}$  can be assigned to

translational, vibrational and rotational of the  $\text{SiO}_4$  units. Fig. 6 shows the Raman spectra of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics at different sintering temperatures. With increasing the sintering temperature from 1873 K to 1923 K, some weak bands become weakening or annihilate, in the meantime the half-width of bands are magnified. It indicates that with increasing the sintering temperature from 1873 K to 1923 K, partial melting occurs on the surface of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics, which causes the increase in the short range disorder degree of structure. As these weak bands correspond to the characteristic peaks of second phase  $\text{La}_2\text{SiO}_5$ , increasing the sintering temperature will decrease the content of second phase  $\text{La}_2\text{SiO}_5$ .

The stretching modes of Raman spectra are particularly sensitive to the neighboring disorders, such as atoms from other sub-lattices or electric defects resulting from substitutions/vacancies, whereas the symmetric bending modes are specifically susceptible to local geometric disorientation. Therefore, the changes in symmetric



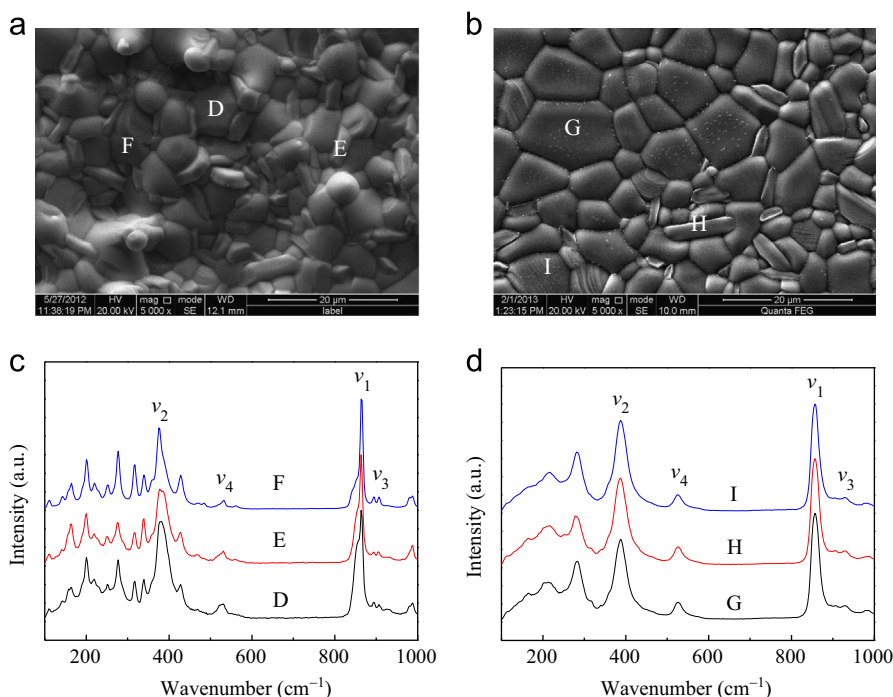


Fig. 5. Microstructures and Raman spectra of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics at different sintering temperatures: (a) microstructures of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics sintered at 1873 K; (b) microstructures of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics sintered at 1923 K; (c) Raman spectra of D, E and F in (a); and (d) Raman spectra of G, H and I in (b).

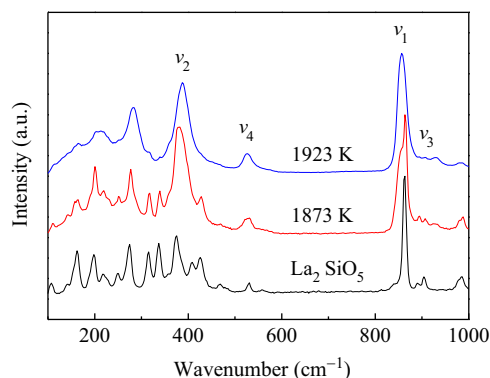


Fig. 6. Raman spectra of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  and  $\text{La}_2\text{SiO}_5$  ceramics sintered at different temperatures.

stretching mode  $\nu_1$  will be able to distinguish the neighboring disorders of oxygen ions defects, which are responsible for electrical conductivity of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics prepared under different sintering conditions. Fig. 7 shows the decomposition of the symmetric stretching mode  $\nu_1$  of  $\text{SiO}_4$  tetrahedral into Lorentzian components for  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics under different sintering conditions. As shown in Fig. 7(a) and (b), the symmetric stretching mode  $\nu_1$  can be decomposed into three main bands at  $849.12\text{ cm}^{-1}$ ,  $856.55\text{ cm}^{-1}$ ,  $864.67\text{ cm}^{-1}$  and  $849.62\text{ cm}^{-1}$ ,  $855.63\text{ cm}^{-1}$ ,  $862.7\text{ cm}^{-1}$ , respectively, which is similar to previous results reported in related literatures [31]. However, the band centered at  $862.7\text{ cm}^{-1}$  is obviously broadened. This indicates that the disorder degree of structure increases with increasing the sintering temperature from 1873 K to 1923 K. Fig. 8 shows the decomposition of the symmetric bending mode

$\nu_2$  of  $\text{SiO}_4$  tetrahedral into Lorentzian components for  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics under different sintering conditions. An additional band shoulder at  $360\text{ cm}^{-1}$  is found in the oxygen-excessive  $\text{La}_{8+x}\text{Sr}_{2-x}(\text{SiO}_4)_6\text{O}_{2+x/2}$  samples with its intensity increasing with increasing  $x$  [32]. As shown in Fig. 8(a) and (b), the fourth band at around  $360\text{ cm}^{-1}$  can be found, all the samples of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  under different sintering temperatures are oxygen-excessive in the present work. In addition, as the intensity of the fourth band in Fig. 8(b) is higher than that in Fig. 8(a), the specimen contains more interstitial oxygen with increasing the sintering temperature from 1873 K to 1923 K.

### 3.3. Electrical responses of as-synthesized oxide ceramics

Fig. 9 shows the impedance plots at 673 K and corresponding equivalent circuit of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics under different sintering conditions. From Fig. 9, all the AC impedance spectra are composed of two interconnected semicircular arcs and an incomplete semicircular. The fitting parameters of grain resistance ( $R_g$ ), grain boundary resistance ( $R_{gb}$ ), grain capacitance ( $CPE_g$ ) and grain boundary capacitance ( $CPE_{gb}$ ) for  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics under different sintering conditions are all acquired by Zview software (Table 2). The ranges of capacitances are from  $1.89 \times 10^{-11}$  to  $7.61 \times 10^{-10}\text{ F cm}^{-1}$  in the high frequency, and from  $6.79 \times 10^{-8}$  to  $1.16 \times 10^{-7}\text{ F cm}^{-1}$  in the medium frequency. These two semicircular arcs correspond to the grain impedance and the grain boundary impedance process, respectively. However, the incomplete semicircular represents the electrode interface diffusion, which is the representative of Wagner ionic diffusion effect. The electrolyte of oxy-apatite type  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics is predominantly conducted by ionic

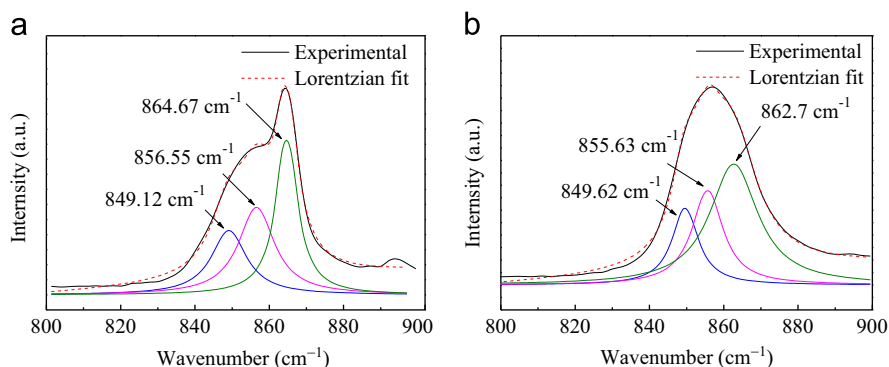


Fig. 7. Decomposition of the symmetric stretching mode  $\nu_1$  of  $\text{SiO}_4$  tetrahedral into Lorentzian components for  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics under different sintering conditions: (a) 1873 K for 10 h; and (b) 1923 K for 10 h.

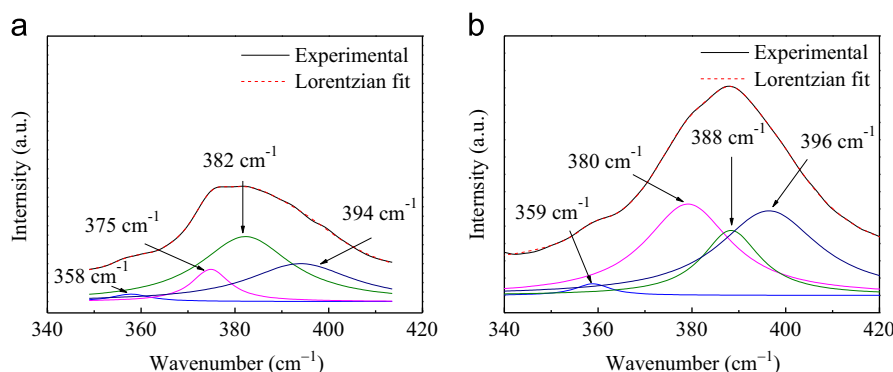


Fig. 8. Decomposition of the symmetric bending mode  $\nu_2$  of  $\text{SiO}_4$  tetrahedral into Lorentzian components for  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics under different sintering conditions: (a) 1873 K for 10 h; and (b) 1923 K for 10 h.

carriers. From Fig. 9(a) and (b), all the semicircular arcs corresponding to the grain impedance and the grain boundary impedance decrease clearly with increasing the sintering temperature from 1873 K to 1923 K, even more for the semicircular arcs correspond to the grain boundary impedance. That is because the cavities within materials are eliminated following the rise of sintering temperature, which is beneficial for grain to grow up. If the size of grain is big, the amount of grain boundary is less for certain bulk specimens. This is concordant with the SEM results in Fig. 2. The big size grains and little amount grain boundaries are all helpful to conducting the interstitial oxygen ions, consequently, the grain impedance and the grain boundary impedance have decreased. It indicates that the grain size plays an important role in the grain impedance of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics. Fig. 9(b)–(d) shows the AC impedance spectra at 1923 K for different sintering time. The semicircular arc corresponding to the grain impedance has no significant change with the sintering time. When the sintering temperature remains unchanged, the grain size has a little change. However, the semicircular arc corresponding to the grain boundary impedance inclines to decrease firstly and then increase. The second phase  $\text{La}_2\text{SiO}_5$  is usually situated at the grain boundaries of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics, and exhibits a negative effect on the conduction of interstitial oxygen ion. Therefore, the grain boundary impedance decreases evidently with decreasing the content of second phase  $\text{La}_2\text{SiO}_5$ . When the sintering time is prolonged from 10 h to 15 h at 1923 K, the content of second phase  $\text{La}_2\text{SiO}_5$  has almost no change, however the grain

boundary impedance increases slightly. As we all know, the grain size usually has an important effect on the macroscopic properties [33], so the importance of the grain size should be considered for electrical properties. The grain and grain boundary conductivity of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics at 673 K under different sintering conditions are shown in Table 3. It can be seen from Table 3 that the grain conductivity of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics sintered at 1923 K for different sintering time are all an order of magnitude higher than that of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics sintered at 1873 K, which indicates that the higher sintering temperature, the bigger grain size, and the higher grain conductivity. In addition, the grain boundary amount at 1923 K is more than that at 1873 K, so the grain boundary conductivity is little higher than that at 1873 K.

Fig. 10 shows the AC impedance plots in the temperature range of 673–1173 K in air and corresponding equivalent circuit of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics sintered at 1923 K for 10 h. Clearly, with increasing the measurement temperature, the semicircular arcs corresponding to the grain and grain boundary impedance decrease evidently and shift to the high frequency. At 873 K, the semicircular arcs corresponding to the grain impedance disappear. In addition, the ray representing electrode interface diffusion becomes to bend down gradually, and then forms a distinct semicircular arc. The transport ability of interstitial oxygen ion increases with increasing the measurement temperature. As the polarization process accelerates, the polarization relaxation time becomes shortened. The polarization relaxation frequencies of both

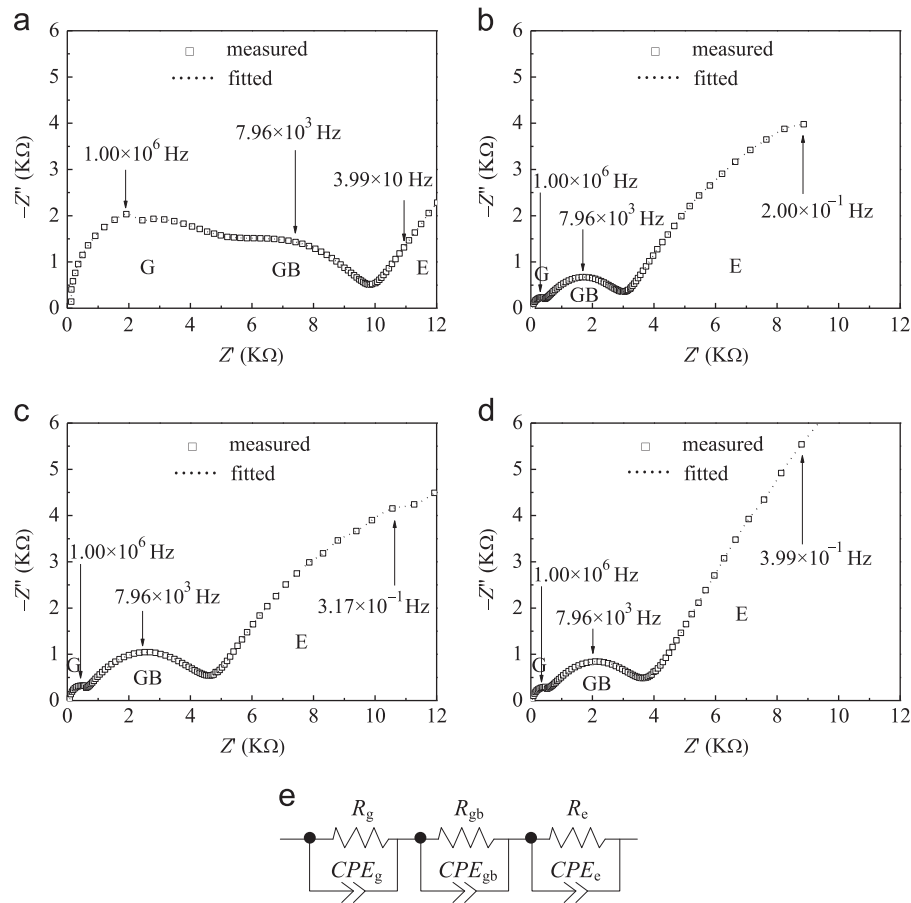


Fig. 9. Impedance plots at test temperature of 673 K and corresponding equivalent circuit of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics under different sintering conditions: (a) 1873 K for 10 h; (b) 1923 K for 10 h; (c) 1923 K for 5 h; (d) 1923 K for 15 h; and (e) equivalent circuit.

Table 2

Fitting parameters of grain resistance ( $R_g$ ), grain boundary resistance ( $R_{gb}$ ), grain capacitance ( $CPE_g$ ) and grain boundary capacitance ( $CPE_{gb}$ ) at 673 K for  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics under different sintering conditions.

Sintering parameters	$R_g$ ( $\Omega$ )	$R_{gb}$ ( $\Omega$ )	$CPE_g$ ( $\text{F cm}^{-1}$ )	$CPE_{gb}$ ( $\text{F cm}^{-1}$ )
1873 K for 10 h	3213	6696	$1.89 \times 10^{-11}$	$6.79 \times 10^{-8}$
1923 K for 10 h	416.4	2583	$7.61 \times 10^{-10}$	$1.16 \times 10^{-7}$
1923 K for 5 h	528.4	4029	$1.83 \times 10^{-10}$	$8.15 \times 10^{-8}$
1923 K for 15 h	511.8	3116	$6.31 \times 10^{-10}$	$9.48 \times 10^{-8}$

Table 3

The conductivity of grain and grain boundary at 673 K for  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics under different sintering conditions.

Sintering parameters	$\sigma_g$ ( $\text{S cm}^{-1}$ )	$\sigma_{gb}$ ( $\text{S cm}^{-1}$ )
1873 K for 10 h	$6.46 \times 10^{-5}$	$3.10 \times 10^{-5}$
1923 K for 10 h	$4.86 \times 10^{-4}$	$7.83 \times 10^{-5}$
1923 K for 5 h	$3.88 \times 10^{-4}$	$5.09 \times 10^{-5}$
1923 K for 15 h	$4.14 \times 10^{-4}$	$6.80 \times 10^{-5}$

grain and grain boundary shift to a high frequency, and finally beyond the upper limit (20 MHz) of measurement frequency. Nevertheless, both grain and grain boundary resistances will decrease with increasing the measurement temperature. At

873 K, the semicircular arcs corresponding to the grain impedance disappear, and the grain capacitance can be neglected. Therefore, the two semicircular arcs correspond to the grain boundary impedance and electrode interface diffusion process. It is concluded that the grain impedance will disappear with increasing the measurement temperature, while the grain boundary impedance is available and decrease gradually.

Arrhenius plots of total conductivity of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics at different sintering temperatures are presented in Fig. 11(a). Clearly, the measured total conductivity at 1923 K is an order of magnitude higher than that at 1873 K. In combination with XRD results, increasing the sintering temperature will decrease the content of second phase  $\text{La}_2\text{SiO}_5$  remarkably. The higher the sintering temperature, the lower the content of second phase  $\text{La}_2\text{SiO}_5$ , the

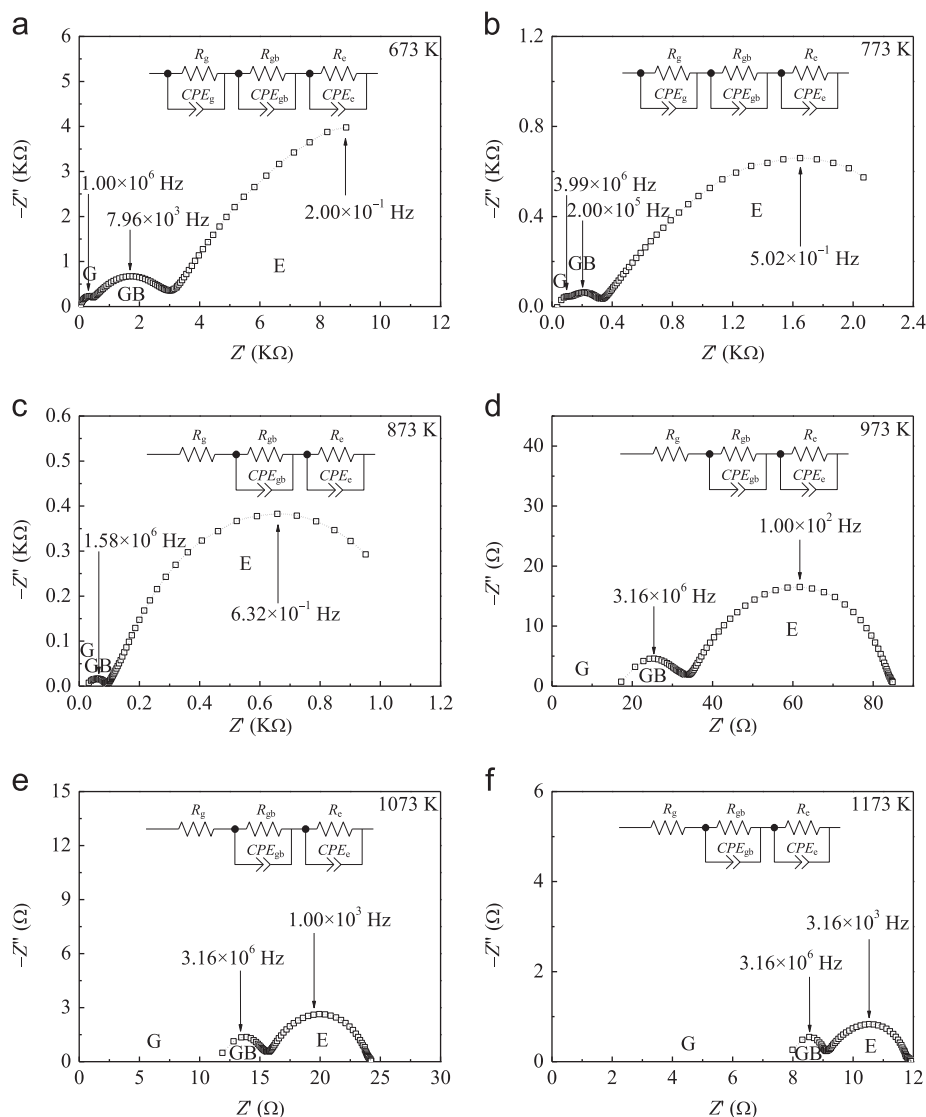


Fig. 10. Impedance plots at different test temperatures and corresponding equivalent circuit of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics sintered at 1923 K for 10 h: (a) 673 K; (b) 773 K; (c) 873 K; (d) 973 K; (e) 1073 K; and (f) 1173 K.

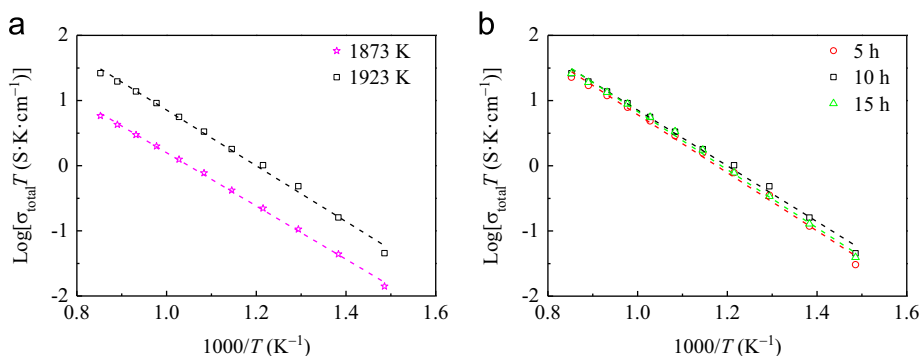


Fig. 11. Arrhenius plots of total conductivity of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics: (a) at different sintering temperatures for 10 h; and (b) at 1923 K for different sintering time.

higher the total conductivity. Therefore, the content of second phase  $\text{La}_2\text{SiO}_5$  is the dominated influencing factor of total conductivity. At 1073 K, the highest electrical conductivity of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics sintered at 1923 K for 10 h reaches

$1.28 \times 10^{-2} \text{ S cm}^{-1}$ , which is higher than that of the sample prepared by a water-based gel-casting route, and is approximate with the sample prepared by freeze-drying method, tape casting combined with reaction sintering under identical conditions



[29,34,35]. Arrhenius plots of total conductivity of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics at 1923 K for different sintering time are presented in Fig. 11(b). The total conductivity first increases evidently with prolonging the sintering time from 5 h to 10 h, and then drops slightly up to 15 h. The content of second phase  $\text{La}_2\text{SiO}_5$  has almost no change when the sintering time is prolonged from 10 h to 15 h, however, the total conductivity still decreases slightly, which may be due to the decrease in the bulk density.

#### 4. Conclusions

- (1) Oxy-apatite  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics were prepared via high temperature solid state reaction and subsequent pressureless pressing. The sintering parameters are optimized to be 1923 K and 10 h to get a high purity of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics.
- (2) Sintering parameters have a distinct influence on both the content of second phase  $\text{La}_2\text{SiO}_5$  and the bulk density of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics. With increasing the sintering temperature, the content of second phase  $\text{La}_2\text{SiO}_5$  and the bulk density of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics decrease obviously. With prolonging the sintering time, the content of second phase  $\text{La}_2\text{SiO}_5$  decreases first and then remains unchanged, however, the bulk density of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics decreases monotonously.
- (3) The content of second phase  $\text{La}_2\text{SiO}_5$  is inversely proportional to total conductivity of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics, which is the dominated influencing factor of total conductivity. The bulk density is directly proportional to total conductivity of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics.
- (4) The content of second phase  $\text{La}_2\text{SiO}_5$  has a certain influence on the grain size of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$ . The second phase distributes mainly at the grain boundaries, which blocks the grain growth of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$ . However, the grain size and grain boundary amount have a distinct influence on total conductivity of  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  ceramics. The grain resistance decreases with increasing the grain size, while the grain boundary resistance increases with increasing the grain boundary amount.

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