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Electrical properties of Sb-doped apatite-type lanthanum silicate materials for SOFCs

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La_{9,33-x}Sb_x(SiO₄)₆O₂ ($0 \le x \le 2.0$) ceramics were fabricated using the standard solid-state synthesis method for solid oxide electrolytes. Increasing the Sb content in apatite-type La_{9,33-x}Sb_x(SiO₄)₆O₂ leads to an increased unit cell volume. The room-temperature structure is hexagonal, space group P6₃ or P6₃/m, with a = 9.728 Å, and c = 7.191 Å for La_{8,33}Sb(SiO₄)₆O₂. The average grain size in sintered specimens was approximately 1.5 to 1.9 µm. La_{9,33-x}Sb_x(SiO₄)₆O₂ (1.5 ≤ x ≤ 2.0) apatite ceramics showed the formation of a second phase of La₂Si₂O₇, due to the volatilization of the Sb atoms. The electrical conductivity at 800 °C and activation energy of La_{8,33}Sb(SiO₄)₆O₂ doped with 1.0 mol% Sb showed a maximum value of 3.3×10^{-3} S cm⁻¹ and 1.47 eV, respectively.

Key words: Solid oxide electrolyte, Apatite-type, Electrical conductivity.

Introduction

Solid electrolytes with oxygen ionic conductivity are key materials in high-temperature electrochemical devices, including solid oxide fuel cells (SOFCs), oxygen pumps, electrolyzers and sensors. In addition, it is known that Lantanium silicate apatite ceramics generally contain a multi-valent element in the form of an ionic conducting material, which is responsible for most of the ionic conduction, due to the number of oxygen channels and A-site vacancies [1-4]. Extensive research is being carried out on the development of more efficient materials as electrolytes in SOFCs in an effort to decrease the high operating temperatures. Generally, a large number of the ions of one species should be mobile. This requires a large number of empty sites, either vacancies or accessible interstitial sites. The empty and occupied sites should have similar potential energies with a low activation energy barrier for jumping between neighboring sites. High activation energy decreases carrier mobility, and very stable sites (deep potential energy wells) lead to carrier localization. Therefore, solid electrolytes with high ionic conductivity normally exhibit low activation energy. Apatite oxides, based on $M_{10}(RO_4)_6O_{2\pm y}$ (M = rare-earth, alkaline-earth, R = Si, Ge), are earth apatite materials that have recently been attracting considerable interest in this regard following the report on silicate and germanate systems exhibiting conductivities higher than the conventional yttria-stabilized zirconia (YSZ) electrolyte at moderate temperatures. The apatite lattice can be

described as a hybrid structure consisting of covalent SiO₄ tetrahedra and ionic-like M/O channels. The oxygen transport in $M_{10-x}(SiO_4)_6O_{2\pm y}$ (M = La-Yb; x = 0-0.67) increases with an increasing M^{3+} radius. while the activation energy decreases [5-8]. The apatite lattice can tolerate a considerable A-site deficiency and extensive doping, thus providing an important tool for further optimization. $La_{10}(SiO_4)_6O_3$ exhibits the highest conductivity among the investigated apatite-type materials. However, silicates are usually prepared through a solid state reaction using La₂O₃ and SiO₂ as raw materials, at high sintering temperatures (approximately 1600 °C). In order to decrease the sintering temperature some authors have doped the apatite structure with transition metal cations (Co, Fe, Mn, Ti) [9-11]. Furthermore, doping studies have shown the importance of nonstoichiometry, either in terms of cation vacancies or an oxygen excess, in maximizing the oxide ion conductivity in these phases [12, 13].

In this study, we fabricated Sb-substituted $La_{9,33-x}(SiO_4)_6O_2$ solid electrolytes in order to improve the conductivity properties and sinterability of apatite ceramics. The role of Sb doping in the apatite lattice might show positive results in terms of ionic conduction as a result of having a larger ionic radius than the La^{3+} ion, and in terms of sinterability due to the low melting temperature of 655 °C. We investigated the doping effects of Sb for the La site in $La_{9,33-x}(SiO_4)_6O_2$ on the oxide ion conductivity.

Experiments

High-purity La₂O₃, SiO₂ and Sb₂O₃ were used to prepare the series of phases La_{9,33-x}Sb_x(SiO₄)₆O₂ $(0 \le x \le 2.0)$ as the starting materials. The raw materials

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were mixed in ethanol with a ball mill using a zirconia ball and plastic pot, dried and then calcined in air at 900 °C for 2 h. The resultant powders were again ballmilled into fine powder. After being dried, the powder was pressed into a pellet under 100 SMPa with a cold isostatic press, and sintered in air at 1400-1450 °C for 2 h. The structural and electrical properties of the specimens, fabricated under optimum sintering conditions, were measured. The materials were characterized using Xray diffraction (XRD, Rigaku D/Max-B diffractometer), and scanning electron microscopy (SEM, Hitachi S-4100). Both sides of each pellet were coated with Pt paste in order to take electrical measurements, and the discs were baked at 950 °C. The electrical properties were measured using a multi-frequency LCR meter (Fluke PM 6306) in the frequency range of 100 Hz to 1 MHz. Conductivities were determined from ac impedance measurements in the temperature range 600 °C to 800 °C.

Results and Discussion

Fig. 1 shows the X-ray diffraction patterns of $La_{9.33-x}Sb_x(SiO_4)_6O_2$. The crystallinity of the compound slightly increases with an increase in the Sb content. $La_{9.33-x}Sb_x(SiO_4)_6O_2$ (0.5 $\leq x \leq 1.0$) apatite ceramics showed the formation of single apatite phases because the doped Sb ions were incorporated into the apatite lattice. In addition, the sintering temperature of these composition materials decreased by approximately 150 °C compared with that of La_{9.33}(SiO₄)₆O₂ materials. However, for the specimens in the range $1.5 \le x \le 2.0$, the second phases of La₂Si₂O₇ are observed at $2\theta = 29^{\circ}$ and 36° due to the volatilization of the Sb atoms [14]. Doping with antimony leads to an increased unit cell volume due to the larger radius of the Sb^{3+} cation compared to La^{3+} , as shown in Table 1 [15].

Fig. 2 shows the surface SEM micrographs of La_{9.33-x}Sb_x(SiO₄)₆O₂ specimens with varying Sb content. With an increase in Sb content, no variations in average grain size were observed (varied from 1.9 μ m to 1.5 μ m). Apparently, no traces of the second phase or segregation of dopant cations at the grain boundaries were found through SEM because of the tiny amount of second phase. These observations are in agreement with the impedance spectroscopy data. At the overlapping semicircles, the component of the intermediate frequency was affected by porosities rather than the second phase.

In order to determine the conductivity, complex plane impedance analysis was performed. Fig. 3 shows the complex impedance spectroscopy of $La_{7,83}Sb_{1.5}(SiO_4)_6O_2$ specimens at different temperatures. Electrode polarization is generally caused by space charge in the low-frequency domain. However, complex impedance was not observed as much in the measurements, because the space charges are located in the deep level of the energy band. Semicircles of the complex impedance

are classified by a phase difference of each component. In the impedance data, the first semicircle produced is not an accurate semicircle, but a thrawart-semicircle because more than two components are overlapped definitely. In addition, another semicircle at low frequency is able to judge through the response of the electrode component. If the first semicircle is not divided distinctly into two components, it can fall into two cases. In the first case, the capacitance values of two components are similar. In the other case, the frequency sizes in the middle range of the semicircle



Fig. 1. X-ray diffraction patterns of (a) $La_{8.83}Sb_{0.5}(SiO_4)_6O_2$, (b) $La_{8.33}Sb_1(SiO_4)_6O_2$, (c) $La_{7.83}Sb_{1.5}(SiO_4)_6O_2$, and (d) $La_{7.33}Sb_2(SiO_4)_6O_2$.

Table 1. Cell parameter data (hexagonal cell) for $La_{9,33-x}Sb_x(SiO_4)_6O_2$ ceramics.

Composition	Sintering temperature	Unit cell parameters	
		a = b (Å)	c (Å)
La _{9.33} (SiO ₄) ₆ O ₂	1600 °C	9.721	7.187
La _{8.83} Sb _{0.5} (SiO ₄) ₆ O ₂	1450 °C	9.723	7.188
$La_{8.33}Sb_1(SiO_4)_6O_2$	1425 °C	9.728	7.191
La _{7.83} Sb _{1.5} (SiO ₄) ₆ O ₂	1400 °C	9.813	7.297
La7.33Sb2(SiO4)6O2	1400 °C	9.833	7.295



Fig. 2. SEM micrographs of (a) $La_{8.83}Sb_{0.5}(SiO_4)_6O_2$ (b) $La_{8.33}Sb_1(SiO_4)_6O_2$ (c) $La_{7.83}Sb_{1.5}(SiO_4)_6O_2$ and (d) $La_{7.33}Sb_2(SiO_4)_6O_2$.



Fig. 3. Complex impedance plots (*Z* and *Z*^{''}), obtained at various temperature for $La_{8,33}Sb_1(SiO_4)_6O_2$ ceramics.



Fig. 4. Conductivity for La_{9,33-x}Sb_x(SiO₄)₆O₂ ceramics at 800 °C.



1000 /T, K¹

Fig. 5. Arrhenius plots of the electrical conductivity for $La_{9,33-x}Sb_x(SiO_4)_6O_2$ ceramics;(a) $La_{8,83}Sb_{0.5}(SiO_4)_6O_2$, (b) $La_{8,33}Sb_1$. (SiO₄)₆O₂, (c) $La_{7,83}Sb_{1.5}(SiO_4)_6O_2$, and (d) $La_{7,33}Sb_2(SiO_4)_6O_2$.

are expanded. In this experiment, there are many porosities, and when the frequency at the highest point of the first semicircle is verified, it doesn't have hundreds of KHz ranges, but dozens of Hz ranges, That's why it was possible to judge using an expansion of the middle range frequency by grain boundaries and porosities. It is known that generally Lantanium silicate apatite ceramics contain a multivalent element in the form of an ionic conducting material, which is responsible for most of the ionic conduction, due to the number of oxygen channels and A-site vacancies [16].

From these results, the total conductivity (the sum of the bulk and grain boundary) was determined by extrapolation to zero reactance of the complex impedance

Table 2. Conductivity and activation energy for $La_{9,33-x}Sb_x(SiO_4)_6O_2$ ceramics.

Composition	$\sigma_{600}{}^o\!{}_C$	$\sigma_{700}{}^o\!{}_C$	$\sigma_{800}{}^o\mathrm{C}$	E _a
		(S cm ⁻¹)		(eV)
La _{8.83} Sb _{0.5} (SiO ₄) ₆ O ₂	$1.5 imes 10^{-4}$	$2.8 imes 10^{-4}$	1.7×10^{-3}	1.46
La _{8.33} Sb(SiO ₄) ₆ O ₂	2.2×10^{-4}	$4.4 imes 10^{-4}$	3.3×10^{-3}	1.47
La7.83Sb1.5(SiO4)6O2	1.3×10^{-4}	2.4×10^{-4}	$8.6 imes 10^{-4}$	1.29
La7.33Sb2(SiO4)6O2	1.0×10^{-4}	2.1×10^{-4}	$7.2 imes 10^{-4}$	1.22

plot. Fig. 4 shows the conductivity of La_{9,33-x}Sb_x(SiO₄)₆O₂ specimens with varying Sb content. The specimen doped with 1.0 mol% Sb showed a maximum value of 3.3×10^{-3} S cm⁻¹. It is suggested that doping with Sb leads to an increase in the oxygen interstitial channel width due to the larger radius of the Sb³⁺ cations compared to La^{3+} in $La_{9,33-x}Sb_x(SiO_4)_6O_2$ apatites. Therefore, as expected, expansion of the interstitial channel width is effective in increasing the mobility of the oxide ion. However, excessive amounts of dopant lead to a decrease in the oxide ion conductivity because disorder in the channel sites and local structural distortions are formed due to the formation of a pyrochlore phase. Therefore, excess doping of Sb is not preferred for high oxide ion conductivity. Thus, the optimized composition for the Sb-substituted specimen seems to be $La_{8.33}Sb(SiO_4)_6O_2$.

Fig. 5 shows the Arrhenius plots of the conductivity in La_{9.33-x}Sb_x(SiO₄)₆O₂ specimens. For La_{9.33-x}Sb_x(SiO₄)₆O₂, a large slope at high temperatures towards larger activation energies is observed in the Arrhenius plot on heating. This behavior is commonly observed in compounds with high ionic conductivities. The reason for this is thought to be that the interstitial oxygens are trapped out into the local structural dislocation below the critical temperature, T_c. However, above T_c, the trapped interstitial oxygens are progressively dissolved into the matrix of oxygen sites through thermal energy [17]. The plot shown in Fig. 5 indicates that T_c is approximately 750 °C for La_{9.33-x}Sb_x(SiO₄)₆O₂ specimens. The La_{8.33}Sb(SiO₄)₆O₂ specimen showed the highest conductivity, suggesting that this material could be a promising electrolyte for use in SOFCs. Although doping with Sb slightly increases the activation energy for ionic transport, as shown in Table 2, the concentration of ionic charge carriers seems essentially unaffected. The variation of the activation energy for ionic transport may be partly related to the incorporation of Sb³⁺, statistically distributed in La_{9.33-} $_{x}Sb_{x}(SiO_{4})_{6}O_{2}$ systems. These results suggest that the oxygen interstitial migration mechanism may be associated with the local structural distortions and compositional inhomogeneity in apatite silicates. Furthermore, the value of $La_{9,33-x}Sb_x(SiO_4)_6O_2$ ceramics is higher than that of La_{9,33}(SiO₄)₆O₂ ceramics [17]. Generally, the activation energy of solid electrolytes decreases with an increase in grain size. However, in this study, we examined the low sintering temperature of $La_{9,33}(SiO_4)_6O_2$ ceramics through the addition of Sb ions, so the specimen has a small grain size due to the low sintering temperature, as shown in Table 1. The area of the grain boundary also increased because of the small grain size.

In general, ionic trapping effects increase a material's activation energy. These facts remarkably occur at low temperatures. However, in lantanium silicate apatite ceramics, an ionic conducting material due to the number of oxygen channels and A-site vacancies, changes in activation energy can also be observed at high temperatures. This is because the ionic trap centers are located in the deep level.

Conclusions

In this paper, $La_{9.33-x}Sb_x(SiO_4)_6O_2$ ceramics were fabricated using the mixed-oxide method, and the low temperature sintering properties as well as the structural and electrical properties with different amounts of Sb were studied. Sintering was carried out at 150 °C lower than the sintering temperature for a basis composition, 1600 °C, with Sb ions being added. The specimens doped with more than $1.5 \text{ mol}\% \text{ Sb}_2\text{O}_3$ showed the formation of a pyrochlore phase, La₂Si₂O₇, due to the volatilization of the Sb atoms. With an increase in the Sb content, no variations in average grain size were observed. The conductivity of the La_{8.33}Sb(SiO₄)₆O₂ specimen showed the highest value, and the excessive amounts of more than 1.5 mol% Sb lead to a decrease in the oxide ion conductivity due to disorder in the channel sites and local structural distortions. Doping with Sb slightly increases the activation energy for ionic transport. Variations in the activation energy for ionic transport may be partly related to the incorporation of Sb^{3+} , statistically distributed in the La_{9.33-x}Sb_x(SiO₄)₆O₂ systems.

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