High Oxide Ion Conductivity in Mg-Doped $La_{10}Si_6O_{27}$ with Apatite-type Structure

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Structure and ionic conductivity of Mg-doped $La_{10}Si_6O_{27}$ was investigated on dense ceramic samples prepared from sol–gel derived powders using two step sintering process. The conductivity was increased by the doping (from 22 to 30–39 mS cm^{-1} at 800 °C) because of expansion of the apatite lattice.

A number of oxide ion conductors have been investigated aiming at application as solid-state electrolytes for fuel cells. $LaGaO_3$-based perovskite-type oxides exhibit extremely high ionic conductivity of about 100 mS cm^{-1} at 800 °C by doping Sr to the La site and Mg to the Ga site to introduce a large amount of oxide ion vacancy.[1] Recently, it has been found that rare earth silicates with an apatite-type structure, $Ln_{10}Si_6O_{27}$, show high oxide ion conductivity.[2] The highest conductivity of these apatite oxides is 10 mS cm^{-1} at 700 °C for $La_{10}Si_6O_{27}$,[3] which is comparable to Y_2O_3-stabilized ZrO_2 (YSZ). Along with the low activation energy, the apatite oxides are considered as potential candidates for solid-state electrolytes at lower temperatures ($<$800 °C). Furthermore, there remains a possibility to increase the conductivity by doping. It has been reported, for example, that Sr doping to the La site enhances the conductivity of $La_{10}Si_6O_{27}$.[4] In this study, we have examined the effects of Mg doping to the Si site on the conductivity and structure of $La_{10}Si_6O_{27}$.

Sintered ceramics of $La_{10}Si_6O_{27}$ with 0, 5, 10, and 15% of Si substituted by Mg ($La_{10}Si_{6-x}Mg_xO_{27-x}$, $x = 0$, 0.3, 0.6, and 0.9) were prepared. A sol–gel process was employed to ensure homogeneity of the powders used for the sintering as shown in Figure 1.[5] $La(NO_3)_3{\cdot}6H_2O$ and $Mg(NO_3)_2{\cdot}6H_2O$ were dissolved in ethanol, added with ethanol solution of tetraethyl orthosilicate (TEOS), sealed and heated at 60 °C for 2 h under vigorous stirring. The obtained clear solution was then unsealed and heated successively at 70 °C to evaporate the solvent until a viscous sol was formed. It turned to a transparent gel after a few days at rt.

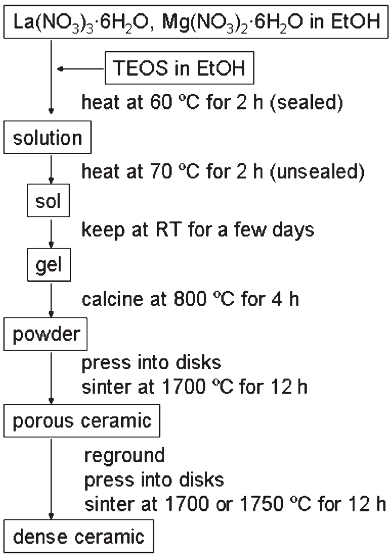

Figure 1. Flow chart of the sample preparation using a sol–gel process.

The gel was calcined at 800 °C for 4 h in air to remove the organic contents. The as-calcined powders were pressed into disks and sintered at 1700 °C for 12 h in air. With the first sintering, porous ceramics were obtained. They were thus reground, pressed into disks of about 13 mm in diameter and 1 mm in thickness, and then sintered again at 1700 or 1750 °C for 12 h. The two-step sintering process made it possible to fabricate dense ceramic samples with apparent densities of 80–90%. MgO-stabilized ZrO_2 was used as setters because of the low reactivity with the samples up to 1750 °C as pointed out by Nakayama et al.[3]

Phases in the samples were analyzed by the powder X-ray diffraction (XRD) method. The lattice parameters were calculated from the XRD profiles by the Rietveld method using RIETAN-2000.[6]

AC impedance measurements were made to determine the ionic conductivity. Platinum-paste electrodes were applied on both faces of the sample disks and fired at 1000 °C. A Solartron 1260 impedance analyzer was used to measure the impedance with frequencies sweeping from 10 MHz to 0.1 Hz at temperatures from rt to 800 °C. The bulk conductivity was calculated from the resistivity in a grain evaluated from Cole–Cole plots of the impedance data.[5]

Table 1 compares the conductivity measured at 800 °C of the samples sintered at 1700 and 1750 °C.[7] The samples of $x =$ 0 and 0.3 show higher conductivities when sintered at 1750 °C, while for $x = 0.6$ and 0.9 the conductivities of the samples sintered at 1700 °C are higher. Basically, the conductivities were increased with higher sintering temperatures owing to development of sintering. On the other hand, at higher temperatures, association of the dopants, formation of the defect complexes, or fluctuation of the compositions may occur and decrease the conductivities of the highly doped samples. The maximum conductivities of $x = 0.3$ and 0.6 are 39 and 30 mS cm^{-1}, respectively, being higher than that of pure $La_{10}Si_6O_{27}$ (22 mS cm^{-1}). This indicates that the conductivity is enhanced by the Mg doping, though it significantly decreases by overdoping with $x =$ 0.9.

Figure 2 shows a variation of the XRD profiles with compo-

Table 1. Conductivity (mS cm^{-1}) of $La_{10}Si_{6-x}Mg_xO_{27-x}$ measured at 800°C

Sintering	Composition, x			
Temp/°C	0	0.3	0.6	0.9
1700	8	23	30	13
1750	22	39	25	5

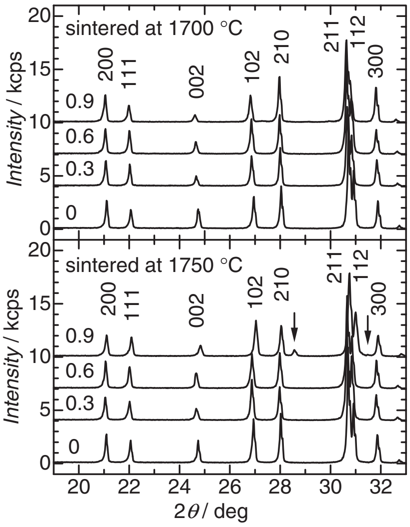

Figure 2. The variation of XRD profiles with composition and sintering temperature.

sition and sintering temperature. Indexing with a hexagonal $P6_3/m$ apatite-type structure is shown as 200, 111, and so on. All the peaks in the profiles but $x = 0.9$ sintered at 1750 °C are attributed to the hexagonal apatite-type structure. This clearly demonstrates a merit of the sol–gel process[5] over the conventional solid-state reaction which yielded a mixture of an apatite phase and a small amount of La_2SiO_5 for $La_{10}Si_6O_{27}$ composition.[3] Detailed observation reveals that the peaks from the apatite-type structure shift to a lower angle with the Mg content. Note that an unknown second phase formed in $x = 0.9$ sintered at 1750 °C as marked by arrows in Figure 2.

Figure 3 shows the lattice parameters which evidently increase with increasing the Mg content. No significant difference with the sintering temperature is observed up to $x = 0.6$. The low a axis parameter of $x = 0.9$ sintered at 1750 °C is caused by the formation of a second phase.

Two mechanisms can be considered for the doping effect on the conductivity enhancement: (i) introduction of oxide ion vacancies and (ii) control of lattice parameters. In the present system, the doping effect on the conductivity enhancement is mainly attributed to the lattice expansion. Divalent Mg ion has a larger ionic radius than tetravalent Si ion and a smaller electrostatic attractive force with oxide ions, thus expanding the apatite lattice and facilitating ion migration.

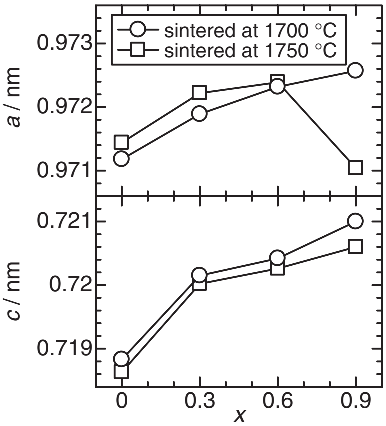

Figure 3. The variation of lattice parameters with composition and sintering temperature.

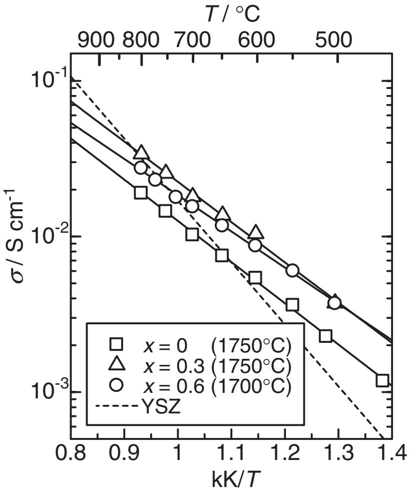

Figure 4. Temperature dependence of the conductivity of $La_{10}Si_{6-x}Mg_xO_{27-x}$ in comparison with YSZ.

It is believed that oxide ions in apatite-type lanthanum silicates migrate via O2a sites lined up along c axis in the $P6_3/m$ apatite-type structure.[1–3] Since all the O2a oxide ion sites are filled in the composition of $La_{9.33}Si_6O_{26}$, extra oxide ions existing at interstitial sites may account for the high ionic conductivity of $La_{10}Si_6O_{27}$.[5] In the $La_{10}Si_{6-x}Mg_xO_{27-x}$ system, however, the Mg doping is supposed to decrease excess oxygen content, showing that the above model is not simply applicable. The same trend has been observed in Sr-doped $La_{10}Si_6O_{27}$.[4] Further studies elucidating the relationship among composition, excess oxygen content and conductivity of the apatite-type lanthanum silicates are in progress.

Figure 4 shows an Arrhenius plot of the conductivities of $x = 0$, 0.3 (sintered at 1750 °C), and 0.6 (sintered at 1700 °C). The conductivity of YSZ (8%) is also shown for comparison. A linear relationship gives an activation energy of 0.60 eV for $La_{10}Si_6O_{27}$, which is much lower than that for YSZ. The activation energies further decrease with the Mg doping as 0.51 eV ($x = 0.3$) and 0.49 eV ($x = 0.6$). The conductivity enhancement is more pronounced at lower temperatures.

The Mg-doped $La_{10}Si_6O_{27}$ exhibit comparable conductivity to YSZ at 800 °C ($x = 0.3$) and 750 °C ($x = 0.6$). Below these temperatures, they have higher conductivity than YSZ. This proves that the Mg-doped $La_{10}Si_6O_{27}$ ($x = 0.3$–0.6) are promising candidates for solid-state electrolytes operating below 800 °C.

References and Notes

1 T. Ishihara, H. Matsuda, and Y. Takita, *J. Am. Chem. Soc.*, **116**, 3801 (1994).
2 S. Nakayama, H. Aono, and Y. Sadaoka, *Chem. Lett.*, **1995**, 431.
3 S. Nakayama and M. Sakamoto, *J. Eur. Ceram. Soc.*, **18**, 1413 (1998).
4 H. Arikawa, H. Nishiguchi, T. Ishihara, and Y. Takita, *Solid State Ionics*, **136**, 31 (2000).
5 S. Tao and J. T. S. Irvine, *Mater. Res. Bull.*, **36**, 1245 (2001).
6 F. Izumi and T. Ikeda, *Mater. Sci. Forum*, **321–324**, 198 (2000).
7 Contribution of Mg^{2+} conduction to the total conductivity could not be ruled out with the AC impedance measurements. It should be evaluated by oxygen gas concentration cell measurements which are in progress.