Study of oxygen diffusion in dense lanthanum oxide ceramics

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A direct oxygen diffusion study using isotopes in dense La₂O₃ ceramics fabricated with the addition of Sr and Ge oxides was performed by secondary-ion mass spectrometry. The experiments using the ¹⁸O isotope were carried out in the temperature range 400–700 °C for 1 h. The surface concentration of ¹⁸O was found to depend on the annealing temperature. The temperature dependence of oxygen diffusion was determined to be expressed as $D^\prime \text{ (cm}^2\text{/s)} = (8.9 \times 10^{-5})\exp(-128.8\text{[kJ/mol]/RT})$, where $D^\prime$ is the diffusion coefficient, $R$ is the gas constant, and $T$ is temperature. On the basis of a comparison with the results of oxygen diffusion studies of CeO₂ and LaGaO₃, we concluded that oxygen diffusion in La₂O₃ occurs via a vacancy mechanism.

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Lanthanum oxide (La₂O₃) is a rare-earth oxide with a hexagonal crystal structure, a wide bandgap, and a large dielectric constant. Because of these characteristics, it has been investigated as a potential gate-insulating material.¹⁻³) Oxygen defects in the lattice of La₂O₃ thin films pose problems for their practical application.¹³) At present, research on the direct diffusion of oxygen in La₂O₃ is technically impossible because La₂O₃ is unstable in air. La₂O₃ reacts with atmospheric water vapor and easily transforms to lanthanum hydroxide [La(OH)₃]. The decomposition of La(OH)₃ has been studied by Ino et al.,⁴) who found that it is decomposed into La₂O₃ by heat treatment at 1000 °C.

La₂O₃ is also used as a main component of oxide-ion and proton conductors. For example, LaGaO₃,⁵⁻⁶) La₅Si₆O₂₇,⁷⁻⁸) LaNbO₄,⁹) and La₂Mo₂O₉¹⁰) contain La₂O₃ as a main component. Among them, LaGaO₃ is an oxide-ion conductor that does not show mixed conduction but does exhibit enhanced ionic conduction due to additives.⁵⁻⁶) The conduction of oxide ions in LaGaO₃ is explained by the oxygen vacancy mechanism, and the activation energy for diffusion represents the oxide-ion migration energy.

Cerium oxide (CeO₂) in the lanthanoid series exhibits the fluorite-type structure and is also an oxide-ion conductor; the relationship between its deviation from stoichiometry and its oxygen diffusion characteristics has been studied.¹¹⁻¹⁴) An extrinsic region for oxygen diffusion in which oxygen diffusion is dominated by the compositional deviation from stoichiometry and by impurities has been found.¹²)

Recently, the shape and mirror surface of densified La₂O₃ was found to be maintained for 3 days when the ambient temperature was less than 15 °C. Furthermore, oxygen diffusion experiments using densified La₂O₃ ceramics were carried out. The present study is the first report of direct oxygen diffusion measurements in La₂O₃ ceramics.

Dense La₂O₃ ceramics were prepared using SrO (0.13 mol %) and GeO₂ (0.13 mol %) via a conventional sintering technique. Reagent-grade powders of La₂O₃, SrCO₃ (High-Purity Chemicals Ltd.), and GeO₂ (Sigma-Aldrich) were used as the starting materials. SrO and GeO₂ were mixed as a sintering aid to improve the disk density of La₂O₃. First, the La₂O₃ powder was dried at 1000 °C for 3 h in air to decompose La(OH)₃ to La₂O₃.⁴) Second, the SrCO₃ and La₂O₃ powders were mixed by ball milling with ethanol as a solvent for 20 h. After drying, the powder mixture was heated at 1260 °C for 5 h in air. Third, GeO₂ was added to the SrO-doped La₂O₃ powder and mixed using the aforementioned ball-milling method. After the drying process, the powders were pressed into disks with a diameter of 10 mm and thickness of 3 mm. A two-step sintering method was carried out to improve the density of the disks. The first step was sintering at 1400 °C for 2 h, and the second step was annealing at 1360 °C for 10 h under flowing O₂. To determine the disk density, the both side of the disk were automatically polished into parallel disks using a polishing machine. As the polishing agent, 9 µm diamond slurry was used. Then, the diameter and the thickness were measured to obtain the volume, and the density was determined from the weight of disk. The disk density reached 6.4 g/cm³. The sintered disks were polished and finished with several grades of diamond paste.

After mirror finishing of the sample surface, the sample
was cleaned with ethanol. To remove the damage introduced near the surface by the mechanical polishing process, the samples were annealed in a furnace at 1100 °C for 1 h under flowing O2. The sample surface was observed using a laser-scanning microscope (Keyence, VK-9710; wavelength: 408 nm). The samples for diffusion experiments were placed in the analytical chamber of a secondary-ion mass spectrometer to maintain their mirror surface.

For oxygen-tracer diffusion experiments, the samples were loaded into an exchange apparatus for performing 18O diffusion. The samples were annealed at 400–700 °C for 1 h. The concentration profiles were measured by secondary-ion mass spectrometry (SIMS). Oxygen intensities of 16O and 18O were measured as a function of time. After the analysis, the SIMS crater depth was measured using a surface profiler (KLA, D-120). The obtained depth profiles were converted to 18O concentration profiles using the following equation: \( C_{18O} = I_{18O} / [I_{16O} + I_{18O}] \), where \( C_{18O} \), \( I_{16O} \), and \( I_{18O} \) are the 18O concentration and the 16O and 18O intensities at depth \( x \). To determine the diffusion coefficient (\( D_x \)), the concentration profile was fitted using a solution to the diffusion equation.15) To evaluate \( D_x \), the concentration profile was fitted using Eq. (1), which is the solution when diffusion is controlled by a rate-limiting reaction at the surface:

\[
\frac{C_x - C_0}{C_g - C_0} = erf_c \left( \frac{x}{2 \sqrt{D_x t}} \right) - \exp \left( \frac{k \cdot x}{D_x} + \frac{k^2 \cdot t}{D_x} \right) \times erf_c \left( \frac{x}{2 \sqrt{D_x t}} + \frac{k}{D_x} \right)
\]

where \( C_g \) and \( C_0 \) are the gas concentration and background concentration, respectively, \( x \) is the depth, \( t \) is the duration of diffusion treatment, and \( erf_c = 1 - erf \) (erf is the Gaussian error function). After the analysis, the sample surface was also observed using a laser-scanning microscope.

**Figure 1** shows the result obtained by the grazing incidence X-ray diffraction (GIXRD) analysis. This method is an advantage to get the information near the surface. The peaks results from the La2O3 and La(OH)3. The sample surface was covered with La(OH)3 formed by the reaction between La2O3 and moisture in air.

**Figure 2** shows a photograph of the sample surface after the SIMS measurement. The La2O3 is dense, and grains with several different sizes are observed on the surface. Some spherically shaped pores are observed in the grains. Also, the SIMS crater with a depth of 5.5 µm is evident in the figure. Notably, the smooth surface was maintained during the experiments.

**Figure 3** shows the concentration profiles of \( C^{18O} \) for samples annealed at 700, 600, 500, and 400 °C for 1 h. The \( C^{18O} \) in the profiles monotonically decreases with increasing depth, indicating that 18O diffused by a simple mechanism. Moreover, the \( C^{18O} \) is confirmed to depend on the annealing temperature. The \( C^{18O} \) near the surface of the sample annealed at 700 °C is 0.67. The \( C^{18O} \) near the surface decreases with decreasing annealing temperature. The \( C^{18O} \) differs substantially between the samples annealed at 500 and those annealed at 400 °C. In the sample annealed at 400 °C, the \( C^{18O} \) near the surface decreased sharply from 0.3 to 0.007 and 18O diffused in the depth direction. The result suggests the presence of an unintentional layer at the surface of this sample. From GIXRD...
spectrum, La(OH)₃ is present on the sample surface and this layer is stable at 400 °C.⁵) ¹⁸O diffuses to La₂O₃ through La(OH)₃. The C[¹⁸O] at the surface of La₂O₃ is 0.007, which is considerably smaller than the value of 0.3 in the La(OH)₃ layer. Especially, the exchange of ¹⁸O from La(OH)₃ to La₂O₃ is slow and this is the rate limiting reaction. The surface concentration of ¹⁸O in the profiles at 500 °C reached to be 0.3. The improvement of ¹⁸O surface concentration at 500–700 °C is due to the products obtained from the decomposition reaction of La(OH)₃. According to the previous studies, the decompose reaction of La(OH)₃ to produce H₂O during the heat treatment at 450 °C. The reactions are described by the equations below.⁴)

\[
2\text{La(OH)}₃ \rightarrow 2\text{LaO(OH)} + 2\text{H₂O}
\]  

(2)

The decomposition products such as LaO(OH) at the surface and H₂O vapor are effective to improve the ¹⁸O surface concentration. Previously, the influence of surface adsorbed water on the surface reaction has been studied with YSZ, CeO₂ and LaGaO₃.⁶,⁷) Their studies show that the oxygen diffusion coefficient is not affected by water, but the surface reaction is greatly improved. The reaction in which ¹⁸O is incorporated into the lattice is as follows.

\[
\text{H}_2\text{O} \rightarrow \text{H}_2\text{Oad} \quad \text{(3)}
\]

\[
\text{H}_2\text{Oad} + \text{¹⁸O}(\text{solid}) \rightarrow \text{¹⁸OHad} + \text{¹⁸OHad} + \text{V}_0
\]  

(4)

\[
\text{¹⁸OHad} + \text{¹⁸OHad} + \text{V}_0 \rightarrow \text{H}_2\text{Oad} + \text{¹⁸O}(\text{solid})
\]  

(5)

\[
\text{H}_2\text{Oad} \rightarrow \text{H}_2\text{Oad}(\text{g})
\]  

(6)

When water molecules are adsorbed on the surface, OH groups are adsorbed and oxygen vacancies are generated on the surface, and ¹⁸O is incorporated into the oxygen vacancy from the OH groups. It is presumed that a reaction that forms oxygen vacancies on the surface is a rate-limiting reaction in a series of reactions. In this study, the surface concentration of ¹⁸O increases with increasing diffusion temperature. This suggests that the oxygen vacancy formation reaction has temperature dependence. To determine the D* values, we analyzed the ¹⁸O diffusion profiles using Eq. (1). The D* values range from 1.1 × 10⁻⁹ cm²/s for the sample annealed at 700 °C and from 9.4 × 10⁻¹³ cm²/s for the sample annealed at 400 °C. The value of k in Eq. (1) is 6.0 × 10⁻⁶ for the sample annealed at 700 °C and 6.0 × 10⁻⁸ cm/s for the sample annealed at 400 °C.

The D* values are summarized in Fig. 4 as a function of the reciprocal temperature. The temperature dependence of D* is represented by the Arrhenius equation: \(D* = D_0 \exp(-\Delta H/R T)\), where \(D_0\), \(\Delta H\), \(R\), and \(T\) are the pre-exponential factor, activation energy, gas constant, and temperature, respectively. The temperature dependence of D* in La₂O₃ ceramics in the temperature range 400–700 °C is expressed as

\[
D*(\text{cm}²/\text{s}) = 8.9 \times 10⁻³ \exp\left[\frac{-128.8 \pm 2.0}{RT} \text{kJ/mol}\right]
\]  

(7)

Figure 4 shows also the results reported by Kamiya et al. for CeO₂. They reported a study showing that oxygen diffusion in CeO₂ at 1100–1300 °C exhibits intrinsic behavior, whereas it exhibits extrinsic behavior at temperatures less than 900 °C. In order to explain these behaviors, the activation energy of diffusion is described in detail as \(\Delta H = \Delta H_f + \Delta H_m\), where \(\Delta H_f\) and \(\Delta H_m\) are defect formation and defect migration energies. The \(\Delta H_m\) reflects the diffusion due to a constant concentration of defects determined by impurities, etc., and is observed when the diffusion experiments are carried out at low temperature, which is an extrinsic behavior. On the other hand, when the diffusion temperature is increased, and then the \(\Delta H_f\) is added in the action energy of diffusion. This region is the intrinsic behavior of diffusion. In case of CeO₂, these behaviors were observed. The oxygen diffusion coefficients in the extrinsic region are on the order of 10⁻¹⁰ cm²/s, and the extrapolation represented by the dashed line in Fig. 4 is almost the same as the diffusion coefficient corresponding to the temperature range 500–600 °C in the present study. The activation energy reported by Kamiya et al. for oxygen diffusion in the extrinsic region (i.e., the oxide-ion migration energy) is 84 kJ/mol. The oxygen diffusion experiments in the present study were performed in the temperature range 400–700 °C, and the activation energy was 128.8 kJ/mol, which is larger than the value from the extrinsic region reported by Kamiya et al.

We also compared our results with those related to the oxygen diffusion in LaGaO₃. In the related studies,⁵,⁶) additives that enhance oxygen diffusion were added to LaGaO₃ and the activation energy for oxygen diffusion exhibited a range of 0.4–1.4 eV (39.6–138.7 kJ/mol). In these LaGaO₃ components, oxygen diffuses via a vacancy mechanism in the extrinsic region and the activation
energy is considered to reflect the migration energy. The activation energy for oxygen diffusion in La$_2$O$_3$ is 128.8 kJ/mol (1.3 eV), which is consistent with the activation energy for oxygen diffusion in LaGaO$_3$. We thus speculated that the oxygen diffusion in La$_2$O$_3$ observed in the present study is a vacancy mechanism and that the activation energy represents the migration energy.

Oxygen defects can be introduced into La$_2$O$_3$ through two pathways. The first pathway is the effect of adding SrO and GeO$_2$. In this study, SrO and GeO$_2$ were added to increase the density of La$_2$O$_3$ ceramics. The reaction equation for the solid solution of SrO and GeO$_2$ is:

$$2\text{SrO} \xrightarrow{\text{La}_2\text{O}_3} 2\text{Sr}_{\text{La}} + 2\text{O}_3 + V_0^+ + h$$

$$2\text{GeO}_2 + V_0^+ \xrightarrow{\text{La}_2\text{O}_3} 2\text{Ge}_{\text{La}} + 4\text{O}_3 + e^-$$

where SrO and GeO$_2$ form a solid solution in La$_2$O$_3$ via oxygen vacancies. A similar reaction has been confirmed in studies of SnO$_2$ in which Zn and Sb are simultaneously dissolved.\(^{18}\) On the basis of reaction Eqs. (8) and (9), we speculate that small amounts of SrO and GeO$_2$ have a small effect on the oxygen vacancies in La$_2$O$_3$. The second pathway to the introduction of oxygen vacancies is the formation of nonstoichiometric La$_2$O$_3$ during sintering. In the present study, La$_2$O$_3$ was synthesized via two-step sintering at 1400°C for 2h and 1360°C for 10h. Under these conditions, the oxygen vacancies are considered to remain in the sample. La$_2$O$_3$ and CeO$_2$ are members of the same lanthanoid series, and the oxygen content of CeO$_2$ is known to deviate from the ideal stoichiometry.\(^{11}\) Oxygen diffusion in La$_2$O$_3$ and CeO$_2$ occurs through a vacancy mechanism. The aforementioned considerations suggest that La$_2$O$_3$ contains oxygen deficiencies introduced during the sintering process.

Finally, the shapes of the samples were observed after the SIMS analysis. Figure 5(a) is a photograph of the sample removed of the sample chamber of the secondary-ion mass spectrometry chamber; (b) is sample the next day. The sample was allowed to stand at room temperature (22°C) in air.

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