

Oxygen Surface Exchange and Diffusion in the New Perovskite Oxide Ion Conductor LaGaO_3

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Introduction. Oxygen ion conductors are important materials for applications such as fuel cells, sensors, and air separation membranes. It is well-known that certain oxides which possess the fluorite structure, e.g. CeO_2 and ZrO_2 , exhibit high oxygen ion conductivity.¹ Recently, we have found that the perovskite LaGaO_3 , acceptor-doped with Sr for La and Mg for Ga, also exhibits high oxygen ion conductivity, comparable to that of CeO_2 doped with Gd_2O_3 .² The great advantage of acceptor-doped LaGaO_3 over similar CeO_2 -based materials is that it is stable in both oxidizing and reducing atmospheres.

Studies of the oxygen exchange behavior of these fast oxygen-conducting ceramics yields two important parameters: the oxygen self-diffusion coefficient, D^* , and the surface exchange coefficient, k . This latter parameter is partly a measure of the activity for the dissociation of oxygen molecules. Exchange studies have been undertaken on fast ion-conducting materials in the past.^{3–5} The mobility of the oxygen ion in cubic zirconia, a typical oxygen ion conductor, has been investigated, and it has been clearly shown, from a comparison of diffusion and electrical conductivity data, that the electrical conductivity is ionic.⁵ One of the aims of these experiments was to verify that the oxygen ion is the majority carrier in LaGaO_3 -based materials, as they are thought to exhibit p-type conductivity in the high oxygen partial pressure range.² Specifically, we have investigated oxygen surface exchange and diffusion in $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-x}$ by ^{18}O isotopic exchange and SIMS at high partial pressures of oxygen (0.1 MPa).

Experimental Details. Ceramic samples of the composition $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-x}$, denoted as LSGM in this paper, were prepared by the solid state reaction of powder mixtures consisting of La_2O_3 , SrCO_3 , MgO , and Ga_2O_3 in stoichiometric proportions. The starting powders were mixed in an Al_2O_3 pestle and mortar and then precalcined at 1273 K for 6 h. The powder was pulverized again with pestle and mortar and pressed into disks of 20 mm diameter and 1.5 mm thickness. After isostatic pressing at 275 MPa, the sample pellets were sintered at 1773 K for 6 h in air. The relative density of the samples used for the isotopic exchange measurement was about 96%. One face of the LSGM pellets was polished with successive grades of diamond abrasive to 0.25 μm , followed by cleaning of the polished surface in a ultrasonic bath. Before exchange with $^{18}\text{O}_2$, the sample was annealed for 12 h in natural oxygen (0.1 MPa) at the temperature intended for the exchange anneal. After cooling to room temperature, the sample chamber was evacuated to high vacuum (5×10^{-6} Pa) and the labeled oxygen

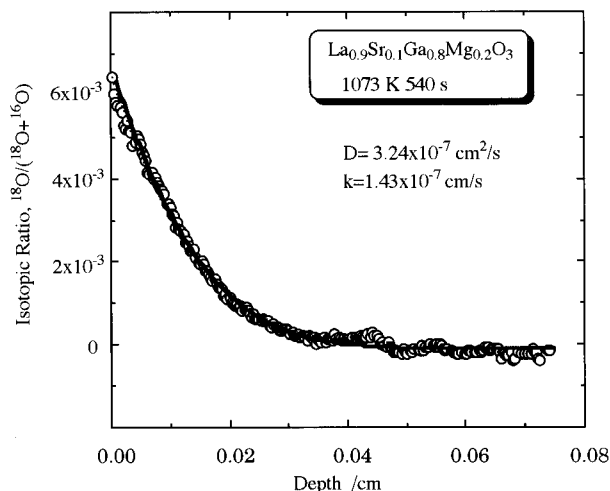


Figure 1. Depth distribution profiles of normalized isotopic fraction for the $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ sample showing the experimental and fitted data. Exchange of ^{18}O was performed at 1073 K for 540 s.

(ca. 80% enriched ^{18}O) was introduced to the cold sample at 0.1 MPa. The sample was quickly reheated and annealed for a set period of time.

Following the anneal, the samples were transversely sectioned and the cut faces were polished using the same regime as mentioned above. The diffusion profile of ^{18}O was measured across the polished cross-section of the exchanged disk by secondary ion mass spectrometer (SIMS) line-scanning in an ATOMIKA-6500 instrument. A 15 kV Xe^{+1} primary beam was used with a current of 3 nA, giving a beam diameter of about 30 μm . The diffusion coefficient and the surface exchange coefficient were determined by fitting the isotopic fraction, corrected for the natural isotopic background and normalized to the gas concentration, to the solution to the diffusion equation for a semi-infinite solid.⁶ The electrical conductivity of the same LSGM ceramics was measured in flowing gas at an oxygen partial pressure of 1 Pa by the two probe ac impedance method with Pt electrode.

Results and Discussion. Figure 1 shows the experimentally determined ^{18}O diffusion profiles in LSGM, following isotopic exchange at 1073 K for 540 s. The solid line in Figure 1 shows the isotopic fraction calculated from the diffusion equation using the values of D and k fitted to the experimental data. Clearly, a good fit of the experimental data has been obtained. The isotopic fraction of ^{18}O at the surface of the sample was as low as 6×10^{-3} , after correcting for the natural isotopic background. In contrast, the diffusion length of ^{18}O was very large and extended to 500 μm . This type of profile suggests that LSGM exhibits a low activity for the surface exchange of oxygen; however, the mobility of the oxide ion in the bulk LSGM is extremely high. These features are typical of other oxide ion conductors, such as stabilized ZrO_2 or doped CeO_2 .^{7,8}

Figure 2 shows an Arrhenius plot of the diffusion and the surface exchange coefficients obtained at 0.1 MPa. The diffusion constants were also calculated from the electrical conductivity data, obtained at $P_{\text{O}_2} = 1$ Pa, by using the Nernst–Einstein relationship. These diffusion constants are also shown for comparison in Figure 2. Both the diffusion coefficient and the surface exchange coefficient increase with increasing temperature. The measured self-diffusion coefficients of oxygen

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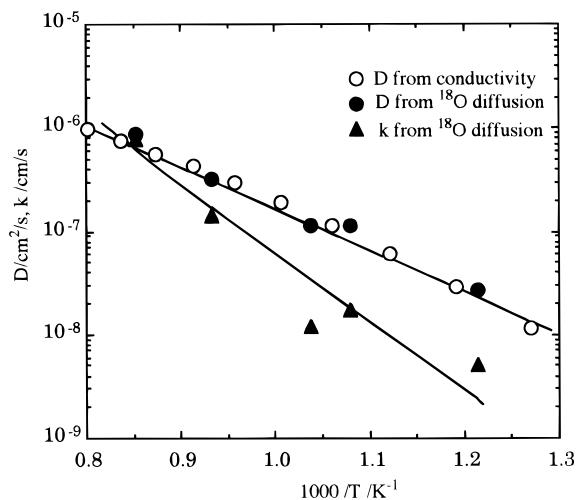


Figure 2. Arrhenius plots of the diffusion and the surface exchange coefficient for the $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ sample.

at 0.1 MPa are in a good agreement with those estimated from electrical conductivity at 1 Pa. This result indicates that the electrical conductivity of LSGM is ionic for the temperature range measured. As mentioned earlier, it had been reported that LSGM exhibits a small amount of hole conductivity in the high oxygen partial pressure range;² however, the good agreement between the measured self-diffusion coefficient with those calculated from electrical conductivity suggests that this is not the case.

The calculated activation enthalpy for the self-diffusion coefficient is 0.79 ± 0.04 eV, which is considerably smaller than that reported for cubic zirconia (1.22 eV)⁵ or thoria (2.77 eV)³ but correlates well with the electrical conductivity data. The calculated activation energy for surface oxygen exchange is almost twice that of the self-diffusion coefficient at 1.57 ± 0.19 eV. Also of interest are the relative values of the surface exchange coefficient and diffusion coefficient, as characterized by the parameter $h = k/D$. For LSGM, at low temperatures, h is found to be smaller than 1. This is typified by very low surface concentrations of tracer.⁹ Similar low-temperature behavior has been recently observed for the fluorite structures $\text{ZrO}_2\text{-Y}_2\text{O}_3$ and $\text{CeO}_2\text{-Gd}_2\text{O}_3$.^{7,8} In contrast, other perovskite oxides, such as acceptor doped LaMnO_3 , LaCoO_3 , SrCeO_3 , CaZrO_3 , and LaYO_3 , the numerical value of the surface exchange coefficient is generally larger than that of diffusion coefficient by orders of magnitude¹⁰⁻¹³ giving rise to $h \gg 1$. The activation enthalpy for oxygen surface exchange also differs between the two groups of materials. For the perovskites listed

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above the activation enthalpy for exchange is less than that for self-diffusion. The reverse is true for the two fluorite-structured oxides. For LSGM, the activation enthalpy for oxygen surface exchange was found to be greater than that observed for self-diffusion, again similar to the two fluorite oxides and in contrast to the perovskite oxides. Before the completion of the present experiments, this difference in exchange behavior was originally thought to lie in differences in structure of the perovskite oxides and the fluorite oxides.⁶ This is obviously not the case, as the present results indicate that surface exchange properties of LSGM are more akin to those of $\text{ZrO}_2\text{-Y}_2\text{O}_3$ and $\text{CeO}_2\text{-Gd}_2\text{O}_3$ than to those of other perovskites. The striking similarity between these three materials is that they are all electrolytes with a very low transport number for electronic species. Given that the mobility of the electrons is much higher than that of the oxide ion, then the electron concentration is very low. The surface exchange of oxygen involves adsorption, a charge transfer process and dissociation, and finally the incorporation of the oxygen ion into a surface vacancy. For ionic conductors, the low electronic carrier concentration will inhibit the charge transfer process, and thus, the formation of electronic species is then rate limiting. This would imply that the surface exchange coefficient for ionic conductors will show a temperature dependence that is related to the electronic band gap and that a P_{O_2} dependence should also be evident. Further work is underway to test this deduction.

In conclusion, these results show that bulk oxygen diffusion in LSGM is very rapid. By a comparison of the oxygen self-diffusivity obtained from tracer and ionic conductivity, the electrical conductivity observed is ionic in the temperature range we have measured. The surface exchange coefficients are anomalous when compared to other perovskite oxides. The activation enthalpy for surface exchange is higher than that for self diffusion coefficient, a finding observed for two other solid oxide electrolytes with the fluorite structure. This behavior is thought to originate in the low electron concentrations found in these electrolyte materials, particularly at the lowest temperatures.

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