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Diffusion of Oxide Ions in $LaFeO_3$ Single Crystal

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The tracer diffusion coefficient, D_O^*, of oxide ions in $LaFeO_3$ single crystal was determined over the temperature range of 900–1100°C by the gas–solid isotopic exchange technique using ^{18}O as a tracer. For the determination of D_O^*, the depth profile of ^{18}O was measured by means of a secondary ion mass spectrometer (SIMS). The surface exchange reaction was found to be slow and the surface exchange rate constant, k, was determined together with D_O^*. It was found that D_O^* at 950°C is proportional to $P_{O_2}^{-0.58}$, where P_{O_2} is an oxygen pressure. The vacancy mechanism was determined for the diffusion of oxide ions from the P_{O_2} dependence. The vacancy diffusion coefficient, D_V, for $LaFeO_3$ was nearly the same as that for $LaCoO_3$ at the same temperature. The activation energy for migration of oxide ion vacancies was 74 kJ · mole^{-1} for both oxides. © 1984 Academic Press, Inc.

Introduction

In a previous paper (*1*), the authors have determined the diffusion coefficient, D_O^*, of oxide ions in $LaCoO_3$. From the oxygen pressure dependence of D_O^*, it was concluded that the diffusion of oxide ions in $LaCoO_3$, proceeds by a vacancy mechanism. The activation energy for migration of oxide ion vacancies, was found to be 74 kJ · mole^{-1}.

Both $LaFeO_3$ and $LaCoO_3$ have the perovskite-type structure. It has been proved that the concentration of oxide ion vacancies in $LaFeO_3$ is smaller than that in $LaCoO_3$ by about 3 orders of magnitude at the same temperature and oxygen partial pressure (*2, 3*). The comparison of their diffusion coefficients is interesting and important in order to elucidate the relation between the diffusivity and the crystal structure.

The purpose of the present work is to determine D_O^* in $LaFeO_3$ by the depth profile measurement by means of SIMS and to make clear the diffusion mechanism.

Experimental

The coprecipitation method was employed for the preparation of $LaFeO_3$. A single crystal was grown by the floating zone method utilizing xenon arc image furnace (*4*).

The crystal was annealed at 1300°C in air for 2 days and cut into slabs of 0.7–0.8 mm thick so that both end surfaces had (1 1 1) planes. The surfaces were successively pol-

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ished with alumina powders down to 0.05 μm in size.

Isotopic exchange was performed using the apparatus already described elsewhere (*1*). In order to obtain the equilibrated defect concentration and remove the mechanical damage on the sample surface, a preannealing was performed in the same atmosphere as that of the subsequent diffusion annealing. The diffusion annealing was then performed in a 73.5% ^{18}O-enriched gas for a definite length of time.

The depth profiles of ^{18}O were measured by SIMS, ATOMIKA A-DIDA 3000. The sample surface was removed by Ar^+ ion sputtering and the oxygen isotopic concentration was determined from the observed intensity ratio of $^{18}O^-$ to $^{16}O^-$. The operational procedure was similar to that by Freer and Dennis (*5*). The depth of the crater was measured by means of a profilometer, Sloan DEKTAK-II.

Results and Discussion

The depth profile of ^{18}O showed that the surface concentration of ^{18}O is always smaller than that in the gas phase. This indicates that the surface exchange reaction would be slow. The data were analyzed so that D_O^* and the surface exchange rate constant, k, can be determined simultaneously (*1*). The results are shown in Table I.

The Arrhenius plot for D_O^* at $P_{O_2} = 53$ Torr is shown in Fig. 1. The Arrhenius equation is

$$D_O^*/\text{cm}^2 \cdot \text{sec}^{-1} = 2.97 \times 10^{-3} \exp\left(-\frac{(214 \pm 34)\ \text{kJ} \cdot \text{mole}^{-1}}{RT}\right) \quad (1)$$

where the figure after ± denotes 2σ. For comparison, D_O^* in $LaCoO_3$ (*1*) is also shown in the same figure. The magnitude of D_O^* in $LaFeO_3$ is smaller than that in $LaCoO_3$ by more than 3 orders of magnitude. The activation energy and the preexponential term are smaller than those for $LaCoO_3$. They are 310 kJ · mole^{-1} and 3.63×10^4 for $LaCoO_3$, respectively.

The oxygen pressure dependence of D_O^* at 950°C is shown in Fig. 2. The figure indicates that D_O^* is proportional to $P_{O_2}^{-(0.58\pm0.15)}$. Mizusaki and his co-investigators have measured the electronic conductivity and the Seebeck coefficient of $LaFeO_3$ as functions of oxygen partial pressure in the temperature range of 1000–1400°C (*6*). According to their defect model, the concentration of oxide ion vacancies, $[V_O^{\cdot\cdot}]$, is proportional to $P_{O_2}^{-0.5}$ in the higher P_{O_2} range of this

TABLE II

TRACER DIFFUSION COEFFICIENTS, D_O^*, SURFACE EXCHANGE RATE CONSTANTS, k, AND VACANCY DIFFUSION COEFFICIENTS, D_V, FOR $LaFeO_3$

t (°C)	P_{O_2} (Torr)	Annealing time (min)	D_O^* (cm^2 sec^{-1})	k (cm sec^{-1})	$[V_O^{\cdot\cdot}]$[a]	D_V (cm^2 sec^{-1})
1100	53	10	2.06×10^{-11}	6.80×10^{-7}	5.75×10^{-6}	1.07×10^{-5}
1050	53	20	1.06×10^{-11}	3.15×10^{-7}	3.51×10^{-6}	9.06×10^{-6}
1000	53	45	5.28×10^{-12}	1.67×10^{-7}	2.13×10^{-6}	7.44×10^{-6}
950	80	90	1.44×10^{-12}	7.39×10^{-8}	1.04×10^{-6}	4.15×10^{-6}
	53	90	1.54×10^{-12}	1.11×10^{-7}	1.27×10^{-6}	3.64×10^{-6}
	34	90	2.20×10^{-12}	8.75×10^{-8}	1.59×10^{-6}	4.15×10^{-6}
	16	80	2.67×10^{-12}	8.78×10^{-8}	2.29×10^{-6}	3.50×10^{-6}
	7	80	5.91×10^{-12}	9.61×10^{-8}	3.44×10^{-6}	5.15×10^{-6}
900	53	150	9.84×10^{-13}	3.89×10^{-8}	7.35×10^{-7}	4.02×10^{-6}

[a] Determined from Ref. (*2*).

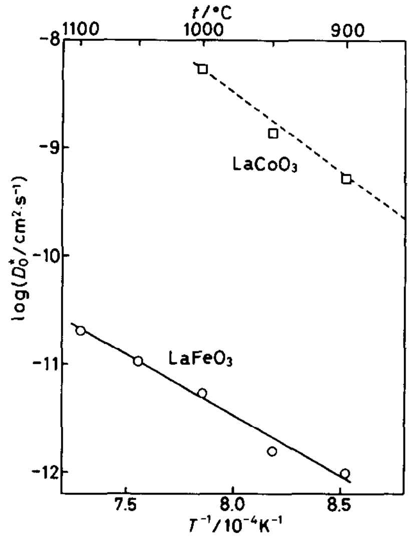

FIG. 1. Arrhenius plot for the tracer diffusion coefficient of oxide ions. ○, $LaFeO_3$; □, $LaCoO_3$, Ref. (*1*).

work. Since it is well known that when diffusion of ions proceeds via randomly distributed point defects, the self-diffusion coefficient should be proportional to the concentration of the point defects, the present result of $D^*_{\text{O}} \propto P_{\text{O}_2}^{-0.58}$ agrees well with the dependence of $[\text{V}_{\text{O}}^{\bullet\bullet}] \propto P_{\text{O}_2}^{-0.5}$, and suggests a vacancy diffusion mechanism.

Assuming that the correlation factor is unity for the diffusion of oxide ions in perovskite-type oxides, D^*_{O} is represented by

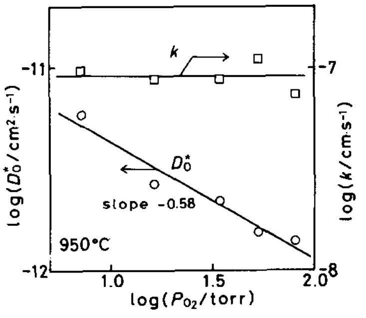

FIG. 2. Oxygen pressure dependences of the tracer diffusion coefficient, D^*_{O}, of the oxide ions and the surface exchange rate constant, *k*.

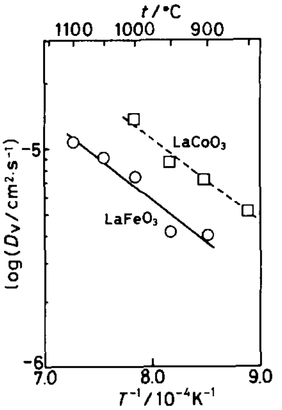

FIG. 3. Arrhenius plot of the diffusion coefficient, D_{V}, of oxide ion vacancies. ○, $LaFeO_3$; □, $LaCoO_3$, Ref. (*1*).

$$D^*_{\text{O}} = N_{\text{V}} D_{\text{V}} = \frac{[\text{V}_{\text{O}}^{\bullet\bullet}]}{3} D_{\text{V}}, \tag{2}$$

where N_{V} and D_{V} are the mole fraction and the diffusion coefficient of oxide ion vacancies, respectively, and [ ] represents the concentration in terms of the number of moles per 1 mole of $LaFeO_3$. Mizusaki and his co-investigators have carried out a thermogravimetric study on the nonstoichiometry of $LaFeO_3$ using the same crystal as is used in the present work and have determined the defect concentration (*2*). The values of $[\text{V}_{\text{O}}^{\bullet\bullet}]$ shown in Table I were determined from their data. The values of D_{V} were calculated by using Eq. (2) and are given in Table I and Fig. 3. The temperature dependence of D_{V} in $LaFeO_3$ is expressed by the equation

$$D_{\text{V}}/\text{cm}^2\cdot\text{sec}^{-1} = 6.96 \times 10^{-3} \exp\left(-\frac{(74 \pm 24)\ \text{kJ}\cdot\text{mole}^{-1}}{RT}\right) \tag{3}$$

For comparison, D_{V} in $LaCoO_3$ is also shown in Fig. 3. The D_{V} values for $LaFeO_3$ are very close to those for $LaCoO_3$ at the same temperature. Moreover, the activation energies, ΔH_{m}, for migration of oxide ion vacancies have the same value, 74 kJ · mole⁻¹.

The activation energy for D_O^* is the sum of formation energy, ΔH_f, of oxide ion vacancies and ΔH_m. Accordingly, the difference in activation energy of D_O^* in Fig. 1 are attributed to the difference in ΔH_f. The values of ΔH_f are estimated to be 137 kJ · mole^{-1} for $LaFeO_3$ and 209 kJ · mole^{-1} for $LaCoO_3$ (*2*, *3*).

It was also found from the measurement by SIMS that the surface exchange rate constant, k, at 950°C is independent of P_{O_2}, as is shown in Fig. 2. The physical meaning of k and its P_{O_2} dependence are not fully understood at present. The temperature dependence is expressed by the equation

$$k/\mathrm{cm}\cdot\mathrm{sec}^{-1} = 5.04 \exp\left(-\frac{(181 \pm 26)\ \mathrm{kJ}\cdot\mathrm{mole}^{-1}}{RT}\right) \quad (4)$$

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