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Diffusion Coefficients of Oxygen in $Nd_2CuO_{4-\delta}$

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The chemical diffusion in $Nd_2CuO_{4-\delta}$ was measured by means of a thermomicrobalance in a temperature range of 650 to 900°C under oxygen pressure of 1 to 0.01 atm, using dense polycrystalline specimens. It was found that the relaxation after a step change in oxygen pressure from 0.3 to 0.01 atm was exponential, and the reduction rate coincided with that of oxidation. From this result, the relaxation was concluded to obey diffusion-controlled kinetics, and the chemical diffusion coefficient was determined. The self-diffusion coefficient of oxygen and the oxygen vacancy diffusion coefficient were calculated from the chemical diffusion coefficient. The self-diffusion coefficient of oxygen in $Nd_2CuO_{4-\delta}$ was slightly larger than that in perovskites, and lower than that of $YBa_2Cu_3O_{6.4}$. The vacancy diffusion coefficient of $Nd_2CuO_{4-\delta}$ is almost the same as that of perovskite-type oxides. © 1991 Academic Press, Inc.

1. Introduction

It is well known that the electrical and superconducting properties of oxide superconductors are strongly dependent on annealing conditions (*1, 2*). Temperature, oxygen pressure, and time are important factors for oxygen annealing. For example, $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ samples annealed at 1050°C in 0.3 atm of oxygen and quenched in liquid nitrogen exhibit semiconducting properties, while those annealed at 1000°C in 10^{-4} atm of oxygen and quenched are superconducting (*3*). The $YBa_2Cu_3O_{7-\delta}$ samples quenched from high temperatures such as 850°C show semiconducting properties, while those slowly cooled to the room temperature are superconducting (*4*).

The length of time t necessary for oxygen annealing is estimated from the chemical diffusion coefficient $\tilde{D}$ and sample thickness l, by an equation $\tilde{D}t \approx l^2$ (*5*). So the determination of chemical diffusion coefficient is important.

The first purpose of the present paper is to determine the chemical diffusion coefficient for $Nd_2CuO_{4-\delta}$. The second one is to calculate the self-diffusion coefficient and the vacancy diffusion coefficient from the chemical diffusion coefficient, in order to elucidate the diffusion mechanism.

2. Experimental

2.1 Sample Preparation

One molar aqueous solutions of $Nd(NO_3)_3$ and $Cu(NO_3)_2$ were mixed in a ratio of 2 : 1 and an oxalic acid–ethanol solution was added so that a water to ethanol ratio of 1 : 3 was obtained to complete the coprecipitation. The aging was carried out at pH 2 for one night with stirring. After the filtration,

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the precipitate was dried at 110°C for several hours and decomposed into oxide at 400°C, and ground. Then, the oxide was heated at 1000°C for 18 hr for the homogenization and examined by means of an X-ray diffractometer to confirm a single phase (*6*).

Samples for use in diffusion measurements were fabricated by pressing $Nd_2CuO_{4-\delta}$ powder into pellets at a pressure of 400 kg/cm^2 and sintering them in air at 1000°C for 72 hr. The cross section of pellets was examined by means of a SEM (scanning electron microscope) to inspect the microstructure, and the density was determined by the Archimedes technique.

2.2 Thermogravimetric Measurement

The oxygen nonstoichiometry and chemical diffusion were measured by means of a vacuum microbalance apparatus equipped with a Shimazu TGA-41 microbalance.

In order to determine the reference point of oxygen nonstoichiometry, the oxygen content of powder samples annealed at 500°C in 1 atom of oxygen for a long period was determined by iodometry. An amount of powder oxide with known oxygen nonstoichiometry was then placed in a platinum basket, suspended from the microbalance, and the equilibrium weight was measured as a function of temperature and oxygen partial pressure. The measurement was carried out in a temperature range of 500 to 1000°C and an oxygen partial pressure range of 1 to 0.01 atm.

The measurements of chemical diffusion were performed using sintered pellets with high relative densities. The size was 9.30 ± 0.02 mm in average diameter and 2.18 ± 0.02 mm in average thickness. A pellet was suspended from the microbalance and equilibrated under a predetermined temperature and oxygen partial pressure. The pressure was then changed stepwise, and the weight change was followed until it reached a new equilibrium. The oxygen partial pressure was changed from 0.3 to 0.01 atm in the reduction run, and it was reversed in the oxidation run.

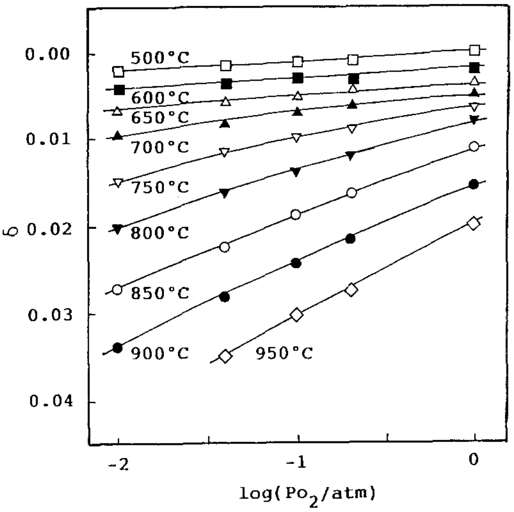

FIG. 1. Oxygen nonstoichiometry of $Nd_2CuO_{4-\delta}$ as a function of oxygen partial pressure and temperature.

When the effect of oxygen deficiency, δ, on the chemical diffusion coefficient was studied, the pressure step was chosen so that the oxygen deficiency changed from $\delta - 0.0025$ to $\delta + 0.0025$.

3. Results and Discussion

3.1 Oxygen Nonstoichiometry

The oxygen content of the reference sample was determined as 4.00 ± 0.004 by chemical analysis. The oxygen deficiency δ in $Nd_2CuO_{4-\delta}$ is illustrated in Fig. 1 as a function of log P_{O_2}. As seen in this figure, δ increases with the decrease in log P_{O_2} and increase in temperature, but the deficiency is only 0.04 even when the temperature is as high as 950°C and the oxygen partial pressure is 4×10^{-2} atm. This value is much smaller than that of $YBa_2Cu_3O_{7-\delta}$ (*7*).

3.2 Chemical Diffusion Coefficient of Oxygen

Figure 2 shows a SEM image of the cross section of specimen. Clearly, pores are

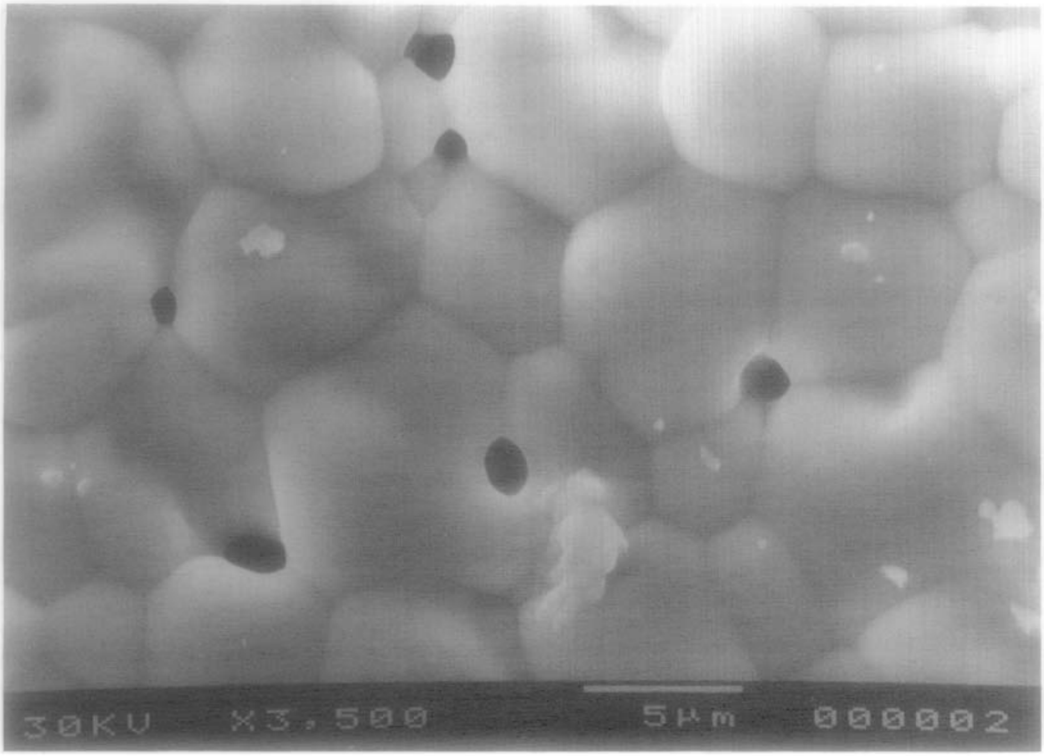

FIG. 2. SEM micrograph of fractured surface.

small and isolated. The relative density found by the Archimedes technique was 94.8%, which is in agreement with the SEM observation.

Figure 3 shows the relaxation curves when the oxygen partial pressure was decreased stepwise from 0.3 to 0.01 atm. The ordinate gives the normalized weight change $\{W(t) - W(\infty)\}/\{W(0) - W(\infty)\}$, where $W(0)$, $W(t)$, and $W(\infty)$ are the weights of specimen at times of zero, t, and ∞, respectively. It is evident that the relaxation rate increases with increasing temperature.

Figure 4 shows the comparison of relaxation curves in oxidation and reduction runs. The curves coincide with each other, and it is concluded that the relaxation is controlled by the diffusion of oxygen in $Nd_2CuO_{4-\delta}$.

In order to investigate the effect of deficiency on relaxation rate the pressure step was chosen so that the deficiency could change from $\delta - 0.0025$ to $\delta + 0.0025$. Figure 5 gives the relaxation curves for $\delta =$

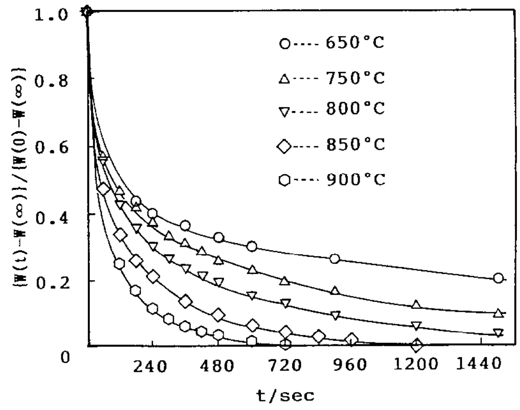

FIG. 3. Relaxation curves at different temperatures.

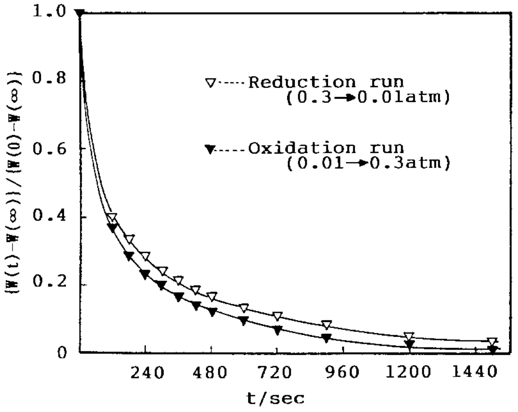

FIG. 4. Relaxation curves in oxidation and reduction runs.

0.0225, 0.0250, and 0.0275 at 900°C. Evidently, the relaxation rate is independent of δ.

Under the boundary condition of tablet, the diffusion equation can not be solved exactly, so an approximation solution is necessary. The tablet has a diameter of 9.30 mm and a thickness of 2.18 mm, so the diffusion occurs maily through the top and bottom surfaces. As the first approximation, the solution for a plane sheet is applicable. It is better to take into account the contribution of diffusion from edge. In the case of a rectangular specimen the size of which is $2a \times 2b \times 2c$, the approximation yields (*8*)

$$\frac{W(t) - W(\infty)}{W(0) - W(\infty)} = \frac{512}{\pi^6} \exp\left\{ -\frac{\pi^2}{4}\left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}\right)\tilde{D}t \right\}, \quad (1)$$

where the left side is the normalized weight change and $\tilde{D}$ is the chemical diffusion coefficient. Setting $d = 2a = 2b$ and $l = 2c$, one has

$$\frac{W(t) - W(\infty)}{W(0) - W(\infty)} = \frac{512}{\pi^6} \exp\left\{ -\pi^2\left(\frac{2}{d^2} + \frac{1}{l^2}\right)\tilde{D}t \right\}, \quad (2)$$

where d and l are the diameter and thickness of pellet. Replacement of a and b by d means that the circular section is approximated by square one. Since $1/l^2$ is 21.0 cm^{-2} and $2/d^2$ is 2.31 cm^{-2}, the term $1/l^2$ is about 10 times larger than $2/d^2$, so the square approximation does not affect the result of the calculation very much and Eq. (2) was adopted for the calculation of $\tilde{D}$.

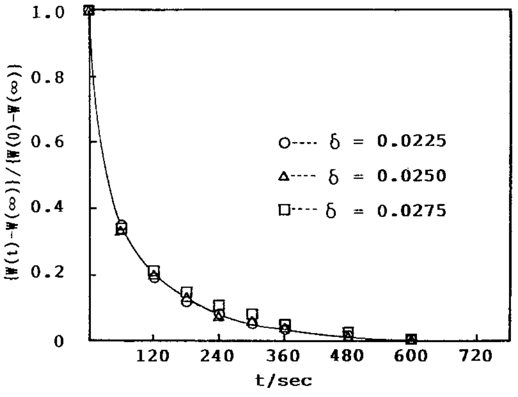

FIG. 5. Relaxation curves for samples with different δ.

When d and l are fixed, the normalized weight can numerically be calculated as a function of $\tilde{D}t$. Also, the normalized weight can experimentally be determined as a function of time. Therefore one can obtain a relation between $\tilde{D}t$ and t. As seen in Fig. 6, all the plots of $\tilde{D}t$ vs t are straight and pass through the origin. The chemical diffusion coefficient $\tilde{D}$ is determined from the slope of the plots, and is given in the second column in Table I. If $\tilde{D}$ and l are known, the equation $\tilde{D}t \approx l^2$ provides t, which is a measure of time necessary for oxygen annealing.

Since $Nd_2CuO_{4-\delta}$ is anisotropic, the chemical diffusion coefficient in the direction of the c-axis, $\tilde{D}_c$, would differ from that in the ab-plane $\tilde{D}_{ab}$. Oxygen seems to diffuse via vacancies in the O-plane sandwiched between two Nd layers, so $\tilde{D}_{ab}$

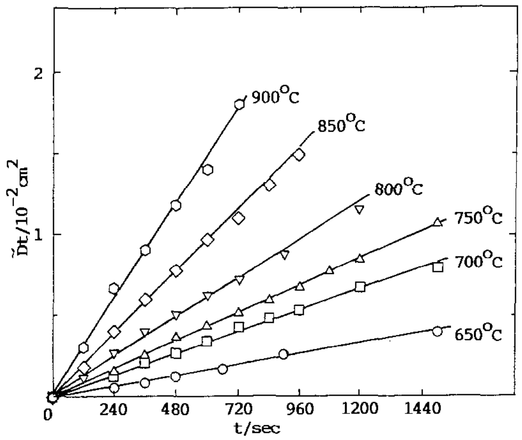

FIG. 6. Relation between t and $\tilde{D}t$.

would be higher than $\tilde{D}_c$, since the specimens employed in this study were polycrystalline and $\tilde{D}$ is a mean value of $\tilde{D}_c$ and $\tilde{D}_{ab}$.

In the case of diffusion in anisotropic media, the diffusion coefficient D, at right angles to surfaces whose normals have direction cosines l, m, n relative to the principal axes of diffusion, is given by (*10*)

$$D = l^2D_1 + m^2D_2 + n^2D_3, \qquad (3)$$

where D_1, D_2, and D_3 are the principal diffusion coefficients. In a $Nd_2CuO_{4-\delta}$ single crystal $D_1 = D_2 = D_{ab}$ and $D_3 = D_c$, so

$$D = (\sin^2\theta)D_{ab} + (\cos^2\theta)D_c. \qquad (4)$$

TABLE I

DIFFUSION COEFFICIENTS OF OXYGEN

Temp (°C)	$\tilde{D}$(cm^2 sec^{-1})	D^*(cm^2 sec^{-1})	D_v(cm^2 sec^{-1})
900	2.39×10^{-5}	4.89×10^{-8}	7.19×10^{-6}
850	1.53×10^{-5}	2.76×10^{-8}	5.17×10^{-6}
800	9.51×10^{-6}	1.27×10^{-8}	3.24×10^{-6}
750	7.54×10^{-6}	7.41×10^{-9}	2.57×10^{-6}
700	5.75×10^{-6}	3.29×10^{-9}	1.90×10^{-6}
650	2.40×10^{-6}	8.84×10^{-10}	7.49×10^{-7}

The sample is polycrystalline, so the diffusion coefficient is obtained by integrating Eq. (4) over a hemisphere in the direction of diffusion. Accordingly the dffusion coefficient D can be expressed as

$$D = \frac{2}{3}D_{ab} + \frac{1}{3}D_c. \qquad (5)$$

Since $D_{ab} > D_c$ for $Nd_2CuO_{4-\delta}$, D appears to be close to D_{ab}. Accordingly $\tilde{D}$ is considered to be close to $\tilde{D}_{ab}$.

Figure 7 gives the Arrhenius plot for $\tilde{D}$. It is expressed by

$$\tilde{D}(\text{cm}^2\,\text{sec}^{-1}) = 5.31 \times 10^{-2} \exp\left\{-\frac{(18 \pm 2)\text{kcal/mol}}{RT}\right\}. \qquad (6)$$

3.3 Self-Diffusion Coefficient of Oxygen

The self-diffusion coefficient D_i^* is calculated from the chemical diffusion coefficient $\tilde{D}$ using (*10*)

$$\tilde{D} = D_i^* \left(\frac{\partial \ln a_i}{\partial \ln C_i}\right), \qquad (7)$$

where a_i and C_i are the activity and concentration of species i, respectively. In the present study, the diffusing species is considered to be oxygen, so Eq. (7) becomes

$$\tilde{D} = \frac{1}{2}D^* \left(\frac{\partial \ln P_{O_2}}{\partial \ln C_O}\right), \qquad (8)$$

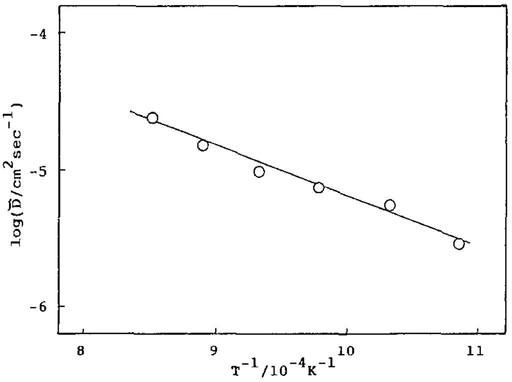

FIG. 7. Arrhenius plot for $\tilde{D}$.

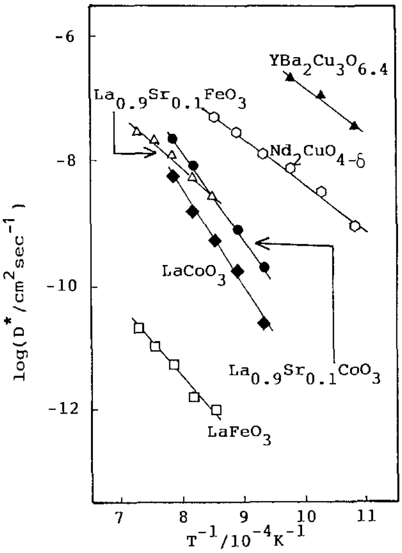

FIG. 8. Arrhenius plot for D^*.

where P_{O_2} and C_O are the oxygen partial pressure and the concentration of oxygen atoms in the oxide, respectively. Since ($\partial \log P_{O_2}/\partial \log C_O$) is calculated from the oxygen nonstoichiometry data shown in Fig. 1, D^* can be calculated from $\tilde{D}$. The self-diffusion coefficients D^* calculated in this way are given in the third column of Table I, and the Arrhenius plot is shown in Fig. 8. The equation is

$$D^*(\mathrm{cm^2\,sec^{-1}}) = 8.51 \times 10^{-2} \exp\left(-\frac{(33 \pm 2)\mathrm{kcal/mol}}{RT}\right). \quad (9)$$

For comparison, D^* of several perovskite-type oxides are also shown in Fig. 8 (*7, 11, 12*). As seen in the figure, D^* of $Nd_2CuO_{4-\delta}$ is slightly larger than those of perovskites.

In the case of $YBa_2Cu_3O_{6.4}$, the oxygen atom migrates on the oxygen lattice points of the Cu(I)–O plane. The self-diffusion coefficient of $YBa_2Cu_3O_{6.4}$ is also given in the same figure. The self-diffusion coefficient of $Nd_2CuO_{4-\delta}$ is not so large as that of $YBa_2Cu_3O_{7-\delta}$.

3.4 Vacancy Diffusion Coefficient

The chemical diffusion coefficient of oxygen can be converted to the vacancy diffusion coefficient D_v by (*13*)

$$\tilde{D} = -\frac{1}{2} D_v \left(\frac{\partial \ln P_{O_2}}{\partial \ln C_v}\right), \quad (10)$$

where C_v is the concentration of oxygen vacancies. The result is given in the fourth column of Table I. The Arrhenius plot for D_v is given in Fig. 9 together with the data of other perovskite oxides (*11, 12*). The plot is expressed by the equation

$$D_v(\mathrm{cm^2\,sec^{-1}}) = 1.63 \times 10^{-2} \exp\left(-\frac{(18 \pm 2)\mathrm{kcal/mol}}{RT}\right). \quad (11)$$

It is noteworthy that D_v of $Nd_2CuO_{4-\delta}$ is close to those of other pervoskites.

Equation (10) is expected at high deviation from stoichiometry. Wagner derived an equation relating $\tilde{D}$ and D_v at low defect concentrations (*14*)

$$\tilde{D} = (1 + z)D_v, \quad (12)$$

where z is the valence of the diffusion ion. For an oxide ion, $z = 2$, so the following relation is expected,

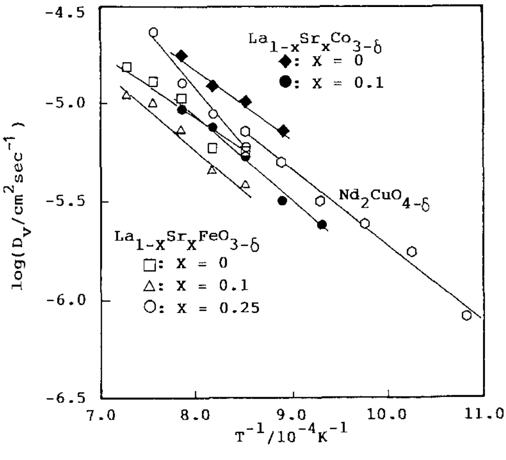

FIG. 9. Arrhenius plot for D_v.

$$\tilde{D} = 3D_v. \qquad (13)$$

In Eqs. (6) and (11) the activation energies are the same. So comparison of the preexponential term gives $\tilde{D}/D_v = 3.25$, which is remarkabley close to 3, expected from Eq. (13).

In $Nd_2CuO_{4-\delta}$, the oxygen vacancies seem to be located mainly on the O-plane and interchange their positions with the neighboring oxygen atoms. If the O-plane is shifted $c/3$ in the c-axis direction, the oxygen sublattice coincides with that of the CuO_2 plane. Therefore, the path of oxygen vacancy is similar to that in perovskites. This would be why D_v of $Nd_2CuO_{4-\delta}$ has nearly the same value as perovskites.

4. Conclusion

(i) The chemical diffusion coefficient $\tilde{D}$ of oxygen in $Nd_2CuO_{4-\delta}$ was determined by the relaxation method. It was found that the temperature dependence of $\tilde{D}$ is expressed by the equation

$$\tilde{D}(\mathrm{cm^2\,sec^{-1}}) = 5.31 \times 10^{-2} \exp\left(-\frac{(18 \pm 2)\mathrm{kcal/mol}}{RT}\right).$$

(ii) The self-diffusion coefficient of oxygen D^* was calculated from $\tilde{D}$. The temperature dependence of D^* was found to be expressed by

$$D^*(\mathrm{cm^2\,sec^{-1}}) = 8.51 \times 10^{-2} \exp\left(-\frac{(33 \pm 2)\mathrm{kcal/mol}}{RT}\right).$$

(iii) The diffusion coefficient of the oxygen vacancy D_v was calculated from $\tilde{D}$. The temperature dependence of D_v was found to be expressed by

$$D_v(\mathrm{cm^2\,sec^{-1}}) = 1.63 \times 10^{-2} \exp\left(-\frac{(18 \pm 2)\mathrm{kcal/mol}}{RT}\right).$$

The activation energies and preexponential term of D_v were nearly the same as those of perovskites.

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