Oxygen selfdiffusion in Fedoped MgO single crystals

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Oxygen self-diffusion coefficients in Fe-doped MgO single crystals were determined by an isotope exchange technique. The results indicated dopant-insensitive diffusion, which was interpreted as due to the vacancy pair mechanism.

I. INTRODUCTION

The self-diffusion coefficient of the Mg ion in MgO has been measured by several investigations.[1-3] All those results so far reported have been interpreted to be due to extrinsic diffusion by free Mg vacancies, which are caused by the presence of cationic impurities with high valences relative to Mg.[3,4] If the oxygen ion in MgO diffuses by the free vacancy mechanism, the oxygen diffusion should be also affected by the presence of those high valence cations. In Oishi *et al.*'s recent measurements,[5] however, two MgO single crystals with different impurity contents exhibited similar oxygen self-diffusion coefficients in the high-temperature regime and also in the low-temperature regime, where major impurities were cations of higher valences than magnesium in both crystals. Oishi *et al.* interpreted that the oxygen diffusion in the high-temperature regime represented as

$$D = 6.76 \exp[-128 \, (\text{kcal/mol})/RT] \, \text{cm}^2/\text{s} \qquad (1)$$

was not due to the simple free vacancy mechanism but due to an impurity insensitive mechanism and that the extrinsic diffusion determined in the low-temperature range was structure sensitive. Dopant insensitive oxygen diffusion was recently determined also for MgO single crystals doped with scandium by Henriksen, Chiang, Kingery, and Petusky.[6]

The present work was undertaken to confirm the high-valence dopant insensitive oxygen diffusion using Fe-doped MgO single crystals. For that purpose a comparison was made in interpretation of the experimental results on the bases of the vacancy pair mechanism and of the free oxygen vacancy mechanism.

II. EXPERIMENTAL

Samples used for the experiment are three MgO single crystals[12] with 310, 2300, and 12 900 ppm Fe from W and C Spicer Ltd., England. (They are designated as SP-310, SP-2300, and SP-12900, respectively.)

Oxygen self-diffusion coefficient was determined under an oxygen pressure of 2×10^4 Pa at a temperature of 1400–1700 °C using an isotope exchange technique similar to the previous determination for undoped MgO single crystals. Diffusion samples were carefully prepared by eliminating subsurface damage using chemical polishing technique.[5]

III. RESULTS AND DISCUSSION

Oxygen self-diffusion coefficients determined for SP-310 and SP-2300 MgO samples are shown in Fig. 1 where

the solid lines represent the previous determination[5] for a MgO single crystal from Norton Company.[13] Figure 2 shows determinations for SP-12900 which exhibited some scatter.

As seen in Figs. 1 and 2, the oxygen self-diffusion coefficients in Fe-doped MgO are similar to or somewhat lower than those in undoped MgO and SP samples exhibit no significant Fe-concentration dependence.

A. Free oxygen vacancy mechanism

One may interpret the results in Fig. 1 that the oxygen diffusion is slower in Fe-doped MgO than in undoped MgO and that is because of the free oxygen vacancy mechanism. This possibility is checked by theoretical calculation of oxygen self-diffusion coefficients on the basis of the assumed free oxygen vacancy mechanism.

The concentration of oxygen vacancies in pure MgO is given by Eq. (2),

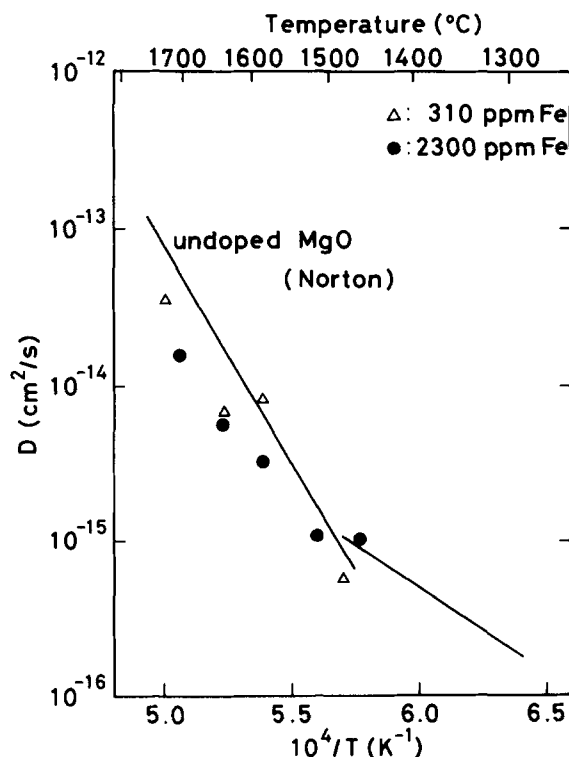$$[V_O^{\cdot\cdot}]_{\text{pure}} = [V_{Mg}'']_{\text{pure}} = K_S^{1/2} , \qquad (2)$$

FIG. 1. Oxygen self-diffusion coefficients in Fe-doped MgO single crystals as a function of temperature.
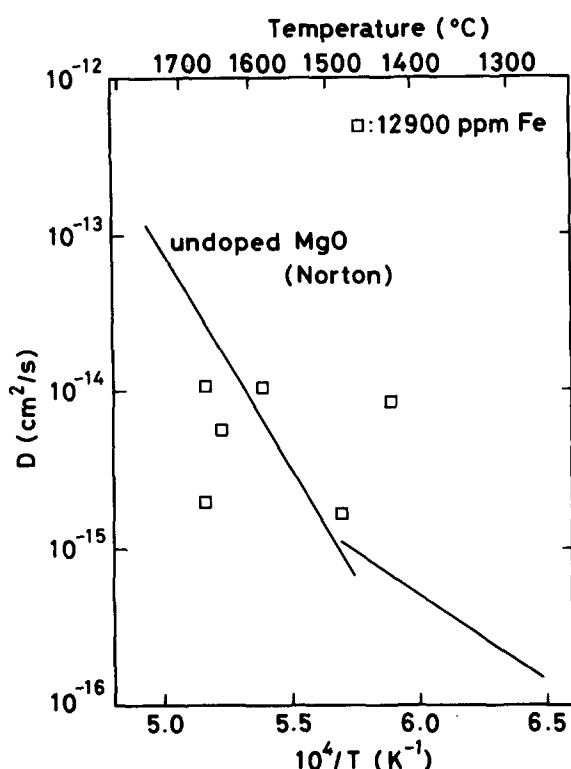
FIG. 2. Comparison of oxygen self-diffusion coefficients in 12 900 ppm Fe-doped MgO and pure MgO.

where K_S is the Schottky equilibrium constant and lattice defects are expressed by Kröger–Vink's notation. When Fe is substitutionally doped in MgO, formed $Fe^{\cdot}_{Mg}$ and V''_{Mg} control the equilibrium for Eq. (2), where the concentration of oxygen vacancies is given by Eq. (3),

$$[V^{\cdot\cdot}_O]_{doped} = \frac{2}{[Fe^{\cdot}_{Mg}]} K_S \ . \tag{3}$$

If the free oxygen vacancy mechanism is the case, the oxygen self-diffusion coefficient, which is proportional to the oxygen vacancy concentration, decreases with increasing $[Fe^{\cdot}_{Mg}]$ as given by Eq. (3).

The ratio of $[V^{\cdot\cdot}_O]_{doped}$ in Eq. (3) and $[V^{\cdot\cdot}_O]_{pure}$ in Eq. (2) gives a relative oxygen self-diffusion coefficient for doped MgO against that for pure MgO as given by Eq. (4),

$$\frac{D_O(doped)}{D_O(pure)} = \frac{[V^{\cdot\cdot}_{O\,doped}]}{[V^{\cdot\cdot}_O]_{pure}} = \frac{2}{[Fe^{\cdot}_{Mg}]} K_S^{1/2}$$

$$= \frac{2}{[Fe^{\cdot}_{Mg}]} \exp\left(\frac{\Delta S_S}{2R}\right) \exp\left(-\frac{\Delta H_S}{2RT}\right) \ , \tag{4}$$

where ΔH_S and ΔS_S are the enthalpy and entropy, respectively, required for formation of Schottky-type vacancies and D_O is the oxygen self-diffusion coefficient. With assumption of $\exp(\Delta S_S/2R) = 1 \sim 10$, the relative oxygen self-diffusion coefficients at 1500 °C calculated by Eq. (4) for $\Delta H_S = 5.5$ eV and $\Delta H_S = 7.5$ eV, respectively, are shown in Fig. 3 as a function of $[Fe^{\cdot}_{Mg}]$ and compared with experimental results, where the experimental relative self-diffusion coefficient is expressed relative to the oxygen self-diffusion coefficient for the

Norton MgO. The concentrations of $Fe^{\cdot}_{Mg}$ necessary for the calculation were taken from the experimental results by Gourdin et al.[8] The discrepancy by factors 10^2–10^7 of the experimental results from the calculated relative self-diffusion coefficients indicates that the free oxygen vacancy mechanism is not the predominant mechanism in the present oxygen diffusion.

Another possibility of the free oxygen defect mechanism is that due to Frenkel-type oxygen defects. However, the formation energy of the Frenkel pair theoretically calculated for the oxygen ion in MgO (12.1 eV)[9] is too high for free defects to be the predominant oxygen defect.

B. Vacancy pair mechanism

As discussed in the previous section, the small difference of the oxygen self-diffusion coefficients determined for Fe-doped and undoped MgO is not properly explained on the basis of the free oxygen vacancy mechanism. The results in Figs. 1 and 2 may be interpreted that the oxygen diffusion is similar in doped and undoped MgO. A diffusion mechanism conceivable for the dopant-insensitive case is the vacancy pair mechanism.

Formation of the vacancy pair from Schottky-type free vacancies is described by Eq. (5),

$$V^{\cdot\cdot}_O + V''_{Mg} \rightleftharpoons (V^{\cdot\cdot}_O \ V''_{Mg})^x \ . \tag{5}$$

Subsequently, the concentration of the vacancy pair is given by Eq. (6),

$$[(V^{\cdot\cdot}_O \ V''_{Mg})^x] = K_S \cdot K_b \tag{6}$$

$$= Z \exp\left[-(\Delta G_S + \Delta G_b)/RT\right] ,$$

$$\approx Z \exp\left[-(\Delta H_S + \Delta H_b)/RT\right] \ , \tag{7}$$

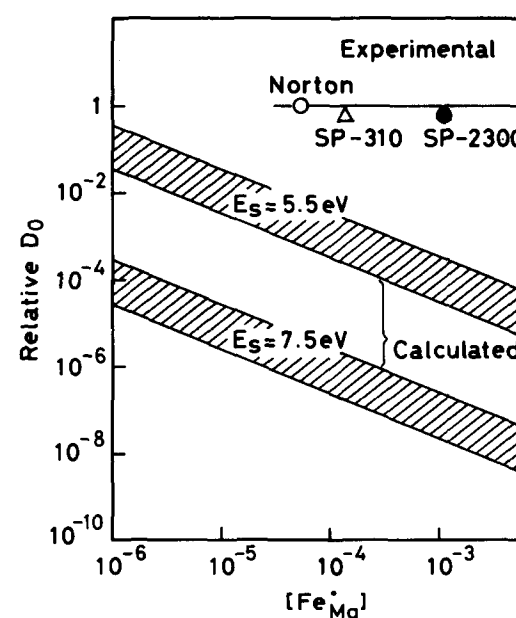where K_S and K_b are constants for the Schottky equilib-

FIG. 3. D_0 in Fe-doped MgO relative to D_0 in pure MgO at 1500 °C calculated for the free oxygen vacancy mechanism.

rium and the equilibrium of Eq. (5), respectively, ΔG_S and ΔG_b corresponding free energy changes, ΔH_S and ΔH_b corresponding enthalpy changes, respectively, and Z is the number of configurations distinguishable with respect to the vacancy pair. Discussion here is made with assumption of the entropy term in the order of 1.

If the present oxygen diffusion is due to the vacancy pair mechanism, the diffusion coefficient should be independent of the dopant concentration, as the vacancy pair concentration is given by Eq. (6). This agrees with the present experimental results and accounts for the oxygen diffusion insensitive to the doped scandium in MgO.[6]

If the vacancy pair mechanism is predominant in the oxygen self-diffusion determined for the Norton MgO, the activation energy determined in the high-temperature regime (128 kcal/mol $= 5.6$ eV)[5] is interpreted to be the sum of the formation and migration energies for the vacancy pair as described by Eq. (8),

$$Q = \text{formation energy } (\Delta H_S + \Delta H_b) + \Delta H_m \quad , \qquad (8)$$

where Q is the experimental activation energy and ΔH_m the migration energy of the vacancy pair. The ΔH_b has been theoretically calculated by Gourdin and Kingery[9] and ΔH_m by Mackrodt.[10] By substituting $\Delta H_m = 2.47$ eV, $\Delta H_b = -2.67$ eV, and $Q = 5.6$ eV in Eq. (8), $\Delta H_S = 5.8$ eV is obtained for the formation energy of Schottky-type free vacancies. This magnitude is not inconsistent with theoretically calculated values (7.4–7.9[11] and 7.7 eV[9]), taking into consideration that the shell model calculation tends to give too high values.[8]

In order that the vacancy pair mechanism is predominant in comparison with the free vacancy mechanism in the present oxygen diffusion, the concentration of the vacancy pair must be higher than that of the free oxygen vacancy, since the migration energy of the vacancy pair is higher than or similar to that of the free oxygen vacancy. The concentration of the vacancy pair relative to the free oxygen vacancy in Fe-doped MgO is given by Eq. (9), as derived from Eqs. (3) and (7) with assumption of the entropy term ≈ 1,

$$\frac{[(V''_{Mg} V^{\cdot\cdot}_O)^x]}{[V^{\cdot\cdot}_O]_{\text{doped}}} = Z \frac{[Fe^{\cdot}_{Mg}]}{2} \exp\left(-\frac{\Delta H_b}{RT}\right) \quad . \qquad (9)$$

In a comparison employing $\Delta H_b = -2.67$ eV, that ratio becomes unity for $[Fe^{\cdot}_{Mg}] \approx 2 \times 10^{-8}$ at 1600 °C, i.e., the presence of Fe^{3+} as low as < 1 ppm readily makes the concentration of the vacancy pair much higher than that of the free oxygen vacancy.

The present oxygen diffusion was determined under an oxygen pressure of 2×10^4 Pa. Variation of oxygen partial pressure introduces the change of $[Fe^{\cdot}_{Mg}]$ in Fe-doped MgO. This, however, should not lead to variation of the oxygen diffusion, since the present oxygen diffusion is insensitive to $[Fe^{\cdot}_{Mg}]$.

ACKNOWLEDGMENTS

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[12]The basic purity of those crystals is of 4N with 70Si, 30Ca, and 10Cr (ppm), according to the supplier.

[13]The Norton single crystal contained 70Fe, 46P, and 37Al other than 210Ca (ppm) as major impurities (Ref. 5). The second high-purity single crystal from ORNL used in the previous work contained 22Si, 15Al, 13P, and 7Fe other than 50Ca (ppm) (Refs. 5 and 7).