Self-Diffusion of Yttrium in Monocrystalline Yttrium Oxide: Y_2O_3

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Yttrium self-diffusion in monocrystalline yttrium oxide (Y_2O_3) is studied by means of the classical radio tracer technique. The few reliable diffusion data obtained in the temperature range 1600–1700°C lead to the following diffusion coefficient

$$D = 3.5 \times 10^{-9} \exp - \frac{72}{RT} \text{ (kcal/mole) m}^2 \text{ sec}^{-1}.$$

Experimental errors on the above numerical values are large and give, for the preexponential and energy terms, respectively:

$$2.10^{-7} < D_0 < 3.10^{-10} \text{ m}^2 \text{ sec}^{-1}$$

$$62 < Q < 82 \text{ kcal/mole}.$$

Nevertheless these results seem in good agreement with those deduced from high-temperature and low-stress creep experiments. The theoretical aspect of self-diffusion of yttrium in Y_2O_3 is studied in terms of point defects and lattice disorder due to the equilibrium between the oxide and its environment. This last part is confined to the restricted range of high oxygen partial pressure in which oxygen interstitials are supposed to be majority defects. Intrinsic and extrinsic diffusion behavior are both considered on the basis of a vacancy diffusion mechanism.

I. Introduction

Yttrium oxide, Y_2O_3, is a high melting point oxide, $T_m = 2450°C$, which possesses stability up to 2250°C.

Some studies concerning point defects disorder (1–5) and self-diffusion (6, 7) have been done in this oxide. Oxygen diffusion experiments have been carried out on small single crystals (6). Previous yttrium diffusion experiments have been carried out on polycrystalline Y_2O_3 (7).

It is only recently that it was possible to grow relatively large yttrium oxide single crystals by the Verneuil method.

Such crystals have been used in a recent study of plastic properties of Y_2O_3 by means of high-temperature creep experiments (9).

The analysis of these creep results is developed in terms of a dislocation climb mechanism which is controlled by the diffusivity of the slowest ion of the oxide.

The present work deals with the study of yttrium self-diffusion in monocrystalline Y_2O_3.

II. Generality

Yttrium oxide has the cubic rare earth type C structure (10, 11) which may be described as a modified fluorite structure.

In this structure, one-fourth of the sites in the anion sublattice are unoccupied. As a consequence of such a defective structure, the unoccupied oxygen sites form nonintersecting strings along the $\langle 111 \rangle$ directions of the crystal. It has been suggested (6) that these strings should provide relatively unimpeded pathways for the migration of oxygen ions through the material. The oxygen diffusion process would therefore be most probably due to the migration along interstitial pathways of oxygen ions.

The yttrium sublattice is F.C.C.

From these crystallographic considerations, and taking into account point defects and lattice disorder in the Y_2O_3 matrix, a clear difference in the diffusion behavior of the two components of the oxide may be expected.

III. Experimental Study

III.1. Material

Stoichiometric $YO_{1.5}$ single crystal elaborated by means of an oxhydric torch (Verneuil method) has been used. The samples have been supplied by the L.E.T.I., Nuclear Center, Grenoble.

An emission spectrographic analysis of the monocrystalline material is given in Table I.

III.2. Experimental Procedure

A tracer sectioning technique was used to measure yttrium self-diffusion. A thin layer of radioactive material was deposited on a monocrystalline lamella 3 mm thick with an area of approximately 50–60 mm².

With such a procedure, the solution of Fick's second law may be written:

$$C(x, t) = \frac{A}{(\pi Dt)1/2} \exp - (x^2/4Dt)$$

where x is the position and A the amount of tracer deposited.

The sectioning device which was used

TABLE I

Elements	Li	Mg	Si	F	Cl	S
ppm	46	450	122	392	50	102

for grinding very thin slices from the surface of the sample is described elsewhere (12).

The isotopes used were ^{91}Y, a β^- emitter of 59 day half-life or ^{88}Y a γ emitter of 108 days half-life supplied by Radio Chemical Center L.T.D., Amersham.

The tracer is in the form of a solution of YCl_3, having a specific activity of 2 mCi/ml. The initial tracer solution is dissolved in distilled water in the ratio 1/10 and then deposited on the surface. The as-received tracer solution has also been deposited by means of under-vacuum evaporation.

After drying, the sample is sealed off in a quartz ampulla under 1/2 atmosphere of air and then maintained at 800°C for 4 hr in order to convert the tracer material to an adherent oxide. Finally, the sample is taken out of the quartz ampulla and then folded with a platinum foil. The activated specimens are heated, in air atmosphere, to diffusion temperature inside a lanthanum chromite resistor furnace running in air up to 1850°C.

Annealing temperatures are monitored with a Pt–10% Rh, Pt–40% Rh thermocouple. The variations of the temperature versus time were always within a 1°C interval.

The duration of the diffusion anneals was more than 10 hr (for instance: 18 hr at 1700°C and 48 hr at 1600°C).

Before starting the sectioning procedure, the edge of the sample is removed up to more than 100 μm depth, in order to avoid effects of surface diffusion. The thickness of the slice removed by the abrasive covered sectioning apparatus is obtained by the classical weight gain method.

A Geiger–Muller tube is used for counting. Every important stage of the experimental procedure is controlled by self radiography of the sample.

III.3. Experimental Results

Many technical problems appeared in the experimental results analysis. Such difficulties are mainly due to the bad internal quality of large Y_2O_3 single crystal.

Tracer concentration in micro-crack present inside the oxide has often been observed by self radiography.

Furthermore, the penetration of the activated yttrium deposited on the surface seems very difficult even for durations of diffusion anneals as long as 50 hr.

Owing to these difficulties, each diffusion test is rigorously controlled at each stage of the experiment.

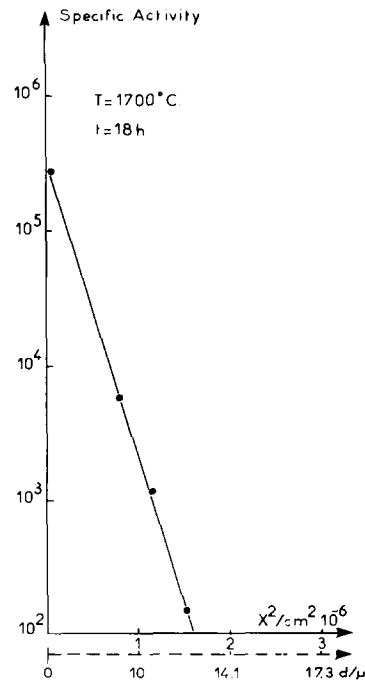The result of such a procedure is the drastic elimination of the majority of the

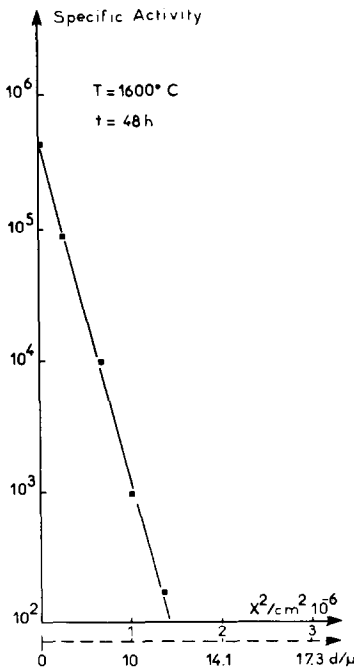FIG. 2. Penetration profile for $T = 1700°C$ and $t = 18$ hr.

FIG. 1. Penetration profile for $T = 1600°C$ and $t = 48$ hr.

diffusion tests. Indeed, among 10 attempts, only two are reliable, one at 1600°C and the other at 1700°C.

The diffusivities calculated from the slopes of penetration profiles for 1600 and 1700°C give the following results (Figs. 1 and 2).

$$D_{1600°C} = 2.92 \times 10^{-17} \text{ m}^2 \text{ sec}^{-1}$$

$$D_{1700°C} = 7.88 \times 10^{-17} \text{ m}^2 \text{ sec}^{-1}.$$

These two values lead to the following diffusion coefficient (Fig. 3).

$$D_y = 3.5 \times 10^{-9} \exp$$
$$- \frac{72}{RT} \text{ (kcal/mole), m}^2 \text{ sec}^{-1}.$$

Taking into account the large experimental errors on these numerical values, the above diffusion coefficient leads to a preexponential and energy terms D_0 and Q which
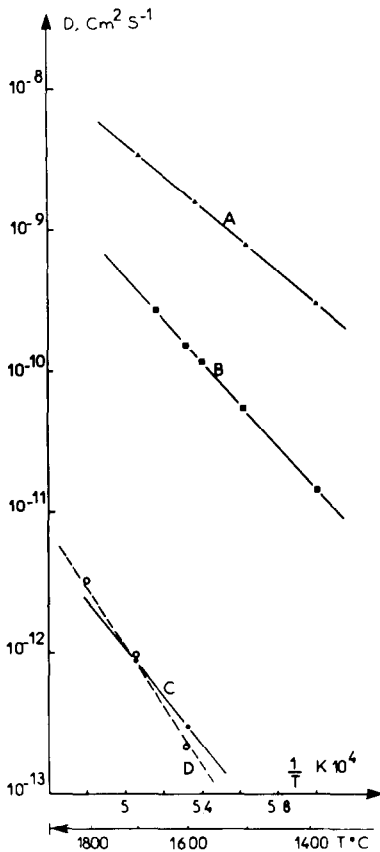
FIG. 3. Logarithm of the diffusion coefficient of yttrium versus the reciprocal of the absolute annealing temperature. Lines A and B: results from (7) and (8) on polycrystals; line C: this work on single crystals; line D: results from creep data (9).

belong, respectively, to the range:

$$2.10^{-7} < D_0 < 3.10^{-10} \text{ m}^2 \text{ sec}^{-1}$$

$$62 < D_0 < 82 \text{ kcal/mole}$$

IV. Theoretical Study

IV.1. Generality

Diffusion in oxides, in general, is due to point defects. Diffusion coefficients are proportional to the defect concentration and may be written as (12):

$$D = A \cdot n_d \exp - \frac{\Delta H_m}{kT} \qquad (1)$$

where A is a constant, ΔH_m is the enthalpy change in the activated process, and n_d is the concentration of point defects responsible for the diffusion mechanism. Depending upon the point defect and the oxygen partial pressure, n_d may be written as:

$$n_d = n_0 \exp \left[- \frac{\Delta H_f}{kT} \right] P_{O_2}^x \qquad (2)$$

H_f is then the enthalpy of formation of the defect and P_{O_2} is the oxygen partial pressure. The exponent x depends on the point defect disorder in the matrix of the oxide.

Hence the diffusion coefficient is:

$$D = A \cdot n_0 P_{O_2}^x \exp - \frac{Q}{kT}. \qquad (3)$$

It is therefore interesting to know, at the thermal equilibrium between the oxide and its surrounding system, the influence of oxygen partial pressure and temperature on the concentration of the point defects.

Depending upon these parameters, more or less important deviation from stoichiometry may occur.

A single point defect model is the most currently suggested to describe the small deviation.

IV.2. Point Defect Disorders and Diffusion in Y$_2$O$_3$

Depending upon temperature and oxygen partial pressure, Y$_2$O$_3$ may show deviation from stoichiometry which could be accommodated through different types of point defect disorder: such disorders are described in the appendix where the well-known formalism of Kroger–Vink is employed (13). As it is currently suggested in the litterature (2, 14) three oxygen partial pressure ranges are considered.

a. High oxygen partial pressure range which leads to the oxide. Y$_2$O$_{3+x}$ or Y$_{2-x}$O$_3$ depending upon the type of point defects controlling the equilibrium. Y$_2$O$_{3+x}$: the majority defects are oxygen interstitials (O$_i''$); this case will be developed latter in

detail. $Y_{2-x}O_3$: yttrium vacancies (V_y'') are majority defects. Equations for the formation of yttrium vacancy lead to the following concentration (for details see the Schottky table in the appendix).

$$[V_y'''] = 3^{-3/4} K_a^{1/4} K_{V_y}^{1/8} P_{O_2}^{3/16} \qquad (4)$$

where yttrium vacancies are assumed to be fully ionized.

b. An intermediate oxygen partial pressure range. Yttrium oxide is stoichiometric: Y_2O_3. Two cases may be distinguished: (a) (O_i'') are majority defects and then: $[O_i''] = [V_o''] = K_{AF}^{1/2}$ through the anti-Frenkel equilibrium (see appendix); and (b) $2[V_o''] = 3[V_y'''] = K_S^{5/2}$ through the schottky equilibrium. In both cases the point defect concentrations are constant.

c. Low oxygen partial pressure range. This leads to the oxide: Y_2O_{3-x} or $Y_{2+x}O_3$.
(a) Y_2O_{3-x}: the majority defects are (V_o''). The reactions lead to:

$$[V_o''] = 4^{-1/3} K_b^{1/3} K_{V_O}^{1/3} P_{O_2}^{-1/6} \qquad (5)$$

(b) $Y_{2+x}O_3$: the majority defects are yttrium interstitials (Y_i'') through the Frenkel disorder. One obtains:

$$[Y_i''] = 3 K_c^{1/4} K_{yi}^{1/8} P_{O_2}^{-3/16}. \qquad (6)$$

From the works of Tallan and Vest (*1*) and Robert (*15*) on electrical conductivity and of Odier *et al.* (*2, 3*) on thermoelectronic emission it has been shown that the anti-Frenkel equilibrium would satisfactorily account for the experimental results. The influence of such defects on the diffusion of yttrium in Y_2O_3 is now developed.

IV.3. Diffusion of Yttrium in Y_2O_3

Previous works dealing with cation diffusion either on Y_2O_3 or quite similar structures strongly suggest an yttrium vacancy diffusion mechanism. Such a process is therefore assumed in the following discussion. The concentration of yttrium vacancies, in both intrinsic and extrinsic cases, is calculated in the high oxygen partial pres-

sure range which corresponds to the experimental conditions of he diffusion study of yttrium in monocrystalline Y_2O_3.

Under these conditions, yttrium oxide exhibits a p-type conduction.

IV.4. Intrinsic Diffusion of Yttrium

The defect equation for the formation of a schottky defect may be written:

$$[V_o'']^3[V_y''']^2 = K_s'' = K_s''^\circ \exp - \frac{\Delta H_s''}{kT} \qquad (7)$$

Introduction of an oxygen into an interstitial site of the matrix leads to the relation

$$[O_i''] p^2 = p_{O_2}^{1/2} K_d K_{O_{i'}}. \qquad (8)$$

Owing to the p-type conduction of this oxide, the electroneutrality equation corresponding to the anti-Frenkel equilibrium is reduced to:

$$p = 2 [O_i'']. \qquad (9)$$

From Eqs. (8) and (9):

$$[O_i''] = \frac{1}{2^{2/3}} p_{O_2}^{1/6} K_d^{1/3} K_{O_i}^{1/3}. \qquad (10)$$

The equation for formation of the Anti-Frenkel defect is:

$$[V_o''][O_i''] = K_{AF}''. \qquad (11)$$

The concentration of double charged oxygen vacancies is obtained from Eqs. (10) and (11):

$$[V_o''] = 2^{2/3} K_{AF}'' K_d^{-1/3} K_{O_i}^{-1/3} P_{O_2}^{-1/6}. \qquad (12)$$

From Eqs. (12) and (7) the concentration of yttrium vacancies is obtained as

$$[V_y'''] = \frac{1}{2} K_s''^{1/2} K_{AF}^{-3/2} K_d^{1/2} K_{O_i}^{1/2} P_{O_2}^{1/4} \qquad (13)$$

when the constants of the low of mass action are developed one obtains:

$$[V_y'''] = \frac{P_{O_2}^{1/4}}{2} \exp \frac{\Delta S_{V_y''}}{2k} \exp$$
$$- \frac{\Delta H_s'' + \Delta H_{O_i} + E_d - 3\Delta H_{AF}''}{2kT}. \qquad (14)$$

The entropy term may be decomposed as:

$$\Delta S_{V_y}''' = \Delta S_s + \Delta S_{O_i} + \Delta S_d - 3\Delta S_{AF}. \quad (15)$$

If the experimental data of electrical conductivity and thermoelectronic emission are considered, namely (1, 3, 15):

$$\Delta H_s'' = 13.7 \text{ eV}; \quad \Delta H_{O_i}$$
$$+ E_d = 5.7 \text{ eV}; \quad \Delta H_{AF}'' = 5 \text{ eV}$$

expression (14) becomes:

$$[V_y'''] = \frac{1}{2} P_{O_2}^{1/4}$$

$$\exp \frac{\Delta S_{V_y'''}}{2k} \exp - \frac{(2.2 \text{ eV})}{kT}. \quad (16)$$

It is worthy of mention that the numerical calculation of this yttrium vacancy concentration strongly depends on the entropy term. In the ionic crystals and oxides the entropy term may be very different than the values proposed for the metals in which $\Delta S/k \simeq 1$. In the oxides, only rough estimations are available. Owing to the exponential dependance of this term, a precise determination of expression (16) is difficult.

For instance, if $\Delta S = 10k$ as suggested for CaF_2 (16) one obtains at 1800°C in Y_2O_3,

$$[V_y'''] = 10^{-1}$$

if $\Delta S = 4k$ as suggested by Berard and Wilder (7) for Y_2O_3:

$$[V_y'''] = 2.4 \times 10^{-4}.$$

From the concentration of yttrium vacancies, the diffusion coefficient of yttrium may be obtained (17):

$$D = \frac{\alpha a_0^2 \nu}{2} P_{O_2}^{1/4} \exp \frac{\Delta S_{V_y} + \Delta S_m}{k} \exp$$

$$- \frac{\Delta H_s'' + \Delta H_{O_i} + E_d - 3\Delta H_{AF}'' + 2\Delta H_m}{2kT}. \quad (17)$$

Comparison with the classical Arrhenius equation,

$$D = D_0 \exp - Q/kT$$

leads to:

$$D_0 = \frac{\alpha a_0^2 \nu}{2} P_{O_2}^{1/4} \exp \frac{\Delta S_{V_y'''} + \Delta S_m}{k}$$

$$Q = 2.2 \text{ (eV)} + H_m. \quad (18)$$

IV.5. Extrinsic Diffusion of Yttrium

The diffusion of yttrium strongly depends on the equation of formation of the Schottky defects (Eq. (7)). Depending on the concentration, the impurities may significantly affect or may completely control the concentration of the two species of an equilibrium.

a. Impurity controling $[V_o^{..}]$. From (Eq. (7)) we have:

$$[V_y'''] = K_s^{1/2} [V_o^{..}]^{-3/2}$$

$$= [V_o^{..}]^{-3/2} \exp \frac{\Delta S_s}{2k} \exp - \frac{\Delta H_s''}{2kT} \quad (19)$$

the diffusion coefficient is then:

$$D = \alpha a_0^2 \nu [V_o^{..}]^{-3/2} \exp$$

$$\frac{\Delta S_s + 2\Delta S_m}{2kT} \exp - \frac{\Delta H_s'' + 2\Delta H_m}{2kT} \quad (20)$$

or:

$$D_0 = \alpha a_0 \nu [V_o^{..}]^{-3/2} \exp \frac{\Delta S_s + 2\Delta S_m}{2k}$$

$$Q = \frac{\Delta H_s''}{2} + \Delta H_m. \quad (21)$$

In general such relations give rise to large values of D_0 and Q.

b. Impurities controlling $[V_y''']$. If the concentration of yttrium vacancies is controlled by the impurities, the diffusion coefficient may be written:

$$D = \alpha a_0^2 \nu [V_y'''] \exp$$

$$\frac{\Delta S_m}{k} \exp - \frac{\Delta H_m}{kT} \quad (22)$$

$$D_0 = \alpha a_0^2 \nu [V_y'''] \exp \frac{\Delta S_m}{k} \quad (23)$$

$$Q = \Delta H_m.$$

These relations lead to low values of D_0 and Q. The diffusion coefficient is independent of oxygen partial pressure.

V. Discussion

According to the assumptions described above, the self-diffusion data of yttrium in the temperature range 1600–1700°C may be condensed in the relation:

$$D_y = 3.5 \times 10^{-9} \exp$$

$$- \frac{72}{RT} \text{ (kcal/mole) m}^2 \text{ sec}^{-1}.$$

It is interesting to compare our diffusion results to those obtained from high-temperature and low-stress creep experiments in Y_2O_3.

Precise study of both, thermal activation of steady-state creep rate and dislocation substructure by means of thermal-chemical (18) etching and electron microscopy, leads to the description of the high-temperature creep behavior of Y_2O_3 in terms of recovery creep due to the evolution of a three-dimensional network of dislocations by a pure-climb mechanism.

The analysis of the creep results has therefore been made using a Nabarro–Herring recovery creep models based on the climb of dislocations (9).

A more developed description of the high-temperature and low-stress creep behavior of Y_2O_3 will be described in another paper (19).

Experimental parameters and yttrium oxide constants have been introduced into the theoretical Nabarro–Herring creep model formalism and a diffusion coefficient, imputed to yttrium diffusion, has been deduced (Fig. 3, line D). The agreement between creep and diffusion values seems good. Yttrium diffusion coefficient may be compared (Fig. 3) to previous results obtained with polycrystalline Y_2O_3 by Berard and Wilder (7).

Taking into account the uncertainty (±10 kcal/mole) of our results concerning the activation energy of diffusion Q, the value which is found, 72 kcal/mole, is similar to that obtained with fully densed polycrystalline Y_2O_3 (Fig. 3, curve B).

Nevertheless, the preexponential term $(3.5 \times 10^{-9} \text{ m}^2 \text{ sec}^{-1})$ obtained with monocrystalline Y_2O_3 is approximately 400 times lower than that of earlier works.

How are these facts to be explained? The difference between our results and these of Berard and Wilder (7, 8) (Fig. 3, A and B) is difficult to explain because of the lack of both experimental uncertainty and details concerning the stoichiometry of the hot-pressing material used in their works.

Analysis of the impurity content of our monocrystalline samples exhibits foreign aliovalent ions, mainly under the form of divalent cation (450 ppm of Mg).

Such a lower valent ion concentration may lead to a decrease of the yttrium vacancy concentration and then to the yttrium self-diffusion coefficient. On the other hand, the material used by Berard and Wilder contains 500 ppm of also a divalent foreign cation: Ca.

Explanation of the different experimental values obtained is therefore not clear in terms of impurity content.

Inasmuch as aliovalent ion concentration may vary from one sample to the other, the difference between our results and these of Berard and Wilder is probably a reflection on both, difference between the polycrystalline and monocrystalline state and difference in the impurity content of the oxides. A hypothetical difference between the stoichiometries may also be argued.

As the present work indicates, the difficulties in obtaining reliable and numerous diffusion data concerning monocrystalline Y_2O_3 are mainly due to the difficulties in growing large and perfect single crystals.

Y_2O_3 exhibits small deviations from stoichiometry and in an attempt to explain such experimental results, on the basis of a mobile defect jump process, point defects and the corresponding lattice disorder due to equilibrium between the oxide and its environment must be considered.

Such a theoretical aspect of the diffusion of yttrium into Y_2O_3 is principally based on the assumption that the diffusion process may be described through a simple point defect model using the Kroger–Vink notations (13).

On this basis, the cation diffusion coefficient of Y_2O_3 strongly depends upon many parameters which are difficult to monitor. In fact, as this work indicates, experimental data in oxides, which are considered to be the same materials, often exhibit considerable discrepencies.

In the restricted range of high oxygen partial pressure, where Y_2O_3 exhibits a p-type conduction and where oxygen interstitial is supposed to be the majority defect through the anti-Frenkel disorder, an interesting theoretical insight concerning the point defect mechanism may be deduced from the P_{O_2} dependance on the diffusion coefficient.

In principle, it might be possible to know the point defect component which is responsible for diffusion. Nevertheless, even in so-called "pure" material aliovalent ions may play a very important role.

With our assumption of a fully ionized cation vacancy diffusion mechanism, ambiguities may appear by considering only the oxygen partial pressure dependence of the diffusion coefficient.

Indeed, depending upon the impurity species and the reducing or oxidizing character of aliovalent ions, the diffusion coefficient may be either independant of P_{O_2} or dependant in exactly the same way as in pure oxide.

Reliable spectroscopic analysis could resolve this problem. Unfortunately, several kinds of aliovalent ions often intervene in the composition and their influence becomes intricate.

Experimental data of yttrium self-diffusion in Y_2O_3 give very low values of the preexponential term D_o.

Small values of D_0 are usually considered to be characteristic of extrinsic behavior where the concentration of cation vacancies is fixed by aliovalent impurities.

An extrinsic diffusion might therefore be an explanation of such experimental data. Unfortunately, the P_{O_2} influence has not been studied in our work.

An alternative is a more complicated intrinsic diffusion mechanism in which point defect complex would be involved. In this case, the preceding models are by no means valid and must be considered in a more sophisticated way.

Nevertheless, in general, a diffusion experiment in oxides is a powerful method to elucidate such difficult problems as the influence of the surrounding atmosphere on physical properties (for instance high-temperature plasticity). In the study of diffusion as a function of oxygen partial pressure, it is customary to calculate the slope of the diffusion coefficient–P_{O_2} curve and to compare this with the theoretical models. The technical difficulties inherent to such experiments added to the basic assumption of the theoretical model often lead to dubious interpretation.

In fact, additional insight concerning the point defect diffusion mechanism and the influence of experimental parameters could be gained by comparison with other types of experiments such as conductivity, thermodefect emission, thermogravimetry, etc. Unfortunately, such systematic studies of an oxide are often lacking and all conclusions concerning the diffusion mechanism and the consequence on other physical properties may therefore be extremely circumspect.

Appendix

The well-known formalism of Kroger and Vink (13) is employed for the description of the point defect disorder present in the matrix of Y_2O_3. With Y_2O_3, the following symbols are used:

V_o^x, V_y^x: Oxygen and yttrium vacancies with zero effective charge on oxygen and yttrium site.

O_i^x, Y_i^x: Neutral interstitial of oxygen and yttrium.

$V_o^{\cdot\cdot}$, $V_y^{\prime\prime\prime}$: Oxygen and yttrium vacancies doubly and triply ionized (effective charge 2+ and 3−).

$O_i^{\prime\prime}$, $Y_i^{\cdot\cdot\cdot}$: Oxygen and yttrium interstitial of actual charge 2− and 3+ (in this case the actual charge is equal to the effective charge).

O: The symbol of the perfect crystal.

The three types of disorder described in the following table may be considered in Y_2O_3.

Schottky	$O = 3V_o^x + 2V_y^x \rightarrow [V_o^x]^3[V_y^x]^2 = K_s$
Frenkel	$Y_y^x = Y_i^x + V_y^x \rightarrow [Y_i^x][V_y^x] = K_F$
Anti-Frenkel	$O_o^x = O_i^x + V_o^x \rightarrow [O_i^x][V_o^x] = K_{AF}$

K_S, F_F, and K_{AF} are the equilibrium constants of each disorder; brackets are the symbol of concentration in unit of site fraction. For details of the characteristic equilibrium of Schottky, Frenkel, and Anti-Frenkel disorder in Y_2O_3, see Refs. (2) and (3).

The characteristic equilibrium of Schottky and Anti-Frenkel, concerning fully ionized, are summarized in the following table:

Schottky	Anti-Frenkel
$3/2\ O_2(g) = 3O_o^x + 2V_y^x \rightarrow K_{V_y}\ (H_{V_y})$	$O_o^x = 1/2\ O_2(g) + V_o^x \rightarrow K_{V_o}\ (H_{V_o})$
$O_o^x = 1/2\ O_2(g) + V_o^x \rightarrow K_{V_o}\ (H_{V_o})$	$1/2\ O_2(g) = O_i^x \rightarrow K_{O_1}\ (H_{O_1})$
$V_y^x = V_y^{\prime\prime\prime} + 3h \rightarrow K_a\ (E_a)$	$V_o^x = V_o^{\cdot\cdot} + 2e \rightarrow K_b\ (E_b)$
$V_o^x = V_o^{\cdot\cdot} + 2e \rightarrow K_b\ (E_b)$	$O_i^x = O_i^{\prime\prime} + 2h \rightarrow K_d\ (E_d)$
$O = 3V_o^{\cdot\cdot} + 2V_y^{\prime\prime\prime} \rightarrow K_s^{\prime\prime}\ (H_s^{\prime\prime})$	$O_o^x = V_o^{\cdot\cdot} + O_i^{\prime\prime} \rightarrow K_{AF}^{\prime\prime}\ (H_{AF}^{\prime\prime})$
$O = e + h \rightarrow k_g\ (E_g)$	$O = e + h \rightarrow K_g\ (E_g)$
$p + 2[V_o^{\cdot\cdot}] = n + 3[V_y^{\prime\prime}]$	$p + 2[V_o^{\cdot\cdot}] = n + 2[O_i^{\prime\prime}]$
$K_s^{\prime\prime} = \dfrac{K_a^2\ K_{V_o}^3\ K_b^3}{K_g^6}$	$K_{AF}^{\prime\prime} = \dfrac{K_b\ K_{V_o}\ K_d\ K_{O_1}}{K_g^2}$

K_i and H_i are the equilibrium constants and enthalpy, respectively, corresponding to each equilibrium; H_i is the enthalpy of formation; and E_i is the energy of ionization.

Acknowledgments

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