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SELF-DIFFUSION OF Er AND Hf IN PURE AND
 HfO_2 -DOPED POLYCRYSTALLINE Er_2O_3

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Based on a M.S. thesis submitted to Iowa State University

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Self-diffusion of Er and Hf in pure and
HfO₂-doped polycrystalline Er₂O₃

by

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ABSTRACT*

Using a tracer sectioning technique, the self-diffusion of Er and Hf was measured over the approximate temperature interval of 1600 to 1970°C in pure and HfO₂-doped polycrystalline Er₂O₃. Up to about 10 m/o HfO₂ dopant level, the Er self-diffusion coefficients followed a relationship based on cation vacancies being the principal mobile defects present and available for cation diffusion. Above 10 m/o HfO₂, deviation from this relationship occurred, which was apparently due to clustering of cation vacancies and oxygen interstitials around the dopant hafnia ion. The activation energy for the self-diffusion of Er in pure Er₂O₃ was 82.2 Kcal/mole and increased with the HfO₂ dopant level present.

The self-diffusion of Hf was measured in pure Er₂O₃ having two impurity levels, and a separation of the grain boundary and volume diffusion was possible. The volume diffusion of Hf showed both extrinsic and intrinsic behavior with the transition temperature increasing with the impurity level present in Er₂O₃. The activation energy for Hf volume diffusion in the intrinsic region was very high, i.e. 235 ± 9.5 Kcal/mole. The grain boundary diffusion was apparently extrinsic over the entire temperature interval. Very low Hf self diffusion rates were found in both pure and HfO₂ doped

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Er_2O_3 compositions apparently due to a strong association between the Hf ions and both the vacant cation sites and interstitial oxygen ions present. Despite this clustering effect, the HfO_2 dopant increased the Hf volume diffusion coefficients approximately one order of magnitude over the values found in pure Er_2O_3 .

INTRODUCTION

The study of diffusion phenomena in the rare earth oxides, particularly in the cubic rare earth oxides such as Er_2O_3 , is a continuing part of a number of investigations at the Ames Laboratory into the behavior of materials possessing fluorite and fluorite-related structures. Er_2O_3 possesses the rare earth oxide Type C (REOC) structure (1). This phase shows a large region of solid solubility for HfO_2 (up to 25% HfO_2), Figure 1 (2). This wide composition range permits the investigation of the effects of dopant level as well as temperature on diffusion processes (including grain boundary diffusion) in polycrystalline Er_2O_3 - HfO_2 solid solutions of the REOC structure.

This study utilized a radioactive tracer serial sectioning technique to measure self-diffusion coefficients for Er and Hf in pure and HfO_2 doped Er_2O_3 in the compositional solid solution region 0-20% HfO_2 over the temperature range 1600-1970°C.

STRUCTURE OF Er_2O_3 AND HfO_2

Erbium, atomic number 68, is a member of the group of elements called the lanthanides (atomic numbers 57 through 71). Erbium has a stable +3 valence and forms the sesquioxide (Er_2O_3), which has the rare earth oxide type C (REOC) structure (1a3) and has a melting point of about 2400°C (2). Hafnium, atomic number 72, has a stable +4 valence and forms the very refractory dioxide (HfO_2) having a melting point in excess of 2800°C (2). Hafnia in pure form can exist in either the monoclinic ($\text{P}2_1/\text{c}$) (3) or the tetragonal (4) structure depending on the temperature. The monoclinic structure is stable below approximately 1700°C , and above 1700°C hafnia undergoes a reversible diffusionless polymorphic transformation to the tetragonal form (5). This transformation takes place over a large temperature interval as shown by hysteresis in thermal expansion upon heating and cooling (6). Because of a specific volume difference of approximately 3% in the two structures, this transformation is destructive to a densely sintered specimen. A number of rare earth oxides including Er_2O_3 as well as CaO , MgO , and Y_2O_3 have been used to "stabilize" HfO_2 by forming a cubic fluorite solid solution structure (2,7). Figure 1 shows that additions of 10 to 50% Er_2O_3 produce a single phase region consisting of a fluorite solid solution.

The phase of interest in this study exists at the other

Figure 1. Proposed phase diagram for the HfO_2 - Er_2O_3 system (2)

end of this binary system. Figure 1 shows the large region of solid solution of the cubic REOC structure type which exists from pure Er_2O_3 to approximately 25% HfO_2 . The REOC structure of pure Er_2O_3 may be described as an altered fluorite structure which has the cations in a face-centered cubic arrangement and the anions in three-fourths of the tetrahedral sites (1). The true fluorite structure ($\text{Fm}\bar{3}\text{m}$) contains anions in all of the tetrahedral locations (8).

The REOC unit cell contains sixteen sesquioxide (Er_2O_3) formula units, and may be viewed as a cube made up of eight face-centered cubic "fluorite" subcells with an ordered omission of one-fourth of the anions in such a way that each erbium is 6-coordinated. The resulting REOC cell has body-centered cubic symmetry. The omission of one-quarter of the anions does give a slight displacement relative to a true fluorite structure of three-fourths of the cations amounting to about 3% of the unit cell edge length (9). The MO_6 groups (consisting of a cube with anion sites at each corner and a cation in the body-centered position) share edges such that the unoccupied oxygen sites are arranged in nonintersecting strings along the four $\langle 111 \rangle$ directions of the cubic cell (10). It can be expected that these nonintersecting strings of unoccupied oxygen sites will be important to diffusion processes in these materials. Two kinds of MO_6 cube groups are present in which the two unoccupied oxygen sites may be

at the extremes of either a face diagonal ($3/4$ of the MO_6 cubes) or a body diagonal ($1/4$ of the MO_6 cubes). The cations occupy essentially the same positions in both REOC and the true fluorite structures. Foex and Traverse (11) have also reported the existence of a high temperature form of Er_2O_3 designated type H and related to the hexagonal type "A" rare earth oxide structure common to the lighter lanthanides at low temperature. This C $\rightleftharpoons$ H transformation is a reversible one, however, occurring around 2250°C .

LITERATURE REVIEW

Diffusion in Rare Earth Oxides and Related Structures

The literature on diffusion in the rare earth oxide systems is limited. Berard and Wilder (12) investigated cation self-diffusion in polycrystalline Er_2O_3 and Y_2O_3 and described the results with the following Arrhenius expressions:

$$\text{For } \text{Er}_2\text{O}_3 \quad D_{\text{Er}} = 1.48 \exp(-102,200/RT) \text{ cm}^2/\text{sec} \quad (1400-1700^\circ\text{C})$$

$$\text{For } \text{Y}_2\text{O}_3 \quad D_{\text{Y}} = 1.65 \times 10^{-2} \exp(-69,200/RT) \text{ cm}^2/\text{sec} \quad (1400-1670^\circ\text{C})$$

The much larger activation energy for the self-diffusion of Er in Er_2O_3 was attributed to a mass effect. Using a thermobalance to observe oxidation-reduction reactions, Berard et al. (13) also measured the diffusion of oxygen in single crystals of Er_2O_3 and Y_2O_3 . These results are described by:

$$\text{For } \text{Er}_2\text{O}_3 \quad D_{\text{O}} = 4.76 \times 10^{-5} \exp(-30,100/RT) \text{ cm}^2/\text{sec} \quad (1060-1292^\circ\text{C})$$

$$\text{For } \text{Y}_2\text{O}_3 \quad D_{\text{O}} = 6.01 \times 10^{-6} \exp(-19,600/RT) \text{ cm}^2/\text{sec} \quad (1064-1276^\circ\text{C})$$

These results show that the phenomenon of rapid anion movement which occurs in the true fluorite structure (14) also occurs in the REOC structure.

Interdiffusion studies have been carried out in several polycrystalline rare earth oxide systems. Schiavi (15) investigated interdiffusion in the Er_2O_3 - HfO_2 system, and by extrapolation of the interdiffusion coefficients to 0% HfO_2 ,

he estimated the impurity diffusion coefficient of Hf in pure Er_2O_3 to be:

$$D_{s,\text{Hf}} = 3.28 \times 10^{10} \exp(-209,000/RT) \text{ cm}^2/\text{sec}$$

There was a large uncertainty associated with this value, but it indicated a very large activation energy to be associated with the movement of Hf in Er_2O_3 . Gessel (16) investigated interdiffusion in the polycrystalline rare earth oxide systems $\text{Er}_2\text{O}_3\text{-Y}_2\text{O}_3$ and $\text{Er}_2\text{O}_3\text{-Ho}_2\text{O}_3$.

Diffusion studies in true fluorite structure materials have been much more numerous. Matzke (17) has reviewed the published results for UO_2 and PuO_2 . Rhodes and Carter (18) have presented results for diffusion of both Ca and Zr in calcia-stabilized zirconia. Numerous diffusion studies have been performed in fluorite structure alkaline earth halides because of their availability in single crystal form. Several studies have been done on the tracer self-diffusion of Ca in CaF_2 (Matzke and Lindner (19), Short and Roy (20), Berard (21), King and Moreman (22), and Kucheria (23)). Aside from Short and Roy, who did work in polycrystalline CaF_2 , the other studies were done in single crystal CaF_2 and gave activation energies of approximately 100 Kcal/mole. Matzke (24), King and Moreman (22), and Kucheria (23) have also measured Ca tracer self-diffusion in CaF_2 doped with hypervalent cations (Sm^{+3} and Y^{+3}). Kucheria especially noted a large increase in D_{Ca}^* as a function of dopant level. In a related study,

Baker and Taylor (25) have investigated the tracer self-diffusion of Sr in CaF_2 , SrF_2 , and BaF_2 . Interdiffusion studies have also been conducted in these systems: CaF_2 - SrF_2 (26), YF_3 - CaF_2 (27), and SrF_2 - BaF_2 (28).

As is true for the REOC structure materials, anion self-diffusion rates are much greater than cation self-diffusion rates in materials possessing the true fluorite structure. Matzke (24) studied the self-diffusion of fluorine in BaF_2 and CaF_2 and found that anion vacancies and interstitials were both much more mobile than cation defects. Using ionic conductivity measurements, the fluorine mobility as well as the predominate defect present in the fluorite structure has been determined in a number of the fluorides (CaF_2 - YF_3 (29), NaF and YF_3 -doped CaF_2 (30), and CaF_2 , SrF_2 , and BaF_2 (31)). The results of these studies showed a low activation energy for the movement of the fluorine ion with the anion-Frenkel defect as the predominant defect in the pure fluoride material. Ionic conductivity measurements have also been used to determine the self-diffusion coefficient of oxygen in calcia-stabilized zirconia (32). In the region of fluorite solid solution, it was shown that the oxygen ion was very mobile with a transference number of about 1.

Grain Boundary Diffusion in Oxides

In polycrystalline materials, grain boundary diffusion can appreciably enhance overall material transport. The

grain boundary diffusion process can be characterized by a diffusion coefficient D_{gb} that is usually considerably larger than the volume diffusion coefficient, D_v . If grain boundary diffusion is responsible for a significant fraction of the total material transport, its contribution can be separated from volume diffusion and the magnitude of D_{gb} can be determined. Levine and MacCallum (33) have shown that, under certain experimental conditions, if D_{gb} is at least 10^4 times greater than D_v , it is possible that the two contributions can be separated in the diffusant concentration profile.

A number of methods for data analysis capable of extracting values of D_{gb} from diffusion profiles have been proposed including those of Fisher (34), Whipple (35), Levine and MacCallum (33), and Suzuoka (36). Details of these methods, particularly the latter, are given below in the section on "Diffusion Theory".

Grain boundary diffusion has been measured in a number of metal systems but in only a very few ceramic systems. An excellent review of grain boundary diffusion in metals has been presented by Gleiter and Chalmers (37). A comparison of grain boundary diffusion and grain boundary widths in metals and ceramics has been presented by Mistler and Coble (38). Using grain growth, sintering, diffusion and/or creep data, they found that in high purity metals the grain boundary widths were on the order of a few atomic diameters, whereas

in ionic materials the effective grain boundary widths were orders of magnitude larger. Both anion (39) and cation (40) grain boundary diffusion have been measured in sodium chloride. Each study found enhanced transport along the grain boundaries due to segregated or precipitated residual impurities. By looking at the energy of activation for host atoms diffusing in the lattice and in the grain boundary, Gupta (41) has investigated the influence of solute segregation on grain-boundary energy and self-diffusion.

Grain boundary diffusion has been studied in several oxide systems. Wuensch and Vasilos (42) have investigated the grain boundary diffusion of Ni and Co in MgO, and have found the grain boundary diffusion to be dependent on the amount of impurities present within the host oxide. An investigation by Rhodes and Carter (18) into the self-diffusion of Zr and Ca in calcia-stabilized zirconia showed grain boundary diffusion enhancement for both cations. Both lattice and grain boundary diffusion of uranium have been measured in UO_2 by Yajima, et al. (43) and in ThO_2 and ThO_2 - UO_2 solid solutions by Furuya (44). The importance of impurity segregation at grain boundaries on the overall enhancement of diffusion movement along grain boundaries appears to be an important factor in most of these studies. This effect combined with the lattice diffusion rate determines whether grain boundary enhancement will be apparent in a material.

Defect Structures

A survey of the defect structures of Er_2O_3 , HfO_2 -doped Er_2O_3 , and similar systems is helpful in understanding the diffusion processes occurring in these materials. Schieltz (45) and Macki (46) have shown the anion-Frenkel defect to be the predominant intrinsic defect in stoichiometric REOC structure materials. Also, in the analogous fluorite materials, Franklin (47) has shown the principal intrinsic defect to be the anion-Frenkel type. The reaction for the formation of this defect can be written as:¹

Tallan and Vest (48) have indicated that Y_2O_3 , which is very similar to Er_2O_3 , will be hyperstoichiometric when heated in air. Under these conditions, they have given the most probable defect reaction as:

The defect structure of HfO_2 -doped Er_2O_3 has been studied by Johnstone (2). He found that, as Hf substituted for Er in Er_2O_3 solid solution, charge neutrality was maintained by formation of an anion interstitial defect, i.e.,

¹The standard Kroeger-Vink notation is used in writing the defect reactions.

In a similar system, ThO₂-doped Gd₂O₃, Macki (46) found two defect structures over the temperature interval of 800°C to 1400°C depending on the prevailing P_{O₂}. At low P_{O₂},

and at high P_{O₂} (1 atm)

It should be noticed that at 1 atmosphere this is the same defect reaction as Johnstone found for HfO₂-doped Er₂O₃. In another similar system, ZrO₂-doped Y₂O₃, Brattan (49) found the predominant defects present to be oxygen interstitials and Subbarao et al. (50) found the same defects in ThO₂-doped Y₂O₃.

Anion interstitials have also been found to be the charge-compensating defects in fluorite materials doped with hypervalent cations, e.g. CaF₂ doped with Y⁺³ (Cheetham et al. (51)) and UO_{2+x} doped with U⁺⁶ (Matzke (52)).

A summary of the results of these studies shows the predominate defect present in pure materials possessing the fluorite and the fluorite related REOC structure to be the anion-Frenkel defect. In materials possessing this structure but doped with a hypervalent impurity, anion interstitials will be the predominate charge compensation defects.

DIFFUSION THEORY

Self-diffusion, i.e. diffusion in the absence of a chemical concentration gradient, can be studied with the use of radioactive tracers. When this is done, the process is commonly referred to as "tracer self-diffusion" with gradients in tracer concentration providing the impetus for changes in the distribution of the tracer species with time.

The analysis of self-diffusion follows the general postulate proposed by Fick (53) for an isothermal, isobaric, binary, single phase system. He described the unidirectional movement of a quantity of a material passing per unit time through a unit area perpendicular to the diffusion direction as being proportional to the negative concentration gradient in the diffusion direction. This is described by the following expression:

$$J_i = -D_i \frac{\partial c_i}{\partial x} \quad (6)$$

Where J_i is the flux of species i , D_i is a proportionality coefficient called the diffusion coefficient for species i , c_i is the concentration of species i , and x is the diffusion distance coordinate. The relationship given in Eq. 6 is usually referred to as Fick's first law, and serves to define the diffusion coefficient in terms of observable quantities. J_i and $(\partial c_i / \partial x)$ are both instantaneous local quantities unless a steady state situation has been achieved.

Fick's second law

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x} \left(D_i \frac{\partial c_i}{\partial x} \right) \quad (7)$$

is used to evaluate the diffusion coefficient under nonsteady-state conditions where the concentration of i at some location is dependent on time.

If the assumption is made that the diffusion coefficient (D_i) is independent of composition (and therefore independent of position), the following expression can be written.

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} \quad (8)$$

The assumption that the diffusion coefficient is independent of position is valid for tracer self-diffusion where there is no gradient in chemical concentration but only of isotopic concentration.¹

Crank (54) and Jost (55) have both developed the solution to Eq. 8 for diffusion from a "thin film" diffusant source, which is derived from the following model. Two semi-infinite rods share an interface at $x=0$. At time $t=0$, all of the diffusant species i is confined to a plane located at $x=0$. The general form of the so-called thin film solution, i.e. the concentration of species i at various locations x after

¹The assumption is made that D_i is the same for all isotopes of species i . This is true unless the ratios of isotopic masses are significantly different from unity as would be the case, e.g., for various isotopes of hydrogen (56).

time t , is given by the following expression:

$$C_i = \frac{\alpha}{2\sqrt{\pi D_i t}} \exp\left[-\frac{x^2}{4D_i t}\right] \quad (9)$$

with the total quantity of diffusant fixed at all times by,

$$\alpha = \int_{-\infty}^{\infty} C_i(x, t) dx \quad (9a)$$

In a tracer self-diffusion experiment, species i would be a radioactive tracer.

Since it is very difficult to sandwich a thin film of a radioactive tracer between two long cylinders, Eq. 9 is modified to describe the more convenient semi-infinite geometry (54). This situation allows the application of a thin tracer film onto one end of a specimen which is thick enough to be considered semi-infinite in extent (thickness $> 5\sqrt{Dt}$). The boundary conditions for the semi-infinite situation are:

$$\begin{array}{lll} x > 0 & C^* \rightarrow 0 & \text{as } t \rightarrow 0 \\ x = 0 & C^* \rightarrow \infty & \text{at } t = 0 \end{array}$$

where superscript (*) indicates that a tracer quantity is being specified. Equation 9a applies where the integral is taken from $x = 0$ to $x = +\infty$. Using reflection and superposition procedure for the boundary $x = 0$, the modification of Eq. 9 is simply the addition of the two solutions for the infinite geometry. This yields the following equation:

$$C_{(x,t)}^* = \frac{\alpha}{\sqrt{\pi D^* t}} \exp\left[-\frac{x^2}{4D^* t}\right] \quad (10)$$

After diffusion has occurred from the thin film source into the semi-infinite specimen for an appropriate length of time, the distribution of tracer as a function of depth is determined by analyzing the tracer concentration in a series of thin sections taken perpendicular to the diffusion direction (x-direction). The tracer self-diffusion coefficient (D^*) is determined from a plot of $\ln A^*$ vs x^2 where A^* is the normalized activity of the section and x is the distance from the surface initially containing the tracer to the midpoint of the section. For pure volume diffusion, i.e. for a uniform medium obeying Eq. 10, this plot should yield a straight line with a slope of $(-1/4D^*t)$ where t is the diffusion anneal time and D^* is the tracer self-diffusion coefficient.

Random Walk Approach

The random walk description of diffusion is based on an atomistic rather than the phenomenological viewpoint previously described. This approach can give additional insight into the atomic-level mechanisms controlling diffusion. For three-dimensional random walk diffusion processes (isotropic medium) the following equation for the self-diffusion coefficient has been developed (57):

$$D = \frac{1}{6} v \ell^2 \quad (11)$$

where v is the total jump frequency and ℓ is the jump distance. A further breakdown of the jump frequency (v) yields

$$v = nv_a P_v \quad (12)$$

where n is the number of adjacent equivalent sites, v_a is the jump attempt frequency to a specific adjacent site, and P_v is the probability that an attempted jump will be successful.

v_a can be expressed as

$$v_a = v_o \exp[-\Delta G_m/RT] = v_o \exp[\Delta S_m/R] \exp[-\Delta H_m/RT] \quad (13)$$

where v_o is the fundamental oscillation frequency of an atom (usually taken as the Debye frequency), and ΔG_m is the free energy associated with the atom being moved into its saddle-point configuration, usually called the energy of motion. P_v can be taken as the probability that the given site toward which a jump is attempted will be unoccupied (and therefore will allow the jump to succeed). If atoms are jumping by means of a vacancy mechanism, P_v can be written (for the intrinsic case) as

$$P_v = \exp[-\Delta G_F/RT] = \exp[\Delta S_F/R] \exp[-\Delta H_F/RT] \quad (14)$$

where ΔG_F is the free energy of formation of mobile vacancies. In the case of doped systems, the expression for P_v can be much more complex than Eq. 14. Recombining and rearranging the terms gives

$$D = \frac{n \lambda^2 v_o}{6} \exp[(\Delta S_F + \Delta S_m)/R] \exp[-(\Delta H_F + \Delta H_m)/RT] \quad (15)$$

An examination reveals the similarity of Eq. 15 with the Arrhenius equation for diffusion.

$$D = D_0 \exp[-Q/RT] \quad (16)$$

where the activation energy Q can be identified as

$$Q = \Delta H_F + \Delta H_m \quad (17)$$

where ΔH_F is an enthalpy term associated with the interplay of the various defect reactions responsible for controlling the concentration of the mobile defects and ΔH_m is the enthalpy of motion for the mobile species.

Grain Boundary Diffusion

The nature of polycrystalline materials with two different "parallel" media through which diffusion proceeds simultaneously, i.e., the crystal (volume diffusion) and the grain boundary, each with different diffusion coefficients, makes Eq. 10 valid only if transport along the boundaries is insignificant. When this is not the case, the diffusion profile resulting from a thin film experimental setup will not be linear when plotted as $\ln A^*$ vs x^2 .

The analysis of grain boundary diffusion from the diffusant concentration profile in a polycrystalline specimen has been carried out in a number of ways. Fisher (34) developed a model for grain boundary diffusion which predicted a linear relationship between $\ln A^*$ and penetration distance. Whipple (35), in further work, proposed that grain boundary diffusion would produce a linear plot of $\ln A^*$ versus penetration distance raised to the 4/3 power. Levine and MacCallum

(33) have also proposed a method for analyzing concentration profiles in polycrystalline specimens in order to extract the grain boundary contribution. All of these analysis methods are based, however, on a semi-infinite diffusant source. Suzuoka (36,58,59) has analyzed the grain boundary diffusion problem for a thin-film diffusant source, and his procedure was applied in this study whenever significant grain boundary effects were present. In this method, the diffusant profiles are plotted as $\ln A^*$ versus $x^{6/5}$, with the linear part of the curve, which occurs at large depths, being due to the pure grain boundary contribution. The slope of this linear portion, γ , has been shown by Suzuoka to be related to D_{gb} and D_v by the following relationship:

$$.973 \log(\Delta-1) = 6.567 - 1.644 \log \gamma - \log D_v t \quad (18)$$

where

$$\Delta = D_{gb}/D_v.$$

When D_v is unknown, as in this study, a method was used which allows the simultaneous determination of D_v and D_{gb} using an assumed standard grain boundary width of 5×10^{-8} cm.¹ The following relationship developed by Suzuoka, which defines the concentration profile of the tracer material in the host structure after some time t , was used in the analysis.

¹Any numerical value for grain boundary width can be used; 5×10^{-8} cm is standard for metal systems, but there is considerable evidence (e.g. 38) that the width in nonmetals may be considerably greater.

$$C(\eta, t) = \frac{\alpha}{\sqrt{\pi D_V t}} \left(C_1 + \frac{1}{n} \bar{C}_2 \right) \quad (19)$$

where $C_1 = \exp(-\eta^2/4)$ and is the concentration factor associated with pure volume diffusion

$$\bar{C}_2 = \int_1^\Delta \left(\frac{\eta^2}{\sigma} - 2 \right) \exp\left(\frac{-\eta^2}{4\sigma}\right) \left(\frac{\Delta-\sigma}{\Delta-1} \left(\frac{e^{-\chi^2}}{\sqrt{\pi}} - \chi \operatorname{erfc}\chi \right) \right) \frac{d\sigma}{\sigma^{3/2}}$$

is the concentration fraction associated with pure grain boundary diffusion.

$$\chi = \sqrt{\frac{\Delta-1}{\Delta-\sigma}} \left(\frac{\sigma-1}{\beta} \right), \quad \eta = \frac{x}{\sqrt{D_V t}}$$

$$n = \frac{b}{\sqrt{D_V t}} \quad \text{and} \quad \beta = 2a(\Delta-1)\sqrt{D_V t}$$

$2a$ = grain boundary thickness which is taken to be 5×10^{-8} cm

$2b$ = mean linear grain size

The numerical values of $\bar{C}_2$, the grain boundary portion, have been tabulated by Suzuoka (36) for a series of values of β and η . Subtracting the grain boundary contribution from the overall diffusion permitted the calculation of the volume diffusion with the standard thin film solution. An example using the Suzuoka analysis is shown in Appendix A.

EXPERIMENTAL PROCEDURE

The Er_2O_3 used in this diffusion study was obtained as a powder from the Ames Laboratory Rare Earth Separation Group. The Er_2O_3 powders were obtained at two levels of purity; level A with a total impurity content of approximately 600 ppm, and level B with a total impurity content of approximately 250 ppm. Table 1 shows the spectrographic and wet chemical analysis of these two powders. The HfO_2 used as a dopant in Er_2O_3 was obtained from the Wah Chang Corporation (Albany, OR) and had the spectrographic analysis shown in Table 2.

All diffusion specimens were fabricated from reprocessed powders prepared by a process developed to give nearly theoretical densities in rare earth oxides (60). The as-received Er_2O_3 was dissolved in nitric acid and this acid solution was diluted to an oxide concentration of approximately 25 g/l. The HfO_2 was obtained as the oxychloride dissolved in a nitric acid solution.

Both pure Er_2O_3 and HfO_2 -doped Er_2O_3 (HDE) powders were made by the same process. The various HfO_2 dopant levels were achieved by mixing the acid solutions of $\text{Er}(\text{NO}_3)_3$ and $\text{Hf}(\text{NO}_3)_4$ together in the appropriate amounts. $\text{Er}(\text{OH})_3$ or $\text{Er}(\text{OH})_3$ - $\text{Hf}(\text{OH})_4$ compositions were precipitated from the acid solutions using dilute NH_4OH . Following precipitation, a washing procedure was followed to prepare a rapidly-drying very friable hydroxide powder. All the washes were carried out using a

Table 1. Emission spectrographic and chemical analyses of Er_2O_3 materials A and B

Element	Concentration (ppm)	
	A	B
Al	<30	<30
Ca ^a	<11	14
Cr	ND ^b	ND
Fe ^a	ND	5
Mg	<26	<26
Ni	30	30
Si ^a	500	194
Ta	<20	<20

^aWet chemical analysis.^bND = not detected.Table 2. Emission spectrographic analysis of HfO_2

Element	Concentration (ppm)	Element	Concentration (ppm)
Al	50	Ni	ND
Ca	500	Si	2000
Cu	150	Ta	ND
Fe	ND ^a	Ti	ND
Mg	150	Zn	320
Nb	ND		

^aND = not detected.

vacuum suction system coupled with a 5 μ m sintered glass filter. The first wash was done with distilled water to remove the soluble ammonium salts from the precipitate. This wash was followed by a series of washes with organic liquids, acetone and toluene. The first organic wash was done with acetone to replace the free water and create a miscible medium for the next wash of toluene. The toluene wash stripped the remaining free water from the hydroxide. A final acetone wash was used to remove the toluene and create a rapid drying medium. The drying and grinding were completed in a single step with a pre-heated (110°C) ceramic mortar and pestle. The ground powders were all sieved to pass 325 mesh.

The hydroxide powders were calcined in platinum crucibles at 960°C in air for three hours to convert them to the oxide form. Fabrication of the diffusion specimens was done with a 3/8" ID tungsten-carbide-lined steel die. One gram of the oxide powder was double-action pressed to about 10,000 PSI followed by ejection and subsequent isostatic pressing to 30,000 PSI.

The sintering of all diffusion specimens was carried out under vacuum of 3×10^{-4} torr in a Centorr (Model 15, Centorr Associates, Suncook, NH) furnace. This furnace consists of a watercooled stainless steel shell with a cylindrical tungsten mesh resistance heating element surrounded by tantalum and molybdenum radiation shields. The furnace temperature was

automatically controlled and monitored with a molybdenum sheathed W5%Re-W26%Re thermocouple.

The specimens were placed in a covered Er_2O_3 crucible and sintered at 2000°C for two hours following a $25^\circ\text{C}/\text{min}$ heating and cooling schedule. Following vacuum sintering, all diffusion specimens were reoxidized in air for a minimum of four hours at 1200°C .

Table 3 shows the sintered density of each composition, the corresponding sintered grain size, and the actual HfO_2 composition at each of the dopant levels as determined by wet chemistry. Densities of the reoxidized pellets were determined by water immersion and are reported as percent theoretical density. The theoretical densities for each composition were calculated from lattice parameters determined by Johnstone (2).

The microstructures of pure Er_2O_3 and each of the HDE compositions are shown in Figure 2. The grain sizes were measured by counting grain boundary intersections using a method described by Fullman (61). The actual HfO_2 compositions, as determined by chemical analysis, are shown to be very close to the nominal 5, 10, and 20 m/o HfO_2 levels based on initial nitrate solution concentrations.

Er-169 and Hf-175 were used as radioactive tracers for the diffusion study. The Er tracer was obtained by neutron activation in the Ames Laboratory Research Reactor, where

Table 3. Chemical compositions and sintered properties of Er_2O_3 and HfO_2 -doped Er_2O_3

Nominal composition (m/o)		Accurate chemical composition (m/o)		Average grain size (μm)	Typical sintered density (% of theoretical)
Er_2O_3	HfO_2	Er_2O_3	HfO_2		
100	-	100	--	269	98.9
95	5	94.96	5.04	10.5	99.8
90	10	89.31	10.69	9.4	99.9
80	20	79.73	20.27	20.5	99.9

Pure Er_2O_3

95 m/o Er_2O_3 5 m/o HfO_2

Figure 2. Microstructures of 0, 5, 10, and 20 m/o HfO_2 -doped Er_2O_3

90 m/o Er_2O_3 10 m/o HfO_2

80 m/o Er_2O_3 20 m/o HfO_2

Figure 2. (Continued)

pure Er_2O_3 was irradiated until 3.46 mg of the oxide powder gave an activity of approximately 50 $\mu\text{Ci/ml}$ when dissolved in dilute HCl . Er-169 has a 9.4 day half-life and decays by β emission to stable Tm-169. The Tm formed as Er-169 decays has the same valence as Er and is very close in size, so there was no influence on the diffusion rates due to transmutation product effects (62,63).

The Hf-175 was purchased as a chloride solution from Amersham-Searle Corp., Arlington Heights, IL. This isotope decays to stable Lu-175 by electron capture and gamma emission with a 75 day half-life. This daughter element (Lu) is also very similar to Er, so it would have no influence on the diffusion rates.

The tracer solution of Er-169 was used without any further dilution or carrier solution. The Hf-175 tracer solution of an approximate activity of 50 $\mu\text{Ci/ml}$ in distilled water was prepared and added to a chloride Er carrier solution having a concentration of 50 mg/ml of dissolved stable Er_2O_3 . Using this tracer level and assuming it to be distributed in a 10 μm thick Er_2O_3 film layer, a determination of the Hf dopant concentration was made. At this activity level, less than 0.1 ppm Hf is present in the Er_2O_3 diffusant source film, so insufficient Hf is introduced into the diffusion zone to significantly influence the defect structure.

Both the Hf-175 and Er-169 tagged thin-film diffusant

sources were formed from 60 μ l of tracer solution pipetted onto the specimen surface, which had first been ground flat by the same procedure used for sectioning described later. Following the grinding procedure the pellet surface was inspected for flaws and etched in dilute H_2SO_4 to give a better surface for the deposition of the tracer layer. The tracer film was slowly dried under controlled humidity and heated in air to 1000°C for two hours to convert all the material to an adherent oxide film. Optical observation at approximately 20X was made to insure that an oxide film was formed which was uniform in appearance. A sectioning analysis of a specimen activated in this manner showed no detectable activity at depths greater than 3 μ m.

All diffusion anneals were carried out with duplicate specimens in covered Er_2O_3 crucibles. Anneals up to 1715°C were performed in air in a gas/air fired Bickley furnace (Model 2150, Bickley Furnaces, Inc., Philadelphia, PA) with a 2 3/4" I.D. horizontal alumina muffle tube. The Er_2O_3 crucibles containing the diffusion specimens were placed inside the muffle tube, with the temperature during the diffusion anneals monitored with a type B thermocouple (Pt6Rh-Pt30Rh). The diffusion anneal temperature was controlled to an accuracy of $\pm 5^\circ C$. At temperatures greater than 1715°C, anneals were performed in a gas/oxygen fired Lemont furnace (Model LOF-3, Lemont Scientific, Inc., Lemont, PA) with a

vertical 3" I.D. stabilized ZrO_2 muffle tube. The Er_2O_3 crucibles containing the diffusion specimens were placed in the center of the furnace on a stabilized ZrO_2 pedestal. Temperatures during these diffusion anneals were monitored with a calibrated automatic optical pyrometer (Photomatic II, Pyrometer Instrument Co. Inc., Northvale, NJ), and the diffusion temperatures were controlled to an accuracy of $\pm 7^\circ\text{C}$. The Bickley furnace was controlled automatically from a set-point temperature, and the Lemont furnace temperature was manually controlled by adjusting the gas and oxygen ratio. The temperatures were recorded continuously in both systems to show any temperature deviations and give an accurate account of the total time of the diffusion anneal. The temperature and durations of the diffusion anneals using Er tracer are shown in Table 4, and the same information for diffusion anneals using Hf tracer is shown in Table 7.

Following a diffusion anneal, each diffusion specimen was mounted on a piece of 1/4" drill stock using Rigidax wax (Type W1, M. Argueso and Co., Inc., Namaroneck, NY) and a jig to insure parallel alignment. The drill stock was mounted in a lathe and the cylindrical surfaces of the specimens were turned to remove any effects of surface diffusion. Serial sectioning of the diffusion specimens was done using the same procedure used in previous diffusion studies (12,20). A turntable arrangement with a drill chuck for holding the dif-

fusion specimens was used for sectioning. 600 grit silicon carbide discs 1 3/4" in diameter were used for grinding off the sections. These discs were weighed prior to and after the sectioning with a Cahn microbalance (model G-2 electrobalance, Cahn Instruments Div., Cerritos, CA). These weights had a standard deviation of $\pm .004$ mg. The drill stock holding the diffusion specimens was mounted in the chuck assembly, and the silicon carbide disc secured in the holder on the turntable. The chuck was mounted slightly off-center on the disc, so that grinding deposited material in a circular pattern on the disc. The diffusion specimen mounted in the chuck was rotated in the opposite direction to the turntable to give uniform grinding of the surface of the diffusion specimen. From 1 to 10 μm was removed with each section, the amount varying with the depth of the section in the profile. The section thickness was based on the section weight, the area of the cylindrical diffusion specimen, and the specimen density. Based on an error of $\pm .00095 \text{ cm}^2$ in the area measurement, and the error involved in the weight measurement, the section thickness was determined to $\pm .08 \mu\text{m}$ (1 standard deviation).

Following sectioning and weighing of the disc, it was covered with transparent Scotch electrical tape (#5, 3-M Co., St. Paul, MN). The β^- radiation of Er-169 was counted by placing the disc under an end-window Geiger-Müller tube.

The output of the Geiger-Müller tube was recorded on a binary scaling unit. The γ radiation of Hf-175 was counted with a NaI (Tl activated) scintillation counter with the output recorded on a digital scaler unit.

Prior to sectioning each specimen, the background radiation was counted and recorded, so it could be subtracted from the total measured activity of each section. This permitted the calculation of the activity due only to the β or γ radiation from the radioactive tracer material present in the section. Since a radioactive decay process follows a Poisson distribution (64, p. 119), the standard deviation on the total number of counts is given by the following expression:

$$\sigma_S = (S)^{1/2} \quad (20)$$

where S is the total counts recorded. Although the total counts recorded was usually much greater, the counting times were adjusted when necessary so the total net counts recorded never fell below 1000. This permitted a maximum limit on the standard deviation of about 3% of the total counts recorded.

RESULTS AND DISCUSSION

Because of the experimental geometry employed, the tracer concentration profiles were expected to follow the thin-film solution to Fick's law (Eq. 10) which described the logarithm of tracer concentration (activity) as decreasing linearly with the square of the distance from the original surface of the diffusion specimen. This relationship will be linear only for pure volume diffusion; however, when additional transport mode such as grain boundary diffusion occur which are sufficiently fast, say 10^4 - 10^5 times faster than volume diffusion, the tracer concentration profiles will deviate from this linear relationship. Suzuoka (36) has shown that a grain boundary contribution will appear as a linear "tail" on a plot of $\ln$ activity vs distance to the $6/5$ power. The linear portion corresponds to a characteristic profile for pure grain boundary diffusion which can then be subtracted from the original profile. Once this is done, a thin film solution can be used in the normal way to determine the volume diffusion coefficients. The details of this procedure are given in Appendix A.

Recasting Eq. 10 in logarithmic form yields;

$$\ln A^* = \ln S + (x^2/4D^*t) \quad (21)$$

where A^* is a normalized activity, which is the measured activity in a section divided by the section thickness, x is the distance to the midpoint of the section, and t is the diffusion anneal time. The value of S is proportional to the

total amount of diffusant activity placed on the diffusion specimen.

The temperature dependence of the diffusion coefficients were fitted to an Arrhenius relationship:

$$D = D_0 \exp(-Q/RT) \quad (22)$$

where D_0 is a constant term called the frequency factor, R is the gas constant, T is the absolute temperature at which diffusion was carried out, and Q is a constant for the diffusion process called the activation energy.

Erbium Diffusion

The self-diffusion of Er was measured in pure Er_2O_3 (material A), and in 5, 10, and 20 m/o HfO_2 -doped Er_2O_3 . Duplicate specimens were used in diffusion anneals performed at 1614, 1715, 1780, and 1900°C. Figure 3 shows a characteristic concentration profile for the self-diffusion of Er in pure Er_2O_3 at 1780°C. On the same plot is shown a second profile for Er diffusion in 20 m/o HfO_2 -doped Er_2O_3 at 1614°C. Appendix B contains the individual profiles for the self-diffusion of Er for all compositions at each temperature. All tracer profiles for Er diffusing in pure Er_2O_3 shows some non-linearity in x^2 at great depths indicating a probable grain boundary diffusion effect. In no case, however, was the effect great enough to allow determination of a grain boundary diffusion coefficient for Er.

Table 4 contains the time of each diffusion anneal and

Figure 3. Concentration profiles for Er self-diffusion in pure Er_2O_3 and HfO_2 -doped Er_2O_3 .

Table 4. $D_{V,Er}^*$ for volume diffusion in pure and HfO_2 -doped Er_2O_3 (cm^2/s)

Temperature (°C)	Time (sec)	HfO ₂ dopant level (m/o)			
		0	5	10	20
1614	187,747	1.34×10^{-12}	1.09×10^{-11}	2.49×10^{-11}	1.08×10^{-11}
		1.99×10^{-12}		1.81×10^{-11}	
1715	234,900	5.56×10^{-12}	5.38×10^{-11}	6.94×10^{-11}	5.99×10^{-11}
		3.29×10^{-12}	5.31×10^{-11}	7.16×10^{-11}	5.81×10^{-11}
1780	16,740	1.24×10^{-11}	9.93×10^{-11}	2.87×10^{-10}	1.84×10^{-11}
			9.87×10^{-11}	1.96×10^{-10}	
1900	10,800	2.84×10^{-11}	2.26×10^{-10}	6.35×10^{-10}	4.68×10^{-10}
		2.68×10^{-11}	2.88×10^{-10}	7.78×10^{-10}	

the volume tracer self-diffusion coefficients ($D_{V,Er}^*$) of Er calculated from each of the concentration profiles using a least squares fit of the data to Eq. 21. The effect of the HfO_2 dopant concentration on the volume self-diffusion coefficients of Er is shown in Figure 4. It is seen that the addition of HfO_2 causes a sharp increase in $D_{V,Er}^*$ at all temperatures. The coefficients reach a maximum at about 10 m/o HfO_2 and then begin to decrease with further HfO_2 additions. The increase in $D_{V,Er}^*$ caused by the addition of 10 m/o HfO_2 is about one order of magnitude when compared with pure material at all temperatures.

In any diffusion process, the concentration of available sites for diffusion of the mobile species as well as the number of possible diffusion paths determine the overall transport of that species. This can be controlled to a certain extent by the intrinsic defects present in a pure material, or by the extrinsic defects generated in a material by the impurities present. An examination of the HfO_2 doping reaction in Er_2O_3 is helpful in understanding the dependence of $D_{V,Er}^*$ on the dopant concentration. When there is sufficient HfO_2 present to dominate intrinsic defects with respect to electrical neutrality requirements the following relationship develops:

$$[Hf_{Er}^{\bullet}] = 2[O_i''] = 2\left(\frac{N_{HfO_2}}{2 - N_{HfO_2}}\right) \quad (23)$$

Figure 4. Compositional dependence of Er volume self-diffusion coefficients in pure Er_2O_3 and HfO_2 -doped Er_2O_3

N_{HfO_2} is the mole fraction HfO_2 in solid solution, the brackets indicate the number of defects per R_2O_3 formula unit of crystal,¹ and the quantity $(N_{\text{HfO}_2}/(2-N_{\text{HfO}_2}))$ equals the fraction of cation sites occupied by Hf. Considering both the anion-Frenkel and the Schottky equilibria, the following reactions must be satisfied:

Writing the equilibrium constants for the reactions

$$K_{\text{AF}} = [\text{V}_\text{O}^{\bullet\bullet}][\text{O}_\text{i}^{\bullet\bullet}] = \exp\left[\frac{-\Delta G_{\text{AF}}}{RT}\right] \quad (26)$$

$$K_{\text{S}} = [\text{V}_{\text{Er}}]^2[\text{V}_\text{O}^{\bullet\bullet}]^3 = \exp\left[\frac{-\Delta G_{\text{S}}}{RT}\right] \quad (27)$$

Substituting Eq. 23 into Eq. 26,

$$K_{\text{AF}} = [\text{V}_\text{O}^{\bullet\bullet}] \frac{2N_{\text{HfO}_2}}{2(2-N_{\text{HfO}_2})} \quad (28)$$

Solving for $[\text{V}_\text{O}^{\bullet\bullet}]$,

$$[\text{V}_\text{O}^{\bullet\bullet}] = K_{\text{AF}} \frac{2-N_{\text{HfO}_2}}{N_{\text{HfO}_2}} \quad (29)$$

Substituting back into the expression for the Schottky equilibrium constant,

¹An R_2O_3 unit of the crystal consists of $\text{Er}_{2-x}\text{Hf}_x\text{O}_{3+x/2}$.

$$K_S = [V_{Er}''']^2 \left(\frac{2 - N_{HfO_2}}{N_{HfO_2}} \right)^3 K_{AF}^3 \quad (30)$$

Rearranging

$$[V_{Er}'''] = \frac{K_S^{1/2}}{K_{AF}^{3/2}} \left(\frac{N_{HfO_2}}{2 - N_{HfO_2}} \right)^{3/2} \quad (31)$$

Finally combining constants (at constant T)

$$[V_{Er}'''] = K' \left(\frac{N_{HfO_2}}{2 - N_{HfO_2}} \right)^{3/2} \quad (32)$$

If it is assumed that Er diffuses by a cation vacancy jump mechanism, the magnitude of $D_{V,Er}^*$ should be directly proportional to $[V_{Er}''']$. This simple analysis predicts a $(N_{HfO_2} / (2 - N_{HfO_2}))^{3/2}$ relationship for the dependence of $D_{V,Er}^*$ on the HfO_2 dopant level in Er_2O_3 .

A comparison of the actual compositional dependence of $D_{V,Er}^*$ with that predicted by Eq. 32 can be made. Table 5 contains a prediction of Er self-diffusion coefficients calculated using the vacancy concentration dependence due to the dopant level present in the following manner. Eqs. 11 and 12, developed from random walk considerations, predict the self-diffusion coefficient at constant temperature for cations moving by a vacancy jump mechanism will be directly proportional to P_V , the fraction of cation sites that are vacant. The fraction of cation sites vacant will simply be equal to $1/2[V_{Er}''']$ or, from Eq. 32,

Table 5. $D_{V,Er}^{**}$ calculated from Eq. 37

m/o HfO ₂	$\frac{N_{HfO_2}}{[2-N_{HfO_2}]}^{3/2}$	1614°C	1715°C	1780°C	1900°C
2	.0010152	2.69×10^{-12}	1.32×10^{-11}	2.45×10^{-11}	6.35×10^{-11}
3	.0018792	4.99×10^{-12}	2.44×10^{-11}	4.53×10^{-11}	1.18×10^{-10}
4	.0029154	7.74×10^{-12}	3.79×10^{-11}	7.03×10^{-11}	1.82×10^{-10}
5 ^a	.0041050	1.09×10^{-11}	5.34×10^{-11}	9.90×10^{-11}	2.57×10^{-10}
6	.0054390	1.44×10^{-11}	7.07×10^{-11}	1.31×10^{-10}	3.40×10^{-10}
7	.0069073	1.83×10^{-11}	8.98×10^{-11}	1.66×10^{-10}	4.32×10^{-10}
8	.0085052	2.26×10^{-11}	1.11×10^{-10}	2.05×10^{-10}	5.32×10^{-10}
9	.0102285	2.71×10^{-11}	1.33×10^{-10}	2.47×10^{-10}	6.40×10^{-10}
10	.0120745	3.21×10^{-11}	1.57×10^{-10}	2.91×10^{-10}	7.56×10^{-10}

^aValues of $D_{V,Er}^{*}$ actually measured at 5 m/o HfO₂.

$$P_V = \frac{1}{2}[V_{Er}'''] = \frac{K'}{2} \left(\frac{N_{HfO_2}}{2 - N_{HfO_2}} \right)^{3/2} = K'' \left(\frac{N_{HfO_2}}{2 - N_{HfO_2}} \right)^{3/2} \quad (33)$$

Thus, $D_{V,Er}^*$ is predicted to be

$$D_{V,Er}^* = \frac{1}{6} n v_o \lambda^2 K'' \left(\frac{N_{HfO_2}}{2 - N_{HfO_2}} \right)^{3/2} \exp\left(\frac{-\Delta G_m}{RT}\right) \quad (34)$$

At constant temperature (where K'' and the exponential term are constants)

$$D_{V,Er}^* = K_T \left(\frac{N_{HfO_2}}{2 - N_{HfO_2}} \right)^{3/2} \quad (35)$$

In order to eliminate K_T at each temperature, the value of $D_{V,Er}^*$ at 5 m/o HfO_2 was chosen as a normalizing factor. Thus,

$$\frac{D_{V,Er}^{**}}{(D_{V,Er}^*)_{5\%}} = \frac{K_T \left(\frac{N_{HfO_2}}{2 - N_{HfO_2}} \right)^{3/2}}{K_T \left(\frac{0.05}{2 - 0.05} \right)^{3/2}} = 243.55 \left(\frac{N_{HfO_2}}{2 - N_{HfO_2}} \right)^{3/2} \quad (36)$$

Where the double asterisk indicates a semi-empirical prediction. And thus, at each temperature,

$$D_{V,Er}^{**} = 243.55 (D_{V,Er}^*)_{5\%} \left(\frac{N_{HfO_2}}{2 - N_{HfO_2}} \right)^{3/2} \quad (37)$$

Plots of predicted diffusion coefficients based on the vacancy model vs mole fraction dopant are shown as solid lines in Figure 5. The experimentally determined diffusion coefficients at each dopant level are also shown on this plot. The

Figure 5. Predicted Er diffusion coefficients based on a vacancy diffusion model (predicted relationship, solid line; actual data, points)

experimentally-determined self-diffusion coefficients are seen to follow the general shape of the relationship developed for the compositional dependence of $[V_{Er}''']$ up to about 10 m/o HfO_2 . The agreement is quite good at 1900 and 1780°C, but somewhat less so at lower temperatures. At dopant levels above 10 m/o HfO_2 , the measured coefficients decreased (Fig. 4) and thus deviate drastically from the vacancy relationship (Fig. 5).

Figure 5 supports the assumption that V_{Er}''' are the primary diffusion sites over at least a limited dopant range, and it might be argued that this is true over a wider compositional range, but with clustering of V_{Er}''' and $Hf_{Er}^\bullet$ becoming more important at higher dopant levels. Hf diffuses more slowly than Er in Er_2O_3 (see next section) and hence such clustering may render a sizable fraction of vacant Er sites relatively immobile, making additional HfO_2 less effective in increasing Er diffusion. This could also account for closer adherence of measured $D_{V,Er}^*$ to predicted values over a wider dopant range at higher temperatures (Fig. 5). The extra thermal energy available at the higher temperatures may be providing the energy necessary to keep the clusters dissociated and most of the V_{Er}''' are mobile until higher dopant levels are involved.

The introduction of HfO_2 dopant increases the number of vacant cation sites, but it also generates O_i'' as the charge

compensating defect, Eq. 3. The introduction of the interstitial oxygens, which are most likely associated with the $\text{Hf}_{\text{Er}}^{\bullet}$, will impede the pathway of the diffusing Er ion. Figure 6 shows three MO_6 groups such as exist in pure Er_2O_3 with a vacant erbium site (V_{Er}''') in the lower right cube. For movement of the Er^{+3} in the left cube to the V_{Er}''' site, the most probable path (least restrictive) will be through or in the direction of the interstitial oxygen site (I^*). However, as HfO_2 is added and the extra oxygen associated with this Hf ion is added into the structure, some interstitial oxygen sites will be filled. Figure 7 shows a situation where a Hf^{+4} has substituted onto an erbium site and the associated oxygen went on the interstitial site (I^*). Now, in order for the Er ion in the left cube to move into the vacancy in the lower right cube, it must pass through a square array of oxygen ions to an intermediate interstitial location directly above the vacancy and then through a second square array of oxygen ions to get to the adjacent vacant cation site. As more HfO_2 is added into the structure, a larger fraction of the Er will be required to move via this more restrictive pathway.

The temperature dependence of the Er self-diffusion coefficients is shown in Figure 8 for each of the compositions investigated. Table 6 contains the Arrhenius constants (D_0 and Q with uncertainties of one standard deviation) calculated using a least squares fit of these data. Berard (10) has made

Figure 6. Configuration of MO_6 groups in pure Er_2O_3 .

Figure 7. Configuration of MO_6 groups in HfO_2 -doped Er_2O_3 showing a substitutional hafnium and oxygen interstitial

Figure 8. Temperature dependence of Er volume diffusion coefficients in pure and HfO_2 -doped Er_2O_3 compositions

Table 6. Arrhenius constants for Er volume diffusion in Er_2O_3 and HfO_2 -doped Er_2O_3

Composition m/o		D_0	Q
Er_2O_3	HfO_2	cm^2/s	Kcal/mole
100 (this study)	-	$5.27^{+1.22}_{-0.92} \times 10^{-3}$	82.2 ± 5.8
100 (12)	-	1.48	102.2
95	5	$1.15^{+0.21}_{-0.18} \times 10^{-1}$	85.5 ± 5.5
90	10	$1.46^{+0.32}_{-0.26} \times 10^1$	102.3 ± 5.5
80	20	$5.16^{+1.09}_{-0.90} \times 10^1$	108.8 ± 7.5

$D_{V,Er}^*$ measurements in pure Er_2O_3 at lower temperatures than this study, and reported an activation energy 20 Kcal/mole greater than found for pure Er_2O_3 here (102.2 Kcal/mole compared to 82.2 Kcal/mole). Both studies were conducted in the same manner, although greater errors in measurement of penetration distances were involved in the earlier study. Berard used hot-pressed Er_2O_3 which had a much smaller grain size and a somewhat lower purity than the Er_2O_3 used in this study. These differences apparently are of importance in activation energy considerations.

The activation energy for the self-diffusion of Er increased with the dopant level present in Er_2O_3 as shown in Figure 9. The addition of HfO_2 up to 5 m/o had apparently only a small effect on the activation energy, increasing it by approximately 3 Kcal/mole. Between 5 m/o HfO_2 and 10 m/o HfO_2 dopant levels there was apparently a significant increase in the activation energy of approximately 18 Kcal/mole. As discussed previously and illustrated in Figures 5 and 6, a possible explanation is that as the diffusion paths become obstructed by O_i'' introduced to compensate for $Hf_{Er}^{\bullet}$, the energy of motion Eq. 34 increases dramatically. The activation energy undergoes an additional but somewhat smaller increase as dopant is increased from 10 m/o to 20 m/o HfO_2 , perhaps as a saturation value is reached. Alternatively, at higher dopant levels, the O_i'' may be clustering preferentially around

Figure 9. Compositional dependence of activation energy for Er self-diffusion in pure and HfO_2 -doped Er_2O_3

substitutional $\text{Hf}_{\text{Er}}^{\bullet}$ and thus having less widespread blocking effects for moving Er ions. It may be significant that 20 m/o HfO_2 is nearly the solubility limit in Er_2O_3 and thus, at this composition, extensive clustering of $\text{Hf}_{\text{Er}}^{\bullet}$ and O_i'' is expected as regions of the crystal take on the configuration of the HfO_2 phase (fluorite) saturated with Er_2O_3 .

In summary, the experimental results for Er diffusing in pure and HfO_2 -doped Er_2O_3 suggest that several competing phenomena are occurring simultaneously. As HfO_2 is added, the tetravalent Hf substituting for trivalent Er causes additional V_{Er}''' to be generated. At the same time, the substitutional $\text{Hf}_{\text{Er}}^{\bullet}$ also introduces O_i'' . The random walk analysis (Eq. 34) shows two factors that are functions of dopant level. The first is $[V_{\text{Er}}''']$ and this increases as $(N_{\text{HfO}_2}/(2-N_{\text{HfO}_2}))^{3/2}$ ¹. However, what is more important is the concentration of mobile V_{Er}''' and this may increase much more slowly with dopant level than is predicted by our simple defect picture, particularly at lower temperatures where appreciable association is to be expected between some of the V_{Er}''' and the relatively immobile $\text{Hf}_{\text{Er}}^{\bullet}$. Also of importance is ΔG_M , the energy of motion of the Er ions, which can be expected to increase as more and more of the interstitial sites (through which Er ions must pass on their way between adjacent normal sites)

¹It is assumed here that K_S and K_{AF} are approximately independent of dopant level.

become blocked by O_i'' introduced by the dopant. If ΔG_M does in fact increase with increasing HfO_2 content, and Figure 9 and Table 6 certainly show this to be probable, then, at a constant temperature, the combined effects of probably clustering of V_{Er}''' and $Hf_{Er}^\bullet$ and of increasing ΔG_M can not only cause $D_{V,Er}^*$ to increase more slowly than predicted by Eq. 35, but to actually reach a maximum and begin to decline. Such a trend is shown in Figure 4.

Hafnium Diffusion

Hafnium self-diffusion was carried out at a series of temperatures from 1601°C to 1970°C in "pure" Er_2O_3 having two levels of impurities present. Er_2O_3 labeled material "A" had a total impurity content of ~600 ppm and Er_2O_3 labeled material "B" had a total impurity content of ~250 ppm (see Table 1). Only a limited amount of material "B" was available so only a few measurements were made in this material. Additional measurements of Hf self-diffusion were carried out at 1704°C in 5, 10, and 20 m/o HfO_2 -doped Er_2O_3 . The overall self-diffusion of Hf was significantly enhanced by diffusion along grain boundaries in pure Er_2O_3 requiring a separation of the grain boundary diffusion contribution in this material. When the Er_2O_3 was doped with HfO_2 , however, the volume diffusion increased to the point where the grain boundary diffusion contribution was no longer a significant factor and could not be separated out.

A characteristic tracer penetration profile for Hf diffusion in pure Er_2O_3 (material A) is shown in Figure 10. The measured profile (square symbols) exhibits the curvature that results from the grain boundary contribution. Using the Suzuoka analysis previously described and discussed in detail in Appendix A, a modified profile was determined in which the grain boundary effects have been subtracted out. The modified profile due to volume diffusion only is also shown in Figure 10 (circular symbols). Appendix C contains the remaining Hf tracer penetration profiles for each of the diffusion specimens.

The Hf grain boundary ($D_{\text{gb,Hf}}^*$) and volume ($D_{\text{V,Hf}}^*$) tracer self-diffusion coefficients for Hf in pure Er_2O_3 calculated from corrected tracer penetration profiles are shown in Table 7. The Suzuoka analysis was applied to generate linear concentration profiles so the standard thin film solution could be used to calculate the volume self-diffusion coefficients. Using the calculated volume self-diffusion coefficient and a grain boundary width ($2a=5 \times 10^{-8}$ cm), a value for the grain boundary diffusion coefficient was calculated with the use of Equation 18.

Values of $D_{\text{V,Hf}}^*$ and $D_{\text{gb,Hf}}^*$ in pure Er_2O_3 are plotted as a function of temperature in Figures 11 and 12 respectively. The temperature dependence of the volume diffusion coefficients (Fig. 11) shows two distinctive regions of diffusion.

Figure 10. Concentration profile for diffusion of Hf in Er_2O_3 . Original data, dashed line; data corrected for grain boundary contribution, solid line

Table 7. Hf volume and grain boundary diffusion in pure Er_2O_3 with two impurity levels

Temp. (°C)	Material A					
	1601°C	1667°C	1807°C	1860°C	1900°C	1970°C
Time (sec)	414,000	576,300	86,400	34,200	33,900	18,000
$D_{V,Hf}^*$ (cm ² /sec)	1.24×10^{-13} 1.52×10^{-13}	2.31×10^{-13} 2.16×10^{-13}	6.68×10^{-13}	1.81×10^{-12} 1.89×10^{-12}	4.25×10^{-12} 4.52×10^{-12}	4.31×10^{-11}
$D_{g.b.,Hf}^*$ (cm ² /sec)	2.06×10^{-8} 6.43×10^{-8}	3.10×10^{-8} 2.89×10^{-8}	2.48×10^{-7}	9.10×10^{-7} 9.64×10^{-7}	8.11×10^{-7} 1.40×10^{-6}	1.85×10^{-6}

Temperature (°C)	Material B	
	1613°C	1693°C
Time (seconds)	750,600	576,900
$D_{V,Hf}^*$ (cm ₂ /sec)	9.66×10^{-15}	2.08×10^{-14}
$D'_{g.b.,Hf}$ (cm ² /sec)	2.16×10^{-10}	1.38×10^{-9}

Figure 11. Temperature dependence of Hf volume diffusion coefficients in pure Er_2O_3 of two different purities (Δ indicates data for Ref. (15))

Figure 12. Temperature dependence of Hf grain-boundary diffusion coefficients in Er_2O_3 of two different purities

For Er_2O_3 "A", with a total impurity content of approximately 600 ppm, a dramatic change in slope occurred at about 1830°C . This sharp change in temperature dependence for $D_{V,\text{Hf}}^*$ probably denotes a transition from extrinsic or impurity controlled diffusion at low temperatures to intrinsic diffusion at temperatures above the slope change. For material "B" (250 ppm impurities), only two experimental values of $D_{V,\text{Hf}}^*$ were determined, and the temperature dependence is parallel to the extrinsic data for material "A" indicating probable impurity control of diffusion for material "B" as well. If the intrinsic (impurity-independent) portion of the curve for material "A" is extrapolated to intersect the curve for material "B", the transition from extrinsic to intrinsic behavior in material "B" can be estimated to take place at about 1740°C . The indication that material "B" behaves intrinsically to a lower temperature than material "A" is consistent with the lower total impurity level in the "B" material.

Table 8 lists the Arrhenius constants calculated for each of the different portions of the curves using a least squares procedure. The activation energy, Q , and D_0 values are listed with uncertainties of one standard deviation. There is a large difference in extrinsic $D_{V,\text{Hf}}^*$ values for the two materials. The additional impurities in material "A" enhanced Hf diffusion by nearly an order of magnitude over that in material "B". The importance of the effect of impurities on dif-

Table 8. Arrhenius constants for Hf diffusion in pure Er_2O_3

	D_0 , cm^2/sec	Q , Kcal/mole
<u>Volume Diffusion</u>		
Extrinsic		
Material A	$1.15^{+.49}_{-.45} \times 10^{-6}$	59.4 ± 3.4
Material B	1.48×10^{-6}	70.6
Intrinsic		
Material A	$2.91^{+.72}_{-.58} \times 10^{12}$	235.6 ± 9.5
(Ref. 15)	$3.28^{+8.53}_{-2.37} \times 10^{10}$	209 ± 45
<u>Grain Boundary Diffusion</u>		
Material A	$2.42^{+1.58}_{-.96} \times 10^4$	103.2 ± 10.1
Material B	1.34×10^{10}	170.8

fusion is shown very dramatically in Figure 11, and is further illustrated by an examination of the magnitude of the activation energies for each of the regions. In the extrinsic region of diffusion, the activation energies were 59.4 ± 3.4 Kcal/mole for material "A" and 70.6 Kcal/mole for material "B"; due to limited data for material "B", this difference may not be significant. On the other hand, in the intrinsic region, there was a sharp increase in the activation energy to 235.6 ± 9.5 Kcal/mole.

In a microprobe interdiffusion study in the same system, Schiavi (15) was able to predict D_{Hf} in pure Er_2O_3 by extrapolation of the concentration-dependent interdiffusion coefficients to "0" dopant levels. These predicted values appear as triangular points in Figure 11. In the present self-diffusion measurements, grain boundary diffusion effects have been accounted for; however, no correction was made for grain boundary diffusion in the interdiffusion measurements, although there was some indication of increased Hf concentration within the grain boundaries. Hf self-diffusion coefficients in pure Er_2O_3 determined by extrapolation of interdiffusion coefficients gave an activation energy of 209 ± 45 Kcal/mole, which is in fair agreement with the value of 235.6 ± 9.5 Kcal/mole determined for $D_{\text{V,Hf}}^*$ in the intrinsic region in this study.

If it is assumed that Hf volume diffusion occurs by a

cation vacancy jump mechanism, the magnitude of $D_{V,Hf}^*$ should be directly proportional to the concentration of Er vacancies in the material. The various defect reactions can be described with the following reactions:

In addition, if equilibrium is established with the surrounding atmosphere, there are several possible stoichiometry modification reactions.

Finally, the presence of tetravalent M impurities leads to

It is possible to write an expression for the observed activation energy, Q , which is the sum of two enthalpy terms, ΔH_f and ΔH_m (see Eq. 17). ΔH_f is the enthalpy associated with the interplay of the various defect reactions responsible for controlling the concentration of the mobile defect (in this case, V_{Er}'''). The various defect reactions (Eq. 38 to Eq. 42) can be grouped into several possible cases for evaluation of ΔH_f depending on which defect reaction predominates. Using the appropriate electrical neutrality approximations for each case, the expressions for ΔH_f can be derived by writing equi-

librium constants for the various defect reactions and solving for $[V_{Er}''']$. Table 9 shows the various possible interpretations of ΔH_f , and includes three possible intrinsic cases and the probable extrinsic case where a tetravalent impurity is present in significant quantities.

Using an electron microprobe, an investigation was conducted into the distribution of the major impurity (Si) in material "A". Narrow regions of increased silicon content were found at distance intervals which were approximately equal to the grain sizes present in pure Er_2O_3 . This indicated probable segregation of Si in grain boundary regions, which is consistent with the observed segregation of Si, Fe, and Ca at grain boundaries reported by Wuensch and Vasilos (42) in polycrystalline MgO. They concluded that grain boundary diffusion was extrinsic due to these impurities present in the grain boundary regions. The temperature dependence of the grain boundary diffusion coefficients in this study (Fig. 12) showed no break, indicating that Hf grain boundary diffusion in "pure" Er_2O_3 was extrinsically controlled over the entire temperature interval. The grain boundary diffusion coefficients determined here were from four to five orders of magnitude larger than the volume diffusion coefficients, and showed grain boundary diffusion coefficients approximately an order of magnitude higher in material "A" (600 ppm impurities) than in the more pure material "B" (250 ppm impurities).

Table 9. Possible interpretations of ΔH_f

Defect producing reactions	Electrical neutrality approximation	ΔH_f
Intrinsic Case I Eqs. 38 and 39	$[O_i''] = [V_o'']$	$(\frac{\Delta H_{38}}{2} - \frac{3\Delta H_{39}}{4})^a$
Intrinsic Case II Eqs. 38, 39, and 41	$2[O_i''] = P$	$(\frac{\Delta H_{38}}{2} - \frac{3\Delta H_{39}}{2} - \frac{\Delta H_{41}}{2})$
Intrinsic Case III, Eq. 40	$3[V_{Er}'''] = P$	$\frac{\Delta H_{40}}{4}$
Extrinsic Case Eqs. 42, 38 and 39	$[O_i''] = \frac{N^b}{2}$	$(\Delta H_{42} + \frac{\Delta H_{38}}{2} - \frac{3\Delta H_{39}}{2})$

^aSubscripts refer to enthalpies of the reactions given in Equations 38 through 42.

^bN is the mole fraction tetravalent impurity.

Hf diffusion was studied in 5, 10, and 20 m/o HfO_2 -doped Er_2O_3 at a single temperature, 1704°C . Grain boundary effects were not detectable in the doped compositions. The values of $D_{V,\text{Hf}}^*$ at the three dopant levels are listed in Table 10 and are plotted in Figure 13. The value for $D_{V,\text{Hf}}^*$ given for 0 m/o HfO_2 at 1704°C was calculated from the Arrhenius expression for intrinsic volume diffusion of Hf in material "A" (see Fig. 11 and Table 8). The effect of dopant addition is seen to increase $D_{V,\text{Hf}}^*$ at first, with a maximum in the coefficients occurring at approximately 5 m/o HfO_2 . Further additions of HfO_2 produces a slight drop from 5 to 10 m/o HfO_2 and little change from 10 to 20 m/o HfO_2 . The maximum at 5 m/o HfO_2 was approximately an order of magnitude larger than in pure material.

If it assumed that substitutional Hf diffuses by jumping into vacant Er sites, then $D_{V,\text{Hf}}^*$ at constant temperature should follow a compositional relationship similar to that developed previously for $D_{V,\text{Er}}^*$ (Eq. 35). An examination of Figure 13 shows that such a relationship would be too simple to describe $D_{V,\text{Hf}}^*$ properly.

The volume self-diffusion of Hf in pure Er_2O_3 exhibited a very large activation energy (235.6 ± 9.5 Kcal/mole) which is much larger than that for the self-diffusion of Er (82.2 ± 5.8 Kcal/mole). Measurement of the self-diffusion coefficients in HfO_2 -doped Er_2O_3 were made at only one temperature, so no

Table 10. D_{V,HfO_2}^* for volume diffusion in pure and HfO_2 -doped Er_2O_3 (cm^2/s)

Temperature °C	Time sec	m/o HfO_2			
		0	5	10	20
1704	520,500	$3.8 \times 10^{-13}{}^a$	4.37×10^{-12}	2.70×10^{-12}	2.01×10^{-12}
			3.55×10^{-12}	2.24×10^{-12}	2.56×10^{-12}

^aValue calculated from Arrhenius constants for $D_{V,Hf}^*$ in pure Er_2O_3 (Table 8).

Figure 13. Compositional dependence of Hf volume diffusion coefficients in pure and HfO_2 -doped Er_2O_3 .

calculation of an activation energy could be made in HfO_2 -doped material.

A number of factors may be responsible for the shape of the composition dependence of $D_{V,\text{Hf}}^*$ (Fig. 13) and for the very large activation energy for Hf diffusion in pure Er_2O_3 . Hafnium substituting on a site normally occupied by an erbium ion in Er_2O_3 constitutes a localized positive effective charge within the crystal. This local positive charge disturbance will tend to attract negative defects to its vicinity and may form associates or defect clusters with them. Two kinds of negatively charged defects are available for possible association with $\text{Hf}_{\text{Er}}^\bullet$, these being O_i'' and V_{Er}''' . There are half as many O_i'' per unit volume of crystal as there are $\text{Hf}_{\text{Er}}^\bullet$ and there are considerably fewer V_{Er}''' . When a Hf ion jumps to an adjacent vacant Er site, it must either "carry along" its associated negative defects or must dissociate from them. In either case, extra energy over and above that needed to simply move an isolated Hf ion will be necessary.

In the case where $\text{Hf}_{\text{Er}}^\bullet$ is strongly associated with V_{Er}''' , the close proximity of the vacancy allows for frequent jumps of the Hf ion. However, since the V_{Er}''' would not tend to move off by random walk after an interchange with the Hf ion due to the attraction between them, the most probable next jump for the Hf ion would be to exchange positions again with the associated V_{Er}''' . This is a situation in which Hf jumps are highly

correlated and the associated V_{Er}''' would tend to orbit about the Hf ion, exchanging with it frequently. Such a situation would not be expected to exhibit a high energy of motion, but most of the Hf ion jumps would not contribute to net movement of the ion, and diffusion would be quite slow.

On the other hand, strong association between $Hf_{Er}^{\bullet}$ and O_i'' , as discussed in the section on Er diffusion and illustrated in Figure 7, would have several effects on Hf diffusion. In the first place, the charge field of O_i'' might act to repel V_{Er}''' and thus set up a sort of "semi-excluded" volume for cation vacancies in the vicinity of the $Hf_{Er}^{\bullet}$ similar to the Debye-Hückel effect. This is probably not very important since the very presence of the $Hf_{Er}^{\bullet}$ defects strongly bonded to O_i'' will tend to keep the crystal locally neutral. A much more important effect of association between $Hf_{Er}^{\bullet}$ and O_i'' would be that the possible Hf diffusion jump pathways would be restricted. This would occur in two ways. First, in Figure 7, the Hf ion shown can jump to only two adjacent cation sites (the front upper left or the front lower right) without increasing its separation distance from the associated O_i'' (I^* site); all ten remaining nearest neighbor cation sites would represent a dissociative jump unless the associated O_i'' also moved along with the Hf ion. For certain of the ten remaining nearest neighbor sites, the movement of the O_i'' could occur in a single jump, for others it could not. The

latter nearest neighbor cation sites are thus effectively unavailable to the Hf ion unless truly dissociative jumps are permitted. In any case, the necessity of carrying along the O_1'' with the Hf ion or of dissociating the complex would result in large energies of motion. When the two remaining undissociative jump sites are considered, Figure 7, it is seen that, if the first part of the jump is to the interstitial position above the lower right cation position, the remaining portion of the jump (either to the left or down, depending on which cation site is the final destination) will be through a tight square array of anions and thus will be quite energetic. The alternate routes for the Hf ion to these two cation sites will require passage through two square arrays and would again be quite energetic. Thus, when all jump possibilities are considered, it is seen that all involve large energies of motion and this is most probably a major factor in the large activation energy measured for Hf diffusion. A second factor in the high activation energy is the necessity to disrupt seven metal-oxygen bonds (on the average) in order to carry Hf^{+4} into its activated state, whereas, for Er^{+3} diffusion, only six metal-oxygen bonds need to be disrupted. This would be partly offset by the smaller ionic radius for Hf^{+4} (.81A) as compared to Er^{+3} (.96A).

As HfO_2 content is increased by doping, the probability of closely-associated $(Hf_{Er}^{\bullet}-O_1''-Hf_{Er}^{\bullet})$ triplets or larger com-

plexes even further restricts the nondissociative jump possibilities for the Hf, and can reduce the enhancing effect of the dopant on $D_{V,Hf}^*$ below that predicted by simple $[V_{Er}''']$ considerations. This is reflected in Figure 13 as an initial enhancement of $D_{V,Hf}^*$ followed by a reversal of the trend above ~ 5 m/o HfO_2 .

A comparison can be made between $D_{V,Er}^*$ and $D_{V,Hf}^*$ in pure Er_2O_3 , and this is done in Figure 14. At most temperatures investigated, $D_{V,Hf}^* < D_{V,Er}^*$, but the great difference in activation energies (235 Kcal/mole vs 82 Kcal/mole) causes the magnitudes of the two coefficients to approach one another at high temperatures. The expected crossover point would come at about $1980^\circ C$, and above this temperature, $D_{V,Hf}^*$ is expected to exceed $D_{V,Er}^*$ up to the melting point ($2400^\circ C$). The possible factors contributing to the great difference in activation energies have been discussed above.

Figure 14. Comparison of temperature dependence of Er and Hf volume diffusion coefficients in pure Er_2O_3 .

CONCLUSIONS

- 1) The self-diffusion coefficients of Er were measured in Er_2O_3 and 5, 10, and 20 m/o HfO_2 -doped Er_2O_3 , and were found to increase with the amount of HfO_2 dopant present. A maximum in the diffusion rates occurred around 10 m/o HfO_2 , which was approximately an order of magnitude larger than the value for pure Er_2O_3 .
- 2) The activation energy for the self-diffusion of Er in pure Er_2O_3 was 82.2 ± 5.8 Kcal/mole, and increased with the amount of HfO_2 dopant present, the largest increase occurring between 5 m/o and 10 m/o HfO_2 .
- 3) Up to 10 m/o HfO_2 , the self-diffusion of Er could be related to the concentration of vacant erbium sites, presumed to be the mobile defect. Above this composition, deviation from this relationship occurred probably due to clustering of cation vacancies and oxygen interstitials around the dopant hafnium ion.
- 4) The self-diffusion of Hf in pure Er_2O_3 showed grain boundary enhancement, so values for both volume and grain boundary diffusion were measured; however, in HfO_2 -doped Er_2O_3 compositions no grain boundary enhancement could be detected.
- 5) The volume diffusion of Hf in pure Er_2O_3 showed both extrinsic and intrinsic behavior with the transition temperature increasing with the impurity level present in Er_2O_3 .

6) Low volume self-diffusion coefficients and a high activation energy (235.6 ± 9.5 Kcal/mole) were found for Hf diffusion in pure Er_2O_3 . In 5 m/o HfO_2 -doped Er_2O_3 , the self-diffusion coefficient increased approximately an order of magnitude over those found in pure Er_2O_3 , but this was followed by a decrease at 10 m/o and 20 m/o HfO_2 -doped Er_2O_3 . These results indicated a probable strong association between the diffusing Hf ion and the oxygen interstitials and erbium vacancies generated by the presence of the hafnium.

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APPENDICES

Appendix A. Determination of D_V and $D_{g.b.}$ Using the Suzukioka Analysis

Suzuoka (36) developed the following relationship between D_V and $D_{g.b.}$.

$$.973 \log(\Delta-1) = 6.567 - 1.644 \log \gamma - \log \sqrt{D_V t} \quad (A1)$$

where $\Delta = D_{g.b.}/D_V$, and γ is the slope of the linear portion of the $\ln A^*$ vs. $x^{6/5}$ plot.

Where D_V is unknown, the following expressions are used to separate out the grain boundary diffusion contribution from the concentration profiles. The total concentration or activity profile of the tracer material can be described by the following expression:

$$C(\eta, t) = \frac{\alpha}{\sqrt{\pi D_V^* t}} (c_1 + \frac{1}{n} \bar{c}_2) \quad (A2)$$

where

$$c_1 = \exp(-\eta^2/4)$$

and is the concentration or activity factor associated with pure volume diffusion, and

$$\bar{c}_2 = \int_1^\Delta \left(\frac{\eta^2}{\sigma} - 2 \right) \exp\left(-\frac{\eta^2}{4\sigma}\right) \frac{\Delta - \sigma}{\Delta - 1} \left[\frac{\exp(-X^2)}{\sqrt{\pi}} - X \operatorname{erfc} X \right] \frac{d\sigma}{\sigma^{3/2}}$$

is the concentration or activity factor associated with pure grain boundary diffusion.

$$X = \frac{\sqrt{\Delta-1}}{\sqrt{\Delta-\sigma}} \frac{(\sigma-1)}{\beta}$$

$$\eta = \frac{x}{\sqrt{D_V t}}$$

2a = grain boundary width

$$n = \frac{b}{\sqrt{D_V t}}$$

$$\beta = 2a(\Delta-1)\sqrt{D_V t}$$

2b = mean linear grain size

σ is an integration constant.

The following is the procedure used for 1667 #2.

1) A value for D_V was estimated by the thin film analysis using five points at shallow depths. This gave a first estimate value for $D_V = 3.6 \times 10^{-13} \text{ cm}^2/\text{sec}$. All slopes were determined by a least squares fit of the points.

2) The value of $\Delta(D_{g.b.}/D_V)$ was determined by the use of Eq. A1 using the estimated value of D_V , the slope of the linear tail on the $\ln A$ vs $x^{6/5}$ plot gave a value for γ . Using a least squares fit on the last eight points gave the following value $\gamma = 1.1566 \times 10^3$. The length of the diffusion anneal was $t = 5.763 \times 10^5 \text{ sec}$, so the following value for Δ was obtained:

$$\Delta = 1.027 \times 10^5$$

3) The value of β and corresponding η for varying depths were determined.

4) With the β values established and η values calculated, the numerical values of $\bar{c}_2$ could be obtained by interpolating values from Table A1 in Suzouka (36).

5) The value of K , which is a multiplying factor ($A^* = K\bar{c}_2$), was determined by comparing $\bar{c}_2$ values with the observed activity (A^*) over the linear portion of the $\ln A^*$ vs $x^{6/5}$ plot:

6) With the value of K , the multiplying factor, the values of A^* at low penetration depths were corrected by subtracting

out $K\bar{c}_2$, the grain boundary portion. $A_1^* = A^* - Kc_2$.

7) A_1^* now becomes the corrected activity and a plot of $\ln A_1^*$ vs x^2 is made and a value for D_V can be determined.

8) Compare the new value of D_V with the original estimate and if they differ significantly repeat the process using the new value of D_V for the first approximation.

9) When a final D_V is determined, Eq.A1 is used to determine the value for $D_{g.b.}$.

Table A1. Values calculated for 1667 #2 using Suzuoka analysis

$\ln A^*$	$x^2 \text{ cm}^2$	$x^{6/5} \text{ cm}^{6/5}$	η	$\bar{c}_2$	$\ln A_1^*$
8.56	1.68×10^{-9}	5.44×10^{-6}	.09	-1.13	8.66
7.35	2.38×10^{-8}	2.67×10^{-5}	.34	-1.03	7.64
6.77	8.71×10^{-8}	5.81×10^{-5}	.65	-.90	7.18
6.74	2.52×10^{-7}	1.10×10^{-4}	1.10	-.68	7.08
5.82	5.75×10^{-7}	1.80×10^{-4}	1.66	-.28	6.16
5.15	1.00×10^{-6}	2.52×10^{-4}	2.20	.035	5.04
5.23	1.55×10^{-6}	3.27×10^{-4}	2.74	.23	4.25
5.18	2.32×10^{-6}	4.17×10^{-4}	3.35	.32	2.81
4.80	3.72×10^{-6}	5.53×10^{-4}	4.24	.32	
4.68	5.82×10^{-6}	7.23×10^{-4}	5.30	.22	
4.51	9.09×10^{-6}	9.45×10^{-4}	6.62	.13	
4.81	1.23×10^{-5}	1.13×10^{-3}	7.71	.08	
3.75	1.56×10^{-5}	1.30×10^{-3}	8.66	.05	
3.96	2.04×10^{-5}	1.53×10^{-3}	9.92	.03	
3.38	2.66×10^{-5}	1.79×10^{-3}	11.3	.02	

Appendix B. Concentration Profiles for Er Self-Diffusion
in Pure Er_2O_3 and HfO_2 -Doped Er_2O_3

Throughout Appendices B and C the numerical designation below the composition heading refers to temperature ($^{\circ}\text{C}$), and A is the activity normalized by a standard time and section thickness.

Appendix C. Concentration Profiles for Hf Self-Diffusion
in Pure Er_2O_3 "A", Pure Er_2O_3 "B", and HfO_2 -Doped Er_2O_3 .
Original Data, Dashed Line (o); Data Corrected for Grain
Boundary Contribution, Solid Line (x)