

O(5') and C(3) atoms. Besides the crystal packing forces, these two weak hydrogen-bonding interactions involving O(1') and O(5') contribute to determine the overall conformation of the phlorizin molecule and the degree of puckering of the glucopyranose ring.

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## Transport Mechanisms of Holmium Sesquioxide-Yttrium Sesquioxide System

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Electrical conductivities of polycrystalline yttrium sesquioxides containing 1.6 and 3.2 mol % of holmium sesquioxides have been measured from 650 to 1050°C under oxygen partial pressures of  $1 \times 10^{-5}$  to  $2 \times 10^{-1}$  atm. Plots of log conductivity vs.  $1/T$  at constant oxygen partial pressures are found to be linear away from the two inflection points. The low- and high-temperature dependences of conductivity show different defect structures of yttrium sesquioxide. The plots of log conductivity vs. log  $P_{O_2}$  are found to be linear at  $P_{O_2}$ 's of  $10^{-5}$  to  $10^{-1}$  atm. The electrical conductivity dependences on  $P_{O_2}$  are found to be  $1/5.3$  at 950-1050 °C,  $1/6$  at 800-950 °C and  $\frac{1}{6.2} - \frac{1}{6.5}$  at 650-800 °C, respectively. The defect structures and conduction mechanisms have been suggested.

### Introduction

Yttrium sesquioxide is the only known oxide in the Y-O system.  $Y_2O_3$  exhibits small deviations from stoichiometry under normal conditions of temperature and pressure. Miller and Danne<sup>1</sup> reported that  $YO_{1.491}$  may be prepared

by arc melting the sesquioxide. The oxygen diffusion in  $YO_{1.491}$  is performed by the oxygen vacancies<sup>2,3</sup>. Berard *et al.*<sup>4,5</sup> have reported yttrium self-diffusion in  $Y_2O_3$ . They found that bulk diffusion predominated.

Tallan and Vest<sup>6</sup> have studied the electrical conductivity as a function of the partial pressure of oxygen. For tempera-

tures above 900°C they found that  $Y_2O_3$  has p-type electronic conduction, however, the ionic contribution to the electrical conductivity increased with decreasing temperature below 900°C. This ionic conduction was also found from emf measurements at 825°C<sup>7</sup>. In connection with Tallan and Vest's studies,  $Y_2O_3$  is in fact a mixed ionic/electronic conductor. Noddack *et al.*<sup>8,9</sup> attempted to measure the ionic contribution to the total conductivity. They found that the ionic transport number in this oxide was less than 0.01 and thus concluded that  $Y_2O_3$  is electronic conductor.

Studies similar to those of Noddack and Walch have more recently been reported by Rao<sup>10</sup>. The authors found that  $Y_2O_3$  has an appreciable difference in the dc and ac conductivities and slightly reduced conductivity on continued electrolysis. From the above observations the authors concluded that  $Y_2O_3$  is mixed ionic/electronic conductor.

$Y_2O_3$  is believed to be p-type semiconductor, however, the conduction mechanism is very much the object of controversy and the nature of defect structures and carriers in  $Y_2O_3$  remains in doubt. In order to clarify the defect structures and transport properties in this sesquioxide, it is desirable to extend the investigations to yttrium sesquioxide with controlled dopant addition.

### Experimental Section

The polycrystalline specimens used in this investigation were prepared in the following method. Specpure  $Y_2O_3$  (Johnson-Matthey Co., 99.99%) and  $Ho_2O_3$  (Johnson-Matthey Co., 99.99%) powders were weighed out, mixed in varying proportions, ball-milled for several hours in ethyl alcohol, and then dried at 300°C. The powder mixture was made into a pellet under a pressure of 600 kg/cm<sup>2</sup> *in vacuo*. The pellets were presintered for 24h at 1200°C and annealed for 72h at 1200°C under atmospheric pressure and then cooled rapidly to room temperature. The samples were given a light abrasive polish on one face and then were turned over and polished until the voids of interface region of the specimen were fully eliminated.  $Y_2O_3$  doped with 1.6 and 3.2 mol%  $Ho_2O_3$  were cut into rectangular forms with dimensions of 1.2×0.8×0.5 cm<sup>3</sup> and 1.3×0.9×0.5 cm<sup>3</sup>, respectively. Pycnometric densities of the specimens show 4–6% of pore volume.

The pellets were etched in dilute  $HNO_3$  and ethyl alcohol solutions, and washed with distilled water, dried, and then connected to the Pt probes. X-ray super-structure lines showed that  $Ho_2O_3$ - $Y_2O_3$  was found to be a uniformly homogeneous, with little evidence for the presence of mixtures of phases or precipitations of either of the components. Spectroscopic comparisons of the starting powders and of the prepared specimens showed that no increase in the concentration of other impurities appeared as a result of this procedure. Starting powders of  $Y_2O_3$  and  $Ho_2O_3$  contained less than 13 ppm of total impurities such as Cu, CO, Ni, Fe and etc., respectively.

According to the valdes technique<sup>11</sup>, electrical conductivity measurement of polycrystalline sesquioxide containing 1.6 and 3.2 mol % of holmium sesquioxides in the temperature

range from 650 to 1050°C under oxygen partial pressures of  $1 \times 10^{-5}$  to  $2 \times 10^{-1}$  atm was measured. The current through the sample was maintained from  $10^{-5}$  to  $10^{-2}$  A by rheostat; also, the potential across the inner two probes was maintained between 0.4 and 1.7 V. The potential difference  $V$  was measured by a Leeds and Northrup 7554-K 4 potentiometer, and the current through the sample was measured by the Keithley Instrument 610B electrometer. Electric furnace employing super kanthal heating element was used in this experiment. Other apparatus were shown in previous articles<sup>12</sup>.

The measurements of electrical conductivity were taken over a complete cycle of the temperature range at a given oxygen partial pressure starting from the low-temperature and proceeding toward the high-temperature end, and then back again to the lower end.

### Results and Discussion

Log conductivities are plotted as a function of the reciprocal of absolute temperature at a constant partial pressure of oxygen. Figure 1 shows that conductivities increase with increasing oxygen partial pressures and temperature on 1.6 mol%  $Ho_2O_3$ - $Y_2O_3$  system. As shown in Figure 3 the conductivity dependences on oxygen partial pressures and temperature are approximately fixed, regardless of mol

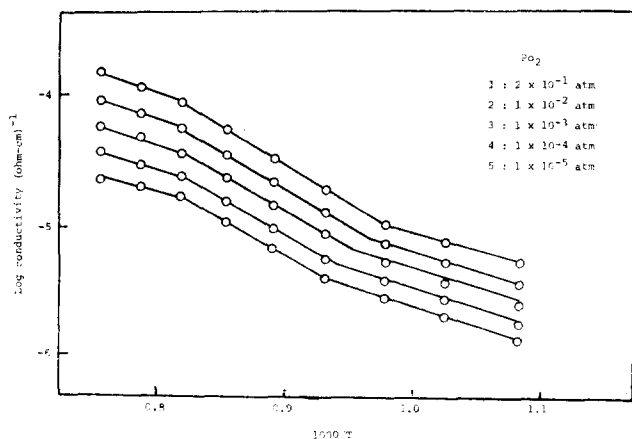


Figure 1. Log conductivity vs.  $1000/T$  for 1.6 mol %  $Ho_2O_3$ - $Y_2O_3$  system under various oxygen pressures.

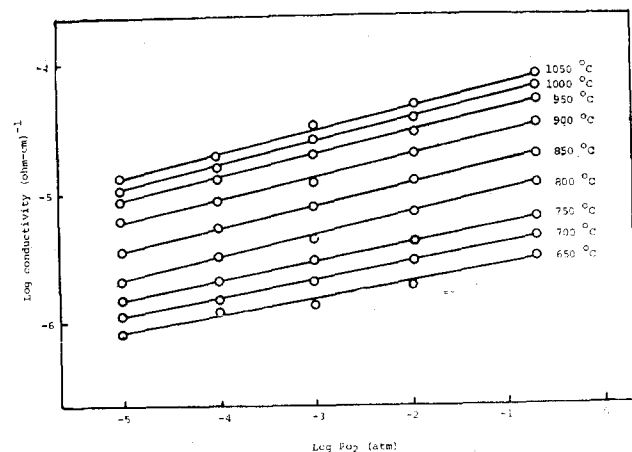


Figure 2. Log conductivity vs.  $\log P_{O_2}$  for 1.6 mol %  $Ho_2O_3$ - $Y_2O_3$  system at various temperatures.

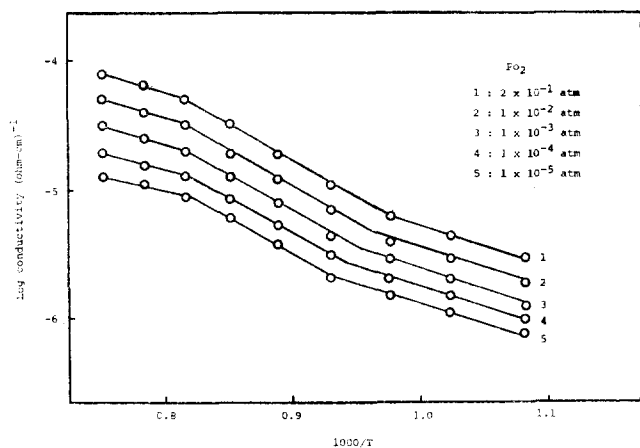


Figure 3. Log conductivity vs.  $1000/T$  for 3.2 mol %  $\text{Ho}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$  system under various oxygen pressures.

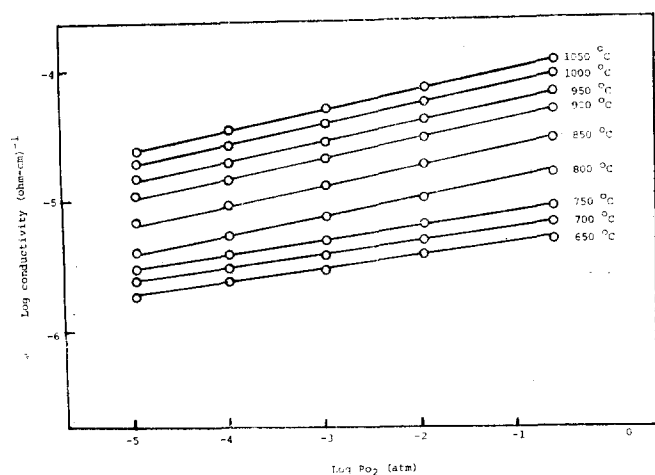


Figure 4. Log Conductivity vs.  $\log P_{\text{O}_2}$  for 3.2 mol %  $\text{Ho}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$  system at various temperatures.

percent of  $\text{Ho}_2\text{O}_3$  doped in  $\text{Y}_2\text{O}_3$ . Each of the curves in Figures 1 and 3 shows a negative slope, and exhibits a discontinuity in slope at the temperatures observed. According to study<sup>13</sup> that both  $\text{Y}_2\text{O}_3$  and  $\text{Ho}_2\text{O}_3$  have rare earth type-cubic structure up to  $2300^\circ\text{C}$ , there was no possibility of phase change in this experiment. It was concluded from this study that conductivity change due to phase transition did not occur in this experiment.

The conductivity isotherms of 1.6 and 3.2 mol %  $\text{Ho}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$  are shown in Figures 2 and 4. Three different dependences of conductivity on oxygen partial pressure are observed from the conductivity isotherms. Tables 1 and 2 show the oxygen partial pressure dependences of the conductivities on 1.6 and 3.2 mol %  $\text{Ho}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$  systems at various temperatures.

**Transport mechanism at 960–1050°C.** As shown in Tables 1 and 2, the oxygen partial pressure dependence of conductivity is  $\frac{1}{5.3}$  at above 950 and below 1050°C. In this temperature region, it is obvious that the  $\text{Y}_2\text{O}_3$  has essentially intrinsic behavior, regardless of  $\text{Ho}_2\text{O}_3$  doped. As shown in Figure 1 and 3, the conductivities increase with increasing oxygen partial pressure. This indicates that  $\text{Y}_2\text{O}_3$  is p-type cha-

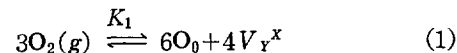
TABLE 1: Oxygen Pressure Dependences for the Conductivities of 1.6 mol %  $\text{Ho}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$  at Various Temperatures

Temperature	$\frac{1}{n}$
1050°C	$\frac{1}{5.3 \pm 0.05}$
1000°C	$\frac{1}{5.3 \pm 0.05}$
950°C	$\frac{1}{6.0 \pm 0.05}$
900°C	$\frac{1}{6.0 \pm 0.05}$
850°C	$\frac{1}{6.0 \pm 0.05}$
800°C	$\frac{1}{6.0 \pm 0.05}$
750°C	$\frac{1}{6.5 \pm 0.1}$
700°C	$\frac{1}{6.6 \pm 0.1}$
650°C	$\frac{1}{6.7 \pm 0.1}$

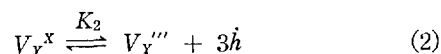
TABLE 2: Oxygen Pressure Dependences for the Conductivities of 3.2 mol %  $\text{Ho}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$  at Various Temperatures

Temperature	$\frac{1}{n}$
1050°C	$\frac{1}{5.3 \pm 0.05}$
1000°C	$\frac{1}{5.3 \pm 0.05}$
950°C	$\frac{1}{6.0 \pm 0.05}$
900°C	$\frac{1}{6.0 \pm 0.05}$
850°C	$\frac{1}{6.0 \pm 0.05}$
800°C	$\frac{1}{6.0 \pm 0.05}$
750°C	$\frac{1}{6.2 \pm 0.1}$
700°C	$\frac{1}{6.3 \pm 0.1}$
650°C	$\frac{1}{6.5 \pm 0.1}$

racteristic. One can assume that the yttrium vacancy can be formed due to the diffusion of oxygen.



In equilibrium(1),  $V_Y^x$  is neutral yttrium vacancy and  $\text{O}_0$  is lattice oxygen. The neutral yttrium vacancy produces easily positively charged electron hole in the valence band by accepting the electron.



In equilibrium(2),  $V_Y'''$  is triply negatively charged yttrium vacancy and  $\dot{h}$  is singly positively charged electron hole. In equilibrium(1), the equilibrium constant is

$$K_1 = \frac{(V_Y^x)^4}{P_{\text{O}_2}^3} \quad (3)$$

and in equilibrium(2), the equilibrium constant is

$$K_2 = \frac{(V_Y''')P^3}{(V_Y^x)} \quad (4)$$

where  $p$  is the concentration of electron hole. In equation(3),

$$V_Y^x = K_1^{1/4} \cdot P_{O_2}^{3/4} \text{ and in equation(4), } P = \frac{K_2^{1/3}(V_Y^x)^{1/3}}{(V_Y''')^{1/3}}$$

The concentration of electron hole can be written as

$$P = \frac{K_2^{1/3} \cdot K_1^{1/2} \cdot P_{O_2}^{1/4}}{(V_Y''')^{1/3}} \quad (5)$$

Applying the electrical neutrality condition to the equilibrium(2), one can find the relation of  $(V_Y''') = \frac{1}{3} p$ . If  $(V_Y''')$  in equation(5) is substituted by above relation, the electron-hole concentration is

$$P = K' P_{O_2}^{1/5.3} \quad (6)$$

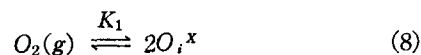
Assuming the electron-hole carrier type in this p-type  $Y_2O_3$ , the electrical conductivity dependence on  $P_{O_2}$  is as follows

$$\sigma \propto P = K' P_{O_2}^{1/5.3} \quad (7)$$

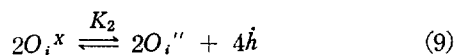
The equation(7) is consistent with the experimental result, *i.e.*,  $\sigma \propto P_{O_2}^{1/5.3}$  at temperatures of 960–1050°C. It is concluded from this coincidence that the transport in yttrium sesquioxide doped with holmium sesquioxide is due to the electron hole which is produced by yttrium vacancy.

*Transport Mechanism at 800–950°C.* The conductivity dependence on oxygen partial pressure is  $\frac{1}{6.0}$  at temperatures from 800 to 950°C as shown in Tables 1 and 2. At temperatures from 800 to 950°C,  $\sigma \propto P_{O_2}^{1/6}$  indicates that the transport of  $Y_2O_3$  has same mechanism for two different doping levels of holmium sesquioxide. The increasing conductivity with increase in oxygen partial pressure, as shown in Figures 1 and 3, shows that  $Y_2O_3$  conserves p-type property at this lower temperatures.

It is assumed that oxygen interstitial is produced by the diffusion of oxygen. This oxygen interstitial can be produced by the following equilibrium.



In equilibrium(8),  $O_i^x$  represents neutral oxygen interstitial. As a result of ionization of this oxygen interstitial the electron hole can be produced as follows



where  $h$  is electron hole and  $O_i''$  represents doubly negatively charged oxygen interstitial. In equilibria(8) and (9), the equilibrium constants are followings

$$K_1 = \frac{(O_i^x)^2}{P_{O_2}} \quad (10)$$

and

$$K_2 = \frac{(O_i'')^2 P^4}{(O_i^x)^2} \quad (11)$$

where  $P$  is the concentration of electron hole. If  $K_3 = K_1 \times K_2$ ,  $K_3$  is represented by the following equation.

$$K_3 = \frac{(O_i'')^2 P^4}{P_{O_2}} \quad (12)$$

In equilibrium(9),  $(O_i'') = \frac{1}{2} P$  and therefore  $K_3$  is  $\frac{1}{4} P^6$ .

The oxygen partial pressure dependence of electron hole can be written

$$P = (4K_3)^{1/6} P_{O_2}^{1/6} \quad (13)$$

If the electron-hole carrier is predominate in this temperature region and the main defect is oxygen interstitial, the electrical conductivity dependence on oxygen partial pressure is

$$\sigma \propto P = K' P_{O_2}^{1/6} \quad (14)$$

This is consistent with the experimentally observed  $\sigma \propto P_{O_2}^{1/6}$  at temperatures of 800 to 950°C. It is reasonable to say that the transport of yttrium sesquioxide doped with holmium sesquioxide is carried out by the electron hole which is formed by the diffusion of oxygen interstitial. The same result, that the defect were changed from oxygen interstitials to metal vacancies by elevating the temperature, was obtained in the study<sup>14</sup> of bare  $Y_2O_3$ .

*Transport Mechanism at 650–790°C.* As shown in Tables 1 and 2, the conductivity dependence on oxygen partial pressure is not regular, saying  $\sigma \propto P_{O_2}^{1/6.2}$  and  $\sigma \propto P_{O_2}^{1/6.7}$ . This irregularity indicates that  $Y_2O_3$  has the extrinsic conductivity by the doping of holmium sesquioxide. In the case of  $Y_2O_3$ – $Ho_2O_3$ , an extrinsic character was exhibited in a lower temperature region than for bare- $Y_2O_3$ . The transport mechanism of  $Y_2O_3$  is very complicated at this extrinsic region by the doping of impurity. As the temperature is lower, the conductivity dependence on oxygen partial pressure is less. This phenomena indicate that  $Y_2O_3$  has the ionic contribution by the doping of impurity. One can not find the correct defects and charge carriers.

It is concluded that in this temperature region the transport of  $Y_2O_3$  is due to the mixed carrier, *i.e.*, electron hole plus ion.

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## Synthesis and Biological Test of the Pheromone of the Asian Corn Borer Moth (*Ostrina Furnacalis*)

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(Z)-12-Tetradecen-1-yl acetate (**1**), (E)-12-tetradecen-1-yl acetate (**2**) and tetradecan-1-yl acetate (**3**), the active components of the sex pheromone of the Asian Corn Borer moth were synthesized by two different methods, one from acetylene and 11-bromo-1-undecanol THP ether by acetylenic route, the other from 12-acetoxy-1-dodecanal and ethyldienetriphenylphosphonium ylide by Wittig route.

### Introduction

Recently O.Saito *et al.*<sup>1</sup> isolated (Z)-12-tetradecen-1-yl acetate (**1**), (E)-12-tetradecen-1-yl acetate (**2**) and tetradecan-1-yl acetate (**3**) (Figure 1) as active components of the female sex pheromone of the Asian Corn Borer moth, *Ostrina furnacalis* Guenee, which is a major economic pest of the corn in Asia.

In 1980, J.A.Klun *et al.*<sup>2</sup> also isolated this pheromone and synthesized the two components, (Z)-12-tetradecen-1-yl acetate (**1**) and (E)-12-tetradecen-1-yl acetate (**2**).

In spite of the natural ratio of 102:117:81 of (Z)-12-tetradecen-1-yl acetate (**1**), (E)-12-tetradecen-1-yl acetate (**2**) and tetradecan-1-yl acetate (**3**), the activity was enhanced by mixing the two compounds in the ratio of 1:1 of (Z)-12-tetradecen-1-yl acetate (**1**) and (E)-12-tetradecen-1-yl acetate (**2**). Including tetradecan-1-yl acetate (**3**) in this natural ratio in pheromone traps resulted in a decrease in trap catches<sup>4</sup>.

Generally pheromonal activity is sensitive to insect species, place and climate. Institute of Agricultural Sciences in Suwon, Korea needed a fair amount of the pheromone of the Asian Corn Borer moth to conduct field test experiments. Therefore we undertook to develop convenient and practical methods for the synthesis of the pheromone of the Asian Corn Borer moth.

Here we wish to report two synthetic routes to the pheromone of the Asian Corn Borer moth and the results of the

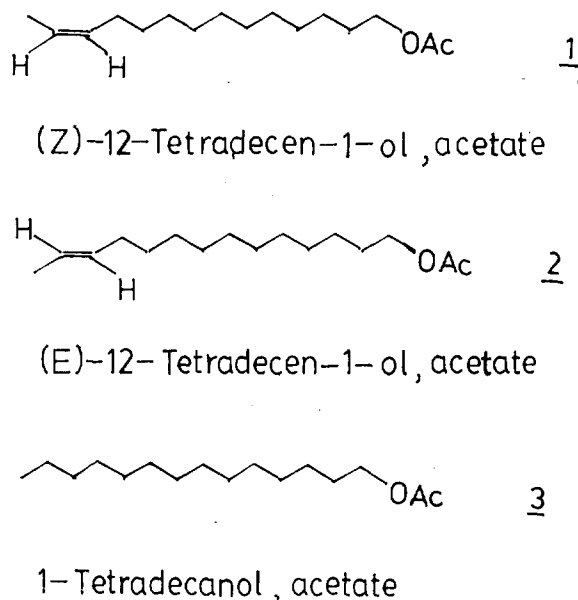


Figure 1

biological activity test of the synthetic pheromones as attractants for males of the Asian Corn Borer moth.

### Results and Discussion

Synthesis by J.A.Klun<sup>2</sup>; The pheromones **1** and **2**, the components of the pheromone the Asian Corn Borer moth, were synthesized by J.A.Klun *et al.* by Grignard coupling reaction of 6-octynylmagnesium bromide and 6-iodo-1-hexanol THP ether, whose preparations are summarized in Scheme 1.

We developed the following two cost-effective synthetic

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