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 conductivites of polycrystalline yttrium sesquioxides containing 1.6 and 3.2 mol % of holmium sesquioxdes have been measured from 650 to 1050C° under oxygen partial pressures of 1×10^{-5} to 2×10^{-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, $\frac{1}{6}$ 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[1] 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[2,3]. Berard *et al*[4,5]. have reported yttrium self-diffusion in Y_2O_3. They found that bulk diffusion predominated.

Tallan and Vest[6] 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[7]. In connection with Tallan and Vest's studies, Y_2O_3 is in fact a mixed ionic/electronic conductor. Noddack et al.[8,9] 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[10]. 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–Mathey Co., 99.99%) and Ho_2O_3 (Johnson–Mathey 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/cm² *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 $1.2\times0.8\times0.5$ cm³ and $1.3\times0.9\times0.5$ cm³, 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[11], 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 1×10^{-5} to 2×10^{-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[12].

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 oxgen. 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
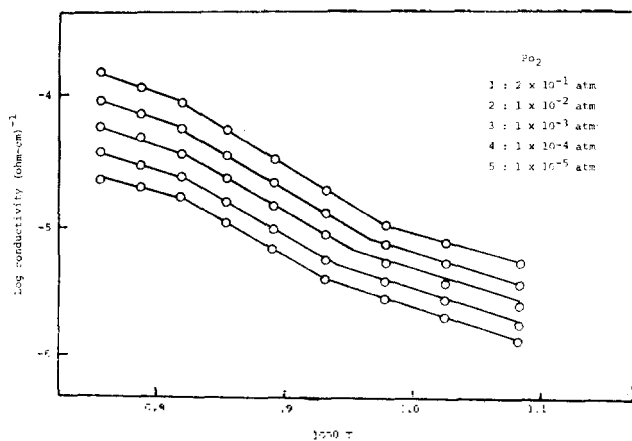

Figure 1. Log conductivity *vs.* 1000/T for 1.6 mol %Ho_3O_2–Y_2O_3 system under various oxygen pressures.
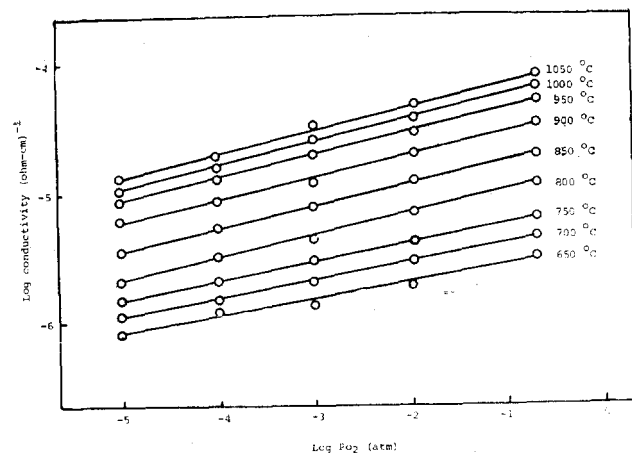

Figure 2. Log conductivity *vs.* log Po_2 for 1.6 mol %Ho_2O_3–Y_2O_3 system at various temperatures.
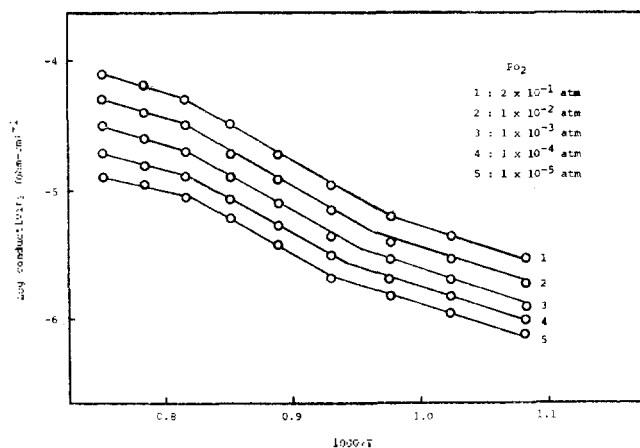
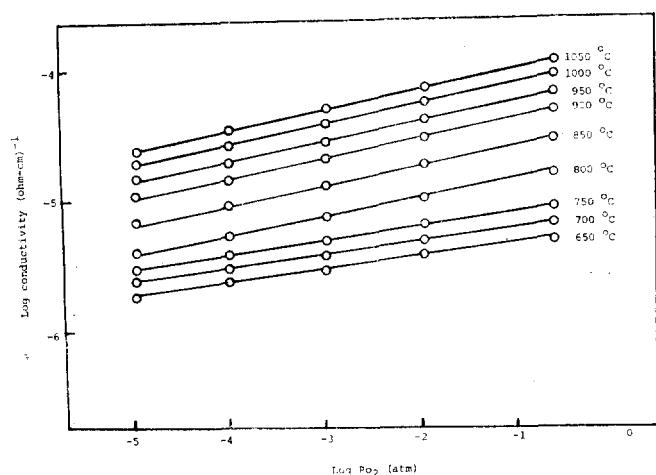**Figure 3.** Log conductivity *vs.* 1000/T for 3.2 mol % Ho_2O_3 -Y_2O_3 system under various oxygen pressures.

Figure 4. Log Conductivity *vs.* log Po_2 for 3.2 mol % Ho_2O_3 -Y_2O_3 system at various temperatures.

percent of Ho_2O_3 doped in Y_2O_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[13] that both Y_2O_3 and Ho_2O_3 have rare earth type–cubic structure up to 2300°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% Ho_2O_3-Y_2O_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% Ho_2O_3-Y_2O_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 Y_2O_3 has essentially intrinsic behavior, regardless of Ho_2O_3 doped. As shown in Figure 1 and 3, the conductivities increase with increasing oxygen partial pressure. This indicates that Y_2O_3 is p–type cha-

TABLE 1: Oxygen Pressure Dependences for the Conductivities of 1.6 mol % Ho_2O_3-Y_2O_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 % Ho_2O_3-Y_2O_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.

$$3O_2(g) \overset{K_1}{\rightleftharpoons} 6O_0 + 4V_Y{}^x \qquad (1)$$
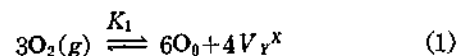
In equilibrium(1), $V_Y{}^x$ is neutral yttrium vacancy and O_0 is lattice oxygen. The neutral yttrium vacancy produces easily positively charged electron hole in the valence band by accepting the electron.

$$V_Y{}^x \overset{K_2}{\rightleftharpoons} V_Y{}''' + 3\dot{h} \qquad (2)$$
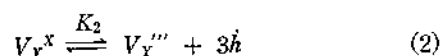
In equilibrium(2), $V_Y{}'''$ is triply negatively charged yttrium vacancy and $\dot{h}$ is singly positively charged electron hole. In equilibrium(1), the equilibrium constant is

$$K_1 = \frac{(V_Y{}^x)^4}{Po_2{}^3} \qquad (3)$$

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),

$V_Y^x = K_1^{\frac{1}{4}} \cdot Po_2^{\frac{3}{4}}$ 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

$$P = \frac{K_2^{\frac{1}{3}} \cdot K_1^{\frac{1}{12}} \cdot Po_2^{\frac{1}{4}}}{(V''')^{1/3}} \quad (5)$$

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

$$P = K' Po_2^{\frac{1}{5.3}} \quad (6)$$

Assuming the electron-hole carrier type in this p-type Y_2O_3, the electrical conductivity dependence on Po_2 is as follows

$$\sigma \ \alpha \ P = K' Po_2^{\frac{1}{5.3}} \quad (7)$$

The equation(7) is consistent with the experimental result, i.e., $\sigma \ \alpha \ Po_2^{\frac{1}{5.3}}$ 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, $\sigma \ \alpha \ Po_2^{\frac{1}{6}}$ 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.

$$O_2(g) \overset{K_1}{\rightleftharpoons} 2O_i{}^x \quad (8)$$
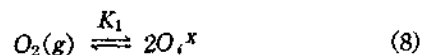
In equilibrium(8), $O_i{}^x$ represents neutral oxygen interstitial. As a result of ionization of this oxygen interstitial the electron hole can be produced as follows

$$2O_i{}^x \overset{K_2}{\rightleftharpoons} 2O_i'' + 4\dot{h} \quad (9)$$
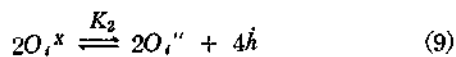
where $\dot{h}$ is electron hole and O_i'' represents doubly negatively charged oxygen interstitial. In equilibria(8) and (9), the equilibrium constants are followings

$$K_1 = \frac{(O_i{}^x)^2}{Po_2} \quad (10)$$

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.

$$K_3 = \frac{(O_i'')^2 P^4}{Po_2} \quad (12)$$

In equilibrium(9), $(O_i'') = \frac{1}{2} P$ and therefore K_3 is $\frac{1}{4} p^6 \cdot po_2^{-1}$.

The oxygen partial pressure dependence of electron hole can be written

$$P = (4K_3)^{1/6} Po_2^{1/6} \quad (13)$$

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

$$\sigma \ \alpha \ P = K' Po_2^{1/6} \quad (14)$$

This is consistent with the experimentally observed $\sigma \ \alpha \ Po_2^{1/6}$ at temperatures of 800 to 950°C. It is reasonable to say that the transport of yttrium sesquioxide doped with holmium sesquixode is carried out by the elctron 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[14] 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 $\sigma \ \alpha \ Po_2^{1/6.2}$ and $\sigma \ \alpha \ Po_2^{1/6.7}$. This irregurality 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 ethylidenetriphenylphosphonium ylide by Wittig route.

Introduction

Recently O.Saito et al[1]. 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[2]. 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 rate of 102:117:81 of (Z)-12-tetradecen-1-yl acetate (1), (E)-12-tetradecen-1-yl acetate(2) and tetradecan-1-yl acetate[1] (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[3] (2). Including tetradecan-1-yl acetate (3) in this natural ratio in pheromone traps resulted in a decrease in trap catches[4].

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
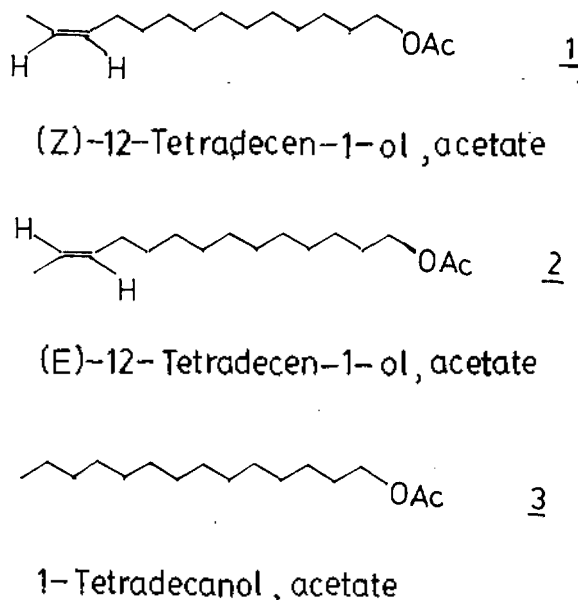
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1-Tetradecanol, acetate

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[2]; 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