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## Electrical Conductivity of the System $\text{ThO}_2\text{-Ho}_2\text{O}_3$

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The electrical conductivity of the system  $\text{ThO}_2\text{-Ho}_2\text{O}_3$  was measured in the temperature range 600-1100°C and  $\text{Po}_2$  range  $10^{-5.2} \times 10^{-1}$  atm. The mean value of activation energy was 1.45 eV. The observed conductivity dependence on  $\text{Po}_2$  was  $\text{Po}_2^{1/4}$  at  $\text{Po}_2$ 's above  $10^{-3}$  atm and was independent on oxygen partial pressure at  $\text{Po}_2$ 's below  $10^{-3}$  atm. It is suggested that these dependences are due to a mixed ionic plus electron hole conduction by Vö defect.

### Introduction

$\text{ThO}_2$  has the fluorite structure up to its melting point<sup>1</sup>, while  $\text{Ho}_2\text{O}_3$  has the rare earth type cubic structure at temperatures lower than 2200°C. The latter changes to hexagonal in the temperature range 2200 to 2300°C<sup>2,3</sup>.

$\text{ThO}_2$  was reported to be an n-type semiconductor by Bransky and Tallan<sup>4</sup> at temperatures above 1600°C and  $\text{Po}_2$ 's below  $10^{-8}$  atm. This n-typeness was also found by Choudhury and Patterson<sup>5</sup> at temperatures below 1400°C and  $\text{Po}_2$ 's lower than  $10^{-20}$  atm.  $\text{Po}_2$  dependence of the electrical conductivity in pure  $\text{ThO}_2$  has also been reported to vary as  $\text{Po}_2^{1/5.4}$  and  $\text{Po}_2^{1/4.5-8}$  at  $\text{Po}_2$ 's higher than  $10^{-3}$  atm. In addition to the  $\text{Po}_2^{1/5}$  dependence at  $\text{Po}_2$ 's higher than  $10^{-3}$  atm, Bransky and Tallan<sup>4</sup> found that the electrical conductivity did not depend on  $\text{Po}_2$  for  $\text{Po}_2$ 's between  $10^{-8}$  and  $10^{-3}$  atm.

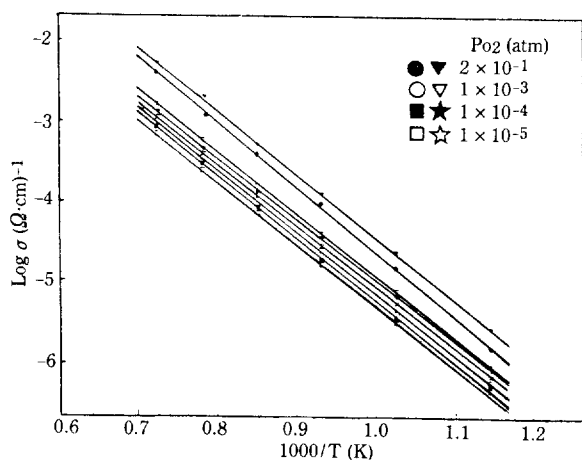
From the electrical conductivity, mixed ionic and electronic conductivity was observed<sup>4</sup>, and activation energies were reported<sup>4</sup> to be 0.98 eV and 0.77 eV at temperatures from 700 to 1000°C and above 1000°C, respectively. Bransky and Tallan<sup>4</sup> reported that the predominant ionic and electronic charge carriers in  $\text{ThO}_2$  were fully ionized metal vacancies and electron holes at  $\text{Po}_2$ 's above  $10^{-8}$  atm. This defect structure was also reported by Bauerle<sup>8</sup> who attributed his  $\text{Po}_2^{1/4}$  dependence to the chemical equilibrium between oxygen gas molecules and fully ionized oxygen vacancies. This defect model and that by Subbarao *et al.*<sup>9</sup> differ significantly from the fully ionized metal vacancy found by Bransky and Tallan<sup>4</sup> and from the anti-Frenkel defect *i.e.*,  $\text{O}_i$  in pure  $\text{ThO}_2$  observed by Lasker and Rapp.<sup>6</sup> Hardaway *et al.*<sup>10</sup> reported the maximum electrical conductivity in  $\text{ThO}_2$  doped with 7.5 mol %  $\text{Y}_2\text{O}_3$  (15 mol %  $\text{YO}_{1.5}$ ) which has already been observed by Lasker and Rapp<sup>6</sup>.

In this work  $\text{ThO}_2\text{-Ho}_2\text{O}_3$  systems were prepared, and their electrical conductivities were measured as a function of temperature and  $\text{Po}_2$ . From the temperature and  $\text{Po}_2$  dependences of electrical conductivity, one defect model and two carrier types are proposed.

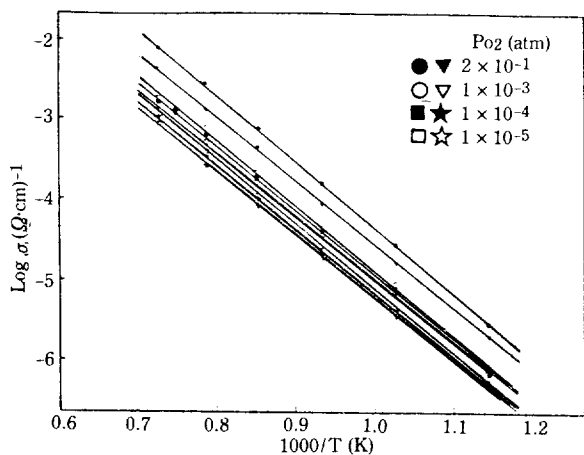
### Experimental

**Sample preparation.**  $\text{ThO}_2$  and  $\text{Ho}_2\text{O}_3$  powders obtained both from the Johnson-Matthey Co. (99.99%) were separately calcinated at 800°C for 6 hr; then weighed, mixed in varying proportions, ballmilled for several hours in  $\text{C}_2\text{H}_5\text{OH}$  solution and then dried at 300°C. The powder mixtures were compacted into pellets under a pressure of 48 MPa in vacuum. Pellets of  $\text{ThO}_2$  containing 5, 8, 10, 12 mol %  $\text{Ho}_2\text{O}_3$  were sintered for 48 hr at 1400°C, annealed for 72 hr at the same temperature under atmospheric pressure, and then quenched to room temperature. The pellets were given a light abrasive polish on both faces until voids on the faces were fully eliminated. The specimens were cut into rectangular forms having dimensions of approximately  $1.5 \times 0.7 \times 0.4$  cm<sup>3</sup>. Four holes were drilled into the largest face at intervals of 0.2 cm. The specimens were etched in dilute  $\text{HNO}_3$  solution, washed with distilled water, and dried in an oven at 200°C for about 24 hr. As Keller *et al.*<sup>11</sup> and Sibieude and Foex<sup>12</sup> reported, X-ray analysis confirmed that all sintered specimens had  $\text{ThO}_2$  type solid solution. Pycnometric densities of specimens are more than 96% of theoretical densities. Spectroscopic analysis of the specimens above showed that total amount of impurity was lower than 20 ppm. Before the sample was introduced into the sample basket, it was always etched in  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and dilute  $\text{HNO}_3$ , and washed with distilled water, dried, and then connected to the Pt probes.

**$\text{Po}_2$  establishment.** The various oxygen partial pressures were established using pure oxygen or nitrogen or a mixture of 0.001% oxygen in nitrogen obtained from Matheson Gas Products. The quartz sample basket was evacuated to a pressure of  $1 \times 10^{-7}$  torr by a diffusion pump<sup>13</sup> at room temperature, and then the temperature of the sample container was increased up to 200°C. A mixture of oxygen and nitrogen, or pure oxygen, was introduced into the sample basket, which was then evacuated again to a pressure of  $1 \times 10^{-6}$



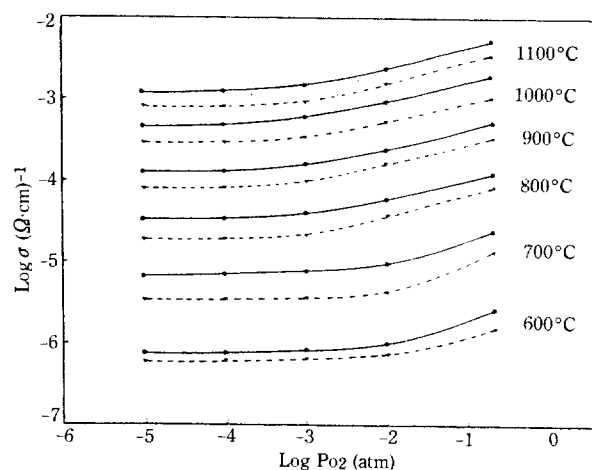
**Figure 1.** Log conductivity vs.  $1000/T$  for 5 mol % ( $\bullet$ ,  $\circ$ ,  $\blacksquare$ ,  $\square$ ) and 8 mol %  $\text{H}_2\text{O}_3\text{-ThO}_2$  ( $\blacktriangledown$ ,  $\triangledown$ ,  $\star$ ,  $\star$ ) under various oxygen pressures.



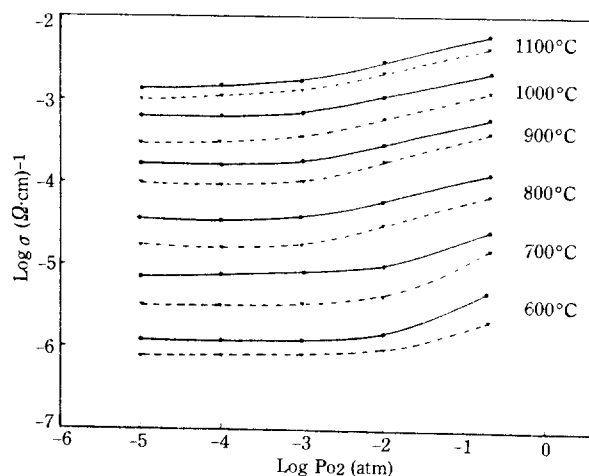
**Figure 2.** Log conductivity vs.  $1000/T$  for 10 mol % ( $\bullet$ ,  $\circ$ ,  $\blacksquare$ ,  $\square$ ) and 12 mol %  $\text{H}_2\text{O}_3\text{-ThO}_2$  ( $\blacktriangledown$ ,  $\triangledown$ ,  $\star$ ,  $\star$ ) under various oxygen pressures.

torr. The introduction and evacuation of gas at  $200^\circ\text{C}$  were performed two or three times, and then total pressure was controlled with 0.001% oxygen in nitrogen in order to establish the required  $\text{Po}_2$ . The pressures of the evacuated sample container and the  $\text{O}_2\text{-N}_2$  mixture were read on a McLeod gauge, a thermocouple gauge, Pirani gauge, and an ultrahigh vacuum ionization gauge, respectively.

**Conductivity measurements.** Measurements of electrical conductivity were performed according to the Valdes' technique<sup>14</sup> as described elsewhere<sup>15,16</sup>. This technique has also been employed to measure the electrical conductivity of other oxide semiconductors; for example,  $\alpha\text{-Fe}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ;  $\text{Cd}^{17-20}$ ,  $\text{La}_2\text{O}_3$ ;  $\text{Cd}^{21}$ ,  $\text{Sm}_2\text{O}_3$ <sup>22</sup>,  $\text{H}_2$ -Reduced Rutile<sup>23</sup>,  $\text{SrTiO}_3$ ;  $\text{Ni/Co}$ -Reduced  $\text{SrTiO}_3$ ;  $\text{Ni}^{24}$ , and  $\text{Tm}_2\text{O}_3$ <sup>25</sup>. Details have been described for the vacuum system<sup>26</sup>, instruments<sup>27</sup>, and the conductivity calculation procedure<sup>15,16</sup>. The sample current was maintained steady at values from  $10^{-6}$  to  $10^{-5}$  A by a rheostat and the corresponding potential drop across the inner two probes was measured; they ranged between 0.2 and 1.8 eV. The potential difference was measured by a Keithley 642 digital multimeter, and the current through the sample was measured by a Keithley 616 digital electrometer. The measurements of electrical conductivity were performed over a cycle in the temperature range  $600\text{-}1100^\circ\text{C}$  under



**Figure 3.** Log conductivity vs.  $\text{log Po}_2$  for 5 mol %  $\text{H}_2\text{O}_3\text{-ThO}_2$  ( $\blacktriangledown$ ) and 8 mol %  $\text{H}_2\text{O}_3\text{-ThO}_2$  ( $\bullet$ ) at various temperatures.



**Figure 4.** Log conductivity vs.  $\text{log Po}_2$  for 10 mol %  $\text{H}_2\text{O}_3\text{-ThO}_2$  ( $\bullet$ ) and 12 mol %  $\text{H}_2\text{O}_3\text{-ThO}_2$  ( $\blacktriangledown$ ) at various temperatures.

$\text{Po}_2$ 's from  $10^{-5}$  to  $2 \times 10^{-1}$  atm, starting from the low temperature and proceeding toward the high temperature end, and then back again. The sample was held at each temperature until equilibrium between the oxygen phase and sample was achieved, as indicated by a constant conductivity.

## Results and Discussion

As shown in Figures 1 and 2,  $\text{log } \sigma$  of each sample shows linear dependences on reciprocal temperature from  $600\text{-}1100^\circ\text{C}$  with characteristic p-type conduction occurring at  $\text{Po}_2$ 's above  $10^{-3}$  atm. At the  $\text{Po}_2$ 's below  $10^{-3}$  atm, the electrical conductivities of all specimens are nearly independent of  $\text{Po}_2$ , and an inflection point does not appear. An average activation energy of 1.47 eV is obtained from slopes of  $\text{log } \sigma$  vs.  $1/T$  at  $\text{Po}_2$ 's above  $10^{-3}$  atm and 1.43 eV is found for  $\text{Po}_2$ 's below  $10^{-3}$  atm. From the analysis of an activation energy, a unique conduction mechanism is expected, however the electrical conductivity dependence on  $\text{Po}_2$ , as shown in Figures 3 and 4, indicates two possible mechanisms.  $\text{Log } \sigma$  vs.  $\text{log Po}_2$  plots (Figures 3 and 4) were drawn with the data obtained from the  $\text{log } \sigma$  vs.  $1/T$  plots. Mean slope value in the  $\text{log } \sigma$  vs.  $\text{log Po}_2$  plots for  $\text{Po}_2$ 's above  $10^{-3}$  atm is  $1/4$  and does not depend on  $\text{Po}_2$  at  $\text{Po}_2$ 's below  $10^{-3}$  atm.

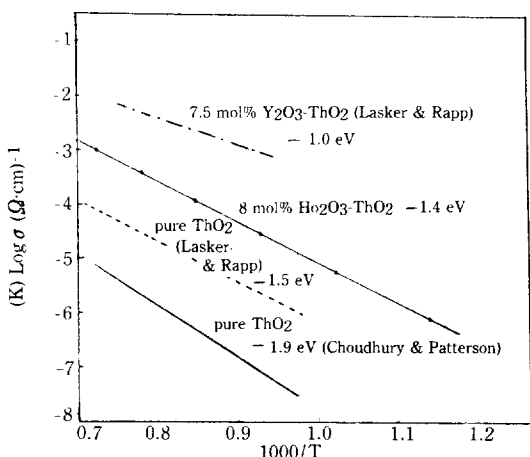
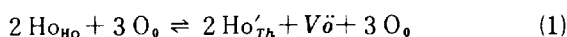


Figure 5. Log conductivity vs.  $1000/T$  plots for ionic conductivity of ThO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>-ThO<sub>2</sub> and ThO<sub>2</sub>-Ho<sub>2</sub>O<sub>3</sub> systems.

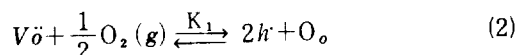
As shown in Figure 5, Choudhury and Patterson<sup>5</sup> reported that the ionic activation energy of pure ThO<sub>2</sub> is 1.9 eV. On the other hand, that of pure ThO<sub>2</sub> obtained by Lasker and Rapp<sup>6</sup> is 1.5 eV. This discrepancy was attributed by Choudhury and Patterson<sup>5</sup> to the different amounts of trace impurities that may have been present in the two sets of specimens.

The average activation energy for the ThO<sub>2</sub>-Ho<sub>2</sub>O<sub>3</sub> system, as determined from slopes in Figures 1 and 2, is below that reported by Choudhury and Patterson<sup>5</sup> for pure ThO<sub>2</sub>. This is to be expected because oxygen vacancy conduction in Ho<sub>2</sub>O<sub>3</sub> doped ThO<sub>2</sub> should include only the energy for migration. In contrast, the migration energy plus the sizable formation energy for defects would be expected in pure ThO<sub>2</sub> system if it were free enough of impurities. As Wachtman<sup>28</sup> reported for the ThO<sub>2</sub>-CaO system, this could be due to a larger amount of energy required to separate the defect pairs in ThO<sub>2</sub>-Ho<sub>2</sub>O<sub>3</sub> as compared to ThO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>.

From the analysis of an activation energy (Figure 5), increasing conductivity with increasing mol % of dopant (Figure 3), and  $\sigma \propto P_{O_2}^{1/4}$  (Figures 3 and 4), it is assumed that an oxygen vacancy may be produced by doping with Ho<sub>2</sub>O<sub>3</sub>. This formation of an oxygen vacancy is represented by the following disorder reaction



where Ho<sub>Th</sub>' is effectively negatively singly charged holmium on thorium site and V $\ddot{o}$  is effectively positively doubly charged oxygen vacancy. Provided that gas phase oxygen may react with this oxygen vacancy, the following equilibrium can exist



where  $h$  represents electron hole. At equilibrium (2),  $K_1 = p^2 / (\text{V}\ddot{o})P_{O_2}^{1/2}$ , where (V $\ddot{o}$ ) is constant, since (V $\ddot{o}$ ) is determined by the amount of dopant in disorder reaction (1). One can easily calculate the electron hole concentration:  $p = K_1^{1/2} (\text{V}\ddot{o})^{1/2} P_{O_2}^{1/4} = K' P_{O_2}^{1/4}$ . Since  $\sigma \propto p$ , the electrical conductivity dependence on  $P_{O_2}$  is  $\sigma = p e \mu = K' e \mu P_{O_2}^{1/4}$  where  $e$  is charge and  $\mu$  is the mobility. If  $e$  and  $\mu$  are constant, the following equation may be conserved.

$$\sigma = K'' P_{O_2}^{1/4} \quad (3)$$

This interpretation above equilibrium (2) is in good agree-

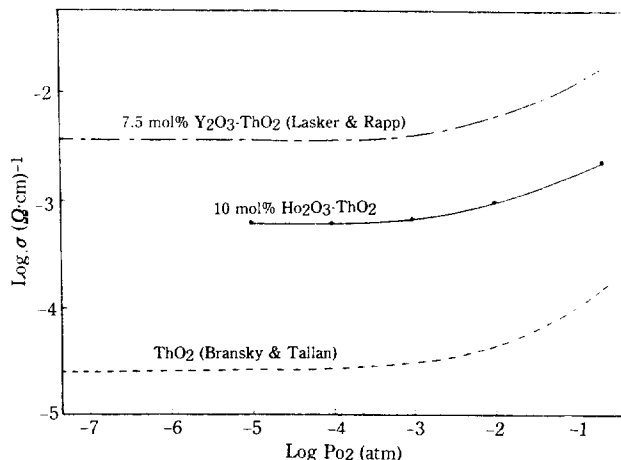


Figure 6. Log conductivity vs.  $\log P_{O_2}$  for ThO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>-ThO<sub>2</sub> and ThO<sub>2</sub>-Ho<sub>2</sub>O<sub>3</sub> systems at 1000°C.

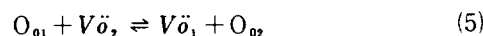
ment with experimentally observed conductivity dependence on  $P_{O_2}$ , i.e.,  $P_{O_2}^{1/4}$ .

An ionic conductivity is essentially independent on  $P_{O_2}$ . It is suggested that an ionic conductivity predominates at  $P_{O_2}$ 's lower than  $10^{-3}$  atm with respect to  $P_{O_2}$  independence of conductivity. As shown in Figure 6, Lasker and Rapp<sup>6</sup> and Bransky and Tallan<sup>4</sup> interpreted their conductivities as being ionic at  $P_{O_2}$ 's lower than  $10^{-5}$  atm for 7.5 mol % Y<sub>2</sub>O<sub>3</sub>-ThO<sub>2</sub> and pure ThO<sub>2</sub>, respectively. For 10 mol % Ho<sub>2</sub>O<sub>3</sub>-ThO<sub>2</sub>, the  $P_{O_2}$  range in which ionic conductivity appears is somewhat different, however, it is difficult to determine the correct  $P_{O_2}$  range in which ionic conductivity predominates. This is the reason why it is difficult to determine the precise  $P_{O_2}$  at which ionic conduction changes to electronic conduction, since more likely occurring is continuously changing mechanism over the entire  $P_{O_2}$  range.

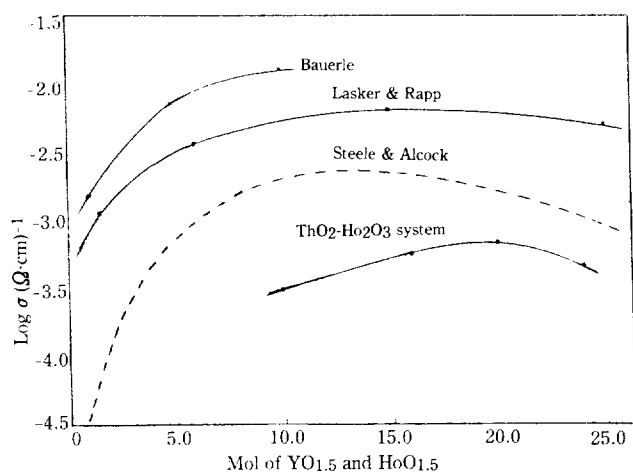
ThO<sub>2</sub> has the large interstitial sites whose presence results in interstitial disorder dominating in this lattice, and since the lower Madelung constant results in the binding of anions to their lattice sites being less strong than that of cations, anion Frenkel pairs are the dominant intrinsic defects in ThO<sub>2</sub>. Lasker<sup>6</sup> reported that the intrinsic defect of ThO<sub>2</sub> is the anion Frenkel defect. As shown in Figure 6, in pure ThO<sub>2</sub>, the conductivity is predominantly ionic at the  $P_{O_2}$  region below  $10^{-5}$  atm. This result might be considered as an intrinsic ionic conduction. The intrinsic ionic conductivity of ThO<sub>2</sub> may be explained by equilibrium (4)



where O'<sub>i</sub> is an interstitial oxygen ion and this is assumed to be the main charge carrier for an ionic conduction. In ThO<sub>2</sub>-Ho<sub>2</sub>O<sub>3</sub> system, an oxygen vacancy is produced by the incorporation of Ho<sub>2</sub>O<sub>3</sub> and then neighboring lattice oxygen is transported through this vacancy. This process is represented by the following



where O<sub>o1</sub> is lattice oxygen and V $\ddot{o}_2$  is oxygen vacancy formed by Ho<sub>2</sub>O<sub>3</sub>. With view to energy level, it is assumed that the energy level of interstitial position is higher than that of lattice site. Consequently, the energy required for reaction (4) to proceed to the right is much more than that for required reaction (5). This assumption is well consistent with the experimental result that the activation energy for the electrical con-



**Figure 7.** Log conductivity ( $1000^{\circ}\text{C}$ ) vs. mol % of  $\text{YO}_{1.5}$  and  $\text{HoO}_{1.5}$  for ionic conductivity of  $\text{ThO}_2\text{-Y}_2\text{O}_3$  and  $\text{ThO}_2\text{-Ho}_2\text{O}_3$  systems.

duction in  $\text{ThO}_2\text{-Ho}_2\text{O}_3$  system is much less than that in pure  $\text{ThO}_2$ . As shown in Figure 6, since  $\text{Po}_2$  dependence of  $\text{ThO}_2\text{-Ho}_2\text{O}_3$  is smaller than pure  $\text{ThO}_2$  and the magnitude of the ionic conductivity of  $\text{ThO}_2\text{-Ho}_2\text{O}_3$  system is larger than that of pure  $\text{ThO}_2$ , it is reasonable to say that the oxygen vacancy concentration produced by doping with  $\text{Ho}_2\text{O}_3$  is larger than that in pure  $\text{ThO}_2$ . It is concluded that the main defect for ionic conduction is an oxygen vacancy produced by doping with  $\text{Ho}_2\text{O}_3$  at  $\text{Po}_2$ 's lower than  $10^{-3}$  atm.

Assuming an ideal solution model, disorder reaction (1) predicts that the ionic conductivity in  $\text{ThO}_2\text{-Ho}_2\text{O}_3$  system would be proportional to the doping ratio of  $\text{Ho}_2\text{O}_3$ , but as shown in Figure 7, it is not a linear function when  $\text{Ho}_2\text{O}_3$  content increases further: The conductivity increases with increasing  $\text{Ho}_2\text{O}_3$  content up to about 10 mol %  $\text{Ho}_2\text{O}_3$  where it goes to a maximum and then decreases with additional doping of  $\text{Ho}_2\text{O}_3$ . In Figure 7, it can be seen that  $\text{ThO}_2\text{-Y}_2\text{O}_3$  system<sup>6,8,31</sup> have the same tendencies as  $\text{ThO}_2\text{-Ho}_2\text{O}_3$  system. The lowering of conductivity of 12 mol %  $\text{Ho}_2\text{O}_3\text{-ThO}_2$  system may originate from decreasing mobility of oxygen ion due to the formation of vacancy ordering<sup>33</sup> or dopant-vacancy interaction<sup>34</sup>.

### Conclusion

The activation energy for an ionic conduction is almost equal to that for an electronic conduction, however, an ionic conductivity is suggested at oxygen partial pressures lower than  $10^{-3}$  atm from  $\sigma$  independent on  $\text{Po}_2$  and an electronic conductivity is confirmed at oxygen partial pressures higher than  $10^{-3}$  atm with  $\sigma \propto \text{Po}_2^{1/4}$ .

The  $\text{ThO}_2\text{-Ho}_2\text{O}_3$  systems investigated have identical defect,  $\text{V}_\text{o}$ , with two different conduction mechanisms, *i.e.*, ionic and electronic.

The charge carriers are an oxygen anion for the ionic conductivity and an electron hole for the electronic conductivity, respectively.

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