

- V. *Cryst. Res. Technol.* **1983**, *18*, 383.
7. Lei, T.; Fanciulli, M.; Molnar, R. J.; Moustakas, T. D.; Graham, R. J.; Scanlon, J. *Appl. Phys. Lett.* **1991**, *59*, 944.
  8. JCPDS File 2-1078.
  9. Elwell, D.; Elwell, M. M. *Prog. Cryst. Growth Charact.* **1988**, *17*, 53.
  10. Karpinski, J.; Jun, J.; Porowski, S. *J. Cryst. Growth* **1984**, *66*, 1.
  11. Akasaki, I.; Amano, H.; Murakami, H.; Sassa, M.; Kato, H.; Manabe, K. *J. Cryst. Growth* **1993**, *128*, 379.
  12. Lei, T.; Moustakas, T. D.; Graham, R. J.; He, Y.; Berkowitz, S. J. *J. Appl. Phys.* **1992**, *71*, 4933.
  13. Kobayashi, A.; Asai, T.; Kawai, S.; Chong, P. J. *MRS Symp. Proc.*; Boston, Symp. Proc.: **1990**, 158, 91; CHE-MICA '90, Auckland, Conf. Proc.: **1990**, 462.
  14. Kim, S. H.; Hwang, J. S.; Chong, P. J.; Choi, J. G. *71st Annual Meeting Kor. Chem. Soc.* **1993**, 47.
  15. Suto, M.; Lee, L. C. *J. Chem. Phys.* **1983**, *78*, 4515.
  16. Vere, A. W.; Rodway, D. C.; Mackey, K. J.; Smith, P. C.; Moores, P. K. *J. Cryst. Growth* **1992**, *121*, 62.
  17. Lee, S. S.; Park, S. M.; Chong, P. J. *J. Mater. Chem.* **1993**, *3*, 347.
  18. Kawabata, T.; Matsuda, T.; Koike, S. *J. Appl. Phys.* **1984**, *15*, 2367.

## Nonstoichiometry of the Terbium Oxide

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The  $x$  values of nonstoichiometric chemical formula,  $Tb_4O_{7-8}$  or  $TbO_{1.5+x}$ , have been determined in temperature range from 600°C to 1000°C under oxygen partial pressure of  $2 \times 10^{-1}$  to  $1 \times 10^{-5}$  atm by using quartz microbalance. The  $x$  values varied from 0.0478 to 0.1964 in the above conditions. The enthalpy of formation for  $x'$  in  $TbO_{1.5+(0.25-x-x')}$ ,  $\Delta H_f$ , was 4.93-3.40 kcal mol<sup>-1</sup> and the oxygen partial pressure dependence was  $-1/8.80 \sim -1/11.8$  under these conditions. The electrical conductivity of the  $TbO_{1.5+x}$  was measured under the same conditions and the values varied from about  $10^{-3}$  to  $10^{-6}$   $\Omega^{-1}cm^{-1}$  within semiconductor range. The activation energies for the conduction increase with oxygen partial pressure from 0.83 to 0.89 eV under the above conditions. The  $1/n$  values obtained from the oxygen pressure dependence of the conductivity are 1/4.4-1/5.2. The conduction mechanism, defect structure, and other physical properties of the oxides are discussed with the  $x$  values, the electrical conductivity values, and the thermodynamic data.

### Introduction

The terbium-oxygen and the praseodymium-oxygen systems have many similarities for physical properties<sup>1</sup>.  $Tb_4O_7$  is dark brown or black solid and contains the equal amounts of  $Tb^{3+}$  and  $Tb^{4+}$ . It dissolves in hot concentrated acids with formation of salts and loses oxygen on heating.

In the terbium-oxygen system, there are many phases with compositions  $TbO_{1.500}$ ,  $TbO_{1.714}$ ,  $TbO_{1.816}$ ,  $TbO_{1.830}$  and  $TbO_2$ . Hyde and Eyring<sup>2</sup> have suggested that these phases belong to a homologous series of  $Tb_nO_{2n-2}$ .  $Tb_2O_3$  possesses the C-type structure up to about 1500°C while  $TbO_2$  crystalized with the fluorite structure. The  $TbO_{1.5+x}$  may contain excess oxygen where  $x$  may have a value up to 0.1 at temperatures of 950-1000°C at 500-600 torr  $O_2$ .

Vasil'eva *et al.*<sup>3</sup> showed the plot of  $-RT \ln P_{O_2}$  vs composition with isotherms and phase regions indicated. Kordis and Eyring<sup>4</sup> reported a partial phase diagram which was derived from an isobaric study using high-temperature X-ray diffraction. They have also confirmed some of the isobaric and isothermal tensiometric studies<sup>5</sup> with a sample ( $TbO_2$ ) of greater purity.

The electrical conductivity for rare earth oxides has been studied<sup>6,7,8</sup>. Subba Rao *et al.*<sup>8</sup> suggested that an electrical conductivity maximum occurs at  $TbO_{1.75}$ , and the result is interpreted in terms of the hopping model and the small polaron theory. The oxide is a p-type semiconductor in the  $TbO_{1.5}$ - $TbO_{1.75}$  range and an n-type semiconductor in the  $TbO_{1.75}$ - $TbO_2$ .

These earlier studies did not include a quantitative evaluation of the relationship between the nonstoichiometric composition and the electrical conductivity. The objective of the present study is to determine the high temperature defect structure of the pure  $Tb_4O_7$  by means of the weight change and electrical conductivity measurements. The electrical conductivity is closely related to the nonstoichiometric compositions of the oxides, and a combination of these measurements gives informations on the defect structure and conduction mechanism. The thermodynamic properties and conduction mechanism of terbium oxide shall be discussed with the nonstoichiometry, the enthalpy of formation of  $x'$ , the oxygen partial pressure dependence of  $x'$ , the activation energy of the electrical conductivity, and the oxygen partial pressure dependence of the electrical conductivity.

## Experimental

Polycrystalline powder of terbium oxide ( $Tb_4O_7$ , Rare Metallic Co., LTD., 99.99%) was compressed under  $3 \text{ ton cm}^{-2}$  pressure into pellets about 0.02 cm and 0.3 cm thick. These pellets were sintered at  $1150^\circ\text{C}$  under an atmospheric air pressure for about 48 hr, and then quenched to room temperature. The 0.02 cm thick pellet was cut into about 0.048 g piece and this piece was used for the nonstoichiometric composition study. The 0.3 cm thick pellet was used for measuring the electrical conductivity. The phase structure of the sample is confirmed as the cubic structure from X-ray diffraction patterns.

Changes in nonstoichiometry have been studied directly through thermogravimetry by measuring the weight change of the specimen as a function of temperature and oxygen partial pressure. Details about the apparatus, measuring procedure and correction for the balance height change due to buoyance and thermomolecular flow were described in previous papers<sup>9,10,11</sup>. The calibration equation for the quartz microbalance used in this study is  $\Delta W (g) = 2.098 \times 10^{-5} \cdot \Delta h (mm) + 3.109 \times 10^{-6}$ , where  $\Delta W$  is the weight in grams read to 0.00001 g and  $\Delta h$  is the balance height change in millimeters read to 0.01 mm using microscopy. The weight changes of the samples have been measured in the temperature range of  $600^\circ\text{C}$  to  $1000^\circ\text{C}$  under several fixed oxygen partial pressures from  $2 \times 10^{-1}$  to  $1 \times 10^{-5}$  atm.

The electrical conductivities of the samples have been measured by the four probe method<sup>9</sup> at the same experimental conditions.

## Results and Discussion

The  $x$  values of the  $TbO_{1.5+x}$  are calculated from the weight changes of the sample by using the quartz microbalance. To distinguish the measuring steps, the nonstoichiometric formula of the  $TbO_{1.5+x}$  is also denoted in terms of  $TbO_{1.5+(0.25-x_0-x')}$ . The  $x^o$  is the nonstoichiometricity of the sintered sample calculated as follows:

$$x^o = \frac{\Delta W^o}{W_s} \times \frac{M}{4 A_o}$$

where  $\Delta W^o$  is the weight change after sintering of  $Tb_4O_7$ ,  $W_s$  the weight of the stoichiometric sample,  $M$  the molecular weight of  $Tb_4O_7$ , and  $A_o$  the atomic weight of oxygen. The  $x'$  value is also calculated as follows:

$$x' = \frac{\Delta W'}{W_s} \times \frac{M}{4 A_o}$$

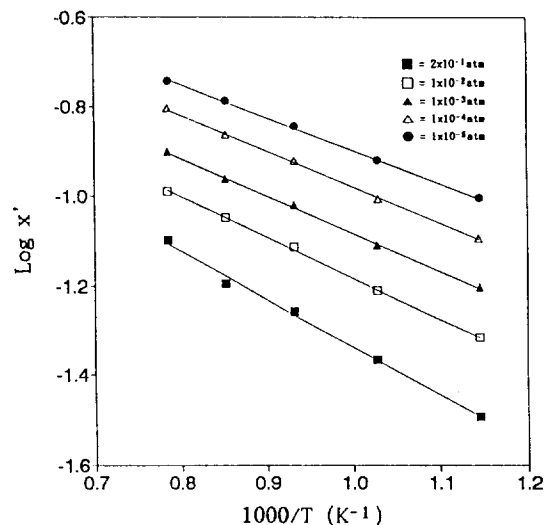
where  $\Delta W'$  is the weight change of the sample in accordance with the temperature and oxygen pressure changes.

Since the  $x^o$  was calculated to 0.0217, the  $TbO_{1.5+(0.25-x_0)}$  should be the  $TbO_{1.5+(0.25-0.0217)}$  or  $TbO_{1.7283}$  after the sintering. The  $x'$  value in the nonstoichiometric composition of the  $TbO_{1.7283-x'}$  can be calculated by the similar way based on the weight change of the sample at the range of 600 to  $1000^\circ\text{C}$  under each oxygen partial pressure. Thus, the  $x$  value for the nonstoichiometric chemical formula,  $TbO_{1.5+x}$ , can be determined from the  $x^o$  and  $x'$  values and is listed in Table 1. The  $x$  values for several temperatures under various oxy-

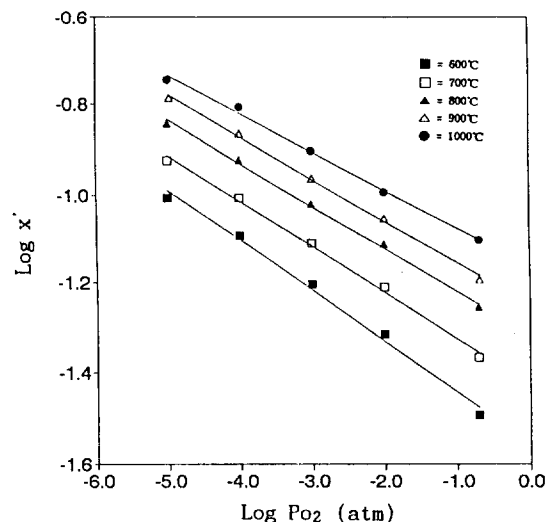
**Table 1.** The  $1.5+x$  Values of the  $TbO_{1.5+x}$  as a Function of Temperature Under Various Oxygen Partial Pressures\*

| Temperature<br>( $^\circ\text{C}$ ) | Oxygen partial pressure (atm) |                    |                    |                    |                    |
|-------------------------------------|-------------------------------|--------------------|--------------------|--------------------|--------------------|
|                                     | $2 \times 10^{-1}$            | $1 \times 10^{-1}$ | $1 \times 10^{-3}$ | $1 \times 10^{-4}$ | $1 \times 10^{-5}$ |
| 600                                 | 1.6964                        | 1.6799             | 1.6658             | 1.6480             | 1.6297             |
| 700                                 | 1.6853                        | 1.6667             | 1.6509             | 1.6297             | 1.6089             |
| 800                                 | 1.6729                        | 1.6515             | 1.6331             | 1.6089             | 1.5847             |
| 900                                 | 1.6644                        | 1.6387             | 1.6191             | 1.5915             | 1.5644             |
| 1000                                | 1.6488                        | 1.6257             | 1.6026             | 1.5712             | 1.5478             |

\* Maximum deviation =  $\pm 0.0001$ .



**Figure 1.** Plot of  $\log x'$  vs  $1000/T$  at various oxygen partial pressures.



**Figure 2.** Plot of  $\log x'$  vs  $\log P_{O_2}$  at various temperatures.

gen partial pressures were not included because thermodynamic equilibria could not be obtained in the temperatures even after several hours. Plot of  $\log x'$  vs  $1000/T$  and of  $\log x'$  vs  $\log P_{O_2}$  are linear as shown in Figures 1 and 2, respectively. The enthalpies of formation of the nonstoichiometric compositions calculated from the slopes of the Arrhe-

**Table 2.** Enthalpies of Formation of  $\text{TbO}_{1.7283-x'}$  Under Various Oxygen Partial Pressures

| Oxygen partial pressure (atm) | Enthalpy of formation (kcal mol <sup>-1</sup> ) |
|-------------------------------|---|
| $2 \times 10^{-1}$            | 4.93  |
| $1 \times 10^{-2}$            | 4.18  |
| $1 \times 10^{-3}$            | 3.87  |
| $1 \times 10^{-4}$            | 3.70  |
| $1 \times 10^{-5}$            | 3.40  |

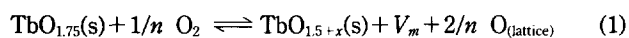
**Table 3.**  $1/n$  Values of the Plot of  $\log x'$  vs  $\log P_{\text{O}_2}$  (or  $\log x' \propto 1/n \log P_{\text{O}_2}$ ) at Various Temperatures

| Temperature (°C) | $1/n$ value |
|------------------|-------------|
| 600              | -1/8.80     |
| 700              | -1/9.68     |
| 800              | -1/10.4     |
| 900              | -1/10.5     |
| 1000             | -1/11.8     |

nius plot are listed in Table 2. Table 3, which shows us the oxygen partial pressure dependence of the nonstoichiometric compositions or the  $1/n$  values obtained from the slopes of the plot of the  $\log x'$  vs  $\log P_{\text{O}_2}$  (or  $\log x' \propto 1/n \log P_{\text{O}_2}$ ). Since the  $x'$  value increases with increasing temperature and decreasing oxygen partial pressure, the mole ratio of the excess oxygen content or the  $x$  value of  $\text{TbO}_{1.5+x}$  decreases with increasing temperature and decreasing oxygen partial pressure from 0.2283 of the  $\text{TbO}_{1.7283}$ .

In general, nonstoichiometric rare earth oxides,  $\text{LnO}_x$ , can be divided into  $p$ -type semiconductors for  $1.50 \leq x \leq 1.75$  and  $n$ -type semiconductors for  $1.75 \leq x \leq 2.00$ , respectively. In the present study, the  $x$  values of the  $\text{TbO}_{1.5+x}$  might be positive at the experimental conditions and thus the  $\text{TbO}_{1.5+x}$  should be a  $p$ -type semiconductor on the basis of the nonstoichiometry. The metal oxides of the  $p$ -type semiconductor have the excess oxygen formed by the defects due to metal vacancy or oxygen interstitial. The enthalpies of formation ( $\Delta H_f$ ) of the nonstoichiometric compositions shown positive values corresponding to the endothermic formation process.

The oxygen partial pressure dependence of the nonstoichiometric compositions can be expressed as



where  $V_m$  is the unionized metal vacancies and  $\text{O}_{(\text{lattice})}$  the interstitial oxygen. By the principle of chemical equilibrium, the constant,  $K_x$ , and the oxygen partial pressure,  $P_{\text{O}_2}$ , are related as follows,

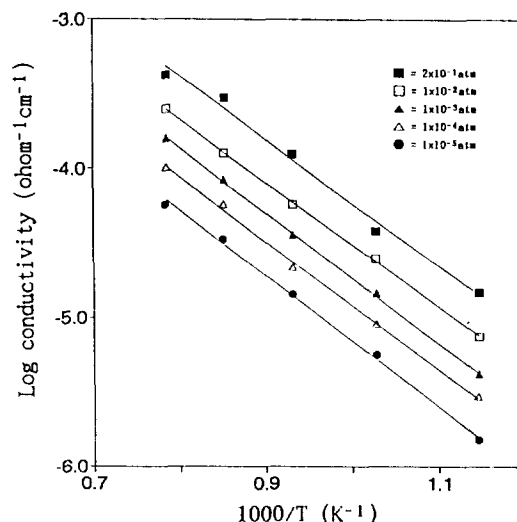
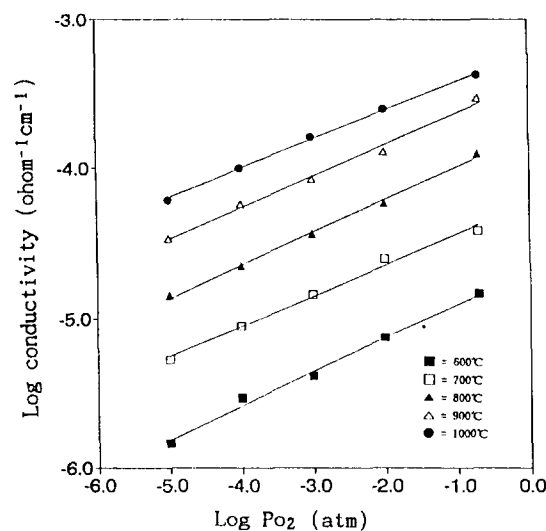
$$K_x = [V_m] P_{\text{O}_2}^{1/n} \quad (2)$$

$$[V_m] = K_x P_{\text{O}_2}^{-1/n} \quad (3)$$

Now the  $x'$  values are proportional to  $[V_m]$ , and thus,

$$x' \propto [V_m] \quad (4)$$

From equations (3) and (4) we obtain,


**Figure 3.** Plot of log conductivity vs  $1000/T$  at various oxygen partial pressures.

**Figure 4.** Plot of log conductivity vs  $\log P_{\text{O}_2}$  at various temperatures.

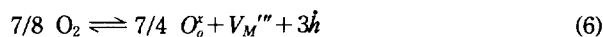
$$x' \propto K_x P_{\text{O}_2}^{1/n} \quad (5)$$

Therefore, the  $x'$  values are proportional to the  $P_{\text{O}_2}^{1/n}$  values and the oxygen pressure dependence or  $1/n$  values increases with increasing the temperature.

Plot of log conductivity vs  $1000/T$  under various oxygen pressures and of log conductivity vs  $\log P_{\text{O}_2}$  at several fixed temperatures are linear as shown in Figures 3 and 4, respectively. The activation energies are obtained from the slopes of the Arrhenius plot. The  $1/n$  values are calculated from the slopes of the plot of log conductivity vs  $\log P_{\text{O}_2}$ . The average activation energy for electrical conductivity was found to be 0.86 eV close to 0.95 eV reported by Subba Rao *et al.*<sup>8</sup> The difference between the activation energies is attributed to the sample preparation conditions, impurity effects, and the ionic contribution to the conductivity.

The electrical conductivity for terbium oxide might be explained in terms of the nonstoichiometry as the main factor. The lower the oxygen pressure, the less lattice oxygen is

formed in the terbium oxide: conversely at the higher oxygen pressures more terbium vacancies are formed. The ionization of metal vacancy to a trivalent positive ion follows the reactions:



where  $O_o^\times$  is the oxygen atom at a lattice site,  $V_M'''$  the metal vacancy ionized to a trivalence and  $\dot{h}$  the positive hole. Applying the mass action law to equation (6) and (7), and assuming the charge neutrality as like,  $P = [\dot{h}] = 3[V_M'''] + 4[V_M''']$ , it may be written as follows:

$$P = (3K)^{1/4} P_{O_2}^{7/32} \quad \text{for } [V_M'''] \gg [V_M''] \quad (8)$$

$$P = (3K)^{1/5} P_{O_2}^{7/40} \quad \text{for } [V_M'''] \gg [V_M'''] \quad (9)$$

Thus the electrical conductivity is given by the following relationship,

$$\sigma = \mu \cdot P \cdot e \quad (10)$$

where  $\mu$  is the hole mobility and  $P$  the positive hole concentration. If  $\mu$  is assumed constant, the conductivity  $\sigma$  can be expressed:

$$\log \sigma \propto 1/4.6 \log P_{O_2} \quad \text{for } [V_M'''] \gg [V_M'''] \quad (11)$$

$$\log \sigma \propto 1/5.7 \log P_{O_2} \quad \text{for } [V_M'''] \gg [V_M'''] \quad (12)$$

As shown in Figure 4, the electrical conductivity increases with oxygen pressure at a given temperature. The oxide shows the typical  $p$ -type characteristics. The  $1/n$  values are 1/4.4-1/5.2 close to the theoretical value of 1/4.6. The difference of the values is ascribed to the ration of  $[V_M'''] \gg [V_M''']$ . Therefore, we concluded that  $Tb_4O_7$  is a positive hole type semiconductor based on the defect model of the ionized metal vacancy. The result is consistent with the nonstoichiometric compositions.

Conclusively, the predominant defects contributing to the nonstoichiometric composition, or the  $x$  value in  $TbO_{1.5+x}$ ,

are the ionized metal vacancies and the nonstoichiometric conduction mechanism is explained by the hopping model<sup>8</sup> and small polaron theory of the positive hole. Thus, in the electrical conductivity of the terbium oxide system, the  $4f^6$  electrons are not the conduction particles<sup>12</sup>, but the positive ion in the 5d band(conduction band) and the negative ions in the 2p band(valence band) provide the charge transfer mechanism.

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## References

1. Kofstad, P. *Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxide*; John Wiley & Sons, Inc.: New York, 1972; p 289.
2. Hyde, B. G.; Eyring, L. *Rare Earth Research III*; Science Publishers, Inc.: New York, 1965; p 289.
3. Vasil'eva, A.; Gerasimov, Y. I.; Maiorova, A. F.; Pervova, I. V. *Dokl. Akad. Nauk SSSR* **1975**, 221(4), 865.
4. Burnham, D. A.; Eyring, L.; Kordis, J. *J. Phys. Chem.* **1968**, 72(13), 4425.
5. Kordis, J.; Eyring, L. *J. Phys. Chem.* **1968**, 72(6), 2030.
6. Chang, S. H.; Yo, C. H.; Choi, J. S.; Pyon, M. S. *J. Kor. Chem. Soc.* **1984**, 28(4), 231.
7. Breuil, H.; Dherbomez, N.; Wilbert, Y. C. *R. Acad. Sci. Ser. C.* **1973**, 277(18), 871.
8. Subba Rao, G. V.; Ramdas, S.; Mehrotra, P. N.; Rao, C. N. R. *J. Solid State Chem.* **1970**, 2, 377.
9. Yo, C. H.; Ko, S. K.; Won, H. J.; Choi, J. S. *J. Phys. Chem. Solids* **1984**, 45(8/9), 899.
10. Yo, C. H.; Kim, C. W.; Lee, E. S.; Pyon, W. B.; Choi, J. S. *J. Phys. Chem, Solids* **1988**, 49(7), 835.
11. Yo, C. H.; Ryu, K. S.; Pyon, W. B.; Pyon, M. S. *J. Phys. Chem. Solids* **1990**, 51(6), 557.
12. Pratap, V.; Verma, B. K.; Lal, H. B. *Proc. Nat. Acad. Sci. India Sect A.* **1978**, 48(1), 20.