

# Thermoelectric Power in Nonstoichiometric Orthorhombic Titanium Oxides

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**Nonstoichiometric orthorhombic titanium oxides (TiO<sub>x</sub>;  $x = 1.86$ – $1.94$ ) prepared by reducing the anatase titanium oxide in H<sub>2</sub> at 950°C are found to show large thermoelectric power. Their Seebeck coefficients are in the range  $-0.060$  to  $-0.518$  mV/K, and theoretical discussions are made based on the assumption that the electronic spin entropy dominating the entropy current is a main factor of the thermoelectric power. The figure of merit for TiO<sub>1.94</sub> at 70°C is estimated at 0.195. The nonstoichiometric orthorhombic titanium oxides, containing no hazardous elements, are promising materials for thermoelectric power generation.**

## I. Introduction

Thermoelectric effects of metal oxides have attracted much attention since the middle of the 1990s. Various kinds of metal oxides, such as Na<sub>x</sub>CoO<sub>4</sub>, Ba<sub>1-x</sub>Sr<sub>x</sub>PbO<sub>3</sub>, and (ZnO)<sub>m</sub>In<sub>2</sub>O<sub>3</sub>, have been found to exhibit high thermo-electromotive force,<sup>1–3</sup> and new theoretical approaches have been developed to derive thermoelectric properties in strongly correlated electron systems.<sup>4–8</sup> The thermoelectric oxides have been extensively investigated also from the viewpoint of applications in thermoelectric devices, which generate electric power from waste heat, because they have advantages in resistance to oxidation and to heat over the conventional thermoelectric alloys.<sup>9,10</sup> From the practical point of view, thermoelectric materials consisting of nonhazardous and inexpensive elements are highly desirable.

Although titanium oxides, having the composition of Ti<sub>n</sub>O<sub>2n-1</sub>, where  $n$  is an integer above 2, have been well known as Magneli phases,<sup>11–14</sup> we have recently found new orthorhombic phases of titanium oxides with nonstoichiometric compositions of TiO <sub>$x$</sub>  ( $x = 1.85$ – $1.94$ ).<sup>15</sup> The new orthorhombic phases were obtained by reducing the anatase or the rutile TiO<sub>2</sub> in H<sub>2</sub> at 950°C, and the O/Ti ratio  $x$  can be controlled in the range 1.85–1.94 by changing the reduction time from 1 to 5 h. Most of the conventional Ti<sub>n</sub>O<sub>2n-1</sub> ( $n = 2$ – $6$ ) exhibit a semiconductor–metal transition at a critical temperature, and thus we have investigated the electrical and optical properties of the new orthorhombic phases first.<sup>16</sup> In the conductivity measurement we discovered an unexpected thermoelectric property of the new orthorhombic titanium oxides comparable to the other of the previously known thermoelectric oxides. It is believed that this is the first observation of thermoelectric effect for the Ti–O system. In this study, we present the thermoelectric properties of the new orthorhombic titanium oxides (TiO <sub>$x$</sub> ,  $x = 1.86$ , 1.88, and 1.94) and give a theoretical discussion on the Seebeck coefficient on the basis of the spin-entropy current.

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## II. Experimental Procedure

According to our previous report,<sup>5</sup> the orthorhombic titanium oxides with the composition of TiO <sub>$x$</sub>  ( $x = 1.94$ , 1.88, and 1.86) were prepared by reducing the anatase titanium oxide in H<sub>2</sub> at 950°C for 1, 3, and 5 h, respectively. The O/Ti ratio  $x$  was determined by thermogravimetry from mass increase accompanied by an oxidation from TiO <sub>$x$</sub>  to TiO<sub>2</sub> in air in the range 430°–570°C. The anatase powder was pressed into pellets ( $\phi 2.5$  mm  $\times$  2–3 mm), and gold electrodes were coated on the top and bottom surfaces and at the two points on the side using gold paste (Tokuriki Chemical Corporation No. 8570, Japan). Reducing the cylindrical powder compacts in H<sub>2</sub> at 950°C yielded dark blue polycrystal pellets, whose relative densities were in the range 55%–64%.

The performance of thermoelectric materials is evaluated by a measure of a material's thermoelectric properties  $Z$ ,

$$Z = S^2 \rho^{-1} \kappa^{-1} \quad (1)$$

where  $S$  is the Seebeck coefficient,  $\rho$  is resistivity, and  $\kappa$  is thermal conductivity.

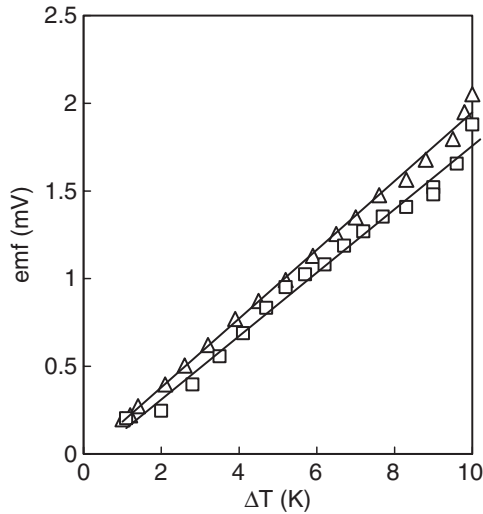
In the present study, the Seebeck coefficient and the resistivity were measured at 25°, 40°, and 70°C, in view of the application to the waste heat recovery. The cylindrical pellet was sandwiched with two copper plates and its bottom was made to contact with a temperature-controlled hot plate. The temperature of both copper plates was measured with thermocouples type K, and the thermoelectromotive force induced between the two plates was measured by an HP34401A electrometer (Hewlett-Packard, Palo Alto, CA). The electromotive force was measured as a function of the temperature difference in the range 0 to ca. 10 K. As for the measurement at 25°C, the Seebeck coefficient was calculated from the slope of the fitted line from 0 to ca. 10 K. On the other hand, as for the measurements at 40° and 70°C, the fitted line from 0 to ca. 3 K was used to calculate the Seebeck coefficient. This is because the slope of the curves measured at 40° and 70°C showed a slight decrease with increasing temperature difference.

The resistivity was measured for the same specimens used in the Seebeck coefficient measurement by the direct current four-probe method. A constant current was made to flow from two outside electrodes using an R6144 current source (Advantest Corporation, Japan), and the electrical potential difference between the two inside electrodes induced by the constant current was measured using an HP34401A electrometer (Hewlett-Packard).

The thermal conductivity was measured for the larger pellets prepared with the same condition using the laser flash method (TC-7000, Ulvac-Riko Corporation, MA).

## III. Results and Discussion

Figure 1 shows the relationship between thermoelectromotive force and the temperature difference at 25°C. The sign of the electromotive force was plus on the higher temperature side, i.e.,



**Fig. 1.** Relationship between thermoelectromotive force and temperature difference at 25°C.  $\Delta$ :  $x = 1.88$ ,  $\square$ :  $x = 1.86$ .

the sign of the Seebeck coefficient was minus, indicating that the specimens were n-type semiconductor. The Seebeck coefficients estimated from the relationship by the least-squares method at 25°, 40°, and 70°C are summarized in Table I. The Seebeck coefficient of  $\text{TiO}_{1.94}$  at 70°C was  $-0.518$  mV/K. This value is greater than that of the  $[(\text{Ca}, \text{Sr}, \text{Bi})_2\text{CoO}_3]_x\text{CoO}_2$  (0.14 mV/K), which has been intensively investigated toward commercial application.<sup>10</sup> In most cases, the present orthorhombic titanium oxides showed the Seebeck coefficients to be greater than 0.1 mV/K.

Theoretical prediction of the Seebeck coefficient based on the Heikes formula in the Hubbard model is given as follows.<sup>17–19</sup> The charge carrier transport in the thermoelectric effect is ascribed to the difference of chemical potential due to the temperature gradient, and the chemical potential is dependent on the entropy current dominated by the electronic spin entropy. On the basis of the assumption of the high-temperature limit of the thermoelectric effect, the Seebeck coefficient is expressed as

$$Q = -\frac{\mu}{qT} \quad (2)$$

where  $\mu$  is the chemical potential and  $q$  is the charge of a carrier. The chemical potential  $\mu$  is given by

$$\frac{\mu}{T} = -\left(\frac{\partial s}{\partial N}\right)_{E,V} \quad (3)$$

where  $s$  is the entropy of the system, and  $E$  and  $V$  are internal energy and volume, respectively. The entropy  $s$  is expressed as

$$s = k_B \ln g \quad (4)$$

where  $g$  is the degeneracy. By substituting Eq. (4) into Eq. (3), we obtain

$$\frac{\mu}{T} = -\left(\frac{\partial \ln g}{\partial N}\right)_{E,V} \quad (5)$$

Thus, the Seebeck coefficient in the high-temperature limit is expressed as

$$Q = -\frac{\kappa_B}{e} \frac{\partial \ln g}{\partial N} \quad (6)$$

where  $e$  is the elementary charge.

**Table I.** The Seebeck Coefficient ( $S$ , mV/K) of  $\text{TiO}_x$  ( $x = 1.86, 1.88, \text{ and } 1.94$ ) at 25°, 40°, and 70°C

	25°C	40°C	70°C
$\text{TiO}_{1.86}$	-0.181	-0.199	-0.483
$\text{TiO}_{1.88}$	-0.196	-0.237	-0.292
$\text{TiO}_{1.94}$	-0.060	-0.170	-0.518

This theory is extendable to the nonstoichiometric titanium oxides,  $\text{TiO}_x$ . The numbers of the configurations of  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$  are defined as  $g_3$  and  $g_4$ , respectively. Since  $\text{Ti}^{3+}$  has one 3d-electron in three  $t_{2g}$  orbitals,  $g_3$  is calculated at six by the product of  $(2S+1)$  and 3, where  $S (= 1/2)$  is the magnitude of spin. Similarly,  $g_4$  is calculated at one because  $\text{Ti}^{4+}$  has no 3d-electron. The total number of the possible states  $g$  is expressed as

$$g = g_3^{N_A - M} g_4^M \frac{N_A!}{M!(N_A - M)!} \quad (7)$$

where  $M$  is the number of  $\text{Ti}^{4+}$  and  $N_A$  is the sum of  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$ . By substituting Eq. (7) into Eq. (5), the Seebeck coefficient of the nonstoichiometric titanium oxides is given by

$$Q = -\frac{k_B}{e} \ln \left( \frac{g_3}{g_4} \frac{x}{1-x} \right) \quad (8)$$

where  $x (= M/N_A)$  is the ratio of  $\text{Ti}^{4+}$ .

The Seebeck coefficients were calculated by applying Eq. (8) to  $\text{TiO}_x$ . The ratio of  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$  was estimated from the average valence of a titanium ion determined by the O/Ti ratio. As shown in Table II, the Seebeck coefficients of  $\text{TiO}_{1.94}$ ,  $\text{TiO}_{1.88}$ , and  $\text{TiO}_{1.86}$  predicted by Eq. (8) were  $-0.326$ ,  $-0.254$ , and  $-0.236$  mV/K, respectively. These theoretical values were found to be rather close to the experimental values at 70°C in Table I.

Here we should note that the theory above is based on the assumption of the high-temperature limit ( $\sim 10\,000$  K). Although such agreement between the theoretical and the experimental values has also been reported for  $\text{NaCo}_2\text{O}_4$ , the fact that the theoretical values ( $\sim 10\,000$  K) are near the experimental ones at 70°C (343 K) is said to be an anomalous behavior. The agreement between these suggests that the system has a tendency to exhibit various phase transitions by doping impurities. Actually, the  $\text{NaCo}_2\text{O}_4$  system has been reported to show spin-density-wave, itinerant ferromagnetism, and superconductivity.<sup>20–22</sup> From this analogy, it is probable that many intriguing physical properties of the nonstoichiometric titanium oxides ( $\text{TiO}_{2-\delta}$ ) remain undiscovered, because there are few researches on the present nonstoichiometric titanium oxides. It is expected that the physical properties of the nonstoichiometric titanium oxides will be a hot area of study from the viewpoint of fundamental solid-state physics as well as for practical applications.

The figures of merit of the present nonstoichiometric titanium oxides is evaluated as follows. The resistivity of  $\text{TiO}_{1.94}$  was 0.0646, 0.0590, and 0.0519  $\Omega \cdot \text{cm}$  at 25°, 40°, and 70°C, respectively. The temperature dependence was semiconductive, which corresponded to the negative sign of the Seebeck coefficients above. The thermal conductivity of  $\text{TiO}_{1.86}$ ,  $\text{TiO}_{1.88}$ , and  $\text{TiO}_{1.94}$

**Table II.** The Theoretically Predicted Seebeck Coefficient ( $S$ , mV/K) of  $\text{TiO}_x$  ( $x = 1.86, 1.88, \text{ and } 1.94$ ) at High-Temperature Limit Based on Eq. (8)

	$\text{Ti}^{3+}$ (%)	$\text{Ti}^{4+}$ (%)	$g_3/g_4$	$x/(1-x)$	$Q$ (mV/K)
$\text{TiO}_{1.86}$	28	72	6	2.57	-0.236
$\text{TiO}_{1.88}$	24	76	6	3.17	-0.254
$\text{TiO}_{1.94}$	12	88	6	7.33	-0.326

**Table III. The Measure of a Material's Thermoelectric Properties ( $Z$ ,  $\times 10^{-5} \text{ K}^{-1}$ ) and the Figure of Merit ( $ZT$ ) for  $\text{TiO}_x$  ( $x = 1.86, 1.88, \text{ and } 1.94$ ) at  $25^\circ\text{C}$ ,  $40^\circ\text{C}$ , and  $70^\circ\text{C}$**

	$Z (\times 10^{-5} \text{ K}^{-1})$			$ZT$		
	$25^\circ\text{C}$	$40^\circ\text{C}$	$70^\circ\text{C}$	$25^\circ\text{C}$	$40^\circ\text{C}$	$70^\circ\text{C}$
$\text{TiO}_{1.86}$	0.43	0.52	3.17	0.0013	0.0016	0.0109
$\text{TiO}_{1.88}$	0.50	0.74	1.16	0.0015	0.0023	0.0040
$\text{TiO}_{1.94}$	0.61	5.38	56.8	0.0018	0.017	0.195

was estimated at  $1.0, 1.0, \text{ and } 0.91 \text{ W} \cdot (\text{m} \cdot \text{K})^{-1}$ , respectively, at  $25^\circ\text{C}$ . Table III shows the measure of a material's thermoelectric properties ( $Z$ ) and the figure of merit ( $ZT$ ). The figure of merit for  $\text{TiO}_{1.94}$  at  $70^\circ\text{C}$  reached  $ZT = 0.195$ . This value is comparable to the other reported n-type materials, such as  $(\text{ZnO})_5$  ( $\text{In}_{0.97}\text{Y}_{0.03}$ ) $_2\text{O}_3$ ,<sup>23</sup>  $\text{Ba}_{1-x}\text{Sr}_x\text{PbO}_3$ , and  $\text{CaMnO}_3$ .<sup>25</sup> It is thought that the present nonstoichiometric titanium oxides have advantages over such thermoelectric materials with regard to environmental loading, because they contain no hazardous heavy metals. Moreover, there is also a possibility of further improvement of performance by optimizing the synthetic condition. In the present study, the polycrystal pellets were employed, aiming at the practical applications, and therefore the performance estimated above may be dependent on some qualities of each pellet, such as porosity, grain size, and inhomogeneity. It can be said that there still remains a need to clarify the theoretical mechanism of thermoelectric oxides. The usage of the single crystals would be more effective to provide theoretical details.

#### IV. Summary

It was found that the nonstoichiometric orthorhombic titanium oxides ( $\text{TiO}_x$ ,  $x = 1.85\text{--}1.94$ ) obtained by reducing anatase  $\text{TiO}_2$  show a large thermoelectric effect. It is believed that this was the first observation of the thermoelectric effect with regard to the Ti–O system. The Seebeck coefficient of  $\text{TiO}_{1.94}$  at  $70^\circ\text{C}$  was  $-0.518 \text{ mV/K}$ , and its figure of merit ( $ZT$ ) was estimated at 0.195. This value is comparable to the other reported thermoelectric materials, and there is still a possibility that titanium oxides with higher performance remain undiscovered. The experimental Seebeck coefficients were compared with the theoretical values predicted by assuming that the entropy current dominated by the electronic spin entropy determines the Seebeck coefficient. Although the theoretical values were close to the experimental ones, there appears to remain a need to formulate the theory to explain the thermoelectric effects of Ti–O system. Further theoretical discussions would be possible by using single crystals of the nonstoichiometric orthorhombic titanium oxides. It can be said that thermoelectric power generation using the nonstoichiometric orthorhombic titanium oxides has advantages with regard to environmental load, not only because they show high performance but also because they contain no hazardous elements.

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