Thermoelectric Properties of Non-stoichiometric Titanium Oxides for Waste Heat Recovery in Steelworks

Noriyuki OKINAKA and Tomohiro AKIYAMA

Center for Advanced Research of Energy Conversion Materials, Hokkaido University, Kita-13, Nishi-8, Kita-ku, Sapporo 060-8628 Japan.
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The thermoelectric properties of a nonstoichiometric titanium oxide (TiO₁.₁) are investigated in terms of materials for high-temperature thermoelectric conversion. The electrical conductivity, σ, of TiO₁.₁ increases to 9000 S/m at 1073 K, is showing semiconducting behavior. The Seebeck coefficient, α, of TiO₁.₁ shows a general trend in which the value increases gradually from 0.4 mV/K at 573 K to 1.0 mV/K at 1223 K. As a consequence, the power factor, α²σ, reaches 8.6×10⁻³ W/(m·K)², the largest value of all reported oxide materials. The thermal conductivity, κ, of TiO₁.₁ increases with temperature, from 1.3 W/(m·K) at 573 K to 7.1 W/(m·K) at 1223 K. In spite of the considerably large values of κ, the figure of merit, Z=α²σ/κ, reaches 1.6×10⁻² K⁻¹ for TiO₁.₁ at 973 K. The extremely large power factor of TiO₁.₁, compared to other metal oxides can be attributed to the optimal carrier density. The dimensionless figure of merit, ZT, of 1.64 attained by TiO₁.₁ at 1073 K is the largest value of all reported other thermoelectric materials in this temperature region. And that TiO₁.₁ has ZT values of nearly unity or greater in the range of 773 to 1223 K, demonstrates the usefulness of the nonstoichiometric titanium oxides for high-temperature thermoelectric conversion.

KEY WORDS: thermoelectric materials; non-stoichiometric titanium oxide; large figure of merit; flash synthesis (FS); waste heat; steelworks.

1. Introduction

In the process of ironmaking and steelmaking, a large amount of heat is exhausted. For example, in a typical steelwork of Japan, the outflow heat is 11,400 MJ/t, however, the recovery ratio of outflow heat is only 17.5% in enthalpy basis and 25.3% in exergy basis. There’s still large room for exhaust heat recovery in steelworks. Thermolectric generator (TEG) is considered to be a promising method to achieve energy savings and waste heat recovery efficiently in steelworks. TEG can convert thermal energy into electric energy directly by Seebeck effect; furthermore they are compact, quiet, rugged, stable, and very reliable. In order to realize the application of TEG in waste heat recovery in steelworks, the materials of TEG should have good heat and oxidation resistance, high energy conversion efficiency, and low production cost. Therefore, oxide becomes the focus of attention for high-temperature application.

TEG converts thermal energy directly into electrical energy via the Seebeck effect induced by the temperature difference in solid materials. The energy balance of thermoelectrics yields the figure of merit, Z=α²σ/κ, where σ is the electrical conductivity, α is the Seebeck coefficient, and κ is the thermal conductivity of the material. The product of Z and the absolute temperature T, ZT, is thereby employed as the most inclusive criterion for evaluating thermolectric materials. Efficient materials have ZT values that are close to unity or greater; the equation ZT=1 corresponds to a conversion efficiency of over 10%; to date, no materials have achieved ZT=2.

In the last three decades, Si–Ge alloys, several metal chalcogenides, transition-metal disilicides and some boron compounds have attracted attention and have been developed as materials for high-temperature thermoelectrics. However, the abovementioned materials have never been applied practically because of expensive surface protection required to prevent oxidation or vaporization and/or inherent temperature limitation due to phase transformation at high temperatures. With regard to the high-temperature operation of thermoelectric transducer, it is apparent that metal oxides are advantageous because of their excellent chemical stability under heat conditions.

Metal oxides are usually considered to be low-mobility materials, primarily because of their highly ionic characters. In reality, however, some oxides exhibit considerably high carrier mobilities, e.g., the reported value of the Hall mobility of SnO₂ single crystals is one-order larger than that of the drift mobility of copper. Hence, we began investigating the thermoelectric properties of oxides.

Titanium oxide is well known to be a conductive oxide. The electrical properties of TiO have particularly attracted considerable attention in a wide range of fields in chemistry and physics. In previous study, we found nonstoichiometric titanium oxide indicated was no longer semimetal but semiconductor. The purpose of this paper is to study the thermoelectric properties of nonstoichiometric titanium oxide at high temperatures from viewpoint of thermoelectrics by revealing the highly promising thermoelectric figure of
merit of the defect-controlled TiO$_{1+x}$ [1]. Here, we discuss the thermoelectric properties, analytical and spectroscopic information, and designing of the defect-controlled microstructures of oxides as a potential material for high-temperature thermoelectrics.

2. Experimental

2.1. Preparation and Characterization of Samples

The titanium oxide TiO$_{1+x}$ were prepared by flash synthesis (FS) [17-19] from Ti and NaClO$_4$ powders of guaranteed grade. The reaction was expressed by the following Eq. (1)

$$\text{Ti} + \frac{1 + x}{4} \text{NaClO}_4 \rightarrow \text{TiO}_{1+x} + \frac{1 + x}{4} \text{NaCl} \quad \text{...(1)}$$

The crystal phases in the samples thus obtained were examined by a powder X-ray diffraction (XRD) study on a JEOL JDX-3500 diffractometer using Cu-K$\alpha$ radiation. Scanning electron microscopy was carried out on a JEOL JSM-T330A instrument equipped with an EDX spectrometer.

2.2. Measurement of Thermoelectric Properties

The samples for electrical measurements were cut from the sintered pellets as rectangular bars of 15×5.0×3.0 mm$^3$, and polished with SiC emery papers. The relative densities of all the samples were measured by Archimedes’ method. The measurements of the electrical conductivity and the Seebeck coefficient were carried out simultaneously in air from 573 to 1 223 K. Briefly, the $\sigma$ values were measured by the dc four-probe technique. The $\alpha$ values were obtained from the least-squares regressions of the thermoelectromotive force as a function of the temperature difference $<$5 K applied by a heater at each measurement temperature. All the measurements were carried out after attaining the steady-state temperature at each step. The thermal conductivity was determined from the thermal diffusivity and the specific heat capacity obtained by the laser flash measurement on an ULVAC TC-7000 instrument from room temperature to 1 273 K for sample disks 10 mm in diameter and 2.0 mm in thickness.

3. Results and Discussions

3.1. Electrical Transport Properties

The temperature dependence of the electrical conductivity, $\sigma$, of TiO$_{1.1}$ is shown in Fig. 1(a). And Arrhenius plot of ln $\sigma$ vs. 1/T for TiO$_{1.1}$ is also shown in Fig. 1(b). The $\sigma$ value of TiO$_{1.1}$ increased sharply with increasing temperature 1 073 K. The behavior of $\sigma$ for TiO$_{1.1}$ was semiconducting.

The Seebeck coefficient, $\alpha$, of TiO$_{1.1}$ is shown in Fig. 2. The $\alpha$ values of all the samples are positive within the whole temperature range examined, indicating $p$-type conduction. The Seebeck coefficient of TiO has values of 5.0 to 12.0 µV/K from room temperature to 1 273 K, and showed no particular dependence on temperature. On the other hand, TiO$_{1.1}$ gave large $\alpha$ values, with a general trend in which the value increased gradually from 400 µV/K at 573 K to 1.0 mV/K at 1 223 K.

The power factor, $\alpha^2\sigma$, which represents the electrical contribution to the overall thermoelectric performance, is
calculated from the results obtained above and depicted in Fig. 3 as a function of temperature. The $\alpha^2\sigma$ value of TiO$_{1.1}$ increases with temperature owing to a large increase in $\sigma$, attains exceedingly large value of $\alpha^2\sigma$, i.e. $8.6 \times 10^{-3}$ W/(m·K$^2$). These values are the largest ever reported on oxide materials, and also surpass those shown by $\beta$-FeSi$_2$ and $\beta$-SiC, which have been proposed as non-oxide candidates for high-temperature thermoelectric materials.

### 3.2. Thermal Transport Properties

The thermal conductivity, $\kappa$, is another fundamental parameter for the evaluation of the thermoelectric performance of materials, and it may cancel out an advantage brought about by a large value of $\sigma$ as is in the case for metals. Actually, the $\kappa$ values of the present oxides are rather high, 1.3 W/(m·K) at 573 K, whereas they increase to 7.1 W/(m·K) at 1223 K with temperature as shown in Fig. 4.

In spite of the relatively high $\kappa$ values, the figure of merit, $Z = \alpha^2\sigma/\kappa$, of the present oxide is revealed to be very prospective, benefiting from the large power factors. The figures of merit of TiO$_{1.1}$ are shown in Fig. 5 as a function of temperature. The $Z$ values for TiO$_{1.1}$ increased with increasing temperature, and $Z$ attained the largest value of $1.6 \times 10^{-3}$ K$^{-1}$ at 973 K. This value is much larger than that of PbSnTe, and is as large as that of the best result reported on $\beta$-FeSi$_2$ which shows a maximum at 873 K. These facts suggest strongly that the electrical properties of the present oxide would be sufficiently advantageous to overcome the unfavorable thermal properties.

The temperature dependence of the dimensionless figure of merit, $ZT$, is shown in Fig. 6. The value $ZT=1.64$ attained at 1073 K for TiO$_{1.1}$ is highest ever recorded. This is the largest value among reported for thermoelectric materials in this temperature range. The thermoelectric performance of the oxide as $ZT=1.64$ at present is evaluated as time and a half of the standard requirement for thermoelectric materials in practical use. In addition to this, TiO$_{1.1}$ has relatively large $ZT$ values of nearly unity or greater in the range of 773 to 1223 K. XRD patterns of TiO$_{1.1}$ before and
after measurements is shown in Fig. 7. All peaks in this figure very well correspond to each other, and there is no peak shift. Therefore the microstructure of TiO\textsubscript{1.1} sample is rather stable under repeated heating conditions.

4. Conclusions

We investigate the thermoelectric properties of a nonstoichiometric titanium oxide, TiO\textsubscript{1.1} for its use as high-temperature thermoelectrics. The magnitude of the electrical conductivity, $\sigma$, of TiO\textsubscript{1.1} increases 9 000 S/m at 1 073 K. The Seebeck coefficient, $\alpha$, of TiO\textsubscript{1.1} increases gradually from 0.4 mV/K at 573 K to ca. 1.0 mV/K at 1 223 K. Hence, the power factor, $\alpha^2\sigma$, reaches $8.6 \times 10^{-3}$ W/(m·K$^2$); this is the largest value that obtained for all reported oxide materials worldwide.

On the other hand, the thermal conductivity, $\kappa$, of TiO\textsubscript{1.1} increases from 1.3 W/(m·K) at 573 K to 7.1 W/(m·K) at 1 223 K by increasing temperature. Despite the consider-

ably large value of $\kappa$, the resulting figure of merit, $Z=\alpha^2\sigma/\kappa$, reaches $1.6 \times 10^{-3}$ K$^{-1}$ for TiO\textsubscript{1.1} at 973 K. The value $ZT=1.64$ attained at 1 073 K for TiO\textsubscript{1.1} is highest ever recorded. This is the largest value among reported for thermoelectric materials in this temperature range.

In addition to this, TiO\textsubscript{1.1} has relatively large $ZT$ values of nearly unity or greater in the range of 773 to 1 223 K. The microstructure of TiO\textsubscript{1.1} sample is rather stable under repeated heating conditions. The results strongly suggested the possibility that the nonstoichiometric defect-controlled titanium oxides without any dopants can be excellent p-type semiconductors as high-temperature thermoelectrics.

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