Fabrication and Thermoelectric Properties of Magneli Phases by Adding Ti into TiO$_2$

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Abstract. In the present study, the TiO$_2$-Ti compacts with Magneli phases Ti$_n$O$_{2n-1}$ were fabricated using the mixed powder of TiO$_2$ powder and addition Ti powder by spark plasma sintering (SPS). The composition and the crystal types of Magneli phases Ti$_n$O$_{2n-1}$ were examined. The results showed that various Magneli phases Ti$_n$O$_{2n-1}$ (single or multi Magneli phases) with the composition of Ti$_{1+y}$O$_{2-x}$ were obtained. The Magneli phases Ti$_n$O$_{2n-1}$ were formed in the transformation from the mother phase rutile TiO$_2$ to TiO with increase in Ti addition fraction. In addition, the thermoelectric properties of the sintered compacts were also measured. The electrical resistivity of the sintered compacts decreased with increase in Ti addition fraction. The thermoelectric performance of the sintered compacts was improved by the formation of Magneli phases Ti$_n$O$_{2n-1}$ with the composition of Ti$_{1+y}$O$_{2-x}$.

Introduction

In recent years, thermoelectric materials have attracted much attention due to their potential applications in conversion between electrical power and heat such as electric power generation from waste heat [1]. The performance of thermoelectric materials is evaluated by the figure of merit $Z$, or by the dimensionless figure of merit $ZT$,

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

(1)

Where $S$ is the Seebeck coefficient, $\rho$ is electrical resistivity, $\kappa$ is thermal conductivity, and $T$ is absolute temperature. Conventionally, power factor $P$ is used to evaluate the performance of thermoelectric materials.

$$P = S^2 \rho^{-1}$$

(2)

For nonstoichiometric titanium oxides TiO$_2$-$x$, the effect of value $x$ on thermoelectric properties has been actively investigated [2-5]. Nonstoichiometric titanium dioxides TiO$_2$-$x$ are expected to be an applicable candidate material because the $ZT$ has reached an exciting value, 1.64 at 1073 K in the case of TiO$_{1.1}$ [2]. Nonstoichiometric titanium dioxide TiO$_2$-$x$ can be obtained by techniques such as sintering of mixed powder of TiO$_2$ and TiO, reduction of TiO$_2$ in carbon or hydrogen reducing atmosphere, among others [4-5]. From the references above, decrease of electrical resistivity and thermal conductivity and improvement of thermoelectric performance can be achieved by increase of value $x$ [2-5].
Besides, titanium oxides with the composition of Ti_nO_{2n-1} (n = 1, 2, 3 ...) have been well known as Magneli phases [6]. They have special crystalline structures, named shear structure, and have become one focus in numerous research fields due to their special properties of metal-nonmetal transition, electrical, thermal, optical property, among others [6-9]. The crystals of Ti_nO_{2n-1} having the composition between Ti_2O_3 and TiO_2 are transferred from the mother phase rutile TiO_2 with decrease of value x of TiO_{2-x} [6]. Furthermore, electrical resistivity of different Magneli phases has different values due to the different n values of Ti_nO_{2n-1}, or different composition phases in the case of multi Magneli phases [7-10]. Ti_nO_{2n-1} can be obtained by reduction reaction [4-5], sintering of mixed powder of TiO_2/TiO [3] or TiO_2/Ti [11-13], and CVD process [14]. The phase transformation, the phase structure and their physical properties have been widely investigated.

In the present study, the compacts with Magneli phases Ti_nO_{2n-1} were fabricated using mixed powder of TiO_2 powder and addition Ti powder by spark plasma sintering (SPS). The composition and the crystalline forms of Magneli phases Ti_nO_{2n-1} were examined. Furthermore, thermoelectric properties were measured and discussed.

**Experimental**

Rutile TiO_2 powder of 0.3 µm in average diameter (purity: 99.0 %) and Ti powder of 35 µm in average diameter (purity: 99.8 %) were used as raw materials. The volume fraction of Ti in the mixed powder was between 0 to 30 %. Firstly, the powder of TiO_2 and Ti was wet-milled in acetone solvent by a planetary ball mill for 2 hours and then was dried for 2 hours. WC (tungsten carbide) balls of 10 mm in diameter and a WC pot were used for wet milling. Secondly, a graphite die of 40 mm in internal diameter was filled up with the mixed powder. Then, the graphite die was put into SPS system (SPS-1030, Sumitomo Coal mining Co., Ltd.) and SPS was carried out. The sintering temperature, pressure and holding time were 1373 K, 27 MPa and 5 min, respectively. The sintered compacts with the dimensions of Φ 40 mm × 2 mm were cut into samples with the dimensions of 40×5×2 mm.

Phase identification was carried out by X-ray diffraction (XRD) (JEOL JDX-3530) and the composition and its distribution were examined by scanning electron microscopy (SEM) (JEOL JSM-5300LA) and electron probe micro-analyzer (EPMA). Electrical resistivity and Seebeck coefficient were measured by the 4-probe method and the static method in the temperature range from 293 to 973 K. Power factor (Eq. (2)) was calculated by electrical resistivity and Seebeck coefficient and used as an evaluation parameter of thermoelectric performance.

**Results and discussion**

**Microstructure and Composition of the sintered Compacts.** The SEM images of the sintered TiO_2-Ti compacts are shown in Fig. 1. It can be seen that the compact without Ti addition has a uniform microstructure (Fig.1 (a)). However, dispersed particles of silvery white inlaid in the uniform matrix of gray color in the case of Ti addition (Fig.1 (b) - (f)). The content of the silvery white phase was less than 2.5 % in volume fraction and did not relate to Ti addition fraction as shown in Table 1.

The composition distributions in the sintered TiO_2-Ti compacts in the cases of 8 vol% and 12 vol% are shown in Fig. 2. It is interesting that the dispersed particle phase of silvery white in SEM images corresponds to tungsten element. Therefore, the particle phase was considered to be WC that was mingled into the mixed powder of TiO_2 and Ti from the WC pot and the WC balls. On the one hand, oxygen element distributes nonuniformly in the case of 8 vol% (Fig.2 (a)), while distributed uniformly in the case of 12 vol% (Fig.2 (b)). On the other hand, titanium distributes uniformly in both of the cases. It suggests that the Ti addition might inset into crystalline lattice and form solid solution during the process of SPS. According to our early work, it can be understood that compacts without Ti addition was TiO_{2-x} with rutile TiO_2 due to carbon reducing from the graphite die [13].
**Magneli phases in the sintered TiO$_2$-Ti compacts.** The XRD patterns of the sintered TiO$_2$-Ti compacts are shown in Fig. 3. The diffraction peaks of Ti cannot be seen in all the XRD patterns. In the case without Ti addition, the mother phase was still rutile TiO$_2$. After addition of Ti powder, Magneli phases Ti$_n$O$_{2n-1}$ were found in the sintered TiO$_2$-Ti compacts. In other words, the mother phase rutile TiO$_2$ transferred to Magneli phases Ti$_n$O$_{2n-1}$. It suggests that the Ti addition might inset into the crystalline lattice of rutile TiO$_2$ and form their solid solution during the process of SPS. The result is in good agreement with the analysis from EPMA (Fig. 2). Therefore, it can be concluded that various Magneli phases Ti$_n$O$_{2n-1}$ (single or multi Magneli phases) can be obtained using the mixed powder of TiO$_2$ powder and addition Ti powder by SPS.

Table 1 lists Ti addition fraction and estimated fraction of the white phase in the compacts. The composition of the sintered TiO$_2$-Ti compacts should be Ti$_{1+y}$O$_{2-x}$ which was different from those prepared in the case of reducing TiO$_2$ to TiO$_x$ (or TiO$_2$-$x$) by carbon or hydrogen reduction [5, 12]. Table 2 lists Ti addition fraction, the atomic ratio $(1+y) / (2-x)$ (the atomic ratio of Ti and O) of Ti$_{1+y}$O$_{2-x}$ and Magneli phases of the sintered TiO$_2$-Ti compacts by XRD. Meanwhile, the atomic...
ration of Ti and O, n/(2n-1) of Magnéli phases Ti$_n$O$_{2n-1}$ is listed in Table 3 for comparison. It can be seen from the tables that the atomic ratio of Ti and O of the Magnéli phases Ti$_n$O$_{2n-1}$ increased with increase in Ti addition fraction. In addition, the Magnéli phases were formed in the transformation from the mother phase rutile TiO$_2$ to TiO with increase in Ti addition fraction.

![XRD patterns of Ti$_n$O$_{2n-1}$ Magnéli phases by TiO$_2$-Ti compacts.](image)

**Fig. 3 XRD patterns of Ti$_n$O$_{2n-1}$ Magnéli phases by TiO$_2$-Ti compacts.**

<table>
<thead>
<tr>
<th>Ti (vol%)</th>
<th>Ti (wt%)</th>
<th>Ti (at.%)</th>
<th>y</th>
<th>x</th>
<th>(1+y)/(2-x)</th>
<th>Magnéli phase (by XRD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.02</td>
<td>TiO$_2$ (rutile)</td>
</tr>
<tr>
<td>5</td>
<td>5.27</td>
<td>8.49</td>
<td>0.08</td>
<td>0.5051</td>
<td>Ti$<em>{10}$O$</em>{19}$, Ti$<em>5$O$</em>{17}$</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>8.41</td>
<td>13.28</td>
<td>0.14</td>
<td>0.5766</td>
<td>Ti$_4$O$_7$, Ti$_3$O$_5$</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10.50</td>
<td>16.37</td>
<td>0.18</td>
<td>0.5979</td>
<td>Ti$_3$O$_3$</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>12.59</td>
<td>19.37</td>
<td>0.23</td>
<td>0.6201</td>
<td>Ti$<em>6$O$</em>{11}$, Ti$_5$O$_5$</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>15.71</td>
<td>23.72</td>
<td>0.30</td>
<td>0.6555</td>
<td>Ti$<em>6$O$</em>{11}$, Ti$_3$O$_5$</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>20.89</td>
<td>30.58</td>
<td>0.43</td>
<td>0.7202</td>
<td>Ti$_4$O$_7$, Ti$_3$O$_5$</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>31.16</td>
<td>43.02</td>
<td>0.74</td>
<td>0.8775</td>
<td>Ti$_2$O$_3$, TiO</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2** Ti addition fraction (volume, weight and atomic), atomic ratio of Ti$_{1+y}$O$_{2-x}$ and Magnéli phases by XRD of TiO$_2$-Ti compacts.

<table>
<thead>
<tr>
<th>Ti$<em>n$O$</em>{2n-1}$</th>
<th>n/(2n-1)</th>
<th>Ti$_{2n-1}$O$_n$</th>
<th>n/(2n-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.5000</td>
<td>Ti$_3$O$_9$</td>
<td>0.5556</td>
</tr>
<tr>
<td>Ti$<em>{10}$O$</em>{19}$</td>
<td>0.5263</td>
<td>Ti$_4$O$_7$</td>
<td>0.5714</td>
</tr>
<tr>
<td>Ti$<em>5$O$</em>{17}$</td>
<td>0.5294</td>
<td>Ti$_3$O$_5$</td>
<td>0.6000</td>
</tr>
<tr>
<td>Ti$<em>5$O$</em>{15}$</td>
<td>0.5333</td>
<td>Ti$_2$O$_3$</td>
<td>0.6667</td>
</tr>
<tr>
<td>Ti$<em>7$O$</em>{13}$</td>
<td>0.5385</td>
<td>TiO</td>
<td>1.0000</td>
</tr>
<tr>
<td>Ti$<em>6$O$</em>{11}$</td>
<td>0.5455</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 3** Atomic ratio of Ti$_n$O$_{2n-1}$ Magnéli phases.
Thermoelectric properties in TiO$_2$-Ti compacts. Electrical resistivity, Seebeck coefficient and power factor of the sintered TiO$_2$-Ti compacts are shown in Fig. 4. Electrical resistivity (Fig. 4(a)) of the sintered TiO$_2$-Ti compacts was lower than those of the compact without addition of Ti. In addition, electrical resistivity decreased with increase in measurement temperature. It should belong to a semiconductor behavior. Similarly to TiO$_{2-x}$ materials [15], the decrease of the electrical resistivity of Magneli phases Ti$_n$O$_{2n-1}$ with the composition of Ti$_{1+y}$O$_{2-x}$ in the sintered TiO$_2$-Ti compacts should result from the increase of the density and mobility of carriers.

Seebeck coefficient of the sintered TiO$_2$-Ti compacts had negative values for all the sintered compacts (n-type semiconductor). The absolute values of Seebeck coefficient (Fig. 4(b)) of the sintered TiO$_2$-Ti compacts were lower than those of the samples without addition of Ti. Power factor (Fig. 4(c)) of the sintered TiO$_2$-Ti compacts increased and then decreased with increase in Ti addition fraction. Power factor of the sintered compacts reached $10 \times 10^{-4}$ Wm$^{-1}$K$^{-2}$ at 973 K when Ti addition fraction were 8 vol% and 10 vol%. It seems that the optimum value of Ti addition fraction was about 10 vol%.

![Fig. 4 Thermoelectric properties of TiO$_2$-Ti compacts.](chart.png)
Conclusions
Various Magneli phases Ti$_{n}$O$_{2n-1}$ (single or multi Magneli phases) with the composition of Ti$_{1+y}$O$_{2-x}$ were obtained by sintering the mixed powder of TiO$_2$ powder and addition Ti powder by SPS. The Magneli phases were formed in the transformation of the mother phase rutile TiO$_2$ to TiO with increase in Ti addition fraction. Electrical resistivity of the sintered TiO$_2$-Ti compacts decreased with increase of Ti addition fraction. Power factor of the sintered TiO$_2$-Ti compacts was increased and the peak value reached 10×10$^{-4}$ Wm$^{-1}$K$^{-2}$ at 973 K when Ti addition fraction was 8 vol% and 10 vol%.

References
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