Thermoelectric properties of nitrogen-doped TiO$_{2-x}$ compounds

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Abstract. The thermoelectric properties of nitrogen-doped TiO$_{2-x}$ containing oxygen defects have been investigated. The oxygen-defective TiO$_{2-x}$ was synthesized by a solid-state reaction of TiO$_2$ and titanium mononitride, TiN. By inducing a sufficient amount of oxygen defects, a sintered sample consisting of the Magneli phase titanium oxide Ti$_n$O$_{2n-1}$ was obtained. While TiO$_2$ is an intrinsically insulating material, the electrical resistivity was reduced by the formation of oxygen defects, which introduce electron carriers. Although the Seebeck coefficient also decreased with an increase in the amount of oxygen defects, the thermoelectric power factor was improved by the further reduction of electrical resistivity. In addition, the thermal conductivity was strongly reduced by phonon scattering at nanometer-spaced periodic planar defects of the Magneli phase crystallographic structure, resulting in the nitrogen-doped TiO$_{2-x}$ exhibiting good n-type performance at high temperatures.

1. Introduction
Thermoelectric devices have recently attracted renewed interest for their potential application in clean energy-conversion systems. Especially, vast amounts of waste heat are targeted for thermoelectric power generation in order to enhance energy utilization efficiency. The conversion efficiency of a thermoelectric device depends mainly on the material’s thermoelectric properties, which are evaluated using the thermoelectric figure of merit $Z = S^2/\rho\kappa$, where $S$ is the Seebeck coefficient, $\rho$ is the electrical resistivity, and $\kappa$ is the thermal conductivity. Thus, the exploration of materials having a high $Z$ value is indispensable for the practical use of thermoelectric technology as an eco-friendly energy recovery system.

Recent discovery of large $S$ coexisting with low $\rho$ in layered cobaltites has opened a route to the exploration of oxides as thermoelectric materials [1–4]. The cobaltites, such as Na$_x$CoO$_2$ and [Ca$_2$Co$_{3}$O$_{6}$]$_{p}$CoO$_2$, which is known as Ca$_3$Co$_4$O$_9$, exhibit p-type conduction and the ZT (where $T$ is the absolute temperature) values are greater than 1 at 1000 K [2-4], which is the required criterion for practical application. In addition, because of their high thermal stability, high tolerance to oxidation, and low toxicity, these oxides are promising candidates for practical use for thermoelectric power generation in air at high temperatures.

On the other hand, in order to construct a thermoelectric device, an n-type thermoelectric oxide material is required. Recently, it has been reported that titanium oxides, such as Nb-doped SrTiO$_3$ and reduced TiO$_2$, show good n-type thermoelectric performance [5-7]. Although these titanium oxides are intrinsically insulating materials, $\rho$ was reduced by the electron doping resulting from the Nb doping...
or the reduction of oxygen content. In addition, a large thermoelectric power factor (PF=S²/ρ) can be obtained by the adjustment of the doping level to keep large S. In addition, κ should be reduced to obtain a large Z value. Since κ in titanium oxide is mainly governed by the lattice thermal conductivity, the enhancement of phonon scattering by the introduction of crystal lattice defects or grain boundaries is effective to reduce the total κ. For titanium dioxide, a relatively wide range of oxygen content can be allowed such as from TiO₂ to TiO. Therefore, an oxygen deficiency and corresponding crystal lattice defects can be easily introduced. Moreover, depending on the oxygen content, the crystallographic structure is deformed. For instance, rutile type TiO₂ was changed to a homologous series of the Magneli phase expressed as TiₙO₂ₙ₋₁ (n=4~10) when a sufficient amount of oxygen defects was introduced [8]. Since the crystallographic structure of the Magneli phase can be described as a shear structure of rutile type TiO₂ [9,10], nanometer-spaced periodic planar defects can be naturally introduced. Then, a strong phonon scattering effect can be expected. In this study, the amount of oxygen defects and the crystallographic phase of titanium oxide were controlled by the solid-state reaction of TiO₂ and titanium mononitride, TiN, and the effect on the thermoelectric properties was investigated.

2. Experimental
The oxygen-defective titanium oxide was synthesized by a solid-state reaction of TiO₂ and TiN. The mixing ratios of these two powders were adjusted to coincide with the chemical compositions of the Magneli phase TiₙO₂ₙ₋₁, as listed in table 1. For instance, aiming to form the Magneli phase of Ti₈O₁₅, the mixing ratio was fixed at TiO₂:TiN=7:1. These raw powders were mixed with ethanol as a lubricant by planetary ball milling at 250 rpm for 20 h. After drying, the mixed powder was sintered at 1473 K for 10 min under a uniaxial pressure of 50 MPa by electric current sintering using a graphite mold. The heating and cooling rates were about 100 K/min. For comparison, a sintered sample made only from TiO₂ powder was also prepared to investigate the oxygen deficiency effect on the thermoelectric properties. The obtained bulk samples, with a typical size of 10 mm in diameter and 2 mm in thickness, were used for measurement of κ and then cut into a bar shape for measurement of ρ and S.

| Table 1. Mixing ratio of raw powders and identified phases by XRD measurement. |
|-----------------|-----------------|-----------------|
| Nominal Composition | Mixing ratio TiO₂:TiN | Identified phase |
| TiO₂ | 1:0 | Rutile |
| Ti₆(O,N)₁₁ | 5:1 | Ti₆O₉, Ti₆O₁₁ |
| Ti₆(O,N)₁₃ | 6:1 | Ti₆O₁₁, Ti₆O₁₃ |
| Ti₈(O,N)₁₅ | 7:1 | Ti₇O₁₃, Ti₈O₁₅ |
| Ti₉(O,N)₁₇ | 8:1 | Ti₈O₁₅ |

Crystallographic structure analysis was performed using X-ray diffraction (XRD) with Cu Kα radiation. The value of ρ was measured in a He atmosphere using a conventional four-probe DC technique. The value of S was calculated from a plot of the thermoelectric voltage against the temperature difference between each end of the bar shaped sample. Two Pt-Pt/Rh (R-type) thermocouples were attached to the sample ends and the Pt wires of the thermocouples were used as voltage terminals. Measured S values were corrected by S for the Pt wires to obtain the net S values of the samples. These measurements of ρ and S were simultaneously conducted using a RZ2001i (Ozawa Science Co. Ltd.) in the temperature range from 350 K to 1150 K. κ was evaluated from the density (D), thermal diffusivity (α), and heat capacity (Cₚ) with the relationship κ=D×α×Cₚ. Of those parameters, D was measured using the Archimedes method; α and Cₚ were evaluated using the laser flash method in the temperature range from 300 K to 550 K.
3. Results and discussion

3.1. Phase identification

XRD measurements were performed on the polished cross section of each sintered sample. As shown in Fig. 1(a), the XRD pattern of the sample made only from TiO$_2$ powder agreed with the reported data for the rutile TiO$_2$ structure, with the exception of the weak diffraction peak (marked with ●) from a secondary phase around $2\theta=26.5^\circ$. Since the sample was sintered in the reductive ambient of a graphite mold, some amount of oxygen should be reduced. In fact, the color of the sample turned to dark blue and $\rho$ was significantly reduced compared to the intrinsically insulating TiO$_2$, as described below. Therefore, the secondary phase can be considered to be a reductive phase of titanium oxide such as the Magneli phase, which gives a strong diffraction peak around the 20 angle of the additional peak.

The XRD patterns of the samples made from the mixture of TiO$_2$ and TiN are clearly different to the rutile phase and agree with the reported data for Magneli phase titanium oxide, with the exception of a weak diffraction peak (marked with ♦) from a secondary phase around $2\theta=20.7^\circ$. This additional peak could not be identified at present. Although the identified majority phase is indicated in Fig. 1, a detailed phase identification confirmed that these samples consisted of more than one Magneli phase, as listed in table 1. It should be noted that the identified phases are described according to the XRD pattern database. These chemical formulas then just express the crystallographic phase, not the actual chemical composition. Since the sintering condition was a reductive atmosphere and titanium oxide is easily reduced at high temperature, the crystallographic phase was formed under unstable conditions. Therefore, samples consisting of a single intended Magneli phase could not be obtained by our sample preparation method. In addition, the $n$ index of the Magneli phase Ti$_n$O$_{2n-1}$ of the identified phase is almost one lower than the nominal composition of the starting mixed powders. This result is also attributed to the reductive reaction during sintering.

![Figure 1](image.png)

Figure 1. XRD pattern (Cu K$\alpha$ radiation) from titanium oxide sintered samples with a nominal composition of a) TiO$_2$, b) Ti$_9$(O,N)$_{17}$, c) Ti$_8$(O,N)$_{15}$, d) Ti$_7$(O,N)$_{13}$, e) Ti$_6$(O,N)$_{11}$. The identified main phase is indicated below each XRD pattern. Peaks not identified are marked with ● or ♦.

In a preliminary composition analysis, a reduction of oxygen content during sintering was detected, while the nitrogen loss was relatively small. The difference in decomposition behavior between
oxygen and nitrogen during sintering seems to be attributed to the difference in chemical stability between TiO₂ and TiN in the reductive atmosphere at high temperatures. A precise composition analysis will be conducted for further investigation of the nitrogen doping effect on the thermoelectric properties of titanium oxide. Although the chemical composition and the crystallographic phase could not be precisely controlled, the results of XRD measurements confirmed that a series of Magneli phase titanium oxides Tiₙ(O,N)₂n₋₁ having a different n index from 8 to 5 can be synthesized by a solid-state reaction of TiO₂ and TiN. In addition, this result also indicates that the amount of oxygen deficiency can be roughly controlled by the mixing ratio of the raw powders of TiO₂ and TiN.

3.2. Electrical properties

Figure 2 shows the temperature dependence of ρ for the samples incorporating different amounts of oxygen defects. All the samples exhibit a semiconducting temperature dependence. The reduction rate of ρ with increasing temperature is reduced by an increase in the amount of oxygen deficiency. This result implies that additional electronic states were introduced into the band gap of the original rutile TiO₂ by the oxygen defects. For the sample made only from TiO₂ powder, the ρ value is significantly lower than that for the intrinsically insulating rutile TiO₂ material. This large reduction of ρ can be attributed to a reduction of the oxygen content during sintering. For the samples consisting of the Magneli phase, a further reduction of ρ was observed. Since the amount of electron doping is directly related to the oxygen deficiency and indirectly related to the n index of the Magneli phase, the monotonic decrease in ρ with decreasing n index is consistent.

![Figure 2](image_url)

**Figure 2.** Temperature dependence of electrical resistivity in titanium oxide sintered samples.

Figure 3 shows the temperature dependence of S. All the samples exhibit a negative S value, resulting from the electron doping effect by the introduction of oxygen defects. The absolute S value, which is generally inversely proportional to the carrier density, decreases with increasing oxygen deficiency because the amount of electron doping is increased by the increase in oxygen reduction level. Although electron doping diminishes S, the further enhancement of electrical conductivity can enhance the thermoelectric power factor PF (=S²/ρ), especially at high temperatures, as shown in Fig. 4. All the samples consisting of the Magneli phase exhibit a higher PF value compared to the rutile phase titanium oxide. The PF value monotonically increases with temperature mainly due to the increase in S at high temperatures. This temperature dependence indicates that the reduced titanium oxide can be a good thermoelectric material at high temperatures.
3.3. Thermal conductivity and thermoelectric performance

In order to estimate the thermoelectric performance of the reductive titanium oxide, the $\kappa$ value was measured as shown in Fig. 5. The $\kappa$ value of the rutile phase titanium oxide sample is much lower than the reported $\kappa$ value in single crystals (7-11 W/mK at 300 K) [9]. This reduction of $\kappa$ can be attributed to the enhancement of phonon scattering at grain boundaries and point defects at oxygen sites, because the sintered sample consists of grains having sizes of several micrometers and contain a certain amount of oxygen defects as mentioned above.

For the sample consisting of the Magneli phase, a further reduction of $\kappa$ was observed. For the sample mainly consisting of the Ti$_{7}$O$_{13}$ Magneli phase (indicated by a nominal composition of Ti$_{8}$(O,N)$_{15}$ and marked with $\bullet$ in Fig. 5), the $\kappa$ value is almost half that for the rutile phase sample. The crystallographic structure of the Magneli phase can be described as a shear structure of the original rutile type TiO$_{2}$ structure. For instance, for the Ti$_{8}$O$_{15}$ (n=8) phase, one planar defect is introduced into every eight pure rutile type titanium dioxide stacking units. This means that nanometer-spaced periodic planar defects can be naturally introduced by the formation of the Magneli phase. Since the distance between the planer defects is the same order as the phonon mean free path in the original rutile TiO$_{2}$, the formation of the Magneli phase structure should have a strong impact on the enhancement of the phonon scattering effect. In fact, the Magneli phase samples exhibit relatively temperature independent $\kappa$ values, as shown in Fig. 5. This result implies that the temperature independent phonon scattering effect of structural defects is much larger than the temperature dependent phonon-phonon scattering effect. Therefore, the large reduction of $\kappa$ can be attributed to the formation of the nanometer-spaced periodic planar defect structure of the Magneli phase.

Finally, the ZT value of the sintered samples was calculated as shown in Fig. 6. Since the lattice part of $\kappa$ and the electrical conductivity of the samples are almost independent of temperature above 600 K, ZT values above 600 K (indicated by open symbols) were estimated using the $\kappa$ value of 550 K. The estimated ZT values increase with increasing temperature mainly due to the enhancement of S at high temperatures. All the samples consisting of the Magneli phase exhibit much larger ZT values compared to the rutile phase sample. The large reduction of $\kappa$ resulting from the formation of the Magneli phase can contribute to the improvement of the ZT value.
4. Conclusions

The thermoelectric properties of rutile type TiO$_2$ having oxygen defects and the Magneli phase Ti$_{2n}$O$_{2n-1}$ were investigated. The amount of oxygen deficiency and the n index of the Magneli phase can roughly be controlled by the solid-state reaction of TiO$_2$ and TiN. The introduction of oxygen deficiency is effective for electron doping, resulting in a significant reduction of $\rho$. Although the electron doping diminishes $S$, a relatively high PF value was obtained at high temperatures due to the increase in $S$ with temperature. The nanometer-order periodic planar defect structure of the Magneli phase can contribute to the strong enhancement of phonon scattering, resulting in a large reduction of $\kappa$. The estimated ZT value reached 0.4 at 1150 K in the sample mainly consisting of the Ti$_7$O$_{13}$ Magneli phase. This ZT value is as high as the reported value for n-type thermoelectric oxide material.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Young Scientists (B) 21760571 from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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