Effect of Addition of Titanium Nitride on Thermoelectric Performance of Yttrium-Doped Strontium Titanate

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We examined the effect of addition of titanium nitride on thermoelectric performance of this material. The samples constructed of Y-doped SrTiO₃ and TiN were prepared by two steps of the solid-state reactions. SrTiO₃ with cubic perovskite structure was formed in all samples. The highest electric conductivity was found for Sr₀.₉Y₀.₁TiO₃-0.1TiN, whereas the largest absolute value in Seebeck coefficient was found for Sr₀.₉Y₀.₁TiO₃. Lower thermal conductivity was found for Sr₀.₉Y₀.₁TiO₃-0.1TiN. The ZT was calculated from the electric conductivity, the Seebeck coefficient, and the thermal conductivity. A high performance was shown in Sr₀.₉Y₀.₁TiO₃-0.1TiN, giving a high electric conductivity and a low thermal conductivity simultaneously. The highest value of ZT was obtained to be 0.26 at 1077 K for this sample.

Keywords: thermoelectric performance, strontium titanate, titanium nitride, solid state reaction, electric conductivity, Seebeck coefficient, thermal conductivity

1. Introduction

The heat energy that we are using is effectively used only by one third of the primary energy, and the remainder is thrown away to the environment as a waste heat.¹ Moreover, the quantity of the supplied primary energy keeps increasing every year. From the viewpoint of effective use of energy and environmental protection, it is necessary that energy is collected from the waste heat thrown away now. However, the waste heat is generated from various places in small scale, and cannot be used in a large-scale device for power generation. Therefore, thermoelectric materials have been thought good for these situations. The thermoelectric material converts the thermal energy directly into the electrical energy, it has no movable part and the structure is simple. These properties are suitable to collect the electrical energy from the waste heat.

Oxide system thermoelectric materials have not been put into practical use, because of a high thermal conductivity.² Recently, Terasaki et al. have found a good thermoelectric oxide material, layered cobaltite.³ After their finding, many p-type layered cobaltites have been developed, and the performance is approaching to the practical usage. However, no n-type oxide thermoelectric material with sufficient performance has been developed yet. We have focused our attention to strontium titanate as a promising n-type thermoelectric oxide material⁴–⁸ in this study. This material has a high ability of thermoelectric performance, but has a high thermal conductivity. In order to make thermal conducting lower, composite concept might be effective because of introduction of phonon scattering centers. In this report, we examined the effect of addition of titanium nitride on thermoelectric performance of this material.

2. Experiment

The composite samples constructed of Y-doped SrTiO₃ and TiN were prepared by two steps of the solid-state reactions. First, Y-doped SrTiO₃ was synthesized by calcination of the mixture containing strontium carbonate (Wako Pure Chemical Industries, Ltd. 99.2%), yttrium oxide (Wako Pure Chemical Industries, Ltd. 99.99%) and titanium oxide (Wako Pure Chemical Industries, Ltd. 99.7%) in proper proportion. Then the Y-doped SrTiO₃ and TiN powders (Japan New Metal Co., Ltd. 97%) were mixed and pelletized under a pressure of 47 MPa, after then sintered at 1573 K for 2 h in a tubular furnace under a nitrogen gas flow. The composition of the samples is shown in Table 1, hereafter Sr₀.₉Y₀.₁TiO₃ and TiN will be abbreviated as YSTO and TN, respectively.

The structure of the samples was characterized by the X-ray diffraction (XRD) (Rigaku, RINT-2500) method at room temperature. The electric conductivity, σ, and Seebeck coefficient, S, were measured at temperatures from 300 to 1100 K by using the thermoelectric properties measuring instrument (ULVAC-RIKO, Inc., ZEM-1). The thermal conductivity, k, was measured by the laser flash apparatus (NETZSCH Inc., LFA 457 MicroFlash), and the SEM images of the samples were observed by EPMA (JEOL Ltd. JXA-8200). The bulk density was determined by using an Archimedean method.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the

Table 1 Composition of the samples prepared in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>x</th>
<th>Mole ratio of Sr₀.₉Y₀.₁TiO₃</th>
<th>Mole ratio of TiN</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSTO</td>
<td>0.0</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>YSTO-0.01TN</td>
<td>0.01</td>
<td>1.0</td>
<td>0.01</td>
</tr>
<tr>
<td>YSTO-0.05TN</td>
<td>0.05</td>
<td>1.0</td>
<td>0.05</td>
</tr>
<tr>
<td>YSTO-0.1TN</td>
<td>0.1</td>
<td>1.0</td>
<td>0.1</td>
</tr>
<tr>
<td>YSTO-0.15TN</td>
<td>0.15</td>
<td>1.0</td>
<td>0.15</td>
</tr>
</tbody>
</table>
samples prepared in this study and that of pure TN powder. YSTO with cubic perovskite structure\(^9\) was formed predominantly in all samples. The peaks of TN\(^{10}\) have become quite weak. And small peaks of Y\(_2\)Ti\(_2\)O\(_7\)\(^{11}\) were observed in YSTO, YSTO-0.01TN and YSTO-0.05TN. Since, Y\(_2\)Ti\(_2\)O\(_7\) peaks in these were relatively small, we assumed the effect of Y\(_2\)Ti\(_2\)O\(_7\) phase is also small. Many cracks occurred in YSTO-0.15TN, therefore, further experiments have not been done for this sample.

Figure 2 shows the SEM images of each sample. The EPMA analyses revealed that there occurred small islands of pyrochlore phase, Y\(_2\)Ti\(_2\)O\(_7\), which can be seen as small white spots on the SEM images as is typically shown in Fig. 2(b). In addition, TiN phases were observed as dark spots as is shown in the circle presented in Fig. 2(c) and (d). These phases were examined by the EPMA analysis. In the cases of YSTO and YSTO-0.01TN, significant pore-growth was not observed. However, a lot of pores or voids were observed in the SEM images for YSTO-0.05TN and YSTO-0.1TN. The origin of these pores has not been clear, but it is probable that the TiN phases have partly decomposed, corresponding to the formation of the voids.

The temperature dependence of the electrical conductivities was shown in Fig. 3. The electrical conductivity values were increased by adding TN at all temperatures examined. Especially, the effect of the TN addition was remarkable in the case of YSTO-0.1TN.

The Seebeck coefficients of the samples were shown in Fig. 4. YSTO was n-type semiconductor, and Seebeck coefficient also indicated negative values in all the samples containing TN. The absolute value of Seebeck coefficient was decreased with increase of TN. The values of Seebeck coefficient of YSTO-0.05TN and YSTO-0.1TN were close to each other, suggesting that these two samples have similar electronic states, e.g. carrier density. On the other hand, the

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**Fig. 1** XRD patterns of the samples prepared in this study and titanium nitride.

**Fig. 2** SEM images of Y-doped SrTiO\(_3\)/TiN composites.
electric conductivities of these two samples were fairly different to each other. This relatively complex behavior of the conductivity may be due to high density of phonon scattering centers embedded in the samples, e.g. substitutions, interfaces, or voids.

The thermal conductivity is shown in Fig. 5 and the bulk density of the sample is shown in Fig. 6. The thermal conductivity of YSTO-0.01TN and YSTO-0.05TN became larger than YSTO. Since TN has a higher thermal conductivity than YSTO, the entire thermal conductivity of the composite YSTO-0.01TN is expected to be larger. However, the entire thermal conductivity of YSTO-0.1TN was smaller than that of YSTO. Since, there were a lot of pores in YSTO-0.1TN, it was thought that this porosity resulted in decrease of thermal conductivity.

The dimensionless figure of merit, $ZT$ of the sample were shown in Fig. 7. $ZT = (S^2\sigma T)/k$ was calculated from the values of conductivity, Seebeck coefficient and thermal conductivity. The value of $ZT$ of YSTO-0.1TN went up to 0.26 at 1077 K. This $ZT$ value was the highest among all the samples. A high performance shown in YSTO-0.1TN may come from a high electric conductivity as well as a low thermal conductivity.

Obara et al. reported the highest $ZT$ of 10% Y-doped SrTiO$_3$ was 0.1 at 490 K.$^{4)}$ However, in our case, the $ZT$ value at corresponding temperature was in the order of $10^{-2}$. The difference in $ZT$ value seems to come mainly from the difference in the electrical conductivity, namely, Obara’s sample showed the electrical conductivity of about $10^5$ Sm$^{-1}$, whereas, ours in the order of $10^3$ Sm$^{-1}$. The origin of this difference is not clear so far. But it showed be noted that Obara et al. used a hot pressing technique to prepare their samples, on the other hand, we used just a conventional ceramics processing. As a result, Obara’s samples were much denser than ours, giving the higher electrical conductivity. The effect of compactness of the samples with this composition on the total thermoelectric performance is quite interesting and worth studying in the future. However, our
main point of discussion of this paper is the effect of addition of titanium nitride in the YSTO system. The effects of addition of titanium nitride on enhancing the thermoelectric performance of YSTO were tentatively considered to be the following two points: one is the increase in electrical conductivity associated with the high electrical conductivity of TN; the other is reduction in the thermal conductivity associated with the formation of a lot of pores.

4. Conclusion

The effect of addition of the titanium nitride on thermoelectric performance of yttrium-doped strontium titanate was experimentally examined. As a result, the electrical conductivity was greatly improved by the addition of titanium nitride to the yttrium-doped strontium titanate. Especially, the conductivity was enhanced in the case of YSTO-0.1TN conductivity. However, the absolute value of Seebeck coefficient has become small as the amount of the titanium nitride increased. Thermal conductivity of YSTO-0.1TN was smaller than that of YSTO. And the highest value of ZT was obtained to be 0.26 at 1077 K for this sample.

Acknowledgement

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