Thermoelectric Device of $\text{Na}(\text{Co}, \text{Cu})_2\text{O}_4$ and $(\text{Ba}, \text{Sr})\text{PbO}_3$

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 $\text{Na}(\text{Co}, \text{Cu})_2\text{O}_4$ と $(\text{Ba}, \text{Sr})\text{PbO}_3$ を用いた酸化物熱電変換素子

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Thermoelectric oxides of $\text{NaCo}_{1.7}\text{Cu}_{0.3}\text{O}_4$ (p-type) and $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{PbO}_3$ (n-type) were coupled to be π -shape device using sinter-forging method with the insertion of Au foil as a diffusion barrier. The high-temperature thermoelectric performance of the device was investigated, and it was stable and showed no appreciable contact resistance at the junction after the thermal cycle at 1000 K in air. The output power for the device was 12 mW when the temperatures of the hot and cold side of the device were 1045 K and 539 K, respectively. High-temperature durability was also tested and the related analysis was also reported.

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1. Introduction

Thermoelectric (TE) materials with high energy-conversion efficiency are investigated for applications as the Peltier coolers and power generators. The performance of TE material is measured by the dimensionless figure-of-merit, ZT , where T is absolute temperature. Z is given by $Z = \alpha^2 \sigma / \kappa$, where α is the thermopower (Seebeck coefficient), σ and κ are the electronic conductivity and thermal conductivity, respectively. For about four decades ago, a ZT of 0.75 was reported, and there has been continuous efforts enhancing the very recent ZT values up to 2.4 at 300 K for the Bi-Te based superlattice thin films.¹⁾ For the real application of TE power generation, it is also inevitable to operate at high temperature with the large temperature difference, making the power and efficiency pulled up drastically from the present level.

Considering the high stability at high temperature in air, easy and low cost process, TE oxides are the best candidates for the TE power generation. Recently, the ZT of oxide materials were surprisingly increased both n-type²⁾⁻⁴⁾ and p-type,⁵⁾⁻⁸⁾ and the research and development on oxide TE are now accelerated by many research groups. Especially for p-type oxides, a series of cobalt oxides, such as NaCo_2O_4 ⁵⁾ and $\text{Ca}_3\text{Co}_4\text{O}_9$,⁷⁾ is the best TE oxide materials. The $\text{Ca}_3\text{Co}_4\text{O}_9$ reported to have the expected ZT of 2.7 whose energy conversion efficiency is calculated to be about 20%.

Authors have also reported a successfully fabricated, directly coupled all-oxide p-n element.⁹⁾ For this element, both the negligibly small resistance of p-n junction and almost ideal thermo-voltage by p-n legs have been confirmed experimentally up to 1070 K. This method is considered to be very suitable for the all-oxide TE device for high temperature operation.⁹⁾⁻¹¹⁾ Before using NaCo_2O_4 as a p-type leg of this element, we should validate some technologies. For instances, whether the NaCo_2O_4 system can replace the p-type leg, how large TE power can be drawn when the device is actually set to a heat source, the degradation problems at high temperature operation. In this study, we report the fabrication of the oxide TE device by coupling

$\text{NaCo}_{1.7}\text{Cu}_{0.3}\text{O}_4$ and $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{PbO}_3$ and its power-generating performance at high temperatures.

2. Experimental procedures

2.1 Materials choice

The $\text{Ba}_x\text{Sr}_{1-x}\text{PbO}_3$ solid solution is the best n-type oxide system³⁾ ever known and the composition of 80% Sr substitution was chosen for its highest thermoelectric figure of merit, $Z = 1.9 \times 10^{-4} \text{ K}^{-1}$ at 680 K. The p-type NaCo_2O_4 is also the best p-type thermoelectric oxide material,⁵⁾ of which recently reported ZT is 1.2 at 800 K,¹²⁾ and the Cu-substituted composition was chosen for its high thermopower.¹³⁾ We prepared the sintered bars of p-n legs separately; p-type $\text{NaCo}_{1.7}\text{Cu}_{0.3}\text{O}_4$ (NCCO) and n-type $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{PbO}_3$ (BSPO). For the sintered body of BSPO, the process of calcination at 1123 K, 12 h, in air and the following sintering at 1123 K again 12 h was used. For the p-leg, from the starting material of NaCO_3 , Co_2O_3 , and CuO were mixed and calcined at 1023 K for 12 h. From this calcined powder, the sintered body was prepared by final firing at 1123 K 12 h. The two sintered bodies of p- and n-legs were joined under uniaxial pressure of 4 MPa, at 1123 K for 10 h in air. For the procedure and details of the element fabrication, see Ref. 9.

2.2 Fabrication of the p-n coupled element and measurement

In our pervious reports of p-n element fabrication, the Li-doped NiO and BSPO was coupled directly without any diffusion barrier between the p- and n-type oxide using the sinter-forging method.⁹⁾ During the sinter-forging process, the liquid phase was formed and the two sintered legs were squeezed down by the load pressure of the hot pressing, and some amount of them spread out. However, in this case of NCCO and BSPO, Two different oxides reacted each other and the direct coupling was failed. To preventing this unwanted reaction between two oxides, a diffusion barrier was introduced. A sheet of Au with the thickness of 30 μm was inserted between two oxides and the sandwich of NCCO/Au/BSPO was hot-pressed. By using Au barrier sheet, the joining two p- and n-oxide was successful.

Fig. 1. Fabrication process and measurement configuration of the coupled single element.

A slit with the width of about 1.5 mm was introduced between NCCO and BSPO by cutting out the Au sheet, and finally pi-shaped elements were prepared, as shown in Fig. 1 (a). The dimension of the element was as follows. The total length of the element was 17.5 mm, and the length of the contact part was 4.5 mm. Both p- and n-type legs had same cross sections of the width $\times$ thickness = $3 \times 3 \text{ mm}^2$.

The current lead at cold side of element was made by silver paste and attached to the alumina slab with glass epoxy. The alumina slab works as not only a binder but also as a cooling fin. The high-temperature TE properties of the element were directly measured by inserting the hot side of the element to electrical furnace. The cold side was naturally cooled by air around alumina slab pressed by metal block, and enough temperature difference was built with this configuration, as shown in Fig. 1 (c). The current-voltage, I - V , characteristics of the TE generator element was measured using variable resistor, increasing the hot-side temperature of the element or module.

3. Results and discussion

As described above, the direct coupling of two legs of BSPO and NCCO was failed by the unwanted reaction between two oxides. We have examined the phase of the reacted parts using the powder XRD peak pattern analysis, see Fig. 2. The reacted parts consist of PbO and $\text{SrCoO}_{2.52}$, with small amount of Sr_2PbO_4 and Ba_2PbO_4 , except the original phase of BSPO and NCCO, indicated as black circles and triangles, respectively. By inserting the diffusion barrier of Au sheet between two oxides, the element of BSPO/Au/NCCO was successfully fabricated without any unwanted reaction. The results of TE power generation reported here is for this element of BSPO/Au/NCCO.

3.1 Power generation from p-n coupled element

Figure 3 shows the thermoelectric voltage with temperature difference and I - V characteristics of an oxide element with the highest hot-side temperatures, which were linear for the whole temperature ranges. The thermoelectric voltage was developed by the temperature difference, ΔT , be-

Fig. 2. Powder XRD peak pattern of the reacted parts at the interface of two oxide legs ($\square$ and $\circ$ are for PbO and $\text{SrCoO}_{2.52}$, respectively).

Fig. 3. I - V characteristics of a coupled oxide element with different hot-side temperatures.

tween hot and cold side of the element, and reached up to 0.14 V with the largest $\Delta T = 506 \text{ K}$. At this condition, the maximum power generated is 12.5 mW for a single element. The large temperature difference of 506 K for this short leg of 2 cm, developed without any intended cooling is noticeable and can be regarded as an advantage of oxide TE generator device.

The total resistance of the element for this temperature, which includes the two contact resistances at cold-side current leads, was evaluated to be 0.396Ω from the I - V curve. This value is larger than the resistance of the p-n coupled element itself which was measured separately at the same time by the four point method, to be 0.25Ω , and the difference was due to the resistance of two contacts of p- and n-legs to the current leads.

The TE output power was calculated for the p-n coupled element, on the assumption that the resistance, R and the thermopower, α of the couple were kept constant at the average temperature 792 K using the high temperature TE properties for NCCO and BSPO. This assumption is reasonable and validated for previous experiments.^{9),11)} The TE properties including the power factors were measured and plotted in the Fig. 4, and the $R (=R_p + R_n)$ and $\alpha_{pn} (= \alpha_p - \alpha_n)$ for 792 K, were 0.443Ω and 0.277 mV/K , respectively. From these data, the maximum output power for a coupled element, $P_{\max} = \{\alpha(T_h - T_c)\}^2 / 4R = (0.277 \times 506)^2 / 1.8$, was

Fig. 4. Thermoelectric properties, upper is conductivity, lower is thermopower of each single element, p- and n-type legs.

calculated to be 11.1 mW. This value is very close to the measured, 12.5 mW, and the p-n coupling seems successful and ideal, i.e., the insertion of Au sheet prohibited unwanted reaction between p- and n-type oxide legs, and did not deteriorate the TE properties of p-n coupled element. From above results and discussion, we proved that this oxide p-n coupled element of NCCO/Au/BSPO worked successfully with large temperature differences and good electrical contacts.

3.2 Efficiency of the TE oxides element

For the real application of TE Power generation, we should validate the adaptability of TE oxides for system design. Furthermore, to estimate the materials parameters such as figure-of-merit and energy conversion efficiency is very important for engineering sense. From the data of NCCO and BSPO above, the efficiency, η , and the Ioffe's figure-of-merit, Z_{Ioffe} , of the p-n couple,¹⁴⁾ were calculated and plotted as shown in Fig. 5. The assumptions are that the temperature of the cold side is 373 K, and that the thermal conductivity, κ , of each p- and n-type oxide legs^{5),6)} are $\kappa_p = \kappa_n = 20 \text{ mW}/(\text{K} \cdot \text{cm})$. Using the reported data of NaCo_2O_4 ¹⁵⁾ and $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{PbO}_3$,³⁾ the same calculation was shown also in the Fig. 5, for the comparison.

Considering that the η of the TE device of Bi-Te system applied for the co-generation using the waste heat, is around 8%, the efficiency of oxides reported in this study is about 1/4 of that of Bi-Te system. Compared with other oxides modules, however, the η in Fig. 5 reached up to about 2% and is higher than that of reported, 1.1%.¹⁰⁾ From the plots of Z values shown in Fig. 5, we could know this low efficiency of the oxides was due to the low Z values of the oxide legs which is almost ten times lower than that of Bi-Te system. However, the large temperature difference reduces the difference in the efficiency. The Z of oxides can increase over 2 times by replacing the p-type leg with the better one. Though the TE properties of the p-type oxide leg in this study were relatively poor than expected, but the recent development of NaCo_2O_4 system are very promising by various advanced processes. Recently, it is reported that the Z

Fig. 5. Calculation of the energy conversion efficiency and figure of merit, Z .

of NaCo_2O_4 system has increased up to $0.88 \times 10^{-3} \text{ K}^{-1}$,¹⁵⁾ which is almost same to that of the state-of-art Bi-Te system. By combining the modified NaCo_2O_4 and the p-n coupling process of this study, we can increase both the power and the efficiency drastically.

3.3 Durability test and analysis

Not only the thermoelectric performance of the couples itself, the high temperature durability of the element including the contacts is also important. For the high-temperature operation, the most possible problem is that a significant change in the electrical resistance of the devices, which leads to the degradation of device performance. In other words, the electrical resistance can be used as an indicator for the degradation of device and this comes from mainly the thermally activated diffusion at the heterogeneous junctions, such as p-n junction or electrode contacts.

The durability of the oxide TE oxide element of NCCO/Au/BSPO for the high temperature operation in air was tested. The power generation properties of the element did not change after the high temperature operation for 7 d, at the hot-side temperature at 1000 K (995–1005 K) in air, with the continuous direct current load, $I = 90\text{--}100 \text{ mA}$, as shown in Fig. 6(a). The power level after the test were almost same to that before the test around 8 mW. From this result, we can conclude that the coupling of these two oxides was very good and there was no increase in resistance at the p-n interface. In this case, the Na diffusion is most fatal problem and the compositional gradient of Na may occur during the operation at high temperature with the continuous direct current. However, no evidence of local distribution of Na was assigned from the EDX analysis shown in Fig. 6(b); the mapping images. However, the question whether the Na loss occurs at the hot side or not was not answered clearly from this quantitative analysis of Na contents for three different parts; the right-side figures.

4. Summary

The thermoelectric device of oxide p-n coupled element of $\text{NaCo}_{1.7}\text{Cu}_{0.3}\text{O}_4$ and $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{PbO}_3$ has been fabricated using direct joining between p-type and n-type. Because of unwanted reaction between the two p- and n-type oxides, the diffusion barrier of Au foil was used and the device was stable and showed no appreciable contact resistance at the

Fig. 6. High-temperature durability test at around 1000 K in air for 7 d. (a) power curves after the operation with the direct current of 100 mA, (b) electron microscopy images and the elemental analysis mapping of the 3 points in p-type leg, NCCO.

junction after the thermal cycle at 1000 K in air. The TE maximum power from the device was 12.5 mW when the temperatures of the hot and cold side of the device were 1045 K and 539 K, respectively. The device showed neither appreciable contact resistance at the junction nor changes in thermopower, after the high-temperature durability test in air.

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