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Thermoelectric power generation using Li-doped NiO and (Ba, Sr)PbO_3 module

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Abstract

A prototype of oxide thermoelectric (TE) module by p–n coupled oxide elements has been fabricated for the first time, for the application of power generation at high-temperatures in air. For the single couple, the π-shaped joints of sintered bodies of Li-doped NiO (p-type) and (Ba, Sr)PbO_3 (n-type) were used. TE performance of both single couple and the module were investigated in the temperature range from 440 to 1060 K. The maximum output power from a single couple was 7.91 mW with the operating temperature difference of 552 K. The assembled module with four elements showing almost four times larger power, 34.4 mW, than that of a single element. The reliability of this oxide couple at high-temperature in air, and an application of module for the power generation using the waste heat from a stove are also reported.

Keywords: Oxide; Thermoelectric module; p–n Coupled element; High-temperature

1. Introduction

Thermoelectric (TE) power generation, direct energy conversion from heat to electrical power, had succeeded in space applications several decades ago. Also on the earth, the researches on using waste heat as new energy sources have been in progress. The attempts to collect the low calorie waste heat by means of TE generator (TEG) with elements of compound semiconductor, such as Bi–Te material [1] have been tired for TEG. However, its conversion efficiency was low because they cannot be used for the application at high-temperature in air, and the deposit of these compound semiconductors is low and some of them are toxic. For the TEG application, it is important fact that high-temperature heat source makes the output power and efficiency pulled up by large temperature difference. In this sense, the promising and the best candidate TE materials for the high-temperature TE generation from waste heat are oxide materials.

Recently, the TE figure-of-merit, Z, of oxide materials were surprisingly increased [2] and the research and development on oxide TE are now accelerated by many research groups, and a series of cobalt oxide were reported to have the ZT of 2.7 whose energy conversion efficiency is expected to be about 20% [3]. Among them, authors have reported a successfully fabricated, directly coupled all-oxide p–n element. For this p–n element, both the negligibly small resistance of p–n junction and almost ideal thermo-voltage by p–n legs were confirmed experimentally up to 1070 K [4]. The TE performance, ZT, of this device is expected to be around 0.15 at 1000 K which same level with that of $FeSi_2$.

Because this oxide device for the high-temperature application is really new, we should check some important properties, which are still in question. The technically important question, for instance, how long the oxide device can work, and or how large TE power can be drawn when the device is actually set to a heat source. In this study, we report the TE performance of oxide element of TEG at high-temperature in air and the durability at high-temperature. Also the properties of newly assembled module with four elements were also evaluated.

2. Element fabrication and measurements

The TEG-element was built-up with a couple of the sintered bodies of p-type alkali-doped NiO (ANO), where

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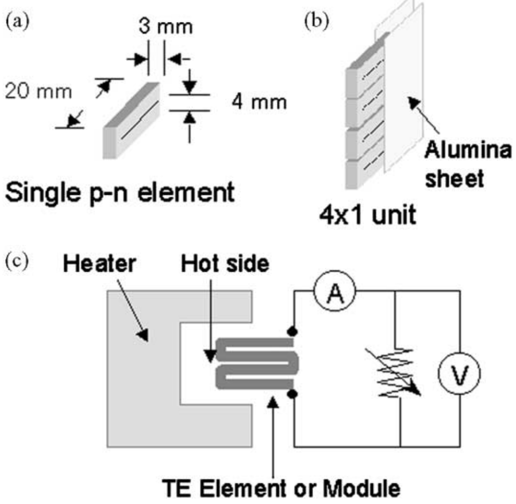

Fig. 1. Fabrication and measurement configuration: (a) a single element, (b) a module of four elements, (c) test set up for the TE power generation.

the alkali element was Li, and n-type $Ba_{0.2}Sr_{0.8}PbO_3$ (BSPO). The $Ba_xSr_{1-x}PbO_3$ solid solution is the best n-type oxide system [5] ever known and the composition of 80% Sr substitution was chosen for its highest power factor, $PF = 3.5 \times 10^{-4}$ W/mK at 1000 K. The p-type ANO is also a promising p-type TE oxide material [6] which can be used over 1200 K. We prepared the sintered bars of ANO and BSPO separately, and they 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 [4].

A slit with the width of about 2 mm was introduced between ANO and BSPO, and finally π-shaped elements were prepared, as shown in Fig. 1(a). The typical dimension of the p–n type element is as follows. The total length of the TEG-element was 20 mm, and the length of the contact part was 6 mm. The width of both legs of ANO and BSPO were 4 mm, and the thickness of them was 3 mm. The module consists of four p–n elements connected in series as shown in Fig. 1(b). 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.

Fig. 1(c) shows a direct measuring method for the high-temperature TE properties of the element in this study. The cold side was naturally cooled by convection of air around alumina fin, and enough temperature difference was built with this configuration. The current–voltage, *I–V*, characteristic of the TE oxide couples was measured using variable resister, increasing the hot-side temperature of the element or module. For the mechanical properties, three-point bending test was used to evaluate the strength of the oxide legs, and their thermal expansion was determined using mechanical dilatometry; the displacement between the ends of a specimen was measured as a function of temperature.

3. TE generator performance

3.1. Single p–n couple

Fig. 2 shows the *I–V* characteristics of an oxide p–n coupled element with various hot-side temperatures, which were linear for the whole temperature ranges. The TE voltage was developed by the temperature difference, ΔT, between hot and cold side of the element, and reached up to 0.116 V with the largest $\Delta T = 552$ K. At this condition, the maximum power generated is 7.91 mW for a single couple. The total resistance of this coupled element for this temperature, which includes the two contact resistances at cold-side current leads, was evaluated to be 0.41 Ω from the *I–V* curve.

The large temperature difference of 552 K without intended cooling is noticeable and can be regarded as a merit of oxide TEG. This high-temperature operation is very attractive and the oxide device was stable at this high-temperature. The TE output power and the efficiency [7] were 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 0.085 Ω and 0.136 mV/K, respectively, which were equal to the values at middle temperature of 750 K, and that the thermal conductivity, κ, of each p- and n-type oxide legs [5,6], were $\kappa_p = \kappa_n = 20$ mW/(K cm). The maximum output power for a coupled element, $P_{max} = \{\alpha(T_h - T_c)\}^2/4R$ was calculated to be 14 mW, and the efficiency, ξ_t, to be 0.64%.

In this study R increased up to 0.41 Ω and P_{max} was 8 mW. This difference of R is due to the resistance of two contacts of p- and n-legs to current leads, and that of the p- and n-legs measured separately to be 0.18 and 0.32 Ω, respectively. This resistance of the legs, 0.18 Ω is larger than the 0.085 Ω taken in above calculation. This because that the resistance of the legs at lower temperature is as large as 1 Ω, when the contact resistance at leads almost unchanged; the contribution of the part in legs at cold side.

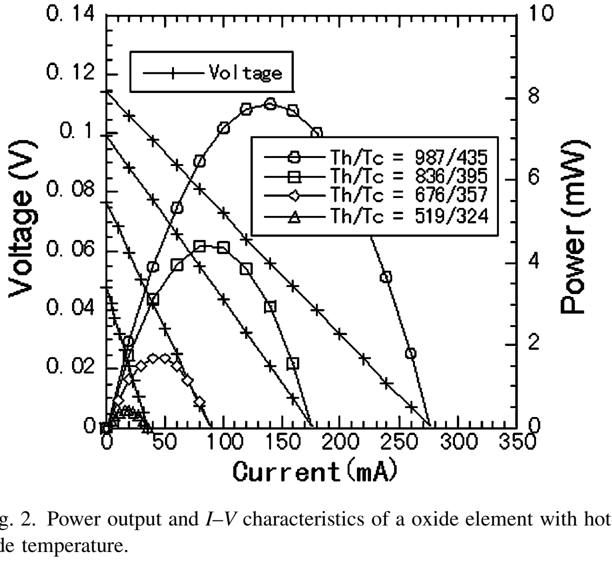

Fig. 2. Power output and *I–V* characteristics of a oxide element with hot-side temperature.

For the size of the p- and n-legs, a two times longer ones, i.e. 40 mm long, were also tested and the built-up temperature difference was nearly same to that of 20 mm long legs. In the case of other high-temperature TE module of $FeSi_2$, the length of the leg was optimized to be 40 mm [8] with neck structure. With this configuration, its built-up ΔT was about 400 K. From above results and discussion, we proved that this oxide p–n element works successfully with large temperature differences and good electrical contacts.

4. Module of four p–n couples

When the module built from this single element, many single couples should be electrically connected in series to get usable level of voltage. For the module made of four elements electrically connected in series, see Fig. 1(b), was assembled and showed almost four times larger power and TE voltage than those of a single couple as shown in Fig. 3. The measured temperature, voltage, and resistance are listed in Table 1, and compared with those of the single couple. The resistance was increased about three times, which was probably owing to difference in size and electrode's contact area of each element.

Table 1
TE power of four p–n coupled module compared with that of a single element

	T_{hot} (K)	ΔT (K)	V_{max} (V)	R (Ω)	P_{max} (mW)
Single p–n element	987	552	0.1138	0.41	7.91
Four p–n module	1164	539	0.394	1.13	34.4

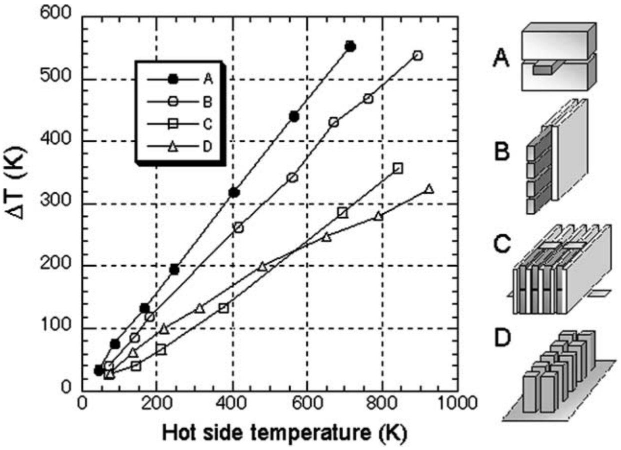

Fig. 4. Hot-side temperature, T_{hot} vs. ΔT for the modules of difference designs. Case A is for a single couple with heat sink of aluminum block.

Though the T_{hot} is higher than that of a single couple, the resistance just increased by four and there was no additional increase in resistance by connecting four couples. And the temperature difference was well developed to make the average of output voltage is same to that of a single one. From these facts, we confirmed that the assembling of in series built-up module was successful, and that the cooling fin of alumina works efficiently. The design becomes important when built-up module and the results shown above is the optimized one. For the other configuration, the built-up temperature difference, ΔT, was relatively small. In Fig. 4, hot-side temperature, T_{hot} versus ΔT for the modules of different designs is plotted, and the single couple with heat sink of aluminum block was also shown as a reference data, the case A. For all the tested cases, B–D, T_{hot} increased up to 1100 K, but their ΔT differ largely. At low-temperature, the case D looks better than the case C, but becomes worse with temperature. This may be due to the transfer by thermal radiation, which became more effective at high-temperature. Among them, the case B was the best design whose ΔT was large and close to that of the case A.

A module of 12 couples were also successfully assembled and tested, using this module of four couples, and the measured P_{max} of this three modules are plotted with hot-side temperature, in Fig. 5. Comparing with the expected power of a module, the three modules showed almost three

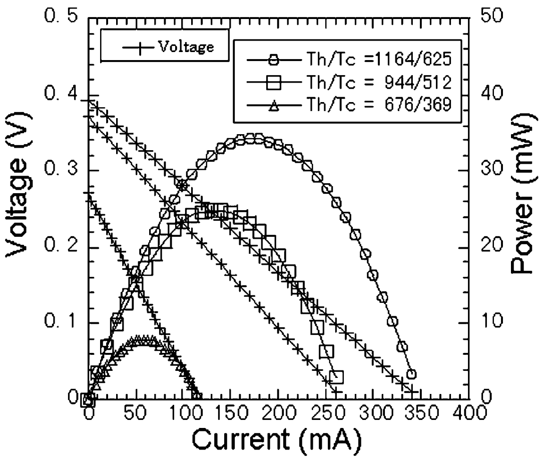

Fig. 3. Power output of the module with four elements in series compared with that of a single element.

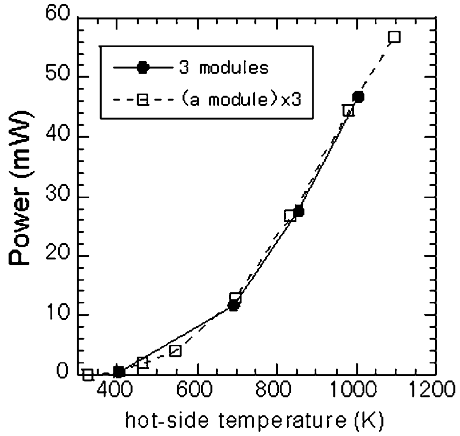

Fig. 5. P_{max} of three times (four couple module) plotted with hot-side temperature; dashed line is epected one, three times P_{max} of a four couple module.

times larger values and this fact can suggest that much more power can be easily drawn by just stacking the modules up. For the highest temperature recorded for a module, however, their hot-side temperature did not reached to this level, because of the small capability of the furnace used in our experiment.

5. Reliability and application

For real application, oxides modules will be not expensive because of its low cost of raw material and its simple processing. If it runs using waste heat, the most important parameter would be how much the module can make electrical power and how the module weight, for engineering sense. For the oxide module shown in this study, a four couple module with alumina fin is 12.5 g and the power per weight = 2.75 mW/g. This is about quarter of the novel $FeSi_2$ module, 12.2 mW/g [8].

Furthermore, not only the TE performance of the couples itself, some other properties of the modules such as high-temperature durability, mechanical strength, and also adaptability for application. These are studied and discussed as below.

6. High-temperature durability

The recent reliability study considered that the TE modules would be less reliable when operated at high-temperature as generator [10]. The major problem is that a significant change in the electrical resistance of the modules, which leads to the degradation of module performance. In other words, the electrical resistance can be used as an indicator for module degradation. The durability of the oxide TE device for the high-temperature operation in air was tested. The TE performance of the oxide element was almost unchanged over 82 h at the hot-side temperature of 990 K in air, as shown in Fig. 6(a). From this result, the coupling of these two oxides is very good and there was not any increase in resistance at the p–n interface.

Considering that some diffusion barriers were adopted for the SiGe TE element [9], it is noticeable that the interface between p- and n-type oxide without any diffusion barrier has no increase of resistance, and that it was very clear boundary. The appearance of the element was also shown in Fig. 6(b) and no morphological change was assigned. Only the color of the BSPO leg's surface changed to red, but it is not harmful and very typical fact occurring after annealing this oxide.

Fig. 7 also shows microscopic observation with the EDX analysis for Ni, Sr, and Pb onto the p–n interface of the couple after the test. The interface was sharp and no signal of inter-diffusion was assigned. The two different grains of p- and n-type oxides seem to hold tightly each other.

7. Mechanical strength

There are other important problems to be investigated when the TE oxide module used for practical applications. First, oxides are in general brittle and can be easily broken during handling or operation. Second, the difference in the thermal expansion could induce cracks in oxides, because its operation undergoes severe thermal cycle from 300 to 1000 K.

Some properties are listed in Table 2 for the each oxide legs of the TE couple. From the facts that the oxide legs were broken first when we handle the π-shaped TE couple, the p–n interface part is considered to be stronger than each legs. The strength of the each legs were evaluated by three-point bending test to be around 50 MPa and that of the p–n interface part would be higher than this value. However, at the interface, the difference in thermal expansion is much critical. Their expansion coefficients investigated using

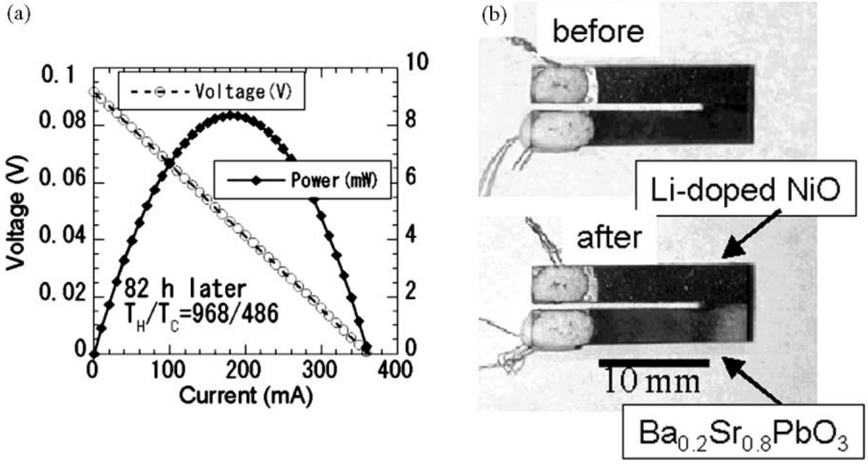

Fig. 6. The 82 h durability test at around 990 K in air; temperatures of hot- to cold-side = 968 to 486 K: (a) power curves after 82 h operation, (b) photos of the tested element.

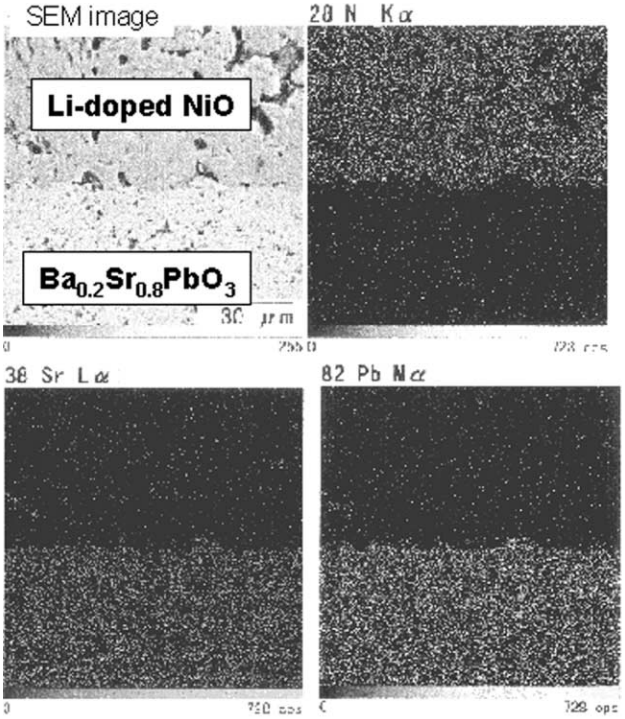

Fig. 7. Electron microscopy images of the interface between p- and n-type oxides with the elemental analysis.

dilatometry were similar at lower temperature but differ at high-temperature region. From the value of the high-temperature region, we can estimate how large stress can be induced. By simple calculation using the difference of thermal expansion coefficient, temperature and the Young's modulus of BPO, the stress induced by temperature difference is $(18.7–14.2) \times 10^{-6}\,K^{-1} \times 500\,K \times 33\,GPa = 74.3\,MPa$, which is larger than the strength of each leg, 50 MPa. More peer analysis and detailed parameters, such as thermal distribution at hot side, should be necessary for the precise evaluation. Actually, during our performance test, there was no failure at the interface part, and the data shown in Table 2 could be guides for practical design.

Table 2
Fracture strength and thermal expansion coefficient data of oxides

	Temp. (°C)	NiO	BPO
	Strength (MPa)		
	20	54 ± 4	47 ± 4
Thermal expansion coefficient ($10^{-6}/K^{-1}$)			
	20–100	9.80	10.7
	20–100	9.80	10.7
	20–100	9.80	10.7
	20–100	9.80	10.7
	20–200	11.5	11.9
	20–300	12.3	12.1
	20–400	13.2	12.6
	20–500	15.1	13.2
	20–600	16.8	13.7
	20–700	18.7	14.2

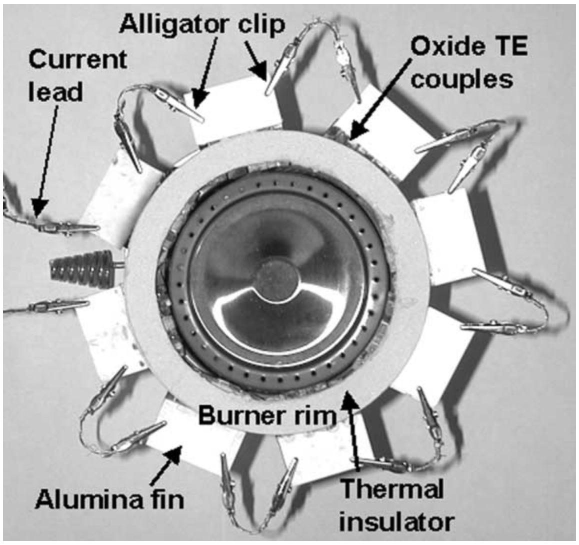

Fig. 8. Photo of the TE generator applied for home stove.

8. Power generation from home stove

Powered from locally available heat sources like kerosene or propane gas, this new oxide TE module can generate electrical power from high-temperature differentials. This can be used for supplying electrical power to safety circuit or microprocessor control system of the heater. We applied our oxide TE module to a home stove. For the specification of the electrical power, a model application, for instance, charging up battery, some 2–3 V and 30–40 mA, that is the power is about 60–120 mW, was considered.

Before the test, we inserted several modules in the stove, and place them around the burner rim and measure the temperature difference built-up. At normal operation condition, the stove burn out heat of some 1000 kcal/h, the TE modules were set around the burner, without rigid contact to burner rim, and the hot and cold temperature built across the module were 823 and 523 K with $\Delta T = 300\,K$. For this experiment, to meet the electrical specification above, eight modules (32 couples) connected in series were set around the burner rim as shown in Fig. 8, and their power generation was examined. The average values of short-circuit current and open-circuit voltage were 100 mA and 2.0 V, with $P_{max} = IV/4 = 50\,mW$. Even after the 20 times cyclic operation, there was no degradation of the power generation performance. This test would be the first application of oxide TE device for power generation.

9. Summary

TE power generation has relatively low conversion efficiency and low power per weight value and expensive at present. However, there can be several exceptions such as when the thermal input energy is just waste heat, or the temperature is very high, or module is made of cheap material like ceramic oxides. In this study, we reported the fabrication of oxide TE module for power generation and its performance. The module was assembled from four p–n couples with Li-doped NiO and (Ba, Sr)PbO_3, with the alumina fin as thermal radiator, and the maximum power generated from this module with the hot-side temperature of 1164 K was 34.4 mW.

This oxide couple was proved to be stable at high-temperature of 990 K in air, and the mechanical strength of its p–n coupled interface was over 50 MPa. Some evaluations on technically important data such as module design and a model application for home stove were also reported here, and this paper would be the first technical reference for development and system design of oxide TE generator.

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