Thermoelectric properties of Ni-based oxides

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In order to discover a new n-type oxide possessing good thermoelectric properties, a high throughput screening technique has been developed. It is found by screening metal-binary systems including 3d transition metals using this technique that $LaNiO_3$ shows the n-type property. Electrical resistivity (ρ) of this oxide is rather low, however, Seebeck coefficient (S) is as low as $-25\mu V/K$. The high throughput screening was carried out in metal-ternary systems of (La, M)NiO_3 to improve S. Bi-substitution is found to be effective to improve both S and ρ.

A thermoelectric unicouple composed of p-type $Ca_3Co_4O_9$ (Co-349) and n-type $LaNiO_3$ (Ni-113) bulks has been constructed. Both p- and n-type legs have been prepared using a hot-pressing technique. Open circuit thermoelectric voltage (V_o) of the unicouple reaches 105 mV at 1118 K of high temperature (T_H) side and 500 K of a temperature difference (ΔT) in air. Resistance of the unicouple (R_I) increases with increasing temperature and is 18 mΩ at 1118 K in air. The V_o values are consistent with those calculated using S values for each oxide leg. Maximum power (P_{max}) is evaluated using a formula of $P_{max} = V_o^2/4R_I$, which increases with temperature and is 152 mW at 1118 K (ΔT= 500K). This value corresponds to 1.07 W/cm^3 and 0.23 W/g of the power density.

Key words: thermoelectric material, oxide, combinatorial chemistry, device, module

1. INTRODUCTION

Humanity urgently requires solutions to energy and environmental problems which are now reaching crisis levels. As one such solution, thermoelectric energy generated from the vast amounts of waste heat emitted by automobiles, factories, and similar sources is expected to be developed in the near future as a resource-conserving form of energy. Waste heat offers a high-quality energy source equal to about 70% of total primary energy, but is difficult to reclaim due to its source amounts being small and widely dispersed. Thermoelectric generation systems provide the only viable method of overcoming these problems by converting heat energy directly into electric energy irrespective of source size and without using turbines or producing CO_2 or radioactive substances. The requirements made of the materials needed for the task, however, are not easily satisfied. Not only they must possess high conversion efficiency, but they must also be composed of non-toxic and abundantly available elements, in addition to having high chemical stability even at high temperatures of 800-1000 K in air. It has been reported that CoO_2-based oxides with layered structures show good p-type thermoelectric properties at high temperatures in air [1-3]. No n-type oxides possessing thermoelectric properties as high as CoO_2-based oxides. In order to realize thermoelectric generation, such n-type oxides are indispensable. Unfortunately, although the exploration of the n-type oxides has been performing eagerly, no n-type oxides with sufficient properties for power application have been discovered.

$LaNiO_3$ and La_2NiO_4, which have perovskite related structure ($A_{n+1}B_nO_{3n+1}$), have been reported to show negative Seebeck coefficient (S) and low resistivity (ρ) values [4]. Although the $LaNiO_3$ (Ni-113) phase has not so high S values ($\sim -25\ \mu V/K$), ρ is low (~ 4.0 mΩ cm) as oxide materials at high temperature. Considering $Ca_3Co_4O_9$ (Co-349) phase shows high S, however, not so low ρ, Ni-113 phase possessing low ρ would be a good partner for the Co-349 phase. This paper shows results of the high throughput screening of substituted (La, M)NiO_3 systems in order to improve S of the $LaNiO_3$ phase. Moreover, construction of thermoelectric unicouples composed of the Co-349 and Ni-113 bulks and their properties are described.

## 2. EXPERIMENTAL

2-1. High throughput screening

The high speed synthesis of oxides for high throughput screening has been shown in Ref. 4. As starting materials, aqueous solutions of metal nitrates were used. The concentration of the solutions was 1.0 metal mol/l. The solutions were distributed using a high-speed library preparation machine. This was designed by the authors and produced by Bio Tech Co., Ltd. in Japan. At most 5 kinds of metals can be mixed and 100 kinds of mixed solutions with different compositions are available within 15 min using this machine. Only a few 100 μg of the metals is included in each solution, which is about 10^{-5} times smaller than the conventional solid state method. After distribution, the

mixed solutions were applied (drawn) on an alumina plate (100 mm x 100 mm) using the same machine. Each sample has a line-shape with length of 10 mm and includes only several μg of metals. The 100 line-shape samples can be applied on the alumina plate within 45 min. Namely, after 1 h from the beginning of distributing the solutions, one precursor library has been prepared (Fig. 1). After application, the precursor libraries were heated at 973-1373 K for 10 h in air. The 1000 kinds of samples (10 libraries) are synthesized using the above method in one day.
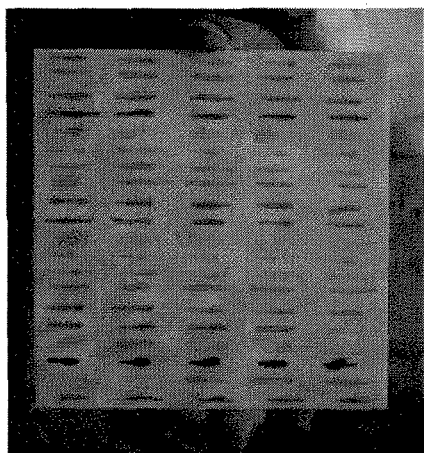
Fig. 1 A precursor library for high throughput screening.

In the high throughput screening technique, evaluating properties of the samples must be as fast as synthesizing them. The evaluation of S is carried out at room temperature using two terminals composed of thermocouples ('Seebeck tester') is this work (Fig. 2). One of the terminals equips a heater (warm side). Temperature difference can be controlled by current flowing in the heater in a region of 5-30 K. The two terminals are touched to both ends of the line-shape samples. The measurement of S of the one library including 100 samples can be finished about 15 min using this system.
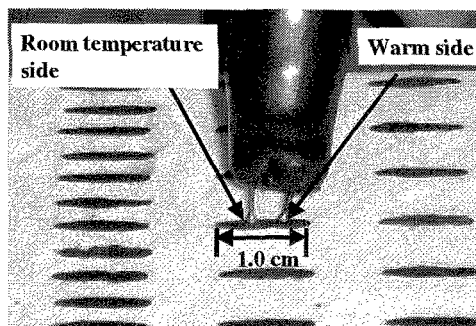
Fig. 2 High-speed evaluation of Seebeck coefficient (Seebeck tester).

For detail investigation, bulk samples consisting of cationic compositions extracted form the libraries, which show good thermoelectric properties have been prepared using a sol-gel method. The metal nitrates as starting materials were weighed and dissolved in distilled water in alumina crucibles. The water was evaporated and the remnant was heated at 1073 K for 10 h in air. The heated samples were ground, pelletized, and sintered at 1173 or 1273 K for 20 h in air.

2-2. Preparation of oxide legs

The p-type Co-349 and n-type Ni-113 bulk materials are prepared using a hot-pressing technique. $CaCO_3$, Bi_2O_3, and Co_3O_4 powders were mixed in a cationic molar ratio of Ca : Bi : Co = 2.7 : 0.3 : 4.0 thoroughly by ball milling. The mixed powder was calcined at 1073 K for 10 h in air. The heated powder was ground, pelletized, and heated at 1153 K for 20 h in an oxygen gas flow (300 ml/min). The heated powder was ground again and pelletized in a plate with dimensions of 20 mm square and 5 mm thick. The plate was hot pressed at 1123 K under a uniaxial pressure of about 10 MPa for 20 h.

The powder of Ni-113 was synthesized using a sol-gel method. $La(NO_3)_3$ $6H_2O$, $Bi(NO_3)_3$ $5H_2O$, and $Ni(NO_3)_3$ $6H_2O$ were weighed in a cationic molar ratio of La : Bi : Ni = 0.9 : 0.1 : 1.0 and solved in distilled water thoroughly in an alumina crucible. The metal nitrate solutions were dried up. The remnant was heated to decomposed nitrates at 1073 K for 10 h in air. The heated powder was ground and pelletized. The pellets were heated at 1273 K for 20 h in the oxygen gas flow of 300 ml/min. The heated samples were ground, pelletized, and heated again under the same condition. After heating the pellets were ground and pelletized in a plate with dimensions of 20 mm square and 5 mm thick. The plate was hot pressed at 1173 K under the uniaxial pressure of about 10 MPa for 20 h in air. The p- and n-type legs were cut out from each hot pressed plate with a dimension of 4.0 mm square and 5.0 mm long. The length direction is perpendicular to the hot pressing axis. Namely, temperature difference was made in the hot pressed plane.

2-3. Preparation of thermoelectric unicouples

Ag paste was applied on the one of 4.0 mm square surfaces for both p- and n-type legs. One couple of the legs was adhered on an alumina plate with a dimensions of 5.0 mm wide, 8.0 mm long, and 1.0 mm thick. One of the surfaces of alumina plate was coated by the Ag paste. The precursor of the thermoelectric unicouple was heated at 1073 K for 15 min in air to solidify the Ag paste. The connection between the legs and the alumina plate was reinforced mechanically using ceramics paste mainly composed of alumina.

2-4. Measurement

Thermoelectric evaluations; open circuit voltage (V_o) and electrical resistance (R_I), were carried out in air. The alumina plate of the unicouple was heated by a planar electrical furnace and another side on which Pt wires for voltage terminals were attached using the Ag paste was cooled by circulated water. Temperature difference (ΔT) between high temperature (T_H) and low temperature (T_L)

sides was 5 to 500 K and increased with increasing T_H. R_I measurement was performed using a DC four terminal method.

3. RESULTS

3-1. Exploration of n-type oxides

Figure 3 shows time dependence of temperature for both warm and room temperature sides and thermoelectric voltage for a Co-349 bulk possessing good thermoelectric properties [5]. Several seconds after attachment of the two terminals of the Seebeck tester, it was found that all values, particularly S, were stable very shortly. The S values evaluated by this method almost agree with those measured by a conventional method. The n-type response is observed in the La-Ni-O library (Fig. 4). The highest S in this library appears around Ni : La = 1 : 1, although it is only about -10 μV/K at room temperature. From X-ray diffraction (XRD) patterns of these samples, it is found that perovskite $LaNiO_3$ phase is mainly formed (Fig. 5).
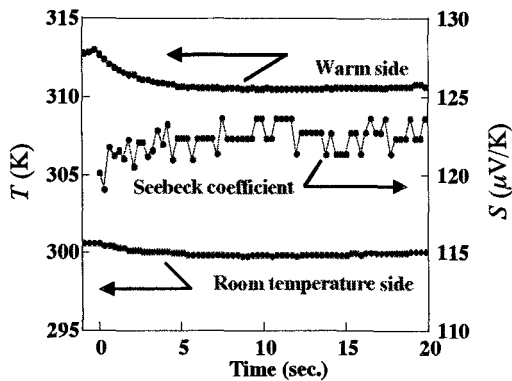
Nd and Bi for La is effective to enhance S. No obvious increase in S, however, is observed in the Sr and Ca substituted samples. For the detail investigation, the substituted bulk samples have been prepared.

Fig. 5   Powder XRD pattern of heated La : Ni = 1 : 1 system

Fig. 3   Time dependence of temperature difference and Seebeck coefficient.

Fig. 6   Seebeck coefficient of $La_{1-x}M_xNiO_3$ libraries.

Powder X-ray diffraction (XRD) patterns of the bulk samples with a composition of $La_{0.9}M_{0.1}NiO_3$ are shown in Fig. 7. In all samples except for Sr and Ca substituted sample, almost peaks are attributed to perovskite ABO_3 structure, although some weak peaks due to secondary phases appear in the no- and Bi substituted samples. In the Sr and Ca substituted samples, perovskite related (La, M)$_2$NiO$_4$ (A$_2$BO$_4$) phase is formed as a main phase.

In all substituted samples except for the Sr, Ca, and Nd substituted ones S values are higher than the no-substituted sample, especially at high temperature (Fig. 8). The increase by K-substitution would come from the decrease in carrier concentration. It has never been clear the reason of the increase in S by Bi-substitution.

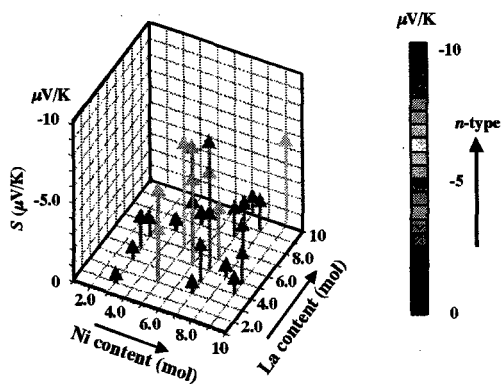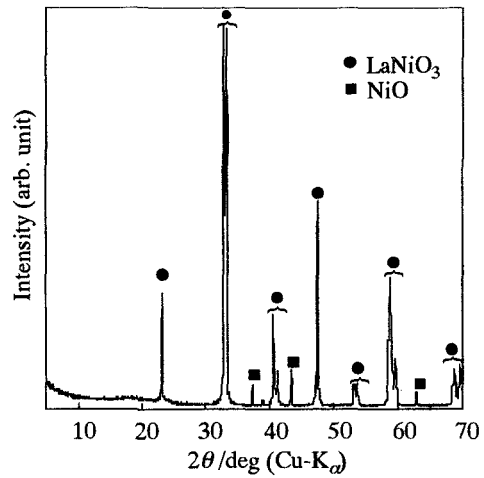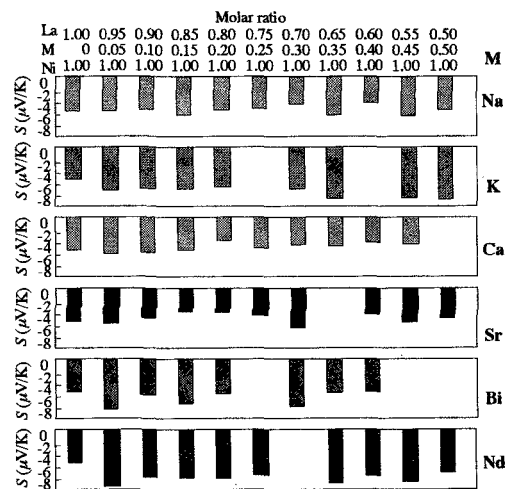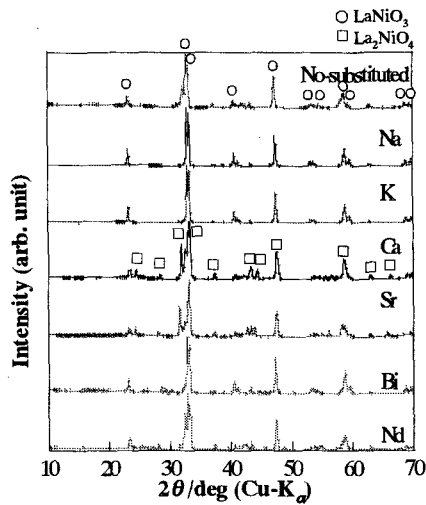**Fig. 4**   Seebeck coefficient of La-Ni-O library.

In order to enhance S values in the $LaNiO_3$ system, high through-put screening was carried out in $La_{1-x}M_xNiO_3$ libraries. Figure 6 shows the S values of the $La_{1-x}M_xNiO_3$ libraries heated at 1073 K for 10 h. It is found by screening libraries that substitution of Na, K,

Fig. 7   Powder XRD patterns of $La_{0.9}M_{0.1}NiO_3$.

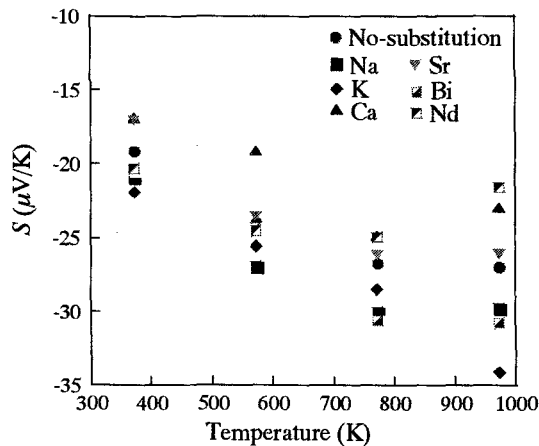**Fig. 8**   Temperature   dependence   of S for $La_{0.9}M_{0.1}NiO_3$.

Figure 9 indicates temperature dependence of ρ. All samples show a metal-like behavior. Bi-substitution is effective to reduce ρ slightly. If oxygen composition is not changed by Bi-substitution and Bi valence is 3+, average Ni valence is same between no- and Bi substituted samples. The reduction of resistivity seems to be caused by structural change or improvement of electrical property at grain boundaries. On the other hand, Na- and K-substitution increases ρ of the LaNiO$_3$ system. In this sample, the average Ni valence is calculated as 3.2, if the oxygen composition is 3.0. This is an incredible high valence for Ni. Therefore, the oxygen deficiency may be present in the Na and K substituted sample. Because no secondary phases are observed in the XRD pattern, the increase in ρ is due to a decrease in carrier (electron) concentration. No-substituted sample would also include the oxygen deficiency, so that the average Ni valence is lower than 3.0. By Na- or K-substitution, the average Ni valence increases, namely the carrier concentration decreases.
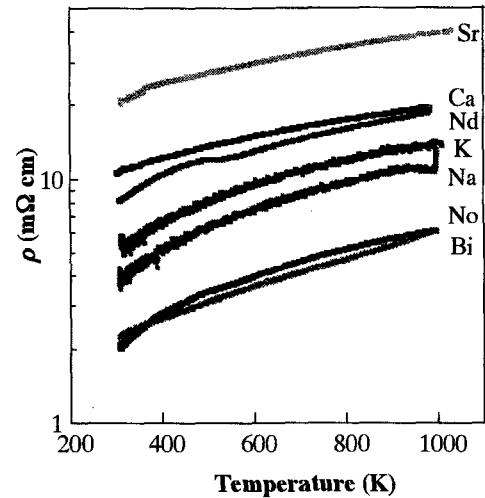

Fig. 9   Temperature   dependence   of ρ for $La_{0.9}M_{0.1}NiO_3$ bulks.

Power factor ($PF = S^2/\rho$) is plotted against temperature (Fig. 10). The Bi-substituted sample possesses the highest PF values in all prepared samples. So hot pressed bulk samples with a composition of $La_{0.9}Bi_{0.1}NiO_3$ were prepared for constructing thermoelectric unicouples.
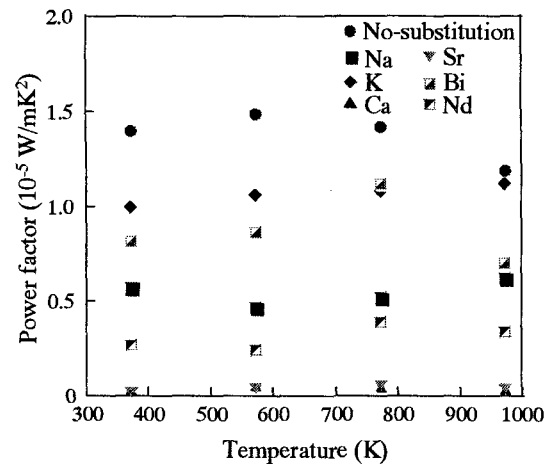

Fig. 10   Temperature   dependence   of PF for $La_{0.9}M_{0.1}NiO_3$.

3-2. Thermoelectric unicouples

Figure 11 shows temperature dependence of S and ρ for the Co-349 ($Ca_{2.7}Bi_{0.3}Co_4O_9$) and Ni-113 ($La_{0.9}Bi_{0.1}NiO_3$) bulk materials. Absolute S values of both materials increase with temperature. Although S is over 200 $\mu V/K$ for the Co-349, it is lower than 30 $\mu V/K$ at high temperature for the Ni-113. ρ for the Co-349 decreases with increasing temperature, on the other hand, the Ni-113 shows a metallic-like behavior. The lowest ρ value is about 5 mΩ cm in the region of measured temperature for the Co-349, however, ρ is suppressed lower than 1.0 mΩ cm for the Ni-113.
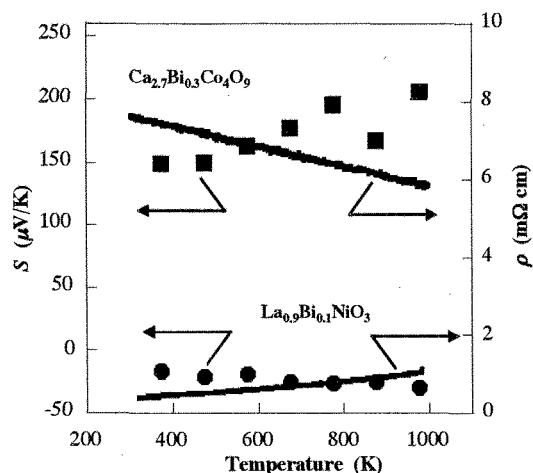
Fig. 11 Thermoelectric properties of p-type Co-349 and n-type Ni-113 legs.

A microscopic photograph for the thermoelectric unicouple is shown in Fig. 12. The V_o values increase with T_H, because S values for both legs increase with increasing temperature and ΔT also with increasing T_H (Fig. 13). The evaluated values of V_o, which is calculated using the integral calculus of sum of S values for both legs against temperature difference, almost agree with the measured V_o. The V_o value reaches 105 mV at 1123 K of T_H and 500 K of ΔT. Temperature dependence of R_I for the thermoelectric unicouple is also shown in Fig. 13. The R_I value increases with temperature and is 18 mΩ at 1118 K.
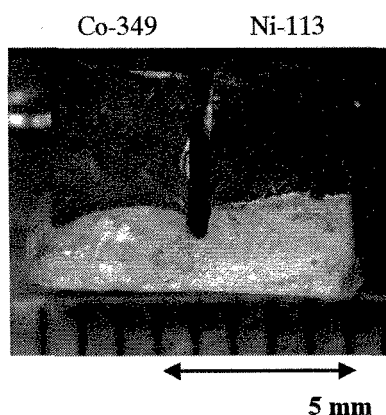

5 mm

Fig. 12 Microscopic image of a thermoelectric unicouple.

Maximum power P_{max} was calculated using a formula of $V_o^2/4R_I$. P_{max} increases with temperature and reaches 152 mW at 1118 K of T_H and 500 K of ΔT (Fig. 14). One of strong points of this unicouple is high power density. Namely, large electrical power can be generated from a small and light thermoelectric module. In the oxide thermoelectric unicouple, the volume power density and the weight power density, specific power, are 1.07 W/cm^3 is 0.23 W/g at 1118 K of T_H, respectively (Fig. 14). These densities are higher than those for some fuel cells or Li ion batteries. However,

the conversion efficiency, which has never been evaluated yet, may be lower than 5 %. In order to improve the efficiency or power density, new n-type oxide materials must be discovered. The high power density indicates that the power application of the oxide thermoelectric materials can be expected to spread to power sources for mobile or ubiquitous items such as cellular phones or potable personal computers, and automobiles.
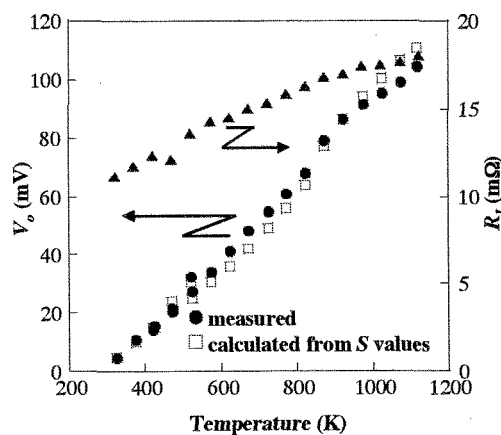

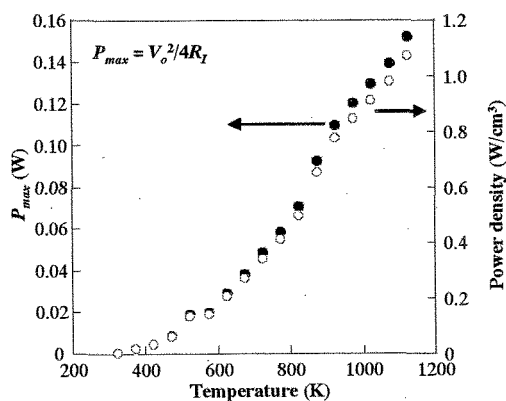**Fig. 13** Temperature dependence of V_o and R_I.

Fig. 14 Temperature dependence of P_{max} (●) and power density (○).

4. CONCLUSION

In order to discover a good n-type oxide, high throughput screening was developed. In the $La_{1-x}M_xNiO_3$ libraries, K-, Na-, and Bi-substitution for La is effective to enhance S. However, ρ is reduced only by Bi-substitution. The hot pressed $La_{0.9}Bi_{0.1}NiO_3$ bulk sample shows lower ρ than 1.0 mΩ cm and S from −20 to −35 μV/K at 373-973 K. PF of this oxide is over 1.0×10^{-4} W/K^{2}m at 773 K in air.

The thermoelectric unicouples composed of the p-type Co-349 and n-type Ni-113 bulk materials have been constructed. The V_o reaches 105 mV and R_I is as low as 18 mΩ at 1118 K of T_H. The unicouple can generate up to 152 mW, and this value correspond to volume and

weight power density of 1.07 W/cm^3 and 0.23 W/g, respectively. Power generation modules composed of the oxide thermoelectric unicouples with the high power density may produce a reformation of small power sources for mobile items or automobiles. Moreover, recovery of electrical energy from waste heat will be realized at factories, incinerators, *etc*.

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