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Design of Seebeck Coefficient Measurement Probe for Powder Library

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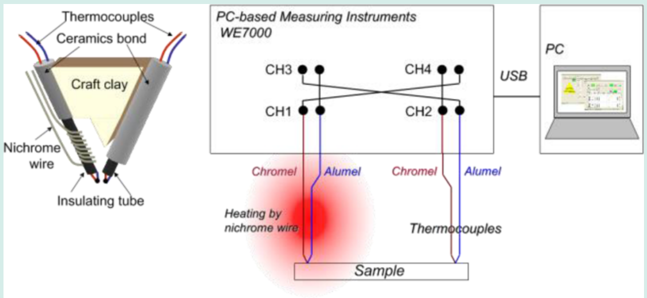
ABSTRACT: A thermoelectric evaluation system, attachable to our developed materials exploration system "M-ist Combi" based on the electrostatic spray deposition method, was designed and established for high-throughput to explore new candidate thermoelectric materials. The developed Seebeck coefficient measurement probe consists of two chromel-alumel thermocouples, and one of thermocouples is able to control its own temperature to ensure a temperature difference between thermocouples. The measurement time for each sample was about 5 s. This provides a stabilized time for the thermoelectric power for each sample. And, it was found that the Seebeck coefficient measurement probe could be used as a high-throughput screening tool for exploring candidate thermoelectric materials.



KEYWORDS: *thermoelectric material, high-throughput evaluation probe, $CaMnO_3$-type compounds, electrostatic spray deposition method, powder library*

1. INTRODUCTION

Thermoelectric materials are well-known for being able to convert exhaust heat into electric energy. Generally, metallic alloys, such as Bi−Sb and Bi_2Te_3, are widely used as thermoelectric materials, and the preparation process of their sintered body has an influence on their physical property.[1] However, the melting point of the metallic alloy is lower than that of oxide. In 1997, it was found that $NaCoO_2$ had properties that made it available as an oxide thermoelectric material. Terasaki et al. reported that the Seebeck coefficient of $NaCoO_2$ showed about 100 μV/K at 300 K as p-type oxide.[2] In addition, p-type $Ca_3Co_4O_9$,[3,4] n-type $Zn_{1-x}Al_xO$[5] and n-type $CaMnO_3$[6] have recently been reported as newly promising thermoelectric materials. As above-mentioned, new oxides are being explored for use as thermoelectric materials. The thermoelectric conversion efficiency of these oxides is lower than their metallic alloys. Therefore, we would like to find new materials with a higher ZT (dimensionless figure of merit) value than the published materials.

The following two equations are examples of indexes for evaluation of the thermoelectric materials:

$$ZT = \frac{S^2\sigma}{\kappa}T \quad (1)$$

$$\text{PF (power factor)} = S^2\sigma \quad (2)$$

S, σ, and κ mean the Seebeck coefficient, the electrical conductivity, and the thermal conductivity, respectively. All equations include the Seebeck coefficient and the electrical conductivity. It is difficult to find candidate thermoelectric materials because thermoelectric property is interrelated with the Seebeck coefficient, thermal conductivity, and electrical conductivity. In particular, it is desired the Seebeck coefficient has a higher value because its value in all equations has to be raised to the second power. Therefore, measurement of the Seebeck coefficient is used as the screening method for candidate thermoelectric materials. Recently, some types of high-throughput screening tools for Seebeck coefficient measurement have been developed to accelerate the measurement speed for

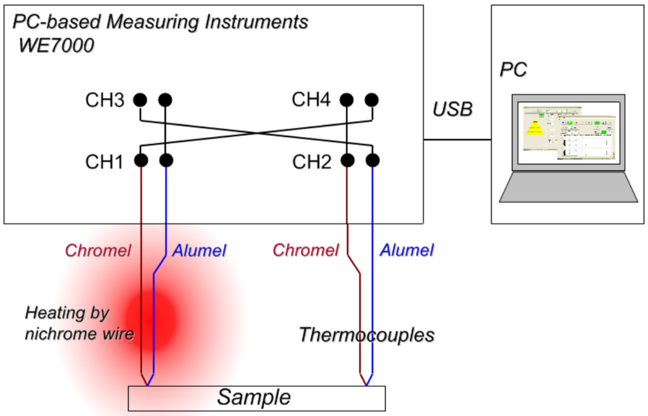


Figure 1. Schematic image of measurement concept for Seebeck coefficient.

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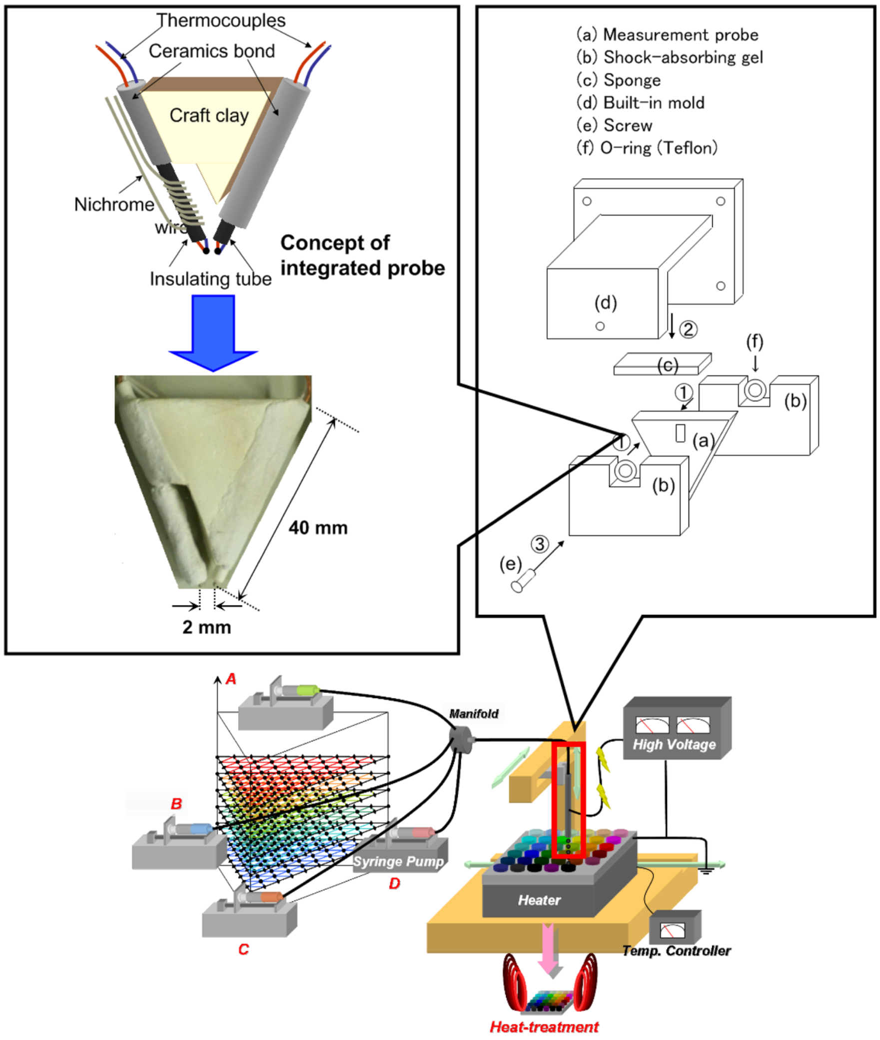

Figure 2. Schematic and actual images of measurement two-point probe and its mounting fixture image.

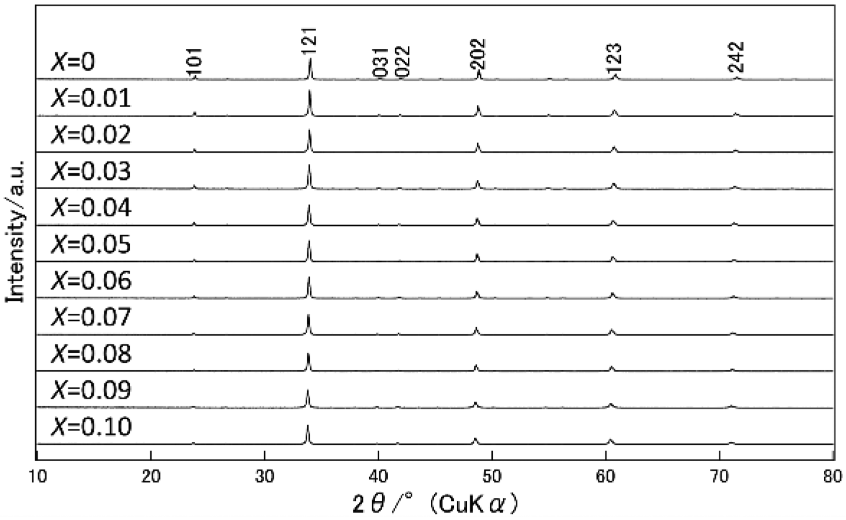

Figure 3. X-ray diffraction patterns of the $Ca_{1-x}La_xMnO_{3-\delta}$ powder obtained by the electrostatic spray deposition method $0 \leq x \leq 0.1$.

many materials. Funahashi et al. developed a high-throughput tester for thick-films.[7] Ohtani et al. developed a four point probe to measure the electrical conductivity and the Seebeck coefficient for thin-film samples.[8] And, Watanabe et al. constructed and developed a high-throughput evaluating method for a thin-film library deposited on a Al_2O_3 substrate that had been embedded with lead wires and local heaters.[9]

Our group has hitherto developed the high-throughput materials exploration system "M-ist Combi" based on the electrostatic spray deposition method.[10] We can obtain liquid, powder, thick-film and thin-film libraries using this M-ist Combi system. The M-ist Combi system is a exchangable triaxial robot hand. Therefore, we can not only prepare a materials library but also evaluate various physical properties in a short time using only this system.[11]

In this study, to evaluate thermoelectric properties in a short time for an uneven powder or film library obtained by our M-ist Combi system, we fabricated a high-throughput evaluation probe, which could be attached to the triaxial robot hand in the M-ist Combi system, and evaluated by n-type oxides.

2. EXPERIMENTAL PROCEDURES

2.1. Fabrication of Seebeck Coefficient Measurement Probe. Figure 1 shows a schematic image of the two-point probe for measurement of the Seebeck coefficient based on the Seebeck tester developed by Funahashi et al.[7] The two-point probe consists of two K-type thermocouples. One thermocouple is covered by a heating element (nichrome wire) and its temperature controlled. These two thermocouples were connected to WE7000 PC-based measurement instrument (Yokogawa Electric Corporation). Each thermocouples were connected to channel CH1 and CH2 in WE7000, respectively. The channel CH1 and CH2 was set to measure temperature of thermocouples. And, the temperature difference was calculated by subtraction from the value of CH1 to that of CH2. Then, two alumel wires and two chromel wires were connected to CH3 and CH4, respectively. Through these interconnections, CH3 and CH4 can measure the thermoelectric power of the alumel- and chromel-wires. From these interconections, Seebeck coefficient can calculate by using the following equation.

$$S[\mu\mathrm{V/K}] = \frac{V_{\mathrm{CH3}}[\mu\mathrm{V}]}{T_{\mathrm{CH1}}[\mathrm{K}] - T_{\mathrm{CH2}}[\mathrm{K}]} + \{-0.0159[\mu\mathrm{V/K^2}] \times (T_{\mathrm{CH1}}[\mathrm{K}] - T_{\mathrm{CH2}}[\mathrm{K}]) - 5.9785[\mu\mathrm{V/K}]\} \quad (3)$$

In the equation, the value of $-0.0159[\mu\mathrm{V/K^2}] \times (T_{\mathrm{CH1}}[\mathrm{K}] - T_{\mathrm{CH2}}[\mathrm{K}]) - 5.9785[\mu\mathrm{V/K}]$ shows the Seebeck coefficient of alumel-wire.

In addition, the division of the difference of channel CH3 and CH4 and the temperature difference of thermocouples was calculated to check whether the two-point probe contact to sample. We can obtain the Seebeck coefficient of the K-type thermocouple (~41 μV/K) if the two-point probe contact to sample. In this study, we consistently checked whether the Seebeck coefficient of the K-type thermocouple was ~41 μV/K when we used the two-point probe.

2.2. Manufacturing the Mounting Fixture of the Seebeck Coefficient Measurement Probe. To attach the Seebeck coefficient measurement probe to the triaxial robot hand of the M-ist Combi system, the mounting fixture was designed and manufactured as shown in Figure 2. The two-point probe manufactured using art clay and insulating tubes was fixed with stainless steel, gel and sponges for shock absorbers. By using the mounting fixture, the Seebeck coefficient could measure stably not only flat film and pelletized powder but also uneven powder aggregates.

Incidentally, all of the operations of the M-ist Combi system can be controlled using software based on the Visual Basic program. In relation to the measurement program of the Seebeck coefficient, the control window made it possible to show the heated thermocouple temperature (CH1), room temperature (CH2), thermoelectric power value (CH3 and CH4) and Seebeck coefficient based on the eq 3.

Table 1. Lattice Constants of $Ca_{1-x}La_xMnO_{3-\delta}$

x	0	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10
nominal comp.	$CaMnO_3$	$Ca_{0.99}La_{0.01}MnO_{3\text{-}\delta}$	$Ca_{0.98}La_{0.02}MnO_{3\text{-}\delta}$	$Ca_{0.97}La_{0.03}MnO_{3\text{-}\delta}$	$Ca_{0.96}La_{0.04}MnO_{3\text{-}\delta}$	$Ca_{0.95}La_{0.05}MnO_{3\text{-}\delta}$	$Ca_{0.94}La_{0.06}MnO_{3\text{-}\delta}$	$Ca_{0.93}La_{0.07}MnO_{3\text{-}\delta}$	$Ca_{0.92}La_{0.08}MnO_{3\text{-}\delta}$	$Ca_{0.91}La_{0.09}MnO_{3\text{-}\delta}$	$Ca_{0.9}La_{0.1}Mn_{0.1}O_{3\text{-}\delta}$
a (nm)	0.5271(4)	0.5380(3)	0.5281(4)	0.5284(5)	0.5288(3)	0.5286(3)	0.5287(6)	0.5294(4)	0.5294(4)	0.5297(3)	0.5301(2)
b (nm)	0.7455(3)	0.7460(2)	0.7463(3)	0.7469(4)	0.7474(2)	0.7474(2)	0.7474(2)	0.7479(3)	0.7490(3)	0.7495(2)	0.7498(2)
c (nm)	0.5268(2)	0.5271(1)	0.5277(2)	0.5280(2)	0.5283(1)	0.5285(1)	0.5285(1)	0.5294(2)	0.5296(2)	0.5303(1)	0.5304(1)
cryst. syst.	ortho.	ortho	ortho	ortho	ortho	ortho	ortho	ortho	ortho	ortho	ortho
space group	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*

2.3. Experimental Section. To prove the effectiveness of the Seebeck coefficient measurement,an n-type (Ca,La)MnO_3 film library were prepared using the M-ist Combi system. Starting materials used were $Ca(NO_3)_2 \cdot 4H_2O$ (99.9%, Wako Pure Chemical Industries), $Mn(NO_3)_2 \cdot 6H_2O$ (99.99%, Wako Pure Chemical Industries), and $La(NO_3)_3 \cdot 6H_2O$ (99.999%, Aldrich). Each nitrate was adjusted to 0.1 mol/L by the mixture of ethanol (C_2H_5OH, 99.5%, Kanto Chemical) and 2-(2-*n*-butoxyethoxy)-ethanol ($C_4H_9(OCH_2CH_2)_2OH$, 98.0%, Kanto Chemical). The mixture ratio of ethanol and buthyl carbitor is 1:4. These solutions were set to the M-ist Combi system, and each mixed solution under applied high voltage was sprayed from a stainless steel nozzle to the grounded and heated (400 °C) YSZ substrate under 8 kV applied voltage. The composition ratio of Ca and La components in (Ca,La)MnO_3 were controlled using the control software in the M-ist Combi. Powders deposited on the YSZ substrate were heat-treated at 950 °C for 6 h. Heat-treated powder library was evaluated using powder X-ray diffraction apparatus (X'pert Pro, Panalytical) with Cu−Kα radiation. Then, these powder sintered at 1300 °C for 12 h after uniaxial pressing.

Prepared sintered bodies, which were about 1 mm in thickness, were arrayed on the measurement stage of the "M-ist combi" system and measured Seebeck coefficient by chenging the robot hand from the electrostatic spray nozzle to the two-point probe. Calculated Seebeck coefficient was retrieved when the two-point probe contacted to sample and the thermal equilibrium confirmed from output data.

3. RESULTS AND DISCUSSION

Figure 3 and Table 1 show thin-film X-ray diffraction patterns and the lattice constant of $Ca_{1-x}La_xMnO_{3-\delta}$, and variation of the lattice constant with the value of x gradually increased. The space group of $Ca_{1-x}La_xMnO_{3-\delta}$ shown to *Pnma*.

Figure 4 shows the Seebeck coefficient of $Ca_{1-x}La_xMnO_{3-\delta}$. In the case of n-type $Ca_{1-x}La_xMnO_{3-\delta}$, the Seebeck coefficient decreased with increase in the substitution quantity of the La component. variation of the Seebeck coefficient by La substitution showed the same tendency as the results obtained by Lan et al.[12] However, there was different between the calculated Seebeck coefficient and the previous report. It is thought that the difference is due to the contact resistance between the two-point probe and the sample is larger than the commonly used Seebeck coefficient measurement apparatus. The increase of the contact resistance conduced to lower Seebeck coefficient than the previous report. However, our established evaluation process for thermoelectric materials is unnecessary for manufacturing normalized sample size. In addition, measurement time for each sample was about 5 s. This time means the stabilized time of thermoelectric power for each sample.

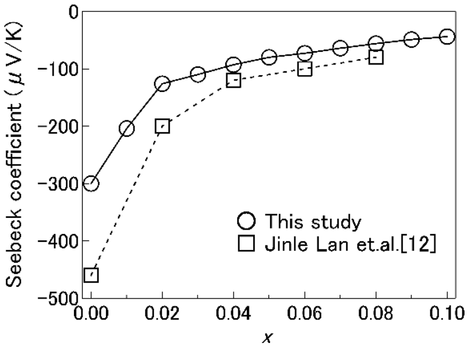

Figure 4. Seebeck coefficient of $Ca_{1-x}La_xMnO_{3-\delta}$ measured using the developed system.

From these results, it is clear the Seebeck coefficient measurement probe can be used as a high-throughput screening tool for exploring candidate thermoelectric materials.

4. CONCLUSION

A Seebeck coefficient measurement probe and system were designed and established in order to achieve a high-throughput evaluation of thermoelectric properties. The probe has two chromel-alumel thermocouples, and one of thermocouples can control its own temperature to ensure a temperature difference between the thermocouples. The probe was made in order to evenly contact any heterogeneous surface, because the materials library obtained by the M-ist Combi system forms a powder and uneven film. n-type La-doped $Ca_{1-x}La_xMnO_{3-\delta}$ obtained using the ESD method were evaluated by the new probe as a verification test. There was different between the calculated Seebeck coefficient and the previously reported data because the contact resistance between the two-point probe and the sample is larger than the commonly used Seebeck coefficient measurement apparatus. However, variation of the Seebeck coefficient by La substitution showed the same tendency as the results obtained by Lan et al.[12] Furthermore, the measurement time for each sample was about 5 s. Therefore, the Seebeck coefficient measurement probe and system are promising as a high-throughput screening tool for exploring thermoelectric materials.

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Notes

The authors declare no competing financial interest.

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