Thermoelectric properties of bismuth-substituted calcium manganite $Ca_{1-x}Bi_xMnO_{3-\delta}$ prepared via the electrostatic spray deposition method

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The thermoelectric properties of $Ca_{1-x}Bi_xMnO_{3-\delta}$ sintered bodies prepared by the electrostatic spray deposition method and sintering technology were evaluated. $Ca_{0.95}Bi_{0.05}MnO_{3-\delta}$ showed the maximum power factor value of 230 μ W·m^{-1·K-2} among $Ca_{1-x}Bi_xMnO_{3-\delta}$ compounds at room temperature. From Seebeck coefficient, Hall coefficient and power generation efficiency measurements on CaMnO_{3-\delta} and Ca_{0.95}Bi_{0.05}MnO_{3-\delta} under high temperature, it was found that the power factor value of $Ca_{0.95}Bi_{0.05}MnO_{3-\delta}$ increased with temperature in the range of 300–873 K, and was 2 to 5 times higher than that of CaMnO_{3-\delta}. The carrier concentration ($n = 5.9 \times 10^{20}$ cm⁻³) of Ca_{0.95}Bi_{0.05}MnO_{3-\delta} is two orders of magnitude higher than CaMnO_{3-\delta} ($n = 7.1 \times 10^{18}$ cm⁻³) at 300 K. The increase in carrier concentration contributed to higher conductivity, power factor and power generation density in the Bi-substituted compound. In thermoelectric performance evaluations, the power density reached 625 mW·cm⁻² for Ca_{0.95}Bi_{0.05}MnO_{3-\delta} with a temperature difference of 444 K, an 11-fold increase compared to the parent compound CaMnO_{3-\delta} (57 mW·cm⁻²).

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1. Introduction

Materials for high temperature (T) thermoelectric generation need high thermoelectric performance index and stable characteristics. Thermoelectric conversion materials are reported among non-oxide and oxide materials. Examples of the former are Bi_2Te_3 ⁽¹⁾ PbTe,⁽²⁾ and Si-Ge,⁽³⁾ and the temperature where their ZT (dimensionless figure of merit, $Z(K^{-1})$ is figure of merit) is about 1 is room temperature, 573 to 773 K and 1173 K, respectively. However, non-oxide materials often are unsuitable for high-T operation since they contain heavy elements and suffer from low melting point, toxicity, oxidation and decomposition under high temperature. Oxide materials are superior to non-oxide materials in oxidative resistance, heat resistance, and chemical stability under high temperature conditions. However, oxide materials were considered to have extremely low thermoelectric performance because localized valence electrons and small overlap of atomic orbitals leads to poor electrical conduction.

In 1997, Funahashi et al.⁴⁾ reported that the ZT of layered cobalt oxide ($[Ca_2CoO_3] \times CoO_2$), a p-type oxide material, reached 1. Now, oxides are recognized as a category of thermoelectric conversion materials. On the other hand, oxide powders with ZT exceeding 1 in n-type oxides have not yet been discovered.

It is well known that thermoelectric effects are observed in perovskite-type CaMnO_{3- δ}. However, the thermoelectric figure of merit of the parent compound is relatively low (*ZT* = 0.01, Power factor (*PF*= σ *S*²) = 5 × 10⁻⁷ W·m⁻¹·K⁻²).⁵) Ohtaki et al. reported that Bi-substitution in (Ca_{0.9}Bi_{0.1})MnO_{3- δ} elevated the power factor to more than 2.8 × 10⁻⁴ W·m⁻¹·K⁻² at 1073 K.⁶) Huang et al. also reported that both substituting Bi and V for Casite and Mn-site increased *ZT* value to 0.1.⁷) Kabir et al. reported that (Ca_{0.97}Bi_{0.03})MnO₃ had a higher power factor (*PF* = 4.67 × 10⁻⁴ W·m⁻¹·K⁻²) at 423 K compared to CaMnO₃ (1.1 × 10⁻⁴ W·m⁻¹·K⁻²).⁸)

We have hitherto studied the electrostatic spray deposition (ESD) method for the fabrication of perovskite-type manganite, and demonstrated CaMnO_{3- δ} thin films were obtained using the ESD method at 1223 K for 1 h. In search for candidate thermoelectric materials among CaMnO_{3- δ} type compounds, a combinatorial A_xCa_{1-x}B_yMn_{1-y}O_{3- δ} (A; La, Bi, Y, Sr) (B; Ni, Ti, V) thin-film library was prepared by the conventional ESD method. In the screening performed, co-doped Bi_{0.02}Ca_{0.98}Mn_{0.98}V_{0.02}O_{3- δ} and Bi_{0.02}Ca_{0.98}Mn_{0.98}Ni_{0.02}O_{3- δ} exhibited somewhat higher conductivity and power factor values than the other materials.⁹

In a follow-up study, we used our M-ist Combi system¹⁰) based on the ESD method to find optimum conditions for obtaining Ca_{1-x}Bi_xMn_{1-y}Ni_yO_{3- δ} (0 \leq x, y \leq 0.1) and then evaluated the thermoelectric properties using our Seebeck-coefficientevaluation probe¹¹) to refine the candidate materials. We also evaluated the σ value used to calculate the *PF* value of the refined candidate materials. However, measurement of the σ value were

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difficult because the powder library obtained by the M-ist combi did not consist of dense sintered bodies. In order to measure electrical conductivity as next step, the powder library was subjected to high-pressure $(200 \text{ MPa})^{12}$ and heat-treated at 1123 K for 1 h in an oxygen atmosphere. The electrical conductivity data indicated that 5%-Bi-substituted CaMnO_{3- δ} has a higher conductivity (63 S·cm⁻¹) than the unsubstituted powder $(13 \text{ S} \cdot \text{cm}^{-1})$. In this study, we prepared Ca_{1-x}Bi_xMnO_{3- δ} (x = 0, 0.01, 0.02, 0.03, 0.04, 0.05 and 0.1) powders using the conventional ESD method. The single-phase perovskite-type Ca_{1-x}-Bi_xMnO_{3- δ} powders were uniaxial pressed and heat-treated, and their thermoelectric properties were studied in sintered bodies.

The ESD method used in this study is a solution-based process. A solution of the starting material in a volatile solvent in a syringe pump is extruded by applying a high voltage to the tip of the stainless steel syringe nozzle. The liquid is positively charge. The electrostatic repulsion breaks the liquid into fine droplets. These are deposited on a heated substrate which is grounded.¹³⁾ The benefit of the EDS method is that it is expected that the function can be improved by enlarging the solid solution region and compositional uniformity.

Experimental

 $Ca_{1-x}Bi_xMnO_{3-\delta}$ powders (x = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1) were prepared by the ESD method. The starting materials were Ca(NO₃)₂·4H₂O (99.9%, Wako Pure Chemical Industries, Ltd.), Mn(NO₃)₂·6H₂O (99.9%, High purity Chemical Lab.), Bi(NO₃)₃·5H₂O (99.999%, Sigma-Aldrich Co.). Solutions at $20 \text{ mmol} \cdot \text{dm}^{-3}$ molarity were prepared by dissolving the nitrates in a mixture of ethanol C₂H₅OH (20 vol.%) and 2-butoxyethanol CH₃(CH₂)₃(OCH₂CH₂)OH (80 vol.%). In the case of Bi(NO₃). 5H₂O, the starting material was first dissolved in dilute nitric acid, as it could not be dissolved by the organic solvents alone. A stoichiometric mixture of the solutions was delivered by a syringe pump to a stainless steel nozzle, and electro-sprayed onto an YSZ reaction plate $(35 \times 35 \times 5 \text{ mm}^{t})$ grounded and heated at 673 K. A voltage of 8 kV was applied to the nozzle by a highvoltage power supply. The solution was pumped at a rate of 8.0 $mL{\cdot}h^{-1}$ for 6.3 h. The obtained powder was heat-treated at 1123 K for 1 h in pure oxygen at atmospheric pressure. The heattreated powder was evaluated by powder X-ray diffractometer (Rigaku Miniflex600, CuK α radiation, 40 kV-15 mA) for phaseidentification and calculation of lattice parameters. Lattice parameters calculation used the Appleman-Evans program.¹⁴⁾

Then, each powder was grounded and uniaxial pressed by applying 70 MPa for 5 min. Pelletized powder (size = 13 mm°) was sintered at 1573 K for 12 h in air at atmospheric pressure.

In thermoelectric property under room temperature, the Seebeck coefficient (S) was evaluated by our developed high-throughput Seebeck measurement probe¹¹⁾ under a temperature difference of 20 K, and the electrical conductivity (σ) was calculated from the resistivity using the four-point probe method (Mitsubishi Chemical Anatlytech, LORESTA-GP) and the size of sintered body.

And, high-temperature thermoelectric properties were measured from room temperature to 873 K using an ADVANCE-RIKO ZEM-2 apparatus. Power generation efficiency was determined using a thermoelectric performance evaluation system (UMTE-1000M, Union Materials Co.). In this evaluation, the temperature of the cold and hot areas were set to 373 and 473– 873 K, respectively. For these thermoelectric property measurements, dense sintered pellets were cut and sanded by sandpaper #800, 2000 and 10000 to final dimensions of $2 \times 2 \times 10$ mm. The temperature difference was set to 40 K.

Hall effect measurements were performed with a ResiTest 8300 instrument (TOYO Corporation) on dense sintered pellets formed to be $10 \text{ mm}^{\varphi} \times 300 \,\mu\text{m}^t$ and polished with sandpaper #800, 2000 and 10000.

Results and discussions

Figure 1 shows powder X-ray diffraction patterns of Ca_{1-x} - $Bi_xMnO_{3-\delta}$ (x = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1). All composition are identified as single phase perovskite-type structures. **Table 1** shows the lattice parameter. The unit cell volume increases with increasing the amount of Bi substitution. **Table 2** summarizes the thermoelectric properties of $Ca_{1-x}Bi_xMnO_{3-\delta}$ (x = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1). The value of absolute Seebeck coefficient (|S|) decreases with increasing the amount of Bi substitution. On the other hand, the electrical conductivity (σ) increases with increasing the amount of Bi substitution. We attribute these trends to the carrier concentration increasing with Bi substitution. Since Bi³⁺ (VIII) (ionic radii: 0.112 nm¹⁵)) is substituted to Ca²⁺ (VIII) (ionic radii: 0.117 nm¹⁵) sites, a part of Mn⁴⁺(VI) (ionic radii: 0.053 nm¹⁵) changes to Mn³⁺(VI)



Fig. 1. Powder X-ray diffraction patterns of $Ca_{1-x}Bi_xMnO_{3-\delta}$ (x = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1) heat-treated at 1223 K for 1 h.

Table 1. Lattice parameter of $Ca_{1-x}Bi_xMnO_{3-\delta}$ powder (x = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1)

x	a/nm	b/nm	c/nm	Vol./nm ³
0	0.5283(2)	0.7463(2)	0.5279(2)	0.20817(8)
0.01	0.5285(2)	0.7468(1)	0.5284(2)	0.20860(7)
0.02	0.5290(2)	0.7470(1)	0.5281(2)	0.20873(7)
0.03	0.5295(2)	0.7472(2)	0.5283(2)	0.20903(8)
0.04	0.5298(2)	0.7474(2)	0.5283(2)	0.20922(8)
0.05	0.5299(1)	0.7479(1)	0.5290(1)	0.20969(6)
0.1	0.5310(3)	0.7491(3)	0.5300(3)	0.2109(1)

Table 2. Thermoelectric property under room temperature of Ca_{1-x} -Bi_xMnO_{3- δ} sintered body (*x* = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1)

x	$S/\mu V \cdot K^{-1}$	$\sigma/{ m S}{ m \cdot}{ m cm}^{-1}$	Power Factor/ μ W·m ⁻¹ ·K ⁻² -
0	-315	4	40
0.01	-186	41	140
0.02	-130	107	107
0.03	-114	100	130
0.04	-106	143	160
0.05	-90	278	230
0.1	-70		



Fig. 2. Temperature dependence of Seebeck coefficience (S) in $Ca_{1-x}Bi_xMnO_{3-\delta}$ (x = 0, 0.05) sintered body.

(ionic radii: 0.0645 nm¹⁵) for charge balance. These conductivity values were more than one order of magnitude higher than the electric conductivity of the powder library in combinatorial technology, and they were close to the values reported by Kabir et al. This is probably because a dense sintered body was obtained by sintering at 1573 K for 12 h after performing uniaxial pressure molding. From these data, we can obtain *PF* values. In this study, Ca_{0.95}Bi_{0.05}MnO_{3- δ} showed maximal value $PF_{max(x=0.05, R.T.)} = 230 \,\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ at room temperature which was about five times higher than the value of CaMnO_{3- δ}.

High-temperature thermoelectric properties were measured for CaMnO_{3- δ} and Ca_{0.95}Bi_{0.05}MnO_{3- δ}, as well as power generation efficiency and Hall effect. Figure 2 shows the temperature dependence of the *S* of CaMnO_{3- δ} and Ca_{0.95}Bi_{0.05}MnO_{3- δ} from room temperature to 873 K. The |*S*| of CaMnO_{3- δ} decreases with increasing temperature. In this poor conductor, the carrier concentration increases with thermal excitation of electrons. On the other hand, the |*S*| of Ca_{0.95}Bi_{0.05}MnO_{3- δ} increases with increasing temperature. Hébert et al. reported the following Mott's formula with $\sigma(E) = n(E)\mu(E)$ in perovskite type compounds expected for metal.¹⁶

$$S = \frac{\pi^2 k_{\rm B}^2 T}{3e} \left[\frac{\delta \ln \sigma(E)}{\delta E} \right]_{E=E_{\rm F}}$$
(1)

n is carrier density, μ is mobility, $k_{\rm B}$ is Boltzmann constant (8.6173 × 10⁻⁵ eV·K⁻¹), and $E_{\rm F}$ is Fermi energy. It is considered that Bi-substitution contributed increasing the carrier concentration, and Ca_{0.95}Bi_{0.05}MnO_{3- δ} shows metallic state. As a result, it seems that $S \propto T$ holds as in this formula.

Figures 3 and **4** show the temperature dependence of the σ , $\ln(\sigma T)$ of CaMnO_{3- δ} and Ca_{0.95}Bi_{0.05}MnO_{3- δ} from room temperature to 873 K. The electrical conductivity of CaMnO_{3- δ} increases with increasing temperature, while that of Ca_{0.95}-Bi_{0.05}MnO_{3- δ} decreases with increasing temperature. The dependence of the electrical conductivity and temperature is expressed by Eq. (2) by Mott and Davis et al.

$$\sigma = \left(\frac{C}{T}\right) \exp\left(\frac{-E_{\rm a}}{k_{\rm B}T}\right) \tag{2}$$

C is the scattering mechanism, E_a is the activation energy for hopping, k_B is the Boltzmann constant, and *T* is the absolute temperature. This equation is transformed as shown in Eq. (3), and E_a is calculated from the inclination of ln (σT) vs. T^{-1} in Fig. 4.



Fig. 3. Temperature dependence of electrical conductivity (σ) in Ca_{1-x}Bi_xMnO_{3- δ} (x = 0, 0.05) sintered body.



Fig. 4. log σT vs. 1000/T plots of $Ca_{1-x}Bi_xMnO_{3-\delta}$ (x = 0, 0.05) sintered body.

$$\ln(\sigma T) = \frac{-E_{\rm a}}{k_{\rm B}T} + \ln C \tag{3}$$

Using the high temperature range in Fig. 4, E_a of CaMnO_{3- δ} and Ca_{0.95}Bi_{0.05}MnO_{3- δ} were found to be 0.21 and 0.05 eV, respectively. The E_a of CaMnO_{3- δ} reported by Ohtaki et al.⁶⁾ is 0.16 eV, which is a close value. Bi-substitution is thought to form impurity levels near the conduction band edge.

Figure 5 shows the temperature dependence of the *PF* of CaMnO_{3- δ} and Ca_{0.95}Bi_{0.05}MnO_{3- δ} from room temperature to 873 K. The *PF* values of CaMnO_{3- δ} and Ca_{0.95}Bi_{0.05}MnO_{3- δ} increase with temperature. Ca_{0.95}Bi_{0.05}MnO_{3- δ} showed the highest *PF* value *PF*_{max(x=0.05, 823 K)} = 340 µW·m⁻¹·K⁻² at 823 K, an enhancement of 2 to 5 times from the *PF* of the unsubstituted CaMnO_{3- δ} in the medium to high temperature range (~873 K). This value compares to 400 µW·m⁻¹·K⁻² of Ca_{0.97}Bi_{0.03}MnO_{3- δ} at 873 K reported by Kabir et al.⁸)

In measurement of Hall coefficient by van der Pauw method, carrier concentration (*n*) and mobility (μ) of CaMnO_{3- δ} and Ca_{0.95}Bi_{0.05}MnO_{3- δ} were determined to be $n = 7.12 \times 10^{18}$ cm⁻³, $\mu = 2.05$ cm²·V·s⁻¹ and $n = 5.90 \times 10^{20}$ cm⁻³, $\mu = 3.19$ cm²·V·s⁻¹, respectively. No significant change was observed in μ , whereas *n* showed two orders of magnitude increase upon Bi substitution. This increase in electrical conductivity due to Bi substitution.



Fig. 5. Temperature dependence of Power Factor (*PF*) in Ca_{1-x} -Bi_xMnO_{3- δ} (x = 0, 0.05) sintered body.

Figure 6 show the power generation capacity of $CaMnO_{3-\delta}$ [Fig. 6(a)] and $Ca_{0.95}Bi_{0.05}MnO_{3-\delta}$ [Fig. 6(b)]. *V* is a voltage, *I* is a current, *W* is the power output obtained from the product of *V* and *I*. From Fig. 6(a), the maximum output W_{max} of $CaMnO_{3-\delta}$ was 2.367 mW and the maximum power density was 57.4 mW·cm⁻². The maximum power W_{max} of $Ca_{0.95}Bi_{0.05}MnO_{3-\delta}$ was 25 mW and the maximum power density was 625 mW·cm⁻², which represent an 11-fold enhancement compared to CaMnO_{3-\delta}. Evidently, there is a dramatic improvement due to the increase in the current value by Bi 5% substitution.

Based on the above results, **Fig.** 7 shows a relationship of the maximum temperature difference output density $(mW \cdot cm^{-2})$ with respect to ΔT (°C). The output density increased as the temperature difference increased, and $Ca_{0.95}Bi_{0.05}MnO_{3-\delta}$ at a temperature difference of 444 K showed more than 10 times larger power density compared with CaMnO_{3-\delta}. Unfortunately, the result are modest (e.g. the power density of n-type Mg₂Si reported by Sakamoto et al.¹⁷) in the same temperature range is 1.43 W·cm⁻²). However, the CaMnO_{3-\delta} type compounds have a stable structure at high temperature range, so it might be possible to achieve better values using a larger temperature difference.

Furthermore, we evaluated the thermoelectric properties of $Ca_{0.95}Bi_{0.05}MnO_{3-\delta}$ sintered bodies with controlled thickness and diameter using a second instrument.¹⁸⁾ In these measurements, PF_{max} of up to $800 \,\mu W \cdot m^{-1} \cdot K^{-2}$ were obtained surpassing the values reported by Kabir et al.⁸⁾

4. Conclusion

The thermoelectric properties of the $Ca_{1-r}Bi_rMnO_{3-\delta}$ sintered bodies prepared by the electrostatic spray deposition method and sintering technology were evaluated using Seebeck coefficient, electrical conductivity, Hall effect and power generation efficiency measurements. 5% Bi-substituted Ca_{0.95}Bi_{0.05}MnO_{3-δ} showed the most promise in the composition range x = 0-0.1, with power factor ranging from 230 to $340 \mu W \cdot m^{-1} \cdot K^{-2}$, and potentially even higher, at the temperature range 300-873 K. Hall effect measurements suggest that the carrier concentration $(n = 5.9 \times 10^{20} \text{ cm}^{-3})$ of Ca_{0.95}Bi_{0.05}MnO_{3- δ} is two orders of magnitude higher than CaMnO_{3- δ} ($n = 7.1 \times 10^{18} \,\mathrm{cm}^{-3}$) and leads to the considerable improvement in thermoelectric performance. The high stability of the compounds at elevated temperatures, combined with the ease of fabrication and the significant tunability of the carrier concentration, make this materials system an excellent target for further research and development.



Fig. 6. Power generation capacity of $CaMnO_{3-\delta}$ and $Ca_{0.95}Bi_{0.05}$ -MnO_{3- δ} sintered bodies (a) $CaMnO_{3-\delta}$, (b) $Ca_{0.95}Bi_{0.05}MnO_{3-\delta}$.



Fig. 7. Correlation of the maximum temperature difference output density (mW·cm⁻²) vs. ΔT (K) of CaMnO_{3- δ} and Ca_{0.95}Bi_{0.05}MnO_{3- δ} sintered bodies.

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