Preparation and Characterization of $\text{Ca}_3(\text{Co},\text{M})_4\text{O}_{9+\delta}$ Type Thermoelectric Materials Using the Electrostatic Spray Deposition Method^{*1}

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$\text{Ca}_3(\text{Co}_{1-x}\text{Al}_x)_4\text{O}_{9+\delta}$, $\text{Ca}_3(\text{Co}_{1-y}\text{Cu}_y)_4\text{O}_{9+\delta}$, $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ thin-films and sintered bodies were prepared by electrostatic spray deposition, a solution-based process. The solid-solution region of $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ was narrower than the presumed region based on the results for single-element-substituted $\text{Ca}_3(\text{Co}_{1-x}\text{Al}_x)_4\text{O}_{9+\delta}$ and $\text{Ca}_3(\text{Co}_{1-y}\text{Cu}_y)_4\text{O}_{9+\delta}$. The electrical conductivity of $\text{Ca}_3(\text{Co}_{0.95}\text{Al}_{0.025}\text{Cu}_{0.025})_4\text{O}_9$ were larger than that of the non-substituted- $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$. The power factor of $\text{Ca}_3(\text{Co}_{0.95}\text{Al}_{0.025}\text{Cu}_{0.025})_4\text{O}_9$ was approximately the same as that of single phase compounds of $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$. This phenomenon was presumed to have resulted from the increased hole concentration and mobility of the material. Our evaluations of the thermoelectric performance showed similar trends for the thin-film and the sintered body. However, we observed uneven thickness and porosity in the prepared thin films. These flaws will have to be resolved through adjustments in the process used to prepare the thin films. [doi:10.2320/matertrans.Y-M2016823]

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1. Introduction

Thermoelectric materials that convert heat directly into electricity have attracted a great deal of attention as materials that can make effective use of the waste heat from factories, automobiles, and so on. Thermoelectric materials can be divided into two types: non-oxide and oxide materials. Bi_2Te_3 ¹⁾ and PbTe ²⁾ are well-known examples of the former. While non-oxide materials have a dimensionless performance index (ZT) of 1 or greater, they also have disadvantages such as the inclusion of heavy elements, low melting points, toxicity, oxidation and decomposition at high temperatures, and element scarcity. Oxide materials, meanwhile, have excellent heat resistance, oxidation resistance, and chemical stability under high-temperature conditions. Favored by these properties, they are seen as promising new candidates as thermoelectric materials. Among these oxide materials, $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ ³⁾, a p-type semiconductor, has been reported to have high thermoelectric performance. The independent control of the electron and phonon in different locations within the crystals is thought to confer this advantage. $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ forms composite crystals with a periodic array consisting of two layers: a CdI_2 type CoO_2 layer with high electrical conductivity and a large Seebeck coefficient, and a block layer with a rock salt-type structure (Ca_2CoO_3) with low thermal conductivity. The lattice constants of the CoO_2 layer, excluding the b-axis, are $a = 0.483$ nm, $c = 1.084$ nm, and $\beta = 98.1^\circ$. Because of a lattice misfit in the b axis direction, b_1 is approximately equal to 0.282 nm for the structure of the CoO_2 layer and b_2 is approximately equal to 0.456 nm for the structure of the Ca_2CoO_3 block layer. As the b-axis length ratio ($p = b_1/b_2$) is an irrational number (0.618...), the crystal structure of this compound

cannot be expressed using a three-dimensional unit cell. For this reason, the crystal structure of this material is noted as a complex crystal with superspace-group symmetry in (3+1) dimensions using a , b_1 , c , b_2 , and β . The b-axis length ratio p , a variable known as the misfit parameter, is sometimes used in the notation for the structural formula, i.e., $[\text{Ca}_2\text{CoO}_3]_p\text{CoO}_2$.

The ZT value of the $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ single-crystal has reported to reach in the range of 1.2–2.7 at 600°C or higher temperatures.⁴⁾ This ZT value qualifies the crystal for practical use as a thermoelectric material, but the plane direction of the crystal strongly affects the material properties. As a consequence, the ZT value reaches only around 0.3 in a polycrystalline body with many crystallites aligned in random patterns.⁵⁾ The performance can be improved, however, by substituting other elements at the Co-sites in $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$.^{6–10)}

In this study we prepared $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ type thin films by electrostatic spray deposition (ESD), a solution-based process, to observe the changes in properties caused by alterations in the crystal structure and microstructure. The ESD method is capable of forming sub-micron-order fine particles of a highly uniform composition and grain size, opening the way to significant improvements in the material properties. In this study, we prepared $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ partly substituting Al and/or Cu for the Co-site in order to increase electrical conductivity. The average valence number of the Co ion in $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ is 3 to 4. We supposed that the substitution of the Co-site with Al^{3+} and Cu^{2+} , these ions not likely to change in valence, would allow us to perform hole doping. We therefore prepared Al- and/or Cu-substituted $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ type thin-films for the Co-site using the ESD method. Note, also, that we made these sintered bodies from fine particle aggregates obtained by the same method to enable comparison with a sintered body obtained using the conventional solid state reaction method. In the ESD method used in this study, the solution used as the starting material is given a positive charge

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to reduce the size of the liquid droplets before the droplets are deposited on a grounded and heated substrate.¹¹⁾ This method has previously been used to synthesize positive electrode materials for lithium-ion secondary batteries¹²⁾ and as a key technology in combinatorial high-speed material exploration.¹³⁾

2. Experimental

2.1 Preparation of $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ thin-film

$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Wako Pure Chemical Industries, Ltd., 99.9%), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Kanto Chemical Co., Inc., 99.95%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aldrich, 99.997%), and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Wako Pure Chemical Industries, Ltd., 99.9%) were dissolved in an organic solvent consisting of a 4:1 ratio of 2-(2-n-butoxyethoxy)ethanol and ethanol to create a 10 mmol·L⁻¹ starting material solution. The starting material solution was then mixed in the stoichiometric proportions and deposited onto a YSZ substrate (1.0 mm^φ × 0.5 mm^l) that had been grounded and heated to 400°C. A 9.0 kV charge was applied to the starting material solution during the electrostatic spray deposition, and the solution was sprayed for 2 hours at a flow rate of 1.0 mL·h⁻¹. The deposited thin-film was heat-treated in atmospheric air at 700°C for 5 hours.

2.2 Preparation of $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ sintered body

A 200 mmol·L⁻¹ starting material solution prepared from the same starting material and organic solvent described in section 2.1 was mixed in the prescribed stoichiometric proportions and deposited onto a YSZ substrate (35 mm × 35 mm × 5 mm^l). An 8.0 kV charge was applied to the starting material solution during the electrostatic spray deposition, and the solution was sprayed for 6 hours at a flow rate of 4.0 mL·h⁻¹. The deposited powder was heat-treated in atmospheric air at 800°C for 4 hours, pelletized under uniaxial pressure, and sintered in atmospheric air at 800–900°C for 12 hours.

2.3 Evaluation of thin-film and sintered body

The thin-film and powder obtained were identified using an X-ray diffraction unit (XRD: PANalytical, X'Pert PRO, CuK α radiation). The chemical composition was calculated by ICP emission spectrophotometry (ICP: Shimadzu, ICPE-9000). The microstructure was observed by field emission scanning electron microscopy (SEM: Hitachi, S-5000)). For the SEM observation, 10 nm of Pt was deposited on each sample in advance using the deposition apparatus. The average film thickness of the thin-film was analyzed by the thin-film FP method for X-ray fluorescence analysis (XRF: SII NanoTechnology Inc., SEA5120A). The electrical conductivity, an index of thermoelectric performance, was calculated with a resistivity meter (Mitsubishi Chemical Analytech Co., Ltd., LORESTA-GP) by the four-point probe method. The Seebeck coefficient was determined with a temperature differential of 20°C using a self-made tester¹⁴⁾. The electrical conductivity and Seebeck coefficient were measured at room temperature.

3. Results and Discussion

3.1 Preparation of $\text{Ca}_3(\text{Co}_{1-x}\text{Al}_x)_4\text{O}_{9+\delta}$ thin-film

Figure 1 shows the thin-film X-ray diffraction pattern of Al-substituted $\text{Ca}_3(\text{Co}_{1-x}\text{Al}_x)_4\text{O}_{9+\delta}$. Within the range of $x = 0 \sim 0.6$, diffraction patterns were indexed as a single phase structure based on $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$. Up to the range of $x = 0.7 \sim 1$, only the diffraction peak of the YSZ substrate was observed. From this result, the Al substituted for the Co-sites had an estimated solid-solution range of $0 \leq x \leq 0.6$. In the case of $x \geq 0.7$, the thin-films obtained appeared to take on an amorphous structure. And as the Al substitution ratio increased, shifts of the diffraction peak to high angles were observed in the $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ at around 8°, 16°, 25°, and 33°. These shifts were thought to result from the smaller ionic radii of Al^{3+} (0.0535 nm¹⁵⁾) relative to that of Co^{3+} (0.0545 nm¹⁵⁾ LS). No CoAl_2O_4 was generated at 700°C¹⁶⁾ in this study.

3.2 Preparation of $\text{Ca}_3(\text{Co}_{1-y}\text{Cu}_y)_4\text{O}_{9+\delta}$ thin-film

Figure 2 shows the thin-film X-ray diffraction pattern of Cu-substituted $\text{Ca}_3(\text{Co}_{1-y}\text{Cu}_y)_4\text{O}_{9+\delta}$. Within the range of $x = 0 \sim 0.3$, a single phase structure based on $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ was obtained. Also, as secondary phase, $\text{Ca}_{0.828}\text{CuO}_2$ was generated up to the range of $x = 0.4 \sim 1$. From this result, the solid-solu-

Fig. 1 X-ray diffraction patterns of $\text{Ca}_3(\text{Co}_{1-x}\text{Al}_x)_4\text{O}_{9+\delta}$ ($0 \leq x \leq 1.0$) thin-films (a) $x = 1.0$, (b) $x = 0.9$, (c) $x = 0.8$, (d) $x = 0.7$, (e) $x = 0.6$, (f) $x = 0.5$, (g) $x = 0.4$, (h) $x = 0.3$, (i) $x = 0.2$, (j) $x = 0.1$, (k) $x = 0$.

Fig. 2 X-ray diffraction patterns of $\text{Ca}_3(\text{Co}_{1-y}\text{Cu}_y)_4\text{O}_{9+\delta}$ ($0 \leq y \leq 1.0$) thin-films (a) $y = 1.0$, (b) $y = 0.9$, (c) $y = 0.8$, (d) $y = 0.7$, (e) $y = 0.6$, (f) $y = 0.5$, (g) $y = 0.4$, (h) $y = 0.3$, (i) $y = 0.2$, (j) $y = 0.1$, (k) $y = 0$.

Fig. 3 Solid-solution regions of $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ thin-films.

Fig. 4 X-ray diffraction patterns of $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ thin-films.

tion region of $\text{Ca}_3(\text{Co}_{1-y}\text{Cu}_y)_4\text{O}_{9+\delta}$ was thought to be $0 \leq x \leq 0.3$. A slight shift of the $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ diffraction peak to a low angle seemed to appear at around 42° as the Cu substitution ratio increased, but an overlapping between the diffraction peaks of the stainless steel sample stage and $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ made this difficult to confirm. The same peak shift has been reported by Y. Huang *et al.*¹⁷⁾

3.3 Preparation of $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ thin-film

From sections 3.1 and 3.2, the solid-solution regions were confirmed to be $0 \leq x \leq 0.6$ for $\text{Ca}_3(\text{Co}_{1-x}\text{Al}_x)_4\text{O}_{9+\delta}$ and $0 \leq x \leq 0.3$ for $\text{Ca}_3(\text{Co}_{1-x}\text{Cu}_x)_4\text{O}_{9+\delta}$. Based on these results, we presumed that a tie-line of the type shown in Fig. 3 could be drawn in the composition of the solid-solution limit conditions of Al and Cu at the Co-sites in $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$, and that a single phase structure based on $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ could be obtained within this range. With this in mind, we prepared a multi-element-substituted $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ thin-film in a slightly broader range than the shaded range. Figure 4 shows the X-ray diffraction patterns for the multi-element-substituted thin-film thus prepared. The patterns confirm two results: first, the single phase structure based on the $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ type; second, a multi-phase of the $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ and $\text{Ca}_{0.828}\text{CuO}_2$ types. Figure 3 shows a reaction phase diagram for $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ – $\text{Ca}_3\text{Al}_4\text{O}_{9+\delta}$ – $\text{Ca}_3\text{Cu}_4\text{O}_{9+\delta}$. The $\text{Al}_{15\%}$ – $\text{Cu}_{20\%}$ substitution product, which we presumed to be within the solid-solution range for the Al and Cu multi-element substitution product, exhibited a multi-phase of $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ and $\text{Ca}_{0.828}\text{CuO}_2$. The actual solid-solution region for $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ was thus confirmed to be narrower than we had presumed.

Fig. 5 SEM images of the $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ thin film (a) surface, (b) surface, (c) cross-section.

Fig. 6 SEM images of $\text{Ca}_3(\text{Co}_{1-x}\text{Al}_x)_4\text{O}_{9+\delta}$ thin film (a) initial particle observation, (b) secondary particle observation.

3.4 SEM observations of $\text{Ca}_3(\text{Co}_{1-x}\text{Cu}_x)_4\text{O}_{9+\delta}$ cross-section and surface

Figure 5, Fig. 6, and Fig. 7 show SEM images of the surfaces and cross-sections of the $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$, $\text{Ca}_3(\text{Co}_{1-x}\text{Al}_x)_4\text{O}_{9+\delta}$, and $\text{Ca}_3(\text{Co}_{1-x}\text{Cu}_x)_4\text{O}_{9+\delta}$ thin-films, respectively. As the SEM images, these crystallites measured approximately 140–200 nm, 80–640 nm, and 100–640 nm,

Fig. 7 SEM images of $\text{Ca}_3(\text{Co}_{1-y}\text{Cu}_y)_4\text{O}_{9+\delta}$ thin film (a) initial particle observation, (b) secondary particle observation.

Fig. 8 Electric conductivity of $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ thin-films.

respectively, confirming their plate-like crystal form. In the $\text{Ca}_3(\text{Co}_{1-x}\text{Al}_x)_4\text{O}_{9+\delta}$ thin-film, the secondary particles form as an island-shaped pattern with visible gaps, resulting in a film of very low density.

3.5 Thermoelectric properties of $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ thin-film

Figure 8 shows the electrical conductivity of the $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ thin-film. An increase in electrical conductivity was observed in the Cu-substituted thin-films but not the Al-substituted thin-films. We attributed the increased electrical conductivity observed in the Cu-substituted materials to the increased hole concentration and hole mobility. The average valence of the Co ion in $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ is approximately 3.1–3.3.¹⁸⁾ We therefore assumed that the hole concentration was increased by the difference in the valence state resulting from the substitution of Cu^{2+} for Co ions. We also assumed that the shift of the X-ray diffraction peak to a low angle (see section 3.2) resulted in a substitution of Cu^{2+} (0.073 nm) by Co^{3+} (0.0545 nm, LS) or Co^{4+} (0.053 nm, HS) with a small ion diameter. This presumably increased both the lattice spacing and hole mobility, thereby increasing the electrical conductivity. The absence of any increase in electrical conductivity in the Al-substituted materials was inexplicable, as the fine crystal grain size and unevenness confirmed in Fig. 6 brought about a scattering of the conduction electrons, which in turn increased the resistivity of the grain boundary.¹⁹⁾

The multi-element-substituted thin-film had higher electrical conductivity in the case of the $\text{Al}_{2.5}\text{Cu}_{2.5}$ -substituted $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ than the non-substituted $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$. The electrical conductivity, however, tended to decrease as the substitution amount for the Co-sites increased. In the multi-element substitution, the increase in electrical conductivity due to Cu substitution was suppressed by the decrease in electrical conductivity due to Al substitution. We

Fig. 9 Seebeck coefficients of $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ thin-films.

Fig. 10 Power factors of $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ thin-films.

think this suppressive effect explains the lack of any distinguished improvement in electrical conductivity. The electrical conductivity could also have been inhibited by the reduced crystallinity and reduced hole mobility resulting from the increase in the substitution ratio, as well as the insulation properties exhibited by the byproduct $\text{Ca}_{0.828}\text{CuO}_2$.

Figure 9 shows the Seebeck coefficient for the $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ thin-films. The Seebeck coefficient increased only in the Cu 5% and 10% substitution for the Co-site. In the other materials, it decreased as the substitution amount for the Co-sites increased. The Seebeck coefficient decreases as the hole concentration increases.⁶⁾ The hole concentration in this study increased due to element substitution, so the behavior of the Seebeck coefficient is a natural result. The effect of the change in Co valence due to the element substitution can also be considered. These results are consistent with the equation from Koshibae *et al.*²⁰⁾ describing thermoelectric force in a layered Co element containing oxides. It may also be possible, therefore, that the Seebeck coefficient decreased as a result of the decrease in Co^{3+} and increase in Co^{4+} due to element substitution.

Figure 10 shows the Power Factor (PF) values for the $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ thin-films. The PF values increased in the Cu-substituted thin-films but not in the Al-substituted thin-films. With regard to the multi-element-substituted materials, the $\text{Al}_{2.5}\text{Cu}_{2.5}$ -substituted $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ exhibited a value comparable to that of the non-substituted-product, but the value decreased as the substitution ratio increased. The absence of any dramatic increase in this study may be linked to the absence of any major increase in electrical conductivity. The compactness of materials is known to have a great influence on the electrical conductivity. The SEM images in Fig. 5 reveal many holes, and the film thickness is uneven at approximately 40–300 nm. Any improve-

Fig. 11 X-ray diffraction patterns of $\text{Ca}_3(\text{Co}_{1-x}\text{Cu}_x)_4\text{O}_{9+\delta}$ ($0 \leq x \leq 0.2$) sintered bodies (at 850°C) (a) $x = 0.2$, (b) $x = 0.1$, (c) $x = 0.05$, (d) $x = 0.025$.

ment in this unevenness in the film thickness would require a more detailed study of the conditions for applying voltage and the concentration setting for the starting material solution in the ESD method. While we were successful in obtaining the anticipated grain size in this experiment, the compactness and unevenness of the film will still need to be resolved by improving the conditions used for thin-film preparation.

3.6 Preparation and thermoelectric properties of $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ sintered body by the ESD method

To resolve the problems with compactness and unevenness and draw out the properties of the material itself, we prepared more sintered pellets and evaluated their thermoelectric properties. The sintered body was formed in the following shape: $10 \text{ mm}^\phi \times 1 \text{ mm}^t$.

Figure 11 shows the powder X-ray diffraction pattern of the $\text{Ca}_3(\text{Co}_{1-y}\text{Cu}_y)_4\text{O}_{9+\delta}$ sintered body heat-treated at 850°C . With $\text{Cu}_{2.5\%}$ substitution, we observed a diffraction pattern of the Co_3O_4 , which was thought to be unreacted. Meanwhile, the $\text{Cu}_{5\%}$ - and $\text{Cu}_{10\%}$ -substituted sintered bodies showed a single phase with a $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ type structure. The $\text{Cu}_{20\%}$ -substituted sintered body, however, induced thermal decomposition of the $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ structure, and the diffraction pattern showed a multi-phase of Co_3O_4 and $\text{Ca}_3\text{Co}_2\text{O}_6$ with a chain-like structure. The CoO_2 layer in the $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ type structure was stabilized by a Co valence of a mixture of $3+$ and $4+$. The addition of Cu^{2+} is assumed to have initially destabilized the structure, inducing a change to a more stable $\text{Co}_3\text{Co}_2\text{O}_6$ structure.²¹⁾ The multi-element-substituted materials exhibited the same tendency shown in Fig. 12. Figure 13 shows the presumed conditions for obtaining a single phase of a $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ type structure based on the powder X-ray diffraction patterns of the $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ sintered body. The line in Fig. 13 plots the temperature at which the single phase structure was obtained when the material was heat-treated at 800 – 900°C . The ideal sintering temperature obtained by the single phase structure decreased as the substitution amount of Co-sites increased, and the same trend was observed in all of the materials in $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$. At 900°C , meanwhile, a single phase structure was obtained in the case of the $\text{Al}_{5\%}$ - and $\text{Al}_{2.5\%}$ - $\text{Cu}_{2.5\%}$ -substituted sintered bodies, but not in the case of the $\text{Cu}_{5\%}$ -substituted sintered bodies. This appeared to be attributable to the higher ionic radii of Cu^{2+} ($0.073 \text{ nm}^{15})$) versus that of Al^{3+} ($0.0535 \text{ nm}^{15})$)

Fig. 12 X-ray diffraction patterns of $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ sintered bodies (at 850°C) (a) $x = 0.1, y = 0.1$, (b) $x = 0.05, y = 0.05$, (c) $x = 0.025, y = 0.025$.

Fig. 13 Single phase conditions of $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ sintered bodies (a) $\text{Ca}_3(\text{Co}_{1-x}\text{Al}_x)_4\text{O}_{9+\delta}$ ($0 \leq x \leq 2$), (b) $\text{Ca}_3(\text{Co}_{1-y}\text{Cu}_y)_4\text{O}_{9+\delta}$ ($0 \leq y \leq 2$), (c) $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ ($0 \leq x + y \leq 2, x = y$).

and the ease with which the crystal structure loses stability.

Figure 14 shows the electrical conductivity of the $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ sintered body. The conductivity of the $\text{Al}_{2.5\%}$ - $\text{Cu}_{2.5\%}$ -substituted material was about the same as that of the non-substituted- $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$. The conductivities of

Fig. 14 Electric conductivity of $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ sintered bodies. Fig. 15 Seebeck coefficients of $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ sintered bodies.

the $\text{Cu}_{2.5\%}$ -, $\text{Cu}_{5\%}$ -, and $\text{Cu}_{10\%}$ -substituted materials were also higher than the conductivity of the non-substituted- $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$. These results followed the same tendency as the thin-films. We also found that the electrical conductivity in the sintered body exceeded that of the thin-film by more than twofold. We attributed this stark difference to the high density and reduced number of internal defects in the sintered body compared to the thin-film. The electrical conductivity did show a tendency, however, to decrease as the substitution amount at the Co-sites increased. We expect that this behavior resulted from the decrease in crystallinity accompanying the increase in the substitution amount in the regions in which a single phase of the $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ structure was obtained. In the case of a multi-phase of $\text{Ca}_3\text{Co}_2\text{O}_6$ and $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$, the electrical conductivity was only about half that of the single-phase $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ structure. This large difference in conductivity was unsurprising, given that the electrical conductivity of the $\text{Ca}_3\text{Co}_2\text{O}_6$ was an order of magnitude lower than that of $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$, and the conduction was thus impeded.

Figure 15 shows the Seebeck coefficient of the $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ sintered body. The Seebeck coefficient decreased as the substitution ratio increased, presumably for the same reason explained in section 3.3.

Figure 16 shows the PF value for the $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ sintered body, calculated based on the results for electrical conductivity and the Seebeck coefficient. The $\text{Al}_{2.5\%}$ - $\text{Cu}_{2.5\%}$ -substituted materials exhibited roughly the same value as the non-substituted product $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$. Moreover, the values for the $\text{Cu}_{2.5\%}$ -, $\text{Cu}_{5\%}$ -, and $\text{Cu}_{10\%}$ -substituted materials were higher than that of the non-substituted $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$. We assume that this discrepancy resulted from the significant effect exerted by the increase in electrical conductivity. For the other materials, the PF value tended to decrease as the substitution amount increased.

Table 1 shows the preparation process and the PF values at 27°C .⁶⁻¹⁰⁾ The PF values for the non-substituted $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$

Fig. 16 Power factor of $\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ sintered bodies.Table 1 $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ Reported examples for the sample doped.

Material name	Synthesis process	Power Factor, $\text{PF}_{300\text{K}} / \text{W m}^{-1} \text{K}^{-2}$
$\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ ⁶⁾	Solid-State reaction method	8.3×10^{-5}
$\text{Ca}_3(\text{Co}_{0.9}\text{Fe}_{0.1})_4\text{O}_{9+\delta}$ ⁶⁾	Solid-State reaction method	19.0×10^{-5}
$\text{Ca}_3(\text{Co}_{0.8}\text{Fe}_{0.2})_4\text{O}_{9+\delta}$ ⁷⁾	Sol-gel method	13.0×10^{-5}
$\text{Ca}_3(\text{Co}_{0.9}\text{Mn}_{0.1})_4\text{O}_{9+\delta}$ ⁶⁾	Solid-State reaction method	9.5×10^{-5}
$\text{Ca}_3(\text{Co}_{0.9}\text{Cu}_{0.1})_4\text{O}_{9+\delta}$ ⁶⁾	Solid-State reaction method	8.7×10^{-5}
$\text{Ca}_3(\text{Co}_{0.8}\text{Cu}_{0.2})_4\text{O}_{9+\delta}$ ⁷⁾	Sol-gel method	14.0×10^{-5}
$\text{Ca}_3(\text{Co}_{0.95}\text{Zn}_{0.05})_4\text{O}_{9+\delta}$ ⁸⁾	Solid-State reaction method	4.0×10^{-5}
$\text{Ca}_3(\text{Co}_{0.8}\text{Zn}_{0.2})_4\text{O}_{9+\delta}$ ⁷⁾	Sol-gel method	8.5×10^{-5}
$\text{Ca}_3(\text{Co}_{0.95}\text{Ga}_{0.05})_4\text{O}_{9+\delta}$ ⁹⁾	Solid-State reaction method	22.0×10^{-5}
$\text{Ca}_3(\text{Co}_{0.8}\text{Cr}_{0.2})_4\text{O}_{9+\delta}$ ⁷⁾	Sol-gel method	6.0×10^{-5}
$\text{Ca}_3(\text{Co}_{0.8}\text{Mo}_{0.2})_4\text{O}_{9+\delta}$ ¹⁰⁾	Sol-gel method	2.8×10^{-5}
$\text{Ca}_3(\text{Co}_{0.8}\text{Ni}_{0.2})_4\text{O}_{9+\delta}$ ⁷⁾	Sol-gel method	6.0×10^{-5}

and $\text{Cu}_{10\%}$ -substituted material were higher than that reported for the sintered body obtained by the conventionally used solid state reaction method. This was not unexpected, as the sintered body obtained with the method in this study had a higher density than the sintered body obtained with the conventionally used solid state reaction method, resulting in a higher PF. From these results, we found that the sintered body obtained in this study could maintain a high density even when element substitution was conducted, and that it may have exhibited higher thermoelectric properties than the sintered body obtained by the conventional solid state reaction method.

4. Conclusions

$\text{Ca}_3(\text{Co}_{1-x-y}\text{Al}_x\text{Cu}_y)_4\text{O}_{9+\delta}$ thin-films and sintered bodies were prepared by electrostatic spray deposition, a solution-based process. The multi-element-substituted materials with Al and Cu were confirmed to have a narrower solid-solution range than had been presumed based on the results of single-element substitution. The evaluation of thermoelectric performance showed similar trends for the thin film and sintered body, but uneven film thickness and porosity were observed in the thin film test specimen, indicating that issues with the material preparation remain to be resolved. Our results did not lead to the discovery of a composition with an thermoelectric performance superior to that of the non-substitution $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$. Among the prepared materials, however, the electrical conductivity of $\text{Ca}_3(\text{Co}_{0.95}\text{Al}_{0.025}\text{Cu}_{0.025})_4\text{O}_9$ exceeded that of the non-substituted $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ in both thin-

films and sintered bodies, and the Power Factor (PF) was also close to that of the non-substituted film.

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