

Thermoelectric properties of Bi and Cu co-doped $\text{Ca}_3\text{Co}_2\text{O}_6$ single crystals

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Abstract Single crystals of Bi and Cu-doped $\text{Ca}_3\text{Co}_2\text{O}_6$ were synthesized in a molten K_2CO_3 flux. Using an obtained single crystal of $(\text{Ca}_{0.985(5)}\text{Bi}_{0.015(5)})_3(\text{Co}_{0.990(3)}\text{Cu}_{0.010(3)})_2\text{O}_6$ elongated to the c -axis direction of the crystal structure, the electric resistivity (ρ) and Seebeck coefficient (S) were measured from room temperature to over 1000 K in air. The single crystal showed p -type semiconducting behavior with ρ values of $1.8 \Omega\text{cm}$ at 303 K and $0.017 \Omega\text{cm}$ at 1000 K. The S values were $+254 \mu\text{VK}^{-1}$ at 325 K, $+360 \mu\text{VK}^{-1}$ at 420 K, and $+214 \mu\text{VK}^{-1}$ at 1000 K. The power factor ($S^2\rho^{-1}$) increased with an increase of temperature and attained $2.70 \times 10^{-4} \text{Wm}^{-1}\text{K}^{-2}$ at 1000 K.

Keywords Thermoelectric materials · $\text{Ca}_3\text{Co}_2\text{O}_6$ · Single crystals · Power factor

The thermoelectric material of oxide is suited for the use in high temperature range, e.g. 700–1000 K, in air due to their high thermal stability in an oxidizing atmosphere. After

the finding of NaCo_2O_4 [1], which has high thermoelectric performance, one has widely surveyed the oxides with high conversion efficiency; $\text{Ca}_3\text{Co}_4\text{O}_9$ [2, 3], (Bi,Pb)-Sr-Co-O compounds [4–6], $(\text{ZnO})_m/\text{In}_2\text{O}_3$ [7, 8], $\text{ZnO}:\text{Al}$ [9]. These oxides exhibited the semiconductor and/or semi-metal with comparatively low electrical resistivity and attracted interest in the quantum well of superlattice structures [10] with respect to their layer structures.

A calcium cobaltite $\text{Ca}_3\text{Co}_2\text{O}_6$ crystallizes in a quasi-one dimensional structure that involves $[\text{Co}_2\text{O}_6]_\infty$ chains and Ca atoms array. The $[\text{Co}_2\text{O}_6]_\infty$ chains, which consist of an alternate face-sharing stack of CoO_6 octahedra and CoO_6 prisms, align parallel to the c axis of the crystal structure and the Ca array separate the chains. Although the $\text{Ca}_3\text{Co}_4\text{O}_9$ has come up for a substance showing thermoelectromotive force, $\text{Ca}_3\text{Co}_2\text{O}_6$ has just been passed over due to the high electric resistivity at room temperature: The resistivities of the $\text{Ca}_3\text{Co}_2\text{O}_6$ single crystal are a few Ωcm in the c -axis direction and the 10^3 – 10^4 times higher in the direction perpendicular to the c axis [11].

Iwasaki et al. [12, 13] measured the electrical resistivity (ρ) and the Seebeck coefficient (S) of the polycrystalline $\text{Ca}_3\text{Co}_2\text{O}_6$ and $\text{Ca}_3\text{Co}_2\text{O}_6$ -based solid solutions in the temperature range up to about 1000 K. They reported that the higher the temperature, the more their power factor ($S^2\rho^{-1}$), and Bi and/or Cu-doped $(\text{Ca}_{1-x}\text{Bi}_x)_3(\text{Co}_{1-y}\text{Cu}_y)_2\text{O}_6$ ($0 < x, y < 0.03$) showed power factors several times larger than in the case of non-doped $\text{Ca}_3\text{Co}_2\text{O}_6$ ($x = 0, y = 0$) [12, 13]. Recently, Mikami et al. [14] and Takahashi et al. [15] measured ρ and S along the c -axis direction of the synthesized $\text{Ca}_3\text{Co}_2\text{O}_6$ single crystals at high temperature ranges. According to their reports, the power factor of the single crystal $\text{Ca}_3\text{Co}_2\text{O}_6$ at 1000 K was about $2.4 \times 10^{-4} \text{Wm}^{-1}\text{K}^{-2}$ [15], which is more than 20 times larger than that of the polycrystalline $\text{Ca}_3\text{Co}_2\text{O}_6$, $0.10 \times 10^{-4} \text{Wm}^{-1}\text{K}^{-2}$ [12].

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In the present study, the preparation of Bi and/or Cu-doped $(\text{Ca,Bi})_3(\text{Co,Cu})_2\text{O}_6$ single crystals was attempted by the flux method. The electric resistivity and Seebeck coefficient of a single crystal were measured in the c -axis direction from room temperature to 1000 K, followed by the power factor was examined.

Single crystals of $(\text{Ca,Bi})_3(\text{Co,Cu})_2\text{O}_6$ were synthesized with CaCO_3 , Co_3O_4 , Bi_2O_3 , and Cu_2O powders with the molar ratios of $\text{Bi}/(\text{Ca}+\text{Bi}) = 0.0 - 0.1$, $\text{Cu}/(\text{Co}+\text{Cu}) = 0.0 - 0.1$, and $(\text{Ca}+\text{Bi})/(\text{Co}+\text{Cu}) = 3.0/2.2$, and quadruple amount of an anhydrous K_2CO_3 powder against the total mass of the other powders. The mixed powders were placed in an alumina crucible and heated to 1193 K in air with a heating rate of $+100 \text{ K h}^{-1}$. After the holding at 1193 K for 48 h, the samples were cooled to 850 K at a cooling rate of -100 K h^{-1} , and then to room temperature in the furnace by shutting off the electric power. Single crystals were mechanically separated from the samples after washing the flux with water. The obtained single crystals of the Bi-doped, Cu-doped, and Bi,Cu co-doped samples, as well as the non-doped $\text{Ca}_3\text{Co}_2\text{O}_6$ single crystals, were black and had needlelike hexagonal or trigonal prismatic shapes elongated to the c -axis direction of the crystal structure. The largest crystal was 10.0 mm long and 0.7 mm wide.

The electron-probe microanalysis (EPMA, JEOL JXA-8200 WD/ED combined Microanalyzer) was carried out for the fracture surface of twenty-three single crystals picked up from various samples. No potassium was detected (detection limit $<0.1 \text{ at}\%$). The $(\text{Ca}+\text{Bi})/(\text{Ca}+\text{Bi}+\text{Co}+\text{Cu})$ molar ratio of the obtained single crystals was 0.60(2) as an average (max 0.68 and min 0.55) and agreed with the expected value (3/5) of Bi and/or Cu-doped $(\text{Ca,Bi})_3(\text{Co,Cu})_2\text{O}_6$. Figure 1 shows the relationships between the molar ratios of Bi/(Ca+Bi) (open symbols) and Cu/(Co+Cu) (solid symbols) in the starting powders and those in the obtained single crystals. It can be seen from Fig. 1 that the concentrations of Bi and/or Cu in the $(\text{Ca,Bi})_3(\text{Co,Cu})_2\text{O}_6$ single crystals were several times less than those in the starting materials, irrespective of cooling rate (-5 K h^{-1} : open/closed squares, -200 K h^{-1} : open circles) and synthesis temperature (at 1213 K: open/closed squares). In addition, it seems to have an upper limit of the Bi and Cu substitution that both x and y of $(\text{Ca}_{1-x}\text{Bi}_x)_3(\text{Co}_{1-y}\text{Cu}_y)_2\text{O}_6$ are around 0.02. These limits are agreed with the case of polycrystalline that the $(\text{Ca}_{1-x}\text{Bi}_x)_3(\text{Co}_{1-y}\text{Cu}_y)_2\text{O}_6$ prepared by the solid state reaction contained impurity phases with $x \geq 0.03$ and $y \geq 0.03$ [12, 13].

We chose a Bi and Cu co-doped single crystal of $(\text{Ca}_{0.985(5)}\text{Bi}_{0.015(5)})_3(\text{Co}_{0.990(3)}\text{Cu}_{0.010(3)})_2\text{O}_6$ (CBCCO here in after) for the measurement of electrical properties. This single crystal was taken from the sample with $\text{Bi}/(\text{Ca}+\text{Bi}) = 0.088$ and $\text{Cu}/(\text{Co}+\text{Cu}) = 0.084$ under holding temperature at 1193 K for 48 h with heating/cooling rates

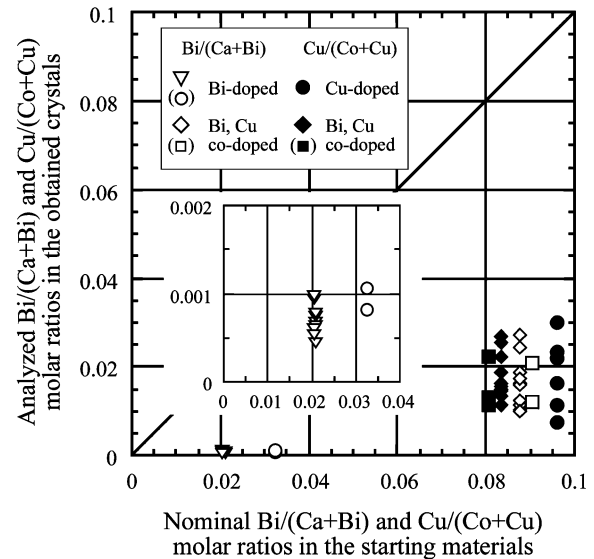


Fig. 1 Molar ratios of Bi/(Ca+Bi) (open symbols) and Cu/(Co+Cu) (solid symbols) of the starting materials and Bi,Cu-doped $\text{Ca}_3\text{Co}_2\text{O}_6$ single crystals synthesized at 1193 K for 48 h with the heating and cooling rate of $\pm 100 \text{ K h}^{-1}$. The Bi/(Ca+Bi) molar ratios of the sample prepared with the cooling rate of -200 K h^{-1} are shown with the open circles. The open/closed squares are resulted in the samples prepared at 1213 K for 48 h with the cooling rate of -5 K h^{-1} . The inset shows the data of small values

of $\pm 100 \text{ K h}^{-1}$. The crystal had 3.0 mm long and 0.0475 mm^2 cross-sectional area with flat and smooth crystal habits. After removing a thin high-electric resistive-layer with a razor knife, one attached Au wire on the crystal with Ag paste as electrodes. Electric resistivity was measured by the direct-current four-probe method and the Seebeck coefficient was performed with a measurement apparatus (Model RZ2001i, Ozawa Science).

Figure 2 shows temperature dependence of the electric resistivity (ρ) of the CBCCO single crystal along the c axis. The semiconducting behavior ($d\rho/dT < 0$) was seen in the measured temperature range (303–1083 K). The ρ values of the CBCCO single crystal at room temperature and 1000 K were 1.8 and $0.017 \text{ }\Omega\text{cm}$, respectively. In the middle temperature range from about 320 K to 800 K, the ρ value of the CBCCO crystal was lower than that of the non-doped one. It should be emphasized that the increasing conductivity in the polycrystalline series is affected not only by the changes of the carrier density from Bi and/or Cu doping, but also the increase of the sintering density with reduction of the grain boundary resistance.

The positive Seebeck coefficient (S) shown in Fig. 3 indicated that the CBCCO single crystal was a p -type semiconductor in the measured temperature range of 325–1065 K. The S value increased from $+254 \text{ }\mu\text{VK}^{-1}$ at 325 K to about $+360 \text{ }\mu\text{VK}^{-1}$ at around 420 K, and then decreased to $+210 \text{ }\mu\text{VK}^{-1}$ at 1000 K. This temperature dependence was similar to that of the non-doped $\text{Ca}_3\text{Co}_2\text{O}_6$ single crystal [15]

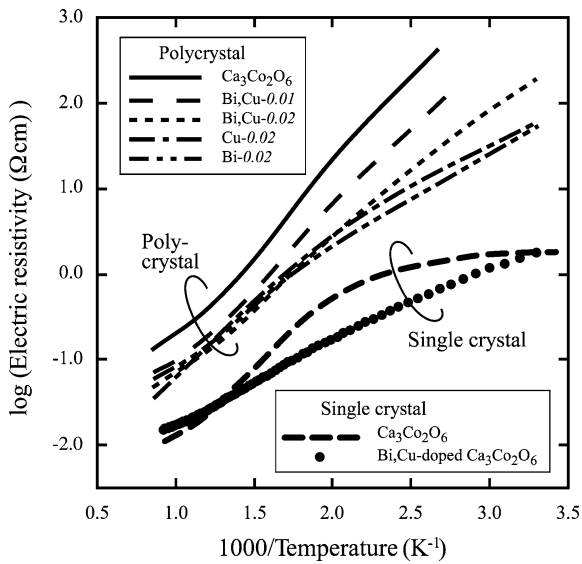


Fig. 2 Temperature dependence of the electrical resistivities for the Bi,Cu-doped $\text{Ca}_3\text{Co}_2\text{O}_6$ (CBCCO) single crystal along the c -axis direction (dots), compared with the data reported for the non-doped $\text{Ca}_3\text{Co}_2\text{O}_6$ single crystal [15] (broken line), the $\text{Ca}_3\text{Co}_2\text{O}_6$ polycrystalline sample [12], and the doped $\text{Ca}_3\text{Co}_2\text{O}_6$ polycrystalline samples [13]

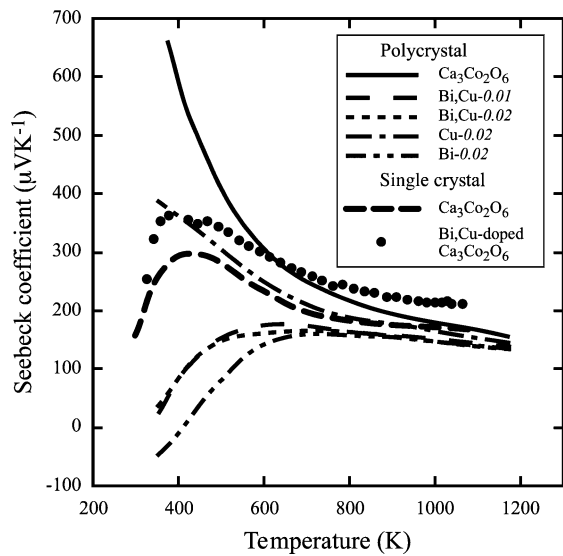


Fig. 3 Temperature dependence of the Seebeck coefficients for the Bi,Cu-doped $\text{Ca}_3\text{Co}_2\text{O}_6$ (CBCCO) single crystal along the c -axis direction (dots), compared with the data reported for the non-doped $\text{Ca}_3\text{Co}_2\text{O}_6$ single crystal [15], the $\text{Ca}_3\text{Co}_2\text{O}_6$ polycrystalline sample [12], and the doped $\text{Ca}_3\text{Co}_2\text{O}_6$ polycrystalline samples [13]

and the doped-polycrystalline samples of $(\text{Ca,Bi})_3\text{Co}_2\text{O}_6$ and $\text{Ca}_3(\text{Co,Cu})_2\text{O}_6$ [12, 13]. The S values of the CBCCO single crystal are higher than those of $\text{Ca}_3\text{Co}_2\text{O}_6$ one in the present temperature range. The S of the polycrystalline samples, on the contrary, decreased with an increase of the amount of dopants [12, 13].

Figure 4 shows the relationship between the power factor ($S^2\rho^{-1}$) and temperature. The power factor of the CBCCO

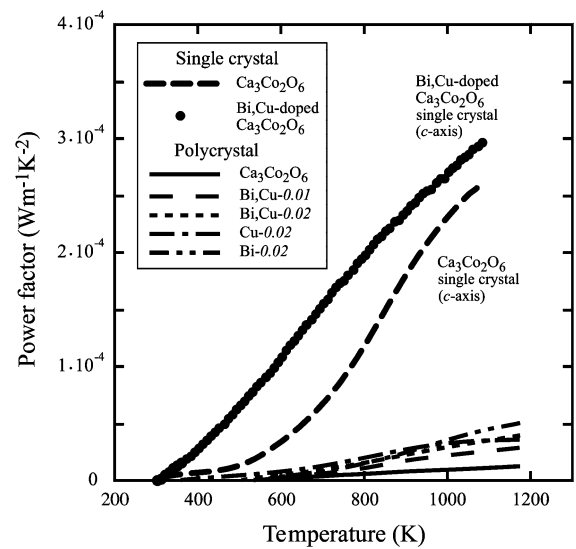


Fig. 4 Temperature dependence of the power factors for the Bi,Cu-doped $\text{Ca}_3\text{Co}_2\text{O}_6$ (CBCCO) single crystal along the c -axis direction (dots), compared with the data reported for the non-doped $\text{Ca}_3\text{Co}_2\text{O}_6$ single crystal [15], the $\text{Ca}_3\text{Co}_2\text{O}_6$ polycrystalline sample [12], and the doped $\text{Ca}_3\text{Co}_2\text{O}_6$ polycrystalline samples [13]

single crystal, as well as the non-doped single crystal [14, 15] and polycrystalline samples [13], increased monotonically with increasing temperature. The $S^2\rho^{-1}$ values of the CBCCO single crystal improved four times larger than the non-doped one in the temperature range from about 410 to 500 K. The $S^2\rho^{-1}$ value of the CBCCO ($2.70 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$) was about 16% higher than that of the non-doped $\text{Ca}_3\text{Co}_2\text{O}_6$ ($2.33 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$) at 1000 K.

The thermal conductivity (κ) of the $\text{Ca}_3\text{Co}_2\text{O}_6$ single crystal (c axis) is estimated to be $2.5 \text{ Wm}^{-1}\text{K}^{-1}$ at 1000 K [14]. If the κ value of the CBCCO single crystal is comparable to this value, the Z ($= S^2\rho^{-1}\kappa^{-1}$) of the CBCCO single crystal is estimated to be $1.08 \times 10^{-4} \text{ K}^{-1}$ ($ZT = 0.108$) at 1000 K.

To summarize, the Bi and/or Cu doped $\text{Ca}_3\text{Co}_2\text{O}_6$ single crystals were prepared by the flux method using K_2CO_3 . The substitution limit was $x \leq 0.02$ and $y \leq 0.02$ for $(\text{Ca}_{1-x}\text{Bi}_x)_3(\text{Co}_{1-y}\text{Cu}_y)_2\text{O}_6$. A co-doped single crystal of $(\text{Ca}_{0.985(5)}\text{Bi}_{0.015(5)})_3(\text{Co}_{0.990(3)}\text{Cu}_{0.010(3)})_2\text{O}_6$ showed a p -type semiconducting behavior in the temperature range of 300–1100 K. The power factor of the co-doped single crystal increased with increasing temperature, and reached $2.70 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$ at 1000 K. The improvement of the power factor by doping was more than 400% at 320–800 K and 116% at 1000 K.

Acknowledgment This work was partially supported by Japan Society for the Promotion of Science, the Grant-in-Aid for Scientific Research, by The Japan Securities Scholarship Foundation, The Thermal and Electric Energy Technology Foundation, and by The Collaborative Research in Center for Interdisciplinary Research, Tohoku University. The authors would like to thank Y. Sato and T. Kamaya for EPMA measurement.

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