Preparation and thermoelectric properties of highly oriented calcium cobalt oxides by solution combustion synthesis with post-spark plasma sintering

LIHUA ZHANG[*a], NORIYUKI OKINAKA[b], TSUYOSHI TOSHO[c], TOMOHIRO AKIYAMA[b]
State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, P. R. China
[a]*School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, P. R. China*
[b]*Center for Advanced Research of Energy Conversion Materials, Hokkaido University, Sapporo 060-8628, Japan*
[c]*Thermoelectric Device Development Inc., Noboribetsu 059-0003, Japan*

In this paper, layered cobalt oxides of $Ca_3Co_4O_9$ and Bi-doped $Ca_3Co_4O_9$ were synthesized by solution combustion synthesis with post-spark plasma sintering method, and the thermoelectric properties of the synthesized materials were analyzed from different directions. The synthesized bulk samples showed a relatively high orientation degree analyzed by XRD degree, and the Lotgering factor of $Ca_3Co_4O_9$ and Bi-doped $Ca_3Co_4O_9$ is 0.70 and 0.91 respectively. Thermoelectric properties measured from different directions show that the power factor and ZT value measured perpendicular to the press direction are relatively higher and the highest ZT value 0.11 was obtained by Bi-doped $Ca_3Co_4O_9$ at 857 K.

1. Introduction

Thermoelectric materials have been concerned a lot in the last decades because it can be applied to thermoelectric device which converts thermal energy into electricity by Seebeck effect and vice versa by Peltier effect. The energy conversion performance of thermoelectric materials is usually characterized by the dimensionless figure of merit $ZT = \alpha^2 \sigma T / \kappa$, where α, σ, T, and κ are Seebeck coefficient ($\mu V \cdot K^{-1}$), electric conductivity ($S \cdot m^{-1}$), absolute temperature (K), and thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$), respectively. Good thermoelectric materials require large Seebeck coefficient (α) and electric conductivity (σ), and a low thermal conductivity (κ) in order to obtain a high ZT. Since the discovery of high power factor in single crystal sodium cobalt oxide $Na_xCo_2O_4$[1], many kinds of oxides have been focused on because of the promising candidate for thermoelectric applications. In these oxides, layered cobalt oxides have been found to show fairly good thermoelectric performances, such as Ca–Co–O, Bi–Sr–Co–O, Tl–Sr–Co–O, Pb–Sr–Co–O, and Ca–Co–Cu–O systems[2-9]. All these compounds show a large Seebeck coefficient, which has been suggested to be related with strong electron-electron correlation[10].

The transport properties of layered cobalt oxides such as $Ca_3Co_4O_9$ are highly anisotropic due to its layered structure[11]. The in-plane electric conductivity is much higher than that out of the plane, suggesting that preferentially grain-aligned ceramics would exhibit higher thermoelectric performance than randomly oriented ceramics with the same composition. Moreover, micro-structural aspects (such as the grain size, grain boundary, and bulk density) of polycrystalline bulk materials have a great influence on their electric conductivity. Therefore, the preparation of highly grain-aligned thermoelectric ceramics with high density is a necessary key technology for practical utilization of polycrystalline materials with layered structure. However, in the reported references, solid-state reaction (SSR) method is usually used as the synthesis method for the layered cobalt oxides. Although SSR method is widely used in production of many electronic ceramics such as PZT, this method is time and energy consuming because it usually need calcinations several times for a long time to obtain a homogeneous production. Therefore, other effective methods were needed. In previous references, solution combustion synthesis (SCS) method was reported to be an appropriate method for layered cobalt oxides. SCS method is one of the most simple solution-based combustion synthesis methods. Notable, the chemical energy released from the redox reaction instantaneously heats up the system, and neither additional heating nor special chemicals are required. Thus, the SCS method is considered to be one of the easiest energy-saving methods to produce ceramics

consisting of fine particles. However, there is rare report about the thermoelectric properties of the SCSed products from different measurement directions. For this consideration, $Ca_3Co_4O_9$ and Bi-doped $Ca_3Co_4O_9$ were synthesized by SCS method and sintered by spark plasma sintering (SPS), and the anisotropic thermoelectric properties of the synthesized oxides were studied in this paper.

2. Experimental

Polycrystalline $Ca_3Co_4O_9$ and Bi-doped $Ca_3Co_4O_9$ were prepared from the raw materials of $Ca(NO_3)_2 \cdot 4H_2O$ (99.9% purity, Kanto Chemical, Tokyo, Japan), $Co(NO_3)_2 \cdot 6H_2O$ (98.0% purity, Kanto Chemical, Tokyo, Japan) and $Bi(NO_3)_3 \cdot 5H_2O$ (99.5% purity, Kanto Chemical, Tokyo, Japan). Stoichiometric amounts of the metal nitrates were dissolved in distilled water, and appropriate amount of fuel was added in the solution. Here it should be mentioned that in the case of $Ca_3Co_4O_9$, $CO(NH_2)_2$ (99.0% purity, Kanto Chemical, Tokyo, Japan) was used as the fuel; while in the case of Bi-doped $Ca_3Co_4O_9$, citric acid (99.9% purity, Kanto Chemical, Tokyo, Japan) was used as the fuel in order to prevent of the hydrolysis of Bi^{3+} ion.

The mixture of raw materials was electromagnetic stirred at 333 K to obtain a homogeneous solution. Then the solution was poured into an Al_2O_3 crucible, after that the crucible was put in a muffle furnace and rapidly heated to 623 K (for $Ca_3Co_4O_9$) and 723 K (for Bi-doped $Ca_3Co_4O_9$), the self-propagating process of smoldering type combustion occurred and completed within several minutes. After the synthesis, the colorless solution changed to black porous bulk. The porous bulk was ground into powder by carnelian mortar and pestle, after which the powder was sintered into pellets with a diameter of 10 mm in a graphite die by SPS (SPS-511S, Sumitomo Coal Mining, Tokyo, Japan) in vacuum condition at the temperature range of 1073−1173 K for 5−15 min, and the sintering pressure was 39 MPa.
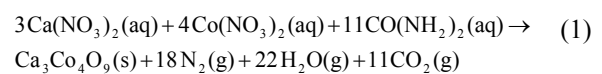
The synthesized samples were characterized by X-ray diffraction analysis (Miniflex, Rigaku, Tokyo, Japan) before and after SPS, using $CuK\alpha_1$ radiation. The morphology of the samples was observed by scanning electron microscope (SEM) (JSM-7000F, JEOL, Tokyo, Japan).

The electric conductivity and the Seebeck coefficient were simultaneously measured by the Seebeck coefficient/electric resistance measuring system (ZEM-2, ULVAC-RIKO, Yokohama, Japan) from room temperature to 865 K. The thermal conductivity was calculated by the density, thermal diffusivity and heat capacity of the sample. The density was measured by the Archimedes method; the thermal diffusivity and heat capacity were measured by laser flash thermal constant analyzer (TC-7000, ULVAC-RIKO, Yokohama, Japan). Because of the crystalline anisotropicity of the product, the thermoelectric properties of $Ca_3Co_4O_9$ and Bi-doped $Ca_3Co_4O_9$ samples were measured in both directions of parallel and perpendicular to the press direction of the sintering.

3. Results and discussion

The SCS of $Ca_3Co_4O_9$ has the following equation in the solution during the synthesis:

$$3Ca(NO_3)_2(aq) + 4Co(NO_3)_2(aq) + 11CO(NH_2)_2(aq) \rightarrow \quad (1)$$
$$Ca_3Co_4O_9(s) + 18N_2(g) + 22H_2O(g) + 11CO_2(g)$$

The urea $(CO(NH_2)_2)$ was acted as fuel and oxidized by the nitrate ions in the process. The equations showed that 11 mol CO_2, 18 mol N_2 and a lot of H_2O released for the production of 1 mol of $Ca_3Co_4O_9$, which resulted to the porous product.

For the preparation of Bi-doped $Ca_3Co_4O_9$, citric acid was used as the fuel because Bi^{3+} ions hydrolyzes with water to form $Bi(OH)^{2+}$ ions. The reactions in the solution are as followings:

$$3A(NO_3)_n + nH_3B \rightarrow A_3B_n + 3nHNO_3 \quad (2)$$

$$4HNO_3 \rightarrow 2H_2O + 4NO_2 + O_2 \quad (3)$$

A is the metal ion, and B is the citrate ion. The corresponding citrates were decomposed and finally the mixture of metal oxides was obtained. In this study, molar ratio of doped Bi is 10%.
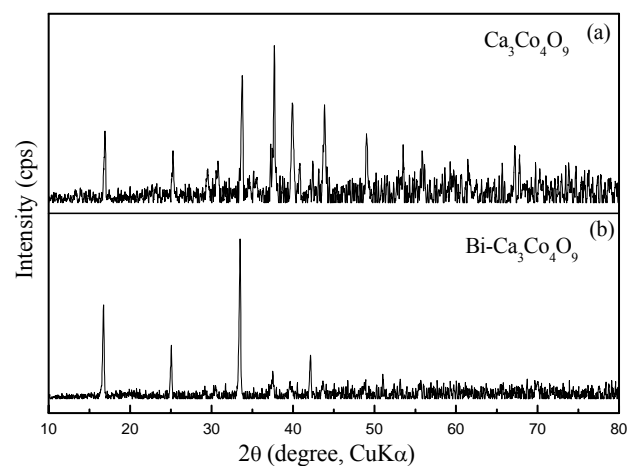

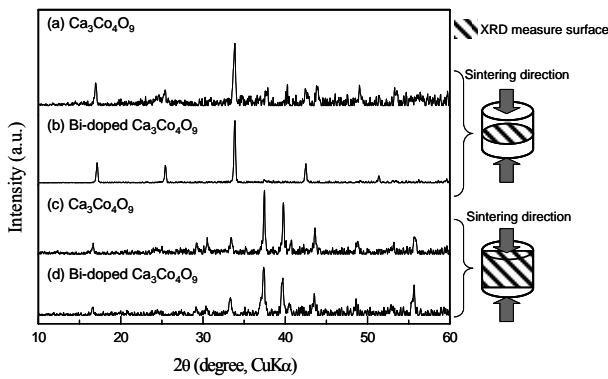Fig. 1. X-ray diffraction patterns of SCSed $Ca_3Co_4O_9$ and Bi-doped $Ca_3Co_4O_9$ powders.

Fig. 2. X-ray diffraction patterns of SPSed Ca$_3$Co$_4$O$_9$ and Bi-doped Ca$_3$Co$_4$O$_9$ measuring in two directions.
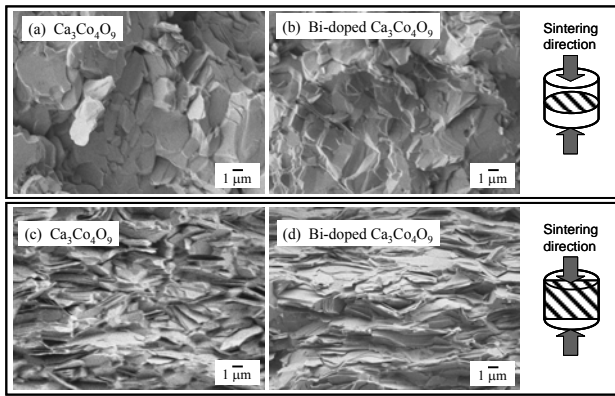

Fig. 3. SEM images of SPSed Ca$_3$Co$_4$O$_9$ and Bi-doped Ca$_3$Co$_4$O$_9$ observed in two directions.

Fig. 1 shows the X-ray diffraction patterns of the SCSed Ca$_3$Co$_4$O$_9$ and Bi-doped Ca$_3$Co$_4$O$_9$ powders. The peaks agree with the data from the literature of Ca$_3$Co$_4$O$_9$ phase[12,13]. This indicated that the high purity Ca$_3$Co$_4$O$_9$ and Bi-doped Ca$_3$Co$_4$O$_9$ powders could be successfully synthesized by SCS. After SPS, the bulk samples were analysized by XRD in two directions as shown in Fig. 2. The peaks are different for both samples measured in two directions, and the peaks in Fig. 2(a) and (b) are mainly on *c* plane, which indicate the textured structure of the synthesized samples. Fig. 3 shows the SEM images of sintered samples. From the XRD figures and SEM images of bulk samples, we can conclude that the bulk samples show well-aligned grains perpendicular to the sintering direction because SPS process allows the control of grain alignment according to the starting processing configuration, i.e. either from powder or pellet[14].

Because of the anisotropic growth of the Ca$_3$Co$_4$O$_9$ and Bi-doped Ca$_3$Co$_4$O$_9$ crystal, the samples exhibited a microstructure consisting plate-like grains with anisotropic shape. Therefore, Ca$_3$Co$_4$O$_9$ and Bi-doped Ca$_3$Co$_4$O$_9$ with textured structure were successfully synthesized by SCS and SPS. As shown in Fig. 5 (a) and (b), the intensity of the (0 0 2) and (0 0 4) peaks

corresponding to the *c*-plane was relatively large compared with the other peaks. This indicated that the *c*-axis direction of each grain of the samples arranged along the pressing direction. The degree of crystallographic orientation of these samples was evaluated by using Lotgering factor[15], which was calculated by following equation:

$$f = \frac{P - P_0}{1 - P_0} \tag{1}$$

where

$$P = \frac{\sum I(00l)}{\sum I(hkl)} \tag{2}$$

when $P_0 = P$, that means $f = 0$, the sample is crystallographically isotropic (randomly oriented); when the *c*-axis directions are completely aligned along the pressing direction, the *f* value is 1. In this study, P_0 was calculated from the peak data of the JCPDS card. The Lotgering factor of the SCSed powers was calculated and as a result that the Lotgering factor of Ca$_3$Co$_4$O$_9$ and Bi-doped Ca$_3$Co$_4$O$_9$ is 0.70 and 0.91 respectively, showing the anisotropic grain growth during the synthesis. Thus, it proved that the SCS method with post-SPS is an effective method to synthesis anisotropic Ca$_3$Co$_4$O$_9$ and Bi-doped Ca$_3$Co$_4$O$_9$ with high purity.
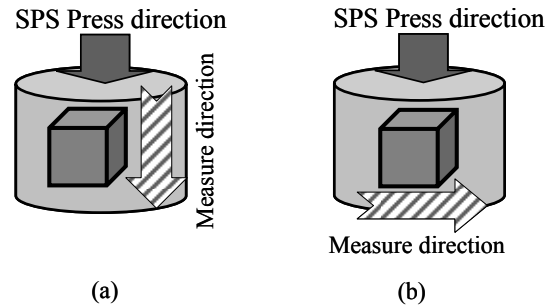

Fig. 4 Schematic diagram of the thermoelectric properties measuring direction: (a) measuring parallel to the press direction; (b) measuring perpendicular to the press direction.
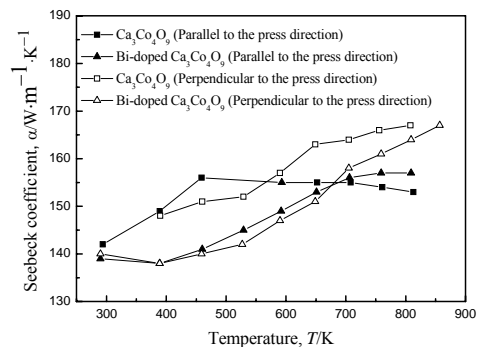

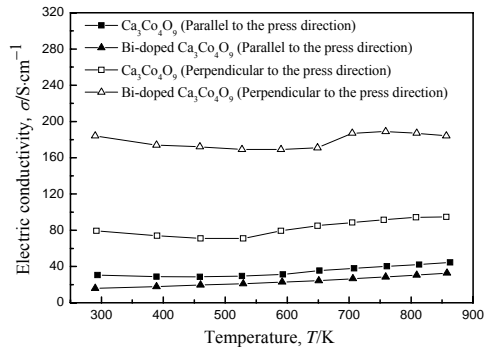*Fig. 5 Temperature dependencies on Seebeck coefficient of Ca$_3$Co$_4$O$_9$ and Bi-doped Ca$_3$Co$_4$O$_9$.*

Fig. 6. Temperature dependencies on electric conductivity of $Ca_3Co_4O_9$ and Bi-doped $Ca_3Co_4O_9$.

particles was formed during the SPS process[11].

Fig. 7 Temperature dependencies on power factor of $Ca_3Co_4O_9$ and Bi-doped $Ca_3Co_4O_9$.

Thermoelectric properties of the samples were measured form different directions, as shown in Fig. 4. Fig. 5 shows the Seebeck coefficient of the SPSed $Ca_3Co_4O_9$ and Bi-doped $Ca_3Co_4O_9$ measured from different directions. Seebeck coefficient was positive in the experimental temperature range, showing p-type materials. In almost all the temperature range measured, $Ca_3Co_4O_9$ shows relatively higher Seebeck coefficient than Bi-doped $Ca_3Co_4O_9$ in the same measuring direction, which was caused by the higher carrier density of doped sample. Comparing the samples measured from different directions, the Seebeck coefficient of the samples measured perpendicular to the press direction was very close to that of the samples measured parallel to the press direction. This shows that the Seebeck coefficient has small difference in the in-plane and out-of-plane directions.

Fig. 6 shows the electric conductivity of the synthesized samples measured from different directions. The electric conductivity shows slight change with temperature increasing. Comparing the Bi-doped $Ca_3Co_4O_9$ sample with $Ca_3Co_4O_9$, the electric conductivity measured perpendicular to the press direction increased a lot with doping elements, which was mainly caused by the increasing of carrier density. Moreover, the electric conductivity of both samples measured perpendicular to the press direction was much higher than that measured parallel to the press direction. Terasaki et al.[1] researched the thermoelectric properties of single crystal $Na_xCo_2O_4$ from different directions. According to their study, the electric conductivity of in-plane direction is higher than that out-of-plane direction in the temperature range from 0 K to 300 K. Therefore, in our study, the higher electric conductivity of the samples measured perpendicular to the press direction was caused by the highly anisotropic crystals and in-plane direction crystals were majority in the measuring direction. It also proved that the sintered products were highly textured. The textured structure was formed from two aspects: one is that the particles by SCS method are regular plate-like; the other is that the particles rearrangement occurred and orientation of the
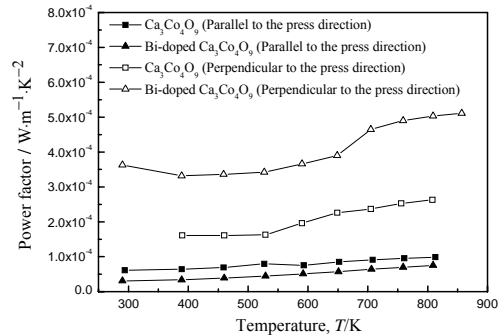
Fig. 7 shows the temperature dependencies on power factor of the SCSed $Ca_3Co_4O_9$ and Bi-doped $Ca_3Co_4O_9$. The power factor increased slightly with temperature, and in all samples the highest power factor was obtained by Bi-doped $Ca_3Co_4O_9$ sample measured perpendicular to the press direction of sintering. The highest power factor, 5.11×10^{-4} W·m^{-1}·K^{-2}, was obtained at 857 K.

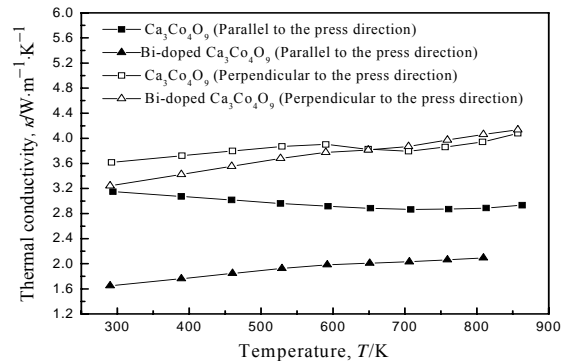*Fig. 8 Temperature dependencies on thermal conductivity of $Ca_3Co_4O_9$ and Bi-doped $Ca_3Co_4O_9$.*
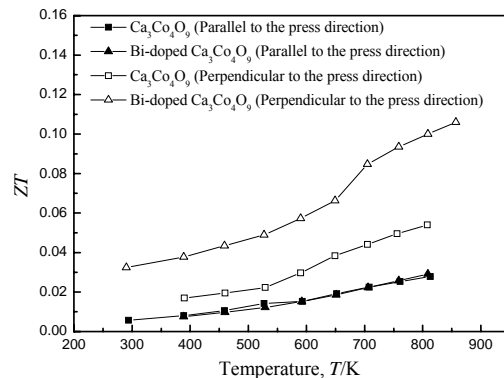
Fig. 9. Temperature dependencies on ZT value of $Ca_3Co_4O_9$ and Bi-doped $Ca_3Co_4O_9$.

Thermal conductivity of the samples was measured and shown in Fig. 8. The samples showed weak temperature dependency; the thermal conductivity increased slightly with temperature except the sample of Bi-doped $Ca_3Co_4O_9$ measured parallel to the press direction. This was probably caused by the different scattering mechanisms of phonon in different directions. Then, ZT value was calculated and shown in Fig. 9. ZT value of all the samples increased with temperature, and the ZT of the samples measured perpendicular to the press direction was higher than that of which measured parallel to the press direction. This was caused by the higher electric conductivity of the former samples. The Bi-doped $Ca_3Co_4O_9$ measured perpendicular to the press direction had the highest ZT among all the samples. The maximum ZT, 0.11, was obtained at 857 K. Although the ZT was not satisfiable at present, the results showed that the combination of SCS and SPS was a proper method to synthesize layered cobalt oxides with high orientation factor for potential thermoelectric application.

4. Conclusions

In this paper, $Ca_3Co_4O_9$ and Bi-doped $Ca_3Co_4O_9$ were synthesized by SCS method combined by SPS, the microstructure and thermoelectric properties of the synthesized $Ca_3Co_4O_9$ and Bi-doped $Ca_3Co_4O_9$ were analyzed. The results show that the dense samples with high orientation degree were successfully obtained with relatively high purity. As for the thermoelectric properties, the power factor and ZT value of both samples measured perpendicular to the press direction are relatively higher. The highest power factor is 5.11×10^{-4} W·m^{-1}·K^{-2} and the highest ZT is 0.11, obtained by Bi-doped $Ca_3Co_4O_9$ at 857 K.

References

[1] I. Terasaki, Y. Sasago, K. Uchinokura, Phys. Rev. B: Condens. Matter. **56,** 12685 (1997).

[2] K. Vidyasagar, J. Gopalakrishnan, C. N. R. Rao, Inorg. Chem. **23**, 1206 (1984).

[3] E. Woermann, A. Muan, J. Inorg. Nucl. Chem. **32**, 1455 (1970).

[4] E. M. Levin, H. F. McMurdie, Phase Diagrams for Ceramists 1975 Supplement, The American Ceramic Society, Ohio, 1975.

[5] T. Itoh, T. Kawata, T. Kitajima, I. Terasaki, Proc. 17th Int. Conf. Thermoelectrics (ICT '98), IEEE, Piscataway 1999.

[6] H. Leligny, D. Grebille, O. Pérez, A. C. Masset, M. Hervieu, C. Michel, B. Raveau, C. R. Acad, Sci. Paris IIc. **2**, 409 (1999).

[7] S. Hébert, S. Lambert, D. Pelloquin, A. Maignan, Phys, Rev. B **64**, 172101 (2001).

[8] D. Pelloquin, A. Maignan, S. Hébert, C. Martin, M. Hervieu, C. Michel, L. B. Wang, B. Raveau, Chem. Mater. **14**, 3100 (2002).

[9] Y. Miyazaki, T. Miura, Y. Ono, T. kajitani, Jpn. J. Appl. Phys. **41**, L849 (2002).

[10] Y. Ando, N. Miyamoto, K. Segawa, T. Kawata I. Terasaki, Phys. Rev. B **60**, 10580 (1999).

[11] Y. Zhang, J. Zhang, Q. Lu, Ceram. Inter. **33**, 1305 (2007).

[12] A. C. Masset, C. Michel, A. Maignan, M. Hervieu, O. Toulemonde, F. Studer, B. Raveau, Phys. Rev. B **62**, 166 (2000).

[13] M. Mikami, E. Guilmeau, R. Funahashi, K, Chong, D. Chateigner, J. Mater. Res. **20**, 2491 (2005).

[14] J. G. Noudem, J. Eur. Ceram. Soc. **29**, 2659 (2009).

[15] F. K. Lotgering, J. Inorg. Nucl. Chem. **9**, 113 (1959).

*Corresponding author: zhanglh@metall.ustb.edu.cn