

Improvements of thermoelectric transport properties for a partially substituted $\text{Ca}_3\text{Co}_4\text{O}_9$ system by spark plasma sintering

Chang-Hyun Lim^{a,b}, Soon-Mok Choi^{a,*}, Won-Seon Seo^a, Kyoung Hun Kim^a, Jong-Young Kim^a and Hyung-Ho Park^b

^aKorea Institute of Ceramic Engineering and Technology (KICET), Seoul 233-5, Korea

^bDepartment of Materials Science and Engineering, Yonsei University, 134 Sinchon-dong, Seodaemun-ku, Seoul 120-749, Korea

Highly-dense and textured $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramic samples were obtained by a spark plasma sintering (SPS) process. The sintering conditions were modified to optimize the degree of orientation and the bulk densities which are important for their thermoelectric performance. Their thermoelectric properties were measured from room temperature to 1,180 K in air. The maximum power factor was achieved at 1,153 K in the SPS-sintered case because of the maximum electrical conductivity owing to both the degree of orientation and bulk density. In order to improve the thermoelectric performance of this SPS-sintered $\text{Ca}_3\text{Co}_4\text{O}_9$ system a doping effect with various dopants was also investigated. $\text{Ca}_3\text{Co}_4\text{O}_9$ samples doped with Ag, Bi, and Na were prepared. Three factors including acceptor doping, a grain boundary phase and elevated mobility caused enhanced electrical conductivities. And these increased electrical conductivities resulted in increased power factors.

Key words: Thermoelectric oxides, Texture structure, $\text{Ca}_3\text{Co}_4\text{O}_9$, Spark plasma sintering.

Introduction

Thermoelectric oxides have been regarded as promising materials for power generation especially at high temperature. In 1997 Terasaki and coworkers reported an oxide material, Na_xCoO_2 , with a high Seebeck coefficient (100 $\mu\text{V/K}$ at 300 K) and a low resistivity (0.2 m Ω at 300 K) [1]. Calcium cobalt oxide $\text{Ca}_3\text{Co}_4\text{O}_9$ was also reported to exhibit excellent conductivity and an extraordinarily large Seebeck coefficient [2]. These results proved that the thermoelectric performance of oxides could be comparable to that of intermetallic compounds. However the high thermoelectric performances of these cobalt oxide systems come from their anisotropic crystal structures, therefore the electrical conductivity of the direction parallel to the laminated layer is much higher than other directions. Then this anisotropy caused a complexity in the manufacture of thermoelectric modules [3]. Besides, the anisotropy can also disturb the higher bulk density of this system after sintering. To overcome these problems, it is worth finding a new manufacturing process where it is both easy to control their textured structures and profitable to elevate their bulk densities. Many researchers devoted their attention to the spark plasma sintering (SPS) process, for examples Song *et al.* [4] and Liu *et al.* [5] reported a high power factor of $5.5 \times 10^{-4} \text{ W/mK}^2$ and a high

dimensionless figure of merit of 0.25 for $\text{Ca}_3\text{Co}_4\text{O}_9$ thermoelectrics at 973 K. The efficiency of a thermoelectric material is determined by its dimensionless thermoelectric figure-of-merit, $ZT = S^2\sigma T/\kappa$, where S , σ , κ , and T are the Seebeck coefficient, electrical conductivity, total thermal conductivity and absolute temperature, respectively. Therefore, good thermoelectric materials should possess a large power factor ($PF = S^2\sigma$) value and a low thermal conductivity value. So in this study $\text{Ca}_3\text{Co}_4\text{O}_9$ thermoelectric oxides were fabricated by a SPS process to modify their laminated structure and elevate their bulk density. Detailed experiments were performed to optimize the sintering conditions.

At the same time, various dopants were substituted into Ca sites to improve the power factor (W/mK^2) by means of increasing the electrical conductivity. $\text{Ca}_3\text{Co}_4\text{O}_9$ oxide is one of the typical mist-layered oxides, and it consists of alternating layers of a distorted CaO-CoO-CaO rock-salt-type layer and a CdI_2 -type CoO_2 layer stacked in the c -axis direction. The electronic structures of the mist-layered $\text{Ca}_3\text{Co}_4\text{O}_9$ include two-dimensionally dispersive e_g bands across the Fermi energy, which yields p -type conduction in the rock-salt Ca_2CoO_3 subsystem, while the Fermi energy lies in the crystal-field gap of the d states in the CoO_2 layer [6]. And the t_{2g} levels further split into another doubly degenerated e_g' levels and a non-degenerated a_{1g} level due to the rhombohedral distortion of the octahedron [7]. Then the edge-shared CoO_2 layers are considered to be responsible for the electrical conduction, whereas the rock-salt-type Ca_2CoO_3 layers are regarded as a charge reservoir to supply charge carriers to the CoO_2 layers [6]. For a pure $\text{Ca}_3\text{Co}_4\text{O}_9$ composition, Ca^{+2} ions at Co^{+3} ion sites in the rock-salt-type Ca_2CoO_3 layer could

*Corresponding author:
Tel : +82-2-3282-2449
Fax: +82-2-3282-2470
E-mail: smchoi@kicet.re.kr

act as acceptor ions and so could produce effectively negative (-) defects in this layered oxide, then the charge valence of Co^{+3} ions in the edge-shared CoO_2 layers may be changed into +4 in proportion to the amount of $\text{Ca}^{+2}_{\text{Co}^{+3}}$ ions. As a result, these mixed valence states between Co^{3+} and Co^{4+} states could increase the carrier concentration in the edge-shared CoO_2 layers in accordance with the Verwey controlled ionic valence principle [8, 9]. And these electrons make this $\text{Ca}_3\text{Co}_4\text{O}_9$ layered oxide a p-type semiconductor. In the case of doping with other acceptors into the Ca sites it may be possible to elevate the electrical conductivity more. So in this study to control the carrier concentration, various amounts of three different dopants Ag^{+1} , Na^{+1} , and Bi^{+3} were doped into the Ca^{2+} sites. The doping effects were investigated in this $\text{Ca}_{1-x}\text{A}_x\text{Co}_4\text{O}_9$ ($\text{A} = \text{Ag}^{+1}$, Na^{+1} , and Bi^{+3}) layered oxide system and the thermoelectric properties were studied.

Experimental Procedures

$\text{Ca}_3\text{Co}_4\text{O}_9$, $\text{Ca}_{2.7}\text{Ag}_{0.3}\text{Co}_4\text{O}_9$, $\text{Ca}_{2.7}\text{Bi}_{0.15}\text{Na}_{0.15}\text{Co}_4\text{O}_9$, and $\text{Ca}_{2.4}\text{Bi}_{0.3}\text{Na}_{0.3}\text{Co}_4\text{O}_9$ powders were prepared by a solid state reaction process. CaCO_3 (99.99%, High-purity Chemical), Co_3O_4 (99.9%, High-purity Chemical), Bi_2O_3 (99.9%, High-purity Chemical), Na_2CO_3 (99.95%, ACROS ORGANICS), and AgNO_3 (99.8%, Hayashi pure chemical industry) powders were used as starting materials. The raw materials were homogeneously mixed by ball milling and calcined at 1,173 K for 12 h in air after hand pressing. The calcined compacts were ground and they were passed through a 325 mesh sieve. These powders of pure $\text{Ca}_3\text{Co}_4\text{O}_9$ composition were sintered by conventional and spark plasma sintering processes. In the conventional sintering process, powders were pressed using the cold isostatic press at 200 MPa for 5 minutes after the compaction and they were sintered at 1,193 K for 24 h in air. For the spark plasma sintering process, powders were loaded into a graphite mold inside an SPS system (SPS-515S, Sumitomo Coal Mining Co., Japan). After applying an initial pressure of 50 MPa, the loaded powders were heated in the sintering temperature range from 1,103 K to 1,173 K for 10 minutes at a heating rate of $100 \text{ K} \cdot \text{minute}^{-1}$ in a vacuum ($< 10^{-5} \text{ Pa}$). $\text{Ca}_{2.7}\text{Ag}_{0.3}\text{Co}_4\text{O}_9$, $\text{Ca}_{2.7}\text{Bi}_{0.15}\text{Na}_{0.15}\text{Co}_4\text{O}_9$ and $\text{Ca}_{2.4}\text{Bi}_{0.3}\text{Na}_{0.3}\text{Co}_4\text{O}_9$ powders were sintered at 1,153 K for 10 minutes at a heating rate of $100 \text{ K} \cdot \text{minute}^{-1}$ under a pressure of 50 MPa in a vacuum ($< 10^{-5} \text{ Pa}$). The sintered samples were cut into rectangle bars with dimensions of $2 \text{ mm} \times 2 \text{ mm} \times 10 \text{ mm}$ to measure the thermoelectric properties.

Their densities were measured by the Archimedes method and an X-ray diffractometer (D/MAX-2500/PC, Rigaku, Japan) was used for analyzing the phases of the sintered bodies. The thermoelectric property was measured by a thermoelectric property measurement system (model

RZ2001i, Ozawa Science, Japan). The electrical conductivity was measured by a 4-point probe method and the Seebeck coefficient was obtained from the slope of the linear relation between ΔV and ΔT , where ΔV is the thermo-electronic motive force produced by a temperature difference ΔT . The thermal conductivity was measured by a laser flash technique (LFA 457, NETZSCH, Germany).

Results and Discussion

Detailed experiments for $\text{Ca}_3\text{Co}_4\text{O}_9$ oxide were performed to optimize their textured structures and bulk densities. Fig. 1 (a)-(d) show XRD results for pure $\text{Ca}_3\text{Co}_4\text{O}_9$ after spark plasma sintering (SPS) at various temperatures from 1,103 K to 1,173 K. The diffraction patterns for all the specimens were indexed as pure $\text{Ca}_3\text{Co}_4\text{O}_9$ and no second phase was detected. As mentioned above the SPS process is effective in promoting a textured structure. As a result, the XRD analysis results for all the specimens showed a highly-oriented structure. To evaluate the degree of orientation for the SPS-sintered specimens, we determined the Lotgering's factors [10], in which the value of f was calculated by using the XRD peak intensities:

$$f = \frac{(P - P_0)}{(1 - P_0)}, \quad P = \frac{\sum I(00l)}{\sum I(hkl)} \quad (1)$$

where P_0 is P for a randomly oriented specimens (JCPDS cards, No. 21-0139).

Calculated degrees of orientation are shown in Fig. 2. As our intention was complete sintering, the degree of orientation for SPS-sintered specimens was much higher than the value for the conventionally sintered case. This

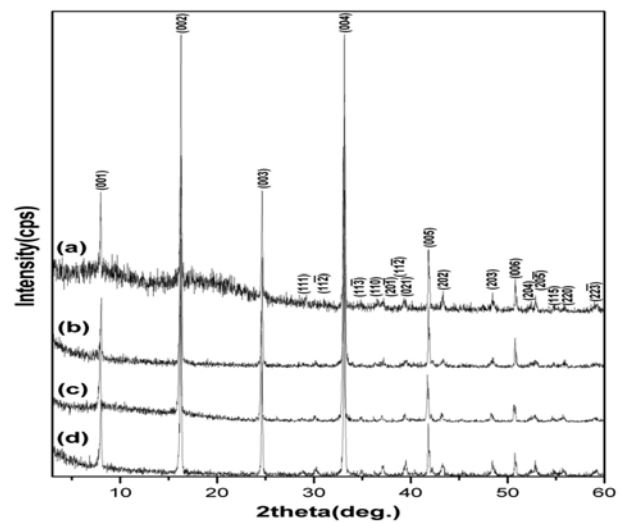


Fig. 1. X-ray diffraction patterns of pure $\text{Ca}_3\text{Co}_4\text{O}_9$ in the perpendicular direction for different SPS processes : (a) 1,103 K (b) 1,123 K (c) 1,153 K (d) 1,173 K.

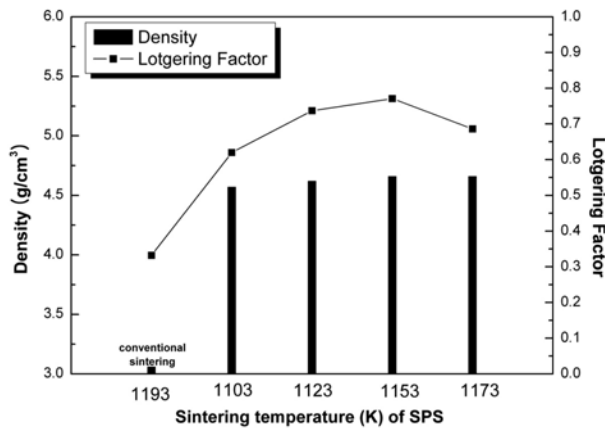


Fig. 2. Relationships of density and Lotgering factor between SPS and conventional processes for pure $\text{Ca}_3\text{Co}_4\text{O}_9$.

enhanced degree of orientation could give a positive effect on the electrical conductivity. Besides, the degree of orientation of SPS-sintered specimens showed a dependence on the SPS temperature. Namely the degree of orientation increased in proportion to the temperature up to 1,153 K SPS-temperature and then the degree of orientation decreased in inverse proportion to the temperature at a higher temperature than 1,153 K SPS temperature. As a result the maximum degree of orientation was achieved at 1,153 K SPS-temperature. This tendency gives a direct effect on the electrical conductivity for pure $\text{Ca}_3\text{Co}_4\text{O}_9$ specimens.

Another important merit of the SPS process considered in this study was the high bulk density of sintered specimens. For all SPS temperatures, the bulk densities for SPS-sintered specimens were much higher than that of the conventionally sintered one as shown in Fig. 2. This improved bulk density could also give a positive effect on the electrical conductivity for pure $\text{Ca}_3\text{Co}_4\text{O}_9$ specimens. And bulk densities also showed an SPS-temperature dependence. Namely the bulk density also increased in proportion to the sintering temperature up to 1,173 K SPS-temperature. The maximum bulk density was acquired in the 1,153–1,173 K SPS-temperature region. This temperature dependence also gave a direct effect on the electrical conductivities of pure $\text{Ca}_3\text{Co}_4\text{O}_9$ specimens, which showed a dependence on the SPS temperature as shown in Fig. 3(a). The electrical conductivity increased in proportion to the SPS temperature owing to an increase of both the degree of orientation and the bulk density value. However, the electrical conductivity of the 1,173 K SPS-sintered one was smaller than the 1,153 K SPS-sintered specimen owing to a decrease of the degree of orientation. Then this temperature dependence gave a direct effect on the power factor for SPS-sintered specimens as shown in Fig. 3(c). As a result the maximum power factor was achieved in the 1,153 K SPS-sintered specimen because of a maximum electrical conductivity owing to a maximum of both the degree of orientation and the bulk density. And obviously as was our intention, the

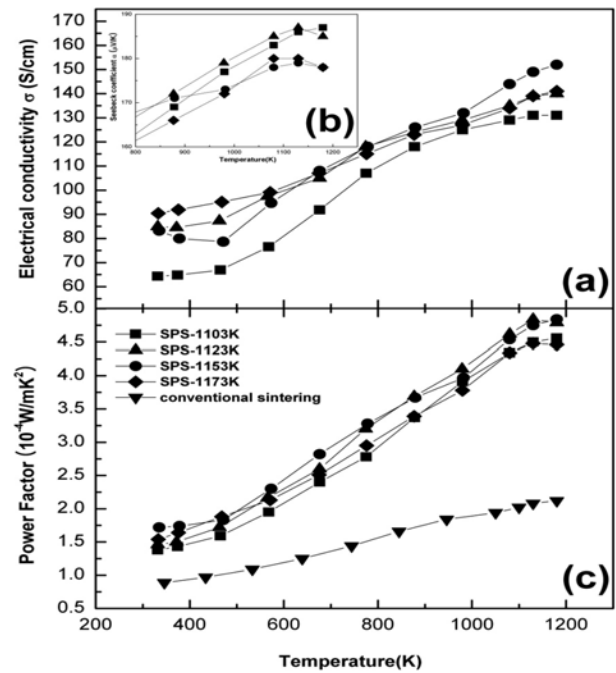


Fig. 3. Temperature dependence of thermoelectric properties for pure $\text{Ca}_3\text{Co}_4\text{O}_9$ samples prepared by different processes : (a) electrical conductivity and (b) Seebeck coefficient, (c) power factor.

maximum power factor values for SPS-sintered specimens $4.84 \times 10^{-4} \text{ W/mK}^2$ was much higher than the conventionally sintered case $2.12 \times 10^{-4} \text{ W/mK}^2$ at a 1,180 K measuring temperature.

To improve the thermoelectric performance of this SPS sintered $\text{Ca}_3\text{Co}_4\text{O}_9$ system we also investigated the doping-effect of various dopants. Three different ions were doped into this $\text{Ca}_3\text{Co}_4\text{O}_9$ system and the SPS-sintering temperatures for these doped $\text{Ca}_3\text{Co}_4\text{O}_9$ systems were all 1,152 K at which the degree of orientation and the bulk density showed a maximum value in the SPS-sintered pure $\text{Ca}_3\text{Co}_4\text{O}_9$ system as mentioned above. Ag^{+1} ions as an acceptor were substituted into Ca^{+2} sites in order to increase the carrier concentration in this system. As mentioned above in the introduction acceptor ions can enhance the electrical conductivity by means of increasing the $\text{Co}^{+4}_{\text{Co}^{+3}}$ concentration. As was our intention, the electrical conductivity for the Ag-doped specimen was higher than the pure specimen as shown in Fig. 4(a). This effect of acceptors on the electrical conductivity gave a direct effect on the power factor values. As a result as shown in Fig. 4(b), the maximum power factor for the Ag-doped specimen was $5.88 \times 10^{-4} \text{ W/mK}^2$ at 1,180 K, which was much higher than that of the pure specimen. In addition, there could be other reasons for the enhanced electrical conductivity of the Ag-doped specimen. Wang *et al.* reported an effect of a grain boundary phase on the total electrical conductivity [11]. In the case of a grain boundary phase having a higher electrical conductivity than the matrix grains, if the grain boundary phase forms a good connection between

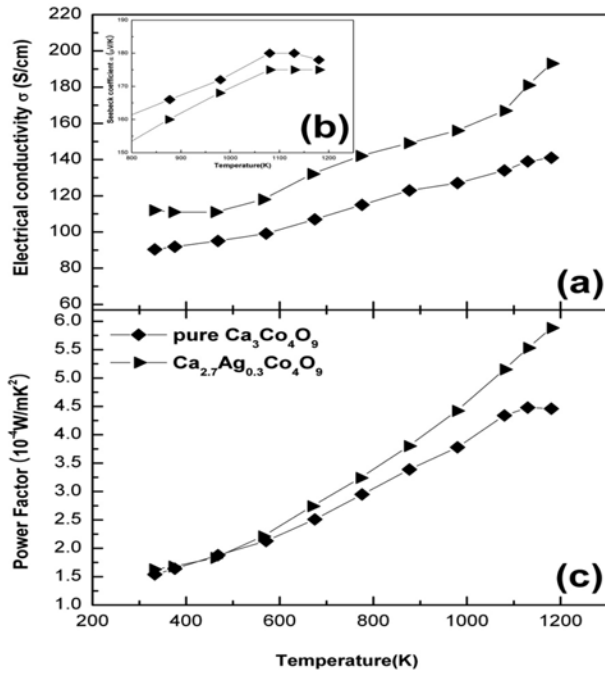


Fig. 4. Temperature dependence of thermoelectric properties for Ag doped $\text{Ca}_3\text{Co}_4\text{O}_9$ samples : (a) electrical conductivity and (b) Seebeck coefficient, (c) power factor.

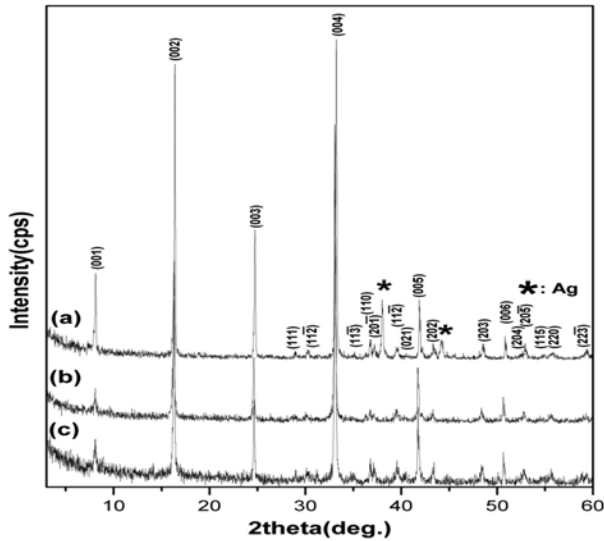


Fig. 5. X-ray diffraction patterns of doped $\text{Ca}_3\text{Co}_4\text{O}_9$ with different doping element in the perpendicular direction : (a) $\text{Ca}_{2.7}\text{Ag}_{0.3}\text{Co}_4\text{O}_9$ (b) $\text{Ca}_{2.7}\text{Bi}_{0.15}\text{Na}_{0.15}\text{Co}_4\text{O}_9$ (c) $\text{Ca}_{2.4}\text{Bi}_{0.3}\text{Na}_{0.3}\text{Co}_4\text{O}_9$.

matrix grains, the carrier scattering at the grain boundaries will be reduced effectively. Then the resistance at the grain boundaries can be diminished, as a result the conductivity of the system would increase [11]. As shown in Fig. 5(a), we may conclude from the results of XRD analysis that not all Ag atoms were substituted into Ca ion sites but some Ag atoms were segregated as a second phase. This grain boundary phase having a higher electrical conductivity could give a positive effect on the total electrical conductivity. The third

reason for an enhanced electrical conductivity for the Ag-doped $\text{Ca}_3\text{Co}_4\text{O}_9$ system might be the effect of the dopant to increase the mobility in this $\text{Ca}_3\text{Co}_4\text{O}_9$ system. As mentioned above CaO-CoO-CaO rock-salt-type layers are not regarded as a conducting path in this $\text{Ca}_3\text{Co}_4\text{O}_9$ system but are regarded as a charge reservoir to supply charge carriers to the CoO_2 layers. Nevertheless, dopant substitution into Ca sites may increase the carrier mobility, which together with the microstructural factor leads to an increase in conductivity [12].

To confirm this effect of dopants on enhancing electrical conductivity by means of elevating mobility, we investigated two more compositions. Bi^{3+} and Na^+ were substituted into Ca^{2+} sites at the same time with the same doing level resulting in stoichiometric compositions. Namely we designed and manufactured two compositions $\text{Ca}_{2.7}\text{Bi}_{0.15}\text{Na}_{0.15}\text{Co}_4\text{O}_9$ and $\text{Ca}_{2.4}\text{Bi}_{0.3}\text{Na}_{0.3}\text{Co}_4\text{O}_9$. The XRD patterns for these two $\text{Ca}_{2.7}\text{Bi}_{0.15}\text{Na}_{0.15}\text{Co}_4\text{O}_9$ and $\text{Ca}_{2.4}\text{Bi}_{0.3}\text{Na}_{0.3}\text{Co}_4\text{O}_9$ specimens all showed a $\text{Ca}_3\text{Co}_4\text{O}_9$ single phase as shown in Fig. 5(b), and (c). The electrical conductivities for these stoichiometric compositions are shown in Fig. 6(a). The electrical conductivity for $\text{Ca}_{2.4}\text{Bi}_{0.3}\text{Na}_{0.3}\text{Co}_4\text{O}_9$ was higher than that for the pure composition. Since the carrier concentration was not changed in these stoichiometric compositions, this enhanced electrical conductivity might be due to increased mobility as mentioned above. The reason for a higher mobility in the $\text{Ca}_{2.4}\text{Bi}_{0.3}\text{Na}_{0.3}\text{Co}_4\text{O}_9$ specimen is not fully understood as yet. It should be commented here, however, that the edge-shared CoO_2 octahedral layers are considered to be responsible for the electrical

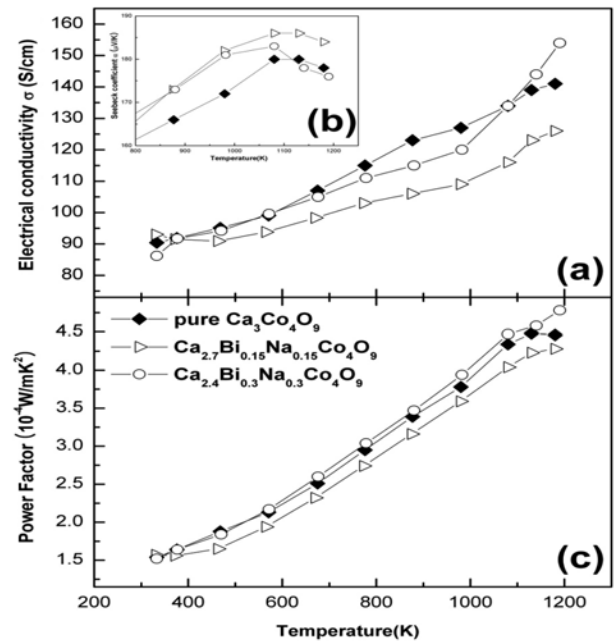


Fig. 6. Temperature dependence of the thermoelectric properties for Bi, Na co-doped $\text{Ca}_3\text{Co}_4\text{O}_9$ samples : (a) electrical conductivity and (b) Seebeck coefficient, (c) power factor.

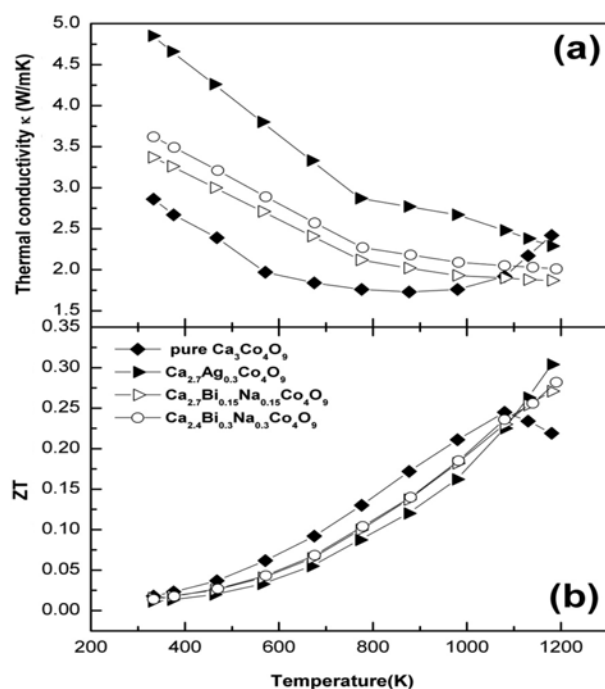


Fig. 7. Temperature dependence of the thermoelectric properties for doped $\text{Ca}_3\text{Co}_4\text{O}_9$ samples with different elements: (a) thermal conductivity, (b) dimensionless figure of merit ZT .

conductivity of this $\text{Ca}_3\text{Co}_4\text{O}_9$. And the distortion of these CoO_2 octahedra might disturb the electronic-hole conduction and decrease the mobility of carriers [13]. Namely the additives might give a positive effect on increasing the mobility of this $\text{Ca}_{2.4}\text{Bi}_{0.3}\text{Na}_{0.3}\text{Co}_4\text{O}_9$ specimen by means of reducing the distortion of the edge-shared CoO_2 octahedra. And this enhanced electrical conductivity gave a positive effect on the power factor for these stoichiometric compositions as shown in Fig. 6(c).

In addition thermal conductivities and dimensionless figure of merit values (ZT) for these doped $\text{Ca}_3\text{Co}_4\text{O}_9$ systems were measured and are shown in Fig. 7(a), (b) respectively. As mentioned above in the introduction good thermoelectric materials should possess a large power factor ($PF = S^2\sigma$) value and a low thermal conductivity value. Although the thermal conductivity for the Ag-doped composition was higher than that of the others, the Ag-doped composition showed a maximum ZT value of 0.30 at 1,180 K higher than any other composition because of its highest power factor value $5.88 \times 10^{-4} \text{ W/mK}^2$ at 1,180 K.

The reason for the increase of the thermal conductivity of the pure $\text{Ca}_3\text{Co}_4\text{O}_9$ specimen at temperatures higher than 980 K is not yet clear. However, it should be commented here that a bipolar transport mechanism could increase thermal conductivity at high temperature or we possibly need to check the reproducibility of the measurement system. More detailed research for optimizing the thermo-electrical performance will be followed as the next study.

Conclusions

Highly-dense and textured $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramic samples were obtained by the SPS process. The electrical conductivity increased in proportion to the SPS temperature owing to an increase of both the degree of orientation and the bulk density value. However, the electrical conductivity for the 1,173 K sample was smaller than for the 1,153 K specimen owing to a decrease of the Lotgering's factor. Also this temperature dependence gave a direct effect on the power factor values for SPS-sintered specimens. The maximum power factor values for SPS-sintered specimen was $4.84 \times 10^{-4} \text{ W/mK}^2$ at 1,180 K, which was much higher than the conventionally sintered case $2.12 \times 10^{-4} \text{ W/mK}^2$ at 1,180 K.

To improve the thermoelectric performance of this SPS-sintered $\text{Ca}_3\text{Co}_4\text{O}_9$ system the doping effect with various dopants was investigated. Three factors including acceptor doping, a grain boundary phase and elevated mobility caused enhanced electrical conductivities. And these increased electrical conductivities gave a direct effect on increasing power factors. The maximum power factor was $5.88 \times 10^{-4} \text{ W/mK}^2$ for a Ag-doped specimen at 1,180 K.

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