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Synthesis and Thermoelectric Properties of the New Oxide Materials $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($0.0 < x < 0.75$)

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A new series of oxides $Ca_{3-x}Bi_xCo_4O_{9+\delta}$, ($x = 0.0-0.75$) with $Ca_2Co_2O_5$-type structures were synthesized, and their structures, electrical properties, Seebeck coefficients, and thermal conductivities were measured. The values of Seebeck coefficients of the new oxides are all positive, showing that they are p-type conductors. Both the electrical conductivity and Seebeck coefficients increase with the increasing Bi contents which can be attributed to the increase of carrier mobility due to the larger size of Bi ion. The electrical conductivity, Seebeck coefficient, and the calculated value of the power factor of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.5$) are 105 S cm^{-1}, 160 μV K^{-1}, and 2.7×10^{-4} W K^{-2} m^{-1} at 700 °C, respectively. The thermal conductivity of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.5$) at room temperature is 1.14 W m^{-1} K^{-1} and increase slightly with the increasing temperature. At 700 °C, the figure of merit of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.5$) is 2.0×10^{-4} K^{-1}.

Introduction

Because of the high stability at high temperature in air, easy manufacture, and low cost, oxides have attracted much attention as the new thermoelectric materials in recent years. Many oxide systems have been investigated, and some of them have good thermoelectric properties. The values of figure of merit (Z) of $(ZnO)_5In_2O_3$,[1] $In_2O_3{\cdot}MO_x$ (M = Cr, Mn, Ni, Y, and Zn),[2] (Zn, Al)O,[3] (Ba, Sr)PbO_3,[4] and $CaMn_{0.9}In_{0.1}O_3$[5] are 1.3×10^{-4} K^{-1} at 850 °C, 0.43×10^{-4} K^{-1} at 1000 °C, 2.4×10^{-4} K^{-1} at 1000 °C, 2.0×10^{-4} K^{-1} at 400 °C, and 1.4×10^{-4} K^{-1} at 900 °C, respectively. However, these values of Z are smaller than those for alloys and semiconductors.[6−8] Koumoto et al. have reported that the Z for porous Y_2O_3 is 1.0×10^{-3} K^{-1} at 950 K; however, the sample exhibited this fine performance only at very narrow temperature range and in a vacuum.[9] All the oxides above are n-type conductors. The reported p-type thermoelectric materials are (La, Sr)FeO_3 and $NaCo_2O_4$. The value of Z for (La, Sr)FeO_3 is only 0.59×10^{-4} K^{-1} at 1000 °C.[10] $NaCo_2O_4$ with Cu substitution has a high figure of merit up to 8.8×10^{-4} K^{-1} at 300 °C.[11] But its content of sodium, which greatly affects the thermoelectric performance, is difficult to control because of the volatility of sodium.[12] From the viewpoint of conduction mechanism, (Zn, Al)O[3] and (Ba, Sr)PbO_3[4] have a broad-band electronic structure, $CaMn_{0.9}In_{0.1}O_3$,[5] (La, Sr)FeO_3,[10] and $In_2O_3{\cdot}MO_x$ are small polaron hopping conducting oxides, and $NaCo_2O_4$ is a strongly correlated electron system.[13,14] The main challenges for researchers are to find new thermoelectric oxide materials and investigate their conduction mechanism to understand the origin of high thermoelectric performance.

$Ca_3Co_4O_{9+\delta}$ ($\delta = 0.33$) is an old oxide which was synthesized first in 1968.[15] It was found that the XRD spectra of $Ca_3Co_4O_{9+\delta}$ is closely similar with that of $Ca_2Co_2O_5$, and all of the peaks can be indexed on the basis of $Ca_2Co_2O_5$ type structures.[16] We found that it has high electrical conductivity and high Seebeck coefficient at high temperatures, and $Z = 0.67 \times 10^{-4}$ K^{-1} at 700 °C. To enhance its thermoelectric performance and understand its conduction mechanism, we substituted Ca with Bi and obtained a new series of p-type conducting oxides $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.3$, 0.5 and 0.75). $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.5$) has $Z = 2.0 \times 10^{-4}$ K^{-1} at 700 °C.

Experimental Section

$Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.0-0.75$) were prepared from reagent-grade $CaCO_3$, Bi_2O_3 and Co_2O_3 powders in stoichiometric ratio.

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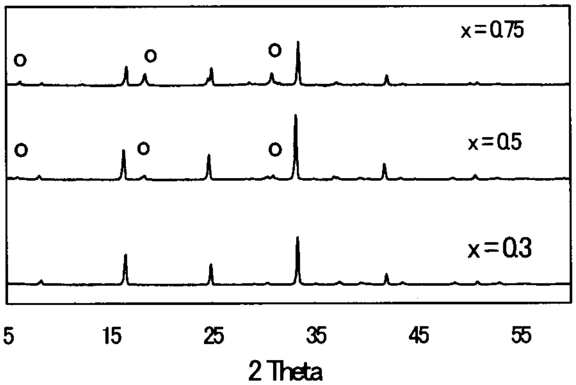

Figure 1. X-ray diffraction spectra of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ (o, second phase).

They were thoroughly mixed by ball milling. The mixture was calcinated at 900 °C in oxygen gas flow for 24 h, ground, and pressed into pellets with a diameter of 18 mm. The pellets for $Ca_3Co_4O_{9+\delta}$ were sintered at 920 °C in oxygen gas flow for 24 h, reground, pressed into pellets, and then sintered at 1100 °C in oxygen gas flow for another 24 h. The pellets for $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.0$, 0.3, 0.5 and 0.75) were sintered at 920 °C in oxygen gas flow for 12 h, reground, pressed into pellets, and then sintered at 960 °C in oxygen gas flow for another 12 h.

X-ray powder diffraction analysis was carried out with a Rigaku diffractometer using Cu Kα ($\lambda = 0.15406$ nm) radiation. Phase composition analysis was made with a Horiba EMAX-5770 EDX system. The specimens for the electric measurements are rectangular bars of 5 × 5 × 15 mm cut out of the sintered pellets. Two Pt−Pt/Rh thermocouples were attached on both end surfaces of the sample bar, and another two Pt electrodes were pasted between them in the standard four-wire arrangement. Electrical conductivity was measured by a dc four-probe technique. For thermoelectromotive force measurement, the temperature gradient in the sample bar was generated by passing cool air in an alumina tube mechanically attached with one end of the sample bar. Thermoelectromotive force measured as a function of temperature difference gave a straight line, and its slope is the Seebeck coefficient. The thermal conductivity was determined from the thermal diffusivity, and the specific heat capacity was measured by laser flash technique.

Results and Discussion

The X-ray power diffraction spectra of oxides $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.3$, 0.5, and 0.75) are presented in Figure 1. The sample with $x = 0.3$ is in single phase with $Ca_2Co_2O_5$- type structure.[16] But several new peaks appear in the XRD spectra of the samples with $x > 0.3$. The new peaks in the sample with $x = 0.5$ are very weak, but those in the sample with $x = 0.75$ are stronger, indicating that the amount of the corresponding phase increase with increasing Bi contents. EDX analysis shows that the amount of the new phase in the samples with $x = 0.5$ and 0.75 is less than 5 and 10%, respectively, and the phase composition is Bi/Ca/Co = 1:1:1 in stoichiometric ratio. Thus, the second phase can be written as $Bi_2Ca_2Co_2O_x$. We analyzed the crystal structure of the 349 phase on the basis of $Ca_2Co_2O_5$-type structure, and the structure parameters are listed in Table 1. All of the oxides crystallized in the orthorhombic system. With increasing Bi content, the parameters a and b increase and c decreases. The cell volume has a maximum for the sample with $x = 0.3$. Because Bi^{3+} is larger than Ca^{2+}, and EDX analysis shows the Bi content in 349 phase increases with increasing x values, the decrease of cell volume perhaps means that some changes in the microstructure or oxygen contents take place when x is larger than 0.3.

Table 1. Structure Parameters of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$

Bi content	system	a (nm)	b (nm)	c (nm)	V (nm^3)
0.0	orthorhombic	1.0893	1.0722	0.7980	0.9320
0.3	orthorhombic	1.0986	1.0801	0.7972	0.9460
0.5	orthorhombic	1.1117	1.0815	0.7696	0.9253
0.75	orthorhombic	1.1157	1.0829	0.7508	0.9071

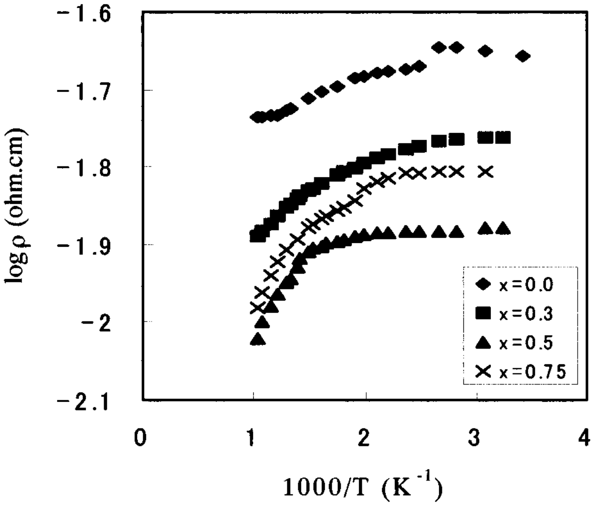

Figure 2. The electrical resistivity vs temperature of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.0-0.75$).

The electrical resistivity of the samples were measured from room temperature to 700 °C. The sample $Ca_3Co_4O_{9+\delta}$ has the lowest electrical resistivity when its pellet was sintered at 1100 °C, but the sintering temperature for the samples with Bi content was 950−960 °C to obtain the lowest resistivity. For easy comparison, the electrical resistivity versus temperature of the samples $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.0-0.75$) sintered at 960 °C is presented in Figure 2. The electrical resistivity of the samples at 700 °C is 18.3 mΩ, cm 12.8 mΩ, cm 9.5, and 10.4 mΩ cm for the sample with $x = 0.0$, 0.3, 0.5, and 0.75, respectively. We measured the electrical resistivity of $Bi_2Ca_2Co_2O_x$ (2202 phase), it is 62 mΩ cm at room temperature and 57 mΩ cm at 700 °C. The increase of electrical resistivity of the sample with $x = 0.75$ can be attributed to the increase of 2202 phase amount.

As shown in Figure 3, the relationship between log ρ and $1/T$ is not linear in the measured temperature range, and the activation energies change with temperatures, indicating that the charge carriers are perhaps thermally activated.[5] Figure 3 presents the plots of log(σT) and $1/T$ for the samples $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.0$, 0.3, and 0.5). In the temperature region above 500 K, the plots for all the three samples lie on straight lines, indicating that the oxides are in hopping conduction.[5,6,17] The electrical conductivity σ of small polaron hopping can be written as

$$\sigma = nea^2(A/T)\exp(-E_h/kT)$$

where n is the carrier concentration, e the electron

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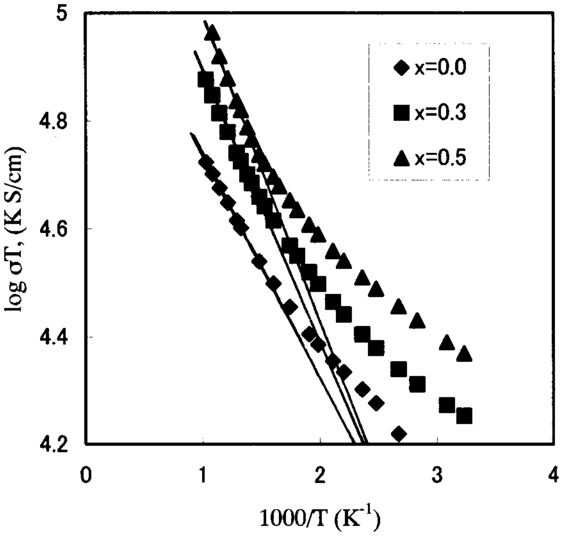

Figure 3. The relation between log (σT) and $1/T$ of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.0-0.5$).

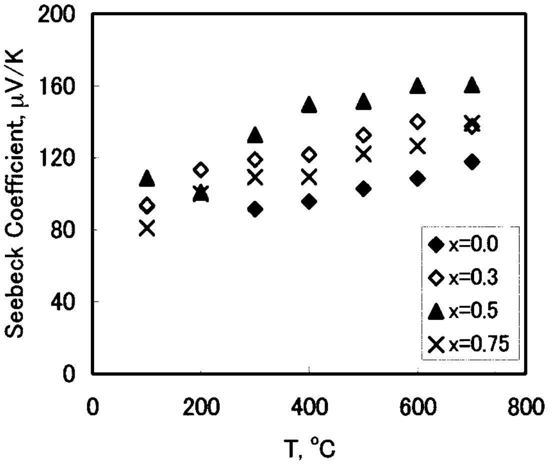

Figure 4. Seebeck coefficients vs temperature of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.0-0.75$).

charge of carrier, a the intersite distance of hopping, E_h the activation energy, and A the preexponential term related to the scattering mechanism.[17] We calculated E_h values of the samples above 500 K, and they are 0.074, 0.086, and 0.116 eV for the sample with $x = 0.0$, 0.3, and 0.5, respectively. The activation energy increases with the increase of Bi contents. If the difference in carrier concentration and in the value of A is sufficiently small, the increase of the electrical conductivity of the samples can be attributed to the increase of the intersite distance of hopping. On the basis of the fact that Bi^{3+} is larger than Ca^{2+}, and the lattice parameters a and b listed in Table 1 increase with increasing Bi contents, it is highly possible that the intersite distance of hopping increase with increasing Bi contents. This implies that the carrier mobility of the samples increase with increasing Bi contents.[5] However, further investigation is needed to measure the carrier concentration, the carrier mobility and the detailed crystal structure to understand the conduction mechanism deeply.

The Seebeck coefficient (S) of oxides $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ versus temperature is presented in Figure 4. The Seebeck coefficient values are all positive, indicating p-type conduction. For all of the samples, the values of Seebeck coefficient increase with increasing temperature over the measured temperature range, and the values above 400 °C are much larger than 100 μV K^{-1}. For example, it is 160 μV K^{-1} at 700 °C for the sample with $x = 0.5$. Similar phenomena has been reported for $LaCrO_3$, (Ca, Bi)MnO_3, (La, Sr)FeO_3, and boron carbides with hopping conduction although the theory of hopping mechanism predicted that Seebeck coefficient is independent of temperature, and the value is around 100 μV K^{-1}.[5,6,18] Meanwhile, the values of Seebeck coefficient increase with increasing Bi content for the samples with $x < 0.5$ but decreases with $x > 0.5$. According to the theory for semiconductors with broad-band electronic structure, the higher carrier mobility leads to larger values of both electrical conductivity and Seebeck coefficient.[19] As discussed above, the substitution of Bi for Ca in the oxides results in the increase of the carrier mobility. This is perhaps the reason that both the Seebeck coefficient and the electrical conductivity increase with increasing Bi contents. The values of power factor, $S^2\sigma$, were calculated, and they are 1.2×10^{-4}, 1.5×10^{-4}, 2.7×10^{-4}, and 1.9×10^{-4} W K^{-2} m^{-1} at 700 °C for the samples with $x = 0.0$, 0.3, 0.5, and 0.75, respectively. The power factor of the second-phase $Ca_2Bi_2Co_2O_x$ appearing in the samples of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.5$ and 0.75) was also measured in our research group; it increases with increasing temperature and reaches 0.28×10^{-4} W K^{-2} m^{-1} at 700 °C. This value is much smaller than those of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$. According to the theoretical analysis by D. J. Bergman et al., the power factor of the composite material of the two thermoelectric materials with similar parameters is entirely determined by the volume fractions, and no enhancement of the power factor is possible.[20] Therefore, the large power factor of the samples $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.5$ and 0.75) is from the (Ca, Bi)$_3Co_4O_{9+\delta}$ phase with $Ca_2Co_2O_5$-type structure.

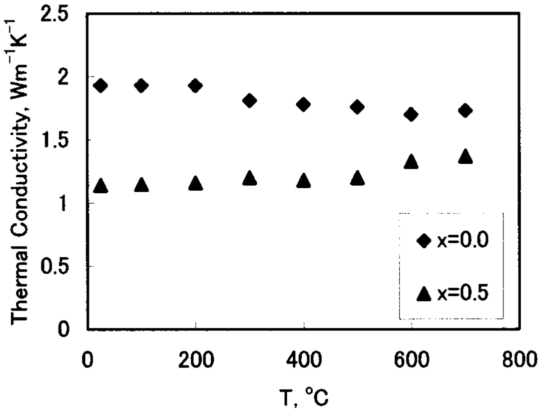

Figure 5. Thermal conductivity vs temperature of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.0$ and 0.5).

Figure 5 presents the thermal conductivity κ of $Ca_3Co_4O_{9+\delta}$ and $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.5$). Because Bi^{3+} is larger and heavier than Ca^{2+}, the substitution of Bi for Ca in $Ca_3Co_4O_{9+\delta}$ reduced its thermal conductivity.[11] At room temperature, the value of thermal conductivity of $Ca_3Co_4O_{9+\delta}$ is 1.70 W K^{-1} m^{-1}, but that of $Ca_{3-x}Bi_xCo_4$-

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$O_{9+\delta}$ ($x = 0.5$) is 1.14 W K^{-1} m^{-1}. As contrasted to that of $Ca_3Co_4O_{9+\delta}$, the thermal conductivity of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.5$) increases slightly with the increasing temperature. The thermal conductivity can be expressed by the sum of a lattice component (κ_l) and an electronic component (κ_e) as $\kappa = \kappa_l + \kappa_e$.[21,22] It is well-known that for semiconductors the electronic contribution in κ is usually lower than 10%. However, because κ_l is proportional to T^{-1} above Debye temperature (this is usually below room temperature), the increase of thermal conductivity of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.5$) should be attributed to the increase of κ_e with increasing temperature. By applying the Wiedemann–Franz law to the electrical conductivity data, the electron thermal conductivity could be estimated as $\kappa_e = L\sigma T$, where L is the Lorenz number (2.44×10^{-8} V^2 K^{-2}), T the temperature and σ the electrical conductivity.[22] The value of κ_e of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.5$) is 0.056 W K^{-1} m^{-1} at room temperature and 0.244 W K^{-1} m^{-1} at 700 °C. It indicates that the increase of κ_e is almost equal to that of κ (it is 1.14 W K^{-1} m^{-1} at room temperature and 1.37 W K^{-1} m^{-1} at 700 °C).

The calculated figure of merit (Z) versus temperature of the oxides $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.0$ and 0.5) is presented in Figure 6. The figure of merit is defined as $Z = S^2\sigma/\kappa$, where S, σ, and κ are Seebeck coefficients, electrical conductivity, and thermal conductivity, respectively. The values of the figure of merit for the two oxides increase with the increasing temperature. This is resulted from the increase in both their Seebeck coefficient and electrical conductivity. The value of figure of merit of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.5$) reaches 2.0×10^{-4} K^{-1} at 700 °C which is about three times of that of $Ca_3Co_4O_{9+\delta}$ and is much larger than that of the commercial high-temperature thermoelectric material $FeSi_2$. It is still increasing toward higher temperature. In fact, $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.5$) is the oxide with the largest figure of merit around 700 °C ever reported to date.[7,8] It can be concluded that $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.5$) is a good oxide material for high-temperature thermoelectric energy conversion.

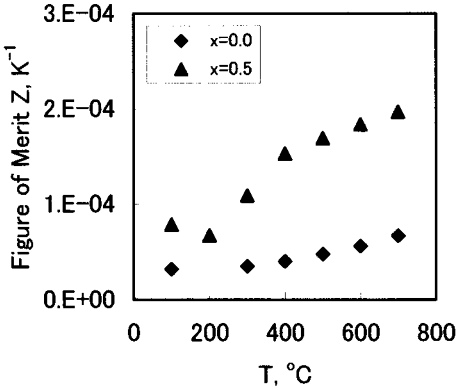

Figure 6. Figure of merit vs temperature of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.0$ and 0.5).

In summary, we have synthesized a new series of oxides $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.0-0.75$), they have high electrical conductivities, large Seebeck coefficients, and low thermal conductivities, indicating that they are promising new thermoelectric materials. For these oxides, the temperature dependence of σ showed a linear relation in plots of $\log(\sigma T)$ versus $1/T$, indicating that the oxides are in hopping conduction. The data of the electrical conductivity, the activation energy E_h, and the crystal structure parameters strongly imply that the carrier mobility of the oxides increases with increasing Bi contents. The Bi substituted sample with $x = 0.5$ has the highest electrical conductivity and largest S in the measured temperature range. Because Bi^{3+} is larger and heavier than Ca^{2+}, the thermal conductivity of $Ca_3Co_4O_{9+\delta}$ was reduced by Bi substitution for Ca. The figure of merit Z of the sample $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ($x = 0.5$) is 2.0×10^{-4} K^{-1} at 700 °C, and ZT reaches 0.2 at this temperature. The value of Z is comparable to the best thermoelectric oxide materials previously reported.

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