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Synthesis and thermoelectric properties of the new oxide ceramics $Ca_{3-x}Sr_xCo_4O_{9+\delta}$ ($x = 0.0$–1.0)

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Abstract

A new series of oxides $Ca_{3-x}Sr_xCo_4O_{9+\delta}$, ($x = 0.0$–$1.0$) were synthesized, and their structures, electrical properties and Seebeck coefficients were measured from room temperature to 700°C. All the oxides have $Ca_2Co_2O_5$ type structure. For all the oxides, both the electrical conductivity and the Seebeck coefficients increase with increasing temperature. The Seebeck coefficients are all positive. The values of Seebeck coefficient decrease with increasing Sr content for the Sr substituted samples. The power factor decreases with increasing Sr content for the samples with $x < 0.5$, but increases for the samples with $x > 0.5$. The Sr substituted sample ($x = 1.0$) has lower thermal conductivity than $Ca_3Co_4O_{9+\delta}$ due to its lower electrical conductivity. At 600°C, the figure of merit for $Ca_2SrCo_4O_{9+\delta}$ is 0.9×10^{-4} K^{-1}, and the value increases toward higher temperature. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

Thermoelectric power generation converts thermal energy directly to electrical energy by the Seebeck effect. The figure of merit Z, defined as $Z = S^2\sigma/\kappa$, where S, σ and κ are the Seebeck coefficient, electrical conductivity, and thermal conductivity respectively, can evaluate the performance of thermoelectric materials. Because these three parameters are dependent on each other and the Seebeck coefficient and electrical conductivity tend to vary in a reciprocal way, it is very difficult to improve the figure of merit dramatically. However, the conversion efficiency of the thermoelectric system can be improved by increasing the temperature difference. High temperature operation is a feasible route to get a high conversion efficiency of thermoelectric system. This is the main reason why more and more attention has been put on oxide ceramics as thermoelectric materials in recent years because oxides are very suitable for long-term use in air at high temperature. Several oxide systems have been investigated, such as $(ZnO)_5In_2O_3$ [1], $In_2O_3 \cdot MO_x$ (M = Cr, Mn, Ni, Zn, Y, Nb, Sn) [2], (Zn,Al)O [3], $(Ba,Sr)PbO_3$ [4] and $(Ca,Ln)MnO_3$ [5], but the values of the figure of merit Z for these systems are smaller than alloys and semiconductors [6]. It has been reported that $NaCo_2O_4$ has a high figure of merit, up to 8.8×10^{-4} K^{-1}, but its application is limited because of the volatility of sodium above 800°C and hygroscopicity in air [7]. For the practical application, further investigations are necessary to find new oxide systems with high thermoelectric performance.

$Ca_3Co_4O_{9+\delta}$ ($\delta = 0.33$) was first synthesized in 1968 [8], and the single crystal of $Ca_3Co_4O_9$ was grown by Woermann in 1970 [9], but no structure analysis and physical property measurement on these oxides have been made up to now. We find that the X-ray powder diffraction patterns of the two oxides are both closely similar with that of $Ca_2Co_2O_5$, which is in layer structure with ordered oxygen vacancies [10]. In this paper, we synthesized a new series of oxide $Ca_{3-x}Sr_xCo_4O_{9+\delta}$ ($x = 0.0$–1.0), and measured their thermoelectric properties.

2. Experimental

$Ca_{3-x}Sr_xCo_4O_{9+\delta}$ ($x = 0.0$–1.0) were prepared from reagent grade $CaCO_3$, $SrCO_3$ and Co_2O_3 powders. They

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were thoroughly mixed by ball milling. The mixture was calcined at 900°C in oxygen gas flow for 24 h, ground, and pressed into pellets with a diameter of 18 mm. The pellets were heated at 920°C in oxygen gas flow for 24 h, and reground, pressed into pellets, and then sintered at 1100°C (for $Ca_3Co_4O_{9+\delta}$) or at 920°C (for the samples with Sr) in flowing oxygen gas for another 24 h.

X-ray powder diffraction analysis was carried out with a Rigaku diffractometer using Cu–K_α (λ = 0.1506 nm) radiation. Silicon powder was used as the internal standard. The specimens for electric measurements were rectangular bars of 5×5×15 mm cut from the sintered pellets. Two Pt–Pt/Rh thermocouples were attached to 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 room temperature air in an alumina tube mechanically attached on one end of the sample bar. Thermoelectromotive force measured as a function of temperature difference gave a straight line, the slope of which is the Seebeck coefficient. The thermal conductivity was determined from the thermal diffusivity and the specific heat capacity measured by laser flash technique.

3. Results and discussion

The X-ray diffraction spectra of $Ca_{3-x}Sr_xCo_4O_{9+\delta}$ show that the oxides are in single phase in the range of x = 0.0–1.0. All the peaks of the oxides can be indexed on the basis of $Ca_2Co_2O_5$-type structure. They crystallize in the orthorhombic system. The X-ray diffraction pattern of $Ca_{3-x}Sr_xCo_4O_{9+\delta}(x=0.3)$ was presented in Fig. 1. $Ca_{3-x}Sr_xCo_4O_{9+\delta}$ can be written as $(Ca, Sr)_{1.5}Co_2O_{4.5+\delta/2}$. It means that 25% of the Ca sites of the $Ca_2Co_2O_5$-type structure are occupied by vacancies in $Ca_{3-x}Sr_xCo_4O_{9+\delta}$. The lattice parameters are listed in Table 1. The lattice volume increases with increasing Sr content. This results from the fact that the Sr ion is larger in diameter than Ca ion. $Ca_3Co_4O_{9+\delta}$ is stable below 1100°C, but the Sr substituted samples have a phase transition from $Ca_2Co_2O_5$-type $(Ca, Sr)_{1.5}Co_2O_{4.5+\delta/2}$ to perovskite-type $(Ca, Sr)CoO_3$ above 1000°C.

The electrical resistivity versus temperature in the range of 20–700°C is presented in Fig. 2. At room temperature, the electrical conductivity of the Sr substituted samples increases slightly with the increasing Sr content because the Sr ion is larger in diameter than Ca ion. However, the electrical conductivity of $Ca_3Co_4O_{9+\delta}$ is higher than all the Sr containing samples. The pellet of $Ca_3Co_4O_{9+\delta}$ is sintered at 1100°C, but those of Sr substituted samples are sintered at 920°C. The higher electrical

Table 1
The lattice parameters of $Ca_{3-x}Sr_xCo_4O_{9+\delta}$

Sr Content	System[a]	A (nm)	B (nm)	C (nm)	V (nm^3)
0.0	Ortho.	1.0893	1.0722	0.7980	0.93202
0.3	Ortho.	1.0906	1.0752	0.8045	0.94338
0.5	Ortho.	1.0904	1.0796	0.8118	0.95565
1.0	Ortho.	1.0943	1.0858	0.8176	0.97146

[a] Orthorhombic system.

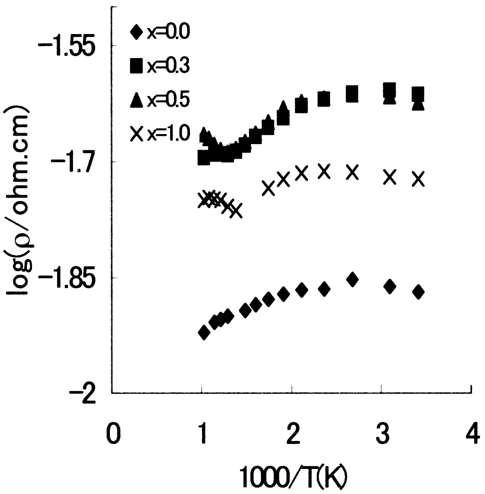

Fig. 2. The electric resistivity vs temperature of $Ca_{3-x}Sr_xCo_4O_{9+\delta}$.

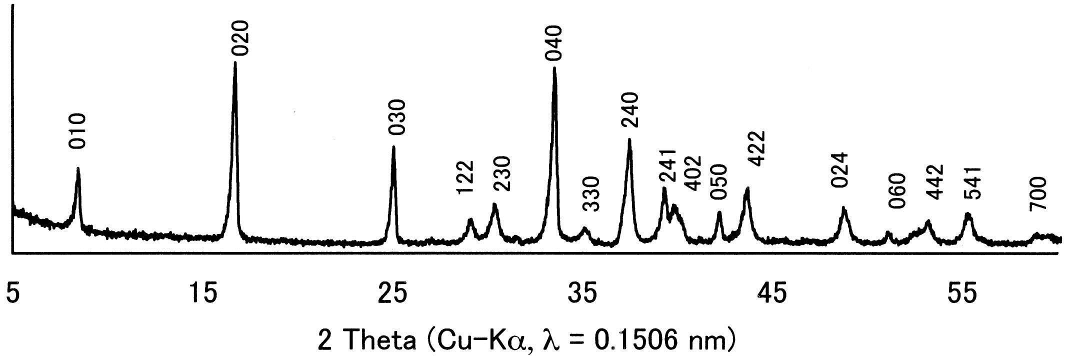

Fig. 1. X-ray diffraction spectra of $Ca_{3-x}Sr_xCo_4O_{9+\delta}(x=0.3)$(Cu-$K_\alpha$ (λ = 0.1506 nm).

conductivity of $Ca_3Co_4O_{9+\delta}$ is perhaps related to its lower intergrain resistivity of the pellet for measurement. The electrical conductivity of $Ca_3Co_4O_{9+\delta}$ increases slightly with increasing temperature, and the value is 83.4 S cm^{-1} at 700°C. A transition of the conducting type from semiconductor to metal was observed above 700 K for the Sr substituted samples with $x = 0.5$ and 1.0. Similar behavior has been reported for other oxides with perovskite type structure, such as $Ln_2Sr Co_2O_7$ and $La_{1-x}Sr_xCoO_3$ [11].

For all the measured oxides, the relationship between log ρ and $1/T$ is not linear in the measured temperature range. But Fig. 3 shows that the plots of log(σ T) vs $1/T$ lie on straight lines below about 150°C and above about 300°C respectively, indicating of the character of hopping conduction mechanism. The electrical conductivity can be expressed as

$$\sigma = (C/T)\exp(-E_a/kT)$$

where E_a is the activation energy of hopping conduction and k is the Boltzmann constant [5]. The slopes of the plots for all the oxides are almost same in the measured temperature range. The E_a values are 0.03 and 0.07 eV below 150°C and above 300°C, respectively.

Fig. 4 presents the values of Seebeck coefficients, S, vs temperature of $Ca_{3-x}Sr_xCo_4O_{9+\delta}$. All the oxides have positive values of S, indicating p-type conduction. For the Sr substituted samples, the values of Seebeck coefficient decrease with increasing Sr content. This tendency is in agreement with that in the electrical conductivity of these oxides which is perhaps related to increases in carrier concentration with the increasing Sr contents. The values of S for $Ca_3Co_4O_{9+\delta}$ increase with increasing temperature, and reach 118 μV K^{-1} at 700°C. But the Seebeck coefficients of the Sr substituted samples peak at 600°C, and the value of S for Sr = 1.0 sample reaches 145 μV K^{-1}. The oxides $Ca_{3-x}Sr_xCo_4O_{9+\delta}$ were prepared in oxygen, and can decompose and change to perovskite-type phase with some cobalt oxide above 1000°C. The appearance of these peaks perhaps has some relation to the change of oxygen contents or the phase transition of $Ca_{3-x}Sr_xCo_4O_{9+\delta}$ in air at high temperature.

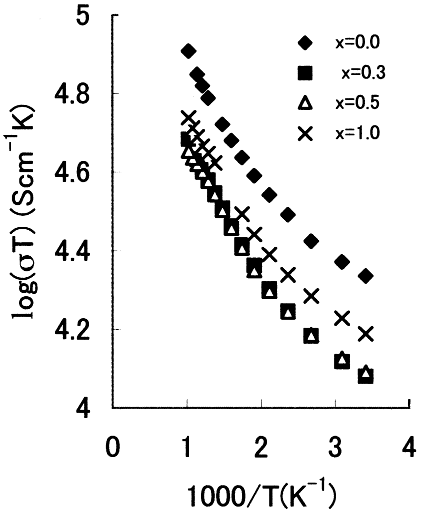

Fig. 3. The electrical properties vs temperature of $Ca_{3-x}Sr_xCo_4O_{9+\delta}$.

The temperature dependence of the power factor, $S^2\sigma$, of the oxides is presented in Fig. 5. The power factor of $Ca_3Co_4O_{9+\delta}$ increases with increasing temperature in the measured temperature range, and the value reaches 1.2×10^{-4} W $K^{-2}m^{-1}$ at 700°C. The power factor of $Ca_{3-x}Sr_xCo_4O_{9+\delta}$ decreases with increasing Sr content for the samples with $x \leqslant 0.5$, but slightly increases with $x > 0.5$. The sample with $x = 1.0$ has the largest power factor at 600°C which is almost equal to that of $Ca_3Co_4O_{9+\delta}$ at 700°C.

The temperature dependence of thermal conductivity of the oxide $Ca_{3-x}Sr_xCo_4O_{9+\delta}$ ($x = 0.0$ and 1.0) is presented in Fig. 6. The substitution of Sr for Ca causes a decrease in the thermal conductivity in the measured temperature range. The value of the thermal conductivity at 300 K is 1.93 W K^{-2} m^{-1} for $x = 0.0$ and

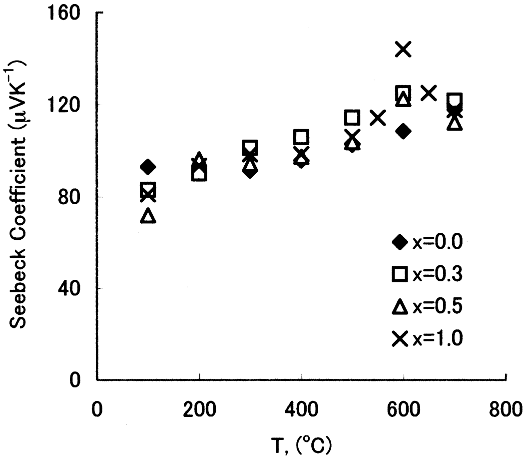

Fig. 4. Seebeck coefficients vs temperature of $Ca_{3-x}Sr_xCo_4O_{9+\delta}$.

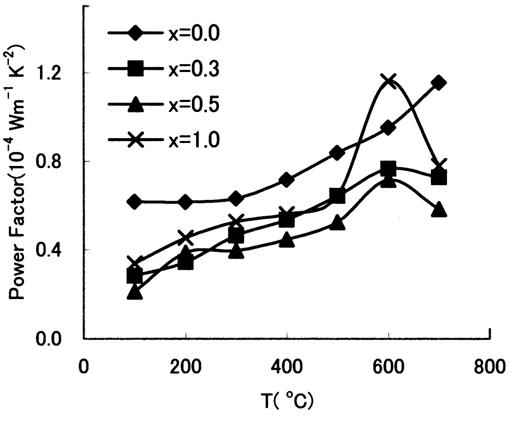

Fig. 5. Power factor vs temperature of $Ca_{3-x}Sr_xCo_4O_{9+\delta}$.

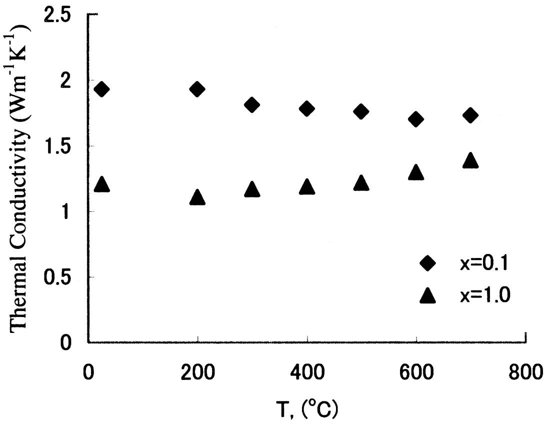

Fig. 6. The thermal conductivity vs temperature of $Ca_{3-x}Sr_xCo_4O_{9+\delta}$.

1.21 W K^{-2} m^{-1} for $x=1.0$. The thermal conductivity of $Ca_{3-x}Sr_xCo_4O_{9+\delta}$ ($x=0.0$) decreases with increasing temperature up to 600°C, where the value is 1.70 Wm^{-1} K^{-1}. At 700°C, the thermal conductivity is 1.72 W m^{-1} K^{-1} which is only a little bigger than that at 600°C. However, the value of the thermal conductivity of the sample with $x=1.0$ increases with increasing temperature, and reaches 1.39 W K^{-2} m^{-1} at 700°C. The thermal conductivity can be expressed by the sum of a lattice component (κ_l) and an electronic component (κ_e) as $\kappa=\kappa_l+\kappa_e$ [4]. Because $\kappa_e=L\sigma T$, where L is the Lorenz number, and the electrical conductivity σ of the sample with $x=1.0$ is smaller than that of the sample with $x=0.0$, the κ_e value of the sample with $x=1.0$ is smaller than that of the sample with $x=0.0$ in the measured temperature range. This is the reason why the Sr doped oxide has lower thermal conductivity, and its κ value increases with the increasing temperature. But the decrease of thermal conductivity of $Ca_3Co_4O_{9+\delta}$ with increasing temperature results from the decrease of the lattice component κ_l which is due to the increase in phonon scattering [4].

The figure of merit Z of the oxides $Ca_{3-x}Sr_xCo_4O_{9+\delta}$ ($x=0.0$ and 1.0) versus temperature is presented in Fig. 7. $Ca_{3-x}Sr_xCo_4O_{9+\delta}$ ($x=1.0$) has the largest value of Z, which is 0.9×10^{-4} K^{-1}, at 600°C, but the value becomes much smaller at 700°C. The values of Z for $Ca_3Co_4O_{9+\delta}$ increases with increasing temperature over the measured temperature range, reaching 0.7×10^{-4} K^{-1} at 700°C, and is still increasing toward higher temperatures. According to the trends shown in Fig. 7, the value of Z for the sample $Ca_3Co_4O_{9+\delta}$ can reach 1.0×10^{-4} K^{-1} at 900–1000°C. The Z-value of $Ca_{3-x}Sr_xCo_4O_{9+\delta}$ ($x=0.0$ and 1.0) is much higher than that of $Ca_{0.9}Bi_{0.1}MnO_3$ and (La,Sr)CrO_3 [5].

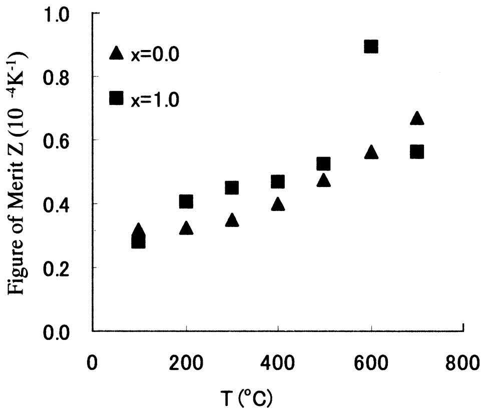

Fig. 7. Figure of merit vs temperature of $Ca_{3-x}Sr_xCo_4O_{9+\delta}$.

4. Conclusions

In summary, we have synthesized a new series of oxide ceramics $Ca_{3-x}Sr_xCo_4O_{9+\delta}$ ($x=0.0$–1.0) with $Ca_2Co_2O_5$ type structure, they have high electrical conductivity, large Seebeck coefficient and low thermal conductivity, showing good thermoelectric performance at high temperature. But the figure of merit is comparatively small for the practical application as the high temperature thermoelectric materials. Further substitution for Ca ion by other elements is required to improve the thermoelectric performance and the phase stability at high temperature.

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