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Synthesis and thermoelectric properties of $(Na_xCa_{1-x})_3Co_4O_9$ ceramics

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Abstract

$(Na_xCa_{1-x})_3Co_4O_9$ ($x = 0.05-0.2$) ceramics with a layered crystal structure were prepared by a sol–gel method followed by a low-temperature sintering procedure. The electrical conductivity and Seebeck coefficient of the complex oxide ceramics were measured from 400 to 900 °C. Their electrical conductivity and power factor increase with increasing temperature, while the thermal conductivity is very weakly dependant on the temperature. Na dopant amount has a remarkable effect on electrical and thermal transport properties. The figure of merit in the ceramic samples is smaller than that of traditional thermoelectric alloys.

Keywords: Electrical conductivity; $(Na,Ca)_3Co_4O_9$; Sol–gel processes; Thermal conductivity; Thermoelectric properties

1. Introduction

The performance of thermoelectric materials is usually evaluated in terms of their thermoelectric figure of merit ZT (dimensionless) defined by

$$ZT = S^2\sigma T/\kappa, \tag{1}$$

where S is the Seebeck coefficent, σ is the electrical conductivity, κ is the total thermal conductivity, and T is the absolute temperature. Since the good thermoelectric performance requires large values of ZT, it is necessary to obtain high S, high σ and low κ. But these three properties are interrelated to each other. For example, an increase in σ ordinarily results in a decrease in S, and high σ leads to high κ. Therefore, it is difficult to get high ZT for the current thermoelectric materials.[1,2] Until now, the doped semiconductors based on bismuth telluride have still been the best known thermoelectric materials with the values of ZT close to one at room temperature among others. Recently, much effort has been made to develop new alloys such as skutterudite (e.g. $CeFe_4Sb_{12}$),[3] $CsBi_4Te_6$,[4] Tl_9BiTe_6,[5] and clathrates (e.g. $Sr_4Eu_4Ga_{16}Ge_{30}$).[6]

On the other hand, oxides have recently been exploited as alternative thermoelectric materials. Because oxides have the merits of long-time use in air at high temperature, they would possibly be regarded as promising thermoelectric materials due to their potential to thermoelectric power generation by waste heat.[7,8] In general, the thermoelectric performance of oxide compounds is always believed to be much lower than that of the semiconductor alloys. However, Terasaki et al.[9] have recently reported a high Seebeck coefficient (100 μV/K at 300 K) and a low resistivity (200 μΩ· cm at 300 K) for $NaCo_2O_4$ single crystal. These data indicate that some semiconducting oxides may be possible for thermoelectric applications. Because of the volatility of sodium above 800 °C and hygroscopicity of $NaCo_2O_4$ in air, its practical application is quite limited. So it is necessary to find new stable oxide systems with good thermoelectric properties.

Among Co-based oxides, crystal structural and physical properties of $Ca_3Co_4O_9$ have been reported recently.[10] This compound is thought to be a misfit-layered oxide consisting of two monoclinic subsystems, namely Ca_2Co_3 layers and CoO_2 layers.[10] The traditional synthesis method of Co-based oxides is solid-state

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processing which is easy to be controlled and operated. But it needs a very long time period to accomplish the synthesis procedure. In this work, we synthesized a series of complex oxides $(Na_xCa_{1-x})_3Co_4O_9$ ($x=0.05-0.2$) by using wet chemical method and measured the thermoelectric properties of polycrystalline $(Na_xCa_{1-x})_3Co_4O_9$ ceramics. Our work shows that $(Na_xCa_{1-x})_3Co_4O_9$ could be promising thermoelectric oxides.

2. Experimental

Oxides $(Na_xCa_{1-x})_3Co_4O_9$ ($x=0.05-0.2$) were synthesized from a stoichiometric mixture of $Ca(NO_3)_2$, $NaNO_3$, and $Co(NO_3)_2$ by sol–gel method. The mixture was thoroughly dissolved in citric acid and heated to a certain temperature with incessant stir. When it formed the gel, it was dried. Then the dried gel was ground and calcined at about 550 °C for an hour in order to remove organic compounds and nitric acid. The powder was reground, pressed into pellets and sintered at 890 °C in air for about 5 h. The sintering temperature was chosen at 890 °C, because $Ca_3Co_4O_9$ is unstable over about 920 °C.

The ceramic microstructure was examined by using X-ray powder diffraction (Cu-K_α radiation) and SEM. Electrical conductivity measurements of the samples (about 10 mm in diameter and 5 mm in thickness) were performed with two-probe method and Pt electrode by applying a DC signal at 400–900 °C in air. Seebeck coefficient values were counted by a graph of the measured thermoelectric voltages (ΔV) versus the temperature differentials (ΔT) across the samples, i.e. $S=\Delta V/\Delta T$. The thermal conductivity measurement was performed using a laser flash technique.

3. Results and discussion

$(Na_xCa_{1-x})_3Co_4O_9$ ($x=0.05-0.2$) powders produced by the sol–gel followed by calcinations method were examined using a X-ray diffractometer. Fig. 1 a shows the X-ray diffraction (XRD) patterns of the calcined powders at different temperatures. The diffraction peaks show that the powder calcined at 350 °C consists of CaO and Co_3O_4 in addition to Na-doped $Ca_3Co_4O_9$. Organic compounds and nitric acid are removed at 350 °C. All of the powders calcined at 400 and 500 °C have the same diffraction peaks as those at 350 °C. However, the XRD patterns of the powder calcined over 600 °C change, and all the peaks correspond to those of $Ca_3Co_4O_9$. The results demonstrate that the samples calcined over 600 °C crystallize in the form of $Ca_3Co_4O_9$-type structure. The particle size of the powder calcined at 600 °C is about 65 nm. The XRD patterns of polycrystalline $(Na_{0.15}Ca_{0.85})_3Co_4O_9$ ceramic is showed in Fig. 1b. All of the exiting peaks can be indexed from the $Ca_3Co_4O_9$-based structure. All XRD patterns for $x=0-0.2$ (not presented here) are the same. $(Na_xCa_{1-x})_3Co_4O_9$ ($x=0.05-0.2$) are shown to be single phase oxide ceramics.

Fig. 2 illustrates a SEM micrograph of a ceramic sample. All of the oxide grains seem to be sheet-like,

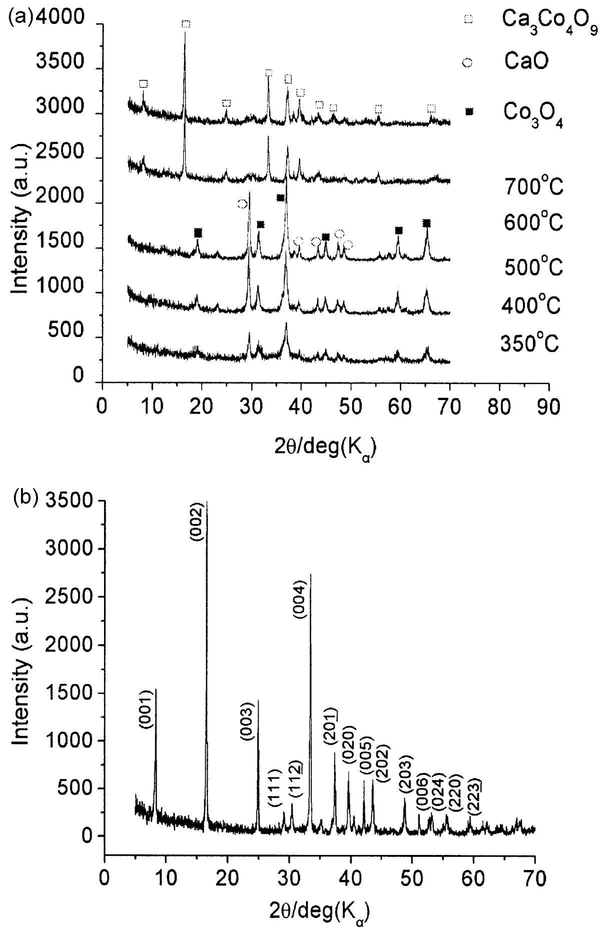

Fig. 1. X-ray diffraction patterns of (a) the powders calcined at temperatures from 350 to 700 °C, and (b) polycrystalline sample sintered at 890 °C, for $(Na_{0.15}Ca_{0.85})_3Co_4O_9$.

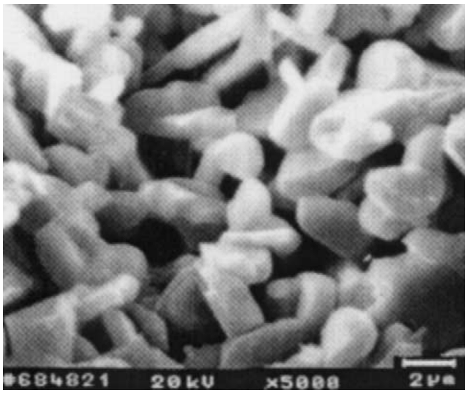

Fig. 2. SEM micrograph of the sintered sample of $(Na_{0.15}Ca_{0.85})_3$-Co_4O_9.

since oxides have layered crystal structure.[10] Though the powder synthesized is nanosized before the sintering process, the grains have grown up to micron level. It can be seen from the micrograph that there are a large numbers of pores in the sample. Because Ca–Co-based oxide is easy to disintegrate at high temperature over 920 °C, it needs to sinter the ceramics at temperatures lower than 920 °C. However, the sintered sample is not much dense on this condition at pressureless sintering. Fig. 3 plots relative densities of the samples as a function of Na dopant content. The relative densities of all pressureless sintered samples are no more than 80% due to low sintering temperature limited by the stability of $Ca_3Co_4O_9$. The pores lead to decrease in both electrical and thermal conductivities of the oxides, and thereby influence the thermoelectric performance of the samples.[11] With the increase in Na-doped amount, the values of the relative densities change slightly. Therefore, in this study, the observed property difference for the samples could not be due to the changes in the microstructure caused by porosity, but mainly the changes in the composition resulting from Na doping.

The measured electrical conductivity versus the temperature is showed in Fig. 4a. The electrical conductivity increases with increasing temperature in the temperature range measured, indicating semiconductor-like conduction behavior. At the same time, the electrical conductivity values of the samples basically increase with increasing Na dopant content at $x \leqslant 0.15$, but slightly drop at $x = 0.2$. It cannot be certain why Na dopant at $x = 0.2$ has led to a little decrease in the electrical conductivity. Accordingly, the linear relationship between $\log(\sigma T)$ and $1/T$ presented in Fig. 4b indicates the character of polaron hopping conductivity mechanism in the oxides. The activation energy values for all

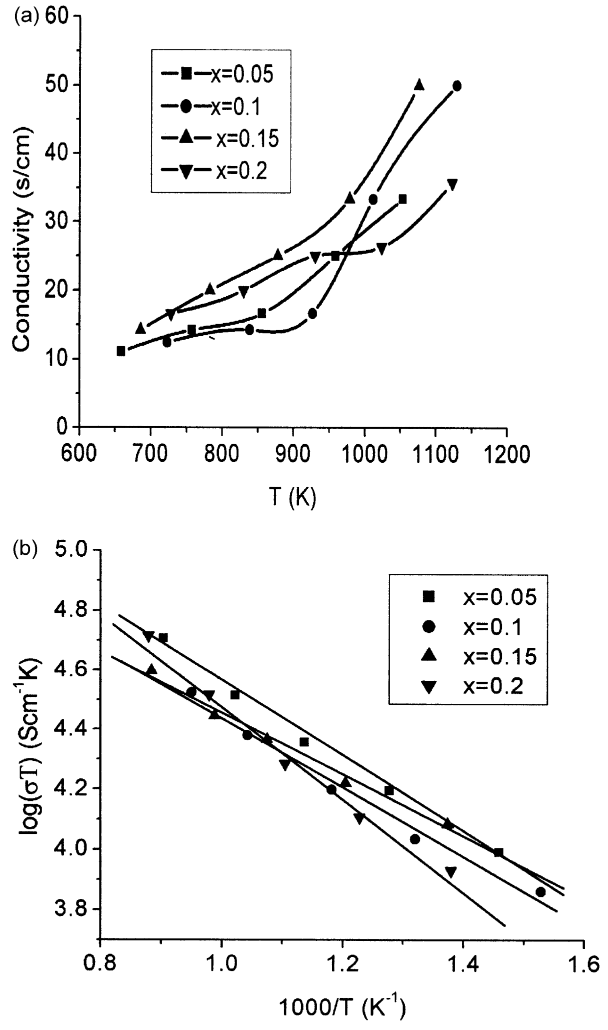

Fig. 4. (a) Temperature dependence of the electrical conductivity σ and (b) $\log(\sigma T)$ versus $1/T$ plots, for $(Na_xCa_{1-x})_3Co_4O_9$.

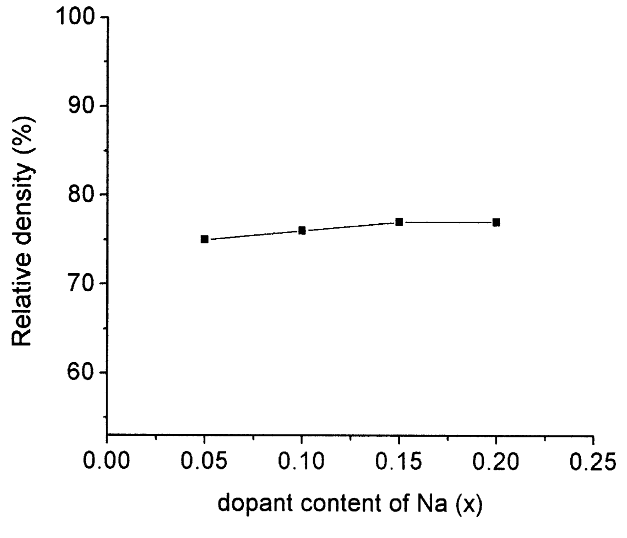

Fig. 3. Relative densities of the samples as a function of Na dopant content.

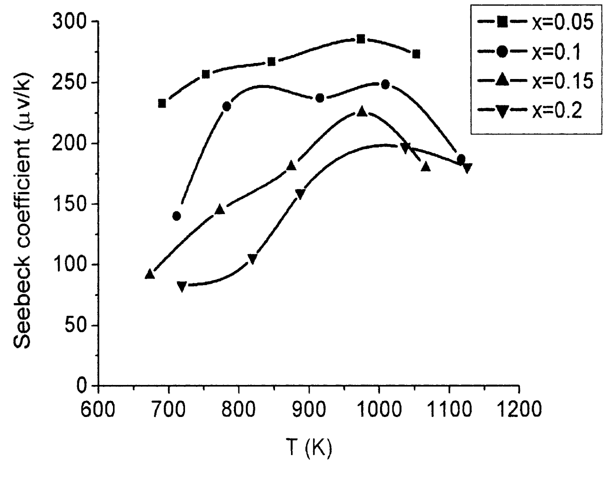

Fig. 5. Seebeck coefficients versus temperature for $(Na_xCa_{1-x})_3Co_4O_9$.

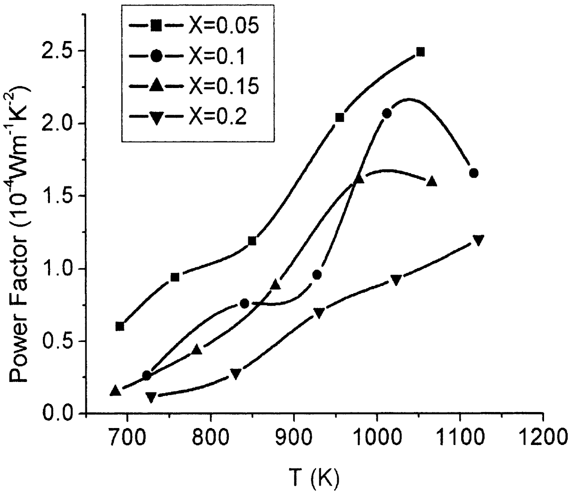

Fig. 6. Power factor versus temperature of $(Na_xCa_{1-x})_3Co_4O_9$.

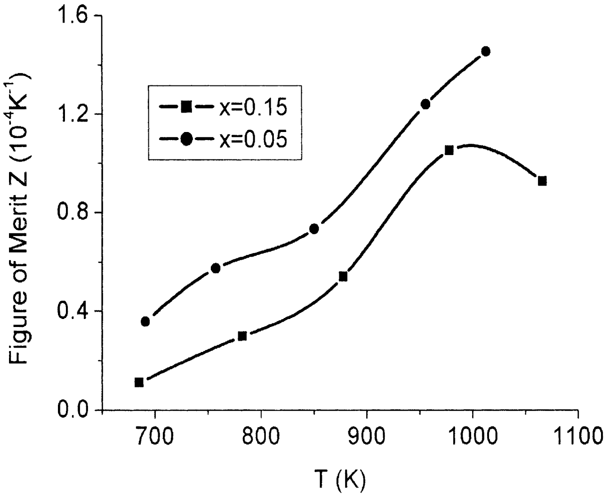

Fig. 8. Temperature dependence of figure of merit for $(Na_xCa_{1-x})_3Co_4O_9$.

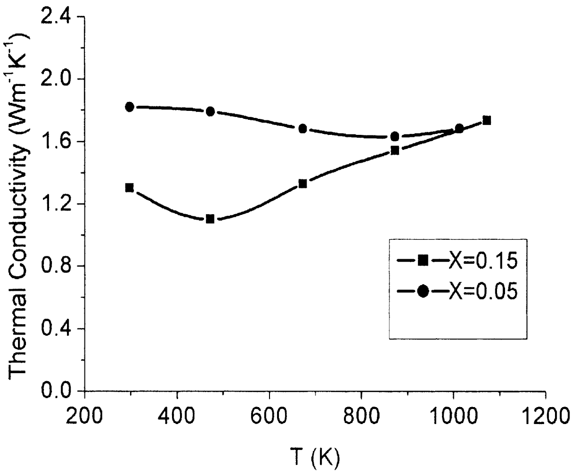

Fig. 7. Thermal conductivity versus temperature of $(Na_xCa_{1-x})_3Co_4O_9$.

the samples with $x=0.05$, 0.1, 0.15, and 0.2 are 0.109, 0.102, 0.089, and 0.114 eV, respectively, which suggests that Na dopant tends to slightly decrease the hopping activation energy at $x \leqslant 0.15$.

The Seebeck coefficients (Fig. 5) of all the samples have positive values, which means that all the oxides are *p*-type semiconductors. It is seen that Seebeck coefficients have the largest values when the temperature exceeds 973 K. The Seebeck coefficients of all the samples increase with increasing temperature, and then decrease beyond 1000 K. With the increase in Na-doped amount, the values of Seebeck coefficients of the samples decrease. The values of S at $x=0.05$ are larger than those of other Na-doped samples. When x value varies from 0.05 to 0.2, the largest value of S decreases from 432 μV/K at 956 K to 197 μV/K at 1037 K. Such a change may be explained from carrier concentration.[9] In the region of $0.05 \leqslant x \leqslant 0.2$, the carrier concentration increases with increasing Na dopant content.

The temperature dependence of the power factor $S^2\sigma$ of these oxide ceramics is showed in Fig. 6. The power factor of the oxides decreases basically with increasing Na doped amount as for the Seebeck coefficients. The values of $S^2\sigma$ of $((Na_xCa_{1-x})_3Co_4O_9$ ($x=0.1$ and 0.15) increase with increasing temperature.

Fig. 7 indicates the temperature dependence of the thermal conductivity for $(Na_xCa_{1-x})_3Co_4O_9$ with $x=0.05$ and 0.15. The thermal conductivity of $(Na_{0.15}Ca_{0.85})_3Co_4O_9$ is lower than that of $(Na_{0.05}Ca_{0.95})_3Co_4O_9$, i.e. the substitution of Na for Ca results in a decrease in the thermal conductivity due to impurity scattering. The thermal conductivity of $(Na_{0.15}Ca_{0.85})_3Co_4O_9$ slightly increases with increasing temperature except around room temperature, and is 1.73 W/mK at 800 °C.

Fig. 8 gives the temperature dependence of the figure of merit Z for the samples $(Na_xCa_{1-x})_3Co_4O_9$ with $x=0.05$ and 0.15. The figure of merit increases with increasing temperature, and reaches 1.2×10^{-4} K^{-1} at 700 °C (i.e. $ZT\sim0.12$). The figure of merit of the oxide ceramics is smaller than that of the traditional thermoelectric alloys such as Bi_2Te_3 and PbTe.[1] The main reason for the low ZT is the low electrical conductivity of the oxide ceramics.

4. Conclusion

$(Na_xCa_{1-x})_3Co_4O_9$ ($x=0.05-0.2$) ceramics have been prepared by a sol–gel procedure followed by low-temperature sintering. The oxide ceramics are *p*-type semiconductors. The Na dopant content has a remarkable effect on electrical and thermal transport properties. The thermoelectric properties measured suggest that Ca–Co-based oxides may be a promising thermoelectric oxides.

The composition and microstructure (e.g. textured ceramics) of the oxide ceramics remains to be optimized to enhance *ZT* of the oxide ceramics.

Acknowledgements

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