

Effect of Gd-doping on thermoelectric properties of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ ceramics

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Abstract A series of $\text{Ca}_{3-x}\text{Gd}_x\text{Co}_4\text{O}_{9+\delta}$ precursor powders were synthesized by the polyacrylamide gel method, and their ceramics were obtained by the Spark Plasma Sintering (SPS). There were lots of defects in the sheet-like grains from SEM and TEM observations. The electrical and the thermal transport properties were obviously affected by the material microstructure. The small polaron hopping conduction mechanism was determined above 600 K, and the hopping activation energy increased with the increase of doping contents. It was found that the Seebeck coefficient and the resistivity of doped samples were markedly enhanced due to the impurity compensation effect, and their thermal conductivities were decreased due to the defects scattering. The maximum figure of merit of $ZT = 0.24$ at 973 K was obtained for $\text{Ca}_{2.7}\text{Gd}_{0.3}\text{Co}_4\text{O}_{9+\delta}$.

Introduction

Thermoelectric generator converts thermal energy directly to electrical energy by thermoelectric materials. The performance of thermoelectric materials is evaluated by the dimensionless figure of merit ZT ($ZT = \alpha^2 \sigma T / \kappa$, where α , σ , κ , and T are the Seebeck coefficient, the electrical

conductivity, the thermal conductivity, and the absolute temperature, respectively). Oxides are very suitable for long-term use at high temperature in air, but the high resistivity impedes their development in thermoelectrics. Several oxide systems have been investigated, such as $(\text{ZnO})_m\text{In}_2\text{O}_3$ [1], $\text{Sr}_{1-x}\text{R}_x\text{TiO}_3$ [2], $\text{CuAl}_{1-x}\text{Mg}_x\text{O}_2$ [3], and $(\text{Sr}_{0.6}\text{Ba}_{0.4})_{1-x}\text{M}_x\text{PbO}_3$ ($M = \text{La}, \text{K}$) [4]. However, the values of ZT of oxides are smaller than semiconductors such as $\text{Ag}(\text{Pb}_{1-y}\text{Sn}_y)_m\text{SbTe}_{m+2}$ [5]. Since Terasaki et al. have reported a high Seebeck coefficient (100 $\mu\text{V}/\text{K}$ at 300 K) and a low-electrical resistivity (0.2 $\text{m}\Omega \text{ cm}$ at 300 K) for a NaCo_2O_4 single crystal, some semiconducting Co-based oxides are possible candidates for thermoelectric applications [6]. Due to the volatility of sodium above 1,073 K and hygroscopicity in air, the practical application of NaCo_2O_4 is quite limited. It is necessary to find other stable oxide systems with good thermoelectric properties. Among Co-based oxides, the crystal structure and the physical properties of $\text{Ca}_3\text{Co}_4\text{O}_9$ have been reported in detail [7]. This compound is thought to be a misfit-layered oxide consisting of two monoclinic subsystems, namely the Ca_2CoO_3 layer and the CoO_2 layer. The Seebeck coefficient and the electrical conductivity are determined by the electronic structure of the CoO_2 layer [8]. The ZT value of the single crystals of $[\text{Ca}_2\text{CoO}_3]_{0.7}[\text{CoO}_2]$ is nearly 0.83, so $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ will be a potential material for thermoelectric applications due to its non-toxicity, low cost, and high-thermoelectric properties [9]. The element doping is an important way to improve thermoelectric properties of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ system [10, 11]. Gd element doping inspires researchers' interest due to its seven unpaired electrons [12]. In this work, we synthesized Gd-doped $\text{Ca}_3\text{Co}_4\text{O}_9$ powders by the polyacrylamide gel method, sintered them by the Spark Plasma Sintering (SPS), and discussed their thermoelectric properties.

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Experimental

The stoichiometric $\text{Ca}(\text{CH}_3\text{COOH})_2 \cdot \text{H}_2\text{O}$, $\text{Co}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$ were dissolved in distilled water. Gd_2O_3 dissolved by HNO_3 was introduced into the above solution. The pH value was controlled at about 6 by using NH_4OH . After completely dissolved, $\text{C}_3\text{H}_5\text{NO}$ (monomer) and $\text{C}_7\text{H}_{10}\text{N}_2\text{O}_2$ (crosslinked agent) were added into the mixture solution. The uniform gel was rapidly gained after $\text{Na}_2\text{S}_2\text{O}_3$ (initiator) was added at 348 K. The moisture of gel was quickly disposed in a microwave oven. Then it was ground and calcined at about 973 K for 3 h in order to remove organic substance. The powders were sintered at 1,023 K for 5 min under 50 MPa by using the SPS.

The $\text{Ca}_{3-x}\text{Gd}_x\text{Co}_4\text{O}_{9+\delta}$ powders were characterized by X ray diffraction (XRD) using a rigaku diffractometer with $\text{Cu K}\alpha$ radiation. The relative densities of all the ceramics were evaluated by the Archimedes method. The Seebeck coefficients were calculated from the thermoelectric voltage and the temperature difference between the two ends of samples. The resistivity was measured by a dc four probes method from 373 K to 1,073 K in air. The cylindrical test samples ($\Phi = 12.72$ mm, $h = 2$ mm) were prepared for measuring thermal conductivity. The thermal conductivity is determined from the specific heat capacity and the thermal diffusivity measured by laser flash technique (METZSCH LFA427) from 373 K to 723 K. The thermal diffusivity is determined by the half rise time, and the specific heat capacity is gained by the comparative method. Percentage of error in experimental measurement of resistivity, thermal conductivity, Seebeck coefficient is 5%.

Results and discussion

Figure 1 shows the XRD patterns of the $\text{Ca}_{3-x}\text{Gd}_x\text{Co}_4\text{O}_{9+\delta}$ powders. All the diffraction peaks of samples are identical to the standard JCPDS card 21-0139 of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$. The diffraction peak (002) shifts from a high angle to a low angle due to the introduced Gd in the inset of Fig. 1. These indicate that Gd element was doped into the lattice of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ and single phase compounds were obtained.

Figure 2 shows the SEM images of the $\text{Ca}_{3-x}\text{Gd}_x\text{Co}_4\text{O}_{9+\delta}$ samples. The micrographs of all the samples fundamentally coincide. The sheet-like grains were orientationally aligned to some degree. The result indicates Gd-doping has no influence on the material micrographs. It is also seen from Fig. 2 that the alveolate micrograph is another character of the samples. Figure 3 shows TEM micrographs and electron diffraction pattern of a $\text{Ca}_{2.7}\text{Gd}_{0.3}\text{Co}_4\text{O}_{9+\delta}$ sample. There are not other phase and non-crystal layer among grains, but there are lots of defects in grains.

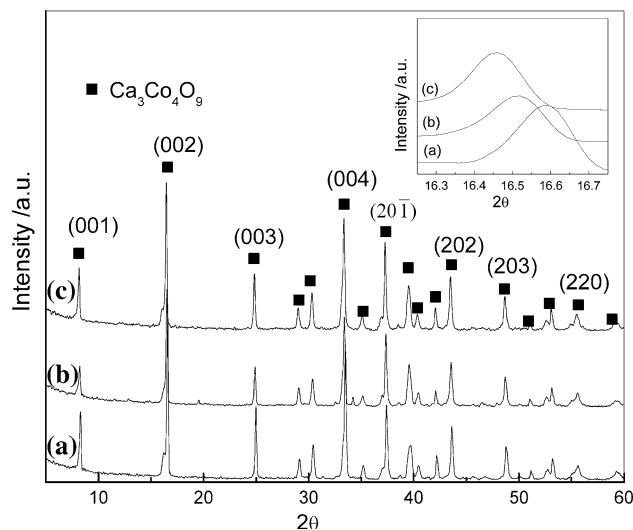


Fig. 1 XRD patterns of $\text{Ca}_{3-x}\text{Gd}_x\text{Co}_4\text{O}_{9+\delta}$ (a) $x = 0$ (b) $x = 0.15$, (c) $x = 0.3$

Figure 4 shows the electrical resistivity of the $\text{Ca}_{3-x}\text{Gd}_x\text{Co}_4\text{O}_{9+\delta}$ samples. The resistivity of the $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ sample shows the positive temperature coefficient below 500 K and the negative temperature coefficient above 500 K. This phenomenon is explained by the spin state change of the material [13]. But the resistivities of the doped $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ samples only show the negative temperature coefficient. The results are in agreement with Wang et al. [14]. This reason need to be studied further. The electrical resistivities of Gd-doped samples obviously increase in comparison with that of the $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ sample. The donor energy level is introduced due to the Gd-doping, and the impurity compensation effect decreases the concentration of hole and increases the resistivity. The resistivity of $\text{Ca}_{2.7}\text{Gd}_{0.3}\text{Co}_4\text{O}_{9+\delta}$ reaches 7.8 $\text{m}\Omega\text{ cm}$ at 1,073 K.

As shown in Fig. 5, The linear relationship between $\ln(\sigma T)$ and $1/T$ in the temperature range above 600 K indicates the hopping conduction mechanism of the materials [15]. The electrical conductivity of the small polaron hopping conduction mechanism can be written as

$$\sigma = nea^2(A/T) \exp(-E_h/\kappa_B T) \quad (1)$$

where n , e , a , E_h , and A are the carrier concentration, the charge of carrier, the intersite distance of hopping, the activation energy, and the pre-exponential term related to the scattering mechanism, respectively.

Through linear fit above 600 K, the hopping activation energy of doped samples increase with the increase of the doped concentration. According to the results from Wang et al., the carriers hop between Co^{3+} and Co^{4+} in the CoO_2 layer for $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ system [16]. The intersite distance of hopping depends directly on proportion between Co^{3+} and Co^{4+} in the CoO_2 layer. The Gd-doping results in decrease

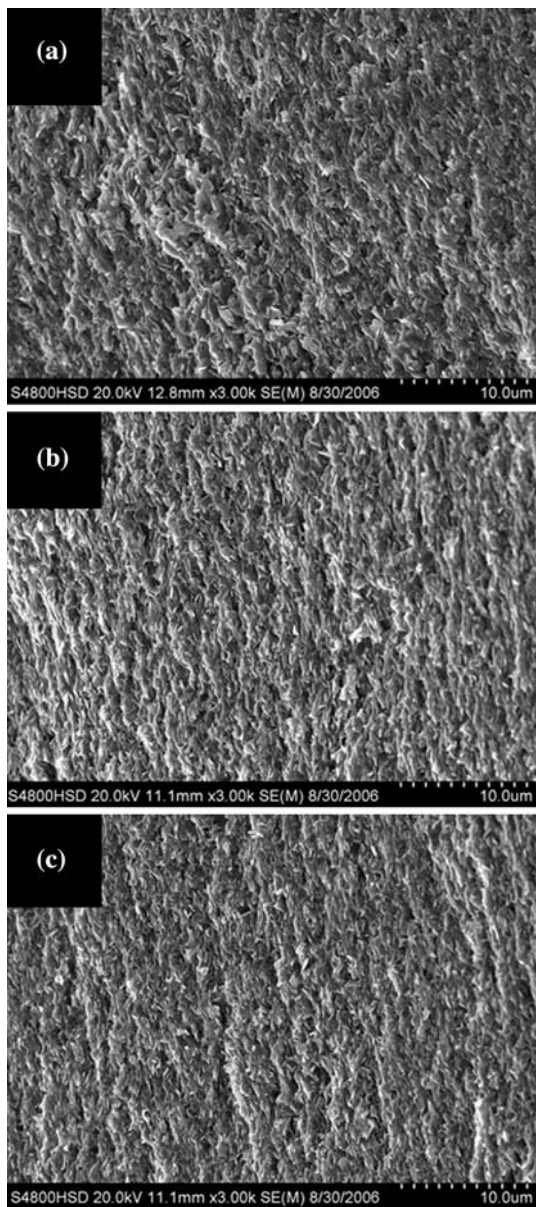


Fig. 2 SEM images of $\text{Ca}_{3-x}\text{Gd}_x\text{Co}_4\text{O}_{9+\delta}$ (a) $x = 0$ (b) $x = 0.15$, (c) $x = 0.3$

of Co^{4+} concentration, and then enhances hopping activation energy.

The positive values of the Seebeck coefficients, as shown in Fig. 6, mean that the major charge carriers in the $\text{Ca}_{3-x}\text{Gd}_x\text{Co}_4\text{O}_{9+\delta}$ ceramics are holes. As the temperature increases from 373 K to 1,050 K, the Seebeck coefficient linearly increases. It is also seen from Fig. 6 that the Seebeck coefficient is enhanced by Gd-doping, the maximum value of 182uV/K is gained for the $\text{Ca}_{2.7}\text{Gd}_{0.3}\text{Co}_4\text{O}_{9+\delta}$ ceramic at 1,073 K.

According to W. Koshibae’s result, the Seebeck coefficient of misfit-layered cobaltite could be ascribed to the degeneracy of the Co^{3+} and Co^{4+} low-spin electronic

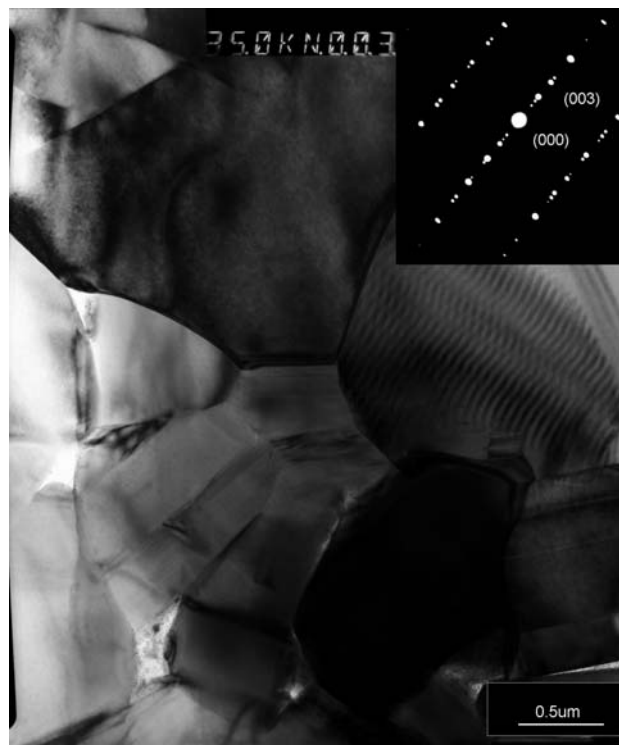


Fig. 3 TEM micrographs and electron diffraction pattern of $\text{Ca}_{2.7}\text{Gd}_{0.3}\text{Co}_4\text{O}_{9+\delta}$ sintered by SPS

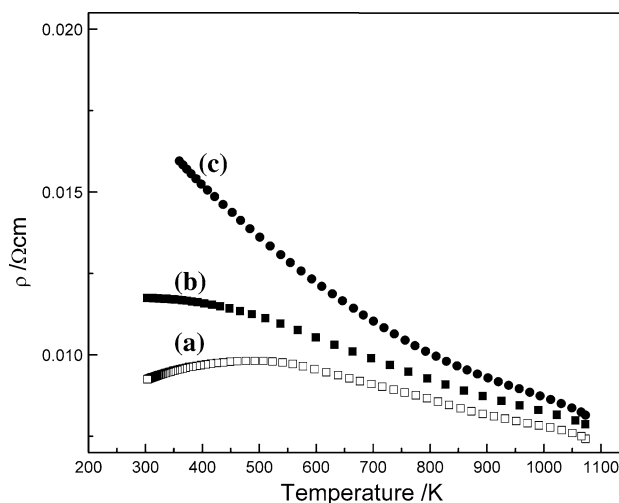


Fig. 4 Temperature dependence of electrical resistivity of $\text{Ca}_{3-x}\text{Gd}_x\text{Co}_4\text{O}_{9+\delta}$ (a) $x = 0$ (b) $x = 0.15$, (c) $x = 0.3$

states together with strong electron correlation [8]. According to their calculation,

$$\alpha_{ab} = \frac{k_B}{e} \ln\left(\frac{g_3}{g_4} \frac{x}{1-x}\right) \tag{2}$$

where k_B is the Boltzmann constant, g_3 , g_4 is the configuration numbers of Co^{3+} , Co^{4+} ions, respectively, x is the Co^{4+} concentration, e is the charge of an electron.

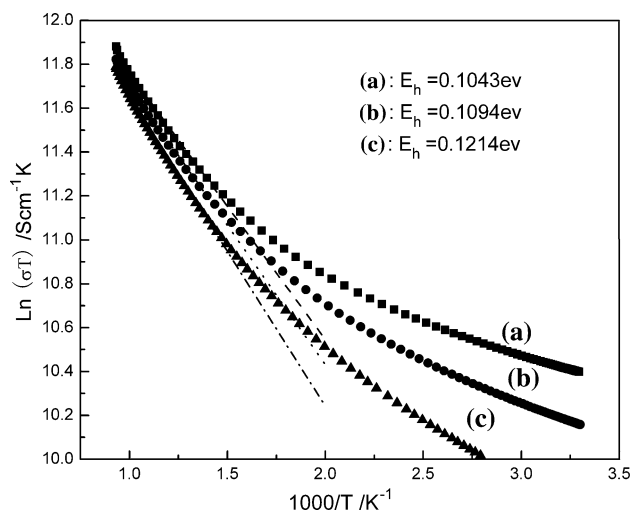


Fig. 5 $\ln(\sigma T)$ versus $1/T$ plots for $\text{Ca}_{3-x}\text{Gd}_x\text{Co}_4\text{O}_{9+\delta}$ (a) $x = 0$ (b) $x = 0.15$, (c) $x = 0.3$

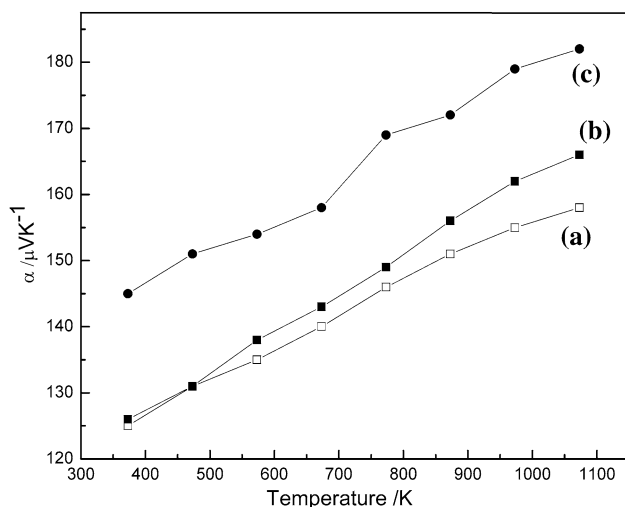


Fig. 6 Temperature dependence of thermoelectric coefficients of $\text{Ca}_{3-x}\text{Gd}_x\text{Co}_4\text{O}_{9+\delta}$ (a) $x = 0$ (b) $x = 0.15$, (c) $x = 0.3$

The higher Seebeck coefficient of Gd-doped samples may result from two factors. One is the reduction of carriers concentration, another is the change of spin state of Co ion in CoO_2 layers [17].

The thermal conductivities of $\text{Ca}_{3-x}\text{Gd}_x\text{Co}_4\text{O}_{9+\delta}$ ceramics are shown in Fig. 7. The thermal conductivities of samples decrease with the increase of temperature and doping concentrations. Great fall of thermal conductivity in doped samples mainly comes from increase of impurity scattering. The thermal conductivity of $\text{Ca}_{2.7}\text{Gd}_{0.3}\text{Co}_4\text{O}_{9+\delta}$ ceramic is $1.4 \text{ W m}^{-1} \text{ K}^{-1}$, the low value maybe attributes to the alveolate micrograph and the defects in grains.

According to $ZT = \alpha^2 T / \rho \kappa$, the ZT values of Gd-doped samples are shown in Fig. 8. The thermoelectric properties of doped samples are obviously enhanced. The maximum

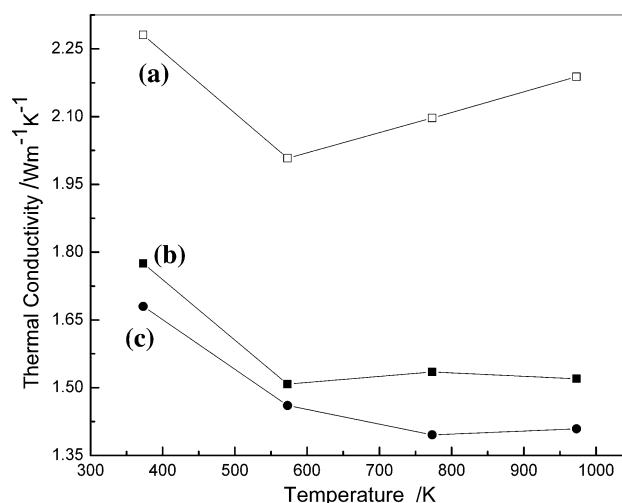


Fig. 7 Temperature dependence of thermal conductivity of $\text{Ca}_{3-x}\text{Gd}_x\text{Co}_4\text{O}_{9+\delta}$ (a) $x = 0$ (b) $x = 0.15$, (c) $x = 0.3$

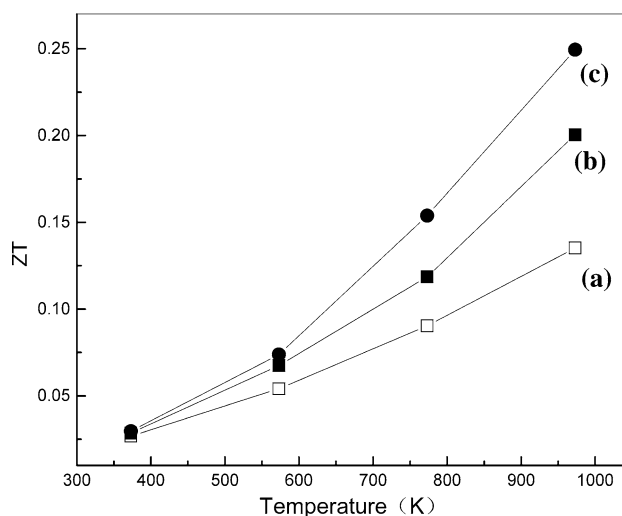


Fig. 8 Temperature dependence of ZT of $\text{Ca}_{3-x}\text{Gd}_x\text{Co}_4\text{O}_{9+\delta}$ (a) $x = 0$ (b) $x = 0.15$, (c) $x = 0.3$

figure of merit of $ZT = 0.24$ at 973 K is obtained for $\text{Ca}_{2.7}\text{Gd}_{0.3}\text{Co}_4\text{O}_{9+\delta}$.

Conclusion

The $\text{Ca}_{3-x}\text{Gd}_x\text{Co}_4\text{O}_{9+\delta}$ precursor powders were synthesized at 973 K by using the polyacrylamide gel method. There was the higher resistivity for Gd-doped samples due to impurity compensation effect. The higher hopping activation energy in doped samples attributed to the bigger intersite distance of hopping. The Seebeck coefficients of doped samples were enhanced, while their thermal conductivities were obviously reduced. The maximum figure

of merit of $ZT = 0.24$ at 973 K was obtained for $\text{Ca}_{2.7}\text{Gd}_{0.3}\text{Co}_4\text{O}_{9+\delta}$.

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