

Synthesis and high temperature thermoelectric properties of $\text{Ca}_{3.0-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$

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Abstract

New polycrystalline $\text{Ca}_{3.0-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$ ($x = 0.0, 0.1, 0.2, 0.3$; $y = 0.0, 0.1$) samples were prepared using a sol–gel method followed by hot-pressing sintering technique. Powder X-ray diffraction analysis showed that all the samples were single phase. The high-temperature (350 to 1073 K) thermoelectric properties of the samples were investigated. The substitution of Nd^{3+} for $\text{Ca}_{2.9}\text{Na}_{0.1}\text{Co}_4\text{O}_{9+\delta}$ resulted in the decrease of the electrical conductivity, thermal conductivity and the increase of the Seebeck coefficient. The electrical conduction was dominated by the small polaron hopping conduction mechanism in the temperature region above 550 K. Compared with Nd or Na single substitution, Nd and Na double substitution can further reduce thermal conductivity of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$. The value of ZT reaches 0.29 for $\text{Ca}_{2.6}\text{Nd}_{0.3}\text{Na}_{0.1}\text{Co}_4\text{O}_{9+\delta}$ at 1073 K.

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1. Introduction

Recently, transition-metal oxides have attracted much interest as promising thermoelectric materials, which are used in clean energy conversion systems. The conversion efficiency of a thermoelectric material is a function of the dimensionless figure of merit ZT ($ZT = S^2\sigma T/\kappa$, where S , σ , κ and T are Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively). As a result, a good thermoelectric material should simultaneously exhibit large S , large σ and small κ , which requires $ZT \geq 1$ for practical use. Thermoelectric conductors, such as Bi–Te system [1], have a high $ZT > 1$ at room temperature, but their instability at high temperatures in air limits their applications. Most oxides with high stability in air at high temperatures are unsuitable for thermoelectric applications because of their low electrical conductivity. In 1997, Terasaki et al. [2] reported that NaCo_2O_4 (whose structure consists of stacking CoO_2 layers

of CdI_2 type with partially filled Na layers) have a large S (100 $\mu\text{V}/\text{K}$ at 300 K) and relative high conductivity (2×10^4 S/m at 300 K). Recently, many oxides have been studied extensively as n-type or p-type candidates [3–11].

The structure of the cobalt $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ was found to be similar to NaCo_2O_4 . The misfit structure is also built up of CdI_2 -type CoO_2 layers which are stacked up with rock salt-type layers. The $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ has been reported [12] to show large Seebeck coefficient and considered to be a good candidate for a thermoelectric material. However, at present the ZT value of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ is too low to be used practically. In order to improve the thermoelectric performance of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$, one effective approach is partial substitution of the Ca site by other elements [13–21]. For instance, the substitution of the heavy rare earth metal Eu for Ca leads to an increase of the Seebeck coefficient and a decrease of thermal conductivity at the same time [13]. The substitution of Na for Ca results in an increase of electrical conductivity due to the increase of carrier concentration [18]. In this paper, we report improved thermoelectric performance of $\text{Ca}_{3.0-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$ by partial substitution of Nd and Na co-doped for Ca, for the first time to our knowledge.

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2. Experimental

Polycrystalline samples $\text{Ca}_{3.0-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$ ($x = 0.0, 0.1, 0.2, 0.3$; $y = 0.0, 0.1$) were prepared using the sol–gel method. Stoichiometric mixtures of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.8 wt%), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9 wt%) and NaNO_3 (99.9 wt%) were thoroughly dissolved in a certain amount of citric acid solution under ultrasonic agitation for 30 min. Nd_2O_3 (99.99 wt%) treated with nitric acid was added to the above solution drop by drop (the molar ratio of metal cations to citric acid in the solution is 1:1.3). The sol solution was heated to form purple gel at 343 K with continuous stirring. The gel was dried in an oven at 373 K for 12 h in air and then was burnt by a self-spread process. The burnt remains were calcined at 823 K for one hour to remove excess organic compounds. The powders were reground then sintered at 1123 K for 6 h in air. To obtain highly dense samples, the powders were pressed and hot-press sintered at 1173 K for 10 h in air under a pressure of about 12 Mpa.

X-ray powder diffraction (XRD) data were collected on a Rigaku D/max-2000 diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm). The chemical composition was determined by X-ray fluorescence spectroscopy (Axiso pw 4400). The relative densities of all the samples were measured using the Archimedes' method. The electrical conductivity of the bar-shaped samples ($15 \times 3 \times 3$ mm³) was measured using the standard four probe method with Pt electrodes by applying a DC signal from 350 to 1073 K in air. Thermoelectromotive force measured as a function of temperature 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 measured by a laser flash technique (NETZSCH LFA427).

3. Result and discussions

Fig. 1 shows the XRD patterns of $\text{Ca}_{3.0-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$ ($x = 0.0, 0.1, 0.2, 0.3$; $y = 0.0, 0.1$). The XRD peaks for all the samples can be indexed on the basis of the standard JCPDS card (21-139) of $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$, indicating the formation of single-phase compound at room temperature. The cell parameters were determined by the Rietveld refinement method based on X-ray powder diffraction, using the GSAS&EXPGUI programs. As listed in Table 1, both lattice parameters a and b_1 for the $\text{Ca}_{2.6}\text{Nd}_{0.3}\text{Na}_{0.1}\text{Co}_4\text{O}_{9+\delta}$ sample are larger than those of the $\text{Ca}_{2.7}\text{Nd}_{0.3}\text{Co}_4\text{O}_{9+\delta}$ sample. With the increase of the amount of Nd-doping, the lattice parameters are almost unchanged because the ionic radius of Nd^{3+} (0.100 nm) is very close to that of Ca^{2+} (0.099 nm).

X-ray fluorescence spectroscopy was used to determine the chemical composition of the prepared samples. The results show that the ratio of Ca (and/or Nd, Na), Co and O in all the samples is around 3.00:3.97:9.22. The oxygen nonstoichiometry was caused by the oxygen-rich atmosphere in air. For the $\text{Ca}_{2.55}\text{Nd}_{0.3}\text{Na}_{0.15}\text{Co}_4\text{O}_{9+\delta}$ sample, the composition of the matrix is $\text{Ca}/\text{Nd}/\text{Na} = 2.55:0.30:0.14$, which matches the nominal composition 2.55: 0.3: 0.15 well.

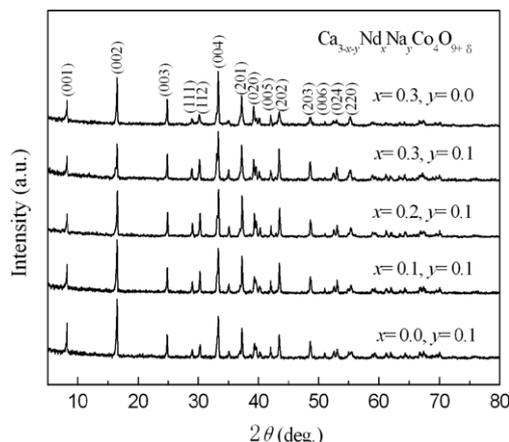


Fig. 1. Powder X-ray diffraction patterns for $\text{Ca}_{3.0-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$ ($x = 0.0, 0.1, 0.2, 0.3$; $y = 0.0, 0.1$) polycrystalline samples.

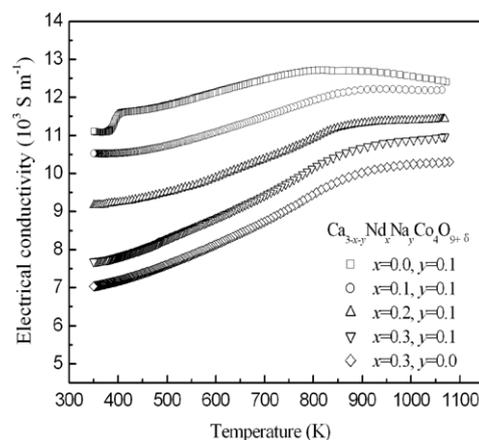


Fig. 2. Temperature dependence of electrical conductivity for $\text{Ca}_{3.0-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$ ($x = 0.0, 0.1, 0.2, 0.3$; $y = 0.0, 0.1$) polycrystalline samples.

The bulk densities of the $\text{Ca}_{3-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$ ($x = 0.0, 0.1, 0.2, 0.3$; $y = 0.0, 0.1$) samples are shown in Table 1. The relative densities of all the samples are around 96%. Therefore, the observed difference in thermoelectric properties discussed in the following discussions mainly result from the composition change caused by Nd and/or Na doping.

Fig. 2 presents the temperature dependence of electrical conductivity (σ) for the as-synthesized samples in the temperature range from 350 to 1173 K. The curves of σ versus T for all the Nd-contained samples show semi-conducting-like behavior above 400 K. The values of σ decrease with increasing Nd-doping amount but increase with increasing Na-doping amount, which could be attributed to the decrease/increase of carrier concentration caused by substitution of $\text{Nd}^{3+}/\text{Na}^+$ for Ca^{2+} . For $\text{Ca}_{2.9}\text{Na}_{0.1}\text{Co}_4\text{O}_{9+\delta}$ sample, there is an obviously abrupt change around 390 K, where the electrical conductivity decrease below 390 K, then increases dramatically above 390 K. This interesting change may be caused by a spin-state transition from low spin (LS, $t_{2g}^3 e_g^2$) to intermediate spin (IS, $t_{2g}^5 e_g^0$) for Co^{4+} and Co^{3+} [12]. Similar phenomenon was also found in the Ag substituted $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ system [21].

Fig. 3 shows the plots of $\log(\sigma T)$ versus $1/T$ for all the samples. The relationship between $\log(\sigma T)$ and $1/T$

Table 1

Lattice parameters a , b_1^a , c , β and relative density for $\text{Ca}_{3-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$ ($x = 0.0, 0.1, 0.2, 0.3$; $y = 0.0, 0.1$)

Samples	Lattice parameters				Relative density (%)
	a (nm)	b_1^a (nm)	c (nm)	β ($^\circ$)	
$\text{Ca}_{2.9}\text{Na}_{0.1}\text{Co}_4\text{O}_{9+\delta}$	0.4840	0.4571	0.1088	98.39	0.2398
$\text{Ca}_{2.8}\text{Nd}_{0.1}\text{Na}_{0.1}\text{Co}_4\text{O}_{9+\delta}$	0.4839	0.4572	0.1087	98.41	0.2400
$\text{Ca}_{2.7}\text{Nd}_{0.2}\text{Na}_{0.1}\text{Co}_4\text{O}_{9+\delta}$	0.4840	0.4572	0.1089	98.40	0.2401
$\text{Ca}_{2.6}\text{Nd}_{0.3}\text{Na}_{0.1}\text{Co}_4\text{O}_{9+\delta}$	0.4841	0.4571	0.1087	98.40	0.2401
$\text{Ca}_{2.7}\text{Nd}_{0.3}\text{Co}_4\text{O}_{9+\delta}$	0.4844	0.4579	0.1088	98.44	0.2405

^a Here b_1 is the b -axis length of the rock salt-type CaCoO_3 subsystem [12].

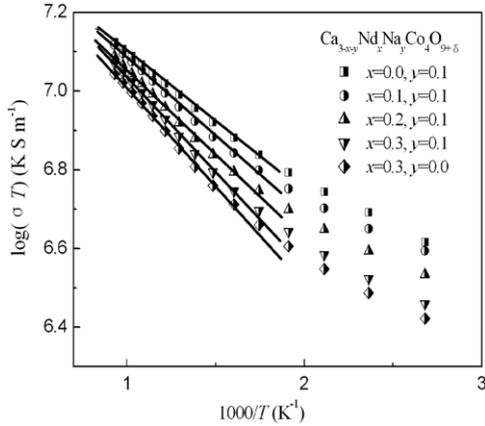


Fig. 3. The relation between $\log(\sigma T)$ and $1/T$ for $\text{Ca}_{3.0-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$ ($x = 0.0, 0.1, 0.2, 0.3$; $y = 0.0, 0.1$) polycrystalline samples.

is non-linear in the whole temperature range measured, but the plots of $\log(\sigma T)$ vs $1/T$ lie on straight lines above 550 K, indicating small polaron hopping conduction (SPHC) mechanism at high temperature. In the frame of the SPHC mechanism, electrical conductivity can be given as: $\sigma = ne^2(A/T) \exp(-E_h/kT)$ [22], where n , e , a , k , E_h and A are the carrier concentration, electron charge of carrier, intersite distance of hopping, Boltzmann constant, activation energy, and a pre-exponential term related to the scattering mechanism, respectively. The values of activation energies (calculated from the slopes of the plots) for $x = 0.0, 0.1, 0.2, 0.3$; $y = 0.1$ and $x = 0.3$; $y = 0.0$ samples are 0.084, 0.088, 0.090, 0.094, 0.096 eV, respectively. It is noted that the difference of activation energies is not larger than 0.02 eV, indicating that the transport mechanism was not changed by Nd and/or Na doping. In the layered $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ system, the CoO_2 layer is responsible for the electrical conduction and the Ca_2CoO_3 layer is responsible for balancing the charge and to stabilizing the structure [21]. In our experiment, the conduction path was not disturbed by substitution of Nd and/or Na for Ca. Therefore, the transport mechanism was not changed.

Fig. 4 presents the temperature dependence of the Seebeck coefficient (S) for $\text{Ca}_{3.0-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$ ($x = 0.0, 0.1, 0.2, 0.3$; $y = 0.0, 0.1$). All the values are positive, indicating that the samples are p -type materials. The values of S increase with increasing temperature over the whole temperature range measured and increase/decrease with increasing Nd/Na-doping amount. Wang et al. [13] explained the effect of Eu substitution on the Seebeck coefficient for $\text{Ca}_{3-x}\text{Eu}_x\text{Co}_4\text{O}_{9+\delta}$ using the

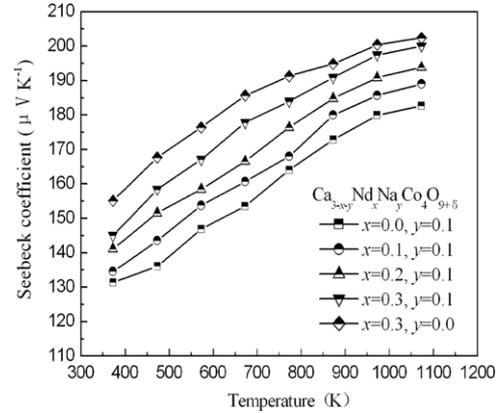


Fig. 4. Temperature dependence of Seebeck coefficient for $\text{Ca}_{3.0-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$ ($x = 0.0, 0.1, 0.2, 0.3$; $y = 0.0, 0.1$) polycrystalline samples.

modified Herke’s formula [23], but recent research has shown that the modified Herke’s formula is only applicable at high temperature [24]. In this paper, we used the modified Mott formula [20] to depict the effect of Nd and/or Na substitution on Seebeck coefficient for $\text{Ca}_{3.0-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$. In the modified Mott formula, the Seebeck coefficient can be expressed as:

$$S = \frac{c_e}{n} + \frac{\pi^2 k_B^2 T}{3e} \left[\frac{\partial \ln \mu(\epsilon)}{\partial \epsilon} \right]_{\epsilon=\epsilon_F} \quad (1)$$

where n , $\mu(\epsilon)$, c_e and k_B are carrier concentration, energy correlated carrier mobility, specific heat and Boltzmann constant, respectively. The formula consists of two terms and the value of first term (c_e/n) is the inverse of carrier concentration. In our experiment, though the carrier mobility $\mu(\epsilon)$ may also play a role in determining S in such layered cobalt oxide [21], the change of S for Nd/Na-doping samples can mainly be explained according to the first term of Eq. (1). The carriers (holes) concentration decrease/increase, resulting in the increase/decrease of S values, with the Nd/Na-doping amount.

Fig. 5 shows the temperature dependence of thermal conductivity (κ) for $\text{Ca}_{3.0-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$ ($x = 0.1, 0.2, 0.3$; $y = 0.0, 0.1$). The thermal conductivities of all the samples show a weak temperature dependence. The κ can be expressed by the sum of a lattice term (κ_1) and an electronic term (κ_e) as: $\kappa = \kappa_1 + \kappa_e$. The κ_e value is estimated using Wiedemann–Franz law as: $\kappa_e = L\sigma T$, where L is the Lorenz number ($2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ for the free-electron model). As shown in the

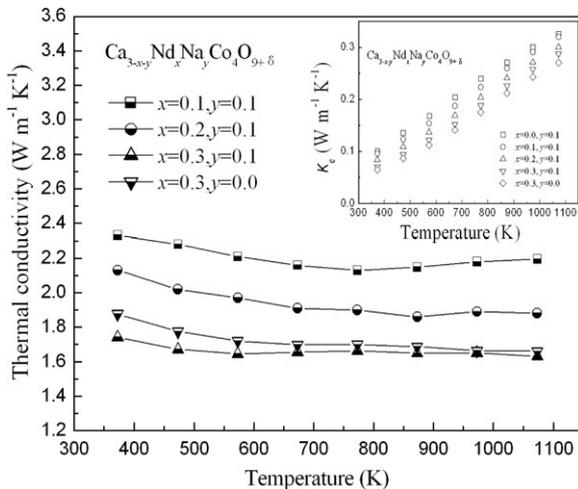


Fig. 5. Temperature dependence of the thermal conductivity for $\text{Ca}_{3.0-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$ ($x = 0.1, 0.2, 0.3$; $y = 0.0, 0.1$) polycrystalline samples. Inset: temperature dependence of the electron term (κ_e) estimated by Wiedemann–Franz law ($\kappa_e = L\sigma T$), where $L = 2.45 \times 10^{-8}$ is the Lorenz number based on the free-electron model.

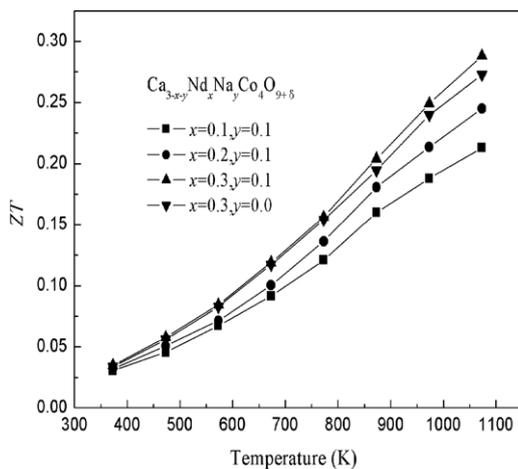


Fig. 6. Temperature dependence of the dimensionless figure of merit (ZT) for $\text{Ca}_{3.0-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$ ($x = 0.1, 0.2, 0.3$; $y = 0.0, 0.1$) polycrystalline samples.

inset of Fig. 5, the values of κ_e decrease/increase gradually with Nd/Na-doping amount because of the decrease/increase of σ (Fig. 2). For $\text{Ca}_{2.9-x}\text{Nd}_x\text{Na}_{0.1}\text{Co}_4\text{O}_{9+\delta}$ samples ($x = 0.0, 0.1, 0.2$ and 0.3), the total κ decreases conspicuously with increasing Nd-doping amount in the whole temperature range because of decreasing κ_e and κ_1 (caused by the lattice vibration of heavy Nd^{3+} , which shorten the average free path of phonon). The total κ for $\text{Ca}_{2.6}\text{Nd}_{0.3}\text{Na}_{0.1}\text{Co}_4\text{O}_{9+\delta}$ is smaller than that of $\text{Ca}_{2.7}\text{Nd}_{0.3}\text{Co}_4\text{O}_{9+\delta}$, indicating the thermal conductivity is further decreased by Nd and Na co-doping.

Fig. 6 illustrates the temperature dependence of the dimensionless figure of merit (ZT) for the $\text{Ca}_{3.0-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$ ($x = 0.1, 0.2, 0.3$; $y = 0.0, 0.1$). The values of ZT increase with increasing temperature and Nd/Na-doping amount as well. The maximum ZT value of the $\text{Ca}_{2.6}\text{Nd}_{0.3}\text{Na}_{0.1}\text{Co}_4\text{O}_{9+\delta}$ sample is 0.29 at 1073 K, which is higher than those of the Nd single substituted samples.

4. Conclusion

New oxides $\text{Ca}_{3.0-x-y}\text{Nd}_x\text{Na}_y\text{Co}_4\text{O}_{9+\delta}$ ($x = 0.0, 0.1, 0.2, 0.3$; $y = 0.0, 0.1$) were prepared and their thermoelectric properties were investigated. XRD analysis confirmed that all the samples were single phase. For $\text{Ca}_{2.9-x}\text{Nd}_x\text{Na}_{0.1}\text{Co}_4\text{O}_{9+\delta}$ ($x = 0.0, 0.1, 0.2$ and 0.3) samples, the electrical conductivity and thermal conductivity decreases while the Seebeck coefficient increases with an increase of Nd doping amount. The electrical conduction was dominated by the small polaron hopping conduction mechanism above 550 K and the transport mechanism was not changed by Nd and/or Na doping. The thermal conductivity was reduced by additional substitution Na for $\text{Ca}_{2.7}\text{Nd}_{0.3}\text{Co}_4\text{O}_{9+\delta}$, which resulted in further improvement of ZT value. The results suggested that Nd and Na co-substituted $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ may be a potential thermoelectric material for application at high temperature.

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