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Effects of Lu and Ni Substitution on Thermoelectric Properties of $Ca_3Co_4O_{9+\delta}$

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Effects of (Lu, Ni) co-doping on the thermoelectric properties of $Ca_3Co_4O_{9+\delta}$ (CCO) have been systematically investigated from 20 K to 350 K. The electrical resistivity and thermopower of (Lu, Ni) co-doped samples increase, while their thermal conductivity is significantly depressed as compared to that of pristine CCO. The figure of merit (*ZT*) of co-doped samples is higher than those of Lu-doped samples and pristine CCO. A maximum *ZT* of 0.0185 is achieved at 350 K for $Ca_{2.9}Lu_{0.1}Co_{3.9}Ni_{0.1}O_{9+\delta}$. We demonstrate that the simultaneous increase of spin entropy and phonon scattering induced by (Lu, Ni) co-doping boosts *ZT* of CCO. This study indicates that (Lu, Ni) co-doping may promise an effective way to improve thermoelectric properties of the CCO system.

Key words: Thermoelectric materials, $Ca_3Co_4O_{9+\delta}$, thermoelectric properties, spin entropy, phonon scattering

INTRODUCTION

Thermoelectric materials, which involve a conversion between thermal and electrical energy, are expected to play increasingly important roles in meeting energy challenges in the future.[1] The conversion efficiency can be determined by the figure of merit $ZT = S^2T/\rho\kappa$, where T, ρ, S, and κ are the absolute temperature, the electrical resistivity, the thermopower, and the thermal conductivity, respectively. Recently, the misfit-layered cobalt oxides have received much attention due to their large thermopower, low thermal conductivity, and good chemical stability.[1,2] In this family, environment-friendly $Ca_3Co_4O_{9+\delta}$ (CCO) system exhibiting excellent thermoelectric performance and high temperature stability has been considered to be a promising candidate thermoelectric materials.[3–7] CCO consists of two alternating subsystems, a rock salt type Ca_2CoO_3 layer and a CdI_2 type CoO_2 sheet, each having the same a, c, and β parameters, but a different lattice parameter b.[4] These two different subsystems provide a way to control the electronic and thermal transport properties separately. However, for practical application, the thermoelectric performance needs to be further improved.[8–11]

So far, partial substitution of different elements at the Ca site[12–23] or Co site[24–28] is a method used to try to improve the thermoelectric properties of CCO. However, very few groups study the effects of simultaneous substitution of two different elements at Ca and Co sites.[29–39] Our group previously demonstrated that (Ce, Ni) co-doping considerably enhanced the thermoelectric performance of CCO compared with those of pure and Ce single-doped CCO.[40] We also studied the thermoelectric properties of the $Ca_{3-x}Lu_xCo_4O_{9+\delta}$ system and found that partial Lu substitution of Ca is an effective approach for improving the thermoelectric properties of the CCO system.[41] In the CCO system, the large thermopower values were found to originate from the spin entropy.[42] In layered cobalt oxides with strong electron–electron interaction, the elementary charge-transport process is the hopping of a hole from Co^{4+} to Co^{3+}, and a large electron–electron on-site repulsion excludes double occupancy of a site by the holes. Because this process

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converts the Co^{4+} (s = 1/2) to a Co^{3+} (s = 0) and vice versa, a spin of −1/2 along with the hole is also transferred, which implies a transfer of the spin entropy $\sigma = k_B \ln 2$. The spin degrees are predicted to produce a large contribution of the Heikes formula[43]:

$$Q = \frac{\mu}{eT} = -\frac{\sigma}{e}, \quad (1)$$

where μ is the chemical potential, and σ (the entropy per electron) equals $k_B \ln(g_s g_c)$ with g_s and g_c the spin and configuration degeneracies, respectively. A previous study suggested that Ni doping can provide a new hopping model for transporting the spin entropy, and as a result the thermopower increases.[44] Thus, simultaneous substitution of Lu and Ni at Ca and Co sites may increase thermopower due to their combined effects on the spin entropy enhancement. Meanwhile, substitutions of Ni at Co site and heavy metal element Lu at Ca site cause effective phonon scattering, causing the thermal conductivity to decrease.[45] Therefore, it is of great interest to investigate the effects of (Lu, Ni) co-doping on the thermoelectric properties of CCO.

In this work, we investigate systematically the effects of (Lu, Ni) co-doping on the thermoelectric properties of CCO. It is found that (Lu, Ni) co-doping is more effective than single rare earth elements doping in improving thermoelectric performance of CCO. The simultaneous increase of spin entropy and phonon scattering induced by (Lu, Ni) co-doping boosts ZT of CCO. This work indicates that (Lu, Ni) co-doping promises an effective way for improving thermoelectric properties of CCO system.

EXPERIMENTAL

$Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$ samples were prepared by a sol–gel chemical solution route as follows: the stoichiometric $CaCO_3$, $Co(NO_3)_2 \cdot 6H_2O$, $Lu(NO_3)_3 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and citric acid monohydrate were dissolved in distilled water. The intensive mixed solution was dehydrated at 335 K for 12 h. The resulting gel was heated at 473 K for 3 h to remove the moisture. The obtained carbonaceous xerogel was crushed and calcined at 823 K for another 3 h in air. The obtained powders were cooled down to room temperature and sintered at 1173 K for 12 h under O_2 atmosphere in corundum crucibles (fused porous alumina). Finally, the powders were pressed into pellets at 15 MPa and annealed at 1173 K for another 36 h under O_2 atmosphere.

X-ray diffraction (XRD, Bruker D8) with Cu Kα radiation was carried out for phase identification. Scanning electron microscope (SEM) investigations were conducted with a FEI Quanta 250F. X-ray photoemission spectroscopy (XPS, PHI 5000 VersaProbe) were performed with a surface sciences instruments spectrometer equipped with a monochromatized Al Kα radiation. All the thermoelectric properties (thermopower, thermal conductivity, electrical resistivity) were measured using the physical property measurement system (PPMS, PPMS-9T EC-II) from 20 K to 350 K.

RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$ samples. All diffraction peaks match to the standard JCDPDS card (no. 21-0139) of CCO. We show the enlarged (002) diffraction peak and (004) peak in the inset of Fig. 1. It is shown that the enlarged (002) and (004) diffraction peaks of co-doped samples shift to higher 2θ values in comparison to the pristine CCO because Lu^{3+} ion (0.98 Å) has a similar ionic radius to Ca^{2+} (1.00 Å) ion.[46] XRD analysis indicates that Lu and Ni are successfully doped into the lattices of CCO. The morphology of $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$ is characterized by SEM (Fig. 2). It is found that the samples are uniform and small pores are present in the matrixes. The particles are combined closely through sintering and twice-annealing. The excellent crystallinity of specimens and the clean surfaces are also identified by the SEM images. Grain sizes of our samples by sol–gel method are smaller than those of other materials prepared by solid state reaction.[47] The densities of our samples are 3.8383 g/cm^3 (x = 0.1, y = 0.1), 3.8260 g/cm^3 (x = 0.1, y = 0.2), 3.8568 g/cm^3 (x = 0.2, y = 0.1), and 3.8093 g/cm^3 (x = 0.2, y = 0.2).

Figure 3 shows the temperature dependence of resistivity (ρ) for $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$. It demonstrates that (Lu, Ni) co-doping leads the ρ to increase. A reentrant is observed for all samples, indicating a typical semiconductor behavior. The transition temperature (T_{min}) is indicated by arrows, shown in Fig. 3. As (Lu, Ni) doping level increases, T_{min} shifts to higher temperature. For semiconductor, ρ is in inverse proportion to the

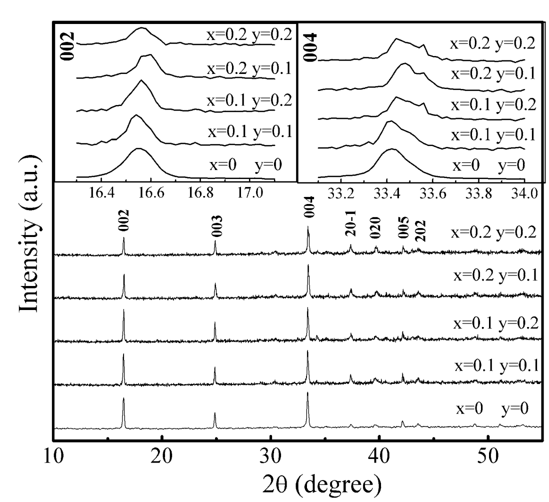

Fig. 1. XRD patterns of $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$. The left inset part shows the enlarged (002) diffraction peak and the right shows the enlarged (004) peak.

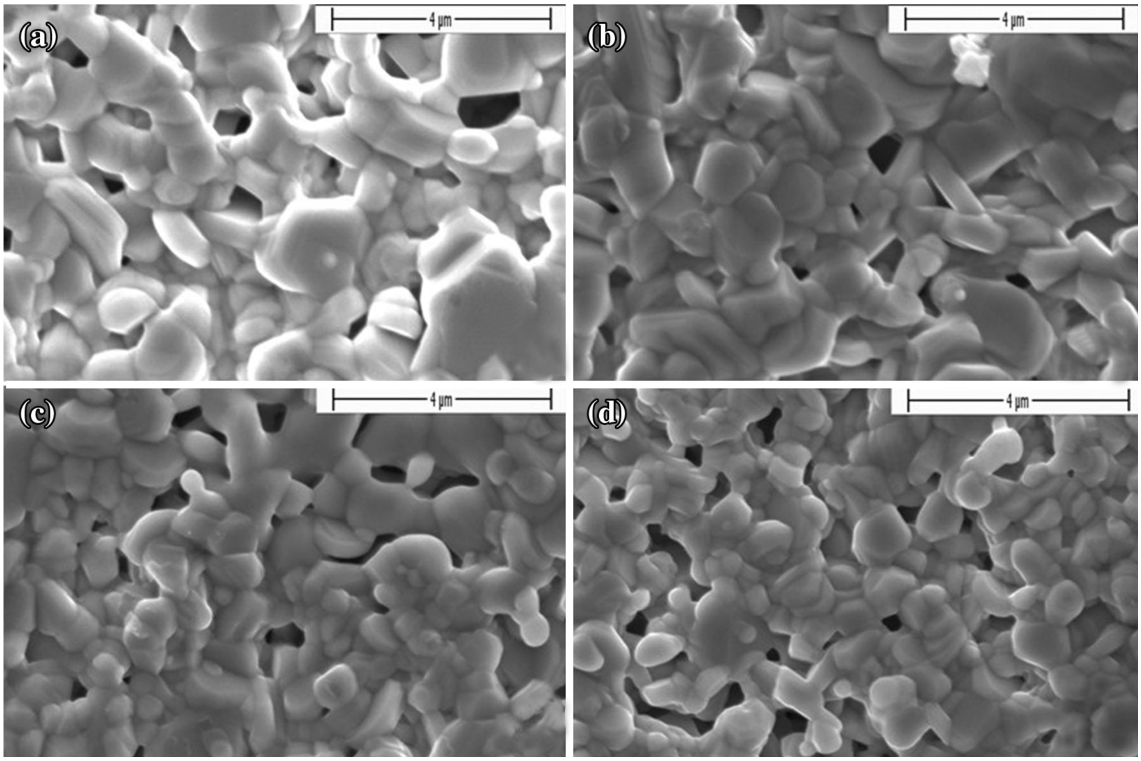

Fig. 2. SEM images showing the fractured cross sections of $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$: (a) $x = 0.1$, $y = 0.1$; (b) $x = 0.1$, $y = 0.2$; (c) $x = 0.2$, $y = 0.1$; (d) $x = 0.2$, $y = 0.2$.

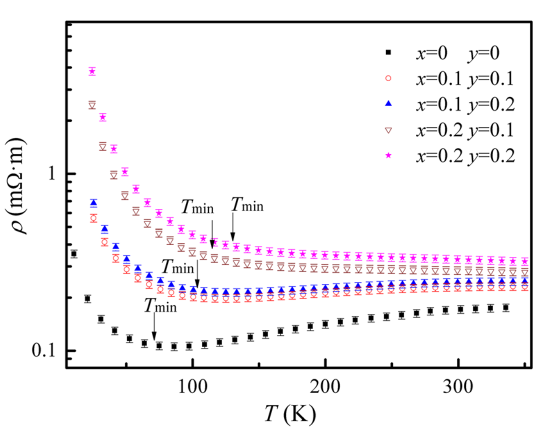

Fig. 3. Temperature dependence of resistivity for $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$.

carrier concentration (n) and the carrier mobility (μ).[48] μ is given by:

$$\mu = \frac{4}{3\pi^{1/2}} \Gamma\left(r + \frac{5}{2}\right) \frac{e\tau_0 (kT)^r}{m^*}, \qquad (2)$$

where m^* and τ_0 are carrier effective mass and relaxation time, and e, k, T, Γ, and r are electron charge, Boltzmann's constant, temperature, gamma function, and scattering law parameter, respectively. Thus, m^* and scattering probability determine the μ. It is considered that impurity ions (Lu, Ni) lead to an increase in impurity scattering.[40] Meanwhile, the substitution of Lu^{3+} for Ca^{2+} increases m^*.[41] Consequently, the μ decreases. Meanwhile, Lu^{3+} doped into Ca^{2+} sites lead n to reduce. As a result, the increase of ρ is observed in (Lu, Ni) co-doped samples.

The temperature dependence of thermopower (S) from 20 K to 350 K for $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$ is shown in Fig. 4. S of all samples increases with the increasing temperature. S of co-doped samples is significantly larger than that of the pristine CCO. In particular, S of $Ca_{2.8}Lu_{0.2}Co_{3.8}Ni_{0.2}O_{9+\delta}$ reaches up to 137.8 μV/K at 350 K. The results indicate that (Lu, Ni) co-doping can effectively enhance S of CCO. The increase in S can be mainly attributed to the enhanced spin entropy.[49] In the high temperature limit, the spin entropy contribution to the thermopower in the strong correlation system can be expressed by the Heikes formula,[50]

$$S = -\frac{k_B}{e} \ln\left[\frac{g_3}{g_4}\left(\frac{c}{1-c}\right)\right], \qquad (3)$$

where g_3 and g_4 are the spin orbital degeneracies for Co^{3+} and Co^{4+} ions, respectively, c is Co^{4+} concentration, k_B is the Boltzmann constant and e is the electron charge. The spin orbital degeneracies $g_3 = 1$ and $g_4 = 6$ are determined according to the low-spin electronic configurations of Co^{3+} and Co^{4+} ions.[50–55] Co 2p XPS spectra of $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$ are shown in Fig. 5. The main peaks

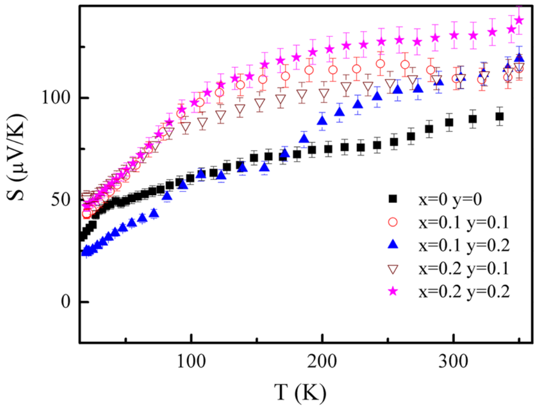

Fig. 4. Temperature dependence of thermopower for $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$.

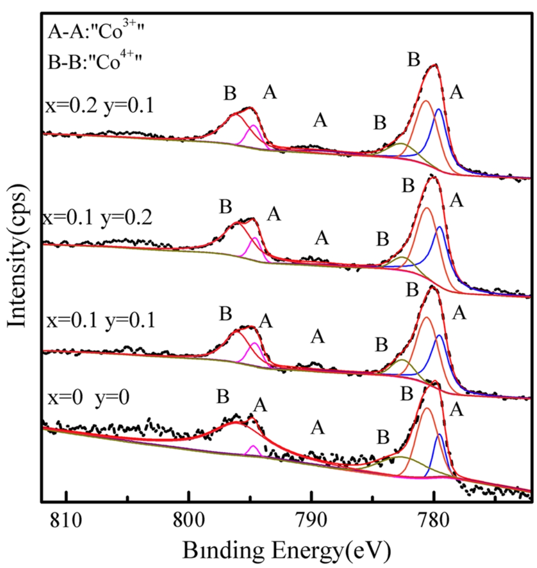

Fig. 5. Co 2p XPS spectra of $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$.

(A) with the binding energy of ca. 779.5 eV, 788.9 eV, 794.6 eV can be identified as Co^{3+}, while the other peaks (B) at ca. 780.5 eV, 782.5 eV, 796 eV are assigned to Co^{4+}.[51] We calculate the ratio of fitting peak area of Co^{4+} to the total Co sites and find that c is reduced by (Lu, Ni) co-doping. According to Eq. 3, the spin entropy enhancement from Co ions can be expected. It is reported that Ni^{2+} and Ni^{3+} coexist in the Ni doped CCO materials.[44] The coexistence of Ni^{2+} and Ni^{3+} ions provides a new hopping model for transporting the spin entropy and induces S to increase, as given by[42]:

$$S = -\frac{k_B}{e}\left\{\frac{g(Co^{3+})}{g(Co^{4+})}\left[\frac{c}{1-c}\right]\right\} - \frac{k_B}{e}\left\{\frac{g(Ni^{2+})}{g(Ni^{3+})}\left[\frac{1-d}{d}\right]\right\}, \tag{4}$$

where $g(Ni^{2+})$ and $g(Ni^{3+})$ are the spin orbital degeneracy for Ni^{2+} and Ni^{3+} ions, d is Ni^{2+} concentration. Ni contributes to the increase of the spin entropy due to spin entropy competition mechanism. Co and Ni make joint contribution to the enhanced spin entropy. A new hopping model provided by magnetic Ni ions further contributes to the increase of the total spin entropy. At low temperature, the undoped $Ca_3Co_4O_{9+\delta}$ has a higher S than doped samples with $x = 0.1$ and $y = 0.2$. The reason needs to be studied further.

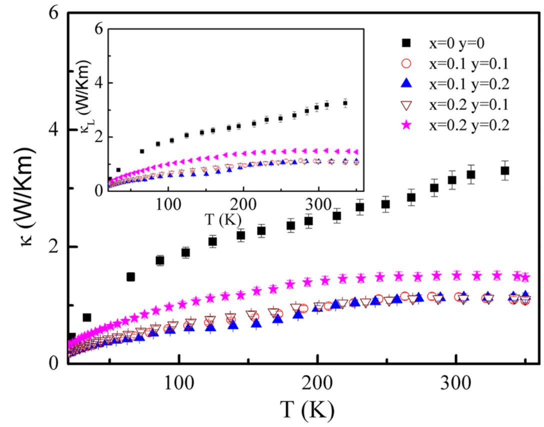

Fig. 6. Temperature dependence of the thermal conductivity for $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$ and the inset shows the temperature dependence of the lattice thermal conductivity for these samples.

Figure 6 shows the temperature dependence of the thermal conductivity (κ) for $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$. κ for all samples increases with increasing temperature. It is found that κ of (Lu, Ni) co-doped samples is much lower than that of pristine CCO. κ of $Ca_{2.9}Lu_{0.1}Co_{3.9}Ni_{0.1}O_{9+\delta}$ sample is 1.077 W/km at 350 K. In general, the total κ consists of the electronic thermal conductivity (κ_e) and lattice thermal conductivity (κ_L). The value of κ_e can be calculated using equation[6]:

$$\kappa_e = L_0 T \sigma, \tag{5}$$

where the Lorentz number (L_0) is equal to 2.44×10^{-8} V^2/K^2, σ and T are the electrical conductivity and the absolute temperature, respectively. κ_L of all samples have been calculated by subtracting κ_e from κ, which is shown in the inset of Fig. 6. It indicates that κ_L is the main source of κ. Therefore, the decrease of κ mainly originates from the reduction of phonon contribution. As shown in Fig. 2, the size of the particles decreases with increasing doping level. Smaller grains cause more effective phonon scattering. Meanwhile, Ni and Lu substitutions contribute the increase of impurity scattering. Therefore, both phenomena are responsible for the observed low thermal conductivity.

The thermoelectric figure of merit (ZT) as a function of temperature for $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$ samples is presented in Fig. 7. ZT of all samples increases with increasing temperature. ZT of (Lu, Ni) co-doped samples is improved as compared with the pristine CCO. The previous data[41] of Lu doped samples is given in Fig. 7 for comparison. ZT of (Lu,

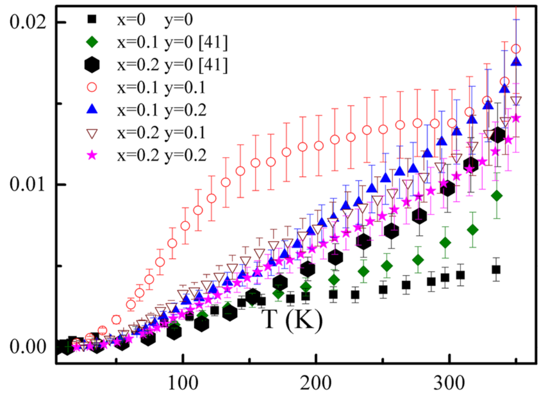

Fig. 7. The thermoelectric figure of merit (*ZT*) as a function of temperature for $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$.

Ni) co-doped samples is higher than Lu doped samples. *ZT* of $Ca_{2.9}Lu_{0.1}Co_{3.9}Ni_{0.1}O_{9+\delta}$ reaches up to 0.0185 at 350 K. These results reveal that (Lu, Ni) co-doping is more effective than single rare earth elements doping in improving thermoelectric performance of CCO.[2] The simultaneous increase of spin entropy and phonon scattering induced by (Lu, Ni) co-doping boosts *ZT* of CCO.

CONCLUSIONS

We have investigated the effects of (Lu, Ni) co-doping on the thermoelectric properties of CCO. The thermopower and resistivity of (Lu, Ni) co-doped samples increase, while their thermal conductivity decreases significantly as compared to that of the pristine CCO. The enhanced thermopower can be attributed to the increase of the spin entropy. Lu and Ni co-doping allows effective phonon scattering, resulting in the decrease of thermal conductivity. The simultaneous increase of the spin entropy and phonon scattering induced by (Lu, Ni) co-doping boosts *ZT* of CCO. $ZT \approx 0.0185$ is achieved at 350 K for $Ca_{2.9}Lu_{0.1}Co_{3.9}Ni_{0.1}O_{9+\delta}$ samples, which is much larger than that of non-doped and Lu doped CCO. This work indicates that co-doping method is a promising way to improve thermoelectric properties of CCO.

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