

# Enhanced thermopower of $\text{YBaCo}_4\text{O}_{7+\delta}$ by Na-for-Ba substitution

S L Leng<sup>1</sup>, X X Wang<sup>2</sup> and H Z Song<sup>2, \*</sup>

<sup>1</sup> College of Material and Chemical Engineering, Tongren University, Tongren 554300, China.

<sup>2</sup> Key Laboratory of Material Physics of Ministry of Education, and Physical Engineering College, Zhengzhou University, Zhengzhou 450052, China.

\* star@zzu.edu.cn

**Abstract.** The electrical resistivity and Seebeck coefficients of  $\text{YBa}_{1-x}\text{Na}_x\text{Co}_4\text{O}_{7+\delta}$  ( $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$ ) ceramic samples prepared by the solid-state reaction method were measured in the temperature range 390-973 K. The results show that with the increase of the Na doping amount, both the electrical resistivity and Seebeck coefficients increased, and that the maximum value of the Seebeck coefficient can reach  $170 \mu\text{VK}^{-1}$ . According to the power factors, the samples with Na doping amount  $x = 0.4$  and  $0.5$  have higher power factors at higher temperature, and the maximum value is  $71 \mu\text{Wm}^{-1}\text{K}^{-2}$  when  $x = 0.4$  at 973 K, being 11% higher than that of the sample without Na doping.

## 1. Introduction

Thermoelectric (TE) materials can convert thermal energy directly into electricity mutually, making it becoming increasingly important in the field of cooling, heating, and recovering waste heat. However, these materials are incapable of wide commercialization because of their poor thermoelectric performance, so enhancing the thermal electrical performance has long been the researchers' study focus. The performance of a TE material is governed by the dimensionless figure-of-merit  $ZT = S^2T / \rho\kappa$ , where  $S$  is the Seebeck coefficient,  $\rho$  the electric resistivity,  $\kappa$  the thermal conductivity and  $T$  the absolute temperature. The parameter  $S^2 / \rho$  is called power factor, which represents the electric transport properties of TE materials. Therefore, good TE materials should possess large power factor as well as low thermal conductivity  $\kappa$ . Reducing electrical resistivity is a common way we take to optimize the electric transport properties, while improving Seebeck coefficient is also another way that should not be ignored. At present, some layered cobalt oxides, such as  $\text{Na}_x\text{CoO}_2$ ,  $\text{Ca}_3\text{Co}_4\text{O}_9$  and  $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ ,<sup>1-3</sup> exhibit better thermoelectric performance due to the layered structure, mixed valence of Co ion and the low spin of  $\text{Co}^{3+}$ ,<sup>4-6</sup> attracting researchers' great attention.

$\text{RBaCo}_4\text{O}_{7+\delta}$  ( $R = \text{Y, Dy-Lu, In, Ca}$ ; abbreviated as R114) synthesized by Valldor et al.<sup>7</sup> is another type of the layered cobalt oxides. Due to their unique structure, favorable physical and chemical properties, R114 compounds have been studied in many fields such as solid oxide fuel cells (SOFCs) and oxygen permeation membranes.<sup>8-15</sup> Especially, much work has been done to investigate their electric transport properties and thermal electric performance.<sup>16-19</sup> It was found that the  $ZT$  value of R114 is much lower than that of conventional non-oxide thermoelectric materials due to their ceramic nature. In our previous study, the influence of R site or Co site doping on the electrical transport properties of R114 has been widely investigated,<sup>19-24</sup> but the investigations of Ba site doping has



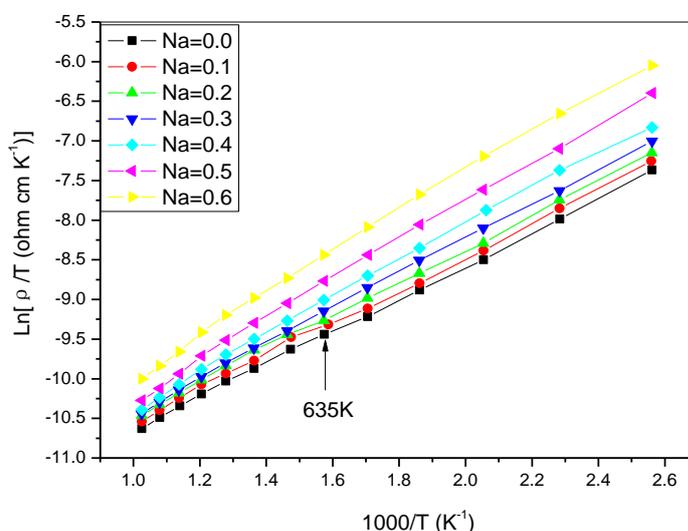
barely been reported. In this paper, the influence of Ba site doping on the electric transport properties of  $\text{YBaCo}_4\text{O}_{7+\delta}$  was studied, and the  $\text{Na}^+$  was selected as the doping element.

## 2. Experimental

$\text{YBa}_{1-x}\text{Na}_x\text{Co}_4\text{O}_{7+\delta}$  ( $x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$ ) ceramic samples were synthesized by the traditional solid-state reaction method. Stoichiometric amounts of  $\text{Y}_2\text{O}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{BaCO}_3$  and  $\text{Co}_3\text{O}_4$  raw materials were mixed thoroughly in an agate mortar. The mixed powder was heated to  $1000^\circ\text{C}$  in a box furnace in air and kept at this temperature for 10 h in order to get rid of carbon. After regrinding, the powder was consolidated into pellets and rectangular bars, and then sintered at  $1140^\circ\text{C}$  in air for 20 h again. The electrical resistivity and Seebeck coefficient were measured simultaneously under He atmosphere from 390 K to 973 K using a LSR-3/800 Seebeck coefficient/electrical resistance measuring system (Linseis, Germany). The rectangular bars with length  $\sim 15$  mm, width  $\sim 4.5$  mm, and height  $\sim 2.0$  mm were prepared for electrical measurements.

## 3. Results and discussion

The relationship between  $\ln(\rho/T)$  and  $1000/T$  was plotted in Figure 1, showing the temperature dependence of the electrical resistivity of  $\text{YBa}_{1-x}\text{Na}_x\text{Co}_4\text{O}_{7+\delta}$  samples from 390 K to 973 K. It was clearly seen that the electrical resistivity of all samples decreases with increase of the temperature, demonstrating semiconducting-like behavior in the measured temperature region. Unfortunately, the electrical resistivity increases with the increase of Na doping amount, which is contrary to our expectation. The phenomena may result from the lattice distortion even the presence of impurity phase leading by the reasonable high doping amount.



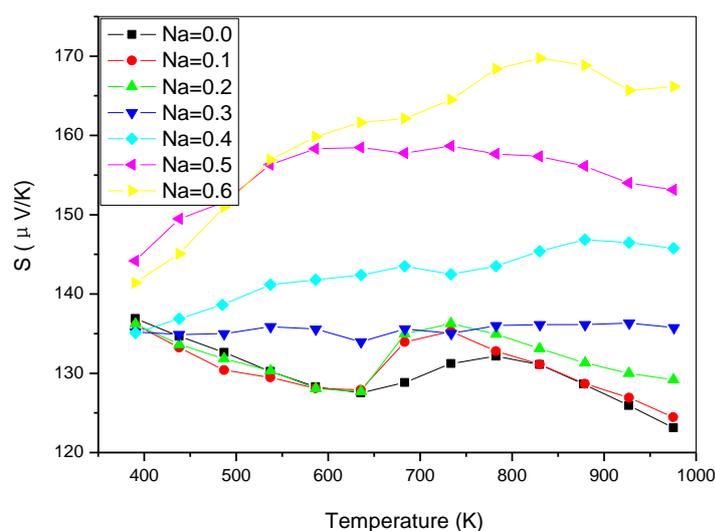
**Figure 1.** Temperature dependence of the electrical resistivity ( $\ln(\rho/T)$  vs  $1000/T$ ) of  $\text{YBa}_{1-x}\text{Na}_x\text{Co}_4\text{O}_{7+\delta}$  samples.

It is also noticed that all the samples have good linear fitting results from 390 K to 635 K. Therefore the conduction mechanism should belong to small polaron hopping conduction mechanism, consistent with our previous study.<sup>19,21,23</sup> The behavior of electrical resistivity versus temperature is expressed as  $\rho = \rho_0 T \exp(E_\sigma / k_B T)$  where  $\rho$  is the electrical resistivity,  $\rho_0$  is a constant,  $T$  is the absolute temperature,  $k_B$  is the Boltzmann constant, and  $E_\sigma$  is the conductive activation energy. However, for temperatures beyond 635 K, the temperature dependence of the electrical resistivity deviates from a straight line, which can be attributed to oxygen absorption/desorption of the samples.

Oxygen absorption cannot exist because the electrical resistivity was measured under He atmosphere. According to previous report,<sup>25</sup> at temperature around 635 K, it begins to appear oxygen desorption from the lattice, resulting in a drop of the carrier concentration, and thus a rise of the resistivity. This can be understood from the defect chemistry where the resistivity of  $\text{RBaCo}_4\text{O}_{7+\delta}$  is related to the oxygen vacancy concentration  $[V_{\text{O}}^{\bullet\bullet}]$  in the ceramic. The reaction during oxygen desorbing can be represented as  $\text{O}_\text{O}^x \Leftrightarrow \frac{1}{2}\text{O}_2 + [V_{\text{O}}^{\bullet\bullet}] + 2e'$ . Thus, oxygen desorption increases the oxygen vacancy

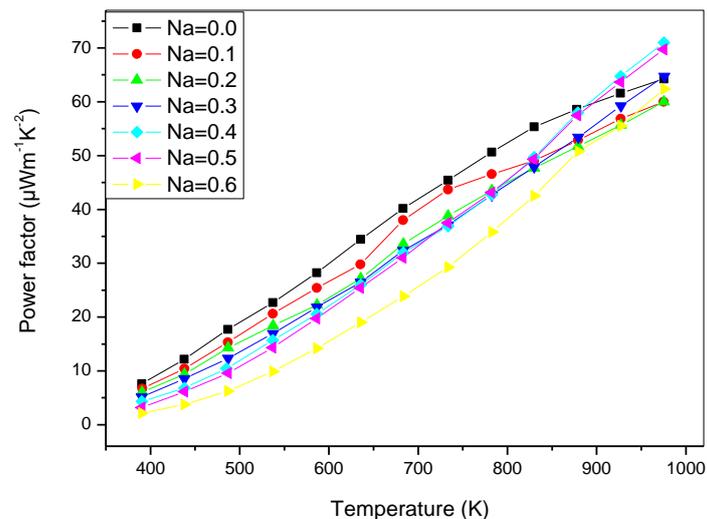
concentration, along with the reduction of hole carriers, resulting in the increment of the resistivity because R114 is *p*-type semiconductor, It seems that this behavior becomes insignificant even disappears as the Na doping amount increases. The reason may be that the increasing Na concentration results in a drop in oxygen adsorption/desorption ability, as shown by the influence of element doping on the oxygen adsorption/desorption properties.<sup>26</sup>

Figure 2 shows the temperature dependence of the Seebeck coefficients of the  $\text{YBa}_{1-x}\text{Na}_x\text{Co}_4\text{O}_{7+\delta}$  samples. It can be seen that the Seebeck coefficients of all the samples are positive for the entire measured temperature range, indicating a *p*-type semiconductor and the conduction mechanism predominantly governed by holes. Moreover, at higher temperature above 635 K, the Seebeck coefficients increase markedly with the increase of the Na concentration corresponding to the evolution of electrical resistivity, which can be attributed to two competing factors. One is the carrier mobility: the carrier mobility should be decreased due to the enhanced scattering effect of carriers in the crystal lattice leading by the Na doping and according to conventional theory for the semiconductor, the smaller carrier mobility leads to smaller Seebeck coefficients. Another is the electron correlation and electron-phonon interactions: the ionic bond of  $\text{Na}^+$  is so strong that its presence makes more and more carriers localization even in a “self-trapped-state”, which will lead to the enhancement of Seebeck coefficient. Moreover, in layered cobaltates it is realized that the electron correlation and electron-phonon interactions will play a very important role in the determination of the Seebeck coefficient.<sup>27</sup> As a result, the Seebeck coefficients increase with the increase of the Na concentration resulting from the predominate contribution of the latter factor. When  $x = 0.6$  at 830 K, the Seebeck coefficient arrives to the maximum value  $170 \mu\text{VK}^{-1}$  in the study range, which is benefit for the improvement of electric transport properties.



**Figure 2.** Temperature dependence of the Seebeck coefficients ( $S$ ) of  $\text{YBa}_{1-x}\text{Na}_x\text{Co}_4\text{O}_{7+\delta}$  samples.

With the electrical resistivity and Seebeck coefficient, power factors ( $PF = S^2 / \rho$ ) have been calculated and the variation with temperature as a function of Nb content has been represented in Figure 3. It is found that, for all the samples, the power factor increases with increase of the temperature, indicating that Y114 exhibit better electrical transport properties at higher temperature. Moreover, at higher temperature range, when  $x = 0.4$  or  $0.5$ , it appears that Na addition produces an important increase of power factor due to the relatively large enhancement of Seebeck coefficient. The sample with  $x = 0.4$  has the maximum  $PF = 71 \mu\text{W m}^{-1} \text{K}^{-2}$  at about 973 K, which is the highest value in the temperature range of our study and is 11% higher than the undoped sample.



**Figure 3.** Temperature dependence of the power factors of  $\text{YBa}_{1-x}\text{Na}_x\text{Co}_4\text{O}_{7+\delta}$  samples.

#### 4. Conclusions

We have synthesized  $\text{YBa}_{1-x}\text{Na}_x\text{Co}_4\text{O}_{7+\delta}$  ( $x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$ ) ceramic samples and investigated their high temperature electrical transport properties. The study demonstrates that the presence of Na produces significant effects on the electric resistivity and Seebeck coefficient. With the increase of the Na doping amount, the electrical resistivity and Seebeck coefficient remarkably increase simultaneously. Moreover, when  $x = 0.4$  or  $0.5$ , the increase magnitude of Seebeck coefficients is higher than that of electric resistivity at higher temperature, resulting an enhancement of the power factor. This phenomenon provides an idea of investigating the influence of double element doping on the electrical transport properties of R114 materials, i.e. Ag-for-Y or Pb-for-Y substitution improves the conductivity<sup>21,24,28</sup> and at the same time Na-for-Ba substitution enhance the thermopower. Thus, the power factor of co-doped  $\text{YBaCo}_4\text{O}_{7+\delta}$  may be enhanced remarkably.

#### Acknowledgments

This work was supported by the Foundation of Henan Educational Committee (Grant No. 16A140036)

#### References

- [1] Terasaki I, Sasago Y and Uchinokura K 1997 *Phys. Rev. B* vol 56 p R12685
- [2] Funahashi R, Matsubara I, Ikuta H, Takeuchi T, Mizutani U and Sodeoka S 2000 *Jpn. J. Appl. Phys.* vol 39 p L1127
- [3] Funahashi R, Matsubara I and Sodeoka S 2000 *Appl. Phys. Lett.* vol 76 p 2385
- [4] He J, Liu Y and Funahashi R 2011 *J. Mater. Res.* vol 26 p 1762

- [5] Zebarjadi M, Esfarjani K, Dresselhaus M S, Ren Z F and Chen G 2012 *Energy Environ. Sci.* vol 5 p 5147
- [6] Doumerc J P, Blangero M, Pollet M, Carlier D, Darriet J, Berthelot R, Delmas C and Decourt R 2009 *J. Electron. Mater.* vol 38 p 1078
- [7] Fergus J W 2012 *J. Euro. Ceram. Soc.* vol 32 p 525
- [8] Valldor M 2004 *Solid State Sci.* vol 6 p 251
- [9] Maignan A, Hébert S, V Caignaert, Pralong V and Pelloquin D 2008 *Solid State Commun.* vol 47 p 470
- [10] Markina M, Vasiliev A N, Nakayama N, Mizota T and Yeda Y 2010 *J. Magn. Magn. Mater.* vol 322 p 1249
- [11] Sarkar T, Caignaert V, Pralong V and Raveau B 2010 *Chem. Mater.* vol 22 p 6467
- [12] Tsipis E, Kharton V and Frade J 2006 *Solid State Ionic* vol 177 p 1823
- [13] Kim Y N, Kim J H, Huq A, Paranthaman M P and Manthiram A 2012 *J. Power Source* vol 214 p 7
- [14] Zhu B, Hao H, Zhang Y, Jia J and Hu X 2010 *J. Rare Earths* vol 28 p 84
- [15] Zhang K, Zhu Z, Ran R, Shao Z, Jin W and Liu S 2010 *J. Alloy. Compd.* vol 492 p 552
- [16] Wong-Ng W, Xie W, Yan Y, Liu G, Kaduk J, Thomas E and Tritt T 2011 *J. Appl. Phys.* vol 110 p 113706
- [17] Tsipis E V, Kharton V V, Frade J R and Núñez P 2005 *J. Solid State Electronchem.* vol 95 p 547
- [18] Hao H S, Chen C Q, Pan L J, Gao J X and Hu X 2007 *Phys. B* vol 387 p 98
- [19] Gao F, He Q L, Wu F, Yang D L, Hu X and Song H Z 2015 *Mod. Phys. Lett. B* vol 29 p 1550154
- [20] Hao H S, Zhang X T, He Q L, Chen C Q and Hu X 2007 *Solid State Commun.* vol 141 p 591
- [21] He Q L, Zhang J, Gao F, Wu F, Hu X and Song H Z 2013 *J. Electron. Mater.* vol 42 p 2570
- [22] Hao H, He Q, Cheng Y and Zhao L 2014 *Mater. Res. Bull.* vol 53 p 84
- [23] He Q L, Gao F, Hu X and Song H Z 2013 *Adv. Mater. Res.* vol 724-725 p 1029
- [24] Chen Y B, Ma R X, Wang K L, Gao F, Hu X and Song H Z 2015 *Int. J. Mod. Phys. B* vol 29 p 1550082
- [25] Song H, Jia J, Zhang S, Yang D, Sun H and Hu X 2012 *Mater. Res. Bull.* vol 47 p 518
- [26] Wang S, Hao H, Zhu B, Jia J and Hu X 2008 *J. Mater. Sci.* vol 43 p 5385
- [27] Schrade M, Fjeld H, Finstad T G and Norby T 2014 *J. Phys. Chem. C* vol 118 p 2915
- [28] Chen Y B, Cao X L, Ma R X, Gao F, Hu X and Song H Z 2015 *J. Electron. Mater.* vol 44 p 3545