Journal of Thermal Analysis and Calorimetry, Vol. 95 (2009) 2, 585–588

EFFECT OF METAL SUBSTITUTION FOR COBALT ON THE OXYGEN ADSORPTION PROPERTIES OF $YBaCo_4O_7$

H. Hao[1,2,3]*, L. Zhao*[2]*, X. Hu*[1*] *and H. Hou*[3]

[1]Key Laboratory of Material Physics of Ministry of Education of China, Zhengzhou University, Zhengzhou 450052, China
[2]Department of Mathematical and Physical Sciences, Henan Institute of Engineering, Zhengzhou 451191, China
[3]Department of Chemistry, Zhengzhou University, Zhengzhou 450052, China

$YBaCo_4O_7$ compound is capable to intake and release a large amount of oxygen in the temperature range of 200–400°C. In the present study, the effect of Zn, Ga and Fe substitution for Co on the oxygen adsorption/desorption properties of $YBaCo_4O_7$ were investigated by thermogravimetry (TG) method. Due to fixed oxidation state of Zn^{2+} ions, the substitution of Zn^{2+} for Co^{2+} suppresses the oxygen adsorption of $YBaCo_{4-x}Zn_xO_7$. The substitution of Ga^{3+} for Co^{3+} also decreases the oxygen absorption capacity of $YBaCo_{4-x}Ga_xO_7$. This can be explained by the strong affinity of Ga^{3+} ions towards the GaO_4 tetrahedron. Compared with Zn- and Ga-substituted samples, the drop of oxygen adsorption capacity is smallest for Fe-substituted samples because of the similar changeability of oxidation states of Co and Fe ions.

Keywords: *metal substitution, oxygen adsorption,* $YBaCo_4O_7$

Introduction

Oxygen content in many transition metal oxides is tunable with the temperature and surrounding oxygen partial pressure because of the variable valence state of transition metals [1, 2]. This oxygen nonstoichiometry makes it possible for oxygen ions to be adsorbed/desorbed in these oxides, which has been utilized in fields such as solid–oxide fuel cells, gas separation and oxygen sensors. Since $RBaCo_4O_7$ (R represents rare earth elements) compounds have been synthesized by Valldor *et al.* [3, 4], studies on their structure, magnetic and electronic properties have been carried on by several groups [5–12]. The crystal structure of $RBaCo_4O_7$ is built up of Kagomé sheets of CoO_4 tetrahedra, linked by triangular layers of CoO_4 tetrahedra [5–7]. The ratio of Co ion numbers in the Kagomé- and triangular-lattices is 3 to 1 and the valences of Co ions are mixed consisting of three Co^{2+} ions and one Co^{3+} ion. Previous studies have shown that $RBaCo_4O_7$ exhibits uncommon oxygen adsorption/desorption behavior in a narrow temperature range of 200–400°C [13, 14]. The compounds are capable to intake and then release 1 to 1.5 extra oxygen atoms per unit formula at ambient and high oxygen pressures, respectively. Such a large oxygen-content reversibility makes the $RBaCo_4O_7$ system a highly potential candidate for various applications such as oxygen storage, gas separation and oxygen sensor [15]. However, the reason of oxygen intake of $RBaCo_4O_7$ is not clear now. Modifying the oxygen intake properties by element substitution will help to clarify the reason. The fixed oxidation states of the R^{3+} and Ba^{2+} ions imply that the extra oxygen atoms must primarily bond with some of the cobalt ions. It has been reported that it is the instability of tetrahedral Co^{3+} in the parent $RBaCo_4O_7$ that drives the strong affinity for oxygen intake [16]. Therefore, substitution for cobalt with other metals is expected to have significant effect on the oxygen adsorption behavior of $RBaCo_4O_7$. In this work, we synthesized M-substituted $YBaCo_{4-x}M_xO_7$ (M=Zn, Ga, Fe) samples and investigated their oxygen adsorption properties by thermogravimetry method.

Experimental

The compositions $YBaCo_{4-x}M_xO_7$ (M=Zn, Ga, Fe) were prepared by the solid-state reaction method. The stoichiometric mixture of Y_2O_3, $BaCO_3$, Co_3O_4, ZnO, Ga_2O_3 and Fe_2O_3 was ground in an agate mortar. After decarbonation at 1000°C, the powder was pressed into pellets, sintered at 1140°C in air for 20 h, and cooled to room temperature. X-ray diffraction (XRD) analysis was carried out with X'tert Pro system using CuK_α radiation (2θ=15–75°, step 0.02°, 10 s/step). TG measurements were performed with a thermo-analyzer (SETARAM, Labsys^{TM}) to investi-

---

[*] Author for correspondence: xhu@zzu.edu.cn

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

gate the oxygen adsorption properties of the samples. In these experiments about 60 mg powder sample was put in an alumina crucible and heated from room temperature to 500°C with a heating rate 1°C min^{-1} in 30 mL min^{-1} oxygen flow.

Results and discussion

XRD results show that three Zn ions can be substituted over the four Co ions of $YBaCo_4O_7$, suggesting that Zn will enter the Co(2) crystallographic sites of the Kagomé layer [4]. However, the solubility limits of Ga and Fe substitution for Co are only 1.0, which suggests a greater Ga and Fe affinity for the Co(1) crystallographic site of the triangular plane [4, 17].

Figure 1 shows the powder XRD patterns of $YBaCo_4O_7$ and $YBaCo_{4-x}M_xO_7$ (M=Zn, Ga, Fe) with their largest M concentration. The lattice parameters and cell volumes were calculated from the XRD data in space group $P6_3mc$ and presented in Table 1. Compared with $YBaCo_4O_7$, Zn substitution slightly increases the cell parameters and cell volume of $YBaCoZn_3O_7$. The result suggests that Zn^{2+} ions (r=0.060 nm) are substituted for Co^{2+} ions with similar ionic radius (r=0.058 nm), so that it does not affect the cell volume too much. Ga and Fe substitutions also increase the cell parameters and cell volumes of $YBaCo_3GaO_7$ and $YBaCo_3FeO_7$. Since the ionic radius of Ga^{3+} is smaller than that of Co^{2+}, so the rise of cell volumes shows that Ga^{3+} ions are substituted for Co^{3+} ions. The increase of the cell volumes caused by Fe substitution can be understood based on the fact that the ionic radii of Fe^{3+} and Fe^{2+} ions are larger than Co^{3+} and Co^{2+} ions, respectively.

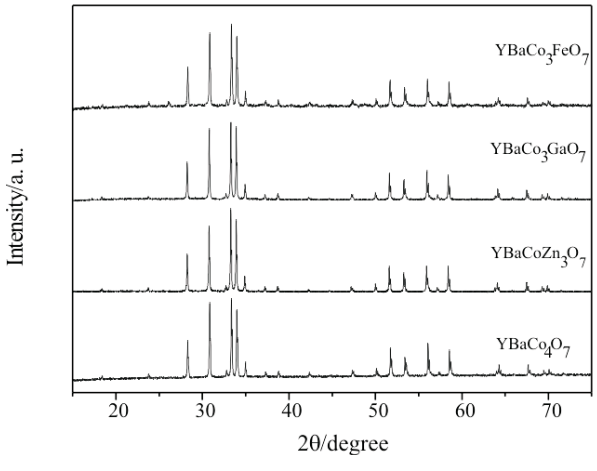

Fig. 1 XRD patterns of $YBaCo_4O_7$, $YBaCoZn_3O_7$, $YBaCo_3GaO_7$ and $YBaCo_3FeO_7$

Figure 2 shows the mass change of $YBaCo_{4-x}M_xO_7$ when heated in oxygen from room temperature to 500°C. It can be seen that $YBaCo_4O_7$ sample begins to adsorb oxygen at about 200°C and the adsorption stops at about 370°C. Then, with the increase of the temperature the sample begins to release oxygen and at about 400°C the mass falls to its initial value. The mass rise in this oxygen adsorption process is about 3.0% of its initial mass, i.e., about 1.1 oxygen ions diffused into a unit cell of $YBaCo_4O_7$. Previous studies have verified that the intake of oxygen in $YBaCo_4O_7$ is the result of oxidation reaction and the adsorption is chemisorption [13, 16]. As seen in Fig. 2a, Zn substitution in $YBaCo_{4-x}Zn_xO_7$ ($0\le x\le 3.0$) samples rapidly decreases the amount of oxygen adsorption and the humps of the oxygen adsorption/desorption almost disappear for the $x\ge 2.0$ samples. In Fig. 2b, one can see that the oxygen absorption capacity of Ga-substituted $YBaCo_{4-x}Ga_xO_7$ ($0\le x\le 1.0$) samples also decreases with the increasing Ga concentration, from 3.0% for $YBaCo_4O_7$ to 1.0% for $YBaCo_3GaO_7$. Although the hump heights of $YBaCo_{4-x}Fe_xO_7$ ($0\le x\le 1.0$) samples are also reduced by Fe substitution (Fig. 2c), the speed of the drop is smaller than Zn and Ga substitution. For $YBaCo_4FeO_7$ sample, its mass change is still 2.1% of its initial mass.

In the parent $YBaCo_4O_7$, all four Co ions are located in CoO_4 tetrahedra and the Co^{2+}/Co^{3+} ratio is 3 to 1. However, tetrahedral coordination of Co^{3+} is extremely rare due to the large crystal field stabilization energy afforded by octahedral coordination. Chmaissem *et al.* have verified that the Co octahedra form by the addition of extra oxygen atoms in $YBaCo_4O_{8.1}$ [16]. The extra oxygen atoms enter the structure to bond with half of the triangular cobalt ions and form zigzag patterns of Co(1) octahedra. In the Kagomé layer, Co(2) octahedra form directly above and below the Co(1)-octahedra to form zigzag ribbons directed along the c-axis. Therefore, Co ions occupy both corner-sharing tetrahedral and edge-sharing octahedral sites in $YBaCo_4O_{8.1}$. All octahedral Co ions and their surrounding first neighbor tetrahedral Co ions are trivalent. Bivalent corner-sharing Co tetrahedral form continuous zigzag

Table 1 Cell parameters and cell volumes of $YBaCo_4O_7$, $YBaCoZn_3O_7$, $YBaCo_3GaO_7$ and $YBaCo_3FeO_7$

Sample	$YBaCo_4O_7$	$YBaCoZn_3O_7$	$YBaCo_3GaO_7$	$YBaCo_3FeO_7$
a/Å	6.308	6.329	6.311	6.314
c/Å	10.240	10.289	10.267	10.276
V/Å^3	352.9	356.89	354.1	354.8

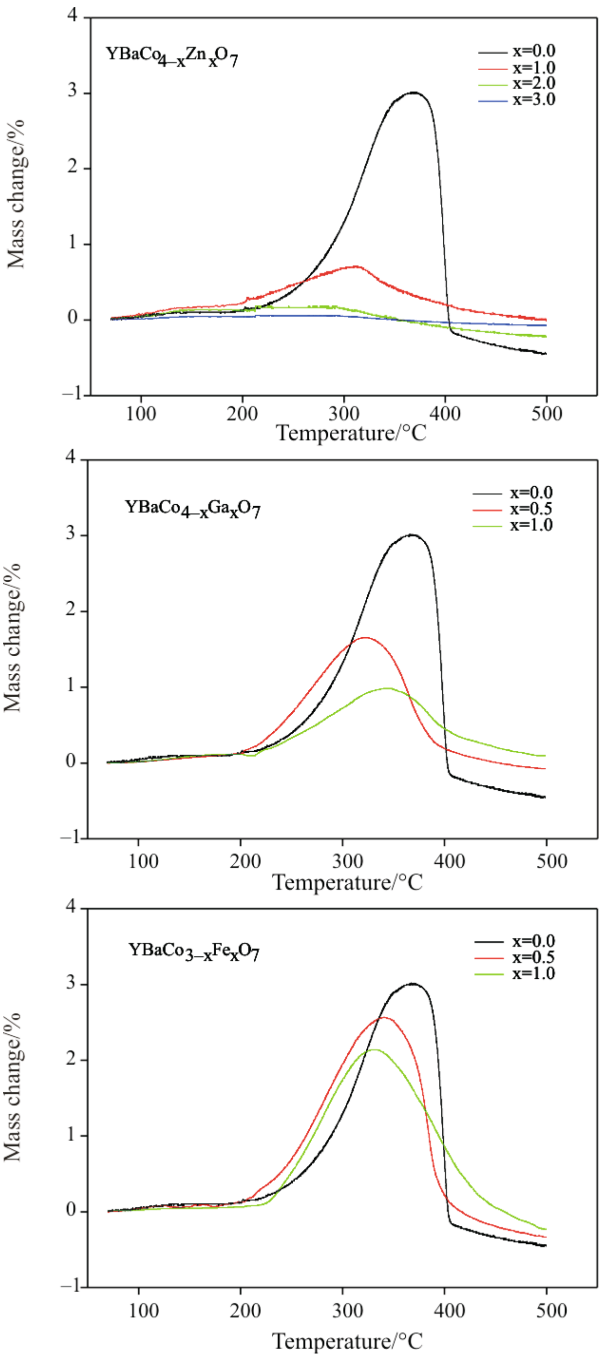

Fig. 2 Mass change of $YBaCo_{4-x}M_xO_7$ (*M*=Zn, Ga, Fe) with temperature in oxygen

ribbons in the b-axis direction, linking the chains of Co^{3+} polyhedra.

When $YBaCo_4O_7$ adsorb one oxygen atom, two Co^{2+} ions will change their oxidation state to Co^{3+}. So, the Co^{2+}/Co^{3+} ratio changes to 1:3 in $YBaCo_4O_8$. Since Zn^{2+} ions with d^{10} electronic configurations can not change their oxidation state from 2+ to 3+, so the substitution of Zn for Co will suppress the oxygen adsorption. When all Co^{2+} ions are substituted by Zn^{2+} ions in $YBaCoZn_3O_7$ sample, its oxygen adsorption phenomenon will be removed, being consistent with the TG result in Fig. 2a. When Co^{3+} ions are substituted by Ga^{3+} (d^{10}) ions which are located in the Co(1) crystallographic site of the triangular plane, Co^{2+} ions will be forced to enter the Co(2) crystallographic site of the Kagomé layer. Although the amount of Co^{2+} ions is not reduced in Ga-substituted samples, this site selectivity will suppress oxygen diffusing into triangular layer due to strong affinity of Ga^{3+} ions towards the fourfold coordination of GaO_4 tetrahedron [17]. Moreover, the absence of the Co(1) octahedra in triangular layer is also unfavorable to the formation of Co(2) octahedra in the Kagomé layer due to these octahedra in the two layers are edge-sharing. So, the oxygen adsorption capacity of $YBaCo_{4-x}Ga_xO_7$ is expected to decrease markedly with the increase of Ga concentration. Although Fe ions also probably enter the Co(1) crystallographic site, the effect of Fe substitution on the oxygen adsorption capacity is weaker than Ga substitution. The reason may be related to the fact that Fe ions have similar variable oxidation states to Co ions. The drop of oxygen adsorption capacity compared with Fe-free $YBaCo_4O_7$ may be caused by the redistribution of Co ions and the distortion of the crystal structure due to Fe substitution.

Conclusions

Zn substitution in $YBaCo_{4-x}Zn_xO_7$ ($0\leq x\leq 3.0$) samples decreases the amount of oxygen adsorption rapidly and the humps of the oxygen adsorption/desorption disappear for the $x\geq 2.0$ samples. The oxygen absorption capacity of Ga-substituted $YBaCo_{4-x}Ga_xO_7$ ($0\leq x\leq 1.0$) samples decreases with the increasing Ga concentration, from 3.0% for $YBaCo_4O_7$ to 1.0% for $YBaCo_3GaO_7$. The hump heights of $YBaCo_{4-x}Fe_xO_7$ ($0\leq x\leq 1.0$) samples are also reduced due to Fe substitution, but the speed of the drop is smaller than Zn and Ga substitution. The effect of metal substitution on the oxygen adsorption properties of $YBaCo_4O_7$ can be explained by the oxidation states of metal ions and their distribution in the crystal structure.

Acknowledgements

This work was partially supported by a Fund of Natural Science of Henan Province, China.

References

1 T. V. Chong, S. Kambe, H. Kawaji, T. Atake and O. Ishii, J. Therm. Anal. Cal., 92 (2008) 425.
2 K. Gavrichev, A. Bolshakov, D. Kondakov, A. Khoroshilov and S. Denisov, J. Therm. Anal. Cal., 92 (2008) 857.
3 M. Valldor and M. Andersson, Solid State Sci., 4 (2002) 923.
4 M. Valldor, Solid State Sci., 6 (2004) 251.
5 A. Huq, J. F. Mitchell, H. Zheng, L. C. Chapon, P. G. Radaelli, K. S. Knight and P. W. Stephens, J. Solid State Chem., 179 (2006) 1136.
6 A. Maignan, V. Caignaert, D. Pelloquin, S. Hébert, V. Pralong, J. Hejtmanek and D. Khomskii, Phys. Rev. B, 74 (2006) 165110.
7 L. C. Chapon, P. G. Radaelli, H. Zheng and J. F. Mitchell, Phys. Rev. B, 74 (2006) 172401.
8 H. S. Hao, C. Q. Chen, L. J. Pan, J. X. Gao and X. Hu, Physica B, 387 (2007) 98.
9 H. S. Hao, X. T. Zhang, Q. L. He, C. Q. Chen and X. Hu, Solid State Commun., 141 (2007) 591.
10 E. V. Tsipis, D. D. Khalyavin, S. V. Shiryaev, K. S. Redkina and P. Nunez, Mater. Chem. Phys., 92 (2005) 33.
11 N. Nakayama, T. Mizota, Y. Ueda, A. N. Sokolov and A. N. Vasiliev, J. Magn. Magn. Mater., 300 (2006) 98.
12 V. Caignaert, A. Maignan, V. Pralong, S. Hebert and D. Pelloquin, Solid State Sci., 8 (2006) 1160.
13 M. Karppinen, H. Yamauchi, S. Otani, T. Fujita, T. Motohashi, Y.-H. Huang, M. Valkeapaa and H. Fjellvag, Chem. Mater., 18 (2006) 490.
14 H. S. Hao, J. H. Cui, C. Q. Chen, L. J. Pan, J. Hu and X. Hu, Solid State Ionics, 177 (2006) 631.
15 T. Motohashi, S. Kadota, H. Fjellvag, M. Karppinen and H. Yamauchi, Mater. Sci. Eng. B, 148 (2008) 196.
16 O. Chmaissem, H. Zheng, A. Huq, P. W. Stephens and J. F. Mitchell, J. Solid State Chem., 181 (2008) 664.
17 A. Maignan, V. Caignaert, V. Pralong, D. Pelloquin and S. Hebert, J. Solid State Chem., 181 (2008) 1220.

DOI: 10.1007/s10973-008-9234-5