OXYGEN BEHAVIOR IN Y$_{1-x}$Zr$_x$BaCo$_4$O$_{7+\delta}$

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Y$_{1-x}$Zr$_x$BaCo$_4$O$_{7+\delta} (x = 0.0, 0.05, 0.1, 0.2, 0.4, 0.6)$ samples were synthesized by the solid state reaction method. The effects of Zr substitution for Y on the oxygen uptake/release properties of these samples were investigated by thermogravimetric (TG) from room temperature to 1150°C. The results show that there exists an optimizing Zr doping amount. The Y$_{0.9}$Zr$_{0.1}$BaCo$_4$O$_{7+\delta}$ sample can uptake more oxygen than the undoped YBaCo$_4$O$_{7+\delta}$ sample at 360°C. Especially, in an oxygen uptake/release cycles between 340°C and 410°C, the mass change of the doped Y$_{0.9}$Zr$_{0.1}$BaCo$_4$O$_{7+\delta}$ sample can reach 5.3% of its original mass and show a stable oxygen uptake/release reproducibility. In addition, in the oxygen uptake/release cycles switched between oxygen and nitrogen atmosphere at 350°C, Y$_{0.9}$Zr$_{0.1}$BaCo$_4$O$_{7+\delta}$ can also adsorb more oxygen. These properties of Y$_{1-x}$Zr$_x$BaCo$_4$O$_{7+\delta}$ make them to be a potential candidate in the field of gas purification and separation.

INTRODUCTION

Recently, a type of oxygen-nonstoichiometric mixed-valence cobalt oxides RBaCo$_4$O$_{7+\delta}$ (R=Y, Dy-Lu and In) synthesized by Välldor et al. [1,2] has attracted much attention because of its abundant physical and chemical properties [3-11]. A more interesting behavior of RBAaCo$_4$O$_{7+\delta}$ is its unique oxygen-storage capability at relatively low temperatures (200-400 °C) as reported by Karpinnen et al. [12] and Hao et al. [13]. The RBAaCo$_4$O$_{7+\delta}$ oxide experiences two processes of oxygen uptake and subsequent release when heated from room temperature to 1100°C in air or oxygen. One is at around 200-450 °C, and the other is at around 650-1000°C. In the lower temperature range (200-450 °C) the RBAaCo$_4$O$_{7+\delta}$ samples show a reversible oxygen uptake/release and 1.5 extra oxygen atoms can uptake or release per unit cell. The possible reason why RBAaCo$_4$O$_{7+\delta}$-type oxides have the unique oxygen adsorption/desorption properties is also explored, and attributed mainly to its mixed-valence cobalt element, excess oxygen ordering with different configurations, and the coexisting of two types of oxygen diffusions [14,15]. This reversible oxygen uptake/release property of RBAaCo$_4$O$_{7+\delta}$ makes them to be potential candidates in fields such as oxygen-storage, gas purification and gas separation because their oxygen uptake/release capability exceeds substantially the conventional oxygen-storage materials such as CeO$_2$-ZrO$_2$ and YBa$_2$Cu$_3$O$_{7+\delta}$ both in the overall magnitude and in the response sensitivity [16,17].

The oxygen uptake/release properties of RBAaCo$_4$O$_{7+\delta}$ can be modified greatly by element substitution or doping [18-21]. In our investigation using low valence Ca$^{+2}$ partial substitution for Y$^{+3}$ in YBaCo$_4$O$_{7+\delta}$ can eliminate obviously the oxygen uptake peak at lower temperature in TG curves [18]. For $Y>0.4$, the low-temperature oxygen hump of Y$_{1-y}$Ca$_y$BaCo$_4$O$_{7+\delta}$ disappears almost completely. This fact suggests that if using high valence Zr$^{+4}$ substitution for Y$^{+3}$ may enhance the low temperature oxygen hump. Therefore, in the present work, we investigate the doping limit and effects on the oxygen uptake/release properties of Zr for Y.

EXPERIMENTAL

Y$_{1-x}$Zr$_x$BaCo$_4$O$_{7+\delta}$ (x = 0.0, 0.05, 0.1, 0.2, 0.4, 0.6) samples were prepared through the solid-state reaction method. Stoichiometric amount of ZrO$_2$, Y$_2$O$_3$, BaCo$_3$, and Co$_3$O$_4$ raw materials were mixed thoroughly in an agate mortar and the mixed powder was heated slowly up to 1000°C in a box furnace and held at this temperature for 10h. After regrinding, the power were pressed into disk-shaped pellets and sintered at 1140°C in air for 20 h again.

X-ray diffraction (XRD, X’pert Pro system using Cu Kα radiation) analysis was carried out on the sample powder to check the phase purity of the samples. TG measurements (SETARAM, Labsys™) were used to investigate the oxygen uptake/release properties of the
samples. About 100 mg sample powder was heated from room temperature to 1150°C with heating rate 5°C/min in 30ml/min oxygen flow. A special heating program was used to test the oxygen uptake/release properties in the temperature range 340°C ~ 410°C. Firstly, the power was heated to 410°C and kept this temperature for a period of time. Then, the temperature was cooled down to 340°C with cooling rate 15°C/min and kept at this temperature for 40 minutes. Afterward, the temperature was rose to 410°C again with heating rate 15°C/min and kept at this temperature for 20 minutes. The 30ml/min oxygen flow was held during whole cycle. In addition, the oxygen uptake/release cycles by switching the atmosphere between N₂ and O₂ at 350°C were also investigated.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns for Y₁₋ₓZrxBaCo₄O₇₊δ (x = 0.0, 0.05, 0.1, 0.2, 0.4, 0.6). It can be seen that with the increase of the amount of Zr the impurity (ZrO₂, marked as *) increases gradually. For the samples with x ≤ 0.2, main phase of Y₁₋ₓZrxBaCo₄O₇₊δ can be maintained. But, for the samples with x ≥ 0.4 obvious impurity peaks arise indicating a limitation of substitution of Zr for Y. Therefore, in the following we only present the oxygen uptake/release properties for the samples with x ≤ 0.4.

![Figure 1. XRD patterns for Y₁₋ₓZrxBaCo₄O₇ samples.](image)

Figure 2 shows the TG curves of Y₁₋ₓZrxBaCo₄O₇ samples (x = 0.0, 0.05, 0.1, 0.2, 0.4) samples from room temperature to 1150°C, which exhibits the oxygen uptake/release properties of the sample with temperature through mass change percent of its original mass. All five TG curves show a very similar oxygen uptake/release behavior. For each Y₁₋ₓZrxBaCo₄O₇ sample, the TG curve exhibits three humps. The main two are at 200-400°C and 650-890°C respectively as reported by Karppinen et al. [12] and Hao et al. [13]. The third small hump at about 950°C was analyzed by Zhu et al. [15]. In this paper, the investigating emphases are focused on the oxygen behavior only at lower temperatures, in which the YBaCo₄O₇₋δ phase is stable even under different oxygen pressures. After all, the YBaCo₄O₇₋δ phase was reported to be thermodynamically unstable and decomposed above 600°C. While, below 600 °C, the thermodynamic decomposition is already hindered by the kinetics [12]. Comparing oxygen uptake/release humps in lower temperature range in Figure 2, it can be seen that the Y₀.9Zr₀.1BaCo₄O₇₋δ sample has the maximal peak with mass change 2.5% of its original mass, which confirms our conjecture that contrary to the substitution of Ca²⁺ for Y³⁺ replacing Y³⁺ by Zr⁴⁺ will enhance the oxygen-storage capability of YBaCo₄O₇₋δ at lower temperature range 200°C ~ 400°C. The reason may be that the proportion of Co²⁺: Co³⁺ in unit cell increases (over 3:1) when part of Y³⁺ is substituted by Zr⁴⁺. However, for the Zr over doped samples the existence of the impurity phase will counteract the effect of Zr doping, therefore, the over doped sample show a reduced oxygen-storage capability as compared with the undoped sample.

![Figure 2. TG curves of Y₁₋ₓZrxBaCo₄O₇ in O₂ atmosphere.](image)

The enhancement of the oxygen-storage capability of the optimum Zr doped sample can be further confirmed by the TG cycle curves between 340°C ~ 410°C. Fig. 3 shows the mass variation percents of YBaCo₄O₇₋δ and Y₀.₉Zr₀.₁BaCo₄O₇₋δ in oxygen flow in such TG cycle. It can be seen that when kept at 340°C for the same time Y₀.₉Zr₀.₁BaCo₄O₇₋δ can uptake more oxygen than YBaCo₄O₇₋δ. The effect of Zr doping is obvious. The mass percentage change can reach 5.3% for Y₀.₉Zr₀.₁BaCo₄O₇₋δ, 20% higher than undoped sample YBaCo₄O₇₋δ (mass percentage change 4.3%). When the temperature is switched from 340°C to 410°C, the fast oxygen release behavior is not changed by the Zr
Oxygen behavior in Y_{1-x}Zr_{x}BaCo_{4}O_{7+δ}
doping, which is desirable for the actual application of
gas separation. From Figure 3 it can be seen also that
the oxygen uptake/release cycles of both samples show
a good reproducibility, which means the materials have
a stable structure under the temperature heating-cooling
cycles. This fact has been reported in [12, 13] the oxygen
uptake/release at lower temperature will not change the
phase structure of the material which is also beneficial
for the actual applications.

Finally, we present the oxygen uptake/release be-
havior of YBaCo_{4}O_{7+δ} and Y_{0.9}Zr_{0.1}BaCo_{4}O_{7+δ}
at 350°C when atmosphere was switched between O_{2} and N_{2}
as shown in Figure 4. As comparing with Figure 3, the oxygen release in N_{2} at 350°C is very slow. Therefore, in
actual applications rising a little temperature to release the oxygen is more efficient.

CONCLUSION

As contrary to the substitution of Ca^{2+} for Y^{3+},
replacing Y^{3+} by Zr^{4+} will enhance the oxygen-storage
capability of YBaCo_{4}O_{7+δ} at lower temperature range
200°C ~ 400°C. However, there exists a Zr doping
limitation, over doping will result impurity phase which
counteracts the effect of Zr doping. There exist an optimum Zr doping amount, Y_{0.9}Zr_{0.1}BaCo_{4}O_{7+δ} has the
remarkable enhanced oxygen-storage capability. Rising
little temperature to release the oxygen is more efficient
than using N_{2} at lower temperature and is recommen-
ded in actual applications.

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