OXYGEN BEHAVIOR IN $Y_{1-x}Zr_xBaCo_4O_{7+\delta}$

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$Y_{1-x}Zr_xBaCo_4O_{7+\delta}$ (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 $Y_{0.9}Zr_{0.1}BaCo_4O_{7+\delta}$ sample can uptake more oxygen than the undoped $YBaCo_4O_{7+\delta}$ sample at 360°C. Especially, in an oxygen uptake/release cycles between 340°C and 410°C, the mass change of the doped $Y_{0.9}Zr_{0.1}BaCo_4O_{7+\delta}$ 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, $Y_{0.9}Zr_{0.1}BaCo_4O_{7+\delta}$ can also adsorb more oxygen. These properties of $Y_{1-x}Zr_xBaCo_4O_{7+\delta}$ 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 $RBaCo_4O_{7+\delta}$ (R=Y, Dy-Lu and In) synthesized by Valldor et al. [1,2] has attracted much attention because of its abundant physical and chemical properties [3-11]. A more interesting behavior of $RBaCo_4O_{7+\delta}$ is its unique oxygen-storage capability at relatively low temperatures (200-400 °C) as reported by Karppinen et al. [12] and Hao et al. [13]. The $RBaCo_4O_{7+\delta}$ 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 $RBaCo_4O_{7+\delta}$ samples show a reversible oxygen uptake/ release and 1.5 extra oxygen atoms can uptake or release per unit cell. The possible reason why $RBaCo_4O_{7+\delta}$-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 $RBaCo_4O_{7+\delta}$ 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 $YBa_2Cu_3O_{7+\delta}$ both in the overall magnitude and in the response sensitivity [16,17].

The oxygen uptake/release properties of $RBaCo_4O_{7+\delta}$ 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 $YBaCo_4O_{7+\delta}$ can eliminate obviously the oxygen uptake peak at lower temperature in TG curves [18]. For y>0.4, the low-temperature oxygen hump of $Y_{1-y}Ca_yBaCo_4O_{7+\delta}$ 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

$Y_{1-x}Zr_xBaCo_4O_{7+\delta}$ (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_2O_3, $BaCO_3$, and Co_3O_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 reground, 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 N_2 and O_2 at 350°C were also investigated.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns for $Y_{1-x}Zr_xBaCo_4O_{7+\delta}$ (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 (ZrO_2, marked as *) increases gradually. For the samples with x ≤ 0.2, main phase of $Y_{1-x}Zr_xBaCo_4O_{7+\delta}$ 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.
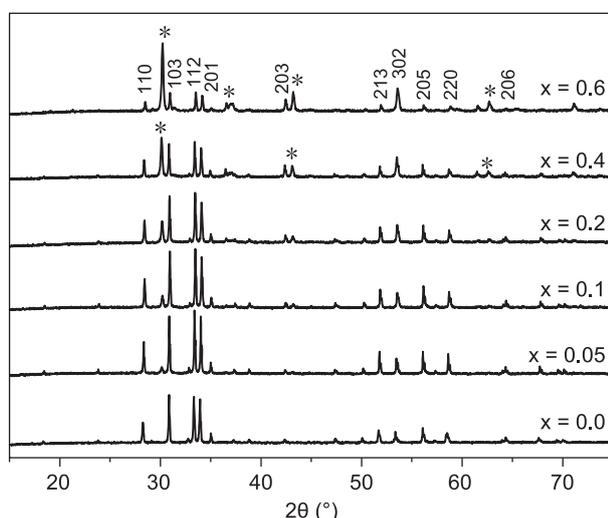

Figure 1. XRD patterns for $Y_{1-x}Zr_xBaCo_4O_7$ samples.

Figure 2 shows the TG curves of $Y_{1-x}Zr_xBaCo_4O_{7+\delta}$ (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 $Y_{1-x}Zr_xBaCo_4O_{7+\delta}$ 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 temperature, in which the $YBaCo_4O_{7+\delta}$ phase is stable even under different oxygen pressures. After all, the $YBaCo_4O_{7+\delta}$ 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 $Y_{0.9}Zr_{0.1}BaCo_4O_{7+\delta}$ sample has the maximal peak with mass change 2.5 % of its original mass, which confirms our conjecture that contrary to the substitution of Ca^{+2} for Y^{+3} replacing Y^{+3} by Zr^{+4} will enhance the oxygen-storage capability of $YBaCo_4O_{7+\delta}$ at lower temperature range 200°C ~ 400°C. The reason may be that the proportion of Co^{+2} : Co^{+3} in unit cell increases (over 3:1) when part of Y^{+3} is substituted by Zr^{+4}. 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.
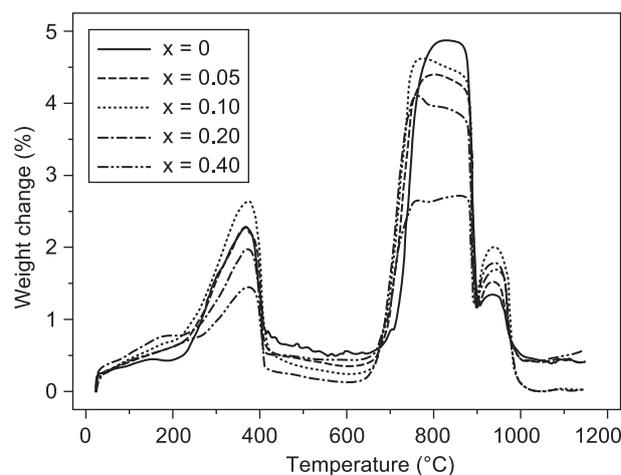

Figure 2. TG curves of $Y_{1-x}Zr_xBaCo_4O_7$ in O_2 atmosphere.

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 $YBaCo_4O_{7+\delta}$ and $Y_{0.9}Zr_{0.1}BaCo_4O_{7+\delta}$ in oxygen flow in such TG cycle. It can be seen that when kept at 340°C for the same time $Y_{0.9}Zr_{0.1}BaCo_4O_{7+\delta}$ can uptake more oxygen than $YBaCo_4O_{7+\delta}$. The effect of Zr doping is obvious. The mass percentage change can reach 5.3 % for $Y_{0.9}Zr_{0.1}BaCo_4O_{7+\delta}$, 20 % higher than undoped sample $YBaCo_4O_{7+\delta}$ (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

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.
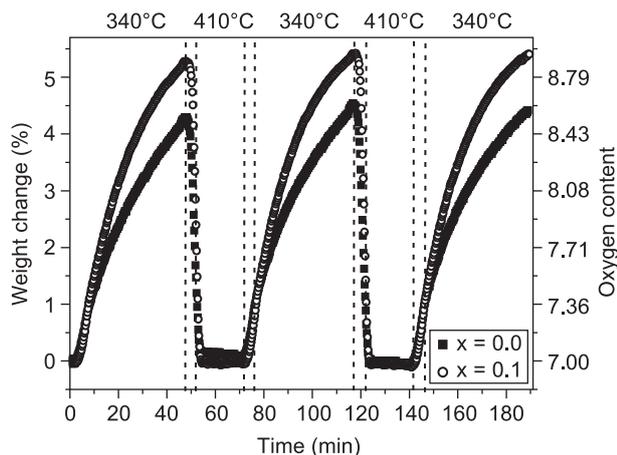

Figure 3. TG curves of $YBaCo_4O_{7+\delta}$ and $Y_{0.9}Zr_{0.1}BaCo_4O_{7+\delta}$ cycling between 340°C and 410°C in O_2 atmosphere.

Finally, we present the oxygen uptake/release behavior of $YBaCo_4O_{7+\delta}$ and $Y_{0.9}Zr_{0.1}BaCo_4O_{7+\delta}$ 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.
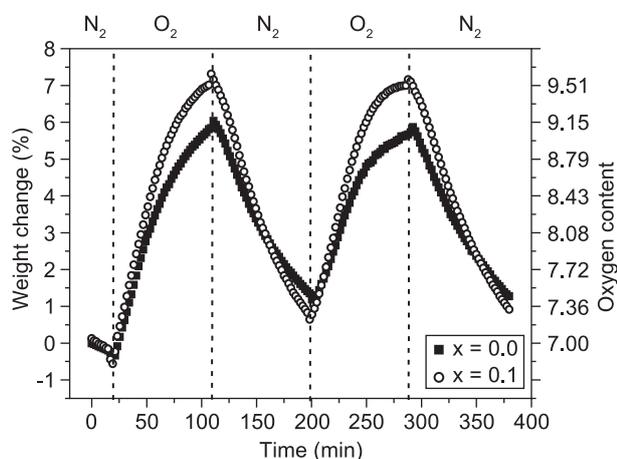

Figure 4. TG curves of $YBaCo_4O_{7+\delta}$ and $Y_{0.9}Zr_{0.1}BaCo_4O_{7+\delta}$ switching between N_2 and O_2 atmosphere at 350°C.

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 $YBaCo_4O_{7+\delta}$ 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, $Y_{0.9}Zr_{0.1}BaCo_4O_{7+\delta}$ 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 recommended in actual applications.

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