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Stability and oxygen-storage characteristics of Al-substituted $YBaCo_4O_{7+\delta}$

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ABSTRACT

A series of Al-substituted $YBa(Co_{1-x}Al_x)_4O_{7+\delta}$ samples was synthesized and characterized with respect to the capability to store large amounts of oxygen at low temperatures (at 200–400 °C) and the phase decomposition upon heating under oxidizing conditions at higher temperatures (above 550 °C). It was revealed that increasing the Al-substitution level up to $x \approx 0.10$ boosts up the phase-decomposition temperature from ~550 to ~700 °C, while the unique oxygen absorption/desorption characteristics remain nearly the same as those of the pristine $YBaCo_4O_{7+\delta}$ phase. The maximum amount of excess oxygen absorbed by the Al-substituted $YBa(Co_{1-x}Al_x)_4O_{7+\delta}$ samples was determined to be as large as $\delta \approx 1.45$ for $x=0.10$ (in 100 atm O_2 at 320 °C). Isothermal annealing experiments carried out for the same $x=0.10$ phase at 300 °C revealed that it could be reversibly charged and discharged with 1.2 oxygen atoms per formula unit by switching the gas flow from N_2 to O_2 and vice versa.

1. Introduction

The ability of the layered $YBaCo_4O_{7+\delta}$ oxide to reversibly absorb/desorb large amounts of oxygen at appreciably low temperatures has made it a highly promising candidate for a new oxygen storage material [1,2]. Through normal-pressure oxygen annealing it is possible to charge the phase with excess oxygen up to $\delta \approx 1.4$ and then discharge it back to $\delta \approx 0.0$ within a narrow temperature range of 200–400 °C. Moreover, taking advantage of high pressures even larger amounts of oxygen (up to $\delta \approx 1.56$) could be loaded into $YBaCo_4O_{7+\delta}$ [3]. Hence the oxygen-storage capacity of $YBaCo_4O_{7+\delta}$ (OSC ≈ 2700 μmol-O/g) substantially exceeds the values reported for the commercial CeO_2-based oxygen-storage material CeO_2–ZrO_2 (OSC ≈ 1500 μmol-O/g) [4] and its recent modification CeO_2–CrO_2 (OSC ≈ 2500 μmol-O/g) [5]. High OSC values have also been reported for rare earth (R) oxysulfates $R_2O_2SO_4$, but the drawback of these compounds is that they operate only at considerably high temperatures [6].

Oxygen-storage materials are already applied in large scale as automotive exhaust catalysts [7]. Novel/better materials are also vigorously searched for applications such as H_2–O_2 fuel cells [8], hydrogen production through solar water splitting [9] and various non-aerobic oxidation processes [10]. In terms of its potential applications the weakest aspect of $YBaCo_4O_{7+\delta}$ is its low-temperature thermodynamical unstability against the more highly oxidized $BaCoO_{3-\delta}$ phase under oxygen-containing atmospheres [1]. Successful synthesis of $YBaCo_4O_{7+\delta}$ requires high temperatures (and preferably low oxygen partial pressures); then at low temperatures it remains only kinetically stabilized against oxidation. The temperature beyond which the $YBaCo_4O_{7+\delta}$ phase readily (i.e. within a finite time) decomposes to $BaCoO_{3-\delta}$ upon heating in an oxygen-containing atmosphere is as low as ~600 °C [1]. We term this temperature as a temperature of oxidative decomposition, $T_{\text{ox-dec}}$. It is an important parameter as it marks the very temperature limit for the safe use of $YBaCo_4O_{7+\delta}$ as an oxygen-storage material. Having the eyes on its potential applications efforts should be made to raise the $T_{\text{ox-dec}}$ value of $YBaCo_4O_{7+\delta}$ [11].

The $YBaCo_4O_{7+\delta}$ phase is rather flexible to accept various cation substitutions, e.g. Ca and the smaller rare earth elements for Y [11–15], and Fe, Ni, Zn, Al and Ga for Co [12,16–18]. Hence it is possible to device a number of different approaches of chemical substitution in order to tailor the $YBaCo_4O_{7+\delta}$ phase towards boosting up the $T_{\text{ox-dec}}$ value. Here we report an increase in $T_{\text{ox-dec}}$ of $YBaCo_4O_{7+\delta}$ by ~150° as achieved through replacing about 10% of Co by Al. Considering the small size of trivalent aluminum ions ($r(Al^{3+})=0.39$ Å in 4-coordination and 0.535 Å in 6-coordination [19]) aluminum indeed most likely substitutes cobalt ($r(Co^{2+})=0.58$ Å in 4-coordination [19]) rather than the larger yttrium ($r(Y^{3+})=0.90$ Å in 6-coordination [19]) or barium ($r(Ba^{2+})=1.52$ Å in 10-coordination [19]) in the $YBaCo_4O_{7+\delta}$ structure. Previous studies focusing on the effects of Al-substitution

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on the crystal structure and magnetic properties of $YBaCo_4O_7$ have moreover concluded that aluminum has a preference—among the two unequivalent cobalt sites—towards the Co1 site (with trivalent cobalt) over the Co2 site (with divalent cobalt) [20].

2. Experimental

A series of $YBa(Co_{1-x}Al_x)_4O_{7+\delta}$ samples with $0.00 \leq x \leq 0.175$ was synthesized by mixing stoichiometric amounts of Y_2O_3, $BaCO_3$, Co_3O_4 and Al_2O_3. After sufficient grinding (for ~1 h) the powder mixtures were pressed into pellets of ~300 mg and fired in an N_2 gas flow at 1050 °C for 12 h. The sample pellets were re-ground and then pressed again into pellets for another heat treatment in an N_2 gas flow at 1050 °C for 20 h. Then they were let slowly cool down to room temperature in the furnace without cutting out the N_2 gas flow. Moreover, in order to guarantee that the samples were in their most reduced state they were additionally annealed in small batches in an N_2 gas flow at 500 °C for 2 h in an air-tight thermobalance. The resultant samples were checked for phase purity by X-ray powder diffraction (XRD; Rigaku: RINT-2000 equipped with a copper rotating anode; 30 kV, 20 mA). The lattice parameters were refined from the XRD data using software JANA2000 in the profile-fitting mode with an accuracy of ±0.02 Å for the unit-cell volume.

Thermogravimetry (TG; Rigaku: Thermo Plus TG 8120) measurements were employed to investigate the low-temperature oxygen absorption/desorption properties and to determine the $T_{\text{ox-dec}}$ value of the samples. In these experiments a sample specimen of ~20 mg was slowly (1 °C/min) heated from room temperature to 1000 °C in an O_2 gas flow. Moreover, isothermal annealing experiments were performed at 300 °C in which the atmosphere was changed between N_2 and O_2 in order to study the reversibility and the speed of oxygen absorption and desorption processes. Some of the samples were additionally oxygenated to the maximum oxygen content by annealing them in an O_2 atmosphere (1–100 atm) at 320 °C. The precise oxygen content was analyzed by iodometric titration [21] for selected samples (both reduced and oxygenated) with an accuracy of ±0.01 for δ based on three to five parallel titration experiments.

Finally the enhanced stability of representative $YBa(Co_{1-x}Al_x)_4O_{7+\delta}$ samples against the oxidative decomposition was verified by heating them in air at different temperatures from 500 to 750 °C in a box furnace for 15 h, followed by quenching to room temperature. X-ray diffraction patterns were then recorded for the quenched samples to detect possible phase decomposition.

3. Results and discussion

The $YBa(Co_{1-x}Al_x)_4O_{7+\delta}$ samples synthesized and subsequently low-temperature annealed in N_2 were found to be of single phase of the $YBaCo_4O_7$-type structure up to x=0.125; XRD patterns for the samples are displayed in Fig. 1. Small peaks due to impurity Al_2O_3 are seen for samples with $x \geq 0.15$, see the right panel of Fig. 1. The fact that aluminum enters the $YBa(Co_{1-x}Al_x)_4O_{7+\delta}$ structure (under the synthesis conditions used) up to $x \approx 0.125$ is also revealed in Fig. 2 where the unit-cell volume of the $YBa(Co_{1-x}Al_x)_4O_{7+\delta}$ phase is plotted against the nominal aluminum content: it decreases linearly with increasing x up to ~0.125, then saturates. Iodometric titration yielded δ values <0.10 for all the single-phase ($0.00 \leq x \leq 0.125$) N_2-annealed $YBa(Co_{1-x}Al_x)_4O_{7+\delta}$ samples.

Thermal behaviors of the samples were investigated in an O_2 gas flow by TG measurements carried out with a slow heating rate of 1 °C/min up to 1000 °C. The resultant TG curves are displayed in Fig. 3. The curves exhibit two humps. The hump in the lower-temperature region of 200–400 °C reflects the ability of the $YBaCo_4O_{7+\delta}$-based compounds to absorb and then to release large amounts of oxygen within a narrow temperature range, while the one in the high-temperature region above 600 °C is due to the oxidative phase decomposition of an $YBaCo_4O_{7+\delta}$-type compound to $BaCoO_{3-\delta}$ (plus debris) [1].

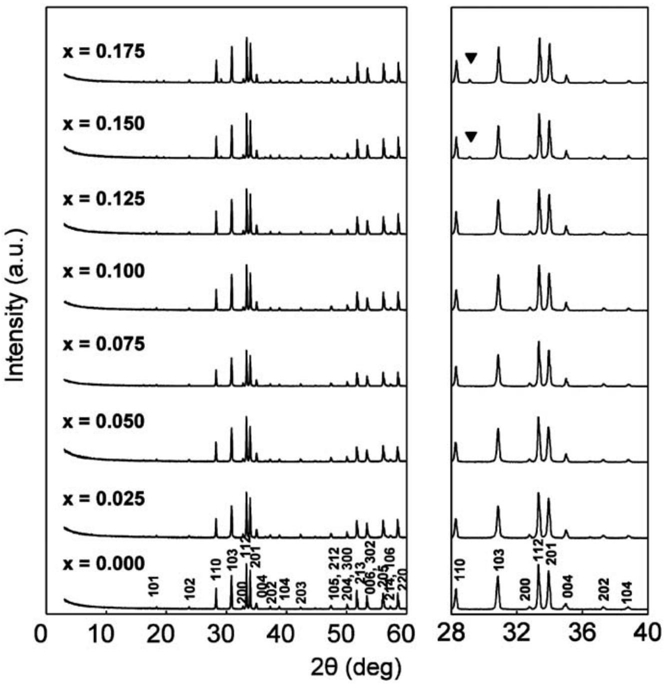

Fig. 1. Evolution of the XRD pattern with increasing Al content x in $YBa(Co_{1-x}Al_x)_4O_{7+\delta}$; the data are for the $\delta \approx 0$ samples obtained through an annealing in an N_2 gas flow at 500 °C. Miller indices are given in space group $P6_3mc$. Peaks due to the Al_2O_3 impurity phase appearing for $x \geq 0.15$ are marked with ▼.

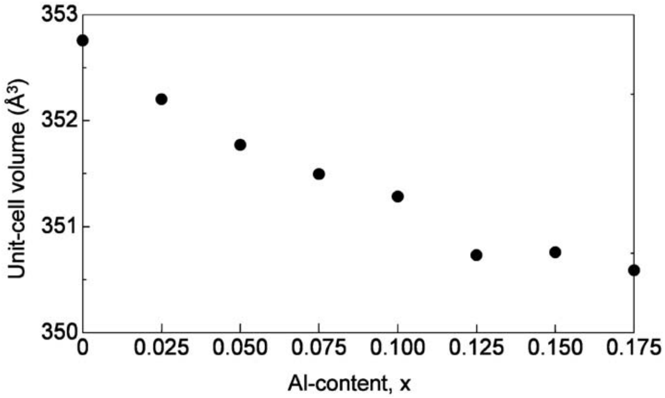

Fig. 2. Decrease of the unit-cell volume with increasing Al content x in $YBa(Co_{1-x}Al_x)_4O_{7+\delta}$; the data are for the $\delta \approx 0$ samples obtained through an annealing in an N_2 gas flow at 500 °C.

From Fig. 3, it is obvious that the higher-temperature hump seen in the TG curves due to the oxidative phase decomposition is drastically affected by the Al-for-Co substitution. Firstly, the magnitude of the hump decreases rapidly as the Al content increases. At the same time, the onset temperature of the weight gain is gradually shifted towards higher temperatures. Hence, increasing the Al-for-Co substitution level (kinetically) stabilizes