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Remarkable Oxygen Intake/Release Capability of $BaYMn_2O_{5+\delta}$: Applications to Oxygen Storage Technologies

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Here, we report the remarkable oxygen intake/release capability of a double perovskite $BaYMn_2O_{5+\delta}$. This oxide rapidly stores/releases a large amount of oxygen (> 3.7 wt %) at moderate temperatures in a perfectly reversible manner. The oxygen intake/release behaviors of $BaYMn_2O_{5+\delta}$ are clearly beyond those of any conventional oxides in terms of the magnitude and sharpness of the processes. It also appeared that this oxide exhibits a significant catalytic activity for flameless combustions of hydrocarbons, presumably owing to its oxygen-storage ability.

Introduction

Oxygen is the most ubiquitous element that is responsible for a huge variety of chemical reactions in energy productions, manufacturing industries, and vital activities. The recent progress in science and technology has required a precise control of redox reactions for novel/better oxygen-related functionalities. Because of increased demands of immediate regulation of oxygen partial pressure [$P(O_2)$] in the gas phase, oxygen-storage materials (OSMs) have attracted great interest.[1−5] These are oxides which reversibly store/release oxygen under oxidative/reductive atmospheres so as to suppress the fluctuation in $P(O_2)$. The CeO_2-ZrO_2 solid solution, the so-called CZ, is the best-known OSM that has been practically used as a three-way catalyst for the effective removal of NO_x, CO, and hydrocarbons from automobile exhausts.[1] OSMs may also be applicable to various redox reactions, e.g., oxidative catalysts, oxidizing agents in anaerobic processes, etc. To realize such applications, novel OSMs with excellent characteristics are highly desirable. Recently, Machida et al. reported a large oxygen-storage capacity (OSC; the amount of mobile oxygen being stored in the crystal lattice) for $Pr_2O_2S/Pr_2O_2SO_4$ (ref 2). However, the drawback of this system is its poor cyclic performance caused by the evaporation of sulfur.[6]

In the present work, we focused on a manganese oxide $BaYMn_2O_{5+\delta}$. The $BaYMn_2O_{5+\delta}$ phase was originally synthesized by Chapman et al.[7] This oxide is categorized as an *A*-site ordered double-perovskite which contains a layered arrangement of smaller yttrium and larger barium ions at the perovskite *A*-site (Figure 1). Oxygen atoms within the yttrium plane are preferentially removed in reductive conditions,[9,10] leading to large oxygen nonstoichiometry ranging from $\delta = 0.0$ to 1.0 (i.e., from O_5 to O_6 forms), which accompanies the variation in Mn valence from +2.5 to +3.5. While the oxygen-nonstoichiometric behavior is also reported for isomorphous iron/cobalt oxides $BaLnM_2O_{5+\delta}$ (Ln = trivalent lanthanide, M = Fe, Co),[11,12] the present manganese oxide shows the widest variation in oxygen content among the double-perovskite oxide members. Because of similarities to colossal magnetoresistive perovskites $Ln_{1-x}AE_xMnO_3$ (AE = Ca, Sr), $BaYMn_2O_{5+\delta}$ and its derivatives ($BaLnMn_2O_{5+\delta}$) have been widely investigated from the viewpoint of physics.[13−16] Nevertheless, the oxygen intake/release characteristics against temperature and the surrounding atmosphere were not well understood. Here, we report

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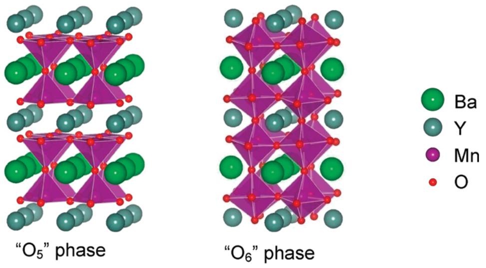

Figure 1. Schematic illustration of the crystal structures of $BaYMn_2O_{5+\delta}$ with oxygen contents $\delta = 0.0$ (left, O_5 phase) and $\delta = 1.0$ (right, O_6 phase). The illustration was drawn with VESTA software[8] based on the structural data in previous literature.

the remarkable oxygen intake/release capability of $BaYMn_2O_{5+\delta}$. This oxide rapidly stores/releases a large amount of oxygen (> 3.7 wt %) at moderate temperatures in a perfectly reversible manner. The oxygen intake/release behaviors are clearly beyond those of any conventional oxides in terms of the magnitude and sharpness of the processes, which make this material a potential candidate for oxygen storage applications.

Experimental Section

Polycrystalline samples of $BaYMn_2O_{5+\delta}$ were synthesized via either a solid-state reaction route utilizing an oxygen-pressure-controlled encapsulation technique (SSR route)[10] or a wet-chemical route with EDTA (ethylenediaminetetraacetic acid) as a complexing agent (EDTA route).[17] For the SSR route, a stoichiometric mixture of $BaCO_3$, Y_2O_3, and Mn_2O_3 preheated in flowing N_2 gas (99.99%) at 1000 °C was used as a precursor. The calcined powder mixture was pressed into pellets and then placed in an evacuated silica ampule together with FeO powder, which acts as a getter for excess oxygen. The silica ampule was heated at 1100 °C for 24 h, followed by rapid cooling to room temperature. For the EDTA route, a stoichiometric amount of $Ba(NO_3)_2$, Y_2O_3, and Mn_2O_3 was dissolved in a concentrated HNO_3 solution in which the EDTA/NH_3 solution was subsequently added. The molar ratio of EDTA/metal ions was 1.5/1.0. The EDTA complex solution was dried and combusted in a porcelain bowl, resulting in a porous solid residue. This solid was ground, pelletized, and then fired at 900−1000 °C in flowing N_2 gas for 12 h.

The as-synthesized product was postannealed at 600 °C in flowing O_2 gas for 12 h to obtain the fully oxygenated O_6 phase. The product thus obtained was further annealed at 500 °C for 12 h in a 5% H_2/95% Ar gas mixture to ascertain whether the incorporated oxygen is removed in a reversible manner. Phase purity and lattice parameters were checked for the resultant products by means of X-ray powder diffraction (XRD; Rigaku Ultima IV; Cu Kα radiation). The Brunauer−Emmett−Teller (BET) specific surface area of the products was determined from N_2 adsorption isotherms measured at 77 K (Quantachrome Instruments Autosorb 6AG).

The oxygen intake/release characteristics of the products were investigated by means of thermogravimetry (TG; Rigaku TG8120GH). The measurements were carried out for ~40 mg specimens with heating/cooling rates of 1 °C/min in flowing O_2 gas or 5% H_2/95% Ar gas mixture. Isothermal TG experiments were also performed upon switching the atmosphere every 10 min between O_2 and 5% H_2/95% Ar to investigate the response and cyclic characteristics of oxygen intake/release processes.

Flameless combustions of hydrocarbons (HC = CH_4 and C_2H_6) were tested to evaluate the catalytic activity of $BaYMn_2O_{5+\delta}$. Approximately 0.5 g of the as-synthesized powder (via the EDTA route; BET surface area = 3.0 $m^2\ g^{-1}$) was diluted with 2 mL of quartz sand and placed in a quartz microreactor (7 mm i.d.ϕ). The activity tests were carried out between 400 and 800 °C in flowing a gas mixture (50 mL min^{-1}) consisting of HC/O_2/H_2O/N_2 = 1.0/0.5/1.0/4.2 in a molar ratio. At each temperature, the specimen was held for ~30 min prior to the analysis to attain the steady state. The outlet gas composition was then analyzed by means of gas chromatography (Shimadzu GC-8A).

Results and Discussion

The synthesis of $BaYMn_2O_{5+\delta}$ was achieved via either a solid-state reaction route utilizing an oxygen-pressure-controlled encapsulation technique or a wet-chemical route with EDTA as a complexing agent. The products prepared by the latter method (EDTA route) exhibited much better oxygen intake/release response than those by the former method (SSR route), although the EDTA route products always contained approximately 5 wt % of $BaMnO_{3-\delta}$ and Y_2O_3 as secondary phases. It should be emphasized that this oxide had never been synthesized through moderate heat treatment becaue of the difficulty in phase formation at low temperatures. Our wet-chemical synthesis led to $BaYMn_2O_{5+\delta}$ products with smaller grain sizes. The BET specific surface areas were 0.50, 1.2, and 3.0 $m^2\ g^{-1}$ for the SSR route product, the EDTA route products prepared at 1000 and 900 °C, respectively. In the present work, fundamental properties (e.g., crystal structure and oxygen nonstoichiometry) were investigated with the SSR route product, while the cyclic performance and catalytic activity were tested with the EDTA route one.

Figure 2 presents X-ray powder diffraction patterns for the as-synthesized (via the SSR route) and postannealed products. The as-synthesized product is essentially the single phase of the oxygen-deficient O_5 phase. All of the diffraction peaks are readily indexed on the basis of the tetragonal $P4/nmm$ space group with the lattice parameters $a = 5.548$ Å and $c = 7.655$ Å, consistent with those previously reported.[9,10] The O_2-annealed product shows a diffraction pattern similar to that of the as-synthesized one, but the position and intensity of some peaks are apparently different. In fact, the pattern is successfully refined with the monoclinic $P2$ model ($a = 5.522$ Å, $b = 5.517$ Å, $c = 7.608$ Å, and $\beta = 90.33°$) that was adopted for the fully oxygenated O_6 phase in previous literature.[10,18] The O_2-annealed product was further annealed in a 5% H_2/95% Ar gas mixture. Small variations are again detected in the diffraction pattern, being identical to that for the as-synthesized product. These findings demonstrate that oxygen intake/release takes place in the course of low-temperature annealing procedures. The similarity in these three patterns implies that the lattice framework

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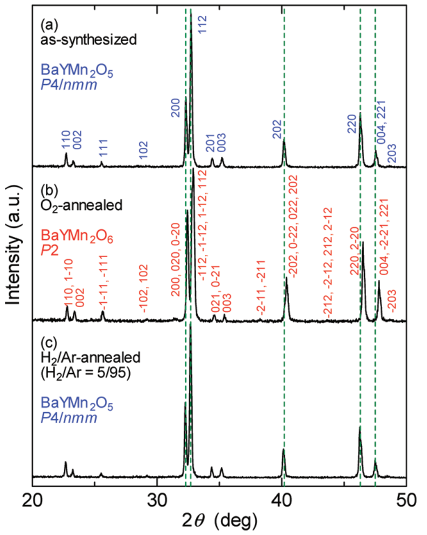

Figure 2. X-ray powder diffraction patterns for the as-synthesized and postannealed $BaYMn_2O_{5+\delta}$ products (via the SSR route). The as-synthesized product (a) was postannealed at 600 °C for 12 h in flowing O_2 gas (b). The product thus obtained was further annealed at 500 °C for 12 h in a 5% H_2/95% Ar gas mixture (c). Diffraction peaks for the as-synthesized and O_2-annealed products are indexed on the basis of tetragonal *P*4/*nmm* and monoclinic *P*2 space groups, respectively.

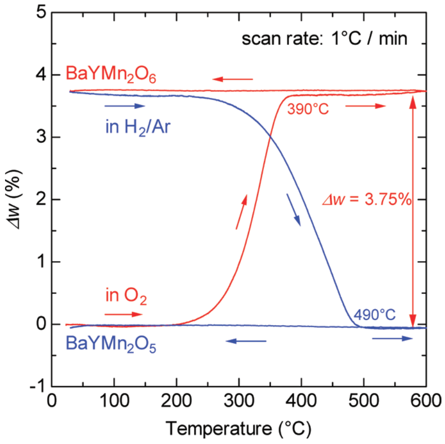

Figure 3. Result of TG analysis for $BaYMn_2O_{5+\delta}$. A portion of the as-synthesized product (via the SSR route) was heated and then cooled in flowing O_2 gas between 25 and 600 °C (scan rate 1 °C/min). The specimen was subsequently heated/cooled in 5% H_2/95% Ar gas mixture with the same temperature scan.

remains essentially unchanged upon oxygen intake/release processes.

Thermogravimetry was carried out both under oxidative/reductive atmospheres (Figure 3). In this analysis, a portion of the as-synthesized product (via the SSR route) was heated and then cooled in O_2 gas between 25 and 600 °C, followed by the same temperature scan in the 5% H_2/95% Ar gas mixture. In flowing O_2 gas, the sample weight starts to increase at about 200 °C and then saturates above 390 °C. The weight gain is most likely attributed to the increase in the oxygen content. The sample weight and accordingly the oxygen content are constant upon cooling in O_2 gas. The magnitude of the weight gain (3.75 wt %) agrees well with the value (3.85 wt %) expected for the O_5-to-O_6 transformation. In the subsequent temperature scan under the reductive atmosphere, the weight loss (i.e., oxygen release) starts and then completes at 200 and 490 °C. Remarkably, the sample weight after the analysis exactly coincides with the initial value.

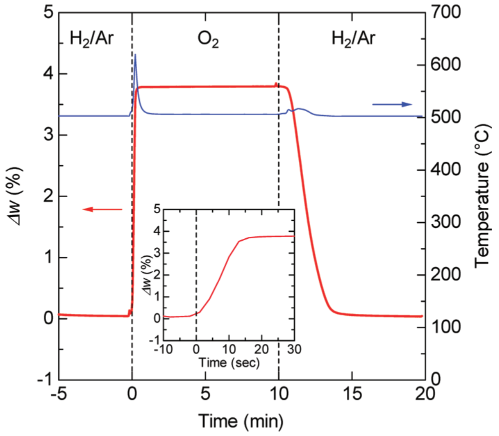

Figure 4. Isothermal TG curve for the $BaYMn_2O_{5+\delta}$ product (via the EDTA route) in 5% H_2/95% Ar, O_2, and then 5% H_2/95% Ar. Time variation in the sample temperature is also plotted. The inset shows the enlargement of the TG curve when the gas flow was switched from 5% H_2/95% Ar to O_2.

All of these results indicate the excellent oxygen intake/release characteristics of $BaYMn_2O_{5+\delta}$. This oxide is featured with a wide range of oxygen nonstoichiometry in which one out of six oxygen atoms per formula unit is incorporated/released. Whereas some perovskite oxides such as $SrCoO_{3-y}$,[19] $CaFeO_{3-y}$,[20] and $LaCuO_{3-y}$[21] are known to exhibit comparably large oxygen nonstoichiometry ($0 \leq y \leq 0.5$), fully oxygenated products ($y = 0$) of these three systems are obtained only with extreme synthesis conditions. Meanwhile, our $BaYMn_2O_{5+\delta}$ allows us to access the whole range of oxygen composition with moderate heat treatments, leading to OSCs as large as 3.8 wt %. This value is indeed much larger than the maximum value for the conventional OSM, CZ (2.8 wt %).[1] A large OSC value is one of the necessary requirements for potential OSMs since it determines the quantity of the material needed for the target redox reaction.

Next, we measured isothermal TG curves of the $BaYMn_2O_{5+\delta}$ products upon switching the atmosphere between O_2 and 5% H_2/95% Ar at 500 °C (Figure 4). It appears that $BaYMn_2O_{5+\delta}$ can store/release ~3.7 wt % of oxygen in response to the variation in surrounding atmosphere. The magnitude of the weight gain is in good agreement with the ideal OSC value (3.85 wt %), indicating that the full amount of mobile oxygen has been involved. More noteworthy, the specimen has completed oxygen intake only within 12 s, i.e., an extremely fast oxidation reaction (see inset of Figure 4). Because of the fast oxidation, large exothermic heat has been produced in a short period, resulting in a sharp rise in the sample temperature by 120 °C. From the TG curve, the oxygen-intake

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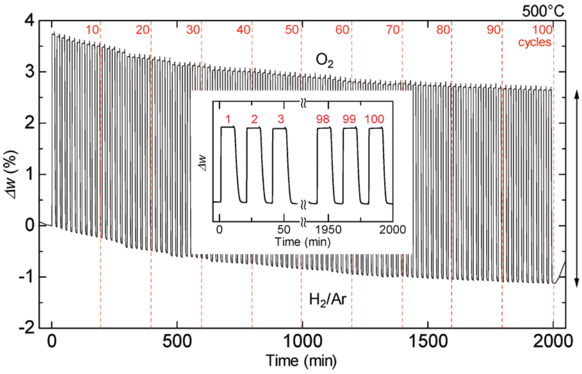

Figure 5. Oxygen intake/release cycles at 500 °C for the $BaYMn_2O_{5+\delta}$ product (via the EDTA route). The TG data were measured while the gas flow was switched every 10 min from O_2 and 5% H_2/95% Ar and vice versa. A gradual decrease in weight is due to an extrinsic cause such as volatilization of carbon residues. The inset shows enlarged TG data at the first, second, third, 98th, 99th, and 100th cycles.

rate is estimated to be ~25 wt % min^{-1} at 500 °C. This value is much larger than those for known OSMs: 9.3 wt % min^{-1} for $Pr_2O_2S/Pr_2O_2SO_4$ (700 °C) and 3.6 wt % min^{-1} for CZ (700 °C).[2] While the oxygen-intake rate was nearly constant in all of the products, the response of oxygen release was found to depend strongly on grain morphology. In fact, as the specific surface area of the product increases, the time required for complete oxygen release is effectively shortened from 20 min (BET surface area: 0.50 m^2 g^{-1}) to 3 min (3.0 m^2 g^{-1}). Taking into account the experimental fact that the oxygen-intake rate is independent of the grain size, the bulk oxygen-diffusion rate is likely to be fast enough. We thus suggest that the formation of H_2O molecules at the grain surface is the rate-limiting factor in the redox processes.

From a practical standpoint, it is important for $BaYMn_2O_{5+\delta}$ to evaluate its cyclic performance in repeating oxygen intake/release processes. Figure 5 shows a long-term isothermal TG curve at 500 °C. Our TG analysis demonstrates a perfect durability upon switching the surrounding atmosphere: neither reduced capacity nor deteriorated response is detectable even after the 100th cycle. We also confirmed that this oxide retains its excellent cyclic characteristics at temperatures as high as 900 °C (see Supporting Information). This finding is somewhat surprising because $BaYMn_2O_{5+\delta}$ may not be a thermodynamically stable phase in flowing O_2 gas, according to the experimental fact that it never forms in oxidative atmospheres. The high stability of $BaYMn_2O_{5+\delta}$ is also confirmed by the previous TG result,[10] in which this compound does not show any signature of phase decomposition in flowing O_2 gas up to 800 °C. The lattice framework with a perovskite-type structure is kinetically robust enough to avoid the thermal instability of $BaYMn_2O_{5+\delta}$ at moderate temperatures.

In terms of the origin of the fast oxygen intake/release of $BaYMn_2O_{5+\delta}$, several important structural features can be pointed out. First, this oxide crystallizes in an oxygen-deficient layered structure in which an ionic conduction pathway inherently exists. Fast oxygen diffusion within the yttrium plane is believed to play a key role in the high sensitivity against temperature and surrounding atmosphere. We note that a fast oxygen-exchange rate was reported also for the isomorphous cobalt oxide $BaLaCo_2O_{5+\delta}$.[22] Second, $BaYMn_2O_{5+\delta}$ is known to possess only three distinct values for its oxygen content, i.e., δ = 0.0, 0.5, and 1.0, presumably due to a strong tendency of oxygen-vacancy ordering.[10,23,24] This feature prohibits a gradual change in the oxygen content and thus induces a steep chemical−potential gradient between oxygen-deficient ($O_5/O_{5.5}$) and fully oxygenated (O_6) domains, leading to significant chemical diffusion at the interface. Such a diffusion mechanism is likely to make positive impact on the oxygen intake/release kinetics.

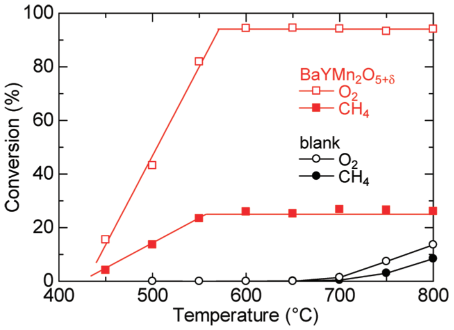

Figure 6. Conversion of CH_4 and O_2 as a function of temperature in the CH_4 combustion experiments. The as-synthesized $BaYMn_2O_{5+\delta}$ powder (via the EDTA route, BET surface area = 3.0 m^2 g^{-1}) without implanted noble metals was used as an oxidative catalyst. For reference, the result of a blank test is also included.

To explore the capability of $BaYMn_2O_{5+\delta}$ as an oxidative catalyst, flameless combustions of hydrocarbons were tested. The as-synthesized $BaYMn_2O_{5+\delta}$ powder (via the EDTA route; BET surface area =3.0 m^2 g^{-1}) without implanted noble metals was used for the CH_4 combustion (i.e., $CH_4 + 2O_2 = CO_2 + 2H_2O$). The feed-gas composition was set to $CH_4/O_2/H_2O/N_2$ = 1.0/0.5/1.0/4.2 in a molar ratio, with anticipation that this oxide effectively acts as an oxidizing agent in reductive (i.e., fuel-rich) atmospheres. Figure 6 presents the conversion of CH_4 and O_2 as a function of temperature (the result of C_2H_6 combustion is given in Supporting Information). Whereas CH_4 combustion never occurs below 700 °C in a blank test, $BaYMn_2O_{5+\delta}$ powder highly promotes the oxidation of CH_4. The conversion values are saturated at 550−600 °C, indicating that the combustion essentially completes above this temperature. We interpret that the significant catalytic activity may be related to the unique feature of $BaYMn_2O_{5+\delta}$. Owing to its oxygen-storage ability, this oxide can provide highly reactive lattice oxygen, which effectively oxidizes CH_4 molecules at the grain surface. It should be emphasized that for our $BaYMn_2O_{5+\delta}$ products no efforts were made to optimize the grain morphology: the BET surface area of ~3.0 m^2 g^{-1} is

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apparently insufficient to achieve the maximum performance. Hence, the catalytic activity could be drastically enhanced as the surface area of the $BaYMn_2O_{5+\delta}$ product is accordingly increased.

Conclusions

The present work revealed remarkable oxygen intake/release capability of a double perovskite $BaYMn_2O_{5+\delta}$. This oxide can rapidly store/release a large amount of oxygen (> 3.7 wt %) at moderate temperatures in a perfectly reversible manner. Owing to this unique ability, various future applications to oxygen-storage technologies are promising. For instance, the great ability to capture O_2 gas is advantageous to practical uses as oxygen scavengers for inert gas purifications[25] or cathode materials in solid oxide fuel cells (SOFC).[26] Also, the facile oxygen release at moderate temperatures may be applied to catalytic oxidizing reactions such as decomposition combustion of volatile organic compounds.

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Supporting Information Available: X-ray powder diffraction patterns for $BaYMn_2O_{5+\delta}$ products prepared by various synthesis routes, SEM images of these products, isothermal TG curves at high temperatures, and the result of the C_2H_6 combustion experiments (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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