Oxygen storage properties and catalytic activity of layer ordered perovskites

BaY_{1-x}Gd_xMn₂O_{5+δ}

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Abstract

Crystal structure, oxygen storage-related and preliminary anaerobic methane combustion studies were conducted for BaY_{1-x}Gd_xMn₂O_{5+δ} (0, 0.25, 0.5, 0.75 and 1) series of oxides prepared by a sol-gel method. All samples were found to possess layered-type A-site cation ordering, with the unit cell volume linearly dependent on the average radius of Y_{1-x}Gd_x for both, the reduced and the oxidized materials. The oxygen content in the temperature range of 400-600 °C indicate change on the order of 1 atomic mole, occurring when the sample's surrounding atmosphere was changed from air to 5 vol.% H₂ in Ar. The time dependence of the reduction shows activated character on temperature, with an activation energy, which seems to be related to the oxygen diffusion in the bulk of the materials. Initial data concerning methane combustion in oxygen-free conditions show promising catalytic activity of BaYMn₂O₆ at elevated temperatures.

Keywords

Oxygen production; Oxygen Storage Materials; Perovskite oxides; Crystal structure; Thermogravimetric analysis; Flameless methane combustion

Introduction

Worldwide market of industrial gases was estimated at 38.0 billion USD in year 2011, and predicted to show a compounded annual growth rate of 6.3% by 2018, up to 58.4 billion USD [1]. Large fraction of the observed market growth, up to 6.1 billion USD by 2018, is related to the oxygen production and consumption due to the increased demand from developing countries. Growth results from the rising industrial demand for oxygen needed in production of steel and non-ferrous metals, chemicals, petrochemicals, glass, ceramics, paper, as well as in healthcare and medical sector [1]. Currently, the need for the oxygen at such large scale is mainly met by usage of cryogenic production method. However, despite high purity of the obtained oxygen (> 99%), very high capital costs, complex production and specific operating conditions (low temperature and high pressure) make the method exceedingly energy-consuming and expensive [2, 3]. Another way for obtaining oxygen from air, applicable on the medium-sized industrial scale, is Pressure Swing Adsorption (PSA), which allows to achieve 85-94% purity of the oxygen. The principle behind PSA process is a difference in chemical affinity of the air components to the adsorber [4, 5]. PSA systems are characterized by a near-ambient working temperature and pressure, and therefore are less complicated in design and cheaper in operation. Besides these two mature technologies, oxygen separation using (dense) Ionic Transport Membranes (ITM) is considered as a promising alternative. The proposed membrane materials are usually ceramics with high oxygen ion conductivity, such as perovskite-type ABO_3 , fluorite-type AO_2 , brownmillerite-type $A_2B_2O_5$, Ruddlesden-Popper series $A_{n+1}B_nO_{3n+1}$, etc. [6-8]. In some designs, a driving force for the O^{2-} diffusion is the oxygen partial pressure difference between both sides of the membrane, while in others, the diffusion is driven by an applied voltage. Presence of electronic component of the

electrical conductivity of the material (MIEC-type membrane) results in a simplification of the engineering design that should reduce operating costs. Currently, perovskite-type oxides are considered among the most attractive materials for ITMs in oxygen separation applications [8].

Recently, excellent oxygen storage properties have been shown for the A-site cation layer-ordered $\text{BaLnMn}_2\text{O}_{5+\delta}$ (Ln: lanthanides and Y) oxides, in which almost complete and reversible change of the oxygen content between the reduced $\text{BaLnMn}_2\text{O}_5$ and the oxidized $\text{BaLnMn}_2\text{O}_6$ occurs at moderate temperatures (300-500 °C) with a change of the oxygen partial pressure (e.g. air and 5 vol.% H_2 in Ar) [9-15]. While Zr- and Ce-based oxygen storage materials (OSM) have been already successfully utilized in three-way catalytic converters [16], these novel $\text{BaLnMn}_2\text{O}_{5+\delta}$ attracted scientific interest, due to their higher reversible oxygen storage capacity (OSC) and faster reaction kinetics, making them attractive from a point of view of application in various technological processes, such as *oxy-fuel* [17] and *chemical looping* [18-20] combustion, which require a precise control of the oxygen partial pressure ($p\text{O}_2$) [10, 12-13]. For $\text{BaYMn}_2\text{O}_{5+\delta}$ compound, the measured value of the reversible OSC was reported near 3.7 wt.% at 500 °C [10-12]. Moreover, catalytic activity for flameless combustions of hydrocarbons was discovered for BaYMn_2O_6 , and it was explained as due to its oxygen storage capability [9].

It seems thus that (high purity) oxygen can be also produced using such OSMs, for instance by a loop-type process, during which the reduced material absorbs O_2 at elevated temperatures from, e.g. the air, and releases the oxygen under low $p\text{O}_2$ conditions, e.g. under vacuum [21]. However, it is yet to be determined if the observed OSC and costs of such systems would be technically and economically reasonable, especially considering larger-scale oxygen production.

In this work, characterization of substituted $\text{BaY}_{1-x}\text{Gd}_x\text{Mn}_2\text{O}_{5+\delta}$ system is presented in terms of crystal structure of the materials (with synchrotron data for $\text{BaYMn}_2\text{O}_{5+\delta}$ and $\text{BaGdMn}_2\text{O}_{5+\delta}$), oxygen storage-related properties (thermogravimetric studies in 400-600 °C range), as well as with initial results concerning anaerobic methane combustion for BaYMn_2O_6 . Choice of chemical composition of the series can be justified as follows: the fastest reduction speed among previously

investigated $\text{BaLnMn}_2\text{O}_6$ (Ln: Pr, Nd, Sm, Gd, Dy, Er and Y) oxides was recorded for $\text{BaGdMn}_2\text{O}_6$ [11], on the other hand, heavier lanthanides limit reversible oxygen storage capacity of the materials. It can be therefore expected that by a partial substitution of Y by Gd some improvement of the oxygen release kinetics may be obtained, while the OSC should remain high.

Experimental

$\text{BaY}_{1-x}\text{Gd}_x\text{Mn}_2\text{O}_{5+\delta}$ (0, 0.25, 0.5, 0.75 and 1) oxides were synthesized by a soft chemistry, sol-gel method. Respective nitrates were dissolved in a small amount of deionized water, with ammonia salt of ethylenediaminetetraacetic acid (EDTA), dissolved in diluted ammonia, used as a complexing agent. As prepared mixtures with pH of around 8 were heated in quartz evaporators in air, up to about 400 °C, resulting in water evaporation, sol-gel transition, decomposition of excessive ammonium nitrite and oxidation of a residual carbon. The obtained precursors were grinded and pressed into pellets. The actual synthesis was performed at 1100 °C for 8 h under reducing atmosphere of 1 vol.% H_2 in Ar, with a gas flow of about $100 \text{ cm}^3 \text{ min}^{-1}$. Relative density of the obtained pellets was ca. 80%. All the presented measurements were carried out on powdered samples, obtained after grinding of the sinters. Before studies the respective powder was sieved on a 100 μm sieve, with the smaller fraction taken for the investigations.

Initial structural studies of the materials were carried out on Panalytical Empyrean diffractometer in 10-110 deg range using CuK_α radiation. High-energy, high-resolution synchrotron X-ray powder measurements for the oxidized (500 °C in air, $\delta \approx 1$) and the reduced (500 °C in 5 vol.% H_2 in Ar, $\delta \approx 0$) $\text{BaYMn}_2\text{O}_{5+\delta}$ and $\text{BaGdMn}_2\text{O}_{5+\delta}$ compounds were conducted at 11-BM station at Argonne's Advanced Photon Source. For Rietveld analysis, GSAS/EXPGUI set of software was used [22, 23]. Preferential orientation correction was utilized in the refinements.

All studies concerning oxygen storage properties were conducted on TA Q5000 IR thermobalance. For the experiments 30-50 mg of the studied powder was placed on the Pt holder. Isothermal reduction (in 5 vol.% H_2 in Ar) and oxidation (in air) runs were conducted in 400-600 °C

temperature range with a gas flow of $100 \text{ cm}^3 \text{ min}^{-1}$. Before studies, the samples were cycled five times isothermally at 500°C . This step was introduced in order to clean surface of the materials from any possible carbon residue from the synthesis, as well as to remove adsorbed gases. As it was shown before [11-14], while during initial several cycles some improvement of the reduction kinetics is observed, the following reduction/oxidation cycles of $\text{BaLnMn}_2\text{O}_{5+\delta}$ materials are practically identical at particular temperature.

Preliminary catalytic tests were conducted on a custom-made setup comprising a furnace, a gas supply system with mixer and mass flow controllers, U-tube quartz sample holder with inner diameter of the catalytic bed zone of 15 mm, and Pfeiffer Vacuum ThermoStar mass spectrometer. For the experiment, ca. 0.25 g of BaYMn_2O_6 sample was mixed with 2.68 g quartz powder and placed in the reactor. Gas flow (pure Ar or 10 vol.% CH_4 in Ar) was kept at constant level of 25 ml min^{-1} .

Results and discussion

Crystal structure

Exemplary synchrotron data together with Rietveld refinements for $\text{BaGdMn}_2\text{O}_5$ and $\text{BaGdMn}_2\text{O}_6$ oxides are presented in Figs. 1a and b. Although preferential orientation-related correction, intensity of (200) reflection could not be refined well. Also, some of the peaks showed evident asymmetry and broadening, likely indicating influence of the internal strain. This can be understood as due to the preparation method of the studied samples, i.e. reduction and oxidation at 500°C . As the temperature, at which the materials were treated, is rather moderate, the crystal lattice might not fully relax after accommodation/removal of 1 mole of the oxygen. Despite the mentioned problems, relatively good quality of the refinements was achieved. The structural parameters of $\text{BaGdMn}_2\text{O}_5$ and $\text{BaGdMn}_2\text{O}_6$, together with data for both Y-containing materials are gathered in Tab. 1. No significant amount of the secondary phases was detected, with BaMnO_3 and YMnO_3 minor impurities visible for the Y-containing materials. Also, no improvement of the refinements was

achieved assuming partial mixing between Ba and Gd (or Y) cations, indicating that the layered arrangement of the Ba-Gd (or Y) cations is well-maintained. The obtained data are in accordance with previous published results [11, 24, 25]. Interestingly, in the case of BaGdMn₂O₆ material, an additional peak was observed in the vicinity of 1.5 deg, which could be successfully refined assuming additional doubling of the unit cell along *c* axis. As can be seen in Fig. 1b inset, the Le Bail-type refinement indicated possibility of presence of such the structure, however, at this point it is not possible to establish partial coordinates of all the atoms in such big (*c* ≈ 15.22 Å) unit cell. Using published data for BaY_{1-x}Gd_xMn₂O_{5+δ} (0.25, 0.5 and 0.75) oxides [25], a dependence of the unit cell volume as a function of the average radius of Y_{1-x}Gd_x (taken for 8-fold coordination, due to the availability of ionic radii data) was evaluated (Fig. 1c). Similarly to the results shown for BaLnMn₂O₅ and BaLnMn₂O₆ (Ln: selected lanthanides) [12-14], the dependence was found to be linear, and more strongly dependent on the chemical composition for the reduced compounds.

Oxygen storage properties

It is well-known that the reduction process for BaYMn₂O_{5+δ} is much longer than the strongly exothermal oxidation [11, 26]. Therefore, considering oxygen storage-related performance, measurements and analysis of the reduction process are of more importance. Detailed information about theoretical and practical OSC on reduction, recorded for all investigated materials, is shown in Tab. 2. It can be noticed that the measured OSC increases with temperature, and in some of the cases exceeds the theoretical value. As it is highly unlikely to introduce more oxygen into the oxidized BaLnMn₂O₆, this can be rather understood as due to reduction of the samples, with oxygen content being below 5 (partial removal of oxygen from square-pyramidal coordination of Mn cations). In general, the data are comparable to previously published for different BaLnMn₂O_{5+δ} [11-14]. Fig. 2a presents reduction curves in 5 vol.% H₂ in Ar, exemplary for BaY_{0.25}Gd_{0.75}Mn₂O₆ compound, recorded in 400-600 °C temperature range. The marked points in the figure correspond to the time needed for achieving 3 wt.% of the weight change. Analogous measurements were

conducted for other $\text{BaY}_{1-x}\text{Gd}_x\text{Mn}_2\text{O}_6$ materials, which allowed to observe that such defined reduction time strongly decreases on temperature. Interestingly, if shown in Arrhenius-type, $\log(T/t)$ vs. $1/T$, coordinates, the reduction time exhibits activated character on temperature, as depicted in Fig. 2b. The calculated values of E_a were found to be in 0.72-0.85 eV range. In addition, it was found that such calculated activation energy increases with the increasing value of the weight change taken as the end point of reduction time measurements, as presented in Tab. 3. However, for assumed larger weight changes, the E_a values are similar. The results support known fact that the mechanism of the oxygen release changes on reduction, and is essentially of a two-phase type with a strong tendency of formation of the oxygen vacancy-ordered $\text{BaLnMn}_2\text{O}_{5.5}$ phase [27]. $\log(T/t)$ vs. $1/T$ coordinates were chosen instead of the standard Arrhenius ones, as they are representative for systems with ionic conduction, in which mobility of the charge carriers μ depends on their charge q , diffusion coefficient D and temperature: $\mu = qD/k_bT$ (k_b - Boltzmann constant). As expected, higher R^2 values were obtained for fitting of the data in such coordinate system.

Unfortunately, as change of the oxygen content is close to one mole per mole of the material during reduction, the recorded characteristics (Fig. 2a) cannot be used as relaxation profiles for fitting values of chemical diffusion coefficient D and surface exchange coefficient k , as both values are expected to change with the proceeding reaction. However, as all studied powders show similar morphology with BET specific surface of $1.4\text{-}2.4\text{ m}^2\text{ g}^{-1}$, and the reduction experiments were conducted in the same conditions, we propose that the calculated E_a allows to compare samples between each other. Furthermore, literature data for perovskite-type oxides suggest that values of k are usually at least 2-3 orders of magnitude higher than the diffusion coefficient values at the respective temperature and that the temperature dependence of k is often not clearly defined [28-32]. Using this information, and taking into consideration morphology of the powders, it can be stated that the oxygen release process in the studied case is expected not to be surface exchange-limited, however, k -limitation cannot be completely ruled out. Considering the simplest approach with mean square displacement of the diffusing species (oxygen) being proportional to the diffusion

coefficient and time, it can be justified that $D_1 \cdot t_1 = D_2 \cdot t_2$, where indexes stand for different temperature. This can be done, as the oxygen release at different temperatures takes place from the same grains of the same sample. Since D shows activated character on temperature, the observed activated character of reduction time is therefore not unexpected. Taking into account that charge carrier mobility is proportional to its diffusion coefficient, for the particular case it can be very roughly approximated that the the calculated activation energy on the order of 0.7-0.8 eV can be related to the activation energy of the oxygen mobility during final stages of the oxygen release.

It should be also added that electrical conductivity of the reduced $\text{BaLnMn}_2\text{O}_5$, in which manganese cations possess Mn^{2+} and Mn^{3+} oxidation states is generally much lower, comparing to the values observed for the oxidized materials with average $\text{Mn}^{3.5+}$ state [12, 33], which may also affect the observed reduction/oxidation characteristics.

Summarizing the oxygen storage-related results, one may notice lack of a clear relationship of the data with the chemical composition of the samples, however, the faster reduction time with 3 wt.% weight change was recorded in 450-600 °C range for the substituted $\text{BaY}_{0.75}\text{Gd}_{0.25}\text{Mn}_2\text{O}_{5+\delta}$, showing OSC, which exceeds 3.5 wt.% in this range.

Anaerobic methane combustion on BaYMn_2O_6

Following paper published by Motohashi et al. [9], a custom-made setup was built to study possibility of methane combustion in oxygen-free conditions using BaYMn_2O_6 as the oxygen carrier and catalyst (see Experimental section for more details). During the experiment, switching of the gas flow from pure Ar to 10 vol.% CH_4 in Ar resulted in an initial increase of methane- and CO_2 -related signals, recorded by a mass spectrometer. Since no oxygen was present in the feed gas, presence of CO_2 in the exhaust gas is a direct proof of catalytic reaction, which can be summarized as:

While the used system was not calibrated for the quantitative analysis, and conditions of the experiment do not allow for elucidation of a nature of the ongoing methane oxidation (i.e., is it occurring in the gas atmosphere with released oxygen or rather on surface on the BaYMn_2O_6), the results prove that the material is active in oxygen-free conditions in relation to the methane conversion. At the present moment no quantitative evaluation could be performed regarding amount of the remaining CH_4 , concentration of CO_2 and H_2O , as well as CO and H_2 , which can be produced in complex reactions taking place during methane oxidation, but the constructed system seems to be appropriate for further studies of the anaerobic methane combustion.

Conclusions

The obtained A-site cation ordered $\text{BaY}_{1-x}\text{Gd}_x\text{Mn}_2\text{O}_{5+\delta}$ (0, 0.25, 0.5, 0.75 and 1) oxides show A-site cation-ordered structure (layered-type). Unit cell volume was found to be linearly dependent on the average radius of $\text{Y}_{1-x}\text{Gd}_x$ for both, the reduced and the oxidized materials, with stronger dependence visible for the reduced samples. The recorded oxygen storage-related performance of the materials is promising, with OSC exceeding 3 wt.% for all studied compounds in 400-600 °C temperature range. The measured reduction time, depending on the used assumptions, shows activated character on temperature, with activation energy values being in 0.72-0.85 eV range (for 3 wt.% change taken as the reference point). While this can be related to the oxygen diffusion in the bulk of the studied materials, no clear dependence on chemical composition of the samples was observed. Additionally, preliminary mass spectroscopy measurements showed that CH_4 can be oxidized with a help of BaYMn_2O_6 even in absence of oxygen in the feed gas stream.

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Figure captions

Fig. 1. Exemplary X-ray synchrotron data with Rietveld refinement for a) $\text{BaGdMn}_2\text{O}_5$ and b) $\text{BaGdMn}_2\text{O}_6$, c) unit cell dependence on the average radius of $\text{Y}_{1-x}\text{Gd}_x$ for reduced and oxidized $\text{BaY}_{1-x}\text{Gd}_x\text{Mn}_2\text{O}_{5+\delta}$.

Fig. 2. a) Reduction characteristics in 5 vol.% H₂ in Ar, recorded in 400-600 °C. Exemplary data for BaY_{0.25}Gd_{0.75}Mn₂O₆. b) Time needed for 3 wt.% change of weight of BaY_{1-x}Gd_xMn₂O_{5+δ} samples presented Arrhenius-type coordinates together with calculated values of the activation energy.

Figure 1a

Figure 1b

Figure 1c

Figure 2a

Figure 2b

Tab. 1. Structural parameters of BaGdMn₂O_{5+δ} and BaYMn₂O_{5+δ} at the room temperature.

composition	BaGdMn ₂ O ₅	BaGdMn ₂ O ₆	BaYMn ₂ O ₅	BaYMn ₂ O ₆
space group	<i>P4/nmm</i>	<i>P4/nmm</i>	<i>P4/nmm</i>	<i>P</i> -1
<i>a</i> [Å]	5.5797(1)	5.5346(1)	5.5489(1)	5.5230(1)
<i>b</i> [Å]				5.5181(1)
<i>c</i> [Å]	7.6862(1)	7.6110(1)	7.6588(1)	7.6125(1)
β [deg] ^a				90.30(1)
<i>V</i> [Å ³]	239.30(1)	233.14(1)	235.82(1)	231.99(1)
Mn(1) (<i>x,y,z</i>)	(0.25,0.25,0.254(1))	(0.25,0.25,0.248(1))	(0.25,0.25,0.276(1))	(0.256(1),0.257(1), 0.258(1))
Mn(2) (<i>x,y,z</i>)	(0.25,0.25,-0.272(1))	(0.25,0.25,-0.260(1))	(0.25,0.25,-0.254(1))	(0.256(1),0.246(1), -0.259(1))
O(1) (<i>x,y,z</i>)	(0.509(1),0.509(1), 0.313(1))	(0.514(1),0.514(1), 0.279(1))	(0.505(1),0.505(1), 0.318(1))	^b
O2 (<i>x,y,z</i>)	(0.25,0.25,-0.007(1))	(0.25,0.25,0.005(1))	(0.25,0.25,0.000(1))	^b
O3 (<i>x,y,z</i>)		(0.25,0.25,0.489(2))		^b
χ^2	4.01	6.68	9.27	9.44

^athe remaining α and γ angles are ≈ 90 deg, ^bdue to lower symmetry, fractional coordinates of the oxygens are not given

Table 2

Tab. 2. Oxygen storage capacity for $\text{BaY}_{1-x}\text{Gd}_x\text{Mn}_2\text{O}_{5+\delta}$ at various temperatures.

composition	theoretical OSC [wt.%]	measured OSC on reduction [wt.%]				
		400 °C	450 °C	500 °C	550 °C	600 °C
$\text{BaYMn}_2\text{O}_{5+\delta}$	3.85		3.56	3.61	3.67	3.72
$\text{BaY}_{0.75}\text{Gd}_{0.25}\text{Mn}_2\text{O}_{5+\delta}$	3.69	3.42	3.58	3.60	3.62	3.63
$\text{BaY}_{0.5}\text{Gd}_{0.5}\text{Mn}_2\text{O}_{5+\delta}$	3.55	3.39	3.50	3.54	3.54	3.53
$\text{BaY}_{0.25}\text{Gd}_{0.75}\text{Mn}_2\text{O}_{5+\delta}$	3.42	3.30	3.43	3.44	3.46	3.48
$\text{BaGdMn}_2\text{O}_{5+\delta}$	3.30	3.22	3.31	3.33	3.34	3.33

Tab. 3. Time needed for 3 wt.% change of weight of $\text{BaY}_{1-x}\text{Gd}_x\text{Mn}_2\text{O}_{5+\delta}$ during reduction at respective temperatures. Values of E_a calculated in $\log(T/t)$ vs. $1/T$ coordinates.

composition	400 °C	450 °C	500 °C	550 °C	600 °C	E_a [eV] 1 wt.% change	E_a [eV] 2 wt.% change	E_a [eV] 3 wt.% change	E_a [eV] 95% of total weight change	E_a [eV] 99% of total weight change
$\text{BaYMn}_2\text{O}_{5+\delta}$		21.75	7.10	3.82	2.53	0.39	0.58	0.85	0.88	0.72
$\text{BaY}_{0.75}\text{Gd}_{0.25}\text{Mn}_2\text{O}_{5+\delta}$	34.37	10.55	5.12	2.92	2.00	0.46	0.59	0.78	0.80	0.79
$\text{BaY}_{0.5}\text{Gd}_{0.5}\text{Mn}_2\text{O}_{5+\delta}$	44.67	18.92	8.40	3.87	2.28	0.46	0.63	0.83	0.85	0.88
$\text{BaY}_{0.25}\text{Gd}_{0.75}\text{Mn}_2\text{O}_{5+\delta}$	33.08	12.25	6.48	3.65	2.48	0.45	0.53	0.72	0.71	0.66
$\text{BaGdMn}_2\text{O}_{5+\delta}$	49.70	13.15	5.88	3.47	2.18	0.53	0.65	0.85	0.82	0.82