Department of Chemistry

YBaCo$_4$O$_{7+\delta}$ and YMnO$_3$$_{3+\delta}$ Based Oxygen-Storage Materials

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Abstract

The threatening exhaustion of the fossil fuel reserves sets demand for developing new solutions for energy production and greener industrial processes. Oxygen-storage materials are a key factor in several established (e.g. three-way catalyst) or novel (e.g. air separation) technologies that help to reduce emissions and lower energy consumption. The wide-range implementation of the applications requires new oxygen-storage materials with enhanced performance and good stability at a proper operation temperature. This thesis reports results of engineering the properties of the two recently discovered oxygen-storage materials, $\text{YBaCo}_4\text{O}_{7+d}$ and $\text{YMnO}_3\text{d}$, as well as a new catalytic application for $\text{YBaCo}_4\text{O}_{7+d}$.

The oxygen-storage capacity of $\text{YBaCo}_4\text{O}_{7+d}$ is outstandingly high but the compound suffers from poor phase stability at high temperatures. The effects of chemical substitutions to each cation site in $\text{YBaCo}_4\text{O}_{7+d}$ phase were systematically studied to reveal that the larger the substituent at the Y and Ba sites and accordingly the larger the crystal lattice is, the larger is the amount the phase can absorb oxygen but at the same time the poorer is the phase stability. On the other hand, all cation substitutions involving the redox-active cobalt atoms in $\text{YBaCo}_4\text{O}_{7+d}$ had a negative effect on the oxygen-storage capacity but some substitutions were highly beneficial for the stability. In particular, for the composition $\text{YBa(Co}_{0.85}\text{Al}_{0.075}\text{Ga}_{0.075})_4\text{O}_{7+d}$ the phase decomposition could be prevented without markedly reducing the oxygen-storage capacity.

A new application possibility for $\text{YBaCo}_4\text{O}_{7+d}$ in industrially relevant catalytic oxidation reactions was also introduced in this thesis. The $\text{YBaCo}_4\text{O}_{7+d}$ catalyst showed an appreciably high activity (60 % conversion) compared to reference materials titanium and cobalt oxides (both < 20 %) in the oxidation of cyclohexene with $\text{H}_2\text{O}_2$. Calorimetric measurements showed that the reason for this high activity is in the interaction between the catalyst and $\text{H}_2\text{O}_2$. Oxygen absorption properties of another new oxygen-storage material candidate, $\text{YMnO}_3\text{d}$, were also investigated in this thesis. The maximum amount of oxygen that could be loaded into the structure through a high oxygen pressure treatment was as high as $d = 0.4$, and with careful adjustments of the annealing parameters essentially phase-pure samples were achieved at $d = 0.35$ with a new crystal structure the nature of which was studied by electron microscopy. To see whether the isostructural $\text{RMnO}_3$ compounds with the smaller rare earth ($R$) cations at the Y site can sustain oxygen-nonstoichiometry a sample series of $R = \text{Ho-Lu}$ was synthesized and treated at various temperatures and oxygen partial pressures. Only the phase $\text{HoMnO}_3\text{d}$ was found to show oxygen hyperstoichiometry similar to the $\text{YMnO}_3\text{d}$ case.

Keywords Oxygen storage, YBaCo407, RMnO3
Tiivistelmä


Koboltaatti YBaCo4O7+d:lla on poikkeuksellisen suuri hapenvarastointikyky, mutta sen heikkous on epästabilisuus korkeassa lämpötiloissa. Tässä työssä tutkittiin systemaattisesti kaikkien kolmen kationipaikan kemiallisen substiuution vaikutusta materiaalin ominaisuuksiin. Todettiin, Y- ja Ba-substituuttiidien tapauksessa kidehilan kasvaminen saa aikaan suuremman hapenabsorbointikyvyn, mutta samaan aikaan yhdisteen stabiilisuus huonenee. YBaCo4O7+d-yhdisteessä koboltti alkuaine, jonka hapetusasteen muuttuminen saa aikaan hapenvarastointikyvyn. Kaikki sen substituutiot laskivat absorboidun hapen määrää, mutta osa näistä substituutioista paransi materiaalin stabiilisuutta. Koostumus YBa(0.85Al0.075Ga0.075)Co4O7+d jossa 15 % koboltista on korvattu galliumin ja halvemman alumiinin seoksella optimoi yhdisteen hapenvarastointikyvyn ja stabiilisuuden.

Tässä väitöskirjatutkimuksessa löydyttiin YBaCo4O7+d:lle myös uusi mahdollinen sollehukse ja yhdesteen katalyyttistä aktiivisuutta (konversio 60 %) sykloheksaanin hapetusasteessa vetyperoksidilla verrattuna referenssimateriaaleihin titaanioksidin ja koboltitioksidin (mol. < 20 %). Kalorimetriset mittaukset osoittivat, että syy aktiivisuuteen on vuorovaikutuksessa vetyperoksidilla eli hapetussa.

Tässä työssä tutkittiin myös toisen uuden hapenvarastointimateriaalikandidaatin, YMnO3+d:n ominaisuuksia. Suurin määrä happea, jonka YMnO3+d pystyy absorboimaan todettiin olevan d = 0.4. Tarkoin kontrolloitujen korkeapainehapotusten avulla saatiin aikaan uusi arvo d = 0.35 vastaava kidehen, jota tutkittiin elektronimikroskopian avulla.

Selvitettiin myös, että yhdisteistä, joissa Y:n paikalla on jokin piennempiokisoihin harvinaisiin maametalleihin (Ho-Lu) yhdistelmästä (Ho - Lu) vain HoMnO3+d:lla voi esiintyä happiin.
The work presented in this thesis was carried out in the Laboratory of Inorganic Chemistry at Aalto University School of Chemical Technology (Helsinki University of Technology) and in the Laboratory of Advanced Materials at University of Alicante, Spain between November 2009 and June 2014. Academy of Finland and Tekniikan edistämissäätiö are gratefully acknowledged for the financial support of this work.

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Seinäjoki, 28.10.2014

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List of Abbreviations and Symbols

BVS  bond valence sum
OSC  oxygen-storage capacity
MIEC mixed electronic-ionic conductor
SOFC solid oxide fuel cell
TG  thermogravimetry
TWC three-way catalyst
XPS X-ray photoelectron spectroscopy
XRD X-ray diffraction
YSZ yttrium stabilized zirconia
List of Publications

In addition to the present review, this thesis includes the following publications (I-V) which are referred to in the text by their corresponding Roman numerals. The original publications are found in Appendices I-V.


III. O. Parkkima, H. Yamauchi and M. Karppinen, Oxygen storage capacity and phase stability of variously substituted YBaCo$_4$O$_{7+\delta}$, Chemistry of Materials 25, 599-604 (2013).

IV. O. Parkkima, A. Silvestre-Albero, J. Silvestre-Albero and M. Karppinen, Oxygen-nonstoichiometric YBaCo$_4$O$_{7+\delta}$ as a catalyst in H$_2$O$_2$ oxidation of cyclohexene, Catalysis Letters, in press.

V. O. Parkkima, S. Malo, M. Hervieu, E.-L. Rautama and M. Karppinen, New RMnO$_{3+\delta}$ ($R = Y$, Ho; $\delta \approx 0.35$) phases with modulated structure, Journal of Solid State Chemistry, 221, 109-115, (2015).
Author’s Contribution

Publication 1: The YBaCo$_4$O$_{7+\delta}$-based functional oxide material family: A review

The author defined the scope of the review together with the co-author. The author had a major role in writing the manuscript.

Publication 2: Ga-for-Co substitution in YBaCo$_4$O$_{7+\delta}$: Effect on high-temperature stability and oxygen-storage capacity

The author defined the research plan together with the co-authors and carried out a major part of the sample preparation and data collection. The results were interpreted together with the co-authors. The author had a minor role in writing the manuscript.

Publication 3: Oxygen storage capacity and phase stability of variously substituted YBaCo$_4$O$_{7+\delta}$

The author defined the research plan together with the co-authors. The author carried out all the experimental work and data collection. The results were interpreted together with the co-authors. The author had a major role in writing the manuscript.

Publication 4: Oxygen-nonstoichiometric YBaCo$_4$O$_{7+\delta}$ as a catalyst in H$_2$O$_2$ oxidation of cyclohexene

The author defined the research plan together with the co-authors and carried out sample preparation and part of the data collection excluding the XPS and calorimetry measurements. The results were interpreted together with the co-authors. The author had a major role in writing the manuscript.

Publication 5: New RMnO$_{3+\delta}$ ($R = Y, Ho; \delta \approx 0.35$) phases with modulated structure

The author defined the research plan together with the co-authors and carried out sample preparation and part of the data collection excluding the electron microscopy measurements. The results were interpreted and the manuscript written together with the co-authors.
1. Introduction

There is an ever-growing demand for greener processes and replacement of fossil fuels in the world today. Development of the solutions calls for various types of materials that can answer to the requirements of the new technologies. Oxygen-storage materials play an essential role in many novel applications that either reduce emissions or costs in a certain process or are related to the new energy technologies. They are able to provide pure oxygen to processes either by releasing the stored oxygen or acting as an oxygen-selective membrane. Together with an oxygen-storage material usually simply air can be used as a source of $O_2$, which means huge savings in the total cost of a process. New and better materials have been actively searched for in recent years.

A common feature of transition metals is that they possess multiple oxidation states; hence many transition metal oxides also show oxygen nonstoichiometry. However, not all of these compounds can be classified as oxygen-storage materials. First, the magnitude of the variation in the oxygen content is finally rather small in most of these compounds. Secondly, even though the oxygen-nonstoichiometric oxides commonly release the excess oxygen upon heating the process is often too slow and gradual whereas in a feasible oxygen-storage material the change in the oxygen content should be fast and occur in a definite and rather narrow temperature range, often preferably at as a low temperature as possible.

The temperature range where the oxygen-storage material is capable of reversibly absorbing and releasing oxygen should naturally match the operation temperature of the application the material is designed for. Most nonstoichiometric oxide materials start to show oxygen-content variation only at high temperatures and one of the major research goals is to find new materials that work at lower temperatures. The various oxygen-storage materials are different also in their requirement for the atmosphere in which they release enough oxygen; some materials release oxygen even upon heating in air whereas others have to be treated in a hydrogen atmosphere for the complete reduction. Having an eye on the potential applications, this is not actually as a crucial feature as it seems to be at the first sight. Namely, there are applications for oxygen-storage materials where e.g. oxide ions need to move through a selective membrane. Here the maximal amount of oxygen the material is able to store is not necessarily of the utmost importance but rather the efficiency of oxide-ion conductivity is the key factor.
In the past essentially more research efforts were focused on the oxide ion conductivity compared to the actual oxygen-storage capacity. The discovery of the unique oxygen-nonstoichiometry characteristics of the YBaCo$_4$O$_{7+\delta}$ family a decade ago was one of the catalysts in accelerating the research on new types of oxygen-storage materials.\textsuperscript{1,2} Since then several new material families with promising oxygen-storage properties have been discovered. Yet, the YBaCo$_4$O$_{7+\delta}$-based materials have remained superior in many material-property aspects most important for the efficient oxygen-storage materials: the oxygen-storage capacity of YBaCo$_4$O$_{7+\delta}$ is essentially better than those for the conventional oxygen-storage materials like cerium oxide, and moreover, the reversible oxygen absorption/desorption process occurs at considerably lower temperatures around 300 °C. The down side of the material is the poor thermal stability. The YBaCo$_4$O$_{7+\delta}$ phase decomposes upon heating in oxygen-containing atmospheres already around 600 °C which may be a crucially too low temperature for many applications. Luckily the peculiar crystal structure of YBaCo$_4$O$_{7+\delta}$ is highly flexible and allows chemical substitutions to each of the metal sites. This has been proven to be a powerful way to enhance the properties of the material.\textsuperscript{1}

More recently another interesting oxide system was highlighted as a possible oxygen-storage material, that is, the hexagonal RMnO$_{3+\delta}$ phases.\textsuperscript{3} Rare earth (\textit{R}) manganites are a largely studied group of materials because of their interesting magnetic and electrical properties. The manganites of the smallest \textit{R} constituents have been traditionally considered oxygen stoichiometric, but thanks to the recent studies it is now known that for the specific \textit{R} compositions the OSC value can exceed those for the conventional materials at appreciably low temperatures of around 250 °C. The RMnO$_{3+\delta}$ material family is particularly interesting because of their thermal stability and non-toxicity.

The ultimate goal of this work was to understand the ways to enhance the important material properties of various oxygen-nonstoichiometric oxide families showing potential for the next-generation oxygen-storage materials. Within the scope of the thesis the two novel oxygen-storage material families, RBaCo$_4$O$_{7+\delta}$ and RMnO$_{3+\delta}$, were investigated. As highlights of the results obtained thereof, (\textit{i}) the poor phase stability of YBaCo$_4$O$_{7+\delta}$ could be greatly improved through proper carefully optimized cation substitutions,\textsuperscript{II,III} and (\textit{ii}) even a new application possibility as a catalyst in a commercially remarkable oxidation reaction was proposed for it.\textsuperscript{IV} In the latter case, substitution studies with different \textit{R} constituents (Y, Ho-Lu) revealed that (\textit{iii}) the RMnO$_{3+\delta}$ phase can be loaded up to $\delta \approx 0.4$ with excess oxygen for \textit{R} = Y and Ho, which then was shown to result in (\textit{iv}) a new modulated crystal structure.\textsuperscript{V} In the following chapters, the most interesting new oxygen-storage material families together with their applications are introduced. The most important experimental methods and results of this thesis are also presented.
2. Oxygen-Storage Materials

In recent years a number of new oxygen-storage material families have been discovered. For a compound to be able to show oxygen-nonstoichiometry there has to be one or more cations that can exist with a more than one oxidation state. Hence, in general all oxygen-storage materials are transition metal oxides but actually one group of oxysulfates has recently been shown to have quite excellent oxygen-storage properties. The oxygen-storage capacity (OSC) of a material is usually presented in moles O per weight of the material (μmolO/g). For the most studied materials, e.g. ceria, the OSC values are experimental and measured under conditions that correspond to the conditions in real processes. For most of the newer materials the OSC values are more theoretical indicating the variation between the stoichiometric phase and the maximal oxygen content the material can sustain.

In this chapter the most interesting new oxygen-storage materials together with ceria, the most well-established material are presented and their properties are compared to each other. The greatest emphasis is given to the YBaCo$_4$O$_{7+δ}$ family because it played a major role in this thesis work. In addition to the materials the most prominent applications of oxygen-storage materials are shortly summarized.

2.1 Ceria

Cerium oxide is one of the most studied oxide materials in general. It has a significant role in the commercial catalytic processes in terms of economic relevance and tonnage. The two major well-established applications of CeO$_2$ are the three-way catalysis (TWC) and fluid catalytic cracking. Still ceria actively investigated as a potential material in new emerging applications.\(^4\)

Cerium oxide has the fluorite (CaF$_2$) structure. It consists of a cubic close-packed array of metal atoms with tetrahedral holes filled with oxygen atoms, as illustrated in Figure 1a. When treated in a reducing atmosphere at elevated temperatures, CeO$_2$ forms a continuum of oxygen-deficient, non-stoichiometric CeO$_{2-δ}$ (δ = 0...0.5) oxides whereas at lower temperatures (\(T < 450 ^\circ C\)) ceria forms a series of discrete compositions. Quite remarkably ceria
maintains its fluorite structure even after a loss of considerable amounts of oxygen from its lattice, i.e. a formation of a large number of oxygen vacancies. The oxygen-deficient compositions are readily oxidized back to the stoichiometric phase in an oxygen-containing atmosphere.\(^5\)

Ceria has various applications but is rarely in alone in applications. The main problem of ceria is the high-temperature stability: as soon a significant sintering of CeO\(_2\) particles occurs, OSC and other catalytic features are inhibited.\(^6\) Among different systems tested, ZrO\(_2\) seems to be the most effective thermal stabilizer.\(^3,6\) Ceria-zirconia solid solutions also have higher reduction efficiency of the redox couple Ce(III)/Ce(IV) and better OSC compared to pure ceria.\(^7-10\) An OSC value of 1500 \(\mu\text{mol O}_2/\text{g}\)\(^11\) was determined for CeO\(_2\)-ZrO\(_2\) at 500 °C by reducing the material first in a H\(_2\) gas flow and then oxidizing in a 50:50 O\(_2\)/N\(_2\) gas flow. In oxygen the OSC value is close to 500 \(\mu\text{mol O}_2/\text{g}\).\(^12\)

### 2.2 Perovskites

Some members of the perovskite oxide family (e.g. SrCoO\(_3\)-\(\delta\),\(^13-14\) SrFeO\(_3\)-\(\delta\)\(^15\) and YBa\(_2\)Cu\(_3\)O\(_7\)-\(\delta\)\(^16\)) exhibit oxygen non-stoichiometry, but usually the variations in the oxygen content are quite small and the kinetics of the absorption/desorption processes are too slow to be utilized in oxygen-storage applications. Perovskites based on Co and Mn were extensively studied in the mid-1970s as potential substituents for noble metals in auto-exhaust catalysts. However the application of perovskite oxides in industrial processes is limited because of their low surface areas and lower resistance to poisoning by water and sulfur. Proper incorporation of a small amount of noble metals (Pt,Rh,Pd) into the perovskite structure could stabilize the metals against sintering, reaction with the support and volatilization.\(^17\) For example rhodium-doped LaMnO\(_3\)-\(\delta\) showed high activity in TWC reactions even though the OSC value is merely 620 \(\mu\text{mol O}/\text{g}\) which is a result from a reversible structural change between hexagonal La(MnRh)O\(_3\)-\(\delta\) and orthorhombic La(MnRh)\(_3\)-\(\delta\).\(^18\) Recent studies show that nickel substitution in LaMnO\(_3\)-\(\delta\) (10-30 % of Mn) could be a good choice. The OSC reaches 800 \(\mu\text{mol O}/\text{g}\) at 500 °C which is 1.5 times the value for CeO\(_2\)-ZrO\(_2\) and in addition the cost of the material is low as well as the stability is at a respectable level.\(^19\)

The B-site ordered double-perovskite compound, Ca\(_2\)AlMnO\(_5\)-\(\delta\) has shown to be a promising candidate material for oxygen storage. It crystallizes in a Brownmillerite-type structure where AlO\(_4\) and MnO\(_6\) polyhedra layers alternate. Ca\(_2\)AlMnO\(_5\)-\(\delta\) can be reversible cycled in mild oxidizing and reducing conditions either switching between oxygen and nitrogen gas flows or between temperatures. The material absorbs oxygen at temperatures between 200 °C and 650 °C and releases all of the oxygen in a single step at higher temperatures. The maximum value for \(\delta\) is 0.45 corresponding to an OSC value of 1900 \(\mu\text{mol O}/\text{g}\).\(^20\)
The structure of the $A$-site ordered double perovskite $\text{BaYMn}_2\text{O}_{5+\delta}$ contains a layered arrangement of yttrium and barium atoms at the $A$-site. Oxygen atoms are removed from the yttrium layer in reductive conditions resulting in a large oxygen nonstoichiometry of $\delta = 0...1$ which corresponds to an OSC value of 2400 $\mu$mol O/g. The phase is oxidized fully in an oxygen flow at temperatures higher than 200 °C and is possible to reversibly reduce back to $\delta = 0$ in an $\text{H}_2/\text{Ar}$ gas flow at the same temperature range. The material has three distinctive crystal forms corresponding to $\delta = 0, 0.5$ and 1.

### 2.3 Hexagonal Manganites

The rare-earth manganese oxide family, $\text{RMnO}_{3+\delta}$, has been a target of intensive research for years due to the exciting properties such as colossal magnetoresistance and ferroelectric effects discovered for several members of the family. Solid state synthesis of $\text{RMnO}_{3+\delta}$ compounds in air results in two different crystal structures. The $\text{RMnO}_{3+\delta}$ phases with the larger rare earths ($\text{La-Dy}$) adopt an orthorhombically-deformed perovskite structure ($Pbnm$), whereas the phases with the smaller $R$ constituents ($\text{Y, Ho-Lu}$) have a nontetrosymmetric hexagonal $P63cm$ structure that is illustrated in the Figure 1d.

Synthesis of the $\text{RMnO}_{3+\delta}$ phases in air has been believed to result in essentially oxygen-stoichiometric samples, except for $R = \text{La}$. Recently it was however discovered by Remsen et al. that for the specific compositions of $(\text{Dy}_{1-x}\text{Y}_x)\text{MnO}_{3+\delta}$ ($0 \leq x \leq 1$) the hexagonal manganites possess oxygen nonstoichiometry; the oxygen-content variation range in $(\text{Dy}_{1-x}\text{Y}_x)\text{MnO}_{3+\delta}$ was $\delta = 0...0.35$ corresponding to an OSC value of up to 2000 $\mu$mol-O/g and hence the system may be considered as a possible candidate for novel oxygen-storage material. In addition to compounds with $R = \text{Dy or Y}$, the $R = \text{Ho}$ phase was also found to be able to sustain oxygen hyper-stoichiometry but the smaller $R = \text{Er – Lu}$ compounds did not.

The temperature range where the oxygen absorption/release takes place in $\text{RMnO}_{3+\delta}$ ($R = \text{Y, Dy, Ho}$) is uniquely low, 200-300 °C. They are also thermodynamically stable and non-toxic which are important characteristics for an oxygen-storage material. A noteworthy downside of the material family might be the slow rate of oxygen release/intake process. In a dynamic TG measurement a heating rate of 0.1 C/min had to be used to get the material to absorb significant amounts of oxygen. In the case of $\text{YBaCo}_4\text{O}_{7+d}$, for example, the rate is at least ten times higher. The sluggishness of the oxygen absorption is probably related to the low temperature range where it is occurring. The mobility of oxide ions is the faster the higher the temperature.
2.4 Delafossites

The delafossite structure $ABO_{2+\delta}$ is capable to accommodate a large number of different $A$ and $B$ cations.$^{34-35}$ Several compounds with the delafossite structure and have quite a wide range of oxygen nonstoichiometry.$^{36,37}$ The $A$ cation is a monovalent ion (Cu, Pt, Pd, Ag) whereas $B$ is a trivalent cation, the ionic radii of which can vary from 0.535 Å (octahedral Al$^{3+}$) up to 1.032 Å (octahedral La$^{3+}$) according to the Shannon’s table of effective ionic radii.$^{38}$ In the delafossite structure $BO_6$ octahedra are connected by edges forming the $BO_2$ layers, which are stacked along the $c$ axis and are connected with triangular metallic planes of $A$ cations (see Figure 1b).$^{37}$

The copper delafossites Cu$BO_{2+\delta}$ have been shown to be able to sustain a large amount of extra interstitial oxygen in the triangular Cu planes with large $B$ cations.$^{36,39}$ The theoretical maximum value for $\delta$ is 0.5 which corresponds to a Cu oxidation state change from +I to +II. The oxygen storage properties are properly studied only with the smaller $B$ cations Al, Fe, Mn and Ga or their mixtures$^{40,41}$ and the maximum $\delta$ values e.g. for $B = Fe$ is 0.18.$^{37}$ The compounds CuFeO$_{2+\delta}$ and CuMnO$_{2+\delta}$ exhibit respectable OSC values (> 600 $\mu$molO/g) above 400 °C but they decompose into Fe and Mn oxides during the oxidation/reduction process which of course prevents their utilization in applications. The compounds with $B = Al$ and Ga seem to be more stable but they started to show similar level of OSC only after 800 °C.$^{40}$

2.5 LuFe$_2$O$_{4+\delta}$

Peculiar magnetic and electric properties have raised interest in the LuFe$_2$O$_{4+\delta}$ compound lately.$^{42-45}$ Magnetic measurements pointed towards oxygen nonstoichiometry and the material’s potential to oxygen storage was revealed recently.$^{46}$ The structure of the oxidized phase is quite complicated including shifts of the cation layers due to the oxygen intercalation/deintercalation process. The stoichiometric compound crystalizes in a monoclinic (C2/m) structure where Lu cations are octahedrally coordinated to form CdI$_2$-type layers that alternate with sheets of trigonal bipyramids of iron.$^{46}$

The oxygen absorption of LuFe$_2$O$_{4+\delta}$ starts upon heating around 200 °C and the OSC corresponding to $\delta = 0...0.5$ is over 1400 $\mu$molO/g. The phase reaches the maximum oxygen content, $\delta = 0.5$ in a dynamic heating process at 500 °C and releases the excess oxygen reversibly in a reducing atmosphere but in a slow manner (in over 5 h) if the temperature is kept constant. The throughout studies of LuFe$_2$O$_{4+\delta}$’s oxygen-storage properties are still in progress and in the future the working conditions of the material should be optimized.$^{46}$
2.6 YBaCo$_4$O$_7$ and Derivatives

The complex cobalt oxide YBaCo$_4$O$_7$ was first synthesized in 2002. The crystal structure of YBaCo$_4$O$_7$ is composed of corner-sharing CoO$_4$ tetrahedra of two kinds with a ratio of 1:3, see Figure 1e. The two kinds of tetrahedra are distinguished by different sets of bond lengths and located in separate Kagome and triangular layers that alternate with each other. Such an arrangement of magnetic cobalt cations on two-dimensional trigonal sublattices forms an exciting system for exploring geometrically frustrated magnetism.

A few years after its discovery the YBaCo$_4$O$_7$ compound was found to be capable in reversibly absorbing and desorbing oxygen up to 1.5 oxygen atoms per formula unit at appreciably low temperatures around 300 °C. This oxygen uptake and release capability substantially exceeded both in the overall magnitude and in the response sensitivity those achieved with conventional oxygen-storage materials. The YBaCo$_4$O$_{7+\delta}$-based compounds have already been investigated for a few applications: as a sorbent material for oxygen-enriched CO$_2$ stream production, a membrane material for oxygen separation, a cathode material for solid oxide fuel cells, and a catalyst in epoxidation reactions requiring active oxygen species.

The only drawback of the YBaCo$_4$O$_7$ family is the instability at high temperatures. The phase decomposes in oxygen-containing atmospheres upon heating at temperatures higher than 600 °C. Having an eye on the applications the enhancement of the thermal stability is an essential issue. Luckily, there are several ways to further modify the properties of YBaCo$_4$O$_{7+\delta}$ as the crystal structure readily accepts various cation substitutions at all the cation sites. Owing to its particular crystal structure, diverse functional properties and chemical flexibility, the YBaCo$_4$O$_{7+\delta}$ phase (and its cation-substituted derivatives) has been a target of increasingly intensive research interest during the last ten years.

2.6.1 Cation Substitutions

One of the most interesting features of the YBaCo$_4$O$_7$ structure is that all the cation sites can be substituted with some other metal ion at least to some extent. Very soon after the YBaCo$_4$O$_7$ compound was discovered a number of isostructural compounds RBa$_4$O$_7$ (R = Ca, In, Dy – Lu; X = Al, Zn, Fe) were synthesized. Actually, a similar structure was first found already in 1996 for the composition, LuBaAlZn$_3$O$_7$ and can also be found in the natural occurring mineral Swedenborgite NaBe$_4$SbO$_7$. All the reported substitutions are presented in Table 1, where also the cell volumes per formula unit are presented. The great variation in the cell volumes from 168.22 Å$^3$ (for InBaCo$_4$O$_{7+\delta}$) to 179.83 Å$^3$ (for YBaFe$_4$O$_{7+\delta}$) highlights the very flexible nature of the crystal structure.
Table 1. Reported chemical substitutions to each metal site in YBaCo$_4$O$_{7+\delta}$. Cell parameters for the phase with the maximum rate of substitution are presented as well as the corresponding cell volume V$_{cell}$ per formula unit.

<table>
<thead>
<tr>
<th>Y site</th>
<th>Solubility limit (%)</th>
<th>Space group</th>
<th>Cell parameters</th>
<th>V$_{cell}$ (Å$^3$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>100</td>
<td>Pbn$_2$</td>
<td>a (Å) 11.040</td>
<td>10.164</td>
<td>175.64</td>
</tr>
<tr>
<td>In</td>
<td>100</td>
<td>P31c</td>
<td>a (Å) 10.087</td>
<td>168.22</td>
<td>56 58</td>
</tr>
<tr>
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<td>a (Å) 6.2962</td>
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</tr>
<tr>
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<td>10.237</td>
<td>176.10</td>
</tr>
<tr>
<td>Er</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td>III 54 58 80 - 82</td>
</tr>
<tr>
<td>Tm</td>
<td>100</td>
<td>P31c</td>
<td>a (Å) 6.276</td>
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</tr>
<tr>
<td>Yb</td>
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<td>P31c</td>
<td>a (Å) 6.267</td>
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<td>174.03</td>
</tr>
<tr>
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</tr>
<tr>
<td>Pr*</td>
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<td>a (Å) 6.304</td>
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</tr>
<tr>
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<td>Pbn$_2$</td>
<td>a (Å) 6.300</td>
<td>10.996</td>
<td>176.69</td>
</tr>
</tbody>
</table>

Ba site

| Sr    | < 15                 | P6$_3$mc    | a (Å) 6.297    | 10.981           | 175.85     | III |
| K**   | ≤ 20                 | Pbn$_2$     | a (Å) 6.297    | 10.199           | 176.31     | 62 |

Co site

| Al    | 12.5                 | P31c        | a (Å) 8.960    |                 | 179.83     | III 53 56 58 60 63 - 66 74 92 |
| Fe    | 100                  | F43m        | a (Å) 17.43    |                 | 95 97 - 102 |
| Zn    | 75                   | P31c        | a (Å) 6.321    | 10.276           | 177.79     | III 54 - 56 58 63 66 69 70 74 |
| Ga    | 30                   | P31c        | a (Å) 6.308    | 10.263           | 176.83     | III 69 96 100 103 104 105 |
| Ni    | < 5                  | P31c        | a (Å) 6.339    | 10.273           | 176.49     | III 106 |
| Mn*** | 50                   | P31c        | a (Å) 6.379    | 10.426           | 183.69     | III 107 |
| Cu    | ≤ 5                  | P31c        | a (Å) 6.293    | 10.3104          | 176.80     | 74 103 |

Li**** ≤ 18.75 P31c a (Å) 6.295 10.3104 176.80 74 103

* In Ca$_x$Ln$_{1-x}$BaCo$_4$O$_{7+d}$
** In Ca$_{1-x}$K$_x$Co$_4$O$_{7+d}$
*** In YBa$_2$Mn$_2$O$_{7+d}$ lower limit 25 %
**** In YBaFe$_3$Li$_{1-x}$O$_{7+d}$

2.6.2 Oxygen Nonstoichiometry

The prototype YBaCo$_4$O$_{7+\delta}$ phase has a unique ability to reversibly absorb and desorb large amounts of oxygen at low temperatures around 300 °C. Oxygen content can vary from $\delta = 0$ to 1.5 which corresponds to the variation of the average cobalt-valence value from 2.25 to 3. Solid state synthesis in air with a slow cooling down to room temperature typically results in seemingly single-phase samples with $\delta \approx 0.1$ possessing a hexagonal structure. The oxygen-stoichiometric ($\delta = 0$) phase can be obtained either by quenching from the synthesis temperature or annealing in pure N$_2$ or Ar at ~500 °C. Through ambient-pressure oxygen annealing it is possible to load the phase with excess oxygen up to $\delta = 1.351$ but to reach the maximal oxygen content of $\delta = 1.5$, an oxygenation heat-treatment period under an elevated oxygen partial pressure or in a solid-medium ultra-high-pressure apparatus in a presence of an external oxygen-releasing material (KClO$_3$) has to be used. In terms of the OSC value the variation from $\delta = 0$ to 1.5 means 2600 μmol O$_2$/g. Even the oxygen...
content value of $\delta = 1.17^2$ that can be obtained just by heating the material in a normal-pressure oxygen gas flow corresponds to an OSC value of 2000 $\mu$molO/g.

It is well established that substituting Y with a smaller cation in YBa-Co$_4$O$_{7+\delta}$ results in a decreased oxygen absorption capability. The fastest oxygen absorption process and the largest resultant oxygen content value realized upon annealing the material in 1 atm O$_2$ gas flow have been obtained for DyBaCo$_4$O$_{7+\delta}$ ($\delta \approx 1.4$), which is the compound with the largest cell volume per formula unit among these phases. Apparently the reason behind this trend is simply in the relatively large size of the oxide anion; the larger the lattice and the wider the cavities in the structure the easier it is for the oxide ions to move in the lattice.

### 2.6.3 Crystal Structure

The crystal symmetry of the parent YBaCo$_4$O$_{7+\delta}$ phase changes according to oxygen content and temperature. At room temperature the oxygen-stoichiometric ($\delta = 0$) phase is orthorhombic with a space group $Pbn21$ ($a = 6.298$ Å, $b = 10.939$ Å, $c = 10.228$ Å). A small amount of excess oxygen ($\delta < 0.1$) is enough to convert the room-temperature structure to trigonal $P31c$ symmetry. The structure was originally labeled as hexagonal $P63mc$ ($a = b = 6.298$ Å, $c = 10.247$ Å) but several neutron diffraction studies have shown that the correct space group is in fact trigonal. The difference between these two symmetries is an O atom moving off from a mirror plane, which is practically unseen by e.g. XRD.

In the YBaCo$_4$O$_7$ structure, CoO$_4$ tetrahedra are found with a 3:1 ratio in the alternating triangular and Kagome layers, as shown in Figure 1e. The oxygen framework can be described as an ABCB-type stacking of closed packed O$_4$ and BaO$_3$ layers whose cavities are occupied by cobalt cations. One might think that divalent Co ions would occupy the site in the triangular layer and trivalent Co ions the site in the Kagome layer because the ratio Co(II):Co(III) in the oxygen-stoichiometric compound is the same as that of the two distinct cobalt sites. Both neutron and XRD data have however indicated that there is no clear charge ordering in the structure; this is also supported by Mössbauer spectroscopy data. Bond valence sum (BVS) calculations typically show intermediate values between 2 and 3 for both the cobalt sites, around 2.3 for Co(1) in the triangle layer and 2.8 for Co(2) in the Kagome layer.

Oxygenation of oxygen-depleted YBaCo$_4$O$_{7+\delta}$ by annealing in air around 300 °C results in YBaCo$_4$O$_8$ which brings about an $a$-axis doubled orthorhombic superstructure ($Pbc21$; $a = 12.790$ Å, $b = 10.845$ Å, $c = 10.149$ Å) corresponding to the addition of two oxide ions to the unit cell. Cobalt ions occupy both corner-sharing tetrahedral and edge-sharing octahedral sites in contrast to the hexagonal structure where only tetrahedral sites exist. Many of the orig-
inal oxygen atoms are also displaced from their initial positions.\textsuperscript{111} The fully-oxygenated YBaCo\textsubscript{4}O\textsubscript{8.5} phase where all cobalt ions are trivalent seems to have a mixed structure and the excess oxygen atoms placed in CoO\textsubscript{6} octahedra form several types of ordering.\textsuperscript{112,113} An intermediate-oxygen-content structure with $\delta = 0.5$ that cannot be stabilized for the unsubstituted parent phase has been isolated for the Ca-for-Y substituted CaBaCo\textsubscript{4}O\textsubscript{7.5} phase but not fully solved yet;\textsuperscript{75} the structure seems to be hexagonal and it bears a resemblance to the $P31c$ phase.

The YBaCo\textsubscript{4}O\textsubscript{7+\delta} family faces structural changes also as a function of temperature. At high temperatures the oxygen-stoichiometric $RBaCo\textsubscript{4}O\textsubscript{7}$ compounds possess a trigonal structure, but with decreasing temperature they experience a transition from the trigonal to orthorhombic symmetry. The transition temperature decreases with decreasing size of the $R$ constituent, from 355 K for Ho\textsuperscript{84} to 160 K for Lu.\textsuperscript{86} For YBaCo\textsubscript{4}O\textsubscript{7} the transition temperature is 310 K,\textsuperscript{114} and the room-temperature structure hence orthorhombic as discussed above. With a further decrease in temperature the $RBaCo\textsubscript{4}O\textsubscript{7}$ compounds experience another symmetry change at low temperatures when magnetic ordering breaks the 90° angle of the orthorhombic phase and the cell becomes monoclinic ($P1121$) around 100 K.\textsuperscript{48,115} It has been shown that a slight oxygen excess ($\delta = 0.08$) suppresses the structural transition and the compound retains its hexagonal symmetry down to at least 6 K.\textsuperscript{116}

In most cases the cation substitutions do not change the basic structure of the YBaCo\textsubscript{4}O\textsubscript{7+\delta} system but they only affect the cell parameters,\textsuperscript{58} the temperature where the structural transitions take place\textsuperscript{86} and/or suppress the transitions.\textsuperscript{104} There are two exceptions: iron at the cobalt sites and calcium at the yttrium site. When all of the cobalt atoms are fully replaced with iron and the oxygen content differs from $\delta = 0$, the symmetry changes to cubic $F43m$ with $a = 8.9595$ Å.\textsuperscript{60} The structure is still closely related to the trigonal one. The stoichiometric iron compound has a tetragonal structure which is stable only in an atmosphere that does not contain any oxygen.\textsuperscript{98}

Divalent calcium at the yttrium site brings about somewhat unusual features regarding the crystal structure. In the CaBaFe\textsubscript{4}O\textsubscript{7+\delta} iron oxides it stabilizes the common $P31c$ trigonal symmetry whereas in the CaBaCo\textsubscript{4}O\textsubscript{7+\delta} cobalt oxides it induces a strong orthorhombic distortion.\textsuperscript{73,117}

2.7 Oxysulfates

Lanthanum oxysulfates $Ln_2O_2S\textsubscript{4}$ ($Ln = \text{La, Pr, Nd, Sm}$) are the only known type of oxygen-storage materials where the valence-changing species is a non-metal ion, namely sulfur ($S(VI) \leftrightarrow S(-II)$).\textsuperscript{118-121} The reduction with hydrogen or hydrocarbons to $Ln_2O_2S$ and a subsequent reoxidation can produce an oxygen storage capacity of 2 mol $O_2$/mol of the oxysulfate phase which e.g. in the case $Ln = \text{La}$ corresponds to an OSC value of 9850 $\mu$molO/g. The clear drawback of
this material family is the high operation temperature ($\geq 700$ °C) it requires.\textsuperscript{118} The operation temperature has been lowered somewhat by impregnating noble metals to the surface.\textsuperscript{119}

The oxysulfate and -sulfide structures resemble each other closely which has been considered to be the reason for the reversible redox process of the material. $\text{La}_2\text{O}_2\text{SO}_4$ exists in a monoclinic $C2/c$ symmetry with $a = 14.349$ Å, $b = 4.285$ Å, $c = 8.386$ Å and $\beta = 107^\circ$. Heating in $\text{H}_2$ stream at 800 °C converts the compound into the single phase $\text{La}_2\text{O}_2\text{S}_2$ with a rhombohedral $P3m1$ structure, which is isostructural with $\text{La}_2\text{O}_3$. Both sulfate and sulfide structures are similar for all the lanthanoids investigated but as expected, the cell parameters change as a function of the radius of the $\text{Ln}$ ion. The structures can be described as an alternating stacking of a $\text{Ln}_2\text{O}_3$ layer and a layer of anion groups; sulfate or sulfide. The phase transformation between these two phases is solemnly the removal or addition of two oxide ions surrounding sulfur atoms.\textsuperscript{118}

The lanthanoid oxysulfates can be synthesized easily by heating commercial $\text{Ln}_2(\text{SO}_4)_2\cdot n\text{H}_2\text{O}$ powders in air or nitrogen flow at 900 °C. All the $\text{LnSO}_4$ compounds have two reactions occurring during the heating in nitrogen or air. First at $T_1$ (e.g. for $\text{Ln} = \text{La}$, 880 °C) occurs the formation of the corresponding oxysulfate, which is used in the synthesis and then at $T_2$ (for $\text{Ln} = \text{La}$, 1210 °C) the decomposition to $\text{Ln}_2\text{O}_3$. $T_2$ decreases with increasing atomic number so the smallest lanthanides have just a very narrow temperature range where the oxysulfate form of the compound is stable. That is why only the compounds with the largest lanthanides (La-Sm) are considered to be interesting in the applications’ point of view. Cerium is an exception; the oxide $\text{CeO}_2$ forms already at $< 700$ °C making the corresponding oxysulfate infeasible in oxygen-storage applications.\textsuperscript{119}

### 2.8 Comparison of Oxygen-Storage Material Candidates

The crystal structures of six transition metal oxides introduced in this chapter are illustrated in Figure 1. Not a single specific structure is a prerequisite for a material to be able to store or conduct oxygen but oxygen-storage materials still have some common features. First, because of the large size of the oxide ion the structure should have relatively large passageways for the ions to move about in the lattice. Secondly, the structure must stand cycling between the reduced and oxidized form. In some materials this means a reversible structural transformation whereas in others oxygen (or cation) vacancies appear and are filled again.
Figure 1. Crystal structures of the transition metal oxides (a) ceria, (b) delafossite CuAlO$_2$, (c) perovskite, (d) hexagonal YMnO$_3$, and (e) YBaCo$_4$O$_{7+\delta}$. The two different kinds of coordination tetrahedras of cobalt atoms in alternating layers are presented for YBaCo$_4$O$_{7+\delta}$.

The OSC values and lowest operation temperatures of the most promising new oxygen-storage materials introduced in this chapter are presented in the Table 2. Many of the newly discovered materials show reasonable OSC values at temperatures lower than 500 °C and among them YBaCo$_4$O$_{7+\delta}$ holds the record for the highest OSC, 2600 μmolO/g. Lanthanum oxysulfates have remarkably high OSC value, but their operation temperatures are as high as those of the conventional oxygen-storage materials. They also need harsh reducing environments, like hydrogen atmosphere.

It should be noted that in this work some of the given OSC values are theoretical, indicating the variation between the stoichiometric phase and the maximal oxygen content the material can sustain. In practise it is not clear whether the material in question could show the whole variation of oxygen content under the certain operation conditions and especially at a desired rate.
<table>
<thead>
<tr>
<th>Material</th>
<th>OSC (μmolO/g)</th>
<th>Operation temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$-ZrO$_2$</td>
<td>500 (-1500*)</td>
<td>500</td>
</tr>
<tr>
<td>Ca$<em>2$AlMnO$</em>{5+6}$</td>
<td>1900</td>
<td>200</td>
</tr>
<tr>
<td>BaYMn$<em>2$O$</em>{5+6}$</td>
<td>2400*</td>
<td>200</td>
</tr>
<tr>
<td>(La$_{1-x}$Rh$<em>x$)MnO$</em>{3+6}$</td>
<td>620</td>
<td>400</td>
</tr>
<tr>
<td>RMnO$_{3+6}$</td>
<td>2000</td>
<td>250</td>
</tr>
<tr>
<td>LuFe$<em>2$O$</em>{4+5}$</td>
<td>1400</td>
<td>200</td>
</tr>
<tr>
<td>YBaCo$<em>4$O$</em>{7+5}$</td>
<td>2600</td>
<td>300</td>
</tr>
<tr>
<td>La$_2$O$_2$SO$_4$</td>
<td>9850*</td>
<td>700</td>
</tr>
</tbody>
</table>

*Requires H$_2$ reduction

From the perspective of possible applications it is not enough just to consider the maximum amount of oxygen an oxygen-storage material is able to absorb and release. A remarkable factor is the rate of the process. For example in the TWC the conditions between oxygen rich and poor states oscillate with a frequency of 1 Hz. This sets the oxygen-storage material requirements that not all of the materials introduced in Table 2 are able to meet. For example the hexagonal manganites require really slow (0.1 °C/min) heating rates to show any absorption in a dynamic measurement. For YBaCo$_4$O$_{7+5}$ under similar conditions the rate can be hundred times faster.

It is impossible to absolutely declare which material would be the best choice for a certain application. In practice there are numerous issues affecting the feasibility of a material: the compatibility with other materials in the device, toxicity, thermal stability and not least the price. Materials with a relatively low OSC values can work well enough in a certain applications, e.g. LaMnO$_{3+5}$ in three-way catalyst (see next section) and because of low price or easy access they might be the best choice. In the next section the most important applications for oxygen-storage materials and the requirements that they set are presented.

### 2.9 Applications of Oxygen-Storage Materials

There are a number of applications for oxygen-storage materials like commercial air separation, car exhaust catalysts, solar water splitting and decomposition of nitrous oxides. New energy related technologies such as fuel cells, chemical looping and production of synthesis gas or hydrogen via partial oxidation of natural gas or methane also require improved oxygen-storage materials. Here the special features of the most important applications and the requirements they set for the oxygen-storage material are presented.
2.9.1 Three-Way Catalyst

The oldest and the most common application for oxygen-storage materials is the three-way catalyst (TWC) that is used to convert the harmful substances into more benign compounds in the exhaust gas flow of car combustion engines. The conditions in the engine alternate between oxygen rich and lean states. When the content of oxygen in the gas stream is high, the oxygen-storage material absorbs oxygen and enhances the conversion of NO\textsubscript{x} to N\textsubscript{2} while the amount of oxygen is insufficient the material releases it to enhance conversion of CO and hydrocarbons to CO\textsubscript{2} and water, see Figure 2. These states oscillate with a frequency of 1 Hz but during driving cycles, especially on acceleration and deceleration longer periods of lean/rich conditions may occur. This means that the oxygen-storage material should have two types of capacity: the total oxygen-storage capacity and dynamic, fast capacity. The former is related to the total degree of reduction at a given temperature and the latter is a measure of the amount of oxygen the material is able to provide during the oscillations the exhaust gas may undergo.

Improvement of TWC activity at low temperature has become necessary to satisfy the ever tightening exhaust emission regulations. To increase the catalytic activity it would be necessary to apply a material that exhibits a high OSC value in a low temperature range. Conventional materials do not show significant OSC values at temperatures lower than 500 °C. This means that the catalyst does not clean the exhaust gas stream before the engine is heated properly, a situation which occurs every time the car is started.

![Figure 2. The working principle of an oxygen-storage material in the TWC. It helps to convert harmful substances that are produced in the combustion process into more benign ones by providing the right amount of oxygen in all conditions.](image)

2.9.2 Air Separation

Development of new technologies for commercial air separation is getting more and more interesting because in addition to conventional consumers of O\textsubscript{2} gas, most large-scale clean combustion technologies require oxygen instead of air as a feed gas. Current commercial method of producing O\textsubscript{2} is cryogenic distillation\textsuperscript{122} which is energy consuming and impractical to integrate with coal gasifier or oxyfuel power plants because of the lower production efficiency.\textsuperscript{52} Oxyfuel is a recently proposed process where high purity O\textsubscript{2} is introduced with
the recycled flue gas and the mixed O$_2$-CO$_2$ gas is feed back fore combustion. The cost of oxygen production is the key to make the oxyfuel process viable in the future.

Dense membranes made of mixed ionic-electric conductor (MIEC) material can continuously deliver pure oxygen under concentration gradients without external electrical loading. Many oxygen-storage materials except for ceria are MIEC type materials (since pure ion conductors are rare) and thus they are usable in this kind of membranes. If the membrane is thin enough the surface kinetics is the rate controlling factor over bulk diffusion for oxygen permeation. These kinetics are naturally facilitated by a material with as good as possible oxygen absorption capability. Low operation temperature of the OS material is desirable because of the lower energy consumption.

### 2.9.3 Solid Oxide Fuel Cell

Fuel cells convert the chemical energy of a fuel (H$_2$, hydrocarbons) to electricity and are one of the most promising ways of reducing the impact of energy production to the environment. The function of solid oxide fuel cells (SOFCs) is based on ceramic materials that conduct oxide ions and are a self-evident application for oxygen-storage materials. The main three parts of a fuel cell are the anode, the cathode and the solid electrolyte between them. Each part has certain requirements for the ceramic material it is made of although oxide-ion conduction plays a role in every part of the cell.

There are three types of SOFCs divided by the conductivity of the electrolyte material, i.e. high-temperature (900 – 1000 °C), intermediate-temperature (700 – 900 °C) or low-temperature (500 – 700 °C) SOFCs. Traditionally the development of SOFCs is concentrated in the first, high-temperature regime because remarkable oxide-ion conductivity usually requires really high temperatures and the most conventional electrolyte material i.e. yttria-stabilized zirconia (YSZ), shows respectable values in this range. Later more materials that work at lower temperatures have successfully been tested for the electrolyte material: e.g. gandolinium-doped ceria and doped lanthanum gallate. The selection for the electrolyte material is limited because it has to be a pure ion conductor and not a MIEC.

In contrast to the electrolyte material, both electrodes need to have both electronic and ionic conductivity. The anode has to also catalyse the oxidation reaction of hydrogen. In most cases the anode material has been a mixture of YSZ or doped ceria and a transition metal, usually nickel. Nickel however suffers from coking and the search for new anode materials is an on-going process. The working environment of the anode is also highly reducing which puts emphasis on the stability of the material. The performance of some MIEC materials has been investigated and they have some advantages over the Ni/YSZ anode: charge transfer may occur over the entire electrode and they are less likely to suffer from sulphur poisoning. It is still challenging to meet all the
requirements, high ion and electronic conductivity and the catalytic activity, at once.\textsuperscript{133}

Majority of the cathode materials studied are perovskites. As the operation temperature is lowered the catalytic activity of the cathode material towards reduction of $\text{O}_2$ and transportation of $\text{O}^{2-}$ ions limit the performance. Replacements for $(\text{La},\text{Sr})\text{MnO}_{3+\delta}$ and $(\text{La},\text{Sr})(\text{Co},\text{Fe})\text{O}_{3-\delta}$ for fuel cells that work under 600 °C are much needed for. For example, $\text{YBaCo}_4\text{O}_{7+\delta}$ based materials have raised a lot of interest.\textsuperscript{53-57}

2.9.4 Removal of Nitrous Oxides

The removal of nitrous oxides ($\text{N}_2\text{O}$) from exhaust streams is a widely studied issue since they contribute greatly to the green-house effect. Direct catalytic decomposition on a metal oxide catalyst is one of the most attractive options because of its low costs and the lack of harmful secondary emissions. The problem with the technique is that the catalyst is easily inhibited by oxygen which is produced when $\text{N}_2\text{O}$ is decomposed into $\text{N}_2$ and $\text{O}_2$. This is why a ceramic, oxygen selective membranes are introduced to the reaction zone. Oxide ions are removed through the membrane and charge neutrality is maintained by a counterdiffusion of electrons. Porous perovskite membranes are already tested in this application.\textsuperscript{126} Nitrous oxides are decomposed at high temperatures so the OS material should be thermally stable at least up to 900 °C.

2.9.5 Hydrogen Production

Hydrogen is both a clean energy source and an important raw material for the chemical industry. Many applications for oxygen-storage materials are actually related to hydrogen production. For example solar radiation is an inexhaustible source of energy but the transportation of the collected energy from the sunny areas to other locations is problematic. Converting the radiation to chemical fuel, favourably $\text{H}_2$, is an intriguing option. Hydrogen could be produced with solar energy by splitting water to $\text{H}_2$ and $\text{O}_2$. The technique requires porous ceramic membranes made of an oxygen-storage material which could separate the two gases selectively. The oxygen-storage material should stand high temperatures (even 1500 °C) without sintering.\textsuperscript{125} Methane is another widely-utilized source of hydrogen. It can be partially oxidized over a solid oxygen-storage material to produce hydrogen or syngas. The partial oxidation requires pure oxygen which is an expensive reactant if it has to be used in the pure gas form. If a solid oxygen-storage membrane is applied air can be used as a source of oxygen on the other side of the membrane.\textsuperscript{130-132}

Third possible method for hydrogen production is the so called chemical-looping. It involves oxidation of a fuel using oxygen from a solid oxygen-storage material (“oxygen-carrier material”) instead of oxygen from air. This
way the products are not diluted with N₂. In practice the oxygen-storage material is circulated between the fuel reactor, where it provides oxygen for the fuel to burn, and the so called air tank where it is loaded back to the oxygen-rich form by air at a proper temperature. The chemical-looping concept is interesting both for CO₂ capture applications in combustion processes, and for H₂ generation through reforming processes. The oxygen-storage material should be stable at the operation temperature and not promote e.g. formation carbon in the fuel reactor.¹²⁸ Even some simple metal oxides (NiO, Fe₂O₃, Mn₃O₄ and CuO) can provide enough oxygen for the reaction but it is believed that introducing a proper oxygen-storage material could be beneficial. SrFeO₃₋₃ based perovskites have been tested in a chemical looping system with a success.¹²⁸,¹²⁹
3. Experimental Procedures

The most essential parts of the experimental work in this thesis included careful synthesis of high-quality samples, engineering and determining the oxygen content of the samples precisely and evaluating the changes in the crystal structure by XRD and Rietveld refinement techniques.

3.1 Sample Synthesis

Both solid-state and sol-gel routes were utilized in sample synthesis. The sol-gel method is based on first dissolving the metal atoms of the starting materials and then complexing them with a chelate forming compound, in this work citric acid or ethylenediaminetetraacetic acid (EDTA). This allows the atomic level mixing of the starting-material cations without precipitation of any insoluble salts. Upon water evaporation the gel ignites spontaneously forming a low-density product that can be pelletized and sintered. Because of the better homogeneity of the starting material mixture, the sol-gel route often results in the desired product at a lower synthesis temperature or reduced firing time compared to the solid-state route. Lower temperatures lead to smaller particle size of the product which could be beneficial in terms of the rate of oxygen absorption. Despite of the advantages of the sol-gel method, the solid-state route was also employed in the sample synthesis because in practice it was an easy and fast and in most cases resulted in good quality products.

The development of the desired phase at different firing temperatures was monitored by XRD measurements. At some points completely single-phase products were impossible to obtain. In these cases the amounts of impurity phases were estimated by Rietveld refinement. Cation substitutions to the original $\text{YBaCo}_4\text{O}_{7+\delta}$ phase were in key role in this thesis. Rietveld or LeBail fittings of XRD data also provided useful information about the success of the synthesis since smooth trends in the cell parameter evolution indicated that the cation substituent was actually sitting at the desired position in the crystal-structure and not for example in the grain boundaries.
3.2 Oxygen Engineering

The precise oxygen content of the oxygen-storage materials is naturally sensitive to the changes in temperature and oxygen partial pressure. That is why the oxygen content of the samples had to be checked after every heat treatment. There were two methods employed for the analysis of the oxygen content of the samples: soluble samples were titrated by iodometric titration whereas the insoluble ones, namely manganites, were analyzed by thermogravimetric (TG) reduction experiments. During this reductive anneal the $RMnO_{3+\delta}$ sample is reduced to $R_2O_3$ and $MnO$ in two steps. First the sample is reduced to the stoichiometric ($\delta = 0$) composition at $\sim 350 ^\circ C$. Decomposition to the binary oxides, $R_2O_3$ and $MnO$, then takes place at around 600 $^\circ C$, see Figure 3a. The oxygen content could be calculated from either one of these mass changes which increased the reliability of the measurement. The reproducibility of the $\delta$ value was $< 0.01$.

In this work two types of materials were studied: $YBaCo_4O_{7+d}$ based cobalt oxides and $RMnO_{3+\delta}$ manganese oxides. The latter samples were found to be (ensured by TG measurements) always in their stoichiometric form right after synthesis whereas the cobalt oxide samples had to be annealed in an Ar gas flow at 500 $^\circ C$ for 10 hours in order to guarantee that the samples were in their reduced form and comparable with each other after synthesis.

The maximal amount of oxygen that the samples were able to absorb was investigated under high-pressure conditions in an autoclave. Different temperatures and durations for the high-pressure treatment were tested. Depending on the temperature (250 - 380 $^\circ C$) a pressure of 90 - 110 bar was reached at the final point. It was found that the manganese oxide samples required much longer periods of time (> 24 h) to reach their maximal oxygen contents compared to the cobalt oxides (a few hours). This is based on the kinetics of the oxygen absorption which are much faster in the case of the $YBaCo_4O_{7+\delta}$ family. The temperature of the treatment also played a crucial role in the high-pressure oxygenation. To get the highest possible oxygen content the temperature had to be in the right range where the compounds were absorbing oxygen. In the case of the $RMnO_3$ compounds even a change of 10 $^\circ C$ resulted in significant differences in crystal structure (observed by XRD) even though the change did not affect greatly to the oxygen content of the sample.

The oxygen absorption/desorption properties were investigated by means of thermogravimetry. There the rate of heating was affecting greatly to the magnitude of oxygen absorption. It was determined that the heating rate of 1 $^\circ C$/min was slow enough for the $YBaCo_4O_{7-\delta}$-based samples (see Figure 3b) to reach the maximum absorption whereas the rate of 0.1 $^\circ C$/min (slower rates were not investigated) had to be used for the manganites. The temperature where the manganites are absorbing oxygen is slightly lower compared to the cobaltites which might explain a part of the difference in the kinetics of absorption.
Figure 3. TG curves recorded for (a) YMnO$_{3.35}$ in H$_2$/Ar flow with a heating rate of 5 °C/min and (b) YBa-Co$_4$O$_{7+\delta}$ in O$_2$ flow with different heating rates. In (a) YMnO$_{3.35}$ is first reduced to the stoichiometric composition and then upon further heating it decomposes to binary oxides. The initial oxygen content can be calculated from either one of these steps. In (b) the effect of the heating rate on the amount of absorbed oxygen is illustrated for YBaCo$_4$O$_{7+\delta}$.

3.3 Phase-Stability Studies

The only significant weakness of YBaCo$_4$O$_{7+\delta}$ is the poor stability at temperatures > 600 °C. The phase is actually metastable at room temperature and decomposes to BaCoO$_{3-\delta}$ plus debris if heated in an oxygen-containing atmosphere. The stability of the samples in respect to temperature was mostly studied by TG method. A typical TG curve recorded for YBaCo$_4$O$_{7+\delta}$ in oxygen flow is presented in Figure 4. The curve has two humps where the mass of the sample increases; first one is due to the oxygen absorption/desorption process and the second one depicts the phase decomposition. The effect of cation substitutions in preventing the decomposition could be judged by the magnitude of the last hump and more importantly from the onset temperature of the latter mass change.

The high-temperature phase stability was additionally confirmed for selected samples by heating them in air at different temperatures from 600 to 1000 °C in a box furnace for 15 hours, followed by quenching to room temperature. X-ray diffraction patterns were then recorded for the quenched samples to detect possible signs of phase decomposition. This method is more sensitive to small changes in the composition that could not be detected from a TG curve.
3.4 Catalytic Evaluation

The activity of YBaCo$_4$O$_{7+\delta}$ as a catalyst was investigated in the oxidation of cyclohexene.\textsuperscript{IV} Catalytic studies were performed using hydrogen peroxide as the primary oxidant which is of a particular interest because of its environmentally benign byproducts. A known amount of octane was also added to the reaction solution, to act as an internal standard. The reaction mixture, where 1-propanol was used as a solvent, was stirred at 70 °C for 2 hours (in some experiments also for a longer period of time). The reaction was terminated by quenching into ice and the reaction products were immediately analyzed by gas-cromatography. The reaction parameters were closely following the results of a previous study\textsuperscript{138} where the selectivity to cyclohexene oxide was optimized.

Immersion calorimetry measurements were performed to understand the nature of YBaCo$_4$O$_{7+\delta}$ as an oxidation catalyst, and more specifically in the activation of the H$_2$O$_2$ molecule.\textsuperscript{IV} In heterogeneous catalysis the degree of the interaction between the reactants and the active sites determine the catalytic behavior, e.g., the activation of the oxidant.\textsuperscript{139} Immersion calorimetry is a powerful technique to estimate the enthalpy of immersion of a liquid molecule on a solid surface; it depends on the surface area available to the liquid (mainly the porosity of the solid) and the specific interactions of the liquid molecule with the solid surface.\textsuperscript{140}
4. Chemical Tailoring of YBaCo$_4$O$_{7+\delta}$

The properties of the YBaCo$_4$O$_{7+\delta}$ were engineered by various cation substitutions in this work. There were two aspects where these enhancements were targeted: maximizing the OSC value and diminishing the phase decomposition that occurs at high temperatures. The factors that affect the both properties were found and the sample that has an optimized composition was successfully synthesized too.

4.1 Cation-Substitution Effects on Oxygen-Storage Capability

The OSC value of the parent YBaCo$_4$O$_{7+\delta}$ phase is outstandingly high, even the value of 2600 μmol/g is reached after oxygenation under elevated oxygen partial pressures. It is well established that substituting Y with a smaller cation in YBaCo$_4$O$_{7+\delta}$ results in a decreased oxygen absorption capability. In this work it was further studied how the smaller-for-larger cation substitution at the Ba site affects the oxygen absorption characteristics. The Ba site is highly under-bonded (BVS = 1.19) thus Ba is not easily replaced by any smaller cation. However a sample series of Y(Ba$_{1-x}$Sr$_x$)Co$_4$O$_{7+\delta}$ ($x = 0$ – 0.2) was successfully synthesized and dynamic TG measurements were performed. The results show that the radius of the cation at the Ba site has similar effect for the oxygen absorption than cation size at the Y site. The higher the substitution rate is the lower is the cell volume and thus the less efficient the oxygen absorption. This finding supports the conclusion that changes in the size of the crystal lattice determine how easily the relatively large oxide anion moves in the cavities of the structure.

The effects of the Co-site substitutions were also studied with several 3$d$ transition metals, i.e. Mn, Fe, Ni and Cu, and also with Zn, Al and Ga. First, samples with 5 % substitution level, YBa(Co$_{0.95}$M$_{0.05}$)Co$_4$O$_{7+\delta}$, were synthesized for all the $M$ substituents and investigated through TG measurements. The TG curves are presented in Figure 5 in III. It was found that for all the substituted samples the maximum oxygen content reached during the dynamic TG run was lower compared to that for the parent YBaCo$_4$O$_{7+\delta}$ phase, the lowest $\delta_{\text{TG-max}}$ value of 0.30 being for the Zn-substituted sample. While the isovalent substi-
tution effects on the Y and Ba sites are most likely related to the sizes of the substituents, those for the metal species replacing cobalt in YBaCo$_4$O$_{7-\delta}$ are probably explained by the redox chemistries (i.e. the different oxidation states) of the substituents. In general the essence of a high OSC value is based on the ability of certain elements to exist with varying valence states and the ability of certain crystal structures to allow these changes. The increase in the oxygen content of YBaCo$_4$O$_{7-\delta}$ is accompanied with a change in the average Co-valence and thus metal species with redox chemistries similar to that of cobalt, namely Fe and Mn affect the oxygen absorption behavior the least. On the other hand, Zn with a fixed oxidation state of II (and no possibility for valence changes) shows a strong reduction in the oxygen absorption capability.

4.2 Cation-Substitution Effects on Phase Stability

It is stated in the last section that the smaller is the crystal cell of the sample the poorer is the capability to reversibly absorb and desorb oxygen at low temperatures. Measurements with the Sr-for-Ba sample series provided information also on the phase stability. They revealed that the smaller cell size leads to higher decomposition temperature and the relation between the phase-decomposition temperature and the cell volume per formula unit is almost inversely linear such that the smaller the cation substituent is the higher is the temperature where the decomposition process starts.

Similar finding has been done for R-for-Y substitution. The oxidative phase decomposition seems to be suppressed if the crystal lattice is made shrunken through an appropriate cation substitution. The roots of this phenomenon are in the strained structure of the YBaCo$_4$O$_{7-\delta}$ phase. The calculations based on BVS values show that even with the smallest possible substituents, e.g. Lu at the Y site, the structure is greatly strained and this is why smaller-for-bigger ion substitutions stabilize it. However, none of the known substitutions to Y or Ba site do prevent the decomposition completely, they only increase the temperature at which it is taking place.

As for the phase-decomposition characteristics, the Co-site substitutions seem to be all advantageous: the phase decomposition temperature was shifted towards higher temperatures for all the substituents (Al, Mn, Fe, Ni, Cu, Zn, Ga) investigated. Most prominently this is seen for Al, Ga and Zn. Interestingly, these three metals are the only substituents that do not exhibit multiple oxidation states. In the main decomposition product of YBaCo$_4$O$_7$, i.e. BaCoO$_3$ s, cobalt is in octahedral coordination while in the YBaCo$_4$O$_7$ structure itself it has tetrahedral coordination; the reason for the enhanced thermal stability is most likely due to the better affinity of divalent Zn and trivalent Al and Ga (compared to cobalt) towards the tetrahedral coordination since all the three cations have symmetrical electronic shells, $d^0$ or $d^{10}$. From these three elements Al favors the tetrahedral coordination mostly because of its small size.
Similarly to YBaCo$_4$O$_{7+5}$ the instability of brownmillerite Sr$_2$Co$_2$O$_5$ was attributed in Ref. 142 to the instability of trivalent Co in tetrahedral oxygen coordination and partial phase stabilization was achieved by means of Ga-for-Co substitution.

It is known that Zn substitution of 25 % to the Co site prevents the phase decomposition of YBaCo$_4$O$_{7+5}$ completely but it also destroys the low-temperature oxygen absorption capability of the material. Having the eye on the possible oxygen-storage applications, the low price of Al metal is definitely an attractive aspect. Unfortunately the solubility limit of Al at the Co sites is only 12.5 % which is not enough to fully prevent the phase decomposition. In this study the solubility limit of Ga-for-Co was found to be close to 30 %. It was also discovered that 20 % substitution is enough to prevent the phase decomposition completely and the oxygen absorption properties of YBaCo$_4$O$_{7+5}$ are still preserved to a respectable extent.

4.3 Co-Substitutions with Multiple Cations

Both zinc and gallium substitutions are efficient in preventing the phase decomposition of YBaCo$_4$O$_{7+5}$ but both also have downsides: zinc the fact that it impairs the oxygen absorption and gallium its high price. Aluminium in contrast is an inexpensive and readily available metal that does not tamper the OSC of the material too much but has a too low solubility limit to the phase. Hence, the co-substitution of Al and Ga was studied further.

A sample series of YBa(Co$_{1-x}$Al$_{x}$/2Ga$_{x}$/2)$_4$O$_{7+5}$, $x = 0 - 0.20$ was synthesized. The most promising co-substituted YBa(Co$_{1-x}$Al$_{x}$/2Ga$_{x}$/2)$_4$O$_{7+5}$ samples of $x = 0.10$ and 0.15 are compared to the corresponding Ga-substituted samples, YBa(Co$_{0.90}$Ga$_{0.10}$)$_4$O$_{7+5}$ and YBa(Co$_{0.85}$Ga$_{0.15}$)$_4$O$_{7+5}$ in Figure 5. It is seen that compared to the Ga-for-Co substitution the co-substitution with Al and Ga prevents the phase-decomposition more efficiently: at $x = 0.15$ no weight gain (or phase-decomposition) occurs in the high-temperature region in the case of co-substitution while for the Ga-substituted sample a trace of weight gain is yet seen. Like it was stated above, trivalent Al favors the tetrahedral coordination more than trivalent Ga and thus the observation that Al and Ga together prevent the phase decomposition of YBaCo$_4$O$_{7+5}$ better than Ga alone is convincing.

It is seen in Figure 5 that in a dynamic TG run the amount of absorbed oxygen for the substituted phases is less ($\delta_{\text{max}} < 1.0$) than that of the unsubstituted YBaCo$_4$O$_{7+5}$ phase ($\delta_{\text{max}} \approx 1.3$, see Figure 4). As for the OSC, like all other cation substitutions in YBaCo$_4$O$_{7+5}$, replacing part of the Co species by Al or Ga or their mixture somewhat suppresses the amount of oxygen absorbed at least during a dynamic TG run. Yet, for e.g. the co-substituted $x = 0.15$ sample, YBa(Co$_{0.85}$Al$_{0.075}$Ga$_{0.075}$)$_4$O$_{7+5}$, the oxygen absorption performance is reasonable, being even a little better than that of the corresponding Ga-substituted YBa(Co$_{0.85}$Ga$_{0.15}$)$_4$O$_{7+5}$ Sample (see Figure 5). Moreover, the maximum oxygen absorption level that the co-substituted samples reached upon thermodynamic
equilibration under high oxygen partial pressure conditions was almost equal to the values for YBaCo₄O₇₊δ. The high-pressure annealing was carried out under oxygen pressure of 100 atm at 280 °C for 10 hours. It seems that the mixed (Al,Ga)-for-Co substitution does not remarkably lower the maximum amount of oxygen allowed for the structure; e.g. for the YBa(0.85Al₀.₀₇₅Ga₀.₀₇₅)₄O₇₊δ sample the δₜₚₑₚ₋ₘₚₓ value was determined at 1.30, being reasonably close to the value observed for the parent YBaCo₄O₇₊δ phase under the same conditions (δₜₚₑₚ₋ₘₚₓ = 1.45). Thus it is concluded that the YBa(0.85Al₀.₀₇₅Ga₀.₀₇₅)₄O₇₊δ material is a highly promising candidate for applications where the high-temperature phase-stability is of importance: it remains stable up to high temperatures, is capable of storing large amounts of oxygen at appreciably low temperatures and contains only minor amounts of the expensive gallium metal.

![Figure 5. TG curves recorded for YBaCo₄O₇₊δ, YBa(0.85Al₀.₀₇₅Ga₀.₀₇₅)₄O₇₊δ and YBa(0.85Al₀.₀₇₅Ga₀.₀₇₅)₄O₇₊δ (x = 0.15 for both) in O₂ gas flow with a heating rate of 1 °C/min. It is seen that the Al:Ga co-substituted sample absorbs more oxygen than the Ga-substituted one. In addition there are traces of the decomposition process detected in the curve of the Ga-substituted sample at 800 °C whereas the mass of the co-substituted sample remains unchanged.](image)

It is known that simultaneous substitutions to more than one site may change the phase stability picture of YBaCo₄O₇₊δ considerably. For example in the case of zinc, YBa(Co₃Zn)O₇₊δ does not decompose at any temperature whereas compounds with Ca or In simultaneously at the Y site do. It was investigated how substitution to the R site concomitant with Al+Ga co-substitution to Co site affects the oxygen absorption properties of the YBaCo₄O₇₊δ material. In this study the multiple site substitution was investigated by synthesizing a sample series of RBa(0.85Al₀.₀₇₅Ga₀.₀₇₅)₄O₇₊δ with R = Y, Dy, Ho and Lu. Surprisingly, the RBa(0.85Al₀.₀₇₅Ga₀.₀₇₅)₄O₇₊δ phase was found to remain stable (upon heating in O₂ up to 1000 °C) only for R = Y and Lu, whereas with the R constituents larger than Y (i.e. Dy and Ho), the phase-decomposition reaction was seen. These findings highlight the fact that the high-temperature stability of the YBaCo₄O₇₊δ family is a structure-related is-
The strain in the structure becomes larger along the ionic radius of $R$ and compounds with larger $R$ need more stabilization from the Co-site substitution to prevent the decomposition reaction.

The co-substitutions of $\text{YBaCo}_4\text{O}_{7+\delta}$ should be studied further in the future. It would be interesting to see how much stabilization from the Co-site substitution the largest Rs (Dy, Ho) need in order to prevent the decomposition at high temperatures. Iron substitution at the Co site is promising in the sense it tampers the oxygen absorption the least. A small amount of Ga or Al in addition of iron at the Co site could stabilize the phase and lead to a new OS material candidate.
5. Catalytic Activity of YBaCo$_4$O$_{7+\delta}$ in Oxidation Reactions

Ceria, the most well-established oxygen-storage material is known to act as a catalyst in several industrial reactions.$^4$ As it is stated above in this review, YBaCo$_4$O$_{7+\delta}$ shows much higher OSC values at lower temperatures than ceria but it had not yet been exploited in heterogeneous catalysis. Catalytic oxidations of hydrocarbons is an important industrial process in both environmental chemistry and fine chemical industry.$^{143-145}$ In these oxidations the homogenous catalyst show high activity and selectivity.$^{146,147}$ Heterogeneous catalysis is, however, more desirable because of the ease of separating the reaction products and recycling the catalyst material. Among the different transition metal catalysts, Ti-based systems have been the most widely investigated.

In this study the catalytic activity of YBaCo$_4$O$_{7+\delta}$ in the oxidation of cyclohexene with H$_2$O$_2$ was investigated.$^{14}$ In the starting point it was known that because the material was synthesized at a relatively high temperature of over 1000 °C the surface area would be really low (later determined to be < 2 m$^2$/g). The activity of a catalyst is greatly affected by the availability of the active sites and thus a large surface area is a typical feature of a feasible catalyst material. For comparison two other materials were examined in the same reaction: binary cobalt oxide sample that was treated under the same synthesis conditions as YBaCo$_4$O$_{7+\delta}$ and a commercial TiO$_2$ sample. The reaction parameters were obtained from a previous study.$^{138}$ Surprisingly, YBaCo$_4$O$_{7+\delta}$ showed outstandingly high conversion in the oxidation of cyclohexene. The activity was more or less three times higher than those with either of the reference materials, see Table 3. Neither of the other two catalyst materials actually improved the conversion of cyclohexene compared to a blank experiment.
Table 3. The conversion of cyclohexene with three different catalyst materials after two hours of reaction at 70 °C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>17.7</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>18.2</td>
</tr>
<tr>
<td>CoO$_{1+5}$</td>
<td>20.3</td>
</tr>
<tr>
<td>YBaCo$<em>4$O$</em>{7+5}$</td>
<td>61.6</td>
</tr>
</tbody>
</table>

The catalytic efficiency of YBaCo$_4$O$_{7+5}$ was also tested with an environmentally friendly reactant-oxidant ratio. YBaCo$_4$O$_{7+5}$ performed well even with a low ratio of 5:1 cyclohexene-H$_2$O$_2$. The drastic reduction of the oxidant amount was compensated by only a two-hour increase in the reaction time to preserve the 60 % conversion. With the initial oxidant-reactant ratio of 1:1, 100 % conversion was achieved in 6 hours whereas the system with the lower ratio reached the 80 % conversion in the same period of time. This corroborates the exceptional behavior of the YBaCo$_4$O$_{7+5}$ catalyst even under lean oxidizing conditions.

In this study the selectivity of the reaction was not studied thoroughly. For both the cobalt-oxide materials, the main reaction products were 2-cyclohexen-1-ol, cyclohexenone, 1,3-cyclohexenedione, 1,2-cyclohexane-diol and 1,2-epoxycyclohexane, although the relative amounts of these components somewhat varied depending on the catalyst material and the catalytic conditions (reaction temperature and time). The selectivity of the reactions and especially the improvement of it is a subject of further studies.

To clarify the roots of the high activity of YBaCo$_4$O$_{7+5}$ and on the other hand the inactivity of especially TiO$_2$, immersion calorimetry experiments with H$_2$O$_2$ were performed. It was known that some titanate systems have problems in activating/dissociating the O-O bond in H$_2$O$_2$ and they work well only with stronger oxidants.$^{149-151}$ It was found out that the enthalpy of H$_2$O$_2$ immersion $\Delta H_{\text{imm}}$ on YBaCo$_4$O$_{7+5}$ was more than two hundred times larger (> 3137 J/g) than that of the commercial titanium oxide (17 J/g) and at least 15 times larger than that of the binary cobalt oxide sample (213 J/g). Actually, the value for YBaCo$_4$O$_{7+5}$ was beyond the detection limit so the ratios could be remarkable greater in reality.

The extremely high enthalpy of immersion of YBaCo$_4$O$_{7+5}$ clearly reflects the presence of associated reaction processes during the calorimetric analysis whereas the small value for the TiO$_2$ sample suggests a physisorption phenomenon without specific liquid-solid interactions. The binary cobalt-oxide catalyst synthesized as a reference material exhibits a little higher enthalpy of immersion, thus reflecting the presence of specific interactions between H$_2$O$_2$ and the Co(II/III) species, in close agreement with the better catalytic behavior of Co versus Ti in oxidation reactions when using H$_2$O$_2$ as an oxidant.

The immersion of H$_2$O$_2$ on the catalyst materials were also performed outside the calorimeter’s reaction chamber to visually observe the difference between different oxide materials. When small amounts of H$_2$O$_2$ and YBaCo$_4$O$_{7+5}$ were put into a test tube (without stirring) a vigorous formation of
bubbles was seen. The gas was most certainly oxygen that forms (in addition to water) in the decomposition of the peroxide. The reaction also produced a remarkable amount of heat which led to boiling of the mixture after a few minutes. The same experiment with the binary cobalt oxide material produced only a few bubbles and a non-detectable amount of heat. After the formation of gas and heat was finished (~20 minutes) YBaCo₄O₇₋₋₅ was dried and measured with XRD to make sure it did not decompose in the process. The same powder sample was also repeatedly made in contact with a fresh batch of H₂O₂ which resulted in a similar formation of gas and heat as the initial experiment. These experiments further confirm that the key to the high activity of YBaCo₄O₇₋₋₅ in the oxidation reaction is the interaction with H₂O₂.

Next step in the catalytic studies with YBaCo₄O₇₋₋₅ is definitely the enhancement of surface area by increasing porosity. A possible way could be templating with an organic material. This should also help to control the selectivity of the reaction, because different pore sizes favour different products and reaction paths.
Rare-earth manganites are a widely studied group of compounds. $\text{RMnO}_{3+\delta}$ compounds crystallize in two different crystal structures. The $\text{RMnO}_{3+\delta}$ phases with the larger rare earths (La-Dy) adopt an orthorhombically-deformed perovskite structure ($Pbnm$), whereas the phases with the smaller $R$ constituents (Y, Ho-Lu) have a noncentrosymmetric hexagonal $P6_3cm$ structure. Synthesis of the $\text{RMnO}_{3+\delta}$ phases in air has been believed to result in essentially oxygen-stoichiometric samples, except for $R = \text{La}$.

Recently it was however discovered by Remsen et al. that for the specific compositions of $(\text{Dy}_{1-x}\text{Y}_x)\text{MnO}_{3+\delta}$ ($0 \leq x \leq 1$) the hexagonal manganites possess oxygen nonstoichiometry; the oxygen-content variation range in $(\text{Dy}_{1-x}\text{Y}_x)\text{MnO}_{3+\delta}$ samples corresponds to OSC value up to 2000 $\mu$mol-O/g. In this work it was investigated whether the smaller members (Y,Ho-Lu) of the rare-earth manganites can possess oxygen hyper-stoichiometry. Moreover the crystal changes in the structure the excess oxygen brings about were elaborated.

High-pressure oxygen annealings for a series of $R = \text{Y} – \text{Lu}$ samples revealed that only the two compounds with the largest $R$s, Y and Ho were able to sustain oxygen-nonstoichiometry. This suggests that also in this case oxygen-nonstoichiometry might be a size-related matter, which was also discovered in the cation substitution experiments with $\text{YBaCo}_4\text{O}_7$. In addition, in a previous study it was found that the compound with a larger $R = \text{Dy}$ absorbs more oxygen than $\text{YMnO}_{3+\delta}$. Suprisingly, in this study dynamic TG measurements (illustrated in Figure 2 in V) showed that $\text{HoMnO}_{3+\delta}$ seemed to absorb more oxygen than $\text{YMnO}_{3+\delta}$. Since the maximum amount of oxygen was determined to be of equal magnitude for both materials ($\delta = 0.4$) the reason must be merely in the kinetics. Also, the difference in size of $\text{Y}^{3+}$ and $\text{Ho}^{3+}$ (CN 6) is minute.

When the materials were treated at elevated oxygen partial pressure (~100 bar) at different temperatures and with varying periods of time it was found that the phases evolve through several steps (similarly to ref. 33) but reach saturation at a certain point ($R = \text{Y}$, 315 °C for 20 h, a somewhat lower temperature for $R = \text{Ho}$), shown in Fig. 3 in V. After this point raising the temperature or duration of the treatment the XRD pattern starts to resemble the ones recorded after lower-temperature treatment. The final phase is obtained also at temperatures between 250 – 300 °C by doubling or tripling the treatment hours; rather a normal behaviour and related to the sluggishness of
the oxygen-absorption kinetics at low temperatures. This is the reason why the pattern obtained at 315 °C was considered to be a final result and phases obtained at 250 – 300 °C as intermediate steps in its formation.

All attempts to find a proper unit cell for the new highly-oxygenated $RMnO_{3+\delta}$, $R = Y$, Ho phase by means of XRD failed. Luckily, employing electron diffraction (ED) revealed some important details of the structure of $YMnO_{3+\delta}$ that help to explain the nature of samples. The analysis of the ED patterns suggests that there might be actually two separate phases in the highly-oxygenated form; the first one resembling closely to the original hexagonal phase and the other being a pyrochlore-like $YMnO_{3.5-\delta}$ or $(Y_2Mn_2O_{7-2\delta})$ phase. This composite structure depends of the oxygen content only acting on the oxidation state of the Mn, which adopt trigonal bipyramidal and octahedral environments. More detailed studies are still needed to reveal the throughout nature of the phase.

The next step in studying the evolvement of the crystal structure of the hyperstoichiometric $RMnO_{3+\delta}$ is to study phases with intermediate oxygen contents between $\delta = 0$ and 0.35. The sample series with varying oxygen contents between could be probably made by heating as-synthesized samples in oxygen and then quenching them at a proper temperature. The ED analysis of the intermediate phases would be most likely the best way to understand the changes in the crystal structure of $RMnO_{3+\delta}$, $R = Y$, Ho during the oxidation process.
7. Conclusions

New energy technologies and the demand for greener processes call for a huge variety of novel functional materials. Understanding the complex relationship between chemistry and properties is essential in developing new material solutions to answer the strict requirements. In this thesis the properties of the new oxygen-storage material $\text{YBaCo}_4\text{O}_{7+\delta}$ were enhanced through cation substitutions. Its utilization in a new catalytic application was also studied. In addition the oxygen-storage properties of another newly-discovered material $\text{YMnO}_{3+\delta}$ were investigated.

Cation substitutions to each of the metal sites in $\text{YBaCo}_4\text{O}_{7+\delta}$ were made and their effect on the oxygen-storage properties and phase stability were investigated by means of TG and XRD techniques. The oxygen absorption was found to be increased in respect to the average size of the cation at either the Y or the Ba site. The effect is most likely related to the size of the crystal lattice and to the wider pathways for oxide ions that the larger cell brings about. On the other hand substitutions to the Y and Ba sites that lead to smaller cell and thus less strained structure were shown to improve the high-temperature stability of the $\text{YBaCo}_4\text{O}_{7+\delta}$ phase by increasing the temperature where the oxidative decomposition to simpler oxides starts. In contrast to the Y and Ba site substitutions, replacement of part of the cobalt with a proper cation was able to prevent the decomposition process completely. In general all Co site substitutions decrease the amount of oxygen the phase absorbs, those cations that have similar variation in the valence states (Fe, Mn) as cobalt the least. The most beneficial substitutent for Co was revealed to be replacing 15 % of it with a 50:50 mixture of aluminium and gallium. This substitution stabilizes the phase for all temperatures and does not hinder the oxygen-storage properties too much.

The $\text{YBaCo}_4\text{O}_{7+\delta}$ compound was also tested as a catalyst material in the oxidation of cyclohexene with $\text{H}_2\text{O}_2$. The conversion of cyclohexene was three times higher with $\text{YBaCo}_4\text{O}_{7+\delta}$ than with with a conventional catalyst material $\text{TiO}_2$ or simple cobalt oxide. Immersion calorimetry measurements showed that the reason for the outstandingly high activity is in the interaction between the catalyst and $\text{H}_2\text{O}_2$: $\text{YBaCo}_4\text{O}_{7+\delta}$ dissociates $\text{H}_2\text{O}_2$ with a really high efficiency.

Very recently it was discovered that hexagonal lanthanum manganites $\text{RMnO}_{3+\delta}$, where $R = \text{Dy, Y}$ are able to show oxygen nonstoichiometry. In this thesis it was shown that also the manganite with $R = \text{Ho}$ can sustain oxygen over the stoichiometric amount whereas the smaller $Rs$ (Er-Lu) cannot even
though they have the same crystal structure. The oxygen absorption properties of HoMnO$_{3+d}$ matched those of the bigger $R$ manganites; they absorb and desorb oxygen at a certain temperature range around 250 °C. The maximum amount of oxygen the phases with $R = Y, Ho$ was found to be $\delta \approx 0.4$. High-pressure oxidations with careful adjustments of the parameters revealed a new composite structure associated with certain conditions and $\delta = 0.35$. 
References

YBaCo$_4$O$_{7+\delta}$ and YMnO$_3$$_{3+\delta}$ Based Oxygen-Storage Materials

Outi Parkkima