Redox energetics of novel perovskite-type oxygen carriers for chemical looping reforming

Dissertation for the degree of Philosophiae Doctor

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Preface

This thesis is submitted in partial fulfillment of the requirements for the degree of Philosophiae Doctor. The study was accomplished during my employment as a Ph.D. candidate at the Department of Chemistry, Centre for Materials Science and Nanotechnology, Faculty of Mathematics and Natural Sciences, University of Oslo. The financial support was provided by the Norwegian Research Council (NFR) through the “RENERGI Programme”.

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Abstract

The present work focuses on the redox energetics of novel perovskite-type oxygen carriers for chemical looping reforming. The aim of this study is to increase the level of knowledge on the redox characteristics of materials for possible applications as the oxygen carriers for the chemical looping processes.

Here we focus on the perovskite-type oxides \((ABO_3)\) with lanthanum on the \(A\)-site and first row transition metals on the \(B\)-site since first row transition metals normally have more than one oxidation state, non-stoichiometry in the perovskite oxides with such metals on the \(B\)-site is common while keeping the same structure. The partial substitution of the cation on the \(B\)-sublattice is studied as a measure to adjust the redox energetics. In the present study partial substitution of cobalt in \(\text{LaCoO}_3\) with \(\text{Mn}\) and \(\text{Fe}\) is chosen. The redox behavior of non-stoichiometric compounds may be assessed from the variation of the oxygen non-stoichiometry with temperature and oxygen partial pressure. Thermogravimetric analyses (TGA) is used for most of the systems but in order to reach higher accuracy, specialized instruments are needed. One of the most accurate techniques to measure the oxygen non-stoichiometry is coulometric titration (CT). A novel CT setup was designed, constructed and validated. This setup was subsequently used to study the oxygen non-stoichiometry of the \(\text{LaMn}_{1-x}\text{Co}_x\text{O}_{3-\delta}\) system at 1223, 1273, and 1373 K. For the \(\text{LaMn}_{1-x}\text{Co}_x\text{O}_{3-\delta}\) system it is found that the observed oxygen non-stoichiometry curve is due to the simultaneous reduction of both manganese and cobalt on the \(B\)-sublattice and the enthalpy of oxidation values show a linear dependence by \(x\) (portion of \(\text{Co}\)). The oxygen non-stoichiometry and redox energetics of the second studied system, \(\text{LaFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}\), just similar to the previous system show no indication of the sequential reduction of the cations occupying the \(B\)-sublattice. The absolute value of the enthalpy of oxidation increases as the iron portion on the \(B\)-sublattice increases, which approves this finding.

In contrast to the experimental approaches, DFT calculations might provide a cost effective tool to examine complex systems and obtain an approximation for the redox thermodynamic properties; according to the following reaction:

\[
\text{LaBO}_{2.5} + \frac{1}{2} \text{O}_2 = \text{LaBO}_3.
\]

It is however necessary to examine the sources of error and the accuracy of the calculations. Therefore a benchmark study was conducted on the formation energetics of lanthanide first row transition metal perovskite-type oxides \((\text{LaBO}_3)\). The benchmark shows that although fundamental errors in the GGA affect the energetics, still with addition of \textit{ad hoc} corrections, it is possible
to obtain values which are in good agreement with the experiment. The benchmark also confirms that as long as the calculations are spin polarized (with any magnetic structure) and performed with the relaxation of the experimental crystal structure, the total energies are reproduced within 15 kJ/(mol $B$).

Turning to the reduced phases, La$BO_{2.5}$, the calculations proved to be much more difficult than the oxidized phases. In contrast with La$BO_3$ phases, a bigger fraction of total energy of the reduced phases is attributed to the magnetic configuration, meaning that a simple magnetic structure (e.g. ferromagnetic) does not predict the ground state reasonably. Still, the biggest challenge is due to the configuration of oxygen vacancies on the oxygen sublattice. Simultaneous presence of oxygen vacancy and spin configurations necessitates a computational algorithm based on statistics, e.g. Monte Carlo method, which was out of the scope of this study given the three year time frame. This however opens up an opportunity for the future works.
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1 Introduction

There is an extensive amount of evidence indicating that the Earth’s climate has changed and the atmospheric mean temperature has increased during the past century [1]. The atmospheric mean temperature is known to be correlated to the concentration of the greenhouse gases [2]. Among all the greenhouse gases, concentration of carbon dioxide has changed extensively, and CO₂ is among the most abundant greenhouse gases (second after water vapor). It is therefore the gas most concerned when analyzing the potential human effects on climate change [1]. In 2007, the Intergovernmental Panel on Climate Change (IPCC) reached the firm conclusion that “most of the observed increase in global average temperature since the mid-20th century is very likely due to the observed increase in anthropogenic greenhouse gas concentrations” [3].

The idea to convert, transmit, store and deliver energy to end-users through carbonless energy carriers has been discussed widely, as the applied way to stabilize the greenhouse gas level. Such systems will either be based on non-fossil primary energy sources (solar, wind, hydroelectric, etc.) or continue to rely on fossil primary energy sources while limiting carbon emissions [4]. From the economical point of view, the electricity produced by fossil energy resources is still much cheaper than the renewable resources or non-fossil ones [5]. Even with the added pollution controls, the cost of fossil energy generated power keeps falling [6]. The existing post-combustion CO₂ capture technologies (e.g. monoethanolamine scrubbing technology [7]) for CO₂ capture from power plants reduce the full power generation by up to 42% [8], and takes more than 70% of the total cost for the overall process of carbon management consisting of capture, transportation, and sequestration [9].

A considerable fraction of the CO₂ capture cost is due to CO₂ separation and concentration. If the carbon dioxide output of a process is not diluted with N₂, the CO₂ capture cost will be much lower. One of the suggested methods is chemical looping [10]. The chemical looping concept is based on splitting the total combustion reaction into two or more separate sub-processes taking place at different temperatures and pressures. In chemical looping processes the primary energy source is still a hydrocarbon fuel while the exhaust CO₂ can be captured. The main idea behind the chemical looping concept is to use of a solid oxygen carrier material...
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instead of oxygen from air (which contains around 80 % N₂) [11]. Conventional cryogenic oxygen production processes demands 31-35 $/ton O₂ for oxygen production [12]. Chemical looping thus has an economical advantage compare to feeding pure O₂ to the combustion reactor in addition to that the air separation equipment is also eliminated [13].

The reduced oxygen-carrying oxide is re-oxidized in air in a second step of the loop (“air reactor”) according to equation (1).

\[ \text{MeO}_{1-x} + \frac{\gamma}{2} \text{O}_2 \rightarrow \text{MeO} \]  

Depending on the specific chemical reaction taking place in the “fuel reactor”, chemical looping processes can be divided into two major subgroups; Chemical looping combustion (CLC) and chemical looping reforming (CLR).

In chemical looping combustion, the hydrocarbon fuel is fully oxidized into CO₂ and H₂O in the fuel reactor according to equation (2) and the main product of this process is therefore heat.

\[ C_nH_m + \left( \frac{2n}{2} + \frac{m}{2x} \right) \text{MeO} \rightarrow (n)\text{CO}_2 + \left( \frac{m}{2} \right)\text{H}_2\text{O} + \left( \frac{2n}{2} + \frac{m}{2x} \right)\text{MeO}_{1-x} \]  

On the other hand, in chemical looping reforming the aimed outcome of the process is not heat, but synthetic gas (syngas), as illustrated by equation (3).

\[ C_nH_m + \left( \frac{2}{x} \right)\text{MeO} \rightarrow (n)\text{CO} + \left( \frac{m}{2} \right)\text{H}_2 + \left( \frac{2}{x} \right)\text{MeO}_{1-x} \]  

A recently proposed variant of CLC is chemical looping hydrogen (CLH) also known as chemical looping steam reforming (CLSR); a water splitting process by partial re-oxidation of the solid oxygen carrier material in “steam reactor” according to equation (4) [14].

\[ \text{H}_2\text{O} + \left( \frac{1}{x-x'} \right)\text{MeO}_{1-x} \rightarrow \text{H}_2 + \left( \frac{1}{x-x'} \right)\text{MeO}_{1-x'} ; x > x' \]  

CLH is a developed form of CLC in which the reduced oxide is used to split water before fully re-oxidized [14]. Although CLH is a modified type of CLC, since the outcome of the
process is both heat and reducing gas (hydrogen), CLH is sometimes considered as a CLR process. CLC, CLR, and CLH processes are schematically presented in figure 1.

Figure 1. Schematic flow sheets for (a) CLC, (b) CLR and (c) CLH.
The separation of the reduction and oxidation reactions by adding an oxygen carrier material necessitates special characteristics for the oxygen carrier material. The hydrocarbon conversion by chemical looping reactions in the absence of gaseous oxygen will be possible only with an oxygen carrier material which exhibits special chemical properties, such as attrition strength, high oxygen mobility, thermal stability, and particular redox properties [13, 15]. The ideal oxygen carrier material should also exhibit considerable amount of transferrable oxygen [9]. Potential oxygen carriers should be stable at high temperatures (600 – 1200 °C), naturally abundant, economically feasible, and environmentally benign. The first materials which attracted much attention were simple metal oxides, especially transition metal oxides, mainly Mn, Fe and Ni oxides. During the past decade, many publications have investigated the oxygen mobility, catalytic selectivity and redox properties of pure transition metal oxides or their mixtures for hydrocarbon conversions [11, 16-19].

Recently the attention has turned to a new series of materials, complex metal oxides [11], despite the fact that some transition metal oxide systems like Fe₂O₃, Mn₃O₄, NiO and CuO show promising results [20]. The reason for this shift is due to the difficulties emerging with the common fluidized bed reactors. Transportation of the oxygen carrier material between the reactors is energy consuming. In addition, the hot gas produced after the air reactor will be transferred to the downstream gas turbine. It is therefore crucial that the gas carries no particles to avoid damaging the sensitive gas turbine [21]. Even if the problems emerging due to harsh reactive conditions (high temperature and pressure) are solved, addition of cyclone to remove the fines from the gas and recirculation of oxygen carrier materials decreases the efficiency. The challenges introduced by the fines, resulted from the inevitable particle attrition, highlights the disadvantages of the fluidized bed reactor [22]. The alternating fixed bed reactors [20] (schematically presented in figure 2) are suggested to solve this problem. In this approach the transport of the oxygen carrier material is removed by switching the fuel and air reactors periodically. Still fixed bed reactors with transition metal oxides as oxygen carrier beds cannot be used. The reason is the products made by reduction of the transition metal oxides, for example reduction of B₂O₃ to the new phase of BO. This phase transformation affects the mechanical properties of the bed drastically. In long terms, the transition metal oxide bed fails mechanically which at best possible scenario decreases the efficiency (if it does not clog the reactor completely).
Perovskite-type oxides with the general formula of $ABO_3$ ($A$ = alkali earth or lanthanide metal and $B$ = transition metal) have attracted a lot of interest as the possible oxygen carrier materials which can overcome the phase transformation difficulties of the binary transition metal oxides. The ideal perovskite structure has the cubic structure, $Pm\bar{3}m$, where the $B$-cations occupy the octahedral sites in the closed pack cubic $A_O_3$ framework. As an alternative, the perovskite structure can be seen as a cube with $A$ cation in the center and $B$ cations on $BO_6$ octahedrons on the edges [23]. The $A$ cation is coordinated with 12 oxygen atoms. The structure of an ideal perovskite-type oxide with the general formula of $ABO_3$ is presented in
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Most of the known perovskite-type compounds do not form the ideal cubic structure and deviations from ideal structures are resulted.

Figure 3. The ideal perovskite structure.

In addition to the required properties for the oxygen carrier material (such as reversible redox, thermal and mechanical stability, and oxygen mobility [24]), perovskites have some advantages over the transition metal oxides. The most important one is the higher oxygen nonstoichiometry many perovskite-type structures accept compared to the binary transition metal oxides. Since first row transition metals normally have more than one oxidation state, non-stoichiometry in the perovskite oxides with such metals on the B-site is common while keeping the same structure [25]. In addition, because of the much larger oxygen non-stoichiometry, the reduction does not happen at a constant oxygen partial pressure, rather gradually over a wide range of oxygen partial pressure. This implies that they can be used to oxidize the fuel with higher partial pressures of oxygen than the transition metal oxides and survive lower oxygen partial pressure conditions.
2 Background

The number of scientific reports on the technological aspects involving perovskites as oxygen carrier materials for chemical looping purposes is remarkable, yet less have focused on the fundamental properties such as the redox energetics. Still our knowledge with regards to the redox energetics of perovskites in general is considerable.

For a simple non-stoichiometric perovskite-type oxide, $ABO_{3-\delta}$, main contributions to the redox energetics are enthalpy of oxidation, non-configurational entropy of oxidation and the configurational entropy due to structural disorder. It is previously shown that a simple solid solution model can describe the main features of oxygen non-stoichiometry isothermal curves versus oxygen partial pressure, for a large number of perovskite-type oxides [26]. In this model enthalpy and non-configurational entropy of oxidation are composition-independent. Bakken et al. [26] have summarized the enthalpies of oxidation for some systems. As illustrated in figure 4, they have shown that the enthalpy of the redox reaction involving $B^{3+}$ and $B^{4+}$ of $La_{1-x}Ae_xBO_{3-\delta}$ ($Ae$ ≡ Ca, Sr and $B$ ≡ Cr, Mn, Fe, Co) varies linearly with the mole fraction of the alkaline earth dopant.

![Figure 4. Enthalpy of oxidation of $La_{1-x}Ae_xBO_{3-\delta}$ as a function of x [26]. Open symbols: non-stoichiometry partial pressure isotherms and the ideal model. Closed symbols: calorimetry.](image)
Background

The isothermal oxygen non-stoichiometry versus oxygen partial pressure curves for these systems are also presented in figure 5. Solid lines in this figure are obtained from the solid solution model. Deviations from the model are typically due to side-reactions like decomposition of the single phase compound as for example observed for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3-\delta}$.

\[ \text{La}_{1-x}\text{Ce}_x\text{BO}_{3-\delta} \]

Figure 5. $3-\delta$ in $\text{La}_{1-x}\text{Ce}_x\text{BO}_{3-\delta}$ as a function of oxygen partial pressure at 1273 K [26].

From the previous studies the main conclusions can be shortlisted as:

- As a rough approximation, the redox behavior is given by the stability of the two oxidation states of the $B$-atoms.
- For a given transition metal, the stability of different valent states depends largely on the structure of the compound. It is also largely related to the size of the cations in the binary and ternary oxides.
- The non-configurational entropy of oxidation does not vary significantly for different systems (unlike enthalpy of oxidation) and can be kept constant.

The ideal solution model can describe the main features of the redox energetics, yet the model fails to explain all details observed for a specific case. For example in the case of $\text{SrFeO}_{3-\delta}$ [27] and $\text{CaMnO}_{3-\delta}$ [28], studies show that correct representation of the configurational entropy is a challenge. The details of the observed redox behavior are influenced by both the nature of the electronic defect species on the $B$-sublattice and local order induced by vacancy-vacancy interactions on the oxygen sublattice.
For the industrial processes shown in figures 1 and 2, it is essential that the perovskite oxygen carrier has a sufficiently large oxygen capacity, as well as the oxygen non-stoichiometry in the oxygen partial pressure ranges suitable for the process. As shown above, the oxygen partial pressure range in which the perovskite is non-stoichiometric is defined by the redox energetics of the material. The redox thermochemistry is thus a fundamental property that should be modified. One possibility is the substitution of the cation occupying the $B$-sublattice, $AB_{1-x}B'_xO_3$. It is often speculated that as a result of this substitution, the complex perovskite shows the average redox properties of two constituent ones, $ABO_3$ and $AB'O_3$, which leads to the oxygen non-stoichiometry isothermal curves very similar to the ones presented in figure 5. Such a curve consists from a single range in which the composition changes; we will call this a “single-step” process. It is on the other hand tempting to suggest that the distinct enthalpies of oxidation of the two different cations on the $B$-sublattice may instead lead to a “two-step” redox process, with separate steps in the redox-isotherms for each cation. If this is the case, this can be an advantage in e.g. the case of hydrogen production by steam reforming in chemical looping hydrogen, see figure 1(c). The main goal of this project is to perform a systematic study on the redox chemistry of ternary perovskite-type oxides in order to gain further knowledge which can be used to modify materials for the aforementioned applications.

Many investigators in the past ten years have studied perovskite-type oxides ($ABO_{3-\delta}$ mostly $A$= La, Sr, Ca & $B$= Mn, Fe, Co) for fundamental properties like high temperature stability, oxygen non-stoichiometry, redox energetics, as well as the thermodynamic assessments of the $A$–$B$–$O$ system [13, 26-31]. So far, LaFeO$_{3-\delta}$ has attracted great attention for the oxidation of carbon monoxide and light hydrocarbons [13, 32-34]. It is e.g. reported that LaFeO$_3$ is up to 95% selective in oxidation of methane to CO and H$_2$ [13], even though the partial oxidation of hydrocarbons in the presence of LaFeO$_{3-\delta}$ decreases by more process cycles [13]. The $A$- and/or $B$-site substituted perovskites have also been the focus of study. Among all the studied compounds, La$_{1-x}$Sr$_x$Fe$_{1-x}$Co$_x$O$_{3-\delta}$ (LSFC) and La$_{1-x}$Sr$_x$Mn$_{1-x}$Co$_x$O$_{3-\delta}$ (LSMC) have been much investigated for their potential applications as electrodes in fuel cells [35-37], as oxygen membranes [38, 39], as catalytic membranes [40], as Fisher-Tropsh catalyst [41], and partial oxidation of light hydrocarbons [11, 41].
3 Objectives

A main objective of this project is to increase the level of knowledge of the redox energetics for perovskites. Here the focus is on the reduction of cations on the $B$-sublattice of the perovskite from 3+ to 2+, and the systems where redox energetic data are not available. This knowledge is of high importance in the selection of novel perovskite-type oxygen carrier materials for chemical looping processes with CO$_2$ capture.

Four main sub-goals are defined:

i) Construction and validation of necessary experimental facilities in order to obtain high precision oxygen non-stoichiometry isothermal curves.

There are several techniques available to measure the oxygen non-stoichiometry of oxides, among which we chose TGA for most of the systems because of the simplicity this technique provides. Coulometric titration method is one of the most accurate techniques (if not the most accurate) to measure the oxygen stoichiometry of oxides at high temperatures, but also one of the most complicated ones to operate. Another challenge remaining is that at this stage coulometric titration setups are not commercially available. We designed, constructed and validated a novel coulometric titration (CT) setup, which we later used to study one of our systems with. This setup provides both simplicity in reloading the sample and also the operation.

It is also important to determine the phase relations for the investigations of the redox mechanisms. At temperatures as high as 1273 K and reducing conditions, not many techniques can be used to investigate the structural stability. A quencher setup is therefore designed, constructed and used to study the phase stability of our systems at high temperatures and reducing conditions.

ii) Determination of the oxygen non-stoichiometry of novel $AB_{1-x}B'_xO_{3-\delta}$ materials over a wide range of oxygen partial pressure (typically $10^{-20}$ to 1 atm).

LaMn$_{1-x}$Co$_x$O$_{3-\delta}$ and LaFe$_{1-x}$Co$_x$O$_{3-\delta}$ systems are chosen for this study. Couples of manganese-cobalt and iron-cobalt are chosen as the occupants of the $B$-sublattice because of the different redox behavior of these elements. Although Co$^{3+}$ ions exists in some perovskite compounds,
still it tends to form the 2+ ion, whereas Mn and Fe are more stable at their 3+ states. These systems provide a suitable match to examine our hypothesis on the redox mechanism, whether the process is “single-step” or “two-step”.

iii) Determination of the enthalpies of oxidation both directly from the isothermal non-stoichiometry curves and through solid solution models. Redox thermodynamic quantities are deducted directly from the oxygen non-stoichiometry isothermal curves. Furthermore solid solution models [26] are applied to the experimentally obtained data to deduce the enthalpies of oxidation in order to fit the cation substitution on the B-sublattice [42].

iv) Providing a benchmark on the potential of density functional theory for determination of redox energetics through mapping the formation energetics of perovskite-type oxides. This will facilitate future calculations of the redox energetics. The experimental approach to study the energetics of complex oxides is both expensive and time consuming. Experimental screening of series of compounds in order to find the suitable candidates cannot fulfill the fast growing technological demand. DFT calculations might provide a cost effective tool to examine complex systems and/or obtain approximate thermodynamic properties. It is however difficult to start directly from the redox reactions. It is crucial first to validate the results of the DFT functionals versus experiment and examine the sources of error (for perovskite-type oxides). Formation energetics of perovskites-type oxides provides a good opportunity. The reason is that more than one reaction pathway (from elements, mono and sesquioxides) can be investigated. Furthermore a large volume of experimental data is available for comparison. Unlike transition metal binary oxides which are well-studied by DFT techniques, not many reports are available on the energetics of lanthanide perovskite-type compounds. Here, we thus studied the formation energetics of the lanthanide first row transition metal perovskite-type oxides as a benchmark.
4 Literature Survey

4.1 LaMnO$_{3-\delta}$ system

LaMnO$_{3+\delta}$ is among the most studied over-stoichiometric perovskite-type compounds. The room temperature oxidative non-stoichiometry of LaMnO$_{3+\delta}$ has been indirectly probed by powder neutron diffraction [25], and the over-stoichiometry suggests that oxygen excess is compensated by vacancies both on La and Mn-sites possibly with partial elimination of La$_2$O$_3$. The composition of over-stoichiometric lanthanum manganite at room temperature is reported therefore to be La$_{1-x}$Mn$_{1-y}$O$_3$ [25]. Although there are evidences suggesting that $x>y$, still simple Schottky equilibrium is the most widely used defect model to describe this phenomenon which leads to the new formula of La$_{1-x}$Mn$_{1-x}$O$_3$ and indicating that the concentration of vacancies on the lanthanum and manganese sites are equal [43-47]. The average valence of manganese in lanthanum manganite at room temperature air is 3.33±0.05 [46, 48-54]. This value decreases by increase of the temperature in air, but even at temperatures as high as 1173 K lanthanum manganite does not become stoichiometric and the average valence of manganese remains at 3.17±0.02 [45].

At temperatures as high as 1173 K, as chemical potential of oxygen in the gas phase decreases, the oxygen content of lanthanum manganite also decreases, and subsequently it goes into the oxygen deficiency region. The oxygen non-stoichiometry of lanthanum manganite in the oxygen deficient region is also investigated broadly by several authors. Suggested defect models are mostly based on the consistent assumption of the simultaneous presence of Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$ on manganese site along with vacancies on the oxygen site [45, 48, 55]. Firstly suggested by Kuo et al. [44], they applied this model on their own experimental non-stoichiometry results from thermogravimetric analysis in the temperature range of 1273 < T/K < 1473. Van Roosmalen and Cordfunke [56] subsequently introduced a cluster model which is based on the assumption of the interaction between oxygen vacancies and the two neighboring $B$ ions in the $ABO_{3-\delta}$ perovskite structure. The neutral cluster may be written as: $B^{2+} - v_O - B^{2+}$. Nowotny and Rekas [55] compared “random-defect model” and “cluster model” in the term of oxygen non-stoichiometry and electrical conductivity. The discrepancy between the experimental data and the cluster model in the electrical conductivity led them to admit the failure of the cluster model. A selection of the available oxygen non-stoichiometry
data for undoped lanthanum manganite at 1273 K versus oxygen partial pressure is presented in figure 6.

![Figure 6. Oxygen non-stoichiometry of LaMnO$_3$$_{3\delta}$ at 1273 K. [44, 45, 47, 48]](image)

### 4.2 LaCoO$_{3-\delta}$ system

Unlike LaMnO$_3$ not many authors have studied the undoped LaCoO$_3$ system. This lack of non-stoichiometric investigations can be described by the short range of oxygen partial pressure in which lanthanum cobaltite is thermodynamically stable. Decomposition oxygen partial pressure of LaMnO$_3$ at 1273 K is reported to be around $10^{15}$ atm whereas for LaCoO$_3$ this value is just around $10^{-5}$ atm [57]. The oxygen non-stoichiometry measurement of LaCoO$_{3-\delta}$ started as early as 1980 by Seppanen et al. report [58] on its dependency from oxygen partial pressures in the temperature range of $1178 < T/K < 1311$. Mizusaki et al. [59] studied the oxygen non-stoichiometry of lanthanum cobaltite by thermogravimetric analysis in the temperature range of $1073 < T/K < 1273$. They have also derived thermodynamic quantities, partial molar enthalpy of oxygen and partial molar entropy of oxygen, directly from the non-stoichiometry curves. Analyzes of the defect structure of LaCoO$_{3-\delta}$ through
thermodynamic modeling by Yang et al. [60] shows that the simple model consisting of compensation of oxygen vacancies by Co\(^{2+}\) fails to fit the experimental data. Similar to previously proposed models for lanthanum manganite they therefore suggested the simultaneous presence of Co\(^{2+}\), Co\(^{4+}\) ions and La, Co and oxygen vacancies. Zuev et al. [61] have measured the oxygen non-stoichiometry of LaCoO\(_{3-\delta}\) as a function of oxygen partial pressure and temperature by coulometric titration technique. They furthermore developed two defect models to describe the non-stoichiometric behavior of lanthanum cobaltite. In the first model oxygen vacancies are compensated by itinerant electronic species, whereas in the second model electrons and holes are localized on the cobalt sites. In another publication by the same authors [62], oxygen ionic conductivity of LaCoO\(_{3-\delta}\) is determined by means of polarization measurements. They have shown that defect clusters or associates containing oxygen vacancies do not form in the oxide, and that the predominant charge carriers in lanthanum cobaltites are electronic defects. A selection of the available oxygen non-stoichiometry data for undoped lanthanum cobaltite at 1273 K versus oxygen partial pressure is presented in figure 7.

![Figure 7. Oxygen non-stoichiometry of LaCoO\(_{3-\delta}\). [58, 61]](image-url)
4.3 \textbf{LaFeO}_{3-\delta} \textit{system}

The crystal structures of LaFeO$_3$ is orthorhombic (Pbnm) [63], and LaFeO$_3$ is stoichiometric at room temperature [34]. The oxygen non-stoichiometry of lanthanum ferrite is not addressed much in the literature, and the reason is that this material does not accept much of oxygen non-stoichiometry [64]. In the oxygen deficient region (LaFeO$_{3-\delta}$) the suggested defect model is based on the assumption of the simultaneous presence of Fe$^{2+}$, Fe$^{3+}$ and Fe$^{4+}$ along with oxygen vacancies [64], just the same as LaMnO$_{3-\delta}$ and LaCoO$_{3-\delta}$. Lanthanum Ferrite is thermodynamically stable over a wide range of oxygen chemical potential. The decomposition oxygen partial pressure of LaFeO$_{3-\delta}$ at 1273 K is around $10^{-16}$ atm [57].

4.4 \textbf{LaMn}_{1-x}\text{Co}_x\text{O}_{3-\delta} \textit{systems}

Sikora \textit{et al.} [65] have studied the valence states of Mn and Co in LaMn$_{1-x}$Co$_x$O$_{3-\delta}$ (0<x<1) by XANES. They have suggested that Co$^{2+}$/Co$^{3+}$ and Mn$^{3+}$/Mn$^{4+}$ mixtures are present in the whole range of solid solution. Oxygen non-stoichiometry dependence of LaMn$_{1-x}$Co$_x$O$_{3-\delta}$ (0<x<1) from oxygen partial pressure has not been addressed in many articles. In a recent publication Bakken \textit{et al.} [42] have reported the oxygen non-stoichiometry of LaMn$_{0.75}$Co$_{0.25}$O$_{3-\delta}$ and LaMn$_{0.25}$Co$_{0.75}$O$_{3-\delta}$ versus oxygen partial pressure at 1273 K obtained by TGA. In the same article the thermodynamic quantities of these materials is investigated. Their extracted values for the enthalpy of oxidation from the solid solution model are in good agreement with the one obtained directly by TG-DSC.

The crystal structure of LaMnO$_3$ and LaCoO$_3$ have been studied extensively and are reported to be orthorhombic and rhombohedral, respectively [66]. LaMnO$_3$ and LaCoO$_3$ are not completely miscible and the stability region is not well established. As shown in figure 8, the LaMnO$_3$-LaCoO$_3$ binary phase diagram in air reported by Jonker [67] shows partial solid solubility at 1273 K. At this temperature LaMn$_{1-x}$Co$_x$O$_3$ have orthorhombic structure for 0<x<0.45, rhombohedral structure for 0.92<x<1, and a two phase region in between [67]. Yet different phase stability regions are reported in different articles. The LaMnO$_3$–LaCoO$_3$ phase diagram at 1373 K shows the two phase region of orthorhombic and rhombohedral for LaMn$_{1-x}$Co$_x$O$_3$ in the range of 0.3<x<0.5 [57]. Two phase region of mixture of orthorhombic and
rhombohedral phases have been reported for the middle ranges of \( x \) even at temperatures as high as 1573 K [68].

![Figure 8. Phase diagram of \( \text{LaMnO}_3-\text{LaCoO}_3 \) system. Figure from [67].](image)

### 4.5 \( \text{LaFe}_{1-x}\text{Co}_x\text{O}_{3-\delta} \) systems

The solubility study of \( \text{LaFeO}_3 \) and \( \text{LaCoO}_3 \) is not addressed in many publications. Yet the few available reports mostly confirm the partial miscibility. The stability region however is not well established. The room temperature two phase region is reported and the range of this two phase region is dependent on synthesis conditions [69]. Troyanchuk \textit{et al.} [69] have reported the two phase region for the range 0.3<\( x \)<0.85, whereas Karpinsky \textit{et al.} [70] report the two phase region in the range 0.4<\( x \)<0.5. Some studies appear to be less accurate and report two single phase regions at room temperature without a two-phase region. For instance both Narasimhan \textit{et al.} [71] and Jia \textit{et al.} [72] report that the system is orthorhombic for \( x \)<0.5.
and rhombohedral for $x>0.5$. The pseudo-ternary phase diagram of $\text{La}_2\text{O}_3 - \text{CoO} - \text{Fe}_2\text{O}_3$ system at 1373 K in air reported by Proskurina et al. [73] shows a partial solubility of $\text{LaFeO}_3$ and $\text{LaCoO}_3$ and a two phase region. At this temperature $\text{LaFe}_{1-x}\text{Co}_x\text{O}_3$ have orthorhombic structure for $0<x<0.225$, rhombohedral structure for $0.75<x<1$, and a two phase region in between [73]. Strangely enough another article by the same research group reports a different two phase region of $0.25<x<0.5$ at the same temperature (figure 9) [57]. This again confirms the fact that the stability region is not well established.

Although quite a few reports are available on this system’s redox investigations, the oxygen non-stoichiometry isotherms are not studied much. Tai et al. [74] have studied the oxygen non-stoichiometry of $\text{LaFe}_{0.8}\text{Co}_{0.2}\text{O}_3$ at 1473 K in a wide range of oxygen partial pressure. For the compounds containing more fraction of cobalt, Kiselev et al. [75] have reported the oxygen non-stoichiometry curve for the $\text{LaFe}_{0.1}\text{Co}_{0.9}\text{O}_{3-\delta}$ composition at 1223 – 1273 K over a narrow range of oxygen partial pressure ($10^{-3}$ – 0.21 atm). In a recent publication, Bakken et al. [42] have studied the oxygen non-stoichiometry of $\text{LaFe}_{0.75}\text{Co}_{0.25}\text{O}_{3-\delta}$ and $\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_{3-\delta}$ versus oxygen partial pressure at 1273 K. They have also obtained the redox enthalpies, directly from TG-DSC and indirectly via thermodynamic modeling.

![Figure 9. Ternary phase diagram of La–Fe–O system at 1373 K. (a) from [73] (b) from [57].](image-url)
4.6 Solid Solution Thermodynamic Model

Several techniques can be used to study the redox behavior of solid oxides, among which presentation of the composition versus oxygen partial pressure at constant temperatures has become a standard. The enthalpy of oxidation for the redox reaction can be directly obtained from such curves, if the data for more than one temperature is available. Extraction of the partial molar thermodynamic quantities is possible by relating the variation of the equilibrium oxygen partial pressure with composition. The change in chemical potential of oxygen relatively to its standard state ($p^\circ O_2 = 1$ atm) can be calculated by

$$\mu_0 - \mu_0^\circ = \frac{1}{2} (\mu_{O_2(g)}^\circ - \mu_{O_2(g)}^\circ) = \frac{1}{2} R \ln(p_{O_2}/p^\circ O_2) \quad (5)$$

$$\mu_0 - \mu_0^\circ = (\text{H}_O - \text{H}_O^\circ) - T(S_O - S_O^\circ) \quad (6)$$

At constant composition (for a specific value of $\delta$), the change in the partial molar enthalpy and the partial molar entropy of oxygen can be calculated using

$$\text{H}_O - \text{H}_O^\circ = \frac{\partial(\mu_0 - \mu_0^\circ)/T}{\partial(1/T)} \quad (7)$$

$$S_O - S_O^\circ = -\frac{\partial(\mu_0 - \mu_0^\circ)}{\partial T} \quad (8)$$

Calorimetry also provides an alternative, even though it is not necessarily possible to link the obtained enthalpy of oxidation with composition and oxygen partial pressure. Another alternative is the use of thermodynamic models. Here we focus on the solid solution thermodynamic models [26]. In this model the Gibbs energy of a non-stoichiometric compound is approximated as a solution of two stoichiometric end-compounds. For a non-stoichiometric perovskite $ABO_{3-\delta}$ (where $A=$ alkaline-earth or rare-earth metal and $B=$ transition metal) the end-phases are $ABO_3$ and $ABO_{2.5}$ [26]. Although $ABO_{2.5}$ is disordered, but the configurational entropy is not included in $\Delta G_{T,nc}^\circ (ABO_{2.5})$, instead in a separate term expresses by $\delta = 0.5$ in the configurational entropy. The configurational entropy of the mixture is dependent on different defect species, and defines the shape of the non-stoichiometry curve. On the other hand, the redox enthalpy is independent from the defect distributions and defines the oxygen partial pressure at which the oxygen nonstoichiometry curve begins to deviate.
from the fully oxidized state of $3-\delta=3$. The non-configurational contribution to the Gibbs energy of $ABO_{3-\delta}$ ($0<\delta<0.5$) (related to the redox process) can be formulated as

$$4ABO_{2.5} \text{(perovskite)} + O_2(g) = 4ABO_3 \text{(perovskite)} \quad (9)$$

$$\Delta G^\circ_{\text{oxidation}} = 4\Delta_f G^\circ_T(ABO_3) - 4\Delta_f G^\circ_{T,\text{nc}}(ABO_{2.5}) - \mu^\circ(O_2) = \Delta_{ox} H^\circ - T\Delta_{ox} S^\circ \quad (10)$$

The main assumption here is that the standard Gibbs energy of the end-compounds $\Delta_f G^\circ_T(ABO_3)$ and $\Delta_f G^\circ_{T,\text{nc}}(ABO_{2.5})$, does not include configurational entropy. All the defects are assumed to be fully charged, and the effect of intrinsic disorder (whether ionic or electronic) is disregarded. The second reaction is the mixing of the produced end-compounds of $ABO_3$ and $ABO_{2.5}$ to form the solid solution of $ABO_{3-\delta}$ ($0<\delta<0.5$).

$$\Delta_f G^\circ_T(ABO_{3-\delta}) = (1 - 2\delta)\Delta_f G^\circ_T(ABO_3) + 2\delta\Delta_f G^\circ_{T,\text{nc}}(ABO_{2.5}) - T\Delta S_{m,c} \quad (11)$$

where $\Delta S_{m,c}$ is the configurational entropy of mixing. The oxygen partial pressure using this model is given by

$$\log(pO_2) = \frac{1}{RT\ln(10)}\{\Delta G^\circ_{\text{oxidation}}\} - \frac{2S_{O,c}}{R\ln(10)} \quad (12)$$

The mixing reaction does not include a non-configurational entropy, rather a mixing Gibbs energy consisting of enthalpy of mixing and the configurational contribution. Based on the assumption of the ideal behavior for the resulted solution, the enthalpy of mixing disappears. The approximations for the configurational entropy is that the configurational entropy consists of contributions due to random distribution of oxygen atoms and oxygen vacancies on the oxygen sublattice and $B^{2+}$ and $B^{3+}$ on the $B$-sublattice according to equation (13).

$$S_{O,c} = -R\ln(10)[2\log(1 - 2\delta) - 2\log(2\delta) - \log\left(\frac{\delta}{3-\delta}\right)] \quad (13)$$

Where the terms $-\log\left(\frac{\delta}{3-\delta}\right)$ and $2\log(1 - 2\delta) - 2\log(2\delta)$, correspond to contributions from the oxygen- and $B$-sublattice, respectively.
5 Experimental Approach

5.1 Cerimetric Titration

The oxygen content of the samples prior to changes in the oxygen activity (using TG or CT, see section 5.3 and 5.4) was measured by cerimetric titration in an inert gas at ambient temperature (as described in [76]). The samples were dissolved in HCl solutions (3M) containing an excess amount of ammonium iron(II) sulfate (Mohr salt). Fe$^{2+}$ reduces the $B^{3+}$ and $B^{4+}$ ($B=\text{Mn, Co}$) in the samples to $B^{2+}$. Fe$^{2+}$ and Fe$^{3+}$ remain unreacted while Fe$^{4+}$ is reduced to Fe$^{3+}$. Ferroin, [Fe($o$-phen)$_3$]SO$_4$, was used as indicator and phosphoric acid to sustain the color of the indicator. The unreacted Fe$^{2+}$ and Fe$^{2+}$ ions from the sample were subsequently titrated by Ce$^{4+}$.

5.2 Quencher

A quencher setup was built to characterize the phase stability at high temperature and reducing conditions. The quencher allowed the use of controlled atmospheres as illustrated schematically in figure 10. The tablets of different samples were quenched from 1273 K at discrete oxygen potentials using an in-house gas mixing system feeding O$_2$(g), N$_2$(g), H$_2$(g), and CO$_2$(g). Bronkhorst mass flow controllers with accuracy 0.01 ml min$^{-1}$ were used to supply the feed gas. A CarboProbeHT oxygen sensor (supplied by Econox) was used to monitor the oxygen partial pressure in-situ. The temperature of the oxygen sensor and the sample was measured by an implanted S-type thermocouple. The tablets were quenched by dropping into a liquid nitrogen cooled copper cup at reducing atmospheres. The quenched pellets were subsequently ground and analyzed by X-ray diffraction. High purity silica (provided by Merck) was used as internal standard.
5.3 Thermogravimetric Analysis

TGA was firstly used to determine the oxygen content of the samples in air at 1223, 1273, and 1323 K, from the room temperature values obtained by cerimetry.

At the next stage the oxygen non-stoichiometry of selected compounds were measured in varying oxygen potentials at three isotherms of 1223, 1273 and 1323 K. In the case of LaMn$_{0.25}$Co$_{0.75}$O$_{3-\delta}$ the oxygen non-stoichiometry was studied using a SETRAM 92-16.18 equipment, and for the LaFe$_{1-x}$Co$_{x}$O$_{3-\delta}$ ($x=0.25$ and 0.75) the oxygen non-stoichiometries were measured by a SETRAM Setsys Evolution equipment. CarboProbeHT oxygen sensors were implanted in both of these devices and were used to monitor the oxygen partial pressure in-situ. The temperature at the oxygen sensor firstly was calibrated for different temperatures using a second thermocouple. The oxygen non-stoichiometry was determined at discrete oxygen potentials by the same in-house gas mixing system as used for the quenching experiments. O$_2$(g) and N$_2$(g) mixtures were fed for the oxygen partial pressure range 0 $<-\log$(pO$_2$/atm) $<5$. For lower partial pressures, a buffer based on a H$_2$(g)/CO$_2$(g) mixture
diluted with N₂ was used in order to reach more reducing atmospheres, \(5 < -\log(p_{O_2}/\text{atm}) < 20\). For all temperatures and oxygen partial pressures the total gas flow was kept at 100 ml min\(^{-1}\). Before each isothermal experiment, the alumina crucibles were calcined at \(>280\) °C in air for 1 hour to remove any adsorbed water before new samples were introduced. Blank experiments with empty crucibles were conducted at all temperatures and gas mixtures in order to determine the correction for the effect of gas buoyancy.

### 5.4 Coulometric Titration

Coulometric titration (CT) is one of the most accurate techniques to measure the oxygen non-stoichiometry of oxides [77]. In the coulometric titration technique, oxygen chemical potential of a confined gas chamber which is in thermodynamic equilibrium with the sample is measured. By counting the number of oxygen molecules which are taken out of the chamber, and monitoring the oxygen partial pressure of the gas, changes in the oxygen non-stoichiometry of the sample can be obtained. We therefore designed, constructed and validated a new coulometric titration setup. The oxygen non-stoichiometry of \(\text{LaMn}_{0.75}\text{Co}_{0.25}\text{O}_{3-\delta}\) was studied using this setup at three temperatures of 1223, 1273, and 1323 K. In the following sections our coulometric titration setup and its accessories are presented. General aspects of coulometric titration techniques are described elsewhere [28, 77, 78].

The primary parts of the present setup, as shown schematically in figure 11, include two yttria-stabilized zirconia (YSZ) tubes (g), an alumina cylinder (e), and a crucible (h). The closed tip of the YSZ tubes (both inside and outside, with approximate area of 1 cm\(^2\)) are brushed with platinum ink, sintered to 0.5mm platinum wires and function as solid electrolytes for oxygen ions. The setup is positioned in a vertical tube furnace in a way that crucible (h), thermocouple (j) and solid electrolytes (i and l) are set in the hot zone of the furnace whereas all the electronic connections and sealing parts in the upper part of the setup remain cooled outside of the furnace. Water cooling system keeps these parts cold during the experiment. The sealing consists of a blind and a female flange coupling (c) with copper gasket (d) as the sealant. Two hollow alumina tubes (k) carry the platinum wires into the hot zone of the apparatus. Crucible is hung up from two solid alumina rods (f) via platinum made clips. Decreasing the empty volume of the cell is beneficial by decreasing the oxygen stored in the cell’s gas. Alumina solid rods (ØD= 8 mm) were used for this purpose to occupy the
Experimental Approach

free volume of the cell as much as possible. An S-type thermocouple (j) is implanted in the cell, measuring the temperature of the area in which sample and solid electrolytes are located, and giving feedbacks to the furnace power supply. The gas inlet and outlet Swagelok valves (b) are used to flush the entire setup with desired gases (e.g. air, O₂, or N₂). Brass-made gas chambers (a) placed on the cold end of the YSZ tubes are used to flush the electrolytes with the reference gases.

The solid electrolytes, thermocouple, and the sample (in the crucible) are within the 40 mm hot zone of the furnace in which the temperature gradient is less than 1 K. Total atmospheric pressure was monitored by an ActiveLine (Pfeiffer vacuum). The electromotive force across the sensor is measured with a National Instruments board (NI 9219). Voltage and current of the pumping YSZ tube were supplied by a National Instruments board (NI9265) with errors specified at less than 10⁻⁶ A. Sensor’s emf and pump’s voltage and current are measured and logged every 5 seconds by an in-house LabView program. At highest current density of 800 mA cm⁻² were used which is safely lower than the values reported as the maximum current densities [79].
Figure 11. Schematic view of the coulometric titration setup and its components.

(a) reference gas chambers
(b) flush valves
(c) flange coupling
(d) gasket
(e) alumina cylinder
(f) alumina rods
(g) YSZ tubes
(h) crucible
(i) oxygen pump
(j) thermocouple
(k) Pt-wire carrier
(l) oxygen sensor
6 DFT Calculations

Understanding the materials properties at the atomic level is the key to controlling them. Density functional theory is an approach towards the basic and fundamental rules governing the behavior of atoms. Quantum behavior of atoms is explained by Schrödinger's equation [80]. Let's focus on the easiest form of the Schrödinger's equation, the time independent Schrödinger equation for a set of atoms in a molecule or a crystal involving interactions between multiple electrons and multiple nuclei. Schrödinger's equation defines the relation between "interactions of electrons and nuclei" and the "electronic wave function" as shown in equation (14) [80].

\[
\left[ \frac{\hbar^2}{2m} \sum_i^N \nabla_i^2 + \sum_i^N V(r_i) + \sum_{i<j}^N U(r_i, r_j) \right] \psi = E \psi
\] (14)

The first part of the Schrödinger's equation consists of a summation of three terms defining the total energy of the electrons in the system:

1) Kinetic energy of each electron.
2) The energy due to the interaction between each electron and a collection of nuclei.
3) The interaction between different electrons.

This equation is a many-body problem, meaning that the individual wave function for each electron cannot be found without considering the wave functions of all other associated electrons. This poses difficulties in solving this problem and finding the true wave functions.

In terms of observation and experiment, it is not possible to observe the wave function directly for any specific set of coordinates. It is only in principle possible to define the probability of the number of electrons at a specific set of coordinates. In addition, experimentally we cannot assign labels to electrons to define which electrons are electron 1, electron 2, etc. This implies that the density of electrons at a specific position, n(r), which is only a function of three coordinates, is physically observable by satisfying the Schrödinger's equation. In the terms of single electron wave functions, density of electrons can be written as

\[
n(r) = 2 \sum_i \psi_i^*(r) \psi_i(r)
\] (15)
Density functional theory relies on two mathematical theories formulated by Kohn and Hohenberg [81]. These theories offer very important information about the relation between ground-state energy from Schrödinger's equation and electron density. According to the first theory, there is one-to-one mapping between the ground-state wave function and the ground-state electron density; i.e. "the ground-state energy from the Schrödinger's equation is a unique functional of the electron density". In other words, all the properties, among which the ground state energy and the ground state wave function, can be determined by the ground-state electron density. The theory doesn't say what this functional is; it just proves the existence of such unique functional. The second theory however describes an important property of this functional. According to the second theory, "the electron density that minimizes the overall functional is the true electron density corresponding to the full solution of the Schrödinger's equation". Still the problem in solving the Schrödinger's equation due to the fact that this is a many-body problem remains untouched. This challenge was eased by Kohn and Sham [82]. They showed that the complication of finding the correct electron density can be reduced by introducing an effective potential. This leads to solving a set of equations, benefitting of having only a single electron involved in each equation, in other words, the solution of Kohn-Sham equations are single-electron wave functions which is only dependent on coordinates. The Kohn-Sham equations have the following form

\[
\left[ \frac{\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{XC}(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r)
\]  

(16)

The effective potential defined by Kohn-Sham approach consists of three potentials:

1) A potential defining the interaction between the electron in the corresponding Kohn-Sham equation and the collection of atomic nuclei.

2) A potential describing the interaction between an electron in the corresponding Kohn-Sham equation and the total electron density which is created by all the electrons. This potential is also known as Hartree potential.

3) The exchange-correlation potential.

The electrons which are focused in every Kohn-Sham equation are part of the total electron density. This means that the interaction of the electron on itself, also known as self-interaction, is also included in the Hartree potential. The first two potentials are known. If the exchange-correlation potential is also known, the ground state can be found by the algorithm illustrated in figure 12.
There is only one difficulty in this brilliant self-consistent approach, the exchange-correlation function. The existence of the true exchange-correlation functional is guaranteed by the Kohn-Hohenberg theory, but the true functional is not known. There is however a simple case that the functional can be derived exactly, the case that the electron density does not alter in local space, i.e. constant. This case doesn't seem to be realistic for any material. In fact this is the difference in the electron density that defines the chemical bonds, but still this is a way to solve the Kohn-Sham set of equations. This approximation is called Local density approximation (LDA), since in this approximation only the local density is used to obtain an approximation for exchange-correlation functional. It should be noted that LDA helps to determine the Kohn-Sham equations completely, but the results are not true solutions to the Schrödinger's equation since it just provides an approximation to the exchange-correlation not the true exchange-correlation functional. LDA is not the only functional used to tackle this problem. Generalized gradient approximation (GGA) is the most known functional after LDA.

Figure 12. Algorithm to determine the ground state in DFT.
In GGA information about the local gradient of the electron density is also included in the functional. There are several ways to utilize this information in the functional, and therefore GGA is a class of wide range of functionals [83]. There are however two functionals which are used most, especially for the case of crystal solids, Perdew-Wang functional (PW91) [84] and Perdew-Burke-Ernzerhof functional (PBE) [85, 86].

An important question to be answered is: what are the biggest sources of uncertainty when using GGA in general and in the case of redox reactions in particular? Non-exact treatment of the exchange term and the self-interaction problem are the biggest challenges within GGA [87, 88]. Self-interaction causes the unpaired electrons to be delocalized over several atoms in order to decrease the Coulomb repulsion [89]. This is a well-known problem especially for narrow band oxides. For example GGA describes a magnetic insulator like NiO as a metal [90]. The ideas to circumvent these errors are based on including the exact exchange from the Hartree-Fock (HF) approach since the self-interaction errors are canceled exactly in the HF calculation. One approach is to employ a HF-like approach for the localized states. This is the idea behind a category of methods called DFT+U. In this method a numerical parameter, $U - J$, is introduced to correct for the electron self-interaction. $U$ and $J$ in this approach are parameters for describing the aspects of the self-interaction. This numerical parameter is de facto empirical and the approach to determine its value is to take a known property of a relevant material, and check what $U - J$ value results in the closest agreement for this property compared to experiment. Another approach to tackle this challenge is by including some portion of HF exchange in the exchange functional which is implemented in the hybrid functionals.

Another source of uncertainty is introduced by the total energy of the $O_2$ molecule. Dissociation energy of the $O_2$ molecule obtained by GGA is 6.08 (PW91) and 6.10 (PBE) whereas with hybrid functionals (B3LYP) this value is reported to be 5.23 eV [91]. The comparison of the dissociation energy obtained experimentally 5.12 eV [92], and from these methods shows that hybrid functionals succeed in describing the O–O bond. On the other hand, GGA results in the value of approximately 1 eV higher.
6.1 Calculational approach

Unlike transition metal binary oxides, which are well-studied by DFT techniques (e.g. [93-95]), in terms of energetics, not many reports are available for DFT calculations on LaBO$_3$ ($B=$ transition metal) system. The few number of research articles on LaBO$_3$ system can be described by the challenges emerging when it comes to DFT calculation of complex systems. For a typical LaBO$_3$, the most obvious challenge is due to the complex magnetic structure of these compounds. Some authors have simply ignored the complex magnetic structures, assuming the nonmagnetic behavior [96]. On the other hand, trying to represent the complex structures requires big supercells, which makes the calculations time consuming and expensive.

The enthalpies of formation of LaBO$_3$ ($B=$ Sc – Cu) as well as the reaction enthalpies corresponding to the formation of the ternary oxides from the monoxides and sesquioxides are calculated according to equations (17), (18), and (19).

$$
\text{La(c) + } B(c) + 1.5O_2(g) = \text{LaBO}_3(c) \\
0.5 \text{La}_2O_3(c) + 0.5B_2O_3(c) = \text{LaBO}_3(c) \\
0.5 \text{La}_2O_3(c) + BO(c) + 0.25O_2(g) = \text{LaBO}_3(c)
$$

The total energies of all species are calculated within the generalized gradient approximation (GGA) to DFT with Perdew-Burke-Ernzehof (PBE) functionals [85, 86]. Projector augmented wave (PAW) [97, 98] pseudopotentials implemented in Vienna Ab-Initio simulation package (VASP 5.2.11) [99] was used. In order to reach converged energies within 5 meV per formula unit, energy cutoff of 550 eV and appropriate k-points were chosen. Atom coordinates, unit cell dimensions, and cell volume were fully relaxed for each structure to obtain ionic forces smaller than 0.01 eV. Gaussian smearing was used with a smearing parameter of 0.2 and 0.05 eV for metallic and insulating compounds, respectively.

In all cases (calculation for metals, metal oxides and lanthanide perovskites), experimentally reported structures were used as starting point and atom coordinates, unit cell dimensions, and cell volume were fully relaxed. For the compounds which the experimental structure is not available, different structures were checked and the most stable one was chosen. For the magnetic perovskite compounds LaBO$_3$ ($B =$ Ti, V, Cr, Mn, and Fe), calculations were
performed in five different magnetic structures; nonmagnetic, ferromagnetic and antiferromagnetic type A, C, and G as described in [100], and in all cases, the magnetic moments are allowed to relax. In order to produce the three different antiferromagnetic structures, supercells were generated by constructing $2 \times 2 \times 1$ conventional unit cell. The total energy of the oxygen molecule is calculated by the relaxation of a triplet $O_2$ molecule in a cubic box with edge length of 1000 pm, starting with the experimental O–O distance of 121 pm [92].
7 Summary of the results and conclusions

The biggest advantage of the novel coulometric titration (CT) setup constructed for this study (presented in section 5.4) is simplicity in operation. In the present setup, oxygen leakage is the biggest source of error when measuring the oxygen non-stoichiometry. The models employed to describe the source of the oxygen leakage suggest that the electrochemical leakage of oxygen through the YSZ tubes is the dominant source of leakage. This can be explained by the fact that a large part of the YSZ tubes in this setup are exposed to reference gas with high oxygen partial pressure. Decreasing the difference in chemical potential of oxygen between inside and outside of the cell is the applied measure to decrease the oxygen leakage. Flushing the pumping YSZ solid electrolyte with N₂ shows a reasonable improvement in term of oxygen leakage. The cell is eventually validated by measuring the oxygen non-stoichiometry of SrFeO₃₋δ at 1273 K in the oxygen partial pressure range of 0.6 < −\( \log(p_{O_2}/\text{atm}) \) < 12. The resulting values are plotted in figure 13 and show a good agreement with the literature.

![Figure 13. Oxygen non-stoichiometry of SrFeO₃₋δ (solid symbols: CT [27, 28, 101], open symbols: TGA [102-104]).](image)

Figure 13. Oxygen non-stoichiometry of \( \text{SrFeO}_3-\delta \) (solid symbols: CT [27, 28, 101], open symbols: TGA [102-104]).
Summary of the results and conclusions

This CT setup was subsequently used to study the oxygen non-stoichiometry of the LaMn$_{1-x}$Co$_x$O$_{3-\delta}$ system at three temperatures of 1223, 1273, and 1373 K. For the LaMn$_{1-x}$Co$_x$O$_{3-\delta}$ system it is found that the observed oxygen non-stoichiometry curve is due to the simultaneous reduction of both manganese and cobalt on the $B$-sublattice. Redox energetics of this system is directly extracted from the experiment and indirectly through the solid solution thermodynamic models. The values for enthalpy of oxidation show a linear dependence by $x$ (portion of Co), which approves the simultaneous reduction of manganese and cobalt. The oxygen non-stoichiometry and redox energetics of the second studied system, LaFe$_{1-x}$Co$_x$O$_{3-\delta}$, just similar to the previous system, show no indication of the sequential reduction of the cations occupying the $B$-sublattice. The absolute value of the enthalpy of oxidation increases as the iron portion on the $B$-sublattice increases, which approves this finding. The enthalpy of oxidation values for LaMn$_{1-x}$Co$_x$O$_{3-\delta}$ and LaFe$_{1-x}$Co$_x$O$_{3-\delta}$ systems are plotted in figure 14.

![Figure 14. Enthalpy of oxidation for LaB$_{1-x}$B'$\delta$O$_3$ versus x. Values for LaMnO$_{3-\delta}$, LaCoO$_{3-\delta}$ and LaFeO$_{3-\delta}$ are deduced from the previous experimental reports; LaMnO$_{3-\delta}$ [45, 48], LaCoO$_{3-\delta}$ [61] and LaFeO$_{3-\delta}$ [64].](image)

The experimental approaches to the investigation of the redox energetics proved to be difficult, time-consuming and expensive. DFT calculations might provide a cost effective tool to examine complex systems and obtain an approximation for the thermodynamic properties. It is however necessary to examine the sources of error and the accuracy of the calculations. A benchmark study was conducted on the formation energetics of lanthanide first row transition metal perovskite-type oxides. Here we studied the influence of the structural relaxation,
magnetic configuration and the sources of error by GGA functionals. The benchmark shows that although fundamental errors in GGA affect the energetics, still with addition of *ad hoc* corrections, it is possible to obtain values which are in agreement to the experiment to a good extent. The comparison of the calculated and experimental values for the formation enthalpies of LaBO$_3$ perovskite-type compounds plotted in figure 15 is an example. Unlike transition metal oxides, here for lanthanide perovskite-type oxides the errors due to over-delocalization of the 3$d$ states are of much smaller magnitude. Therefore formation enthalpies calculated from DFT are in a very good agreement with the experiment.

![Figure 15. Calculated enthalpy of formation for LaBO$_3$ versus experiment.](image)

The experimental data is extracted from [105-113].

Figure 16 shows the energy scatter of different magnetic structures for the LaBO$_3$ compounds. The one with the lowest energy for each compound is set as zero. As shown in figure 16, the difference between the energy of different magnetic configurations, is not very large. The difference remains within 15 kJ/(mol B) for all the magnetic compounds. Hence, as long as the calculations are spin polarized (with any magnetic structure) and performed with the relaxation of the experimental crystal structure, the formation enthalpies are reproduced within 15 kJ/(mol B). In other words, any presumably small magnetic unit cell gives reasonable total energies. This is particularly interesting since the uncertainty of the
experimental data mostly introduces higher magnitudes of error. Another outcome of the figure 16 is the effect of the spin-polarized calculations versus the non-magnetic ones. As the magnetic moment of $B$-cation increases, the deviation of the energy between non-magnetic calculations and the ground state increases significantly. In the cases of $B=$Cr, Mn, and Fe, it becomes non-negligibly higher than the ground state by 101.6, 113.6 and 69.3 kJ/(mol $B$), respectively.

![Figure 16. Energy difference between different spin configurations for LaBO$_3$ ($B$=Ti, V, Cr, Mn and Fe).](image)

In order to obtain the redox energetics, the same calculations as performed for LaBO$_3$ should be done for the reduced phases, LaBO$_{2.5}$, which is much more challenging. The calculations for LaBO$_{2.5}$ show that in comparison with LaBO$_3$, a bigger fraction of total energy of the reduced phases is attributed to the magnetic configuration. This implies that a simple magnetic structure (e.g. ferromagnetic) does not produce the formation enthalpies with the same accuracy as for LaBO$_3$. Configuration of oxygen vacancies on the oxygen sublattice contributes even more than spin ordering to the total energy. Huge number of possible states caused by simultaneous presence of both oxygen vacancy and spin configurations requires computational algorithms based on statistical methods.
8 References

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