ABSTRACT

AIR SEPARATION AND OXYGEN STORAGE PROPERTIES OF HEXAGONAL RARE-EARTH MANGANITES

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This dissertation presents evaluation results of hexagonal \(Y_{1-x}R_x\text{MnO}_{3+\delta}\) \((R = \text{Er, Y, Dy, Pr, La, Tb and Ho})\) rare-earth manganites for prospective air-separation applications. In these materials, oxygen content is sensitively dependent on the surrounding conditions of temperature and/or oxygen partial pressure, and therefore they exhibit the ability to selectively absorb, store, and release significant amounts of separated oxygen from air. This study presents a full characterization of their thermogravimetric characteristics and air-separation capabilities. With the expected potential impact of oxygen content on the physical properties of these materials, the scope of this work is expanded to explore other relevant properties such as magnetic, transport, and dilatometric characteristics.

Single-phase polycrystalline samples of these materials were achieved in the hexagonal \(\text{P}_6\text{3}cm\) phase through solid state reaction at elevated temperatures. Further annealings under reducing conditions were required for samples with large rare-earth cations in order to suppress the competing perovskite structure and form in the anticipated hexagonal phase.
Thermogravimetric measurements in oxygen atmospheres demonstrated that samples with the larger $R$ ionic radii show rapid and reversible incorporation of significant amounts of excess oxygen ($0.41 > \delta > 0$) at an unusual low temperature range ~190-325 °C. The reversible oxygen storage characteristics of HoMnO$_{3+\delta}$ and related materials shown by the fast incorporation and release of interstitial oxygen at easily accessible elevated temperatures of ~300 °C demonstrate the feasibility and potential for low-cost thermal swing adsorption TSA process for oxygen separation and enrichment from air. Neutron and X-ray powder diffraction measurements confirmed the presence of three line compounds $RMnO_{3+\delta}$, the oxygen stoichiometric P6$_3$cm ($\delta = 0$ for all $R$), the intermediate oxygen content superstructure phase R3c ($\delta \sim 0.28$ for $R = \text{Ho, Dy, Dy}_{0.5}\text{Y}_{0.5}$, and $\text{Dy}_{0.3}\text{Y}_{0.7}$) constructed by tripling the c-axis of the original unit cell, and the highly oxygen-loaded Pca2$_1$ phase ($\delta = 0.40$ for all $R$). In-situ synchrotron diffraction showed thermal stability of these single phases and their coexistence ranges, demonstrating that the stability of the $\delta = 0.28$ phase increases with the ionic size of the $R$ ion. The magnetic properties of the multiferroic $RMnO_{3+\delta}$ were found to be dependent on the oxygen content of these compounds. Below the magnetic ordering temperatures, samples with higher oxygen content showed slightly decreased magnetization relative to the less oxygenated ones. Dilatometry measurements suggest that the thermal expansion coefficient TEC of the oxygen-loaded Pca2$_1$ phase is slightly larger than that of the stoichiometric P6$_3$cm phase. The calculated Pca2$_1$ to P6$_3$cm chemical expansion coefficient 14.38 x 10$^{-3}$ [mole-O]$^{-1}$ was found to be within the expected range for the hexagonal $Y_{0.97}\text{La}_{0.03}MnO_{3+\delta}$ sample.
AIR SEPARATION AND OXYGEN STORAGE PROPERTIES OF HEXAGONAL RARE-EARTH MANGANITES

BY

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To my Family
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CHAPTER 1: INTRODUCTION

1.1 High-purity Oxygen Production and Air-separation

Atmospheric oxygen levels are maintained through a delicate and highly synchronized process called photosynthesis. This mechanism, utilized by plants and other primary producers, is the main source of oxygen besides photolysis in which oxygen is liberated from its water molecules upon interaction with ultraviolet radiation in the earth’s atmosphere [1].

The first industrial-scale attempt to separate oxygen from air was conducted by the German scientist Carl Linde in 1895 [2]. He employed the Joule-Thomson effect to cool filtered-air below the boiling points of its main constituents (Figure 1.1), i.e. oxygen (-183.0°C),

![Figure 1.1: Composition of earth’s atmosphere by volume [3].](image)

"Figure 1.1: Composition of earth’s atmosphere by volume [3]."
nitrogen (-195.8°C), and argon (-189.3°C), thus liquefying each component one at a time in a technique called cryogenic distillation. In this process, air is initially compressed into a thermally insulated compartment of volume $V_1$, pressure $P_1$, and temperature $T_1$, and is then allowed to expand in a continuous-flow and steady-state arrangement through a porous plug restriction so as to fill the entire volume $V_2$ of an adjacent compartment of pressure $P_2$ and temperature $T_2$, where $V_2 > V_1$ and $P_1 > P_2$. According to laws of thermodynamics, this fundamentally irreversible process proceeds along a constant enthalpy curve where gas does a net work $W$ by displacing itself across the restriction. Since the system consisting of gas and container is adiabatically insulated, the heat exchange is zero; i.e., $Q = 0$.

It follows from the 1st law of thermodynamics

$$Q = \Delta E + W$$

where

$$E = \text{the total internal energy of the system}$$

and

$$W = P_2 V_2 - P_1 V_1$$

that

$$(E_2 - E_1) + (P_2 V_2 - P_1 V_1) = 0.$$  

Using:

$$H = E + PV$$

we conclude that $H_2 = H_1$, and hence enthalpy $H$ is conserved.
For the gas under investigation here, the final temperature $T_2$ after the throttling process, i.e. the expansion through the restriction, may increase or decrease depending on the initial thermodynamical parameters $P_1$ and $T_1$ of the system. Figure 1.2 [4] depicts the pressure-temperature relationship of the nitrogen gas, as an example, where different curves in the plot correspond to different constant values of enthalpy $H$ in the $P$-$T$ plane of the gas. According to this diagram, the temperature will decrease upon throttling only if the expansion occurred within the region confined by the inversion curve, as shown on the graph. Within this region, the slope

![Figure 1.2: Curves of constant enthalpy H in the P-T plane of nitrogen gas.](image)
of the curve, also known as the Joule-Thompson coefficient $\mu$, is positive in value, indicating a prompt cooling upon expansion as is the case for all the other air components. Thus, cooling upon throttling is viable for air, and cryogenic distillation was the method of choice to deploy for commercial air-separation.

The rapid technological developments witnessed during the past few decades in different fields of industry, especially in the steel and chemical production sectors, have resulted in a significant increase in the demand on pure oxygen. The chemical industry has become the primary consumer of pure oxygen with an estimated consumption of 106 Mega tons annually, or 74% of the total world’s annual consumption of pure oxygen [5]. In addition to this increased demand on pure oxygen, the threat of global warming as a result to the increasing levels of atmospheric flue gases has established a new necessity for alternative oxygen separation systems, which are suitable for low-cost efficient production of high-purity oxygen relative to the mature and costly cryogenic distillation method, and also for providing the proof of principle necessary for the establishment of new “clean” technologies to harvest the energy of fossil fuel with minimum or no carbon print, and therefore, minimizing environmental impact. Pressure Swing Adsorption (PSA) and Vacuum Swing Adsorption (VSA) have emerged as new potential technologies for oxygen separation with projected $\sim 52\%$ lowering in capital relative to cryogenic distillation [5]. In PSA, beds of adsorbent material, typically zeolite for oxygen separation from air, selectively adsorb a specific element (nitrogen) from a mixture of gases (air) at elevated pressures. The trapped nitrogen is then desorbed upon swinging to lower pressures after separating the oxygen enriched gas. This mechanism has been deployed to enrich oxygen (90% purity) in portable oxygen concentrators used by emphysema patients.
Polymeric membranes have been also introduced as another alternative for oxygen enrichment or depletion of air. Oxygen depletion is a new approach to fire prevention in buildings and airplanes; polymeric membranes can be utilized as future coatings for the fuel tanks in airplanes, for example. The polyphenylene oxide and the polyimides are two typical polymeric membrane materials widely utilized by Parker Gas Inc and Air Products Inc, respectively [6]. The mechanism of air separation in polymeric membranes is based on preferred dissolution and diffusion of oxygen over nitrogen in these compounds. The operational temperature is limited by the thermal stability of the polymer type. Despite the low ~ 40% purity of the produced oxygen, small-scale applications related to the health sector are possible where the low purity of the produced oxygen is no longer an issue.

Ionic Transport Membranes (ITM) technology is the newest technique anticipated for the oxygen production through air separation. Still, this technology is in the development stage and preliminary results demonstrated oxygen production with the highest achieved purities, so far. With a projected 17% lowering in capital, this technique suggests major improvements over the well-established cryogenic distillation. One of the advantages of the ITM technology is the possibility of local decentralization of oxygen production to small-scale plants, especially for chemical processes which account for the consumption of 74% of the total produced oxygen. Therefore, the transport of oxygen over public roads will be eliminated. The ionic transport membrane is typically made of a good catalytic material which dissociates the oxygen molecule into two oxygen ions (surface reaction) on the feed side of the membrane. The oxygen ions are then diffused through the bulk to recombine at the permeate side of the membrane, giving away two pairs of electrons which return to the feed side. Therefore, a good candidate ITM material is a mixed ionic and electronic conductor. The air is compressed at the feed side of the membrane
to maintain sufficient oxygen partial pressure difference across the membrane, a driving force linearly related to the diffused ions. The structural family of Ruddlesden-Popper compounds $A_{n+1}B_nO_{3n+1}$ (A and B represent rare-earth and/or transition metals) presents the majority of the ITM materials. The end members of this family, the cubic perovskites, represent an important class of mixed ionic and electronic conductor MIEC materials suitable for ITM technology. The ionic diffusion is achieved in these compounds through the formation of oxygen vacancy defects. In the oxygen deficient $ABO_{3-\delta}$ perovskites, oxygen ion vacancies diffuse across the bulk through a thermally assisted hopping mechanism. Typically, this mechanism is significant at temperatures well above $\sim 700 \, ^{\circ}C$. Amongst all the investigated MIEC materials, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}O_{3-\delta}$ (BSCF) system has demonstrated the highest separated oxygen flux $\sim 3 \, \text{mLmin}^{-1}\text{cm}^{-2}$ at $\sim 900 \, ^{\circ}C$ and $\sim 20 \, \text{KPa}$ transmembrane oxygen partial pressure differential. Geometry of the synthesized membranes was found to affect the produced oxygen fluxes of these materials. The hollow-fiber geometry of the BSCF perovskite system boosted the oxygen flux to $\sim 9 \, \text{mLmin}^{-1}\text{cm}^{-2}$, a significant improvement over the previously achieved $\sim 3 \, \text{mLmin}^{-1}\text{cm}^{-2}$ oxygen flux for the BSCF disc geometry. However; BSCF is unstable at temperatures below $\sim 825 \, ^{\circ}C$ leading to structural instability; and therefore, membrane mechanical failure. The more stable $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}O_{3-\delta}$ (LSCF) is preferred over the BSCF system although on the expense of the reduced obtained oxygen flux $\sim 1 \, \text{mLmin}^{-1}\text{cm}^{-2}$ for the hollow-fiber geometry. It represents the best compromise between stability, durability, and produced oxygen flux [5-6].

The growth of new oxygen separation materials will strongly impact the development of crucial energy-related technologies, such as chemical looping combustion (CLC) and fuel cells, to minimize the environmental impact which has raised serious concerns in the research community. CLC is one of the promising techniques which have been intensely developed.
Envisaged applications of the oxygen storage materials, including CLC, will be discussed in section 1.2. The continuous dependence on pure oxygen and the wide range of envisaged oxygen-related applications will ensure a continuous need for the development of new oxygen-storage material.

In this dissertation, a new class of ceramic materials (hexagonal rare-earth manganites) are evaluated and proposed as new potential oxygen-storage materials for commercial low-cost high-purity oxygen production through air-separation. This new technology is anticipated to be introduced in the medium to large scale production range. Characterizations of related physical properties associated with these complex oxides, such as magnetic and transport properties, in which a possible impact of oxygen content on their physical properties is expected, are also discussed. The investigated materials in this study are also characterized as multiferroics, an important class of functional materials in which a strong coupling between the magnetic and ferroelectric order parameters was discovered.
1.2 Applications of Oxygen-storage Materials

Complex oxides have generated a great deal of interest within the research community during the past few decades. They exhibit a wide range of interesting phenomena including superconductivity [7], colossal magnetoresistance [8], metal-insulator transitions [9], multiferroicity [10], and mixed ionic-electronic conductivity [5], due to a strong interaction between orbital, magnetic, charge, and structural degrees of freedom. Recently, oxygen storage properties have been discovered in ceramic oxides. The growth of these interesting materials will have a great impact on the development of crucial technologies such as oxygen production and important technological and energy-related applications.

Rare-earth manganites have been recently considered as new potential oxygen-storage materials. In these materials, oxygen content is sensitively dependent on the surrounding conditions of temperature and/or oxygen partial pressure [11]. They exhibit the ability to selectively absorb, store, and release significant amounts of oxygen under specific conditions of temperature and/or oxygen partial pressure which, in principle, can be conveniently optimized. An ideal candidate material must possess a large oxygen storage capacity (OSC, measured in moles of oxygen per molar weight of material) with reversible oxygen storage/release capability, preferably at low and narrow temperature range near atmospheric pressure. They must also exhibit stability under strong reducing conditions and in elevated temperatures.

An overview of some of the envisaged applications related to these materials is described in the following sections.
1.2.1 Thermal Swing Adsorption (TSA) for Air-separation

Oxygen non-stoichiometry in complex oxides is achieved through two different mechanisms that are intrinsically related to the crystal structure of the material under investigation. The first mechanism is common in the archetypal perovskite materials $ABO_{3-\delta}$ ($A$ and $B$ are typically large rare-earth and/or transition metals) where significant amounts of oxygen vacancies are accommodated within the structures [12]. The introduction of a lower valence cation on the A site results in the formation of interstitial and/or lattice site oxygen vacancies causing frenkel and/or schottky defects. The synthesis of non-stoichiometric oxygen deficient material, capable of swinging between two oxygen contents $\delta_1$ and $\delta_2$, is the essence of many important applications such as solar-water splitting, fuel cells, and air-separation using the prototype ceria-zirconia solid-solution. Oxygen diffusion through the deficient $ABO_{3-\delta}$ perovskites depends on oxygen ion hopping between the oxygen vacancy sites. The activation energy of this process is typically $> 1$ eV, while the activation energy of interstitial oxygen is around 0.2 - 0.5 eV [13]. In rare occasions, like in the case of perovskite La$_{1-x}$Sr$_x$MnO$_{3+\delta}$, excess oxygen rather than vacancies was observed in TG measurements, and was attributed to the creation of intrinsic frenkel and/or schottky vacancy-defects on the A and B sites with equal proportions [12]. For the LaMnO$_3$ system (Kröger-Vink notation is used), the introduction of excess oxygen ($\delta$) and the conservation of electric charge will imply the following equilibrium relation per formula unit:

$$\text{LaMnO}_3 + \frac{\delta}{2} \text{O}_2 = (\text{La} V_{\text{La} \langle \delta/3 \rangle}) (\text{Mn} V_{\text{Mn} \langle \delta/3 \rangle}) \text{O}_{3+\delta}$$  

$$= \frac{3 + \delta}{3} \{ (\text{La}_{3+(3+\delta)} V_{\text{La} \langle \delta(3+\delta) \rangle}) (\text{Mn}_{3+(3+\delta)} V_{\text{Mn} \langle \delta(3+\delta) \rangle}) \text{O}_3 \}$$
letting \( \gamma = \frac{(3+\delta)}{3} \)

equal vacancies are obtained on both the \( A \) and \( B \) sites:

\[
= \frac{(3+\delta)}{3} \{\text{La}_{1-\gamma} \text{Mn}_{1-\gamma} \text{O}_3\}
\]

This method allows material to absorb and accommodate extra oxygen at relatively high and wide range of temperatures sufficient to create these defects, and hence causing serious integration challenges for practical applications. The other technique, on the other hand, is utilized in the hexagonal rare-earth manganites. They absorb and store excess oxygen within the

**Figure 1.3:** Schematic diagram of thermal swing adsorption (TSA) with AMnO\(_3\) sorbent material.
interstitial sites of their structures. Relative to their perovskite counterparts, the oxygen ions in hexagonal manganites are less constricted. Thus, the incorporation and expulsion of oxygen proceed along shorter and lower temperature ranges, making these compounds unique and ideal for thermal swing adsorption (TSA) applications. In TSA, two beds of sorbent cycle in between two chambers separated by a temperature gradient $\Delta T = T_2 - T_1$ (Figure 1.3). These two temperature points define the temperature range suitable for the rapid incorporation (in the oxygen-rich chamber) and expulsion (in the oxygen-deficient chamber) of excess oxygen in the sorbent material.

According to literature [14], ceria-zirconia solid solutions have been widely used as the oxygen storage material of choice for air-separation. The OSC of this material is related to the ability of CeO$_2$ fluorite structure to accommodate a significant number of oxygen vacancies when doped. They are utilized at temperature $\sim 500$ °C and have OSCs in the range of $\sim 400$-$500 \, \mu$mol-O/g measured in oxygen atmosphere [15]. The best OSCs of $\sim 2700 \mu$mol-O/g have been reported for the $RBaCo_4O_{7+\delta}$ ($R = Y, Dy, Ho, Er, Lu$) compounds which were found to completely desorb at $\sim 425$ °C in oxygen atmosphere. These compounds, however, decompose at relatively low temperatures $\sim 725$ °C; and therefore, causing durability challenges. Introducing Al on the Co sites, on the other hand, has resulted in improving the stability and recoverability of these compounds [16].
1.2.2 Solar Water Splitting

The thermochemical reaction in which water is separated into oxygen and hydrogen is generally known as water splitting. Solar-driven water splitting using non-stoichiometric oxides has emerged within the research community as an efficient and attractive “clean” mechanism to harvest the potentially limitless source of solar energy, with little or no carbon footprint, and therefore minimum environmental impact.

At its simplest level, this fuel production process relies on the basic thermodynamical principle that partial reduction of the oxide takes place at high temperature while oxidation, in this case by water steam, occurs at lower temperature. Therefore, the concentrated solar energy provides the heat necessary for the expulsion of oxygen from the bulk of the catalyst material, see Figure 1.4 [17] for ceria based water splitting cell in the first half-cycle, and hydrogen is

![Ceria based solar-driven two steps fuel production cycle through water-splitting.](image)
released upon oxygenation at lower temperature in the second half-cycle. The ideal catalyst material should demonstrate high sensitivity in oxygen content, as well as high oxygen diffusivity and fast kinetics. Ceria oxide had been widely considered for this technology. However, the extreme temperatures required for the creation of suitable levels of reduction, i.e. oxygen vacancies, in ceria introduced challenges in reactor design and operation [18]. La$_{1-x}$Sr$_x$MnO$_3$-$\delta$ perovskites, however, have been introduced as better candidates for this technology. The doping of lower valence Sr on the La site introduces oxygen vacancies in the orthorhombic structure. Structural phase transitions to the rhombohedral, tetragonal, and then to the cubic phase were found to occur with the introduction of strontium at doping levels of $0.47 > x$, $0.7 > x$, and $1 > x$, respectively [18]. This system was found to provide a reduced operation temperature range and enhanced fuel production capacities reaching 9 ml g$^{-1}$ for the Sr$_{0.4}$ doped composition between 1400 – 800 °C. Increasing doping of Sr decreased the fuel production rate, suggesting that the intermediate compositions provide the best compromise between fuel production and energy penalty [18].

Water splitting is a key component in our envisaged hydrogen economy, where pure oxygen is the waste-product of a fuel production process.
1.2.3 Chemical Looping Combustion (CLC)

Traditional combustion of fossil fuel with air releases significant amounts of pollutants, primarily NO$_x$ and SO$_x$, and therefore increasing the environmental impact of this essential and important source of energy. Different techniques were considered to minimize the release of these toxic waste-products ranging from automobile exhaust catalysts to Flue-Gas Desulfurization (FGD) technologies.

Figure 1.5: Schematic drawing of a chemical looping combustion (CLC) process.
Chemical looping combustion (CLC) not only reduces the emissions of these oxides, but eliminates them. In this process, fossil fuel combusts with high partial pressure of oxygen instead of with ambient air, resulting in \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) as waste products which are easier to capture and process compared to the \( \text{NO}_x \) and \( \text{SO}_x \) flue gases. Figure 1.5 [19] represents a schematic drawing of the CLC method. The ceramic material, commonly called oxygen carriers for this technique, picks up oxygen in the air reactor in a manner similar to the oxygenation occurring in TSA. The oxygen-loaded material gets reduced in the fuel reactor releasing pure oxygen to combust with the fuel in the second step of this two-step combustion technique.

Once the combustion is initiated, this cycle proceeds autothermally by utilizing the reactor waste heat increasing the efficiency of this process. Perovskite lanthanum cobaltites have been intensively evaluated as potential oxygen storage materials for CLC applications. Beside their large oxygen storage capacity, they also exhibit stability and recoverability in elevated temperatures and under strong reducing conditions similar to the physical conditions encountered in the reactor.
1.2.4 Hydrogen-Oxygen Fuel Cells

Typical oxygen storage materials are often good ionic conductors of oxygen but are electrically insulating. The development of fuel cells relies on the existence of a suitable electrolyte material with the aforementioned properties. The mixed ionic electronic conductors MIEC family provide excellent candidates for the cathode materials, giving that chemical and structural stabilities are maintained.

Fuel cells are electrochemical devices that convert chemical energy stored in fuel gas into electricity upon interaction with an oxidizing agent. They are different from the conventional batteries in the sense that they require a continuous flow of fuel gas, in this case hydrogen, and

![Schematic drawing of a hydrogen-oxygen fuel cell](image)

**Figure 1.6**: Schematic drawing of a hydrogen-oxygen fuel cell [20].
oxygen (air) to ensure a constant flow of electricity. They typically consist of three components, cathode, anode, and electrolyte, stacked in layers between the two terminals of an electric load (Figure 1.6). Oxygen storage materials can also be used as cathodes to separate oxygen from air.

Although fuel cells were invented in the mid-nineteenth century, they were not practically deployed until recently by the national aeronautics and space administration NASA to generate power for a variety of equipment, ranging from probes to space capsules. Moreover, they are suitable as primary and secondary power sources for commercial and residential buildings in developing and rural areas around the world. In these fuel cells, oxygen is separated from air at the cathode and subsequently gets reduced by the free electrons from the anode. On the other hand, hydrogen is oxidized at the anode from the oxygen anions, reaching from the cathode where they react to form water releasing two electrons which conduct through the external interconnect from the anode to the cathode, therefore generating electricity. As previously mentioned, this process requires an electrolyte material that conducts oxygen anions but is electrically insulating.

There are some limitations which stood as a barrier against further wide-adaptation of this technology. First and foremost, the fuel cells operate at relatively high temperatures (600-1000°C) making them hard to implement for efficient practical applications. Additionally, the typical process apparatus requires the stacking of different materials, thus generating chemical reactions between layers causing disintegration concerns. Finally, there is a thermal-expansion mismatch between the layers which goes effective with the slightest temperature gradients.
1.3 How Do We Explore the Materials We Want?

The scientific method is the standard criteria followed to construct a realistic theory of natural phenomena through unbiased perception and explanation. It first starts with an observation of a new phenomenon unexplainable by previously existing theories or laws of that field. The inability to model that observation will consequently prompt the formulation of a new hypothesis in the form of a possible mechanism, or a mathematical model, that fits the descriptions.

![Diagram of Property vs. Composition](image)

**Figure 1.7**: Schematic drawing represents the results of a general research criteria encountered in science.
This new hypothetical model is then used to quantitatively predict new results of new observations. Finally, the ultimate test to verify the validity of these predictions is carried out through proper experiments conducted independently by different performers. If the results of this experiment matched those of the hypothesis, then a theory can be established and accepted as a universal law of science.

A general result of a research criteria often encountered in science is presented in Figure 1.7 [21]. There are regions of instability that prevent the researcher from directly achieving or exploring the desired phenomenon, within that region, using standard procedures. The instability region, where the observed data line diverges from the expected one, requires us asking the principal question: what essential parameters are necessary for a reliable description of the phenomenon? With the proper designation of the right parameters, and a logical comprehension of the research’s problem, one could minimize the boundaries of the instability region where further exploration becomes possible. The acquired knowledge of that particular problem will be consequently stretched, either by building upon previously established foundations or by establishing new concepts that better describes the natural phenomena.

Our goal of the research described in this dissertation is to control the structural and physical behavior of oxygen ordered phases by utilizing the chemical variables and synthesis conditions, in attempt to optimize the operation conditions required in these materials for a variety of applications, as was previously explained in section 1.2.
CHAPTER 2: EXPERIMENTAL METHODS

The goldshmidt tolerance factor $t$ was utilized to estimate the degree of structural distortion, and therefore to predict the possible formability of our designed $R\text{MnO}_3 \,(R = \text{Rare-earth elements})$ structures. It is expressed as: $t = \frac{<R-O>}{\sqrt{2}<\text{Mn-O>}}$, where the $<R-O>$ and $<\text{Mn-O}>$ are average bond lengths preferably obtained from NPD measurements. Hexagonal $R\text{MnO}_3$ structures were found to be feasible in the tolerance factor ($t$) limit $t < 0.855$, while the perovskite structure was more likely to form in the limit $t > 0.855$ as was the case for all the large size rare-earth elements (i.e. Dy, La, Pr, Tb, and Gd). Samples were prepared following conventional ceramic synthesis methods. Stoichiometric amounts of high purity (99.999 %) metal oxides ($R_2O_3$ and MnO) were thoroughly mixed in an agate mortar then pressed into high-density pellets. The heat treatment consisted of several calcinations in air, with intermediate grindings, in a temperature range of 800-1300 °C with the final firing held at 1300 °C for 12 hours followed by natural cooling in the furnace. All samples that did not form in the anticipated hexagonal $P6_3\text{cm}$ phase were subsequently fired in ultrahigh-purity argon at 1300 and 1400 °C. Under these conditions, the perovskite phase was successfully suppressed. High-pressure oxygen annealings were conducted using a home-built system. About 2 cm$^3$ alumina crucibles containing a total ~ 1-2 g of small pellet chunks of the air-synthesized samples were loaded into a stainless-steel high-pressure containment vessel placed in a high temperature furnace within a sealed chamber. Annealing was performed under 190 bar of pure oxygen at 400 °C followed by slow cooling (0.1 deg/min) to room temperature. Synthesis and experimental reaction gases consisted
of different mixtures of ultra-high purity argon, hydrogen, oxygen, and air (21% O₂ balanced with Ar) flowed at a rate of 100 ccm using a MKS flow-meter.

To examine the phase purity of our samples, x-ray diffraction (XRD) experiments were carried out using a Rigaku D/MAX powder diffractometer with CuKα radiation in the 2θ = 20-70° range. XRD is a powerful technique allows for careful examination of the crystal structure of the investigated material. Unlike amorphous material, long-range periodicity in crystals helps diffract x-ray beams according to Bragg’s law:

\[ \lambda = 2d_{hkl} \sin \theta \]

where \( \lambda \), \( d_{hkl} \), and \( \theta \) represent the x-ray wavelength, interplanar spacing, and incident angle, respectively. Constructive interference of the diffracted waves, at specific incident angles, is illustrated as sharp peaks in the generated XRD pattern. Each peak corresponds to a specific plane in the unit cell, typically labeled by miller indices. In a typical diffractometer, like our

![Bragg-Brentano Geometry](image)

**Figure 2.1**: Schematic drawing showing the geometry typically used in XRD diffractometers.
Rigaku, the Bragg-Brentano geometry is used in the instrument, see Figure 2.1. In this geometry, the diffraction vector (\(s\)), i.e. the vector that bisects the angle between the incident and diffracted beams, is always normal to the surface of the sample which is shown in yellow in figure 2.1. The x-ray tube is fixed in position while the sample and detector rotate at \(\theta/\text{min}\) and \(2\theta/\text{min}\), respectively; and hence, the name \(\theta:2\theta\) instrument is designated for this arrangement. As shown in figure 2.1, \(\theta\) is the incident angle of the x-ray beam while \(2\theta\) is the angle between the incident and diffracted beams. Theoretical x-ray patterns were generated using Powdercell v 2.4.

Absolute oxygen content and the oxygen storage capacity (OSC, measured in moles of oxygen per molar weight of material) of our samples were investigated by thermogravimetric analysis (TGA) using Cahn TG171 and Cahn TherMax700 thermobalances with a 2 \(\mu\)g precision. In the TGA system, the sample’s temperature is gradually changed using the desired rates required by the design of the experiment. The weight of the investigated sample is measured using an analytical balance located outside of the furnace, and is simultaneously communicated to the user as a function of time and/or temperature using specially designed software. For increased accuracy, broken chunks of the samples as large as 1g were placed in cylindrical alumina crucibles suspended on a sapphire rod at one side of the thermobalance. Depending on the reaction gases used in the TG experiment, Pt, Au, or Mo wire was used in hanging the alumina crucible to the thermobalance. Empty-cup runs were performed for calibration and buoyancy corrections. The absolute oxygen contents of samples produced at various synthesis and annealing conditions were determined during the final TGA experiment by reducing the oxygenated samples in 42% \(\text{H}_2/\text{Ar}\) to their reduction products of \(R_2\text{O}_3\) and MnO as verified by
subsequent XRD measurements. Hence, the oxygen content was normalized using the weight difference between the oxygenated samples and their reduction products.

High-resolution time-of-flight neutron powder diffraction (NPD) data were collected over two frames of d-spacing (0.1 - 3 and 1 - 6 Å) at low and room temperatures at the Australian Nuclear Science and Technology Organization (ANSTO) and the spallation neutron source of Oak Ridge National Laboratory using the 11A-POWGEN powder diffractometer, respectively. While x-ray diffraction XRD probes the bulk of the material through interaction with its atomic electron-clouds, NPD probes the crystals with enhanced resolution. Unlike XRD, NPD is based on the scattering of neutrons with the nuclei in the unit cell. Therefore, NPD is inherently more sensitive to light elements such as oxygen. Neutrons are also neutral, and yet exhibit an intrinsic magnetic moment making them ideal to study the magnetic and structural properties of materials. In the time-of-flight apparatus, the detector is fixed at specific angle and the variables in Bragg equation are the neutron wavelength and d spacing. The time needed for the scattered neutrons to arrive at the detector bank depends on their wavelengths according to De Broglie’s equation, \( \lambda = \frac{h}{mv} \). Powgen, for example, uses a pulsed neutron source with a wide range of wavelengths produces neutrons that arrive at the counter at different times based on their wavelengths, i.e velocities. Moreover, while the scattering amplitude of x-rays depends on the scattering angle, time-of-flight neutrons on the other hand scatter isotropically with minimum dependence on the angle of scattering. The General Structure Analysis System (GSAS) and the user graphical interface (EXPGUI) suite were used to analyze NPD data using the Rietveld method [22-23]. Background, peak width, and absorption were all refined together with the lattice parameters, atomic positions, oxygen site occupancies, and isotropic temperature factors. Visual representations of all the refined structures were made using the visual electronic and structural
analysis VESTA software [24], while IsoDistort and Isotropy [25] were utilized to perform group theoretical analysis in search of possible isotropy subgroups originating from the parent structure.

In-situ high-flux synchrotron data were collected for selected $RMnO_{3+δ}$ samples at the Advanced Photon Source (APS) of Argonne National Laboratory on beam line 11-ID-C using temperature profiles similar to those used in the samples’ TG measurements. The synchrotron diffraction data was processed and plotted with OriginPro software [26]. Dilatometry measurements were conducted on samples few millimeters in length using Linseis Differential Dilatometer L75 with 1μm precision. Ultra-high-purity (99.999 %) oxygen was used as a reaction gas flowed at an approximate rate of roughly 100 ccm. For increased accuracy, “zero” dilatometry runs performed with a piece of alumina close in length to the sample’s length were subtracted from the raw data to account for the thermal behavior associated with the alumina piston and sample holder of the dilatometer in similar temperature and atmosphere profiles.

Thin films were fabricated using pulsed laser deposition (PLD) system located in a class-100 clean room. Targets of perovskite SrRuO$_3$ were epitaxially deposited on (001) silicon wafers at 900 °C and in 100 mTorr of O$_2$ at different laser frequencies. Preliminary characterization of the synthesized films consisted of atomic force microscopy (AFM) using a Quesant Q-scope 350 AFM/MFM. Scans were processed with Scan Atomic software. A high-vacuum Scanning Electron Microscope (Tescan, model Vega II SBH) equipped with a liquid nitrogen-free INCAx-act Analytical Standard EDS Detector (Oxford Instruments) was used to investigate the porosity and morphology of our samples.
Magnetic measurements were performed using Quantum Design’s Magnetic Property Measurement System (MPMS) in the temperature range 2-400 K. Transport measurements were made in collaboration with AGH University of Science and Technology, Poland.
CHAPTER 3: OXYGEN STORAGE, STRUCTURAL, MAGNETIC, AND TRANSPORT PROPERTIES OF HEXAGONAL Dy$_{1-x}$Y$_x$MnO$_{3+\delta}$

3.1 Introduction

Research on single-valent rare earth manganites (RMnO$_3$, where $R$ is a rare earth or Y) has gained increasing importance over the past few years [27]. The particular interest in these materials is primarily due to their vast potential in the development of technologically and industrially critical fields like spintronics [28], air separation [29], and energy related technologies such as chemical looping [30-32], fuel-cells [33], and solar water splitting [34] which is a key component of the hydrogen economy. Two distinct equilibrium phases are obtained when synthesized in air under normal conditions as a function of the $R$ ionic size: a perovskite structure for large rare-earth elements (e.g. La, Pr, Gd, Dy) and a hexagonal structure for the smaller ionic size elements (e.g. Ho, Er, Y, Lu). The hexagonal structure is best described as layers of corner-shared trigonal-bipyramids (TBP) of MnO$_5$ polyhedra, separated by layers of 8-fold coordinated $R^{3+}$ cations surrounded by six basal and two inequivalent apical oxygen ligands. Figure 3.1 shows a schematic drawing of the hexagonal structure of Dy$_{1-x}$Y$_x$MnO$_3$ along with the results of a thermogravimetric heating/cooling cycle in oxygen for $x = 0.3$. The temperatures $T_{\text{Red}}$ (on heating) and $T_{\text{Oxi}}$ (on cooling) define the temperature range...
Figure. 3.1: Schematic drawing of the hexagonal crystal structure of \( \text{Dy}_{1-x}\text{Y}_x\text{MnO}_{3+\delta} \) with the Mn atoms centered at the trigonal-bipyramidal positions (left panel). Thermogravimetric measurement of low-temperature oxygen adsorption/desorption capability in the temperature range \( T_{\text{Oxi}} - T_{\text{Red}} \) for \( \text{Dy}_{0.7}\text{Y}_{0.3}\text{MnO}_{3+\delta} \) in pure \( \text{O}_2 \) (right panel).

where the thermal swing absorption process can be utilized to separate oxygen from air.

Electronic 3\(d\) orbital configurations have been reported for the Mn\(^{3+}\) ions in both their TBP and octahedral coordination in the hexagonal and perovskite crystal structures, respectively [35]. In the octahedral geometry, the crystal field splits the degenerate 3\(d\) orbitals into two stabilized sets, \( t_{2g} \) orbitals (\( d_{xy}, d_{xz}, d_{yz} \)) with lower energy relative to the barycenter, and \( e_g \) orbitals (\( d_{x^2-y^2}, d_{z^2} \)) at higher energies. The symmetry is further lowered in the perovskite structure by lifting the two-fold degeneracy of the \( e_g \) orbitals in response to Jahn-Teller effects, leading to an elongated \( c \)-axis and three different (Mn-O) bond lengths [36]. These distortions are accommodated by rotating and tilting the polyhedra along the \( ab \) plane and about the \( c \)-axis.
[37], which result in considerably smaller than 180° Mn-O-Mn bond angles with a large impact on the transport and magnetic properties of the system [38].

Stabilization of the electronic orbitals with the TBP coordination is achieved when the 3d⁴ orbitals of Mn³⁺ are split into three sets a' (dz²), e' (dx²-y², dxz, dxy), and e'' (dxz, dyz) in a high-spin e'² e''² state, which results in compressed apical (Mn-O) bond lengths that are much shorter than the basal (Mn-O) bonds in which the electrons experience a stronger repulsive force [39]. Unlike their perovskite counterparts, hexagonal rare-earth manganites exhibit multiferroic properties due to the opposite and unequal displacements of the R³⁺ ions and the associated tilt of the TBP polyhedra relative to the c-axis [40]. Antiferromagnetic ordering occurs in these materials for both the Mn³⁺ and R³⁺ ions at T_N ~ 70-130 K and ~ 5-10 K, respectively, while ferroelectricity occurs at much higher temperatures of T_C ~ 573-923 K [41-45]. In addition, distant layers of MnO₅ polyhedra allow for a less constricted oxygen environment that results in easily movable interstitial oxygen ions leading to better oxygen storage/release capabilities at low temperatures.

A convenient description of the average distortions from the perovskite cubic structure can be expressed in terms of the tolerance factor, t = <R-O>/√2<Mn-O>, where the <R-O> and <Mn-O> are average bond lengths preferably obtained from NPD measurements. The tolerance factor also explains the relative stability of the perovskite and hexagonal phases at the synthesis temperatures as demonstrated in our previous study [46]. Based on that study, we determined that the hexagonal and perovskite structures of Dy₁₋ₓYₓMnO₃ can be obtained for t < 0.855 and t
> 0.855, respectively. Synthesis of hexagonal Dy$_{1-x}$Y$_x$MnO$_{3-\delta}$ over the full solubility range can be achieved when the $<$Mn-O$>$ bond length gets elongated while partially reducing the valence state of Mn$^{3+}$ in inert atmospheres to Mn$^{2+}$ and; therefore, by decreasing the tolerance factor. In this chapter, we discuss the thermogravimetric, structural, and magnetic properties of stoichiometric and oxygenated Dy$_{1-x}$Y$_x$MnO$_{3+\delta}$ compounds, which were purposely synthesized in the hexagonal structure using reducing conditions as previously established by the tolerance factor design rules.
3.2 Results and Discussion

X-ray diffraction confirmed that high temperature synthesis in argon tends to favor the formation of the hexagonal phase, while synthesis in oxygen tends to favor the perovskite phase. Figure 3.2 shows XRD patterns for the as-made single-phase Dy$_{1-x}$Y$_x$MnO$_{3.0}$ samples with peaks indexed by the hexagonal P6$_3$cm structure for all samples, x = 0, 0.3, 0.5, 0.7, and 1.

![X-ray diffraction patterns for stoichiometric Dy$_{1-x}$Y$_x$MnO$_3$ with peak indices corresponding to the P6$_3$cm phase.](image)

**Figure 3.2:** X-ray diffraction patterns for stoichiometric Dy$_{1-x}$Y$_x$MnO$_3$ with peak indices corresponding to the P6$_3$cm phase.
3.2.1 Thermogravimetric Measurements

The as-made samples were annealed to 500 °C in a TGA thermobalance under high purity oxygen with slow heating and cooling rates of 0.1 °C/min. Consecutive oxygen absorption and desorption steep steps upon heating are shown in Figure 3.3 to take place in a narrow and exceptionally low temperature range of 200 - 380°C. The argon synthesized Dy-rich samples show total oxygen contents slightly below 3.0, in agreement with our anticipation of some Mn\(^{2+}\) formation. Noticeably, the oxygen absorption/desorption process for the Dy-rich samples takes place at higher temperatures and all compositions become oxygen stoichiometric \((\text{Dy}_{1-x}\text{Y}_x\text{MnO}_3)\) above 380°C. Samples quenched from these temperatures exhibit the well known \(P6_3\)cm hexagonal symmetry, which will be briefly discussed in the next section.

Upon slow cooling, samples reabsorb oxygen below 360°C over a considerably narrower temperature range, and then they remain largely unchanged in their oxygen content upon further cooling. A clear correlation between the increasing average ionic size of the \(R^{3+}\) cations and the increasing temperature at which the oxygen-loaded phases are stabilized is again observed. The amount of excess oxygen intake is significantly larger in samples with larger \(R^{3+}\) cationic sizes, resulting in a higher oxidation state of Mn up to 3.6+ and OSC of 1233 \(\mu\)mol-O/g (or about 2% by weight) for \(\text{Dy}_{0.7}\text{Y}_{0.3}\text{MnO}_{3+\delta}\). This trend of increased oxidation state as a function of increased \(R^{3+}\) cationic size is remarkably similar to the behavior of the perovskite counterparts when synthesized in oxygen. The latter phases form significant amounts of lattice defects (cation vacancies) as a function of increasing the \(R^{3+}\) cationic size to result in an average Mn oxidation state up to +3.3 for \(R = \text{La}\) [47].
Figure 3.3: TGA measurements of oxygen content for Dy$_{1-x}$Y$_x$MnO$_{3+\delta}$ as a function of temperature using heating and cooling rates of 0.1°C/min in pure O$_2$. The arrows indicate the direction of the temperature sweep.

However, achieving these oxidation states requires much higher temperatures and wider temperatures ranges. For the perovskite LaMnO$_{3+\delta}$, TG data shows that accommodation of excess oxygen commenced upon heating in oxygen around 550 °C and then to saturate around 820 °C. Upon further heating, oxygen was desorbed at slow rate that stoichiometry could not be achieved even at elevated temperature as high as 1400 °C. Cooling to room temperature demonstrated slow reabsorption of excess oxygen to reach the stabilized oxygen-loaded phase.
Figure 3.4: TGA measurements of oxygen content for perovskite $\text{RMnO}_{3+d}$ as a function of temperature in pure $\text{O}_2$. Excess oxygen is accommodated by the creation of cation vacancies $v$ in equal proportions at the R and Mn sites. The arrows indicate the direction of the temperature sweep [47].

with maximum oxygen content of $\delta = 0.15$, indicating an average $+3.3$ oxidation state for the manganese cation, see Figure 3.4.

High pressure oxygen annealing at 250 bar and 400 °C resulted in a drastic boost to the total oxygen content in the samples (up to 3.38 oxygen atom per formula unit) and enhanced the
Figure 3.5: TGA reduction of oxygenated YMnO$_{3+\delta}$ in 42% H$_2$ to Y$_2$O$_3$ and MnO.

OSC up to $\sim$1700 µmol-O/g (or 2.7% by weight). Tests of Dy$_{1-x}$Y$_x$MnO$_{3+\delta}$ materials under several reducing atmospheres showed stability of the oxygen loaded phases to temperatures as high as 300 °C when heated in Ar and the stability of the stoichiometric O$_3$ phase in air or Ar to higher temperatures of at least 1100 °C. They also showed the stability of the oxygen loaded phase in 42% H$_2$ [see Figure 3.5 for $x = 1$] up to 200 °C and with oxygen contents O$_{3.00}$-O$_{2.80}$ to 500 °C [40]. The TGA experiments on samples with richer Dy contents ($0 < x < 0.5$) revealed the existence of a stable oxygen plateau near O$_{3.25}$-O$_{3.29}$, which could indicate the possible ordering of a new structural phase which we later identify as Hex1. Figure 3.6 (curve 1) shows a
**Figure 3.6:** TGA reduction of high pressure oxygenated Dy$_{0.7}$Y$_{0.3}$MnO$_{3+\delta}$ (curve 1) in 21% O$_2$ atmosphere with a heating rate of 1°C/min up to 375°C. Curve 2 shows an absorption/desorption TGA run for the same sample in high-purity O$_2$ with heating and cooling rates of 0.1°C/min. The Plateau at $\delta = 0.29$ corresponds to a stable structural phase, Hex1.

The TGA reduction run for the high-pressure oxygenated Dy$_{0.7}$Y$_{0.3}$MnO$_{3+\delta}$ sample. The reduction was conducted in 21% O$_2$ balanced with Ar, with heating rate of 1°C/min up to 375 °C. The plateau observed around ~ 300 °C (corresponding to oxygen content ~ O$_{3.29}$) is consistent with the stability of the oxygen content observed around O$_{3.29}$ in the absorption/desorption cycle (Figure 3.6, curve 2) for the same sample. The possible formation of a charge ordered phase of Dy$_{0.7}$Y$_{0.3}$Mn$_{0.4}^{3+}$Mn$_{0.6}^{4+}$O$_{3.29}$ should thus be considered. Preliminary structural analysis of the Hex1 phase using XRD data suggested general symmetry lowering as indicated by the increased number of Bragg peaks in Hex1 relative to the stoichiometric parent P6$_3$cm phase. Figure 3.7(a)
Figure 3.7(a): XRD patterns for Dy$_{0.7}$Y$_{0.3}$MnO$_{3+\delta}$ where $\delta = 0$ (top) and 0.29 (bottom) correspond to the P6$_3$cm and Hex1 phases, respectively. Splitting, shifts and increased number of peaks in Hex1 is indicative of general lowering in symmetry relative to the parent P6$_3$cm phase.
Figure 3.7 (b): Comparison of XRD patterns for both phases in the $2\theta = 26-34^\circ$ range.

depicts the XRD patterns for the parent P6$_3$cm Dy$_{0.7}$Y$_{0.3}$MnO$_3$ and the Hex1 Dy$_{0.7}$Y$_{0.3}$MnO$_{3.29}$ phases, respectively.

To help identify the set of new peaks corresponding to this new phase, an overlay of these patterns in the $2\theta = 26-34^\circ$ range is shown in Figure 3.7(b).

The relative similarity in the peak positions and intensities of the new phase to that of the parent structure suggests that Hex1 is structurally related to the parent material. However, a
Table 3.1: Comparison table of selected oxygen storage materials reported in literature [35],[48-50].

<table>
<thead>
<tr>
<th>Material</th>
<th>δ-Ox</th>
<th>OSC (µmol-O/g)</th>
<th>$T_{\text{Oxi}}$ (°C)</th>
<th>$T_{\text{red}}$ (°C)</th>
<th>*Cost ($/g$)</th>
<th>Toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBaCo$<em>4$O$</em>{7+δ}$</td>
<td>1.25</td>
<td>2178</td>
<td>300</td>
<td>420</td>
<td>0.061</td>
<td>Yes</td>
</tr>
<tr>
<td>YBaCo$<em>{3.4}$Al$</em>{0.3}$Ga$<em>{0.3}$O$</em>{7+δ}$</td>
<td>0.5</td>
<td>881</td>
<td>400</td>
<td>480</td>
<td>0.071</td>
<td>Yes</td>
</tr>
<tr>
<td>Ca$<em>2$AlMnO$</em>{5+δ}$</td>
<td>0.5</td>
<td>2065</td>
<td>300</td>
<td>650</td>
<td>0.002</td>
<td>No</td>
</tr>
<tr>
<td>YMnO$_{3+δ}$</td>
<td>0.14</td>
<td>730</td>
<td>150</td>
<td>290</td>
<td>0.056</td>
<td>No</td>
</tr>
<tr>
<td>DyMnO$_{3+δ}$</td>
<td>0.25</td>
<td>942</td>
<td>350</td>
<td>390</td>
<td>0.673</td>
<td>No</td>
</tr>
<tr>
<td>Dy$<em>{0.7}$Y$</em>{0.3}$MnO$_{3+δ}$</td>
<td>0.31</td>
<td>1274</td>
<td>250</td>
<td>360</td>
<td>0.527</td>
<td>No</td>
</tr>
</tbody>
</table>

*: Based on current pricing of metals available at mineralprices.com (2013).

lattice-sublattice crystallographic relationship is not necessary when dealing with two samples that are chemically different. Detailed structural analysis of all these single-phase samples is discussed in the following section.

Table 3.1 presents several selected oxygen storage materials reported in the literature along with their oxygen storage capacity measured in pure O$_2$. While the OSC of Dy$_{1-x}$Y$_x$MnO$_{3+δ}$ does not exceed the highest reported OSC value, the present system clearly has the lowest reported reduction temperature which is significantly lower than the best reported reduction temperature for YBaCo$_4$O$_{7+δ}$ (with high OSC value) and presents a key advantage towards the development of thermal swing applications for oxygen separation. Upon further comparison with YBaCo$_4$O$_{7+δ}$ which decomposes at a relatively low temperature of about 600 °C, Dy$_{1-x}$Y$_x$MnO$_{3+δ}$ has by far superior stability up to at least 1100 °C in air. Additionally, from the toxicity and cost point of view, manganites are preferred over the cobaltites. Unlike most OSC materials, the large change in Mn oxidation state in hexagonal Dy$_{1-x}$Y$_x$MnO$_{3+δ}$ does not rely
on the formation of oxygen-ion vacancies at elevated temperatures, but on the reversible phase transitions between several hexagonal structures with the metal ions in variable coordination which, in principle, could be optimized by suitable chemical substitution to allow for even better oxygen storage capacities and lower material costs. Optimization of properties of oxygen storage materials will be discussed in chapter 4.
3.2.2 Crystal Structural Analysis

As previously mentioned, the starting structural model used in the refinements of oxygen stoichiometric samples was that of the parent YMnO$_3$. The structure crystallizes in the hexagonal space group P6$_3$cm (N. 185), which we subsequently confirmed, through Rietveld refinements and using neutron powder diffraction data, as being appropriate for all the stoichiometric materials under investigation here. Typical best-fit Rietveld refinement plots are presented in Figures 3.8(a,b) for Dy$_{0.3}$Y$_{0.7}$MnO$_3$ and Dy$_{0.5}$Y$_{0.5}$MnO$_3$, respectively. Atomic coordinates, lattice parameters, site occupancies, atomic sites, and agreement factors obtained from the refinements are listed in Table A1 in the attached Appendix.

As expected, the monotonically changing values of the lattice parameters and unit cell volume correlate well with the average ionic size of the $R$-site; thus, confirming the formation of a continuous solid solution. Mn-O bond lengths are presented in Figure 3.9 together with their geometric $<\text{Mn-O}>_g$ average. Figure 3.9 shows that the apical (Mn-O1) and (Mn-O2) bond lengths are markedly shorter than the in-plane Mn-O bonds. This is in conformity with the 3$d^4$ electronic configuration of the Mn$^{3+}$ ion when in a non-degenerate high-spin state $e''^2 e'^2$ as expected in the trigonal-bipyramidal coordination.

Determining the crystal structure of the oxygen-loaded phase (Hex1) was proven to be challenging due to the complexity of this structure and the relatively poor quality of the collected NPD data which is intrinsically related to the presence of highly neutron absorbing dysprosium.
Figure 3.8.(a,b) Neutron powder diffraction patterns for \( \text{Dy}_{1-x} \text{Y}_x \text{MnO}_3 \) (\( x = 0.7 \) and 0.5). Star symbols represent the experimental data and the red solid line shows the calculated intensities. The blue solid line at the bottom shows the difference between the experimental data and the best fit obtained from the Rietveld refinement. Tick marks below the data show the location of the Bragg peaks.
The initial refinement trials for this structure were conducted for the Dy$_{0.7}$Y$_{0.3}$MnO$_{3.29}$ sample in the parent P6$_3$cm model while varying the lattice parameters in attempt to accommodate the extra oxygen ions. This attempt failed to index a significant number of the diffracted peaks in the NPD pattern. Satisfactory fitting results were achieved; however, after considering a superstructure model constructed by tripling the $c$-axis of the original stoichiometric cell, using the symmetry of the R3c space group (# 161). Our final refinement results of this superstructure are plotted in Figure 3.10 and the corresponding structural parameters listed in Table 3.2, along with reliability factors confirming the validity of this model.

Refinements of the cations and oxygen site occupancies showed that all the atoms except O1 are essentially full within one to three standard deviations; and thus indicating no sign of any cation vacancy formation. For these atoms, full site occupancies were then assumed and kept fixed in subsequent and final refinement cycles. On the other hand, the in-plane O1 refined site occupancy was surprisingly low even when we successfully determined the location of the excess oxygen O6, Figure 3.11. The resulting refined oxygen occupancies reflect a total oxygen content of O$_{3.31}$ for our sample, which is in reasonable agreement with the measured value O$_{3.29}$ in TGA experiments.

Our refinement results also identify the in-plane site O6 as preferred intercalation site of the oxygen ion over the other possible apical sites. This preference may be rationalized following arguments described in references [40],[51] related to the coordination requirements of the $R$ and Mn cations.
Figure 3.9: Mn-O bond lengths and $<\text{Mn-O}>$ and $<R\text{-O}>$ geometric averages ($R = \text{Y and Dy}$) for $\text{Dy}_{1-x}\text{Y}_x\text{MnO}_3$. Error bars are within the symbols.

Figure 3.10: Neutron powder diffraction pattern for $\text{Dy}_{0.7}\text{Y}_{0.3}\text{MnO}_{3.29}$. Star symbols represent the experimental data and the red solid line shows the calculated intensities. The blue solid line at the bottom shows the difference between the experimental data and the best fit using R3c as obtained from the Rietveld refinements. Tick marks below the data show the location of the superstructure Bragg peaks.
### Table 3.2: Atomic coordinates, space group, lattice parameters, site occupancies, thermal factors, and agreement factors for the oxygenated sample Dy$_{0.7}$Y$_{0.3}$MnO$_{3.29}$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>n</th>
<th>$U_{iso}$ ($\text{Å}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy1/Y1</td>
<td>6a</td>
<td>0</td>
<td>0</td>
<td>-0.0819(4)</td>
<td>0.7/0.3</td>
<td>-0.002(9)</td>
</tr>
<tr>
<td>Dy2/Y2</td>
<td>6a</td>
<td>0</td>
<td>0</td>
<td>0.0944(3)</td>
<td>0.7/0.3</td>
<td>-0.003(6)</td>
</tr>
<tr>
<td>Dy3/Y3</td>
<td>6a</td>
<td>0</td>
<td>0</td>
<td>0.2345(7)</td>
<td>0.7/0.3</td>
<td>0.001(3)</td>
</tr>
<tr>
<td>Mn</td>
<td>18b</td>
<td>0.2749(9)</td>
<td>-0.0477(6)</td>
<td>0</td>
<td>1</td>
<td>0.033(2)</td>
</tr>
<tr>
<td>O1</td>
<td>6a</td>
<td>0</td>
<td>0</td>
<td>0.1669(3)</td>
<td>0.578</td>
<td>0.082(9)</td>
</tr>
<tr>
<td>O2</td>
<td>6a</td>
<td>0</td>
<td>0</td>
<td>0.9931(2)</td>
<td>1</td>
<td>0.027(6)</td>
</tr>
<tr>
<td>O3</td>
<td>6a</td>
<td>0</td>
<td>0</td>
<td>0.3380(9)</td>
<td>1</td>
<td>0.058(7)</td>
</tr>
<tr>
<td>O4</td>
<td>18b</td>
<td>0.2943(3)</td>
<td>-0.0295(7)</td>
<td>0.0481(9)</td>
<td>1</td>
<td>-0.006(7)</td>
</tr>
<tr>
<td>O5</td>
<td>18b</td>
<td>0.0051(8)</td>
<td>0.3159(5)</td>
<td>0.2757(2)</td>
<td>1</td>
<td>0.013(6)</td>
</tr>
<tr>
<td>O6</td>
<td>18b</td>
<td>0.2787(2)</td>
<td>0.3972(7)</td>
<td>0.3281(1)</td>
<td>0.483</td>
<td>0.035(2)</td>
</tr>
</tbody>
</table>

Lattice parameters ($\text{Å}$)

- $a = 6.2253(6)$, $c = 33.2426(9)$
- $V(\text{Å}^3) = 1115.7228 (7)$

Reliability factors

- $R_p = 5.89\%$, $R_{exp} = 5.15\%$, $\chi^2 = 2.554$  

Based on these arguments, the competing coordination sites of $R$ and Mn result in intercalating oxygen ions from in-plane sites, where oxygen is strongly attached to manganese and weakly bonded to dysprosium/yttrium.
Table 3.3: Bond Valence Sums (BVS) calculated for the Anion sites of $\text{Dy}_{0.7}\text{Y}_{0.3}\text{MnO}_{3.29}$.

<table>
<thead>
<tr>
<th>Anions</th>
<th>O1</th>
<th>O2</th>
<th>O3</th>
<th>O6</th>
<th>Apical Sites</th>
<th>O4</th>
<th>O5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn (BVS)</td>
<td>0.52</td>
<td>1.89</td>
<td>1.77</td>
<td>1.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dy/Y (BVS)</td>
<td>0.57</td>
<td>0.28</td>
<td>0.19</td>
<td>0.26</td>
<td></td>
<td>1.23</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Our Bond Valence Sum (BVS) [52] evaluation of the anion sites for $\text{Dy}_{0.7}\text{Y}_{0.3}\text{MnO}_{3.29}$ (see Table 3.3) is in accord with our observations in the oxygen refinements. BVS analysis was also conducted for the Mn cations with 5-fold and 8-fold coordinations as identified in the P6$_3$cm and R3c structures, respectively.

Figure 3.11: Portion of the R3c superstructure in the $c$ range $= 0.27611 - 0.42829$ showing the oxygen ion intercalation site (O6) in the $a$-$b$ plane around the Mn sites.
Table 3.4: Bond valence sum analysis calculated for Mn ions using 5-fold and 8-fold coordinations for P6\(_{3}\)cm and R3c crystal structures, respectively. \(r_0\) values were taken from ref [52], where \(r_{01}\), \(r_{02}\), and \(r_{03}\) are the tabulated parameters for Mn\(^{2+}\), Mn\(^{3+}\), and Mn\(^{4+}\), respectively.

<table>
<thead>
<tr>
<th>P6(_{3})cm ((\delta = 0))</th>
<th>5-Fold coordinated Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Dy}_{1-x}\text{Y}_x\text{MnO}_3^{3+}\delta)</td>
<td>(r_{01} = 1.790(3) \text{ Å})</td>
</tr>
<tr>
<td>(x = 0)</td>
<td>3.1671(78)</td>
</tr>
<tr>
<td>(x = 0.3)</td>
<td>3.0007(50)</td>
</tr>
<tr>
<td>(x = 0.5)</td>
<td>3.0989(35)</td>
</tr>
<tr>
<td>(x = 0.7)</td>
<td>3.0858(81)</td>
</tr>
<tr>
<td>(x = 1)</td>
<td>3.0796(94)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R3c ((\delta = 0.29))</th>
<th>8-Fold coordinated Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Dy}_{1-x}\text{Y}_x\text{MnO}_3^{3+}\delta)</td>
<td>(r_{01} = 1.790(3) \text{ Å})</td>
</tr>
<tr>
<td>(x = 0.3)</td>
<td>3.5187(91)</td>
</tr>
</tbody>
</table>

Possible manganese oxidation states are listed in Table 3.4. Bond lengths obtained from NPD refinements were used in the calculations.
3.2.3 Magnetic Measurements

Although oxygen storage properties are the primary subject of this work, we find it necessary to put the magnetic (this section) and the transport (next section) oxygen-content dependent properties of these oxides under the scope. \( \text{RMnO}_3 \) ceramics are one of the most heavily researched materials for their multiferroic characteristics. Interesting coupling between magnetic and ferroelectric order parameters has been discovered in these materials. Therefore, a complete characterization of these important ceramic compounds was intended in which new, interesting properties may be discovered.

Magnetic measurements were performed on stoichiometric hexagonal Dy\(_{1-x}\)Y\(_x\)MnO\(_3\) (\( x = 0 \) and 0.5) samples air-quenched from 400 °C. Zero field-cooled (ZFC) and field-cooled (FC) measurements collected in the temperature range 2-400 K under an applied magnetic field of \( H = 1 \) kOe are presented in Figure 3.12 (a, b) and magnified around the low-temperature phase transition temperatures in Figure 3.13. A transition at \( T = 8 \) K is visible as a local minimum in the magnetization temperature derivative, \( dM/dT \), (see inset of Figure 3.12(a)) for DyMnO\(_3\), which is presumably a ferrimagnetic transition of Dy\(^{3+}\) ions, as described in Ref. [43], in contrast to the perovskite DyMnO\(_3\) which is antiferromagnetic below 9.5 K [53]. For Dy\(_{0.5}\)Y\(_{0.5}\)MnO\(_3\), this transition is observed at \( T_C \sim 4 \) K (see: inset of Figure 3.12(b)). Additional magnetic transitions have been reported for hexagonal DyMnO\(_3\) in the intermediate temperature phase at \( T_N \sim 68 \) K [54] related to the antiferromagnetic ordering of Mn\(^{3+}\) spins, and at \( T_{SR} \sim 40 \) K suggested to be related to a possible spin reorientation of the Mn\(^{3+}\) ions similar to what has been reported for the hexagonal HoMnO\(_3\) multiferroic prototype [55]. A different transition has
Figure 3.12.a: “zero-field-cooled” (ZFC) and “field-cooled” (FC) magnetization for DyMnO$_3$ measured in $H = 1$ kOe in the temperature range 2-400K. The insets, in each panel, show the temperature dependence of the inverse molar susceptibility and the temperature derivative of magnetization for each sample.

been found at $T_N \approx 70$ K for hexagonal HoMnO$_3$ attributed to Mn$^{3+}$ magnetic ordering [55]. The anticipated anomalies in dc susceptibility in the paramagnetic region associated with those transitions are hardly visible in our data for Dy$_{1-x}$Y$_x$MnO$_3$. It is possible that the reported 40 K transition may be the signature of potential impurities such as Mn$_3$O$_4$, for example, which exhibits a ferrimagnetic behaviour at $T \sim 42$ K [40].
Figure 3.12.b: “zero-field-cooled” (ZFC) and “field-cooled” (FC) magnetization for Dy<sub>0.5</sub>Y<sub>0.5</sub>MnO<sub>3</sub> measured in H = 1 kOe in the temperature range 2-400K. The insets, in each panel, show the temperature dependence of the inverse molar susceptibility and the temperature derivative of magnetization for each sample.

Our XRD measurements showed no trace of this oxide in any of our samples. Neutron data need to be collected at the temperature range 3-70 K to determine the exact ordering of the Mn and Dy magnetic sublattices. We note, however, that Nandi et. al. determined six possible magnetic representations using element-specific x-ray resonant magnetic scattering technique to be compatible with the P6<sub>3</sub>cm structure of DyMnO<sub>3</sub> [44]. They suggest the low-temperature phase magnetic representation Γ<sub>3</sub> (P6’<sub>3</sub>cm’) for Dy<sup>3+</sup> spins in the hexagonal c-direction, and the Γ<sub>6</sub> (P6<sub>3</sub>) representation for the spins aligned in the ab plane.
Figure 3.13: “zero-field-cooled” (ZFC), “field-cooled” (FC) and remanent (rem) magnetization (open symbols) for DyMnO$_3$ and the FC magnetization for Dy$_{0.5}$Y$_{0.5}$MnO$_3$ (filled symbols).

Isothermal magnetization measurements at $T = 2$ K show small hysteresis consistent with weak ferrimagnetism superimposed on a paramagnetic field dependence background roughly following the Brillouin function, Figure 3.14. The data suggest that only part of Dy$^{3+}$ ions are ferrimagnetically ordered. The effect of dilution of Dy magnetism with the nonmagnetic yttrium on the isothermal magnetization is also observed; for Dy$_{0.5}$Y$_{0.5}$MnO$_3$ both the high field magnetization and coercivity field are close to half of their respective values for DyMnO$_3$. 
Figure 3.14: Isothermal magnetization of DyMnO$_3$ and Dy$_{0.5}$Y$_{0.5}$MnO$_3$ at T=2 K.

The temperature dependence of the molar susceptibility for Dy$_{1-x}$Y$_x$MnO$_3$ (see insets of Figure 3.12), in the temperature range 100 – 395 K was analyzed using the modified Curie-Weiss (CW) law: $\chi = \frac{C}{T-\theta} + \chi_o$ (where $C$, $\chi_o$, and $\theta$ represent the Curie constant, background susceptibility, and Curie-Weiss temperature, respectively). The deviation from the Curie-Weiss law below 100 K could indicate the presence of fluctuations related to a two-dimensional short range magnetic ordering [56].

The effective paramagnetic moment $\mu_{\text{eff}}$ was calculated from the fit using the formula $\mu_{\text{eff}} = 2.828 \, \text{C}^{1/2}$, Figure 3.15. The experimental magnitudes of $\mu_{\text{eff}}$ correspond reasonably well to the
Figure 3.15: The values of the effective paramagnetic moment $\mu_{\text{eff}}$ versus $x$ in $\text{Dy}_{1-x}\text{Y}_x\text{MnO}_3$. The solid line represents the calculated $\mu_{\text{eff}}$ for Dy$^{3+}$ and Mn$^{3+}$.

Nominal values calculated for Dy$^{3+}$ ($\mu_{\text{eff}}^{\text{Dy}} = 10.6 \, \mu_B$) and Mn$^{3+}$ ($\mu_{\text{eff}}^{\text{Mn}} = 4.9 \, \mu_B$) using the formula $\mu_{\text{eff}}^2 = (1-x)(\mu_{\text{eff}}^{\text{Dy}})^2 + (x)(\mu_{\text{eff}}^{\text{Mn}})^2$ (presented in Figure 3.15 as a solid line). The Curie-Weiss temperature is generally independent of $x$ and roughly equal to -20 K, which points to weak antiferromagnetic interactions in the paramagnetic state.
As was previously discussed in section 1.2.4, the development of a dependable electrochemical fuel-cell highly depends on the growth of a suitable electrolyte material. An ideal electrolyte is the conductor of a single ion (typically $\text{O}^{2-}$ or $\text{H}^+$) and electronic insulator. It passes an ionic current inside the cell that equals an electronic current flowing in an external circuit between the two electrodes of the cell. Typically the electrolyte is exposed to air on the cathode side and hydrogen on the anode side. The electrolyte thus has to be chemically stable in a wide range of oxygen pressures. Cathode material, on the other hand, must be good ionic and electronic conductor. The voltage across the two sides of the electrolyte $V_o$ is related to the difference in the oxygen free energy $\Delta G$ across the opposite sides which is intrinsically related to the oxygen chemical potential:

$$V_o = -t_o/(nF) \Delta G$$

$t_o$ : the transport number

$F$ : Faraday’s constant

$n$ : the number of electrons involved in the redox reaction

The transport number represents the fraction of the total conductivity of the electrolyte that is due to the ionic conduction. Electronic conductivity adds to the voltage drop across the electrolyte, and hence; a good electrolyte material must have a transport number $t_o \sim 1$. A typical polarization curve in a solid oxide fuel cell is presented in Figure...
3.16(a) (taken from reference [57]). The voltage loss \( \eta(I) \) increases with the current at different rates as illustrated in the figure. The voltage drops illustrated in regions (i) and (iii) correspond to the activation energy required to overcome the barrier to mass transfer through the electrolyte and to the inability of the reactants to diffuse fast enough to sustain the current in the depletion region, respectively. The slope of the curve in region (ii) represents the area resistance (the bulk resistance per area = \( L/\sigma \), where \( L \) and \( \sigma \) represent the electrolyte’s spacing and conductivity, respectively) of the electrolyte material.
Although electronic and ionic conductivities may follow the same behavior and yield similar temperature curves, the two phenomena are intrinsically different in nature. Electronic conductivity $\sigma_e$ was found to be achieved through different mechanisms depending on the type of the material under investigation. Phonon-assisted, small polaron conduction, and semiconducting behavior are three exemplary models through which electronic conduction has been explained in distinct classes of materials. It mainly depends on the electronic band structure of the material under investigation. Ionic conductivity $\sigma_i$, on the other hand, is related to the crystal structure and to the order-disorder transition abilities of the investigated materials. In general, electronic insulators exhibit large energy gap $E_g$ separating the valence-band from the conduction-band. Moreover, in contrast to electronic conductors, the conductivity of semiconductors, for example, increases with the increasing temperature as more electrons are gaining enough kinetic (thermal) energy to overcome the energy gap, and therefore; to reach the conduction state. In analogy, the energy $\Delta H_g$ required to excite an ion into the available vacancy or interstitial sites of the ionic insulator material is large. The ionic conductivity is given by Ohm’s law where the electrolyte resistance $R = L / (\sigma_i A)$ is proportional to the ratio of its thickness $L$ to its area $A$. Therefore, the choice of ceramics over other liquid or polymer candidate materials for electrolytes have the advantage of synthesis flexibility to systematically fabricate a ceramic membrane with the desired mechanical strength while minimizing the ratio $L/A$ to reduce resistivity. In ionic conductors, the diffusivity “mobility” of the ions is given by the Nernst-Einstein equation $\mu_i = qD / (kT)$, where $q$, $k$, and $T$ represents the charge, Boltzmann’s constant, and the absolute temperature, respectively, while $D$ is the diffusion coefficient which contains the motional free energy for an ion jump. It follows that: $\sigma_i = (B/T) e^{E_a/kT}$ where $E_a$ is the activation energy as given by the Arrhenius equation.
We have investigated several compositions of DyIn$_{1-x}$M$_x$O$_3$ ($M = \text{Ni, Mn, and Co}$) to study the effect of $M$ doping on the transport properties through its influence on the distortion and band structure of the trigonal-bipyramidal TBP polyhedra of the original host hexagonal oxide. Geometric ferroelectricity was discovered in hexagonal $RMnO_3$ ($R = \text{Rare-earth cation}$) and was attributed to the alternating $R$-O bond lengths along the c-axis of the structure. Moreover, the cooperative tilting of the TBP and the different apical Mn-O bond lengths along the c-direction enhanced the ferroelectric order parameter in these structures. Indium commonly
exists with fixed oxidation state as In$^{3+}$ ion. Manganese Mn and cobalt Co, on the other hand, are known to exhibit both 3+ and 4+ oxidation states, while Ni is usually in 2+ or 3+ oxidation states. Single phase hexagonal samples of DyIn$_{1-x}$M$_x$O$_3$ were achieved over different solubility ranges, see figure 3.17 for XRD patterns for M = Ni, Mn, and Co.

Figure 3.18 represents high-temperature impedance spectroscopy performed on selected samples of hexagonal DyInO$_3$, DyIn$_{0.9}$Co$_{0.1}$O$_3$, DyIn$_{0.9}$Ni$_{0.1}$O$_3$, and DyIn$_{0.75}$Mn$_{0.25}$O$_3$ to determine their total conductivities in the temperature range 25-800 °C. The natural logarithm of the measured conductivity was modeled as a function of the inverse-temperature for our samples.
Table 3.5: Activation energies in their respective temperature ranges based on the fitted conductivity data.

<table>
<thead>
<tr>
<th>Material</th>
<th>Activation Energy $E_a$ (eV)</th>
<th>Temperature range ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DyInO$_3$</td>
<td>1.91</td>
<td>480-800</td>
</tr>
<tr>
<td>DyIn$<em>{0.9}$N$</em>{0.1}$O$_3$</td>
<td>1.28</td>
<td>400-680</td>
</tr>
<tr>
<td>DyIn$<em>{0.75}$Mn$</em>{0.25}$O$_3$</td>
<td>1.10</td>
<td>320-720</td>
</tr>
<tr>
<td>DyIn$<em>{0.9}$Co$</em>{0.1}$O$_3$</td>
<td>0.47</td>
<td>100-580</td>
</tr>
</tbody>
</table>

using a model similar to the semiconducting behavior. High-quality fits yielded for all the investigated samples in which activation energies were determined from the slopes. The activation energy was found to decrease from the undoped material DyInO$_3$ to the slightly doped one. The doping of Ni, Co, or Mn on the indium sites could have possibly created either mobile interstitial or mobile vacancy sites, and therefore; reducing the ionic motional enthalpy within the structure of the doped materials in contrast to the suppressed ionic motion by the ionic ordering in DyInO$_3$. No sharp first-order transitions in those curves were observed, but smooth continuous transitions to fast ionic conduction illustrating a complex order-disorder phenomenon in these compounds. With the introduction of Ni, Co, and Mn transition ions on the indium sites, there is possibility for the electronic contribution to the measured conductivity of the investigated samples. From the observed data, it is clear that if there was any contribution of electronic conductivity it would be rather small as the impedance data for the doped and undoped
materials is relatively similar, suggesting that ionic conductivity is the dominant component of the measured total conductivity.

Surprisingly, intense bright blue color was observed over much of the DyIn\(_{1-x}\)Mn\(_x\)O\(_3\) solid-solution range when Mn was introduced on the original In sites. The end compounds of this solid solution, DyInO\(_3\) and DyMnO\(_3\), are white and black in color, respectively. At doping manganese levels of < 0.1, light blue color was obtained for the sample. The intensity (darkness) of this blue color was found to increase as a function of the increasing Mn doping level. To understand this behavior, two detailed features of the isostructural hexagonal DyInO\(_3\) and DyMnO\(_3\) must be taken into account. While the basal Mn-O bond lengths are significantly longer than the apical Mn-O bonds in their trigonal-bipyramidal TBP structure, all the In-O bonds are essentially equal in length within the experimental error. In DyMnO\(_3\), crystal stabilization is achieved in the TBP geometry when the Mn\(^{3+}\) degenerate 3d\(^4\) orbitals are split into three sets a’ (d\(_{z^2}\)), e’ (d\(_{x^2-y^2}\), d\(_{xy}\)), and e” (d\(_{xz}\), d\(_{yz}\)) in a high-spin e’\(^2\) e”\(^2\) state, which results in compressed apical (Mn-O) bond lengths relative to the longer basal (Mn-O) bonds in which the electrons experience stronger repulsive force, see figure 4.1. In the bigger In\(^{3+}\) configuration, the d\(_{z^2}\) orbitals are filled, and hence; longer apical In-O bond lengths are expected relative to the apical Mn-O bonds where manganese d\(_{z^2}\) orbitals are unoccupied. The e’ \(\rightarrow\) a’ energy splitting depends on the length of the apical Mn/In-O bond through its influence on the d\(_{z^2}\) orbital. Hence; by introducing the Mn\(^{3+}\) on the In\(^{3+}\) trigonal-bipyramidal sites of the host material, a new manganese 3d\(_{z^2}\) orbital is introduced in the energy-gap of the In band structure. Subramanian et al [58], reported the same blue colors in hexagonal YIn\(_{1-x}\)Mn\(_x\)O\(_3\). They attributed the absorbance peak around \(\sim 2\text{eV}\) in their diffuse reflectance measurements on lightly Mn doped YInO\(_3\) to the transition between the valence-band maximum e’ and the lowest unoccupied energy level a’ that
lies in the band gap of YInO$_3$. It is the absence of this mid-gap energy level in pure YInO$_3$ that leaves it colorless (white). By increasing the Mn$^{3+}$ doping level in DyInO$_3$, the mid-gap narrow band formed from the Mn 3 d$_{z^2}$ orbitals is broadened, and thus, the observed blue color is darkening.
3.3 Conclusion

We have successfully prepared a solid solution of Dy\(_{1-x}Y_x\)MnO\(_3\) materials under reduced oxygen pressure conditions that favor the formation of a hexagonal phase over its perovskite counterpart. This is in agreement with our tolerance factor rules and the (Mn-O) bond-lengths dependence on the oxygen content, where reducing conditions are necessary to elongate the manganese bonds enough to bring the tolerance factor below the (0.855) limit. Room temperature bond lengths derived from NPD data for oxygen stoichiometric samples were found to be consistent with the non-degenerate high-spin state \(e''^2e'^2\) of Mn\(^{+3}\) in trigonal-bipyramidal coordination where the compressed apical bond lengths are considerably shorter than the in-plane bonds. Our hexagonal materials exhibit large oxygen storage/release capabilities (within about 2.7% by weight) at exceptionally low oxidation/reduction temperatures of ~ 200-400 °C. These properties reveal the potential for low-cost thermal swing absorption processes for oxygen separation from air. A phase transition to the oxygen-loaded R3c superstructure was observed to take place for \(\delta \sim 0.29\) in the Dy-rich samples. Structural analysis using NPD and XRD allowed us to determine the location of the extra oxygen atoms O6 that occupy one of the previously empty in-plane triangular sites in the parent structure. At low temperatures, our magnetic data indicates the formation of magnetic Dy sublattice at ~ 8 K and ~4 K for DyMnO\(_3\) and Dy\(_{0.5}\)Y\(_{0.5}\)MnO\(_3\), respectively. The magnetic properties are diluted by the partial substitution of non-magnetic yttrium at the magnetic Dy sites in Dy\(_{1-x}Y_x\)MnO\(_3\). In transport measurements, the activation energy was found to decrease from the undoped material DyInO\(_3\) to the slightly doped one. The doping of Ni, Co, or Mn on the indium sites could have possibly created either mobile...
interstitial or mobile vacancy sites, and therefore; reducing the ionic motional enthalpy within the structure of the doped materials in contrast to the suppressed ionic motion by the ionic ordering in DyInO$_3$. Further optimization of properties is necessary for this system of oxygen storage material; either by increasing the OSC or by decreasing the oxygenation-reduction temperature range in the thermogravimetric cycle. Moreover, as was previously established in table 3.1, the high cost of dysprosium makes this system unattractive for future implementation as sorbent beds for thermal swing adsorption applications, thus; the search for a less expensive new rare-earth element to substitute for the Dy while developing the previously achieved results may be crucial for complete adaptation of these oxygen storage materials. In the next chapter, we discuss the optimization of properties and controlling of structural and physical behavior of the previously achieved hexagonal Dy$_{1-x}$Y$_x$MnO$_{3+\delta}$ system by controlling the chemical variables and synthesis conditions.
CHAPTER 4: OPTIMIZATION OF DESIGN-PROPERTY RELATIONSHIP IN HEXAGONAL AND PEROVSKITE $Y_{1-x}R_xMn_{1-y}E_yO_{3+\delta}$ ($R = \text{La, Pr, Tb, Ce, Er, Dy, Sr}$; and $E = \text{Fe, Co, In, Ru}$) FOR OXYGEN STORAGE APPLICATIONS

4.1 Introduction

The family of rare-earth manganites $RMnO_{3+\delta}$, ($R$ is Rare-Earth or Y) in both hexagonal and perovskite structures has increasingly attracted significant attention over the past few years [27]. These materials exhibit fascinating physical properties including charge and orbital ordering [59], colossal magnetoresistance [8], multiferroicity [11], and insulator to metal transitions [9]; in response to an elaborate interaction between orbital, magnetic, charge, and structural degrees of freedom. In chapter three, large changes of oxygen contents $\delta = 0 - 0.4$ at slightly elevated temperatures of $T = 200 - 400 \degree C$ were shown for hexagonal manganites $Dy_{1-x}Y_xMnO_{3+\delta}$, which can sensitively affect the physical properties and are suggestive of superior oxygen storage/release capacities (OSC) for prospective industrial oxygen-separation applications from air [60].

With more than 100 million tons of O$_2$ separated annually from air for industrial uses [61], the development of a functional oxygen storage and carrier material is crucial to efficiently keep up with the expanding demand for pure O$_2$, and for the advancement of important technologies. Hexagonal manganites have proven their definite potential to compete with the currently employed cryogenic distillation [62] and pressure swing adsorption technologies [63].
for the commercial production of high purity oxygen by reversible oxidation/reduction processes at atmospheric conditions. They present several advantages over other important candidates reported in the literature such as the fluorite Ce$_{1-x}$Zr$_x$O$_{2+\delta}$, YBaCo$_{3.4}$Al$_{0.3}$Ga$_{0.3}$O$_{7+\delta}$, and Ca$_2$AlMnO$_{5+\delta}$ [60].

The non-centrosymmetric hexagonal $P6_3cm$ structure of rare-earth manganites $RMnO_3$ is described as layers of corner-shared MnO$_5$ trigonal-bipyramids (TBP), separated by layers of 8-fold coordinated $R^{3+}$ cations [60] as shown in the top part of Figure 4.1. The 3d$^4$ orbitals in hexagonal manganites are split into three sets a’ (d$_z^2$), e’ (d$_{x^2-y^2}$, d$_{xy}$), and e” (d$_{xz}$, d$_{yz}$) in a high-spin e’$^2$e”$^2$ state as shown in the figure. The apical Mn-O bond length significantly affects the e’-a’ energy splitting through its influence on the d$_z^2$ orbital. This energy splitting can explain the interesting colors observed in Mn-doped hexagonal ABO$_3$ compounds.

On the other hand, crystal stabilization is achieved differently for the 6-fold coordinated Mn$^{3+}$ ions in the perovskite orthorhombic $Pbnm$ structure, as described in Fig. 1 (bottom). In that electronic configuration, the energy gap ($\Delta_c$) between the two sets of 3d orbitals is typically of the order 2-3 eV, which is larger than predicted by the ionic model of crystal field theory in which the energy difference between transition metal $d$ orbitals is attributed to the resultant electrical potentials of a point-like negative charges of the surrounding oxygen ions. This energy gap, however, is better explained using the ligand field theory model in which interactions between the metal and the surrounding ligands are covalent in nature, resulting in some degree of orbital overlapping within the octahedral complex.
Figure 4.1: Schematic drawings of the hexagonal (top) and perovskite (bottom) RMnO$_3$ rare-earth manganites with their corresponding Mn$^{3+}$ 3d orbital configurations.

Moreover, the non-polar lattice distortions in these materials; such as the cooperative tilt of the manganese polyhedra and the buckling of the R-O planes, induce ferroelectricity which persists at elevated temperatures up to $T_c \sim 573 - 923$ K. The rare coexistence of antiferromagnetic and ferroelectric order parameters makes these compounds of particular interest. Complex long-range magnetic orderings associated with the Mn$^{3+}$ and $R^{3+}$ cations were reported to occur at relatively low temperature ranges. The magnetic spins associated with the manganese sublattice were found to order in a frustrated triangular antiferromagnetic structure at
Neel temperature $T_N \sim 70 - 130$ K where each spin is rotated by $90^\circ$ from its nearest neighbor in the a-b plane. The magnetic ordering associated with the $R^{3+}$ was found to occur at lower temperatures $\sim 5-10$ K depending on the type of the rare-earth element [64-68].

In the previous chapter, we discussed the synthesis and oxygen content dependent properties of hexagonal $\text{Dy}_{1-x}\text{Y}_x\text{MnO}_{3+\delta}$ where we confirmed through x-ray diffraction (XRD) and thermogravimetric (TG) measurements the formation of two new structural phases denoted as Hex1 and Hex2 at $\delta \sim 0.25$ and $\delta \sim 0.39$, respectively. Analysis of the x-ray and neutron diffraction (NPD) data using Rietveld refinements for the Hex1 phase indicated the formation of a large superstructure by tripling the $c$-axis of the original $P6_3cm$ unit cell. Modeling of the Hex1 superstructure was successful in a structural symmetry consistent with the noncentrosymmetric space group $R3c$ (#161). However, the presence of highly neutron absorbent Dy and the inherent low sensitivity of x-rays for light elements such as oxygen resulted in relatively low quality refinements from NPD and XRD measurements, respectively. In this chapter, we elaborate on the synthesis of high quality single-phase oxygen-loaded samples of $R\text{MnO}_{3+\delta}$ in the Hex1 and Hex2 structures for $R = \text{Ho, Er, and Y}$, having significantly smaller neutron absorption cross sections than Dy. Detailed results of their oxygen content, NPD structural, and magnetic properties are discussed. Moreover, we embark on the results of a systematic chemical doping performed on the A and B sites ($\text{ABO}_{3+\delta}$) of the original $\text{Dy}_{1-x}\text{Y}_x\text{MnO}_{3+\delta}$ oxygen storage system which was executed in an attempt to optimize the design-property relationship of this oxygen storage system; primarily by lowering the oxygenation-reduction temperature range necessary for the thermal swing adsorption process, and also, by increasing the oxygen storage capacity OSC exhibited in these materials. Dilatometry measurements were also carried out for selected
samples to determine both their thermal (TLC) and chemical (CE) expansion coefficients. Thermal and chemical expansion data are necessary for a successful design of the cathode and electrolyte materials utilized in important technologies such as fuel-cells. Further exploration of these materials was initiated for selected samples in the tolerance factor \((t) > 0.855\) region, where samples are no longer in the hexagonal P6\(_3\)cm form but crystallized in the perovskite structure. Thin films of perovskite strontium ruthenate (SRO) were achieved using pulsed laser deposition (PLD) technique in an attempt to study the reduced dimensionality, and the geometrical confinement and physical proximity effects of these important superconductors.
4.2 RESULTS AND DISCUSSION

4.2.1 Oxygen Storage Capability of RMnO$_{3+\delta}$ (R = Y, Ho, and Er)

To keep track of changes in the thermogravimetric characteristics of the new samples relative to the old Dy$_{1-x}$Y$_x$MnO$_{3+\delta}$ system, the YMnO$_{3+\delta}$ sample was included here as a reference. To demonstrate the dependence of oxygen content on temperature, and therefore to measure the OSC in oxygen-rich atmospheres, the as-made P6$_3$cm samples were initially annealed up to 500 °C in a TGA thermobalance and then cooled to room temperature with slow heating and cooling rates of 0.1 °C/min (see Figure 4.2). A clear absorption/desorption behavior is observed on the TGA curves to take place within an exceptionally low and narrow temperature range between ~180 and up to 320 °C. Samples begin absorbing oxygen upon heating around 180 °C, achieve maximum oxygen content around 240 - 290 °C and then rapidly desorb oxygen, resulting in stoichiometric compositions above the reduction temperature $T_{\text{red}}$ of 260, 290, and 320 °C for Er, Y and Ho, respectively. All materials quenched in separate experiments from temperatures above $T_{\text{red}}$ were found to exhibit the single-phase P6$_3$cm structure as verified by XRD.

Upon cooling, absorption of oxygen starts below 220, 260, and 300 °C for Er, Y and Ho, respectively. It proceeds over a short temperature range to reach the stabilized oxygen-loaded phases at $T_{\text{oxi}}$ of 150, 160, and 190 °C for Er, Y and Ho, respectively.
Figure 4.2: Temperature dependence of oxygen content for RMnO$_{3+δ}$ (R = Er, Ho, and Y) with heating (a) and cooling (b) rates of $0.1^{\circ}C/min$ in $O_2$. $T_{red} - T_{oxi}$ represents the temperature range utilized in Thermal Swing Absorption process for air separation.
Below $T_{\text{oxi}}$, the samples remain relatively constant in their oxygen content upon further cooling probably due to kinetic reasons. Noticeably, the amount of excess oxygen intake is strongly dependent on the $R^{3+}$ ionic size of $R\text{MnO}_{3+\delta}$ and the resulting OSC increases considerably even for very small increases in $R^{3+}$ ionic size; from 111 μmol-O/g for Er (0.951Å) to 678 μmol-O/g for Y (0.963Å) and 1083 μmol-O/g (or 1.73% by weight) for Ho (0.967Å) [see discussion of figure 4.14 for details on ionic radii]. Such a strong dependence on the ionic size of $R^{3+}$ is also consistent with our previous results for $\text{Dy}_{1-x}\text{Y}_x\text{MnO}_{3+\delta}$ showing a very strong correlation between the increase of the excess oxygen intake and the average ionic size of Dy and Y [60]. TGA data indicate that the initial oxygen content of the as-made samples obtained by natural cooling in air is only slightly above 3 meaning that the final oxygen content of samples obtained from high temperature synthesis is strongly dependent on the cooling rate and oxygen atmosphere as well as the ionic size of $R^{3+}$ and possibly on the sample’s grain size, porosity and morphology. However, electron microscopy images presented in Figure 4.3 show no significant differences in the investigated samples morphology that could have accounted for possible variations in the specific surface area of the grains and the solid-state diffusion length of oxygen among our samples, and consequently, this possibility was ruled out.

The absorption/desorption kinetics of the excess oxygen ions also shows clear dependence on the ionic size of the $R$ cations as indicated by the increasing slope $\frac{d(\text{Oxy. Cont.})}{dT}$ in the TG curve. This trend of enhanced oxygen absorption/desorption amounts and rates, in samples with larger $R$ ionic size could be attributed to the increased distortion of the
Figure 4.3: Scanning electron microscopy (SEM) images at 5 μm scale for $R\text{MnO}_3$ samples with $R = \text{Ho}, \text{Y}$, and $\text{Er}$ in (a), (b) and (c), respectively. (d) Typical sample morphology at 50 μm for $\text{YMnO}_3$.

stoichiometric P6$_3$cm phase caused by the increasing ionic size of the $R^{+3}$ cations. Since the oxygen ion diffusion is a function of temperature and activation energy [69], a direct comparison of the absorption/desorption rates for these samples is not rigorous, knowing that the absorption/desorption occur at different temperatures for the different samples. Yang et al [70],
on the other hand, showed that the time rates required to achieve equilibria in the redox reactions involved in the perovskite strontium-doped lanthanum manganites are intrinsically related to the thermodynamic order parameters, where reactions of lowest reduction enthalpy achieved the highest reduction rates. It’s similarly possible that the observed differences in our samples’ kinetics could be attributed to differences in their reduction and oxygenation enthalpies. It is not possible, however, to derive these thermodynamic parameters from our data as it reflects the temperature dependence of oxygen content rather than the oxygen partial pressure dependence necessary to provide the Arrhenius plot.

In order to measure the OSC achieved under high-pressure oxygen atmosphere, samples were annealed under 190 bar of oxygen at 400 °C for 12 hours and then slowly cooled to room temperature at a rate of 0.1 °C/min. Although our as-synthesized samples showed different kinetics and thus exhibited different amounts of maximum oxygen content when annealed in oxygen on TGA, they all showed similarly enhanced oxygen content when annealed under high-pressure oxygen atmosphere as shown in Figure 4.4. All high-pressure-annealed samples showed similar stability in their oxygen content around 3.38 up to 250 °C upon heating in pure O₂ atmosphere on TGA before rapidly reducing and becoming stoichiometric in oxygen content above 300 °C. The HoMnO₃⁺δ sample showed a clear plateau in the TGA curve around ~ O₃.28, as shown in the inset of Figure 4.4.
Figure 4.4: TG curves of oxygen content vs. temperature for heavily oxygenated RMnO$_{3+\delta}$ (R= Er, Ho, and Y) after high-pressure oxygen annealing at 190 bars and 400 °C. Samples were heated up to 350 °C in O$_2$ with heating rate of 0.1 °C/min. Stability in oxygen content was observed for all samples at O$_{3.00}$ and ~ O$_{3.38}$. HoMnO$_{3+\delta}$ showed another plateau around O$_{3.28}$, as shown in the inset.

Similar plateaus were previously observed for Dy$_{1-x}$Y$_x$MnO$_{3+\delta}$ (x ≤ 0.5) and were associated with the thermal stability of the Hex1 phase [60]. The stability of the oxygen content O$_{3.38}$ up to 250 °C indicate the formation of a second stable Hex2 phase [71]. Our room temperature XRD measurements, (see Figures 4.5 and 4.6), revealed extra peaks of the Hex1 and
Figure 4.5: XRD patterns of HoMnO$_{3+\delta}$ (with $\delta = 0$, 0.28, and 0.38). A magnification of the pattern in the range $2\theta = 26$-$34^\circ$ is shown in the inset for $\delta = 0.28$ (Hex1) phase. Hex2 phases for R = Ho and Y when compared to the stoichiometric ($\delta = 0$) P6$_3$cm phase for samples prepared with various excess oxygen contents. An observed increased number of Bragg peaks indicated general lowering in symmetry and the formation of Hex1 and Hex2 superstructures. Structural analysis and details of these oxygen-loaded phases are discussed in the following section. Figure 4.7 shows an overlay of Bragg peaks corresponding to P6$_3$cm, Hex1, and Hex2 for comparison.
Figure 4.6: XRD patterns of YMnO$_{3+\delta}$ (with $\delta = 0$, 0.13, 0.25, and 0.36). A magnification of the patterns in the range $2\theta = 26$-$34^\circ$ is shown in the insets for comparison reason.
Figure 4.7: Overlay of the XRD patterns of P6₃cm, Hex1, and Hex2 phases in the 2θ range (28-34) where peaks corresponding to the Hex1 and Hex2 structures can be compared relative to the parent P6₃cm phase.

Our TGA results indicate the achievement of significant property improvements in HoMnO₃₊δ for prospective applications for oxygen separation over the previously reported Dy₁₋ₓYₓMnO₃₊δ system [60]. First, although both systems allow the intake of similar amounts of oxygen under similar conditions, HoMnO₃₊δ has lower oxidation (T_{oxi}) and reduction (T_{red}) temperatures, which define the operational temperature range of ΔT = T_{red} - T_{oxi} suitable for thermal swing absorption applications for air separation, see Figure 4.2. Second, the synthesis conditions in air for HoMnO₃₊δ are less demanding than their Dy₁₋ₓYₓMnO₃₊δ counterparts (x ≤
0.5), which require careful firings under reducing conditions to slightly reduce Mn$^{3+}$ and elongate the Mn-O bond lengths. Such reducing conditions are necessary to bring the tolerance factor below the limit of perovskite phase stability (0.855) as was earlier established by our design rules [72].
4.2.2 Crystal Structure of RMnO$_{3+\delta}$ (R = Y, Ho, and Er)

As mentioned above, the oxygen stoichiometric samples of our investigated materials were confirmed to crystallize in the hexagonal space group symmetry of P6$_3$cm (N. 185). Figure 4.5 shows a compilation of XRD patterns collected for HoMnO$_{3+\delta}$ at $\delta = 0$, 0.28, and 0.38. In agreement with the oxygen content stability regions observed in the TG curves (see figure 4.4); XRD demonstrates the appearance of extra Bragg peaks corresponding to the formation of the previously identified Hex1 and Hex2 phases for $\delta = 0.28$ and 0.38, respectively [60]. To help discriminate between these new phases, magnified XRD patterns in the 2θ range (26-34°) are shown in the insets of figures 4.5 and 4.6. Patterns of other $R_xMn_y^{+4}Mn_{1-y}^{+3}O_{3+\delta}$ systems (e.g. pyrochlore $R_2Mn_2O_7$, RMn$_2$O$_5$, and $R_2$MnO$_4$) and manganese oxides, which could account for the increase in oxygen content, were compared to these new phases. No traces of any of these structures were observed.

Samples of HoMnO$_{3.28}$ quenched from 270 °C are nearly single-phase in Hex1, as verified with XRD, and thus were utilized for further structural investigation. Neutron powder diffraction data were collected up to a d-spacing of 6 Å. Preliminary analyses of the data confirmed the superstructure formation. Satisfactory fitting results were achieved when the refinement was carried out using a symmetry model consistent with the space group R3c (N. 161), after considering a superstructure constructed by tripling the c-axis of the original
Figure 4.8: NPD pattern for HoMnO$_{3.28}$. The stars are the observed data and the bottom line is the difference profile between experimental data and best fit calculated from the Rietveld refinement method.

Our final refinement results for HoMnO$_{3.28}$ are presented in Table 4.1 along with the reliability factors. Atomic sites, lattice parameters, and peak widths were refined together with absorption, isotropic thermal factors and site occupancies, while a 20-term function type 1
Table 4.1: Atomic coordinates, space groups, lattice parameters, site occupancies, thermal factors, and agreement factors of HoMnO$_{3.28}$ obtained from GSAS [22,23].

<table>
<thead>
<tr>
<th>R 3 C</th>
<th>HoMnO$_{3.28}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom</td>
<td>Position</td>
</tr>
<tr>
<td>Ho1</td>
<td>6a</td>
</tr>
<tr>
<td>Ho2</td>
<td>6a</td>
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<tr>
<td>O4</td>
<td>18b</td>
</tr>
<tr>
<td>O5</td>
<td>18b</td>
</tr>
</tbody>
</table>

| $<\text{Mn-O}_g$ (Å) | 1.98247(9) |
| Lattice parameters (Å) | a = 6.1987(5), c = 33.2176(5) |
| V (Å$^3$) | 1105.37032(1) |

(Shifted Chebyshev) was used to account for the background. Small peaks from the vanadium containers were identified in all patterns; these were not included in the refinement. It was noticed that the refined occupancies of the cations and the original oxygen ions (i.e. O1, O2, O3, O4, and O5) remained essentially full within one to three standard deviations, except for the O1 ion, and thus were fixed at unity during following refinement cycles. The intercalated extra oxygen (O6) was found to prefer the 18b site derived from the superstructure. With the introduction of extra oxygen, a clear interplay takes place in this layer between the two oxygen ions O1 and O6 to accommodate proper cation to oxygen coordinations and reasonable Mn-O,
Figure 4.9: (a) A top view of a 2D layer in the R3c superstructure showing the arrangement of oxygen ions and Mn cations. O6 represents the excess interstitial oxygen in 3-fold arrangement around the original oxygen O1 ion. (b) Schematic drawing of the R3c structure of HoMnO$_{3.28}$.

Further investigations on the Hex1 structure were carried out using bond valence sum (BVS) analysis conducted on both the Mn cations and oxygen anions. The BVS method...
describes bonding between ions in the crystal based on the assumption that the anion-cation interactions within the polyhedral complexes are ionic in nature. Bond valence sum is calculated using the equation

\[ V(R) = \sum_{i=1}^{n} e^{(r_o - r_i)/B} \]

where \( R \) denotes the ion of valence \( V \), \( n \) is the number of ligands attached to the cation \( R \) in the polyhedron, \( B \) is an empirically established constant, and \( r_o \) is the tabulated constant by Brown et al.\[73\] which depends on the type of the bond constituents. The determination of the required \( i^{th} \) ionic bond lengths \( r_i \) are preferably achieved from the NPD data using the rietveld structural refinement method. The BVS evaluation of the anion sites were found to be in good agreement with our observations in the oxygen refinements. Possible manganese oxidation states are listed in table 4.2. Bond lengths obtained from our NPD refinements were used in the calculations.
Table 4.2: Bond valence sum analysis calculated for Mn ions using 7-fold coordinations for Pca2₁ and R3c crystal structures. $r_0$ values were taken from ref [73], where $r_{o1}$, $r_{o2}$, and $r_{o3}$ are the tabulated bond valence parameters for Mn$^{+2}$, Mn$^{+3}$, and Mn$^{+4}$, respectively.

<table>
<thead>
<tr>
<th>Crystal Structure</th>
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<tbody>
<tr>
<td>YMnO$_{3+\delta}$</td>
<td>0.41</td>
<td>$r_{o1} = 1.790(3)$ Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$r_{o2} = 1.760(5)$ Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$r_{o3} = 1.753(6)$ Å</td>
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<td>BVS (Mn)</td>
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<td></td>
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<td>3.81(1)</td>
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<td>3.74(1)</td>
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<tr>
<td>ErMnO$_{3+\delta}$</td>
<td>0.38</td>
<td>$r_{o1} = 1.790(3)$ Å</td>
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<tr>
<td></td>
<td></td>
<td>$r_{o2} = 1.760(5)$ Å</td>
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<td></td>
<td></td>
<td>$r_{o3} = 1.753(6)$ Å</td>
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<tr>
<td>BVS (Mn)</td>
<td></td>
<td>4.22(1)</td>
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<tr>
<td></td>
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<td>3.89(3)</td>
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<td>3.82(1)</td>
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<td>HoMnO$_{3+\delta}$</td>
<td>0.28</td>
<td>$r_{o1} = 1.790(3)$ Å</td>
</tr>
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<td>$r_{o2} = 1.760(5)$ Å</td>
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</table>

Samples of YMnO$_{3.41}$ and ErMnO$_{3.38}$ fired at 400 °C under high pressure oxygen atmosphere and then slowly cooled to room temperature exhibited structures that were single-phase in Hex2 (see YMnO$_{3+\delta}$ in Figure 4.6, for example). The overall similarities of the XRD pattern for this Hex2 phase relative to the stoichiometric RMnO$_{3.0}$ parent phase (see: figure 4.6).
prompted the use of $P6_3cm$ for our starting structural refinement models. Albeit a reasonable fit was obtained, this model was ruled out because of the unrealistic and meaningless refined atomic thermal factors and oxygen site occupancies. Although similar, we note that some of the Bragg peaks have shifted significantly with respect to those of the parent structure as demonstrated in Figure 4.6 and that the two structures must be different. It’s clear that the insertion of extra oxygen into the structure must have produced significant strains, cooperative atomic displacements and other subtle structural re-arrangements. The failure to fit our NPD data in the $P6_3cm$ space group suggested that the overall similarity in the diffraction patterns could be reasoned out if the excess oxygen ions didn’t produce a first order phase transition, and that they were accommodated in positions which induced strains, atomic displacements, and possibly oxygen ordering consistent with a continuous second order phase transition. Relying on this hypothesis, the deployment of group theoretical analysis to elucidate the transition path and to search for possible isotropy subgroups (distorted symmetries) originating from a parent structure that is chemically different can be justified since the transition in question is continuous.

A quick inspection of Figure 4.6 reveals the disappearance of the (102) reflection from the $YMnO_{3.41}$ pattern. This peak is present in the diffraction patterns of the stoichiometric materials and its absence can be attributed to a symmetry-lowering structural transition caused by a $(\sqrt{3}a \times a)$ distortion as previously suggested by Gibbs et al.[74]. The inset of Figure 4.10a shows such a change in unit cells’ basis vectors, giving rise to a possible orthorhombic superstructure.
Figure 4.10(a): NPD pattern for YMnO$_{3.41}$. The stars are the observed data and the bottom line is the difference profile between experimental data and best fit calculated from the Rietveld refinement method. Inset shows an orthorhombic sublattice (red) with basis vectors (a x √a) originating from a hexagonal parent lattice with basis vector (a x a), both unit cells have the same c vector.

In a symmetry-lowering structural transition, those symmetry elements which persist from the parent space group form the isotropy subgroups associated with distinct classes of physical order parameters, characterized by strain, atomic displacements, and occupancies. IsoDistort program, part of the Isotropy suite software package [25], was utilized to identify the distortion symmetries available to the P6$_3$cm parent structure based on calculated irreducible
representations associated with each k point in the parent’s first brillouin zone. It was noticed that the orthorhombic subgroups were only induced by symmetry modes derived from the M or Γ points of the first brillouin zone. Several models were constructed and tested against our NPD data, each at a time, and it was immediately noticed that all C-centered sublattices failed to index major peaks in the diffraction patterns, and thus they were discarded. The set of order parameters and symmetry modes that allowed for a phase transition to be continuous, according to rules of Landau theory and the rules of renormalization group theory, induced the subgroup Pca2₁ (N. 29) with a shifted origin at (1/2,0,0).

The results of the model refined in this space group are plotted in Figures 4.10(a,b), and the corresponding structural data are presented in Table A2 (in the appendix) for YMnO₃.₄₁ and ErMnO₃.₃₈. The refined occupancies of all the original ions refined to unity within one to three standard deviations, and were consequently fixed in subsequent refinement cycles. Excess oxygen was determined to occupy the O₅ sites depicted in Figure 4.11, which shows a schematic drawing of the orthorhombic Pca2₁ supercell. It’s worth noting that the refined oxygen contents of O₃.₃₅ and O₃.₃₇ were in good agreement with the nominal oxygen contents, obtained from our TG measurements, for both ErMnO₃.₃₈ and YMnO₃.₄₁, respectively. BVS evaluations of the cation and anion oxidation states in the Pca2₁ supercell yielded reasonable results that indeed strengthened the validity of this model. Possible Mn oxidation states are listed in Table 4.2.
Figure 4.10(b): NPD pattern for ErMnO$_{3.38}$ in the d-spacing range (0.3-3) Å. The stars are the observed data and the bottom line is the difference profile between experimental data and best fit calculated from the Rietveld refinement method.
To the best of our knowledge, there hasn’t been any model reported in the literature for the Hex 2 structure. Parkkima et al [75], on the other hand, have recently reported the appearance of satellites in the electron diffraction pattern of a heavily oxygenated YMnO$_{3.35}$ sample and have suggested that these satellites are associated with modulated structures with different propagation vectors. At present, it’s unclear whether or not the TEM observations represent local ordering for specific domains. However, we note that the absence of commensurate or in-commensurate long-
range ordering peaks in our data combined with a cell rotation of the lower symmetry orthorhombic Pca2₁ sublattice are consistent with short range local-ordering capable of giving rise to modulated structures in diverse propagation directions for this compound.

In-situ high-flux synchrotron diffraction measurements were conducted on select samples to better understand the phase transitions observed in our TG and neutron diffraction data by providing a qualitative description of the evolution of the x-ray patterns. Figure 4.12a presents the synchrotron data for heavily oxygenated HoMnO₃⁺δ collected on slow heating in O₂. Below 300 °C, the set of shifted peaks that correspond to the Hex 2-Pca2₁ phase is clearly visible in the 2θ range (28-36°). Upon further heating around 300 °C, it is equally noticeable the formation of a new set of peaks that correspond to the Hex 1-R3c phase at lower oxygen content. With further heating, the material becomes stoichiometric in its oxygen content as noted by the recovery of the original P6₃cm peaks. Close inspection of the contour lines reveals the thermal effect on the lattice parameters, expressed by the slightly shifting peak positions evidenced by the slight bending of these contour lines. Figure 4.12b shows synchrotron data collected for HoMnO₃⁺δ upon cooling from ~400 °C. The high-temperature stoichiometric phase reabsorbs oxygen until reaching the stable oxygen-loaded R3c phase, around 300 °C, as predicted by our TG measurements. The ErMnO₃⁺δ synchrotron data are presented in Figure 4.13. Upon slow heating in O₂, the heavily oxygenated material goes through an intermediate mixed phase combination of Hex2 and P6₃cm (identified here as Hex0) slightly above 200 °C. No Hex1 phase is observed at any oxygen content between 3.38 and 3.00. The material goes back to
Figure 4.12 (a): High-flux in-situ synchrotron data collected for HoMnO$_{3+\delta}$ while slowly heating in O$_2$. 
**Figure 4.12 (b):** High-flux in-situ synchrotron data collected for HoMnO$_{3+\delta}$ while slowly cooling in O$_2$. 
Figure 4.13: High-flux in-situ synchrotron data collected for ErMnO$_{3+\delta}$ while slowly heating in O$_2$. 
Figure 4.14: Schematic phase diagram. Ionic radii were obtained from neutron powder diffraction data of the stoichiometric $RMnO_3$ materials.

stoichiometric at temperature exceeding $\sim 320 \, ^\circ C$, which is again in complete agreement with the TG results. A schematic phase diagram is presented in Figure 4.14. The thermal stability temperature range of the $RMnO_{3+\delta}$ Hex 1 phase is directly proportional to the average ionic radius of the $R$ cation. As described in reference [72], there is a significant uncertainty in the reported ionic radii of the rare-earth cations under investigation here attributed to the inconsistent $R$-coordination to oxygen numbers on which the reported radii were based. The ionic radius of a
certain cation is dependent on its coordination with the surrounding anions. For increased accuracy, the ionic radii of the cations reported here were extracted from neutron powder diffraction data of the stoichiometric P63cm RMnO3 materials reported for $R = \text{Ho}$, Er, and Dy$_{1-x}Y_x$ in references [76], [77], and [60], respectively. For consistency, geometric averaging rather than the algebraic mean was utilized to determine the average $<R-O>$ bond lengths, and hence the corresponding ionic radii, in 8-coordinated cations and 3-coordinated oxygen anions geometry for each sample.
4.2.3 Magnetic Measurements of RMnO$_{3+\delta}$ ($R = Y$, Ho, and Er)

Although magnetic properties of the RMnO$_{3+\delta}$ compounds may fall outside the scope of this dissertation, a brief analysis related to these properties is necessary for this category of multiferroic materials where physical properties are sensitively affected by the oxygen content. The structural and electronic differences between the hexagonal and perovskite manganites were discussed previously. The 5-fold coordinated Mn$^{3+}$ cations are not Jahn-Teller active, which results in compressed apical (Mn-O) bond lengths relative to the longer basal bonds where the electrons experience stronger repulsive forces. Perhaps, the most significant difference lies in the source of the electric polarization associated with these important multiferroics. While the “geometric” ferroelectricity in hexagonal RMnO$_3$ is generated in response to a nonpolar lattice distortions; such as the cooperative tilts of the manganese polyhedra and the buckling of the R-O planes, it can be traced; however, to a magnetic origin in their perovskite counterparts [78]. In the latter compounds, it was found that the observed electric polarization below the Neel temperature is a result to the breaking of the inversion symmetry induced by an incommensurate helicoidal spin-density-wave SDW of a frustrated magnet, implying stronger coupling between the magnetic and electric order parameters [79]. Moreover, the degree of magnetic frustration can be structurally tuned by controlling the $R^{3+}$ cationic size which effectively manipulates the super-exchange interactions between the Mn$^{3+}$ ions by alternating the O-Mn-O angle within the polyhedron complex. For large size $R$ (i.e. $R = $ La), the manganese magnetic moments arranged in a type A ferromagnetic structure within the (a-b) plane of the perovskite RMnO$_3$ unit cell, while exhibiting antiferromagnetic coupling between layers. As the $R^{3+}$ decreases in size, an increase in magnetic frustration indicated by the significant drop of the $T_N$ temperature from $\sim$
150 k for $R = \text{La}$ to $\sim 40$ k for $R = \text{Eu}$ was observed [80]. Although the amount of induced electric polarization in these materials is two to three orders lower in magnitude than typical ferroelectrics, they show the strongest magnetoelectric coupling among the known multiferroics due to the magnetic nature of the electric polarization, in contrast to the rest majority of multiferroics where ferroelectricity and magnetism exclusively coexist and $P$ and $M$ are associated with different ions in the compound.

Data of the magnetic susceptibility ($\chi$) dependence on temperature within the range 2-400 K, and the isothermal magnetizations at 5 K were collected for the $RMnO_{3+\delta}$ ($R = \text{Ho, Y}$) samples in their corresponding stoichiometric and oxygen-loaded phases with $\delta = 0, 0.28,$ and $\sim 0.4$.

Figures 4.15 and 4.16 show the “zero-field cooled” (ZFC) and “field-cooled” (FC) susceptibility measurements performed under an external applied magnetic field of 1 kOe for $\text{HoMnO}_{3+\delta}$ and $\text{Y MnO}_{3+\delta}$, respectively. As expected, a characteristic paramagnetic behavior is observed for all the investigated samples above the Neel temperature $T_N \sim 72$ K. The manganese sublattice in rare-earth manganites has been reported to order in a canted antiferromagnetic structure around $T_N \sim 72$ K. Another transition temperature, around $T_{\text{SR}} \sim 42$ K, was also
Figure 4.15: “zero-field-cooled” (ZFC) and “field-cooled” (FC) magnetizations for HoMnO$_{3+\delta}$ ($\delta = 0.28$ and 0.38) measured in $H = 1$ kOe in the temperature range 2-400K. The inset shows the two curves magnified around the transition temperature.

reported for the HoMnO$_3$ and was attributed to a sudden reorientation of the Mn$^{3+}$ moments in a direction perpendicular to their original orientation in the basal plane [76]. At lower temperatures, the rare-earth cations $R^{3+}$ were reported to become polarized typically below $\sim 30$ K, in response to the R-Mn exchange. For the HoMnO$_{3+\delta}$ data presented in the insets of Figures 4.17(a,b), the absence of the anticipated anomaly in the temperature-derivative of the
Figure 4.16: “zero-field-cooled” (ZFC) and “field-cooled” (FC) magnetizations for YMnO$_{3+\delta}$ ($\delta = 0$, 0.28, and 0.41) measured in $H = 1$ kOe in the temperature range 2-400 K. The inset shows the curves magnified around the transition temperature.

The magnetization curve (dM/dT) around the transition temperature of the manganese moments was strongly argued to be due to the masking of the manganese moments by the much higher paramagnetic susceptibility associated with the Ho$^{3+}$ moments. However, the same absence of this anomaly in the YMnO$_{3+\delta}$ data, (see: Figures 4.18(a,b)) , with only non-magnetic yttrium present in the A site, suggested a possible lowering in the transition temperature of the manganese ordering in a trend similar to what has been described by Brinks et al [81] for the
lowering of $T_N$ of the manganese moments in orthorhombic $RMnO_3$ from ~ 141 K for La to ~ 40 K for Tb, in accord with the tendency of decreasing Neel temperature with the decreasing cationic radii exhibited in rare-earth titanates, vanadites, and orthoferrites [82]. It is also possible that some impurities which are compatible with the synthesis procedure of our samples, such as $Mn_3O_4$ which is ferrimagnetically ordered around ~ 43 K, could explain the kink in the $dM/dT$ curve around the $T_{SR}$ transition temperature. No trace of this oxide was detected in any of our XRD profiles.

In the low temperature range below ~ 30 K, several kinks are clearly observed in the $dM/dT$ curves of the investigated samples, implying a complex temperature dependent magnetism. The ZFC and FC curves of the susceptibility measurements overlap over a large temperature range down to ~ 10 K at which they diverge in a manner consistent with weak ferromagnetism. The possibility of a spin-glass (SG) behavior should be tested for these samples by performing a sequence of $\chi_{ac}$ vs. T measurements at different frequencies, in which observing any distinct shift in the susceptibility cusps could be attributed to the signature behavior of SG materials.
**Figure 4.17:** The temperature derivative of magnetization for HoMnO$_{3.28}$ (a) and HoMnO$_{3.39}$ (b), and the temperature dependence of the inverse molar susceptibility (c). Isothermal magnetizations at $T = 2$ K is presented for both samples in (d).
Figure 4.18: The temperature derivative of magnetization for YMnO$_3$\textsubscript{4.41} (a), YMnO$_3$\textsubscript{3.25} (b), and YMnO$_3$ (d). The temperature dependence of the inverse molar susceptibility for all samples is shown in (c).
The modified Curie-Weiss (CW) law:  \( \chi = \frac{C}{T-\theta} + \chi_o \) (where \( C, \chi_o, \) and \( \theta \) represent the Curie constant, background susceptibility, and Curie-Weiss temperature, respectively) was used to analyze the temperature dependence of the molar susceptibility in the range 100-395 K. The effective paramagnetic moment \((\mu_{\text{eff}})_{\text{tot}}\) was calculated from the fit using the formula \((\mu_{\text{eff}})_{\text{tot}} = 2.828 \, C^{1/2}\) as presented in Table 4.3. As a first approximation, the theoretical values of the total effective paramagnetic moments \((\mu_{\text{eff}})_{\text{tot}}\) were calculated based on a nominal ionic amounts of \((2\delta)\) \(\text{Mn}^{4+}\) and \((1-2\delta)\) \(\text{Mn}^{3+}\) in the oxygen-loaded \(\text{RMnO}_{3+\delta}\) samples, both in their high-spin electronic configurations. Their individual \(\mu_{\text{eff}}\) moments were calculated using the formula: \( P = g \left( J (J+1) \right)^{1/2} \) (where \( P, g, \) and \( J \) represent the magnetic moments in Bohr magnetons, the g-factor, and the total angular momentum, respectively) and were found to be \(3.8 \, \mu_B (\mu_{\text{eff}}^{\text{Mn}^{4+}})\) and \(4.9 \, \mu_B (\mu_{\text{eff}}^{\text{Mn}^{3+}})\) using \( J \) values of 3/2 and 2, respectively. The \((\mu_{\text{eff}})_{\text{tot}}\) was then calculated using the formula: \((\mu_{\text{eff}})_{\text{tot}}^2 = (2\delta) \left( \mu_{\text{eff}} \right)^2_{\text{Mn}^{4+}} + (1-2\delta) \left( \mu_{\text{eff}} \right)^2_{\text{Mn}^{3+}} + \left( \mu_{\text{eff}} \right)^2_{\text{R}^{3+}}\).

Our experimental values for the total effective paramagnetic moments \((\mu_{\text{eff}})_{\text{tot}}\) were in poor agreement with their corresponding theoretical values, see Table above. This inconsistency could be due to the large error bars of our calculations as a result of the oversimplification in the CW fitting performed, in which we combined all three terms of \((\chi) = \sum_{i=1}^{3} \left( \left( \mu_{\text{eff}} \right)^2 \frac{1}{8 (I_i-\alpha_i)} \right)\) in just one “average” term: \( \chi = \frac{C}{(T-\theta)} + \chi_o. \) Moreover, the \(\text{Mn}^{3+}\) ions are no longer stable in their trigonal-bipiramidal configuration as in the case of stoichiometric \(\text{P6}_3\text{cm}\) structure, and the electronic high-spin state upon which we based our theoretical values for the \((\mu_{\text{eff}})_{\text{tot}}\) is possibly not the case in the new more complex oxygen-loaded superstructures.
Isothermal magnetization measurements for HoMnO$_{3+\delta}$ at 2 K show a small hysteresis (coercive field $H_{\text{coer}} = 740$ Oe and 880 Oe for $\delta = 0.28$ and 0.39, respectively) consistent with weak ferromagnetism roughly following the Brillouin function, Figure 14(d). The magnetizations of both samples were found to increase linearly up to $\sim 20$ kOe and to not fully saturate up to $\sim 70$ kOe. The effect of the increasing oxygen content was found to slightly decrease the magnetization as shown in Figure 4.17(d). Relative to the theoretical values of the Brillouin
function, our data implies that only part of the Ho$^{3+}$ ions are magnetically ordered at that temperature.
4.2.4 Optimization Results For Hexagonal $Y_{1-x}R_xMn_{1-y}M_yO_3^{3+\delta}$ (R = La, Pr, Tb, Ce, Dy and M = Fe, Co, In) Oxygen-storage Materials

In this section, we explore chemical doping on both the A and B sites of the original $\text{ABO}_{3+\delta}$ ($\text{Dy}_{1-x}Y_x\text{MnO}_{3+\delta}$) system, primarily to achieve further lowering in the oxidation-reduction temperature range and also to increase the oxygen storage capacity OSC of these materials. Although the results shown for the $\text{Dy}_{0.7}Y_{0.3}\text{MnO}_{3+\delta}$ sample demonstrated exceptional low reduction-oxidation temperature range and large OSC compared to the best reported materials in literature, the cost of raw dysprosium element may be prohibitive for deploying this system as a sorbent material for mass production of high purity oxygen. A less expensive system should probably be found for commercial air separation. The substituent ions were chosen to achieve possible solid solubility range with the substituted ion. Generally, the criterion of choosing the substituent ion requires close similarities in the ionic size, valence, electronegativity, group number, and structural properties of the substitution constituents. For exploration of enhanced properties we have selected the Y-based compounds because of the lower molecular weight and reasonable cost of yttrium.

Figure 4.19 shows the thermogravimetric behavior of selected hexagonal substituted samples at slow heating and cooling rates in oxygen atmosphere. In contrary to the buckled layers of corner shared $\text{MnO}_6$ octahedra in the perovskite unit cell, the separated layers of the $\text{MnO}_3$ bipyramids in the hexagonal structure allows for less constricted oxygen environment and easier absorption and desorption of interstitial oxygen ions at much lower temperature ranges.
Figure 4.19: TG measurements of Hexagonal (Top) and Perovskite (Bottom) RMnO$_{3+\delta}$ with slow heating and cooling rates in oxygen atmosphere.
as indicated in the figure. Remarkably similar, the temperature needed to achieve maximum oxygen content is dependent on the ionic size of the rare-earth elements in both structures. Compositions with smaller-size ions seem to saturate in their oxygen content at relatively higher temperatures. The hexagonal LaMnO$_{3+\delta}$ sample, for example, has achieved excess oxygen approximately twice the amount achieved in its perovskite counterpart at significantly lower temperature range. This is because excess oxygen is accommodated differently in the perovskite than in hexagonal structures. The mechanism depends on the creation of schottky and/or frenkel vacancy defects with equal proportions on the A and B sites of the perovskite ABO$_3$ material, see: section 1.2.1 for details. Noticeably, as in LaMnO$_{3+\delta}$, not only the achieved oxygen storage capacities are significantly less in the perovskites relative to their hexagonal counterparts, but they also require much higher temperature ranges necessary for the creation of these vacancy defects. Even at temperatures high as 1400 °C, RMnO$_{3+\delta}$ manganites seem to not completely reduce to stoichiometric oxygen content.

Figure 4.19 demonstrates superior OSC achieved for both the Y$_{0.7}$Tb$_{0.3}$MnO$_{3+\delta}$ and Y$_{0.97}$La$_{0.03}$MnO$_{3+\delta}$ samples with OSC of 1927 and 1448 µmol-O/g, respectively, when compared to DyMnO$_{3+\delta}$ (OSC of 942 µmol-O/g). For example, although Y$_{0.97}$La$_{0.03}$MnO$_{3+\delta}$ accommodates less interstitial oxygen content, its molar weight is smaller and shows better thermogravimetric characteristics as it exhibits lower oxidation-reduction temperature range closer to ambient conditions.

The starting oxygen content of the hexagonal Y$_{0.96}$Pr$_{0.04}$MnO$_{3+\delta}$ obtained from synthesis in Ar atmosphere shows (similar to the DyMnO$_{3+\delta}$ sample) slight oxygen deficiency as noted in the below-stoichiometric (O$_3$) starting value in figure 4.19 (Top). This is in accord with our
Figure 4.20: TG cycles of $Y_{1-x}Ce_xMnO_{3+\delta}$ samples achieved at slow heating and cooling rates of 0.1°C/min in oxygen.

arguments of the tolerance factor design rules [12] which require certain reduction in the Mn cation necessary to establish longer <Mn-O> bond lengths and hence bringing the tolerance factor below the 0.855 limit.

Another A-site substitutions, with Ce$^{4+}$ for Y$^{3+}$, were also done to potentially increase the amount of interstitial oxygen. Solid solutions of $Y_{1-x}Ce_xMnO_{3+\delta}$ were achieved over a solubility range of $0 < x < 0.2$. Figure 4.20 shows results of the thermogravimetric cycles for this system.
Figure 4.21: TG reduction cycle of $Y_{0.9}Ce_{0.1}MnO_{3+\delta}$ sample achieved at slow heating rate in 5% hydrogen balanced with argon atmosphere.

under slow heating and cooling rates of 0.1°C/min in oxygen. To assign the proper oxygen content for our samples during TG measurements, oxygenated samples were reduced, see: figure 4.21 for $Y_{0.9}Ce_{0.1}MnO_{3+\delta}$ sample for example, to their primary constituent products. Hence, the absolute oxygen content was normalized using the weight difference between the oxygenated samples and the reduction products. Upon heating, the stoichiometric samples start to pick up oxygen fast over a relatively short temperature range between ~100 – 310 °C before achieving maximum oxygen content. Upon further heating, samples start to desorb oxygen at a relatively slower rate. The cerium doping level was found to affect the oxygen absorption/desorption
kinetics as evident from the sharper slope for the \( x = 0.2 \) sample relative to the other samples where achieving the maximum oxygen content occurred at slightly higher temperatures. Noticeably, in contrast to the previous studied oxygen storage systems, all samples (even for the \( \text{Y}_{0.99}\text{Ce}_{0.01}\text{MnO}_{3+\delta} \) with the slightest cerium substitution) never achieved stoichiometry even after heating up to 500 °C. Further heating beyond 500 °C doesn’t seem to help achieve stoichiometry in oxygen content for these samples as predicted from the extrapolation of the TG curves. The amount of oxygen nonstoichiometry \( \delta \) predicted as a result to the Ce\(^{4+} \) substitution for trivalent Y\(^{3+} \) is \( \delta = x/2 \), where \( x \) is the number of moles of substituted yttrium. The observed oxygen nonstoichiometry was noted, however, to be significantly larger than predicted. The observed increase in oxygen content was argued to be related to the cerium coordination-to-oxygen anions which could possibly require a coordination number larger than 8 as is the case for the other R\(^{3+} \) cations investigated in this work. On the other hand, preliminary XRD measurements conducted on these samples showed patterns with peaks similar to those corresponding to the heavily oxygenated \( \text{Hex}_2 \text{RMnO}_{3.4} \) phase. Since x-rays are inherently not sensitive to oxygen; a neutron powder diffraction measurement is more adequate to study the crystal structures; and therefore, the cerium coordination of these compounds. The amount of excess oxygen achieved in the Ce-substituted samples can be also explained if charge ordering is considered. The introduction of \( \delta \approx 0.44 \) moles of oxygen in the \( \text{Y}_{0.8}\text{Ce}_{0.2}\text{MnO}_{3+\delta} \) for example suggests the possible formation of a charge ordered phase of \( \text{Y}^{3+}_{0.8}\text{Ce}^{4+}_{0.2}\text{Mn}^{3+}_{0.7}\text{Mn}^{4+}_{0.3}\text{O}_{3.44} \).

Cerium substitution has been found to induce interesting thermogravimetric behavior on the host material. Even the slightest amount of cerium has its profound effect on the thermogravimetric cycle as shown in figure 4.22. Although the oxygen storage capacity was
Figure 4.22: TG cycles of $Y_{0.92}La_{0.03}Ce_{0.05}MnO_{3+\delta}$ and $Y_{0.97}La_{0.03}Mn_{0.97}Co_{0.03}O_{3+\delta}$ samples achieved at slow heating and cooling rates of 0.1°C/min in oxygen.

dramatically increased by the introduction of cerium on the yttrium sites ($Y_{0.8}Ce_{0.2}MnO_{3+\delta}$ sample exhibits the highest achieved oxygen storage capacity so far: 2177.67 µmol-O/g considering total excess oxygen $\delta = 0.44$), the wide oxidation-reduction temperature range and the “locking” of oxygen anions at high temperature, which prevented the samples from achieving $\delta = 0$ stoichiometry at elevated temperatures, indicate a technical problem for deployment in thermal swing adsorption applications.
Figure 4.23: TG cycles of YMn$_{1-x}$M$_x$O$_{3+\delta}$ samples achieved at slow heating and cooling rates of 0.1°C/min in oxygen.

Figure 4.23 summarizes evaluation results of YMn$_{1-x}$M$_x$O$_{3+\delta}$ for M = Co, In, and Fe introduced on the B-site of the ABO$_{3+\delta}$ system. The thermogravimetric characteristics of these samples do not exceed in quality any of the previous studied system which prompts the termination of any further doping on the B-site. The multi-valence nature of the Mn cation which occupies the B-site of the oxygen storage system makes it a key component in maintaining the
desired reversible oxygen storage properties of the materials under investigation; and therefore, it is concluded that any substitution must be performed on the A-site.

A summary of oxygen storage capacities, oxidation and reduction temperatures, expected cost of fabrication, and toxicity of selected materials is presented in table 4.4. We note that unlike the rest of the listed materials, OSC of ceria-zirconia was measured in O2-H2 reduction
and oxygenation cycle instead of thermal-swinging in oxygen. So far, the Y$_{0.97}$La$_{0.03}$MnO$_{3+δ}$ system exhibits the most desired thermogravimetric characteristics which promote this material as a strong candidate to compete for prospective deployment as sorbent beds for thermal swing adsorption applications for air separation.
4.2.5 Dilatometry Measurements

In general, crystal lattice undergoes two types of structural expansion; the first type is the thermal expansion -designated here as (TE)- which is attributed to the elongation of bond lengths in response to the increased vibrational energy of the constituent ions as a result to the increasing temperature. The second type is the chemical expansion –designated here as (CE)- which occurs as a result to the change in chemical composition within the unit cell, mostly due to change in oxygen stoichiometry, where the valence, and thus the size of A or M ion change.

Expansion of the crystal lattice has a significant impact on the material’s magnetic, transport, and structural properties [83-85]. Dilatometry studies of rare-earth manganites are very rare although necessary. A successful design of an application requires careful knowledge of the expansion coefficients of the involved materials. For example, the geometry involved in the fuel cells design requires a stacking arrangement of cathode, electrolyte, and anode materials, therefore; information on their expansion coefficients is crucial to maintain operation and to avoid mechanical damage to the apparatus as a result to possible expansion mismatch between the different cell components.

Conventionally, the reported expansion coefficients of materials in literature are the net results which contain both the thermal TEC and chemical CE expansion coefficient components of that material. Since both expansions may take place simultaneously at similar rates, discrimination between the two types could be cumbersome. Moreover, measuring the chemical expansion of the material can be established at a fixed temperature level while varying the oxygen content as a function of oxygen partial pressure; therefore, one can then separate the
chemical component of the expansion from the thermal component for that material. Doing so, however, requires knowledge of the thermogravimetric behavior of the material as a function of temperature, and also requires a relatively long time window.

For our samples, chemical and thermal expansion coefficients were measured differently. The thermogravimetric cycles of the hexagonal rare-earth manganites show two discrete regions of thermally stable phases, one for the oxygenated material and the second corresponding to the stoichiometric one, see: figure 4.24 for Y\(_{0.97}\)La\(_{0.03}\)MnO\(_{3+\delta}\) sample, separated by a relatively short temperature range. Each phase extends over a relatively large temperature range with nearly fixed oxygen content. The stability of oxygen content over that specific temperature range for each phase allows us to measure the thermal expansion coefficient for each phase. Moreover, the effective chemical expansion of the sample can be measured over the narrow temperature range where phase transition from the stable oxygen-loaded phase to the stoichiometric one took place simply by subtracting the small values of TEC from the observed value of CE.

Dilatometry measurements were conducted on selected RMnO\(_{3+\delta}\) samples in the temperature range 20 - 550 °C under the same conditions as used in the samples’ TG measurements. An exemplary Dilatometry results are reported here for the Y\(_{0.97}\)La\(_{0.03}\)MnO\(_{3+\delta}\) sample in figure 4.25. A diamond saw was utilized to carefully cut dense pellets of the investigated material into small cuboids ~ 3.14 mm * 3.2 mm * 3.2 mm in volume with smooth sides for increased accuracy. The cuboids samples were deliberately achieved to be relatively similar in size to the small chunks’ of the same material used in the TG measurement; so
Figure 4.24: TG cycle for $Y_{0.97} La_{0.03} MnO_{3+\delta}$ upon slow heating in oxygen to 500 °C. Red bars separate regions of oxygen content stability, at $\delta \sim 0.39$ (below 250 °C) and $\delta \sim 0.00$ (above 340 °C) corresponding to Hex 2 and Hex 0 phases, respectively; from the region of unstable oxygen content where chemical expansion is dominant.

to eliminate any possible kinetic oxygen exchange effect between the TG and Dilatometry measurements that could arise from varying surface area or diffusion lengths among samples used in each measurement. The following equation was used to calculate the TEC and CE coefficients:

$$ TEC = \frac{1}{L_0} \frac{1}{n-m} \sum_{i=m}^{n} \frac{\Delta L_{i+1} - \Delta L_i}{T_{i+1} - T_i} $$
Figure 4.25: Dilatometry results for $Y_{0.97}La_{0.03}MnO_{3+\delta}$ measured upon slow heating in oxygen. In analogy to the TG measurement of this sample, red bars separate regions of thermal expansion TEC from regions of chemical expansion CE.

measured in K$^{-1}$, where $L_0$, $\Delta L$, and $T$ correspond to the sample’s starting length, the change in length, and temperature, respectively; and the m-n define the starting and final temperature points of the measured temperature range, respectively. The CE was calculated using the equation:

$$CE = \frac{1}{\Delta \delta} \left( \frac{\Delta L}{L_0} - <TEC > \Delta T \right)$$

where CE is measured in (moles of O)$^{-1}$, $\Delta \delta$ is the absolute change in oxygen content across the designated temperature range of CE, and $<TEC>$ is the average TEC of the two stable oxygen content regions.
The resulting thermal expansion coefficient TEC of the Hex 2 phase was found to be $2.16 \times 10^{-6} \text{ K}^{-1}$ which is slightly larger than that of the stoichiometric Hex 0 phase, $1.55 \times 10^{-6} \text{ K}^{-1}$. This is in accord to previous results reported by Remsen et al [35] for the DyMnO$_{3+\delta}$ hexagonal system in which TEC for the oxygen-loaded phase ($\delta = 0.29$) exceeded that of the stoichiometric($\delta = 0$) P6$_3$cm phase.

Calculations of the CE coefficient yielded results which also were in good agreement with recently published work [35] for the DyMnO$_{3+\delta}$ hexagonal system. CE upon the phase transition from the Hex 2 phase to the P6$_3$cm phase was found to be $14.38 \times 10^{-3} \text{ [mole-O]}^{-1}$. 
4.2.6 Pulsed Laser Deposition PLD

So far, we explored and characterized oxygen storage, transport, structural, and magnetic properties of the RMnO$_{3+\delta}$ systems in the lower $t < 0.855$ limit of the tolerance factor ($t$) region where material crystallizes in the hexagonal structure. A strong impact on the physical properties of the material is expected upon transition to the upper limit $t > 0.855$ region where material exhibits the well-known perovskite structure. As was previously shown, achieving this transition can be done through systematically controlling the synthesis conditions in which reducing atmospheres may be utilized to elongate the critical R-O bond necessary to obtain the desired $t$ value.

In this section, we summarize the results of a preliminary research on perovskite strontium ruthenate SrRuO$_3$ (SRO) samples intended to define the synthesis requirements for epitaxial SRO thin films using pulsed laser deposition PLD technique. Also, to initiate and construct the blue print for perspective future work on these important complex transition metal oxides.

With the rapidly developing thin film technology in the field of Material Science, research paths have been developed to solve current technological challenges or to initiate new projects intended to develop superior industrially relevant materials. Research in the field of magnetic oxide thin films and multilayered heterostructures is one of these promising avenues in which a great deal of interest has been generated due to a wide range of phenomena exhibited in these artificial structures. This expected interesting transition in the physical properties is
attributed to the reduced dimensionality, geometrical confinement and physical proximity effects. Phenomena, in strongly correlated transition metal oxides, such as Exchange Bias, Spin Flop transitions and Giant magnetoresistance (GMR) play a significant role in the field of spintronics. The particular interest in giant magnetoresistive films is primarily due to their potential in enhanced data storage applications and computer reading heads. The GMR effect is observed as a significant change in the electrical resistance of the material depending on whether the magnetization of adjacent ferromagnetic (or ferrimagnetic) layers is in parallel or antiparallel alignment. SRO thin films are expected to exhibit enhanced magnetism compared to their bulk material [86] which is dependent on the degree of lattice distortion imposed by the orientation of the underlying substrate.

Epitaxial thin films of SRO can be deposited on single crystal substrates, like SrTiO$_3$ (STO) (001) which presents a lattice mismatch of less than 1%, thus allowing the epitaxial growth of the film in either layer-by-layer or step-flow modes. Polycrystalline SrRuO$_3$, however, could be deliberately deposited on other less lattice-matching substrates, like the abundantly available Si (001) wafers. Of the various methods available for thin film deposition, PLD has advantages over other techniques that include the capability of reactive deposition in ambient gases, which enables control of the chemical deposition of the films. In this technique, large target pellets (1 inch in diameter) of the materials under investigation are assembled on a specially designed carousel located within a stainless-steel chamber that is capable of witholding low vacuum pressures. On one side of this chamber, there is an opening leading to the laser chamber through a special pipe connection. Another opening is located on the other side of the chamber which is designed as an inlet for the synthesis-reaction gases and for purging the
system as well. Deposition parameters and chamber pressures are controlled through special software with a graphical user interface.

Synthesis of SRO PLD films started with optimum deposition parameters reported in literature for SRO samples grown on Si (001) substrates. The resulting synthesized films were then characterized using atomic force microscopy AFM to roughly study the films morphology and to assess the fabrication of the epitaxial thin film. Figure 4.26 shows a typical AFM image conducted on epitaxial transition metal oxide film.

Further characterization is conducted on the produced films using x-ray diffraction measurements XRD. This is to absolutely verify the formation of the desired epitaxial films by evaluating the spectra peaks in the XRD pattern.
Our XRD results for the SRO film grown on the Si (001) substrate are shown in figure 4.27. The corresponding peaks belong to the perovskite phase. The XRD results of this thin film suggest an excellent epitaxy as indicated by the spectra that only show SRO film peaks with the same orientation as the underlying substrates.

These results suggest that the 900 oC temperature and the 100 mTorr pressure of O2 which were utilized in the film fabrication are the optimum deposition parameters necessary
Figure 4.27: XRD diffraction pattern of epitaxial SrRuO$_3$ thin films shown in the 2θ range 20-70 with peaks corresponding to the perovskite phase.

to establish high quality epitaxial SRO films for further characterization.
Single-phase polycrystalline samples of stoichiometric $Y_{1-x}R_xMnO_{3+\delta}$ ($R = \text{Er, Y, Dy, Pr, La, Tb and Ho}$) were achieved in the hexagonal $P6_3cm$ structure through solid state reaction at elevated temperatures. Thermogravimetric measurements in oxygen atmospheres demonstrated that samples with the larger $R$ ionic radii show rapid and reversible incorporation of significant amounts of excess oxygen ($0.41 > \delta > 0$) at unusual low temperature range $\sim$190-325 °C. The reversible oxygen storage characteristics of HoMnO$_{3+\delta}$ and related materials showed by the fast incorporation and release of interstitial oxygen at easily accessible elevated temperatures of $\sim$300 °C demonstrate the feasibility of deploying them as bed sorbents for generating oxygen enriched gas from air through temperature swing adsorption TSA process. Further increase in the excess oxygen intake to $\delta \sim 0.39$ was achieved for all the investigated materials when annealed under high-pressure oxygen. Neutron and X-ray powder diffraction measurements confirmed the presence of three line compounds $RMnO_{3+\delta}$; the oxygen stoichiometric $P6_3cm$ ($\delta = 0$ for all $R$), the intermediate oxygen content superstructure phase $R3c$ ($\delta \sim 0.28$ for $R = \text{Ho, Dy, Dy}_{0.5}Y_{0.5}$, and $\text{Dy}_{0.3}Y_{0.7}$) constructed by tripling the c-axis of the original unit cell, and the highly oxygen-loaded $Pca2_1$ phase ($\delta = 0.40$ for all $R$). In-situ synchrotron diffraction showed thermal stability of these single phases and their coexistence ranges, demonstrating that the stability of the $\delta = 0.28$ phase increases with the ionic size of the $R$ ion. Structural refinements using neutron powder diffraction for oxygen excess phases suggest the formation of a superstructure by tripling the c-axis of the original parent unit cell. The symmetry of $R3c$ (space group #161) was found to fit that of the $RMnO_{3.28}$ ($R = \text{Ho}$) phase. Modeling of the $RMnO_{3.38}$ oxygen-loaded phase
converged on a structural model consistent with the symmetry of Pca2₁ (space group #29). Optimization attempts of design-property relationship through chemical doping on the B-site of the ABO₃₊δ system suggest quality lowering in the desired properties and that the Mn is the cation of choice for the B site. The magnetic properties of the multiferroic RMnO₃₊δ were found to be dependent on the oxygen content of these compounds. Below the magnetic ordering temperatures, samples with higher oxygen content showed slightly decreased magnetization relative to the less oxygenated ones. Dilatometry measurements suggest that the thermal expansion coefficient TEC of the oxygen-loaded Hex 2 phase is slightly larger than that of the stoichiometric P6₃cm phase. The calculated Hex2 to Hex0 chemical expansion coefficient 14.38 x 10⁻³ [mole-O]⁻¹ was found to be within the expected range for the hexagonal Y₀.97La₀.0₃MnO₃₊δ sample. Pulsed laser deposition technique was found feasible for the fabrication of high quality epitaxial thin films of SrRuO₃ SRO deposited on the abundantly available silicon Si (001) substrates. Optimum deposition parameters were found to be 900 °C for the required synthesis temperature, and an oxygen pressure of 100 mTorr. Post-annealing for the deposited films for a relatively short period of time and then furnace cooling in atmospheric oxygen pressures is recommended to minimize the creation of any oxygen vacancies which in return could affect the structural integrity of the film.
REFERENCES


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<tr>
<td>[17]</td>
<td>Solar energy laboratory, University of Minnesota.</td>
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[26] OriginLab, Northampton, MA.


[77] B. Van Aken, A. Meetsma, T. Palstra, Acta Crystallographica Sec. E ISSN 1600-5368


APPENDIX
Table A1: Atomic coordinates, lattice parameters, and agreement factors for Dy$_{1-x}$Y$_x$MnO$_3$.

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<tr>
<th>Dy$_{1-x}$Y$_x$ =</th>
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<th>Dy$<em>{0.3}$Y$</em>{0.7}$</th>
<th>Dy$<em>{0.5}$Y$</em>{0.5}$</th>
<th>Dy$<em>{0.7}$Y$</em>{0.3}$</th>
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<td>a (Å)</td>
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<td>6.1644(7)</td>
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<tr>
<td>c (Å)</td>
<td>11.4544(6)</td>
<td>11.4304(3)</td>
<td>11.4204(5)</td>
<td>11.4129(0)</td>
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<td>V (Å$^3$)</td>
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<td>376.1700(6)</td>
<td>374.7638(5)</td>
<td>373.8755(2)</td>
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**Dy/Y1 (0 0 z)**

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**Dy/Y2 (1/3 2/3 z)**

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**Mn (x 0 0)**

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**O1 (x 0 z)**

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<td>0.3323(9)</td>
<td>0.3413(5)</td>
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**O3 (0 0 z)**

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**O4 (1/3 2/3 z)**

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Reliability factors

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<td>$\chi^2$</td>
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<td>1.674</td>
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Table A2: NPD results for (Y/Er)MnO$_{3+\delta}$ in Hex 2 phase.

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<th>Position</th>
<th>N</th>
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<td>0.7479(1)</td>
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<td>12.2(2)</td>
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<td>0.4212(5)</td>
<td>0.0034(3)</td>
<td>2.3(1)</td>
<td>15.5(5)</td>
<td>-2.2(8)</td>
</tr>
<tr>
<td>O1-3</td>
<td>4a</td>
<td>1</td>
<td>0.4382(1)</td>
<td>0.7592(9)</td>
<td>-0.0021(4)</td>
<td>6.7(3)</td>
<td>4.0(2)</td>
<td>1.8(5)</td>
</tr>
</tbody>
</table>

Lattice Parameters: (Å) a = 6.1557(1) b = 10.6660(9) c = 11.1689(7)
Unit cell volume: (Å$^3$) 733.32356(6)
Reliability factors: Rp = 7.32%, Rwp = 4.23%, $\chi^2$ = 1.536