Ca$_{1-x}$A$_x$MnO$_3$ (A= Sr and Ba) Perovskite Based Oxygen Carriers for Chemical Looping with Oxygen Uncoupling (CLOU)

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Abstract

Operated under a cyclic redox mode with an oxygen carrier, the chemical looping with oxygen uncoupling (CLOU) process offers the potential to effectively combust solid fuels while capturing CO$_2$. Development of oxygen carriers capable of reversibly exchanging their active lattice oxygen (O$^{2-}$) with gaseous oxygen (O$_2$) under varying external oxygen partial pressure (P$_{O2}$) is of key importance to CLOU process performance. This article investigates the effect of A-site dopants on CaMnO$_3$ based oxygen carriers for CLOU. Both Sr and Ba are explored as potential dopants at various concentrations. Phase segregations are observed with the addition of Ba dopant even at relatively low concentrations (5% A-site doping). In contrast, stable solid solutions are formed with Sr dopant at a wide range of doping level. While CaMnO$_3$ perovskite suffers from irreversible change into Ruddlesden-Popper (Ca$_2$MnO$_4$) and spinel (CaMn$_2$O$_4$) phases under cyclic redox conditions, Sr doping is found to effectively stabilize the perovskite structure. In-situ XRD studies indicate that the Sr doped CaMnO$_3$ maintains a stable orthorhombic perovskite structure under an inert environment (tested up to 1,200 °C). The same oxygen carrier sample exhibited high recyclability over 100 redox cycles at 850 °C. Besides being highly recyclable, Sr doped CaMnO$_3$ is found to be capable of releasing its lattice oxygen at a temperature significantly lower than that for CaMnO$_3$, rendering it a potentially effective oxygen carrier for solid fuel combustion and carbon dioxide capture.

Keywords: chemical looping, oxygen uncoupling, perovskite, solid fuel

1. Introduction

Climate change caused by anthropogenic carbon dioxide emissions along with the ever increasing demand for energy requires new power generation processes with lower carbon footprints. Of the various carbon capture technologies under development, chemical looping combustion (CLC) has emerged as a potentially promising option.[1,2] The CLC processes utilize a solid oxygen carrier to transfer oxygen from the air to the fuel. This is achieved using interconnected fluidized bed or moving bed reactors.[3–8] In the first reactor, commonly termed
the reducer/fuel reactor, the oxidized form of the oxygen carrier is reacted with the fuel to form carbon dioxide and water vapor. The oxygen depleted carrier is then transported to a second reactor referred to as the oxidizer/air reactor. Here, air is used to regenerate the oxygen depleted carrier while producing heat for power generation.

While most oxygen carriers are effective for gaseous fuel combustion, they tend to be less active in converting solid fuels such as biomass or coal due to mass transfer and kinetic limitations. To enhance the combustion rate for solid fuels, two methods are typically used. In the first method, solid fuel is gasified into syngas by steam, carbon dioxide, or oxygen. The resulting syngas is then reacted with the oxygen carrier at a faster rate than direct solid-solid interactions. [6–11] A variety of oxygen carriers including Fe [8,10,12–14], Mn [13,15], and Ni [16,17] based oxides have been used in the conversion of solid fuels via such an in-situ gasification approach. An even faster approach to combust solids fuel is the so-called chemical looping with oxygen uncoupling (CLOU). [3,18,19] The CLOU process takes the advantage of oxygen carriers with high equilibrium oxygen partial pressure (P_{O2}). As a result, solid fuels are combusted with gaseous oxygen released from the oxygen carrier, resulting in significantly improved reaction kinetics. Typical oxygen carriers that exhibit CLOU properties include oxides and mixed oxides containing Cu, Mn, and/or Co. [18–30]

Despite possessing excellent oxygen uncoupling properties, copper oxides face challenges including a low melting point of the reduced Cu phase which can lead to agglomeration and defluidization. Supports, such as MgAl_{2}O_{4}, SiO_{2}, and Al_{2}O_{3}, have been shown to help prevent sintering and defluidization while maintaining the oxygen uncoupling properties of the copper oxide. [19,26–28] Nevertheless, the relatively high cost of copper oxide may limit its applications. Cobalt oxides, while potentially feasible, are typically avoided due to their low decomposition temperature, toxicity, and negative environmental impact. [18,23] Manganese oxides hold advantages over copper oxides in terms of high availability and low cost. However, pure manganese oxide is difficult to regenerate with air due to its high equilibrium P_{O2}. Formation of mixed oxide phases through the addition of secondary metal oxides such as Fe, Ni, Mg, and Ca to manganese oxides has been shown as an effective approach to improve the regenerability and structural stability of Mn based oxygen carriers. [15,19,21–25,31–36]

More recently, perovskite structured oxygen carriers have received increasing attentions as oxygen carriers for redox applications. [23,31,33–54] Typical perovskites take the form of ABO_{3−δ}, where A is a large cation of either the alkali earth or rare earth metal and B is a smaller transition metal cation.[55] As a support, mixed ionic and electronic conductive (MIEC) perovskites such as La_{1−x}Sr_{x}FeO_{3} (LSF) have shown to enhance the redox activity of iron oxides by nearly two orders of magnitude.[51–54] Perovskite and perovskite supported iron oxide have also been explored as redox catalysts for syngas generation and water-splitting.[56,57] In terms of CLOU applications, La containing perovskite supports are reported to be effective to enhance the oxygen donation properties of mixed Mn-Fe and Co-Fe oxides.[23] Up to 8.8% decrease in initial decomposition temperature was reported for perovskite supported mixed metal oxides. As
a standalone oxygen carrier, perovskites of the CaMnO$_3$ family are extensively studied for CLOU and CLC applications.[20,29–39,49,58–62] While its oxygen uncoupling capacity is smaller than copper oxides, CaMnO$_3$, which can be synthesized from abundantly available manganese ores and Ca precursors [29,61], has been reported to be active for solid fuel conversions.[29,31,34,36] A challenge to CaMnO$_3$ is its lack of long term stability and activity with fuels. Undoped CaMnO$_3$ has been reported to undergo irreversible phase change to CaMn$_2$O$_4$ and Ca$_2$MnO$_4$ phases, leading to eventual deactivation of the oxygen carrier.[19,20,32,59,60] In addition, CaMnO$_3$ has been shown to deactivate in the presence of sulfur, a common constituent of coal, through formation of CaSO$_4$.[32,36,60] Prevention of irreversible phase transition has been investigated by doping secondary metals into the A and B-sites of the CaMnO$_3$ parent material. The dopants can also be used to increase the activity of the oxygen carrier. The most common elements used to stabilize the structure are Ti and Mg.

Pishahang et al. investigated Ca$_{1.5+y}$Mn$_{1.4}$Ti$_x$O$_{3.5}$ oxygen carriers under fixed bed conditions using syngas as the fuel. [38] The authors reported that adding Ti and decreasing the Ca content increased stability of the oxygen carrier. 95% conversion of the syngas was achieved with no observable coke formation. Ryden et al. studied a CaMn$_{0.875}$Ti$_{0.125}$O$_{3.5}$ oxygen carrier for CLOU.[35] The oxygen carrier exhibited oxygen uncoupling at temperature above 720°C in a fluidized bed with a maximum oxygen uncoupling rate of 0.03 L$_3$/min at 950°C. The maximum oxygen concentration was 4 vol. %. Besides the good uncoupling properties, the oxygen carrier exhibited good redox activity and stability for methane conversion. Kallen et al. used Mg doped CaMnO$_3$ and tested the oxygen carrier in a 10kW$_{th}$ gas-fired CLC unit. [37] The synthesized oxygen carrier released oxygen at above 700°C. The oxygen carrier did not agglomerate for 120 hrs. at hot conditions (including 55hrs. of reaction) and formation of fines (<45 μm.) was below 0.01%, indicating possible longevity in the particle’s lifetime. Another study using Mg, Ti, and Fe dopants conducted by Hallberg et al. shows good activity with methane and syngas while releasing 0.3-0.5% by weight gaseous oxygen at 900°C. [33] A maximum oxygen release of ~1 w.t.% was reported at 1,000°C. The authors noted CaMn$_2$O$_4$ spinel formation after testing the oxygen carrier’s CLOU properties in three cycles and activity for methane conversion in a single cycle. Hallberg et al. also investigated the addition of both Ti and Mg in a 300W fluidized bed system using natural gas as the fuel. [62] The designed oxygen carriers showed higher conversion of the fuel than Ni oxides while showing little attrition, however, it was determined that the spent particles contained a noticeable amount of the spinel CaMn$_2$O$_4$ phase. Pour et al. examined different oxygen carriers created by combining cheap manganese ores with Ca(OH)$_2$. [29] While the primary phase was CaMnO$_3$-$\delta$, the manganese ores also contained Al, Fe, K, Ti, Mg, etc. in small quantities. In reaction with methane, ores containing high concentrations of Al showed poor performance due to spinel formation between Al and Mn. The best performing oxygen carrier made from a South African manganese ore, which was mainly composed of Fe, Si, Ca, Mg, and Mn, had an oxygen capacity of 1.5 w.t. % in methane. Oxygen uncoupling capacity was between 0.37-0.68 w.t.% for the various oxygen carriers investigated.
Although extensive studies on B-site dopants were performed, limited studies using A-site dopants have been conducted. Arjmand et. al. investigated Ca$_{1-x}$La$_x$Mn$_3$M$_{1-3}$O$_{3-\delta}$ (M=Mg, Ti, Fe, or Cu) oxygen carriers for CLOU properties between 900-1,000°C in a laboratory scale fluidized bed.[31] The authors characterized the oxygen carriers’ capability to release oxygen by measuring oxygen concentration in the product gas stream during the uncoupling step. It was determined that pure CaMnO$_3$ had the highest oxygen release capability (~0.7% after 360 s). La-doped CaMnO$_3$ had a lower oxygen concentration of ~0.5% after 360 s. Doping of both A and B-sites caused even further decrease in oxygen release except for copper doping which exhibited higher oxygen concentration than CaMnO$_3$. However, copper caused the perovskite materials to defluidize when fuel was added. The authors did detect small amounts of spinel CaMn$_2$O$_4$ although its effect on the oxygen carrier performance was not documented. To summarize, further studies on the effect of A-site substitution using low cost alkali earth metals are desired in order to obtain a more informed strategy to develop oxygen carriers with lower cost and improved CLOU performance.

This article investigates the effect of A-site dopants on CaMnO$_3$ based oxygen carriers for CLOU applications. Both Sr and Ba are explored as potential dopants at various concentrations. The impacts of A-site dopants on phase stability, oxygen release properties, redox stability, and reactivity of the Ca$_{1-x}$A$_x$MnO$_3$ (A= Sr and Ba) based oxygen carriers are investigated using an in-situ X-ray diffraction (XRD) instrument, a thermogravimetric analyzer (TGA), and a fluidized bed reactor. It is determined that Sr dopant can enhance the stability of the perovskite structure while providing facile oxygen release for solid fuel conversions.

### 2. Experimental:

#### 2.1 Oxygen Carrier Synthesis:

Mixed oxides with a general formula of Ca$_{1-x}$A$_x$MnO$_3$ (A= Ba or Sr and x=0, 0.05, 0.25, 0.5, 0.75, and 1) are prepared using a citric acid sol-gel method. General procedure for the sol-gel samples includes dispersion of cation precursors Ca(NO$_3$)$_2$·4H$_2$O (Sigma-Aldrich), Ba(NO$_3$)$_2$ (Sigma Aldrich), Sr(NO$_3$)$_2$ (ACS Reagent, Noah), and Mn(NO$_3$)$_2$·4H$_2$O (Sigma Aldrich) in distilled water followed by addition of citric acid. In the synthesis procedure used, citric acid (Sigma Aldrich) is added to the solution in a molar ratio of 2.5:1 (citric acid: total cations) as a chelating agent. After a short time, ethylene glycol (Sigma Aldrich) is used as a gel promoter in a molar ratio of 1.5:1 (ethylene glycol: citric acid) at a temperature of 80°C. After most of the water is boiled out, the sol-gel sample is dried in a vacuum oven for 12 hours to remove any extra moisture. The dried sample is then annealed in air at 1,200°C for 12 hours. The resulting powder is crushed and sieved to under 75 micron particle size.

A solid state reaction (SSR) method is used to scale up the synthesis process. The SSR method procedure requires powder preparation, followed by pelletization, and annealing/solid state reaction. Preparation of a Ca$_{0.75}$Sr$_{0.25}$MnO$_3$ oxygen carrier was conducted by mixing calculated
amounts of CaCO$_3$ (≥99.0%, Sigma-Aldrich), SrCO$_3$ (99.0%, Noah), and Mn$_3$O$_4$ (99.0%, Noah) precursors for 12 hours in a planetary ball mill (XBM4X, Columbia International) at a rotation speed of 250 rpm. The mixture is then pressed into ¾” pellets by a hydraulic press (YLJ-1ST, MTI Corporation) at a pressure of 20MPa and sintered in a high temperature furnace (GSL-1500-X50, MTI Corporation) at 1,200°C for 12 hours. After annealing, the particles are fractured and sieved into a range of 90-250 microns.

2.2 Oxygen Uncoupling Experiments

Initial oxygen uncoupling properties of the oxygen carriers are characterized in a TGA. Two primary experiments are conducted in the TGA: (1) temperature programmable desorption TPD experiments using inert helium (5.0, Airgas) up to 1,000°C at a ramp of 20°C/min and (2) isothermal experiments between 650-950°C. Isothermal experiments are conducted at various temperatures to determine the oxygen uncoupling capabilities at low to high temperatures. At each temperature, 5 cycles of switching between pure inert and 10% O$_2$ (Extra Dry, Airgas) balanced with a mixture of argon (5.0, Airgas) and helium are conducted for short term recyclability of the oxygen carrier. Best performing oxygen carriers are also tested for 100 cycles at 850°C to demonstrate the oxygen uncoupling performance of the perovskite oxygen carriers over the long term.

2.3 Fluidized Bed Experiments

A laboratory-scale fluidized-bed reactor is used for solid fuel conversion experiment (Figure S1). The quartz fluidized-bed reactor has an outer diameter of 25.4 mm. The reactor is heated through external heating from a tube furnace (MTI OTF-1200X-S-VT). Temperature is measured inside the reactor with an Inconel (Type K) thermocouple to set the temperature of the reactor to 850°C. A 3.75mm ID stainless steel tube is used for solid fuel injection into the reactor. A gas mixing panel is used to send the desired ratio of gases from both the bottom of the reactor for fluidization and through the smaller stainless steel tube for solid fuel injection. For maintaining fluidization, flow rates of 1,080 and 1,200 mL/min (at S.T.P) are used for solid fuel conversion (inert environment) and oxidation cycles, respectively. The flow rates correspond to 6-7 times the calculated minimum fluidization velocity, $U_{mf}$, of the synthesized oxygen carrier. Prior to experiments, the reactor bed is loaded with 16 mesh silicon carbide (Kramer Industries) at the bottom of the reactor. The SiC particles act as a gas preheater and distributor. The SiC layer also supports the oxygen carrier bed. After the SiC layer is placed, approximately 15 grams of the oxygen carrier is placed into the reactor.

For redox reactions of solid fuel, bituminous coal (Asbury Inc.) is converted into devolatized coal char through heating in the reactor at 800°C in a N$_2$ environment. Injection of the coal is conducted in a pulse mode by loading from the top of the reactor through the small stainless steel tube and is pulsed into the bottom of the oxygen carrier layer of the reactor bed using N$_2$. 10 redox cycles are tested using the fluidized bed reactor conducting two experiments in those 10
cycles. During cycles 1, 3, 5, and 10 solid fuel conversion is tested. Cycles 2, 4, and 6-9 are examining the oxygen uncoupling properties. Exhaust gas concentrations are measured using a quadrupole mass spectrometer (MKS Cirrus 2) and a near-IR based gas analyzer (Emerson X-Stream).

2.4 Sample Characterizations

Phase identification of the oxygen carriers is conducted using X-ray powder diffraction. Powdered samples are prepared and tested using a Rigaku SmartLab X-ray diffractometer with Cu-Kα (λ=0.1542nm) radiation operating at 40kV and 44mA. A scanning range of 20-80° (2θ) with a step size of 0.1° holding for 3.5 seconds at each step is used to generate the XRD patterns. To examine phase properties during TPD experiments, in-situ X-ray diffraction was conducted using an Empyrean PANalytical XRD using a similar Cu-Kα radiation operating at 45kV and 40mA. A 2θ range of 20-80° is used at a ramp rate of 0.1° holding each step for 0.1s. A TPD experiment is conducted in the in-situ XRD by heating the sample at 5°C/min in pure argon. XRD scans are conducted the entire length of the ramp to 1,200°C.

2.5 DFT Calculations

Density functional theory (DFT) calculations are conducted to interpret the oxygen uncoupling behavior of cubic CaMnO$_3$ and hexagonal BaMnO$_3$. The calculations are performed using the Vienna ab initio simulation package (VASP) [63,64] in which a plane-wave basis set is used. The electron-ion interaction is modeled by the projector-augmented wave (PAW) method.[65,66] The Perdew-Burke-Enzerhoff (PBE) form of the generalized-gradient approximation (GGA) is used for the exchange and correlation functional.[67] The plane-wave cutoff energy is set to 425 eV. To calculate the O vacancy (O$_V$) formation energy, 1x2x2 and 2x2x2 supercells are chosen for BaMnO$_3$ and CaMnO$_3$ systems, respectively. A 4x2x2 Γ-centered k-mesh and a 4x4x4 Monkhost-Pack k-mesh are used to the BaMnO$_3$ and CaMnO$_3$ supercells, respectively. In our calculations, both the ferromagnetic (FM) and the antiferromagnetic (AFM) order are used for considered perovskite structures. Here, A-type AFM and G-type AFM spin configurations are adopted by BaMnO$_3$ and CaMnO$_3$, respectively. In this work, removal of one O atom from the perfect structure is done to create a defect. The formation energy of the O vacancy is defined as

$$E_{O_V} = E_{AmnO_5-\delta} + \frac{1}{2}E_{O_2} - E_{AmnO_5}$$

where $E_{AmnO_5-\delta}$ is the total energy of the perovskite supercells with one O vacancy (A= Ba, Ca and δ= 0.125), $E_{O_2}$ is the energy of the isolated O$_2$ molecules in the spin-polarized triplet state, and $E_{AmnO_5}$ corresponds to the energy of the perfect AMnO$_3$.

3. Results and Discussions

3.1 Motivation for Dopant Addition
Previous studies indicate that CaMnO$_3$ undergoes an irreversible phase transition into CaMn$_{2}$O$_{4-\delta}$ and Ca$_2$MnO$_4$ under redox conditions.[59] Since perovskites can accommodate significant amount of oxygen vacancies, the decomposition would occur in two steps. In the first step, manganese undergoes reduction from a 4+ valence state (CaMnO$_3$) to 3+ (CaMnO$_{2.5}$) with the perovskite structure maintained. Further reduction of Mn will result in the formation of new phases:

$$6\text{CaMnO}_{2.5} \leftrightarrow 2\text{CaMn}_2\text{O}_{4-\delta} + 2\text{Ca}_2\text{MnO}_4 + (\delta-0.5)\text{O}_2$$  \hspace{1cm} \text{Reaction 1}

One potential approach to avoid such an undesired transition is to add dopants that enhance the stability of the perovskite phase. By inspection of the Goldschmidt or bond-valence model (BVM) tolerance factor, it is possible to project dopant effect on the structural stability of perovskites semi-empirically. The Goldschmidt tolerance factor is defined in equation 1 [68]:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$  \hspace{1cm} (Eq. 1)

Where $r_A$, $r_B$, and $r_O$ are the ionic radii of the A-site ion, B-site ion, and oxygen ion. BVM tolerance factor replaces the summations of effective ionic radii in Equation 1 with ideal A-O and B-O bond distances.[69] Based on the report by Dabrowski et. al.[70] CaMnO$_3$ has a tolerance factor of 0.985. While this value is within the suitable range to form stable cubic perovskites (0.9$\leq$$t$$<1$), further increase of the tolerance factor towards an ideal value of 1 for cubic perovskite can potentially enhance the stability of the oxygen vacant Ca$_{1-x}$A$_x$MnO$_{2.5}$ perovskite. It is apparent from Equation 1 that larger A-site dopants such as Ba and Sr should render such an effect. It is also noted that the ionic radius of Ba$^{2+}$ (1.61 angstrom) is significantly larger than Mn$^{3+}$ (0.58 angstrom under low spin) and Ca$^{2+}$ (1.34 angstrom). Therefore, significant doping of Ba will lead to a tolerance factor larger than 1, resulting in a hexagonal perovskite structure.

Effect of A-site dopant on stability of CaMnO$_3$ perovskite family can also preliminarily be understood from DFT calculations. The BaMnO$_3$/CaMnO$_3$ structures have different magnetic ordering patterns over different temperature ranges. Table 1 shows the oxygen vacancy formation energies for BaMnO$_3$ and CaMnO$_3$ in both FM and AFM states. It can be seen that O vacancy is easier form in CaMnO$_3$ ($E_{Ov}$ = 1.20 eV and 2.28 eV, respectively) than in BaMnO$_3$ ($E_{Ov}$ = 2.79 eV and 3.18 eV, respectively) regardless of the magnetic state adopted. We found that both CaMnO$_3$ and BaMnO$_3$ with AFM ordering need more energy to release oxygen than the corresponding one with FM ordering. Indeed, the AFM ordered state can only be remained at a relatively low temperature (below the Néel temperature). The computational results implies that the structural stability coupled with the oxygen donation capability can potentially be changed by substituting Ca in the A-site with larger cations such as Sr or Ba. In addition, the doping effect is likely to be correlated to the experimental temperature. Since Sr has an ionic radius slightly larger than Ca but smaller than Ba, one could anticipate Sr addition to Ca$_x$A$_1$. 
MnO$_3$ causing similar effects as Ba addition, but to a lesser extent. Although stability of the perovskite can only be accurately estimated by comparing the relative stability of original and decomposed phases, vacancy formation energy calculations together with semi-empirical analysis give important clues to the selection of potentially effective dopants (like Sr and Ba) for the CaMnO$_3$ parent structure.

Table 1. Oxygen vacancy (O$_V$) formation energy of BaMnO$_3$ and CaMnO$_3$ under FM (ferromagnetic) and AFM (antiferromagnetic) orders

<table>
<thead>
<tr>
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<th>$E_{O_V}$, FM (eV)</th>
<th>$E_{O_V}$, AFM (eV)</th>
</tr>
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<tbody>
<tr>
<td>BaMnO$_3$</td>
<td>2.79</td>
<td>3.18</td>
</tr>
<tr>
<td>CaMnO$_3$</td>
<td>1.20</td>
<td>2.28</td>
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3.2 Thermal Stability of CaMnO$_3$

Although previous studies revealed irreversible decomposition of CaMnO$_3$ to Ruddlesden-Popper and spinel phases, the decomposition was observed under extended redox cycles at relatively low temperatures (<1,000 °C).[31] An alternative approach that can conveniently quantify phase stability of perovskites without undergoing extended redox cycles would be desirable for efficient screening of perovskite based oxygen carriers. In the current study, temperature programmed desorption (TPD) and in-situ XRD are used to determine the stability of perovskites as well as their initial oxygen uncoupling temperature and rate of oxygen uncoupling. Figure 1 shows the TPD and in-situ XRD results. The sample weight loss profile in TPD indicates an initial decomposition temperature at approximately 800°C followed with significant release of lattice oxygen. This is corroborated by the in-situ XRD spectra, which exhibit significant increase in lattice parameter (decreasing 2θ angles) at above 800 °C. When heated above 1,000°C, the CaMnO$_3$ phase decomposes into undesired Ca$_2$MnO$_4$ and CaMn$_2$O$_4$ structures as evidenced by the peaks formed at or near 29.5, 33, 34.5, 37.7, 39, 40.4, 43.2, and etc. 2θ angles.
3.3 Effect of A-Site Dopants on Oxygen Uncoupling Properties

Figure 2- Normalized differential thermal gravimetric (DTG) curves of (a) Ba-doped and (b) Sr-doped CaMnO$_3$ ramped to 1,000°C at a rate of 20°C/min in a pure helium atmosphere. Sample weight: 20mg; Gas flow rate: 100mL/min. He (5.0 Grade).
Perovskite samples with various dopant amounts are tested using TPD to observe initial oxygen release temperature and total amount of oxygen released. Differential thermal gravimetry (DTG) curves of selected samples are shown in Figure 2. The area under the DTG curves is the total weight loss exhibited by the oxygen carriers. As can be seen, CaMnO$_3$ exhibits a significant decomposition peak at around 800°C. A similar feature is also observed for Ca$_{0.95}$Ba$_{0.05}$MnO$_3$. Both Sr and Ba dopant affect the initial decomposition temperature, oxygen release rate, and total oxygen release of Ca$_{1-x}$A$_x$MnO$_3$. Both pure SrMnO$_3$ and BaMnO$_3$ are more stable than CaMnO$_3$ and, as a result, release less total oxygen. BaMnO$_3$ offers about 7 times less total oxygen release and SrMnO$_3$ offers about 3.5 times less oxygen compared to pure CaMnO$_3$. When Sr and Ba are doped to the A-site, properties of both oxides can be observed. Ba and Sr doped samples tend to decompose at significantly lower temperatures (<700°C) than Ca based perovskites. When Ba is doped, the trend is apparent to shift between pure CaMnO$_3$ and pure BaMnO$_3$. While 0.05 Ba doping does not significantly affect the properties of oxygen uncoupling, increasing the dopant amount to 0.25 can shift the initial reduction temperature by approximately 200°C. Total oxygen release for Ca$_{0.75}$Ba$_{0.25}$MnO$_3$ is 3 w.t.% during the TPD experiment. This is only slightly lower than the 3.7 w.t.% oxygen release by pure CaMnO$_3$. The rate of oxygen release in the high temperature ranges (>750°C), however, is significantly slower for Ca$_{0.75}$Ba$_{0.25}$MnO$_3$. Another intriguing property is the significant weight loss observed at low temperatures (<600°C) in which almost 0.5 w.t.% of the sample is released in the form of oxygen (Figure 2a). Further doping of Ba onto the perovskite follows a trend to reduce total oxygen release and oxygen donation rate in the high temperature range. Sr-doped samples follow a trend similar to that exhibited by the Ba-doped samples. Rates of oxygen release at high temperatures are slightly faster than the Ba-doped samples, although still slower than pure CaMnO$_3$. Doping up to 0.25 Sr does not significantly affect the total oxygen released. Initial temperature for oxygen release; on the other hand, is lowered. For instance, Ca$_{0.75}$Sr$_{0.25}$MnO$_3$ exhibits significant weight loss in two distinct temperature regions, i.e. 300 – 450 °C and > 600 °C. The low temperature oxygen release could be associated with chemisorbed oxygen in the lattice structure. Figure 3 summarizes the total oxygen release and initial decomposition temperature for several representative perovskite samples.

![Figure 3](image-url)

Figure 3- Total oxygen release and initial decomposition temperature comparisons between
CaMnO$_3$ and Sr- and Ba-doped synthesized oxygen carriers. Sample weight: 20 mg; Gas flow rate: 100mL/min. He (5.0 Grade).

**Structural and Stability Studies**

Effectiveness of dopant addition largely relies on the compatibility of the dopant and its parent structure. Ideally, dopant should be fully incorporated into the host structure to form a homogeneous solid state solution. Figure 4 illustrates the XRD patterns for the oxygen carriers for Ba and Sr doped CaMnO$_3$ at a range of x=0 to x=1. As can be seen, Ba cannot be fully incorporated into the CaMnO$_3$ structure in most cases. Even at small dopant levels (x<0.1), a secondary hexagonal BaMnO$_3$ phase can be identified. When doped further, ternary phases, such as Mn oxides, are observed until A-site is fully occupied by Ba. Sr-doped CaMnO$_3$, on the other hand, forms a relatively homogenous solid-solution. Sr doping up to x=0.25 exhibits complete incorporation of Sr into CaMnO$_3$ while shifting the structure from cubic to orthorhombic. At x=0.5, co-existence of SrMnO$_3$ and CaMnO$_3$ structures are observed. At higher doping levels (>0.5), a single orthorhombic SrMnO$_3$ phase is observed.

![XRD patterns](image)

Figure 4- XRD of various doped CaMnO$_3$ with (a) Sr doping and (b) Ba doping. Phases: (●) SrMnO$_3$, (x) CaMnO$_3$, (▲) BaMnO$_3$, and (★) Mn$_3$O$_4$.

The primary motivation for dopant addition is to stabilize the CaMnO$_3$ structure and prevent the formation of stable spinel phases at high temperatures. Figure 5 investigates the *in-situ* XRD of the Sr- and Ba-doped CaMnO$_3$. For the Sr-doped sample, the structure of the perovskite phase is maintained even at a high temperature of 1,200 °C. To compare, CaMnO$_3$ is decomposed at 1,000 °C. Significant shift of 20 angles, which are indicative of oxygen release, begins at approximately 600°C. This is consistent with TPD observations. Ca$_{1-x}$Ba$_x$MnO$_3$ sample with a low dopant level (x=0.05) was chosen for *in-situ* XRD due to the difficulty to incorporate Ba into the CaMnO$_3$ host structure. As shown in Figure 5, the Ba-doped sample, similar to CaMnO$_3$, exhibited phase decomposition at 1,000°C. It is therefore concluded that Sr is likely to be a more suitable dopant for CaMnO$_3$, since it readily incorporates into the host structure and helps to...
enhance the stability of the perovskite phase. Ba-doped samples, on the other hand, do not exhibit the desired CLOU properties. This may have resulted from the significant differences in ionic sizes between Ba$^{2+}$ and Ca$^{2+}$, which can lead to large lattice distortions and stresses.

Figure 5- *In-situ* XRD of the (a) Ca$_{0.75}$Sr$_{0.25}$MnO$_3$ and (b) Ca$_{0.95}$Ba$_{0.05}$MnO$_3$ in argon at a ramping rate of 5°C/min to 1,200°C. Gas flow rate: 50mL/min Ar (Grade. 5.0)

### 3.4 Redox Testing

CLOU performance of an oxygen carrier can be characterized by its oxygen donation properties under cyclic redox conditions. In order to determine the oxygen donation properties of the reference (CaMnO$_3$) and Sr doped (Ca$_{0.75}$Sr$_{0.25}$MnO$_3$) oxygen carrier samples, short-term isothermal redox experiments are carried out at 650°C, 750°C, 850°C, and 950°C. The results are summarized in Figure 6.
As can be seen, undoped CaMnO$_3$ does not observe any noticeable weight loss at 650°C. Once the temperature reaches 850°C, significant oxygen release is observed. When the temperature is increased even further, the oxygen carrier exhibits even higher oxygen donation. When doping Sr and Ba into CaMnO$_3$, different phenomena are observed. When Ba is doped, there is no indication that the material is being reoxidized to any extent at any temperature using 10% O$_2$. From XRD of the reduced sample, the formation of spinel CaMn$_2$O$_4$ phase is observed. This may indicate that Ba could be distorting the structure to promote the decomposition of the cubic CaMnO$_3$ phase. In-situ XRD (Figure 5b) also corroborates the formation of spinel and reduced perovskite phases at a lower temperature than pure CaMnO$_3$. When Sr is doped into the CaMnO$_3$ structure, it promotes oxygen donation at a much lower temperature while still being able to reoxidize. While at 650°C, ~0.1 w.t.% oxygen release is observed. Once the material is heated to 850 and 950°C, total oxygen release becomes more significant. In pure CaMnO$_3$, near complete oxidation using 10% oxygen is achieved. However, Sr-doped CaMnO$_3$ is only able to restore roughly 99% of the initial weight. Each sample was cycled 5 times at each temperature and no change in performance was observed.

In chemical looping schemes, long term cycling is important due to the need to replenish the solid oxygen carriers over time. Figure 7 examines the Sr-doped perovskite at 850°C for 100 uncoupling cycles. Over 100 cycles, the material has no observable deactivation and is very stable throughout all 100 cycles. After 100 cycles are performed, oxygen release is still observed at lower temperatures 650°C and 750°C. The oxygen capacity and rate of oxygen release at these lower temperatures are comparable to what was observed in Figure 6. XRD analysis shows a small amount of SrMnO$_3$ appearing after the 100 cycles (See Figure S2). However, no spinel or Ruddlesden-Popper phases were identified.
Initial coal char reactions were conducted in a TGA. Coal char was well mixed with the oxygen carrier and placed in the TGA and heated to 250°C to remove any moisture. The TGA is then heated to 950°C in helium and the reaction is allowed to proceed to completion. Figure 8 examines the results of pure CaMnO\textsubscript{3} versus a Sr-doped sample. The Sr-doped oxygen carrier has an initial reaction temperature of approximately 100°C lower compared to the undoped CaMnO\textsubscript{3} oxygen carrier. Besides the lower reaction temperature, the Sr-doped has a higher activity in reaching full conversion of solid char.

Figure 8- Char combustion using TGA of pure and Sr-doped CaMnO\textsubscript{3}. Heating in inert to 250°C for drying, then heated at a rate of 20°C/min. in helium to 950°C. Sample weight: 20mg for the oxygen carrier and 0.2mg of coal char. Gas flow rates: 100mL/min He (5.0 Grade).
Fluidized bed results are shown in Figure 9. Examination of the solid char cycles of the Ca$_{0.75}$Sr$_{0.25}$MnO$_3$ reveals nearly 100% conversion of the coal char in every cycle. This is confirmed through no observable CO$_2$ during the oxidation step (see Figure S3). Further comparison of the CO$_2$ to CO selectivity reveals around 90% selectivity during every cycle. The fluidized bed results confirm the viability of the Ca$_{0.75}$Sr$_{0.25}$MnO$_3$ oxygen carrier in CLOU applications.

![Graph showing Char Conversion and CO$_2$ Selectivity](image)

Figure 9- Char conversion and CO$_2$ selectivity of the Ca$_{0.75}$Sr$_{0.25}$MnO$_3$ oxygen carrier in a fluidized bed reactor. Sample weight: 17 gms, Ca$_{0.75}$Sr$_{0.25}$MnO$_3$ and 10mg of char Temperature: 850°C Gas Flow Rates: nitrogen: 800mL/min (Grade 5.0) and helium (Grade 5.0): 280mL/min (Char Reduction) and oxygen (Extra dry grade): 120mL/min (during oxidation only).

4. Conclusions

The present study investigates the redox properties of doped CaMnO$_3$ as oxygen carriers for CLOU processes. The effects of A-site substitution with Sr and Ba dopants on structural stability, oxygen carrying capacity, and oxygen donation temperature of the oxygen carriers are investigated. The A-site dopants are chosen through both a semi-empirical approach and DFT calculations for oxygen vacancy formation energy. Ba addition to the CaMnO$_3$ structure is found to be ineffective due to the inability of Ba to incorporate into the CaMnO$_3$ structure. Sr, on the other hand, is found to form homogeneous solid solutions with the CaMnO$_3$ host structure. Sr-doped samples are also found to be effective in preventing irreversible decomposition of the parent perovskite structure to the Ruddlesden-Popper (Ca$_2$MnO$_4$) and spinel (CaMn$_2$O$_4$) phases. Excellent stability is observed for Sr doped sample (Ca$_{0.75}$Sr$_{0.25}$MnO$_3$) through various conditions including heating to 1,200°C, 100 isothermal redox cycles, and reaction with solid...
fuels. Besides the increased stability of the structure, Sr-doped oxygen carriers exhibit noticeable oxygen release at significantly lower temperature than that observed for pure CaMnO$_3$. Due to its various advantages compared to undoped CaMnO$_3$, Sr-doped CaMnO$_3$ oxygen carrier offers a potentially viable option for solid fuel conversion in CLC schemes.

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