

# Novel perovskite ceramics for chemical looping combustion application



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## ABSTRACT

New modified calcium manganese (CM) perovskite structures applicable in chemical looping combustion were synthesized in this study. These modifications were applied by doping the A-site with lanthanum and strontium and B-site by iron and zirconium (CLMF, CLMZ, CSMF, and CSMZ). TGA, XRD, SEM and BET techniques have been used to characterize the prepared structures. According to the results obtained from TGA analysis, the oxygen capacity of the samples ranged between 1.2 for CLMZ and 1.75 for CSMF. All prepared samples showed to possess a porous surface and the perovskites phase formation was confirmed by XRD results. Iodometric titration experiments were also conducted for evaluating the manganese ion charge and its variability in association with different doping elements. Reactivity and oxygen uncoupling behaviors of the prepared samples were also evaluated using a fluidized bed chemical looping reactor using methane as the fuel at four different temperatures (800, 850, 900, 950 °C).

All of the oxygen carriers showed oxygen uncoupling behavior and they were able to capture and release oxygen. Mass-based conversion of the perovskites was calculated and temperature increase proved to increase the mass-based conversion rate in all of the samples under study. Gas yield was calculated at 950 °C as well, and results showed that CLMZ, CM and CSMF showed 100% gas yields and CLMF and CSMZ showed approximately 85% yield in fluidized bed reactor, which is a high and acceptable quantity.

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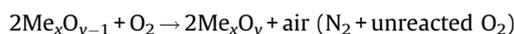
## 1. Introduction

Chemical looping combustion (CLC) is a novel method of pure CO<sub>2</sub> production during carbonaceous fuel combustion with the least energy penalty among currently introduced methods. This system is commonly composed of two interconnected fluidized bed reactors, called air and fuel reactors. In order for the combustion to occur, the oxygen in the air reactor, should be transferred to the fuel reactor (containing carbonaceous fuel, C<sub>n</sub>H<sub>2m</sub>) using metal oxides (Me<sub>x</sub>O<sub>y</sub>) called oxygen carriers. These materials are oxidized in the presence of air in the air reactor and are then transferred to the fuel reactor. In the fuel reactor, the fuel reacts with the oxygen carriers, utilizing their captured oxygen and consequently fuel oxidation and oxygen carrier reduction occur

simultaneously. Afterwards, the oxygen carriers are transferred to the air reactor for reoxidation and a new cycle begins [1–3].

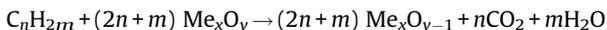
There are several factors that make CLC superior to a conventional combustion process. As mentioned earlier, in CLC oxygen is transferred between reactors and hence the combustion occurs in the presence of pure oxygen. This way, the only products of the combustion reaction are CO<sub>2</sub> and water vapor which can be separated by using a simple condensation unit, as opposed to a combustion that takes place in air which can have several byproducts and CO<sub>2</sub> separation requires energy intensive utilities. It is also of great interest in CLC processes that the sum of the heat released during the oxidation and reduction reactions is the same as the heat released during a normal combustion process [2].

The two main reactions during oxidation and reduction are shown below:

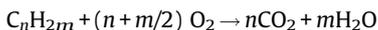
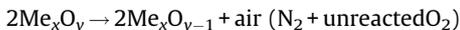


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The Chemical Looping Combustion with Oxygen Uncoupling (CLOU) process is also a CLC technology with a different mechanism for burning the fuel. In CLOU, the fuel reacts with the oxygen released by the oxygen carriers via the following oxidation and reduction reactions [4,5]:



As mentioned earlier, oxygen carriers are responsible for oxygen transport between reactors. As a result, an effective oxygen carrier is one of the main determinants of a successful CLC process and hence there have been numerous studies investigating various oxygen carriers applicable in CLC. For an efficient CLC process, these oxygen carriers should have specific qualifications such as: high reactivity with the fuel to result in complete combustion, stability, resistance to agglomeration, durability throughout multiple oxidation and reduction cycles and mechanical strength. They should also be non-toxic, environmentally friendly and cost effective [2]. Oxides of transition metals (Ni, Fe, Co, Mn, Cu) [6,7] and their combinations; natural ores such as ilmenite [8]; and mixed metal oxides called perovskites [9–11] have been investigated by many research groups and have proven to be viable options as oxygen carriers for chemical looping purposes. In recent years, special attention has been devoted to perovskite ceramics because of their special characteristics [2,12–14]. These structures are important because they are composed of a combination of metal oxides with different features. It is also of great importance to know that around 90% of elements in the periodic Table can be successfully incorporated into a perovskite structure [15]. This provides us with a wide range of elements to choose from and tune the properties of the perovskites as desired for their intended applications. Perovskite materials have a general formula of ABO<sub>3</sub>, in which A and B are both cations, with A as a larger cation than B. Transition metals will usually locate on the B-site, whereas larger cations (such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>) will be located on the A-site [14,16]. In recent years, several studies have been conducted in order to synthesize more efficient perovskites applicable to CLC as oxygen carriers [10]. The most promising material that has been used extensively during the past decade is CaMnO<sub>3</sub> [17,18]. In this structure, the release and capture of oxygen is due to the transformation of Mn<sup>4+</sup>–Mn<sup>3+</sup>, thereby facilitating the oxygen release within the fuel reactor. However, this structure is subject to change into Ca<sub>2</sub>MnO<sub>4</sub> and CaMn<sub>2</sub>O<sub>4</sub>, which might cause a decrease in the perovskite efficiency during oxidation–reduction cycles at high temperatures. According to the literature, to resolve this problem, transition metals such as Ti, Fe, Zr and Cu can be doped with the B-site cation (Mn), leading to a more stable structure during the process [2].

Although, the ideal perovskite structure is cubic, the small ionic radius of the doped ions, compared with the voids between the octahedral, will result in a cooperative tilting of the corner shared octahedral, such that structure distorts into the orthorhombic space group *Pnma* [19].

In ternary oxides, the BO<sub>6</sub> octahedral tilting is possible when employing smaller A-site cations in the ABO<sub>3</sub> structure. If tilting occurs, the BO<sub>6</sub> octahedral distort such that the B–O–B bonds are no longer equal to 180° [19,20]. Distortion in ABO<sub>3</sub> type perovskites can occur by changes in B–O bond lengths. This will result in deviation from the ideal cubic structure. These types of distortions are prompted by orbital degeneracies, polar distortions, bond-valence requirements, and/or valence fluctuations. Changes in B–O bond lengths in the systems with *d*<sup>4</sup> or *d*<sup>7</sup> electronic configurations on their B atoms are possible and expected. These

changes can lead to Jahn–Teller-type anti-symmetric breathing of the BO<sub>6</sub> octahedral [21].

It is also important to note that the degree of distortion and the properties of the perovskites are highly dependent on the synthesis conditions. As a result, several methods of synthesis have been introduced for perovskite production to date, which strongly influence its surface physicochemical properties, surface area, porosity, purity, stability and crystal size [22,23]. Of all the proposed techniques, the solid state reaction, the sol-gel method, the combustion method, mechanical–chemical processing, the Pechini method and the microwave route are the most common [24]. An important feature of the preparation method is the scale up capacity of it. Most of the preparation methods cited above are developed for laboratory scale production. Currently, the preparation methods planned for oxygen-carrier preparation at large-scale production are spray drying and impregnation [3]. Extrusion is an important forming technique in the ceramics industry owing to its ability to provide complex shapes and forms with dimensional accuracy, and to its flexibility for mass production [25]. One of the main goals of the proposed method is to use the mass production capability of extrusion technique. Therefore, the extrusion technique is selected for production of oxygen carriers in the present study.

There is a relationship between composition, structure and properties, which have been well studied in recent years [2,26,27]. However, many questions remain in this relationship that need to be explored in the future.

As discussed earlier, several studies have tried to improve the stability and oxygen capacity of CaMnO<sub>3</sub> [2]. Although, some of them have been successful in addressing the stability of calcium manganese by doping the A- or B-sites, the oxygen capacity has decreased as a result of doping [17,28–30]. Here, we have tried to find doping elements that can increase both the oxygen capacity and stability of CaMnO<sub>3</sub> by investigating the effect of ion size on A- and B-site positions of this perovskite structure i.e., replacing the Mn and Ca sites with larger cations, such as Zr and Sr respectively. Undoped calcium manganese is also prepared for comparison (CM) purposes, while a lanthanum and iron doped sample (CLMF) is chosen to identify the effects of starch optimization and preparation method on physical properties of the samples. CLMF has been reported by Arjmand et al. [28] using rotary evaporation as the mixing method with the starch amount not being optimized.

## 2. Experimental procedure

The perovskite-based oxygen carrier particles, which are investigated in this study, are synthesized as follows. Ca(OH)<sub>2</sub> (Alfa-Aesar, 95 wt%) and MnCO<sub>3</sub> (Alfa-Aesar, 99 wt%) powders with an average particle size of ~46 μm (325 mesh) are mixed in an appropriate weight ratio with or without La<sub>2</sub>O<sub>3</sub> (Alfa-Aesar, 99.9 wt%), Fe<sub>2</sub>O<sub>3</sub> (Alfa-Aesar, 99 wt%), ZrO<sub>2</sub> (Acros Organics, 99 wt%), and SrCO<sub>3</sub> (Alfa-Aesar, 99 wt%), to make 500 g batches of the final product in each case. A simple coding label C(S or L)M(F or Z) is used for each sample, where C=Ca, S=Sr, L=La, M=Mn, F=Fe and Z=Zr. Hence the synthesized samples are CLMF, CLMZ, CSMF, CSMZ and CM. The list of

**Table 1**  
EDS analysis of the samples (single perovskite) investigated in this work (at%).

Element	CM	CLMF	CLMZ	CSMF	CSMZ	Computational data
Ca	18.63	16.63	16.94	16.12	17.67	18
Mn	18.75	15.74	17.03	15.30	17.57	18
O	62.62	63.84	62.20	65.10	61.43	60
La	–	1.91	1.95	–	–	2
Fe	–	1.88	–	1.91	–	2
Sr	–	–	–	1.57	1.64	2
Zr	–	–	1.87	–	1.68	2

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