



# Synthesis and preliminary study of pure and Zr-doped $\text{YMnO}_3$ compounds as Solid Oxide Fuel Cells electrode



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## ABSTRACT

The  $\text{Y}_{1-x}\text{Zr}_x\text{MnO}_3$  series ( $0 \leq x \leq 0.30$ ) has been studied to be used as possible SOFC electrode material. These compounds adopt a layered structure of hexagonal symmetry in which the manganese cations are located in trigonal bi-pyramidal coordination of oxygen atoms, different from that of the classical perovskite. The synthesis of the materials has been carried out by solid state reaction and X-ray diffraction technique reveals that pure phases can be obtained until  $x=0.10$ . For  $x \geq 0.10$ , an additional YSZ phase is formed, similar to the SOFC electrolyte material. HT-XRD technique and thermogravimetric analysis of pure or Zr-doped  $\text{YMnO}_3$  indicate that, in diluted dry  $\text{H}_2$  for  $T > 600$  °C, these compounds are unstable, what precludes their use as anode material. On the other hand, reactivity studies at high temperature ( $T = 1300$  °C) between  $\text{Y}_{1-x}\text{Zr}_x\text{MnO}_3$  ( $x = 0, 0.05$  and  $0.1$ ) and 8YSZ show a chemical compatibility in which the formation of an electrically insulating phase does not take place, but a crossed diffusion of  $\text{Y}^{3+}/\text{Mn}^{3+}$  and  $\text{Zr}^{4+}$  at the interface between both materials. Thermomechanical compatibility in air between YSZ and  $\text{Y}_{1-x}\text{Zr}_x\text{MnO}_3$  is also demonstrated from RT to 850 °C.

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## 1. Introduction

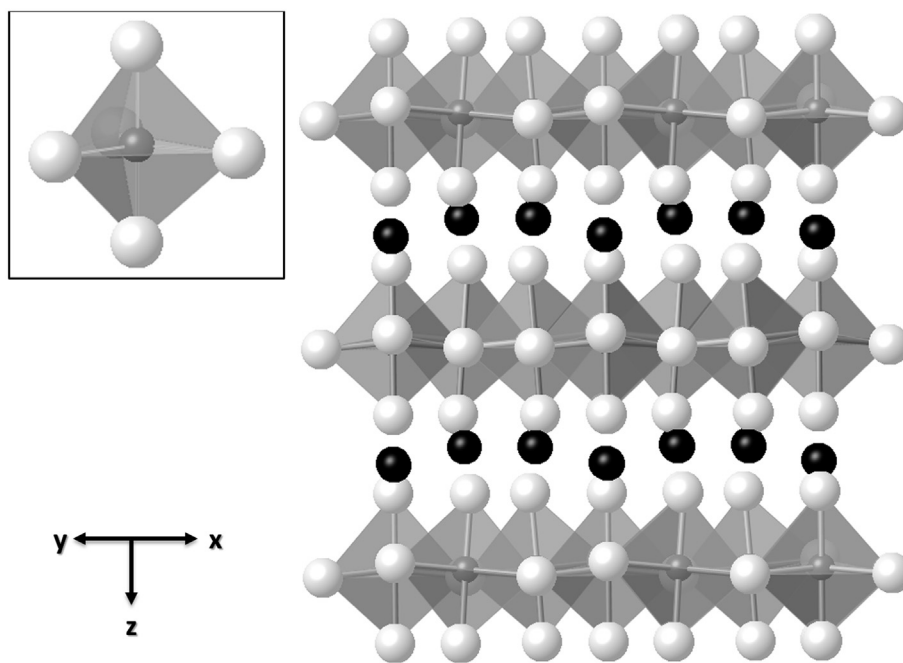
Given the increasing of different environmental problems and the possibility of a global energetic crisis, finding ways that are more efficient for energy generation is of major importance for generations to come. The Solid Oxide Fuel Cells (SOFC) are considered as one of the most viable solutions for the future, as it can operate either with hydrogen, the non-polluting fuel by excellence, or with any organic fuel, fossil or synthetic, with a relatively higher efficiency of conversion than other more classical technologies [1–3]. Unfortunately, the state-of-the-art materials used to fabricate SOFCs are already not giving complete satisfaction in terms of efficiency and durability, especially because of chemical reactivity at the interfaces during cell preparation or *in operando*; this is especially the case at the cathode side, the main degradation occurring from the reactivity between the electrode and both electrolyte or interconnect [4,5]. Moreover, the Ni/YSZ cermet (YSZ = yttria-doped zirconia) currently employed at the anodic side

presents many problems during redox cycling and Ni coarsening in temperature, in addition to issues related to complex organic fuel utilization (coking, poisoning with sulfur, ...) [6].

While most of the research done in the area is focused on perovskite oxides, this study goes aboard on the study of manganites of a different structure type. Indeed,  $\text{REMnO}_3$  oxides can crystallize into two distinct ways depending on the size of the rare earth (RE) cation with respect to Mn: when the RE ionic radius is large (La–Tb) the structure adopts the perovskite arrangement, but if it is small (Dy–Lu, Y, Sc), the material becomes layer-type [7,8]. In particular,  $\text{YMnO}_3$  crystallizes in the hexagonal  $P6_3cm$  space group. As depicted in Fig. 1, the structure is built of  $[\text{MnO}_5]$  trigonal bi-pyramids (instead of octahedra in perovskites) linked by their three equatorial vertices to form layers. The latter are in turn separated by layers of  $\text{Y}^{3+}$  cations in 8-fold bi-capped trigonal antiprisms of oxygen (instead of 12-fold for the RE site in perovskites), the  $[\text{YO}_8]$  polyhedra being linked to the apical oxygen ions of the bi-pyramids [7]. The stability of the hexagonal layered structure of  $\text{REMnO}_3$  stoichiometry with respect to the perovskite is mainly due to the low value of the Goldschmidt tolerance factor ( $t < 0.855$ ) because of a small RE cation [9,10]. Indeed,  $\text{YMnO}_3$  can be prepared in both structural types, but the hexagonal layered compound (h- $\text{YMnO}_3$ ) is

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**Fig. 1.** Representation of hexagonal  $\text{YMnO}_3$  structure. Buckled layers of Y atoms (black) in 8-fold coordination of O atoms (light gray) separate the  $[\text{MnO}_5]$  trigonal bi-pyramids (dark gray) layers in which each polyhedron is linked to three other by their equatorial vertices.

more stable in usual temperature and pressure conditions. As an example,  $h\text{-YMnO}_3$  can be synthesized by solid state method in air at  $1200^\circ\text{C}$  under ambient pressure [8] whereas the orthorhombic perovskite structure is stabilized by either low-temperature [11], high-pressure synthesis [12], or even epitaxial thin film growth [13].

According to literature,  $\text{YMnO}_3$  can be doped by aliovalent cations, as in the case in which  $\text{Y}^{3+}$  cations are replaced by  $\text{Zr}^{4+}$ , forming a hexagonal solid solution for  $x < 0.3$  compositions [14–18]. According to Van Aken *et al.* [14], the doping the structure with  $\text{Zr}^{4+}$  conduces to  $\text{Mn}^{2+}/\text{Mn}^{3+}$  mixed valence with a decrease of lattice parameters. Nevertheless, another work indicates that single phased materials cannot be obtained for concentrations higher than  $x = 0.1$  in the  $\text{Y}_{1-x}\text{Zr}_x\text{MnO}_3$  series; beyond such value, precipitation of  $\text{ZrO}_2$ -type material occurs [15]. Some authors also indicate the possibility of substituting  $\text{Ca}^{2+}$  or  $\text{Sr}^{2+}$  for  $\text{Y}^{3+}$  and forming the  $\text{Y}_{1-x}\text{A}_x\text{MnO}_3$  ( $\text{A} = \text{Ca}, \text{Sr}$ ) solid solution hexagonal structure for  $x < 0.22$  [16,17]. In this case, acceptor doping induces a  $\text{Mn}^{3+}/\text{Mn}^{4+}$  mixed valence that provides p-type carriers and higher conductivity level respect to that of Zr-doping [14]. However, other studies claim that Ca-doping is not possible in  $\text{YMnO}_3$  and such substitution always gives a mixture including an orthorhombic perovskite phase [17]. Moreover, Sr-doping in  $\text{YMnO}_3$  would induce, as in the case of Sr-doped  $\text{LaMnO}_3$  (LSM), a strong chemical reactivity with the YSZ electrolyte [18]; such reactivity would be probably the case for Ca-doping too, which is not acceptable for the application.

Finally, different results describe the non-stoichiometry possibilities in  $\text{REMnO}_3$  hexagonal manganites; according to T. Atsumi *et al.* [19],  $\text{YMnO}_{3-\delta}$  can be oxygen deficient until the maximum value  $\delta \sim 0.04$ , confirmed more recently by the parent composition  $\text{DyMnO}_{3-\delta}$  by Remsen *et al.* [20]. The latter work also describe that the  $\text{RMnO}_3$  family displays oxygen excess considerable oxygen positive non-stoichiometry, until  $\delta \sim 0.18$  for  $\text{R} = \text{Dy}$  in air, which gives insight of some aptitude for donor doping. On the other hand, the soft chemistry reduction of  $\text{YMnO}_3$  using a calcium hydride

probe to be stable until  $\text{YMnO}_{2.80}$  and interesting structural features give hope for a possible Mixed Ionic Electronic Conducting (MIEC) behaviour *i.e.* the possibility to use such manganites as SOFC electrode materials: (i) the reduced compounds present oxygen vacancies localized in the equatorial planes with an increasing disorder in the tilting that could be associated to higher oxygen (or oxygen vacancy) mobility; (ii) the reduction induces a structural change to the more symmetrical space group  $P6_3/mmc$  for which the  $[\text{MnO}_5]$  bi-pyramids are not yet cooperatively tilted and the Y planes not buckled [21].

The aim of this preliminary study is to clarify the possibility of doping Zr for Y in  $\text{YMnO}_3$  but also to evaluate the possible use of such pure or donor-doped materials as anode and/or cathode component in Solid Oxide Fuel Cells, based on tests of chemical and thermomechanical compatibility with SOFC electrolyte YSZ and reducibility in diluted hydrogen atmosphere.

## 2. Materials and methods

Non-doped  $\text{YMnO}_3$  powder was prepared by solid-state reaction using  $\text{Y}_2\text{O}_3$  (Alfa Aesar, 99.9%, previously treated at  $1000^\circ\text{C}$  for 3 h) and  $\text{MnO}_2$  (Alfa Aesar, 99.9%, dried at  $150^\circ\text{C}$  for 3 h) as precursors. Stoichiometric amounts of the corresponding powders were thoroughly weighed, mixed and ground together before being pressed into pellets that were placed on alumina foils using sacrificial powder bed. The heat treatment were performed at  $1400^\circ\text{C}$  during 12 h in air using heating and cooling rates of  $4^\circ\text{C min}^{-1}$ . For the doped  $\text{Y}_{1-x}\text{Zr}_x\text{MnO}_3$  samples ( $x = 0.05, 0.1, 0.15, 0.2$  and  $0.3$ , thereafter referred as YZM), Zr (IV) isopropoxide (Alfa Aesar, 99.9%), previously treated at  $1000^\circ\text{C}$  for 3 h was used as zirconium source. In this case, the pressed pellets were placed on platinum foils due to greater reactivity with alumina, then treated in air at  $1400^\circ\text{C}$ ,  $1450^\circ\text{C}$  and finally  $1500^\circ\text{C}$ , each time for 12 h, with intermediate grinding steps.

Phase analysis was performed after synthesis by X-ray diffraction at room temperature using a BRUKER D8 ADVANCE powder

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