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Preparation, thermal and phase evolution and functional properties of non-stoichiometric strontium-doped lanthanum manganite perovskite ceramics

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ABSTRACT

Powders of $(La_{0.85}Sr_{0.15})_{0.98}MnO_{3-\delta}$ (LSM85) and $(La_{0.80}Sr_{0.20})_{0.98}MnO_{3-\delta}$ (LSM80) perovskites have been synthesized and characterized in detail, and then sintered to evaluate their electrical and magnetic properties at low temperatures and at near room temperature. Microstructural observations/analyses after the dilatometric essays show that the perovskites have compositions that deviate from the nominal ones. Furthermore, magnetic characterization of both samples reveals a ferromagnetic behavior with a Curie temperature above 300 K for LSM80 and of 260 K for LSM85. In addition, LSM85 is insulator from 15 up to 300 K, whereas LSM80 is metallic up to 160 K and insulator up to 300 K. This significant discrepancy of behaviour is attributable to structural and compositional differences between the two perovskites.

1. Introduction

There is currently great interest in the development of new oxides with perovskite structure and formula ABO_3, where the B-site cation occupies the interstitial site of an octahedron of oxygen anions, and the A-site cation fits in the large cavity at the centre of the 12 coordination site [1,2]. Interestingly, these perovskites can exhibit a wide range of possible oxygen stoichiometries which provides them with an attractive combination of ionic and electronic conductivity, so that they find application in several fields such as catalysis, fuel cells, oxygen sensors, and membranes for gas separations [3,4], to name a few. There is also great attention put today on investigating the wide variety of appealing electrical and magnetic properties of the perovskite oxides [5,6], and in their possible utilization as electrode materials for solid-oxide fuel cells (SOFCs) [7–12]. Strontium-doped lanthanum manganite (i.e., $La_{1-x}Sr_xMnO_3$, or simply LSM) is known to be a very promising cathode for those SOFCs based on stabilized zirconia electrolyte because of its high electrical conductivity, elevated chemical and thermal stabilities, and high catalytic activity for the oxygen reduction, as well as for its compatibility with the zirconia electrolyte. Stoichiometric nominal compositions of $La_{1-x}Sr_xMnO_3$ with $x < 0.2$ are normally used in the present generation of SOFCs [13], despite non-stoichiometric LSMs are more sinterable and densifiable and also have higher electrical conductivity. In addition, due to their magnetic properties LSM ceramics are also suitable materials as magnetic field sensors [14] and in hyperthermia applications [15], so that the control of the composition and the formation of different oxidic phases result appealing. However, the information about synthesis, thermal evolution, sintering behavior and the relationships with their functional properties (particularly electrical and magnetic features) of the non-stoichiometric LSMs is still very scarce [16]. This is therefore the objective of the present work, which, seeking to expand the existing knowledge on non-stoichiometric LSMs, specifically investigates all these aspects on both LSM nanopowders and bulks with nominal composition given by $(La_{0.85}Sr_{0.15})_{0.98}MnO_{3-\delta}$ and $(La_{0.80}Sr_{0.20})_{0.98}MnO_{3-\delta}$. We have chosen two materials with two compositions very close each other but belonging to two different regions in the magnetic phase diagram of $La_{1-x}Sr_xMnO_3$ [17], although there must be taken into account that non-stoichiometric perovskites are considered in this work.

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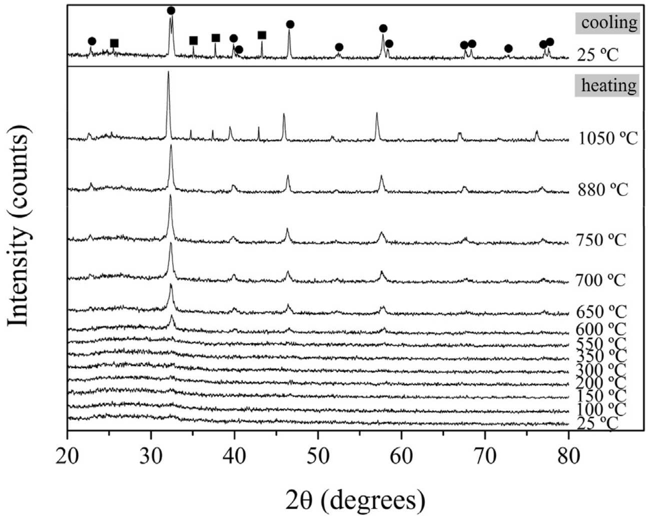

Fig. 1. XRTD patterns of the as-synthesized LSM85 powder collected in-situ at different temperatures (as indicated) in the range 25–1050 °C. Peak assignations are included for relevant peaks (solid circles for LSM, and solid squares for the Al_2O_3 holder).

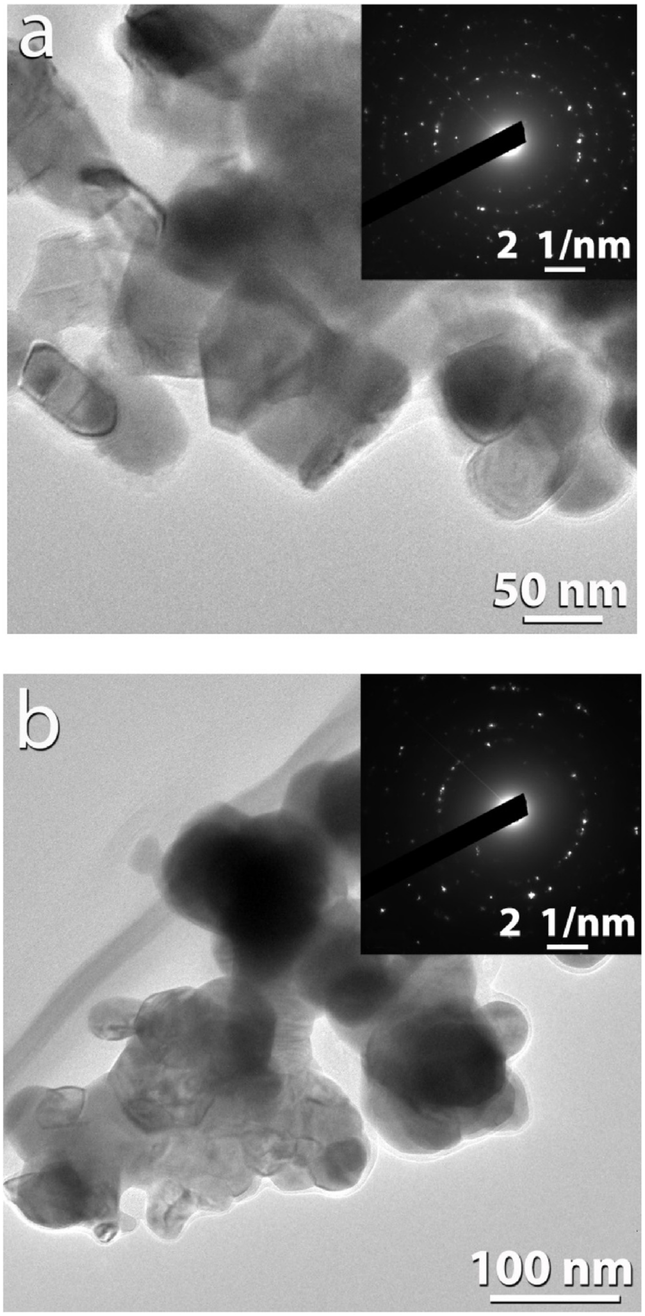

Fig. 2. TEM images of the (a) LSM80 and (b) LSM85 powders after calcination in air at 1000 °C for 1 h. The insets show the corresponding SAED patterns.

2. Experimental procedure

2.1. Powder synthesis

Non-stoichiometric LSM powders with nominal compositions given by $(La_{0.85}Sr_{0.15})_{0.98}MnO_{3-\delta}$ and $(La_{0.80}Sr_{0.20})_{0.98}MnO_{3-\delta}$ (hereafter labelled simply as LSM85 and LSM80, respectively) were synthesized by the complexation of metal ions with citric acid and polyesterification between the acid and poly-ethylene-glycol. To that end, solutions of the relevant nitrates—namely $La(NO_3)_3{\cdot}6H_2O$, $Sr(NO_3)_2$, and $Mn(NO_3)_3{\cdot}4H_2O$, the three of analytical-reagent grade, from Aldrich, Germany—were first standardized by total reflection X-ray fluorescence (TXRF S2 PicoFox, Bruker, Germany), and then combined with citric acid and polyethylene-glycol in sufficient quantities to bind all the cations (the citric acid: metal ions ratio was 1:1). After metal nitrates were dissolved in deionized water and stirred at 90 °C to obtain a clear solution, aqueous citric acid and ethylene glycol solutions were sequentially added to the solution containing the metal ions. The mixture was stirred at 90 °C for 2 h until gelation occurred. Next, the gel was dehydrated (at 150 °C) to remove the water that was produced by the polyesterification between ethylene glycol and citric acid. The resulting deep-brown gel, which was dried overnight in an oven at 180 °C, formed a sponge-like polymeric resin. The resulting powders hereafter will be referred to as-synthesized powders. Finally, the resin was calcined at 500 °C for 1 h in air (heating and cooling rate of 5 °C/min) to remove any remaining organics, and micro-milled for 3 h, and sieved up to 63 μm. Then, the resulting powders were re-calcined at 1000 °C for 1 h in air, crushed with a pestle and sieved again up to 63 μm.

2.2. Powder characterization

The as-synthesized LSM powders were investigated using X-ray diffractometry (XRD, D8 Advance, Bruker AXS, Germany), and the LSM85 powder by X-ray thermo-diffractometry (XRTD) as well. XRD was aimed at elucidating the amorphous or crystalline nature of the LSM powders; if required, phase identification was performed with the aid of the PDF2 database. The XRTD patterns [18] were collected at different temperatures in the range 25–1050 °C (heating ramp of 5 °C/s). XRTD was aimed at investigating in-situ the thermal evolution. The LSM powders calcined at 500 °C and those re-calcined at 1000 °C were also, once crushed, characterized by XRD, with the same goals and procedures as in the case of the as-synthesized powders. After calcination at 500 °C for 1 h, the powders suspended in ethanol and sonicated for 1 min were studied by laser diffraction (Mastersizer S, Malvern, UK) to determine their particle size distribution. Those powders were also subjected to micro-milling for different times (1, 2, 3, and 4 h) in order to choose an adequate milling time. We consider 3 h as the best milling time since the resulting particle distribution was monomodal, centred at the lowest average particle size, and the narrowest if we compare with the distributions for the rest of the studied times. After milling the particles of the LSM80 powder have sizes ranging from ~200 nm to 20.0 ± 0.5 μm, with the average particle size being 3.0 ± 0.5 μm, while the particle sizes of the LSM85 powder

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