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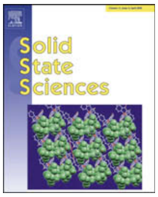

Cation-deficient lanthanum manganite oxides: Experimental and theoretical studies

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ABSTRACT

Cation-deficient lanthanum manganite oxides with $0.8 \leq La/Mn \leq 1.25$ were synthesized using a multi-step decomposition of gel precursors and investigated from experimental and theoretical point of view. The XRD (X-Ray Diffraction) analysis of the mixed $LaMnO_3$ oxide crystal concludes to a hexagonal structure, space group R-3c, excluding the presence of pure oxides such as La_2O_3, Mn_2O_3, or MnO_2 whatever the ratio La/Mn is. Oxides with nominal formulae $La_{1-x}MnO_{3+y}$ and $LaMn_{1-x'}O_{3+y}$ contain more than one defect structure involving valence defect (holes $h^{\bullet}$), anionic vacancies as well as cationic vacancies in A and B sublattices of the perovskite structure. With the increase of La or Mn non-stoichiometry, the oxygen content *y* decreases more with La-deficient compositions than with Mn-deficient ones. The La/Mn ratio influences strongly the relationship between $[h^{\bullet}]$, $[V_O^{\bullet\bullet}]$, $[V_{La}^{'''}]$ and $[V_{Mn}^{'''}]$.

The DFT-GGA (Density functional Theory, Generalized-Gradient Approximation) simulation of these compounds using VASP (Vienna Ab-initio Simulation Package) concludes that the electronic structure for the optimized stoichiometric $La_6Mn_6O_{18}$ is not optimal, relative to that expected considering Mn(III) ions with four alpha electrons each. The non-stoichiometry is the easiest way of reducing the Jahn–Teller instability by depopulating the half-filled e_g orbitals. A partial oxidation is then stabilizing. Creation of defects, either an O insertion or a cationic vacancy, allows finding an ideal count. In the case of pure cationic defects (missing a La(III) or a Mn(III) cation), the amount of vacancies is one missing cation upon twelve. The compact nature of lanthanum manganite oxide does not allow oxygen insertion within the bulk structure and oxidation can only be achieved at the surface without O penetration. The formation of antisites is endothermic. The creation of mixed vicinal vacancies, one oxygen and one cationic vacancy (La or Mn), is exothermic for a concentration of defects of one defect per twelve cations.

1. Introduction

Perovskites of ABO_3 type like $LaMnO_3$ have received considerable attention as efficient heterogeneous catalysts [1–12] as electrode materials for solid oxide fuel cells [13–17] and other electrochemical applications. During the last two decades, they have been consistently proposed as alternative catalysts for hydrogen-involving reactions as hydrogenolysis of hydrocarbon [18] as well as for reaction combustion of carbon monoxide and light hydrocarbon [4,11,19–23].

Lanthanum manganite oxides $LaMnO_{3+y}$ exhibit non-stoichiometry on one or more sublattice [24–28] due to the fact that manganese on the B-site can have the valences Mn^{2+}, Mn^{3+} or Mn^{4+}. This means that the perovskite can be either oxidized or reduced as a function of temperature and oxygen partial pressure. At high temperature and low oxygen partial pressure, Mn^{3+} is reduced to Mn^{2+} and the negative deviations from stoichiometry are explained by the presence of oxide ion vacancies. However, when oxygen is in excess with respect to the ideal formula, it still occupies the lattice sites. Interstitial oxygen is indeed hardly likely, since the $LaMnO_3$ structure consists of a close packed LaO_3 lattice with Mn in the O_6 octahedral sites. Oxidative non-stoichiometry is then possible through cation vacancies.

In a previous study [29] on $LaMnO_{3+y}$, we proposed, in order to explain the experimentally determined densities of investigated samples with a wide range of *y* values, that the overstoichiometry originates from cation vacancies with equal concentration on the A and B-sites in the perovskite structure. This can be expressed, according to Kröger–Vink notation for defect equilibra as:

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$$1/2O_2 = Oo^x + 1/3V'''_{La} + 1/3V'''_{Mn} + 2h^{\bullet} \quad (1)$$

This also can be expressed referring to Mn_2O_3 or MnO_2 as

$$LaMnO_3 + 3x/2O_2 \rightarrow La_{1-x}Mn_{1-x}O_3 + x/2La_2O_3 + x/2Mn_2O_3 \quad (1a)$$

$$LaMnO_3 + 7x/4O_2 \rightarrow La_{1-x}Mn_{1-x}O_3 + x/2La_2O_3 + xMnO_2 \quad (1b)$$

Then, the notation $LaMnO_{3+y}$ is somewhat misleading, as it indicates an excess of oxygen instead of cation vacancies. So the above shortcut formula corresponds in fact to equal vacancy concentration in A and B sublattices ($La_{1-\varepsilon}Mn_{1-\varepsilon}O_3$ where $\varepsilon = y/3 + y$) with Mn^{4+} content equaling $2y$. Moreover, the partial substitution of the La(III) site with cations of lower valance, e.g. Ca(II) has been shown to greatly alter the catalytic properties in the methane combustion reaction [2]. This type of acceptor doping leads to charge compensation by an increase in the valence of the Mn site and/or the formation of oxygen vacancies [29]. Clearly the role of defects and doping, as well as the Mn^{4+}/Mn^{3+} ratio to create electronic species, are crucial to the fundamental understanding of the catalytic behavior of $LaMnO_{3+y}$ material and considerable speculation discussed about the role of oxygen species or defects in the partial and complete oxidation of various reducing compounds (e.g. alkenes, alcanes, aromatics and ammonia) [4]. Even for manganite samples with nominally equal Mn^{4+} contents, Malavasi et al. [30,31] have shown that magnetic properties as Curie temperature are strongly dependent on the cation vacancy distribution over the A and B sites of pure and doped manganite perovskites. For this purpose, De Souza et al. [32] investigated the nature of the oxidative non-stoichiometry of $LaMnO_3$. They have shown from atomistic simulation studies that it originates from lanthanum and manganese vacancies rather than from excess of oxygen. They found a tendency of forming more lanthanum vacancies than manganese vacancies. Let us however remark that La_2O_3 oxide formation has not been observed experimentally.

A majority of works was devoted to pure and partially lanthanum substituted perovskite compounds where the atomic ratio A:B = 1:1 (equal number of La and Mn vacancies). The various results obtained with these materials do not form a consistent picture probably due to the difficulty in controlling accurately the La/Mn ratio and in synthesizing these compounds. As, both cation and oxygen non-stoichiometry are possible [25,33,34] information concerning their interdependencies is usually incomplete and sometimes contradictory. Although the most complete data are available for La/Mn = 1:1 composition with a variable oxygen content, a few systematic research on the variation of the relative content of Mn^{4+} ion and oxygen non-stoichiometry were reported for La and Mn-deficient compounds.

Compounds with lanthanum or manganese non-stoichiometry of formula $La_{1-x}MnO_{3+y}$ or $LaMn_{1-x'}O_{3+y}$ present considerable interest from the point of view of potential applications as well as illustrating fundamental problems of composition–structure–properties correlations [27] . In this case, average oxidation state n of Mn formally can change through two dimensional area (x,y): $n = 3 + 3x + 2y$. The homogeneity limits are conditioned not only by cation stoichiometry but by oxygen content as well.

The aim of this paper is to employ a combined experimental and computational approach to investigate the defect distribution in the lanthanum manganite perovskite oxide as a function of La/Mn atomic ratio. The first objective is to synthesize a series of non-stoichiometric manganites with nominal formulae $La_{1-x}MnO_{3+y}$ and $LaMn_{1-x'}O_{3+-}$ ($0 \le x,x' \le 0.2$) and with accurately controlled La/Mn ratio. The second objective is to investigate theoretically the nature of defects and its distributions in the lanthanum manganite sublattices. Taking into account these computational results, the interpretation of the composition of La and Mn-deficient synthesized compounds is the third objective of this work.

2. Experimental

2.1. Synthesis and characterization of lanthanum manganite ($0.8 \le La/Mn \le 1.25$)

In order to make comparison of their properties reliable and to control the La/Mn ratio accurately, all samples considered in this work have been prepared and annealed under the same conditions. $La_{1-x}MnO_{3+y}$ and $LaMn_{1-x'}O_{3+y}$ samples designed by LMr, r = La/Mn ranging from 0.80 ± 0.01 to 1.25 ± 0.01 (La/Mn ratio given below are those determined by inductively coupled plasma emission analysis for which the accuracy is about 1%), have been prepared in polycrystalline form from aqueous solutions of lanthanum nitrate hexahydrate (Fluka) and manganese(III) acetate dihydrate (Fluka). La and Mn precursors were mixed intimately on a molecular scale. The obtained solution, with La/Mn atomic ratio equal to r, was maintained under constant stirring for 2 h. Upon removal of the excess solvent by heating at 343 K, a black gel containing the metals in solid solution was formed. The gel was dried at 383 K for 24 h. Final samples used in this study were obtained after a pretreatment conducted in two steps. First, solids were treated for 2 h at 723 K in air followed by grinding. This treatment enables the total elimination of organic and nitrate materials. Next, the powders were calcinated for 24 hours at 973 K in air and rapidly cooled to room temperature. This operation allows higher homogeneity and stabilization of the surface morphology.

This procedure is outlined in the flow chart of Fig. 1.

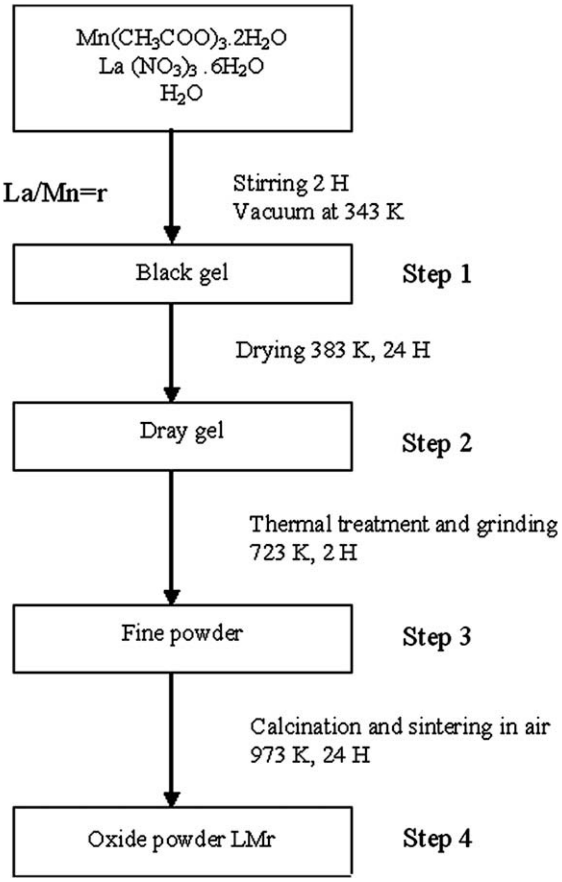

Fig. 1. A flow chart illustrating the multi-step decomposition of a gel precursor for LMr preparation.