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Crystal structure and mixed ionic–electronic conductivity of $La_{1-x}Ca_xMnO_3$ $(0 \leq x \leq 0.8)$ produced by mechanosynthesis

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Abstract

The aim of this work was to study the relationship between the crystalline structure, the mixed ionic–electronic conductivity and the calcium content in calcium-doped lanthanum manganites (CLM, $La_{1-x}Ca_xMnO_3$) synthesized by reactive ball milling. Mechanosynthesis was employed to produce nanocrystalline CLM with varying calcium content (x = 0–0.8 in increments of 0.1). Powders of Mn_2O_3, La_2O_3 and CaO mixed in the stoichiometric ratio were used as raw materials. The mechanosynthesis was carried out using a high-energy shaker mixer/mill. X-ray powder diffraction and Rietveld refinement were used to determine the crystalline structure as a function of calcium content. The four-point probe resistivity test was used to measure the electrical resistivity of the compacted and sintered powders using a DC milli-ohm meter. The results showed that the substitution of the La^{3+} ion by the Ca^{2+} ion during mechanosynthesis only changed the lattice parameters but not the orthorhombic *Pnma* structure. The mixed ionic–electronic conductivity increased with the Ca^{2+} content. The best conductivity was observed for the composition of $La_{0.2}Ca_{0.8}MnO_3$.

Keywords: Lanthanum manganites; Mechanosynthesis; Crystal structure; X-ray diffraction; Mixed ionic–electronic conductivity

1. Introduction

Manganites such as $REMnO_3$ (RE = rare earth) have been the subject of recent research due to their magnetic and electrical–electronic properties [1] along with their great potential for use in a wide range of applications including sensors, permanent magnets, catalysts and pigments [1–4]. These properties have also been the reason for research regarding their giant magnetoresistance (GMR) [5–8] and their use as electrode materials for solid-oxide fuel cells (SOFC) [9,10]. Such manganites have very good mixed conductivity and magnetic properties if the REs are partially substituted by alkaline earth atoms with similar ionic radii and different oxidation numbers than the RE in A sites [11–14]. They are capable of forming vacancies that, with other intrinsic and extrinsic defects, give rise to very high electronic and ionic flow and generate magnetic fields. The magnetic and electrical properties are not only closely related to the crystalline structure and stoichiometry of the manganites but also to their defect formation and electronic–ionic flow. Therefore, these materials are mainly used in electronic and microelectronic devices [15–17]. To obtain doped manganites, several synthetic methods have been developed [18–24]. The mechanochemical process (MCP) is an effective, economical and versatile way to produce CLMs using powder oxide mixtures [25–27]. Recently, the high-energy ball milling technique was proven effective in the mechanosynthesis of nanostructured manganites from oxides through a mechanical activation [2,27–29].

Zhang and Saito [30] successfully synthesized $LaMnO_3$ by grinding the mixture of La_2O_3, MnO_2 and Mn_2O_3 powders at room temperature using a high-energy ball mill. The physical and chemical properties of $La_{1-x}Sr_xMnO_3$ were reportedly dependent on the values of x.

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The aim of this work was to establish the relationship between the calcium concentration, the crystalline structure and the mixed ionic–electronic conductivity in the CLM powder synthesized by high-energy ball milling and the possibility of using this material as a SOFC cathode.

2. Materials and methods

Five grams of a mixture of Mn_2O_3 (Sigma Aldrich, 99% purity, 5 μm particle size), La_2O_3 (Sigma Aldrich, >99.9% purity, 7 μm particle size) and CaO (Sigma Aldrich, >99.9% purity, 9 μm particle size) powders was used as raw material. The powders were mixed in a stoichiometric ratio according to Eq. (1) with the x values ranging from 0 to 0.8 in increments of 0.1, as reported in previous work [29].

$$0.5Mn_2O_3 + 0.5(1-x)La_2O_3 + xCaO + 0.25xO_2 \rightarrow Ca_xLa_{1-x}MnO_3 \qquad (1)$$

The mixture was placed in a steel vial with a volume of 6×10^{-5} m^3 that contained steel balls with a diameter of 0.0127 m. The ball-to-powder weight ratio was 10:1 and ball milling was performed in air. The vial was sealed and shaken in a SPEX 8000D shaker mixer/mill without any control agent for the mechanical energy to initiate the chemical reactions. The powders were milled for 270 min according to the procedure used in previous works [27,28].

The milled powders were characterized at room temperature using a Rigaku D-MAX 2100 diffractometer with a 2θ range of 20–70° at an increment of 0.02° and a 5° angle of incidence. A Cobalt-Kα (λ = 1.7889 Å) target was used. Rietveld refinement was performed on all X-ray patterns using MAUD software [31] to determine the crystal structure and lattice parameters as a function of the milling time.

The milled powder was compacted at 400 MPa by uniaxial pressing to obtain cylindrical test specimens that were 15 mm in diameter and 3 mm in height. The specimens were subsequently sintered in air at 1400 °C for 2 h. The four-point probe resistivity test was used to measure the electrical resistance of the sintered compacts from room temperature to 1413 K; the test was performed using a GW Instek milli-ohmmeter (model GOM-802) with platinum contacts. The total conductivity was reported, which included both the ionic and the electronic conductivities [32].

3. Results and discussion

Table 1 shows the lattice parameters and interplanar distances of the (2 0 0) diffraction plane of the CLM. The specimens with x from 0.1 to 0.8 were milled for 270 min and the lattice parameter a was seen to vary with the Ca^{2+} content. A modification in lattice parameter a was observed when Ca^{2+} was introduced to the $LaMnO_3$ structure by mechanosynthesis, especially between $x = 0.7$ and 0.8. Nevertheless, the three lattice parameters of the structure between $x = 0$ and 0.8 slightly decreased in the same order of magnitude. In addition, the structure maintained the same orthorhombic *Pnma* unit cell in the transition from $LaMnO_3$ ($x = 0.0$) to $La_{0.2}Ca_{0.8}MnO_3$ ($x = 0.8$). The substitution of Ca^{2+} at the positions originally occupied by La^{+3} changed the cell parameters due to the different ionic radii between Ca^{2+} (with an ionic radius of 0.99 Å) and La^{3+} (with an ionic radius of 1.06 Å).

Table 1
Lattice parameter and interplanar distances of the (2 0 0) diffraction plane of the $La_{1-x}Ca_xMnO_3$, for x from 0 to 0.8, milled for 270 min.

Diffraction plane		Lattice parameters (A)			c/a
Ca content (x)	$d_{(2\,0\,0)}$ (nm)	*a*	*b*	*c*	
0.1	2.7649	5.5183	7.7203	5.5643	1.008
0.2	2.7511	5.5133	7.7395	5.5304	1.003
0.3	2.7411	5.4862	7.7243	5.5197	1.006
0.4	2.7318	5.4482	7.6877	5.5225	1.013
0.5	2.7178	5.4750	7.6563	5.4963	1.0038
0.6	2.7097	5.4571	7.6403	5.4734	1.0029
0.7	2.6999	5.3912	7.5927	5.5057	1.042
0.8	2.6899	5.3989	7.5733	5.4856	1.0072

In previous studies [29], the width of the peak corresponding to the close-packed (2 0 0) plane of the orthorhombic structure was observed to increase as Ca content increased (Fig. 1). The increase was because the interplanar distances of certain planes were close to the mean point; that is, the structure became closer to $CaMnO_3$ than $LaMnO_3$ as the Ca content increased. Therefore, the mixture had a wider reflection due to the different interplanar distances caused by the Ca atoms. This caused the crystal structure to be distorted by the volumetric strain induced by the calcium substituted at the lanthanum positions.

The crystal structure and space group by calculating the c/a parameter are shown in Table 1. The lattice distortion changed the axial symmetry from $c/a > \sqrt{2}$ to $c/a < \sqrt{2}$ without changing the *Pnma* space group. The orbitally ordered phase was designated as orthorhombic in all the studied compositions according to the refined structural results. This agreed with the t calculations, in which the tolerance factor was 0.85 and 0.825 for $LaMnO_3$ and $CaMnO_3$, respectively; both values were within the range of

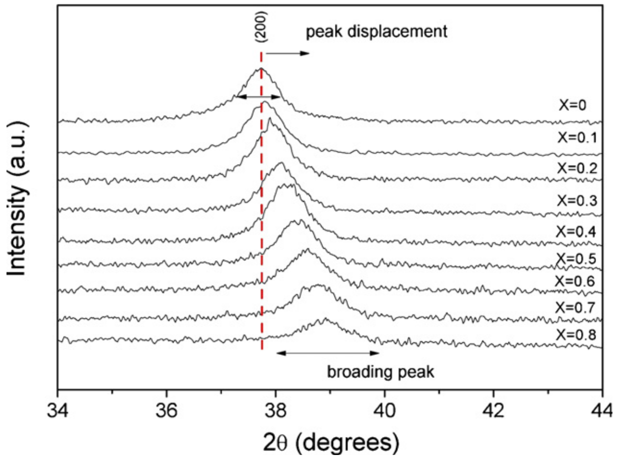

Fig. 1. X-ray diffraction patterns of $Ca_xL_{a1-x}MnO_3$ at various values of x.