

YPSZ-LSM interactions in spark plasma sintered ceramics

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The objective of the present study is to analyze the interactions between yttria partially stabilized zirconia and strontium-doped lanthanum manganite (YPSZ-LSM) and lanthanum manganite (LM), after processing by spark plasma sintering. LSM ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3\pm\delta}$ with $x = 0.15$) and LM ($\text{LaMnO}_{3\pm\delta}$) were obtained by a mechanosynthesis process using two different types of manganese oxide as precursors: MnO (II) and MnO_2 (IV). The manganite powders were mixed with YPSZ in a 1:1 weight ratio. The mixed powders were uni-axial compacted at 16 MPa and spark plasma sintered (SPS) at 1000 °C and 1300 °C. Results of the interaction between YPSZ and LSM were obtained and are reported from XRD and SEM analyses. For samples that have been sintered at 1000 °C, only those that contain LM and LSM that has been synthesized from manganese (IV) show the formation of lanthanum zirconate; in contrast, all of the samples that have been sintered at 1300 °C give raise to lanthanum zirconate. Cubic zirconia is present at room temperature in 15% Sr-doped lanthanum manganite mixtures (1300 °C SPS).

Key words: Lanthanum manganites, Structure, Yttria stabilized zirconia, Spark plasma sintering.

Introduction

The most used pair of materials found which together are widely used in ceramic-ceramic conduction devices is strontium-doped lanthanum manganite (LSM) with yttria-stabilized zirconia (YSZ) [1-5]. Examples of these devices are solid oxide fuel cells and sensors. One of the challenges for this technology is to reach the maximum oxygen conduction through the interface while maintaining chemical and thermo-mechanical compatibility between the components. This combination has some reactivity limitations at high operation temperatures; the lanthanum atoms from the manganite migrate to the zirconia structure, which forms the pyrochlore lanthanum zirconate, $\text{La}_2\text{Zr}_2\text{O}_7$ (LZ), which is one of the obstacles to optimal operation. Although there are some reports on the high ionic conductivity of LZ [6, 7] with gadolinium and lanthanum in the A sites, it has been found that the conductivity of the lanthanum and strontium zirconates is lower than the LSM or YSZ. [8, 9] This migration of the lanthanum into the zirconia structure is favored by non-stoichiometry in the lanthanum manganite due to the oxidation ratio for the manganese ion [10] or changes to the rare or alkaline earth atoms in the A sites [11, 12]. In some reports, different properties of lanthanum manganites that have been produced by mechanosynthesis from different manganese oxides have been found that obtain a mixed Mn oxidation number in perovskite [13-15].

On the other hand, the relationship between the synthesis and processing of the components with their final properties has been discussed [16]. In this respect, there are some reports on the increase in the three-phase boundaries (TPB) [1, 11, 17] that concern maximizing the reduction of oxygen at the LSM-YPSZ interface.

Spark plasma sintering is a process in which ceramic powders can be compacted and quickly sintered to almost full density. By means of this process, heat and mass transfer take place faster than in conventional furnace heating, so that the formation of a new species can be diminished due to the short diffusion time [18]. Additionally, there are some reports on the modification of the microstructure in films of YSZ by SPS [19].

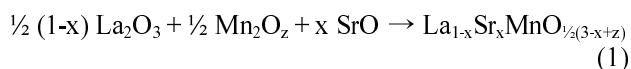
The goal of this study is to find the right conditions in order to avoid the diffusion of lanthanum from lanthanum manganite into the zirconia structure. LSM-YPSZ spark plasma sintered mixtures are prepared and analyzed so as to find out the conditions that avoid the formation of lanthanum zirconate besides the morphology of the pores that conveniently increase the TPB. The reason for the use of partially stabilized zirconia is to find out the effect of the cubic and tetragonal zirconia structure on the formation of the lanthanum pyrochlores. A comparison between samples spark plasma sintered (SPS) and conventionally heating (CH) is also presented.

Experimental procedure

Lanthanum manganites were prepared by mechanosynthesis, which uses precursor powders (La_2O_3 300 mesh, MnO_2 60-230 mesh, SrO -60 mesh and MnO -60 mesh, Sigma-Aldrich) of 99.9% purity, that

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follows the procedure that has been reported elsewhere [13]. The reaction is as follows:



where z is equal to the oxidation number of Mn (II) and Mn (IV) and x corresponds to the atomic fraction of strontium in the A sites, which is either 0 or 0.15.

Lanthanum manganite samples prepared by this method will be referred to hereafter as LM2 when MnO is used as precursor, $z = 2$ and $x = 0$ in eq. 1; LSM2 when $z = 2$ and $x = 0.15$ (doping with 15 atomic percent of Sr in the La sites); LM4 when MnO_2 is used as precursor, $z = 4$ and $x = 0$ in eq. 1; LSM4 when $z = 4$ and $x = 0.15$ (based on MnO_2 and doping with 15 atomic percent of Sr in the La sites).

A SPEX 8000D mixer mill was used to synthesize lanthanum manganite from the precursor powders under atmospheric conditions with a 10:1 ball to powder weight ratio while using balls of steel as the milling medium.

Lanthanum manganites were mechanosynthesized according to methodology reported in previous work [13]. Powder mixtures with $z = 2$ were milled for 240 minutes and were subsequently calcined at 1050 °C for nine hours in an air atmosphere. LM or LSM compounds with $z = 4$ were obtained in a single step with 270 minutes of milling. The manganites that have been synthesized have a mixture of crystalline phases (cubic, orthorhombic and rhombohedral), even after calcining in an air atmosphere (1050 °C/9 h). However, rhombohedral structures predominate for $z = 2$ and cubic structures dominate for $z = 4$ [13].

LM or LSM compounds were mixed with YPSZ (TZ3Y tetragonal zirconia with 3% mol of Y_2O_3 , TOSOH Corp., particle size 0.5 μm , specific surface area 15 m^2/g , which has a tetragonal phase in a 1:1 weight ratio in a high energy ball mill SPEX 8000 for 10 minutes. Thus, the powder mixtures obtained were sintered by two methods: (a) spark plasma sintering at 1000 °C and 1300 °C applying 5 kN, 200A and 2 V in a Dr. Sinter 5000 with 6×10^{-2} Pa vacuum, a heating rate of 191 $\text{K}/\text{minute}^{-1}$ and 10 minutes of holding time, in a 10 mm diameter graphite matrix, without shrinkage, in which the temperature was measured with a pyrometer (b) conventionally heat sintered (CH) at 1000 °C and 1300 °C with a heating rate of 10 $\text{K}/\text{minute}^{-1}$ and a dwell time of two hours in air at atmospheric pressure.

The crystalline structure analysis of sintered ceramics was carried out by X-ray diffraction (Bruker D8 Advance with linxeye detector) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), and values of 2θ ranging from 20 to 90 ° in increments of 0.02 °. Rietveld refinement of the X-ray diffraction patterns was done using MAUD 2.47 software.

Finally, microstructural characterization of the heat-treated samples was carried out by scanning electron

microscopy (Philips-XL30 ESEM) with backscattered electrons.

Results and discussion

Fig. 1 shows a comparison of X-ray diffraction patterns of YPSZ-lanthanum manganite mixtures spark plasma sintered (SPS) at 1000 ° for 10 minutes versus mixtures conventionally heated (CH) at 1000 ° for 2 hours. On the XRD patterns of the lanthanum manganite from $\text{MnO} + \text{La}_2\text{O}_3$ and from $\text{MnO}_2 + \text{La}_2\text{O}_3$ (LM2, LM4, LM2SPS, LM4SPS) mixtures which are both manganites without strontium before and after spark plasma sintering, we can observe the peaks that correspond to cubic zirconia (CZ) at $31.3 \pm 2^\circ$ prevail after sintering, while after conventional heating at 1000 °C cubic zirconia peaks disappear. On the other hand, in the XRD patterns of the mixtures with strontium LSM2 SPS (15% strontium-doped lanthanum manganite from $\text{MnO} + \text{La}_2\text{O}_3 + \text{SrO}$) and LSM4 SPS (15% strontium-doped lanthanum manganite from $\text{MnO}_2 + \text{La}_2\text{O}_3 + \text{SrO}$) spark plasma sintered, only the peaks of tetragonal zirconia and lanthanum manganite are found. But an interesting fact occurs with conventional heating of the mixture LSM4, where monoclinic and cubic zirconia peaks remain in the XRD patterns. Due to the initial XRD patterns with cubic, tetragonal and monoclinic phases of zirconia present, we can deduce that the stabilization of the cubic phase of zirconia at 1000 °C is only promoted by manganites with a stoichiometry and structure that is given by equation 1 for $z = 2$ and 4 and $x = 0$ with the spark plasma sintering process and by manganite with a

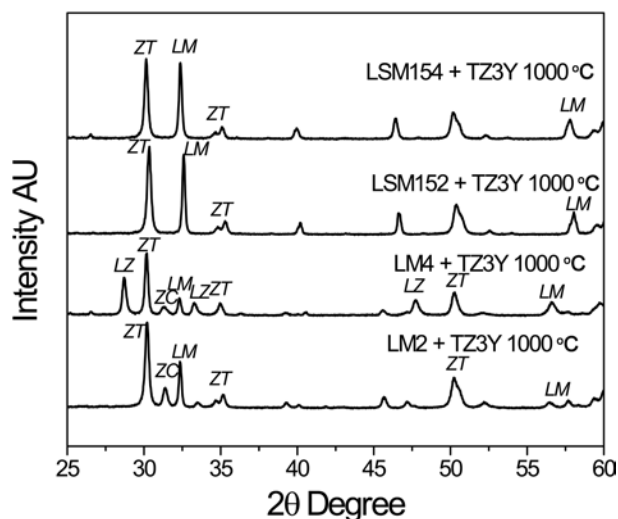


Fig. 1. X-ray diffraction of lanthanum manganite - yttria stabilized zirconia mixtures. LM2 and LM4 as milled and mixed; LM2SPS, LSM2SPS, LM4SPS and LSM4SPS spark plasma sintered at 1000 °C for 10 minutes; LM2CH, LSM2CH, LM4CH and LSM4CH conventionally heat treated at 1000 °C for 2 hours. LM: lanthanum manganite, LZ: lanthanum zirconate, MZ: monoclinic zirconia, TZ: tetragonal zirconia, CZ: cubic zirconia.

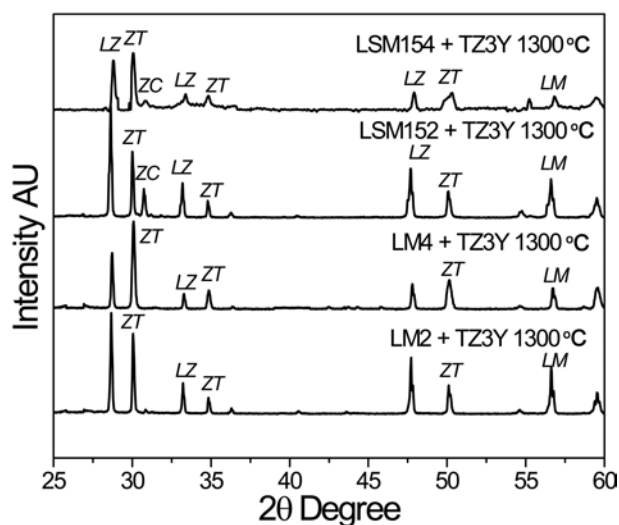


Fig. 2. X-ray diffraction of lanthanum manganite - yttria stabilized zirconia mixtures, which have been spark plasma sintered at 1300 °C for 10 minutes. LM2: lanthanum manganite from $\text{MnO} + \text{La}_2\text{O}_3$; LM4: lanthanum manganite from $\text{MnO}_2 + \text{La}_2\text{O}_3$; LSM2: 15% strontium-doped lanthanum manganite from $\text{MnO} + \text{La}_2\text{O}_3 + \text{SrO}$; LSM4: 15% strontium-doped lanthanum manganite from $\text{MnO}_2 + \text{La}_2\text{O}_3 + \text{SrO}$.

stoichiometry of $z = 4$ and $x = 0.15$ by the conventional sintering process.

There is a notable shifting of the lanthanum manganite peak (LM) from 32.3 to 32.6° in the LSM2 SPS mixture, with respect to the other mixtures. This shifting is due to the combination of crystalline structures that are obtained for lanthanum manganite from mechanosynthesis [13].

Only the mixture of partially stabilized zirconia with manganite from $\text{MnO}_2 + \text{La}_2\text{O}_3$ (LM4 + TZ3Y) both conventionally and spark plasma sintered at 1000 °C presents the peaks for lanthanum zirconate (LZ).

In addition, there is a difference in the relative height between the lanthanum manganite peaks with respect to zirconia peaks. In undoped LM2 and LM4 samples, the relative height of the mean LM peak is lower for the conventional sintering than SPS and mixtures as milled. Although the relative height of the LM peak in LM2 is lower than in the doped samples, its height is

greater than the same peak in LM4. For LM4, we could attribute this height decrease to the formation of lanthanum zirconate (LZ) due to the lanthanum atoms migration into the zirconia structure. The manganese migration stabilizes the cubic zirconia structure. In the LM2 mixture, the zirconate (LZ) peaks are not present but the relative height of the LM peak is lower than for the doped samples. In studies of the stoichiometry of the lanthanum manganites by energy dispersive X ray spectrometry (EDS), we observe a diminution in the lanthanum atomic composition with respect to the stoichiometric relationship. The reason for the diminution in the relative height is that the excess manganese migrates to the zirconia structure and stabilizes the zirconia cubic crystalline phase.

In Fig. 2, the XRD patterns for the 1300 °C conventional (2 h) and spark plasma sintered (10 minutes) samples are shown. In this figure, the absence of the lanthanum manganite peaks can be observed in those samples spark plasma sintered. This event could be due to either the migration of the lanthanum atoms into the zirconia structure (which forms lanthanum zirconate), the partial diffusion of manganese (which stabilizes the cubic/tetragonal phase) or the partial instantaneous evaporation of manganese (as has been reported by Kušèer, *et al.* [21]). This fact is not observed for conventionally treated samples.

The evaporation of manganese oxide in a conventional heat treatment has been reported at 1450 °C. Instead of the samples SP sintered at 1000 °C, we can observe in both of the samples that have been SP sintered at 1300 °C (see Fig. 2) the presence of cubic zirconia when they have been doped with 15% strontium. The LM2 and LM4 samples, which have been SPS at 1300 °C, only present the lanthanum zirconate and tetragonal zirconia phases.

Fig. 3 shows the microstructure of a spark plasma sintered mixture of YPSZ + LaMnO_3 from MnII samples (LM2). A sample SP sintered at 1000 °C (showed in Fig. 3 left) present a continuous phase only with submicrometre pores. Samples spark plasma sintered at 1300 °C, present a continuous phase morphology but contrast shows only two components in the mixture (Fig. 3 right). Samples SP

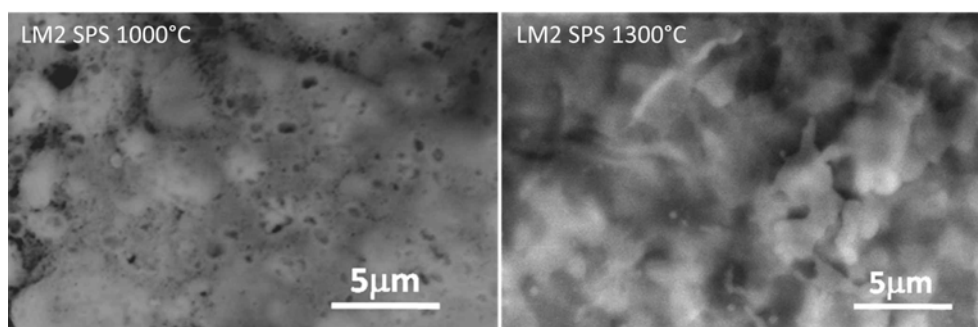


Fig. 3. Microstructure of mixtures of lanthanum manganite synthesized from MnO with TZ3Y, which have been spark plasma sintered at 1000 °C and 1300 °C for 10 minutes.

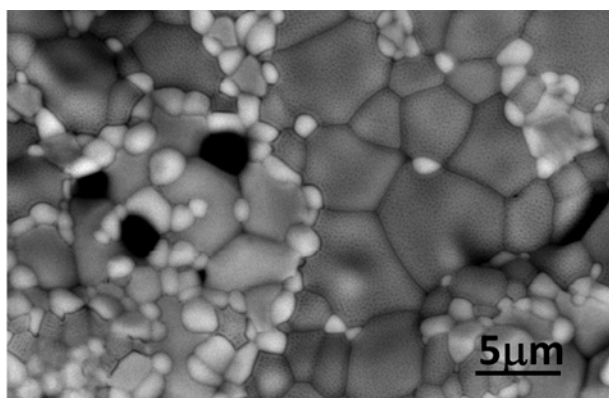


Fig. 4. Microstructure of mixtures of lanthanum manganite synthesized from MnO with TZ3Y, which have been conventionally heat treated at 1300 °C for 2 h.

sintered at 1300 °C show a liquid-like morphology without clear definition of grains. A chemical analysis of the brighter phase indicates a greater content of La than the darker. By comparing the molecular weight, we conclude that the brighter phase is lanthanum zirconate and the gray phase is tetragonal zirconia. This precipitation is of lanthanum zirconate and the gray continuous phase is tetragonal zirconia with smaller lines of cubic zirconia. In general, the spark plasma sintering, together with the small particle size, allows quick sintering of the samples at 1300 °C.

Fig. 4 shows the morphology for a mixture of YPSZ + LaMnO₃ from MnII samples (LM2) conventionally sintered at 1300 °C for two hours. In this image we can observe a clear definition of grains in which the darkest grains with small dots correspond to cubic zirconia [22], the middle-dark and smooth grains correspond to lanthanum manganite and at the interface between the last, the brightest grains correspond to lanthanum zirconates which are observed to grow at the LM-CZ interfaces.

Spark plasma sintering is a technique for materials processing that applies a lot of energy to a powder sample in a short time period. If the powder is small enough, the compounds tend to reach equilibrium, which results in reactions with lower energy levels for the compounds.

Conclusions

The SPS is a technique that is capable of providing more energy than conventional heating when processing the LSM-YPSZ; this process results in a new structure and morphology. The SPS at 1000 °C promotes compact porosity that could be convenient for molecular oxygen transport in fuel cells. Also, samples both conventionally and spark plasma sintered at 1000 °C (except for the LM4-TZ3Y mixture) do not form lanthanum zirconate. Conversely, all of the samples that have been sintered at 1300 °C form lanthanum zirconate while the lanthanum manganite almost disappears. Cubic zirconia was found

for spark plasma sintered samples at 1000 °C only in LM, but samples with strontium inhibit the formation of cubic zirconia, contrary to the treatment at 1300 °C, in which only strontium doped samples present cubic zirconia phase.

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