

Estabilización estructural y caracterización eléctrica de materiales basados en CaMnO_3

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La conductividad mixta (iónica y electrónica) es un requerimiento importante para un material como buen electrodo; con el objeto de asegurar alta actividad electrocatalítica y buen rendimiento cuando se usa en aplicaciones de estado sólido. En aire, la mayoría de las perovskitas ensayadas muestran alta conductividad electrónica (por mecanismos de saltos) y además deficiencia de oxígeno, que es la responsable de la conducción oxígeno-ión. En particular, CaMnO_3 puede acomodar alta concentración de vacantes de oxígeno, formando canales que producen alta movilidad de oxígeno. Sin embargo, las composiciones deficientes en oxígeno obtenidas mediante condiciones reductoras no son estables en atmósferas oxidantes, siendo la recuperación del oxígeno muy rápida a alta temperatura.

En este trabajo se recogen los intentos preliminares de estabilizar composiciones CaMnO_{3-x} ($0 \leq x \leq 0.5$) a alta temperatura, incluyendo la sustitución parcial de Sr por Ca (hasta 0.5). DRX, ATD, TG y medidas de conductividad eléctrica fueron utilizadas para caracterizar los procesos redox.

Palabras clave: manganita de calcio, estabilización, propiedades eléctricas.

Structural Stabilization and electrical characterization of CaMnO_3 based materials

Mixed (ionic and electronic) conductivity is an important requirement of a good electrode material, to ensure a high electrocatalytic activity and very good performance when used in solid state devices. In air, most perovskites tested as electrodes show high electronic conductivity (by hopping mechanism) and also some oxygen deficiency, which is responsible for oxygen-ion conduction. In particular, CaMnO_3 can accommodate high amounts of oxygen vacancies, forming channels which can give high oxygen mobility. However, the oxygen-deficient compositions obtained in reducing conditions are not stable in oxidizing atmospheres and the recovery of oxygen is very fast at high temperatures.

In this work preliminary attempts to stabilize CaMnO_{3-x} ($0 \leq x \leq 0.5$) compositions at high temperatures are reported, including partial substitution of Sr for Ca (up to 0.5). XRD, TGA, DTA, and electrical conductivity measurements were used to characterize the redox process.

Key words: calcium manganites, stabilization, electrical properties

1. INTRODUCTION

Solid Oxide Fuel Cells (SOFCs) are expected to become competitive devices for electrical power generation, but successful commercialization is still dependent on increasing the general efficiency, mostly by increasing the cathodic performances by using different ceramic materials. It is now well known that a good electrocatalytic behavior of cathodic processes is achieved if the cathode material is a mixed conductor (electronic and oxygen-ion) (1,2).

In air most perovskites tested as cathode materials show enough electronic conductivity, and a few systems based on LaCoO_3 seem to have also high ionic conductivity, as demonstrated by oxygen diffusion measurements (3) or permeability tests (4). This high

oxygen mobility seems to be related with high oxygen vacancy concentrations in the lattice, created by nonstoichiometry and/or doping effects. However, these promising materials have serious problems of instability in contact with yttria stabilized zirconia (YSZ) electrolytes, due to a large thermal expansion mismatch and a high degree of chemical reactivity at processing or working temperatures (5).

On seeking for similar perovskites having high oxygen deficiency, CaMnO_3 based materials seem to be very promising, due to the ability of accommodate a large number of oxygen vacancies (6,7), forming interesting channels which might be responsible for a high oxygen mobility. However, the electrical conductivity of these compositions is generally low when compared with other perovskite systems as rare-earth manganites or cobaltates (8), and

up to now there is no experimental evidence of a significant ionic conductivity. Moreover, the oxygen-deficient compositions are formed by exposure the stoichiometric materials to reducing conditions or by performing the synthesis directly in reducing conditions, but in both cases the recovery of oxygen in oxidising working conditions of a typical cathode is very fast, especially at high temperatures (above 300 °C) (6). Although this oxygen sensitivity may preclude utilisation as a cathode, there is also a possibility of operation under anodic conditions.

Some attempts to increase the stability of oxygen-deficient compositions and/or the electrical conductivity involving the partial substitution of Ca cation by iso or heterovalent species. For example, Esaka et al. (9) reported some results on $\text{Ca}_{1-x}\text{Ce}_x\text{MnO}_{3-y}$ compositions ($x \leq 0.15$), and concluded that the Ce for Ca substitution tends to increase the oxygen deficiency. Typical electrical conductivities at room temperature were about 10^{-2} S/cm, and were attributed to hopping mechanism.

In this work preliminary attempts to stabilize the $\text{CaMnO}_{2.5}$ or similar CaMnO_{3-x} ($0 \leq x \leq 0.5$) compositions at high temperatures are reported, including partial substitution of Sr for Ca (up to 0.5). XRD, TGA, DTA, and electrical conductivity measurements were used to characterize the redox process.

2. EXPERIMENTAL

Several Sr-doped CaMnO_3 compositions (containing 0, 5, 10, 20, 40, and 50 mol% Sr) were prepared by solid state reaction from CaCO_3 , MnCO_3 , and SrCO_3 , following the steps:

- Mixing and milling in alcohol media during 2 hours;
- Calcination at 1000 °C during about 10 hours;
- Milling as in a).

Structural characterization of the calcined powders were studied by X-Ray Diffraction (Rigaku, Stoe Stadi-P), to determine the extent of formation of solid solution by Sr for Ca substitution and also to estimate the oxygen deficiency in the lattice. Structural changes were also evaluated after annealing treatments in reducing atmospheres (using flowing H_2) and at temperatures around 300-400 °C.

TGA/DTA analyses on previously calcined powders were used to detect redox temperatures and evaluate the possible effect of Sr for Ca substitution. These analyses were performed in different atmospheres, from air to H_2 .

Electrical conductivity of sintered pellets (1400 °C during 5 hours) was measured by a van der Pauw four-probe technique between room temperature and 1000 °C.

3. RESULTS

3.1. Structure

CaMnO_3 and derived compounds have orthorhombic perovskite-type structure (7,11). However, the X-Ray analysis of calcined powder shows a more complex structure than expected for CaMnO_3 stoichiometric composition (Figure 1), in accordance with the existence of some oxygen deficiency, as expected for similar perovskites prepared in air.

Promoting Sr for Ca substitution seems to increase the oxygen deficiency, as can be seen in Figure 2 for $\text{Ca}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$. However, the samples having Sr contents higher than 20 %mol denote simultaneous formation of SrMnO_{3-x} and $\text{CaMnO}_{3-x'}$ probably due to incomplete reaction of reagents. Attempts to impro-

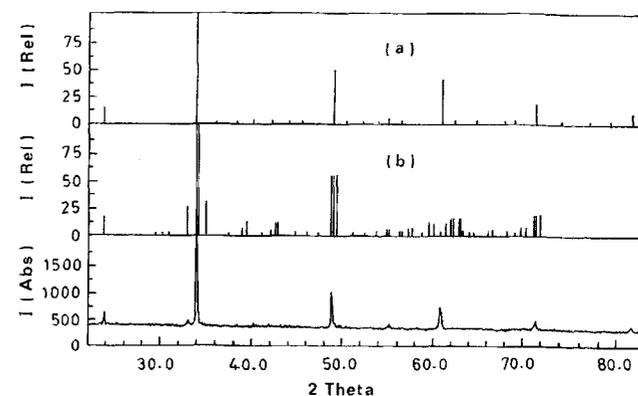


Fig. 1: X-Ray diffraction of CaMnO_3 powder after calcination in air at 1100 °C. For comparison, standard results of JCPDS files are also given: (a) stoichiometric CaMnO_3 composition; (b) $\text{CaMnO}_{2.5}$.

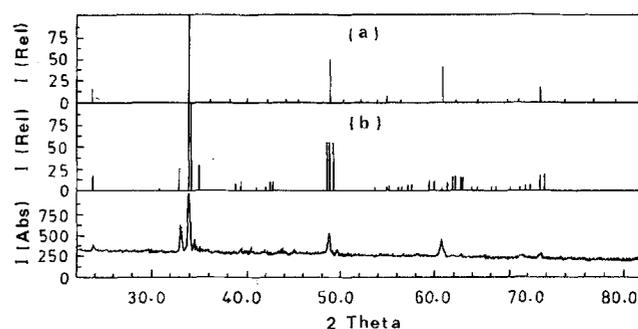


Fig. 2: X-Ray diffraction of $\text{Ca}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ powder after calcination in air at 1100 °C. For comparison, standard results of JCPDS files are also given: (a) stoichiometric CaMnO_3 composition; (b) $\text{CaMnO}_{2.5}$.

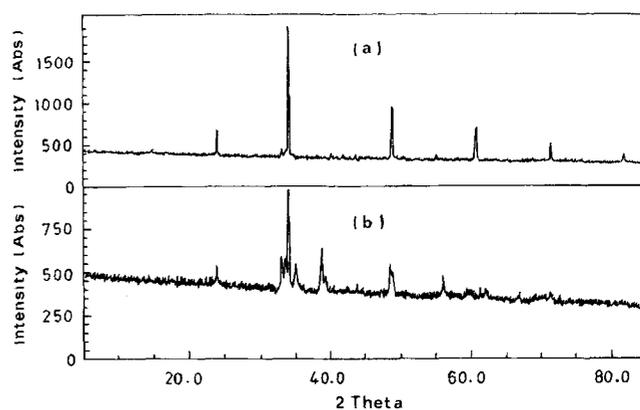


Fig. 3: X-Ray diffraction of CaMnO_3 powder before (a), and after (b) annealing treatment in reducing atmospheres (310 °C, 4 days, H_2 flowing).

ve the reactivity and solid solution formation of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (increasing the firing temperature up to 1400 °C and/or the calcination time) were not very successful. Previous works on similar compositions (6,10) suggest the need of much longer calcination periods, in some cases during 8 or more days.

3.2. Reducing Tests

CaMnO_3 and $\text{Ca}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ samples were annealed in H_2 atmospheres at 310 °C for 96 and 48 hours, respectively. The beha-

vior of the undoped sample is similar than predicted from Poeppelmeier results (6), denoting a strong increase of oxygen deficiency near the $\text{CaMnO}_{2.5}$ structure (Figure 3). The reversibility of this process was tested after reoxidation at 1000 °C for 2 hours, with an almost perfect recovery of the structure previously obtained after calcination in air. The Sr-doped sample also shows some increase of oxygen deficiency, but less pronounced than in the case of the undoped sample (the annealing periods were different). This tendency can be ascribed to the increase of oxygen deficiency previously created by Sr for Ca substitution (see Figure 2), and might also be related with an increase of stability of nonstoichiometric phase by Sr doping, causing a change of temperature for the redox transition.

DTG/DTA analyses of CaMnO_3 sample performed in oxygen up to 1000 °C denotes only two minor steps at 300 and 600 °C, involving a change of 0.1% weight each, probably due to minor losses from CO_2 or H_2O picked up on standing. Further analysis in H_2 atmosphere is much more relevant (Figure 4) and shows two clear peaks at 487 and 623 °C, for a total weight loss of about 10.7%, slightly less than theoretical predictions (11%) for a complete reduction to Mn^{2+} , corresponding to the composition CaMnO_2 . The complete reduction process involves two different steps (6):



A similar test performed with $\text{Ca}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ (Figure 5) denotes a change in the position of both peaks to lower temperatures (421 and 561 °C). This confirms the ionic substitution in perovskite structure, and the lower total weightloss (9.94%) probably arises from a combination of a lack of pretreatment in O_2 and to an increase of nonstoichiometry after calcination in air (Figure 3).

In both compositions, the oxidation (from air to O_2) seems to be more difficult than the reduction (from air to H_2), probably because the later process is not affected by diffusion rate.

3.3. Electrical properties

Figure 6 shows the evolution of electrical conductivity with temperature for undoped and 10 and 20% Sr samples, in air and between room temperature and 1000 °C. The values of conductivity at maximum temperature are about 1-10 S/cm, more than one order of magnitude lower than that found for lanthanum manganites (1,8).

The shape of the curves is rather unusual for this type of perovskites, denoting a slight increase of conductivity with increasing temperature in the low and moderate temperature region (up to about 400-600 °C, depending on composition), and then a strong increase for higher temperatures. Normally, similar Co or Mn-based perovskites show an inverse evolution, with a flat-type behavior at high temperatures (>800°C) due to semiconductor/metallic transitions (8). The change in slope for CaMnO_3 based materials might be related with increasing oxygen deficiency, as structural transitions are not expected in this temperature region (11). The defect structure of these perovskite-type compounds is dominated by Schottky disorder (12):

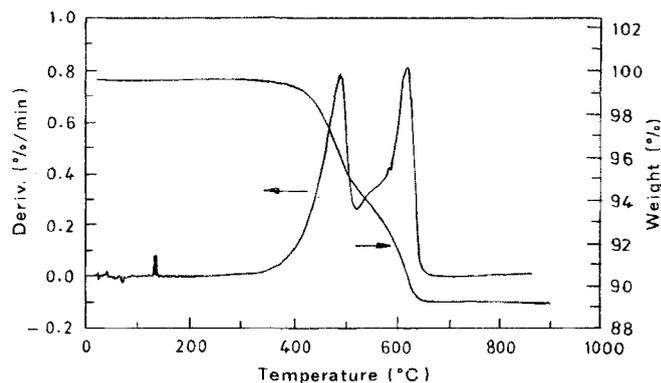
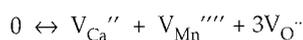


Fig. 4: TGA/DTA analyses of CaMnO_3 performed in H_2 between room temperature and 1000 °C for a sample previously treated in O_2 atmosphere. The total weight loss is about 10.7%, in good accordance with theoretical predictions for complete reduction of manganese to Mn^{2+} (11%).

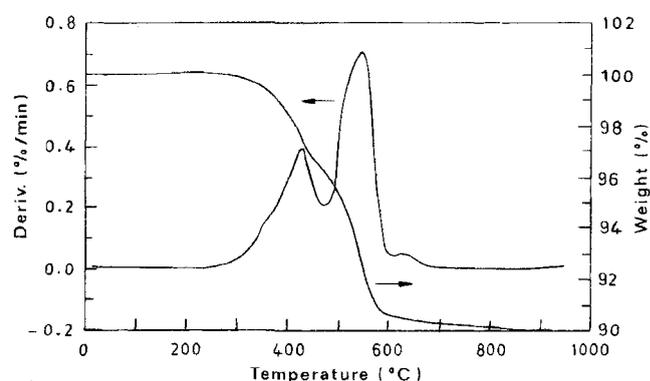


Fig. 5: TGA/DTA analyses of $\text{Ca}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ performed in H_2 between room temperature and 1000 °C. The total weight loss is about 9.9%.

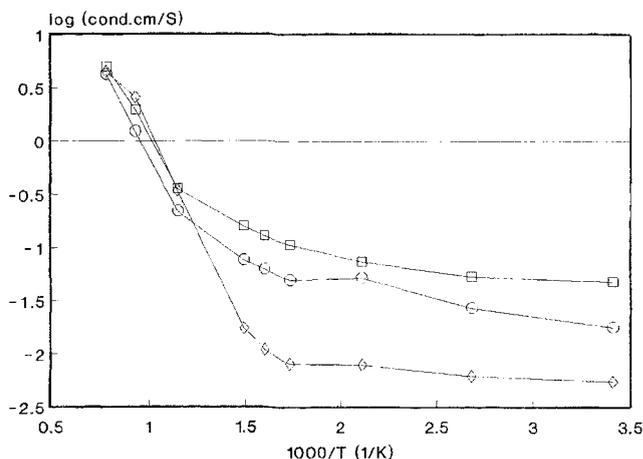
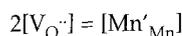


Fig. 6: Electrical conductivity of $\text{Ca}_{1-x}\text{Sr}_x\text{MnO}_3$ as a function of temperature. (○ - $x=0$; □ - $x=0.1$; ◇ - $x=0.2$).

and the dominant conduction hopping mechanism involves polaron changes between Mn^{4+} ($\text{Mn}_{\text{Mn}}^{4+}$) and Mn^{3+} ($\text{Mn}_{\text{Mn}}^{3+}$) ionic sites. Theoretically, the electronic conductivity should be maximum when the concentration of both Mn species is equal ($[\text{Mn}^{3+}] = [\text{Mn}^{4+}]$) and there is a tendency for increasing the amount of trivalent manganese ions as the oxygen-deficiency increases. Assuming a constant amount of cation vacancies, the charge elec-

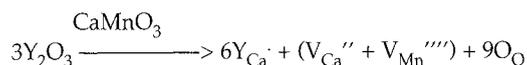
troneutrality in the lattice for oxygen vacancy creation (oxygen-deficiency) is obtained by simultaneous reduction of manganese ions (increasing $[Mn^{3+}]$):



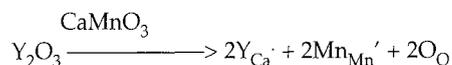
and an increase of electrical conductivity is expected with increasing oxygen deficiency. The change of slope in conductivity-temperature curves might be related with starting oxygen deficiency, as predicted from TGA/DTA curves.

The effect of Sr for Ca substitution on defect structure is predictably low because these cations are isovalent, but the stabilization of more oxygen-deficient structures at lower temperatures might contribute to improving the electronic conductivity, as shown in Figure 6 for 10% Sr-doped sample, in agreement with few literature results (9). The change in slope of 20% Sr-doped sample tends to occur at lower temperatures, in agreement with TGA/DTA results. At high temperatures this composition presents maximum conductivities.

A stronger effect on electronic and oxygen ion conductivities should be obtained promoting the Ca substitution by heterovalent cations, trying to not affect or even increase the structural stability of the oxygen-deficient phase. For example, Y for Ca substitution seems to decrease oxygen deficiency, as predicted by,

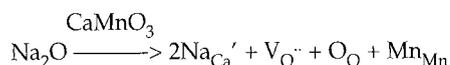


or,



for oxidising and reducing atmospheres, respectively. However, this decrease of oxygen deficiency might be compensated by an increase of electronic conductivity (by hopping).

On the other hand, Na for Ca substitution should increase both ionic conductivity and stability of oxygen-deficient compositions but probably giving a decrease of electronic conductivity,



The study of effects of these type of substitutions is now in progress.

4. CONCLUSIONS

Formation of solid solution by Sr for Ca substitution is possible by solid state reaction at 1000 °C up to a level of 20 %mol Sr. Stronger doped samples require calcination at higher temperatures, or the use of a different preparation procedure (chemical route). All the compositions seem to show some oxygen deficiency after calcination in air, with a slight increase of this tendency created by Sr doping.

Structural changes after annealing treatments in H₂ and at 310 °C seem to be more important in undoped samples, but it is possible to increase the oxygen deficiency in all the compositions. However, the reoxidation process is very fast in air and at high temperatures, and not affected by Sr-doping.

Electrical conductivity at room temperature is about 10⁻² S/cm, in close agreement with few literature results on similar compositions (9). At high temperatures the conductivity is still very low when compared with more common perovskites tested as cathode materials, and the effect of Sr doping is less pronounced.

Ca substitution by heterovalent cations should be a more promising alternative to increase the oxygen-deficient stability and also the electrical properties. ♦

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