Effect of the A cation size disorder and synthesis conditions on the properties of an iron perovskite series

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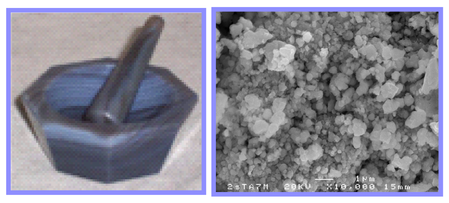
Introduction

Solid state chemistry thrives on a rich variety of solids that can be synthesized using a wide range of techniques. It is well known that the preparative route plays a critical role on the physical and chemical properties of the reaction products, controlling the structure, morphology, grain size and surface area of the obtained materials. This is particularly important in the area of ABO_3 perovskite compounds given that they have for long been at the heart of important applications [1]. Particularly, perovskite systems such as $La_{1-x}Sr_xFeO_3$ (LSF) are now receiving researchers attention for their interesting applications [2-4] such as ceramic membranes (CMs) for oxygen separation, solid oxide fuel cells (SOFCs) electrodes for efficient power generation, catalysts for complete oxidation of CO in vehicle engines, etc. In order to develop these advanced materials, combustion methods (glycine-nitrate, urea based, and other modifications) have been proposed as one of the most promising methods for their synthesis [5,6]. The characteristics (including purity, structure and size) of the combustion synthesis oxide powders are typically determined by several synthetic parameters, such as the species of fuel and oxidizer reactants, the fuel/oxidizer ratio, and the subsequent sintering treatment after combustion process [7,8]. In the other hand, physical properties of these perovskite materials are very sensitive to changes in the doping level (x), the average size of the A cations ($<r_A>$), and the effects of A cation size disorder ($\sigma^2(r_A)$) quantified as $\sigma^2(rA) = <r_A^2> - <r_A>^2$ [9].

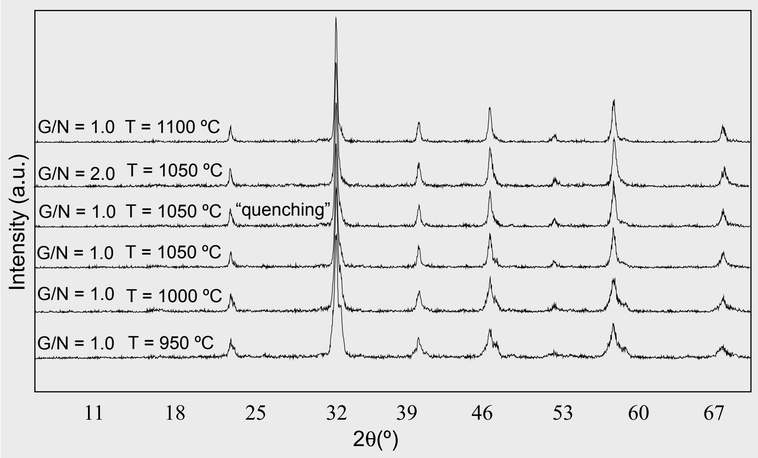
Scientific Approach

Our searching approach to find the optimum synthetic conditions for new materials within the LSF system has been based on the study of only one of the indicated parameters isolated from the rest. In this sense, this study is focused in the synthesis of new compositions with higher values of A cation size disorder ($La_{0.15}Sm_{0.35}Sr_{0.08}Ba_{0.42}FeO_{3-\delta}$) varying the calcinations temperature, fuel/oxidizer ratio and cooling rate.

Polycrystalline samples



XRD



X-ray diffraction patterns for $La_{0.15}Sm_{0.35}Sr_{0.08}Ba_{0.42}FeO_{3-\delta}$ perovskites sintered by glycine nitrate combustion method at different synthetic conditions.

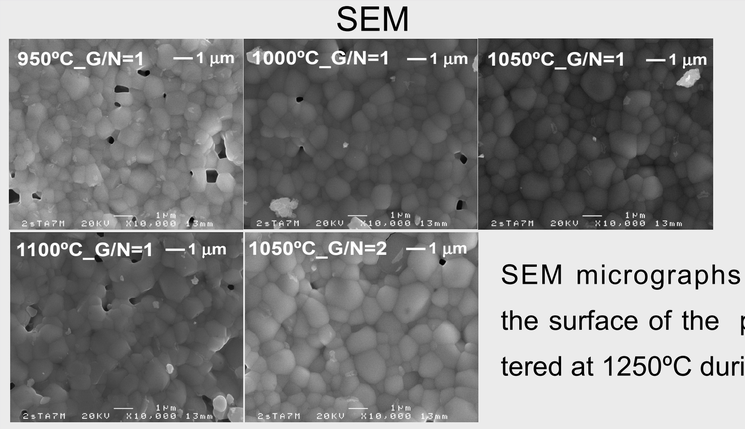
Synthesis

Glycine nitrate combustion (GNC) process for $La_{0.15}Sm_{0.35}Sr_{0.08}Ba_{0.42}FeO_{3-\delta}$ samples preparation.

- The solutions (metal nitrates dissolved) were mixed in a 1 litre glass beaker, which was placed on a hot plate, under constant stirring, to evaporate excess water. The synthesis was carried out varying the calcinations temperature (950, 1050 and 1100ºC), fuel/oxidizer ratio (G/N = 1 and 2) and cooling rate (slow cooling and air-quenched).
- The resulting viscous liquid autoignited after placing the glass beaker directly in a preheated plate (at 450ºC).
- The resulting powders were pelletized and calcined in air between 950 and 1100ºC for 5 hours to obtain the pure sample.

1250ºC (12 h)

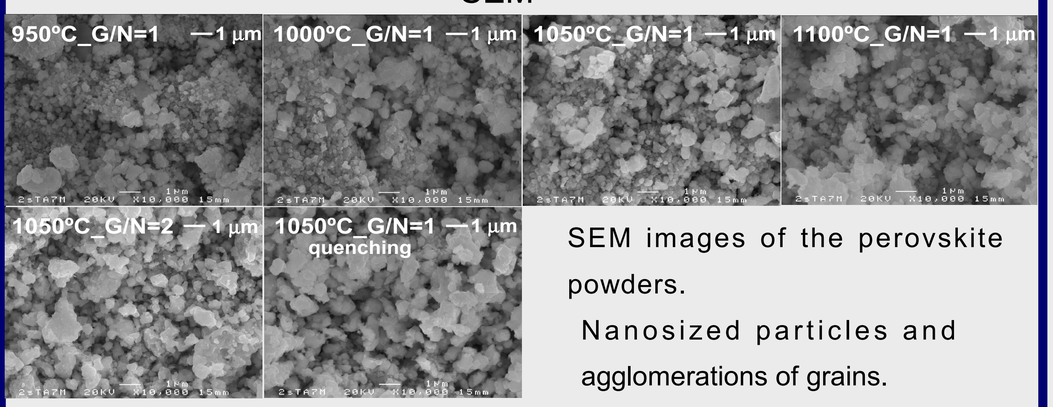
SEM



SEM micrographs taken on the surface of the pellets sintered at 1250ºC during 12 h.

Grain sizes ranging between 0.77 µm for sample obtained at 950ºC to 0.92 µm for the obtained at 1100ºC.

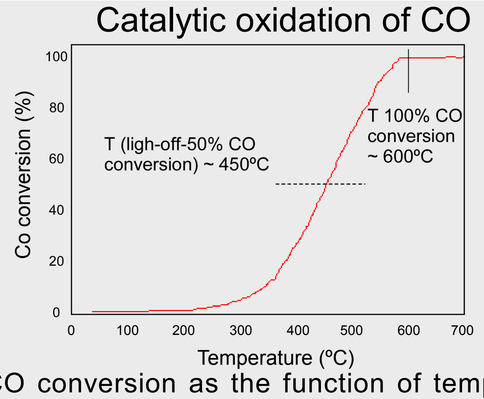
SEM



SEM images of the perovskite powders.

Nanosized particles and agglomerations of grains.

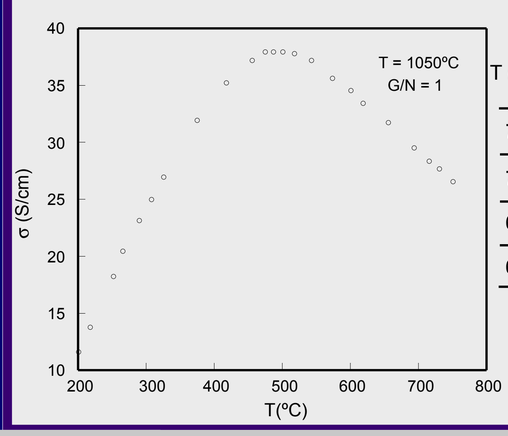
Catalytic oxidation of CO



CO conversion as the function of temperature over catalyst obtained at 1050ºC and with G/N = 1.

Electrical conductivity

Electrical conductivity as a function of temperature and current applied measured by the four-point method.



T (ºC)	σ (S/cm) G/N = 1 10, 50 and 100 mA	G/N = 2 10 and 50 mA	G/N = 2 100 mA
750	26.5	13.3	12.7
700	29.5	13.8	13.6
650	31.7	15.1	14.7
600	34.5	16.0	15.5

Conductivity decreases when a current of 100 mA is applied.

BET

BET specific surface areas of the samples

$T_{synthesis}$ (ºC)	G/N	S_{BET} (m^2/g)
950	1	8.22
1000	1	2.81
1050	1	2.11
1050 with quenching	1	1.72
1050	2	1.99
1100	1	1.56

S_{BET} decreases with calcination temperature.

Acknowledgements

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Conclusions

Six $La_{0.15}Sm_{0.35}Sr_{0.08}Ba_{0.42}FeO_{3-\delta}$ compounds have been obtained by glycine-nitrate method varying the calcinations temperature, fuel/oxidizer ratio and cooling rate, in order to study the effect on the structural, morphological, electrical and catalytic properties.

By the combustion method a well-necked morphology of the powders which are composed of nanosized particles and agglomerations of grains has been obtained.

Catalytic oxidation tests for the sample obtained at 1050ºC and with G/N = 1, has shown a value of light off temperature (T50%) about 450ºC reaching 100% CO combustion at approximately 600°C.

The BET specific surface areas of the samples decreases as calcination temperature increases.

The material obtained with G/N = 1.0 shows higher specific conductivity than obtained with G/N = 2.

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