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EFFECT OF ATTRITION MILLING AND CALCINATION TEMPERATURE ON PHASE COMPOSITION OF STRONTIUM- AND MAGNESIUM-DOPED LANTHANUM GALLATE

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Abstract. Oxygen-ion conductors based on strontium- and magnesium-doped lanthanum gallate have been proposed to be used as solid electrolyte in solid oxide fuel cells operating at intermediate temperatures (500-700 ºC), due to their high ionic conductivity and stability over a wide range of oxygen partial pressures. In this work, the effect of attrition milling on phase composition of powder and consolidated specimens prepared by solid state synthesis has been investigated. The results show that both the attrition milling and the calcination temperature play a major role in the phase composition. Powders with negligible amount of secondary phases were obtained after two steps of calcination at high temperature followed by attrition milling.

Introduction

Lanthanum gallate with partial substitutions of strontium and magnesium (LSGM) is a promise solid electrolyte for application in solid oxide fuel cells operating at intermediate temperatures (IT-SOFC), because of the combination of its properties like high ionic conductivity and ion transport number, chemical stability in a wide range of oxygen partial pressures and good mechanical strength [1-3].

The main drawback of LSGM is related to the usually found secondary phases that seem to be independent on the method of preparation. The secondary phases reported in the literature are: $LaSrGaO_4$, $LaSrGa_3O_7$, $LaGa_2O_9$ and free MgO [4,5]. These secondary phases are responsible for lowering of the ionic conductivity, thereby influencing the overall cell performance [6].

There are several indications that whatever the method of preparation the secondary phases will be always detected in the bulk of LSGM by thermodynamic as well as kinetics limitations. Another factor contributing for impurity phase formation is the vaporization of gallium, which is prone to occur in temperatures in excess of 1400ºC [7].

One of the most employed methods for the preparation of LSGM is the conventional mixing of starting materials followed by solid state reactions at high temperatures [1,8]. This method consists of one or more steps of mixing or milling and calcination before sintering, and has the advantage of high production rate along with simplicity. In this work, the composition $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$, hereafter called simply by LSGM, was prepared by the conventional ceramic method using attrition milling and different temperatures of calcination. The main purpose of this study is to verify the influence of the milling and temperature of calcination in the phase assemblage of LSGM.

Experimental

The composition $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) was prepared from La_2O_3 (99.9%), Ga_2O_3 (99.99%), MgO and $SrCO_3$ starting materials. The lanthanum oxide powder was heat treated at 1000ºC before use. Three routes, designated as R1-1, R1-2 and R2, were evaluated. The main processing steps of each route are shown in Fig. 1.

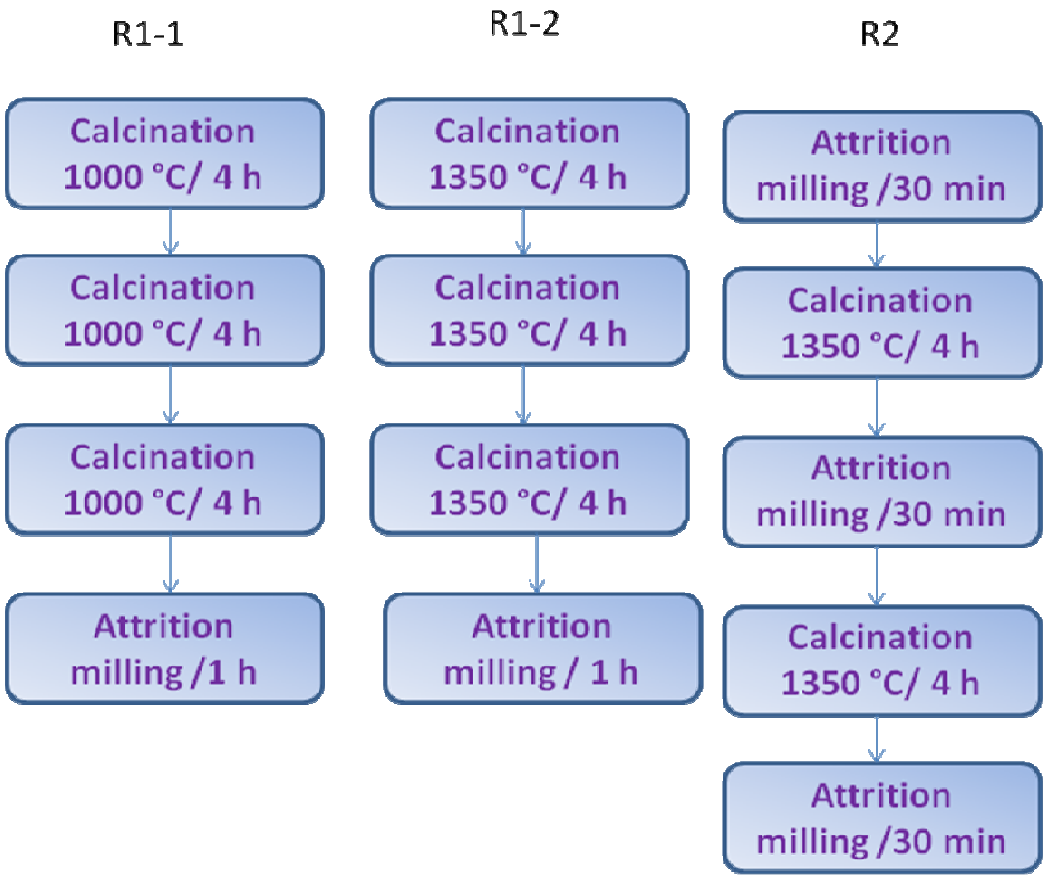

Fig. 1: Flowchart of the processing routes.

The main difference between routes R1-1 and R1-2 is the temperature of calcinations, settled in 1350ºC in the latter. In the processing route designated as R2, the calcinations was intermediated by attrition and the temperature of calcination was fixed at 1350 ºC.

Characterization of the powders prepared by the three routes was carried out by X-ray diffraction (D8 Advance, Bruker-AXS) using a Cu Kα radiation source in the 20-80º 2θ range for phase analysis, and scanning electron microscopy, SEM (XL30, Philips) for morphology observation.

Results and discussion

Fig. 2 shows X-ray diffraction powder patterns after each processing step for route R1-1. The identification of phases was carried out by comparison of the experimental patterns with ICSD files. As can be seen, the phase LSGM was not formed after following this route, because of the lower temperature of thermal treatments.

SEM micrographs of powder mixtures after each processing step of route R1-1 are shown in Fig. 3.

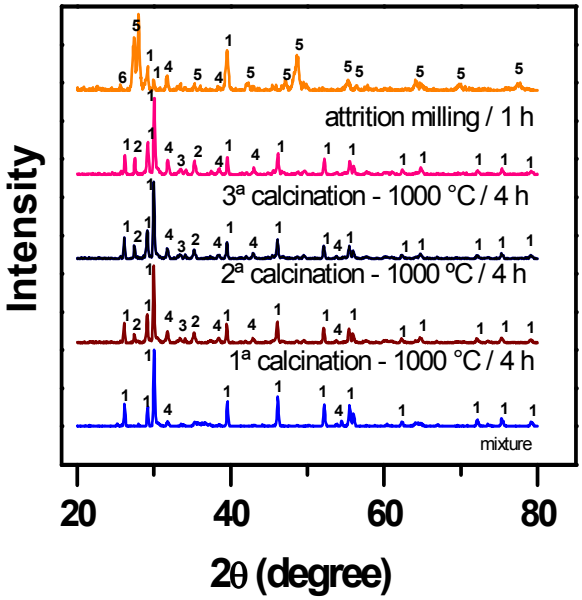

Fig. 2: X-ray diffraction patterns of powder mixtures after each processing step of route R1-1. 1-La_2O_3, 2-$SrCO_3$, 3-$SrLaGaO_4$, 4-Ga_2O_3, 5-$La(OH)_3$ e 6-$La_4Ga_2O_9$.

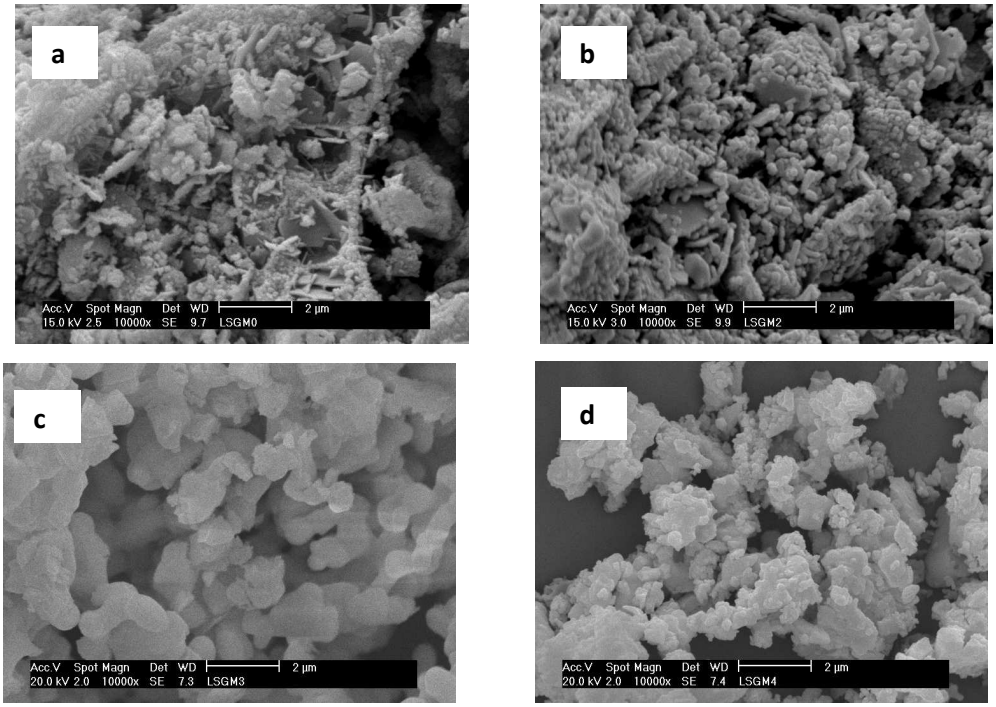

Fig. 3: SEM micrographs of powder mixtures after processing steps of route R1-1. a) before calcination, b) after the second calcination, c) after the third calcination, and d) after attrition milling.

The powder particles of the starting materials (Fig. 3a) are quite different in shape and size hindering a good homogeneity among them. After the second calcination (Fig. 3b) the morphology resembles that of the original mixture, but the third calcination (Fig. 3c) favored the start of neck formation. Reasonable homogeneity of the powder mixture was obtained only after attrition milling (Fig. 3d).

Fig. 4 shows X-ray diffraction patterns of powder mixtures prepared according to the route R1-2. After the first step of calcination at 1350ºC, the LSGM phase has already been formed. However, the reaction was incomplete and diffraction peaks of the starting reagents are detected.

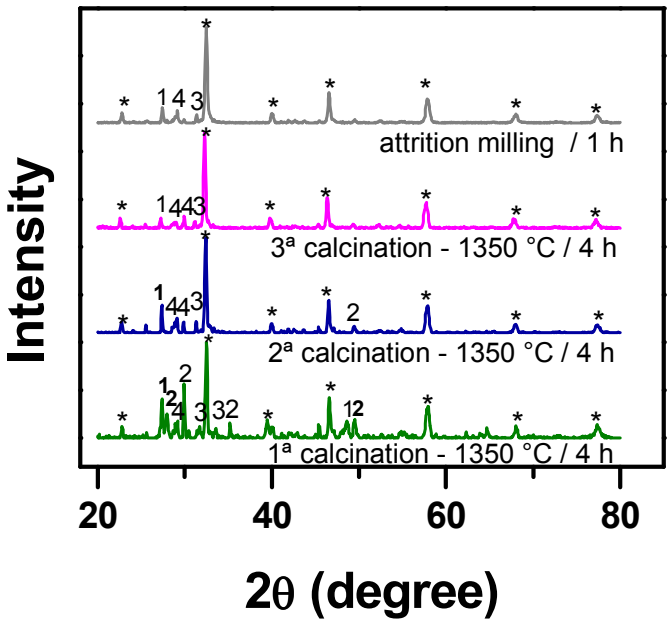

Fig. 4: X-ray diffraction patterns of powder mixtures after each processing step of route R1-2. 1-$La(OH)_3$, 2-$SrLaGa_3O_7$. 3-$SrLaGaO_4$, 4-La_2O_3 e * - LSGM.

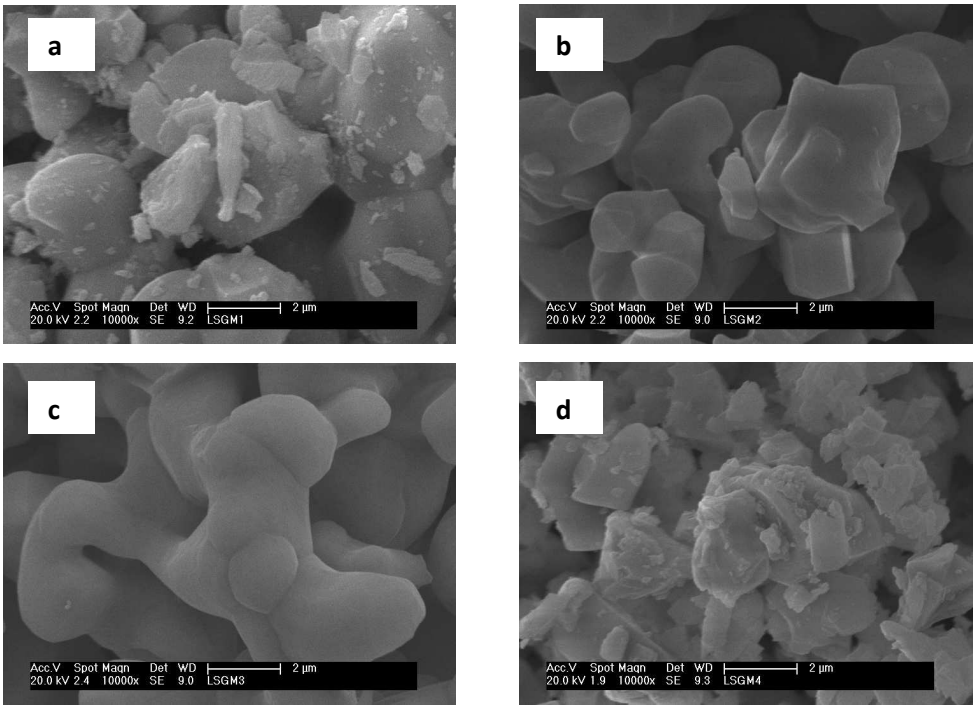

Fig. 5: SEM micrographs of powder mixtures after processing steps of route R1-2. a) after the first calcination, b) after the second calcination, c) after the third calcination, and d) after attrition milling.

The LSGM phase becomes more evident during subsequent calcinations and predominates at the end of the processing steps.

Fig. 5 shows SEM micrographs of powder mixtures after processing steps according to the route R1-2. The sintering of the powder particles may be seen even after the first calcination (Fig. 5a), because of the relatively high temperature. Subsequent calcinations resulted in continuous growing of the particles/grains. The particle/grain growth process occurs very fast at this temperature, and then it was decided to intercalate a step of attrition milling between two successive calcinations.

Fig.6 shows X-ray diffraction patterns of powder mixtures prepared according to the route R2.

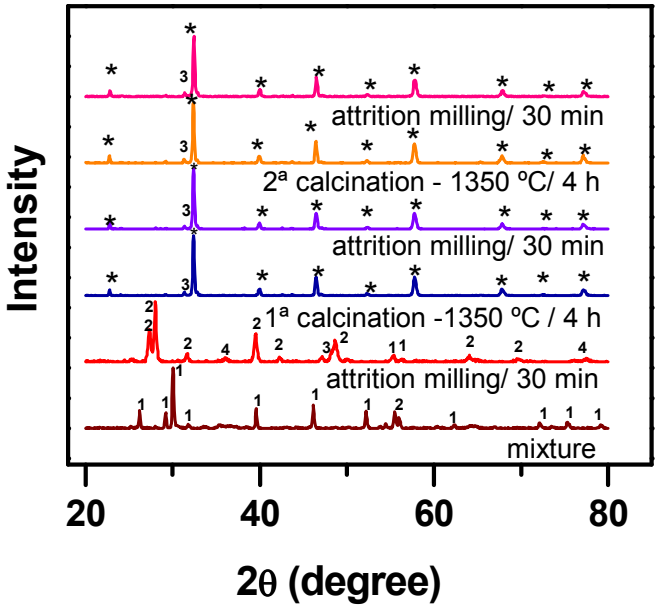

Fig. 6: X-ray diffraction patterns of powder mixtures after each processing step of route R2. 1-La_2O_3, 2-$La(OH)_3$ 3-$SrLaGaO_4$, 4-Ga_2O_3 e * - LSGM.

The processing route R2 allowed for obtaining the LSGM phase yet after the first calcination, similarly to the route R2-1. In this case, however, the secondary phase content, estimated by X-ray diffraction data, is smaller. The persistent secondary phase is $SrLaGaO_4$.

Observation of the morphology of the powder particles for this route resulted in the micrographs shown in Fig. 7. The attrition milling of the starting mixture (Fig. 7a) produced particles with homogeneous size and shape, which contributed to the formation of the LSGM phase. After the first (Fig. 7b) and the second calcinations (Fig. 7c), the morphology of the particles is similar due to the attrition milling between them. After the final attrition milling (Fig. 7d) the powder particles still possess a mix nature exhibiting loose particles along with neck between larger particles.

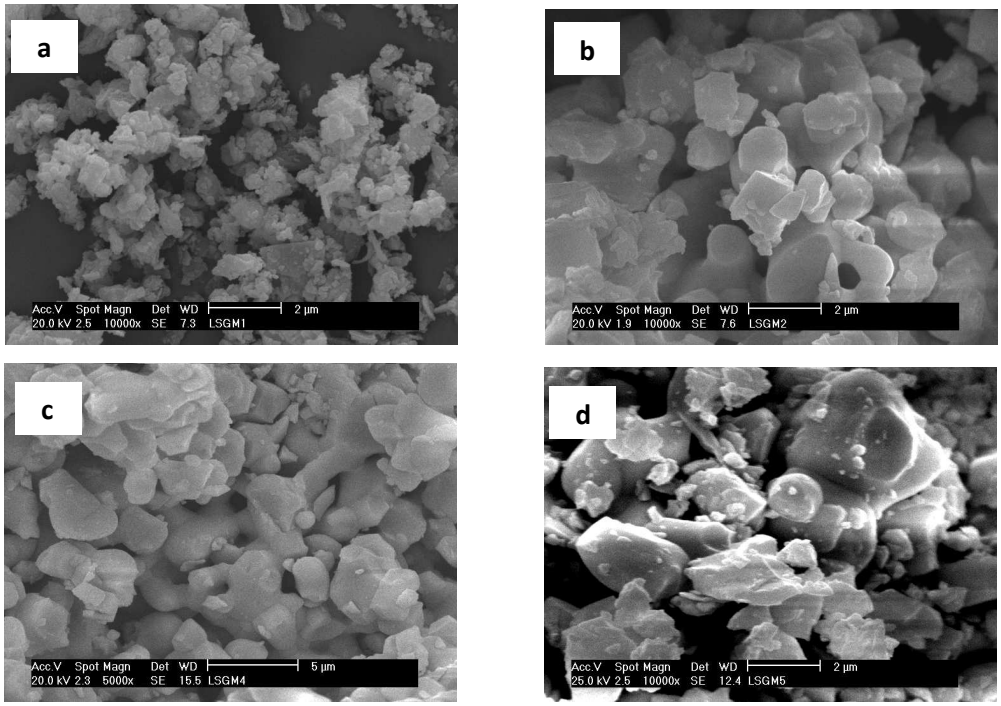

Fig. 7: SEM micrographs of powder mixtures after processing steps of route R2. a) after attrition milling, b) after the first calcination, c) after the second calcination, and d) after attrition milling.

Conclusions

Three processing routes were employed to prepare LSGM powders varying the calcination temperature and milling. The use of low temperatures did not resulted in the LSGM phase. Introduction of the milling step between successive calcinations reduced the amount of secondary phases in the produced powders.

Acknowledgements

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