Effect of synthesis process on the densification, microstructure, and electrical properties of $\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_3$ ceramics

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Abstract

$\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_3$ thermoelectric materials have been prepared, through a classical solid state sintering method, from attrition, and ball milled precursors. After calcination step, microstructural observations have shown that attrition milled precursors possess much smaller particle sizes than the obtained by ball milling. Smaller precursors sizes lead to higher reactivity, producing higher density, hardness, and thermoelectric phase content in the sintered materials. The thermoelectric properties reflect the microstructural features, decreasing electrical resistivity in the attrition milling prepared samples without a drastic decrease of Seebeck coefficient. As a consequence, power factor values are higher than the obtained in the classical solid state method samples. Moreover, the highest power factor values at 800 °C are much higher than the best results obtained in this CaMnO_3 family. As a result, it has been found that it is possible to tailor the thermoelectric properties of $\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_3$ ceramics by designing the appropriate preparation procedure while keeping in mind its industrial scalability.

Keywords: Densification; Electroceramics; Electrical properties; Hardness.

Running head: Synthesis of $\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_3$ ceramics

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1. Introduction

Thermoelectric (TE) materials can directly transform a thermal gradient to electrical energy without moving parts. They are considered very promising to raise the energy transforming systems efficiency, decreasing their CO₂ emissions. As a consequence, they can help to fight against global warming, reducing the greenhouse gases release. For these applications, it is necessary to obtain highly efficient TE materials, being quantified through the figure-of-merit, ZT , which is defined as $TS^2/\rho\kappa$, where T , S , ρ , and κ , are absolute temperature, Seebeck coefficient, electrical resistivity, and thermal conductivity, respectively.¹

In the last years, different semiconducting and intermetallic compounds have been used to build high performance TE modules. On the other hand, they possess some drawbacks, as the presence of heavy or toxic elements (Sb, As, Te ...) ² with low melting point and/or reduced chemical stability at moderate temperatures under air. Moreover, their low relative abundance in earth's crust and high prices, drastically limit their large scale applications. Some of these inconveniences were surpassed by the discovery of attractive thermoelectric performances in Na_xCoO₂ ceramic.³ These materials are composed of non-toxic, cheaper, more abundant, and environmentally friendly elements than the intermetallic ones. Furthermore, they possess high thermal and chemical stability under air. As a consequence of these advantages, the search for new oxide materials possessing high TE performances led to new materials, such as [Ca₂CoO₃][CoO₂]_{1.62} or [Bi_{0.87}SrO₂]₂[CoO₂]_{1.82},^{4,5} with *p*-type conduction. On the other hand, *n*-type ones are mainly represented by MnO or SrTiO₃-based ceramics.^{6,7} The main drawback of these ceramics is their relatively low performances when compared with the intermetallic ones. As a consequence, their TE properties have to be substantially increased before being

considered for practical applications. Many processing techniques have been applied to improve the performances of anisotropic materials by aligning the grains in a preferential direction, such as hot uniaxial pressing,^{8,9} or the electrically assisted laser floating zone melting.^{10,11} On the other hand, not too many works explore the effect of precursors on the final properties of these materials, even if it is well established that their characteristics may greatly influence their performances. Most commonly, TE ceramics are prepared through the solid state route,⁸ which involves repeated mixing, milling and thermal treatments. Nevertheless, incomplete reaction, and compositional inhomogeneities are typical trademarks of this method. On the other hand, more complex solution methods have been used to increase precursors homogeneity and reactivity,^{12,13} leading to increased electrical performances in the final materials.

The objective of this work is producing high performance $\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_3$ thermoelectric materials, which show improved TE properties,¹⁴ using the attrition milling process, which is a very simple and industrially scalable modification of one of the steps of the classical solid-state method. The microstructural, mechanical, and electrical properties of the sintered bodies will be determined and compared with the obtained through the classical solid-state method using the ball milling process.

2. Experimental

The initial $\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_3$ mixtures used in this work were prepared from commercial CaCO_3 ($\geq 99\%$, Aldrich), Mn_2O_3 (99 %, Aldrich), and Yb_2O_3 (99.9 %, Aldrich) powders. They were weighed in the appropriate proportions, mixed and milled for 3 h in an attrition mill at 600 rpm for the modified solid-state method, and

in a ball mill for 3 h at 300 rpm for the classical solid-state one. In both cases, the milling procedure has been performed in water media. After the milling process, both slurries were totally sieved to separate the grinding media and dried using infrared radiation until soft brownish powders were obtained. The resulting powders were then subjected to a thermal treatment at 900 °C for 12 h in order to decompose the CaCO_3 . It should be noted that infrared spectroscopy has shown that a second thermal treatment in the same conditions was necessary for the classical solid-state method to reach the same starting composition in both types of samples. After the thermal treatments, the powders were manually milled and pressed in form of pellets under 400 MPa applied pressure. These green bodies were sintered at 1300 °C and different dwell times, some of the samples were maintained at this temperature for 1.5 h, while others were sintered for 12 h. Phase identification in the sintered materials has been performed using powder X-ray diffraction (XRD) utilizing a Rigaku D/max-B X-ray powder diffractometer ($\text{CuK}\alpha$ radiation) with 2θ ranging between 10 and 70 degrees. Apparent density of the different samples has been determined in several samples for each experimental procedure using Archimedes method. Microstructural observations were performed on the precursor powders after the thermal treatments in order to establish their differences before sintering. Moreover, fractured and polished surfaces were also studied using a Field Emission Scanning Electron Microscope (FESEM, Zeiss Merlin) fitted with an energy dispersive spectrometry (EDS) device. Microhardness has been measured on several samples for each synthesis conditions using 15 seconds dwell time and 9.81 N applied load.

Electrical resistivity and Seebeck coefficient were simultaneously determined in all samples using the steady state mode, by the standard dc four-probe technique in a

LSR-3 apparatus (Linseis GmbH) between 50 and 650 °C. Moreover, Power Factor ($PF = S^2/\rho$) has been calculated from the electrical resistivity and Seebeck coefficient to evaluate their TE performances.

3. Results and discussion

The effect of the different precursors and sintering process duration can be easily observed in Fig. 1, where the green ceramics, together with the ones sintered for 1.5 and 12 h, obtained from the different precursors are presented. As it can be easily observed, all sintered samples volumes are smaller than the green ceramics ones, due to the densification produced during the thermal treatment. Moreover, no drastic changes in their dimensions can be observed when comparing samples sintered 1.5 and 12 h, independently of the synthesis method. On the other hand, it is also clear that the attrition milled precursors lead to higher densification due to their smaller particle sizes and, consequently, to their higher reactivity. These characteristics have been confirmed by FESEM observations of the different precursor powders and illustrated in Fig. 2. As it can be easily observed in these pictures, the grain sizes are much larger in the classical solid state method precursors (around 700 nm) than in the attrition milling ones (about 200 nm). These differences are due to the fact that attrition milling leads to very small particle sizes¹³ and to the two calcination steps necessary to decompose the CaCO_3 in the classical solid state method. As a consequence of their lower grain sizes, it is easy to deduce that their chemical reactivity and cation diffusion rates should be much higher than using the classical solid state precursors.

After sintering procedure, powder XRD patterns displayed in Fig. 3 show that all samples are very similar. As it can be observed in the graph, major peaks (indicated

by their diffraction planes) belong to the thermoelectric $\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_3$ phase with orthorhombic Pnma space group, in agreement with previously reported data,^{14,15} independently of the synthesis route and the sintering duration. Moreover, no evident secondary phase formation has been detected in any of the patterns, clearly indicating that the synthesis conditions have been adequate to produce very high content of thermoelectric phase in all samples.

FESEM observations on fractured surfaces of all samples were performed and some representative micrographs are displayed in Fig. 4. As it can be deduced from these images, the microstructure clearly fits with the general aspect of samples shown in Fig. 1. The samples produced from the attrition milled precursors possess no evident porosity even after only 1.5 h sintering (Fig. 4a) while in the classical solid state one there is still a relatively high porosity content after 12 h sintering (Fig. 4b). As a consequence of these observations, it can be easily deduced that the larger shrinkage produced in samples produced from the attrition milled precursors is due to the higher reactivity of these powders, reflected in nearly porosity-free materials. In order to confirm these observations, apparent density has been measured in all the materials and the mean results, together with their standard error, are illustrated in Table 1. From these data, it is evident that samples produced using the attrition milled precursors possess much higher densities than their counterparts prepared via classical solid state method, confirming the previous observations. Moreover, as it should be expected, density of samples produced with each type of precursors is increased when the sintering time is longer.

Representative FESEM images of polished surfaces of all samples are displayed in Fig. 5. In these images the features observed in the previous micrographs can be also seen, very low porosity in samples produced from the attrition milled

precursors and a clear grain growth and decrease of porosity when the sintering time is longer. These results are in clear agreement with previous reported results in ceramic materials.^{16,17} Moreover, major contrast is the grey one (indicated by #1) in all samples and corresponds to the thermoelectric $\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_3$ phase (through EDS analysis). Samples produced from the attrition milled precursors are only composed of this phase, while the obtained through the classical solid state method present a white contrast (#2 in Figs. 5c, and d) which is an Yb-rich phase with approximate $\text{Ca}_{0.5}\text{Yb}_{0.5}\text{MnO}_3$ composition after 1.5 h sintering, and slightly lower Yb content after 12 h. This last phase has not been detected through XRD, probably due to its low amount, to the fact that an important fraction of this phase is inside the grains, surrounded by the grey one (thermoelectric phase, see Figs. 5c, and d), and the similar pattern of both compositions.

All these microstructural observations are reflected in the mechanical properties measured using Vickers microhardness, as it is illustrated in Table 2. From these data, it is clear that the hardness is much higher in the samples prepared from the attrition milled precursors due to the very low content of porosity, which is responsible of the low hardness measured in the classically prepared samples. Moreover, the raise of hardness when the sintering time is longer is associated to a decrease of porosity, more important in the latter samples due to their higher porosity. Furthermore, these results are comparable to the obtained in sintered and Spark Plasma Sintered (SPS) $\text{Ca}_{0.95}\text{Sm}_{0.05}\text{MnO}_3$ materials, 0.13 and 0.85 GPa, respectively,¹⁸ confirming the above statements.

Electrical resistivity evolution with temperature for all samples is displayed in Fig. 6. From the data presented in the graph, it is clear that the resistivity values clearly agree with the previous discussed characteristics, they are lower when the samples

density is higher. Moreover, they are also lower for samples with higher thermoelectric phase content. As a consequence, the lowest values have been determined in the attrition milled samples sintered for 12 h at 1300 °C in the whole measured temperature range. On the other hand, only small differences in the general behaviour of resistivity can be observed, all samples show metallic-like one ($dp/dT > 0$), with the only exception of the classically prepared samples sintered for 1.5 h, which show semiconducting-like behaviour ($dp/dT < 0$) at high temperatures (> 700 °C). The difference can be associated to the lower density and higher amount of secondary phases found in these samples, compared with the other ones. In any case, all samples possess much lower electrical resistivity at room temperature than the sintered undoped CaMnO_3 (125 m Ω .cm).¹⁹ The minimum resistivity values measured in this work at room temperature (2.2 m Ω .cm) are lower than the determined in Yb-doped sintered materials (3.5-7 m Ω .cm),^{14,15,20} or the best results obtained in SPS samples (10 m Ω .cm).²¹ Furthermore, they are similar to the reported for the best codoped CaMnO_3 sintered materials (around 2.3 m Ω .cm).²²⁻²⁴

When evaluating the values at 800 °C, the minimum resistivity values measured in this work (4.2 m Ω .cm) are much lower than the pristine CaMnO_3 (35 m Ω .cm),¹⁹ the best measured in Yb-doped sintered materials (7-9 m Ω .cm),^{14,15,20} or prepared through SPS (8 m Ω .cm).²¹ On the other hand, they are comparable to the best reported results in codoped CaMnO_3 (between 3.6 and 6.5 m Ω .cm).²²⁻²⁴ From these data, it is clear that attrition milled precursors are very useful to obtain samples with very low electrical resistivity due to the microstructural improvements induced by using small particle size precursors.

Fig. 7 displays the variation of the Seebeck coefficient as a function of temperature for the different samples. All of them exhibit negative values in the whole measured temperature range, confirming a dominating conduction mechanism by electrons. As it can be observed, the S values increase when the temperature is increased in all cases. The highest S values are measured in the classically prepared samples sintered for 1.5 h, in agreement with their higher electrical resistivities. At room temperature, the maximum values ($-90 \mu\text{V/K}$) are much lower than the reported in undoped materials ($-350 \mu\text{V/K}$)¹⁹ which clearly reflects the low carrier concentration in CaMnO_3 . The electron doping promoted by Yb substitution, enhances the carrier concentration and is the responsible for this low Seebeck coefficient. On the other hand, the values measured in this work at room temperature are comparable to the obtained in Yb-doped sintered samples (-90 to $-100 \mu\text{V/K}$),^{14,20} prepared using SPS ($-90 \mu\text{V/K}$),²¹ or in codoped materials (-70 to $-120 \mu\text{V/K}$).²²⁻²⁴ When comparing the values at high temperature (800°C), the values measured in this work ($-160 \mu\text{V/K}$) are still lower than in the pure samples ($-225 \mu\text{V/K}$),¹⁹ but higher than the measured in Yb-doped sintered samples (-140 to $-150 \mu\text{V/K}$),^{14,20} or sintered by SPS ($-145 \mu\text{V/K}$).²¹ Moreover, they are higher than most of the reported values for codoped CaMnO_3 materials (-95 to $-160 \mu\text{V/K}$).²²⁻²⁴

Using the electrical resistivity and Seebeck coefficient data, PF variation with temperature has been calculated for all samples and presented in Fig. 8. This graph clearly shows that samples prepared from the attrition milled precursors possess much higher PF values than the classically prepared ones. Moreover, the former ones possess very similar values at low and high temperatures, differing only between 350 and 750°C where the samples sintered for 12 h possess higher performances. The maximum values at room temperature ($0.27 \text{ mW/K}^2\text{m}$) are

higher than the reported for the undoped CaMnO_3 ($0.1 \text{ mW/K}^2\text{m}$),¹⁹ Yb-doped sintered materials ($0.20\text{-}0.23 \text{ mW/K}^2\text{m}$),^{14,20} or prepared through SPS ($0.08 \text{ mW/K}^2\text{m}$).²¹ On the other hand, they are lower than the best reported values in codoped CaMnO_3 ($0.13\text{-}0.42 \text{ mW/K}^2\text{m}$).²²⁻²⁴ Finally, at high temperatures (800°C) both attrition milled samples display the same value ($0.50 \text{ mW/K}^2\text{m}$), drastically higher than the measured in the pristine CaMnO_3 ($0.17 \text{ mW/K}^2\text{m}$),¹⁹ in Yb-doped sintered materials ($0.22\text{-}0.25 \text{ mW/K}^2\text{m}$),^{14,20} or sintered using SPS ($0.26 \text{ mW/K}^2\text{m}$).²¹ Moreover, the maximum values obtained in this work clearly exceed the reported in codoped materials ($0.095\text{-}0.35 \text{ mW/K}^2\text{m}$).²²⁻²⁴

From these data, it is worth to mention that the very high thermoelectric performances reached in these materials have been obtained using a relatively economic and scalable preparation technique. As a consequence, $\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_3$ sintered materials prepared from attrition milled precursors can be seen as very promising candidates for practical applications in high temperature thermoelectric devices.

4. Conclusions

$\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_3$ thermoelectric materials were prepared by attrition milling, and classical solid state method. Microstructural studies of precursors after the calcination process have shown that attrition milling method produced very small particle size precursors, compared with the obtained by the classical solid state route. These small particle sizes lead to very low porosity sintered bodies, with very high hardness values, due to their high reactivity. The electrical resistivity is much lower than the measured in solid state sintered materials, independently of the sintering process duration, without drastic modifications of Seebeck coefficient. As a

consequence, PF values for samples produced from attrition milled precursors are much higher than the obtained in the classically solid-state prepared samples. Moreover, the highest PF values at 800 °C are the highest obtained in CaMnO_3 , $\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_3$ or codoped CaMnO_3 sintered materials reported in the literature. Besides these improvements, it is important to highlight that they have been produced using an economic and scalable preparation technique which allows decreasing the number and duration of thermal treatments when compared with the classical solid state route. As a result, it is clear that it is possible to tailor the thermoelectric properties of CaMnO_3 ceramics by an appropriate design of the ceramic preparation route and doping processes.

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References

1. Rowe DM. Thermoelectric Handbook: Macro to Nano. 1st ed. Boca Raton, FL: CRC Press; 2006.
2. Wang H, Hwang J, Snedaker ML, Kim I-H, Kang C, Kim J, Stucky GD, Bowers J, Kim W. High Thermoelectric Performance of a Heterogeneous PbTe Nanocomposite. *Chem Mater*. 2015;27:944-949.
3. Terasaki I, Sasago Y, Uchinokura K. Large thermoelectric power in NaCo_2O_4 single crystals. *Phys Rev B*. 1997;56:12685-12687.
4. Masset AC, Michel C, Maignan A, Hervieu M, Toulemonde O, Studer F, Raveau B, Hejtmanek J. Misfit-layered cobaltite with an anisotropic giant magnetoresistance: $\text{Ca}_3\text{Co}_4\text{O}_9$. *Phys Rev B*. 2000;62:166-175.
5. Diez JC, Rasekh Sh, Madre MA, Guilmeau E, Marinel S, Sotelo A. Improved thermoelectrical properties of Bi-M-Co-O (M=Sr, Ca) misfit compounds by laser directional solidification. *J Electron Mater*. 2010;39:1601-1605.
6. Zhu YH, Su WB, Liu J, Zhou YC, Li J, Zhang X, Du Y, Wang CL. Effects of Dy and Yb co-doping on thermoelectric properties of CaMnO_3 ceramics. *Ceram Int*. 2015;41:1535-1539.
7. Liu J, Wang CL, Li Y, Su WB, Zhu YH, Li JC, Mei LM. Influence of rare earth doping on thermoelectric properties of SrTiO_3 ceramics. *J Appl Phys*. 2013;114:223714.
8. Wang H, Sun X, Yan X, Huo D, Li X, Li J-G, Ding X. Fabrication and thermoelectric properties of highly textured $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ ceramic. *J Alloys Compds*. 2014;582:294-298.

9. Rubesova K, Hlasek T, Jakes V, Huber S, Hejtmanek J, Sedmidubsky D. Effect of a powder compaction process on the thermoelectric properties of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ ceramics. *J Eur Ceram Soc.* 2015;35:525-531.
10. Costa FM, Ferreira NM, Rasekh Sh, Fernandes AJS, Torres MA, Madre MA, Diez JC, Sotelo A. Very large superconducting currents induced by growth tailoring. *Cryst Growth Des.* 2015;15:2094-2101.
11. Ferreira NM, Rasekh Sh, Costa FM, Madre MA, Sotelo A, Diez JC, Torres MA. New method to improve the grain alignment and performance of thermoelectric ceramics. *Mater Lett.* 2012;83:144-147.
12. Wu NY, Holgate TC, Nong NV, Pryds N, Linderoth S. High temperature thermoelectric properties of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ by auto-combustion synthesis and spark plasma sintering. *J Eur Ceram Soc.* 2014;34:925-931.
13. Sotelo A, Rasekh Sh, Torres MA, Bosque P, Madre MA, Diez JC. Effect of synthesis methods on the $\text{Ca}_3\text{Co}_4\text{O}_9$ thermoelectric ceramic performances. *J Solid State Chem.* 2015;221:247-254.
14. Flahaut D, Mihara T, Funahashi R, Nabeshima N, Lee K, Ohta H, Koumoto K. Thermoelectrical properties of A-site substituted $\text{Ca}_{1-x}\text{Re}_x\text{MnO}_3$ system. *J Appl Phys.* 2006;100:084911.
15. Wang Y, Sui Y, Cheng J, Wang X, Lu Z, Su W. High Temperature Metal-Insulator Transition Induced by Rare-Earth Doping in Perovskite CaMnO_3 . *J Phys Chem C.* 2009;113:12509-12516.
16. Jung Y-I, Yoon D Y, Kang S-J L. Coarsening of polyhedral grains in a liquid matrix. *J. Mater. Res.* 2009;24:2949-2959.

17. Yoon B-K, Lee B-A, Kang S-J L. Growth behavior of rounded (Ti,W)C and faceted WC grains in a Co matrix during liquid phase sintering. *Acta Mater.* 2005;53:4677-4685.
18. Noudem JG, Kenfaui D, Quetel-Weben S, Sanmathi CS, Retoux R, Gomina M. Spark Plasma Sintering of n-Type Thermoelectric $\text{Ca}_{0.95}\text{Sm}_{0.05}\text{MnO}_3$. *J Amer Ceram Soc.* 2011;94:2608-2612.
19. Kabir R, Tian R, Zhang T, Donelson R, Tan TT, Li S. Role of Bi doping in thermoelectric properties of CaMnO_3 . *J Alloys Compds.* 2015;628:347-351.
20. Kabir R, Wang D, Zhang T, Tian R, Donelson R, Tan TT, Li S. Tunable thermoelectric properties of $\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_3$ through controlling the particle size via ball mill processing. *Ceram Int.* 2014;40:16701-16706.
21. Quetel-Weben S, Retoux R, Noudem JG. Thermoelectric $\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_{3-\delta}$ grain growth controlled by spark plasma sintering. *J Eur Ceram Soc.* 2013;33:1755-1762.
22. Zhang B, Chang A, Zhao Q, Ye H, Wu Y. Synthesis and Thermoelectric Properties of Yb-doped $\text{Ca}_{0.9-x}\text{Yb}_x\text{La}_{0.1}\text{MnO}_3$ Ceramics. *J Electron Mater.* 2014;43:4048-4055.
23. Wang H, Wang C. Synthesis of Dy doped $\text{Yb}_{0.1}\text{Ca}_{0.9}\text{MnO}_3$ ceramics with a high relative density and their thermoelectric properties. *Mater Res Bull.* 2012;47:2252-2256.
24. Zhu Y, Wang C, Wang H, Su W, Liu J, Li J. Influence of Dy/Bi dual doping on thermoelectric performance of CaMnO_3 ceramics. *Mater Chem Phys.* 2014;144:385-389.

Table 1. Evolution of the mean density of the different $\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_3$ samples as a function of the preparation procedure, together with their standard errors.

Precursor	Sintering time (h)	Density (g/cm^3)	Standard error
Attrition	1.5	4.62	0.02
	12	4.67	0.03
Solid State	1.5	3.28	0.04
	12	4.12	0.20

Table 2. Evolution of the mean Vickers hardness of the different $\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_3$ samples as a function of the preparation procedure, together with their standard errors.

Precursor	Sintering time (h)	Hardness (GPa)	Standard error
Attrition	1.5	7.52	0.09
	12	7.61	0.07
Solid State	1.5	1.35	0.02
	12	1.91	0.05

Figure captions

Figure 1. Image of a green ceramic pellet, together with the sintered ones at 1300 °C for 1.5 and 12 h, prepared through the classical solid-state method or from attrition milling.

Figure 2. FESEM micrographs of precursor powders after the thermal treatments for the a) classical solid state; and b) attrition milling methods.

Figure 3. Powder XRD patterns of $\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_3$ samples after the different sintering procedures: a, and b) attrition milled precursors sintered at 1300 °C for 1.5 and 12 h, respectively; c, and d) classical solid state method sintered at 1300 °C for 1.5 and 12 h, respectively.

Figure 4. FESEM micrographs performed in representative fractured surfaces of each synthesis method: a) attrition milling after 1.5 h at 1300 °C; and b) classical solid state method after 12 h at 1300 °C.

Figure 5. FESEM micrographs performed in representative polished surfaces after the sintering procedures: a, and b) attrition milling after 1.5, and 12 h at 1300 °C, respectively; and c, and d) classical solid state method after 1.5, and 12 h at 1300 °C, respectively. The different phases are indicated by numbers, #1 $\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_3$; #2 Yb-rich phase with approximate $\text{Ca}_{0.5}\text{Yb}_{0.5}\text{MnO}_3$ composition.

Figure 6. Electrical resistivity evolution with temperature for each preparation method: classical solid state method sintered at 1300 °C for (●) 1.5, and (■) 12 h; and attrition milling sintered at 1300 °C for (◆) 1.5, and (▼) 12h.

Figure 7. Seebeck coefficient evolution with temperature for each preparation method: classical solid state method sintered at 1300 °C for (●) 1.5, and (■) 12 h; and attrition milling sintered at 1300 °C for (◆) 1.5, and (▼) 12h.

Figure 8. PF evolution with temperature for each preparation method: classical solid state method sintered at 1300 °C for (●) 1.5, and (■) 12 h; and attrition milling sintered at 1300 °C for (◆) 1.5, and (▼) 12h.

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