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Effect of the sintering conditions on the morphology of $La_{9.33}Si_2Ge_4O_{26}$ oxyapatite for SOFCs electrolytes

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Solid oxide fuel cells (SOFCs) are devices that allow direct conversion of chemical to electrical energy through an electrochemical reaction in a cleaner and more efficient way than conventional processes (eg. gas turbines) [1]. They are characterized by the use of a solid oxide material as the electrolyte. Yttria-stabilised zirconia (YSZ) has traditionally been used in SOFCs electrolytes at temperatures in the range of 850-1000 °C. Recent research is being focused on the development of new materials with increased ionic conductivity at intermediate temperatures (500-800ºC) as alternative materials to YSZ. Rare earth silicates with an apatite-type structure, such as doped lanthanum oxides of general formula $La_{10}(MO_4)_6O_2$, where M = Ge, Co, Si, Al, or P, are among these materials [2]. The major limitation associated with the manufacture of these materials is their poor sinterability, which requires high sintering temperatures (1600ºC).

The present work concerns the production of $La_{9.33}Si_2Ge_4O_{26}$ dense materials from La_2O_3 (99.9%), SiO_2 (99.4%) and GeO_2 (99.9%) powders by mechanical alloying (MA) followed by conventional and microwave hybrid sintering at 1350ºC. Dry mechanical milling was carried out in protective atmosphere (argon at 200 kPa) by using a rotating speed of 350 rpm for 15h. Prior to the synthesis of the $La_{9.33}Si_2Ge_4O_{26}$ mixture, the starting materials were milled separately at 350 rpm in argon at 50 kPa in order to achieve low particle size distributions with a greater ability for sintering. The MA mixture was compacted by uniaxial pressing at 390 MPa followed by sintering for 1 h at 1350 °C. Density of the $La_{9.33}Si_2Ge_4O_{26}$ pellets was determined by the boiling test method. SEM/EDS, XRD and atomic force microscopy (AFM) were used for samples characterization.

The bulk densities and the open porosities of the pellets (EF and MW for conventional and microwave hybrid sintering, respectively) are presented in Table 1. Dense pellets were obtained in both cases. However, sample MW showed higher density and, consequently, lower porosity than sample EF. Both mechanically alloyed samples are formed by an apatite phase. This phase remains stable during sintering. However, traces of a second phase (La_4GeO_8) were detected after sintering. This phase was already referred in previous work [3]. Figure 1 shows the morphology of the two samples obtained by SEM and AFM as well as the corresponding particles size distributions. The sintered samples were as-polished and thermal etched in air at 1300 ºC, for 10 min., for detailed microstructural observation. SEM images at low amplification confirm that sample EF is more porous than sample MW (Figure 1 (a) and (b), respectively). Although the same sintering temperature was used in both sintering processes, sample MW has a coarser grain size (Figure 1 (c) to (f)). This feature was already been reported in previous work [4]. Mean values of 0.9 and 1.9 μm were determined for samples EF and MW, respectively.

As conclusion, one may say that microwave hybrid sintering is a novel suitable process for the densification of $La_{9.33}Si_2Ge_4O_{26}$ powders for application in SOFCs electrolytes.

References

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Table 1. Density and open porosity of the sintered samples.

Sample identification	T. sintering (º C)	Sintering density ($g.cm^{-3}$)	Open Porosity (%)
EF	1350	5.13	6.15
MW	1350	5.36	1.11

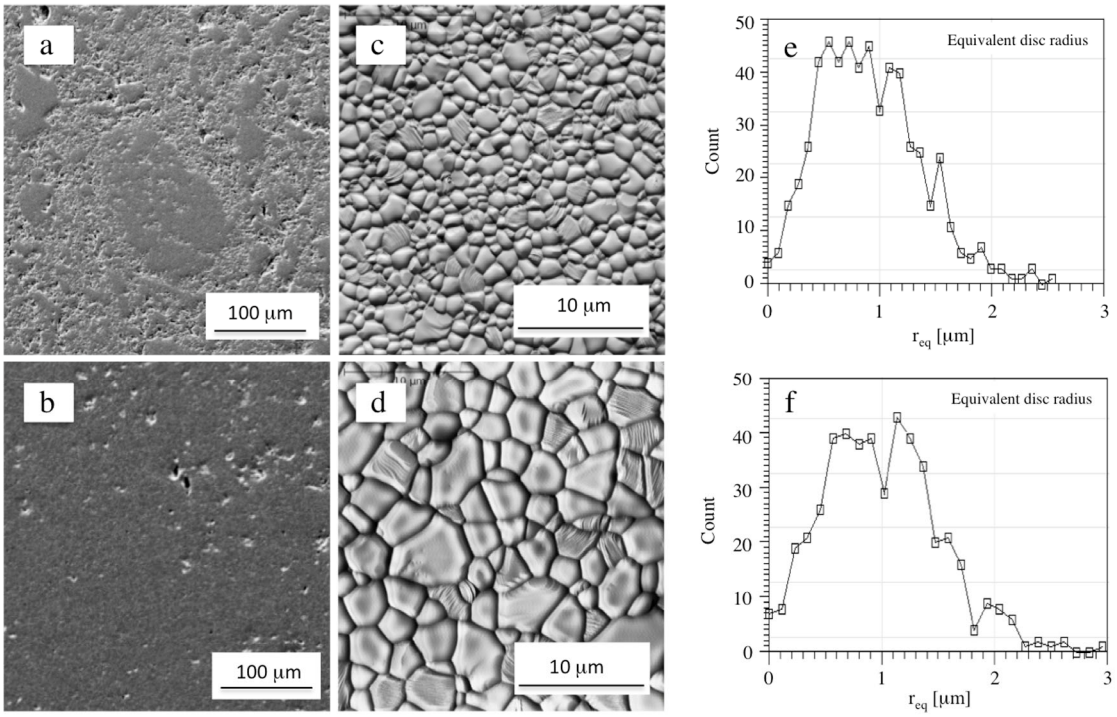

Figure 1. SEM ((a) and (b)) and AFM ((c) and (d)) images of the sintered pellets ((a) and (c) concern EF sample and (b) and (d) to MW sample). (e) and (f) correspond to the grain size analysis of samples EF and MW, respectively.

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