Effect of milling process on the density, microstructure and electrical properties of $Ca_{0.9}Yb_{0.1}MnO_3$ thermoelectric ceramics

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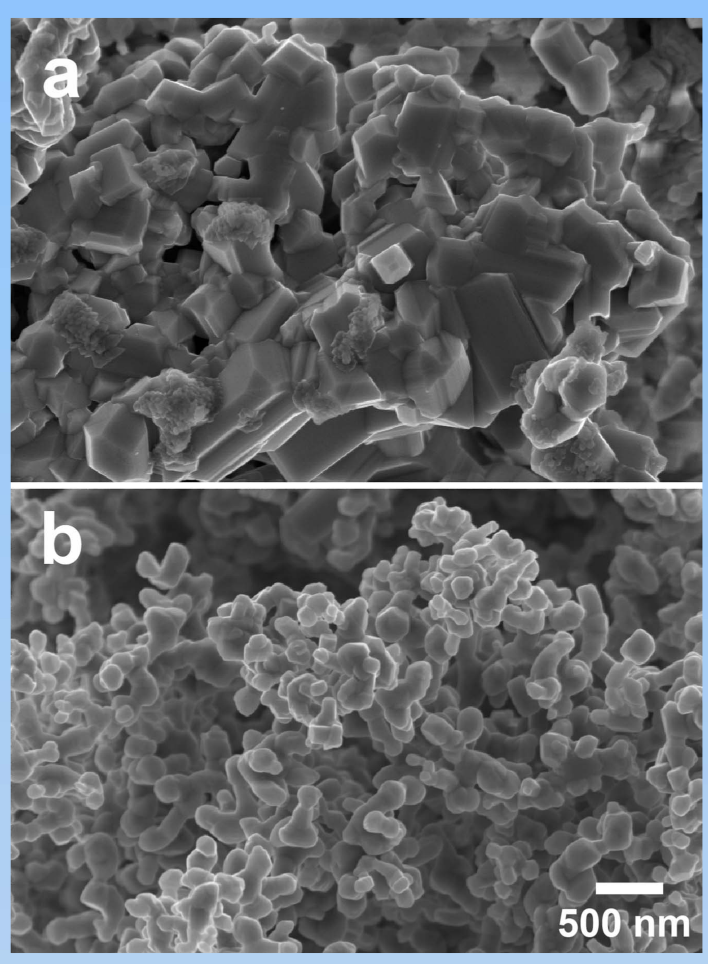
Objectives

Thermoelectric modules are composed of several materials (structural ceramic, metallic conductors, and p- and n-type thermoelements). Among these thermoelements, p-type ones typically possess higher thermoelectric performances than n-type ones, evaluated through the dimensionless figure of merit, ZT, ($=S^2T/\rho\kappa$, where S is Seebeck coefficient, T absolute temperature, ρ electrical resistivity, and κ thermal conductivity). However, sometimes it is also used the power factor, PF ($=S^2/\rho$).

In this work, it will be studied the influence of the milling process on the structure and microstructure of sintered samples, evaluating the effect on the parameters defining the PF.

Methodology

$CaCO_3$, Yb_2O_3, and Mn_2O_3 raw materials were used to prepare $Ca_{0.9}Yb_{0.1}MnO_3$ samples using two different milling processes, ball milling and attrition milling. In both cases, precursors were weighed, mixed and milled for 3h at 300 and 600rpm, respectively, in water media. The mixtures were dried under IR radiation and calcined at 900ºC for 12h (two times for the ball milled precursors) to decompose the carbonates, and manually milled. Finally, the powders were cold uniaxially pressed in form of pellets, sintered at 1300ºC for 1.5 and 12h, and characterized.



FESEM micrographs of precursor powders after the thermal treatments for:
a) Ball milling
b) Attrition milling
showing the much lower particle sizes in attrition milled precursors.

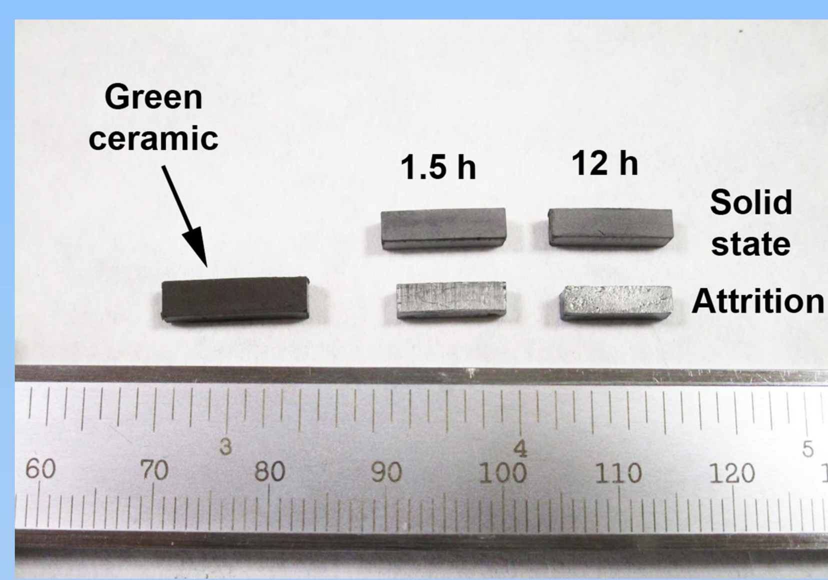
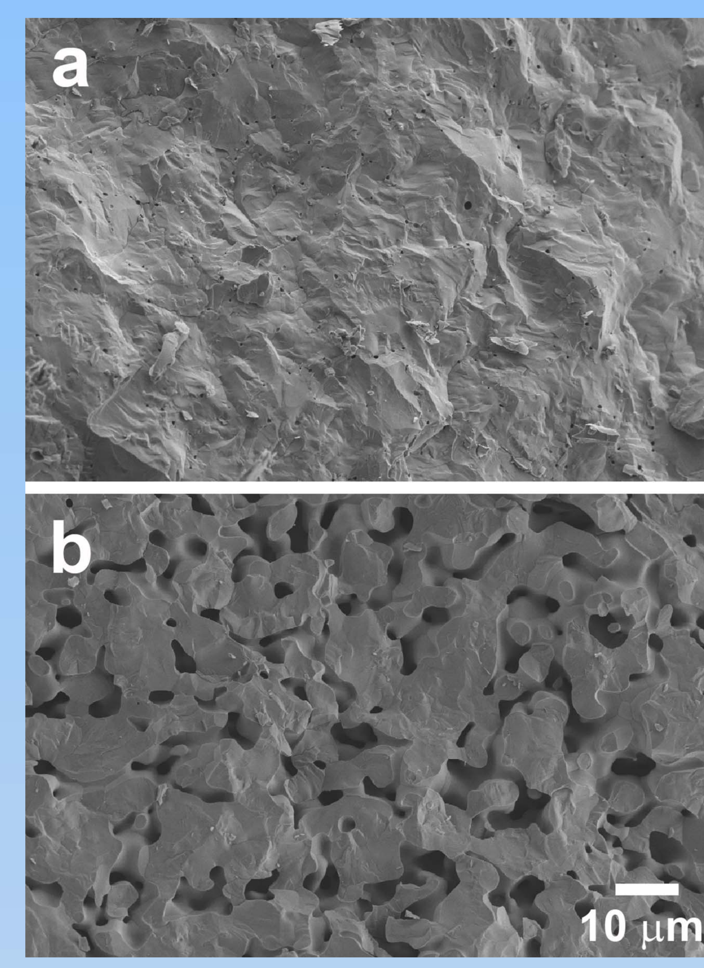
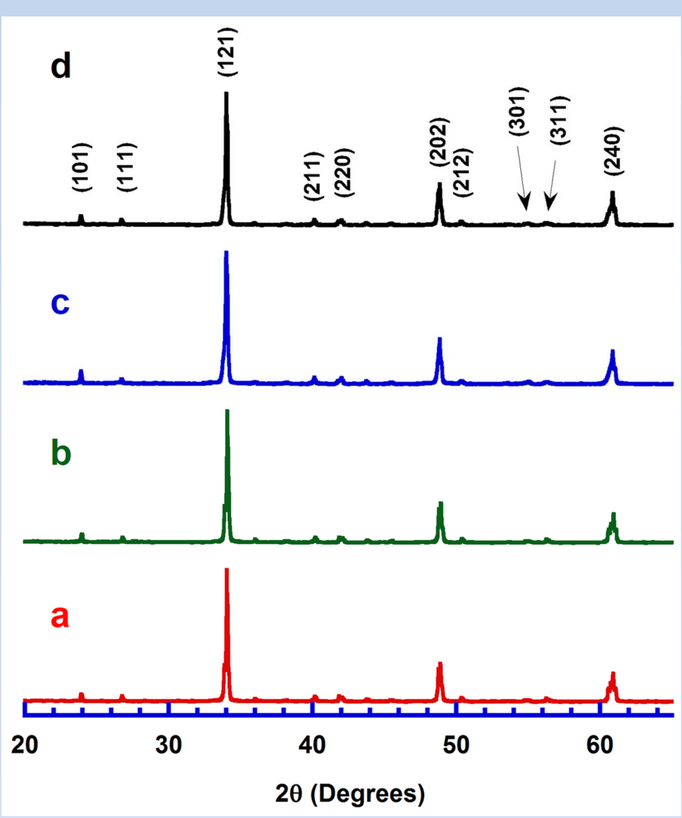


Image of pellets in the different steps as a function of milling procedure and sintering time.
Densification is higher in samples produced by attrition milling due to their smaller starting particle sizes.
These results have been confirmed through Archimedes' method.

Precursor	Sintering time (h)	Density (g/cm³)	Standard error
Attrition milled	1.5	4.62	0.02
Attrition milled	12	4.67	0.03
Ball milled	1.5	3.28	0.04
Ball milled	12	4.12	0.20



FESEM micrographs of fractured surfaces of sintered specimens for:
a) 1.5h (attrition milled precursors)
b) 12h (ball milled precursors)
illustrating the higher densification in samples from attrition milled precursors.

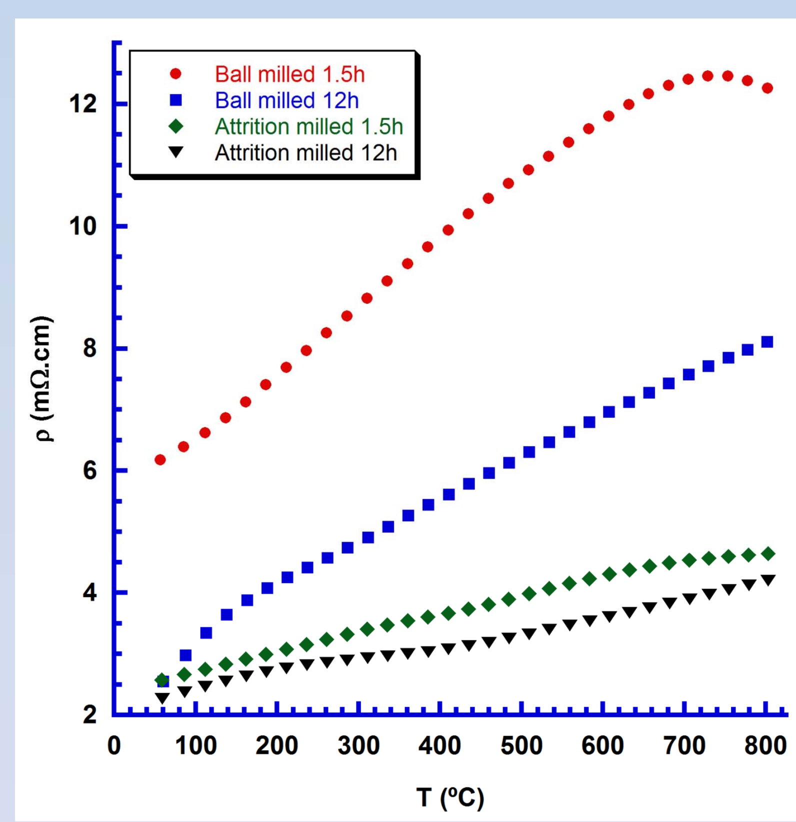


Powder XRD patterns of $Ca_{0.9}Yb_{0.1}MnO_3$ produced from:
a) and b) attrition milled precursors; and c) and d) ball milled precursors; sintered at 1300ºC for:
a) and c) 1.5h; and b) and d) 12h.

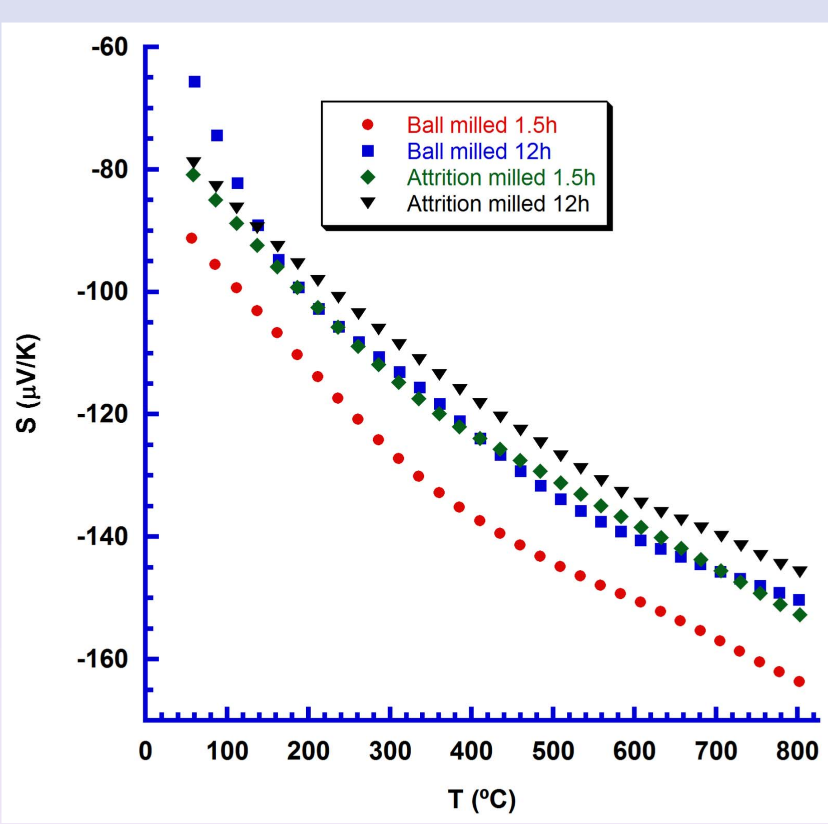
Diffraction planes show the peaks associated to the thermoelectric phase, and no secondary phases have been identified.

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

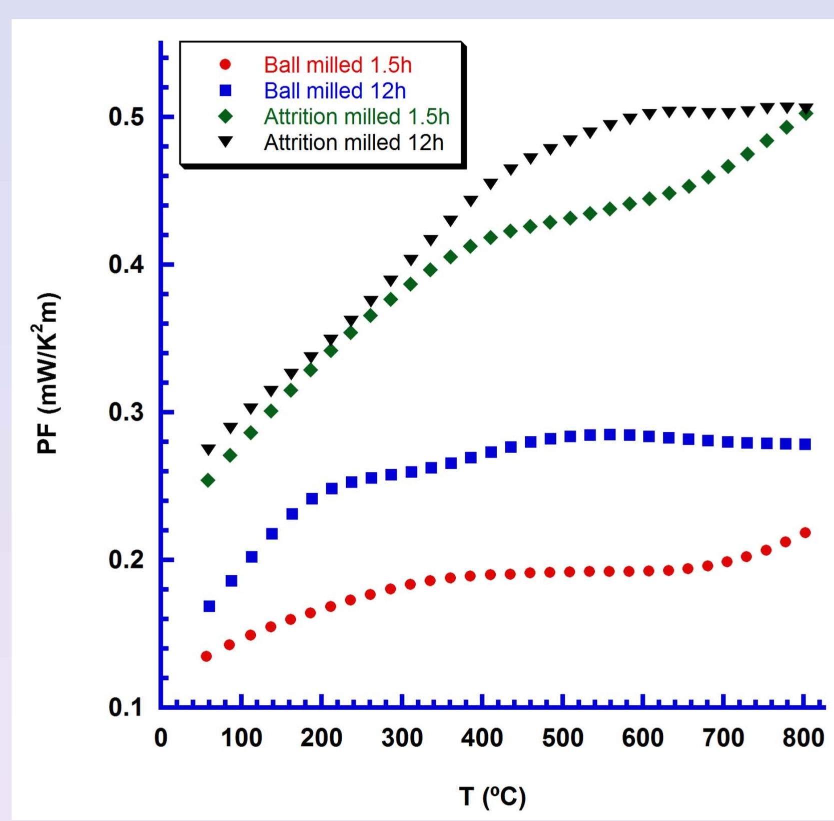
Vickers microhardness for all sintered samples.
The high porosity of samples prepared from ball milled precursors drastically decreases their hardness.



Electrical resistivity for the different samples.
It is drastically decreased with sintering time for ball milled precursors. Moreover, attrition milled ones further decrease it even at short sintering times.
The lowest ρ at 800ºC (4.2mΩ cm) is lower than the reported for SPS samples with the same composition (8mΩ cm)[1]



Seebeck coefficient is negative for all samples ➔ Charge carriers are electrons.
Absolute S is higher for the samples produced from ball milled precursors and sintered at 1300ºC for 1.5h due to their lower charge carrier mobility (reflected in their higher electrical resistivity).
The highest absolute S at 800ºC (-160μV/K) is higher than the reported for SPS samples with the same composition (-145μV/K)[1]



Power factor for the different samples. It is increased with the sintering time, especially for the ball milled samples.
It is dramatically raised for samples produced from attrition milled precursors.
The highest PF at 800ºC (0.50 mW/K²m) is higher than the reported for samples with the same composition classically sintered or SPS processed, 0.22-0.25[2,3], and 0.26 mW/K²m[1], respectively.

Conclusions

- Attrition milling ➔ Small particle size ➔ high density sintered bodies.
- Higher hardness and lower resistivity than ball milled precursors. Negligible S variation.
- Maximum PF higher than the reported in the literature for sintered or SPS prepared samples.

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References

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