Improvement of thermoelectric properties of Ca$_{0.9}$Gd$_{0.1}$MnO$_3$ by powder engineering through K$_2$CO$_3$ additions

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Abstract

Oxide materials based on calcium manganite show clear prospects as thermoelectrics, provided by their stability at high temperatures and inherent flexibility in tuning the relevant electrical and thermal transport properties. Donor-doped CaMnO$_3$ is an n-type semiconductor with a perovskite structure and relatively high thermoelectric performance. In this work, the precursor powders have been modified through potassium carbonate additions to produce Ca$_{0.9}$Gd$_{0.1}$MnO$_3$ pellets without the usual delamination problems occurring during the compaction process. In order to demonstrate the relevant effects, several samples with different amounts of potassium carbonate (0-15wt.%) have been prepared. The results showed that potassium additions significantly facilitate the compaction procedure, while also improving the thermoelectric performances. The results also highlight the importance of porosity control for improving ZT, by decreasing the thermal conductivity without reduction of the electrical performance. The highest ZT values were observed for the samples processed at 15wt.% of potassium carbonate addition, exhibiting an improvement at least 30% at 800ºC when compared to the pure samples.

Keywords

Oxide Thermoelectric; powder engineering; Calcium Manganite; thermoelectric performance; porosity
**Introduction**

Thermoelectric (TE) materials are gaining interest due to their intrinsic advantages to increase energy transforming systems efficiency, by harvesting wasted heat into useful electric power. Among the different TE materials, oxides are among the most promising, due to their high thermal and chemical stability when working under air, and are effective at high temperatures [1]. One of the most promising compounds is CaMnO₃, an $n$-type semiconductor oxide with perovskite structure [2]. On the other hand, this compound possesses limited TE performances due to its low carrier concentration. Consequently, many studies have been carried out in order to improve its thermoelectric properties using dopants [1,3]. These studies are essentially focused on the improvement of the electrical conductivity, without affecting the Seebeck coefficient or thermal conductivity [2]. The addition of dopants has already proved to increase the electrical conductivity and simultaneously reduce the thermal conductivity [4,5].

It is known that preparation routes present a significant impact on the thermoelectric performance. Microstructural tuning is quite effective for decreasing the electrical resistivity and thermal conductivity, while increasing, or maintaining practically constant, Seebeck coefficient [6]. Consequently, in ceramic materials good and clean grain connections should be obtained to avoid adverse effects on the carrier mobility, improving the electrical conductivity without drastically modifying the thermal conductivity. Moreover, porosity control in the bulk material can help to tailor the thermal conductivity values. The formation of strong grain boundaries in relatively low density materials has already been successfully achieved in several ceramic materials [7].

On the other hand, to the best of our knowledge, the literature lacks the details about pressing procedures and associated problems. Based on our experience, obtaining green compacts from these powders and, in particular, manganites, is not a trivial task. In order to improve the compacts quality various approaches have been used, including low compaction pressures, leading, however, to low-density sintered bodies [8]; adding binders, which should be eliminated before sintering [9]; or using more complex procedures [8,10].

Present study focuses on the modification of precursor powders of Ca$_{0.9}$Gd$_{0.1}$MnO$_3$ thermoelectric ceramics, aiming to facilitate the production of the green compacts while avoiding the previously mentioned drawbacks. Further changes should proceed during the calcining step in order to avoid any adverse effects during the sintering procedure.
Taking into account the typical calcining temperature in this family (900 °C) [8,10], K$_2$CO$_3$ is a good candidate as it melts below 900°C [11]. Moreover, previous studies in cobaltites thermoelectric have shown that K$_2$CO$_3$ vanishes at 900 °C even during sintering of compact pellets, having no detrimental effect on the thermoelectric performances [12]. Herein, a very facile and scalable sintering method for producing highly-performing thermoelectric ceramics with controlled porosity has been developed [12] through the addition of different amounts of K$_2$CO$_3$ to the initial powders mixture. In the present work, somewhat similar approach was implemented for manganite-based ceramics. The corresponding microstructural evolution is linked to the thermoelectric performance.

**Experimental**

Ca$_{0.9}$Gd$_{0.1}$MnO$_3$ + x wt.% K$_2$CO$_3$ samples (x= 0, 5, 10, and 15) were prepared using CaCO$_3$ (Panreac, 99,5%), MnO (Panreac, 99%), Gd$_2$O$_3$ (Aldrich, 99.9 %), and K$_2$CO$_3$ (Panreac, 99%) commercial powders. They were weighed in stoichiometric proportions, and ball milled in aqueous media for 30 min at 300 rpm. The resulting suspension was dried using a rapid infrared evaporation system described elsewhere [12]. Some part of the powders obtained after water evaporation was kept for further characterization. The other part was calcined at 900 °C for 12h, to decompose the carbonates (CaCO$_3$ and K$_2$CO$_3$), as reported in previous works [12,13]. After grinding in the mortar, these powders were uniaxially cold pressed at 400 MPa in form of pellets (3 x 3 x 14 mm$^3$) which were then sintered at 1300°C for 24h, with a final furnace cooling. It is worth to mention that the pellets with at least 10 wt.% K$_2$CO$_3$ content have been easily obtained, while for lower additions PVA (PolyVinyl Alcohol) has to be added as a binder to facilitate the compaction. Otherwise the delamination was observed, as illustrated in Fig. 1.

Powder X-ray diffraction (XRD) analysis was performed between 10 and 70 ° from room temperature until 1200 °C, using a Panalytical X’pert PRO3 (CuK$_\alpha$1 radiation) with a temperature chamber from Anton Paar, on the dry powders after milling procedure to evaluate the relevant effects of potassium carbonate addition. The carbonate decomposition has been studied by FTIR analysis using a Bruker IFS 28 Spectrometer, on calcined powders. Moreover, particle size distribution has also been performed on these powders using a laser beam diffraction method, with a Coulter LS230 equipment at room temperature. This technique is based on the Fraunhoffer
diffraction principle, which allows evaluating the particle size as a function of a laser beam diffraction angle when it crosses a set of particles.

Phase identification of the sintered materials was performed by powder XRD at room temperature, using the similar experimental procedure as described above.

Figure 1 – Photograph showing the delamination of bars after pressing the powders without additions.

Microstructural studies were performed in a FESEM (Zeiss Merlin) on calcined powders to observe the grains evolution with the K₂CO₃ content. Moreover, longitudinal polished sections of samples were studied in a SEM (Su-70, Hitachi) equipped with an energy dispersive spectrometry (EDS) system (Bruker) in order to determine the phases content and distribution. Apparent density was measured on bulk sintered samples, using Archimedes method at room temperature.

Electrical resistivity and Seebeck coefficient were simultaneously measured on sintered samples, using the steady state mode, by the standard DC four-probe technique in a LSR-3 apparatus (Linseis GmbH) between 50 and 800 °C under He atmosphere. Thermal conductivity measurements were performed at room temperature, using a transient plane source technique (Hot Disk TPS 2500 s). This method involves an electrically conducting element, acting both as a temperature sensor and heat source, insulated with two thin layers of Kapton (70 μm). The transient plane source element is sandwiched between two similar samples, with both faces being in contact with the samples surfaces.

Finally, figure of merit (ZT) was calculated, using electrical resistivity, Seebeck coefficient, and thermal conductivity data. It should be noticed that the thermal conductivity value, measured at room temperature, was used for ZT estimation at higher temperatures, assuming the thermal conductivity constant, independently of the temperature [12]. This rough assumption leads to clear underestimation of the real ZT values, as the thermal conductivity of manganites is decreasing when the temperature is raised [14,15], but in the present work it was used for comparison purposes.
Results & discussion

The results of SEM analysis of the powders after calcination clearly illustrate the effect of potassium carbonate additions on the Ca$_{0.9}$Gd$_{0.1}$MnO$_3$ microstructure, as shown in Fig. 2. K$_2$CO$_3$ promotes a significant coalescence of the particles up to 10 wt.%, leading to large particles agglomerates with individual sizes larger than 500 nm. On the other hand, higher K$_2$CO$_3$ content increases the agglomerates sizes, as well as the size of the individual particles.

![SEM micrographs](image)

Figure 2 – SEM micrographs of the powders with various K$_2$CO$_3$ addition content after calcination at 900 ºC for 12h.

Particle size analysis, presented in Figure 3 has shown that the samples containing 10 wt.% of K$_2$CO$_3$ present the highest mean particle diameter, while samples without additions present the lowest particle diameters. These results clearly indicate the influence of potassium carbonate which promotes the grain growth during the calcination procedure.

In order to determine if carbonates are still present on the samples after calcination, FTIR analysis was performed on all samples and the results are presented in Figure 4. Two strong bands at 1635 and 1415cm$^{-1}$ represent the vibration for the ionized carboxylate symmetric and asymmetric C–O stretching [16,17]. Furthermore, the content of calcium and potassium carbonates increased with K$_2$CO$_3$ load. This effect can be attributed to the fact that the calcination process was performed under static air. Consequently, the CO$_2$ partial pressure on the atmosphere in close contact with the powders is raised, hindering the total carbonate decomposition.
The effect of temperature on the powders evolution has been further evaluated by XRD analysis at different temperatures, and the obtained patterns are presented in Figure 5 for the samples without (0 wt.%) and with 10 wt.% K₂CO₃ addition. As it can be deduced from the diffractograms presented in the figure, both samples evolve differently, illustrating the effect of potassium carbonate addition. K₂CO₃ addition to the
initial powders promotes the formation of CaMnO$_3$ phase at low temperatures (700ºC), confirmed by the absence of this phase in the potassium-free sample. However, after reaching 1200 ºC and cooling down to room temperature, several phases can be detected in all samples due to the short time heating and cooling process, which leads to incomplete reaction. It is worth to mention that these data highlight the phases evolution with temperature, but the amount of the final products after calcining procedure should be different due to the longer time and lower temperature of this process (900 ºC, 12 h).

Figure 5. Powder XRD diffractograms from room temperature to 1200 ºC for samples with a) 0 wt% and b) 10 wt.% K$_2$CO$_3$ addition.
After the sintering of these calcined powders at 1300 ºC for 12 h, the powder XRD analysis was performed and the results are shown in Figure 6. All samples present as the major phase $\text{Ca}_{0.9}\text{Gd}_{0.1}\text{MnO}_3$ (PDF card: 04-015-8452), with orthorhombic crystalline structure. Moreover, small amounts of $\text{Ca}_2\text{Mn}_2\text{O}_5$ secondary phase (card: 04-010-2534), with orthorhombic structure are also identified.

Similar phase composition was previously reported for the $\text{CaMnO}_3$ system, processed under similar thermal conditions [8]. From the results displayed in these patterns, it can be also observed that the amount of secondary phase is decreasing with potassium carbonate content. This evolution clearly evidence the influence of $\text{K}_2\text{CO}_3$ on the reaction kinetics to produce the thermoelectric perovskite phase, as discussed above (see Fig. 5). This effect can be promoted by the formation of a $\text{K}_2\text{CO}_3$-based liquid phase, which enhances cation mobility and interdiffusion during the thermal treatments [12].

![Figure 6– Powder XRD diffractograms at room temperature for sintered samples with different potassium carbonate additions, ● = CaMnO₃ phase and ● = Ca₂Mn₂O₅ secondary phase.](image)

The potassium carbonate additions also have an impact on the ceramics density, as displayed in Fig. 7. From these results, it is possible to observe that the increase of potassium carbonate amount in the samples first increases the density up to 5 wt.%, while decreasing for higher additions. Furthermore, 5 and 10 wt.% $\text{K}_2\text{CO}_3$ -loaded samples present higher density than the sample without addition. This result can be expected if considering previous studies [18], where potassium carbonate has been mixed with copper powder to produce open pore cell structure in the bulk material after sintering. Moreover, porosity volume was increased when potassium carbonate was added, corroborating the results obtained in this work.
Figure 7 – Relative density of samples, as a function of K$_2$CO$_3$ addition, after sintering at 1300 °C for 12h.

Figure 8 shows representative micrographs of the sintered samples surfaces. These images are not conclusive regarding the effect of potassium carbonate additions on the microstructure of sintered samples. This is due to the small density variation between the different samples, as previously discussed. On the other hand, EDS analysis did not reveal the presence of potassium in the samples after sintering, indicating its total loss during this process. Taking into account that FTIR results showed that samples with 10 and 15 wt.% K$_2$CO$_3$ additions still contain a fraction of potassium carbonate after calcination (see Fig. 4), it may indicate that potassium carbonate played an important role in the cations mobility during the sintering procedure.

Figure 8 – Representative SEM micrographs taken at the surfaces of sintered samples with different K$_2$CO$_3$ additions.
Thermal properties of sintered samples at room temperature as a function of K₂CO₃ content are summarized in Table 1, where thermal conductivity (κ), thermal diffusivity (D) and heat capacity (Cₚ) values are presented. The values obtained for the thermal conductivity agree well with those reported for pure and doped CaMnO₃ phase [1,19,20]. Moreover, the thermal conductivity evolution with the K₂CO₃ content is the same observed with the samples density, clearly showing that lower porosity of samples leads to higher κ values, in agreement with previously published results [1]. This effect is because pores act as insulating medium for heat transport, limiting the thermal conductivity in the bulk samples. Thus, the highest density sample possesses the highest diffusivity, leading to the highest κ values [1,18].

### Table 1 - Thermal parameters determined in the different samples at room temperature: thermal conductivity (k), thermal diffusivity (D) and heat capacity (Cp).

| Wt.% K₂CO₃ | K (W/m K) | D (mm²/s) | Cₚ (MJ/(m³ K)) |
|------------|-----------|-----------|-----------------|
| 0          | 0.64      | 0.49      | 1.33            |
| 5          | 1.22      | 0.79      | 1.56            |
| 10         | 0.91      | 0.57      | 1.62            |
| 15         | 0.68      | 0.50      | 1.35            |

In Fig. 9, the electrical resistivity evolution of samples with temperature, as a function of K₂CO₃ content is presented. All samples present metallic behaviour in the whole measured temperature range, in accordance with the literature data [3,6,8,21]. The results suggest that K₂CO₃ addition drastically decreases electrical resistivity values. This behaviour apparently illustrates the effect of a liquid phase (mainly K₂CO₃), leading to low resistivity of the grain boundaries. On the other hand, it also reflects the consequence of a liquid excess, which starts to increase the porosity in the sintered samples, with adverse effects on the electrical properties and density. The lowest values determined in this work at room temperature (~ 4 mΩ.cm) have been observed for 5 wt.% K₂CO₃-loaded samples. These values are lower than those measured in sintered CaMnO₃ (125 mΩ.cm) [22], or in spark plasma sintered (SPS) materials (10 mΩ.cm) [23]. On the other hand they are within the best results observed for doped or co-doped CaMnO₃ (2.3-7.0 mΩ.cm) [4,24-26].
Figure 9 – Electrical resistivity evolution with temperature for sintered samples with different K₂CO₃ additions.

The evolution of Seebeck coefficient (S) with temperature is displayed in Fig. 10. The S values are negative at all temperatures, showing that dominant carriers are electrons in all samples. Furthermore, absolute values are increasing with the temperature, which is the typical behaviour in the manganites family [6,21,27,28]. In addition, all samples display very similar values at the measured temperatures, indicating that Mn likely possesses the same oxidation states in all of them, independently of K₂CO₃ addition. The highest values at room temperature (-80 µV/K) are clearly lower than the determined in pure CaMnO₃ (-350 µV/K) [1], reflecting the higher carrier concentration in the doped materials. On the other hand, they are in the order of those reported in doped or co-doped materials prepared through different techniques (between -70 and -120 µV/K) [4,23-26]. These results indicate that K₂CO₃ addition, besides the porosity and grains connectivity modification discussed above has negligible effect on the thermoelectric phase.

Electrical performances of the samples determined by the power factor (PF=S²/ρ, not shown here) are within those reported in the literature [1,28]. Moreover, the lowest values are obtained in samples without K₂CO₃ additions, while the highest were determined with 5 wt.% additions, in agreement with their lower electrical resistivity.
Finally, Fig. 11 compares the thermoelectric performances of the studied samples, evaluated through their ZT. As previously mentioned in the experimental section, the ZT values at high temperatures can be significantly underestimated, since typically the thermal conductivity of manganites decreases when the temperature is raised [14,15]. Despite of the higher electrical performances of the 5 and 10 wt.% K$_2$CO$_3$ samples, the highest ZT values have been determined in the 15 wt.% samples, due to the lower thermal conductivity. The maximum ZT determined in this work corresponds to ~ 0.12, and 0.17 at room temperature and 800 ºC, respectively. These values are within the range described in the literature for CaMnO$_3$ system [3,27,28].

The obtained results clearly show the benefits of K$_2$CO$_3$ addition to the initial powders, not only by facilitating the compaction of the materials, but also by increasing their thermoelectric performances thought improved grains connectivity and porosity control. This synergy appears very attractive for processing of bulk oxide thermoelectrics, where simultaneous improvement of thermoelectric properties and compaction procedure is achieved by using relatively inexpensive additions. Further efforts might be focused on the application of the proposed approach to other oxide materials with reasonable thermoelectric performance, with more emphasis on the porosity control. Such powder engineering is also expected to be attractive for ceramists focused on other applications, where powder compaction step and control of the electrical performance are crucial.
Conclusions

Ca$_{0.9}$Gd$_{0.1}$MnO$_3$ thermoelectric materials have been prepared through the classical solid state method. It has been found that K$_2$CO$_3$ addition to the precursors mixture promotes compaction without the need of organic binders, which allows to avoid the detrimental effects of organics decomposition during thermal processing. Moreover, K$_2$CO$_3$ produces the formation of a liquid phase, which enhances cation mobility and interdiffusion, reflected in higher densities (up to 10 wt.%) and lower electrical resistivity, compared with the samples without additions. Microstructure and Seebeck coefficient were found to be very similar in all samples, confirming that K$_2$CO$_3$ addition has negligible effect on the thermoelectric phase. On the other hand, in spite of the large increase of thermal conductivity due to the better electrical connectivity of grains, the relatively slight decrease of density in samples with 15 wt.% K$_2$CO$_3$ additions leads to thermal conductivities very similar to those measured in the pure samples. The highest thermoelectric performances have been obtained for the samples containing 15 wt.% of K$_2$CO$_3$ addition, with an improvement of around 30 % at 800 ºC as compared to the pure samples.

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