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Tailoring $Ca_3Co_4O_9$ microstructure and performances using a transient liquid phase sintering additive

A. Sotelo [a], F.M. Costa [b], N.M. Ferreira [b], A. Kovalevsky [c], M.C. Ferro [c], V.S. Amaral [d], J.S. Amaral [d], Sh. Rasekh [a], M.A. Torres [a], M.A. Madre [a,*], J.C. Diez [a]

[a] ICMA (CSIC-Universidad de Zaragoza), C/Maria de Luna 3, 50018 Zaragoza, Spain
[b] i3N, Physics Department, University of Aveiro, Aveiro, 3810-193, Portugal
[c] CICECO—Aveiro Institute of Materials, Department of Materials and Ceramic Engineering, University of Aveiro, 3810-193 Aveiro, Portugal
[d] CICECO—Aveiro Institute of Materials, Physics Department, University of Aveiro, 3810-193 Aveiro, Portugal

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ABSTRACT

A flexible, adaptable, economical and easily scalable processing route, allowing microstructural control, is presented. It involves classical solid state sintering method and addition of liquid promoting compound. Controlled porosity and high thermoelectric performance have been attained in $Ca_3Co_4O_9$ by K_2CO_3 additions, drastically improving the sintering procedure. K_2CO_3 behaves as transient liquid phase, providing microstructural benefits, vanishing during sintering. Electrical resistivity was improved by enhanced grains connectivity and growth. Significant increase in Seebeck coefficient at high temperatures has been produced while lattice thermal conductivity was unaffected. The best ZT value, estimated at 800 °C, assuming the thermal conductivity value at 140 °C, is 0.35 for 5 wt.% K_2CO_3 samples. These values are significantly higher than that obtained in highly-dense textured materials at the same temperature. The results suggest that this approach is very effective for preparing highly-performing $Ca_3Co_4O_9$-based thermoelectric materials with relatively high porosity to control thermal conductivity.

1. Introduction

Since the discovery of promising thermoelectric (TE) properties in $NaCo_2O_4$ ceramics [1], with the ability to operate at high temperatures under air atmosphere without degradation, many works have been focused on this Co-based TE family. Those intense studies resulted in the discovery of new cobalt oxide-based thermoelectrics, which today are an important subject of research [2,3]. The performance of these thermoelectric materials is usually evaluated through the dimensionless figure of merit, ZT ($=S^2T/\rho\kappa$), where S, T, ρ, and κ are Seebeck coefficient, absolute temperature, electrical resistivity, and thermal conductivity, respectively. As bulk materials, these oxides usually demonstrate quite low thermoelectric performance, which make them no feasible for any practical applications. Envisaging the increment of ZT, many processing and structural engineering routes were attempted, including cationic substitution in solid state sintered materials [4,5], or taking advantage of their crystallographic nature to align the grains into a preferential direction using well-known techniques such as templated grain growth (TGG) [6], hot-pressing [7], spark plasma sintering (SPS) [8], laser floating zone (LFZ) [9], or the recently developed electrically assisted laser floating zone (EALFZ) [10]. These texturing techniques have been reported to produce high density bulk materials with well oriented grains, leading to enhanced electrical conductivity.

An important discovery from all these studies is the fact that, indeed, new preparation routes allow a significant increase in the thermoelectric performance, while the coupling between electrical and thermal properties can also be overcome. These methods aim at decreasing the electrical resistivity and thermal conductivity, while increasing, or maintaining practically constant, Seebeck coefficient. Consequently, in these materials good and clean grain connections should be obtained to avoid its hindering effect on carrier mobility, improving the electrical conductivity without drastically modifying S. Moreover, a relatively high porosity to decrease thermal conductivity of the bulk material is also favorable. The formation of strong grain boundaries has been already successfully achieved in several ceramic materials, by the formation of liquid phase, promoted by metallic Ag addition to the bulk material [11,12]. In the case of $Ca_3Co_4O_9$ ceramic materials, it is essential to find an additive compatible with this phase, with a melting point close to the sintering temperature, and which is not reacting with any

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[*] Corresponding author. Fax: +34 976761957.
E-mail address: amadre@unizar.es (M.A. Madre).

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one of the matrix components. In the literature, many examples of these kind of materials can be found as part of the fluxes used to grow $Ca_3Co_4O_9$ single crystals [13,14]. Among these materials, K_2CO_3 possess melting point (899 °C) [15] very close to the optimal $Ca_3Co_4O_9$ materials sintering temperature, as reported in previous works [16]. Furthermore, these studies have shown that K_2CO_3 has not a detrimental effect on the thermoelectric performances of single crystals. Herein, a very facile and scalable sintering method for producing highly-performing and relatively porous $Ca_3Co_4O_9$ thermoelectric ceramics has been developed. The effect of relatively small additions of K_2CO_3, as liquid phase promoter during the sintering process, to the thermoelectric $Ca_3Co_4O_9$ bulk ceramics has been studied in this work. The structural and microstructural features are related with the thermoelectric properties.

2. Experimental

Polycrystalline $Ca_3Co_4O_9$ samples, pure and containing 5 and 10 wt.% K_2CO_3, were prepared by the classical solid state route from $CaCO_3$ (≥99%, Aldrich), Co_3O_4 (99.5%, Panreac), and K_2CO_3 (≥99%, Aldrich) commercial powders. After mixing in stoichiometric proportions, the precursors were milled in aqueous media in an agate ball mill for 30 min at 300 rpm. The resulting suspension was then collected and completely dried using a rapid infrared evaporation system. This adjusted procedure allows very fine distribution of K_2CO_3 particles in the resulting precursor powder after evaporation of the solvent, provided by the high solubility of potassium carbonate in water and rapid drying. The dry powdered mixtures were annealed at 750 and 800 °C for 12 h, with an intermediate manual grinding, to decompose $CaCO_3$, as reported in previous works [17]. The resulting powder was uniaxially compacted at ~400 MPa in form of pellets (around 3 mm × 3 mm × 14 mm), followed by sintering at 900 °C for 24 h. During the sintering step the samples were horizontally placed on an alumina powder bed.

Phases in sintered materials were identified by powder X-ray diffraction (XRD) analysis, using a Rigaku D/max-B X-ray powder diffractometer (CuKα radiation) with 2θ ranging between 10 and 60°. Microstructural observations and comparative analysis of element distribution were performed on longitudinal polished sections of samples in a FESEM (Zeiss Merlin), equipped with an energy dispersive spectrometry (EDS) system (INCA 350, Oxford Instruments). Additional HRTEM (JEOL model JEM-2200FS) studies of the 5 wt.% K_2CO_3 samples were conducted to identify the structural features, with emphasis on possible effects provided by potassium ions. Apparent density was measured using Archimedes' principle for each composition, at least for four ceramic samples, and compared to the theoretical density (4.677 g/cm^3) [18].

Electrical resistivity and Seebeck coefficient were simultaneously measured for all samples, using the steady state mode, by the standard DC four-probe technique in a LSR-3 apparatus (Linseis GmbH) in the range from 50 to 800 °C under He atmosphere. Thermoelectric performance was evaluated and compared through the power factor, as $PF = S^2/\rho$. Thermal conductivity measurements were performed at 25–140 °C, using a transient plane source technique (Hot Disk TPS 2500 s). This method involves an electrically conducting pattern element, acting both as a temperature sensor and heat source, insulated with two thin layers of Kapton (70 μm). The TPS element is sandwiched between two similar samples, with both faces being in contact with the samples surfaces. The measurements were performed using heating power from 7 to 9 W and measurement time from 20 to 80 s. ZT values were calculated at 25–140 °C, based on the data of power factor and thermal conductivity. As the thermal conductivity of $Ca_3Co_4O_9$-based material is known to decrease on heating [19,20], with relatively weak temperature dependence at $T > 200–300$ °C, the ZT values have been estimated at higher temperatures and compared to the best up-to-date literature data.

3. Results and discussion

A simplified sketch of the expected sintering mechanism is given in Fig. 1. Heating of the prepared compacts up to 900 °C is accompanied by the formation of liquid K_2CO_3 phase, coexisting with solid calcium cobaltite grains. Classical mechanism of the liquid phase sintering involves wetting of the solid phase, penetration of the liquid into the pores, driven by an interplay between capillary forces, viscosity and gravity, rearrangement of the grains to closer packing and progressive annihilation of pores [21], resulting in the material densification and rigid bonding between the grains. Partial solution of the matrix material in the melt and softening of the solid phase, provided by appropriate treatment conditions, can further assist the densification. In classical approach, on cooling the liquid solidifies to form a composite microstructure with tailored properties.

An interesting feature of the prepared materials refers to the chemical composition at the microscale level. According to the results of detailed SEM/EDS studies performed on sintered fractured and polished ceramics, the potassium concentration, both at the grain boundaries and in intragranular space, was below the detection limit of the equipment, roughly 0.1% mass concentration. Although, one should not completely exclude possible presence of potassium impurities, additional TEM imaging confirms compositional homogeneity of the samples. A representative TEM micrograph, showing typical grain boundaries and corresponding EDS mapping results, are presented in Fig. 2. The nominal composition of this sample corresponds to 5 wt.% of K_2CO_3, which is fairly above the EDS detection limit for potassium cations.

Among the factors which facilitate vanishing of the liquid phase, at least, it can be considered partial volatilization of K_2CO_3 under sintering conditions. The literature data suggest significant weight losses for K_2CO_3 even below melting point, mainly provided by decomposition reaction and partially due to congruent sublimation process [22]. Potassium oxide, as a product of decomposition, could easily react with moisture traces to produce KOH. Moreover, under discussed sintering conditions, potassium carbonate itself can undergo the hydrolysis reaction. In general, volatilization of the molten K_2CO_3 is known as one the factors that limit the performance of molten carbonate fuel cells (MCFC), even operating at lower temperatures [23]. The carbonate losses in this case are further facilitated by the presence of water traces, due to the formation of alkali hydroxides, which have a vapor pressure of about an order of magnitude higher than the corresponding carbonates.

On the other hand, as sintered materials still possess a noticeable level of porosity as will be discussed below, the melt can be also forced to flow downwards against the capillary forces under the gravity effect, and infiltrate into the alumina powder bed, used as a support. This might also contribute as a plausible explanation for the transient behavior of the liquid phase during sintering. In order to verify this hypothesis, the alumina bed where a bar-shaped sample was sintered in a horizontal position is presented in Fig. 3. Three visually distinct regions, including the one beneath the sample (right side of Fig. 3, indicated by #1), were further analysed by EDS. The results, presented in Table 1, clearly confirm presence of potassium in the alumina bed, with decreasing concentration when the distance from the sample position is raised. At the same time, no signs of calcium and/or cobalt diffusion into the alumina bed were observed. It should be highlighted that prevailing mechanism for potassium depletion might still be based on the volatilization losses, as it can also result in the enrichment of the alumina bed with potassium.