High temperature stability of hot-pressed Sr-doped $\text{Ca}_3\text{Co}_4\text{O}_9$ samples

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Abstract

$\text{Ca}_{2.93}\text{Sr}_{0.07}\text{Co}_4\text{O}_9$ bulk textured samples have been successfully prepared by hot uniaxial pressing, followed by a thermal treatment at 800°C under air between 0 and 1532 h. The microstructural, thermoelectric and mechanical properties as well as density of all the samples were evaluated as a function of the thermal treatment length. Scanning electron microscope characterization has shown that samples are mainly composed by Sr-doped $\text{Ca}_3\text{Co}_4\text{O}_9$ thermoelectric (TE) phase, accompanied by minor amounts of Sr-free $\text{Ca}_3\text{Co}_2\text{O}_6$ secondary phase. After an initial decrease of density after the first aging treatment, it remains practically constant for longer times. This behaviour is reflected in the mechanical properties, which slightly decrease after 12 h thermal treatment, when compared with the as-hot pressed ones, and remain practically constant for larger times. However, TE properties are not affected by the aging process, and are within the typical errors, independently of the aging time. Moreover, power factor values at 850°C are between the highest obtained so far in this kind of materials ($> 0.60\text{mW/K}^2\text{m}$)

Keywords: thermoelectricity; cobalt oxide; power factor; flexural strength;
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INTRODUCTION

Global energy consumption, 13.8 billion tons of oil equivalents (toe) in 2015, is increasing about 1.7% per year [1,2], being more than 80% provided by fossil fuels. Consequently, CO₂ is continuously increasing in the Earth's atmosphere leading to global warming. In the way to green fuels-based new economy (mainly solar and wind energy [3]), these emissions can be reduced by increasing the energy conversion systems efficiency. Thermoelectric (TE) materials can help in this task generating electric power from wasted heat, usually evaluated through their figure-of-merit ZT , defined as $ZT = (S^2 T)/(\rho \kappa)$, where S is Seebeck coefficient; T , absolute temperature; ρ , electrical resistivity; and, κ thermal conductivity [4].

At present, intermetallic bulk materials as Bi₂Te₃ or CoSb₃ [5] show high ZT values and are used in commercial devices. However, these conventional intermetallic materials are not only based on scarce and heavy metals, but also show working temperature limitations. The discovery of attractive TE characteristics in Na₂Co₂O₄ ceramic [6], based on abundant elements and with no heavy metals, allowed higher working temperature. Moreover, in spite of their lower performances, great efforts have been made in the study of CoO-based materials, such as Ca-Co-O, Bi-Sr-Co-O, Bi-Ca-Co-O, or Bi-Ba-Co-O, with attractive TE properties [7-14]. Ca₃Co₄O₉ crystal structure is formed by two layers, CdI₂-type CoO₂ and rock-salt-type (RS), with common a - and c -axis lattice parameters and β angles but different b -axis length, causing a misfit along the b -direction [15]. This general structure has direct effects on the electric properties of these materials; it is well known that isovalent substitutions in the RS layer can modify ρ , and S by changing its lattice parameters [8,16].

Moreover, Co oxidation state in the conducting layer also plays a crucial role on the electric performances of $\text{Ca}_3\text{Co}_4\text{O}_9$ materials, and can be modified through aliovalent substitutions or the atmosphere during sintering [17-20]. Finally, due to the $\text{Ca}_3\text{Co}_4\text{O}_9$ anisotropy, the alignment of grains along their conducting planes can also enhance TE properties, with techniques as spark plasma sintering [21], or hot-pressing [22,23].

In future practical applications, thermoelectric modules built using these CoO-based materials should support hard service conditions, mainly characterized by high temperatures under air. Accordingly, it is required to acquire a better knowledge about their thermal stability under this atmosphere. In this work, the microstructural, thermoelectric and mechanical evolution of textured Sr-doped $\text{Ca}_3\text{Co}_4\text{O}_9$ samples, produced through uniaxial hot-pressing technique, has been studied as a function of the thermal treatment length at 850°C under air (between 0 and 1532 h).

EXPERIMENTAL

Based on previous results of Sr-doped $\text{Ca}_3\text{Co}_4\text{O}_9$ sintered materials [8], the initial $\text{Ca}_{2.93}\text{Sr}_{0.07}\text{Co}_4\text{O}_9$ stoichiometry has been prepared through the standard ceramic route. As precursors, CaCO_3 ($\geq 99\%$, Aldrich), SrCO_3 ($\geq 98\%$, Aldrich), and CoO (99.99%, Aldrich) commercial powders were employed. After weighing in the appropriate amounts, they were mixed and milled for 30 min in water medium using an agate ball mill. The slurry was then quickly dried using infrared radiation, followed by manually-grinding in an agate mortar. The mixture was subjected to two subsequent thermal treatments: 12 h at 750°C and 12 h at 800°C under air atmosphere, with an intermediate manual milling. The main objective of these thermal treatments is the decomposition of CaCO_3

and SrCO_3 . The calcined powders were cold uniaxially pressed at 250 MPa in form of discs (25 mm diameter and ~ 4 mm thick), which were hot uniaxially pressed in the optimal conditions experimentally determined, 850 °C and 30 MPa for 14 h under air. After this process, the hot-pressed discs (~ 28 mm diameter and ~ 3 mm thick) were cut with a diamond saw into small pieces ($\sim 2 \times 2 \times 15 \text{ mm}^3$) for their posterior survey. For this study, 5 discs have been prepared, producing 65 samples after cutting. All these samples have been mixed and 10 samples were used for each condition of the aging thermal treatment at 850°C under air for 0, 24, 96, 384 and 1536h.

Microstructural evolution was carried out on polished longitudinal surfaces and transversal fractures of all samples using a Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss Merlin), while the phases were analyzed with an energy dispersive spectrometer (EDS) system.

Density values have been determined through the Archimedes' method (9 samples for each condition), taking 4.677 g/cm^3 as the theoretical one [15]. Mechanical properties of samples were evaluated using the three point bending test in an Instron 5565 machine with a 10mm loading span fixture and a $30 \mu\text{m/min}$ punch displacement speed. Flexural strength was computed from the maximum load, according to the strength of materials theory for an elastic beam of rectangular section. Due to the brittle nature of these polycrystalline ceramics, at least five samples for each condition were tested to obtain accurate values.

Electrical resistivity and Seebeck coefficient were simultaneously measured in a LSR-3 system (Linseis GmbH) by the four-probe DC technique in the steady state mode between 50 and 800°C, by heating, under He atmosphere. With

these data, power factor (PF) defined as $PF = S^2/\rho$, where S is the Seebeck coefficient and ρ the electrical resistivity, of all samples was calculated to determine the temporal evolution of their thermoelectric performances at high temperature.

RESULTS AND DISCUSSION

Representative SEM micrographs, performed on longitudinal polished sections, are displayed in Figs. 1a, and b. They show two different contrasts, the major one in all samples (light grey contrast, #1) has been identified by EDS as the Sr-doped $\text{Ca}_3\text{Co}_4\text{O}_9$ TE phase, while minor one (dark grey contrast, #2) is the $\text{Ca}_3\text{Co}_2\text{O}_6$ secondary phase, in agreement with CaO-CoO phase diagram [24]. The presence of this phase, despite the stoichiometric proportion of elements, is due to the fact that $\text{Ca}_3\text{Co}_4\text{O}_9$ phase formation requires oxygen absorption and its diffusion is hindered by the hot pressing process. In this processing step, the largest samples surfaces are shielded from the atmosphere by the press pistons, drastically decreasing the oxygen diffusion. Moreover, it is important to note that no Sr has been detected in this secondary phase, within the EDS detection limit, indicating that all Sr is incorporated in the TE phase substituting Ca. Consequently, due to the stoichiometric proportions of Ca and Co used as starting composition, some cobalt oxide should remain unreacted in these samples, even if it has not been found in our microscopical analysis. Furthermore, samples should possess a relatively high density, as only a small amount of porosity is possible to distinguish, mainly produced by the polishing process. On the other hand, when observing Figs. 1c, and d, where representative transversal fractures of samples are shown, it is clear that all

possess a good grain orientation, with their *ab*-planes tending to align perpendicularly to the pressing direction. Furthermore, besides a slight grain growth with time, no significant differences can be observed among them.

Density measurements shown in Table I have confirmed the low porosity observed in the micrographs previously discussed. From these data, it seems evident that besides a slight decrease of density after the first thermal treatment, density remains practically constant, independently of the thermal treatment duration. This evolution can be due to absorption of oxygen in the grain boundaries. Moreover, remaining stresses in the samples after the hot-pressing procedure can be released during the heat treatments, leading to stress-free samples.

In order to evaluate the mechanical behaviour evolution of the samples, three point flexural strength tests were performed in all samples. The mean values, together with their standard errors are presented in Fig. 2, as a function of time. Mechanical strength suddenly decreases from ~ 300 MPa (mean strength for the samples after hot-pressing process) to a constant value of ~ 250 MPa for all the aged samples. This value seems to be independent of the aging treatment duration in the whole time range studied (1536 h). Consequently, this fact corroborates the previous results indicating that negligible microstructural evolution was produced in the samples. As a result, it confirms the assumption of temperature-driven stress release after the hot-pressing process. Anyway, the lowest mean strength value found in this work for the aged samples is high enough to ensure proper mechanical integrity in typical thermoelectric applications. Moreover, these values are much higher than the obtained in conventionally sintered samples (20-40 MPa) [25,26], mainly associated to the

larger density of hot-pressed samples. On the other hand, they are in the range of the spark plasma sintered (SPS) specimens (200-285 MPa) [27], due to their similar density values. Therefore, mechanical properties are within the highest values reported in the literature.

Fig. 3a presents the electrical resistivity evolution with temperature for all samples. From the data presented in the graph, it is easy to deduce that all samples display very similar values and present semiconducting-like behaviour ($dp/dT < 0$) in the whole measured temperature range. Moreover, the slight differences found between the samples are inside the typical error in this kind of measurements $\pm 8\%$ [27]. This asseveration is confirmed with Fig. 3b, where the mean electrical resistivity values at room temperature (RT, dots) and 800°C (squares) are presented (with $\pm 8\%$ error bars) as a function of the aging treatment duration. The black horizontal lines represent the total mean value obtained from all the samples, clearly showing that all the measured values are between $\pm 8\%$ error. The mean RT values obtained in this work (8.6 mΩ.cm) are lower than the reported for sintered specimens (15-30 mΩ.cm) [26,28], or prepared through alternative methods (11-15 mΩ.cm) [29,30], due to the higher density and grain orientation of samples. On the other hand, they are comparable to the reported in SPS materials (7-8 mΩ.cm) [26,31,32], due to the similar characteristics of both types of samples. When comparing the mean high-temperature values determined in this work (5.9 mΩ.cm) with literature, the same behavior described at RT is found. These results, clearly evidence that the materials prepared in this work possess well oriented grains and good electrical connectivity between them, independently of the aging time.

The evolution of Seebeck coefficient as a function of the temperature for all the samples is shown in Fig. 4a. The S values are positive in the whole measured temperature range, in agreement with a predominant hole conduction mechanism. Moreover, all samples show very similar values, with nearly lineal dependence with temperature, in agreement with previously published data [28]. On the other hand, the slight differences between the samples are in the typical uncertainty for this kind of measurements $\pm 6\%$ [27]. This fact can be easily seen in Fig. 4b, where the mean Seebeck at RT (dots) and 800°C (squares) are presented (with $\pm 6\%$ error bars) for each aging time. The black horizontal lines show the total mean Seebeck coefficient, showing that all measurements are within the $\pm 6\%$ error. When comparing these mean S values at RT and 800°C (149 and 192 $\mu\text{V/K}$, respectively), they are in the order of the reported for sintered, prepared through alternative methods or SPS (125-150, and 155-230 $\mu\text{V/K}$, respectively) [26,28-32].

PF evolution as a function of temperature, calculated from the electrical resistivity and Seebeck coefficient, is displayed in Fig. 5a. All the samples show very similar behaviour (PF is increasing with temperature) and values. The small variations between the data are well inside the typical uncertainty for this kind of measurements (14%) [27]. This fact is emphasized in Fig. 5b, where the mean PF at RT (dots) and 800°C (squares) are presented (with $\pm 14\%$ error bars) for each aging time. The black horizontal lines show the total mean PF , illustrating that all measurements are within the $\pm 14\%$ error. The maximum PF values at 800°C ($> 0.6 \text{ mW/K}^2\text{m}$) are much higher than the best reported in textured materials prepared by SPS (0.45 $\text{mW/K}^2\text{m}$) [31], or by alternative methods (0.44 $\text{mW/K}^2\text{m}$) [30].

All these results indicate that hot forging textured $\text{Ca}_{2.93}\text{Sr}_{0.07}\text{Co}_4\text{O}_9$ materials are good bulk ceramic candidates for applications in thermoelectric generators working at high temperatures under air for long periods of time.

4. Conclusions

High density and well textured $\text{Ca}_{2.93}\text{Sr}_{0.07}\text{Co}_4\text{O}_9$ bulk samples were successfully prepared by a hot-pressing method, using pre-reacted solid state powders as starting material. SEM characterization has shown that samples are mainly composed by Sr-doped $\text{Ca}_3\text{Co}_4\text{O}_9$ TE phase, accompanied by minor amounts of Sr-free $\text{Ca}_3\text{Co}_2\text{O}_6$ secondary phase. Density values decrease with the first aging thermal treatment, being practically constant for larger times. This behavior is reflected in the mechanical properties of aged samples, which are slightly lower than the obtained after hot-pressing but they are maintained practically constant over time. However, thermoelectric properties are within the typical errors, independently of the aging time. Moreover, PF values at 800°C are the highest obtained so far in this kind of materials ($> 0.60\text{mW/K}^2\cdot\text{m}$). These characteristics make these materials good candidates for practical applications in power generation devices.

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Figure captions

Figure 1. Representative SEM micrographs of longitudinal polished samples (a, and b) and transversal fractured sections (c, and d). Different contrasts are #1: grey one, associated to the TE $\text{Ca}_3\text{Co}_4\text{O}_9$ phase; and #2: dark grey, associated to the secondary $\text{Ca}_3\text{Co}_2\text{O}_6$ phase.

Figure 2. Mechanical performance (three point bending) of Sr-doped $\text{Ca}_3\text{Co}_4\text{O}_9$ textured samples, together with their standard error, as function of time at 800°C.

Figure 3. a) Temperature dependence of the electrical resistivity, as a function of aging time; b) Electrical resistivity at RT (■) and 800°C (●), together with its error bar (8%). The horizontal black lines represent the mean values at RT and 800°C for all samples.

Figure 4. a) Temperature dependence of Seebeck coefficient, as a function of aging time; b) Seebeck coefficient at RT (■) and 800°C (●), together with its error bar (6%). The horizontal black lines represent the mean values at RT and 800°C for all samples.

Figure 5. a) Temperature dependence of power factor, as a function of aging time; b) Power factor at RT (■) and 800°C (●), together with its error bar (14%). The horizontal black lines represent the mean values at RT and 800°C for all samples.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5