Effect of Na doping on the $\text{Ca}_3\text{Co}_4\text{O}_9$ thermoelectric performance

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Abstract

$\text{Ca}_{3-x}\text{Na}_x\text{Co}_4\text{O}_9$ polycrystalline thermoelectric ceramics with small amounts of Na ($x = 0, 0.01, 0.03, 0.05, 0.07$, and 0.10) have been prepared using the classical solid state method. Microstructural characterization has shown that Na has been incorporated into the $\text{Ca}_3\text{Co}_4\text{O}_9$ phase and that no Na-based secondary phases have been produced. It has also been found that Na addition promotes grain growth and favours sintering due to the formation of a small amount of liquid phase. Electrical resistivity decreases when Na content increases until 0.07Na addition while Seebeck coefficient is maintained practically unchanged. The improvement in electrical resistivity leads to higher power factor values than the usually obtained in samples prepared by more complex and expensive techniques.

Keywords: Sintering; Doping; Electrical properties; Seebeck coefficient.

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1. Introduction

Thermoelectric (TE) materials are characterized by their ability to directly transform a temperature gradient to electrical power due to the Seebeck effect. The conversion efficiency of such materials is usually quantified by the dimensionless figure of merit ZT , $TS^2/\rho\kappa$ (where the electrical part S^2/ρ is also called power factor, PF), where S , ρ , κ , and T are Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively [1]. This characteristic has attracted attention to this type of materials for applications in waste heat recovery devices or solar thermoelectric generators [2-4].

Considering the ZT expression, a high performance thermoelectric material should possess a large Seebeck coefficient together with low electrical resistivity and thermal conductivity. The low electrical resistivity is necessary to avoid Joule heating while the low thermal conductivity is required to maintain a large temperature gradient in the thermoelectric device.

Nowadays, TE devices are based on intermetallic materials, such as Bi_2Te_3 or CoSb_3 , with high ZT values [5-7], and can be industrially used at relatively low temperatures, e.g. in vehicles exhaust. On the other hand, these intermetallic materials show some important drawbacks, as their scarcity in earth's crust [8] or their degradation and/or liberation of heavy elements at high temperatures under air [4]. These problems lead to the limitation of their working temperatures constraining their effective performances. These temperature limitations were surpassed by the discovery, in 1997, of attractive thermoelectric properties in $\text{Na}_2\text{Co}_2\text{O}_4$ ceramics [9] which have higher chemical stability at high temperatures. Moreover, they are composed of cheaper, more environmentally friendly, and abundant elements than the intermetallic ones. This discovery

boosted the search for new ceramic materials with high thermoelectric performance. Nowadays, different thermoelectric ceramics are studied as promising materials for practical applications, such as MnO-, SrTiO₃-, or CoO-based ceramics [10-13]. The MnO- and SrTiO₃-based ceramics are well known as n-type thermoelectric elements while the CoO-based ones, as p-type. In this last type, the research is now focused on materials with high thermoelectric performances and high thermal stability, such as Ca₃Co₄O₉, with very interesting thermoelectric properties [14,15].

Crystallographic studies have demonstrated that Co-based materials possess a monoclinic structure which is, in turn, composed of two different layers. These layers are a common conductive CdI₂-type hexagonal CoO₂ layer with a two-dimensional triangular lattice and a block layer composed of insulating rock-salt-type (RS) layers. The two sublattices (RS block and CdI₂-type CoO₂ layer) are alternatively stacked to form the crystal structure. Moreover, they possess common a- and c-axis lattice parameters and β angles, but different b-axis length, causing a misfit along the b-direction [16,17].

Studies performed on these CoO-based ceramics have demonstrated that the Seebeck coefficient values are governed by the incommensurability ratio and/or the charge of the RS block layer [18]. This effect provides the basis for tuning up the thermoelectric properties by chemical substitutions in this family [19-24]. On the other hand, it is well established that electrical resistivity is drastically affected by the presence of secondary phases, porosity, and grains connectivity [25]. As a consequence, some metallic additions producing a small amount of liquid phase during sintering are usually employed to decrease electrical resistivity by improving the electrical connectivity between the grains [26].

Other important characteristic associated to the high crystallographic anisotropy of these materials is the formation of plate-like grains during the sintering process. This shape anisotropy opens the route to align preferentially the grains using physical, mechanical and/or chemical processes. Such processes should allow the alignment of the conducting planes leading to macroscopic properties comparable to the obtained on single crystals. Numerous methods have been reported to be efficient in producing well aligned bulk materials, such as hot uniaxial pressing [27,28], spark plasma sintering (SPS) [29,30], laser floating zone melting (LFZ) [31,32], electrically assisted laser floating zone (EALFZ) [33,34], templated grain growth (TGG) [35], *etc.* The main advantage of these techniques is the production of materials with very low electrical resistivity values due to the preferential alignment of conducting planes with the current flow direction. On the other hand, these methods possess some drawbacks, as the high price of the spark plasma device and the relatively long processing time of the hot uniaxial pressing or the TGG. In the case of the melt-growth processes, it has been reported that the final electrical properties are strongly dependent with the growth speed [36,37].

The aim of this work is to study the effect of doping on the microstructural and thermoelectric properties of $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramics prepared by a simple and cheap procedure. With this goal, $\text{Ca}_{3-x}\text{Na}_x\text{Co}_4\text{O}_y$ ($x=0, 0.01, 0.03, 0.05, 0.07$, and 0.10) polycrystalline ceramics will be prepared using the classical solid state route. The structural and microstructural modifications produced by the Na addition will be related with the changes on the thermoelectric performances.

2. Experimental

$\text{Ca}_{3-x}\text{Na}_x\text{Co}_4\text{O}_9$ polycrystalline ceramic materials, with $x = 0.00, 0.01, 0.03, 0.05, 0.07$, and 0.10 , were prepared by the conventional solid state route using CaCO_3 (Panreac, 98 + %), Na_2CO_3 (Panreac, 98 + %), and Co_2O_3 (Aldrich, 98 + %) commercial powders as starting materials. They were weighed in the appropriate proportions, well mixed and ball milled for 30 minutes at 300 rpm, in acetone media, in an agate ball mill. The obtained suspension has then been dried under infrared radiation until all the acetone has been evaporated. The resulting powder mixture was manually milled, to break the agglomerates, and subsequently thermally treated at 750 and 800°C for 12h under air, with an intermediate manual milling to decompose the carbonates [15]. After the thermal treatments, the powders were uniaxially pressed at 400 MPa for 1 minute in order to obtain green ceramic parallelepipeds (3 mm x 2.5 mm x 14 mm), with an adequate size for their thermoelectric characterization. The green ceramics were then sintered in the optimal conditions found in previous works, consisting in one step heating at 900 °C during 24 h with a final furnace cooling [38].

Powder X-ray diffraction (XRD) patterns have been systematically recorded in order to identify the different phases in the sintered materials. Data have been collected at room temperature, with 2θ ranging between 5 and 60 degrees, using a Rigaku D/max-B X-ray powder diffractometer working with Cu K α radiation. Apparent density measurements have been performed on several samples for each composition after sintering, using 4.677 g/cm³ as theoretical density [39].

Microstructural observations were performed on the samples surface, using a Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss Merlin) fitted

with an energy dispersive spectrometer (EDS). Several micrographs of the samples have been used to estimate grain sizes in all the samples by the line intercept method using Image-Pro Plus software. Electrical resistivity and Seebeck coefficient were simultaneously determined by the standard dc four-probe technique in a LSR-3 measurement system (Linseis GmbH), in the steady state mode between 50 and 800 °C under He atmosphere. From the resistivity values, the activation energy and the relative carrier concentration for each composition have been estimated. Moreover, with the electrical resistivity and Seebeck coefficient data, the power factor has been calculated in order to determine the samples performances. These properties have been compared with the results obtained in undoped samples and with those reported in the literature.

3. Results and discussion

Powder XRD patterns for the different $\text{Ca}_{3-x}\text{Na}_x\text{Co}_4\text{O}_9$ samples are displayed in Fig. 1 (from 5 to 40° for clarity). In these graphs, it is clear that all the samples have very similar diffraction patterns. In all cases major peaks are associated to the thermoelectric $\text{Ca}_3\text{Co}_4\text{O}_9$ phase, indicated by its reflection planes in Fig. 1f, in agreement with previously reported data [40]. Moreover, it is accompanied by small amounts of $\text{Ca}_3\text{Co}_2\text{O}_6$ (peaks shown by * in Fig 1e) [40], while the peak marked by # belongs to the (111) diffraction plane of Si, used as reference. On the other hand, careful observation of these diagrams shows that there is no Na-based secondary phase indicating that Na should have been incorporated into the crystal structure of $\text{Ca}_3\text{Co}_4\text{O}_9$ and/or $\text{Ca}_3\text{Co}_2\text{O}_6$ phases. Furthermore,

no peaks shift has been detected with Na doping, probably due to the very small difference in the ionic radii of Na^+ and Ca^{2+} .

Fig. 2 shows SEM micrographs performed on all samples surfaces. In the figure, it can be clearly seen that they are composed by randomly oriented plate-like grains. Moreover, their grain sizes seem to increase when the Na content is raised. In order to confirm these observations, grain sizes were measured using the intercept method in several micrographs for each composition. The estimated mean grain sizes, together with their standard deviation, are displayed in Table I. From these data, it is clear that measured mean grain sizes are increased when the Na amount is raised. This effect can be associated to the formation of a small fraction of liquid phase during the sintering procedure, promoted by the Na additions. As a consequence, cations mobility is raised promoting a higher grain growth rate. On the other hand, when observing the samples in more detail, it has been found that major phase is the thermoelectric $\text{Ca}_3\text{Co}_4\text{O}_9$ one, observed as well defined plate-like grains in Fig. 2. Moreover, $\text{Ca}_3\text{Co}_2\text{O}_6$ secondary phase cannot be observed in these micrographs due to its small amounts. In order to assess its presence, it is shown as an insert in Fig. 2b at higher magnifications. As can be easily seen in the insert, this phase shows different morphological aspect from the observed in the $\text{Ca}_3\text{Co}_4\text{O}_9$ one. All these observations are in good agreement with the above discussed XRD data. On the other hand, EDS analysis of both $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_3\text{Co}_2\text{O}_6$ phases has shown that Na incorporation is only produced in the $\text{Ca}_3\text{Co}_4\text{O}_9$. Moreover, the Na content found in these phases is only slightly lower than the nominal composition.

Other interesting feature which can be observed in Fig. 2 is that the samples are not fully dense and some porosity can be observed in the micrographs. The presence of this high amount of porosity can be explained taking into account the phase equilibrium diagram for the CaO-CoO system [41]. In the diagram, the maximum stability temperature of $\text{Ca}_3\text{Co}_4\text{O}_9$ phase is $\sim 926^\circ\text{C}$, slightly higher than the sintering temperature in this work (900°C). On the other hand, the eutectic temperature in this system is about 1350°C , where liquid phase appears. The great difference between the sintering temperature and the eutectic one leads to a very slow densification process. As a consequence, a relatively high porosity should be expected in these samples.

In order to confirm these observations and discussion, apparent density measurements have been performed on at least 4 samples for each composition. They were measured and weighed for three times to minimize the measurement errors. The calculated mean apparent densities, together with their standard error, are presented in Table II. As it can be observed in these data, in spite of substituting Ca by a lighter element (Na), the samples density is raised from around 71 to 73 % of $\text{Ca}_3\text{Co}_4\text{O}_9$ theoretical density when Na content is increased from 0 to 0.10. These results clearly indicate that Na favours a higher densification of the bulk samples at the sintering temperatures. In any case, these variations are small enough to assume that they should have practically no effect on the electrical behaviour of the samples.

Fig. 3 shows the variation of the Seebeck coefficient with the temperature, as a function of the Na doping. In the plot, it can be clearly seen that the sign of the Seebeck coefficient is positive for the entire measured temperature range, confirming a conduction mechanism mainly governed by holes. The values of

the Seebeck coefficient increase with temperature, with the same behaviour for all the samples. The room temperature values are approximately the same for all samples, independently of Na content. This measured value (around 135 $\mu\text{V/K}$) is slightly higher than those reported elsewhere at room temperature for 0, 0.3, and 0.5Na-doped hot uniaxial pressed samples ($\sim 120 \mu\text{V/K}$) [42]. Moreover, they show the same values found in Cu and Na codoped samples (about 135 $\mu\text{V/K}$) prepared by SPS [43]. On the other hand, when considering the maximum S values at 800 °C ($\sim 215 \mu\text{V/K}$), they are higher than the obtained in Bi and Na substituted samples processed by SPS (around 185 $\mu\text{V/K}$) [44], or by TGG followed by hot uniaxial pressing (about 185 $\mu\text{V/K}$) [45]. It is worthy of mentioning that the similar S values obtained for the undoped and the Na-doped samples indicate that Na doping does not affect, in a great extent, the $\text{Ca}_3\text{Co}_4\text{O}_9$ conduction band [22].

The temperature dependence of electrical resistivity, as a function of Na content, is shown in Fig. 4. As it can be clearly seen, the $\rho(T)$ curves show a decrease of resistivity from 0.00 to 0.07Na substitution. Higher Na contents slightly increases resistivity, compared with the 0.07Na-doped samples. All the curves reflect a slope change at about 400 °C, from semiconducting-like ($d\rho/dT < 0$) to metallic-like ($d\rho/dT > 0$) behaviour. The decrease of room temperature resistivity values with increasing Na content is in agreement with previous works which demonstrate that the raise in the rock-salt layer dimensions produce a decrease of resistivity [31]. Moreover, the substitutions in the RS layer using cations with lower oxidation state than the original one, also lead to lower electrical resistivity due to the raise in the amount of Co^{4+} in the conducting layer [24]. In any case, the lowest measured room temperature resistivity values

(~ 12.5 mΩ.cm for the 0.07Na-substituted samples) is around 40 % lower than the undoped samples prepared in this work. Moreover, they are lower than the best values obtained for Ca₃Co₄O₉ samples sintered and textured by spark plasma sintering (15-18 mΩ.cm) [47]. Furthermore, the values at 800 °C (~ 14 mΩ.cm) are also lower than the obtained in Na-doped samples prepared by sol-gel method (about 20 mΩ.cm) [48].

In order to explain the resistivity behaviour of these samples, it should be considered that the temperature dependence of the electrical conductivity, in the semiconducting behaviour zone, can be described as:

$$\sigma.T \propto \exp (-E/k_B.T)$$

where E, k_B, and T are the activation energy, Boltzmann constant, and absolute temperature, respectively. The activation energy values are obtained from the log (σT) *versus* 1/T plot as the curve fit slope in the different samples below T*, as illustrated in Fig. 5, where the log (σT) *versus* 1000/T is represented. T* is defined as the temperature where the behaviour of the samples changes from semiconducting-like to metallic-like one. The calculated values have been found to be around 40 meV in all cases, confirming that Na additions do not appreciably modify the Ca₃Co₄O₉ conduction band, in agreement with previous works [20]. Moreover, Na additions do not produce modifications in the T* values, independently of the Na amount. On the other hand, in the figure it can be seen that the represented data are higher when the Na content is raised until they reach a maximum for the 0.07Na-doped samples. Further Na additions slightly decrease these values. Under the assumption that these changes are mainly due to variations on the holes concentration, the estimated carrier

concentration is increased when Na is added to the samples in agreement with the electrical resistivity evolution.

In order to evaluate the thermoelectric performances of these materials, power factor has been calculated from electrical resistivity and Seebeck coefficient data. The temperature dependence of power factor, as a function of Na content, is plotted in Fig. 6. When considering PF values at around 50 °C (~ room temperature), it can be clearly seen that all the Na-doped samples possess higher PF values than the undoped ones. The maximum increase is obtained for the 0.07 and 0.10Na-doped samples (~ 75 % higher than the undoped ones). The maximum PF value at room temperature (about 0.14 mW/K².m) is slightly lower than the values found in Cu and Na codoped prepared by sol-gel and consolidated by SPS (around 0.17 mW/K².m) [43]. On the other hand, the highest PF value obtained at 800 °C (around 0.32 mW/K².m) for the 0.07Na-doped samples is lower than the obtained in Bi and Na cosubstituted samples prepared by TGG followed by hot uniaxial pressing (about 0.60 mW/K².m) [45], but much higher than the measured in samples with the same composition prepared by TGG and consolidated by cold isostatic pressing (~ 0.12 mW/K².m). Moreover, this value is about 70 % higher than the obtained in this work for the undoped samples.

4. Conclusions

This work demonstrates that Na can substitute Ca in Ca_{3-x}Na_xCo₄O₉ in small proportions without appreciably modifying the crystal structure. It has been found that Na substitution promotes grain growth and favours sintering due to the formation of a small amount of liquid phase. These effects are reflected in a

marked decrease of electrical resistivity without appreciably modifying Seebeck coefficient. The optimal Na for Ca substitution has been determined using the values of the power factor at 800 °C, which is maximum for the 0.07Na-doped samples with values around 0.32 mW/K².m, which is about 70 % higher than the obtained for the undoped samples. Moreover, PF values are also higher than the typical ones obtained by complex and more expensive techniques.

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Figure captions:

Figure 1. Powder X-ray diffraction patterns obtained in the $\text{Ca}_{3-x}\text{Na}_x\text{Co}_4\text{O}_9$ samples with $x = 0.00$ (a); 0.01 (b); 0.03 (c); 0.05 (d); 0.07 (e); and 0.10 (f). The diffraction planes indicate the $\text{Ca}_3\text{Co}_4\text{O}_9$ phase, and those marked with a * the $\text{Ca}_3\text{Co}_2\text{O}_6$ one. The # symbol denotes the (111) peak of Si, used as internal reference.

Figure 2. Surface SEM micrographs of $\text{Ca}_{3-x}\text{Na}_x\text{Co}_4\text{O}_9$ samples for $x = 0.00$ (a); 0.01 (b); 0.03 (c); 0.05 (d); 0.07 (e); and 0.10 (f) showing the randomly oriented $\text{Ca}_3\text{Co}_4\text{O}_9$ plate-like grains. The insert in (b) shows the $\text{Ca}_3\text{Co}_2\text{O}_6$ microstructural aspect.

Figure 3. Temperature dependence of the Seebeck coefficient as a function of Na content in $\text{Ca}_{3-x}\text{Na}_x\text{Co}_4\text{O}_9$ samples, for $x = 0.00$ (▲); 0.01 (▼); 0.03 (■); 0.05 (◆); 0.07 (●); and 0.10 (▲).

Figure 4. Temperature dependence of the electrical resistivity, as a function of Na content in $\text{Ca}_{3-x}\text{Na}_x\text{Co}_4\text{O}_9$ samples, for $x = 0.00$ (▲); 0.01 (▼); 0.03 (■); 0.05 (◆); 0.07 (●); and 0.10 (▲).

Figure 5. $\text{Log}(\sigma T)$ versus $1000/T$ plot for all the $\text{Ca}_{3-x}\text{Na}_x\text{Co}_4\text{O}_9$ samples, for $x = 0.00$ (▲); 0.01 (▼); 0.03 (■); 0.05 (◆); 0.07 (●); and 0.10 (▲). The slopes of the fittings are nearly the same in all cases, below T^* . T^* indicates the metallic-to-semiconducting transition temperature. The drawn lines are guides for eyes.

Figure 6. Temperature dependence of the power factor as a function of Na content in $\text{Ca}_{3-x}\text{Na}_x\text{Co}_4\text{O}_9$ samples, for $x = 0.00$ (▲); 0.01 (▼); 0.03 (■); 0.05 (◆); 0.07 (●); and 0.10 (▲).

Table I. Evolution of the mean grain sizes, together with their standard deviation, determined in the bulk sintered $\text{Ca}_{3-x}\text{Na}_x\text{Co}_4\text{O}_9$ samples.

x	Mean grain size (μm)	Standard deviation
0.00	3.14	1.19
0.01	3.29	1.19
0.03	3.78	1.53
0.05	3.86	0.82
0.07	4.07	1.26
0.10	4.43	1.14

Table II. Evolution of samples density, together with their standard error, determined in the bulk sintered $\text{Ca}_{3-x}\text{Na}_x\text{Co}_4\text{O}_9$ samples.

x	Mean apparent ρ (g/cm³)	Standard error	% Theor. ρ
0.00	3.30	0.01	70.6
0.01	3.30	0.01	70.6
0.03	3.32	0.01	71.0
0.05	3.35	0.01	71.6
0.07	3.36	0.01	71.8
0.10	3.39	0.01	72.5

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6