Doping effect in $\text{Ca}_3\text{Co}_{4-x}\text{Zn}_x\text{O}_y$ ceramics

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Abstract

$\text{Ca}_3\text{Co}_{4-x}\text{Zn}_x\text{O}_y$ ($x = 0.01, 0.03$, and 0.05) polycrystalline thermoelectric ceramics have been prepared by the classical solid state method. XRD data have shown that $\text{Ca}_3\text{Co}_4\text{O}_9$ is the major phase, with small amounts of the $\text{Ca}_3\text{Co}_2\text{O}_6$ one. Moreover, it has been found that the Zn has been incorporated into these two phases. Slight Zn doping decreases electrical resistivity compared with the values obtained in undoped samples. The minimum values have been obtained for the 0.01-Ni doped samples, increasing for further Zn substitution. Seebeck coefficient does not appreciably change in all the measured temperature range, independently of Zn content. The improvement in electrical resistivity leads to higher power factor values for the 0.01 Zn-doped samples (about 30 %) than for the undoped ones. The maximum power factor at 800 °C, around 0.27 mW/K².m is significantly higher than the best results obtained in Zn doped samples reported in the literature.

Keywords: Ceramics; Cobaltites; Electrical resistivity; Power factor.

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1. Introduction

Nowadays, thermoelectric (TE) materials are receiving high interest as they can harvest wasted heat from many energy transforming processes. Moreover, these materials can directly transform a temperature difference to electrical power, without moving parts, due to the Seebeck effect. The energy conversion efficiency of TE materials is quantified using the figure of merit ($ZT = TS^2/\rho\kappa$). In this expression, S is the Seebeck coefficient, ρ electrical resistivity, κ thermal conductivity, and T is the absolute temperature [1]. If only the electrical part of this expression is considered (S^2/ρ), it is called power factor (PF) which is often used to characterise the materials performances when the thermal conductivity is difficult to be measured. Furthermore, the intrinsic characteristics of these materials have centered the efforts for their use in practical applications as waste heat recovery devices [2] or solar thermoelectric generators [3].

Intermetallic TE materials are currently employed in several practical applications as, for example, energy harvesters in vehicles exhaust. However, due to their degradation and/or oxidation at high temperature under oxidative environment, they cannot be used in these conditions. Finally, these kinds of materials are often composed of heavy, scarce, and toxic elements, as Te, Sb, etc. The working temperature limitation of these materials was surpassed by the discovery of relatively high TE performances in the Na-Co-O ceramic system [4]. Since then, many works have been made on the cobalt-based ceramics for high temperature applications, mainly on the $\text{Ca}_3\text{Co}_4\text{O}_9$ [5,6], $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_x$ [7,8], $\text{Bi}_2\text{Ca}_2\text{Co}_2\text{O}_x$ [9,10], and $\text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_x$ [11,12] systems with high thermoelectric properties and working temperatures.

Crystallographic studies of these cobalt-based materials have demonstrated that they can be described by a monoclinic structure which is, in turn, composed of two stacked alternating layers. They are a conductive CdI₂-type hexagonal CoO₂ layer with a two-dimensional triangular lattice, and an insulating rock-salt-type (RS) one. These two sublattices possess common a- and c-axis lattice parameters and β angles, but different b-axis length which produces a misfit along the b-direction [13]. The high structural anisotropy of these materials leads to the formation of plate-like grains with very large dimensions in the ab plane and very small ones in the c direction. As a consequence, this effect can be exploited to preferentially align these grains to obtain bulk properties close to those obtained in single crystals. Many different techniques have been explored to produce well aligned grains in bulk materials, as hot uniaxial pressing [14], spark plasma sintering [15], laser floating zone melting (LFZ) [16], electrically assisted laser floating zone [17], *etc.* The main drawbacks of these methods are due to different factors, as the relatively long treatments, the high costs associated with the processes and/or the strong properties dependence on the growth or the texturing speed [14,15,18,19].

On the other hand, previous works have demonstrated that the Seebeck coefficient and/or electrical resistivity values can be influenced by changes in the incommensurability ratio and/or the effective charge of the RS block layer between the CoO₂ ones [20]. These studies have provided the basis for the TE properties modification using cationic substitution. The most common ones are based on the substitution of an alkaline-earth [21,22], Co [23,24], or Bi [25,26] which have been effective in improving the materials performances.

The aim of this work is studying the effect of small substitutions of Co by Zn on the structural, microstructural, and high temperature thermoelectric properties of $\text{Ca}_3\text{Co}_{4-x}\text{Zn}_x\text{O}_y$ when it is prepared using the classical solid state synthesis route.

2. Experimental

$\text{Ca}_3\text{Co}_{4-x}\text{Zn}_x\text{O}_y$ polycrystalline ceramic materials, with $x = 0.00, 0.01, 0.03$, and 0.05 , were prepared from commercial CaCO_3 (Panreac, 98 + %), Co_2O_3 (Aldrich, 98 + %), and ZnO (Carlo Erba, 99.5 %) powders as starting materials using the classical solid state route. They were weighed in the appropriate proportions, mixed and ball milled for 30 minutes in acetone media at 300 rpm. The resulting slurry has been heated under infrared radiation to evaporate the acetone. The dry mixture was subsequently manually milled and thermally treated twice at 750 and 800 °C for 12h under air, with an intermediate manual grinding. This thermal treatment has been found in previous works to be adequate to decompose the CaCO_3 [27]. After thermal treatment, the powders were uniaxially pressed at 400 MPa for 1 minute in form of parallelepipeds (approximately 3 mm x 3 mm x 14 mm) and sintered at 900 °C for 24 h with a final furnace cooling.

Powder X-ray diffraction (XRD) patterns have been recorded in order to identify the different phases in the thermoelectric 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.

Microstructural observations were performed on polished longitudinal sections of the samples, using a Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss Merlin) fitted with an energy dispersive X-ray spectrometer (EDX). Micrographs of the samples have been used to analyze the different phases and their distribution. Apparent density measurements have been performed on several samples for each composition after sintering, using 4.677 g/cm^3 as theoretical density [28].

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 and at temperatures ranging from 50 to 800 °C under He atmosphere. Moreover, with the electrical resistivity and thermopower data, power factor has been calculated in order to determine the samples performances. These properties have been compared with the results obtained in the undoped samples and with those reported in the literature at room temperature ($\sim 50 \text{ °C}$), where oxygen diffusion is negligible, to avoid the influence of the atmosphere on the compared values.

3. Results and discussion

Powder XRD patterns for the different $\text{Ca}_3\text{Co}_{4-x}\text{Zn}_x\text{O}_y$ samples are displayed in Fig. 1 (from 5 to 40° for clarity). From these data, it is clear that all the samples have very similar diffraction patterns. As can be seen in Fig. 1a, corresponding to the undoped samples, the highest peaks have been associated to the thermoelectric $\text{Ca}_3\text{Co}_4\text{O}_9$ phase, indicated by the reflection planes, in agreement with previously reported data [29], where a monoclinic unit cell (#12, C12/m1) has been used. On the other hand, the peak at around 28.65 degrees

(indicated by • in Fig. 1d) corresponds to the (111) diffraction plane of Si used as reference. Moreover, the peaks identified by * in Figs. 1a, and d, have been associated to the $\text{Ca}_3\text{Co}_2\text{O}_6$ phase, accordingly to previously reported data [30], with a rhombohedral unit cell (#167, $R\bar{3}cH$). From these data, it seems that only a slight increase in the amount of the $\text{Ca}_3\text{Co}_2\text{O}_6$ phase can be found with Zn addition. The most evident differences between the XRD patterns obtained for all samples are due to the preferential orientation of the plate-like grains. These changes in the preferential orientation lead to the observed variation in the relative intensities between the different crystallographic planes. This is a typical effect associated with the preparation of powdered samples when they are composed of very anisotropic grains (as plate-like ones) which can induce different preferential grain orientations in the powders. Moreover, it explains the fact that some of the diffraction planes, associated to the $\text{Ca}_3\text{Co}_2\text{O}_6$ secondary phase, appear while others disappear. Taking into account this effect, it can be deduced that the Zn doping does not appreciably change the phases proportions. On the other hand, no Zn based secondary phase has been detected with this technique, which is a clear indication that Zn has been incorporated in the $\text{Ca}_3\text{Co}_4\text{O}_9$ and/or $\text{Ca}_3\text{Co}_2\text{O}_6$ crystal structures.

General SEM observations performed on representative longitudinal polished sections of the samples are shown in Fig. 2. In these images, it can be observed that all samples possess very similar microstructure, indicating that Zn doping does not influence, in an important manner, the samples microstructure. Moreover, it is evident that grain size is not homogeneous all along the samples, reflecting the well known drawbacks of the solid state synthesis methods. Other feature observed in these micrographs is the porosity, observed

as very dark contrast in the figure, which seems to increase with raising the Zn content. In order to confirm this observation, apparent density measurements have been performed for all samples. At least four samples for each composition were measured for three times to minimize measurement errors. The obtained results showed that the samples progressively decrease their densities when the Zn amount is increased, from about 70 % of the theoretical one for the undoped samples, until around 58 % for the 0.05 Zn-doped ones. This evolution clearly agrees with the microstructural aspects discussed previously. Moreover, the relatively low densities found also agree with previous works [31] and can be explained due to the fact that the sintering temperature (910 °C) is far from the melting temperature of this system (~ 1350 °C), as can be observed in the phase equilibrium diagram [32].

Other interesting feature which can be observed in these micrographs is that only two different phases have been found, the major one (grey contrast) has been identified by EDX as $\text{Ca}_3\text{Co}_4\text{O}_9$, while the minor one possess very similar contrast and different shape (indicated by #1 Fig.2d), being identified as the $\text{Ca}_3\text{Co}_2\text{O}_6$ secondary phase. Moreover, EDX analysis has shown that Zn is found substituting Co in the $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_3\text{Co}_2\text{O}_6$ phases in variable proportions all along the samples but always in higher content in this last one.

Fig. 3 shows the variation of the Seebeck coefficient with the temperature, as a function of the Zn doping. In the plot, it can be clearly seen that the sign of the thermopower is positive for the entire measured temperature range, which confirms a conduction mechanism mainly governed by holes. The Seebeck coefficient increases with temperature, with very similar values and behaviour for all the samples. The obtained values at room temperature (~ 135 $\mu\text{V/K}$) are

slightly higher than those reported elsewhere ($\sim 125 \mu\text{V/K}$) at the same temperature [33]. On the other hand, the maximum Seebeck coefficient ($\sim 220 \mu\text{V/K}$) obtained in this work at 800°C is significantly higher than the measured in $\text{Ca}_3\text{Co}_4\text{O}_9$ samples prepared by autocombustion method and consolidated by spark plasma sintering (150 and $165 \mu\text{V/K}$ measured parallel and perpendicular to the applied load, respectively) at the same temperature [34]. The similar values obtained for all samples indicate that small Zn addition does not affect, in a great extent, the $\text{Ca}_3\text{Co}_4\text{O}_9$ conduction band [31].

The temperature dependence of electrical resistivity, as a function of the Zn content, is shown in Fig. 4. The $\rho(T)$ curves show a decrease of resistivity when 0.01 Zn is added, compared with the undoped samples. Further Zn addition raises resistivity values compared with the 0.01 Zn doped ones. The decrease of room temperature resistivity values with Zn addition is in agreement with previous works which demonstrate that the raise in the rock-salt layer dimensions (due to the higher ionic radii of Zn^{2+} , compared with the Co^{2+} one) produce a decrease of resistivity [21]. The raise of resistivity for Zn contents higher than 0.01 is related with the increase on the crystal defects which decrease the carriers mobility.

All the curves in Fig. 4 show a semiconducting-like ($d\rho/dT < 0$) behaviour, from room temperature to around 400°C , in agreement with previously reported data in this system where the charge transport process is a hole hopping from Co^{4+} to Co^{3+} [35]. At higher temperatures, this behaviour changes to a metallic-like ($d\rho/dT > 0$) one where the charge carriers are transported in the valence or conduction band [24]. The lowest measured room temperature resistivity values ($\sim 16 \text{ m}\Omega\cdot\text{cm}$ for the 0.01 Zn-substituted samples) are close to the values

obtained for $\text{Ca}_3\text{Co}_4\text{O}_9$ samples produced by spark plasma sintering ($\sim 13 \text{ m}\Omega\cdot\text{cm}$) [15]. The obtained resistivity values are more impressive when taking into account that they have been obtained in samples prepared by the solid state method, with low densities, and are compared with the obtained in spark plasma sintering prepared ones, with about 98 % of the theoretical density. As a consequence, the resistivity values obtained in the 0.01 Zn doped samples are much lower than the expected from their measured densities.

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

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

where E , k_B , and T are the activation energy, Boltzmann constant, and absolute temperature, respectively. The activation energy values are obtained from the $\log (\sigma T)$ *versus* $1/T$ plot as the curve fit slope in the different samples below T^* , as illustrated in Fig. 5. T^* is defined as the temperature where the behaviour of the samples changes from semiconducting to metallic one, which is shifting to lower temperatures for all the doped samples, compared with the undoped ones. The calculated activation energies values have been about 34 meV for the Zn doped samples, while for the undoped ones this value is around 36 meV, confirming that Zn doping has not a strong influence on the $\text{Ca}_3\text{Co}_4\text{O}_9$ conduction band [31]. Under the assumption that these changes in conductivity are mainly due to variations on the hole concentration, the carrier concentration is clearly increased by small Zn additions. The maximum increase is obtained for the 0.01 Zn-doped samples, with values around 20 % higher than for the pure ones, decreasing for higher Zn doping.

In order to evaluate the thermoelectric performances of these materials, the power factor has been calculated using the electrical resistivity and Seebeck coefficient data and plotted as a function of temperature in Fig. 6. When considering PF values at about 50 °C (~ room temperature), it can be clearly seen that the 0.01 Zn-doped samples possess higher PF values than the undoped ones (around 40 %). The highest PF value obtained at 800 °C (around 0.27 mW/K².m) for the 0.01 Zn-doped samples is ~ 30 % higher than the obtained in the undoped ones. This maximum PF value is around 35 % higher than the obtained in Zn substituted samples prepared by a sol-gel method (~ 0.19 mW/K².m at 700 °C) [24] which is known for producing higher quality samples than the classical solid state one.

All these data indicate that very small Zn additions are adequate to improve, in a significant manner, the thermoelectric performances of Ca₃Co₄O₉ ceramics.

4. Conclusions

This work demonstrates that very small Zn substitutions for Co in Ca₃Co₄O₉ thermoelectric ceramics improve its performances by significantly decreasing electrical resistivity without appreciably modifying the Seebeck coefficient values. The optimal Zn for Co substitution has been determined using the power factor values at 50 and 800 °C, which are maximum for the 0.01 Zn-doped samples. The raise in PF, compared with the undoped samples, is around 30 %. Moreover, the measured PF values at 800 °C are about 35 % higher than the best ones reported in the literature, measured in Zn-doped Ca₃Co₄O₉ prepared by a sol-gel method which provides high homogeneous precursors.

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Figure captions:

Figure 1. Powder X-ray diffraction patterns obtained for the $\text{Ca}_3\text{Co}_{4-x}\text{Zn}_x\text{O}_y$ samples; $x = 0.00$ (a); 0.01 (b); 0.03 (c); and 0.05 (d). The diffraction planes indicate the $\text{Ca}_3\text{Co}_4\text{O}_9$ phase and the * the $\text{Ca}_3\text{Co}_2\text{O}_6$ ones. The • symbol identifies the (111) diffraction peak of Si, used as reference.

Figure 2. SEM micrographs performed on representative longitudinal polished sections of $\text{Ca}_3\text{Co}_{4-x}\text{Zn}_x\text{O}_y$ samples, for $x = 0.00$ (a); 0.01 (b), 0.03 (c), and 0.05 (d).

Figure 3. Temperature dependence of the Seebeck coefficient, as a function of Zn content, in $\text{Ca}_3\text{Co}_{4-x}\text{Zn}_x\text{O}_y$ samples, for $x = 0.00$ (●); 0.01 (■); 0.03 (◆); and 0.05 (▲).

Figure 4. Temperature dependence of the electrical resistivity, as a function of Zn content, in $\text{Ca}_3\text{Co}_{4-x}\text{Zn}_x\text{O}_y$ samples, for $x = 0.00$ (●); 0.01 (■); 0.03 (◆); and 0.05 (▲).

Figure 5. Log (σT) *versus* $1000/T$ plot as a function of Zn content in $\text{Ca}_3\text{Co}_{4-x}\text{Zn}_x\text{O}_y$ samples, for $x = 0.00$ (●); 0.01 (■); 0.03 (◆); and 0.05 (▲).

Figure 6. Temperature dependence of the power factor, as a function of Zn content, in $\text{Ca}_3\text{Co}_{4-x}\text{Zn}_x\text{O}_y$ samples, for $x = 0.00$ (●); 0.01 (■); 0.03 (◆); and 0.05 (▲).

Figure 1

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