Thermoelectric properties of rare earth doped $\text{Ca}_{3-x}\text{RE}_x\text{Co}_4\text{O}_9$ (RE=Dy, Er, Gd, and Tb; x=0, 0.01, 0.03, and 0.05)

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Abstract

$\text{Ca}_{3-x}\text{RE}_x\text{Co}_4\text{O}_9$ thermoelectric ceramics with different rare earth (RE= Dy, Er, Gd, and Tb) substitution for Ca have been successfully produced by the classical solid state method. All these rare earths in small proportions produce the same effects on the thermoelectric phase, reflected on a similar and significant decrease of the electrical resistivity, compared with the undoped samples. The Seebeck coefficient slightly decreases with all the studied substitutions while the power factor values appreciably increase at high temperatures for small amounts (0.01) of doping elements. Further doping produces the decrease of power factor which indicates that the optimal doping level has been determined to be 0.01 for all the tested rare earths which produces, approximately, the same improvement, around 20 % of the power factor obtained in the undoped samples at 800 °C.

Keywords: Doping, Electrical properties, Microstructure, Thermopower, Cobaltites.

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1. Introduction

Thermoelectric (TE) materials for practical electric power generation systems should possess high energy conversion efficiency. Thermoelectric energy conversion has shown important advantages to be applied in harvesting waste heat in industrial applications. Moreover, it can be used to transform solar energy into electricity at lower cost than photovoltaic energy [1]. The conversion efficiency of TE materials is usually quantified using the dimensionless figure of merit ZT , which is defined as $TS^2/\rho\kappa$ (in which S^2/ρ is also called power factor, PF), where S is the Seebeck coefficient (or thermopower), ρ the electrical resistivity, κ the thermal conductivity, and T is the absolute temperature [2]. From this expression, it is clear that an adequate TE material for practical applications must involve high thermopower and low electrical resistivity, with low thermal conductivity.

The discovery of large thermoelectric power in Na_xCoO_2 [3], with a high ZT value at 300K (about 0.26), has opened a new research field. From this discovery, great efforts have been made to explore new ceramic families with high thermoelectric performances. In the last years, many studies have been performed in other layered cobaltites, such as misfit $[\text{Ca}_2\text{CoO}_3][\text{CoO}_2]_{1.62}$, $[\text{Bi}_{0.87}\text{SrO}_2]_2[\text{CoO}_2]_{1.82}$ and $[\text{Bi}_2\text{Ca}_2\text{O}_4][\text{CoO}_2]_{1.65}$ which also exhibit attractive thermoelectric properties [4-7]. In these systems, the crystal structure is formed by two different layers, showing an alternate stacking of a common conductive CdI_2 -type CoO_2 layer with a two-dimensional triangular lattice and a block layer, composed of insulating rock-salt-type (RS) layers. Both sublattices (RS block and CdI_2 -type CoO_2 layer) possess common a - and c -axis lattice parameters and β angles but different b -axis length, causing a misfit along the b -direction [8,9].

One of the main factors affecting the thermoelectric performances of this kind of materials is the electrical resistivity which should be maintained as low as possible. The resistivity values in ceramic materials are influenced by a number of different parameters as content and distribution of secondary phases, porosity, oxygen content, etc. As a consequence, many different synthetic methods have been used in order to synthesize thermoelectric and other layered ceramic materials [4,10-14]. On the other hand, layered cobaltites are materials with a strong crystallographic anisotropy; therefore the alignment of plate-like grains by mechanical and/or

chemical processes has been studied to attain macroscopic properties comparable to those obtained on single crystals mainly due to the electrical resistivity decrease. Some techniques have been shown to be adequate to obtain a good grain orientation in several oxide ceramic systems, such as templated grain growth (TGG) [9], microwave texturing [15], hot pressing [16], spark plasma sintering [17], or directional growth from the melt [18,19]. Other possibilities arising from the crystallographic structure of these materials are the cationic substitutions in the RS layer, which can change the misfit relationship between the two layers and, as a consequence, modifying the values of the thermopower [20]. From this point of view, it is clear that this kind of substitutions can be useful in order to improve thermoelectric performances of ceramic materials, as it is reported for the substitution of Gd and Y [21] or Sb [22] for Ca in $[\text{Ca}_2\text{CoO}_3][\text{CoO}_2]_{1.62}$, Pb for Bi [23,24] or Sr by Ca [25] in $[\text{Bi}_2\text{Ca}_2\text{O}_4][\text{CoO}_2]_{1.65}$.

Taking into account these previously discussed effects, the aim of this work is studying the effect produced by the substitution of small amounts of Ca by different rare earths (Dy, Er, Gd, and Tb) on the microstructure and thermoelectric characteristics of $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramic materials.

2. Experimental

The initial $\text{Ca}_{3-x}\text{RE}_x\text{Co}_4\text{O}_9$ (RE= Dy, Er, Gd, and Tb; $x=0, 0.01, 0.03$, and 0.05) polycrystalline ceramics were prepared from commercial CaCO_3 (> 98.5 %, Panreac), Co_3O_4 (99.7 %, Alfa Aesar), Dy_2O_3 (99.9 %, Alfa Aesar), Er_2O_3 (99.9 %, Aldrich), Gd_2O_3 (99.9 %, Aldrich), and Tb_3O_5 (99.9 %, Aldrich) powders by the classical solid state method. They were weighed in the appropriate proportions, well mixed and ball milled for 30 minutes at 300 rpm, in acetone media, in a planetary agate ball mill. The obtained slurry has been heated in a rapid evaporation system equipped with infrared radiation until all the acetone has been evaporated. The dry mixture was then manually milled in order to avoid the presence of agglomerates in the next steps, favouring the alkaline earth carbonates decomposition. After milling, the homogeneous mixture was thermally treated twice at 750 and 800°C for 12h under air, with an intermediate manual milling in order to assure the total decomposition of carbonates, as reported previously [4], which improve the mixture reactivity in the sintering processes. 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 subsequently sintered in the optimal conditions found in previous works with the help of the CaO-CoO phase diagram [26], and consisting in one step heating at 900 °C for 24 h with a final furnace cooling which are the best determined conditions to produce the $\text{Ca}_3\text{Co}_4\text{O}_9$ phase [27,28].

Powder X-ray diffraction (XRD) patterns have been systematically 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 $K\alpha$ radiation. Apparent density measurements have been performed on several samples for each composition after sintering, using 4.677 g/cm^3 as theoretical density [29].

Microstructural observations were performed on the surfaces of all samples, using a Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss Merlin) fitted with an energy dispersive spectrometry (EDS) analyzer. 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. From the resistivity values, the activation energy for each sample has been estimated in the semiconductor-like behaviour region. Moreover, with the electrical resistivity and thermopower data, the 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 low temperatures ($\sim 50 \text{ °C}$), where oxygen diffusion is negligible, to avoid the influence of the atmosphere on the compared values.

3. Results and discussion

Powder XRD patterns for all $\text{Ca}_{3-x}\text{RE}_x\text{Co}_4\text{O}_9$ (RE= Dy, Er, Gd, and Tb; $x=0, 0.01, 0.03$, and 0.05) samples have been performed in the same conditions. In Fig. 1, the XRD plots for the Dy-doped samples (from 10 to 40° for clarity), which are representative of the structural evolution of all the rare earths substitutions, are shown. As can be seen in Fig. 1a, corresponding to the undoped samples, all the

peaks can be associated to the thermoelectric $\text{Ca}_3\text{Co}_4\text{O}_9$ phase, indicated by the reflection planes, and in agreement with previously reported data [30], where a monoclinic unit cell (#12, $C12/m1$) has been used. This space group is an approximation, as a superspace formalism should be done for the $\text{Ca}_3\text{Co}_4\text{O}_9$ phase [31]. Only one peak, associated to the $\text{Ca}_3\text{Co}_2\text{O}_6$ phase has been identified at about 21° indicated by a * in Fig. 1a [32], where a rhombohedral unit cell (#167, $R\bar{3}cH$) has been used. When Dy is added to the samples, three new peaks of the $\text{Ca}_3\text{Co}_2\text{O}_6$ phase appear (indicated by * in Fig 1d), indicating a slight increase of this phase. The peak indicated by a • in this pattern corresponds to the (111) peak of Si, used as internal reference. In spite of this raise on the $\text{Ca}_3\text{Co}_2\text{O}_6$ phase content, it is clear that the cobaltite phase appears as the major one, independently of Dy content. Moreover, when observing in detail these XRD patterns, no shift can be observed in the cobaltite peaks with the rare earth additions, certainly due to the small proportion of rare earth.

Scanning electron microscopy has been performed on the surfaces of all samples after the sintering process. The microstructural evolution of samples, as a function of the rare earth substitution, is very similar for all of them. As a consequence, the microstructural features will be discussed for one rare earth substitution and can be extended to the other ones, as can be observed in Table 1 where the composition determined by EDX for the different contrasts, are displayed. In Fig. 2, representative micrographs of Tb doped $\text{Ca}_3\text{Co}_4\text{O}_9$ samples are displayed. As it can be seen in Fig. 2a, major phase corresponds to the $\text{Ca}_3\text{Co}_4\text{O}_9$ one (#1, grey contrast), accompanied by small amounts of $\text{Ca}_3\text{Co}_2\text{O}_6$ (#2, slightly clearer grey contrast surrounded by a line for clarity). This is a typical feature found in the solid state sintered samples, as reported in previous works [33]. When Tb (or other rare earth) is added, the undoped $\text{Ca}_3\text{Co}_4\text{O}_9$ phase coexists with Tb-doped $\text{Ca}_3\text{Co}_2\text{O}_6$ and $\text{Ca}_3\text{Co}_4\text{O}_9$ (this last one is indicated by #3 in Fig. 2d). The Tb-doped $\text{Ca}_3\text{Co}_4\text{O}_9$ phase is easily distinguishable by its shape and due to its light grey contrast. Moreover, its amount is increased when the Tb nominal content is raised.

Another feature that can be observed in Fig. 2 is that porosity seems to increase with the Tb amount. In order to confirm this evolution, apparent density measurements were performed on more than four samples for each composition. The mean values obtained, together with their standard error, are displayed in Fig. 3

as a function of the doping amount. As it can be clearly seen in the plot, apparent density decreases when the amount of rare earth is increased, compared with the undoped samples. With these density values, the calculated relative one of the samples is ranging from 74 % of the theoretical density for the undoped samples, to 65 % measured in the 0.05 Dy doped samples. The other samples possess intermediate relative densities but much closer to 70 % for 0.01 and 0.03 rare earth substitution.

In order to have a global view of the effect of the different rare earths and their amounts on the thermoelectric properties, the electrical resistivity, Seebeck coefficient and power factor values at room temperature and 800 °C, together with the estimated activation energies (between room temperature and 200 °C), are summarized in Table 2. As can be clearly seen in the table, in spite of very small variations in the Seebeck coefficient and activation energies for all samples, electrical resistivity values decrease, in an important manner (~ 20%), for the 0.01 rare earth doped samples which lead to a raise on the power factor values (~ 30% at room temperature and 800 °C), compared with the undoped ones. Further doping produces a decrease of both characteristics, compared with the 0.01 rare earth doped samples. This effect is due to the competition between the raise on the carrier concentration induced by the rare earth substitution (RE^{3+}) for Ca^{2+} , and the decrease on the carrier mobility as a consequence of the scattering produced by the introduction of defects on the crystal structure. Due to the above mentioned results, the following discussions will be centered on the lowest doped samples, $Ca_{2.99}RE_{0.01}Co_4O_9$, as they show the best thermoelectric properties when evaluated by the PF (see Table 2).

When considering the effect of temperature on the evolution of electrical resistivity, for the undoped and 0.01 rare earth doped samples, shown in Fig. 4, all curves reflect a slope change at about 400 °C, from semiconducting-like ($dp/dT \leq 0$) to metallic-like ($dp/dT \geq 0$) behaviour, typical characteristic in sintered materials [34]. The 0.01 substituted samples show very similar room temperature resistivities (about 17 m Ω .cm), which are lower than the measured on the undoped ones (~ 21 m Ω .cm). Moreover, these values are around the best values obtained in 0.1 Dy or Er substituted $Ca_3Co_4O_9$ samples (~ 14 m Ω .cm) [35] and lower than the measured

in 0.3 Gd, 0.2 Er, and 0.2 Tb substituted samples (20, 40, and 36 mΩcm, respectively) at the same temperature [36,37].

The Seebeck coefficient values, as a function of temperature, for the undoped and 0.01 rare earth doped samples, are shown in Fig. 5. 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 in all cases, showing very similar values for all the samples indicating that rare earth substitution does not affect, in a great extent, the $\text{Ca}_3\text{Co}_4\text{O}_9$ conduction band. On the other hand, Seebeck coefficient values in all samples are the same, except for the 0.01 Tb-doped samples, which is about 3 % higher. In any case, the values can be considered the same in all cases as the difference is in the measurement error range. The Seebeck coefficient values at 800 °C, for the 0.01 doped samples, is higher than the best values obtained for $\text{Ca}_3\text{Co}_4\text{O}_9$ samples consolidated by spark plasma sintering ($\sim 175 \mu\text{V/K}$) at 600 °C [17].

In order to evaluate the thermoelectric performances of the 0.01 doped sintered ceramic materials, variation of power factor with temperature has been calculated from the resistivity and Seebeck coefficient values and displayed in Fig. 6. As it was found in the Seebeck coefficient measurements, PF increases with temperature in all the measured range. In the plot, the undoped samples present the lowest PF values in all the measured range and their increase with temperature possess a lower slope than the observed in the doped samples. On the other hand, the all doped samples possess the same behaviour, except in the case of the Tb-doped samples which show slightly higher PF values in the whole temperature range. When considering PF values at around 50 °C ($\sim$ room temperature), the maximum increase is obtained for the 0.01 Tb-doped samples ($\sim 20\%$ higher than the undoped ones). The highest PF value obtained at 800 °C (around $0.27 \text{ mW/K}^2\cdot\text{m}$) for the 0.01 Tb-doped samples is about 35% higher than the obtained on the undoped samples, and only slightly lower than the reported values at 800 °C using the hot-pressing technique in 0.1 Dy or Er substituted samples (~ 0.38 and $0.31 \text{ mW/K}^2\cdot\text{m}$, respectively) [35] which show much higher density. The improvement produced by rare earth doping in these solid state sintered materials can help to approach their practical applications.

4. Conclusions

This paper demonstrates that $\text{Ca}_3\text{Co}_4\text{O}_9$ thermoelectric materials with small rare earth (Dy, Er, Gd, and Tb) substitutions by Ca (0, 0.01, 0.03, and 0.05) can be produced successfully by the solid state route. It has been determined that all the rare earths produce very similar effects on the thermoelectric phase, which is reflected on a decrease of the electrical resistivity, compared with the undoped samples for samples with 0.01 rare earth doping. On the other hand, the Seebeck coefficient slightly decreases by the rare earth additions. The power factor values increase for small amounts of doping elements, determining the optimal doping level as 0.01 for all the rare earths. The highest PF improvement, around 35%, compared with the undoped samples, has been obtained in 0.01 Tb-doped samples at 800 °C.

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Figure captions

Figure 1. Powder XRD diagrams for the $\text{Ca}_{3-x}\text{Dy}_x\text{Co}_4\text{O}_9$ sintered samples with $x =$ a) 0; b) 0.01; c) 0.03; and d) 0.05. Crystallographic planes have been indicated on the peaks corresponding to the $(\text{Ca,Dy})_3\text{Co}_4\text{O}_9$ phase. Other peaks indicated by symbols correspond to: * $(\text{Ca,Dy})_3\text{Co}_2\text{O}_6$ phase, and • Si (111) peak used as reference.

Figure 2. Scanning electron micrographs from longitudinal polished sections of $\text{Ca}_{3-x}\text{Tb}_x\text{Co}_4\text{O}_9$ sintered samples with $x =$ a) 0; b) 0.01; c) 0.03; and d) 0.05. The different phases in the micrographs are: #1 pure $\text{Ca}_3\text{Co}_4\text{O}_9$; #2 $\text{Ca}_3\text{Co}_2\text{O}_6$ with different Tb amounts; and #3 Tb substituted $\text{Ca}_3\text{Co}_4\text{O}_9$.

Figure 3. Mean apparent density values, together with their standard error, obtained as a function of the doping amount for each of the rare earths: ● Dy; ▲ Er; ▼ Gd; and ■ Tb.

Figure 4. Temperature dependence of the electrical resistivity for $\text{Ca}_{2.99}\text{RE}_{0.01}\text{Co}_4\text{O}_9$ sintered samples for RE= ● Dy; ▲ Er; ▼ Gd; and ■ Tb. The undoped samples, shown as reference are indicated by ◆.

Figure 5. Temperature dependence of the Seebeck coefficient measured in $\text{Ca}_{2.99}\text{RE}_{0.01}\text{Co}_4\text{O}_9$ sintered samples for RE= ● Dy; ▲ Er; ▼ Gd; and ■ Tb. The undoped samples, shown as reference are indicated by ◆.

Figure 6. Temperature dependence of the power factor determined in $\text{Ca}_{2.99}\text{RE}_{0.01}\text{Co}_4\text{O}_9$ sintered samples for RE= ● Dy; ▲ Er; ▼ Gd; and ■ Tb. The undoped samples, shown as reference are indicated by ◆.

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