Improvement of thermoelectric properties in $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramics by Ba doping

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Abstract

$\text{Ca}_{3-x}\text{Ba}_x\text{Co}_4\text{O}_9$ bulk polycrystalline thermoelectric ceramics with $x=0.00, 0.01, 0.03$ and 0.05 have been prepared through a classical solid state method. Microstructural characterizations of sintered samples have shown that Ba has been incorporated into the $\text{Ca}_3\text{Co}_4\text{O}_9$ and/or $\text{Ca}_3\text{Co}_2\text{O}_6$ structures and that no Ba-based secondary phases have been produced. The apparent density values increase when the amount of barium is raised with respect to the undoped samples, reaching a maximum value of around 77 % of the $\text{Ca}_3\text{Co}_4\text{O}_9$ theoretical density, for samples with the highest amount of barium. Electrical resistivity of doped samples decreases in the whole measured temperature range with respect to the undoped ones, while Seebeck coefficient remains practically unchanged. In conclusion, the improvement in resistivity leads to power factor values which are higher than the ones measured in undoped samples, fact which makes this bulk polycrystalline compound a promising candidate for high-temperature power generation applications in oxidative environments.

Keywords: Thermoelectric cobaltites; Doping; Solid state synthesis; Electrical properties; Power factor.

1. Introduction

Thermoelectric (TE) materials can directly transform a temperature gradient into electrical power, due to the well-known Seebeck effect. The conversion efficiency of such materials is usually quantified by the dimensionless figure of merit, $ZT = TS^2/\rho\kappa$ (in which the electrical part S^2/ρ is known as power factor, PF), where S is the Seebeck coefficient, ρ the electrical resistivity, κ the thermal conductivity and T the absolute temperature [1]. This type of direct solid-state energy-conversion has focused attention on this type of materials in recent years, as they can be used in high-temperature applications like waste heat recovery devices [2] or solar thermoelectric generators [3]. Furthermore, they can also be used as heating/refrigeration devices [4].

Taking into account the above ZT expression, a high-performance thermoelectric material should possess a large Seebeck coefficient, together with low electrical resistivity and low thermal conductivity. Furthermore, the absolute working temperature should be as high as possible to increase ZT values. Low electrical resistivity is necessary to minimize Joule heating, while a low thermal conductivity helps to maintain a large temperature gradient between the hot and cold sides in a thermoelectric device, raising its performances.

Nowadays, TE devices based on intermetallic compounds, such as Bi_2Te_3 or CoSb_3 , with high ZT values, are industrially used at relatively low temperatures, for example in vehicles exhaust. However, they cannot be applied in devices working at high temperatures under air due to the degradation and/or evaporation of heavy metals. These temperature limitations found in classical thermoelectric materials applications were overcome by the discovery, in 1997, of attractive TE properties in $\text{Na}_2\text{Co}_2\text{O}_4$ ceramics [5]. From this discovery, many works have been performed on the CoO-based ceramic families as promising thermoelectric materials for high temperature applications in oxidative environments, such as Bi-AE-Co-O (AE: alkaline earth) [6-8], and the very promising $\text{Ca}_3\text{Co}_4\text{O}_9$ compound [9,10].

Crystallographic studies performed on those CoO-based materials have demonstrated that they are intrinsically nanostructured. Moreover, they can be described by a monoclinic structure which is, in turn, composed of two different alternatively-stacked layers (along the c -axis), which have the same lattice parameters, except for the b -axis lengths, which are different (hence the misfit characteristic of these TE cobaltites) [11,12]. The triple distorted insulating rock salt-type (RS) $[\text{Ca}_2\text{CoO}_3]$ layer is regarded as the first subsystem, while the common conductive hexagonal CdI_2 -type $[\text{CoO}_2]$ layer is regarded as the second one. The misfit (incommensurability) ratio is given by the two different b -axis

lengths (b_1/b_2). Furthermore, it has also been found that the Seebeck coefficient values are governed by the incommensurability ratio and/or the charge of the RS-type block layers between the $[\text{CoO}_2]$ ones [13]. This is the basis for the modification of thermoelectric properties of a given material via chemical substitutions, such as Sb^{3+} for Ca^{2+} in $\text{Ca}_3\text{Co}_4\text{O}_9$ [14], or Pb^{2+} for Bi^{3+} in $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ or $\text{Bi}_2\text{Ca}_2\text{Co}_{1.7}\text{O}_x$ [15-17]. On the other hand, electrical resistivity improvements can be produced by metallic Ag additions, where an increase on the materials performances is produced by raising the electrical connectivity between the grains [18,19].

As it is well-known, the high crystallographic anisotropy of these materials leads to the formation of plate-like grains, growing along the ab plane, during the sintering processes. This shape anisotropy opens the route to preferentially align the grains by different methods. Such processes should allow the alignment of the conducting and large ab planes, leading to macroscopic properties of polycrystalline samples comparable to those obtained in single crystals. Numerous methods have been reported to be efficient in producing well-aligned grains in bulk materials, in these or in similar anisotropic systems, such as hot uniaxial pressing [20,21], spark plasma sintering (SPS) [22,23], microwave texturing [24], laser floating zone melting (LFZ) [25-27], electrically assisted laser floating zone (EALFZ) [28,29], templated grain growth (TGG) [30], *etc.* The main advantage of these techniques is the production of materials with very low electrical resistivity values, due to the alignment of conducting planes with the current-flow direction. On the other hand, they possess some drawbacks, as the high price of SPS device and the relatively long processing time of the hot uniaxial pressing or the TGG. In the case of the processes involving samples melting, it has been reported that the electrical properties strongly depend on the growth rate [24,27,31-33].

The aim of this work is to study the effect of small amounts of Ba for Ca substitution on the microstructure and high-temperature thermoelectric properties of $\text{Ca}_{3-x}\text{Ba}_x\text{Co}_4\text{O}_9$ ceramics, prepared through a simple method, as the classical solid state route. The structural and microstructural modifications produced by the Ba incorporation in the crystal structure will be related with the changes on the thermoelectric performance.

2. Experimental

$\text{Ca}_{3-x}\text{Ba}_x\text{Co}_4\text{O}_9$ polycrystalline ceramic materials, with $x = 0.00, 0.01, 0.03$ and 0.05 , were prepared through a conventional solid state synthesis. Stoichiometric amounts of CaCO_3 (Aldrich, ≥ 99

%), BaCO₃ (Panreac, 98 %), and CoO (Panreac, 99.5 %) commercial powders were used as precursors. They were weighed in the appropriate proportions, well-mixed and ball-milled for 30 minutes at 300 rpm, using an agate ball mill and acetone media. The obtained slurry has been heated under infrared radiation until all the acetone has been evaporated. The dry mixture was then manually ground in order to avoid the presence of agglomerates in the next steps. After milling, the homogeneous mixture was thermally treated at 750 and 800°C for 12h in air, with an intermediate manual milling in order to assure the total decomposition of carbonates, as reported previously [10]. The resulting 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 the adequate size for their thermoelectric characterization. These green ceramics were subsequently sintered in the optimal conditions found in previous works, consisting in one step heating at 900 °C for 24 h with a final furnace cooling [10].

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 the Ca₃Co₄O₉ theoretical density [34].

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). Moreover, several micrographs of each sample have been used to analyze the different phases and their distribution. The oxygen content has been determined through cerimetric titrations, in order to obtain the mean cobalt valence (Co³⁺+Co⁴⁺) in the conductive [CoO₂] layers, at room temperature, following the procedure described in previous works [35].

The 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 temperatures ranging from 50 to 800 °C under He atmosphere. Using the resistivity values, the activation energy for each sample has been estimated. Moreover, with the electrical resistivity and Seebeck coefficient data, PF 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.

3. Results and discussion

Powder XRD patterns for the different $\text{Ca}_{3-x}\text{Ba}_x\text{Co}_4\text{O}_9$ samples are displayed in Fig. 1 (from 5 to 40° for clarity). From these data, it is clear that all the samples exhibit very similar diffraction patterns. In Fig. 1a, corresponding to the undoped samples, major peaks are associated to the thermoelectric $\text{Ca}_3\text{Co}_4\text{O}_9$ phase, indicated by its reflection planes, in agreement with previously reported data [36]. When Ba is added, some new peaks appear (shown by * in Fig. 1d), indicating the $\text{Ca}_3\text{Co}_2\text{O}_6$ phase formation [36]. On the other hand, careful observations of these diffractograms show that there are no Ba-containing secondary phases, which is a clear indication that Ba has entered 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. However, this Ba incorporation into the two structures has no noticeable effect on the 2θ angles at which the cobaltite peaks appear, probably due to the very small amounts of Ba used in this work.

Fig. 2 shows representative SEM micrographs performed on the surfaces of $\text{Ca}_{3-x}\text{Ba}_x\text{Co}_4\text{O}_9$ samples, with $x = 0.00$ (Fig. 2a), 0.01 (Fig. 2b), 0.03 (Fig. 2c) and 0.05 (Fig. 2d). In the figure, it can be clearly seen that the porosity, indicated by the black contrast, seems to be slightly decreased when barium content is raised. This porosity evolution can be explained when observing the CaO-CoO [37] and $\text{BaCO}_3\text{-CaCO}_3$ [38] equilibrium phase diagrams and the melting point of the barium carbonate (811°C). In these diagrams, the CaO-CoO system eutectic point is found at $\sim 1350^\circ\text{C}$, which is far higher than the sintering temperature used for the $\text{Ca}_{3-x}\text{Ba}_x\text{Co}_4\text{O}_9$ samples (900°C). On the other hand, the temperature of $\text{BaCO}_3\text{-CaCO}_3$ eutectic point (800°C) and the melting temperature of the barium carbonate (811°C) are lower to that used for the sintering process (900°C). Therefore, this situation might have promoted the formation of a small amount of liquid phase, which could have helped the densification process during sintering process and establish a better connectivity between the grains. As a consequence, the samples density is expected to slightly rise with increasing contents of barium.

The EDS analyses have shown that the undoped samples are mainly composed by the $\text{Ca}_3\text{Co}_4\text{O}_9$ phase (grey contrast in Fig. 2a). In Ba-doped samples, major phase was also found to be the $\text{Ca}_3\text{Co}_4\text{O}_9$ one, accompanied by small amounts of $(\text{Ca}+\text{Ba})_3\text{Co}_2\text{O}_y$ (slightly darker grey contrast in Figs. 2b-d), fact which suggests that Ba^{2+} ions have mainly entered into the $\text{Ca}_3\text{Co}_2\text{O}_y$ structure, substituting the calcium ions in the $[\text{Ca}_2\text{CoO}_3]$ RS-type layers. Moreover, SEM-EDS results agree with the powder XRD ones, discussed previously, which showed a slight increase of the $\text{Ca}_3\text{Co}_2\text{O}_y$ phase content in the Ba-doped samples.

Typical features of the classical solid-state synthesis route can also be distinguished in the representative micrographs displayed in Fig. 2, where the morphology of the grains can also be seen. In the figure, it is clear that all the samples are composed by randomly-oriented plate-like grains of different sizes and that barium substitution do not seem to modify the grains morphology. The mean grain-sizes have been estimated using image analysis for all samples. It has been found that they are in the range of ~ 1 to $5\ \mu\text{m}$, in the planar dimension (crystallographic a - b plane) and $\sim 0.5\ \mu\text{m}$ in thickness (along the c -axis), in agreement with other works found in the literature [39-41]. On the other hand, the apparent thickness along the c -axis is given by the stacking of very-thin plate-like grains of $\text{Ca}_3\text{Co}_4\text{O}_9$, each one having a thickness of around 35 nm, estimated for similar layered cobalt oxides using Scherrer's formula [42]. This fact confirms that the preferential crystal-growth is produced along the a - b crystallographic plane.

As mentioned previously in the SEM-EDS section, the doped samples seemed to have lower porosity than the undoped ones. In order to confirm these observations, apparent density measurements have been performed on at least three samples for each composition and the results are shown in Fig. 3. As can be observed in the figure, these determinations have been shown to be very reproducible as the mean standard error has only been ± 0.01 . Moreover, the density values of all the doped samples are higher than that of the undoped ones, slightly increasing when Ba-content is raised. When considering the relationship of the obtained values with the theoretical density of the $\text{Ca}_3\text{Co}_4\text{O}_9$ compound (ρ_{th}), the calculated mean apparent densities for these samples are ranging from $\sim 72\ \% \rho_{th}$, for the undoped, to $\sim 77\ \% \rho_{th}$, for the 0.05 Ba-doped ones. This evolution of the apparent density indicates that the small substitutions performed in this work were successful for improving the densification process during sintering, probably due to the formation of a liquid phase which could have helped the densification process.

The variation of the Seebeck coefficient with the temperature for all Ba-doped samples can be seen in Fig. 4. In the plot, it can be clearly seen that S is positive in the whole measured-temperature range, which confirms a conduction mechanism mainly governed by holes. Furthermore, the values of the Seebeck coefficient for all samples are very close and increase almost linearly with the temperature. The approximately linear dependence of the Seebeck coefficient with temperature could be associated with the typical behavior of a metallic compound described by the expression [43]:

$$S \approx \frac{\pi^2 k_B^2 T}{e E_F}, \quad (\text{Eq. 1})$$

where E_F is the energy of electrons at the Fermi level, k_B the Boltzmann constant, e the electron charge and T the absolute temperature. All the samples roughly present the same S values at room temperature, fact which can be explained by the isovalent nature of the substitution, and confirmed by the cerimetric titrations, which gave a mean cobalt valence of around 3.11 in all cases. Usually, the increase in S can be attributed to a lower fraction of Co^{4+} in the conducting CdI_2 -type $[\text{CoO}_2]$ layer [44] of $\text{Ca}_3\text{Co}_4\text{O}_9$, as given by the modified Heikes formula [45], which expresses the high-temperature thermoelectric power. All the doped samples, especially the 0.01 and the 0.05 Ba-doped ones, present slightly higher S values after around 500 °C, fact which can probably be explained by the fact that the Seebeck coefficient values are affected by subtle changes in the electronic structure of the conducting $[\text{CoO}_2]$ layers. These changes could be associated to modifications of the cell parameters (very small ones due to the low amounts of Ba, and not detected in this work), when a bigger divalent alkaline-earth ion substitutes the smaller Ca^{2+} ones in the $\text{Ca}_3\text{Co}_4\text{O}_9$ compound [46,47]. For the same type of Ba-doped samples, the higher S values could also be explained by the increase in the effective mass of charge carriers [46]. It has been reported that the electronic specific heat could also contribute to increase S , due to the doping-induced distortion of the electronic density of states [48], which can affect the conduction mechanism of this compound.

The obtained values for the Ba-doped samples at room temperature ($\sim 134 \mu\text{V/K}$) are very similar to others found in the literature, for 0.2 Ba-doped bulk $\text{Ca}_3\text{Co}_4\text{O}_9$ samples, fabricated by a citrate acid sol-gel and SPS method, at the same temperature [49]. Furthermore, all the values obtained at room temperature are slightly higher than those reported elsewhere ($\sim 125 \mu\text{V/K}$), at the same temperature, for undoped $\text{Ca}_3\text{Co}_4\text{O}_9$ samples obtained through different methods [41,50]. On the other hand, the highest value of the Seebeck coefficient ($\sim 210 \mu\text{V/K}$) obtained at 800 °C for the 0.01 Ba-substituted samples is significantly higher (27 %) than the one obtained for the 0.2 Ba-doped bulk samples, fabricated by a citrate acid sol-gel method and SPS processed, at $\sim 727 \text{ °C}$ ($\sim 165 \mu\text{V/K}$) [49]. In any case, the relatively similar values obtained for all the Ba-doped samples in all the measured-temperature range indicate that small substitutions of Ba do not affect, in a great extent, the conduction band of the bulk $\text{Ca}_3\text{Co}_4\text{O}_9$ samples.

The temperature dependence of the electrical resistivity, as a function of the Ba-content, is shown in Fig. 5. As it can be seen in this graph, between room-temperature to around 420 °C, all the $\text{Ca}_{3-x}\text{Ba}_x\text{Co}_4\text{O}_9$ samples show a semiconducting-like behavior ($dp/dT < 0$), followed by a metallic-like one

($dp/dT > 0$) at higher temperatures. The electrical resistivity values of all doped samples are lower than those of the undoped ones, in all the measured temperature range, and increase from the 0.01 to the 0.03 Ba-doped samples, slightly decreasing for the 0.05 Ba-doped ones.

As it was previously reported for this type of materials, the charge transport process in the semiconducting regime is represented by a thermally-activated hole hopping mechanism from Co^{4+} to Co^{3+} [51], while in the metallic one the charge carriers are transported in the valence or conduction bands [52]. The resistivity curves from Fig. 5 can be explained by the highly anisotropic properties of the $\text{Ca}_3\text{Co}_4\text{O}_9$ compound, which is known to exhibit a metallic-like behavior in the crystallographic a - b plane and a semiconducting-like one along the c -axis [53]. The behavior shown by all the electrical resistivity curves is the typical one of an extrinsic semiconductor in the saturation area and is in agreement with the linear evolution of the Seebeck coefficient with temperature, explained previously. Furthermore, as Ca^{2+} and Ba^{2+} are isovalent, the resistivity values measured for the doped samples are expected to be almost identical with the ones of the undoped samples. On the other hand, it has been reported that this type of substitution can induce lattice distortions (due to different ionic radii), which are anisotropic, due to the misfit nature of this compound. In other words, the change in the b_2 -axis (corresponding to the $[\text{Ca}_2\text{CoO}_3]$ layer) is considerably larger than the one in the b_1 -axis (corresponding to the $[\text{CoO}_2]$ layer). The resulting interfacial incompatibility, developed between the conductive and insulating layers, would create an induced in-plane stress which, in turn, could change the bond angle between the Co-O bond pairs in the conductive $[\text{CoO}_2]$ layers. This situation can lead to a decrease in the effective mass of the charge carriers [46,54], therefore qualitatively explaining the low resistivity values of all the doped samples, with respect to the undoped ones.

Furthermore, the low resistivity values of all the doped samples, with respect to the undoped ones, are in agreement with the apparent density values discussed earlier, which showed that all the doped samples have slightly higher values, than the undoped ones. This fact suggests that, for the Ba-doped samples, a slightly better grain-connectivity could also contribute to the lower resistivity values measured in all the doped samples.

The lowest measured room temperature resistivity value ($\sim 15.8 \text{ m}\Omega\text{cm}$, for the 0.01 Ba-substituted samples) is around the best ones obtained for $\text{Ca}_3\text{Co}_4\text{O}_9$ samples produced by more sophisticated methods, like, for example, spark plasma sintering ($15\text{-}18 \text{ m}\Omega\text{cm}$) [38], or solution synthesis ($\sim 16 \text{ m}\Omega\text{cm}$) [10], and about 15 % lower than the undoped samples prepared in this work.

From the measured resistivity values, the activation energy for the different $\text{Ca}_{3-x}\text{Ba}_x\text{Co}_4\text{O}_9$ samples has been estimated and compared with the one of the undoped samples, in the semiconductor-like behaviour regime, in which the temperature dependence of electrical conductivity can be described as:

$$\sigma T \propto \exp(-E/k_B T), \quad (\text{Eq. 2})$$

where E , k_B , and T are the activation energy, Boltzmann constant, and absolute temperature, respectively. The activation energy values are obtained from the $\ln(\sigma T)$ versus $1/T$ plots (not shown), as the curve fit slopes below T^* , the semiconducting-to-metallic transition temperature. T^* is clearly indicated in the different $\ln(\sigma T)$ versus $1000/T$ Arrhenius plots illustrated in Fig. 6, in which the curve fit slopes (linear fits are guides for eyes) from the metallic-like behavior regime are also shown, for a clearer determination of T^* .

In Fig. 6, it is clear that T^* corresponds to the transition temperature found in the resistivity curves and that the slopes of the fittings below it are nearly identical in all cases. The calculated activation energy values were found to be 36 meV for the undoped samples, and 38, 39, and 40 meV for the 0.01, 0.03, and 0.05 Ba-doped ones, respectively. These values indicate that Ba substitution has an almost negligible influence on the hopping process activation energy. All these points clearly agree with the determined electrical resistivity values discussed previously.

In order to evaluate the thermoelectric performances of these materials, PF has been calculated from the Seebeck coefficient and electrical resistivity data, and plotted in Fig. 7. As it was expected, the PF values of Ba-doped samples are higher than the ones of the undoped ones, due to the improvements in electrical resistivity. The maximum PF values are obtained for the 0.01 Ba-doped samples, in the whole measured temperature range. On the other hand, the 0.03 and 0.05 Ba-doped samples show slightly lower PF values, with respect to the 0.01 Ba-doped ones, due to their higher electrical resistivity. The highest PF value at 800 °C ($\sim 0.28 \text{ mW/K}^2\text{m}$) for the 0.01 Ba-doped samples is about 40 % higher than the obtained for the undoped ones ($\sim 0.20 \text{ mW/K}^2\text{m}$). Furthermore, the room temperature values are 22 % (for the 0.01 Ba-doped samples) and 11 % (for the 0.03 and 0.05 Ba-doped ones) higher than the ones obtained in the pure ones.

4. Conclusions

In this work, $\text{Ca}_{3-x}\text{Ba}_x\text{Co}_4\text{O}_9$ polycrystalline samples with $x=0.00, 0.01, 0.03$ and 0.05 were successfully synthesized through the classical solid-state route. It has been found that barium has mainly entered into the crystal structure of $\text{Ca}_3\text{Co}_2\text{O}_6$, substituting the Ca^{2+} cations in the RS-type layers. The apparent density values of all the doped samples are higher than the measured in undoped ones, progressively increasing from the 0.01 to 0.05 Ba-containing samples, probably due to the formation of a small amount of liquid phase during sintering, which could have helped the densification process. PF values were found to increase from the undoped samples to the ones with 0.01 Ba. For samples with 0.03 and 0.05 Ba, the PF values slightly decrease with respect to the 0.01 Ba-doped ones, due to the higher electrical resistivity values found in these samples. In any case, the PF values of all the doped samples are higher than of the undoped ones, due to the improvements in electrical resistivity, mainly caused by their higher density. The optimal Ba^{2+} for Ca^{2+} substitution was established to be 0.01, using the highest PF values obtained at 50 and 800 °C, ~ 0.11 and $\sim 0.28 \text{ mW/K}^2\text{m}$, respectively, which are between 20 and 40 % higher than the ones obtained in undoped samples.

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Figure captions:

Fig. 1 Powder X-ray diffraction patterns of $\text{Ca}_{3-x}\text{Ba}_x\text{Co}_4\text{O}_9$ samples, with $x = 0.00$ (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 those marked with *asterisk* (*) belong to the $\text{Ca}_3\text{Co}_2\text{O}_6$ one.

Fig. 2 SEM micrographs of representative longitudinal polished sections of $\text{Ca}_{3-x}\text{Ba}_x\text{Co}_4\text{O}_9$ samples, with $x=0.00$ (a), 0.01 (b), 0.03 (c) and 0.05 (d).

Fig. 3 Apparent density values of $\text{Ca}_{3-x}\text{Ba}_x\text{Co}_4\text{O}_9$ samples, together with their standard errors, as a function of the Ba-content.

Fig. 4 Temperature dependence of the Seebeck coefficient for $\text{Ca}_{3-x}\text{Ba}_x\text{Co}_4\text{O}_9$ samples, with $x=0.00$ (*filled circle*), 0.01 (*filled square*), 0.03 (*filled diamond*) and 0.05 (*filled triangle*).

Fig. 5 Temperature dependence of the electrical resistivity for $\text{Ca}_{3-x}\text{Ba}_x\text{Co}_4\text{O}_9$ samples, with $x=0.00$ (*filled circle*), 0.01 (*filled square*), 0.03 (*filled diamond*) and 0.05 (*filled triangle*).

Fig. 6 Modified Arrhenius plots ($\ln(\sigma T)$ versus $1000/T$) for $\text{Ca}_{3-x}\text{Ba}_x\text{Co}_4\text{O}_9$ samples, with $x=0.00$ (*filled circle*), 0.01 (*filled square*), 0.03 (*filled diamond*) and 0.05 (*filled triangle*). The slopes of the fittings below T^* are nearly the same in all cases. T^* indicates the metallic-to-semiconducting transition temperature.

Fig. 7 Temperature dependence of the power factor for $\text{Ca}_{3-x}\text{Ba}_x\text{Co}_4\text{O}_9$ samples, with $x=0.00$ (*filled circle*), 0.01 (*filled square*), 0.03 (*filled diamond*) and 0.05 (*filled triangle*).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7