Effect of Ga addition on Ca-deficient $\text{Ca}_3\text{Co}_4\text{O}_y$ thermoelectric materials

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Abstract

$\text{Ca}_{3-x}\text{Ga}_x\text{Co}_4\text{O}_y$ polycrystalline thermoelectric ceramics with small amounts of Ga have been synthesized by the classical solid state method. XRD data have shown that all the Ga has been incorporated into the $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_3\text{Co}_2\text{O}_6$ thermoelectric phases and no Ga-containing secondary phases have been produced. Moreover, for Ga contents ≥ 0.07 , the $\text{Ca}_3\text{Co}_2\text{O}_6$ phase disappears. Apparent density measurements have revealed that all samples are very similar, with densities around 70 % of the theoretical one. Electrical resistivity decreases in all Ga-doped samples, compared with the pure ones, while Seebeck coefficient is practically the same for all samples, except for the 0.12 and 0.15 Ga substituted ones, at high temperatures which present slightly higher values. Both factors in the 0.15 Ga-substituted samples lead to power factor values around $0.35 \text{ mW/K}^2\text{m}$ at 800°C which is about 70 % higher than the obtained for the undoped samples.

Keywords: Powders: solid state reaction; Sintering; Platelets; Electrical properties; Thermopower.

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1. Introduction

Thermoelectric (TE) materials possess the ability to transform, without mobile elements, a temperature difference to electrical power due to the well-known Seebeck effect. The conversion efficiency of these materials is quantified by a dimensionless coefficient called the figure-of-merit, ZT . This parameter 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 [1]. Nowadays, these materials are attracting interest in order to be used in several applications as waste heat recovery devices [2] or solar thermoelectric generators [3] due to the global warming problem. Furthermore, they can also be used as heating/refrigeration devices [4].

At present, the practical applications of TE devices based on intermetallic materials, such as Bi_2Te_3 , with high ZT values, involve heat harvesting in relatively low temperature environments, e.g. in vehicles exhaust. However, due to their degradation under air at high working temperatures, they cannot be applied in devices working in such conditions. As a consequence some of the most important sources of wasted heat (for example, thermal power stations) cannot be used. These temperature limitations were overcome by the discovery of attractive thermoelectric properties in $\text{Na}_2\text{Co}_2\text{O}_4$ ceramics [5]. Since the discovery of this thermoelectric oxide, much work has been performed on the cobalt-based ceramics as promising thermoelectric materials for high temperature applications. The intense research work devoted on those ceramics led to the discovery and optimization of new compositions, such as

$\text{Ca}_3\text{Co}_4\text{O}_9$ [6,7] $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_x$ [8,9], $\text{Bi}_2\text{Ca}_2\text{Co}_2\text{O}_x$ [10,11] and $\text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_x$ [12,13] with interesting thermoelectric properties and high working temperatures.

Crystallographic studies performed on those Co-based materials have demonstrated that they possess a monoclinic structure which is, in turn, composed of two different layers. These layers show an alternate stacking of a common conductive CdI_2 -type hexagonal CoO_2 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 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 [14]. The high structural anisotropy of these materials, together with their preferential growth habit through the ab plane, leads to the formation of plate-like grains during the crystallisation process. This shape anisotropy opens the route to preferentially align the grains using physical, mechanical and/or chemical processes. Such processes should allow the alignment of the conducting planes which could allow reaching macroscopic properties comparable to those obtained on single crystals. Numerous methods have been reported to be efficient to produce well aligned bulk materials, in these or in similar anisotropic systems, such as hot uniaxial pressing [15], templated grain growth (TGG) [16], spark plasma sintering [17], microwave texturing [18], laser floating zone melting (LFZ) [19], electrically assisted laser floating zone [20], *etc.* On the other hand, these methods possess some drawbacks due to different factors, as the relatively long treatments required for the first two ones, or the high costs associated with the equipment and the strong dependence of thermoelectric properties on the growth or the texturing speeds for the other ones [13,18,21-23].

Another possibility arising from the crystal structure of these materials has been put in evidence in some studies reporting that the Seebeck coefficient values are governed by the incommensurability ratio and/or the charge of the RS block layer between the CoO_2 ones [24]. This characteristic provides the basis for the modification of thermoelectric properties of a given material via chemical substitutions. The most common ones substitute an alkaline-earth by a rare-earth or a semimetal, as Yb or Sb for Ca in $\text{Ca}_3\text{Co}_4\text{O}_9$ [25,26], or Co by another transition metal, as Cu or Cr for Co in $\text{Ca}_3\text{Co}_4\text{O}_9$ [27,28]. Other usual substitutions are Pb for Bi in $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ or $\text{Bi}_2\text{Ca}_2\text{Co}_{1.7}\text{O}_x$ [29-31], or metallic Ag additions in $\text{Ca}_3\text{Co}_4\text{O}_9$ or $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ [32,33].

The aim of this work is to study the effect of Ga addition, in Ca-deficient $\text{Ca}_3\text{Co}_4\text{O}_y$ samples ($\text{Ca}_{3-x}\text{Ga}_x\text{Co}_4\text{O}_y$), on the microstructural, electric and thermoelectric characteristics of sintered bulk materials when they are prepared by the classical solid state synthesis route.

2. Experimental

$\text{Ca}_{3-x}\text{Ga}_x\text{Co}_4\text{O}_y$ polycrystalline ceramic materials, with $x = 0.00, 0.01, 0.03, 0.05, 0.07, 0.10, 0.12, 0.15$, and 0.17 , were prepared by the conventional solid state route using commercial CaCO_3 (Panreac, 98 + %), Co_2O_3 (Aldrich, 98 + %), and Ga_2O_3 (Aldrich, 99.9 %) 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. Then, the slurry was heated in a rapid evaporation system under infrared radiation until all the acetone was evaporated. The dry mixture was manually milled and thermally treated twice at 750 and 800°C for 12h under air, with an intermediate manual grinding in order

to assure the total decomposition of calcium carbonate, as reported previously [7]. After thermal treatment, the powders were uniaxially pressed at 400 MPa for 1 minute in order to obtain green tetragonal ceramic bodies (~ 3 mm x 3 mm x 14 mm), with an adequate size and shape for their thermoelectric characterization. These materials were subsequently sintered in the optimal conditions for this system, consisting in one step heating at 910 °C for 24 h with a final furnace cooling.

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 α radiation.

Microstructural observations were performed on longitudinal polished and fractured surfaces of the samples, using a Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss Merlin) fitted with an energy dispersive spectrometry (EDS) device. Several representative micrographs have been used to analyze the different phases content and their distribution. Moreover, apparent density measurements have been performed on several samples for each composition after sintering, using 4.677 g/cm³ as theoretical density [34]. 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. 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 room temperature ($\sim 50\text{ }^{\circ}\text{C}$), where oxygen diffusion is negligible, to avoid the influence of the atmosphere on the compared values.

3. Results and discussion

Powder XRD patterns for some of the $\text{Ca}_{3-x}\text{Ga}_x\text{Co}_4\text{O}_y$ samples are displayed in Fig. 1 (from 5 to 40° for clarity). These plots show the general evolution of the samples with Ga doping, indicating that all the samples have very similar diffraction patterns with small differences. In all samples the highest peaks are associated to the thermoelectric $\text{Ca}_3\text{Co}_4\text{O}_9$ phase, indicated by the reflection planes in Fig. 1d, in agreement with previously reported data [35]. In this figure, it has also been indicated the peak at around 28.65 degrees (#) which corresponds to the (111) diffraction plane of Si used as internal reference. On the other hand, some peaks, belonging to the $\text{Ca}_3\text{Co}_2\text{O}_6$ phase [35], appear (identified by * and the diffraction planes in Fig 1b) in the undoped sample. The intensity of these peaks is reduced when Ga is added, disappearing for Ga contents of 0.07 . This is a clear indication that Ga addition reduces the amount of secondary phases and leads to the production of nearly single $\text{Ca}_3\text{Co}_4\text{O}_9$ phase. On the other hand, no Ga-based secondary phases have been found in the XRD diagrams indicating that all added Ga has been incorporated in the $\text{Ca}_3\text{Co}_4\text{O}_9$ structure.

SEM micrographs performed on representative polished (a-c) and fractured (d) sections of some of the samples are presented in Fig. 2. In the figure, it can be clearly seen that all samples are composed by randomly oriented plate-like grains with similar sizes. When observing the samples in more detail, it has

been found that major phase is the thermoelectric $\text{Ca}_{3-x}\text{Ga}_x\text{Co}_4\text{O}_y$ one (grey contrast, #1) which can be observed as well defined plate-like grains. Ga-free $\text{Ca}_3\text{Co}_2\text{O}_6$ secondary phase (#2) can be also seen in Fig. 2a as a slightly darker grey contrast with different shape. This phase disappears for Ga contents ≥ 0.07 and, as a consequence, it cannot be observed in the other micrographs (see Fig. 2b and c). This microstructural evolution is in clear agreement with the above discussed XRD data. Finally, for high Ga contents, ≥ 0.17 , a new phase appears as dark grey contrast (#3 in Fig. 2c) corresponding to CoO with very small amounts of Ca and Ga. This phase has not been observed in the XRD plots due to its small amount ($< 1\%$) for this Ga substitution level. As indicated previously, the samples are mainly composed by randomly oriented plate-like grains. This is illustrated in Fig. 2d where a representative fractured surface of the pure sample is shown. Other feature which can be observed in these micrographs is that the porosity in the samples does not appreciably change with the Ga addition. This effect is due to the fact that the temperature stability range for this compound (peritectoid point at $\sim 925^\circ\text{C}$) is far from the melting point ($\sim 1350^\circ\text{C}$ associated to an eutectic point), as observed in previous works [27].

In order to determine the effect of Ga content on the density of the bulk sintered materials, 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 mean density values have shown a good reproducibility as the calculated standard error was determined to be $\pm 0.01 \text{ g/cm}^3$ in all cases. The density for all samples has been very similar, around 3.30 g/cm^3 , which corresponds to about 70 % of the theoretical

density of $\text{Ca}_3\text{Co}_4\text{O}_9$ phase. These results are in agreement with the SEM observations discussed previously which showed no evident difference on the porosity of the different samples.

Fig. 3 shows the variation of the Seebeck coefficient with the temperature, as a function of the Ga addition. 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, except for the 0.12 and 0.15 Ga which show a slightly higher value than the other samples at higher temperatures ($> 600\text{ }^\circ\text{C}$). The maximum Seebeck coefficient value ($\sim 220\text{ }\mu\text{V/K}$) obtained in this work at $800\text{ }^\circ\text{C}$ is significantly higher than the best values obtained for $\text{Ca}_3\text{Co}_4\text{O}_9$ samples consolidated by spark plasma sintering ($170\text{--}175\text{ }\mu\text{V/K}$) at about $625\text{ }^\circ\text{C}$ [36].

The temperature dependence of electrical resistivity, as a function of the Ga content, is shown in Fig. 4. The $\rho(T)$ curves show a decrease of resistivity when Ga is added, compared with the undoped samples. The curves show a semiconducting-like ($d\rho/dT < 0$) behaviour, from room temperature to around $350\text{ }^\circ\text{C}$ for samples with small Ga content (≤ 0.05), changing to a metallic-like one at higher temperatures. Samples with higher Ga content seem to progressively lose their semiconducting-like behaviour, with a slope change in the curves at around $350\text{ }^\circ\text{C}$. In all the doped samples, room temperature resistivity values decrease significantly (up to $\sim 50\%$ of the undoped one resistivity). In any case, the lowest measured room temperature resistivity values ($\sim 11\text{ m}\Omega\cdot\text{cm}$ for the ≥ 0.07 Ga-substituted samples) is lower than the best values obtained for $\text{Ca}_3\text{Co}_4\text{O}_9$ samples produced by no so simple and

cheap methods. As examples, it can be considered the values obtained in samples consolidated by spark plasma sintering (15-18 mΩ.cm) [36] or produced by solution methods (~ 16 mΩ.cm) [7]. The electrical resistivity evolution can be explained by the increase of Ca₃Co₄O₉ phase content in the samples, together with the disappearance of the Ca₃Co₂O₆ secondary phase, in agreement with the XRD data and SEM observations discussed previously. 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:

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

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. T* is defined as the temperature where the behaviour of the samples changes from semiconducting to metallic one, which is shifting to lower temperatures from the undoped sample (T₁*) to the ≥ 0.07 Ga-substituted ones (T₂*). The calculated activation energies values have shown to be around 40 meV for samples with Ga contents ≤ 0.05, while for the higher doped samples this value is around 32 meV (about 20 % lower). These results agree with all the previously discussed data and confirm that the Ca₃Co₂O₆ secondary phase disappearance, leading to pure Ca₃Co₄O₉ phase samples improves the electrical behaviour of these samples by decreasing activation energy values. Under the assumption that these changes in conductivity are mainly due to variations on the hole concentration, the carrier concentration is clearly increased by Ga addition, as can be easily seen in Fig. 5. The maximum

increase is obtained for the 0.10, 0.12 and 0.15 Ga-doped samples, with values around 80 % higher than for the pure ones, reinforcing the above considerations.

In order to evaluate the thermoelectric performances of these materials, the power factor has been calculated using the data displayed in Figs. 3 and 4 and plotted in Fig. 6. When considering PF values at around 50 °C (~ room temperature), it can be clearly seen that all the Ga-doped samples possess higher PF values than the undoped ones. As it can be observed in the figure, PF values at this temperature are increased with Ga content until they reach the maximum values (~ 0.15 mW/K².m) for Ga contents ≥ 0.07 which is about 65 % higher than the obtained for the undoped samples. The highest PF value obtained in these samples is reached at 800 °C (around 0.34 mW/K².m) for the 0.12 Ga-doped samples and is about 70 % higher than the obtained for the undoped samples. This value is higher than the obtained in samples produced by spark plasma sintering (~ 0.32 mW/K².m) which possess much higher density [36]. The improvement in PF obtained in these samples is mainly due to the important decrease on the electrical resistivity, discussed previously, as all the samples possess practically the same Seebeck coefficient values.

All the obtained data show that optimal Ga additions can significantly improve the thermoelectric performances of Ca₃Co₄O₉ ceramics, thus approaching them for next future practical applications.

4. Conclusions

This paper demonstrates that Ga additions to Ca-deficient Ca₃Co₄O₉ samples can improve their thermoelectric properties. Ga contents ≥ 0.07 lead to the

disappearance of the $\text{Ca}_3\text{Co}_2\text{O}_6$ secondary phase, producing $\text{Ca}_{3-x}\text{Ga}_x\text{Co}_4\text{O}_9$ pure phase samples. This microstructural modification decreases the electrical resistivity of the samples due to the raise on the carrier concentration and diminishing the activation energy values. The optimal Ga addition has been determined using the values of the power factor at 50 and 800 °C, which is maximum for the 0.12 Ga-doped samples with values around 0.15 and 0.34 $\text{mW/K}^2\cdot\text{m}$, respectively, which are about 70 % higher than the obtained for the undoped samples and slightly higher than the values obtained in higher density samples produced by spark plasma sintering.

Acknowledgements

The authors wish to thank the Gobierno de Aragón (Research Groups T12 and T87) for financial support. The technical contributions of C. Estepa, and C. Gallego are also acknowledged. Sh. Rasekh acknowledges a JAE-PreDoc 2010 grant from CSIC.

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Figure captions:

Figure 1. Powder X-ray diffraction patterns obtained for the $\text{Ca}_{3-x}\text{Ga}_x\text{Co}_4\text{O}_y$ samples; $x = 0.00$ (a); 0.05 (b); 0.10 (c); and 0.15 (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 the surface of representative $\text{Ca}_{3-x}\text{Ga}_x\text{Co}_4\text{O}_y$ samples; $x = 0.01$ (a); 0.07 (b); and 0.17 (c). A higher magnification micrograph illustrating the shape and random orientation of the plate-like grains is shown in (d). Grey contrast (#1) corresponds to the $\text{Ca}_{3-x}\text{Ga}_x\text{Co}_4\text{O}_y$ phase; darker grey (#2) to the $\text{Ca}_3\text{Co}_2\text{O}_6$, and the darkest grey (#3) to the CoO ($\text{CaO}, \text{Ga}_2\text{O}_3$) solid solution.

Figure 3. Temperature dependence of the Seebeck coefficient, as a function of Ga content, in $\text{Ca}_{3-x}\text{Ga}_x\text{Co}_4\text{O}_y$ samples, for $x = 0.00$ ($\square$); 0.01 ($\odot$); 0.03 ($\blacktriangle$); 0.05 ($\blacktriangledown$); 0.07 ($\blacklozenge$); 0.10 ($\bullet$); 0.12 ($\blacksquare$); 0.15 ($\blacktriangleright$); and 0.17 ($\blacktriangleleft$).

Figure 4. Temperature dependence of the electrical resistivity, as a function of Ga content, in $\text{Ca}_{3-x}\text{Ga}_x\text{Co}_4\text{O}_y$ samples, for $x = 0.00$ ($\square$); 0.01 ($\odot$); 0.03 ($\blacktriangle$); 0.05 ($\blacktriangledown$); 0.07 ($\blacklozenge$); 0.10 ($\bullet$); 0.12 ($\blacksquare$); 0.15 ($\blacktriangleright$); and 0.17 ($\blacktriangleleft$).

Figure 5. $\log(\sigma T)$ versus $1000/T$ plot as a function of Ga content in $\text{Ca}_{3-x}\text{Ga}_x\text{Co}_4\text{O}_y$ samples, for $x = 0.00$ ($\square$); 0.01 ($\odot$); 0.03 ($\blacktriangle$); 0.05 ($\blacktriangledown$); 0.07 ($\blacklozenge$); 0.10 ($\bullet$); 0.12 ($\blacksquare$); 0.15 ($\blacktriangleright$); and 0.17 ($\blacktriangleleft$). T_1^* and T_2^* indicate the metallic-to-

semiconducting transition temperature for the pure samples and those with Ga content ≥ 0.07 , respectively.

Figure 6. Temperature dependence of the power factor, as a function of Ga content, in $\text{Ca}_{3-x}\text{Ga}_x\text{Co}_4\text{O}_y$ samples, for $x = 0.00$ ($\square$); 0.01 ($\odot$); 0.03 ($\blacktriangle$); 0.05 ($\blacktriangledown$); 0.07 ($\blacklozenge$); 0.10 ($\bullet$); 0.12 ($\blacksquare$); 0.15 ($\blacktriangleright$); and 0.17 ($\blacktriangleleft$).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6