# Improvement of textured $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\mathrm{x}}$ thermoelectric performances by metallic Ag additions 

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#### Abstract

$\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\mathrm{x}}$ thermoelectric ceramics with small Ag additions ( 0 , 1 , and 3 $w t . \%$ ) have been successfully grown from the melt, using the laser floating zone method. Microstructure has shown a reduction on the amount of secondary phases and a better alignment, with the growth direction, for Ag contents of 3 $\mathrm{wt} . \%$. The microstructural evolution, as a function of Ag content, is confirmed with the electrical resistivity values which show an important decrease for the 3 wt .\% Ag samples, leading to maximum power factor values of about 0.42 $\mathrm{mW} / \mathrm{K}^{2} . \mathrm{m}$ at $650^{\circ} \mathrm{C}$, which is among the best results obtained in this type of materials.


Keywords: A. Grain growth; B. Platelets; B. Microstructure-final; C. Electrical properties.

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## 1. Introduction

Thermoelectric (TE) materials with high energy conversion efficiency are strongly required for electric power generation. Thermoelectric energy conversion is now showing very important advantages to harvest waste heat in a wide number of applications. Moreover, it can transform solar energy into electricity at lower cost than photovoltaic energy [1]. The conversion efficiency of such materials is quantified by the dimensionless figure of merit ZT , which is defined as $\mathrm{TS}^{2} / \rho \kappa$ (in which $\mathrm{S}^{2} / \rho$ is also named power factor, PF ), where S is the Seebeck coefficient (or thermopower), $\rho$ the electrical resistivity, $\kappa$ the thermal conductivity, and T is the absolute temperature [2]. As higher ZT higher the efficiency, an adequate TE material for practical applications must involve, therefore, high thermopower and low electrical resistivity, with low thermal conductivity.

The discovery of large thermoelectric power in $\mathrm{Na}_{\mathrm{x}} \mathrm{CoO}_{2}$ [3], which was found to posses a high ZT value of about 0.26 at 300 K , has opened a broad research field and from that moment on, great efforts have been devoted to explore new cobaltite families with high thermoelectric performances. Some other layered cobaltites, such as misfit $\left[\mathrm{Ca}_{2} \mathrm{CoO}_{3}\right]\left[\mathrm{CoO}_{2}\right]_{1.62},\left[\mathrm{Bi}_{0.87} \mathrm{SrO}_{2}\right]_{2}\left[\mathrm{CoO}_{2}\right]_{1.82}$ and $\left[\mathrm{Bi}_{2} \mathrm{Ca}_{2} \mathrm{O}_{4}\right]\left[\mathrm{CoO}_{2}\right]_{1.65}$ were also found to exhibit attractive thermoelectric properties [4-8]. The crystal structure is composed of two different layers, with an alternate stacking of a common conductive $\mathrm{Cdl}_{2}$-type $\mathrm{CoO}_{2}$ layer with a twodimensional triangular lattice and a block layer, composed of insulating rock-salt-type (RS) layers. Both sublattices (RS block and $\mathrm{Cdl}_{2}$-type $\mathrm{CoO}_{2}$ layer) possess common a- and c-axis lattice parameters and $\beta$ angles but different baxis length, causing a misfit along the b-direction [9-11].
As layered cobaltites are materials with a strong crystallographical anisotropy, the alignment of plate-like grains by mechanical and/or chemical processes is necessary to attain macroscopic properties comparable to those obtained on single crystals. Some techniques have been shown to be adequate to obtain a good grain orientation in several oxide ceramic systems, such as template grain growth (TTG) [10], sinter-forging [12], spark plasma [13], or directional growth from the melt [14]. On the other hand, it is interesting to explore cationic substitutions in the RS layer, which can change the misfit relationship between
these two layers and, as a consequence, modifying the values of the thermopower [7]. 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 [12], as it is reported for the substitution of Gd and Y for Ca [15], or Pb for Bi [16]. Moreover, metallic Ag additions have also shown to improve, in an important manner, the mechanical and thermoelectrical properties of this system [17] and other similar materials [18] which nearly do not react with Ag. Taking into account these previously discussed effects, the aim of this work is producing high performances TE materials by the addition of metallic Ag to the optimally Pb doped $\mathrm{Bi}-\mathrm{Sr}-\mathrm{Co}-\mathrm{O}$ compound $[16,19]$, followed by a texturing process performed by the Laser Floating Zone (LFZ) technique.

## 2. Experimental

The initial $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\mathrm{x}}$ with small amounts of silver ( 0,1 , and $3 \mathrm{wt} . \% \mathrm{Ag}$ ) polycrystalline ceramics were prepared from commercial $\mathrm{Bi}\left(\mathrm{NO}_{3}\right)_{3} \cdot 5 \mathrm{H}_{2} \mathrm{O}(\geq 98$ \%, Aldrich), $\mathrm{SrCO}_{3}$ (98.5 \%, Panreac), $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ (98 \%, Panreac), and metallic Ag (99 \%, Aldrich) powders by a sol-gel via nitrates method. They were weighed in the appropriate proportions and suspended in distilled water. Concentrated $\mathrm{HNO}_{3}$ (analysis grade, Panreac) was added dropwise into the suspension until it turned into a clear pink solution. Citric acid (99.5 \%, Panreac), and ethylene glycol (99 \%, Panreac), were added to this solution in the adequate proportions. Evaporation of the solvent was performed slowly in order to decompose the nitric acid excess, which allows the polymerization reaction between ethylene glycol and citric acid, forming a pink gel [20,21]. The dried product was then decomposed (slow self combustion) by heating at 350$400^{\circ} \mathrm{C}$ for 1 h . The remaining powder was mechanically ground and calcined at 750 and $800^{\circ} \mathrm{C}$ for 12 h , with an intermediate grinding. This step is especially important when texturing is performed using the LFZ technique: it has been designed to decompose the alkaline-earth carbonates which, otherwise, would decompose in the molten zone disturbing the solidification front. The soobtained powders were cold isostatically pressed in form of cylinders ( $\sim 120 \mathrm{~mm}$ long and 2-3 mm diameter) under an applied pressure of about 200 Mpa for 1 minute.

The green ceramic cylinders were subsequently used as feed in a LZF texturing system used succesfully in previous works [22-24] and described in detail elsewhere [25]. On the other hand, growth rate has been chosen taking into account previous results obtained in layered ceramic samples [26,27]. As a consequence, all samples were grown downwards at $15 \mathrm{~mm} / \mathrm{h}$, with a seed rotation of 3 rpm , in order to maintain the cylindrical geometry in the final textured material, while the feed has been rotating at 15 rpm , in the opposite direction, to improve the molten zone homogeneity. After texturing process, long (more than 150 mm ) cylindrical and geometrically homogeneous samples have been obtained. These textured materials were then cut into shorter pieces with the adequate sizes for their characterization ( $\sim 15 \mathrm{~mm}$ long).
The structural identification of all the samples was performed by powder XRD utilizing a Rigaku D/max-B X-ray powder diffractometer (CuK $\alpha$ radiation) with $2 \theta$ ranging between 10 and 70 degrees. Microstructural observations were performed on polished samples using a Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss Merlin) fitted with energy dispersive spectrometry (EDS) analysis. Micrographs of these samples have been recorded to analyze the different phases and their distribution. From these pictures, an estimation of the amount of the different phases, have been performed using Digital Micrograph software.

Steady-state simultaneous measurements of resistivity and thermopower were determined by the standard dc four-probe technique in a LSR-3 apparatus (Linseis GmBh ) between 50 and $650^{\circ} \mathrm{C}$ under He atmosphere. From these data, PF values as a function of temperature were calculated in order to evaluate the final samples performances.

## 3. Results and discussion

Powder XRD patterns for all $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\mathrm{x}}$ samples with different amounts of Ag are plotted (from 10 to $40^{\circ}$ for clarity) in Fig. 1. They show very similar patterns where the most intense peaks correspond to the misfit cobaltite $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\times}$phase, in agreement with previous reported data [16,28]. From this figure, it is clear that the cobaltite phase appears as the major one, independently of Ag content. Peaks marked with a $\bullet$ in the plot correspond to the Co -free $\mathrm{Bi}_{0.75} \mathrm{Sr}_{0.25} \mathrm{O}_{1.375}$ secondary phase [29]. Moreover, for samples with

1 and $3 \mathrm{wt} . \% \mathrm{Ag}$, a new peak appears in the XRD plots at around 38 degrees, which corresponds to the metallic Ag (111) plane (indicated by ■) [30]. This peak also indicates that Ag does not react with the thermoelectric ceramic, leading to the formation of a ceramic matrix composite with metallic particles distributed inside the matrix, as observed in similar ceramic systems [18,27,31]. Scanning electron microscopy has been performed on polished longitudinal sections of all samples after the growth process. The microstructural evolution of samples, as a function of Ag content, can be easily observed in Fig. 2 where representative micrographs of longitudinal polished sections of all samples are presented. In these general views, it can be clearly seen that all samples are composed by three contrasts, which correspond to different phases, identified by EDS and numbered, for clarity, in Fig. 2a. Grey contrast (\#1) corresponds to the thermoelectric $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\times}$phase, and white (\#2) and dark grey (\#3) ones to the $\mathrm{Bi}_{2.2} \mathrm{SrO}_{y}$ and $\mathrm{SrCoO}_{z}$ secondary phases, respectively, which is in agreement with the previously discussed XRD data. Moreover, it can be observed that the amount and size of these secondary phases is reduced when the Ag content is increased. The approximate content of these secondary phases is about 14 vol. $\%$ of $\mathrm{Bi}_{2.2} \mathrm{SrO}_{\mathrm{y}}$ and 1.5 vol. $\%$ of $\mathrm{SrCoO}_{\mathrm{z}}$ for the pure samples, which are reduced to around 12 and $1.3 \mathrm{vol} . \%$ for the $1 \mathrm{wt} . \% \mathrm{Ag}$ ones, and 7 and 0.5 vol. $\%$ found in the $3 \mathrm{wt} . \% \mathrm{Ag}$ samples.

Other interesting feature that can be observed in this figure is the $\mathrm{Bi}_{2.2} \mathrm{SrO}_{y}$ change in shape, from thick and relatively short grains in the pure $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\mathrm{x}}$ samples, to thinner and better aligned grains with respect to the growth direction when Ag is added. The reduction in thickness and good alignment of this secondary phase increases the effective area of the thermoelectric phase. This effect, together with an improved alignment of the thermoelectric phase, leads to the raise of transport properties.
On the other hand, Ag is not easy to see in the micrographs displayed in Fig. 2 due to their low magnification. In order to observe the Ag shape and distribution, higher magnification micrographs have been recorded for samples with $3 \mathrm{wt} . \%$ Ag, and presented in Fig. 3a. In this micrograph, some Ag particles are indicated by arrows for clarity, as they show a very similar contrast to that of the thermoelectric phase. Furthermore, some regions with an eutectic-like microstructure can be also observed in Fig. 3a, surrounded by a broken line.

This marked zone has been enlarged and displayed in Fig. 3b, where it can be clearly seen a homogeneous distribution of metallic Ag spherical particles in a $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\mathrm{x}}$ thermoelectric ceramic matrix. This result is in agreement with previously reported works in similar ceramic materials which does not react with Ag but produces an eutectic detected experimentally by DTA analysis but not observed microstructurally before [32].

The temperature dependence of the electrical resistivity as a function of the Ag content is represented in Fig. 4. As it can be easily seen, the $\rho(T)$ curves show very similar behaviour for samples with 0 and $1 \mathrm{wt} . \% \mathrm{Ag}$, with only a slight reduction of resistivity for the samples with $1 \mathrm{wt} . \%$ Ag. Both curves display a semiconducting-like behaviour ( $\mathrm{d} \rho / \mathrm{dT}$ < 0 ) from room temperature to about 550 ${ }^{\circ} \mathrm{C}$ and a metallic-like one ( $\mathrm{d} \rho / \mathrm{dT}>0$ ) at higher temperatures. On the other hand, samples with 3 wt . \% Ag additions reduce significantly the resistivity values and change their behaviour radically showing a mettallic-like one ( $\mathrm{d} \rho / \mathrm{dT}$ $>0)$ in all the measured temperature range. This important reduction of electrical resistivity is consistent with the reduction of the secondary phases content already mentioned in the microstructure discussion (see Fig. 2) and the higher grain alignment, which has been also observed in similar ceramic systems [17, 31]. The minimum resistivity value at room temperature, $\sim 7$ $\mathrm{m} \Omega . \mathrm{cm}$, is obtained for samples with $3 \mathrm{wt} . \% \mathrm{Ag}$, while for the 0 and $1 \mathrm{wt} . \% \mathrm{Ag}$ is about two times higher, 13 and $12 \mathrm{~m} \Omega . \mathrm{cm}$, respectively. In any case, these values are lower than the obtained in pure $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\mathrm{x}}$ processed by the same technique with higher growth speed [16]. Moreover, the minimum value is comparable to that obtained in single crystals with similar composition without Ag [33].

Fig. 5 displays the variation of the Seebeck coefficient as a function of temperature for all the samples. In this figure, it is clear that the sign of the Seebeck coefficient is positive for the whole measured temperature range, which confirms a conduction mechanism predominantly governed by holes. The values increase with temperature, with a slight change in the curve slope at about $300^{\circ} \mathrm{C}$ for all the samples. Moreover, the room temperature values are very similar for the 0 and $1 \mathrm{wt} . \% \mathrm{Ag}$ samples while it is lower for the $3 \mathrm{wt} . \% \mathrm{Ag}$ added samples, which is in agreement with the room temperature values of
resistivity. In all cases, these room temperature values are higher than the measured in single crystals with similar composition without Ag (about 100 $\mu \mathrm{V} / \mathrm{K})$ [33]. The reason for obtaining such high values is the formation of considerable amounts of oxygen vacancies on the thermoelectric phase when samples are textured using the LFZ technique [22]. This effect has also been observed in the misfit phase $\left[\mathrm{Ca}_{2} \mathrm{CoO}_{3}\right]\left[\mathrm{CoO}_{2}\right]_{1.62}$ which contains considerable amounts of oxygen vacancies when it is thermally treated under reducing atmosphere [34]. The raise on the oxygen vacancies changes the Co oxidation state from $\mathrm{Co}^{4+}$ to $\mathrm{Co}^{3+}$, thus increasing S values, in agreement with Koshibae equation [35].

In order to evaluate the thermoelectric performances of the textured ceramic materials, variation of Power Factor with temperature has been calculated from the resistivity and Seebeck coefficient values and displayed, as a function of the Ag content, in Fig. 6. As it was found in the resistivity and Seebeck factor measurements, samples with 0 and $1 \mathrm{wt} . \%$ Ag show very similar values with a minimum value, at room temperature, of about $0.16 \mathrm{~mW} / \mathrm{K}^{2} . \mathrm{m}$, higher than the obtained values in single crystals with similar composition to the pure one (~ $0.14 \mathrm{~mW} / \mathrm{K}^{2} . \mathrm{m}$ ) [33]. Moreover, it is about $50 \%$ higher than the obtained for the pure $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\mathrm{x}}$ material processed by the LFZ technique at higher growth speeds [16]. On the other hand, samples with 3 wt. \% Ag additions increase the power factor values, at room temperature, in around $50 \%$ the obtained values in Ag-free samples. This result indicates that small Ag additions can be very useful in order to strongly reduce electrical resistivity and, as a consequence raising the thermoelectric performances.
The maximum PF value obtained in these samples, $\sim 0.42 \mathrm{~mW} / \mathrm{K}^{2} . \mathrm{m}$ is among the best results obtained in this type of materials so far, making them good candidates to be applied in practical thermoelectric devices.

## 4. Conclusions

This paper demonstrates that $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\mathrm{x}}$ thermoelectric materials with small Ag additions ( 0,1 , and $3 \mathrm{wt} . \%$ ) can be directionally grown by the laser floating zone method. It has been determined that the optimal Ag content in the textured materials is $3 \mathrm{wt} . \%$. Microstructural evolution shows that this amount of

Ag reduces significantly the amount of secondary phases and induces their alignment with the growth direction. Moreover, the electrical resistivity data clearly indicated that this Ag amount simultaneously enhances the metallic behaviour of samples, together with an important reduction of their resistivity. All these factors lead to a raise in the Power Factor, with a maximum value of $\sim$ $0.42 \mathrm{~mW} / \mathrm{K}^{2} . \mathrm{m}$ which is among the best results obtained in this type of materials so far.

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## Figure captions

Fig. 1. Powder $X R D$ diagrams for the $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\mathrm{x}}$ textured samples with a) 0 ; b) 1 ; and c) $3 \mathrm{wt} . \%$ Ag. Crystallographic planes have been indicated on the peaks corresponding to the $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{x}$ phase. Other phases are indicated by symbols: • Co-free $\mathrm{Bi}_{0.75} \mathrm{Sr}_{0.25} \mathrm{O}_{1.375}$ secondary phase; and $\boldsymbol{\square} \mathrm{Ag}$.

Fig. 2. Scanning electron micrographs from longitudinal polished textured samples $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\mathrm{x}}$ with different Ag contents: a) 0 ; b) 1 ; and c) 3 $w t . \%$. The different phases are indicated by arrows, 1) $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\mathrm{x}} ; 2$ ) $\mathrm{Bi}_{2.2} \mathrm{SrO}_{y}$; and 3 ) $\mathrm{SrCoO}_{z}$.

Fig. 3. Scanning electron micrographs from longitudinal polished samples $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\mathrm{x}}$ with $3 \mathrm{wt} . \% \mathrm{Ag}$. Ag particles are indicated by arrows in (a). Broken line indicates the zone represented in (b), where an eutectic-like structure can be distinguish ( Ag particles in a $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\mathrm{x}}$ phase matrix).

Fig. 4. Temperature dependence of the electrical resistivity for textured $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\mathrm{x}}$ with different Ag contents. - 0 ; 1; and ■ $3 \mathrm{wt} . \%$.

Fig. 5. Temperature dependence of the Seebeck coefficient for textured $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\mathrm{x}}$ with different Ag contents. - 0 ; 1; and ■ $3 \mathrm{wt} . \%$.

Fig. 6. Temperature dependence of the power factor for textured $\mathrm{Bi}_{1.6} \mathrm{~Pb}_{0.4} \mathrm{Sr}_{2} \mathrm{Co}_{1.8} \mathrm{O}_{\mathrm{x}}$ with different Ag contents. - 0; 1; and ■ $3 \mathrm{wt} . \%$.

Figure 1


Figure 2


Figure 3


Figure 4


Figure 5


Figure 6


