High thermoelectric performance in Bi$_{2-x}$Pb$_x$Ba$_2$Co$_2$O$_y$ promoted by directional growth and annealing

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Abstract

Bi$_{2-x}$Pb$_x$Ba$_2$Co$_2$O$_y$ (x=0.0, 0.2, 0.4, and 0.6) misfit compounds were grown by the laser floating zone technique. Microstructural analysis has shown the formation of thermoelectric grains together with high amount of secondary phases. Thermoelectric grains orientation is increased until 0.4Pb, while further substitution drastically destroys the preferential grain orientation. Electrical resistivity is very low compared with the values obtained in sintered materials, spectacularly increasing power factor. Moreover, the performance of these materials was further improved subjecting the as-grown samples to a postannealing step due to the rise of thermoelectric phase content. These microstructural modifications led to a high decrease of electrical resistivity, improving power factor in around a factor two at room temperature, compared with the as-grown samples. Moreover, the low thermal conductivity of the textured annealed samples leads to a maximum estimated ZT value of 0.53 for the 0.2 Pb-doped samples, much higher than the reported in literature.

Keywords: Ceramics; Doping; Grain growth; Electrical properties; Thermopower

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1. Introduction

Nowadays, there is a great and growing interest in the development of new and clean energy sources in order to fight against global warming. These green energy sources should decrease the release of greenhouse gases, as CO₂, produced in the classical energy transforming systems. On the other hand, it is still difficult to avoid the use of fossil fuels in many applications, as in automobiles or electrical power production, with a relatively low efficiency (∼ 40 %) [1]. In this scenario, thermoelectric (TE) energy conversion, based on the well-known Seebeck effect, can be used to transform solar energy into electricity at lower cost than photovoltaic energy [2]. Moreover, it has shown important advantages (for example, they are silent and have non moving parts) to be applied in harvesting waste heat in these classical energy transforming systems [3]. The efficiency characterization of these TE materials is performed through the dimensionless figure of merit, ZT, which is calculated as $T S^2 \rho^{-1} \kappa^{-1}$, where $T$, $S$, $\rho$, and $\kappa$ are the absolute temperature, Seebeck coefficient, electrical resistivity and thermal conductivity, respectively [4]. As a consequence, a high performance TE material should have low thermal conductivity, high power factor (PF = $S^2 \rho^{-1}$), and high working temperatures. At present, some practical applications of TE devices can be found in vehicles exhausts and in cooling systems. These TE devices are formed by different intermetallic or semiconducting materials, as Bi-Te-based ones, with high associated costs, and relatively low working temperatures. Moreover, most of these materials are composed of scarce, heavy, and/or toxic elements which are not environmental friendly. Nevertheless, since the discovery in 1997 of good TE properties in NaₓCoO₂ [5], many studies have been performed in transition metal oxide (TMO’s) based materials. These materials, such as Bi₂Ca₂Co₂Oₓ [6,7], Bi₂Sr₂Co₂Oₓ [8,9], Bi₂Ba₂Co₂Oₓ [10], or Ca₃Co₄O₉ [11,12], are based in cheaper, more abundant and environmentally friendly, and chemically stable at high temperatures under air. All these characteristics have greatly increased the interest in these TMO’s-based materials. Crystallographic studies of these materials have shown that they can be described by a monoclinic structure formed by two different sublattices which are alternately stacked [13]. One is the CoO₂ conductive layer with CdI₂-type
structure, while the other one is an insulating rock-salt-type. Both sublattices possess the same lattice parameters, except in the b-axis length, leading to a misfit along this direction [14]. As it is well-known, these materials show a very important crystallographic anisotropy which is reflected in a high electrical conductivity one. As a consequence, the alignment of grains along their conducting planes can be used to drastically reduce the electrical resistivity in the bulk materials. This process would allow enhancing ZT to values close to the obtained in single crystals. Many techniques have been used to produce such grain alignment, as hot-pressing [15], spark plasma sintering (SPS) [16], laser floating zone (LFZ) [17], or the electrically assisted laser floating zone [18], which have shown their ability to improve TE performance of bulk materials by the alignment of grains.

On the other hand, doping processes have been also shown that TE properties can be tuned up by using the adequate dopants and proportions, as it is the case of different metals for Ca substitution in Ca$_3$Co$_4$O$_9$ [19], or Pb for Bi in Bi$_2$Sr$_2$Co$_{1.8}$O$_x$ [20]. Moreover, the synthesis techniques can also drastically modify the grain sizes and their connectivity, leading to improved properties in the final bulk materials [21].

Taking into account the above considerations, the aim of the present work is studying the effect of relatively low Pb substitutions for Bi in the Bi$_2$Ba$_2$Co$_2$O$_x$ thermoelectric material. Pb has been selected as dopant due to its unique properties which make it essential in many compounds and applications, as for example in PZT piezoelectrics [22], or as dopant, stabilizing the High-Tc Bi-2223 superconducting phase [23]. It has been prepared by a polymer solution method developed in our laboratory [24], followed by texturing using the laser floating zone melting technique [17]. Moreover, as it was determined in previous works in similar systems, the as grown materials possess a high amount of secondary phases [25]. As a consequence, some samples were annealed to increase the amount of the thermoelectric phase. The thermoelectric properties of these Bi$_2$$_x$Pb$_x$Ba$_2$Co$_2$O$_y$ textured ceramics (with $x$=0, 0.2, 0.4, and 0.6), before and after annealing, have been determined and correlated with their structure and microstructure.

2. Experimental
The Bi$_{2-x}$Pb$_x$Ba$_2$Co$_2$O$_y$ ceramics (with x=0, 0.2, 0.4, and 0.6) were prepared from Bi(CH$_3$CO$_2$)$_3$ (99.99 + %, Aldrich), Pb(CH$_3$CO$_2$)$_2$ • 3H$_2$O (≥ 99%, Aldrich), Ba(CH$_3$CO$_2$)$_2$ (≥ 99%, Aldrich), and Co(CH$_3$CO$_2$)$_2$ • 4H$_2$O (98%, Panreac) commercial powders. They were weighed in the appropriate proportions and dissolved in a mixture of distilled H$_2$O and glacial acetic acid (ACS Reagent, Panreac). To the clear pink solution, Polyethyleneimine (PEI) (50% aqueous, Aldrich) was added to the above solution which turned darker immediately due to the nitrogen-metal bond formation. Partial evaporation of water and acetic acid has been performed in a rotary evaporator until a final volume of around 20% of the initial one. The concentrated solution was then placed onto a hot plate for further solvent evaporation until a very dark pink paste appeared. Further heating turned this paste to violet colour, followed by a slow autocombustion with the release of brown fumes (nitrogen oxides). The mixture was manually milled and thermally treated at 700 and 750°C for 12 h, with an intermediate milling, following the procedure described elsewhere [26] to decompose the alkaline earth carbonates. This decomposition step is very important to produce well aligned grains by the laser floating zone, due to the fact that the remaining carbonates would decompose during the texturing process inside the molten zone. As a consequence, the melt would be disturbed by the CO$_2$ bubbles produced in the decomposition process, leading to the growth front destabilization and producing grains misalignments.

The final powder was then isostatically pressed under 200 MPa during one minute to produce cylindrical green ceramics (2-3 mm diameter). These cylinders were used as feed in a LFZ device equipped with a continuous power Nd:YAG laser (λ = 1064 nm), following the experimental procedure described elsewhere [27]. All the LFZ-grown samples were processed at 30 mm h$^{-1}$ under air with a seed rotation of 3 rpm to maintain the cylindrical geometry. Moreover, the feed was rotated at 15 rpm in the opposite direction, in order to ensure compositional homogeneity of the molten zone. After the texturing process, long (> 150 mm) and geometrically homogeneous textured cylindrical rods of around 2 mm diameter were produced. The textured bars were cut into suitably sized pieces for their TE characterization (~ 15 mm long). As mentioned previously, as-grown materials are characterized by a relatively high amount of secondary
phases. As a consequence, some of the samples were annealed at 700 °C for 24 h, in air atmosphere, to increase the proportion of the thermoelectric phase in the samples.

The identification of the main phases in the textured samples was performed by powder X-ray diffraction (XRD) utilizing a Rigaku D/max-B X-ray powder diffractometer (CuKα radiation) with 2θ ranging between 10 and 70 degrees. In order to determine the adequate temperature for annealing the as-grown samples, DTA analyses were performed in a TA Instrument (SDT Q600) system between room temperature and 800 °C.

Microstructural observations were performed on polished as-grown and annealed samples using backscattered electrons in a Zeiss Merlin field emission scanning electron microscope (FESEM) equipped with an energy dispersive spectrometry (EDS) analysis system. Micrographs of these samples have been recorded to analyze the different phases and their distribution.

Steady-state simultaneous measurements of resistivity and Seebeck coefficient were determined by the standard dc four-probe technique in a LSR-3 apparatus (Linseis GmbH) between 50 and 650 °C under He atmosphere, with an estimated error of 4 % in each parameter. From these data, samples performances were determined using PF values.

Finally, thermal conductivity was determined at room temperature in the annealed samples using the transient plane source technique (Hot Disk TPS 2500 s), which possess an accuracy better than 5 %, as indicated by the system manufacturer. This method uses an electrically conducting pattern element acting both as a temperature sensor and heat source, insulated with two thin layers of Kapton (70 µm). The TPS element is assembled between two samples of similar characteristics with both faces in contact with the two samples surfaces. The measurements were performed with heating power ranging from 7 to 9 W and measurement time from 20 to 80 s. From the PF and κ values, ZT has been determined at room temperature and estimated at higher temperatures, together with its calculated error from the uncertainties of each physical parameter (S, ρ, and κ). For this estimation, the κ behaviour with temperature has been consulted in other works where it has been found to be nearly constant [28] or decreasing [29] when the temperature is increased. As a
consequence it has been assumed that, in the worst case, \( \kappa \) would be unchanged with \( T \).

3. Results and discussion

3.1. As-grown samples

Powder XRD data for as-grown samples with different Pb content are plotted (from 10 to 40° for a better clarity) in Fig. 1. They show similar patterns where most of the peaks correspond to the (00l) planes of the misfit cobaltite \( \text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_y \) \cite{28}. Even if minor differences are found in weak peaks, the cobaltite phase appears as the major one, independently of the Pb content. Peak marked with a * in the plot corresponds to a Bi-Ba-O solid solution with P121/n1 space group \cite{30}. Moreover, the proportion of the secondary phase is decreasing, compared to the thermoelectric one, when the Pb content in the samples is raised, as can be observed by the decrease of its (200) peak intensity.

Scanning electron microscopy was performed on longitudinal polished sections of the as-grown samples, and representative images of all samples are displayed in Fig. 2. In these images, three main contrasts can be seen (indicated by numbers in Fig. 2a for clarity). The major phase in all samples (grey contrast, #1) has been identified by EDS as the misfit thermoelectric \( (\text{Bi,Pb})_2\text{Ba}_2\text{Co}_2\text{O}_y \) one. In the case of the Pb-doped samples, this phase has a Pb content of around 0.4 for the 0.2Pb-doped one, slightly decreasing for higher Pb nominal composition. Dark grey contrast (#2) corresponds to the \( \text{Ba}_2\text{Co}_3\text{O}_z \) secondary phase, while the white contrast (#3) has been identified as \( \text{Bi}_5\text{Ba}_4\text{O}_x \), in agreement with the XRD data. Moreover, this last phase has an increasing Pb content with the nominal one, reaching a Bi:Ba:Pb proportion of 5:4:1 for the highest Pb nominal composition. This type of phases (plumbate-like ones) are well common in other Pb-doped systems \cite{31} for their ability to admit very high Pb proportions, which can explain the slight decrease of Pb in the thermoelectric \( (\text{Bi,Pb})_2\text{Ba}_2\text{Co}_2\text{O}_y \) phase. Finally, in 0.6Pb-doped samples, a new contrast appears (black one, #4) which corresponds to Co-oxide. Other feature that can be observed in these microstructures is the decrease of \( \text{Ba}_2\text{Co}_3\text{O}_z \) secondary phase when Pb content is raised while the thermoelectric one increases, in agreement with the XRD data. On the other hand, the plumbate-
like phase content seems to slightly increase with Pb-content. All these features are maintained until 0.4 Pb nominal content and further Pb substitution produces new phases (#4 in Fig. 2d) and clearly destroys the grain orientation in the bulk material. In any case, it can be easily seen that the best aligned grains are those found in samples with 0.2 Pb substitution.

The temperature dependence of the electrical resistivity, as a function of the Pb content, is given in Fig. 3. As it can be easily seen, $\rho(T)$ curves show a semiconducting-like behaviour ($d\rho/dT < 0$) in the whole temperature range. Moreover, the curve slope tends to be lower when Pb content is raised. This is in agreement with previous works which showed that Bi substitution by Pb increases the hole carrier concentration in similar systems [20,32]. This is due to the fact that Pb$^{2+}$ is substituting Bi$^{3+}$ in the RS structure leading to a decrease on the effective charge in this structure. As a consequence, the charge in the conducting layer has to be raised in order to compensate the changes in the RS layer, increasing the relative proportion of Co$^{4+}$ in this layer. From Koshiba expression [33], the higher relationship between Co$^{4+}$ and the total Co in the conducting layer (Co$^{3+}$+Co$^{4+}$) increases the carrier concentration, leading to lower electrical resistivity values at room temperature. On the other hand, the evolution of resistivity for the Pb doped samples clearly agree with the SEM and EDS data discussed previously. In fact, the lowest resistivity is measured on 0.2Pb doped samples due to their higher grain orientation (see Fig. 2) and to the fact that Bi$_2$Ba$_2$Co$_2$O$_y$ thermoelectric phase has the highest Pb content. Further Pb substitution produces higher grain misalignment and a slight decrease of Pb in the thermoelectric phase, leading to increased resistivity values compared to the 0.2Pb doped samples. The minimum resistivity value (≈ 11 mΩ cm) at 650 °C has been obtained for the 0.2Pb doped samples, which is slightly higher than the best results obtained in pure Bi$_2$Ba$_2$Co$_2$O$_y$ textured by the LFZ technique at low rates (≈ 8.5 mΩ cm) [34], but much lower than the obtained in sintered materials (≈ 33 mΩ cm) [28].

Fig. 4 displays the variation of Seebeck coefficient with temperature as a function of Pb content. As can be easily seen in the plot, S is positive in the whole measured temperature range, indicating a conduction mechanism mainly governed by holes. Moreover, all the samples show similar S values at room
temperature (\(\sim 130 \, \mu V \, K^{-1}\)) which are slightly higher than the obtained in textured materials grown by the LFZ technique at low rates (\(\sim 120 \, \mu V \, K^{-1}\)) [34], and much higher than the measured in sintered materials at the same temperature (\(\sim 85 \, \mu V \, K^{-1}\)) [28]. On the other hand, different behaviours can be observed for the undoped and for the doped samples. The raise of S with temperature for the undoped samples is much lower than for the Pb doped ones. As a consequence, all the Pb doped samples reach higher S values at 650 °C than the undoped ones. The highest S value at 650 °C has been obtained for the 0.4Pb doped samples (\(\sim 205 \, \mu V \, K^{-1}\)), which is around 35 % higher than the obtained in the undoped samples, and slightly higher (\(\sim 5 \%\)) than the measured in the other Pb doped ones. Moreover, this value is slightly higher than the obtained in textured materials grown by the LFZ technique at low rates (\(\sim 185 \, \mu V \, K^{-1}\)) [34], and much higher than the measured in sintered materials at the same temperature (\(\sim 110 \, \mu V \, K^{-1}\)) [28].

From the above data, PF has been calculated and presented, as a function of Pb content, in Fig. 5, where it can be clearly seen that the PF of the 0.2Pb doped samples raise, in a very important manner, with respect to the values obtained in undoped ones (\(\sim 100 \%\) in the whole measured temperature range). Further Pb doping starts to decrease PF values with respect to the 0.2Pb doped ones. This evolution is in clear agreement with the microstructural features discussed previously which showed that the best oriented grains and the highest amount of TE phase was obtained in the 0.2Pb doped samples. The highest PF values at room temperature and at 650 °C (around 0.12 and 0.34 mW K^{-2} m^{-1}, respectively) are much higher than the obtained in solid state sintered materials (\(\sim 0.035\) and 0.040 mW K^{-2} m^{-1}, respectively) [28]. Moreover, they are also higher than the obtained at different growth rates. On the other hand, they are very close to the values obtained in pure Bi$_2$Ba$_2$Co$_2$O$_y$ materials textured at low rates (about 0.40 mW K^{-2} m^{-1} at 650 °C) [34].

It is important to highlight that all the above described results are around the best ones obtained in Bi$_2$Ba$_2$Co$_2$O$_y$ materials. Taking into account that the amount of secondary phases in the studied samples is relatively high, an annealing process could promote the formation of a higher proportion of TE phase. Consequently, this thermal treatment would decrease the amount of
secondary phases leading, at least, to a lower electrical resistivity. In order to
determine the adequate annealing temperature, DTA analysis has been
performed on the as-grown samples (diagrams not shown). All the curves
showed a continuous endothermic behaviour in the high temperature range. As
a consequence, the best annealing temperature for the thermal treatment of as-
grown samples has been experimentally found to be 700 °C.

3.2. Annealed samples
After annealing at 700 °C for 24 h with a final cooling inside the furnace,
powdered samples were characterized by XRD, and the results are plotted in
Fig. 6. As can be observed in the plot, all the samples exhibit patterns similar (to
the as-grown ones, where most of the peaks correspond to the (00l) planes of
the misfit cobaltite Bi$_2$Ba$_2$Co$_2$O$_y$ [28] which is the major one, independently of
Pb content. The peak marked with a * in the plot corresponds to a Bi-Ba-O solid
solution with P121/n1 space group [30], which is decreasing in intensity,
compared to the thermoelectric one, when the Pb content in the samples is
raised. Moreover, the intensity of this (002) peak is clearly smaller than the one
obtained in as-grown samples, indicating a decrease of secondary phase
content with the thermal treatment.

Scanning electron microscopy performed on longitudinal polished sections of
annealed samples has confirmed the evolution described in the XRD
discussion, as can be observed in the representative images displayed in Fig. 7.
In the pictures, three main contrasts can be observed (indicated by numbers in
Fig. 7a for clarity). The major phase in all samples (grey contrast, #1) has been
identified by EDS as the misfit thermoelectric (Bi,Pb)$_2$Ba$_2$Co$_2$O$_y$ one. In the case
of the Pb-doped samples, this phase has a Pb content of around 0.4 in all
cases. Dark grey contrast (#2) corresponds to the Ba$_2$Co$_5$O$_7$ secondary phase
which possesses higher Co content than in the as-grown samples, while the
white contrast (#3) has been identified as Bi$_2$Ba$_4$O$_x$ with lower Bi content than in
the as-grown ones. Moreover, this last phase has an increasing Pb content with
the nominal one, reaching a Bi:Ba:Pb proportion of 2:4:1 for the highest Pb
nominal composition. In any case, the amount of this plumbate-like phase is
very low in the case of 0.2 and 0.4 Pb doped samples due to the Pb
incorporation in the thermoelectric phase (which is around 0.4Pb in all cases).
The temperature dependence of the electrical resistivity as a function of Pb content for the annealed samples is shown in Fig. 8. As it can be easily seen, Pb addition clearly decreases the electrical resistivity values in the whole measured temperature range, in agreement with previous reports [35]. Moreover, the \( \rho(T) \) curves show nearly a metallic-like behaviour (\( d\rho/dT > 0 \)) in the whole studied temperature range. This behaviour is totally different to the one observed in the as-grown samples (see Fig. 3) and can be associated to the higher amount of thermoelectric phase in the annealed ones, together with a higher oxygen content. This is in agreement with previous works which showed that LFZ processing of these materials generates oxygen vacancies in larger content than in bulk samples synthesized by a classic solid-state reaction [17]. As a consequence, the annealing process can lead to an increase of oxygen in the structure, in agreement with the decrease of electrical resistivity in the annealed samples, compared with the as-grown ones (see Figs. 3 and 8). The lowest resistivity value at 650 ºC has been obtained in the 0.2 Pb doped annealed samples (~ 6 mΩ cm) which is nearly half of the obtained in the as-grown ones (around 11 mΩ cm). Moreover, it is much smaller than the measured in sintered materials (about 33 mΩ cm) [28], in Bi\(_{1.8}\)Pb\(_{0.2}\)Ba\(_2\)Co\(_2\)O\(_y\) materials annealed under 0.1% O\(_2\) atmosphere (around 70 mΩ cm) [36], or in highly textured materials grown by LFZ at low rates (~ 8.5 mΩ cm) [34].

Fig. 9 displays the variation of the Seebeck coefficient as a function of temperature for all the annealed samples. As it can be observed, all samples possess, approximately, the same S values in the whole measured temperature range. At first sight, the most remarkable difference can be found in the drastic change in Seebeck coefficient between as-grown and annealed undoped samples. This effect can be due to the fact that Pb\(^{2+}\) substitution for Bi\(^{3+}\) should lead to a decrease of the total oxygen content in the thermoelectric phase, leading to a lower effect of the LFZ processing on the oxygen vacancies. This explanation is in agreement with the small changes in the Seebeck coefficient between as-grown and annealed Pb doped samples (see Figs. 4 and 9). Moreover, the Seebeck coefficient values at room temperature for the annealed samples (around 115 µV K\(^{-1}\)) are lower than the obtained in as-grown ones (about 130 µV K\(^{-1}\)) which clearly agree with the increase in oxygen in the
structure produced by the annealing process discussed previously. In any case, the highest S value at 650 °C has been obtained for the undoped samples (~185 μV K⁻¹) which is the same value obtained in textured materials grown by the LFZ technique at low rates (~185 μV K⁻¹) [34], and much higher than the measured in sintered materials at the same temperature (~110 μV K⁻¹) [28], or in Bi₁.₈Pb₀.₂Ba₂Co₂O₇ materials annealed under 0.1 % O₂ atmosphere (around 120 μV K⁻¹) [36].

From the electrical resistivity and Seebeck coefficient data, PF has been calculated and represented, as a function of temperature, in Fig. 10. As it can be observed in the graph, the drastic decrease of electrical resistivity of annealed samples with only a slight decrease of Seebeck coefficient, leads to a higher PF values than the ones obtained in as-grown samples. At room temperature, annealed samples show PF values about two times higher in all cases. Moreover, the maximum PF value at 650 °C (about 0.45 mW K⁻² m⁻¹) for the 0.2 Pb doped samples is 30 % higher than the best value obtained in the best as-grown ones (see Fig. 5). More interesting, this value is much higher than the one obtained in solid state sintered materials (~0.040 mW K⁻² m⁻¹) [28] or in Bi₁.₈Pb₀.₂Ba₂Co₂O₇ materials annealed under 0.1 % O₂ atmosphere (around 0.030 mW K⁻² m⁻¹) [36] and slightly higher than those measured in pure Bi₂Ba₂Co₂O₇ materials textured at low rates (about 0.40 mW K⁻² m⁻¹) [34] at the same temperature.

Thermal conductivity values at room temperature in all the textured-annealed samples were 0.493, 0.561, 0.505, and 0.623 W K⁻¹ m⁻¹ for the 0.0, 0.2, 0.4, and 0.6 Pb-doped samples, respectively. On the other hand, as it is well known, the thermal conductivity can be expressed by a sum of lattice component (κₗ) and electronic component (κₑ), κ = κₗ + κₑ, and κₑ = LσT, where L is Lorenz number, σ electrical conductivity, and T absolute temperature. As Pb substitution increases the electrical conductivity, compared with the undoped samples, κₑ of Pb-doped samples is expected to be larger than that of Pb-free ones, explaining the higher thermal conductivity of Pb-doped samples. In any case, the measured values are much lower than the obtained in the Bi₂Ba₂Co₂O₇ sintered materials (~1 W K⁻¹ m⁻¹ at room temperature) [28], or in Bi₁.₈Pb₀.₂Ba₂Co₂O₇
materials annealed under 0.1% O$_2$ atmosphere (∼ 1 W K$^{-1}$ m$^{-1}$ at room temperature) [36].

With PF and $\kappa$ data, ZT has been calculated at room temperature, which showed the values 0.014, 0.031, 0.028, and 0.019 for the 0.0, 0.2, 0.4, and 0.6 Pb-doped samples, respectively. These values are very small for practical applications, but it should be considered that thermoelectric oxides are adequate for high temperature devices. Moreover, when compared with the reported values in the literature at this temperature (0.0021, and 0.0075 for 0.0, and 0.2 Pb-doped samples, respectively [36]), the values achieved in this work are more than four times higher than the previously presented. Moreover, with the approximation of $\kappa$ constant with temperature, estimated ZT values at 650 ºC would be 0.38, 0.53, 0.52, and 0.34 for the 0.0, 0.2, 0.4, and 0.6 Pb-doped samples, respectively. Taking into account this consideration, estimated ZT values are presented in Fig. 11. As it can be observed, 0.2 and 0.4 Pb-doped samples possess very similar ZT values, clearly higher than the undoped ones while the 0.6 Pb-doped ones show the lowest values. The maximum ZT value obtained in these samples, 0.53 for the 0.2 Pb-doped ones is about two times higher than the obtained in solid state sintered Bi$_2$Ba$_2$Co$_2$O$_y$ materials (∼ 0.25) [28]. Moreover, all the textured-annealed samples prepared in this work show higher ZT than these sintered materials. It is clear that this calculated value has an uncertainty is determined by the individual physical parameters uncertainties used to get the ZT result, specifically electrical resistivity, Seebeck coefficient and thermal conductivity. This way, the relative error of ZT was determined by the principle of error propagation. Moreover, taking into account the number of measurements performed at each temperature, the value of error corresponds to the upper limit of the error. Using this procedure, it is possible to forecast the maximum uncertainty associated to the determined value. The electrical resistivity error estimation obtained was 4 % taking into account the sensitivity of the measuring apparatus and the inaccuracy in measuring the dimensions of the samples and the distance between the contacts. An error of around 4% was also estimated for Seebeck coefficient, which is also influenced by the error of the thermocouples in determining the temperature difference of the cold and hot sides of the sample. For the error in the thermal conductivity ($k$) better accuracy
than 5% is stated by the equipment manufacture. Hence, considering all these values together in the mathematical formula of error propagation a maximum 16 % error for ZT was estimated. It is important to highlight that this error value is in accordance to the international analysis of ZT measurements that have conclude that the uncertainty in ZT values is around 15 % [37,38]. Noteworthy, all these results indicate that textured and annealed Bi$_{1.8}$Pb$_{0.2}$Ba$_2$Co$_2$O$_y$ materials are good bulk ceramic candidates for applications in thermoelectric generators.

4. Conclusions
Textured Pb doped Bi$_{2-x}$Pb$_x$Ba$_2$Co$_2$O$_y$ materials, with x= 0, 0.2, 0.4, and 0.6 were successfully prepared by the laser floating zone method. XRD and SEM characterization have shown that as-grown materials are mainly composed of the thermoelectric (Bi,Pb)$_2$Ba$_2$Co$_2$O$_y$ phase accompanied of several secondary phases. The amount of these secondary phases decreases with Pb addition until 0.4Pb, increasing the proportion of thermoelectric phase. Further decrease of the amount of secondary phases has been performed by annealing at 700 ºC, leading to higher thermoelectric performance than the measured in the as-grown samples. The best PF values obtained at 650 ºC for the 0.2 Pb doped samples is the highest reported in the best of our knowledge, around 10 times higher than the obtained in solid state sintered materials and about 10 % higher than the measured in pure laser grown Bi$_2$Ba$_2$Co$_2$O$_y$ materials at low rates. The low thermal conductivity of the textured annealed samples leads to a maximum estimated ZT value of 0.53 for the 0.2 Pb-doped samples, which is about two times higher than the obtained in solid state sintered undoped ones reported in the literature. This raise in ZT is very important even if the real value could be decreased by a maximum of 16 % due to the measurements error.

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Figure captions

Figure 1. Powder XRD plots of the Bi$_{2-x}$Pb$_x$Ba$_2$Co$_2$O$_x$ as-grown samples with different Pb contents. $x = 0.0$ (a), 0.2 (b), 0.4 (c), and 0.6 (d). Diffraction planes indicates the Bi$_2$Ba$_2$Co$_2$O$_x$ phase while * shows the peak corresponding to the BiBaO$_3$ secondary phase.

Figure 2. Scanning electron micrographs obtained on transversal polished sections of Bi$_{2-x}$Pb$_x$Ba$_2$Co$_2$O$_x$ as-grown samples with $x = 0.0$ (a), 0.2 (b), 0.4 (c), and 0.6 (d). Different contrasts are #1: grey one, associated to the thermoelectric (Bi,Pb)$_2$Ba$_2$Co$_2$O$_x$ phase; #2: dark grey, Ba$_2$Co$_3$O$_{y}$; #3: white, Bi$_5$Ba$_4$O$_z$ with plumbate-like composition (around Bi$_5$Ba$_4$PbO$_z$) in the Pb-substituted samples; and #4: black, Co-oxide.

Figure 3. Temperature dependence of the electrical resistivity for the as-grown Bi$_{2-x}$Pb$_x$Ba$_2$Co$_2$O$_x$ samples, for $x = 0.0$ ■; 0.2 ● 0.4 ▲; and 0.6 ▼.

Figure 4. Temperature dependence of the Seebeck coefficient for the as-grown Bi$_{2-x}$Pb$_x$Ba$_2$Co$_2$O$_x$ samples, for $x = 0.0$ ■; 0.2 ● 0.4 ▲; and 0.6 ▼.

Figure 5. Temperature dependence of power factor for the as-grown Bi$_{2-x}$Pb$_x$Ba$_2$Co$_2$O$_x$ samples, for $x = 0.0$ ■; 0.2 ● 0.4 ▲; and 0.6 ▼.

Figure 6. Powder XRD plots of the Bi$_{2-x}$Pb$_x$Ba$_2$Co$_2$O$_x$ as-grown samples with different Pb contents. $x = 0.0$ (a), 0.2 (b), 0.4 (c), and 0.6 (d). Diffraction planes indicates the Bi$_2$Ba$_2$Co$_2$O$_x$ phase while * shows the peak corresponding to the BiBaO$_3$ secondary one.

Figure 7. Scanning electron micrographs obtained on transversal polished sections of Bi$_{2-x}$Pb$_x$Ba$_2$Co$_2$O$_x$ annealed samples with $x = 0.0$ (a), 0.2 (b), 0.4 (c), and 0.6 (d). Different contrasts are #1: grey one, associated to the thermoelectric (Bi,Pb)$_2$Ba$_2$Co$_2$O$_x$ phase; #2: dark grey, Ba$_2$Co$_3$O$_{y}$; #3: white, and Bi$_2$Ba$_4$O$_z$ with plumbate-like composition (around Bi$_2$Ba$_4$PbO$_z$) in the Pb-substituted samples.
Figure 8. Temperature dependence of the electrical resistivity for the annealed Bi$_{2-x}$Pb$_x$Ba$_2$Co$_2$O$_x$ samples, for $x = 0.0$ ■; 0.2 ● 0.4 ▲; and 0.6 ▼.

Figure 9. Temperature dependence of the Seebeck coefficient for the annealed Bi$_{2-x}$Pb$_x$Ba$_2$Co$_2$O$_x$ samples, for $x = 0.0$ ■; 0.2 ● 0.4 ▲; and 0.6 ▼.

Figure 10. Temperature dependence of power factor for the annealed Bi$_{2-x}$Pb$_x$Ba$_2$Co$_2$O$_x$ samples, for $x = 0.0$ ■; 0.2 ● 0.4 ▲; and 0.6 ▼.

Figure 11. Estimated temperature dependence of ZT for the annealed Bi$_{2-x}$Pb$_x$Ba$_2$Co$_2$O$_x$ samples, for $x = 0.0$ ■; 0.2 ● 0.4 ▲; and 0.6 ▼.
Figure 1
Figure 3

The graph shows the relationship between the resistivity (\(\rho\) in m\(\Omega\).cm) and temperature (T in °C). The data is represented by different markers and lines, each possibly indicating a different material or condition. The x-axis represents temperature ranging from 0 to 700 °C, while the y-axis represents resistivity from 35 to 10 m\(\Omega\).cm. The graph exhibits a downward trend, indicating an increase in resistivity with increasing temperature.
Figure 4

The graph shows the relationship between temperature (T °C) and the electrical conductivity (S [μV/K]). There are four distinct lines representing different conditions or materials, each indicated by a different symbol and color.

- Line 1 (red dots): Increasing conductivity with temperature, reaching a peak around 500 °C and then decreasing slightly.
- Line 2 (black triangles): Gradually increasing conductivity with a steady rise until around 600 °C.
- Line 3 (blue circles): A steep increase in conductivity at lower temperatures, peaking sharply and then decreasing.
- Line 4 (green inverted triangles): A moderate increase in conductivity with a slight plateau around 400 °C and then a steady rise.

The y-axis represents the conductivity in microwatts per Kelvin (μV/K), ranging from 120 to 220, while the x-axis represents temperature in degrees Celsius (°C), ranging from 0 to 700.
Figure 6
Figure 8

The graph shows the relationship between electrical resistivity $\rho$ (in $\text{m}\Omega\text{cm}$) and temperature $T$ (in °C). The data is represented by different symbols and lines for varying conditions or materials. The resistivity increases with temperature, indicating a positive temperature coefficient of resistance. The specific trends and values for each condition are detailed in the accompanying text.
Figure 11