Preparation of high performances $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ thermoelectric materials from nanosized precursors

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Abstract

$\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ thermoelectric materials were prepared by three different synthesis methods producing nanosized precursors: coprecipitation (with ammonium carbonate or oxalic acid), and attrition milling, which were compared with the obtained by the classical solid state method. Microstructure has shown that precursors produced by coprecipitation and attrition milling methods produced nanometric precursors, much smaller than the typical sizes produced by the solid state route. The thermoelectric properties are in agreement with the microstructural features, leading to lower resistivity in all the samples, compared with the solid state ones while Seebeck coefficient is maintained practically unchanged in all cases. As a consequence, maximum power factor values of around four times higher than the obtained in the classical solid state method ones have been determined. Moreover, the highest power factor value at 650 °C is higher than the best results obtained in as-grown textured materials produced by the laser floating zone technique.

Keywords: Ceramics; Synthesis; Electric properties; Microstructure; Power factor.

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1. Introduction

Thermoelectricity provides an attractive technology to directly transform thermal to electrical energy without moving parts. As a consequence, the thermoelectric (TE) systems are one of the most promising ones to increase the efficiency in the energy transforming systems. Furthermore, the TE systems can be used in solar clean energy generation [1]. In any case, they can help reducing CO₂ emissions, decreasing the release of greenhouse gases. On the other hand, before any practical application of TE materials it is necessary to raise their performances. The efficiency of these materials is determined using the dimensionless figure-of-merit, $ZT (=TS^2/\rho\kappa$; T , S , ρ , and κ , are absolute temperature, Seebeck coefficient, electrical resistivity, and thermal conductivity, respectively [2]). The electrical part of ZT expression (S^2/ρ), called power factor, PF, is also often used to determine the materials TE performances when thermal conductivity measurements are not possible to be measured.

Today it is possible to find thermoelectric modules with high performance based on different alloys and/or intermetallic materials. Unfortunately, many of these materials are composed of heavy and/or toxic elements [3,4] which can be volatilized and/or oxidized at high temperatures and, as a consequence, their working temperature is drastically limited. This is a very important drawback for the practical applications of these intermetallics due to the fact that most of the wasted heat is produced in industrial processes involving high temperatures [5]. Moreover, they are also limited by their relatively low abundance in earth's crust and, consequently, high prices, drastically limiting their commercial exploitation [6]. These limitations were surpassed with the discovery of attractive thermoelectric performances in Na_xCoO₂ ceramic material [7], which has higher chemical stability

at high temperatures and is composed of cheaper, environmentally friendly, and more abundant elements than the intermetallic ones. This discovery boosted the search for new ceramic materials with high thermoelectric performance. Nowadays, different thermoelectric ceramics are studied as promising materials for practical applications, such as MnO-, SrTiO₃-, or CoO-based ceramics [8-10]. In any case, their bulk performances should be drastically raised to achieve values close to the obtained in single crystals before seriously been considered for mass production [11].

In the case of the Co-based ceramics, it has been found that their crystal structure can be described by a monoclinic system which is formed by the alternating stacking of two different subsystems. One is of a common conductive CdI₂-type CoO₂ layer with a two-dimensional triangular lattice and the other, a block layer composed of insulating rock-salt-type (RS) layers. Both sublattices (RS and CdI₂-type layer) possess common a- and c-axis lattice parameters and β angles but different b-axis length, causing a misfit along the b-direction [12]. As a consequence of their crystal structure, layered cobaltites are characterized by a very important crystallographic and electrical anisotropy. Several methods have been used to take advantage of this anisotropy aligning the grains along their ab planes to improve the electrical transport. Among these processes, it is possible to highlight the template grain growth (TGG) [13], hot-pressing [14], spark plasma sintering (SPS) [15], laser floating zone (LFZ) [16], or the electrically assisted laser floating zone melting (EALFZ) [17]. In spite of the good TE performances obtained through these processes, the industrial production still remains an important challenge due to the relatively long processing times and/or the prices of these systems.

Many authors have decided to follow another different way to improve the TE properties of these ceramic materials without the need of these expensive systems. In this case, they exploit the fact 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 [18]. This characteristic provides the basis for the modification of thermoelectric properties of a given material via chemical substitutions as Sr by Ca or Pb by Bi in $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_x$ [19,20] or by substituting Ca or Co in $\text{Ca}_3\text{Co}_4\text{O}_9$ [21,22] leading to better performance than the obtained in the pure material.

On the other hand, it is well known that precursor characteristics may greatly influence the properties of the final products, but only a small amount of work has been done in exploring the synthesis methods. Usually, TE oxides are prepared by the classical solid state route [23-25], which involves repeated mixing, milling and calcinations. Nevertheless, incomplete reaction, and compositional inhomogeneities are typical trademarks of this process. Some other methods have been used to surpass these problems, mainly based on sol-gel techniques [10,15,26,27] while much less bibliography is dealing with other more complex techniques [28,29].

Taking into account the above considerations and previously reported data in similar systems [30], the comparison between three different synthesis methods which produce precursor powders with very high surface/volume relationship will be shown in this work. These processes are: coprecipitation with oxalic acid, coprecipitation with ammonium carbonate, and attrition milling. Moreover, classical solid state preparation method will be also used to produce reference samples. The bulk TE properties will be determined in the sintered bodies, related with the microstructure, and compared with those obtained on solid state prepared samples and with the best results found in the literature for the $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ ceramics.

2. Experimental

2.1. Samples preparation

The $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ samples used in this work were prepared by the different methods described in detail in the following paragraphs:

- (i) *Coprecipitation with oxalic acid*: Bi_2O_3 (99.9%, Aldrich), SrCO_3 ($\geq 99\%$, Aldrich), and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$, Aldrich) were dissolved in a mixture of HNO_3 (Fluka, PA) and distilled water. Oxalic acid ($\text{HOOC}\text{COOH} \cdot 2\text{H}_2\text{O}$; Panreac, $\geq 99.5\%$) was added to the solution until a pH value of around 2.4 was obtained. In order to produce the total precipitate of cations, pH was then adjusted to around 5.3 by the addition of 30 wt.% NH_3 solution in water (Panreac, PA), and finally to 7.1 by adding $(\text{NH}_4)_2\text{CO}_3$ (Panreac, PRS-CODEX). The resulting suspension was kept for about 15 minutes at 75°C with continuous stirring to produce the precipitates agglomeration. The slurry was then filtered and washed several times with distilled water to isolate a light pink solid. The product was dried at $\sim 150^\circ\text{C}$ and heated at 450°C for 1 hour to decompose the organic material.
- (ii) *Coprecipitation with ammonium carbonate*: Bi_2O_3 (99.9%, Aldrich), SrCO_3 ($\geq 99\%$, Aldrich), and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$, Aldrich) were dissolved in a mixture of HNO_3 (Fluka, PA) and distilled water. Once a clear solution was obtained, $(\text{NH}_4)_2\text{CO}_3$ (Panreac, PRS-CODEX) was added stepwise until a pH value of around 6.7 has been obtained to precipitate all the cations. The slurry was then kept at 75°C for 15 minutes with continuous stirring to age the precipitate. After this process, the resulting suspension was filtered to separate the solid product which was subsequently washed several times with distilled water. The light violet solid product

was dried at $\sim 150\text{ }^{\circ}\text{C}$ and heated at $450\text{ }^{\circ}\text{C}$ for 1 hour to decompose the organic material.

(iii) *Attrition milling*: Bi_2O_3 (99.9%, Aldrich), SrCO_3 ($\geq 99\%$, Aldrich), and Co_3O_4 (99.5%, Panreac) were mixed and attrition milled, using ZrO_2 balls as milling media in water, for 2 h. The resulting slurry was then sieved and the balls were washed several times with distilled water to separate the grinding media and the milled solid. The suspension was then totally dried under infrared radiation until a soft brownish powder was obtained.

(iv) *Classical solid state method*: Bi_2O_3 (99.9%, Aldrich), SrCO_3 ($\geq 99\%$, Aldrich), and Co_3O_4 (99.5%, Panreac) were mixed and milled in an agate ball mill for 2 h at 300 rpm in acetone media. The resulting slurry was then sieved and the balls were washed with acetone to separate the grinding media and the powders mixture. The suspension was then totally dried under infrared radiation until a soft brownish powder was obtained.

The obtained powders from the different methods were then thermally treated at 750 and $800\text{ }^{\circ}\text{C}$ for 12 h with an intermediate manual milling, to decompose the SrCO_3 , pressed in form of parallelepipeds at about 400 MPa, followed by a sintering process performed at $800\text{ }^{\circ}\text{C}$ for 24 h with a final furnace cooling.

Hereafter, samples produced by the coprecipitation method with oxalic acid will be named S1, with ammonium carbonate, S2, the ones by attrition milling, S3, and the classical solid state ones, S4.

2.2. Characterization

The precursors evolution has been followed in the different processing steps through DTA-TGA (TA Instruments, SDT Q600) between room temperature (RT)

and 800 °C at a heating rate of 10 °C/min. FTIR (Bruker Vertex 70) has been used to identify the products obtained after each processing stage. Moreover, the powders microstructure and grain size evolution has been studied in a Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss Merlin).

Phase identification in the sintered materials has been performed using powder X-ray diffraction (XRD) utilizing a Rigaku D/max-B X-ray powder diffractometer (CuK α radiation) with 2 θ ranging between 10 and 70 degrees. Microstructural observations were performed on the samples surface in a FESEM fitted with an energy dispersive spectrometry (EDS) device used to determine the elemental composition of each phase.

Electrical resistivity and Seebeck coefficient were simultaneously determined in all samples using the steady state mode, by the standard dc four-probe technique in a LSR-3 apparatus (Linseis GmbH) between 50 and 650 °C under He atmosphere. Moreover, with the electrical resistivity and Seebeck coefficient data, PF has been calculated to evaluate the TE performances.

3. Results and discussion

3.1. Precursor powders

After drying the precipitates obtained by filtering the S1 and S2 solutions, FTIR analysis has been used to determine the species produced in the precipitation process. The absorbance graphs, as a function of wavenumber, are displayed in Fig. 1. The absorbance bands have shown that S1 precipitate (Fig. 1a) is formed by a mixture of Bi, Sr and Co(II) oxalates [31], with common peaks centered at about 1630-1610 (strong), and 1330-1310 (medium) cm⁻¹. Other peaks at 1450-1430 (weak) and 800-780 (weak) cm⁻¹ are associated to the Bi and Sr oxalates, 1380-

1360 (weak) cm^{-1} to the Co(II) and Sr oxalates, and 840-820 (weak) cm^{-1} to the Co(II) oxalate. On the other hand, in the S2 precipitate (Fig. 2b) spectrum major absorbance peaks (at about 1300 and 1050 cm^{-1}) can be associated to ammonium carbonate, with the weak ones at 880-860 and 730-750 cm^{-1} associated to Co and Sr carbonates, at 850-830 cm^{-1} to Bi basic carbonate, and 710-730 cm^{-1} to Co carbonate [31]. Moreover, the evolution of precursors with the thermal treatments is illustrated in Fig. 1c-e for the S3 precursors. The compositional evolution observed in these spectra is the same for the S1, and S2 precursors after the thermal treatment at 450 °C for 1 h, as well as for the S4 after drying. As it can be clearly seen in the figure, in a first step (after drying in this particular case, Fig. 1c) the S3 precursors are composed by Bi and Co oxides (undetected with this technique), together with Sr carbonate identified through its peaks at around 1450 (strong), and 850 cm^{-1} (medium) [31]. On the other hand, after the thermal treatment at 750 °C for 12 h, no evident signal of Sr carbonate can be identified (Fig. 1d), clearly indicating that its amount is fairly below the detection limit of this technique. As a consequence, the graph obtained after the second thermal treatment at 800 °C (Fig. 1e) for 12 h used for further decomposition of carbonates, shows the same absence of Sr carbonate peaks.

In order to know the thermal evolution of these two precipitates, DTA-TGA measurements were performed under air atmosphere and the results are displayed in Fig. 2a and b. As can be clearly observed in the plot, both precursors loss about 10 wt.% until around 200 °C which can be associated to solvent losses. Further heating produces a broad mass loss of around 25 and 15 % for the S1 and S2 precursors, respectively, due to the organic material decomposition. This step is confirmed by the presence of sharp exothermic peaks found in the DTA (insert in

Fig. 2) at about 290 and 250 °C for S1 and S2, respectively. The difference in weight loss for both precursors is in agreement with the rapid decomposition of Bi, Sr, and Co oxalates and the formation of Sr carbonate, and Bi and Co oxides, in the S1 materials, while for the S2 only ammonium carbonate is decomposed at this temperature. On the other hand, the gradual weight loss produced between 250 and 600 °C in the S2 precursors is due to the Bi and Co carbonates decomposition to produce their oxides [29,32]. Finally, from around 600 °C the SrCO_3 decomposition is starting. The evolution of precursors with the different thermal treatments is illustrated in Fig. 2c and d, where their TGA graphs are displayed. As it can be easily observed in the figure, after the thermal treatment at 450 °C for 1 h (Fig. 2c), samples loss about 10 wt.% from 400 to 600 °C, probably due to some undecomposed organic material. From 600 °C, a slight weight loss of about 2 wt.% is produced until 800 °C, due to the strontium carbonate decomposition. As a consequence, the temperatures for the subsequent thermal treatments were fixed in 750 and 800 °C, for 12 h each, with an intermediate manual milling to assure the carbonates decomposition. After the thermal treatment at 750 °C, TGA shows less than 1 wt.% loss between 750 and 800 °C (see Fig. 2d), clearly indicating that most of the carbonates have disappeared.

SEM observations have been performed on S1 and S2 precursors to study the microstructural modifications produced with the thermal treatment at 450 °C for 1 h (to decompose the organic material) and compared with the dry S3 and S4 ones. Representative images of samples in the different conditions are displayed in Fig. 3. In the micrographs, very important differences can be observed when comparing S1 and S2 precipitates (Figs. 3a and b, respectively). The S1 precipitates are formed by large (more than 1 μm length) columnar-like grains corresponding to the different

oxalates while S2 ones show an bulky matrix where small metallic carbonate grains (as previously discussed for their FTIR spectra) seem to appear as inclusions in the matrix. When these precursors are subjected to the thermal treatment to decompose the organic material, it is clear that small particles (less than 100 nm), probably Bi and Co oxides and Sr carbonate, appear (see Figs. 3c and d). They are forming agglomerates which, approximately, keep the same shape observed before the thermal treatment. On the other hand, the dry S3 and S4 precursors are presented in Figs. 3e and f, respectively. From these images, it is clear that S1 and S2 precursors are formed by much smaller grains than S3 and S4 ones (see Figs. 3c-e). Moreover, S3 grains are still smaller than S4 ones, as expected from the milling procedure.

In the case of microstructure, great differences have been found between them, depending on the preparation route. As a consequence, they have been studied and compared after each thermal treatment in order to easily visualize their thermal evolution. The microstructural observations performed in all the powder precursors after the thermal treatment at 750 °C for 12 h are illustrated in Fig. 4. As it can be easily seen in the figure, in the S1 and S2 powders big plate-like grains coexist with very small ones with different aspect. Moreover, the sizes of these plate-like are similar to the obtained in the S4 precursors, which are the largest ones in this step. On the other hand, S3 precursor powders have only slightly grown when compared with the other ones, possessing the smallest grain sizes. These effects are due to the high reactivity of the S1 and S2 precursors as a consequence of the intimate cation mixture, and the relatively large grain sizes produced in the S4 ones after milling.

After the thermal treatment at 800 °C for 12 h, further reaction is produced in the different precursors, as illustrated in Fig. 5 where representative micrographs of powders produced by the different methods, are shown. At a first sight, it is easy to see that the small grains present in S1 and S2 precursors, after the thermal treatment at 750 °C for 12 h, have totally disappeared. Moreover, the grains have grown in all cases (see Figs. 4 and 5), leading to similar grain sizes for precursors S1, S2, and S4, while they are much smaller for the S3 samples. This can be explained by a slight grain growth in the S4 precursors due to their initial large size, and to a rapid diffusion in the S1 and S2 precursors promoted by the presence of very small grains which tend to disappear. In the case of S3 precursors, their intermediate sizes, together with the fixed composition of each grain, lead to a slower diffusion and, consequently, to a lower grain growth.

As it was mentioned previously, after thermal treatments, the powders are carbonates-free and, therefore, they can be used to prepare the thermoelectric bulk materials.

3.2. Sintered materials

Powder XRD plots for sintered samples obtained for the different synthesis methods are represented (from 10 to 40 degrees for clarity) in Fig. 6. From the data represented in the figure it is very clear that all the samples show similar patterns where the most intense peaks correspond to the crystallographic planes of the $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ phase [33], indexed in the plot. On the other hand, only very small amounts of secondary phases are found, indicated by the presence of the small peaks marked with a * in the graph (associated to the $\text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_y$ phase, with $R\bar{3}mH'$ space group [34]). Moreover, it seems that S1 and S4 precursors possess a

higher amount of $\text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_y$ phase, due to the higher relative intensity of peaks associated to this secondary phase. In any case, these results clearly show that $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ is the major phase in all cases, indicating that the synthesis conditions used are adequate to produce a high amount of the thermoelectric phase, independently of the processing route.

SEM micrographs of representative surfaces of the sintered materials prepared with the different precursors are presented in Fig. 7. In these images it can be clearly observed that three different contrasts can be identified (numbered in Fig. 7a for clarity). These contrasts have associated, through EDS, to different compositional regions. Grey contrast (#1) corresponds to the thermoelectric $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ phase and is the major one in all samples. White contrast (#2) has been associated to the Bi-Sr-O solid solution with an approximate Bi:Sr cation relationship 3:1, in agreement with the XRD data discussed previously. Finally, dark grey contrast (#3) shows a Ca-Co-O composition with an approximate Ca:Co relationship 1:1. This last phase has not been observed in the XRD patterns, probably due to its small particle size (see dark contrast in Fig. 7d). On the other hand, it is also clear from these micrographs that the amount of these secondary phases changes with the synthesis method. The highest amount is found in S4 samples, reflecting the well-known drawbacks of the classical solid state synthesis method while the lowest ones are found for the S2 and S3 methods, probably due to the higher homogeneity of the starting mixtures. In the case of the S1 samples, the presence of a relatively high amount of secondary phases can be associated to a different cationic precipitation rate, leading to local compositional inhomogeneities.

Other interesting feature which can be observed in these micrographs is that S1, S2 and S4 samples show approximately the same grain sizes while S3 ones possess

much lower grain sizes. This fact can be associated to the higher reactivity of S1 and S2 samples due to the intimate cation mixture produced in the precipitation process, while in the S4 ones these sizes are typical for this synthesis route. The very small grain sizes in samples S3 can be associated to a higher distance between the different cations, when compared with the mixtures produced by the coprecipitation methods.

These microstructural features are reflected in the electrical properties of samples, as can be observed in Fig. 8 where their electrical resistivity evolution with temperature is displayed. As it can be easily observed in the graph, the highest resistivity values in the whole measured temperature range correspond to S4 samples, due to their highest amount of secondary phases, as shown in Fig. 7. Moreover, it displays semiconducting-like behaviour ($dp/dT < 0$) in the whole measured temperature range, in agreement with previous results [35]. On the other hand, when comparing the electrical resistivity for samples S1 and S3 and their microstructures (see Figs. 7a and c), it can be deduced that grain boundaries possess a higher effect on the electrical properties than the presence of secondary phases in relatively low amounts. Moreover, this high number of grain boundaries leads to a semiconducting-like behaviour from RT to 450 °C, changing to a metallic-like ($dp/dT > 0$) at higher temperatures, while it is slightly metallic-like for S1 samples in the whole measured temperature range. As a consequence, electrical resistivity of S3 samples is higher than the measured in S1 ones. Finally, the decrease of the number of grain boundaries and secondary phases, leads to the lowest resistivity values measured in S2 samples, with a metallic-like behaviour in the whole measured temperature range.

The minimum measured values in these samples at RT ($\sim 20 \text{ m}\Omega\cdot\text{cm}$), is lower than the obtained in laser floating zone (LFZ) grown materials ($45 \text{ m}\Omega\cdot\text{cm}$) [36], but higher than the obtained after annealing these samples ($18 \text{ m}\Omega\cdot\text{cm}$) [36]. Moreover, they are approximately the same obtained in samples produced by solution methods (around $21 \text{ m}\Omega\cdot\text{cm}$) [37], and very close to the values obtained in sintered materials under oxygen atmosphere (about $15 \text{ m}\Omega\cdot\text{cm}$) [13] or in single crystals ($\sim 20 \text{ m}\Omega\cdot\text{cm}$) [33]. Furthermore, these values are much lower than the one obtained in sinter-forged materials (around $40 \text{ m}\Omega\cdot\text{cm}$) [38]. From these data, it can be deduced that samples produced by S2 method are between the best ones reported in the literature from the point of view of their electrical resistivity. This is in agreement not only with the very low amount of secondary phases, and large grain sizes found in these samples, but also pointing out to enhanced grains connectivity and clean grain boundaries.

Fig. 9 displays the variation of Seebeck coefficient with temperature for the different samples. All of them exhibit positive values in the whole measured temperature range, confirming a dominating hole conduction mechanism. All samples exhibit very similar S values, with only minor differences at RT. The S values are ranging from around $120 \text{ }\mu\text{V/K}$ to $210 \text{ }\mu\text{V/K}$ at RT and $650 \text{ }^\circ\text{C}$, respectively, in all cases. These values are approximately the same obtained in samples produced by solution methods at both temperatures (130 and $210 \text{ }\mu\text{V/K}$) [37], and higher than the values measured in sintered materials under oxygen atmosphere ($40 \text{ }\mu\text{V/K}$ at $650 \text{ }^\circ\text{C}$) [13] or in single crystals (20 and $120 \text{ }\mu\text{V/K}$ at RT and $650 \text{ }^\circ\text{C}$, respectively) [33]. Moreover, they are lower than the obtained in laser floating zone (LFZ) grown materials at RT ($140 \text{ }\mu\text{V/K}$) but higher at $650 \text{ }^\circ\text{C}$ ($140 \text{ }\mu\text{V/K}$) [36]. The fact that LFZ grown materials possess so high S values at RT is due to the high number of

oxygen vacancies produced by this LFZ method, as a consequence the holes concentration is decreased due to the reduction of Co^{4+} to Co^{3+} leading to high Seebeck coefficient. This effect is in agreement with previous works which showed that, under reducing conditions, the misfit phase $[\text{Ca}_2\text{CoO}_3][\text{CoO}_2]_{1.62}$ (close to this misfit system) contains considerable amounts of oxygen vacancies [39] leading to much higher Seebeck coefficients than the measured in sintered materials with equilibrium oxygen vacancies.

From the electrical resistivity and Seebeck coefficient values, PF variation with temperature has been calculated for all the samples and represented in Fig. 10. In the graph, it is clear that S4 samples possess the lowest PF values in all the measured temperature range due to their highest resistivity, as a consequence of their microstructural drawbacks discussed previously. S1 and S3 samples show very similar PF values due to their similar electrical behaviour produced by different microstructural features, in the S1 samples it is due to the presence of secondary phases while for the S3 ones, it is coming from the higher amount of grain boundaries. On the other hand, as mentioned in the SEM discussions, S2 samples show a reduced number of grain boundaries when compared with S3 ones, and lower amount of secondary phases than S1 samples. As a consequence, samples produced by the S2 method show improved TE properties, reflected in the highest PF values of all studied samples. The maximum PF values at 650 °C ($\sim 0.15 \text{ mW/K}^2\cdot\text{m}$) obtained S2 samples is about 100, 100 and 400 % higher than the measured in S1, S3, and S4 samples, respectively. Moreover, it is around 200 % higher than the measured on LFZ textured materials ($0.06 \text{ mW/K}^2\cdot\text{m}$) but about 25 % lower than the obtained in textured and annealed samples ($0.20 \text{ mW/K}^2\cdot\text{m}$) at the same temperature [36].

These high PF values obtained with relatively economic and scalable preparation techniques make these $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ sintered materials very promising candidates for practical applications in high temperature thermoelectric devices.

4. Conclusions

$\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ thermoelectric materials were prepared by three different synthesis methods: coprecipitation with ammonium carbonate, with oxalic acid, attrition milling, and compared with those prepared by the classical solid state method. Microstructural studies of precursors have shown that both coprecipitation methods and attrition milling produced very small particle size precursors, compared with the typically obtained using the classical solid state route. These small particle sizes lead to lower amount of secondary phases after sintering. Thermoelectric properties clearly agree with the microstructural features found in these materials. The measured electrical resistivity is lower than the measured in solid state sintered materials in all cases while nearly no modification of Seebeck coefficient has been found. As a consequence, the best PF values measured in samples produced by coprecipitation with ammonium carbonate are around four times higher than the obtained in the classically prepared ones. Moreover, they are about two times higher than the measured in the other two types of samples. Furthermore, they are higher than the best values obtained on as-grown LFZ textured $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ materials reported in the literature.

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Figure captions

Figure 1. FTIR spectra of the dry products obtained after filtering the precipitates of (a) S1; and (b) S2 precursors; and evolution of S3 precursors after drying (c); and after the thermal treatments at 750 °C for 12 h (d); and 800 °C for 12 h (e).

Figure 2. TGA plots vs. temperature of the dry products obtained after filtering the S1 precipitates (a); and S2 precursors after drying (b); and after the thermal treatments at 450 °C for 1 h (c); and at 750 °C for 12 h (d). The insert shows the DTA graph obtained for the S1 (a); and S2 (b) precursors after drying.

Figure 3. Representative SEM micrographs of powders obtained in different conditions: a) S1; and b) S2 after drying the precipitates; c) S1; and d) S2 after thermal treatment at 450 °C for 1 h; e) S3; and f) S4 after drying the suspensions.

Figure 4. Representative SEM micrographs obtained in the different powder precursors after the thermal treatment at 750 °C for 12 h. a) S1; b) S2; c) S3; and d) S4.

Figure 5. Representative SEM micrographs obtained in the different powder precursors after the thermal treatment at 800 °C for 12 h. a) S1; b) S2; c) S3; and d) S4.

Figure 6. Powder XRD plots of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ sintered specimens obtained with the different synthesis methods. a) S1; b) S2; c) S3, and d) S4. Crystallographic planes

indicate the peaks for the $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ phase and the * shows those belonging to the $\text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_y$ secondary one.

Figure 7. Representative SEM micrographs obtained on the surfaces of sintered materials prepared with the different precursors S1 (a), S2 (b), S3 (c), and S4 (d).

Figure 8. Electrical resistivity vs. temperature of sintered materials prepared with the different precursors (♦) S1, (●) S2, (■) S3, and (▼) S4.

Figure 9. Seebeck coefficient vs. temperature of sintered materials prepared from the different precursors (♦) S1, (●) S2, (■) S3, and (▼) S4.

Figure 10. Power factor vs. temperature of sintered materials prepared from the different precursors (♦) S1, (●) S2, (■) S3, and (▼) S4.

Figure 1

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