Use of laser technology to produce high thermoelectric performances in $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$

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Abstract

Intrinsically nanostructured $\text{Bi}_2\text{Sr}_2\text{Co}_{1.7}\text{O}_x$ bulk polycrystalline ceramics were prepared by a polymer solution method and by directional growth. Moreover, the effect of annealing on the as-grown materials has been studied.

Microstructure has shown randomly oriented grains in the classical sintered materials while in the textured samples they were well oriented with their c-axis nearly perpendicular to the growth direction. Furthermore, the annealed samples showed much lower amount of secondary phases than the as-grown ones. These microstructural changes are reflected on the thermoelectric properties which increase with the grain orientation and with the decrease on the secondary phases content mainly due to the electrical resistivity reduction. As a consequence, a raise on the power factor of about 2 and 5 times, compared with the classically sintered samples, were obtained for the as-grown and annealed samples, respectively. The maximum power factor obtained at

650 °C in the annealed samples ($\sim 0.20 \text{ mW/K}^2\text{m}$) is much higher than the obtained in sinter-forged textured materials at the same temperature.

Keywords: Grain growth, Sintering, Microstructure; Electrical resistivity; Thermopower

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1. Introduction

Thermoelectric (TE) materials are attracting attention due to their ability to transform a temperature gradient into electrical power due to the well-known Seebeck effect. Their inherent characteristics have focused attention on these materials to be applied in practical applications as waste heat recovery devices [1] or solar thermoelectric generators [2]. Furthermore, they can also be used as heating/refrigeration devices [3]. The conversion efficiency of such materials is usually quantified by the dimensionless figure of merit ZT , $TS^2/\rho\kappa$ (in which the electrical part, S^2/ρ , is 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 [4].

Nowadays, the commercial applications of thermoelectric devices are based on the use of alloys and/or intermetallic materials, such as Bi_2Te_3 or CoSb_3 , with high thermoelectric performances at relatively low temperatures. On the other hand, these materials possess some drawbacks, as they can be degraded at high temperatures under air and/or releasing toxic or heavy elements. These problems lead to the limitation of their working temperature limiting their effective performances, as can be deduced from the ZT expression. The temperature limitation was surpassed in 1997 by the discovery of high thermoelectric properties in the Na-Co-O system [5]. From the discovery of this thermoelectric oxide, much work has been performed on the CoO-based ceramics as promising thermoelectric materials for high temperature applications. The intense research work continues on these families, such as $\text{Ca}_3\text{Co}_4\text{O}_9$, LaCoO_3 , $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_9$ and $\text{Bi}_2\text{Ca}_2\text{Co}_2\text{O}_y$ with interesting thermoelectric properties and high working temperatures [6-9].

The crystal structure of these CoO families is composed of two different layers, with an alternate stacking of a common conductive CdI₂-type CoO₂ 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 CdI₂-type CoO₂ layer) possess common *a*- and *c*-axis lattice parameters and β angles but different *b*-axis length, causing a misfit along the *b*-direction [10]. It has been reported that the misfit factor and/or the charge of the RS block layer between the CoO₂ ones govern the Seebeck coefficient values [11]. These crystallographic characteristics provide the basis for the modification of thermoelectric properties of a given material via chemical substitutions. The most common ones substitute an alkaline-earth by other cation, as Ca for Sr in Bi₂Sr₂Co_{1.8}O_x [12] or La for Ca in Ca₃Co₄O₉ [13], or Co by another transition metal, as Cu or Cr for Co in Ca₃Co₄O₉ [14,15]. Other usual substitutions are Pb for Bi in Bi₂Ca₂Co_{1.7}O_x [16].

On the other hand, 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, as Template Grain Growth (TTG) [17], spark plasma sintering [18], hot pressing [19], laser floating zone melting (LFZ) [20], or electrically assisted laser floating zone (EALFZ) [21].

The aim of the present work is studying the modification of microstructure as well as the thermoelectric properties of Bi₂Sr₂Co_{1.8}O_x when comparing the

classically sintered materials with the laser floating zone textured and textured-annealed ones.

2. Experimental

The polycrystalline $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ ceramics used for this study have been prepared by the polymer solution method route [22]. To a suspension of $\text{Bi}(\text{CH}_3\text{CO}_2)_3$ (99.99 + %, Aldrich), $\text{Sr}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ (Reagent grade, Alfa Aesar), and $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ (98 %, Panreac) powders in distilled H_2O , glacial acetic acid (ACS Reagent, Panreac) was added until a pink clear solution was formed. Polyethyleneimine (PEI) (50 % aqueous, Aldrich) was added to the above solution, which turned darker immediately due to the nitrogen-metal coordination. After partial evaporation (~80 vol. %) of water and acetic acid in a rotary evaporator, the concentrated solution, with a very high viscosity, was placed onto a hot plate until a very dark pink paste appeared. Further heating turned this paste to violet color, followed by a slow combustion with the release of brown fumes (nitrogen oxides). The resulting powder has then been thermally treated twice at 750 and 800 °C for about 12 hours under air, with an intermediate manual milling, in order to assure the complete decomposition of the carbonates. This thermal treatment is necessary and it has been designed specifically to avoid the presence of carbonates in the following steps [23]. These as-prepared powders were then used for the different processed samples:

a) *Classical sintering process*: The powders were uniaxially pressed at 400 MPa for 1 minute in order to obtain green ceramic parallelepipeds (~ 3 mm x 3 mm x 14 mm), with an adequate size and shape for their thermoelectric

characterization. These green bodies were subsequently sintered in the optimal conditions for this system, consisting in one step heating at 810 °C for 24 h with a final furnace cooling [8].

b) *Texturing process*: The resulting powders were then cold isostatically pressed into latex tubes at ~200 MPa for around 2 minutes to obtain green ceramic cylinders which were subsequently used as feed in a LFZ device equipped with a continuous power Nd:YAG laser ($\lambda = 1.06 \mu\text{m}$). The processing of the different samples has been performed in the same conditions; they were directionally grown downwards from the melt at 30 mm/h with a seed rotation of 3 rpm. Moreover, in order to assure compositional homogeneity of the molten zone, an opposite feed rotation of 15 rpm has also been performed. Finally, after the texturing process, long (more than 15 cm) and geometrically homogeneous (~2 mm diameter) textured cylindrical rods have been produced as reported in previous works [24]. These bars were cut into pieces with the adequate dimensions for the thermoelectric measurements (~ 15 mm long).

c) *Texturing-annealing process*: Part of the samples obtained in the texturing process were subjected, after cutting, to a thermal treatment consisting in one step heating at 810 °C for 24 h with a final furnace cooling to reduce the amount of secondary phases, as reported in previous works [25].

The identification of the main phases in all the samples was carried out using powder XRD in a Rigaku D/max-B X-ray powder diffractometer ($\text{CuK}\alpha$ radiation), between 10 and 70 degrees. Microstructure evolution has been observed using a scanning electron microscope (JEOL 6000) equipped with an energy dispersive X-ray spectroscopy (EDS) device, used to determine the elemental composition of the different phases. Polished sections of all samples

have been observed to analyze the microstructural evolution with the different treatments. Electrical resistivity and Seebeck coefficient were simultaneously determined by the standard dc four-probe technique in a LSR3 measurement system (Linseis GmbH), in the steady state mode, at temperatures ranging from 50 to 650 °C. With the electrical resistivity and Seebeck coefficient data, the power factor ($PF = S^2/\rho$) has been calculated in order to determine the samples performances.

3. Results and discussion

Powder XRD patterns for all the $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ samples (from 10 to 40 degrees, for clarity), are displayed in Fig. 1. From these data, it is clear that the most intense peaks correspond to the $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ phase (indicated by their diffraction planes in Fig. 1a, in agreement with previously published data [26]. On the other hand, peaks marked with • and ♦ in Fig. 1a correspond to the $\text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_y$ [27] and $\text{Sr}_6\text{Co}_5\text{O}_{14.3}$ [28] secondary phases, respectively. When observing carefully the patterns displayed in the figure, it can be clearly seen that the relative intensity of reflections attributed to the secondary phases decrease from the samples prepared by the classical solid state method (Fig. 1a) to the textured ones (Fig. 1b). Moreover, the annealing treatment still decreased the amount of secondary phases, as can be observed by the nearly total disappearance of the peaks corresponding to the secondary phases (see Fig. 1c). This result clearly indicates that the temperature and time are adequate to produce nearly pure phase textured thermoelectric materials. On the other hand, it can also be observed the disappearance of some peaks belonging to the $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ phase with the annealing process. As it is well

known, the thermoelectric grains mostly grow along the ab planes, as reported in previous works [29], producing plate-like grains. As a consequence, the preparation of powdered samples can induce different preferential grain orientations in the powders. This is a typical effect associated with samples composed of very anisotropic grains (as plate-like ones).

Representative SEM micrographs of longitudinal sintered and as-grown fractured samples are shown in Fig. 2. In these micrographs it can be easily seen the microstructural evolution with the different processing processes. Classical sintered samples (Fig. 2a) show small (5-10 μm in the ab plane) randomly oriented plate-like grains while the as-grown ones possess very large (more than 100 μm in the ab plane) well aligned grains stacked long their ab planes (Fig. 2b). In any case, it is difficult to establish the grains dimensions in the c axis, even when observing at higher magnification (see Fig. 2c) where it can be observed that all the grains are formed by very thin plate-like grains perfectly stacked along their ab planes. Due to the difficulty inherent to the determination of thickness of each individual grain by SEM observations, an estimation of their thickness has been performed from the XRD results applying Scherrer's formula using the (006) and (0010) diffraction peaks. The obtained mean value for the grain thickness is about 35 nm in all cases, which confirms that the crystal preferential growth is produced along the ab plane.

Representative SEM micrographs of longitudinal sintered and as-grown polished samples are shown in Fig. 3. In these images it is clear that the grain sizes of the sintered samples (Fig. 3a) are much lower than for the textured ones (Fig. 3b and c). Moreover, it can be observed that grey contrast (#1), associated by EDS to the thermoelectric $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ phase, is the major one

in all cases. The other contrasts correspond to secondary phases and they are dark grey (#2) with $\text{Sr}_3\text{Co}_4\text{O}_x$ composition, light grey (#3) with different composition in the sintered ($\text{Bi}_{0.75}\text{Sr}_{0.22}\text{O}_y$) or textured samples (Bi_2SrO_x).

Finally, black contrast (#4) has been identified as CoO .

Other feature that can be observed in the micrographs is the relatively high porosity in the sintered specimens while nearly no porosity can be observed in the textured and textured annealed samples. Moreover, in the textured annealed samples thermoelectric phase amount is higher than in the textured ones without losing their grain orientation.

The effect of the different processing methods on the thermoelectric properties of these ceramics has been determined by electrical resistivity and Seebeck coefficient measurements. The temperature dependence of the electrical resistivity, as a function of the preparation method, has been measured and represented in Fig. 4. As it can be easily observed in the plot, two different behaviours can be observed, one for the classically sintered and as-grown samples and another one for the textured and annealed ones. The first ones show a marked semiconducting-like behaviour ($d\rho/dT < 0$) in all the measured temperature range. In the case of the textured and annealed samples, they show a clear metallic-like behaviour ($d\rho/dT > 0$) in all the measured temperature range, with lower resistivity values than the obtained in the other samples. The evolution of resistivity with the different processing can be explained taking into account the microstructural features discussed previously. The behaviour of the classically sintered materials is the typical observed in this kind of materials when they are formed by randomly oriented grains and possess an appreciable amount of isolating secondary phases. The as-grown samples show a good

grain orientation and lower number of grain boundaries due to their larger size. As a consequence, and in spite of an important raise on the secondary phases content, the resistivity values decrease, indicating that grain orientation and lower amount of grain boundaries have higher influence on the electrical resistivity than the amount of secondary phases. Moreover, when the as-grown samples are annealed, further decrease on the electrical resistivity is produced by the reduction on the secondary phases content. In any case, this decrease is lower than the produced by the texturing process, confirming that the secondary phases affect, in a lower extent than the grain orientation and size, the electrical resistivity values. The lowest resistivity values at 650 °C measured in the textured and annealed samples ($\sim 20 \text{ m}\Omega\cdot\text{cm}$) are close to the values obtained in sintered materials under oxygen ($\sim 15 \text{ m}\Omega\cdot\text{cm}$) [17] or single crystals ($\sim 18 \text{ m}\Omega\cdot\text{cm}$ at room temperature) [30]. Moreover, they are much lower than the measured on sinter-forged materials ($\sim 40 \text{ m}\Omega\cdot\text{cm}$) [31].

Fig. 5 displays the Seebeck coefficient variation with temperature, as a function of the processing method. It is evident that the sign of the thermopower is positive for the entire measured temperature range for all the samples which confirms a conduction mechanism mainly governed by holes. In this case, the sintered and the textured annealed samples possess similar Seebeck coefficient and behaviour. On the other hand, the as-grown ones show a very different behaviour and lower Seebeck values at high temperatures. The difference between both groups of samples can be explained by the higher amount of secondary phases found in the as-grown ones which reduce the thermoelectric phase content. On the other hand, the sintered and textured annealed samples possess higher amount of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ thermoelectric

phase. The highest Seebeck coefficient has been obtained for the sintered samples at 650 °C ($\sim 205 \mu\text{V/K}$), very close to the obtained in textured annealed ones ($\sim 200 \mu\text{V/K}$) and higher than the obtained in sinter-forged materials ($\sim 150 \mu\text{V/K}$) [31]. Moreover, the room temperature values are much higher than the obtained in sintered materials under oxygen at the same temperature ($\sim 40 \mu\text{V/K}$) [17].

In order to evaluate the thermoelectric performances of these materials, PF has been calculated from the resistivity and Seebeck coefficient values and plotted in Fig. 6. When considering PF values at about 50 °C ($\sim$ room temperature), it can be clearly seen that sintered samples show the lowest values (around $0.02 \text{ mW/K}^2\text{m}$). The texturing process promotes a very important increase at this temperature, reaching around $0.05 \text{ mW/K}^2\text{m}$, while the annealing produces further increase until about $0.10 \text{ mW/K}^2\text{m}$. In any case, these values are much higher than the obtained in sintered materials under oxygen at the same temperature ($\sim 0.01 \text{ mW/K}^2\text{m}$) [17]. Moreover, the maximum PF value at 650 °C ($\sim 0.20 \text{ mW/K}^2\text{m}$) for the textured annealed samples is around the best obtained in sinter-forged materials at the same temperature ($\sim 0.06 \text{ mW/K}^2\text{m}$) [31].

4. Conclusions

The effect of the processing method on the microstructure and thermoelectric properties of intrinsically nanostructured $\text{Bi}_2\text{Ca}_2\text{Co}_{1.7}\text{O}_x$ ceramic materials has been studied. The microstructure has shown that all samples possess $\text{Bi}_2\text{Ca}_2\text{Co}_{1.7}\text{O}_x$ thermoelectric phase as the major one. Moreover, the thermoelectric grains are formed by the close stacking of nanometric grains (around 35 nm) in the c-direction. Sintered samples showed randomly oriented

grains while the textured ones have very well oriented grains with their c-axis nearly perpendicular to the growth direction. The observed microstructures have an important impact on the thermoelectric properties, which increase from the sintered samples to the as-grown and the annealed ones. This effect is mainly produced by the decrease on the electrical resistivity of these samples.

Maximum PF values at 650 °C (about 0.20 mW/K²m) are much higher than the best ones reported in the literature for hot-forged textured materials. All these results show that Bi₂Sr₂Co_{1.8}O_x directionally grown and annealed ceramics are promising materials for practical applications.

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Figure captions

Figure 1. XRD plots of all the samples: a) classically sintered at 810 °C for 24 h; b) as-grown textured sample; and c) textured and annealed at 810 °C for 24 h. Crystallographic planes have been indicated on the peaks corresponding to the $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ thermoelectric phase. • and ♦ indicate the $\text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_y$, and $\text{Sr}_6\text{Co}_5\text{O}_{14.3}$ secondary phases, respectively.

Figure 2. Representative SEM micrographs of longitudinal fractured samples a) sintered at 810 °C for 24 h; b) textured by the LFZ technique; and c) high magnification of the textured sample.

Figure 3. Representative SEM micrographs of longitudinal polished samples a) sintered at 810 °C for 24 h; b) textured by the LFZ technique; and c) textured by LFZ and annealed at 810 °C for 24 h. #1 (grey contrast) $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ thermoelectric phase; #2 (dark grey) $\text{Sr}_3\text{Co}_4\text{O}_x$; #3 (light grey) $\text{Bi}_{0.75}\text{Sr}_{0.22}\text{O}_y$ (in a) or Bi_2SrO_x (in b and c); and #4 (black) CoO .

Figure 4. Temperature dependence of the electrical resistivity of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ samples, as a function of the processing technique. • sintered at 810 °C for 24 h; ♦ textured by the LFZ technique; and ■ textured and annealed at 810 °C for 24 h.

Figure 5. Temperature dependence of the Seebeck coefficient of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ samples, as a function of the processing technique. • sintered at 810 °C for 24

h; ♦ textured by the LFZ technique; and ■ textured and annealed at 810 °C for 24 h.

Figure 6. Temperature dependence of the power factor of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ samples, as a function of the processing technique. • sintered at 810 °C for 24 h; ♦ textured by the LFZ technique; and ■ textured and annealed at 810 °C for 24 h.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6