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Improvement of $Bi_2Sr_2Co_{1.8}O_x$ thermoelectric properties by laser floating zone texturing

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ABSTRACT

Thermoelectric performances of cobaltite ceramics can be improved raising the electrical conductivity. This can be performed by increasing the size of grains and aligning them along a preferential direction by the Laser Floating Zone (LFZ) method. In this work, $Bi_2Sr_2Co_{1.8}O_x$ ceramics have been directionally grown at three different speeds, *i.e.* 15, 30 and 50 mm/h. Their microstructure and thermoelectric properties are significantly influenced by the LFZ growth conditions. In all cases, the microstructure exhibits alternate cobaltite layers with secondary phases and small CoO inclusions, particularly when the growth is performed at high speeds (30 and 50 mm/h). The thermopower is, nevertheless, higher than usual while electrical resistivity values are similar to those obtained by conventional solid state routes, leading to relatively high power factor values. This result is probably linked to the stacking of different BiSrCoO layers and/or to oxygen vacancies.

1. Introduction

Thermoelectric materials are able to convert thermal energy to electrical one, accordingly the well-known Seebeck effect. This physical property is exploited to produce, environmental friendly, electrical power from a thermal gradient subjected to a thermoelectric device. The performance of thermoelectrics is commonly quantified by the figure of merit ZT, which is defined as $S^2T/\rho\kappa$, where S is the thermopower or Seebeck coefficient, T the absolute temperature, ρ the electrical resistivity, and κ the thermal conductivity.

Since the discovery of large thermoelectricity in Na_xCoO_2 [1], enthusiastic efforts have been devoted to explore new Co oxides of high thermoelectric performances, and some layered cobaltites, such as $[Ca_2CoO_3][CoO_2]_{1.62}$ and $[Bi_{0.87}SrO_2]_2[CoO_2]_{1.82}$ were found to exhibit good thermoelectric (TE) properties as well [2–5]. Moreover, these materials can operate at high temperature in air without degradation as compared to intermetallic thermoelectric compounds.

The crystal structure of these layered cobaltites is composed of an alternate stacking of a common conductive CdI_2-type CoO_2 layer with a two-dimensional triangular lattice and a block layer, composed of insulating rock-salt-type (RS) layers [6–8]. The two RS and CoO_2 layers have common a and c axes, while the b-axis lengths of the two layers are different. Moreover, this RS block layer can induce chemical pressure to the CoO_2 layer through the lattice misfit, which is suggested to introduce disorder into the conducting layers. Due to the high structural anisotropy of this crystal lattice, the alignment of plate-like grains using physical, mechanical and/or chemical processes is required to attain macroscopic properties as near as possible than those obtained on single crystals. It has been established that the Laser Floating Zone (LFZ) technique is adequate to obtain a good grain orientation in several oxide ceramic systems [9–12], especially in Bi-based cuprate superconductors which are very close systems compared to misfit cobaltites. Therefore, a significant decrease of the electrical resistivity of these misfit cobaltites is thus expected when they are adequately textured by this technique.

In this paper, we report the results obtained on textured $Bi_2Sr_2Co_{1.8}O_x$ ceramic bars processed by the LFZ technique with different pulling rates. The microstructural and phase composition analyses of the textured ceramics have been performed by scanning electron microscopy (SEM-EDS). Their thermoelectric properties were also measured as a function of temperature and discussed accordingly to the microstructure.

2. Experimental

Polycrystalline thermoelectric ceramics, with nominal composition $Bi_2Sr_2Co_{1.8}O_x$, have been prepared using the conventional solid state synthesis route using commercial Bi_2O_3 (Panreac, 98 + %), $SrCO_3$ (Panreac, 98+%) and Co_2O_3 (Aldrich, 98+%) powders. They were weighed in the adequate proportions, ball milled mixed and thermally treated twice at 750 and 800 °C for 12 h in air, with an intermediate manual and ball milling, to assure the total elimination of the CO_2 from the carbonates. This is a critical step to avoid their decomposition during the LFZ growth process, which can lead to bubble formation inside the melt and, as a consequence, disturb the solidification front. The resulting powder mixture was then cold isostatically pressed at 200 MPa in order to obtain green ceramic cylinders (longer than

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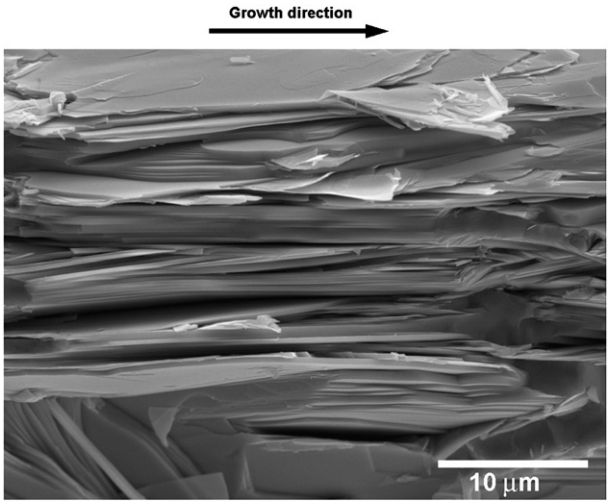

Fig. 1. SEM micrograph of a longitudinal fractured sample grown at 30 mm/h, showing the orientation of the misfit platelike grains. The arrow indicates the growth direction.

100 mm) with variable diameters between 2 and 4 mm, depending on the rubber tube size used as dye. These cylinders were subsequently used as feed in a LFZ device [13] equipped with a continuous power Nd:YAG laser ($\lambda = 1.06$ μm).

The growth processes have been performed downwards using three different growth rates (15, 30 and 50 mm/h), with no rotation of the seed. In order to ensure the compositional homogeneity of the melt, a feed rotation of 15 rpm has been implemented. Finally, after the texturing process, long (~10 to 30 cm, depending on the relative speed between feed and seed) and geometrically homogeneous textured cylindrical rods (from 1 to 4 mm in diameter) were obtained.

In order to identify the phases composition, transversal and longitudinal polished surfaces were observed with a JEOL 6000 scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS) device, INCAx-sight from Oxford Instruments. Electrical resistivity measurements were performed using the standard dc four-probe technique at temperatures between 5 and 400 K, in the absence of an applied external field, in a Physical Properties Measurement System (PPMS) from Quantum Design. Thermopower has been measured at temperatures between 5 and 300 K in an experimental setup described elsewhere [14].

3. Results and discussion

The good grain alignment in these materials can be illustrated by the micrograph displayed in Fig. 1, where the longitudinal fracture of a textured bar is shown. The platelet like grains are well oriented with their *ab* planes along the bar axis.

Fig. 2 shows the polished transversal surface of the textured bars grown at 15 (Fig. 2a and d), 30 (Fig. 2b and e) and 50 (Fig. 2c and f) mm/h. Typical microstructures in the directionally grown $Bi_2Sr_2Co_{1.8}O_x$ bars show a dense and compact microstructure with low porosity, as a consequence of their crystallization from the melt. On the other hand, it can be observed the formation of secondary phases (dark contrasts) linked to a slightly unstable solidification front. This instability becomes more and more important with increasing the pulling rate as higher amounts of secondary phases are clearly observed. In other words, at higher growth speeds, the solidification front is flatter than for lower speeds. This phenomenon reduces the radial thermal gradient (inherent to this process) and an homogeneous distribution of the secondary phases is observed. The observations at higher magnification (Fig. 2d, e and f), indicate that two distinct contrasts can be actually seen on the darkest zones. The black one has been identified as CoO phase whereas the darkest grey is

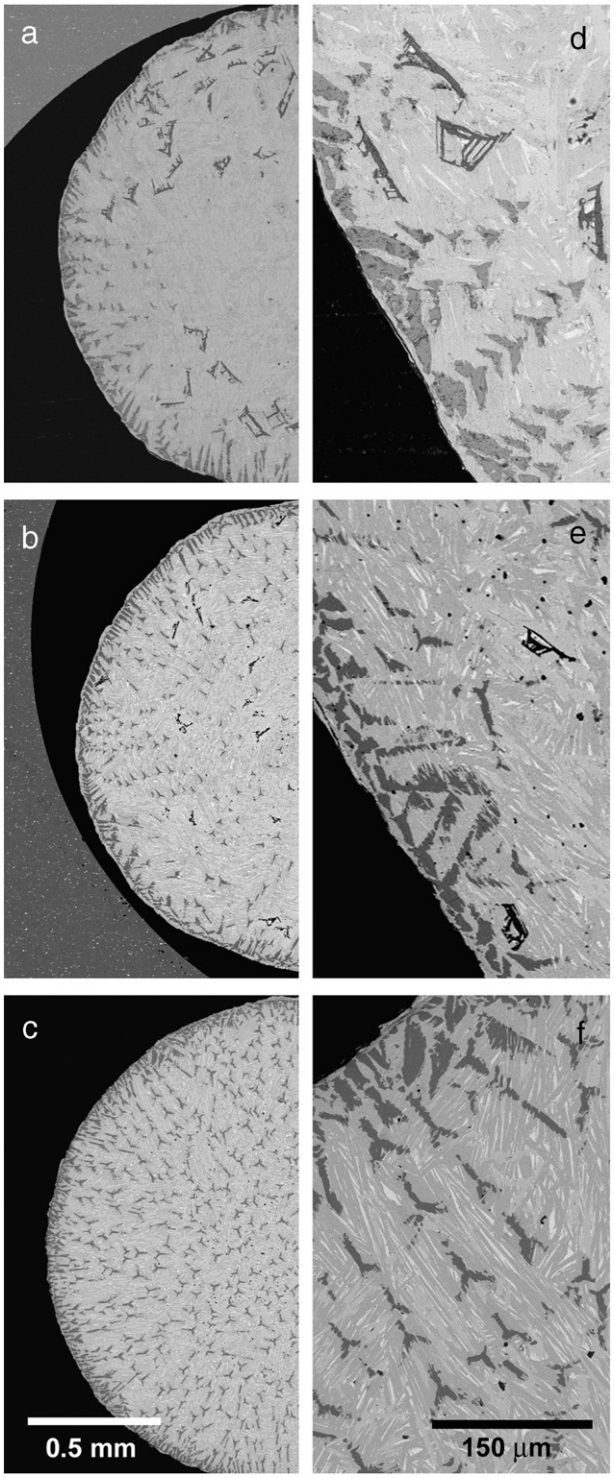

Fig. 2. SEM micrographs of transversal polished sections of a sample grown at: a) and d) 15; b) and d) 30; and c) and f) 50 mm/h.

associated to the $Sr_3Co_4O_x$ phase. Despite the presence of these secondary phases, the samples are mainly composed of highly textured Bi–Sr–Co–O grains as seen in Fig. 3 where the polished longitudinal section of the center of the textured bars is displayed. The Fig. 3a, corresponding to the sample grown at 15 mm/h, shows the presence of two different main phases, grey and light grey, corresponding to the $Bi_2Sr_2Co_2O_x$ and $Bi_2Sr_2Co_{1.3}O_x$, respectively, which are well-aligned with the growth direction and stacked as alternated layers. When the growth speed is increased, the alignment