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Improvement of textured $Bi_{1.6}Pb_{0.4}Sr_2Co_{1.8}O_x$ thermoelectric performances by metallic Ag additions

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Abstract

$Bi_{1.6}Pb_{0.4}Sr_2Co_{1.8}O_x$ thermoelectric ceramics with small Ag additions (0, 1, and 3 wt%) have been successfully grown from the melt, using the laser floating zone method. Microstructure has shown a reduction in the amount of secondary phases and a better grain alignment with respect to the growth direction for an Ag content of 3 wt%. The microstructural evolution, as a function of Ag content, is confirmed with the electrical resistivity values, which show an important decrease for the 3 wt% Ag samples, leading to maximum power factor values of about 0.42 mW/K^2 m at 650 °C, which are among the best results obtained in this type of material.

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

1. Introduction

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

The discovery of large thermoelectric power in Na_xCoO_2 [3], which was found to possess a high ZT value of about 0.26 at 300 K, has opened a broad research field and from that moment on, great efforts have been devoted to explore new cobaltite families with high thermoelectric performances. Some other layered cobaltites, such as misfit $[Ca_2CoO_3][CoO_2]_{1.62}$, $[Bi_{0.87}SrO_2]_2[CoO_2]_{1.82}$ and $[Bi_2Ca_2O_4][CoO_2]_{1.65}$ were also found to exhibit attractive thermoelectric properties [4–8]. The crystal structure is composed of two different layers, with the 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. Both sublattices (RS block and CdI_2-type CoO_2 layer) possess common *a*- and *c*-axis lattice parameters and β angles but different *b*-axis length, causing a misfit along the *b*-direction [9–11].

As layered cobaltites are materials with a strong crystallographical anisotropy, the alignment of plate-like grains by mechanical and/or chemical processes is necessary to attain macroscopic properties comparable to those obtained on single crystals. Some techniques have been shown to be adequate to obtain a good grain orientation in several oxide ceramic systems, such as template grain

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growth (TTG) [10], sinter-forging [12], spark plasma [13], and directional growth from the melt [14]. On the other hand, it is interesting to explore cationic substitutions in the RS layer, which can change the misfit relationship between these two layers and, as a consequence, modify the values of the thermopower [7]. From this point of view, it is clear that this kind of substitution can be useful in order to improve thermoelectric performances of ceramic materials [12], as is reported for the substitution of Gd and Y for Ca [15], or Pb for Bi [16]. Moreover, metallic Ag additions have also been shown to improve, in an important manner, the mechanical and thermoelectrical properties of this system [17] and other similar materials [18] which nearly do not react with Ag.

Taking into account these previously discussed effects, the aim of this work is producing high performance TE materials by the addition of metallic Ag to the optimally Pb doped Bi–Sr–Co–O compound [16,19], followed by a texturing process performed by the laser floating zone (LFZ) technique.

2. Experimental

The initial $Bi_{1.6}Pb_{0.4}Sr_2Co_{1.8}O_x$ with small amounts of silver (0, 1, and 3 wt% Ag) polycrystalline ceramics were prepared from commercial $Bi(NO_3)_3 \cdot 5H_2O$ ($\geq 98\%$, Aldrich), $SrCO_3$ (98.5%, Panreac), $Co(NO_3)_2 \cdot 6H_2O$ (98%, Panreac), and metallic Ag (99%, Aldrich) powders by a sol–gel via nitrates method. They were weighed in the appropriate proportions and suspended in distilled water. Concentrated HNO_3 (analysis grade, Panreac) was added dropwise into the suspension until it turned into a clear pink solution. Citric acid (99.5%, Panreac), and ethylene glycol (99%, Panreac), were added to this solution in adequate proportions. Evaporation of the solvent was performed slowly in order to decompose the excess nitric acid, which allowed the polymerisation reaction between ethylene glycol and citric acid, forming a pink gel [20,21]. The dried product was then decomposed (slow self combustion) by heating at 350–400 °C for 1 h. The remaining powder was mechanically ground and calcined at 750 and 800 °C for 12 h, with an intermediate grinding. This step is especially important when texturing is performed using the LFZ technique: it has been designed to decompose the alkaline-earth carbonates which, otherwise, would decompose in the molten zone disturbing the solidification front. The so-obtained powders were cold isostatically pressed in the form of cylinders (~120 mm long and 2–3 mm in diameter) under an applied pressure of about 200 Mpa for 1 min.

The green ceramic cylinders were subsequently used as feed in a LZF texturing system used successfully in previous works [22–24] and described in detail elsewhere [25]. On the other hand, the growth rate has been chosen taking into account previous results obtained in layered ceramic samples [26,27]. As a consequence, all samples were grown downwards at 15 mm/h, with a seed rotation of 3 rpm, in order to maintain the cylindrical geometry in the final textured material, while the feed was rotated at 15 rpm in the opposite direction, to improve the molten zone homogeneity. After the texturing process, long (more than 150 mm) cylindrical and geometrically homogeneous samples were obtained. These textured materials were then cut into shorter pieces of adequate sizes for their characterisation (~15 mm long).

The structural identification of all the samples was performed by powder XRD utilising a Rigaku D/max-B X-ray powder diffractometer (CuKα radiation) with 2θ ranging between 10° and 70°. Microstructural observations were performed on polished samples using a field emission scanning electron microscope (FE-SEM, Carl Zeiss Merlin) fitted with energy dispersive spectrometry (EDS) analysis. Micrographs of these samples have been recorded to analyse the different phases and their distribution. From these pictures, an estimation of the amount of the different phases has been made using the Digital Micrograph software.

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

3. Results and discussion

Powder XRD patterns for all $Bi_{1.6}Pb_{0.4}Sr_2Co_{1.8}O_x$ samples with different amounts of Ag are plotted (from 10° to 40° for clarity) in Fig. 1. They show very similar patterns where the most intense peaks correspond to the misfit cobaltite $Bi_{1.6}Pb_{0.4}Sr_2Co_{1.8}O_x$ phase, in agreement with previous reported data [16,28]. From this figure, it is clear that the cobaltite phase appears as the major one, independently of Ag content. Peaks marked with a ● in the plot correspond to the Co-free $Bi_{0.75}Sr_{0.25}O_{1.375}$ secondary phase [29]. Moreover, for samples with 1 and 3 wt% Ag, a new peak appears in the XRD plots at around 38°, which corresponds to the metallic Ag (111) plane (indicated by ■) [30]. This peak also indicates that Ag does not react with the thermoelectric ceramic, leading to the formation of a ceramic matrix composite with metallic particles distributed inside the matrix, as observed in similar ceramic systems [18,27,31].

Scanning electron microscopy has been performed on polished longitudinal sections of all samples after the growth process. The microstructural evolution of samples, as a function of Ag content, can be easily observed in Fig. 2 where representative micrographs of longitudinal polished sections of all samples are presented. In these general views, it can be clearly seen that all samples are composed by three contrasts which correspond to different phases, identified by EDS and numbered, for clarity, in Fig. 2a. Grey contrast (♯1) corresponds to the thermoelectric $Bi_{1.6}Pb_{0.4}Sr_2Co_{1.8}O_x$