Mechanical and Thermoelectric Environmental Evolution Properties of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ Ceramics Textured by Laser Floating Zone Technique

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Abstract

$\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ ceramics have been synthesized through solid-state reaction methods and directionally grown from the melt by laser floating zone technique. Mechanical and thermoelectric characteristics of this material were determined by three point bending tests and the four probe technique, respectively. The mechanical and thermoelectric properties of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ were determined as a function of the environmental conditions, air and water. Flexural strength data show that textured materials possess a high degradation resistance due to the low porosity of the external part of the rods ($\sim 65\mu\text{m}$), which avoids water infiltration and, as a consequence, the internal degradation. Moreover, power factor values are maintained practically unchanged for the samples immersed in water for 24h.

Keywords: $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$, laser floating zone, flexural strength, thermoelectricity

1.Introduction

Since Terasaki et al. [1] reported that $\text{Na}_x\text{Co}_2\text{O}_4$ had shown large thermoelectric power coexisting with low electrical resistivity, increased attention has been attracted to other layered cobalt oxides such as $\text{Ca}_3\text{Co}_4\text{O}_9$, $\text{Bi}_2\text{Sr}_3\text{Co}_2\text{O}_9$, $\text{Bi}_2\text{Ca}_2\text{Co}_2\text{O}_x$, $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$, and $\text{Bi}_2\text{Ca}_2\text{Co}_{1.7}\text{O}_x$ due to their high performances [2-10]. Layered cobalt oxides possess fairly good thermoelectric (TE) properties, and they are thermally and chemically stable at high temperatures under air. Their crystal structure 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 layers. This structure shows high crystalline anisotropy, which is reflected in their thermoelectric properties and preferential grain growth along the *ab*-planes, which are also the conducting ones [7]. TE performances are usually evaluated through a dimensionless parameter known as the figure of merit ($ZT = TS^2/\rho\kappa$) where *S* is the Seebeck coefficient, *T* the absolute temperature, ρ the electrical resistivity, and κ the thermal conductivity. According to this formula, high *S*, low ρ , and low κ are required to obtain high TE performances [11]. Although single crystals present high TE performances along the *ab* plane, *ZT* of polycrystalline materials with randomly oriented grains is still relatively low, restricting their practical applications. Numerous methods have been reported to increase *ZT* through the improvement of grain orientation using texturing techniques. Some of these involve solid-state reactions, such as hot forging [12] and template grain growth [13]. On the other hand, it is also possible to obtain well-oriented grains by directional solidification from molten material, as the laser floating zone (LFZ) process [3,4] and the electrically assisted laser floating zone (EALFZ) technique [14].

Until now, investigations of the mechanical properties of ceramic materials have been neglected and attention was mainly focused on the search for material synthesis, processing, crystallographic structure and thermoelectric properties. Knowledge of the thermal and mechanical properties is essential for their practical applications [9]. On the other hand, it is necessary to take into account their reactivity to moisture, which can lead to their chemical degradation and, as a consequence, affect their thermoelectric and mechanical properties [15,16].

In this work, the chemical stability of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ textured rods grown by a LFZ technique has been studied by means of the immersion of some of the samples in

water while others were kept in air. A comparison of mechanical and thermoelectric properties of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ materials as a function of the environmental conditions has been made.

2. Experimental

$\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ TE ceramics have been prepared from commercial Bi_2O_3 (Panreac, 98+%), SrCO_3 (Panreac, 98 + %), and Co_2O_3 (Aldrich, 98+%) powders. Conventional solid state synthesis of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ powders is described in detail elsewhere [8]. The resulting powders were then used to prepare cylindrical precursors, 120 mm long and 2-3 mm diameter by cold isostatic pressing at an applied pressure of 200 MPa for around 2 min. Precursor rods were subsequently used as feed in a LFZ equipment. The samples were grown by the laser floating zone method using a continuous power Nd:YAG laser ($\lambda = 1.06 \mu\text{m}$) under air, as reported in previous works [17]. They were directionally grown downwards from the melt at 30 mm/h with a seed rotation of 3 rpm to maintain the cylindrical geometry. Moreover, in order to assure compositional homogeneity of the molten zone, an opposite feed rotation of 15 rpm has also been applied. Finally, after the texturing process, long and geometrically homogeneous textured cylindrical rods have been produced. These bars were cut into pieces with the adequate size (about 15 mm long) for their characterization. The identification of main phases was carried out using powder X-ray diffraction in a Rigaku D/max-B device, working with Cu K α radiation and 2θ ranging between 10 and 40°. The fractured surfaces were examined in a scanning electron microscope (JEOL JSM 6400). Mechanical characterization has been performed by flexural strength, using the three-point bending test in an Instron 5565 machine with a 10 mm loading span fixture. The flexural strength of textured $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ thin rods was measured as a function of the environmental conditions, air and water, at room temperature. Loading rates spanning three orders of magnitude (1, 10 and 100 $\mu\text{m}/\text{min}$) were used to explore their susceptibility to the environmental conditions. The rods tested in water conditions were immersed in distilled water during 1 h before test. A drop of distilled water added with a syringe, covered the central section of the rods during mechanical tests to ensure that the fracture region was immersed in water during the test. The flexural strength was computed from the maximum load achieved in the test according to the strength of materials theory for an elastic beam of circular section. Thermoelectric

characterization has been performed in the as-grown samples, as well as in 24 h and 24 days water immersed ones. Electrical resistivity and Seebeck coefficient were simultaneously determined in a LSR-3 measurement system (Linseis GmbH) between room temperature (RT) and 650 °C under He atmosphere. Power factor ($PF=S^2/\rho$) has been calculated in order to determine the samples performances.

3. Results and Discussion

XRD patterns of the different samples have shown no differences between them, independently of the environmental conditions. In Fig.1 the representative powder XRD pattern for the $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ samples, corresponding to the as-grown one, is displayed. As can be observed in the figure, the most intense peaks correspond to the thermoelectric phase (indicated by their diffraction planes), in agreement with previously reported data [18,19]. The minor peaks have been associated to non-thermoelectric $\text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_y$ and $\text{Sr}_6\text{Co}_5\text{O}_{14.3}$ secondary phases (indicated by * and #, respectively) [20,21]. The presence of these relatively high amount of secondary phases is due to the typical incongruent melting found in this and other similar Bi-based systems [22,23].

Microstructural studies of transversal broken surfaces have shown that the microstructure is practically the same for all samples, independently of the environmental conditions. The typical $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ fractured surface, performed in as-grown samples, is displayed in Fig.2. As it can be clearly observed in the figure, two different regions can be distinguished and described as an outer ring surrounding inner zone. The inner region is composed by large and well aligned grains with their c-axis nearly perpendicular to the growth direction. On the other hand, outer ring with ~65 μm thickness possess lower grain sizes and porosity. Moreover, this external region can be of the main importance in these samples, as can act as a protective layer against water diffusion to the internal region, minimizing the possibility of chemical degradation by water.

Mechanical characterization of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ samples has been performed using the flexural strength (three-point bending test), σ_f , which is defined as $8FL/\pi d^3$, where F is the applied load, L the span, and d the bar diameter. In order to evaluate the mechanical behaviour evolution with the environment, flexural strength tests were made on different environment (air and water) and loading rates (1,10 and 100

µm/min). Due to the brittle nature of this ceramic material, 10 samples for each condition were used to get more accurate values. The mean strength values together with its corresponding standard error are represented in Fig.3 for the different samples. As it can be clearly seen mean flexural strength values decrease when loading rate is reduced in both cases (air and water) due to a subcritical crack growth process. This change can be related to the chemical degradation with environmental water vapour for the dry samples, while it is due to a higher interaction of water with the samples in the water tested ones. This behaviour is in agreement with a stress corrosion cracking process which allows the interpretation of the mechanical behaviour of this material. For samples measured under air, there is significant dependence of the mean flexural strength with the loading rate, ($\Delta \approx 17\%$, from 121.2 to 141.7 MPa), while there is a stronger dependence in case of the water tested samples ($\Delta \approx 25\%$, from 105 to 130.9 MPa). Moreover, mean flexural strength values are slightly lower for the samples treated in water than as-grown, confirming the environmental damage produced by water.

The stable growth of cracks under applied stresses lower than that for fast fracture (slow crack growth, SCG) is usually studied by means of a power-law function ($v = da/dt = AK_I^n$) where v , a , and t are the crack growth velocity, crack size and time, respectively. K_I is the stress intensity factor. A and n are parameters depending on the material and environment. The n values have been computed from the slope of the $\log(\sigma_f)$ versus $\log(d\mathcal{E}/dt)$, where $(d\mathcal{E}/dt)$ is the strain rate [24,25]. For the tests performed under air an n value of 30 has been obtained, confirming the significant differences found in the flexural strength experiments. A lower n value of 21, has been obtained for the water tests, in agree with the stronger dependence of the flexural strength with the loading rate described previously. Anyway, these crack growth exponents found for this ceramic material containing a very reactive cation as is the Sr^{2+} , are high enough, and are close to the values found in more inert ceramics, as for example the Al_2O_3 [24].

The temperature dependence of the electrical resistivity is shown in Fig. 4 for all the samples. As it can be clearly seen in the figure, all curves show the same semiconductor-like behaviour ($\delta\rho/\delta T < 0$) in the whole temperature range. This semiconducting behaviour is in agreement with earlier reports on these cobaltite systems [26]. Moreover, the electrical resistivity increases with the time the samples

are immersed in water, due to a possible slight superficial degradation. The measured resistivity values, 36, 43 and 64 m Ω cm, at room temperature (RT) for as-grown, and water immersed for 24 h and 24 days samples, respectively, are lower than the reported ones for sintered specimens [27,28], which show resistivities around 80-100 m Ω cm at RT. Moreover, the obtained values for the as-grown and 24 h water immersed samples are lower than the measured in textured materials (around 45 m Ω .cm) at RT [3]. The relatively high values measured in these materials can be associated with the presence of secondary phases (usually not present in adequately sintered materials) and with a reduction of the oxygen content in comparison with sintered specimens, typical for laser grown materials [29].

Fig.5 displays the Seebeck coefficient variation with temperature as a function of the environmental conditions. It is evident that the sign of the Seebeck coefficient is positive for whole measured temperature range for all samples, which confirms a conduction mechanism mainly governed by holes. In all cases, it is observed the values of the Seebeck coefficient decrease when temperature is raised from RT to around 450 $^{\circ}$ C, followed by an increase for higher temperatures. The measured Seebeck coefficients at RT have been 134, 134, and 142 μ V/K for the as-grown, and water immersed for 24h and 24 days samples, respectively. As-grown and 24 h water immersed samples show the same value, while it is slightly higher for those immersed in water for 24 days, reflecting the slight superficial degradation produced in these last samples. Seebeck coefficient values at RT obtained for all samples are higher than those reported for sintered specimens in the literature [27] and are not common in these systems, confirming the resistivity discussion and agreeing with previous works [29].

In order to evaluate the thermoelectric performances of samples, PF has been calculated from the electrical resistivity and Seebeck coefficient data and represented as a function of temperature in Fig. 6. In this plot, it can be observed that all of the samples show similar evolution. In the case of as-grown samples, the values of the PF increase when temperature is raised from RT to around 200 $^{\circ}$ C, followed by a decreases with temperature until about 400 $^{\circ}$ C, increasing again for higher temperatures. The measured values at RT have been 0.048, 0.040 and 0.028 mW/K 2 m for the as-grown, and water immersed for 24h and 24 days samples, respectively. These values are higher than the ones reported for sintered specimens ($\sim$ 0.03 mW/K 2) [28].

Conclusions

The LFZ method has been successfully applied for growing highly textured bulk samples with homogeneous dimensions. Powder XRD has shown no differences between the samples kept in air and those immersed in water, with no indication of decomposition products. Microstructural observation has revealed that the samples are formed by two different regions, a highly textured internal one and a low porosity outer one with $\sim 65\mu\text{m}$ thickness. Mechanical tests showed that flexural strength of the samples depends on the environment tested in air and water loading rate. On the other hand, it has been determined that these materials possess an unexpected degradation resistance which can be related with low porosity of the external region, which avoids the internal degradation by water infiltration. Room temperature electrical resistivity values are lower than those obtained in sintered bulk ceramics, while S and PF values are higher than the measured in sintered ceramics. The obtained results indicate that the LFZ process is a very useful and promising technique to obtain high mechanical and thermoelectric performances in $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_x$ materials.

Acknowledgements

The authors acknowledge financial support from the Gobierno de Aragón and the Fondo Social Europeo (Consolidated Research Groups T12 and T87) and MINECO-FEDER (Project MAT2013-46505-C3-1-R). The technical contribution of C. Estepa, and C. Gallego are also acknowledged. F. Kahraman acknowledges a financial grant from the Council of Higher Education (YÖK) in Turkey for international mobility. Authors would like to acknowledge the use of Servicio General de Apoyo a la Investigación-SAI, Universidad de Zaragoza.

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Figure Captions

Figure 1. Representative XRD pattern of $\text{Bi}_2\text{Sr}_2\text{Co}_{1-8}\text{O}_x$ samples corresponding to the as-grown ones. Peaks indicated by their reflection planes correspond to the $\text{Bi}_2\text{Sr}_2\text{Co}_{1-8}\text{O}_x$ thermoelectric phase. Peaks associated to the non-thermoelectric $\text{Bi}_{0.75}\text{Sr}_{0.25}\text{O}_y$ and $\text{Sr}_6\text{Co}_5\text{O}_{14.3}$ secondary phases are shown by * and #, respectively.

Figure 2. Typical microstructure of a textured $\text{Bi}_2\text{Sr}_2\text{Co}_{1-8}\text{O}_x$ fractured surface where the outer and inner zones can be clearly distinguished.

Figure 3. Mean flexural strength of $\text{Bi}_2\text{Sr}_2\text{Co}_{1-8}\text{O}_x$ textured materials, together with their standard error, as a function of loading rate. The lines in the figure are a guide for the eye.

Figure 4. Temperature dependence of the electrical resistivity as a function of the environmental conditions. (●) As-grown, and water immersed for (■) 24h, and (◆) 24 days samples.

Figure 5. Temperature dependence of the Seebeck coefficient as a function of the environmental conditions. (●) As-grown, and water immersed for (■) 24h, and (◆) 24 days samples

Figure 6. Temperature dependence of the PF as a function of the environmental conditions. (●) As-grown, and water immersed for (■) 24h, and (◆) 24 days samples.

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