Enhancement of electrical conductivity of $\text{Ca}_{2.93}\text{Sr}_{0.07}\text{Co}_4\text{O}_9$ thick films via hot uniaxial pressing

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Abstract

Sr-doped $\text{Ca}_3\text{Co}_4\text{O}_9$ thermoelectric thick films have been prepared by dip-coating technique, followed by sintering and hot uniaxial pressing. XRD patterns are very similar in both types of samples, with only differences in the relative intensity of peaks, pointing out to a better grain orientation in hot-pressed films. Moreover, SEM observation showed a drastic decrease of the hot-pressed films thickness. Electrical resistivity is decreased in textured materials due to the higher grain orientation and density, confirmed through Hall measurements. On the other hand, Seebeck coefficient is maintained practically unchanged. Power factor at 800 °C is much higher in textured materials (0.44 mW/K²m) than the determined in sintered films (0.30 mW/K²m), and in the order of the best typically reported in the literature (0.43 mW/K²m).

Keywords: Ceramics; Oxides; Thick films; Microstructure; Electrical properties; Thermoelectrics

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1. INTRODUCTION

In recent years, the use of fossil fuels has been drastically increased after a period of lower consumption due to the past economic crisis. Moreover, most of them are used to produce energy in systems with low efficiency, consuming high amounts of fuel which produce large quantities of CO₂ and waste heat. These facts play against the new low (or renewable)-energy-consumption policy of many countries. In this scenario, thermoelectric (TE) materials can play an important role in decreasing the fuels consumption harvesting the waste heat and producing useful electric power.¹ On the other hand, these applications require materials with high conversion efficiency, usually evaluated through the figure-of-merit, ZT , which involves several electrical and thermal parameters in the form of:

$$ZT = \frac{S^2 T}{\rho \kappa} \quad (\text{Eq. 1})$$

where S , T , ρ , and κ are Seebeck coefficient, absolute temperature, electrical resistivity, and thermal conductivity, respectively.²

Although TE phenomena have been discovered long time ago,³ these materials are only used in very specific niches, and usually at relatively low temperatures. This is due to the fact that the highest TE performances are achieved in intermetallic alloys,^{4,5} characterized by a relatively low chemical stability under air.¹ On the other hand, the discovery of unexpectedly high TE performances in Na₂Co₂O₄ ceramic material⁶ opened new possibilities for practical applications as these materials possess many advantages, when compared with the intermetallic ones. They can work at higher temperatures without degradation, have no heavy metals, are cheaper, more environmentally friendly, and larger relative abundance.⁷ In spite of the large number of

ceramic systems with TE characteristics,⁸⁻¹⁰ their performances are lower than the reported in intermetallic materials. Consequently, the thermoelectric performances of these ceramic materials need to be improved before they can be used in practical applications. As a result, many efforts have been performed to achieve this goal using different approaches, as decreasing starting particle sizes via synthesis methods,¹¹ doping processes,¹² or texturing.¹³

Among these TE families, $\text{Ca}_3\text{Co}_4\text{O}_9$ materials display the most interesting properties for practical applications due to their easy preparation and simple chemical composition. Moreover, they can be textured to exploit their crystal anisotropy, which is reflected in the anisotropy of electrical and thermal properties.¹⁴ Furthermore, they can be produced in form of thick films, decreasing the raw materials needs,¹⁵ and allowing automatic production.

The aim of this study is fabricating $\text{Ca}_{2.93}\text{Sr}_{0.07}\text{Co}_4\text{O}_9$ thick films by dip-coating process,¹⁶ and textured through the hot-uniaxial-pressing technique. Their structural, and microstructural characteristics will be related with their thermoelectric properties, using sintered thick films as reference.

2. EXPERIMENTAL PROCEDURE

$\text{Ca}_{2.93}\text{Sr}_{0.07}\text{Co}_4\text{O}_9$ nominal composition has been used due to previous results, indicating the enhancement of the Seebeck coefficient without drastic modifications of electrical resistivity.^{17,18} The initial suspension, with 29 %vol. of solid, was prepared from CaCO_3 (≥ 99 %, Aldrich), SrCO_3 (≥ 98 %, Aldrich), and CoO (99.99 %, Aldrich) commercial powders following previous procedure.¹⁹ Polycrystalline Al_2O_3 substrates

were used for deposition, as they provide the highest amount of TE phase after sintering. They were cleaned by sonication, followed by immersion in a dilute HNO₃ acid, and rinsed sequentially with water and acetone.

These substrates were then coated with the suspension by the dip-coating technique as previously reported,¹⁹ and totally dried under air at 50 °C for 24 h. All samples were then thermally treated under air at 450 °C for 2 h to eliminate organics, and sintered at 900 °C for 24 h, followed by slow cooling to room temperature (sintered films). Some of these sintered films were subsequently hot uniaxially pressed at 850 °C for 1 h under 25 MPa applied pressure, using graphite to avoid sticking between alumina piston and the thermoelectric coating, and final slow cooling to room temperature (textured films).

Sintered and textured films were characterized through surface XRD in a theta-theta PANalyticalX'Pert Pro (CuK α radiation, $\lambda=1.54059$ Å) between 5 and 60 degrees.

Microstructural studies have been made on transversal surfaces in a Field Emission Scanning Electron Microscope (FESEM, Zeiss Merlin). Moreover, textured samples have been observed after etching in HCl 5 M for 5 s to reveal grain orientation. Carrier concentration and mobility have been determined by Hall measurements at room temperature (22 °C) in a L79/HCS system (Linseis GmbH) under air. Seebeck coefficient and electrical resistivity were simultaneously determined between 50 and 800 °C in a LSR-3 system (Linseis GmbH) under He atmosphere. From the electrical resistivity values, the activation energy for these samples has been estimated in the semiconductor-like behaviour regime, using the expression:

$$\sigma T \propto \exp \left(-\frac{E}{k_B T} \right) \quad (\text{Eq. 2})$$

where E , k_B , and T are the activation energy, Boltzmann constant ($\approx 8.62 \cdot 10^{-5}$ eV/K), and absolute temperature, respectively. Finally, power factor, $PF (= S^2/\rho)$, was calculated to determine the TE performances of samples.

3. RESULTS AND DISCUSSION

The ceramic slurry, with 29 vol.% solid content, prepared for this work shows shear-thinning flow behavior from 1 s^{-1} to 1000 s^{-1} , determined from its viscosity curve, confirming that it is a weakly flocculated suspension. Consequently, it will allow the production of homogeneous coatings, as it shows low viscosity during the substrates coating, which will be increased during the organics evaporation avoiding suspended particles movement.

XRD data obtained on sintered and textured coatings surfaces are presented in Fig. 1. As it can be observed in the patterns, all peaks can be related to the diffraction planes of $\text{Ca}_3\text{Co}_4\text{O}_9$ phase.²⁰ On the other hand, in spite of the similarity observed between both patterns, they considerably differ in the peaks intensity. Consequently, Lotgering factor has been calculated using the expression,²¹ for $2\theta < 43^\circ$:

$$f = \frac{(P-P_0)}{(1-P_0)}; \text{ being } P_i = \frac{\sum I\{00l\}}{\sum I\{hkl\}} \quad (\text{Eq. 3})$$

where P_0 is the relationship for randomly oriented powder extracted from the 21-0139 JCPDS card, and P is extracted from the data obtained for the prepared coatings. The data have shown an increase of texture from 59 % determined for the sintered specimens, to 72 % in the hot-pressed coatings (13 % improvement). These results clearly point out to a significant rise of grain orientation induced by the hot uniaxial pressing process.

Microstructural observations performed on transversal sections of samples using secondary electrons, are presented in Fig. 2. It should be highlighted that all samples showed the same dimensions after sintering ($272.56 \pm 20.15 \mu\text{m}$ thickness, see insert) and possessed the same microstructure observed in Fig. 2a. When these samples are subjected to the uniaxial hot pressing process, the thickness ($14.0 \pm 1.2 \mu\text{m}$) is drastically decreased, and the grain orientation is increased, as presented in Fig. 2b. This reduction is due to two effects, firstly an increase of density due to the pressure effect, and secondly, the coating plastic deformation without any change of the substrate size. This plastic deformation produces a partial flow of the $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramic beyond the substrate limits, being lost. Both processes are simultaneously produced during the hot-pressing process. Moreover, even if there is no significant grain size modification between both types of samples, an improvement on the grain orientation can be observed when comparing the insert in Fig. 2a, and Fig. 2b (etched with HCl for clearer grains observation), confirming the results obtained through the Lotgering factor calculations. On the other hand, the microstructural modification has been also accompanied by an increase of density, from around $40 \pm 5 \%$ of the theoretical one (4.68 g/cm^3)⁸ for the sintered specimens, to about $97 \pm 2 \%$ for the textured ones. These values also confirm the relatively large amount of material lost due to the plastic flow during the texturing process.

The structural and microstructural features previously described are reflected in the electrical resistivity evolution, as a function of temperature, displayed in Fig. 3. Despite similar semiconducting behavior of both types of samples, in agreement with previous reports,^{22,23} the values are much lower for textured samples than for sintered ones. This

decrease can be explained by the higher density and better grain alignment obtained in hot-pressed specimens which aligns, at the same time, the conducting planes of $\text{Ca}_3\text{Co}_4\text{O}_9$ phase.²⁴ The minimum resistivity values (8.7 m Ω .cm) have been obtained at 675 °C in textured samples, which is much lower than the measured at 800 °C in bulk sintered materials (40 m Ω .cm).²⁵ On the other hand, they are close to the reported for bulk textured materials produced by hot uniaxial pressing or spark plasma sintering (SPS), 6.9, and 7 m Ω .cm, respectively.^{25,26} Furthermore, they are higher than the obtained in multilayer materials prepared through tape casting and processed by hot-pressing (5.9 m Ω .cm).¹⁵

These differences between the two types of samples have been confirmed through Hall measurements at room temperature. As it is well known, electrical conductivity can be determined through the expression:

$$\sigma = n e \mu \quad (\text{Eq. 4})$$

where n is the charge carrier concentration, e the electron charge, and μ the charge carrier mobility. These measurements have shown that carrier concentration and mobility are enhanced in textured materials, when compared with the sintered ones (from $4.221 \cdot 10^{19}$ to $6.072 \cdot 10^{19}$ /cm³, and from 3.099 to 4.588 cm²/V s, respectively). The increase on the carrier mobility in the textured films can be easily explained by the grain alignment along the conducting plane. On the other hand, the higher charge carrier concentration can be due to the same effect observed in bulk textured materials which present higher Co oxidation state in the surface than in the bulk material.²⁷ It is also necessary to highlight that substituting these charge carrier concentration and mobility values in equation 4, the calculated electrical conductivity values for textured and

sintered films, 44.6 and 21.0 S/cm, respectively, clearly show the enhancement of conductivity induced by the hot pressing process. On the other hand, the corresponding resistivity values are higher than the measured in the LSR-3 system, but it can be explained by the higher resistivity of contacts in the Hall apparatus (made using spring-pressured pins in the sample corners), and the lower measurement temperature.

As it is well known, the conduction mechanism in these compounds is a charge-transport process by hopping. Moreover, this hopping conduction is accompanied by phonon-assisted jump of carriers among Co ions in the conducting layer.²⁸ The activation energy values for the different samples were calculated from the curve fit slopes below T^* (semiconducting regime), which is defined as the temperature where the behaviour of the samples changes from semiconducting to metallic. As it can be observed in the modified Arrhenius plots shown Fig. 4, texturing process increases the T^* value from 115 °C for the sintered materials (T_1^*), to 200 °C for the textured ones (T_2^*), probably influenced by a different oxygen content in the samples induced by the graphite used in the hot pressing process. On the other hand, the slopes of both curves in the metallic and semiconducting regions are very similar, leading to calculated activation energy values of around 43, and 45 meV (in the semiconducting regime), and 80, and 94 meV (in the metallic region) for the sintered, and textured films, respectively. The slightly higher thermal activation energies in textured films indicate that hopping carriers are more thermally activated than in the sintered ones.²⁹ However, these high values obtained in the metallic region are lower than the lowest reported in the literature for bulk textured materials (123, and 158 meV),^{30,31} and in the order of the sintered specimens.³² These results clearly show that texturing process has no significant effect

on the activation energy of the hopping process, and the decrease with respect to the bibliographic results can be associated to the Sr doping which can modify the valence band.

Fig. 5 illustrates the evolution of Seebeck coefficient as a function of temperature in both kinds of samples. S is positive in the whole measured temperature range, pointing out to holes as major charge carriers. Moreover, it is not observed any effect of the processing route on the S values, which increase with temperature, in agreement with previous works.^{19,22} The highest S value has been reached at 800 °C in the sintered coatings (204 $\mu\text{V/K}$), slightly higher than the measured in textured ones (198 $\mu\text{V/K}$). Furthermore, these values are higher than the reported in bulk sintered (between 180 and 190 $\mu\text{V/K}$),^{23,25} or textured materials by hot-pressing or SPS (170,²⁵ and 165 $\mu\text{V/K}$,²⁶ respectively).

The samples performances evolution with temperature has been determined through PF, shown in Fig. 6. PF is increased when the temperature is raised, being higher for the textured films provided by their lower electrical resistivity, when compared with the sintered ones. The highest value at 800 °C for the textured materials (0.44 $\text{mW/K}^2\text{m}$) is about 45 % higher than the obtained for the sintered films. Moreover, this high value is of the order of the highest ones typically reported in literature (0.43 $\text{mW/K}^2\text{m}$).^{26,33,34}

4. SUMMARY

Sintered and textured thick films of Sr-doped $\text{Ca}_3\text{Co}_4\text{O}_9$ materials have been prepared using the dip-coating technique. XRD data have shown that all samples have $\text{Ca}_3\text{Co}_4\text{O}_9$ phase as the major one, with only differences in the relative intensity of peaks. These

differences indicate, through Lotgering factor calculations, that hot-pressing enhances grain alignment from 59 to 72 %. Microstructural observations have demonstrated that textured materials possess much higher density than sintered ones, as the film thickness is reduced from 272.56 to 14.0 μm . These modifications are reflected in the electrical resistivity, which is lower for the textured films in the whole measured temperature range, provided by a higher charge carrier concentration and mobility. On the other hand, no significant modification of the Seebeck coefficient has been detected. The highest PF value determined at 800 °C (0.44 mW/K²m) is of the order of the best results typically reported in literature.

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Figure Captions

Figure 1. XRD patterns obtained on the different films surfaces a) sintered; and b) after texturing.

Figure 2. Representative SEM micrographs taken on longitudinal sections of $\text{Ca}_3\text{Co}_4\text{O}_9$ films: a) sintered; and b) textured. The insert shows the whole thickness of the sintered film.

Figure 3: Temperature dependence of the electrical resistivity for the different films.

Figure 4: Modified Arrhenius plot for the different types of samples. The linear fits in the metallic-like behavior regime are only shown for a clear visualization of T^* in both cases.

Figure 5: Temperature dependence of the Seebeck coefficient for the different films.

Figure 6: Temperature dependence of power factor for the different films.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6