



# Decrease of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ thermal conductivity by Yb-doping

G. Klirat<sup>a</sup>, M.A. Aksan<sup>a</sup>, Sh. Rasekh<sup>b</sup>, M.A. Madre<sup>b,\*</sup>, J.C. Diez<sup>b</sup>, A. Sotelo<sup>b</sup>

<sup>a</sup>Inonu Universitesi, Fen Edebiyat Fakultesi, Fizik Bolumu, 44280 Malatya, Turkey

<sup>b</sup>ICMA (CSIC-Universidad de Zaragoza), Maria de Luna, 3. 50018 Zaragoza, Spain

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## Abstract

In this study, the effect of Yb-substitution on the structural, electrical and thermal transport properties of the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  system has been investigated in the low temperature region (between 10 and 300 K). The resistivity of samples increases with raising the Yb-concentration in the system. All the samples show a metal-semiconductor transition below 85 K. In the analysis based on *Strongly Correlated Fermi Liquid Model*, an increased bandwidth and a reduced electronic correlation are found. It has also been found that the energy gap,  $E_0$ , value also decreases with Yb-substitution. The samples show positive thermoelectric power, indicating that dominant charge carriers are holes in all the samples. The thermoelectric power value decreases with Yb-substitution. From Mott equation, it is determined that the Fermi energy and hole concentration decrease in the Yb-substituted samples, compared to the undoped ones. Thermal conductivity,  $\kappa$ , is decreased in about 50% of the measured in undoped samples for the 0.01 and 0.03 Yb-doped samples at 300 K. Highest figure of merit, ZT, value is found to be  $5.4 \cdot 10^{-3}$  at 300 K for the unsubstituted sample and the ZT value decreases by the substitution.

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## 1. Introduction

Thermoelectric (TE) materials for practical electric power generation systems should possess high energy conversion efficiency. TE energy conversion has important advantages to be used to transform solar energy into electricity at lower cost than photovoltaic energy [1]. The TE materials conversion efficiency is quantified by the dimensionless figure of merit ZT, defined as  $S^2T/\rho\kappa$ , where  $S$  is the thermoelectric power,  $\rho$  electrical resistivity,  $\kappa$  thermal conductivity, and  $T$  is absolute temperature [2]. From this expression, it is clear that a TE material for practical applications must involve high thermoelectric power and low electrical resistivity, with low thermal conductivity and high working temperatures.

The discovery of large  $S$  values in  $\text{Na}_x\text{CoO}_2$  [3], with high ZT at 300 K, has opened a new research field. From this discovery, great efforts have been made to explore new ceramic families with high thermoelectric performances. In the last years, many

studies have been performed in other layered cobaltites, such as  $[\text{Ca}_2\text{CoO}_3][\text{CoO}_2]_{1.62}$ ,  $[\text{Bi}_{0.87}\text{SrO}_2]_2[\text{CoO}_2]_{1.82}$  and  $[\text{Bi}_2\text{Ca}_2\text{O}_4][\text{CoO}_2]_{1.65}$  which also exhibit attractive thermoelectric properties [4–6]. In these systems, the crystal structure is formed by two different layers, showing an alternate stacking of a common conductive  $\text{CdI}_2$ -type  $\text{CoO}_2$  layer with a two-dimensional triangular lattice and a block layer, composed of insulating rock-salt-type (RS) layers. Both sublattices (RS and  $\text{CdI}_2$ -type layers) possess common  $a$ - and  $c$ -axis lattice parameters and  $\beta$  angles but different  $b$ -axis length, causing a misfit along the  $b$ -direction [7,8].

One of the main factors affecting the thermoelectric performances of this kind of materials is the electrical resistivity which should be maintained as low as possible to avoid Joule heating. The resistivity values in ceramic materials are influenced by a number of different parameters as content and distribution of secondary phases, porosity, oxygen content, etc. As a consequence, many different synthesis methods have been used in order to prepare thermoelectric and other layered ceramic materials [4,9–12]. On the other hand, layered cobaltites are materials with a strong crystallographic anisotropy; therefore the

\*Corresponding author. Tel.: +34 976762617; fax: +34 976761957.

E-mail address: [amadre@unizar.es](mailto:amadre@unizar.es) (M.A. Madre).

alignment of plate-like grains by mechanical and/or chemical processes has been studied to attain macroscopic properties comparable to those obtained on single crystals mainly due to the decrease of their electrical resistivity. Some techniques have been shown to be adequate to obtain a good grain orientation in several oxide ceramic systems, such as templated grain growth (TGG) [8], hot pressing [13], spark plasma sintering (SPS) [14], laser floating zone [15] or electrically assisted laser floating zone [16]. Other possibilities arising from their crystallographic structure are the cationic substitutions in the RS layer, which can modify the misfit relationship. From this point of view, it is clear that these substitutions can modify the thermoelectric performances, as it is reported for substitutions of B [17] or Sb [18] for Ca in  $[\text{Ca}_2\text{CoO}_3][\text{CoO}_2]_{1.62}$ , Pb for Bi [19] or Sr by Ca [20] in  $[\text{Bi}_2\text{Ca}_2\text{O}_4][\text{CoO}_2]_{1.65}$ .

The aim of this work is studying the effect produced by the substitution of small amounts of Yb for Ca on the microstructure and thermoelectric characteristics of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramic materials.

## 2. Experimental

The initial  $\text{Ca}_{3-x}\text{Yb}_x\text{Co}_4\text{O}_{9+\delta}$  ( $x=0.00, 0.01, 0.03, \text{ and } 0.05$ ) polycrystalline ceramics were prepared from commercial  $\text{CaCO}_3$  (> 98.5%, Panreac),  $\text{Co}_3\text{O}_4$  (99.7%, Alfa Aesar), and  $\text{Yb}_2\text{O}_3$  (99.9%, Aldrich) powders by the classical solid state method. The powders were weighed in the appropriate proportions, well mixed and ball milled for 30 min at 300 rpm, in acetone media, in a planetary agate ball mill. The obtained slurry has been heated in a rapid evaporation system equipped with infrared radiation until the acetone has been totally evaporated. The dry mixture was then manually milled in order to avoid the presence of the agglomerates in the next steps and, as a consequence, favouring the alkaline earth carbonates decomposition. After milling, the fine powdered mixture has been thermally treated, in a two steps process, at 750 °C and 800 °C for 12 h under air, with an intermediate manual milling. The objective of this thermal treatment is assuring the total decomposition of calcium carbonates, as reported previously [21], which improve the mixture reactivity in the sintering processes. After the thermal treatments, the powders were milled again and uniaxially pressed at 400 MPa for 1 min in order to obtain green ceramic parallelepipeds (approximately 3 mm × 2.5 mm × 14 mm), with an adequate size for their thermoelectric characterization. The green ceramics were subsequently sintered in the optimal conditions found in previous works with the help of the CaO–CoO phase diagram [22], and consisting in one step heating at 900 °C for 24 h with a final furnace cooling which are the best determined conditions to produce the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  phase [23].

Powder X-ray diffraction (XRD) patterns have been systematically recorded in order to identify the different phases in the thermoelectric sintered materials. Data have been collected at room temperature, with  $2\theta$  ranging between 5 and 40°, using a Rigaku D/max-B X-ray powder diffractometer working with  $\text{Cu K}_\alpha$  radiation.

Microstructural investigations were performed using a Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss Merlin) fitted with an energy dispersive spectrometry (EDS) analyzer.

Temperature dependence of resistivity ( $\rho-T$ ), thermoelectric power ( $S-T$ ) and thermal conductivity ( $\kappa-T$ ) of the samples were measured simultaneously with 9T Quantum Design physical properties measurement system (PPMS) between 10 and 300 K.  $S$  was determined by dividing the voltage difference ( $\Delta V$ ) to the temperature gradient ( $\Delta T$ ) between the two ends of the sample ( $S=\Delta V/\Delta T$ ). Thermal conductivity measurements were carried out using the steady-state method.

## 3. Results and discussion

The XRD patterns for the  $\text{Ca}_{3-x}\text{Yb}_x\text{Co}_4\text{O}_{9+\delta}$  samples are shown in Fig. 1. It is obvious that all the samples have very similar diffraction patterns. All the materials mainly consist of the thermoelectric  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  phase with monoclinic symmetry [24] which is in agreement with previously reported data [25]. However, a small amount of secondary phase,  $\text{Ca}_3\text{Co}_2\text{O}_6$ , (marked with \* and situated at  $\sim 31^\circ$ ) is also obtained [25,26]. It should be mentioned that the peak indicated with ● corresponds to the (111) diffraction plane of Si used as internal reference.

Fig. 2 shows SEM micrographs performed on the surface of the samples. It can be clearly seen that all samples are composed by randomly oriented plate-like grains with a relatively broad grain sizes distribution, which is a typical  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$

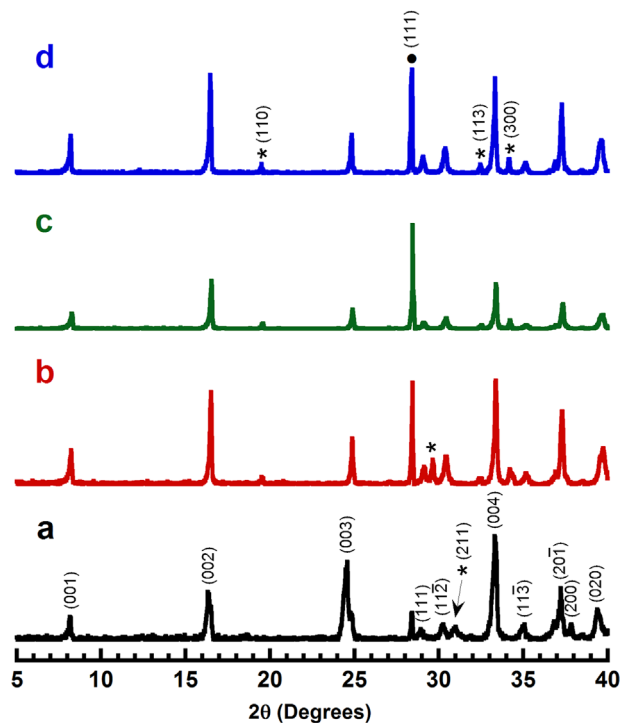


Fig. 1. Powder X-ray diffraction patterns obtained for the  $\text{Ca}_{3-x}\text{Yb}_x\text{Co}_4\text{O}_{9+\delta}$  samples; (a)  $x=0.00$ , (b) 0.01, (c) 0.03 and (d) 0.05. The diffraction planes indicate the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  phase, those indicated by a \* the  $\text{Ca}_3\text{Co}_2\text{O}_6$  one. The ● symbol denotes the (111) plane of Si used as internal reference.

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