ORIGINAL PAPER

# Effect of precursor calcination temperature on the microstructure and thermoelectric properties of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> ceramics

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Received: 1 August 2012/Accepted: 1 October 2012/Published online: 10 October 2012 © Springer Science+Business Media New York 2012

Abstract Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> (CCO) powder precursors were prepared by the chemical sol-gel route and calcined at various temperatures between 923 K (CCO-923 K) and 1,073 K (CCO-1,073 K). The calcination temperature was found to be a critical factor affecting the microstructure and thermoelectric properties of CCO ceramic bulk samples. The grain size increases with calcination temperature. The nano-crystals with size about 100 nm in the powders calcined at 923 K promote large crystal growth and texture development during sintering. Bulk pellets made from CCO-923 K powder have large crystal grains, uniform grain size distribution, and a high degree of crystal alignment. By contrast, pellets made from CCO powders at higher calcination temperatures have a bimodal distribution of large and small grains and a large amount of randomly oriented grains. Transmission electron microscopy analysis shows that each crystal grain (identified in SEM images) consists of bundles of CCO nano-lamellas. The nanolamellas within one bundle share the same *c*-axis orientation and have fiber texture. The electrical resistivity of CCO-923 K is weakly dependent on operating temperature. Compared to the CCO-1,073 K sample, the CCO-923 K

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sample has the highest power factor, a lower thermal conductivity, and higher electrical conductivity.

**Keywords** Sol–gel methods · Cobalt oxide · Calcination · Thermoelectric properties · Nanostructure

## **1** Introduction

Thermoelectric (TE) materials directly convert heat into electricity through the Seebeck effect. The energy conversion efficiency of a TE material is described by the dimensionless figure-of-merit,  $ZT = S^2 \sigma T/\kappa$ , where S, T,  $\sigma = l/\rho$ ,  $\rho$  and  $\kappa$  are the Seebeck coefficient, absolute temperature, electrical conductivity, electrical resistivity, and thermal conductivity, respectively. Layered metal oxides have attracted much attention since the discovery of the high TE performance of  $\gamma$ -Na<sub>x</sub>CoO<sub>4</sub> by Terasaki et al. [1]. However, due to the volatility at elevated temperatures and poor resistance to humidity, practical application of y-NaCo<sub>2</sub>O<sub>4</sub> for power generation is quite limited. Currently, another cobaltite, Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> (CCO) is considered to be one of the most promising candidates of p-type TE material due to its chemical stability and non-toxicity at higher temperatures [2, 3]. The crystal structure of CCO is a misfit-layered structure consisting of an electrically conductive CdI<sub>2</sub>-type CoO<sub>2</sub> layer and an insulating rocksalt-type  $Ca_2CoO_3$  layer [4].  $CoO_2$  sheets have a strongly correlated electron system that serve as electronic transport layers, while Ca<sub>2</sub>CoO<sub>3</sub> misfit layers serve as phonon scattering centers for reducing thermal conductivity. A CCO single crystal has very good TE performance with an extrapolated ZT of 0.8 at 973 K [4], and it is highly stable in air up to 1,199 K [5]. But single crystals are not practical, thus, the challenge is to improve the conversion

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efficiency of polycrystalline CCO, which is currently low in comparison with that of single crystals.

Because of the large anisotropy in the electrical transport properties of CCO single crystals, it is critical to sinter polycrystalline CCO bulk ceramics in a way that promotes densification and crystal texture simultaneously. In order to optimize the microstructure and TE performance of CCO materials, special fabrication methods for bulk materials were investigated, such as hot-pressing [6], cold high pressure pressing [7, 8], magnetic alignment [9], and spark plasma sintering process [10]. The CCO powder precursor for these methods could be made either using sol-gel chemical solution or solid state reaction methods. The solgel chemical solution route offers lower fabrication cost and simpler control of stoichiometry. For powders made using both methods, it is critical to determine the effect of processing variables on the microstructure and texture development of the sintered ceramics. For the sol-gel chemical routes, so far, the influence of some key processing parameters on the microstructure and TE properties of the sintered pellets are largely unexplored. One such key processing parameter is the calcination temperature of the precursor powder.

In this study, experiments were conducted to examine the effect of calcination temperature of powder precursors synthesized using a sol–gel method on the microstructure and TE performance of cold-pressed CCO pellets. The key nanostructure of the powders responsible for promoting the development of uniform grain distribution and a high degree of crystal texture is identified.

## 2 Experimental procedure

The CCO powder precursor was prepared using a sol-gel method by dissolving citric acid and stoichiometric amounts of Ca(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O in deionized water, followed by the addition of ethylene glycol [11]. The mixture was first heated to  $\sim 323$  K and stirred on a hot stage until complete dissolution, and then heated at  $\sim$  363 K for 3 h to remove most of the water from the solution, thus obtaining a gel. The gel was ashed at 773 K for 2 h in air in a box furnace. The ash was grounded and calcined for 4 h with an oxygen flow. Four different calcining temperatures starting from 923 K, 973 K, 1,023 K, and up to 1,073 K are chosen in the study. 923 K was chosen as the lowest calcination temperature at which the CCO crystal phase start to form [12]. For calcination, all the precursor powders were heated up at a rate of  $10 \text{ K min}^{-1}$  to the desired temperatures. The calcined powders were then re-grounded, mixed with polyvinylidene fluoride (PVDF, Sigma-Aldrich) as a binder, and uniaxially pressed into pellets at 930 MPa and 298 K. All four pellets, made from the powders calcined at 923 K (CCO-923 K, hereafter), 973 K (CCO-973 K), 1,023 K (CCO-1,023 K), and 1,073 K (CCO-1,073 K) were sintered at 1,193 K for 12 h in a tube furnace with oxygen flow. The sintering process was program-controlled using two ramp rates of 5 and 2.7 K/min for ramping furnace temperature from 298 to 873 K and from 873 to 1,193 K, respectively. During the ramping, the furnace temperature was held at 873 K for 3 h to remove the residual PVDF. After sintering, the pellets were cooled down along with the furnace in air.

The phase identification of the samples was made using a Bruker D8 Discovery X-ray diffractor with Cu K<sub> $\alpha$ </sub> radiation at room temperature. Both the morphology of the powders and bulk samples were examined using a JEOL JSM-7600F scanning electron microscope (SEM). The nanostructure of the calcined powder and the sintered pellets were analyzed using transmission electron microscopy (TEM). TEM samples were prepared by mechanically polishing and ion milling the pellets in a liquid-nitrogen cooled holder. Electron diffraction, diffraction contrast, high-resolution TEM imaging, and chemistry analysis were performed in a JEM-2100 operated at 200 kV.

The electrical properties were measured from 315 to 973 K in the direction parallel to the pressed plane of the pellets. The absolute Seebeck coefficient *S* and electrical resistivity  $\rho$  of the pellets were examined using Linseis LSR-1100 in a low pressure He environment. Thermal conductivity were measured by the equation  $\kappa = \lambda C_p \rho$ where  $C_p$  is specific heat,  $\lambda$  is thermal diffusivity, and  $\rho$  is density. The specific heat  $C_p$  and thermal diffusivity  $\lambda$  were measured from 323 to 973 K using a Laser Flash Analyzer Linseis-1200. The measurement of the thermal properties was conducted in the directions both parallel and perpendicular to the pressed plane of the pellets.

## 3 Results and discussion

#### 3.1 Nanostructure of the powders

SEM images for CCO powder precursors calcined at different temperatures are shown in Fig. 1. All of the calcined powders contain facetted rectangular shaped crystal grains. The size of the crystals increases as calcination temperature increases. The average grain size of the CCO-923 K powders is 100 nm, while the average grain size increases to 500 nm for CCO-1,073 K.

TEM taken of CCO-923 K is shown in Fig. 2. The high resolution TEM image and the electron diffraction pattern clearly show that even when calcined at the relative low temperature of 923 K, the powder is well crystallized. Figure 2 also reveals that each facetted crystal, with a size



Fig. 1 SEM morphology of pellets made from powders a CCO-923 K, b CCO-973 K, c CCO-1,023 K, and d CCO-1,073 K



Fig. 2 TEM image and the electron diffraction taken from the sample made from CCO-923 K powders

of about 100 nm as shown in the SEM image in Fig. 1, is actually composed of nano-lamellas. The nano-lamellas within each grain have widths of several nanometers and lengths of about 100 nm. The nano-lamellas share the same c-axis orientation, but have different in-plane orientations.

### 3.2 Pellet microstructure

The apparent densities of sintered pellet samples (pellet mass divided by volume), and the relative density (apparent density divided by the theoretical density of 4.68 g cm<sup>-3</sup>

Table 1 The apparent densities of sintered pellets

Sample	Calcination temperature of powders (K)	Sintering temperature of pellets (K)	Apparent density (g cm <sup>-3</sup> )	Relative density (%)
ССО-923 К	923	1,193	3.67	78
ССО-973 К	973	1,193	3.66	78
CCO- 1,023 K	1,023	1,193	3.71	79
ССО- 1,073 К	1,073	1,193	3.84	82

[13]) are listed in Table 1. It is clear that under the same pelletizing and sintering processes, the pellet density slightly increases with increasing calcination temperature of the powder precursor.

All the diffraction peaks from the XRD pattern of CCO pellets can be indexed as those from  $Ca_3Co_4O_9$  phase (PDF: #23-110) with monoclinic symmetry. Figure 3 shows the representative XRD diffraction patterns taken from the pressed planes and fracture surfaces of samples CCO-923 and CCO-1,073 K. XRD patterns from the pressed plane of pellet of CCO-973 show strong intensity from peaks corresponding to the (00 *l*) plane family of the CCO-349 monoclinic, suggesting that the pellet has a well-defined texture, i.e., a strong preferential growth orientation along the crystallographic *c*-axis. By contrast, the pellet of CCO-1,073 is with the strong peaks, of (201) and (202), from the none (00 *l*) plane family.

SEM images of the pressed surface of pellets calcined at different temperatures are shown in Fig. 4. For all four samples, the grains are plate-shaped. CCO-923 K has large crystal grains of about 5–10  $\mu$ m. CCO-923 K also has uniform grain size distribution and exhibits certain degree of crystal texture having grains with a well-proportioned disk surface perpendicular to the pressing direction. For calcination temperatures 973 K and higher, the grain size in the pressed surface starts to exhibit a bimodal distribution. For example, CCO-1,073 K has small grains less than 1  $\mu$ m and larger grains ~10  $\mu$ m. In comparison with CCO-923 K, pellets made from CCO-973 to CCO-1,073 K have more randomly orientated grains.

Cross-sectional SEM images taken from the fractured surface of the pellets are shown in Fig. 5. The microstructure displays a complicated trend as the calcination temperature increases. For CCO-923 K, the grain size is relatively large and the size distribution is uniform. The size of the bundle in Fig. 5a is larger than the size of the grains shown in the corresponding plan-view image in Fig. 4a. Accordingly, those big bundles most likely consist of several grains shown in Fig. 4a with the same or similar orientation. For CCO-973 K, the grain size seen in Fig. 5b is much smaller than for CCO-923 K. For CCO-1,023 K



**Fig. 3** XRD patterns of the pressed planes (**a**) and fractured surface (**b**) of the samples CCO-923 K and CCO-1,073 K

and CCO-1,073 K samples, the pellets have bi-modal distribution consisting of both large and small grains.

TEM examination was conducted on pellets made of CCO-923 K and CCO-1,073 K powders. The diffraction contrast images in Fig. 6a show the nanostructure of crystal grains in CCO-923 K. TEM images indicate that each crystal grain shown in the SEM images of Fig. 4a actually consists of bundle of lamellas. Each lamella has a length over one micron and a width of several tens of nanometers. Selected area electron diffraction patterns taken from two



Fig. 4 SEM morphology of the pressed plane of the pellets made from powders a CCO-923 K, b CCO-973 K, c CCO-1,023 K, and d CCO-1,073 K

different regions (Regions B and C) are shown in Fig. 6b, c, respectively. As it can be seen in Fig. 6b, Region B is a CCO crystal with corresponding electron diffraction indexed as being from the [110] direction of the CCO phase. By contrast, Region C has several lamellar-shaped CCO-grains with different orientations. As it can be concluded from Fig. 6c, the electron diffraction pattern from Region C is indexed as a complex pattern of [110] and [310] axes of CCO phase. The electron diffraction pattern in Fig. 6c also indicates that within one bundle (see Fig. 6a), all of the lamellas share the same *c*-axis orientation. In other words, the nano-lamellas in the same bundle have fiber texture. Such a fiber texture and the common c-axis (labeled in Fig. 6a) of different lamellas are confirmed by high resolution TEM (HRTEM) images shown in Fig. 7. A diffraction contrast image taken from the CCO-1,073 K is shown in Fig. 8. Within each bundle, the lamellas still have fiber texture. Furthermore, the widths of the nano-lamellas are in the range of several nanometers up to several hundred nanometers.

TEM analysis clearly demonstrates that the size of the nano-lamellas inside the crystal bundle in the pellets is significantly larger than the size of nano-lamellas in the calcined powders. Apparently, the CCO crystals experience significant crystal growth and texture development during the sintering process. Under the same pelletizing condition and sintering heat-treatment, the pellet made of CCO-923 K powders developed the most grain growth, and the highest degree of crystal texture. Such microstructure development in different pellets can be related to the nanostructure of the precursor powders. During sintering, by eliminating pores, the specific area of the powders decreases. On the other hand, the grain boundaries are another type of surfaces that also contribute to Gibbs free energy. In order to reduce the free energy contribution, the specific grain boundary area must decrease. Hence, grain growth competes with densification during sintering. Powders calcined at 923 K have the smallest crystal grain size and relatively high specific surface area. Since the sintering driving force is larger for small particles, which tend to shrink more than larger ones, both sintering and grain growth tend to be vigorous for pellets made of CCO-923 powders.

Instead of having well-defined symmetrical particle shapes, such as spheres, cubes or tetrakaidecahedrons, CCO nano-crystals have unsymmetrical lamellas. These lamellas are present in the nano-crystal of calcined powders and in the sintered pellets as well. Since the calcined



Fig. 5 SEM cross-sectional view of the fractured surface of the pellets a CCO-923 K, b CCO-973 K, c CCO-1,023 K, and d CCO-1,073 K

powders were re-grounded before being pressed to form pellets, the closely packed powders are assumed to have random crystal orientation. However, it is obvious that the nano-crystals rotate their crystal orientation during the crystal growth that accompanies the sintering process, to reduce the magnitude of misorientation between neighboring grains. Apparently, the particle rotations and the crystal rotations occur during sintering, thus promoting texture development and microstructure evolution.

The formation of anisotropy shaped nano-lamellas in precursor powders and sintered pellets has important implications on grain boundary energy as well. The rotation of crystalline particles is influenced by grain boundary diffusion and grain boundary energy, both of which are significantly dependent on the crystallographic orientation. The crystal rotation is driven by torques arising from anisotropic grain boundary energy [14, 15]. The anisotropic grain boundary coefficient promotes anisotropic shrinkage, resulting in crystal sthat are arranged in a preferred orientation in the sintered body. For CCO, with its layered structure and monoclinic unit cell, the presence of nano-lamellas and the *c*-axis fiber texture clearly indicate that the in-plane grain boundary energy, associated with the misorientation in the *a-b*-plane, is significantly higher than the out-of-plane grain boundary energy existing in between neighboring nano-lamellas along the *c*-axis. Accordingly, grain boundaries with in-plane misorientation may serve as preferred segregation sites for dopants and impurities that further affect the transport properties.

Because of the smallest crystal size in CCO-923 K, the CCO-923 K grains experiences the largest crystal growth, the largest crystal rotation, and the highest degree of texture development during sintering. Upon calcination at higher temperatures, the pellets have smaller grain sizes and non-uniform grain size distribution. Therefore, it can be seen that the nanostructure of the crystals in the precursor powders have a critical impact on the densification and microstructure development of the pellets. For the broad class of sintered materials, no unique trend exists between the initial powder size and densification [16]. However, initial powder size is significant for sol-gel materials in which surface atomic diffusion is more important than in conventional materials, especially in the early stage of sintering, when necks between particles begin to develop, particularly due to the high initial surface area. The present study shows that in order to promote significant grain growth and texture development in the sintered body, the critical size of crystals in the precursor should be about 100 nm or less. Furthermore, the present **Fig. 6** TEM image and electron diffractions of pellet made of CCO-923 K powder (**a**) TEM image, (**b**) and (**c**) of electron diffraction patterns taken from region *B* and region *C*, respectively, as indicated in the TEM image



study shows that the size of the crystals in the precursor can be controlled by the calcination temperature.

#### 3.3 Thermoelectric performance

The electrical resistivity  $\rho$ , Seebeck coefficient S, and power factor  $(S^2/\rho)$  as a function of temperature for the sintered pellets are shown in Fig. 9a, b, c, respectively. Despite having the lowest density of all the samples, the electrical resistivity of CCO-923 K is significantly lower than that of the pellets with higher density and made from powders calcined at higher temperature. Furthermore, the resistivity of CCO-923 K exhibits very weak temperature dependence from 74.7  $\mu\Omega$ ·m at 315 K to 88.3  $\mu\Omega$ ·m at 973 K. The samples made from powders calcined at higher temperatures show gradually metal-semiconductor transition around 473 K, which is consistent with the literature [17]. The lowest electrical resistivity in CCO-923 K is attributed to its larger grain size and better crystal alignment. The pellet made of CCO-1,073 K, having the highest packing density, has the highest electrical resistivity (1.5 times that of the CCO-923 K sample). Such high resistivity can be explained in terms of large amounts of randomly orientated grains. The Seebeck coefficient *S* of all the samples as a function of temperature from 293 to 973 K is given in Fig. 9b. For all the samples, *S* increases with temperature up to 973 K. While the pellets made of CCO-923 K have the highest power factor (0.306 mWm<sup>-1</sup>K<sup>-2</sup>, and the pellets made of CCO-1,023 K have the lowest power factor (0.255 mWm<sup>-1</sup>K<sup>-2</sup>) as shown in Fig. 9c.

The larger electrical resistivity measured from the CCO-1,073 K sample that is with more random oriented crystal grains could be explained in term of the layered structure and strong anisotropy of the Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>. The monoclinic structure of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> is comprised of two misfit layered subsystems: a distorted rock salt-type Ca<sub>2</sub>CoO<sub>3</sub> layer sandwiched between two CdI<sub>2</sub>-type CoO<sub>2</sub> layers along the *c*-axis. CoO<sub>2</sub> nanosheets possessing a strongly correlated electron system serve as electronic transport layers (i.e., high electrical conductivity  $\sigma$ ) and Ca<sub>2</sub>CoO<sub>3</sub> misfit layers serve as phonon scattering regions resulting in low thermal conductivity  $\kappa$ . The two dimensional layered structure



Fig. 7 High resolution TEM image taken from pellet made of CCO-923 K powder



Fig. 8 TEM diffraction contrast taken from the pellet made of CCO-1,073 K powder

resulted in two dimensional electrical conductive characters. Textured  $Ca_3Co_4O_9$  is highly anisotropic, with in-plane electrical conductivity up to 5–10 times higher than outof-plane electrical conductivity [2, 3]. As such, the highest power factor from CCO-923 K sample is attributed to the better crystal alignment and texture, in comparison with other samples.

Thermal conductivity is calculated by the equation  $\kappa = C_p \lambda \rho$  where  $C_p$  is specific heat,  $\lambda$  is thermal diffusivity, and  $\rho$  is the density. For CCO-923 and CCO-1,073 K along directions parallel and perpendicular to the pressing plane, thermal conductivity as a function of temperature are shown in Fig. 10. Strong anisotropy of thermal



Fig. 9 Temperature dependence of **a** resistivity  $\rho$  **b** Seebeck coefficient *S* and **c** power factor  $S^2/\rho$  for the samples calcined at various temperatures



Fig. 10 Temperature dependence of thermal conductivity for the samples calcined at 923 and 1,073 K. The measurements performed in the directions parallel and perpendicular to the pressed planes are indicated by symbols // and  $\perp$ , respectively; and the *arrows* of connecting two data sets indicate those data are taken from same sample



Fig. 11 Temperature dependence of figure of merit ZT for the samples calcined at 923 and 1,073 K

conductivity was observed in the CCO-923 K sample. The CCO-923 K sample shows higher values of  $\kappa$  (2.19 W m<sup>-1</sup>K<sup>-1</sup> at 323 K and 2.06 W m<sup>-1</sup>K<sup>-1</sup> at 973 K) along the pressed plane. By contrast, the CCO-923 K sample shows very low value of  $\kappa$  (1.32 W m<sup>-1</sup>K<sup>-1</sup> at 323 K and 1.3 W m<sup>-1</sup>K<sup>-1</sup> at 973 K) in the direction perpendicular to the pressed plane. In comparison with CCO-923, CCO-1,073 K exhibits smaller anisotropy but higher thermal conductivity along both directions about, 1.7 and 2.4 W m<sup>-1</sup>K<sup>-1</sup> at 973 K, respectively. Thus, in the CCO-923 K sample, lower electrical resistivity is accompanied with lower thermal conductivity. These results are in

agreement with literature [18], showing that in CCO the contribution of electrons and/or holes carriers transporting heat  $(\kappa_e)$  to the total thermal conductivity  $\kappa$  is smaller than the contribution of phonons travelling through the lattice  $(\kappa_{\rm I})$ . Plots of ZT as a function of temperature are shown in Fig. 11. The ZT values were calculated using the electrical resistivity, Seebeck coefficient, and thermal conductivity measured all from the pressed plane of the pellets. ZT of 0.14 and 0.1 are obtained for CCO-923 and CCO-1,073 K at 973 K. For undoped pure CCO, the ZT value of 0.14 at 923 K is approaching the highest reported value for the pure CCO bulk samples synthesized using some special techniques including reactive-templated grain growth [19-21]. In comparison with reactive-templated grain growth (which is limited by the very thin as-prepared textured sheet) the sol-gel method in conjunction with the coldpressing pelletization presented in this study, are more versatile for large scale production. Most importantly, the sol-gel chemical solution route offers lower fabrication cost and simpler control of the stoichiometry. Therefore, the sol-gel route is very promising for synthesis of doped CCO using various dopants to further improve the performance of CCO.

#### 4 Conclusions

In summary, the calcination temperature of powder precursor has a critical effect on the microstructure and thermoelectric properties of sintered CCO bulk materials. The size of the crystals increases as the calcination temperature increases. The nano-crystals with size about 100 nm in the powders calcined at 923 K promote large crystal growth and texture development during sintering. Despite having the lowest packing density, pellet made of CCO-923 K powders have the lowest electrical resistivity as well as relatively weak temperature dependence. Furthermore, the higher electrical conductivity of pellet made of CCO-923 K powder is not accompanied with higher thermal conductivity, which suggests that thermal conductivity is controlled by phonon scattering. Therefore, CCO-923 K combines the benefit of high electrical conductivity and low thermal conductivity due to its crystal texture and efficient phonon scattering.

Acknowledgments Air-Force Summer Faculty Fellowship, West Virginia-Energy Materials Program (Grant EPS08-01), and West Virginia University Advanced Energy Initiative.

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