**Influence of processing on stability, microstructure and thermoelectric properties of Ca3Co4-xO9+δ**

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**Abstract**

Due to high figure of merit, Ca3Co4-xO9+δ (CCO) has potential as p-type material for high-temperature thermoelectrics. Here, the influence of processing including solid state sintering, spark plasma sintering and post-calcination on stability, microstructure and thermoelectric properties is reported. By a new post-calcination approach, single-phase materials were obtained from precursors to final dense ceramics in one step. The highest *zT* of 0.11 was recorded at 800 °C for CCO with 98 and 72 % relative densities. *In situ* high-temperature X-ray diffraction in air and oxygen revealed a higher stability of CCO in oxygen ( ̴ 970 °C) than in air ( ̴ 930 °C), with formation of Ca3Co2O6 which also showed high stability in oxygen, even at 1125 °C. Since achievement of phase pure high density CCO by post-calcination method in air is challenging, the phase stability of CCO in oxygen is important for understanding and further improvement of the method.

Keywords: Ca3Co4-xO9+δ, post calcination, phase stability, microstructure, thermoelectric performance

1. **Introduction**

The transfer of heat to electricity by thermoelectricity is a well-known phenomenon used for harvesting waste heat [1]. In order to increase the efficiency of the harvesting process, three parameters need to be taken into account: Seebeck coefficient (*S*), electrical (*σ*) and thermal conductivities (*κ*), given in the figure of merit (*zT= σS2T/κ*), which explains the thermoelectric performance for a material [1, 2]. The product *σS2* is known as the thermoelectric power factor (*P*). Currently the best thermoelectric (TE) materials are Bi2Te3-based giving high *zT* value (1.41) in the low-temperature range [3]. Tellurides, however contain heavy metals introducing environmental challenges and they are unstable at high temperatures due to decomposition and oxidation limiting the application range. To overcome these issues, metal oxides like cobalt-based ones have been proposed as alternative thermoelectric materials where layered cobaltites *e.g.* Ca3Co4-xO9+δ (CCO) are among the most promising p-type candidates. CCO belong to a family of misfit-layer structures, containing two different sub-lattices where the first one creates a CoO2 network of edge-sharing CoO6-octahedra, and the second one contains two-dimensional Ca2CoO3 rock salt blocks [4, 5]. The single-phase CCO composition has a Ca:Co ratio of 3:3.93 [4, 6]. The CoO2 sub-lattice exhibits metallic conduction being responsible for the large thermoelectric power factor, while the disordered Ca2CoO3 sub-lattice lowers the thermal conductivity and increases the *zT* and therefore efficiency [4, 5, 6]. Hence, Ca3Co4-xO9+δ is one of the most promising oxide p-type conductors for thermoelectric generators.

Since oxides possess good stability at high temperature, a necessity for high-temperature applications, phase transitions and stability are important factors to determine application limits. The homogeneity range of CCO, according to the phase diagram becomes narrower with increasing temperature and ends up in a single point at 926 °C [7]. Above that temperature, CCO decomposes to Ca3Co2O6 and CoO. According to Woermann et al. further heating to 1026 °C results in a decomposition into solid solutions of CaO and CoO [8]. However, limited information is available on crystallographic data of CCO in air at high temperatures and there is no available data in pure oxygen, according to our literature survey. A *zT* of 0.87 has been reported for CCO single crystals in the *a-b* plane at 700 °C [9]. Due to a plate-like morphology of the grains and a low decomposition temperature, sintering of CCO to high density is challenging. Conventional sintering gives low densities, around 74 % when processed at 900 °C for 24 h [10] giving *zT* values of around 0.11 [11]. Alternative techniques have been used for densification, including spark plasma sintering (SPS) and hot pressing (HP), which significantly enhance the densification rate achieving densities from 95 to 97 % [12] [13]. For polycrystalline ceramics processed by SPS, *zT* values around 0.24 are reported at 800 °C, where the thermal and electrical conductivities and the Seebeck coefficient reached 2.2 W/mK, 132 S/m and 180 μV/K, respectively [14].

Due to the challenges related to obtaining high density CCO materials, post-calcination routes at temperatures above the decomposition temperature during densification followed by an annealing to regenerate the single CCO phase have been explored by Madre et al. [15] and Kang et al. [16]. Madre used laser floating zone (LFZ) to align the CCO particles followed by melting and long-time annealing at 900 °C for 72 h, resulting in a final density of 98 %. Kang et al. used solid state sintering at a maximum temperature of 1200 °C, combined with cooling below 700 °C and post-calcination at 900 °C, and a maximum density of 92 % was obtained for single-phase CCO [16]. Schulz et al. reported single-phase material with 93 % density by solid state sintering at 1200 °C followed by calcination at 900 °C for 70 h, without cooling below 700 °C [11]. However, the post calcination route is insufficiently described in the literature in terms of maximum achievable density and phase purity.

Here, a careful study of the thermoelectric properties of CCO with densities varying from 46 to 98 % of the theoretical value is reported, which has been motivated by the challenges to obtain phase pure and dense CCO ceramics. No comprehensive study of the electrical conductivity, Seebeck coefficient and thermal conductivity of these materials as a function of density is available in the literature. The thermal conductivity is decreasing with increasing porosity being beneficial for the *zT*, but on the other hand, the electrical conductivity is expected to decrease with increasing porosity being detrimental to the thermoelectric properties. A discussion on how the dependencies of these two parameters influence the *zT* is included. To be able to prepare the material with higher density, the post-calcination route was improved and challenges with respect to obtaining phase pure CCO are discussed. Since the partial pressure of oxygen plays an important role for oxygen diffusion and phase transitions in CCO, *in situ* high-temperature X-ray diffraction was preformed to understand the post-calcination process, aiming at preparing single-phase CCO with high density.

1. **Materials and Methods**

*2.1 Materials synthesis*

CCO powder was synthesized using solid state reaction (SSR), by mixing CaCO3 (Inframat Advanced Materials) and Co3O4 (Inframat Advanced Materials, 99.9 %) with isopropanol and zirconia balls. After drying in rotavapor (Büchi R-210), pellets of the precursor mixture were prepared by uniaxial pressing (5 MPa) and calcined three times at 880 °C for 14 h in ambient air with intermediate grinding (conventional furnace, Entech Super Kanthal 2). The final SSR powder was prepared by grinding the final pellet in a mortar followed by sieving (250 m).

Four ceramic samples with different densities (CCO46%, CCO72%, CCO89% and CCO98%) were prepared by the following routes: For CCO46%, the powder prepared by SSR was uniaxially pressed into pellets and bars at 5 MPa. Sintering was conducted at 900 °C for 10 h using heating and cooling rates of 200 °C/h. For CCO72% and CCO89%, green pellets and bars were prepared by uniaxial pressing at 5 MPa, followed by cold-isostatic pressing (CIP) at 200 MPa. Thermal treatment for CCO72% was the same as for CCO46% except that the dwelling time was 8 h. Thermal treatment of CCO89% was conducted using similar post-calcination route published by Kang et al. [16], where a mixture of precursors instead of phase pure CCO powder was used. The mixture of the precursors (CaCO3 and Co3O4) where heated at 1100 °C for 24 h, followed by 30 min at 650 °C and thereafter at 900 °C for 12 h. Heating and cooling rates were 60 h/°C. Spark plasma sintering for 2 min at 750 °C and 75 MPa was used for the CCO98% sample. Spark plasma sintering was carried out in a graphite die (20 mm) in vacuum (Dr Sinter 825). The preparation and sintering parameters for the different samples are summarized in Table S1 (Supplementary data).

*2.2 Characterization*

Phase purity of the CCO powders and materials was characterized by powder X-ray diffraction (Bruker D8 DaVinci). Using CuKα1 radiation, the diffraction patterns were recorded in the range 15-50° 2θ with a scanning rate 1°/min. For CCO46%, CCO72% and CCO89% XRD patterns were recorded in both the direction parallel and perpendicular to the uniaxial pressing direction. Particle size and morphology of the powders were characterized by SEM (Hitachi S-3400N). Thermal dilation of the sample using the post-calcination method were recorded using Netzsch DIL 402 dilatometer in ambient air. The density of the sintered samples were measured by Archimedes method using isopropanol. The ceramic samples (CCO46%, CCO72%, CCO89% and CCO98%) were casted in epoxy and polished to 50 nm (Al2O3 solution from BUEHLER, Master-Prep Polishing Suspension) for 1 h using VibroMet 2 from BUEHLER. Chemical etching of the polished surfaces was done by using HNO3 (concentrated) for 5, 7, 7 and 10 min for CCO46%, CCO72%, CCO89% and CCO98%, respectively. Etched surfaces were carbon coated using LEICA EM SCD 500. Microstructure of the etched samples was analyzed by field-emission scanning electron microscope (JEOL JSM-6700F), where randomly chosen 10 grains/pores were measured for each sample to give an approximate grain and pore size.

All thermoelectric measurements were performed in ambient air, from 100 to 800 °C with steps of 100 °C, where the bar shaped samples (18 x 5 x 2 mm), (10, 5, 2 mm) and pellets (12.7 mmwith 2 mm thickness) were used for electrical conductivity, Seebeck coefficient and thermal diffusivity measurements, respectively. The measurements were performed in the direction parallel to the pressing direction. Thermal conductivity was determined by the laser flash method (Netzsch LFA 457 MicroFlash). The Seebeck coefficient ΔV/ ΔT was measured by using a Probostat (NorECs AS), where the temperature gradient was dependent on the working temperature in a vertical furnace and decreased as the temperature increased [17]. Electrical conductivity was measured using four-point measurements in a home-made device [18] in a horizontal furnace, using Keithley multimeter and software.

The thermal stability of CCO and evolution of secondary phases were analyzed by high-temperature X-ray diffraction (HT-XRD). The data were recorded using a θ-θ Bruker D8 ADVANCE diffractometer with CuKα radiation and a VANTEC-1 position sensitive detector. Measurements were done in air and pure oxygen from room temperature to 1125 °C, where steps of 100 °C were used up to 900 °C and 25 °C for higher temperatures. The uncertainty in temperature was < ±15 °C. The diffraction data were recorded in the range 10 – 75° 2θ using a step size of 0.016° and 0.4 s/step giving a total collection time of 29 min per scan. Cell parameters of CCO were refined using Pawley fitting and the P2(3) space group for CCO using the Topas 5 software. Sample displacement and Cherbychev polynomial background function were defined.

1. **Results**

*3.1 Powder characteristics*

Phase pure plate-like CCO powder with a broad particle size distribution (approximately 1 to 5 μm) with an average around 3.5 μm was obtained by the SSR synthesis (Fig. 1).

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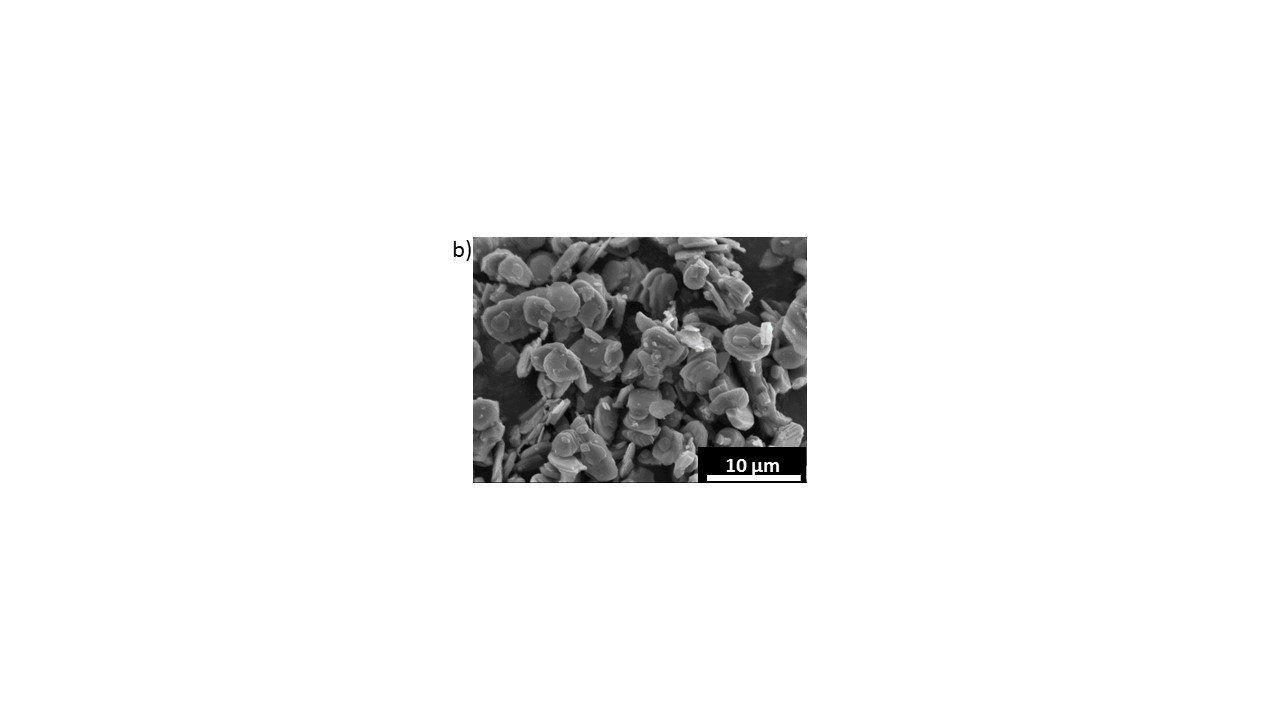
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Fig. 1 a). XRD pattern of CCO powder produced by SSR. Diffraction lines from pdf-file [24] is included and b) SEM image of CCO powder prepared by SSR.

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Fig. 2 HT-XRD patterns of CCO powder recorded in a) ambient air and b) pure oxygen. Phase identifications are included using diffraction lines from pdf-files: [19] CCO, [20] Ca3Co2O6, [21] CaO, [22] CoO.

HT-XRD patterns of the CCO powder from 925 °C in air are shown in Fig. 2a. According to the diffraction pattern at 925 °C, CCO is still phase pure while at 950 °C, CCO decomposes into Ca3Co2O6 and CoO(ss) (solid solution with CaO) according to the reaction 1:

CCO → Ca3Co2O6 + 2 CoO(ss)+ O2(g)(1)

Since the diffraction lines from the secondary phases are quite developed at 950 °C, we propose that the decomposition of CCO occurs just above 925 °C. At 975 °C, only Ca3Co2O6 andCoO(ss) are observed. Reflections due to CaO(ss) appear at 1075 °C, demonstrating the first sign of the instability of Ca3Co2O6.At 1125 °C almost no Ca3Co2O6 is present as it decomposes according to reaction 2:

2 Ca3Co2O6 → 4 CoO(ss)+ 6 CaO(ss) + O2(g)(2)

Fig. 2b presents X-ray diffractograms of CCO recorded in pure oxygen in the temperature range 925 - 1125 °C, including room temperature. The first decomposition products Ca3Co2O6 and CoO(ss) are observed at 975 °C, while CCO is observed up to 1000 °C and disappears at 1025 °C. Comparing the XRD patterns at 975 °C recorded in air and oxygen shows an increased stability of CCO in oxygen with a temperature difference of at least 35 °C. At 1125 °C, only Ca3Co2O6 and CoO(ss) are present, which demonstrate the enhanced stability of Ca3Co2O6 in pure oxygen. The stability fields for CCO and Ca3Co2O6 in air and oxygen based on the HT-XRD data are summarized in Table S2 (Supplementary data).

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Fig. 3. Cell parameters of CCO in ambient air and pure oxygen as a function of temperature. Open and filled symbols are related to air and oxygen, respectively. Dotted and dashed vertical lines represents stability limits of CCO in air (925 °C) and in oxygen (975 °C), respectively. The size of the symbols represents the maximum error.

Lattice parameters of CCO obtained by from the HT-XRD patterns are presented as a function of temperature in air and oxygen in Fig. 3. The *a* and *c* lattice parameters continuously increase with temperature up to 925 °C and 975 °C, respectively, which demonstrate the stability limit (vertical dotted and dashed lines) of CCO. Thermal expansion coefficient (TEC) was calculated for *a* and *c* lattice parameters: TEC (*a* in oxygen) = 15.0\*10-6 K-1; TEC (*a* in air) = 14.7\*10-6 K-1; TEC (*c* in oxygen) = 15.1\*10-6 K-1; TEC (*c* in air) = 15.3\*10-6 K-1.The *b* parameter shows a shallow minimum at ~700 °C in ambient air and at ~500 °C in oxygen. Different behavior of the *b* parameter could be explained due to the CCO structure with the two subsystems (Ca2CoO3 and CoO2). The parameters *a* and *c* are the same in both subsystems, while the *b* parameter of the CCO unit cell contains *bCa2CoO3*and *bCoO2*, giving a mismatch in lattice parameter where the overall lattice must be understood as an incommensurable complex structure [23] [24]. Since the formation of oxygen vacancies occurs only on oxygen sites next to Co2+ in the Ca2CoO3 subsystem, oxygen non-stoichiometry mostly influences the valence of cobalt from the rock-salt layer where mostly *bCa2CoO3* is affected increasing the mismatch between *bCa2CoO3* and *bCoO2*, showing non-linear trend with temperature. The rock-salt layer can accept up to 5 % oxygen vacancies according to Shimoyama et al. [5].

*3.2 Materials processing and microstructure*

The green density of CCO46% and CCO72% was 43 % and 65 %, respectively, hence the heat treatment of these samples mostly resulted in coarsening and only a minor degree of densification. Besides the low decomposition temperature, conventional sintering is also limited due to the plate-like morphology of CCO which deteriorates initial green packing and further densification. Cold isostatic pressing (CIP) resulted in higher green and final densities, which demonstrates that the green body density affects the final density more than the sintering time in this case with the very low densities where CCO72% reached higher final density with even shorter dwelling time than CCO46%.

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C:\Users\sathyaps\Desktop\nikola paper fig\heating 2.tifFig. 4 a) Temperature program for the post-calcination of CCO with heating and cooling rates of 60 °C/h. Isothermal hold 1: 24 h at 1100 °C; isothermal hold 2: 0.5 h at 650 °C; isothermal hold 3: 12 h at 900 °C and b) sintering curve for post-calcination of CCO according to the temperature program presented in a). Regions without temperature scale in between dotted lines, represents three isothermal holds. A magnified part of the curve starting from the end of the first isothermal hold until the start of the third isothermal hold is included in the insert.

The sintering curve for the post-calcination following the temperature program in Fig. 4a is presented in Fig. 4b. For clarity, the initial and final time for the three isothermal holds are marked with vertical dashed lines where no temperature scale is present in between. During heating of the green body, which is a mixture of Co3O4 and CaCO3, decomposition of carbonates starts at ~ 700 °C while densification starts at ~ 950 °C and continues until 1100 °C. The hold in densification observed at 930 °C corresponds to the decomposition temperature observed by HT-XRD (Table 2) due to partial reduction of cobalt to Co2+. During the isothermal hold at 1100 °C for 24 h, densification of the multiphase material composed of CoO(ss) and CaO(ss) reaches a total linear shrinkage of about 30 %. Re-formation of CCO occurs at 925 °C while decreasing the temperature from 1100 °C to 650 °C. During the isothermal hold at 650 °C, no dimensional change is observed, while a further oxidation of cobalt results in an elongation occurring around 800 °C, during the following heating. Reaching the isothermal hold at 900 °C, no further changes in dimension are observed and a final density of 89 % of theoretical was obtained.

Microstructural analysis of CCO46% shows that coarsening has occurred resulting in large open pores with large size distribution (4 - 18 m). The grain size is in the range from 2 to 7 m (Fig. 5a). Micrograph of CCO72% (Fig. 5b) shows a lower but still open porosity compared to CCO46% with uniform pore size distribution (2 - 5 m), while the grain size is in the range from 2 to 6 m. The microstructure of CCO89% (Fig. 5c) demonstrates that grain growth has occurred, and a wide grain size distribution from 3 to 11 m are present compared to the samples with lower density. The pores (1-7 mm) contributes to 6 % open and 5 % closed porosity. The micrographs of the CCO98% sample prepared by SPS (Fig. 5d-top view and 5d-side view) confirm a high relative density of 98 % as measured by Archimedes method and well packed and oriented plate-like grains perpendicular to the pressing direction. The visual impression of the grain size looks larger than real due to stacking of the grains connected in one direction. The grains are estimated to have a length from approximately 3 to 5 m and the thickness from 0.5 to 2 m as intra-grain features are revealed during the etching. The microstructure of CCO98% has significant texture as can be seen from Fig. 5 d and also from the XRD patterns recorded parallel and perpendicular to the pressing direction during SPS presented in Fig. 6 , For CCO72% and CCO89% no significant texture was observed in the XRD patterns also provided in Fig. 6.The density and microstructure characteristics of the samples are summarized in Table S1.

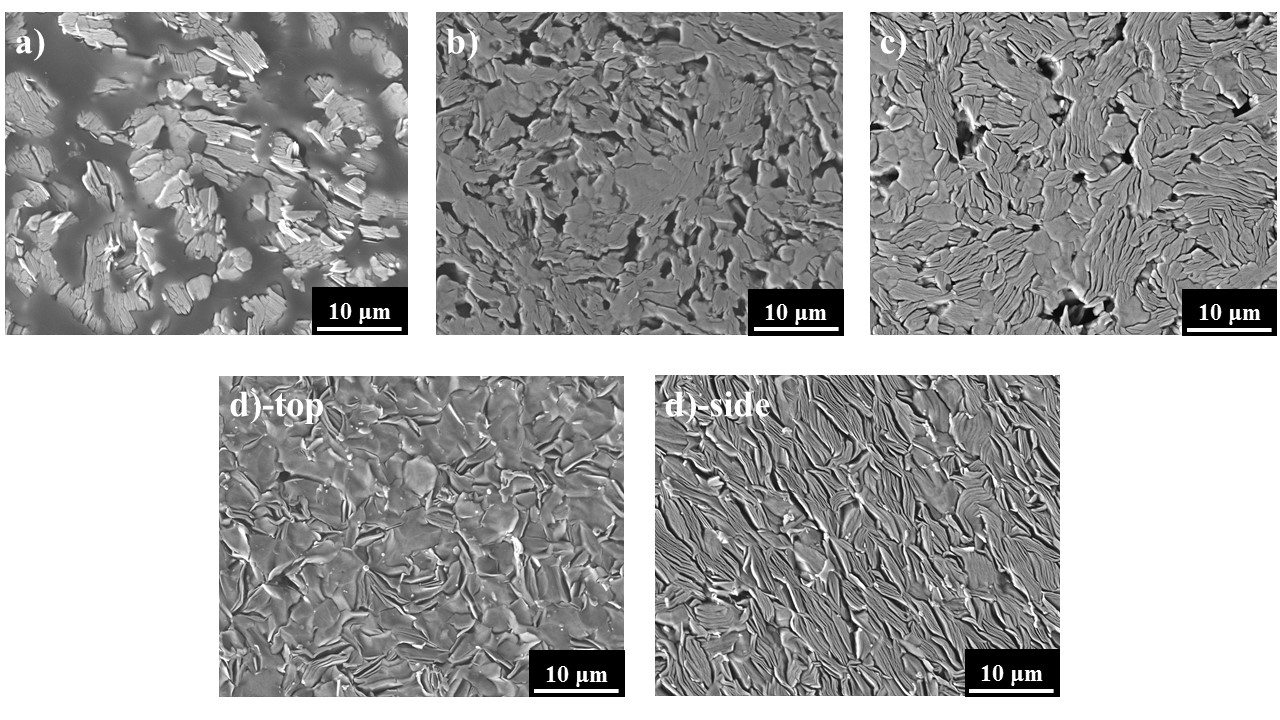


Fig. 5. SEM micrographs of polished and chemically etched surfaces of: a) CCO46%, b) CCO72%, c) CCO89%, d) CCO98% from top view and d)-side CCO98% from side view.



Fig. 6. XRD patterns of CCO72%, CCO89 and CCO98% in the directions parallel (ǁ) and perpendicular (﬩) to the pressing direction during uniaxial pressing and SPS (for CCO98%).

*3.3 TE characteristics*

The four samples with different porosities and microstructures were characterized with respect to Seebeck coefficient, thermal and electrical conductivities to evaluate the TE performance. Significant influence of temperature, density and microstructure on the thermal conductivity was observed in Fig. 7a and b. Thermal conductivity increases with increasing density and generally decreases with increasing temperature. CCO98% has the highest thermal conductivity of 2.70 Wm-1K-1 at 100 °C, while CCO46% showed a minimum value of 0.39 Wm-1K-1 between 300 and 500 °C. Included in the Fig. 7a is also data recorded for a 98 % dense sample reported by Lim et al. [14], which shows lower thermal conductivity than CCO98%. CCO46% shows increasing thermal conductivity above 700 °C corresponding to contribution from radiation due to the large porosity. The influence of grain orientation in



Fig. 7. Thermal conductivity of CCO samples with different densities a) as a function of temperature and b) as a function of density. Data from Lim et al. [14] is included for comparison.

CCO98% will cause different thermal conductivity in the directions perpendicular and parallel to the pressing direction. Our thermal conductivity measurements were done in the direction parallel to the pressing direction, where a lower value is expected since Bittner et al. showed a noticeable effect of texture on electrical conductivity [25] [26]. The effect of porosity on thermal conductivity is more dominant than the effect of grain size since CCO98% has smaller grain size than CCO89% but still higher thermal conductivity. The electrical conductivity of CCO46%, CCO72% and CCO89% presented in Fig. 8a is almost independent of temperature but shows a slight increase up to 500 – 600 °C followed by a decrease at even higher temperatures. This behavior may be explained by a combination of charge carrier mobility (holes) and the relation between oxygen stoichiometry and concentration of charge carriers as explained by Schrade et al. [6]. They showed that in air the conductivity will be virtually independent of temperature at T<600 °C whereas a moderate reduction in conductivity will take place at T>600 °C. For samples with a high porosity it is reasonable to assume that the oxygen stoichiometry is in chemical equilibrium with the prevailing partial pressure of oxygen (air), thus defining the concentration of the charge carriers. However, for high density samples with closed porosity (CCO 98%) it is equally reasonable to assume that the kinetics of oxygen exchange is hampered by slow kinetics corresponding to a virtually fixed concentration of charge carriers due to a fixed (“frozen”) concentration of oxygen vacancies. Schrade et al. [6] have reported a general increase in hole mobility for CCO at T>550 °C. Assuming that our CCO 98% sample exhibit a virtually fixed concentration of holes we suggest that the pronounced increase in conductivity at elevated temperatures (Fig. 8a) is governed by enhanced mobility. A similar behavior was also observed for the 98 % density sample by Lim et al. [14] even though their sample showed a lower conductivity at low temperature. Electrical conductivity increases linearly with the density of samples up to 89 % (Fig. 8b), from where the trend is different for the temperatures shown (100, 500 and 800 °C). Sample CCO46% has a significantly lower electrical conductivity due to the lower degree of contiguity between the grains.

The temperature influence on the Seebeck coefficient, S, is given in Fig. 9a, and compared to the data by Lim et al. [14]. A positive Seebeck coefficient over the whole temperature range is observed for all samples, confirming that the major charge carriers are electron holes. The Seebeck coefficient increases with temperature in the range 200 - 700 °C, and the highest measured Seebeck coefficient was approximately 160 μV/K for CCO98% at 700 °C. The value of S is inversely proportional to the carrier concentration as shown in Eq. (1) [27]

 (1)

where kB is the Boltzmann constant, e is the elementary charge, n is the carrier concentration, h is Plank´s constant, m\* is the effective mass of charge carrier, C is an integral constant and T is the absolute temperature. The concentration of charge carriers should decrease with increasing porosity consistent with the moderate increase in S observed for porosities in the range from 46 to 89% in Fig. 9a. This simple approach do not, however, explain why the CCO98% sample show the highest Seebeck coefficient. The deviation associated with the CCO 98% sample may originate from the synthesis method, since this material is anisotropic with alignment of the layers perpendicular to the pressing direction and the enhanced Seebeck coefficient may be explained by a more sophisticated analysis of the electronic structure in the aligned layers. Such an analysis is beyond the scope of this paper.

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Fig. 8. Electrical conductivity of CCO samples with different densities as a function of a) temperature and b) density. Data from Lim et al. [14] is included for comparison. The uncertainty is within ±1%.

As shown in Fig. 9b, *zT* increases with temperature, where the highest *zT* value of 0.11 was obtained for CCO98% and CCO72% at 800 °C. At low temperatures, where the electrical conductivity is low, CCO72% shows the best performance with the optimum combination of low thermal conductivity and sufficient electrical conductivity for obtaining maximum *zT* = 0.11. At temperatures above 400 °C, the higher electrical conductivity of CCO98% contributing strongly to *zT* and increasing the *zT* to the same level at CCO72%. The data from Lim et al. [14] shows a higher zT value reaching 0.24.

1. **Discussion**

*4.1 Post-calcination, maximum achievable density vs phase purity*

The post-calcination method is more efficient than conventional sintering in terms of densification as the densification is occurring above the decomposition temperature. The method is further developed, compared to Schultz et al. and Kang et al. [11] [16], since a reaction sintering is used starting from CaCO3 and Co3O4 precursors, while they started from single-phase powder, which first needs to be synthesized. With our continuous method, there is no need for initial time-consuming powder synthesis and coarsening of the powders during synthesis before doing post-calcination. In order to obtain phase-pure material after calcination, all cobalt needs to be re-oxidized and this is identified as the critical step using the post-calcination method. Oxidation first occurs at the surface of the specimen, and further towards the interior of the sample, where the oxidation is more dominant when oxygen diffuses through a porous material than through the bulk of the material. Hence, kinetics of re-oxidation is dependent on the density of the material. CCO89% still has 6 % open porosity (Table S1) and complete re-oxidation of the sample is possible during slow cooling with only 30 min holding at 650 °C, followed by 12 h calcination at 900 °C. On the other hand, single-phase CCO above 90 % density was not completely achieved even after 72 h of calcination, opposed to Madre et al. [15] and Schultz et al. [11]. The surface of the samples was single-phase CCO, but by crushing and grinding the samples, XRD revealed multiple phases in the interior. By increasing the densification temperature from 1100 °C to 1140 °C, the obtained density was 94 %, but secondary phase of Ca3Co2O6 was still present in the interior the pellet. Since the main challenges by the post-calcination method is re-oxidation of the interior of the sample, calcination (region 3 in Fig. 4a) in oxygen at 950 °C could be a proper solution for achieving phase purity also in the interior of the material. Calcination in pure oxygen will provide stability of CCO to higher temperatures as shown in Fig. 2 and Table S2 and enhance the kinetics of oxygen diffusion, which was limited by the temperature (900 °C) in air. The thickness of the sample is also an important issue which should be taken into account due to the influence of the diffusion distance. All post-calcination attempts performed resulting in secondary phases are summarized in Table S3 (Supplementary information). The relation between phase purity and achievable density is limited to a density of about 92 %, above which closed porosity will dominate. Especially for densities above 92 %, re-oxidation is hampered by slow oxygen diffusion trough the bulk. It is believed however that post-calcination treatment can be modified and used as a new fast solid state synthesis method for powders, where traditional time consuming SSR synthesis can be replaced by the new approach. By reducing the first heat treatment temperature from 1100/1200 °C to 1030 - 1050 °C for a shorter time, single-phase powder could be prepared.

*4.2 TE performance vs microstructure and temperature*

Since the Seebeck coefficient shows only a small variation with density, the *zT* value (Fig. 9b) is to a large extent determined by a combination of thermal conductivity and electrical conductivity. *zT* is highest for CCO98% and CCO72% caused by a combination of lower thermal conductivity, for CCO72% and a higher power factor for CCO98%. At low temperatures where the electrical conductivity is low, CCO72% shows the best performance with the optimum combination of low thermal conductivity and sufficient electrical conductivity. At temperatures above 400 °C, the higher electrical conductivity of CCO98% contributes strongly to zT and increasing the zT to the same level at CCO72%. The microstructure of CCO98% could further be improved by decreasing the grain size, which will give mutual effect of lowering thermal conductivity while enhancing power factor through the Seebeck coefficient. CCO72% contains optimum, fraction of porosity to obtain low thermal conductivity, and the *zT* could be further improved by enhancing the electrical conductivity e.g. by doping. These results show the importance of optimizing all parameters influencing the *zT* to obtain a high performance TE material.

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Fig. 9. a) Seebeck coefficient of CCO samples with different densities and b) figure of merit, zT, for CCO samples with different densities as a function of temperature. Data from Lim et al. [14] is included for comparison. The uncertainty in the measurement of the Seebeck coefficient is within ±5 %.

1. **Conclusion**

CCO samples were processed by solid state sintering, spark plasma sintering and post-calcination method to obtain materials with a wide range of densities from 46 to 98 % with different microstructures. By post-calcination method we were able to prepare pure phase CCO starting from the precursors via continuous process to dense material. Cooling from 1100 °C to 650 °C presents a necessary step before calcination at 900 °C, providing phase purity up to 92 % of theoretical density. The stability of CCO is higher in pure oxygen than in air, where the CCO is stable to ̴ 970 °C, hence we propose calcination in oxygen at 950 °C in order to obtain completely phase pure material with high density. Formation of secondary phases is shifted towards higher temperatures, where Ca3Co2O6 is stable even at 1125 °C in oxygen. The highest zT was observed for CCO98% and CCO72% caused by a combination of lower thermal conductivity for CCO72% and a higher power factor for CCO98%. An optimization of all parameters influencing the zT is important to obtain a high performance TE material.

**Acknowledgments**

Financial support from The Research Council of Norway under the program Nano2021 to the project (Number 228854) "Thermoelectric materials: Nanostructuring for improving the energy efficiency of thermoelectric generators and heat-pumps" (THELMA). Professor Mats Johnsson, Stockholm University is acknowledged for support on SPS. Antoine R. M. Dalod (NTNU) is acknowledged for fruitful discussions.

**References**

[1] S. Walia, S. Balendhranet, H. Nili, S. Zhuiykov, S. Rosengarten, Q.-H. Wang, M. Bhaskaran S. Sriram, M.S. Strano K. Kalantar-Zadehal, Transition metal oxides – Thermoelectric properties, Prog. Mater. Sci. 58 (2013) 1443 – 1489.

[2] J.R. Sootsman, D.Y. Chung, M.G. Kanatzidis, New and Old Concepts of Thermoelectric Materials,Angew. Chem. Edit. 48(2009) 8616 - 39.

[3] O. Yamashita, S. Tomiyoshi, K. Makita,Bismuth telluride compounds with high thermoelectric figures of merit,Jpn. J. Appl. Phys. 93 (2003) 368- 374.

[4] Y. Miyazaki, Crystal structure and thermoelectric properties of the misfit-layered cobalt oxides, Solid State Ionics, 172 (2004) 463 - 467.

[5] J. Shimoyama, S. Horu, L. Otzschi, M. Sano, K. Kishio, Oxygen Nonstoichiometry in Layered Cobaltite Ca3Co4Oy, Jpn. J. Appl. Phys. 42 (2003) 194 - 197.

[6] M. Schrade, H. Fjeld, T.G. Finstad, T. Norby, Electronic Transport Properties of [Ca2CoO3−δ]q[CoO2],J. Phys. Chem. C 118 (2014) 2908 - 2918.

[7] D. Sedmidubsky, V. Jakes, O. Jankovsky, J. Leitner, Z. Sofer, J. Hejtmanek, Phase equilibria in Ca–Co–O system,J. Solid State Chem. 194 (2012) 199 - 205.

[8] E. Woermann, A. Muan, Phase Equilibria in the system CaO-cobalt oxide in air,J. Inorg. Nucl. Chem. 32 (1970) 1455 - 1459.

[9] M. Shikano, R. Funahashi, Electrical and thermal properties of single-crystalline (Ca2CoO3)0.7CoO2 with a Ca3Co4O9 structure, Appl. Phys. Lett. 82 (2003) 1851 - 1853.

[10] A. Sotelo, G. Constantinescu, Sh. Rasekh, M.A. Torres, J.C. Diez, M.A. Madre, Improvement of thermoelectric properties of Ca3Co4O9 using soft chemistry synthetic methods, J. Eur. Ceram. Soc. 32 (2012) 2415 - 2422.

[11] T. Schulz, J. Topfer, Thermoelectric properties of Ca3Co4O9 ceramics prepared by an alternative pressure - less sintering/annealing method, J. Alloy. Compd. 659 (2016) 659 122 - 126.

[12] D. Wang, L. Chen, Q. Wang, J. Li, Fabrication and thermoelectric properties of Ca3−xDyxCo4O9+δ System,J. Alloy. Compd. 376 (2004) 58 - 61.

[13] M. Prevel, S. Lemonnier, Y. Klein, S. Hebert, D. Chateigner, Textured Ca3Co4O9 thermoelectric oxides by thermoforging process, J. Appl. Phys. 98 (2005) 093706-1-4.

[14] C-H. Lim, S-M. Choi, W-S. Seo, K.H. Kim, J-Y Kim, H-H Park, Improvements of thermoelectric transport properties for a partially substituted Ca3Co4O9 system by spark plasma sintering*,* J. Ceram. Process. Res. 13 (2012) 197 - 201.

[15] M.A. Madre, F.M. Costa, N.M. Ferreira, A. Sotelo, M.A. Torres, G. Constantinescu, Sh. Rasekh, J.C. Diez, Preparation of high-performance Ca3Co4O9 thermoelectric ceramics produced by a new two-step method, J. Eur. Ceram. Soc. 33 (2013) 1747 - 1754.

[16] M-G. Kang, K-H. Cho, J-S. Kim, S. Nahm, S-J. Yoon, C-Y. Kang, Post-calcination, a novel method to synthesize cobalt oxide-based thermoelectric material, Acta Mater.73 (2014) 251 - 258.

[17] V. Øygarden, T. Grande, Crystal structure, electrical conductivity and thermal expansion of Ni and Nb co-doped LaCoO3, Dalton T. 42 (2013) 2704 – 2715.

[18] I. Wærnhus, P.E. Wullum, R. Holmestad, T. Grande, K. Wiik, Electronic properties of polycrystalline LaFeO3. Part 1: "Experimental results and the quantitative role of Schottky defects", Solid State Ionics 176 (2005) 2783 – 2790.

[19] Y.-G. Kang, Department of Materials Science and Engineering, Seoul National University, Gwanak-gu, South Korea, Private Communication (2011).

[20] H. Fjellvåg, E. Gulbrandsen, S.O. Aasland, A.Olsen, B.C. Hauback, Crystal structure and possible charge ordering in one-dimensional Ca3Co2O6, J. Solid StateChem. 124 (1996) 190 - 194.

[21] M.C. Verbraeken, E.Suard, J.T.S. Irvine, Structural and electrical properties of calcium and strontium hydrides, J. Mater. Chem. 19 (2009) 2766 - 2770.

[22] R. Grimes, A. Fitch, Thermal decomposition of cobalt(II) acetate tetrahydrate studied with time-resolved neutron diffraction and thermogravimetric analysis, J. Mater. Chem. 1 (1991) 461 - 468.

[23] G.M. Kale, S.S. Pandit, K.T. Jacob, Thermodynamics of cobalt (II, III) oxide (Co3O4): Evidence of phase transition, T. Jpn. I. Met. 29(1988) 125 - 132.

[24] M. Schrade, S. Casolo, P.J. Graham, C. Urlich, S. Li, O-M. Løvik, T.G. Finstad, T. Norby, Oxygen nonstoichiometry in (Ca2CoO3)0.62(CoO2): A combined experimental and computational Study, J. Phys. Chem. C. 118 (2014) 18899 - 1889907.

[25] M. Bittner, L. Helmich, F. Nietschke, B. Geppert, O. Oeckler, A. Feldhoff, Porous Ca3Co4O9 with enhanced thermoelectric properties derived from sol–gel synthesis, J. Eur. Ceram. Soc. 37 (2017) 3909 - 3915.

[26] J-W. Moon, D. Nagahama, Y. Masuda, W-S. Seo, K. Koumoto, Anisotropic thermoelectric properties of crystal-axis oriented ceramics of layer-structured oxides in the Ca-Co-O system*,* J. Ceram. Soc. Jpn. 109 (2001) 647 - 650.

[27] F.P. Zhang, Q.M. Lu, X. Zhang, J.X. Zhang, First principle investigation of electronic structure of CaMnO3 thermoelectric compound, J. Alloys Compd. 509 (2011) 542-545.

**Figure captions:**

Fig. 1 a). XRD pattern of CCO powder produced by SSR. Diffraction lines from pdf-file [24] is included and b) SEM image of CCO powder prepared by SSR.

Fig. 2 HT-XRD patterns of CCO powder recorded in a) ambient air and b) pure oxygen. Phase identifications are included using diffraction lines from pdf-files: [19] CCO, [20] Ca3Co2O6, [21] CaO, [22] CoO.

Fig. 3. Cell parameters of CCO in ambient air and pure oxygen as a function of temperature. Open and filled symbols are related to air and oxygen, respectively. Dotted and dashed vertical lines represents stability limits of CCO in air (925 °C) and in oxygen (975 °C), respectively. The size of the symbols represents the maximum error.

Fig. 4 a) Temperature program for the post-calcination of CCO with heating and cooling rates of 60 °C/h. Isothermal hold 1: 24 h at 1100 °C; isothermal hold 2: 0.5 h at 650 °C; isothermal hold 3: 12 h at 900 °C and b) sintering curve for post-calcination of CCO according to the temperature program presented in a). Regions without temperature scale in between dotted lines, represents three isothermal holds. A magnified part of the curve starting from the end of the first isothermal hold until the start of the third isothermal hold is included in the insert.

Fig. 5. SEM micrographs of polished and chemically etched surfaces of: a) CCO46%, b) CCO72%, c) CCO89%, d) CCO98% from top view and d)-side CCO98% from side view.

Fig. 6. XRD patterns of CCO72%, CCO89 and CCO98% in the directions parallel (ǁ) and perpendicular (﬩) to the pressing direction during uniaxial pressing and SPS (for CCO98%).

Fig. 7. Thermal conductivity of CCO samples with different densities a) as a function of temperature and b) as a function of density. Data from Lim et al. [14] is included for comparison.

Fig. 8. Electrical conductivity of CCO samples with different densities as a function of a) temperature and b) density. Data from Lim et al. [14] is included for comparison. The uncertainty is within ±1 %.

Fig. 9. a) Seebeck coefficient of CCO samples with different densities and b) figure of merit, zT, for CCO samples with different densities as a function of temperature. Data from Lim et al. [14] is included for comparison. The uncertainty in the measurement of the Seebeck coefficient is within ±5 %.