



Phase evolution and thermoelectric performance of calcium cobaltite upon high temperature aging

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Abstract

Crystal phase transformation and their nanostructure evolutions were studied for baseline thermoelectric ceramic $\text{Ca}_3\text{Co}_4\text{O}_9$, and for a sample aged at 1283 K, which is significantly higher than the $\text{Ca}_3\text{Co}_4\text{O}_9$ decomposition temperature of 1199 K. X-ray diffraction from both samples only reveals peaks from $\text{Ca}_3\text{Co}_4\text{O}_9$ phase. TEM examination reveals that in the aged sample, CaO nano-phase exists between neighboring $\text{Ca}_3\text{Co}_4\text{O}_9$ nano-lamella grains. Moreover, a small amount of Co_3O_4 and $\text{Ca}_2\text{Co}_2\text{O}_5$ phase were also observed in the aged sample. The $\text{Ca}_2\text{Co}_2\text{O}_5$ phase does not exhibit the same lamella nanostructure as $\text{Ca}_3\text{Co}_4\text{O}_9$ and displayed few crystal defects. Except for $\text{Ca}_3\text{Co}_4\text{O}_9$, $\text{Ca}_2\text{Co}_2\text{O}_5$, and Co_3O_4 , no other Ca–Co–O cobaltite phase, such as $\text{Ca}_3\text{Co}_2\text{O}_6$, was found in the aged sample. Electrical and thermal properties of both baseline and aged sample were measured over the temperature range of 320–1033 K.

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1. Introduction

Thermoelectric (TE) oxide materials, [1–6] such as bismuth based cobaltites [7,8] and particularly newly developed calcium cobaltites, [9–13] are promising for on-board heavy-duty vehicle applications and high temperature waste heat harvesting from power plants, because they are lightweight, inexpensive, highly efficient, non-toxic and stable at high temperatures in air. In comparison with other promising oxides, calcium cobaltite has some unique features. For example, BiCuSeO has gained ever-increasing attention in recent years, with the ZT value significantly increased from 0.5 to 1.4 from year 2010 to year 2014. [14] However, the thermal stability of BiCuSeO is a concern, and BiCuSeO-based TE materials could not be used in air for an extended periods as a conventional oxide at high temperatures, apparent decomposition occurred in the BiCuSeO samples when heated to 773 K, although at 573 K the

oxidation was limited to the surface accompanied by the formation of bismuth oxide. [15,16] On the other hand, the calcium cobaltite single crystal shows very good TE behavior with an extrapolated figure of merit ZT of 0.8 at 973 K [2].

The extraordinary TE performance of $\text{Ca}_3\text{Co}_4\text{O}_9$ is attributed to its layered structure. [3] $\text{Ca}_3\text{Co}_4\text{O}_9$ contains layers of single CdI_2 -type CoO_2 and triple rock salt-type Ca_2CoO_3 subunits that are alternately stacked in the c -direction with a misfit relationship. [3] In the $\text{Ca}_3\text{Co}_4\text{O}_9$, CoO_2 sheets, possessing a strongly correlated electron system, serve as electronic transport layers, while Ca_2CoO_3 layers serve as phonon scattering regions to give low thermal conductivity. The misfit relationship between the CoO_2 layer and Ca_2CoO_3 layer leads to an incommensurate structure with the subunits sharing the same a , c and β parameters but different b lattice parameters ($b_1/b_2=1.61$). [3] The subunit of CoO_2 from $\text{Ca}_3\text{Co}_4\text{O}_9$ phase are also shared by other Ca–Co–O cobaltite, including $\text{Ca}_2\text{Co}_2\text{O}_5$, [17–22] CaCo_2O_4 , [23,24] Ca_xCoO_2 , [25] and $\text{Ca}_3\text{Co}_2\text{O}_6$. [26–28] In the pseudo-binary Ca–Co–O system, stable phases have been synthesized for Ca/Co ranging

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between 1.5 and 0.75 of Ca_xCoO_2 , [25] $\text{Ca}_3\text{Co}_2\text{O}_6$, [28] $\text{Ca}_2\text{Co}_2\text{O}_5$, [17–20] and $\text{Ca}_3\text{Co}_4\text{O}_9$. [3] Among those similar cobaltite phases, $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_2\text{Co}_2\text{O}_5$ exhibit the best TE behavior. It is herein proposed that during the synthesis of the $\text{Ca}_3\text{Co}_4\text{O}_9$ phase, the formation of the above-mentioned phases of calcium cobalt oxide phases are dependent on the sintering temperature, with the $\text{Ca}_3\text{Co}_4\text{O}_9$ phase being stable up to 1199 K. Above 1199 K, it decomposes into a $\text{Ca}_3\text{Co}_2\text{O}_6$ phase, which is stable up to 1300 K. [29] In practical applications, for example the waste heat recovery from the power plants, the generators are expected to work in the harsh environments including high temperatures of 923–1273 K. Accordingly, it is essential to understand the thermal stability in air of sintered $\text{Ca}_3\text{Co}_4\text{O}_9$ materials, the phase transformation between different cobaltite Ca–Co–O phases, and their property and structure evolution upon long term high temperature operation and overheating above the reported decomposition temperature of 1199 K. [30]

The present work reports on the nanostructure and TE performance of polycrystalline $\text{Ca}_3\text{Co}_4\text{O}_9$ bulk samples aged at high temperature in air. Specifically, thermal stability and nanostructure evolution were studied for a $\text{Ca}_3\text{Co}_4\text{O}_9$ sample that was heat-treated at 1283 K, which is 84 K higher than the

$\text{Ca}_3\text{Co}_4\text{O}_9$ decomposition temperature as indicated in the CaO–CoO phase diagram. [30]

2. Experimental procedure

The precursor powders with nominal composition $\text{Ca}_3\text{Co}_4\text{O}_9$ were prepared by a sol–gel chemical solution route. Stoichiometric amounts of calcium nitrate tetrahydrate (Acros Organics, CAS: 13477-34-4) and cobalt nitrate hexahydrate (Acros Organics, CAS: 10026-22-9) were dissolved in de-ionized water with additions of citric acid (BDH, CAS: 5949-29-1) and ethylene glycol (BDH, CAS: 107-21-1). The solution was heated at 350 K with constant mechanical stirring for 3 h to obtain a gel. The gel was ashed at 773 K in a box furnace. Finally, the ash products were calcined at 923 K in a tube furnace for 4 h with oxygen flow to form precursor powders. The calcined powders were then re-ground and uniaxially pressed into pellets under a pressure of 930 MPa at 298 K. The pellets were then submitted to heat treatment in two conditions, respectively. One is the baseline sample that was sintered at 1193 K for 12 h. The second sample was sintered at 1193 K for 12 h, and then further heat-treated at 1283 K for another 12 h.

X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), and high resolution Transmission Electron Microscope (TEM) equipped with Energy Dispersive X-ray Spectroscopy (EDS) were used to examine the structure and chemistry of the two samples from the micron to the atomic scale. The planes perpendicular to the pressed plane were selected for TEM analyses in this work. TEM samples were prepared by mechanical polishing and ion milling 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 absolute Seebeck coefficient and electrical resistivity of the pellets were measured in low pressure He gas from 320 K to 1033 K using a Linseis LSR-1100. The thermal conductivity was measured and evaluated from 323–1023 K using a Laser Flash Analyzer (LFA) Linseis-1200.

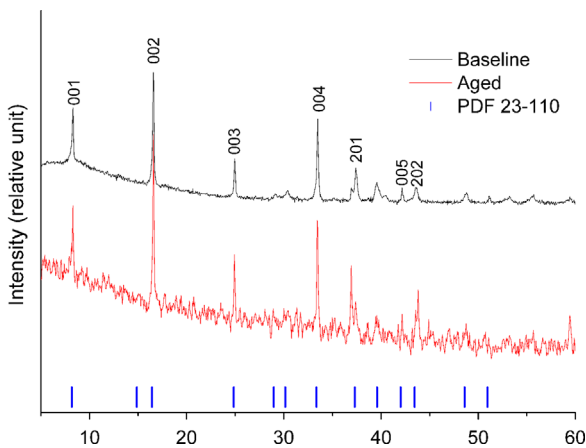


Fig. 1. XRD pattern of the baseline sample and the sample aged at 1283 K.

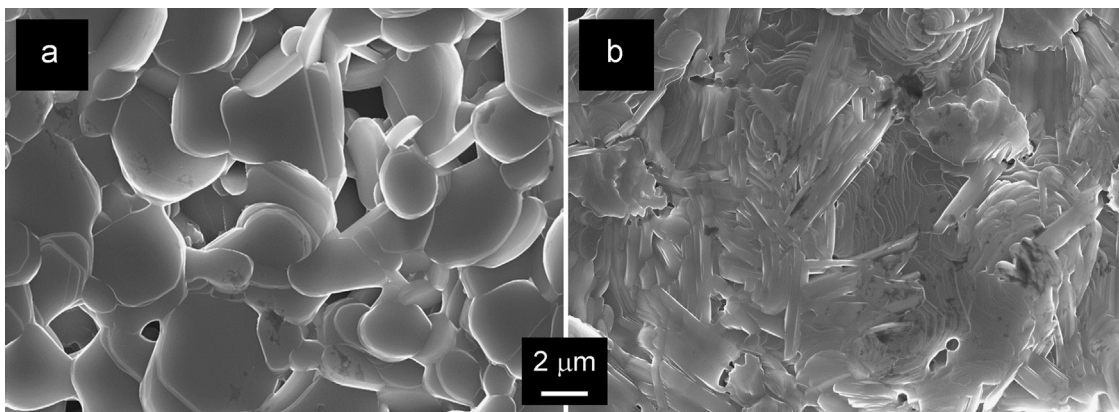


Fig. 2. Morphologies of the pressed surface taken from (a) the baseline sample and (b) the aged sample.

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