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Effects of Synthesis and Spark Plasma Sintering Conditions on the Thermoelectric Properties of $Ca_3Co_4O_{9+\delta}$

NINGYU WU,[1,2] TIM C. HOLGATE,[1] NGO VAN NONG,[1] NINI PRYDS,[1] and SØREN LINDEROTH[1]

1.—Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark. 2.—e-mail: niwu@dtu.dk

$Ca_3Co_4O_{9+\delta}$ samples were synthesized by solid-state (SS) and sol–gel (SG) reactions, followed by spark plasma sintering under different processing conditions. The synthesis process was optimized and the resulting materials characterized with respect to their microstructure, bulk density, and thermoelectric transport properties. High power factors of about 400 μW/m·K^2 and 465 μW/m·K^2 (at 800°C) were measured for SS and SG samples, respectively. The improved thermoelectric performance of the SG sample is believed to originate from the smaller particle sizes and better grain alignment. The SG method is suggested to be a beneficial means of obtaining high-performance thermoelectric materials of $Ca_3Co_4O_{9+\delta}$ type.

Key words: Thermoelectric, spark plasma sintering, $Ca_3Co_4O_{9+\delta}$, solid-state reaction, sol–gel reaction

INTRODUCTION

Thermoelectric materials have provided a means to convert thermal energy into electrical energy. The performance of a thermoelectric material can be evaluated by the dimensionless figure of merit $ZT = S^2T/\rho\kappa$, which consists of the Seebeck coefficient (S), the electrical resistivity (ρ), the thermal conductivity (κ), and the absolute temperature (T). Shikano and Funahashi[1] first brought attention to $Ca_3Co_4O_{9+\delta}$ as a high-temperature thermoelectric candidate by reporting a ZT of 0.83 (at 800°C) for a single crystal. $Ca_3Co_4O_{9+\delta}$ has a misfit-layered structure with a CdI_2-type hexagonal CoO_2 subsystem and a rock-salt-type Ca_2CoO_3 subsystem. The electronic conduction takes place mainly in the CoO_2 layer while the Ca_2CoO_3 subsystem dominates the phononic conduction and may therefore be tuned to reduce the lattice thermal conductivity. However, the two-dimensional character of this layered structure can result in anisotropy in the thermal and electrical transport properties.[1,2]

So far, many efforts have focused on $Ca_3Co_4O_{9+\delta}$ to achieve higher thermoelectric performance by either mastering the ion doping or by choice of the processing route, i.e., solid-state (SS) or sol–gel (SG) reactions.[3–14] For pure $Ca_3Co_4O_{9+\delta}$ synthesized by SS, the resulting improvement has led to its thermoelectric properties reaching ρ = 9 mΩ·cm, S = 180 μV/K, and power factor PF = 370 μW/m·K^2 at 800°C, leading to a ZT of 0.25.[13] On the other hand, for $Ca_3Co_4O_{9+\delta}$ synthesis by SG, it was shown that ρ = 6.1 mΩ·cm, S = 165 μV/K, and PF = 445 μW/m·K^2 at 700°C, but unfortunately no data on the thermal conductivity were reported and therefore no value for ZT is available.[4] Recently, Kenfaui et al.[15] conducted a systematic study by varying the conditions of the spark plasma sintering (SPS) process, such as applied pressures and sintering temperatures, discovering that the thermoelectric properties increase with increasing sintering temperature and pressure up to 50 MPa, reaching a PF of 315 μW/m·K^2 at about 550°C. Many other attempts have been made to improve the thermoelectric properties of this type of material.[16,17] However, more detailed study of the processing parameters along with their relationship to the resulting thermoelectric properties is still needed.

In this work, the thermoelectric properties of samples synthesized by SS and SG followed by

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