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Thermoelectric Properties of $Ca_{3-x}Dy_xCo_4O_{9+\delta}$ with $x = 0.00$, 0.02, 0.05, and 0.10

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Polycrystalline samples of $Ca_{3-x}Dy_xCo_4O_{9+\delta}$ (x = 0.00, 0.02, 0.05, and 0.10) have been prepared by conventional solid-state synthesis. The x-ray diffraction (XRD) results revealed that all the samples are single phase. The thermoelectric properties were measured at 25 K to 300 K. The thermopower of all the samples was positive, indicating that the predominant carriers are holes over the entire temperature range. The electrical resistivity of all the samples exhibited the nonmetal-to-metal transition at below 75 K. The electrical resistivity decreased and the thermopower increased with increasing Dy^{3+} content. Among all the samples, $Ca_{2.9}Dy_{0.10}Co_4O_{9+\delta}$ had the highest dimensionless figure of merit of 0.044 at 300 K.

Key words: Thermoelectric materials, sintering, thermoelectric, thermal conductivity, x-ray diffraction, figure of merit

INTRODUCTION

Thermoelectric energy conversion can be used to generate electricity from waste heat. The efficiency of thermoelectric materials in this process is determined by their dimensionless thermoelectric figure of merit, $ZT = S^2\sigma T/\kappa$, where S, σ, T, and κ are the Seebeck coefficient, the electrical conductivity, the absolute temperature, and the thermal conductivity, respectively.[1] Wide attention has been focused on exploration of thermoelectric materials recently. Good thermoelectric materials require large thermopower (S) to generate a large thermal voltage, low electrical resistivity (ρ) to minimize Joule heating, and low thermal conductivity (κ) to retain heat at the junctions.[2] Besides, thermoelectric materials are required to be stable at high temperatures. In recent years, layered cobalt oxides have gained great attention since $NaCo_2O_4$ single crystal was found to exhibit good thermoelectric properties.[3] Recently, the misfit cobalt oxides ($Ca_3Co_4O_{9+\delta}$) have been investigated extensively as potential thermoelectric materials because of their large S, low ρ, and low κ.[4–9] The crystal structure of the $Ca_3Co_4O_{9+\delta}$ system consists of two subsystems, viz. the distorted NaCl-type (Ca_2CoO_3) sublattice and the CdI_2-type (CoO_2) sublattice, alternately stacking along the c-axis.[10] Polycrystalline bulk $Ca_3Co_4O_{9+\delta}$ samples are still at a relatively low level for industrial applications. Many attempts have been made to optimize the thermoelectric performance of $Ca_3Co_4O_{9+\delta}$ by either partially substituting cations or using appropriate fabrication methods such as hot pressing (HP)[11] or spark plasma sintering (SPS) techniques.[12] Partial replacement of cations in $Ca_3Co_4O_{9+\delta}$ has been carried out on either the Ca site[13–24] or the Co sites.[5,8,25–28] It has been reported that partial substitution for Ca by heavier ions with trivalence such as Eu^{3+},[13] Nd^{3+},[14] Bi^{3+},[15] Y^{3+},[21] or Yb^{3+},[22] is effective in improving the thermoelectric properties. There are a few reports regarding the high-temperature (> 300 K) thermoelectric properties of the $Ca_{3-x}Dy_xCo_4O_{9+\delta}$ system with higher doping level ($x \geq 0.10$).[9,29,30] Therefore, it is interesting to investigate the low-temperature (< 300 K) thermoelectric properties of the $Ca_{3-x}Dy_xCo_4O_{9+\delta}$ system. We report herein the low-temperature thermoelectric properties of the $Ca_{3-x}Dy_xCo_4O_{9+\delta}$ ($0 \leq x \leq 0.10$) system.

EXPERIMENTAL PROCEDURES

Polycrystalline samples of $Ca_{3-x}Dy_xCo_4O_{9+\delta}$ (x = 0.00, 0.02, 0.05, and 0.10) were synthesized by

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