Journal of ELECTRONIC MATERIALS, Vol. 42, No. 7, 2013
DOI: 10.1007/s11664-013-2585-0

Grain-Oriented $Ca_3Co_4O_9$ Thermoelectric Oxide Ceramics Prepared by Solid-State Reaction

KOHEI OBATA,[1] YASUNORI CHONAN,[1] TAKAO KOMIYAMA,[1] TAKASHI AOYAMA,[1] HIROYUKI YAMAGUCHI,[1,3] and SHIGEAKI SUGIYAMA[2]

1.—Department of Electronics and Information Systems, Akita Prefectural University, 84-4 Tsuchiya-Ebinokuchi, Yurihonjo City, Akita 015-0055, Japan. 2.—Akita Industrial Technology Center, 4-11 Arayamachi-Sanuki, Akita City, Akita 010-1623, Japan. 3.—e-mail: yamaguchi@akita-pu.ac.jp

We studied a method to enhance the degree of grain orientation of $Ca_3Co_4O_9$ thermoelectric oxide ceramics. Ceramic specimens were prepared by solid-state reaction with different growth conditions. Large-grained $Ca_3Co_4O_9$ powders were obtained by using "heavy-calcination" and "moderate-grinding" steps before pelletizing, and these large-grained powders contributed to the enhancement of the degree of orientation. Scanning electron microscopy (SEM) observation results showed that plate-like crystal grains were stacked up in layers for the heavily calcined ceramics, while no such anisotropic structure was found for those that were lightly calcined. x-Ray diffraction (XRD) analysis also indicated that the specimen obtained by heavy-calcination and moderate-grinding steps had a high degree of (002) orientation. The effect of the heavy-calcination and moderate-grinding steps was clearly evidenced by the electrical resistivity ρ. The electrical resistivity ρ at 700°C for the higher-oriented ceramics was 73% of that for the lower-oriented ceramics. Since ρ was reduced without deterioration of the Seebeck coefficient S, the power factor (S^2/ρ) at 700°C for the former was increased by 29% compared with that for the latter.

Key words: $Ca_3Co_4O_9$, thermoelectric oxide, solid-state reaction method, large-grained powder, grain-oriented ceramics, electrical resistivity

INTRODUCTION

$Ca_3Co_4O_9$ is one of the most promising p-type thermoelectric materials because of its high dimensionless figure of merit[1] $ZT = S^2T/\rho\kappa$, where S is the Seebeck coefficient, T is the absolute temperature, ρ is the electrical resistivity, and κ is the thermal conductivity. This material shows strong anisotropy in its thermoelectric properties due to the layer structure.[2] Therefore, it is a desirable material for fabricating grain-oriented ceramics for practical use. When prepared by conventional sintering,[3] the degree of grain orientation of ceramics is apt to deteriorate. So, some research groups have reported fabrication of grain-oriented ceramics by the: (1) magnetic alignment method,[4] (2) hot-forging technique,[5] (3) single-crystal composite method,[6] and (4) multisheet cofiring technique.[7] These approaches achieved improvement of the orientation degree by innovations in the pelletizing or sintering process. The approaches share a common feature: $Ca_3Co_4O_9$ powders are prepared by the solid-state reaction method before pelletizing; however, the preparation conditions of the $Ca_3Co_4O_9$ powders vary.

Some researchers have focused on the preparation of $Ca_3Co_4O_9$ powders. Mikami et al.[8] reported the validity of using large-grained $Ca_3Co_4O_9$ powder for producing grain-oriented $Ca_3Co_4O_9$ ceramics. At first, they prepared $Ca_3Co_4O_9$ powders by solid-state

(Received July 6, 2012; accepted March 21, 2013; published online May 7, 2013)