

Preparation and characterization of calcium cobaltite for thermoelectric application.

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Abstract

Calcium and sodium cobaltites had been reported recently as the good candidates for oxide thermoelectric application because of high figure of merit. However, little is known about that compounds: calcium cobaltite could form at least three different compounds with diversified Ca:Co cations ratio, formation temperature and details of ceramic processing are not clear. The aim of the work was to study temperature dependence of cobaltites formation, their characterization and stability in air at room temperature. Starting powders of CaCO_3 with different Ca:Co ratio and three different sources of Co_3O_4 were mixed and calcined at 700-1100°C. DTA/TG, mass changes, density, grain size distribution, phase composition were examined. It has been found that phase composition of the resulted product was dependent on calcination temperature and properties of starting cobalt oxide. Three stages of cobaltite formation were established: simultaneous decomposition of CaCO_3 with $\text{Ca}_3\text{Co}_4\text{O}_9$ formation (800-900 °C), decomposition of $\text{Ca}_3\text{Co}_4\text{O}_9$ and formation of $\text{Ca}_3\text{Co}_2\text{O}_6$ (about 950 °C) and the last stage at 1050°C was dependent on starting cation ratio and source of cobalt (II,III) oxide. It has been found that total decomposition of the previous phases was observed in the batches with Ca:Co=1:1 ratio if very pure Co_3O_4 was used for preparation. Replacement of pure Co_3O_4 by cobalt oxide contaminated by cobalt hydroxide lead to re-formation of $\text{Ca}_3\text{Co}_4\text{O}_9$ phase at 1050 °C in 1:1 batches. Residual Co_3O_4 and CaO was always present in calcined specimens. It seems that prolonged heat treatment did not lead to better reaction degree. Some reactions were promoted by solid state diffusion, the others were of heterogenic nature and grain size and surface area were of significance.