

Abstract

Exploring the High-Temperature Thermoelectric Performance of La-Substituted $\text{Ca}_3\text{Co}_4\text{O}_9$ Bulk Ceramics [†]

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It is well-known that the electrical properties of the $\text{Ca}_3\text{Co}_4\text{O}_9$ thermoelectric (TE) compound are strongly influenced by the valence of the substituting cation, while its solubility and “functional” impact depend largely on the preparation and/or processing methods used. Furthermore, this material’s hybrid crystal structure allows for different cation substitutions in/from different sublattices. This research work presents the relevant effects of different La substitutions for the Ca ions from the insulating rock salt type [Ca_2CoO_3] crystal component (considered as a “charge reservoir” for the conductive [CoO_2] layers) for a series of bulk samples prepared and processed via a solid-state method, chosen for simplicity. The results show that the actual level of La substitutions does not exceed 0.03 ($x < 0.03$), in $\text{Ca}_{3-x}\text{La}_x\text{Co}_4\text{O}_9$ samples with $x = 0.01, 0.03, 0.05$ and 0.07 , and that beyond this limit, simultaneous $\text{Ca}_3\text{Co}_4\text{O}_9$ phase decomposition and secondary $\text{Ca}_3\text{Co}_2\text{O}_6$ and $(\text{La,Ca})\text{CoO}_3$ phase formation take place. The morpho-structural features were found to be quite moderate, with a negligible effect on the charge carries transport. The electrical measurements and average oxidation state of cobalt (~ 3.11) suggest that the substitutions with La have only a minor effect on the charge carrier concentration. The electrical resistivity of the samples with $x = 0.01, 0.03$ and 0.05 is found to be ~ 1.3 times lower than of pristine $\text{Ca}_3\text{Co}_4\text{O}_9$, while the changes in the Seebeck coefficient values are only moderate in the whole measured temperature range. The highest power factor, representing the electrical counterpart of the TE performance, was found for the $\text{Ca}_{2.99}\text{La}_{0.01}\text{Co}_4\text{O}_9$ samples ($\sim 0.28 \text{ mW/K}^2\text{m}$, at $800 \text{ }^\circ\text{C}$), being among the best found in the literature for similar materials. Our results suggest that low substitutions with rare-earth cations in the “charge reservoir” layers of the $\text{Ca}_3\text{Co}_4\text{O}_9$ compound can be promising in designing and improving these p-type oxides, provided by the strongly correlated nature of their conduction mechanism.

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