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Synthesis and Structural Characterization of Ca3Co4O9 based Thermoelectric Oxide

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Among all oxide the misfit layered oxide Ca3Co4O9 exhibits one of the highest figures of merit been one of the most promising thermoelectric material. In one of its layer the cobalt atoms are surrounded by other six oxygen atoms in an octahedral site, forming the compost CoO2. In another layer, Ca, Co and O form the compost Ca2CoO3+δ in a face centered cubic structure. Crystals with this kind of structures are considered natural super lattices. Interesting electronic properties of these materials result from charge transfer between the two subsystems, leading to a mixed valent cobalt state within the CoO2 layer. At high temperatures, the electronic properties of many oxide materials are influenced by reduction: thermal creation of effectively positively charged oxygen vacancies and the accompanying change in the concentration of electronic charge carriers.

In this work, nanostructured Ca3Co4O9 samples with different pHs (0 to 2) were prepared by the polymeric precursors method, also known as Pechini. The effects of the pH on the Ca3Co4O9 structure were analyzed. The samples were characterized by X-ray diffraction, thermal analysis, scanning electron microscope (SEM), RAMAN spectroscopy and Hall effect measurements. The parameters of the synthesis were determined by the thermal analyzis. The X-ray diffraction and the RAMAN results show that the Ca3Co4O9 has been successfully obtained. As the pH increase the SEM data reveals that the granularity of the samples reduces drastically, resulting in an opened structure. Thermal treatments in oxygen atmosphere over the prepared samples revels that the opened structure were more suitable to changes in the oxygen stoichiometry. These data were confirmed by appearance of oxygen vacancy related mode at the RAMAN spectra and changes in the carrier density changes determined by Hall measurements.

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