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Impact of $BiBO_3$, NaF and BiF_3 Doping on the Thermoelectric Properties of $Bi_2Ca_2Co_2O_y$ Ceramics

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Extended Abstract

Due to the increasing global energy demand and climate change issues, the importance of environmentally friendly renewable energy technologies is growing. Many studies in this field focus on thermoelectric materials that can directly convert waste heat into electric power. Doping via sol-gel chemistry, leading to exceptionally high chemical homogeneity, is a promising approach for enhancing the heat-to-electricity conversion efficiency of thermoelectric materials. In this work, for the first time, we studied the impact of (i) partial substitution of bismuth oxide (Bi_2O_3) by bismuth borate ($BiBO_3$), (ii) dual-substitution of Bi_2O_3 by $BiBO_3$ and sodium fluoride (NaF), and (iii) dual-substitution of Bi_2O_3 by $BiBO_3$ and bismuth (III) fluoride (BiF_3) on the thermoelectric characteristics of $Bi_2Ca_2Co_2O_y$ layered cobaltite. Samples with a nominal composition of $Bi_2Ca_2Co_2O_y$ (reference), $Bi_{1.9925}Ca_2Co_2(BiBO_3)_{0.0075}O_y$, $Bi_{1.8925}Ca_2Co_2(NaF)_{0.10}(BiBO_3)_{0.0075}O_y$, and $Bi_{1.8925}Ca_2Co_2(BiF_3)_{0.10}(BiBO_3)_{0.0075}O_y$, were prepared using the sol-gel method with citric acid and ethylene glycol as chelating agents. The phase composition of prepared materials was examined using X-ray diffraction analysis. Grain size distribution, surface morphology, and elemental compositions were studied by a scanning electron microscope (SEM) coupled with an energy-dispersive X-ray spectrometer (EDS). A homemade setup was used to determine the temperature dependence of the Seebeck coefficient and electrical resistivity in the temperature range of 293 K to 973 K. Thermal conductivity was measured from 293 K to 573 K. Finally, values of power factor ($PF = S^2/\rho$) and figure of merit ($ZT = S^2T/\rho k$) were calculated with S, ρ, T, and k representing Seebeck coefficient, electrical resistivity, absolute temperature, and thermal conductivity, respectively. The XRD analysis confirms that all the samples consist of a nearly pure $Bi_2Ca_2Co_2O_y$ phase. SEM/EDS analysis reveals that prepared materials consist of plate-like grains with a sizes of around 6 µm, which constitute the $Bi_2Ca_2Co_2O_y$ phase. Additionally, there are smaller grains with dimensions of 1÷2 µm, mainly containing a cobalt compound. When compared to the reference and $BiBO_3$-doped samples, dual NaF/$BiBO_3$ and BiF_3/$BiBO_3$ doping significantly reduces the concentration of smaller grains. Dual NaF/$BiBO_3$ doping leads to a sharp decrease in ρ due to the partial substitution of NaF for Bi_2O_3, which increases the concentration of charge carriers (holes). At the same time, partial substitution of BiF_3 for Bi_2O_3 led to a decrease in hole concentration and, hence, an increase in ρ. Seebeck coefficients were positive for all the samples, indicating p-type conductivity. The value of S for the NaF/$BiBO_3$ co-doped composition at 973 K is 4–6 % lower than that of the reference, $BiBO_3$-doped, and BiF_3/$BiBO_3$ co-doped samples. Although the NaF/$BiBO_3$ co-doped sample possesses a slightly lower Seebeck coefficient and higher thermal conductivity than the ones studied, the reduced resistivity has a greater impact on the thermoelectric performance, leading to an improved power factor and figure of merit. The maximum PF and ZT values achieved in the NaF/$BiBO_3$ co-doped composition are 18% and 13% higher, respectively, than the reference $Bi_2Ca_2Co_2O_y$.

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