THERMOELECTRIC PROPERTIES OF LAYERED CALCIUM COBALTITE DOPED BY PARTICLES OF COBALT, COPPER, AND THEIR OXIDES

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Layered nanostructured calcium cobaltite ($Ca_3Co_4O_{9+\delta}$) is prospective oxide thermoelectric for high-temperature applications, and its thermoelectric performance may be essentially improved, particularly, via doping by micro- and nanoparticles of semiconductors (B_4C, TiC), metal oxides (ZrO_2, $CaZrO_3$) or noble metals (Ag, Au) **[1, 2]**. In this work the results of attempt of enhancing of thermoelectric properties of $Ca_3Co_4O_{9+\delta}$ through doping by particles of transition metals (Co, Cu), and their oxides (Co_2O_3, Co_3O_4, Cu_2O, CuO) are presented.

Ceramic samples of layered calcium cobaltite with different dopants (see above) were prepared using ceramic method and sintered at different conditions at temperatures below and above of temperature of peritectoid decomposition of $Ca_3Co_4O_{9+\delta}$ (T_p = 926 °C in air) and their electrical conductivity (σ) and thermo-EMF (S) were measured within 25 – 825 °C. Effect of nature of dopants and their content in composites, as well as thermal prehistory of the samples on their phase composition, microstructure, porosity, electrotransport (σ and S) and thermoelectric properties (power factor (P), $P = S^2\sigma$) was analyzed.

All the prepared materials were p-type semiconductors like parent layered calcium cobaltite. It had been found that σ values of ceramics are enhanced at increasing of sintering temperature of the samples which is due to the decreasing of their porosity. Thermo-EMF coefficient values of obtained materials increases at creation in them phase inhomogeneity and this is more pronounced when role of dopant among oxides plays Co_2O_3, and copper oxides (Cu_2O and CuO). So, porosity of $Ca_3Co_4O_{9+\delta}$ ceramics sintered at $T > T_p$ decreases more than 2 times comparing to the ceramics sintered at common conditions ($T < T_p$) which results in appropriate increasing of its σ and P values: ≈ 300 and 140 μW/m·K^2 at 775 °C. Values of power factor of ceramics having $Ca_3Co_4O_{9+\delta}$ + 8 mas. % Co_2O_3 and $Ca_3Co_4O_{9+\delta}$ + 8 mas. % Cu_2O sintered at $T < T_p$ are equal ≈ 220 and 210 μW/m·K^2 respectively at 775 °C which is about 1.5 time larger than for parent $Ca_3Co_4O_{9+\delta}$ cobaltite.

Our results demonstrate that using unexpensive additives and varying thermal prehistory of ceramics based on the layered calcium cobaltite one can essentially improve its thermoelectric performance. That may be used for development of new high-temperature oxide thermoelectrics based on $Ca_3Co_4O_{9+\delta}$ which will be prospective for effective conversion of high-temperature heat into electrical energy.

References

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[2] F. Kahraman, M. A. Madre, Sh. Rasekh, *et al*. J. Eur. Ceram. Soc., 2015, 35, 3835-3841.