MceMge12-002

Microstructure influences on thermal conductivity of CaMn0.96V0.04O3 thermoelectric ceramics

Gelfuso, M.V.(1); Torres, S.O.A.(1); Rosa, J.P.M.M.(1); Thomazini, D.(1);
(1) UNIFEI;

Thermoelectric materials can convert thermal energy directly into electrical energy. Calcium manganite perovskites (CaMnO3-CMO) are considered one of the most promising thermoelectric ceramics due to their high Seebeck coefficient and electrical conductivity values as well as their low thermal conductivity (k). Also, doping with a pentavalent transition metal ion (V5+) is an alternative to enhance CMO thermoelectric properties, as a consequence of the decrease in thermal conductivity. This study aims to report the synthesis of CaMn0.96V0.04O3 (CMO-V) ceramics by the modified Pechini method, a chemical synthesis developed by the Functional Materials Development Group (GDMaF). The raw precursors CaCO3, MnO, and V2O5 were solubilized in citric acid [2.5 M], nitric acid [6.0 M], and citric and nitric acid 1:1 mixture of aqueous solutions, respectively. The final solution was dried at 343 K for 24 h, producing a non-crystalline powder. This powder was calcined for 3 h at 1073 K, a temperature defined by differential thermal analysis. The calcined powder was used to prepare the CMO-V ceramics. The samples were formed by uniaxially pressing at 175 MPa into discs, with 12 mm diameter and 2 mm thickness, which presented between 43 % and 53 % of theoretical densities. Afterward, dilatometric analysis was accomplished to determine the temperature that promotes the highest rate of sample shrinkage, representing the best sintering temperature. The samples were sintered at 1673 K in a tubular resistive furnace with sintering times of 1, 3, 6, 12, and 24 h with airflow by natural convection. The structural analysis of the calcined powders and sintered ceramics was performed by X-ray diffraction. It was noted a small CaMn2O4 amount in calcined powder and sintered ceramics, but CaMnO3 is the major phase, which suggests that the modified Pechini method was effective for obtaining CMO as the main phase. A scanning electron microscopy, assisted by energy dispersive spectroscopy was performed to obtain micrographs and semiquantitative analysis of chemical elements. In calcined powder, the average particle size was 475±15 nm. The sintered ceramics showed average grain sizes of 2.55±1.31 ?m, 5.69±3.86 ?m, 4.27±1.35 ?m, 5.44±0.38 ?m and 5.16±0.80 ?m for the ceramics sintered for 1, 3, 6, 12 and 24 h, respectively. The sintered samples exhibit relative apparent densities between 74 and 87 % of theoretical density. Thermal conductivity values, k, were measured by the pulsed laser technique from 323 K to 873 K. The k values decreased with increasing temperature due to the Umklapp process. Furthermore, CMO-V ceramics sintered for longer sintering times (12 and 24 h) present higher thermal conductivities (~ 4.4 W/mK) than that sintered for 1, 3 or 6 h(3.0 - 3.5W/mK). The porosity was a microstructural parameter with great influence on k values of CMO-V ceramics.