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Electrical conduction by polaron hopping mechanism in CaMnO3 perovskites

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Thermoelectric materials are a propitious solution for world society energetic generation crisis, since they can harvest wasted energy dissipated by thermal generators using the Seebeck effect. On this wise, calcium manganite (CaMnO3 or CMO) is a promising n-type semiconductor metallic oxide for thermoelectric applications, however, its electrical properties need more studies for its potential applications. Thus, in this study, an electrical characterization of CaMnO3 perovskites was performed. CaMnO3 powders were produced by the modified Pechini method. CaCO3 and MnO were the precursors, which were solubilized in citric acid [2.5 M] and nitric acid [6 M] solutions, respectively. The earlier solutions were mixed and so, the final solution was dried at 343 K for 24 h. The non-crystalline powder obtained was calcined at 1073 K for 3 h. From this calcined powder, samples were uniaxially pressed under 175 MPa. After, the samples were sintered in the resistive conventional furnace at 1543 K for 1, 12 and 24 h, at atmospheric air. According to X-ray diffractometry, it was confirmed that the CaMnO3 phase was predominant; however, a small amount of CaMn2O4 was obtained (~14 %). Scanning electron microscopy was used for microstructural evaluation. The average grain sizes were 1.04±0.69 ?m, 2.64±1.39 ?m and 4.85±0.35 ?m for the CMO perovskites sintered for 1, 12 and 24 h, respectively. For all ceramics, geometrical densities achieved values higher than 73 % of calculated theoretical densities. Although, increasing sintering time from 12 h to 24 h, density slightly decreases due to grain growth phenomenon. Seebeck coefficient (S) was measured, and the analysis of its values concluded that the conduction mechanism is due to the large polarons hopping. Electrical conductivity (?) was measured at 873 K, and its values reached 316 S/m and 1295 S/m for the ceramic sintered for 1 h and for 24 h, respectively. Also, ? values shown significantly increments at temperatures above 673 K, which indicates the conduction mechanisms transition from polaron variable range hopping (VRH) to polaron nearest neighbor hopping (NNH). The activation energy for conduction (EA), for hopping (EH) and charge carrier generation (ES) values were calculated for the NNH mechanism. The ceramics were analyzed by impedance spectroscopy (20 Hz to 5 MHz) to determine real and imaginary relative dielectric permittivity (?r), and loss factor (tan?). EA was greater than ES: this non-equivalence affirms that charge transport is mostly dominated by thermally activated carriers hopping. EH values for all ceramics are greater than kBT, so charge carrier tunneling was negligible. Activation energy for dipolar interactions (Em) was calculated and this value was higher than EH, which justified the electrically conductive behavior of CaMnO3 and high tan? values. Polaron radii (rP) were calculated and these values are greater than lattice parameters, which confirmed large polaron instead of small ones.