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Synthesis of $La_{1-x}Sr_xMnO_3$ powders via polymerizable complex process: effect of molar ratio of citric acid to metal oxides

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Abstract – It was studied the polymerizable complex route based on polyesterification between citric acid/ethylene glycol and metal ions with different molar ratios (CA:MO) to synthesize LSM perovskite nanopowders. XRD results showed that powders exhibited single LSM phase formation only for samples with CA:MO ratio of 3, with crystallite sizes of 12-21 nm. The microstructure of the powder samples revealed by SEM analysis consisted of agglomerates formed by fine particles of different shapes. It was also evaluated the porosity and electrical conductivity of the sintered pellets with different strontium contents.

Sr-doped $LaMnO_3$ (LSM) has been extensively studied for using as cathode material in Solid Oxide Fuel Cells (SOFCs), which are promising efficient, energy-saving, and environment-friendly energy conversion devices that generate electricity and heat [1]. In nanosized crystals, LSM presents good properties such as chemical and thermal stabilities, high catalytic activity for the oxygen reduction, thermal expansion coefficient reasonably similar to that of solid electrolyte (YSZ) and high electrical conductivity. In this work, powders of $La_{1-x}Sr_xMnO_3$ (x = 0.2, 0.3 and 0.4) with nanometric crystallite sizes were obtained from the resins synthesized by the Pechini-type polymerization process of citritc acid/metal oxide and ethylene glycol. The process occurs in three major steps: complexation of metal ions with citric acid, polyesterification with formation of a polymeric network where metallic ions are evenly distributed and finally decomposition of this polymer matrix [2]. Molar ratios of citric acid to metal oxides (CA:MO) were varied, and the resulting effects on the powder's properties were studied using X-ray diffraction (XRD), TGA/DTA, SEM and specific surface area (BET method).

XRD patterns (Figure 1) showed that CA:MO ratio of 3 is the most favorable ratio for the synthesis of LSM, in accordance with the literature [3], which points out that the resin contains a lower fraction of monodentate ligand and a higher portion of C-C-O structure obtained from ethylene glycol, making it possible to synthesize the LSM phase at low temperature and better microstructure formation. The powder exhibited a pure phase of LSM, with rhombohedral structure, a crystallite size of about 15 nm and a specific surface area of 10 m^2/g. SEM micrographs of the LSM powders (Figure 2) showed smaller grain size and larger porosity for CA:MO ratio of 3. Nanopowders were sintered at 1100^oC to produce porous pellets. The porosity, particle size and microstructure of LSM sintered bodies are strongly dependent on the ratio of CA:MO in the polymeric matrix formation. The sintered samples presented small particle sizes and porosity of about 40-50%. The electrical conductivity, measured by two probe technique, increased with increasing the strontium content.

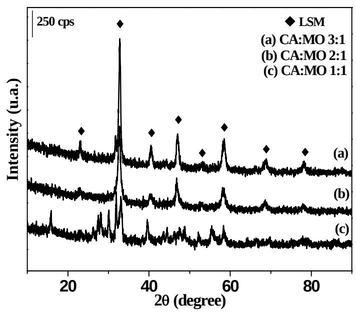

Figure 1: XRD of LSM powders synthesized with different ratios of CA: MO (a) 3:1 (b) 2:1 and (c) 1:1, calcined at 750 °C.

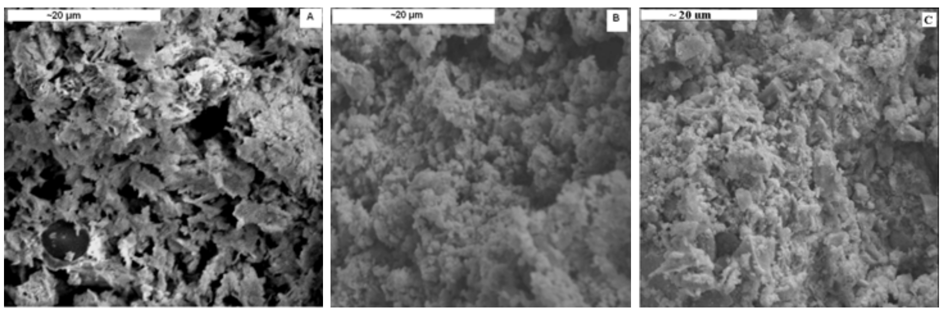

Figure 2: Micrographs of LSM samples with different ratios of CA: OM: (A) 1:1, (B) 2:1 and (C) 3:1, calcined at 900 ° C/10h in air flow.

References

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