Synthesis of Sr-doped $LaMnO_3$ and $LaCrO_3$ powders by combustion method: structural characterization and thermodynamic evaluation

(Síntese de pós de $LaMnO_3$ e $LaCrO_3$ dopados com Sr pelo método de combustão: caracterização estrutural e avaliação termodinâmica)

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Abstract

Lanthanum strontium manganite (LSM) and chromite (LSC) powders, as well as the corresponding non-doped samples, were synthesized by the combustion method, using two different fuels (urea and glycine). The ignition of the reagent mixture with urea takes a longer time and the maximum temperature is higher than using glycine, for doped samples. The theoretical calculations of exothermic heat and adiabatic flame temperatures indicate favorable conditions for combustion to occur. However, calcination is an essential step for a good crystallization of perovskite phase. X-ray diffraction patterns showed formation of only perovskite phase for the samples synthesized with urea. The crystallite sizes are in the range of 19-25 nm, with smaller values when urea was used as fuel. Scanning electron microscopy showed the presence of agglomerates, formed by fine particles of different shapes. Thermogravimetric analysis revealed that the weight loss is much higher for manganites, with complete burn out of organics at 850-900 ^oC.
Keywords: perovskites, combustion synthesis, X-ray diffraction, thermogravimetric analysis, microstructure.

Resumo

Manganita de lantânio dopada com estrôncio (LSM) e cromita (LSC) em pó, bem como as correspondentes amostras não dopadas, foram sintetizadas pelo método de combustão, usando dois diferentes combustíveis (ureia e glicina). A ignição da mistura reacional com ureia leva mais tempo e a temperatura máxima é maior do que usando glicina, para as amostras dopadas. Os cálculos teóricos de calor de reação e temperatura de chama adiabática indicam condições favoráveis à combustão. No entanto, a calcinação é uma etapa essencial para uma boa cristalização da fase perovskita. Os padrões de difração de raios X mostraram a formação apenas da fase perovskita para as amostras sintetizadas com uréia. Os tamanhos de cristalitos estão na faixa de 19-25 nm, com valores menores quando a ureia é usada como combustível. Análises de microscopia eletrônica de varredura mostraram a presença de aglomerados, formados por partículas finas de diferentes formas. A análise termogravimétrica revelou que a perda de peso é muito maior para as manganitas, com queima completa dos orgânicos em 850-900 ^oC.
***Palavras-chave**: perovskitas, síntese de combustão, difração de raios X, análise termogravimétrica.*

INTRODUCTION

Perovskites are mixed ceramic oxides with ABO_3 type crystal structure where cations with a large ionic radius have 12 coordination to oxygen atoms and occupy A-sites, and cations with smaller ionic radius have 6 coordination and occupy B-sites [1]. A and O form a cubic packing and B is contained in the octahedral voids in the packing. The perovskite structure may undergo atomic distortion leading to orthorhombic or rhombohedral unit cells [2]. Perovskites like lanthanum manganite and chromite are interesting materials for application in solid oxide fuel cells (SOFC) due to chemical and thermal stability, mechanical strength and high electrical conductivity [2, 3]. The electrical conductivity of these materials can be enhanced by substituting a lower valence ion, such as Sr, on the La site. Sr-doped $LaMnO_3$ (LSM) and $LaCrO_3$ (LSC) are currently the preferred ceramic materials for cathode and interconnect in the SOFC [3, 4].

Different synthesis methods have been developed for the production of perovskite powders, like solid-state reaction, sol-gel technique, hydrothermal synthesis, co-precipitation, and combustion [5-8]. Combustion synthesis is characterized by fast heating rates, high temperatures and short reaction times [9, 10]. It is a straightforward preparation process to produce homogeneous, very fine, crystalline and unagglomerated multicomponent oxide nanopowders, without intermediate decomposition steps [11]. In the solution combustion synthesis, an aqueous solution of the desired metal salts is heated together with a suitable organic fuel, until the mixture ignites and a fast combustion reaction takes off [9, 12]. Several fuels have been used in the combustion synthesis of perovskites, like glycine, urea, oxalyl-hydrazine, citric acid and sucrose [8,