SYNTHESIS AND CHARACTERIZATION OF ALKALINE EARTH METALS DOPED $La_2Mo_2O_9$ CERAMICS

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Oxide-ion conductors have attracted considerable interest due to their potential applications as components of solid oxide fuel cells (SOFCs), oxygen sensors, oxygen pumps and oxygen-permeable membrane catalysts [1]. SOFCs are characterized as devices with high energy-conversion efficiency and a positive environmental impact. However, electrolyte materials for SOFCs have to meet some requirements: exhibit high ion conductivity, which in turn implies very specific structural features only met by a restricted number of solid oxides [2]. Nowadays, most widely used materials for SOFC electrolyte are gadolinium-doped ceria (GDC) and yttria-stabilized zirconia (YSZ). However, these ceramic materials require high-operating temperatures (~1273 K) to obtain high oxide-ion conductivity. Such conditions have some disadvantages like as seal in high temperature, interface reaction between components of SOFC, the sintering of the electrodes and more [3]. Moreover, in recent years, the $La_2Mo_2O_9$-type compounds, known as the LAMOX family, which was originally reported by Lacorre et al., have also attracted great interest due to their high oxygen-ion conductivity at medium temperatures. $La_2Mo_2O_9$ undergoes a reversible transition from monoclinic α to cubic β structure at ~ 853 K, leading to an increase in the ionic conductivity up to two orders of magnitude and reaching values higher than those corresponding to YSZ (0.06 S/m at 1073 K). Besides, YSZ or GDC generate oxygen vacancies by doping other metal cations, while lanthanum molybdate possesses intrinsic oxygen vacancies, and the vacant intrinsic oxygen sites allow accommodation of oxygen excess in the structure thus resulting the high-ionic conductivity [3, 4]. Nevertheless, the phase transition between these structures clearly limits their potential application in SOFCs. The stabilization of cubic β phase at room temperature was a hard task of many scientists, nevertheless, it was found that the doping of different elements in the La, Mo and O sites stabilizes the high-temperature crystal phase indefinitely. It was observed that La site substitution with lower valence cations such as Ca^{2+}, Sr^{2+}, Ba^{2+} and another could stabilize cubic phase and increase oxygen-vacancy concentration [5, 6]. In such case, the obtained transport properties of $La_2Mo_2O_9$ strongly depend on preparation technique of final ceramic. Usually, unfavorable effect could be caused by impurities, porosity and low connectivity between the grains. To avoid such problems there is possible to use so called sol-gel synthesis, which provides both a good homogenization between starting materials and a high purity of the final ceramic.

This is the main reason why in this paper we report environmentally friendly and simple aqueous sol-gel synthesis of La–M–Mo–O tartrate gel precursors (M= Ca^{2+}, Sr^{2+} and Ba^{2+}) for $La_{2-x}M_xMo_2O_{9-\delta}$ ceramics. Herein is important to note that the use of tartaric acid in the sol-gel processing makes a possibility to reduce interactions between the individual components avoiding the formation of precipitates during the evaporation stage from the reaction mixture. Moreover, using this method there is possible to synthesize $La_2Mo_2O_9$ compound homogeneously substituted by Ca^{2+}, Sr^{2+} and Ba^{2+} ions, controlling their amount and the crystallinity of the final ceramics. In order to obtain dense and fully crystalline ternary oxide the as-prepared gels were heat-treated at 1273 K for 5 hours. Next to that, the obtained powders were additionally pelletized and sintered in air at 1473 K for 5 h. In order to investigate the crystallization and thermal decomposition mechanism of La–M–Mo–O tartrate gel precursors, the thermogravimetry and differential scanning calorimetry (TG–DSC) analysis was applied. Besides, in order to confirm the phasic transition between room-temperature α-$La_2Mo_2O_9$ and high-temperature β-$La_2Mo_2O_9$ phases, the investigation of as-prepared powders using DSC and XRD methods was performed. Additionally, all samples sintered at 1427 K temperature were investigated by scanning electron microscopy (SEM) in case to see whether there is a dense surface of sintered ceramics and how dopant amount can affect their surface morphology.

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