

Abstract

Proton conducting electrolyte materials studied in this thesis have unique protonic conductivity and dielectric properties useful for a solid oxide fuel cell (SOFC) and also ceramic capacitor industry. In this regard, the Barium Zirconate ($BaZrO_3$) already presents an ideal example of proton conducting electrolyte material in the temperature range 300 to 600 °C due to its high proton conductivity and excellent chemical stability. But, the microstructural parameters such as small grain size and highly resistive grain boundaries seriously limit its practical application as an electrolyte in proton conducting SOFCs. However, the effective proton conductivity can be tailored with the substitution of a trivalent cation at Zr^{4+} sites in a perovskite lattice, synthesis route and sintering procedure via controlling the effect of oxygen vacancies, grain sizes and grain boundaries. Therefore, a proper substitution of trivalent cation at Zr^{4+} sites in a perovskite lattice can offer additional oxygen vacancies in $BaZrO_3$, which play an important role for proton conduction in the humidified atmosphere particularly. In view of the above, a compound with a proper substituent such as Ho^{3+} at Zr^{4+} in $BaZrO_3$ is a simple choice to integrate proton conductivity and dielectric features. In this investigation, we prepared $BaZr_{(1-x)}Ho_xO_3$ by flash pyrolysis route (modified combustion route) to tailor the effective properties. The synthesized $BaZr_{(1-x)}Ho_xO_3$ ($x = 0, 0.05, 0.10, 0.15$ and 0.20) were characterized in terms of their electrical and dielectric properties. It was found that there is no structural change occurring in $BaZrO_3$ after Ho substitution. Furthermore, the fine and coarse grains appear in the microstructure of Ho substituted $BaZrO_3$ perovskite, which is obtained by conventionally sintering at 1600 °C for 4 h and 8 h. The relative density and grain size of Ho substituted $BaZrO_3$ samples obtained by conventionally sintering at 1600 °C for 8 h are decreased with increasing Ho content in $BaZrO_3$ perovskite. The Raman spectroscopic study of Ho substituted $BaZrO_3$ sintered at 1600 °C exhibit the BO_6 octahedra distortion of ABO_3 perovskite due to substitution of larger Ho^{3+} atoms at Zr^{4+} site. As a result, the more oxygen vacancies are generated. The comprehensive impedance and modulus spectroscopic studies provide the effect of grain and grain boundary contributions to the overall electrical response (conduction and relaxation processes) in all samples. It is found that the frequency and temperature dependent dielectric signatures of Ho substituted $BaZrO_3$ can be explained by Maxell-Wagner (M-W) model due to the insulating and conducting nature of grain boundary as well as grain, respectively. The proton conductivity of Ho substituted $BaZrO_3$ samples obtained by conventionally sintering at 1600 °C for 8 h in 3% humidified O_2 atmosphere is found to be increased with Ho content in $BaZrO_3$ due to additional oxygen vacancies in $BaZrO_3$ and can be explained by Grotthus mechanism. However, the relative density of spark plasma sintered $BaZr_{(1-x)}Ho_xO_3$ ($x = 0.10$ and 0.20) samples at 1600 °C for 20 min are found higher than the conventionally sintered sample. The conductivity of the spark plasma sintered $BaZr_{(1-x)}Ho_xO_3$ ($x = 0.20$) sample in 3% humidified O_2 atmosphere is obtained to be $8.5 \times 10^{-2} S \cdot cm^{-1}$ at 800 °C, which is higher than conventionally sintered samples. The $BaZr_{(1-x)}Ho_xO_3$ ($x = 0.20$) sample obtained by spark plasma sintering at 1600 °C for 20 min is found with enhanced conductivity can be used as a proton conducting electrolyte for proton conducting SOFCs.

Keywords: Proton conducting electrolyte, Flash pyrolysis route, Spark plasma sintering, Grain and grain boundary, Dielectric and impedance spectroscopy.