

## **The Effect of Cation Nonstoichiometry on the Electrical Conductivity of CaZrO<sub>3</sub>**

Solid state oxygen ion conductors with little electronic conductivity, high thermal stability, and good chemical inertness are required to measure oxygen potentials at high temperature and in various oxygen partial-pressure ( $P_{O_2}$ ). Calcium zirconate with a perovskite structure has the required high thermal and chemical stability, and the good thermal shock resistance. CaZrO<sub>3</sub> is a mixed p-type and oxygen ionic conductor in high  $P_{O_2}$  but a stable ionic conductor in low  $P_{O_2}$ . It exhibits protonic conduction under hydrogen-containing atmosphere at elevated temperature, if the zirconium in the oxides was partially replaced by aliovalent cations. Thus it has been used as a refractory material, a microwave dielectric, a solid electrolyte and a proton conductor. However, the phase homogeneity region for this compound has been reported to be very narrow. Thus, there are still controversies regarding to the electrical conductivity as a function of Ca/Zr ratio.

In this study, the electrical conductivities of Ca<sub>1-x</sub>ZrO<sub>3-δ</sub> systems were measured by using impedance spectroscopy as a function of Ca/Zr ratio ( $0 \leq x \leq 0.1$ ) and temperature (550°C~1100°C). Stoichiometric CaZrO<sub>3</sub> revealed poor sinterability due possibly to the free CaO observed at grain junctions. With decreasing Ca/Zr ratio, the free CaO disappeared and the sintered density increased. The total electrical conductivity rapidly decreased, ~100 times at 1100°C, when the Ca content decreased below 0.98. The impedance measurement revealed that the decrease is due mostly to the increase in the grain boundary resistivity. The activation energy of grain boundary resistivity also rapidly increased with decreasing Ca/Zr ratio. In other words, the grain boundary resistivity was very sensitive to Ca/Zr ratio. It is suggested that the single phase composition is near Ca<sub>0.98</sub>ZrO<sub>3</sub>.