



EFFECT OF LANTHANIDE DOPING ON ELECTRICAL PROPERTIES OF PYROCHLORE-TYPE $\text{Gd}_2\text{Zr}_2\text{O}_7$ FOR SOLID OXIDE FUEL CELL ELECTROLYTES

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ABSTRACT

Oxides $\text{A}_2\text{B}_2\text{O}_7$ with the pyrochlore crystal structure represent an interesting group of ceramic materials because of their high compositional diversity, structural flexibility and intrinsic concentration of oxygen vacancies. Considered as a superstructure of an anion deficient fluorite structure, oxygen conducting pyrochlores present lower activation energies for migration than the fully disordered fluorite materials of the same composition; e.g., the E_{dc} is significantly lower in the defect pyrochlore-type gadolinium zirconate ($\text{P-Gd}_2\text{Zr}_2\text{O}_7$) than in its fully disordered analogue, the fluorite-type $\text{F-Gd}_2\text{Zr}_2\text{O}_7$. The aim of the present contribution is to study the role played by the average A cation size on the electrical properties of $\text{P-Gd}_2\text{Zr}_2\text{O}_7$, a well known high-temperature solid oxide ion conductor. Several compositions with the general formulae $\text{Gd}_{2-y}\text{Ln}_y\text{Zr}_2\text{O}_7$ ($\text{Ln} = \text{Er}^{3+}, \text{Y}^{3+}, \text{Dy}^{3+}, \text{Sm}^{3+}, \text{Nd}^{3+}$ and La^{3+}) having Gd partially replaced by different lanthanides, were prepared by mechanically milling stoichiometric mixtures of the corresponding elemental oxides. Electrical properties were analyzed on sintered samples as a function of frequency and temperature by using impedance spectroscopy. We found that $\text{P-Gd}_2\text{Zr}_2\text{O}_7$ is highly tolerant to a large number of A-site lanthanide substitutions; thus, whereas Gd substitution by smaller lanthanides induces a pyrochlore to fluorite phase transition, using larger dopant cations yields partially disordered pyrochlores. Despite of higher structural disorder, ionic conductivity values measured for the fluorite-type materials are lower than those observed for pyrochlores whereas activation energies for oxygen migration in the series decrease monotonically as the average size of the A cation increases.

Keywords: Pyrochlores, Gadolinium Zirconate, Lanthanides, Ionic Conductivity, Anion Deficient Fluorites