Synthesis and Characterization of Mixed Conducting Praseodymia-Doped Yttria-Stabilized Zirconia

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Mixed conductors based on yttria-stabilized zirconia are potential electrode materials in YSZ-electrolyte fuel cells because they are chemically and mechanically compatible with YSZ. Mixed conductivity in YSZ has been obtained by introducing mixed-valence cations, such as Ce^{3+}/Ce^{4+} (1), Ti^{3+}/Ti^{4+} (2) and Tb^{3+}/Tb^{4+} (3). In this work, praseodymia has been doped into yttria stabilized zirconia to introduce p-type electronic conductivity. Praseodymia-doped yttria-stabilized zirconia (YZPr) is prepared using a co-precipitation method.

The structure and lattice parameter of praseodymia-doped yttria-stabilized zirconia (YZPr) have been studied using X-ray diffraction. The lattice parameter of YZPr with a fixed Y content increases with the Pr concentration (Fig.1). The lattice parameter of YZPr is larger than the lattice parameters of YZTb (3) because the Pr cation is larger than the Tb cation. The lattice parameter of YZPr with a fixed zirconium content increases with the Pr concentration (Fig.2), and the lattice parameter of YZPr with a fixed Pr content also increases with the Y concentration.
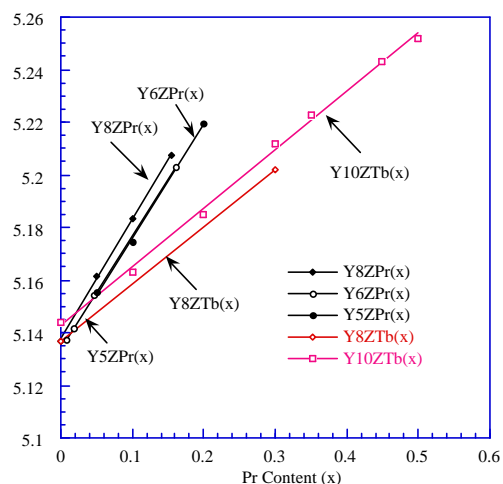

Fig.1. Lattice-parameter Variations of Y5ZPr(x) ($Zr_{0.90-x}Y_{0.10}Pr_xO_{2-\delta}$), Y6ZPr(x) ($Zr_{0.89-x}Y_{0.11}Pr_xO_{2-\delta}$) and Y8ZPr(x) ($Zr_{0.86-x}Y_{0.14}Pr_xO_{2-\delta}$) with Pr content. Lattice parameters of Y8ZTb(x) and Y10ZTb(x) (3) are for comparison.

Pr^{3+} (1.14 Å) has a larger ionic radius than Y^{3+} (1.02 Å), while the Pr^{4+} (0.96Å) has a smaller ionic radius than Y^{3+} (1.02 Å) (4). The increase of the lattice parameter of $Zr_{1-\alpha}Y_{\alpha-x}Pr_xO_{2-\delta}$ (α=0.15, 0.20, 0.30) with the Pr concentration (Fig.2) indicates that most of Pr cations are in the Pr^{3+} states in YZPr.

The pyrocholore structure appears in YZPr when the Pr concentration is increased. Compared to the terbia-doped zirconia that forms only short range ordering in $Tb_2Zr_2O_{7+\delta}$ (5), praseodymia doped zirconia begins to
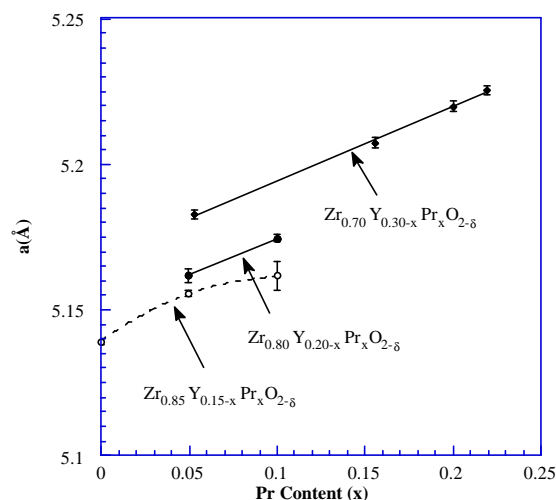

Fig.2. Variations of the lattice parameters of YZPr with 85 mole% of Zr ($Zr_{0.85}Y_{0.15-x}Pr_xO_{2-\delta}$), YZPr with 80 mole% of Zr ($Zr_{0.80}Y_{0.20-x}Pr_xO_{2-\delta}$) and YZPr with 70 mole% of Zr ($Zr_{0.70}Y_{0.30-x}Pr_xO_{2-\delta}$) with the Pr content

form a pyrochlore phase at 35 mole% of the Pr content. The ionic radii and the ratio of ionic radius over the Zr^{4+} radius ($r(M^{3+})/r(Zr^{4+})$) are plotted for some trivalent cations in Fig.3. The larger rare earth dopants (La, Pr, Nd, Sm and Gd with $r(M^{3+})/r(Zr^{4+})>1.25$ form the pyrochlore phase (6) because they prefer a higher oxygen coordination number (7) and leave to the oxygen vacancy for the Zr cation.
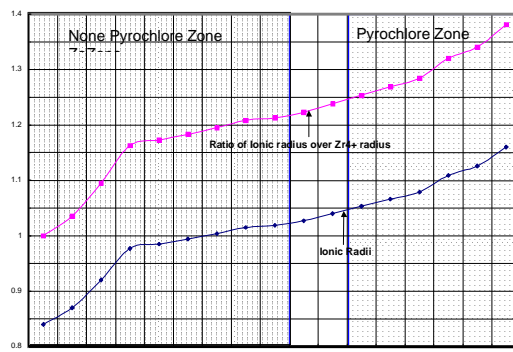

Fig.3. The ionic radii of trivalent cations (4) and the ratios of the ionic radius of trivalent cation over Zr^{4+} radius.

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