Understanding the Effect of Ce and Zr on Chemical Expansion in Yttrium doped Strontium Cerate and Zirconate by Density Functional Theory and High Temperature X-Ray Analysis

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<Purpose>

Proton conducting oxides which have perovskite structure (ABO_3) are expected to be applied to fuel cells or steam electrolysis because of superiority of proton conduction in the temperature range between 400 °C and 700 °C[1]. Proton conducting oxides have oxygen vacancies and they start to be filled with water due to hydration below approximately 600 °C in wet atmosphere. Hydration is the origin of the proton conduction to take place in the materials, however, this also leads to chemical expansion. Because chemical expansion causes damage to the components of the fuel cells and the steam electrolyzers, it is desirable that the chemical expansion is as small as possible. In this study, we investigated the influence of cerium and zirconium at *B*-site on chemical expansion by density functional theory (DFT). The calculation results were compared with the ones by high-temperature X-ray diffraction (HT-XRD) analysis.

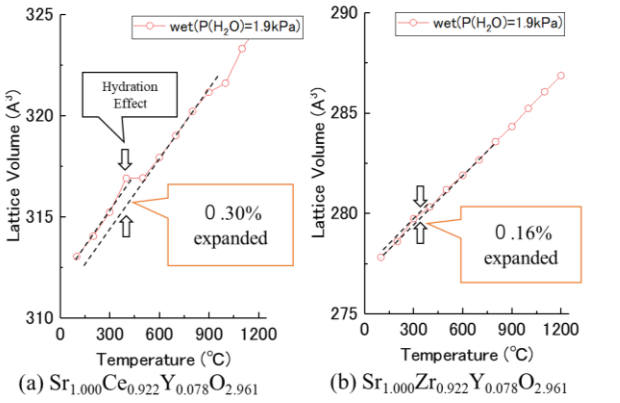
<Methodology>

$Sr_{32}Ce_{30}Y_2O_{95}$ (yttrium doped strontium cerate) supercell and $Sr_{32}Zr_{30}Y_2O_{95}$ (yttrium doped strontium zirconate) supercell were evaluated for chemical expansion coefficient before and after hydration. The Perdew-Burke-Ernzer-hof (PBE) exchange-correlation functional was employed based on the projector augmented wave (PAW) method. The cutoff energy for the plane wave basis set was 500 eV for all calculations.

For comparison with experimental results, powdered $Sr_{1.000}Ce_{0.922}Y_{0.078}O_{2.961(3-\delta)}$ and $Sr_{1.000}Zr_{0.922}Y_{0.078}O_{2.961(3-\delta)}$ which have the same composition ratio above supercells were prepared by solid state reaction method. HT-XRD analysis to evaluate chemical expansion coefficient were conducted for each powdered sample in a wet N_2. X-ray diffraction profiles every 100°C were obtained from 1200 °C to 100 ° C, and lattice volume at each 100°C was calculated.

<Results and Discussion>

Chemical expansion coefficient calculated by DFT was 0.24% and 0.21% for $Sr_{32}Ce_{30}Y_2O_{95}$ and $Sr_{32}Zr_{30}Y_2O_{95}$, respectively. On the other hand, as shown in Figure1, chemical expansion coefficient obtained by HT-XRD analysis was 0.30% and 0.16% for $Sr_{1.000}Ce_{0.922}Y_{0.078}O_{2.961(3-\delta)}$ and $Sr_{1.000}Zr_{0.922}Y_{0.078}O_{2.961(3-\delta)}$, respectively. The chemical expansion coefficient of yttrium doped strontium cerate tends to be larger than zirconate by DFT and HT-XRD analysis. The above different tendency can be explicable from the viewpoints of covalency in the bond between Zr/Ce at *B*-site and the nearest oxygen.



(a) $Sr_{1.000}Ce_{0.922}Y_{0.078}O_{2.961}$ (b) $Sr_{1.000}Zr_{0.922}Y_{0.078}O_{2.961}$

Figure1 The lattice volume of respective composition at each temperature in wet N_2 obtained by high temperature X-ray analysis

[1] Hudish,G., Manerbino,A., Coors,W.G. & Ricote, S.*J.Am.Ceram. Soc.* **101,** 1298–1309 (2018)

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