# STRUCTURAL ANALYSIS OF $Ce_{1-x}M_xO_{2-0.5x-\delta}$ (M=Gd, Sm, Y) BY HIGH TEMPERATURE XRD UNDER VARIOUS OXYGEN PARTIAL PRESSURES

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Various applications of doped-ceria ($Ce_{1-x}M_xO_{2-0.5x-\delta}$, M: trivalent cations) to solid oxide fuel cells (SOFCs) have been proposed. In such applications, expansion mismatch with other constituting materials, especially the reduction expansion, should be considered since the SOFC operating conditions include reducing atmospheres with very low oxygen partial pressure, $P(O_2)$.

In this work, crystal structure and lattice constants of $Ce_{1-x}M_xO_{2-0.5x-\delta}$ (M=Gd, Sm, Y; x=0, 0.1, 0.2) were investigated with high temperature XRD under various $P(O_2)$. By combining with oxygen nonstoichiometry data, dependence of lattice constants on $\delta$ was calculated and the expansion feature was discussed.

The pure $CeO_2$ powder from Rare Metallic Co. Japan, $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ (CGO10), $Ce_{0.8}Gd_{0.2}O_{1.9-\delta}$ (CGO20), $Ce_{0.9}Sm_{0.1}O_{1.95-\delta}$ (CSO10) and $Ce_{0.8}Sm_{0.2}O_{1.9-\delta}$ (CSO20) powders from Rhodia Co. Japan and $Ce_{0.9}Y_{0.1}O_{1.95-\delta}$ (CYO10) and $Ce_{0.8}Y_{0.2}O_{1.9-\delta}$ (CYO20) powders provided by Prof. Mizusaki, Tohoku University were examined. X-ray diffraction at room temperature (Rigaku Co., Ltd, RINT2500; CuKα, 50 kV, 250 mA) revealed that all the specimens were single phase with cubic fluorite structure.

High temperature X-ray diffraction measurements were performed using Rigaku RINT-2500 (CuKα, 50 kV, 250 mA) in temperature range of 25~1000℃. The atmosphere was controlled by flowing $O_2/N_2$ mixtures for high $P(O_2)$ range and $N_2/H_2/H_2O$ mixtures for low $P(O_2)$ one. $P(O_2)$ was monitored by a zirconia oxygen sensor set at downstream of the X-ray diffraction chamber. The lattice constant was determined from the Bragg angle of 422 peak which appeared in 2θ range of 85~89°. Because the Pt sample holder is easy to be deformed and the position of sample may differ in deferent settings, the calibration of diffraction angle is necessary and is completed by comparing the Bragg angle obtained at 30℃ to that obtained with room-temperature-attachment that has a glass plate sample holder to give good reproducibility of sample position.

Temperature dependence of lattice constants under various atmospheres was studied. Fig. 1 shows the representative result for CSO10. In $N_2$ or $O_2$, almost linear increase of lattice constant was observed. The average thermal expansion coefficient (TEC) from room temperature to 1000℃ is $12.3 \times 10^{-6}$ $K^{-1}$ for CSO10. Since TEC of both CGO10 and CYO10 are $12.2 \times 10^{-6}$ $K^{-1}$, the effect of different dopants is not obvious. Tendency of TEC increase with doping content was observed; TEC increases from $11.8 \times 10^{-6}$ $K^{-1}$ of $CeO_2$ to $12.4 \times 10^{-6}$ $K^{-1}$ of CSO20. This indicates that the chemical bond in the lattice is weakened by the introduction of oxygen vacancies. Although the expansion behavior below 600℃ in reducing atmospheres with various $H_2/H_2O$ is similar to the expansion in $N_2$, abrupt increase of lattice constant was observed at higher temperatures. A larger $H_2/H_2O$ ratio results in a larger reduction expansion.

At 700℃, the reduction expansion of CSO10 is smaller than that of CSO20. At 800℃, expansion of CSO10 and CSO20 almost coincides with each other. At 900 and 1000℃, however, CSO10 shows a larger expansion. This shows that CSO10 has a lager dependence on temperature, i.e., the energy necessary for removing oxygen from the lattice of CSO10 is larger than that of CSO20. Similarly, the temperature dependence of $CeO_{2-\delta}$ was found larger than that of CSO10. Therefore it is concluded that Sm doping weakened the bond energy of oxygen in the lattice.

In order to analyze dependence of lattice constants on $\delta$, the TG data from literatures were used. (1-5) Fig. 2 shows the dependence of lattice constant on total oxygen vacancy concentration, which includes the effects of both casino doping and reduction. For the same vacancy concentration it is obvious that pure ceria expands more than doped ceria, owing to the larger radius of $Ce^{3+}$ ion (1.14 Å) than the dopant ions ($Sm^{3+}$ (1.09 Å), $Gd^{3+}$ (1.06 Å), $Y^{3+}$ (1.015 Å)). Pure $CeO_2$, and the 10mol% doped samples show a two-step expansion feature and CGO10 showed the closest feature as pure ceria. The bending point of expansion behavior seems to be located on the oxide vacancy content value of 0.1. For 20mol% doped samples, linear reduction expansion was observed, because the oxide ion vacancies created by doping has reached to bending point without reduction.
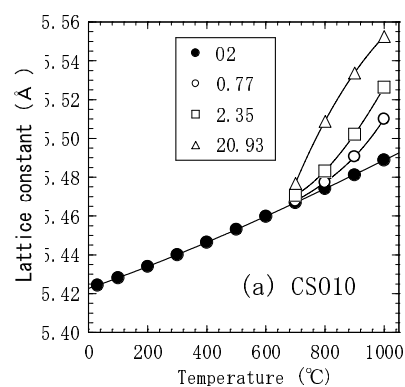


Fig. 1 Lattice constant of CSO10 as a function of temperature. The numbers in the legend show the $H_2/H_2O$ ratios in the reducing atmospheres
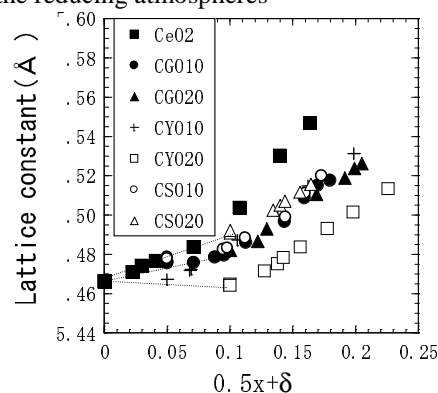


Fig.2. Lattice constant as a function of total concentration of oxide ion vacancies.

[1] S.Wang, H. Inaba, H. Tagawa, and T. Hashimoto, *J. Electrochem. Soc.* **144**, 4076 (1997).
[2] S. Wang, H. Inaba, H. Tagawa, M. Dokiya, and T. Hashimoto, *Solid State Ionics*, **107**,73 (1998).
[3 T. Kobayashi, S. Wang, M. Dokiya, H. Tagawa, and T. Hashimoto, *Solid State Ionics*, **126**,349 (1999).
[4] R. J. Panlener, R. N. Blumenthal and J. E. Garnier, *J. Phys. Chem. Solids*, **36**, 1213 (1975).
[5] D. J. M. Bevan and J. Kordis, *J. Inorg. Nucl. Chem.*, **26**, 1509 (1964).
[6] S. Wang, M. Katsuki, T. Hashimoto, and M. Dokiya, *J. Electrochem. Soc.,* submitted.