Atomic displacement parameters and structural disorder of oxygen ions in the \( \text{Ce}_x\text{Zr}_{1-x}\text{O}_2 \) solid solutions \((0.12 \leq x \leq 1.0)\): Possible factors of high catalytic activity of ceria-zirconia catalysts

Masatomo YASHIMA\(^1\,*\) and Takahiro WAKITA\(^1,2\)

\(^1\) Department of Materials Science and Engineering, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa, 226-8502, Japan;
\(^2\) Daichii Kigenso Kagaku Kogyo Co. Ltd., Hirabayashi-Minami 1-6-38, Suminoe-ku, Osaka, 559-0025, Japan

\* yashima+@+materia.titech.ac.jp

**Introduction**

Ceria-zirconia \((\text{Ce}_x\text{Zr}_{1-x}\text{O}_2)\) catalysts are widely used in the cleaning of exhaust gases from automobiles. The development of improved catalysts requires a better understanding of crystal structure and oxygen-ion diffusion in ceria-zirconia materials. Here we report a high-angular-resolution synchrotron x-ray powder diffraction study of \( \text{Ce}_x\text{Zr}_{1-x}\text{O}_2 \) \((x=0.12, 0.4, 0.5, 0.6, 0.7, 0.8 \text{ and } 1.0)\) to clarify the structural origin of greater catalytic activity of this material.

(M. Yashima and T. Wakita, “Atomic displacement parameters and structural disorder of oxygen ions in the \( \text{Ce}_x\text{Zr}_{1-x}\text{O}_2 \) solid solutions \((0.12 \leq x \leq 1.0)\): Possible factors of high catalytic activity of ceria-zirconia catalysts”, *Appl. Phys. Lett.*, 94, [14] 171902 (3 pages) (2009).)

**Experiments**

High-angular-resolution synchrotron x-ray powder diffraction analyses \((\delta d/d = 0.0022\%\text{, where } d \text{ and } \delta d \text{ are the lattice spacing and peak width, respectively})\) were performed using the multiple-detector system installed at the BL-4B2 beam line of the Photon Factory operated by the High Energy Accelerator Research Organization (KEK), Japan. A monochromatized 1.20645(5) Å x-ray beam was utilized. The crystal structure was refined by the Rietveld method with a computer program RIETAN-2000. Electron-density distribution was studied by a maximum-entropy method (MEM).

**Results and discussion**

As shown in Fig. 1, the isotropic atomic displacement parameter of the oxygen atoms \( U(O) \) in tetragonal \( \text{Ce}_x\text{Zr}_{1-x}\text{O}_2 \) and cubic \( \text{CeO}_2 \) was larger than that of \( \text{Ce} \) and \( \text{Zr} \) atoms \( U(\text{Ce}, \text{Zr}) \) in the whole compositional range of \( 0.12 \leq x \leq 1.0 \). The \( \text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2 \) composition has the highest \( U(O) \) value in the \( \text{Ce}_x\text{Zr}_{1-x}\text{O}_2 \) solid solutions \((x=0.12, 0.4, 0.6, 0.7, 0.8 \text{ and } 1.0)\), suggesting higher bulk diffusivity of the oxygen ions in \( \text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2 \) compared with those at other compositions. Figures 2(a), 2(b) and 2(c) show the electron density contour maps on the (100) and (110) planes of tetragonal \( \text{Ce}_x\text{Zr}_{1-x}\text{O}_2 \) \((x=0.12 \text{ and } 0.5)\) and cubic \( \text{CeO}_2 \), respectively. The results reveal that the oxygen ions in \( \text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2 \) are spread over a wide area compared with \( \text{Ce}_x\text{Zr}_{1-x}\text{O}_2 \), which suggest higher bulk diffusivity of the oxygen ions in \( \text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2 \). The greater \( U(O) \) and large spatial distribution of oxygen ions in \( \text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2 \) are possible factors of its higher catalytic activity.

---


**Materials Science**