

## Crystal structure and the structural disorder of ceria

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Ceria (cerium dioxide, CeO<sub>2</sub>)-based compounds are attractive materials for potential use as electrolytes in solid oxide fuel cells (SOFCs) and gas sensors, because the materials have a higher oxide ion (O<sup>2-</sup>) conductivity than that of stabilized zirconia and a lower cost comparing with lanthanum gallate-based phases. Other promising applications of ceria-based materials include the SOFCs anode materials, solid-electrolyte oxygen pumps, and mixed-conducting membranes for oxygen separation and partial oxidation of hydrocarbons. The ceria-based materials are widely used as automotive catalysts. The development of the ceria-based materials requires a better understanding of the conduction mechanism, and crucial to this is the knowledge of the structural disorder of mobile ions at high temperatures where the materials work efficiently. The crystal structure of the CeO<sub>2</sub> at high temperatures has been investigated by some researchers. In the present work [1-3], we have reanalyzed the structure with a split-atom model leading to a better fit, because the oxide ions have an anisotropic thermal motion as described below.

Neutron powder diffraction experiments were carried out in air in the temperature range from 400 to 1497°C. Neutron powder diffraction measurements were conducted in air with a 150-detector system, HERMES, installed at the JRR-3M reactor in Japan Atomic Energy Research Institute, Tokai, Japan. Neutrons with wavelength 1.8207 Å were obtained by the (311) reflection of a Ge monochromator. The experimental data were analyzed by a combination technique of Rietveld analysis, the maximum-entropy method (MEM), and the MEM-based pattern fitting.

Rietveld analysis was carried out assum-

ing two structural models with the Fm-3m symmetry. One was the ideal fluorite-type structured model where the Ce and O atoms were put at 4a 0,0,0 and at 8c 1/4,1/4,1/4, respectively. The other was a split-atom model where the O atoms were distributed at the 8c 1/4,1/4,1/4 and at the 32f  $x,x,x$  positions ( $x=1/4+\delta$ ). The isotropic atomic displacement parameters were used for all the atoms. The Rietveld analysis with the split-atom model yielded a better fit than that with the ideal fluorite model. The unit-cell parameter increased with an increase of temperature. The positional parameter  $x$  of oxide ion at the 32f site  $x(O_2)$  varied little with temperature. With increasing of temperature the occupancy of oxide ion at the 32f site  $g(O_2)$  did not change much between 400 and 703°C, while the  $g(O_2)$  increased above 703°C. The increase of  $g(O_2)$  indicates an increase of the disorder of oxide ions at the 8c and 32f sites. Both the isotropic atomic displacement parameters for the Ce atom  $B(Ce)$  and for the O atom  $B(O)$  also increased with temperature. At higher temperatures the  $B(O)$  was larger than the  $B(Ce)$ , suggesting a larger diffusion coefficient of oxide ions.

MEM analysis was carried out using the structure factors obtained in the Rietveld analysis with the split-atom model. Number of structure factors derived in the analysis was 11. The present results reveal that the oxide ions in the CeO<sub>2</sub> have a complicated disorder and spread over a wide area, comparing with Ce ions. The spatial distribution of oxide ions is larger at higher temperatures (Figs. 4 and 5), corresponding to the larger displacement parameters and larger occupancy  $g(O_2)$ . Bulges in the 1/4- $\delta$ , 1/4- $\delta$ , 1/4+ $\delta$  directions ( $\delta > 0$ ) are clearly seen in Figs. 4 and 5, indicating anisotropic thermal motions

around an ideal  $8c$  position. The direction of bulges of oxide ions is opposite side of the Ce ion and the oxide ions shift to the position of the cavity at  $1/2, 1/2, 1/2$  position. The bulges are attributable to the repulsion between the Ce and oxide ions. Other small bulges in the  $1/4$ - $\delta$ ,  $1/4$ - $\delta$ ,  $1/4$ + $\delta$  directions ( $\delta > 0$ ) can be seen at the lower density level, which might be due to the experimental error. The bulges in the  $1/4$ - $\delta$ ,  $1/4$ - $\delta$ ,  $1/4$ + $\delta$  directions indicate a possible diffusion mechanism where the oxide ions move through a face of the surrounding Ce tetrahedron to the octahedral cavity and then re-entering a neighboring anion site).

#### References

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