Crystallography

4B2/2005G157,2005G158,2004G256,2004G058

Electron density distribution in $Ce_{0.8}Zr_{0.2}O_2$ solid solution through synchrotron powder diffraction data

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Introduction

Three-way catalyst has been known to oxidize CO and HC, and to reduce NOx at the same time. CeO_2-ZrO_2 solid solutions are used as the subcatalysts for purification of automotive exhaust gases. The development of CeO_2-ZrO_2 catalysts requires a better understanding of the diffusion mechanism of oxide ions.The crystal structure of the CeO_2-ZrO_2 solid solutions has been investigated by Yashima et al. [1-5].They reported the existence of three metastable tetragonal forms of t, t' and t''. The three tetragonal forms belong to the $P4_2/nmc$ space group. However, the crystal structure and electron density distribution of the $Ce_{0.8}Zr_{0.2}O_2$ at high temperatures have not yet been investigated *in situ*. The purpose of this study is to investigate the crystal structure and electron-density distribution in the $Ce_{0.8}Zr_{0.2}O_2$ at 1823 K using the synchrotron powder diffraction data

Experiment

Synchrotron powder diffraction experiment was conducted using the multiple-detector system installed at the beamline BL-4B$_2$ of the Photon Factory, KEK, Japan. A furnace with $MoSi_2$ heaters [6] was placed on the sample table, and used for synchrotron powder diffraction measurements 1823 K. Monochromatized 1.200063(2) Å X-ray was used for the diffraction experiment. The diffraction data were analyzed by Rietveld method, with a computer program RIETAN-2000. The electron-density distribution was studied by a maximum-entropy method (MEM) using the structure factors obtained in the Rietveld analysis. The calculation was performed by a computer program PRIMA with 64×64×64 pixels.

Results and discussion

Structure refinements of the $Ce_{0.8}Zr_{0.2}O_2$ were successfully performed assuming the space group $Fm\bar{3}m$ (Fig.1). Unit-cell parameters were refined to be a=5.4506(3) Å. The weighted reliability factor R_{wp} was 16.34 %. The MEM density map indicates anisotropic thermal motions around the ideal 8c position. The direction of bluges of oxide ions is opposite side of the Ce and Zr cations and the oxide ions shift to the position of the cavity, 1/2.1/2,1/2 (Fig. 2).

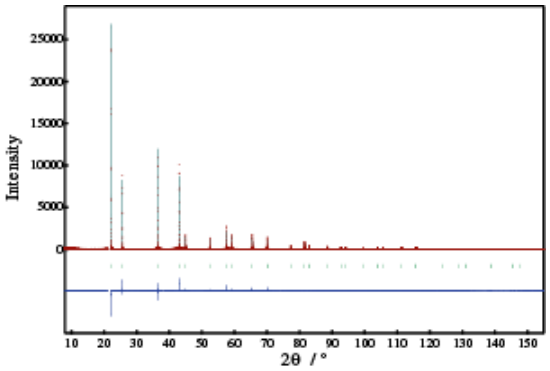

Figure 1. Rietveld fitting pattern for synchrotron powder diffraction data of the $Ce_{0.8}Zr_{0.2}O_2$ solid solution measured at 1823 K.

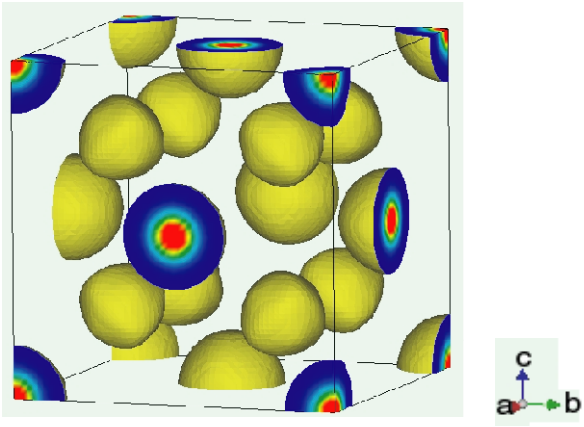

Figure 2. Equicontour electron density surfaces at 1.0 e/Å^3 of the $Ce_{0.8}Zr_{0.2}O_2$ solid solution measured at 1823 K.

References

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