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The local structure of $(Ce_{1-x}Zr_x)O_2$ solid solutions

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We have investigated the local structure of $(Ce_{1-x}Zr_x)O_2$ $(0 \leq x \leq 0.3)$ solid solutions. The local structure around the Ce atom is different from that of the central Zr atom and also from the average structure obtained from XRD measurements.

1 Introduction

CeO_2 has a cubic structure while ZrO_2 shows polymorphs such as monoclinic, tetragonal and cubic structure. The XRD measurements shows that the solid solution $(Ce_{1-x}Zr_x)O_2$ with x less than 0.4 maintains the cubic structure where the lattice constant decreases lineally from 5.4113 Å at x=0 to 5.3110 Å at x=0.4. [1] We attempt to investigate $(Ce_{1-x}Zr_x)O_2$ from the viewpoint of local structure.

2 Experiment

The solid solutions $(Ce_{1-x}Zr_x)O_2$ $(0 \leq x \leq 0.3)$ were prepared from CeO_2 and ZrO_2 powders with the purity of 4N by solid state reaction. A mixture of them were ground in an alumina mortar and then mechanically milled in a stainless steel vial of a vibratory ball mill with stainless steel balls for 5 hours. The powders were calcined at 1400 °C for 20 hours in air. They were pulverized in the mortar and again fired at 1400 °C for 20 hours in air. We carried out X-ray powder diffraction (XRD) and XAFS measurements at room temperature to investigate the crystallographic and local structure.

3 Results and Discussion

X-ray powder diffraction shows that $(Ce_{1-x}Zr_x)O_2$ $(0 \leq x \leq 0.3)$ has the cubic fluorite structure (space group *Fm-3m*). We have obtained the linear decrease of the lattice constant with increasing x by the Rietveld analysis of XRD patterns. This agrees with the previous report. [1]

XANES spectra for Ce L_3 and Zr K edges indicate that both of Ce and Zr ions in $(Ce_{1-x}Zr_x)O_2$ $(0 \leq x \leq 0.3)$ keep tetravalent independent of Zr content.

Figure 1 represents the radial structure function around the Zr atom. The first peak around 1.5 Å comes from the nearest neighbor O atoms. The second peak at 3.5 Å for x=0.1, which we attribute to both of Zr and Ce neighbors, splits by further x to the two sub-peaks: Zr-Zr and Zr-Ce pairs contribute to the sub-peaks at 3.3 and 3.5 Å respectively. This is consistent with the XRD result that shows a linear decrease of the lattice constant with increasing x.

The radial structure function of $(Ce_{1-x}Zr_x)O_2$ at the Ce K edge is shown in Fig. 2. The peak near 1.7 Å is attributed to the first O neighbor, which hardly moves at all despite an increase in the Zr content. The second peak around 3.5Å, which consists of Ce-Zr and Ce-Ce pairs, hardly shifts and splits in contrast to the Zr surroundings. The behavior around the Ce atom is also much different from change in the average structure from XRD with the Zr content. These results may suggest that the local structure around Ce ions differs from that of Zr atoms and from the average structure derived from XRD.

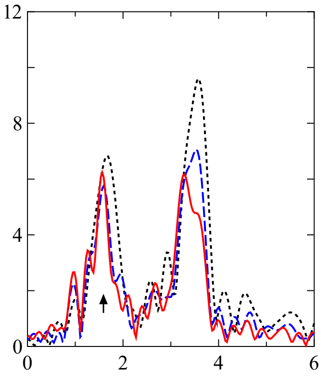

Fig. 1: Radial structure function of $(Ce_{1-x}Zr_x)O_2$ for the Zr K edge at 300 K.

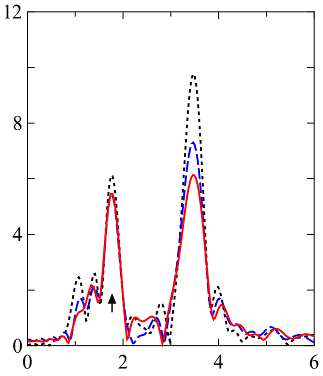

Fig. 2: Radial structure function of $(Ce_{1-x}Zr_x)O_2$ for the Ce K edge at 300 K.

References

[1] A. Varez *et al.*, *J. Euro. Ceram. Soc.* **27**, 3677 (2007).

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