

Local structures of 10 mol% Y₂O₃ doped ceria ceramics by XAFS spectroscopy

Yarong WANG¹, Hiroyuki KAGEYAMA*², and Toshiyuki MORI¹

¹ Ecomaterials Center, National Institute for Materials Science,
Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

² National Institute of Advanced Industrial Science and Technology (AIST),
Midorigaoka 1-8-31, Ikeda, Osaka 563-8577, Japan

Introduction

Rare-earth doped ceria with a fluorite structure, has been considered more promising electrolyte materials than ZrO₂-based materials such as Y₂O₃ doped ZrO₂ (YSZ), especially for application in solid oxide fuel cells (SOFCs) operating at intermediate temperatures [1]. It is said that the ionic conductivity of rare-earth doped ceria largely depends on the dopant cations and their concentration [2]. Besides, microstructure of the sintered body, such as average grain size, is also known to have significant effects on the ionic conductivity. These phenomena are considered to relate to the local structural changes.

In this work, the local structures around Ce and Y atoms in 10 mol% Y₂O₃ doped ceria ceramics were studied by XAFS spectroscopy using samples with average grain sizes of about 150 nm and about 700 nm.

Experimental

Powder samples of 10 mol% Y₂O₃ doped ceria (YDC) were prepared by sintering at temperatures of 1273 K for 6 hours (average grain sizes of about 150 nm, YDC(150)) and 1723 K for 4 hours (average grain sizes of about 700 nm, YDC(700)), respectively [3].

The local structures around Ce and Y atoms in the samples were examined by Y-K and Ce-K XAFS analysis at room temperature and at 773 K, respectively. The measurement of Ce K-XAFS was done at the Beamline BL01B1 of the SPring-8 (Proposal No. 2003A0045-NX-np). The k³-weighted EXAFS function in the k-region from 2 to 14 Å⁻¹ for room temperature and that from 2 to 12 Å⁻¹ for 773 K were used for the calculation of radial structure functions (RSFs), respectively. The curve fitting analysis was performed for the RSF typically from 1.0 to 3.3 Å (in R-space) using the theoretical phase shifts and amplitude functions derived from FEFF code.

Results and Discussion

The comparison of the RSFs and the results of curve fitting for Ce K-edge indicated that the local structure around Ce cation in the YDC is similar to that of Ce cation in the fluorite CeO₂ structure though the coordination number of Ce-O tends to be smaller than 8. On the other hand, the comparison of the RSFs and the results of curve fitting for Y K-edge suggested that the local structure around Y cation in the YDC is significantly different and bears more resemblance to that of the Y

cation in the C-type Y₂O₃ structure. A more accurate description of the local structures around Y cation can be given by analyzing the Y-K edge EXAFS spectra based on the C-type Y₂O₃ structure with three Y-O and two Y-cation shells as shown in Table1. The smaller σ value and goodness-of-fit factor R_f successfully supported our assumption above.

Table1. Fitting Results of Y-K edge EXAFS for pure C-type Y₂O₃ and 10mol% Y₂O₃ doped ceria (YDC(150)) based on C-type Y₂O₃ structure model [4].

Sample	Bond	Coordination number CN*	Bond length R (Å)	Mean square relative displacement σ (Å)	
Y ₂ O ₃ At RT	Y-O (1)	2.0	2.22	0.04	
	Y-O (2)	2.0	2.28	0.04	
	Y-O (3)	2.0	2.36	0.04	
	Y-Y (1)	6.0	3.51	0.07	
	Y-Y (2)	6.0	4.02	0.07	
YDC (150) At RT	Y-O (1)	2.0 (2.0)	2.24	0.04	
	Y-O (2)	2.0 (2.0)	2.32	0.04	
	Y-O (3)	2.0 (2.0)	2.41	0.04	
	Y-Y	2.4 (9.0)	3.98	0.10	
	Y-Ce	9.6 (3.0)	3.76	0.10	
	At HT	Y-O (1)	2.0 (1.7)	2.24	0.09
		Y-O (2)	2.0 (2.0)	2.34	0.09
		Y-O (3)	2.0 (1.5)	2.37	0.09
		Y-Y	2.4 (7.2)	4.09	0.10
		Y-Ce	9.6 (4.7)	4.12	0.10

*The data outside the () were the initial values while those inside were calculated from the last several cycles of fitting.

References

- [1] B. C. H. Steel et al., Nature 414, 345-352 (2001).
- [2] T. Kudo et al., J. Electrochem. Soc. 122, 142-147 (1975).
- [3] Y. Wang, et al., J. Mater. Res., 18, 1239-1246 (2003).
- [4] Y. Wang, et al., J. Solid State Ionics, in press.

*h-kageyama@aist.go.jp