

Local Crystal Structure of Super Ionic Conductors by EXAFS

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Introduction

Zirconia-based super ionic conductors have been utilized as an electrolyte material in Solid Oxide Fuel Cells, which has a great possibility to support energy for the future because of high efficiency and the environmental sensitivity. High ionic conductivity of solid electrolyte occurs in the range from 600 to 1000°C, which is operating temperature of SOFCs. It is necessary to obtain a fundamental understanding of the factors to control the fast oxide ion transport in the oxide ion conducting materials. In this study, the local structure around Zr, Sc, Y in 11mol%Sc₂O₃-doped (11ScSZ) and 8mol%Y₂O₃-doped ZrO₂(8YSZ) were analyzed by XAFS spectroscopy at high temperature.

Experimental

The samples were prepared by the co-precipitation method. The starting materials were Sc₂O₃, Y₂O₃ and ZrOCl₂·8H₂O. The dry precipitates were calcined at 800°C for 1h to convert the metal hydroxides to oxides. The powders were pressed isostatically into a disk under a pressure of 170 MPa followed by sintering at 1700°C for 12h. X-ray absorption spectra were obtained in the BL01B1 station. The XAS near Zr(K), Sc(K) and Y(K)-edge were measured by the conventional transmission method. High temperature XAS measurements were performed in a range from 25 to 1000°C using the high temperature sample holder and muffle furnace in N₂ gas flow. This furnace has the ability to heat the temperature up to 1700°C.

Results

Scandia doped zirconia(11ScSZ) shows the highest conductivity in the zirconia-based electrolytes, which is nearly twice as high as other electrolytes. Figure 1 shows the Fourier transforms of Zr(K)-edge EXAFS of high temperature measurement for 8YSZ and 11ScSZ. The change in Zr-cation coordination number for 11ScSZ showed a remarkable decrease with increasing temperature, compared with the case of 8YSZ. It suggests that the size mismatch between host and dopant cations determines the distortion of Zr network. The details are now under investigation.

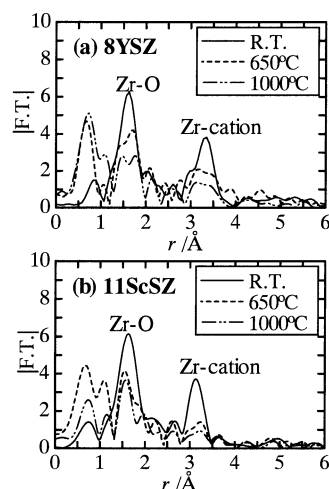


Fig.1. Fourier transforms of Zr-Kedge EXAFS for (a)8YSZ and (b)11ScSZ at various temperatures.

XAFS Studies on the Titanium Oxide Thin Film Photocatalysts Including Metal Ions Prepared by Magnetron Sputtering Method Which Is Capable of Operating under Visible Light Irradiation

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Metal ion-implantation technique has been successively applied to modify the electronic structure of the titanium oxide-based photocatalysts in order to the design and develop the new photocatalytic reaction systems which enable to efficiently absorb the visible light and operate effectively under solar beam or visible light irradiation. In the present study, Ag ion-implanted TiO₂ thin film photocatalysts prepared by magnetron sputtering method were characterized by the Ag K-edge XAFS measurements. The XAFS spectra were measured at the BL01B1 facility in the transmission mode at room temperature using Si(311) monochromator.

The UV-Vis absorption band of TiO₂ thin film photocatalysts prepared by magnetron sputtering method were shifted toward the longer wavelength region by ion-implantation of Ag ion. Visible light irradiation of these Ag ion implanted TiO₂ thin film photocatalyst in the presence of NO was found to initiate the decomposition of NO into N₂, O₂ as well as N₂O linearly against the irradiation time, suggesting that the decomposition reaction take place photocatalytically by visible light irradiation. These results show that Ag ions implanted do not work as the electron-hole recombination center.

We have also investigated the local structure of Ag ions implanted into the deep

bulk of the TiO₂ thin films by measuring the Ag K-edge XAFS spectra. The edge position of the Ag K-edge XANES spectrum of Ag ion-implanted TiO₂ thin film photocatalyst is quite similar to that of Ag₂O powder, indicating that the Ag species exist as Ag⁺. Fourier transform of the EXAFS spectrum of the Ag ion-implanted TiO₂ thin film photocatalyst shows intense peak attributed to the Ag-O bond as well as the peak attributed to the Ag-O-Ti bond with weak intensity. These results show that the Ag⁺ ions which exist in a highly dispersed state in the bulk TiO₂ play a significant role in the modification of the electronic properties of the TiO₂ thin film photocatalyst.

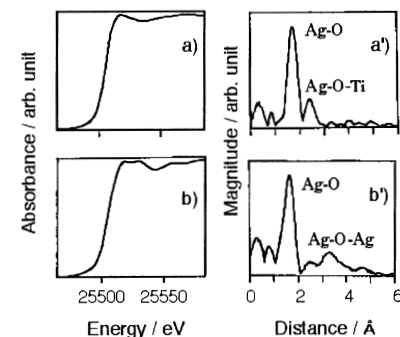


Fig. Ag K-edge XANES and FT-EXAFS of the Ag ion-implanted TiO₂ thin film photocatalyst (a, a') and Ag₂O powder (b, b').