

Local structure analysis of ultra dilute trivalent dopants in ceramics

Isao Tanaka (7888)^{1)*}, Akihito Kuwabara (17103)¹⁾,
Masahiro Kunisu (7702)¹⁾, Satoru Yoshioka (9595)¹⁾,
Toshihiro Okajima (4122)²⁾, Norimasa Umesaki (3515)³⁾

1) Department of Materials Science & Engineering, Kyoto University, Yoshida, Sakyo, Kyoto 606-8501, Japan

2) Industry Promotion Division, Saga Prefectural Government, 1-1-59 Jyonai, Saga 840-8570 Japan

3) JASRI, SPring-8, 1-1-1 Kouto, Mikazuki-cho, Sayo-gun, Hyogo 679-5198, Japa

Introduction

Characterization of local environments of rare earth elements is essential for design and full utilization of optical materials. In the present study we focus our efforts on the study of Eu^{3+} dopants in borosilicate glasses using L_3 -edge XAFS. The materials are important model systems for fluorescent materials.

Method

Eu L_3 -edge XANES spectra from 0.3 % Eu-doped borosilicate glass were measured using a Si (111) double-crystal monochromator at BL01B1 of SPring-8. Experiments were carried out by the transmission mode and the Total Fluorescence Yield mode, in which Eu $L\alpha$ fluorescent emissions were collected with a 19-elements Ge solid-state detector. The samples were sintered at 923 K to 1023 K. Measurements were made at room temperature in air.

Results

Prior to the XAFS measurements, Eu L_3 -edge XANES spectra of reference oxides were measured by the transmission mode. Figure 1 shows observed Eu L_3 -edge XANES spectrum of Eu_2O_3 in comparison to the theoretical spectrum obtained in the present study. Spin-polarized FP-LAPW method was employed, in which core-hole and relativistic effects were carefully taken into consideration. Because two kinds of different sites (A : B = 3:1) are present in the Eu_2O_3 crystal with a bixbyite structure, two sets of calculations for different Eu sites were performed. It is

noteworthy that the theoretical spectra from sites A and B show different peak positions. The calculated spectrum reproduces a basic shape of the experimental spectrum. However, the energy resolution of the experimental spectrum is not good enough to discuss detailed features. Some ways of deconvolution are required when one wants to use the Eu L_3 -edge XANES spectrum. Analysis on the local environment of the various Eu dopants in glasses is in progress using EXAFS.

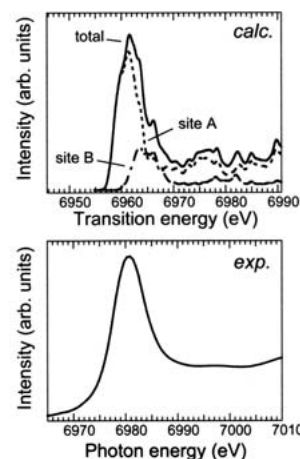


Fig. 1 Eu L_3 -edge XANES from Eu_2O_3 . Top and bottom panels are calculation and experiment, respectively.

XAFS study on the self-regeneration mechanism of perovskite catalysts for automotive emissions (VI)

Masashi Taniguchi^{a)} (8753), Hirohisa Tanaka^{a)} (7263), Mari Uenishi^{a)} (7265),
Yoshikazu Iseki^{a)} (14736), Yasuo Nishihata^{b)} (1166), Jun'ichiro Mizuki^{b)} (302)

^{a)} Daihatsu Motor Co. Ltd, Ryuo, Gamo-gun, Shiga 520-2593, Japan.

^{b)} JAERI/SPring-8, Mikazuki, Sayo-gun, Hyogo 679-5148, Japan

Catalytic converters are widely applied to control automotive emissions, such as nitrogen oxides (NO_x), carbon monoxide (CO), and unburned hydrocarbons (HC). The conventional catalyst usually deteriorates because of the agglomeration and growth of precious metal particles on support materials during vehicle use. It was demonstrated by x-ray diffraction and XAFS techniques that Pd-containing perovskite-based catalysts, $\text{LaFe}_{0.57}\text{Co}_{0.38}\text{Pd}_{0.05}\text{O}_3$ and $\text{LaFe}_{0.95}\text{Pd}_{0.05}\text{O}_3$, retain high metal dispersion due to structural responses to the inherent redox fluctuation in exhaust-gas composition with the modern gasoline engines [1-4]. We have been investigating another intelligent catalyst with Rh. However, as for the Rh-perovskite with Fe in the B-site, it was a problem that the amount of segregation of Rh was a little.

Rh-containing perovskite oxides, $\text{AB}_{0.95}\text{Rh}_{0.05}\text{O}_3$ (A = Alkaline-earth metal, B = +4 valence metal) were prepared by the alkoxide method. The each powdered catalyst was oxidized in air at 800 °C. The

powder catalyst was then divided into five samples that were reduced in 2.5 % hydrogen and 7.5 % carbon monoxide balanced with nitrogen gas at 800 °C for 1 hour. X-ray absorption spectra were measured at RT in transmission mode near Rh K-edge.

By changing the B-site of the perovskite from Fe (+3 valence) ion to the +4 valence metal, it has been found that the amount of segregation of Rh is much improved. It is thought that because the valence of the B-site was changed from +3 to +4, Rh in the B-site of the perovskite crystal became unstable and easy to segregate. Further analysis is now in progress.

References

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