Local structure analysis of ultra dilute trivalent dopants in ceramics

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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 \(L_2\)-edge XAFS. The materials are important model systems for fluorescent materials.

Method

Eu \(L_2\)-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 \(L\alpha\) fluorescence emissions were collected with a 19-element 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 \(L_2\)-edge XANES spectra of reference oxides were measured by the transmission mode. Figure 1 shows observed Eu \(L_2\)-edge XANES spectrum of EuO\(_2\) 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 EuO\(_2\) 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 \(L_2\)-edge XANES spectrum. Analysis on the local environment of the various Eu dopants in glasses is in progress using EXAFS.

Fig. 1 Eu \(L_2\)-edge XANES from EuO\(_2\). Top and bottom panels are calculation and experiment, respectively.

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

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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, LaFe\(_{1-x}\)Co\(_x\)O\(_3\)-Pd\(_{0.2}\)O\(_2\), retain high metal dispersion due to structural responses to the inherent redox fluctuation in exhaust gas compositions. In modern gasoline engines, \(^1\) we have been investigating another intelligent catalyst with Rh. However, as for the Rh-perovskite with Fe in B-site, it was a problem that the amount of segregation of Rh was small.

Rh-containing perovskite oxides, ABO\(_{3}\)Rh\(_{0.5}\)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 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