

## Structural Analysis of Tb doped Alumina during a Preparation Process by Combined in situ XAFS and XRD

Kyoko K. Bando (AIST), Tetsuya Kodaira (AIST), Eiichi Kobayashi (SAGA-LS), Naofumi Nagai (Kawaken Fine Chem. Co. Ltd.)

kk.bando@aist.go.jp

Alumina is one of the most important industrial materials. It has been used for various products like insulators, reactors, binders, catalyst supports and so on. Recently, a method to produce sols composed of fibrous boehmite nanoparticles was developed (Nagai, et al., *J. Mater. Chem.*, **2011**, *21*, 14884). It is possible to make a transparent self-standing film out of this sol, which enables application of the material to optical devices. In addition, when Tb ions were doped, the film acquires photoluminescent (PL) properties and emits bright green light due to the  $f-f$  transition of Tb by UV irradiation. Since the PL performance changed with pretreatment conditions, it is important to know how the PL active structure was formed during the process. In addition, it was found that the PL intensity normalized by the Tb content significantly decreased when the Tb content was increased from 2 mol% to 3 mol% to Al. To elucidate how the active structure was formed during the preparation process, combined in situ XAFS and XRD analysis was conducted and changes of both the local structure around Tb and the crystal structure of alumina were observed.

A boehmite sol composed of fibrous nanoparticles of 1400 nm in length (F1000) was provided by Kawaken Fine Chem. Tb was added to this sol with aqueous solution of Tb nitrate. The mixture was spread on a plastic mold and dried at 60 °C to make films. The content of Tb was varied from 0.5 mol% to 5 mol% to Al. In situ XAFS and XRD measurements were conducted at BL11 in SAGA LS and BL9A and 12C at PF in Japan. A cell designed for in situ XAFS and XRD measurements was used. Tb  $L_{III}$ -edge XAFS spectra and diffracted X-ray spectra at  $2\theta = 32^\circ$  were collected simultaneously while the temperature of the sample was raised from r.t. to 600 °C in a flow of He.

Phase transformation of the substrate from boehmite to  $\gamma$  was observed from 300 °C to 500 °C, which was confirmed by disappearance of 051 diffraction of boehmite and emergence of 400 diffraction of  $\gamma$  phase. In situ Tb  $L_{III}$ -edge XANES spectra were compared to this phase transformation. The valence state of Tb was trivalent and unchanged during the process. However, the change in the second peak around 7552 eV was different depending on the Tb content. For the 5mol% sample, the intensity decreased monotonously prior to the phase transformation of the substrate, indicating segregation of Tb from alumina. On the other hand, for the samples with a Tb content less than 2 mol%, while the intensity at 7552 eV at 500 °C was lower than that at 300 °C, a maximum was observed in the process. The temperature which gave the maximum became lower with the Tb content. Fourier transform of EXAFS indicated certain stretch-contraction of Tb – O bonding in the same period. Tb ions for the samples with the lower Tb content were isolated and dispersed between alumina fibers. Such an environment was thought to have an influence on the Tb local structure.

This work is supported by JSPS KAKENHI (c) Grant number 24510162. The XAFS experiments were conducted with an approval of PF- PAC proposal number 2015G581, 2013G130, and SAGA LS proposal number 1411125F, 1511110F, and 1610133F.