

## Short Note

**Effect of Excitation Wavelength on Photoemission Properties of Eu-doped  $Zr_{1-x}Ce_xO_2$  ( $x = 0-0.2$ ) Nanoparticles**Masakuni OZAWA<sup>1\*</sup>, Masashi MATSUMOTO<sup>2</sup> and Masatomo HATTORI<sup>1</sup><sup>1</sup>Institute of Materials and Systems for Sustainability, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan.<sup>2</sup>Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan.

Received December 3, 2017; Revised January 14, 2018; Accepted January 18, 2018

**ABSTRACT**

Eu-doped  $ZrO_2$  and  $Zr_{1-x}Ce_xO_2$  ( $x = 0-0.2$ ) nanoparticles were prepared by a hydrothermal method. The photoemission spectra of  $Zr_{1-x}Ce_xO_2:Eu^{3+}$  nanocrystalline samples showed the typical emission of  $Eu^{3+}$  ions assigned to  ${}^5D_0 \rightarrow {}^7F_1$  (590 nm) and  ${}^5D_0 \rightarrow {}^7F_2$  (610 nm) transitions and additional emissions of  ${}^5D_0 \rightarrow {}^7F_1$  with higher J. The spectra were measured at two excitation wavelength of 340 nm (indirect) and 467 nm (direct), and the direct excitation emission was less sensitive compared with 340 nm-induced emission. Asymmetry ratio which was measured by indirect excitation was more effective for monitoring a local lattice distortion in  $CeO_2$ - $ZrO_2$ . This is a fundamental knowledge about luminescent spectra for evaluating the nature of catalytic properties.

**KEY WORDS**Photoluminescence, Eu,  $ZrO_2$ ,  $CeO_2$ , Oxygen storage capacity**1. Introduction**

The local structure in host materials is the main factor that controls the photoemission spectra and intensity of luminescent materials.  $Eu^{3+}$  is a major emission center and the photoluminescence properties depend on the symmetry of host crystal lattices. There have been several attempts to prepare small particles of  $Eu^{3+}$ -doped  $ZrO_2$ <sup>1-3)</sup>, and our interest is in the luminescence properties of  $Eu^{3+}$ -doped  $ZrO_2$  and  $Zr_{1-x}Ce_xO_2$  ( $x = 0-0.2$ ) with different symmetries<sup>4,5)</sup>. The interatomic distance, which depends on the Ce concentration in the same crystal structure (tetragonal  $ZrO_2$ ), especially in such materials comprising fine particles with low crystallinity, should affect the luminescent and other properties including catalysis. Nanoparticles of  $ZrO_2$ - and  $CeO_2$ -based materials are interesting for many applications, especially support and subcatalyst in automotive catalysts<sup>6-8)</sup>. Recently, the optical property is used for analysis of local structure of  $CeO_2$ -stabilized  $ZrO_2$  catalysts with oxygen storage capacity (OSC)<sup>9,10)</sup>. The lattice distortion will be a factor in the un-stabilization of lattice oxygens in the host, resulting in better OSC catalyst.

In this study, the hydrothermally prepared nanocrystal samples were analyzed about the luminescence behavior of  $Zr_{1-x}Ce_xO_2:Eu^{3+}$  nanoparticles with different Ce concentrations and discussed in relation to their crystal structural characteristics. Especially, the effect

of excitation wavelength on photoemission spectra and asymmetry factor are examined for analyzing a local structure in this system.

**2. Experimental**

A series of  $Zr_{1-x}Ce_xO_2:Eu^{3+}$  ( $x = 0, 0.05, 0.1, 0.15, 0.2$ ) samples with 3 mol% Eu were prepared by a modified hydrothermal process, as previously described<sup>5,11)</sup>. The samples were heat-treated at 400°C for 3 h in air (calcined). The structural characteristics of the nanocrystalline samples were examined from their X-ray diffraction (XRD) patterns obtained using a MiniFlex II (Rigaku) system with  $Cu-K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at 15 mA and 30 kV. The fluorescence spectra obtained were measured at room temperature using a fluorescence meter (JASCO PF8500) with a 150 W Xe lamp as an excitation source. The emission spectra of calcined  $Zr_{1-x}Ce_xO_2:Eu^{3+}$  samples were measured at two excitation wavelengths at 340 and 466 nm. The excitation spectra was evaluated for the  ${}^5D_0 \rightarrow {}^7F_1$  transition of  $Eu^{3+}$  at 590 nm.

**3. Results and discussion**

The XRD patterns of the calcined  $Zr_{1-x}Ce_xO_2:Eu^{3+}$  ( $x = 0-0.2$ ) samples corresponded to the diffraction intensities of apparently a pseudocubic fluorite structure<sup>5)</sup>. The  $d_{(111)}$  interatomic distance of tetragonal compounds in  $Zr_{1-x}Ce_xO_2$  with 3mol%  $Eu^{3+}$  increased from 0.296 to 0.300 nm with the increase in the doping concentration of  $CeO_2$  from  $x = 0$  to 0.2. This is due to the radius of  $Ce^{4+}$  (0.097 nm)

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\*\* The content of this article had been presented at JSPMIC2017.