



Photoemission properties of Eu-doped $Zr_{1-x}Ce_xO_2$ ($x = 0-0.2$) nanoparticles prepared by hydrothermal method

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Photoluminescent Eu-doped ZrO_2 and $Zr_{1-x}Ce_xO_2$ ($x = 0-0.2$) nanoparticles were prepared by a hydrothermal method. X-ray diffraction and Raman spectra indicated the formation of tetragonal crystals of ZrO_2 and its solid solutions with a grain size of less than 10 nm diameter after heat treatment at 400 °C. 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 ${}^5D_0 \rightarrow {}^7F_J$ with higher J of 3–5. Increasing the CeO_2 concentration reduced the emission intensity, and the emission peak shift was affected by a local lattice distortion, i.e., CeO_2 concentration. The present study provided fundamental knowledge that is expected to enable the fabrication of ZrO_2 -based nanocrystal phosphor materials and a measure for controlling the emission peak shift and intensity in oxide fluorite-based phosphor. © 2018 The Japan Society of Applied Physics

1. Introduction

Zirconium dioxide (zirconia; ZrO_2) has been widely investigated owing to its high chemical and thermal stabilities, and its highly cationic conductive, catalytic, and biocompatible materials.^{1–5} Eu^{3+} -doped ZrO_2 is attractive owing to its stable photoluminescence properties, and several studies were performed with Eu-doped monoclinic and tetragonal ZrO_2 ceramics.^{6–16} The crystal structure of ZrO_2 is the main factor that controls the emission spectra and intensity of this luminescent material. In general, the photoluminescence properties of an emission center (Eu^{3+}) change depending on the symmetry of host crystal lattices and the interatomic distance. Also, heat treatment at elevated temperatures over 600 °C is required for the preparation of ZrO_2 -based ceramics. There have been several attempts to prepare small particles of Eu^{3+} -doped ZrO_2 on the nanoscale, and the luminescence properties of such particles doped with Eu^{3+} seem to depend on the preparation method used to obtain the nanocrystalline state.^{7,15,16}

Our interest is in the preparation of Eu^{3+} -doped ZrO_2 and $Zr_{1-x}Ce_xO_2$ ($x = 0-0.2$) in the nanocrystalline state and in their luminescence properties, as well as the control of such properties for their application as luminescent materials. Possible controlling factors and effects on the Eu^{3+} luminescence emission center may be expected when Eu^{3+} is introduced into the $Zr_{1-x}Ce_xO_2$ host by modifying a local site (e.g., interatomic distance). The interatomic distance, which depends on the Ce concentration in the same crystal structure (tetragonal ZrO_2), especially in practical materials comprising fine particles with low crystallinity, should affect the luminescent properties. Also, CeO_2 -stabilized ZrO_2 particles have been useful as supporting materials in three-way catalysis, because of their capability to store and release oxygen through redox processes involving the Ce^{4+}/Ce^{3+} couple.^{17–21} In a previous study, we observed the luminescence of heavily Ce-doped ZrO_2 with Eu ($Ce_{0.5}Zr_{0.5}O_2:Eu^{3+}$) showing the typical emission of Eu^{3+} ions, the intensity of which was affected by local distortion at high Eu concentrations.²² A possible relationship between the local structure and catalytic properties was expected; however, the intensity of photoemission itself was too low for a phosphor material.

Nanoparticles of ZrO_2 -based materials with rare-earth cations such as Ce^{4+} and Eu^{3+} added into ZrO_2 lattices are interesting for many applications, especially photoluminescence, if the increased intensity and emission spectra (wavelength) can be controlled.

In this study, a series of nanocrystalline Eu^{3+} -doped ZrO_2 and $Zr_{1-x}Ce_xO_2$ ($x = 0-0.2$) samples were prepared by the hydrothermal method. As-dried and calcined nanocrystal samples were prepared to analyze 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.

2. Experimental procedure

2.1 Preparation

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.^{21,22} The starting materials were cerium nitrate hexahydrate [$Ce(NO_3)_3 \cdot 6H_2O$, Wako], zirconium oxynitrate hexahydrate [$ZrO(NO_3)_2 \cdot 6H_2O$, Wako], and europium nitrate pentahydrate [$Eu(NO_3)_3 \cdot 5H_2O$, Wako]. A total of 7 mmol of stoichiometric amounts of the starting materials and 7 mmol of potassium oleate ($C_{33}H_{17}COOK$, 19% solution, Wako) were dissolved in 30 mL of distilled water. The solutions were mixed by vigorously stirring, followed by the addition of 10 mL of 25 wt% aqueous ammonia solution (NH_3 , 25% solution, Wako). Then, the solution mixture containing precipitates was transferred to a Teflon-lined stainless-steel autoclave. Subsequently, the mixture was heated at 200 °C for 48 h with stirring at a rate of 800 rpm in the sealed autoclave. After the system was naturally cooled to room temperature, the precipitates were separated from the solution by centrifugation and then washed with distilled water. The samples were dried at 95 °C for 24 h in air (as-dried), and others were heat-treated at 400 °C for 3 h in air (calcined).

2.2 Characterization

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. Morphological observation of the nanoparticles was carried out using a