

Structural and photoluminescence properties of solution combustion-processed novel ZrO_2 doped with Eu^{3+} and Al^{3+}

S.J. Yoon, J.W. Pi, K. Park*

Faculty of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul 143-747, South Korea



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ABSTRACT

High-quality nanosized $\text{Zr}_{1-x}\text{O}_2:\text{xEu}^{3+}$ ($0.05 \leq x \leq 0.13$), $\text{Zr}_{0.89-x}\text{O}_2:0.11\text{Eu}^{3+},\text{xAl}^{3+}$ ($0 \leq x \leq 0.060$), and $\text{Zr}_{0.96-x}\text{O}_2:\text{xEu}^{3+}, 0.04\text{Al}^{3+}$ ($0.05 \leq x \leq 0.13$) phosphors were prepared by solution combustion method. The partial substitution of Eu^{3+} for Zr^{4+} in zirconia (ZrO_2) stabilized the tetragonal and cubic structures at room temperature. The prepared phosphors were effectively excited by near-ultraviolet (393 nm) and exhibited red emission characteristics. The photoluminescence (PL) properties of $\text{Zr}_{1-x}\text{O}_2:\text{xEu}^{3+}$ phosphors were substantially improved by controlling the Eu^{3+} concentration and adding Al^{3+} as a sensitizer. The incorporation of Al^{3+} was highly effective for improving the PL properties and reducing the optimal concentration of Eu^{3+} . Compared with Al^{3+} -free $\text{Zr}_{1-x}\text{O}_2:\text{xEu}^{3+}$ phosphors, $\text{Zr}_{0.87}\text{O}_2:0.09\text{Eu}^{3+}, 0.04\text{Al}^{3+}$ phosphor exhibited impressive PL properties that render it a strong candidate red-emitting phosphor for white light-emitting diodes and solid-state lighting applications.

1. Introduction

White light-emitting diodes (WLEDs) were first reported in the 1960s [1,2]. In recent years, significant attention has been paid to the fabrication of WLEDs because of numerous advantages, such as long lifetime, high color rendering index (CRI), high luminosity efficiency, and environmental friendliness [3]. WLEDs are widely used in solid-state lighting, backlights of liquid crystal displays, automobile headlights, traffic-signal lights, urban landscape lighting, and indoor and outdoor lighting [2,4]. WLEDs show particularly high potential for the replacement of conventional incandescent and fluorescent lamps because of their aforementioned advantages, as well as their relatively low operating temperature, high reliability, and low energy consumption [5–9].

WLEDs can be produced by combining a blue LED chip with a broad-band yellow $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor [4,10]. However, this combination faces the problems of low CRI (< 80), blue/yellow color separation, and luminous efficiency [2,3,11]. An alternative approach is to combine a blue or near-ultraviolet (UV) LED chip with multi-chromatic blue, green, and red phosphors to generate white light [3–5]. Conventional phosphors for this application are $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$, $\text{ZnS}:\text{Cu}^+/\text{Al}^{3+}$, and $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ for blue, green, and red light, respectively [12]. Among these phosphors, $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ phosphor showed lower efficiency than blue and green phosphors, as well as short working lifetime and instability due to the release of sulfide [12,13].

Thus, developing efficient red-emitting phosphors with high photoluminescence (PL) intensity, strong absorption in blue or near-UV LED chips, and high chemical stability is very important for WLED.

Oxide phosphors are reportedly strong candidate materials for photonic devices. In particular, zirconia (ZrO_2) is attracting special attention because of its high refractive index, high optical transparency, wide band gap (4–5 eV), high photothermal stability, high chemical stability, and low phonon energy (470 cm^{-1}). These features render ZrO_2 an appropriate host medium for highly efficient luminescent materials [14–20]. A low phonon energy enhances the possibility of high efficient luminescence of activators incorporated into a host [20,21]. To extend the applications of ZrO_2 as phosphors, the PL properties of ZrO_2 doped with Tb^{3+} , Dy^{3+} , Eu^{3+} , Er^{3+} , Ce^{3+} , and Ti^{4+} ions have been extensively studied [22–26]. Yoon and Park [22] investigated the PL properties of $\text{Zr}_{1-x}\text{O}_2:\text{xTb}^{3+}$ ($0.03 \leq x \leq 0.13$) phosphors prepared by the solution combustion method, depending on Tb^{3+} concentration and annealing temperature. Upon excitation at 296 nm, $\text{Zr}_{1-x}\text{O}_2:\text{xTb}^{3+}$ phosphors showed intense green emission peaks caused by the $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 3, 4, 5,$ and 6) transitions of Tb^{3+} , i.e., $^5\text{D}_4 \rightarrow ^7\text{F}_6$ (489 nm), $^5\text{D}_4 \rightarrow ^7\text{F}_5$ (545 nm), $^5\text{D}_4 \rightarrow ^7\text{F}_4$ (587 nm), and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ (617 nm). The most efficient emission properties were obtained for $\text{Zr}_{0.95}\text{O}_2:0.05\text{Tb}^{3+}$ phosphor annealed at 900 °C. Das et al. [23] synthesized $\text{ZrO}_2:\text{Dy}^{3+},\text{Eu}^{3+}$ phosphors for near-UV excited WLED applications. The emission color was tuned from yellow to near white light, and eventually to warm-white light by changing the concentration of

* Corresponding author.

E-mail address: kspark@sejong.ac.kr (K. Park).

Dy³⁺. This tunable emission was attributed to the variation in site symmetry due to the Dy³⁺ and Eu³⁺ co-doping and efficient energy transfer from Dy³⁺ to Eu³⁺. López-Luke et al. [24] studied the up-conversion emission of ZrO₂:Er³⁺ phosphor upon excitation at 968 nm. Strong green emission was produced by the transition ²H_{11/2} + ⁴S_{3/2} → ⁴I_{15/2} and explained by cooperative energy transfer between neighboring ions. Tetragonal crystal structure and small crystallite size were more favorable for the up-conversion emission. Das et al. [25] synthesized bluish green-emitting ZrO₂:Ce³⁺ phosphors through a microemulsion route. Nanosized ZrO₂:Ce³⁺ phosphors were formed as the aqueous micelles confined the constituent cations during crystallization. The phosphors emitted bluish green light (487 nm) under UV excitation. The microemulsion-processed ZrO₂:Ce³⁺ phosphors were suitable for optoelectronic applications. Cong et al. [26] prepared a long-lasting afterglow ZrO₂:Ti⁴⁺ phosphor through the conventional solid-state reaction method. Upon 254 nm irradiation, a bluish white broad emissive band was observed, which was caused by the recombination of electrons trapped by F⁺ centers and the holes created in the valence band. A bluish-white long-lasting phosphorescence (LLP) with a persistent time of 1 h was found after removing the 254 nm light. PL and LLP properties were improved by substituting Ti⁴⁺ for Zr⁴⁺ due to the creation of anion vacancies.

Traditionally, the high-temperature solid-state reaction method has been used to prepare ZrO₂ phosphors doped with trivalent rare-earth ions for WLED applications. Yin et al. [27] synthesized Zr_{1-x}Eu_xO₂ and Zr_{1-2x}Eu_xM_xO₂ (M = Nb, Ta; 0.01 ≤ x ≤ 0.13) phosphors via the solid-state reaction method. The monoclinic Zr_{1-2x}Eu_xM_xO₂ (x = 0.05) showed approximately five times stronger red emission under 395 nm or 469 nm excitation at room temperature in comparison with M⁵⁺ ion-free Zr_{0.95}Eu_{0.05}O₂. The incorporation of M⁵⁺ ions into Zr_{1-x}Eu_xO₂ reduced the tetragonal phase and eliminated oxygen vacancies, substantially improving the PL intensity and quantum yield. This solid-state reaction method was suitable for large-scale production. However, resultant powders were usually characterized by inhomogeneous composition, large agglomerated particles, low-surface area, irregular morphologies, and presence of crystal defects and impurities, which were detrimental to PL properties [28]. Consequently, various chemical methods, such as solution combustion [28,29], sol-gel [30,31], spray pyrolysis [32], polyol [33], sol-emulsion-gel [34], co-precipitation [35,36], and hydrothermal processes [37,38], have been used to prepare ultra-fine, high purity ZrO₂-based phosphors. In particular, a solution combustion method has been considered promising for preparing high-quality ZrO₂ phosphors doped with trivalent rare-earth ions. This method uses heat energy liberated by the self-sustaining exothermic redox reaction in a homogeneous aqueous solution of oxidizer (nitrates) and fuel. This method offers the advantages of simple apparatus, small input energy, cost-effectiveness, short reaction time, low synthesis temperature, and high flexibility in fuel choice, and is a suitable process for synthesizing various high-purity nanoscale inorganic materials [22,39–41].

In the present work, to investigate the effect of Eu³⁺ concentration on ZrO₂, we prepared ZrO₂ phosphors doped with various Eu³⁺ concentrations through solution combustion method. To further improve the PL properties, we doped an Al³⁺ ions as a sensitizer into Zr_{0.89}O₂:0.11Eu³⁺ phosphor and then investigated its crystal structure, luminescence, and color chromaticity. We then compared the PL properties of singly Eu³⁺-doped Zr_{1-x}O₂:xEu³⁺ phosphors with those of Eu³⁺/Al³⁺-co-doped Zr_{0.96-x}O₂:xEu³⁺, 0.04Al³⁺ phosphors.

2. Experimental

Zr_{1-x}O₂:xEu³⁺ (0.05 ≤ x ≤ 0.13), Zr_{0.89-x}O₂:0.11Eu³⁺, xAl³⁺ (0 ≤ x ≤ 0.060), and Zr_{0.96-x}O₂:xEu³⁺, 0.04Al³⁺ (0.05 ≤ x ≤ 0.13) phosphors were prepared by solution combustion method. ZrO (NO₃)₂·2H₂O, Al(NO₃)₃, and Eu₂O₃ were used as starting materials for the synthesis, and citric acid (C₃H₄(OH)(COOH)₃) was used as a

combustion fuel. Eu₂O₃ was dissolved in HNO₃ to form Eu(NO₃)₃. ZrO (NO₃)₂·2H₂O, Al(NO₃)₃, Eu(NO₃)₃, and citric acid were separately dissolved in deionized water. After mixing the nitrate solutions together, the obtained nitrate solutions and citric acid solution were placed in a beaker. The molar ratio of the metal nitrates to citric acid was controlled to be 1.0. The mixed solutions were heated slowly on a magnetic hot plate at 200 °C under stirring until excess free water evaporated to form highly viscous gel precursors. Upon further heating, the precursors spontaneously ignited to produce Zr_{1-x}O₂:xEu³⁺, Zr_{0.89-x}O₂:0.11Eu³⁺, xAl³⁺, and Zr_{0.96-x}O₂:xEu³⁺, 0.04Al³⁺ powders. These powders were calcined at 300 °C for 4 h in air to remove residual impurities and then annealed at 900 °C for 4 h in air. The crystal structure of the prepared phosphors was investigated by X-ray powder diffraction (XRD) and Rietveld diffraction profiles. XRD patterns were obtained with an X-ray diffractometer (Rigaku RINT 2000) with Cu K_α radiation (λ = 0.15418 nm). For Rietveld refinement, the XRD patterns were measured using an X-ray diffractometer (XPRT-PRO, Pan Analytical, UK) with Cu K_α radiation (λ = 1.5406 Å) and operated at 40 kV and 30 mA over a wide 2θ range (20°–100°) at a scan rate of 0.02°/m. Experimental data were refined through the Rietveld method by using the Fullprof software. The morphology and size of the annealed phosphors were investigated with a field-emission scanning electron microscopy (FE-SEM) system (Hitachi S4700). UV-Visible absorption spectra were obtained with a UV-Visible spectrophotometer (Varian, Cary 5000) in the wavelength of 200–800 nm. PL excitation and emission spectra were recorded with a spectrofluorometer (QM-4/2005SE, PTI, USA) equipped with a 75 W Xenon lamp.

3. Results and discussion

Fig. 1 shows the room-temperature XRD patterns of Zr_{1-x}O₂:xEu³⁺ (0.05 ≤ x ≤ 0.13) phosphors prepared by the solution combustion method in comparison with Joint Committee on Power Diffraction Standards (JCPDS) cards (tetragonal JCPDS card 50–1089 and cubic JCPDS card 49–1642). Clearly, the incorporation of Eu³⁺ ions affects the crystal structure of ZrO₂. Zr_{1-x}O₂:xEu³⁺ (0.05 ≤ x ≤ 0.11) and Zr_{0.87}O₂:0.13Eu³⁺ phosphors form the tetragonal and cubic crystal structures, respectively. No XRD peaks corresponding to the monoclinic phase are observed. ZrO₂ is known to form three crystalline phases, i.e., the monoclinic phase with the P21/c (14) space group (< 1170 °C), the tetragonal phase with the P42/nmc (137) space group (1170–2370 °C), and the cubic phase with the Fm3m (225) space group (≥ 2370 °C) [23]. Among them, the cubic phase is the most symmetric, and the monoclinic phase is lower symmetric than the tetragonal and

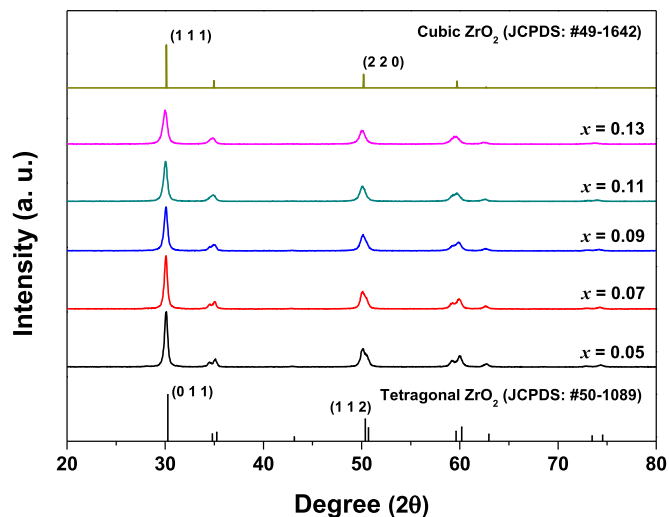


Fig. 1. XRD patterns of the Zr_{1-x}O₂:xEu³⁺ phosphors with various Eu³⁺ concentrations.

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