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## Short communication

# Fluorescence property of $ZrO_2:Ti$ phosphor and its enhancement in fluorescent intensity by adding phosphorus

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## ABSTRACT

It was investigated how the PL of the blue phosphor,  $ZrO_2:Ti$ , was affected by the change in addition amounts of Ti. The 1000 ppm Ti doped  $ZrO_2$ , ( $ZrO_2 + 1000$  ppm Ti), showed the strongest PL, which was 5.4 times higher than that of the pure  $ZrO_2$ . This strong PL was further improved by the addition of P, Sn, Se, B and Si to the ( $ZrO_2 + 1000$  ppm Ti) phosphor. The improvement was achieved by the ( $ZrO_2 + 1000$  ppm Ti + 4000 ppm P) phosphor, and its absorptivity, internal quantum efficiency and external quantum efficiency were 53, 59 and 31% at room temperature, respectively, when excited at 280 nm.

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## 1. Introduction

Titanium doped  $ZrO_2$  ( $ZrO_2:Ti$ ) has been attracting increasing interest as a blue phosphor. Of particular interest is mechanoluminescence from stress-activated  $ZrO_2:Ti$ , which was reported by Akiyama et al. in 2002 [1]. From the observation that the PL intensity and the PL integrated intensity of the  $ZrO_2:Ti$  are comparatively high, its possible application to industry has been proposed. Another point worth noting about the  $ZrO_2:Ti$  is that it is a novel long-lasting afterglow phosphor, as was reported by Cong et al. [2], Chandra [3], Wang et al. [4] and Nikiforov et al. [5]. The PL mechanism generally

accepted to date is that the replacement of Zr by Ti produces anion vacancies, resulting in the enhanced PL and long lasting PL. Cong et al. investigated the blue PL of the ( $ZrO_2 + x$  ppm Ti) phosphors in the range of  $x = 0-2000$  ppm (0–0.5 mol% Ti) and found that the strongest PL is observed for the about 2000 ppm (0.5 mol%) Ti doped phosphor [2]. However, the effect of the Ti amount beyond 2000 ppm on the PL has not been investigated. So, in the present work, we prepared the ( $ZrO_2 + x$  ppm Ti) phosphors with  $x$  being 0–50,000 ppm and their PL spectra were examined. Moreover, because an enhancement of PL intensity by the P addition to  $ZrO_2:Ti$  phosphor was found, it reports on the effect of P addition.

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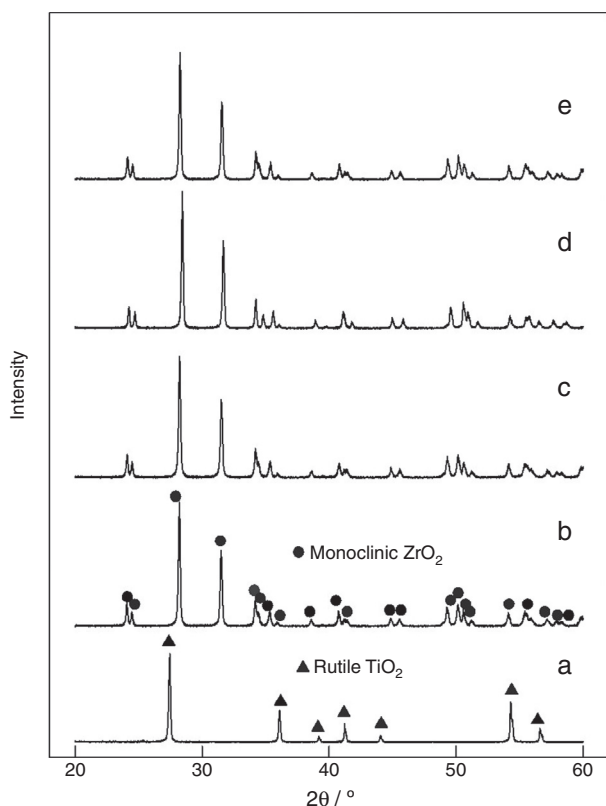
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## 2. Experimental

Various  $\text{ZrO}_2\text{:Ti}$  phosphors ( $(\text{ZrO}_2 + x \text{ ppm Ti})$  phosphors, hereafter) were prepared from  $\text{ZrO}_2$  (purity 99.9%, TZ-0, Tosoh Co.) and 0–50,000 ppm  $\text{TiO}_2$  (99.9%) powders. Analytical grade  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ ,  $\text{SnO}_2$ ,  $\text{SeO}_2$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$  or  $\text{Ta}_2\text{O}_5$  powder was added to the  $(\text{ZrO}_2 + 1000 \text{ ppm Ti})$  phosphor in the range of 0–10,000 ppm as another additive to prepare the ternary phosphors ( $(\text{ZrO}_2 + 1000 \text{ ppm Ti} + x \text{ ppm M})$  phosphor ( $M = \text{P, Sn, Se, B, Si, Al, Nb}$  or  $\text{Ta}$ ), hereafter). These component powders were mixed using a ball-mill and heat-treated at  $1400^\circ\text{C}$  for 2 h in an air atmosphere.

X-ray powder diffraction data were obtained using a diffractometer (XRD, MiniFlex II, Rigaku Co.) with  $\text{Cu-K}\alpha_1$  radiation ( $\lambda = 0.154050 \text{ nm}$ ). Excitation and emission spectra were measured on an FP-6500 spectrofluorometer (JASCO Co.). Quantum efficiencies were determined with a Qunataurus-QY system C11347-01 (Hamamatsu Photonics K.K.). The morphology of the powder was examined using a scanning electron microscope (FE-SEM, JEOL 7500F) fitted with an energy dispersive X-ray analyzer (EDX). Electronic states of  $\text{Ti}2p$  and  $\text{P}2p$  were investigated by X-ray photoelectron spectroscopy (XPS, PHI5000 VersaProb, ULVAC-PHI, Inc) using  $\text{Al-K}\alpha$  X-ray source.

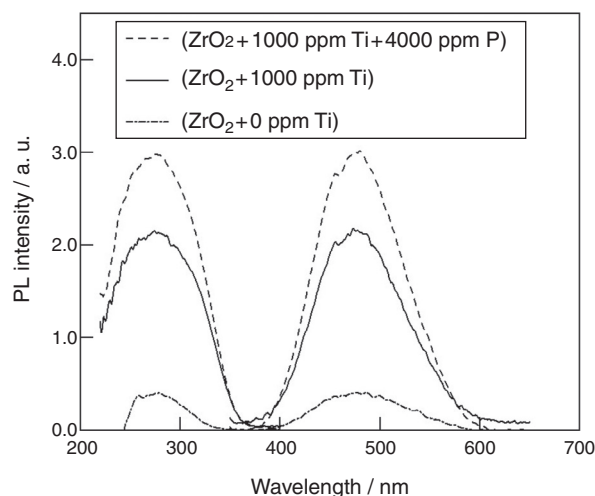


**Fig. 1** – X-ray diffraction patterns of  $\text{TiO}_2$  (a),  $\text{ZrO}_2$  (b),  $(\text{ZrO}_2 + 1000 \text{ ppm Ti})$  (c),  $(\text{ZrO}_2 + 50,000 \text{ ppm Ti})$  (d) and  $(\text{ZrO}_2 + 1000 \text{ ppm Ti} + 4000 \text{ ppm P})$  (e) phosphors. Closed triangle: ICDD no. 21-1276 (rutile  $\text{TiO}_2$ ) and closed circle: ICDD no. 37-1484 (monoclinic  $\text{ZrO}_2$ ).

## 3. Results and discussion

### 3.1. $(\text{ZrO}_2 + x \text{ ppm Ti})$ phosphors ( $x = 0\text{--}50,000$ )

Typical XRD results of  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $(\text{ZrO}_2 + 1000 \text{ ppm Ti})$  and  $(\text{ZrO}_2 + 50,000 \text{ ppm Ti})$  are shown in Fig. 1. Diffraction peaks attributable to  $\text{TiO}_2$  are not observed in the XRD patterns of both  $(\text{ZrO}_2 + 1000 \text{ ppm Ti})$  and  $(\text{ZrO}_2 + 50,000 \text{ ppm Ti})$ , which are similar to that of monoclinic  $\text{ZrO}_2$ , suggesting that Ti atoms were dissolved into the  $\text{ZrO}_2$  lattice. Typical excitation and emission spectra are shown for the  $\text{ZrO}_2$  without any dopants and the  $(\text{ZrO}_2 + 1000 \text{ ppm Ti})$  phosphor in Fig. 2. Both excitation and emission spectra of  $\text{ZrO}_2$  were essentially little changed with the excitation and emission maxima being at around 280 nm and 475 nm, respectively, when Ti was added as a dopant. The relationship between the additive amount of Ti and the PL intensity was examined by measuring PL spectra of the  $(\text{ZrO}_2 + x \text{ ppm Ti})$  ( $x = 0\text{--}50,000$ ) phosphors. Results are given in Fig. 3. The present  $(\text{ZrO}_2 + x \text{ ppm Ti})$  ( $x = 0\text{--}50,000$ ) phosphors prepared by sintering at  $1400^\circ\text{C}$  for 2 h in an air atmosphere also emitted bluish white light under the excitation by UV light and the PL intensity was the strongest for the  $(\text{ZrO}_2 + 1000 \text{ ppm Ti})$  phosphor (5.4 times stronger than  $\text{ZrO}_2$ ), whereas Cong et al. reported that the  $(\text{ZrO}_2 + 2000 \text{ ppm Ti})$  phosphor gave the strongest intensity when the  $(\text{ZrO}_2 + x \text{ ppm Ti})$  ( $x = 0\text{--}2000$ ) phosphors were sintered at  $1250^\circ\text{C}$  for 3 h [2]. The PL mechanism of the  $\text{ZrO}_2\text{:Ti}$  phosphor has been proposed by several groups [1–5]. According to Cong et al. [2], Ti ions exist in the mixed valence states of  $\text{Ti}^{4+}$  and  $\text{Ti}^{3+}$ , when  $\text{TiO}_2$  was dissolved into  $\text{ZrO}_2$ , and the substitution of two  $\text{Ti}^{3+}$  ions for a  $\text{Zr}^{4+}$  ion produces one anion vacancy for charge compensation, that is, the concentration of anion vacancies in the  $\text{ZrO}_2\text{:Ti}$  is higher than that in the pure  $\text{ZrO}_2$  to enhance the emission intensity at around 475 nm. Wang et al. also reported that the emission observed for the as-purchased  $\text{ZrO}_2$  materials is



**Fig. 2** – Excitation (left) and emission (right) spectra of the  $(\text{ZrO}_2 + 0 \text{ ppm Ti})$ ,  $(\text{ZrO}_2 + 1000 \text{ ppm Ti})$  and  $(\text{ZrO}_2 + 1000 \text{ ppm Ti} + 4000 \text{ ppm P})$  phosphors. Cutting filter ( $<320 \text{ nm}$ ) was used. Emission wavelength for excitation spectral measurement: 475 nm, Excitation wavelength for emission spectral measurement: 280 nm.

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