Short communication

Fluorescence property of ZrO$_2$:Ti phosphor and its enhancement in fluorescent intensity by adding phosphorus

Susumu Nakayama$^{a,*}$, Masatomi Sakamoto$^b$

$^a$ Department of Applied Chemistry and Biotechnology, National Institute of Technology, Niihama College, Niihama, Japan

$^b$ Material and Biological Chemistry, Graduate School of Science and Engineering, Yamagata University, Yamagata, Japan

A R T I C L E  I N F O

Article history:
Received 5 November 2015
Accepted 16 March 2016
Available online 15 April 2016

Keywords:
Photoluminescence
Zirconia
Titanium doped zirconia
Phosphorus doping

A B S T R A C T

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 B, 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.

© 2016 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

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%) 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.

* Corresponding author.
E-mail: nakayama@chem.niihama-nct.ac.jp (S. Nakayama).

http://dx.doi.org/10.1016/j.jmrt.2016.03.005
2. Experimental

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

X-ray powder diffraction data were obtained using a diffractometer (XRD, MiniFlex II, Rigaku Co.) with Cu-K$_\alpha$ radiation (λ = 0.154050 nm). Excitation and emission spectra were measured on an FP-6500 spectrofluorometer (JASCO Co.). Quantum efficiencies were determined with a Quan-taurus-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 Ti2p and F2p were investigated by X-ray photoelectron spectroscopy (XPS, PHI5000 VersaProbe, ULVAC-PHI, Inc) using Al-K$_\alpha$ X-ray source.

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

3. Results and discussion

3.1. ([ZrO$_2$ + x ppm Ti] phosphors (x = 0–50,000))

Typical XRD results of TiO$_2$, ZrO$_2$, (ZrO$_2$ + 1000 ppm Ti) and (ZrO$_2$ + 50,000 ppm Ti) are shown in Fig. 1. Diffraction peaks attributable to TiO$_2$ are not observed in the XRD patterns of both (ZrO$_2$ + 1000 ppm Ti) and (ZrO$_2$ + 50,000 ppm Ti), which are similar to that of monoclinic ZrO$_2$, suggesting that Ti atoms were dissolved into the ZrO$_2$ lattice. Typical excitation and emission spectra are shown for the ZrO$_2$ without any dopants and the (ZrO$_2$ + 1000 ppm Ti) phosphor in Fig. 2. Both excitation and emission spectra of 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 (ZrO$_2$ + x ppm Ti (x = 0–50,000)) phosphors. Results are given in Fig. 3. The present (ZrO$_2$ + x ppm Ti (x = 0–50,000)) phosphors prepared by sintering at 1400 °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 (ZrO$_2$ + 1000 ppm Ti) phosphor (5.4 times stronger than ZrO$_2$), whereas Cong et al. reported that the (ZrO$_2$ + 2000 ppm Ti) phosphor gave the strongest intensity when the (ZrO$_2$ + x ppm Ti (x = 0–2000)) phosphors were sintered at 1250 °C for 3 h [2]. The PL mechanism of the ZrO$_2$: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 Ti$^{4+}$ and Ti$^{3+}$, when TiO$_2$ was dissolved into ZrO$_2$, and the substitution of two Ti$^{3+}$ ions for a Zr$^{4+}$ ion produces one anion vacancy for charge compensation, that is, the concentration of anion vacancies in the ZrO$_2$:Ti is higher than that in the pure ZrO$_2$ to enhance the emission intensity at around 475 nm. Wang et al. also reported that the emission observed for the as-purchased ZrO$_2$ materials is
attributed to Ti$^{3+}$ centers because they inevitably contain a trace amount (about 0.1 wt%) of TiO$_2$ [4]. PL intensity of the present phosphors was decreased with an increase of additive amount of Ti above 1000 ppm (see also Fig. 3). This is due to the concentration quenching effect [2].

3.2. (ZrO$_2$ + 1000 ppm Ti + x ppm M) phosphors (M = P, Sn, Se, B, Si, Al, Nb or Ta)

The (ZrO$_2$ + 1000 ppm Ti + x ppm M) phosphors (M = P, Sn, Se, B, Si, Al, Nb or Ta) were prepared by adding (NH$_4$)$_2$HPO$_4$, SnO$_2$, SeO$_2$, H$_3$BO$_3$, SiO$_2$, Al$_2$O$_3$, Nb$_2$O$_5$ and Ta$_2$O$_5$ powders in the range of 0–10,000 ppm to the mixture of (ZrO$_2$ + 1000 ppm Ti), which is the composition showing the strongest PL intensity as described in Section 3.1, and their PL spectra were recorded in order to investigate whether the intensity of (ZrO$_2$ + 1000 ppm Ti) phosphor is enhanced by the addition of the second additive. There was no significant influence of Al, Nb and Ta. Maximal enhancement factors for (ZrO$_2$ + 1000 ppm Ti + x ppm B) and (ZrO$_2$ + 1000 ppm Ti + x ppm Si) were 1.09 and 1.05 to (ZrO$_2$ + 1000 ppm Ti), respectively. Results for the (ZrO$_2$ + 1000 ppm Ti + x ppm M) phosphors (M = P, Sn and Se) are given in Fig. 4, which shows that maximal enhancement factors of 1.37, 1.31 and 1.15 are obtained for M = P (x = 4000), Sn (x = 500) and Se (x = 2000), respectively. In the (ZrO$_2$ + 1000 ppm Ti + 4000 ppm P) phosphor, which exhibits the strongest PL intensity (see Fig. 2), absorptivity, internal quantum efficiency and external quantum efficiency were estimated to be 53, 59 and 31% at room temperature, respectively. Further enhancement in PL intensity by the P addition to the (ZrO$_2$ + 1000 ppm Ti) phosphor may be explained on the analogy of electronic conduction mechanism proposed for the TiO$_2$–P$_2$O$_5$ glass, in which the Ti$^{3+}$ sites are increased by the co-existence of P [6,7]. Absorptivity, internal quantum efficiency and external quantum efficiency of the (ZrO$_2$ + 1000 ppm Ti + 4000 ppm P) phosphor were decreased with the increase of temperature: 30, 36 and 11% at 80 °C, and

![Fig. 3 - Effect of additive amount of Ti on the PL intensity of the (ZrO$_2$ + x ppm Ti) phosphors (x = 0–50,000). Excitation wavelength: 280 nm. Inserted italic values: maximal emission wavelength.](image)

![Fig. 4 - Effect of additive amount of P, Sn and Se on the PL intensity of the (ZrO$_2$ + 1000 ppm Ti + x ppm M) phosphors (M = P, Sn and Se). Excitation wavelength: 280 nm. Inserted italic values: maximal emission wavelength.](image)

![Fig. 5 - XPS wide spectrum (a) and P2p XPS spectrum (b) of the (ZrO$_2$ + 1000 ppm Ti + 4000 ppm P) phosphor.](image)
3, 10 and 0.3% at 150 °C, respectively. The XRD measurements were made for the (ZrO₂ + 1000 ppm TiO₂ + x ppm P) phosphors. Typical XRD pattern is shown for the (ZrO₂ + 1000 ppm Ti + 4000 ppm P) phosphor in Fig. 1(e). When x is 7000 ppm or less, the (ZrO₂ + 1000 ppm Ti + x ppm P) phosphors gave the XRD pattern similar to that of ZrO₂, as was also the case in the (ZrO₂ + 1000 ppm Ti) phosphor, suggesting that P atoms were dissolved into ZrO₂. The XRD peaks of ZrPO₄(OH) were observed, when x was 10,000 ppm or more. Fig. 5 shows XPS spectra of the (ZrO₂ + 1000 ppm Ti + 4000 ppm P) phosphor. No Ti2p peak was detected because the additive amount of Ti was small. Regarding the XPS spectra of phosphorus, Viswanathan and Pulikottil [8] reported that the P2p peak binding energies of P³⁺ and P⁵⁺ in Zeolite ZSM-5 are 130.2 eV and 135.9 eV, respectively, and Nakahira et al. [9] reported that P³⁺ and P⁵⁺ on the surface of P-doped TiO₂ film give the P2p peaks at 128.4 eV and 133 eV, respectively. From these reports, it is reasonable to suppose that the P2p peak at 133.87 eV for the (ZrO₂ + 1000 ppm Ti + 4000 ppm P) phosphor corresponds to P⁵⁺ (see Fig. 5(b)). Existence of P³⁺ was not recognized from the XPS measurement.

4. Conclusions

PL spectra of the ZrO₂:Ti phosphors (represented by (ZrO₂ + x ppm Ti) phosphors) prepared at 1400 °C in an air atmosphere were measured in the range of x = 0–50,000 ppm. Effects of the second additives (P, Sn, Se, B, Si, Al, Nb and Ta) were investigated. Results are summarized as follows:

1. The strongest PL intensity was obtained in the (ZrO₂ + 1000 ppm Ti) phosphor and its PL intensity was 5.4 time stronger that of pure ZrO₂.
2. Further enhancement of the PL intensity was observed by adding P, Sn, Se, B and Si to the (ZrO₂ + 1000 ppm Ti) phosphor. The addition of P was the most effective for the enhancement and maximal enhancement factor of 1.37 was obtained for the (ZrO₂ + 1000 ppm Ti + 4000 ppm P) phosphor.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgements

The authors appreciate the help received from Hamamatsu Photonics K.K. with data of quantum efficiencies.

References