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Luminescent properties of Pr doped $ZrSiO_4$ phosphors

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Abstract

Mixtures of ZrO_2, SiO_2, Pr_2O_3, and H_3BO_3 were fired at the temperature of 1150–1350 °C under H_2 atmosphere. A single phase $ZrSiO_4$:Pr phosphors could be achieved at the firing temperature above 1150 °C. Crystallinity and PL properties strongly depended on the flux amounts, firing temperature, and dopant concentrations. $ZrSiO_4$:Pr phosphors showed a strong red emission at 615 nm and a weak red emission at 622 nm with an excitation wavelength of 295 and 450 nm, respectively. Two sets of the emission bands and excitation spectra originated from Pr^{3+} ions at Zr and Si sites, respectively.

Keywords: A. Powders: solid-state reaction; C. Optical properties; D. Silicate; D. ZrO_2

1. Introduction

$ZrSiO_4$ has been widely investigated due to several physical properties of interest such as low thermal conductivity, high permittivity, high chemical stability, and high melting point. Also, it is a good refractory material with low thermal expansion coefficient and good thermal shock resistance [1–3].

$ZrSiO_4$ has two crystallographic phases of zircon and scheelite. It is reported that, at ambient pressure, $ZrSiO_4$ has a zircon structure, but converts into a scheelite structure at high pressure. Zircon phase related to our experiment is a body-centered tetragonal structure ($I4_1/amd$) composed of four $SiO_4{}^{4-}$ and four $ZrO_8{}^{12-}$ groups in a unit cell [4–6].

$ZrSiO_4$:RE (rare earth) ceramics have been well-known as pigments, which exhibit various colors according to RE ions. For example, blue, yellow, and pink pigments could be made by adding vanadium (V), praseodymium (Pr), and iron (Fe) in $ZrSiO_4$ crystal lattice, respectively [2,7]. Especially, Pr is a trivalent ion that has a tendency to become tetravalent. With the substitution of Pr for Zr, electrical neutrality is preserved and additional charge-balancing substitutions are not required [6–8].

However, luminescent properties of $ZrSiO_4$:RE were rarely investigated until now. Zircon's crystal chemistry strongly favors the incorporation of RE in Zr^{4+} site. And so the RE impurities easily become luminescent centers in a crystallographic environment of the host lattice [4].

In this experiment, $ZrSiO_4$:Pr powders were synthesized by solid-state reaction with H_3BO_3 as a flux under H_2 atmosphere. The effects of H_3BO_3, firing temperatures, and dopant concentrations on the synthesis and luminescent properties of $ZrSiO_4$:Pr were investigated.

2. Experimental procedure

ZrO_2 (TERIO, 99.9%), SiO_2 (High Purity Chemical, 99.9%), Pr_2O_3 (United International Inc., 99.9%), and H_3BO_3 (Aldrich, 99.99%) were used as raw materials. ZrO_2 and SiO_2 were mixed together by 1:1 mole ratio and H_3BO_3 was added as a flux. The mixture was ball-milled for 24 h and fired at 1150–1350 °C for 3 h under 5% H_2 atmosphere. Luminescent properties were investigated by changing flux amounts and dopant concentrations.

The crystalline phase of prepared powders was analyzed by XRD (X-ray diffractometer, SIEMENS D5005) using Cu Kα radiation ($\lambda = 1.5406$ Å). PL (Photoluminescence) properties were measured by PL (PSI Darsa 5000) system. Excitation source of PL was a Xe lamp and various excitation wavelengths were refracted by a monochromator.

3. Results and discussion

Since $ZrSiO_4$ is a high temperature material, it requires high firing temperature and/or long firing time [1,9]. To lower the

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firing temperature and shorten the duration time, in this experiment, H_3BO_3 was added as a flux into the mixture of ZrO_2 and SiO_2.

A flux method is well-known for a single-crystal growth and accelerates the kinetics of the formation of the desired compounds by enhancing diffusion coefficients. This method is very simple and easy to synthesize powders with desirable characteristics, including very fine size, narrow size distribution, single-crystal particles, high purity, and good chemical homogeneity [10]. For phosphors, it enables spherically shaped powders, leading to the enhancement of luminescent properties [11].

Fig. 1 shows XRD patterns of $ZrSiO_4$:Pr (1 mol%) powders with various amount of H_3BO_3 after firing at 1150 °C for 3 h under 5% H_2 gas. When H_3BO_3 was not added, only ZrO_2 and SiO_2 phases were observed, but $ZrSiO_4$ phase was not as shown in Fig. 1(a). By adding 5 wt% H_3BO_3, SiO_2 peaks disappeared, and $ZrSiO_4$ as well as ZrO_2 were observed as shown in Fig. 1(b), but the intensity of $ZrSiO_4$ XRD peaks were still very weak. With increasing the amount of H_3BO_3 more than 10 wt% in Fig. 1(c and d), ZrO_2 perfectly disappeared and a single phase $ZrSiO_4$ could be achieved. Consequently, we could verify that the adding a flux (H_3BO_3) had strong influence on the synthesis of $ZrSiO_4$ phase by the following mechanism.

H_3BO_3 transformed to B_2O_3 liquid phase by evaporating H_2O below the synthesizing temperature for $ZrSiO_4$ because of its low melting temperature of 186 °C. B_2O_3 liquid phase caused a strong fluxing action during firing the mixture of ZrO_2 and SiO_2, which enabled an increase in process flexibility and a drop in firing temperatures by accelerating the reaction of ZrO_2 and SiO_2. But an excess of H_3BO_3 can be the source for the undesired secondary phases and affect PL properties [10–12].

Excitation spectra of $ZrSiO_4$:Pr (1 mol%) fired at 1150 °C for 3 h with 10 wt% H_3BO_3 is shown in Fig. 2. Two excitation peaks were observed at 295 and 450 nm. Relative intensities of two excitation peaks were different depending on the emission peaks, 615 and 622 nm. The intensity of 295 nm excitation peak was stronger than that of 450 nm for 615 nm emission, but inverse relation to that for 622 nm. It was quite probable that the electronic configuration of Pr ion was a trivalent (Pr^{3+}), but not Pr^{4+}, because the firing process was carried under H_2 reduction atmosphere in this experiment. In addition, $ZrSiO_4:Pr^{4+}$ powders are well-known for the yellow ceramic pigments and non-radiative, but our samples were white powders emitting the red light.

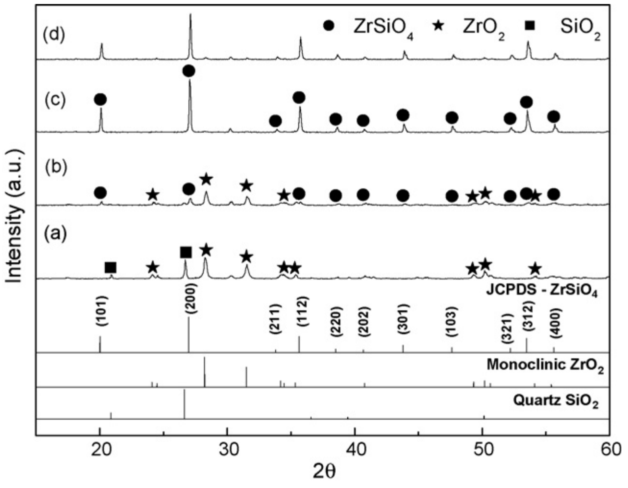

Fig. 1. XRD patterns of $ZrSiO_4$:Pr (1 mol%) powders fired at 1150 °C for 3 h under 5% H_2 atmosphere with various H_3BO_3 contents. (a) 0 wt%, (b) 5 wt%, (c) 10 wt%, and (d) 20 wt%.

Two excitation peaks implied that two activation centers coexisted in $ZrSiO_4$:Pr. Theoretically, a trivalent cation, Pr^{3+}, can be substituted not only for Zr, but also for Si sites. Andres et al. [13] reported that the substitution energy (ΔE) of Pr^{3+} for Zr^{4+} was −0.5748 a.u. (atomic units), and that for Si^{4+} was +0.0413 a.u., so Pr^{3+} preferred the substitution for Zr sites to Si ones. Nevertheless, the possibility of the substitutions of Pr^{3+} for Si sites could not be absolutely excluded. Conclusively, $ZrSiO_4:Pr^{3+}$ had two excitation peaks due to Pr^{3+} ions substituted for Zr and Si sites, which served as activation centers.

Two red emissions around 615 and 622 nm with the excitation wavelength of 295 and 450 nm are shown in Fig. 3, respectively. 615 nm emission was much stronger than 622 nm emission. It demonstrated that strong 615 nm and weak 622 nm emissions originated from Pr^{3+} at Zr and Si sites, respectively, because Pr^{3+} strongly favored Zr sites thermodynamically, but a little Si ones. Accordingly, two excitation peaks of 295 and 450 nm were attributed to Pr^{3+} ions at Zr and Si sites, respectively. For two red emissions, the energy of 615 and 622 nm emissions were 16260 and 16077 cm^{-1}, respectively, which were generated from the same energy transition of $^1D_2 \rightarrow {}^3H_4$ of Pr^{3+} ions [14,15]. The small difference between two emission wavelengths was ascribed to the different ligands surrounding each Pr^{3+} ion at Zr and Si site, leading to the distinctive crystal field. A similar case is reported for Pr doped Ln_2O_3 (Ln = Y, Sc, Gd) phosphors [16]. There are two crystallographically different cation sites in Ln_2O_3, and Pr^{3+} can occupy two distinct sites in Ln_2O_3, contributing to the existence of two sets of excitation and emission spectra due to two different luminescent centers.

The broad and weak greenish-blue emission band around 490 nm generated from $ZrSiO_4$ host material [17,18]. However,

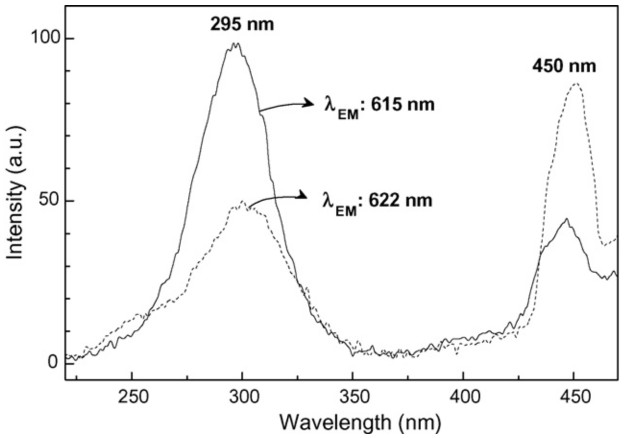

Fig. 2. Excitation spectra of $ZrSiO_4$:Pr (1 mol%) fired at 1150 °C for 3 h with 10 wt% H_3BO_3 under 5% H_2 atmosphere.

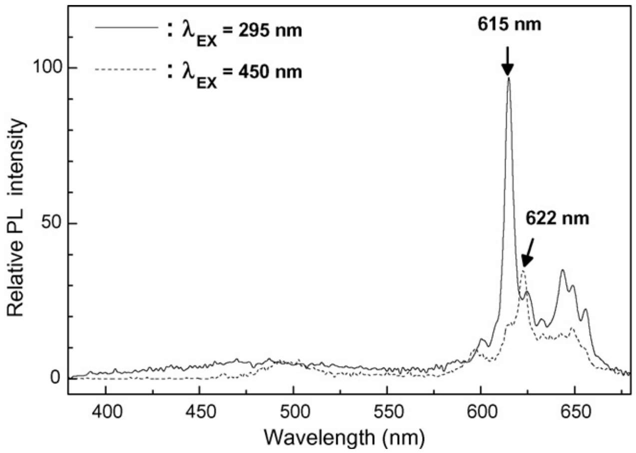

Fig. 3. PL spectra of $ZrSiO_4$:Pr (1 mol%) fired at 1150 °C for 3 h with 10 wt% H_3BO_3 under 5% H_2 atmosphere.

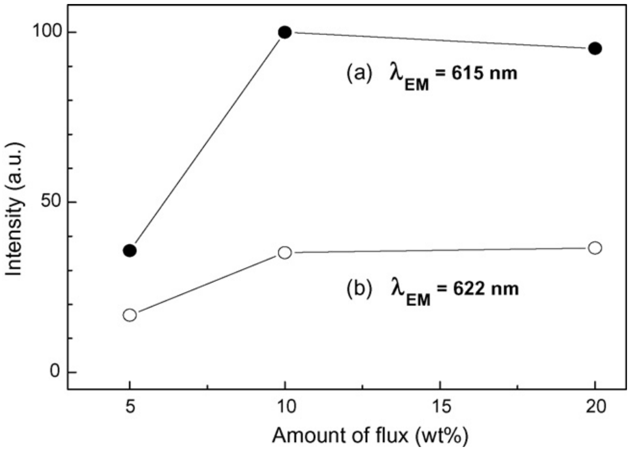

Fig. 4. PL intensity of 1 mol% Pr doped $ZrSiO_4$ fired at 1150 °C for 3 h with various H_3BO_3 amounts under 5% H_2 atmosphere. (a) $\lambda_{EX} = 295$ nm, ● and (b) $\lambda_{EX} = 450$ nm, ○.

the intensity was so weak that it did not affect PL properties of $ZrSiO_4$:Pr^{3+}.

Fig. 4 shows PL spectra of $ZrSiO_4$:Pr^{3+} powders fired at 1150 °C for 3 h with various amounts of flux. PL intensity increased with increasing flux amounts, but there was little difference between 10 and 20 wt% H_3BO_3. This meant that more than 10 wt% flux was not effective to enhance PL properties.

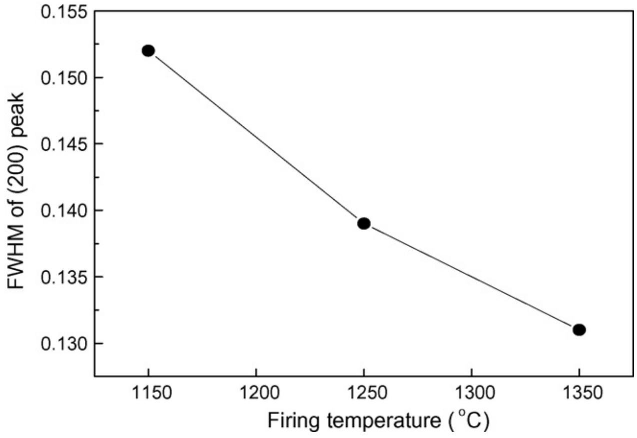

Fig. 5. FWMH of (2 0 0) peak of $ZrSiO_4$:Pr (1 mol%) fired for 3 h with 10 wt% H_3BO_3 as a function of firing temperatures under 5% H_2 atmosphere.

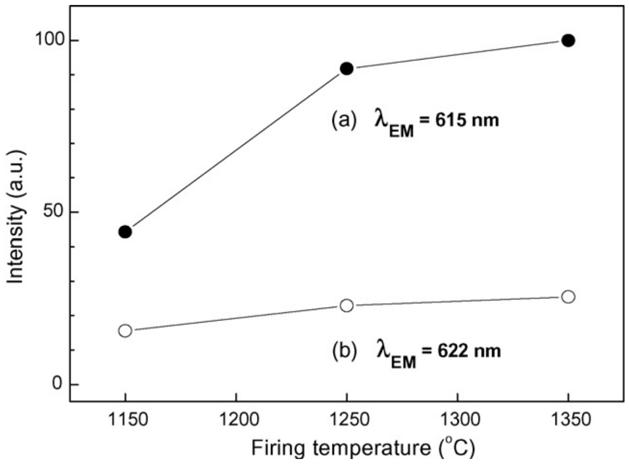

Fig. 6. PL intensity of 1 mol% Pr doped $ZrSiO_4$ with 10 wt% H_3BO_3 fired for 3 h as a function of firing temperatures under 5% H_2 atmosphere. (a) $\lambda_{EX} = 295$ nm, ● and (b) $\lambda_{EX} = 450$ nm, ○.

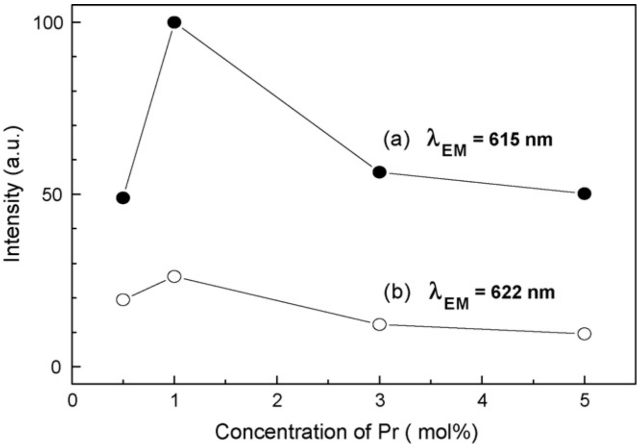

Fig. 7. PL intensity of Pr doped $ZrSiO_4$ with 10 wt% H_3BO_3 fired at 1350 °C for 3 h with various Pr contents. (a) $\lambda_{EX} = 295$ nm and (b) $\lambda_{EX} = 450$ nm.

Full width of half maximum (FWHM) of (2 0 0) peak as a function of the firing temperature is shown in Fig. 5. FWHM values decreased with increasing firing temperatures, and so the crystallinity was improved, leading to the enhancement of PL as shown in Fig. 6. PL intensity of $ZrSiO_4$:Pr (1 mol%) increased with increasing the firing temperature. This is in well accordance with FWHM values of XRD (2 0 0) peak in Fig. 5.

PL spectra of $ZrSiO_4$ fired at 1350 °C for 3 h with various Pr contents are shown in Fig. 7. PL intensity increased with increasing Pr concentrations, and then peaked at 1 mol%. At more than 1 mol%, PL decreased due to the concentration quenching effects.

4. Conclusion

Pr^{3+} doped $ZrSiO_4$ phosphors were synthesized by firing the mixture of ZrO_2, SiO_2, Pr_2O_3, and H_3BO_3 in 5% H_2

atmosphere. According to XRD data, a single phase of $ZrSiO_4$ was observed by firing at 1150 °C with more than 10 wt% H_3BO_3 as a flux. Pr^{3+} preferred the substitution for Zr sites to Si ones thermodynamically. Nevertheless, the possibility of the substitutions of Pr^{3+} for Si sites could not be absolutely excluded. Conclusively, $ZrSiO_4:Pr^{3+}$ had two excitation peaks due to Pr^{3+} ions substituted for Zr and Si sites, leading to two red emission bands at 615 and 622 nm. By comparing the relative intensity of two emission peaks, it could be confirmed that strong 615 nm emission originated from Pr^{3+} at Zr site, while weak 622 nm from Pr^{3+} at Si site. PL intensity strongly depended on the firing temperature, flux amounts, and the concentration of Pr ions.

Acknowledgement

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