Chemistry Letters Vol.38, No.11 (2009)

Synthesis of New Green-emitting Phosphors Based on Zirconium Oxide Phosphate

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New green-emitting phosphors, $Zr_2O(PO_4)_2$:x%Tb^{3+} ($1 \leq x \leq 10$), were synthesized in a single-phase form by a liquid-phase method and photoluminescence properties were characterized. The excitation spectrum consisted of a strong broad band from 220 to 290 nm, corresponding to the 4f–5d transition of Tb^{3+}. The phosphors exhibit typical emission peaks assigned to the transition from $^5D_4$ to ^7F_J ($J = 6, 5, 4$, and 3) of Tb^{3+}. The maximum peak intensity was obtained for $Zr_2O(PO_4)_2$:3%Tb^{3+}.

A number of rare-earth-doped materials have been widely studied for their applications as phosphors. It is well known that trivalent rare earth ions display sharp line emission spectra because the 4f-electrons are well shielded from the surroundings by the filled 5s and 5p orbitals. Among such trivalent rare earth ions, Tb^{3+} has been commonly employed as a green-emitting activator because of the efficient emission originated from the $^5D_4$–^7F_J ($J = 6$, 5, 4, and 3) transitions. For example, $LaPO_4$:Ce^{3+},Tb^{3+} has been widely applied in tricolor fluorescent lamps.[1]

In order to design new luminescent materials, it is significant to select the crystal structure thoughtfully. In previous work, we have reported red- and green-emitting phosphors based on hexagonal (type-II) rare earth oxycarbonates.[2–8] These oxycarbonate phosphors can show high emission intensity, due to the layer structure, in which the $(R_2O_2{}^{2+})_n$ layers (R: rare earths) are separated by carbonate groups ($CO_3{}^{2-}$ ions) in the direction of the c axis.[9] In this structure, energy transfer from an excited luminescent ion to another across the $CO_3{}^{2-}$ layer is inhibited, because of the long R^{3+}–R^{3+} distance. Accordingly, phosphors based on such a layer structure should be resistant to concentration quenching.

In the present study, we have focused on zirconium oxide phosphate, $Zr_2O(PO_4)_2$, as a host material of the phosphor. There are two different structures in $Zr_2O(PO_4)_2$; α-form (monoclinic $I2/m$)[10] and β-form (orthorhombic $Cmca$).[11] Among these two structures, the β-form is expected to be a suitable structure for phosphors, because it has a layer structure similar to that of the hexagonal rare earth oxycarbonates, in which the ZrO_7 polyhedron layers are separated by the PO_4 tetrahedron groups in the direction of the c axis.[10,12] The ZrO_7 coordination polyhedron is a slightly distorted pentagonal bipyramid with a mean Zr–O distance of 0.2147 nm,[11] and a part of the Zr^{4+} sites in the $Zr_2O(PO_4)_2$ lattice is substituted with Tb^{3+}. Furthermore, it has been elucidated in our laboratory that $Zr_2O(PO_4)_2$ has high thermal and chemical stabilities at high temperatures (up to 1600 °C) in air,[13] where it is advantageous for obtaining phosphor particles of high crystallinity. In this letter, therefore, new green-emitting phosphors based on β-$Zr_2O(PO_4)_2$:x%Tb^{3+} ($1 \leq x \leq 10$) have been synthesized by a liquid-phase method, and the photoluminescence properties have been characterized.

An aqueous solution of 0.5 mol L^{-1} $(NH_4)_2HPO_4$ was added dropwise to a stoichiometric mixture of 1.0 mol L^{-1} aqueous $ZrOCl_2 \cdot 8H_2O$ and 0.1 mol L^{-1} aqueous $Tb(NO_3)_3 \cdot 6H_2O$ solutions, in which the amount of Tb^{3+} was adjusted between 1 and 10%. After stirring at 80 °C for 12 h, the solvent water was evaporated at 130 °C, and the solid residue was dried at 80 °C for 12 h. The resultant powder was first calcined at 800 °C for 9 h and then at 1000 °C for 12 h in air. After calcination, the sample was reground in a mortar and heated again at 1300 °C for 12 h in air.

The samples were characterized by X-ray powder diffraction (XRD; Rigaku Multiflex) to identify the crystal structure, and the sample composition was analyzed by X-ray fluorescence spectroscopy (XRF; Rigaku ZSX100e). Photoluminescence (PL) excitation and emission spectra were measured at room temperature with a spectrofluorophotometer (Shimadzu RF-5300PC), where the emission spectra were obtained for excitation at 254 nm, and the excitation spectra were recorded for the emission peak at 543 nm.

Figure 1 shows the XRD patterns of $Zr_2O(PO_4)_2$:3%Tb^{3+} synthesized at 1000 and 1300 °C. The sample obtained by calcination at 1000 °C resulted in a two-phase mixture of α-$Zr_2O(PO_4)_2$ and NASICON-type[14] phosphate. In contrast, the XRD pattern of the sample synthesized at 1300 °C is in good agreement with that of the single-phase β-$Zr_2O(PO_4)_2$ structure with high crystallinity, and no diffraction peaks evident of impurities are present in this pattern. All of the samples calcined at 1300 °C were confirmed to be single β-phase by the XRD measurements. In addition, it is reasonable to consider that the charge compensation is achieved by the formation of oxide anion defects in the β-$Zr_2O(PO_4)_2$ lattice, because the formal valences of the Zr and Tb ions are 4+ and 3+, respectively.

Figure 2 depicts the photoluminescence excitation and emission spectra of the β-$Zr_2O(PO_4)_2$:3%Tb^{3+} phosphor synthesized

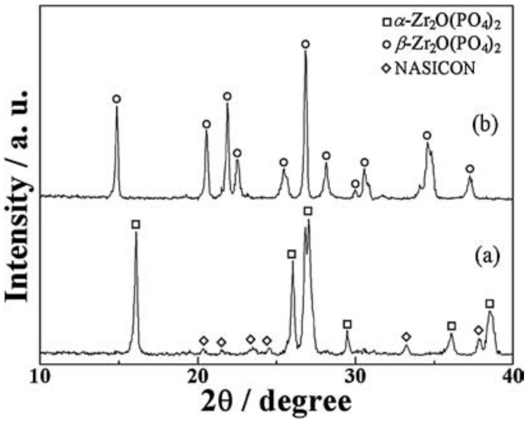

Figure 1. X-ray powder diffraction patterns of $Zr_2O(PO_4)_2$: 3%Tb^{3+} synthesized at 1000 (a) and 1300 °C (b).

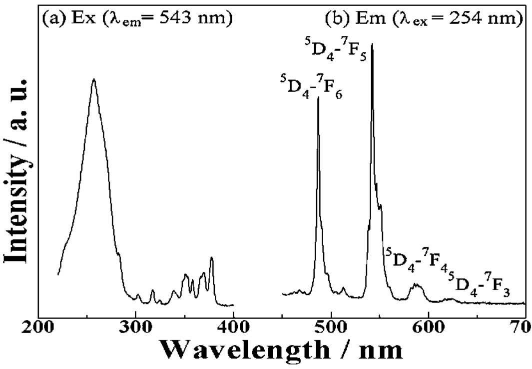

Figure 2. Photoluminescence excitation (a) and emission (b) spectra of the β-$Zr_2O(PO_4)_2$:3%Tb^{3+} phosphor.

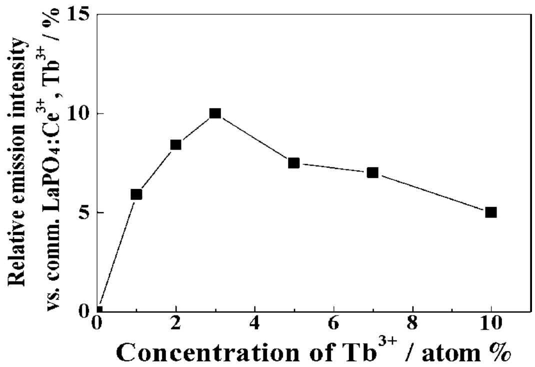

Figure 3. Dependence of the emission intensity on the Tb^{3+} concentration in the β-$Zr_2O(PO_4)_2$:x%Tb^{3+} ($1 \leq x \leq 10$) phosphors. The excitation wavelength is 254 nm for both β-$Zr_2O(PO_4)_2$:x%Tb^{3+} and $LaPO_4$:Ce^{3+},Tb^{3+}.

at 1300 °C. The excitation spectrum consists of a strong broad band from 220 to 290 nm, which corresponds to the energy transition from the $4f^8$ to $4f^7 5d$ configuration of Tb^{3+}. Some small peaks between 300 and 400 nm correspond to the 4f–4f transition of Tb^{3+}. This β-$Zr_2O(PO_4)_2$:3%Tb^{3+} phosphor exhibits a well-known characteristic Tb^{3+} ion emission under excitation at 254 nm, and no self-activated emission is observed in the undoped sample. The emission peaks at 487, 543, 586, and 620 nm correspond to the transition from the $^5D_4$ excited level to $^7F_6$, $^7F_5$, $^7F_4$, and $^7F_3$ ground levels of Tb^{3+}, respectively.

The dependence of the emission intensity on the Tb^{3+} concentration in the β-$Zr_2O(PO_4)_2$:x%Tb^{3+} ($1 \leq x \leq 10$) phosphors is shown in Figure 3. The luminescent intensity increases with the amount of Tb^{3+} until it reaches a maximum and then decreases due to concentration quenching. The maximum emission was obtained at a composition of β-$Zr_2O(PO_4)_2$:3%Tb^{3+}, where the relative intensity was 10% compared to that of a commercial $LaPO_4$:Ce^{3+},Tb^{3+} phosphor.

As mentioned above, the critical Tb^{3+} concentration is 3%, above which concentration quenching of the luminescence occurs. Since the concentration quenching is caused by energy transfer from one activator to another until an energy sink in the lattice is reached, there is a critical energy-transfer distance between Tb^{3+} ions in β-$Zr_2O(PO_4)_2$:x%Tb^{3+} that yields the highest emission intensity. The critical energy-transfer distance (R_c) in phosphors, in which the activator is introduced solely on the zirconium ion sites in the present case, can be estimated approximately using the following equation:[15]

$$R_c = 2\left(\frac{3V}{4\pi x_c N}\right)^{\frac{1}{3}} \qquad (1)$$

where V is the volume of the unit cell, x_c is the critical concentration of Tb^{3+}, and N is the total number of zirconium and terbium ions in the β-$Zr_2O(PO_4)_2$ lattice. The critical energy-transfer distances of Tb^{3+} in β-$Zr_2O(PO_4)_2$:3%Tb^{3+} is calculated using the experimental and analytical values of V (0.6852 nm^3), x_c (0.03), and N (8), and the R_c value is estimated to be 1.76 nm. This is almost equivalent to that found in $CsYP_2O_7$:5%Tb^{3+} (1.9 nm), in which a weak concentration quenching is observed due to the relatively long distance between Tb^{3+} ions.[16]

In summary, new green-emitting phosphors based on zirconium oxide phosphate were synthesized by a liquid-phase method. The samples obtained in the present study have the stable β-$Zr_2O(PO_4)_2$ structure in a single phase with high crystallinity. The photoluminescence spectra showed emissions from the $^5D_4$ exited state to the ^7F_J ground states of Tb^{3+}, and the emission reached the maximum intensity for the $Zr_2O(PO_4)_2$:3%Tb^{3+} composition. Although the emission intensity of this phosphor is not sufficient at the present stage, improvement of the optical properties is expected by optimization of the preparation and modification of the crystal field around the Tb^{3+} ions by doping different cations in the Zr^{4+} ion site.

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