

Title Synthesis and photoluminescence properties of Mn^{2+} co-doped white emitting $(\text{Sr},\text{Sn})\text{ZnP}_2\text{O}_7$ phosphor

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Rare earth-free white emitting $(\text{Sr},\text{Sn})(\text{Zn},\text{Mn})\text{P}_2\text{O}_7$ phosphors were synthesized in a single phase form by a conventional solid-state reaction method and photoluminescent properties were characterized. These phosphors showed three broad band in emission spectra at 340, 440, and 690 nm, and the ratio of emission intensity between blue-green light and red light changes with Mn^{2+} content increasing because of energy transfer from Sn^{2+} to Mn^{2+} . The emission color of the phosphors varied from blue-white to orange-white with the increase in the Mn^{2+} content and the emission color of the $(\text{Sr}_{0.90}\text{Sn}_{0.10})(\text{Zn}_{0.97}\text{Mn}_{0.03})\text{P}_2\text{O}_7$ phosphor was very close to white light.

Key words: Rare earth free phosphor, White emission, SrZnP_2O_7 .

Introduction

Rare earth doped phosphors have been widely used in various optical devices as a light source due to their high luminescence efficiency and high emission color purity. However, rare earth elements are very expensive compared with another metal elements, because rare earth supply was limited all over the world. Therefore, many investigations have been devoted to search for new phosphor material without rare earth ions.

Recently, transition metal ions have been widely investigated as a luminescence ion an alternative to rare earth ions. In particular, Mn^{2+} ion has attracted much attention as luminescence ion because Mn^{2+} -doped phosphors show wide-ranging emission, from 500 to 700 nm, depending on the crystal field of the host materials [1-3]. However, the luminescent efficiency with the direct excitation due to the d-d transition of Mn^{2+} is not sufficient because the d-d transition of Mn^{2+} is the spin-forbidden transitions [4, 5]. Therefore, Mn^{2+} -doped phosphors were generally co-doped with rare earth ions, mainly Ce^{3+} and Eu^{2+} which have high efficiency for both excitation and emission to enhance the emission efficiency by the energy transfer from the rare earth ions to Mn^{2+} ion. On the other hand, ns^2 -type transition metal ions, such as Ga^+ , In^+ , Tl^+ , Sn^{2+} , and Pb^{2+} , doped phosphors show suitable broad emission band by the direct excitation [6, 7]. It is well known that the ns^2 -type transition metal ions doped phosphors present four absorption bands, and the three lower

bands are called A, B, and C bands in the order of increasing energy, which have been attributed to inter-ionic transitions from the $^1\text{S}_0$ ground state to the $^3\text{P}_1$ (spin-orbit allowed), $^3\text{P}_2$ (vibrationally allowed), and $^1\text{P}_1$ (dipole allowed) excited states of the ns^2 -type transition metal ions, respectively [8, 9], and the higher absorption band (D band) is usually ascribed to a charge transfer transition [10, 11]. Therefore, the photoluminescence of compounds containing metal ions with ns^2 -type configuration can be used in fluorescent lamp, low pressure Hg lamps, and X-ray imaging devices.

Among them, in this study, we focused on divalent Sn^{2+} ion as a luminescence ion to realize a rare earth free white emitting phosphor with high luminescent efficiency. The Sn^{2+} -doped phosphors have been previously used in fluorescent mercury lamps as a commercial phosphor materials [4-6]. In addition, it is well known that Sn^{2+} -doped phosphors showed strong broad emission band in wide-ranging wavelength from 330 to 680 nm [5, 12], which indicates that Sn^{2+} ion is expected to be a luminescence ion for the white emitting phosphors. Furthermore, we focused on strontium zinc pyrophosphate, SrZnP_2O_7 , as a host material of phosphors. The crystalline form of strontium zinc pyrophosphate adopts a monoclinic structure with a space group of $P2_1/n$ [13-15]. In the crystal structure, the P_2O_7 groups all fall on 3-fold axes with the bridging oxygen ions on inversion centers and Zn^{2+} shows a square-pyramidal coordinated with five oxygen atoms, and ZnO_5 and P_2O_7 build a three-dimensional framework with channels, and the Sr^{2+} ions occupy the channels surrounded by eight oxygen atoms, as illustrated in Figure 1. In addition, the ionic radius of Sr^{2+} (0.126 nm for 8 coordination [17]) is similar to that of Sn^{2+} (0.123 nm for 8 coordination

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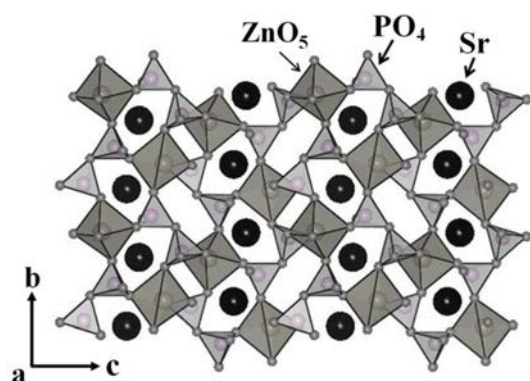


Fig. 1. Crystal structure of monoclinic SrZnP_2O_7 [16].

[17]), which indicates that Sn^{2+} can be easily substituted into the Sr^{2+} site in the SrZnP_2O_7 lattice to form solid solutions. Furthermore, it is possible to modify the luminescence properties by doping different cations in the Zn^{2+} ion site.

In this paper, therefore, rare earth free white-emitting $(\text{Sr},\text{Sn})\text{ZnP}_2\text{O}_7$ phosphors were synthesized and the photoluminescent properties were characterized. Furthermore, partial substitution of the Zn^{2+} site with Mn^{2+} was carried out to improve the luminescence efficiency.

Experimental

$(\text{Sr}_{1-x}\text{Sn}_x)(\text{Zn}_{1-y}\text{Mn}_y)\text{P}_2\text{O}_7$ ($0.01 \leq x \leq 0.10$, $0 \leq y \leq 0.05$) phosphors were synthesized by the conventional solid-state reaction method. SrCO_3 , ZnO , $\text{NH}_4\text{H}_2\text{PO}_4$, SnO , and MnCO_3 were mixed in a stoichiometric ratio using a mortar with acetone for obtaining a homogeneous chemical mixture. The mixture was pressed into pellets and calcined at 980°C for 12 hrs in a flow of pure N_2 gas, and then the samples were reground in a mortar.

The crystal structure of the samples was identified by X-ray powder diffraction (XRD; Mac Science Ltd. MX-Labo) analysis. The emission (PL) and excitation (PLE) spectra were measured at room temperature with a spectrofluorometer (Jasco Corp. FP-6500/6600), where the emission spectrum was obtained for excitation at 254 nm, and excitation spectrum was obtained for emission at 330 nm. The Commission International de l'Eclairage (CIE) chromaticity coordinate data for the phosphors were measured at room temperature with a luminescence colorimeter (Hamamatsu C7473-36 PMA-11).

Results and Discussion

The X-ray powder diffraction (XRD) patterns of the $(\text{Sr}_{1-x}\text{Sn}_x)\text{ZnP}_2\text{O}_7$ ($0.01 \leq x \leq 0.10$) phosphors were in good agreement with a single phase of high crystalline monoclinic SrZnP_2O_7 structure. Photoluminescence excitation and emission spectra of the $(\text{Sr}_{1-x}\text{Sn}_x)\text{ZnP}_2\text{O}_7$ ($0.01 \leq x \leq 0.10$) phosphors are shown in Figure 2. The

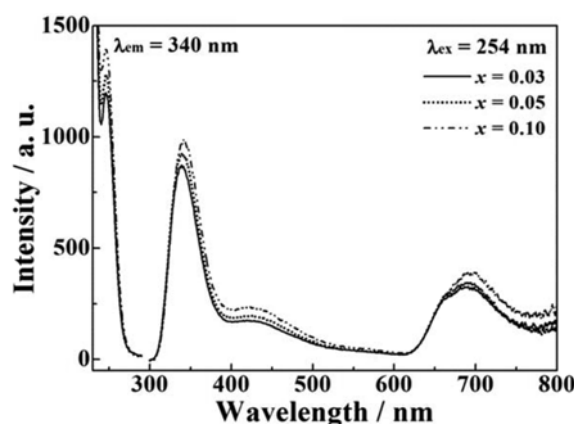


Fig. 2. Photoluminescence excitation and emission spectra of the $(\text{Sr}_{1-x}\text{Sn}_x)\text{ZnP}_2\text{O}_7$ ($0.03 \leq x \leq 0.10$) phosphors.

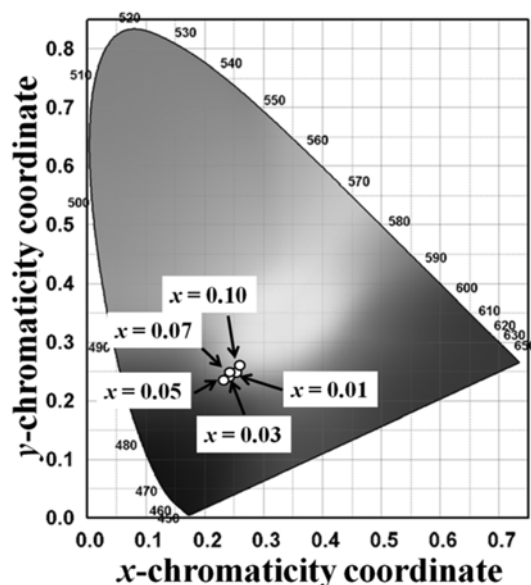


Fig. 3. CIE chromaticity diagram for the $(\text{Sr}_{1-x}\text{Sn}_x)\text{ZnP}_2\text{O}_7$ ($0.01 \leq x \leq 0.10$) phosphors.

emission spectra of all samples consists of three broad peaks at 340, 440, and 690 nm, corresponding to the transition from the $^3\text{P}_J$ ($J = 1$ and 0) excited level to $^1\text{S}_0$ ground level of Sn^{2+} [12]. In addition, the emission peak intensity increased by the increases in the amount of Sn^{2+} , and highest emission peak intensity was obtained for $(\text{Sr}_{0.90}\text{Sn}_{0.10})\text{ZnP}_2\text{O}_7$. The CIE chromaticity coordinate values for the $(\text{Sr}_{0.90}\text{Sn}_{0.10})\text{ZnP}_2\text{O}_7$ phosphor were $x = 0.26$ and $y = 0.26$ under excitation at 254 nm UV light (Fig. 3) and this phosphor showed blue-white light emission.

In order to improve the luminescence properties of the $(\text{Sr}_{0.90}\text{Sn}_{0.10})\text{ZnP}_2\text{O}_7$ phosphor, Mn^{2+} was doped into the Zn^{2+} site in the host SrZnP_2O_7 lattice. Figure 4 shows XRD patterns of the $(\text{Sr}_{0.90}\text{Sn}_{0.10})(\text{Zn}_{1-y}\text{Mn}_y)\text{P}_2\text{O}_7$ ($0 \leq y \leq 0.05$) phosphors. The XRD patterns of all samples were in good agreement with a single phase of highly crystalline monoclinic SrZnP_2O_7 structure, and no diffraction peaks evident of impurities are present in

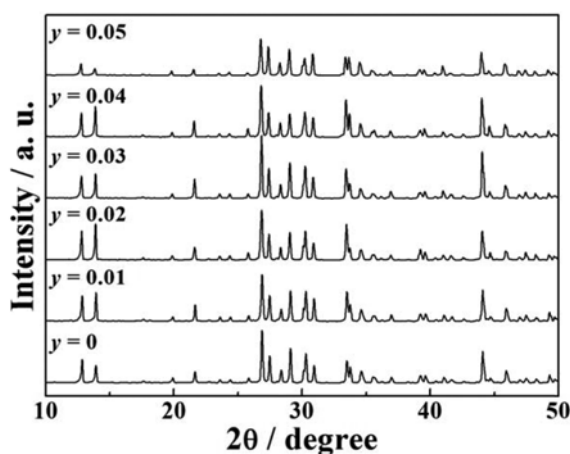


Fig. 4. XRD patterns of the $(\text{Sr}_{0.90}\text{Sn}_{0.10})(\text{Zn}_{1-y}\text{Mn}_y)\text{P}_2\text{O}_7$ ($0 \leq y \leq 0.05$) phosphors.

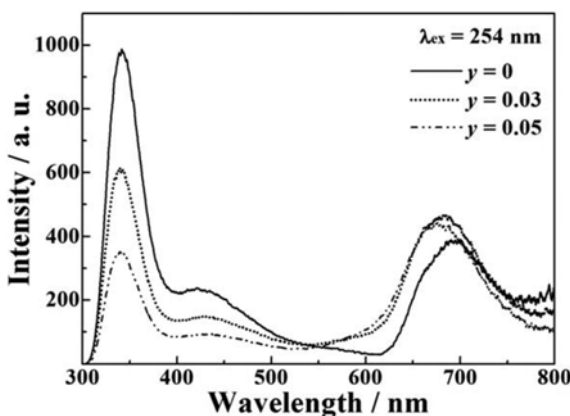


Fig. 5. Photoluminescence emission spectra of the $(\text{Sr}_{0.90}\text{Sn}_{0.10})(\text{Zn}_{1-y}\text{Mn}_y)\text{P}_2\text{O}_7$ ($0 \leq y \leq 0.05$) phosphors.

the XRD patterns. In addition, Zn^{2+} ion has an ionic radius of 0.068 nm for 5 coordination [17], while Sr^{2+} ion has an ionic radius of 0.126 nm for 8 coordination [17]. Therefore, in the case of present phosphors, the doping Mn^{2+} ions preferably occupy the Zn^{2+} site in the host SrZnP_2O_7 lattice, because the ionic radius of Mn^{2+} (0.075 nm for 5 coordination and 0.096 nm for 8 coordination [17]) is similar to that of Zn^{2+} (0.068 nm) which is much smaller than that of the Sr^{2+} ion (0.126 nm).

Figure 5 illustrates the emission spectra of the $(\text{Sr}_{0.90}\text{Sn}_{0.10})(\text{Zn}_{1-y}\text{Mn}_y)\text{P}_2\text{O}_7$ ($0 \leq y \leq 0.05$) phosphors under excitation wavelength at 254 nm. In the emission spectra, the emission peak intensity at 690 nm was effectively enhanced by Mn^{2+} doped into the host lattice, while the emission peak intensity at 340 and 440 nm decreased, which can be explained by the energy transfer from Sn^{2+} to Mn^{2+} . It is well known that the Sn^{2+} emission band in blue to green regions overlaps the excitation band of Mn^{2+} [18–20] and the increase of peak intensity at 690 nm by the Mn^{2+} doping was attributed to the red emission due to the $^4\text{T}_{1g}(4\text{G}) \rightarrow ^6\text{A}_{1g}(^6\text{S})$ transition of Mn^{2+} .

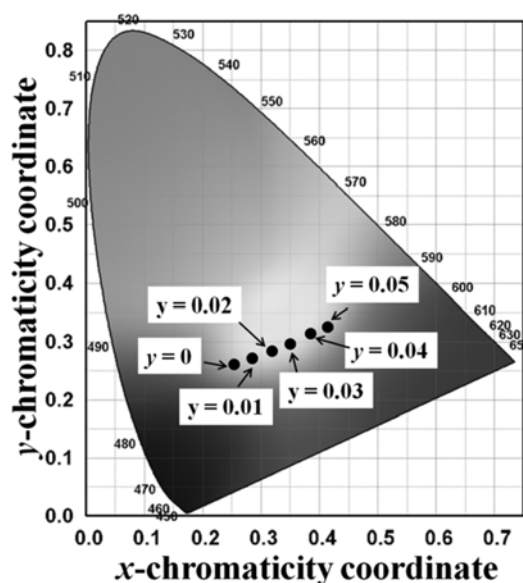


Fig. 6. CIE chromaticity diagram for the $(\text{Sr}_{0.90}\text{Sn}_{0.10})(\text{Zn}_{1-y}\text{Mn}_y)\text{P}_2\text{O}_7$ ($0 \leq y \leq 0.05$) phosphors.

Furthermore, the emission peak wavelength at 690 nm shifts to the shorter wavelength side with increasing Mn^{2+} content in the phosphors, which can be attributed to the change of the crystal field strength around Mn^{2+} in the host lattice. The crystal field strength decreases with increasing the amount of Mn^{2+} in the host SrZnP_2O_7 lattice due to lattice expansion, because Zn^{2+} (ionic radius: 0.068 nm for 5 coordination [17]) in the host material is partially substituted with the larger Mn^{2+} (ionic radius: 0.075 nm for 5 coordination [17]) to form solid solutions (Fig. 3).

As previous studies, they are reported that the red-emission of Mn^{2+} in strontium zinc phosphate is attributed to the $^4\text{T}_{1g}(4\text{G}) \rightarrow ^6\text{A}_{1g}(^6\text{S})$ transition of Mn^{2+} located on Sr^{2+} site in the host lattice [21, 22], because Sr^{2+} ions site is surrounded by eight oxygen atoms, while Zn^{2+} shows a square-pyramidal coordinated with five oxygen atoms (ZnO_5) in the crystal structure (Fig. 1). From the viewpoint of ionic radius, however, it is considered that the Mn^{2+} ion was hard to substitute into the Sr^{2+} site in these crystal structure, because the ionic radius of Mn^{2+} (0.096 nm for 8 coordination [17]) was much smaller than that of the Sr^{2+} (0.126 nm for 8 coordination [17]). It is well known that Mn^{2+} gives a green or red emission in a lot of inorganic materials, and the wavelength position of the emission bands is significantly dependent on the crystal structure of host material. For tetrahedrally coordinated Mn^{2+} , it generally exhibits a green emission [23], whereas it shows a yellow to red emission for octahedrally coordinated Mn^{2+} [24, 25]. However, in the case of the $(\text{Sr}_{0.90}\text{Sn}_{0.10})(\text{Zn}_{1-y}\text{Mn}_y)\text{P}_2\text{O}_7$ ($0 \leq y \leq 0.05$) phosphors, the emission peak intensity at 690 nm was effectively enhanced by Mn^{2+} doping into the host lattice, while the emission peak intensity at 340 and 440 nm was decreased, although Mn^{2+} is substituted into

the Zn^{2+} site in the host SrZnP_2O_7 lattice. This is considered that the ZnO_5 unit may exist as distorted ZnO_6 octahedron form in the $(\text{Sr}_{0.90}\text{Sn}_{0.10})(\text{Zn}_{1-y}\text{Mn}_y)\text{P}_2\text{O}_7$ lattice. However, unfortunately, we do not have any direct evidence to explain the doping site of Mn^{2+} in the $(\text{Sr}_{0.90}\text{Sn}_{0.10})(\text{Zn}_{1-y}\text{Mn}_y)\text{P}_2\text{O}_7$ lattice. Therefore, further studies are necessary to unveil the doping site of Mn^{2+} from a structure point of view.

Figure 6 presents the CIE chromaticity diagram for the $(\text{Sr}_{0.90}\text{Sn}_{0.10})(\text{Zn}_{1-y}\text{Mn}_y)\text{P}_2\text{O}_7$ ($0 \leq y \leq 0.05$) phosphors under excitation at 254 nm UV light. With Mn^{2+} content increasing, the ratio of emission intensity between blue-green light and red light changes because of energy transfer from Sn^{2+} to Mn^{2+} . As a result, the CIE chromaticity coordinate values change from ($x = 0.26$, $y = 0.26$) to ($x = 0.42$, $y = 0.32$) for $y = 0$ and $y = 0.05$, respectively, and the emission color of the phosphors varied from blue-white to orange-white. The emission color of the $(\text{Sr}_{0.90}\text{Sn}_{0.10})(\text{Zn}_{0.97}\text{Mn}_{0.03})\text{P}_2\text{O}_7$ phosphor with $y = 0.03$ is very close to white light and the CIE chromaticity coordinate values for the phosphor were $x = 0.35$ and $y = 0.29$ under excitation at 254 nm UV light, which is close to the standard white chromaticity ($x = 0.33$, $y = 0.33$) for the NTSC system.

Conclusions

Rare earth free white emitting $(\text{Sr}_{1-x}\text{Sn}_x)(\text{Zn}_{1-y}\text{Mn}_y)\text{P}_2\text{O}_7$ ($0.01 \leq x \leq 0.10$, $0 \leq y \leq 0.5$) phosphors were synthesized by the conventional solid-state reaction method. The phosphors obtained in this study adopt the monoclinic SrZnP_2O_7 structure and consist of a single phase with high crystallinity. These phosphors showed three broad band in emission spectra at 340, 440, and 690 nm, and the ratio of emission intensity between blue-green light and red light changes with Mn^{2+} content increasing because of energy transfer from Sn^{2+} to Mn^{2+} . The emission color of the samples phosphors varied from blue-white to orange-white with the increase in the Mn^{2+} content and the emission color of the $(\text{Sr}_{0.90}\text{Sn}_{0.10})(\text{Zn}_{0.97}\text{Mn}_{0.03})\text{P}_2\text{O}_7$ phosphor is very close to white light.

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