

Luminescence properties of $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{Mn}^{2+}$ phosphor and the improvement by co-doping Bi^{3+}

Renping Cao^{a,*}, Wudi Wang^a, Jinlong Zhang^a, Yujiao Ye^a, Ting Chen^a, Siling Guo^a, Fen Xiao^b, Zhiyang Luo^b

^a College of Mathematics and Physics, Jingtangshan University, Ji'an, 343009, China

^b College of Mechanical Manufacture and Automation, Jingtangshan University, Ji'an, 343009, China



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ABSTRACT

$\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{R}$ ($\text{R} = \text{Bi}^{3+}$, Mn^{2+} , and $\text{Bi}^{3+}/\text{Mn}^{2+}$) phosphors are synthesized by a solid-state reaction method in air. $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{Bi}^{3+}$ phosphor with excitation 380 nm shows blue light and its emission band peaking at ~445 nm is observed. Under excitation at 355 and 416 nm, $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{Mn}^{2+}$ phosphor shows red emission with a single broad emission band peaking at ~630 nm in the range of 500–800 nm owing to the ${}^4\text{T}_1(\text{G}) \rightarrow {}^6\text{A}_1$ transition of the Mn^{2+} ion. The optimal Mn^{2+} ion content in $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{Mn}^{2+}$ phosphor is ~0.05 and the lifetime of $\text{Sr}_2\text{Mg}_{2.95}\text{P}_4\text{O}_{15}:0.05\text{Mn}^{2+}$ phosphor is ~6.17 ms. After Bi^{3+} ion is co-doped, emission intensity of $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{Mn}^{2+}$ phosphor can be enhanced obviously due to energy transfer (ET) from Bi^{3+} to Mn^{2+} , which is confirmed by the luminescence properties and lifetimes of $\text{Sr}_2\text{Mg}_{3-x}\text{P}_4\text{O}_{15}:\text{Bi}^{3+}$, Mn^{2+} phosphor. Luminous mechanism and ET process of $\text{Sr}_2\text{Mg}_{3-x}\text{P}_4\text{O}_{15}:\text{Bi}^{3+}$, Mn^{2+} phosphor are explained by the simple energy level diagram of Bi^{3+} and Mn^{2+} ions.

1. Introduction

The solid-state lighting sources based on white light emitting diodes (W-LEDs) fabricated using blue and/or near ultraviolet (UV) LED chips coated with phosphors have been widely studied in recent years owing to the high luminous efficiency, environmental friendliness, long lifetime, energy saving and small volume [1–5]. Typically, the W-LEDs products are generated by two methods in order to obtain good white light: a combination of an UV LED chip coated with red, green, and blue tricolor phosphors, and a combination of a GaN-based blue LED chip with $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG:Ce) yellow phosphor [6–9]. So, luminescence properties of phosphors are one of important influence factors to applications of W-LEDs. Host materials and activators are two important influence factors to phosphors.

Phosphate compounds have been used as host materials of phosphors for many years due to their easy synthesis, low material cost, and excellent stability [10,11]. $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$ as a phosphate was first researched in the system of $\text{SrO}-\text{MgO}-\text{P}_2\text{O}_5$ by Hoffman [12]. $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$ is used as host of phosphors has also been investigated, such as $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{Eu}^{2+}$ and $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{Eu}^{2+}$, Mn^{2+} , which are synthesized in reducing atmosphere [13–15]. The special electronic structure of Mn^{2+} ions enables them to show green, yellow, orange or red broadband emission, depending on the influence of the host

materials crystal field [16–18]. In order to improve the luminescence properties of phosphors, energy transfer (ET) is usually a good method [19–21]. Here, we research the luminescence properties improvement of $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{Mn}^{2+}$ phosphor by ET between Bi^{3+} and Mn^{2+} ions when Bi^{3+} ion is co-doped.

In this work, a series of $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{R}$ ($\text{R} = \text{Mn}^{2+}$, Bi^{3+} , and $\text{Bi}^{3+}/\text{Mn}^{2+}$) phosphors are synthesized by a high temperature solid-state reaction method in air. The crystal structures, fluorescence lifetimes, and luminescence properties are investigated. The dependence of emission intensity on Mn^{2+} ion concentration is discussed. ET between Bi^{3+} and Mn^{2+} ions in $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{Bi}^{3+}$, Mn^{2+} phosphor is investigated by spectrum. Luminous mechanism and ET process are explained by the simple energy level diagrams of Bi^{3+} and Mn^{2+} ions.

2. Experimental section

2.1. Raw materials

The raw materials are SrCO_3 (99.9%, Aladdin chemical), MgO (99.5%, Aladdin chemical), $\text{NH}_4\text{H}_2\text{PO}_4$ (99.5%, Aladdin chemical), MnCO_3 (99.9%, Aladdin chemical), and Bi_2O_3 (99.9%, Aladdin chemical), which are used directly to prepare the samples without further purification.

* Corresponding author.

E-mail address: jxcrp@163.com (R. Cao).

2.2. Samples synthesis

$\text{Sr}_2\text{Mg}_{3-x}\text{P}_4\text{O}_{15}:\text{xMn}^{2+}$ ($x = 0, 1, 2, 3, 4, 5,$ and 6 mol%), $\text{Sr}_{1.96}\text{Mg}_3\text{P}_4\text{O}_{15}:0.04\text{Bi}^{3+}$, and $\text{Sr}_{2-y}\text{Mg}_{2.95}\text{P}_4\text{O}_{15}:0.05\text{Mn}^{2+}, \text{yBi}^{3+}$ ($y = 2, 4,$ and 6 mol%) phosphors are synthesized by a solid-state reaction method in air. All synthesis conditions are the same. The synthesis process is as follows:

The raw materials are weighed accurately $5\text{ g} \rightarrow$ ground for 15 min in an agate mortar \rightarrow placed in a crucible \rightarrow heated in air at $650\text{ }^\circ\text{C}$ for $4\text{ h} \rightarrow$ reground for $15\text{ min} \rightarrow$ sintered at $1050\text{ }^\circ\text{C}$ for $5\text{ h} \rightarrow$ cooled to room temperature \rightarrow The products are obtained.

2.3. Characterization

X-ray powder diffractions (XRD) of the samples are measured using XRD powder diffractometer (Philips Model PW1830) with $\text{Cu-K}\alpha$ radiation at 40 kV and 40 mA to identify the crystal phase. The XRD patterns data are collected in the 2θ range of $10\text{--}90^\circ$ at room temperature. Luminescence properties as well as decay curves of the samples are investigated by using a steady-state FLS980 spectrofluorimeter (Edinburgh Instruments, UK, Edinburgh) with a high spectral resolution (signal to noise ratio $> 12000:1$) at room temperature. A 450 W ozone free xenon lamp is used as the excitation source for steady-state spectrum measurement. A microsecond pulsed xenon flash lamp μF900 with an average power of 60 W is available to record the decay curves for lifetimes.

3. Results and discussion

The crystal structures and the phase purity of phosphors are characterized by powder X-ray diffraction in the experiment. As representatives, only the XRD patterns of $\text{Sr}_2\text{Mg}_{3-x}\text{P}_4\text{O}_{15}:\text{xMn}^{2+}$ ($x = 0, 3,$ and 6 mol%) and $\text{Sr}_{1.94}\text{Mg}_{2.95}\text{P}_4\text{O}_{15}:0.05\text{Mn}^{2+}, 0.06\text{Bi}^{3+}$ phosphors are shown in Fig. 1. All the XRD diffraction peaks of the samples are found to match well with that of joint committee on powder diffraction standards (JCPDS) no. 21–964. We do not observe other XRD peaks derived from the impurity phase or starting materials. So, we confirm that the doping Mn^{2+} ions does not cause any significant change in the host $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$ structure and all samples are a pure phase $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$. The ionic radii (Mg^{2+} : $\sim 0.72\text{ \AA}$, Mn^{2+} : $\sim 0.75\text{ \AA}$, Sr^{2+} : $\sim 1.13\text{ \AA}$, and Bi^{3+} : $\sim 1.08\text{ \AA}$) have been known [22]. According to the ionic radius similarity principle, we infer that Mn^{2+} and Bi^{3+} ions will replace Mg^{2+} and Sr^{2+} ions sites in host $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$ lattice, respectively.

Fig. 2(a) shows photoluminescence (PL) and PL excitation (PLE) spectra of $\text{Sr}_{1.96}\text{Mg}_3\text{P}_4\text{O}_{15}:0.04\text{Bi}^{3+}$ phosphor ($\lambda_{\text{ex}} = 380\text{ nm}$, $\lambda_{\text{em}} = 445\text{ nm}$) at room temperature. With excitation 380 nm , $\text{Sr}_{1.96}\text{Mg}_3\text{P}_4\text{O}_{15}:0.04\text{Bi}^{3+}$ phosphor emits blue light with the Commission Internationale Ed l'eclairage (CIE) chromaticity coordinate $(0.179, 0.176)$. A broad PL band peaking at $\sim 445\text{ nm}$ can be observed in the range of $400\text{--}600\text{ nm}$, which is attributed to the $^3\text{P}_1 \rightarrow ^1\text{S}_0$ electron

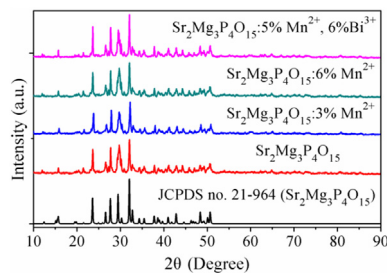


Fig. 1. The XRD profile of JCPDS standard card no. 21–964, the XRD patterns of $\text{Sr}_2\text{Mg}_{3-x}\text{P}_4\text{O}_{15}:\text{xMn}^{2+}$ ($x = 0, 3,$ and 6 mol%), and $\text{Sr}_{1.94}\text{Mg}_{2.95}\text{P}_4\text{O}_{15}:0.05\text{Mn}^{2+}, 0.06\text{Bi}^{3+}$ phosphors.

transition of Bi^{3+} ion [23]. Monitored at 445 nm , two PLE bands in the region from 220 nm to 420 nm are observed, which are assigned to the $\text{O}^{2-} \rightarrow \text{Bi}^{3+}$ charge transfer band (CTB) ($220\text{--}320\text{ nm}$) and the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ transition ($320\text{--}420\text{ nm}$) of Bi^{3+} ion, respectively [24].

Fig. 2(b) PL and PLE spectra of $\text{Sr}_2\text{Mg}_{2.95}\text{P}_4\text{O}_{15}:0.05\text{Mn}^{2+}$ phosphor ($\lambda_{\text{ex}} = 355$ and 416 nm , $\lambda_{\text{em}} = 630\text{ nm}$) at room temperature. $\text{Sr}_2\text{Mg}_{2.95}\text{P}_4\text{O}_{15}:0.05\text{Mn}^{2+}$ phosphor shows red emission with excitation 355 and 416 nm . Its CIE chromaticity coordinate is about $(0.594, 0.405)$. In the PL spectrum with excitation 355 and 416 nm , a single broad PL band peaking at $\sim 630\text{ nm}$ is observed in the region from 500 nm to 800 nm due to the $^4\text{T}_1(\text{G}) \rightarrow ^6\text{A}_1$ transition of Mn^{2+} ion [25,26]. Monitored at 630 nm , we can observed four PLE bands in the PLE spectrum region from 220 nm to 600 nm , which is assigned to the $\text{O}^{2-} \rightarrow \text{Mn}^{2+}$ CTB ($220\text{--}300\text{ nm}$) and the $^6\text{A}_1 \rightarrow ^4\text{T}_2(\text{D})$ ($320\text{--}395\text{ nm}$), $^6\text{A}_1 \rightarrow [^4\text{A}_1(\text{G}), ^4\text{E}(\text{G})]$ ($395\text{--}455\text{ nm}$), and $^6\text{A}_1 \rightarrow ^4\text{T}_1(\text{G})$ ($455\text{--}600\text{ nm}$) transitions of Mn^{2+} ion, respectively [27–30]. According to PL and PLE spectra in Fig. 2, it can also be found that PL spectrum of $\text{Sr}_{1.96}\text{Mg}_3\text{P}_4\text{O}_{15}:0.04\text{Bi}^{3+}$ phosphor has an overlap with PLE spectrum of $\text{Sr}_2\text{Mg}_{2.95}\text{P}_4\text{O}_{15}:0.05\text{Mn}^{2+}$ phosphor in the range of $400\text{--}600\text{ nm}$. The meaningful result indicates that ET can be occurred between Bi^{3+} and Mn^{2+} ions when Bi^{3+} and Mn^{2+} ions are co-doped into $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}$.

PL spectra of $\text{Sr}_2\text{Mg}_{3-x}\text{P}_4\text{O}_{15}:\text{xMn}^{2+}$ phosphors with changing Mn^{2+} ion concentration from 1 mol\% to 6 mol\% and the relation between Mn^{2+} ion concentration and PL intensity at room temperature are shown in Fig. 3. $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{Mn}^{2+}$ phosphor with excitation 416 nm shows red emission. The PL spectral shape and peak position are the same with changing Mn^{2+} ion concentration. It can also be found that PL intensity strongly depend on the Mn^{2+} ion concentration, first increasing with Mn^{2+} ion concentration in the range of $1\text{--}5\text{ mol\%}$ and reaching a maximum at $x = 0.05$, then decreasing with further increasing Mn^{2+} ion concentration because of the concentration quenching. The result indicates that the optimal Mn^{2+} ion concentration is about 5 mol\% . The phenomenon may be explained by the critical distance R_c between Mn^{2+} ions, which is calculated to study the energy transfer mechanism between Mn^{2+} ions. R_c can be approximately calculated on the basis of the relation Equation (1) suggested by Blasse et al. [27].

$$R_c \approx 2[3V/(4\pi X_c N)]^{1/3} \quad (1)$$

where V is the volume of the unit cell, X_c is the critical concentration of Mn^{2+} ion, N is the number of sites available for the dopant in the unit cell.

Fig. 4 shows the room temperature decay curve of $\text{Sr}_2\text{Mg}_{2.95}\text{P}_4\text{O}_{15}:0.05\text{Mn}^{2+}$ phosphor monitored at 630 nm and excited at 416 nm . The red curve is a fit of the experimental data to a first order exponential decay equation. The decay curve of $\text{Sr}_2\text{Mg}_{2.95}\text{P}_4\text{O}_{15}:0.05\text{Mn}^{2+}$ phosphor is fitted directly via the software in steady-state FLS980 spectrofluorimeter based on a first-order exponential decay equation (2) [31] and the lifetime value is about 6.17 ms .

$$I(t) = I_{(0)} \exp(-t/\tau) + A \quad (2)$$

where, $I(t)$ is the luminescence intensity at time t , $I_{(0)}$ is the initial luminescence intensity, t is the time, A is the value for different fitting, and τ is the decay time for the exponential components.

It is well know that ET is an important method to improve luminescence properties of phosphors. In order to research ET from Bi^{3+} to Mn^{2+} ions in $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{Bi}^{3+}, \text{Mn}^{2+}$ phosphor, PL spectra of $\text{Sr}_{2-y}\text{Mg}_{2.95}\text{P}_4\text{O}_{15}:0.05\text{Mn}^{2+}, \text{yBi}^{3+}$ ($y = 0, 2, 4,$ and 6 mol\%) phosphors with excitation 355 nm are investigated at room temperature, which are shown in Fig. 5. It can be seen that PL intensity of $\text{Sr}_2\text{Mg}_3\text{P}_4\text{O}_{15}:\text{Mn}^{2+}$ phosphor with excitation 355 nm can be enhanced obviously when Bi^{3+} is co-doped. PL intensity is getting stronger with increasing Bi^{3+} concentration from 2 mol\% to 6 mol\% . The reason is due to ET from Bi^{3+} to Mn^{2+} ions, which is consistent with the observation results in Fig. 2.

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