

Phase conversion and spectral properties of long lasting phosphor $\text{Zn}_3(\text{PO}_4)_2:\text{Mn}^{2+}, \text{Ga}^{3+}$

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Abstract A red long lasting phosphor $\text{Zn}_3(\text{PO}_4)_2:\text{Mn}^{2+}, \text{Ga}^{3+}$ (ZPMG) was prepared by ceramic method, and phase conversion and spectral properties were investigated. Results indicated that the phase conversion from $\alpha\text{-Zn}_3(\text{PO}_4)_2$, $\beta\text{-Zn}_3(\text{PO}_4)_2$ to $\gamma\text{-Zn}_3(\text{PO}_4)_2$ occurs with different manganese concentration incorporated and sinter process. The structural change induced by the phase transformation results in a remarkable difference in the spectral properties. The possible luminescence mechanism for this red LLP with different forms has been illustrated.

During the last decade, long lasting phosphorescent materials have attracted more and more attention for their commercial applications in many fields, such as, emergent-lighting, military installation and traffic signs [1–4]. Since the green long lasting phosphor $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ was reported in 1996 [5], scientists have been focusing their attention on rare earth doped aluminate, silicate and sulfide systems [6–10]. However, transition metal ion Mn^{2+} can be excited by almost all the common excitation methods, viz., X-ray, electron bombardment, UV-irradiation and electric field, and shows efficient luminescence and highly saturated color in many matrix hosts [11–13]. The study on the luminescent properties for manganese activated

phosphors have drawn considerable attention in recent years. The most successful application is the halophosphate $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}):\text{Sb}^{3+}, \text{Mn}^{2+}$ which was used as a classic low pressure mercury vapor lamp [14]. The luminescence of Mn^{2+} is ascribed to the electronic transition from the excited state ${}^4\text{T}_{1g}$ to the ground ${}^6\text{A}_{1g}$. The emission color depends on the coordination number (CN) of Mn^{2+} in the compound, when CN = 4, the emission color is green; and the color is red for CN = 6 [15]. For example, Xiao et al. [16] reported the long persistent phosphors, $\text{CaAl}_2\text{O}_4:\text{Mn}^{2+}, \text{Ce}^{3+}$, $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Mn}^{2+}, \text{Ce}^{3+}$, and $\text{MgSiO}_3:\text{Mn}^{2+}, \text{Eu}^{2+}, \text{Dy}^{3+}$. Since the ligand field and CN of Mn^{2+} in the three matrixes are different, the emission colors are green, yellow and red, respectively.

As well known, zinc orthophosphate has three crystalline modifications, labeled as α , β and γ forms. The coordination number of Zn^{2+} are 4, 4, 4(α), 6, 5, 4(β) and 6, 4, 4(γ), the emission colors and luminescence properties in the three forms doped with Mn^{2+} are different. Photoluminescence and cathodoluminescence properties of Mn^{2+} activated phosphors in three forms have been intensively investigated [17–20]. Furthermore, Wang et al. [21] reported red long lasting phosphorescent properties of $\beta\text{-Zn}_3(\text{PO}_4)_2:\text{Mn}^{2+}_{0.05}, \text{M}^{3+}(\text{M} = \text{Al}, \text{Ga})$. This offered a new system to the development of red LLP materials. However, Zinc orthophosphate has three crystalline modifications, and the spectral properties of the three forms are various: there's no phosphorescent emission in α form, on the contrary, there is red phosphorescent emission both in β and γ forms. Furthermore, β and γ forms can converse for each other under specific condition and preparative procedure. In this paper, the phase conversion mechanism and effects on the preparation

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of $\text{Zn}_3(\text{PO}_4)_2: \text{Mn}^{2+}, \text{Ga}^{3+}$ (ZPMG) are well investigated. Results showed that annealing or quenching temperature and manganese amount doped in the structure affect the crystalline structure of ZPMG. The excitation, emission and phosphorescence spectra of all the three forms phosphors have been measured. It can be clearly observed that the photoluminescence color of γ -ZPMG is green, and after removing the excited source, the LLP color is red. The study on the possible luminescent mechanism showed that Mn^{2+} doped in the γ -ZPMG co-exist tetrahedral and octahedral coordination.

Experimental

Samples preparation

Powder samples were prepared by solid-state reaction at high temperature. The stoichiometric amounts of the raw materials ZnO (A.R.), $(\text{NH}_4)_2\text{HPO}_4$ (A.R.), MnCO_3 (A.R.), Ga_2O_3 (99.99%) were thoroughly mixed and ground in an agate mortar. Then the mixtures were transferred into a corundum crucible and pre-fired at 500°C for 3 h in a furnace. After cooling to the room temperature, the samples were thoroughly reground again in the agate mortar. The mixtures were finally transferred into the corundum crucible and sintered under different conditions to obtain α , β or γ -ZPMG.

Measurements

All the crystalline structures of the samples were measured by a Rigaku D/max-II B X-ray powder diffractometer with $\text{CuK}\alpha_1$ ($\lambda = 1.5405 \text{ \AA}$) radiation and were coincident with α - $\text{Zn}_3(\text{PO}_4)_2$ (JCPDS:29-1390), β - $\text{Zn}_3(\text{PO}_4)_2$ (JCPDS:30-1489) and γ - $\text{Zn}_3(\text{PO}_4)_2$ (JCPDS:30-1490), respectively. The excitation and emission spectra were measured by a HITACHI F-4500 fluorescence spectrofluorometer equipped with a 150 W Xe lamp. The LLP experiments were performed on a HITACHI F-4500 fluorescence spectrofluorometer, too. The relative intensity was measured by PR-302 relative brightness meter. All the experiments were performed at room temperature.

Results and discussion

Phase conversion conditions

All of the three forms, α , β and γ - $\text{Zn}_3(\text{PO}_4)_2$ belong to monoclinic system. Changing the sintering temperature

and the amount of Mn^{2+} doped in the crystal structure, the different phase states can be obtained. From Fig. 1, it can be observed that when there was more than 0.3 mol% MnCO_3 , γ -ZPMG was obtained when the mixtures were sintered at 850°C under a thermal-carbon reducing atmosphere for 3 h, When the sintering temperature raised to 970°C with the same other conditions as the preparation of γ -ZPMG, the product is β -ZPMG. When there was no or less than 0.3 mol% MnCO_3 added into the raw materials, the product is α form under the sintering temperature at either 850 or 970°C .

Structure analysis

The effect of annealing and quenching on the crystal structure of $\text{Zn}_3(\text{PO}_4)_2$ has been shown in Fig. 2. The product is a single γ phase of $\text{Zn}_3(\text{PO}_4)_2$ when sample was sintered at 850°C , which consistent with the JCPDS(30-1490) under the sintering process of both annealing and quenching; when the raw materials was sintered at 970°C , the synthesized-sample was a single β phase of $\text{Zn}_3(\text{PO}_4)_2$ both annealing and quenching; when the sintering temperature raised from 850°C to 970°C , the sample was composed with γ - $\text{Zn}_3(\text{PO}_4)_2$ and β - $\text{Zn}_3(\text{PO}_4)_2$ under the condition of quenching, but a single γ phase for annealing. All the experiments above have been done based on the condition that the concentration of $\text{Mn}^{2+} > 0.3 \text{ mol\%}$. This conversion can be interpreted as follows: β phase is a metastable phase at room temperature when the temperature below to approximately 942°C , where there exists a sluggish, reversible transition from β phase to α phase [17]. So lowering the temperature rapidly is contributed to the

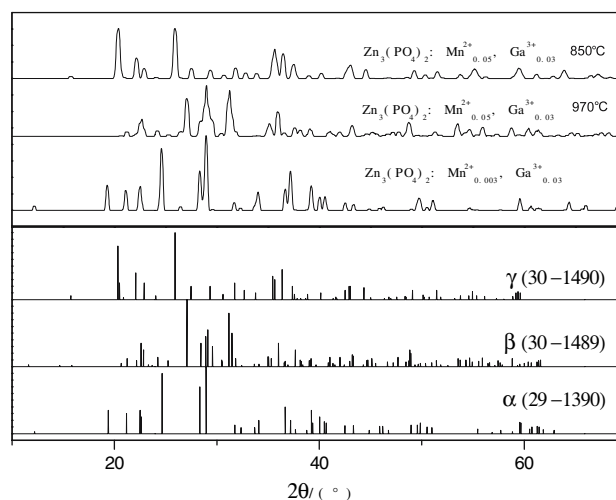


Fig. 1 XRD patterns of ZPMG at different temperature and concentration of Mn^{2+}

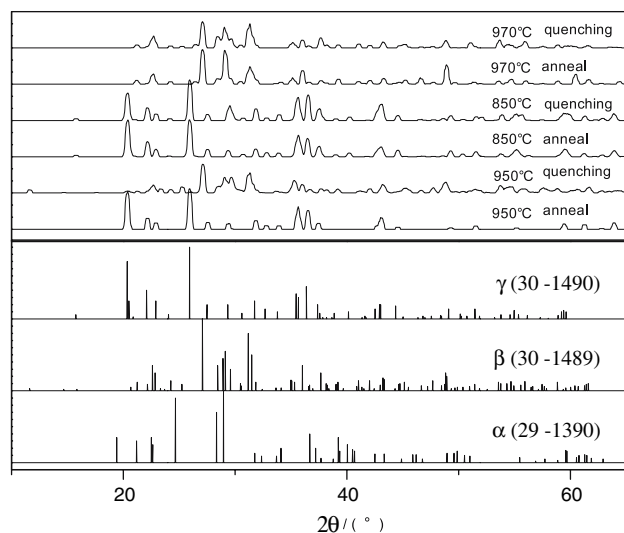


Fig. 2 XRD patterns of ZPMG by anneal or quenching at different temperature

formation of β phase. But there's no α - $\text{Zn}_3(\text{PO}_4)_2$ form occurred in the process mentioned above due to the concentration of Mn^{2+} higher than 1 mol%. A.L. Smith reported that $\text{Zn}_3(\text{PO}_4)_2$ without any manganese addition does not show any phase change even up to the point of fusion, and the X-ray diffraction pattern corresponds to the α form [19]. The phase conversion of the ZPMG occurred when the doped concentration of Mn^{2+} is up to 0.3 mol% and sintered at 970 °C. Furthermore, the concentration of Mn^{2+} for the phase conversion is changeable, changing with the co-doped ions. In our present work, when the co-doped ions are Eu^{2+} and Dy^{3+} , the product still keep α form with the concentration of Mn^{2+} up to 0.3 mol%, but β form at 0.5 mol%.

In our present work, the samples were sintered under reducing environment, so quenching has been taken, then the phase conversion from β to γ form is dependent on sintering temperature. The X-ray diffraction curves were shown in Fig. 3. At 850 °C only the γ form is produced. Between 850 °C and 950 °C, both β and γ form co-exist in the $\text{Zn}_3(\text{PO}_4)_2:\text{Mn}^{2+}, \text{Ga}^{3+}$. Up to 970 °C, the conversion to β form finished completely. But above 1,000 °C, the sample becomes molten state.

Excitation and emission spectra

Figure 4 shows the excitation spectra of the three different phase states by monitoring 507, 616, 616 nm for α , β and γ form, respectively. For comparison, the overall excitation spectra are divided into three parts: The first one in the range from 200 nm to 250 nm ascribed to the charge transfer band (CTB) of

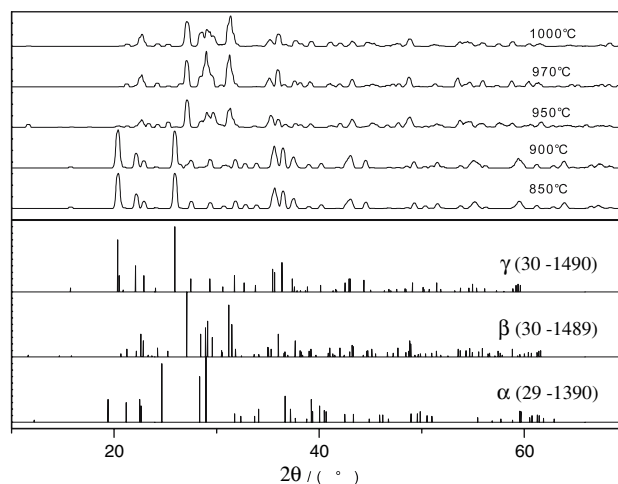


Fig. 3 XRD patterns of $\text{Zn}_2(\text{PO}_4)_3$ converting from γ to β as temperature increasing

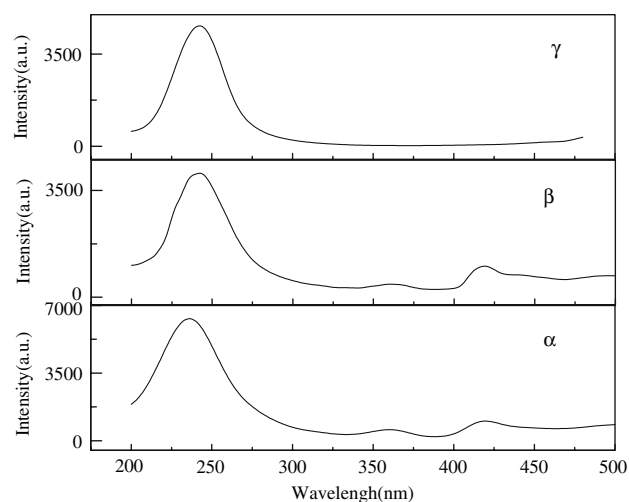


Fig. 4 Excitation spectra for the three forms of α , β and γ -ZPMG. α : $\lambda_{\text{em}} = 507$ nm, 246 nm; β : $\lambda_{\text{em}} = 616$ nm, $\lambda_{\text{ex}} = 234$ nm; γ : $\lambda_{\text{em}} = 616$ nm, $\lambda_{\text{ex}} = 246$ nm

$\text{Mn}^{2+} \rightarrow \text{O}^{2-}$. And that the host absorption as the edge of the optical absorption band for $\text{Zn}_3(\text{PO}_4)_2$ is situated at 6.9 eV (180 nm) beyond the detection of our instrument [18]. The second one between 350 nm and 380 nm originates from the splitting of ${}^4\text{T}_{2g}$ (${}^4\text{D}$) levels. The third one in the range from 400 nm to 450 nm is associated with the splitting of ${}^4\text{E}_g$ - ${}^4\text{A}_{1g}$ (${}^4\text{G}$) levels. Furthermore, in the order of α , β and γ , the peaks in the region from 300 to 450 weakened gradually, and disappeared completely as a results of their different sintering temperatures and crystal structures.

Figure 5 shows the emission spectra of the three forms excited at 234 nm(α), and 246 nm(β and γ), The emission peaks at 507 nm occurs in the three forms of α , β and γ . Another sharp peak at both 616 nm occurs

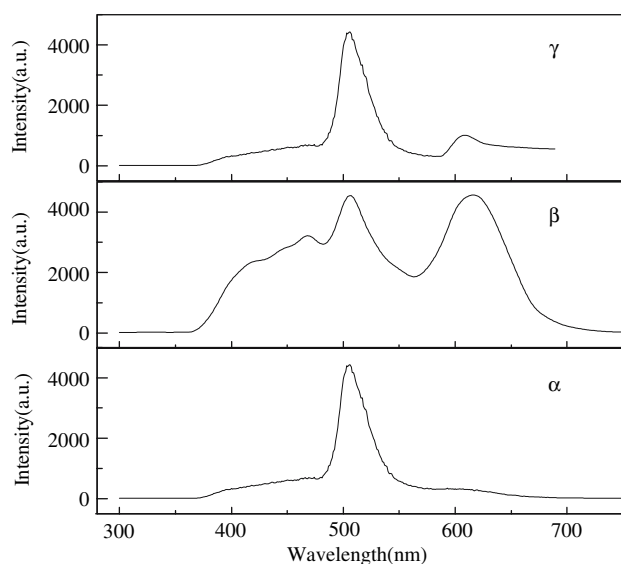


Fig. 5 The emission spectra for the three forms of α , β and γ -ZPMG. $\lambda_{em}(\alpha) = 507$ nm; $\lambda_{em}(\beta) = 507$ nm and 616 nm; $\lambda_{em}(\gamma) = 507$ and 616 nm

in the two forms of β and γ . Both the two typical peaks are attributed to the ${}^4T_1 \rightarrow {}^6A_1$ transition of Mn^{2+} .

As a luminescent center Mn^{2+} is usually characterized by green or red emissions, which attributed to the transition of Mn^{2+} from the excited ${}^4T_{1g}({}^4G)$ to the ground ${}^6A_{1g}({}^6S)$ state in the energy group $3d^5$. The emission color is strongly dependent on the coordination environment of Mn^{2+} in the host lattice, such as the strength of the ligand field and coordination number (CN). The stronger the ligand field, the higher the emission peak will be [22]. In addition, the coordination number (CN) also has a great effect on the emission color: the Mn^{2+} ion emits green light when it is tetrahedrally coordinated (CN = 4) in the lattice, whereas it emits red light in octahedral coordination (CN = 6) [15]. For example, Li has reported that the emission spectrum with a maximum at about 525 nm of ZSBM-G is attributed to the ${}^4T_1 \rightarrow {}^6A_1$ transition of Mn^{2+} in a tetrahedral site, while the spectrum peaking at about 606 nm of ZSBM-R is ascribed to a same transition of Mn^{2+} in an octahedral site by substituting for the cation Zn^{2+} [23]. In the present case, the similar optical features indicate that the Mn^{2+} would also occupy a tetrahedral site or an octahedral site in the three forms.

Although the three forms all belong to monoclinic system, there are equivalent cation sites in the three forms. In α - $Zn_3(PO_4)_2$, both unique cation sites are tetrahedrally coordinated [24, 25], leading the only green emitting occurs at 507 nm in the emission spectra. However, the limited solubility of Mn^{2+} in the α form implies either considerable distortions upon substitution or a preference of Mn^{2+} for an interstitial

site [17]. In β form, there are three nonequivalent cation sites, i.e., Zn (1), Zn (2), and Zn (3). Zn (1) and Zn (3) are coordinated with four and five oxygen atoms, respectively, while Zn (2) is coordinated with six oxygen atoms [17]. Therefore, the broad emission band peaking at 507 and 616 nm are assigned to the ${}^4T_{1g}({}^4G) \rightarrow {}^6A_{1g}({}^6S)$ transition of Mn^{2+} in the Zn (1) and Zn (2) sites with tetrahedral and octahedral coordination, respectively. The γ form shows the same average cation coordination number as that of β - $Zn_3(PO_4)_2$, but in this case the cation coordination numbers are 6, 4, and 4. So the similar peaks locate at the same positions. However, the red emission at 616 nm is weaker than that in β - $Zn_3(PO_4)_2$ as the decrease of Zn^{2+} that octahedrally coordinated.

Long-lasting phosphorescence

Figure 6 shows the LLP emission spectra of α , β and γ -ZPMG taken immediately after removal of excitation source. It can be observed that there is no long-lasting phosphorescent phenomenon in the α form as a result of no octahedrally coordinated Mn^{2+} in this structure. On the contrary, in the β and γ -ZPMG, the long-lasting phosphorescent emission peaking at 616 nm can be clearly observed, due to the existence of octahedral coordination which is assigned to the transition ${}^4T_{1g}({}^4G) \rightarrow {}^6A_{1g}({}^6S)$ of Mn^{2+} . But the phosphorescent intensity in β form is stronger than that in γ form. The decay curves of β and γ -ZPMG in Fig. 7 show that the decay curves of β and γ -ZPMG can be divided into two processes: a fast and a slow one. And

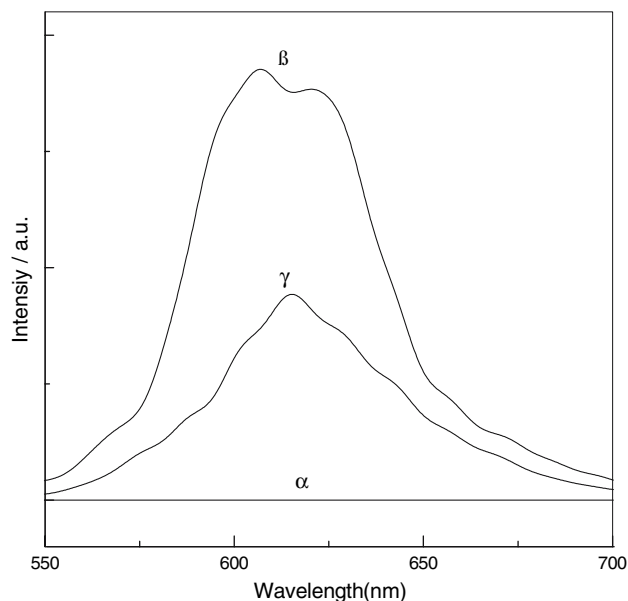


Fig. 6 LLP emission spectra of α , β and γ -ZPMG after the removal of UV lamp peaking at 254 nm

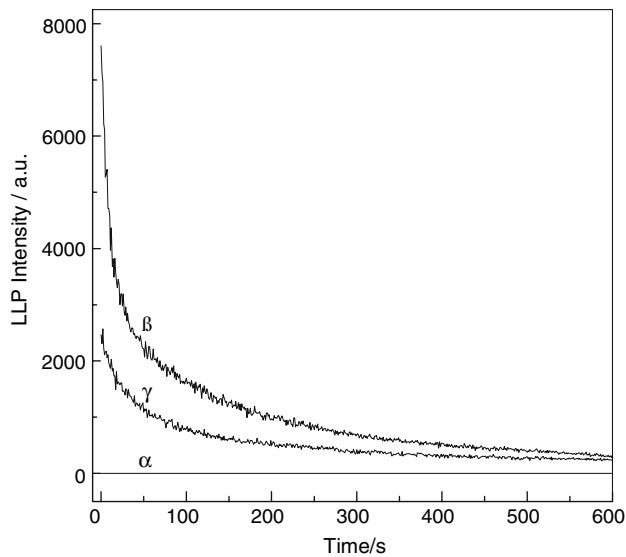
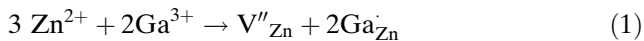


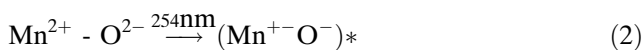
Fig. 7 The decay curves of α , β and γ -ZPMG by monitoring the emission at 616 nm

the phosphorescence time of β form is longer, too. In the β form, the red phosphorescence is still observed in the dark for no less than 30 min by the naked eye, whose limitation of light perception is about 0.32 mcd m^{-2} , but only about 15 min for γ -ZPMG.

Wang et al. [19] figured out that, in order to achieve long lasting phosphorescence, the incorporation of the auxiliary codopants with different valences and ionic radii from the host cation is often undertaken. In the present case, both in β and γ -ZPMG, Ga^{3+} ion would non-equivalently replace the Zn^{2+} ions as they are doped into $\text{Zn}_3(\text{PO}_4)_2$. In order to keep the charge balance, two Ga^{3+} ions will substitute three Zn^{2+} ions (the total charge of two trivalent Ga^{3+} ions is equal to that of three Zn^{2+} ions). Hence, one vacancy defect of V_{Zn}'' with two negative charges and two positive defects of $\text{Ga}_{\text{Zn}}^{\cdot}$ would be created by each substitution of every two Ga^{3+} ions in the compound:



An electron–hole recombination model is proposed to interpret the red LLP phenomenon of β and γ -ZPMG, the electron–hole pair is created after exciting with 254 nm UV lamp for 5 min.



The electron–hole pair dissociates after excitation, and then the electron and hole are separately trapped. The electron would be trapped at the positive defect $\text{Ga}_{\text{Zn}}^{\cdot}$ whereas the hole would be captured at the negative compensating defect V_{Zn}'' .



Under the thermal fluctuations, the trapped holes are released:



The released holes recombine with the trapped electrons, and the released energy from the recombination of electrons and holes was transferred to Mn^{2+} finally, resulting in the phenomenon of red LLP of Mn^{2+} as shown in Fig. 6.

Conclusion

The three forms α , β and γ -ZPMG were prepared by means of high-temperature solid-state reaction. The emission peaks of the three forms locate at 508 nm (α), 508 nm and 616 nm (β and γ). But in the LLP emission spectra, there is no LLP emitting for α form, because there is no octahedrally coordinated Mn^{2+} in this structure. For the β and γ -ZPMG, the long-lasting phosphorescent emission band is also derived from the ${}^4\text{T}_{1g}({}^4\text{G}) \rightarrow {}^6\text{A}_{1g}({}^6\text{S})$ transition of Mn^{2+} in the host. The decay curves of β and γ -ZPMG can be divided into two processes: a fast and a slow one. After irradiated by UV lamp for 5 min, the red phosphorescence of Mn^{2+} , Ga^{3+} co-doped β -ZPMG and γ -ZPMG are still observed in the dark for no less than 30 and 15 min, respectively.

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