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Phosphorescence behavior and photoluminescence mechanism of Dy^{3+} sensitized β-$Zn_3(PO_4)_2$: Mn^{2+} phosphor

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ABSTRACT

A red long persistent phosphor (LPP) of β-$Zn_3(PO_4)_2$: Mn^{2+}, Dy^{3+} was synthesized conventionally via homogeneous coprecipitation and conventional solid-state sintering methods. The emission peak of phosphor was found at 620 nm, which can be assigned to the $^4T_{1g} \rightarrow {}^6A_{1g}$ transition of Mn^{2+}. The decay curves of phosphors show that Dy^{3+} ions co-doping can largely improve the performance of the red LLP of β-$Zn_3(PO_4)_2$: Mn^{2+}. This red long-persistent luminescence was observed for about 4 h in the limit of light perception for naked eyes when excited under 254 nm UV light for 5 min. Thermoluminescence analysis indicates that the dopant of Dy^{3+} ions produced suitable trap depth of defects that enhanced the luminescence of LPP. It is hypothesized that Dy^{3+} as a sensitizer transfers its energy to the luminescent center of Mn^{2+}. We propose that the emission mechanism of LPP experiences a series process of electron–hole pairs: production, release, movement and combination. The decay time of LPP has close relationship with the life span of electron–hole pairs during their releasing time from traps and moving length on their path.

1. Introduction

The long persistent phosphor (LPP) is a kind of photoluminescence material which exhibits particular light storing and releasing properties [1,2]. Over the past decades, rare-earth (especially Eu) ions activated LPP materials have been widely studied and applied in safety indication, graphic arts, road signs, interior decoration, radiation detection, structural damage sensors and optical storage media [3–6]. Up to now, more and more realms such as solar energy utilization and in vivo bio-imaging have used long-lasting phosphors to solve correlative questions [7,8]. LPP can exhibit variety of colors in the darkness, most especially blue ($CaAl_2O_4$: Eu^{2+}, Nd^{3+}) and green ($SrAl_2O_4$: Eu^{2+}, Dy^{3+}) [9–11]. Although many red LPP materials, such as Y_2O_2S: Eu^{3+}, Mg^{2+}, Ti^{4+} [12], Y_2O_3: Eu^{3+}, Ho^{3+} [13], $CaTiO_3$: Eu^{3+} [14], $CaTiO_3$: Pr^{3+} [15] and β-$Zn_3(PO_4)_2$: Mn^{2+}, Sm^{3+} [16] have been reported, red LPP materials are still far beyond practical application since their phosphorescence persisting times are very short. According to the trichromatic theory of color vision, the combination of red, green and blue in appropriate intensities can create various colors. Thus, red LPP materials can have a wide range of practical applications. In previous researches, rare earth ions based red persistent luminescence has attracted great concern while there is still much limited investigation on the Mn^{2+}-doped long-lasting phosphors. Manganese compounds are low cost, easily synthesized and environmentally friendly. Therefore, Mn^{2+}-activated LPP materials will have price and health advantage over rare earth elements activated LPP materials.

Mn^{2+} ion is usually characterized by green or red emission in oxides. It consists of a 3d–3d broad band corresponding to the transition of Mn^{2+} from the excited $^4T_{1g}$ (^4G) state to the ground $^6A_{1g}$ (^6S) state. It is well-known that the emission color is strongly dependent on the coordination environment of Mn^{2+} in the host lattice. The reported results have revealed that a Mn^{2+} ion at a site tetrahedrally surrounded by oxygen gives rise to green emission and a Mn^{2+} ion at a site octahedrally surrounded by oxygen leads to red emission [17]. In compounds of Zn_2GeO_4 and $ZnSiO_4$, the replacement of Zn^{2+} on a tetrahedral site by Mn^{2+} will produce the green emission spectrum at 535 nm and 525 nm, respectively [18,19]. In phosphors of $Zn_3(PO_4)_2$ and Mg_2SiO_4, Mn^{2+} ion substitutes the cation Zn^{2+} or Mg^{2+} on a distorted octahedral site, with the emission center at 616 nm or 620 nm, respectively [16,20].

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Rare earth ions are widely used as activators in different hosts due to their high luminescence properties. Dy^{3+} ion is well known as an activator and emission center for many inorganic lattices. It has a $4f^9$ electron configuration, and usually exhibits two principal emission bands in the visible region: one in the blue region (470–500 nm) and another in the yellow region (570–600 nm), attributed to $^4F_{9/2}$–$^6H_{13/2}$ and $^4F_{9/2}$–$^6H_{15/2}$ transitions of Dy^{3+} ions, respectively. Some researchers have reported luminescence properties of Dy^{3+}, such as Mg_2SiO_4: Mn^{2+}, Dy^{3+} [20], YPO_4: Pr^{3+}, Ln^{3+} (Ln = Nd, Er, Ho, Dy) [21], $K_3Y(VO_4)_2$: Dy [22] and $B_4Si_3O_{12}$: Dy [23]. The dopant of Dy^{3+} can improve the initial phosphorescence and afterglow time of Mn^{2+}-LPP. Additionally, Dy^{3+} ion can serve as trap center [20].

Rare earth ions doped phosphates have unique luminescent properties resulting from their stability and high emission quantum yield. The red LPP of β-$Zn_3(PO_4)_2$: Mn^{2+} was first reported by Su's group [16]. Sm^{3+}, Zr^{4+}, Ga^{3+} or Al^{3+} co-doped $Zn_3(PO_4)_2$: Mn^{2+} have been investigated thoroughly [16,24–27]. Owing to the forbidden transition ($^4T_1$–$^6A_1$) required by the selection rule, Mn^{2+} singly doped β-$Zn_3(PO_4)_2$ phosphor cannot show considerable emission performance. However, co-doping Sm^{3+}, Zr^{4+}, Al^{3+}, Ga^{3+} or Zn^{2+} ions can largely enhance the luminescent properties of β-$Zn_3(PO_4)_2$: Mn^{2+} [16,24,25,27]. It has been reported that Dy^{3+} as a promising sensitizer can enhance the luminescence intensity of Mn^{2+} in many hosts, such as Mg_2SiO_4: Mn^{2+}, Dy^{3+} [20]. In this work, we report a LPP material of β-$Zn_3(PO_4)_2$: Mn^{2+}, Dy^{3+} in which Mn^{2+} is acted as a luminescence center and Dy^{3+} as a sensitizer.

2. Experimental

2.1. Materials and synthesis

The β-$Zn_3(PO_4)_2$: Mn^{2+}, Dy^{3+} phosphors were synthesized through homogeneous coprecipitation and conventional solid-state sintering methods. The reactants ZnO (A. R. (Analytic Reagent)), $MnCO_3$ (A. R.), $(NH_4)_2HPO_4$ (A. R.) and Dy_2O_3 (99.5%), were employed as starting materials in this research. The Mn^{2+} concentration was fixed at 3.0 mol% since it can show the best red LLP in β-$Zn_3(PO_4)_2$: x mol% Mn^{2+} (x = 1.0–5.0) and Dy^{3+} concentrations varied between 1.0 mol% and 6.0 mol% of Zn^{2+} ions in $Zn_3(PO_4)_2$. The raw materials were weighed according to the stoichiometric ratios. Then, all of the above materials were completely dissolved in water or nitric acid to obtain homogeneous solution. Ammonium hydroxide was added dropwise to the homogeneous solution until no precipitation occurred. The resultant white fluffy precipitate was filtered and washed with distilled water, and subsequently dried at 373 K for 5 h. Finally, the coprecipitation precursors were finally transferred into the corundum crucible and sintered in a thermal-carbon reducing atmosphere to obtain white powder of phosphors.

2.2. Measurements

The structures of all the synthesized samples were analyzed by a XRD using Cu $K\alpha_1$ (λ = 0.15406 nm) radiation. The excitation and emission spectra of the obtained powders were measured on a Hitachi F-4600 spectrofluorometer equipped with 150 W Xe lamp as the excitation. Each sample was irradiated with UV excitation light for 5 min and phosphorescence emission was recorded with a fluorometer, using the kinetic analysis mode. The decay curves of samples were detected immediately using a weak photometer of BPCL-2-JZ-TGC, after being exposed to UV light (254 nm) for 5 min, with 4.07 mW/cm^2 power rating. The thermoluminescence (TL) spectra were measured on a miniature heater with automatic temperature control system and a weak photometer of BPCL-2-JZ-TGC. The temperature rose with a heating rate of 0.2 K/s from 300 to 573 K. The TL spectra were measured after the samples had been irradiated for 5 min by UV lamp (254 nm) with a power of 15 W and then decayed for 30 min. All measurements except TL spectrum were performed at room temperature.

3. Results and discussions

3.1. Phase characterization

The XRD patterns of samples are shown in Fig. 1. It could be observed that when the $Zn_3(PO_4)_2$: Mn^{2+}, Dy^{3+} and $Zn_3(PO_4)_2$: Mn^{2+} were sintered at 1223 K under a thermal-carbon reducing atmosphere for 3 h, the β-$Zn_3(PO_4)_2$ (JCPDS standard card NO. 30-1489) was obtained with small amount of γ phase (JCPDS standard card NO. 30-1490). However, $Zn_3(PO_4)_2$: Mn^{2+}, Dy^{3+} appeared in main phase of γ with small amount of β when the sintering time was prolonged or the sintering temperature was increased.

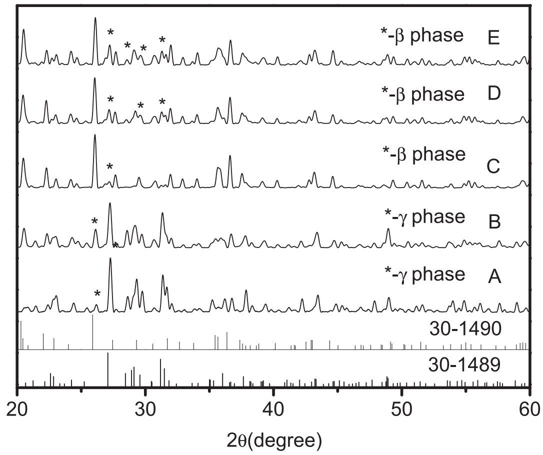

Fig. 1. The XRD of samples in various synthesized condition. $Zn_3(PO_4)_2$: Mn^{2+} ((A) 1223 K, 3 h); $Zn_3(PO_4)_2$: Mn^{2+}, Dy^{3+} ((B) 1223 K, 3 h, (C) 1233 K, 3 h, (D) 1223 K, 4 h, and (E) 1223 K, 5 h).

3.2. Luminescence analysis

Mn^{2+} can give red luminescence in octahedral coordination (CN = 6) and green emission in tetrahedral coordination (CN = 4) [17]. Fig. 2(a) illustrates the emission spectrum and the excitation spectrum of the β-$Zn_3(PO_4)_2$: Mn^{2+} and β-$Zn_3(PO_4)_2$: Mn^{2+}, Dy^{3+}. As shown in Fig. 2, the emission spectrum is dominated by a red emission band at 620 nm, which is assigned to the transition from the lowest excited state to the ground state of the Mn^{2+} ions, i.e., the $^4T_{1g} \rightarrow {}^6A_{1g}$ transition. The excitation spectrum monitored at 620 nm consists of several bands in the UV and visible regions. These bands are due to the spin-forbidden transitions in the $3d^5$ electron configurations of the Mn^{2+} ions. According to the Orgel diagram for Mn^{2+}, these bands appearing at 382.5, 411, (436, 452) and 477 nm are attributed to the transition from the ground state $^6A_{1g}$ to the excited states of $^4T_{2g}$, (^4E_g–$^4A_{1g}$), $^4T_{2g}$ and $^4T_{1g}$ energy levels, respectively [28,29]. One broad band dominates the wavelength range from 200 to 250 nm when monitored via the emission at 620 nm. It is assigned to the charge transfer state (CTS) of Mn^{2+}–O^{2-} [29] rather than the host absorption because the edge of the host absorption band for β-$Zn_3(PO_4)_2$ is situated at 180 nm [28].

The emission and excitation spectra of $Zn_3(PO_4)_2$: Dy^{3+} were displayed in Fig. 2(b). The excitation spectra fall in the range of 250–450 nm, monitored at 482 nm. These 4f–4f transitions of Dy^{3+} correspond to $^6H_{15/2}$–$^4F_{3/2}$ (305 nm), $^6H_{15/2}$–(^4F, $^4D)_{5/2}$ (338 nm), $^6H_{15/2}$–$^6P_{7/2}$ (352 nm), $^6H_{15/2}$–$^6P_{5/2}$ (369 nm), $^6H_{15/2}$–$^4F_{7/2}$ (381 nm), $^6H_{15/2}$–$^4G_{11/2}$ (400 nm) and $^6H_{15/2}$–$^4I_{15/2}$ (437 nm) [30], respectively. The main emission peak at 482 nm is corresponded to spin forbidden 4f–4f transitions of Dy^{3+} ($^4F_{9/2}$–$^6H_{15/2}$, magnetic dipole) [31]. In Fig. 2(c), the emission bands of $^4F_{9/2}$–$^6H_{15/2}$ (around 480 nm) transitions in the $Zn_3(PO_4)_2$: Dy^{3+} are close to the excitation bands corresponding to $^6A_{1g} \rightarrow {}^4T_{1g}$ (around 470 nm) transition in the $Zn_3(PO_4)_2$: Mn^{2+}, which makes it possible for Dy^{3+} as a sensitizer to transfer its energy to the luminescence center of Mn^{2+}. It will be deeply discussed in the part of "Luminescence Mechanism".