Mn-ion-enhanced red spectral emission from yttrium aluminum garnet doped cerium phosphor

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Mn ions were co-doped in yttrium aluminum garnet doped cerium (YAG:Ce) phosphors as a co-activator and host lattice element using the co-precipitation method. These ions broadened the emission spectra of the pure YAG:Ce phosphor, which is caused by the $^2E-^4A_2$, $^5E-^5T_2$ or $^1T_2-^5T_2$ transition. From our X-ray diffraction results, we observed that Ce^{3+} (1.032 Å) was substituted at the Y^{3+} (0.900 Å) site, and Mn^{4+} (0.538 Å) and Mn^{3+} (0.67 Å) were substituted at the Al^{3+} (0.535 Å) site. The chromaticity color co-ordinates of YAG:Ce_{0.06} is (0.203, 0.167), and the indices of YAG:Ce_{0.06}Mn_{0.04} and YAG:Ce_{0.06}Mn_{0.08} are (0.249, 0.181) and (0.233, 0.194), respectively. The manganese co-doped yttrium aluminum garnet doped cerium blended with the YAG:Ce phosphor showed improved white light emission.

phosphor, LED, manganese, YAG:Ce

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Ce-doped yttrium aluminum garnet (YAG) $Y_3Al_5O_{12}$ has been widely used in solid-state laser materials and phosphors [1,2]. However, YAG:Ce is also a promising candidate for use in cathode-ray tubes (CRTs), field emission displays (FEDs), vacuum fluorescent displays (VFDs), and white light-emitting diodes (WLEDs) [3–5]. In contrast to single Ce doped YAG phosphor, which can convert blue light to yellowish-green light [2], some co-doped YAG:Ce phosphors have been studied that increase the emission efficiency and broaden luminosity spectra. The materials use rare earth elements, such as Pr^{3+} , Sm^{3+} , or Tb^{3+} ions [6–9]. However, few studies examine YAG:Ce phosphors co-doped with transition elements.

The ions of manganese, which is a transition element with various common ionization states, are well-known activators used in YAG mainly to produce tunable solid-state laser media [10]. The different charges of the Mn ions (2+,

3+, and 4+) have different luminescence properties, depending on the charge state of the co-dopants and content of the growth environment. Similar to the $^6A_1-^4A_1$ and $^6A_1-^4T_2$ transitions, Mn^{2+} can be excited between 400 and 520 nm [11]. The luminescence spectrum of Mn^{4+} ions can be excited in the band that peaks between 460 and 480 nm, which is caused by the $^2E-^4A_2$ transitions [12]. However, the luminescence of Mn^{3+} in the octahedral sites of Al- in the garnet lattice usually results in intensive luminescence caused by the $^5E-^5T_2$ or $^1T_2-^5T_2$ transition in the orange-red spectral range [13,14]. Although the co-doped YAG:Ce phosphor has been previously studied, to the best of our knowledge few studies of the luminescence in YAG:Ce,Mn phosphors have been published.

We attempted to develop YAG:Ce,Mn phosphors excitable via blue light for application in white light LEDs. YAG phosphor powders are usually produced via solid state reactions [15], the sol-gel method [16], the glycothermal method [17], spray pyrolysis [18], or the co-precipitation method

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[19]. In this experiment, YAG:Ce and YAG:Ce,Mn phosphors were synthesized via a co-precipitation method: appropriate amounts of MnCl_2 , $\text{Ce}(\text{NO}_3)_3$, $\text{Y}(\text{NO}_3)_3$, and $\text{Al}(\text{NO}_3)_3$ solutions were mixed. These solutions were prepared by dissolving the corresponding nitrate salts in distilled water or dissolving them in HNO_3 and HCl .

1 Experiment

1.1 Materials

Y_2O_3 (99.99%, Changchun Hai Puri Co. Ltd., Changchun, China) and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (A.R., Shanghai Zhanyun Chemical Co. Ltd., Shanghai, China) were used as rare earth sources. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (A.R., Shanghai Zhanyun Chemical Co. Ltd., Shanghai, China), which was used as the source of Al, and MnO_2 (98%, Sino-Chemical Reagent Company, Shanghai, China) were used as the transition element sources for YAG:Ce,Mn. The synthesis method is as follows.

High purity Y_2O_3 and MnO_2 were dissolved in HNO_3 and HCl , respectively, through stirring and heating. Cerium and aluminum nitrate solutions were prepared by dissolving $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in distilled water. The multi-cation solution was prepared using the stoichiometric proportion: $\text{Y}_{3-x}\text{Ce}_x\text{Al}_5\text{O}_{12}$ ($x=0.02, 0.04, 0.06, 0.08, 0.10$) and $\text{Y}_{2.94}\text{Ce}_{0.06}\text{Al}_{5-y}\text{Mn}_y\text{O}_{12}$ ($y=0.02, 0.04, 0.06, 0.08$). The total cation concentration was 0.16 mol/L.

The concentration of ammonium hydrogen carbonate (AHC), which was used as the precipitant solution dissolved in the distilled water, was 2 mol/L.

1.2 Powder synthesis

Precursors were produced by dripping 300 mL of the precipitant solution (AHC) into 300 mL of the multi-cation solution at 2 mL/min under magnetic stirring at room temperature. The solution was stirred for another 60 min after all of the AHC was added. After aging for 4 h at 25°C, the resulting suspensions were filtered and washed three times with distilled water, rinsed three times with ethyl alcohol, and dried at 110°C for 10 h. Then, the precursors were sintered at 1200°C for 2 h in air.

1.3 Powder characterization

X-ray powder diffraction (XRD) was carried out on a Bruker D8 Advance diffract meter (Germany; 40 kV, 40 mA) using $\text{Cu K}\alpha$ radiation ($\lambda=0.15406$ nm) at a scanning rate of 0.02°/s. Field-emission scanning electron microscope (FE-SEM) images were taken with a JEOL instrument (JEOL-6700F, Japan) at an accelerating voltage of 10 kV. The excitation and emission spectra were obtained with a FluoroMax-4 luminescence spectrometer (Horiba Jobin Yvon Co. Ltd., France) and the photoelectricity tests were

performed using a PMS-50 (Everfine Co., Shanghai, China). All the measurements were carried out at room temperature.

2 Results and discussion

The Ce-doped YAG phosphors ions were prepared at 1200°C for 2 h. Figure 1 shows the emission (Figure 1(a)) and excitation (Figure 1(b)) spectra of the YAG:Ce phosphors. As the concentration of Ce ions increased, the excitation and emission intensities showed similar changes. The intensities of emission and excitation were especially similar for the YAG:Ce_{0.06}, YAG:Ce_{0.08}, and YAG:Ce_{0.1} phosphors. Although the concentrations of Ce ions are different, the emission spectra have the same peaks at 528 nm in each case, originating from the $^2\text{T}_{2g}(5d) \rightarrow ^2\text{F}_{7/2}, ^2\text{F}_{5/2}(4f)$ transition of the Ce^{3+} ions, which was excited at a fixed excitation wavelength of 460 nm. The maximum emission intensity was demonstrated via the YAG:Ce_{0.06} phosphor. This is shown in Figure 1(a). The emission intensities of YAG:Ce_{0.08} and YAG:Ce_{0.1} were not as high as that of YAG:Ce_{0.06} because of concentration quenching [20]. Figure 1(b)

Figure 1 Emission (a) and excitation (b) spectra of YAG:Ce_{0.02} (1), YAG:Ce_{0.04} (2), YAG:Ce_{0.06} (3), YAG:Ce_{0.08} (4), and YAG:Ce_{0.1} (5) phosphors.

shows the excitation spectra for excitation at 528 nm. In these spectra, the excitation peaks at 340 and 460 nm can be seen.

Figure 1(a) shows that the emission of YAG:Ce_{0.06} was more intense than that of the other YAG:Ce_x ($x=0.02, 0.04, 0.08, 0.10$) phosphors. Therefore, the Mn ions were doped into YAG:Ce_{0.06}. Figure 2 shows the X-ray powder diffraction patterns for the YAG:Ce_{0.06} and YAG:Ce_{0.06}Mn_y ($y=0.02, 0.04, 0.06, 0.08$) phosphors. All the diffraction peaks were indexed based on the pure YAG phase (Figure 2, JCPDS file 33-0040), with no impurity peaks. The phase of the YAG:Ce_{0.06}Mn_y ($y=0.02, 0.04, 0.06, 0.08$) phosphors was the same as that of YAG:Ce_{0.06}, which indicates that the refined lattice parameters did not undergo significant changes following Mn-ion co-doping. In addition, the patterns of YAG:Ce_{0.06}Mn_y ($y=0.02, 0.04, 0.06, 0.08$) (Figure 2(b)–(e)) showed clear shifts to lower 2θ angles, compared with the peaks of YAG:Ce_{0.06} (Figure 2(a)). Previous studies suggest that the shift was caused by substituting larger dopant ions at the sites [12]. Because the phosphor samples were prepared in air, the co-doped Mn ions had mainly +3 and +4 charges [11]. Based on the radii of Mn⁴⁺ (0.538 Å) and Mn³⁺ (0.645 Å), and compared with those of Y³⁺ (0.900 Å) and Al³⁺ (0.535 Å), we can prove that Al-sites would be substituted mainly by the Mn⁴⁺ and Mn³⁺ ions, which can explain why there is a shift to a lower 2θ angle.

The sizes of YAG:Ce_{0.06} (Figure 3(a)) and YAG:Ce_{0.06}Mn_{0.08} (Figure 3(b) and (c)) are shown in Figure 3. The morphology and microstructure of the samples were examined using FE-SEM. Figure 3(a) and (b) shows low-magnification (10000×) SEM images that present a full view of the samples. The size distribution broadened to 200–500 nm, with the increase of the Mn ion concentration. The material also became spherical with the addition of the Mn ions. All of the microspheres have similar sizes and morphologies. This suggests that the structure may be superior for some applications. Figure 3(c) shows a higher magnification

Figure 2 Powder X-ray diffraction patterns of (a) YAG:Ce_{0.06}, (b) YAG:Ce_{0.06}Mn_{0.02}, (c) YAG:Ce_{0.06}Mn_{0.04}, (d) YAG:Ce_{0.06}Mn_{0.06}, and (e) YAG:Ce_{0.06}Mn_{0.08} phosphor.

Figure 3 SEM of (a) YAG:Ce_{0.06} and (b), (c) YAG:Ce_{0.06}Mn_{0.08} phosphor.

(30000×) SEM image of the YAG:Ce_{0.06}Mn_{0.08}.

Co-doped YAG:Ce_{0.06} phosphors with various Mn concentrations were excited at 390 and 460 nm. The excitation at 390 nm occurs only for the Mn³⁺ ions, in contrast to the excitation wavelengths of Mn²⁺ and Mn⁴⁺ ions [21]. By contrast, excitation at 460 nm only occurs for Mn⁴⁺ [12] and Ce³⁺. We observed from the emission spectra corresponding to 460-nm excitation (Figure 4(a)) that YAG:Ce has a broad band emission with a peak at 538 nm and sharp emission peaks at 504, 625, and 691 nm. Using the emission spectrum of YAG:Ce_{0.06} (Figure 1(a)) as a reference, the addition of Mn ions at the Al site resulted in a significant red shift with the emission maxima shifting from 528 to 538 nm because of the ²E–⁴A₂, ⁵E–⁵T₂, and ¹T₂–⁵T₂ transitions [12], and also for the peaks at 504, 625, and 691 nm. With increasing Mn-ion concentration, the emission intensity of the YAG:Ce,Mn generally increased. This is shown in Figure 4(a). Figure 4(b) shows the excitation spectra of YAG:Ce_{0.06}Mn_{0.06} detected at 504, 538, 625, and 691 nm. The range of the excitation spectra is from 320 to 490 nm, which indicates that the YAG:Ce,Mn phosphors can also be excited using blue light. Figure 5 shows the emission spectra of YAG:Ce_{0.06} and YAG:Ce_{0.06}Mn_{0.08}. From the spectra, we

Figure 4 (a) Emission spectra of YAG:Ce,Mn for excitation at 460 nm. 1, YAG:Ce_{0.06}Mn_{0.02}; 2, YAG:Ce_{0.06}Mn_{0.04}; 3, YAG:Ce_{0.06}Mn_{0.06}; and 4, YAG:Ce_{0.06}Mn_{0.08} phosphor. (b) Excitation spectra of YAG:Ce_{0.06}Mn_{0.06} detected at 504, 538, 625, 691 nm.

can see that the full width at half maximum (FWHM) of YAG:Ce_{0.06} is 92 nm and the FWHM of YAG:Ce_{0.06}Mn_{0.08} is 103 nm. When excited with near-UV light at 390 nm (Figure 6(a)), Mn-codoped YAG:Ce phosphors showed the characteristic Mn³⁺ peaks at 531, 641, and 744 nm, which cannot be excited in pure YAG:Ce. The excitation spectra of YAG:Ce_{0.06}Mn_{0.06} are shown in Figure 6(b). The detected emission wavelengths of 531, 641, and 744 nm represent the excitation peaks from 336 to 490 nm. Generally, increasing the concentration of Mn ions enhanced the bandwidth of the emission spectra of the YAG:Ce,Mn phosphors.

Table 1 lists the photoelectricity parameters for YAG:Ce_{0.06}Mn_y ($y=0, 0.02, 0.04, 0.06, 0.08$). The chromaticity color co-ordinates shifted toward the optimum white light emission region for the YAG:Ce,Mn phosphors compared with that of YAG:Ce. The CIE chromaticity comprises two color co-ordinates, x and y , which specify the point on the chromaticity diagram in Figure 7. The CIE color co-ordinates of YAG:Ce and YAG:Ce,Mn phosphors, which were excited

Figure 5 FWHM of (a) YAG:Ce_{0.06} and (b) YAG:Ce_{0.06}Mn_{0.08}.

Figure 6 (a) Emission spectra of YAG:Ce,Mn for excitation at 390 nm. 1, YAG:Ce_{0.06}Mn_{0.02}; 2, YAG:Ce_{0.06}Mn_{0.04}; 3, YAG:Ce_{0.06}Mn_{0.06}; and 4, YAG:Ce_{0.06}Mn_{0.08} phosphor. (b) Excitation spectra of YAG:Ce_{0.06}Mn_{0.06} detected at 531, 641 and 744 nm.

using a blue LED, are shown in Figure 7. When the YAG:Ce_{0.06} phosphor with a co-ordinate of (0.203, 0.167) was co-doped with Mn ions, the color co-ordinate of the

Table 1 Photoelectric parameters of YAG:Ce_{0.06}Mn_x phosphor

Concentration of Mn (mol/L)	Color co-ordinate x	Color co-ordinate y
0	0.203	0.167
0.02	0.207	0.157
0.04	0.249	0.181
0.06	0.22	0.173
0.08	0.233	0.194

Figure 7 CIE color co-ordinates for YAG:Ce_{0.06} (a), YAG:Ce_{0.06}Mn_{0.04} (b), and YAG:Ce_{0.06}Mn_{0.08} (c) phosphors.

emitted light was shifted to (0.249, 0.181) for the YAG:Ce_{0.06}Mn_{0.04} and (0.233, 0.194) for the YAG:Ce_{0.06}Mn_{0.08}, which are closer to the value for standard white light. This shows that by using a fixed excitation light (460 nm), bright white light with different color co-ordinates can be obtained using YAG:Ce,Mn phosphors.

3 Conclusion

The properties of YAG:Ce phosphors were altered through the co-doping of Mn ions. Compared with that of YAG:Ce phosphor, Mn co-doped YAG:Ce phosphors red-shifted about 10 nm because of the ²E–⁴A₂, ⁵E–⁵T₂, and ¹T₂–⁵T₂ transitions of the Mn ions. We found that as the concentration of the Mn ions increased, the emission intensity also increased. The CIE color co-ordinates for YAG:Ce_{0.06}Mn_{0.04} and YAG:Ce_{0.06}Mn_{0.08} are (0.249, 0.181) and (0.233, 0.194), respectively. This is in contrast to the CIE color co-ordinates for YAG:Ce_{0.06} (0.203, 0.167). Therefore, cerium-manganese-co-doped yttrium aluminum garnet blended with cerium-doped yttrium aluminum garnet phosphor has an improved white light emission spectrum, which is promising for use in white LEDs.

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