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# A novel red-emitting phosphor $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}:\text{Ce}^{3+}/\text{Mn}^{2+}$ for blue chip-based white LEDs

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Traditional white light-emitting diodes (LEDs) (blue chip + YAG:Ce<sup>3+</sup> yellow phosphor) have the limitation of red deficiency, which limits their application in the illumination field. The single cation/anion substitution or co-doping of activators can increase the red component; however, the large energy loss is attributed to the ultra-long Stokes shift and energy transfer. This work attempts to utilize the short-distance Stokes shift and a small amount of energy transfer to increase the red component in two steps. First, based on a large number of previous research results, the  $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}:\text{Ce}^{3+}$  phosphor is selected. Second, additional enhancement of the red component in the emission spectrum was achieved by ion co-doping Mn<sup>2+</sup> into  $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}:\text{Ce}^{3+}$ . The emission peaks for samples  $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}:\text{Ce}^{3+},\text{Mn}^{2+}$  shift from 600 to 635 nm with increase in the concentration of Mn<sup>2+</sup>, and the emission spectra intensity of  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{ Ce}^{3+},0.03\text{ Mn}^{2+}$  anomalously increased by ~37%, which was attributed to the increase in the distance between Ce<sup>3+</sup> ions because of the doping of Mn<sup>2+</sup> ions, and reduction in the concentration of defects in the crystal, resulting in the energy loss decreases of Ce<sup>3+</sup>. The emission peak of  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{ Ce}^{3+},0.03\text{ Mn}^{2+}$  shifts to 618 nm and the quantum efficiency was as high as 83.07%. Furthermore, this sample has high thermal stability and the emission intensity was still 80.14% at 120 °C. As such, it has great potential in the application of white LEDs.

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## 1 Introduction

Traditional white LEDs (the blue-chip + YAG:Ce<sup>3+</sup> yellow phosphor) have superior properties of high brightness and low cost and are extensively used in transportation, lighting displays, medical devices, electronic products and other fields. However, because of the lack of red-light components, color rendering and color temperature of white LEDs is insufficient to meet the increasing lighting requirements. For example, in the field of high-color restored lighting or warm white lighting, it cannot compete with other white lighting solutions.<sup>1–6</sup> In general, the red light component of the phosphor can be increased by co-doping other activating ions, *e.g.*, Jia *et al.* reported the YAG:Ce<sup>3+</sup>,Mn<sup>2+</sup> phosphor with the two emission peaks at 540 nm (Ce<sup>3+</sup>) and 594 nm (Mn<sup>2+</sup>), which increases the red component of the emission with increasing Mn<sup>2+</sup> concentration.<sup>7</sup> However, adding sufficient red components requires Ce<sup>3+</sup> to transfer a large amount of energy to enhance the emission intensity of

Mn<sup>2+</sup> ions.<sup>8–11</sup> However, it causes a large amount of energy loss, which reduces the overall luminous intensity of the phosphor. Furthermore, the substitution of anions/cations to adjust the crystal field environment of Ce<sup>3+</sup> ions can regulate the emission spectrum of Ce<sup>3+</sup> ions to the long-wave direction and increase the red component. A large number of researchers have adjusted the emission spectrum of YAG:Ce<sup>3+</sup> by this method and obtained a large number of results to achieve the movement of the emission peak from 532 to 622 nm.<sup>12–14</sup> However, with the redshift of the emission spectrum, its Stokes shift increases, the quenching effect increases, and the emission intensity of the phosphor gradually decreases, which limits the application of the phosphor. The energy loss caused by the ultra-long Stokes shift and a large amount of energy transfer is extremely large. Either method cannot obtain high-efficiency phosphors alone; this work attempts to combine two methods to prepare a highly efficient red phosphor in two steps. Firstly, initially improve the red component of Ce<sup>3+</sup> ion emission spectrum using structural fine-tuning, while ensuring that the phosphor has relatively strong luminescence intensity. Pan *et al.* reported an orange (600 nm) emitting phosphor  $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}:\text{Ce}^{3+}$  with quantum efficiency as high as 58.3%;<sup>15</sup> as such, the  $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}:\text{Ce}^{3+}$  phosphor is selected based on a large number of previous research results. Second, additional enhancement in the red component of the emission spectrum

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by co-doping  $\text{Mn}^{2+}$  with  $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}:\text{Ce}^{3+}$ ; moreover, it is desired to obtain a highly efficient red phosphor. Finally, when the doping concentration of  $\text{Mn}^{2+}$  is 0.03, the emission peak of  $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}:\text{Ce}^{3+}, \text{Mn}^{2+}$  shifts to 618 nm, and the quantum efficiency is as high as 83.07%. Furthermore, the emission intensity of the sample  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07 \text{ Ce}^{3+}, 0.03 \text{ Mn}^{2+}$  is still 80.14% at 120 °C, indicating that this sample has a higher thermal stability. By mixing this sample with  $\text{YAG}:\text{Ce}^{3+}$ , a warm white light with a high color index of 78 and abundant red light components is obtained, stimulated by the 460 nm-sized blue chip. It has great potential in applying white LEDs.

## 2 Sample preparation and characterization

A series of  $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}$ ,  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07 \text{ Ce}^{3+}, y\text{Mn}^{2+}$  ( $y = 0, 0.01, 0.02, 0.03, 0.04, 0.06, 0.08, 0.12, 0.16$ ) and  $\text{Mg}_{1.97}\text{Y}_{2-x}\text{Al}_2\text{Si}_2\text{O}_{12}:x\text{Ce}^{3+}, 0.03 \text{ Mn}^{2+}$  ( $x = 0, 0.001, 0.005, 0.01, 0.03, 0.05, 0.07$ ) samples were synthesized by a high temperature solid-state method. The raw materials were  $\text{MgO}$  (A.R.),  $\text{Y}_2\text{O}_3$  (99.999%),  $\text{Al}_2\text{O}_3$  (A.R.),  $\text{SiO}_2$  (A.R.),  $\text{CeO}_2$  (99.999%), and  $\text{MnCO}_3$  (A.R.). Firstly, the raw materials were weighed as per the stoichiometric ratio, and then they were placed in an agate mortar and ground for 20 min; the ground powders were placed in a corundum, and then placed in a box furnace for sintering by heating to 1650 °C and held for 5 h. Finally, the samples were naturally cooled to room temperature, and the samples were taken out and placed in an agate mortar for grinding to obtain powder samples for the subsequent measurements.

### 2.1 Phase structure characterization

The phase structures of the samples were characterized using a Bruker D8 X-ray diffractometer. The radiation source was Cu target  $\text{K}\alpha$  ( $\lambda = 0.15406 \text{ nm}$ ), and the working voltage and current were 40 kV and 40 mA, respectively. The scan range  $2\theta$  and the step size were 10–80° and  $0.02^\circ \text{ s}^{-1}$ , respectively.

### 2.2 Optical properties

The steady-state spectra of the samples were measured using a Hitachi F-4600 fluorescence spectrometer. The sample thermoluminescence spectra (TL) were measured using an FJ-427A1 type thermoluminescence meter, and the measurement range and heating rate were 50–300 °C and  $1^\circ \text{ C s}^{-1}$ , respectively. The samples were irradiated for 5 min under UV light and then placed in a dark room for 10 min before thermoluminescence measurements were taken.

### 2.3 Fluorescence lifetime and quantum efficiency

The lifetimes of samples were monitored using a Horiba FL3 instrument. The lifetime of  $\text{Ce}^{3+}$  was achieved using 320 and 455 nm nano-LEDs as exciting sources, and the lifetime of  $\text{Mn}^{2+}$  was measured using a Xe lamp as the light source. The quantum efficiencies of samples were measured using the Hitachi F-7000 fluorescence spectrophotometer and a Hitachi 5J0-0148 integrating sphere.

## 3 Results and discussion

### 3.1 XRD pattern and crystal structure

Fig. 1(a) shows the unit cell of  $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}$ . There are three different lattice positions in the stability of the garnet structure. The Y/Mg atom has eight coordination oxygen atoms together to form a dodecahedron with two different bond lengths. The length

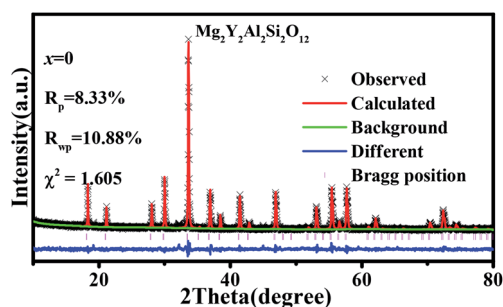


Fig. 2 XRD refinement of  $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}$ .

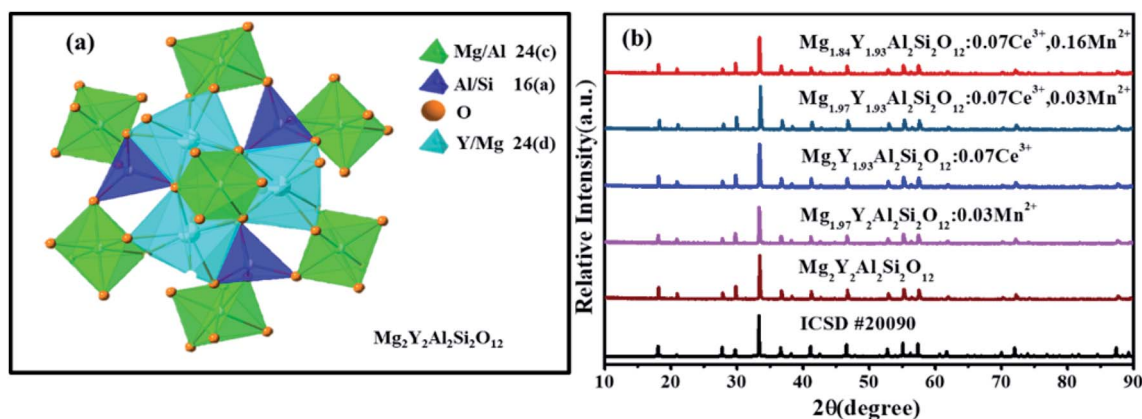


Fig. 1 (a) The unit cell of  $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}$ . (b) XRD patterns of  $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}$ ,  $\text{Mg}_{1.97}\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}:0.03 \text{ Mn}^{2+}$ ,  $\text{Mg}_2\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07 \text{ Ce}^{3+}$ ,  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07 \text{ Ce}^{3+}, 0.03 \text{ Mn}^{2+}$ ,  $\text{Mg}_{1.84}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07 \text{ Ce}^{3+}, 0.16 \text{ Mn}^{2+}$ .



of the four shorter keys is  $m$  and the length of four longer keys is  $n$ . The Y/Mg atom occupies 24(c) sites in the unit cell. The Mg/Al atom has six coordination oxygen atoms together to form an octahedron, which has the same bond length  $p$  and occupies 16(a) sites in the unit cell. The Al/Si atom occupies the 24(d) site and has four coordinating oxygen atoms to form a tetrahedron, which has the same bond length  $q$ . Fig. 1(b) shows the XRD patterns of representative samples  $\text{Mg}_2\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}$ ,  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.03\text{Mn}^{2+}$ ,  $\text{Mg}_2\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}$ ,  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, 0.03\text{Mn}^{2+}$  and  $\text{Mg}_{1.84}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, 0.16\text{Mn}^{2+}$ . The XRD diffraction peak positions of the synthetic samples match well with the diffraction peak in the standard card  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (ICSD#20090), indicating that all the samples have a single-crystal phase and that the  $\text{Ce}^{3+}$  and  $\text{Mn}^{2+}$  ions do not destroy the crystal structure. The XRD patterns of samples are subjected to refinement using the standard card  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (ICSD#20090) as a standard, and the obtained refinement data are within the accurate range and are shown in Fig. 2–4.

### 3.2 Luminescence properties of $\text{Mg}_2\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}$ and $\text{Mg}_{1.97}\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}:0.03\text{Mn}^{2+}$

Fig. 5(a) and (b) show the excitation spectra and emission spectra of  $\text{Mg}_2\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}$  two luminescence

centers. The luminescence centers come from the  $\text{Ce}^{3+}$  ions substituting  $\text{Y}^{3+}$  ions to occupy eight coordination sites.<sup>15</sup> The emission spectra of  $\text{Ce}^{3+}$  in fluorides and oxides can generally move from the ultraviolet region to the blue region. However, in the environment of strong covalent and crystal field, the 5d energy level of  $\text{Ce}^{3+}$  ions can move to a lower energy range; therefore,  $\text{Ce}^{3+}$  can emit yellow or even red fluorescence color.<sup>7,8,16</sup> In the study of sulfides and nitrides, the 5d energy levels of  $\text{Ce}^{3+}$  ions can be divided into two to five energy levels, and the number of separations depend on the symmetry of the lattice containing  $\text{Ce}^{3+}$  ligands. In the cubic symmetry crystal structure, such as garnet structure, the 5d state is split into two energy levels ( $e_g$  and  $t_g^2$ ), and the crystal field can be split further in the twisted cubic crystal.<sup>17–22</sup> The unique longwave emission (green yellow-orange) of  $\text{Ce}^{3+}$  in the garnet is attributed to the splitting of the crystal field of the energy level  $e_g$  into a lower  $5d_1$  level and a higher energy  $5d_2$  level with an interval of about  $8000\text{ cm}^{-1}$ . It is precise because of this energy level splitting the emission from the highest energy  $5d_2$  level is in the blue-violet spectral region; the emission from the lowest energy  $5d_1$  level is in the green yellow-orange spectral region.<sup>23–27</sup> It is seen from Fig. 5(a), under the excitation of 332 nm, the emission spectrum of  $\text{Ce}^{3+}$  extends from 350 to 700 nm, and the emission peak is

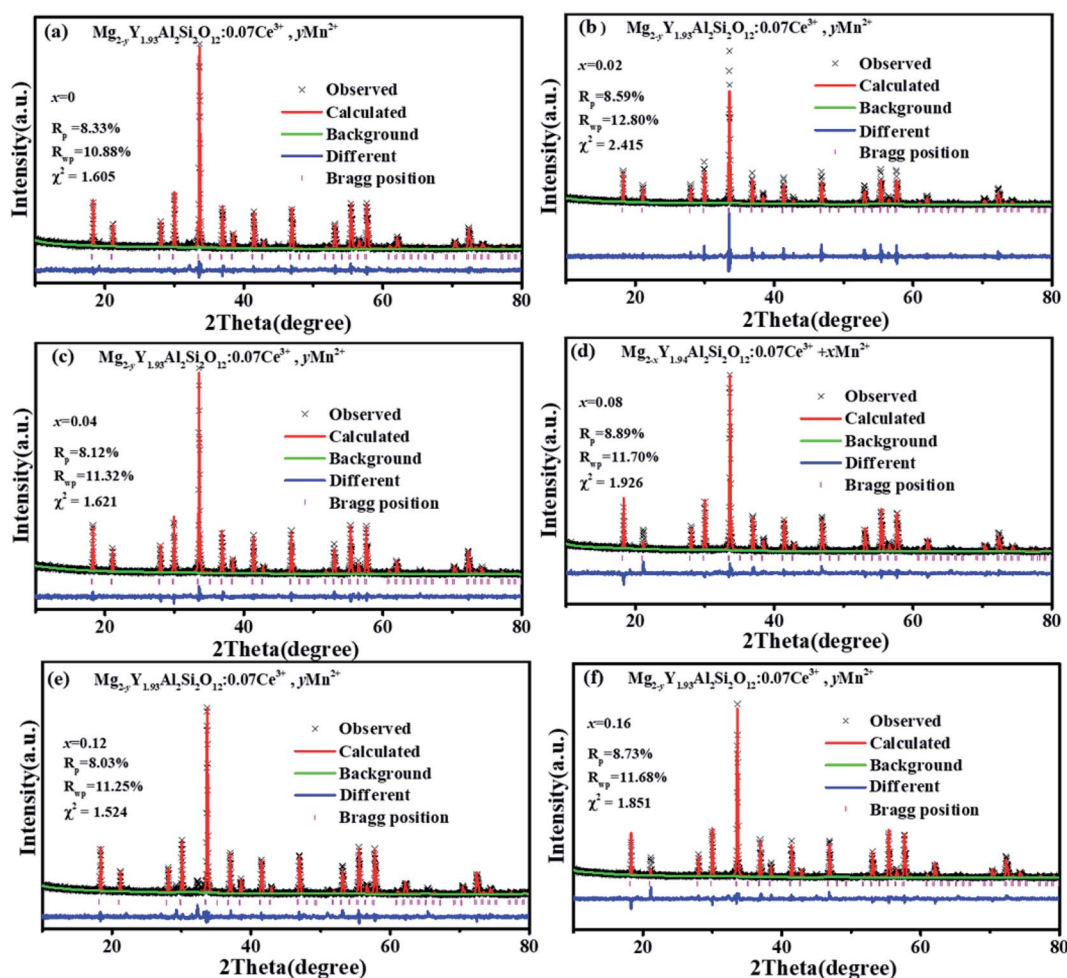


Fig. 3 XRD refinement of  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, y\text{Mn}^{2+}$  ( $y = 0, 0.02, 0.04, 0.12, 0.16$ ).





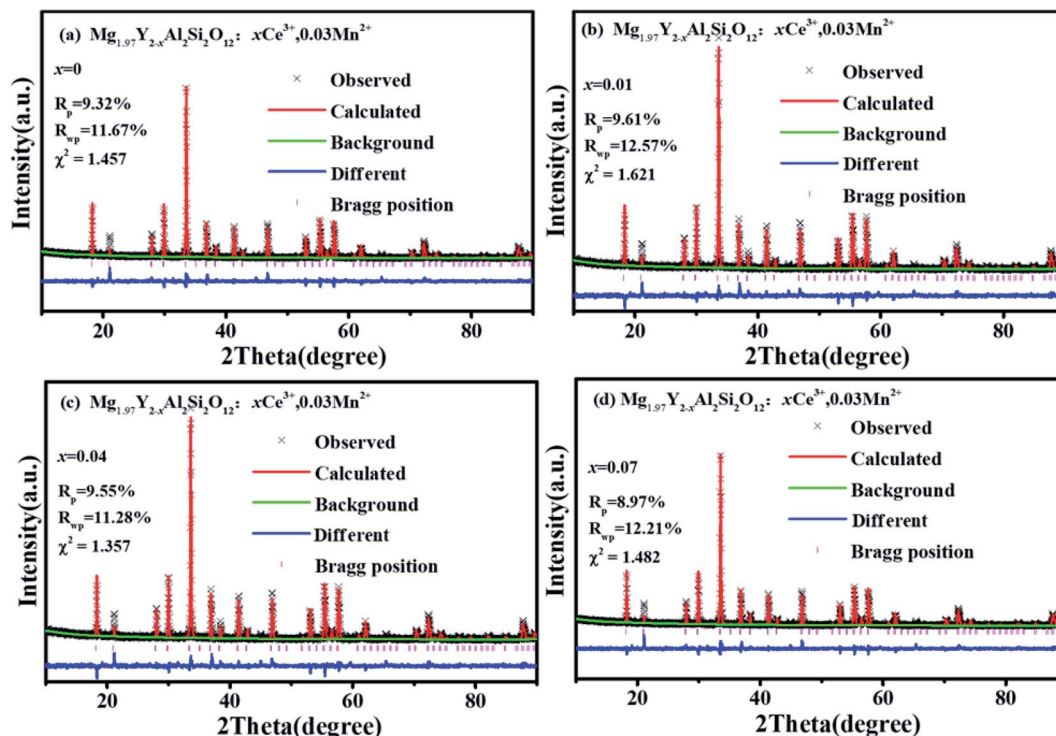


Fig. 4 XRD refinement of  $\text{Mg}_{1.97}\text{Y}_{2-x}\text{Al}_2\text{Si}_2\text{O}_{12}:x\text{Ce}^{3+},0.03\text{Mn}^{2+}$  ( $x = 0, 0.01, 0.03, 0.07$ ).

located at 405 nm. By monitoring the 405 nm emission peak, the excitation spectrum ranges from 200 to 400 nm, and the strongest excitation peak is 332 nm, which is formed by the electron transition from the ground state to  $5d_2$  energy level. The tailing of 500–650 nm comes from the emission spectrum of electrons from  $5d_2$  level relaxing to  $5d_1$  level and then downward. In Fig. 5(b), under the excitation of 470 nm, it is seen that the emission spectrum extends from 500 nm to 800 nm and the emission peak is at 600 nm. For the 600 nm emission peak, the corresponding excitation spectrum extends from 200 nm to 550 nm. It is obvious that there are two excitation peaks in the excitation spectrum: one is  $\sim 332$  nm, which is attributed to the electronic transition from the ground state to the  $5d_2$  level, and the other one is at 470 nm, which is attributed to the electron transition from the ground state to the  $5d_1$  level.

In the previous work, it has been proven that  $\text{Mn}^{2+}$  ions can occupy the tetracoordinate, hexacoordinate and octagonal sites of  $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}$  and emit green light (536 nm), red light (635 nm) and deep red light (735 nm). When the amount of  $\text{Mn}^{2+}$  is  $> 0.2$ , the deep red light will be generated. The purpose of this work is to develop a red-light-compensated phosphor; hence, the amount of  $\text{Mn}^{2+}$  ions is not  $> 0.2$ . Fig. 5(c) and (d) show the excitation spectra and emission spectra of  $\text{Mg}_{1.97}\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}:0.03\text{Mn}^{2+}$ . According to the literature, Mn ions can occupy four, six and eight coordination in garnet structure.<sup>42</sup> In this work,  $\text{Mn}^{2+}$  occupies eight coordination sites to form the luminescence center Mn1. Under the excitation of 421 nm, the emission spectrum extends from 470 to 700 nm, and the primary peak is located at 635 nm. By monitoring the 635 nm emission peak, the excitation spectrum from 200 nm to 500 nm

is obtained, and the peak is at 421 nm. The 536 nm emission peak is derived from the luminescence center Mn2 formed by  $\text{Mn}^{2+}$  occupying a tetracoordinate position, as shown in Fig. 5(d). For the luminescence center Mn2, the emission spectrum extends from 500 to 750 nm under the 456 nm excitation radiation; furthermore, the peak is at 536 nm. For the 536 nm emission peak, a broad excitation band is observed from 200 nm to 500 nm, and the primary peak is at 456 nm.

Fig. 5 show that the emission spectrum of  $\text{Ce}^{3+}$  overlaps with the excitation spectrum of  $\text{Mn}^{2+}$  in the yellow- and green-shaded region and that the luminescence center formed by  $\text{Ce}^{3+}$  may transfer energy to the luminescence centers Mn1 and Mn2. Moreover, the emission peak of  $\text{Mn}^{2+}$  ion is closer to the long-wave direction; furthermore, the red component of  $\text{Mg}_2\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}$  can be enhanced by co-doping  $\text{Mn}^{2+}$ . In addition, under the same measurement conditions, the ratio of the relative emission intensity of  $\text{Ce}^{3+}$  to  $\text{Mn}^{2+}$  is  $\sim 100 : 1$ .

### 3.3 Luminescence properties of $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},0.03\text{Mn}^{2+}$

Fig. 6(a) shows the emission spectrum of  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},0.03\text{Mn}^{2+}$  under the 470 nm excitation and the primary peak is at 618 nm. Compared with the emission peak of  $\text{Mg}_2\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}$  is at 600 nm in Fig. 5(b), the emission spectrum of  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},0.03\text{Mn}^{2+}$  results in a significant redshift. No characteristic emission spectrum of  $\text{Mn}^{2+}$  is observed in the spectrum, and the characteristic excitation of  $\text{Mn}^{2+}$  ions could not be observed by monitoring the emission peaks of 635 (Mn1) and 536 nm (Mn2).



It may be because the luminescence intensity of  $\text{Mn}^{2+}$  is considerably smaller than the luminescence intensity of  $\text{Ce}^{3+}$ . To avoid this interference, the emission spectrum of the sample  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},0.03\text{Mn}^{2+}$  is measured under the excitation of 332 nm. Fig. 6(b) shows the 635 nm characteristic emission of Mn1 with the 332 nm excitation, which indicates that  $\text{Mn}^{2+}$  can normally emit. To further confirm that  $\text{Mn}^{2+}$  ions form luminescence centers in  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},0.03\text{Mn}^{2+}$ , the lifetimes of Mn1 and Mn2 are measured; furthermore, the lifetimes can be calculated using the following formula<sup>28–30</sup>

$$\tau = \frac{\int_0^\infty I(t)dt}{\int_0^\infty I(t)dt} \quad (1)$$

$I$  refers to the emission intensity of the illuminating center at time  $t$ ,  $t$  is time, and  $\tau$  is the lifetime. The calculated lifetimes of Mn1 and Mn2 are 3.63 and 0.97 ms, respectively, as shown in Fig. 6(c). It is confirmed that  $\text{Mn}^{2+}$  ions do form the luminescent centers in the sample and that the emission spectra of the sample  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},0.03\text{Mn}^{2+}$  is attributed to the interaction of  $\text{Ce}^{3+}$  and  $\text{Mn}^{2+}$  luminescence centers.

Fig. 7(a) shows the emission spectra of  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},y\text{Mn}^{2+}$  under 470 nm excitation. There is an obvious red shift, which can be observed with  $\text{Mn}^{2+}$  concentration increased, and the emission peaks of  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},y\text{Mn}^{2+}$  shifting from 600 to 635 nm, as shown in Fig. 7(b). The reasons may be explained below:

(1) When doped with  $\text{Mn}^{2+}$  ions, the crystal structure of the sample changes, resulting in a change in the emission spectra of  $\text{Ce}^{3+}$ , which causes the redshift of the emission spectra.

(2)  $\text{Ce}^{3+}$  ions transfer energy to the luminescence center of Mn1, and the emission intensity of Mn1 increases, which causes the emission spectra to move toward the long-wave direction.

For specific reasons, the following experiments were performed.

### 3.4 Analyze the conjecture (1)

Under the 470 nm excitation, the emission spectrum of Mn1 is indistinguishable from the large-area overlap of the emission spectrum of the  $\text{Ce}^{3+} 5d_1$  level. To reduce the effect of the emission spectrum of the  $5d_1$  level, the emission spectra of the samples were measured under 332 nm excitation. Fig. 8(a) shows that the emission peak of the right emission spectrum is at 635 nm, which is attributed to the luminescence center Mn1. As the doping concentration of  $\text{Mn}^{2+}$  increases, the crystal structure may change; furthermore, the emission spectrum of Mn1 shifts to the long-wave direction. Because  $\text{Ce}^{3+}$  and Mn1 occupy the same position, the emission spectrum of  $\text{Ce}^{3+}$  may move in the longwave direction with increase in  $\text{Mn}^{2+}$  doping concentration. Furthermore, verifying the above conclusions from the perspective of the crystal structure. Many factors describe the change in the crystal field; however, the most influential two factors are the average bond length of the polyhedral unit cell and the degree of distortion of the unit cell. The relationship between the average bond length and the splitting of the luminescent center level orbit can be calculated using the following formula<sup>31</sup>

$$\varepsilon_{\text{cfs}} = \beta_{\text{poly}} R^{-2} \quad (2)$$

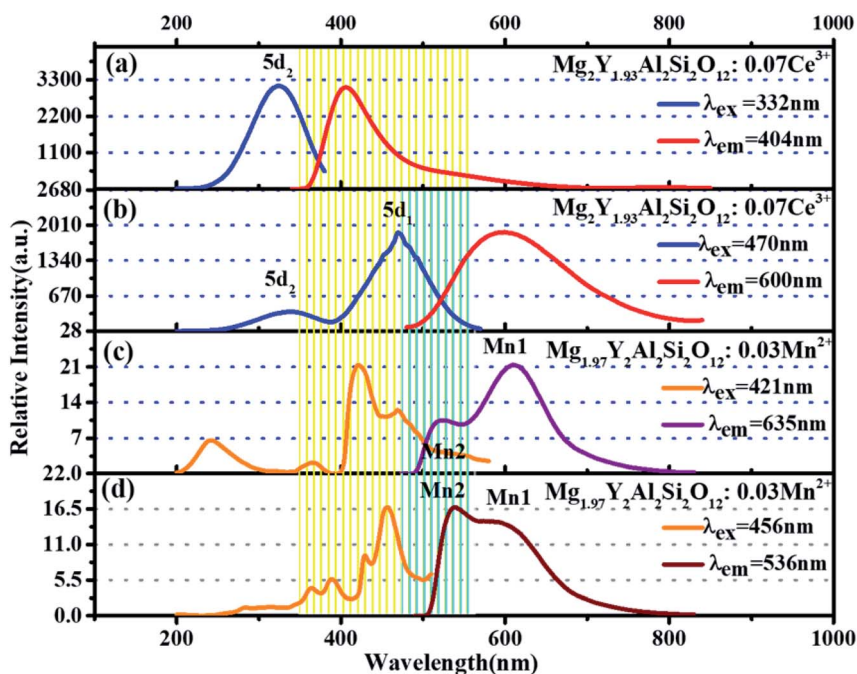


Fig. 5 (a and b) Excitation spectra and emission spectra of  $\text{Mg}_2\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}$ . (c and d) Excitation spectra and emission spectra of  $\text{Mg}_{1.97}\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}:0.03\text{Mn}^{2+}$ .



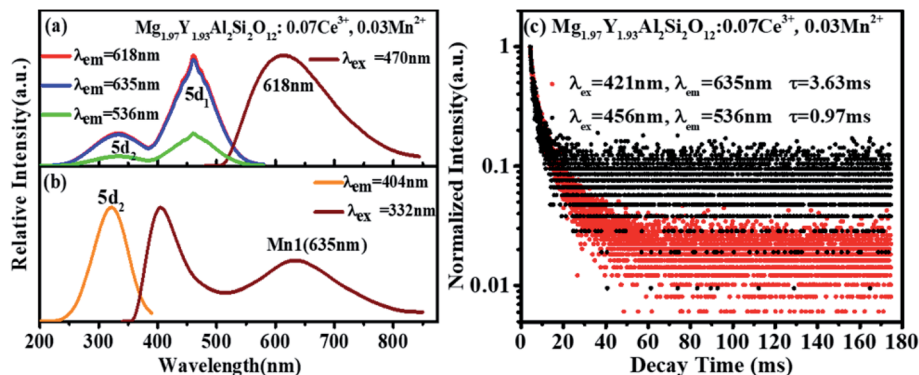


Fig. 6 (a and b) Excitation spectra and emission spectra  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, 0.03\text{Mn}^{2+}$ ; (c) lifetime decay spectra of Mn1 and Mn2 in  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, 0.03\text{Mn}^{2+}$ .

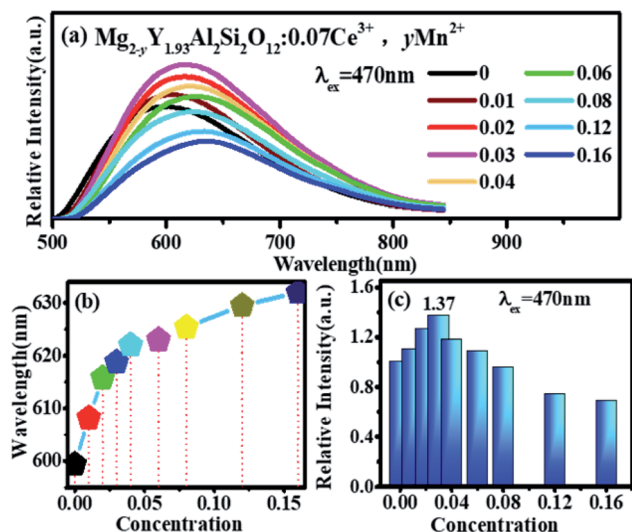


Fig. 7 (a) Emission spectra of  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, y\text{Mn}^{2+}$  ( $y = 0, 0.01, 0.02, 0.03, 0.04, 0.06, 0.08, 0.12, 0.16$ ) ( $\lambda_{\text{ex}} = 470\text{nm}$ ). (b) A shift diagram of the emission peaks of  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, y\text{Mn}^{2+}$  ( $y = 0, 0.01, 0.02, 0.03, 0.04, 0.06, 0.08, 0.12, 0.16$ ) ( $\lambda_{\text{ex}} = 470\text{nm}$ ). (c) A change in emission intensity of  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, y\text{Mn}^{2+}$  ( $y = 0, 0.01, 0.02, 0.03, 0.04, 0.06, 0.08, 0.12, 0.16$ ) ( $\lambda_{\text{ex}} = 470\text{nm}$ ).

$\epsilon_{\text{cfs}}$  is the crystal field splitting and  $\beta_{\text{poly}}$  is a constant, which depends on the type of polyhedron; generally,  $\beta_{\text{octa}} = 1.35 \times 10^9 \text{ pm}^2 \text{ cm}^{-1}$  (octahedron). The  $\beta_{\text{poly}}$  of other polyhedral cells can be derived from the octahedral  $\beta_{\text{octa}}$ :  $\beta_{\text{cub}} = 0.89\beta_{\text{octa}}$  (cube),  $\beta_{\text{dh}} = 0.79\beta_{\text{octa}}$  (dodecahedron).  $R^{-2}$  is the average bond length; therefore, the degree of the orbital splitting of the activated ions increases as  $R$  decreases.

As for the crystal distortion, the change in the bond length and bond angle in the crystal can cause the symmetry of the crystal decreasing and lead to the crystal field to split. Conversely, the symmetry of crystal increasing indicates the distortion degree of the crystal decreasing, which reduces the split in the crystal field. It can be calculated using the formula (3),<sup>32,33</sup> and the degree of distortion is affected by the bond length

$$\text{Key length : } D = \frac{1}{n} \sum_{i=1}^n \frac{|l_i - l_{\text{av}}|}{l_{\text{av}}} \quad (3)$$

where  $l_i$  represents the bond length of the central atom and the ligand,  $l_{\text{av}}$  represents the average bond length, and  $n$  represents the coordination number. Table 1 shows the XRD refinement data of  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, y\text{Mn}^{2+}$  ( $y = 0, 0.02, 0.04, 0.08, 0.12, 0.16$ ) and the calculated distance between  $\text{Ce}^{3+}$  ions. The energy level splitting and distortion of  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, y\text{Mn}^{2+}$  ( $y = 0, 0.02, 0.04, 0.08, 0.12, 0.16$ ) was

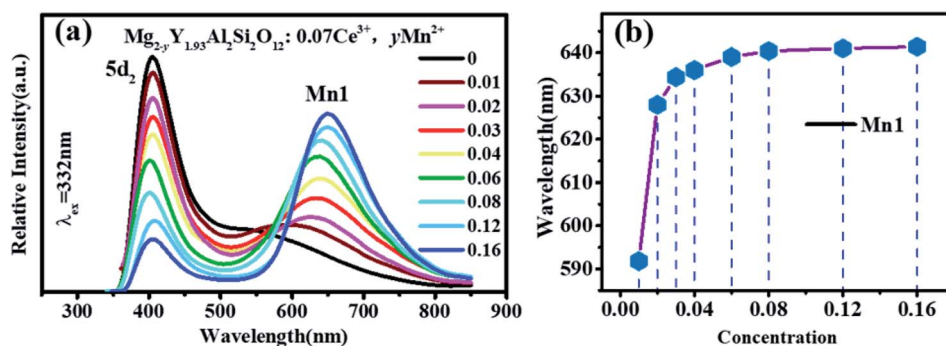


Fig. 8 (a) The emission spectra of the samples  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, y\text{Mn}^{2+}$  ( $y = 0, 0.01, 0.02, 0.03, 0.04, 0.06, 0.08, 0.12, 0.16$ ) at 332 nm excitation; (b) the emission peak shifts of the Mn1 emission spectra.



**Table 1** XRD refinement data of  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},y\text{Mn}^{2+}$  ( $y = 0, 0.02, 0.04, 0.08, 0.12, 0.16$ ) and the calculated distance between  $\text{Ce}^{3+}$  ions

	0	0.02	0.04	0.08	0.12	0.16
$x$						
$\chi^2$	1.605	2.415	1.621	1.926	1.524	1.851
$R_{\text{wp}}$	10.88%	12.8%	11.32%	11.7%	11.25%	11.68%
$R_p$	8.3%	8.59%	8.12%	8.89%	8.03%	8.73%
$a/b/c$ (Å)	11.990	11.992	11.993	11.994	11.995	11.997
$V$ (Å <sup>3</sup> )	1723.665	1724.339	1724.819	1725.282	1725.900	1726.763
Eight-coordinated bond lengths $m$ (Å)	2.313	2.313	2.315	2.317	2.319	2.321
Eight-coordinated bond lengths $n$ (Å)	2.4265	2.428	2.431	2.435	2.439	2.443

calculated and the data is shown in Table 2. The crystal field splitting decreases with an increase in the  $\text{Mn}^{2+}$  concentration; however, at the same time, the unit cell distortion gradually increases, which causes the energy level splitting to increase. In fact, the crystal distortion in the dodecahedral structure of the garnet has a stronger influence on the luminescence center, which makes the emission spectrum shift toward the long-wave direction. The above analyses indicate that speculation (1) is correct. When doped with  $\text{Mn}^{2+}$  ions, the crystal structure of the sample changes, resulting in the emission redshift of  $\text{Ce}^{3+}$  and  $\text{Mn}^{2+}$ .

### 3.5 Analyze the conjecture (2)

It can be clearly seen from Fig. 8(a) that the  $\text{Ce}^{3+}$  ions transfer energy to Mn1 under excitation at 332 nm. However, under excitation at 470 nm, the emission spectra of Mn1 cannot be distinguished from the  $5d_1$  emission spectra of  $\text{Ce}^{3+}$ . To confirm that there is an energy transfer between the  $5d_1$  emission spectra of  $\text{Ce}^{3+}$  and the emission spectra of Mn1; the lifetime changes of  $\text{Ce}^{3+}$  and  $\text{Mn}^{2+}$  luminescent centers were measured. The lifetimes of Mn1, Mn2, the electron of  $5d_1$  and  $5d_2$  (using 320 nm and 455 nm external LED pulse lamps) level in  $\text{Mg}_{1.97}\text{Y}_{2-x}\text{Al}_2\text{Si}_2\text{O}_{12}:x\text{Ce}^{3+},0.03\text{Mn}^{2+}$  and  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},y\text{Mn}^{2+}$  were measured with an increase in the  $\text{Mn}^{2+}$  concentration. Fig. 9(a) shows the lifetimes of the luminescence center Mn1. The results show that the lifetimes of the luminescence center Mn1 gradually increases with increase in  $\text{Ce}^{3+}$  concentration.

Fig. 5 shows that the emission spectrum of Mn2 overlaps with the excitation and emission spectra of  $\text{Ce}^{3+}$  ions, indicating that the photon energy emitted by the two is close. Therefore, Mn2 may transfer energy to  $\text{Ce}^{3+}$  ions, and  $\text{Ce}^{3+}$  may transfer

energy to Mn2. The experiment verified the relevant information, and a large number of studies reported that  $\text{Ce}^{3+}$  transfers energy to  $\text{Mn}^{2+}$  and examples of  $\text{Mn}^{2+}$  ion transferring energy to  $\text{Ce}^{3+}$  have not been found.<sup>34–39</sup> Furthermore, the experiment measured the lifetime change of Mn2 luminescence center with  $\text{Ce}^{3+}$  doping, as shown in Fig. 9(b). With increase in  $\text{Ce}^{3+}$  ion doping concentration, the lifetime of Mn2 luminescence center has a slight increase, indicating that  $\text{Ce}^{3+}$  is in the material and it is possible to transfer energy to Mn2.

Fig. 9 (c–f) show the lifetimes of the  $5d_1$  and  $5d_2$  level electrons of  $\text{Ce}^{3+}$  in  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},y\text{Mn}^{2+}$ . When the  $\text{Mn}^{2+}$  concentration is increased, the lifetimes of  $\text{Ce}^{3+}$  decrease overall (the abnormality of lifetimes is explained in detail below). Consequently,  $\text{Ce}^{3+}$  ions transfer energy to  $\text{Mn}^{2+}$  ions, and the emission intensity of Mn1 increases, which causes the emission spectra of the samples  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},y\text{Mn}^{2+}$  to move toward the long-wave direction.

Therefore, the primary reasons for the spectral shift are as follows: (1) as the  $\text{Mn}^{2+}$  ion concentration increases, the distortion of the dodecahedral unit cell increases such that the  $5d_1$  level of  $\text{Ce}^{3+}$  splitting and the crystal field splitting of Mn1 luminescence center increase, the emission spectra move toward the direction of long waves. (2) The  $\text{Ce}^{3+}$  luminescence center transferred energy to the Mn1 luminescence center, and the luminescence intensity of Mn1 increases, which causes the emission spectra to move toward the long-wave direction. Under the combined action of the two, the emission spectra move toward the long-wave direction as the  $\text{Mn}^{2+}$  concentration increases.

Moreover, as shown in Fig. 8(a) and 6(a), the energy transfer of  $\text{Ce}^{3+}$  to Mn1 is more efficient than the Mn2 luminescence center, which indicated that  $\text{Ce}^{3+}$  has little effect on the luminescence properties of Mn2. This may be attributed to Mn2 being located at the center of the fully symmetric tetrahedron, which greatly weakens the influence of external Mn2 luminescence center. Conversely, it can be considered that the effect of Mn2 on the overall luminescent property of  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},y\text{Mn}^{2+}$  is weak.

In Fig. 7(a) and (c), under the excitation of 470 nm, the emission intensities of  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},y\text{Mn}^{2+}$  abnormally increases with increase in  $\text{Mn}^{2+}$  concentration. In Fig. 5, under the same test conditions (photomultiplier voltage is 460 V, excitation end slit width is 2.5 nm, and receiving end slit width is 2.5 nm), the relative emission intensity of  $\text{Mn}^{2+}$  is

**Table 2** The energy level splitting and distortion of  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},y\text{Mn}^{2+}$  ( $y = 0, 0.02, 0.04, 0.08, 0.12, 0.16$ )

Concentration	Energy level splitting $\varepsilon_{\text{cfs}}$ ( $10^9\text{ pm}^2\text{ cm}^{-1}$ )	Distortion $D$
0	0.1899	0.0239
0.02	0.1898	0.0243
0.04	0.1894	0.0244
0.08	0.1889	0.0248
0.12	0.1885	0.0253
0.16	0.1880	0.0255



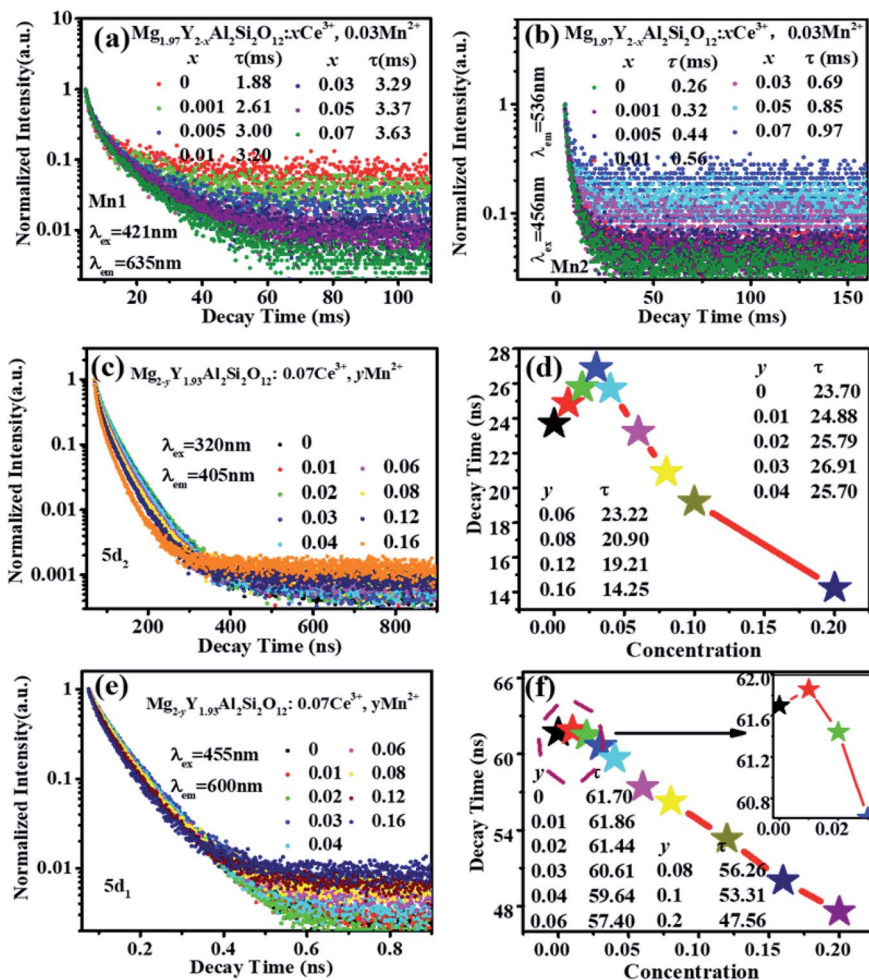


Fig. 9 (a) Lifetimes of Mn1 luminescence center in  $\text{Mg}_{1.97}\text{Y}_{2-x}\text{Al}_2\text{Si}_2\text{O}_{12}:\text{xCe}^{3+}, 0.03\text{Mn}^{2+}$  ( $\lambda_{\text{ex}} = 421 \text{ nm}$ ,  $\lambda_{\text{em}} = 635 \text{ nm}$ ); (b) the lifetimes of Mn2 luminescence center in  $\text{Mg}_{1.97}\text{Y}_{2-x}\text{Al}_2\text{Si}_2\text{O}_{12}:\text{xCe}^{3+}, 0.03\text{Mn}^{2+}$  ( $\lambda_{\text{ex}} = 456 \text{ nm}$ ,  $\lambda_{\text{em}} = 536 \text{ nm}$ ); (c and d) the lifetimes of the  $5d_2$  level electrons of  $\text{Ce}^{3+}$  in  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, y\text{Mn}^{2+}$  and the corresponding line graph ( $\lambda_{\text{ex}} = 320 \text{ nm}$ ,  $\lambda_{\text{em}} = 405 \text{ nm}$ ); (e and f) the lifetime of the  $5d_1$  level of  $\text{Ce}^{3+}$  in  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, y\text{Mn}^{2+}$  and the corresponding line graph ( $\lambda_{\text{ex}} = 455 \text{ nm}$ ,  $\lambda_{\text{em}} = 600 \text{ nm}$ ).

much smaller than that of  $\text{Ce}^{3+}$ . The emission intensities of  $\text{Mn}^{2+}$  are negligible compared to the overall  $\text{Ce}^{3+}$  emission spectra. Though  $\text{Ce}^{3+}$  can transfer energy to the Mn1 luminescence center, the energy utilization efficiency must be generally <100%, which will lose energy. Namely, the number of photons

absorbed by the Mn1 luminescence center will be higher than the number of photons radiated. If there are no other factors, as the  $\text{Mn}^{2+}$  concentration increases, the transfer energy increases and the energy loss increases under the 470 nm excitation; therefore, the overall emission intensity of the sample should

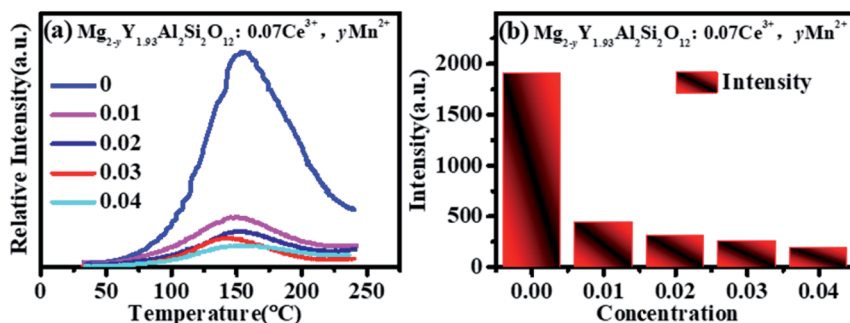


Fig. 10 (a) Thermoluminescence spectra of  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, y\text{Mn}^{2+}$  ( $y = 0, 0.01, 0.02, 0.03, 0.04$ ). (b) The thermoluminescence intensity of  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, y\text{Mn}^{2+}$  as a function of  $\text{Mn}^{2+}$  concentration.



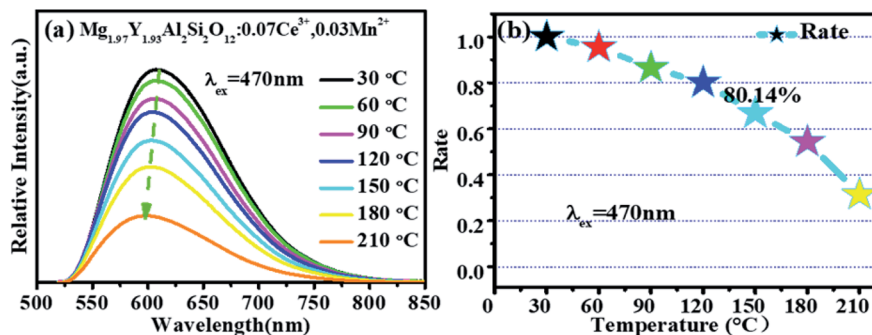


Fig. 11 (a) Temperature spectra of  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, 0.03\text{Mn}^{2+}$ . (b) The emission intensity of  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, 0.03\text{Mn}^{2+}$  as a function of temperature.

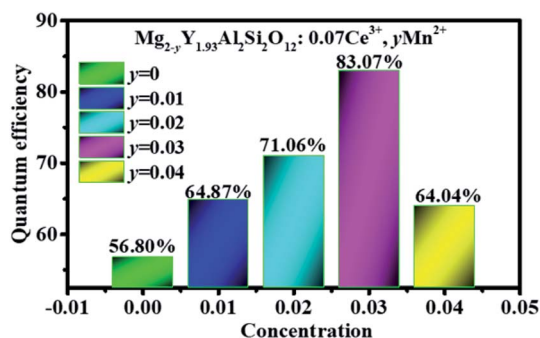


Fig. 12 Quantum efficiency of  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, y\text{Mn}^{2+}$  ( $y = 0, 0.01, 0.02, 0.03, 0.04$ ).

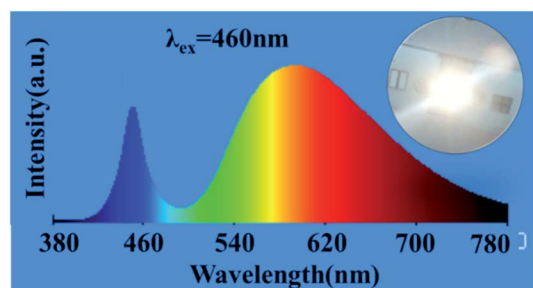


Fig. 13 Mixed phosphor of  $\text{YAG}:\text{Ce}^{3+}$  and  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, 0.03\text{Mn}^{2+}$  is excited by the 460 nm chip.

gradually decrease. However, it is observed that the emission intensities of the samples abnormally increase under the 470 nm excitation with an increase in the  $\text{Mn}^{2+}$  concentration and reach a maximum at 0.03, as shown in Fig. 7(c). It can be inferred that other factors cause an abnormal increase in the luminescence intensity of samples under the same excitation radiation. The luminescence centers in the sample are only  $\text{Ce}^{3+}$  and  $\text{Mn}^{2+}$ ; hence, the possibilities causing the enhanced abnormal luminescence intensity of  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, y\text{Mn}^{2+}$  are as follows:

(1) The luminescence intensity of the  $\text{Mn}^{2+}$  luminescence center itself (excluding the energy transfer of  $\text{Ce}^{3+}$ ) in the  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}, y\text{Mn}^{2+}$  is considerably improved

compared to luminescence intensity in the  $\text{Mg}_{2-y}\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}:y\text{Mn}^{2+}$ . Thus, the emission intensity of co-doping of  $\text{Ce}^{3+}$  and  $\text{Mn}^{2+}$  is higher than that of single-doped  $\text{Ce}^{3+}$  ions under 470 nm excitation.

(2)  $\text{Mn}^{2+}$  doping into  $\text{Mg}_2\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}$  increases the emission intensity of  $\text{Ce}^{3+}$  ions itself, which improves the overall luminescence intensity.

Next, it will be proved and explained one by one. Fig. 6 shows that the characteristic excitation and emission of Mn1 and Mn2 cannot be observed under excitation of 470 nm when co-doped with  $\text{Ce}^{3+}$  and  $\text{Mn}^{2+}$ , which indicates that the luminescence efficiency of  $\text{Mn}^{2+}$  is relatively weak. Therefore, reasons (1) and (3) are excluded. As such, the reason for the abnormal enhancement of the emission of the sample may be the conjecture (2):  $\text{Mn}^{2+}$  ions doping into  $\text{Mg}_2\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+}$  increase the emission intensity of  $\text{Ce}^{3+}$  ions, which improves the overall luminescence intensity. The details of the energy loss between  $\text{Ce}^{3+}$  ions can be described as  $\text{Ce}^{3+}$  acts as an active ion in the host because the activated ions at the same excited states are close enough with increasing activator concentration, which can easily result in energy transfer among the energy states. Due to the energy transfer between activator and activator, the energy will go through the quenching center of impurity and be consumed in the lattice vibration of the host, which can further result in a decrease in the emission intensity. In addition, the activating  $\text{Ce}^{3+}$  ions and defects in the matrix can be used as quenching centers.

Therefore, three factors can improve the emission intensity of  $\text{Ce}^{3+}$  ions: other ions transfer energy to  $\text{Ce}^{3+}$ ; or the energy loss of  $\text{Ce}^{3+}$  decreases the quenching center, or  $\text{Ce}^{3+}$  transferred energy to other luminescent centers decreases. The change of the  $\text{Ce}^{3+}$  lifetimes can reflect the energy change of the  $\text{Ce}^{3+}$  luminescence center. This work analyzes the lifetime change of  $\text{Ce}^{3+}$  ions to determine which factor affects the energy change of the  $\text{Ce}^{3+}$  luminescence center. This relationship can be expressed by the following formula<sup>40</sup>

$$\frac{1}{\tau} = \frac{1}{\tau_0} + P_{\text{nr}} + P_{\text{t}} \quad (4)$$

where  $\tau$  represents the lifetime of the luminescent center,  $\tau_0$  describes the lifetime of the free ion of the luminescent center and is constant.  $P_{\text{nr}}$  represents the probability of a non-radiative



transition of the luminescent center under the action of the quenching center (negative), and  $P_t$  means the probability that the illuminating center absorbs (positively) or outward (negatively). In Fig. 9(d) and (f), the lifetimes of the  $5d_1$  and  $5d_2$  level electrons of  $\text{Ce}^{3+}$  in the sample  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},y\text{Mn}^{2+}$  increase at first, reaching the maximum at  $y = 0.03$ , and then gradually decrease. No luminescence centers can transfer energy to  $\text{Ce}^{3+}$ , and  $\text{Ce}^{3+}$  ions also transfer energy to  $\text{Mn}^{2+}$  ions, so  $P_t$  is negative. As the  $\text{Mn}^{2+}$  concentration increases, the  $P_t$  value decreases. When doped with a small number of  $\text{Mn}^{2+}$  ions, the lifetime of  $\text{Ce}^{3+}$  increases, which proves that there is a certain factor that makes the  $P_{nr}$  to increase, namely, the energy loss of the  $\text{Ce}^{3+}$  ion in the quenching center to decrease. The quenching center of  $\text{Ce}^{3+}$  can be the other  $\text{Ce}^{3+}$  ions surrounding the  $\text{Ce}^{3+}$  luminescence center or the quenching center composed of defects in the matrix structure. So, the reasons for the reduction in energy loss of the corresponding  $\text{Ce}^{3+}$  luminescence center are as the  $\text{Mn}^{2+}$  concentration increases, the distance between  $\text{Ce}^{3+}$  ions increase, which weakens the multipole interaction between  $\text{Ce}^{3+}$  ions;  $\text{Mn}^{2+}$  ions reduce the concentration of defects, the number of  $\text{Ce}^{3+}$  quenching centers and the energy loss of the  $\text{Ce}^{3+}$  luminescence center. Using the volume of the sample unit cell in Table 1, the distances between the  $\text{Ce}^{3+}$  ions were calculated using the formula for the critical distance between ions<sup>41</sup>

$$R_c \approx 2 \left( \frac{3V}{4\pi\chi_c N} \right)^{\frac{1}{3}} \quad (5)$$

where  $R_c$  is the distance between the doped particles,  $V$  is the unit cell volume,  $\chi_c$  is the doping ion concentration, and  $N$  is the number of cations in the unit cell.  $\chi_c = 0.06$ ,  $N = 8$ , and the volume is obtained by refinement data, as shown in Table 1. The distances between  $\text{Ce}^{3+}$  ions are calculated to be 9.0299, 9.0300, 9.0302, 9.0305, 9.0308, 9.0311, which correspond to  $x = 0, 0.02, 0.04, 0.08, 0.12, 0.16$ , respectively. The distances between  $\text{Ce}^{3+}$  ions gradually increase, which means that the interaction probability between  $\text{Ce}^{3+}$  ions decrease, and the energy loss of the  $\text{Ce}^{3+}$  luminescence center is reduced.

The thermoluminescence intensity is used to characterize the number of defects in  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},y\text{Mn}^{2+}$  ( $y = 0, 0.01, 0.02, 0.03, 0.04$ ), as shown in Fig. 10. It can be seen that as the  $\text{Mn}^{2+}$  ions are doped into the material, the number of defects in the sample gradually decreases. Meanwhile, the defect-quenching center number of the  $\text{Ce}^{3+}$  may be decreasing, which reduces the energy loss of the  $\text{Ce}^{3+}$  luminescent center. Briefly, with doping of  $\text{Mn}^{2+}$  ions, the distance between  $\text{Ce}^{3+}$  particles increase, the interaction between  $\text{Ce}^{3+}$  particles decrease, the quenching center of defect formation decreases, and the energy loss of  $\text{Ce}^{3+}$  luminescence center decreases. At low concentration, the energy saved by the quenching center is more than the energy lost by the energy transfer, so that the emission intensities increase. Otherwise, when the doping concentration is relatively high, the energy saved by the quenching center is less than the energy lost by the energy transfer, hence the emission intensity decreases.

### 3.6 Temperature stability and quantum efficiency

Fig. 11 shows that the emission intensity of  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},0.03\text{Mn}^{2+}$  gradually decreases with an increase in the temperature, under the excitation of 470 nm light. The emission spectrum intensity remains 80.14% at 120 °C, which means that it has a higher temperature stability.

Fig. 12 shows the quantum efficiency of  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},y\text{Mn}^{2+}$  ( $y = 0, 0.01, 0.02, 0.03, 0.04$ ). Under the 470 nm excitation, the quantum efficiencies of the samples  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},y\text{Mn}^{2+}$  increase at first and then decreases with increasing  $\text{Mn}^{2+}$  concentration, which is the same as the changing trend of the emission spectra. When doped with 0.03  $\text{Mn}^{2+}$ , the internal quantum efficiency is as high as 83.07%, which reaches the level of commercial application.

To verify that  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},0.03\text{Mn}^{2+}$  phosphor can supplement the red component of blue-chip + YAG: $\text{Ce}^{3+}$ , the mixed phosphor of YAG: $\text{Ce}^{3+}$  and  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},0.03\text{Mn}^{2+}$  was excited by the 460 nm chip, and a warm white LED with the color temperature of 3005 K was successfully obtained, as shown in Fig. 13. Moreover, the color rendering index was raised to 78, and the effect of adding red components was remarkable.

## 4 Conclusions

A series of  $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}$  and  $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}$  doped with  $\text{Ce}^{3+}$  and  $\text{Mn}^{2+}$  were synthesized by the high-temperature solid-phase method. Two phenomena about the emission spectra of the samples  $\text{Mg}_{2-y}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},y\text{Mn}^{2+}$  are emphatically discussed. The one phenomenon is that the emission spectra are shifted from 600 nm to 635 nm under the excitation of 470 nm, wherein, two reasons are causing the spectra red-shift. Firstly, as the  $\text{Mn}^{2+}$  ions enter the crystal structure, the energy transfer from the  $\text{Ce}^{3+}$  ion to the  $\text{Mn}^{2+}$ , the emission intensity of  $\text{Ce}^{3+}$  decreases and the emission intensity of  $\text{Mn}^{2+}$  increases, so the emission peak shift toward the long-wave direction. Secondly, with the entry of  $\text{Mn}^{2+}$  ions, crystal distortion of the dodecahedral unit cells of  $\text{Ce}^{3+}$  and  $\text{Mn}^{2+}$  increases, which leads to the energy level split of the  $\text{Ce}^{3+}$  and  $\text{Mn}^{2+}$  luminescence center increasing, and the emission spectra shift toward the long wave. Another phenomenon is that the emission spectrum intensity of the sample  $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}:\text{Ce}^{3+},\text{Mn}^{2+}$  anomalously increased by about 37%, compared with the emission spectrum intensity of the sample  $\text{Mg}_2\text{Y}_2\text{Al}_2\text{Si}_2\text{O}_{12}:\text{Ce}^{3+}$ , which is because that doping of  $\text{Mn}^{2+}$  ions increases the distance between the  $\text{Ce}^{3+}$  ions, and that lowers the concentration of defects in the crystal, resulting in the reduction in the energy loss of the  $\text{Ce}^{3+}$  quenching center. When the doping concentration of  $\text{Mn}^{2+}$  is 0.03, the emission peak of the sample  $\text{Mg}_{1.97}\text{Y}_{1.93}\text{Al}_2\text{Si}_2\text{O}_{12}:0.07\text{Ce}^{3+},0.03\text{Mn}^{2+}$  shifts to 618 nm and the quantum efficiency was as high as 83.07%. In addition, this sample has high thermal stability, while the emission intensity was still at 80.14% at 120 °C. Finally, warm white light with a high color index of 78 was obtained with abundant red light components by mixing this phosphor with YAG: $\text{Ce}^{3+}$ , stimulated by a blue light chip. It has great potential in the application of white LEDs.



## Conflicts of interest

The authors declare no competing financial interest.

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