



Cite this: *RSC Adv.*, 2017, 7, 52995

# Luminescence properties and energy transfer behavior of colour-tunable white-emitting $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phosphors with co-doping of $\text{Eu}^{2+}$ , $\text{Eu}^{3+}$ and $\text{Mn}^{4+}$

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$\text{Eu}^{2+}$ ,  $\text{Eu}^{3+}$  and  $\text{Mn}^{4+}$  co-doped  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  phosphors were synthesized in air by high temperature solid-state reaction. The coexistence of  $\text{Eu}^{2+}$ ,  $\text{Eu}^{3+}$  and  $\text{Mn}^{4+}$  in  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  was detected and verified from X-ray photoelectron spectra (XPS), photoluminescence (PL)/photoluminescence excitation (PLE) spectra and diffuse reflection spectra. The crystal structure, luminescence properties and energy transfer between  $\text{Eu}^{2+}$  and  $\text{Mn}^{4+}$  were investigated scientifically. Under ultraviolet excitation, a broad emission band with peak at 496 nm was ascribed to a  $4f^65d-4f^7$  transition of  $\text{Eu}^{2+}$ , and another five narrow emission bands were attributed to  $4f-4f$  transitions of  $\text{Eu}^{3+}$ . The sharp emission band with peak at 659 nm was generated from the spin-forbidden electronic transition  ${}^2E_g-{}^4T_2$  of  $\text{Mn}^{4+}$ . The energy transfer between  $\text{Eu}^{2+}$  and  $\text{Mn}^{4+}$  was demonstrated following the nonradiative electric dipole-dipole interaction, and the energy transfer efficiency reached 58.16%. The emission colour of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu},\text{Mn}^{4+}$  can be tuned from blue-green (0.2396, 0.3332) to white (0.3465, 0.2906) with increasing concentrations of  $\text{Mn}^{4+}$ .

Received 20th July 2017  
 Accepted 3rd November 2017

DOI: 10.1039/c7ra07970b

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## 1 Introduction

With the ever-increasing demands of humankind for illumination quality, white light-emitting diodes (WLEDs) are replacing the incandescent and fluorescent lamps gradually and becoming a new generation of solid state lighting sources for buildings and scenery lighting, LCD backlighting, interior lighting, automobiles, agriculture, medicine and aerospace.<sup>1-4</sup> At present, the commercial method to generate white light emission is exciting the yellow-emitting  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$  ( $\text{YAG}:\text{Ce}^{3+}$ ) with an InGaN light-emitting diode (LED) chip which emits blue light with the wavelength between 450 nm and 480 nm typically.<sup>5,6</sup> Because of the emission deficiency in the red region, this WLED shows poor colour rendering and appears a simple cool white. Another feasible method is combining blue, green and red phosphors with a near-ultraviolet (n-UV) chip which emits ultraviolet with the wavelength between 380 nm and 420 nm.<sup>7-9</sup> This combination improves the colour rendering performance, but poor chemical stability will be shown as it ages due to the different chemical properties of the three phosphors. Compared with other approaches, studies on

the preparation of direct-white-emitting light phosphors have been carried out due to their excellent thermal stability and colour rendering properties.

To the best of our knowledge, aluminate has becoming an important host material because of its excellent thermostability, non-poisonous and competitive price.<sup>10-13</sup> Peng<sup>14</sup> firstly found the coexistence of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  in  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  prepared in air. Two broad bands peaking at 400 nm and 490 nm attributed to the  $4f-5d$  transition of  $\text{Eu}^{2+}$ , and line emissions in the region of 550-700 nm belong to the  $f-f$  transitions of  $\text{Eu}^{3+}$ . Xu<sup>15</sup> reported the non-RE activated  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Mn}^{4+}$  phosphor prepared by solid-state method in air. The  $\text{Al}^{3+}$  ions in the  $[\text{AlO}_6]$  octahedral sites of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  were substituted by  $\text{Mn}^{4+}$  ions in the crystal lattice, and the emission spectrum measurement excited by 365 nm showed that the sharp emission peak at 651 nm was ascribed to the  ${}^2E-{}^4A_2$  transition of  $\text{Mn}^{4+}$  ion, and a broad band at 662 nm was attributed to the phonon sideband transition. Based on the above experimental results, the authors believe that there should be an energy transfer between  $\text{Eu}^{2+}$  and  $\text{Mn}^{4+}$  in  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ . Meanwhile, there has been no one, by far, reporting its luminescence properties and potential applications. The previous studies provide the access to obtain direct white emission for WLED by the coexistence of  $\text{Eu}^{2+}$ ,  $\text{Eu}^{3+}$  and  $\text{Mn}^{4+}$  in  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ .

In our work, a series of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{xEu},\text{Mn}^{4+}$  phosphors were synthesized in air through the high temperature solid-state

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reaction. The coexistence of  $\text{Eu}^{2+}$ ,  $\text{Eu}^{3+}$  and  $\text{Mn}^{4+}$  was revealed by X-ray photoelectron spectroscopy (XPS), diffuse reflection spectra and photoluminescence (PL) spectra. The influences of  $\text{Mn}^{4+}$  on the luminescence properties were discussed in detail, and the fluorescence lifetime, energy transfer between  $\text{Eu}^{2+}$  and  $\text{Mn}^{4+}$  and applications in WLED were studied respectively.

## 2 Experimental

Series of  $\text{Eu}^{3+}$  ions single-doped  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:x\text{Eu}$  ( $x = 0.005, 0.01, 0.02, 0.04, 0.06, 0.08$ ) and co-doped  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:0.01\text{Eu}_y\text{Mn}^{4+}$  ( $y = 0.0002, 0.0005, 0.001, 0.002, 0.003, 0.005, 0.01, 0.02$ ) were synthesized by conventional solid-state reaction in air with  $\text{SrCO}_3$ (A.R.),  $\text{Al}(\text{OH})_3$ (A.R.),  $\text{MnCO}_3$ (A.R.),  $\text{H}_3\text{BO}_3$ (A.R.) and  $\text{Eu}_2\text{O}_3$ (4N). The stoichiometric amount of raw materials were well homogenized in an agate mortar, and the  $\text{H}_3\text{BO}_3$  was added as a flux. All samples were pre-sintered in alumina crucibles in air at  $700^\circ\text{C}$  for 2 h, and further heat-treated at  $1400^\circ\text{C}$  for 5 h with sufficient grindings in the processes.

The phase purity of synthesized phosphors were checked by X-ray diffraction (XRD) with a D8 Advance diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) by the step of  $4^\circ \text{ min}^{-1}$  at room temperature. The X-ray photoelectron spectroscopy (XPS) was obtained on an ESCALAB 250xi (ThermoFisher, England) electron spectrometer. The emission and excitation spectra were analyzed on a Hitachi F-4600 fluorescence spectrophotometer with a 400 nm cut-off filter. The diffuse reflection spectra were detected by a Shimadzu UV-3600 UV-vis-NIR spectrophotometer attached with an integral sphere. The photoluminescence decay curves were recorded on a Horiba JOBIN YVON FL3-21 spectrofluorometer.

## 3 Results and discussion

Fig. 1 shows the XRD patterns of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:x\text{Eu}$  ( $x = 0, 0.005, 0.01, 0.02, 0.04, 0.06$ ) and  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:0.01\text{Eu}_y\text{Mn}^{4+}$  ( $y = 0.0002, 0.0005, 0.001, 0.002, 0.003, 0.005, 0.01$ ) synthesized at  $1400^\circ\text{C}$

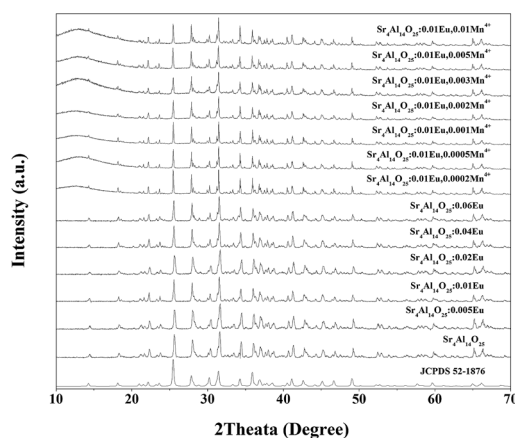


Fig. 1 XRD patterns of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:x\text{Eu}$  ( $x = 0, 0.005, 0.01, 0.02, 0.04, 0.06$ ) and  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:0.01\text{Eu}_y\text{Mn}^{4+}$  ( $y = 0.0002, 0.0005, 0.001, 0.002, 0.003, 0.005, 0.01$ ) synthesized at different temperatures, and the standard pattern JCPDS 52-1876.

for 5 h in air. The reference pattern of the standard JCPDS Card no. 52-1876 for  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  was also listed in Fig. 1 as a reference. It is observed that the samples synthesized in various conditions are all in pure  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  phase, and the change of doping of  $\text{Eu}^{3+}$  and  $\text{Mn}^{4+}$  ions would not impact the host structure.

It has been found that the  $\text{Mn}^{4+}$  ion is more likely to achieve stability once it is accommodated and stabilized in an octahedral site. Usually, there will be strong absorption and emission spanning from 250 nm to 500 nm and 630 nm to 735 nm respectively when  $\text{Mn}^{4+}$  substitutes an octahedral site.<sup>16,17</sup> The fragments of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  unit cell are exhibited in Fig. 2.  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  is orthorhombic structure with space group  $Pmma$ . The structure contains two Sr sites and six Al sites. Sr(1) and Sr(2) are both coordinated by ten oxygen atoms. Al(1), Al(2) and Al(3) form tetrahedrons with four coordinations, while Al(4), Al(5) and Al(6) are six-coordinated that form rigid octahedrons.<sup>18</sup> Because the radius difference between  $\text{Eu}^{2+}$  and  $\text{Sr}^{2+}$  ions is much smaller than that of  $\text{Eu}^{2+}$  and  $\text{Al}^{3+}$ , and the ionic size of  $\text{Mn}^{4+}$  is much smaller than that of  $\text{Sr}^{2+}$  but close to  $\text{Al}^{3+}$ , it is reasonable to consider the  $\text{Eu}^{2+}$  ions are substituted in  $\text{Sr}^{2+}$  sites, while  $\text{Mn}^{4+}$  ions tend to occupy the octahedral sites of  $\text{Al}^{3+}$ .

Fig. 3 shows the observed (black squares), calculated (red lines), and difference (bottom) XRD profiles for the Rietveld refinement of  $\text{Sr}_{3.96}\text{Al}_{13.9972}\text{O}_{25}:0.04\text{Eu}^{2+}, 0.0028\text{Mn}^{2+}$  with  $\lambda = 1.5406 \text{ \AA}$  by TOPAS program. Almost all peaks can be indexed by hexagonal cell with parameters close to  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ , herein the structural parameters of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  are used as initial parameters in the Rietveld analysis. The final refinement is stable and convergent well with low residual factors  $R_{\text{exp}} = 6.281\%$ ,  $R_{\text{wp}} = 17.843\%$ ,  $R_p = 13.770\%$  and  $\chi^2 = 2.841$ , indicating the single phase with no unidentified diffraction peaks from impurity.

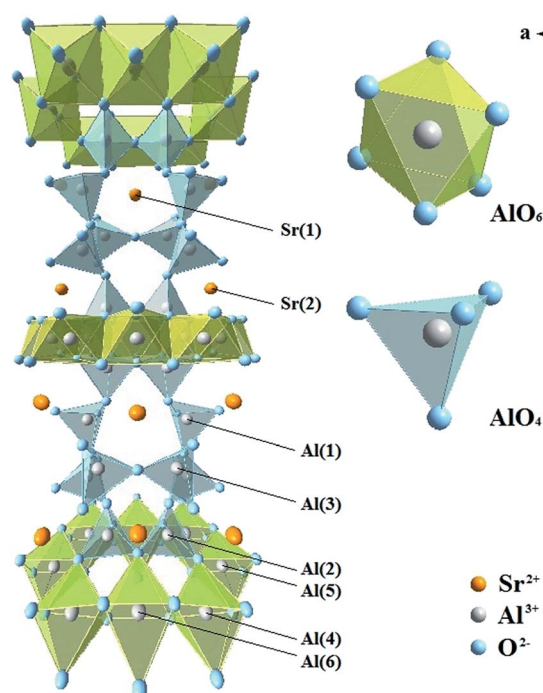


Fig. 2 The crystal structures of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ .



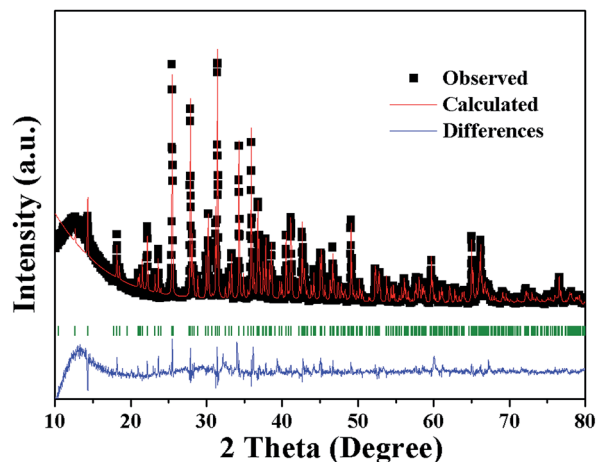


Fig. 3 Power XRD pattern of  $\text{Sr}_{3.96}\text{Al}_{13.9972}\text{O}_{25}:\text{0.04Eu}^{2+},\text{0.0028Mn}^{2+}$  with corresponding Rietveld refinement (red) and residuals (blue).

The final refined crystallographic data are listed in Table 1. The cell parameters are determined to be  $a = 24.7177 \text{ \AA}$ ,  $b = 8.4810 \text{ \AA}$ ,  $c = 4.8847 \text{ \AA}$  and  $V = 1026.22 \text{ \AA}^3$ . The crystallographic site coordinates, occupancy factors, and equivalent isotropic displacement parameters are summarized in Table 2.

To examine the valence state of europium and manganese in  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ , the XPS spectra of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:x\text{Eu}$  ( $x = 0.01, 0.02, 0.06$ ) and  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{0.01Eu},y\text{Mn}^{4+}$  ( $y = 0.005, 0.01, 0.02$ ) is recorded in Fig. 4(a) and (b). It is evident from Fig. 4(a) that the broad bands peaking at 1136.5 eV ascribed to  $\text{Eu}^{3+} 3d_{5/2}$  are observed, and the bands peaking at 1127.5 eV consistent with  $\text{Eu}^{2+} 3d_{5/2}$  emerge gradually with the increasing doping of  $\text{Eu}^{3+}$  ions.<sup>19</sup> The peak intensities of  $\text{Mn}^{4+} 2p_{3/2}$  and  $2p_{1/2}$  at 642.5 eV and 654.5 eV, as shown in Fig. 4(b), increase with the increasing content of  $\text{Mn}^{2+}$  ions, and no  $\text{Mn}^{2+}$  peaks are observed as the value of  $y$  varies. We can deeply confirm that there is an coexistence of  $\text{Eu}^{2+}$ ,  $\text{Eu}^{3+}$  and  $\text{Mn}^{4+}$  in  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  phosphors.

Fig. 5 shows the excitation and emission spectra of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$ . We doped the Eu ions originally into the host in the form of  $\text{Eu}_2\text{O}_3$ , and we found that the trivalent and bivalent Eu ions co-existed in  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$  prepared in air at 1400 °C for 5 h. Under 496 nm monitoring, as shown in Fig. 5(a), the broad

Table 1 Main parameters of processing and refinement of the  $\text{Sr}_{3.96}\text{Al}_{13.9972}\text{O}_{25}:\text{0.04Eu}^{2+},\text{0.0028Mn}^{2+}$  sample

Sp.Gr.	<i>Pmma</i>
$a, \text{ \AA}$	24.7177 (8)
$b, \text{ \AA}$	8.4810 (3)
$c, \text{ \AA}$	4.8847 (2)
$V, \text{ \AA}^3$	1026.22 (6)
$2\theta$ -interval, °	10–80
No. of reflections	313
No. of refined parameters	47
$R_{wp}, \%$	17.843
$R_p, \%$	13.770
$R_{exp}, \%$	6.281
$\chi^2$	2.841
$R_B, \%$	4.593

Table 2 Fractional atomic coordinates and isotropic displacement parameters ( $\text{ \AA}^2$ ) of  $\text{Sr}_{3.96}\text{Al}_{13.9972}\text{O}_{25}:\text{0.04Eu}^{2+},\text{0.0028Mn}^{2+}$  sample

$\text{Sr}_{3.96}\text{Al}_{13.9972}\text{O}_{25}:\text{0.04Eu}^{2+},\text{0.0028Mn}^{2+}$	$x$	$y$	$z$	$B_{iso}$	Occ.
Sr1	0.1387	1/2	0.0355	2.98	0.99
Eu1	0.1387	1/2	0.0355	2.98	0.01
Sr2	0.1204	0	0.1143	1.16	0.99
Eu2	0.1204	0	0.1143	1.16	0.01
Al1	0.1851	0.1956	0.6284	3.68	0.9998
Mn1	0.1851	0.1956	0.6284	3.68	0.0002
Al2	0.0677	0.3178	0.5066	0.35	0.9998
Mn2	0.0677	0.3178	0.5066	0.35	0.0002
Al3	1/4	0.2451	0.4131	1.38	0.9998
Mn3	1/4	0.2451	0.4131	1.38	0.0002
Al4	0	0.1671	0	2.21	0.9998
Mn4	0	0.1671	0	2.21	0.0002
Al5	0	0	1/2	2.98	0.9998
Mn5	0	0	1/2	2.98	0.0002
Al6	0	1/2	0	4.29	0.9998
Mn6	0	1/2	0	4.29	0.0002
O1	0.0462	0.1867	0.3054	1.10	1
O2	0.1359	0.3187	0.5089	1.10	1
O3	0.1904	0.2482	0.9582	1.10	1
O4	1/4	0.2957	0.1281	1.10	1
O5	0.0340	0	0.8224	1.10	1
O6	0.0527	1/2	0.3277	1.10	1
O7	0.1582	0	0.5656	1.10	1
O8	0.0442	0.3234	0.8311	1.10	1
O9	1/4	1/2	0.0580	1.10	1

excitation band from 250 nm to 450 nm with maximum at 362 nm originates from the f–d transition of  $\text{Eu}^{2+}$ .<sup>20</sup> The other excitation spectra monitored at 619 nm consists of the broad bands from 200 nm to 350 nm, which is generated from the charge-transfer band (CTB) between  $\text{Eu}^{3+}$  and  $\text{O}^{2-}$  with the peak at 261 nm, and the series of narrow bands from 350 nm to 550 nm form from the f–f transition of  $\text{Eu}^{3+}$  within its  $4f^6$  configuration.<sup>21</sup> The PL spectra with different excitation factors are demonstrated in Fig. 5(b). The characteristic peaks of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  are both observed in emission spectra with the change of excitation wavelength. The band emission peaking at 469 nm stems from  $4f^65d-4f^7$  transition of  $\text{Eu}^{2+}$ , and the other five typical line emissions peaking at 596 nm, 620 nm, 652 nm, 688 nm and 707 nm are attributed to  $4f-4f$  transition of  $^5d_0-^7f_J$  ( $J = 1, 2, 3, 4$ ) of  $\text{Eu}^{3+}$ .<sup>22,23</sup> The strongest emission generated from the transition of  $^5d_0-^7f_2$  of  $\text{Eu}^{3+}$  belongs to the electric dipole transition, which reflects that the electric dipole transition is the dominant factor in the luminescence process of  $\text{Eu}^{3+}$ .<sup>24</sup>

The PL spectra of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:x\text{Eu}$  ( $x = 0.005, 0.01, 0.02, 0.04, 0.06, 0.08$ ) prepared at 1400 °C for 5 h and the dependence of the relative emission intensities of  $\text{Eu}^{2+}$  (496 nm) and  $\text{Eu}^{3+}$  (594 nm) in the  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  phosphors are labelled in Fig. 6. All investigated phosphors were monitored at an excitation wavelength of 325 nm. It is found that the PL intensities of red and blue emissions change obviously with the concentration variation of the Eu dopant. The emissions of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  enhance with the increase of  $\text{Eu}^{3+}$  ions concentration, and the former reaches the maximum at 1 mol% due to the concentration



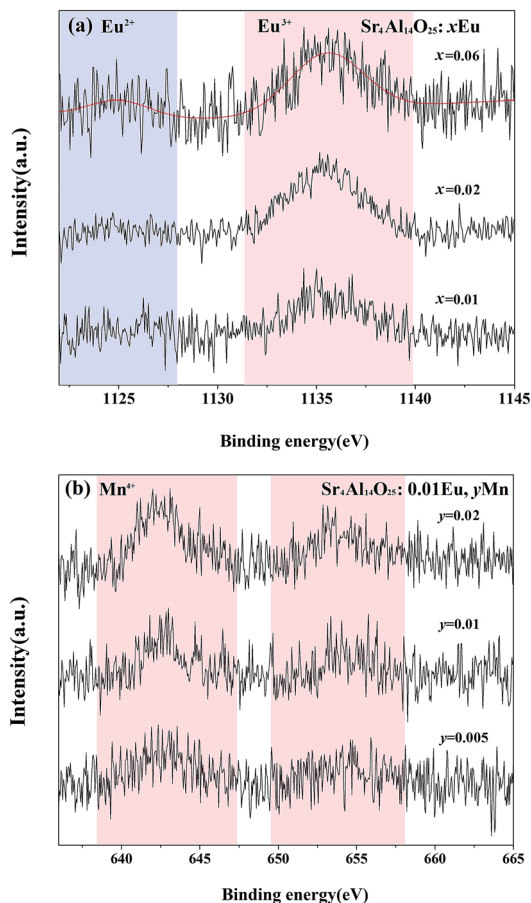


Fig. 4 High-resolution Eu 3d XPS spectra of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:x\text{Eu}$  ( $x = 0.01, 0.02, 0.06$ ) (a) and Mn 2p XPS spectra of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:0.01\text{Eu},y\text{Mn}$  ( $y = 0.005, 0.01, 0.02$ ) (b).

quenching.<sup>25</sup> This observation indicates that the increasing doping of  $\text{Eu}^{3+}$  ions spawn the  $V''_{\text{Sr}}$  and electrons which can combine with  $\text{Eu}^{3+}$  ions and promotes the self-reduction reaction in some extent. The self-reduction process can be presented in the following equations:<sup>26</sup>

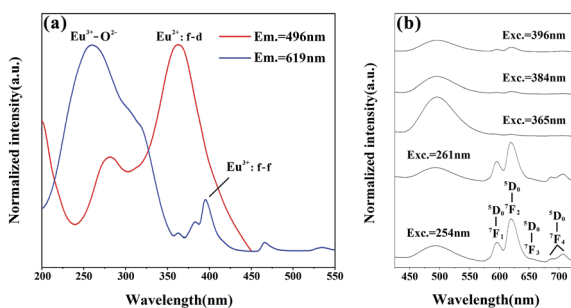
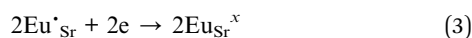
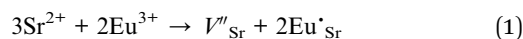


Fig. 5 PLE spectra of  $\text{Eu}^{3+}$  (619 nm) and  $\text{Eu}^{2+}$  (496 nm) of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:0.01\text{Eu}$  (a) and PL spectra with different excitations (b).

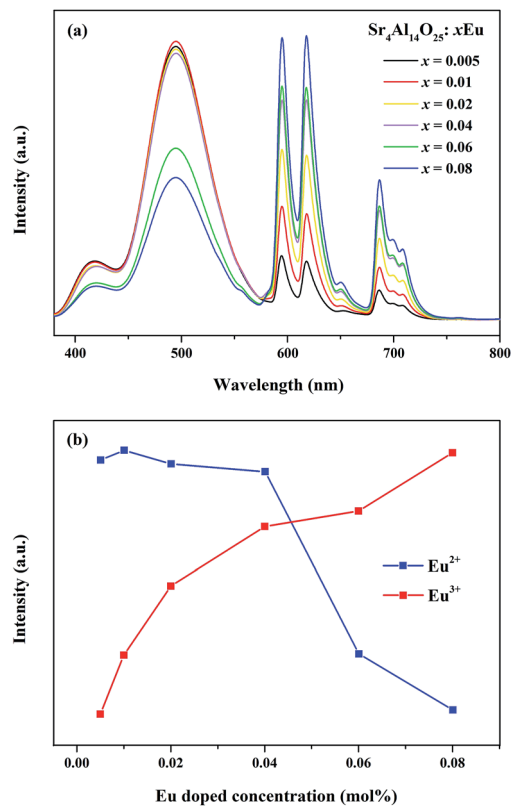


Fig. 6 PL spectra of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:x\text{Eu}$  ( $x = 0.005, 0.01, 0.02, 0.04, 0.06, 0.08$ ) under ultraviolet excitation (325 nm) (a) and dependence of relative emission intensity of  $\text{Eu}^{2+}$  (496 nm) and  $\text{Eu}^{3+}$  (619 nm) in  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  phosphors as a function of  $\text{Eu}^{3+}$  doped concentration (b).

As the  $\text{Mn}^{2+}$  is singly doped in  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  host, the PL and PLE spectra of synthesized phosphor ( $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:0.002\text{Mn}^{4+}$ ) are shown in the Fig. 7. It contains two excitation bands from 250 nm to 550 nm, which are due to the spin-allowed electronic transition  ${}^4\text{A}_2-{}^4\text{T}_1$  and  ${}^4\text{A}_2-{}^4\text{T}_2$  of  $\text{Mn}^{4+}$ .<sup>27</sup> The optimal excitation wavelength of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:0.002\text{Mn}^{4+}$  is 325 nm, and the half-band width is approximately 85 nm, much wider than the emission band of UV LED chips. It is indicated that the excitation wavelength at 325 nm can be an alternative for the typical commercial chips in the future market. The sharp emission

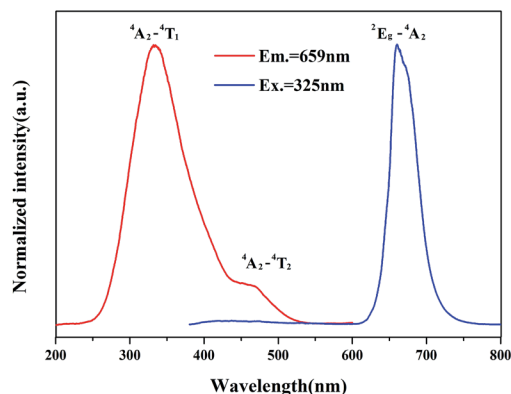


Fig. 7 The spectral pattern of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:0.002\text{Mn}^{4+}$ .





band peaking at 659 nm generates from the spin-forbidden electronic transition  ${}^2E_g-{}^4T_2$  of  $Mn^{4+}$ .<sup>28</sup>

As revealed in Fig. 8, series of phosphors with varied  $Eu^{3+}$  and  $Mn^{4+}$  concentrations are synthesized and their PL spectra are recorded upon excitation of 325 nm for the investigation of the energy transfer (ET) between  $Eu^{2+}$  and  $Mn^{4+}$ . We can see that the intensities of the  $Eu^{2+}$  and  $Eu^{3+}$  emissions are found to decrease monotonically with increasing  $Mn^{4+}$  content due to the conspicuous energy transfer between  $Eu^{2+}$  and  $Mn^{4+}$ . The simplified diagram of the energy transfer process from  $Eu^{2+}$  to  $Mn^{4+}$  in  $Sr_4Al_{14}O_{25}$  phosphors is illustrated in Fig. 9. As indicated in this diagram, the relationship of energy transfer between  $Eu^{2+}$  and  $Mn^{4+}$  ions can be attributed to the similar energy level values between the excited 5d state of  $Eu^{2+}$  and the  ${}^4T_{1g}$  levels of  $Mn^{4+}$  ions.<sup>29</sup>

Meanwhile, the PL intensity of the  $Mn^{4+}$  increases with the doping of  $Mn^{4+}$  ions, and comes to a maximum value at  $y = 0.001$ . Then the concentration quenching leads to the weakening of PL intensity. The synthesized phosphors can be tuned expediently from blue-green to white by the co-existence of  $Eu^{2+}$ ,  $Eu^{3+}$  and  $Mn^{4+}$ . To observe the characteristic of change in colour after doping  $Mn^{4+}$  more visually, as shown in Table 3 and Fig. 10, the Commission Internationale de l'Eclairage (CIE) chromaticity coordinates, correlated colour temperature (CCT) and CIE chromaticity diagram of  $Sr_4Al_{14}O_{25}:0.01Eu,yMn^{4+}$

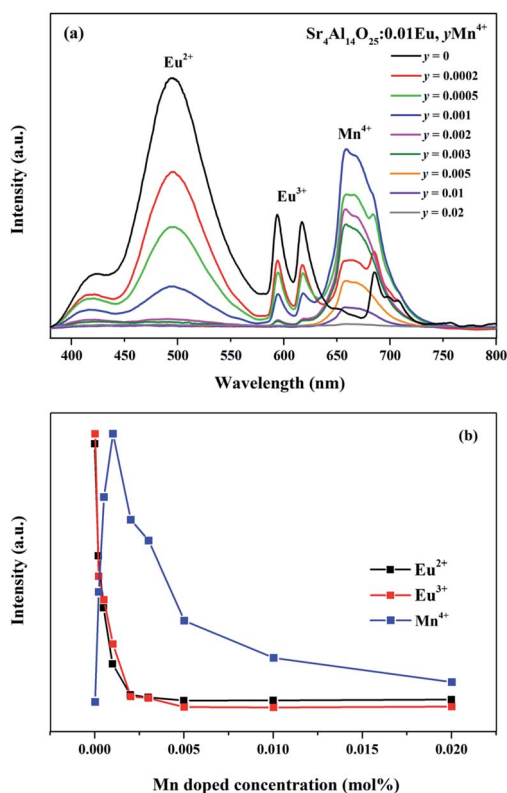


Fig. 8 PL spectra of  $Sr_4Al_{14}O_{25}:0.01Eu,yMn^{4+}$  ( $y = 0, 0.0002, 0.0005, 0.001, 0.002, 0.003, 0.005, 0.01, 0.02$ ) under ultraviolet excitation (325 nm) (a) and dependence of relative emission intensity of  $Eu^{2+}$  (496 nm),  $Eu^{3+}$  (619 nm) and  $Mn^{4+}$  (659 nm) in  $Sr_4Al_{14}O_{25}$  phosphors as a function of  $Mn^{4+}$  doped concentration (b).

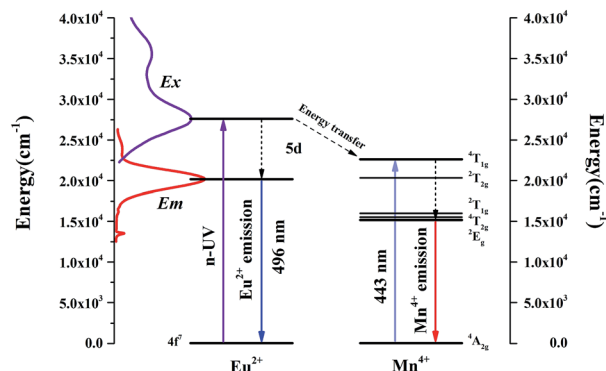


Fig. 9 The energy level structure of  $Eu^{2+}$  and  $Mn^{4+}$  and the energy transfer mechanism among them.

Table 3 The CIE chromaticity coordinates ( $x, y$ ) and correlated colour temperature (CCT) of  $Sr_4Al_{14}O_{25}:0.01Eu,yMn^{4+}$  ( $y = 0, 0.0002, 0.0005, 0.001$ )

Sample no.	Composition ( $y$ )	CIE coordinates ( $x, y$ )	CCT (K)
1(a)	0	(0.2396, 0.3332)	11 489
2(b)	0.0002	(0.2723, 0.3191)	9380
3(c)	0.0005	(0.3266, 0.3040)	5798
4(d)	0.001	(0.3465, 0.2906)	4554

( $y = 0, 0.0002, 0.0005, 0.001$ ) phosphors are calculated and plotted respectively. As summarized in Table 2, the series of chromaticity coordinates of the  $Sr_4Al_{14}O_{25}:0.01Eu,yMn^{4+}$  are calculated from the corresponding datum of emission spectra. The phosphors can be regulated from blue-green (0.2396, 0.3332) to white (0.3465, 0.2906) with the increasing concentration of  $Mn^{4+}$ , corresponding to the correlated colour temperature from 11 489 K to 4554 K as listed in Table 3.

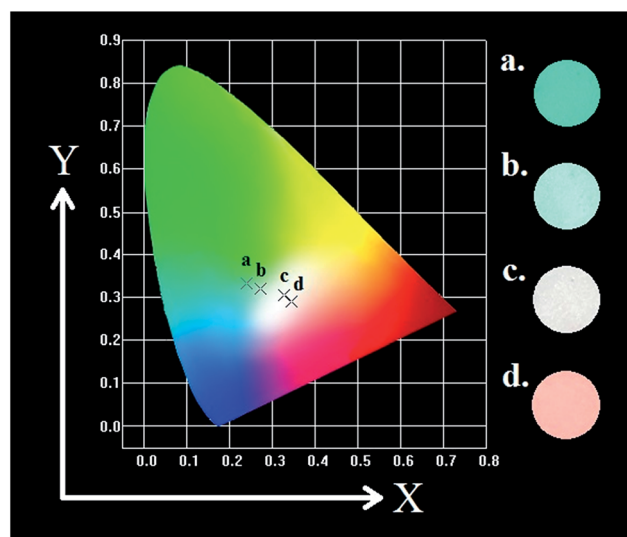


Fig. 10 CIE chromaticity diagram of  $Sr_4Al_{14}O_{25}:0.01Eu,yMn^{4+}$  ( $y = 0, 0.0002, 0.0005, 0.001$ ) under 325 nm excitation and digital images in UV box.



To further verify the existence of energy transfer between  $\text{Eu}^{2+}$  and  $\text{Mn}^{4+}$  in  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:0.01\text{Eu},y\text{Mn}^{4+}$  ( $y = 0, 0.0005, 0.001, 0.002, 0.003, 0.005, 0.01, 0.02$ ), we investigated the luminescence decay curves of  $\text{Eu}^{2+}$  496 nm emission and the corresponding lifetimes of  $\text{Eu}^{2+}$  with the doping of  $\text{Mn}^{4+}$ . Additionally, the energy transfer efficiency is also listed next to the lifetimes in Fig. 11(a). All the decay curves can be well fitted ground on the following non-exponential equation:<sup>30,31</sup>

$$\tau = \frac{\int_0^{\infty} I(t)dt}{I(t)dt} \quad (4)$$

where  $I(t)$  stands for the PL intensities at time  $t$ . The effective decay lifetimes monitored at 496 nm of  $\text{Eu}^{2+}$  are calculated to be 1478.69, 1242.81, 888.22, 794.80, 720.49, 652.35, 643.00 and 618.70 ns for  $y = 0, 0.0005, 0.001, 0.002, 0.003, 0.005, 0.01, 0.02$ , respectively. The lifetimes of  $\text{Eu}^{2+}$  emission are monotonically decreasing with the doping of  $\text{Mn}^{4+}$ , which indicates that the energy transfer between  $\text{Eu}^{2+}$  and  $\text{Mn}^{4+}$  ions occurs in the  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  host, and the estimate the  $\text{Eu}^{2+}$ - $\text{Mn}^{4+}$  ET probability ( $P_{\text{Eu-Mn}}$ ) can be fitted to the following equation:<sup>32,33</sup>

$$P_{\text{Eu-Mn}} = \frac{1}{\tau_y} - \frac{1}{\tau_0} \quad (5)$$

where  $\tau_y$  and  $\tau_0$  stand for the corresponding lifetimes of  $\text{Eu}^{2+}$  ions with and without  $\text{Mn}^{4+}$  ions doping for the constant sensitizer concentration. The values of the estimated  $P_{\text{Eu-Mn}}$  are plotted in Fig. 11(b). The consecutive increasing of the ET probabilities with the various  $\text{Mn}^{4+}$  content manifests an enhanced ET process between  $\text{Eu}^{2+}$  and  $\text{Mn}^{4+}$  because of the decrease in the average distance between the ions.<sup>34</sup> Furthermore, the energy transfer efficiency  $\eta$  from a donor  $\text{Eu}^{2+}$  to acceptor  $\text{Mn}^{4+}$  would be estimated according to the expression as follows:<sup>35</sup>

$$\eta = 1 - \frac{\tau_s}{\tau_{s_0}} \quad (6)$$

where  $\eta$  stands for the energy transfer efficiency.  $\tau_s$  and  $\tau_{s_0}$  mean the lifetimes of  $\text{Eu}^{2+}$  with and without the doping of  $\text{Mn}^{4+}$  ions. As shown in the Fig. 11(a), the energy transfer efficiency decreases constantly from 15.95% to 58.16% with the increasing concentration of  $\text{Mn}^{4+}$ . The result is ascribed to the shortening distance between the  $\text{Eu}^{2+}$  ions and  $\text{Mn}^{4+}$  ions.

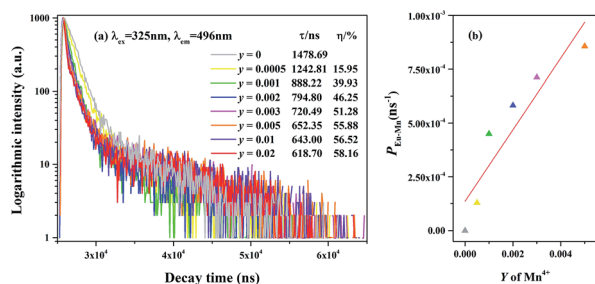


Fig. 11 Decay curves, lifetime and energy transfer efficiency ( $\eta$ ) of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:0.01\text{Eu},y\text{Mn}^{4+}$  ( $y = 0, 0.0005, 0.001, 0.002, 0.003, 0.005, 0.01, 0.02$ ) under excitation of 325 nm (a). Energy transfer probability ( $P_{\text{Eu-Mn}}$ ) as a function of  $\text{Mn}^{4+}$  doped concentration.

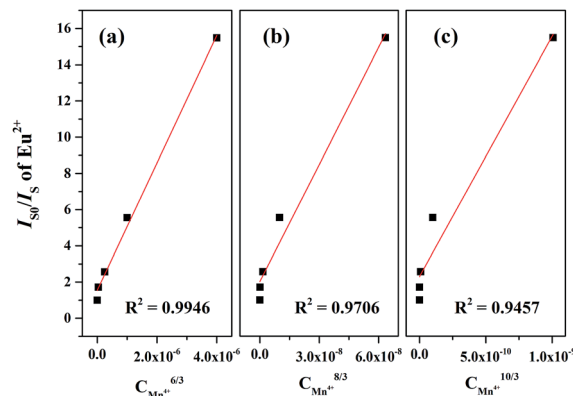


Fig. 12 Dependence of  $I_{s_0}/I_s$  of  $\text{Eu}^{2+}$  on  $C_{\text{Mn}}^{6/3}$ ,  $C_{\text{Mn}}^{8/3}$  and  $C_{\text{Mn}}^{10/3}$ .

Generally, the energy transfer mechanism between the sensitizer ( $\text{Eu}^{2+}$ ) to activator ( $\text{Mn}^{4+}$ ) ions and the relation can be revealed by the Dexter's energy transfer theory:<sup>36-38</sup>

$$\frac{I_{s_0}}{I_s} \propto C^n \quad (7)$$

in which  $I_{s_0}$  and  $I_s$  mean the PL intensities of  $\text{Eu}^{2+}$  with and without activator  $\text{Mn}^{4+}$  ions, separately.  $C$  stands for the doping content of  $\text{Mn}^{4+}$  ions, and the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions correspond to  $n = 6, 8$ , and  $10$ , respectively. The fitting curves of  $I_{s_0}/I_s$  versus  $C^{n/3}$  are shown in Fig. 12(a-c), which reveal a linearity only when  $n = 6$ , demonstrating that the energy transfer mechanism from  $\text{Eu}^{2+}$  to  $\text{Mn}^{4+}$  in the  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  host follows a nonradiative electric dipole-dipole interaction.

Fig. 13 presents the diffuse reflection spectra of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ ,  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:0.01\text{Eu}$  and  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:0.01\text{Eu},0.003\text{Mn}^{4+}$ . It is observed that the energy absorption of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  host occurs in ultraviolet region, and the band gap is estimated to be 3.701 eV based on the fitting line of the absorption edge.<sup>39,40</sup> A strong energy absorption band can be seen obviously in the 200–350 nm region from the host material. With the doping of  $\text{Eu}^{3+}$  ions, an obvious absorption appears around 200–300 nm in the near-UV region as a result of the 4f–5d transition of  $\text{Eu}^{2+}$ ,

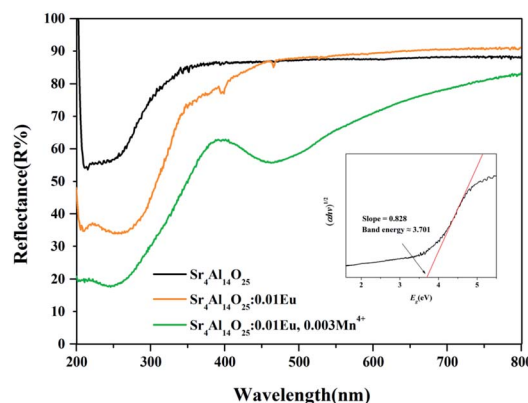


Fig. 13 Diffuse reflectance spectra of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ ,  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:0.01\text{Eu}$  and  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:0.01\text{Eu},0.003\text{Mn}^{4+}$ .



and the relatively weak absorption peaking at 391 nm results from the f–f transition of  $\text{Eu}^{3+}$ , which is in accordance with the excitation spectra of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$ . When the  $\text{Mn}^{4+}$  doped into the host, it exhibits an obvious absorption from 390 nm to 550 nm assigned to the spin-forbidden electronic transition of the  $\text{Mn}^{4+}$  ions. Above results indicates the potential of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu},\text{Mn}^{4+}$  for solid-state lighting.

## 4 Conclusion

Series of colour-tunable direct-white-emitting phosphors  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu},\text{Mn}^{4+}$  were synthesized in air by conventional high temperature solid state reactions. The coexistence of  $\text{Eu}^{2+}$ ,  $\text{Eu}^{3+}$  and  $\text{Mn}^{4+}$  was proved, and the self-reduction process of  $\text{Eu}^{3+}$  was discussed. The luminescence properties were investigated, and three groups of emissions in  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  ascribed to  $\text{Eu}^{2+}$ ,  $\text{Eu}^{3+}$  and  $\text{Mn}^{4+}$  were observed under ultraviolet excitation. The energy transfer between  $\text{Eu}^{2+}$  and  $\text{Mn}^{4+}$  originated from a nonradiative electric dipole–dipole interaction, and the energy transfer efficiency could reach 58.16%. The emission colour of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:0.01\text{Eu},\gamma\text{Mn}^{4+}$  ( $\gamma = 0, 0.0002, 0.0005, 0.001$ ) could be modulated from blue-green (0.2396, 0.3332) to white (0.3465, 0.2906), corresponding to the colour temperature from 11 489 K to 4554 K with the increasing concentration of  $\text{Mn}^{4+}$ . These results manifest that the prepared  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu},\text{Mn}^{4+}$  phosphor can be regarded as a potential approach to obtain colour-tunable direct-white emissions through adjusting the content of  $\text{Mn}^{4+}$ .

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

We thank the National Natural Science Foundation of China (Grant No. 51472223) and the Fundamental Research Funds for Central Universities (Grant No. 2652015090).

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