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# Synthesis, structure, and luminescence characteristics of far-red emitting Mn<sup>4+</sup>-activated LaScO<sub>3</sub> perovskite phosphors for plant growth

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Far-red emitting phosphors LaScO<sub>3</sub>:Mn<sup>4+</sup> were successfully synthesized *via* a high-temperature solid-state reaction method. The X-ray powder diffraction confirmed that the pure-phase LaScO<sub>3</sub>:Mn<sup>4+</sup> phosphors had formed. Under 398 nm excitation, the LaScO<sub>3</sub>:Mn<sup>4+</sup> phosphors emitted far red light within the range of 650–800 nm peaking at 703 nm (14 225 cm<sup>-1</sup>) due to the <sup>2</sup>E<sub>g</sub> → <sup>4</sup>A<sub>2g</sub> transition, which was close to the spectral absorption center of phytochrome P<sub>FR</sub> located at around 730 nm. The optimal doping concentration and luminescence concentration quenching mechanism of LaScO<sub>3</sub>:Mn<sup>4+</sup> phosphors was found to be 0.001 and electric dipole–dipole interaction, respectively. And the CIE chromaticity coordinates of the LaScO<sub>3</sub>:0.001Mn<sup>4+</sup> phosphor were (0.7324, 0.2676). The decay lifetimes of the LaScO<sub>3</sub>:Mn<sup>4+</sup> phosphors gradually decreased from 0.149 to 0.126 ms when the Mn<sup>4+</sup> doping concentration increased from 0.05 to 0.9 mol%. Crystal field analysis showed that the Mn<sup>4+</sup> ions experienced a strong crystal field in the LaScO<sub>3</sub> host. The research conducted on the LaScO<sub>3</sub>:Mn<sup>4+</sup> phosphors illustrated their potential application in plant lighting to control or regulate plant growth.

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## Introduction

Nowadays, to meet the continuous increasing needs of people, the greenhouse industry has been developed. In the agriculture field, when it comes to conditions for plant growth, moderate sunlight, air, and moderate moisture are usually mentioned as the basic conditions.<sup>1–4</sup> The blue (≈ 400–500 nm), red (≈ 600–690 nm) and far red (≈ 700–740 nm) light in sunlight can affect the growth process of natural plants, such as phototropic processes and photomorphogenesis.<sup>5–7</sup> There exist two kinds of phytochrome, P<sub>R</sub> and P<sub>FR</sub>, and P<sub>R</sub> is the biologically inactive state, whereas P<sub>FR</sub> is the biologically active state.<sup>4,8</sup> These two phytochromes can be converted into each other by absorbing different wavelengths of light, in which the P<sub>R</sub> was sensitive to red light and can turn into P<sub>FR</sub> by absorbing light with wavelength peaking at around 660 nm, whereas P<sub>FR</sub> should absorb far red light peaking at around 730 nm to switch to P<sub>R</sub>.<sup>9,10</sup> It is known that in order to blossom, short-day plants need to stay in the dark for a longer time than long-day plants.<sup>11–13</sup> So plant growth progress can be controlled by changing the spectral composition in artificial light.

The proportion of red light in the natural sunlight is higher than far red light.<sup>9</sup> Meanwhile, with the development of science and technology in the world, the far red light become even less due to the night lighting, which means the far-red light is

insufficient for plant cultivation and even influence the entire life style of the plant.<sup>4</sup> Thus, finding artificial light to meet the requirement of plant growth is urgent, especially in the greenhouse industry. In the past, the light emitted by traditional gas-discharge lamps cannot match well with the absorption spectrum of phytochrome, especially the P<sub>FR</sub>. But the solid state light-emitting diodes (LEDs) device with long lifetime and low power consumption,<sup>14–21</sup> which can exhibit various colors by coating different phosphors onto the blue/near-ultraviolet LED chip,<sup>22–30</sup> can make up for this drawback. That means the light from the specific LEDs can match well with the absorption spectrum of phytochrome. Many research efforts have already been conducted to develop the red phosphors, such as K<sub>2</sub>-NaAlF<sub>6</sub>:Mn<sup>4+</sup> (630 nm),<sup>31</sup> Na<sub>3</sub>MgZr(PO<sub>4</sub>)<sub>3</sub>:Eu<sup>3+</sup> (611 nm),<sup>32</sup> and Sr<sub>2</sub>MgAl<sub>22</sub>O<sub>36</sub>:Mn<sup>4+</sup> (658 nm),<sup>33</sup> which emit red light in the range of 610–660 nm. In contrast, relatively less attention has been paid to the far-red phosphors with emission wavelength within 660–730 nm, which can be used for the plant growth. So it is important to find novel phosphors that can emit far-red light to meet the requirement of far-red light.

Mn<sup>4+</sup> ions in particular host materials with octahedral structures can emit red light and even deep red light due to the <sup>2</sup>E<sub>g</sub> → <sup>4</sup>A<sub>2g</sub> transition,<sup>34–37</sup> such as Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Mn<sup>4+</sup> (652 nm),<sup>38</sup> NaMgGdTeO<sub>6</sub>:Mn<sup>4+</sup> (697 nm),<sup>39</sup> Ca<sub>3</sub>La<sub>2</sub>W<sub>2</sub>O<sub>12</sub>:Mn<sup>4+</sup> (711 nm),<sup>40</sup> La<sub>2</sub>MTiO<sub>6</sub>:Mn<sup>4+</sup> (M = Mg and Zn; 710 nm),<sup>41</sup> and Ba<sub>2</sub>GeO<sub>4</sub>:Mn<sup>4+</sup> (667 nm).<sup>42</sup> Considering that the structure of the LaScO<sub>3</sub> compound with [ScO<sub>6</sub>] octahedral structure is similar to LaAlO<sub>3</sub> and Mn<sup>4+</sup>-doped LaAlO<sub>3</sub> phosphors can emit far-red emission,

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so the  $\text{LaScO}_3$  compound has been chosen as the host for  $\text{Mn}^{4+}$  doping.<sup>43,44</sup> Thus, in this work,  $\text{LaScO}_3$  and  $\text{Mn}^{4+}$  ions had been chosen for the host material and activator, respectively, and a series of  $\text{LaScO}_3:\text{xMn}^{4+}$  ( $x = 0.0005\text{--}0.0090$ ) phosphors with different  $\text{Mn}^{4+}$  doping concentration had been synthesized. These prepared phosphors can be well excited by 398 nm and emit far-red light peaking at 703 nm with CIE chromaticity coordinates of (0.7324, 0.2676). The crystal structure of the  $\text{LaScO}_3$ , decay lifetimes and luminescence properties had also been investigated in detail, and the results indicated the  $\text{LaScO}_3:\text{Mn}^{4+}$  phosphors could be serve as the far-red emitting phosphor in plant growth LEDs.

## Experimental section

$\text{LaScO}_3:\text{xMn}^{4+}$  ( $x = 0.0005\text{--}0.009$ ) phosphors were prepared by a facile solid-state reaction method using  $\text{Sc}_2\text{O}_3$  (analytical reagent, AR),  $\text{MnCO}_3$  (AR), and  $\text{La}_2\text{O}_3$  (99.99%) as the starting materials. The raw materials were weighed according to the stoichiometric ratio. The mixed starting materials was ground in an agate mortar and transferred to  $\text{Al}_2\text{O}_3$  crucible to sinter at 1500 °C for 10 h in air. And then, the products were cooled down to room temperature and reground into powders to get the target phosphors  $\text{LaScO}_3:\text{xMn}^{4+}$ .

The X-ray powder diffraction (XRD) results of  $\text{LaScO}_3:\text{xMn}^{4+}$  phosphors were measured on an X-ray diffractometer (Bruker D8 Advance) with  $\text{Cu-K}\alpha$  radiation. The room-temperature photoluminescence (PL)/PL excitation (PLE) spectra and luminescence decay lifetimes of  $\text{LaScO}_3:\text{xMn}^{4+}$  phosphors were recorded by using the same Edinburgh FS5 spectrofluorometer, equipping with a 150 W continued-wavelength Xenon lamp and a pulsed Xenon lamp, respectively. The internal quantum efficiency (IQE) of the  $\text{LaScO}_3:0.001\text{Mn}^{4+}$  phosphors were measured by the Edinburgh FS5 spectrofluorometer with an integrating sphere.

## Results and discussion

Fig. 1 showed the XRD patterns of the  $\text{LaScO}_3:\text{xMn}^{4+}$  ( $x = 0, 0.0005, 0.001, \text{ and } 0.005$ ) phosphors and the standard data of  $\text{LaScO}_3$  (JCPDS: 26-1148). It could be seen that all the diffraction peaks of the samples matched well with the standard data of  $\text{LaScO}_3$ . There was no excess crystal phase formation, which illustrated the  $\text{Mn}^{4+}$  ions could be successfully doped into the  $\text{LaScO}_3$  host.  $\text{Mn}^{4+}$  ions can replace specific cationic sites of the specific host, where cationic sites have a coordination number (CN) of six, such as  $\text{Nb}^{5+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Te}^{6+}$ , and  $\text{W}^{6+}$  ions.<sup>39,40,45–48</sup> Considering the cationic radius and the coordination environment of  $\text{Mn}^{4+}$  ( $r = 0.535 \text{ \AA}$ , CN = 6) and  $\text{Sc}^{3+}$  ( $r = 0.745 \text{ \AA}$ , CN = 6),<sup>43,49,50</sup> the  $\text{Mn}^{4+}$  ions could replace the  $\text{Sc}^{3+}$  sites in the  $\text{LaScO}_3$  host.

In order to identify the structure of the as-prepared sample, the Rietveld refinement for the  $\text{LaScO}_3$  host and  $\text{LaScO}_3:0.001\text{Mn}^{4+}$  phosphors were conducted. Fig. 2(a) and (b) depict the Rietveld refinement results of  $\text{LaScO}_3$  host and  $\text{LaScO}_3:0.001\text{Mn}^{4+}$ , respectively. From the values of  $R_p$  and  $R_{wp}$  ( $R_p = 8.13\%$  and  $R_{wp} = 7.55\%$  for  $\text{LaScO}_3$  host;  $R_p = 4.86\%$  and  $R_{wp} = 3.50\%$

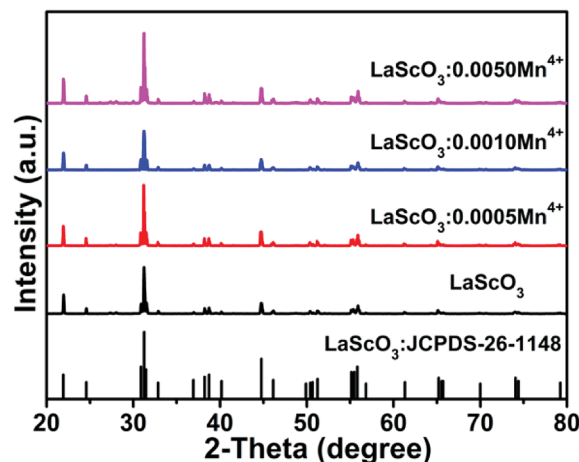


Fig. 1 XRD patterns of  $\text{LaScO}_3:\text{xMn}^{4+}$  ( $x = 0, 0.0005, 0.001, \text{ and } 0.005$ ) phosphors and the stand pattern of  $\text{LaScO}_3$  (JCPDS: 26–1148).

for  $\text{LaScO}_3:0.001\text{Mn}^{4+}$  phosphors), we could know that the obtained results were reliable. The refined crystallographic parameters of the  $\text{LaScO}_3$  host and  $\text{LaScO}_3:0.001\text{Mn}^{4+}$  phosphors were listed in Table 1 and Table 2, respectively. It could be seen that the parameters of  $\text{LaScO}_3$  host and  $\text{LaScO}_3:0.001\text{Mn}^{4+}$  phosphors changed slightly due to the difference in ions radii between  $\text{Sc}^{3+}$  and  $\text{Mn}^{4+}$  ions. The crystal systems of the  $\text{LaScO}_3$  host and  $\text{LaScO}_3:0.001\text{Mn}^{4+}$  phosphors were orthorhombic with a space group of  $Pbnm$ . Fig. 2(c) and (d) show the crystal structure of the  $\text{LaScO}_3$  host and the  $[\text{ScO}_6]$  octahedron, respectively. In the unit cell, one  $\text{Sc}^{3+}$  ion was surrounded by six  $\text{O}^{2-}$  ions to form  $[\text{ScO}_6]$  octahedral units and the  $\text{Mn}^{4+}$  ions could substitute for  $\text{Sc}^{3+}$  ions to form the  $\text{LaScO}_3:\text{Mn}^{4+}$  compound. All the results illustrated the formation of  $\text{LaScO}_3:\text{Mn}^{4+}$  phosphors.

The PLE and PL spectra of the  $\text{LaScO}_3:0.001\text{Mn}^{4+}$  phosphors were shown in Fig. 3(a). When monitored at 703 nm, the obtained excitation spectrum of the  $\text{Mn}^{4+}$  ions in  $\text{LaScO}_3$  was an asymmetric absorption band, which could be fitted to four peaks though Gaussian fitting, namely, peaks at 346 nm ( $28\,902 \text{ cm}^{-1}$ ;  $\text{Mn}^{4+}\text{--O}^{2-}$  transition), 392 nm ( $25\,510 \text{ cm}^{-1}$ ;  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$  dominant transition), 462 nm ( $21\,645 \text{ cm}^{-1}$ ;  ${}^4\text{A}_{2g} \rightarrow {}^2\text{T}_{2g}$  transition), and 543 nm ( $18\,416 \text{ cm}^{-1}$ ;  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$  transition).<sup>48,51</sup> Under the excitation of 398 nm or 549 nm, the  $\text{LaScO}_3:0.001\text{Mn}^{4+}$  phosphors emitted deep red light peaking at 703 nm ( ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$  transition; see Fig. 3(a)) with the CIE chromaticity coordinates of (0.7324, 0.2676) (see Fig. 3(b)). Fig. 3(c) shows the absorption spectra of  $\text{P}_R$  and  $\text{P}_{FR}$  as well as the emission spectrum of the  $\text{LaScO}_3:0.001\text{Mn}^{4+}$  phosphor. Obviously, the PL spectrum of the  $\text{LaScO}_3:0.001\text{Mn}^{4+}$  phosphor was located within the absorption spectrum of the  $\text{P}_{FR}$ . Importantly, the dominant emission peak of  $\text{LaScO}_3:0.001\text{Mn}^{4+}$  phosphor at 703 nm was close to the peak wavelength (around 730 nm) of the absorption spectrum of  $\text{P}_{FR}$ . So it was meaningful to apply  $\text{LaScO}_3:\text{Mn}^{4+}$  phosphors to plant growth LEDs.

To find the optimal doping concentration of  $\text{Mn}^{4+}$  ions in  $\text{LaScO}_3:\text{Mn}^{4+}$  phosphors, a series of  $\text{LaScO}_3:\text{xMn}^{4+}$  ( $x = 0.0005\text{--}0.009$ ) phosphors were synthesized and the corresponding PL

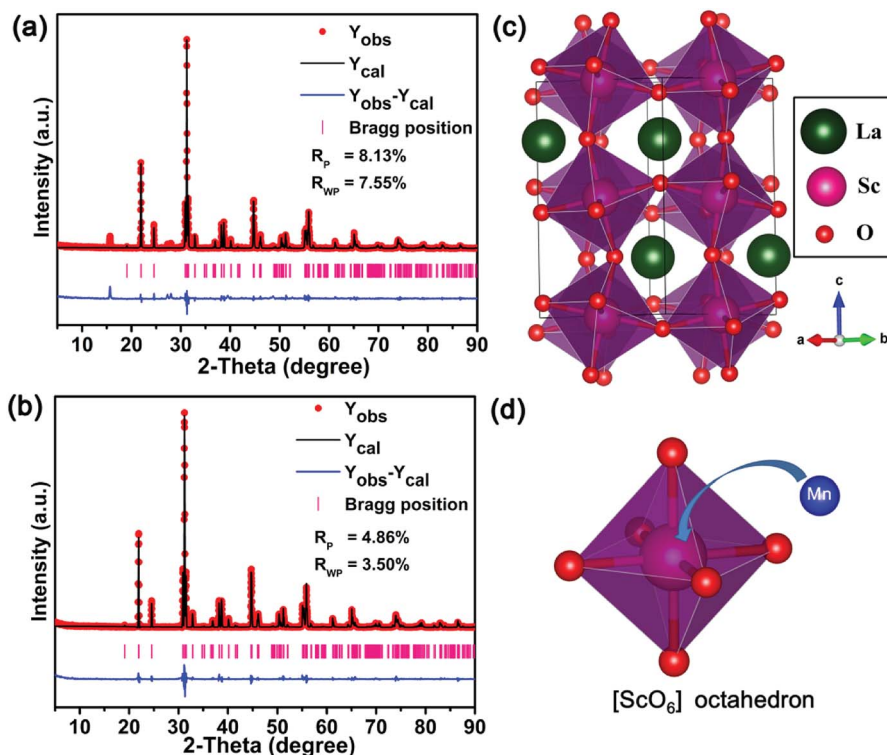


Fig. 2 Rietveld refinement of  $\text{LaScO}_3$  host (a) and  $\text{LaScO}_3:0.001\text{Mn}^{4+}$  (b) using the Fullprof suit software. The structure of (c)  $\text{LaScO}_3$  host and (d)  $[\text{ScO}_6]$  octahedron.

spectra were shown in Fig. 3(d). It could be found that the PL intensity of the  $\text{LaScO}_3:x\text{Mn}^{4+}$  phosphors firstly increased as  $\text{Mn}^{4+}$  concentration increased and then decreased, and the optimal-doping concentration reached when  $x = 0.001$ , which was attributed to the concentration quenching in the  $\text{LaScO}_3:x\text{Mn}^{4+}$  phosphors. The IQE of the  $\text{LaScO}_3:0.001\text{Mn}^{4+}$  phosphor was 15%. The optical doping concentration of  $\text{Mn}^{4+}$  is much lower than rare-earth doped phosphors, because the d-electron wave functions of transition metals (*e.g.*,  $\text{Mn}^{4+}$  ions) extend more widely than 4f electrons of rare earths (*e.g.*,  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions).<sup>52,53</sup> Due to the energy transfer between the nearest  $\text{Mn}^{4+}$  and ends with energy transfer to traps or killing sites,

concentration quenching occurs in  $\text{LaScO}_3:x\text{Mn}^{4+}$  phosphors.<sup>47,54</sup> Considering the concentration quenching occurred in  $\text{LaScO}_3:x\text{Mn}^{4+}$  phosphors, the critical distance ( $R_c$ ) of  $\text{Mn}^{4+}$  ions in the  $\text{LaScO}_3:x\text{Mn}^{4+}$  phosphors was calculated using the following equation:<sup>55,56</sup>

$$R_c = 2 \left( \frac{3V}{4\pi x_c N} \right)^{1/3} \quad (1)$$

where  $V$  and  $N$  represents the volume and the number of host cations of the unit cell, respectively;  $x_c$  refers to the optimal doping concentration of  $\text{Mn}^{4+}$  ions. Herewith,  $V = 266.251(14) \text{ \AA}^3$ ,  $N = 4$ , and  $x_c = 0.001$ . Hence, the  $R_c$  of  $\text{Mn}^{4+}$  ions in

Table 1 Refined crystallographic parameters of  $\text{LaScO}_3$  host

Formula		$\text{LaScO}_3$								
Crystal system		Orthorhombic								
Space group		$pbnm$								
Lattice parameters		$a = 5.68010(17) \text{ \AA}$ , $b = 5.79022(16) \text{ \AA}$ , $c = 8.0952(2) \text{ \AA}$ , $V = 266.244(13) \text{ \AA}^3$								
$U_{\text{aniso}} (\text{Å}^2)$										
Atom	$x$	$y$	$z$	Occ.	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
La1	0.01060	0.95680	0.25	1	0.01218	0.00649	-0.00259	-0.00656	0.00000	0.00000
Sc1	0.00000	0.5	0.00000	1	0.00448	-0.00362	0.00289	-0.00681	-0.00587	-0.00140
O1	0.71276	0.28618	0.01023	1	-0.05698	0.04639	-0.04425	-0.01988	0.00000	0.00000
O2	0.90808	0.52065	-0.01828	1	0.04604	-0.02305	0.00770	0.02371	0.02416	0.03004

Table 2 Refined crystallographic parameters of  $\text{LaScO}_3:0.001\text{Mn}^{4+}$  phosphors

Formula					$\text{LaScO}_3:0.001\text{Mn}^{4+}$					
Crystal system					Orthorhombic					
Space group					$pbnm$					
Lattice parameters					$a = 5.67879(18) \text{ \AA}$ , $b = 5.79140(16) \text{ \AA}$ , $c = 8.0956(3)$ , $V = 266.251(14) \text{ \AA}^3$					
					$U_{\text{aniso}} (\text{Å}^2)$					
Atom	$x$	$y$	$z$	Occ.	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
La1	0.00909	0.95617	0.25	1	0.00781	-0.00411	0.00299	-0.00040	0.00000	0.00000
Sc1	0.00000	0.5	0.00000	0.999	0.01333	-0.00843	-0.00312	0.00057	0.00554	-0.00207
Mn1	0.00000	0.5	0.00000	0.001	0.01333	-0.00843	-0.00312	0.00057	0.00554	-0.00207
O1	0.91109	0.52509	0.25000	1	-0.00405	-0.02970	-0.00531	-0.00072	0.00000	0.00000
O2	0.70010	0.30343	0.01124	1	0.02081	0.03995	-0.02703	-0.02709	-0.00394	0.00625

$\text{LaScO}_3:x\text{Mn}^{4+}$  was calculated to be about  $50.29 \text{ \AA}$  ( $>5 \text{ \AA}$ ), which was comparable with that in other  $\text{Mn}^{4+}$  doped phosphors, such as  $\text{KMgLaTeO}_6:\text{Mn}^{4+}$  ( $33.83 \text{ \AA}$ ),<sup>57</sup>  $\text{Ba}_2\text{TiGe}_2\text{O}_8:\text{Mn}^{4+}$  ( $40.1 \text{ \AA}$ ),<sup>49</sup>  $\text{Li}_2\text{MgZrO}_4:\text{Mn}^{4+}$  ( $33.8 \text{ \AA}$ ),<sup>48</sup> indicating that the luminescence concentration quenching derived from the electric multipole interaction.<sup>25</sup>

To determine whether the electric multipole interaction was electric dipole–dipole (d–d), or dipole–quadrupole (d–q), or quadrupole–quadrupole (q–q) interactions, the following equation could be used to get the exact form:<sup>58,59</sup>

$$\frac{I}{x} = k [1 + \beta(x)^{\theta/3}]^{-1} \quad (2)$$

where  $I$  represents the PL intensity;  $\beta$  and  $k$  are constants for a given host lattice;  $\theta = 6, 8$  and  $10$  stands for electric d–d, d–q, and q–q interactions, respectively;  $x$  is the dopant content of  $\text{Mn}^{4+}$  ions in  $\text{LaScO}_3$  host. The relationship between  $\log(I/x)$  and  $\log(x)$  was plotted in Fig. 3(e) and the slope of the fitting result was found to be  $-1.71990$  ( $=-\theta/3$ ), revealing that the value of  $\theta$  was about 5.16. Thus, the luminescence concentration quenching mechanism of  $\text{Mn}^{4+}$  ions in  $\text{LaScO}_3$  host was electric d–d interaction.

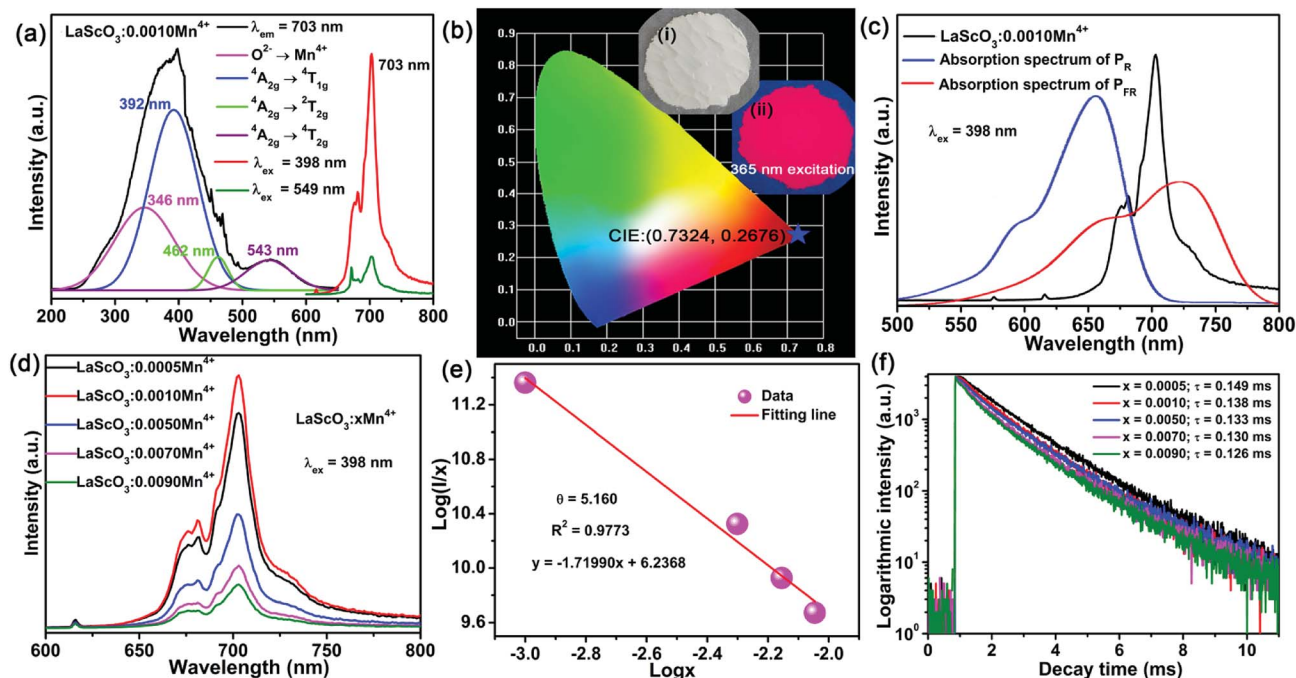


Fig. 3 (a) The PLE spectrum of  $\text{LaScO}_3:0.001\text{Mn}^{4+}$  phosphors monitored at 703 nm. The four curves represent the Gaussian fitting curves. (b) The CIE chromaticity diagram of  $\text{LaScO}_3:0.001\text{Mn}^{4+}$  phosphors. The insets show the phosphor digital pictures under the 365 nm excitation (ii) and daylight (i). (c) The room-temperature PL spectrum of  $\text{LaScO}_3:0.001\text{Mn}^{4+}$  sample excited at 398 nm and the absorption spectra of phytochrome  $\text{P}_R$  and  $\text{P}_{FR}$ . (d) The PL spectra of  $\text{LaScO}_3:x\text{Mn}^{4+}$  ( $x = 0.0005–0.009$ ) phosphors excited at 398 nm. (e) Plot of  $\log(I/x)$  vs.  $\log(x)$  of  $\text{Mn}^{4+}$  ions in  $\text{LaScO}_3:x\text{Mn}^{4+}$  phosphors. (f) The luminescence decay curves of  $\text{LaScO}_3:x\text{Mn}^{4+}$  ( $x = 0.0005–0.009$ ) phosphors under the test condition of  $\lambda_{\text{em}} = 703 \text{ nm}$  and  $\lambda_{\text{ex}} = 398 \text{ nm}$ .



Fig. 3(f) exhibits the luminescence decay curves of Mn<sup>4+</sup> 703 nm emissions in LaScO<sub>3</sub>:xMn<sup>4+</sup> ( $x = 0.0005\text{--}0.009$ ) phosphors. The decay lifetimes of the LaScO<sub>3</sub>:xMn<sup>4+</sup> samples were obtained by the following double-exponential model:<sup>60</sup>

$$I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (3)$$

where  $I$  refers to the luminescent emission intensities at time  $t$ ;  $A_1$  and  $A_2$  are constants; and  $\tau_1$  and  $\tau_2$  are the decay time for the exponential component, respectively. The decay lifetimes of the LaScO<sub>3</sub>:xMn<sup>4+</sup> phosphors were calculated to be 0.149 ms ( $x = 0.0005$ ), 0.138 ms ( $x = 0.001$ ), 0.133 ms ( $x = 0.005$ ), 0.130 ms ( $x = 0.007$ ), and 0.126 ms ( $x = 0.009$ ). Obviously, the decay lifetimes decreased as the concentration  $x$  increased, revealing the non-radiative energy-migration of Mn<sup>4+</sup> ions in the LaScO<sub>3</sub>:xMn<sup>4+</sup> phosphors.

To explore the influence of the octahedral coordination environment of LaScO<sub>3</sub>:xMn<sup>4+</sup> phosphors on the 3d<sup>3</sup> energy level of Mn<sup>4+</sup> ions, Fig. 4(b) shows the Tanabe–Sugano energy-level diagram of Mn<sup>4+</sup> ions in the octahedral site of LaScO<sub>3</sub> host together with the simple energy level diagram of Mn<sup>4+</sup> ions. Based on the <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub> (18 416 cm<sup>-1</sup>) transition energy gap, the crystal-field strength ( $Dq$ ) of the LaScO<sub>3</sub>:xMn<sup>4+</sup> phosphors can be roughly estimated by the following equation:<sup>64</sup>

$$Dq = E(^4A_{2g} \rightarrow ^4T_{2g})/10 \quad (4)$$

Based on the PLE spectrum of the LaScO<sub>3</sub>:0.001Mn<sup>4+</sup> phosphors, the energy difference between the <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>1g</sub> (25 510 cm<sup>-1</sup>) and <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub> (18 416 cm<sup>-1</sup>) was about 7094 cm<sup>-1</sup>. Therefore, the Racah parameter  $B$  can be obtained by the following expression:<sup>62</sup>

$$\frac{Dq}{B} = \frac{15(x-8)}{(x^2-10x)} \quad (5)$$

in which the  $x$  can be calculated by:

$$x = \frac{E(^4A_{2g} \rightarrow ^4T_{1g}) - E(^4A_{2g} \rightarrow ^4T_{2g})}{Dq} \quad (6)$$

From the PL spectrum of the LaScO<sub>3</sub>:0.001Mn<sup>4+</sup> phosphors, the energy of the <sup>2</sup>E<sub>g</sub> → <sup>4</sup>A<sub>2g</sub> (14 225 cm<sup>-1</sup>) was acquired and the Racah parameter  $B$  was evaluated by the following expression:<sup>47,63</sup>

$$\frac{E(^4E_g \rightarrow ^4A_{2g})}{B} = \frac{3.05C}{B} + 7.9 - \frac{1.8B}{Dq} \quad (7)$$

According to the eqn (4)–(7), the crystal field parameters  $Dq$ ,  $B$ , and  $C$  were 1842, 701, and 3006 cm<sup>-1</sup>, respectively. Thus the value of the  $Dq/B$ , which represented the intensity of the crystal field, was about 2.628 (>2.2), indicating that the Mn<sup>4+</sup> ions experienced strong crystal strength in LaScO<sub>3</sub> host than those in Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> ( $Dq/B = 1.98$ ),<sup>64</sup> Ba<sub>2</sub>YSbO<sub>6</sub> ( $Dq/B = 1.88$ ),<sup>65</sup> and Ca<sub>2</sub>-LaNbO<sub>6</sub> ( $Dq/B = 2.31$ ).<sup>66</sup>

The emission energy of the <sup>2</sup>E<sub>g</sub> → <sup>4</sup>A<sub>2g</sub> transition of Mn<sup>4+</sup> ions in specific host could be affected by the nephelauxetic effect.<sup>67</sup> The nephelauxetic effect can be described as the parameter  $\beta_1$ , which was established by Brik *et al.*<sup>63</sup> And the value of  $\beta_1$  can be calculated by the following expression:<sup>68</sup>

$$\beta_1 = \sqrt{\left(\frac{B}{B_0}\right)^2 + \left(\frac{C}{C_0}\right)^2} \quad (8)$$

where  $B_0 = 1160$  cm<sup>-1</sup> and  $C_0 = 4303$  cm<sup>-1</sup>, which was the Racah parameter of the free Mn<sup>4+</sup> ions. Thus, the value of  $\beta_1$  in the LaScO<sub>3</sub> host was about 0.924. Brik *et al.* also have presented the linear relationship [ $E(^2E_g) = -880.49 + 16\,261.92\beta_1 \pm \sigma$ ;  $\sigma = 332$  cm<sup>-1</sup>] between the <sup>2</sup>E<sub>g</sub> energy level of Mn<sup>4+</sup> ions in different hosts.<sup>63</sup> Fig. 4(a) depicts the relationship between the <sup>2</sup>E<sub>g</sub> energy level of Mn<sup>4+</sup> ions and  $\beta_1$  in different hosts. All the points were located around the line  $E(^2E_g) = -880.49 + 16\,261.92\beta_1$ , indicating the data were acceptable. The detailed data of these phosphors, which used in Fig. 4(a), were listed in Table 3. It can

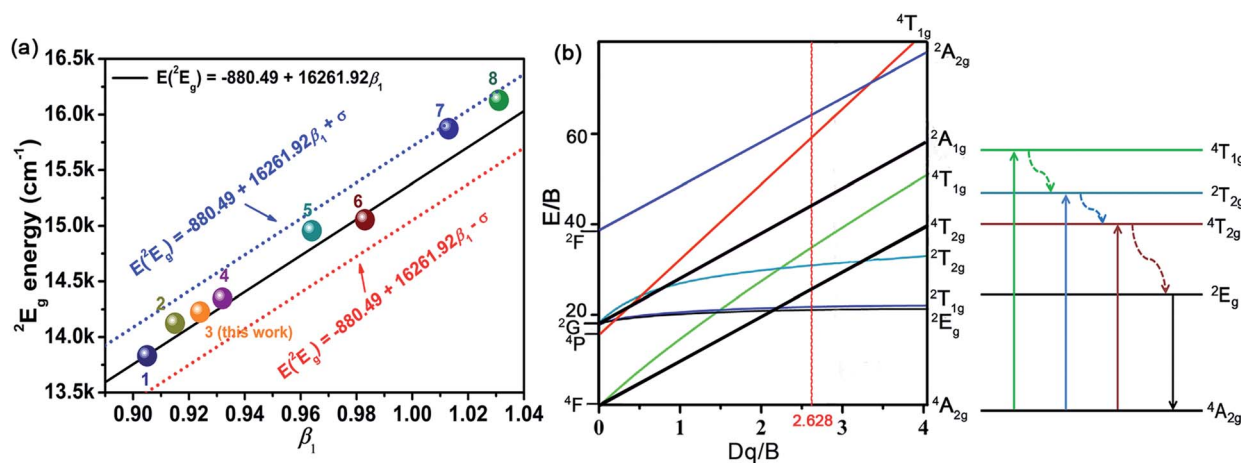


Fig. 4 (a) Dependence of the <sup>2</sup>E<sub>g</sub> energy level of Mn<sup>4+</sup> ions on the nephelauxetic ratio  $\beta_1$  in different hosts including LaScO<sub>3</sub> [ $E(^2E_g) = -880.49 + 16\,261.92\beta_1 \pm \sigma$ ;  $\sigma = 332$  cm<sup>-1</sup>]. (b) (Left side) Tanabe–Sugano energy-level diagram of Mn<sup>4+</sup> ions in the octahedral site of LaScO<sub>3</sub> host and (right side) the simple energy level diagram of Mn<sup>4+</sup> ions.

Table 3 The spectroscopic parameters of Mn<sup>4+</sup> ions in different host

No.	Hosts	$Dq/\text{cm}^{-1}$	$B \text{ cm}^{-1}$	$C / \text{cm}^{-1}$	$Dq/B$	$\beta_1$	$E(^2E_g)/\text{cm}^{-1}$	Ref.
1	SiTiO <sub>3</sub>	1818	719	2839	2.529	0.905	13 831 (723 nm)	69
2	La(MgTi) <sub>1/2</sub> O <sub>3</sub>	2053	700	2959	2.933	0.915	14 124 (708 nm)	9
3	LaScO <sub>3</sub>	1842	701	3006	2.628	0.924	14 225 (703 nm)	This work
4	NaMgGdTeO <sub>6</sub>	2083	727	2971	2.865	0.932	14 347 (697 nm)	39
5	Y <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	2000	600	3500	3.333	0.964	14 956 (669 nm)	63 and 70
6	CaZrO <sub>3</sub>	1850	754	3173	2.454	0.983	15 054 (664 nm)	67
7	K <sub>2</sub> SiF <sub>6</sub>	2197	599	3750	3.668	1.013	15 873 (630 nm)	63
8	KTeF <sub>5</sub>	2267	567	3904	3.998	1.031	16 129 (620 nm)	71

be seen clearly from Table 3 and Fig. 4(a) that with the increasing of  $\beta_1$ , the value of the energy level of <sup>2</sup>E<sub>g</sub> increased. And the value of the nephelauxetic effect in LaScO<sub>3</sub>:xMn<sup>4+</sup> phosphors was close to the La(MgTi)<sub>1/2</sub>O<sub>3</sub>:Mn<sup>4+</sup>, NaMgGdTeO<sub>6</sub>:Mn<sup>4+</sup>, and SiTiO<sub>3</sub>:Mn<sup>4+</sup>, indicating the similar coordination environments of Mn<sup>4+</sup> ions in these phosphors. Based on the Tanabe–Sugano energy-level diagram in the left diagram of Fig. 4(b), the simple schematic diagram of the Mn<sup>4+</sup> energy level transition in the LaScO<sub>3</sub> host was illustrated in the right diagram of Fig. 4(b). The electrons at the ground state <sup>4</sup>A<sub>2g</sub> (from the <sup>4</sup>F term) absorbed the energy of the excited light (398 nm or 549 nm) and then were pumped to the excited level <sup>4</sup>T<sub>1g</sub> (from the <sup>4</sup>F term), <sup>2</sup>T<sub>2g</sub> (from the <sup>2</sup>G term), and <sup>4</sup>T<sub>2g</sub> (from the <sup>4</sup>F term), after which the electrons could relax to the lowest excited state level <sup>2</sup>E<sub>g</sub> (from the <sup>2</sup>G term) through non-radiative transitions process <sup>4</sup>T<sub>1g</sub> → <sup>2</sup>T<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub> → <sup>2</sup>E<sub>g</sub>, and finally released the energy by radiation transitions process with a red light emission at 703 nm.<sup>64</sup>

## Conclusions

In conclusion, LaScO<sub>3</sub>:xMn<sup>4+</sup> (x = 0.0005–0.009) far-red emitting phosphors have been successfully synthesized *via* high-temperature solid-state reaction process. The crystal structure of the host and LaScO<sub>3</sub>:0.001Mn<sup>4+</sup> phosphors had been discussed and the XRD patterns of the LaScO<sub>3</sub>:xMn<sup>4+</sup> proved that they all were pure phase. Monitored at 703 nm, the obtained PLE spectrum of the LaScO<sub>3</sub>:0.001Mn<sup>4+</sup> phosphors exhibited four Gaussian fitting peaks, centering at 346 nm (28 902 cm<sup>-1</sup>; Mn<sup>4+</sup>–O<sup>2-</sup> transition), 392 nm (25 510 cm<sup>-1</sup>; <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>1g</sub> dominant transition), 462 nm (21 645 cm<sup>-1</sup>; <sup>4</sup>A<sub>2g</sub> → <sup>2</sup>T<sub>2g</sub> transition), and 543 nm (18 416 cm<sup>-1</sup>; <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub> transition). Upon 398 nm excitation, the PL spectrum of LaScO<sub>3</sub>:0.001Mn<sup>4+</sup> phosphors showed a far-red emission peaking at 703 nm within the 650–800 nm range, which was very close to the central absorption wavelength of the P<sub>FR</sub> at around 730 nm. The optimal doping concentration of Mn<sup>4+</sup> ion was 0.001 in LaScO<sub>3</sub> host and the electric d–d interaction contributed to the concentration quenching mechanism. All the results indicated that the LaScO<sub>3</sub>:Mn<sup>4+</sup> phosphors are promising far-red emitting materials for plant growth LEDs application.

## Conflicts of interest

There are no conflicts to declare.

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## Notes and references

- R. J. Bula, R. C. Morrow, T. W. Tibbitts and D. J. Barta, *HortScience*, 1991, **26**, 203–205.
- D. E. Macey and J. T. Arnott, *Can. J. For. Res.*, 1986, **16**, 949–954.
- C. A. Jaleel, P. Manivannan, B. Sankar, A. Kishorekumar, R. Gopi, R. Somasundaram and R. Panneerselvam, *Colloids Surf., B*, 2007, **60**, 7–11.
- C. Kami, S. Lorrain, P. Hornitschek and C. Fankhauser, *Curr. Top. Dev. Biol.*, 2010, **91**, 29–66.
- L. Ma, D.-j. Wang, Z.-y. Mao, Q.-f. Lu and Z.-h. Yuan, *Appl. Phys. Lett.*, 2008, **93**, 144101.
- J. Chen, N. Zhang, C. Guo, F. Pan, X. Zhou, H. Suo, X. Zhao and E. M. Goldys, *ACS Appl. Mater. Interfaces*, 2016, **8**, 20856–20864.
- M. J. Kasperbauer, *Plant Physiol.*, 1987, **85**, 350–354.
- P. F. Devlin, J. M. Christie and M. J. Terry, *J. Exp. Bot.*, 2007, **58**, 3071–3077.
- Z. Zhou, J. Zheng, R. Shi, N. Zhang, J. Chen, R. Zhang, H. Suo, E. M. Goldys and C. Guo, *ACS Appl. Mater. Interfaces*, 2017, **9**, 6177–6185.
- A. M. Srivastava, M. G. Brik, H. A. Comanzo, W. W. Beers, W. E. Cohen and T. Pocock, *ECS J. Solid State Sci. Technol.*, 2017, **7**, R3158–R3162.
- T. Nakajima and T. Tsuchiya, *ACS Appl. Mater. Interfaces*, 2015, **7**, 21398–21407.
- G. D. Massa, *HortScience*, 2008, **43**, 1951–1956.
- H. Smith, *Nature*, 2000, **407**, 585–591.
- X. Huang, *Nat. Photonics*, 2014, **8**, 748–749.
- C. Yu, Z. Yang, J. Qiu, Z. Song and Z. Dacheng, *J. Am. Ceram. Soc.*, 2018, **101**, 612–623.
- X. Wu, Y. Jiao, O. Hai, Q. Ren, F. Lin and H. Li, *J. Alloys Compd.*, 2018, **730**, 521–527.

- 17 J. Han, L. Li, M. Peng, B. Huang, F. Pan, F. Kang, L. Li, J. Wang and B. Lei, *Chem. Mater.*, 2017, **29**, 8412–8424.
- 18 D. Wen, H. Kato, M. Kobayashi, S. Yamamoto, M. Mitsuishi and M. Kakihana, *J. Mater. Chem. C*, 2017, **5**, 4578–4583.
- 19 P. Du, L. Luo, X. Huang and J. S. Yu, *J. Colloid Interface Sci.*, 2018, **514**, 172–181.
- 20 P. Du, X. Huang and J. S. Yu, *Inorg. Chem. Front.*, 2017, **4**, 1987–1995.
- 21 X. Huang, *J. Alloys Compd.*, 2017, **690**, 356–359.
- 22 H. Guo, X. Huang and Y. Zeng, *J. Alloys Compd.*, 2018, **741**, 300–306.
- 23 P. Du, X. Huang and J. S. Yu, *Chem. Eng. J.*, 2018, **337**, 91–100.
- 24 X. Huang and H. Guo, *Dyes Pigm.*, 2018, **154**, 82–86.
- 25 S. G. Prasanna Kumar, R. Hari Krishna, N. Kottam, P. Krishna Murthy, C. Manjunatha, R. Preetham, C. Shivakumara and T. Thomas, *Dyes Pigm.*, 2018, **150**, 306–314.
- 26 J. Zhong, S. Zhou, D. Chen, J. Li, Y. Zhu, X. Li, L. Chen and Z. Ji, *Dalton Trans.*, 2018, **47**, 8248.
- 27 X. Huang, H. Guo and B. Li, *J. Alloys Compd.*, 2017, **720**, 29–38.
- 28 X. Huang, B. Li, H. Guo and D. Chen, *Dyes Pigm.*, 2017, **143**, 86–94.
- 29 H. Guo, B. Devakumar, B. Li and X. Huang, *Dyes Pigm.*, 2018, **151**, 81–88.
- 30 X. Huang, S. Wang, B. Li, Q. Sun and H. Guo, *Opt. Lett.*, 2018, **43**, 1307–1310.
- 31 L. Y. Wang, E. H. Song, T. T. Deng, Y. Y. Zhou, Z. F. Liao, W. R. Zhao, B. Zhou and Q. Y. Zhang, *Dalton Trans.*, 2017, **46**, 9925–9933.
- 32 G. Zhu, Z. Li, C. Wang, F. Zhou, Y. Shi, Y. Wen and S. Xin, *J. Mater. Sci.: Mater. Electron.*, 2017, **29**, 2216–2221.
- 33 R. Cao, M. Peng, E. Song and J. Qiu, *ECS J. Solid State Sci. Technol.*, 2012, **1**, R123–R126.
- 34 Q. Sun, S. Wang, B. Li, H. Guo and X. Huang, *J. Lumin.*, 2018, **203**, 371–375.
- 35 J. Liang, P. Du, H. Guo, L. Sun, B. Li and X. Huang, *Dyes Pigm.*, 2018, **157**, 40–46.
- 36 K. Sankarasubramanian, B. Devakumar, G. Annadurai, L. Sun, Y.-J. Zeng and X. Huang, *RSC Adv.*, 2018, **8**, 30223–30229.
- 37 X. Huang, J. Liang, B. Li, L. Sun and J. Lin, *Opt. Lett.*, 2018, **43**, 3305–3308.
- 38 M. Peng, X. Yin, P. A. Tanner, M. G. Brik and P. Li, *Chem. Mater.*, 2015, **27**, 2938–2945.
- 39 K. Li, H. Lian and R. V. Deun, *J. Lumin.*, 2018, **198**, 155–162.
- 40 X. Huang and H. Guo, *Dyes Pigm.*, 2018, **152**, 36–42.
- 41 Y. Takeda, H. Kato, M. Kobayashi, H. Kobayashi and M. Kakihana, *Chem. Lett.*, 2015, **44**, 1541–1543.
- 42 R. Cao, W. Luo, Q. Xiong, S. Jiang, Z. Luo and J. Fu, *Chem. Lett.*, 2015, **44**, 1422–1424.
- 43 D. Lybye, P. Finn Willy and M. Mogens, *Solid State Ionics*, 2000, **128**, 91–103.
- 44 J. Du, O. Q. De Clercq, K. Korthout and D. Poelman, *Materials*, 2017, **10**, 1422.
- 45 C. Wu, J. Li, H. Xu, J. Wu, J. Zhang, Z. Ci, L. Feng, C. Cao, Z. Zhang and Y. Wang, *J. Alloys Compd.*, 2015, **646**, 734–740.
- 46 M. H. Du, *J. Mater. Chem. C*, 2014, **2**, 2475–2481.
- 47 L. Qin, S. Bi, P. Cai, C. Chen, J. Wang, S. I. Kim, Y. Huang and H. J. Seo, *J. Alloys Compd.*, 2018, **755**, 61–66.
- 48 R. Cao, Z. Shi, G. Quan, T. Chen, S. Guo, Z. Hu and P. Liu, *J. Lumin.*, 2017, **188**, 577–581.
- 49 R. Cao, Y. Ye, Q. Peng, G. Zheng, H. Ao, J. Fu, Y. Guo and B. Guo, *Dyes Pigm.*, 2017, **146**, 14–19.
- 50 B. Wang, H. Lin, F. Huang, J. Xu, H. Chen, Z. Lin and Y. Wang, *Chem. Mater.*, 2016, **28**, 3515–3524.
- 51 B. Wang, H. Lin, J. Xu, H. Chen and Y. Wang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 22905–22913.
- 52 U. B. Humayoun, S. N. Tiruneh and D.-H. Yoon, *Dyes Pigm.*, 2018, **152**, 127–130.
- 53 M. Inokuti and F. Hirayama, *J. Chem. Phys.*, 1965, **43**, 1978–1989.
- 54 S. Zhang, Y. Hu, H. Duan, Y. Fu and M. He, *J. Alloys Compd.*, 2017, **693**, 315–325.
- 55 B. Li, X. Huang, H. Guo and Y. Zeng, *Dyes Pigm.*, 2018, **150**, 67–72.
- 56 X. Huang, B. Li and H. Guo, *J. Alloys Compd.*, 2017, **695**, 2773–2780.
- 57 K. Li, H. Lian and R. Van Deun, *Dalton Trans.*, 2018, **47**, 2501–2505.
- 58 C. Wang, Y. Jin, Y. Lv, G. Ju, L. Chen, Z. Li and Y. Hu, *J. Lumin.*, 2017, **192**, 337–342.
- 59 S. K. Hussain, T. T. H. Giang and J. S. Yu, *J. Alloys Compd.*, 2018, **739**, 218–226.
- 60 S. Liang, M. Shang, H. Lian, K. Li, Y. Zhang and J. Lin, *J. Mater. Chem. C*, 2016, **4**, 6409–6416.
- 61 X. Zhang, J. Nie, S. Liu, Y. Li and J. Qiu, *J. Am. Ceram. Soc.*, 2017, 1–9.
- 62 C. Yang, Z. Zhang, G. Hu, R. Cao, X. Liang and W. Xiang, *J. Alloys Compd.*, 2017, **694**, 1201–1208.
- 63 M. G. Brik, S. J. Camardello and A. M. Srivastava, *ECS J. Solid State Sci. Technol.*, 2014, **4**, R39–R43.
- 64 L. Zhou, C. Shen, L. Shen, S. Liu, J. Liu, L. Ding, J. Du, W. Xiang and X. Liang, *J. Alloys Compd.*, 2018, **769**, 686–693.
- 65 J. Zhong, D. Chen, S. Yuan, M. Liu, Y. Yuan, Y. Zhu, X. Li and Z. Ji, *Inorg. Chem.*, 2018, **57**, 8978–8987.
- 66 Z. Lu, H. Wang, D. Yu, T. Huang, L. Wen, M. Huang, L. Zhou and Q. Wang, *Opt. Laser Technol.*, 2018, **108**, 116–123.
- 67 M. G. Brik and A. M. Srivastava, *ECS J. Solid State Sci. Technol.*, 2013, **2**, R148–R152.
- 68 M. G. Brik, S. J. Camardello, A. M. Srivastava, N. M. Avram and A. Suchocki, *ECS J. Solid State Sci. Technol.*, 2015, **5**, R3067–R3077.
- 69 Z. Brykner, V. Trepakov, Z. Potůček and L. Jastrabík, *J. Lumin.*, 2000, **87–89**, 605–607.
- 70 M. G. Brik, A. M. Srivastava and N. M. Avram, *Opt. Mater.*, 2011, **33**, 1671–1676.
- 71 T. T. Deng, E. H. Song, J. Su, Y. Y. Zhou, L. Y. Wang, S. Ye and Q. Y. Zhang, *J. Mater. Chem. C*, 2018, **6**, 4418–4426.