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Synthesis, structure, and luminescence characteristics of far-red emitting Mn⁴⁺-activated LaScO₃ perovskite phosphors for plant growth

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Far-red emitting phosphors LaScO₃:Mn⁴⁺ were successfully synthesized *via* a high-temperature solid-state reaction method. The X-ray powder diffraction confirmed that the pure-phase LaScO₃:Mn⁴⁺ phosphors had formed. Under 398 nm excitation, the LaScO₃:Mn⁴⁺ phosphors emitted far red light within the range of 650–800 nm peaking at 703 nm (14 225 cm⁻¹) due to the ²E_g → ⁴A_{2g} transition, which was close to the spectral absorption center of phytochrome P_{FR} located at around 730 nm. The optimal doping concentration and luminescence concentration quenching mechanism of LaScO₃:Mn⁴⁺ phosphors was found to be 0.001 and electric dipole–dipole interaction, respectively. And the CIE chromaticity coordinates of the LaScO₃:0.001Mn⁴⁺ phosphor were (0.7324, 0.2676). The decay lifetimes of the LaScO₃:Mn⁴⁺ phosphors gradually decreased from 0.149 to 0.126 ms when the Mn⁴⁺ doping concentration increased from 0.05 to 0.9 mol%. Crystal field analysis showed that the Mn⁴⁺ ions experienced a strong crystal field in the LaScO₃ host. The research conducted on the LaScO₃:Mn⁴⁺ 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.^{1–4} 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.^{5–7} There exist two kinds of phytochrome, P_R and P_{FR}, and P_R is the biologically inactive state, whereas P_{FR} is the biologically active state.^{4,8} These two phytochromes can be converted into each other by absorbing different wavelengths of light, in which the P_R was sensitive to red light and can turn into P_{FR} by absorbing light with wavelength peaking at around 660 nm, whereas P_{FR} should absorb far red light peaking at around 730 nm to switch to P_R.^{9,10} 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.^{11–13} 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.⁹ 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.⁴ 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_{FR}. But the solid state light-emitting diodes (LEDs) device with long lifetime and low power consumption,^{14–21} which can exhibit various colors by coating different phosphors onto the blue/near-ultraviolet LED chip,^{22–30} 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 K₂-NaAlF₆:Mn⁴⁺ (630 nm),³¹ Na₃MgZr(PO₄)₃:Eu³⁺ (611 nm),³² and Sr₂MgAl₂₂O₃₆:Mn⁴⁺ (658 nm),³³ 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.

Mn⁴⁺ ions in particular host materials with octahedral structures can emit red light and even deep red light due to the ²E_g → ⁴A_{2g} transition,^{34–37} such as Sr₄Al₁₄O₂₅:Mn⁴⁺ (652 nm),³⁸ NaMgGdTeO₆:Mn⁴⁺ (697 nm),³⁹ Ca₃La₂W₂O₁₂:Mn⁴⁺ (711 nm),⁴⁰ La₂MTiO₆:Mn⁴⁺ (M = Mg and Zn; 710 nm),⁴¹ and Ba₂GeO₄:Mn⁴⁺ (667 nm).⁴² Considering that the structure of the LaScO₃ compound with [ScO₆] octahedral structure is similar to LaAlO₃ and Mn⁴⁺-doped LaAlO₃ phosphors can emit far-red emission,

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so the LaScO_3 compound has been chosen as the host for Mn^{4+} doping.^{43,44} Thus, in this work, LaScO_3 and 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 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 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 Sc_2O_3 (analytical reagent, AR), MnCO_3 (AR), and La_2O_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 Al_2O_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 LaScO_3 (JCPDS: 26-1148). It could be seen that all the diffraction peaks of the samples matched well with the standard data of LaScO_3 . There was no excess crystal phase formation, which illustrated the Mn^{4+} ions could be successfully doped into the LaScO_3 host. Mn^{4+} ions can replace specific cationic sites of the specific host, where cationic sites have a coordination number (CN) of six, such as Nb^{5+} , Zr^{4+} , Ti^{4+} , Te^{6+} , and W^{6+} ions.^{39,40,45–48} Considering the cationic radius and the coordination environment of Mn^{4+} ($r = 0.535 \text{ \AA}$, CN = 6) and Sc^{3+} ($r = 0.745 \text{ \AA}$, CN = 6),^{43,49,50} the Mn^{4+} ions could replace the Sc^{3+} sites in the LaScO_3 host.

In order to identify the structure of the as-prepared sample, the Rietveld refinement for the 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 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 LaScO_3 host; $R_p = 4.86\%$ and $R_{wp} = 3.50\%$

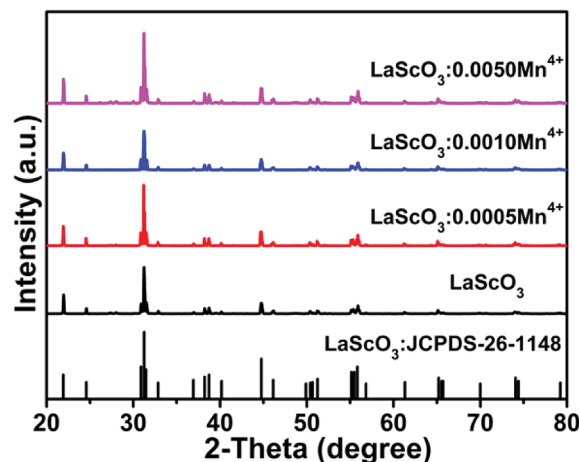


Fig. 1 XRD patterns of $\text{LaScO}_3:\text{xMn}^{4+}$ ($x = 0, 0.0005, 0.001, \text{ and } 0.005$) phosphors and the stand pattern of LaScO_3 (JCPDS: 26–1148).

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 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 LaScO_3 host and $\text{LaScO}_3:0.001\text{Mn}^{4+}$ phosphors changed slightly due to the difference in ions radii between Sc^{3+} and Mn^{4+} ions. The crystal systems of the 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 LaScO_3 host and the $[\text{ScO}_6]$ octahedron, respectively. In the unit cell, one Sc^{3+} ion was surrounded by six O^{2-} ions to form $[\text{ScO}_6]$ octahedral units and the Mn^{4+} ions could substitute for 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 Mn^{4+} ions in 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).^{48,51} 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 P_R and 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 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 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 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



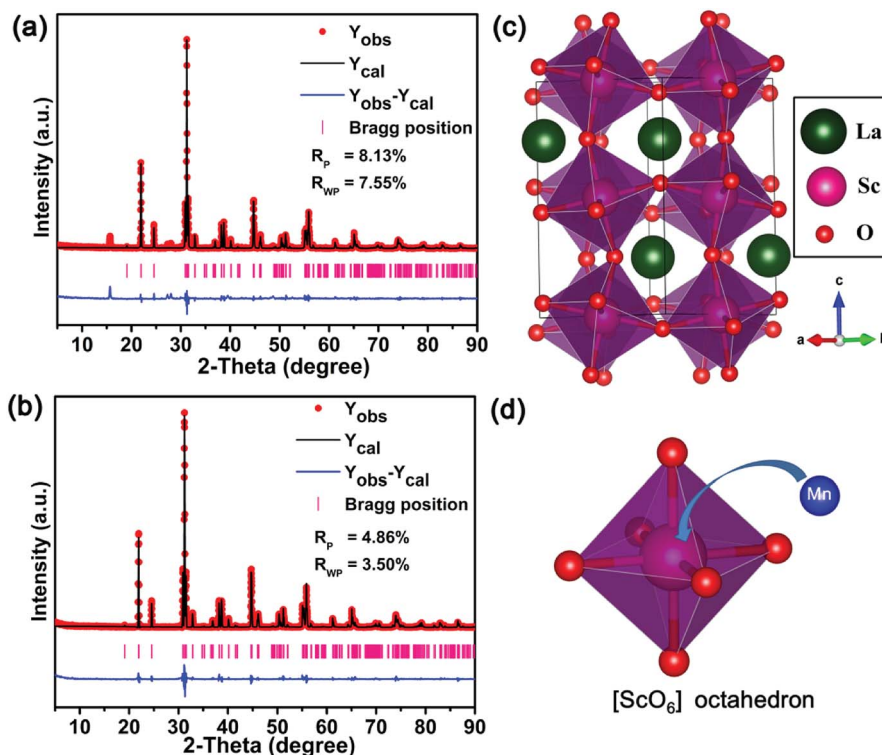


Fig. 2 Rietveld refinement of LaScO₃ host (a) and LaScO₃:0.001Mn⁴⁺ (b) using the Fullprof suit software. The structure of (c) LaScO₃ host and (d) [ScO₆] octahedron.

spectra were shown in Fig. 3(d). It could be found that the PL intensity of the LaScO₃:xMn⁴⁺ phosphors firstly increased as Mn⁴⁺ concentration increased and then decreased, and the optimal-doping concentration reached when $x = 0.001$, which was attributed to the concentration quenching in the LaScO₃:xMn⁴⁺ phosphors. The IQE of the LaScO₃:0.001Mn⁴⁺ phosphor was 15%. The optical doping concentration of Mn⁴⁺ is much lower than rare-earth doped phosphors, because the d-electron wave functions of transition metals (*e.g.*, Mn⁴⁺ ions) extend more widely than 4f electrons of rare earths (*e.g.*, Eu³⁺ and Tb³⁺ ions).^{52,53} Due to the energy transfer between the nearest Mn⁴⁺ and ends with energy transfer to traps or killing sites,

concentration quenching occurs in LaScO₃:xMn⁴⁺ phosphors.^{47,54} Considering the concentration quenching occurred in LaScO₃:xMn⁴⁺ phosphors, the critical distance (R_c) of Mn⁴⁺ ions in the LaScO₃:xMn⁴⁺ phosphors was calculated using the following equation:^{55,56}

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

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 Mn⁴⁺ ions. Herewith, $V = 266.251(14) \text{ \AA}^3$, $N = 4$, and $x_c = 0.001$. Hence, the R_c of Mn⁴⁺ ions in

Table 1 Refined crystallographic parameters of LaScO₃ host

Formula		LaScO ₃								
Crystal system		Orthorhombic								
Space group		<i>pbnm</i>								
Lattice parameters		$a = 5.68010(17) \text{ \AA}$, $b = 5.79022(16) \text{ \AA}$, $c = 8.0952(2) \text{ \AA}$, $V = 266.244(13) \text{ \AA}^3$								
$U_{\text{aniso}} (\text{\AA}^2)$										
Atom	<i>x</i>	<i>y</i>	<i>z</i>	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 LaScO₃:0.001Mn⁴⁺ phosphors

Formula					LaScO ₃ :0.001Mn ⁴⁺					
Crystal system					Orthorhombic					
Space group					<i>pbnm</i>					
Lattice parameters					<i>a</i> = 5.67879(18) Å, <i>b</i> = 5.79140(16) Å, <i>c</i> = 8.0956(3), <i>V</i> = 266.251(14) Å ³					
					<i>U</i> _{aniso} (Å ²)					
Atom	<i>x</i>	<i>y</i>	<i>z</i>	Occ.	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> 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

LaScO₃:*x*Mn⁴⁺ was calculated to be about 50.29 Å (>5 Å), which was comparable with that in other Mn⁴⁺ doped phosphors, such as KMgLaTeO₆:Mn⁴⁺ (33.83 Å),⁵⁷ Ba₂TiGe₂O₈:Mn⁴⁺ (40.1 Å),⁴⁹ Li₂MgZrO₄:Mn⁴⁺ (33.8 Å),⁴⁸ indicating that the luminescence concentration quenching derived from the electric multipole interaction.²⁵

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:^{58,59}

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

where *I* represents the PL intensity; β 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 Mn⁴⁺ ions in LaScO₃ 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 θ was about 5.16. Thus, the luminescence concentration quenching mechanism of Mn⁴⁺ ions in LaScO₃ host was electric d–d interaction.

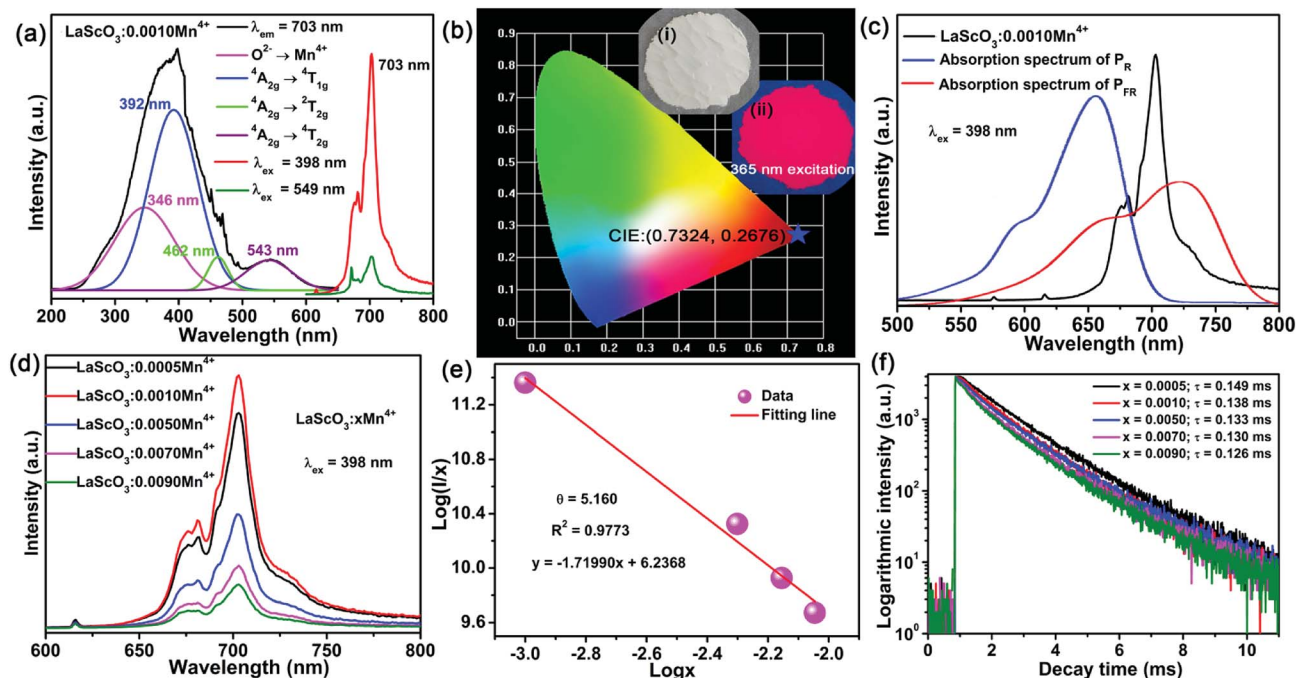


Fig. 3 (a) The PLE spectrum of LaScO₃:0.001Mn⁴⁺ phosphors monitored at 703 nm. The four curves represent the Gaussian fitting curves. (b) The CIE chromaticity diagram of LaScO₃:0.001Mn⁴⁺ phosphors. The insets show the phosphor digital pictures under the 365 nm excitation (ii) and daylight (i). (c) The room-temperature PL spectrum of LaScO₃:0.001Mn⁴⁺ sample excited at 398 nm and the absorption spectra of phytochrome P_R and P_{FR}. (d) The PL spectra of LaScO₃:*x*Mn⁴⁺ (*x* = 0.0005–0.009) phosphors excited at 398 nm. (e) Plot of log(*I*/*x*) vs. log(*x*) of Mn⁴⁺ ions in LaScO₃:*x*Mn⁴⁺ phosphors. (f) The luminescence decay curves of LaScO₃:*x*Mn⁴⁺ (*x* = 0.0005–0.009) phosphors under the test condition of $\lambda_{em} = 703$ nm and $\lambda_{ex} = 398$ nm.



Fig. 3(f) exhibits the luminescence decay curves of Mn⁴⁺ 703 nm emissions in LaScO₃:xMn⁴⁺ (x = 0.0005–0.009) phosphors. The decay lifetimes of the LaScO₃:xMn⁴⁺ samples were obtained by the following double-exponential model:⁶⁰

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

where I refers to the luminescent emission intensities at time t ; A_1 and A_2 are constants; and τ_1 and τ_2 are the decay time for the exponential component, respectively. The decay lifetimes of the LaScO₃:xMn⁴⁺ 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 Mn⁴⁺ ions in the LaScO₃:xMn⁴⁺ phosphors.

To explore the influence of the octahedral coordination environment of LaScO₃:xMn⁴⁺ phosphors on the 3d³ energy level of Mn⁴⁺ ions, Fig. 4(b) shows the Tanabe–Sugano energy-level diagram of Mn⁴⁺ ions in the octahedral site of LaScO₃ host together with the simple energy level diagram of Mn⁴⁺ ions. Based on the ⁴A_{2g} → ⁴T_{2g} (18 416 cm⁻¹) transition energy gap, the crystal-field strength (Dq) of the LaScO₃:xMn⁴⁺ phosphors can be roughly estimated by the following equation:⁶⁴

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

Based on the PLE spectrum of the LaScO₃:0.001Mn⁴⁺ phosphors, the energy difference between the ⁴A_{2g} → ⁴T_{1g} (25 510 cm⁻¹) and ⁴A_{2g} → ⁴T_{2g} (18 416 cm⁻¹) was about 7094 cm⁻¹. Therefore, the Racah parameter B can be obtained by the following expression:⁶²

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

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 LaScO₃:0.001Mn⁴⁺ phosphors, the energy of the ²E_g → ⁴A_{2g} (14 225 cm⁻¹) was acquired and the Racah parameter B was evaluated by the following expression:^{47,63}

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

According to the eqn (4)–(7), the crystal field parameters Dq , B , and C were 1842, 701, and 3006 cm⁻¹, 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 Mn⁴⁺ ions experienced strong crystal strength in LaScO₃ host than those in Y₃Al₅O₁₂ ($Dq/B = 1.98$),⁶⁴ Ba₂YSbO₆ ($Dq/B = 1.88$),⁶⁵ and Ca₂-LaNbO₆ ($Dq/B = 2.31$).⁶⁶

The emission energy of the ²E_g → ⁴A_{2g} transition of Mn⁴⁺ ions in specific host could be affected by the nephelauxetic effect.⁶⁷ The nephelauxetic effect can be described as the parameter β_1 , which was established by Brik *et al.*⁶³ And the value of β_1 can be calculated by the following expression:⁶⁸

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

where $B_0 = 1160$ cm⁻¹ and $C_0 = 4303$ cm⁻¹, which was the Racah parameter of the free Mn⁴⁺ ions. Thus, the value of β_1 in the LaScO₃ 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⁻¹] between the ²E_g energy level of Mn⁴⁺ ions in different hosts.⁶³ Fig. 4(a) depicts the relationship between the ²E_g energy level of Mn⁴⁺ ions and β_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

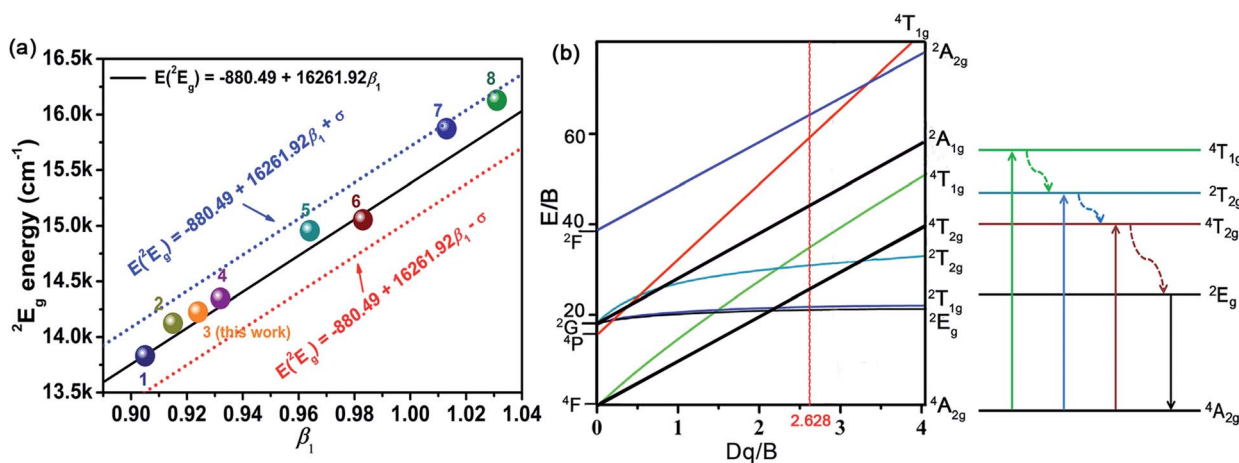


Fig. 4 (a) Dependence of the ²E_g energy level of Mn⁴⁺ ions on the nephelauxetic ratio β_1 in different hosts including LaScO₃ [$E(^2E_g) = -880.49 + 16\,261.92\beta_1 \pm \sigma$; $\sigma = 332$ cm⁻¹]. (b) (Left side) Tanabe–Sugano energy-level diagram of Mn⁴⁺ ions in the octahedral site of LaScO₃ host and (right side) the simple energy level diagram of Mn⁴⁺ ions.



Table 3 The spectroscopic parameters of Mn⁴⁺ ions in different host

No.	Hosts	Dq/cm^{-1}	$B \text{ cm}^{-1}$	C / cm^{-1}	Dq/B	β_1	$E(^2E_g)/\text{cm}^{-1}$	Ref.
1	SiTiO ₃	1818	719	2839	2.529	0.905	13 831 (723 nm)	69
2	La(MgTi) _{1/2} O ₃	2053	700	2959	2.933	0.915	14 124 (708 nm)	9
3	LaScO ₃	1842	701	3006	2.628	0.924	14 225 (703 nm)	This work
4	NaMgGdTeO ₆	2083	727	2971	2.865	0.932	14 347 (697 nm)	39
5	Y ₂ Ti ₂ O ₇	2000	600	3500	3.333	0.964	14 956 (669 nm)	63 and 70
6	CaZrO ₃	1850	754	3173	2.454	0.983	15 054 (664 nm)	67
7	K ₂ SiF ₆	2197	599	3750	3.668	1.013	15 873 (630 nm)	63
8	KTeF ₅	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 β_1 , the value of the energy level of 2E_g increased. And the value of the nephelauxetic effect in LaScO₃:xMn⁴⁺ phosphors was close to the La(MgTi)_{1/2}O₃:Mn⁴⁺, NaMgGdTeO₆:Mn⁴⁺, and SiTiO₃:Mn⁴⁺, indicating the similar coordination environments of Mn⁴⁺ 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 Mn⁴⁺ energy level transition in the LaScO₃ host was illustrated in the right diagram of Fig. 4(b). The electrons at the ground state $^4A_{2g}$ (from the 4F term) absorbed the energy of the excited light (398 nm or 549 nm) and then were pumped to the excited level $^4T_{1g}$ (from the 4F term), $^2T_{2g}$ (from the 2G term), and $^4T_{2g}$ (from the 4F term), after which the electrons could relax to the lowest excited state level 2E_g (from the 2G term) through non-radiative transitions process $^4T_{1g} \rightarrow ^2T_{2g} \rightarrow ^4T_{2g} \rightarrow ^2E_g$, and finally released the energy by radiation transitions process with a red light emission at 703 nm.⁶¹

Conclusions

In conclusion, LaScO₃:xMn⁴⁺ ($x = 0.0005\text{--}0.009$) far-red emitting phosphors have been successfully synthesized *via* high-temperature solid-state reaction process. The crystal structure of the host and LaScO₃:0.001Mn⁴⁺ phosphors had been discussed and the XRD patterns of the LaScO₃:xMn⁴⁺ proved that they all were pure phase. Monitored at 703 nm, the obtained PLE spectrum of the LaScO₃:0.001Mn⁴⁺ phosphors exhibited four Gaussian fitting peaks, centering at 346 nm (28 902 cm⁻¹; Mn⁴⁺–O²⁻ transition), 392 nm (25 510 cm⁻¹; $^4A_{2g} \rightarrow ^4T_{1g}$ dominant transition), 462 nm (21 645 cm⁻¹; $^4A_{2g} \rightarrow ^2T_{2g}$ transition), and 543 nm (18 416 cm⁻¹; $^4A_{2g} \rightarrow ^4T_{2g}$ transition). Upon 398 nm excitation, the PL spectrum of LaScO₃:0.001Mn⁴⁺ 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_{FR} at around 730 nm. The optimal doping concentration of Mn⁴⁺ ion was 0.001 in LaScO₃ host and the electric d–d interaction contributed to the concentration quenching mechanism. All the results indicated that the LaScO₃:Mn⁴⁺ 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. Bryknař, V. Trepakov, Z. Potuřek and L. Jastrabik, *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.

