Synthesis, structure, and luminescence characteristics of far-red emitting Mn$^{4+}$-activated LaScO$_3$ perovskite phosphors for plant growth

Liangling Sun, Balaji Devakumar, Heng Guo, Jia Liang, Bin Li, Shaoying Wang, Qi Sun and Xiaoyong Huang

Far-red emitting phosphors LaScO$_3$:Mn$^{4+}$ were successfully synthesized via a high-temperature solid-state reaction method. The X-ray powder diffraction confirmed that the pure-phase LaScO$_3$:Mn$^{4+}$ phosphors had formed. Under 398 nm excitation, the LaScO$_3$:Mn$^{4+}$ phosphors emitted far red light within the range of 650–800 nm peaking at 703 nm (14 225 cm$^{-1}$) due to the $^2$E$_g$ → $^4$A$_{2g}$ 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 LaScO$_3$:Mn$^{4+}$ phosphors was found to be 0.001 and electric dipole–dipole interaction, respectively. And the CIE chromaticity coordinates of the LaScO$_3$:0.001Mn$^{4+}$ phosphors were (0.7324, 0.2676). The decay lifetimes of the LaScO$_3$:Mn$^{4+}$ phosphors gradually decreased from 0.149 to 0.126 ms when the Mn$^{4+}$ doping concentration increased from 0.05 to 0.9 mol%. Crystal field analysis showed that the Mn$^{4+}$ ions experienced a strong crystal field in the LaScO$_3$ host. The research conducted on the LaScO$_3$:Mn$^{4+}$ phosphors illustrated their potential application in plant lighting to control or regulate plant growth.

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. 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. There exist two kinds of phytochrome, P$_R$ and P$_{FR}$, and P$_a$ is the biologically inactive state, whereas P$_{FR}$ is the biologically active state. These two phytochromes can be converted into each other by absorbing different wavelengths of light, in which the P$_a$ is 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$_R$.

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. 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. 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. 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, which can exhibit various colors by coating different phosphors onto the blue/near-ultraviolet LED chip, 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$_2$NaAlF$_6$:Mn$^{4+}$ (630 nm), Na$_2$MgZr(PO$_4$)$_3$:Eu$^{3+}$ (611 nm), Sr$_2$MgAl$_2$O$_6$:Mn$^{4+}$ (658 nm), 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$^{4+}$ ions in particular host materials with octahedral structures can emit red light and even deep red light due to the $^2$E$_g$ → $^4$A$_{2g}$ transition, such as Sr$_2$Al$_2$O$_4$:Mn$^{4+}$ (652 nm), NaMgGdTeO$_4$:Mn$^{4+}$ (697 nm), Ca$_2$La$_2$W$_2$O$_{12}$:Mn$^{4+}$ (711 nm), La$_2$MTHO$_5$:Mn$^{4+}$ (M = Mg and Zn; 710 nm), and Ba$_2$GeO$_5$:Mn$^{4+}$ (667 nm). Considering that the structure of the LaScO$_3$ compound with [ScO$_6$] octahedral structure is similar to LaAlO$_3$ and Mn$^{4+}$-doped LaAlO$_3$ phosphors can emit far-red emission,
so the LaScO₃ compound has been chosen as the host for Mn⁴⁺ doping.⁴³,⁴⁴ Thus, in this work, LaScO₃ and Mn⁴⁺ ions had been chosen for the host material and activator, respectively, and a series of LaScO₃ₓMn₄⁺⁺ (x = 0.0005–0.0090) phosphors with different Mn⁴⁺ 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 LaScO₃ host, decay lifetimes and luminescence properties had also been investigated in detail, and the results indicated the LaScO₃:Mn⁴⁺ phosphors could be serve as the far-red emitting phosphor in plant growth LEDs.

**Experimental section**

LaScO₃ₓMn₄⁺⁺ (x = 0.0005–0.009) phosphors were prepared by a facile solid-state reaction method using Sc₂O₃ (analytical reagent, AR), MnCO₃ (AR), and La₂O₃ (99.99%) as the starting materials. The raw materials were weighed according to the stoichiometric ratio. The mixed starting materials were ground in an agate mortar and transferred to Al₂O₃ 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 LaScO₃ₓMn₄⁺⁺.

The X-ray powder diffraction (XRD) results of LaScO₃ₓMn₄⁺⁺ phosphors were measured on an X-ray diffractometer (Bruker D8 Advance) with Cu-Kα radiation. The room-temperature photoluminescence (PL)/PL excitation (PLE) spectra and luminescence decay lifetimes of LaScO₃ₓMn₄⁺⁺ 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 LaScO₃:0.001Mn⁴⁺⁺ phosphors were measured by the Edinburgh FS5 spectrofluorometer with a integrating sphere.

**Results and discussion**

Fig. 1 showed the XRD patterns of the LaScO₃ₓMn₄⁺⁺ (x = 0, 0.0005, 0.001, and 0.005) phosphors and the stand pattern of LaScO₃ (JCPDS: 26–1148). It could be seen that all the diffraction peaks of the samples matched well with the standard data of LaScO₃. There was no excess crystal phase formation, which illustrated the Mn³⁺ ions could be successfully doped into the LaScO₃ host. Mn⁴⁺ ions can replace specific cationic sites of the specific host, where cationic sites have a coordination number (CN) of six, such as Nb⁵⁺, Zr⁴⁺, Ti⁴⁺, Te⁶⁺, and W⁶⁺ ions.⁴⁹,⁶⁰,⁶¹ Considering the cationic radius and the coordination environment of Mn⁴⁺ (r = 0.535 Å, CN = 6) and Sc³⁺ (r = 0.745 Å, CN = 6), from the values of R_p and R_wp (R_p = 8.13% and R_wp = 7.55% for LaScO₃ host; R_p = 4.86% and R_wp = 3.50% for LaScO₃:0.001Mn⁴⁺⁺ phosphors), we could know that the obtained results were reliable. The refined crystallographic parameters of the LaScO₃ host and LaScO₃:0.001Mn⁴⁺⁺ phosphors were listed in Table 1 and Table 2, respectively. It could be seen that the parameters of LaScO₃ host and LaScO₃:0.001Mn⁴⁺⁺ phosphors changed slightly due to the difference in ions radii between Sc³⁺ and Mn⁴⁺ ions. The crystal systems of the LaScO₃ host and LaScO₃:0.001Mn⁴⁺⁺ phosphors were orthorhombic with a space group of Pbam. Fig. 2(c) and (d) show the crystal structure of the LaScO₃ host and the [ScO₆] octahedron, respectively. In the unit cell, one Sc³⁺ ion was surrounded by six O²⁻ ions to form [ScO₆] octahedral units and the Mn⁴⁺ ions could substitute for Sc³⁺ ions to form the LaScO₃,Mn⁴⁺ compound. All the results illustrated the formation of LaScO₃:Mn⁴⁺ phosphors.

The PLE and PL spectra of the LaScO₃:0.001Mn⁴⁺⁺ phosphors were shown in Fig. 3(a). When monitored at 703 nm, the obtained excitation spectrum of the Mn⁴⁺ ions in LaScO₃ was an asymmetric absorption band, which could be fitted to four peaks though Gaussian fitting, namely, peaks at 346 nm (28 902 cm⁻¹; Mn⁴⁺–O²⁻ transition), 392 nm (25 510 cm⁻¹; 4A₂g → 4T₁g dominant transition), 462 nm (21 645 cm⁻¹; 4A₂g → 4T₂g transition), and 543 nm (18 416 cm⁻¹; 4A₂g → 4T₂g transition).⁴⁹ Under the excitation of 398 nm or 549 nm, the LaScO₃:0.001Mn⁴⁺⁺ phosphors emitted deep red light peaking at 703 nm (2Eg → 4A₂g 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_F as well as the emission spectrum of the LaScO₃:0.001Mn⁴⁺⁺ phosphor. Obviously, the PL spectrum of the LaScO₃:0.001Mn⁴⁺⁺ phosphor was located within the absorption spectrum of the P_F. Importantly, the dominant emission peak of LaScO₃:0.001Mn⁴⁺⁺ phosphor at 703 nm was close to the peak wavelength (around 730 nm) of the absorption spectrum of P_F. So it was meaningful to apply LaScO₃:Mn⁴⁺ phosphors to plant growth LEDs.

To find the optimal doping concentration of Mn⁴⁺ ions in LaScO₃:Mn⁴⁺ phosphors, a series of LaScO₃ₓMn₄⁺⁺ (x = 0.0005–0.009) phosphors were synthesized and the corresponding PL
Spectra were shown in Fig. 3(d). It could be found that the PL intensity of the LaScO$_3$:Mn$^{4+}$ phosphors firstly increased as 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 LaScO$_3$:Mn$^{4+}$ phosphors. The IQE of the LaScO$_3$:0.001Mn$^{4+}$ phosphor was 15%. The optical doping concentration of Mn$^{4+}$ is much lower than rare-earth doped phosphors, because the $d$-electron wave functions of transition metals (e.g., Mn$^{4+}$ ions) extend more widely than 4f electrons of rare earths (e.g., Eu$^{3+}$ and Tb$^{3+}$ ions). Due to the energy transfer between the nearest Mn$^{4+}$ ions and ends with energy transfer to traps or killing sites, concentration quenching occurs in LaScO$_3$:Mn$^{4+}$ phosphors. Considering the concentration quenching occurred in LaScO$_3$:Mn$^{4+}$ phosphors, the critical distance ($R_c$) of Mn$^{4+}$ ions in the LaScO$_3$:Mn$^{4+}$ phosphors was calculated using the following equation:

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

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 Mn$^{4+}$ ions. Herewith, $V = 266.251(14)$ Å$^3$, $N = 4$, and $x_c = 0.001$. Hence, the $R_c$ of Mn$^{4+}$ ions in
LaScO$_3$:xMn$^{4+}$ was calculated to be about 50.29 Å ($>5$ Å), which was comparable with that in other Mn$^{4+}$ doped phosphors, such as KMgLaTeO$_6$:Mn$^{4+}$ (33.83 Å), Ba$_2$TiGe$_2$O$_8$:Mn$^{4+}$ (40.1 Å), Li$_2$MgZrO$_4$:Mn$^{4+}$ (33.8 Å),$^{98}$ 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:$^{58,59}$

$$I \propto k \left(1 + \beta(x) \theta^3/3 \right)^{-1}$$

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 Mn$^{4+}$ ions in 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 Mn$^{4+}$ ions in LaScO$_3$ host was electric $d$–$d$ interaction.

### Table 2

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

<table>
<thead>
<tr>
<th>Formula</th>
<th>Crystal system</th>
<th>Space group</th>
<th>Lattice parameters</th>
</tr>
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<tr>
<td>LaScO$_3$:0.001Mn$^{4+}$</td>
<td>Orthorhombic</td>
<td>$pbnm$</td>
<td>$a = 5.67879(18)$ Å, $b = 5.79140(16)$ Å, $c = 8.0956(3)$ Å, $V = 266.251(14)$ Å$^3$</td>
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</table>

<table>
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<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Occ.</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
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<td>0.95617</td>
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<td>0.00781</td>
<td>-0.00411</td>
<td>0.00299</td>
<td>-0.00400</td>
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<td>Sc1</td>
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<td>0.5</td>
<td>0.00000</td>
<td>0.999</td>
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<td>-0.00843</td>
<td>-0.00312</td>
<td>0.00057</td>
<td>0.00554</td>
<td>-0.00207</td>
</tr>
<tr>
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<td>0.5</td>
<td>0.00000</td>
<td>0.001</td>
<td>0.01333</td>
<td>-0.00843</td>
<td>-0.00312</td>
<td>0.00057</td>
<td>0.00554</td>
<td>-0.00207</td>
</tr>
<tr>
<td>O1</td>
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<td>0.52509</td>
<td>0.25000</td>
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<td>-0.00405</td>
<td>-0.02970</td>
<td>-0.00531</td>
<td>0.00072</td>
<td>0.00000</td>
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</tr>
<tr>
<td>O2</td>
<td>0.70010</td>
<td>0.30343</td>
<td>0.01124</td>
<td>1</td>
<td>0.02081</td>
<td>0.03995</td>
<td>-0.02703</td>
<td>-0.02799</td>
<td>-0.00394</td>
<td>0.00625</td>
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Fig. 3 (a) The PLE spectrum of LaScO$_3$:0.001Mn$^{4+}$ phosphors monitored at 703 nm. The four curves represent the Gaussian fitting curves. (b) The CIE chromaticity diagram of LaScO$_3$:0.001Mn$^{4+}$ phosphors. The insets show the phosphor digital pictures under the 365 nm excitation (ii) and daylight (i). (c) The room-temperature PL spectrum of LaScO$_3$:0.001Mn$^{4+}$ sample excited at 398 nm and the absorption spectra of phytochrome PR and PFR. (d) The PL spectra of LaScO$_3$:xMn$^{4+}$ ($x = 0.0005–0.009$) phosphors excited at 398 nm. (e) Plot of log($I/x$) vs. log($x$) of Mn$^{4+}$ ions in LaScO$_3$:xMn$^{4+}$ phosphors. (f) The luminescence decay curves of LaScO$_3$:xMn$^{4+}$ ($x = 0.00005–0.009$) 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 = 0.005–0.009) phosphors. The decay lifetimes of the LaScO₃:xMn⁴⁺ samples were obtained by the following double-exponential model:⁶⁰

\[ I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \]  

(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 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(a) 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 \(^{4}A_{2g} \rightarrow ^{4}T_{2g}\) (18 416 cm⁻¹) transition energy gap, the crystal-field strength \( D_q \) of the LaScO₃:xMn⁴⁺ phosphors can be roughly estimated by the following equation:⁶⁴

\[ D_q = E(^{4}A_{2g} \rightarrow ^{4}T_{2g})/10 \]  

(4)

Based on the PLE spectrum of the LaScO₃:0.001Mn⁴⁺ phosphors, the energy difference between the \(^{4}A_{2g} \rightarrow ^{4}T_{1g}\) (25 510 cm⁻¹) and \(^{4}A_{2g} \rightarrow ^{4}T_{2g}\) (18 416 cm⁻¹) was about 7094 cm⁻¹. Therefore, the Racah parameter \( B \) can be obtained by the following expression:⁶⁵

\[ D_q/B = 15(x - 8)/(x^2 - 10x) \]  

(5)

in which the \( x \) can be calculated by:

\[ x = \frac{E(^{4}A_{2g} \rightarrow ^{4}T_{1g}) - E(^{4}A_{2g} \rightarrow ^{4}T_{2g})}{D_q} \]  

(6)

From the PL spectrum of the LaScO₃:0.001Mn⁴⁺ phosphors, the energy of the \(^{2}E_{g} \rightarrow ^{4}A_{2g}\) (14 225 cm⁻¹) was acquired and the Racah parameter \( B \) was evaluated by the following expression:⁶⁴,⁶⁵

\[ \frac{E(^{2}E_{g} \rightarrow ^{4}A_{2g})}{B} = \frac{3.05C}{B} + 7.9 - \frac{1.8B}{D_q} \]  

(7)

According to the eqn (4)–(7), the crystal field parameters \( D_q, B, \) 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 Y₂Al₅O₁₂ (\( Dq/B = 1.98)⁶⁴, Ba₂YSbO₆ (\( Dq/B = 1.88)⁶⁵, and Ca₂LaNbO₆ (\( Dq/B = 2.31)⁶⁵.

The emission energy of the \(^{2}E_{g} \rightarrow ^{4}A_{2g}\) transition of Mn⁴⁺ ions in specific host could be affected by the nephelauxetic effect.⁶⁷ The nephelauxetic effect can be described as the parameter \( \beta_1 \), which was established by Brik et al.⁶⁵ And the value of \( \beta_1 \) can be calculated by the following expression:⁶⁵

\[ \beta_1 = \sqrt{\left(\frac{B}{B_0}\right)^2 + \left(\frac{C}{C_0}\right)^2} \]  

(8)

where \( B_0 = 1160 \text{ cm}^{-1} \) and \( C_0 = 4303 \text{ cm}^{-1} \), which was the Racah parameter of the free Mn⁴⁺ ions. Thus, the value of \( \beta_1 \) in the LaScO₃ host was about 0.924. Brik et al. also have presented the linear relationship \( [E(^{2}E_{g}) = -880.49 + 16 261.92 \beta_1 \pm \sigma; \sigma = 332 \text{ cm}^{-1}] \) between the \(^{2}E_{g}\) energy level of Mn⁴⁺ ions in different hosts.⁶⁵ Fig. 4(a) depicts the relationship between the \(^{2}E_{g}\) energy level of Mn⁴⁺ ions and different hosts. All the points were located around the line \( E(^{2}E_{g}) = -880.49 + 16 261.92 \beta_1 \), indicating the data were acceptable. The detailed data of these phosphors, which used in Fig. 4(a), were listed in Table 3. It can

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Fig. 4 (a) Dependence of the \(^{2}E_{g}\) energy level of Mn⁴⁺ ions on the nephelauxetic ratio \( \beta_1 \) in different hosts including LaScO₃: \( E(^{2}E_{g}) = -880.49 + 16 261.92 \beta_1 \pm \sigma; \sigma = 332 \text{ cm}^{-1} \). (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 Mn$^{4+}$ ions in different host

<table>
<thead>
<tr>
<th>No.</th>
<th>Hosts</th>
<th>$Dq$/cm$^{-1}$</th>
<th>$B$ cm$^{-1}$</th>
<th>$C$ /cm$^{-1}$</th>
<th>$Dq/B$</th>
<th>$\beta_1$</th>
<th>$E(^2E_g)/$cm$^{-1}$</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>SiTiO$_3$</td>
<td>1818</td>
<td>719</td>
<td>2839</td>
<td>2.529</td>
<td>0.905</td>
<td>13 831 (723 nm)</td>
<td>69</td>
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<tr>
<td>2</td>
<td>La(MgTi)$_{1/2}$O$_3$</td>
<td>2053</td>
<td>700</td>
<td>2959</td>
<td>2.933</td>
<td>0.915</td>
<td>14 124 (708 nm)</td>
<td>9</td>
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<tr>
<td>3</td>
<td>LaScO$_3$</td>
<td>1842</td>
<td>701</td>
<td>3006</td>
<td>2.628</td>
<td>0.924</td>
<td>14 225 (703 nm)</td>
<td>This work</td>
</tr>
<tr>
<td>4</td>
<td>NaMgGdTeO$_6$</td>
<td>2083</td>
<td>727</td>
<td>2971</td>
<td>2.865</td>
<td>0.932</td>
<td>14 347 (697 nm)</td>
<td>39</td>
</tr>
<tr>
<td>5</td>
<td>Y$_2$Ti$_2$O$_7$</td>
<td>2000</td>
<td>600</td>
<td>3500</td>
<td>3.333</td>
<td>0.964</td>
<td>14 956 (669 nm)</td>
<td>63 and 70</td>
</tr>
<tr>
<td>6</td>
<td>CaZrO$_3$</td>
<td>1850</td>
<td>754</td>
<td>3173</td>
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<td>0.983</td>
<td>15 054 (644 nm)</td>
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<tr>
<td>7</td>
<td>K$_2$SiF$_6$</td>
<td>2197</td>
<td>599</td>
<td>3750</td>
<td>3.668</td>
<td>1.013</td>
<td>15 873 (630 nm)</td>
<td>63</td>
</tr>
<tr>
<td>8</td>
<td>KTeF$_3$</td>
<td>2267</td>
<td>567</td>
<td>3904</td>
<td>3.998</td>
<td>1.031</td>
<td>16 129 (620 nm)</td>
<td>71</td>
</tr>
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</table>

be seen clearly from Table 3 and Fig. 4(a) that with the increasing of $\beta_1$, the value of the energy level of $^2E_g$ increased. And the value of the nephelauxetic effect in LaScO$_3$:Mn$^{4+}$ phosphors was close to the La(MgTi)$_{1/2}$O$_3$:Mn$^{4+}$, NaMgGdTeO$_6$:Mn$^{4+}$, and SiTiO$_3$:Mn$^{4+}$, indicating the similar coordination environments of Mn$^{4+}$ 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$^{4+}$ energy level transition in the LaScO$_3$ host was illustrated in the right diagram of Fig. 4(b). The electrons at the ground state $^4A_{2g}$ (from the $^6$T 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 $^6$F term), $^2T_{2g}$ (from the $^4$G term), and $^4T_{2g}$ (from the $^4$F term), after which the electrons could relax to the lowest excited state level $^2E_g$ (from the $^4$G 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.

Conclusions

In conclusion, LaScO$_3$:xMn$^{4+}$ ($x = 0.0005$–$0.009$) far-red emitting phosphors have been successfully synthesized via high-temperature solid-state reaction process. The crystal structure of the host and LaScO$_3$:0.001Mn$^{4+}$ phosphors had been discussed and the XRD patterns of the LaScO$_3$:xMn$^{4+}$ proved that they all were pure phase. Monitored at 703 nm, the obtained PLE spectrum of the LaScO$_3$:0.001Mn$^{4+}$ phosphors exhibited four Gaussian fitting peaks, centering at 346 nm (28 902 cm$^{-1}$; Mn$^{4+}$–O$^2-$ transition), 392 nm (25 510 cm$^{-1}$; $^4A_{2g} \rightarrow ^4T_{1g}$ dominant transition), 462 nm (21 645 cm$^{-1}$; $^4A_{2g} \rightarrow ^4T_{2g}$ transition), and 543 nm (18 416 cm$^{-1}$; $^4A_{2g} \rightarrow ^4T_{2g}$ transition). Upon 398 nm excitation, the PL spectrum of LaScO$_3$:0.001Mn$^{4+}$ 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 Mn$^{4+}$ ion was 0.001 in LaScO$_3$ host and the electric d–d interaction contributed to the concentration quenching mechanism. All the results indicated that the LaScO$_3$:Mn$^{4+}$ 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

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